

## Electronic Supplementary Information (ESI)

### General remarks:

NMR spectra were recorded on a *Bruker* AMX 400 spectrometer at 25°C (1H NMR: 400 MHz, 13C NMR: 100 MHz). Chemical shift values ( $\delta$ ) are expressed in parts per million using the internal standard tetramethylsilane (1H NMR,  $\delta_{\text{H}} = 0.00$ ) or the solvent as reference (13C NMR,  $\delta_{\text{C}} = 77.00$  for CDCl<sub>3</sub>). The following abbreviations reflect the multiplicity of the signals obtained: s = singlet, d = doublet, t = triplet, m = multiplet, combination dd = doublet of doublets. Infrared (FT-IR) spectra were recorded on a *Perkin-Elmer* FTIR Spectrum 2000, absorptions are reported in cm<sup>-1</sup>. Mass spectra were measured on a *Varian* Saturn 2000. Electrochemistry was performed using a *Metrohm* Autolab PGSTAT 10 Potentiostat. In CV-measurements, all potentials were internally referenced to the ferrocene/ferricinium couple (Fc/Fc<sup>+</sup>). Melting points were determined using a *Büchi* B-545 apparatus. Elemental analyses were performed on an *Elemental Vario EL* (Ulm University). Preparative flash column chromatography was performed using glass columns packed with silica gel 60 (particle size 40–63 nm, *Merck*).

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### Chemicals:

2-Chloromethyl-2,3-dihydro-thieno[3,4-b][1,4]dioxine<sup>[1]</sup> **1** and ethynyl-ferrrocene<sup>[2]</sup> **3c** were synthesized according literature. Hex-1-yne **3a** was purchased from *Merck*. 2-But-3-ynyl-isoindole-1,3-dione **3b**, and Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> were purchased from *Aldrich*.

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### Synthesis of azidomethyl-EDOT 2:

**2-Azidomethyl-2,3-dihydro-thieno[3,4-b][1,4]dioxine 2:** Under inert argon atmosphere, 2.42 g (37.2 mmol) sodium azide were added to a magnetically stirred solution of 3.55 g (18.6 mmol) 2-chloromethyl-2,3-dihydro-thieno[3,4-b][1,4]dioxine **1** in 180 mL abs. DMF. The reaction mixture was heated up to 120°C for 3 h. After cooling, the solvent was removed by rotary evaporation under vacuum. Then, 200 mL water were added to the residue and the product was extracted twice with 150 mL diethyl ether each. The organic phases were combined, washed with 100 mL water, and dried using MgSO<sub>4</sub>. Subsequently, the diethyl ether was evaporated yielding 3.56 g (97 %) of a nearly colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 6.36$  (AB-system,  $J_{AB} = 3.7$  Hz, 2H, Th), 4.30 (m, 1H, CH-O), 4.18 (dd,  $J_1 = 11.7$  Hz,  $J_2 = 2.3$  Hz, 1H, CH<sub>2</sub>-O), 4.04 (dd,  $J_1 = 11.7$  Hz,  $J_2 = 6.9$  Hz, 1H, CH<sub>2</sub>-O), 3.56 (dd,  $J_1 = 13.1$  Hz,  $J_2 = 6.0$  Hz, 1H, CH<sub>2</sub>-N<sub>3</sub>), 3.47 (dd,  $J_1 = 13.1$  Hz,  $J_2 = 5.2$  Hz, 1H, CH<sub>2</sub>-N<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 141.0$ , 140.6, 100.21, 100.04, 72.4, 65.7, 50.5; EI-MS: m/e = 197 (M<sup>+</sup>, 100 %); elemental analysis: C<sub>7</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>S (M<sub>w</sub> 197.2), calc.(%) C 42.63, H 3.58, N 21.31, found C 42.87, H 3.65, N 21.22.

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### Synthesis of 1,2,3-triazolo-functionalized EDOTs 4a-c (general description)

Azidomethyl-EDOT **2**, alkyne **3**, and tetrakis(acetonitrile)copper(I) hexafluorophosphate in a molar ratio of 1:1:0.05 were dissolved in acetonitrile. One equivalent of copper powder was added and the mixture was stirred for three days at room temperature. Subsequently, the mixture was diluted with dichloromethane or chloroform. After separation of elemental copper by filtration, the solvent was evaporated and the residue was purified by recrystallization or column chromatography on silica gel. Yields were 84 % for **4a**, 73 % for **4b** and 64 % for **4c**.

