SUPPORTING INFORMATION

Self-assembled multilayers of CdSe nanocrystals and carboxylate-handled phenylene-based molecules: optical, electrochemical and photoconductive properties †

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Preparation of some linkers

The compounds dimethyl 2-nitrobiphenyl-4,4'-dicarboxylate[1], and 4,4'-dibromoazobenzene[2] were prepared according to literature prescriptions.

All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. NMR spectra were recorded on a Bruker FT 300 (300 MHz for ^{1}H); chemical shifts value are given in parts per million.

2-Nitrobiphenyl-4,4'-dicarboxylic acid (NPh2CA2).

This compound was obtained from the corresponding dimethyl ester by hydrolysis with NaOH in ethanol/water, followed by acidification with hydrochloric acid. Anal. Calcd for $C_{14}H_9NO_6$: C, 58.54; H, 3.16; N, 4.88%. Found: C, 58.45; H, 3.02; N, 4.73%. ^{1}H NMR (DMSO-d6) : δ 7.52 (d, 2H), 7.72 (d, 1H), 8.03 (d, 2H), 8.27 (br d, 1H), 8.47 (broad s, 1H), 13.39 (br s, 2H). MS, *m/e* 287 ($M^{\bullet+}$).

Dimethyl 2',3',5',6'-tetrafluoro-*p*-terphenyl-4,4''-dicarboxylate.

4-Methoxycarbonylphenylboronic acid pinacol ester (170 mg, 0.64 mmol) and $PdCl_2(PPh_3)_2$ (4.5 mg) were added to a solution of 1,4-dibromo-tetrafluorobenzene (100 mg, 0.32 mmol) in toluene (4 mL) in a Schlenk tube. After addition of 2M aqueous solution of K_2CO_3 (2.5 mL) and a catalytic amount of TEBA, the reaction mixture was refluxed overnight under stirring. The mixture was poured into water and extracted with $CHCl_3$ (3 X 100 ml). The combined organic layer was dried ($MgSO_4$), and the solvent was evaporated at reduced pressure. Crystallization of the residue with toluene afforded the title compound as a white solid (87 mg, 68% yield). ^1H NMR ($CDCl_3$): δ 3.97 (s, 6H), 7.60 (d, 4H, J=8.9 Hz), 8.19 (d, 4H, J=8.9 Hz). Anal. Calc for $C_{22}H_{14}F_4O_4$: C, 63.14; H, 3.37; F, 18.17%. Found: C, 63.41; H, 3.52; F,17.91%. MS, *m/e* 418 ($M^{\bullet+}$).

2,7-Bis(4-methoxycarbonyl-phenyl)-fluoren-9-one.

4-methoxycarbonylphenylboronic acid pinacol ester (155 mg, 0.59 mmol) and $Pd(PPh_3)_4$ (6.6 mg) were added to a solution of 2,7-dibromo-9-fluorenone (100 mg, 0.29 mmol) in toluene (4 mL) in a Schlenk tube. After addition of 2M aqueous solution of K_2CO_3 (2.5 mL) and a catalytic amount of TEBA, the reaction mixture was refluxed overnight under stirring. After addition of CH_2Cl_2 (10 mL), the solid precipitated was filtered, and washed several times with water and with $CHCl_3$ to give the title compound as an orange solid (91 mg, 70% yield). ^1H NMR (DMF-d6, 110 °C): δ 3.97 (s, 6H), 8.08-7.85 (br m, 10H), 8.14 (d, 4H, J=8.45 Hz). Anal. Calc for $C_{29}H_{20}O_5$: C, 77.68; H, 4.49%. Found: C, 77.41; H, 5.19. MS, *m/e* 448 ($M^{\bullet+}$).

2,7-Bis(4-methoxycarbonyl-phenyl)-9,9-dioctyfluorene.

4-Methoxycarbonylphenylboronic acid pinacol ester (100 mg, 0.38 mmol) and $Pd(PPh_3)_4$ (6.6 mg) were added to a solution of 2,7-dibromo-9,9-dioctyfluorene (104 mg, 0.29 mmol) in toluene (4 mL) in a Schlenk tube. After addition of 2M aqueous solution of K_2CO_3 (2.5 mL) and a catalytic amount of TEBA, the reaction mixture was refluxed overnight under stirring. The mixture was poured into water and extracted with CH_2Cl_2 (3 X 100 ml). The combined organic layer was dried ($MgSO_4$), and the solvent was evaporated at reduced pressure. Flash chromatography (silica gel, hexane/CH_2Cl_2 8:2) of the residue afforded the title compound (134 mg, 70% yield). ^1H NMR ($CDCl_3$) δ 0.71(m, 4H), 0.78 (t, 6H, *J* = 6.6 Hz), 1.18-1.07 (m, 20H), 2.09-2.03 (m, 4H), 3.96 (s, 6H), 7.63 (dd,, 2H, J=7.89, J=1.6 Hz), 7.75 (d, 4H, J= 7.59 Hz), 7.81 (d, 2H, J=7.89 Hz), 8.14 (d, 4H, J= 7.59 Hz). Anal. Calc for $C_{45}H_{54}O_{54}$: C, 82.06; H, 8.21%. Found: C, 82.41; H,8.52%. MS, *m/e* 658 ($M^{\bullet+}$).

