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High-Yield Formation of Giant Bis(bicyclic) and Crypt-tris(bicyclic) Molecules under Normal Reaction Conditions

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We report the unexpected result of the reaction of 1,3-bis[(9-anthrylmethoxy)methyl]benzene (**1a**) or 1,3,5-tris[(9-anthrylmethoxy)methyl]benzene (**1b**) with tris(2-maleimidoethyl)amine (**2**) in homogeneous solution leading to giant bis(bicyclic) and crypt-tris(bicyclic) molecules. The anticipated, intractable solids are obtained in a condensed state reaction using an oscillating mill.

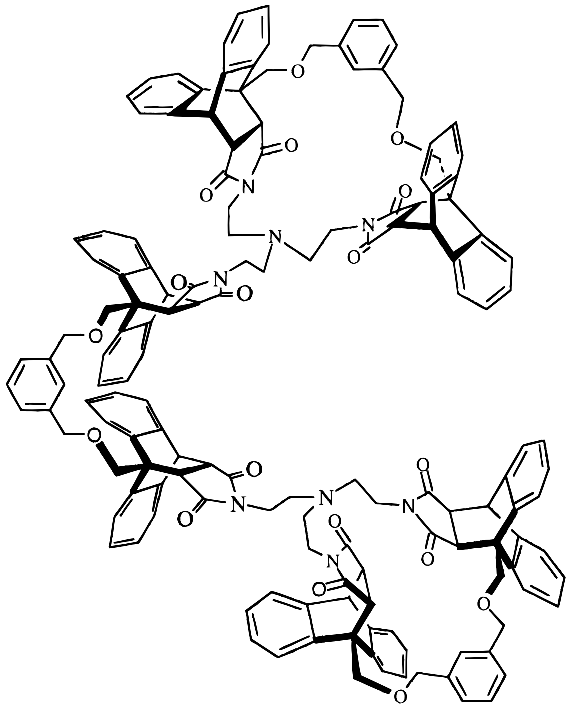
Introduction

Recently we started investigating the preparation of new three-dimensional extended organic solids via reversible Diels−Alder polymerization reactions.[1] In this context we studied the Diels−Alder reaction of 1,3-bis[(9-anthrylmethoxy)methyl]benzene (**1a**)[2] and 1,3,5-tris[(9-anthrylmethoxy)methyl]benzene (**1b**)[2,3] with tris(2-maleimidoethyl)amine (**2**).[4,5] As the preparation of highly cross-linked polymers in solution is often hampered by the precipitation of small oligomers at an early stage of the polymerization, we performed the reaction of **1** with **2** under several conditions. One set of experiments was devoted to the reaction of **1** with **2** in toluene solution, while another set of experiments involved reactions in the condensed state. Depending upon the conditions applied, one can obtain either exotic macrocyclic structures or cross-linked polymers. This report emphasizes the unusual observation of the former.

Results and Discussion

Reactions of 1a and 1b with 2 in Toluene Solution. When a toluene solution of **1a** and **2** (**1a**:**2** = 3:2) or **1b** and **2** (**1b**:**2** = 1:1) was heated at reflux for 24 h, surprisingly the reaction mixture remained clear but, on occasion, deposited a trace of fine precipitate after cooling to room temperature. Filtration showed that the precipitate accounted for a maximum of only 8% of the mass balance. Evaporation of the mother liquors afforded a pale yellow solid, whose spectroscopic data (^{1}H, ^{13}C NMR, IR, and UV−vis) indicated the formation of Diels−Alder adduct(s) without residual anthracene or maleimide moieties. The products were readily soluble in common solvents, which is in sharp contrast to the intractability of the cycloadducts obtained from reaction of **1** with **2** in the absence of solvent (see below). However, the IR spectra of the cycloadducts obtained from toluene solution match those of the products obtained from solid-state reaction (see Figure 1), despite the difference in physical properties.

