Tetraphenylethene-Derived Columnar Liquid Crystals and Their Oxidative Photocyclization

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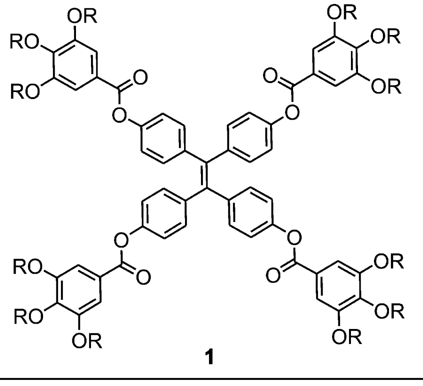
The synthesis of novel tetraphenylethenes **9a–f**, **13**, and **18a**,**b** bearing ether, biphenyl, and 4-cyanobiphenyl moieties via a McMurry reaction and Suzuki coupling as key steps is described. Mesogenic properties of these compounds were studied by differential scanning calorimetry (DSC), optical polarizing microscopy, and X-ray diffraction. Ether-substituted derivatives **9a**,**b** with chain lengths C_8 or C_9 were non-mesogenic. Compounds **9c–f** with longer alkyl chains displayed hexagonal columnar mesophases. Whereas cyanobiphenyl derivative **13** was non-mesogenic, the corresponding biphenyl systems **18a**,**b** with decyloxy and dodecyloxy chains, respectively, formed hexagonal columnar mesophases. Oxidative photocyclization of compounds **1f**, **9c**, **13**, and **18a** were investigated. Upon irradiation in the presence of iodine tetraphenylethenes **1f**, **9c** gave the corresponding phenanthrenes **22a**,**b**. The mesomorphic properties of **22a**,**b** were strongly dependent on the substituent. Whereas ether **22a** displayed only isotropic melting, a hexagonal columnar mesophase was found for ester **22b**.

Introduction

There is considerable interest in the development of novel columnar liquid crystals[1] resulting from their unique one-dimensional transport properties such as electrical conductivity[2] and photo-conductivity.[3,4] For a long time the presence of a large flat aromatic core connected with flexible side chains was assumed to be an ultimate prerequisite for the formation of thermotropic columnar mesophases. However, contributions from several laboratories over the last couple of years indicated that even molecules devoid of a disk-like core region can be used as columnar mesogens[5] because the major driving force for mesophase formation is microsegregation of the polar cores from the lipophilic alkyl side chains rather than intracolumnar π−π stacking between the core regions.[6] We have recently discovered that tetraphenylethenes condensed with gallic acid derivatives (**1**) represent a novel class of columnar liquid crystals, despite the twisting of the aryl rings (Scheme 1).[7] Thus it seemed attractive to study the scope of this mesogenic subunit. In addition we were particularly interested in the oxidative photocyclization of tetraphenylethenes because this reaction should provide a novel mesogenic unit. *cis*-Stilbenes and tetraphenylethenes are well-known to undergo oxidative photocyclization to phenanthrenes.[8−10] However, to the best of our knowledge this cyclization has not been used for the preparation of liquid crystalline phenanthrenes.[11] Here we describe the synthesis and mesomorphic properties of tetraphenylethenes and their photocyclization towards phenanthrenes.



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1	**a**	**b**	**c**	**d**	**e**	**f**	**g**
R=	C_5H_{11}	C_6H_{13}	C_7H_{15}	C_8H_{17}	C_9H_{19}	$C_{10}H_{21}$	$C_{12}H_{25}$

Scheme 1. Tetraphenylethene esters **1a−g**

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Results and Discussion

In order to explore the scope and limitations of the tetraphenylethene mesogenic subunit, it was decided to prepare the corresponding ether, biphenyl, and 4-cyanobiphenyl derivatives and to compare them with the esters **1**. As the key step for the formation of the tetraphenylethene moiety the McMurry reaction of suitable modified 4,4′-disubstituted benzophenones was chosen.[7,12,13]

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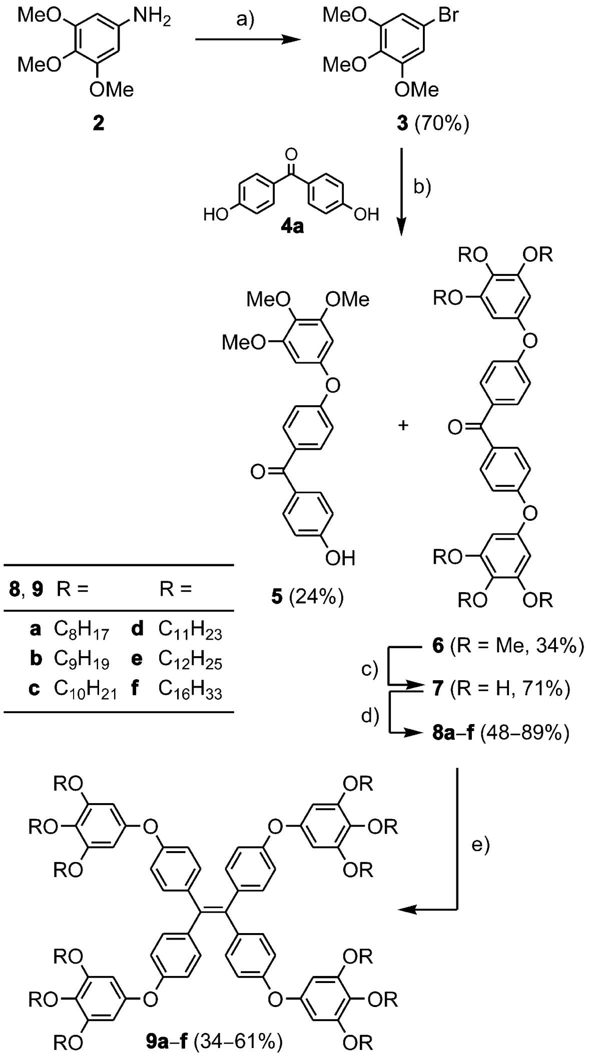
As outlined in Scheme 2, compound 3,4,5-trimethoxyaniline (**2**) was treated with $NaNO_2$ under acidic conditions following the procedure by Banwell. Subsequent Sandmeyer reaction of the diazonium salt with CuBr under reflux gave the bromide **3** in 70% yield.[14] Coupling of bromide **3** with 4,4′-dihydroxybenzophenone (**4a**) was achieved by heating the compounds with CuO in the presence of K_2CO_3 in pyridine at 140 °C.[15] After 5 days, a mixture of the bis-arylated compound **6** (34%) and the mono-arylated product **5** (24%) was obtained, which could be separated by flash chromatography. The methoxy groups in **6** were removed with BBr_3 in CH_2Cl_2, yielding the hexahydroxy derivative **7** in 71%, which was alkylated under standard conditions using K_2CO_3 in DMF at 80 °C to give the corresponding hexaalkyloxybenzophenones **8a−f** in moderate to good yields (Table 1). Final McMurry coupling of benzophenones **8a−f** was achieved with $TiCl_4$ and Zn powder in CH_2Cl_2 in the presence of pyridine to afford the tetraphenylethenes **9a−f** in 34−61% (Table 2).

The mesomorphic properties of tetraphenylethene ethers **9a−f** and their precursors **8a−f** were studied by differential scanning calorimetry (DSC) and optical polarizing microscopy. As shown in Table 1, benzophenones **8a−e** did not show any mesomorphic properties. Compound **8f** displayed two endothermic peaks at 45 °C and 53 °C upon first heating, which may be correlated to crystal → crystal and crystal → isotropic liquid transitions, respectively. These two transitions reappear during the cooling cycle at 41 °C and 39 °C. On further heating only isotropic melting at 44 °C was observed. Microscopy revealed no characteristic textures between 53 °C and 45 °C.



Scheme 2. Tetraphenylethene ethers **9**: a) 1. $NaNO_2$, H_2SO_4, H_2O, 10 °C, 2. CuBr, H_2O, reflux, 30 min; b) CuO, pyridine, K_2CO_3, 140 °C, 5 d; c) BBr_3 (7 equiv.), CH_2Cl_2, −60 °C, 1 h, then room temp., 16 h; d) K_2CO_3 (13 equiv.), DMF, RBr (6 equiv.), 80 °C, 40 h; e) $TiCl_4$, Zn, pyridine, CH_2Cl_2, 60 °C, 20 h

Table 1. Yields and phase-transition temperatures of benzophenones **8**

8[a]	Yield (%)	Temp.[b] [°C] for Cr → I[c]
a	83	37
b	73	33
c	48	50
d	89	44
e	58	42
f	65	45

[a] Preparation of **8** from **7** under the reaction conditions shown in Scheme 2. [b] Transition temperatures were determined by DSC upon first heating (heating rate 10 K·min^{-1}). [c] The following phases were observed: Cr (crystalline), I (isotropic).

The phase transition temperatures of tetraphenylethenes **9a−f** are summarized in Table 2. Whereas the octyl- and nonyl-substituted derivatives **9a**,**b** show only isotropic melting upon heating, the compounds **9c−f** with longer alkoxy chains displayed an interesting phase behavior. During first heating of the decyloxy-substituted tetraphenylethene **9c** isotropic melting at 38 °C was observed. Upon cooling of the isotropic phase below 4 °C a columnar mesophase appeared, which could not be transformed into the crystalline phase even upon prolonged cooling and storage at subambient temperatures. When the columnar mesophase was reheated, a clearing transition at 16 °C was observed. This cycle could be repeated several times. Compounds **9d**,**e** behaved similarly. In contrast, derivative **9f** displayed only crystal → isotropic liquid phase transitions in DSC. However, upon rapid cooling from the isotropic phase fan-shaped textures indicative for columnar mesophases were

Table 2. Yields and phase-transition temperatures of tetraphenylethenes **9**

9[a]	Yield (%)	Temp. cycle	Temp.[b] [°C]	Enthalpies [kJ·mol^{-1}]	Transitions[c]
a	55	1st heating	54[d]	–[e]	Cr → I
b	57	1st heating	43[d]	–[e]	Cr → I
c	49	1st heating	38	6.90	Cr → I
c		1st cooling	4	−3.88	I → Col$_h$
c		2nd heating	16	7.98	Col$_h$ → I
d	51	1st heating	42	134	Cr → I
d		1st cooling	11	−7.14	I → Col$_h$
d		2nd heating	17	6.58	Col$_h$ → I
e	34	1st heating	52	158	Cr → I
e		1st cooling	17	−9.15	I → Col$_h$
e		2nd heating	23	8.78	Col$_h$ → I
f	61	1st heating	43	224	Cr → I
f		1st cooling	36	−220	I → Cr [f]
f		2nd heating	43	212	Cr → I[f]

[a] Preparation of **9** from **8** under the reaction conditions shown in Scheme 2. [b] Transition temperatures were determined by DSC (heating rate 10 K· min^{-1}). [c] The following phases were observed: Cr (crystalline), Col$_h$ (hexagonal columnar), I (isotropic). [d] Phase transitions were determined by optical polarizing microscopy. [e] Not determined. [f] A hexagonal columnar mesophase was observed during microscopy.

detected for **9f**. Similar optical results were obtained for **9c**−**e**.[16] As a typical example the texture of **9e** at 11 °C is shown in Figure 1.

