

Synthesis of novel donor–acceptor twins

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Donor acceptor dimers **1a–f** were prepared in four steps by coupling 1-(bromohexyloxy)-9,10-anthraquinone **5c** to 2-hydroxy-3,6,7,10,11-pentakis(alkyloxy)triphenylenes **2a–f**. Whereas differential scanning calorimetry and optical polarizing microscopy of those derivatives **1a–d** with short alkyl chains revealed only crystal to soft plastic crystal transitions followed by isotropic melting, **1e,f** with long alkyl chains possess a mesophase. Weak intramolecular charge-transfer interactions in solution were deduced from NMR and UV spectra.

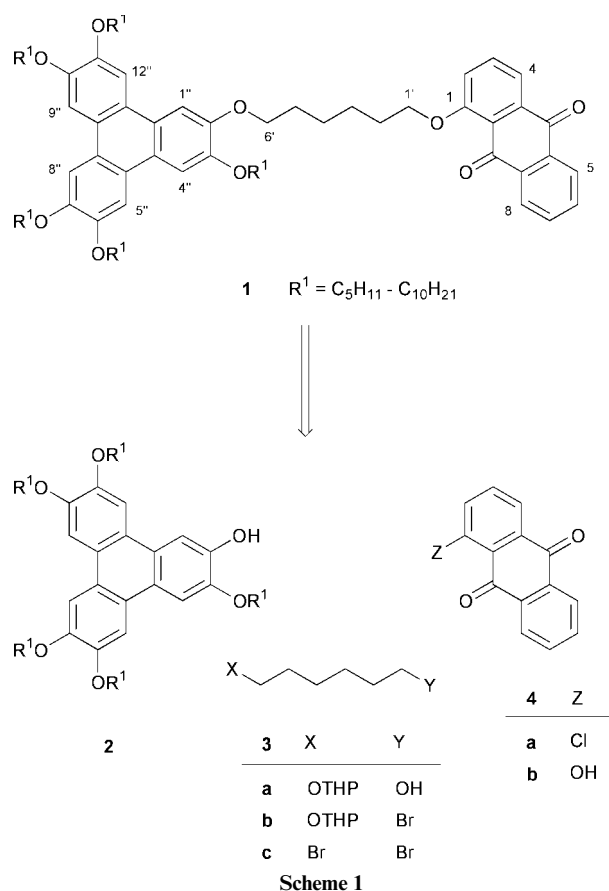
Introduction

The discovery of the first non-polymeric organic metal, a charge-transfer complex containing tetrathiafulvalene and tetracyanoquinodimethane¹ initiated a tremendous amount of research effort on organic electronically active materials.^{2,3} In particular a broad variety of tetrathiafulvalene derivatives have been used for intramolecular charge-transfer complexes.^{4,5} Liquid crystalline charge-transfer complexes have been known since 1968.⁶ It was found that electron transfer can have a profound effect on the induction and stabilization of mesophases.^{7,8} These liquid crystals were usually rod-shaped (calamitic)^{9,10} and only a few examples of disc-shaped (discotic) mesogenic charge-transfer complexes have been described.¹¹ Most charge-transfer interactions in liquid crystals were induced by separate donor (or acceptor) moieties and doping them with the corresponding (non)mesogenic acceptor (or donor). Thus the question arises whether donor and acceptor can be linked by a tether in one mesogenic unit to form a liquid crystalline dimer, a so-called twin.^{12,13} This issue has been addressed independently by three groups. Ringsdorf and co-workers studied discotic charge-transfer twins from pentaalkoxytriphenylene tethered to 2,4,7-trinitrofluorenone^{14,15} and prepared Langmuir-Blodgett films from these compounds.¹⁶ A very high intracolumnar stacking order as a result of charge-transfer interactions and hydrogen bonds in 2,3,4-tris(alkyloxy)-benzaldehyde-2',4'-dinitrophenylhydrazone was observed by Praefcke and Gündogan.¹⁷ Tschierske investigated liquid crystalline macrocycles, which undergo charge-transfer-induced phase transitions.¹⁸ A mesogenic donor–acceptor twin containing azobenzene for optical storage was reported by Wendorff and co-workers.¹⁹ In contrast, quinone derivatives have not been used as acceptors in such donor–acceptor systems. Therefore, we chose donor–acceptor twin **1** bearing a pentakis(alkoxy)triphenylene as donor unit tethered to an anthraquinone as acceptor unit (Scheme 1). The results concerning synthesis and mesomorphic properties of **1** are reported below.

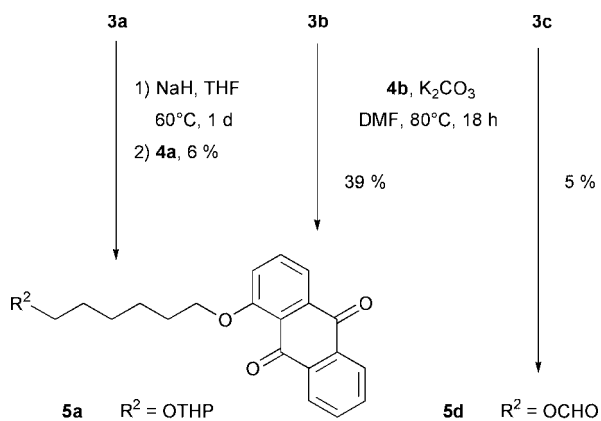
Results and discussion

Synthesis of the donor–acceptor twins

For the synthesis of compound **1** the strategy outlined in Scheme 1 was envisaged. The spacer **3** should be attached first



