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Electropolymerized Star-Shaped Benzotrithiophenes Yield π -Conjugated Hierarchical Networks with High Areal Capacitance

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ABSTRACT

High-surface-area π -conjugated polymeric networks have the potential to lend outstanding capacitance to supercapacitors because of the pronounced faradaic processes that take place across the dense intimate interface between active material and electrolytes. In this report, we describe how benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (**BTT**) and tris(ethylenedioxythiophene)benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (**TEBTT**) can serve as 2D (trivalent) building blocks in the development of electropolymerized hierarchical π -conjugated frameworks with particularly high areal capacitance. In comparing electropolymerized networks

of **BTT**, **TEBTT**, and their copolymers with EDOT, we show that **TEBTT**/EDOT-based copolymers, *i.e.* P(**TEBTT**/EDOT), can achieve higher areal capacitance (e.g., as high as 443.8 mF cm⁻² at 1 mA cm⁻²) than those achieved by their respective homopolymers (**PTEBTT** and PEDOT) in the same experimental conditions of electrodeposition (**PTEBTT**: 271.1 mF cm⁻² (at 1 mA cm⁻²) and PEDOT: 12.1 mF cm⁻² (at 1 mA cm⁻²)). For example, P(**TEBTT**/EDOT)-based frameworks synthesized in a 1:1 monomer-to-comonomer ratio show a ca. 35x capacitance improvement over PEDOT. The high areal capacitance measured for P(**TEBTT**/EDOT)-based frameworks can be explained by the open, highly porous hierarchical morphologies formed during the electropolymerization step. With >70% capacitance retention over 1,000 cycles (up to 89% achieved), both **PTEBTT**- and P(**TEBTT**/EDOT)-based frameworks are resilient to repeated electrochemical cycling and can be considered promising systems for high life cycle capacitive electrode applications.

INTRODUCTION

Of all electrochemical devices capable of storing charge and delivering power, high-power-density and high-energy-density supercapacitors with extensive life cycles are especially attractive for applications such as portable electronics and electric vehicle powertrains.^{1, 2} Comparatively, high-power densities (*i.e.*, fast charge-discharge rates) can be more readily achieved than high-energy densities in electrochemical capacitors because of the nature of the charge storage process.³ For supercapacitors, a wide range of material systems, including metal oxides³ and conjugated polymers,^{4,5} are being explored for their inclusion in the development of higher-performing electrode materials that combine high energy and power densities. Some pseudocapacitive materials can yield energy densities as high as 300 Wh kg⁻¹ (at power densities

of 0.47 kW kg^{-1}),⁶ while pure-electric double-layer capacitors yield significantly lower figures of *ca.* 10 Wh kg^{-1} (at 1 A g^{-1}).⁷ In addition to the intrinsic pseudocapacitive properties of oxides and polymers, their nano- and meso-scale morphologies and the interplay between material surface and electrolytes are 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.⁸⁻¹⁰ Electropolymerization approaches using monomer solutions can be performed reproducibly, while incorporating ions and counterions in the process of forming open, porous nanostructured films.^{11, 12} Thus, several studies have emphasized the range of achievable morphologies using conjugated polymers such as polyaniline (PANI),^{13, 14} polypyrrole,^{14, 15} polythiophene,¹⁶ and poly(3,4-ethylenedioxythiophene) (PEDOT)^{17, 18}, derived from the electropolymerization of commercially available monomers. For example, varying the experimental conditions for the synthesis of PANI induces considerable morphological changes that impact material capacitance (i.e., nanospheres to nanorods to nanofibers).¹⁹

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.^{20, 21} For example, phenylenevinylene-,²⁰ phenylethynylene-,²¹ and triazine-based²¹ motifs have been shown to yield highly porous morphologies with specific surface values $>1,000 \text{ m}^2 \text{ g}^{-1}$ in specific experimental electrodeposition conditions, while trivalent motifs such as 1,3,5-tris(oligothienyl)benzene^{22, 23} and triarylamine²⁴⁻²⁷ are amenable to synthesizing efficient capacitive conjugated networks. In parallel, the copolymerization of monomers with comparable