Figure 1. Fan-shaped texture of tetraphenylethene **9e** as seen between crossed polarizers at 11 °C upon cooling (cooling rate: 0.1 K·min^{-1}) from the isotropic liquid (magnification 200 ×)

Non-oriented samples of **9d**,**e** were investigated by X-ray studies at 14 °C and 19 °C, respectively, during the second heating run. Only one reflection (d = 2.97 nm for **9d** and d = 3.33 nm for **9e**) could be detected. With respect to the texture observation these reflections were indexed as 10 reflections of a hexagonal lattice leading to the lattice parameters a_{hex} = 3.43 nm and a_{hex} = 3.85 nm.[17]

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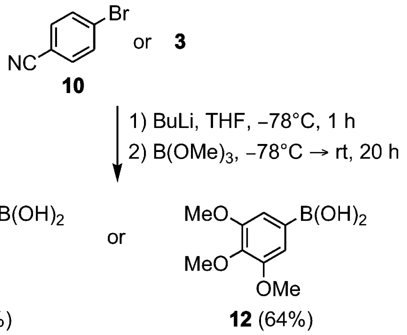
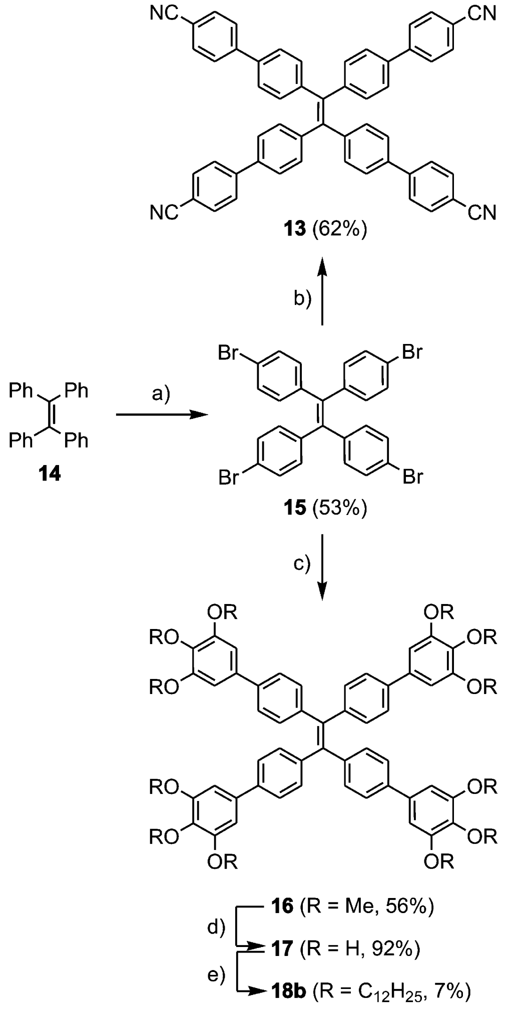
For the synthesis of the biphenyl derivatives a Suzuki coupling was chosen.[18] As shown in Scheme 3, the required boronic acids **11** and **12** were prepared in 37% and 64% yield, respectively, from 4-bromobenzonitrile (**10**) and 3,4,5-trimethoxybenzene (**3**) by treatment with BuLi in THF, followed by quenching with trimethylborate. Suzuki coupling of tetrakis(*p*-bromophenyl)ethene (**15**), easily available by neat bromination of tetraphenylethene (**14**) according to a procedure by Morris,[19] with boronic acid **11** gave the desired 4-cyanobiphenyl derivative **13** in 62% yield (Scheme 4).



Scheme 3

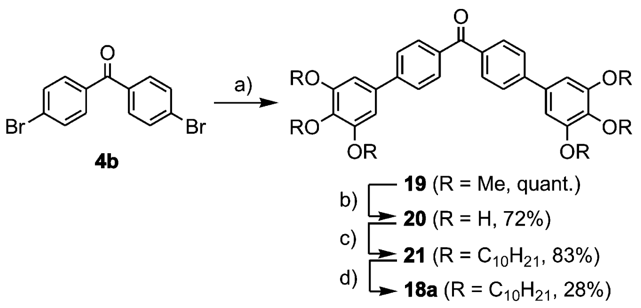
Compound **13** did not show any mesomorphic properties. Upon heating isotropic melting at 337 °C was observed. Due to decomposition above the melting point, no cooling cycles could be studied by DSC.

The uneventfully proceeding Suzuki coupling of boronic acid **12** with tetrabromide **15** afforded the tetraphenylethene **16** in 56% yield. Removal of the methoxy groups with BBr_3 as described above was achieved in 92%. Disappointingly, upon alkylation of dodecahydroxy derivative **17** with dodecycl bromide only 7% of the desired tetraphenylethene **18b** could be obtained. In order to improve the yield, we decided to prepare alternatively a fully functionalized benzophenone precursor which should undergo final McMurry coupling to the tetraphenylethene derivative **18a**. As shown in Scheme 5, compound 4,4′-dibromobenzophenone (**4b**) almost quantitatively underwent Suzuki coupling with boronic acid **12** to ketone **19**. Deprotection and alkylation



Scheme 4. Preparation of tetraphenylethene derivatives: a) Br_2, room temp., 16 h; b) **11**, $Pd(PPh_3)_4$ (15 mol %), Na_2CO_3, DME, H_2O, 100 °C, 18 h; c) **12**, $Pd(PPh_3)_4$ (15 mol %), Na_2CO_3, DME, H_2O, 100 °C, 24 h; d) BBr_3 (13 equiv.), CH_2Cl_2, -60 °C → room temp., 16 h; e) K_2CO_3 (25 equiv.), DMF, $C_{12}H_{25}Br$ (12 equiv.), 80 °C, 3 days

with decyl bromide proceeded in 72% and 83%, respectively, and the final McMurry coupling of **21** gave the tetraphenylethene **18a** in 28% yield.



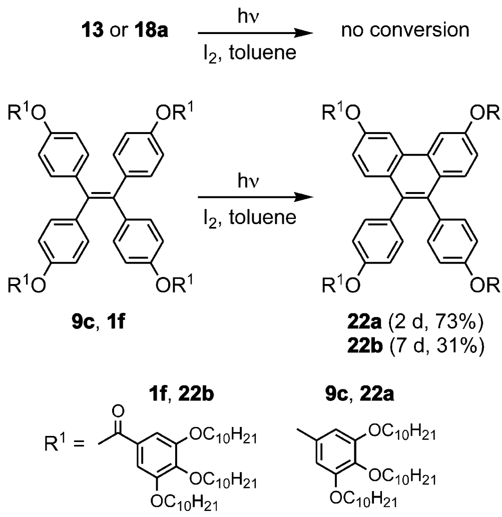
Scheme 5. Tetrakis[4-(3,4,5-trisdecyloxyphenyl)phenyl]ethene: a) **12**, $Pd(PPh_3)_4$ (8 mol %), Na_2CO_3, DME, H_2O, 100 °C, 60 h; b) BBr_3 (7 equiv.), CH_2Cl_2, -78 °C → room temp., 18 h; c) K_2CO_3 (12 equiv.), DMF, $C_{10}H_{21}Br$ (6 equiv.), 80 °C, 4 d; d) $TiCl_4$, Zn, pyridine, CH_2Cl_2, 50 °C, 24 h

In the DSC experiment biphenyl derivative **18b** displayed a melting transition at 49 °C (131.2 kJ·mol^{-1}) and an enantiotropic clearing transition at 65 °C (10.5 kJ·mol^{-1}). During subsequent cooling and heating cycles no crystalline phase was observed, but the clearing transition between mesophase and isotropic liquid was fully reversible. This observation agreed well with the optical investigations. Upon slow cooling from the isotropic liquid a fan-shaped texture was observed.[16] Further support came from X-ray studies of non-oriented samples. The diffraction pattern could be traced back to a hexagonal columnar lattice with a lattice parameter $a_{\text{hex}} = 3.5$ nm for **18b**.[17]

Photocyclization to Phenanthrene Derivatives 22

The results of the oxidative photocyclizations of tetraphenylethenes **13**, **18a**, **9c**, and **1f** (R = $C_{10}H_{21}$) are summarized in Scheme 6. Following the procedure by Olsen and Buckles,[20] solutions of the tetraphenylethenes **13**, **18a**, **9c**, or **1f** in toluene were irradiated with a daylight lamp in the presence of 1 equiv. of iodine. Whereas the 4-cyanobiphenyl derivative **13** and trisalkoxybiphenyl derivative **18a** did not give any trace of the desired phenanthrene, photocyclizations of ether **9c** and ester **1f** were successful. However, compounds **9c** and **1f** differed remarkably in their reactivity. Upon irradiation of ether **9c** the corresponding phenanthrene **22a** was isolated after 2 days in 73% yield. In contrast, irradiation of ester **1f** gave phenanthrene **22b** after 7 days in only 31% yield. The different reaction rates could even be observed in the solid state. Solutions of tetraphenylethenes **9c** or **1f** in CH_2Cl_2 were dropped onto cover glasses and the solvent was evaporated. The solid samples were irradiated overnight in the presence of air at $\lambda = 254$ nm (commercial UV lamp). Reaction monitoring by TLC indicated almost complete conversion of **9c** to **22a** after 12 h. In contrast, conversion of **1f** to **22b** was only poor, showing mainly starting material **1f**. In the photocyclizations no trace of the corresponding dibenzo[*g*,*p*]chrysenes was found in the crude products. This result agrees well with earlier works of Davidson[21] and Mitchell.[22] The latter author reported that the failure of 9,10-diphenylphenanthrene derivatives to undergo a second photocyclization to the corresponding dibenzo[*g*,*p*]chrysenes is not due to steric hindrance of the *ortho* hydrogen atoms. In contrast, under Scholl conditions ($AlCl_3$, nitrobenzene) 9,10-diphenylphenanthrenes are clearly converted into the dibenzo[*g*,*p*]chrysenes. However, the chrysene derivatives turned out to be very sensitive towards oxygen. Thus, Mitchell concluded that even if the chrysenes are formed during double oxidative photocyclization, they immediately decompose under the reaction conditions. This is probably true in our cases as well.