to the anthraquinone **4** followed by coupling with the triphenylene moiety **2**. Mono-*O*-tetrahydropyranyl-protected hexanediol **3a**²⁰ was deprotected with NaH in refluxing THF, followed by addition of 1-chloroanthraquinone **4a** (Scheme 2). However, only 6% of the desired product **5a** could be obtained.²¹ In contrast, coupling of THP-protected bromide **3b**²² with 1-hydroxyanthraquinone in the presence of K₂CO₃ provided **5a** in 39% yield. Deprotection of **5a** with TsOH was performed in MeOH–CH₂Cl₂ for solubility reasons to give alcohol **5b** in 98% yield. Subsequent conversion of **5b** to the bromide **5c** was achieved under Appel conditions²³ with CBr₄–PPh₃ in 56% yield. Attempts to avoid the use of THP-protected



1, 2	R^1	Yield of 1 [%]
a	C_5H_{11}	88
b	C_6H_{13}	90
c	C_7H_{15}	49
d	C_8H_{17}	78
e	C_9H_{19}	52
f	$\text{C}_{10}\text{H}_{21}$	72

Scheme 2

precursor **3b** were unsuccessful. Employing 1,6-dibromohexane **3c** in the etherification with **4b** yielded nothing of the desired product **5c**. However, the formate **5d** was obtained instead (5%). The synthesis was finished by treatment of bromide **5c** with 2-hydroxy-3,6,7,10,11-pentakis(alkyloxy)triphenylenes **2a-f**²⁴ to give the donor–acceptor twins **1a-f** in 49–90% yield.

Spectroscopic and calorimetric properties of twins (**1**)

Several characteristic features of donor–acceptor twins **1** were observed when comparing the spectroscopic data of **1** with those of the anthraquinone precursor **5c**. The ¹H NMR signals of **1** at ambient temperature displayed high field shifts for the anthraquinone moiety as compared to the “triphenylene-free” precursor **5c**. In particular the signals of 3-H, 5-H, 6-H, 7-H and 8-H are shifted up field 0.1–0.13 ppm. The corresponding shifts for 2-H and 4-H were much smaller ($\Delta\delta = 0.01$ –0.04 ppm). On the other hand small down-field shifts were detected for the triphenylene moiety in **1** as compared to hexakis(alkyloxy)triphenylenes.^{24–26} 4''-H was shifted by 0.08 ppm and 1''-H, 9''-H, 12''-H were shifted by 0.03 ppm. Similar shifts could also be detected in the ¹³C NMR spectra, albeit the effects were smaller than those in the ¹H NMR spectra. Thus the signals of C-2, C-3, C-4, C-5, C-6, C-7 and C-8 are shifted up-field ($\Delta\delta = 0.2$ ppm), whereas C-1'', C-9'', C-12'', C-4'' are shifted down-field ($\Delta\delta = 0.1$ –0.4 ppm). The above mentioned NMR shifts are probably attributable to charge-transfer interactions

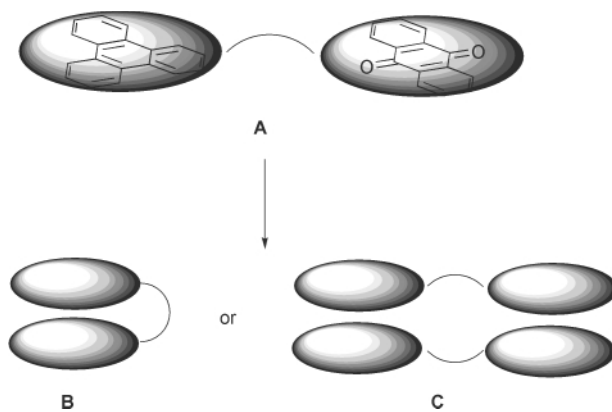
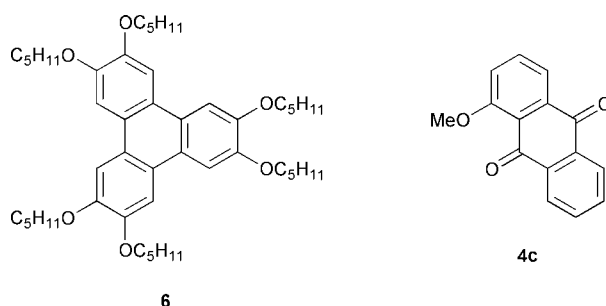


Fig. 1

between anthraquinone and triphenylene, either intra- or intermolecular, resulting in stacked orientation (**B**) or dimer formation (**C**) (Fig. 1).

In addition, a small shift of the carbonyl stretching band to lower frequencies ($\Delta\nu \leq 4\text{ cm}^{-1}$) was detected in the IR spectra of **1a-f**, as compared to the corresponding band of **5a-c**.²⁷ In order to detect even weak charge-transfer absorptions UV spectra were taken from compounds **1a-f** and compared with those of 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene **6**,^{15,28} 1-methoxy-9,10-anthraquinone **4c**,^{29–31} and an equimolar mixture of **6** and **4c**. At a concentration of $10^{-5}\text{ mol dm}^{-3}$ in acetonitrile



the UV spectrum of the (1 : 1) mixture **6-4c** does not contain any additional bands as compared to the spectra of the separate donor **6** and acceptor **4c**, except that the intensity of the absorption at 346 nm increased (see Experimental section for details).³² The UV spectra of compounds **1a-f** were almost identical to those of **6-4c**. However upon increasing the concentration to $10^{-4}\text{ mol dm}^{-3}$ and keeping the solutions for 1 day the spectra of **1** and **6-4c** displayed an additional shoulder at 320 nm.^{33–35} Due to partial overlap with absorptions caused by the triphenylene moiety, determination of molar absorption coefficients was not possible.³⁶

