Supplementary Material for

"Electron Donors and Acceptors via 2,7-Functionalized Pyrene-4,5,9,10-tetraone"

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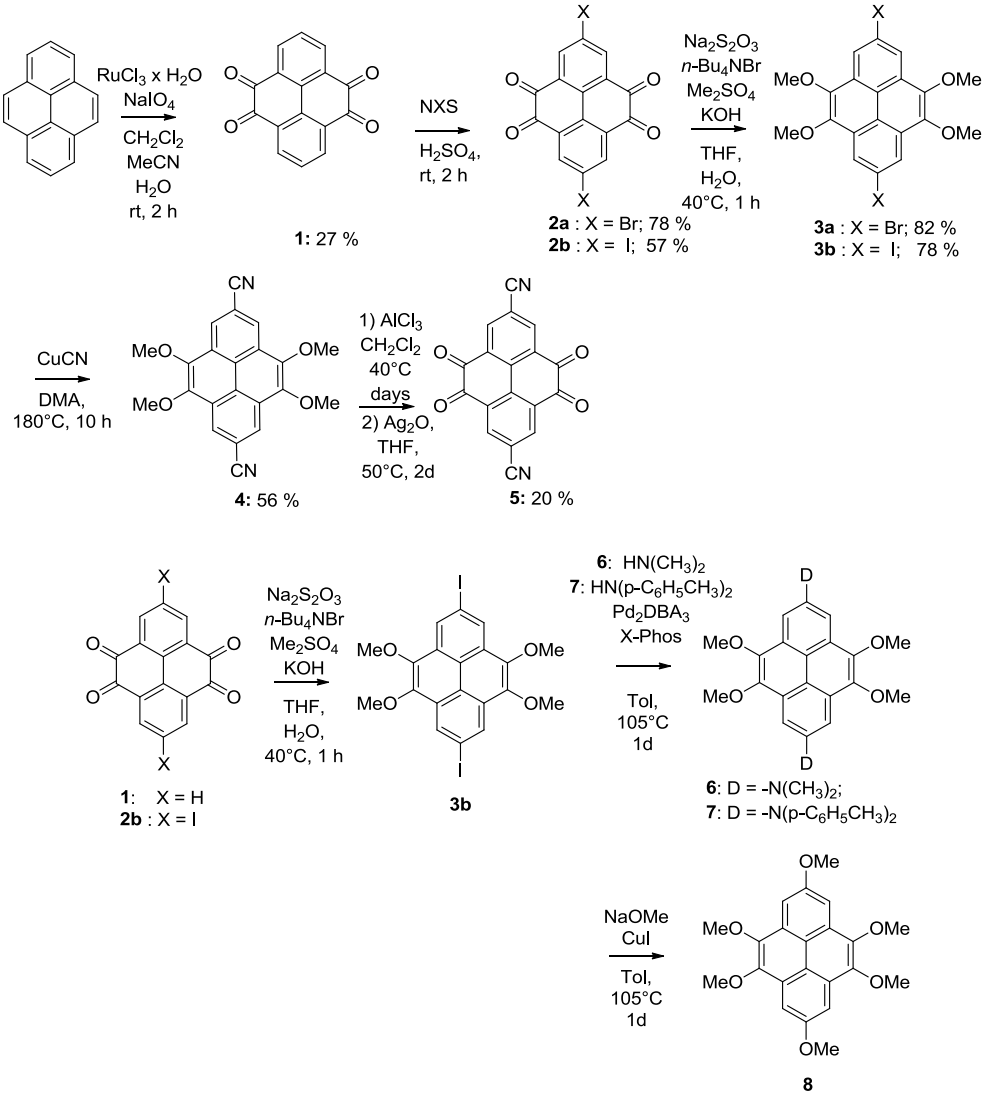
S1. Experimental Details

Commercially available reagents were used without further purification unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX250 or Bruker AMX500. Mass spectra were obtained using FD on a VG Instruments ZAB 2 SE-FPD. UV-visible spectra were obtained on a Perkin-Elmer lambda 9 spectrophotometer at room temperature. Cyclovolatammetry was measured on a Princeton Applied Research Parstat 2273 instrument with anhydrous solvents under argon atmosphere. Data collections for the crystal-structure analysis were performedon a Nonius KCCD diffractometer equipped with a Cryostream cooler with graphite monochromated MoKa radiation. The structures were solved by direct methods (Shelxs) and refined on F with anisotropic temperature factors for the nonhydrogen atoms. The H atoms were refined with fixed isotropic temperature factors in the riding mode.

S1. Experimental details, continued

Scheme S1: Synthesis of pyrene based donors and acceptors (**1-8**):



Compund **1** was prepared according to the reported literature procedures.[1, 2]

[1] J. Hu, D. Zhang and F. W. Harris, *The Journal of Organic Chemistry* **2004**, *70*, 707
[2] A. Berg, H. J. Jakobsen and S. R. Johansen, *Acta Chemica Scandinavica* **1969**, *23*, 567-575

2,7-Dibromopyrene-4,5,9,10-tetraone (2a): In a 25 mL Schlenk-flask, pyrene-4,5,9,10-tetraone (0.20 g, 0.76 mmol) was added into H_2SO_4 (3 mL) and then NBS (0.30 g, 1.7 mmol) was added into the mixture. The resulting mixture was stirred at 40 ^oC for 1 h. The reaction was quenched with water (100 mL) and the precipitate was collected by the filtration. The residue was purified by recrystallization from CH_2Cl_2 and subsequently recrystallized from ether to give desired product (0.25 g) as a yellow powder. Yield = 78%.
FD-MS (8 KV): m/z 420.1 (100%), calcd 420.0.
^{1}H-NMR ($C_2D_2Cl_4$, 500 MHz, 140 ºC): δ = 8.61 (s, 2H).
^{13}C-NMR (THF-d_8, 175 MHz): δ = 125.9, 133.4, 134.8, 137.6, 176.3.

2,7-Diiodopyrene-4,5,9,10-tetraone (2b): In a 25 mL Schlenk-flask, pyrene-4,5,9,10-tetraone (0.20 g, 0.76 mmol) was added into H_2SO_4 (3 mL) and then NIS (0.67 g, 3 mmol) was added into the mixture. The resulting mixture was stirred at 40 ^oC for 3 h. The reaction was quenched with water (100 mL) and the precipitate was collected by filtration. The residue was washed successively with water, ethanol, DCM and THF. The product was obtained as an orange powder with a yield of 72%.
FD-MS (8 KV): m/z 513,4 (100%), calcd 513.8.
^{1}H-NMR (THF-d_8, 300 MHz): (δ = 8.49 (s, 1H).
^{13}C-NMR (THF-d_8, 75 MHz): δ =, 125.57, 133.08, 134.61, 137.03, 175.94.

2,7-Dibromo-4,5,9,10-tetraomethoxypyrene (3a): A mixture of 2,7-dibromopyrene-4,5,9,10-tetraone (0.30 g, 0.71 mmol), *n*-Bu_4NBr (0.16 g, 0.50 mmol), $Na_2S_2O_4$ (0.75 g, 4.3 mmol), THF (5 mL), and water (3 mL) was stirred at 25 ºC for 5 min. Dimethyl sulfate (0.94 g, 7.4 mmol) and aqueous sodium hydroxide (2 mL, 18 mmol) were added to the solution and the mixture was stirred at 40 ºC for 4 h. Then, toluene and water were added and the organic phase was washed by brine (3 times), dried with $MgSO_4$, and concentrated in vacuum. The residue was purified by crystallization from CH_2Cl_2 and methanol to give a white product (0.28 g) in 82% yield.
FD-MS (8 KV): m/z 480.4 (100%), calcd 480.2.
^{1}H-NMR (CD_2Cl_2, 250 MHz): δ = 4.18 (s, 12H), 8.55 (s, 4H).
^{13}C-NMR (CD_2Cl_2, 175 MHz): δ = 111.8, 119.3, 120.8, 121.5, 123.5, 162.2.

