Surface and Interface Engineering of Conjugated Polymers and Nanomaterials

in Applications of Supercapacitors and Surface-Functionalization

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ABSTRACT

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In this dissertation, three aspects about surface and interface engineering of conjugated polymers and nanomaterials will be discussed.

(i) There is a significant promise for electroactive conjugated polymers (ECPs) in applications of electrochemical devices including energy harvesting, electrochromic displays, etc. Among these, ECPs has also been developed as electroactive materials in electrochemical supercapacitors (ESCs). Compared with metal oxides, ECPs are attractive because they have good intrinsic conductivity, low band-gaps, relatively fast doping-and-undoping process, the ease of synthesis, and tunable electronic and structural properties through structural modifications.

Here, Multiple-branch-chain 3,4-ethylenedioxythiophene (EDOT) derivatives was designed as crosslinkers in the co-electropolymerization of EDOT to optimize its morphology and improve the cycling stability of PEDOT in the supercapacitor applications. High-surface-area π-conjugated polymeric networks can be synthesized via the electrochemical copolymerization of the 2D (trivalent) motifs benzo[1,2-b:3,4-b':5,6-b'']trithiophene (BTT) and tris-EDOT-benzo[1,2-b:3,4-b':5,6-b'']trithiophene (TEBTT) with EDOT. Of all the material systems studied, P(TEBTT/EDOT)-based frameworks

achieved the highest areal capacitance with values as high as 443.8 mF cm^{-2} (at 1 mA cm^{-2}), higher than those achieved by the respective homopolymers (PTEBTT and PEDOT) in the same experimental conditions of electrodeposition (PTEBTT: 271.1 mF cm^{-2} (at 1 mA cm^{-2}); PEDOT: 12.1 mF cm^{-2} (at 1 mA cm^{-2}).

(ii) In electrochemical process, the suitable choice of appropriate electrolytes to enlarge the safe working potential window with electrolyte stability is well known to improve ECPs' performance in ESCs applications. Ionic liquids (ILs) are ion-composed salts and usually fluid within a wide temperature range with low melting points. There are many unique characteristics for these intrinsic ion conductors, including high ionic conductivity, wide electrochemical voltage windows in neutral conditions, fast ion mobility in redox reaction process (>10-14 m2 V-1 s-1), low vapor pressure, and environmental stability. These properties qualified ambient-temperature ILs to be applied as supporting medium for various devices and materials processing applications in both industry and academia, overcoming the limitation of volatile organic compounds (VOCs). Especially, ILs have been utilized as superior medium to electrodeposit metals, alloys, semiconductors and ECPs in the application of supercapacitors.

Electropolymerization of EDOT and its derivative 4,4'-dimethoxy-3,3'-bithiophene (BEDOT) have been studied in three kinds of imidazolium-based ionic liquids and conducting salt in VOCs with different anions both as the growth medium and the supporting electrolyte, to assess the influence of these anions on their morphology and electrochemical activity. It is found these thiophene polymers grown in ILs with higher viscosity and lower diffusion shows much slower growth rate and orderly morphologies

than in Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) dissolved in acetonitrile (ACN), and gives better electrochemical performance via cyclic voltammetry (CV) and galvanostatic charge-and-discharge (CD) studies. Polymers displayed multiple redox peaks in several cases, the possible reasons and origins are discussed. The synthesized polymer can be affected greatly by both the ILs with different anion/cation, and its mutal interation with targeted monomer.. As far as known, there is no systematic study on how the anions of ILs and common organic solution could play a role as a medium both for polymerization and post-polymerization electrolyte for PEDOT and its derivatives. This study can be used as an easy reference and provide experimental diagnositc data when selecting ionic liquids to investigate and optimize thiophene-based electrochemical systems, such as batteries and supercapactiors.

(iii) Another aspect about interface chemistry of direct functionalization of nanodiamond with maleimide has also been addressed. Functional nanodiamonds are promising candidates for extensive practical applications in surface science, photonics and nanomedicine. Here, a protocol of direct functionalization is described by which maleimide-derivatized substituents can be appended to the outer shell of thermally annealed nanodiamonds through Diels-Alder reaction. This protocol can be carried out in room temperature, ambient atmosphere, without catalyst, and provide functionalized nanodiamonds with good solubility in organic solution. Also, this method can be applied for other maleimide derivatives,e.g.m aleimide-fluorescene, which can be applied in fluorescence labeling, sensing, and drug delivery. A series of techniques, especially Fourier transform infrared spectroscopy (FTIR), and Solid State Nuclear Magnetic Resonance

(SS-NMR) was conducted for the analysis of surface chemistry and the investigation of the

two-point binding strategy in details.

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[bmim][PF$_6$]	1-butyl-3-methylimidazolium hexafluorophosphate
[bmim][Tf$_2$N]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[bmim][TfO]	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
0D	zero-dimensional
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
AC	activated carbon
BTT	Benzo[1,2-b:3,4-b':5,6-b'']trithiophene
CD	galvanostatic charge-discharge
CE	counter electrode
CNT	carbon nanotube
CP	Carbon paper
CV	cyclic voltammetry
DDNPs	detonation diamond nanoparticles

ECP	electroactive conjugated polymers
ECSs	Electrochemical supercapacitors
EDLC	electrochemical double layer capacitor
EES	Electrochemical energy storage
PEDOT	poly(3,4-ethylenedioxythiophene)
ESR	equivalent series resistance
FS	faradaic supercapacitors
GC	glassy carbon
ITO	indium tin oxide
PAni	polyaniline
PPy	polypyrrole
PTp	polythiophene
RE	reference electrode
RT	room temperature
SEM	scanning electron microscopy
SSA	specific surface area

TBAP	tetrabutylammonium perchlorate
TBAPF$_6$	tetrabutylammonium hexafluorophosphate
TEBTT	tris-EDOT-benzo[1,2-b:3,4-b':5,6-b'']trithiophene
TEM	transmission electron microscopy
TGA	thermo gravimetric analysis
WE	working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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oxidation features; the values italicized point to oxidation features that are not well resolved but occur reproducibly between experiments.

Figure 2.3 SEM images of the morphologies of electrodeposited polymer films prepared from several monomer solutions of different BTT/EDOT monomer compositions: (**a**) 1:0, (**b**) 3:1, (**c**) 1:1, (**d**) 1:3, (**e**) 1:6, and (**f**) 0:1. Electrodeposition conditions: 50 mM monomer solutions in ACN; 20 deposition cycles in a voltage window of -0.7 – +1.5 V (vs. Ag/Ag+), on carbon cloth electrodes; deposition scan rate of 50 mV s-1.

Figure 2.4 (**a, b**) Cyclic voltammograms of electrodeposited PBTT, PEDOT, and several P(BTT/EDOT) copolymers prepared from several solutions of different BTT/EDOT monomer compositions: 1:0 (black), 3:1 (red), 1:1 (blue), 1:3 (magenta), 1:6 (green), and 0:1 (dark blue) at a scan rate of 20 mV s-1. Electrodeposition conditions: 50 mM monomer solutions in ACN; 20 deposition cycles in a voltage window of -0.7 – +1.6 V (vs. Ag/Ag+), on carbon cloth electrodes; deposition scan rate of 50 mV s-1. Each voltammogram is normalized to the extent of functionalized surface area. (**c**) Galvanostatic charge-discharge curves collected for the polymers at a current density of 5 mA cm-2; the areal capacitance values inferred are indicated on the plot.

Figure 2.5 (**a**) Cyclic voltammograms of PTEBTT films electropolymerized on various working electrodes and voltage windows (collected in ACN). Electrodeposition conditions: 1 mM monomer solutions in DCM; 120 deposition cycles; deposition scan rate of 50 mV s-1. (**b**) Cyclic voltammograms of PTEBTT films on glassy carbon button electrodes as a function of the number of electrodeposition cycles (collected in ACN). Electrodeposition conditions: 1 mM monomer solutions in DCM; 120 deposition cycles in a voltage window

of -1.0 − +1.2 V (vs. Ag/Ag+); deposition scan rate of 50 mV s-1. (**c**) Cyclic voltammograms of PTEBTT films on glassy carbon button electrodes as a function of scan rate (collected in ACN). Electrodeposition conditions: 1 mM monomer solutions in DCM; 20 deposition cycles in a voltage window of -1.0 − +1.2 V (vs. Ag/Ag+); deposition scan rate of 50 mV s-1. Inset: anodic (Ipa) and cathodic (Ipc) current intensity variations of the first redox couple of PTEBTT as a function of the square root of the scan rate.

Figure 2.6 Cyclic voltammograms of electrodeposited PBTT and PTEBTT. Electrodeposition conditions of PBTT: scan rate of 50 mV s-1, 20 cycles, voltage window -0.7–+1.6 V (vs. Ag/Ag+), 50 mM monomer in ACN. Electrodeposition conditions of PTEBTT: scan rate of 50 mV s-1, 120 cycles, voltage window -1.0–+1.2 V (vs. Ag/Ag+), 1 mM monomer in DCM. Each voltammogram is normalized to the extent of functionalized surface area.

Figure 2.7 SEM images of the morphologies of electrodeposited polymer films prepared from several monomer solutions of different TEBTT/EDOT monomer compositions: (**a**) 1:0, (**b**, **e**) 1:1, (**c**, **f**) 1:9, and (**d**) 0:1. Electrodeposition conditions: 1 mM monomer solutions in DCM; 120 deposition cycles in a voltage window of -1.0 − +1.2 V (vs. Ag/Ag+), on glassy carbon button electrodes; deposition scan rate of 50 mV s-1.

Figure 2.8 (**a**) Cyclic voltammograms of electrodeposited PTEBTT, PEDOT, and several P(TEBTT/EDOT) copolymers prepared from several solutions of different TEBTT/EDOT monomer compositions: 1:0 (black), 3:1 (red), 1:1 (blue), 1:3 (magenta), 1:9 (green), and 0:1 (dark blue); curves collected at a scan rate of 20 mV s-1. Electrodeposition conditions: 1 mM monomer solutions in DCM; 120 deposition cycles in

a voltage window of -1.0 − +1.2 V (vs. Ag/Ag+), on glassy carbon button electrodes; deposition scan rate of 50 mV s-1. (**b**) areal capacitance vs. current density increments for several P(TEBTT/EDOT) copolymers. (**c**) areal capacitance vs. cycle number for several P(TEBTT/EDOT) copolymers (at 2 mA cm-2).

Figure 3.1 Cyclic voltammograms during electropolymerization of EDOT with increased cycles prepared from (**a**) TBAPF6/ACN, (**b**) [bmim][Tf2N], (**c**) [bmim][TfO], and (**d**) [bmim][PF6] Electrodeposition conditions: 25 mM monomer solutions in supporting medium; 20-180 deposition cycles in a voltage window of -1.0 − +1.2 V (vs. Ag/Ag+), on carbon paper electrodes; deposition scan rate of 50 mV s-1. Each voltammogram is normalized to the extent of functionalized surface area.

Figure 3.2 Cyclic voltammograms of PEDOT electrodeposited and post-electropolymerization CV in different combinations of ILs and organic solvents. (**a**) [bmim][Tf2N] as electrodeposition medium and TBAPF6/ACN as post-electropolymerization electrolyte; (**b**) TBAPF6/ACN as both electrodeposition medium and post-electropolymerization electrolyte; (**c**) TBAPF6/ACN as electrodeposition medium and [bmim][Tf2N] as post-electropolymerization electrolyte; (**d**) TBAPF6/ACN as both electrodeposition medium and post-electropolymerization electrolyte, with a voltage window of -1.0 − +1.2 V (vs. Ag/Ag+) and scan rate of 20 mV s-1. Each voltammogram is normalized to the extent of functionalized surface area.

Figure 3.3 Galvanostatic charge-discharge curves collected for the PEDOT electrodeposited in ILs or organic solvents. (**a**) [bmim][Tf2N] as electrodeposition medium and TBAPF6/ACN as post-electropolymerization electrolyte; (**b**) TBAPF6/ACN as both

electrodeposition medium and post-electropolymerization electrolyte; (**c**) TBAPF6/ACN as electrodeposition medium and [bmim][Tf2N] as post-electropolymerization electrolyte; (**d**) TBAPF6/ACN as both electrodeposition medium and post-electropolymerization electrolyte, at a current density of 2 mA cm-2; the areal capacitance values inferred are indicated on the plot.

Figure 3.4 Summary of galvanostatic charge-discharge values collected for the PEDOT electrodeposited in ILs or organic solvents. (**a**) [bmim][Tf2N] as electrodeposition medium and TBAPF6/ACN as post-electropolymerization electrolyte; (**b**) TBAPF6/ACN as both electrodeposition medium and post-electropolymerization electrolyte; (**c**) TBAPF6/ACN as electrodeposition medium and [bmim][Tf2N] as post-electropolymerization electrolyte; (**d**) TBAPF6/ACN as both electrodeposition medium and post-electropolymerization electrolyte, at a current density of 2, 5, and 10 mA cm-2; the percentage numbers indicated on the plot are the attenuation degree of capacitance values with the increased current density.

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Figure 3.8 Cyclic voltammograms during electropolymerization of BEDOT with increased cycles prepared from (**a**) TBAPF6/ACN, (**b**) [bmim][Tf2N], (**c**) [bmim][TfO], and (**d**) [bmim][PF6] Electrodeposition conditions: 25 mM monomer solutions in supporting medium; 20-100 deposition cycles in a voltage window of -1.0 − +1.2 V (vs. Ag/Ag+), on carbon paper electrodes; deposition scan rate of 50 mV s-1. Each voltammogram is normalized to the extent of functionalized surface area.

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Figure 4.1 a) Size distribution pattern of the ball-milled DDNPs measured by DLS in MilliQ water (tuned to pH~3.8 by HCl solution). **b)** TEM image (bright field, 150keV) of the corresponding DDNPs (scale bar: 50 nm). Figure adapted with permission.[158]

Figure 4.2 a) FTIR spectra and **b)** Raman spectra (1 scan, t= 20s/scan, λ= 325 nm) of thermally annealed DDNPs. [1] DDNPs prior to ball-milling (black curve), [2] ball-milled DDNPs (blue curve), [3] DDNPs thermally annealed at 500oC for 1h (purple curve), [4] DDNPs thermally annealed at 600oC for 1h (green curve), [5] DDNPs thermally annealed at 700oC for 1h (orange curve), [6] DDNPs thermally annealed at 800oC for 1h (red curve), and [7] DDNPs thermally annealed at 900oC for 1h (pink curve). Spectra given on an arbitrary scale. Note: Significant degradation of the sample was observed with increasing power and number of scans by Raman under the UV laser beam (i.e., upon longer times of exposure) − the peak maximum shifting towards higher frequencies (from ca. 1590 cm-1, G-band contribution from the *graphite-like* outer-shell → to 1640 cm-1, −OH). Oxidative degradation mechanisms may be the source of degradation.

Figure 4.3 FTIR spectra of [1] ball-milled DDNPs (control), [2] thermally annealed GDNPs(800), [3] GDNPs(800) treated with the functional maleimide EHM (EHM-GDNP), and [4] the free EHM substituent. The molecular structure and main characteristic vibrations of EHM are indicated on the plot.

Figure 4.4 XRD patterns of the DDNP and GDNP(800) precursors. (arbitrary scale) The characteristic peaks of the crystal planes of diamond at 2Θ = 44.3° (111), 75.5° (220), and 91.7° (311) indicate that the diamond-like carbon structure (sp3) of the DDNPs is preserved upon annealing at 800°C for 1h.

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Figure 4.8 a) 1D ^{13C} CP/MAS solid-state NMR spectrum of thermally annealed GDNPs(800); b) 2D $^{13C}\{^{1H}\}$ HETCOR spectra of the GDNPs(800); c) 1D ^{13C} CP/MAS solid-state NMR spectrum of GDNPs(800) treated with the control unsubstituted maleimide M (M-GDNP); d) 2D $^{13C}\{^{1H}\}$ HETCOR spectra of the M-GDNPs; e) 1D ^{13C} CP/static solid-state NMR spectrum of the M-GDNPs; f) 1D ^{13C} CP/MAS solid-state NMR spectrum of GDNPs(800) treated with the functional maleimide EHM (EHM-GDNP). The molecular structures and peak assignments are indicated on the spectra.

Figure 4.9 a) 1D ^{13C} MAS solid-state NMR spectrum of thermally annealed GDNPs(800). In the absence of ^{1H} decoupling, the resonance observed in Fig. 2a (at *ca.* 47.3 ppm) and pertaining to hydrogen-substituted carbons (CH, CH2) cannot be observed. Here, a 1D ^{13C} CP/MAS analysis is required to account for the low content of hydrogen-substituted carbons located at the nanodiamond surface (also see Fig. 4.9b). b) 1D 1H MAS

solid-state NMR spectrum **of** thermally annealed GDNPs(800). c) 1H-1H double-quantum (DQ) analysis of M-treated GDNPs(800) treated with the control unsubstituted maleimide M *(*M-GDNP). DQ signals in the w1 dimension are observed at frequencies corresponding to the sum of single quantum (SQ) frequencies of protons that are close to one another in space and will correlate in the w2 dimension with the corresponding ordinary proton resonances. DQ correlation analyses can serve to identify equivalent protons, and is useful here to **differentiate between** CH and CH2 moieties. d) 2D 13C{1H} HETCOR spectra of GDNPs(800) treated with the functional maleimide EHM (EHM-GDNP). The molecular structure (EHM) and peak assignments are indicated on the 2D spectrum.

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Figure 4.13 a) UV-Vis and b) Fluorescence spectra (in solution) of thermally annealed GDNPs(800) (red curve), the unfunctionalized fluorescein-5-maleimide (F5M) dye (green curve), and GDNPs(800) treated with F5M (F5M-GDNP) (blue curve).

Figure 4.14 Fluorescence microscopy images of **a)** thermally annealed GDNPs(800) and **b)** the GDNPs(800) treated with the fluorescent F5M dye (F5M-GDNP); spun-coated

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respectively.

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Chapter 1

Introduction and Background

1.1 Energy Reality and Energy Storage Demanding

Traditional industry society has been largely relying on the substantial energy consuming derived from the combustion of fossil fuels, which is non-renewable energy. Due to the limitation of the fossil fuel reserves as well as the environmental and ecology impact of the combustion for energy production, there has been intense activities and significant advancement in electricity harvested from renewable energy in recent decades, including solar energy, wind energy, water power, and so on. However, these energy resources are not constant and reliable power supply because of their variable nature and inherent intermittency, which causes significant challenges for the practically usage of electrical equipment and appliance. [1-3] The whole energy supply procedure can be simply described as "generation – transmission - distribution". At this point, electrical energy storage techniques s is emerging as the bridge to provide continuous and steady energy supply from energy generation systems to various distributions, which could be modern technologies, e.g. hybrid electric vehicles, portable electronic devices, and telecommunication.[4]

1.2 Electrochemical energy storage: batteries and supercapacitors

1.2.1 Classification of Energy Storage Techniques

Electrical energy generated through the conversion of solar, wind, and other sources can be transformed and stored in various ways, including in mechanical, thermal and chemical forms as shown in **Figure 1.1**.
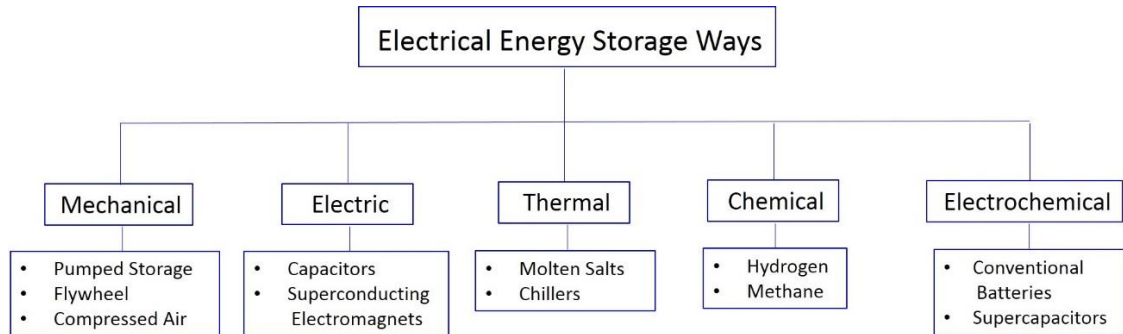
Figure 1.1 Classification of Electrical Energy Storage Methods.

Electrochemical energy storage (EES) is the most traditional energy storage system, which can be classified into three categories: primary batteries (zinc-carbon battery) – unrechargeable dry voltaic cell which is composed of a zinc shell as the anode and a graphite rod as the cathode, secondary batteries (lead-acid battery) – voltaic cell which can be recharged, and fuel cells – a device requires continuous feeding of fuel and oxygen for the convertion of fuel's chemical energy into electricity.[5, 6] The primary common feature for batteries and fuel cells is to obtain electrical energy through the chemical energy stored.

Batteries are the most widely investigated and appllied devices in EES systems for their large energy density and economical affordability. However, batteries and fuel cells suffer from inherent disadvantages which is low power density and short cycling life. [7, 8] A capacitor is a device consisting of two or more conductive plates segmented by dielectric separator. When electric current flows through the capacitor, the potential energy is stored electrostatically between these conducting plates. When the capacitor connects to an external circuit, electric current will be discharged quickly. As illustrated in **Figure 1.2**, typically the relative higher energy density could only be achieved at the sacrifice of power density, and vice verse. So, high power-density devices should be complemented by dielectric capacitors or EDLCs to enhance the interfacial storage of charge on its working electrode surface. [5, 9] Batteries and supercapacitors both rely on electrochemical processes, although separate electrochemical mechanisms determines their relative energy and power density. Due to supercapacitor's physical/chemical charge storage mechanism and slow reaction kinetics for batteries and fuel cells, supercapacitors are expected to provide greater power density and sustainable life cycle compared with batteries and fuel cells but lower energy densities. On the other hand, supercapacitors can offer higher energy density compared with conventional energy storage devices. Thus, electrochemical supercapacitors (ESCs) are featured as critical components to complement and fill between the gap between batteries and conventional capacitors. They provide the prospects of maintaining the relatively high energy density comparable to batteries meanwhile can be charged and discharged rapidly to afford robust power densities.[3, 8] Due to these characteristic, ESCs can be utilized conveniently and portably as the high-power electrical supplier for various stationary and mobile apparatus.
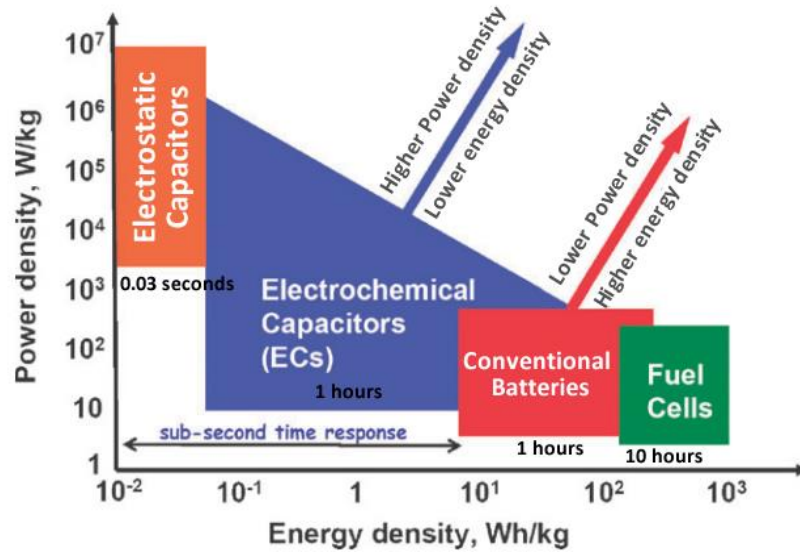
Figure 1.2 Simplified Ragone plot: the characteristics of various energy storage devices with the comparison of both energy density and power density.[5, 9]

1.2.2 Classification of Capacitors

Depending on the choice of electrode and electrolyte, three major categories can be classified for the capacitors, which are electrostatic capacitors, electrolytic capacitors and supercapacitors. They can be further divided into subgroups according to the specific materials used as electrode and electrolyte.

