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Impact on the mesophase transition temperatures of 1,4-bis(naphthyl)-1,3-butadiyne of the attachment of terminal alkoxy chains

Hsiu-Fu Hsu[a]; Ying-Hui Lai[a]; Shu-Yu Lin[a]; Wei-Chung Lin[a]; Jen-Fon Chen[a]
[a] Department of Chemistry, Tamkang University, Tamsui, Taiwan ROC,

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HSIU-FU HSU*, YING-HUI LAI, SHU-YU LIN, WEI-CHUNG LIN, and
JEN-FON CHEN
Department of Chemistry, Tamkang University, Tamsui, Taiwan ROC

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The synthesis of 1,4-bis(2-naphthyl)-1,3-butadiynes, containing terminal alkoxy chains, is reported. The mesomorphism of these compounds has been characterized by differential scanning calorimetry and polarizing optical microscopy. The introduction of terminal alkoxy chains, significantly lowers the melting temperature of the analogous core without terminal chains. The induction of a smectic phase occurred when two decyloxy chains were attached. The solid state structures and packing arrangements of the butyloxy derivative and the chainless core were determined by single crystal X-ray diffraction, and revealed greater layer interpenetration for the substituted material.

1. Introduction

Materials with high birefringence are potentially valuable as additives in liquid crystal mixtures for display applications. A variety of functional groups, including ethynyl and naphthalene units, are reported to show high optical anisotropy [1–6]. A compound containing four high birefringence units, 1,4-bis(2-naphthyl)-1,3-butadiyne, and no terminal alkyl chains, was reported to give a nematic phase at 273.6°C upon heating. No clearing point was detected since polymerization occurred in the liquid crystalline state to yield a black polymer [7]. A lower clearing point may be achieved and thermal polymerization suppressed by attaching terminal chains onto the naphthyl groups to increase dispersive forces between the molecules. In addition, although the dependence of mesophase behaviour on the length of alkyl chains has often been discussed for liquid crystal materials [8], the effect of terminal chains, compared with the analogous material without any chains, has seldom been studied due to the scarcity of liquid crystal materials without chains [9, 10]. In this context, the synthesis and phase behaviour of the alkoxyl derivatized compounds, **2a–2f**, have been studied to probe the effects of the terminal chains on mesophase behaviour. Also, the solid state structures and packing arrangements of compound **2a** and its chainless analogue have been compared.

2. Results and discussion

The symmetric system **2** was prepared according to the scheme. Alkoxy-containing compounds **1a–1f** were derived from 2-bromo-6-alkoxy-naphthalene, which was prepared by the alkylation of its hydroxy analogue. Subsequent coupling to trimethylsilylacetylene using Sonogashira conditions, followed by removal of the trimethylsilyl group with K_2CO_3 in methanol, gave the corresponding ethynyl derivatives **1**. The coupling of two units of **1** using copper acetate gave the symmetric mesogenic compounds **2** in good yields.

The thermal data for series **2** investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) are summarized in the table. When viewed under the microscope, all compounds are observed to exhibit solely nematic behaviour except for compound **2f** which also shows a smectic C phase. In the DSC analysis of compounds **2a–2e**, only the Cr–N transitions were detected while the absence of N–I transitions suggests a highly disordered fluid mesophase. For the compound with the longest terminal chains, **2f**, two enantiotropic transitions, Cr–SmC and N–I were observed but only the SmC–N transition was detected in the heating DSC trace. An odd–even effect was also observed. For even values of *n*, both the melting and clearing temperatures decrease with increasing chain length, but a more significant influence on the clearing points was found.

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*Author for correspondence; e-mail: hhsu@mail.tku.edu.tw

