Room temperature liquid crystalline perylene diester benzimidazoles with extended absorption[†]

André Wicklein, Mathis-Andreas Muth and Mukundan Thelakkat*

Received 27th May 2010, Accepted 30th July 2010 DOI: 10.1039/c0jm01626h

The synthesis, characterization and thermotropic properties of novel asymmetrically substituted discotic molecules, perylene diester benzimidazoles (**PDBIs**), are presented. **PDBIs** were designed with an imidazole unit at 3,4 positions and a bisester moiety at 9,10 positions of the perylene tetracarboxylic acid core. By attaching linear or branched aliphatic substituents at the ester moiety and two alkyl or alkoxy substituents at the benzimidazole unit, sufficient solubility and the flexibility to obtain mesophases was guaranteed. Thermotropic behaviour, which is strongly influenced by the nature of the respective substituents at the diester and benzimidazole moiety, was investigated using differential scanning calorimetry (DSC), polarization optical microscopy (POM) and X-ray diffraction measurements (XRD). All **PDBIs** under investigation self-organize into liquid crystalline columnar hexagonal phases (Col_h), among them **PDBI-3** even at room temperature. Also the formation of a room temperature columnar plastic phase (Col_{hp}) and the formation of a lamellar phase was observed. Due to extension of the π -conjugation system, the absorption of these well soluble discogens is significantly extended to longer wavelengths in the visible regime up to 680 nm.

Introduction

Self-organizing organic semiconductor molecules like discotic liquid crystals (LCs)¹⁻³ have found increased interest as solution processable materials for organic semiconductor applications in areas like light emitting diodes,4 field effect transistors5 or photovoltaic devices.⁶ The uniaxial conducting properties along the π - π stacking axis in self-assembled columnar superstructures of disc-like molecules, consisting of a rigid aromatic core with flexible side-chains attached at the periphery of the mesogen, provide the high charge carrier mobility within the bulk phase which is decisive in organic electronics.7-9 In such materials charge carrier mobilities up to $0.1-1.3 \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$ in their liquid crystalline mesophases have been measured.^{8,10-12} Liquid crystalline organization also increases the local order without creating too many grain boundaries on the macroscopic level as in the case of crystalline materials. It is also desirable to have room temperature LC materials, so that devices can be processed from isotropic melt at high temperatures and the LC order can be maintained at room temperature. However, most discotic semiconductor materials are good hole transporting materials (ptype), while the number of suitable electron transporting materials (n-type) is still very limited.¹³⁻¹⁵ In this context discotic mesogens derived from perylene bisimides^{16,17} (PBI) and related molecules are a promising class of dyes. This is in view of their high electron affinity making them highly attractive as n-type semiconductors and their favourable absorption properties in the visible wavelength regime. Unfortunately, high solubility of PBIs

is often gained at the expense of planarity and loss of strong $\pi - \pi$ interactions, by incorporating substituents at the bay position, which results in twisting of the perylene core. However strong $\pi - \pi$ interactions are required for intermolecular order and efficient charge carrier transport. Very recently we reported on a series of highly soluble discotic liquid crystalline **PBIs** carrying swallowtail *N*-substituents.¹⁸

Another class of liquid crystalline perylene dyes are tetraalkyl esters of perylene tetracarboxylic acid (PTE).¹⁹ But PTEs absorb only in the blue region and are less electron deficient compared to PBIs.²⁰ Therefore it is of fundamental interest to improve the electron deficiency and extend the absorption to longer wavelength region in this class of materials. One elegant way to achieve this is to introduce a fused benzimidazole moiety to the perylene core. It was recently demonstrated for bisimides to get a new class of n-type semiconductors.²¹ Taking these facts into account, we decided to design new soluble asymmetric molecules based on a perylene diester benzimidazole (PDBI) structure in which liquid crystalline organization along with an extended absorption in the red region of visible spectrum was realized. The electron affinity could also be maintained close to that of PBI.18 A substitution at the bay positions of the pervlene core was avoided in all cases in order to maintain planarity and to promote strong π - π interactions.

