Long-range self-assembly of bis(imidazole)-annulated terphenyls

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Received 16th June 2006, Accepted 18th August 2006
First published as an Advance Article on the web 30th August 2006
DOI: 10.1039/b608593h

In our study, we present the synthesis and characterisation of the first bis(imidazole)-annulated terphenyl disc-shaped molecules, which self-organise into columnar structures throughout long-range ordered domains during cooling from the isotropic phase. Two derivatives substituted with 3,7-dimethyloctyl and 2-decyltetradecyl substituents have been prepared. Concentration dependent UV/vis investigations indicated pronounced aggregation of both compounds in solution. The structural analysis of mechanically aligned samples revealed columnar supramolecular order with favoured helical stacking of the discs with a pitch of four molecules independent of the substituents. On the other hand, significant differences in the self-organisation during solidification from the isotropic phase were observed. The bulkier the alkyl side chains, the lower the growth rate and the higher the macroscopic order of the domains. These novel bis(imidazole)-annulated terphenyls are promising candidates for field-effect transistor applications because of the pronounced molecular packing and the formation of macroscopically aligned domains with edge-on arranged molecules.

Introduction

Organic semiconductors have gained increasing attention in the development of electronic devices.[1] One advantage of organic conjugated polymeric materials is the ease with which they can be processed at low cost.[2,3] However, since the long-range order between the electrodes is essential for undisturbed charge carrier transport, many polymer-based field-effect transistors (FETs) demonstrated relatively poor performance due to the high disorder of the conjugated polymer chains. It has been shown previously that discotic liquid crystals are promising alternatives for use in electronics because of their ability to self-organise into highly ordered superstructures *via* π-interactions.[4] In these structures the molecules assemble into columnar arrays which form a percolation pathway for electrons and holes.[5] High charge carrier mobilities along the one-dimensional stacks have been measured with values of up to 1.1 $cm^2\ V\ s^{-1}$.[6] The variation of the core substitution allows fine tuning of the bulk properties and processibility of these materials from solution or from the isotropic phase.[7] A major advantage of discotics is the formation of a liquid crystalline phase which promotes self-healing of macroscopic defects.[8] In contrast to other organic semiconductors, it is also possible to control the organisation of the disc-shaped molecules on surfaces. Thereby, the discs can arrange themselves in an edge-on manner, which is important in FETs,[9] or face-on, leading to a homeotropic phase,[10] which is required in photovoltaic cells.

It has been reported that the formation of complex superstructures of liquid crystalline terphenyls can be successfully tailored by the nature and the position of the substituents.[11] These ternary block molecules self-organised due to a nano-separation between the rigid terphenyl unit and flexible polar and non-polar substituents.[11] Here we present the synthesis of the first bis(imidazole)-annulated terphenyl as a planar disc-shaped building block and its self-assembly into long-ranged columnar superstructures when processed from the melt. The observed pronounced intracolumnar packing of these molecules and the formation of well-ordered and large domains are desired for the implementation of discotic materials in FET devices.

Results and discussion

Most of the previously described heteroaromatic discotic materials have been prepared either by condensation reactions or by oxidative cyclodehydrogenation of suitable precursor materials.[7a,12] Here, the palladium-catalysed intramolecular amination of chlorinated terphenyls **6a/b** with two imidazole substituents to give the planarised polycyclic compounds **1a/b** (Scheme 1) is demonstrated. The terphenyl core **4** was synthesised by a Suzuki coupling of dibromoterephthaldehyde (**2**) with 2-chlorobenzene-boronic acid (**3**) to yield the dichloroterphenyl **4**. To introduce solubility and phase formation, alkyl chains were introduced into the side-groups of the discotic material by alkylation of 4,4′-dihydroxybenzil with 3,7-dimethyloctylbromide and 2-decyltetradecylbromide. The imidazole rings of **6a** and **6b** were generated by condensation of the aldehyde groups of **4** with the benzil functionalities of **5a** and **5b**, respectively. This reaction was performed with ammonium acetate, as an ammonia source, in acetic acid. The molecules **6a** and **6b** were planarised successfully by an intramolecular Buchwald-type reaction.[13] The intramolecular C–N bond formation using palladium(II) acetate, triethylphosphine and sodium *tert*-butoxide proceeded in 87% and 72% yield to produce **1a** and **1b** respectively. This catalyst system was utilised, as the use of bulky ligands like 2-(di-*tert*-butylphosphino)biphenyl did not lead to product formation.

