The influence of hydrogen bonding and π–π stacking interactions on the self-assembly properties of C_3-symmetrical oligo(*p*-phenylenevinylene) discs†

Jeroen van Herrikhuyzen, Pascal Jonkheijm, Albertus P. H. J. Schenning* and E. W. Meijer*

Received 19th December 2005, Accepted 8th February 2006
First published as an Advance Article on the web 3rd March 2006
DOI: 10.1039/b517993a

Three C_3-symmetrical discotics containing a 1,3,5-benzenetricarboxamide unit functionalized with π-conjugated oligo(*p*-phenylenevinylene)s (OPV)s have been synthesized and fully characterized. For the two amide OPV discs a two-step transition from helical stacks to molecularly dissolved species was observed and surprisingly, the topology of the amide determines the stability and helicity of the fibers in solution and the length of the fibrils at a surface. In case of the bipyridine disc, aggregates were formed that show little chiral ordering while the stacks remain present over a large temperature range. At a surface, completely disordered structures exist probably as a result of competing types of π–π stacking interactions that differ in strength and orientation. The results show that the design of functional self-assembled architectures based on hydrogen bonding and π–π stacking interactions is an extremely delicate matter and reveal that special demands have to be taken into account to balance the topology, directionality and strength of multiple secondary interactions.

Introduction

Discotic molecules have intensely been used as building blocks in self-assembled cylindrical shaped fibers.[1] Such fibers are attractive for nano-sized electronics because they possess the necessary one-dimensionality leading to anisotropic properties.[2] An interesting class of fibers consists of aggregates based on C_3-symmetrical discs containing a 1,3,5-benzenetricarboxamide unit.[3] Solvophobic effects, hydrogen bonding and π–π stacking interactions, have been used to organise the building blocks into fibers.[3,4] These compounds are liquid crystalline and by introducing chiral side chains helical fibers can be constructed. Some of these aggregates form organogels: entangled three-dimensional, continuous networks of fibers or are used as nucleation agents for polyolefins.[5] Interestingly, some long fibers can be homeotropic aligned with an electric field, presumably because of a net dipole moment that exists as a result of hydrogen bonding in the stacking direction.[3c,i] These features motivated us to synthesize C_3-symmetrical discotics containing a 1,3,5-benzenetricarboxamide unit functionalized with chiral oligo(*p*-phenylenevinylene)s (OPVs). Three different building blocks have been synthesized (Scheme 1, **OPV1**, **OPV2** and **OPV3**) and the influence of hydrogen bonding and π–π stacking interactions on the self-assembly behavior has been studied. The first two differ only in topology of the amide moieties and the third one contains an additional bipyridine π-fragment coplanarized by intramolecular hydrogen bonds.

Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands. E-mail: A.P.H.J.Schenning@tue.nl, E.W.Meijer@tue.nl

† Electronic supplementary information (ESI) available: Figures showing: optical microscopy image of **3**, temperature dependent UV-Vis, CD and PL measurements of **OPV3** in dodecane, Tapping mode AFM height image of drop-cast films of **OPV1** and GPC chromatogram of **OPV3**. See DOI: 10.1039/b517993a

Results and discussion

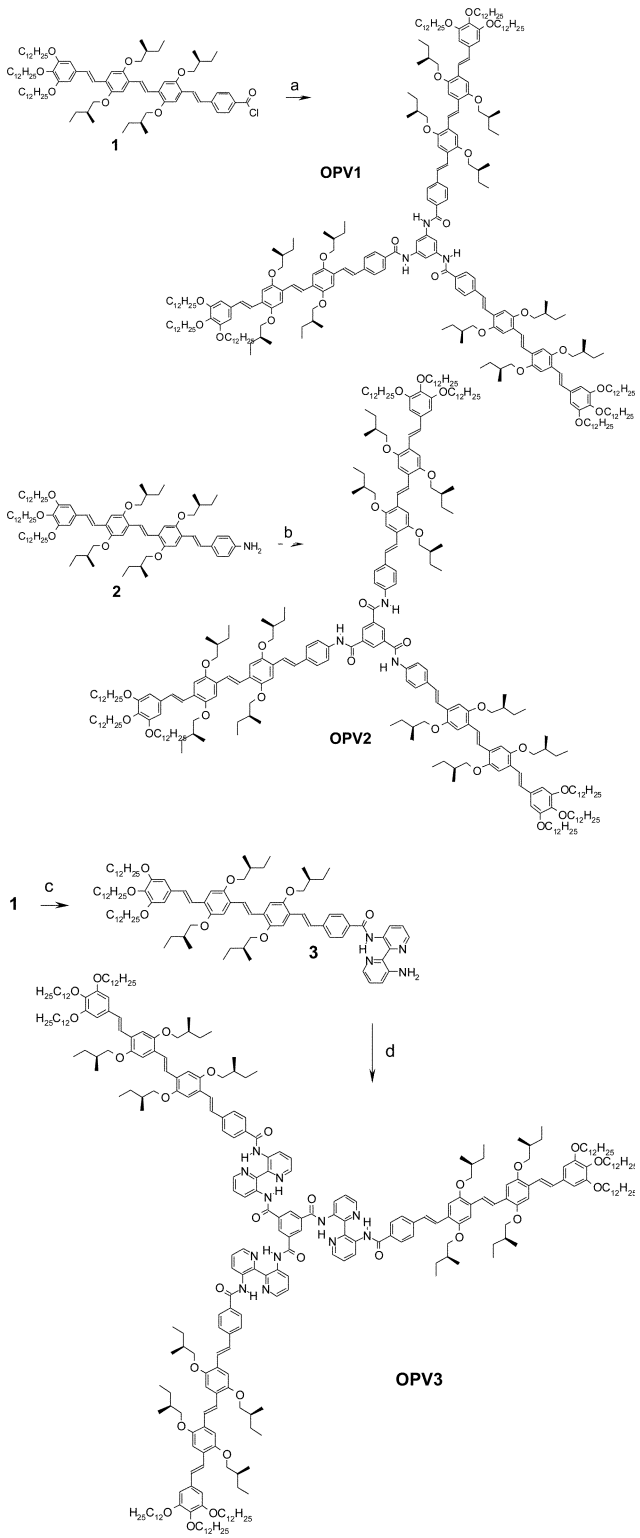
Synthesis

OPV1 was synthesized by the reaction of 1,3,5-triaminobenzene with OPV acid chloride **1**.[6] The disc with the reversed amide linkage, **OPV2**, was synthesized by reacting 1,3,5-trimesic acid trichloride, with OPV amine **2**.[6] From precursor **1** also OPV aminobipyridine **3** was made by reacting it in equimolar amounts with 3,3′-diamino-2,2′-bipyridine.[3a] Finally, after purification by column chromatography this compound was reacted with 1,3,5-trimesic acid trichloride, to yield the OPV-substituted C_3-symmetrical disc **OPV3**.

