Supporting information for:

Novel, low-cost, highly soluble n-type semiconductors: tetraazaanthracene tetraesters

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Characterization techniques

Solution spectra of new compounds, dissolved in chloroform (POCh-Poland, dried with calcium chloride and distilled), as well as the solid state spectra of their thin films deposited on quartz plate or an ITO electrode were recorded on a Varian Cary 5000. In UV-vis and spectroelectrochemical measurements the baseline was determined using quartz cuvette with chloroform/quartz plate and spectroelectrochemical cell with ITO in 0.1 M Bu₄NBF₄ acetonitrile, respectively. The infrared spectra were recorded using a Perkin Elmer (System 2000) spectrometer using the pressed pellets technique.

Cyclic voltammetry studies were carried out for the $5x10^{-4}$ M solutions in 0.1 M Bu₄NBF₄/CH₂Cl₂. The electrolyte was placed in a one-compartment, three electrode electrochemical cell with a platinum disk working electrode of the surface area of 3 mm², a platinum mesh counter electrode and an Ag/0.1 M Ag⁺/acetonitrile reference electrode. The measurements were performed using an Autolab potentiostat (Eco Chemie). All operations involving the electrolyte preparation and electrochemical measurements were carried out under dry argon atmosphere. The choice of the solvent was governed by the solubility of the molecules investigated. The use of a methylene chloride-based electrolyte in combination with an acetonitrile-based reference may introduce an additional junction potential. For this reason the potential of the reference *vs* Fc/Fc⁺ redox couple was checked at the end of each experiment.

As for cyclic voltammetry in thin layer, thin films of new compounds were deposited on a platinum electrode by casting from chloroform solution. The measurements were carried out in 0.1 M Bu₄NBF₄/ CH₃CN, in the same electrochemical cell and using the same set of working, counter and reference electrodes as described above. The potential of the reference *vs* Fc/Fc⁺ redox couple was checked at the end of each experiment.

For UV-vis-NIR spectroelectrochemical investigations, thin layers were deposited by casting on an ITO electrode. In the measurements the same counter (Pt) and reference (Ag/0.1 M Ag⁺) electrodes, as in the case of cyclic voltammetry studies were used. The measurements were carried out in 0.1 M Bu_4NBF_4/CH_3CN electrolyte. The used UV-vis spectroelectrochemical cell was of rectangular shape (30 mm x 14 mm x 6 mm). All three electrodes were in close vicinity, so the iR drop was negligible. The potential of the reference electrode was verified using the ferrocene couple at the end of each set of spectroelectrochemical investigations. The UV-vis-NIR spectra were recorded on a Varian Cary 5000.

Reagents and reaction techniques

Carbon tetrachloride (reagent grade), acetic acid (reagent grade), dioxane (reagent grade), o-dichlorobenzene (spectroscopy grade), dimethyl tartrate¹ (99%), diethyl tartrate (99%), 2-octyldodecanol (97%) and 1,2,4,5benzenetetramine tetrahydrochloride (technical grade, >80%) were purchased from Aldrich and used as received. Dibutyl tartrate was purchased from Acros Organics and used as received². N-bromosuccinimide (NBS) was purchased from Fluka or Alfa Aesar and used as received. None of the reactions require argon atmosphere. Highest possible grade for solvents and reagents is not strictly required. The reaction mixtures were heated using an oil bath. The temperatures given in procedures are <u>internal</u> temperatures. Reactions, where possible, where monitored using TLC plates developed with chloroform or chloroform:alcohol 20:1 v/v as eluent.

Synthesis of dibutyl dioxosuccinate (1a) (simplified procedure)



In a three-necked 100 ml flask equipped with large magnetic stir bar was put 2.62g (0.01 mol) of dibutyl tartrate, 7.12 g (0.04 mol) of NBS and 20 ml of CCl_4^3 . The resulting mixture was stirred overnight at 75 - 78 °C⁴. After a while the reaction mixture changes color to deep red due to liberation of bromine by NBS. Next the mixture was cooled to room temperature and diluted with 40 ml of hexanes. Everything was carefully filtered and the filtrate was evaporated at 50 °C to yield 2.8 g of yellow orange highly viscous liquid. The crude product was suitable to be used in the next step. NMR and IR studies showed that procedure was reproducible and the crude product contained 80 % of **1a** (2.24 g, 86.8 % yield), contaminated mainly with succinimide.