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3 oxidation potentials, such as 2,2'-bithiophene and triphenylamine (10 mol%) motifs,²⁶ is another
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5 promising strategy for the preparation of tunable capacitive polymeric frameworks.
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8 In this report, we compare the electropolymerization patterns of two 2D (trivalent) building
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10 blocks—benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (**BTT**) and
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12 tris(ethylenedioxythiophene)benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (**TEBTT**) (Scheme 1)—and
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14 their copolymerization with 3,4-ethylenedioxythiophene (EDOT). We also describe the
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16 experimental conditions required to form hierarchical π -conjugated frameworks with particularly
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18 high areal capacitance. Based on the basic characterization of **BTT**-based well-defined
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20 oligomers^{28, 29} and **TEBTT** homopolymers from previous reports,³⁰ we clarify the fundamental
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22 differences between electropolymerized homopolymer and copolymer networks made from these
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24 two building motifs, and emphasize their use for the synthesis of high-capacitance,
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26 nanostructured 3D polymeric networks that are resilient to repeated electrochemical cycling. In
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28 particular, comparing **BTT**- and **TEBTT**-based networks, we find that **TEBTT**-based
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30 homopolymers and copolymers with EDOT are substantially more capacitive (reaching up to
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32 271.1 mF cm⁻² and 443.8 mF cm⁻² (1 mA cm⁻²), respectively) and stable upon cycling (up to 73%
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34 and 89% capacitance retention after 1,000 cycles, respectively) than their **BTT** counterparts.
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Scheme 1 (a) Schematic representation of 3,4-ethylenedioxythiophene (EDOT), benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene (BTT), tris(ethylenedioxythiophene)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.

METHODS

Synthetic Procedures. Benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene²⁷ (**BTT**) and tris(ethylenedioxythiophene)benzo[1,2-*b*:3,4-*b'*:5,6-*b''*]trithiophene³⁰ (**TEBTT**) were synthesized according to previously reported methods. The Supporting Information (SI) provides the details of the synthetic protocols. All monomers were characterized by ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) on a Bruker Advance III Ultrashielded 400 Plus instrument at room temperature. The ¹H, ¹³C NMR 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.

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 AgNO₃ and 100 mM tetrabutylammonium perchlorate (TBAP) solution] was used as the reference electrode, and a platinum wire was used as the counter electrode. The working electrode consisted of a gold button electrode (7 mm-diameter electrode fitted with 3 mm-diameter gold disc), a carbon cloth (*ca.* 1 cm²), a platinum button electrode (7 mm-diameter electrode fitted with 3 mm-diameter platinum disc), or a glassy carbon electrode (7 mm-diameter

electrode fitted with 3 mm-diameter glassy carbon disc). Figure S11 shows the cyclic voltammogram of Ferrocene, used as standard; measurements performed in 100 mM tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile (ACN). All electrolyte solutions were prepared using anhydrous ACN or dichloromethane (DCM) solvents and with 100 mM TBAPF₆ as the supporting electrolyte.

Linear scan voltammograms of **BTT**, **TEBTT**, and EDOT were collected on gold button electrodes at a scan rate of 20 mV s⁻¹ from solutions of 5, 1, and 5 mM in DCM respectively (a lower molarity of **TEBTT** was used for solubility reasons). The (**BTT**/EDOT)-based copolymers, *i.e.* P(**BTT**/EDOT), were electrodeposited on highly porous conducting carbon cloth from several monomer solutions of different **BTT**/EDOT monomer compositions (1:0, 3:1, 1:1, 1:3, 1:6, and 0:1). The electrodeposition experiments (20 cycles) were performed in ACN in a potential window of -0.7—+1.6 V and with a scan rate of 50 mV s⁻¹. P(**TEBTT**/EDOT) was prepared on glassy carbon electrodes from several monomer solutions (see Table 1) of different **TEBTT**/EDOT monomer compositions (1:0, 3:1, 1:1, 1:3, 1:9, 5:95, and 0:1) in DCM, and 20 deposition cycles at a scan rate of 50 mV s⁻¹ in a voltage window of -1.0—+1.2 V (vs. Ag/Ag⁺) unless otherwise specified. The analysis of the capacitive performances of the electrodeposited materials was performed in ACN.

The areal capacitance (*Ca*) of electrodeposited polymeric materials was calculated from the charge-discharge curves using the following general equation:³¹

$$Ca = I^* \Delta t / \Delta V ,$$

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).³¹ 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.

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.

RESULTS AND DISCUSSION

Electrochemical Characterizations of BTT and TEBTT

Figure 1a 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 Figures 1b and 1c, 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/AgCl)³⁰ and $+1.55$ V (vs.

