

Novel, Low-Cost, Highly Soluble n-Type Semiconductors: Tetraazaanthracene Tetraesters

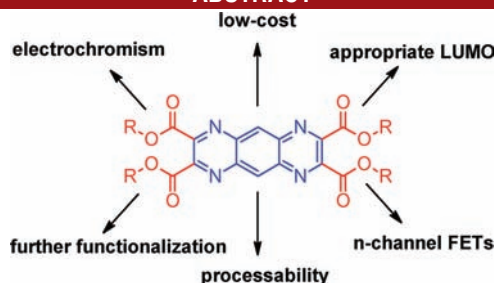
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ABSTRACT



New tetraester derivatives of 1,4,5,8-tetraazaanthracene have been prepared and characterized by spectroscopic and electrochemical techniques. The LUMO level of the compounds is close to -4 eV (the so-called air operating stability border in n-channel field effect transistors). Tetraesters were obtained with reasonable yields without the necessity of using high-quality reactants or solvents, resulting in their low cost.

In recent years organic synthesis has greatly contributed to the development of new semiconducting materials for n-channel field effect transistors.¹ This includes, among others, azaacenes, which seem very promising in this respect as evidenced by theoretical calculations.² Many of azaacene derivatives studied theoretically are difficult to obtain or even might not be obtainable by synthetic methods developed to date. However, azaacenes containing a tetraazaacene core (alternatively named pyrazinoquinoxaline) can be readily prepared using the condensation reactions between aromatic di- or tetraamines and diketones.³

Thus, we have synthesized a series of new tetraester derivatives of 1,4,5,8-tetraazaanthracene, taking into account

that the presence of the ester substituents in fused aromatic compounds greatly improves their solution processability. We demonstrate that these new compounds can serve as precursors of other derivatives showing interesting electronic properties.

Dioxosuccinates have rarely been used for condensation⁴ and, to the best of our knowledge, never used in a 2-fold reaction. Such a process introduces four ester groups in positions 2, 3, 6, and 7 to the 1,4,5,8-tetraazaanthracene core. The ester groups may potentially be submitted to further conversion. It is noteworthy that the tetraesters described here are obtainable in two steps only, using very simple reactions (Scheme 1). Importantly, none of the steps require an argon atmosphere, costly substrates like transition metal catalysts, and highest quality, dry solvents. This contributes to the lowering of the

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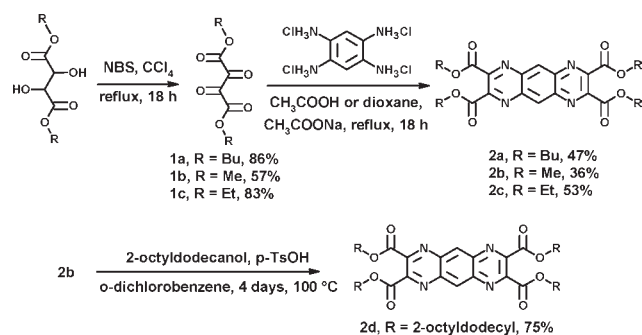
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Scheme 1. Synthetic Route to the Novel Tetraazaanthracene Tetraesters



semiconductor's price. According to the literature such an approach is used almost exclusively for nonsoluble n-type materials,⁵ whereas our compounds are solution processable. Finally, it is not common to introduce heteroatoms and electron-accepting groups in one step.

To prepare dioxosuccinic acid esters (**1a–1c**), we have used the oxidation of the tartaric acid esters with *N*-bromosuccinimide modifying the procedure reported by Khurana and Kandpal.⁶ As compared to the original procedure, the molar ratio between the tartrate and NBS needed to be increased from 1:3 to 1:4. Additionally, the reaction time had to be extended from 3 to 18 h, to ensure reproducibility. Obtained **1a–1c** were contaminated with succinimide and unreacted NBS, which were difficult to remove. Fortunately, the yield of the next reaction was practically unaffected by the purity of **1a–1c**, so it was decided crude diesters would be used in the next and final step.⁷