2,7-Diiodo-4,5,9,10-tetraomethoxypyrene (3b): A mixture of 2,7-diiodoopyrene-4,5,9,10-tetraone (0.35 g, 0.68 mmol), *n*-Bu_4NI (0.18 g, 0.55 mmol), $Na_2S_2O_4$ (0.82 g, 4.7 mmol), THF (5 mL), and H_2O (3 mL) was stirred at 25 ºC for 5 min. Dimethyl sulfate (0.78 ml, 8.2 mmol) and aqueous sodium hydroxide (2 mL, 18 mmol) were added to the solution and the mixture was stirred at 40 ºC for 4 h. Then, toluene and water was added and the organic phase was washed by brine (3 times) and dried with $MgSO_4$ and concentrated in vacuum. The residue was purified by crystallized from CH_2Cl_2 and methanol to give a white product (0.28 g) in 82% yield. **FD-MS** (8 KV): m/z 480.4 (100%), calcd 480.2. **^{1}H-NMR** (CD_2Cl_2, 250 MHz): δ = 4.18 (s, 12H), 8.55 (s, 4H). **^{13}C-NMR** (CD_2Cl_2, 175 MHz): δ = 111.8, 119.3, 120.8, 121.5, 123.5, 162.2.

2,7-Dicyano-4,5,9,10-tetraomethoxypyrene (4): 2,7-Dibromo-4,5,9,10-tetraomethoxypyrene (0.58 g, 1,2 mmol) and CuCN (0.32 g, 3.6 mmol) was added to *N*,*N*-dimethylacetamide (5 mL) under argon and the resulting mixture was refluxed at 180 °C for 10 h. After cooling, aqueous solution of $FeCl_3$ (1 M, 300 mL) and CH_2Cl_2 were added to the mixture. Then the organic phase was washed with brine (100 mL×3) and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by column chromatography using CH_2Cl_2 as eluent to give the final product (0.25 g) in 56% yield.
FD-MS (8 KV): m/z 372.5 (100%), calcd 372.4. **^{1}H-NMR** (CD_2Cl_2, 250 MHz): δ = 4.22 (s, 12H), 8.75 (s, 4H).
^{13}C-NMR (CD_2Cl_2, 175 MHz): δ = 142.5, 123.4, 121.5, 113.4, 32.7, 30.6.

2,7-Dicyanopyrene-4,5,9,10-tetraone (5): To a solution of $AlCl_3$ (0.60 g, 4.5 mmol) in CH_2Cl_2 (10 mL) at 0 ºC, a solution of 2,7-dicyano-4,5,9,10-tetraomethoxypyrene (0.20 g, 1.2 mmol) in CH_2Cl_2 (80 mL) was added dropwise. The resultant mixture was stirred at room temperature for 4 d. The solvent was removed by evaporation and THF and brine was added to the residue. The organic phase was washed with brine (100 mL×3) and dried over Na_2SO_4. The residue was precipitated in DMSO to give the desired dicyano-tetrahydroxypyrene, which was subjected to the following oxidation without further purification.
FD-MS (8 KV): m/z 316.3 (100%), calcd 316.3. **^{1}H-NMR** (THF-d_8, 250 MHz): δ = 8.63 (s, 4H), 8.99 (s, 4H).

To a solution of the 2,7-dicyano-4,5,9,10-tetraohydroxypyrene (0.14 g, 0.43 mmol) in THF (8 mL) under argon, Ag_2O **(**1.0 g, 4.3 mmol) was added and the resultant mixture was stirred at 50 ºC for 30 min. The precipitate was filtered off and the filtrate was purified by column chromatography using ethyl acetate : hexane = 3 : 2 as eluent providing the desired product **5** (28 mg) in 20% yield.
FD-MS (8 KV): m/z 312.1 (100%), calcd 312.2.
^{1}H-NMR (THF-d_8, 250 MHz): δ = 8.77 (s).
^{13}C-NMR (THF-d_8, 75 MHz): δ = 116.3, 117.1, 134.0, 135.8, 137.2, 175.1.

2,7-Bis(dimethylamino)-4,5,9,10-tetramethoxypyrene (6): To a solution of 2,7-diiodo-4,5,9,10-tetramethoxypyrene (0.2 g, 0.35 mmol), palladium acetate (3.2 mg, 13.9 µmol) 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (*XPhos*) (13.3 mg, 27.9 µmol) and sodium *tert*-butoxide (0.15 g, 1.53 mmol) in dry toluene (40 ml) was added a 2 M solution of diemethylamine in THF (0.76 mL, 1.53 mmol). The resulting mixture was stirred at 105 °C for 10 h. After cooling, the raw product was poured on ice water. The phases were separated and the aqueous phase was extracted with DCM (50 mL×3). The combined organic phases were washed with brine (50 mL×2) and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by column chromatography (10:1 hexane/ethyl acetate) to give the desired product **6** (0.62 g) in 43% yield; FD-MS (8 KV): m/z 408.7 (100%), calcd 408.2; ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 7.68 (s, 4H), 4.14 (s, 13H), 3.21 (s, 12H); ^{13}C NMR (CD_2Cl_2, 175 MHz): δ = 149.21, 145.40, 128.36, 114.90, 104.02, 61.33, 54.00, 41.61.

2,7-Bis(di-*p*-tolylamino)-4,5,9,10-tetramethoxypyrene (7): In a 100 ml Schlenk tube 2,7-diiodo-4,5,9,10-tetramethoxypyrene (0,2 g, 0,35 mmol), di-(p-tolyl)amine (399 mg, 2.08 mmol), palladium acetate (3.2 mg, 13.9 µmol) 2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (*XPhos*) (13.3 mg, 27.9 µmol) and sodium *tert*-butoxide (0.15 g, 1.53 mmol) were added and dissolved in dry toluene (50 ml). The resulting mixture was stirred at 105 ºC for 12 h. After cooling, the raw product was poured on ice water. The phases were separated; the aqueous phase was extracted with DCM (50 mL×3). The combined organic phases was washed with brine (50 mL×2) and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by repeated column chromatography (1:1 hexane/ethyl acetate) to give the desired product (0.42 g) in 21% yield; FD-MS (8 KV): m/z 711.9 (100%), calcd 712.3; ^{1}H NMR (CD_2Cl_2, 250 MHz): δ =

7.93 (s, 4H), 7.16 – 7.05 (m, *J* = 6.2 Hz, 17H), 3.97 (s, 12H), 2.35 (s, 13H); ^{13}C-NMR (CD_2Cl_2, 175 MHz): δ = 146.89, 146.43, 145.09, 133.24, 130.47, 129.20, 124.95, 117.54, 114.50, 61.54, 21.13.

2,4,5,7,9,10-Hexamethoxypyrene (8): In a 100 ml Schlenk tube 2,7-diodo-4,5,9,10-tetramethoxypyrene (1 g, 1.74 mmol) was dissolved at elevated temperatures (≈ 65 ºC) in 40 ml dry DMF and 15 ml dry toluene. Copper iodide (0.1 g, 0.52 mmol) was added and the flask resealed. 2 ml dry sodium methylate solution in methanol (30 vol.%) was added. The mixture was stirred 6 h at 100 ºC. After cooling, the raw product was poured on ice water. The phases were separated; the aqueous phase was extracted with DCM (100 mL × 3). The combined organic phases were washed with water (150 mL × 3), brine (150 mL) and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by column chromatography (toluene) to give the desired hexamethoxy-pyrene **8** (0,22 g) in 33% yield; FD-MS (8 KV): m/z 382,5 (100%), calcd 382.1; ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 7.91 (s, 4H), 4.16 (s, 12H), 4.10 (s, 6H); ^{13}C NMR (CD_2Cl_2, 175 MHz): δ = 158.59, 145.42, 129.40, 116.73, 105.24, 61.51.

