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Electron donors and acceptors based on 2,7-functionalized pyrene-4,5,9,10-tetraone†

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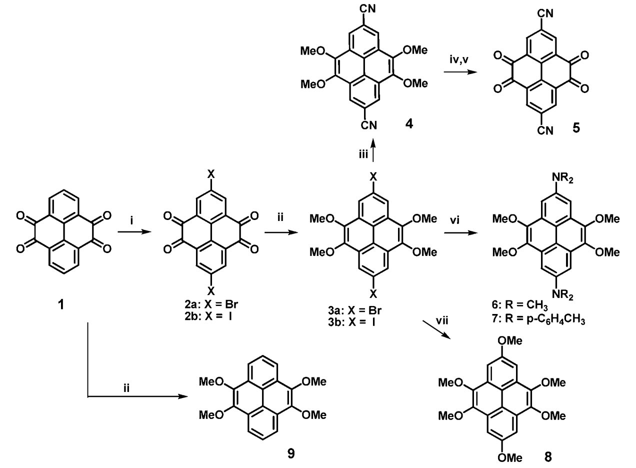
An efficient synthesis of 2,7-dibromo- and diiodo-pyrene(4,5,8,19)-tetraones led to strong donors and acceptors based on pyrene. They are versatile building blocks for conjugated materials and can be further applied in molecular electronics.

Polycyclic aromatic hydrocarbons (PAHs) have long played an important role in modern organic chemistry from a synthetic, theoretical and applied viewpoint.[1] More recently, PAH derivatives have been intensively studied as active components of electronic and optoelectronic devices.[2] In this regard, pyrenes are probably the best known organic chromophores,[3] while anthracenes[4] are used as emitters in organic light emitting diodes and pentacenes[5] are outstanding semiconductors in field effect transistors. Optimizing PAHs for electron and hole transport requires the synthesis of derivatives with either an electron rich or electron poor character. In the family of PAHs, pyrene itself is known as an electron donor,[6] and the conventional approach to functionalise this molecule is applied predominantly at the 1,3,6,8-positions.[7] There exist very few reports where other positions have been tackled, like the inactive 2,7 positions (due to the nodal plane of the frontier orbitals) by introducing *tert*-butyl or pinacolborone both directed by steric demands, or the 4,5,9,10-positions which most easily became accessible *via* the pyrene tetraone and its condensation with diamines.[8,9] Here, we present a new synthetic strategy for creating a variety of both, electron deficient and electron rich pyrene derivatives **2–8**.



Scheme 1 (i) (2a) *N*-bromosuccinimide, H_2SO_4, at 45 °C, 2 h, 78%; (2b) *N*-iodosuccinimide, H_2SO_4, at 45 °C, 2 h, 74%; (ii) $Na_2S_2O_4$, $(n\text{-Bu})_4NBr$, $(CH_3O)_2SO_2$, KOH, THF, H_2O, 40 °C, 1 h, 82%; (iii) CuCN, NMP, at 180 °C, 10 h, 56%; (iv) $AlCl_3$, CH_2Cl_2, at 40 °C, 4 days; (v) Ag_2O, THF, at 50 °C, 30 min, 20% for two steps; (vi) $HN(CH_3)_2$ in THF (6), $HN(p\text{-}C_6H_5CH_3)_2$ (7) Pd_2DBA_3, toluene, 95 °C, 18 h; (vii) NaOMe, CuI, toluene–DMF, 95 °C, 18 h, 62%.