Clearly, reaction in toluene solution leads to the formation of soluble structures which must be macrocyclic.[6] The smallest macrocycles that fit the stoichiometry of the reaction are **7** and **8** (Scheme 1), although the simultaneous formation of larger oligomers is still possible.



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After a series of experiments designed to obtain hyperbranched polymers or oligomers, we always isolated **7** and **8** from the crude. The latter was subjected to column chromatography (SiO_2, $CHCl_3$) to yield white

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[1] (a) By allowing the propagation reaction of the polymerization to proceed via a reversible addition reaction, one may achieve a thermodynamic minimum of the bonding network comprising the macroscopic solid, thereby introducing special properties such as exceptional hardness and thermal stability. (b) Sastre, A.; Srdanov, G.; Wudl, F. *Chem. Eur. J.* **1999**, *5*, 289−296.

[2] Prepared from 9-hydroxymethylanthracene and 1,3-bis(bromomethyl)benzene or 1,3,5-tris(bromomethyl)benzene.[3]

[3] Fourmigué, M.; Johannsen, I.; Boubekeur, K.; Nelson, C.; Batail, P. *J. Am. Chem. Soc.* **1993**, *115*, 3752.

[4] Kossmehl, G.; Nagel, H.-I.; Pahl, A. *Angew. Makromol. Chem.* **1995**, *227*, 139.

[5] For reports about linear anthracene/maleimide polymers see: (a) Stevens, M. P. *J. Polym. Sci., Part C: Polym. Lett.* **1984**, *22*, 467, and references therein. (b) Simionescu, C. I.; Grigoras, M. *J. Polym. Sci., Part C. Polym. Lett.* **1990**, *28*, 39.

10.1021/jo991783d CCC: $19.00

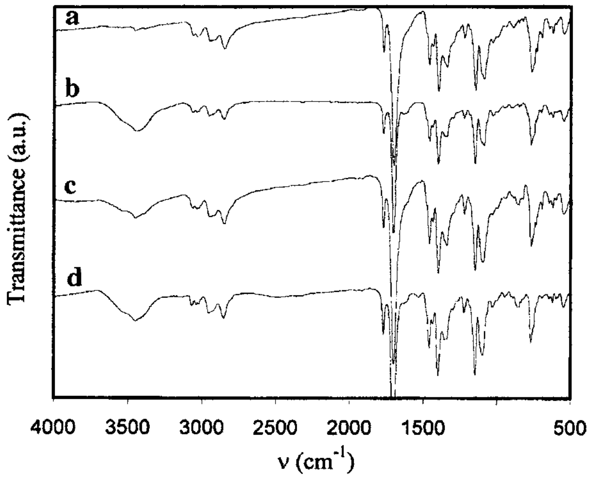
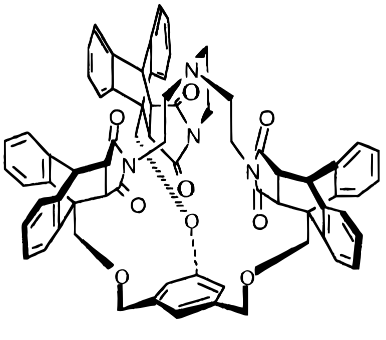


Figure 1. FTIR spectra as KBr mulls of reactions of **1a** and **1b** with **2**. Spectrum a, solid-state reaction of bis(anthracene) **1a** with tris(maleimide) **2**; spectrum b, solution reaction of bis(anthracene) **1a** with **2**; spectrum c, solid-state reaction of tris(anthracene) **1b** with tris(maleimide) **2**; spectrum d, solution reaction of tris(anthracene) **1b** with **2**.