S2. Fluorescence spectra of donors **6-8** in DCM.

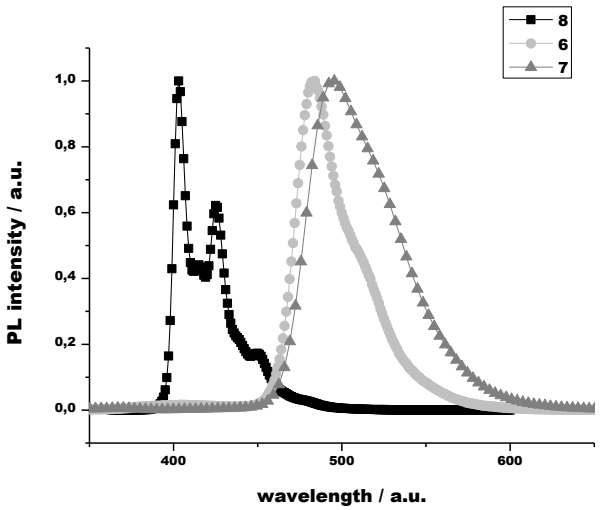


Figure S1. Fluorescence spectra of compounds **6- 8**.

S3. Cyclic voltammetry of target structures

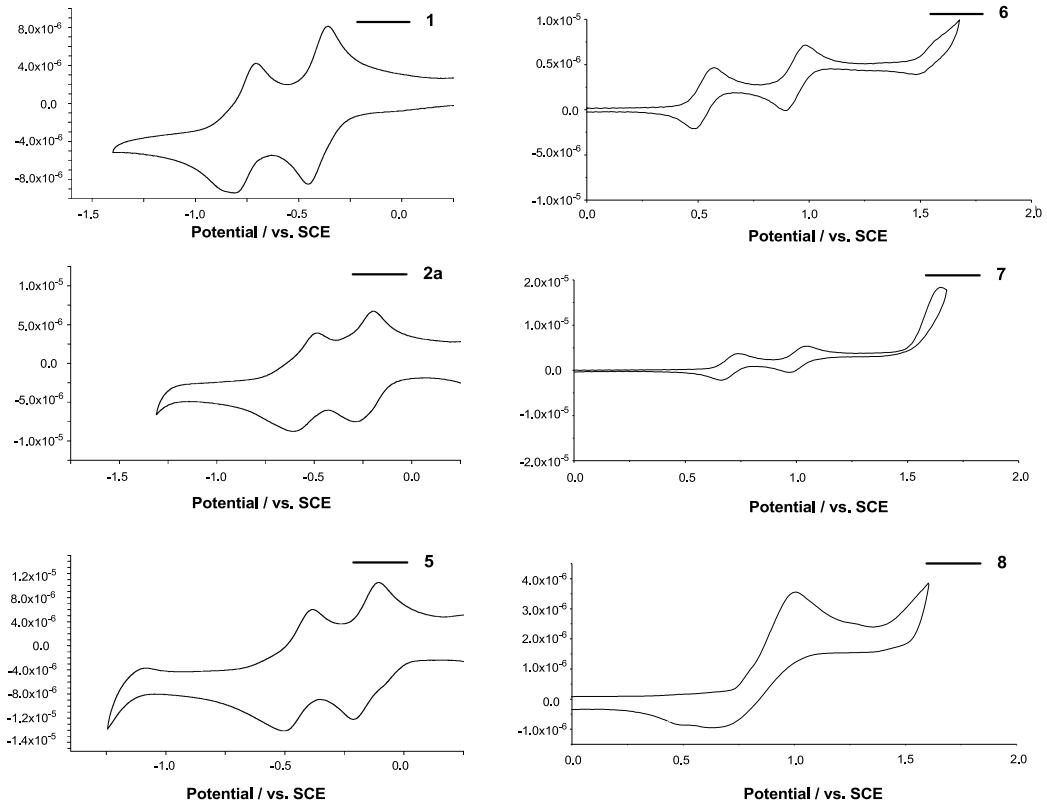
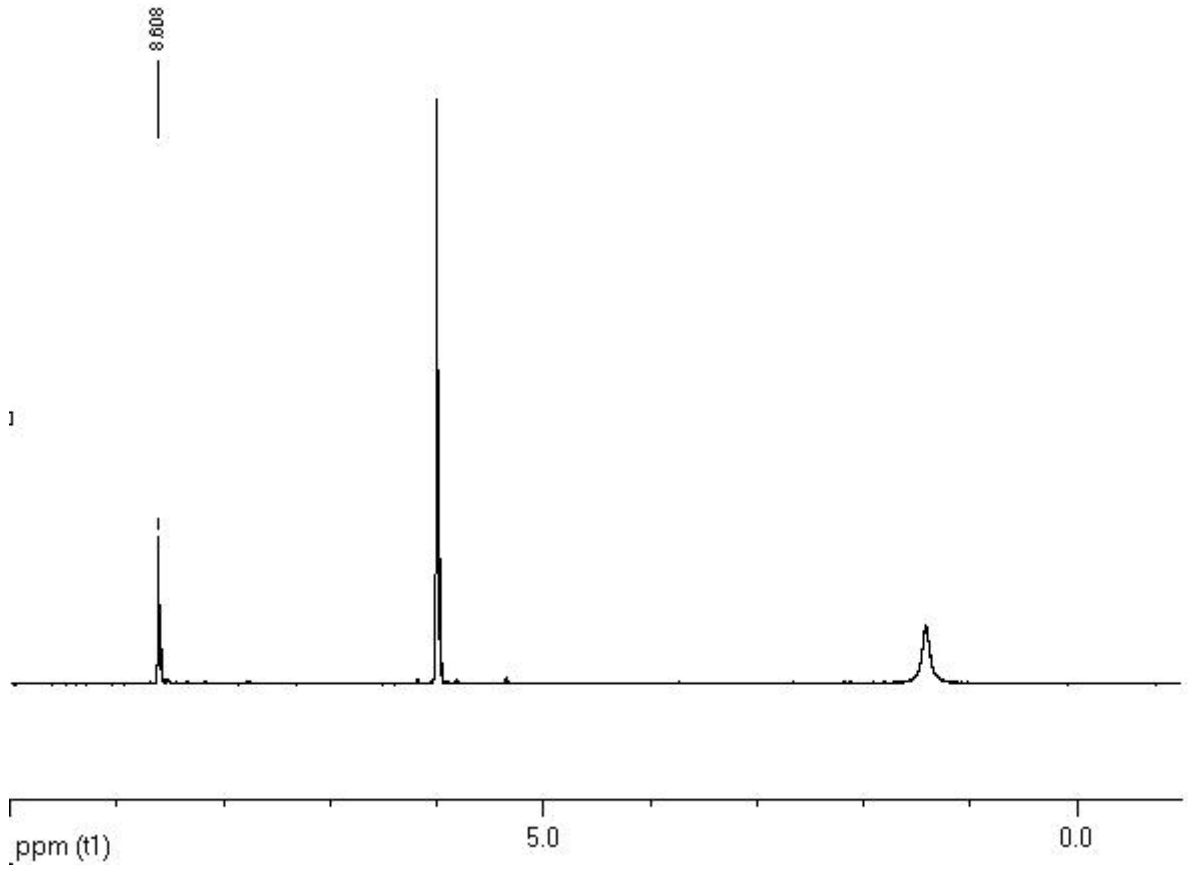


