Purification of 2,3,6,7,10,11-Hexamethoxytriphenylene and Preparation of Hexakiscarbonylmethyl and Hexakiscyanomethyl Derivatives of 2,3,6,7,10,11-Hexahydroxytriphenylene

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2,3,6,7,10,11-Hexamethoxytriphenylene (**1**) was subjected to an improved purification procedure and demethylated to give 2,3,6,7,10,11-hexahydroxytriphenylene (**2**) as the relatively stable trihydrate. Compound **2** was alkylated with reactive halogen reagents giving 2,3,6,7,10,11-hexakis(cyanomethyl)triphenylene (**3**), 2,3,6,7,10,11-hexakis(*N*,*N*-diethylcarbamoylmethyloxy)triphenylene (**4**) and 2,3,6,7,10,11-hexakis(ethoxycarbonylmethyloxy)triphenylene (**5**). Reduction of **4** gave 2,3,6,7,10,11-hexakis(diethylaminoethyloxy)triphenylene (**6**) and reduction of **5** followed by acetylation gave 2,3,6,7,10,11-hexakis(acetyloxyethyloxy)triphenylene (**7**). Hydrolysis of **5** gave 2,3,6,7,10,11-hexakis(carboxymethyloxy)triphenylene (**8**). Compound **8** could be converted to its corresponding active *N*-hydroxysuccinimide ester (**9**) by the DCC method. Compound **9** was found to be a versatile core molecule that could be coupled with glycine-*t*-butyl ester, L-phenylalanine and L-phenylalanine-*t*-butyl ester giving compounds **10**, **11** and **12**.

Compound **1** was first isolated as a result of a study of the pigment in *Ustilago maydis* spores by Piattelli et al.[1] who also reported a demethylation procedure to yield **2** (Scheme 1). Procedures for the preparation of **1** were later reported, first by Marquardt[2] and then by Musgrave et al.[3] Compound **2** is of strong interest as a starting material for the preparation of materials such as discotic liquid crystals,[4,5] semiconductors from doped hexaalkoxytriphenylenes[6,7] or applications where advantage is taken of the molecular properties that the triphenylene nucleus possesses. An example is the strong fluorescence[8] that is often associated with triphenylene derivatives or the triplet ground state dication[9,10] of the triphenylene system. Improved preparative procedures for **1** have been published recently.[11-13] The oxidation of 1,2-dimethoxybenzene to form **1** is accompanied by the formation of a myriad of polyalkoxy-dibenzo-naphthacenequinone molecules as shown by Musgrave et al.[3,14] Associated with these molecules are certain analytical problems such as: insolubility, failure to volatilize during mass spectral analysis, failure to combust when subjected to elemental analysis and a very strong interaction with silica as pointed out by Musgrave et al.[3,14] The purity of the crude product is thus hard to establish by conventional methods. The removal of the polyalkoxy-dibenzo-naphthacenequinone molecules is absolutely necessary if contamination of the desired product with structurally similar molecules is to be avoided.

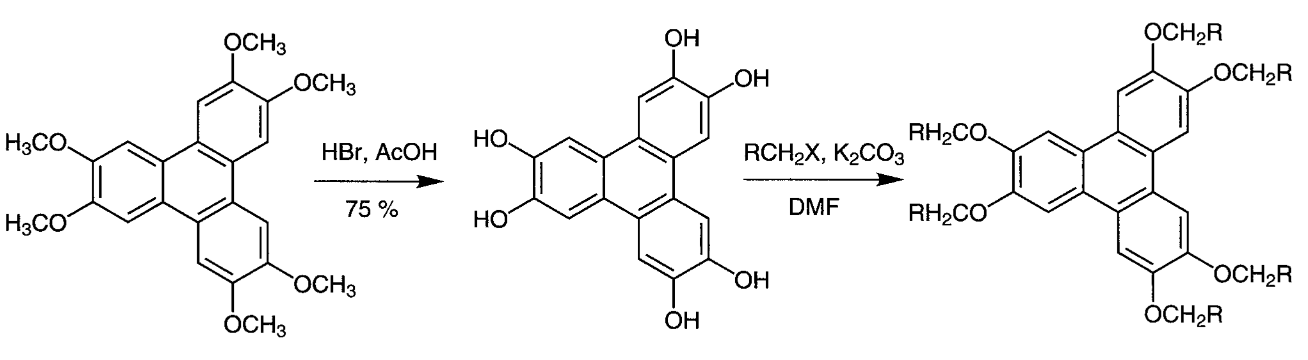
Ringsdorf and co-workers[15] have described the properties of compounds such as **5** and analogues of **8**, but no experimental details for their synthesis were given.

In this paper we describe how large amounts of **1** can be purified such that the quinoid products mentioned above are eliminated. This was done by taking advantage of the strong interaction of these quinoid products with silica by boiling the crude product with silica in $CHCl_3$. The solids thus obtained were air-dried thus ensuring complete oxidation of the quinoid products followed by Soxhlet extraction of the solids. A crude sample prepared by the method of Boden et al.[12] and a crude sample prepared by the method of Naarmann et al.[13] were sub-

Table. The Distribution of Products Obtained in the Synthesis of **2** by Three Methods

Method by	Phenols[a] (%)	**2** (%)	Other[b] (%)
Naarmann[13]	2	95	3
Boden[12]	7	90	3
Our	11[c]	89	0

[a] The amount of penta-, tetra- and trimethoxytriphenylene present.
[b] The amount of naphthacenequinones.
[c] In our case only the pentamethoxytriphenylene was found.