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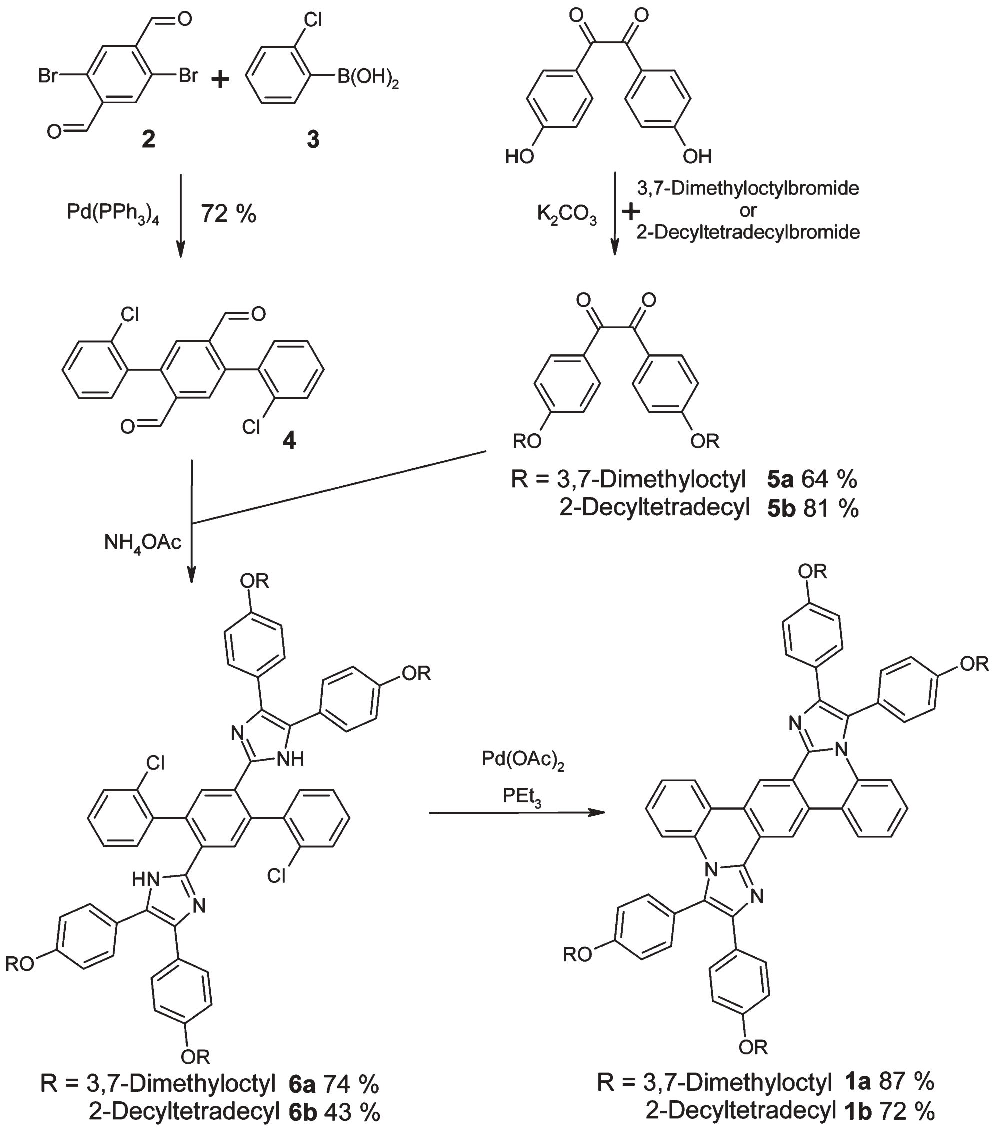

Scheme 1 Synthetic route toward the planarised bis(imidazoles) **1a** and **1b**.

Due to their identical core structure, both compounds (**1a** and **1b**) exhibited identical UV/vis spectra in solution (THF) with a well resolved vibronic structure (Fig. 1). The absorption maxima of **1a** were located at 328 nm, 342 nm, 370 nm and 384 nm, which were the same as the maxima of **1b**. In comparison, the open precursors **6a** and **6b** showed only broad absorption bands with maxima at 377 nm, indicating a less rigid chromophore. The photoluminescence spectra of **1a** and **1b** at high concentrations (20 μmol L^{-1} and 11.6 μmol L^{-1} respectively) revealed broad emission bands with maxima at 468 nm and 467 nm respectively and a vibrational sideband at 447 nm. As the concentration of **1b** was decreased from 11.6 μmol L^{-1} to 0.12 μmol L^{-1}, a new sharp fluorescence band appeared at 416 nm. Similarly, an additional fluorescence band appeared at 417 nm for **1a** when the concentration was reduced from 20 μmol L^{-1} to 0.2 μmol L^{-1}. The vibronic features and the missing hypsochromic shift of the low energy band at lower concentrations suggests that the changes in the photoluminescence spectra did not originate from aggregation. The reason for the additional high energy band at low concentration remains unclear, but we speculate that this high energy band might be due to a transition from a higher vibrational level ($v > 0$) of the first excited state S_1 into the vibrational levels of the ground state S_0.

