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An Efficient Route to Stable Room-Temperature Liquid-Crystalline Triphenylenes

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Fourfold 2,3,6,10-alkoxycarbonyl-substituted triphenylenes are synthesised in five concise steps from 4-methylcyclohexanone by selective monoformylation of 2,6,10-trimethyltriphenylene, followed by oxidation in aqueous dichromate solution. Their low symmetry leads to mesogenic self assembly in a columnar liquid-crystalline state at or near room temperature, depending on the choice of alkyl group. These materials unite several properties that are desirable in charge-transporting thin films for organic optoelectronics: room-temperature self assembly into structures of good charge mobility and high viscosity, low electron density in the aromatic core, smooth synthetic access, and optical transparency.

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Introduction

The interest in the chemistry, physics and therapeutic effects of functionalised triphenylenes has increased continuously over the last decades, and they have gained considerable importance in such diverse fields as birefringent films for LCDs,[1] charge transporters in organic optoelectronics[2,3] and potential HIV inhibitors in AIDS therapy.[4]

The synthetically easily accessible triphenylene hexaethers and related materials are, together with octa- and tetrasubstituted phthalocyanines, the most extensively explored class of columnar liquid crystals since their invention in 1977,[5] and the extraordinary charge transport properties of columnar liquid crystals have first been demonstrated with triphenylene hexathioethers in 1994.[2] But in contrast to the hexaethers and thioethers (which are donor-type charge transporters), triphenylenecarboxylic acid derivatives with more than three carboxylic substituents (which reduce the electron density of the aromatic core and lead to a more acceptor-type character) are unknown to this date.

Triphenylenes are of particular interest for organic optoelectronics where relatively large aromatic systems with their good electronic overlap between neighbouring molecules are to be combined with the absence of absorption in the visible wavelength range (for example for blue-emitting organic LEDs): Amongst benzo-annelated areneoligocarboxylic esters, only benzene, naphthalene, phenanthrene and triphenylene derivatives do not absorb part of the visible spectrum in the condensed state.

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We have recently shown that the dehydrating cyclotrimerisation of 4-methylcyclohexanone followed by dehydrogenation and oxidation with dichromate yields triphenylene-2,6,10-tricarboxylic acid (**1**; Scheme 1), whose alkyl esters **2** show to a limited extent columnar and nematic liquid-crystalline phases.[6] This self assembly into columns gives rise to unidirectional charge transport,[2,3] and the enhanced photostability of arenecarboxylic acid derivatives[7] compared to arene ethers and thioethers makes such materials a preferred choice for robust devices.

The usefulness of triphenylene triesters **2** is limited because the liquid-crystalline temperature ranges are small, and mesophases that are thermodynamically stable at room temperature could not be obtained: Only a monotropic (i.e. metastable) mesophase is formed by the triethyl, tri-*n*-propyl and tri-*n*-butyl esters (columnar in the first case, nematic in the two others), triesters with longer *n*-alkyl chains are not mesogenic, and a thermotropic (i.e. stable) mesophase is obtained only by chain branching, the tris(2-ethyl)-hexyl ester showing a columnar mesophase in a narrow temperature range (see Table 1).

We therefore aimed to develop non-absorbing room-temperature columnar arenecarboxylates by increasing the number of carboxylate substituents and dissymmetrising the substitution pattern on **2**.

Results and Discussion

We have now found that 2,6,10-trimethyltriphenylene (**3**) is readily and regioselectively monoformylated at the peripheral 3-position, giving rise to a polar tetrasubstituted intermediate **4** which is readily oxidised with aqueous dichromate in a conventional stirred benchtop autoclave to give triphenylene-2,3,6,10-tetracarboxylic acid.