Intermediate **3** and the disc molecules **OPV1**, **OPV2** and **OPV3** were characterized by ^{1}H and ^{13}C NMR, APT, ^{1}H–^{1}H COSY, HETCOR,[7] infrared, mass spectroscopy and gel permeation chromatography (GPC). In contrast to **OPV1** and **OPV2**, broad ^{1}H NMR spectra for the large **OPV3** were obtained at 25 °C in different solvents, such as deuterated chloroform, 1% methanol in chloroform and THF. This is probably the result of the strong stacking of the discs in these solvents. At 50 °C in chloroform the peaks in ^{1}H NMR were sharper. The ^{13}C NMR spectrum at 50 °C in chloroform, however, only showed sharp peaks in the aliphatic region while the aromatic signals are extremely broadened. The NMR study indicates that **OPV1** and **OPV2** are molecularly dissolved under the conditions used, while **OPV3** is aggregated. Surprisingly, for the new disc molecules no clear liquid crystalline phase could be determined by polarization microscopy. Intermediate **3** showed, however, a clearing temperature of 56–58 °C and upon slow cooling (1 °C min^{-1}) a liquid crystalline cone-like texture was observed between crossed polarizers.[8]

Self-assembly in solution

The self-assembly of the disc-shaped derivatives **OPV1** and **OPV2** in methylcyclohexane (MCH) was studied by a variety of optical



Scheme 1 Synthesis of three C_3-symmetrical oligo(*p*-phenylenevinylene) (OPV) discs. (a) 1,3,5-Triaminobenzene, NEt_3, CH_2Cl_2; (b) 1,3,5-trimesic acid trichloride, NEt_3, CH_2Cl_2; (c) 3,3′-diamino-2,2′-bipyridine, NEt_3, CH_2Cl_2; (d) 1,3,5-trimesic acid trichloride, NEt_3, CH_2Cl_2.

techniques. The UV-Vis absorption and circular dichroism (CD) experiments in MCH pointed out that **OPV1** is aggregated over a large concentration range (10^{-3}–10^{-8} M).[7] In the absorption spectrum a diagnostic shoulder at higher wavelengths was present while in CD a bisignated Cotton effect was observed having a positive sign at high wavelength and a negative sign at low wavelength. The CD measurements show that the chiral packing of the *S*-2-methylbutoxy side chains causes a helical packing of the OPV segments. Temperature dependent UV-Vis, CD and PL (photoluminescence) measurements showed a transition from aggregated to molecularly dissolved species upon heating (Fig. 1). The vibronic shoulder in UV-Vis as well as the CD-effect gradually disappeared. Furthermore, the fluorescence simultaneously shifted towards a spectrum similar to the one recorded in THF with the maximum at $\lambda = 493$ nm and the shoulder at $\lambda = 524$ nm, typically for molecularly dissolved OPVs.[7] The transition temperatures observed in UV-Vis and PL were 50 °C and 49 °C, respectively; whereas in CD this transition temperature is lower[9] indicating that helical stacking occurs in two steps. First, non-helical stacks are formed which subsequently rearrange into a helical conformation. Remarkably, this has previously not been observed for apolar analogues lacking the OPV segments[3a,4b] but only for discs equipped with polar ethylene oxide tails in butanol.[10]

The two-step assembly process is also observed for **OPV2** (Fig. 2). Remarkably, the transition from molecular dissolved species to non-helical stacks is much broader when compared to **OPV1**, while the melt temperature ($T_m = \sim 80$ °C) is higher. In contrast with the strong bisignated CD spectrum of **OPV1** only a small positive Cotton effect exists below 54 °C. This behavior illustrates that a subtle difference like an amide sequence alternation has significant influence on the self-assembly behavior.

To shed more light on this remarkable phenomenon, we performed infrared experiments to see if hydrogen bonds exist in both OPV systems (Fig. 3). In case of **OPV2** (MCH, 10^{-3} M), the N–H stretch vibration is present at 3225 cm^{-1} similar as found earlier for the C_3-analogues lacking the oligo(*p*-phenylenevinylene)s, indicating hydrogen bonds. Surprisingly, for **OPV1** (MCH, 10^{-3} M), this vibration is positioned at 3422 cm^{-1} which is typical for non-hydrogen-bonded species. Similarly, the C=O stretch vibration for **OPV2** was found at 1648 cm^{-1} whereas for **OPV1** this vibration was situated at 1671 cm^{-1} showing again that only hydrogen bonds are present in case of **OPV2**. When **OPV1** and **OPV2** are dissolved in THF solution, the N–H and C=O stretch vibration of both molecules are positioned at 3422 cm^{-1} and 1671 cm^{-1}, respectively, indicating non-hydrogen bonded species. It is not easy to relate this difference in hydrogen bonding to electron or steric effects. In addition, it was not seen in the related C_3 symmetrical discs lacking the OPV segments. In this case, both isomers show hydrogen bonding upon aggregation.[4b,11] The aggregation of our disc molecules is probably mainly caused by π–π interactions of the OPV segment. In case of **OPV2**, a more planar core, as a result of conjugation, can be expected since the carbonyl functionalities are directly linked to the benzene core. In contrast to **OPV1**, stacking of the OPV segment in **OPV2** probably causes an orientation that allows hydrogen bonding.

