Concise Synthesis of [1,1′-Biisoquinoline]-4,4′-diol *via* a Protecting Group Strategy and Its Application for Potential Liquid-Crystalline Compounds

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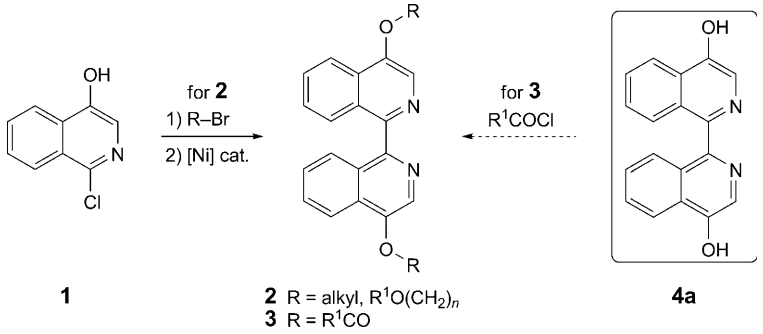
Dedicated to Prof. *Helmut Schwarz* on the occasion of his 65th birthday

The [1,1′-biisoquinoline]-4,4′-diol (**4a**), which was obtained as hydrochloride **4a** · 2 HCl in two steps starting from the methoxymethyl (MOM)-protected 1-chloroisoquinoline **8** (*Scheme 3*), opens access to further O-functionalized biisoquinoline derivatives. Compound **4a** · 2 HCl was esterified with 4-(hexadecyloxy)benzoyl chloride (**5b**) to give the corresponding diester **3b** (*Scheme 4*), which could not be obtained by Ni-mediated homocoupling of **6b** (*Scheme 2*). The ether derivative **2b** was accessible in good yield by reaction of **4a** · 2 HCl with the respective alkyl bromide **9** under the conditions of *Williamson* etherification (*Scheme 4*). Slightly modified conditions were applied to the esterification of **4a** · 2 HCl with galloyl chlorides **10a**–**h** as well as etherification of **4a** · 2 HCl with 6-bromohexyl tris(alkyloxy)benzoates **11b**,**d**–**h** and [(6-bromohexyl)oxy]-substituted pentakis(alkyloxy)triphenylenes **14a**–**c** (*Scheme 5*). Despite the bulky substituents, the respective target 1,1′-biisoquinolines **12**, **13**, and **15** were isolated in 14–86% yield (*Table*).

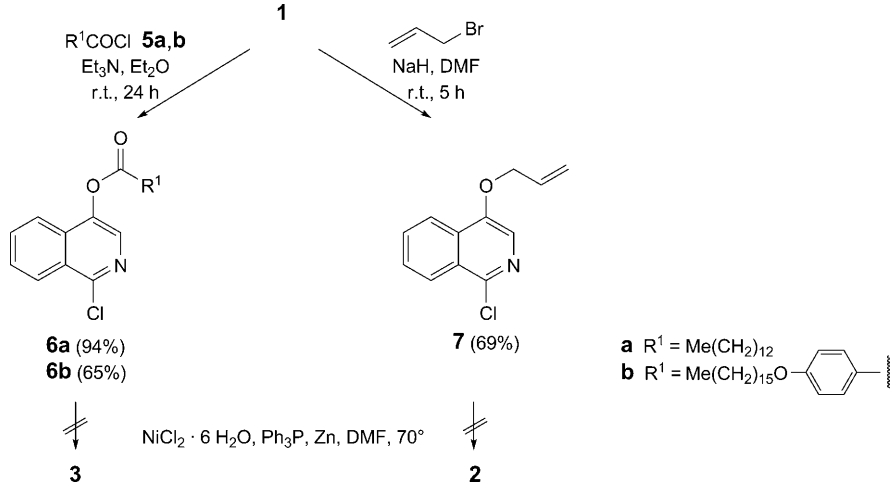
Introduction. – Biisoquinolines are highly attractive ligands for metal complexes because of their strong structural resemblance with bipyridines [1] and BINOL-derived ligands [2] (BINOL = [1,1′-binaphthalene]-2,2′-diol). However, in contrast to the latter, the chemistry of biisoquinolines has been explored to a much lesser extent. For example, *Kotora* and co-workers reported a sequence of *Sonogashira* coupling of α,ω-diynes with 1-chloroisoquinolines followed by a *Vollhardt* cyclization and oxidation with 3-chloroperbenzoic acid to give the corresponding bis-N-oxide, which was utilized in an asymmetric allylsilane addition to aldehydes [3]. *Knochel* and co-workers developed a *Negishi* coupling for 8,8′-biquinolines [4], while *Hashim* and *Kappe* published a microwave-assisted Ni-catalyzed homocoupling to [4,4′-biquinolin]-2-ones [5], and *Blakemore et al.* reported the enzymatic resolution of [8,8′-biquinoline]-7,7′-diols [6]. Very recently, we described the convenient synthesis of 4,4′-bifunctionalized 1,1′-biisoquinolines **2** from 1-chloroisoquinolin-4-ol (**1**) *via Williamson* etherification and Ni-mediated homocoupling (*Scheme 1*) [7].

The sequence **1** → **2** proceeded well for alkyl substituents even with long chain lengths, whereas (aryloxy)alkyl-substituted isoquinoline could still be coupled but with dramatically decreased yields [7]. The Ni-mediated homocoupling of the corresponding ester-functionalized isoquinoline to give **3**, however, failed completely (*Scheme 2*). Thus, in order to expand the scope of O-substituents in the 4,4′-positions of the 1,1′-

Scheme 1



Scheme 2



biisoquinoline, a more flexible approach is required. For this purpose, we envisioned [1,1′-biisoquinoline]-4,4′-diol (**4a**) as the key subunit (*Scheme 1*), which might be extended towards liquid-crystalline compounds (for reviews, see [8]). The results are discussed below.

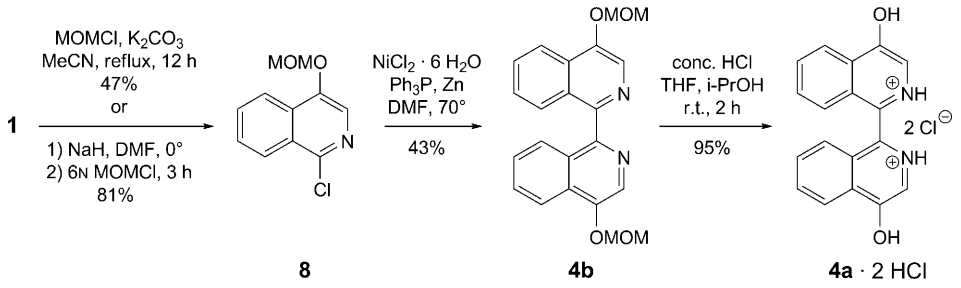
Results and Discussion. – Initial attempts to obtain [1,1′-biisoquinoline]-4,4′-diol (**4a**) by deprotection of 4,4′-diethoxy-1,1′-biisoquinoline (**2a**, R = Et) with HBr/AcOH under reflux for 42 h according to the method of *Fukuda et al.* [9a] resulted in incomplete ether cleavage. Deprotection with BBr_3 and MeOH by using the procedure of *Finn* and co-workers [9b] provided a violet solid, from which the desired product **4a** could not be isolated. The direct homocoupling of 1-chloroisoquinolin-4-ol (**1**) with $NiCl_2 \cdot 6\,H_2O$, Ph_3P, and Zn in DMF at 70° following a procedure of *Bolm et al.* [10] did not yield any trace of **4a**. It should be noted that *Naumann* and *Langhals* obtained the homocoupling product from 3-bromoisoquinolin-4-ol under similar conditions in 27%

yield, whereas the 2-bromoquinolin-3-ol gave the homocoupling product only in trace amounts [11].

With regard to the analogous pyridine-3-ol, only O-protected derivatives were used for the Ni-mediated homocoupling [12]. Consequently, we prepared as potential homocoupling precursors both the ester derivatives **6a**,**b** and the allyl ether **7** from **1** by standard esterification [13] with acid chlorides **5a**,**b** in the presence of Et_3N in Et_2O and by treatment with allyl bromide and NaH in DMF, respectively (*Scheme 2*). However, neither the 1-chloroisoquinolin-4-yl carboxylates **6** nor the allyl protected isoquinoline **7** reacted under the usual Ni-mediated coupling conditions. Presumably, the ester and allylic moiety interfere with the Ni complex.

Therefore, we introduced the methoxymethyl (MOM) protecting group in **1**. Whereas treatment of **1** with dimethoxymethane in the presence of P_2O_5 in CH_2Cl_2 or acetone [14] at room temperature did not give any conversion due to the poor solubility of the starting material in both solvents, the methoxymethylation with MOMCl and K_2CO_3 in refluxing MeCN [13b] yielded product **8** in 47% (*Scheme 3*). The yield could be further improved to 81% analogously to [13b], where MOMCl was generated *in situ* from acetyl chloride, MeOH, and dimethoxymethane as described by *Amato et al.* [15]. Under the usual conditions, **8** was then coupled to give the 4,4′-MOM-protected biisoquinoline **4b** in 43% yield. Deprotection with conc. HCl in THF/i-PrOH at room temperature [16] provided the dihydrochloride **4a** · 2 HCl in 95% yield as a crystalline solid[1]) [17].

Scheme 3



In preliminary attempts, we demonstrated that [1,1′-biisoquinoline]-4,4′-diol (**4a** · 2 HCl) indeed may act as a precursor for further *O*-functionalization (*Scheme 4*). O-Acylation of **4a** · 2 HCl with 4-(hexadecyloxy)benzoyl chloride (**5b**) in the presence of Et_3N gave the target biisoquinoline diester **3b** in 16% yield. Also ether derivative **2b**, which was isolated under the homocoupling conditions only in very poor yields of 4% [7], was accessible in 50% yield from **4a** · 2 HCl by *Williamson* etherification with the respective bromide **9** and NaH in DMF at room temperature.