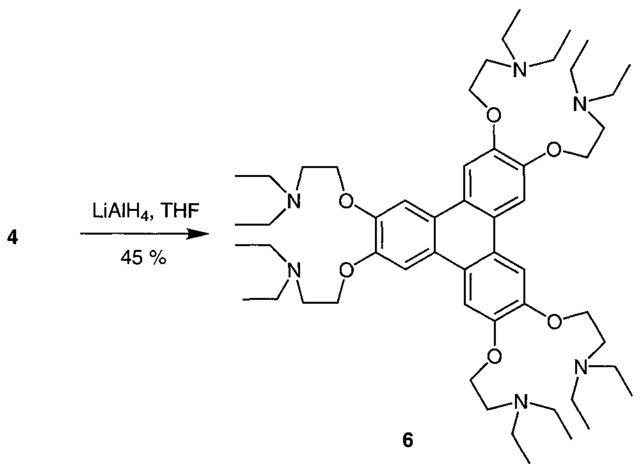
1

2

3 (R = CN, X = Cl), 60 %
4 (R = $CONEt_2$, X = Cl), 43 %
5 (R = COOEt, X = Br), 50 %

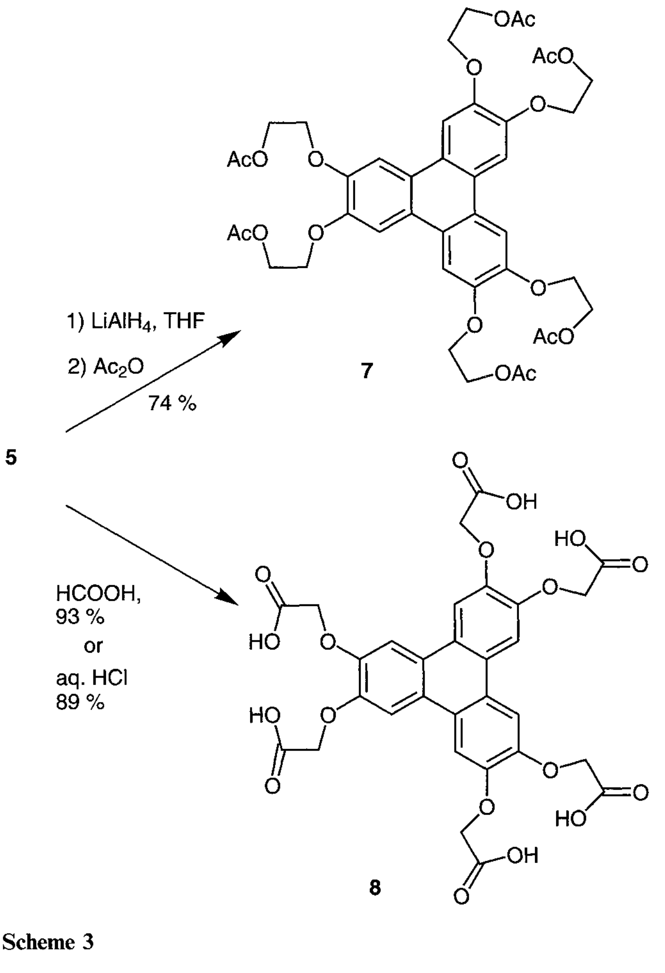
Scheme 1

jected to reverse phase HPLC using an acetonitrile/water solvent system. Common to the samples prepared by the two methods was a noticeable degree of demethylation. The purity by HPLC of the crude product as compared to a sample purified by our method and the distribution of the impurities is presented in the Table. Subsequent derivatization of **2** with reactive halogen alkylating agents gave **3**, **4** and **5** (Scheme 1). Reduction of **4** gave **6** (Scheme 2).



Scheme 2

Reduction of **5** followed by acetylation yielded **7**, whereas transesterification or hydrolysis of **5** yielded **8**. Direct alkylation of **2** with α-haloacetic acid to give **8** is associated with the same problems as encountered in the case of the preparation of 1,2-bis(carboxymethyloxy)benzene,[16] where it is known that sodium and potassium ions bind strongly to the product and are not easily removed. The indirect method published here is thus preferable also when considering that the role of formic acid in the transesterification of **5** to give **8** is not only to accept the ethyl groups but also to serve as an antioxidant. Compound **8** could be transformed to its corresponding active ester **9** by reaction with *N*-hydroxysuccinimide/DCC. Compound **9** was found to be a versatile reagent that could be reacted with various mild nucleophiles such as amino acids and amino acid esters thus in principle allowing for the triphenylene system to be incorporated into polymers or supramolecular systems. Compound **9** was reacted with glycine-*t*-butyl ester, L-phenylalanine and L-phenylalanine-*t*-butyl ester giving compound **10**, **11** and **12**. The *t*-butyl esters were prepared by esterification of the *N*-phthaloyl protected amino acids followed by deprotection.[17] The advantage of the *t*-butyl esters lies in the increased solubility of the product. Finally we have verified the earlier observation[15] that **5** exhibits a liquid crystalline mesophase beween 126 °C and 179 °C and found that compounds **3**, **4**, **6**, **7**, **8**, **9**, **10**, **11** and **12** exhibit no such phase.