2,7-Bis(4-carboxyphenyl)-9,9-dioctyfluorene (Ph2FlCA2).

This compound was obtained from the corresponding dimethyl ester by hydrolysis with KOH in dioxane/water at 95 °C, followed by acidification with hydrochloric acid. ^{1}H NMR (DMF-d6) δ 0.71(m, 4H), 0.74 (t, 6H, *J* = 6.6 Hz), 1.07 (m, 20H), 2.06 (m, 4H), 7.85 (d,, 2H, J=7.97 Hz), 8.07-7.97 (m, 8H), 8.15 (d, 4H, J= 8.35 Hz).

4,4'-Bis(4-carboxyphenyl)-azobenzene (Ph4N2CA2).

4-Carboxyphenylboronic acid pinacol ester (550 mg, 2.22 mmol) and $Pd(PPh_3)_4$ (35 mg) were added to a solution of 4,4'-dibromoazobenzene (250 mg, 0.74 mmol) in DME (15 mL) in a Schlenk tube. After addition of 1M aqueous solution of Na_2CO_3 (2.5 mL) and a catalytic amount of TEBA, the reaction mixture was heated at 90 °C overnight under stirring. The solid precipitated was filtered, and washed with DME and water. The obtained product was suspended in water (10 mL) and acetic acid (1 mL) and the resulting mixture was kept under stirring for 2 days. The solid was filterd and washed with water to give the title compound (246 mg, 79% yield). Anal. Calcd for $C_{26}H_{16}N_2O_4$: C, 74.28; H, 3.84; N, 6.66%. Found: C, 74.19; H, 3.91; N, 6.52%. HREIMS calcd, 420.1110; found 420.1103.

NaphCA4

Reaction of 1,4,5,8-naphthalenetetracarboxylic acid with triethylamine has previously given the half-deprotonated dianion salt (see Scheme S1).[3] We have similarly prepared the dianion tetrabutylammonium salt (NaphCA4) from the anhydride (NTCA) using tetrabutylammonium hydroxide (TBAOH). In details, suspension of 10 mg of NTCA in 10 ml EtOH, upon addition of 2 TBAOH equivalents after 1-2 hour stirring and warming becomes colorless clear. The colorless salt obtained from evaporation of the solvent has been identified as follows.

The FTIR pattern of the solid (Fig. S2) shows the strong carbonyl band at 1780 cm^{-1} of the anhydride (characteristic CO–O–CO stretching vibration) transformed into a similarly strong band at 1714 cm^{-1}. Strong bands at 1604, 1486, 1348 and 1270 cm^{-1} are also present. Since the tetracid displays its ν(C=O) and ν (C-O) stretching bands at 1693 and 1284 cm^{-1} respectively,[4] we assign the bands at 1714 and 1270 cm^{-1} to these modes of vibration. The bands at 1604 and 1486 cm^{-1} are due to vibration of the aromatic ring[5] and to the CH2 scissoring of the TBA cation (along with the strong CH2 stretching bands at 2930 and 2850 cm^{-1}). Finally a broad band at ca 3300 cm^{-1} is assigned to the O$\cdots$H$\cdots$O stretching of the H-bridged carboxylate moieties. All these data confirm that the compound is the expected H-bridged dianion.

Ph3F4CA2, Ph2FlOCA2, Ph2FlCA2 and Ph4N2CA2

These long-chain linkers have been used in the acid form dissolved in DMF. Whereas Ph2FlCA2 and Ph4N2CA2 were directly produced as the acid, Ph3F4CA2 and Ph2FlOCA2, prepared as the methyl ester form, were hydrolyzed to the dianion tetrabutylammonium salts with TBAOH and subsequently protonated with $HClO_4$ to yield the acid. Typically, a suspension of 4 mg of Ph3F4CA2 in 10 ml THF, upon addition of 2 TBAOH equivalents becomes clear and subsequent addition of $HClO_4$ in slight excess causes the precipitation of the acid form, which is filtered, washed with EtOH and dried.

