

## Research Article

# Synthesis and Characterization of Nonsymmetric Liquid Crystal Dimer Containing Biphenyl and Azobenzene Moiety

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Calamitic liquid crystalline dimer containing azobenzene moiety and a decyloxy biphenyl linked by flexible spacers {4-[7-(4'-decyloxy-biphenyl-4-yloxy)-alkyloxy]-phenyl}-(4-decyl-phenyl)-diazene has been synthesized and characterized by spectroscopic methods. The transition temperatures and phase behaviours were studied by Differential Scanning Calorimeter (DSC) and Polarizing Optical Microscope (POM). The synthesized compounds exhibited enantiotropic liquid crystal phase with higher spacer display nematic and smectic C phases while lower spacer shows nematic and smectic A phases.

## 1. Introduction

The liquid crystalline state is characterized by the orientational ordering of its constituent molecules, and transitions between different mesophases are accompanied by changes in the local molecular order. These transitions are usually marked by changes in various anisotropic properties, but depending on the order of the transition they may also be accompanied by changes in scalar quantities such as enthalpy content or density. The alternations in density and thermal expansivity which accompany the nematic to isotropic phase transition have been the subjects of a number of investigations [1–7]. The architecture and functionalization are the essential aspects in the molecular engineering of liquid crystal for the control of important physical properties such as optical anisotropy, dielectric anisotropy, supramolecular order, and thermal stability of mesophases. The initial interest in liquid crystal dimers arose, therefore, from their potential use as model compounds with which to understand the more complex polymeric systems. It quickly became apparent, however, that the dimers themselves were of significant interest in their own right as they exhibited quite different behaviour to conventional low molar mass liquid crystals [7, 8]. The liquid crystal dimer consists of mesogenic units separated by flexible spacers, normally alkyl

chains [9]. Nonsymmetry is usually introduced in to a dimer by connecting two different mesogenic units, by changing the length of the terminal chains or by using different terminal groups or varying the length and parity of spacer group [10]. These polymers have been the focus of considerable research interest not only for their technological potential [11] but also on a more fundamental level because they exhibit a range of unusual liquid crystalline behaviour. This includes the dramatic dependence of their transitional properties on the length and parity of the flexible spacers linking the mesogenic units [12], the observation of a nematic-nematic transition [13], and the occurrence of alternating smectic phases [14]. Particularly, molecules containing azo groups are well known to show reversible isomerization transformations upon irradiation with ultraviolet and visible light [15, 16]. The azobenzene class of chromophores is characterized by the azo linkage (–N=N–) that bridges two phenyl rings. This extended aromatic structure gives rise to azobenzene's intense optical absorption and related optical properties [17]. Strictly, “azobenzene” refers only to the parent molecule, though the term is now frequently used to refer to the entire class of substituted azo molecules. Biphenyl is a widely used building block for the construction of calamitic liquid crystals. It acts as a supportive entity for hermochromism.

TABLE 1: Phase transitions temperatures ( $^{\circ}\text{C}$ ) and the corresponding enthalpies (J/g) of liquid crystalline dimers.

Compound	$n$	Cr	Heating/cooling	SmC	Heating/cooling	SmA	Heating/cooling	N	Heating/cooling	I
C-4	4	•	152.7 [17.2]	—	—	•	166.1 [3.2]	•	189.3 [2.3]	•
			135.5 [15.9]				162.7 [2.6]		186.3 [2.6]	
C-5	5	•	169.5 [23.1]	•	155.7 [2.3]	—	—	•	175.0 [3.1]	•
			150.4 [14.6]		159.2 [3.9]				177.9 [2.3]	
C-6	6	•	153.0 [51.2]	—	—	•	163.0 [1.9]	•	179.0 [3.6]	•
			141.3 [49.9]				160.7 [2.0]		181.4 [2.5]	
C-7	7	•	131.6 [34.6]	•	149.5 [4.1]	—	—	•	171.4 [4.0]	•
			138.6 [29.1]		152.6 [3.6]				173.6 [4.7]	
C-8	8	•	167.0 [19.5]	—	—	•	153.1 [3.1]	•	183.0 [6.1]	•
			140.6 [21.6]				151.3 [1.8]		179.1 [5.8]	
C-9	9	•	149.3 [39.4]	•	140.4 [2.9]	—	—	•	169.3 [4.5]	•
			131.4 [25.7]		143.9 [3.1]				172.3 [5.6]	
C-10	10	•	132.8 [19.1]	—	—	•	136.7 [4.1]	•	168.3 [3.5]	•
			119.9 [22.4]				137.1 [4.9]		171.9 [4.6]	
C-11	11	•	112.9 [20.3]	•	142.5 [3.0]	—	—	•	167.0 [2.9]	•
			124.4 [27.8]		139.6 [4.9]				165.4 [3.7]	
C-12	16	•	112.5 [19.1]	—	—	•	134.5 [2.4]	•	163.5 [4.3]	•
			99.4 [30.9]				137.4 [3.0]		162.2 [3.9]	

