Supporting Information for:

Synthesis, Crystal structure and Transistor Performance of Tetracene Derivatives

Hyunsik Moon,[†] Roswitha Zeis,[†] Evert-Jan Borkent,[†] Celine Besnard,[‡] Andrew J. Lovinger,[†] Theo Siegrist,[†] Christian Kloc,[†] Zhenan Bao[,§]*

[†]Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974, [‡]Department of Materials Chemistry, Lund University, Sweden and [§]Department of Chemical Engineering, Stanford University, Stanford, California 94305
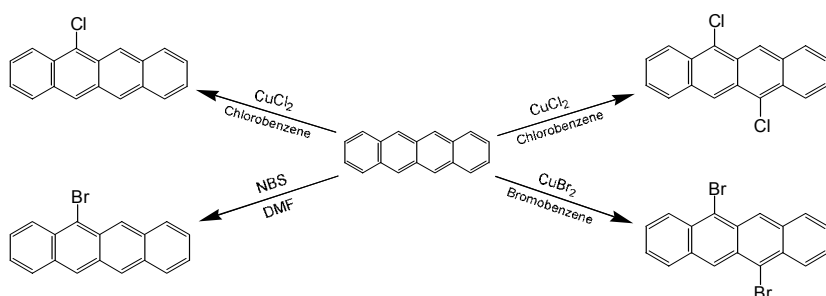
E-mail; zbao@chemeng.stanford.edu

Experimental

All chemicals were purchased from Aldrich Chemical Co. and used without further purification. The reaction apparatus was flame-dried and the reactions were carried out under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Bruker 360 MHz spectrometer and chemical shifts were measured relative to trimethylsilane in $CDCl_3$ as solvent unless otherwise noted. Cyclic voltammetry (CV) was performed with a Princeton Applied Research Potentiostat model 263A interfaced to a PC computer. The solvent was dry CH_3CN, and the supporting electrolyte was tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.10 M). A Pt wire was used as a counter electrode and $Ag/AgNO_3$ (0.10 M) as a reference electrode. The reported potentials are vs the ferrocene/ferrocenium (Fc/Fc^+, 4.8 V) couple, obtained by adding a crystal of ferrocene to the solution. Element analysis was performed by Roberson Microlit Laboratories, Madison, NJ. Melting points were uncorrected. Flash column chromatography was carried out using silica gel (Aldrich, 200-400 mesh). Single crystals of tetracene derivatives were grown either from solution or vapor phase.

5-Chloroteracene Anhydrous copper chloride ($CuCl_2$, 1.77 g, 13.2 mmol) and tetracene (3 g, 13.2 mmol) were placed in a flask containing chlorobenzene (100 mL) under N_2. The mixture was stirred at 100 ºC for 3 h. After toluene (50 mL) was added, the resulting mixture was filtered to remove unreacted copper chloride and the solvents were removed by rotary evaporation. The solid residue was chromatographed with CH_2Cl_2:hexane (v/v: 1:10) and subsequently recrystallized from $CHCl_3$:methanol (v/v: 3:1) to afford platelet-shaped orange crystals (1.20 g, 34.8%). mp 182 ºC. ^{1}H NMR δ 7.43 (m, 3H), 7.52 (t, 1H), 7.98 (t, 2H), 8.07 (d, 1H), 8.47 (d, 1H), 8.62 (s, 1H), 8.65 (s, 1H), 9.12 (s, 1H). Elemental anal. Found: C, 82.16; H, 4.21; Cl, 13.38. Calcd for $C_{18}H_{11}Cl$: C, 82.29; H, 4.22; Cl, 13.49.

5-Bromotetracene In absence of light, a solution of NBS (0.81 g, 4.38mmol) in DMF (25 mL) was added dropwise to a solution of tetracene (1 g, 4.38 mmol) in DMF (200 mL) at 80 ºC and the reaction mixture was stirred at 100 ºC for 6 h. The mixture was poured into ice water (500 mL) and filtered to obtain the solids. Column chromatography with CH_2Cl_2:hexane (v/v: 1:10) and subsequent recrystallization from toluene afforded platelet-shaped orange crystals (0.70 g, 52.0%). mp 157 ºC. ^{1}H NMR δ 7.44 (m, 3H), 7.52 (t, 1H), 7.98 (t, 2H), 8.08 (d, 1H), 8.48 (d, 1H), 8.66 (s, 1H), 8.67 (s, 1H), 9.15 (s, 1H). Elemental anal. Found: C, 70.58; H, 3.40; Br, 26.33. Calcd for $C_{18}H_{11}Br$: C, 70.38; H, 3.61; Br, 26.01.

Scheme. Reactions for the synthesis of tetracene derivatives.

5,11-Dichlorotetracene This compound was synthesized with anhydrous copper chloride ($CuCl_2$), tetracene and chlorobenzene according to literature procedures.[1,2] mp 225 ºC. ^{1}H NMR δ 7.47 (t, 2H), 7.56 (t, 2H), 8.07 (d, 2H), 8.46 (d, 2H), 9.12 (s, 2H). Elemental anal. Found: C, 73.01; H, 3.32; Cl, 23.48. Calcd for $C_{18}H_{10}Cl_2$: C, 72.75; H, 3.39; Cl, 23.86.