However, the most surprising result was discovered by examining compounds **22a**,**b** by microscopy and DSC. Ether-substituted phenanthrene **22a** did not show any mesomorphic properties. During several heating and cooling cycles only isotropic melting from the crystalline phase at 49 °C was observed. In contrast, ester-substituted phenanthrene **22b** displayed a fan-shaped texture between 110



Scheme 6. Photocyclization

°C and 121 °C under the microscope (Figure 2). The DSC curves of **22b** revealed another interesting feature of this novel mesogenic subunit. As can be seen from Table 3, the clearing enthalpy for a given temperature cycle is much larger than the corresponding melting enthalpy. Usually the reverse is true for columnar liquid crystals[1] as exemplified by the transition enthalpies of tetraphenylethene **18b**. The large clearing enthalpy of **22b** is probably caused by relatively strong long-range orientational order of the columnar mesophase, which is evident in the extremely high viscosity. The X-ray diffraction displays two weak reflections at d = 4.3 nm (first order) and d = 2.15 nm (second order) after slow cooling from the isotropic state into the liquid crystalline one. This pattern would indicate a layer structure. But with respect to the texture of the phase the pattern has been evaluated on the basis of a Col$_{hex}$ structure because often the √3 reflection is of extreme low intensity and cannot be observed. A lattice parameter a = 4.96 nm of the hexagonal cell was obtained. Simultaneously with the Bragg reflections a diffuse scattering can be seen in the small angle region which indicates the presence of the isotropic phase.[16] Obviously, the formation of the mesophase is kinetically hindered in these systems. This would also explain why an extremely slow cooling rate is required in order to obtain a suitable mesophase.

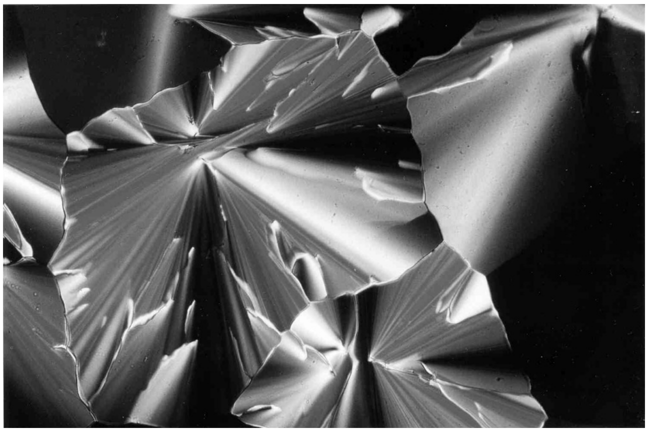


Figure 2. Fan-shaped texture of phenanthrene **22b** as seen between crossed polarizers at 116 °C upon cooling (cooling rate: 0.1 K·min^{-1}) from the isotropic liquid (magnification 200 ×)

Thus, rigidifying the mesogenic core of the tetraphenylethene to the phenanthrene moiety resulted in a strong increase of the melting and clearing points together with decreased width of the mesophase. While the former result seems reasonable, the latter outcome is somewhat unexpected. In Figure 3 possible arrangements of tetraphenylethenes **1f**, **9c**, and phenanthrenes **22a**,**b** are shown. Presumably C_2-symmetrical tetraphenylethenes **9c**, **1f** can better accommodate the columnar orientation in the mesophase, by stacking neighboring tetraphenylethenes, which are rotated against each other by 90° (Figure 3, a). Slight deviations from the 90° angle are tolerated in this case. However, two neighboring phenanthrenes **22a**,**b** must be rotated by 180° against each other in order to maintain sufficient space between the planar phenanthrene system and the twisted aryl rings (Figure 3, b). There are no deviations from the 180° angle possible and thus the tendency to crystallize is strongly enhanced. Of course the crystalline phase is further

Table 3. Phase transition temperatures of tetraphenylethenes **18a** (R = C$_{10}$H$_{21}$), **18b** (R = C$_{12}$H$_{25}$) and phenanthrenes **22a**,**b** (R = C$_{10}$H$_{21}$)

18, **22**[a]	Temp. cycle	Temp.[b] [°C] (enthalpies [kJ·mol^{-1}])				
18a	1st heating	Cr	65 (9.85)	I[c]		
18a	1st cooling	I	54 (−8.71)	Cr		
18a	2nd heating	Cr	61 (8.60)	I		
18b	1st heating	Cr	49 (131.2)	Col$_h$	65 (10.5)	I
18b	1st cooling	I	61 (−9.65)	Col$_h$		
18b	2nd heating	Col$_h$	66 (10.1)	I		
22a	1st heating	Cr$_1$	29 (0.44)	Cr$_2$	49 (84.0)	I
22a	1st cooling	I	48 (−82.8)	Cr		
22a	2nd heating	Cr$_2$	47 (61.6)	I		
22b	1st heating	Cr$_2$	110 (1.91)	Col$_h$	121 (26.2)	I
22b	1st cooling	I	119 (−24.7)	Col$_h$	101 (−0.73)	Cr$_2$ 97 (−1.19) Cr$_1$
22b	2nd heating	Cr$_1$	98 (2.35)	Cr$_2$	106 (−2.43)	Col$_h$ 121 (−25.0) I

[a] Preparation of **18**, **22** under the reaction conditions shown in Schemes 4−6. [b] Transition temperatures were determined by DSC (heating rate 10 K·min^{-1}). [c] The following phases were observed: Cr, Cr$_1$, Cr$_2$ (crystalline), Col$_h$ (hexagonal columnar), I (isotropic).

stabilized by the increased π−π stacking interaction of phenanthrenes **22a**,**b** as compared to tetraphenylethenes **9c**, **1f**.[23] In order to maximize overlap between neighboring phenanthrenes **22**, antiparallel stacking is required, resulting in a larger lattice parameter for **22b** as compared to tetraphenylethenes **9c**, **1f**. Comparison of the molecular diameters of **9d**,**e** and **18b**, which were estimated from Corey−Pauling−Kolton (CPK) models (**9d**: 4.1 nm, **9e**: 5.2 nm, **18b**: 5.0 nm), with the experimental lattice parameter suggests a partial interdigitation of the aliphatic side chains of neighboring columns. In contrast, the columnar arrangement for compound **22b** (Figure 3, b) has a diameter of 5.2 nm based on CPK models. This corresponds well with experimental lattice parameter, proposing only little overlap between the side chains. It should be mentioned that Artal et al.[24] studied $FeCl_3$-mediated cyclization of alkoxy-substituted 1,2,4,5-tetraphenylbenzenes to the corresponding tetrabenz[*a*,*c*,*h*,*j*]anthracenes. Whereas the tetraphenylbenzenes displayed only isotropic melting behavior, the board-like tetrabenz[*a*,*c*,*h*,*j*]anthracenes formed crystal B and hexagonal columnar mesphases.

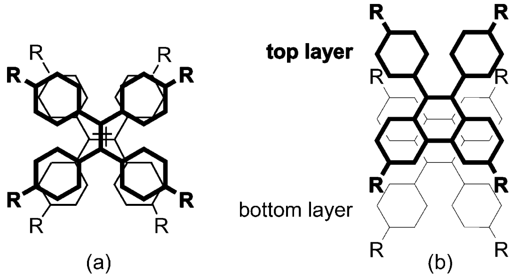


Figure 3. Possible arrangements of tetraphenylethenes **1f**, **9c** (a) and phenanthrenes **22a**,**b** (b) in the hexagonal columnar mesophase

In conclusion, the scope of the novel tetraphenylethene mesogenic subunit has been extended to ether and biphenyl substituents. The pendant trialkoxybenzene groups seem to play a major role in stabilizing the columnar mesophase. In addition ether and ester tetraphenylethenes, such as **9c**, **1f** can undergo oxidative photocyclization to phenanthrenes **22a**,**b**. Particularly, phenanthrene **22b** provides a novel mesogenic core unit.

Experimental Section

General: For general experimental conditions and preparation of **1f** see ref.[7] Tetraphenylethene (**14**) (98% pure) was purchased from Aldrich. The X-ray patterns were recorded by a Guinier film camera which is equipped with a heating stage. The wavelength of the Cu-*Kα* line has been used. The exposure time was about 2 h.

1-Bromo-3,4,5-trimethoxybenzene (3): To an ice-cooled suspension of 3,4,5-trimethoxyaniline (**2**) (18.3 g, 0.10 mol) in H_2O (80 mL) and concd. H_2SO_4 (10 mL) was added dropwise a solution of $NaNO_2$ (6.90 g, 0.10 mol) in H_2O (120 mL) while keeping the temperature at 5−10 °C. The precipitate was dissolved by addition of ice-cold H_2O (150 mL). The resulting solution was added dropwise over 30 min to a refluxing aqueous solution of CuBr (prepared by refluxing a mixture of $CuSO_4$ (9.99 g, 0.04 mol), copper shavings (2.03 g, 32.0 mmol), NaBr (15.4 g, 0.15 mol), concd. H_2SO_4 (1.6 mL), and H_2O (100 mL) for 3 h). The mixture was refluxed for additional 30 min, cooled to room temp. and diluted with Et_2O (250 mL). The aqueous layer was extracted with Et_2O (2 × 250 mL) and the combined organic layers were washed with sat. $NaHCO_3$ (2 × 250 mL), dried ($MgSO_4$), and the solvents evaporated. Flash chromatography on SiO_2 (hexanes/ethyl acetate, 3:1) yielded 17.3 g (70%) of a colorless solid; m.p. 78 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 6.70 (s, 2 H, 4-,6-H), 3.83, 3.80 (s, 9 H, OCH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 153.9 (C-1, C-3), 137.7 (C-2), 116.1 (C-5), 108.9 (C-4, C-6), 60.8, 56.3 (OCH_3) ppm. MS (EI): *m*/*z* (%) = 248 (96), 246 (100) [M^+], 233 (60), 231 (62), 205 (20), 203 (22), 190 (14), 188 (18), 175 (10), 173 (12), 157 (3), 137 (3), 124 (18), 109 (5), 94 (3), 81 (5). Analytical data were in accordance with the literature.[14]

4,4′-Bis(3,4,5-trimethoxyphenyloxy)benzophenone (6): A mixture of **4a** (1.50 g, 7.00 mmol), **3** (3.45 g, 14.0 mmol), CuO (1.68 g, 21.0 mmol), and K_2CO_3 (1.94 g, 14.0 mmol) in pyridine (30 mL) was heated at 140 °C for 5 days. The mixture was then cooled to room temp., diluted with CH_2Cl_2 (200 mL), and filtered. The organic layer was stirred for 2 h with 10% HCl (2 × 200 mL), washed with sat. $NaHCO_3$ (200 mL) and H_2O (200 mL), dried ($MgSO_4$), and the solvents evaporated. After purification by flash chromatography on SiO_2 (CH_2Cl_2/ethyl acetate, 10:1) and recrystallization from CH_2Cl_2/hexanes, compounds **5** (0.64 g, 24%) and **6** (1.29 g, 34%) were obtained as colorless solids.

