

Butterfly-mesogens: *para*-cyclophane based macrocyclic metallomesogens forming smectic and columnar liquid crystalline phases†

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The combination of two different molecular architectures, the rather rod-like *para*-cyclophanes and two half disc-like 1,3-diketone units fused *via ortho*-palladation leads to new liquid crystalline materials with a quite unusual molecular shape. By increasing the number of attached alkyl chains a discontinuous transition from a lamellar to a columnar organisation of the molecules was observed. Compounds with twelve alkyl chains are the first *para*-cyclophane derivatives that show thermotropic columnar mesophase behaviour.

Introduction

After the discovery of disc-like liquid crystals in 1977¹ the incorporation of macrocyclic structures into such molecules became an important challenge. This is because it was hoped that the combination of their special molecular structures, which enables them to stack in columns, can be combined with the ability of macrocycles to enclose guest molecules and ions,² effects, which might reinforce potential technological applications of such systems in the field of molecular electronics, photonics and ion transport.³ A large number of such macrocyclic liquid crystals are structurally related to completely rigid porphyrins and phthalocyanines, rigid but not flat cyclotrimeratrylenes (CTV's), semiflexible cyclotetraeratrylenes (CTTV's) and calixarenes, or flexible crown ethers and azacrowns.⁴ Recently, another, more unconventional type of macrocyclic compound exhibiting mesomorphic properties has been reported. In these macrocycles conformationally rigid⁵ or flexible⁶ rod-like units are connected by flexible spacers, *e.g.* polyether- and/or alkyl chains. Due to the fixation of the rod-like segments at their terminal ends inside the cyclic structure, they exhibit nematic and smectic mesophases that are much more stable than those of the corresponding low and high molecular mass open chain liquid crystals. Additionally, the combination of different rigid units allows the introduction of special properties, such as donor-acceptor properties^{7a} and to construct novel metallomesogens.^{7b}

However, exclusively nematic and smectic mesophases have been realised with these materials up to now.

†The procedures and analytical data for all compounds are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/jm/b0/b003594g/>