Based on the data above, we propose that **OPV1** forms helical stacks similar as previously found for related fibers based on the same chiral OPVs.[12] However, the positive couplet found in the CD spectra of **OPV1** reveals right handed helical whereas the previously reported fibers have the opposite handedness.[12] In case of **OPV2** the stacks are more stable probably as a result of additional hydrogen bonds. However, the small Cotton effect

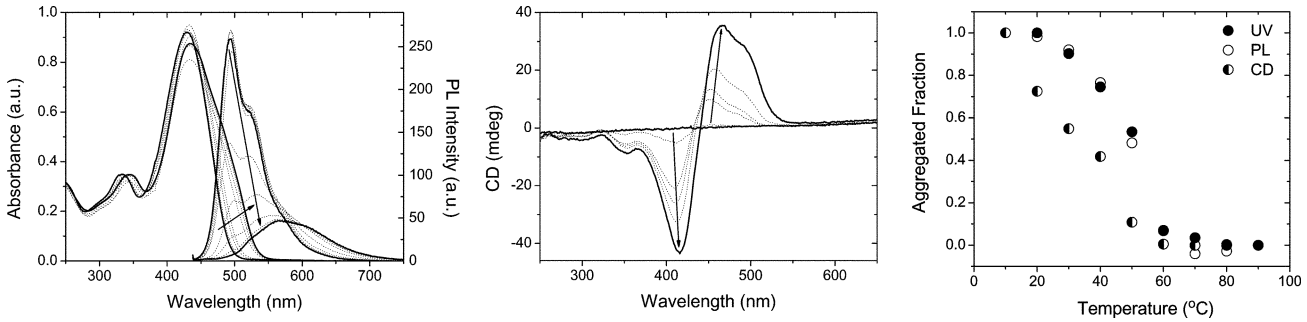


Fig. 1 Temperature dependent UV-Vis (left), PL (left) CD (middle) measurements and the melting curve (right) of **OPV1** in MCH (5.3×10^{-6} M). The aggregated fraction (ϕ) was determined by using the intensity of the UV-vis signal at 520 nm, the PL signal at 494 nm and the CD signal at 416 nm and normalizing these intensities at 10 °C to 1, and at 90 °C to 0.

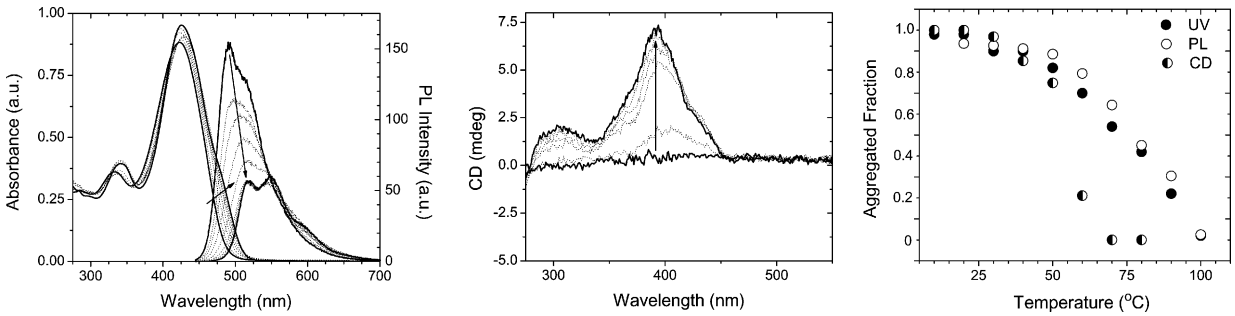


Fig. 2 Temperature dependent UV-Vis (left), PL (left) and CD (middle) measurements and melting curves (right) of **OPV2** in MCH (5.3×10^{-6} M). The aggregated fraction (ϕ) was determined by using the intensity of the UV-Vis signal at 490 nm, the PL signal at 500 nm and the CD signal at 400 nm and normalizing these intensities at 0 °C to 1, and at 100 °C to 0.

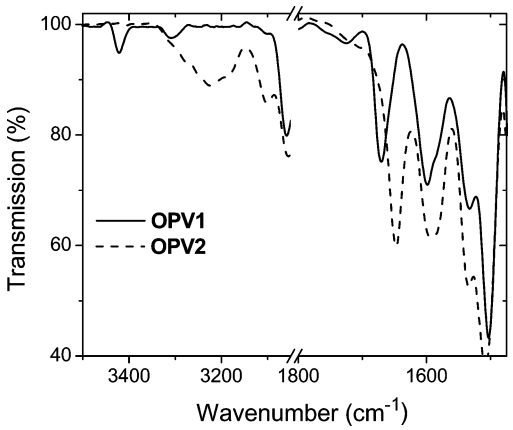


Fig. 3 IR spectra of **OPV1** and **OPV2** recorded at 23 °C in MCH.

and the broad melting curve indicate that non-helical stacks are present which are formed in a less cooperative fashion. Apparently, π–π interactions between adjacent OPV molecules only allow such a helical arrangement if hydrogen bonding and π–π interactions both exist in the stacking direction (**OPV2**) and the strength and the precise direction of both interactions compete, resulting in non-helical stacks. This behavior could be similar to previously reported oligo(*p*-phenylenevinylene) systems where π–π stacking interactions are frustrated by covalent linkers between adjacent stacked oligomers.[12]

This conflicting nature between different secondary interactions is even more pronounced in the self-assembly properties of bipyridine disc **OPV3**. The fluorescence of **OPV3** in THF[8] shows a maximum at $\lambda_{em,\,max} = 504$ nm and a shoulder at $\lambda = 550$ nm, typical for molecularly dissolved OPV tetramers.[7] In MCH at room temperature using the same concentration as in THF, the fluorescence of the OPV segments is quenched and the maximum is red-shifted indicating aggregated species (Fig. 4).[7] Upon heating, a gradual transition towards molecularly dissolved species took place as the observed fluorescence increased and shifted to the blue. However, at 90 °C the fluorescence is still approximately three times quenched with respect to THF. Surprisingly, only a very weak bisignated CD effect is observed, which remains very weak even at high temperatures.[8] This emphasises that the aggregates possess only a little chiral ordering. UV-Vis measurements showed that upon heating a blue shift is observed instead of the expected red shift towards the THF absorption maximum where molecularly dissolved species are present.[8] These optical studies show that for bipyridine disc **OPV3** aggregation takes place without a clear transition temperature to a molecularly dissolved state. From earlier work it is know that the bipyridyl parts are planar in the C_3 symmetrical core due to intramolecular hydrogen bonds and contribute to the stability of the self-assembled stacks.[3a] It could well be that in case of **OPV3**, the strength and directionality of the π–π stacking caused by the bipyridyl and the OPV segments are so different that it results in ill-defined objects (*vide infra*).

Self-assembly at surfaces

The self-assembly properties of our disc molecules were also studied as individual fibers at surfaces by atomic force microscopy

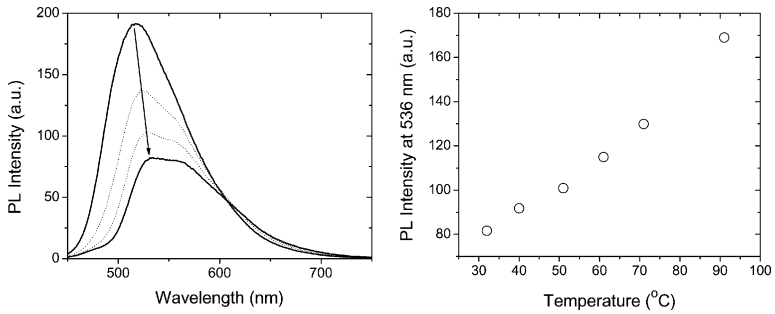


Fig. 4 Temperature dependent PL measurements (left) and the PL intensity at 536 nm *versus* the temperature (right) of **OPV3** in MCH (5.3×10^{-6} M).