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### 4-Butyl-1-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-

[1,2,3]triazole **4a**: colorless solid, m.p. 83°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 7.40$  (s, 1H, triazole), 6.39 (AB-system,  $J_{AB} = 3.7$  Hz, 2H, Th), 4.63 (m, 2H, EDOT-CH<sub>2</sub>-N), 4.56 (m, 1H, CH-O), 4.27 (dd,  $J_1 = 11.9$  Hz,  $J_2 = 2.1$  Hz, 1H, CH<sub>2</sub>-O), 3.85 (dd,  $J_1 = 11.9$  Hz,  $J_2 = 6.2$  Hz, 1H, CH<sub>2</sub>-O), 2.73 (t,  $J = 7.7$  Hz, 2H,  $\alpha$ -CH<sub>2</sub>), 1.67 (m, 2H,  $\beta$ -CH<sub>2</sub>), 1.39 (m, 2H,  $\gamma$ CH<sub>2</sub>), 0.94 (t,  $J = 7.3$  Hz, 2H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 148.8$ , 140.8, 140.2, 122.0, 100.46, 100.45, 71.9, 65.4, 49.7, 31.5, 25.3, 22.3, 13.8; EI-MS: m/e = 279 (M<sup>+</sup>, 100 %); elemental analysis: C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S (M<sub>w</sub> 279.3), calc.(%) C 55.89, H 6.13, N 15.04, found C 55.70, H 5.99, N 14.91.

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### 2-[2-[1-(2,3-Dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-

[1,2,3]triazol-4-yl]-ethyl}-isoindole-1,3-dione **4b**: colorless solid, m.p. 70 159°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 7.78$  (m, 2H, Ph), 7.68 (m, 2H, Ph), 7.53 (s, 1H, triazole), 6.35 (AB-system,  $J_{AB} = 3.7$  Hz, 2H, Th), 4.62 (m, 2H,

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EDOT-CH<sub>2</sub>-N), 4.51 (m, 1H, CH-O), 4.23 (dd,  $J_1 = 11.9$  Hz,  $J_2 = 2.1$  Hz, 1H, CH<sub>2</sub>-O), 4.02 (t,  $J = 7.0$  Hz, 2H, CH<sub>2</sub>-CH<sub>2</sub>), 3.80 (dd,  $J_1 = 11.9$  Hz,  $J_2 = 6.5$  Hz, 1H, CH<sub>2</sub>-O), 3.16 (t,  $J = 7.0$  Hz, 2H, CH<sub>2</sub>-CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 168.1$ , 140.9, 140.2, 133.9, 131.9, 123.2, 122.8, 100.5, 100.3, 71.8, 65.3, 49.8, 37.4, 24.8; CI-MS: m/e = 397 (HM<sup>+</sup>, 100 %); IR:  $\nu$  (cm<sup>-1</sup>) = 1770, 1708 (C=O, Val.); elemental analysis: C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>S (M<sub>w</sub> 396.4), calc.(%) C 57.57, H 4.07, N 14.13, found C 57.46, H 4.11, N 13.95.

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**4-Ferrocenyl-1-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethyl)-1H-[1,2,3]triazole 4c**: pale orange solid, m.p. 172°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 7.57$  (s, 1H, triazole), 6.40 (AB-system,  $J_{AB} = 3.7$  Hz, 2H, Th), 4.72 (m, 2H, Fe), 4.65 (m, 2H, EDOT-CH<sub>2</sub>-N), 4.61 (m, 1H, CH-O), 4.30 (m, 2H, 85 Fe), 4.29 (dd,  $J_1 = 11.9$  Hz,  $J_2 = 2.1$  Hz, 1H, CH<sub>2</sub>-O), 4.07 (s, 5H, Fe), 3.89 (dd,  $J_1 = 11.9$  Hz,  $J_2 = 6.1$  Hz, 1H, CH<sub>2</sub>-O); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta = 147.2$ , 140.9, 140.2, 120.3, 100.60, 100.53, 75.0, 71.9, 69.6, 68.7, 66.7, 65.5, 49.8; EI-MS: m/e = 407 (M<sup>+</sup>, 52 %), 408 (HM<sup>+</sup>, 100 %); elemental analysis: C<sub>19</sub>H<sub>17</sub>FeN<sub>3</sub>O<sub>2</sub>S (M<sub>w</sub> 407.3), calc.(%) C 56.03, H 4.21, N 10.32, 90 found C 55.90, H 4.22, N 10.29.

### Polymerization of azidomethyl-EDOT 2:

In a three electrode single compartment cell with Pt-tip working, Pt wire counter and a Ag/AgCl reference electrode N<sub>3</sub>-EDOT **2** (5x10<sup>-3</sup> M in 95 acetonitrile/0.1 M TBAHFP) was electropolymerized potentiodynamically between -1.0 V and +1.5 V (vs. Ag/Ag<sup>+</sup>) in several cycles with the polymer film left in a partially oxidized state by applying -0.2 V. The electrodes were removed, washed with acetonitrile and dried in vacuo. Finally polymer films of azidomethyl-PEDOT **P2** were characterized 100 electrochemically in acetonitrile / 0.1 M TBAHFP.

### Attempted polymerization of 1,2,3-triazolo-functionalized EDOTs 4a-c:

The same electrochemical set-up as described in the polymerisation of **2** was used. Electrolyte solutions of monomers **4a**, **4b** and **4c** (5x10<sup>-3</sup> M in 105 acetonitrile/0.1 M TBAHFP) were applied in potentiodynamic scanning between -1.0 V and +1.65 V (vs. Ag/AgCl). After 10 cycles ending at a potential of -0.2 V the electrodes were removed without precipitation of a polymer film.