4-Hydroxy-4′-(3,4,5-trimethoxyphenyloxy)benzophenone (5): M.p. 173 °C. IR (KBr): $\tilde{\nu}$ = 1630 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.8 Hz, 2 H, 2′-,6′-H), 7.75 (d, *J* = 8.8 Hz, 2 H, 2-,6-H), 7.03 (d, *J* = 8.8 Hz, 2 H, 3′-,5′-H), 6.94 (d, *J* = 8.6 Hz, 4 H, 3-,5-H), 6.34 (s, 2 H, 2′′-,6′′-H), 3.86 (s, 3 H, OCH_3), 3.81 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.2 (CO), 161.5 (C-4), 160.6 (C-4′), 154.0 (C-3′′, C-5′′), 151.5 (C-1′′), 134.8 (C-1′), 132.7 (C-2, C-6′), 132.3 (C-2′, C-6′), 129.7 (C-1), 116.7 (C-3′, C-5′), 115.3 (C-3, C-5), 97.9 (C-2′′, C-6′′), 61.0, 56.2 (OCH_3) ppm. MS (EI): *m*/*z* (%) = 380 (100) [M^+], 365 (80), 337 (6), 190 (3), 149 (3), 121 (24), 93 (4). $C_{22}H_{20}O_6$ (380.39): calcd. C 69.45, H 5.30; found C 69.57, H 5.36.

4,4′-Bis(3,4,5-trimethoxyphenyloxy)benzophenone (6): M.p. 125 °C. IR (KBr): $\tilde{\nu}$ = 1636 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.8 Hz, 4 H, 2-,6-H), 7.02 (d, *J* = 8.8 Hz, 4 H, 3-,5-H), 6.34 (s, 4 H, 2′-,6′-H), 3.84 (s, 6 H, OCH_3), 3.81 (s, 12 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.1 (CO), 161.6 (C-4), 154.1 (C-3′, C-5′), 151.4 (C-1′), 135.0 (C-1), 132.2 (C-2, C-6), 132.0 (C-4′), 116.7 (C-3, C-5), 97.9 (C-2′, C-6′), 61.0, 56.1 (OCH_3) ppm. MS (EI): *m*/*z* (%) = 546 (100) [M^+], 531 (44), 503 (2), 473 (3), 394 (20), 379 (15), 351 (1), 287 (1), 279 (4), 258 (6), 230 (2), 167 (4), 149 (10), 135 (3), 83 (4). $C_{31}H_{30}O_9$ (546.57): calcd. C 68.11, H 5.54; found C 67.58, H 5.54.

4,4′-Bis(3,4,5-trihydroxyphenyloxy)benzophenone (7): To a solution of **6** (1.00 g, 1.83 mmol) in CH_2Cl_2 (20 mL) at −60 °C was added dropwise BBr_3 (12.8 mL, 12.8 mmol, 1.0 M solution in CH_2Cl_2), and the resulting solution was stirred for 1 h at −60 °C and additional 16 h at room temp. The mixture was hydrolyzed under ice-cooling by dropwise addition of H_2O (40 mL) and CH_2Cl_2 (20 mL). The precipitate was isolated and dissolved in ethyl acetate (100 mL). The organic layer was washed with 2 N HCl (100 mL) and H_2O (100 mL), dried ($MgSO_4$), and the solvents evaporated. After recrystallization from ethyl acetate/CH_2Cl_2 0.60 g (71%) of a pale red solid was isolated, m.p. 212 °C. IR (KBr): $\tilde{\nu}$ = 3395, 3388, 3315, 1626 cm^{-1}. ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ = 8.13 (s, 4

H, 3′-,5′-OH), 7.78 (d, *J* = 8.8 Hz, 4 H, 2-,6-H), 7.30 (s, 2 H, 4′-OH), 7.04 (d, *J* = 8.8 Hz, 4 H, 3-,5-H), 6.21 (s, 4 H, 2′-,6′-H) ppm. ^{13}C NMR [100 MHz, (CD$_3$)$_2$CO]: δ = 194.0 (CO), 163.1 (C-4), 148.7 (C-1′), 147.5 (C-3′, C-5′), 132.8 (C-2, C-6), 132.7 (C-1), 131.0 (C-4′), 117.2 (C-3, C-5), 100.8 (C-2′, C-6′) ppm. MS (EI): *m*/*z* (%) = 462 (100) [M$^+$], 338 (70), 322 (4), 284 (2), 256 (2), 245 (37), 231 (14), 216 (6), 171 (3), 126 (13), 121 (36), 93 (5). $C_{25}H_{18}O_9$ (462.41): calcd. C 64.92, H 3.93; found C 64.87, H 3.53.

General Procedure for the Preparation of 4,4′-Bis(3,4,5-trialkyloxyphenyloxy)benzophenones 8a−f: A suspension of ketone **7** (0.50 g, 1.08 mmol), alkyl bromide (6.49 mmol), and K_2CO_3 (1.80 g, 13.0 mmol) in DMF (20 mL) was heated at 80 °C for 44 h. After cooling to room temp., the mixture was poured onto ice (50 g). The resulting precipitate was isolated by filtration, washed with H_2O, and redissolved in CH_2Cl_2 (100 mL). The organic layer was dried ($MgSO_4$), evaporated, and purified by flash chromatography on SiO_2.

4,4′-Bis(3,4,5-trioctyloxyphenyloxy)benzophenone (8a): Flash chromatography (hexanes/ethyl acetate, 25:1) yielded 1.02 g (83%) of a colorless solid; m.p. 37 °C. IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, *J* = 8.6 Hz, 4 H, 2-,6-H), 7.01 (d, *J* = 8.8 Hz, 4 H, 3-,5-H), 6.30 (s, 4 H, 2′-,6′-H), 3.95 (t, *J* = 6.6 Hz, 4 H, OC*H*$_2$CH$_2$), 3.90 (t, *J* = 6.6 Hz, 8 H, OC*H*$_2$CH$_2$), 1.82−1.72 (m, 12 H, CH$_2$), 1.52−1.42 (m, 12 H, CH$_2$), 1.36−1.23 (m, 48 H, CH$_2$), 0.90−0.84 (m, 18 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 194.3 (CO), 161.8 (C-4), 153.9 (C-3′, C-5′), 150.9 (C-1′), 135.2 (C-1), 132.2 (C-2, C-6), 131.9 (C-4′), 116.6 (C-3, C-5), 99.1 (C-2′, C-6′), 73.5, 69.1 (O*C*H$_2$CH$_2$), 31.9, 31.8, 30.3, 29.5, 29.4, 29.3, 29.2, 26.9, 26.1, 26.0, 22.7, 22.6 (CH$_2$), 14.1 (CH$_3$) ppm. MS (EI): *m*/*z* (%) = 1135 (6) [M$^+$], 787 (100), 674 (34), 562 (5), 461 (3), 449 (26), 338 (12), 309 (3), 149 (3), 121 (38). $C_{73}H_{114}O_9$ (1135.70): calcd. C 77.19, H 10.12; found C 77.04, H 10.24.

4,4′-Bis(3,4,5-trinonyloxyphenyloxy)benzophenone (8b): Flash chromatography (hexanes/ethyl acetate, 30:1) yielded 1.36 g (73%) of a colorless solid; m.p. 33 °C. IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, *J* = 8.8 Hz, 4 H, 2-,6-H), 7.01 (d, *J* = 8.8 Hz, 4 H, 3-,5-H), 6.30 (s, 4 H, 2′-,6′-H), 3.95 (t, *J* = 6.6 Hz, 4 H, OC*H*$_2$CH$_2$), 3.90 (t, *J* = 6.6 Hz, 8 H, OC*H*$_2$CH$_2$), 1.82−1.72 (m, 12 H, CH$_2$), 1.51−1.42 (m, 12 H, CH$_2$), 1.37−1.21 (m, 60 H, CH$_2$), 0.90−0.86 (m, 18 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 194.2 (CO), 161.8 (C-4), 153.9 (C-3′, C-5′), 150.8 (C-1′), 135.2 (C-1), 132.2 (C-2, C-6), 131.9 (C-4′), 116.5 (C-3, C-5), 99.1 (C-2′, C-6′), 73.5, 69.1 (O*C*H$_2$CH$_2$), 31.9, 30.3, 29.7, 29.6, 29.4, 29.3, 26.9, 26.1, 26.0, 22.7 (CH$_2$), 14.1 (CH$_3$) ppm. MS (EI): *m*/*z* (%) = 1219 (1) [M$^+$], 843 (100), 717 (24), 467 (21), 341 (20), 214 (39), 121 (50). $C_{79}H_{126}O_9$ (1219.86): calcd. C 77.77, H 10.42; found C 77.63, H 10.60.

4,4′-Bis(3,4,5-trisdecyloxyphenyloxy)benzophenone (8c): Flash chromatography (hexanes/ethyl acetate, 30:1) yielded 0.68 g (48%) of a colorless solid; m.p. 50 °C. IR (KBr): $\tilde{\nu}$ = 1653 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, *J* = 8.8 Hz, 4 H, 2-,6-H), 7.01 (d, *J* = 8.8 Hz, 4 H, 3-,5-H), 6.30 (s, 4 H, 2′-,6′-H), 3.95 (t, *J* = 6.7 Hz, 4 H, OC*H*$_2$CH$_2$), 3.90 (t, *J* = 6.4 Hz, 8 H, OC*H*$_2$CH$_2$), 1.82−1.74 (m, 12 H, CH$_2$), 1.49−1.41 (m, 12 H, CH$_2$), 1.38−1.23 (m, 72 H, CH$_2$), 0.89−0.86 (m, 18 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 194.3 (CO), 161.8 (C-4), 153.9 (C-3′, C-5′), 150.9 (C-1′), 135.2 (C-1), 132.2 (C-2, C-6), 131.9 (C-4′), 116.6 (C-3, C-5), 99.1 (C-2′, C-6′), 73.6, 69.2 (O*C*H$_2$CH$_2$), 31.9, 30.3, 29.7, 29.6, 29.4, 29.3, 26.1, 26.0, 22.7 (CH$_2$), 14.1 (CH$_3$) ppm. MS (EI): *m*/*z* (%) = 1305 (10) [M$^+$], 899 (100), 759 (8), 517 (12), 277 (5), 206 (7), 121 (6), 73 (40). $C_{85}H_{138}O_9$ (1304.02): calcd. C 78.28, H 10.67; found C 77.65, H 10.74.