The differential scanning calorimetry (DSC) scans for both compounds (**1a** and **1b**), Fig. 2, revealed only one phase transition from the columnar phase to the isotropic state. The small exothermic cold-crystallisation peak prior to the main endothermic one was attributed to a supercooling of the sample.[14] The isotropisation temperature decreased from 162 °C ($\Delta H_{\text{2nd heating}}$ = 32.0 J g^{-1}) for **1a** to 114 °C ($\Delta H_{\text{2nd heating}}$ = 5.7 J g^{-1}) for **1b** with increasing steric demand of the dovetailed side chains. Furthermore, the enthalpy decrease of the phase transition indicated a lowering of the order in the solid phase by the introduction of longer alkyl substituents. Additionally, **1a** and **1b** exhibit high thermal stability up to 350 °C.

Two-dimensional wide-angle X-ray diffraction (2D-WAXS) experiments were performed on an extruded fibre to

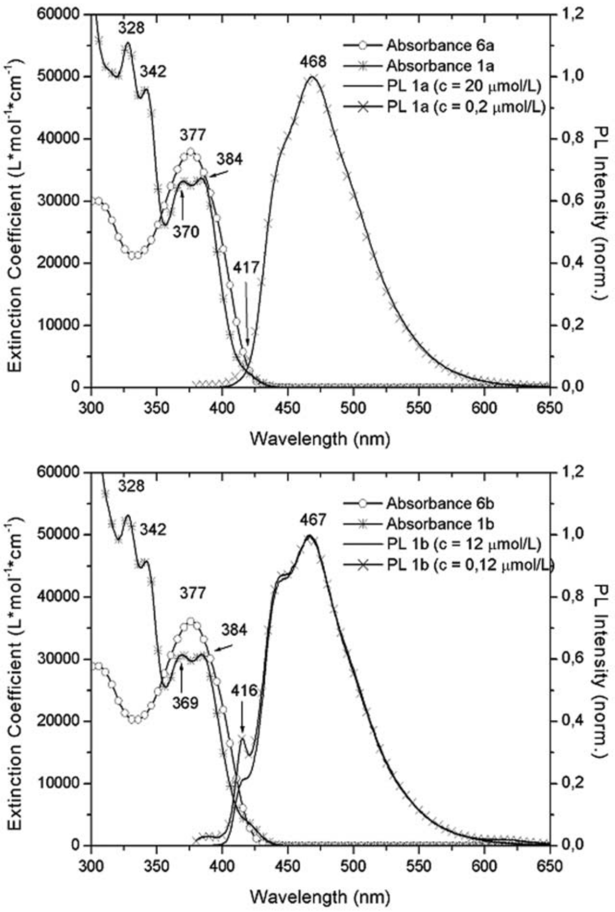

Fig. 1 UV and PL spectra of **1a** and **1b** and UV spectra of the precursors **6a** and **6b** (THF).

investigate the supramolecular structure of the self-assembled molecules (Fig. 3).[15] The 2D lateral tetragonal unit cells, describing the intercolumnar organisation, were assigned from the positions of the sharp equatorial reflections, which were fitted to the characteristic correlation of $1 : \sqrt{2} : 2$ (see Table 1). Packing parameters of a = 2.76 nm for **1a** and of a = 2.86 nm for **1b** were found to be dependent on the length of the side chains. Strong meridional wide-angle reflections at 0.38 nm for **1a** and 0.45 nm for **1b** correspond to face-to-face distances between the disc-shaped molecules and indicate an orthogonal arrangement of their molecular planes relative to the columnar axis. The alkyl chain correlation is in the same range, but appears as an amorphous halo in the X-ray pattern. Middle-range meridional reflections relating to periodicities of 1.82 nm for **1a** and 2.16 nm for **1b** suggest additional intracolumnar correlations between every 5th disc (for **1b** 2.16/0.45 ~ 5). Further multiple meridional reflections confirm a helical arrangement of the molecules along the columns (see Table 1).[16] This helical organisation was formed by a slight rotation of each disc relative to each other, induced by the high steric hindrance of the phenyl rings attached at the corona. In general, a helical arrangement of discotics enhances the molecular packing, leading to higher charge carrier mobilities along the columnar structures.[4]

