



# Liquid Crystals



# Discogens Possessing Aryl Side Groups Synthesized by Suzuki Coupling of Triphenylene Triflates and Their Self-Organization Behavior

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**Abstract:** Pd-catalyzed Suzuki cross-coupling reactions between arylboronic acids and bromoarenes have been applied widely in the synthesis of liquid-crystalline materials. However, aryl triflate derivatives have been less used despite their high chemical tolerance, reactivity, and chemical accessibility. In this report, three series of discogens have been synthesized in good yields from appropriate triphenylene triflate precursors by Suzuki coupling reactions with various commercial arylboronic acids (e.g., aryl = phenylene, thiophene, naphthalene, triarylamine, carbazole, and fluorene). The synthesized discogens display broad mesophase ranges and high thermal stabilities. Moreover, those bearing triarylamine, carbazole, and fluorene side groups are also blue-light emitters. The availability of the triflate precursors coupled with their highly efficient cross-coupling with commercial arylboronic acids make this strategy extremely versatile and attractive for the design of new functional materials.

## Introduction

In recent decades, discotic liquid crystal (DLC) derivatives based on polycyclic  $\pi$ -conjugated triphenylene (TP) have become the most important discotic representatives and have attracted considerable research interest<sup>[1–12]</sup> because of their exceptional self-organizational behavior, defect-self-healing character, and high charge-carrier transportation along the assembled cylindrical columns.<sup>[13–18]</sup> The highly symmetrical TP core is an ideal scaffold for the development of various discotic functional materials with interesting electronic properties, and various molecular systems based on TP have shown a wide range of commercial applications, including optical compensating films,<sup>[19]</sup> organic photovoltaic (OPV) devices,<sup>[20,21]</sup> organic fieldeffect transistors (OFET),<sup>[22]</sup> and organic light-emitting diodes (OLEDs).<sup>[23,24]</sup>

Hexa(alkoxy)triphenylenes ( $R_6$ -TP,  $R = OC_nH_{2n+1}$ ) and simple related derivatives are the workhorses of DLCs:<sup>[1-4]</sup> their synthesis conditions are versatile, and purification methods for largescale TP derivatives have been developed.<sup>[25]</sup> Although,  $R_6$ -TP discogens have good solubilities in most organic solvents, they exhibit hexagonal columnar mesophases (Col<sub>hex</sub>) over narrow temperature ranges and with low phase-transition tempera-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201600270. tures.<sup>[1]</sup> In contrast, more sophisticated hexaaryl-substituted triphenylenes, Ar<sub>6</sub>-TP, and corresponding fused-ring DLCs, prepared from hexabromotriphenylene followed by oxidation reactions, exhibit low solubilities in classical organic solvents but possess high phase-transition temperatures, high thermal stabilities, and wide mesophase ranges.<sup>[26,27]</sup> However, they have been less investigated owing to their unalterable and limited molecular designs and evident synthetic difficulties.

Alternatively, it is anticipated that mixed alkoxy/aryltriphenylenes would display physical and chemical properties intermediate between those of pure Ar<sub>6</sub>-TP and those of pure R<sub>6</sub>-TP, of interest for the development of new materials for electronic devices, but such systems have not been investigated widely.<sup>[28,29]</sup> The replacement of only one alkyl or alkoxy group by H in R<sub>6</sub>-TPs already compromises their mesomorphism.<sup>[30–33]</sup> However, the replacement of some of the diverging alkoxy chains by radial  $\pi$ -conjugated groups (e.g., cyano, ethynyl, or aromatic) results in mixed TP systems, in which the mesomorphism is maintained, with higher clearing temperatures than those of the parent R<sub>6</sub>-TP compounds.<sup>[31]</sup> The extension of the TP core with  $\pi$ -conjugated groups is also beneficial to mesophase induction/formation and the enhancement of the mesophase stability.<sup>[28,31]</sup> To date, bromo-substituted TP derivatives<sup>[26,27,30-33]</sup> have mostly been used as key intermediates for the synthesis of such  $\pi$ -extended TPs, mainly by Suzuki crosscoupling reactions. However, these bromo-TPs are not readily accessible, as their previously reported synthesis is tedious, low yielding, and involves hydroxyl activation, catalytic hydrogenation, and aromatic bromination.<sup>[30-35]</sup> In contrast, aryl triflates are suitable alternative substrates for the Suzuki cross-coupling reaction.<sup>[36–38]</sup> Indeed, their synthesis is shorter and more direct than that of their bromo-TP homologs, as they can be obtained

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directly in one-step from the corresponding and readily available hydroxytriphenylenes<sup>[1]</sup> by reaction with triflic anhydride.<sup>[37]</sup> Triphenylenyl triflates and nonaflates have been used for  $C-N^{[39]}$  and C-C bond<sup>[40]</sup> construction, respectively, in functional material synthesis. In this context, TP triflate derivatives would seem to be more useful and relevant starting materials for the synthesis of mixed alkoxy/aryltriphenylenes.

Functional molecules containing units such as triarylamine,<sup>[41-43]</sup> carbazole,<sup>[44-46]</sup> and fluorene<sup>[47]</sup> have been investigated extensively as photoconductors, charge-carrier transporters, photo- and electroluminescent materials, and photorefractive materials. They have displayed enormous academic and economic values. DLCs containing these functional units possess not only their own dynamics and order but also electron-rich and light-emitting features, which increase their applicability. It may be expected that the enlargement of the  $\pi$ -conjugated system of the semiconducting discogens will provide a more efficient overlap and result in a higher thermal stability of the columnar mesophase and faster charge-carrier mobility.<sup>[48,49]</sup>

With these ideas in mind, we designed a series of TP discogens, which contain various aryl moieties with electron-donating and electron-withdrawing groups. We first synthesized triphenylene mono(triflate), bis(triflate), and tris(triflate) derivatives in high yields by the reaction of the appropriate hydroxytriphenylene with triflic anhydride (M**0**, D**0**, and T**0**, respectively; Tables 1, 2, and 3). We subsequently applied Suzuki cross-coupling reactions between these TP triflates and various arylboronic acids to synthesize the corresponding series of mixed alkoxy/aryltriphenylenes (M**n**, D**n**, and T**n**), which possess radial electron-rich or electron-deficient phenylenes, as well as triphenylamine, carbazole, and fluorine groups, in good-to-excellent yields (Tables 1, 2, and 3). More importantly, these mixedside-group triphenylenes have been characterized by differential scanning calorimetry (DSC), polarized optical microscopy

C <sub>6</sub> H <sub>13</sub> O	$\begin{array}{c} \text{OH} \\ \text{OC}_{6}\text{H}_{13} \\ \text{OC}_{6}\text{H}_{13} \\ \text{OC}_{6}\text{H}_{13} \end{array}$	$\begin{array}{c} O, \\ O, \\ N, CH_2Cl_2 \\ \hline 91\% \\ C_6H_{13}O \\ \hline \end{array}$	$SO_2CF_3$ $OC_6H_{13}$ $OC_6H_{13}$	ArB(OH) <sub>2</sub> , Pd(PPh <sub>3</sub> ) <sub>4</sub> K <sub>2</sub> CO <sub>3</sub> , THF/H <sub>2</sub> O C <sub>6</sub> H <sub>13</sub> O Ar	OC <sub>6</sub> H <sub>13</sub> OC <sub>6</sub> H <sub>13</sub>
C	Л	C C	о 0	Ai D1-D1	7
Compound	Ar	Yield (%)	Compound	Ar	Yield (%)
D1		81	D <b>10</b>	C5H11	77
D <b>2</b>	<b>S</b>	77	D <b>11</b>	MeO MeO	79
D <b>3</b>		58	D <b>12</b>	C <sub>5</sub> H <sub>11</sub> O C <sub>5</sub> H <sub>11</sub> O	76
D <b>4</b>	NC	75	D <b>13</b>	<b>N</b> -()	61
D <b>5</b>	F	64	D <b>14</b>		59
D <b>6</b>	F	85	D <b>15</b>		48
D <b>7</b>	FF	87	D <b>16</b>	<b>N</b> -( <b>)</b>	66
D <b>8</b>		85	D <b>17</b>		49
D <b>9</b>		67			

Table 1. Molecular structures and synthetic yields of 2,7-diaryltriphenylenes D1-D17.





#### Table 2. Molecular structures and synthetic yields of 2-aryltriphenylenes M1-M5.



Table 3. Molecular structures and synthetic yields of 2,6,10-triaryltriphenylenes T1-T4.



(POM), and small-angle X-ray scattering (SAXS), and most of them (25/29) exhibit hexagonal columnar mesophases over large temperature ranges with higher clearing temperatures than those of the hexa(hexyloxy)triphenylene parent.

## **Results and Discussion**

## Synthesis of Aryltriphenylenes from Triphenylenyl Triflates

The synthesis of hydroxytriphenylenes can usually be performed by three different methods, namely, *o*-terphenyl intramolecular oxidation, benzene–biphenyl intermolecular oxidation, and statistical *o*-dialkoxybenzene oxidative trimerization.<sup>[1,50]</sup> The benzene–biphenyl route possesses a higher selectivity than the statistical method, and 2-hydroxy-3,6,7,10,11pentakis(hexyloxy)triphenylene and 2,7-di(hydroxy)-3,6,10,11tetrakis(hexyloxy)triphenylene were synthesized by this route (Schemes 1 and 2) and obtained in good yields.<sup>[51,52]</sup> 2-Methoxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene was prepared by FeCl<sub>3</sub> oxidative coupling between 1-methoxy-2-hexyloxybenzene and 3,3',4,4'-tetra(hexyloxy)biphenyl, followed by selective demethylation with LiPPh<sub>2</sub> to produce 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene (Scheme 1). 3,6,10,11-Tetrakis(hexyloxy)-2,7-bis(methyloxy)triphenylene was synthesized by the FeCl<sub>3</sub>-mediated oxidative cyclodehydrogenation between 1,2-bis(hexyloxy)benzene and 3,3'-bis(hexyloxy)-4,4'-



dimethoxybiphenyl, followed by selective demethylation with LiPPh<sub>2</sub> (Scheme 2). Finally, 2,6,10-tri(hydroxy)-3,7,11-tris(hexy-loxy)triphenylene was prepared by the statistical method (Scheme 3). First, 2,6,10-tris(hexyloxy)-3,7,11-tri(methoxy)triphenylene was synthesized by the FeCl<sub>3</sub>-mediated oxidative trimerization of 1-methoxy-2-hexyloxybenzene, followed by column chromatographic separation of the unsymmetrical isomer. Then, selective demethylation with LiPPh<sub>2</sub> yielded 2,6,10-tri-(hydroxy)-3,7,11-tris(hexyloxy)triphenylene.