(AFM) operated in tapping mode. For **OPV1**, fibers with a length of approximately 20 nm and a uniform height were observed on graphite after drop-casting a 1×10^{-5} M MCH solution.[8] Extended fibers ranging from 50 to 100 nm were observed for **OPV2** when a 5.3×10^{-6} M MCH solution was drop-cast (Fig. 5). A dense network of fibers was found from a 1×10^{-5} M MCH solution. The height of the fibers is on average 5 nm, which is in fairly good agreement with a CPK model that predicts 5.2 nm when the dodecyloxy tails are tilted and comparable to related OPV fibers.[7] Drop-cast films from MCH at different concentrations of bipyridine **OPV3** on several substrates resulted in all cases in ill-defined structures.

In solution, self-assembled stacks of **OPV2** are more stable than that of **OPV1** which is also expressed in the solid state. On graphite the **OPV2** stacks are longer than those of **OPV1** showing the importance of additional hydrogen bond interactions. This agreement between stacks in solution and on surfaces is also present for **OPV3**.

Conclusions

Three C_3-symmetrical discotics substituted with π-conjugated tetra(*p*-phenylenevinylene)s were synthesized and fully characterized. Infrared, absorption, circular dichroism and fluorescence studies in methylcyclohexane revealed that a competition exists between the different supramolecular interactions of adjacent discs. In the case of the bipyridine disc, aggregates were formed that show little chiral ordering and remain present over a large temperature range while in the solid state, completely disordered structures exist probably as a result of different types of π–π stacking interactions that differ in strength and orientation. For both amide OPV discs in solution a transition from aggregated to molecularly dissolved species was observed. Surprisingly, the topology of the amide determines strongly the stability and helicity of the fibers in solution and the length of the fibrils at a graphite surface.

Importantly, our results show that the design of functional self-assembled architectures based on hydrogen bonding and π–π

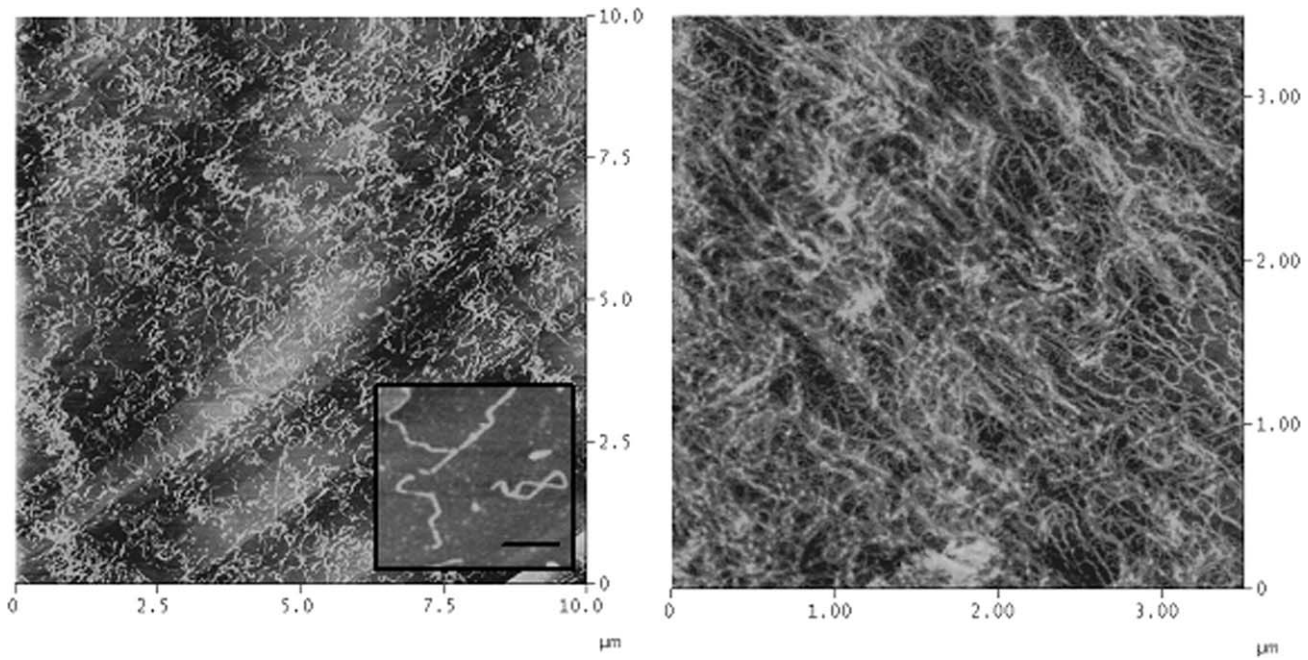


Fig. 5 Tapping mode AFM height image of 10.0 × 10.0 μm (left) with inset to show smaller area (bar = 250 nm) of drop-cast films of **OPV2** from a 5.3×10^{-6} M MCH solution on a graphite substrate and a height image of 3.5 × 3.5 μm (right) from a 1×10^{-4} M MCH solution, both showing the formation of fiber-like structures.

stacking interactions is an extremely delicate matter and reveal that special demands have to be taken into account to balance the topology, directionality and strength of multiple secondary interactions.

Experimental

General: UV/Vis, fluorescence and circular dichroism measurements were performed on a Perkin Elmer Lambda 40 UV/Vis Spectrometer, a Perkin Elmer LS-50 B and a JASCO J-600 spectropolarimeter respectively. Atomic force microscopy (AFM) measurements were carried out at room temperature with a Digital Instruments Nanoscope IV controller operating in the tapping mode. Substrates were freshly cleaved and used as such. Solutions of **OPV1**, **OPV2** and **OPV3** in MCH were drop-cast on highly oriented pyrolitic graphite (HOPG) substrates. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25.0 °C on a Varian Gemini (300 MHz) or a Varian Mercury Vx (400 MHz). Additionally ^{1}H–^{1}H COSY, APT and HETCOR experiments were carried out to assign all peaks. Chemical shifts (δ) are given in ppm relative to tetramethylsilane, which was used as internal standard. Abbreviations used are s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet and br = broad. Infrared spectra were run on a Perkin Elmer Spectrum One UATR FT-IR spectrophotometer. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilising an α-cyano-4-hydroxycinnamic acid matrix; mode of operation: reflector (**3**, **OPV1** and **OPV2**) and linear (**OPV3**); polarity: positive. Optical properties were studied using a Jeneval polarisation microscope equipped with crossed polarisers and a Linkam THMS 600 hot stage. All solvents were of AR quality and chemicals were used as received.