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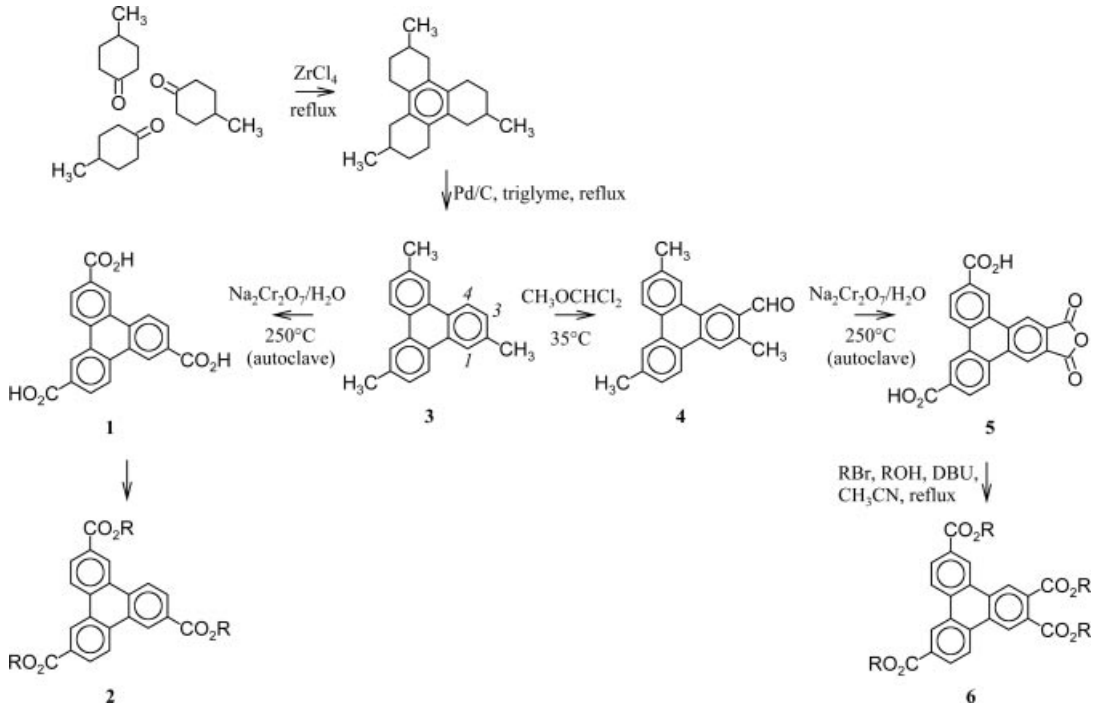

Scheme 1. Synthesis of tri- and tetraalkyl triphenylenetri- and -tetracarboxylates **2** and **6**.

Table 1. Phase-transition temperatures [°C] of **6a**–**6h** and **2a**–**2h**[6] (by differential scanning calorimetry, on heating).[a]

R	**6a**–**h**	**2a**–**h**
Ethyl (**a**)	cr-70-col$_h$-218-i	cr-161-[col$_h$-135-]i
n-Propyl (**b**)	cr-59-col$_h$-186-i	cr-137-[n-82-]i
n-Butyl (**c**)	cr-49-col$_h$-147-i	cr-86-[n-59-]i
n-Pentyl (**d**)	cr-50-col$_h$-109-i	cr-111-i
n-Hexyl (**e**)	cr-58-col$_h$-91-i	cr-101-i
n-Heptyl (**f**)	cr-46-col$_h$-64-i	cr-93-i
n-Octyl (**g**)	cr-50-i	cr-77-i
rac-2-Ethylhexyl (**h**)	col$_h$-121-i	cr-111-col$_h$-124-i

[a] cr = crystalline, col$_h$ = hexagonal columnar liquid-crystalline, n = nematic liquid-crystalline, i = isotropic liquid; monotropic phases are in square brackets.

