Supplementary Material (ESI) for Chemical Communications

# One polymer for all: Benzotriazole Containing Donor-Acceptor Type Polymer as a Multi-Purpose Material

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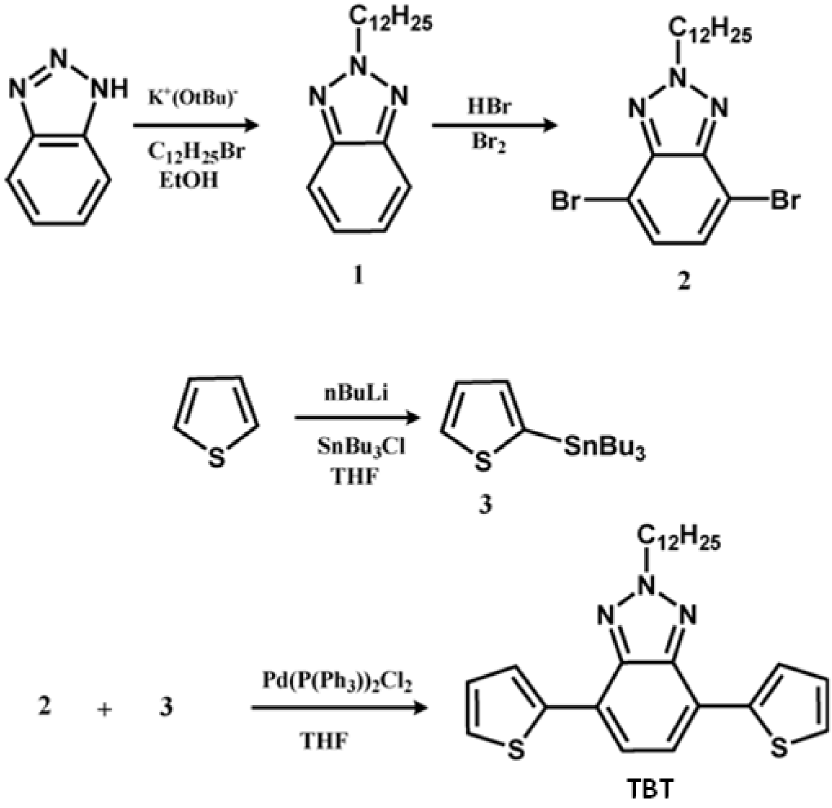
## Electronic Supplementary Information

## Experimental

### General

All chemicals were purchased from Aldrich except THF which was purchased from Acros. Tributyl(thiophene-2-yl)stannane was synthesized according to a previously described method.[1] All reactions were carried out under argon atmosphere unless otherwise mentioned. All electrochemical studies were performed under ambient conditions using a Voltalab 50 potentiostat. Electropolymerization was performed in a three-electrode cell consisting of an Indium Tin Oxide doped glass slide (ITO) as the working electrode, platinum wire as the counter electrode, and Ag wire as the reference electrode. $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 Spectrometer. Chemical shifts were given in ppm downfield from tetramethylsilane. Varian Cary 5000 UV–Vis spectrophotometer was used to perform the spectroelectrochemical studies of the polymer. Fluorescence measurements were conducted using a Varian Eclipse spectrofluorometer. Column chromatography of all products was performed using Merck Silica Gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). Reactions were monitored by thin layer chromatography using fluorescent coated aluminum sheets. Solvents used for spectroscopy experiments were spectrophotometric grade. Colorimetry measurements were done via Minolta CS-100 Spectrophotometer. Mass analysis was carried out on a Bruker time of flight (TOF) mass spectrometer with an electron impact ionization source. Average molecular weight was determined by gel permeation chromatography (GPC) using a Polymer Laboratories GPC 220.