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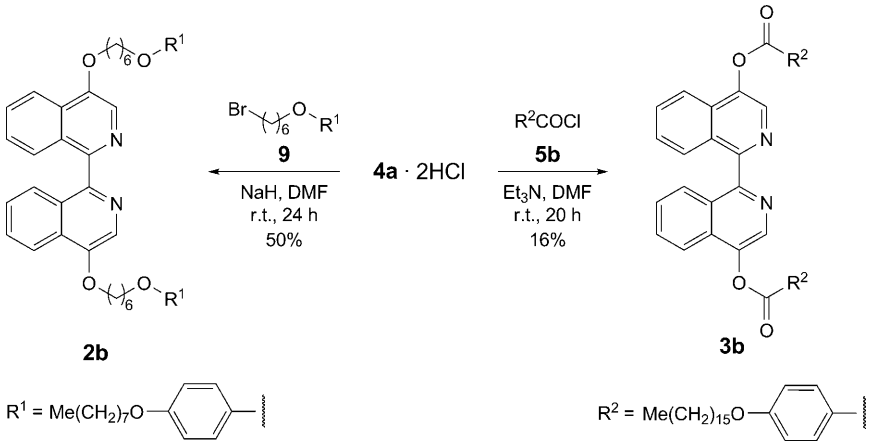
[1]) CCDC-701631 and 701632 contain the crystallographic data (excluding structural factors) of **4a** and those of 4,4′-diethoxy-1,1′-biisoquinoline (**2a**) [7]. These data can be obtained free of charge *via* [17].

Scheme 4

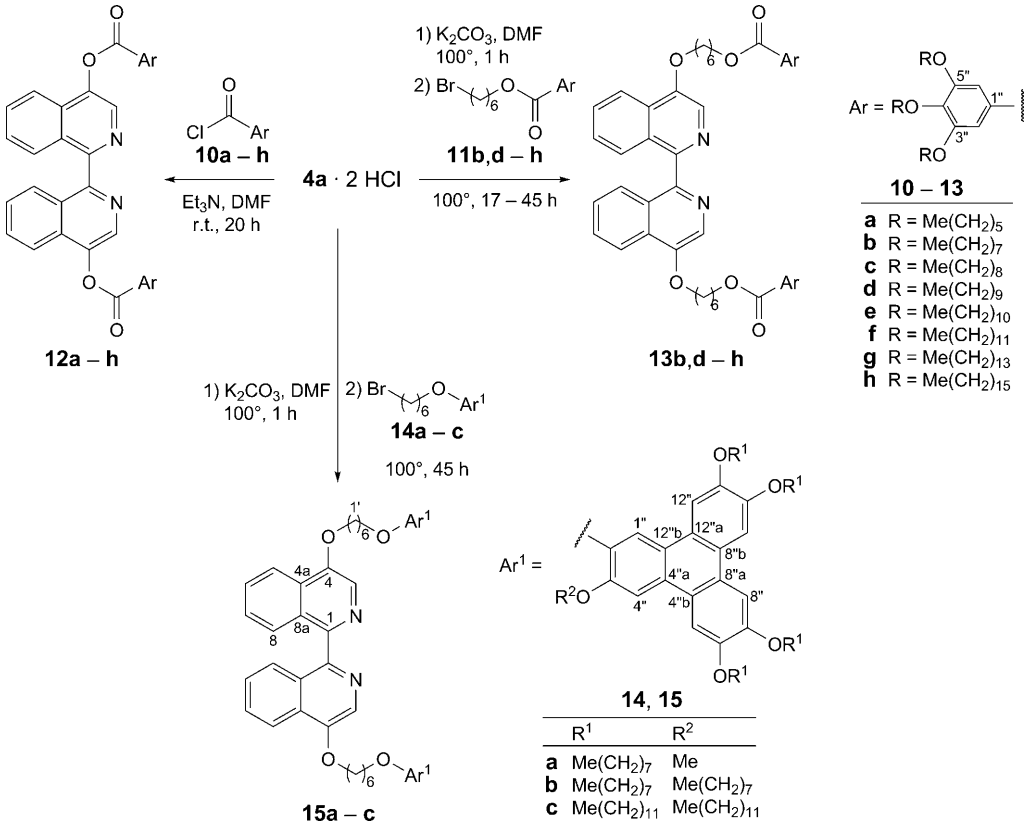


Based on these results, we extended the method to the derivatization of **4a** · 2 HCl with mesogenic gallic acid (= 3,4,5-trihydroxybenzoic acid) derivatives **10** and **11** as well as (alkyloxy)triphenylenes **14** with regard to liquid-crystalline compounds (*Scheme 5*; *Table*). O-Acylation of **4a** · 2 HCl with galloyl chlorides **10a**–**h** (which were easily obtained from the respective acids by chlorination with $SOCl_2$ [18]) in the presence of Et_3N afforded the 1,1′-biisoquinolinediyl diesters **12a**–**h** in 48–86% yield. The alkylation reagents **11b**,**d**–**h** were prepared by esterification of the galloyl chlorides **10b**,**d**–**h** with 6-bromohexan-1-ol in analogy to [19]. Bromides **11** and **4a** · 2 HCl were linked *via* the hexyloxy chains in the presence of K_2CO_3 in DMF at 100° to give biisoquinolines **13b**,**d**–**h** in yields between 18 and 77%. Under the same

Table. *O-Functionalization of* **4a** · *2 HCl* via *Esterification and Etherification* (for details, see *Scheme 5*)

Halide	R	R^1	Product	Yield [%]	M.p. [°]
10a	$Me(CH_2)_5$		**12a**	63	94
10b	$Me(CH_2)_7$		**12b**	74	76
10c	$Me(CH_2)_8$		**12c**	69	79
10d	$Me(CH_2)_9$		**12d**	84	81
10e	$Me(CH_2)_{10}$		**12e**	86	85
10f	$Me(CH_2)_{11}$		**12f**	49	88
10g	$Me(CH_2)_{13}$		**12g**	51	82
10h	$Me(CH_2)_{15}$		**12h**	48	82
11b	$Me(CH_2)_7$		**13b**	77	34
11d	$Me(CH_2)_9$		**13d**	32	69
11e	$Me(CH_2)_{10}$		**13e**	18	32
11f	$Me(CH_2)_{11}$		**13f**	21	52
11g	$Me(CH_2)_{13}$		**13g**	60	58
11h	$Me(CH_2)_{15}$		**13h**	36	67
14a	$Me(CH_2)_7$	Me	**15a**	69	101
14b	$Me(CH_2)_7$	$Me(CH_2)_7$	**15b**	31	69
14c	$Me(CH_2)_{11}$	$Me(CH_2)_{11}$	**15c**	14	66

Scheme 5



conditions, *O*-alkylation of **4a**·2 HCl with 2-[(6-bromohexyl)oxy]-3,6,7,10,11-pentakis-(alkyloxy)triphenylenes **14a**–**c** gave a third series of biisoquinolines **15a**–**c** bearing pentakis(alkyloxy)triphenylene moieties in the substituents. Triphenylenes **14** were accessible by trimerization of bis(alkyloxy)benzenes [20] to give the respective pentakis(alkyloxy)triphenylen-2-ols, which were converted with 1,6-dibromohexane in analogy to a method of *Kumar et al.* [21].

Conclusion. – A synthetic route to [1,1′-biisoquinoline]-4,4′-diol (**4a**) *via* protection with *in situ* generated MOMCl solution followed by Ni-catalyzed homocoupling and acidic deprotection could be established. Diol **4a**, isolated as hydrochloride **4a**·2 HCl, was found to be a key building block for *O*-alkylations and *O*-acylations resulting in a series of 1,1′-biisoquinolines **2**, **3**, **12**, **13**, and **15** tethered to (alkyloxy)benzenes, gallic acids, and triphenylenes. These substituents were chosen with regard to potential mesogenic properties. The physical investigations are currently under way.

Generous financial support by the *Deutsche Forschungsgemeinschaft*, the *Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg* ('Landesgraduierten' fellowship

for *E. K.*), and the *Fonds der Chemischen Industrie* is gratefully acknowledged. We would like to thank *Robert Hoffmann* for his experimental contribution.

Experimental Part

1. *General*. Commercial reagents were used without further purification unless otherwise indicated. All solvents were distilled prior to use. Reactions were performed in oven-dried glassware. Flash chromatography (FC): silica gel *60* (230–400 mesh; *Fluka*). M.p.: *Büchi SMP 20*; uncorrected. IR Spectra: *Bruker-Vector-22*-FT-IR spectrophotometer; ATR = attenuated total reflection; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-Avance-300* and *-500* instrument; at 300 (^1H) and 75 (^{13}C) and 500 (^1H) and 125 MHz (^{13}C), resp.; δ in ppm, J in Hz; signal assignments are based on DEPT and COSY experiments. MS and ESI-MS: *Finnigan MAT 95*, *Varian MAT 711*, and *Bruker Daltonics micrOTOF_Q*; APCI = atmospheric pressure chemical ionization; in *m/z* (rel. %). GC/MS: *Thermo-Electron-Corporation-Trace-DSQ* apparatus with *Macherey-Nagel-Optima-5-MS* column (30 m × 0.25 mm).

2.1. *1-Chloroisoquinolin-4-yl Tetradecanoate* (**6a**). To a suspension of **1** (718 mg, 4 mmol) in anh. Et_2O (40 ml), Et_3N (0.62 ml, 446 mg, 4.4 mmol) was added dropwise followed by tetradecanoyl chloride (**5a**; 1.0 ml, 1.08 g, 4.4 mmol) at 0°. After stirring at r.t. for another 24 h, 1M aq. $NaHCO_3$ (28 ml) was added and the org. layer washed with H_2O (28 ml). The combined aq. layer was extracted with Et_2O (2 × 40 ml) and the extract dried (Na_2SO_4) and concentrated: **6a** (1.46 g, 94%). Colorless solid. M.p. 75°. FT-IR (ATR): 2916*s*, 2849*s*, 1772*m*, 1471*m*, 1309*m*, 1258*m*, 1227*m*, 1119*m*, 1087*s*, 1021*m*, 963*m*, 913*m*, 772*s*, 744*m*, 717*m*, 641*m*. ^1H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, *J* = 6.7, Me); 1.24–1.50 (*m*, 10 CH_2); 1.80–1.90 (*m*, CH_2); 2.75 (*t*, *J* = 7.5, $COOCH_2$); 7.70–7.87 (*m*, H–C(6), H–C(7), H–C(5) or H–C(8)); 8.17 (*s*, H–C(3)); 8.33–8.37 (*m*, H–C(5) or H–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (CH_2); 34.2 ($COOCH_2$); 121.1, 126.8, 128.9, 131.5 (C(5), C(8), C(6), C(7)); 127.5, 131.8 (C(4a), C(8a)); 134.2 (C(3)); 142.3, 148.1 (C(1), C(4)); 171.6 (C=O). GC/EI-MS: 389 (1, M^+), 354 (3, $[M-Cl]^+$), 211 (24, $[C_{13}H_{27}CO]^+$), 179 (100, $[M+H-C_{13}H_{27}CO]^+$), 123 (10), 85 (20), 71 (36), 57 (34). Anal. calc. for $C_{23}H_{32}ClNO_2$ (389.21): C 70.84, H 8.27, Cl 9.09, N 3.59 found: C 71.02, H 8.41, Cl 8.98, N 3.29.