Phase transitions of **1a-f** were determined by differential scanning calorimetry (DSC) and polarizing microscopy (Table 1). Compounds **1a,b,d** displayed two phase transitions in the temperature range of 40–52 and 53–67 °C respectively. The first transition presumably corresponds to a crystal to soft plastic crystal conversion. Microscopic investigations revealed no characteristic textures. In contrast, heptyl-substituted derivative **1c** showed isotropic melting. For the derivatives **1e,f** with long alkyl chains three phase transitions were observed, the former ones probably resemble a crystal to crystal conversion and the latter one a clearing process from a mesophase. Under the optical microscope compound **1f** appeared as a highly viscous anisotropic material. The double refraction disappeared at the clearing temperature. Upon slow cooling from the isotropic liquid to 58 °C fiber-like structures were observed. Unfortunately, the exact type of mesophase or soft plastic crystal phase could not be determined by X-ray diffraction until now.

In conclusion donor–acceptor dimers **1a-f** were available in four steps by a convergent approach. NMR, UV and IR data of

Table 1 Phase transitions of dimers **1**^a

1	R	Transition temperatures/°C (and enthalpies/kJ mol ⁻¹) of 1 ^b						
		K ₁	K ₂	M _x	I			
a	C ₅ H ₁₁	—	·	43 (22.7)	·	67 (2.83)	·	
b	C ₆ H ₁₃	—	·	52 (14.6)	·	61 (0.70)	·	
c	C ₇ H ₁₅	—	·	38 (39.9)	—	—	·	
d	C ₈ H ₁₇	—	·	40 (30.4)	·	53 (3.04)	·	
e	C ₉ H ₁₉	·	21 (1.11)	·	31 (0.26)	·	44 (21.3)	·
f	C ₁₀ H ₂₁	·	37 (4.01)	·	49 (13.7)	·	63 (0.50)	·

^a Transition temperatures were determined by differential scanning calorimetry. Heating rates: 3 K min⁻¹ for **1a,b** and 10 K min⁻¹ for **1c–f**. Temperatures were observed upon first heating (**1a–c**) or second heating (**1d–f**). ^b The following phases were observed: K₁, K₂ (crystalline); M_x (mesophase), I (isotropic).

1a–f indicate a weak intramolecular charge-transfer interaction (**B** in Fig. 1) in solution between the triphenylene π -donor system and the anthraquinone acceptor.

Experimental

General

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Merck Si 254 F plates (0.25 mm thickness) and the products were visualized by spraying with a solution of phosphomolybdic acid in EtOH (5%, v/v). Flash chromatography³⁷ was carried out with Merck silica gel 60 (230–400 mesh). NMR spectra: Bruker AM 400 (¹H: 400 MHz, ¹³C: 100 MHz). Chemical shifts are reported in ppm, *J* values are given in Hz. Multiplets in ¹³C NMR spectra were assigned with the aid of DEPT experiments. Differential scanning calorimetry: Rheometric Scientific DSC SP, heating and cooling rate: 10 K min⁻¹ and 3 K min⁻¹ (for **1a,b**). IR spectra: Nicolet 320 FT-IR spectrometer. MS: Finnigan Model MAT 8430 (EI). UV: Hewlett-Packard 8452 diode array spectrometer (*d* = 0.1 dm). GC: Hewlett-Packard HP6890, HP5-fused silica capillary column (id 0.32 mm, length 30 m). Temperature program: 220 °C at 1 °C min⁻¹ up to 280 °C, then isothermal for 20 min. Polarizing microscopy: Olympus BX50 polarizing microscope combined with a Linkam LTS350 hot stage and Linkam TP 93 central processor. The following compounds were prepared according to literature procedures: 2-hydroxy-3,6,7,10,11-pentakis(alkyloxy)triphenylenes **2a–f**,²⁴ 6-(tetrahydropyran-2-yloxy)hexan-1-ol **3a**,²⁰ 6-bromo-1-(tetrahydropyran-2-yl-oxy)hexane **3b**,²² 1-methoxy-9,10-anthraquinone **4c**,^{29,30} and 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene **6**.²⁵

1-[6-(Tetrahydropyran-2-yloxy)hexyloxy]-9,10-anthraquinone (**5a**)

Method A. To a suspension of NaH (0.24 g, 10.0 mmol, 60% suspension in mineral oil) in THF (5 mL) was added dropwise over 5 min **3a** (2.02 g, 10.0 mmol). After refluxing the mixture overnight a solution of 1-chloro-9,10-anthraquinone **4a** (2.40 g, 10.0 mmol) in THF (40 mL) was added dropwise and the mixture was refluxed for another 2 d. Then the mixture was poured in H₂O (100 mL) and the aqueous layer was extracted with Et₂O (4 × 100 mL). The combined organic layers were dried over MgSO₄ and evaporated. The crude product was purified by flash chromatography on SiO₂ (hexanes–ethyl acetate 10:1) and recrystallization (THF–hexanes 20:1) to yield a yellow solid (0.26 g, 0.60 mmol, 6%).