***Scheme ESI-1.*** Synthesis of 1, 2, 3 and TBT.

### Synthesis of 2-dodecylbenzotriazole:

Synthesis of 2-dodecylbenzotriazole was performed according to methodology described in literature.[2] 1,2,3-Benzotriazole (5.0 g, 42 mmol), potassium tert-butoxide (5.0 g, 44 mmol) and bromododecane (12.2 g, 49 mmol) were dissolved in methanol (50 mL). The reaction mixture was refluxed for 12 h and monitored by TLC. After removal of the solvent by evaporation, the residue was dissolved in $CHCl_3$ and extracted with water. The organic extract was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. Column chromatography on silica gel was performed to obtain 2-dodecylbenzotriazole as a colorless oil (3.7g, 31%). $^1H$ NMR (400MHz, $CDCl_3$, $\delta$): 7.76 (m, 2H), 7.26 (m, 2H), 4.62 (t, *J*=7.1Hz 2H), 2.12 (m, 2H), 1.25-1.15 (m, 18H), 0.78 (t, *J*=6.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3, δ): 144.3, 126.1, 117.9, 56.6, 31.8, 30.0, 29.5, 29.4, 29.4, 29.3, 29.3, 29.0, 26.5, 22.6, 14.0.

**Synthesis of 4,7-dibromo-2-dodecylbenzotriazole:** [2]

2-Dodecylbenzotriazole (3.7g, 13.1mmol) and an aqueous HBr solution (5.8 M, 15 ml) were added to a flask, and the mixture was stirred for 1 h at 100°C. Bromine (5.9 g, 36 mmol) was added, and the mixture was stirred for 12 h at 135°C. After cooling the mixture to room temperature, an aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. With column chromatography, 4,7-dibromo-2-dodecylbenzotriazole was obtained as light yellow oil (4.3 g, 75%). $^{1}$H NMR (400MHz, $CDCl_3$, δ): 7.36 (s, 2H), 4.60 (t, *J*=7.0 Hz, 2H), 2.10 (m, 2H), 1.38-1.12 (m, 18H), 0.80 (t, *J*=6.9 Hz, 3H). $^{13}$CNMR (100 MHz, $CDCl_3$, δ): 143.7, 129.4, 109.9, 57.4, 31.8, 30.1, 29.5, 29.5, 29.4, 29.4, 29.3, 28.9, 26.4, 22.6, 14.0.

**Synthesis of 2-dodecyl-4,7-di(thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (TBT):**

4,7-Dibromo-2-dodecylbenzotriazole (100 mg, 0.224mmol), and tributyl(thiophen-2-yl) stannane were dissolved in anhydrous THF (100 ml) and dichlorobis(triphenylphosphine)-palladium(II) (50 mg, 0.045 mmol) was added at room temperature. The mixture was refluxed for 12 hours under argon atmosphere. Solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel to obtain 75 mg (74%) TBT. $^{1}$H NMR (400MHz, $CDCl_3$, δ): 8.01 (d, *J*=5.6 Hz, 2H), 7.52 (s, 2H), 7.28 (d, *J*=6.0 Hz, 2H), 7.09 (t, $J_A$=8.8 Hz, $J_B$ = 4.8, 2H), 4.60 (t, *J*=7.0 Hz, 2H), 2.10 (m, 2H), 1.38-1.15 (m, 18H), 0.80 (t, *J*=6.9 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, δ): 142.4, 140.2, 128.4, 127.3, 125.8, 123.9, 123.0, 57.1, 32.2, 30.3, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 26.9, 22.9, 14.4. MS (*m*/*z*): 451 [M+]

## Chemical polymerization of TBT (PII)

100 mg TBT was dissolved in 10 mL of $CHCl_3$ under argon atmosphere. $FeCl_3$ (142 mg) were suspended in 10 mL of nitromethane and slowly added to the monomer solution. Yellow solution slowly turned to deep green and finally deep blue. Mixture was stirred for 4 h and then added into 200 mL methanol. The precipitate was dissolved in $CHCl_3$ and extracted with water several times. Organic phase was dried with magnesium sulfate and evaporated. Residue was dissolved in 50 mL THF and 50 mL hydrazine monohydrate was added. In order to de-dope the polymer completely, mixture was stirred for 12 h and during this period solution turned to dark red. THF was evaporated under reduced pressure. Chloroform was added to the residue and the organic phase was extracted several times with water. Combined organic phases were evaporated and the residue was stirred in acetone to remove unreacted monomers. The polymer was filtered and dried under vacuum to give PII as dark-red solid. $^1H$ NMR (400MHz, $CDCl_3$, $\delta$): 7.50 (benzotriazole), 7.2 (thiophene), 7.0 (thiophene), 4.6 (N-$CH_2$), 1.5-0.8 (pendant alkyl chain).