Scheme 3

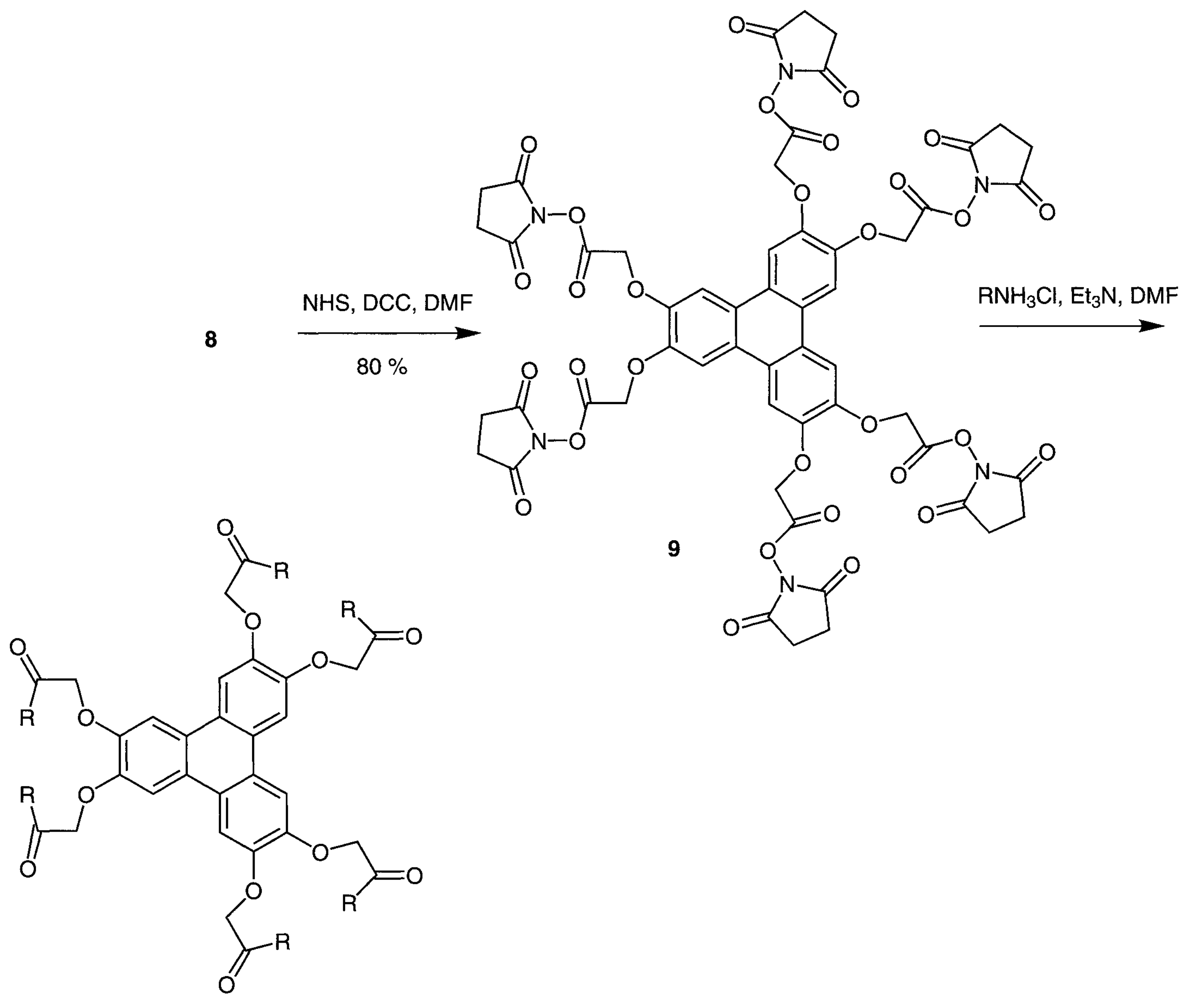
THF was dried by distillation from benzophenone/Na and DMF was dried by distillation from CaH_2. CH_2Cl_2 was dried by passage through basic alumina. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 250 MHz NMR spectrometer. Melting points were determined using a melting point microscope. Differential scanning calorimetry was recorded on a Perkin-Elmer DSC7 and are reported only for compounds where no decomposition was observed upon heating. Mass spectra were recorded on a JEOL JMS HX110-110T mass spectrometer. HPLC separations were performed on a Shimadzu chromatographic system comprising a pump (LC-10AD), column oven (CTO-10A), photodiode array detector (SPD-M10A) and a homepacked column.

Experimental Conditions for HPLC

The column contained Nucleosil 5 μ C18, column dimensions 250 mm × 4.6 mm ID. The mobile phase was MeCN containing H_2O (30 %) and TFA (0.03 %). The flow rate was 1 mL/min and the temperature was 40 °C. The purity was based on the optical absorption at 280 nm.