4,4′-Bis(3,4,5-trisundecyloxyphenyloxy)benzophenone (8d): Flash chromatography (hexanes/ethyl acetate, 30:1) yielded 1.34 g (89%) of a colorless solid; m.p. 44 °C. IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, *J* = 8.8 Hz, 4 H, 2-,6-H), 7.01 (d, *J* = 8.8 Hz, 4 H, 3-,5-H), 6.30 (s, 4 H, 2′-,6′-H), 3.94 (t, *J* = 6.7 Hz, 4 H, OC*H*$_2$CH$_2$), 3.90 (t, *J* = 6.6 Hz, 8 H, OC*H*$_2$CH$_2$), 1.82−1.74 (m, 12 H, CH$_2$), 1.50−1.43 (m, 12 H, CH$_2$), 1.36−1.21 (m, 84 H, CH$_2$), 0.90−0.85 (m, 18 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 194.3 (CO), 161.8 (C-4), 153.9 (C-3′, C-5′), 150.9 (C-1′), 135.2 (C-1), 132.2 (C-2, C-6), 131.9 (C-4′), 116.6 (C-3, C-5), 99.1 (C-2′, C-6′), 73.6, 69.1 (O*C*H$_2$CH$_2$), 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 29.3, 26.9, 26.1, 26.0, 22.7 (CH$_2$), 14.1 (CH$_3$) ppm. MS (EI): *m*/*z* (%) = 1388 (8) [M$^+$], 1234 (1), 1079 (1), 955 (100), 800 (8), 647 (7), 492 (24), 338 (15), 214 (6), 121 (60). $C_{91}H_{150}O_9$ (1388.19): calcd. C 78.72, H 10.90; found C 78.81, H 11.13.

4,4′-Bis(3,4,5-tridodecyloxyphenyloxy)benzophenone (8e): Flash chromatography (hexanes/ethyl acetate, 30:1) yielded 0.93 g (58%) of a colorless solid; m.p. 42 °C. IR (KBr): $\tilde{\nu}$ = 1649 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, *J* = 8.8 Hz, 4 H, 2-,6-H), 7.01 (d, *J* = 8.6 Hz, 4 H, 3-,5-H), 6.30 (s, 4 H, 2′-,6′-H), 3.94 (t, *J* = 6.6 Hz, 4 H, OC*H*$_2$CH$_2$), 3.90 (t, *J* = 6.4 Hz, 8 H, OC*H*$_2$CH$_2$), 1.82−1.72 (m, 12 H, CH$_2$), 1.50−1.41 (m, 12 H, CH$_2$), 1.36−1.21 (m, 96 H, CH$_2$), 0.89−0.86 (m, 18 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 194.3 (CO), 161.8 (C-4), 153.9 (C-3′, C-5′), 150.9 (C-1′), 135.2 (C-1), 132.2 (C-2, C-6), 131.9 (C-4′), 116.6 (C-3, C-5), 99.1 (C-2′, C-6′), 73.6, 69.1 (O*C*H$_2$CH$_2$), 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 29.3, 26.1, 26.0, 22.7 (CH$_2$), 14.1 (CH$_3$) ppm. MS (FAB): *m*/*z* (%) = 1472 (4) [M$^+$], 1011 (1), 749 (1), 461 (2), 421 (4), 329 (14), 307 (18), 176 (46), 154 (100). $C_{97}H_{162}O_9$ (1472.35): calcd. C 79.12, H 11.10; found C 79.11, H 11.24.

4,4′-Bis(3,4,5-trihexadecyloxyphenyloxy)benzophenone (8f): Flash chromatography (hexanes/ethyl acetate, 30:1) yielded 1.03 g (65%) of a colorless solid; m.p. 44 °C. IR (KBr): $\tilde{\nu}$ = 1653 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, *J* = 8.8 Hz, 4 H, 2-,6-H), 7.01 (d, *J* = 8.6 Hz, 4 H, 3-,5-H), 6.30 (s, 4 H, 2′-,6′-H), 3.94 (t, *J* = 6.6 Hz, 4 H, OC*H*$_2$CH$_2$), 3.90 (t, *J* = 6.4 Hz, 8 H, OC*H*$_2$CH$_2$), 1.80−1.74 (m, 12 H, CH$_2$), 1.49−1.43 (m, 12 H, CH$_2$), 1.37−1.22 (m, 144 H, CH$_2$), 0.89−0.86 (m, 18 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 194.3 (CO), 161.8 (C-4), 153.9 (C-3′, C-5′), 150.9 (C-1′), 135.2 (C-1), 132.2 (C-2, C-6), 131.9 (C-4′), 116.6 (C-3, C-5), 99.1 (C-2′, C-6′), 73.6, 69.2 (O*C*H$_2$CH$_2$), 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 29.3, 26.2, 26.1, 22.7 (CH$_2$), 14.1 (CH$_3$) ppm. MS (EI): *m*/*z* (%) = 1807 (1) [M$^+$], 1583 (0.1), 1359 (0.1), 1235 (11), 1011 (3), 788 (1), 561 (3), 335 (7), 285 (4), 169 (23), 83 (48), 58 (100). $C_{121}H_{210}O_9$ (1808.99): calcd. C 80.33, H 11.71; found C 80.49, H 11.92.

General Procedure for the Preparation of Tetrakis[4-(3,4,5-trialkyloxyphenyloxy)phenyl]ethenes 9a−f: To a solution of $TiCl_4$ (0.50 mL, 0.50 mmol, 1.0 M solution in CH_2Cl_2) in THF (3.5 mL) were successively added Zn powder (65.4 mg, 1.00 mmol), pyridine (31 μL, 0.38 μmol), and a solution of benzophenone **8** (0.44 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred at 60 °C for 20 h. Then were added K_2CO_3 (10 mL, 10% aqueous solution) and 10 mL H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed in vacuo. The crude products were purified by flash chromatography on SiO_2 (hexanes/ethyl acetate, 30:1).

Tetrakis[4-(3,4,5-trioctyloxyphenyloxy)phenyl]ethene (9a): 0.27 g (0.12 mmol, 55%) of a pale yellow solidifying oil, m.p. 54 °C. IR (KBr): $\tilde{\nu}$ = 1593, 1495 cm^{-1}. UV: λ_{max} (ε_{max}) = 362 (1.05), 330

(1.99), 296 (2.27), 266 (4.56), 208 (19.45) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 8.6 Hz, 8 H, 2-,6-H), 6.73 (d, *J* = 8.8 Hz, 8 H, 3-,5-H), 6.20 (s, 8 H, 2′-,6′-H), 3.92−3.85 (m, 24 H, $OC\mathit{H_2}CH_2$), 1.79−1.70 (m, 24 H, CH_2), 1.49−1.40 (m, 24 H, CH_2), 1.36−1.23 (m, 96 H, CH_2), 0.90−0.86 (m, 36 H, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (C-4), 153.6 (C-3′, C-5′), 152.3 (C-1′), 139.1 (C=C), 138.4 (C-1), 134.4 (C-4′), 132.6 (C-2, C-6), 117.3 (C-3, C-5), 98.1 (C-2′, C-6′), 73.5, 69.1 ($O\mathit{C}H_2CH_2$), 31.9, 31.8, 30.3, 29.6, 29.4, 29.3, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m*/*z* = 2237.7 [M$^+$], 2260.7 [M$^+$ + Na]. $C_{146}H_{228}O_{16}$ (2239.41): calcd. C 78.29, H 10.27; found C 78.42, H 10.56.

Tetrakis[4-(3,4,5-trinonyloxyphenyloxy)phenyl]ethene (9b): 0.30 g (0.12 mmol, 57%) of a pale yellow solidifying oil, m.p. 43 °C. IR (KBr): ṽ = 1593, 1495 cm^{-1}. UV: λ_{max} (ε_{max}) = 330 (1.84), 300 (1.98), 266 (4.52), 208 (20.35) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 8.6 Hz, 8 H, 2-,6-H), 6.73 (d, *J* = 8.8 Hz, 8 H, 3-,5-H), 6.19 (s, 8 H, 2′-,6′-H), 3.91−3.85 (m, 24 H, $OC\mathit{H_2}CH_2$), 1.79−1.70 (m, 24 H, $OCH_2C\mathit{H_2}CH_2$), 1.48−1.40 (m, 24 H, CH_2), 1.37−1.21 (m, 120 H, CH_2), 0.90−0.86 (m, 36 H, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (C-4), 153.6 (C-3′, C-5′), 152.3 (C-1′), 139.1 (C=C), 138.4 (C-1), 134.4 (C-4′), 132.6 (C-2, C-6), 117.3 (C-3, C-5), 98.1 (C-2′, C-6′), 73.5, 69.1 ($O\mathit{C}H_2CH_2$), 31.9, 30.3, 29.7, 29.6, 29.4, 29.3, 26.2, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m*/*z* = 2405.9 [M$^+$], 2427.9 [M$^+$ + Na], 2467.9 [M$^+$ + Na + K]. $C_{158}H_{252}O_{16}$ (2407.73): calcd. C 78.81, H 10.56; found C 78.93, H 10.86.

Tetrakis[4-(3,4,5-trisdecyloxyphenyloxy)phenyl]ethene (9c): 0.24 g (0.09 mmol, 49%) of a pale yellow oil, m.p. 38 °C. IR (KBr): ṽ = 1593, 1495 cm^{-1}. UV: λ_{max} (ε_{max}) = 354 (1.16), 330 (1.67), 278 (3.63), 266 (4.24), 208 (19.66) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 8.6 Hz, 8 H, 2-,6-H), 6.73 (d, *J* = 8.8 Hz, 8 H, 3-,5-H), 6.19 (s, 8 H, 2′-,6′-H), 3.91−3.85 (m, 24 H, $OC\mathit{H_2}CH_2$), 1.79−1.70 (m, 24 H, $OCH_2C\mathit{H_2}CH_2$), 1.50−1.39 (m, 24 H, CH_2), 1.37−1.21 (m, 144 H, CH_2), 0.90−0.86 (m, 36 H, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (C-4), 153.6 (C-3′, C-5′), 152.3 (C-1′), 139.1 (C=C), 138.4 (C-1), 134.4 (C-4′), 132.6 (C-2, C-6), 117.3 (C-3, C-5), 98.1 (C-2′, C-6′), 73.5, 69.1 ($O\mathit{C}H_2CH_2$), 31.9, 30.3, 29.8, 29.7, 29.6, 29.4, 29.3, 26.2, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m*/*z* = 2574.1 [M$^+$], 2597.1 [M$^+$ + Na]. $C_{170}H_{276}O_{16}$ (2576.05): calcd. C 79.25, H 10.81; found C 79.00, H 11.02.

