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Design and Synthesis of Novel Calamitic and Discotic Materials Based on the Photorefractive Carbazole Unit

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The incorporation of photorefractive molecular units, such as carbazole, into anisotropic materials (liquid crystals) may offer many advantages over conventional electrical poling of photorefractive polymers. Thus, a series of symmetric 3,6-disubstituted carbazole derivatives with well-known biphenyl and triphenylene liquid-crystalline moieties was synthesized and characterized. These modifications were achieved by the esterification of bishydroxy carbazole derivatives with monoalkylated biphenyl carboxylic acids and alkylation of bisacylated bromo- derivatives of carbazole with monohydroxy pentaalkoxy triphenylene. The pure compounds are not liquid-crystalline, even when doped with trinitrofluorenone (TNF), unlike triphenylene/carbazole materials that we reported previously. These compounds, although not liquid-crystalline, may be of interest in the field of photorefractivity.

Keywords Anisotropic ordering; calamitic liquid crystals; carbazole; discotic liquid crystals; mesogenic; photorefractive

Introduction

Due to their extensive biological activity, carbazole derivatives and their chemistry have been studied at length [1]. However, it is only recently that they have been studied in terms of their material properties [1,2] and in particular their photorefractive properties [3]. The interest in photorefractive materials [4] lies in their numerous potential technological applications [5] such as high-density optical data storage, optical image processing, phase-conjugated mirrors, dynamic holography, optical computing, parallel optical logic, and pattern recognition. Thus, recent studies on carbazole materials have been concerned with electroluminescence [6], nonlinear optics [7], and photoconductivity [8]. Amorphous organic photorefractive materials

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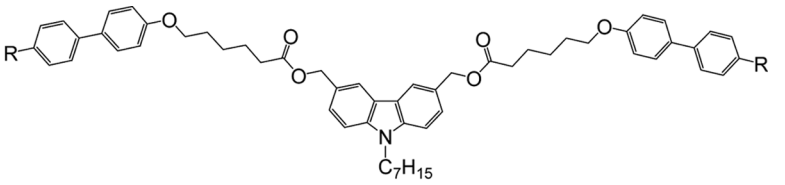
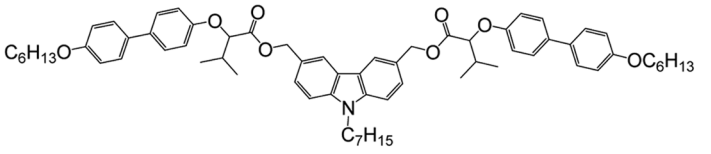
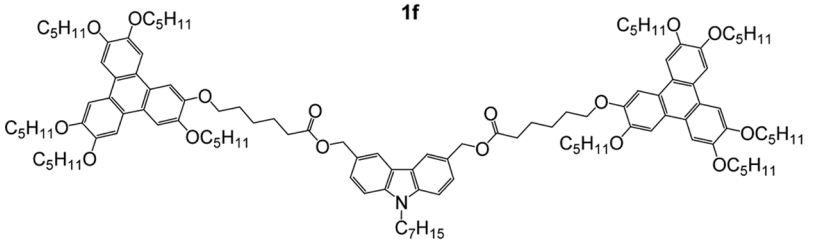
[9] have many advantages over crystalline inorganic [3] and latterly crystalline organic [10] photorefractive materials on which the early research was carried out. These advantages include large opitical nonlinearities, low dielectric constants, low cost, structural flexibilty, and ease of fabrication. However, the major drawback of the amorphous organic photorefractive materials is that a low T_g is required in order that the material can be aligned by a DC electric field to induce a degree of anisotropic ordering [11]. The chemical modification of the carbazole moiety to induce liquid crystallinity is attractive in order to combine the advantages of the amorphous materials with anisotropic ordering. However, to date there are only a few examples in which the carbazole moiety has been incorporated into thermotropic low-molecular-weight [12] and polymeric liquid-crystalline materials [13] and into lyotropic liquid crystals [14]. Thus, one of the approaches that we are adopting [15] to induce hexagonal columnar discotic and calamitic mesophases in carbazole



1a R = OC_5H_{11}
1b R = OC_6H_{13}
1c R = OC_8H_{17}
1d R = $OC_{12}H_{25}$
1e R = CN



1f



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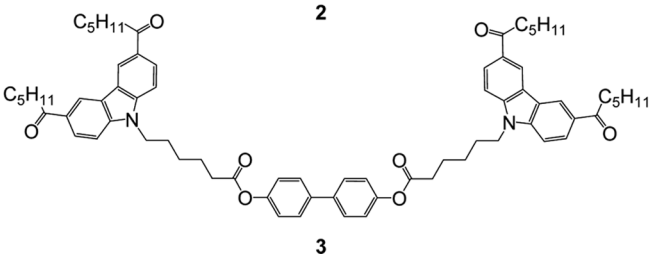

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Figure 1. Carbazole-based biphenylene and triphenylene derivatives **1a-f**, **2–3**.

derivatives is to covalently modify the carbazole moiety with well-known [16] discotic triphenylene and calamitic biphenyl derivatives [17].

Previously, we have reported [15] the synthesis of several carbazole based triphenylene hybrid structures in which one, two, three, and six carbazole units were covalently linked to the periphery of the triphenylene core; the induced mesophase behavior of some of these carbazole derivatives when "complexed" with trinitrofluorenone (TNF) [15,18], and later we also studied transient photoconductivity properties of these complexes [19]. We have also recently reported on the preparation of triphenylene/carbazole mesogens that have been chemically modified on the 3 and 6 positions of the carbazole moiety and their solution electrochemistry [20]. We have also reported a study of the incorporation of carbazole as the central unit in a first and second generation of mesogenic bent structures [21] in order to pursue banana-shaped liquid crystals [22–24]. In this present article we report on the synthesis of carbazole/biphenyl and carbazole/triphenylene hybrid structures. The chemical structures of the carbazole derivatives are shown in Fig. 1.

