Electronic Supplementary Information for the paper

New Stable Donor-Acceptor Dyads for Molecular Electronics

Mykola Kondratenko, Andrey G. Moiseev and Dmitrii F. Perepichka*

Department of Chemistry and Centre for Self-Assembled Chemical Structures, McGill University, 801 Sherbrooke Street West, Montreal, Qc, Canada H3A 2K6

Synthesis of auxiliary reagents

**N-2-Ethylhexyl-1,4,5,8-naphthalenetetracarboxyimide anhydride (6a).** Monoimide 6a was prepared following a literature procedure,\textsuperscript{47} from commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride 5 (10.0 g, 37.3 mmol) and 2-ethyl-1-hexylamine (5.35 g, 41.3 mmol). The product was purified by column chromatography (silica; hexane/ethylacetate gradient) to afford the desired product 6a as yellowish solid (first fraction) (6.1 g, 43%) along with symmetric diimide 7 as a side product (second fraction) (5.9 g, 32%). 6a: m.p. 166–169 °C; \( \delta_H \) (400 MHz, CDCl\(_3\)) 8.81 (4H, s), 4.15 (2H, m), 2.32 (2H, m), 1.61 (4H, m), 1.30 (24H, m).
N-(2-Ethylhexyl)-N’-p-bromophenyl 1,4,5,8-naphthalenetetracarboxydiimide (8a). Compound 6a (6.1 g, 16.1 mmol) and p-bromoaniline (2.80 g, 16.1 mmol) were dissolved in dry DMF (150 ml) and the reaction mixture was stirred at reflux overnight under nitrogen atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure. After column chromatography on silica (CH2Cl2:EtOAc eluent, gradient), afforded the desired diimide 8a (6.5 g, 76%). m.p.: 203–204°C; δH (500 MHz, CDCl3) 8.75 (4H, s), 4.15 (4H, m), 1.94 (2H, t, J 6.0 Hz), 1.43-1.22 (16H, m), 0.95 (6H, t, J 7.4 Hz), 0.89 (6H, t, J 7.2 Hz). HR-MS (ESI): calculated for C28H25BrN2O4 533.1070, found 533.1058.

N-(6-(tert-butylsulfanyl)hexyl-1,4,5,8-naphthalenetcarboxyimide anhydride (6b). To a solution of 5 (1.0 g, 3.7 mmol) in dry DMF (150 ml) was slowly added (during 3 h) a solution of amine 17 (0.65 g, 3.5 mmol) in dry DMF (40 ml) under nitrogen atmosphere and reaction mixture was refluxed overnight. After cooling to room temperature, reaction mixture was placed in the fridge for 2-3 h (–10°C). Precipitate (corresponding diimide side product) was filtered out and then the solvent was removed under reduced pressure. Crude product was dissolved in acetone and resulted solution was kept in the fridge overnight to precipitate more of diimide. The filtrate was concentrated and resulted solid was purified by column chromatography on silica (CH2Cl2:EtOAc eluent, gradient) resulting in desired monoimide 6b as a yellow solid (0.88 g, 59%). M.p.: 218–220°C; δH (400 MHz, CDCl3) 8.81 (4H, s), 4.21 (2H, t, J 7.6), 2.53 (2H, t, J 7.2), 1.77 (2H, t, br), 1.7–1.4 (6H, m), 1.31 (9H, s); δC (75.0 MHz, CDCl3) 162.1, 158.8, 138.1, 131.2, 128.8, 127.9, 122.7, 41.7, 41.1, 30.9, 29.7, 29.1, 28.2, 27.9, 26.9.

N-(6-(tert-butylsulfanyl)hexyl-N’-p-bromophenyl-1,4,5,8-naphthalenetcarboxydiimide (8b). NDI 6b (0.88 g, 2.0 mmol) and p-bromoaniline (1.0 g, 5.8 mmol) were dissolved in dry DMF (100 mL) and the reaction mixture was stirred under nitrogen atmosphere at reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure and the crude product was dried under vacuum. After column chromatography on silica (CH2Cl2:EtOAc eluent, gradient), desired diimide 8b was obtained as dark yellow solid (0.75 g, 63%). M.p.: 237–239°C; δH (400 MHz, CDCl3) 8.81 (4H, s), 7.72 (2H, d, J 8.8 Hz), 7.23 (2H, d, J 8.8 Hz), 4.21 (2H, m), 2.53 (2H, t, J 7.2), 1.77 (2H, m), 1.62-1.39 (6H, m), 1.32 (9H, s); δC (75.0 MHz, CDCl3) 163.1, 162.8, 131.0, 131.0, 130.0, 127.1, 126.4, 123.3, 41.5, 40.3, 31.0, 29.2, 28.9, 28.2, 27.3, 26.8; HR-MS (ESI): calculated for C30H29BrN2O4S 592.1026, found 592.1033.