Tetrakis[4-(3,4,5-trisundecyloxyphenyloxy)phenyl]ethene (9d): 0.31 g (0.11 mmol, 51%) of a pale yellow solid. IR (KBr): ṽ = 1593, 1495 cm^{-1}. UV: λ_{max} (ε_{max}) = 328 (1.64), 300 (1.86), 264 (4.17), 208 (18.70) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 8.8 Hz, 8 H, 2-,6-H), 6.73 (d, *J* = 8.8 Hz, 8 H, 3-,5-H), 6.19 (s, 8 H, 2′-,6′-H), 3.91−3.85 (m, 24 H, $OC\mathit{H_2}CH_2$), 1.79−1.70 (m, 24 H, CH_2), 1.49−1.40 (m, 24 H, CH_2), 1.36−1.20 (m, 168 H, CH_2), 0.89−0.86 (m, 36 H, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (C-4), 153.6 (C-3′, C-5′), 152.3 (C-1′), 139.1 (C=C), 138.4 (C-1), 134.3 (C-4′), 132.6 (C-2, C-6), 117.4 (C-3, C-5), 98.1 (C-2′, C-6′), 73.5, 69.1 ($O\mathit{C}H_2CH_2$), 31.9, 30.3, 29.7, 29.5, 29.4, 29.3, 26.2, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m*/*z* = 2742.2 [M$^+$], 2765.2 [M$^+$ + Na]. $C_{182}H_{300}O_{16}$ (2744.37): calcd. C 79.64, H 11.03; found C 79.64, H 11.31.

Tetrakis[4-(3,4,5-tridodecyloxyphenyloxy)phenyl]ethene (9e): 0.22 g (0.08 mmol, 34%) of a pale yellow solid. IR (KBr): ṽ = 1592, 1498 cm^{-1}. UV: λ_{max} (ε_{max}) = 358 (0.47), 330 (1.80), 286 (2.90), 266 (4.23), 208 (18.62) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 8.8 Hz, 8 H, 2-,6-H), 6.73 (d, *J* = 8.8 Hz, 8 H, 3-,5-H), 6.19 (s, 8 H, 2′-,6′-H), 3.91−3.85 (m, 24 H, $OC\mathit{H_2}CH_2$), 1.79−1.72 (m, 24 H, $OCH_2C\mathit{H_2}CH_2$), 1.49−1.40 (m, 24 H, CH_2), 1.36−1.23 (m, 192 H, CH_2), 0.90−0.86 (m, 36 H, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (C-4), 153.6 (C-3′, C-5′), 152.4 (C-1′), 139.1 (C=C), 138.4 (C-1), 134.3 (C-4′), 132.6 (C-2, C-6), 117.3 (C-3, C-5), 98.1 (C-2′, C-6′), 73.5, 69.1 ($O\mathit{C}H_2CH_2$), 31.9, 30.3, 29.7, 29.5, 29.4, 29.3, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m*/*z* = 2910.3 [M$^+$], 2933.3 [M$^+$ + Na]. $C_{194}H_{324}O_{16}$ (2912.70): calcd. C 79.99, H 11.22; found C 79.67, H 11.35.

Tetrakis[4-(3,4,5-trihexadecyloxyphenyloxy)phenyl]ethene (9f): 0.48 g (0.13 mmol, 61%) of a pale yellow solid. IR (KBr): ṽ = 1594, 1496 cm^{-1}. UV: λ_{max} (ε_{max}) = 328 (1.35), 290 (2.18), 264 (3.89), 208 (19.50) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98 (d, *J* = 8.6 Hz, 8 H, 2-,6-H), 6.73 (d, *J* = 8.8 Hz, 8 H, 3-,5-H), 6.19 (s, 8 H, 2′-,6′-H), 3.91−3.85 (m, 24 H, $OC\mathit{H_2}CH_2$), 1.77−1.72 (m, 24 H, CH_2), 1.47−1.41 (m, 24 H, CH_2), 1.37−1.20 (m, 288 H, CH_2), 0.90−0.86 (m, 36 H, $CH_2C\mathit{H_3}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (C-4), 153.6 (C-3′, C-5′), 152.4 (C-1′), 139.1 (C=C), 138.4 (C-1), 134.3 (C-4′), 132.6 (C-2, C-6), 117.4 (C-3, C-5), 98.1 (C-2′, C-6′), 73.5, 69.1 ($O\mathit{C}H_2CH_2$), 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 29.3, 26.2, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m*/*z* = 3583.1 [M$^+$], 3607.2 [M$^+$ + Na]. $C_{242}H_{420}O_{16}$ (3585.99): calcd. C 81.04, H 11.81; found C 81.10, H 11.97.

4-Cyanophenylboronic Acid (11): To a cooled solution of 4-bromobenzonitrile (**10**) (9.10 g, 0.05 mol) in THF (150 mL) was added dropwise at −78 °C *n*BuLi (20 mL, 0.05 mol, 2.5 M solution in *n*-hexane) and the solution was stirred for 1 h at −78 °C. Then was added dropwise $B(OMe)_3$ (5.70 mL, 0.05 mol) at −78 °C. The cooling bath was removed and the mixture was stirred for 20 h at room temp. After hydrolysis with 10% HCl (150 mL), the layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 150 mL). The combined organic layers were washed with H_2O (250 mL), dried ($MgSO_4$), and the solvents evaporated. The residue was washed with hot hexanes (30 mL) and recrystallized from H_2O (300 mL) to give 2.75 g (37%) of a colorless solid, m.p. 280 °C (dec.). ^{1}H NMR (200 MHz, CD_3COCD_3): δ = 7.90 (d, *J* = 7.8 Hz, 2 H, 3-,5-H), 7.62 (d, *J* = 8.0 Hz, 2 H, 2-,6-H), 7.42 (s, 2 H, OH) ppm. ^{13}C NMR (50 MHz, CD_3COCD_3): δ = 135.4, 131.7 (C-2, C-3, C-5, C-6), 119.4, 114.3 (C-1, C-6, CN) ppm. MS (EI): *m*/*z* (%) = 147 (46), 146 (10) [M$^+$], 130 (3), 120 (1), 103 (100), 102 (6), 76 (14), 75 (4).

3,4,5-Trimethoxyphenylboronic Acid (12): To a cooled solution of **3** (4.94 g, 0.02 mol) in THF (50 mL) was added dropwise at −85 °C *n*BuLi (8.00 mL, 0.02 mol, 2.5 M solution in *n*-hexane) and the solution was stirred for 1 h at −85 °C. Then was added dropwise $B(OMe)_3$ (2.30 mL, 0.02 mol) at −85 °C. The cooling bath was removed and the mixture was stirred for 18 h at room temp. After hydrolysis with 10% HCl (150 mL), the layers were separated and the aqueous layer was extracted with ethyl acetate (2 × 120 mL). The combined organic layers were washed with H_2O (150 mL), dried ($MgSO_4$), and concentrated to a volume of 30 mL. Precipitation was completed by addition of *n*-hexane (50 mL). After filtration, 2.73 g (64%) of a colorless solid were isolated, m.p. 247 °C. IR (KBr): ṽ = 3448, 3373, 1585, 1510 cm^{-1}. ^{1}H NMR (400 MHz, CD_3COCD_3): δ = 7.19 (s, 2 H, 2-,6-H), 7.14 (s, 2 H, OH), 3.82 (s, 6 H, OCH_3), 3.74 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, CD_3COCD_3): δ = 153.9, 141.4 (C-1, C-3, C-4, C-5), 112.1 (C-2, C-6), 60.4 (4-OCH_3), 56.3 (OCH_3) ppm. MS (EI): *m*/*z* (%) = 582 (100), 581 (63), 580 (16), 334 (34), 319 (23), 291 (8), 212 (63) [M$^+$], 197 (36), 168 (50), 153 (30), 110 (14), 86 (15). $C_9H_{13}BO_5$ (212.01): calcd. C 50.99, H 6.18, B 5.10; found C 51.42, H 6.37, B 5.30.

Tetrakis[4-(4′-cyanophenyl)phenyl]ethene (13): To a solution of **15** (320 mg, 0.50 mmol) in degassed DME (20 mL) were added sequentially a solution of 2 M Na_2CO_3 (20 mL, in degassed H_2O), $Pd(PPh_3)_4$ (87 mg, 75.0 μmol), and **11** (440 mg, 3.00 mmol), and the resulting mixture was heated at 100 °C for 18 h. After cooling to room temp., H_2O (100 mL) was added and the aqueous layer was extracted with Et_2O (3 × 100 mL) and CH_2Cl_2 (3 × 100 mL). The CH_2Cl_2 layer was dried ($MgSO_4$), evaporated, and the residue was purified by flash chromatography on SiO_2 (hexanes/ethyl acetate, 2:1; then CH_2Cl_2) to give 230 mg (62%) of a pale yellow solid, m.p. 337 °C (dec.). IR (KBr): $\tilde{\nu}$ = 2225, 1606, 1573, 1492 cm^{-1}. UV: λ_{max} (ε_{max}) = 404 (0.53), 370 (2.39), 352 (3.43), 326 (5.27), 314 (5.82), 286 (6.13), 272 (5.52), 202 (13.02) nm (10^4 $L\cdot mol^{-1}\cdot cm^{-1}$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.6 Hz, 8 H, 2′-,6′-H), 7.65 (d, *J* = 8.6 Hz, 8 H, 3′-,5′-H), 7.42 (d, *J* = 8.6 Hz, 8 H, 2-,6-H), 7.22 (d, *J* = 8.6 Hz, 8 H, 3-,5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 143.6, 137.4 (C-1, C-4, C-1′), 140.7 (C=C), 132.6 (C-3′, C-5′), 132.1 (C-3, C-5), 127.4 (C-2′, C-6′), 126.7 (C-2, C-6), 118.8 (CN), 110.9 (C-4′) ppm. MS (EI): *m/z* (%) = 736 (14) [M^+], 635 (100). $C_{54}H_{32}N_4$ (736.87): calcd. C 88.01, H 4.38, N 7.61; found C 88.02, H 4.41, N 7.24.