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Results and discussion

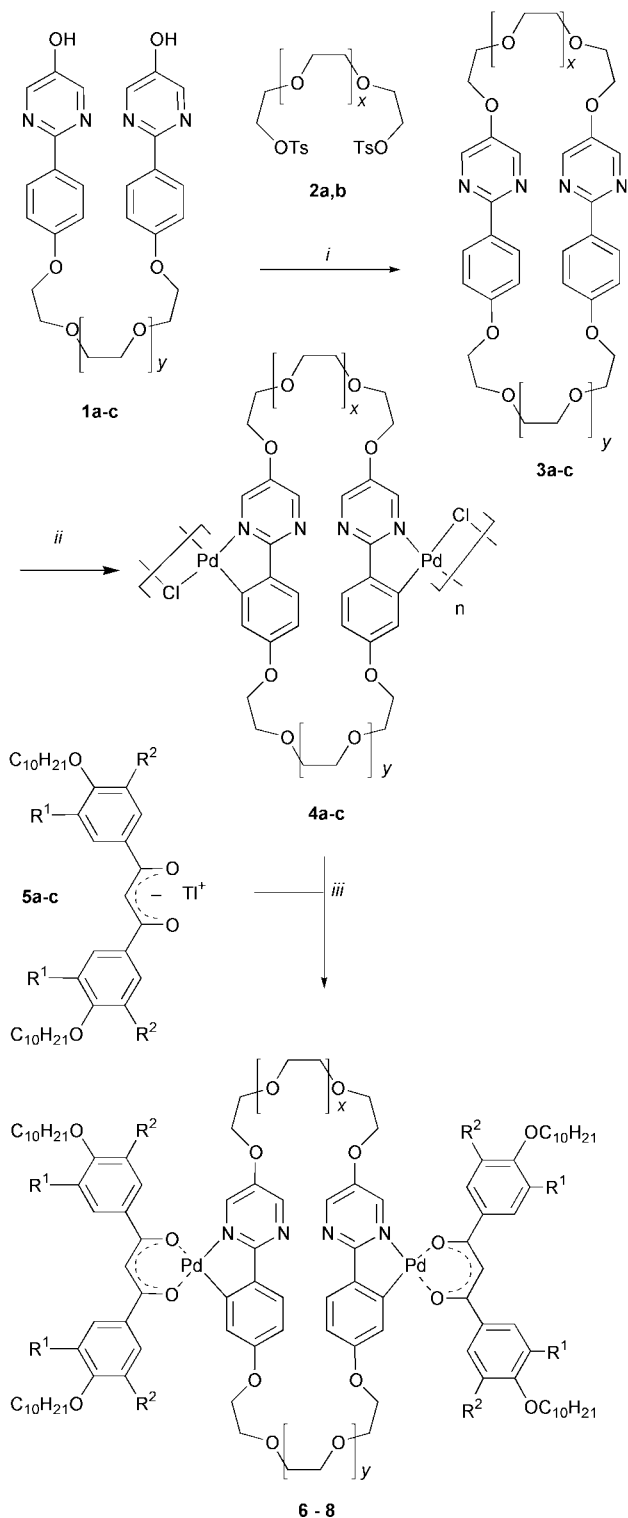
Synthesis

In an attempt to create new types of metal containing liquid crystals with new and unusual molecular shapes we have synthesised novel macrocyclic molecules combining two half-disc units *via* flexible polyether chains. For this purpose macrocyclic polyether cyclophanes combining two 2-phenylpyrimidine units (compounds **3a–3c**) have been synthesised. They were obtained as shown in Scheme 1 by cyclisation of **1a–1c**⁸ with **2**⁹ under high dilution conditions in the presence of potassium toluene-4-sulfonate (K⁺OTos[−]) as template and result in yields of 25% to 40%. The two 2-phenylpyrimidine units incorporated in the macrocyclic structures of compounds **3a–3c** were *ortho*-palladated by treatment with [Pd(C₆H₅CN)₂Cl₂] in ethanol.¹⁰ Insoluble pale yellow polymeric materials¹¹ (compounds **4**) were obtained, which decompose without melting on heating above 360 °C. Treatment of these polymers of fused macrocycles with thallium(I) salts of aromatic 1,3-diketones (**5**)^{12,13} results in the formation of the bright yellow dinuclear Pd-complexes **6–8** (Scheme 1). To study the influence of the number of alkoxy chains on the mesophase behaviour we used 1,3-diketones with two, four or six alkoxy chains. Thus, we obtained compounds **6–8** with four, eight and twelve long alkyl chains connected with the macrocycle.

Liquid crystalline properties

All compounds were investigated by optical microscopy between crossed polarisers. The transition temperatures of the macrocycles **3a–c** are listed in Table 1. On heating, all three *para*-cyclophanes melt to isotropic liquids, and only on cooling a monotropic (metastable) nematic phase could be observed.

The mesomorphic properties of the dinuclear Pd-complexes are summarised in Table 2. Compound **6a** with only four alkyl chains exhibits a typical fan-like texture, which can easily be



Scheme 1 Synthesis of compounds **6-8**; labelling of the compounds: **1a**: $y=1$, **1b**: $y=2$, **1c**: $y=3$; **2a**: $x=1$, **2b**: $x=3$; **3a-c**, see Table 1; **4a**: $x=3$, $y=1$, **4b**: $x=1$, $y=2$, **4c**: $x=1$, $y=3$, **5a**: $R^1, R^2=H$, **5b**: $R^1=C_{10}H_{21}O$, $R^2=H$, **5c**: $R^1, R^2=C_{10}H_{21}O$; compounds **6-8**, see Table 2; reagents and conditions: (i) K_2CO_3 , K^+OTs^- , DMF, $80^\circ C$, high dilution; (ii) $[Pd(C_6H_5CN)_2Cl_2]$, ethanol, $25^\circ C$; (iii) CH_2Cl_2 , $25^\circ C$.

homeotropically aligned giving optically isotropic domains. These are characteristic features of an S_A -type layer structure. On cooling compound **8a** with twelve chains from the isotropic liquid the development of a mosaic-like texture, quite characteristic for some columnar mesophases can be observed (see Fig. 1). The same textures were observed for compounds **8b** and **8c**, which have different lengths of polyether chains connecting both 2-phenylpyrimidine units. Surprisingly, how-