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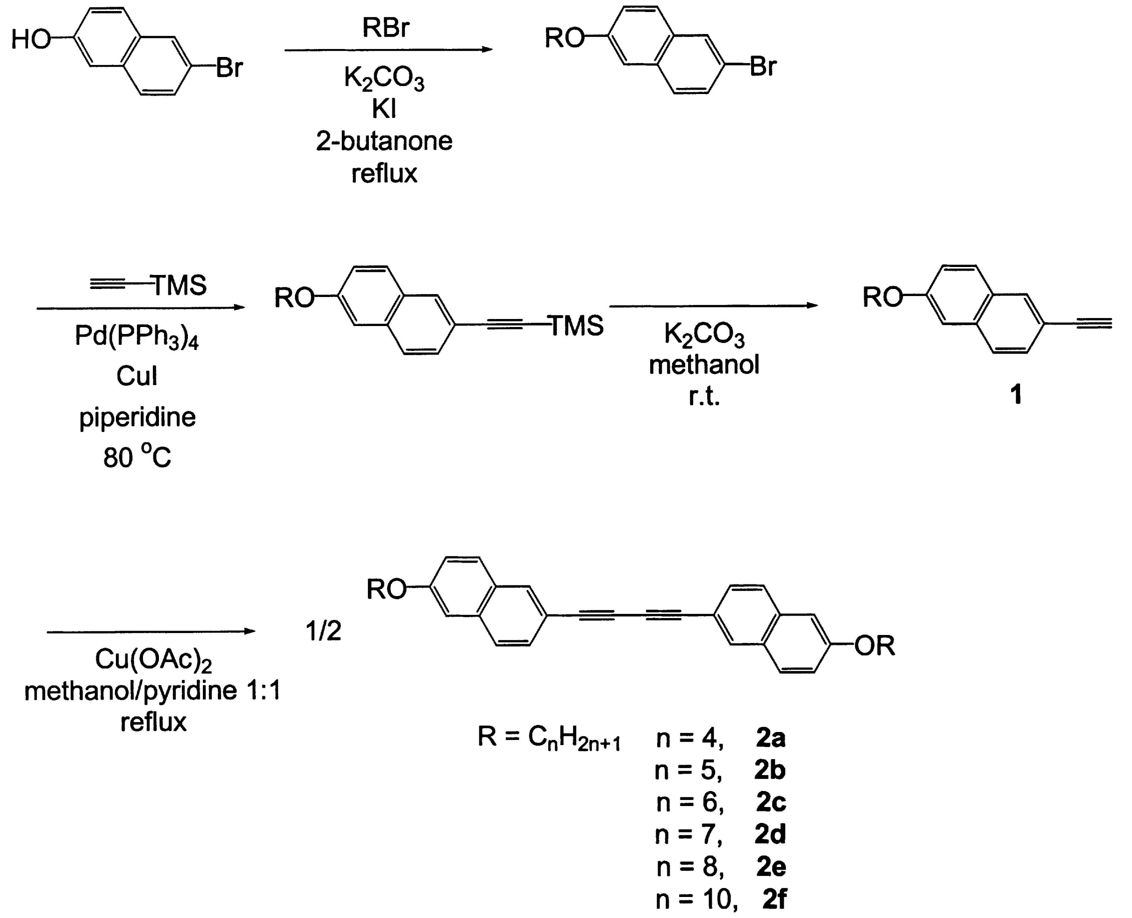

Scheme. Synthesis of compounds **2a–2f**.

Table. Phase behaviour of compounds **2a–2f**. Transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{-1}) were determined by DSC at 10°C min^{-1}. Cr, Cr1, and Cr2, crystalline phases; SmC, smectic C; N, nematic; I, isotropic; *n* denotes the length of the alkoxy chains.