References

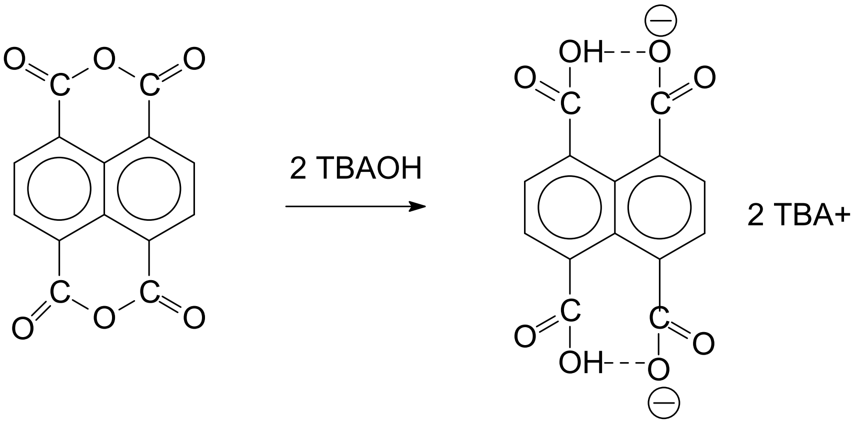
(1) V. K. Ol'klovik, A. A. Pap, V. A. Vasilevskii, N. A. Galinovskii, S. N. Tereshko, *Russ.J.Org.Chem.*, 2008, 1172.

(2) T. Yamamoto, I. Nishiyama, H. Yokoyama, *Chem.Lett.*, 2007, 1108.

(3) J. R. Li, Y. Tao, Q. Yu, X. H. Bu, *Crystal Growth & Design*, 2006, **6**, 2493.

(4) Z. S. Wang, C. H. Huang,.F. Y. Li, S. F. Weng, K. Ibrahim, F. Q. Liu, *J.Phys.Chem.B*, 2001, **105**, 4230.

(5) D. Yan, J. Lu, M. Wei, J. Ma, D. G. Evans, X. Duan, *Phys.Chem.Chem.Phys.,* 2009,**11**, 9200 .



Scheme S1 – Preparation of NaphCA4 dianion.

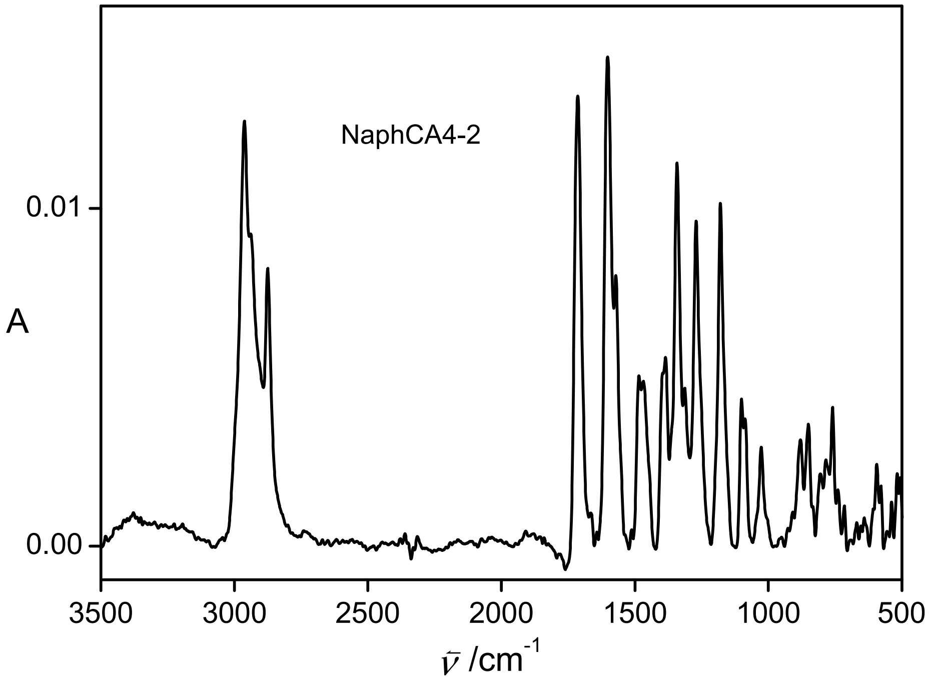


Fig. S2 – FTIR spectrum of NaphCA4 dianion.