The product is well soluble in hexane, ether, THF, acetic acid and chlorinated solvents. It may be stored for a few weeks in refrigerator, but it is best to use it directly after preparation.

Note: Although not required, the purification of **1a** is troublesome, regardless of the technique used.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ: 4.18 - 4.38 (m, 4H); 1.58 - 1.78 (m, 4H); 1.30 -1. 50 (m, 4H); 0.84 - 1.00 (m, 6H).

¹ Any enantiomeric or racemic dialkyl tartrates may be used.

² Dibutyl tartrate may be prepared also as follows: 15 g of tartaric acid (any enantiomer or racemic) and 50 ml of butanol (not necessarily anhydrous) and 1 ml of sulphuric acid were refluxed for 2 hours. After that, liberated water (*ca.* 4 ml) was removed with excessive butanol azeotropically in about 2 hours. When distillation was finished the pale yellow reaction mixture was cooled and diluted with 10 ml of diethyl ether. The resulting solution was shaken two times with 50 ml of water and dried with anhydrous magnesium sulphate. After evaporation of ether, the residue was vacuum distilled (146 °C/ 2 mm Hg) to yield 19 g of very pure dibutyl tartrate (72 %).

³ Usage of carbon tetrachloride is commonly criticized. We are currently checking if it can be replaced with 1,2dichloroethane. It has similar boiling point, but it is several times less expensive and much less toxic. According to initial runs, the reaction proceeds similarly in this solvent.

⁴ At 70 °C the oxidation is not complete.

Synthesis of dimethyl dioxosuccinate (1b) (simplified procedure)



In a three-necked 100 ml flask equipped with large magnetic stir bar was put 3.56 g (0.02 mol) of dimethyl tartrate, 14.24 g (0.08 mol) of NBS and 20 ml of CCl₄. The resulting mixture was stirred overnight at 75 - 78 °C. After a while the reaction mixture changes color to deep red due to liberation of bromine by NBS. Next the mixture was cooled to room temperature and solvent was evaporated. Residue was flooded with 50 ml of diethyl ether and left to stand for a few hours. The ether solution was decanted and the residue was treated in the same way two more times. Combined ether solution was evaporated at 50 °C to yield 4 g of white slurry solid. NMR and IR studies showed that procedure was reproducible and the crude product contained 50 % of **1b** (2 g, 57.4%). The product was used for next step without further purification. The crude product is quite well soluble in ether, THF, acetic acid and chlorinated solvents. It is very poorly soluble in hexane. It may be stored for a few weeks in refrigerator, but it is best to use it directly after preparation.

Note: Although not required, the purification of **1b** is troublesome, regardless of the technique used. <u>¹H NMR (400 MHz, CDCl₃) δ : 3.91 (s, 6H).</u>

Synthesis of diethyl dioxosuccinate (1c) (simplified procedure)

In a three-necked 100 ml flask equipped with large magnetic stir bar was put 4.12 g (0.02 mol) of diethyl tartrate, 14.24 g (0.08 mol) of NBS and 20 ml of CCl₄. The resulting mixture was stirred overnight at 75 - 78 °C. After a while the reaction mixture changes color to deep red due to liberation of bromine by NBS. Next the mixture was cooled to room temperature and diluted with 40 ml of diethyl ether⁵. Everything was carefully filtered and the filtrate was evaporated at 50 °C to yield 5 g of yellow orange highly viscous liquid. The crude product was suitable to be used in the next step. NMR and IR studies showed that procedure was reproducible and the crude product contained 67 % of **1c** (3.35 g, 83 % yield), contaminated mainly with succinimide.

The product is slightly miscible with hexane, and well soluble in ether, THF, acetic acid and chlorinated solvents. It may be stored for a few weeks in refrigerator, but it is best to use it directly after preparation.

Note: Although not required, the purification of 1c is troublesome, regardless of the technique used.