Results and discussion

Synthesis

Herein, we describe the synthesis of asymmetrically substituted perylene diester benzimidazoles **PDBIs 1–3** (Fig. 1) and their structural, thermotropic, optical and electrochemical properties. **PDBIs** were designed with an imidazole unit at 3,4 positions and a bisester moiety at 9,10 positions of the perylene tetracarboxylic acid core. We attached linear or branched aliphatic substituents

Department of Macromolecular Chemistry I – Applied Functional Polymers, University of Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany; Web: http://afupo.de/index.php. E-mail: mukundan. thelakkat@uni-bayreuth.de; Fax: (+49) 921-55-3206

[†] Electronic supplementary information (ESI) available: Synthesis and characterization of intermediates. Additional figures. See DOI: 10.1039/c0jm01626h



Fig. 1 Synthesis of asymmetric perylene diester benzimidazoles **PDBIs 1–3** i) 1. KOH, H₂O. 2. HCl, pH 8–9. 3. R₁-Br, Aliquat 336, KI, 100 °C ii) *p*TsOH · H₂O, *n*-dodecane/toluene (5 : 1), 95 °C. iii) **2**, Zn(OAc)₂, DMAc, 300 Watt, 160 °C, 20 Min.

at the ester moiety and two alkyl or alkoxy chains at the benzimidazole unit in order to guarantee sufficient solubility and flexibility to obtain mesophases. All these molecules selfassemble into discotic columnar structures also at low temperatures and have an extended absorption range up to 680 nm.

The synthesis of **PDBIs** is carried out by partial hydrolysis of symmetrically substituted perylene tetraesters **PTEs** with pTosOH·H₂O allowing access to diester-anhydrides **1a**, **b** (Fig. 1).²² The benzimidazole moiety was subsequently introduced by condensation of 1,2-diaminophenyls **2a**, **b** with the respective anhydride **1a**, **b** in DMAc using zinc acetate under microwave irradiation conditions to afford highly soluble **PDBIs 1–3** in good yields (> 60%). All three compounds were fully characterized by means of ¹H-, ¹³C-NMR spectroscopy, IR, GPC, MS and microanalyses after thorough purification by column chromatography (for details see Experimental Section). The details of synthesis of perylene tetraesters, diester anhydrides and aromatic *ortho*-diamines are given in ESI.[†]



Fig. 2 UV-vis absorption spectra of **PTE-1** and **PDBIs 1–3** measured in 1.0×10^{-5} M CHCl₃ solution. All **PDBIs** exhibit high molar extinction coefficient values in the whole range from 450 to 600 nm.

Optical and electronic properties

The UV-vis absorption spectra of PDBIs 1-3 and PTE-1 in CHCl₃ solution are presented in Fig. 2. Both tetraesters PTE-1 and PTE-2 exhibit similar absorption spectra as pervlene bisimide with characteristic vibronic bands, but with a blue shift of 54 nm ($\lambda_{max} = 471$ nm). The incorporation of the fused benzimidazole unit significantly extends the absorption of PDBIs 1-3 to longer wavelengths, up to 680 nm. This is almost 100 nm redshifted compared to perylene bisimides (PBIs). The alkoxy substituted PDBIs 2 and 3 exhibit a better absorption range than PDBI-1 carrying only alkyl substituents. All derivatives posses high molar extinction coefficients (ɛ) in the visible range; for instance **PDBI-2** $\epsilon = 3.32 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at $\lambda_{\text{max}} = 554 \text{ nm}$. Thus the extended absorption range of these dyes can be used for efficient light-harvesting in photovoltaic devices. PDBI-2 and 3 absorb in the same wavelength regime but have different fine structures, for instance absorption maxima are located at 554 nm for PDBI-2 and at 516 nm for PDBI-3. As expected the fluorescence maxima are also red-shifted and compared to PDBI-1, PDBI-3 exhibits a higher Stokes-shift (see ESI[†]). For PDBI-2 no fluorescence could be observed in solution.



Fig. 3 (a) Cyclic voltammograms of PDBIs 1–3, showing the first and second reduction peaks. The measurements were conducted in CH_2Cl_2 containing 0.1 M Bu₄NPF₆ with respect to ferrocene–ferrocenium couple (Fc/Fc⁺) at a scan rate of 50 mVs⁻¹. (b) Energy band level diagram showing HOMO- and LUMO- energy levels with corresponding bandgaps of perylene tetraester PTE-1²⁴ and perylene diester benzimidazoles PDBIs 1–3.



Fig. 4 (a) DSC thermograms of **PDBIs 1–3** (scan rate 10 Kmin⁻¹) showing the second heating (solid curves) and first cooling cycle (dashed curve). (b–e) Optical microscopic images of textures of **PDBIs 1–3** (under crossed polarizers). (b) Focal conic texture of Col_h phase of **PDBI-1** at 169 °C. (c) Mosaic texture of Col_h phase of **PDBI-3** at 175 °C. (d) Mixture of mosaic and pseudo focal conic textures representing the Col_h-phase of **PDBI-2** at 220 °C and (e) same film region showing the Col_{hp} phase of **PDEI-2** at 130 °C.