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solids whose MALDI-TOF spectroscopic analysis (Figure 2) differed significantly from those of the cycloadducts obtained from solid-state reaction (Figure 4). For example, for the reaction of **1a** and **2**, the product obtained from toluene displayed intense signals at 2328 and 2352 amu, which can be ascribed to bis(bicycle) **7** [calcd for $C_{150}H_{127}N_8O_{18}$ (M + H)$^{\bullet+}$ 2330 and calcd for $C_{150}H_{126}N_8NaO_{18}$ (M + Na$^{\bullet+}$) 2352]. For the product obtained from solid-state reaction the MALDI-TOF spectrum contained many signals of relatively low mass and the signal at 2330 was only very weak. Similar trends could be observed for the reaction of **1b** with **2**. The MALDI-TOF spectrum of the cycloadduct obtained from toluene contained an intense signal at 1126, which could be ascribed to cryptand **8** [calcd for $C_{72}H_{61}N_4O_9$ (M + H$^{\bullet+}$) 1126], while this signal was only very weak for the product obtained from solid-state reaction.

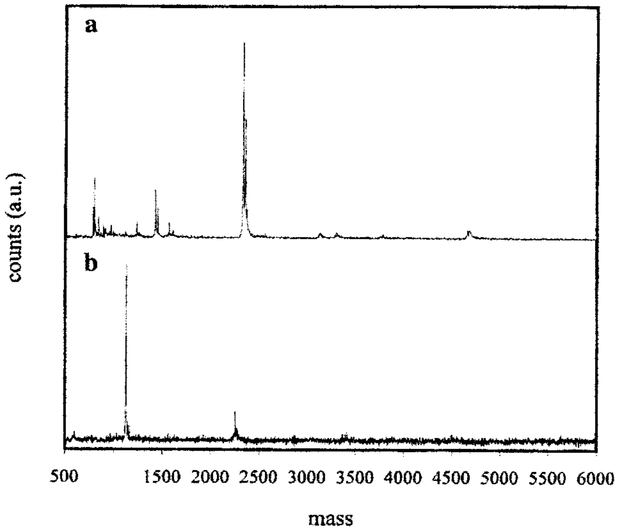

Figure 2. MALDI-TOF mass spectra of toluene solution reactions. Spectrum a, solution reaction of bis(anthracene) **1a** with tris(maleimide) **2**; spectrum b, solution reaction of tris(anthracene) **1b** with **2**.

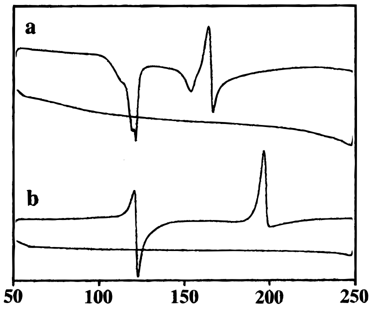

Figure 3. Differential scanning calorimetry of solid-state reactions recorded at 10 °C/min. Trace a, bis(anthracene) **1a** with tris(maleimide) **2**; trace b, tris(anthracene) **1b** with **2**.

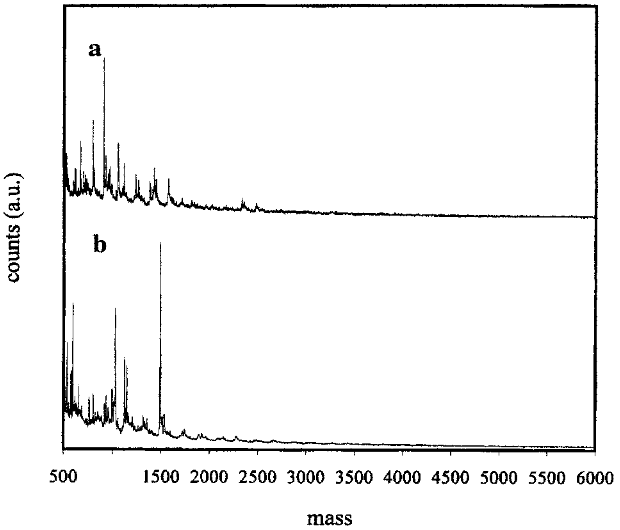

Figure 4. MALDI-TOF mass spectra of solid-state reactions. Spectrum a, bis(anthracene) **1a** with tris(maleimide) **2**; spectrum b, tris(anthracene) **1b** with **2**.