The synthesis of the target structures **2–8** is depicted in Scheme 1 and is based on pyrene-4,5,9,10-tetraone (**1**) which can be prepared in gram scales.[9] While pyrenes are usually halogenated in the 1,3,6,8-positions, our approach utilized the direct bromination or iodination in the 2,7-positions of **1**, opening a new pathway for derivatives of pyrenes. The synthesis of 2,7-dibromopyrene-4,5,9,10-tetraone (**2a**) and 2,7-diiodopyrene-4,5,9,10-tetraone (**2b**) was easily performed by halogenation with *N*-bromo- or *N*-iodosuccinimide in sulfuric acid, respectively.[10] Direct cyanation of **2a** using CuCN to synthesize 2,7-dicyano-pyrene-4,5,9,10-tetraone (**5**) was not successful and resulted in an unidentified black solid. Therefore, the ketone-functions of compound **2a** were protected with methyl groups *via* reductive alkylation with $Na_2S_2O_4$ and dimethyl sulfate.[11] The resulting product, 2,7-dibromo-4,5,9,10-tetra-methoxypyrene (**3a**), was obtained in a very good yield (82%). Subsequently, cyanation of compound **3a** with CuCN led to 2,7-dicyano-4,5,9,10-tetramethoxypyrene (**4**) (56%).[12] After deprotection with aluminium trichloride and subsequent oxidation with

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† Electronic supplementary information (ESI) available: Experimental details, fluorescence spectra, cyclic voltammograms, X-ray structures and details, DFT calculations. CCDC 847344 (**2a**), 857532 (**5**), 857533 (**6**), 857534 (**7**), 857535 (**8**), 857537 (and mixed TCNQ cocrystals with **8**) and 857536 (**9**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc39141h

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silver oxide, 2,7-dicyano-pyrene-4,5,9,10-tetraone (**5**) was successfully isolated in 20% yield.

The diiodo derivative **3b** was prepared in analogy to **3a** using the precursor compound **2b**. **3b** turned out to be an excellent precursor for Ullmann[13] and Buchwald–Hartwig[14]-type cross coupling reactions, thus opening a viable route to strong donors based on pyrene. The amino-derivatives 2,7-bis(dimethylamino)-4,5,9,10-tetra-methoxypyrene (**6**) and 2,7-bis(di-*p*-tolylamino)-4,5,9,10-tetramethoxypyrene (**7**) were synthesized *via* palladium catalyzed amination using the appropriate secondary amine. When applying a copper(I)-catalyzed methoxylation 2,4,5,7,9,10-hexamethoxypyrene (**8**) was obtained (67%). As a reference for the donors **6–8**, 4,5,9,10-tetramethoxy-pyrene (**9**) was synthesised to compare the effects of additional substituents in positions 2 and 7.

The products were identified using ^{1}H- and ^{13}C-NMR spectroscopy as well as field desorption mass spectroscopy (FD-MS, see ESI†). The tetraone acceptors **1**, **2a**/**b**, and **5** are soluble in polar solvents such as THF, 1,4-dioxane, DMF, and DMSO, while the donor derivatives **6–8** showed improved solubility in chlorinated solvents (DCM, chloroform) as well as in THF.

The UV-Vis absorption spectra of the pyrene tetraones **1**, **2a**, and **5** recorded in DMF are shown in Fig. 1a. Similar to 9,10-phenanthrenedione,[15] they are characterized by the π–π* transitions at around 290 nm and the n–π* transitions at around 350–380 nm which are considerably less intense than the former. The UV-Vis absorption properties of the donors **6–8** were studied in dichloromethane and are depicted in Fig. 1b. Strong π–π* absorptions (300 to 350 nm) attributed to the pyrene core were observed. Here the maximum extinction coefficient of compounds **6** ($\log\varepsilon = 5.42$) and **7** ($\log\varepsilon = 5.43$), however, was one order of magnitude larger than the one for compound **8** ($\log\varepsilon = 4.11$). The longest wavelength transition was observed above 450 nm for **6** and **7** due to the higher HOMO level, while it occurred at 399 m for the hexamethoxypyrene **8**. Therefore the fluorescence spectra also showed a pronounced blue shift when the donor residue in positions 2 and 7 were changed from the amino groups in **6** (λ_{max} = 483 nm) or **7** (λ_{max} = 495 nm) to methoxy **8** (λ_{max} = 402 nm), respectively (see ESI,† Fig S2).