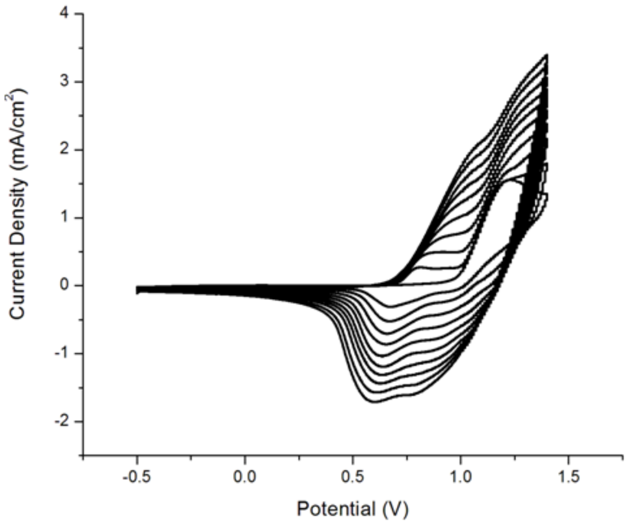


***Figure ESI-1.*** Repeated potential-scan electropolymerization of TBT in 0.1 M ACN/$TBAPF_6$ solvent-electrolyte system at a scan rate of 100 mVs$^{-1}$ on ITO electrode.

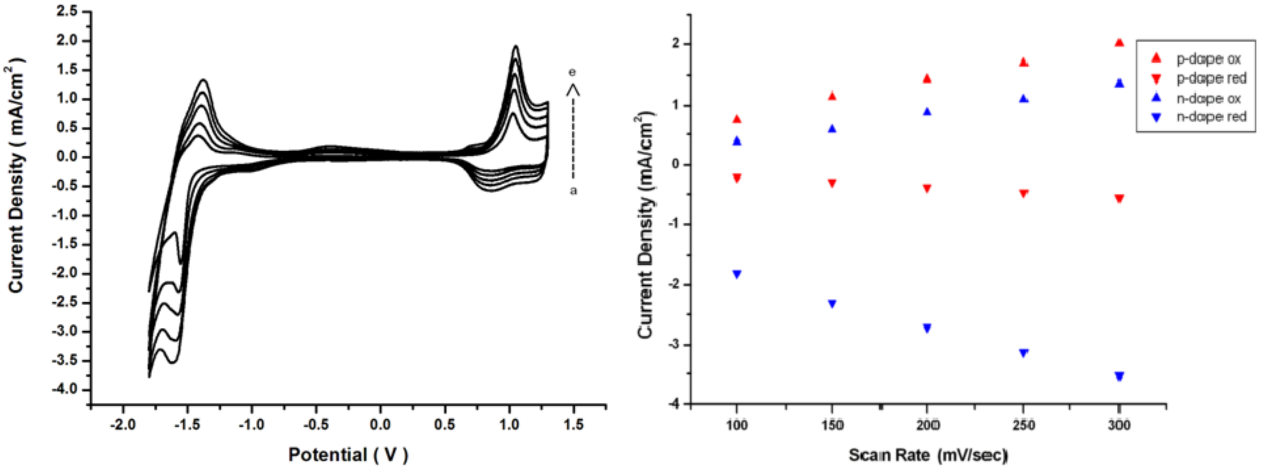


***Figure ESI-2.*** Linear variation of anodic and cathodic peak currents for both p and n doping as a function of scan rate for PI film in ACN / $TBAPF_6$ (a) 100, (b) 150, (c) 200, (d) 250 and (e) 300 mVs$^{-1}$