Further the electrochemical stability and reversibility of redox processes were studied using cyclic voltammetry (CV). All the compounds exhibit two reversible reduction peaks. Fig. 3a shows the cyclic voltamogramms of PDBIs 1-3 and Fig. 3b shows the HOMO- and LUMO- energy levels with corresponding bandgaps. In order to calculate the LUMO levels, the first reduction potentials were calibrated with respect to ferroceneferrocenium couple Fc/Fc⁺, which has a quasi-calculated HOMO-energy level of 4.8 eV.23 The HOMO levels were estimated from the optical band gap and the respective LUMO values. The respective optical band gaps, were determined from the absorption edges of absorption spectra of diluted CHCl₃ solutions. The extension of the π -conjugation system between the perylene core and the benzimidazole unit generally accounts for a narrowing of the HOMO-LUMO gap of the PDBI dyes. Moreover, the lowering of band-gap in **PDBIs** is mainly caused by a positive shift in HOMO-value rather than a negative shift in LUMO values. For PDBIs 2 and 3, the band-gap could further be decreased by 0.2 eV by introduction of electron-donating alkoxy substituents at the benzimidazole moiety. This is highly desired if energy loss during charge transfer from donor molecules to PDBI is to be minimized and can also contribute to high open-circuit voltages in photovoltaic devices using PDBIs as acceptors.

Thermotropic properties

PDBIs are highly thermally stable as shown by the high onset decomposition temperatures (T_{on} between 303 and 319 °C) in

thermogravimetric analysis (TGA; see ESI[†]). Thermotropic behaviour of **PDBIs** was analyzed by a combination of differential scanning calorimetry (DSC) and polarization optical microscopy (POM). Additionally temperature dependent small and wide angle X-ray scattering (SAXS and WAXS) experiments were performed to unequivocally determine the structure of the mesophases on the molecular level. All of the derivatives under investigation exhibit thermotropic liquid crystalline mesophases; two of them maintaining their liquid crystalline behavior even at room temperature. DSC thermograms of all **PDBIs** are summarized in Fig. 4a and phase transition temperatures with corresponding transitions enthalpies are presented in Table 1.

Table 1Summary of the thermal behaviour, phase transition tempera-
tures with corresponding transitions enthalpies and phases a of investi-
gated PDBIs 1–3

PDBI	phase transitions ^b (T [°C]/ Δ H [kJmol ⁻¹])
PDBI-1	$\operatorname{Cr}_{L}(120/49.4) \to \operatorname{Col}_{h}(172/3.9) \to \mathrm{I}$
PDBI-2	$\begin{array}{c} 1 \ (168/-2.4) \rightarrow \text{Col}_{h} \ (89/-51.9) \rightarrow \text{Cr}_{L} \\ \text{Cr} \ (-16/18.8) \rightarrow \text{Col}_{hp} \ (165/2.1) \rightarrow \text{Col}_{hd} \ (235/4.5) \rightarrow \text{I} \end{array}$
PDBI-3	I (232/-4.6) → Col _{hd} (160/-2.6) → Col _{hp} (-23/-17.4) → Cr Col _h (183/1.2) → I
	$I(168/-1.9) \rightarrow Col_h$
$a \operatorname{Cr} =$	crystalline phase; $Cr_L = crystalline$ lamellar phase; $Col_h = r_h$ because r_h disordered columnar

"Cr = crystalline phase; Cr_L = crystalline lamellar phase; Col_h = columnar hexagonal mesophase; Col_{hd} = disordered columnar hexagonal mesophase; Col_{hp} = columnar plastic phase; I = isotropic phase. ^b Obtained from DSC measurements at a heating rate of 10 Kmin⁻¹ under nitrogen atmosphere.