### Post-functionalization of azidomethyl-PEDOT **P2** with alkynes 3a-c:

Electrodes coated with azidomethyl-PEDOT **P2** obtained by 5 repetitive cycles were dipped into a solution of alkyne **3** (0.6 mMol) and Cu (CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (5 Mol%) in 1.2 mL acetonitrile to which copper powder (0.3 mMol) was added. After 3 days at room temperature with occasional 115 gentle swirling the coated electrodes were steeped and rinsed with acetonitrile several times, washed with methanol and diethyl ether and dried in vacuum. Finally, the electrochemical characterization of the post-functionalized PEDOT **P4a-c** were carried out using the same electrode set up and monomer-free electrolyte solution (CH<sub>3</sub>CN / 0.1 M TBAHFP. All potentials were referenced to ferrocene (Fc/Fc<sup>+</sup>).

### References

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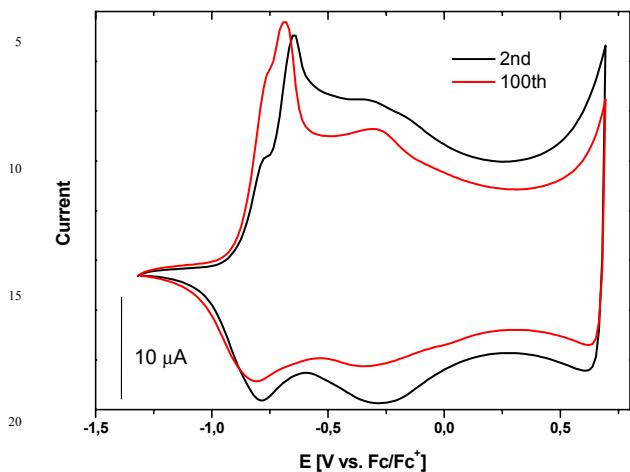
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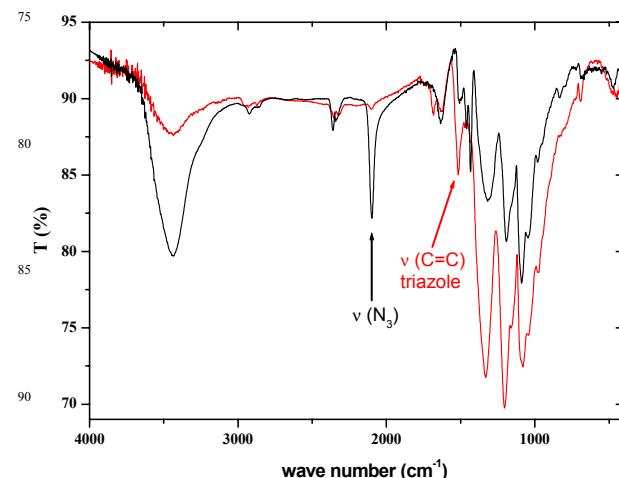
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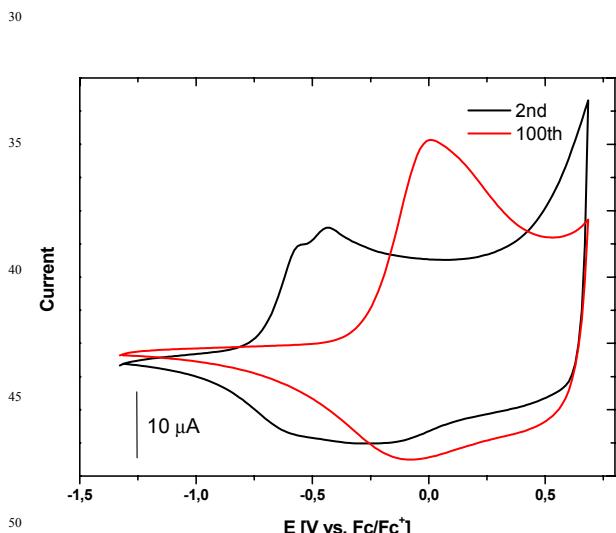
Figures



**Fig. S1** Cyclic voltammograms of polymer **P2** in acetonitrile/TBAHFP, 2<sup>nd</sup> scan (black line) and 100<sup>th</sup> (red line). The decrease of polymer charging capacity is after 100 cycles 18% so that 82% of electroactivity remain.



**Fig. S3** IR-spectrum of precursor polymer P(N<sub>3</sub>-EDOT) **P2** in KBr (black) and 4-butyl-1,2,3-triazole-modified PEDOT **P4a** after derivatization (red). The black arrow indicates the strong N<sub>3</sub>-absorption at 2098 cm<sup>-1</sup> in **P2** and the red arrow the C=C-absorption at 1514 cm<sup>-1</sup> in **P4a**.



**Fig. S2** The electroactivity of polymer **P4a** (prepared under the same conditions than **P2**) in acetonitrile/TBAHFP 2<sup>nd</sup> scan (black line) and 100<sup>th</sup> (red line). The decrease of polymer charging capacity is after 100 cycles 9% so that 91% of electroactivity remain. E<sub>p</sub><sup>Ox</sup> is shifted from -0.43 V to 0.01 V and E<sub>onset</sub> from -0.91 V to 0.54 V.

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