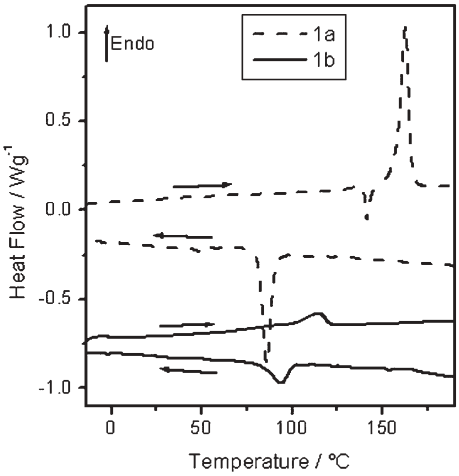

Fig. 2 DSC scans of **1a** and **1b** during first cooling and second heating (10 °C min⁻¹). Arrows indicate the cooling and heating directions.

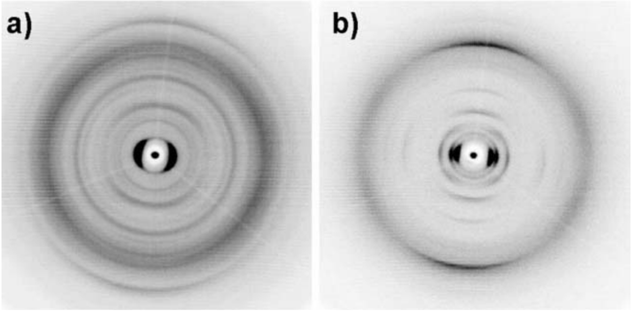

Fig. 3 2D-WAXS patterns of **1a** and **1b** prepared by filament extrusion.

On the basis of the X-ray results, **1a** was a crystalline powder in its solid phase. The phase characterisation of **1b** was less clear. Whereas **1b** was waxy and soft at room temperature, which is characteristic for a mesophase, the rather complex intracolumnar organisation of this material excluded its classification as a liquid crystalline phase. Therefore, compound **1b** was considered to be plastic crystalline.[17]

The accessible isotropisation temperature of both compounds allowed the investigation of the self-assembly from the melt by polarised optical microscopy (POM) at different cooling rates. Close to the crystallisation temperature of **1a**, well-ordered spherulites nucleated randomly over the whole

Table 1 Miller indices (*hkl*) and *d*-spacings (nm) from 2D-WAXS of extruded fibres. The calculated values are given in brackets

	1a	1b
Equatorial reflections		
100	2.76 (2.76)	2.86 (2.86)
110	1.90 (1.96)	2.08 (2.02)
200	1.35 (1.39)	1.43 (1.43)
120	1.19 (1.24)	—
Meridional reflections		
*hk*1	1.82	2.16
*hk*2	0.95	1.13
*hk*3	0.63	0.74
*hk*4	0.38	0.45