As shown in **Figure 1.3,** Electrostatic capacitors are firstly developed way for electrical energy storage. Consisting of two conductive electrodes (films, foils, sintered beads of metal or conductive electrolyte, etc.) separated by an dielectric or insulating material (ceramic, glass, plastic film, vacuum/air, paper, oxide layer mica, etc.). In this type of capacitors, electric charges can be accumulated and stored inside the concentrated electric field between two paralel electrodes. The equivalent series resistance (ESR) and equivalent

series inductance (ESL) has low values for this arrangment. Discharge time could be within tens of microseconds and power delivering is on the order of 1.5 mWh/kg and 2 mWh/L.[10]

Different from the bulk insulators of conventional electrostatic capacitors, current electrolytic capacitors are normally polarized capacitors, the anode electrode of which are composed of a special metal with an insulating oxide layer performs as the dielectric. The surface of the oxide layer is covered by a solid or liquid electrolyte, serving as cathode electrode. Due to this the dielectric oxide layer is very thin with enlarged anode surface, electrolytic capacitors generally provide energy density on the order of 30 mWh/kg and 120 mWh/L, respectively, which are much higher than that of the electrostatic capacitors, however, much smaller value than electrochemical supercapacitors.[10]

For supercapacitors, electrical energy is stored and released electrochemically by charge seperation in the nanoscale at the interface between working electrode material and the surrounding electrolyte. Generally, a supercapacitor device is constructed of two working electrodes separated by a porous separator made of dielectric porous film, all of which is saturated with electrolyte. The electrolyte is usually an aqueous or organic solvents containing a large amount of homogenously dispersed ions. So, the ionic can flow between the electrodes carrying the currents and keep the currents from discharging the cell. The core structure of a supercapacitor is the electroactive materials on the working electrode. [11] The Structures, components, properties, pros and cons of capacitor catalog is summarized in **Figure 1.3**. Since the focus of this dissertation, more details on supercapacitor will be further discussed in the following section.

Classification of Capacitors

| Electrostatic Capacitors | Electrolytic Capacitors | Supercapacitors |

d ↔ plates/foil, dielectric

$C = \varepsilon \cdot \dfrac{A}{d}$

d dx — Al2O3 / electrolyte

d' — electrode, electro-active materials, seperator

- Two-terminal electrical conductors
- store energy electrostatically

- a thin metal oxide as dielectric layer instead of an insulator.
- store energy electrostatically and electrochemically

- two electrodes separated by a insulator.
- store energy store energy electrostatically and/or electrochemically at the interface

- operated at high voltages
- almost unlimited lifetime
- Low energy densities

- lower voltage
- Limited life time
- larger energy density

- Voltage largely depend on the electrolyte
- Limited life time depend on the electrode material
- largely improved power densities

Figure 1.3 Classification and Comparison of Capacitors.

1.2.3 Classification and General Properties of Supercapacitors

While traditionally batteries offer high energy densities, and conventional electrostatic capacitors offer high power densities, supercapacitors, also named as electrochemical supercapacitors or ultracapacitors, fill the gap of the two types of energy storage devices and improve the charge-and-discharge rates and cycle life. [5-8, 12] Electrochemical capacitors can be distinguished according to the two main mechanisms of energy storage ways: (i) electrochemical double-layer capacitors (EDLCs) by accumulating surface ions electrostatically at the interface between electrode composed of high-surface carbonaceous materials and its surrounding electrolyte, and (ii) pseudocapacitors based on surface redox (faradic) reactions of electro-active materials typically transition metal oxide/hydroxide and conducting polymers. [8, 13-15]

1.2.3.1 Electrochemical Double-Layer Capacitors (EDLCs)

Surface area of carbonaceous materials (activated carbons (ACs), carbon nanotubes (CNTs), graphene, etc.) can be tuned by designing different morphologie and have been utilized as working electrodes for electrochemical double layer capacitors (EDLCs).[16, 17] The mechanism of charge generation for EDLCs includes surface dissociation and ion adsorption from crystal lattice defects or electrolyte.[8] Electrical charges take place only on the surface by electrostatic accumulation. From **Figure 1.3**, the capacitance of EDLCs generated from electroactive materials of the working electrode, which includes interfacial contacting area of the carbon materials and electrolyte. Electrical charges is just accumulated on these interfaces. In the charging process, the accumulated electrons can be transferred from the negative side to the positive side of electrode via an external voltage. Within the supporting medium, cations transfer towards negative side and anions travel towards positive side. In the case of discharge, the whole processes continue in a reverse mode. By this mechanism, accumulated electrons and enery is accumulated and stored in the double-layer interface. In this type of ECSs, there is no charge transfer through the bulk electrode materials and electrolyte interface. Also, there is no net ion exchanges occur between the bulk electrode and the electrolyte. It can give an indication that the concentration of the electrolyte does not fluctuate in the charge-and-discharge processes.[18]
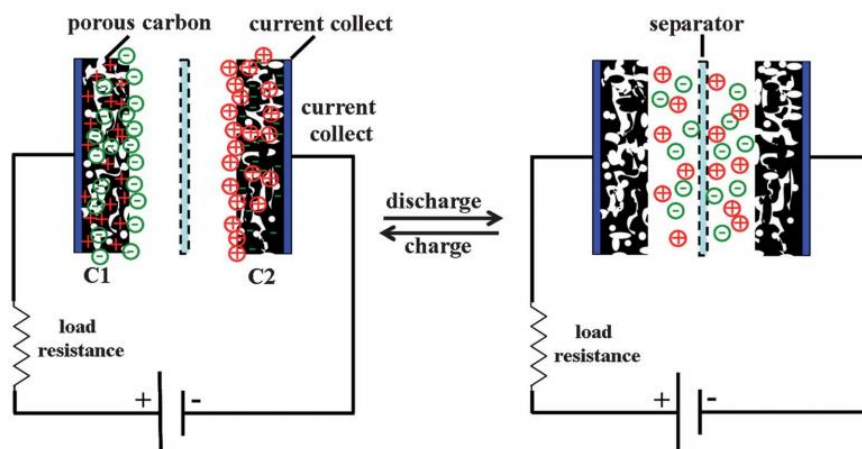
Figure 1.4 Scheme of electric double layer capacitor (EDLC).[19]

The energy density of EDLCs is much higher than conventional dielectric capacitors because the thicker thickness of the double layer is able to store more energy. EDLCs can store a substantial amount of electrical charges which is able to be delivered at higher power density compared with rechargeable batteries.[11] There are lots of other advantages for EDLCs, e.g. fast charge-and-discharge rates, high cycle life, lightweight, high stability and affordability. However the charge accumulated is purely electrostatic so it will limit the energy density for the restriction of surface area of the carbon materials.[16, 20] Due to this shortcoming, the application of pseudocapacitive materials has been investigated with higher energy density and capacitance.

1.2.3.2 Pseudocapacitors

The working mechanism of pseudocapacitors or faradaic supercapacitors (FS) is different from electrostatic EDLC. With the apply of an additional potential, redox reactions together with faradaic reactions would take place in the pseudo-materials, resulting in charge transfer reactions through the electrodes. This process resembles the charge-discharge processes in batteries. Pseudo-materials undergoing such kind of redox

reactions include a few transition metal oxides/hydroxides/chalcogenide,[6, 15] including ruthenium oxide (RuO_2), manganese dioxide (MnO_2),[21, 22] cobalt oxide (Co_3O_4)[23] and $NiCo_2S_4$,[24, 25] as well as conducting polymers, which could be polyaniline (PAni) and polypyrrole (PPy) and polythiophene (PTp).[20, 26, 27]

Faradaic processes can be divided into three major types, which are reversible adsorption, e.g hydrogen adsorption on platinum/gold surfaces, redox reactions of transition metal oxides/hydroxides, and reversible electrochemical doping and dedoping processes of conjugated conducting polymers.[6] For the third type, redox processes occur both on the surfaceand in the bulk near the surface of these pseudo-materials. It has been demonstrated that the energy storage mechanism based on Faradic mechanism can not only provide an enlarged working voltage window, but also enhance capacibility and energy densities compared with EDLCs.[28] As reported, the capacibility of a supercapacitor based on Faradaic mechanism can be 10 to 100 times higher compared with EDLC based on electrostatic accumulation mechanism.[29] Eventhough, also because of the energy storage mechanism, an FS is typically disadvantage in power density compared with EDLC because it takes relatively longer time for faradaic processes than nonfaradaic processes.[30] Moreover, similar to batteries, also due to the redox reactions occuring near the electrode, the phase of pseudocapacitance materials often changes within the electrode, which limits their stability during cycling and power densities.

1.2.3.3 Hybrid Supercapacitors

In recent decades, the hybrid design of EDLCs carbon materials and pseudocapacitance materials has inspired new types of so-called hybrid electrochemical capacitors (HECs). [15]

The advantages of the kind of hybrid structure is contributed by both non-Faradic and Faradic materials, where the synergistic effects of both EDLCs and faradaic capacitance mechanisms can make a contribution. For pseudocapacitance materials, charges are accumulated via faradic electrochemical process with capacitance increasement and working voltage window enlargement. Meanwhile, the incorporation of carbon material insure the stability and life time of the whole device. For both of the two mechanisms, to achieve high capacitance values, large surface area, suitable pore-size distribution, and high conduting properties is necessarily required, which will be further discussed in **Chapter 2**.

1.2.3.3.1 Metal Oxide- Carbon Composite Nanomaterials

In the metal oxide-carbon composite nanostructures, carbon nanotubes, graphene, active carbon and other electrical conducting carbon materials can be chosen as the hybrid with metal oxides in view of their superior mechanical and electrochemical stability.[16, 31] There are two major ways to form the hybrids for carbon materials.

One way is to coat carbon layers onto the oxide surface, e.g. soaking oxides into carbohydrate solution or under hydrothermal/solvothermal methods.[32-35] Despite the convinience and affordablity of this method, the synthesized carbon materials are usually too amorphous and less conducting.[36] Besides, carbon layers can easily react with multivalent metal oxides in the process of carbonization, therefore their components and feeding ration should be precisely determined. Graphene and metal oxide encapsulation by electrostatic interaction as well as in-situ grown of metal/metal oxide and carbon nanotubes shows improved electrical conductivity and mechanical integrity.[37-39] Coaxial carbon core-

oxide shell nanostructures is the other route. This hybrid configuration has several important merits, which are excellent conductivity for the structure of carbon core; homogeneous electrochemical accessibility without the usage of binders and other non-conducting materials; a dual energy-storage mechanism.[40]

1.2.3.3.2 Metal Oxide- Conducting Polymer Hybrids

Electroactive conjugated polymers also known as conducting polymers are also promising candidates to supplement metal oxides in the application of energy storage.[41] It can provide a buffering layer with flexibility and increase the hybrid's conducting ability when mixed with metal oxides. However, the disadvantage of conducting polymers is that the mechanical and electrochemical stability is poor in aqueous electrolytes. As a result, conducting polymers has shorter cycle life compared with carbon materials, which is one of the major obstacles for real applications.[42] There are various ways and combinations for conducting polymers and metal oxides hybrids to harvest their synergetic effects, e.g. the sandwich structure of PANI between layers of MnO_2, polymers decorated by metal oxide.
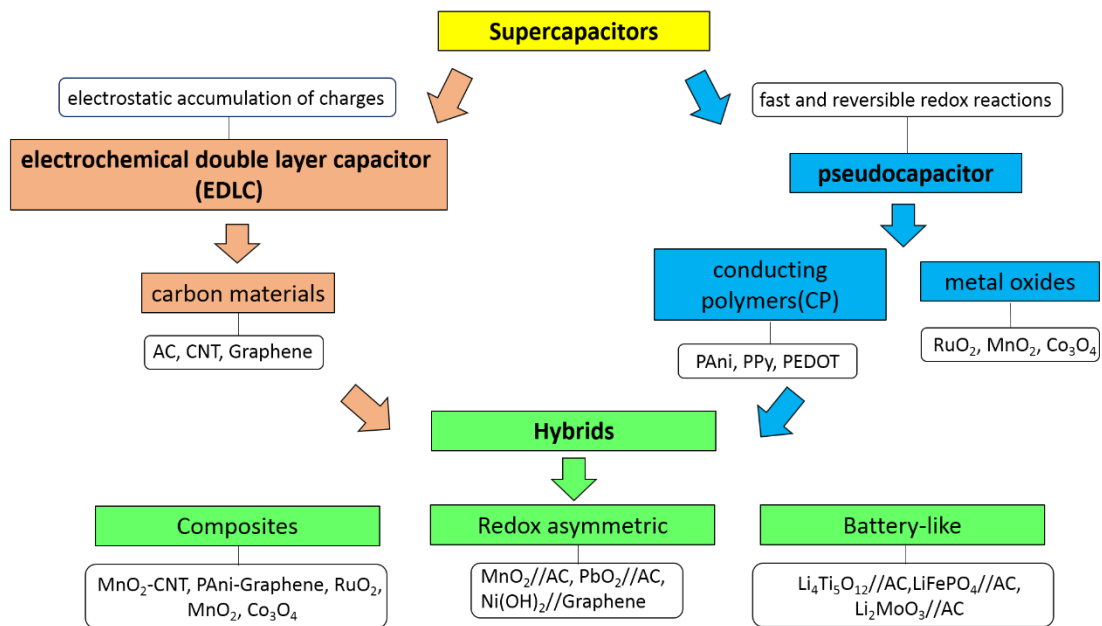
Figure 1.5 Classification of supercapacitors.

1.3 Techniques to Synthesis Electronically Conducting Polymer Electrodes for Supercapacitors

1.3.1 Chemically oxidation

There are several routes to produce conducting polymers, e.g. electrochemical oxidation, photopolymerization, and chemical oxidation. Electrochemical polymerization is ideal to synthesize nice polymer films in a controlled manner on the conducting substrate, while chemical polymerization can be applied to synthesize colloidal dispersions of polymers, which is much more amendable for production in large scale.

Because of conjugated bonding structures, conjugated polymers such as polypyrrole, polyaniline, polydioxythiophene, show high electronic conductivity. These polymers can be produced by electrochemically oxidize the corresponding monomers. In-situ deposition

of PEDOT can occur in an acetonitrile solution with EDOT monomer and iron (III) chloride oxidant as shown in **Scheme 1.1**. Doping is a subsequently process after EDOT is polymerized.
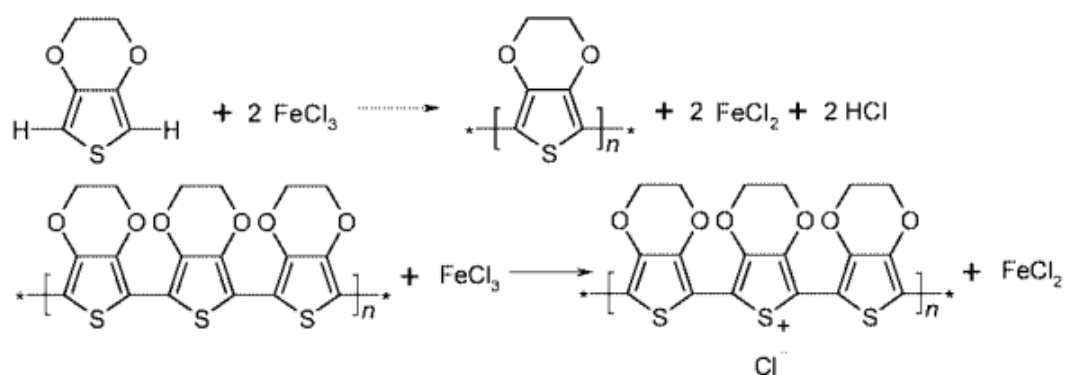
Scheme 1.1 Chemical oxidation process of EDOT and the doping process of PEDOT polymer.[43]

1.3.2 Electrochemical polymerization

Electrochemical polymerization can also bring high oxidation state to the polymer in its growth process, and the doping/dedoping of ions from the electrolyte can be realized through trapping/escaping from the polymer chains. When cycling in the appropriate votage potential windows, these polymers is able to go through a doping and dedoping reversible switching process, which make the polymers as well as this polymerization techniques can be utilized in electrochemical capacitors, electrochromic, batteries, and so on.

POLYACETYLENE (reduction or ' n - doping ') :

POLYACETYLENE (oxidation or ' p - doping ') :

POLYPYRROLE (oxidation or ' p - doping ') :

POLYTHYOPHENE (oxidation or ' p - doping ') :

$X^- = ClO_4^-$, BF_4^- , ...
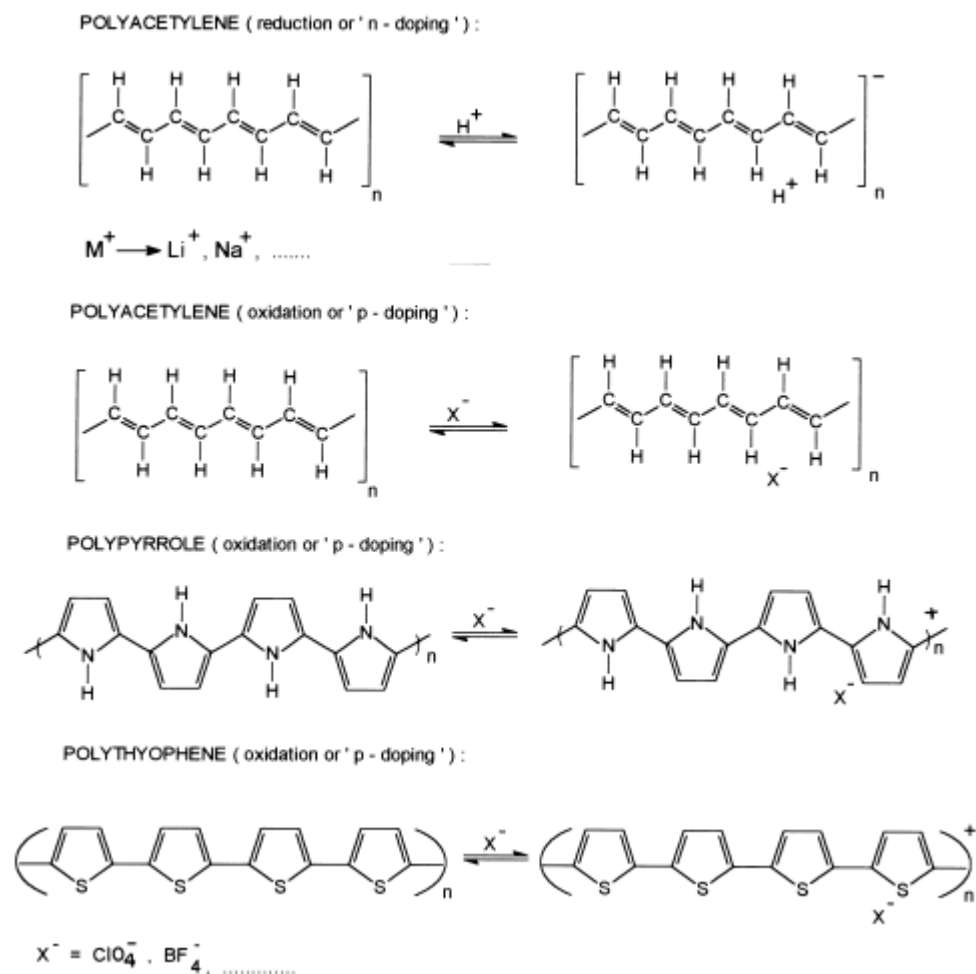
Figure 1.6 Schemes of n-doping and p-doping (reduction and oxidation) processes of conducting polymers in electrochemical reactions.[27]

1.3.2.1 Choice of monomers

To synthesize conducting polymers through electrochemcial techniques, the monomers should have π-conjugated structures and relatively low anodic oxidation potential for efficient polymerization, the structure of which is prone for electrophilic substitution reaction. Especially, aromatic-structure monomers can undergo electrophilic substitution reactions while still maintaining the aromatic framework. Such monomers which are

difficult to polymerize by chemical routes can be oxidized by electrochemical polymeriztion process. Relative low potential of oxidation can avoid of the oxidative decomposition of the supporting electrolyte and other side reactions of the solvent during electropolymerization process.[27]

1.3.2.2 Choice of the growth medium and supporting electrolyte

Redox reactions can take place for monomers during the electropolymerization process, and these reactions is carried out via radical cation intermediates. It is reasonable to consider that the properties of growth medium and supporting electrolyte, especially their nucleophilic charaters plays an important role in the polymerization redox reactions. Poor nucleophilic solvents, e.g. aprotic specise, which could be benzonitrile and acetonitrile, is usually prefered. Meanwhile, solvents with strong nucleophilic anions, e.g. cyanide, acetate, alkoxide, and hydroxide could not be the ideal medium to produce polymer films in good quality. Soluble oligmers and polymers will be produced and dispersed throughout the whole solution. However, by adding suitable protic acid, some of the highly nucleophilic aprotic solvents, e.g. hydroxylic solvents, Dimethylformamide, Dimethyl sulfoxide, can still be applied in these kind of reactions. For some farily nucleophilic solvents, e.g. halides species, it is not easy to deposite nice films onto the substrate because halides species are more prone to be oxidized than the targeted monomers. Besides the nucleophilic properties of solvents, the choice of the growth medium and supporting electrolyte should also be considered based on the solubility of electrolytic salts and monomors for polymerization. For the electrolytic salts, quarternary ammonium salts (R_4NX, R= Alkyl, Aryl radical; X = BF_4^-, PF_6^-, Cl^-, ClO_4^-, Br^-, I^-, $CF_3SO_3^-$, $CH_3C_6H_4SO_3^-$)

show high solubility in these nucleophilic aprotic solvents, and have usually been chosen as supporting electrolytes. In contrast, sodium and potassium compound commonly has low solubility in these solvents.[27]

1.3.2.3 Electrodes

For a standard three-electrode electrochemical system, it contains three main parts, a working electrode, a counter electrode, and a reference electrode. A working electrode is typically a conducting substrate/steel providing a site for polymer electrodeposition, Since redox reactions take place for the formation of polymeric film on the working electrode, inert electrodes, e.g. Pt, Au, or glassy carbon is generally used as substrates would obtain a layer of conducting polymers on the surface, in the same time, concurrent oxidation of electrode materials can be avoided. However, inexpensive and more available substrate materials are usually choosed for practical applications such as supercapacitors, which can be ITO, carbon paper, carbon cloth and stainless substrates. A counter electrode is usually a metallic steel/foil made of inert and conducting metals, e.g. platnum, gold, and nickel. A reference electrode can be Ag/AgCl or saturated calomel electrode (SCE).
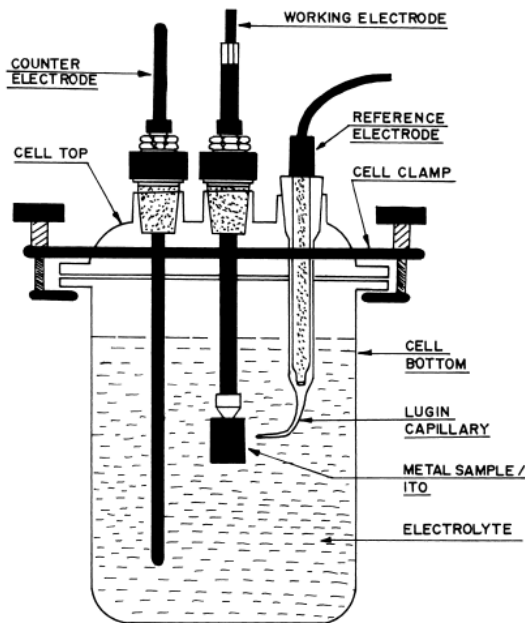
Figure 1.7 General set-up for electrochemical polymerization.[27]

1.3.2.4 Attractive features of Electrochemical Polymerization

One of the most attractive features for electrochemical polymerization technique is it requires the choice of supporting electrolyte. The two main functions of supporting electrolyte in ECP is, firstly, the supporting electrolyte is usually conducting salts, which can be dissolved in the electrolytic solution and make the whole solution conducting. Secondly, the supporting electrolyte can be a source of counterions, and the synthesized polymer unite can be doped by anion/cation intercalation. "Dopant ions" can be adjusted accordingly by the wide choice of cations and anions from the suitable electrolyte. The doping process takes place simultaneously with the formation of polymers. However in conventional routes, polymer synthesis and doping process are subsequent and independent process.