Triphenylene can be regarded as an assembly of three fairly independent benzene moieties, linked by bonds that have mainly single-bond character.[8] It is therefore likely that substitution with deactivating groups may proceed beyond one-fold reaction, giving a mixture of mono-, di- and trisubstituted products. The Friedel–Crafts acetylation of triphenylene for example is known to yield either 2-acetyl- or 2,6-(or 2,7-)diacetyltriphenylene, depending on the temperature (refluxing carbon disulfide/refluxing 1,2-dichloroethane).[9]

In trimethyltriphenylene **3**, the 2-methyl group renders positions 3 (peripheral) and 4 (internal) sterically more similar than in triphenylene. We therefore performed Friedel–Crafts acetylations to check whether the regioselectivity of the reaction is maintained in **3**. We found that only the peripheral positions are reactive, yielding either 3-acetyl-2,6,10-trimethyltriphenylene or 3,7-diacetyl-2,6,10-trimethyltriphenylene, depending on the reaction conditions. We then had the choice to obtain **4** by applying the known 4-step synthesis of triphenylene-2-carboxaldehyde [(i) acylation, (ii) dichromate oxidation to the acid, (iii) $LiAlH_4$ reduction to the alcohol, (iv) Sarett oxidation],[10] or to attempt direct formylation. We found that formylation with dichloromethyl methyl ether and $TiCl_4$ conveniently yields the monoformylated product **4** smoothly without traces of regioisomers or of dialdehyde, the only critical parameter being the temperature: tarry byproducts reduce the yield if the reaction is carried out in refluxing dichloromethane, whereas a satisfying yield of 59% is obtained at 35 °C. Given that the two previous steps leading to trimethyltriphenylene **3**, i.e. the dehydrating cyclotrimerisation of refluxing 4-methylcyclohexanone with catalytic $ZrCl_4$ (where we simplified the reported procedure[11] by avoiding to work under pressure) and the aromatisation with Pd, can both be performed on a large scale (10–50 g), a tetrasubstituted triphenylene is thus accessible in three easy steps and convenient quantities. It should be noted that the cyclotrimerisation of 4-methylcyclohexanone can only give the regiosymmetrical 2,6,10-trimethyl hydrocarbon, which forms, as is evident from the ^{13}C NMR spectrum, in two diastereomers [(*R*,*R*,*R*/*S*,*S*,*S*) and (*R*,*R*,*S*/*S*,*S*,*R*)] of approximately equal abundance.

Whereas Friedman's oxidation of methyl-substituted arenes such as **3** with sodium dichromate in water at 250 °C under pressure had been reported to be efficient only in a shaken autoclave (the viscosity of the reaction medium and the phase separation of the starting hydrocarbon with the medium reportedly rendering stirred autoclaves inefficient),[12] we managed to obtain a reasonable yield of oxidation of **4** to the tetraacid or its monoanhydride **5** in a

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simple magnetically stirred benchtop autoclave (oxidation plus esterification to the soluble and well purifiable alkyl ester **6b** give an overall yield of 45%). We presumed initially that the ease of oxidation of the formyl substituent to a base-soluble carboxylate group greatly contributes to this improved reactivity by quickly solubilising the starting material and homogenising the reaction mixture. But when we tested this hypothesis by applying the same conditions to the oxidation of the apolar hydrocarbon **3**, we found that triacid **1** is obtained in similar yield (48% of **2b** from **3** via **1**). It seems thus that the presence of several oxidisable methyl groups contributes as well to an improved reactivity and therefore leads to good yields with standard benchtop equipment.

The final esterifications of the so obtained tri- and tetraacids were performed with the corresponding alkyl bromide (or iodide, in the case of ethyl) and the corresponding alkyl alcohol in acetonitrile with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as base, because we found potassium carbonate as well as triethylamine to be ineffective to achieve the heterogeneous esterification of insoluble **6** with long alkyl alcohols of limited polarity, such as 2-ethylhexanol.

The tetraalkyl esters **6** not only are more prone to form columnar liquid-crystalline phases than the corresponding trisubstituted triphenylenes **2**[13] due to the additional flexible substituent, they also are of particularly low symmetry which disfavours crystallisation entropically. This leads to low melting points and extended columnar temperature ranges in the *n*-alkyl derivatives **6a**–**6f** and to a mesophase that is stable at room temperature with the branched-chain 2-ethylhexyl derivative **6h** (Table 1). The columnar mesophase is of hexagonal symmetry in all liquid-crystalline derivatives, as is illustrated by the room-temperature X-ray diffractogram of **6h** (which shows, besides the broad disk spacing peak 001 and the main lattice peak 100, an unambiguously hexagonal 210 lattice peak, Figure 1), and by its growth pattern in thin films and droplets (Figure 2).

