Covalently linked donor–acceptor mesogens based on disc-shaped penta-alkynes

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The synthesis and thermal properties of novel discotic donor–acceptor mesogens are described which are characterized by covalently linked penta-alkyne and trinitrofluorenone sub-units.

Electron-rich discotic systems such as triphenylenes and multialkynylbenzene derivatives form charge-transfer complexes with rather flat but non-liquid crystalline electron acceptors like 2,4,7-trinitrofluorenone (TNF).[1] Such donor–acceptor interactions are known to cause a stabilization as well as an induction of hexagonal-columnar mesophases.[1–4] Furthermore, binary systems of disc-like donor and acceptor molecules have been reported to exhibit a nematic-columnar (N_c) phase,[4–7] which in contrast to the common nematic-discotic (N_D) mesophase,[8] is characterized by a columnar stacking of the molecules. However, these columns do not form two-dimensional lattice structures. They display a positional short range order and an orientational long range order.[5] Although it is known that the combination of different structural elements in a single molecule may lead to rather unexpected supramolecular structures[9] the only examples of discotic charge transfer twins known so far are those which contain tiphenylene sub-units as the donor molecular part.[10] Here the first representatives of donor–acceptor mesogens based on covalently linked discotic penta-alkynes and trinitrofluorenones are reported.

The synthetic route to these novel discotic donor–acceptor molecules **2** is given in Fig. 1. The synthesis was carried out by esterification (DCC; DMAP) of the terminal hydroxy substituted pentakis(arylethynyl)benzene derivatives **1**† with β-(2,4,7-trinitro-9-fluorenylideneaminooxy)propionic acid.‡[10]

Structural modifications were performed at the peripheries of the pentayne units in order to influence the diameter of the donor molecular part in this way. The spacer length between the disc-shaped donor and the acceptor sub-units was kept constant.

The phase transition data of the penta-alkyne charge-transfer twin molecules **2** as obtained by differential scanning calorimetry are summarized in Table 1.

It was found that the thermal behaviour of the donor–acceptor molecules **2a–c** strongly depends on the substitution pattern of the pentayne donor molecular part. Optical microscopy and calorimetric studies revealed that an enantiotropic mesophase exists for compound **2a** which is stable even at room temperature. The observed fan-shaped textures are typical for a higher ordered columnar mesogenic structure usually characterized by a parallel alignment of the columns with a two-dimensional either hexagonal or rectangular lattice symmetry.[8] In addition, a monotropic mesophase is observed by polarizing microscopy during cooling from the isotropic melt. It displays either a nematic Schlieren or a marbled texture.

The fivefold methyl substituted discotic donor–acceptor molecule **2b** melts at temperatures close to the decomposition temperature which makes the observation of mesomorphism impossible. An enantiotropic polymorphism was detected for the laterally unsubstituted donor–acceptor pentayne **2c** by microscopy and DSC. The clearing enthalpy is similar to those found for charge transfer induced N_c phases of binary systems from unsubstituted multialkynyl benzene compounds and TNF.[4–6] This suggests the occurrence of a N_c phase for compound **2c**. Optical textures indicate that the low temperature mesophase is a higher ordered discotic-columnar one, similar to compound **2a**. Obviously, it can be presumed that the chemical linkage of the donor and acceptor leads to an alternating arrangement of the molecules in neighbouring columns (Fig. 2) giving rise to the N_c phase as well as to the in addition observed

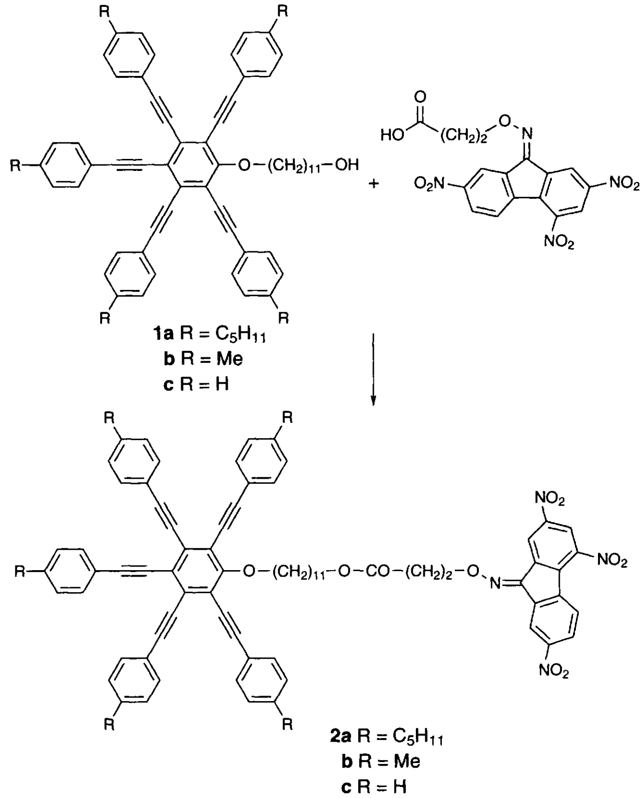

Fig. 1 Synthesis of the discotic donor–acceptor penta-alkynes **2a–c**

Table 1 Phase transition data for the discotic donor–acceptor compounds **2a–c**. Transition temperatures (°C) were determined by DSC on heating at 5 K min^{-1}, transition enthalpies (kJ mol^{-1}) are given in parenthesis