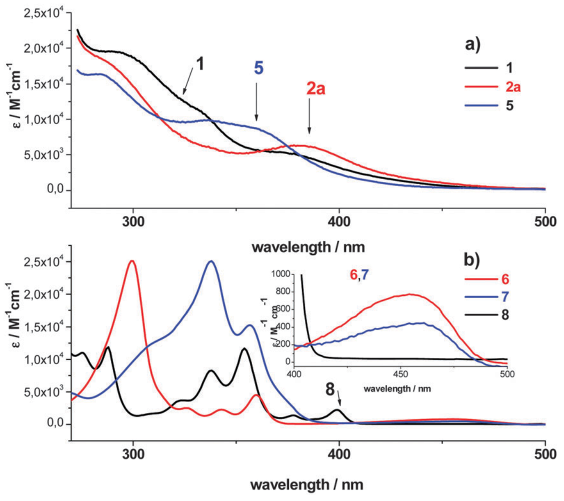

Fig. 1 Absorption spectra of (a) pyrene tetraones **1**, **2a**, and **5**, (b) pyrene donors **6–8**.

The reduction properties of **1–5** were investigated in DMF solutions using cyclic voltammetry ([n-Bu$_4$NClO$_4$] = 0.1 M, 100 mV s^{-1}). All molecules showed two reversible one-electron reduction steps (ESI,† Fig. S3). The pyrene-4,5,9,10-tetraone derivative **1** had a low first reduction potential, E_{R1}, at −0.41 V (*vs.* SCE for all the compounds discussed below), which was 0.19 V lower than that of 9,10-phenanthrenedione (−0.60 V).[15] Further electron-withdrawing substituents such as halogens or cyano groups led to more easy reduction of **2a** and **5**, with E_{R1} of −0.24 V and −0.16 V, respectively. For direct comparison the strong electron-acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ)[16] was also studied under these conditions. Thereby, TCNQ still demonstrated more easy reduction by 0.42 V due to the quinoidal structure[17] which is missing in the dicyano derivative **5**. Cyclic voltammetry investigations of the donors **6–8** were conducted in DCM solutions ([n-Bu$_4$NPF$_6$] = 0.1 M 50 mV s^{-1}). A two-electron oxidation was observed in the case of the amino donors **6** and **7** (see Table 1). For **8** a one-electron oxidation was observed. The half wave oxidation potential was determined to be E_O = +0.85 V. In none of the three studied donors the reduction wave was resolved before solvent decomposition.

For the acceptors, it is noteworthy that the LUMO of the dicyano derivative **5** reached −4.24 eV which is comparable with many other strong acceptors as benzo-TCNQ (−4.10 eV),[16] 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) (−3.70 eV),[17] bis[1,2,5]thiadiazolo-tetracyanoquinodimethane (BTDA) (−4.38 eV),[18] dicyano-substituted perylene-tetracarboxydiimide (−4.33 eV),[19] and a perfluorinated copper phthalocyanine at −4.27 eV.[20] As suggested by Marks *et al.*[21] the requirement for n-type semiconductors with thermodynamically air-stable charge carriers is a LUMO level within the range of −4.0 to −4.4 eV as found here.

Single crystals of compounds **2a** and **5** were grown by slow evaporation of a THF solution at room temperature. The dibromo derivative **2a** exhibits π–π stacking with a distance of 0.34–0.35 nm (ESI,† Fig. S4). The dicyano derivative **5** shows a stacking with the cyano groups oriented in an anti-parallel fashion (Fig. 2a). The closest C–C distance between the molecules

Table 1 Optical absorption maxima, optical gap, redox potentials *vs.* SCE, together with HOMO and LUMO energies of the main targets