Result and Discussion

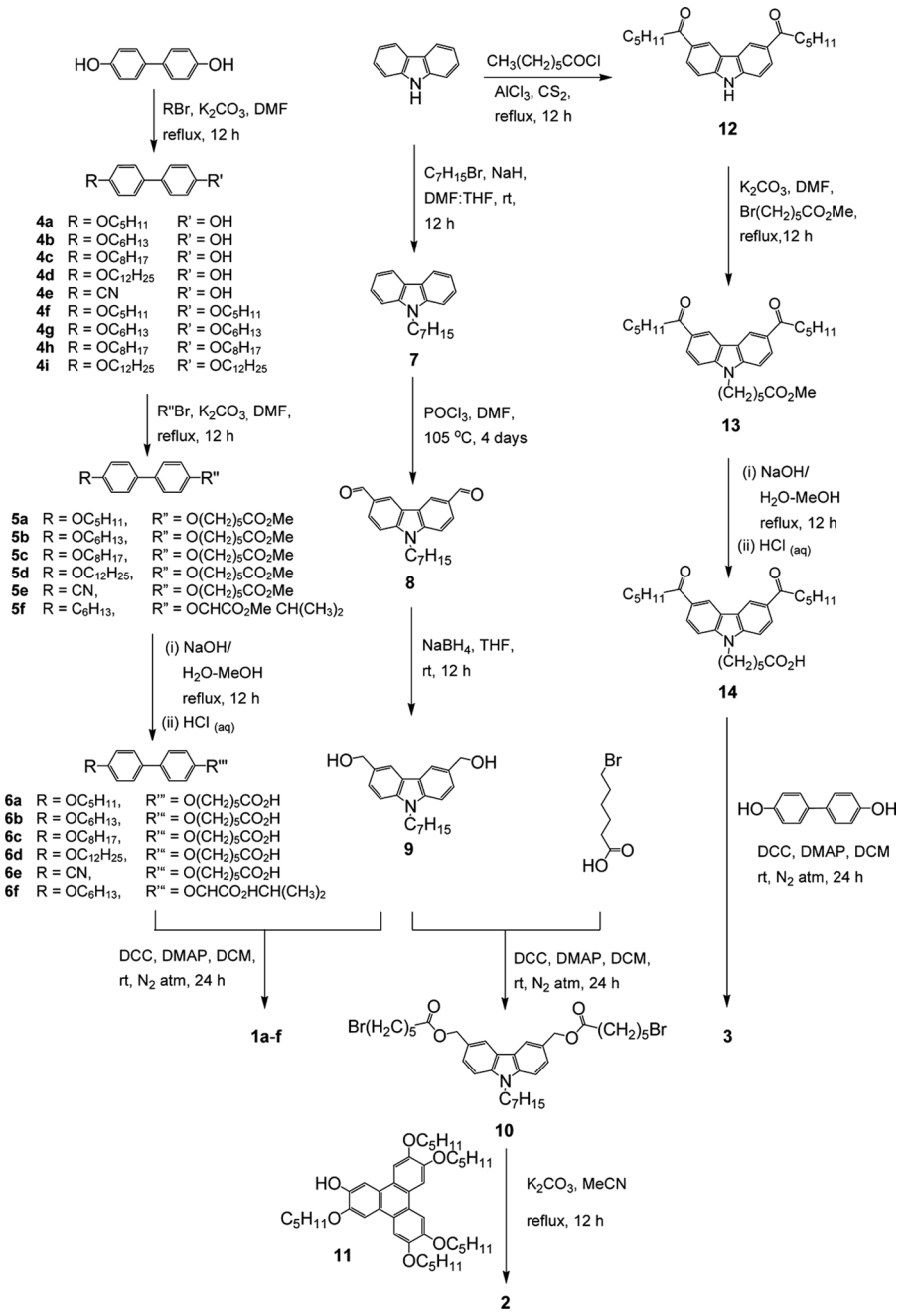
Molecular Design

Previously it has been reported that the introduction of substituents on the 3- and 6-positions of carbazole represents a possible approach for designing carbazole-based photorefractive materials [9]. Thus, combining a carbazole unit with well-known biphenyl and triphenylene liquid-crystalline moieties represents a possible approach toward developing novel materials that are liquid-crystalline and have photorefractive properties. Hence, the molecules investigated here are hybrids of triphenylene/biphenyl and carbazole moieties that are linked by an alkyl spacer. For molecules **1a-f** and **2**, the central core comprises a carbazole that is substituted on the 3 and 6 positions with biphenyl or triphenylene units, and **3**, contains a biphenyl moiety as the central core with substitutents in the 4 and 4′ positions that consist of 3,6-disubstituted carbazole moieties, leading to an H-shaped molecular structure.

The presence of the alkyl chains as spacers between the aromatic components (biphenyl or triphenylene and carbazole) provides flexibility, elongate the molecule and provides a balance between the aromatic and alkyl components within the molecular design [25]. As previously reported for triphenylene/carbazole [20] based materials, the lack of mesophase behavior was envisaged to be partly the result of the larger proportion of π-surface relative to the alkyl chain. Thus, the addition of the alkyl chain as spacers will provide a more balanced system. In all of the molecules, apart from **1f**, the pentyl chain has been selected as the spacer, which is attached to the central core *via* an ester linkage. Whilst in molecule **1f**, a branched alkyl chain has been introduced as the spacer in order to lower the melting point. Furthermore, to investigate the effect of the length of the spacer on the mesophase behavior a range of alkyl chain lengths has been used (**1a-e**).

Synthesis

The synthesis of the new carbazole based biphenyl (rod-like) and triphenylene (disc-like) compounds **1a-f**, **2**, and **3** were achieved *via* a series of reactions as illustrated in Scheme 1. Alkylation of commercially available biphenyl-4,4-diol with



Scheme 1. Synthetic routes to the triphenylene and biphenylene derivatives **1a-f**, **2–3**.

n-bromopentane, *n*-bromohexane, *n*-bromooctane, and *n*-bromdodectane, respectively, was performed under basic conditions (K_2CO_3), affording white crystalline solids **4a-d** and dialkylated biphenyl derivatives **4f-i**. Similar conditions were then used to perform a second alkylation on the free hydroxyl group of compounds **4a-e**, with 6-bromohexanoate or methyl 2-bromo-3-methylbutanoate affording

the biphenyl esters **5a-f**. These esters were subsequently hydrolyzed under basic conditions to afford the carboxylic acids **6a-f**.

The N-alkylation of carbazole with n-bromoheptane afforded 9-heptylcarbazole **7**. The N-alkylated carbazole was necessary in order to perform the following formylation step [26]. The formylation step involved the symmetric functionalization of the carbazole core on the 3 and 6 positions, giving rise to the introduction of two aldehyde functional groups, affording 3,6-diformyl-9-heptylcarbazole **8**. The bisformylation was performed in the presence of phosphorus oxychloride ($POCl_3$) in DMF at 0°C under a N_2 atmosphere [27]. The 3,6-diformyl compound **8** was reduced to bis-3,6-dihydroxy methyl derivative **9**, using $NaBH_4$ as a reducing agent. Compound **9** was esterified with the acids **6a-f** using 1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) to afford the respective esters **1a-f**.

The commercially available 6-bromohexanoic acid was directly esterified with bishydroxy carbazole **9**, using DCC and DMAP, to afford the bis-bromo ester **10**. Alkylation of this bis-bromo ester **10** with monohydroxy pentyloxy triphenylene **11** in the presence of K_2CO_3 afforded the bistriphenylene carbazole **2** as a white solid.

Commercially available carbazole was bisacylated under Freidel-Crafts conditions [27] with hexanoic acid chloride to afford **12**. This bisacylated carbazole derivative was subsequently N-alkylated with 6-bromohexanoate to afford **13**. This ester was then hydrolyzed under basic conditions to the acid **14**. The acid was esterified with 4,4′-biphenol *via* DCC coupling to afford **3**.

Thermal Properties

Thermal analysis was carried out on compounds **1a-f**, **2**, **3**, **4a-d**, **5a-f**, and **6a-f** using a variable-temperature optical polarized microscope (OPM) between crossed

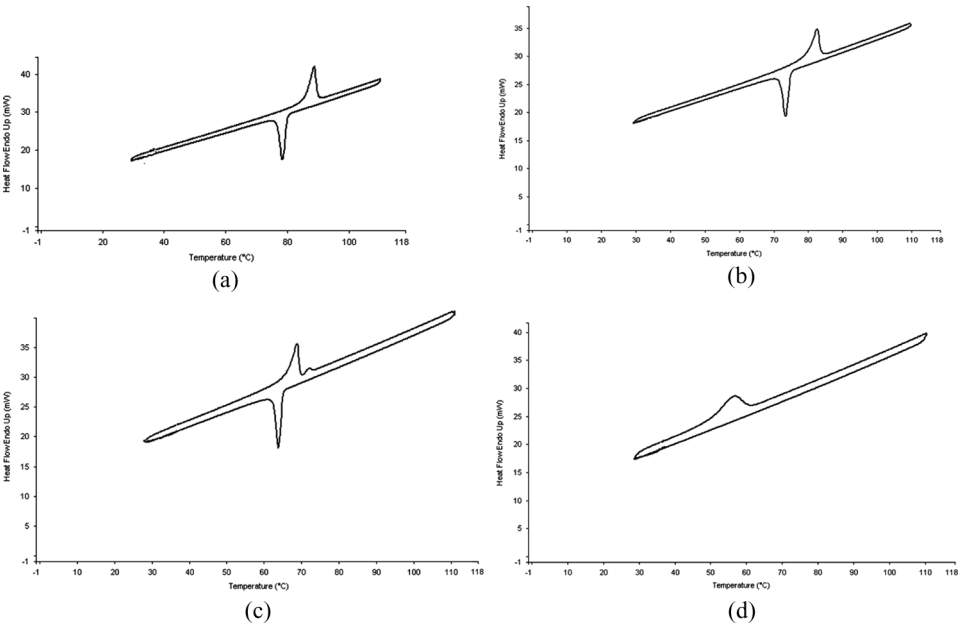


Figure 2. DSC traces for compounds **1a**, **1b**, **1c**, and **2** (second heating cycle at a rate 10°C/min).