The DSC heating curve of PDBI-1 shows two reversible transitions at 120 °C (49.4 kJ/mol) and 172 °C (3.9 kJ/mol). The corresponding transitions on cooling are observed at 168 °C and 89 °C (Fig. 4a). POM experiments upon cooling from the isotropic melt (Fig. 4b) gave evidence for a columnar hexagonal $(Col_{\rm h})$ ordering in the high temperature phase (*ca.* 120–172 °C). As can be seen, large focal conic textures were observed. Also X-ray diffraction experiments are in accordance with a columnar hexagonal ordering of the mesogens. The diffractogram of PDBI-1 in the mesophase and at room temperature (dashed curve) is presented in Fig. 5a. At 140 °C, we observed a 2D hexagonal lattice with $a_{hex} = 32.9$ A which is in reasonable agreement with the (100), (110) and (210) Bragg reflections with the typical ratios of the *d*-values of $1:\sqrt{3}:\sqrt{7}$ (For details see ESI^{\dagger}). The relatively broad reflection at 25.3° in the wide angle regime depicts a moderate intracolumnar long-range order with a π - π stacking distance of $d_{\pi\pi} = 3.52$ Å. Upon further cooling to 95 °C, PDBI-1 forms spherulites under crossed polarizers (see ESI[†]). This texture remains the same on cooling down to room temperature. X-ray diffraction experiments at RT show (001) and its corresponding higher-order reflections, up to (006) as shown in Fig. 5a (dashed curve). This corresponds to one dimensional translational order^{25,26} with a layer distance of 41.6 Å. The d-spacings estimated from the position of Bragg reflections are exactly in the ratios 1: 1/2: 1/3: 1/4, etc. Thus PBBI-1 exhibits a lamellar ordering below 95 °C. Nevertheless the mixed reflexes in the wide-angle regime could not yet be assigned.

PDBI-2 carrying alkoxy substituents at the benzimidazole moiety depicts a quite different thermotropic behaviour. Here three reversible transitions can be observed in DSC measurements, at -16 °C (18.8 kJ/mol), 165 °C (2.1 kJ/mol) and 235 °C (4.5 kJ/mol) during heating. From POM and XRD the transitions can be assigned as $Cr \rightarrow Col_{hp} \rightarrow Col_{hd}$. Thus compared to **PDBI-1**, **PDBI-2** exhibits additionally a transition from a highly ordered liquid crystalline columnar plastic phase $(Col_{hp})^{27}$ to a columnar hexagonal disordered phase (Col_{hd}) at 165 °C.

The fact that the enthalpy for the $Col_{hp} \rightarrow Col_{hd}$ transition is small compared to the enthalpy of the $Col_{hd} \rightarrow I$ transition at 235 °C supports the existence of a Col_{hp} phase between -16 °C and 165 °C.3,28 This is in line with the loss of shear ability of the texture in POM when the sample is cooled under 165 °C. In the Col_{hd} phase PDBI-2 features a mixture of mosaic and pseudo focal conic textures under crossed polarizers (Fig. 4d) and only negligible textural changes are observable for the transition at 165 °C to the plastic phase (Fig. 4e). XRD measurements in the Col_{hp} phase (cf. Fig. 5b dashed curve) indicates that the cores of the mesogen are regularly stacked as can be deduced from the relatively sharp reflection peak at 24.5°. This corresponds to a stacking distance of $d_{\pi\pi} = 3.50$ Å. The absence of any peaks in the wide angle regime between 165 °C and 235 °C is characteristic for a disordered nature of the columns in the Colhd phase (solid curve). For both phases the Bragg reflections in the small-angle regime correspond to a 2D hexagonal lattice (see ESI[†]).



Fig. 5 X-ray diffraction patterns of (a) **PDBI-1** in Col_h phase (140 °C) and crystalline lamellar Cr_L phase (RT). (b) **PDBI-2** in Col_{hd} phase (200 °C) and Col_{hp} phase (120 °C). (c) **PDBI-3** in Col_h phase at 160 °C and RT. (d) Schematic representation of 2D discotic columnar hexagonal packing.

PDBI-3 with two branched alkyl chains at the ester groups possess only one reversible phase transition at 183 °C in DSC upon heating. Here mosaic textures can be observed at 175 °C in POM (Fig. 4c), indicating a Colh phase. Further characteristic dendritic textures are given in ESI[†]. It is also worthy to note that **PDBI-3** shows a partial homeotropic alignment of the columns as observed in POM micrographs employing a $\lambda/4$ plate (see ESI[†]). Here X-ray diffraction gave evidence for the existence of a liquid crystalline columnar hexagonal lattice in the whole temperature range below the transition to the isotropic phase. Fig. 5c depicts the diffractograms at 160 °C and at RT. It is obvious that the intracolmnar ordering (see 001 reflection) increases with lowering of temperature. The fact that PDBIs 2 and 3 are liquid crystalline even at RT is highly interesting for applications requiring high order in molecular arrangement. 2D lattice parameters and $\pi - \pi$ stacking distances $d_{\pi\pi}$ of all **PDBIs** are summarized in Table 2.

