Electronic supplementary Information (ESI)

Functionalized highly electron-rich redox-active electropolymerized 3,4-propylenedioxythiophenes as precursors and targets for bioelectronics and supercapacitors

Tolga Karazehir,[1] Baran Sarac,[2] Hans-Detlev Gilsing,[3] Selin Gumrukcu,[4] Jürgen Eckert,[2,5†] and A. Sezai Sarac[6]*

[1]Department of Energy System Engineering, Adana Alparslan Türkeş Science and Technology University, 01250 Saricam, Adana, Turkey

[2]Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, 8700 Leoben, Austria

[3]Institute of Thin Film and Microsensoric Technology (IDM), 14513 Teltow, Germany

[4] Department of Chemistry, Istanbul Technical University, 34469 Istanbul, Turkey

[5] Department of Materials Science, Chair of Materials Physics, Montanuniversität Leoben, 8700 Leoben, Austria

[6]Polymer Science and Technology, Istanbul Technical University, 34469 Istanbul, Turkey

[†]Adjunct with National University of Science and Technology «MISiS», Leninsky Prosp., 4, 119049, Moscow, Russia

*Corresponding author: A.Sezai Sarac (sarac@itu.edu.tr)

Synthesis of the ProDOT monomers

3-(p-Tolylsulfonyloxymethyl)-3-methyl-3,4-dihydro-2H-thieno[3.4-b][1,4]dioxepine ***2***

To a solution of 0.60 gr. (3.0 mmol) of 3-(Hydroxymethyl)-3,4-dihydro-3-methyl-2*H*-thieno [3.4-*b*][1,4]dioxepine **1** in 40 mL of pyridine an amount of 0.76 gr. (4.0 mmol) of p-toluenesulfonyl chloride was added in portions at 0-5°C. The mixture was allowed to reach room temperature and was stirred for 20 h. The dark red solution was poured into 1 L of ice water containing 50 mL of concentrated hydrochloric acid. The solid precipitating was collected, dissolved into diethyl ether, dried, concentrated and purified by column

chromatography on silica gel using n-heptane/ethyl acetate 3:1 as eluent giving 0.70 gr. (=66%) of **2** as a colorless solid.

mp. 150-151°C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.0 Hz, *J* = 1.7 Hz, 2H, 2x Ar-H); 7.34 (d, *J* = 8.0 Hz, 2H, 2x Ar-H); 6.47 (s, 2H, 2x CH); 4.13 (s, 2H, $C(CH_2O)$); 3.95 (d, *J* = 12.1 Hz, 2H, OCH_2); 3.64 (d, *J* = 12.1 Hz, 2H, OCH_2); 2.44 (s, 3H, Ar-CH_3); 0.95 (s, 3H, $C(CH_3)$) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.5 (Th-C2/5); 144.9 (Ar-C4); 132.6 (Ar-C1); 129.9 (Ar-C3/5); 127.9 (Ar-C2/6); 106.1 (Th-C3/4); 75.8 (2x OCH_2); 72.0 (CH_2OSO_2); 42.9 ($(H_3C)\underline{C}(CH_2O)$); 21.6 (Ar-$CH_3$); 16.7 ($C(\underline{C}H_3)$ ppm.π

IR (neat) ν = 3130, 2972, 2868, 1597, 1562, 1487, 1452, 1405, 1386, 1373, 1351, 1333, 1215, 1190, 1173, 1135, 1096, 1023, 967, 931, 848, 834, 819, 789, 764, 665, 626 cm^{-1}.

*3-(Bromomethyl)-3-methyl-3,4-dihydro-2H-thieno[3.4-b][1,4]dioxepine **3***

To a solution of 0.13 gr. (0.5 mmol) of triphenylphosphine in 20 mL of dichloromethane 0.025 mL (0.5 mmol) of bromine was added at -20°C. After stirring for 5 min 0.07 mL (0.5 mmol) of triethylamine was added and stirring was continued for further 5 min. A solution of 0.10 g (0.5 mmol) of **1** in 5 mL of dichloromethane was added dropwise with stirring for 15 min at the same temperature. The mixture was warmed up to room temperature and stirring was continued for 15 min. The solution was washed with 4x 25 mL of water, dried over Na_2SO_4, filtrated and evaporated. The residue was separated by column chromatography on silica gel using n-heptane/ ethyl acetate 8:1 as eluent yielding 0.05 gr. (=38%) of **3** as a colorless solid. An amount of 0.05 g or **1** was recovered.

mp. 64-65°C

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.51 (s, 2H, 2x CH); 4.06 (d, *J* = 11.8 Hz, 2H, OCH_2); 3.76 (d, *J* = 11.8 Hz, 2H, OCH_2); 3.63 (s, 2H, $C(CH_2O)$); 1.01 (s, 3H, $C(CH_3)$) ppm.