Table 1. Transition temperatures (onset values) and enthalpy values ΔH (kJ/mol) were recorded on the second heating by DSC (10°C/min) for compounds **1a, 1b**, and **1c**. However, for compound **2**, the onset temperature and enthalpy values were recorded from the first heating because the compound decomposed over first heating

Entry	K → I/°C	ΔH
1a	86	34.8
1b	77	23.2
1c	66	26.1
2	56	19.6

polarizers and differential scanning calorimetry (DSC). Monoalkylated **4a-d**, dialkylated biphenyl **5a-f**, and acid derivatives **6a-f** did not show any mesophase by OPM. The new carbazole-based bis-biphenyl, triphenylene dimers **1a-f**, **2**, and biphenyl based bis-carbazole **3**, as single components, did not show any birefringent liquid phases either. This was not a total surprise because none of the compounds that were reported previously [15,20,21] exhibited a mesophase as a single component. DSC revealed that upon cooling the I → K transition was observed at slightly lower temperatures, confirming the lack of any mesophase formation. However, for a few of the compounds **1d**, **1e**, **1f**, and **3** the I → K transition was not observed. These results suggests that these compounds decomposed through the K → I transition. In the case of compound **1c** an additional peak was originally observed during K → I transition in the DSC trace; however, this peak was not reproducible in the third heating cycle. As expected, for all the derivatives, the K → I transition decreased with increasing carbon chain length. The DSC traces are illustrated in Fig. 2 and the melting points are listed in Table 1.

However, it was expected that doping with TNF would induce a mesophase, as it did with the previously reported [15] compounds. Unfortunately, doping **1a-f**, **2**, and **3** with TNF [28] did not produce any mesophases. Thus, our design criteria of introducing two mesogenic moieties to the carbazole units to enhance the discotic and calamitic mesophases did not lead to liquid-crystalline molecules. It should be pointed out that previously we have derivatized carbazole [21] at the 3 and 6 positions to afford banana-shaped liquid crystals. To date, all attempts to induce mesophases in these materials have not succeeded. Thus, a 3,6-disubstituted carbazole may be inherently non-mesogenic.

Conclusions

The synthesis of several mesogenic units containing carbazole **1a-f**, **2**, and **3** derivatives has been described. The pure compounds were found not to be liquid-crystalline in nature. Furthermore, it was not possible to induce a mesophase by doping with TNF.

Having synthesized and investigated several carbazole derivatives in which the carbazole unit is at the periphery [15,20,21] of a triphenylene/biphenyl core separated by a spacer in the form of an alkyl chain or vice versa, both designs showed

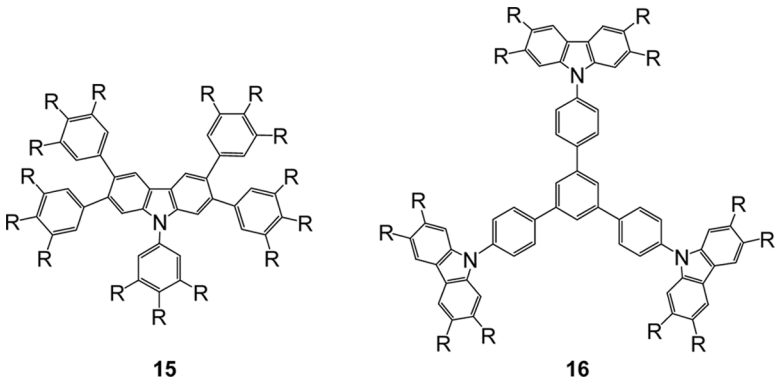


Figure 3. Proposed structure of carbazole liquid crystals.

limited success in forming mesophases. Therefore, it can be concluded that these molecular architectures are no longer worth pursuing. Presently, we are working on the synthesis of two carbazole derivatives illustrated in Fig. 3. Both are based on disc-like structures and thus are expected to display columnar mesophases. Structure **15** comprises of 2,3,6,7,9-pentaphenylcarbazole derivative as the disc-like central core. Each of the phenyl moieties are further substituted in the 3, 4, and 5 positions with alkyl chains. For structure **16**, the central core comprises of 1,3,5-triphenylbenzene onto which 2,3,6,7-tetraalkylsubstituted carbazole moieties are attached *via* the nitrogen, leading to a bulky aromatic disc-like core with alkyl moieties substituted onto the carbazole to further elongate the molecule. In both cases a range of alkyl chains can be investigated such as pentyl, hexyl, etc., to obtain the optimum balance between aromatic and alkyl components.

Experimental

General Procedures

The starting materials, which were commercially available, were purchased from Sigma-Aldrich (Gillingham, UK) and used as received. The solvents were purchased from Fisher Scientific (CH_2Cl_2, EtOAc, Et_2O THF and MeOH) or Aldrich. Solvents were either used as received or dried; DCM was distilled from $CaCl_2$ under a N_2 atmosphere. Yields refer to chromatographically pure products. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 (Merck 5554 mesh). Column chromatography was performed on silica gel 60 (Merck 230–400). Microanalyses were performed by the University of Birmingham microanalytical services. High-performance liquid chromatography (HPLC) studies were recorded on a Dionex Summit System with Chromeleon Software, coupled to a Summit UV 170 s UV/visible multichannel detector with an analytical flow cell. Analytical HPLC runs were performed on a Luna (Phenomenex), C_{18}, 250 mm × 4.6 mm ID, with 10 μm pore size column using a gradient of MeCN/H_2O 50/50 over 60 min. Electron impact (EI) mass spectra were recorded at 70 eV on a VG ProSpec mass spectrometer. Liquid secondary ion mass spectra (LSIMS) were recorded on a VG ZaBSpec mass spectrometer equipped with a cesium ion source and utilizing *m*-nitrobenzyl alcohol containing a trace of sodium acetate as the liquid matrix.

^{1}H NMR spectra were recorded either on a Bruker AC 300 (300 MHz), Bruker AMX400 (400 MHz), or Bruker DRX500 (500 MHz), spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC 300 (75 MHz), Bruker AMX400 (100 MHz), or Bruker DRX500 (125 MHz) spectrometer. The chemical shift values are expressed as δ values and the coupling constant values (J) are in Hertz (Hz). The following abbreviations are used for the signal multiplicities or characteristics: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, muliplet; q, quartet; quint; quintet; br, broad. Transition temperatures were measured using a Mettler FP82 HT hot stage and central processor in conjunction with Leitz DMFRT polarizing microscope as well as differential scanning calorimetry (DSC7 Perkin-Elmer). 2-Hydroxy-3,6,7,10-pentakis (pentyloxy) triphenylene **11** [29], compounds **12**, **13**, and **14** were synthesized according to literature procedures [20,27].