2.2. *1-Chloroisoquinolin-4-yl 4-(Hexadecyloxy)benzoate* (**6b**). As described for **6a**, from **1** (359 mg, 2 mmol), 4-(hexadecyloxy)benzoyl chloride (**5b**, 914 mg, 2.4 mmol), and Et_3N (0.33 ml, 240 mg, 2.4 mmol): 681 mg (65%) of **6b**. Colorless solid. M.p. 115°. FT-IR (ATR): 2916*s*, 2850*s*, 1725*s*, 1604*s*, 1508*m*, 1468*m*, 1316*m*, 1257*s*, 1166*s*, 1152*m*, 1093*s*, 1039*m*, 1019*m*, 1001*m*, 958*m*, 901*m*, 844*m*, 760*s*, 721*m*, 691*m*, 675*m*, 640*m*. ^1H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, *J* = 6.7, Me); 1.23–1.43 (*m*, 12 CH_2); 1.44–1.54 (*m*, CH_2); 1.80–1.89 (*m*, CH_2); 4.08 (*t*, *J* = 6.6, CH_2O); 7.00–7.05 (*m*, H–C(3′), H–C(5′)); 7.71–7.81 (*m*, H–C(6), H–C(7)); 7.91–7.95 (*m*, H–C(5) or H–C(8)); 8.22–8.27 (*m*, H–C(2′), H–C(6′)); 8.29 (*s*, H–C(3)); 8.36–8.39 (*m*, H–C(5) or H–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 26.0, 29.1, 29.4, 29.57, 29.61, 29.67, 29.71, 31.9 (CH_2); 68.5 (CH_2O); 114.6 (C(3′), C(5′)); 120.3, 127.6, 132.1 (C(1′), C(4a), C(8a)); 121.3, 126.7 (C(5), C(8)); 128.9, 131.5 (C(6), C(7)); 132.6 (C(2′), C(6′)); 134.5 (C(3)); 142.7, 148.2 (C(1), C(4)); 164.1, 164.3 (C=O, C(4′)). EI-MS (pos.): 523.3 (7, M^+), 488.3 (1, $[M-Cl]^+$), 345.3 (100, $[C_{16}H_{33}OC_6H_4CO]^+$), 121.1 (35, $[OHC_6H_4CO]^+$), 43.3 (10). Anal. calc. for $C_{32}H_{42}ClNO_3$ (523.28): C 73.33, H 8.08, Cl 6.76, N 2.67; found: C 73.42, H 8.04, Cl 6.77, N 2.58.

2.3. *[1,1′-Biisoquinoline]-4,4′-diyl Bis(4-(Hexadecyloxy)benzoate* (**3b**). As described for **6a**, from **4a** · 2 HCl (29 mg, 0.08 mmol), **5b** (63 mg, 0.17 mmol), and Et_3N (0.06 ml, 44 mg, 0.44 mmol). Purification by dissolving in warm CH_2Cl_2 and precipitation with EtOH, yielded 13 mg (16%) of **3b**. Colorless solid. M.p. 110°. FT-IR (ATR): 1579*m*, 1561*m*, 1504*m*, 1447*m*, 1392*m*, 1311*m*, 1282*m*, 1158*m*, 1111*m*, 1079*m*, 1022*m*, 984*m*, 912*s*, 874*m*, 858*m*, 800*m*, 760*s*, 739*s*, 666*m*, 609*s*, 565*m*. ^1H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 2 Me); 1.24–1.41 (*m*, 24 CH_2); 1.46–1.53, 1.82–1.91 (2*m*, 2 CH_2); 4.10 (*t*, *J* = 6.5, 2 CH_2O); 7.50–7.08, 8.31–8.34 (2*m*, 8 H, H–C(2′), H–C(3′), H–C(5′), H–C(6′)); 7.53–7.59, 7.72–7.77 (2*m*, 4 H, H–C(6), H–C(7)); 7.93–7.96, 8.03–8.06 (2*m*, 4 H, H–C(5), H–C(8)); 8.71 (*s*, 2 H, H–C(3)). ^{13}C-NMR (125 MHz, $CDCl_3$): 14.1 (Me); 22.7, 26.0, 29.1, 29.38, 29.39, 29.58, 29.62, 29.67, 29.71, 31.9 (CH_2); 68.5 (CH_2O); 114.6, 132.7 (C(2′), C(3′), C(5′), C(6′)); 120.6, 128.9, 131.2 (C(4a), C(8a), C(1′)); 120.8, 127.6 (C(5), C(8)); 128.1, 130.8 (C(6), C(7)); 134.8 (C(3)); 143.0, 155.2, 164.0, 164.6 (C(1),

C(4), C(4′), C=O). ESI-MS: 977.64 ($[M+H]^+$), 858.42, 666.38, 617.38, 345.28. HR-ESI-MS (pos.): 977.6403 ($[M+H]^+$, $C_{64}H_{84}N_2O_6^+$; calc. 977.6402).

2.4. *[1,1′-Biisoquinoline]-4,4′-diyl Bis[(3,4,5-tris(alkyloxy)benzoates* **12a**,**c**–**f**. The bis-benzoates **12a**,**c**–**f** were prepared as described below for **12b**,**g**,**h**. For yields and m.p.s. of **12a**–**h**, see *Table*.

2.5. *[1,1′-Biisoquinolin]-4,4′-diyl Bis[3,4,5-tris(octyloxy)benzoate]* (**12b**). As described for **6a**, from **4a** · 2 HCl (50 mg, 0.138 mmol), **10b** (160 mg, 0.304 mmol), and Et_3N (1.0 ml, 726 mg, 7.21 mmol) in DMF (2 ml). Purification by FC (SiO_2, hexanes/AcOEt 20:1 and 10:1; R_f 0.28) yielded 129 mg (74%) of **12b**. Light yellow waxy solid. FT-IR (ATR): 3065*w*, 2954*m*, 2920*s*, 2852*s*, 1736*s*, 1623*w*, 1584*s*, 1429*s*, 1335*s*, 1193*s*, 1115*s*, 1095*s*, 752*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87–0.93 (*m*, 6 Me); 1.26–1.43 (*m*, 24 CH_2); 1.48–1.58 (*m*, 6 CH_2); 1.76–1.92 (*m*, 6 CH_2); 4.12 (*t*, *J* = 6.5, 8 H, $CH_2O-C(3'')$, $CH_2O-C(5'')$); 4.13 (*t*, *J* = 6.5, 4 H, $CH_2O-C(4'')$); 7.58 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(7)); 7.59 (*s*, 4 H, H–C(2″), H–C(6″)); 7.76 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.95 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H–C(8)); 8.03 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(5)); 8.69 (*s*, 2 H, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.69, 22.72, 26.08, 26.12, 29.31, 29.33, 29.37, 29.40, 29.5, 30.4, 31.8, 31.9 (CH_2); 69.4 (CH_2O); 73.7 (CH_2O); 108.9 (C(2″), C(6″)); 120.9 (C(5)); 123.0 (C(1″)); 127.6 (C(8)); 128.1 (C(7)); 129.0 (C(8a)); 130.9 (C(6)); 131.1 (C(4a)); 134.9 (C(3)); 143.1 (C(4)); 143.6 (C(4″)); 153.2 (C(3″), C(5″)); 155.4 (C(1)); 164.8 (COO). APCI-MS: 1265.9 ($[M+H]^+$), 1145.9, 777.5 ($[M+2H-R]^+$), 693.4 ($[M+H-R-C_8H_{17}]^+$), 493.4. Anal. calc. for $C_{80}H_{116}N_2O_{10}$ (1265.78): C 75.91, H 9.24, N 2.21; found: C 75.82, H 9.12, N 2.21.

2.6. *[1,1′-Biisoquinoline]-4,4′-diyl Bis[3,4,5-tris(tetradecyloxy)benzoate]* (**12g**). As described for **6a**, from **4a** · 2 HCl (50 mg, 0.138 mmol), **10g** (236 mg, 0.304 mmol), and Et_3N (1.0 ml, 726 mg, 7.21 mmol) in DMF (2 ml). Purification by FC (SiO_2, hexanes/AcOEt 20:1 and 10:1; R_f 0.47, yielded 125 mg (51%) of **12g**. FT-IR (ATR): 2920*s*, 2851*s*, 2185*w*, 1978*w*, 1732*s*, 1586*s*, 1430*s*, 1335*s*, 1194*s*, 1118*s*, 1056*s*, 758*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.91 (*m*, 6 Me); 1.26–1.43 (*m*, 60 CH_2); 1.47–1.57 (*m*, 6 CH_2); 1.76–1.92 (*m*, 6 CH_2); 4.12 (*t*, *J* = 6.5, 8 H, $CH_2O-C(3'')$, $CH_2O-C(5'')$); 4.12 (*t*, *J* = 6.5, 4 H, $CH_2O-C(4'')$); 7.57 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(7)); 7.59 (*s*, 4 H, H–C(2″), H–C(6″)); 7.76 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.95 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(8)); 8.03 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(5)); 8.69 (*s*, 2 H, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1, 14.2 (Me); 21.1, 22.7, 26.11, 26.13, 29.3, 29.38, 29.41, 29.43, 29.6, 29.67, 29.68, 29.73, 29.8, 30.4, 31.9 (CH_2); 69.4 (CH_2O); 73.7 (CH_2O); 108.9 (C(2″), C(6″)); 120.9 (C(5)); 122.9 (C(1″)); 127.6 (C(8)); 128.2 (C(7)); 129.0 (C(8a)); 130.9 (C(6)); 131.2 (C(4a)); 134.8 (C(3)); 143.1 (C(4)); 143.6 (C(4″)); 153.2 (C(3″), C(5″)); 155.3 (C(1)); 164.8 (COO). APCI-MS: 1895.4, 1771.4 ($[M+H]^+$), 1729.5, 1550.2, 1431.2, 1387.2, 886.7, 741.7, 545.5, 351.3. Anal. calc. for $C_{166}H_{188}N_2O_{10}$ (1770.74): C 78.68, H 10.70, N 1.58; found: C 78.57, H 10.53, N 1.48.