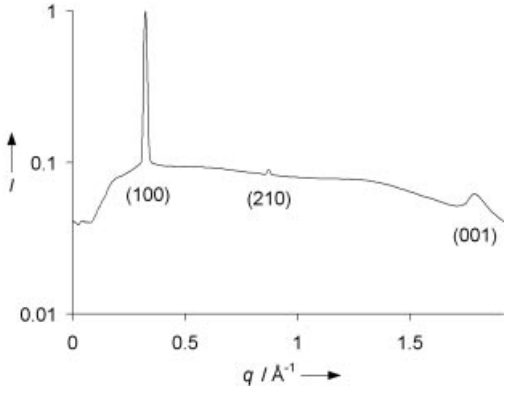

Figure 1. X-ray powder diffraction pattern of **6h** at 25 °C.

If the alkyl chains in **6** exceed a certain length and if they are all linear, the columnar mesophase is no longer present, because the molecular shape is no longer disk-like enough to induce the formation of the liquid-crystalline state. Thus,

Figure 2. Growth of a hexagonal columnar liquid-crystalline domain in homeotropic orientation (columns perpendicular to substrate) of **6h** upon cooling through the isotropic-to-LC phase-transition temperature on a silicon wafer, observed by differential interference contrast (DIC) microscopy in reflection (200 μm × 150 μm).

the *n*-octyl derivative **6g** lacks any mesophase (Table 1). This effect of chain length on self assembly is similar to the one that occurs in the triesters **2** at shorter chain lengths, where the ethyl, *n*-propyl and *n*-butyl triesters show ephemeral monotropic mesophases on cooling, whereas no liquid-crystalline behaviour is observed with *n*-pentyl or longer chains.

Conclusion

In summary, we have elaborated a straightforward synthetic pathway to triphenylene-2,3,6,10-tetracarboxylic acid and its tetraalkyl esters, and we have shown that by varying the degree of branching of the alkyl periphery, the propensity to liquid-crystalline self assembly can be adjusted efficiently to obtain a stable room-temperature mesophase. The physical study of the alignment[14] and wetting properties of **6h** in sub-micron thin films on semiconductor and electrode surfaces is currently under way.

Experimental Section

2,6,10-Trimethyl-dodecahydrotriphenylene: 4-Methylcyclohexanone (40 g, 0.35 mol) was refluxed with zirconium tetrachloride (4 g, 17 mmol) overnight. Water was formed during the reaction, creating a biphasic mixture. After cooling to room temperature, hot chloroform (100 mL) was added and the gumlike solids were filtered off. The solvent was distilled off, and the product was recristallised from butanol. Yield: 23.3 g (82 mmol, 69%) of a 1:1 mixture of the C_3-symmetrical (*R*,*R*,*R*/*S*,*S*,*S*) and the dissymmetrical (*R*,*R*,*S*/*S*,*S*,*R*) diastereomer, which are recognisable in the ^{13}C NMR spectrum, where the aliphatic signals tend to split into four peaks, of which one (of the *sym* isomer) is three times as large as the three others. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.86–2.40 (m, 9 H), 2.20–2.00 (m, 3 H), 1.96–167 (m, 6 H), 1.46–1.22 (m, 3 H),

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1.14–1.03 (m, 9 H, CH_3) ppm. ^{13}C NMR (300 MHz, APT, $CDCl_3$): δ = 131.8–131.7 (2×C_{Ar}*sym*, 6×C_{Ar}*dissym*), 36.2 (CH_2*sym*), 36.0 (CH_2*dissym*), 35.5 (CH_2*dissym*), 35.3 (CH_2*dissym*), 31.6 (CH_2*sym*), 31.4 (2×CH_2*dissym*), 31.0 (CH_2*dissym*), 29.2 (CH*sym*), 29.1 (CH*dissym*), 29.0 (CH*dissym*), 28.6 (CH*dissym*), 27.6 (CH_2*sym*), 27.3 (CH_2*dissym*), 26.7 (CH_2*dissym*), 26.1 (CH_2*dissym*), 22.6 (CH_3*sym*), 22.4 (2×CH_3*dissym*), 21.8 (CH_3*dissym*) ppm. $C_{21}H_{30}$ (282.46): calcd. C 89.29, H 10.71; foundC 89.51; H 10.49.