Table 1. Results of the Optimization of the Synthesis of the Compounds Studied

entry	compd	solvent	base	time	temp	yield
1	2a	CH ₃ COOH	None	18 h	120 °C	20%
2	2a	CH ₃ COOH	None	18 h	80 °C	5%
3	2a	CH ₃ COOH	CH ₃ COONa	18 h	120 °C	47%
4	2a	ethanol	CH ₃ COONa	18 h	80 °C	30%
5	2b	CH ₃ COOH	CH ₃ COONa	18 h	120 °C	20%
6	2b	dioxane	CH ₃ COONa	18 h	100 °C	36%
7	2c	CH ₃ COOH	CH ₃ COONa	18 h	120 °C	24%
8	2c	dioxane	CH ₃ COONa	4 h	100 °C	53%

The second step required optimization (Table 1), since initial results were mostly unsatisfactory. The first solvent used for the synthesis of **2a** was acetic acid. The yield did not exceed 20% but was reproducible (entry 1). At lower temperatures, **2a** was barely formed (entry 2). Later, we found that much better results were obtained when the

amine groups in 1,2,4,5-benzenetetraamine tetrahydrochloride were unblocked with a base, sodium acetate (entry 3). Still a high temperature was required, since even with the presence of this base the yield was clearly diminished when a lower boiling solvent was used (entry 4). During the reaction, considerable amounts of deep red colored byproducts formed, but **2a** was easily separable from them as it eluted faster on a chromatography column. After running one column only, residual impurities were perfectly removed by crystallization with small amounts of hot ethanol, which is attractive for a medium laboratory scale. **2a** has excellent solubility in solvents like chloroform, dichloromethane, chlorobenzenes, dioxane, THF, acetonitrile, and toluene. It is insoluble in methanol and ethanol at rt.

The optimized procedure was directly used to synthesize **2b**; the yield was however poor (entry 5). Additionally, the suppressed solubility of **2b** excluded chromatographic purification of amounts larger than a few hundred milligrams. Therefore, we developed an alternative procedure, resulting in better yields of **2b** (entry 6) of practically similar purity, which in addition did not require chromatographic purification. This modification not only reduced costs of tetraazaacenes synthesis but also turned out to be more suitable for the preparation of larger quantities of **2b**. **2b** is fairly soluble in chlorinated solvents, especially chloroform.

Similarly as in the case of **2a** and **2b**, the yield of **2c** was found to be solvent dependent (entries 7 and 8). Additionally, the reaction time was significantly reduced (entry 8). **2c** is readily soluble in chlorinated solvents.

Compound **2b** was used for further derivatization. Our test reactions proved that a methyl group can be interchanged with appreciable yields. We managed to perform transesterification to obtain **2d**. It should be pointed out that it was actually possible to exchange all four groups despite the fact that the process was sterically demanding and a rather weak nucleophile was used. More importantly, the rather poor solubility of **2b** did not limit its usefulness. **2d** was obtained as an orange viscous liquid.

The structures of the tetraesters were confirmed by spectroscopic techniques, and their purity was checked by elemental analysis.

Spectroscopic features of the synthesized compounds are typical for a tetraazaacenes family.^{3b,8} Two bands could be distinguished in the solution spectra of **2a–2d**: a stronger one at 271 nm and a weaker one at 376 nm (see Figure 1). The length of the alkyl group did not affect the position of the absorption maxima (Table 2). At low concentrations (10⁻⁶–10⁻⁴ M) the absorbance maxima linearly changed with dilution, suggesting significant steric repulsion induced by the bulkiness of the ester groups. In comparison to the related tetraalkyl derivative,⁹ ester groups provided a more pronounced bathochromic shift of the bands ascribed to the tetraaza core. Interestingly, the

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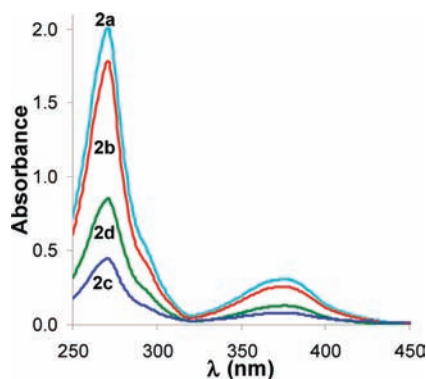


Figure 1. UV–vis spectra of chloroform solutions of **2a** (2.0×10^{-5} M), **2b** (2.0×10^{-5} M), **2c** (0.5×10^{-5} M), and **2d** (1.35×10^{-5} M).