Compound	Phase transitions
2a (*n* = 4)	$\mathrm{Cr}\ \underset{144.6\ (-9.51)}{\overset{153.4\ (11.29)}{\rightleftharpoons}}\ \mathrm{N}\ \underset{247.0^{b}}{\overset{264.2^{b}}{\rightleftharpoons}}\ \mathrm{I}$ (partial decomposition)
2b (*n* = 5)	$\mathrm{Cr}\ \underset{153.8\ (-18.09)}{\overset{164.4\ (19.38)}{\rightleftharpoons}}\ \mathrm{N}\ \underset{218.9^{b}}{\overset{232.4^{b}}{\rightleftharpoons}}\ \mathrm{I}$ (partial decomposition)
2c (*n* = 6)	$\mathrm{Cr}\ \underset{134.9\ (-9.36)}{\overset{140.5\ (13.6)^{a}}{\rightleftharpoons}}\ \mathrm{N}\ \underset{225.4^{b}}{\overset{229.1^{b}}{\rightleftharpoons}}\ \mathrm{I}$
2d (*n* = 7)	$\mathrm{Cr1}\ \underset{129.4\ (-9.8)}{\underleftarrow{\xrightarrow{129.8\ (7.73)}\ \mathrm{Cr2}\ \xrightarrow{140.0\ (10.58)}}}\ \mathrm{N}\ \underset{212.0^{*}}{\overset{215.3^{*}}{\rightleftharpoons}}\ \mathrm{I}$
2e (*n* = 8)	$\mathrm{Cr}\ \underset{135.1\ (-9.51)}{\overset{139.7\ (12.31)^{a}}{\rightleftharpoons}}\ \mathrm{N}\ \underset{204.6^{b}}{\overset{211.3^{b}}{\rightleftharpoons}}\ \mathrm{I}$
2f (*n* = 10)	$\mathrm{Cr}\ \underset{124.9\ (-10.59)}{\overset{128.5\ (10.36)}{\rightleftharpoons}}\ \mathrm{SmC}\ \underset{163.0^{b}}{\overset{163.6\ (0.01)}{\rightleftharpoons}}\ \mathrm{N}\ \underset{192.6\ (-0.53)}{\overset{193.8\ (0.49)}{\rightleftharpoons}}\ \mathrm{I}$

[a] Two overlapped peaks with the stronger peak at 140.0°C.

[b] Observed by POM studies but not detected in DSC measurements.

By the introduction of alkoxy terminal chains at both ends of the parent compound, 1,4-bis(2-naphthyl)-1,3-butadiyne, the nematic phase was retained. Although the clearing temperature of the parent compound was not reported due to thermal polymerization in its liquid crystal state, attachment of two terminal alkoxy chains does lower the clearing temperature such that it can now be determined. Partial thermal polymerization was observed for compounds with shorter chains, **2a** and **2b**, as evidenced by the formation of sparse orange dots when viewed under the POM at the clearing temperature and by irreversible DSC runs. Apparently, the dispersive forces arising from these shorter chains were not sufficient to prevent adjacent molecules from undergoing thermal polymerization. However, no polymerization was detected for **2c**–**2f** up to 250°C, presumably due to more significant dispersive forces arising from the longer chains. Furthermore, the photostability of compound **2f** was examined with UV radiation in its nematic temperature range, and little decomposition was detected after exposure to radiation for twelve hours using a mercury lamp.

Most importantly, the impact on mesophase transition temperatures of the introduction of terminal alkoxy chains does not follow the trends in the transition temperatures of the even or odd series. A significant decrease of the Cr–N phase transition temperature by at least 109°C (273.6°C for the parent compound and 164.4°C for C_5 analogue **2b**) was achieved. The large decrease in the melting temperatures cannot be predicted by extrapolation of the trends in the melting points of either the even or odd series. This may be ascribed to the increase in molecular thickness resulting from the introduction of alkoxy chains.

The layered arrangement of **2c** in its smectic phase was further verified using powder X-ray diffraction (XRD); its diffractogram at 142°C is shown in figure 1. One broad small angle peak and a diffuse wide angle halo were found. The halo at 4.46 Å is characteristic of liquid-like correlations in the liquid crystalline state. The small angle peak at 36.54 Å represents the layer and is much shorter than the estimated extended molecular length of 44.34 Å [11]. The smaller layer spacing may result from layer interpenetration, tilting between the molecular axis and the layer normal, or more likely a combination of both.

The molecular structure of **2a** was determined by single crystal XRD and is shown in figure 2. The two naphthalene units are coplanar and can be interchanged