Scheme 1. Synthesis of 2-hydroxy-3,6,7,10,11-penta(hexyloxy)triphenylene: (i) NaOH,  $H_2O_2$ ,  $H_2O$  (91.1 %); (ii)  $n-C_6H_{13}Br$ ,  $K_2CO_3$ , DMF (80–90 %); (iii) 1: Mg, THF; 2: Ni(PPh\_3)\_2Cl\_2, THF (70 %); (iv) FeCl\_3,  $H_2SO_4$ ,  $CH_2Cl_2$  (50–60 %); (v) LiPPh\_2, THF, tBuCl (80–90 %).



Scheme 2. Synthesis of 2,7-dihydroxy-3,6,10,11-tetrakis(hexyloxy)triphenylene: (i) *m*-CPBA,  $CH_2CI_2$  (81.7 %); (ii) *n*-C<sub>6</sub>H<sub>13</sub>Br, K<sub>2</sub>CO<sub>3</sub>, DMF (88.5 %); (iii) 1: Mg, THF; 2: Ni(PPh<sub>3</sub>)<sub>2</sub>CI<sub>2</sub>, THF, HCI (67.2 %); (iv) FeCI<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>2</sub>CI<sub>2</sub> (57.1 %); (v) LiPPh<sub>2</sub>, THF, tBuCl (80.9 %).

Triphenylene-2,7-diyl triflate (D**0**) was synthesized in a yield of 91 % through the reaction of triphenylene-2,7-diol with triflic anhydride (Table 1).<sup>[37]</sup> Similarly, M**0** and T**0** were synthesized in almost quantitative yields (Tables 2 and 3). The corresponding mixed alkoxy/aryltriphenylenes were synthesized through





Scheme 3. Synthesis of 2,6,10-tri(hydroxy)-3,7,11-tris(hexyloxy)triphenylene: (i) n-C<sub>6</sub>H<sub>13</sub>Br, K<sub>2</sub>CO<sub>3</sub>, DMF (90 %); (ii) FeCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> (50–60 %), separation of the isomers by column chromatography; (iii) LiPPh<sub>2</sub>, THF, tBuCl (80–90 %).

Suzuki cross-coupling reactions.<sup>[36–38]</sup> Generally, the TP triflate and arylboronic acid (1.2 equiv. per triflate group) reacted in tetrahydrofuran/H<sub>2</sub>O (THF/H<sub>2</sub>O, 4:1) with Pd(PPh<sub>3</sub>)<sub>4</sub> (8 mol-%) as the catalyst and K<sub>2</sub>CO<sub>3</sub> as the base.

The 2,7-diaryltriphenylene derivatives D1-D17 were synthesized in yields of 48 to 87 % (Table 1). Considering the twofold cross-coupling characteristic of the reaction, the yields are acceptable. Two major advantages of this cross-coupling reaction can be emphasized: it (1) possesses a simple catalytic system and (2) has a large functional-group tolerance; for example, chloro (D9), cyano (D4), and thiophene (D2) derivatives were synthesized in good yields. Furthermore, both electron-rich and electron-deficient arylboronic acids react smoothly, and the yields are also high, considering their bulkiness. However, the stereochemistry has a moderate effect on the synthetic yield: D13-D17 with bulky aryl groups are synthesized in moderate yields. Monoaryltriphenylenes M1-M5 were synthesized in yields of 60-94 % (Table 2), and the triaryltriphenylene discogens T1-T4 were obtained in yields of 62-85 % (Table 3) with a high tolerance to bulky substituents, as for series D1-D17.

All of the synthesized compounds were characterized by <sup>1</sup>H NMR and IR spectroscopy; the new intermediates and target compounds were characterized by high-resolution mass spectroscopy [Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) with MALDI or ESI], and the analytical data are in good agreement with the chemical structures (Figures S4–S64 in the Supporting Information).

#### Mesomorphism Investigation by POM, DSC, and SAXS

We first investigated the mesomorphism of these sophisticated discogens by POM. All but D16, D17, T3, and T4 displayed typical fan-shaped or pseudo-focal-conical textures, which indicate the presence of discotic columnar mesophases (Figure 1). The phase transitions were characterized comprehensively by DSC (Figure 2), and the transition temperatures and enthalpy changes are summarized in Table S1 and Figures S1–S3. The columnar nature of the mesophases of some representative compounds was further proved by SAXS (Figure 4 and Table 4). The synthesized discogens crystallized from organic solvents, and on the first heating runs they displayed crystal  $\rightarrow$  mesophase and mesophase  $\rightarrow$  isotropic (I) liquid transitions. On the first cooling run, they displayed isotropic liquid  $\rightarrow$  mesophase transitions, but crystallization is not always observed as the aryl







Figure 1. POM images of some representative samples (for a cooling rate of 3 °C/min from isotropic liquid). (A) M1 at 98 °C with homeotropic alignment behavior (face-on orientation of the discotic columns on the glass surface); (B) M1 at 96 °C with parallel polarizers, showing sixfold symmetrical domains of the  $Col_{hex}$  mesophase; (C) M4 at 88 °C, the black textures show face-on orientation of the columns; (D) D12 at 125 °C, the fan-shaped texture shows the edge-on orientation of the discotic columns; (E) D5 at 90 °C, the texture shows the homeotropic alignment behavior of the fluorophenyltriphenylene; (F) T2 at 120 °C, big fan-shaped texture; (G) D14 at 140 °C, small fan-shaped texture with propeller-like assembly; (H) D14 at 180 °C, the growth of developable domains from the isotropic liquid.



Figure 2. Representative DSC curves depicting the first cooling run and the second heating run of M2, M4, D3, D6, D8, T1, and T2. The peaks in the first cooling runs represent isotropic liquid to columnar phase transitions ( $I \rightarrow Col_{hex}$ ); and the peaks in the second heating run show columnar phase to isotropic liquid transitions ( $Col_{hex} \rightarrow I$ ).

groups are larger than the alkyl chains and the target discogens are highly viscous. However, some discogens showed cold crystallization during the second heating run (Table S1).

Table 4. Small-angle X-ray data for the mesophases of M2, D8, D12, D13, D14, and T2.

	$d_{\rm meas}$ [Å] <sup>[a]</sup>	Ι (ξ, Å) <sup>[b]</sup>	hk/D <sub>i</sub> /h <sub>i</sub> <sup>[c]</sup>	d <sub>calcd.</sub> [Å] <sup>[d]</sup>	Mesophase parameters <sup>[e]</sup>
M <b>2</b>	20.44	vs (sh)	10	20.20	$\operatorname{Col}_{\operatorname{hex}}(T = 25 \ ^{\circ}\mathrm{C})$
	14.1	m (60)	D		$a = 23.3 \text{ Å}; S = 471 \text{ Å}^2 (Z = 1)$
	11.64	w (sh)	11	11.66	$V_{\rm mol} = (1610 \pm 50) \text{ Å}^3$
					$(\varrho = 1.01 \pm 0.03)$
	10.11	vw (sh)	20	10.10	$h_{\rm mol} = (3.42 \pm 0.14)$ Å
	7.57	w (sh)	21	7.63	
	4.4	vs (10)	$h_{ch}+h_{ar}$		
	3.50	s (80)	$h_{\pi}$		
D <b>12</b>	22.10	vs (sh)	10	21.90	$Col_{hex}$ (T = 25 °C)
	14.6	m (60)	D		a = 25.35 Å; $S = 555$ Å <sup>2</sup> ( $Z = 1$ )
	11.02	vw (sh)	20	10.95	$V_{\rm mol} = (1850 \pm 60) \text{ Å}^3$
					$(\varrho = 1.01 \pm 0.03)$
	8.17	m (sh)	21	8.28	$h_{\rm mol} = (3.33 \pm 0.14)$ Å
	7.25	vw (sh)	30	7.30	
	4.5	vs. (10)	$h_{ch}+h_{ar}$		
	3.53	vs (100)	$h_{\pi}$		
	21.85	vs (sh)	10	21.70	$Col_{hex}$ (T = 150 °C)
	14.6	m (40)	D		$a = 25.05 \text{ Å}; S = 544 \text{ Å}^2 (Z = 1)$
	10.76	vw (sh)	20	10.85	$V_{\rm mol} = (2020 \pm 70) \text{ Å}^3$
					$(\varrho = 0.93 \pm 0.03)$
	8.10	w (sh)	21	8.20	$h_{\rm mol} = (3.71 \pm 0.16) \text{ Å}$
	4.5	vs (10)	$h_{ch}+h_{ar}$		
	3.74	vs (40)	$h_{\pi}$		
T <b>2</b>	23.42	vs (sh)	10	23.15	$Col_{hex}$ (T = 25 °C)
	14.6	s (40)	D		$a = 26.7 \text{ Å}; S = 619 \text{ Å}^2 (Z = 1)$
	11.53	w (sh)	20	11.58	$V_{\rm mol} = (2080 \pm 60) \text{ Å}^3$
					$(\rho = 1.02 \pm 0.03)$
	8.64	m (sh)	21	8.75	$h_{\rm mol} = (3.36 \pm 0.14)$ Å
	6.57	vw (sh)	22	6.68	
	4.4	s (10)	$h_{ch}+h_{ar}$		
	3.52	s (100)	h <sub>π</sub>		
D <b>8</b>	29	m (50)	$D_2$		$Col_{bex}$ (T = 170 °C)
	18.20	vs (sh)	10	18.20	$a = 21.0 \text{ Å}; S = 382 \text{ Å}^2 (Z = 1)$
	14.4	m (70)	D		$V_{\rm mol} = (1480 \pm 50) \text{ Å}^3$
					$(\rho = 1.00 \pm 0.03)$
	4.4	vs (10)	$h_{ch} + h_{ar}$		$h_{\rm mol} = (3.86 \pm 0.16) \text{ Å}$
	3.71	s (50)	h <sub>-</sub>		
D <b>1</b> 3	20.10	vs (sh)	10	20.10	$Col_{hav}$ (T = 50 °C)
	14.3	m (80)	D		a = 23.2 Å: $S = 467$ Å <sup>2</sup> ( $7 = 1$ )
	4.4	vs (10)	h <sub>sh</sub> +h <sub>ar</sub>		$V_{\rm mal} = (1825 + 80) \text{ Å}^3$
		15 (10)	···Cli ····dl		$(\rho = 1.02 \pm 0.05)$
	3.60	s (50)	h		$h_{\rm max} = (3.91 \pm 0.20) \text{ Å}$
D14	2016	100 (sh)	10	20.18	$Col_{1}$ (T = 160 °C)
U <b>14</b>	140	m (100)	D	20.10	$a = 233 \text{ Å} \cdot \text{S} = 470 \text{ Å}^2 (7 - 1)$
	764	w (sh)	21	763	$V = (1920 + 80) Å^3$
	,	** (311)	21		$(\alpha - 0.96 \pm 0.04)$
	50_11	vs (10)	h.⊥h		$h_{\rm e} = 0.90 \pm 0.04$
	3.64	vs (10) c (40)	h h		11mol - (4.09 ± 0.20) A
	2.01	3 (-10)	'π		

[a] Measured periodicities of reflections from columnar lattice (*hk*) of scattering signals from short-range correlated structure  $D_i$  and from lateral distances between molecular segments  $h_i$ . [b] Intensity of reflections and scattering signals (VS: very strong, S: strong, m: medium, w: weak, vw: very weak) and associated correlation length  $\xi$  (sh indicates a sharp reflection). [c] Miller indices, short-range correlated periodicities D and  $D_2 = 2D$ , lateral distances between chains ( $h_{ch}$ ), rigid segments of substituents ( $h_{ar}$ ), and face-to-face triphenylene rings ( $h_{\pi}$ ). [d] Calculated spacing from optimized lattice parameter. [e] Type of mesophase, temperature, lattice parameter (*a*), lattice area (S), number of molecule stacks per lattice (*Z*), calculated molecular volume from reference data ( $V_{mol}$ ), density ( $\varrho$ ), and columnar slice thickness ( $h_{mol}$ ).