5-Hexyl-bisEDOT (10a). Compound 10a was prepared according to literature procedure49 from bis-EDOT (2 g) and 1-iodohexane (1.17 g, 7.1 mmol) Purification was performed by column chromatography on silica using hexanes:EtOAc (5:1) as eluent resulting in final product 10a as a yellow powder (0.95 g, 37 %) and 9
as a by-product (26%). 10a: M.p. 118-120 °C (lit10 120 °C); \( \delta_H \) (400 MHz, CDCl\(_3\)) 6.22 (s, 1H), 4.3-4.19 (m, 8H), 2.63 (t, 2H, \( J = 7.6 \)Hz), 1.6-1.61 (m, 4H), 1.4-1.36 (m, 4H), 0.88 (t, 3H, \( J = 7.2 \)Hz). 9: \( \delta_H \) (400 MHz, CDCl\(_3\)) 4.3-4.19 (m, 8H), 2.63 (t, 2H, \( J = 7.6 \)Hz), 1.6-1.61 (m, 4H), 1.4-1.36 (m, 4H), 0.88 (t, 3H, \( J = 7.2 \)Hz).

The NMR suggests some impurities of the disubstituted bisEDOT, which, however, are easier to remove at the later stage.

6-(tert-butylsulfanyl)hexyl-bisEDOT (10b). To a solution of bis-EDOT (1.0 g, 3.54 mmol) in dry THF (100 ml) at -78 °C a 2.5 M solution of \( t \)-BuLi (1.45 ml, 3.6 mmol) was added dropwise and reaction mixture was stirred at -40 °C for 2h under nitrogen atmosphere. Then reaction mixture was cooled to -78 °C and compound 15 (1.06 g, 3.54 mmol) was slowly added. Mixture was stirred at -40 °C overnight (at the end the temperature raised to -10 °C). Then reaction was quenched with water, diluted with EtOAc and organic phase was washed sequentially with water and brine, dried with MgSO\(_4\). Solution was filtered and concentrated under reduced pressure affording crude brown oil as a mixture of starting bisEDOT, monoalkylated and dialkylated bis-EDOT. Purification was performed by column chromatography on silica (hexanes:EtOAc eluent, gradient) resulted in product 10b as a yellowish greasy solid (0.68g, 42%). \( \delta_H \) (400 MHz, CDCl\(_3\)) 6.22 (s, 1H), 4.3-4.19 (m, 8H), 2.6 (2H, \( J = 7.5 \)Hz), 2.51 (t, 2H, \( J = 7.6 \)Hz), 1.6-1.55 (m, 4H), 1.4-1.36 (m, 4H), 1.31 (s, 9H). The NMR suggests some impurities of the disubstituted bisEDOT, which, however, are easier to remove at the later stage.

5-Tributylstannyl-5’-hexyl-bisEDOT (11a). To a solution of 10a (0.27g, 0.74 mmol) in dry diethyl ether (150 mL) at –78°C a solution of 1.7 M \( n \)-BuLi (0.52 mL, 0.88 mmol) was slowly added and reaction mixture was warmed up to -40 °C and stirred for 3–4 h under nitrogen atmosphere. After cooling the reaction mixture to –78°C tributylstannyl chloride (0.24 g, 0.74 mmol) was added and reaction mixture was slowly (overnight) warmed to room temperature. After quenching reaction with water, organic phase was extracted with diethyl ether, washed with water, brine and dried over MgSO\(_4\). Crude product (0.46 g) was used without further purification for synthesis of 2a and 3a. \( \delta_H \) (400 MHz, CDCl\(_3\)) 4.3-4.19 (m, 8H), 2.62 (t, 2H, \( J = 7.5 \)Hz), 1.65-1.45 (m, 8H), 1.2-1.4 (m, 12H), 1.15-1.0 (m, 6H), 0.88 (m, 12H).