In the study described here, we combine azobenzene and alkoxy biphenyl units through flexible alkyl spacer to produce a calamitic nonsymmetric liquid crystalline dimer with the aim to study the liquid crystalline properties.

## 2. Results and Discussions

The identification of the mesophases and determination of phase transition temperatures were achieved with the help of polarizing optical microscope (POM). The sample placed between a clean untreated glass slide and a cover slip was used for this particular study. The mesophase assignment was based on the observation of birefringence and fluidity when examined under POM. To confirm the transition temperatures and to determine their associated enthalpies, a differential scanning calorimeter (DSC) calibrated using pure indium was employed. The peaks observed in DSC traces (obtained at a rate of  $10^{\circ}\text{C}/\text{min.}$ ) due to phase transition were reproducible and peak temperatures were consistent with those deduced from the optical experiments.

In an effort to understand the structure-property relations the chain lengths of the paraffinic spacer have been varied and both the terminal alkyl and alkoxy tails have been unvaried. The thermal behaviour and phase transition temperatures of the dimeric compounds are summarized in Table 1. It is clear from Table 1 that all the dimers exhibit enantiotropic mesomorphism, especially the nematic (N) behavior. The DSC thermograms show three exothermal transitions on heating to the isotropic liquid and three endothermic transitions on cooling indicating that the even spacer length of the dimer exhibited enantiotropic behaviour for nematic and smectic A phase and the odd spacer length for nematic and smectic C phases. The smectic A phase was characterized by the formation of focal conic texture (Figure 1)

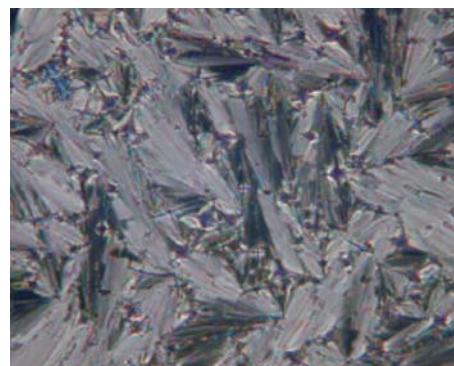


FIGURE 1: Polarising optical microscope textures of SmA focal conic at  $160.7^{\circ}\text{C}$  exhibited by the compound C-6.

as observed under polarized light. Nematic phases were assigned from their schlieren optical texture containing both types of point singularities, which flashed when subjected to mechanical stress, combined with the high mobility of the phase. The smectic C phase was characterized by the schlieren texture (Figure 2). The increase of the spacer length of the dimer promotes smectic behaviour.

All the dimers show enantiotropic nematic phase. Dimers with even spacer exhibit higher transition temperature than the odd spacer. The odd spacers C-5, C-7, C-9, and C-11 exhibit smectic C to nematic and nematic to isotropic phase transitions whereas the even spacers C-4, C-6, C-8, C-10, and C-12 exhibit smectic A to nematic and nematic to isotropic phase transitions. The dimers having  $\text{C}_4$  alkylene spacer show the highest clearing temperatures followed by the dimers with  $\text{C}_8$  and  $\text{C}_6$  alkylene spacers. All the synthesized liquid crystal compounds are highly stable. The effects of the spacer length on the transition temperatures and phase behaviour



FIGURE 2: Polarising optical microscope textures of SmC schlieren at 139.6°C exhibited by the compound C-11.