## Mesomorphism of 2,7-Diaryl-Substituted Triphenylenes D1–D17

The 2,7-diaryl-substituted triphenylenes contain neutral aryls (D1–D3), electron-deficient aryls (D4–D9), electron-rich aryls (D10–D12), and the bulky triphenylamine (D12), carbazole (D14, D16, and D17), and fluorene (D15) groups (Table 1). Triphenylene-2,7-diyl triflate (D0) displays a columnar (Col<sub>hex</sub>) phase at 124–179 °C and a plastic columnar (Col<sub>x</sub>) phase below 124 °C (Figure S1).

Diphenyl-TP (D1) can be regarded as the parent compound of the 2,7-diaryl-substituted derivatives. Compound D1 exhibits melting and clearing temperature of 10 and 120 °C, that is 50 °C below and 20 °C above the respective transition temperatures of hexakis(hexyloxy)TP (R<sub>6</sub>-TP, R = OC<sub>6</sub>H<sub>13</sub>).<sup>[53]</sup> The temperature range of the mesophase is also considerably broader than those of other disubstituted isomers: the 3,6-isomer displays a columnar phase between 71 and 136 °C, and the 2,3-isomer is nonmesomorphic with a melting point of 104 °C.<sup>[28]</sup>

For D2, possessing 3-thiophene substituents, the mesophase range shifts somewhat to higher temperature (between 68 and 148 °C), consistent with previously reported findings for the 3,6isomer (I  $\rightarrow$  Col<sub>hex</sub> 147 °C, Col<sub>hex</sub>  $\rightarrow$  glass 55 °C) and 2,3-isomer (monotropic with a m.p. of 87 °C).[28] This shift is evidently related to the enhanced interactions between the thiophene rings, whereas D3 instead demonstrates the effect of a further molecular extension of the conjugated moieties from phenyl to 2-naphthalenyl substituents. As expected, the extension further delayed the transition to the isotropic liquid phase (202 °C), and the melting temperature increased moderately (37 °C), resulting in much higher mesophase stability than those for D1 and D2. In D4, the phenyl rings are terminated with electron-withdrawing cyano functions, which are well-known promoters of mesomorphism through dipolar association.[31,32,54] Logically, the enhanced interactions increase both the clearing and the melting temperature (by 88 and 64 °C, respectively) and enlarge the mesophase range somewhat. The ratio with other substitution patterns is similar to that for D1, as the 2,3-isomer is non-mesomorphic with a melting temperature of 217 °C, and the 3,6isomer displays a clearing temperature of 186 °C with a mesophase range of 10 °C.<sup>[28]</sup> Comparing the mesomorphism of 2,7diaryl-TPs D1, D2, and D4 with those of their 2,3- and 3,6-isomers, the most influential structural features for the induction and stabilization of mesomorphism is the larger separation between both substitution positions rather than the molecular symmetry alone. For example, the 2,7- and 3,6-isomers, which favor a more homogeneous distribution of the aliphatic continuum between the columns, are less perturbed than they would be if the substituents were closer to each other, as in the 2,3isomer.<sup>[55,56]</sup>

For the electron-deficient aryl systems such as the fluorophenyl (D**5** to D**8**) and chlorophenyl (D**9**) derivatives, the beneficial impact of electron-withdrawing substituents on the clearing temperatures is obvious: D**5** to D**8** possess one to three fluoro groups on the phenyl rings, and their clearing temperatures increase from 162–214 °C, and the transition increases to 219 °C for D**9** with the even more withdrawing chloro group. Such a relationship between the electron-withdrawing charac-



ter of the substituents and the extension of the columnar mesomorphism to higher temperature was previously investigated for close discotic systems.<sup>[55,56]</sup>

The deleterious effect of weakly electron-donating groups such as alkyl and alkoxy chains was pointed out in the same report, but the series of substituents involved no longer chains than a methyl group. On the contrary, D10 and D12 show extended Colhex ranges owing to their pentyl chains, which insert into the aliphatic periphery and contribute to isolating the discogens at the nodes of the lattice. Conversely, the methoxy chains of D11 are insufficient to screen out interactions between the substituents of neighboring columns and lead to the appearance of a broad three-dimensional "plastic Col" mesophase followed by a narrow Colhex range. The derivatives with bulkier electron-rich substituents such as diphenylaminophenyl (D13) and phenylcarbazole (D14, D16, and D17) are either nonmesomorphic with crystalline phases that melt at high temperature (D13, D16, and D17) or show a tiny Col<sub>hex</sub> range above a three-dimensional mesophase (D14). In the crystalline carbazole derivatives, the substituents are attached through the phenyl rings; therefore, the entire carbazole rings are pendant from the triphenylene core, and this allows self-association in regular, crystalline networks. Conversely, mesomorphism persists for the compound with the side-attached carbazole moiety and is even improved for the dimethylfluorene derivative (D15), for which side-attachment combines with the space requirement of the methyl groups to hamper interactions between the fluorene rings. This derivative exclusively shows the Colhex phase in the broadest range of the series, presumably because the triphenylene columns are surrounded by a swollen periphery of molten chains and disorganized fluorene substituents.

## Mesomorphism of 2-Aryltriphenylenes M0-M5

The starting compound, triphenylen-2-yl triflate (MO), displays a Colhex phase from room temperature to 173 °C, that is, to a much higher temperatures than that for R<sub>6</sub>-TP. All five synthesized 2-aryltriphenylenes also exhibit Colhex phases over broad ranges, again up to temperatures well above that of R<sub>6</sub>-TP (Figure S2). The transition to the isotropic liquid is indeed delayed by the molecular extension of the mesogens; thus, the transitions are intermediate between those of the disubstituted analogues and R<sub>6</sub>-TP (see above and Figure 3). The broadening of the mesomorphic range actually comes from a significant decrease of the melting temperature: for instance, M4 melts at 84 °C on first heating, but the D16 analogue melts at 232 °C, and R<sub>6</sub>-TP at melts 68 °C. On cooling, none of the monosubstituted derivatives crystallize, and only two of them (M1 and M3) give rise to cold crystallization on the second heating. In these monosubstituted derivatives, the disorder introduced by the insertion of substituents between the aliphatic chains seems to be the dominant effect, and this explains the suppression of crystalline arrangements. In particular, the proportion of substituents appears too low to efficiently promote 3D arrangements through self-association processes.







Figure 3. Comparative phase diagram of selected compounds of the three series of TP derivatives bearing the same substituents.

#### Mesomorphism of 2,6,10-Triaryltriphenylenes T0-T4

The starting compound for the triaryl-TPs, TO, displays a plastic Col phase (Col<sub>x</sub>) with a high clearing temperature of 222 °C. In line with findings for derivatives with fewer alkyl chains, the transitions to the isotropic liquid phase are further delayed with regard to those of the disubstituted derivatives (Figure 3). For the alkyl-chain-terminated derivatives T1 and T2, the Col<sub>bex</sub> phase is maintained and even extended to higher clearing temperatures. The derivatives with side-attached phenylcarbazole and dimethylfluorene moieties, T3 and T4, only show crystalline phases with very high melting temperatures (271 and 239 °C, respectively, Figure S3) owing to the self-association of the macrocycles. Therefore, the proportion of aliphatic segments is not enough to counterbalance these bulky aryls and allow the appearance of mesophases. Therefore, in this series, the bulkiness of the substituents is very deleterious to mesomorphism but contrarily helps with the stabilization of the crystalline state.

#### Characterization of the Mesophases by SAXS

The mesomorphism of a selection of aryl-TP compounds (i.e., M**2**, D**8**, D**12**–D**14**, and **T2**) was investigated by SAXS. In particular, the assignments of  $Col_{hex}$  mesophases on the basis of the optical textures were confirmed by the sharp small-angle reflections and the wide-angle scattering profiles (Figure 4 and Table 4). In addition to the broad scattering maximum at ca. 4.5–5 Å owing to the liquidlike lateral distances between molten chains ( $h_{ch}$ ) and between the rigid moieties of the substituents ( $h_{ar}$ ), the wide-angle region contains a semidiffuse peak at ca. 3.5 Å for the triphenylene rings stacked into columns ( $h_{\pi}$ ). The columns then arrange at the nodes of a hexagonal lattice with a mixed periphery of chains and aromatic residues, as definitively demonstrated by the indexation of the small-angle reflections to (10), (11), (20), (21), (30), and (22). However, the number of detectable reflections is variable: three or four were

observed for the alkyl-chain-terminated substituents, that is, for columns extended by aromatic segments that are entirely enveloped by the chains. This architecture logically promotes sharp interfaces with the aliphatic periphery and, thus, the presence of higher-order reflections. On the contrary, substituents devoid of terminal chains just insert in the periphery without contributing to nanosegregation boundaries. Therefore, the interfaces are rather irregular for these systems, and, consequently, no or only one higher-order reflection is detectable in the SAXS patterns.



Figure 4. Representative SAXS profiles.