5-tributylstannyl-5’-(6-(tert-butylsulfanyl)hexyl)-bisEDOT (11b). To a solution of 10b (0.46 g, 1.0 mmol) in dry THF (150 mL) at –78°C was slowly added a solution of 2.5 M \( n \)-BuLi (0.4 mL, 1.0 mmol). Then reaction mixture was warmed up to -40 °C and stirred for 3–4 h. After cooling the reaction mixture to –78°C tributylstannyl chloride (0.33 g, 1.0 mmol) was added and reaction mixture was slowly (overnight) warmed to room temperature. After quenching reaction with water, resulted solution was extracted with ethyl acetate, organic phase was washed with water, brine and dried over MgSO\(_4\). Crude product (0.7 g) was used without further purification for the next step. \( \delta_H \) (400 MHz, CDCl\(_3\)) 4.3-4.19 (m, 8H), 2.62 (2H, t, \( J = 7.5 \)), 2.51 (t, 2H, \( J = 7.6 \)Hz), 1.68-1.55 (m, 10H), 1.45-1.25 (m, 19H), 1.2-1.0 (m, 6H), 0.88 (t, 9H, \( J = 7.2 \)Hz).

2-Tributylstannyl-EDOT (12). To a solution of EDOT (5.0 g, 35.2 mmol) in dry diethyl ether (300 mL) at –78°C was slowly added a solution of 2.5 M \( n \)-BuLi (14.1 mL, 35.2 mmol) reaction mixture was warmed up to room temperature and stirred for 1.2 h. After cooling the reaction mixture to –78°C tributylstannyl chloride (11.5 g, 35.2 mmol) was added and reaction mixture was slowly (overnight) warmed to room temperature. After quenching reaction with water, resulted solution was extracted with diethyl ether, organic phase was washed with water, brine and dried over MgSO\(_4\). Crude product was filtered through short pad.
silica gel and used without further purification for the next step (10.1 g, 67%). \( \delta_H \) (400 MHz, CDCl\(_3\)) 6.6 (s, 1H), 4.2-4.14 (m, 4H), 1.65-1.40 (m, 6H), 1.4-1.2 (m, 6H), 1.2-1.0 (m, 6H), 0.88 (t, 9H, \( J \) 7.2 Hz)

**tert-Butylsulfanylhexyl-6-chloride (14).** To a solution of 1-bromo-2-chlorohexane (8.4 g, 42.1 mmol) and tert-butyl mercaptane (3.8 g, 41.2 mmol) in DMF well-grounded potassium carbonate (6.0 g, 55.6 mmol) was added and the reaction mixture was stirred at room temperature overnight. After all starting 6-bromohexyl chloride was consumed, reaction mixture was diluted with water and resulted solution was extracted with EtOAc, washed with water and brine. Organic phase was dried over MgSO\(_4\). Evaporation of the solvent gave desired product as colorless oil (8.37 g, 95%), which had sufficient purity (GC-MS) to use it for further transformation. \( \delta_H \) (400 MHz, CDCl\(_3\)) 3.52 (t, 2H, \( J \) 6.8 Hz), 2.52 (t, 2H, \( J \) 7.2 Hz), 1.86 (2H, m), 1.57 (m, 2H), 1.50-1.38 (m, 4H), 1.37 (s, 9H). \( \delta_C \) (75.0 MHz, CDCl\(_3\)) 44.9, 41.7, 32.4, 30.9, 29.6, 28.4, 28.0, 26.5. HRMS (APCI) calculated for C\(_{10}\)H\(_{22}\)ClS 209.1125 found 209.1128

**tert-Butyl-(6-iodohexyl)sulfane (15).** To a solution of tert-butylsulfanyl-6-chloride (14) (8.37 g, 40.2 mmol) from previous step in acetone was added NaI (7.0 g, 47 mmol) and the reaction mixture was stirred at reflux overnight. Completion of the reaction was followed by \( ^1H \) NMR and GC-MS analysis. Then reaction mixture was diluted with water and resulted solution was extracted with EtOAc. Organic phase was washed with water, brine, and then was dried over MgSO\(_4\). Solvent was evaporated resulting in desired product as a yellow oil (11.0 g, 91%); \( \delta_H \) (400 MHz, CDCl\(_3\)) 3.18 (t, 2H, \( J \) 6.9 Hz), 2.52 (t, 2H, \( J \) 7.2 Hz), 1.94-1.80 (m, 2H), 1.6-1.57 (m, 2H), 1.45-1.38 (m, 4H), 1.37 (s, 9H); \( \delta_C \) (125.0 MHz, CDCl\(_3\)) 41.9, 33.3, 30.9, 30.1, 29.5, 28.2, 28.1, 7.0. HRMS (APCI) calculated for C\(_{10}\)H\(_{22}\)I 301.0481 found 301.0477.