Purification of 2,3,6,7,10,11-Hexamethoxytriphenylene (1):

The crude product was obtained by adding veratrole (109 g, 0.79 mol), dissolved in anhyd CH_2Cl_2 (0.5 L), over a period of 2 h to a mechanically stirred suspension of anhyd $FeCl_3$ (330 g, 2.03 mol) and CF_3COOH (100 mL) in CH_2Cl_2 (1.5 L). It was important that the addition was done dropwise and not faster than 2 h otherwise a thick mass formed preventing proper mixing of the reactants. Immediately after the addition began, a deep blue colour developed due to the radical cation of the triphenylene. The HCl (g) which formed was removed in a well-ventilated place with a hose. After the addition the mixture was left to stir overnight. The thick greenish-black precipitated 2,3,6,7,10,11-hexamethoxytriphenylenium tetrachloroferrate was filtered on a large sintered funnel and washed with CH_2Cl_2 (2 × 500 mL). The salt was added in small portions to MeOH (500 mL) with stirring. The MeOH serves to reduce the salt (exothermic, CH_2O boils off). The colour changed to pale yellow. The product was filtered and washed with H_2O (300 mL), sodium dithionite solution (300 mL, 0.05 M) to reduce the quinoid byproducts and finally H_2O (300 mL). The moist product was transferred to a 1 L flask containing $CHCl_3$ (0.5 L) and silica (20 g). The mixture was refluxed for 1 h and the solids



10 (R = $NHCH_2COO$-t-Bu), 92 %
11 (R = NHCH(Bz)COOH), 50 %
12 (R = NHCH(Bz)COO-t-Bu), 33 %

Scheme 4

containing the major part of the product were filtered. The filtrate contained only a little of **1** (4 g) which was obtained by drying the $CHCl_3$ phase ($MgSO_4$), treating with activated carbon and filtering through silica (20 g) while hot. Upon cooling **1** crystallizes from the light yellow $CHCl_3$ solution. The solids containing the major part of the product were left to dry in the air for 7 days (this is important!) in the dark. After this period of time the solids were transferred to a large Soxhlet apparatus and extracted with $CHCl_3$. After a few hours **1** began to crystallize in the extract as slightly yellow crystals. The extraction time depends on the design of the Soxhlet etc. but in our case 48 h was sufficient. The extract was allowed to cool. One volume of MeOH was added and the product was filtered and recrystallized from $CHCl_3$/EtOH (5:1). Colourless crystals were obtained (58.8 g, 54%); HPLC: retention volume 7.25 mL, purity 88.7%. This product contained 11% 2-hydroxy-3,6,7,10,11-pentamethoxytriphenylene and had a purity of 99.7% with respect to 2,3,6,7,10,11-hexaoxytriphenylene. Remethylation of the product was done by stirring the purified product (1 g), dried powdered K_2CO_3 (5 g), and MeI (2 mL) in DMF (0.15 L) for two days at ambient temperature under Ar. The mixture was poured into H_2O (0.5 L) and the precipitated product was filtered and dried. The remethylated product was 99.97% pure **1** (0.96 g, 96% yield based on the triphenylene core). Analytical data are in accordance with literature.[1–3,11–13]

2,3,6,7,10,11-Hexahydroxytriphenylene (2) · $3H_2O$: 2,3,6,7,10,11-Hexamethoxytriphenylene[3,11–13] (**1**) (7.32 g, 19 mmol) obtained as described above was suspended in 47% HBr (aq) (250 mL) and HOAc (250 mL). The suspension was deoxygenated by passing a stream of Ar through the suspension for 5 min. The mixture was refluxed overnight under Ar. After 24 h, the dark solution was allowed to cool slowly under Ar. After another 5 h the crystals were filtered and washed with Et_2O. The product was recrystallized from H_2O/HOAc (3:2, 500 mL) by treating with activated carbon, followed by filtration. Colourless needles were obtained (5.4 g, 75%). The crystals are somewhat sensitive to air and should be stored under Ar; mp: > 360 °C.[1,11] The remaining analytical data is in accordance with the literature.[1]

Anal. Calcd for $C_{18}H_{12}O_6$, $3H_2O$ (378.33): C, 57.14; H, 4.79; Found: C, 56.9; H, 4.19.

2,3,6,7,10,11-Hexakis(cyanomethyl)triphenylene (3):
2-Chloroacetonitrile (2.64 g, 35 mmol) and dried powdered K_2CO_3 (13.8 g, 100 mmol) were mixed in DMF (100 mL) and deoxygenated by passing a rapid stream of Ar through the suspension. After 5 min, compound **2** · $3H_2O$ (1.89 g, 5 mmol) was added and the suspension was stirred under Ar for 48 h at r.t. The mixture was poured into H_2O (1 L) and the resulting mixture was neutralised with H_2SO_4 (5 M) which made filtration easier. The product was filtered, washed with H_2O (3 x 100 mL) and dried. The crude product thus obtained was recrystallized by dissolution in refluxing MeCN (500 mL), treatment with activated carbon and filtering while hot. This gave compound **3** (1.68 g, 60 %) as white crystals; mp: 318–320 °C.