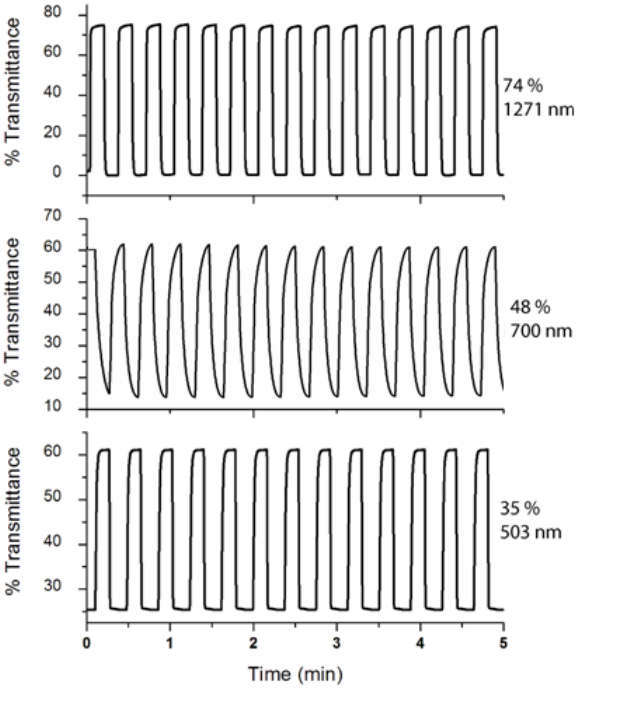


***Figure ESI-3.*** Electrochromic switching: optical absorbance change monitored at 503, 700 and 1271 nm for PI in 0.1 M TBAPF$_6$/ACN while switching between its fully reduced and oxidized states.

***Table ESI-1.*** L,a,b values for distinctive colors of PI at different oxidation states.

| Colors | L | a | b |
|---|---|---|---|
| Red (p) | 43.98 | 58.99 | 16.53 |
| Brown (p) | 55.59 | 17.26 | 16.67 |
| Black (p) | 67.32 | 0.148 | 1.72 |
| Green (p) | 69.26 | -34.14 | 31.29 |
| Blue (p) | 64.71 | -6.1 | -38.72 |
| Blue (n) | 77.48 | -7.64 | -21.21 |
| Transmissive (n) | 86.67 | 2.78 | -16.94 |

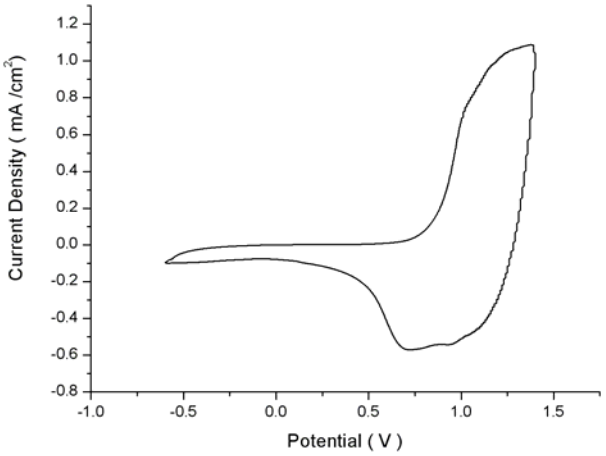


***Figure ESI-4.*** Single scan cyclic voltammetry of PII on an ITO electrode at 100 mV s$^{-1}$ in 0.1M TBAPF$_6$/ACN.

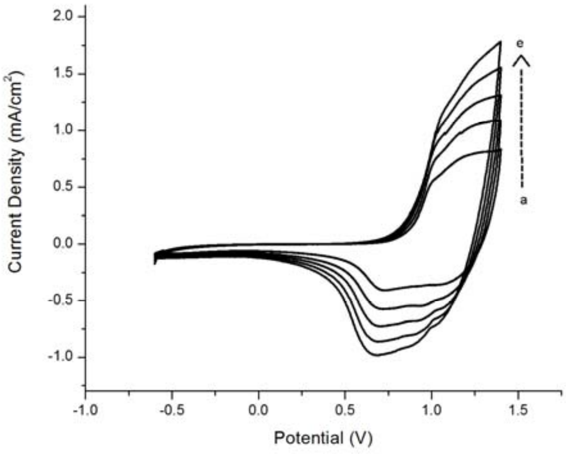


***Figure ESI-4.*** Scan rate dependence of PII film on ITO, in TBAPF$_6$/ACN at : (a)100, (b)150, (c)200, (d)250 and (e) 300 mV s$^{-1}$

In order to probe the optical changes upon doping, spectral changes were investigated by UV-vis- NIR spectrophotometer in a monomer free, 0.1 M TBAPF$_6$, ACN solution.