Compound ***4a***. A suspension of K_2CO_3 (11.12 g, 80.65 mmol) in a solution of 4,4′-biphenol (5.00 g, 26.88 mmol) and *n*-bromopentane (4.06 g, 26.88 mmol) in MeCN (100 mL) was stirred and heated under reflux overnight. The resultant brown mixture was allowed to cool to room temperature and concentrated *in vacuo* (30 mL). Water (250 mL) was added and the aqueous layer was extracted by washing with Et_2O (3×100 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered, and solvent removed *in vacuo*, yielding a colorless solid as the crude product. The crude product was purified by silica gel column chromatography (gradient elution: 0 to 50% CH_2Cl_2 in EtOAc, increase polarity in increments of 25% per 150 mL of eluent used). The solvent was removed *in vacuo* to yield a white solid **4a** (2.50 g, 36%). Mp 138–140°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 2H, $J = 7.9$ Hz), 7.42 (d, 2H, $J = 7.9$ Hz, 2H), 6.94 (d, 2H, $J = 7.9$ Hz, 2H), 6.88 (d, 2H, $J = 7.9$ Hz), 4.81 (brs, 1H), 3.98 (t, 2H, $J = 6.4$ Hz), 1.82–1.78 (m, 2H), 1.34–1.23 (m, 4H), 0.95–0.91 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 158.3, 154.6, 133.8, 133.2, 127.9, 127.7, 115.6, 114.8, 68.1, 29.0, 28.2, 22.5, 14.0. MS (EIMS) m/z 256 $[M]^+$.

The same procedure used for the preparation of **4a** was followed for the synthesis of **4b**, **4c**, and **4d**.

Compound ***4b***. From 4,4′-biphenol (5.00 g, 26.88 mmol), K_2CO_3 (11.12 g, 80.64 mmol), and *n*-bromohexane (4.43 g, 26.88 mmol). This yielded a white solid **4b** (2.20 g, 30%). Mp 129–131°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.42 (d, 2H, $J = 8.8$ Hz), 7.39 (d, 2H, $J = 8.8$ Hz), 6.91 (d, 2H, $J = 8.8$ Hz), 6.85 (d, 2H, $J = 8.8$ Hz), 4.76 (s, 1H), 3.96 (t, 2H, $J = 6.6$ Hz), 1.83–1.71 (m, 2H), 1.51–1.39 (m, 2H), 1.38–1.25 (m, 4H), 0.88 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 158.3, 154.5, 133.8, 133.2, 127.9, 127.7, 115.6, 114.8, 68.1, 31.6, 29.3, 25.7, 22.6, 14.0. MS (EIMS) m/z 270 $[M]^+$.

Compound ***4c***. From 4,4′-biphenol (5.00 g, 26.88 mmol), K_2CO_3 (11.12 g, 80.64 mmol), and *n*-bromooctane (4.81 g, 26.88 mmol). This yielded a white solid **4c** (2.00 g, 26%). Mp 121–124°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.44 (d, 2H, $J = 7.9$ Hz), 7.42 (d, 2H, $J = 7.9$ Hz), 6.94 (d, 2H, $J = 7.9$ Hz), 6.88 (d, 2H, $J = 7.9$ Hz), 4.79 (s, 1H), 3.98 (t, 2H, $J = 6.4$ Hz), 1.81–1.77 (m, 2H), 1.46–1.23 (m, 10H), 0.88–0.86 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, 25°C) δ 158.4, 154.6, 133.9, 133.3, 128.0, 127.8, 115.7, 114.9, 68.2, 31.9, 29.5, 29.4, 29.3, 26.2, 22.7, 14.2. MS (EIMS) m/z 298 $[M]^+$.

Compound ***4d***. From 4,4′-biphenol (5.00 g, 26.88 mmol), K_2CO_3 (11.12 g, 80.64 mmol) and *n*-bromododecane (6.70 g, 26.88 mmol). This yielded a white solid **4d** (2.20 g, 23%). Mp 100–112°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.44 (d, 2H, $J = 8.0$ Hz), 7.42 (d, 2H, $J = 8.0$ Hz), 6.94 (d, 2H, $J = 8.0$ Hz), 6.88 (d, 2H, $J = 8.0$ Hz), 4.76 (s, 1H), 3.98 (t, 2H, $J = 6.4$ Hz), 1.82–1.76 (m, 2H), 1.49–1.23 (m, 18H), 0.88–0.86 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, 25°C) δ 157.6, 156.5, 132.7, 130.8, 127.2, 127.0, 115.7, 114.8, 67.5, 31.3, 29.1, 29.0, 28.8, 28.7, 25.6, 22.1, 14.0. MS (EIMS) m/z 354 $[M]^+$.

Dialkylated biphenyl compounds **4f-4i** were obtained as by-products from the synthesis of **4a-4d**.

Compound ***4f***. Obtained by column chromatography by using CH_2Cl_2 as eluent to yield **4f** (3.00 g, 40%) as microcrystalline white power. Mp 162–165°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.47 (d, 4H, $J = 8.7$ Hz), 6.95 (d, 4H, $J = 8.7$ Hz), 3.99 (t, 4H, $J = 6.6$ Hz), 1.86–1.77 (m, 4H), 1.51–1.35 (m, 8H), 0.95 (t, 6H, $J = 7.05$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 158.2, 133.2, 127.6, 114.8, 68.1, 29.0, 28.2, 22.5, 14.0. MS (EIMS) m/z 326 $[M]^+$.

Compound ***4g***. Obtained by column chromatography by using CH_2Cl_2 as eluent to yield **4 g** (2.50 g, 35%) as microcrystalline white powder. Mp 159–162°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.47 (d, 4H, $J = 8.7$ Hz), 6.95 (d, 4H, $J = 8.7$ Hz), 3.96 (t, 4H, $J = 6.6$ Hz), 1.86–1.76 (m, 4H), 1.52–1.43 (m, 4H), 1.42–1.29 (m, 8H), 0.88 (t, 6H, $J = 7.01$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 158.2, 133.3, 127.6, 114.8, 68.1, 31.6, 29.3, 25.7, 22.6, 14.0. MS (EIMS) m/z 354 $[M]^+$.

Compound ***4h***. Obtained by column chromatography by using CH_2Cl_2 as eluent to yield **4 h** (2.50 g, 35%) as microcrystalline white power. Mp 155–157°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 4H, $J = 8.8$ Hz), 6.94 (d, 4H, $J = 8.8$ Hz), 3.98 (t, 4H, $J = 6.4$ Hz), 1.84–1.75 (m, 4H), 1.41–1.23 (m, 20H), 0.89 (m, 6H, $J = 6.9$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 158.2, 133.3, 127.6, 114.8, 68.1, 31.8, 29.4, 29.3, 29.2, 26.1, 22.6, 14.1. MS (EIMS) m/z 410 $[M]^+$.

Compound ***4i***. Obtained by column chromatography by using CH_2Cl_2 as eluent to yield **4i** (2.10 g, 32%) as microcrystalline white power. Mp 150–151°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.46 (d, 4H, $J = 8.7$ Hz), 6.94 (d, 4H, $J = 8.7$ Hz), 3.98 (t, 4H, $J = 6.5$ Hz), 1.84–1.74 (m, 4H), 1.51–1.28 (m, 36H), 0.88 (t, 6H, $J = 6.68$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 157.6, 156.5, 132.7, 130.8, 127.2, 127.0, 115.7, 114.8, 67.5, 31.3, 29.1, 29.0, 28.8, 28.7, 25.6, 22.1, 14.0. MS (EIMS) m/z 522 $[M]^+$.

The same procedure for **4a** was followed for the synthesis of **5a**, **5b**, **5c**, **5d**, **5e**, and **5f**.

Compound ***5a***. From **4a** (1.20 g, 4.68 mmol), K_2CO_3 (0.65 g, 4.68 mmol), and methyl 6-bromohexanoate (0.98 g, 4.68 mmol). This yielded a white solid **5a** (0.70 g, 39%). Mp 111–112°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 4H, $J = 7.2$ Hz), 6.93 (d, 4H, $J = 7.2$ Hz), 3.99 (t, 4H, $J = 6.1$ Hz), 3.67 (s, 3H), 2.35 (t, 2H, $J = 7.4$ Hz), 1.84–1.69 (m, 6H), 1.51–1.38 (m, 6H), 0.90–0.88 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 174.0, 158.3, 158.1, 133.5, 133.3, 127.6, 114.7, 68.1, 67.7, 51.5, 34.0, 29.0, 28.2, 25.7, 24.7, 22.5, 14.0. MS (EIMS) m/z 384 $[M]^+$.