Method B. A mixture of 1-hydroxy-9,10-anthraquinone **4b** (5.07 g, 22.6 mmol), K₂CO₃ (12.5 g, 90.0 mmol) and 6-bromo-1-(tetrahydropyran-2-yloxy)hexane **3b** (6.00 g, 22.6 mmol) in

DMF (80 mL) was heated at 80 °C for 18 h and then poured onto ice (200 g). The precipitate was filtered *via* Celite and dissolved in CH₂Cl₂ (300 mL). After drying over MgSO₄, evaporation of the solvent and purification by flash chromatography on SiO₂ (hexanes–ethyl acetate (10:1, then 3:1) of a yellow solid (3.57 g, 8.70 mmol, 39%) was obtained; mp 68–69 °C (Found: C, 73.60; H, 6.87. C₂₅H₂₈O₅ requires C, 73.51; H 6.91%); $\lambda_{\max}(\text{CH}_3\text{CN})/\text{nm}$ 380 (log ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 3.68), 320 (3.40), 254 (4.47), 216 (4.36), 202 (4.39); $\nu_{\max}/\text{cm}^{-1}$ 1676 (C=O); δ_{H} (400 MHz, CDCl₃) 8.27–8.20 (2H, m, 5-H, 8-H), 7.93–7.91 (1H, m, 4-H), 7.77–7.64 (3H, m, 3-H, 6-H, 7-H), 7.32–7.29 (1H, m, 2-H), 4.57 (1H, t, *J* 4.4, 2'-H), 4.15 (2H, t, *J* 6.7, 1'-H), 3.90–3.84 (1H, m, 6'-H_a), 3.80–3.74 (1H, m, 6'-H_b), 3.52–3.47 (1H, m, 6'-H_b), 3.45–3.40 (1H, m, 6'-H_b), 2.02–1.95 (2H, m), 1.84–1.44 (12H, m); δ_{C} (100 MHz, CDCl₃) 183.2 (CO), 181.8 (CO), 159.6 (C-1), 135.3, 134.7, 132.1, 121.3 (C-4a, C-8a, C-9a, C-10a), 134.5, 133.8, 132.7 (C-3, C-6, C-7), 126.8, 126.2 (C-5, C-8), 119.2, 118.8 (C-2, C-4), 98.5 (C-2''), 69.2, 67.1, 62.0 (C-1', C-6', C-6''), 30.4, 29.3, 28.7, 25.6, 25.4, 25.1, 19.3; *m/z* 408 (M⁺, 8%), 324 (72), 224 (100), 196 (14), 151 (12), 139 (24), 99 (8).

1-(6-Hydroxyhexyloxy)-9,10-anthraquinone (**5b**)

A solution of **5a** (0.41 g, 1.00 mmol) and TsOH·H₂O (19.0 mg, 0.10 mmol) in MeOH (10 mL) and CH₂Cl₂ (1 mL) was stirred for 18 h at room temperature and then hydrolyzed with saturated NaHCO₃ (50 mL). The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL) and the combined organic layers were dried over MgSO₄ and evaporated. The crude product was purified by flash chromatography on SiO₂ (hexanes–ethyl acetate 5:1, then 1:1) to yield 0.32 g (0.98 mmol, 98%) of a yellow solid; mp 105.5–106.5 °C (Found: C, 73.98; H, 6.20. C₂₀H₂₀O₄ requires C, 74.06; H, 6.21%); $\lambda_{\max}(\text{CH}_3\text{CN})/\text{nm}$ 380 (log ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 3.69), 324 (3.42), 254 (4.49), 216 (4.37), 198 (4.40); $\nu_{\max}/\text{cm}^{-1}$ 3533 (OH), 1677 (C=O); δ_{H} (400 MHz, CDCl₃) 8.25–8.18 (2H, m, 5-H, 8-H), 7.92–7.89 (1H, m, 4-H), 7.76–7.63 (3H, m, 3-H, 6-H, 7-H), 7.30–7.28 (1H, m, 2-H), 4.16 (2H, t, *J* 6.4, 1'-H), 3.68 (2H, t, *J* 6.4, 6'-H), 2.01–1.94 (2H, m, 2'-H), 1.82 (1H, s, OH), 1.66–1.59, 1.54–1.48 (6H, m, 3'-H, 4'-H, 5-H); δ_{C} (100 MHz, CDCl₃) 183.4 (CO), 182.1 (CO), 159.8 (C-1), 135.5, 134.9, 132.3, 121.4 (C-4a, C-8a, C-9a, C-10a), 134.7, 134.0, 133.0 (C-3, C-6, C-7), 127.0, 126.4 (C-5, C-8), 119.5, 119.0 (C-2, C-4), 69.4, 62.6 (C-1', C-6'), 32.4, 28.9, 25.6, 25.3 (C-2', C-3', C-4', C-5'); *m/z* 324 (M⁺, 40%), 224 (100), 196 (14), 151 (12), 168 (13), 139 (13), 99 (9).