Table 2. Basic Optical Properties of the Tetraesters

compd	λ_{\max} (CHCl ₃) (nm)	λ_{\max} (quartz) (nm)
2a	271, 376	267, 371
2b	271, 376	289, 392
2c	271, 376	285, 376
2d	271, 376	275, 374

bands did not show a vibronic structure, with the exception of a distinguishable shoulder at *ca.* 290 nm (Figure 1).

In the thin film spectra¹⁰ these two bands showed very small shifts with simultaneous broadening. The band of higher energy exhibited a more pronounced decrease in intensity. In the spectrum of **2b** the largest shift was observed, since the methoxycarbonyl substituent is the smallest possible, allowing stronger π -stacking interactions. The spectrum of **2a** showed a weak blue shift of the two peaks. It is possible that, in this case, the packing of the molecules alters the angles between aromatic moieties, weakening π - π interactions. The UV–vis data are listed in Table 2.

Next, we checked the influence of the functional groups on the electrochemical properties of these new derivatives. We expected that electron-withdrawing ester groups combined with the presence of four nitrogen atoms in the core would significantly shift the reduction potentials to less negative values, in comparison to the majority of the existing tetraazaanthracene derivatives.^{8,11} The cyclic voltammograms of all compounds are shown in Figure 2. The potentials of the observed redox couples are listed in Table 3.

(10) See Supporting Information.

(11) Other heteroacenes: (a) Hu, J.; Zhang, D.; Jin, S.; Cheng, S. Z. D.; Harris, F. W. *Chem. Mater.* **2004**, *16*, 4912–4915. (b) Liang, Z.; Tang, Q.; Liu, J.; Li, J.; Yan, F.; Miao, Q. *Chem. Mater.* **2010**, *22*, 6438–6443. (c) Gao, B.; Wang, M.; Cheng, Y.; Wang, L.; Jing, X.; Wang, F. *J. Am. Chem. Soc.* **2008**, *130*, 8297–8306.

(12) Cycling upon potential -2.2 V did not reveal additional redox couples. Also measurements in positive potential range up to 1.5 V did not show clear oxidation processes.

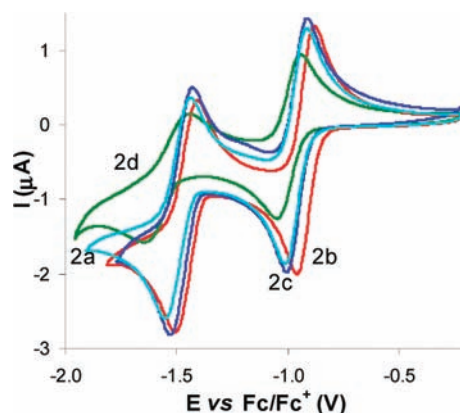


Figure 2. Representative cyclic voltammograms of **2a**, **2b**, **2c**, and **2d** (5×10^{-4} M in 0.1 M Bu₄NBF₄ CH₂Cl₂).