Ag/AgCl):²⁹ we note that the oxidation feature observed in the prior study³⁰ was somewhat broad and likely encompassed oxidation peaks E_{ox1} and E_{ox2} similar to those shown in Figure 1b (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; Fig. 1a) and similar to that reported for terthiophene (*ca.* +1.0 V; vs. Ag/Ag⁺).^{32, 33} This oxidation onset of **BTT** is, however, significantly lower than that of single-ring thiophene motifs (*ca.* +1.75 V; vs. Ag/Ag⁺),³³ illustrating how redox potential depends on conjugation length and HOMO-LUMO gap reduction in more extended **BTT** π -systems.³³ The second and third oxidation features in the linear scan of **BTT** occur at $E_{ox2} = +1.59$ V and $E_{ox3} = +2.04$ V. The origin of these sequential oxidations is unclear, as those may arise from a sequential oxidation of the thiophene rings of **BTT** to radical cations or stem from the formation of coupled products resulting from the initial oxidation step (thiophene-based cation radicals to form oligomeric species).³⁴

Figure 1 (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** (Fig. 1c) 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/AgCl)³⁰. Figure 1c provides further insight on the consecutive oxidation features in **TEBTT**, although it should be noted that the second and third oxidation features ($E_{\text{ox}2} = +0.71$ V and $E_{\text{ox}3} = +1.32$ V) are somewhat convoluted in the broad redox response of **TEBTT** in this voltage window. While the first oxidation peaks ($E_{\text{ox}1} = +0.49$ V) can be assigned to the oxidation of an EDOT motif in **TEBTT**, several processes can be at the origin of the three following oxidation features ($E_{\text{ox}2} = +0.71$ V, $E_{\text{ox}3} = +1.32$ V, and $E_{\text{ox}4} = +1.98$ V) and those discussions are beyond the scope of this study.

Copolymerization of BTT and EDOT

Considering the close oxidation potentials of **BTT** ($E_{\text{ox}1} = +1.28$ V; Fig. 1b) and EDOT (+1.02 V; Fig. 1a), 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,^{1,17,35} 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) 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 illustrate the morphologies of the electrodeposited **PBTT** (Fig. 2a; 1:0 ratio in **BTT**/EDOT), **BTT**/EDOT-based copolymers (Fig. 2b, 2c, 2d, and 2e; 3:1, 1:1, 1:3, and

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3 1:6 ratios, respectively), and PEDOT (Fig. 2f; 0:1 ratio). Comparing the film depositions
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5 achieved in Figures 2a (**PBTT**) and 3f (PEDOT), the contrasts in electrodeposition yields and
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7 morphologies formed on the carbon cloth electrodes are rather obvious, and it is interesting to
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9 note that **BTT** may not electropolymerize as efficiently as EDOT in spite of their comparable
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11 onsets of oxidation. This might be explained by the lower conductivity of **PBTT** compared to
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13 PEDOT (although challenging to measure in non-continuous electropolymerized films), which
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15 may affect the propensity of the **BTT** monomer to electropolymerize further once a critical
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17 amount of **PBTT** is deposited on the carbon cloth. In contrast to the dense nodular morphology
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19 and large aggregates (700–2,500 nm) obtained on electropolymerizing EDOT (Fig. 2f), sparser
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21 aggregates with high aspect ratios are observable for **PBTT** (width dispersion: 80–160 nm;
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23 length: 400–700 nm). Looking at the intermediate morphologies that develop on copolymerizing
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25 **BTT** and EDOT (depicted in Figures 2b, 2c, 2d, and 2e), it is worth noting however that
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27 electrodeposited films of P(**BTT**/EDOT) are more densely nanostructured than those of their
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29 **PBTT** counterpart, showing significant differences in aggregate size distributions. In general,
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31 blending **BTT** and EDOT leads to the electrodeposition of aggregate patterns that are somewhat
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33 smaller in size (i.e., more nanostructured) compared to PEDOT films and dependent on the
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35 initial **BTT**/EDOT monomer ratios (Fig. 2b, 3:1 ratio in **BTT**/EDOT, aggregates: 30–300 nm;
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37 clusters: 500–1,000 nm; Fig. 2c, 1:1 ratio in **BTT**/EDOT, clusters: 400–2,000 nm; Fig. 2d, 1:3
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39 ratio in **BTT**/EDOT, aggregates: ca. 40 nm; clusters: 1,000–2,000 nm; Fig. 2e, 1:6 ratio in
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41 **BTT**/EDOT, clusters: 200–1,400 nm).
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Figure 2 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)