2.7. *[1,1′-Biisoquinoline]-4,4′-diyl Bis[3,4,5-tris(hexadecyloxy)benzoate]* (**12h**). As described for **6a**, from **4a** · 2 HCl (50 mg, 0.138 mmol), **10h** (262 mg, 0.304 mmol), and Et_3N (1.0 ml, 726 mg, 7.21 mmol) in DMF (2 ml). Purification by FC (SiO_2, hexanes/AcOEt 20:1 and 10:1; R_f 0.51, yielded 126 mg (48%) of **12h**. Light yellow waxy solid. FT-IR (ATR): 2916*s*, 2849*s*, 1737*s*, 1587*s*, 1503*s*, 1467*s*, 1430*s*, 1385*m*, 1336*s*, 1199*s*, 1122*s*, 1096*s*, 751*s*, 720*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.91 (*m*, 6 Me); 1.26–1.43 (*m*, 72 CH_2); 1.47–1.57 (*m*, 6 CH_2); 1.76–1.92 (*m*, 6 CH_2); 4.12 (*t*, *J* = 6.5, 8 H, $CH_2O-C(3'')$, $CH_2O-C(5'')$); 4.12 (*t*, *J* = 6.5, 4 H, $CH_2O-C(4'')$); 7.57 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(7)); 7.59 (*s*, 4 H, H–C(2″), H–C(6″)); 7.76 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.95 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(8)); 8.03 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(5)); 8.69 (*s*, 2 H, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1, 14.2 (Me); 22.7, 26.10, 26.14, 29.3, 29.38, 29.44, 29.6, 29.7, 29.8, 30.4, 31.9 (CH_2); 69.4 (CH_2O); 73.7 (CH_2O); 108.9 (C(2″), C(6″)); 120.9 (C(5)); 122.9 (C(1″)); 127.6 (C(8)); 128.2 (C(7)); 128.9 (C(8a)); 131.0 (C(6)); 131.2 (C(4a)); 134.7 (C(3)); 143.1 (C(4)); 143.6 (C(4″)); 153.2 (C(3″), C(5″)); 155.1 (C(1)); 164.8 (COO). APCI-MS: 2063.6, 1939.6 ($[M+H]^+$), 970.8, 825.8, 601.5, 379.3. Anal. calc. for $C_{128}H_{212}N_2O_{10}$ (1939.06): C 79.28, H 11.02, N 1.44; found: C 79.08, H 10.80, N 1.42.

3.1. *1-Chloro-4-(prop-2-en-1-yloxy)isoquinoline* (**7**). A soln. of **1** (718 mg, 4 mmol) in anh. DMF (2 ml) was slowly added dropwise to a suspension of NaH (192 mg, 4.8 mmol) in anh. DMF (4 ml) at 0°. After stirring of the green soln. at r.t. for 1 h, 3-bromoprop-1-ene (0.7 ml, 968 mg, 8 mmol) was added at 0° (green → reddish-brown). The mixture was stirred at r.t. for another 5 h. Then, H_2O (20 ml) and CH_2Cl_2 (60 ml) were added. The org. layer was dried (Na_2SO_4), the solvent evaporated, and the residue purified by FC (SiO_2, hexanes/AcOEt 6:1, R_f 0.47): **7** (607 mg, 69%). Colorless solid. M.p. 94°. IR (ATR): 2916*s*, 2849*m*, 1735*m*, 1605*m*, 1579*m*, 1510*m*, 1469*m*, 1250*s*, 1168*s*, 1150*m*, 1127*m*, 1076*s*, 1038*m*,

914*m*, 844*m*, 757*s*, 719*m*, 689*m*, 660*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.76–4.78 (*m*, CH_2); 5.36–5.41, 5.49–5.57 (2*m*, CH=CH_2); 6.09–6.22 (*m*, C*H*=CH_2); 7.68–7.79 (*m*, H–C(6), H–C(7)); 7.81 (*s*, H–C(3)); 8.25–8.28 (*m*, H–C(5), H–C(8)). ^{13}C-NMR (125 MHz, $CDCl_3$): 69.6 (CH_2); 118.3 (CH=*C*H_2); 121.9, 126.0 (C(5), C(8)); 122.4 (C(3)); 127.0, 130.4 (C(4a), C(8a)); 128.8, 130.3 (C(6), C(7)); 132.3 (*C*H=CH_2); 142.7, 149.4 (C(1), C(4)). EI-MS (pos.): 219.0 (44, M^+), 184.1 (72, $[M-Cl]^+$), 150.0 (100). Anal. calc. for $C_{12}H_{10}ClNO$ (219.67): C 65.61, H 4.59, N 6.31, Cl 16.14; found: C 65.52, H 4.63, N 6.38, Cl 16.25.

3.2. *4,4′-Bis{[6-[4-(octyloxy)phenoxy]hexyl}oxy}-1,1′-biisoquinoline* (**2b**). As described for **7**, from **4a**·2 HCl (36 mg, 0.1 mmol) in anh. DMF (2 ml), NaH (18 mg, 0.44 mmol), and 1-[(6-bromohexyl)oxy]-4-(octyloxy)benzene (**9**; 85 mg, 0.2 mmol) in anh. DMF (2 ml): 45 mg (50%) of **2b**. Spectroscopic data: in accordance with those in [7].

4. *1-Chloro-4-(methoxymethoxy)isoquinoline* (**8**). *Method A*. K_2CO_3 (5.53 g, 40.0 mmol) was added to a suspension of **1** (1.79 g, 10.0 mmol) in anh. MeCN (50 ml), and the mixture was heated under reflux for 30 min. Then, MOMCl (1.2 ml, 1.21 g, 15.0 mmol) was added and the mixture heated under reflux for another 12 h and filtered without cooling. The residue was washed with CH_2Cl_2 (3 × 20 ml) and the combined filtrate concentrated. The residue was taken up in CH_2Cl_2 (60 ml), the soln. washed with 0.5N aq. NaOH (2 × 25 ml) and H_2O (2 × 25 ml) and dried (Na_2SO_4), the solvent evaporated, and the residue purified by FC (SiO_2, hexanes/AcOEt 5:1, R_f 0.43); **8** (1.06 g, 47%). Yellowish solid.

Method B. A soln. of **1** (179 mg, 1 mmol) in anh. DMF (2 ml) was slowly added dropwise to a suspension of NaH (44 mg, 1.1 mmol) in anh. DMF (1.5 ml) at 0°, and the green mixture was stirred at r.t. for 1 h. Then, a 6N soln. of MOMCl [14] (0.2 ml, 1 mmol) was added at 0° (green → yellow). The mixture was stirred at r.t. for another 3 h, and then H_2O (10 ml) and CH_2Cl_2 (20 ml) were added. The org. layer was dried (Na_2SO_4) and the solvent evaporated: **8** (182 mg, 81%). Yellowish solid. M.p. 66°. FT-IR (ATR): 1312*m*, 1285*m*, 1211*m*, 1174*m*, 1151*m*, 1082*m*, 936*s*, 876*s*, 760*s*, 741*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.56 (*s*, Me); 5.40 (*s*, CH_2); 7.68 (*ddd*, *J* = 8.3, 6.9, 1.3, H–C(6) or H–C(7)); 7.75 (*ddd*, *J* = 8.3, 6.9, 1.3, H–C(6) or H–C(7)); 8.07 (*s*, H–C(3)); 8.21 (*ddd*, *J* = 8.3, 1.3, 0.8, H–C(5) or H–C(8)); 8.24 (*ddd*, *J* = 8.3, 1.3, 0.8, H–C(5) or H–C(8)). ^{13}C-NMR (63 MHz, $CDCl_3$): 56.5 (Me); 95.3 (CH_2); 121.7 (C(3)); 125.1, 126.2 (C(5), C(8)); 127.1, 130.7 (C(4a), C(8a)); 128.7, 130.5 (C(6), C(7)); 143.6, 148.3 (C(1), C(4)). EI-MS: 223 (28, M^+), 193 (4, $[C_{10}H_{11}ClNO]^+$), 150 (10), 45 (100, $[MeOCH_2]^+$). HR-ESI-MS (pos.): 246.0299 ($[M+Na]^+$, $C_{11}H_{10}ClNaO_2^+$; calc. 246.0298). Anal. calc. for $C_{11}H_{10}ClNO_2$ (223.66): C 59.07, H 4.51, Cl 15.85, N 6.26; found: C 59.16, H 4.54, Cl 15.76, N 6.01.

5. *4,4′-Bis(methoxymethoxy)-1,1′-biisoquinoline* (**4b**). A soln. of $NiCl_2 \cdot 6H_2O$ (808 mg, 3.40 mmol) in degassed anh. DMF (15 ml) was heated at 70° (bath temp.), and Ph_3P (3.56 g, 13.7 mmol) and Zn (237 mg, 3.65 mmol) were added. The mixture became brown and was heated at 70° for 1 h. Then, a soln. of **8** (525 mg, 2.79 mmol) in degassed anh. DMF (5 ml) was added and the mixture stirred at 70° for 4 h (TLC control). After cooling to r.t., the mixture was quenched with 5% NH_3 soln. (21 ml). The aq. layer extracted with CH_2Cl_2/Et_2O 2:1 (3 × 25 ml), the combined org. phase concentrated, and the residue taken up in CH_2Cl_2 (15 ml), washed with H_2O (4 × 8 ml) and brine (1 × 10 ml), dried (Na_2SO_4), and concentrated. The crude product was purified by FC (SiO_2, hexanes/AcOEt 1:2; R_f (AcOEt) = 0.54): **4b** (220 mg, 43%). M.p. 135°. FT-IR (ATR): 1579*m*, 1292*m*, 1279*m*, 1150*s*, 1085*m*, 1063*s*, 1018*m*, 960*s*, 928*m*, 902*m*, 861*m*, 773*m*, 687*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.62 (*s*, Me); 5.51 (*s*, CH_2); 7.49 (*ddd*, *J* = 8.4, 7.0, 1.3, H–C(6) or H–C(7)); 7.71 (*ddd*, *J* = 8.4, 7.0, 1.3, H–C(6) or H–C(7)); 7.79 (*ddd*, *J* = 8.4, 1.3, 0.7, H–C(5) or H–C(8)); 8.33 (*ddd*, *J* = 8.4, 1.3, 0.7, H–C(5) or H–C(8)); 8.48 (*s*, H–C(3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 56.5 (Me); 95.2 (CH_2); 121.2, 127.0 (C(5), C(8)); 125.7 (C(3)); 127.6, 129.6 (C(6), C(7)); 128.6, 129.3 (C(4a), C(8a)); 148.2, 151.7 (C(1), C(4)). GC/EI-MS: 376 (100, M^+), 345 (12), 331 (94, $[M-CH_2OMe]^+$), 315 (10), 301 (40, $[M+H-CH_2OMe-OMe]^+$), 287 (38, $[M+H-2CH_2OMe]^+$), 270 (48), 258 (24), 242 (12), 229 (22), 214 (20), 207 (46), 191 (18), 176 (26), 150 (8), 130 (10), 115 (8), 78 (20, Ph^+). HR-ESI-MS (pos.): 377.1499 ($[M+H]^+$, $C_{22}H_{20}N_2O_4^+$; calc. 377.1496).