^{13}C-NMR (100 MHz, $CDCl_3$) δ 149.4 (Th-C2/5); 106.6 (Th-C3/4); 76.6 (2x OCH_2); 43.4 ($(H_3C)\underline{C}(CH_2Br)$); 35.2 ($C(\underline{C}H_2Br)$; 19.3 ($C(\underline{C}H_3)$) ppm.

IR (neat) v = 3102, 3037, 2962, 2897, 2887, 1554, 1480, 1455, 1447, 1433, 1393, 1379, 1365, 1321, 1302, 1253, 1205, 1186, 1171, 1134, 1086, 1020, 958, 919, 904, 877, 851, 790, 758, 674, 658, 625 cm^{-1}.

A solution of 2.15 gr. (14.9 mmol) of 3,4-dimethoxythiophene, 5.46 gr (29.8 mmol) of 2-bromomethyl-2-methylpropane-1,3-diol and 0.29 gr (1.5 mmol) of *p*-toluenesulfonic acid monohydrate in 200 mL of toluene was refluxed for 15 h with vapor phase adsorption of the evolving methanol on molecular sieves 4A°. After cooling to room temperature the reaction mixture was washed with 3x 100 mL of water, dried over Na_2SO_4, filtrated and evaporated. The crude product was purified by column chromatography on silica gel using n-heptane/ ethyl acetate 8:1 as eluent yielding 2.84 gr. (=72%) of **3** as a colorless solid.

*3-[(Benzyloxy)methyl]-3-methyl-3,4-dihydro-2H-thieno[3.4-b][1,4]dioxepine **4***

To a suspension of 0.14 gr. (5.8 mmol) of sodium hydride (60% in mineral oil) in 25 mL of dimethylformamide 0.31 gr. (2.9 mmol) of benzyl alcohol were introduced and the mixture was stirred and heated to 110°C until the evolution of hydrogen stopped. After cooling to 50°C a solution of 0.50 gr. (1.9 mmol) of **3** in 25 mL of dimethylformamide was added dropwise. After completion stirring at 110°C was continued for 2 h. After cooling to room temperature the solution was evaporated and the residue was taken up in 100 mL of ethyl acetate. The organic phase was washed with 3x 100 mL of a 10% aqueous solution of $NaHCO_3$, dried over Na_2SO_4, filtrated and evaporated. The crude oil was purified by column chromatography on silica gel using n-heptane/ethyl acetate 8:1 as eluent to give a viscous oil solidifying upon trituration with petroleum ether to yield 0.36 g (=65%) of **4** as a colorless powder.

mp. 44-45°C

^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.38-7.26 (m, 5H, Ar-H); 6.73 (s, 2H, 2x CH); 4.51 (s, 2H, OCH_2Ph); 3.95 (d, *J* = 11.9 Hz, 2H, OCH_2); 3.69 (d, *J* = 11.9 Hz, 2H, OCH_2); 3.47 (s, 2H, $C(CH_2O)$); 0.93 (s, 3H, $C(CH_3)$) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6) δ 149.6 (Th-C2/5); 138.4 (Ar-C1); 128.2 (Ar-C3/5); 127.3 (Ar-C2/6); 127.2 (Ar-C4); 106.0 (Th-C3/4); 76.2 (2x OCH_2); 72.5 (OCH_2Ph); 72.1 ($C(\underline{C}H_2O)$; 42.9 ($(H_3C)\underline{C}(CH_2O)$); 16.8 ($C(\underline{C}H_3)$ ppm.

IR (neat) ν = 3115, 2967, 2940, 2881, 2850, 1566, 1497, 1479, 1445, 1410, 1392, 1379, 1366, 1309, 1282, 1245, 1199, 1168, 1107, 1075, 1033, 1026, 1014, 993, 965, 910, 878, 852, 778, 766, 743, 699, 669, 639, 623 cm^{-1}.