Conclusion

In summary, we synthesized three discotic molecules belonging to a novel class of semiconductors, perylene diester benzimidazoles. All these molecules exhibit extended absorption up to 680 nm. Even compared to perylene bisimides, these materials thus exhibit longer wavelength absorption with 130 nm red-shift due to further extension of π -conjugation via the benzimidazole group. The decrease in band gap energy was essentially achieved by a shift of the HOMO value. All PDBIs self-organize into liquid crystalline columnar hexagonal phases (Col_b) at higher temperatures below 250 °C; PDBIs 2 and 3 even at room temperature. Also the existence of a columnar plastic phase (Col_{hp}) for PDBI-2 and a lamellar ordering for PDBI-1 was observed at room temperature. This self-assembling behaviour should allow for an orientation of PDBIs 2 and 3 in the high temperature liquid crystalline phase and for a transfer of the orientation during cooling to a highly ordered phase at room temperature. All of these properties make n-type semiconducting PDBIs promising candidates for applications in organic electronics.

Table 2 X-ray diffraction data of liquid crystalline mesophases of **PDBIs 1–3**. 2D Lattice parameters and π - π stacking distance $d_{\pi\pi}$ as determined from temperature dependent X-ray diffraction experiments

PDBI	T [°C]	lattice parameters ^a [Å]	$d_{\pi\pi}{}^{b}[A]$	phase ^c
PDBI-1	120	$a_{hex} = 32.9$	3.52	Col_h
	RT	$d_{L} = 41.6$	-	CrL
PDBI-2	200	$a_{hex} = 34.0$	-	Col _{hd}
	120	$a_{hex} = 35.9$	3.50	Colhp
PDBI-3	160	$a_{hex} = 30.6$	3.49	Colh
	RT	$a_{hex} = 31.8$	3.49	Col _h

^a Hexagonal lattice parameter

$$a_{hex} = \sqrt[2]{\frac{d}{a}} d_{\pi\pi}^2.$$

 b From (001) reflex. c Col_{ho} = ordered columnar hexagonal; Col_{hd} = disordered columnar hexagonal; Col_{hp} = columnar plastic; Cr_L = crystalline lamellar phase.

Experimental section

Materials and methods

The starting materials, perylenetetracarboxylic acid dianhydride PTCDA, 1-bromododecane, 3-(bromomethyl)heptane, Aliquat 336, Catechol, dibenzo-18-crown-6, hydrazine monohydrate, palladium on carbon (10% Pd), *p*-toluenesulfonic acid monohydrate, zinc acetate and solvents were purchased from Aldrich, Fluka, Acros or TCI and used without any further purification. Solvents used for precipitation and column chromatography were distilled under normal atmosphere. DMAc (anhydrous with crowncap, 99.5%) and *ortho*-dichlorobenzene (anhydrous with crowncap, 99.0%) were purchased from Fluka and Aldrich.

¹H- and ¹³C-NMR spectra were recorded on a Bruker AC 300 spectrometer (300 MHz and 75 MHz, respectively). Chemical shifts are reported in ppm at room temperature using CDCl₃ as solvent and tetramethylsilane as internal standard unless indicated otherwise. Abbreviations used for splitting patterns are s = singlet, d = dublett, t = triplet, qui = quintet, m = multiplet. FTIR-spectra were recorded with a Perkin Elmer Spectrum 100 (FTIR) in the range of 400–4000 cm⁻¹. Oligomeric size exclusion chromatography (Oligo-SEC) was used to determine the purity of synthesized perylene bisimides. Oligo-SEC measurements were performed utilizing a Waters 515-HPLC pump with stabilized THF as eluent at a flow rate of 0.5 ml/min. 20 µl of a solution with a concentration of approx. 1 mg/ml were injected into a column setup, which consists of a guard column (Varian; 5×0.8 cm; mesopore gel; particle size 3 μ m) and two separation columns (Varian; 30×0.8 cm; mesopore gel; particle size 3 μ m). The compounds were monitored with a Waters 486 tunable UV detector at 254 nm and a Waters 410 differential RI detector. Mass spectroscopic (MS) data were obtained from a FIN-NIGAN MAT 8500 instrument. UV-vis spectra were recorded with a Perkin Elmer Lambda 900 spectrophotometer. Photoluminescence spectra were acquired on a Shimadzu RF 5301 PC spectrofluorophotometer. The thermal degradation was studied using a Mettler Toledo TGA/SDTA 851e with a heating rate of 10 Kmin⁻¹ under N₂ atmosphere. Differential scanning calorimetry (DSC) was carried out with a Perkin Elmer differential scanning calorimeter (Diamond) with heating and cooling rates of 10 K/min under N₂ atmosphere. The instrument was calibrated with indium standards before measurements. Phase transitions were also examined by a polarization optical microscope (POM) Nikon Diaphot 300 with a Mettler FP 90 temperature-controlled hot stage. X-ray diffraction measurements were performed on a Huber Guinier Diffraktometer 6000 equipped with a Huber quartz monochromator 611 with Cu- $K_{\alpha 1}$: 1.54051 Å. For cyclic voltammetry (CV) experiments, a conventional three-electrode assembly using a Ag/AgNO₃ reference electrode was used. CH₂Cl₂ containing 0.1 M Bu₄NPF₆ was used as solvent. All measurements were carried out under N2-atmosphere at a scan rate of 0.05 Vs⁻¹ at 25 °C and all redox potentials were calibrated to ferrocene/ferrocenium couple (Fc/Fc⁺).