6. *[1,1′-Biisoquinoline]-4,4′-diol Hydrochloride (1:2)* (**4a**·2 HCl). Conc. HCl soln. (0.2 ml) was added to a soln. of **4b** (36 mg, 0.096 mmol) in THF/i-PrOH 1:1 (10 ml), and the mixture was stirred at r.t. for 7 h. The solvent was evaporated: **4a**·2 HCl (33 mg, 95%). Yellow solid. M.p. >240°. FT-IR (ATR): 2860*m*, 2324*m*, 1984*m*, 1581*s*, 1495*m*, 1454*m*, 1389*s*, 1358*s*, 1265*m*, 1084*m*, 842*m*, 771*s*, 716*m*, 584*m*. ^{1}H-NMR (300 MHz, CD_3OD): 7.70–7.73 (*m*, 2 H, H–C(5) or H–C(8)); 7.81–7.86, 8.05–8.10 (2*m*, 4 H,

H–C(6), H–C(7)); 8.26 (*s*, 2 H, H–C(3)); 8.60–8.63 (*m*, 2 H, H–C(5) or H–C(8)). ^{13}C-NMR (125 MHz, (D_6)DMSO): 121.2 (C(3)); 122.1, 127.0 (C(5), C(8)); 130.2, 132.2 (C(6), C(7)); 128.1, 129.0 (C(4a), C(8a)); 141.5, 152.0 (C(1), C(4)). ESI-MS: 289.10 ($[M+H]^+$), 311.08 ($[M+Na]^+$). Anal. calc. for $C_{18}H_{14}Cl_2N_2O_2$ (361.23): C 59.85, H 3.91, Cl 19.63, N 7.76; found: C 59.71, H 4.05, Cl 19.39, N 7.63.

7.1. *6-Bromohexyl 3,4,5-Tris(alkyloxy)benzoates* **11d–f**. The benzoates **11d–f** were prepared as described below for **11b**,**g**,**h**.

7.2. *6-Bromohexyl 3,4,5-Tris(octyloxy)benzoate* (**11b**). In analogy to [19], **10b** (877 mg, 1.67 mmol) was added to a soln. of 6-bromohexan-1-ol (0.18 ml, 0.25 g, 1.41 mmol) and Et_3N (0.5 ml, 0.37 g, 3.61 mmol) in CH_2Cl_2 (10 ml), and the mixture was stirred at r.t. for 2 h. The solvent was evaporated and the residue purified by FC (SiO_2, hexanes/AcOEt 40:1; R_f 0.48): **11b** (651 mg, 64%). M.p. 10°. FT-IR (ATR): 2923*s*, 2855*s*, 2366*w*, 2168*w*, 2003*w*, 1715*s*, 1586*s*, 1499*m*, 1465*m*, 1428*s*, 1381*m*, 1332*s*, 1212*s*, 1110*s*, 1043*m*, 1008*m*, 853*m*, 764*s*, 723*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.91 (*m*, 3 Me); 1.24–1.40 (*m*, 12 CH_2); 1.43–1.54 (*m*, 10 H, CH_2, 2 H–C(3′), 2 H–C(4′)); 1.70–1.94 (*m*, 10 H, CH_2, 2 H–C(2′), 2 H–C(5′)); 3.42 (*t*, *J* = 6.8, 2 H–C(6′)); 4.01 (2*t*, *J* = 6.5, CH_2O–C(3″), CH_2O–C(4″), CH_2O–C(5″)); 4.30 (*t*, *J* = 6.7, 2 H–C(1′)); 7.24 (*s*, H–C(2″), H–C(6″)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.2, 26.06, 26.11, 26.9, 27.8, 28.6, 29.30, 29.33, 29.4, 29.5, 30.3, 31.8, 31.9, 32.6 (CH_2, C(2′), C(3′), C(4′), C(5′)); 33.6 (C(6′)); 64.8 (C(1′)); 69.2 (CH_2O); 73.5 (CH_2O); 108.0 (C(2″), C(6″)); 124.9 (C(1″)); 142.4 (C(4″)); 152.8 (C(3"), C(5″)); 166.5 (COO). ESI-MS: 669.4 ($[M+H]^+$), 507.4 ($[M+H-BrC_6H_{13}]^+$), 395.3 ($[M+2H-BrC_6H_{13}-C_8H_{17}]^+$). HR-ESI-MS: 669.4080 and 671.4067 ($[M+H]^+$, $C_{37}H_{65}BrO_5^+$; calc. 669.4088 and 671.4075).

7.3. *6-Bromohexyl 3,4,5-Tris(tetradecyloxy)benzoate* (**11g**). As described for **11b**, from **10g** (1.04 g, 1.34 mmol), 6-bromohexan-1-ol (0.18 ml, 0.25 g, 1.41 mmol), and Et_3N (0.5 ml, 0.37 g, 3.61 mmol): 497 mg (37%) of **11g**. R_f 0.61 (hexanes/AcOEt 20:1). M.p. 41°. FT-IR (ATR): 2915*s*, 2849*s*, 2362*w*, 1703*s*, 1585*m*, 1466*m*, 1429*s*, 1346*s*, 1334*s*, 1255*s*, 1219*s*, 1121*s*, 994*s*, 767*s*, 725*m*, 651*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 3 Me); 1.26–1.38 (*m*, 30 CH_2); 1.43–1.54 (*m*, 10 H, CH_2, 2 H–C(3′), 2 H–C(4′)); 1.69–1.94 (*m*, 10 H, CH_2, 2 H–C(2′), 2 H–C(5′)); 3.42 (*t*, *J* = 6.8, 2 H–C(6′)); 4.01 (2*t*, *J* = 6.5, CH_2O–C(3″), CH_2O–C(4″), CH_2O–C(5″)); 4.30 (*t*, *J* = 6.7, 2 H–C(1′)); 7.24 (*s*, H–C(2″), H–C(6″)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.3, 26.1, 27.8, 28.6, 29.36, 29.39, 29.43, 29.6, 29.66, 29.69, 29.73, 30.4, 32.0, 32.6 (CH_2, C(2′), C(3′), C(4′), C(5′)); 33.6 (C(6′)); 64.8 (C(1′)); 69.2 (CH_2O); 73.5 (CH_2O); 108.1 (C(2″), C(6″)); 125.0 (C(1″)); 142.5 (C(4″)); 152.8 (C(3″), C(5″)); 166.5 (COO). (APCI)-MS: 923.7 ($[M+H]^+$), 773.7, 759.7 ($[M+H-BrC_6H_{13}]^+$), 727.5, 577.48, 563.5, 519.5, 367.3, 323.3. HR-APCI-MS: 921.6869 and 923.6867 ($[M+H]^+$, $C_{55}H_{101}BrO_5^+$; calc. 921.6905 and 923.6899).

7.4. *6-Bromohexyl 3,4,5-Tris(hexadecyloxy)benzoate* (**11h**). As described for **11b**, from **10h** (3.00 g, 3.48 mmol), 6-bromohexan-1-ol (0.18 ml, 0.25 g, 1.41 mmol), and Et_3N (0.5 ml, 0.37 g, 3.61 mmol): 2.18 g (62%) of **11h**. R_f 0.52 (hexanes/AcOEt 20:1). M.p. 46°. FT-IR (ATR): 2916*s*, 2849*s*, 2169*w*, 1975*w*, 1707*s*, 1587*m*, 1502*m*, 1467*s*, 1429*s*, 1335*s*, 1219*s*, 1121*s*, 988*m*, 765*m*, 721*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 3 Me); 1.26–1.38 (*m*, 36 CH_2); 1.43–1.54 (*m*, 10 H, CH_2, 2 H–C(3′), 2 H–C(4′)); 1.69–1.94 (*m*, 10 H, CH_2, 2 H–C(2′), 2 H–C(5′)); 3.42 (*t*, *J* = 6.8, 2 H–C(6′)); 4.01 (2*t*, *J* = 6.5, CH_2O–C(3″), CH_2O–C(4″), CH_2O–C(5″)); 4.30 (*t*, *J* = 6.7, 2 H–C(1′)); 7.24 (*s*, H–C(2″), H–C(6″)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.2, 26.08, 26.11, 27.8, 28.6, 29.3, 29.40, 29.43, 29.6, 29.67, 29.69, 29.74, 30.3, 32.0 (CH_2, C(2′), C(3′), C(4′), C(5′)); 33.6 (C(6′)); 64.8 (C(1′)); 69.2 (CH_2O); 73.5 (CH_2O); 108.0 (C(2″), C(6″)); 124.9 (C(1″)); 142.4 (C(4″)); 152.8 (C(3″), C(5″)); 166.5 (COO). APCI-MS: 1007.8 ($[M+H]^+$), 961.8, 843.8 ($[M+H-BrC_6H_{13}]^+$), 825.8, 783.5, 619.5, 575.5, 395.3, 351.3. HR-MS (APCI): 1005.7830 and 1007.7835 ($[M+H]^+$, $C_{61}H_{113}BrO_5^+$; calc. 1005.7844 and 1007.7841).