3′-[(*E*,*E*,*E*)-4-<4-{4-(3,4,5-Trisdodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]-styryl}-2,5-bis[(*S*)-2-methylbutoxy]-styryl>benzoylamino]-2,2′-bipyridine-3-amine (3)

To an ice-cooled solution of 3,3′-diamino-2,2′-bipyridine[3a] (24 mg, 0.13 mmol) and triethylamine (0.5 ml) in dry dichloromethane (15 ml) a solution of benzoyl chloride derivative **1**[6] (170 mg, 0.13 mmol) in dry dichloromethane (10 ml) was added dropwise under an argon atmosphere. After complete addition the ice bath was removed and the mixture was stirred at room temperature for 4 hours. The mixture was evaporated *in vacuo* and purification by column chromatography on silica gel (ethyl acetate–hexane 1 : 3) yielded pure **3** (90 mg, 48%) (Chart 1). $R_f = 0.5$. $T_{cl} = 56$–58 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.89 (t, 9 H, *1* and *13*), 1.03 (m, 12 H, *41*, *46*, *59* and *64*), 1.13 (m, 12 H, *39*, *44*, *57* and *62*), 1.2–1.4 (m, 24 H, *2–9* and *14–21*), 1.5 (m, 6 H, *10* and *22*), 1.68 (m, 8 H, *40*, *45*, *58* and *63*), 1.83 (m, 6 H, *11* and *23*), 2.0 (m, 4 H, *38*, *43*, *56* and *61*), 3.85–3.95 (m, 8 H, *37*, *42*, *55* and *60*), 3.95–4.05 (m, 6 H, *12* and *24*), 6.62 (br, 2 H, *83*), 6.75 (s, 2 H, *27*), 7.04 (d, $J = 16.5$ Hz, 1 H, *29*), 7.11–7.25 (m, 7 H, *32*, *35*, *47*, *48*, *65*, *80* and *81*), 7.32 (dd, 1 H, *79*), 7.40 (d, $J = 16.5$ Hz, 1 H, *30*), 7.54 (s, 2 H, *50* and *53*), 7.62 (d, $J = 16.2$ Hz, 1 H, *66*), 7.67 (d, $J = 8.2$ Hz, 2 H, *68*), 8.08 (m, 3 H, *69* and *76*), 8.33 (dd, 1 H, *75*), 9.30 (dd, 1 H, *74*), 14.69 (br, 1 H, *72*). ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ {11.30 (1 C), 11.39 (1 C), 11.43 (2 C)} (*41*, *46*, *59* and *64*), 14.00 (3 C, *1* and *13*), {16.69 (1 C), 16.77 (3 C)} (*39*, *44*, *57* and *62*), {29.26, 29.29, 29.34 (8 C), 29.56, 29.61, 29.66 (17 C)} (*2–9*, *11* and *14–21*), 26.03 (3 C, *10* and *22*), 26.30 (4 C, *40*, *45*, *58* and *63*), 30.36 (1 C, *23*), {34.87 (1 C), 34.99 (1 C), 35.05 (2 C)} (*38*, *43*, *56* and *61*), 69.00 (2 C, *12*), 73.45 (1 C, *24*), {73.99 (1 C), 74.10 (1 C), 74.31 (1 C), 74.39 (1 C)} (*37*, *42*, *55* and *60*), 104.99 (2 C, *27*), 109.52 (1 C, *48*), 109.82 (1 C, *47*), 110.32 (1 C, *32*), 111.00 (1 C, *35*), 122.39 (2 C, *30* and *50*), {122.67, 125.14, 127.20, 134.76, 136.26, 138.50, 140.61, 143.43, 145.04} (9 × 1 C, *73–82*), 122.94 (1 C, *53*), 124.03 (1 C, *81*), 125.66 (1 C, *66*), 125.98 (1 C, *52*), 126.43 (2 C, *68*), 126.83 (1 C, *49*), 127.49 (1 C, *34*), 127.84 (2 C, *69*), 128.17 (1 C, *31*), 128.46 (1 C, *65*), 128.54 (1 C, *29*), 133.12 (1 C, *28*), 134.00 (1 C, *70*), 138.07 (1 C, *25*), 141.39 (1 C, *67*), {150.86 (1 C), 151.02 (1 C), 151.06 (1 C), 151.46 (1 C)} (*33*, *36*, *51* and *54*), 153.16 (2 C, *26*), 165.86 (1 C, *71*). IR (UATR): ν (cm^{-1}): 3448, 3212, 3058 (N–H stretch); 2957, 2922, 2853 (C–H stretch); 1660 (C=O stretch); 1598, 1574, 1520, 1504 (C=C stretch); 1466, 1434, 1421, 1397, 1334, 1306, 1295, 1241, 1202 (C–O–C), 1152, 1116, 1068, 1040, 1010, 962, 917, 893, 854, 838, 808, 796, 773, 761, 731, 697, 672. MALDI-TOF MS (MW = 1494.24): *m*/*z*: 1494.07 $[M]^+$. Anal. Calcd. For $C_{97}H_{144}N_4O_8$: C 77.97, H 9.71, N 3.75. Found: C 77.39, H 9.85, N 3.51%.