For any substituent, the aromatic segments and the chains connected to the triphenylene unit alternate in the column region around the triphenylene cores. This alternation of highand low-electronic-density segments gives rise to its own scattering signal identified as the broad small-angle peak, D (Figure 4). The width of the signal implies that the associated structure is limited to the local range, and the correlation lengths are between three and eight alternations. Consequently, the cylindrical symmetry of the long-range-correlated arrangement of columns is not affected, and the mesophase can still be considered as a classical Col<sub>hex</sub> phase with only an increased rough-



ness of the nanosegregation interfaces. As previously found for other closely related discotic systems,<sup>[57]</sup> the molecular organization in the mesophase appears to be ruled by the stacking of the mesogenic units, which prevails over the development of a regular structure between the substituents.

Nevertheless, substituents without terminal chains (D8) and especially those with large peripheral macrocycles (D13 and D14) perturb the columnar stacking, as indicated by the induction of crystalline phases and the restriction of the mesomorphism to small Colhex ranges (or even only monotropic, as for D13), whereas the ranges are enlarged by the alkyl-chain-terminated substituents in M2, D12, and T2 (see above). Within the mesomorphic domains, the perturbation of the stacking should lead to a modified relationship between the stacking distance at the local range,  $h_{\pi}$ , and the molecular-slice thickness of the columns  $h_{mol}$  (i.e., the ratio between the molecular volume,  $V_{\rm mol}$ , calculated from reference data, and the lattice area, S).<sup>[58]</sup> Both heights are similar with alkyl-chain termination and are associated with relatively large correlation lengths; therefore, the triphenylene rings form rather straight and untilted columns. In addition, the geometrical interface areas per chain are ca. 21 Å<sup>2</sup> at room temperature and 23 Å<sup>2</sup> for D12 at 150 °C, that is, in good agreement with the natural cross-section of the alkyl chains. This favorable packing geometry is consistent with the broad Colhex ranges, in contrast to substituents without terminal chains, which show  $h_{\rm mol}$  values significantly above  $h_{\pi}$  and areas per chain that exceed their space requirement. These findings confirm a perturbed stacking, which is clearly related to enhanced interactions between the substituents.

## Photophysical Properties of Aryltriphenylene Derivatives Bearing Chromophores – UV/Vis Absorption and Fluorescent Emission

As some of the discogens contain light-emitting functional units, we measured the UV/Vis absorption and fluorescent emission spectra of M**3**–M**5**, D**13**, D**15**, D**16**, T**3**, and **T4** in dilute THF solution ( $1 \times 10^{-6}$  m). The spectra are displayed in Figure 5, and the data are summarized in Table 5. The spectra display the absorptions of the TP core and the triphenylamine, carbazole, or fluorene units: all of these compounds have an absorption peak at  $\lambda = 284$  nm that originates from the absorption of the TP core; the other absorption bands at  $\lambda = 325$ –360 nm are characteristic bands of triarylamine, carbazole, and fluorine moieties. The absorptions are redshifted compared with that of pure hexakis(hexyloxy)TP. As the number of aryl substituents increases from one to three, the absorptions at  $\lambda = 300$ –400 nm also strengthen accordingly.

In solution, the maximum emissions occur in the  $\lambda = 350$ – 500 nm range with a peak at  $\lambda \approx 425$  nm, and the fluorescence intensities are enhanced with the increasing number of aryl groups; T**3** displays the strongest absorption and emission (Figure 5). The broad fluorescence emission bands of the target compounds at  $\lambda = 375$ –500 nm demonstrate that these compounds emit blue light and can be used as light-emitting discotic materials. To complete this investigation, the fluorescence of films of the corresponding compounds was also recorded.





Figure 5. UV/Vis and fluorescence spectra of R6-TP and aryl-TPs (in solution in THF,  $1.0 \times 10^{-6}$  M): (a) diphenylaminophenyl-TP, (b) carbazoylphenyl-TP, (c) dimethylfluorenyl-TP.

With a few exceptions (Table 5 and Supporting Information), no great differences could be observed between the fluorescence properties of the films and solutions. Indeed, almost identical spectral features were observed for the triarylamine- and carbazole-substituted TP compounds, whereas the largest divergence was recorded for the carbazole-2,7-distubstituted TP (D16), for which the emission was redshifted by ca. 20 nm. The films of all of the fluorene derivatives (M5, D15, and T4) show redshifted emissions compared with the solution emissions

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Table 5. Summary of the UV/Vis absorption and fluorescence spectroscopic properties of discogens in solutions and films.

	λ <sub>abs</sub> [nm]	Е [L mol <sup>-1</sup> cm <sup>-1</sup> ]	$\lambda_{ m ex}/\lambda_{ m em}$ [nm] (intensity) <sup>[a]</sup>	$\lambda_{ m ex}/\lambda_{ m em}$ [nm] <sup>[b]</sup>	Quantum efficiency $(\lambda_{ex}, nm)^{[c]}$
R <sub>6</sub> -TP	278	$1.3 \times 10^{5}$	278/383	-	-
	308	$2.6 \times 10^{4}$	$(8.4 \times 10^{5})$		
M <b>3</b>	282	$1.3 \times 10^{5}$	340/412	340/402, 418	0.47 (340)
	347	$5.5 \times 10^{4}$	(4.1 × 10 <sup>6</sup> )		
D <b>13</b>	296	$1.1 \times 10^{5}$	362/425	362/426	0.50 (362)
	346	$5.5 \times 10^{4}$	(9.5 × 10 <sup>6</sup> )		
T <b>3</b>	286	$1.3 \times 10^{5}$	348/411	345/410	0.67 (345)
	349	$1.3 \times 10^{5}$	(11.9 × 10 <sup>6</sup> )		
M <b>4</b>	283	$1.3 \times 10^{5}$	340/408	340/406	0.30 (340)
	341	$6.1 \times 10^{4}$	(1.6 × 10 <sup>6</sup> )		
D <b>16</b>	286	$1.5 \times 10^{5}$	343/408	343/427	0.42 (340)
	342	$4.4 \times 10^{4}$	(1.6 × 10 <sup>6</sup> )		
M <b>5</b>	288	$8.9 \times 10^{4}$	340/405	340/418	0.38 (340)
	340	$4.0 \times 10^{4}$	$(1.7 \times 10^{6})$		
D <b>15</b>	290	$8.7 \times 10^{4}$	340/422	340/452	0.24 (340)
	348	$5.7 \times 10^{4}$	$(1.7 \times 10^{6})$		
T <b>4</b>	316	$1.5 \times 10^{5}$	344/388, 404	345/418	0.22 (345)
	340	$1.2 \times 10^{5}$	$(5.7 \times 10^{6})$		
			5.8 × 10 <sup>6</sup> )		

[a] Solution fluorescence with excitation and emission peaks. [b] Film fluorescence with excitation and emission peaks. [c] The fluorescence absolute quantum efficiency was measured for THF solutions of the samples at a concentration of  $1 \times 10^{-6}$  mol/L.

(10–30 nm), probably because of the possible aggregation of the molecules. This aggregation has also been indicated by the decreased fluorescence quantum efficiencies caused by aggregation quenching (Table 5).

# Conclusions

Three new series of DLCs, namely, 2-aryl-, 2,7-diaryl-, and 2,6,10triaryl/alkoxytriphenylenes, have been designed and synthesized. The first application of Suzuki cross-coupling reactions between the readily accessible triflate derivatives 2-TfO-TP, 2,7-(TfO)<sub>2</sub>-TP, and 2,6,10-(TfO)<sub>3</sub>-TP (M0, D0, and T0) and various arylboronic acids resulted in the synthesis of the target discogens in good-to-excellent yields. The three precursory TP triflates (M0, D0, and T0) display Col<sub>hex</sub> mesophases or plastic Col<sub>x</sub> phases with high clearing temperatures. Among the 26 synthesized aryl-substituted triphenylene discogens, 22 exhibit a Colhex mesophase. The clearing temperatures increase with the increased number of aryl substituents. On cooling from the isotropic liquids, the discogens exhibit Colhex phases in broad temperature ranges down to room temperature. We have demonstrated for the first time that both electron-rich and electrondeficient aryl substituents on the TP core enhance the mesophase formation and stability. The successful combination of one, two, and three triarylamine, carbazole, and fluorene units to the central triphenylene core has resulted in functional DLCs, which have potential applications in the field of mesophase semiconducting materials with high charge-carrier transport. Furthermore, we expect that aryl triflates, as equivalent bromoarene synthons, will be used more widely as substrates for Pd-catalyzed cross-coupling reactions in the synthesis of liguid crystals or even other functional molecular materials.

# **Experimental Section**

Instruments: High-resolution mass spectra were measured with an IonSpec (now Varian) FTICR mass spectrometer (7.0 T) with MALDI or ESI. The <sup>1</sup>H NMR (400 MHz) spectra were recorded with a Varian UNITY INOVA-400 spectrometer, CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> were used as the solvents, and tetramethylsilane (TMS) was used as the internal standard. The phase transitions and enthalpy changes were measured by DSC with a TA-DSC Q100 instrument at heating and cooling rates of 10 °C/min under a N2 atmosphere. Liquid-crystalline optical textures were observed with an OLYMPUS BX41 polarizing optical microscope installed with a HCS302-GXY heating plate and an INSTEC STC200 temperature controller. The SAXS patterns were recorded with a Rigaku Smartlab (3) X-ray diffractometer with a TCU 110 temperature controller (±1 K) and a Cu-K radiation source ( $\lambda$  = 0.154 nm) operated at 40 kV with a scanning speed of 10 K/min. The fluorescence was measured with a HORIBA Fluoromax-4p spectrometer, and the quantum efficiencies were measured with a HORIBA-F-3029 integrating sphere.

**Chemicals:** The intermediate 2-hydroxy-3,6,7,10,11-pentakis(hexy-loxy)triphenylene<sup>[51]</sup> and 2,6,10-tri(hydroxy)-3,7,11-tris(hexyloxy)triphenylene<sup>[52]</sup> were prepared according to our previously reported methods (Schemes 1 and 3). All chemicals, including the arylboronic acids and solvents, were commercial products, which were used directly without further purification.