Further support for the structural assignment of crypt-tris(bicyclic) **8** was based on fluorescence of the product. CPK models of **8** indicated that its cavity was large enough to host various transition metal cations. Upon photoexcitation, the interaction of the encapsulated metal ion(s) with the photoexcited host molecule should induce drastic quenching of the emission intensity, thereby opening a way of fluorescence-sensing the cryptate formation.[7] In a preliminary study it was demonstrated

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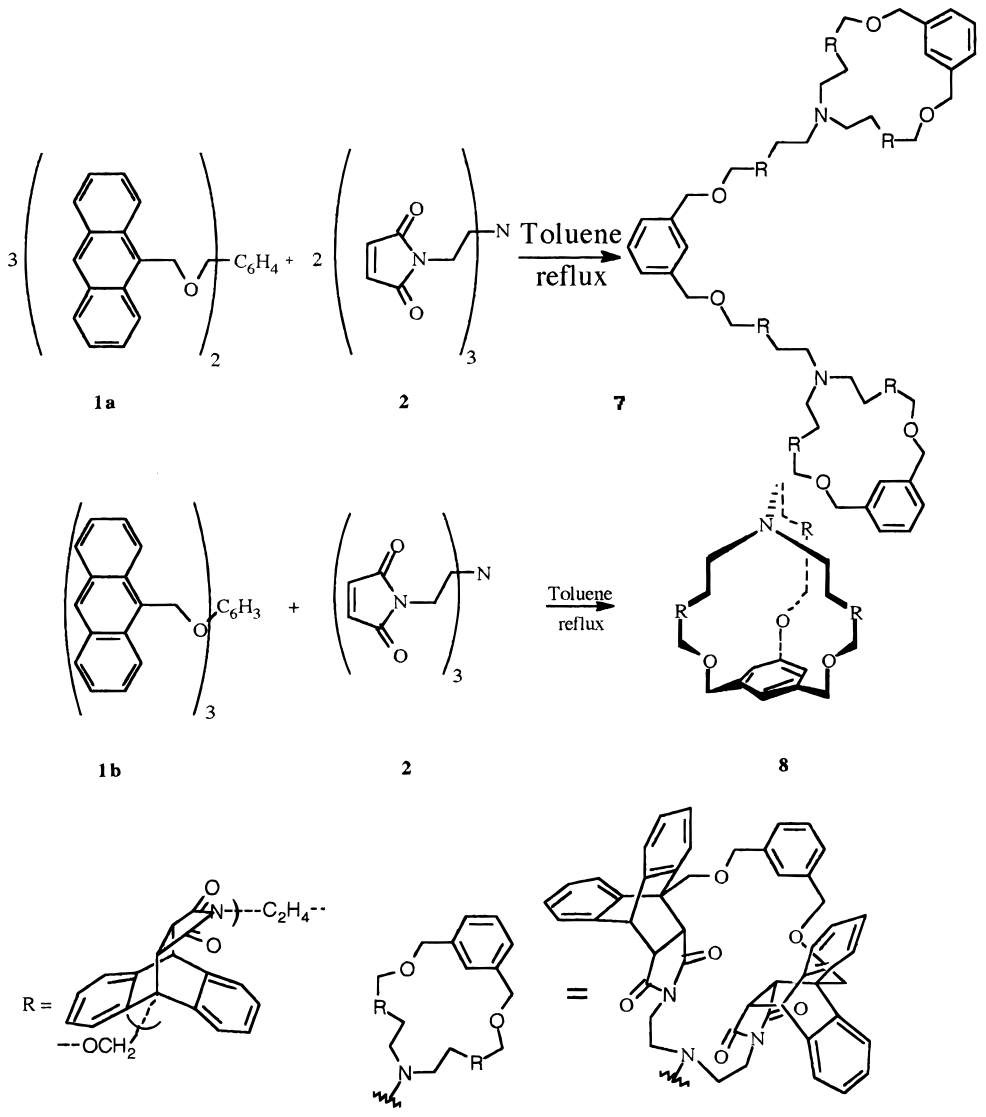
(6) The small amount of insoluble material described above could be hyperbranched polymers expected from this combination of functionality: (a) Kim, Y. H. *J. Polym. Sci. A: Polym. Chem.* **1998**, *36*, 1685. (b) Hawker, C. J. *Macromolecular Architectures* **1999**, *147*, 113. (c) Hult, A.; Johansson, M.; Malmstrom, E. *Branched Polymers II* **1999**, *143*, 1.