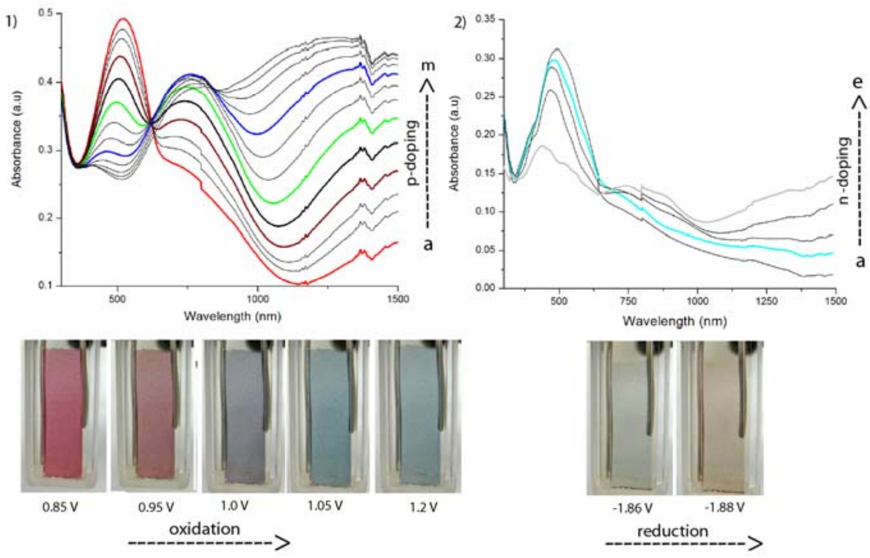


***Figure ESI-6.*** Electronic absorption spectra of PII film on ITO coated glass slide in monomer free, 0.1M TBAPF$_6$ /ACN electrolyte-solvent couple at applied potentials (V). 1) p-doping (a) 0.850, (b) 0.875, (c) 0.900, (d) 0.950, (e) 1.00, (f) 1.05, (g) 1.10, (h) 1.15, (i) 1.20, (j) 1.25, (k) 1.30, (l) 1.35 and (m) 1.40V. 2) n-doping (a) -1.84, (b) -1.85, (c) -1.86, (d) -1.87, (e) -1.88.

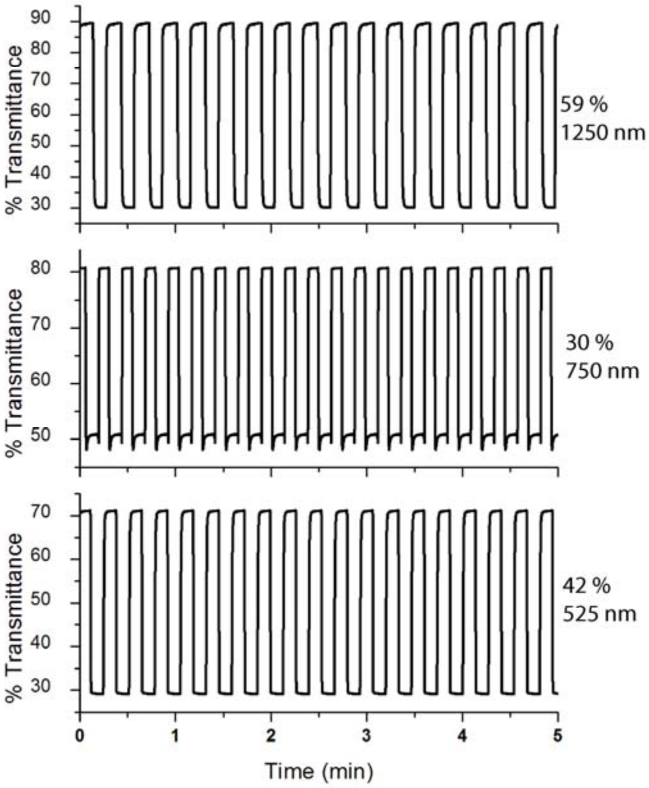


***Figure ESI-7.*** Electrochromic switching: optical absorbance change monitored at 525, 750 and 1250 nm for PII in 0.1 M TBAPF$_6$/ACN while switching between its fully reduced and oxidized states.