5-Bromo-2-methoxyphenol:<sup>[59]</sup> 5-Bromo-2-methoxybenzaldehyde (10 g, 50.5 mmol) in dichloromethane (30 mL) was cooled to 0 °C. Then, a solution of 3-chloroperoxybenzoic acid (m-CPBA, 11.9 g, 69.0 mmol, 85 %) in dichloromethane (100 mL) was added dropwise with stirring at this temperature, and the mixture was stirred at ambient temperature for 72 h. The white solid was removed by filtration, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (40 mL, 2 м) was added, and stirring was continued for another 2 h. The CH<sub>2</sub>Cl<sub>2</sub> was removed with a rotary evaporator, and the residue was dissolved in diethyl ether and washed with  $Na_2SO_3$  solution (3  $\times$  10 mL, 1  $\mbox{m})$  and a solution of NaHCO<sub>3</sub> (3  $\times$  10 mL); the organic phase was extracted with NaOH solution (3  $\times$  20 mL, 2 M). The pH of the aqueous phase was adjusted to 3–4 and it was extracted with diethyl ether (3  $\times$  20 mL), dried with MgSO<sub>4</sub>, and filtered. The solvent was removed by distillation, and the compound was purified by column chromatography (light petroleum/CH<sub>2</sub>Cl<sub>2</sub> 1:1) to yield a white solid (7.12 g, 81.7 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.06 (d, J = 2.40 Hz, 1 H, ArH), 6.96 (dd, J = 2.40, J = 8.40 Hz, 1 H, ArH), 6.71 (d, J = 8.40 Hz, 1 H, ArH), 5.67 (s, 1 H, OH), 3.87 (s, 3 H, OCH<sub>3</sub>) ppm.

**4-Bromo-2-hexyloxy-1-methoxybenzene:** A mixture of 5-bromo-2-methoxyphenol (2 g, 10.8 mmol),  $K_2CO_3$  (4.5 g, 32.3 mmol), and 1-bromohexane (1.94 g, 12.9 mmol) in *N*,*N*-dimethylformamide (DMF, 45 mL) was stirred at 80 °C for 24 h. The inorganic compounds were removed by filtration, the solvent was removed by distillation, and the product was collected by reduced pressure distillation to yield the product as a pale liquid (3.1 g, 88.5 %).

**3,3'-Di(hexyloxy)-4,4'-bis(methyloxy)biphenyl:** To magnesium chips (420 mg, 17.4 mmol) was slowly added a solution of 4-bromo-1-methoxy-2-(hexyloxy)benzene (9.5 g, 33.0 mmol) in THF (10 mL) under N<sub>2</sub>. The mixture was stirred under reflux until the magnesium chips disappeared. Then, it was cooled to room temperature, and Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (140.2 mg, 0.28 mmol) was added. The mixture was stirred at 45 °C for 12 h. Diluted hydrochloric acid was added dropwise until the mixture was acidic. The organic phase was extracted with ethyl acetate and dried with anhydrous MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure to afford the crude product, which was recrystallized from methanol to afford the biphenyl





as a white solid, yield 3.9 g (67.2 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 7.01 (dd, *J* = 0.80, 2.00 Hz, 1 H, ArH), 6.99 (dd, *J* = 0.80, 2.00 Hz, 1 H, ArH), 6.98 (s, 1 H, ArH), 6.97 (s, 1 H, ArH), 3.97 (t, *J* = 6.80 Hz, 4 H, OCH<sub>2</sub>), 3.83 (d, *J* = 0.80 Hz, 6 H, OCH<sub>3</sub>), 1.87–1.80 (m, 4 H, CH<sub>2</sub>), 1.47–1.41 (m, 4 H, CH<sub>2</sub>), 1.37–1.31 (m, 8 H, CH<sub>2</sub>), 0.92–0.88 (m, 6 H, CH<sub>3</sub>) ppm.

**2,7-Bis(methyloxy)-3,7,10,11-tetrakis(hexyloxy)triphenylene:** To a mixture of 4,4'-bis(methyloxy)-3,3'-bis(hexyloxy)-1,1'-biphenyl (10.0 g, 24.1 mmol) and 1,2-bis(hexyloxy)benzene (26.9 g, 96.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), FeCl<sub>3</sub> (30.6 g, 188.3 mmol) and a catalytic amount of H<sub>2</sub>SO<sub>4</sub> were added, and the mixture was stirred at room temperature for 2 h. Then, the mixture was quenched with cold methanol, and water was added. The organic layer was extracted and dried with anhydrous MgSO<sub>4</sub>. The mixture was purified by chromatography to yield the dimethoxytriphenylene derivative as a white solid, yield 9.51 g (57.1 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 7.85 (s, 4 H, ArH), 7.80 (s, 2 H, ArH), 4.24 (t, *J* = 6.40 Hz, 8 H, OCH<sub>2</sub>), 4.12 (s, 6 H, OCH<sub>3</sub>), 1.98–1.91 (m, 8 H, CH<sub>2</sub>), 1.62–1.54 (m, 8 H, CH<sub>2</sub>), 1.45–1.34 (m, 16 H, CH<sub>2</sub>), 0.94 (dd, *J* = 1.60, 7.20 Hz, 12 H, CH<sub>3</sub>) ppm.

2,7-Dihydroxy-3,6,10,11-tetrakis(hexyloxy)triphenylene: Lithium (small particles, 3.1 g, 435.5 mmol) was added to a solution of PPh<sub>3</sub> (45.73 g, 174.2 mmol) in dry THF (100 mL). The mixture was stirred for 1 h, and the Li disappeared; tBuCl (16.13 g, 174.2 mmol) was added in three portions, and the mixture was heated under reflux for 1 h. 2,7-Dimethoxy-3,6,10,11-tetrakis(hexyloxy)triphenylene (12 g, 17.42 mmol) was added under a nitrogen atmosphere, and the mixture was stirred for 12 h at 70 °C. Then, the mixture was poured carefully into ice water, acidified with 10 % HCl solution (100 mL), and extracted with diethyl ether. The organic layer was dried with magnesium sulfate and filtered, and the organic solvent was removed under vacuum. Purification through silica gel column chromatography afforded the product as a white solid, yield 9.32 g (80.9 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 7.96 (s, 2 H, ArH), 7.81 (s, 2 H, ArH), 7.73 (s, 1 H, ArH), 7.71 (s, 1 H, ArH), 5.89 (s, 2 H, OH), 4.28 (dd, J = 6.40, 12.80 Hz, 4 H, OCH<sub>2</sub>), 4.20 (t, J = 6.40 Hz, 4 H, OCH<sub>2</sub>), 1.97-1.90 (m, 8 H, CH<sub>2</sub>), 1.58-1.52 (m, 8 H, CH<sub>2</sub>), 1.42-1.38 (m, 16 H, CH<sub>2</sub>), 0.96–0.92 (m, 12 H, CH<sub>3</sub>) ppm.

**3,6,10,11-Tetra(hexyloxy)triphenylene-2,7-diyl Triflate (D0):** To a stirred solution of 2,7-dihydroxy-3,6,10,11-tetra(hexyloxy)triphenylene (1.0 g, 1.51 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added triethylamine (1.28 mL, 12.1 mmol) at room temperature under an argon atmosphere. The mixture was cooled to -40 °C, and Tf<sub>2</sub>O (1.28 mL, 3.02 mmol) was added. The mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica column chromatography (dichloromethane/petroleum ether 1:2) to yield D**0** as a gray solid (1.26 g, 90.6 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.21 (s, 2 H, ArH), 7.88 (s, 2 H, ArH), 7.68 (s, 2 H, ArH), 4.28 (t, *J* = 6.4 Hz, 4 H, OCH<sub>2</sub>), 4.23 (t, *J* = 6.4 Hz, 4 H, OCH<sub>2</sub>), 1.99–1.93 (m, 8 H, CH<sub>2</sub>), 1.62–1.56 (m, 8 H, CH<sub>2</sub>), 1.45–1.37 (m, 16 H), 0.96–0.93 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>44</sub>H<sub>58</sub>F<sub>6</sub>O<sub>10</sub>S<sub>2</sub> [M]<sup>+</sup> 924.34; found 924.3375.

**D1:** Under argon, D**0** (100 mg, 0.11 mmol), phenylboronic acid (30.8 mg, 0.262 mmol),  $K_2CO_3$  (354.0 mg, 2.67 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (15.8 mg, 0.01 mmol) were added to a reaction tube. Degassed water (3 mL) and THF (10 mL) were injected into the reaction mixture. The mixture was stirred at 80 °C for 24 h. Then, it was cooled, extracted with EtOAc and dried with MgSO<sub>4</sub>. The organic solvent was removed by distillation, and the residue was purified by silica gel column chromatography (light petroleum/CH<sub>2</sub>Cl<sub>2</sub> 1:1) to yield D**1** as a white solid (68.5 mg, 80.7 %). The other compounds of the

series, D2–D17, were all prepared accordingly. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.39 (s, 2 H, ArH), 7.99 (s, 2 H, ArH), 7.93 (s, 2 H, ArH), 7.74 (d, J = 8.00 Hz, 4 H), 7.51 (t, J = 7.60 Hz, 4 H), 7.42 (t, J = 7.20 Hz, 2 H), 4.21 (dd, J = 6.40, J = 15.60 Hz, 8 H, OCH<sub>2</sub>), 1.95–1.80 (m, 8 H, CH<sub>2</sub>), 1.51–1.47 (m, 8 H, CH<sub>2</sub>), 1.39–1.32 (m, 18 H, CH<sub>2</sub>), 0.93–0.89 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>54</sub>H<sub>68</sub>O<sub>4</sub> [M]<sup>+</sup> 780.51; found 780.5115.

**D2:** The coupling of D**0** (100 mg, 0.11 mmol) with (thiophen-3-yl)boronic acid (33.4 mg, 0.262 mmol) resulted in D**2** (67.1 mg, 76.9 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.53 (s, 2 H, ArH), 7.94 (s, 2 H, ArH), 7.93 (s, 2 H, ArH), 7.80 (d, *J* = 4.00 Hz, 2 H), 7.65 (d, *J* = 8.00 Hz, 2 H), 7.44 (dd, *J* = 2.80, 2.00 Hz, 2 H), 4.27–4.21 (m, 8 H, OCH<sub>2</sub>), 1.97–1.90 (m, 8 H, CH<sub>2</sub>), 1.61–1.52 (m, 8 H, CH<sub>2</sub>), 1.41–1.37 (m, 16 H, CH<sub>2</sub>), 0.93 (t, *J* = 8.00 Hz, 12 H, OCH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>50</sub>H<sub>64</sub>O<sub>4</sub>S<sub>2</sub> [M]<sup>+</sup> 792.42; found 792.4246.