Table 1 Phase transition temperatures $T/^\circ C$ of compounds **3**, as determined by polarised light microscopy (K=crystalline solid, N=nematic phase, I=isotropic liquid); values in parentheses refer to monotropic (metastable) mesophases

Comp.	x	y	Phase transitions
3a	3	1	K 154 (N 123) I
3b	1	2	K 164 (N 126) I
3c	1	3	K 149 (N 112) I

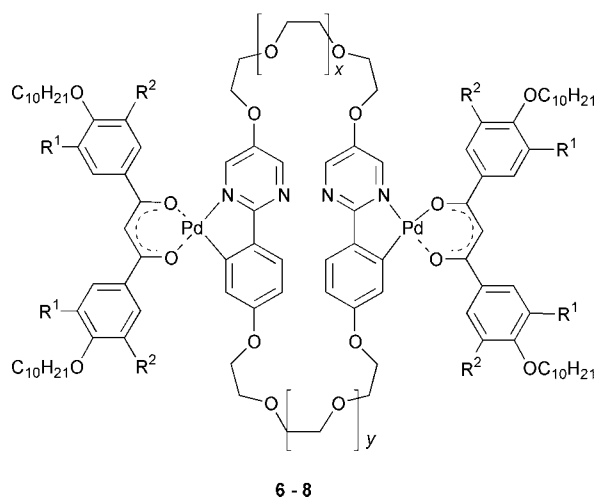
ever, compound **7a** with eight alkoxy chains does not exhibit any liquid crystalline properties. Even on cooling below the melting point only crystallisation was observed which sets in at $105^\circ C$. The transition temperatures of these novel metallo-mesogens¹⁴ are summarised in Table 2. It shows, that by increasing the number of alkyl chains a discontinuous transition from a lamellar to a columnar organisation of the molecules in the mesophase takes place.

To additionally confirm the columnar structure of the mesophases of compounds **8a-8c**, X-ray diffraction experiments were carried out with compound **8b**. In the wide angle region a broad diffuse scattering of low intensity was found as characteristic for liquid crystalline phases. It indicates the liquid-like disorder of the alkyl chains and also indicates that there is no long range periodicity within the columns. As the wide angle scattering is unusually broad in comparison to columnar mesophases of other disc-like compounds it points to a strong disorder within the columns. In the small angle region three sharp reflexes corresponding to a ratio of their position of $1:\sqrt{3}:2$ (Guinier film camera, $110^\circ C$) indicate a hexagonal lattice with a lattice parameter $a_{hex} = 3.72$ nm (Fig. 2a), a result that is confirmed as well by X-ray diffraction experiments on an aligned sample of **8b** (2D detector, Fig. 2b). Thus, the molecules **8b** should be organised in nearly cylindrical columns. Using equation (1) it was calculated that exactly one molecule is found in the diameter of the columns (N_A =Avogadro-constant, M =molecular mass, $h=0.45$ nm corresponding to the height of a hypothetical segment of the columns which is required by the diameter of the alkyl chains, the density ρ is assumed to be 1 g cm^{-3}).

$$n = \frac{a_{hex}^2}{2} \sqrt{3} h \frac{N_A}{M} \rho \quad (1)$$

This is also in good agreement with the estimated molecular dimensions. The square planar coordination geometry of $Pd(II)$ should provide two nearly planar metallo-organic cores in each molecule. In the crystal structures of related aromatic $Pd(II)$ -1,3-diketonates the phenyl rings are only slightly tilted ($3-12^\circ$) with respect to the plane of the $Pd(II)$ diketonate core structure.¹⁶ Therefore, it is reasonable to assume that the two half parts of the molecules adopt a nearly planar, half-disc-

Table 2 Phase transition temperatures T/C , as determined by polarised light microscopy, and transition enthalpies $\Delta H/kJ\ mol^{-1}$ (lower lines in italics) of compounds **6–8** (K = crystalline solid, S_A = smectic A phase, Col_h = hexagonal columnar phase, I = isotropic liquid)