1-(6-Bromohexyloxy)-9,10-anthraquinone (**5c**)

To a vigorously stirred solution of CBr₄ (205 mg, 0.62 mmol) in THF (10 mL) were added PPh₃ (162 mg, 0.62 mmol) and **5b** (200 mg, 0.62 mmol), and the mixture was stirred at room temperature overnight. After removal of the precipitate by filtration the solvent was removed *in vacuo*. The residue was dissolved in CH₂Cl₂ (50 mL) and washed with H₂O (2 × 40 mL). The organic layer was dried over MgSO₄ and evaporated. Purification of the crude product by flash chromatography on SiO₂ (hexanes–ethyl acetate 10:1) and recrystallization (CH₂Cl₂–hexanes 30:1) yielded 134 mg (0.35 mmol, 56%) of yellow crystals; mp 85 °C (Found: 386.0510 (mass spectrum), C₂₀H₁₉BrO₃ requires 386.0518%); $\lambda_{\max}(\text{CH}_3\text{CN})/\text{nm}$ 380 (log ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 3.67), 322 (3.40), 254 (4.46), 216 (4.36), 202 (4.38); $\nu_{\max}/\text{cm}^{-1}$ 1677 (C=O); δ_{H} (400 MHz, CDCl₃) 8.26–8.20 (2H, m, 5-H, 8-H), 7.93–7.91 (1H, m, 4-H), 7.77–7.65 (3H, m, 3-H, 6-H, 7-H), 7.31–7.29 (1H, m, 2-H), 4.15 (2H, t, *J* 6.4, 1'-H), 3.44 (2H, t, *J* 6.4, 6'-H), 1.99–1.89, 1.68–1.52 (8H, m, 2'-H, 3'-H, 4'-H, 5'-H); δ_{C} (100 MHz, CDCl₃) 183.4 (CO), 182.1 (CO), 159.8 (C-1), 135.6, 135.0, 132.4, 121.6 (C-4a, C-8a, C-9a, C-10a), 134.8, 134.1, 133.0 (C-3, C-6, C-7), 127.1, 126.5 (C-5, C-8), 119.6, 119.0 (C-2, C-4), 69.3 (C-1'), 33.8, 32.5, 28.9, 27.7, 25.1 (C-2', C-3', C-4', C-5', C-6'); *m/z* 386

(M⁺, 17%), 307 (7), 237 (100), 224 (97), 196 (15), 149 (9), 122 (18), 106 (7).

1-(6-Formyloxyhexyloxy)anthraquinone (5d)

A mixture of **4b** (5.61 g, 25.0 mmol), K₂CO₃ (13.8 g, 0.10 mol) and 1,6-dibromohexane **3c** (12.2 g, 50.0 mmol) in DMF (60 mL) were heated at 80 °C for 2 d and then poured onto ice (150 g). The precipitate was filtered *via* Celite and dissolved in CH₂Cl₂ (100 mL). After drying over MgSO₄, evaporation of the solvent and purification by flash chromatography on SiO₂ (hexanes–ethyl acetate (10:1, then 5:1) 0.45 g (1.30 mmol, 5%) of a yellow solid was obtained; mp 100.5–101.0 °C (Found: C, 71.48; H, 5.70. C₂₁H₂₀O₅ requires C, 71.58; H, 5.72%); λ_{max}(CH₃CN)/nm 380 (log(ε/dm³ mol⁻¹ cm⁻¹) 3.70), 322 (3.43), 254 (4.48), 216 (4.38), 204 (4.41); ν_{max}/cm⁻¹ 1721, 1677 (C=O); δ_H (400 MHz, CDCl₃) 8.28–8.21 (2H, m, 5-H, 8-H), 8.07 (1H, s, CHO), 7.95–7.93 (1H, m, 4-H), 7.79–7.66 (3H, m, 3-H, 6-H, 7-H), 7.33–7.30 (1H, m, 2-H), 4.23–4.15 (4H, m, 1'-H, 6'-H), 2.01–1.94, 1.79–1.62, 1.55–1.47 (8H, m, 2'-H, 3'-H, 4'-H, 5'-H); δ_C (100 MHz, CDCl₃) 183.5 (CO), 182.1 (CO), 161.1 (CHO), 159.8 (C-1), 135.6, 135.0, 132.4, 121.5 (C-4a, C-8a, C-9a, C-10a), 134.8, 134.1, 133.0 (C-3, C-6, C-7), 127.1, 126.4 (C-5, C-8), 119.6, 119.0 (C-2, C-4), 98.5 (C-7'), 69.3, 63.9 (C-1', C-6'), 28.9, 28.3, 25.5 (C-2', C-3', C-4', C-5'); *m/z* 352 (M⁺, 100%), 237 (14), 225 (18), 224 (76), 196 (12), 151 (7), 139 (18).

General procedure for the preparation of donor–acceptor twins (1a–f)

To a solution of 2-hydroxy-3,6,7,10,11-pentakis(alkyloxy)triphenylene **2** (0.74 mmol) in DMF (10 mL) were added K₂CO₃ (0.41 g, 3.00 mmol) and **5c** (0.29 g, 0.74 mmol), and the mixture was stirred for 20 h at 80 °C. Then the mixture was poured onto ice (30 g), the precipitate was filtered *via* Celite and redissolved in CH₂Cl₂ (50 mL). After drying over MgSO₄ the solvent was removed *in vacuo* and the crude product was purified by flash-chromatography on SiO₂ (hexanes–ethyl acetate 10:1).