^{1}H NMR ($CDCl_3$): $\delta = 5.6$ (s, 12H, OC*H*$_2$CN), 8.46 (s, 6H, Ar*H*).

^{13}C NMR ($CDCl_3$): $\delta = 56.14$ (*C*H$_2$), 110.60 (Ar*C*H), 117.43 (*C*N), 125.46 (Ar*C*), 147.57 (Ar*C*O).

MS: (EI) 558 (M$^+$) 20 %; HPLC: retention volume, 25.30 mL, purity 97.3 %.

Anal. Calcd for $C_{30}H_{18}N_6O_6$ (558.51): C, 64.52; H, 3.25; N, 15.06; Found: C, 64.23; H, 3.25; N, 15.20.

2,3,6,7,10,11-Hexakis(*N*,*N*-diethylcarbamoylmethoxy)triphenylene (4):
N,*N*-Diethylchloroacetamide (7.2 g, 48 mmol) and dried powdered K_2CO_3 (20 g, 140 mmol) were mixed in DMF (300 mL) and deoxygenated by passing a rapid stream of Ar through the suspension. After 5 min, compound **2** · $3H_2O$ (3.0 g, 8.0 mmol) was added and the suspension was stirred under Ar at r.t. for 48 h. The brown, very fine suspension was poured into H_2O (1 L). The mixture was then extracted with CH_2Cl_2 (4 x 300 mL). The organic phases were combined, washed with H_2O (0.5 L) and dried ($MgSO_4$). The brownish organic phase with a green fluorescence was filtered through 40 cm^3 of flash silica gel and evaporated to give a brown oil which crystallized into a light yellow compound when suspended in a 1 : 1 mixture of toluene and light petroleum (bp 80–100 °C). The crude product was filtered and recrystallized from toluene/light petroleum (bp 80–100 °C) (500 mL) using activated carbon to give **4** as fine white needles (3.79 g, 43 %). Differential scanning calorimetry (DSC) showed melting in the interval 171.3–185.4 °C, onset at 179.3 °C, peak at 180.8 °C, 63.0 kJ/mol.

^{1}H NMR ($CDCl_3$): $\delta = 1.1$ (t, 18H, 7 Hz, C*H*$_2$), 1.2 (t, 18H, 7 Hz, C*H*$_3$), 3.3–3.4 (q, 12H, 7 Hz, NC*H*$_2$CH$_3$), 3.5–3.6 (q, 12H, 7 Hz, NC*H*$_2$CH$_3$), 4.95 (s, 12H, OC*H*$_2$C=O), 7.95 (s, 6H, Ar*H*).

^{13}C NMR ($CDCl_3$): $\delta = 12.68$ (*C*H$_3$), 14.15 (*C*H$_3$), 40.10 (N*C*H$_2$), 41.48 (N*C*H$_2$), 68.67 (O*C*H$_2$), 107.74 (Ar*C*H), 123.89 (Ar*C*), 147.55 (Ar*C*O), 166.90 (*C*=O).

MS: (FAB$^+$) 1003 (M$^+$) 100 %; HPLC: retention volume, 6.14 mL, purity 96.2 %.

Anal. Calcd for $C_{54}H_{78}N_6O_{12}$ (1003.24): C, 64.64; H, 7.83; N, 8.37; Found: C, 63.80; H, 7.66; N, 8.16.

2,3,6,7,10,11-Hexakis(ethoxycarbonylmethoxy)triphenylene (5):
Ethyl bromoacetate (10 g, 60 mmol) and dried powdered K_2CO_3 (20 g, 140 mmol) were mixed in DMF (500 mL) and deoxygenated by passing a rapid stream of Ar through the suspension. After 5 min, compound **2** · $3H_2O$ (3.0 g, 8 mmol) was added and the suspension was stirred under Ar at r.t. for 48 h. The brown, very fine suspension was poured into H_2O (1 L) and stirred for 5 min. The yellow-white powdery product was filtered (time consuming) and washed with H_2O. The product was dissolved in refluxing EtOH (100 mL), treated with activated carbon, filtered, and left to crystallize in the freezer. The hair-fine colourless crystals were filtered, dried, and recrystallized from toluene/light petroleum (bp 50–70 °C) (750 mL) (3.8 g, 50 % yield). Differential scanning calorimetry (DSC) showed a wax temperature (mesophase transition) in the interval 105.0–129.1 °C, onset at 121.2 °C, peak at 124.4 °C. 39.2 kJ/mol, and melting in the interval 157.5–172.5 °C, onset at 165.4 °C, peak at 166.9 °C, 13.5 kJ/mol.

^{1}H NMR ($CDCl_3$): $\delta = 1.3$–1.4 (t, 18H, 7 Hz, C*H*$_3$), 4.3–4.4 (q, 12H, 7 Hz, OC*H*$_2$CH$_3$), 4.85 (s, 12H, OC*H*$_2$C=O), 7.55 (s, 6H, Ar*H*).

^{13}C NMR($CDCl_3$): $\delta = 14.06$ (*C*H$_3$), 61.12 (O*C*H$_2$CH$_2$), 66.59 (O*C*H$_2$–C=O), 108.32 (Ar*C*H), 123.83 (Ar*C*), 147.09 (Ar*C*O), 168.79 (*C*=O).