Scheme 1



that the addition of Ag(I) triflate to a dichloromethane solution of the reaction product quenches its fluorescence. No change in fluorescence is observed when Ag(I) triflate is added to a CH_2Cl_2 solution of the noncyclic Diels–Alder adducts **4**, **6**, and **7** (Scheme 2). The result that the purified product interacts more strongly with the metal ion than the other macrocycles can be explained by the presence of a cryptand structure proposed for **8**.

Reaction of Neat 1 with 2. It was envisioned that pyrolytic Diels–Alder reactions of **1** with **2** could occur either in the solid state or in the melt (Table 1). The tethered anthracenes **1** melt (sharp endotherm) before decomposing (shallow exotherm followed by a continuous endotherm). Tris(maleimide) **2** first melts and then slowly starts to polymerize at approximately 200 °C (shallow exotherm) before decomposition occurs at 400 °C.

The DSC trace of an equimolar mixture of **1b** and **2**, previously ground together in a mortar, is depicted in Figure 3b. It can be seen that as soon as **2** starts to melt (onset at 118 °C), it reacts with tris(anthracene) **1b**. However the reaction is not complete, as indicated by the melting of unreacted **1b** at 196 °C. The DSC trace of a mixture of **1a** and **2** (**1a**:**2** = 3:2) is similar, although more complex (Figure 3a). For example, reaction of **2** with **1a** (onset at 105 °C) starts at a lower temperature than reaction of **2** with **1b**. In addition, the polymodal form of the observed exotherm indicates that several different reactions are involved in the process. Again, the reaction is not complete, as indicated by the melting of the unreacted **1a**.

Table 1. DSC and TGA Data of Compounds 1, 2, 4, 6, 7, and 8

	DSC^a (°C)	TGA^{b,c} (°C)
1a	166,^{d} 280^e	340
1b	196,^{d} 320^e	320
2	124,^{d} 200^e	415
4a	340^e	340
4b	310,^{f} 350^e	320
6	294,^{d} 320^e	355
1a + **2** (vib. mill)	340^e	380
1b + **2** (vib. mill)	350^e	370
1a + **2** (toluene) (**7**)	355^e	370
1b + **2** (toluene) (**8**)	350^e	376

[a] 50–400 °C; 10 °C·min^{-1}. [b] 50–700 °C; 10 °C·min^{-1}. [c] 5% weight loss. [d] Melting. [e] Decomposition. [f] Sublimation.

The incomplete reaction of **1** with **2** might be due to the fact that grinding the two compounds together does