Chapter 2

Multiple-Branch-Chain 3, 4-Ethylenedioxythiophene Derivatives Designed as Crosslinkers in the co-Electropolymerization of EDOT Yields High Capacitance

2.1 Introduction of Conducting Polymers and EDOT in Supercapacitor Applications

Of all electrochemical energy storage (EES) systems, Electrochemical supercapacitors (ECSs) is well suited for renewable energy-storage applications owing to the high charge and discharge rate, good energy-storage efficiency, steady cycle life and can be intergrated with renewable energy sources. [7, 8] These properties allows them to supply stable power under fluctuating energy sources, e.g. wind and solar power generation.[5-8, 12] As discussed in **Chapter 1**, **Section1.2.3**, Three different families of supercapacitors can be differentiated depending on the electro-active material employed.[13, 20, 44] Pseudo-materials provide much higher energy density than carbonaceous materials due to their energy-storage mechanism is based on Faradic reaction. One type of electro-active materials for pseudocapacitors are transition metal oxides/hydroxides/chalcogenides.[6, 15] Huge

gravimetric capacitive performance can be achieved by RuO2, MnO2,[21, 22] V2O5,[45] Co3O4[23] and NiCo2S4,[24, 25]. However, there would also be some difficulties when metal oxides are used as capacitence materials. Firstly, these metal oxides are wide bandgap semiconductors or insulators which show less conducting ability.[46] Less conductivity will not only put an detrimental effect for capacitance performance, but also generate joule heat of substantial amount in the repeated charging and discharging actions. Then, metal oxides are usually suffering from poor ion transportion.[47] To provide sufficient and larger contact area between the electrode matrix and electrolyte solution, metal oxides are typically synthesized with porous morphologies and hierarchical structures in nanoscale, which could offer sufficient ion transport pathways inside. However, in this case, due to the increased amount of grain boundaries, the rise of electrical resistivity will inevitably happen.[48, 49] Typically, metal oxides suffer from severe volume swelling and shrinking during charge and discharge processes, which can damage and even pulverize the polymer film.[50] Most of these extensively studied oxides belong to transition metals which is rare and prohibitive in price, e.g. RuO_2 pseudocapacitor has the highest specific capacitance (~1000 F/g) in this class, but is a vehicle-sized ESC of RuO_2 would cost more than \$1 million.[51] As a result, efforts is driving to develop more sustainable electroactive conjugated polymers (ECPs) for improvement of energy-storage capacity per unit cost.[20, 26, 52]

There is a significant promise for ECPs in applications of electrochemical devices including energy harvesting,[53] electrochromic displays, [54] etc. Among these, ECPs has also been developed as electroactive materials in electrochemical supercapacitors (ESCs).[6, 55] Compared with metal oxides, ECPs are attractive because they have good intrinsic

conductivity, namely, from a few S cm−1 to 500 S cm^{-1} in the doped state,[56, 57] much lower

band gaps compared with conventional polymers, [54] relatively fast doping and undoping

process, the ease of synthesis, and tunable electronic and structural properties through

structural modifications.[26, 58, 59]

Besides the usage of electroactive polymers reported initially for redox-reaction based

supercapacitors,[58, 60, 61] There has been increasing effort devoted to develop new conjugated

monomers/polymers with different structures, especially for polythiophene, polyaniline,

and polypyrrole.[20, 26, 27, 62] The advantage of polyaniline is that it has the ability to store

charges and energy in both aqueous and nonaqueous electrolyte solutions. In contrast,

polythiophene has shown electrochemical instability which limited their application in

energy storage devices, electron-rich derivatives of polythiophene, especially poly (3,4-

ethylenedioxythiophene) (PEDOT) has attracted tremedous attention contributed to their

superior features including fast redox switching speeds, relative higher electrochemical

stability and capacibility.[63] Motivation for the use of polythiophene instead of polyaniline

or polypyrrole in such devices stems from the fact that a higher cell voltage can be achieved

with the polythiophene as most of these can be n- and p-doped because of a smaller band

gap. Consequently, derivatives and analogues of poly (3, 4-alkylenedioxythiophene)s of

similar structures with PEDOT have been studies for electrochemical devices.

In addition to the intrinsic pseudocapacitive properties of ECPs, their nano- and meso-

scale morphologies and the interplay between material surface and electrolytes is also

critical to optimizing the capacitance of electrode material and thus, overall supercapacitor

performance. Considering both morphology and material/electrolyte interactions,

conjugated polymers that can be electropolymerized into highly porous networks are promising pseudocapacitive materials for use in the construction of supercapacitors for specific applications.[64-66] Electropolymerization approaches using monomer solutions can be performed reproducibly, while incorporating ions and counterions in the process of forming open, porous nanostructured films.[67, 68] Thus, several studies have emphasized the range of achievable morphologies using conjugated polymers derived from the electropolymerization of commercially available monomers such as polyaniline (PANI),[69, 70] polypyrrole,[70, 71] polythiophene,[72] and poly(3,4-ethylenedioxythiophene) (PEDOT).[73, 74] For example, varying the electrodeposition conditions of PANI induces considerable morphological changes that impact film capacitance (i.e., nanospheres to nanorods to nanofibers).[75]

Another approach to tuning polymer film morphology relies on the development of functional monomers that can adopt other specific electrodeposition patterns upon electrochemical polymerization including multivalent monomers or comonomers that form 2D or 3D covalent networks.[76, 77] For example, phenylenevinylene-,[76] phenylethynylene-,[77] and triazine-based[77] motifs have been shown to yield highly porous morphologies with specific surface values $>1,000$ $m^2\,g^{-1}$ in specific experimental electrodeposition conditions, while trivalent motifs such as 1,3,5-tris(oligothienyl)benzene[78, 79] and triarylamine[80-83] are amenable to synthesizing efficient capacitive conjugated networks. In parallel, the copolymerization of monomers with comparable oxidation potentials, such as bithiophene and triphenylamine (10 mol%) motifs,[82] is another promising strategy for the preparation of tunable capacitive polymeric frameworks.

2.2 9,9'-Spirobi[9H-fluorene] 3, 4-Ethylenedioxythiophene Derivative as Crosslinker in the co-Electropolymerization of EDOT

In this report, we compare the electropolymerization patterns of two 2D (trivalent) building blocks—benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (BTT) and tris-EDOT-benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (TEBTT) (**Figure 2.1**)—and their copolymerization with 3,4-ethylenedioxythiophene (EDOT). We also describe the experimental conditions required to form hierarchical π-conjugated frameworks with particularly high areal capacitance. Based on the basic characterization of BTT-based well-defined oligomers[84, 85] and TEBTT homopolymers from previous reports,[86] we clarify the fundamental differences between electropolymerized homopolymer and copolymer networks made from these two building motifs, and emphasize their use for the synthesis of high-capacitance, nanostructured 3D polymeric networks that are resilient to repeated electrochemical cycling. In particular, comparing BTT- and TEBTT-based networks, we find that TEBTT-based homopolymers and copolymers with EDOT are substantially more capacitive (reaching up to 271.1 mF cm^{-2} and 443.8 mF cm^{-2} (1 mA cm^{-2}), respectively) and stable upon cycling (up to 73% and 89% capacitance retention after 1,000 cycles, respectively) than their BTT counterparts.

(a)

(b)
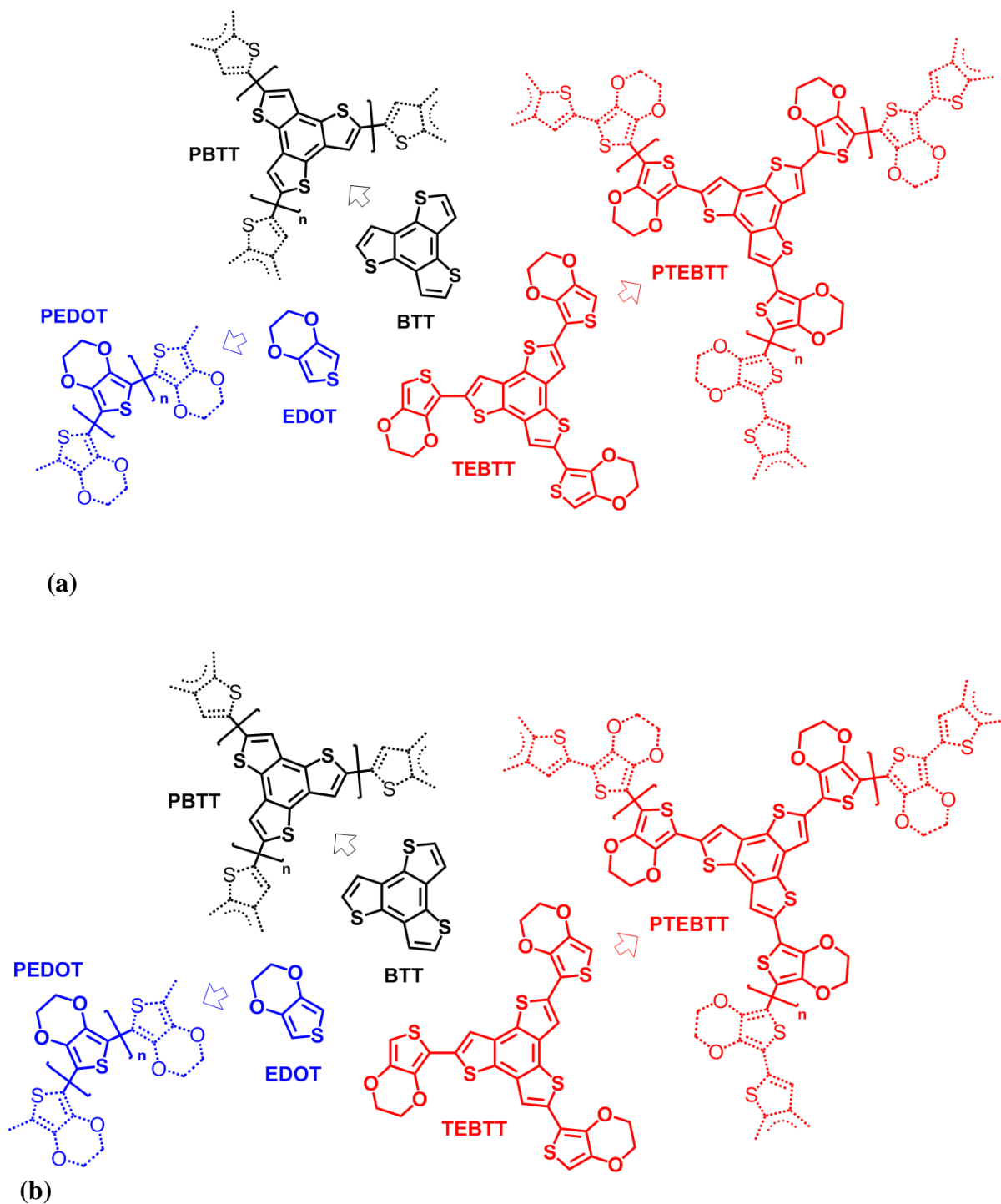
Figure 2.1 (a) Schematic representation of 3,4-ethylenedioxythiophene (EDOT), benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene (BTT), tris-EDOT-benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene (TEBTT), and their respective polymers (PEDOT, PBTT, and PTEBTT).

(**b**) Schematic representation of the random copolymerization of BTT and TEBTT with EDOT.

2.2.1 Experimental Section

2.2.1.1 Synthetic Procedures

Benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene[83] (BTT) and tris-EDOT-benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene[86] (TEBTT) were synthesized in the lab. All monomers were characterized by ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) on a Bruker Advance III Ultrashielded 400 Plus instrument at room temperature. The ^{1}H, ^{13}C spectra were referenced according to the tetramethylsilane (TMS) internal standards. High-resolution mass spectrometry (HRMS) data was recorded using an LTQ Orbitrap Velos MS (Thermo Fisher Scientific) in the positive atmospheric pressure photoionization (+APPI) mode. Elemental analyses were performed on a Flash 2000 - Thermo Scientific CHNO Analyzer.

2.2.1.2 Electrochemical Measurements

The electrochemical characterizations were performed in a standard three-electrode cell placed in a nitrogen-filled glovebox to which a Versastat 4 potentiostat/galvanostat (Princeton Instrument) was connected. In all three-electrode cell experiments, a nonaqueous Ag/Ag$^+$ electrode [consisting of a Ag wire immersed in a 10 mM AgNO$_3$ and 100 mM tetrabutylammonium perchlorate (TBAP) solution in acetonitrile (ACN)] was used as the reference electrode, and a platinum wire was used as the counter electrode. All electrolyte solutions were prepared using anhydrous solvents [ACN, dichloromethane

(DCM)] and with 100 mM tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte.

The specific areal capacitance (*Ca*) of electrodeposited polymeric materials was calculated from the charge-discharge curves through the following general equation:[87]

$$Ca = \frac{I* \Delta t}{\Delta V}$$

where *Ca* is expressed in mF cm^{-2} and the constant current (I) is applied in mA cm^{-2}; Δt is the discharging time (in seconds) and ΔV is the potential change (in V).[87] In this report, we discuss and emphasize *Ca* values (as opposed to the specific gravimetric capacitance *Cs*) by using a measurement of the functionalized surface area that is more accurate than measuring the exact mass of the electrodeposited polymeric material.

2.2.1.3 Imaging Characterization

Electrodeposited polymer film morphologies were characterized with a Quanta 600 scanning electron microscope (SEM) (FEI). Prior to imaging the samples, the supporting electrolyte was washed from the electropolymerized thin film by successive rinsing steps in neat ACN, and a 5 nm layer of gold was sputtered onto the polymer films (to minimize charging effects). The SEM was operated at a working distance of 5 mm and an accelerating potential of 10 kV.

2.2.2 Results and Discuss

2.2.2.1 Electrochemical Characterizations of BTT and TEBTT

   Figure 2.2a shows the linear scans in potential and actual onsets of oxidation for BTT, TEBTT, and EDOT (control scan); the various oxidation features observed for BTT and TEBTT on scanning linearly in the -2.0 − +2.5 V potential window (vs. Ag/Ag$^+$) are detailed directly on the plots in **Figure 2.2b** and **Figure 2.2c**, respectively (oxidation potentials taken at the maximum peak height). In all three experiments, a dark electrodeposited film forms on the gold button electrode, indicating that electropolymerization is occurring during linear scans. BTT exhibits three well-pronounced oxidation peaks at +1.28 V (E_{ox1}), +1.59 V (E_{ox2}), and +2.04 V (E_{ox3}). Interestingly, prior studies of BTT-based systems via cyclic voltammetry (CV) have only described one oxidation peak, albeit at different potentials of +1.39 V (vs. Ag/Ag$^+$)[86] and +1.55 V (vs. Ag/Ag$^+$):[85] we note that the oxidation feature observed in the prior study[86] was somewhat broad and likely encompassed oxidation peaks E_{ox1} and E_{ox2} similar to those shown in **Figure 2.2b** (no cyclic voltammogram was provided in the later study). The first oxidation peak seen for BTT (E_{ox1} = +1.28 V) is sharp and has an onset at +1.11 V, on the same order of that observed for EDOT (+1.02 V; **Figure 2.2a**) and similar to that reported for terthiophene (*ca.* +1.0 V; vs. Ag/Ag$^+$).[88, 89] This oxidation onset is, however, significantly lower than that of single-ring thiophene motifs (*ca.* +1.75 V; vs. Ag/Ag$^+$),[89] illustrating how redox potential depends on conjugation length and HOMO-LUMO gap reduction in more extended BTT π-systems.[89] The second and third oxidation features in the linear scan of BTT (E_{ox2} = +1.59 V and E_{ox3} = +2.04 V) suggest a sequential oxidation

of the three thiophene rings of BTT to radical cations, whereby each subsequent oxidation becomes less favored in response to the presence of previously formed positive charges.
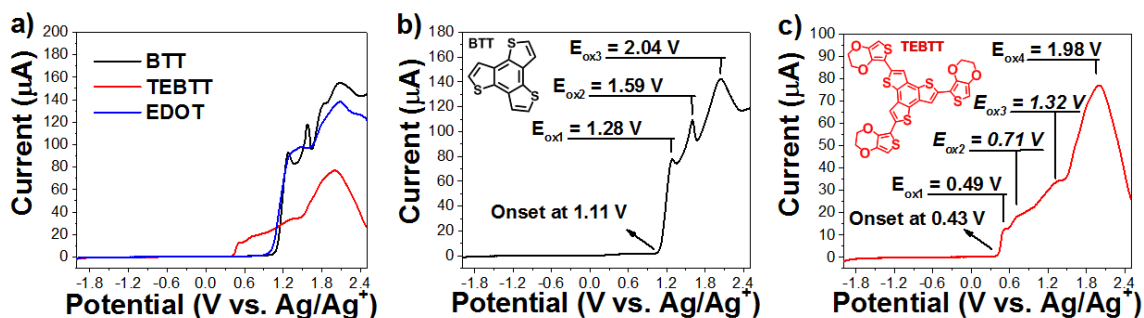
Figure 2.2 (**a**) Linear scan voltammograms collected on gold button electrodes at a scan rate of 20 mV s^{-1} from a solution of BTT (5 mM), TEBTT (1 mM), and EDOT (5 mM) in DCM. (**b, c**) Individual linear scan voltammograms detailing (**b**) BTT's and (**c**) TEBTT's oxidation features; the values italicized point to oxidation features that are not well resolved but occur reproducibly between experiments.

The early oxidation onset of TEBTT (**Figure 2.2c**) at +0.43 V is comparably much lower than that of BTT, which is expected because of the EDOT unit substitution on the BTT core, further extending the π-conjugated motif. Here, the oxidation potential of TEBTT measured by linear scan is lower than that reported in earlier work by CV (+0.78 V; vs. Ag/Ag$^+$),[86] and we note that experimental uncertainties are not uncommon when measuring redox potentials via conventional CV methods. **Figure 2.2c** provides further insight on the consecutive oxidation features in TEBTT, although it should be noted that the second and third oxidation features (E_{ox2} = +0.71 V and E_{ox3} = +1.32 V) are somewhat convoluted in the broad redox response of TEBTT in this voltage window. While the first two oxidation peaks (E_{ox1} = +0.49 V and E_{ox2} = +0.71 V) can be assigned to the oxidation of the EDOT motifs in TEBTT, the third oxidation feature (E_{ox3} = +1.32 V) occurs at a

potential close to that of the first oxidation of the BTT motif (E_{ox1} = +1.28 V; **Figure 2.2b**) and can, therefore, reasonably be assigned to the oxidation of a thiophene ring at the core. Consistent with the oxidation peak attribution in BTT at higher potentials (E_{ox3} = +2.04 V; **Figure 2.2b**), the fourth oxidation feature seen for TEBTT (E_{ox4} = +1.98 V) suggests a sequential oxidation of the other thiophene rings at the core.

2.2.2.2 Copolymerization of BTT and EDOT

Considering the close oxidation potentials of BTT (E_{ox1} = +1.28 V; **Figure 2.2b**) and EDOT (+1.02 V; **Figure 2.2a**), the concurrent electropolymerization of the two motifs can be expected to yield copolymers with random compositions. Because PEDOT is one of the most conductive and capacitive polymers reported to date,[73, 90, 91] copolymers of BTT and EDOT may combine high-capacitance, nanostructured networks that are inherently distinct from those of their respective homopolymers (PBTT and PEDOT). Thus, we examined the electrodeposition of P(BTT/EDOT) copolymers prepared from several monomer solutions of different BTT/EDOT monomer compositions; experiments were performed in ACN on highly porous conducting carbon cloth with a potential window of -0.7–+1.5 V and a scan rate of 50 mV s^{-1} for 20 cycles. The SEM images shown in **Figure 2.3** illustrate the morphologies of the electrodeposited PBTT (**Figure 2.3a**; 1:0 ratio in BTT/EDOT), P(BTT/EDOT) copolymers (**Figure 2.3b-e**; 3:1, 1:1, 1:3, and 1:6 ratios, respectively), and PEDOT (**Figure 2.3f**; 0:1 ratio). Comparing the film depositions achieved in **Figure 2.3a** (PBTT) and **Figure 2.3f** (PEDOT), the contrasts in electrodeposition yields and morphologies formed on the carbon cloth electrodes are rather obvious, and it is interesting to note that BTT may not electropolymerize as efficiently as EDOT in spite of their

comparable onsets of oxidation. This might be explained by the lower conductivity of PBTT compared to PEDOT (although challenging to measure in non-continuous electropolymerized films), which may affect the propensity of the BTT monomer to electropolymerize further once a critical amount of PBTT is deposited on the carbon cloth. In contrast to the dense nodular morphology and large aggregates (700–2,500 nm) obtained on electropolymerizing EDOT (**Figure 2.3f**), sparser aggregates with high aspect ratios are observable for PBTT (width dispersion: 80–160 nm; length: 400–700 nm). Looking at the intermediate morphologies that develop on copolymerizing BTT and EDOT (depicted in **Figure 2.3b-e**), it is worth noting however that electrodeposited films of P(BTT/EDOT) are more densely nanostructured than those of their PBTT counterpart, showing significant differences in aggregate size distributions. In general, blending BTT and EDOT leads to the electrodeposition of aggregate patterns that are somewhat smaller in size (i.e., more nanostructured) compared to PEDOT films and dependent on the initial BTT/EDOT monomer ratios (**Figure 2.3b**, 3:1 ratio in BTT/EDOT, aggregates: 30-300 nm; clusters: 500-1,000 nm; **Figure 2.3c**, 1:1 ratio in BTT/EDOT, clusters: 400-2,000 nm; **Figure 2.3d**, 1:3 ratio in BTT/EDOT, aggregates: ca. 40 nm; clusters: 1,000-2,000 nm; **Figure 2.3e**, 1:6 ratio in BTT/EDOT, clusters: 200-1,400 nm).
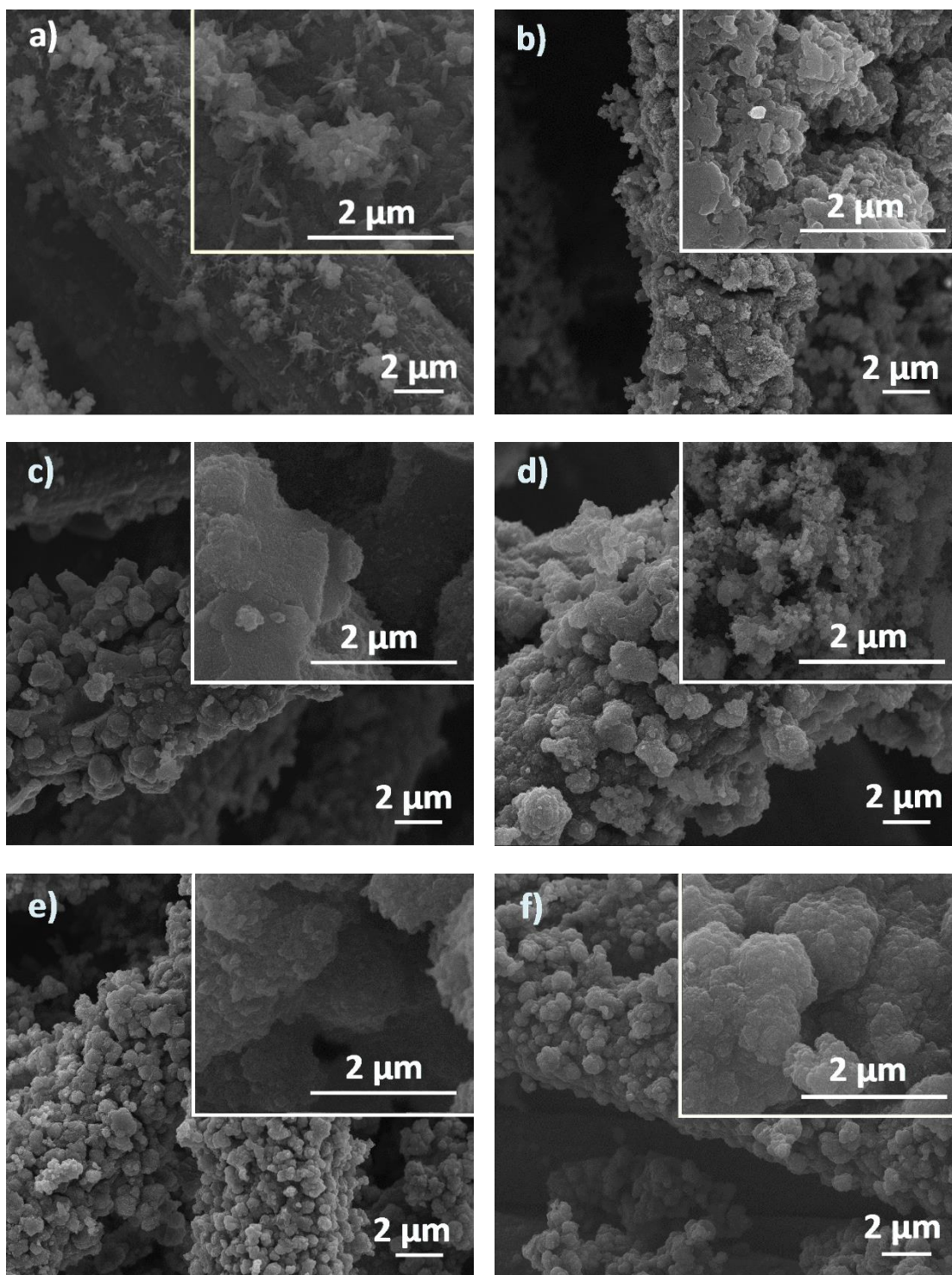
Figure 2.3 SEM images of the morphologies of electrodeposited polymer films prepared from several monomer solutions of different BTT/EDOT monomer compositions: (**a**) 1:0, (**b**) 3:1, (**c**) 1:1, (**d**) 1:3, (**e**) 1:6, and (**f**) 0:1. Electrodeposition conditions: 50 mM monomer

solutions in ACN; 20 deposition cycles in a voltage window of -0.7 − +1.5 V (vs. Ag/Ag$^+$), on carbon cloth electrodes; deposition scan rate of 50 mV s^{-1}.