¹<u>H NMR (400 MHz, CDCl₃) δ: 4.30 - 4.40 (m, 4H), 1.28 - 1.40 (m, 6H).</u>

⁵ When hexane was used the yield was very low.

Synthesis of tetrabutyl ester of 1,4,5,8-tetraaza-2,3,6,7-anthracenetetracarboxylic acid (2a)



0.75 g of 1,2,4,5-tetraaminobenzene tetrahydrochloride (2.6 mmol, assuming 100 % quality), 1.96 g of crude **1a** (6 mmol assuming 80% quality), 0.86 g of sodium acetate (10.4 mmol) and 40 ml of acetic acid were heated for 18 hours at 120 °C⁶. The mixture was cooled and solvent evaporated at 50°C. The residue was dissolved in chloroform and directly⁷ filtered through 40 cm high silica gel column using chloroform as eluent⁸. Yellow-orange colored fraction⁹, which eluted first, was collected (about 300 ml) and evaporated obtaining 0.80 g of quite pure **2a** as yellow powder¹⁰. It was crystallized from 10 ml of hot ethanol. After cooling in refrigerator bright yellow needles were filtered off, washed with 3 x 10 ml of methanol and dried, obtaining 0.73 g of pure **2a** (47.4 %, assuming 100 % quality of tetrahydrochloride).

¹<u>H NMR</u> (400 MHz, CDCl₃) δ : 9.22 (s, 2H); 4.52 (t, 8H, J = 6.8 Hz); 1.76 - 1.94 (m, 8H); 1.40-1.60 (m, 8H); 1.00 (t, 12H, J = 7.2 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 164.3 ; 146.7 ; 140.4 ; 131.9 ; 67.3 ; 30.6 ; 19.2 ; 13.8.

<u>IR</u> (KBr disk, cm⁻¹): 3452; 3421; 2961; 2933; 2874; 1743; 1721; 1576; 1509; 1471; 1452; 1417; 1345; 1305; 1281; 1262; 1201; 1085; 1069; 948; 886; 825; 784.

UV-vis (CHCl₃): 376 nm, 271 nm.

Elemental analysis calculated C 61.84; H 6.57; N 9.52 found C 61.24 H 6.75; N 9.32.

Another example:

1 g of 1,2,4,5-tetraaminobenzene tetrahydrochloride (3.5 mmol, assuming 100 % quality), 2.84 g of crude **1a** (8.8 mmol, assuming 80 % quality), 1.16 g of sodium acetate (14 mmol) and 40 ml of acetic acid were submitted to the same procedure as above. 0.86 g of pure **2a** was obtained (42 %, assuming 100 % quality of tetrahydrochloride). Elemental analysis found C 61.68; H 6.39; N 9.62.

⁶ For **2a-2c** TLC (chloroform or chloroform/ethanol 20:1) indicated no change after 2 - 4 hours.

⁷ If the reaction scale is larger (tetrachloride>1g) copious amounts of liberated sodium chloride will clog the column, hence chloroform solution should be filtered first to remove insoluble impurities. Extraction with water is not very effective and difficult because dark colors mask completely phase separation border.

⁸ If the reaction proceeded well, separation of main fraction did not require TLC monitoring for **2a-2d**. Plates were developed in chloroform with some alcohol added.

⁹ In the case of **2a**, fraction containing tetraester was directly followed with deep-red colored fraction, which contained negligible amounts of tetraester and was rejected.

¹⁰ If the powder obtained was dark orange, red or brown it was necessary to stir it with methanol and centrifuge before crystallization. Hence, second chromatography is not required. If the user still wants to use column, only half amount of silica gel is necessary in comparison to the first column.