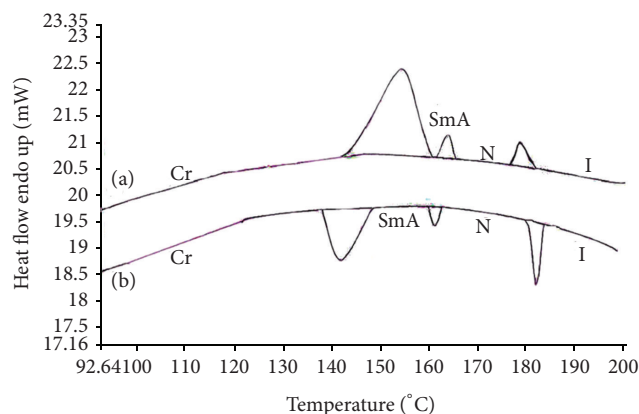


FIGURE 3: Differential scanning calorimetric thermogram of compound C-6 obtained at a rate of  $10^{\circ}\text{C min}^{-1}$ : (a) heating cycle (b) cooling cycle.

observed in this series are in accord with those observed for conventional low molar mass mesogens. As a representative case the DSC scans obtained at a rate of  $10^{\circ}\text{C/min}$  for the C-6 sample are shown in Figure 3.

The effects of the spacer length on the transition temperatures and phase behaviour observed in this series are in accord with those observed for conventional low molar mass mesogens. There is a pronounced odd-even effect in the nematic transition temperatures in which the even members have the greater values and as expected this alternation attenuates with increasing spacer length, whereas the odd spacers have lower transition temperature. In Figure 4, the dependence of the transition temperature of the nematic phase on the spacer length for the C-n series is compared (Scheme 1).

### 3. Conclusion

We have synthesized liquid crystalline dimers possessing two nonsymmetrical entities connected by flexible spacers. Molecular design of this dimer incorporates the biphenyl and azo benzene segments interconnected through methylene spacers. All the compounds exhibit enantiotropic mesophases and the transition temperatures for the even spacers are higher than the odd spacer.

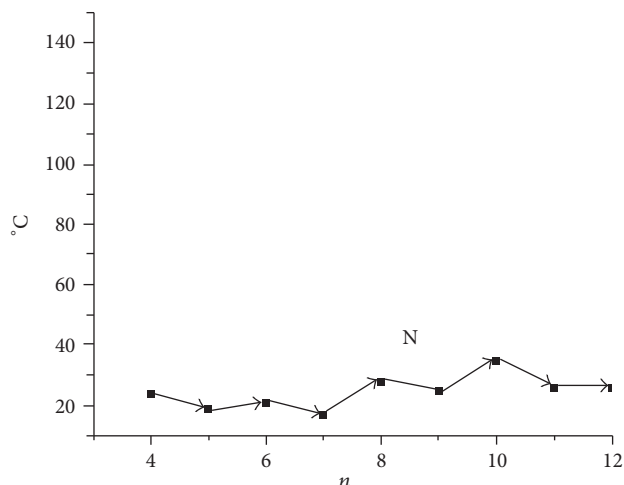


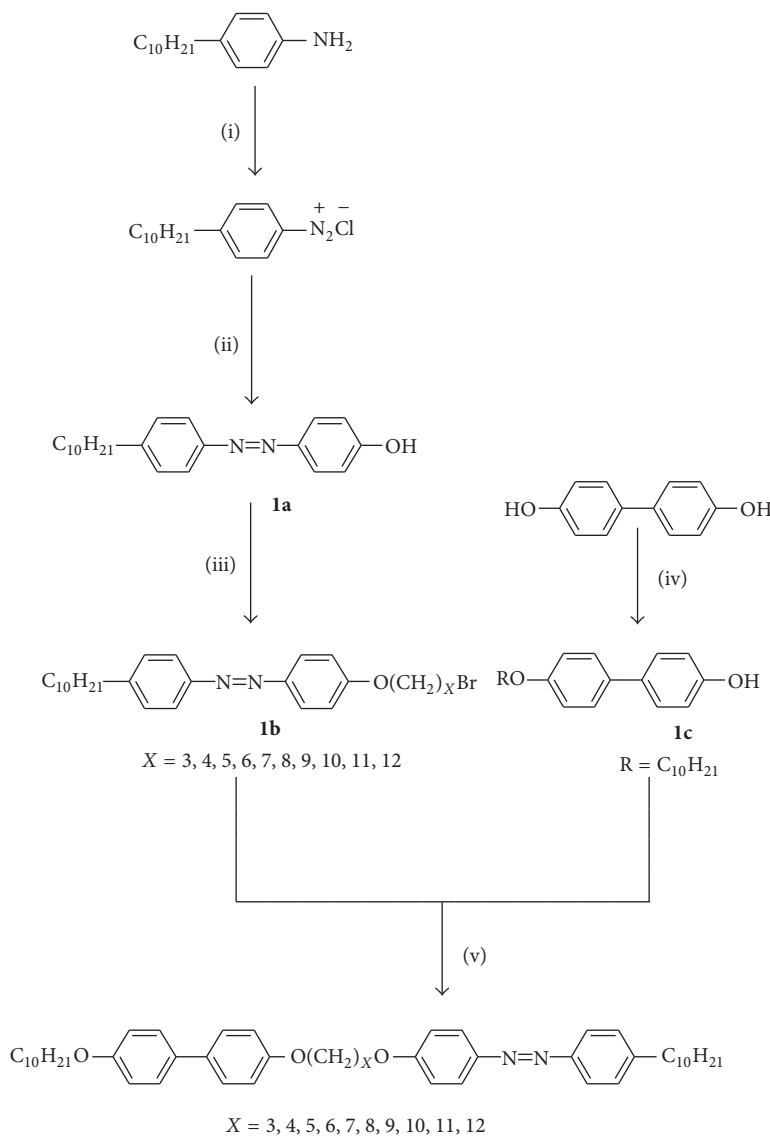
FIGURE 4: Dependence of nematic to isotropic transition temperature for the C-n series.