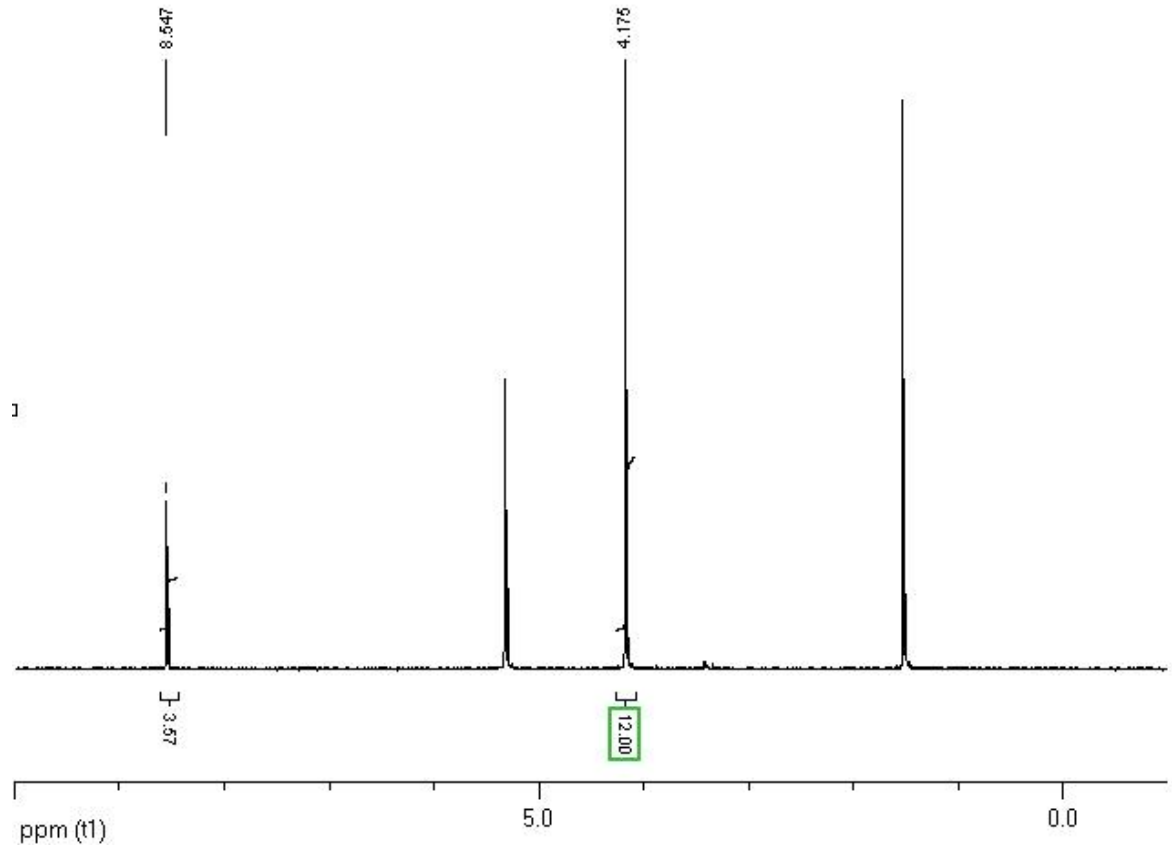
Figure S2: Cyclic voltammograms of **TCNQ**, **1**, **2a**, **5**, **8**, **6**, and **7** in DMF; [*n*-Bu_4NClO_4] = 0.1 M, 100 mV/s, and ferrocene was used as an internal standard. On-set of reduction and oxidations peaks were used to determine LUMO and HOMO energies, respectively (see table 1) .

S4. NMR data of the products 2-8.

2a



3a



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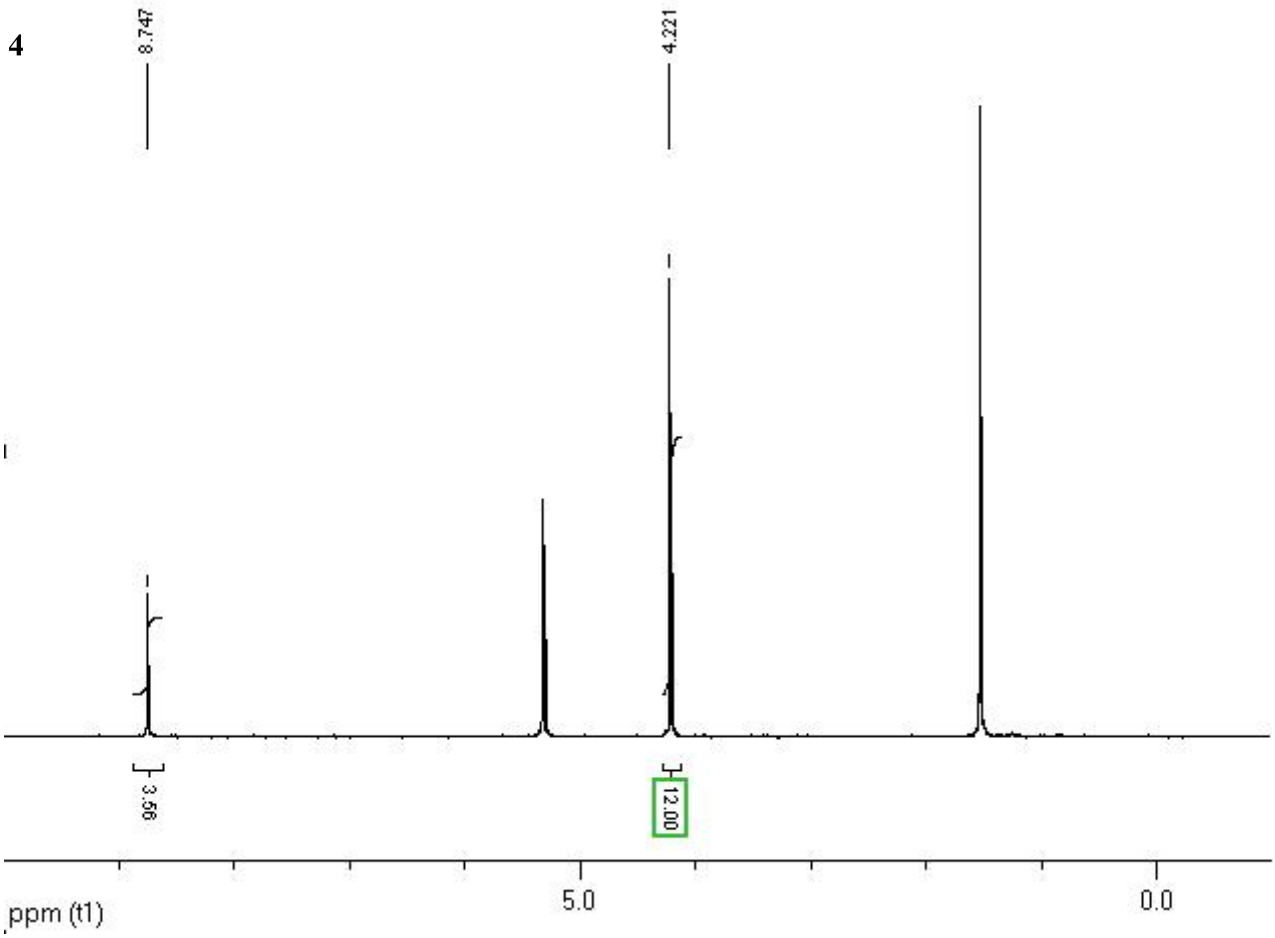