*Compound **5b**.* From **4b** (1.20 g, 4.44 mmol), K_2CO_3 (0.61 g, 4.44 mmol), and methyl 6-bromohexanoate (0.93, 4.44 mmol). This yielded a white solid **5b** (1.00 g, 57%). Mp 108–110°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 4H, $J = 8.7$ Hz), 6.94 (d, 4H, $J = 8.7$ Hz), 3.98 (t, 4H, $J = 6.5$ Hz), 3.67 (s, 3H), 2.35 (t, 2H, $J = 7.5$ Hz), 1.83–1.66 (m, 6H), 1.56–1.42 (m, 4H), 1.38–1.31 (m, 4H), 0.91 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 174.0, 158.3, 158.1, 133.5, 133.3, 127.6, 114.7, 68.1, 67.7, 51.5, 34.0, 31.6, 29.3, 29.0, 25.7, 25.6, 24.7, 22.6, 14.0. MS (EIMS) m/z 398 $[M]^+$.

*Compound **5c**.* From **4c** (1.20 g, 4.03 mmol) K_2CO_3 (0.56 g, 4.03 mmol), and methyl 6-bromohexanoate (1.20 g, 4.03 mmol). This yielded a white solid **5c** (1.00 g, 58%). Mp 109–111°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 4H, $J = 7.4$ Hz), 6.93 (d, 4H, $J = 7.4$ Hz), 3.98 (t, 4H, $J = 6.4$ Hz), 3.67 (s, 3H), 2.35 (t, 2H, $J = 7.4$ Hz), 1.84–1.69 (m, 6H), 1.51–1.28 (m, 12H), 0.88–0.87 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 173.7, 158.1, 157.7, 133.3, 133.1, 128.7, 116.2, 69.4, 69.2, 52.0, 34.8, 32.8, 30.3, 30.2, 29.9, 27.0, 26.6, 25.7, 23.5, 14.5. MS (EIMS) m/z 426 ($[M]^+$, 25%).

*Compound **5d**.* From **4d** (1.20 g, 3.39 mmol), K_2CO_3 (0.47 g, 3.39 mmol), and methyl 6-bromohexanoate (0.71 g, 4.03 mmol). This yielded a white solid **5d** (0.90 g, 55%). Mp 111–113°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 4H, $J = 7.6$ Hz), 7.42 (d, 4H, $J = 7.6$ Hz), 3.98 (t, 4H, $J = 6.4$ Hz), 3.67 (s, 3H), 2.35 (t, 2H, $J = 7.4$ Hz), 1.86–1.74 (m, 6H), 1.53–1.26 (m, 20H), 0.87 (t, 3H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, DMSO-d_6, 25°C) δ 174.3, 158.0, 132.6, 127.2, 115.2, 67.9, 67.7, 33.4, 31.2, 28.9, 28.8, 28.6, 28.5, 25.5, 25.2, 24.3, 22.0, 13.8. MS (ESMS) m/z 505 $[M + Na]^+$.

*Compound **5e**.* From **4e** (1.20 g, 6.15 mmol), K_2CO_3 (0.85 g, 6.15 mmol), and methyl 6-bromohexanoate (1.29 g, 6.15 mmol). This yielded a white solid **5e** (0.80 g, 40%). Mp 267°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.66 (d, 2H, $J = 8.6$ Hz), 7.61 (d, 2H, $J = 8.6$ Hz), 7.51 (d, 2H, $J = 8.6$ Hz), 6.91 (d, 2H, $J = 8.6$ Hz), 3.99 (t, 2H, $J = 6.4$ Hz), 3.67 (s, 3H), 2.34 (t, 2H, $J = 7.5$ Hz), 1.88–1.77 (m, 2H), 1.76–1.68 (m, 2H), 1.55–1.49 (m, 2H). (75 MHz, $CDCl_3$, 25°C) δ 173.9, 159.7, 145.2, 132.5, 131.3, 128.3, 127.0, 119.0, 115.0, 110.0, 67.8, 51.4, 33.9, 28.8, 25.6, 24.6. MS (EIMS) m/z 323 $[M]^+$.

*Compound **5f**.* From **4b** (1.20 g, 4.44 mmol), K_2CO_3 (0.61 g, 4.44 mmol), and methyl 2-bromo-3-methybutanoate (0.87 g, 4.44 mmol). This yielded a white solid **5f** (0.80 g, 47%). Mp 90–92°C. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 7.44 (d, 4H, $J = 8.6$ Hz), 6.94 (d, 4H, $J = 8.8$ Hz), 4.40 (d, 1H, $J = 5.8$ Hz), 3.98 (t, 2H, $J = 6.6$ H), 3.75 (s, 3H), 2.33–2.26 (m, 1H), 1.82–1.76 (m, 2H), 1.56–1.42 (m, 2H), 1.37–1.33 (m, 4H), 1.11 (d, 3H, $J = 6.8$ Hz), 1.10 (d, 3H, $J = 6.8$ Hz), 0.91 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C) δ 171.9, 158.4, 157.8, 134.5, 133.1, 127.8 127.7, 115.4, 114.8, 81.9, 68.1, 52.0, 31.7, 31.6, 29.3, 25.7, 22.6, 18.6, 17.8, 14.0. MS (EIMS) m/z 384 $[M]^+$.

*Compound **6a**.* To a solution of **5a** (0.80 g, 2.08 mmol) in MeOH (150 mL), an aqueous solution of sodium hydroxide (15 mL^{-1}, 2.10 mol L^{-1}) was added. The mixture was stirred and heated under reflux overnight. The resultant colorless solution was allowed to cool to room temperature and HCl (2 M) was added dropwise to acidify the solution, whereupon a white precipitate was formed, which was filtered off. The filtrate was concentrated *in vacuo* (~20 mL) and H_2O

(100 mL) was added. The aqueous layer was extracted with Et_2OAc (3×100 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), and filtered. The solvent was removed *in vacuo*, yielding a white solid **6a** (0.50 g, 65%). Mp 160°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.51 (d, 4H, $J = 7.2$ Hz), 6.93 (d, 4H, $J = 7.2$ Hz), 3.99–3.98 (m, 4H), 2.41 (t, 2H, $J = 7.4$ Hz), 1.83–1.68 (m, 6H), 1.56–1.38 (m, 6H), 0.93 (t, 3H, $J = 7.0$ Hz). (75 MHz, $CDCl_3$, 25°C) δ 179.2, 158.3, 158.1, 133.5, 133.3, 127.7, 114.8, 68.1, 67.7, 33.8, 29.0, 28.2, 25.6, 24.4, 22.5, 14.0. MS (EIMS) m/z 370 $([M\text{-}H]^+$.

The same procedure used for the preparation of **6a** was followed for the synthesis of **6b**, **6c**, **6d**, **6e**, and **6f**.

*Compound **6b***. From compound **5b** (0.80 g, 2.01 mmol) and sodium hydroxide (15 mL, 2.18 mol L^{-1}). This yielded a white solid (0.60 g, 78%). Mp 155–158°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.51 (d, 4H, $J = 8.7$ Hz), 6.93 (d, 4H, $J = 8.7$ Hz), 3.99–3.98 (m, 4H), 2.41 (t, 2H, $J = 7.4$ Hz), 1.83–1.68 (m, 6H), 1.59–1.42 (m, 4H), 1.38–1.27 (m, 4H), 0.93 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 178.6, 158.3, 158.1, 133.5, 133.3, 127.7, 114.7, 68.1, 67.7, 33.7, 31.6, 29.3, 29.0, 25.7, 25.6, 24.4, 22.6, 14.0. MS (EIMS) m/z 407 $[M + Na]^+$.