## 4. Experimental

**4.1. Materials.** 4-decyylaniline,  $\alpha$ ,  $\omega$ -dibromoalkane, 4,4'-Dihydroxybiphenyl, and 4-decyloxy benzoic acid were purchased from Aldrich Chemical Co. All other solvents and reagents were purchased commercially and used without purification. Dichloromethane and ethanol obtained were purified and dried as per the standard procedures.

**4.2. Measurements.** IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. NMR spectra were recorded using Bruker AMX-400 (400 MHz). The identification of the mesophases and determination of phase transition temperatures were achieved with the help of polarizing optical microscope (Leica DMLP) provided with a heating stage (Mettler FP90). The sample placed between a clean untreated glass slide and a cover slip was used for this particular study. The mesophase assignment was based on the observation of birefringence and fluidity when examined under POM. To confirm the transition temperatures and to determine their associated enthalpies, a differential scanning calorimeter (Perkin Elmer DSC7) calibrated using pure Indium was employed. The peaks observed in DSC traces (obtained at a rate of  $10^{\circ}\text{C/min}$ .) due to phase transition were reproducible and peak temperatures were consistent with those deduced from the optical experiments.

**4.3. Synthesis of Dimer.** The target dimers were purified by column chromatography and recrystallization choosing appropriate mixture of solvents, while the intermediates were purified by column chromatographic technique. Chromatography was performed using either silica gel (100–200, 230–400 mesh). Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel, 60F254). Infra red spectra were recorded on a Perkin-Elmer Spectrum 1000 FTIR spectrometer; the spectral positions (absorption maxima) are given in wave



SCHEME 1: Scheme C-n. Reagents and condition: (i) sodium nitrite, HCl, 0–2°C; (ii) phenol, aq. NaOH, Na<sub>2</sub>CO<sub>3</sub>, 0–2°C; (iii) 1,10-dibromodecane, anhy. K<sub>2</sub>CO<sub>3</sub>, acetone reflux, 18 h; (iv) 1-bromodecane, anhy. K<sub>2</sub>CO<sub>3</sub>, butanone reflux, 14 h; (v) anhy. K<sub>2</sub>CO<sub>3</sub>, DMF reflux, 22 h.

numbers (cm<sup>-1</sup>). NMR spectra were recorded using Bruker AMX 400 (400 MHz) spectrometer. For <sup>1</sup>H NMR spectra, the chemical shifts are reported in parts per million relative to Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard and coupling constants are presented in hertz. Elemental analysis was performed using a Eurovector model EA 3000 CHNS elemental analyzer.

The azo benzene intermediates (**1a** and **1b**) were synthesized in two steps. Firstly, 4-decylaniline was diazotized using hydrochloric acid, sodium nitrite; sodium hydroxide and sodium carbonate provide the compound (**1a**). Alkylation of this compound with α, ω-dibromoalkane gives the intermediate (**1b**). The hydroxyl intermediate was synthesized by the O-alkylation of 4,4'-dihydroxybiphenyl using 1-bromodecane. These upon reacting with the intermediate (**1b**) furnished the target dimer.