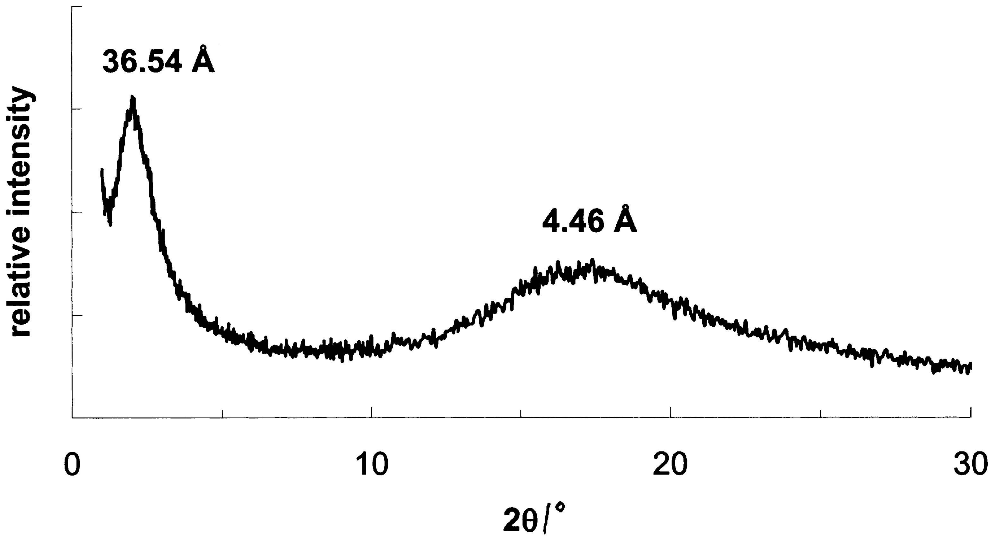

Figure 1. X-ray diffractogram of **2f** in the mesophase at 142°C.

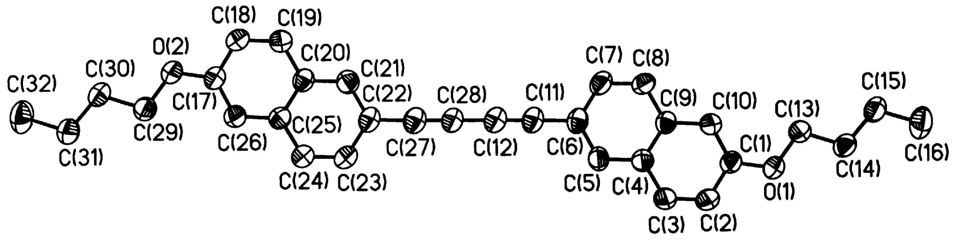

Figure 2. X-ray structure of **2a**. ORTEPs shown at 50% probability; hydrogen atoms are omitted for clarity.

by an inversion centre and a C_2 rotation axis. The packing diagram is shown in figure 3 in which the molecules align along the molecular axis. The molecular structure of **2a** has the same features as that of the parent molecule 1,4-bis(2-naphthyl)-1,3-butadiyne. However, the molecular packing motifs for these two are quite different. Without terminal chains, the molecules pack in distinctive layers with no overlap between layers; the introduction of terminal chains blurred the layer structure by layer interpenetration.

3. Summary and conclusion

The introduction of terminal alkoxy chains to the symmetric 1,4-bis(2-naphthyl)-1,3-butadiyne core has significant impact on transition temperatures, and lowers both the melting and clearing temperatures. The induction of a smectic phase did not occur until the chain length reached $n = 10$. In the solid state, the packing motifs of the butyloxy modified compound **2a** showed a higher degree of layer interpenetration than in the chainless parent compound.

4. Experimental

4.1. *General*

All chemicals and solvents were reagent grade (Aldrich Chemical Co.) and used without further purification. Series **1** was synthesized following literature procedures [12, 13]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm relative to residual $CHCl_3$ ($\delta = 7.24$, ^{1}H; 77.0, ^{13}C). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). DSC scans were obtained using a Perkin-Elmer Pyris1 with heating and cooling rates of 5–10°C min^{-1}. Optical microscopy was carried out on a Nikon Eclipse E600 POL with a Mettler FP90/FP82HT hot stage system. Mass spectra were obtained on a Finnigan MAT-95XL. Elemental analyses were carried out on a Heraeus CHN-O-Rapid Analyzer.

Powder XRD data were collected on the wiggler beamline BL17A of the Synchrotron Radiation Research Center (SRRC), Taiwan, using a triangular bent Si(1 1 1) monochromator and a wavelength of 1.32633 Å. The sample in a 1 mm capillary was mounted on a Huber 5020 diffractometer. An air stream heater was fitted to the BL17A beamline and the temperature controller was programmable by a PC with a PID feedback system.