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3 1:1, (d) 1:3, (e) 1:6, and (f) 0:1. Electrodeposition conditions: 50 mM monomer solutions in
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5 ACN; 20 deposition cycles in a voltage window of -0.7 – +1.5 V (vs. Ag/Ag⁺), on carbon cloth
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7 electrodes; deposition scan rate of 50 mV s⁻¹.
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11 The electroactivity and capacitive properties of **PBTT**, PEDOT, and P(**BTT**/EDOT) were
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13 measured by CV; the corresponding voltammograms are shown in Figures 3a and 3b. For ease of
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15 comparison, each voltammogram is normalized to the extent of functionalized surface area, and
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17 in Figure 3c the areal capacitance (*Ca*) of the electrodeposited polymers is extracted from
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19 galvanostatic charge-discharge measurements (the values are shown directly on the plot). By
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21 comparing all electrodeposited systems in Figure 3, we note that **PBTT** homopolymers exhibit
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23 only a modest capacitance value of 73 mF cm⁻² (at 5 mA cm⁻²), which is consistent with the lack
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25 of reversibility of the broad redox process in the 0.0 to +0.8 V voltage window and with the
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27 smaller amount of material deposited on the carbon cloth electrode (Fig. 2a). It is interesting to
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29 note, however, that considering recently published studies on electropolymerized material
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31 systems for supercapacitor applications,³⁵⁻³⁸ *Ca* values >50 mF cm⁻² inferred for **PBTT** remain
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33 significant. For comparison, polypyrrole/graphene oxide nanocomposites have been shown to
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35 yield 22.8 mF cm⁻² (at 0.1 mA cm⁻²),³⁸ while poly(3,4-propylenedioxyppyrrrole)/SWCNT
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37 composites attain 16.4 mF cm⁻² (at 0.9 mA cm⁻²);³⁶ capacitance values that are expected to drop
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39 significantly at higher current densities, such as those at which we estimate the capacitance of
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41 **PBTT** (i.e., 5 mA cm⁻²).
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49 Following the same experimental conditions as those used for the electrodeposition of **PBTT**,
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51 PEDOT-functionalized carbon cloth electrodes yield *Ca* values of 733 mF cm⁻² (at 5 mA cm⁻²),
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53 confirming that **PBTT** homopolymers perform more modestly than PEDOT. Here again, these
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55 differences may arise from the lower electronic conductivity of **PBTT** compared to PEDOT,
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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 3c (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 couplings in unsubstituted thiophene-based motifs subjected to oxidative polymerization conditions are known to affect conjugation, and subsequently lower the conductivity, electrochemical cycling stability, and capacitive performance of thiophene-based polymers.^{33, 39, 40} In parallel, and as shown in Figure 3, the capacitive cycles of the several P(**BTT**/EDOT) copolymers (see Scheme 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 3 (a, b) Cyclic voltammograms of electrodeposited **PBTT**, PEDOT, and several **BTT/EDOT**-based 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} (Note: insets **a**) and **b**) show different potential windows). Electrodeposition conditions: 50 mM monomer solutions in ACN; 20 deposition cycles in a voltage window of $-0.7 - +1.6 \text{ V}$ (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.

Copolymerization of **TEBTT** and **EDOT**

As an alternative to **BTT**, and to mitigate the probability of α - β and β - β 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.³³ As a result, and as previously discussed from Figure 1c, **TEBTT** exhibits a lower oxidation potential ($E_{\text{ox1}} = +0.49$ V). Because **TEBTT** is a more extended π -conjugated system, π -stacking and aggregation make it 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 1. Figure 4a 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 S12). As emphasized in Table 1 and Figure 4a, 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 1). **PTEBTT** films electrodeposited on the GC electrode exhibit an oxidation onset at +0.20 V (Fig. 4a) and a broad quasi-reversible redox couple ($E_{\text{ox1}} = +0.62$ V – $E_{\text{red1}} = +0.27$ V) followed by an irreversible oxidation (and related reduction $E_{\text{red2}} = +0.69$ V on the reverse cycle). The SEM image in Figure 5a 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 Figures 4b and 4c. 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, Figures 4b and 4c 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 Fig. 4b) and for films cycled over a wide range of scan rates (Fig. 4c). These results indicate that films of electropolymerized **PTEBTT** are not limited by electronic conductivity or electrolyte diffusion aspects. As illustrated in Figure 4c, 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.⁴¹ The interpolations calculated give $I_{\text{pa}} = -0.13(3) v^{1/2} + 2.26(4)$ and $I_{\text{pc}} = -0.21(2) v^{1/2} - 1.63(3)$ with *v* representing the scan rate investigated.

Figure 4 (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.