General procedure for the preparation of perylene diester benzimidazoles PDBI 1 to 3

A mixture of the respective diester anhydride 1a, b (0.3 mmol) and zinc acetate (0.5 mmol) were dissolved in dry DMAc (6 mL)

in a microwave pressure tube and the respective ortho-diamine 2a, b (0.4 mmol) was added. The condensation was carried out under microwave irradiation conditions for 25 min at 160 °C and 300 W. The violet crude product was precipitated in methanol (300 mL) and filtered. The residue was washed with H2O (2×30 mL) and methanol (3×30 mL) and dried over night at 60 °C in vacuo. The crude product was purified *via* column chromatography.

Synthesis of bisdodecyl-perylene-3,4-(4,5-bisdodecyl-1,2-benzimidazole)-9,10-dicarboxylate PDBI-1

1a (0.22 g, 0.3 mmol) and diamine 2a (0.20 g, 0.4 mmol) were allowed to react according to the general procedure. The crude product was purified via column chromatography (silica flashgel, eluent CHCl₃:acetone 20 : 1 v/v). Yield: 0.27 g (80%) as violet solid. Calcd. for C₇₈H₁₁₀N₂O₅: C 80.06, H 9.59, N 2.42. Found: C 80.58, H 9.66, N 2.16. EI-MS (70 eV): m/z 1155 ([M+], 8%). IR (ATR): v = 2915 (s), 2848 (s), 1714 (s), 1690 (s), 1596 (m), 1468 (s), 1358 (s), 1171 (s), 743 (s) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, 298 K) $\delta = 8.74 - 8.65$ (m, 2H, H_{Ar}), 8.48 - 8.36 (m, 4H, H_{Ar}), 8.28 -8.24 (m, 1H, H_{Ar}), 8.12-8.06 (m, 2H, H_{Ar}), 7.61-7.57 (m, 1H, H_{Ar}), 4.36 (t, ${}^{3}J = 6.9$ Hz, 4H, O-CH₂), 2.80–2.69 (m, 4H, benzimidazol-CH₂), 1.90-1.78 (m, 4H, OCH₂-CH₂), 1.76-1.62 (m, 4H, benzimidazole-CH2-CH2), 1.53-1.15 (m, 72H, CH2), 0.95- $0.84 (m, 12H, CH_3) \text{ ppm.}^{13}\text{C-NMR} (75 \text{ MHz}, CDCl_3, 298 \text{ K}) \delta =$ 168.3 (2C, O-C=O), 159.4 (1C, N-C=O), 147.6 (1C, N-C=N), 142.1, 139.4, 139.0, 135.9, 132.5, 132.3, 131.8, 131.0, 130.3, 130.0, 129.8, 129.0, 128.6, 127.4, 126.6, 126.1, 122.4, 121.8, 120.3, 119.2, 115.1 (26C, CAr), 65.8 (2C, O-CH₂), 32.8, 32.0, 31.3, 30.9, 30.0, 29.8, 29.7, 29.6, 29.4, 28.7, 26.1, 22.7 (42C, CH₂), 14.1 (4C, CH₃) ppm.