2,6,10-Trimethyltriphenylene (3): The mixture of dodecahydro isomers (15 g, 53 mmol) was refluxed with 10% Pd/C (1.5 g, 1.4 mmol) in 50 mL of triglyme under argon for several hours until the end of gas formation. After cooling to room temperature, chloroform (250 mL) was added and the mixture was heated to reflux to redissolve the partially precipitated product. The mixture was filtered hot, the chloroform was evaporated and the product was recrystallised from butanol. Yield: 11.0 g (41 mmol, 77%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8 Hz, 3 H, ArH), 8.36 (s, 3 H, ArH), 7.40 (d, *J* = 8 Hz, 3 H, ArH), 2.58 (s, 9 H, CH_3) ppm. ^{13}C NMR (300 MHz, APT, $CDCl_3$): δ = 136.9 (C_{Ar}), 130.1 (C_{Ar}), 128.2 ($C_{Ar}H$), 127.1 (C_{Ar}), 123.2 (2×$C_{Ar}H$), 21.9 (CH_3) ppm. $C_{21}H_{18}$ (270.37): calcd. C 93.29, H 6.71; found C 93.47, H 6.53.

2,6,10-Trimethyltriphenylene-3-carboxaldehyde (4): At 0 °C, a 1 M solution of titanium tetrachloride in dichloromethane (50 mL) was slowly added under argon to a vigorously stirred suspension of **3** (10 g, 37 mmol) in dichloromethane (75 mL). Then 1,1-dichloromethyl methyl ether (50 mL, 0.55 mol) was added slowly at 0 °C and the mixture was stirred at room temperature overnight. The mixture was finally stirred at 35–40 °C for 90 min (reflux temperature is to be avoided as it reduces the yield). After dilution with dichloromethane (125 mL), the mixture was poured onto ice/water with stirring, the phases were separated, the aqueous phase was washed with dichloromethane, the united organic fractions were dried with sodium sulfate, the sulfate was filtered off, the solvent was evaporated and the product was purified by column chromatography (silica gel, dichloromethane). Yield: 6.5 g (22 mmol, 59%). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.48 (s, 1 H, CHO), 8.87 (s, 1 H, ArH), 8.58 (d, *J* = 8 Hz, 1 H, ArH), 8.50 (d, *J* = 8 Hz, 1 H, ArH), 8.48 (s, 1 H, ArH), 8.41 (s, 1 H, ArH), 8.29 (s, 1 H, ArH), 7.63 (d, *J* = 8 Hz, 1 H, ArH), 7.60 (d, *J* = 8 Hz, 1 H, ArH), 2.96 (s, 3 H, CH_3), 2.83 (s, 3 H, CH_3), 2.81 (s, 3 H, CH_3) ppm. ^{13}C MR (300 MHz, APT, $CDCl_3$): δ = 192.7 (CHO), 138.5 (C_{Ar}), 137.5 (2×C_{Ar}), 137.3 (C_{Ar}), 133.9 (C_{Ar}), 132.4 (C_{Ar}), 131.3 (C_{Ar}), 129.4 (C_{Ar}), 128.9 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.4 ($C_{Ar}H$), 127.4 (C_{Ar}), 127.3 (C_{Ar}), 125.8 ($C_{Ar}H$), 124.1 ($C_{Ar}H$), 123.2 (3×$C_{Ar}H$), 22.0 (CH_3), 21.8 (CH_3), 20.0 (CH_3) ppm. $C_{22}H_{18}O$ (298.38): calcd. C 88.56, H 6.08; found C 88.70, H 6.19.