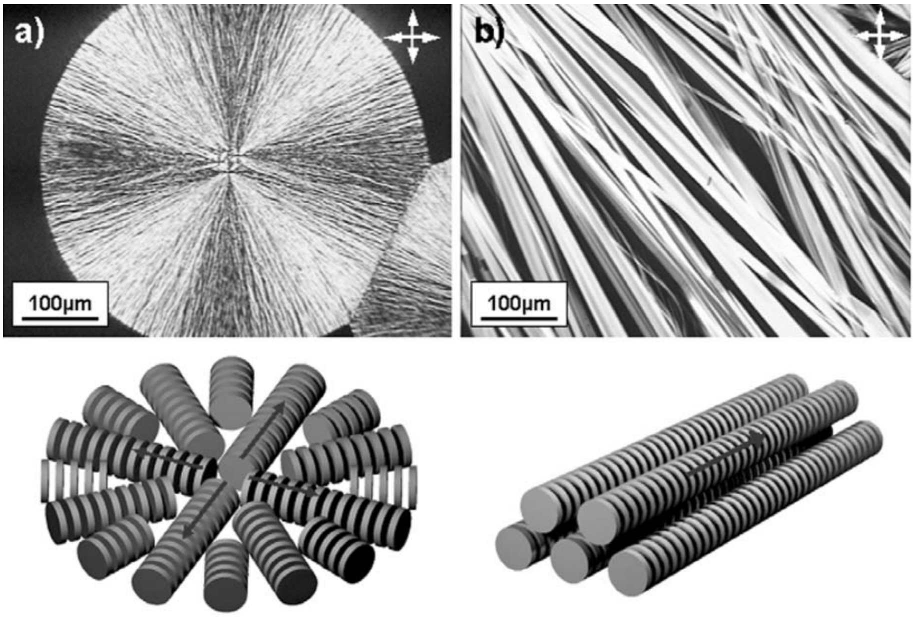

Fig. 4 Cross-polarised optical microscopy images and schematic illustrations of the supramolecular organisations in the structures of a) **1a** and b) **1b** after non-isothermal cooling at rates of 1 °C min^{-1} and 0.1 °C min^{-1}, respectively. The arrows in the drawings represent the assembly directions of the columns during solidification. The samples were prepared between two glass slides.

sample area (Fig. 4a). The high optical anisotropy and the appearance of the Maltese cross indicate pronounced macroscopic order. The extinction along the analyser/polariser direction suggests a radial alignment of the columnar structures from the centre and an edge-on arrangement of the molecules.[18] The atomic force microscopy (AFM) image confirmed this assumption, revealing the topography of the spherulites with growth structures that expanded radially from the nucleation centre (Fig. 5b). Recently, structural studies of spherulites, formed by disc-shaped molecules self-assembled into columnar structures, by using microfocus synchrotron radiation verified the analysis of the POM and AFM experiments.[19] The study of the crystallisation kinetics showed a maximum growth rate at 130 °C, at which domains with sizes of several hundred micrometres were obtained (Fig. 5a). A comparison to the growth rate of polymers is not possible in this case due to significant differences between both systems in macroscopic organisation. In contrast, during slow cooling **1b** formed long and highly birefringent "quasi-crystalline" fibres with lengths exceeding several millimetres (Fig. 4b), in which the columns were oriented uniaxially along the fibre axes. The observed morphology indicated a great tendency of **1a** and **1b** to self-organise over macroscopic dimensions. In comparison, discotic hexa-*peri*-hexabenzocoronenes and perylenetetracarboxydiimides, substituted by short aliphatic side chains, form smaller and less ordered domains with defect structures which possess low uniform birefringence in the POM.[20] The bulkier the alkyl substituents, the weaker the interaction between the molecules, resulting in a lower growth rate and thus in the establishment of domains with improved long-range order.

In conclusion, we have developed a new discotic material based on a planar bis(imidazole)-annulated terphenyl, with

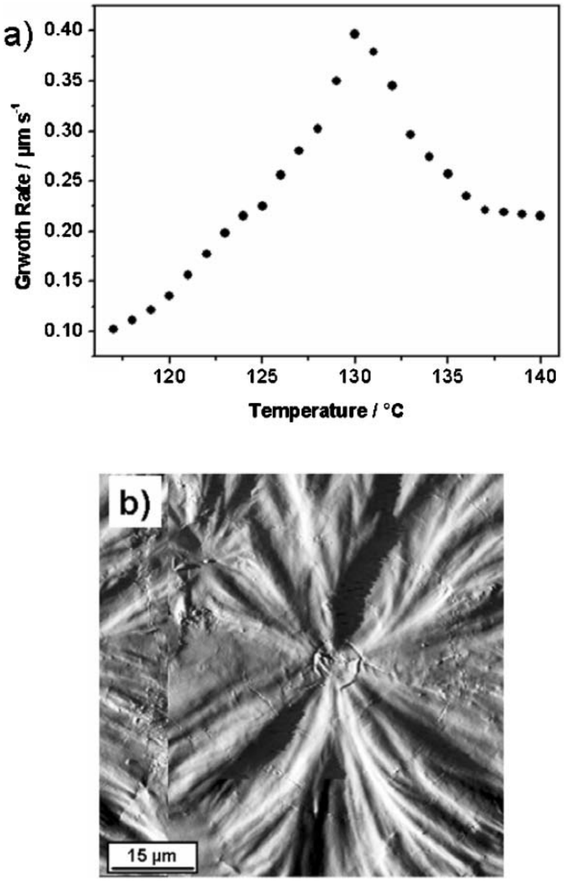

Fig. 5 a) Spherulite growth kinetics of **1a** based on isothermal crystallisation and b) topography image from AFM of **1a** after crystallisation from the isotropic phase (the image was taken in tapping mode).

good solubility and a low isotropisation temperature, allowing facile processibility. The self-assembly took place *via* π-stacking of the rigid cores into columnar superstructures. The compounds **1a** and **1b** showed, independent of the alkyl substituents, favourable helical packing within the columns, which is considered to enhance the one-dimensional charge carrier transport. Additionally, **1a** and **1b** revealed pronounced self-assembly into well-oriented structures over macroscopic dimensions due to directional growth of the material when processed from the melt. In principle, the distance between the electrodes in a device of several tenths of micrometres can be spanned by these "self-aligned" highly ordered supramolecular structures, making the novel bis(imidazole)-annulated terphenyls promising candidates for electronic applications.