2.2.2.3 Electroactivity and Capacitive Properties of PBTT, PEDOT and P(BTT/EDOT)

The electroactivity and capacitive properties of PBTT, PEDOT, and the P(BTT/EDOT) copolymers were measured by CV; the corresponding voltammograms are shown in **Figure 2.4a-b**. For ease of comparison, each voltammogram is normalized to the extent of functionalized surface area, and in **Figure 2.4c** the areal capacitance (*Ca*) of the electrodeposited polymers is extracted from galvanostatic charge-discharge measurements (the values are shown directly on the plot). By comparing all electrodeposited systems in **Figure 2.4**, we note that PBTT homopolymers exhibit only a modest capacitance value of 73 mF cm^{-2} (at 5 mA cm^{-2}), which is consistent with the lack of reversibility of the broad redox process in the 0.0 to +0.8 V voltage window and with the smaller amount of material deposited on the carbon cloth electrode (**Figure 2.3a**). It is interesting to note, however, that considering recently published studies on electropolymerized material systems for supercapacitor applications,[59, 90, 92, 93] *Ca* values >50 mF cm^{-2} inferred for PBTT remain significant. For comparison, polypyrrole/graphene oxide nanocomposites have been shown to yield 22.8 mF cm^{-2} (at 0.1 mA cm^{-2}),[93] while poly(3,4-propylenedioxypyrrole/SWCNT composites attain 16.4 mF cm^{-2} (at 0.9 mA cm^{-2});[92] capacitance values that are expected to drop significantly at higher current densities, such as those at which we estimate the capacitance of PBTT (i.e., 5 mA cm^{-2}).

Following the same experimental conditions as those used for the electrodeposition of PBTT, PEDOT-functionalized carbon cloth electrodes yield *Ca* values of 733 mF cm^{-2} (at 5 mA cm^{-2}), confirming that PBTT homopolymers perform more modestly than PEDOT. Here again, these differences may arise from the lower electronic conductivity of PBTT compared to PEDOT, noting that the thiophene rings in BTT motifs are not in direct conjugation because the central phenyl interferes with the conjugation path between thiophenes. The significant voltage drops (IR-drop) visible in **Figure 2.4c** (2x that seen for PEDOT electropolymerized in the same conditions) reflect energy losses due to internal resistance in films of electrodeposited PBTT, further supporting the argument consistent with the idea that PBTT films may be less conductive than those of PEDOT. It should also be noted that the occurrence of α-β and β-β side-couplings in unsubstituted thiophene-based motifs subjected to electrochemical and oxidative polymerization conditions are known to affect conjugation, and subsequently lower the conductivity, electrochemical cycling stability, and capacitive performance of thiophene-based polymers.[89, 94, 95] In parallel, and as shown in **Figure 2.4**, the capacitive cycles of the several P(BTT/EDOT) copolymers (see **Figure 2.1b**) electrodeposited and characterized by CV reflect redox behaviors that are somewhat intermediate between those of PBTT and PEDOT. A similar pattern is observed for areal capacitance values, suggesting that long segments of the two homopolymers formed on the carbon cloth electrode.

Figure 2.4 (**a, b**) Cyclic voltammograms of electrodeposited PBTT, PEDOT, and several P(BTT/EDOT) copolymers prepared from several solutions of different BTT/EDOT monomer compositions: 1:0 (black), 3:1 (red), 1:1 (blue), 1:3 (magenta), 1:6 (green), and 0:1 (dark blue) at a scan rate of 20 mV s^{-1}. Electrodeposition conditions: 50 mM monomer solutions in ACN; 20 deposition cycles in a voltage window of -0.7 − +1.6 V (vs. Ag/Ag$^+$), on carbon cloth electrodes; deposition scan rate of 50 mV s^{-1}. Each voltammogram is normalized to the extent of functionalized surface area. (**c**) Galvanostatic charge-discharge curves collected for the polymers at a current density of 5 mA cm^{-2}; the areal capacitance values inferred are indicated on the plot.

As an alternative to BTT, and to mitigate the probability of α-β and β-β side-couplings between the thiophene moieties, we turn to the TEBTT motifs, where EDOT units were appended to the BTT core, extending the conjugation of the π-system and further reducing its HOMO/LUMO gap. As a result, and as previously discussed from **Figure 2.2c**, TEBTT exhibits a lower oxidation potential (E_{ox1} = +0.49 V). Because TEBTT is a more extended π-conjugated system, it is only moderately soluble in ACN, but its solubility was found sufficient in DCM (solubility up to 1.25 mM), and the later was used for the electrochemical polymerization of all TEBTT-based polymers. Next, the electrodeposited films were carefully rinsed with DCM and characterized in ACN for consistency with the characterization protocol used for all BTT-based polymers.

First, we studied the optimal conditions for the electrochemical deposition of PTEBTT as a function of voltage window, cycle number, and working electrode with the goal of achieving the best possible *Ca* values. The corresponding experimental conditions and obtainable *Ca* values are summarized in **Table 2.1**. **Figure 2.5a** shows the CV curves of PTEBTT films electrodeposited on various working electrodes and voltage windows. In contrast to the lack of reversibility of the broad redox process previously discussed for PBTT, the redox processes for PTEBTT were found to be inherently more reversible (see **Figure 2.6**). As emphasized in **Table 2.1** and **Figure 2.5a**, a voltage window of -0.2–+0.8 V was found optimal for PTEBTT with respect to the *Ca* performance values. The choice of the working electrode (WE) was also found to be an important parameter, with glassy carbon (GC) button electrodes producing polymer films that are electroactive and reversibly cycled over a broader voltage range, suggesting a more adhered, more densely electropolymerized polymeric network (found to yield higher *Ca* values). In contrast,

attempts to electrodeposit TEBTT on carbon cloth and indium tin oxide (ITO) electrodes did not yield comparably promising results and thus, were not pursued further. Furthermore, because films electrodeposited via alternative deposition techniques such as potentiostatic and pulsed potentiostatic techniques showed only modest capacitive characteristics, we concentrated on CV protocols (**Table 2.1**). PTEBTT films electrodeposited on the GC electrode exhibit an oxidation onset at +0.20 V (**Figure 2.5a**) and a broad quasi-reversible redox couple (E_{ox1} = +0.62 V − E_{red1} = +0.27 V) followed by an irreversible oxidation (and related reduction E_{red2} = +0.69 V on the reverse cycle). The SEM image in **Figure 2.6a** shows a distinctly structured morphology on micron-sized fibers densely distributed across the GC surface (width dispersion: 150-200 nm; length: 1,200-1,600 nm) accompanied by some nodular aggregates (800-1,600 nm). From the optimized conditions (WE: glassy carbon button electrode, voltage window: -1.0–+1.2 V, scan rate: 50 mV s^{-1}), we studied the dependence of the capacitive response of PTEBTT as a function of the number of electrodeposition cycles and the scan rate; the corresponding CV curves are shown in **Figure 2.5b-c**. Overall, with PTEBTT, *Ca* values are found to increase with the number of electrodeposition cycles as more electroactive material is deposited on the GC electrode, reaching areal capacitance values as high as 271.1 mF cm^{-2} (1 mA cm^{-2}) after 120 cycles, which represents a 10-fold improvement compared to PBTT. In addition to the high *Ca* values achieved, **Figure 2.5b-c** emphasize the reversibility of the first redox couple in PTEBTT, which is maintained for films obtained over large numbers of deposition cycles (up to 120 shown in **Figure 2.5b**) and for films cycled over a wide range of scan rates (**Figure 2.5c**). These results indicate that films of electropolymerized PTEBTT are not limited by electronic conductivity or electrolyte

diffusion aspects. As illustrated in **Figure 2.5c**, the redox peak intensities (anodic, I_{pa}, and cathodic, I_{pc}) for electrodeposited films of PTEBTT were found to vary linearly with the square root of the scan rate (correlation factors given in inset), consistent with a reversible system.[96] The interpolations calculated give $I_{pa} = -0.13(3)\ v^{1/2} + 2.26(4)$ and $I_{pc} = -0.21(2)$ $v^{1/2} - 1.63(3)$ with v representing the scan rate investigated.
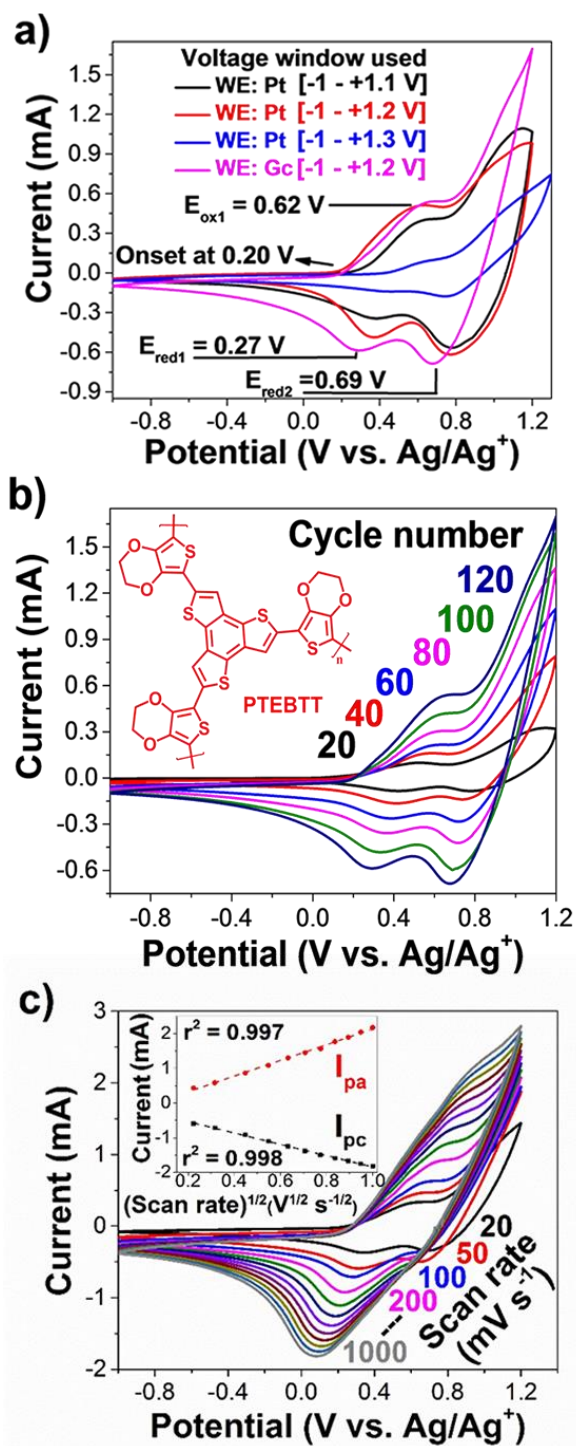
2.2.2.4 Copolymerization of TEBTT and EDOT

Figure 2.5 (**a**) Cyclic voltammograms of PTEBTT films electropolymerized on various

working electrodes and voltage windows (collected in ACN). Electrodeposition conditions:

1 mM monomer solutions in DCM; 120 deposition cycles; deposition scan rate of 50 mV

s^{-1}. (**b**) Cyclic voltammograms of PTEBTT films on glassy carbon button electrodes as a

function of the number of electrodeposition cycles (collected in ACN). Electrodeposition

conditions: 1 mM monomer solutions in DCM; 120 deposition cycles in a voltage window

of -1.0 – +1.2 V (vs. Ag/Ag$^+$); deposition scan rate of 50 mV s^{-1}. (**c**) Cyclic voltammograms

of PTEBTT films on glassy carbon button electrodes as a function of scan rate (collected

in ACN). Electrodeposition conditions: 1 mM monomer solutions in DCM; 20 deposition

cycles in a voltage window of -1.0 – +1.2 V (vs. Ag/Ag$^+$); deposition scan rate of 50 mV

s^{-1}. Inset: anodic (I_{pa}) and cathodic (I_{pc}) current intensity variations of the first redox couple

of PTEBTT as a function of the square root of the scan rate.
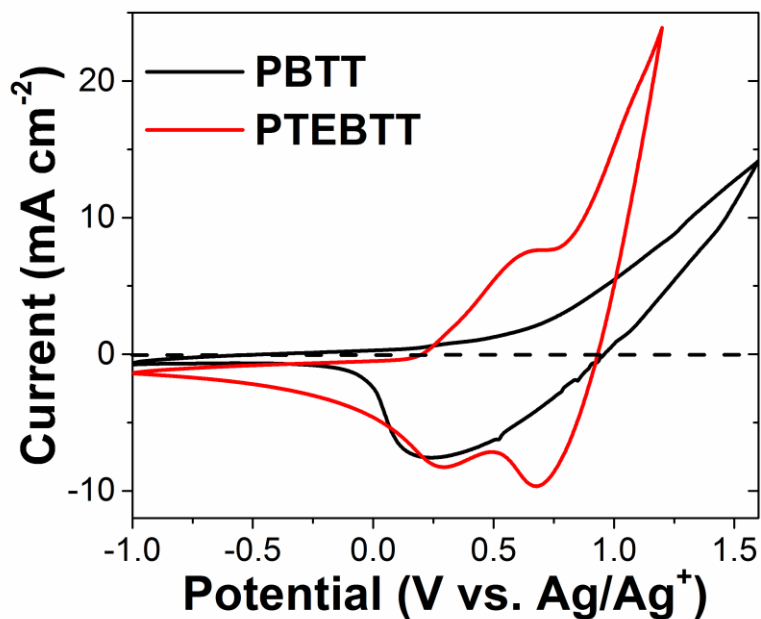

Figure 2.6 Cyclic voltammograms of electrodeposited PBTT and PTEBTT.

Electrodeposition conditions of PBTT: scan rate of 50 mV s^{-1}, 20 cycles, voltage window

-0.7–+1.6 V (vs. Ag/Ag$^+$), 50 mM monomer in ACN. Electrodeposition conditions of

PTEBTT: scan rate of 50 mV s^{-1}, 120 cycles, voltage window -1.0–+1.2 V (vs. Ag/Ag$^+$), 1 mM monomer in DCM. Each voltammogram is normalized to the extent of functionalized surface area.

Table 2.1 Summary of electrodeposition conditions for PTEBTT, PEDOT, and several P(TEBTT/EDOT) copolymers prepared from several solutions of different TEBTT/EDOT monomer compositions (in DCM) and the associated areal capacitance (*Ca*) values on various working electrodes (WE). Experimental details: deposition scan rate of 50 mV s^{-1}; all measurements performed in ACN.

Monomer Solution Composition / Concentration	WE	Condition of Electrodeposition	Time/Number of Deposition Cycles	*Ca* (mF cm^{-2})	Conditions of Measurement
TEBTT/EDOT 1:0 1 mM	Pt	Potentiostatic I = 1.2 V	20 min 40 min 50 min	15.6 mF cm^{-2} 44.6 mF cm^{-2} 21.3 mF cm^{-2}	1 mA cm^{-2} between [0 – 0.8 V]
TEBTT/EDOT 1:0 1 mM	Pt	Pulsed potentiostatic I$_1$ = 1.2 V (1s) I$_2$ = - 1.0 V (2s)	600 (I$_1$ - I$_2$) 1200 (I$_1$ - I$_2$) 1800 (I$_1$ - I$_2$)	40.6 mF cm^{-2} 45.3 mF cm^{-2} 44.1 mF cm^{-2}	1 mA cm^{-2} between [0 – 0.8 V]
TEBTT/EDOT 1:0 1 mM	Pt	Cycling [-1 – 1.1 V]	40 cycles 80 cycles 120 cycles	41.6 mF cm^{-2} 124.0 mF cm^{-2} 184.5 mF cm^{-2}	1 mA cm^{-2} between [0 – 0.8 V]
TEBTT/EDOT 1:0 1 mM	Pt	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	61.0 mF cm^{-2} 141.0 mF cm^{-2} 186.0 mF cm^{-2}	1 mA cm^{-2} between [0 – 0.7 V]
TEBTT/EDOT 1:0 1 mM	Pt	Cycling [-1 – 1.3 V]	40 cycles 80 cycles 120 cycles	20.6 mF cm^{-2} 55.0 mF cm^{-2} 17.9 mF cm^{-2}	1 mA cm^{-2} between [0 – 0.8 V]
TEBTT/EDOT 1:0 1 mM	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	29.5 mF cm^{-2} 99.0 mF cm^{-2} 271.1 mF cm^{-2}	1 mA cm^{-2} between [0 – 0.8 V]
TEBTT/EDOT 3:1 1 mM	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	53.7 mF cm^{-2} 193.6 mF cm^{-2} 323.4 mF cm^{-2}	1 mA cm^{-2} between [-0.2 – 0.8 V]
TEBTT:EDOT 1:1 2.5 mM	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	139.0 mF cm^{-2} 383.8 mF cm^{-2} 443.8 mF cm^{-2}	1 mA cm^{-2} between [-0.2 – 0.8 V]
TEBTT:EDOT 1:3	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles	99.8 mF cm^{-2} 127.1 mF cm^{-2}	1 mA cm^{-2}

5 mM			120 cycles	356.7 mF cm^{-2}	between [-0.2 – 0.8 V]
TEBTT:EDOT 1:9 5 mM	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	59.0 mF cm^{-2} 127.1 mF cm^{-2} 218.0 mF cm^{-2}	1 mA cm^{-2} between [-0.2 – 0.8 V]
TEBTT:EDOT 5:95 5 mM	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	57.7 mF cm^{-2} 125.7 mF cm^{-2} 189.3 mF cm^{-2}	1 mA cm^{-2} between [-0.2 – 0.8 V]
TEBTT:EDOT 0:1 5 mM	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	24.0 mF cm^{-2} 40.3 mF cm^{-2} 55.9 mF cm^{-2}	1 mA cm^{-2} between [-0.2 – 0.8 V]
TEBTT:EDOT 0:1 1 mM	GC	Cycling [-1 – 1.2 V]	120 cycles	12.1 mF cm^{-2}	1 mA cm^{-2} between [0.1 – 0.8 V]

Pt: platinum button electrode; GC: glassy carbon electrode.
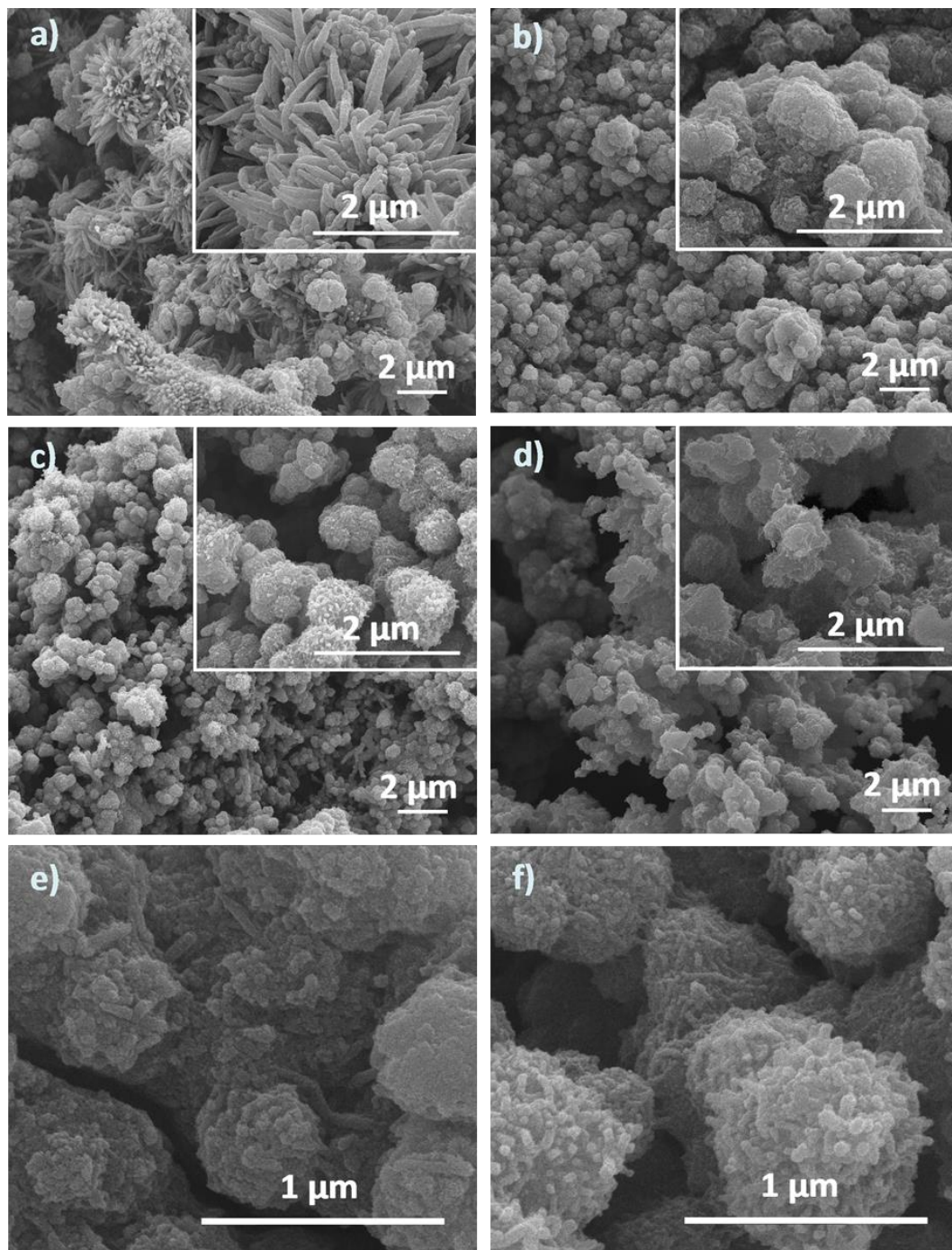
Figure 2.7 SEM images of the morphologies of electrodeposited polymer films prepared from several monomer solutions of different TEBTT/EDOT monomer compositions: (**a**) 1:0, (**b**, **e**) 1:1, (**c**, **f**) 1:9, and (**d**) 0:1. Electrodeposition conditions: 1 mM monomer

solutions in DCM; 120 deposition cycles in a voltage window of -1.0 − +1.2 V (vs. Ag/Ag$^+$), on glassy carbon button electrodes; deposition scan rate of 50 mV s^{-1}.