5,11-Dibromotetracene This compound was prepared with anhydrous copper bromide ($CuBr_2$), tetracene and bromobenzene according to literature procedures.[1,3] ^{1}H NMR δ 7.48 (t, 2H), 7.56 (t, 2H), 8.07 (d, 2H), 8.47 (d, 2H), 9.23 (s, 2H). Elemental anal. Found: C, 55.83; H, 2.36; Br, 41.04. Calcd for $C_{18}H_{11}Br_2$: C, 56.00; H, 2.61; Br, 41.39.

Single Crystal X-ray Data Collection

The data collections were carried out using MoKα radiation on a Sapphire-2 CCD detector (Xcalibur 2 diffractometer, Oxford Diffraction) at room temperature. No absorption correction was applied. The integration was carried out in the CrysAlis software (Oxford Diffraction). The structure was solved using SIR-92[4] and the refinements were carried out in CRYSTALS.[5] Due to the low scattering power of the crystals, the number of significant reflections available for the refinement is low. Anisotropic displacement parameters were anyway chosen for all non hydrogen atoms due to the high anisotropy. The positions of the hydrogen atoms were calculated and their parameters were constrained or fixed during the refinement.

5-Chlorotetracene (CCDC 245498) $P2_1/c$, a = 10.7752(15) Å, b = 14.371(2) Å, c = 8.067(12) Å, β = 93.868(11)°. Reflections (total/unique with I>2σ): 26776/1092. Refinement by full least square on F using 172 parameters and 1092 unique reflections with final indices for reflections with I>2σ: R = 3.90, wR = 4.18, GOF = 1.1525, and for all reflections: R = 21.12, wR = 14.40. Hydrogen atoms: riding model.

5-Bromotetracene (CCDC 245497) $P2_1/c$, a = 10.8526 (15) Å, b = 14.396(2) Å, c = 8.1770(12) Å, β = 93.091(11)°. Reflections (total/unique with I>2σ): 27422/1575. Refinement by full least square on F using 172 parameters and 1575 unique reflections with final indices for reflections with I>2σ: R = 4.37, wR = 4.90, GOF = 1.0519, and for all reflections: R = 10.09, wR = 9.92. Hydrogen atoms: riding model.

5,11-Dichlorotetracene (CCDC 245496) $P-1$, a = 3.8607(12) Å, b = 8.664(3) Å, c = 19.686(5) Å, α = 93.37(3)°, β = 92.02(2)°, γ = 99.47(3)°. Reflections (total/unique with I>2σ): 5777/492. Refinement by full least square on F using 181 parameters and 939 unique reflections with final indices for all reflections R = 9.05, wR = 9.85, GOF=0.9959, and for reflections with I>2σ: R = 3.90, R = 4.03, wR = 7.15. Hydrogen atoms: fixed parameters.

References:

1. Tanimoto, I.; Kushioka, K.; Kitagawa, T.; Maruyama, K. *Bull. Chem. Soc. Japan* **1979**, *52*, 3586.
2. Ware, J. C.; Borchert, E. E. *J. Org. Chem.* **1961**, *26*, 2267.

3. Mitchell, R. H.; Lai, Y.-H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.
4. Altomare, A.; Burla, M. C.; Camalli, G.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.
5. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkins, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.

Table S1. Semi-empirical calculations with a PM3 hamiltonian in Spartan '04

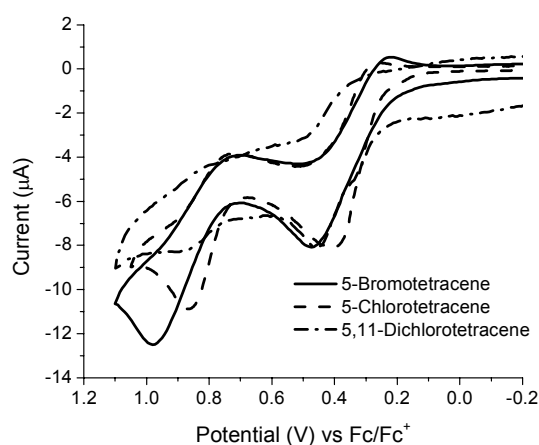|	HOMO	LUMO
Tetracene	-7.75 eV	-1.24 eV
5-Chlorotetracene	-7.82 eV	-1.41 eV
5,11-Dichlorotetracene	-7.89 eV	-1.56 eV
5-Bromotetracene	-7.88 eV	-1.45 eV
5,11-Dibromotetracene	-8.01 eV	-1.65 eV

Figure S1. Cyclic voltammogram of tetracene derivatives.

Table S2. Thin film transistor performance

	Substrate Temp	SiO$_2$		OTS[a] treated SiO$_2$		PTS[b] treated SiO$_2$	
		Mobility[c] (cm^2/Vs)	On/off	Mobility (cm^2/Vs)	On/off	Mobility (cm^2/Vs)	On/off
5-Chlorotetracene	0	No gate effect Cloudy film					
	25						
5,11-Dichlorotetracene	0	3×10^{-5}	40	1×10^{-3}	500	1×10^{-4}	30
	50	No gate effect		6×10^{-5}	~10	No gate effect	

[a] Octadecyltrimethoxysilane.
[b] Phenyltrimethoxysilane.
[c] Calculated in saturation regions.
[d] The crystallinity of all films was investigated with X-ray diffraction. Only dichlorotetracene on OTS treated SiO$_2$ showed preferred orientation peaks at 9.6 Å and 4.8 Å.