8. *3-Methoxy-6,7,10,11-tetrakis(octyloxy)triphenylen-2-ol.* In analogy to [20b], anh. $FeCl_3$ (13.4 g, 0.120 mol) was added portionwise to a soln. of 1,2-bis(octyloxy)benzene (10.0 g, 29.9 mmol) and guaiacol (=2-methoxyphenol; 7.42 g, 59.8 mmol) in anh. CH_2Cl_2 (80 ml) at 0°, while N_2 was passed through the soln. The mixture was stirred at r.t. for 2 h, then poured in cold MeOH (100 ml), and the CH_2Cl_2 was evaporated. The dark green precipitate was filtered off and separated by FC (SiO_2, hexanes/AcOEt 40:1, 20:1, 10:1, and 5:1): 3,6,7,10,11-pentakis(octyloxy)triphenylen-2-ol (145 mg, 2%), 2,3,6,7,10,11-hexakis(octyloxy)triphenylene (3.66 g, 36%), and the title product (774 mg, 10%). R_f 0.35 (hexanes/AcOEt 10:1). M.p. 109°. FT-IR (ATR): 3535*m*, 2919*s*, 2850*s*, 2184*w*, 1974*w*, 1617*m*, 1514*s*, 1448*s*, 1427*s*, 1386*m*,

1259*s*, 1166*s*, 1043.7s, 835s, 792s. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87–0.92 (*m*, 4 Me); 1.26–1.47 (*m*, 16 CH_2); 1.51–1.61 (*m*, 4 CH_2); 1.90–1.99 (*m*, 4 CH_2); 4.13 (*s*, MeO); 4.18–4.25 (*m*, CH_2O–C(6″), CH_2O–C(7″), CH_2O–C(10″), CH_2O–C(11″)); 5.86 (br. *s*, OH); 7.78–7.96 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 26.17, 26.23, 29.4, 29.47, 29.51, 29.6, 30.9, 31.9 (CH_2); 56.1 (MeO); 69.2, 69.7, 69.9 (CH_2O); 103.5, 106.6, 107.4, 107.5, 107.6 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 123.0, 123.3, 123.59, 123.61, 123.7, 124.1 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 145.1 (C(2″)); 146.4 (C(3″)); 148.8, 148.9, 149.1, 149.2 (C(6″), C(7″), C(10″), C(11″)). APCI-MS: 787.58 ($[M+H]^+$), 675.5 ($[M+H-C_8H_{18}]^+$), 658.5, 563.3, 451.2, 433.2, 339.1. Anal. calc. for $C_{51}H_{78}O_6$ (787.16): C 77.82, H 9.99; found: C 77.63, H 9.84.

9.1. *3,6,7,10,11-Pentakis(octyloxy)triphenylen-2-ol.* In analogy to [20a], bis(octyloxy)benzene (10.0 g, 29.9 mmol) was added to a suspension of anh. $FeCl_3$ (14.5 g, 90.0 mmol) and conc. H_2SO_4 (3 drops) in anh. CH_2Cl_2 (80 ml) at 0°, while N_2 was passed through the soln. The mixture was stirred at r.t. for 1 h, then cold MeOH was added, and the CH_2Cl_2 was evaporated. The precipitate was filtered off and separated by FC (SiO_2, hexanes/AcOEt 50:1, and 40:1): 2,3,6,7,10,11-hexakis(octyloxy)triphenylene (5.56 g, 56%) and the title product (1.36 g, 15%). The spectroscopic data were in accordance with those in [22].

9.2. *3,6,7,10,11-Pentakis(dodecyloxy)triphenylen-2-ol.* As described in *9.1*, from bis(dodecyloxy)benzene (12.0 g, 26.8 mmol): 2.95 g (28%) of the title product. R_f 0.72 (hexanes/AcOEt 10:1). M.p. 84°. FT-IR (ATR): 3557*w*, 2917*s*, 2849*s*, 2368*w*, 2119*w*, 1975*w*, 1617*m*, 1515*s*, 1437*s*, 1259*s*, 1168*s*, 1044*s*, 835*s*, 721*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 5 Me); 1.21–1.46 (*m*, 40 CH_2); 1.51–1.61 (*m*, 5 CH_2); 1.88–1.98 (*m*, 5 CH_2); 4.18–4.24 (*m*, 5 CH_2O); 5.90 (br. *s*, OH); 7.76–7.96 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 26.16, 26.20, 26.23, 29.37, 29.40, 29.5, 29.57, 29.64, 29.66, 29.70, 29.72, 29.8, 31.9 (CH_2); 69.1, 69.6, 69.7, 69.9 (CH_2O); 106.5, 107.2, 107.3, 107.4, 107.6 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 123.0, 123.2, 123.5, 123.59, 123.61, 123.7, 123.9 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 145.2, 145.8, 148.7, 148.9, 149.0, 149.1 (C(2″), C(3″), C(6″), C(7″), C(10″), C(11″)). APCI-MS: 1166.0 ($[M+H]^+$), 997.8 ($[M+H-C_{12}H_{26}]^+$), 829.6, 661.4, 643.4, 493.3, 475.3, 325.1. HR-APCI-MS: 1166.0088 ($[M+H]^+$, $C_{78}H_{132}O_6^+$; calc. 1166.0097).

10.1. *2-[(6-Bromohexyl)oxy]-3-methoxy-6,7,10,11-tetrakis(octyloxy)triphenylene* (**14a**). In analogy to [21], a suspension of anh. K_2CO_3 (0.93 g, 6.70 mmol) and 3-methoxy-6,7,10,11-tetrakis(octyloxy)triphenylen-2-ol (739 mg, 934 μmol) in butan-2-one (60 ml) was stirred at 95° for 30 min. Then, 1,6-dibromohexane (2.12 g, 8.93 mmol) was added and the mixture stirred at 95° for another 16 h. The mixture was filtered and the residue washed with CH_2Cl_2. The filtrate was concentrated and the residue purified by FC (SiO_2, hexanes/AcOEt 40:1, 20:1, 10:1): **14a** (790 mg, 89%). R_f 0.48 (hexanes/AcOEt 10:1). M.p. 44°. FT-IR (ATR): 3098*w*, 2920*s*, 2850*s*, 2366*w*, 2179*w*, 1974*w*, 1617*m*, 1517*s*, 1428*s*, 1258*s*, 1165*s*, 1048*s*, 836*s*, 723*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87–0.92 (*m*, 4 Me); 1.28–1.47 (*m*, 16 CH_2); 1.53–1.62 (*m*, 12 H, CH_2, 2 H–C(3′), 2 H–C(4′)); 1.89–2.00 (*m*, 12 H, CH_2, 2 H–C(2′), 2 H–C(5′)); 3.44 (*t*, $J=6.8$, 2 H–C(6′)); 4.10 (*s*, MeO); 4.23 (*m*, 5 CH_2O); 7.80–7.85 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.4, 26.2, 28.0, 29.2, 29.4, 29.5, 31.9, 32.7 (CH_2, C(2′), C(3′), C(4′), C(5′)); 33.8 (C(6′)); 56.3 (MeO); 69.1 (C(1′)); 69.70, 69.74, 69.8 (CH_2O); 105.0, 106.4, 107.3, 107.4 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 123.4, 123.45, 123.52, 123.7 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 148.3, 149.0, 149.1, 149.2 (C(2″), C(3″), C(6″), C(7″), C(10″), C(11″)). APCI-MS: 951.6 ($[M+H]^+$), 839.5 ($[M+H-C_8H_{18}]^+$), 787.6 ($[M+H-BrC_6H_{13}]^+$), 727.3, 675.5, 597.2, 563.3, 451.2, 339.1. HR-APCI-MS: 949.5911 and 951.5907 ($[M+H]^+$, $C_{57}H_{89}BrO_6^+$; calc. 949.5915 and 951.5910).

10.2. *2-[(6-Bromohexyl)oxy]-3,6,7,10,11-pentakis(octyloxy)triphenylene* (**14b**). As described for **14a**, from 3,6,7,10,11-pentakis(octyloxy)triphenylen-2-ol (988 mg, 1.12 mmol) and 1,6-dibromohexane (2.12 g, 8.93 mmol): 1.01 g (86%) of **14b**. R_f 0.78 (hexanes/AcOEt 10:1). M.p. 53°. FT-IR (ATR): 2917*s*, 2849*s*, 1616*m*, 1517*s*, 1434*s*, 1258*s*, 1171*s*, 1029*s*, 855*s*, 603*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88–0.92 (*m*, 5 Me); 1.26–1.47 (*m*, 20 CH_2); 1.53–1.66 (*m*, 14 H, CH_2, 2 H–C(3′), 2 H–C(4′)); 1.89–1.98 (*m*, 14 H, CH_2, 2 H–C(2′), 2 H–C(5′)); 3.44 (*t*, $J=6.8$, 2 H–C(6′)); 4.20–4.25 (*m*, 6 CH_2O); 7.84 (*s*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.4, 26.2, 28.0, 29.4, 29.5, 31.9, 32.8 (CH_2, C(2′), C(3′), C(4′), C(5′)); 33.7 (C(6′)); 69.5, 69.7, 69.76, 69.80 (CH_2O, C(1′)); 107.3, 107.4 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 123.6, 123.68, 123.70, 123.8 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 148.9,

149.01, 149.04, 149.1 (C(2″), C(3″), C(6″), C(7″), C(10″), C(11″)). APCI-MS: 1049.7 ($[M+H]^+$), 937.6 ($[M+H-C_8H_{18}]^+$), 885.7 ($[M+H-BrC_6H_{13}]^+$), 825.4, 773.6, 713.3, 661.4, 601.2, 549.3, 531.3, 489.1, 437.2, 325.1. HR-APCI-MS: 1047.7023 and 1049.7017 ($[M+H]^+$, $C_{63}H_{103}BrO_6^+$; calc. 1047.7077 and 1049.7009).

10.3. *2-[(6-Bromohexyl)oxy]-3,6,7,10,11-pentakis(dodecyloxy)triphenylene* (**14c**). As described for **14a**, from 3,6,7,10,11-pentakis(dodecyloxy)triphenylen-2-ol (1.38 g, 1.19 mmol) and 1,6-dibromohexane (2.12 g, 8.93 mmol): 1.38 g (87%) of **14c**. R_f 0.74 (hexanes/AcOEt 10:1). M.p. 49°. FT-IR (ATR): 3102*w*, 2918*s*, 2849*s*, 2546*w*, 2369*w*, 2179*w*, 1976*w*, 1617*m*, 1516*s*, 1436*s*, 1387*s*, 1259*s*, 1172*s*, 1045*s*, 836*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 5 Me); 1.23–1.47 (*m*, 40 CH_2); 1.52–1.63 (*m*, 14 H, CH_2, 2 H–C(3′), 2 H–C(4′)); 1.89–1.98 (*m*, 14 H, CH_2, 2 H–C(2′), 2 H–C(5′)); 3.44 (*t*, *J* = 6.8, 2 H–C(6′)); 4.22 (*t*, *J* = 6.6, 4 CH_2O); 4.23 (*t*, *J* = 6.4, CH_2O); 7.83 (*s*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.4, 26.2, 28.0, 29.3, 29.4, 29.5, 29.6, 29.70, 29.72, 29.8, 32.0, 32.8 (CH_2, C(2′), C(3′), C(4′), C(5′)); 33.7 (C(6′)); 69.5, 69.6, 69.72, 69.74 (OCH_2, C(1′)); 107.2, 107.4 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 123.56, 123.57, 123.63, 123.65, 123.72 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 148.8, 148.9, 148.97, 148.99, 149.00, 149.01 (C(2″), C(3″), C(6″), C(7″), C(10″), C(11″)). APCI-MS: 1330.0 ($[M+H]^+$), 1161.8 ($[M+H-C_{12}H_{26}]^+$), 993.6, 825.4, 643.4, 475.3, 325.1. Anal. calc. for $C_{84}H_{143}BrO_6$ (1328.93): C 75.92, H 10.85, N 6.01; found: C 76.12, H 10.72, N 5.93.