Following the conditions of electropolymerization employed earlier in ACN, now applied in DCM, films of electrodeposited PEDOT yield lower *Ca* values (**Table 2.1**) than those obtained earlier from ACN: PEDOT electrodeposited on carbon cloth from 1 mM and 5 mM monomer solutions yield capacitance values of *ca.* 12 mF cm^{-2} and *ca.* 55 mF cm^{-2} (at 1 mA cm^{-2}), respectively (**Table 2.1**). These lower *Ca* values may result from the lower propensity of the monomer to undergo electropolymerization in the lower dielectric constant solvent DCM ($\varepsilon = 8.9$)[97] (ACN: $\varepsilon = 36.6$),[97] combined with the effect of using a WE that is inherently less porous (on going from carbon cloth to the GC button electrode).[98, 99] The SEM image in **Figure 2.7d** shows aggregate patterns in a relatively wide size distribution (650-1,000 nm) spread across films that are several micrometers thick.

Next, we prepared P(TEBTT/EDOT) copolymers by electrodepostion from several solutions of different TEBTT/EDOT monomer compositions; electrodeposition conditions: 1 mM monomer solutions in dichloromethane (DCM); 120 deposition cycles in a voltage window of -1.0 − +1.2 V (vs. Ag/Ag$^+$), on glassy carbon (GC) button electrodes; deposition scan rate of 50 mV s^{-1}. As depicted by the SEM images shown in **Figure 2.7b** and **Figure 2.6c**, the P(TEBTT/EDOT) copolymers exhibit morphologies that are fairly distinct from those of their homopolymer counterparts, PTEBTT and PEDOT. In particular, the higher-magnification SEM images shown in **Figure 2.7e-f** indicate that the aggregate patterns formed are highly nanostructured (**Figure 2.7b&e**, 1:1 ratio in

TEBTT/EDOT, aggregates: <100 nm; clusters: 500-1,200 nm; **Figure 2.7c&f**, 1:9 ratio in

TEBTT/EDOT, aggregates: <50 nm; clusters: 600-1,000 nm). Here, we note that the dense,

highly textured hierarchical P(TEBTT/EDOT) networks formed are consistent with the

values of high areal capacitance given in **Table 2.1**. The CV curves of the electrodeposited

P(TEBTT/EDOT) polymers shown in **Figure 2.7a** reflect inherently more capacitive

material systems compared to their homopolymer counterparts, PTEBTT or PEDOT;

observations consistent with the higher *Ca* values obtained for the copolymers and

summarized in **Table 2.1**, reaching up to 443.8 mF cm^{-2} (at 1 mA cm^{-2}) (1:1 ratio in

TEBTT/EDOT). In particular, copolymers that result from the addition of only 5 mol.% of

TEBTT in the initial TEBTT/EDOT monomer solution exhibit significantly higher *Ca*

values compared to PEDOT: 189 mF cm^{-2} vs. 12 mF cm^{-2} (at 1 mA cm^{-2}), respectively,

representing a ca. 15-fold capacitance increase. These results suggest that TEBTT motifs

play a critical role in the development of open, hierarchical morphologies required to

maximize areal capacitances and promote electrolyte diffusion in conventional

electropolymerized π-conjugated systems such as PEDOT. **Figure 2.8** also shows how the

capacitive cycles of the several P(TEBTT/EDOT) copolymers electrodeposited and

characterized by CV reflect redox behaviors that are not intermediate between those of

PTEBTT and PEDOT—an observation that points to a random integration of TEBTT and

EDOT monomers during the electropolymerization step.

    Figure 2.8b-c depict the areal capacitance of PTEBTT, PEDOT, and the

P(TEBTT/EDOT) copolymers obtained from the electropolymerization of several

TEBTT/EDOT monomer compositions (3:1, 1:1, 1:3, and 1:9 ratios) as a function of

current density (**Figure 2.8b**) and cycle number (**Figure 2.8c**). It is interesting to note that

several P(TEBTT/EDOT) copolymers (1:1, 1:3, and 1:9 ratios) undergo only little capacitance variations with current density increments, suggesting excellent electrolyte diffusion within the highly porous P(TEBTT/EDOT)-based frameworks. **Figure 2.8c** shows that films of electrodeposited PTEBTT are relatively resilient to repeated electrochemical cycling with *ca.* 73% of capacitance retained (at 2 mA cm^{-2}) over 1,000 cycles (vs. 96% for PEDOT over 1,000 cycles (at 2 mA cm^{-2}). Here, we note that our estimate of the stability of the homopolymer PTEBTT is on the low end of the capacitance retention reported in prior work (ca. 95% over 1,400 cycles),[86] a difference that is likely to stem from the significantly thicker films examined in this study: PTEBTT is electrodeposited in 120 cycles between -1.0 and +1.2 V vs. only 8 cycles between 0.0 and +1.0 V in earlier work.[86] Likewise, all of the P(TEBTT/EDOT) copolymers show >70% of capacitance retention (at 2 mA cm^{-2}) over 1,000 cycles (with up to ca. 89% achieved), demonstrating satisfying long-term stability upon repeated electrochemical cycling. These stability figures, ranging between those of PTEBTT and PEDOT, are greater than those reported for some of the more conventional conjugated polymers such as 50% capacitance retention over 1,000 cycles (at 2 mA cm^{-2}) for polypyrrole,[65] 84% capacitance retention after 200 cycles for poly(3-methylthiophene) (longer cycling times not provided), and 70% capacitance retention after 1,000 cycles for PANI.[26, 65] Last, we note that the mechanical stability and long-term cycling performances of the P(TEBTT/EDOT)-based frameworks may be further improved in hybrid carbon-based composite systems including carbon nanotubes or graphene oxide; however this falls beyond the scope of this report.[66]
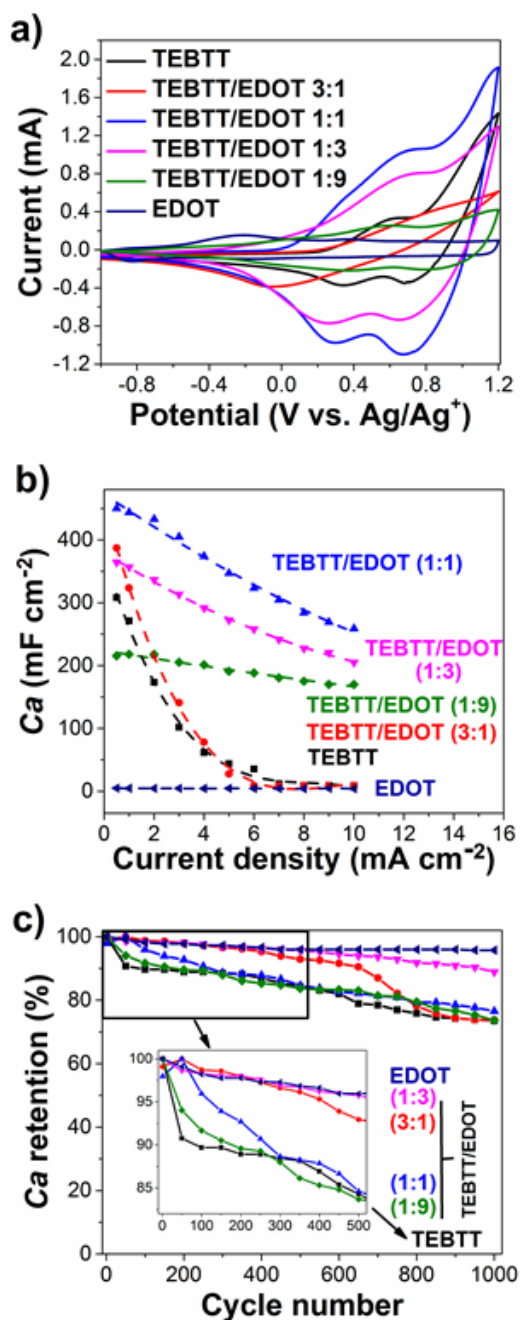
Figure 2.8 (**a**) Cyclic voltammograms of electrodeposited PTEBTT, PEDOT, and several P(TEBTT/EDOT) copolymers prepared from several solutions of different TEBTT/EDOT monomer compositions: 1:0 (black), 3:1 (red), 1:1 (blue), 1:3 (magenta), 1:9 (green), and 0:1 (dark blue); curves collected at a scan rate of 20 mV s^{-1}.

Electrodeposition conditions: 1 mM monomer solutions in DCM; 120 deposition cycles in a voltage window of -1.0 – +1.2 V (vs. Ag/Ag$^+$), on glassy carbon button electrodes; deposition scan rate of 50 mV s^{-1}. (**b**) areal capacitance vs. current density increments for several P(TEBTT/EDOT) copolymers. (**c**) areal capacitance vs. cycle number for several P(TEBTT/EDOT) copolymers (at 2 mA cm^{-2}).

2.2.3 Conclusion

In summary, we have shown that high-surface-area π-conjugated polymeric networks can be synthesized via the electrochemical copolymerization of the 2D (trivalent) motifs benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene (BTT) and tris-EDOT-benzo[1,2-*b*:3,4-*b*':5,6-*b*'']trithiophene (TEBTT) with EDOT. Of all the material systems studied, P(TEBTT/EDOT)-based frameworks achieved the highest areal capacitance with values as high as 443.8 mF cm^{-2} (at 1 mA cm^{-2}), higher than those achieved by the respective homopolymers (PTEBTT and PEDOT) in the same experimental conditions of electrodeposition (PTEBTT: 271.1 mF cm^{-2} (at 1 mA cm^{-2}); PEDOT: 12.1 mF cm^{-2} (at 1 mA cm^{-2}). The high areal capacitance achieved with P(TEBTT/EDOT) copolymers—with up to *ca.* 30-fold capacitance increases compared to PEDOT—can be related to the open, highly porous hierarchical π-conjugated frameworks formed during the electropolymerization step. We find that both PTEBTT- and P(TEBTT/EDOT)-based frameworks are resilient to repeated electrochemical cycling, maintaining >70% capacitance over 1,000 cycles (up to 89% achieved), making them promising systems for high life cycle capacitive electrode applications. Lastly, the use of 2D motifs such as TEBTT in the synthesis of electropolymerized hierarchical π-conjugated frameworks with

particularly high areal capacitance may be applicable to other established capacitive polymeric systems such as polythiophenes, polypyrrole, and PANI.

Chapter 3

How Doping Influences EDOT and its Derivative's Electrochemical Properties – the role of anions in the Electropolymerization process

3.1 Introduction and Background

Besides tremedous interests and potentials in investigations of organic devices from energy harvesting[53] to electrochromic displays,[54, 100] electroactive conjugated polymers (ECPs) are emerging as attractive candidates for electrochemical energy storage applications.[6, 55] This is contributed to their good intrinsic conductivity in the doped state,[56, 57] much lower band gaps compared with conventional polymers (10 eV),[54] relatively fast doping and undoping process, the ease of synthesis, and tunable electronic and structural properties through structural modifications[26, 58, 59] and high specific capacitances.[63]

In electrochemical process, the suitable choice of appropriate electrolytes to enlarge the safe working potential window with electrolyte stability is well known to improve ECPs' performance in ESCs applications. Ionic liquids (ILs) are ion composed salts and usually fluid over a wide temperature range with low melting points. Protected with inert gas to
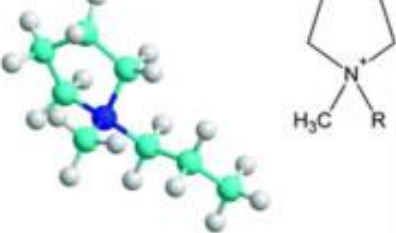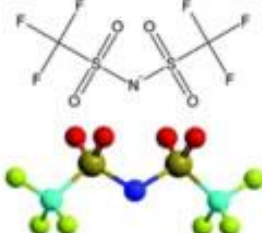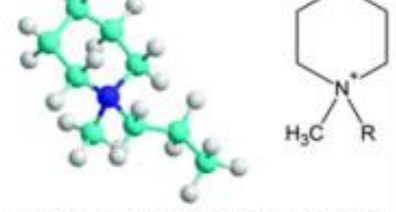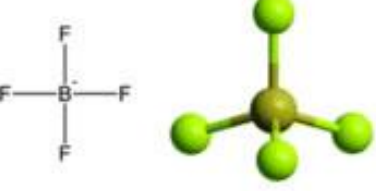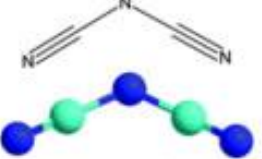
avoid the gaseous products generated at cathode and anode, the working potential window when ILs is used as supporting electrolyte can be improved by almost 1.5–2 times than that of aqueous electrolytes with acid-base [101] ILs have been applied as supporting medium for various devices and materials processing applications in both industry and academia, overcoming the limitation of volatile organic compounds (VOCs).[102-104] Especially, ILs have been utilized as superior medium to electrodeposit metals, alloys, semiconductors and ECPs in the application of supercapacitors.[105-108] This is mainly contributed to their unique characteristics including intrinsic ion and high ionic conductivity, broad electrochemical voltage windows in neutral conditions, instant ion mobility during redox reaction processes, extremely low vapor pressure, environmental stability; [103, 106, 107, 109, 110] and numerous, however partly understood, cation/anion effects plays a role to influence the hierachical morphology and particle size of deposits.

It is well known that for an IL, the size and symmetry of cation plays an important role for its physical properties (e.g. melting point) whereas the anion has more influence towards its stability and chemical reactivity.[107] Due to the combinations of various cations and anions, there is a plethora of different ILs already available and can still be a tremendous long list of potential ILs, the ionic structures and properties of which can be designed and adjusted artificially to accommodate different purposes and applications.[104, 107] Considering the usage of ILs for the ECPs synthesis, there has been some investigations based on relative small varieties of ILs. The magnitude of the cation can be adjusted accordingly by tailoring the alkyl substituent's chain length. Usually, planar aromatic cations, represented by imidazolium is preferred rather than its analogues with non-planar configurations which can be pyrrolidinium, due to the enhanced cation intercalation,

superior fluidity and conductivity of the plane configuation.[106, 111] **Table 3.1** shows the range of nitrogen-based cations which are commonly used. Also, during the polymer growth process and electrochemical cycling, it is interesting to note that the nature of these anions can act as dopants, which play a role in the extent of their intercalation into the polymers.[106] Together with doping effect of anions, it is possible that cation/anion is able to influence the polymer's crystal size and as a consequence the morphology of those deposits, which plays a crucial role for the overall electroactive performance of ECP. Motivation for the use of PTh instead of PAn or PPy in supercapacior application stems from the fact that a relative broader potential window (~1.2 V) can be achieved with PTh, as most of these can be n- and p-doped because of a smaller band gap.[112, 113] Amongst PTh-based organic conducting polymers, poly (3,4-ethylenedioxythiophene) (PEDOT) and its derivatives have been explored as a most popular and extensively studied electroactive material due to their high electrochemical stability and fast cycle switching speed.[100, 114] Polythiophene, as well as substituted polythiophenes, have been synthesized by electrochemical polymerization and characterized in ILs, containing Trifluoromethanesulfonate [OTf]-, hexafluorophosphate [PF$_6$]-, sulfonated aromatics or bis(trifluoromethanesulfonyl)amide [NTf$_2$]- anions and so on, to yield significant increased currents and higher stability than carried out in common organic solvents dissolving conducting salts, making them of tremendous interest for electrochemical supercapcitor.[106, 108, 111, 115-122] Electropolymerization of thiophenes have been studied in imidazolium or pyrrolidinium-based ionic liquids as the growth medium and the supporting electrolyte, to assess the influence of the anions on morphology formation and electrochemical activity of these conducting polymers.[111, 119] However, there is no systematic study on how the

anions of ILs and common organic solution with salt could play a role as a medium both for polymerization and post-polymerization electrolyte for PEDOT and PEDOT-similarity. Here we put an effort to study the electrochemical behavior of PEDOT in ILs for fundamental investigation. There is tremendous potential to clarify the role of the separate anions and cations and how they would affect the electrochemical behavior of electroactive polymers. In this study, imidazolium-based ionic liquids with three different types of anions which are 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]), 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][TfO]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) were used as growth medium and supporting electrolyte to assess the influence of the nature of these anions on the morphology and electrochemical activity of PEDOT. It is found PEDOT produced in ILs shows much slower growth rate and orderly morphologies than grown in an organic electrolyte with $TBPPF_6$. Some CVs of the polymers show multiple redox peaks, the possible reasons and origins are discussed. The synthesized polymer can be affected greatly by both the ILs with different anion/cation, and its mutal interation with targeted monomer. The same protocol has been carried out for a PEDOT-similarity, which is 4,4'-dimethoxy-3,3'-bithiophene (BEDOT). It can be pertinent to refer to this study when designing suitable ionic liquids for PEDOT and its analogues for investigation and optimization of electrochemical systems, such as batteries and supercapactiors.

Table 3.1 A selection of cations and anions used to make ionic liquids.

Cations	Anions
N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium, [DEME]⁺	Bis(fluorosulfonyl)imide, [FSI]⁻
N-methyl-N-alkyl pyrrolidinium, [CₙmpyrⳠ)	Bis(trifluoromethanesulfonyl)amide, [NTf₂]⁻
N-methyl-N-alkyl piperidinium, [Cₙmpip]⁺	Tetrafluoroborate, [BF₄]⁻
1-alkyl-3-methylimidazolium, [Cₙmim]⁺ R=Et [emim]⁺ R=Bu [bmim]⁺ R=Hex [hmim]⁺	Dicyanamide, [dca]⁻

* R groups – typically ethyl, propyl, butyl.

3.2 The Study on Electropolymerization of EDOT and BEDOT and the Post-polymerization Electrochemical Properties

3.2.1 Experimental Section

3.2.1.1 Synthetic Procedures

4,4'-dimethoxy-3,3'-bithiophene (BEDOT) were synthesized in the lab. All monomers were characterized by ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) on a Bruker Advance III Ultrashielded 400 Plus instrument at room temperature. The ^{1}H, ^{13}C spectra were referenced according to the tetramethylsilane (TMS) internal standards. High-resolution mass spectrometry (HRMS) data was recorded using an LTQ Orbitrap Velos MS (Thermo Fisher Scientific) in the positive atmospheric pressure photoionization (+APPI) mode. Elemental analyses were performed on a Flash 2000 - Thermo Scientific CHNO Analyzer.

3.2.1.2 Electropolymerization Procedure and Electrochemical Measurements

All electrochemical measurements were performed in a standard three-electrode cell which is connected with a Versastat 4 potentiostat/galvanostat (Princeton Instrument). Carbon paper (CP) was cut into strips and sonicated in ethanol, afterwards dried overnight at 60 ^{o}C under vacuum. Each strip was wrapped partially by parafilm with a bare surface area ~0.7×0.7 cm^2 on the front edge. These parafilm covered CP strips were used as working electrode substrates for electrodeposition. A platinum wire was the counter electrode, and the reference electrode was a nonaqueous Ag/Ag+ electrode, consisting of a silver wire immersed in an acetonitrile solution of 10 Mm AgNO3 and 0.1 M

tetrabutylammonium perchlorate (TBAP). Ionic liquids of HPLC grade and 3,4-ethylenedioxythiophene monomers (EDOT, 97%) was purchased from Sigma Aldrich and used as received. In this study, Ionic liquids of 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf$_2$N]), 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim][TfO]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) was used. Anhydrous acetonitrile (ACN) from Sigma Aldrich with 100 mM tetrabutylammonium hexafluorophosphate (TBAPF$_6$) is applied as supporting electrolyte. To investigate the how ILs and organic electrolyte affect the growth and electroactivity of EDOT and its similarity, 25 mM EDOT dissolved in [bmim][Tf$_2$N] or TBAPF$_6$/ACN was applied as the growth medium in a standard three-electrode cell. PEDOT was electro-deposited onto CP electrode by cyclic voltammetry with scanning potential between -1.0 and $+1.2$ V vs. Ag/Ag$^+$ and varied potential cycles (scan rate 50 mV/s). After electrochemical cycling, CP substrate's bare surface uncovered by parafilm was deposited with PEDOT. In order to remove the residues and unreacted monomers, CP substrate was rinsed with dropcasted fresh IL or acetonitrile which is consistent with the growth medium. Either [bmim][Tf$_2$N] or TBAPF$_6$/ACN is used as supporting electrolyte for electrochemical measurements. The same protocol has been carried out for EDOT in [bmim][TfO] and [bmim][PF$_6$]. The presence of oxygen can affect the electrochemical synthesis of a conducting polymer for the possibility to form hydroxide at the electrode and react with radical intermediates of polymers.[106] All of the experiment was carried out in an Ar-protected glovebox.

In the post-polymerization cyclic voltammetric experiments, each electrode was scanned with scan rate of 20 mV/s for three times. In the charge and discharge experiments

the polymer film was cycled three times wthin the potential range consisted with **CV** window.

The areal capacitance (***Ca***) of electrodeposited polymeric materials was calculated from the charge-discharge curves through the following general equation:[87]

$$Ca = \frac{\mathrm{I}^* \, \Delta t}{\Delta V} \; ,$$

where *Ca* is expressed in mF cm^{-2} and the constant current (I) is applied in mA cm^{-2}; Δt is the discharging time (in seconds) and ΔV is the potential change (in V).[87] In this report, we discuss and emphasize *Ca* values (as opposed to the gravimetric capacitance *Cs*) by using a measurement of the functionalized surface area that is more accurate than measuring the exact mass of the electrodeposited polymeric material.

3.2.2 Results and Discussion

3.2.2.1 Electrochemical Polymerization and Characterizations of EDOT

It is widely accepted that the electrochemical performance of ECPs-based supercapacitor can be largely determined by the interaction of the electroactive conjugated polymers with the electron collector. Electron collectors are usually conducting substrate/steel, which can be carbon cloths, carbon fibers, porous carbon papers (CPs). In this experiment, in order to minimize the effect of other parameters, CPs have been chosen as electrode substrate. **Figure 3.1a-d** shows the cyclic voltammograms for increased polymerization cycles at a scan rate of 50 mV/s for CP electrodes in a solution of 25 mM EDOT monomer in ACN containing 100 mM TBAPF$_6$ or pure ILs, which are

[bmim][Tf$_2$N], [bmim][TfO] and [bmim][PF$_6$], respectively. As known, if there are more electroactive materials deposited onto the electrode, there will be higher current signals in correspond with the linearly swept voltage. It can be shown from the cyclic voltammograms of PEDOT electrochemical deposited in these different kinds of ILs or organic electrolyte, that the highest redox currents of polymer was obtained during the deposition in TBAPF$_6$/ACN in **Figure 3.1a**, and the lowest from [bmim][PF$_6$] in **Figure 3.1d**. However, it is also interesting to note that in TBAPF$_6$/ACN, the current density per surface area quickly saturated within the first 40 cycles, and decreased with additional cycles, which indicate PEDOT underwent faster polymerization process compared with ionic liquids until the grown film is too thick. Beside [bmim][PF$_6$], which shows very tiny current density and not significant increase over cycling, PEDOT electropolymerized in [bmim][Tf$_2$N] (**Figure 3.1b**) and [bmim][TfO] (**Figure 3.1c**) shows smooth and continuous increase of current over additional cycles, which may contribute to the slowly and gradually growth of PEDOT in these ILs. In electrochemical polymerization process, the radical coupling and oxidation of monomers took place at the interface of the CP electrode surface and electrolyte where PEDOT deposition were accumulated. Due to the strong electrostatic and other interaction forces, ILs' viscosity is 10 to 100 times higher compared with water and organic solvents, which affects on the diffusion rate within the ILs and results in the smaller diffusion coefficients and lower ionic conductivity.[104] Hence, it is reasonable to envision viscosity of ILs can also play a significant role in the electrochemical polymerization process. According to diffusion rates, it could be expected that in the low viscous organic solvent electrolyte, these accumulated polymers and oligomers near the electrode will be more easily to diffuse away than in ILs species.