N,*N*″,*N*″-Tris{3[3′-[(*E*,*E*,*E*)-4-<4-{4-(3,4,5-trisdodecyloxystyryl)-2,5-bis[(*S*)-2-methyl-butoxy]-styryl}-2,5-bis[(*S*)-2-methylbutoxy]-styryl>benzoylamino]benzene (OPV1)

1,3,5-Triaminobenzene was synthesized in a Parr reactor from 3,5-dinitroaniline by reduction with H_2 and a catalytic amount of 10% Pd/C in methanol. After filtration and evaporation *in vacuo* it was dissolved in dry dichloromethane (5 ml) and added dropwise to a solution of benzoyl chloride **1**[6] (110 mg, 0.082 mmol)

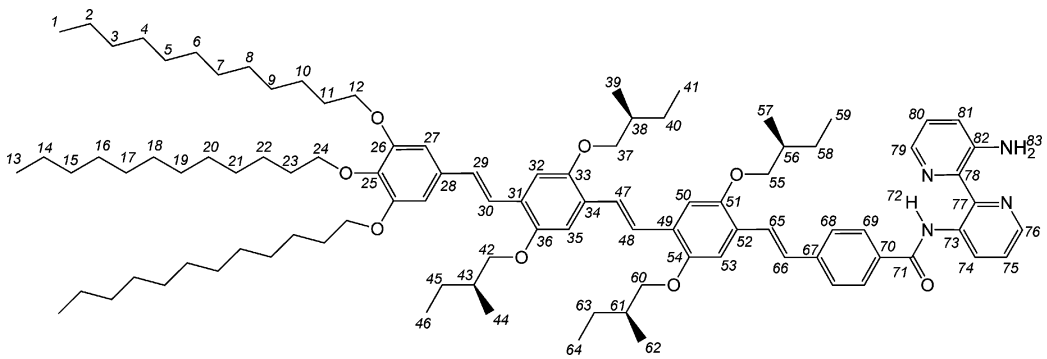


Chart 1 Numbering of the protons and carbon atoms of **3**.

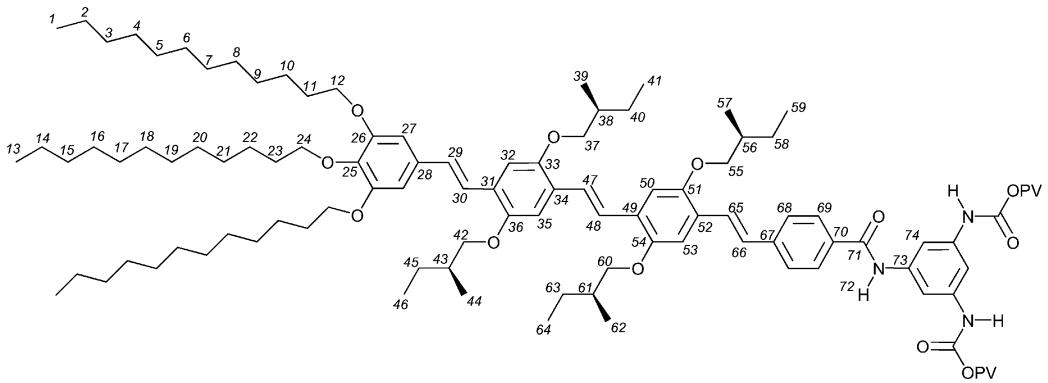


Chart 2 Numbering of the protons and carbon atoms of **OPV1**.

and triethylamine (13 μl) in dry dichloromethane (5 ml). The mixture was stirred at room temperature for 4 hours, evaporated *in vacuo*. Purification by column chromatography on silica gel (dichloromethane–pentane 3 : 1) yielded pure **OPV1** (46 mg, 42%) (Chart 2). T_g = 249–253 °C. ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.89 (t, 27 H, *1* and *13*), 1.03 (m, 36 H, *41*, *46*, *59* and *64*), 1.13 (m, 36 H, *39*, *44*, *57* and *62*), 1.2–1.4 (m, 72 H, *2–9* and *14–21*), 1.5 (m, 18 H, *10* and *22*), 1.68 (m, 24 H, *40*, *45*, *58* and *63*), 1.84 (m, 18 H, *11* and *23*), 2.0 (m, 12 H, *38*, *43*, *56* and *61*), 3.85–3.95 (m, 24 H, *37*, *42*, *55* and *60*), 3.95–4.05 (m, 18 H, *12* and *24*), 6.75 (s, 6 H, *27*), 7.04 (d, J = 16.2 Hz, 3 H, *29*), 7.11 (s, 3 H, *32*), 7.14 (s, 3 H, *35*), 7.17 (d, J = 15.8 Hz, 3 H, *47*), 7.20 (d, J = 15.9 Hz, 3 H, *65*), 7.24 (d, J = 15.8 Hz, 3 H, *48*), 7.40 (d, J = 16.2 Hz, 3 H, *30*), 7.54 (s, 6 H, *50* and *53*), 7.63 (d, J = 15.9 Hz, 3 H, *66*), 7.63 (d, J = 8.1 Hz, 6 H, *68*), 7.89 (d, J = 8.1 Hz, 6 H, *69*), 8.11 (s, 3H, *74*), 8.22 (s, 3H, *72*). ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ {11.31 (3 C), 11.37 (3 C), 11.43 (6 C)} (*41*, *46*, *59* and *64*), 14.00 (9 C, *1* and *13*), {16.68 (3 C), 16.74 (3 C), 16.77 (6 C} (*39*, *44*, *57* and *62*), {22.58 (9 C), [29.26, 29.29] (9 C), 29.33 (9 C), [29.55, 29.60, 29.65] (42 C), 31.95 (9 C)} (*2–9*, *11* and *14–21*), 26.03 (9 C, *10* and *22*), 26.29 (12 C, *40*, *45*, *58* and *63*), 30.24 (3 C, *23*), {34.87 (3 C), 34.98 (3 C), 35.05 (6 C)} (*38*, *43*, *56* and *61*), 68.99 (6 C, *12*), 73.45 (3 C, *24*), {73.94 (3 C), 74.08 (3 C), 74.30 (3 C), 74.36 (3 C)} (*37*, *42*, *55* and *60*), 105.0 (6 C, *27*), 109.5 (3 C, *48*), 109.8 (3 C, *47*), 110.3 (3 C, *32*), 110.9 (3 C, *35*), 122.4 (6 C, *30* and *50*), 123.0 (3 C, *53*), {125.8, 126.0, 126.5, 126.8, 127.1, 127.2, 127.4, 128.3, 128.5} (36 C, *29*, *31*, *34*, *49*, *52*, *65*, *66*, *68*, *69*, *73*, *74*), 132.7 (3 C, *28*), 133.1 (3 C, *70*), 138.1 (3 C, *25*), 141.8 (3 C, *67*), {150.9 (3 C), 151.0 (3 C), 151.1 (3 C), 151.5 (3 C)} (*33*, *36*, *51* and *54*), 153.2 (6 C, *26*), 165.5 (3 C, *71*). IR (UATR): ν (cm^{-1}): 3347, 3061 (N–H stretch); 2958, 2922, 2822, 2853 (C–H stretch); 1649 (C=O stretch); 1604, 1579, 1540, 1504 (C=C stretch); 1465, 1422, 1386, 1340, 1258, 1238, 1201 (C–O–C), 1152, 1116, 1068, 1040, 1010, 962, 917, 893, 854, 838, 808, 796, 773, 761, 731, 697, 672. MALDI-TOF MS (MW = 4047.18): m/z = 4046.36 [M]$^+$, 4069.24 [M + Na]$^+$. Anal. Calcd. For $C_{267}H_{411}N_3O_{24}$: C 79.24, H 10.24, N 1.04. Found: C 78.46, H 10.40, N 1.08%.