Synthesis of tetramethyl ester of 1,4,5,8-tetraaza-2,3,6,7-anthracenetetracarboxylic acid (2b)



Method A:

0.7 g of 1,2,4,5-tetraaminobenzene tetrahydrochloride (2.5 mmol, assuming 100 % quality), 1.96 g of crude **1b** (5.6 mmol, assuming 50 % quality), 0.83 g of sodium acetate (10 mmol) and 40 ml of acetic acid were heated for 18 hours 120 °C. The mixture was cooled and solvent evaporated at 50 °C. The residue was dissolved in chloroform and directly filtered through 20 cm silica gel column using chloroform as eluent. Yellow-orange colored fraction, which eluted first, was collected (about 100 ml) and evaporated. Residue was washed with methanol and dried to obtain 0.23 g of quite pure **2b** as yellow powder. Everything was dissolved in 20 ml of boiling chloroform and about 10 ml of methanol was added. After cooling, the precipitate was centrifuged and washed with acetone and dried obtaining 0.15 g of pure **2b** as yellow powder (14.5 %, assuming 100 % quality of tetrahydrochloride). The filtrate was evaporated to yield another 0.06 g (5.8 %) of **2b**, suitable for test reactions.

¹<u>H NMR (400 MHz, $C_2D_2Cl_4$ or CDCl₃) δ : 9.25 (s, 2H); 4.14 (s, 12H).</u>

¹³C NMR (100 MHz, C₂D₂Cl₄) δ: 164.3; 145.9; 140.1; 131.8; 54.0.

<u>IR</u> (KBr disk, cm⁻¹): 3486; 3432; 3131; 3081; 3027; 2962; 1749; 1725; 1582; 1509; 1455; 1445; 1409; 1389; 1351; 1295; 1279; 1267; 1219; 1187; 1091; 1067; 954; 889; 883; 846; 823; 799; 786; 769; 726; 559; 429. UV-VIS (CHCl₃): 376 nm, 271 nm.

Elemental analysis calculated C 52.18; H 3.41; N 13.52, found C 51.92; H 3.10; N 13.34.

Method B, excluding chromatography techniques:

0.7 g of 1,2,4,5-tetraaminobenzene tetrahydrochloride (2.5 mmol, assuming 100 % quality), 4 g of crude **1b** (11.3 mmol, assuming 50 % quality), 0.83 g of sodium acetate (10 mmol) and 40 ml of dioxane were heated for 18 hours at 100 °C. The mixture was cooled and solvent evaporated at 50°C. The residue was centrifuged with 50 ml of methanol, then 50 ml of water and finally 50 ml of acetone. The residue was dissolved in 40 ml of boiling chloroform and filtered hot through funnel filled with cotton wool. Filtrate was evaporated to give 0.38 g of **2b**. It was dissolved again in 40 ml of hot chloroform and 20 ml of methanol was added. After cooling the precipitate was centrifuged and washed with acetone obtaining 0.18 g of pure **2b** as yellow powder. The filtrate was evaporated to yield another 0.19 g of **2b** of almost identical purity. The total yield was 35.7 %. Elemental analysis found C 51.86 H 3.08 N 13.34.

Synthesis of tetraethyl ester of 1,4,5,8-tetraaza-2,3,6,7-anthracenetetracarboxylic acid (2c)



1 g of 1,2,4,5-tetraaminobenzene tetrahydrochloride (3.5 mmol, assuming 100 % quality), 2.5 g of crude **1c** (8.3 mmol assuming 67 % quality), 1.15 g of sodium acetate (14 mmol) and 40 ml of acetic acid were heated for 18 hours at 120 °C. The mixture was cooled and solvent evaporated at 50°C. The residue was dissolved in chloroform and directly filtered through 30 cm high silica gel column using chloroform as eluent. Yellow-orange colored fraction, which eluted first, was collected (about 150 ml) and evaporated obtaining 0.5 g of quite pure **2c** as yellow-orange powder. It was dissolved in chloroform and small portions of hexane were added to initialize crystallization using slow evaporation/cooling technique. Bright yellow fluffy solid obtained, was filtered off and washed with 3 x 10 ml of methanol and dried, yielding 0.40 g of pure **2c** (24 %, assuming 100 % quality of tetrahydrochloride).

¹<u>H NMR</u> (400 MHz, CDCl₃) δ: 9.23 (s, 2H); 4.60 (q, 8H, J = 5.4 Hz); 1.51 (t, 12H, J = 7.2 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 164.0, 146.5; 140.3; 131.7; 63.4; 14.1.