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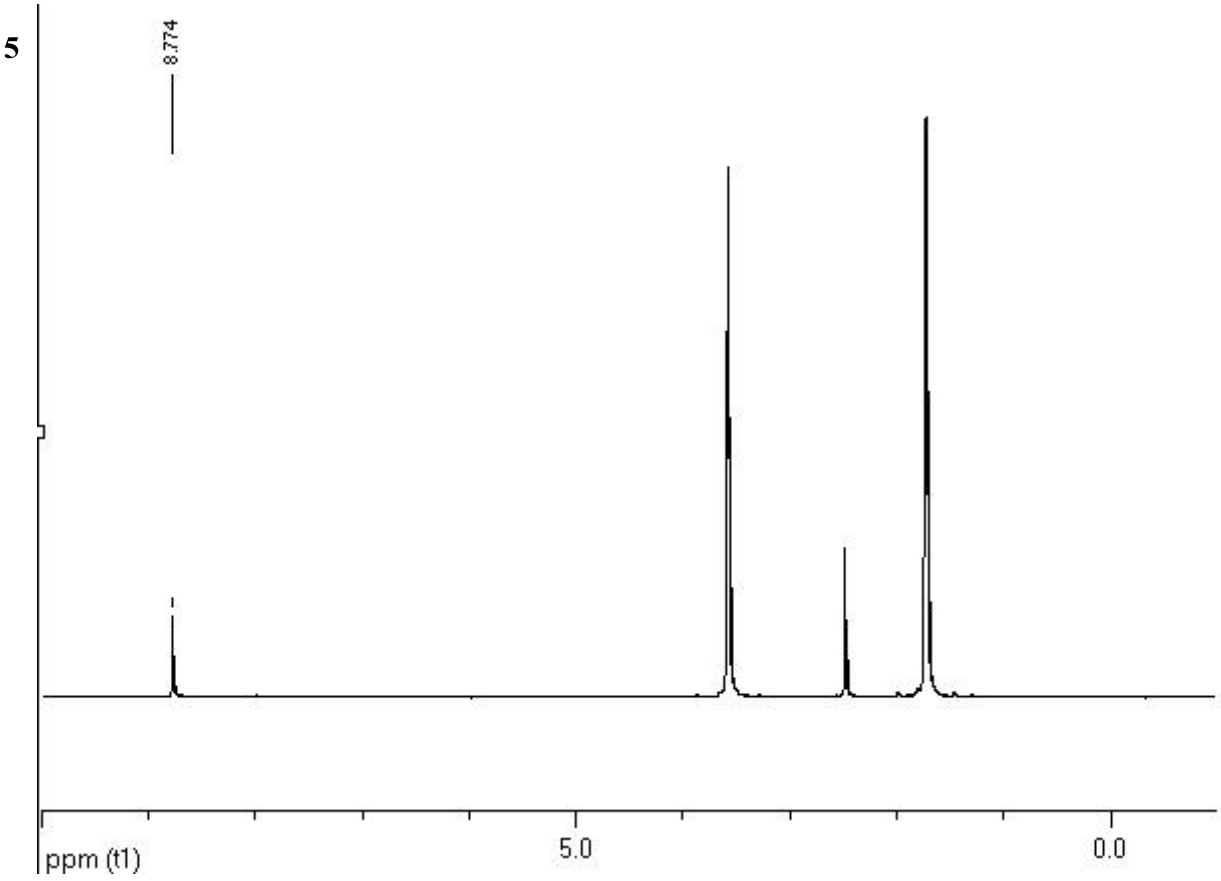
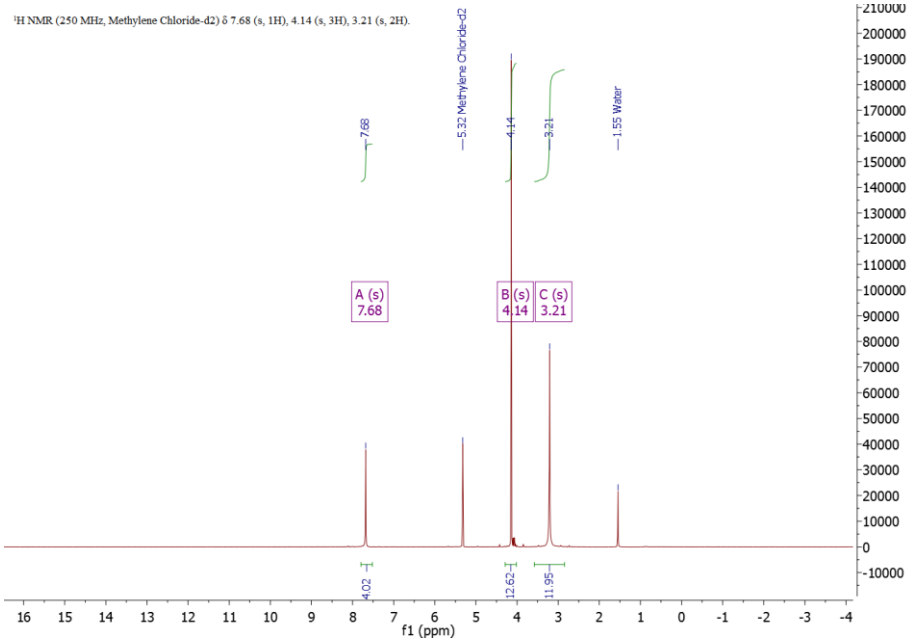
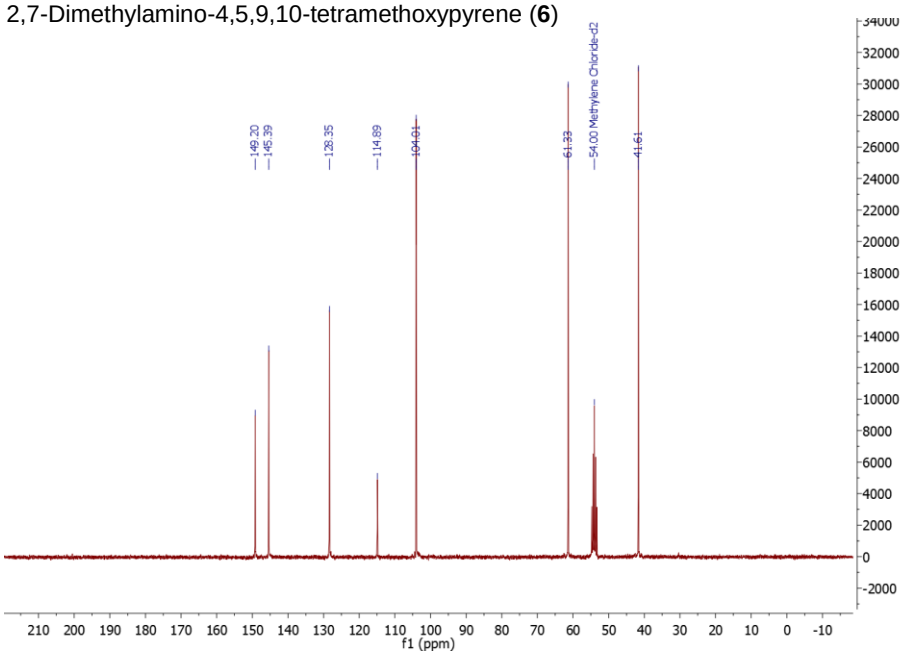