**D3:** The coupling of D**0** (50 mg, 0.054 mmol) with (naphthalen-2yl)boronic acid (22.53 mg, 0.131 mmol) resulted in D**3** (27.9 mg, 58.3 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.50 (s, 2 H, ArH), 8.18 (s, 2 H, ArH), 8.05 (s, 2 H, ArH), 7.97–7.92 (m, 8 H, ArH), 7.90 (s, 1 H, ArH), 7.88 (s, 1 H, ArH), 7.54 (t, *J* = 4.00 Hz, 4 H, ArH), 4.25–4.19 (m, 8 H, OCH<sub>2</sub>), 1.94–1.80 (m, 8 H, CH<sub>2</sub>), 1.55–1.46 (m, 8 H, CH<sub>2</sub>), 1.36– 1.30 (m, 16 H, CH<sub>2</sub>), 0.91–0.86 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>62</sub>H<sub>72</sub>O<sub>4</sub> [M]<sup>+</sup> 880.54; found 880.5428.

**D4:** The coupling of D**0** (50 mg, 0.054 mmol) with (4-cyanophenyl)boronic acid (19.2 mg, 0.131 mmol) resulted in D**4** (33.5 mg, 74.6 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.35 (s, 2 H, ArH), 7.98 (s, 2 H, ArH), 7.90 (s, 2 H, ArH), 7.85 (d, *J* = 8.40 Hz, 4 H, ArH), 7.80 (d, *J* = 8.40 Hz, 4 H, ArH), 4.25–4.19 (m, 8 H, OCH<sub>2</sub>), 1.96–1.81 (m, 8 H, CH<sub>2</sub>), 1.56–1.43 (m, 8 H, CH<sub>2</sub>), 1.38–1.33 (m, 16 H, CH<sub>2</sub>), 0.93–0.89 (m, 8 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>56</sub>H<sub>66</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup> 830.50; found 830.5018.

**D5:** The coupling of D**0** (50 mg, 0.054 mmol) with (4-fluorophenyl)boronic acid (18.33 mg, 0.131 mmol) resulted in **D5** (28.5 mg, 64.2 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.34 (s, 2 H, ArH), 7.96 (s, 2 H, ArH), 7.92 (s, 2 H, ArH), 7.69 (dd, *J* = 5.60, 2.80 Hz, 4 H, ArH), 7.19 (t, *J* = 8.80 Hz, 4 H, ArH), 4.22–4.20 (m, 8 H, OCH<sub>2</sub>), 1.95–1.80 (m, 8 H, CH<sub>2</sub>), 1.57–1.47 (m, 8 H, CH<sub>2</sub>), 1.38–1.33 (m, 16 H, CH<sub>2</sub>), 0.93–0.89 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>54</sub>H<sub>66</sub>F<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup> 816.49; found 816.4928.

**D6:** The coupling of D**0** (50 mg, 0.054 mmol) with (3,4-difluorophenyl)boronic acid (20.69 mg, 0.131 mmol) resulted in D**6** (39.2 mg, 84.6 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.34 (s, 2 H, ArH), 7.94 (s, 2 H, ArH), 7.90 (s, 2 H, ArH), 7.30–7.27 (m, 2 H, ArH), 7.24 (s, 2 H, ArH), 6.89–6.84 (m, 2 H, ArH), 4.23 (t, *J* = 6.40 Hz, 8 H, OCH<sub>2</sub>), 1.97–1.83 (m, 8 H, CH<sub>2</sub>), 1.61–1.51 (m, 8 H, CH<sub>2</sub>), 1.40–1.34 (m, 16 H, CH<sub>2</sub>), 0.94–0.89 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>54</sub>H<sub>64</sub>F<sub>4</sub>O<sub>4</sub> [M]<sup>+</sup> 852.47; found 852.4738.

**D7:** The coupling of D**0** (50 mg, 0.054 mmol) with (3,5-difluorophenyl)boronic acid (20.69 mg, 0.131 mmol) resulted in D**7** (40.5 mg, 87.4 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.32 (s, 2 H, ArH), 7.95 (s, 2 H, ArH), 7.90 (s, 2 H, ArH), 7.60–7.54 (m, 2 H, ArH), 7.44–7.41 (m, 2 H, ArH), 7.31–7.25 (m, 2 H, ArH), 4.24–4.21 (m, 8 H, OCH<sub>2</sub>), 1.96–1.82 (m, 8 H, CH<sub>2</sub>), 1.55–1.46 (m, 8 H, ArH), 1.39–1.34 (m, 16 H, CH<sub>2</sub>), 0.94–0.89 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>54</sub>H<sub>64</sub>F<sub>4</sub>O<sub>4</sub> [M]<sup>+</sup> 852.47; found 852.4739.

**D8:** The coupling of D**0** (50 mg, 0.054 mmol) with (3,4,5-trifluorophenyl)boronic acid (23.8 mg, 0.131 mmol) resulted in D**8** (41.1 mg, 85.1 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.29 (s, 2 H, ArH), 7.93 (s, 2 H, ArH), 7.88 (s, 2 H, ArH), 7.36 (t, *J* = 7.20 Hz, 2 H, ArH), 4.23 (t, *J* = 6.40 Hz, 8 H, OCH<sub>2</sub>), 1.96–1.85 (m, 8 H, CH<sub>2</sub>), 1.56–1.49 (m, 8





H, CH<sub>2</sub>), 1.40–1.36 (m, 16 H, CH<sub>2</sub>), 0.92 (t, J = 6.40 Hz, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>54</sub>H<sub>62</sub>F<sub>6</sub>O<sub>4</sub> [M]<sup>+</sup> 888.46; found 888.4548.

**D9:** The coupling of D**0** (100 mg, 0.11 mmol) with (3,4-dichlorophenyl)boronic acid (50.4 mg, 0.261 mmol) resulted in D**9** (66.4 mg, 66.7 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.31 (s, 2 H, ArH), 7.92 (s, 2 H, ArH), 7.89 (s, 2 H, ArH), 7.84 (s, 2 H, ArH), 7.55 (t, *J* = 8.00 Hz, 4 H, ArH), 4.21 (t, *J* = 6.40 Hz, 8 H, OCH<sub>2</sub>), 1.96–1.82 (m, 8 H, CH<sub>2</sub>), 1.60–1.51 (m, 8 H, CH<sub>2</sub>), 1.39–1.35 (m, 16 H, CH<sub>2</sub>), 0.92 (t, *J* = 6.80 Hz, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>54</sub>H<sub>64</sub>Cl<sub>4</sub>O<sub>4</sub> [M]<sup>+</sup> 916.36; found 916.3556.

**D10:** The coupling of D**0** (30 mg, 0.033 mmol) with (4-pentyl-phenyl)boronic acid (15.0 mg, 0.078 mmol) resulted in D**10** (23.5 mg, 77.3 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.39 (s, 2 H, ArH), 7.97 (s, 2 H, ArH), 7.93 (s, 2 H, ArH), 7.66 (d, *J* = 8.00 Hz, 4 H, ArH), 7.33 (d, *J* = 8.00 Hz, 4 H, ArH), 4.20 (d, *J* = 4.00, 8 Hz, OCH<sub>2</sub>), 2.71 (t, *J* = 8.00 Hz, 4 H, CH<sub>2</sub>), 1.53–1.48 (m, 12 H,CH<sub>2</sub>), 1.41–1.34 (m, 24 H, CH<sub>2</sub>), 0.95–0.90 (m, 18 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>64</sub>H<sub>88</sub>O<sub>4</sub> [M]<sup>+</sup> 920.67; found 920.6679.

**D11:** The coupling of D**0** (50 mg, 0.054 mmol) with (3,4-dimethoxyphenyl)boronic acid (23.9 mg, 0.131 mmol) resulted in D**11** (38.7 mg, 79.1 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.38 (s, 2 H, ArH), 7.98 (s, 2 H, ArH), 7.94 (s, 2 H, ArH), 7.34 (d, *J* = 2.00 Hz, 2 H, ArH), 7.28 (d, *J* = 4.00 Hz, 1 H, ArH), 7.26 (d, *J* = 2.00 Hz, 1 H, ArH), 7.04 (s, 1 H, ArH), 7.02 (s, 1 H, ArH), 4.23–4.18 (m, 8 H, OCH<sub>2</sub>), 3.98 (d, *J* = 5.2.0 Hz, 12 H, OCH<sub>3</sub>), 1.94–1.84 (m, 8 H, CH<sub>2</sub>), 1.58–1.49 (m, 8 H, CH<sub>2</sub>), 1.38–1.33 (m, 16 H, CH<sub>2</sub>), 0.93–0.88 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>58</sub>H<sub>76</sub>O<sub>8</sub> [M]<sup>+</sup> 900.55; found 900.5538.

**D12:** The coupling of D**0** (50 mg, 0.054 mmol) with [3,4-bis(pentyloxy)phenyl]boronic acid (38.34 mg, 0.131 mmol) resulted in D**12** (40.5 mg, 87.4 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.37 (s, 2 H, ArH), 7.96 (s, 2 H, ArH), 7.93 (s, 2 H, ArH), 7.34 (d, *J* = 4.00 Hz, 2 H, ArH), 7.25 (d, *J* = 4.00 Hz, 1 H, ArH), 7.23 (d, *J* = 4.00 Hz, 1 H, ArH), 7.03 (s, 1 H, ArH), 7.01 (s, 2 H, ArH), 4.20 (dd, *J* = 8.00, 4.00 Hz, 8 H, OCH<sub>2</sub>), 4.11–4.07 (m, 8 H, OCH<sub>2</sub>), 1.95–1.82 (m, 16 H, CH<sub>2</sub>), 1.55– 1.33 (m, 40 H, CH<sub>2</sub>), 0.98–0.90 (m, 24 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>74</sub>H<sub>108</sub>O<sub>8</sub> [M]<sup>+</sup> 1124.80; found 1124.8045.

**D13:** The coupling of D**0** (50 mg, 0.054 mmol) with [4-(diphenyl-amino)phenyl]boronic acid (37.9 mg, 0.131 mmol) resulted in D**13** (37 mg, 61.1 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS, 400 MHz):  $\delta$  = 8.43 (s, 2 H, ArH), 7.82 (s, 2 H, ArH), 7.77 (s, 2 H, ArH), 7.41 (d, J = 2.00 Hz, 2 H, ArH), 7.39 (d, J = 2.00 Hz, 2 H, ArH), 6.88 (d, J = 2.00 Hz, 2 H, ArH), 6.87 (d, J = 2.00 Hz, 2 H, ArH), 6.77 (dd, J = 1.20, 8.80 Hz, 8 H, ArH), 6.66 (t, J = 7.20 Hz, 8 H, ArH), 6.46 (t, J = 7.20 Hz, 4 H, ArH), 3.62 (t, J = 6.40 Hz, 4 H, OCH<sub>2</sub>), 3.45 (t, J = 6.40 Hz, 4 H, OCH<sub>2</sub>), 1.35–1.23 (m, 8 H, CH<sub>2</sub>), 1.12–1.06 (m, 4 H, CH<sub>2</sub>), 1.04–0.96 (m, 4 H, CH<sub>2</sub>), 0.94–0.79 (m, 16 H, CH<sub>2</sub>), 0.52–0.46 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>78</sub>H<sub>86</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup> 1114.66; found 1114.6588.