**4-Hydroxy-4-decylazo Benzene (1a)**. 4-Decylaniline (1 g, 0.004 mol) was dissolved in 200 mL of a 1:1 mixture of water and acetone and 2.5 mL of concentrated HCl. To the cooled solution, NaNO<sub>2</sub> (0.29 g, 0.004 mol) in 3 mL of water was added dropwise. The solution was allowed to stand for 30 minutes in an ice bath with temperature 0–2°C. The resulting diazonium ion solution was added to a cold solution of phenol (0.4 g, 0.004 mol), NaOH (0.33 g, 0.004 mol), and Na<sub>2</sub>CO<sub>3</sub> (1 g) in 14 mL of cold water. The precipitate was filtered, dried, and recrystallised from aqueous ethanol. Yield: 84%; a yellow solid; m.pt: 75°C. IR (KBr pellet): 3432, 2857, 1652, and 1025 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ: 7.75 (d, J = 9.2 Hz, 2H, Ar), 7.30 (m, 4H, Ar), 7.72 (d, J = 8.4 Hz, 2H, Ar), 2.66 (t, 2H, 1XAr-CH<sub>2</sub>), 1.71–1.56 (m, 14H, 7XCH<sub>2</sub>), 1.47 (m, 2H, 1XCH<sub>2</sub>), 0.95 (t, 3H, 1XCH<sub>3</sub>).



*4- $\omega$ -Bromoalkyloxy-4-decylazobenzene (1b)*. Potassium carbonate (1 equiv, 0.046 mol) was added to a solution of 4-hydroxy-4-decylazo benzene and  $\alpha$ ,  $\omega$ -dibromoalkane (4 equiv, 0.070 mol) in acetone (180 mL). The reaction mixture was refluxed at 50°C for 18 h and then poured into ice cold water. The crude product was extracted in to dichloromethane and dried over sodium sulphate and the solvent removed in vacuo. The crude residue was purified by column chromatography on silica gel (100–200 mesh), eluting with hexane and dichloromethane to afford pure compound.

*4- $\omega$ -Bromododecyloxy-4-decylazobenzene*. Yield: 89%; a yellow solid; IR (KBr pellet): 2810, 1610, 1265, 1039, and 804  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.71–7.60 (m, 2H, Ar), 7.29–7.20 (m, 4H, Ar), 6.69–6.62 (m, 2H, Ar), 4.20 (t, 2H, 1XAr–OCH<sub>2</sub>), 3.22 (t, 2H, 1XCH<sub>2</sub>Br), 2.62 (t, 2H, 1XAr–CH<sub>2</sub>), 1.79–1.73 (m, 38H, 19XCH<sub>2</sub>), 0.97 (t, 3H, 1XCH<sub>3</sub>).

*4-n-decyloxy-4'-hydroxybiphenyl*. 4,4'-Dihydroxybiphenyl (1 g, 0.005 mol), n-bromodecane (0.4 g, 0.002 mol), and potassium carbonate (3.5 g, 0.026 mol) were refluxed for 14 h under nitrogen atmosphere using butanone and was filtered through Celite bed when hot. The filtrate was evaporated to get the solid residue and purified by column chromatography on silica gel (100–200 mesh) and recrystallised from ethanol.

Yield: 55%; IR (KBr pellet): 3305, 2920, 2854, 1619, 1503, 1251, and 832  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.47 (d,  $J = 8.6$  Hz, 2H, Ar), 7.43 (d,  $J = 8.5$ , 2H, Ar), 6.91 (d,  $J = 8.7$ , 2H, Ar), 6.87 (d,  $J = 8.6$ , 2H, Ar), 4.79 (s, 1H, 1XOH), 3.98 (t, 2H, 1XAr–OCH<sub>2</sub>), 2.0–1.25 (m, 16H, 8XCH<sub>2</sub>), 0.91 (t, 3H, 1XCH<sub>3</sub>).