Tetrakis(4-bromophenyl)ethene (15): Powdered tetraphenylethene **14** (5.00 g, 15.0 mmol) was treated with bromine (7.50 mL, 0.15 mol) and the mixture was kept for 16 h at room temp. The resulting solid was dissolved in hot toluene (120 mL), the solution was concentrated to 20 mL and the precipitate was isolated and washed with hexanes. After flash chromatography on SiO_2 (hexanes/CH_2Cl_2, 20:1), 5.12 g (53%) of a colorless solid was obtained, m.p. 247 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.6 Hz, 8 H, 3-,5-H), 6.84 (d, *J* = 8.6 Hz, 8 H, 2-,6-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.4 (C-1), 139.6 (C=C), 132.7 (C-3, C-5), 131.3 (C-2, C-6), 121.3 (C-4) ppm. MS (EI): *m/z* (%) = 652 (12), 650 (58), 648 (94), 646 (66), 644 (14) [M^+], 572 (33), 570 (88), 568 (95), 566 (30), 490 (25), 488 (27), 486 (10), 410 (30), 408 (28), 329 (34), 327 (78), 325 (24), 254 (12), 252 (100), 250 (42), 163 (75), 149 (39), 111 (22), 83 (34).

Tetrakis[4-(3,4,5-trimethoxyphenyl)phenyl]ethene (16): To a solution of **15** (500 mg, 0.77 mmol) in degassed DME (30 mL) were added sequentially a solution of 2 M Na_2CO_3 (30 mL in degassed H_2O), $Pd(PPh_3)_4$ (133 mg, 0.12 mmol), and **12** (0.98 g, 4.63 mmol) and the resulting mixture was heated at 100 °C for 24 h. After cooling to room temp., H_2O (100 mL) was added and the aqueous layer was extracted with Et_2O (100 mL) and ethyl acetate (2 × 150 mL). The ethyl acetate layer was washed with H_2O (100 mL), dried ($MgSO_4$), evaporated, and the residue was purified by flash chromatography on SiO_2 (CH_2Cl_2/ethyl acetate, 10:1 → 4:1), recrystallization from CH_2Cl_2/*n*-hexane and by flash chromatography on SiO_2 (CH_2Cl_2/ethyl acetate, 5:1) to give 0.43 g (56%) of a pale yellow solid, m.p. 264 °C. IR (KBr): $\tilde{\nu}$ = 1586, 1554, 1497 cm^{-1}. UV: λ_{max} (ε_{max}) = 390 (1.06), 348 (3.38), 302 (7.51), 200 (19.37) nm (10^4 $L\cdot mol^{-1}\cdot cm^{-1}$). ^1H NMR (400 MHz, CD_3COCD_3): δ = 7.38 (d, *J* = 8.3 Hz, 8 H, 3-,5-H), 7.19 (d, *J* = 8.3 Hz, 8 H, 2-,6-H), 6.77 (s, 8 H, 2′-,6′-H), 3.90 (s, 24 H, OCH_3), 3.87 (s, 12 H, OCH_3) ppm. ^{13}C NMR (100 MHz, CD_3COCD_3): δ = 153.4 (C-3′, C-5′), 140.2 (C=C), 142.8, 139.0, 137.7, 136.4 (C-1, C-1′, C-4, C-4′), 131.8 (C-3, C-5), 126.3 (C-2, C-6), 104.1 (C-2′, C-6′), 60.9 (OCH_3), 56.2 (OCH_3) ppm. MS (EI): *m/z* (%) = 997 (100) [M^+], 982 (1), 831 (2), 498 (15), 303 (1), 284 (3), 230 (3), 168 (8), 83 (12). $C_{62}H_{60}O_{12}$ (997.15): calcd. C 74.67, H 6.07; found C 75.16, H 6.19.

Tetrakis[4-(3,4,5-trihydroxyphenyl)phenyl]ethene (17): To a cooled solution of **16** (300 mg, 0.30 mmol) in CH_2Cl_2 (20 mL) was added dropwise at −78 °C BBr_3 (4.20 mL, 4.20 mmol, 1.0 M solution in CH_2Cl_2), and the resulting mixture was stirred for 1 h at −78 °C and 40 h at room temp. Then H_2O (2 × 10 mL) and CH_2Cl_2 (10 mL) were added dropwise under ice-cooling and the precipitate was isolated, washed with a minimum amount of H_2O and CH_2Cl_2 and redissolved in ethyl acetate (100 mL). The layers were separated and the organic layer was washed with 2 N HCl (100 mL) and H_2O (100 mL), dried ($MgSO_4$), and the solvents evaporated. Recrystallization from ethyl acetate/CH_2Cl_2 yielded 230 mg (92%) of a yellow solid, m.p. 353 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3417, 1613, 1542, 1505 cm^{-1}. UV: λ_{max} (ε_{max}) = 396 (0.64), 350 (2.53), 306 (5.43), 210 (10.31), 194 (9.31) nm (10^4 $L\cdot mol^{-1}\cdot cm^{-1}$). ^1H NMR (400 MHz, CD_3OD): δ = 7.30 (d, *J* = 8.5 Hz, 8 H, 3-,5-H), 7.07 (d, *J* = 8.5 Hz, 8 H, 2-,6-H), 6.59 (s, 8 H, 2′-,6′-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 147.2 (C-3′, C-5′), 141.5 (C=C), 143.6, 140.6, 134.1, 133.1 (C1, C1′, C-4, C-4′), 132.9 (C-3, C-5), 126.6 (C-2, C-6), 106.8 (C-2′, C-6′) ppm. MS (EI): *m/z* (%) = 828 (3) [M^+], 812 (1), 416 (100), 400 (7), 215 (44), 185 (14), 81 (14). $C_{50}H_{36}O_{12}$ (828.83): calcd. C 72.44, H 4.38; found C 73.31, H 4.52.

Tetrakis[4-(3,4,5-tridodecyloxyphenyl)phenyl]ethene (18b): A suspension of K_2CO_3 (0.83 g, 6.00 mmol), **17** (0.20 g, 0.24 mmol), and dodecyl bromide (0.72 g, 2.90 mmol) in DMF (20 mL) was heated at 80 °C for 3 days. After cooling to room temp., H_2O (20 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL) and the combined organic layers were washed with H_2O (2 × 100 mL), dried ($MgSO_4$), and azeotropically codistilled with toluene (4 × 30 mL). After flash chromatography on SiO_2 (hexanes/ethyl acetate, 30:1), the crude product was dissolved in CH_2Cl_2 (2 mL), then EtOH (50 mL) was added. The resulting yellow solidifying oil was isolated after decanting the solvent. Yield: 46 mg (7%). IR (KBr): $\tilde{\nu}$ = 1586, 1498 cm^{-1}. UV: λ_{max} (ε_{max}) = 354 (3.35), 308 (7.29), 210 (14.36) nm (10^4 $L\cdot mol^{-1}\cdot cm^{-1}$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.3 Hz, 8 H, 3-,5-H), 7.14 (d, *J* = 8.3 Hz, 8 H, 2-,6-H), 6.75 (s, 8 H, 2′-,6′-H), 4.01 (t, *J* = 6.4 Hz, 16 H, OCH_2CH_2), 3.97 (t, *J* = 6.6 Hz, 8 H, OCH_2CH_2), 1.84−1.74 (m, 24 H, CH_2), 1.51−1.44 (m, 24 H, CH_2), 1.37−1.22 (m, 192 H, CH_2), 0.90−0.86 (m, 36 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4 (C-3′, C-5′), 140.2 (C=C), 142.7, 139.1, 138.0, 135.8 (C-1, C-1′, C-4, C-4′), 131.8 (C-3, C-5), 126.2 (C-2, C-6), 105.6 (C-2′, C-6′), 73.5 (OCH_2CH_2), 69.3 (OCH_2CH_2), 31.9, 30.4, 29.8, 29.7, 29.5, 29.4, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m/z* = 2846.5 [M^+]. $C_{194}H_{324}O_{12}$ (2848.70): calcd. C 81.79, H 11.47; found C 81.71, H 11.55.

4,4′-Bis(3,4,5-trimethoxyphenyl)benzophenone (19): To a solution of 4,4′-dibromobenzophenone **4b** (950 mg, 2.80 mmol) in degassed DME (50 mL) were added sequentially a solution of 2 M Na_2CO_3 (50 mL in degassed H_2O), $Pd(PPh_3)_4$ (240 mg, 0.21 mmol), and **12** (1.48 g, 7.00 mmol) and the resulting mixture was heated at 100 °C for 60 h. After cooling to room temp., H_2O (200 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layers were washed with H_2O (100 mL), dried ($MgSO_4$), evaporated, and purified by flash chromatography on SiO_2 (hexanes/ethyl acetate, 1:1) to give 1.47 g (quant.) of a pale yellow solid, m.p. 149 °C. IR (KBr): $\tilde{\nu}$ = 1656 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.3 Hz, 4 H, 2-,6-H), 7.68 (d, *J* = 8.3 Hz, 4 H, 3-,5-H), 6.84 (s, 4 H, 2′-,6′-H), 3.95 (s, 12 H, OCH_3), 3.91 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7 (CO), 153.6 (C-3′, C-5′), 145.3 (C-4), 138.4, 135.8 (C-1′, C-4′), 136.3 (C-1), 130.6 (C-2, C-6), 126.9 (C-3, C-5), 104.6 (C-2′, C-6′), 60.9, 56.2 (OCH_3) ppm. MS (EI): *m/z* (%) = 514 (100)

[M$^+$], 499 (36), 471 (7), 441 (5), 413 (2), 272 (1), 271 (10), 257 (4), 243 (2), 213 (4), 128 (3). $C_{31}H_{30}O_7$ (514.57): calcd. C 72.35, H 5.88; found C 72.38, H 5.97.

4,4′-Bis(3,4,5-trihydroxyphenyl)benzophenone (20): To a cooled solution of **19** (1.29 g, 2.50 mmol) in CH_2Cl_2 (30 mL) was added dropwise at −78 °C BBr_3 (17.5 mL, 17.5 mmol, 1.0 M solution in CH_2Cl_2), and the resulting mixture was stirred for 1 h at −78 °C and 18 h at room temp. Then H_2O (2 × 30 mL) and CH_2Cl_2 (20 mL) were added dropwise under ice-cooling and the precipitate was isolated and redissolved in ethyl acetate (250 mL). The layers were separated and the organic layer was washed with 2 N HCl (200 mL) and H_2O (200 mL), dried ($MgSO_4$), and the solvents evaporated. Recrystallization from acetone/CH_2Cl_2 gave 0.77 g (72%) of a pale green solid, m.p. 327 °C. IR (KBr): $\tilde{\nu}$ = 3441, 3330, 1635 cm^{-1}. ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ = 8.10 (s, 4 H, 3′-,5′-OH), 7.84 (d, *J* = 8.6 Hz, 4 H, 2-,6-H), 7.72 (d, *J* = 8.6 Hz, 4 H, 3-,5-H), 7.61 (s, 2 H, 4′-OH), 6.83 (s, 4 H, 2′-,6′-H) ppm. ^{13}C NMR [100 MHz, $(CD_3)_2CO$]: δ = 195.6 (CO), 147.1 (C-3′, C-5′), 145.9 (C-4), 136.7 (C-1′), 134.5 (C-1), 131.8 (C-4′), 131.2 (C-2, C-6), 127.0 (C-3, C-5), 107.1 (C-2′, C-6′) ppm. MS (EI): *m/z* (%) = 430 (100) [M$^+$ + H], 429 (6), 413 (3), 382 (1), 373 (3), 305 (2), 229 (56), 215 (49), 201 (6), 183 (8), 155 (19), 104 (10), 91 (12), 77 (8). $C_{25}H_{18}O_7$ (430.41): calcd. C 69.75, H 4.22; found C 69.64, H 4.49.