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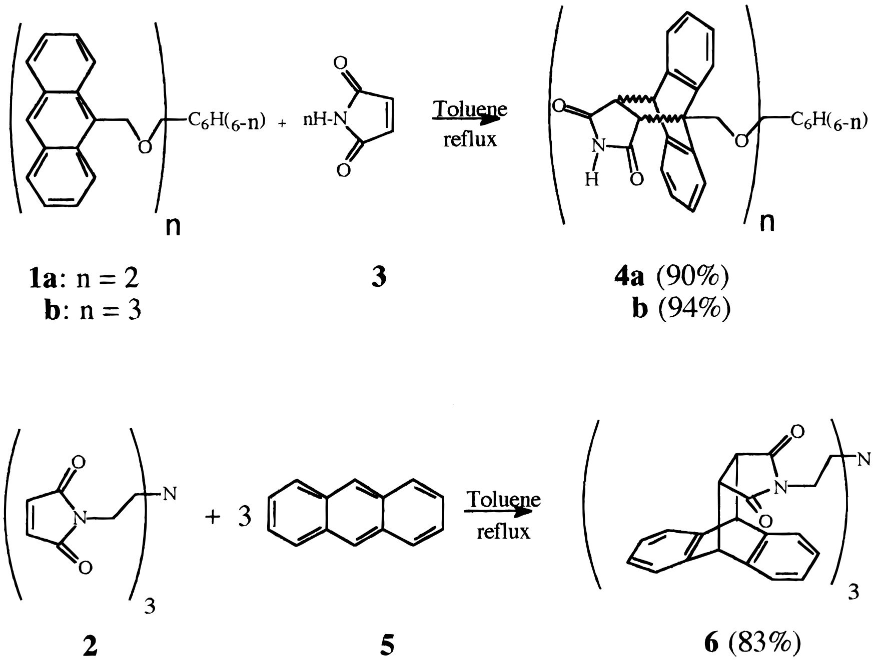
(7) Labbrizzi, L.; Licchelli, M.; Parodi, L.; Poggi, A.; Taglietti, A. *Eur. J. Inorg. Chem.* **1999**, 35.

Scheme 2



not furnish a homogeneous mixture. To improve homogeneity, **1** and **2** were mixed in a vibration mill ("wiggle bug" 58.3 Hz, 1.5 h). Surprisingly, the DSC traces of the powders did not exhibit endotherm(s) or exotherm(s) (50−250 °C). These results suggest that the action of the vibration mill forces the Diels−Alder reaction between **1** and **2** to completion, as has been reported recently for cycloaddition reactions of C_{60}.[8] Proof that the solid-state reaction products were indeed Diels−Alder adducts was based on their IR spectra, which match those of the cycloadducts **4** (obtained from **1** and maleimide derivative **3**) and **6** (obtained from **2** and anthracene derivative **5**) (see Scheme 2).

The powders obtained from the vibration mill experiments are intractable, as can be expected for cross-linked polymers; for example, solubility in hexanes, benzene, toluene, ether, THF, acetone, chloroform, dichloromethane, ethyl acetate, DMF, DMSO, and methanol is insufficient to allow NMR or UV−vis spectroscopic analysis. The MALDI-TOF spectrum of the solid-state cycloadduct of **1a** with **2** is depicted in Figure 4, where it is clear that there are only relatively low mass signals. Some of these signals can be ascribed to small fragments of the expected cross-linked polymers, as for example *m*/*e* 904 (**1a**:**2** = 1:1), 1425 (**1a**:**2** = 2:1), and 2330 (**1a**:**2** = 3:2) in Figure 4a and 1126 (**1b**:**2** = 1:1) in Figure 4b. These could also be side products encapsulated upon cross-linking and released in the MS process.

Summary and Conclusions

The results obtained above show that in toluene solution, at concentrations that are not usually associated with macrocyclizations (0.02−0.01 M), and without the need to resort to syringe pumps nor other sophisticated, high-dilution techniques, Diels−Alder additions to produce complex macrocyclic structures compete very effectively with hyperbranching polymerization reactions. In attempts to explain these observations, we designed experiments aimed at determining if the solvent was acting as a template. The reactions were carried out in a number of solvents of different size and electronic character. Since we did not observe unusual effects, we were forced to conclude that the solvent was not "templating" the macrocyclizations. We believe the explanation ultimately rests on the exceptional rigidity of our systems because molecular models showed that once one anthracene moiety of **1** has reacted with one maleimide moiety of **2**, a combination of imposed rigidity and intramolecular interactions (either charge-transfer or quadrupolar interactions)[9] between the remaining anthracene and maleimide moieties preorganizes these fragments with a geometry close to that of the transition state for the formation of macrocyclic structures such as **7** and **8**.