MS: (EI) 840 (M$^+$) 100 %.

HPLC: retention volume, 10.53 mL, purity 90.3 %.

Anal. Calcd. for $C_{42}H_{48}O_{18}$ (840.83): C, 60.00; H, 5.75; Found: C, 59.58; H, 5.76.

2,3,6,7,10,11-Hexakis(diethylaminoethoxy)triphenylene (6):
$LiAlH_4$ pellets (1.44 g, 36 mmol) were dissolved in anhyd THF (125 mL) in a dry flask under Ar by stirring the mixture overnight. Compound **4** (2.0 g, 2 mmol) dissolved in anhyd THF (75 mL) was added to form a cloudy slightly green coloured solution. The mixture was refluxed for 1 day and left to stir for two days. The mixture was hydrolyzed by the dropwise addition of H_2O (4 mL) (caution!), whereby the colour changed to light yellow. NaOH (10 g) dissolved in H_2O (100 mL) was added. The light yellow organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 200 mL). The organic phases were combined and dried (K_2CO_3, 50 g) and evaporated to give a light yellow viscous oil (1.45 g). The product was dissolved in HCl (aq) (100 mL, 20 %) and washed with Et_2O (2 x 100 mL) and CH_2Cl_2 (2 x 100 mL). The acidic aqueous phase containing the product was poured onto a mixture of ice (300 g) and NaOH (200 mL, 5 M). The mixture was extracted with $CHCl_3$ (3 x 150 mL). The combined organic phase was dried (K_2CO_3, 15 g) and filtered through silica (20 g). The filtrate was evaporated to give a light yellow oil which crystallized slowly (0.82 g, 45 % yield). Differential scanning calorimetry (DSC) showed melting in the interval 32.7–88.2 °C, onset at 68.4 °C, peak at 74.4 °C, 39.5 kJ/mol.

^{1}H NMR ($CDCl_3$): $\delta = 1.1$ (t, 36H, 7 Hz, C*H*$_3$), 2.7 (q, 24H, 7 Hz, NC*H*$_2$CH$_3$), 3.0 (t, 12H, 7 Hz, OCH$_2$C*H*$_2$N), 4.3 (t, 12H, 7 Hz, OC*H*$_2$CH$_2$N), 7.9 (s, 6H, Ar*H*).

^{13}C NMR ($CDCl_3$): $\delta = 11.86$ (*C*H$_3$), 47.79 (N*C*H$_2$CH$_3$), 51.78 (*C*H$_2$NEt$_2$), 67.83 (Ar*C*O), 106.62 (Ar*C*H), 123.45 (Ar*C*), 148.43 (Ar*C*O).

MS: (EI) 100 (100 %), 86 (31 %) 820 (7 %), 721 (3 %), 919 (M$^+$, 3 %), 622 (2 %).

HPLC: retention volume, 1.96 mL, purity 93.6 %.

Anal. Calcd. for $C_{54}H_{90}N_6O_6$ (919.34): C, 70.57; H, 9.87; N, 9.15; Found: C, 69.90; H, 9.94; N, 9.00.

2,3,6,7,10,11-Hexakis(acetoxyethoxy)triphenylene (7):
Compound **5** (2.2 g, 2.6 mmol) was dissolved in anhyd THF (75 mL) in a dry flask under Ar. The solution was stirred while $LiAlH_4$ (2.0 g, 58 mmol) was added. Hydrogen was evolved and the temperature rose somewhat. The mixture was stirred for 4 days at ambient temperature after which it was hydrolyzed by the dropwise addition of H_2O (caution!). Aqueous HCl (37 %, 4 mL) was then added. After standing for 1 h the THF was decanted from the aluminium salts and the product. The THF contained 100 mg of byproducts. The precipitate was stirred overnight with aq HCl (200 mL, 1 M). A solid precipitated and the suspension was evaporated to dryness in vacuo. The solid was refluxed for 2 h with Ac_2O (200 mL, 2.12 mol) and pyridine (20 mL, 0.25 mol). H_2O (100 mL) was added dropwise through the condenser to hydrolyse the Ac_2O (caution!). The light yellow solution was poured into crushed ice (1 kg) and the precipitated white product was filtered, washed with H_2O and dried over H_2SO_4 (conc.) in a vacuum desiccator overnight. Recrystallization from refluxing $CHCl_3$/light petroleum ether (bp 80–100 °C) (100 mL) gave compound **7** as fine white needles (1.6 g, 74 % yield); mp 137.5 °C.

^{1}H NMR ($CDCl_3$): $\delta = 2.15$ (s, 18H, C*H*$_3$C=O), 4.4–4.6 (double t, 24H, ArOC*H*$_2$C*H*$_2$OAc), 7.9 (s, 6H, Ar*H*).

^{13}C NMR ($CDCl_3$): $\delta = 20.79$ (CH_3), 62.61 (ArOCH_2), 67.35 ($CH_2OC{=}O$), 108.17 (ArCH), 123.98 (ArC), 148.28 (ArCO), 170.95 ($C{=}O$).

MS: (EI) 840 (M^+) 100%.

HPLC: retention volume, 6.55 mL, purity 97.1%; Anal. Calcd for $C_{42}H_{48}O_{18}$ (840.83): C, 60.00; H, 5.75; Found: C, 59.96; H, 5.77.