**D14:** The coupling of D**0** (100 mg, 0.11 mmol) with (9-phenyl-9*H*-carbazol-3-yl)boronic acid (74.9 mg, 0.261 mmol) resulted in D**14** (65.9 mg, 58.7 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.53 (s, 2 H, ArH), 8.21 (s, 2 H, ArH), 8.19 (s, 2 H, ArH), 8.08 (s, 2 H, ArH), 8.01 (t, *J* = 9.60 Hz, 6 H, ArH), 7.73 (d, *J* = 8.40 Hz, 4 H, ArH), 7.59 (t, *J* = 8.40 Hz, 4 H, ArH), 7.49–7.45 (m, 4 H, ArH), 7.33 (t, *J* = 7.20 Hz, 4 H, ArH), 4.34–4.26 (m, 8 H, OCH<sub>2</sub>), 1.99–1.90 (m, 8 H, CH<sub>2</sub>), 1.59–1.54 (m, 8 H, CH<sub>2</sub>), 1.43–1.37 (m, 16 H, CH<sub>2</sub>), 0.92 (t, *J* = 7.20 Hz, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>78</sub>H<sub>82</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup> 1110.63; found 1110.6275.

**D15:** The coupling of D**0** (100 mg, 0.11 mmol) with (9,9-dimethyl-9*H*-fluoren-2-yl)boronic acid (74.9 mg, 0.261 mmol) resulted in D**15** (53.5 mg, 48.4 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS, 400 MHz):  $\delta$  = 8.92 (s, 2 H, ArH), 8.39 (s, 2 H, ArH), 8.23 (s, 2 H, ArH), 8.09 (s, 2 H, ArH), 7.89 (d,

J = 7.6 Hz, 2 H, ArH), 7.79 (d, J = 8.0 Hz, 2 H, ArH), 7.67 (d, J = 6.8 Hz, 2 H, ArH), 7.30 (d, J = 7.6 Hz, 2 H, ArH), 7.24 (t, J = 6.8 Hz, 4 H, ArH), 4.10 (t, J = 6.0 Hz, 4 H, OCH<sub>2</sub>), 3.93 (t, J = 6.0 Hz, 4 H, OCH<sub>2</sub>), 1.78–1.65 (m, 8 H, CH<sub>2</sub>), 1.54 (s, 12 H, CH<sub>3</sub>), 1.51–1.36 (m, 8 H, CH<sub>2</sub>), 1.31–1.17 (m, 16 H, CH<sub>2</sub>), 0.89 (t, J = 6.4 Hz, 6 H, CH<sub>3</sub>), 0.84 (t, J = 6.4 Hz, 6 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>72</sub>H<sub>84</sub>O<sub>4</sub> [M]<sup>+</sup> 1012.64; found 1012.6372.

**D16:** The coupling of D**0** (100 mg, 0.11 mmol) with [4-(9*H*-carbazol-9-yl)phenyl]boronic acid (74.9 mg, 0.261 mmol) resulted in D**16** (81.2 mg, 66.4 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.54 (s, 2 H, ArH), 8.21 (d, *J* = 7.60 Hz, 4 H, ArH), 8.08 (s, 2 H, ArH), 8.04 (s, 2 H, ArH), 8.01 (d, *J* = 2.00 Hz, 2 H, ArH), 7.99 (d, *J* = 2.00 Hz, 2 H, ArH), 7.73 (d, *J* = 2.00 Hz, 2 H, ArH), 7.72 (d, *J* = 2.00 Hz, 2 H, ArH), 7.60 (d, *J* = 8.00 Hz, 4 H, ArH),7.47 (t, *J* = 8.00 Hz, 4 H, ArH), 7.34 (t, 4 H, ArH), 4.35–4.26 (m, 8 H, OCH<sub>2</sub>), 2.00–1.91 (m, 8 H, CH<sub>2</sub>), 1.60–1.53 (m, 8 H, CH<sub>2</sub>), 1.45–1.35 (m, 16 H, CH<sub>2</sub>), 0.94–0.91 (m, 12 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>78</sub>H<sub>82</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup> 1110.63; found 1110.6273.

**D17:** The coupling of D**0** (100 mg, 0.11 mmol) with [3-(9*H*-carbazol-9-yl)phenyl]boronic acid (74.9 mg, 0.261 mmol) resulted in D**17** (59.6 mg, 48.8 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.47 (s, 2 H, ArH), 8.18 (d, *J* = 7.60 Hz, 4 H, ArH), 8.00 (t, *J* = 2.00 Hz, 4 H, ArH), 7.94 (s, 2 H, ArH), 7.83 (s, 1 H, ArH), 7.81 (s, 1 H, ArH), 7.74 (d, *J* = 8.00 Hz, 2 H, ArH), 7.60 (t, *J* = 8.00 Hz, 4 H, ArH), 7.56 (s, 2 H, ArH), 7.43 (t, *J* = 8.00 Hz, 4 H, ArH), 7.31 (t, *J* = 7.60 Hz, 4 H, ArH), 7.43 (t, *J* = 8.00 Hz, 4 H, ArH), 7.31 (t, *J* = 7.60 Hz, 4 H, ArH), 4.28-4.20 (m, 8 H, OCH<sub>2</sub>), 1.95–1.85 (m, 8 H, CH<sub>2</sub>), 1.45–1.36 (m, 16 H, CH<sub>2</sub>), 1.29–1.17 (m, 8 H, CH<sub>2</sub>), 0.90 (t, *J* = 7.20 Hz, 6 H, CH<sub>3</sub>), 0.82 (t, *J* = 7.20 Hz, 6 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>78</sub>H<sub>82</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup> 1110.63; found 1110.6272.

**3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-yl Triflate (M0):** To a solution of triphenylen-2-ol (2.0 g, 2.68 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) was added triethylamine (2.23 mL) at room temperature under argon. The mixture was stirred for 10 min, and Tf<sub>2</sub>O (2.3 mL, 13.4 mmol) was added at -40 °C. The mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (light petroleum/CH<sub>2</sub>Cl<sub>2</sub> 1:1) to afford the triphenylen-2-yl triflate as a gray solid, yield 1.96 g (83.4 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.18 (s, 1 H, ArH), 7.85 (s, 1 H, ArH), 7.80 (s, 1 H, ArH), 7.79 (s, 2 H, ArH), 7.69 (s, 1 H, ArH), 4.28-4.21 (m, 10 H, OCH<sub>2</sub>), 1.99-1.91 (m, 10 H, CH<sub>2</sub>), 1.60-1.59 (m, 10 H, CH<sub>2</sub>), 1.45-1.37 (m, 20 H, CH<sub>2</sub>), 0.94 (t, *J* = 6.8 Hz, 15 H, CH<sub>3</sub>) ppm. HRMS: calcd. for C<sub>49</sub>H<sub>71</sub>F<sub>3</sub>O<sub>8</sub>S [M]<sup>+</sup> 876.48; found 876.4819.

M1: Under argon, M0 (150 mg, 0.171 mmol), (4-pentylphenyl)boronic acid (39.4 mg, 0.205 mmol), K<sub>2</sub>CO<sub>3</sub> (354.0 mg, 2.67 mmol), and  $Pd(PPh_3)_4$  (15.8 mg, 0.0574 mmol) were added to a reaction tube. Degassed water (3 mL) and THF (10 mL) were injected into the reaction mixture. The mixture was stirred at 80 °C for 24 h, cooled, extracted with EtOAc, and dried with MgSO<sub>4</sub>. The organic solvent was removed by distillation, and the residue was purified by silica gel column chromatography (light petroleum/CH<sub>2</sub>Cl<sub>2</sub> 1:1) to afford M1 as a white solid (140.3 mg, 93.6 %). The other compounds of the series, M2-M5, were all prepared accordingly. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.37 (s, 1 H, ArH), 7.93 (s, 2 H, ArH), 7.84 (s, 3 H, ArH), 7.65 (d, J = 8 Hz, 1 H, ArH), 7.32 (d, J = 8 Hz, 2 H, ArH), 4.25-4.19 (m, 10 H, OCH<sub>2</sub>), 2.70 (t, J = 7.6 Hz, 2 H, CH<sub>2</sub>), 1.99-1.90 (m, 8 H, CH<sub>2</sub>), 1.87-1.80 (m, 2 H, CH<sub>2</sub>), 1.75-1.67 (m, 2 H, CH<sub>2</sub>), 1.63-11.47 (m, 10 H, CH2), 1.41-1.25 (m, 26 H, CH2), 0.96-0.87 (m, 18 H, CH<sub>2</sub>) ppm. HRMS (ESI): calcd. for  $C_{59}H_{86}O_5$  [M]<sup>+</sup> 874.65; found 874.6420.

**M2:** The coupling of M**0** (150 mg, 0.171 mmol) with [3,4-bis(pentyloxy)phenyl]boronic acid (60.3 mg, 0.205 mmol) resulted in M**2** 





(152.1 mg, 91 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.35 (s, 1 H, ArH), 7.93 (s, 2 H, ArH), 7.86 (d, *J* = 8 Hz, 3 H, ArH), 7.32 (d, *J* = 2, 0.5 Hz), 7.21 (dd, *J* = 1.6, *J* = 8.4 Hz, 1 H, ArH), 7.02 (d, *J* = 8.4 Hz, 1 H, ArH), 4.27–4.17 (m, 10 H, OCH<sub>2</sub>), 4.11–4.06 (m, 4 H, OCH<sub>2</sub>), 1.99–1.81 (m, 16 H, CH<sub>2</sub>), 1.63–1.32 (m, 45 H, CH<sub>2</sub>), 0.98–0.86 (m, 21 H, CH<sub>2</sub>) ppm. HRMS (ESI): calcd. for C<sub>64</sub>H<sub>96</sub>O<sub>7</sub> [M]<sup>+</sup> 976.72; found 976.7035.