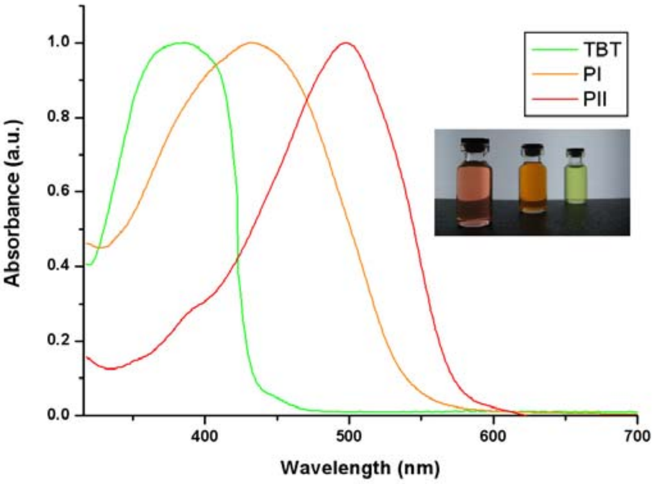


***Figure ESI-8.*** Solution optical absorbance spectra of TBT, PI, PII in CHCl$_3$.

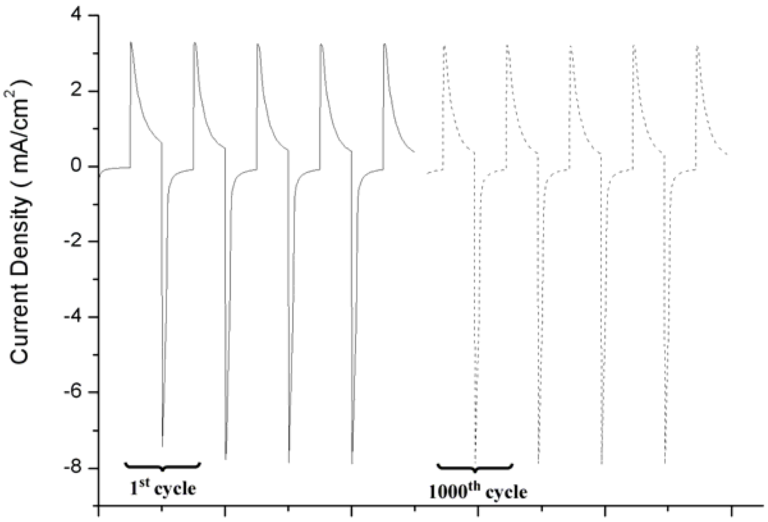


***Figure ESI-9:*** Chronoamperometry experiment for PI on ITO glass in 0.1 M $TBAPF_6$/ACN while switching between reduced and oxidized states. The first four cycles and the ones after the 1000$^{th}$ cycle are presented. Each interval on the x axes stands for 5 s.

***Table ESI-2.*** GPC Molecular weight determination for PI and PII (in THF, using PS standards).

| Polymer | $M_n$ (g/mol) | $M_w$ (g/mol) | PDI | Avg. No. Rep. Un. |
|---|---|---|---|---|
| PI | 13000 | 23370 | 1.79 | 28 |
| PII | 43970 | 239640 | 5.45 | 97 |

1) S. S. Zhu, T. M. Swager, *J. Am. Chem. Soc.* 1997**, 119**, 12568-12577.
2) a) A. Balan, G. Gunbas, A. Durmus, L. Toppare, *Chem. Mater.* 2008, **20**, 7510. b) Çetin G. A., Balan, A.; Gunbas, G.; Durmus, A.; Toppare, L. *Org. Electron.* 2009, **10**, 34. c) A. Tanimoto, T. Yamamoto, *Macromolecules* 2006, **39**, 3546.