<u>IR</u> (KBr disk, cm⁻¹): 3449; 3417; 3067; 2985; 2941; 2907; 1745; 1720; 1575; 1511; 1475; 1452; 1422; 1389; 1370; 1303; 1288; 1283; 1265; 1207; 1118; 1089; 1067; 1017; 1015; 906; 889; 868; 863; 824; 797; 723; 550; 453.

UV-vis (CHCl₃): 376 nm, 271 nm.

Elemental analysis calculated C 56.17; H 4.71; N 11.91, found C 56.19; H 4.67; N 11.86.

Method B (optimized and recommended)

0.72 g of 1,2,4,5-tetraaminobenzene tetrahydrochloride (2.5 mmol, assuming 100 % quality), 2 g of crude **1c** (6.6 mmol assuming 67 % quality), 0.82 g of sodium acetate (10 mmol) and 20 ml of dioxane were heated for 4 hours at 100 °C. The mixture was cooled and solvent evaporated at 50 °C. The residue was dissolved in chloroform and directly filtered through 30 cm high silica gel column using chloroform as eluent. Yellow-orange colored fraction was collected (about 150 ml) and evaporated obtaining 0.75 g of quite pure **2c** as yellow-orange powder. Everything was crystallized from 40 ml of boiling chloroform:ethanol 1:1 v/v and after cooling overnight in refrigerator yellow transparent needles were filtered off, washed with 3 x 10 ml of ethanol and dried to yield 0.5 g of very pure **2c**. The combined filtrate was evaporated and residue washed with small amounts of ethanol and dried. 0.15 g of pale yellow residue was dissolved in 10 ml of chloroform and a few ml of hexane were added with subsequent cooling. The first crop (95 mg, bright yellow fluffy solid) was collected and washed with 3x10 ml of ethanol. To the combined filtrate some chloroform was added to clarify the suspension and another 5 ml of hexane was introduced. Upon cooling second and final crop appeared and was recovered as the first one (40 mg). The total yield of very pure **2c** was 0.635 g (52.9 %).

Elemental analysis found C 56.23; H 4.80; N 11.92.

Synthesis of tetra(2-octyldodecyl) ester of 1,4,5,8-tetraaza-2,3,6,7-anthracenetetracarboxylic acid (2d)



30 mg of **2b** (0.0725 mmol), 0.5 g of 2-octydodecanol (1.6778 mmol) and a small crystal of p-toluenesulphonic acid in 1 ml of o-dichlorobenzene were heated for 100°C for 4 days in a small, loosely capped vial. The progress of reaction was conveniently monitored by TLC using chloroform as eluent. Each day additional very small crystal of p-toluenesulphonic was added. After 3 days TLC indicated only one spot and reaction was terminated after another day. Reaction mixture was directly filtered through 20 cm silica gel column using chloroform as eluent. 100 ml of orange colored fraction was collected and evaporated. It was filtered again through 15 cm silica gel column and 100 ml of collected fraction was evaporated to yield 80 mg (74.6%) of orange oil.

¹<u>H NMR</u> (400 MHz, CDCl₃) δ: 9.22 (s, 2H); 4.40 (t, 8H, J = 5.6 Hz); 1.82 - 1.90 (m, 4H); 1.18 - 1.42 (m, 152H); 0.86 (apparent t, 24H, J = 6.8 Hz).

¹³C NMR (100 MHz, CDCl₃) δ: 164.3 ; 146.6 ; 140.3 ; 131.8 ; 70.2, 37.3 ; 31.9 ; 31.0 ; 30.0 ; 29.7 ; 29.6 (2C) ; 29.3 ; 26.7 ; 22.7 ; 14.1. Not all aliphatic carbons could be resolved.

<u>IR</u> (coated on KBr disk, cm⁻¹): 3445; 2955; 2924; 2854; 1759; 1738; 1731; 1576; 1509; 1464; 1456; 1415; 1378; 1342; 1295; 1263; 1200; 1166; 1085; 1065; 957; 892; 819; 789; 722.

UV-vis (CHCl₃): 376 nm, 271 nm.

Elemental analysis calculated C 76.21; H 11.30; N 3.78 found C 76.13 H 11.47; N 3.61.