Meanwhile, the unreacted monomers are also more flexible to diffuse onto the interfacial place and more materials can be polymerized and deposited. It is speculated ILs with higher viscosity is helpful for further oligomers oxidation and polymers deposition onto the electrode by accumulation, while lower viscosity facilitates fast polymerization to diffuse away into the bulk distributed in the whole medium. It can be observed after the first several cycles that EDOT monomer solution of $TBAPF_6$/ACN turned dark thoroughly while EDOT/IL solution was brown with transparency. ILs composed by larger ions or charge delocalized ions usually have lower viscosity, so ILs with anions such as $(CF_3SO_2)N^-$ and $CF_3SO_3^-$ tend to be more viscous than that of PF_6^-.[106] The viscosities of these imidazolium type ILs is [bmim][Tf_2N] (69 η/cP) < [bmim][TfO] (93 η/cP) < and [bmim][PF_6] (450 η/Cp).[123, 124] The preference of high viscosity is not always the case seen for [bmim][PF_6] and there are other factors.
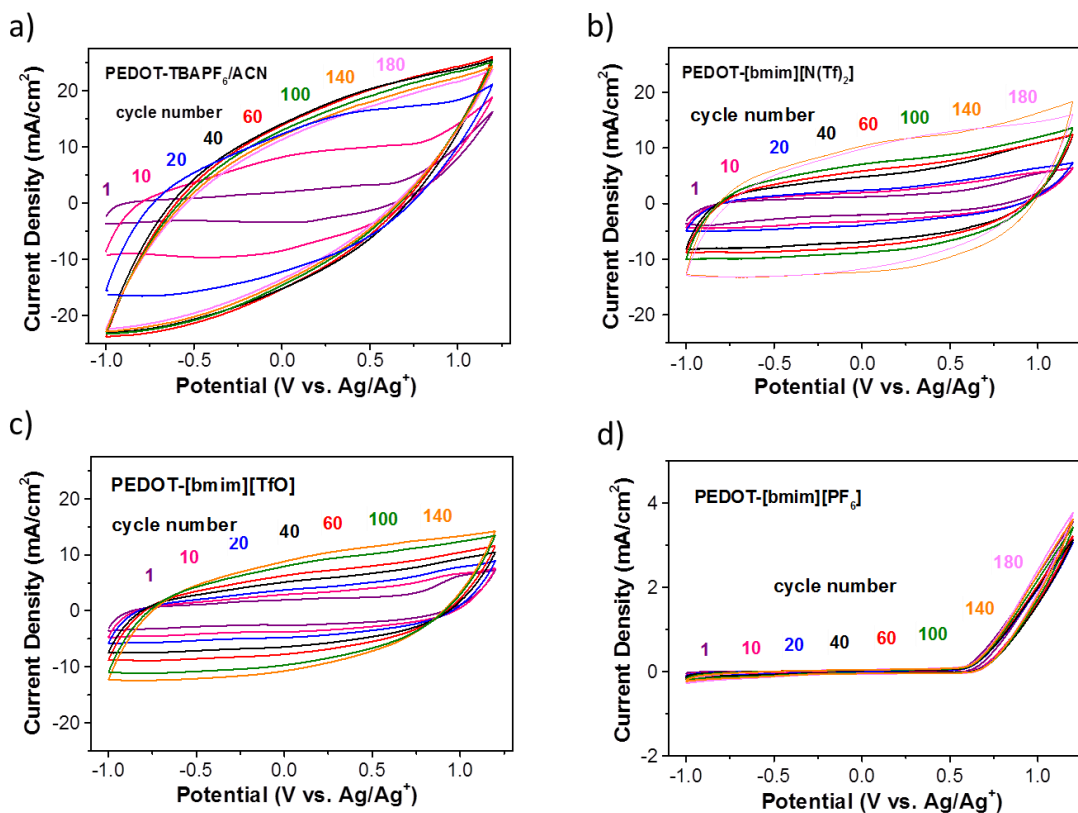
Figure 3.1 Cyclic voltammograms during electropolymerization of EDOT with increased cycles prepared from (**a**) TBAPF$_6$/ACN, (**b**) [bmim][Tf$_2$N], (**c**) [bmim][TfO], and (**d**) [bmim][PF$_6$] Electrodeposition conditions: 25 mM monomer solutions in supporting medium; 20-180 deposition cycles in a voltage window of -1.0 – +1.2 V (vs. Ag/Ag$^+$), on carbon paper electrodes; deposition scan rate of 50 mV s^{-1}. Each voltammogram is normalized to the extent of functionalized surface area.

To assess the electrochemical activities of these conducting polymer films deposited on the substrate and its redox process, cyclic voltammetry (CV) process is carried out. The CVs collected during the electrochemical deposition and increased cycling of EDOT in four kinds of supporting electrolyte is shown in **Figure 3.1 (a)-(d)**. The electrolyte system used as cycling medium can strongly affect the electrochemical response of the polymers. It can

be seen that in **Figure 3.1(a)-(c)**, the growth CVs of PEDOT shows an increase in current density with successive cycles,indicating continuous PEDOT deposition and succesful film growth on the substrate. Among these, EDOT electrodeposited in TBAPF$_6$/ACN shows the highest current density, wheras in **Figure 3.1 (d)**, PEDOT electrodeposited in [bmim][TfO], the current density is extremely low and there is almost no significant current increase. This can be explained by little PEDOT deposited in this kind of ionic liquid.

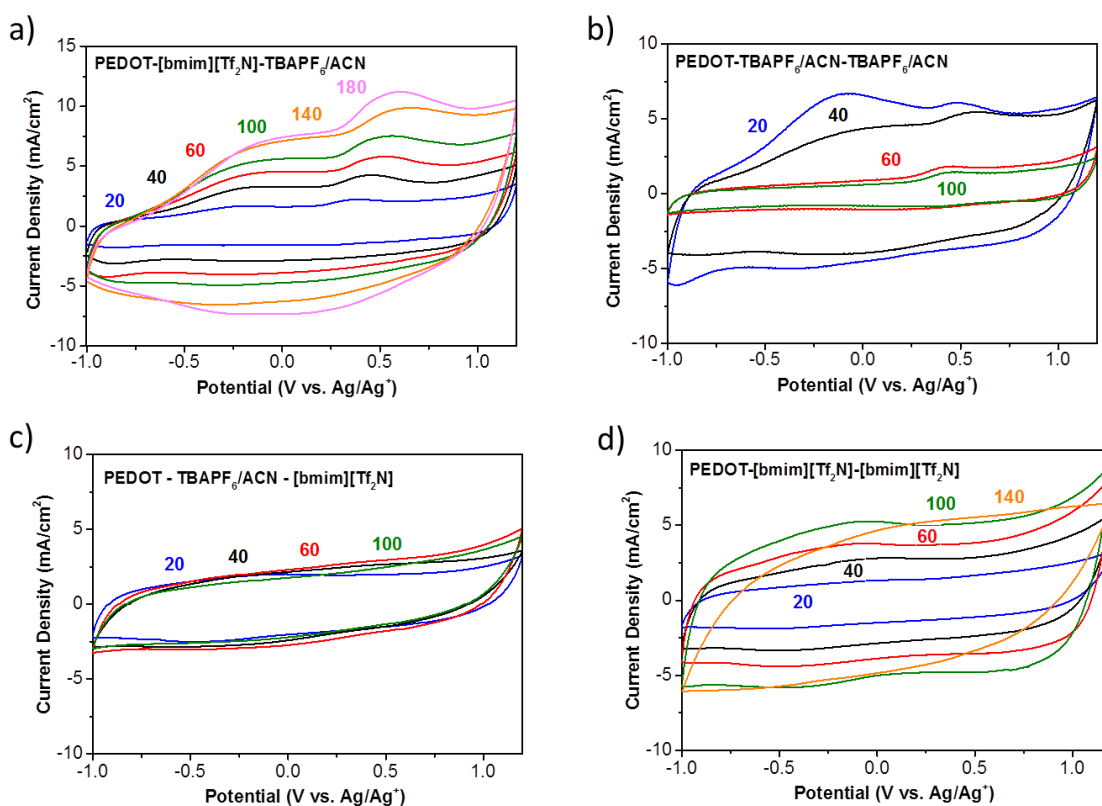**Figure 3.2** Cyclic voltammograms of PEDOT electrodeposited and post-electropolymerization CV in different combinations of ILs and organic solvents. (**a**) [bmim][Tf$_2$N] as electrodeposition medium and TBAPF$_6$/ACN as post-electropolymerization electrolyte; (**b**) TBAPF$_6$/ACN as both electrodeposition medium and post-electropolymerization electrolyte; (**c**) TBAPF$_6$/ACN as electrodeposition medium

and [bmim][Tf$_2$N] as post-electropolymerization electrolyte; (**d**) TBAPF$_6$/ACN as both electrodeposition medium and post-electropolymerization electrolyte, with a voltage window of -1.0 – +1.2 V (vs. Ag/Ag$^+$) and scan rate of 20 mV s^{-1}. Each voltammogram is normalized to the extent of functionalized surface area.

In **Figure 3.2a**, following the electropolymerization, the carbon paper composed of the deposited PEDOT polymer film in [bmim][Tf$_2$N] was removed from the growth electrolyte. PEDOT prepared in [bmim][Tf$_2$N], was rinsed with ACN and transferred into monomer-free ACN/TBAPF$_6$ in which the post-polymerization CVs were carried out. This batch of sample is named PEDOT-[bmim][Tf$_2$N]-ACN/TBAPF$_6$. When either ACN/TBAPF$_6$ or [bmim][Tf$_2$N] was used as the growth medium and ACN/TBAPF$_6$ is used as after-growth CV electrolyte (**Figure 3.2a-b**), polymer films grown in [bmim][Tf$_2$N] gives higher current response, this can be contributed to a slower, more ordered polymer structure growth, which is consistent with the electropolymerization results in **Figure 3.1a-b**. The same trend can be observed in **Figure 3.2c-d**. It can also be noted that the redox current charge during the post-polymerization CV is much higher in ACN/TBAPF$_6$ than [bmim][Tf$_2$N], when comparing PEDOT-ACN/TBAPF$_6$-ACN/TBAPF$_6$ (**Figure 3.2b**) and PEDOT-ACN/TBAPF$_6$-[bmim][Tf$_2$N] (**Figure 3.2c**), as well as PEDOT-[bmim][Tf$_2$N]-ACN/TBAPF$_6$ (**Figure 3.2a**) and PEDOT-[bmim][Tf$_2$N]-[bmim][Tf$_2$N] (**Figure 3.2d**), suggesting superior electrochemical activity in lower viscous organic solvent. It is known from the growth CVs in Figure 3.1a-d that the electrochemical response of PEDOT depends greatly on the nature of the ionic liquid applied. So, the post-polymerization CVs of PEDOT shows there is influence for both the growth medium in which PEDOT

deposited, and the nature of the supporting electrolyte used in the post-polymerization cycling.[106, 117] CVs of these polymer films in the [bmim][Tf$_2$N] or ACN/TBAPF$_6$ indicate not only an influence of the nature of the counter ions on the polymer growth but also its effect as the supporting solvent for the post-polymerizaiton cycling.

Cyclic voltammetry can provide valuable information to analysis the structure of the PEDOT formed. In **Figure 3.2b**, It can be noticed the voltamogramms of PEDOT-[bmim][Tf$_2$N]-ACN/TBAPF$_6$ displays two anodic peak currents, although only one broad cathodic peak can be observed may because peaks merged into one. The shape and current intensity of the CV is very different comparing to PEDOT-[bmim][Tf$_2$N]-[bmim][Tf$_2$N] in **Figure 3.2d**, which used ILs as growth medium and supporting electrolyte. From **Figure 3.2a-d**, it has been noted that the redox peaks of the post-polymerization CVs for PEDOT grown in [bmim][Tf$_2$N] or ACN/TBAPF$_6$ varied significantly depending on whether monomers were cycled in molecular solvent system or in ionic liquid, in which the counter ions intercalated into polymer films need a transfering time for equilibration in the new solvent.. This phenomenon is mainly related to the different extent polymer can expand in various supporting electrolyte, which affect the size of response.[117]. What's more, the two distinct anodic peaks displayed in **Figure 3.2a** indicate that at least two redox reaction mechanisms have been involved in oxidation. During redox reaction of a conducting polymer, there is a principal limiting mechanism of the electronic charge compensation: expulsion of cation/anion originally presented in the polymer film together with incorporation of anion/cation from the surrounding electrolyte during oxidation/reduction process to maintain electroneutrality. In the first step of this experiment which is electropolymerization of EDOT in IL shown in **Figure 3.1a**, the ionic liquid of

[bmim][Tf$_2$N] as cycling electrolyte can actively involve in the redox response of deposited polymer, resulting in counter-ion intercalation/de-intercalation near the polymer backbones. For the positive doping process, electrons would be exchanged in oxidation process, meanwhile [Tf$_2$N]$^-$ would be intercalated in the polymer film instead of electrons. As shown in **Scheme 3.1**. The viscosity and conductivity of the supporting solution, the nature and mobility of the counter ions, , and ability of the supporting solution to swell the polymer film, is able to significantly influence the doping process and deposited polymer's electrochemical behavior in electropolymerization cycling and its afterwards post-polymerization CV process.[125]
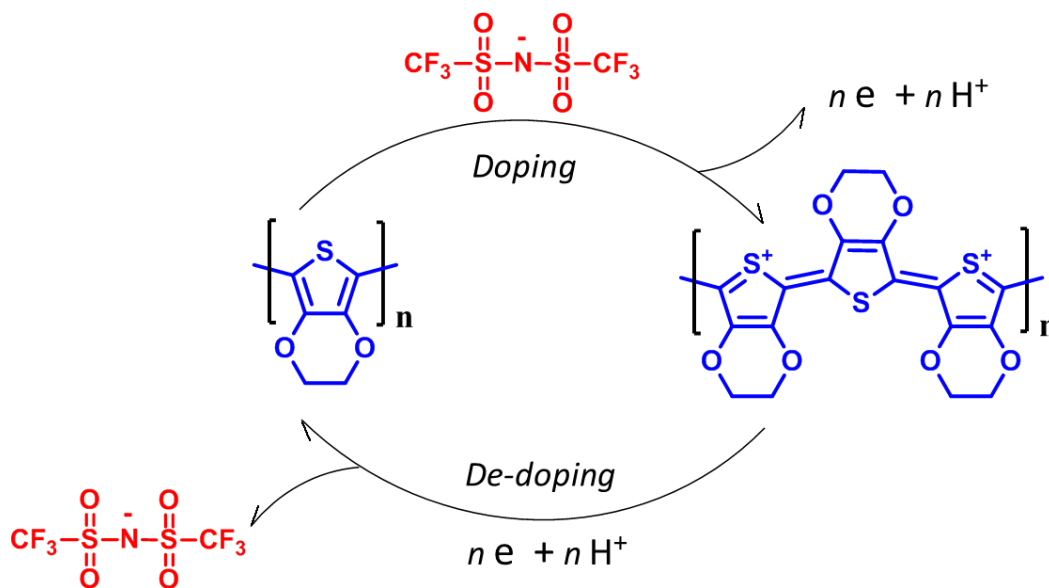
Scheme 3.1 Positive Doping/De-doping Process of PEDOT in [bmim][Tf$_2$N].

However, cases are more complex for the post-polymerizaiton CV in a different medium. It has been observed in **Figure 3.2** that there are multiple redox peaks in the PEDOT polymer films synthesized in ionic liquids. The "two-peaks" phenomenon can only be observed in PEDOT-[bmim][Tf$_2$N]-ACN/TBAPF$_6$ and PEDOT- ACN/TBAPF$_6$-

ACN/TBAPF$_6$ when organic solvent was used as post-polymerization CV electrolyte. Considering what is the reason for the multiple redox peaks oberseved for poly(thiophene), there is extensive investigations in the literatures however these discussions have not reached to an agreement yet and still under debate. It has been proposed that in PEDOT polymers the polymer chains can be highly conjugated and well-growed, but also it can be shorter with a more open configuration. As a result, the polymer stucture is composed of two zones, one is rigid and the other is loosely packed. [117, 118, 126, 127-130] The presence of two zones in the polymer structure could explaine the presense of two peaks in oxidation and reduction process for PEDOT. Also, these multiple redox peaks could be explained by the transitions between polaron, bipolaron neutral, and metallic states of the polymer,[131] An additional possibility is speculated that the presence of doping and de-doping in polymer's redox processes because of the ionic liquid cation. This can be related to the interchain cavity and the solvation energy of the polymer in different mediums.

Figure 3.3 Galvanostatic charge-discharge curves collected for the PEDOT electrodeposited in ILs or organic solvents. (**a**) [bmim][Tf$_2$N] as electrodeposition medium and TBAPF$_6$/ACN as post-electropolymerization electrolyte; (**b**) TBAPF$_6$/ACN as both electrodeposition medium and post-electropolymerization electrolyte; (**c**) TBAPF$_6$/ACN as electrodeposition medium and [bmim][Tf$_2$N] as post-electropolymerization electrolyte; (**d**) TBAPF$_6$/ACN as both electrodeposition medium and post-electropolymerization electrolyte, at a current density of 2 mA cm^{-2}; the areal capacitance values inferred are indicated on the plot.

PEDOT films electrochemcially deposited in ILs have shown an increase of galvanostatic charge-discharge performance as shown in **Figure 3.3** As deposited PEDOT

cycling in TBAPF$_6$/ACN shows higher capacitance than cycling in ILs, suggests higher

extent of polymer swelling and faster ion transfer into and out of the polymer chains.

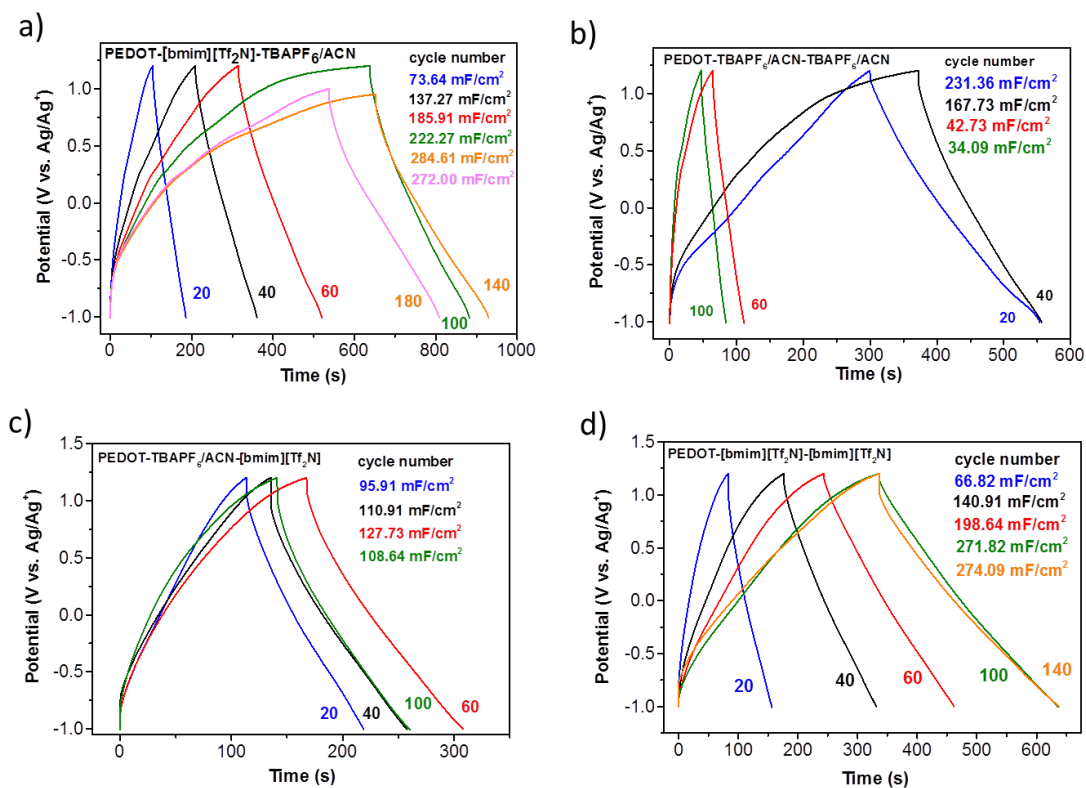**Figure 3.4** Summary of galvanostatic charge-discharge values collected for the PEDOT

electrodeposited in ILs or organic solvents. (**a**) [bmim][Tf$_2$N] as electrodeposition medium

and TBAPF$_6$/ACN as post-electropolymerization electrolyte; (**b**) TBAPF$_6$/ACN as both

electrodeposition medium and post-electropolymerization electrolyte; (**c**) TBAPF$_6$/ACN

as electrodeposition medium and [bmim][Tf$_2$N] as post-electropolymerization electrolyte;

(**d**) TBAPF$_6$/ACN as both electrodeposition medium and post-electropolymerization

electrolyte, at a current density of 2, 5, and 10 mA cm^{-2}; the percentage numbers indicated

on the plot are the attenuation degree of capacitance values with the increased current density.

Figure 3.5 Summary of galvanostatic charge-discharge values collected for the PEDOT electrodeposited in [bmim][TfO] or TBAPF$_6$/ACN, at a current density of (**a**) 2, (**b**) 5, and (**c**) 10 mA cm^{-2}.

Figure 3.6 SEM images of the morphologies of electrodeposited PEDOT films grown in (**a**) (**c**) TBAPF$_6$/ACN, (**b**) (**d**) [bmim][Tf$_2$N]. Electrodeposition conditions: 25 mM monomer solutions in electrolyte; 100 deposition cycles in a voltage window of -1.0 – +1.2 V (vs. Ag/Ag$^+$), on carbon paper electrodes; deposition scan rate of 50 mV s^{-1}. The scale bar in (a) and (b) is 2 μm; (c) and (d) is 50μm.

Films grown in ILs could give different morphologies.[119, 121] In addition to the intrinsic pseudocapacitive properties of ECPs, the interfacial electrochemistry between ECPs and the electrolyte also plays a significant role for its overall capacitance performance, which

can be enhanced by morphology adjustments. Synthesis of nano or meso-scale structures with hierarchical porosity can not only provide sufficient specific surface area (SSA) as electroactive sites for faradaic reactions, but also to ensure the effectively participation of electrolyte ions and electrons in the interface.[44] Therefore, the surface of PEDOT film electrochemically deposited on the carbon paper electrode was examined by scanning electron microscope (SEM), as shown in **Figure 3.6**. There is a distinct effect of the anion (and a less clear effect of the solvent) on the morphology of the PEDOT layers. The film produced in the neat ILs was more compact and homogeneous than that from the organic solution medium with higher electrochemically activity and heavier doped. The films electropolymerized in the TBAPF$_6$/ACN solutions shows a granular depositions whereas the film grown in ILs appeared to be very smooth and in order.

3.2.2.1 Electrochemical Characterizations of BEDOT

In order to clarify and confim the effect of anions on PEDOT and its derivatives, 4,4'-dimethoxy-3,3'-bithiophene (BEDOT) were synthesized, and the same protocol has been carried out. **Figure 3.7** shows the linear scans in potential and actual onsets of oxidation for BEDOT, where the various oxidation features on scanning linearly in the -2.0 – +2.5 V potential window (vs. Ag/Ag$^+$) are detailed directly on the plots. PBEDOT dark films can be deposited on the glassy carbon button electrode in [bmim][Tf$_2$N] and [bmim][TfO], indicating that electropolymerization is occurring during linear scans.)

Figure 3.7 Linear scan voltammograms collected on glassy button electrodes at a scan rate of 20 mV s^{-1} from a solution of **BEDOT** (5 mM) detailing oxidation features, in (**a**) [bmim][Tf$_2$N], [bmim][TfO], TBAPF$_6$/ACN and (**b**) [bmim][PF$_6$].

Figure 3.8 Cyclic voltammograms during electropolymerization of BEDOT with increased cycles prepared from (**a**) TBAPF$_6$/ACN, (**b**) [bmim][Tf$_2$N], (**c**) [bmim][TfO],

and (**d**) [bmim][PF$_6$] Electrodeposition conditions: 25 mM monomer solutions in

supporting medium; 20-100 deposition cycles in a voltage window of -1.0 – +1.2 V (vs.

Ag/Ag$^+$), on carbon paper electrodes; deposition scan rate of 50 mV s^{-1}. Each

voltammogram is normalized to the extent of functionalized surface area.

Figure 3.9 Summary of galvanostatic charge-discharge values collected for the

PBEDOT electrodeposited in ILs or organic solvents. (**a**) [bmim][Tf$_2$N] as

electrodeposition medium and TBAPF$_6$/ACN as post-electropolymerization electrolyte;

(**b**) TBAPF$_6$/ACN as both electrodeposition medium and post-electropolymerization

electrolyte; (**c**) TBAPF$_6$/ACN as electrodeposition medium and [bmim][Tf$_2$N] as post-

electropolymerization electrolyte; (**d**) TBAPF$_6$/ACN as both electrodeposition medium

and post-electropolymerization electrolyte, at a current density of 2, 5, and 10 mA cm^{-2}; the percentage numbers indicated on the plot are the attenuation degree of capacitance values with the increased current density.