11.1. *[1,1′-Biisoquinoline]-4,4′-diylbis(oxyhexane-6,1-diyl) Bis[(3,4,5-tris(alkyloxy)benzoates]* **13d**–**f**. Bis-benzoates **13d**–**f** were prepared as described below for **13b**,**g**,**h**. For yields and m.p.s. of **13b**,**d**–**h**, see *Table*.

11.2. *[1,1′-Biisoquinoline]-4,4′-diylbis(oxyhexane-6,1-diyl) Bis[(3,4,5-tris(octyloxy)benzoate]* (**13b**). In analogy to [19], a suspension of **4a**·2 HCl (185 mg, 275 μmol) and anh. K_2CO_3 (230 mg, 1.66 mmol) in anh. DMF (10 ml) was stirred at 100° for 1 h. After addition of **11b** (185 mg, 275 μmol), the mixture was stirred at 100° for another 17 h. The mixture was hydrolyzed with H_2O (10 ml) and extracted with CH_2Cl_2 (3 × 10 ml). The org. layer was washed with H_2O and brine (10 ml each), dried (Na_2SO_4), and concentrated. The residue was purified by FC (SiO_2, hexanes/AcOEt 10:1, 5:1, and 2:1): **13b** (156 mg, 77%). R_f 0.53 (hexanes/AcOEt 2:1). FT-IR (ATR): 3066*w*, 2951*s*, 2919*s*, 2825*s*, 2366*w*, 2169*w*, 1981*w*, 1707*s*, 1588*s*, 1579*s*, 1503*s*, 1468*s*, 1455*s*, 1428*s*, 1332*s*, 1296*s*, 1247*s*, 1218*s*, 1118*s*, 1097*s*, 985*s*, 858*m*, 780*s*, 764*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 6 Me); 1.26–1.38 (*m*, 24 CH_2); 1.43–1.52 (*m*, 6 CH_2); 1.57–1.67 (*m*, 4 H, 2 H–C(4′)); 1.69–1.92 (*m*, 20 H, CH_2, 2 H–C(3′), 2 H–C(5′)); 1.97–2.08 (*m*, 4 H, 2 H–C(2′)); 4.02 (*t*, *J* = 6.6, 4 H, CH_2O–C(4″)); 4.02 (*t*, *J* = 6.5, 8 H, CH_2O–C(3″), CH_2O–C(5″)); 4.34 (*t*, *J* = 6.3, 4 H, 2 H–C(1′)); 4.36 (*t*, *J* = 6.8, 4 H, 2 H–C(6′)); 7.28 (*s*, 4 H, H–C(2″), H–C(6″)); 7.47 (*ddd*, *J* = 8.5, 6.9, 1.3, 2 H, H–C(7)); 7.68 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.74 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(8)); 8.24 (br. *s*, 2 H, H–C(3)); 8.33 (*ddd*, *J* = 8.5, 1.3, 0.8, 2 H, H–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.68, 22.70, 25.9, 26.0, 26.06, 26.10, 28.8, 29.29, 29.33, 29.4, 29.5, 30.3, 31.8, 31.9 (CH_2, C(2′), C(3′), C(4′), C(5′)); 65.0 (C(6′)); 68.7 (C(1′)); 69.2 (CH_2O); 73.5 (CH_2O); 108.1 (C(2″), C(6″)); 121.3 (C(5)); 122.5 (C(3)); 125.0 (C(1″)); 126.9 (C(8)); 127.7 (C(7)); 128.5 (C(8a)); 129.1 (C(4a)); 129.4 (C(6)); 142.4 (C(4″)); 149.9 (C(4)); 150.4 (C(1)); 152.8 (C(3″), C(5″)); 166.5 (COO). ESI-MS: 1467.0 ($[M+H]^+$), 1353.9 ($[M-C_8H_{18}]^+$), 1253.8, 1141.7, 959.6, 877.6 ($[M+H-R]^+$), 765.4, 665.3, 489.4, 377.3, 289.1. Anal. calc. for $C_{92}H_{140}N_2O_{12}$ (1466.10): C 75.37, H 9.62, N 1.91; found: C 75.12, H 9.52, N 1.88.

11.3. *[1,1′-Biisoquinoline]-4,4′-diylbis(oxyhexane-6,1-diyl) Bis[(3,4,5-tris(tetradecyloxy)benzoate]* (**13g**). As described for **13b**, from **4a**·2 HCl (185 mg, 275 μmol) and **11g** (301 mg, 304 μmol): 163 mg (60%) of **13g**. R_f 0.53 (hexanes/AcOEt 2:1). FT-IR (ATR): 2916*s*, 2849*s*, 1712*s*, 1579*s*, 1428*s*, 1335*s*, 1300*s*, 1212*s*, 1095*s*, 993*m*, 767*s*, 720*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 6 Me); 1.26–1.38 (*m*, 60 CH_2); 1.43–1.52 (*m*, 6 CH_2); 1.57–1.67 (*m*, 4 H, 2 H–C(4′)); 1.69–1.92 (*m*, 20 H, CH_2, 2 H–C(3′), 2 H–C(5′)); 1.97–2.08 (*m*, 4 H, 2 H–C(2′)); 4.01 (*t*, *J* = 6.6, 2 CH_2O); 4.02 (*t*, *J* = 6.5, 4 CH_2O); 4.34 (*t*, *J* = 6.3, 4 H, 2 H–C(1′)); 4.35 (*t*, *J* = 6.8, 4 H, 2 H–C(6′)); 7.28 (*s*, 4 H, H–C(2″), H–C(6″)); 7.47 (*ddd*, *J* = 8.5, 6.9, 1.3, 2 H, H–C(7)); 7.68 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.74 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(8)); 8.24 (*s*, 2 H, H–C(3)); 8.33 (*ddd*, *J* = 8.5, 1.3, 0.8, 2 H, H–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.9, 26.0, 26.1, 28.8, 29.3, 29.38, 29.43, 29.6, 29.67, 29.73, 30.4, 32.0 (CH_2, C(2′), C(3′), C(4′), C(5′)); 64.9 (C(6′)); 68.8 (C(1′)); 69.3 (CH_2O); 73.5 (CH_2O); 108.1 (C(2″), C(6″)); 121.4 (C(5)); 122.4 (C(3)); 125.0 (C(1″)); 126.9 (C(8)); 127.8 (C(7)); 128.5 (C(8a)); 129.2 (C(4a)); 129.5 (C(6)); 142.5 (C(4″)); 150.0 (C(4)); 150.4 (C(1)); 152.9 (C(3″), C(5″)); 166.5 (COO). APCI-MS: 1971.6 ($[M+H]^+$),

1775.4 ([$M+H-C_{14}H_{30}$]$^+$), 1591.2, 1394.0, 1212.9, 1129.8 ([$M+2H-R$]$^+$), 933.6, 741.7, 545.5, 349.2, 289.1. Anal. calc. for $C_{128}H_{212}N_2O_{12}$ (1971.06): C 78.00, H 10.84, N 1.42; found: C 78.03, H 10.74, N 1.40.

11.4. *[1,1′-Biisoquinoline]-4,4′-diylbis(oxyhexane-6,1-diyl) Bis[(3,4,5-tris(hexadecyloxy)benzoate]* (**13h**). As described for **13b**, from **4a**·2 HCl (185 mg, 275 μmol) and **11h** (613 mg, 609 μmol): 216 mg (36%) of **13h**. R_f 0.64 (hexanes/AcOEt 2:1). FT-IR (ATR): 2916*s*, 2848*s*, 2185*w*, 1973*w*, 1709*s*, 1579*m*, 1467*s*, 1429*s*, 1330*s*, 1302*s*, 1219*s*, 1116*s*, 1099*s*, 991*m* 866*m*, 767*s*, 720*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.86–0.90 (*m*, 6 Me); 1.26–1.38 (*m*, 72 CH_2); 1.43–1.52 (*m*, 6 CH_2); 1.57–1.67 (*m*, 4 H, 2 H–C(4′)); 1.69–1.92 (*m*, 20 H, CH_2, 2 H–C(3′), 2 H–C(5′)); 1.97–2.08 (*m*, 4 H, 2 H–C(2′)); 4.02 (*t*, *J* = 6.6, 2 CH_2O–C(4″)); 4.02 (*t*, *J* = 6.5, 8 H, CH_2O–C(3″), CH_2O–C(5″)); 4.34 (*t*, *J* = 6.3, 4 H, 2 H–C(1′)); 4.36 (*t*, *J* = 6.8, 4 H, 2 H–C(6′)); 7.28 (*s*, 4 H, H–C(2″), H–C(6″)); 7.47 (*ddd*, *J* = 8.5, 6.9, 1.3, 2 H, H–C(7)); 7.68 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.74 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(8)); 8.24 (*s*, 2 H, H–C(3)); 8.33 (*ddd*, *J* = 8.5, 1.3, 0.8, 2 H, H–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 25.9, 26.0, 26.09, 26.12, 28.8, 29.2, 29.36, 29.38, 29.44, 29.6, 29.67, 29.68, 29.73, 29.8, 30.4, 31.9 (CH_2, C(2′), C(3′), C(4′), C(5′)); 64.9 (C(6′)); 69.0 (C(1′)); 69.3 (CH_2O); 73.5 (CH_2O); 108.1 (C(2″), C(6″)); 121.6 (C(5)); 122.4 (C(3)); 125.0 (C(1″)); 127.0 (C(8)); 128.2 (C(7)); 128.4 (C(4a), C(8a)); 129.4 (C(6)); 142.5 (C(4″)); 149.8 (C(4)); 150.3 (C(1)); 152.9 (C(3″), C(5″)); 166.5 (COO). APCI-MS: 2139.8 ([$M+H$]$^+$), 1915.5 ([$M+H-C_{16}H_{34}$]$^+$), 1703.3 , 1237.0, 1213.9, 989.7, 825.8, 601.5, 379.3. Anal. calc. for $C_{140}H_{236}N_2O_{12}$ (2139.38): C 78.60, H 11.12, N 1.31; found: C 78.40, H 11.00, N 1.27.