**N-(6-(tert-Butylsulfanyl)hexyl)phthalimide (16).** To a solution of 15 (1.0 g, 4 mmol) in acetone (100 ml) at reflux, was added potassium phthalimide (1.0 g, 5.4 mmol) in small portions under nitrogen atmosphere. Reaction mixture was stirred at reflux for 4–6 h. Then it was cooled down to room temperature. Precipitate (formed KBr) was filtered off, and the solvent was evaporated under reduced pressure. Residue was purified by column chromatography on silica giving compound 16 as a white-beige greasy solid (1.15 g, 87% yield). \( \delta_H \) (400 MHz, CDCl\(_3\)) 7.83 (m, 2H), 7.69 (m, 2H), 3.67 (t, 2H, \( J \) 7.2), 2.52 (t, 2H, \( J \) 6.6 ), 1.67 (m, 2H), 1.55 (m, 2H), 1.5-1.3 (m, 4H), 1.35 (9H, s); \( \delta_C \) (125.0 MHz, CDCl\(_3\)) 168.4, 133.8, 132.1, 123.1, 41.7, 37.9, 30.9, 29.7, 28.8, 28.5, 28.1, 26.5. HR-MS (CI) calculated for C\(_{18}\)H\(_{25}\)O\(_2\)NSNa 342.1498 found 342.1508.

**tert-Butylsulfanyl-6-hexylamine (17).** To a suspension of compound 16 (1.15 g, 3.60 mmol) in methanol (100 ml) was added hydrazine monohydrate (0.5 ml, 10 mmol) and reaction mixture was stirred at reflux for 2 h. Then solvent was evaporated and residue was dissolved in CH\(_2\)Cl\(_2\), washed with 10% KOH, water and brine, dried over MgSO\(_4\). Evaporation of CH\(_2\)Cl\(_2\) under reduced pressure resulted in desired product 17 as a yellow oil (0.77 g, 100 %). \( \delta_H \) (300 MHz, CDCl\(_3\)) 2.68 (t, 2H, \( J \) 7.5Hz), 2.52 (t, 2H, \( J \) 8 Hz), 1.57 (m, 2H), 1.5-1.26 (m, 6H), 1.31 (s, 9H), 1.19 (s, br, 2H); \( \delta_C \) (125.0 MHz, CDCl\(_3\)) 42.2, 41.8, 33.7, 30.9, 29.8, 29.1, 28.2, 26.6; HR-MS (ESI) calculated for C\(_{10}\)H\(_{23}\)NS (M+1) 190.1551, found 190.1607.
Cyclic voltammograms of dyads 3 and 4, in solution and in SAMs.

**Figure S1.** CV of dyads 3a and 4a (0.1 M Bu₄NPF₆ in DCM vs Ag/AgCl)
Figure S2. Linear dependence of the first reduction peak of the SAM of dyad 3 on the scan rate (on Au electrode).

Figure S3. Multiple scanning of the SAM of the dyad 3.
**Figure S4.** Spectroelectrochemistry of the dyad 2 (reduction of the NDI moiety) in DMF (0.1 M Bu₄NPF₆).

**Figure S5.** Absorption spectra of the dyad of dyad 3 in SAMs on semitransparent gold electrode (red) and differential absorbance between two gold slides showing a residual plasmonic band of gold nanoislands (a deep at ca 600 nm) (black).
**Figure S6.** TGA analysis of the dyad 2.

**Figure S7.** Fluorescence of the dyad 2 in toluene.
Dyad 1
pad=10 run with find20 before acquisition
Sample: 478
Sample ID: service_8_01
Files: /home/walkup/chemsys/data/service/478_01.txt
Pulse Sequence: s2pul
Solvent: cdc13
Ambient temperature
Sample FS, Operator: service
Files: 478_01
Mercury-390 "m390"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.984 sec
Delay 9000 repetitions
Observe 1H, 75.4468872 MHz
DECRPPE H1, 290.05664214 MHz
Power 35 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 2 hr, 38 min, 46 sec
Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is (c) The Royal Society of Chemistry 2010