Compd	λ_{max}^{a}/nm	ΔE^{b}/eV	E_{R1}^{c}/V	E_{R2}^{c}/V	E_{O1}^{d}/V	HOMO/eV	LUMO/eV
1	290, 371	2.65	−0.41	−0.76	—	−6.64	−3.99^{f}
2a	290, 380	2.49	−0.24	−0.55	—	−6.65	−4.16^{f}
5	290, 336	2.48	−0.16	−0.44	—	−6.72	−4.24^{f}
6	462	2.59	—	—	+0.55	−4.85^{e}	−2.26
7	465	2.55	—	—	+0.69	−5.03^{e}	−2.48
8	399	3.02	—	—	+0.85	−5.14^{e}	−2.12

^{a} Optical absorption maxima (in DMF). ^{b} Onset of optical absorptions. ^{c} E_{R1} or E_{R2} = (E_{pa} + E_{pc})/2, reduction potentials *vs.* SCE. ^{d} Oxidation potential *vs.* SCE. ^{e} Determined *vs.* vacuum level from E_{HOMO} = −4.40 eV − E_{O1}. ^{f} Determined from vacuum level from E_{LUMO} = −4.40 eV − E_{R1}.

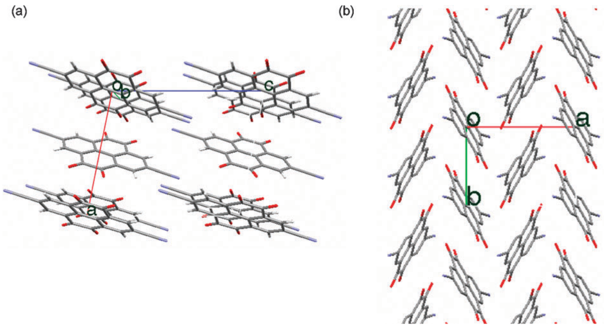

Fig. 2 Single crystal structure of **5**: (a) viewed along the *b* axis; (b) herringbone packing.

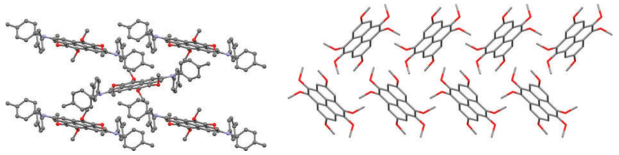

Fig. 3 Single crystal structures of the prepared donor molecules **7** and **8**, H atoms omitted for clarity.

was determined to be *ca.* 0.32 nm, with a very small π-overlap and a herringbone-like geometry (Fig. 2b).

The electron-rich compounds **6–8** were crystallized by vapor diffusion of hexane into a DCM solution of the respective compound, and structures **7** and **8** are juxtaposed in Fig. 3. The packing of **7** shows an interaction between the pyrene core of one layer and one of the tolyl-residues in the next layer. The shortest C–C distance was found to be 0.36 nm. **8** crystallized like **5** in a herringbone structure with the smallest intermolecular C–C distance determined to be 0.33 nm.

Some donor acceptor cocrystals of **8** and **9** with TCNQ became available[22] and served for in depth comparison of thin films and crystallites of various compositions by exciting physical studies such as UPS, HAXPES, and NEXAFS techniques.[22b,c]

In conclusion, we have presented a new synthesis of pyrene derivatives acting as donors or acceptors, starting from the pyrene-4,5,9,10-tetraone and its direct halogenation in positions 2 and 7 (Br, I) which otherwise is difficult to address in pyrene chemistry. They even enable their insertion in the main chain donor and alternating donor acceptor conjugated copolymers.[10a] CV measurements revealed that the LUMO level of 2,7-dicyanopyrene-4,5,9,10-tetraone **5** (−4.24 eV) is comparable to that of dicyano-perylene derivatives and PCBM. New donor moieties **6–8** were developed from the pyrene core with high lying HOMO but yet air stable. From the above outline there are two further options to follow: (i) the combination of these building blocks with other extended conjugated systems and (ii) the synthesis of even stronger donors and acceptors based on the pyrene core.

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