Single crystal XRD data were collected on a Siemens SMART-1000 automated diffractometer. Structure solution and refinement were performed with the integrated program package SHELXTL [14]; absorption corrections were applied using SADABS. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. Crystal data for **2a**: triclinic, space group $P-1$, $a = 9.8503(13)$, $b = 11.2447(16)$, $c = 11.5387(16)$ Å, $\alpha = 89.693(3)$, $\beta = 80.289(3)$, $\gamma = 79.546(3)^\circ$, $T = 293(2)$ K, $Z = 2$, 6497 reflections measured, 4321 independent reflections, final R_1, wR_2, and GOF were 0.0386, 0.01448, and 0.891.

4.2. *Synthesis of 1,4-bis(2-alkoxy-2′-naphthyl)-1,3-butadiynes*

To a 100 ml Schlenk flask fitted with a condenser with nitrogen inlet and containing pyridine/methanol (1/1, 40 ml), was added 2-butyloxy-6-ethynyl-naphthalene (0.60 mmol) and copper acetate (1.51 mmol). The mixture was heated at reflux for 18 h, then filtered and the filtrate dried under reduced pressure. The product was purified by column chromatography (SiO_2, hexanes/chloroform 6/1) and was recrystallized from methanol/chloroform to afford white crystals of the respective butadiyne product **2**.

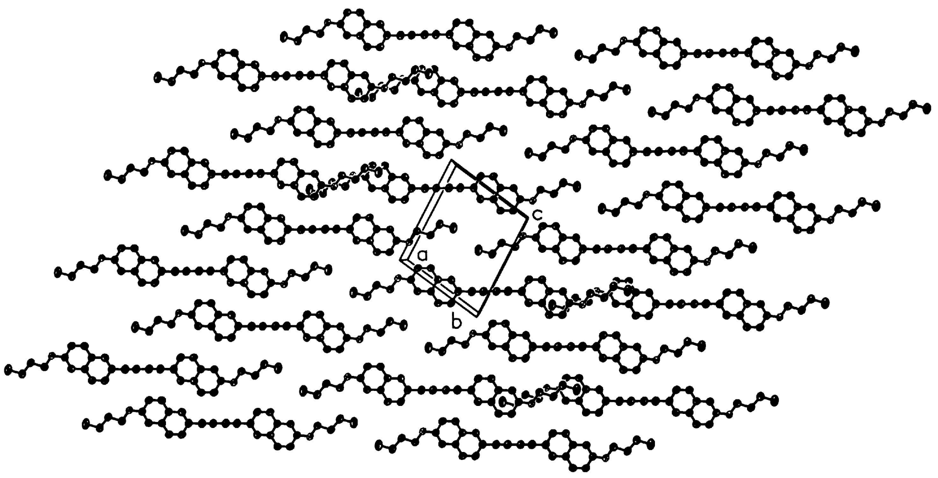

Figure 3. Packing diagram of **2a**.

4.3. *1,4-Bis(2-butyloxy-2′-naphthyl)-1,3-butadiyne*

2a: yield 55%, white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.99 (s, 2H), 7.70 (d, $J = 8.9$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.50 (dd, $J = 8.4$, 1.5 Hz, 2H), 7.17 (dd, $J = 8.9$, 2.4 Hz, 2H), 7.10 (d, $J = 2.4$ Hz, 2H), 4.09 (t, $J = 6.5$ Hz, 4H), 1.85 (m, 4H), 1.54 (m, 4H), 1.01 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.3, 134.7, 132.8, 129.4, 129.1, 128.3, 126.9, 119.9, 116.6, 106.7, 82.3, 73.9, 67.9, 31.3, 19.3, 13.9. HRMS (EI) calc. for $C_{32}H_{30}O_2$ 446.2246, found 446.2243. Elemental analysis: calc. for $C_{32}H_{30}O_2$ C 86.06, H 6.77; found C 85.68, H 6.75%.

2b: yield 58%, white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.00 (s, 2H), 7.70 (d, $J = 9.0$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.51 (dd, $J = 8.4$, 1.7 Hz, 2H), 7.17 (dd, $J = 9.0$, 2.4 Hz, 2H), 7.10 (d, $J = 2.4$ Hz, 2H), 4.09 (t, $J = 6.6$ Hz, 4H), 1.86 (m, 4H), 1.45 (m, 8H), 0.96 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.3, 134.7, 132.8, 129.4, 129.1, 128.3, 126.9, 119.9, 116.6, 106.7, 82.3, 73.9, 68.2, 28.9, 28.3, 22.5, 14.0. HRMS (EI) calc. for $C_{34}H_{34}O_2$ 474.2559, found 474.2550. Elemental analysis: calc. for $C_{34}H_{34}O_2$ C 86.04, H 7.22; found C 85.65, H 7.26%.