Synthesis of bisdodecyl-perylene-3,4-(4,5-bisdodecyloxy-1,2benzimidazole)-9,10-dicarboxylate PDBI-2

1a (0.30 g, 0.4 mmol) and diamine 2b (0.29 g, 0.6 mmol) were allowed to react according to the general procedure. The crude product was purified via column chromatography (silica flashgel, eluent CHCl₃:acetone 20:1 v/v). Freeze-drying from benzene gave the violet product PDBI-2. Yield: 0.28 g (59%) as violet solid. Calcd. for C₇₈H₁₁₀N₂O₇: C 78.88, H 9.33, N 2.36. Found: C 78.75, H 9.32, N 2.30. EI-MS (70 eV): m/z 1187 ([M+], 5%). IR (ATR): $\nu = 2917$ (s), 2849 (s), 1720 (s), 1677 (s), 1592 (m), 1465 (s), 1364 (m), 1293 (s), 1170 (s), 746 (s) cm⁻¹. ¹H-NMR (300MHz, CDCl₃, 298 K) $\delta = 8.69$ (d, ${}^{3}J = 8.12$ Hz, 2*H*, H_{Ar}), 8.50–8.38 (m, 4H, H_{Ar}), 8.13–8.05 (m, 3H, H_{Ar}), 7.34 (s, 1H, H_{Ar}), 4.36 (t, ${}^{3}J =$ 6.8 Hz, 4H, O-CH₂), 4.22-4.09 (m, 4H, benzimidazole-OCH₂), 2.01-1.89 (m, 4H, OCH2-CH2), 1.89-1.78 (m, 4H, benzimidazole-CH₂-CH₂), 1.52-1.14 (m, 72H, CH₂), 0.97-0.82 (m, 12H, CH₃) ppm. ¹³C-NMR (75 MHz, CDCl₃, 298 K) $\delta = 168.3$ (2C, O-C=O), 159.5 (1C, N-C=O), 148.8 (1C, N-C=N), 147.0, 139.4, 137.8, 136.3, 132.5, 132.2, 131.9, 131.3, 131.0, 130.4, 130.2, 129.2, 128.7, 127.4, 126.4, 126.1, 125.6, 122.4, 121.8, 120.6, (26C, CAr), 69.7, 69.5 (2C, benzimidazole-O-CH2), 65.8 (2C, O-CH2), 31.9, 31.3, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.6, 26.1, 22.7 (40C, CH₂), 14.1 (4C, CH₃) ppm.

Synthesis of bis(2-ethylhexyl)-perylene-3,4-(4,5-bisdodecyl-oxy-1,2-benzimidazole)-9,10-dicarboxylate PDBI-3

1b (0.50 g, 0.8 mmol) and diamine 2b (0.80 g, 1.7 mmol) were allowed to react according to the general procedure. Then, CHCl₃ (100 mL) was added to the mixture and the violet crude product was washed with water (2 \times 100 mL). The organic layer was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. The crude product was purified via column chromatography (silica flashgel, eluent CHCl₃:MeOH 95 : 5 v/v). Freeze-drying from benzene gave the violet product PDBI-3. Yield: 0.55 g (65%) as violet solid. Calcd. for $C_{70}H_{94}N_2O_7$: C 78.17, H 8.81, N 2.60. Found: C 77.26, H 8.93, N 2.46. EI-MS (70 eV): m/z 1074 ([M⁺], 29%). IR (ATR): $\nu = 2922$ (s), 2853 (s), 1710 (s), 1687 (s), 1592 (m), 1455 (s), 1364 (w), 1290 (s), 1169 (s), 745 (m) cm⁻¹. ¹H-NMR (300 MHz, CDCl₃, 298 K) $\delta = 8.76-8.64$ (m, 2H, H_{Ar}), 8.54–8.41 (m, 4H, H_{Ar}), 8.15–8.07 (m, 3H, H_{Ar}), 7.36 (s, 1H, H_{Ar}), 4.37-4.26 (m, 4H, O-CH₂), 4.23-4.10 (m, 4H, benzimidazole-O-CH2), 2.00-1.88 (m, 2H, OCH2-CH), 1.87-1.77 (m, 4H, benzimidazole-CH₂-CH₂), 1.61-1.23 (m, 52H, CH₂), 1.05–0.86 (m, 18H, CH₃) ppm. ¹³C-NMR (75 MHz, $CDCl_3$, 298 K) $\delta = 168.4$ (2C, O–C=O), 159.9 (1C, N–C=O), 148.8 (1C, N-C=N), 147.1, 137.9, 136.4, 132.4, 132.3, 131.9, 131.3, 131.1, 130.2, 129.9, 129.2, 128.8, 127.4, 126.4, 126.1, 125.7, 122.6, 121.8, 120.6, 103.7, 100.1 (26C, CAr), 69.7, 69.5 (2C, benzimidazole-O-CH₂), 68.0 (2C, O-CH₂), 38.8 (2C, O-CH₂-CH), 32.0, 30.5, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 26.1, 23.9, 23.0, 22.7 (28C, CH₂), 14.1, 11.0 (6C, CH₃) ppm.