1-{6-[3,6,7,10,11-Pentakis(pentyloxy)triphenylen-2-yloxy]-hexyloxy}-9,10-anthraquinone (1a). Orange solid (0.64 g, 0.65 mmol, 88%) (Found: C, 77.12; H, 8.28. C₆₃H₈₀O₉ requires C, 77.11; H, 8.22%); λ_{max}(CH₃CN)/nm 380 (log(ε/dm³ mol⁻¹ cm⁻¹) 3.68), 346 (3.78), 308 (4.42), 280 (4.84), 272 (4.84), 260 (4.81), 214 (4.68), 200 (4.69); ν_{max}/cm⁻¹ 1673 (C=O); δ_H (400 MHz, CDCl₃) 8.14–8.09 (2H, m, 5-H, 8-H), 7.89–7.87 (1H, m, 4-H), 7.82–7.79 (5H, m, 1-H, 5''-H, 8''-H, 9''-H, 12''-H), 7.75 (1H, s, 4''-H), 7.63–7.55 (3H, m, 3-H, 6-H, 7-H), 7.28–7.26 (1H, m, 2-H), 4.28 (2H, t, *J* 6.4, 1'-H), 4.24 (2H, t, *J* 5.9, 6'-H), 4.22–4.15 (10H, m, OCH₂CH₂), 2.04–1.89 (14H, m), 1.82–1.73 (4H, m), 1.59–1.41 (20H, m), 1.00–0.94 (15H, m, CH₂CH₃); δ_C (100 MHz, CDCl₃) 183.3 (CO), 182.0 (CO), 159.8 (C-1), 148.9, 148.8 (C-2'', C-3'', C-6'', C-7'', C-10'', C-11''), 135.6, 134.8, 132.2, 121.4 (C-4a, C-8a, C-9a, C-10a), 134.6, 133.9, 132.8 (C-3, C-6, C-7), 127.0, 126.2 (C-5, C-8), 123.5, 123.4 (C-1a'', C-4a'', C-5a'', C-8a'', C-9a'', C-12a''), 119.4, 118.8 (C-2, C-4), 107.2, 107.0 (C-1', C-4'', C-5'', C-8'', C-9'', C-12''), 69.6, 69.4, 69.1, 69.0 (C-1', C-6', OCH₂CH₂), 29.2, 29.1, 29.0, 28.9, 28.3, 26.9, 25.4, 25.3, 22.6, 22.5, 14.0 (CH₃); *m/z* 981 (M⁺, 100%), 910 (5), 773 (6), 757 (20), 604 (5), 533 (6), 463 (16), 393 (15), 323 (16), 295 (18), 266 (6), 225 (12).

1-{6-[3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yloxy]-hexyloxy}-9,10-anthraquinone (1b). Orange solid (0.53 g, 0.50 mmol, 90%) (Found: C, 77.51; H, 8.79. C₆₈H₉₀O₉ requires C, 77.68; H, 8.63%); λ_{max}(CH₃CN)/nm 378 (log(ε/dm³ mol⁻¹ cm⁻¹) 3.67), 346 (3.75), 308 (4.41), 280 (5.03), 270 (4.92), 260 (4.86), 214 (4.68), 196 (4.79); ν_{max}/cm⁻¹ 1674 (C=O); δ_H (400 MHz, CDCl₃) 8.14–8.10 (2H, m, 5-H, 8-H), 7.90–7.87 (1H, m, 4-H), 7.83–7.80 (5H, m, 1'-H, 5''-H, 8''-H, 9''-H, 12''-H), 7.76 (1H, s, 4''-H), 7.65–7.55 (3H, m, 3-H, 6-H, 7-H), 7.29–7.27 (1H, m,

2-H), 4.28 (2H, t, *J* 6.4, 1'-H), 4.24 (2H, t, *J* 5.9, 6'-H), 4.21–4.15 (10H, m, OCH₂CH₂), 2.04–1.99 (4H, m), 1.98–1.87 (10H, m), 1.78–1.73 (4H, m), 1.63–1.52 (10H, m), 1.45–1.34 (20H, m), 0.95–0.83 (15H, m, CH₂CH₃); δ_C (100 MHz, CDCl₃) 183.4 (CO), 182.0 (CO), 159.9 (C-1), 149.0, 148.9, 148.8 (C-2'', C-3'', C-6'', C-7'', C-10'', C-11''), 135.6, 134.9, 132.3, 121.5 (C-4a, C-8a, C-9a, C-10a), 134.7, 133.9, 132.8 (C-3, C-6, C-7), 127.0, 126.3 (C-5, C-8), 123.6, 123.5 (C-1a'', C-4a'', C-5a'', C-8a'', C-9a'', C-12a''), 119.4, 118.9 (C-2, C-4), 107.3, 107.2 (C-1', C-4'', C-5'', C-8'', C-9'', C-12''), 69.7, 69.6, 69.5, 69.2, 69.1 (C-1', C-6', OCH₂CH₂), 31.6, 29.6, 29.4, 29.3, 29.2, 29.0, 25.8, 25.5, 25.4, 22.6, 14.0 (CH₃); *m/z* 1050 (M⁺, 100%), 966 (4), 881 (2), 826 (6), 744 (5), 659 (4), 575 (4), 491 (10), 407 (8), 323 (10), 295 (24), 225 (20).