Table 1 Summary of electrodeposition conditions for **PTEBTT**, PEDOT, and several **TEBTT**/EDOT-based 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	<i>Ca</i> (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 5 mM	GC	Cycling [-1 – 1.2 V]	40 cycles 80 cycles 120 cycles	99.8 mF cm ⁻² 127.1 mF cm ⁻² 356.7 mF cm ⁻²	1 mA 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 5 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 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 1). These lower *Ca* values may result from the lower propensity of the monomer to undergo electropolymerization in the lower dielectric constant solvent DCM ($\epsilon = 8.9$)⁴² (ACN: $\epsilon = 36.6$)⁴² combined with the effect of using a WE that is inherently less porous (on going from carbon cloth to the GC button electrode).^{43,44} The SEM image in Figure 5d 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) by electrodeposition 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 Figures 5b and 5c, the P(**TEBTT**/EDOT)-based framework exhibit morphologies that are fairly distinct from those of their homopolymer counterparts, **PTEBTT** and PEDOT. In particular, the higher-magnification SEM images shown in Figures 5e and 5f indicate that the aggregate patterns formed are highly nanostructured (Fig. 5b and 5e, 1:1 ratio in

TEBTT/EDOT, aggregates: <100 nm; clusters: 500-1,200 nm; Fig. 5c and 5f, 1:9 ratio in **TEBTT**/EDOT, aggregates: <50 nm; clusters: 600-1,000 nm). Here, we note that the dense, highly textured hierarchical networks formed by P(**TEBTT**/EDOT) are consistent with the values of high areal capacitance given in Table 1. The CV curves of the electrodeposited P(**TEBTT**/EDOT) shown in Figure 6a reflect inherently more capacitive material systems compared to their homopolymer counterparts, **PTEBTT** or PEDOT; observations consistent with the higher C_a values obtained for the copolymers and summarized in Table 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 C_a 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 6 also shows how the capacitive cycles of the several **TEBTT**/EDOT-based 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.

Figures 6b and 6c depict the areal capacitance of **PTEBTT**, PEDOT, and the **TEBTT**/EDOT-based 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 (Fig. 6b) and cycle number (Fig. 6c). It is interesting to note that several **TEBTT**/EDOT-based copolymers (1:1, 1:3, and 1:9 ratios) undergo only little capacitance variations with current density increments,

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3 suggesting excellent electrolyte diffusion within the highly porous P(**TEBTT**/EDOT)-based
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5 frameworks. Figure 6c shows that films of electrodeposited **PTEBTT** are relatively resilient to
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7 repeated electrochemical cycling with *ca.* 73% of capacitance retained (at 2 mA cm⁻²) over 1,000
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9 cycles (vs. 96% for PEDOT over 1,000 cycles (at 2 mA cm⁻²). Here, we note that our estimate of
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11 the stability of the homopolymer **PTEBTT** is on the low end of the capacitance retention
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13 reported in prior work (*ca.* 95% over 1,400 cycles),³⁰ a difference that is likely to stem from the
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15 significantly thicker films examined in this study: **PTEBTT** is electrodeposited in 120 cycles
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17 between -1.0 and +1.2 V vs. only 8 cycles between 0.0 and +1.0 V in earlier work.³⁰ Likewise,
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19 all of the **TEBTT**/EDOT-based copolymers show >70% of capacitance retention (at 2 mA cm⁻²)
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21 over 1,000 cycles (with up to *ca.* 89% achieved), demonstrating satisfying long-term stability
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23 upon repeated electrochemical cycling. These stability figures, ranging between those of
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25 **PTEBTT** and PEDOT, are greater than those reported for some of the more conventional
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27 conjugated polymers such as 50% capacitance retention over 1,000 cycles (at 2 mA cm⁻²) for
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29 polypyrrole,⁹ 84% capacitance retention after 200 cycles for poly(3-methylthiophene) (longer
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31 cycling times not provided), and 70% capacitance retention after 1,000 cycles for PANI.^{5,9} Last,
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33 we note that the mechanical stability and long-term cycling performances of the
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35 P(**TEBTT**/EDOT)-based frameworks may be further improved in hybrid carbon-based
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37 composite systems including carbon nanotubes or graphene oxide; however this falls beyond the
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39 scope of this report.¹⁰
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Figure 6 (a) Cyclic voltammograms of electrodeposited **PTEBTT**, PEDOT, and several **TEBTT**/EDOT-based 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 $-1.0 - +1.2 \text{ V}$ (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 **TEBTT**/EDOT-based copolymers. **(c)** areal capacitance vs. cycle number for several **TEBTT**/EDOT-based copolymers (at 2 mA cm^{-2}).

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(ethylenedioxythiophene)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—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. 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.

ASSOCIATED CONTENT

Supporting Information. Detailed syntheses of **BTT** and **TEBTT** with their respective ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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