N,*N*″,*N*″-Tris{3[3′-[(*E*,*E*,*E*)-4-<4-{4-(3,4,5-trisdodecyloxystyryl)-2,5-bis[(*S*)-2-methyl-butoxy]-styryl}-2,5-bis[(*S*)-2-methylbutoxy]-styryl>}benzene-1,3,5-carboxamide (OPV2)

To a solution of OPV aniline **2**[6] (200 mg, 0.15 mmol) and triethylamine (21 μl) in dry dichloromethane (10 ml) a solution of 1,3,5-benzenetricarboxylic acid chloride (11.8 mg, 0.045 mmol) was added dropwise. The mixture was stirred for 6 hours and the solvent was evaporated *in vacuo*. Purification by column chromatography on silica gel (dichloromethane–pentane 3 : 1) and BioBeads SX-1 (dichloromethane) yielded pure **OPV2** (150 mg, 82%) (Chart 3). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 0.89 (t, 27 H, *1* and *13*), 1.03 (m, 36 H, *41*, *46*, *59* and *64*), 1.13 (m, 36 H, *39*, *44*, *57* and *62*), 1.2–1.4 (m, 72 H, *2–9* and *14–21*), 1.5 (m, 18 H, *10* and *22*), 1.68 (m, 24 H, *40*, *45*, *58* and *63*), 1.84 (m, 18 H, *11* and *23*), 2.0 (m, 12 H, *38*, *43*, *56* and *61*), 3.85–3.95 (m, 24 H, *37*, *42*, *55* and *60*), 3.95–4.05 (m, 18 H, *12* and *24*), 6.75 (s, 6 H, *27*),

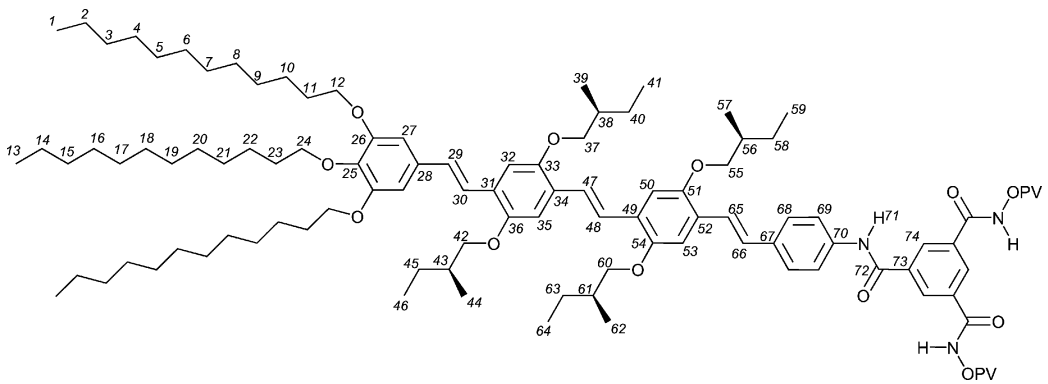


Chart 3 Numbering of the protons and carbon atoms of **OPV2**.

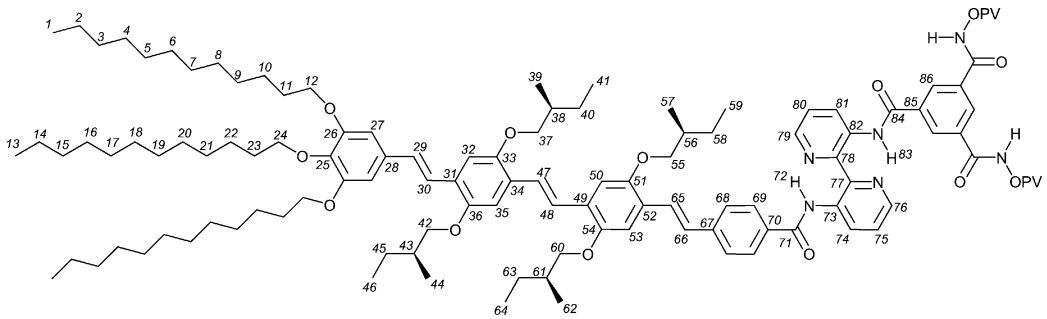


Chart 4 Numbering of the protons and carbon atoms of **OPV3**.

7.02 (s, 3 H, *32*), 7.06 (d, $J = 16.2$ Hz, 3 H, *29*), 7.11 (s, 3 H, *35*), 7.15 (d, $J = 15.8$ Hz, 3 H, *47*), 7.20 (d, $J = 15.9$ Hz, 3 H, *65*), 7.24 (d, $J = 15.8$ Hz, 3 H, *48*), 7.43 (d, $J = 16.2$ Hz, 3 H, *30*), 7.50 (d, $J = 15.9$ Hz, 3 H, *66*), 7.53 (s, 6 H, *50* and *53*), 7.58 (d, $J = 8.1$ Hz, 6 H, *68*), 7.73 (d, $J = 8.1$ Hz, 6 H, *69*), 8.27 (s, 3H, *74*), 8.62 (s, 3H, *71*). IR (UATR): ν (cm^{-1}): 3634, 3347 (N–H stretch); 3061, 2957, 2922, 2853 (C–H stretch); 1649 (C=O stretch); 1589, 1504 (C=C stretch); 1466, 1422, 1388, 1339, 1247, 1201 (C–O–C), 1157, 1117, 1043, 962, 914, 852, 810, 719, 695. MALDI-TOF MS (MW = 4047.18): $m/z = 4046.65$ $[M]^+$.