The authors acknowledge financial support from the Deutsche Forschungsgemeinschaft (Schwerpunkt Feldeffekt-transistoren) and EU project NAIMO Integrated Project No. NMP4-CT-2004-500355.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 or Bruker AMX 300 with the solvent residual proton or carbon signal as the internal standard. Melting points were determined on a Büchi hot stage apparatus and are not corrected. Mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD by using field desorption (FD). Elemental analyses were carried out on a Foss Heraeus Vario EL. All starting materials were used as purchased from commercial sources. The solvents were dried following standard procedures. 2,5-Dibromoterephthalaldehyde (**2**) and 4,4′-dihydroxybenzil were synthesised according to literature procedures. UV/vis and PL spectra were recorded using a Perkin–Elmer Lambda 9 spectrophotometer and SPEX Fluorolog 2 type F212 spectrometer, respectively.

DSC was performed using a Mettler DSC 30 apparatus with a heating rate of 10 K min^{-1} from −100 °C to 250 °C for **1a**, and from −20 °C to 200 °C for **1b**. The optical textures of the compounds were investigated using a Zeiss microscope with polarising filters equipped with a Hitachi KP-D50 colour digital CCD camera. The samples were sandwiched between two glass slides and then thermally treated on a Linkam hot stage regulated with a Linkam TMS 91 temperature controller. The topography images were obtained in tapping mode by atomic force microscopy (AFM) using a Digital Instruments Nanoscope IIIa MultiMode scanning probe microscope. The 2D-WAXS experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with pinhole collimation and a 2D Siemens detector. A double graphite monochromator for the Cu-Kα radiation (λ = 0.154 nm) was used.

2,2″-Dichloro-[1,1′,4′,1″]terphenyl-2′,5′-dicarbaldehyde (4)

2-Chlorophenylboronic acid (1 g, 6.3 mmol), **2** (888 mg, 3.04 mmol) and Pd(PPh$_3$)$_4$ (73 mg, 0.063 mmol) were dissolved in a degassed mixture of aqueous K$_2$CO$_3$ (2 M, 16 mL) and THF (48 mL). The reaction was stirred under reflux for 48 h and then quenched with HCl (2 M). The mixture was extracted with dichloromethane and the organic fractions were dried with MgSO$_4$. The solvent was removed under reduced pressure and the product was purified by column chromatography (10% ethyl acetate in hexane) and subsequent recrystallisation from ethanol to provide 782 mg (72%) of the title product as a yellow solid, mp 217 °C. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 9.89 (s, 2H), 7.99 (s, 2H), 7.55 (m, 8H). ^{13}C NMR (75.46 MHz, CD$_2$Cl$_2$): δ = 190.86, 142.46, 137.22, 135.96, 133.70, 132.14, 130.67, 130.51, 130.06, 127.66. Anal. Calcd for C$_{20}$H$_{12}$Cl$_2$O$_2$: C, 67.63; H, 3.41. Found: C, 67.49; H, 3.43.

4,4′-Bis(3,7-dimethyloctyloxy)benzil (5a)

4,4′-Dihydroxybenzil (4 g, 16.5 mmol) and K$_2$CO$_3$ (4.58 g, 33.1 mmol) were dissolved in DMF (30 mL) and stirred for 30 min at RT. 3,7-Dimethyloctylbromide (8.05 g, 36.4 mmol) was added and the reaction mixture was stirred for 3 days at 80 °C. The reaction was quenched by the addition of water and the products extracted with dichloromethane. The organic fractions were dried over MgSO$_4$ and the solvent was removed under reduced pressure. The product was purified by column chromatography (5% ethyl acetate in hexane) to give the title compound as a yellow oil (5.51 g, 64%). FD-MS: *m*/*z* = 522.8 [M$^+$] (calcd 522.78), ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): 7.91 (d, J = 8.8 Hz, 4H), 6.98 (d, J = 9.1 Hz, 4H), 4.08 (t, J = 5.95 Hz, 4H, OCH$_2$), 1.85–1.16 (m, 20H), 0.88 (m, 18H, CH$_3$). ^{13}C NMR (75.46 MHz, CD$_2$Cl$_2$): δ = 193.97, 164.98, 132.57, 126.43, 115.11, 67.37, 39.61, 37.59, 36.30, 30.22, 28.38, 25.03, 22.83, 22.73, 19.76.