Fig. S3 FT-IR spectrum of 2a





Fig. S6 FT-IR spectrum of 2b



Fig. S9 FT-IR spectrum of 2c





Fig. S12 IR spectrum of 2d



Fig. S13 DSC plot of a) **2a**, b) **2b**, c) **2c**, d) **2d**



Fig. S14 UV-vis spectra of thin films of a) 2a and 2b, b) 2c and 2d



Fig. S15 Cyclic voltammetry of **2b** coated on platinum electrode in 0.1 M Bu₄NBF₄ CH₃CN: a) linear, b) differential



Fig. S16 UV-vis-NIR spectra of **2b** deposited on ITO registered in the potential range: a) from E = -0.75 V to E = -1.25 V, b) from E = -1.25 V to E = -1.55 V. Electrolyte: 0.1 M Bu₄BF₄ in CH₃CN; E *vs* Fc/Fc⁺

Deposition of ordered layers

Thin films of the studied semiconductors were deposited on a glass substrate previously washed in an ultrasonic washing stand using a three step procedure (chloroform, isopropanol, chloroform). Layers of **2a** were deposited from three different solvents: chloroform, toluene and chlorobenzene (concentration 2 mg/ml). Self assembly, crystallization and continuity of the layers obtained from different solvent, was studied using a polarized optical microscope (POM, Biolar microscope, PZO) (see Fig. S17).



Fig. S17. Polarized optical microscopy images of **2a** films, obtained by drop-casting from a) chloroform b) toluene, c) chlorobenzene. White arrows show orientation of polarization planes of the polarizer and the analyzer.

Optimal deposition parameters, established on the basis of the drop casting tests (concentration of the solution and as well as its temperature of the temperature of the substrates) were then used for the preparation of oriented polycrystalline layers by the zone-casting technique.



Fig. S18. Polarized optical microscopy images of highly oriented **2a** films, obtained from chlorobenzene by drop casting method (upper row) and zone casting technique (lower row). White arrow indicates the crystals growth direction, black arrows show orientation of polarization planes of the polarizer and the analyzer.

The zone casting method allowed producing oriented crystalline layers on large surface area (>20 cm²), in a reproducible manner. Atomic force microscopy (AFM, SOLVER PRO scanning probe microscope, NT-MDT) measurements confirmed unidirectional orientation of the crystals in the polycrystalline structure (Fig. S19). The AFM studies showed that morphology (crystals width and thickness) of the crystals changed depending on the method of casting. The drop-casting technique allowed us to produce crystals with high size range (from 100 to 500 nm) and 5-20 μ m wide. By the zone-casting method crystals ranging size from 100 to 200 nm and 5-40 μ m wide were fabricated.



Fig. S19. Atomic force microscopy images of **2a** films obtained by a) drop casting method, b) zone casting technique

The OFETs based on **2a** and **2c** were fabricated applying the top-gate bottom-contact structure. First the gold source and drain electrodes were evaporated on top of cleaned glass substrates with a thickness of about 40 nm. Next the **2a** or **2c** oriented layer was deposited by zone-casting. Then 1 μ m thick Parylene C film (used a dielectric layer) was evaporated. Finally, the gate Al electrode was than evaporated on top with a thickness of about 100 nm. The devices were fabricated and measured under ambient conditions. (room temperature: T~26°C, relative humidity: RH ~ 40 -70%). Different channel length was used: 30, 40, 50, 60, 80 and 100 μ m, channel width: 4 mm. The OFETs based on the tetraazaanthracene derivatives show typical *n*-type behavior. The charge carrier mobility (without the device architecture optimization) calculated from saturation region were estimated for **2a** $\mu_{\text{FET}} = 1 \times 10^{-4} \text{cm}^2/(\text{V}\text{s})$. The values, ON/OFF ratio and threshold voltage were $3x10^2$ and 120 V respectively. The parameters for **2c** were estimated to be $\mu_{\text{FET}} = 5 \times 10^{-4} \text{cm}^2/(\text{V}\text{s})$, ON/OFF = $2x10^3$, $V_T = 110 \text{ V}$.



Fig. S20. Output characteristic of the OFETs based on 2c deposited by zone-casting method, measured in air