N,*N*″,*N*″-Tris{3[3′-[(*E*,*E*,*E*)-4-<4-{4-(3,4,5-trisdodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]-styryl}-2,5-bis[(*S*)-2-methylbutoxy]-styryl > benzoylamino]-2,2′-bipyridyl]}benzene-1,3,5-tricarbonamide (OPV3)

To a solution of **3** (80 mg, 0.054 mmol) and triethylamine (8 µl) in dry dichloromethane (5 ml) a solution of 1,3,5-benzenetricarboxylic acid chloride (4.3 mg, 0.016 mmol) in dry dichloromethane (0.5 ml) was added dropwise. The mixture was heated under reflux for 18 hours and evaporated *in vacuo.* Purification by column chromatography on silica gel (ethyl acetate–hexane 1 : 3, product comes off first), preparative size-exclusion chromatography (Bio-Beads) with tetrahydrofuran as eluent and finally precipitation from methanol yielded pure **OPV3** (32 mg, 43%) (Chart 4). $T_g = 253$–254 °C. ^{1}H-NMR (300 MHz, $CDCl_3$, 50 °C, TMS): δ 0.89 (t, 27 H, *1* and *13*), 1.03 (m, 36 H, *41*, *46*, *59* and *64*), 1.12 (m, 36 H, *39*, *44*, *57* and *62*), 1.2–1.4 (m, 72 H, *2–9* and *14–21*), 1.5 (m, 18 H, *10* and *22*), 1.66 (m, 24 H, *40*, *45*, *58* and *63*), 1.79 (m, 18 H, *11* and *23*), 1.96 (m, 12 H, *38*, *43*, *56* and *61*), 3.80–3.90 (m, 24 H, *37*, *42*, *55* and *60*), 3.95–4.05 (m, 18 H, *12* and *24*), 6.73 (s, 6 H, *27*), {6.98 (6 H), [7.04, 7.08] (6 H), [7.15, 7.17] (6 H)} (*29*, *32*, *35*, *47*, *48*, *65*), {7.34 (3H), 7.43 (m, 9 H), 7.50 (9 H)} (*30*, *50*, *53*, *66*, *68*, *75*), 7.86 (d, 6 H, *69*), 8.14 (br, 3 H, *80*), 8.31 (br, 3 H, *86*), 8.82 (br, 3 H, *76*), 9.03 (br, 3 H, *79*), 9.39 (br, 6 H, *74* and *81*), 14.64 (br, 3 H, *72*), 15.30 (br, 3 H, *83*). IR (UATR): ν (cm^{-1}): 3644, 3412, 3060 (N–H stretch); 2957, 2923, 2872, 2854 (C–H stretch); 1725, 1674 (C=O stretch); 1600, 1568, 1505 (C=C stretch); 1467, 1444, 1423, 1374, 1331, 1300, 1260, 1242, 1233, 1202 (C–O–C), 1158, 1116, 1073, 1041 (br), 961, 915, 859, 802, 775, 768, 756, 730, 719, 693, 663. MALDI-TOF MS (MW = 4638.83): m/z: 4633.17 $[M]^+$.

Acknowledgements

3,3′-Diamino-2,2′-bipyridine was kindly provided by Judith van Gorp. Henk Eding and Xianwen Lou are acknowledged for the elemental analysis and mass spectrometry respectively.

References

1 For some recent reviews, see: (*a*) A. Ciferri, *Liq. Cryst.*, 2004, **31**, 1487; (*b*) C. D. Simpson, J. Wu, M. D. Watson and K. Müllen, *J. Mater. Chem.*, 2004, **14**, 494; (*c*) H. M. Keizer and R. P. Sijbesma, *Chem. Soc. Rev.*, 2005, **34**, 226; (*d*) T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2005, **45**, 38; (*e*) R. J. Bushby and O. R. Lozman, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 343.
2 A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2005, 3245.
3 (*a*) A. R. A. Palmans, J. A. J. M. Vekemans, E. E. Havinga and E. W. Meijer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2648; (*b*) A. R. A. Palmans, J. A. J. M. Vekemans, H. Fischer, R. A. Hikmet and E. W. Meijer, *Chem.–Eur. J.*, 1997, **3**, 300; (*c*) A. R. A. Palmans, J. A. J. M. Vekemans, R. A. Hikmet, H. Fischer and E. W. Meijer, *Adv. Mater.*, 1998, **10**, 873; (*d*) M. P. Lightfoot, F. S. Mair, R. G. Pritchard and J. E. Warren, *Chem. Commun.*, 1999, 1645; (*e*) J. Y. Chang, J. R. Yeon, Y. S. Shin, M. J. Han and S.-K. Hong, *Chem. Mater.*, 2000, **12**, 1076; (*f*) Y. Yasuda, E. Iishi, H. Inada and Y. Shirota, *Chem. Lett.*, 1996, 575; (*g*) K. Hanabusa, C. Koto, M. Kimura, H. Shirai and A. Kakehi, *Chem. Lett.*, 1997, 429; (*h*) Y. Matsunaga, N. Miyajima, Y. Nakayasu, S. Sakai and M. Yonenaga, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 207; (*i*) M. L. Bushey, T.-Q. Nguyen, W. Zhang, D. Horoszewski and C. Nuckolls, *Angew. Chem., Int. Ed.*, 2004, **43**, 5546; (*j*) A. Sakamoto, D. Ogata, T. Shikata and K. Hanabusa, *Macromolecules*, 2005, **38**, 8983.
4 (*a*) L. Brunsveld, A. P. H. J. Schenning, M. A. C. Broeren, H. M. Janssen, J. A. J. M. Vekemans and E. W. Meijer, *Chem. Lett.*, 2000, 292; (*b*) J. J. Van Gorp, J. A. J. M. Vekemans and E. W. Meijer, *J. Am. Chem. Soc.*, 2002, **124**, 14759.
5 M. Blomenhofer, S. Ganzleben, D. Hanft, H.-W. Schmidt, M. Kristiansen, P. Smith, K. Stoll, D. Mader and K. Hoffmann, *Macromolecules*, 2005, **38**, 3688.
6 A. El-ghayoury, E. Peeters, A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2000, 1969.
7 P. Jonkheijm, F. Hoeben, R. Kleppinger, J. van Herrikhuyzen, A. P. H. J. Schenning and E. W. Meijer, *J. Am. Chem. Soc.*, 2003, **125**, 15941.
8 See supporting information†.
9 It should be noted that it is not clear if the CD signal is at its maximum at low temperature which could indicate that not all aggregates are fully helical at this temperature. Therefore it is not possible to accurately determine the melting temperature.
10 L. Brunsveld, H. Zhang, M. Glasbeek, J. A. J. M. Vekemans and E. W. Meijer, *J. Am. Chem. Soc.*, 2000, **122**, 6175.
11 J. J. van Gorp, J. A. J. M. Vekemans and E. W. Meijer, *Mol. Cryst. Liq. Cryst.*, 2003, **397**, 491.
12 A. P. H. J. Schenning, P. Jonkheijm, E. Peeters and E. W. Meijer, *J. Am. Chem. Soc.*, 2001, **123**, 409.