Comp.	x	y	R^1	R^2	Phase transitions
6a	3	1	H	H	K 197 S_A 207 I
7a	3	1	$OC_{10}H_{21}$	H	K 137 I
8a	3	1	$OC_{10}H_{21}$	$OC_{10}H_{21}$	K 110 Col_h 178 I [4.5] [6.2]
8b	1	2	$OC_{10}H_{21}$	$OC_{10}H_{21}$	K 108 Col_h 211 I [2.4] [6.3]
8c	1	3	$OC_{10}H_{21}$	$OC_{10}H_{21}$	K 110 Col_h 208 I [1.4] [4.6]

like average conformation, which should facilitate the arrangement of the molecules in columns. Additionally, these semirigid half-discs are connected by the two rather flexible polyether chains, which restrict the possible positions of the half-disc units to each other. An idealised planar conformation which resembles a butterfly is shown in Fig. 3. Like the wings of a butterfly the two half-disc units can adopt different orientations relative to each other and also a sandwich-like conformation with both half-disc units on top of each other (like a butterfly sitting on a flower), in addition to other conformations could be found along the columns. Additionally, a staggered arrangement (both half-discs are not in one plane) may be possible. Hence, these molecules can adopt quite different conformations which could be the reason for the disorder within the columns. As the central cores of the molecules of **6–8** are built up by a combination of Pd-1,3-diketone units, heterocycles, ether functionalised aromatic units and polyether chains, they are rather polar and microsegregation¹⁷ of these polar regions from the lipophilic chains should be very efficient. Therefore the segregation of the polar centres from their lipophilic surrounding should additionally facilitate the organisation of these flexible molecules in their liquid crystalline phases. However, a certain minimum number of chains is necessary to completely surround the central core regions cylindrically. If this is not possible, the columnar phases get lost (compound **7a**) or an arrangement in layers becomes possible (compound **6a**). Here, the central units are randomly distributed within polar layers which are separated from the layers of the fluid alkyl chains.

Conclusions

In summary, it was found that the combination of two different molecular architectures, the rather rod-like *para*-cyclophanes and two half disc-like 1,3-diketone units, fused *via ortho*-palladation, leads to new liquid crystalline materials with a quite unusual molecular shape, which suggest to denote them

as butterfly-mesogens. By increasing the number of attached alkyl chains a discontinuous transition from a lamellar to a columnar organisation of the molecules was observed, but no cubic phase could be detected as intermediate phase as known for polycatenar molecules¹⁸ and amphiphilic compounds.¹⁹ Probably, because of the significant flexibility provided by the central macrocyclic structure also lamellocolumnar²⁰ and discotic lamellar phases²¹ could not be found. Moreover, compounds **8a–8c** are the first *para*-cyclophane derivatives that show thermotropic columnar mesophase behaviour.^{22,23} Though these molecules may at first glance look funny, they may open new possibilities to build well-defined self-assembled structures incorporating transition metals and ion channels in close proximity to each other, embedded in an isolating lipophilic surrounding.²⁴ Hence, further optimisation of the molecular structure could possibly lead to useful materials for the design of supermolecular devices.

Experimental section

General methods

1,3-Bis(4-decyloxyphenyl)propane-1,3-dione,²⁵ 1,3-bis(3,4-didecyloxyphenyl)propane-1,3-dione,²⁵ 1,3-bis(3,4,5-tridecyloxyphenyl)propane-1,3-dione^{25,26} and the oligoethylene glycol bistosylates **2**⁹ were synthesised according to literature procedures. The thallium ethoxide (Aldrich) was used as received. Solvents were dried prior to use.

Confirmation of the structures of the products was obtained by ¹H and ¹³C NMR spectroscopy (Varian Gemini 200, Varian Unity 400 and Varian Unity 500) and mass spectroscopy (Intectra GmbH, AMD 402, electron impact, 70 eV; Finnigan MAT LCQ Spectrometer). Microanalyses were performed using a CHNS-932 (Leco Co.) elemental analyser.

Transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot 2 polarising microscope and these were confirmed

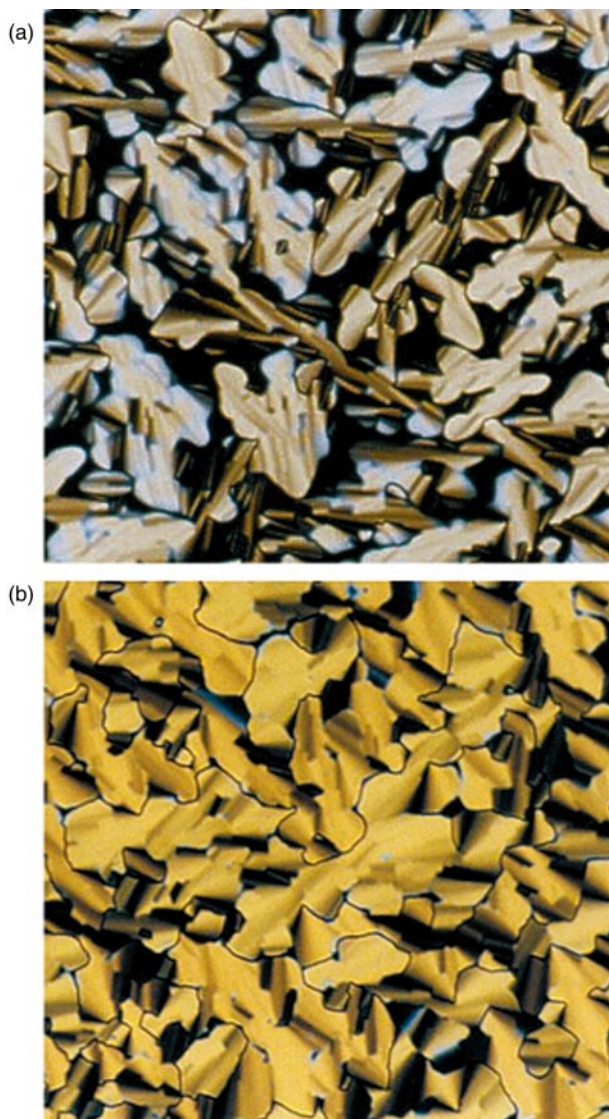


Fig. 1 Polarised light optical micrograph of the hexagonal columnar phase of **8a**: a) at 175 °C, b) at 103 °C.

using differential scanning calorimetry (Perkin-Elmer DSC-7, heating and cooling rate: 10 K min⁻¹).

X-Ray diffraction patterns were obtained on a Guinier film camera (Huber) operating with a Cu-K α_1 beam. Oriented samples were investigated with a two dimensional detector (HI-STAR, Siemens).

The complete experimental procedure is given for the synthesis of compound **8a** and its intermediates, as a representative example. The procedures and analytical data of all other compounds are available as supplementary material.†

Synthesis of the *para*-cyclophane **3a**

A solution of 1,8-bis[4-(5-hydroxypyrimidin-2-yl)phenoxy]-3,6-dioxaoctane **1a**⁸ (0.3 mmol, 147 mg) and 1,14-bis(4-tolylsulfonyl)-3,6,9,12-tetraoxatetradecane (**2b**, $x=3$, 0.3 mmol, 164 mg) in dry DMF (110 ml) was added at 80 °C to a suspension of potassium carbonate (3 mmol, 414 mg) and potassium toluene-*p*-sulfonate (3 mmol, 630 mg) in dry DMF (20 ml) over a period of 24 hours under an Ar atmosphere. The resulting solution was stirred at this temperature for an additional 172 hours. After cooling to room temperature the solvent was removed under reduced pressure and the residue was partitioned between CH₂Cl₂ and water (150 ml/75 ml). The layers were separated and the organic layer was washed