4,4′-Bis(3,4,5-trisdecyloxyphenyl)benzophenone (21): A suspension of K_2CO_3 (1.93 g, 14.0 mmol), **20** (0.50 g, 1.16 mmol), and decyl bromide (1.54 g, 7.00 mmol) in DMF (20 mL) was heated at 80 °C for 4 days. Then the mixture was poured onto ice (50 g), the precipitate was filtered through Celite, washed with H_2O and redissolved in CH_2Cl_2 (150 mL). The organic layer was dried ($MgSO_4$), evaporated, and purified by flash chromatography on SiO_2 (hexanes/ethyl acetate, 20:1) to give 1.23 g (83%) of a colorless solid. IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.3 Hz, 4 H, 2-,6-H), 7.67 (d, *J* = 8.3 Hz, 4 H, 3-,5-H), 6.82 (s, 4 H, 2′-,6′-H), 4.06 (t, *J* = 6.4 Hz, 8 H, OCH_2CH_2), 4.02 (t, *J* = 6.6 Hz, 4 H, OCH_2CH_2), 1.88−1.75 (m, 12 H, CH_2), 1.54−1.47 (m, 12 H, CH_2), 1.36−1.22 (m, 72 H, CH_{23}), 0.91−0.87 (m, 18 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8 (CO), 153.5 (C-3′, C-5′), 145.4 (C-4), 138.8, 135.2 (C-1′, C-4′), 136.2 (C-1), 130.6 (C-2, C-6), 126.8 (C-3, C-5), 106.2 (C-2′, C-6′), 73.6, 69.4 (OCH_2CH_2), 31.9, 30.4, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 26.0, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (EI): *m/z* (%) = 1272 (94), 1271 (100) [M$^+$], 1131 (11), 991 (10), 851 (5), 709 (12), 569 (8), 429 (16), 401 (3), 285 (1), 229 (3), 111 (1). $C_{85}H_{138}O_7$ (1272.03): calcd. C 80.25, H 10.94; found C 79.63, H 10.87.

Tetrakis[4-(3,4,5-trisdecyloxyphenyl)phenyl]ethene (18a): To a solution of $TiCl_4$ (0.75 mL, 0.75 mmol, 1.0 M solution in CH_2Cl_2) in THF (3.5 mL) were successively added Zn powder (98.1 mg, 1.50 mmol), pyridine (46.5 µL, 0.57 µmol) and a solution of **21** (0.84 g, 0.66 mmol) in CH_2Cl_2 (3 mL). The resulting mixture was stirred at 50 °C for 24 h. Then were added K_2CO_3 (10 mL, 10% aqueous solution) and 10 mL H_2O and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried ($MgSO_4$), evaporated, and purified by flash chromatography on SiO_2 (hexanes/ethyl acetate, 25:1) to give 230 mg (28%) of a yellow solid. IR (KBr): $\tilde{\nu}$ = 1586, 1493 cm^{-1}. UV: λ_{max} (ε_{max}) = 352 (2.28), 300 (6.41), 210 (13.97) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, *J* = 8.1 Hz, 8 H, 2-,6-H), 7.14 (d, *J* = 8.4 Hz, 8 H, 3-,5-H), 6.75 (s, 8 H, 2′-,6′-H), 4.01 (t, *J* = 6.4 Hz, 16 H, OCH_2CH_2), 3.97 (t, *J* = 6.7 Hz, 8 H, OCH_2CH_2), 1.84−1.74 (m, 24 H, CH_2), 1.51−1.44 (m, 24 H, CH_2), 1.38−1.22 (m, 144 H, CH_2), 0.90−0.86 (m, 36 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4 (C-3′, C-5′), 142.7, 139.1 (C-4, C-1′), 140.2 (C=C), 138.0 (C-1), 135.8 (C-4′), 131.8 (C-2, C-6), 126.1 (C-3, C-5), 105.6 (C-2′, C-6′), 73.5, 69.3 (OCH_2CH_2), 31.9, 30.4, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m/z* = 2510.3 [M$^+$], 2533.3 [M$^+$ + Na]. $C_{170}H_{276}O_{12}$ (2512.05): calcd. C 81.27, H 11.08; found C 81.11, H 11.25.

3,6-Bis(3,4,5-trisdecyloxyphenyloxy)-9,10-bis[4-(3,4,5-trisdecyloxyphenyloxy)phenyl]phenanthrene (22a): A solution of **9c** (100 mg, 38.8 µmol) and iodine (9.85 mg, 38.8 µmol) in toluene (15 mL) was irradiated for 2 days with a daylight lamp. Then the mixture was washed with sat. Na_2SO_3 (20 mL) and H_2O (20 mL), dried ($MgSO_4$) and the solvents evaporated. Flash chromatography on SiO_2 (hexanes/ethyl acetate, 30:1) yielded 70 mg (73%) of a colorless solid. IR (KBr): $\tilde{\nu}$ = 1595, 1519, 1494 cm^{-1}. UV: λ_{max} (ε_{max}) = 372 (0.37), 354 (0.41), 326 (1.97), 316 (2.84), 294 (4.74), 262 (11.67), 208 (26.94) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 2.3 Hz, 2 H, 4-,5-H), 7.58 (d, *J* = 8.8 Hz, 2 H, 1-,8-H), 7.18 (dd, *J* = 9.1/2.2 Hz, 2 H, 2-,7-H), 7.09 (d, *J* = 8.6 Hz, 4 H, 2″-,6″-H), 6.88 (d, *J* = 8.6 Hz, 4 H, 3″-,5″-H), 6.31 (s, 4 H), 6.22 (s, 4 H, 2′-,2‴-,6′-,6‴-H), 3.96−3.85 (m, 24 H, OCH_2CH_2), 1.81−1.71 (m, 24 H, CH_2), 1.49−1.40 (m, 24 H, CH_2), 1.36−1.22 (m, 144 H, CH_2), 0.90−0.85 (m, 36 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 156.0 (C-3, C-6, C-4″), 153.8, 153.7 (C-3′, C-3‴, C-5′, C-5‴), 152.7, 152.6 (C-1′, C-1‴), 135.4, 134.1 (C-9, C-10, C-1″), 134.5, 134.4 (C-4′, C-4‴), 132.3 (C-2″, C-6″), 131.0, 128.3 (C-1a, C-4a, C-8a, C-9a), 129.5 (C-1, C-8), 118.9 (C-2, C-7), 117.6 (C-3″, C-5″), 98.0 (C-2′, C-2‴, C-6′, C-6‴), 73.5, 69.1 (OCH_2CH_2), 31.9, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m/z* = 2572.3 [M$^+$], 2595.4 [M$^+$ + Na]. $C_{170}H_{274}O_{16}$ (2574.04): calcd. C 79.31, H 10.74; found C 79.24, H 10.92.

3,6-Bis(3,4,5-trisdecyloxybenzoyloxy)-9,10-bis[4-(3,4,5-trisdecyloxybenzoyloxy)phenyl]phenanthrene (22b): A solution of tetraphenylethene **1f** (500 mg, 0.19 mmol) and iodine (47.2 mg, 0.19 mmol) in toluene (65 mL) was irradiated for 7 days with a daylight lamp. Then the mixture was washed with sat. Na_2SO_3 (50 mL) and H_2O (50 mL), dried ($MgSO_4$), and the solvents evaporated. Flash chromatography on SiO_2 (hexanes/ethyl acetate, 25:1) and recrystallization from CH_2Cl_2/EtOH yielded 160 mg (31%) of a pale yellow solid. IR (KBr): $\tilde{\nu}$ = 1732, 1587, 1501 cm^{-1}. UV: λ_{max} (ε_{max}) = 358 (0.23), 334 (0.37), 308 (4.11), 278 (9.88), 266 (9.03), 218 (16.48), 192 (10.85) nm (10^4 L·mol^{-1}·cm^{-1}). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 2.3 Hz, 2 H, 4-,5-H), 7.67 (d, *J* = 9.1 Hz, 2 H, 1-,8-H), 7.48, 7.43 (s, s, 8 H, 2′-H, 2‴-H, 6′-H, 6‴-H), 7.38 (dd, *J* = 9.1/2.2 Hz, 2 H, 2-,7-H), 7.29 (d, *J* = 8.3 Hz, 4 H, 2″-,6″-H), 7.18 (d, *J* = 8.6 Hz, 4 H, 3″-,5″-H), 4.09−4.05 (m, 24 H, OCH_2CH_2), 1.87−1.76 (m, 24 H, CH_2), 1.52−1.47 (m, 24 H, CH_2), 1.38−1.21 (m, 144 H, CH_2), 0.91−0.86 (m, 36 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 165.0 (CO), 153.0 (C-3′, C-3‴, C-5′, C-5‴), 149.8 (C-3, C-6, C-4″), 143.1, 143.0 (C-4′, C-4‴), 136.7, 136.0 (C-1″, C-9, C-10), 132.0 (C-2″, C-6″), 130.8, 130.1 (C-1a, C-4a, C-8a, C-9a), 129.5 (C-1, C-8), 123.8, 123.7 (C-1′, C-1‴), 121.8 (C-2, C-7), 121.3 (C-3″, C-5″), 115.1 (C-4, C-5), 108.6, 108.5 (C-2′, C-2‴, C-6′, C-6‴), 73.6, 69.3 (OCH_2CH_2), 31.9, 30.4, 29.7, 29.6, 29.4, 29.3, 26.1, 22.7 (CH_2), 14.1 (CH_3) ppm. MS (MALDI-TOF): *m/z* = 2707.1 [M$^+$ + Na]. $C_{174}H_{274}O_{20}$ (2686.08): calcd. C 77.79, H 10.29; found C 77.44, H 10.29.

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