4,4′-Bis(2-decyltetradecyloxy)benzil (5b)

4,4′-Dihydroxybenzil (6 g, 24.7 mmol), K$_2$CO$_3$ (6.85 g, 49.56 mmol), DMF (40 mL) and 2-decyltetradecylbromide (22.75 g, 54.5 mmol) were treated in the same way as for compound **5a**. The product was purified by column chromatography (5% ethyl acetate in hexane) to give the title compound as a yellow oil 18.54 g (∼81%). *m*/*z* = 916.5 [M$^+$] (calcd 915.53). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 7.91 (d, J = 8.78 Hz, 4H), 8.98 (d, J = 8.8 Hz, 4H), 3.93 (d, J = 5.65 Hz, 4H), 1.80 (m, 2H), 1.26 (m, 80H), 0.87 (t, J = 5.95 Hz, 12H). ^{13}C NMR (75.46 MHz, CD$_2$Cl$_2$): δ = 194.01, 165.22, 132.54, 126.38, 115.12, 71.84, 38.20, 32.32, 31.61, 30.34, 30.06, 30.03, 29.98, 29.74, 27.15, 23.08, 14.26.

2,2″-Dichloro-2′,5′-bis(4,5-bis(4-(3,7-dimethyloctyl)phenyl) imidazol-2-yl)-[1,1′,4′,1″]terphenyl (6a)

Benzil **5a** (1.91 g, 3.66 mmol), **4** (500 mg, 1.41 mmol), ammonium acetate (1.54 g, 54 mmol) and conc. acetic acid (30 mL) were heated at 120 °C for 18 h under argon. After the reaction was cooled, ice (50 mL) was added and the mixture was made basic with aqueous ammonia. The solution was extracted with dichloromethane and dried over MgSO$_4$. The solvent was removed under reduced pressure and the product was purified by column chromatography (10% ethyl acetate in hexane) to give the title compound as a yellow solid (1.42 g, 74%). *m*/*z* = 1360.5 [M$^+$] (calcd 1360.8). ^{1}H NMR (250 MHz, CD$_2$Cl$_2$): δ = 8.31 (m, 2H), 8.14 (d, J = 5.35 Hz, 2H), 7.55

(m, 12H), 6.95 (d, *J* = 8.47 Hz, 4H), 6.77 (d, *J* = 7.22 Hz, 8H), 3.97 (m, 8H, OCH_3), 1.81–1.17 (m, 40H), 0.87 (m, 36H, CH_3). ^{13}C NMR (75.46 MHz, $C_2D_2Cl_4$, 100 °C): δ = 158.93, 143.83, 140.16, 135.85, 134.42, 132.04, 130.73, 130.49, 130.13, 128.93, 128.84, 127.91, 115.24, 67.18, 39.56, 37.63, 36.64, 30.40, 28.12, 24.81, 22.81, 22.75, 19.98. Anal. Calcd for $C_{88}H_{112}Cl_2N_4O_4$: C, 77.67; H, 8.30; N, 4.12. Found: C, 77.70; H, 8.34; N, 4.26.

2,3,11,12-Tetrakis(4-(3,7-dimethyloctyl)phenyl)imidazo[1,2-*f*]imidazo[1′,2′:1,2]quino[4,3-*j*]phenanthridine (1a)