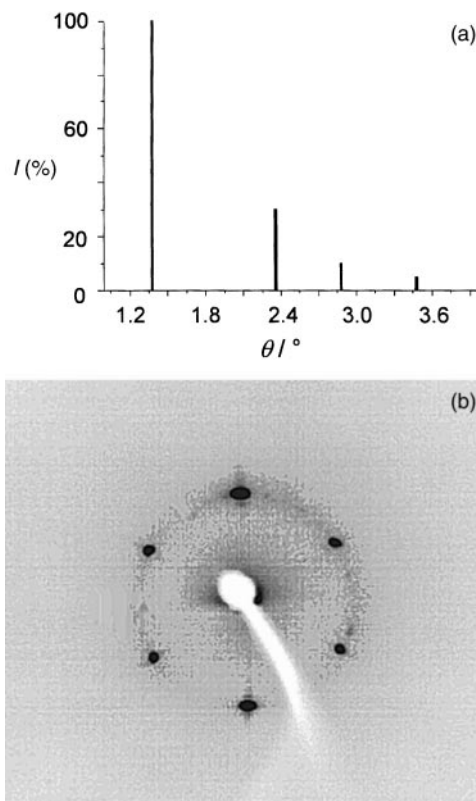


Fig. 2 Small-angle X-ray diffraction pattern of **8b**: a) sketch of the diffraction pattern obtained by the Guinier film method at 110 °C, b) aligned sample (2D detector) at the same temperature.

successively with 20 ml portions of 5 M HCl, saturated sodium bicarbonate solution, distilled water, and brine and was dried over Na₂SO₄. Evaporation of the solvent resulted in a crude product which was purified by column chromatography (silica gel, CH₂Cl₂-ethanol=10:0.5 to 10:2) and repeated crystallisation from *n*-heptane to give **3a** (84 mg, 40%). ¹H NMR (200 MHz, CDCl₃, 27 °C, TMS): δ =8.37 (s, 4H, Py-H), 8.10 (d, ³*J*(H,H)=8.9 Hz, 4H, Ph-H), 6.82 (d, ³*J*(H,H)=8.9 Hz, 4H, Ph-H), 4.20 (t, ³*J*(H,H)=4.5 Hz, 4H, PyOCH₂), 4.02 (t, ³*J*(H,H)=4.7 Hz, 4H, PhOCH₂), 3.89 (t, ³*J*(H,H)=4.5 Hz, 4H, PyOCH₂CH₂), 3.82–3.51 (m, 4H, PhOCH₂CH₂), 3.74–3.68 (m, 8H, OCH₂), 3.67–3.62 (m, 8H, OCH₂); ESI-MS *m/z* (%): 731 [M+K]⁺ (9), 715 [M+Na]⁺ (51), 693 [M+H]⁺ (100);

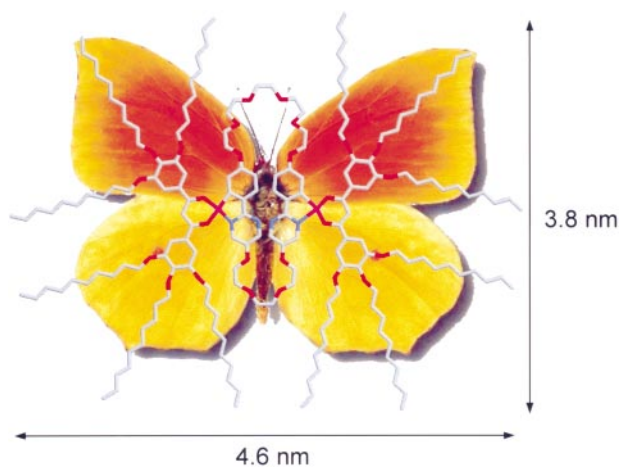


Fig. 3 Molecular dimensions of compound **8c** in its most extended conformation with all-*trans* conformation of the alkyl chains (hydrogen atoms are omitted for clarity) and comparison of its molecular shape with a butterfly (*Gonepteryx cleopatra* L.-*peridae*).¹⁵ The colour of the lower part of the wings corresponds to the colour of compounds **6–8** in the crystalline state.

Elemental analysis for $C_{36}H_{44}N_4O_{10} \cdot 0.5H_2O^{27}$ (692.77): calcd: C 61.61, H 6.46, N 7.98; found: C 61.53, H 6.50, N 7.97%.