Experimental Section

All experiments were performed in flame-dried glassware under a nitrogen atmosphere using standard Schlenk techniques. 1,3,5-Tris(bromomethyl)benzene (**9**)[3] was prepared according to literature. Tris(2-maleimidoethyl)amine (**2**)[4] was prepared according to literature and recrystallized three times from acetone prior to use. All other reagents, maleimide (**3**), anthracene (**5**), 9-hydroxymethylanthracene (**10**), 1,3-bis(bromomethyl)benzene (**11**), sodium hydride (60% dispersion in mineral oil), *N*,*N*-dimethylformamide (anhydrous), toluene, $CHCl_3$, Et_2O, EtOAc, and MeOH (Aldrich) were used as purchased. Melting points are uncorrected. Elemental analyses were provided by Desert Analytics, Tucson, AZ.

1,3-Bis[(9-anthrylmethoxy)methyl]benzene (1a). At 0 °C, NaH (1.08 g, 60% dispersion in mineral oil, 27.0 mmol) was added to a solution of 9-hydroxymethylanthracene (**10**: 5.21 g, 25.6 mmol) and 1,3-bis(bromomethyl)benzene (**11**: 3.15 g, 11.9 mmol) in DMF (50 mL). The mixture was stirred at

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[8] (a) Wang, G.-W.; Murata, Y.; Komatsu, K.; Wan, T. S. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2059. (b) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583. (c) Murata, Y.; Fujiwara, K.; Kato, N.; Komatsu, K. *9th Int. Symp. Nov. Arom. Comput. (ISNA)*, 2−7 Aug, Hong-Kong P.R.C.

[9] Heaton, N. J.; Bello, P.; Herradón, B.; Del Campo, A.; Jiménez-Barbero, J. *J. Am. Chem. Soc.* **1998**, *120*, 12371.

room temperature for 24 h. The reaction mixture was poured into H_2O (500 mL) and filtered over a glass sintered funnel. The residue was washed with H_2O, dried in vacuo, and subjected to column chromatography (SiO_2, $CHCl_3$). The eluate was filtered and concentrated in vacuo, and the residue was recrystallized from toluene to furnish pale yellow crystals. Yield: 1.88 g (61%); mp 166 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.46 (s, 2H), 8.31 (m, 4H), 8.00 (m 4H), 7.42 (m, 12H), 5.49 (s, 4H), 4.72 (s, 4H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 138.7, 131.5, 131.1, 129.0, 128.7, 128.5, 127.6, 127.4, 126.2, 125.0, 124.4, 72.4, 64.2. UV–vis (CH_2Cl_2): λ = 224, 258 (λ_{max}), 333, 349, 367, 387. FT-IR (KBr, main peaks): v = 3082–3028, 2968, 2926, 2891, 2868, 1624 cm^{-1}. EI m/z = 518 ($[M]^{•+}$, 10%) calcd for $C_{38}H_{30}O_2$: 518.2246. Found: 518.2231. Anal. Calcd for $C_{38}H_{30}O_2$ (mol wt 518.67): C, 88.00; H, 5.83. Found: C, 88.07; H, 5.82.

1,3,5-Tris[(9-anthrylmethoxy)methyl]benzene (1b). 1b was prepared from NaH (0.60 g, 60% dispersion in mineral oil, 15 mmol) and a solution of 9-hydroxymethylanthracene (**10**: 3.02 g, 14.5 mmol) and 1,3,5-tris(bromomethyl)benzene (**9**: 1.70 g, 4.76 mmol) in DMF (50 mL) and purified as described for **1a**. Yield: 1.70 g (48%) of pale yellow crystals; mp 196 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.44 (s, 3H), 8.28 (m, 6H), 7.98 (m, 6H), 7.39 (m, 15H), 5.48 (s, 6H), 4.70 (s, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 138.9, 131.5, 131.1, 129.0, 128.7, 128.4, 126.9, 126.2, 125.0, 124.4, 72.3, 64.3. UV–vis (CH_2Cl_2): λ = 224, 258 (λ_{max}), 333, 349, 367, 387. FT-IR (KBr, main peaks): v = 3082, 2858, 2794, 1624 cm^{-1}. FAB calcd for $C_{54}H_{42}O_3$ ($[M]^{•+}$): 738.3134. Found: 738.3148. Anal. Calcd for $C_{54}H_{42}O_3$ (mol wt 738.94): C, 87.78; H, 5.73. Found: C, 87.74; H, 5.73.