*{4-[7-(4'-Decyloxy-biphenyl-4-yloxy)-alkyloxy]-phenyl}-(4-decyl-phenyl)-diazene*. Compound **1b** (1 equiv, 0.0003 mol), compound **1c** (1 equiv, 0.0004 mol), and potassium carbonate (3 equiv, 0.0007 mol) were refluxed for 22 h under nitrogen atmosphere using dimethylformamide. Water was added to the reaction mixture at room temperature. The product was filtered and purified by column chromatography on silica gel (100–200 mesh) and recrystallised from dichloromethane/ethanol.

C-3. Yield: 45%; a yellow solid [found C, 79.77; H, 8.97; N, 4.06.  $\text{C}_{47}\text{H}_{64}\text{N}_2\text{O}_3$  requires C, 80.07; H, 9.15; N, 3.97]. IR (KBr pellet): 2854, 2816, 1625, 1257, 1041, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.79 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.29 (d,  $J = 8.1$  Hz, 2H, Ar), 6.94 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H, 3XOCH<sub>2</sub>), 2.51 (t, 2H, 1XAr–CH<sub>2</sub>), 1.77–1.74 (m, 32H, 16XCH<sub>2</sub>), 1.24 (t, 2H, 1XCH<sub>2</sub>), 0.99–0.96 (m, 6H, 2XCH<sub>3</sub>).

C-4. Yield: 49%; a yellow solid [found C, 79.93; H, 9.57; N, 3.7.  $\text{C}_{48}\text{H}_{66}\text{N}_2\text{O}_3$  requires C, 80.18; H, 9.25; N, 3.90]. IR (KBr pellet): 2854, 2806, 1625, 1259, 1041, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80

(d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.29 (d,  $J = 8.1$  Hz, 2H, Ar), 6.94 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H, 3XOCH<sub>2</sub>), 2.51–2.53 (m, 2H, 1XAr–CH<sub>2</sub>), 1.77–1.74 (m, 32H, 16XCH<sub>2</sub>), 1.24–1.22 (m, 4H, 2XCH<sub>2</sub>), 0.99–0.96 (m, 6H, 2XCH<sub>3</sub>).

C-5. Yield: 52%; a yellow solid [found C, 80.03; H, 9.65; N, 4.12.  $\text{C}_{49}\text{H}_{68}\text{N}_2\text{O}_3$  requires C, 80.28; H, 9.35; N, 3.82]. IR (KBr pellet): 2856, 2806, 1625, 1259, 1051, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.29 (d,  $J = 8.1$  Hz, 2H, Ar), 6.94 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H, 3XOCH<sub>2</sub>), 2.52–2.55 (m, 2H, 1XAr–CH<sub>2</sub>), 1.77–1.74 (m, 32H, 16XCH<sub>2</sub>), 1.24–1.22 (m, 6H, 3XCH<sub>2</sub>), 0.99–0.96 (m, 6H, 2XCH<sub>3</sub>).

C-6. Yield: 55%; a yellow solid [found C, 80.13; H, 9.74; N, 3.52.  $\text{C}_{50}\text{H}_{70}\text{N}_2\text{O}_3$  requires C, 80.38; H, 9.44; N, 3.75]. IR (KBr pellet): 2856, 2806, 1625, 1259, 1051, and 848  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.28 (d,  $J = 8.1$  Hz, 2H, Ar), 6.94 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H, 3XOCH<sub>2</sub>), 2.50 (t, 2H, 1XAr–CH<sub>2</sub>), 1.77–1.74 (m, 32H, 16XCH<sub>2</sub>), 1.24–1.20 (m, 8H, 4XCH<sub>2</sub>), 0.99–0.96 (m, 6H, 2XCH<sub>3</sub>).

C-7. Yield: 64%; a yellow solid [found C, 80.67; H, 9.83; N, 3.42.  $\text{C}_{51}\text{H}_{72}\text{N}_2\text{O}_3$  requires C, 80.48; H, 9.53; N, 3.68]. IR (KBr pellet): 2856, 2806, 1625, 1260, 1051, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.28 (d,  $J = 8.1$  Hz, 2H, Ar), 6.94 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H, 3XOCH<sub>2</sub>), 2.49–2.52 (m, 2H, 1XAr–CH<sub>2</sub>), 1.77–1.74 (m, 32H, 16XCH<sub>2</sub>), 1.24–1.20 (m, 10H, 5XCH<sub>2</sub>), 0.99–0.96 (m, 6H, 2XCH<sub>3</sub>).