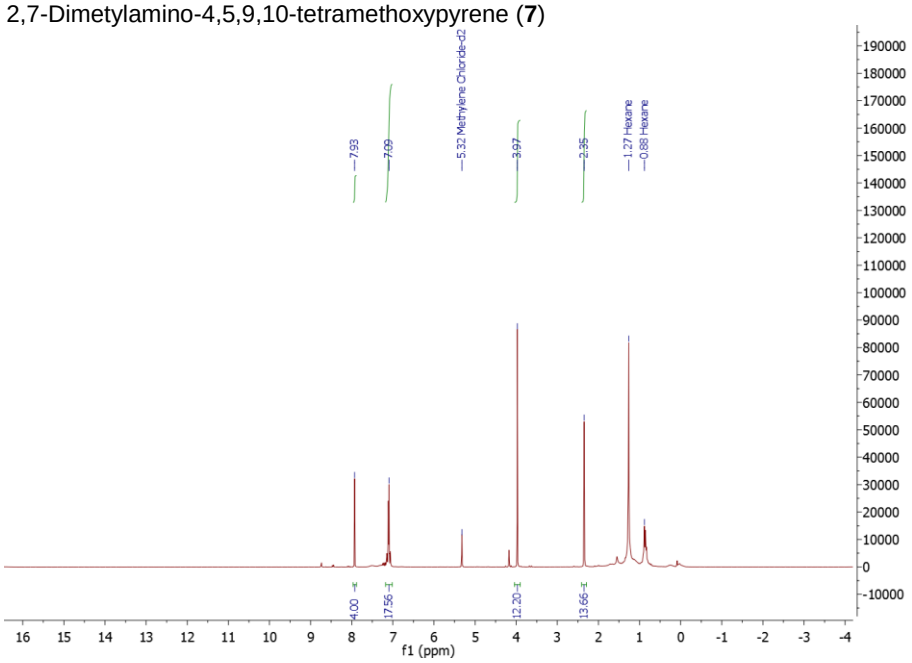
2,7-Dimethylamino-4,5,9,10-tetramethoxypyrene (**6**)



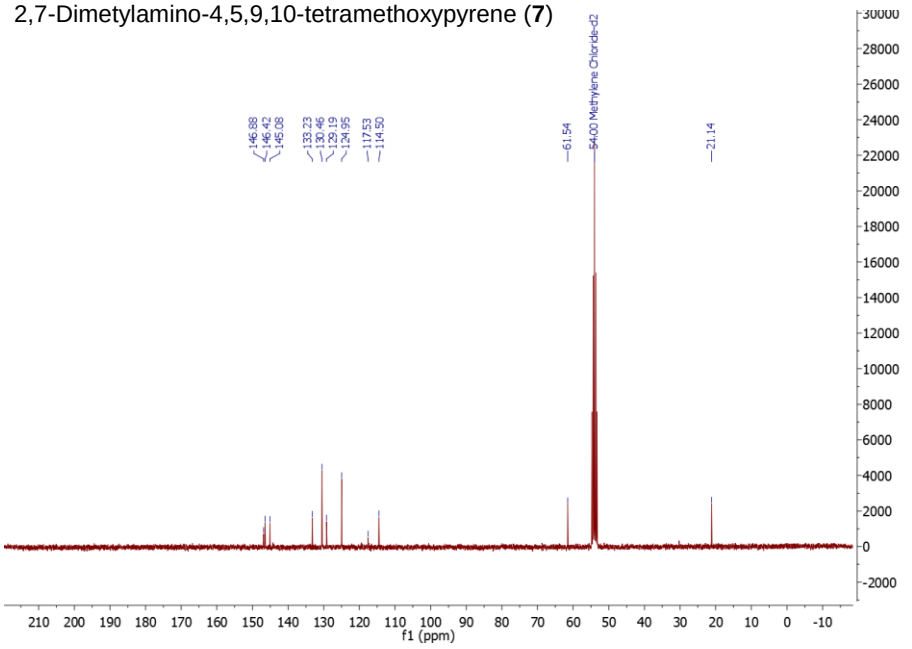
2,7-Dimethylamino-4,5,9,10-tetramethoxypyrene (**6**)



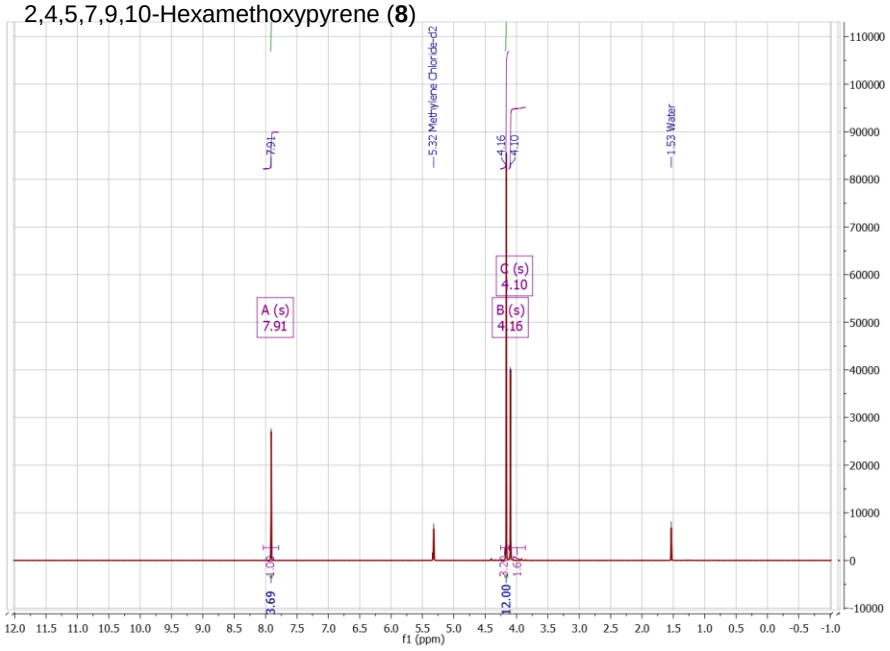
2,7-Dimetylamino-4,5,9,10-tetramethoxypyrene (**7**)



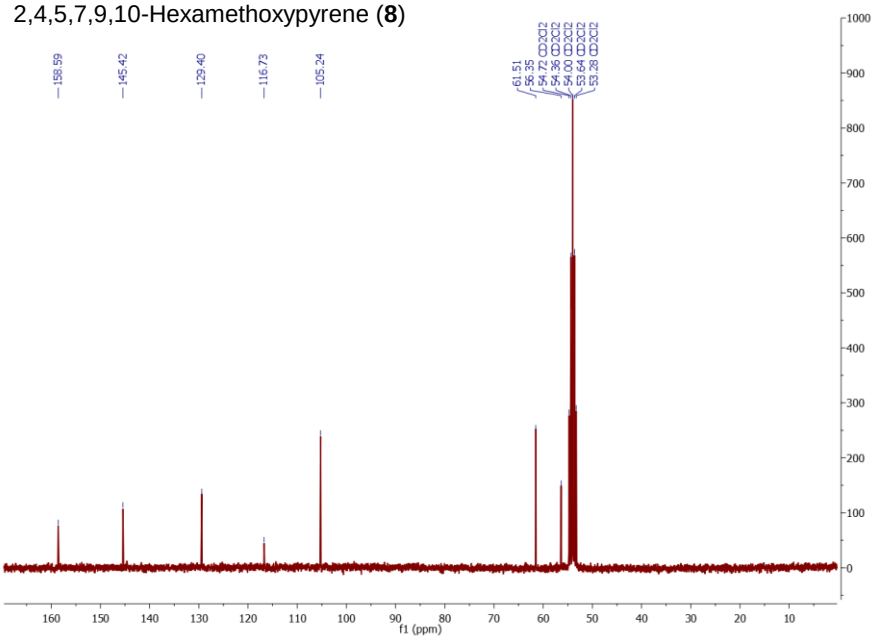
2,7-Dimetylamino-4,5,9,10-tetramethoxypyrene (**7**)



2,4,5,7,9,10-Hexamethoxypyrene (**8**)



2,4,5,7,9,10-Hexamethoxypyrene (**8**)



S5. X-ray crystal structures and details.