Tetrapropyl Triphenylene-2,3,6,10-tetracarboxylate (6b): To a vigorously stirred suspension of **4** (3.5 g, 12 mmol) in water (56 mL), sodium dichromate dihydrate (19.0 g, 64 mmol) was slowly added in small portions. The resulting red suspension was transferred to a 100-mL stirred autoclave ("Model I" from Carl Roth GmbH & Co KG, Karlsruhe) and stirred at 250 °C overnight. The internal pressure rose to about 45 bar during heat-up and remained approximately constant during the reaction. After cooling to room temperature, the autoclave contents were washed out with water, the green chromium salts were filtered off and the formed triphenylene-2,3,6,10-tetracarboxylic acid was precipitated by addition of excess concd. hydrochloric acid. After filtration and vacuum drying at 100 °C, 3.8 g of crude triphenylene-2,3,6,10-tetracarboxylic acid 2,3-anhydride was obtained, which was powdered and added to a stirred solution of propyl bromide (20 g, 0.16 mol), propanol (14 g, 0.23 mol) and DBU (16 g, 0.11 mol) in acetonitrile (200 mL). The mixture was refluxed overnight, the solvent and volatile reagents were evaporated, methanol (700 mL) was added, the precipitate was filtered off and purified by column chromatography (silica gel, chloroform/ethyl acetate, 9:1) and recrystallisation from methanol. Yield: 3.0 g (5.2 mmol, 45%). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.39 (d, *J* = 1 Hz, 1 H, ArH), 9.36 (d, *J* = 1 Hz, 1 H, ArH), 9.06 (s, 1 H, ArH), 9.03 (s, 1 H, ArH), 8.80 (d, *J* = 9 Hz, 1 H, ArH), 8.73 (d, *J* = 9 Hz, 1 H, ArH), 8.38 (dd, *J* = 9 Hz, *J* = 1 Hz, 1 H, ArH), 8.36 (dd, *J* = 9 Hz, *J* = 1 Hz, 1 H, ArH), 4.43–4.37 (m, 8 H, 4×OCH_2), 1.92–1.82 (m, 8 H, 4×CH_2), 1.10 (t, *J* = 7 Hz, 6 H, 2×CH_3), 1.07 (t, *J* = 7 Hz, 3 H, CH_3), 1.06 (t, *J* = 7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (400 MHz, APT, $CDCl_3$): δ = 167.6 (2×CO_2), 166.3 (2×CO_2), 133.7 (C_{Ar}), 132.7 (C_{Ar}), 131.9 (C_{Ar}), 131.7 (C_{Ar}), 130.8 (C_{Ar}), 130.6 (C_{Ar}), 130.3 (C_{Ar}), 129.9 (C_{Ar}), 129.6 (C_{Ar}), 128.9 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.6 (C_{Ar}), 126.1 ($C_{Ar}H$), 125.9 ($C_{Ar}H$), 125.6 ($C_{Ar}H$), 124.9 ($C_{Ar}H$), 124.2 ($C_{Ar}H$), 123.8 ($C_{Ar}H$), 67.7 (2×OCH_2), 67.1 (2×OCH_2), 22.2 (2×CH_2), 22.0 (2×CH_2), 10.6 (4×CH_3) ppm. $C_{34}H_{36}O_8$ (572.65): calcd. C 71.31, H 6.34; found C 71.11, H 6.46.