3.2.3 Conclusion

Electropolymerization of EDOT and its derivative 4,4'-dimethoxy-3,3'-bithiophene (BEDOT) have been studied in three kinds of imidazolium-based ionic liquids and conducting salt in volatile organic compounds with different anions both as the growth medium and the supporting electrolyte, to assess the influence of these anions on their morphology and electrochemical activity. It is found these thiophene polymers grown in ILs with higher viscosity and lower diffusion shows much slower growth rate and orderly morphologies than in TBAPF$_6$ dissolved in ACN, and gives better electrochemical performance via cyclic voltammetry (CV) and galvanostatic charge-and-discharge (CD) studies. Polymers displayed multiple redox peaks in several cases, the possible reasons and origins are discussed. The synthesized polymer can be affected greatly by both the ILs with different anion/cation, and its mutal interation with targeted monomer. As far as known, there is no systematic study on how the anions of ILs and common organic solution could play a role as a medium both for polymerization and post-polymerization electrolyte for PEDOT and its derivatives. This study can be used as an easy reference and provide experimental diagnositc data when selecting ionic liquids to investigate and optimize thiophene-based electrochemical systems, such as batteries and supercapactiors.

Chapter 4

Direct Functionalization of Nanodiamonds with Maleimide

4.1 Introduction

Diamond materials span a wide range of attractive physical properties, including large mechanical resistance, high thermal conductivity, and tunable optoelectronic behaviour when suitably doped.[132, 133] Down to the nanoscale, embedded diamond nanoparticles find use in surface coatings, nanocomposites, and are promising building elements in nanophotonic device engineering.[134] In parallel, their excellent chemical stability and anticipated compatibility in biological systems make them particularly attractive for biomedical applications.[133] Thus, a number of recent studies have emphasized the perspectives of nanodiamonds as drug-delivery vehicles, templates for biological sensing, and probes in bioimaging.[132] The nature of the solubilizing substituents and specific functional groups appended to the nanodiamond surface defines the function of the nanoparticle, and in turn its field of applicability.

Synthetic nanodiamonds prepared by detonation protocols, so-called detonation diamond nanoparticles (DDNPs), are composed of primary nanocrystals (2-10 nm) and their aggregates (10-100 nm).[132] As synthesized, DDNPs show a relatively heterogeneous surface, composed of amorphous carbon forms (*a*-C), hydroxyls (–OH), alkoxy/ether

groups (C–O–C), carbonyls (C=O), sp^2 moieties (C=C), and a non-negligible content of dangling bonds (–C*, unsatisfied valence).[135-140] Thus, DDNPs are generally subjected to a chemical surface-treatment in order to selectively produce short functionalities (*e.g.,* –OH, –CO$_2$H, –COCl, –NH$_2$) to which larger substituents can be appended, most commonly by esterification or amidation.[141] The reductive C-C coupling between aryl diazonium salts and hydrogenated diamond films,[142] and *graphitized/* hydrogenated DDNPs,[143-145] are examples of direct functionalization. Further derivatization with functional substituents can be achieved by catalyzed cross-coupling at the aryl site. As an alternative, functional aryls can also be appended to diamond films (*e.g.* via cycloadditions, [4+2] or [2+2]),[146-152] and to the π-system of thermally annealed nanodiamonds,[153, 154] albeit using specific reagents and elevated temperature conditions.[155] Here, we report on a protocol of direct functionalization by which maleimide-derivatized substituents can be appended to the outer shell of thermally annealed nanodiamonds under ambient conditions. Noting that a wide range of functional maleimides can readily be made from the commercial precursor maleic anhydride,[156] this direct approach to functionalizing nanodiamonds should be amenable to the preparation of nanomaterials with a manifold of functions.

4.2 Experimental Section

4.2.1 Preparation of the Nanoparticle Precursors

Materials: Synthetic nanodiamonds with nominal primary particle sizes of less than 10 nm were sourced from Sigma Aldrich (catalogue # 636428-5G). MilliQ water (18 MΩ)

was used as the dispersive medium in the ball-milling step. All other reagents were ACS reagent grade and sourced from Sigma Aldrich.

Methods: *Ball-milling procedure* – Concentrated solutions of diamond nanoparticles were prepared according to the salt-milling protocol described by Pentecost *et al.*[157] The nanodiamonds were mixed with NaCl in a 1:7 ratio and then transferred into a steel jar (50 mL volume; Retsch Co.), along with stainless steel grinding balls (50 g, 6 mm diameter). The milling was carried out at 400 rpm for 15h (by 1h intervals, and 30min pauses between milling intervals) in a Planetary Ball Mill PM 200 (Retsch Co.). Next, the mixture was charged in a glass beaker filled with hydrochloric acid (HCl) (37% in volume), diluted with deionized water, and sonicated in a sonication bath (Branson 5510, Bransonic) for 30 min in order to remove iron contaminants produced during the milling step (from the steel balls and jar). The resulting solution of nanoparticles was then centrifuged in an ultra-centrifugation system (Superspin 610 rotor, WX Ultra 90, Thermo Scientific) to precipitate the nanodiamonds. The nanoparticles were collected, re-dispersed in deionized water and centrifuged again. This cleaning step was repeated several times until a negative silver nitrate test (0.1N) was obtained. The ball-milled and purified nanodiamonds were dispersed in aqueous HCl solutions (pH~3.8) and sonicated with an ultrasonic probe for 1.5h[2] (Ultrasonic Processor Q500, Qsonica; ϕ1.27 cm Standard probe; Maximum out-put power 400W, used at 60% amplitude). *Thermal annealing protocol* – The ball-milled nanodiamonds (DDNPs) were charged in a quartz vessel, placed in a furnace (V.S. Technologies), and subjected to distinct annealing temperatures for 1h under vacuum (10^{-2} Torr): T=500°C → GDNP(500), T=600°C → GDNP(600), T=700°C → GDNP(700), T=800°C → GDNP(800), T=900°C → GDNP(900).

**4.2.2 Characterization of the Nanoparticle Precursors**

The size distribution of the ball-milled nanodiamond precursors was estimated by dynamic light scattering (DLS) (Zetasizer Nano ZS, Malvern). As DLS measurements were found to be sensitive to the concentration of nanoparticles in solutions,[158] the concentration of each sample solution was adjusted by tuning the absorbance of the sample to optical density (OD)~1.0 at the wavelength of 350 nm (Ocean Optics Inc., light source DH-2000-Bal, 1 cm path-length cuvette) through dilution with an aqueous HCl solution (pH~3.8) before each DLS measurement. A Lemis ViscoDens VDM-300 was used to measure the solvent viscosity and density of pH~3.8 HCl solutions, and the measured parameters were input in the DLS method. Over 90 DLS measurements (20 seconds per run) were averaged to avoid environmental perturbation and obtain stable data. The size and shape of the primary nanoparticles was further examined by high-resolution transmission electron microscopy (HR-TEM; Titan G2 80-200, FEI Co.). Aqueous solutions of nanodiamonds were deposited on 300 mesh Au grids (Ted Pella Inc., USA) and the nanodiamonds were analyzed under an acceleration voltage of 300 kV. Fourier transform infrared spectroscopy (FTIR) analyses were carried out on a Nicolet iS10 from Thermo Scientific equipped with a Smart iTR compartment for ATR analysis. The spectra were collected at 4 cm^{-1} resolution with 64 cumulative scans in the 4000-600 cm^{-1} spectral range. Raman analyses were carried out on a LabRAM Aramis (Horiba Jobin Yvon) micro-Raman system. The spectra were acquired in a backscattering configuration. A 40X objective was used to focus and collect scattered light from the substrate, and the excitation source consisted of a He-Cd laser (325 nm). Typical laser power at the sample position was 1D (~1 Mw) and the data acquisition time was 20 s per scan. Note: Significant degradation of the sample was observed with

increasing power and number of scans by Raman under the UV laser beam (i.e., upon longer times of exposure) – the peak maximum shifting towards higher frequencies (from ca. 1580 cm^{-1}, G-band → to 1640 cm^{-1}, –OH). Oxidative degradation mechanisms may be the source of degradation. X-ray diffraction analyses (XRD) were performed on a BRUKER D8 Advance (CuλKα1 =1.5406 Å; increments: 0.01 degree/step; scan speed: 1 s/step). X-ray photoelectron spectroscopy (XPS) studies were performed on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source ($hv = 1486.6$ eV) operating at 150 W, a multichannel plate and delay line detector under a vacuum of 1 x 10^{-9} mbar. The measurements were performed in hybrid mode using electrostatic and magnetic lenses. All spectra were recorded using an aperture slot of 300 μm × 700 μm. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively and quantified using empirically derived relative sensitivity factors provided by Kratos analytical. The data were analyzed with the software CASAXPS. The individual peaks were fitted by a Gaussian (70%)–Lorentzian (30%) (GL30) function after applying Shirley-type background subtraction. Thermogravimetric analyses (TGA) were conducted in Al$_2$O$_3$ crucibles under argon flow (Netzsch, TG 209 F1 with ASC). A heating rate of 5 °C/min and sample mass of ca. 12mg were set for all experiments.

4.2.3 Synthesis of the Maleimide EHM

Materials and Methods: All reagents from commercial sources were used without further purification. Reactions were carried out under a nitrogen atmosphere. Solvents were dried and purified using standard techniques. Flash chromatography was performed with analytical-grade solvents using Silicycle SiliaFlash P60 (particle size 40-63 μm, 60 Å, 230

– 400 mesh) silica gel. Flexible plates PE SilG/UV 250 μm from Whatman® were used for TLC. Compounds were detected by UV irradiation or staining with I_2, unless otherwise stated. All compounds were characterized by ^1H NMR and ^{13}C NMR at room temperature on a Bruker Avance III Ultrashielded 600 Plus instrument (respectively at 600 MHz and 150 MHz) or on a Bruker Avance III 500 equipped with a 13C-1H *cryoprob* (at 500 MHz for proton and 125 MHz for carbon). High-resolution mass spectrometry (HRMS) accurate data were recorded using a Bruker LC-MS MicroTOF II in positive electro spray ionization mode (+ESI). Elemental analyses were carried out on a Flash 2000 - Thermo Scientific CHNO Analyzer.
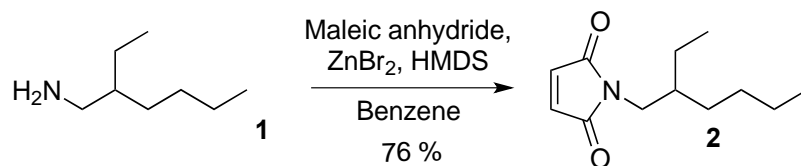
Synthesis of 1-(2-ethylhexyl)-1*H*-pyrrole-2,5-dione[159] (2) – EHM: A solution of 2-ethylhexan-1-amine 1 (1.5 mL, 9.2 mmol) in dry benzene (5 mL) was added to a stirred solution of maleic anhydride (1 g, 10.12 mmol) in dry benzene (100 mL) at room temperature over a *ca.* 15 min period. After an additional 1 h stirring at 30°C, ZnBr₂ (2.28 g, 9.7 mmol) was added in one portion, and the mixture was stirred for another *ca.* 10 min. A solution of hexamethyldisilazane (HMDS) (2.75 mL, 13.415 mmol) in dry benzene (15 mL) was added slowly at 30°C over a period of 30 min (the reaction mixture changed from clear to turbid). Next, the reaction temperature was increased to 80°C, and the mixture was refluxed for an additional 2 h. After being cooled to room temperature, the reaction mixture was poured into 0.5 M HCl (70 mL). The aqueous phase was extracted with ethyl acetate (2x50 mL). The combined organic extracts were washed successively with 40 mL of

saturated $NaHCO_3$ and 40 mL of brine and then dried over anhydrous $MgSO_4$ and concentrated under vaccuo. The oily residue was purified by column chromatography (hexane/EtOAc 5:1) to yield compound 2 (1.6 g, 76%) as a clear oil. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.68 (s, 2H); 3.40 (d, 2H, $J = 7.5$ Hz); 1.72-1.69 (m, 1H); 1.27-1.21 (m, 8H); 0.87 (t, 6H, $J = 7.5$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 170.8; 133.6; 41.3; 37.7; 29.9; 28.0; 23.3; 22.6; 13.6; 9.9. HRMS/ESI: m/z calcd for $C_{12}H_{20}NO_2^+$: 210.1489 [M+H]+, found: 210.1483.

4.2.4 Functionalization Procedure

Methods: Following the annealing step, 50 mg of GDNPs were dispersed and sonicated for 60 min (sonication bath, Branson 5510) in 5 mL of acetonitrile (ACN), under ambient conditions. Next, the functional imide (EHM or M, 1 g) was added to the colloidal solution of diamond nanoparticles, and the mixture was stirred briefly. Assuming functionalization had occurred, the mixture of GDNPs and (excess) imide substituents was subjected to 5 washing cycles by centrifugation (Eppendorf 5702, 4400 rpm) in acetone (15 mL/washing-cycle) in order to remove the free imide substituents (excess). Next, the nanoparticles were dried under vacuum overnight (10^{-2} mBar, 25°C). Note: Unfunctionalized EHM or M substituents can be recovered upon centrifugation in acetone. The DLS, FTIR, XPS and TGA measurements were performed as per the experimental described for the nanodiamond precursors.

4.2.5 SS-NMR Analyses

1D ^{1}H MAS and ^{13}C CP/MAS spectra were recorded on a Bruker AVANCE III spectrometer operating at resonance frequencies of 400 and 100 MHz for ^{1}H and ^{13}C, respectively, and using a conventional double resonance 4 mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 17 and 10 KHz for the ^{1}H and ^{13}C analyses, respectively. NMR chemical shifts are reported with respect to TMS as the external reference. For CP/MAS ^{13}C NMR experiments, the following sequence was used: i) 90^0 pulse on the proton (pulse length 2.4 s), then ii) cross-polarization step with a contact time of typically 2 ms, and iii) acquisition of the ^{13}C signal under high-power proton decoupling. The delay scans was set to 5 s to allow the complete relaxation of the ^{1}H nuclei, and 3,000-5,000 scans were performed for a carbon experiment and 32 for a proton experiment. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

2D ^{13}C{^{1}H} heteronuclear correlation (HETCOR) analyses were conducted on a Bruker AVANCE III spectrometer using a 3.2 mm MAS probe. The following protocol was employed: i) 90^0 proton pulse, ii) t_1 evolution period, iii) cross-polarization (CP) to carbon spins, and iv) detection of carbon magnetization under two pulse phase modulation (TPPM) decoupling.[160, 161] For the cross-polarization step, a ramped radio frequency (RF) field centered at 75 KHz was applied to protons, while the carbon RF field was matched to obtain optimal signal. A total of 32 t_1 increments with 2000 scans each were collected. The sample spinning frequency was 8.5 kHz. A 2D Fourier transformation gives through space

between pairs of neighboring carbon (in F2) and proton (in F1) nuclei. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment is expected to be quite selective, that is to lead to correlation only between pairs of connected ^{1}H-^{13}C spins (C-H directly bonded).

^{1}H-^{1}H double-quantum (DQ) experiments were recorded on a Bruker AVANCE III-600 spectrometer with a conventional double resonance 3.2 mm CPMAS probe, according to the following general protocol:[162] i) excitation of DQ coherences, ii) t_1 evolution, iii) Z-filter, and iv) detection. The spectra were recorded in a rotor-synchronized fashion in t_1; that is the t_1 increment was set equal to one rotor period (4.545 μs). One cycle of the standard back-to-back (BABA) recoupling sequence was used for the excitation and reconversion period. Quadrature detection in w_1 was achieved using the States-TPPI method. A spinning frequency of 22 KHz was used. The 90^0 proton pulse length was 2.5 μs, while a recycle delay of 5 s was used. A total of 128 t_1 increments with 32 scans each were recorded. DQ proton spectroscopies under fast MAS have recently been shown to be a powerful technique to probe the structural information and dynamics inherent to proton-proton dipolar couplings. The DQ frequency in the w_1 dimension corresponds to the sum of two single-quantum (SQ) frequencies of the two coupled protons and correlates in the w_2 dimension with the two corresponding proton resonances.

4.2.6 Preparation and Characterization of F5M-GDNPs

Materials: Fluorescein-5-maleimide (F5M) was purchased from Life Technology (CAS: 75350-46-8).

Methods: 10 mg of GDNPs(800) were dispersed and sonicated for 60 min (sonication bath, Branson 5510) in 1 mL of acetonitrile (ACN), under ambient conditions. Next, Fluorescein-5-maleimide (F5M, 5 mg) was added to the colloidal solution of diamond nanoparticles, and the mixture was stirred briefly. The mixture of GDNPs and (excess) F5M dye molecules was subjected to washing cycles by centrifugation (Eppendorf 5702, 4400 rpm) in acetonitrile until the supernatant solution showed no residual optical absorption by UV-Vis. Next, the nanoparticles were dried under vacuum overnight (10^{-2} mBar, 25°C) or dissolved in a mixture of acetonitrile/DMF for further characterizations.

Characterization of the DDNPs Functionalized with F5M: Fluorescence microscopy images were collected with an Olympus BX43 Upright Fluorescence Microscope (Software: QCapture). Samples of F5M, GDNPs(800) and F5M-GDNPs were spun-cast from acetonitrile on glass substrates. UV-Vis spectra were collected with a Cary 100 (DMF solutions). Fluorescence spectra (from DMF solutions) were acquired with a Cary Eclipse ($\lambda_{Ex} = 455$ nm; $\lambda_{max} = 550$ nm). FTIR analyses were carried out on a Nicolet iS10 from Thermo Scientific equipped with a Smart iTR compartment for ATR analysis. The spectra were collected at 4 cm^{-1} resolution with 64 cumulative scans in the 4000-600 cm^{-1} spectral range.

4.3 Results and Discussion on Direct Functionalization of Nanodiamond with Maleimide

4.3.1 Thermal Anealing and Characterization of detonation diamond nanoparticles (DDNPs)

Considering DDNPs, the extent of sp^2 moieties at the nanodiamond surface can be increased by high-temperature annealing treatment under vacuum, a procedure by which the sp^2 carbon content (*graphite-like*) develops from shell to core, at the expense of the sp^3 diamond carbon.[163-165] The *graphite-like* surface of fullerenes, such as carbon nanotubes (CNTs) and buckminsterfullerene (C60), is known to be amenable to addition reactions with various molecular partners, including substituted furfuryl and maleimide derivatives.[166] Here, DDNPs were de-aggregated by ball-milling (see **Figure 4.1**) and subjected to distinct annealing temperatures under vacuum (10^{-2} Torr), yielding various samples of *graphitized* diamond nanoparticles (GDNPs); the evolution of the surface composition was monitored by FTIR and Raman spectroscopy. As shown in **Figure 4.2**, thermal annealing induces i) a reduction of the extent of surface carbonyls (1715 cm^{-1}; **Figure 4.2a**), along with ii) a concomitant development and broadening of the main band (1500-1650 cm^{-1}; **Figure 4.2b**) as the peak maximum shifts towards lower frequencies (from *ca.* 1640 cm^{-1} (–OH) to 1590 cm^{-1} (G-band contribution)) – features characteristic of the formation of sp^2 bonding patterns.[167]
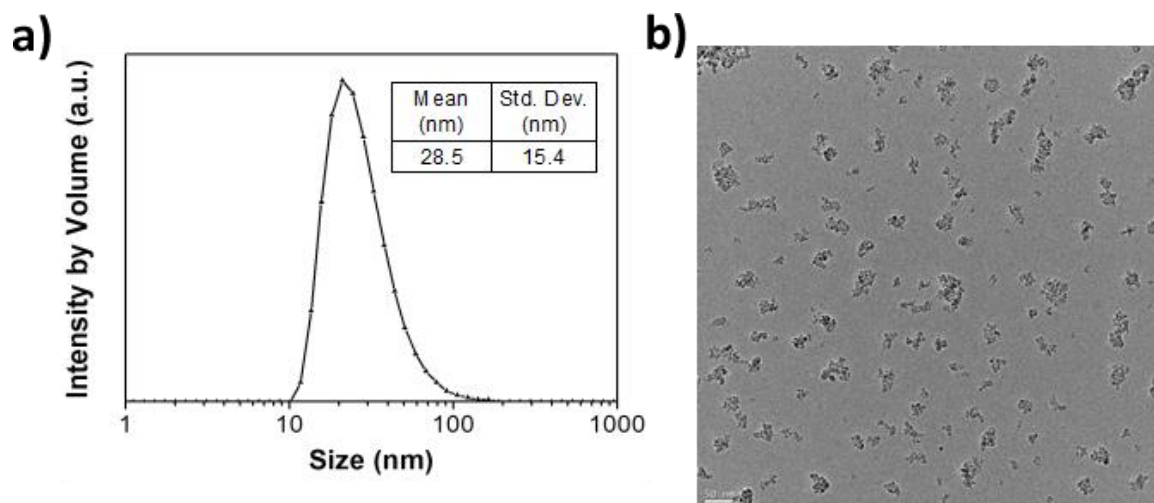
Figure 4.1 a) Size distribution pattern of the ball-milled DDNPs measured by DLS in MilliQ water (tuned to pH~3.8 by HCl solution). **b)** TEM image (bright field, 150keV) of the corresponding DDNPs (scale bar: 50 nm). Figure adapted with permission.[158]
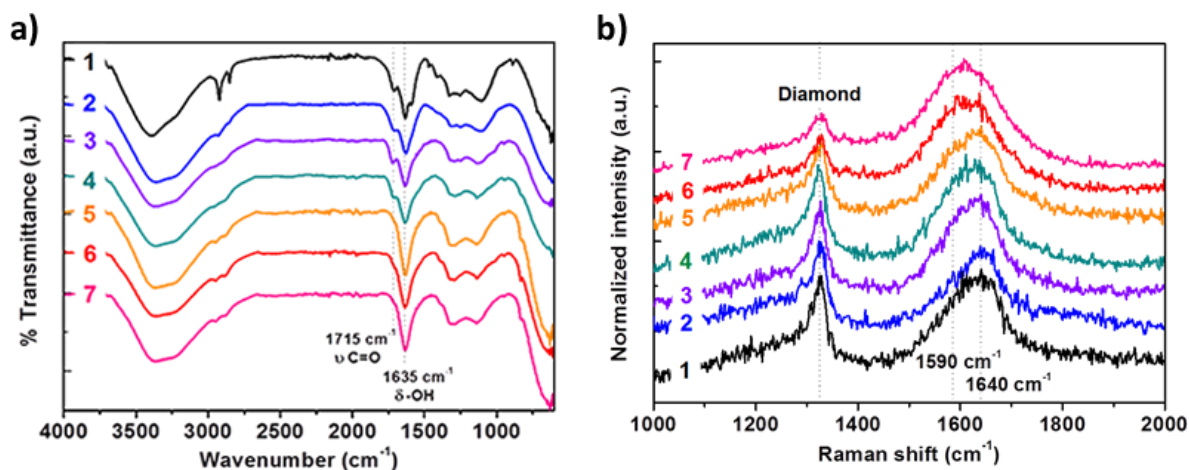
Figure 4.2 a) FTIR spectra and **b)** Raman spectra (1 scan, t= 20s/scan, λ= 325 nm) of thermally annealed DDNPs. [1] DDNPs prior to ball-milling (black curve), [2] ball-milled DDNPs (blue curve), [3] DDNPs thermally annealed at 500°C for 1h (purple curve), [4] DDNPs thermally annealed at 600°C for 1h (green curve), [5] DDNPs thermally annealed at 700°C for 1h (orange curve), [6] DDNPs thermally annealed at 800°C for 1h (red curve), and [7] DDNPs thermally annealed at 900°C for 1h (pink curve). Spectra given on an

arbitrary scale. Note: Significant degradation of the sample was observed with increasing power and number of scans by Raman under the UV laser beam (i.e., upon longer times of exposure) – the peak maximum shifting towards higher frequencies (from ca. 1590 cm^{-1}, G-band contribution from the *graphite-like* outer-shell → to 1640 cm^{-1}, –OH). Oxidative degradation mechanisms may be the source of degradation.