Crytallographic Dara for compounds **2** (CCDC 847344), **5** CCDC 857532), **6**-**8** (CCDC 857533-857535), and CT complexes of **8** and **9** with TCNQ (CCDC 857537, CCDC 857536) are available free of charge through the Cambridge Crystallographic Data Center.

2,7-Dibromo-pyrene-4,5,9,10-tetraone (**2a**) crystallized from THF at room temperature in the triclinic space group P-1 with cell parameters a= 6.5579(4) Å, b= 8.2137(5) Å, and c= 10.2782(5) Å. The shortest C-C contact between neighboring pyrenes is 3.41 Å. Layers of pyrenes with short contacts are interrupted by THF solvent molecules.

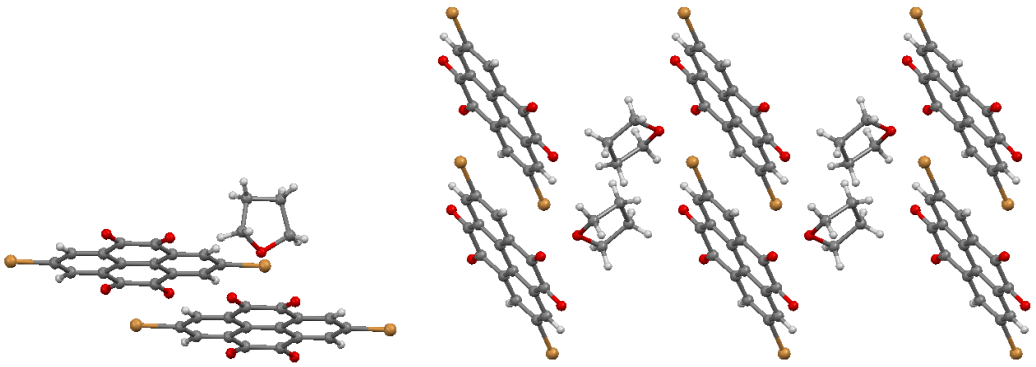


Figure S3: A single crystal structure of **2a**: (a) Two neighboring pyrene derivatives ; (b) 2D packing viewed along the *b* axis where the π-π distance (short contacts) of neighboring pyrene planes is about 0.34 - 0.35 nm.

2,7-Dicyano-pyrene-4,5,9,10-tetraone (**5**) crystallized out of THF in a monoclinic symmetry space group P 21/a with cell parameters a= 9.3552(5) Å, b= 6.6260(4) Å, and c= 11.1029(5) Å. (CCDC..), see Figure 2 in main text.

2,7-Bis(dimethylamino)-4,5,9,10-tetramethoxypyrene (**6**) crystallized in P21/n space group. The cell parameters are a= 16.0033(9) Å, b= 6.9362(4) Å, c= 20.1144(9) Å.

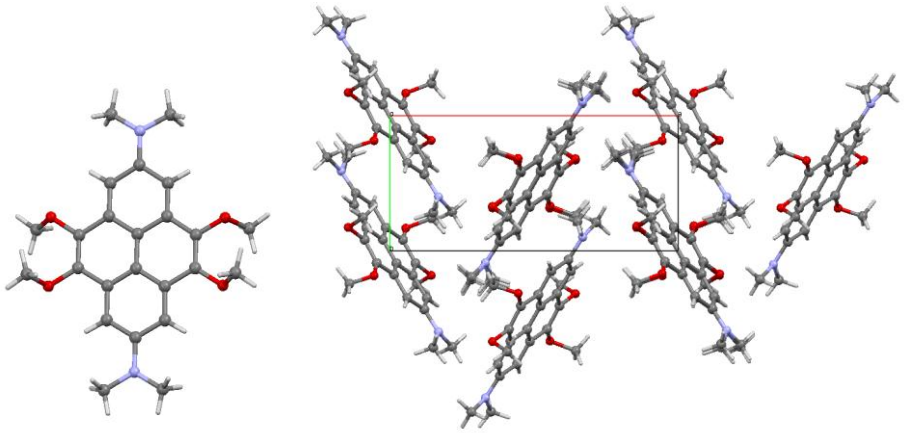


Fig S4. Structure of **6** and its packing viewed along the c-axis.

2,7-Bis(di-*p*-tolylamino)-4,5,9,10-tetramethoxypyrene (**7**) crystallized in the space group P 1 21/n 1 with cell parameters a= 13.9727(4) Å, b= 9.7974(3) Å, c =14.0930(4) Å.

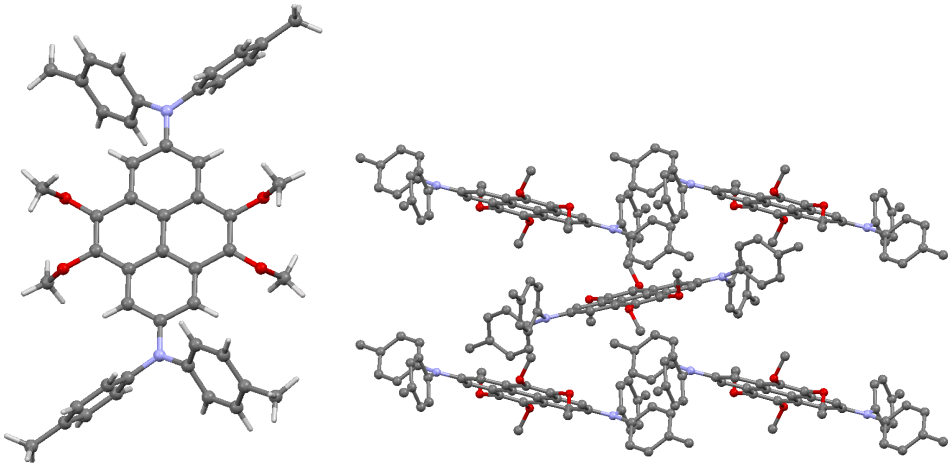


Figure S5: The bis(ditolylamino) pyrene **7** and its packing, showing that the tolyl entitites hinder a close π-stacking.

2,4,5,7,9,10-Hexamethoxypyrene (**8**) crystallized in monoclinic symmetry space group n 'P 1 21/c 1 with unit cell parameters a= 8.1780(4) Å, b= 7.8530(2) Å, and c= 14.2480(6) Å. The methoxy groups at 2,7 positions are nearly in the plane of pyrene with very small torsion (3-5 degrees) while the methoxy groups at positions 4,5,9, and 10 are heavily twisted out of the plane of pyrene (~ 80 degrees). The C-O bond length is in the typical range for methoxy-aryls of 1.371-1.380 Å.

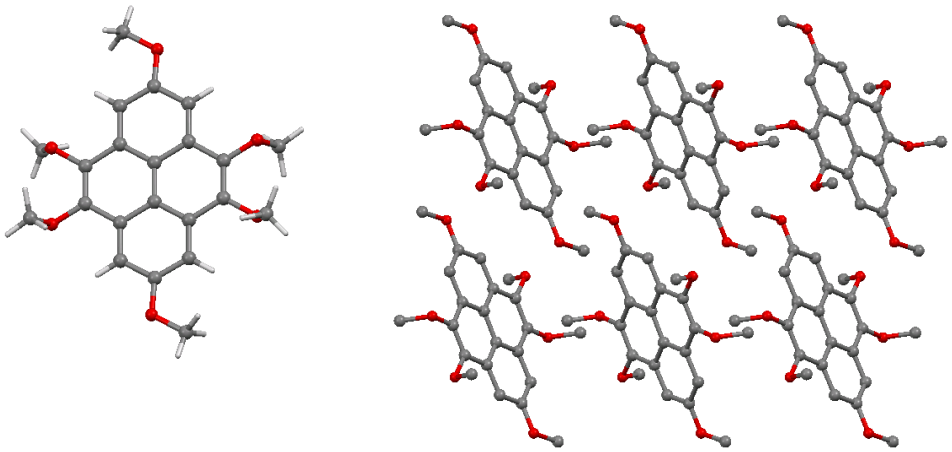


Figure. S6: X-ray crystal structure **8**, and packing (without H atoms) viewed along b axes.