*Comopound **6c***. From compound **5c** (0.80 g, 1.88 mmol) and sodium hydroxide (15 mL, 2.18 mol L^{-1}). This yielded a white solid (0.70 g, 90%). Mp 155–157°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 4H, $J = 7.7$ Hz), 6.93 (d, 4H, $J = 7.7$ Hz), 3.99–3.97 (m, 4H), 2.41 (t, 2H, $J = 7.4$ Hz), 1.84–1.69 (m, 6H), 1.51–1.28 (m, 12H), 0.88–0.87 (m, 3H). ^{13}C NMR (75 MHz, DMSO-d_6, 25°C) δ 174.3, 157.7, 132.2, 127.1, 114.8, 67.4, 67.3, 33.6, 33.2, 28.7, 28.4, 25.5, 25.1, 24.2, 22.0, 13.9. MS (EIMS) m/z 412 $[M]^+$.

*Compound **6d***. From compound **5d** (0.80 g, 1.66 mmol) and sodium hydroxide (15 mL, 2.18 mol L^{-1}). This yielded a white solid (0.60 g, 77%). Mp 152–153°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.45 (d, 4H, $J = 7.7$ Hz), 7.42 (d, 4H, $J = 7.7$ Hz), 3.99–3.96 (t, 4H, $J = 6.4$ Hz), 2.41 (t, 2H, $J = 7.4$ Hz), 1.85–1.71 (m, 6H), 1.55–1.26 (m, 20H), 0.88–0.85 (t, 3H, $J = 6.6$ Hz).^{13}C NMR (75 MHz, DMSO-d_6, 25°C) δ 174.0, 157.6, 132.1, 126.9, 114.7, 67.4, 67.3, 33.4, 31.0, 28.7, 28.5, 28.4, 28.2, 25.2, 24.9, 24.0, 21.8, 13.6. MS (EIMS) m/z 468 $[M]^+$.

*Compound **6e***. From compound **6e** (0.80 g, 2.48 mmol) and sodium hydroxide (15 mL, 2.18 mol L^{-1}). This yielded a white solid (0.60 g, 78%). Mp 152–153°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.69 (d, 2H, $J = 8.6$ Hz), 7.63 (d, 2H, $J = 8.6$ Hz), 7.52 (d, 2H, $J = 8.6$ Hz), 6.98 (d, 2H, $J = 8.6$ Hz), 4.01 (t, 2H, $J = 6.6$ Hz), 2.41 (t, 2H, $J = 7.4$ Hz), 1.87 (qt, 2H, $J = 6.6$ Hz), 1.74 (qt, 2H, $J = 6.6$ Hz), 1.60–1.52 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, & DMSO-d_6, 25°C) δ 174.7, 160.4, 145.6, 133.2, 128.2, 128.9, 127.6, 117.6, 115.7, 68.4, 33.8, 29.3, 25.9, 25.0. MS (EIMS) m/z 309 $[M]^+$.

*Compound **6f***. From compound **5f** (0.80 g, 2.08 mmol) and sodium hydroxide (15 mL, 2.18 mol L^{-1}). This yielded a white solid (0.70 g, 91%). Mp 170–172°C. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 7.46 (d, 2H, $J = 9.1$ Hz), 7.44 (d, 2H, $J = 9.1$ Hz), 6.96 (d, 2H, $J = 8.8$ Hz), 6.94 (d, 2H, $J = 8.8$ Hz), 4.48 (d, 1H, $J = 5.0$ Hz), 3.99 (t, 2H, $J = 6.6$ Hz), 2.39–2.33 (m, 1H), 1.8–1.78 (m, 2H), 1.50–1.46 (m, 2H), 1.38–1.36 (m, 4H), 1.15 (d, 3H, $J = 6.6$ Hz), 1.12 (d, 3H, $J = 6.6$ Hz), 0.94 (t, 3H, $J = 7.1$ Hz). (125 MHz, $CDCl_3$, 25°C) δ 176.8, 158.4,

157.1, 134.8, 133.0, 127.8, 127.7, 115.5, 114.8, 81.2, 68.1, 31.6, 29.3, 25.7, 22.6, 18.7, 17.5, 14.0. MS (EIMS) m/z 393 $[M + Na]^+$.

Compound 7. To a solution of carbazole (1.00 g, 5.90 mmol), in DMF:THF (1:2, 25 mL), was added sodium hydride (0.28 g, 11.67 mmol, 60% in oil) at room temperature. The mixture was stirred for 15 min before addition of 1-bromoheptane (7.30 g, 0.02 mmol) and was stirred for 10 h. The reaction was quenched with MeOH (25 mL) and the solvent removed *in vacuo*. The residue was partitioned with CH_2Cl_2(50 mL)-3 M HCl aq (50 mL). The organic layer was separated and washed with H_2O (60 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was subjected to silica gel column chromatography (eluent: hexane/CH_2Cl_2, 1:1) to afford **7** (0.51 g, 32%) as a white microcrystalline power. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.09 (d, 2H, $J = 7.8$ Hz), 7.50–7.40 (m, 4H), 7.27–7.20 (m, 2H), 4.28 (t, 2H, $J = 7.3$ Hz), 192–1.84 (m, 2H), 1.41–1.21 (m, 8H), 0.87 (t, 3H, $J = 6.9$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 140.5, 125.6, 122.8, 120.3, 118.7, 108.6, 43.1, 31.1, 29.1, 29.0, 27.3, 22.6, 14.0. MS (EIMS) m/z 265 $[M]^+$.

*Compound **8**.* The compound was synthesized following a preparation method as reported in literature [20,27]. Phosphorus oxychloride (59.79 g, 72.91 mmol) was added dropwise over 1 h to anhydrous DMF (30.11 g, 41.25 mmol) at 0°C, under an N_2 atmosphere. The mixture was warmed to room temperature and 1,2-dichloroethane (44 mL) was added. Finally 9-heptyl-9H-carbazole **7** (5.14 g, 19.40 mmol) was added to the solution. The resulting solution was heated under reflux for 4 days under a N_2 atmosphere. The reaction mixture was poured very slowly over 5 min in H_2O/ice (150 mL) and extracted with EtOAc (3×50 mL). The aqueous layer was further extracted with EtOAc (150 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude product was purified by recrystallization from EtOAc/hexane to yield a pale brown solid **8** (4.53 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 10.14 (s, 2H), 8.67 (s, 2H), 8.09 (dd, 2H, $J = 8.5$, 1.6 Hz), 7.56 (d, 2H, $J = 8.5$ Hz), 4.39 (t, 2H, $J = 7.2$ Hz), 1.92–1.88 (m, 2H), 1.36–1.24 (m, 8H), 0.85 (t, 3H, $J = 6.6$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 190.0, 143.6, 128.5, 126.7, 123.1, 122.0, 42.6, 30.5, 27.8, 26.0, 21.4, 12.8. MS (LSIMS) m/z 322 $[M + H]^+$.

*Compound **9**.* A solution of **8** (2.10 g, 6.54 mmol) in THF-ethanol (40 mL:20 mL) was added to $NaBH_4$ (1.42 g, 37.37 mmol). The resultant suspension was stirred at room temperature for 10 h. The solution was poured into water (300 mL) and the resulting precipitate was collected and dried ($MgSO_4$). The residue was subjected to silica gel column chromatography (eluent: hexane/CH_2Cl_2, 1:1) to afford **9** (1.60 g, 75%). Mp 260°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.09 (s, 2H), 7.59 (d, 2H, $J = 8.5$ Hz), 7.39 (d, 2H, $J = 8.5$ Hz), 5.30 (s, 2H), 4.85 (d, 4H, $J = 5.2$ Hz), 4.29 (t, 2H, $J = 7.2$ Hz), 1.83 (q, 2H, $J = 7.2$ Hz), 1.34–1.23 (m, 8H), 0.85 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 140.5, 134.7, 125.4, 122.5, 118.9, 109.1, 64.9, 43.0, 32.0, 27.3, 14.5. MS (EIMS) m/z: 325 $[M]^+$.