Acknowledgements

Financial Support from SPP 1355 (DFG) is kindly acknowledged.

Notes and references

- S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Haegele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, *Angew. Chem., Int. Ed.*, 2007, 46, 4832–4887.
- 2 S. Kumar, Chem. Soc. Rev., 2006, 35, 83-109.
- 3 C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121–146.
- 4 G. Lüssem and J. H. Wendorff, Polym. Adv. Technol., 1998, 9, 443-460.
- 5 H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Slegrist, W. Li, Y. Y. Lin and A. Dodabalapur, *Nature*, 2000, **404**, 478–481.
- 6 L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, 293, 1119–1122.
- 7 P. Wojciech, Z. Matthias, C. Ji Young, M. Klaus and Z. Rudolf, Macromol. Rapid Commun., 2009, 30, 1179–1202.
- 8 S. Sergeyev, W. Pisula and Y. H. Geerts, *Chem. Soc. Rev.*, 2007, 36, 1902–1929.
- 9 D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbachi, H. Ringsdorf and D. Haarer, *Nature*, 1994, **371**, 141–143.
- 10 J. M. Warman, M. P. de Haas, G. Dicker, F. C. Grozema, J. Piris and M. G. Debije, *Chem. Mater.*, 2004, **16**, 4600–4609.
- 11 B. A. Jones, M. J. Ahrens, M.-H. Yoon, A. Facchetti, T. J. Marks and M. R. Wasielewski, Angew. Chem., Int. Ed., 2004, 43, 6363–6366.
- 12 M. Gsänger, J. H. Oh, M. Könemann, H. W. Höffken, A.-M. Krause, Z. Bao and F. Würthner, *Angew. Chem. Int. Ed.*, 2010, 49, 740–743.
- 13 Y.-D. Zhang, K. G. Jespersen, M. Kempe, J. A. Kornfield, S. Barlow, B. Kippelen and S. R. Marder, *Langmuir*, 2003, **19**, 6534–6536.
- 14 R. J. Chesterfield, J. C. McKeen, C. R. Newman, P. C. Ewbank, D. A. da Silva Filho, J.-L. Bredas, L. L. Miller, K. R. Mann and C. D. Frisbie, *J. Phys. Chem. B*, 2004, **108**, 19281–19292.

- 15 M. J. Sienkowska, J. M. Farrar, F. Zhang, S. Kusuma, P. A. Heiney and P. Kaszynski, J. Mater. Chem., 2007, 17, 1399– 1411.
- 16 H. Langhals, Helv. Chim. Acta, 2005, 88, 1309-1343.
- 17 F. Würthner, Chem. Commun., 2004, 1564-1579.
- 18 A. Wicklein, A. Lang, M. Muth and M. Thelakkat, J. Am. Chem. Soc., 2009, 131, 14442–14453.
- 19 S. Benning, H.-S. Kitzerow, H. Bock and M.-F. Achard, *Liq. Cryst.*, 2000, **27**, 901–906.
- 20 M. Oukachmih, P. Destruel, I. Seguy, G. Ablart, P. Jolinat, S. Archambeau, M. Mabiala, S. Fouet and H. Bock, *Sol. Energy Mater. Sol. Cells*, 2005, **85**, 535–543.
- 21 A. Wicklein, P. Kohn, L. Ghazaryan, T. Thurn-Albrecht and M. Thelakkat, *Chem. Commun.*, 2010, 46, 2328.

- 22 C. Xue, R. Sun, R. Annab, D. Abadi and S. Jin, *Tetrahedron Lett.*, 2009, **50**, 853–856.
- 23 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, Adv. Mater., 1995, 7, 551–554.
- 24 X. Mo, H.-Z. Chen, Y. Wang, M.-M. Shi and M. Wang, J. Phys. Chem. B, 2005, 109, 7659–7663.
- 25 K. Ohta, H. Muroki, A. Takagi, K.-I. Hatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 1986, 140, 131–152.
- 26 H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, 1988, 163, 211–219.
- 27 S. K. Prasad, D. S. S. Rao, S. Chandrasekhar and S. Kumar, *Mol. Cryst. Liq. Cryst.*, 2003, **396**, 121–139.
- 28 D. M. Collard and C. P. Lillya, J. Am. Chem. Soc., 2002, 113, 8577– 8583.