4,5,9,10-Tetramethoxypyrene (**9**) crystallized in monoclinic symmetry space group C 1 2/c 1 with unit cell parameters a= 15.5468(10) Å, b= 10.7779(10) Å, and c= 10.2340(8) Å.

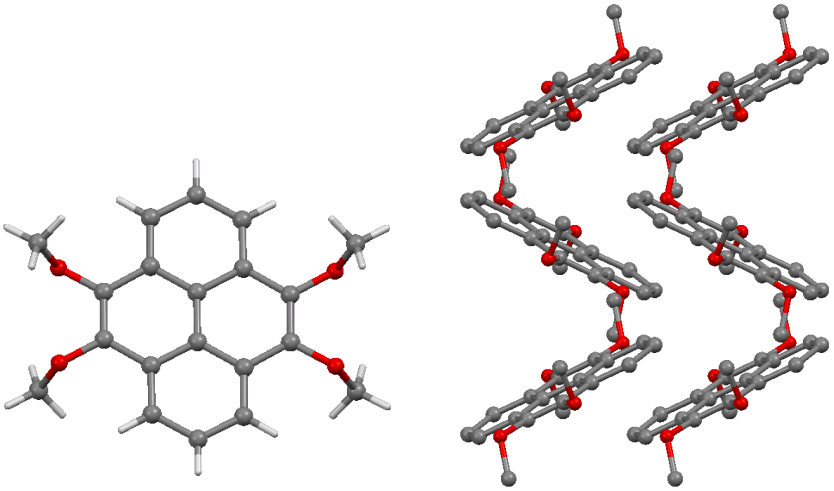


Figure S7: Crystal structure of **9** and its packing.

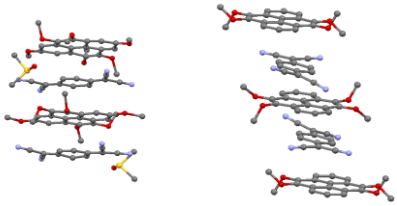


Figure S8. Structure of CT cocrystals consisting of the donors **8** (a) or **9** (b) with the acceptor TCNQ**.**

A co-crystal of hexamethoxypyrene **(8)** and TCNQ was grown out of DMSO solution. Crystallographic data indicate a mixed stack arrangement with one DMSO solvent molecule intercalated in each TCNQ layer. The mixed complex with 1:1 ratio crystallized in monoclinic form with P 1 n 1 space group and unit cell parameters of _cell_length_a= 13.1830(7) Å,_cell_length_b= 12.9270(9) Å,_and cell_length_c= 19.6250(9) Å. As in the isolated HMP (**8**) the methoxy groups at positions 2 and 7 are nearly in plane with the pyrene core (± 6 degrees), while the 4 methoxy groups at positions 4,5,9,10 are heavily twisted out of the pyrene plane with 65-85 degrees. The shortest π-π (C-C) distance is 3.133 Å but many short contacts are found in average with 3.2-3.5 Å. From the packing it turns out that neighboring alternating columns are arranged in such a way that in plane always a HMP donor molecule comes next to a TCNQ acceptor molecule.

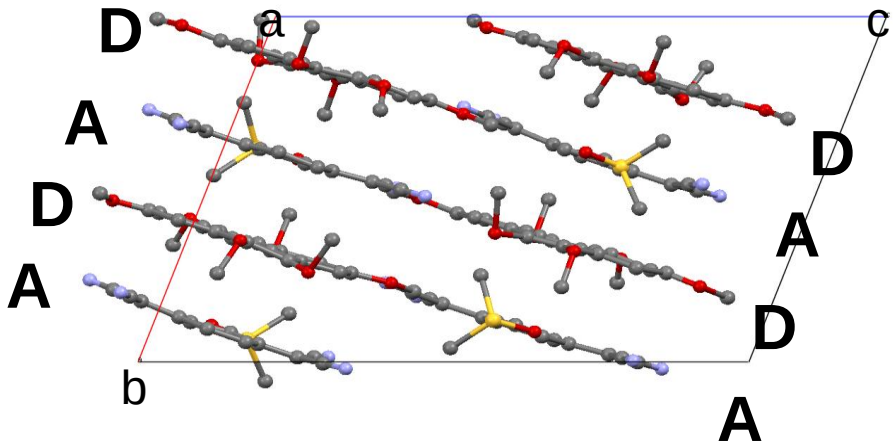


Figure S9: Packing of **8**/TCNQ showing the in plane alternating arrangement between D/A columns.

A cocrystal of **TMP-9** and **TCNQ** was grown by vapour diffusion of hexane into DCM and in contrast to HMP/TCNQ obtained without intercalated solvent molecules. The 1:1 complex crystallized in the same monoclinic space group P1n1 with cell parameters of a= 14.2441(5) Å, b= 14.6744(7) Å, and c= 13.2556(4) Å. Here the π-π distances are slightly larger with 3.32 Å as shortest contact, which can be found both for the distance of TCNQ to a TMP on top and to a TMP below. Thus no dimerization is obvious.
The packing however demonstrates a detailed difference to HMP/TCNQ since the neighbouring alternating stacks show TMP donor next to donor and TCNQ acceptor next to acceptor, such that layers of donors and layers of acceptors are formed. Another difference is found in the fact that one dicyanomethylene group is slightly twisted out of the pyrene plane (~ 10 degrees).

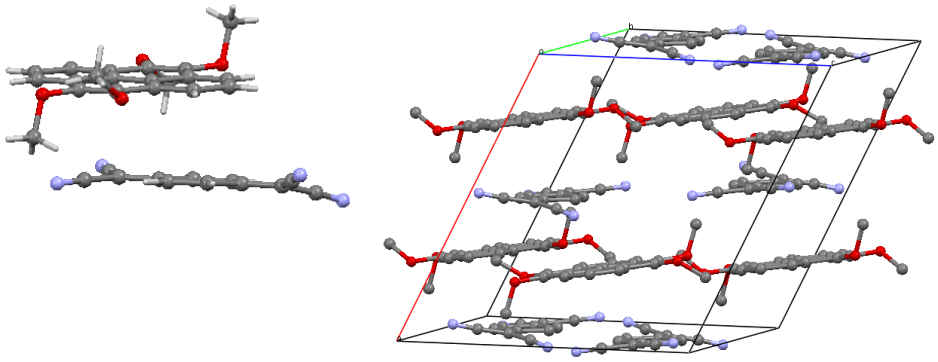


Figure S10: The alternating stack a) of TMP-**9** and TCNQ with packing b) demonstrating layers of TMP and of TCNQ

S5. DFT calculations of HOMOs and LUMOs

For the DFT calculations the hybrid functional B3LYP was used and the basis set 6-31G*.

Table S1. The calculated HOMO and LUMO values in eV[a].

Compd.	HOMO	LUMO
1	-7.05	-3.54
2(a)	-7.12	-3.84
5	-7.76	-4.35
6	-4.50	-1.07
7	-4.52	-1.32
8	-5.05	-1.33
9	-5.37	-1.71
TCNQ		-4.82

[a] The density functional theory (DFT) calculations have been performed using the Gaussian 03 program (Frisch, M. J. et al.) with the B3LYP hybrid functional (Becke 3-Parameter, Lee, Yang and Parr), and a basis set 6-31G* for the ground state geometry optimization.

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