C-8. Yield: 67%; a yellow solid [found C, 80.28; H, 9.83; N, 3.91.  $\text{C}_{52}\text{H}_{74}\text{N}_2\text{O}_3$  requires C, 80.57; H, 9.62; N, 3.61]. IR (KBr pellet): 2856, 2806, 1635, 1260, 1051, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.28 (d,  $J = 8.1$  Hz, 2H, Ar), 6.95 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H, 3XOCH<sub>2</sub>), 2.54 (t, 2H, 1XAr–CH<sub>2</sub>), 1.77–1.74 (m, 32H, 16XCH<sub>2</sub>), 1.24–1.20 (m, 12H, 6XCH<sub>2</sub>), 0.99–0.96 (m, 6H, 2XCH<sub>3</sub>).

C-9. Yield: 70%; a yellow solid [found C, 80.47; H, 9.45; N, 3.67.  $\text{C}_{53}\text{H}_{76}\text{N}_2\text{O}_3$  requires C, 80.66; H, 9.71; N, 3.55]. IR (KBr pellet): 2856, 2806, 1635, 1260, 1051, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.28 (d,  $J = 8.1$  Hz, 2H, Ar), 6.95 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H, 3XOCH<sub>2</sub>), 2.49 (t, 2H, 1XAr–CH<sub>2</sub>), 1.77–1.74 (m, 32H, 16XCH<sub>2</sub>), 1.24–1.20 (m, 14H, 7XCH<sub>2</sub>), 0.99–0.96 (m, 6H, 2XCH<sub>3</sub>).

C-10. Yield: 70%; a yellow solid [found C, 80.56; H, 9.94; N, 3.79.  $\text{C}_{54}\text{H}_{78}\text{N}_2\text{O}_3$  requires C, 80.75; H, 9.79; N, 3.49].

IR (KBr pellet): 2856, 2806, 1635, 1268, 1051, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.42 (m, 4H, Ar), 7.28 (d,  $J = 8.1$  Hz, 2H, Ar), 6.96 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H,  $3\text{XOCH}_2$ ), 2.50 (t, 2H,  $1\text{XAr-CH}_2$ ), 1.77–1.74 (m, 32H,  $16\text{XCH}_2$ ), 1.24–1.19 (m, 16H,  $8\text{XCH}_2$ ), 0.99–0.96 (m, 6H,  $2\text{XCH}_3$ ).

C-11. Yield: 72%; a yellow solid [found C, 81.14; H, 9.72; N, 3.72.  $\text{C}_{55}\text{H}_{80}\text{N}_2\text{O}_3$  requires C, 80.83; H, 9.87; N, 3.43]. IR (KBr pellet): 2856, 2806, 1635, 1268, 1071, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.85 (d,  $J = 8.6$  Hz, 2H, Ar), 7.81 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.29 (d,  $J = 8.1$  Hz, 2H, Ar), 6.96 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.80 (m, 4H, Ar), 4.20 (t, 6H,  $3\text{XOCH}_2$ ), 2.54 (t, 2H,  $1\text{XAr-CH}_2$ ), 1.77–1.74 (m, 32H,  $16\text{XCH}_2$ ), 1.24–1.19 (m, 18H,  $9\text{XCH}_2$ ), 0.99–0.96 (m, 6H,  $2\text{XCH}_3$ ).

C-12. Yield: 75%; a yellow solid [found C, 80.78; H, 10.12; N, 3.57.  $\text{C}_{56}\text{H}_{82}\text{N}_2\text{O}_3$  requires C, 80.91; H, 9.94; N, 3.37]. IR (KBr pellet): 2862, 2806, 1635, 1268, 1071, and 841  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz): 7.86 (d,  $J = 8.6$  Hz, 2H, Ar), 7.80 (d,  $J = 8.2$  Hz, 2H, Ar), 7.44–7.41 (m, 4H, Ar), 7.28 (d,  $J = 8.1$  Hz, 2H, Ar), 6.96 (d,  $J = 8.4$  Hz, 2H, Ar), 6.84–6.81 (m, 4H, Ar), 4.20 (t, 6H,  $3\text{XOCH}_2$ ), 2.53 (t, 2H,  $1\text{XAr-CH}_2$ ), 1.77–1.75 (m, 32H,  $16\text{XCH}_2$ ), 1.24–1.19 (m, 20H,  $10\text{XCH}_2$ ), 0.99–0.96 (m, 6H,  $2\text{XCH}_3$ ).

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