Compound 2	Cr[a]		M[a]		N_C[a]		I[a]
a[b]	—		●	67.4 (2.4)	—		●
	—		●	[50][c]	●	[59][c]	●
b[d]	●	224.6 (71.7)					●
c	●	118.0 (4.6)	●	124.5 (1.5)	●	134.0 (0.8)	●

[a] Cr crystalline phase; M columnar mesophase with either hexagonal or rectangular lattice; N_C nematic-columnar mesophase; I isotropic phase. [b] Heating rate 10 K min^{-1}. [c] Monotropic phase transitions; observed by polarizing microscopy during cooling, not detectable by DSC. [d] Melts with decomposition.

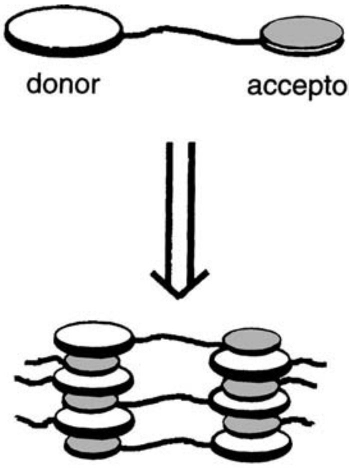

Fig. 2 Two-dimensional structure model for the columnar arrangement of the donor–acceptor molecules **2**

higher ordered columnar mesophases, the latter probably exhibiting either a hexagonal or a rectangular lattice.

The polymorphism observed for the charge transfer molecules **2a** and **2c** has also to be attributed to the chemical fixation of the penta-alkyne donor and the acceptor sub-units. The equimolar charge transfer complexes of the hydroxy substituted pentaynes **1a** and **1c** with TNF, which are comparable to the twin molecules **2a** and **2c** with respect to the molar ratio of the donor and of the acceptor, are monomesomorphic. The equimolar mixture of the fivefold pentyl substituted penta-alkynyl alcohol **1a** and TNF was found to form a hexagonal-columnar as ordered (D_{ho}) mesophase[4] whereas the appropriate mixture of the lateral unsubstituted pentayne **1c** and TNF exhibits a N_c phase,[11] exclusively.

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Footnotes

† The hydroxy substituted penta-alkynes **1a** and **1c** have already been described previously.[4,11] The fivefold methyl modified pentayne **1b** was prepared according to the method given in ref. 4. Phase transition data (°C) of **1b**; transition enthalpies (kJ mol^{-1}) in brackets: Cr 171.6 (43.9) N_D 226.6 (0.5) I. Cr crystalline; N_D nematic-discotic; I isotropic.

‡ A typical procedure is as follows. For 11-[Pentakis(phenylethynyl)-phenoxy]-undecyl-β-(2,4,7-trinitro-9-fluorenylideneaminooxy) propionate **2c**: **1c** 500 mg (0.654 mmol) and β-(2,4,7-trinitrofluorenylideneaminooxy) propionic acid (900 mg) were dissolved in dioxane (10 ml) by heating. After the addition of CH_2Cl_2 (5 ml) the mixture was cooled to 0 °C. Under a nitrogen atmosphere DMAP (a few mg) dissolved in CH_2Cl_2 (1 ml) were added followed by the dropwise addition of DCC (460 mg, 2.24 mmol) in CH_2Cl_2 (2 ml) with stirring. After complete addition the reaction mixture was stirred at ambient temperature for 70 h. The resulting precipitate was removed by filtration and washed with CH_2Cl_2. The combined solutions were evaporated *in vacuo*. The residue was purified by two flash chromatographies using light petroleum–ethyl acetate (10:3) as eluent followed by recrystallization from ethanol–CH_2Cl_2. $C_{73}H_{56}N_4O_{10}$ (M_W 1149.28), 460 mg (61.20% yield). IR (KBr) ν/cm^{-1} 2210 (C≡C), 1735 (COO), 1530 (NO_2) and 1340 (NO_2). ^1H NMR (300 MHz, $CDCl_3$) δ 1.29–1.47 (m, 12 H, CH_2), 1.67 (m, 4 H, CH_2), 1.97 (m, 2 H, CH_2), 2.90 (t, 2 H, CH_2COO, *J* 6.4 Hz), 4.17 (t, 2 H, CH_2OCO, *J* 6.4 Hz), 4.33 (t, 2 H, CH_2O-phenyl, *J* 6.1 Hz), 4.79 (t, 2 H, CH_2ON, *J* 6.4 Hz), 7.44 (m, 15 H, phenyl), 7.63 (m, 10 H, phenyl) and 8.13–9.28 (m, 5 H, TNF).

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