1-{6-[3,6,7,10,11-Pentakis(heptyloxy)triphenylen-2-yloxy]-hexyloxy}-9,10-anthraquinone (1c). Orange solid (0.33 g, 0.29 mmol, 49%) (Found: C, 78.17; H, 9.16. C₇₃H₁₀₀O₉ requires C, 78.18; H, 8.99%); λ_{max}(CH₃CN)/nm 378 (log(ε/dm³ mol⁻¹ cm⁻¹) 3.71), 346 (3.81), 308 (4.43), 280 (5.04), 270 (4.93), 260 (4.87), 214 (4.71), 196 (4.79); ν_{max}/cm⁻¹ 1673 (C=O); δ_H (400 MHz, CDCl₃) 8.14–8.10 (2H, m, 5-H, 8-H), 7.90–7.88 (1H, m, 4-H), 7.82–7.80 (5H, m, 1-H, 5''-H, 8''-H, 9''-H, 12''-H), 7.75 (1H, s, 4''-H), 7.65–7.54 (3H, m, 3-H, 6-H, 7-H), 7.29–7.27 (1H, m, 2-H), 4.28 (2H, t, *J* 6.4, 1-H), 4.24 (2H, t, *J* 5.9, 6'-H), 4.21–4.15 (10H, m, OCH₂CH₂), 2.05–2.00 (4H, m), 1.98–1.87 (10H, m), 1.79–1.73 (4H, m), 1.62–1.51 (10H, m), 1.42–1.30 (30H, m), 0.93–0.88 (15H, m, CH₂CH₃); δ_C (100 MHz, CDCl₃) 183.3 (CO), 182.0 (CO), 159.8 (C-1), 148.9, 148.8 (C-2'', C-3'', C-6'', C-7'', C-10'', C-11''), 135.6, 134.8, 132.2, 121.5 (C-4a, C-8a, C-9a, C-10a), 134.6, 133.9, 132.8 (C-3, C-6, C-7), 127.0, 126.3 (C-5, C-8), 123.5 (C-1a'', C-4a'', C-5a'', C-8a'', C-9a'', C-12a''), 119.4, 118.8 (C-2, C-4), 107.3, 107.1 (C-1', C-4'', C-5'', C-8'', C-9'', C-12''), 69.7, 69.6, 69.5, 69.1, 69.0 (C-1, C-6, OCH₂CH₂), 31.8, 29.4, 29.2, 29.1, 29.0, 26.1, 25.4, 25.3, 22.5, 14.0 (CH₃); *m/z* 1120 (M⁺, 100), 1022 (4), 913 (12), 896 (30), 814 (6), 715 (4), 617 (4), 519 (14), 421 (10), 323 (15), 250 (10), 224 (22).

1-{6-[3,6,7,10,11-Pentakis(octyloxy)triphenylen-2-yloxy]-hexyloxy}-9,10-anthraquinone (1d). Orange solid (0.47 g, 0.39 mmol, 78%) (Found: C, 78.54; H, 9.50. C₇₈H₁₁₀O₉ requires C, 78.61; H, 9.30%); λ_{max}(CH₃CN)/nm 382 (log(ε/dm³ mol⁻¹ cm⁻¹) 3.66), 346 (3.74), 308 (4.40), 280 (5.02), 270 (4.91), 260 (4.85), 214 (4.68), 196 (4.80); ν_{max}/cm⁻¹ 1721, 1677 (C=O); δ_H (400 MHz, CDCl₃) 8.14–8.09 (2H, m, 5-H, 8-H), 7.89–7.87 (1H, m, 4-H), 7.83–7.80 (5H, m, 1-H, 5''-H, 8''-H, 9''-H, 12''-H), 7.75 (1H, s, 4''-H), 7.64–7.55 (3H, m, 3-H, 6-H, 7-H), 7.28–7.26 (1H, m, 2-H), 4.29 (2H, t, *J* 6.4, 1'-H), 4.24 (2H, t, *J* 5.9, 6'-H), 4.21–4.15 (10H, m, OCH₂CH₂), 2.04–1.99 (4H, m), 1.98–1.87 (10H, m), 1.78–1.73 (4H, m), 1.62–1.51 (10H, m), 1.46–1.25 (40H, m), 0.92–0.83 (15H, m, CH₂CH₃); δ_C (100 MHz, CDCl₃) 183.3 (CO), 182.0 (CO), 159.9 (C-1), 148.9, 148.8 (C-2'', C-3'', C-6'', C-7'', C-10'', C-11''), 135.6, 134.8, 132.2, 121.5 (C-4a, C-8a, C-9a, C-10a), 134.6, 133.9, 132.8 (C-3, C-6, C-7), 127.0, 126.3 (C-5, C-8), 123.6, 123.5 (C-1a'', C-4a'', C-5a'', C-8a'', C-9a'', C-12a''), 119.4, 118.8 (C-2, C-4), 107.3, 107.1 (C-1', C-4'', C-5'', C-8'', C-9'', C-12''), 69.7, 69.6, 69.5, 69.2, 69.1 (C-1', C-6', OCH₂CH₂), 31.8, 29.6, 29.4, 29.3, 29.2, 29.0, 26.1, 25.4, 22.6, 14.0 (CH₃); *m/z* 1191 (M⁺, 100), 1078 (4), 1002 (5), 966 (20), 884 (6), 771 (6), 741 (3), 659 (4), 548 (5), 547 (10), 435 (10), 323 (15), 295 (10), 224 (30).

1-{6-[3,6,7,10,11-Pentakis(nonyloxy)triphenylen-2-yloxy]-hexyloxy}-9,10-anthraquinone (1e). Orange solid (0.34 g, 0.27 mmol, 52%) (Found: C, 78.97; H, 9.58. C₈₃H₁₂₀O₉ requires C, 79.00; H, 9.59%); λ_{max}(CH₃CN)/nm 382 (log(ε/dm³ mol⁻¹ cm⁻¹) 3.59), 346 (3.70), 308 (4.35), 280 (4.98), 270 (4.87), 260 (4.80), 214 (4.64), (4.76); ν_{max}/cm⁻¹ 1674 (C=O); δ_H (400 MHz, CDCl₃) 8.14–8.09 (2H, m, 5-H, 8-H), 7.90–7.87 (1H, m, 4-H), 7.82–7.79 (5H, m, 1'-H, 5''-H, 8''-H, 9''-H, 12''-H), 7.75 (1H, s, 4''-H), 7.65–