To a mixture of compound **6a** (0.5 g, 0.36 mmol) and NaO*t*Bu (99 mg, 1.03 mmol) in degassed toluene (10 mL) was added, under argon, palladium acetate (4 mg, 0.018 mmol) and triethylphosphine (0.55 mL, 1 M in THF). The reaction was stirred at 115 °C (oil bath) for 48 h and then quenched with HCl (2 M). The solution was extracted with dichloromethane and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was purified by column chromatography (10% ethyl acetate in hexane) to provide 411 mg (87%) of **1a** as a yellow solid. *m*/*z* = 1287.4 [M$^+$] (calcd 1287.88). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 9.68 (s, 2H), 8.78 (d, *J* = 7.53 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 4H), 7.38 (m, 8H), 7.22 (t, *J* = 8.15 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 4H), 6.82 (d, *J* = 8.77 Hz, 4H), 4.13 (m, 4H, OCH_3), 2.98 (m, 4H, OCH_3), 1.94–1.18 (m, 40H), 1.02–0.89 (m, 36H, CH_3). ^{13}C NMR (75.46 MHz, $C_2D_2Cl_4$, 100 °C): δ = 160.40, 158.72, 142.22, 141.51, 134.21, 133.24, 131.87, 129.17, 128.63, 127.97, 127.57, 125.33, 125.27, 124.88, 124.01, 122.77, 118.10, 117.80, 115.91, 114.40, 67.00, 66.72, 39.69, 39.67, 37.76, 37.72, 36.69, 30.38, 30.35, 28.42, 28.40, 25.11, 25.07, 22.88, 22.86, 22.79, 22.76, 19.91, 19.84. Anal. Calcd for $C_{88}H_{110}N_4O_4$: C, 82.07; H, 8.61; N, 4.35. Found: C, 82.13; H, 8.81, N, 4.30.

2,2″-Dichloro-2′,5′-bis(4,5-bis(4-(2-decyltetradecyl)phenyl) imidazol-2-yl)-[1,1′,4′,1″]terphenyl (6b)

Benzil **5b** (3.35 g, 3.66 mmol), **4** (0.2 g, 0.56 mmol), ammonium acetate (1.54 g, 54 mmol) and conc. acetic acid (15 mL) were treated in the same way as for compound **6a**. The product was purified by column chromatography (5% ethyl acetate in hexane) to give the title compound as a yellow solid (515 mg, 43%). *m*/*z* = 2144.3 [M$^+$] (calcd 2146.32), ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ = 8.17–6.74 (m, 24H), 3.73 (d, *J* = 5.05 Hz, 8H), 1.68 (m, 4H), 1.18 (br s, 160H), 0.79 (t, *J* = 6.63 Hz, 24H). ^{13}C NMR (75.46 MHz, CD_2Cl_2): δ = 159.30, 143.73, 140.14, 135.86, 134.40, 132.06, 130.77, 130.49, 130.16, 128.83, 127.94, 115.26, 72.06, 38.47, 32.06, 31.89, 30.19, 29.80, 29.77, 29.43, 27.16, 22.77, 14.14. Anal. Calcd for $C_{144}H_{224}Cl_2N_4O_4$: C, 80.58; H, 10.52; N, 2.61. Found:, 80.06; H, 10.98; N, 2.76.

2,3,11,12-Tetrakis(4-(2-decyltetradecyl)phenyl)imidazo[1,2-*f*]imidazo[1′,2′:1,2]quino[4,3-*j*]phenanthridine (1b)

To a mixture of **6b** (340 mg, 0.158 mmol) and NaO*t*Bu (43 mg, 0.44 mmol) in degassed toluene (7 mL) under argon was added palladium acetate ($\sim$2 mg, 8 $\times$ 10^{-6} mol) and triethylphosphine (0.24 mL, 1 M in THF). The reaction was performed in a similar way to that for compound **1a**. The product was purified by column chromatography (5% ethyl acetate in hexane) to provide 474 mg (72%) of **1b** as a yellow wax. *m*/*z* = 2073.7 [M$^+$] (calcd 2073.4). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 9.48 (s, 2H), 8.52 (d, *J* = 9.15 Hz, 2H), 7.50 (d, *J* = 8.53 Hz, 4H), 7.26 (m, 6H), 7.06 (m, 6H), 6.78 (d, *J* = 8.53 Hz, 4H), 3.92 (m, 4H, $ArOCH_2$), 3.71 (m, 4H, $ArOCH_2$), 1.81 (br s, 4H, alkyl), 1.19 (br s, 160H, alkyl), 0.81 (m, 24H, CH_3). ^{13}C NMR (62.89 MHz, CD_2Cl_2): δ = 160.67, 159.01, 142.27, 141.65, 134.40, 133.20, 129.18, 128.07, 127.49, 125.40, 125.18, 125.09, 124.97, 124.12, 122.82, 118.20, 117.87, 115.97, 114.46, 71.63, 71.34, 38.49, 38.41, 32.33, 31.81, 31.75, 30.46, 30.09, 30.06, 29.77, 27.34, 27.26, 23.09, 14.27. Anal. Calcd for $C_{144}H_{222}N_4O_4$: C, 83.42; H, 10.79; N, 2.70. Found: C, 83.21; H, 10.90; N, 2.79.

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