2,3,6,7,10,11-Hexakis(carboxymethoxy)triphenylene (8):
Compound **5** (4.20 g, 5 mmol) was dissolved in formic acid (75 mL). Three drops of methanesulfonic acid were added and the solution was refluxed for 5 h and cooled to r.t. To ensure complete precipitation H_2O was added (100 mL). The white product was filtered on a Büchner funnel and washed with H_2O (3 × 100 mL), EtOH (2 × 100 mL), Et_2O (100 mL) and then dried in air to constant weight. This gave compound **8** (3.21 g, 93% yield). The product obtained by this method is very pure but it can be recrystallized from H_2O (800 mL per gram). The compound crystallizes as a monohydrate, the crystal H_2O of which can seemingly be removed reversibly. In one experiment, a large portion of this compound was prepared (12.53 g, 18.14 mmol monohydrate) and this was dried in an oven at 110 °C for 3 h causing it to lose weight, exactly matching the calculated amount of H_2O (0.33 g, 18.32 mmol H_2O). After being stored for 3 h in contact with air at ambient temperature the weight increased by 0.33 g corresponding to one mole equivalent of H_2O being taken up. **Alternative route:** compound **5** (1.0 g, 1.2 mmol) was suspended in aq HCl (37%, 25 mL). The mixture was refluxed with stirring for 2 days, cooled and the precipitate filtered. After drying on the filter the product was boiled with $CHCl_3$/EtOH (5:1) (100 mL), and DMF (20 mL) was added to bring the solid into solution. The solution was left in the freezer and the crystals were collected after 3 days (0.8 g, 89%); mp: 254 °C (dec.) darkens at 220 °C.

^{1}H NMR (DMSO-d_6): $\delta = 5.01$ (s, 12H, OCH_2C=O), 8.01 (s, 6H, ArH), 13.0 (b, 6H, COOH).

^{13}C NMR (DMSO-d_6): $\delta = 65.83$ (CH_2), 108.01 (ArCH), 123.37 (ArC), 147.52 (ArCO), 170.33 ($C{=}O$).

Mass spectral analysis and HPLC on this compound was not possible.

Anal. Calcd. for $C_{30}H_{26}O_{19}$ (690.52): C, 52.18; H, 3.80; Found: C, 52.18; H, 3.80.

2,3,6,7,10,11-Hexakis(*N*-succinimidyloxycarbonylmethoxy)triphenylene · MeCN · 2H_2O (9):
Compound **8** (4.14 g, 6 mmol) and *N*-hydroxysuccinimide (5.52 g, 48 mmol) were dissolved together in anhyd DMF (60 mL). Dicyclohexylcarbodiimide (DCC) (9.9 g, 48 mmol) was added while stirring. After the addition, stirring was continued for 16 h at r.t. The precipitated dicyclohexylurea (DCU) was filtered off by suction filtration and washed with MeCN (100 mL). The filtrate and washing were transferred to an Erlenmeyer flask (1 L) and heated to just below reflux temperature. Refluxing MeCN (700 mL) was added quickly to the filtrate and washing with stirring. When the mixing was complete the stirring was stopped. Nearly colourless crystals formed immediately after the addition. The solution was allowed to cool to r.t. and stored at −15 °C for 3 days. The product was filtered, washed with MeCN, and dried in a desiccator over $CaCl_2$. This gave compound **9** (6.39 g, 80%). The product is scarcely soluble in MeCN (0.8 g/L at reflux temperature) and decomposes on Soxhlet extraction with this solvent; mp: 166–172 °C (dec.).

^{1}H NMR ($CHCl_3$): $\delta = 2.14$ (s, 3H, MeCN), 2.94 (s, 24H, N(COCH_2)$_2$), 5.68 (s, 12H, OCH_2C=O), 8.28 (s, 6H, ArH).

^{13}C NMR ($CHCl_3$): $\delta = 26.58$ (CH_2CH_2), 64.78 (OCH_2), 109.19 (ArCH), 124.61 (ArC), 147.61 (ArCO), 166.34 ($CH_2C{=}O$), 171.19 (NC=O).

Mass spectral analysis and HPLC on this compound was not possible.

Anal. Calcd. for $C_{56}H_{49}N_7O_{32}$ (1332.03): C, 50.50; H, 3.71; N, 7.36; Found: C, 50.61; H, 3.49; N, 7.29.

2,3,6,7,10,11-Hexakis[*N*-(*tert*-butoxycarbonylmethyl)aminocarbonylmethoxy]triphenylene · 2.5H_2O (10):
Compound **9** (3.24 g, 2.43 mmol) was dissolved in anhyd DMF (50 mL) together with *t*-butyl glycinate hydrochloride (2.68 g, 16 mmol). While stirring an excess of Et_3N (1.8 g, 18 mmol) was added. Stirring was continued at r.t. for 24 h. The mixture was poured onto crushed ice (0.2 kg) causing a white precipitate to form. The product was filtered, washed with H_2O (2 × 25 mL) and recrystallized from EtOH (50 mL). This gave compound **10** (3.12 g, 92%); mp: 201–203 °C gas evolution (2-methylpropene), followed by melting of the acid at 237–239 °C (dec.) with darkening at 230 °C.