Table 3. Redox Potentials (vs Fc/Fc⁺) and the Energies of the LUMO/HOMO Levels (vs the Vacuum Level) of the Tetraesters

compd	E_{red1} (V)	E_{red2} (V)	E_{ox2} (V)	E_{ox1} (V)	$E_{\text{red1onset}}$ (V)	LUMO (eV)	HOMO (eV)
2a	-0.95	-1.49	-1.39	-0.87	-0.81	-3.99	-6.91
2b	-0.91	-1.46	-1.36	-0.83	-0.76	-4.04	-6.96
2c	-0.95	-1.47	-1.38	-0.87	-0.81	-3.99	-6.91
2d	-1.00	-1.60	-1.40	-0.89	-0.85	-3.95	-6.87

Contrary to the first reversible reduction, the second one is quasi-reversible.¹² Spectroelectrochemical investigations confirmed consecutive formation of a radical anion and then a dianion.¹⁰ Interestingly, **2b** shows its reduction peaks clearly shifted toward higher potentials in comparison to **2a**. It seems that in **2a** the butyl groups provide a greater inductive donating effect toward the carbonyl ester groups. As for **2d**, using similar reasoning, the branched alkyl chain induces a larger donating effect, weakening slightly the electron-accepting power of the ester group. Between **2b** and **2d**, the difference approaches 100 mV, which is a phenomenon almost never observed for n-type molecules, where changing of alkyl substituents usually barely influences the reduction potential.

From the first reduction onsets it was possible to calculate the LUMO levels of the azaacenes (Table 3). The onsets were determined by the method described previously (LUMO = $-e(E_{\text{red1onset}} \text{ vs Fc/Fc}^+ + 4.8 \text{ V})$).¹³ **2a–2d** satisfy the conditions required for the semiconductors used in the air-operable devices. Using the absorption edge, the HOMO levels were calculated with the following formula: HOMO = LUMO – 1240/ λ_{offset} , where λ_{offset} =

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425 nm. The obtained band gap value (2.92 eV) is typical of the related compounds.^{8,11b}

For **2b**, it was possible to record the voltammogram in a thin layer.¹⁰ Again, two reduction potentials were observed at -0.89 and -1.45 V. During the reduction a deep red colored product was formed. To elucidate these changes electrochemical investigations were carried out.¹⁰ In the spectrum of the reduced form, two bands were distinguishable: a sharp one at 480 nm (giving red color) and a broad vibronic one with a maximum at 881 nm attributed to the presence of radical anions. Further reduction was manifested by the appearance of a new band at 319 nm, possibly ascribed to the formation of a dianion.

2a and **2c** exhibit a high tendency for self-organization. Hence, it was possible to prepare polycrystalline thin films with highly oriented crystal wires by different solution processing methods: drop casting and zone casting.¹⁰ The preoptimization process, carried out for spin-coating experiments, allowed us to indentify the best solvent (chlorobenzene) and to establish the optimum concentration and temperature of the solution. These conditions were then applied to the zone casting¹⁴ of oriented **2a** layers. In both methods the semiconductor layers exhibited reproducible orientation on surface areas exceeding 20 cm^2 . Polarized optical microscope images showed the optical birefringence of the polycrystalline films. The morphology of the layers was further analyzed by AFM.¹⁰ Our results unequivocally confirm the unidirectional orientation of the crystals. Using the zone-casting method, we were able to produce crystals of a size ranging from 100 to 200 nm and $5\text{--}40\text{ }\mu\text{m}$ wide.

To verify the applicability of our new semiconductors in organic electronics, we have fabricated top gate-bottom contact transistors¹⁰ from **2a** and **2c**, using Parylene C as a dielectric. The best measured charge carriers mobility was $5 \times 10^{-4}\text{ cm}^2/(\text{V}\cdot\text{s})$. Taking into account that neither the substrate–semiconductor nor semiconductor–dielectric interface was optimized, we expect the large area of potential improvement in the electron mobility.

To conclude, we have developed a simple two-step, low-cost procedure for the preparation of tetraazaanthracene tetraesters, new organic semiconductors of potential use in organic electronics. Incorporation of the heteroatoms to the conjugated core, in combination with the presence of electron-withdrawing substituents in one molecule, seems to be a promising approach. To the best of our knowledge, this is the first case where the electron-withdrawing substituents significantly contribute to the improvement of the solution processability of the prepared semiconductor and allows for its further functionalization. Such studies are in progress.

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Supporting Information Available. Experimental procedures, ¹H NMR, ¹³CNMR, IR spectra, DSC plots, additional electrochemical and spectroelectrochemical diagrams, POM and AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>