**M3:** The coupling of M**0** (50 mg, 0.057 mmol) with [4-(diphenylamino)phenyl]boronic acid (19.8 mg, 0.068 mmol) resulted in M**3** (36.8 mg, 72 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.38 (s, 1 H, ArH), 7.95 (s, 1 H, ArH), 7.93 (s, 1 H, ArH), 7.87 (s, 1 H, ArH), 7.84 (s, 2 H, ArH), 7.64 (d, *J* = 8.4 Hz, 2 H, ArH), 7.29 (t, *J* = 7.6 Hz, 4 H, ArH), 7.20 (d, *J* = 8.0 Hz, 6 H, ArH), 7.05 (t, *J* = 7.2 Hz, 2 H, ArH), 4.23 (dd, *J* = 7.6, *J* = 14.4 Hz, 10 H, OCH<sub>2</sub>), 1.98–1.82 (m, 10 H, CH<sub>2</sub>), 1.63–1.48 (m, 10 H, CH<sub>2</sub>), 1.41–1.33 (m, 20 H, CH<sub>2</sub>), 0.96–0.88 (m, 15 H, CH<sub>2</sub>) ppm. HRMS (ESI): calcd. for C<sub>66</sub>H<sub>85</sub>NO<sub>5</sub> [M]<sup>+</sup> 971.64; found 971.6428.

**M4:** The coupling of M**0** (150 mg, 0.171 mmol) with [4-(9*H*-carbazol-9-yl)phenyl]boronic acid (58.9 mg, 0.205 mmol) resulted in M**4** (142.5 mg, 93.1 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS, 400 MHz):  $\delta$  = 8.48 (s, 1 H, ArH), 8.20 (s, 1 H, ArH), 8.18 (s, 1 H, ArH), 8.00 (s, 1 H, ArH), 7.96 (d, J = 1.2 Hz, 2 H, ArH), 7.95 (d, J = 5.6 Hz, 2 H, ArH), 7.87 (s, 2 H, ArH), 7.70 (d, J = 4.4 Hz, 2 H, ArH), 7.58 (d, J = 8.0 Hz, 2 H, ArH), 7.46 (t, J = 8.0 Hz, 2 H, ArH), 7.32 (t, J = 7.6 Hz, 2 H, ArH), 4.29–4.24 (m, 10 H, OCH<sub>2</sub>), 2.01–1.87 (m, 10 H, CH<sub>2</sub>), 1.64–1.51 (m, 10 H, CH<sub>2</sub>), 1.47– 1.34 (m, 20 H, CH<sub>2</sub>), 0.97–0.89 (m, 15 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>66</sub>H<sub>83</sub>NO<sub>5</sub> [M]<sup>+</sup> 969.63; found 969.6268.

**M5:** The coupling of M**0** (50 mg, 0.057 mmol) with (9,9-dimethyl-9*H*-fluoren-2-yl)boronic acid (16.3 mg, 0.068 mmol) resulted in M**5** (31.6 mg, 60.1 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS, 400 MHz):  $\delta$  = 8.90 (s, 1 H, ArH), 8.35 (s, 1 H, ArH), 8.25 (d, *J* = 3.6 Hz, 2 H, ArH), 8.20 (d, *J* = 4.0 Hz, 2 H, ArH), 8.08 (s, 1 H, ArH), 7.89 (d, *J* = 8.0 Hz, 1 H, ArH), 7.79 (d, *J* = 7.6 Hz, 1 H, ArH), 7.67 (d, *J* = 7.6 Hz, 1 H, ArH), 7.29–7.21 (m, 3 H, ArH), 4.18 (t, *J* = 6.4 Hz, 2 H, OCH<sub>2</sub>), 4.14–4.08 (m, 4 H, OCH<sub>2</sub>), 4.02 (t, *J* = 6.4 Hz, 2 H, OCH<sub>2</sub>), 3.93 (t, *J* = 6.4 Hz, 2 H, OCH<sub>2</sub>), 1.90–1.80 (m, 6 H, CH<sub>2</sub>), 1.79–1.72 (m, 2 H, CH<sub>2</sub>), 1.68–1.63 (m, 2 H, CH<sub>2</sub>), 1.59–1.56 (m, 2 H, CH<sub>2</sub>), 1.53 (s, 6 H, CH<sub>3</sub>), 1.49–1.42 (m, 4 H, CH<sub>2</sub>), 1.40–1.16 (m, 24 H, CH<sub>2</sub>), 0.91 (dd, *J* = 12, 5.6 Hz, 12 H, CH<sub>3</sub>), 0.83 (t, *J* = 6.4 Hz, 3 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>63</sub>H<sub>84</sub>O<sub>5</sub> [M]<sup>+</sup> 920.63; found 920.6318.

**3,7,11-Tris(hexyloxy)triphenylene-2,6,10-triyl Triflate (T0):** To a solution of TP-2,6,10-triol (600 mg, 1.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added triethylamine (0.86 mL, 8.32 mmol) at room temperature under an argon atmosphere. The mixture was stirred for 10 min, and Tf<sub>2</sub>O (2.63 mL, 15.6 mmol) was added at -40 °C. The mixture was warmed to room temperature and stirred for 6 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuum. The residue was purified by column chromatography (light petroleum/CH<sub>2</sub>Cl<sub>2</sub> 1:3) to yield the product T**0** as a white solid, yield 900.4 mg (93.3 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.01 (t, *J* = 5.6 Hz, 3 H, ArH), 7.52 (t, *J* = 7.00 Hz, 3 H, ArH), 4.24 (t, *J* = 6.4 Hz, 6 H, OCH<sub>2</sub>), 2.01–1.93 (m, 6 H, CH<sub>2</sub>), 1.62–1.54 (m, 8 H, CH<sub>2</sub>), 1.44–1.40 (m, 12 H, CH<sub>2</sub>), 0.96 (t, *J* = 7.2 Hz, 9 H, CH<sub>3</sub>) ppm.

**T1:** The coupling of TP-2,6,10-triyl triflate (50 mg, 0.054 mmol) with (4-pentylphenyl)boronic acid (37.3 mg, 0.194 mmol) resulted in **T1** (40.8 mg, 78.2 %). The other compounds of the series, **T2**–**T4**, were prepared accordingly. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta = 8.46$  (s, 3 H, ArH), 7.97 (s, 3 H, ArH), 7.67 (d, J = 7.6 Hz, 6 H, ArH), 7.33 (d, J = 8.00 Hz, 6 H, ArH), 4.17 (t, J = 6.4 Hz, 6 H, OCH<sub>2</sub>), 2.70 (t, J = 7.6 Hz, 6 H, CH<sub>2</sub>), 1.86–1.79 (m, 6 H, CH<sub>2</sub>), 1.75–1.68 (m, 6 H, CH<sub>2</sub>), 1.42–1.39 (m, 12 H, CH<sub>2</sub>), 1.34–1.31 (m, 10 H, CH<sub>2</sub>), 0.92 (dd, J = 8.4,

J= 15.2 Hz, 18 H, CH\_3) ppm. HRMS (ESI): calcd. for  $C_{69}H_{90}O_3~[M]^+$  966.69; found 966.6888.

**T2:** The coupling of **T0** (50 mg, 0.054 mmol) with [3,4-bis(pentyloxy)phenyl]boronic acid (57.2 mg, 0.194 mmol) resulted in **T2** (46.1 mg, 67.1 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.45 (s, 3 H, ArH), 7.98 (s, 3 H, ArH), 7.34 (s, 3 H, ArH), 7.25 (d, *J* = 8.4 Hz, 3 H, ArH), 7.04 (d, *J* = 8.4 Hz, 3 H, ArH), 4.18 (t, *J* = 6.4 Hz, OCH<sub>2</sub>), 4.10 (dd, *J* = 6.4, *J* = 4.4 Hz, 12 H, OCH<sub>2</sub>), 1.93–1.80 (m, 18 H, CH<sub>2</sub>), 1.57– 1.38 (m, 34 H, CH<sub>2</sub>), 1.33–1.32 (m, 12 H, CH<sub>2</sub>), 0.98–0.89 (m, 27 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>84</sub>H<sub>120</sub>O<sub>9</sub> [M]<sup>+</sup> 1272.89; found 1272.8929.

**T3:** The coupling of **T0** (100 mg, 0.18 mmol) with [4-(diphenyl-amino)phenyl]boronic acid (112.4 mg, 0.389 mmol) resulted in **T3** (114.9 mg, 84.5 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 400 MHz):  $\delta$  = 8.52 (s, 3 H, ArH), 7.80 (s, 3 H, ArH), 7.43 (d, *J* = 8.4 Hz, 6 H, ArH), 8.91 (d, *J* = 8.8 Hz, 6 H, ArH), 6.79 (d, *J* = 5.6 Hz, 12 H, ArH), 6.68 (t, *J* = 7.6 Hz, 12 H, ArH), 6.48 (t, *J* = 7.2 Hz, 6 H, ArH), 3.37 (t, *J* = 6.00 Hz, OCH<sub>2</sub>), 1.21–1.14 (m, 6 H, CH<sub>2</sub>), 1.00–0.91 (m, 6 H, CH<sub>2</sub>), 0.91–0.80 (m, 12 H, CH<sub>2</sub>), 0.51 (t, *J* = 7.2 Hz, 9 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>90</sub>H<sub>87</sub>N<sub>3</sub>O<sub>3</sub> [M]<sup>+</sup> 1257.67; found 1257.6748.

**T4:** The coupling of **T0** (50 mg, 0.054 mmol) with (9,9-dimethyl-9*H*-fluoren-2-yl)boronic acid (55.7 mg, 0.194 mmol) resulted in **T4** (36.9 mg, 61.9 %). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS, 400 MHz):  $\delta = 8.99$  (s, 3 H, ArH), 8.27 (s, 3 H, ArH), 8.11 (s, 3 H, ArH), 7.90 (d, J = 8.0 Hz, 3 H, ArH), 7.79 (d, J = 7.6 Hz, 3 H, ArH), 7.65 (d, J = 7.6 Hz, 3 H, ArH), 7.30 (d, J = 6.8 Hz, 3 H, ArH), 7.24 (dd, J = 6.8, J = 2.0 Hz, 6 H, ArH), 3.90 (t, J = 6.0 Hz, 6 H, OCH<sub>2</sub>), 1.63–1.57 (m, 6 H, CH<sub>2</sub>), 1.54 (s, 18 H, CH<sub>3</sub>), 1.37–1.30 (m, 6 H, CH<sub>2</sub>), 1.24–1.11 (m, 12 H, CH<sub>2</sub>), 0.82 (t, J = 6.8 Hz, 9 H, CH<sub>3</sub>) ppm. HRMS (ESI): calcd. for C<sub>81</sub>H<sub>84</sub>O<sub>3</sub> [M]<sup>+</sup> 1104.64; found 1104.6418.

**Supporting Information** (see footnote on the first page of this article): Phase diagrams; summary of thermotropic behavior; <sup>1</sup>H NMR, HRMS, and emission spectra.

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