2c: yield 65%, white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.99 (s, 2H), 7.70 (d, $J = 8.9$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.51 (dd, $J = 8.4$, 1.6 Hz, 2H), 7.17 (dd, $J = 8.9$, 2.4 Hz, 2H), 7.10 (d, $J = 2.4$ Hz, 2H), 4.08 (t, $J = 6.6$ Hz, 4H), 1.85 (m, 4H), 1.53 (m, 4H), 1.38 (m, 8H), 0.93 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.3, 134.7, 132.8, 129.4, 129.1, 128.3, 126.0, 119.9, 116.6, 106.7, 82.3, 73.9, 68.2, 31.6, 29.2, 25.8, 22.6, 14.0. HRMS calc. for $C_{36}H_{38}O_2$ 502.2872, found 502.2873. Elemental analysis: calc. for $C_{36}H_{38}O_2$ C 86.02, H 7.62; found C 85.86, H 7.64%.

2d: yield 57%, white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.99 (s, 2H), 7.69 (d, $J = 9.0$ Hz, 2H), 7.66 (d, $J = 8.5$ Hz, 2H), 7.51 (dd, $J = 8.5$, 1.6 Hz, 2H), 7.17 (dd, $J = 9.0$, 2.4 Hz, 2H), 7.10 (d, $J = 2.4$ Hz, 2H), 4.08 (t, $J = 6.6$ Hz, 4H), 1.86 (m, 4H), 1.51 (m, 4H), 1.35 (m, 12H), 0.91 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.3, 134.7, 132.8, 129.4, 129.1, 128.3, 126.9, 119.9, 116.6, 106.7, 82.3, 73.9, 68.2, 31.8, 29.2, 29.1, 26.1, 22.6, 14.1. HRMS calc. for $C_{38}H_{42}O_2$ 530.3185, found 530.3179. Elemental analysis: calc. for $C_{38}H_{42}O_2$ C 85.99, H 7.98; found C 86.08, H 8.00%.

2e: yield 55%, white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.99 (s, 2H), 7.70 (d, $J = 9.0$ Hz, 2H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.51 (dd, $J = 8.4$, 1.6 Hz, 2H), 7.17 (dd, $J = 9.0$, 2.4 Hz, 2H), 7.10 (d, $J = 2.4$ Hz, 2H), 4.08 (t, $J = 6.5$ Hz, 4H), 1.85 (m, 4H), 1.50 (m, 4H), 1.33 (m, 16H), 0.90 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.3, 134.7, 132.8, 129.3, 129.1, 128.3, 126.9, 119.9, 116.5, 106.7, 82.3, 73.9, 68.2, 31.8, 29.4, 29.2, 29.2, 26.1, 22.7, 14.1. HRMS calc. for $C_{40}H_{46}O_2$ 558.3498, found 558.3497. Elemental analysis: calc. for $C_{40}H_{46}O_2$ C 85.98, H 8.30; found C 85.73, H 8.28%.

2f: yield 87%, white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.99 (s, 2H), 7.70 (d, $J = 9.0$ Hz, 2H), 7.66 (d, $J = 8.7$ Hz, 2H), 7.51 (dd, $J = 8.7$, 1.3 Hz, 2H), 7.17 (dd, $J = 9.0$, 2.4 Hz, 2H), 7.09 (d, $J = 2.4$ Hz, 2H), 4.07 (t, $J = 6.6$ Hz, 4H), 1.85 (m, 4H), 1.48 (m, 4H), 1.29 (m, 24H), 0.89 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 158.3, 134.7, 132.8, 129.3, 129.1, 128.3, 126.9, 119.9, 116.5, 106.7, 82.3, 73.9, 68.2, 31.9, 29.6, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1. HRMS for $C_{44}H_{54}O_2$ 614.4124, found 614.4125. Elemental analysis: calc. for $C_{44}H_{54}O_2$ C 85.94, H 8.85; found C 85.83, H 8.88%.

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