Tetrakis(2-ethylhexyl) Triphenylene-2,3,6,10-tetracarboxylate (6h): Because the well crystallising propyl derivative **6b** is more easily purified after the oxidation/esterification sequence than the higher homologues, tetraesters with alkyl chains longer than propyl were synthesised from **6b** by alkyl group exchange: **4** (3 g) was refluxed in 10% ethanolic potassium carbonate solution (300 mL) for 1 d, the solvent was evaporated, the residue was dissolved in water (200 mL) and an excess of concd. hydrochloric acid was added to precipitate the gelatinous tetraacid, which was filtered off, washed with water and dried under vacuum at 100 °C to yield 2.5 g of crude triphenylenetetracarboxylic acid anhydride, which was powdered and added to a stirred solution of 2-ethylhexyl bromide (20 g, 0.10 mol), 2-ethylhexanol (14 g, 0.11 mol) and DBU (16 g, 0.11 mol) in acetonitrile (200 mL). The mixture was refluxed overnight, the solvent was evaporated, methanol (700 mL) was added, the precipitate was filtered off and purified by column chromatography (silica gel, dichloromethane/pentane, 1:1) and reprecipitation from ethanol. Yield: 2.7 g (3.2 mmol, 60%). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.41 (d, *J* = 1 Hz, 1 H, ArH), 9.38 (d, *J* = 1 Hz, 1 H, ArH), 9.07 (s, 1 H, ArH), 9.05 (s, 1 H, ArH), 8.82 (d, *J* = 9 Hz, 1 H, ArH), 8.75 (d, *J* = 9 Hz, 1 H, ArH), 8.40 (dd, *J* = 9 Hz, *J* = 1 Hz, 1 H, ArH), 8.38 (dd, *J* = 9 Hz, *J* = 1 Hz, 1 H, ArH), 4.44–4.29 (m, 8 H, 4×OCH_2), 1.90–1.73 (m, 4 H, 4×CH), 1.60–1.25 (m, 32 H, 16×CH_2), 1.05–0.85 (m, 24 H, 8×CH_3) ppm. ^{13}C NMR (400 MHz, APT, $CDCl_3$): δ = 167.9 (CO_2), 167.5 (CO_2), 166.4 (2×CO_2), 133.6 (C_{Ar}), 132.8 (C_{Ar}), 132.1 (C_{Ar}), 130.9 (C_{Ar}), 130.6 (C_{Ar}), 130.4 (C_{Ar}), 130.1 (C_{Ar}), 129.7 (C_{Ar}), 129.6 (C_{Ar}), 129.0 ($C_{Ar}H$), 128.8 ($C_{Ar}H$), 128.7 (C_{Ar}), 126.2 ($C_{Ar}H$), 126.0 ($C_{Ar}H$), 125.7 ($C_{Ar}H$), 125.0 ($C_{Ar}H$), 124.3 ($C_{Ar}H$), 124.1 ($C_{Ar}H$), 68.8 (2×OCH_2), 68.0 (2×OCH_2), 39.1 (2×CH), 38.9 (2×CH), 30.8 (2×CH_2), 30.6 (2×CH_2), 29.2 (4×CH_2), 24.2 (2×CH_2), 24.0 (2×CH_2), 23.1 (4×CH_2), 14.2 (4×CH_3), 11.2 (4×CH_3) ppm. $C_{54}H_{76}O_8$ (853.18): calcd. C 76.02, H 8.98; found: C 75.89, H 8.91.

Tripropyl Triphenylene-2,6,10-tricarboxylate (2b): 2b was obtained from **3** (3.2 g, 12 mmol) in exactly the same way as **6b** from **4**. Yield: 2.8 g (5.8 mmol, 48%). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.38 (s, 3 H, ArH), 8.80 (d, *J* = 8 Hz, 3 H, ArH), 8.36 (d, *J* = 8 Hz, 3 H, ArH), 4.42 (t, *J* = 7 Hz, 6 H, OCH_2), 1.91 (sext, *J* = 7 Hz, 6 H, CH_2), 1.12 (t, *J* = 7 Hz, 9 H, CH_3) ppm. ^{13}C NMR (400 MHz, APT, $CDCl_3$): δ = 166.3 (CO_2), 133.5 (C_{Ar}), 129.4 (C_{Ar}), 128.8 (C_{Ar}), 128.5 ($C_{Ar}H$), 125.9 ($C_{Ar}H$), 123.8 ($C_{Ar}H$), 67.0 (OCH_2), 22.2 (CH_2), 10.6 (CH_3) ppm. $C_{30}H_{30}O_6$ (486.56): calcd. C 74.06, H 6.21; found: C 74.10, H 6.29.

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