11.5. *4,4′-Bis{{6-{[3-methoxy-6,7,10,11-tetrakis(octyloxy)triphenylen-2-yl]oxy}hexyl}oxy}-1,1′-biisoquinoline* (**15a**). As described for **13b**, from **4a**·2 HCl (100 mg, 207 μmol), **14a** (579 mg, 609 μmol), and K_2CO_3 (612 mg, 4.43 mmol) with stirring for 45 h and purification by FC (SiO_2, hexanes/AcOEt 20:1, 10:1, 5:1, 4:1, 3:1, 2:1, 1:1, and 2:3): 387 mg (69%) of **15a**. R_f 0.60 (hexanes/AcOEt 1:1). FT-IR (ATR): 3069*w*, 2921*s*, 2852*s*, 2367*w*, 2186*w*, 1970*w*, 1616*m*, 1507*s*, 1427*s*, 1258*s*, 1162*s*, 1042*s*, 835*s*, 767*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.87–0.92 (*m*, 8 Me); 1.28–1.47 (*m*, 32 CH_2); 1.53–1.63 (*m*, 8 CH_2); 1.75–1.80 (*m*, 8 H, 2 H–C(3′), 2 H–C(4′)); 1.90–1.99 (*m*, 8 CH_2); 2.04–2.13 (*m*, 8 H, 2 H–C(2′), 2 H–C(5′)); 4.10 (*s*, 2 MeO); 4.23 (*t*, *J* = 6.6, 4 H, CH_2O–C(6″)); 4.24 (*t*, *J* = 6.6, 12 H, CH_2O–C(7″), CH_2O–C(10″), CH_2O–C(11″)); 4.32 (*t*, *J* = 6.4, 4 H, 2 H–C(6′)); 4.37 (*t*, *J* = 6.3, 4 H, 2 H–C(1′)); 7.46 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(7)); 7.66 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.73 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(8)); 7.81–7.86 (*m*, 12 H, H–C(1″), H–C(4″), H–C(5″), H–C(8″), H–C(9″), H–C(12″)); 8.26 (*s*, 2 H, H–C(3)); 8.34 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 26.08, 26.13, 26.2, 29.4, 29.5, 31.9 (CH_2, C(2′), C(3′), C(4′), C(5′)); 56.3 (MeO); 68.7 (C(1′)); 69.2 (C(6′)); 69.7, 69.8 (CH_2O); 105.0, 106.4, 107.3, 107.5 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 121.4 (C(5)); 122.4 (C(3)); 123.4, 123.46, 123.54, 123.65, 123.68 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 126.9 (C(8)); 127.8 (C(7)); 128.5 (C(8a)); 129.1 (C(4a)); 129.5 (C(6)); 148.4, 148.99, 149.01, 149.03, 149.1, 149.2 (C(2″), C(3″), C(6″), C(7″), C(10″), C(11″)); 150.1 (C(4)); 150.4 (C(1)). APCI-MS: 2027.4 ([$M+H$]$^+$), 1902.2, 1838.2, 1201.8, 1014.7. Anal. calc. for $C_{132}H_{188}N_2O_{14}$ (2026.91): C 78.22, H 9.35, N 1.38; found: C 78.27, H 9.30, N 1.37.

11.6. *4,4′-Bis{{6-{[3,6,7,10,11-pentakis(octyloxy)triphenylen-2-yl]oxy}hexyl}oxy}-1,1′-biisoquinoline* (**15b**). As described for **13b**, from **4a**·2 HCl (100 mg, 207 μmol), **14b** (639 mg, 609 μmol), and K_2CO_3 (612 mg, 4.43 mmol) with stirring for 45 h and purification by FC (SiO_2, hexanes/AcOEt 20:1, 10:1, 5:1, and 4:1): 193 mg (31%) of **15b**. R_f 0.47 (hexanes/AcOEt 4:1). FT-IR (ATR): 2882*s*, 1682*m*, 1558*s*, 1485*s*, 1407*s*, 1350*s*, 1188*m*, 1086*s*, 929*s*, 743*s*, 679*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.85–0.92 (*m*, 10 Me); 1.27–1.47 (*m*, 40 CH_2); 1.53–1.63 (*m*, 10 CH_2); 1.75–1.80 (*m*, 8 H, 2 H–C(3′), 2 H–C(4′)); 1.90–1.99 (*m*, 10 CH_2); 2.03–2.11 (*m*, 8 H, 2 H–C(2′), 2 H–C(5′)); 4.23 (*t*, *J* = 6.6, 16 H, CH_2O–C(6″), CH_2O–C(7″), CH_2O–C(10″), CH_2O–C(11″)); 4.24 (*t*, *J* = 6.5, 4 H, CH_2O–C(3″)); 4.30 (*t*, *J* = 6.4, 4 H, 2 H–C(6′)); 4.37 (*t*, *J* = 6.3, 4 H, 2 H–C(1′)); 7.46 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(7)); 7.65 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6)); 7.74 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(8)); 7.83–7.87 (*m*, 12 H, H–C(1″), H–C(4″), H–C(5″), H–C(8″), H–C(9″), H–C(12″)); 8.25 (*s*, 2 H, H–C(3)); 8.34 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(5)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 26.1, 26.2, 29.4, 29.5, 31.9 (CH_2, C(2′), C(3′), C(4′), C(5′)); 68.8 (C(1′)); 69.6 (C(6′)); 69.6, 69.7, 69.8 (OCH_2); 107.2, 107.3, 107.35, 107.42 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 121.4 (C(5)); 122.4 (C(3)); 123.60, 123.64, 123.7 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 126.9 (C(8)); 127.8 (C(7)); 128.5 (C(8a)); 129.1 (C(4a)); 129.5 (C(6)); 148.9, 149.0 (C(2″), C(3″), C(6″), C(7″), C(10″), C(11″)); 150.0 (C(4)); 150.4 (C(1)). APCI-MS: 2223.6 ([$M+H$]$^+$),

1971.5, 1338.9, 1299.9, 1186.9, 1160.9, 1112.8, 1070.8, 1026.8, 985.8, 967.8, 873.7, 855.7. Anal. calc. for $C_{146}H_{216}N_2O_{14}$ (2223.28): C 78.87, H 9.79, N 1.26; found: C 78.73, H 9.65, N 1.22.

11.7. *4,4′-Bis{[6-{[3,6,7,10,11-pentakis(dodecyloxy)triphenylen-2-yl]oxy}hexyl]oxy}-1,1′-biisoquinoline* (**15c**). As described for **13b**, from **4a** · 2 HCl (100 mg, 207 μmol), **14c** (809 mg, 609 μmol), and K_2CO_3 (612 mg, 4.43 mmol) with stirring for 45 h and purification by FC (SiO_2, hexanes/AcOEt 20:1, 10:1, 8:1, 5:1, and 2:1): 105 mg (14%) of **15c**. R_f 0.56 (hexanes/AcOEt 4:1). FT-IR (ATR): 3077*w*, 2918*s*, 2849*s*, 2559*w*, 2368*w*, 2119*w*, 1969*w*, 1617*m*, 1517*s*, 1436*s*, 1387*s*, 1259*s*, 1172*s*, 1044*m*, 836*s*, 721*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.83–0.90 (*m*, 10 Me); 1.22–1.47 (*m*, 80 CH_2); 1.52–1.62 (*m*, 10 CH_2); 1.75–1.80 (*m*, 8 H, 2 H–C(3′), 2 H–C(4′)); 1.90–1.99 (*m*, 10 CH_2); 2.03–2.13 (*m*, 8 H, 2 H–C(2′), 2 H–C(5′)); 4.23 (*t*, *J* = 6.6, 16 H, CH_2O–C(6″), CH_2O–C(7″), CH_2O–C(10″), CH_2O–C(11″)); 4.24 (*t*, *J* = 6.5, 4 H, CH_2O–C(3″)); 4.30 (*t*, *J* = 6.4, 4 H, 2 H–C(6′)); 4.37 (*t*, *J* = 6.3, 4 H, 2 H–C(1′)); 7.46 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6) or H–C(7)); 7.65 (*ddd*, *J* = 8.5, 6.9, 1.2, 2 H, H–C(6) or H–C(7)); 7.74 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(5) or H–C(8)); 7.83–7.87 (*m*, 12 H, H–C(1″), H–C(4″), H–C(5″), H–C(8″), H–C(9″), H–C(12″)); 8.25 (*s*, 2 H, H–C(3)); 8.34 (*ddd*, *J* = 8.5, 1.2, 0.8, 2 H, H–C(5) or H–C(8)). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.1 (Me); 22.7, 26.16, 26.23, 29.4, 29.5, 29.6, 29.70, 29.73, 29.8, 31.9 (CH_2, C(2′), C(3′), C(4′), C(5′)); 68.8 (C(1′)); 69.6 (C(6′)); 69.7 (CH_2O); 107.2, 107.4 (C(1″), C(4″), C(5″), C(8″), C(9″), C(12″)); 121.4 (C(5)); 122.4 (C(3)); 123.6, 123.7 (C(4″a), C(4″b), C(8″a), C(8″b), C(12″a), C(12″b)); 126.9 (C(8)); 127.8 (C(7)); 128.5 (C(8a)); 129.1 (C(4a)); 129.5 (C(6)); 148.9, 149.0 (C(2″), C(3″), C(6″), C(7″), C(10″), C(11″)); 150.0 (C(4)); 150.4 (C(1)). APCI-MS: 2785.3 ($[M+H]^+$), 2658.0, 2596.1, 2475.9, 2223.6, 2122.0, 1992.5, 1648.2. HR-APCI-MS: 2785.2624 ($[M+H]^+$, $C_{186}H_{296}N_2O_{14}^+$; calc. 2785.2652).

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Received March 12, 2009