4.3.2 Functionalization of Annealed DDNPs with Maleimide

In a control experiment, a batch of DDNPs annealed at higher temperature (800°C) – GDNP(800) – was treated with a simple alkyl-substituted maleimide derivative (EHM; **Figure 4.3**) for a few minutes under ambient conditions. A detailed experimental can be found in **Section 4.2.4**; the XRD analysis of the GDNP(800) precursor (**Figure 4.4**) confirmed the integrity of the diamond core upon thermal annealing. With the observation of a net change in nanoparticle dispersion in solution (see **Figure 4.5**), the treated GDNPs were further inspected by FTIR. **Figure 4.3** shows a number of characteristic features pointing to an effective association between EHM and the nanodiamond surface. The FTIR spectra of the ball-milled DDNPs [1] and thermally annealed GDNPs(800) [2], prior to EHM-treatment, are shown along with those of the EHM-treated GDNPs(800) [3] and the free EHM substituent [4]. At a first level of observation, the association between EHM and the nanodiamond surface is supported by the presence of the characteristic stretching modes of maleimide[168] in EHM-treated GDNPs [3]: υ(C=O): ca. 1700 cm^{-1}, υ_s(C,C>N-): ca. 1405 cm^{-1}, and υ_{as}(C,C>N-): ca. 1165 cm^{-1} (Imide I, II and III). Further, a notable shift of the υ_{as}(C,C>N) asymmetric stretch from ca. 1165 cm^{-1} [4] to ca. 1180 cm^{-1} [3] suggests a structural change at the alkene site (C=C) of maleimide. Assuming that an addition

reaction occurred across the alkene, maleimide would be converted to its saturated analog, succinimide − an assumption supported by the apparent loss of the bending modes characteristic of maleimide at 693 cm^{-1} (ring-bend) and 827 cm^{-1} (☐(=CH), out-of-plane) in EHM-treated GDNPs [3] (marked with red box).[169] X-ray photoelectron spectroscopy (XPS) analyses (see **Figure 4.6** and **Table 4.1**) indicate a non-negligible increase in relative oxygen (O: 3.7 at%) and nitrogen (N: 2.3 at%) contents in EHM-treated GDNPs(800) compared to the untreated GDNP(800) precursor (O: 3.0 at%; N: 1.5 at%), thus providing additional support for the change in surface composition inferred from the FTIR data. The thermogravimetric analyses (TGA) of EHM-treated GDNPs(800), the untreated GDNP(800) precursor and the free EHM substituent are provided in the **Figure 4.7**.
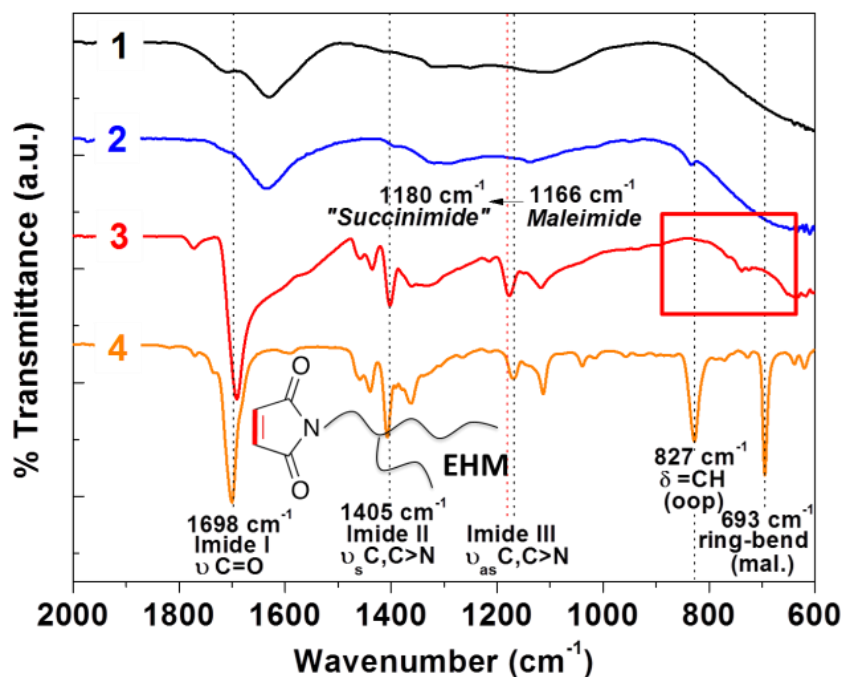
Figure 4.3 FTIR spectra of [1] ball-milled DDNPs (control), [2] thermally annealed GDNPs(800), [3] GDNPs(800) treated with the functional maleimide EHM (EHM-

GDNP), and [4] the free EHM substituent. The molecular structure and main characteristic

vibrations of EHM are indicated on the plot.
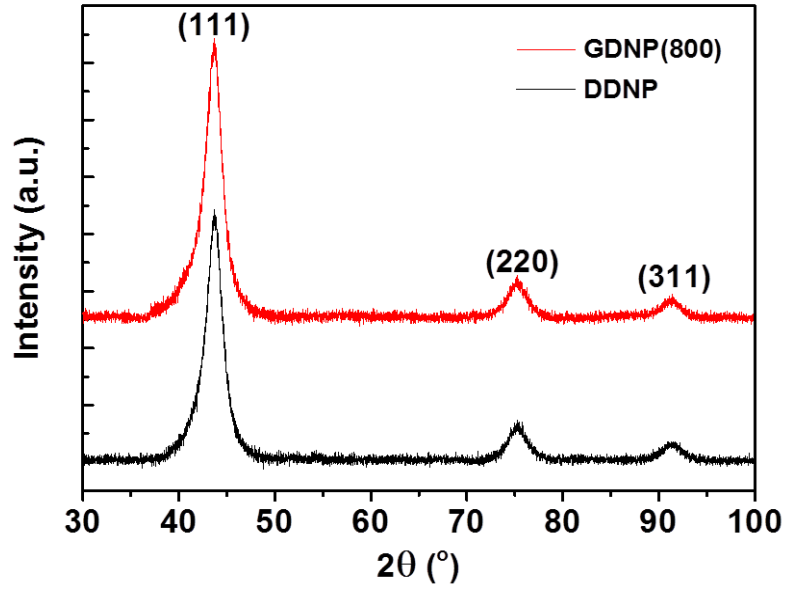
Figure 4.4 XRD patterns of the DDNP and GDNP(800) precursors. (arbitrary scale) The

characteristic peaks of the crystal planes of diamond at $2\Theta = 44.3°$ (111), 75.5° (220), and

91.7° (311) indicate that the diamond-like carbon structure (sp^3) of the DDNPs is preserved

upon annealing at 800°C for 1h.

Figure 4.5 Dilute solutions of DDNPs (left), GDNPs(800) (center) and EHM-treated GDNPs(800) (right) in chlorobenzene (same initial concentration). After 3 days, the colloidal solution of EHM-GDNPs remains stable, while the unfunctionalized DDNP and GDNP precursors precipitated and settled at the bottom of the quartz cuvettes (white circled).

Figure 4.6 XPS survey spectra of **a)** GDNP(800) and **b)** EHM-GDNP(800). High-resolution XPS analyses and deconvolutions of the C1s peaks of **c)** GDNP(800) and **d)** EHM-GDNP(800).

Table 4.1 XPS analyses of the GDNPs(800) and of the EHM-treated GDNPs(800).

	Atomic content (at%)		
	C	O	N
GDNP(800)	95.5	3.0	1.5
EHM-GDNP(800)	94.0	3.7	2.3

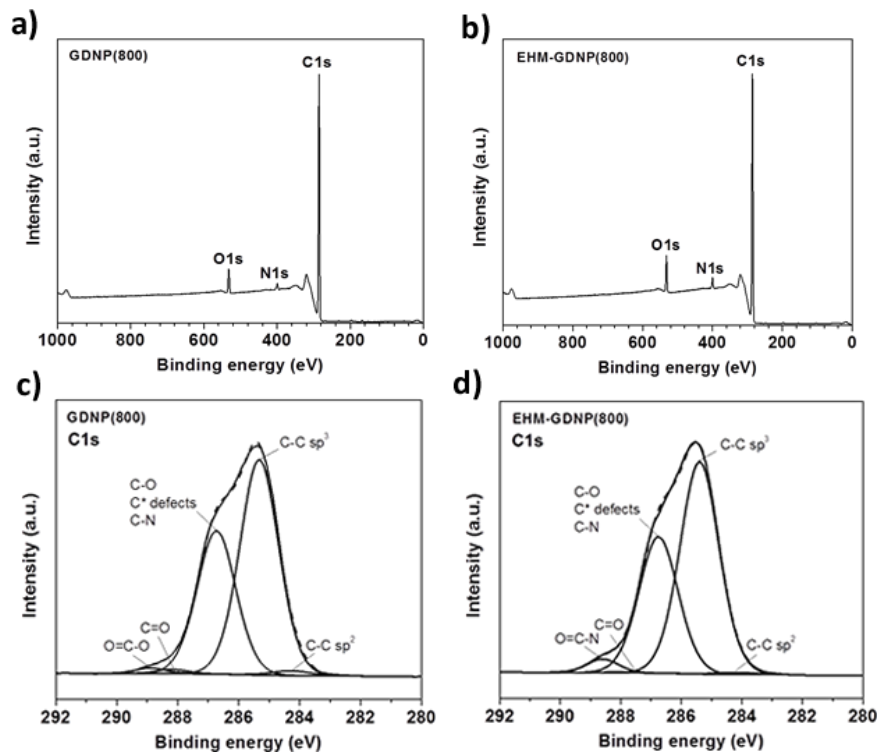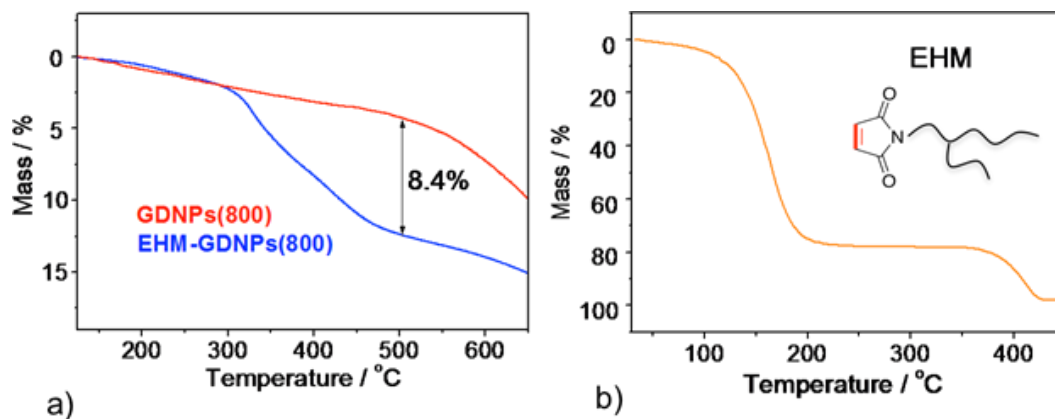**Figure 4.7** Thermogravimetric analysis (TGA) of **a)** thermally annealed GDNPs(800) (control system, red curve) and GDNPs(800) treated with the functional maleimide EHM (EHM-GDNP, blue curve), and **b)** the free EHM substituent. Note: the onset of evaporation of the free EHM substituents is observed at ca. 125 °C, while the onset of weight loss of EHM-GDNPs(800) shows beyond 300 °C (not seen in unfunctionalized GDNPs(800)).

4.3.3 Binding Strategy Investigation through Solid-state NMR (SS-NMR)

A number of solid-sate NMR (SS-NMR) analyses were performed to validate the apparent bond-forming reaction taking place between EHM and the nanodiamond surface (**Figure 4.8** and **Figure 4.9**). In **Figure 4.9**, the 1D ^{13}C magic-angle spinning (MAS) NMR spectrum of the thermally annealed GDNPs(800) (**Figure 4.9a**) shows only one resonance at 33.4 ppm, characteristic of the sp^3-hybridized carbon content of the nanodiamond precursor.[135-139] Meanwhile, the 1D ^{1}H MAS spectrum of the GDNPs (**Figure 4.9b**) shows a broad resonance in the range 1-4 ppm, consisting of an overlap of several peaks, including resonances associated to CH$_X$ groups.[135-139, 170] The presence of CH$_X$ surface groups (such as CH and CH$_2$) can be confirmed by 1D ^{13}C cross-polarization (CP)/MAS[135-139, 170, 171] (**Figure 4.8a**, peak at 47.3 ppm), and by 2D ^{13}C{^{1}H} heteronuclear correlation (HETCOR)

spectroscopy (**Figure 4.8b**) analyses (here, the use of a short contact time for the CP step in this through-space dipolar correlation experiment is expected to lead to correlations between pairs of connected ^1H–^{13}C spins only[172-174]). In **Figure 4.8b**, the clear ^1H-^{13}C correlations at 0.8(^1H) and 45.2(^{13}C) ppm, and at 2.1(^1H) and 48.2(^{13}C) ppm, can be ascribed to the CH_2 and CH groups, respectively.

Figure 4.8c shows the 1D ^{13}C CP/MAS spectrum of the thermally annealed GDNPs(800) treated by an unsubstituted maleimide (M). In comparison with the 1D ^{13}C CP/MAS spectrum of the GDNP precursors prior to M-treatment (**Fig. 4.8a**), the spectrum of M-treated GDNPs shows an additional peak of pronounced intensity at 173 ppm (C2/blue dot), characteristic of the C=O group pertaining to the control maleimide substituent M; the solution 13C NMR spectrum of M (**Figure 4.10**) is provided. However, it is worth noting that the second peak at 135 ppm, characteristic of the alkene in M (**Figure 4.10**), is absent in the 1D ^{13}C CP/MAS spectrum of M-treated GDNP – an observation consistent with the apparent loss of the bending modes at 693 cm^{-1} and 827 cm^{-1} seen earlier in the FTIR spectrum of EHM-treated GDNPs (**Figure 4.3**). While the occurrence of extra sp^3-hybridized carbons (C1/red dot) at the nanodiamond surface upon binding of M is likely convoluted in the GDNP resonances at 34.5 and 47.3 ppm (**Figure 4.8c**), the 2D $^{13}C\{^1H\}$ HETCOR spectrum shown in **Figure 4.8d** indicates a new ^1H-^{13}C correlation at 1.5(^1H) and 33(^{13}C) ppm, that is not initially present in the 2D $^{13}C\{^1H\}$ HETCOR spectrum of non-functionalized GDNPs (**Figure 4.8b**) – a result which confirms the occurrence of new sp^3-hybridized carbons (C1/red dot) appended to the nanodiamond surface. The resonance at ca. 47(^{13}C) ppm is assigned to the CH_2 and CH groups that are initially present on the GDNP surface. Importantly, both the 1D ^{13}C CP/MAS and 2D $^{13}C\{^1H\}$ HETCOR spectra

of M-treated GDNP point to the occurrence of only one new type of sp^3-hybridized carbon (CH or CH_2) at the nanodiamond surface upon binding of M. In **Figure 4.9c**, the ^1H-^1H double-quantum (DQ) spectrum of M-treated GDNP shows a single autocorrelation peak for the proton resonance at 0.8 ppm, which corresponds to the CH_2 surface groups initially present at the nanodiamond outer shell. In contrast, the protons at 2.1 and 1.5 ppm (marked with red box) in **Figure 4.8d** do not show any autocorrelation footprint by ^1H-^1H DQ analysis – a result which validates both the identity of the new sp^3-hybridized carbons that occur upon binding: CH groups (C1/red dot, **Figure 4.8c**), and the binding scheme: a two-point binding reaction at the nanodiamond surface. This result was confirmed by examining the ^{13}C chemical shift anisotropy (CSA) of the C=O groups in M-treated GDNPs, which provides clear insight into the dynamics and the nature of the binding pattern.[175] In **Figure 4.8e**, the static ^{13}C NMR spectrum of M-GDNPs shows a broad structureless resonance in the region of interest (centered at *ca.* 173 ppm; circled red). While a one-point binding scheme would allow for axial rotations of M in the magnetic field, resulting in a sharp and isotropic C=O resonance (*i.e.* wide range of local orientations at the nuclear site), here the powder-like pattern observed in the static 13C NMR spectrum of M-GDNPs indicate a fixed molecular orientation with respect to the external magnetic field. It can thus be concluded that a two-point binding scheme – most likely a concerted addition reaction – is taking place between maleimide and the outer shell of the nanodiamonds. The same demonstration applies to the GDNPs(800) treated with the functional maleimide derivative EHM, for which the 1D ^{13}C CP/MAS spectrum is provided as **Figure 4.8f**. Here, the large number of aliphatic carbons in EHM gives rise to several additional peaks (C3-C10/green dots) at lower chemical shift (11, 17, 10, 25 ppm) and changes the peak lineshape of the

broader resonance common to M-GDNPs (30-50 ppm); the 2D 13C{1H} HETCOR analysis in the (**Figure 4.9d**) allows for the detailed peak assignment. As in M-GDNPs, the 1D ^{13}C CP/MAS spectrum of EHM-treated GDNPs shows a peak of pronounced intensity at 173 ppm (C2/blue dot), characteristic of the C=O group pertaining to EHM, and is in agreement with the presence of bound EHM at the nanodiamond surface. This step shows that the protocol of direct functionalization with maleimide is applicable to other substituted derivatives, such as the solubilizing alkyls commonly used to improve the stability of a variety of nanoparticles in solution.[176]

Figure 4.8 a) 1D ^{13}C CP/MAS solid-state NMR spectrum of thermally annealed GDNPs(800); b) 2D ^{13}C{^{1}H} HETCOR spectra of the GDNPs(800); c) 1D ^{13}C CP/MAS solid-state NMR spectrum of GDNPs(800) treated with the control unsubstituted maleimide M (M-GDNP); d) 2D ^{13}C{^{1}H} HETCOR spectra of the M-GDNPs; e) 1D ^{13}C CP/static solid-state NMR spectrum of the M-GDNPs; f) 1D ^{13}C CP/MAS solid-state NMR

spectrum of GDNPs(800) treated with the functional maleimide EHM (EHM-GDNP). The

molecular structures and peak assignments are indicated on the spectra.

Figure 4.9 a) 1D ^{13}C MAS solid-state NMR spectrum of thermally annealed

GDNPs(800). In the absence of ^{1}H decoupling, the resonance observed in Fig. 2a (at *ca.*

47.3 ppm) and pertaining to hydrogen-substituted carbons (CH, CH$_2$) cannot be observed.

Here, a 1D ^{13}C CP/MAS analysis is required to account for the low content of hydrogen-

substituted carbons located at the nanodiamond surface (also see Fig. 4.9b). **b)** 1D ^{1}H MAS

solid-state NMR spectrum of thermally annealed GDNPs(800). **c)** ^{1}H-^{1}H double-quantum

(DQ) analysis of M-treated GDNPs(800) treated with the control unsubstituted maleimide

M (M-GDNP). DQ signals in the w1 dimension are observed at frequencies corresponding

to the sum of single quantum (SQ) frequencies of protons that are close to one another in

space and will correlate in the *w2* dimension with the corresponding ordinary proton resonances. DQ correlation analyses can serve to identify equivalent protons, and is useful here to differentiate between CH and CH_2 moieties. **d)** 2D $^{13}C\{^1H\}$ HETCOR spectra of GDNPs(800) treated with the functional maleimide EHM (EHM-GDNP). The molecular structure (EHM) and peak assignments are indicated on the 2D spectrum.
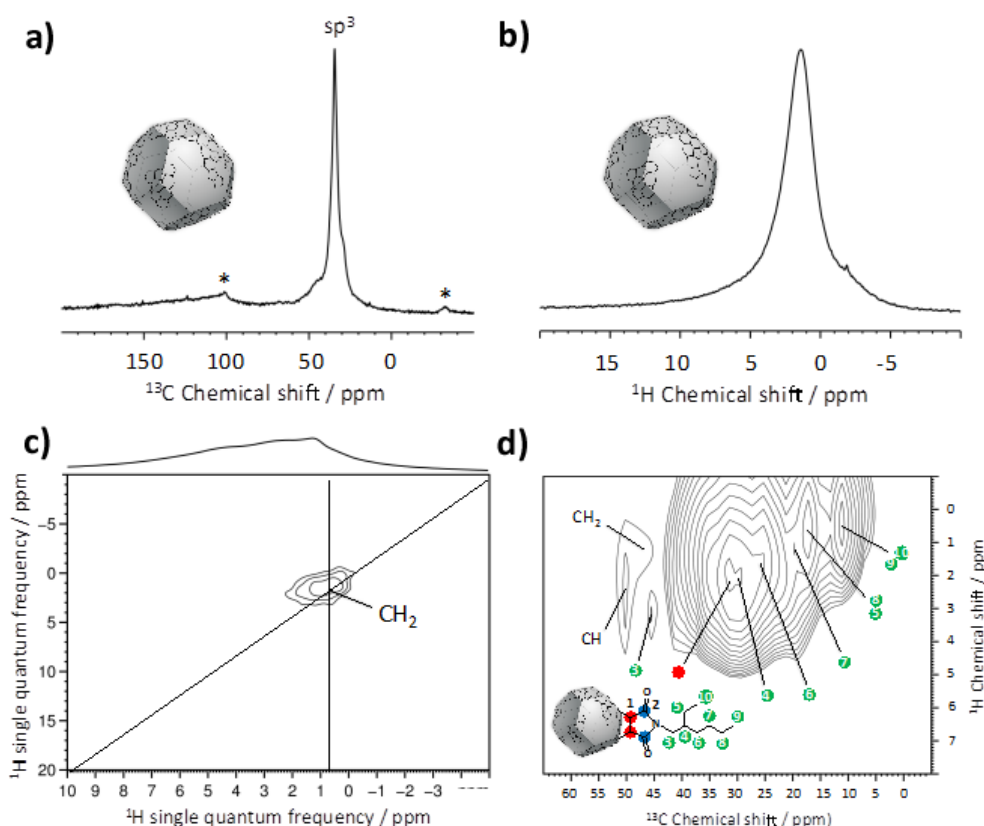

Figure 4.10 Solution ^{13}C NMR spectrum of maleimide M (free substituent).

4.3.4 Functionalization of Annealed DDNPs with Maleimide-derivatized Fluorescein Dye

In parallel, **Figure 4.11** shows that thermally annealed GDNPs labeled with a maleimide-derivatized fluorescein dye (**Figure 4.11a**) can yield fluorescent nanodiamonds (**Figure 4.11b**), which pave the path to the use of nanodiamond templates for sensing and

bioimaging.[1a] FTIR, UV-Vis and fluorescence spectra, fluorescence microscopy images are provided in the **Figure 4.12**, **Figure 4.13** and **Figure 4.14**.

Figure 4.11 a) Fluorescein-5-maleimide (F5M); b) bright-field and c) fluorescence microscopy images of the GDNPs(800) treated with the fluorescent F5M dye (F5M-GDNP), and spun-coated on glass.

Figure 4.12 FTIR spectra of thermally annealed GDNPs(800) (red curve), the unfunctionalized fluorescein-5-maleimide (F5M) dye (green curve), and GDNPs(800) treated with F5M (F5M-GDNP) (blue curve).

Figure 4.13 a) UV-Vis and b) Fluorescence spectra (in solution) of thermally annealed GDNPs(800) (red curve), the unfunctionalized fluorescein-5-maleimide (F5M) dye (green curve), and GDNPs(800) treated with F5M (F5M-GDNP) (blue curve).

Figure 4.14 Fluorescence microscopy images of **a)** thermally annealed GDNPs(800) and **b)** the GDNPs(800) treated with the fluorescent F5M dye (F5M-GDNP); spun-coated on glass. **c)** and **d)** Bright-field microscopy images of the GDNPs(800) and F5M-GDNP, respectively.

4.4 Conclusion

In summary, using a combination of FTIR and SS-NMR analyses, we have shown that maleimide-derivatized substituents can be effectively appended to the *graphite-like* outer shell of thermally annealed nanodiamonds. From the 2D ^{13}C{^{1}H} HETCOR, ^{1}H-^{1}H DQ and CAS NMR analyses performed, the step of direct functionalization between maleimide and the nanodiamond surface can be described as a two-point binding reaction involving

the alkene of the functional imide. Taking our fluorescein-substituted GDNP as a model system, this direct approach to functionalizing nanodiamonds under ambient conditions is amenable to the preparation of nanomaterials with tunable functional substituents, as required in the development of nanocomposites, surface coatings, nanoscale photonic devices, and sensing/imaging nanoprobes.

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