*Compound **10**.* To a solution of 6-bromohexanoic acid (0.30 g, 1.54 mmol) in dry CH_2Cl_2 (10 mL) cooled to 0°C under a N_2 atmosphere, 1,3-dicyclohexylcarbodiimide (0.32 g, 1.54 mmol) and a catalytic amount of 4-dimethylaminopyridine were added. The resultant suspension was stirred for 30 min and **9** (0.50 g, 1.54 mmol) was added over 10 min, followed by further stirring for 24 h under an N_2 atmosphere at room

temperature. The white precipitate was filtered and the filtrate was diluted with CH_2Cl_2 (30 mL) and washed with H_2O (3 × 30 mL), followed by 10% $NaHCO_3$ (aq) (10 mL) and brine (5 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluent: hexane/CH_2Cl_2, 1:3) to yield **10** (0.62 g, 60%) as a white solid. Mp 129°C. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 8.10 (s, 2H), 7.49 (d, 2H, $J = 8.5$ Hz), 7.37 (d, 2H, $J = 8.5$ Hz), 4.28 (t, 2H, $J = 7.2$ Hz), 3.37 (t, 4H, $J = 6.8$ Hz), 2.38 (t, 4H, $J = 7.4$ Hz) 1.90–1.86 (m, 4H), 1.73–1.63 (m, 4H), 1.51–1.43 (m, 4H), 1.35–1.24 (m, 4H), 0.85 (t, 6H, $J = 6.6$ Hz). MS (LSIMS) m/z 679 $[M]^+$.

*Compound **1a**.* To a solution of **9** (0.10 g, 0.31 mmol) in dry CH_2Cl_2 (30 mL), cooled in an ice bath under an N_2 atmosphere, compound **6a** (0.34 g, 0.92 mmol), 1,3-dicyclohexylcarbodiimide (0.12 g, 0.62 mmol), and 4-dimethylaminopyridine (catalytical amount) were added. The solution was stirred at room temperature under an N_2 atmosphere for 24 h. HCl (50 mL, 1 mol dm^{-3}) was added, which yielded a white solid. MeOH (10 mL) was added to dissolve the precipitate. The aqueous layers were extracted with CH_2Cl_2 (3 × 30 mL), dried ($MgSO_4$), and filtered. The solvent was removed *in vacuo* to yield a brown solid. The solid was absorbed onto silica and purified by silica gel column chromatography (gradient elution: 0 to 10% EtOAc in hexane, increase polarity in increments of 5% per 150 mL of eluent used). The solvent was removed *in vacuo* to yield a white solid (0.06 g, 19%). Mp 86°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.11 (s, 2H), 7.48 (d, 2H, $J = 8.4$ Hz), 7.43 (d, 4H, $J = 8.4$ Hz), 7.41 (d, 4H, $J = 8.4$ Hz), 7.36 (d, 2H, $J = 8.4$ Hz), 6.93 (d, 4H, $J = 8.4$ Hz), 6.88 (d, 4H, $J = 8.4$ Hz), 5.30 (s, 4H), 4.25 (t, 2H, $J = 7.2$ Hz), 3.98 (t, 4H, $J = 6.5$ Hz), 3.93 (t, 4H, $J = 6.4$ Hz), 2.40 (t, 4H, $J = 7.4$ Hz), 1.84–1.70 (m, 14H), 1.57–1.24 (m, 20H), 0.94 (t, 6H, $J = 6.0$ Hz), 0.86 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 173.6, 158.3, 158.1, 140.7, 133.4, 133.3, 127.6, 126.9, 126.7, 122.7, 121.2, 114.7, 108.9, 68.1, 67.7, 67.0, 43.3, 34.4, 31.7, 29.0, 28.9, 28.2, 27.2, 25.7, 24.7, 22.5, 22.4, 14.0. MS (LSIMS) m/z 1030 $[M]^+$. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 99.8% pure.

The same procedure used for the preparation of **1a** was followed for the synthesis of **1b**, **1c**, **1d**, **1e**, and **1f**.

*Compound **1b**.* This compound was prepared from compound **9** (0.10 g, 0.31 mmol), compound **6b** (0.35 g, 0.92 mmol), 1,3-dicyclohexylcarbodiimide (0.12 g, 0.61 mmol) in dry CH_2Cl_2 (50 mL) to yield a white solid (0.05 g, 15%). Mp 77°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.11 (s, 2H), 7.48 (d, 2H, $J = 8.4$ Hz), 7.43 (d, 4H, $J = 8.4$ Hz), 7.42 (d, 4H, $J = 8.4$ Hz), 7.37 (d, 2H, $J = 8.4$ Hz), 6.93 (d, 4H, $J = 8.4$ Hz), 6.88 (d, 4H, $J = 8.4$ Hz), 5.30 (s, 4H), 4.25 (t, 2H, $J = 7.2$ Hz), 3.98 (t, 4H, $J = 6.5$ Hz), 3.93 (t, 4H, $J = 6.4$ Hz), 2.40 (t, 4H, $J = 7.3$ Hz), 1.84–1.70 (m, 14H), 1.57–1.24 (m, 26H), 0.94 (t, 6H, $J = 6.0$ Hz), 0.86 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 173.6, 158.3, 158.1, 140.7, 133.4, 133.3, 127.6, 126.9, 126.7, 122.7, 121.2, 114.8 108.9, 68.1, 67.7, 67.0, 43.3, 34.4, 31.7, 31.6, 29.3, 29.0, 27.2, 25.7, 25.6, 24.7, 22.6, 22.5, 14.0. MS (LSIMS) m/z 1080 $[M]^+$. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 99.7% pure.

*Compound **1c**.* From compound **9** (0.10 g, 0.31 mmol), compound **6c** (0.38 g, 0.92 mmol) and 1,3-dicyclohexylcarbodiimide (0.12 g, 0.62 mmol) in dry CH_2Cl_2 (50 mL) to yield a white solid (0.06 g, 18%). Mp 66°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.11 (s, 2H), 7.44 (d, 2H, $J = 8.4$ Hz), 7.41 (d, 4H, $J = 8.4$ Hz),

7.40 (d, 4H, $J = 8.4$ Hz), 7.36 (d, 2H, $J = 8.4$ Hz), 6.93 (d, 2H, $J = 8.4$ Hz), 6.88 (d, 2H, $J = 8.$ 4 Hz), 5.29 (s, 4H), 4.25 (t, 2H, $J = 7.2$ Hz), 3.95 (t, 4H, $J = 6.5$), 3.93 (t, 4H, $J = 6.4$ Hz), 2.40 (t, 4H, $J = 7.2$ Hz), 1.81–1.59 (m, 14H), 1.51–1.29 (m, 20H), 0.89–0.85 (t, 9H, $J = 6.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 173.6, 158.3, 158.1, 140.7, 133.4, 133.3, 127.6, 126.9, 126.7, 122.7, 121.2, 114.8, 114.7, 108.9, 68.1, 67.7, 67.0, 43.3, 34.3, 31.8, 31.7, 29.3, 29.2, 29.0, 27.2, 26.1, 25.7, 24.7, 22.6, 22.4, 14.1, 14.0. MS (LSIMS) 1114 $[M]^+$. Found C: 78.70%; N; 1.25%; H: 8.53. calcd. C, 78.22%; N, 1.53%; H, 8.05%. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 99.8% pure.