1,3-Bis(3,4,5-tridecyloxyphenyl)propane-1,3-dionato thallium(I) 5c

Prepared in analogy to a published procedure¹³ from 1,3-bis(3,4,5-tridecyloxyphenyl)propane-1,3-dione^{25,26} and thallium ethoxide. Mp 36 °C; Elemental analysis for $C_{75}H_{140}O_8Tl$ (1374.32): calcd: C 65.55, H 10.27; found: C 65.24, H 8.99%.

Synthesis of the dinuclear Pd-compound 8a

To a suspension of **3a** (28.6 μ mol, 20 mg) in dry ethanol (4 ml), $Pd(PhCN)_2Cl_2$ (57.0 μ mol, 22.2 mg) suspended in dry ethanol (2 ml) was added. The mixture was stirred for 24 h at 20 °C. The resulting yellow precipitate was filtered under suction and washed subsequently with ethanol, acetone and petroleum ether. Drying and crystallisation from CH_2Cl_2 -ethanol gave 21 mg of the polymer **4a**, which was used without further purification for the next step. A solution of **5c** (43 μ mol, 59 mg) in dry CH_2Cl_2 (5 ml) was added at once to a suspension of **4a** in dry CH_2Cl_2 (5 ml). The mixture was stirred for 120 h at 25 °C. Removal of the solvent resulted in a yellow solid, which was purified by column chromatography (silica gel, CH_2Cl_2 -ethanol = 10:0.2) and repeated crystallisation from ethyl acetate-ethanol (5:2) to give **8a** (28 mg, 41%). ¹H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.40 (d, ⁴J(H,H) = 3.3 Hz, 2H, Py-H), 8.24 (d, ⁴J(H,H) = 3.3 Hz, 2H, Py-H), 7.33 (d, ³J(H,H) = 8.4 Hz, 2H, Ph-H), 7.10 (s, 4H, Ar-H), 7.03 (s, 4H, Ar-H), 6.97 (d, ⁴J(H,H) = 2.3 Hz, 2H, Ph-H), 6.49 (dd, ³J(H,H) = 8.4 Hz, ⁴J(H,H) = 2.3 Hz, 2H, Ph-H), 6.33 (s, 2H, CH), 4.07–4.00 (m, 32H, OCH_2), 3.75 (t, ³J(H,H) = 4.7 Hz, 4H, $PhOCH_2$), 3.72–3.64 (m, 20H, $ArOCH_2$), 1.83–1.73 (m, 24H, $ArOCH_2CH_2$), 1.53–1.44 (m, 24H, $ArOCH_2CH_2CH_2$), 1.43–1.25 (m, 144H, CH_2), 0.89–0.84 (m, 36H, CH_3); ¹³C NMR (100 MHz, $CDCl_3$, 27 °C, TMS): δ = 182.72 (C), 182.41 (C), 167.62 (C), 160.57 (C), 153.97 (C), 153.91 (C), 153.84 (C), 150.14 (C), 147.11 (CH), 142.01 (C), 141.93 (C), 136.75 (C), 136.21 (C), 135.51 (C), 127.76 (CH), 116.70 (CH), 112.99 (CH), 107.51 (CH), 107.03 (CH), 96.21 (CH), 74.02 (CH_2), 72.36 (CH_2), 72.04 (CH_2), 71.88 (CH_2), 71.83 (CH_2), 70.77 (CH_2), 70.61 (CH_2), 70.35 (CH_2), 70.29 (CH_2), 70.21 (CH_2), 69.49 (CH_2), 67.97 (CH_2), 32.86 (CH_2), 32.83 (CH_2), 31.38 (CH_2), 30.70 (CH_2), 30.64 (CH_2), 30.58 (CH_2), 30.56 (CH_2), 30.51 (CH_2), 30.49 (CH_2), 30.31 (CH_2), 30.29 (CH_2), 27.19 (CH_2), 27.18 (CH_2), 27.08 (CH_2), 26.99 (CH_2), 23.57 (CH_2), 14.95 (CH_3); Elemental analysis for $C_{186}H_{304}N_4O_{26}Pd_2$ (3225.31): calcd: C 69.26, H 9.50, N 1.74; found: C 69.27, H 9.44, N 1.58%.

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