^{1}H NMR ($CHCl_3$): $\delta = 1.49$ (s, 54H, C(CH_3)$_3$), 3.95–3.97 (d, 12H, NCH_2C=O), 4.99 (s, 12H, OCH_2C=O), 8.30 (s, 6H, ArH), 8.56 (t, 6H, NH).

^{13}C NMR ($CHCl_3$): $\delta = 28.79$ (CH_3), 42.19 (OC(CH_3)$_3$), 69.55 (OCH_2), 81.82 (NCH_2), 109.69 (ArCH), 124.80 (ArC), 148.47 (ArCO), 169.36 (NC=O), 169.80 (OC=O).

MS: (FAB$^+$) 1351 (M^+) 61%.

HPLC: retention volume, 11.62 mL, purity 90.8%.

Anal. Calcd. for $C_{66}H_{95}N_6O_{26.5}$ (1396.50): C, 56.77; H, 6.86; N, 6.02; Found: C, 56.80; H, 6.82; N, 6.16.

2,3,6,7,10,11-Hexakis[*N*-(1-carboxy-1-benzylmethyl)aminocarbonylmethoxy]triphenylene · 3H_2O (11):
Compound **9** (1.38 g, 1 mmol) was dissolved in anhyd DMF (20 mL) together with L-phenylalanine hydrochloride (1.16 g, 7 mmol). While stirring an excess of Et_3N (1.4 g, 14 mmol) was added. Stirring was continued at r.t. for 24 h. The mixture was poured into H_2O (100 mL) resulting in a clear solution. Addition of aq HCl (37%, 2 mL) caused a voluminous white precipitate to form. The product was filtered, washed with H_2O (2 × 20 mL) and recrystallized from EtOH (25 mL). This gave compound **11** (0.78 g, 50%) as off-white microcrystals; mp: 189 °C.

^{1}H NMR (90 MHz, DMSO-d_6): $\delta = 3.15$ (d, 12H, PhCH_2), 4.56–4.62 (d, 6H, NCH(Bz)COO), 4.87 (s, 12H, OCH_2CON), 7.17 (br s, 30H, PhH), 8.14 (s, 6H, ArH), 8.39 (d, 6H, NH).

MS: (FAB$^+$) 1554/1555, (M^+ and MH^+), 55%.

HPLC on this compound was not possible.

Anal. Calcd. for $C_{84}H_{84}N_6O_{27}$ (1609.61): C, 62.68; H, 5.26; N, 5.22; Found: C, 62.60; H, 5.53; N, 5.52.

2,3,6,7,10,11-Hexakis[*N*-(1-*tert*-butoxycarbonyl-1-benzylmethyl)aminocarbonylmethoxy]triphenylene (12):
Compound **9** (2.0 g, 1.5 mmol) was dissolved in anhyd DMF (50 mL) together with *t*-butylphenylalanine hydrochloride (2.58 g, 10 mmol). While stirring an excess of Et_3N (1.1 g, 11 mmol) was added. Stirring was continued at r.t. for 24 h. The mixture was poured onto crushed ice (0.2 kg) causing a white precipitate to form. Due to the very high solubility in common organic solvents, compound **12** was purified as follows. The crude precipitate was filtered, washed with H_2O (2 × 50 mL) and dried. Dissolution in THF (100 mL) followed by passage through a short column of basic alumina (20 g) and evaporation of the filtrate gave a nearly colourless oil. This was taken up in a small volume of Et_2O (5 mL) and diluted with light petroleum ether (30 mL) and cooled. After 24 h, the product was filtered and dried in the air. The mother liquor contains an almost equal amount of product which can be combined advantageously with later crops prior to the column purification. This gave compound **12** (0.95 g, 33%). Differential scanning calorimetry (DSC) showed melting in the interval 56.99–97.52 °C, onset at 65.39 °C, peak at 68.44 °C, 34.898 kJ/mol.

^{1}H NMR ($CDCl_3$): $\delta = 1.39$ (s, 54H, C(CH_3)$_3$), 3.07 (d, 12H, PhCH_2), 4.67–5.07 (m, 18H, NCH(Bz)COO and OCH_2CON), 7.00–7.18 (m, 30H, PhH), 7.30–7.45 (s, 6H, NH), 7.83 (s, 6H, ArH).

^{13}C NMR ($CDCl_3$): $\delta = 28.51$ (CH_3), 37.94 (OC(CH_3)$_3$), 54.95 (BzCH_2), 69.34 (OCH_2), 81.91 (NCH_2), 109.69(ArCH), 124.84 (ArC), 127.50 (*p*-BzCH), 129.16 (*o*-BzCH), 130.19 (*m*-BzCH), 138.09 (BzCCH$_2$), 148.60 (ArCO), 168.96 (NC=O), 171.34 (OC=O).

MS: (FAB$^+$) 1892, (M^+), 26%.

HPLC: retention volume, 6.56 mL, purity 94.4%.

Anal. Calcd. for $C_{108}H_{126}N_6O_{24}$ (1892.21): C, 68.55; H, 6.71; N, 4.44; Found: C, 67.90; H, 6.68; N, 4.39.

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