Compound ***1d***. From compound **9** (0.10 g, 0.31 mmol), compound **6d** (0.43 g, 0.92 mmol) and 1,3-dicyclohexylcarbodiimide (0.12 g, 0.61 mmol) in dry CH_2Cl_2 (50 mL) to yield a white solid (0.06 g, 15%). Mp56°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.10 (s, 2H), 7.46 (d, 2H, $J = 8.4$ Hz), 7.42 (d, 4H, $J = 8.4$ Hz), 7.41 (d, 4H, $J = 8.4$ Hz), 7.36 (d, 2H, $J = 8.4$ Hz), 6.93 (d, 4H, $J = 8.4$ Hz), 6.87 (d, 4H, $J = 8.4$ Hz), 5.29 (s, 4H), 4.24 (t, 2H, $J = 7.3$ Hz), 3.97 (t, 4H, $J = 6.6$ Hz), 3.93 (t, 4H, $J = 6.4$ Hz), 2.39 (t, 4H, $J = 7.4$ Hz), 1.84–1.70 (m, 14H), 1.51–1.20 (m, 20H), 0.88 (t, 6H, $J = 6.9$ Hz), 0.84 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 173.6, 158.3, 158.1, 140.7, 133.4, 133.3, 127.6, 126.9, 126.7, 122.7, 121.2, 114.8, 114.7, 108.9, 68.1, 67.7, 67.0, 43.3, 34.4, 31.9, 31.7, 29.6, 29.4, 29.3, 29.0, 28.9, 27.2, 26.1, 25.7, 24.7, 22.6, 22.5, 14.1, 14.0. MS (LSIMS) m/z 1225 $[M + Na]^+$. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 99.7% pure.

Compound ***1e***. This was prepared from compound **9** (0.10 g, 0.31 mmol), compound **6e** (0.28 g, 0.92 mmol) and 1,3-dicyclohexylcarbodiimide (0.10 g, 0.62 mmol) in dry CH_2Cl_2 (50 mL) to yield a white solid (0.08 g, 28%). Mp 58°C. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.09 (s, 2H), 7.65 (d, 4H, $J = 8.4$ Hz), 7.58 (d, 4H, $J = 8.4$ Hz), 7.48–7.44 (m, 6H), 7.36 (d, 2H, $J = 8.4$ Hz), 6.91 (d, 4H, $J = 8.4$ Hz), 5.29 (s, 4H), 4.25 (t, 2H, $J = 7.2$ Hz), 3.96 (t, 4H, $J = 6.5$ Hz), 2.40 (t, 4H, $J = 7.4$ Hz), 1.83–1.70 (m, 10H), 1.57–1.21 (m, 12H), 0.86 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 173.5, 158.7, 145.2, 140.7, 132.5, 131.3, 128.3, 127.0, 126.9, 126.7, 122.7, 121.2, 119.0, 115.1, 110.1, 108.9, 67.8, 67.0, 43.3, 34.3, 31.6, 29.0, 28.9, 28.8, 27.2, 25.6, 24.7, 22.5, 14.0. MS (LSIMS) m/z 930 $[M + Na]^+$. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 99.6% pure.

Compound ***1f***. From compound **9** (0.10 g, 0.31 mmol), compound **6f** (0.42 g, 0.92 mmol) and 1,3-dicyclohexylcarbodiimide (0.12 g, 0.61 mmol) in dry CH_2Cl_2 (50 mL) to yield a pale yellow oil (0.70 g, 27%). ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 7.99 (d, 2H, $J = 6.3$ Hz), 7.39–7.30 (m, 12H), 6.89 (d, 4H, $J = 7.4$ Hz), 6.87 (d, 4H, $J = 7.4$ Hz), 5.36–5.29 (m, 4H), 4.41 (d, 2H, $J = 7.4$ Hz), 4.20 (d, 2H, $J = 7.2$ Hz), 3.97 (t, 4H, $J = 6.5$ Hz), 2.34–2.27 (m, 2H), 1.82–1.77 (m, 6H), 1.49–1.46 (m, 2H), 1.08 (d, 6H, $J = 6.8$ Hz), 1.05 (d, 6H, $J = 6.8$ Hz), 0.93 (t, 6H, $J = 7.0$ Hz), 0.86 (t, 12H, $J = 7.0$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C) δ 171.3, 158.3, 157.3, 140.7, 134.2, 133.1, 127.6, 127.0, 126.1, 122.6, 121.3, 115.4, 114.7, 108.8, 81.8, 68.1, 67.6, 43.2, 31.7, 31.6, 29.3, 29.0, 28.9, 27.2, 25.7, 22.6, 22.5, 18.6, 17.8, 14.0. MS (LSIMS) m/z 1029 $[M]^+$. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 100% pure.

Compound ***2***. A suspension of K_2CO_3 (0.81 g, 0.59 mmol) in a solution of **11** (0.10 g, 0.14 mmol) and **10** (0.40 g, 0.59 mmol) in MeCN (100 mL) was stirred and heated

under reflux overnight. The resultant brown mixture was allowed to cool to room temperature and concentrated *in vacuo* (30 mL). H_2O (150 mL) was added and the aqueous layer was extracted with Et_2O (3×100 mL). The combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and solvent removed *in vacuo*, yielding a colorless solid as the crude product. The crude product was purified by silica gel column chromatography (gradient elution: 0 to 50% CH_2Cl_2 in EtOAc, increase polarity in increments of 30% per 150 mL of eluent used). The solvent was removed *in vacuo* to yield a colorless solid **2** (0.10 g, 36%). Mp 56°C. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 8.08 (s, 2H), 7.81 (d, 2H, $J = 6.6$ Hz), 7.45 (d, 2H, $J = 8.5$ Hz), 7.29 (d, 2H, $J = 8.5$ Hz), 5.19–5.28 (m, 8H), 4.24–4.17 (m, 24H), 2.34 (t, 4H, $J = 3.3$ Hz), 1.97–1.90 (m, 28H), 1.82–1.75 (m, 6H), 1.64–1.42 (m, 54H), 1.24–1.19 (m, 8H), 0.99–0.95 (m, 30H), 0.83 (t, 3H, $J = 6.7$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, 25°C) δ 173.6, 149.7, 149.0, 140.7, 126.8, 126.5, 123.6, 122.6, 121.1, 108.9, 107.3, 69.7, 69.4, 67.1, 43.2, 34.4, 31.7, 29.1, 28.9, 28.9, 28.4, 27.2, 25.8, 24.8, 22.6, 14.1 MS (LSIMS) m/z 1866 $[M]^+$. Found C: 75.84%; N; 0.68%; H: 9.19. calcd. C, 76.56%; N, 0.73%; H, 8.95%. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 99.9% pure.

Compound 3. The same procedure used for the preparation of **1a** was followed for the synthesis of **3**. From biphenyl-4,4′-diol (0.10 g, 0.54 mmol), compound **14** (0.65 g, 1.39 mmol) and 1,3-dicyclohexylcarbodiimide (0.44 g, 2.15 mmol) in dry CH_2Cl_2 (50 mL) to yield a white solid (0.40 g, 68%). Mp 92°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.79 (d, 4H, $J = 1.5$ Hz), 8.17 (dd, 4H, $J = 8.7$, 1.5 Hz), 7.50 (d, 4H, $J = 8.6$ Hz), 7.45 (d, 4H, $J = 8.7$ Hz), 7.04 (d, 4H, $J = 8.6$ Hz), 4.38 (t, 4H, $J = 7.5$ Hz), 3.09 (t, 8H, $J = 7.3$ Hz), 2.54 (t, 4H, $J = 7.3$ Hz), 1.99–1.96 (m, 4H), 1.85–1.78 (m, 12H), 1.53–1.37 (m, 20H), 0.93 (t, 12H, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.9, 171.8, 150.0, 143.7, 138.0, 129.7, 128.0, 126.9, 123.0, 121.8, 121.6, 43.3, 38.6, 34.0, 31.7, 28.7, 26.6, 24.5, 22.6, 14.0. MS (EIMS) m/z 1106 $[M]^+$. Found C: 78.41%; N; 2.51%; H: 7.52. calcd. C, 78.22%; N, 2.53%; H, 7.65%. HPLC run in 50% MeCN and 50% H_2O showed that the compound was 99.8% pure.

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