7.53 (3H, m, 3-H, 6-H, 7-H), 7.29–7.27 (1H, m, 2-H), 4.28 (2H, t, *J* 6.4, 1'-H), 4.23 (2H, t, *J* 5.9, 6'-H), 4.21–4.15 (10H, m, OCH₂CH₂), 2.04–1.99 (4H, m), 1.98–1.89 (10H, m), 1.79–1.73 (4H, m), 1.61–1.51 (10H, m), 1.40–1.25 (50H, m), 0.91–0.85 (15H, m, CH₂CH₃); δ_{C} (100 MHz, CDCl₃) 183.3 (CO), 182.0 (CO), 159.9 (C-1), 148.9, 148.8 (C-2'', C-3'', C-6'', C-7'', C-10'', C-11''), 135.6, 134.8, 132.2, 121.5 (C-4a, C-8a, C-9a, C-10a), 134.6, 133.9, 132.8 (C-3, C-6, C-7), 127.0, 126.3 (C-5, C-8), 123.6, 123.5 (C-1a'', C-4a'', C-5a'', C-8a'', C-9a'', C-12a''), 119.4, 118.8 (C-2, C-4), 107.3, 107.2 (C-1'', C-4'', C-5'', C-8'', C-9'', C-12''), 69.7, 69.6, 69.5, 69.2, 69.1 (C-1', C-6', OCH₂CH₂), 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 26.2, 26.1, 25.4, 22.6, 14.0 (CH₃); *m/z* 1261 (M⁺, 100%), 1039 (4), 1037 (7), 954 (5), 827 (4), 783 (2), 701 (3), 575 (10), 449 (8), 323 (12), 295 (8), 225 (30).

1-{6-[3,6,7,10,11-Pentakis(decyloxy)triphenylen-2-yloxy]-hexyloxy}-9,10-anthraquinone (1f). Orange solid (0.48 g, 0.36 mmol, 72%) (Found: C, 79.22; H, 9.76. C₈₈H₁₃₀O₉ requires C, 79.35; H, 9.84%); λ_{max} (*n*-hexane)/nm 378 (log (ϵ /dm³ mol⁻¹ cm⁻¹) 3.54), 346 (3.68), 306 (4.34), 278 (4.93), 268 (4.85), 258 (4.82), 212 (4.66), 198 (4.66); ν_{max} /cm⁻¹ 1675 (C=O); δ_{H} (400 MHz, CDCl₃) 8.15–8.10 (2H, m, 5-H, 8-H), 7.90–7.88 (1H, m, 4-H), 7.83–7.79 (5H, m, 1''-H, 5''-H, 8''-H, 9''-H, 12''-H), 7.75 (1H, s, 4-H), 7.66–7.53 (3H, m, 3-H, 6-H, 7-H), 7.30–7.27 (1H, m, 2-H), 4.29 (2H, t, *J* 6.4, 1'-H), 4.24 (2H, t, *J* 5.9, 6'-H), 4.21–4.15 (10H, m, OCH₂CH₂), 2.05–2.01 (4H, m), 1.98–1.89 (10H, m), 1.76–1.73 (4H, m), 1.60–1.50 (10H, m), 1.42–1.27 (60H, m), 0.90–0.78 (15H, m, CH₂CH₃); δ_{C} (100 MHz, CDCl₃) 183.4 (CO), 182.0 (CO), 159.9 (C-1), 149.0, 148.9, 148.8 (C-2'', C-3'', C-6'', C-7'', C-10'', C-11''), 135.6, 134.9, 132.3, 121.5 (C-4a, C-8a, C-9a, C-10a), 134.7, 133.9, 132.8 (C-3, C-6, C-7), 127.0, 126.3 (C-5, C-8), 123.6, 123.5 (C-1a'', C-4a'', C-5a'', C-8a'', C-9a'', C-12a''), 119.5, 118.9 (C-2, C-4), 107.4, 107.3, 107.2 (C-1'', C-4'', C-5'', C-8'', C-9'', C-12''), 69.7, 69.5, 69.2, 69.1 (C-1', C-6', OCH₂CH₂), 34.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 26.9, 26.2, 25.5, 25.4, 22.9, 22.8, 22.7, 22.6, 22.3, 14.1 (CH₃); *m/z* 1331 (M⁺, 100%), 1303 (10), 1107 (12), 884 (4), 743 (4), 605 (2), 603 (10), 463 (12), 323 (20), 224 (82), 168 (27).

1-Methoxy-9,10-anthraquinone (4c)

λ_{max} (CH₃CN)/nm 378 (log (ϵ /dm³ mol⁻¹ cm⁻¹) 3.69), 324 (3.41), 268 (4.17), 254 (4.48), 214 (4.36).

2,3,6,7,10,11-Hexakis(pentyloxy)triphenylene (6)

λ_{max} (CH₃CN)/nm 346 (log (ϵ /dm³ mol⁻¹ cm⁻¹) 3.56), 308 (4.40), 280 (5.06), 270 (4.89), 212 (4.45), 194 (4.67).

(1:1) Mixture of (6) and (4c)

λ_{max} (CH₃CN)/nm 378 (log (ϵ /dm³ mol⁻¹ cm⁻¹) 3.72), 346 (3.80), 308 (4.44), 278 (5.08), 270 (4.96), 260 (4.87), 214 (4.70), 198 (4.81).

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