3-[(4'-Carbethoxy)phenoxy]-3,4-dihydro-3-methyl-2H-thieno[3.4-b][1,4]dioxepine ***5***

To a suspension of 0.28 gr. (11.7 mmol) of sodium hydride (60% in mineral oil) in 100 mL of dimethylformamide 0.96 gr. (5.7 mmol) of ethyl 4-hydroxybenzoate were introduced and the mixture was stirred and heated to 110°C until the evolution of hydrogen stopped. The solution was cooled to room temperature and a solution of 1.00 gr. (3.8 mmol) of **3** in 100 mL of dimethylformamide was added dropwise. After completion the reaction mixture was stirred at 110°C for 12 h and after cooling stirring was continued at room temperature for further 12 h. The solution was evaporated and the residue was taken up in 100 mL of ethyl acetate to precipitate sodium bromide. The mixture was filtered and evaporated. The crude product was purified by column chromatography on silica gel using n-heptane/ethyl acetate 8:1 as eluent giving 0.93 g (=71%) of **5** as a colorless solid.

mp. 63-64°C

^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.91 (dd, *J* = 7.0, 2.2 Hz, 2H, Ar-3/5H); 7.09 (dd, *J* = 6.8, 2.0 Hz, 2H, Ar-2/6H); 6.78 (s, 2H, 2x CH); 4.27 (q, *J* = 7.0 Hz, 2H, $OC\underline{H}_2CH_3$); 4.13 (s, 2H,

C(CH_2O)); 4.09 (d, *J* = 11.8 Hz, 2H, OCH_2); 3.78 (d, *J* = 11.8 Hz, 2H, OCH_2); 1.31 (t, *J* = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$); 1.01 (s, 3H, C(CH_3)) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6) δ 165.3 (COO); 162.5 (Ar-C4); 149.6 (Th-C2/5); 131.1 (Ar-C2/6); 122.3 (Ar-C1); 114.5 (Ar-C3/5); 106.0 (Th-C3/4); 75.8 (2x OCH_2); 69.8 (C($\underline{C}H_2O$); 60.3 ($O\underline{C}H_2CH_3$); 42.7 ((H_3C)$\underline{C}$(CH_2O)); 16.4 (C($\underline{C}H_3$)); 14.2 ($OCH_2\underline{C}H_3$) ppm.

IR (neat) ν = 3092, 2956, 2907, 2867, 1706, 1606, 1580, 1558, 1512, 1483, 1450, 1423, 1407, 1368, 1275, 1251, 1216, 1195, 1174, 1143, 1106, 1031, 977, 911, 878, 848, 794, 768, 756, 694, 606, 652, 626 cm^{-1}.

3-[(4'-Hydroxymethyl)phenoxy]-3,4-dihydro-3-methyl-2H-thieno[3.4-b][1,4]dioxepine ***6***

To a solution of 0.20 gr. (0.57 mmol) of **5** in 40 mL of toluene a solution of 5.00 mL (5.00 mmol) of diisobutylaluminium hydride (1m in dichloromethane) in 25 mL of toluene was added dropwise at 0°C. After completion the mixture was stirred at 0°C for 1 h. For quenching of the reaction, 50 mL of 1m hydrochloric acid were added dropwise until the evolution of hydrogen stopped. The mixture was allowed to reach room temperature and was stirred for 1 h. After partition of the organic phase the aqueous phase was extracted with 3x 50 mL of diethyl ether. The combined extracts were washed consecutively with 3x 50 mL of saturated aqueous $NaHCO_3$ and 3x 50 mL saturated aqueous NaCl, dried over Na_2SO_4, filtrated and evaporated yielding 0.17 g (=97%) of the pure product as a colorless solid.

mp. 84-85°C

^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.22 (dd, *J* = 6.7, 2.0 Hz, 2H, Ar-3/5H); 6.91 (dd, *J* = 6.6, 2.0 Hz, 2H, Ar-2/6H); 6.77 (s, 2H, 2x CH); 5.02 (t, *J* = 5.6 Hz, 1H, $CH_2O\underline{H}$); 4.40 (d, *J* = 5.6 Hz, 2H, $C\underline{H}_2OH$); 4.07 (d, *J* = 11.9 Hz, 2H, OCH_2); 4.01 (s, 2H, CH_2OPh); 3.77 (d, *J* = 11.9 Hz, 2H, OCH_2); 1.01 (s, 3H, C(CH_3)) ppm.

^{13}C-NMR (100 MHz, DMSO-d_6) 157.7 (Ar-C4); 149.6 (Th-C2/5); 134.8 (Ar-C1); 127.8 (Ar-C2/6); 114.2 (Ar-C3/5); 106.3 (Th-C3/4); 75.9 (2x OCH_2); 69.7 (C($\underline{C}H_2O$); 62.5 (CH_2OH); 42.7 ((H_3C)$\underline{C}$(CH_2O)); 16.5 (C($\underline{C}H_3$)) ppm

IR (neat) ν = 3304, 3114, 2937, 2863, 1612, 1584, 1557, 1514, 1486, 1466, 1444, 1402, 1375, 1322, 1296, 1236, 1218, 1206, 1186, 1175, 1160, 1134, 1112, 1037, 1023, 971, 943, 914, 847, 830, 812, 788, 766, 722, 658, 625, 609 cm^{-1}.