Maleimide and Bis[(9-anthrylmethoxy)methyl]benzene (4a). A suspension of **1a** (0.1464 g, 0.283 mmol) and maleimide (**3**: 0.0548 g, 0.565 mmol) in toluene (10 mL) was heated and became homogeneous within a minute of heating to 80 °C. The reaction was kept at reflux for 18 h. The turbid white reaction mixture was allowed to cool to room temperature and filtered over a sintered glass funnel. The residue was washed with toluene (2 × 5 mL) and dried in vacuo to furnish a white powder. Yield: 0.131 g (65%); mp 340 °C, decomp. UV–vis (CH_2Cl_2): λ = 230 (λ_{max}), 258, 272. FT-IR (KBr, main peaks): v = 3424–3041, 2960, 2912, 2860, 1776, 1720 cm^{-1}. FAB calcd for $C_{46}H_{37}N_2O_6$ ($[M + H]^{•+}$): 713.2652. Found: 713.2659. Anal. Calcd for $C_{46}H_{36}N_2O_6$ (mol wt 712.81): C, 77.51; H, 5.09; N, 3.93. Found: C, 75.80; H, 5.24; N, 4.84.

Maleimide and Tris[(9-anthrylmethoxy)methyl]benzene (4b). **4b** was prepared from a suspension of **1b** (0.1389 g, 0.188 mmol) and **3** (0.0584 g 0.0565 mmol) in toluene (10 mL) and purified as described for **4a**. Yield: 0.135 g (94%) of a white powder; mp 350 °C, decomp. ^{1}H NMR (200 MHz, [D_6] DMSO): δ 10.81 (s, 3H), 7.58 (s, 3H), 7.12 (bm, 18H), 4.94 (s, 6H), 4.86 (s, 6H), 4.70 (s, 3H), 3.26 (m, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 138.9, 131.5, 131.1, 129.0, 128.7, 128.4, 126.9, 126.2, 125.0, 124.4, 72.3, 64.3. UV–vis (CH_2Cl_2): λ = 229 (λ_{max}), 225 (s), 262 (s), 272 (s). FT-IR (KBr, main peaks): v = 3424–3041, 2958, 2922, 2858, 1778, 1720 cm^{-1}. Anal. Calcd for $C_{66}H_{51}N_3O_9$ (mol wt 1030.16): C, 76.95; H, 4.99; N, 4.08. Found: C, 76.78; H, 5.18; N, 3.83.

Trismaleimide and Anthracene (6). A solution of anthracene (**5**: 0.1390 g, 0.780 mmol) and **2** (0.1000 g, 0.259 mmol) in toluene (10 mL) was heated at reflux for 6 h. The reaction mixture was allowed to cool to room temperature to furnish a pale yellow solution and a white precipitate. The precipitate was filtered off, dissolved in a minimum of $CHCl_3$, and applied to a SiO_2 column. The column was washed with $CHCl_3$ and eluted with $CHCl_3$/EtOAc (3:1). The eluate was filtered and concentrated in vacuo to furnish a white solid. Yield: 0.170 g (71%); mp 294 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.38 (m, 6H), 7.26 (m, 6H), 7.18 (m, 12H), 4.76 (s, 6H), 3.20 (s, 6H), 2.86 (bt, $^{3}J_{HH}$ = 6.2 Hz, 6H), 1.53 (bt, $^{3}J_{HH}$ = 6.2 Hz, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 176.6, 141.6, 138.8, 127.1, 126.7, 125.1, 124.3, 50.0, 46.9, 45.7, 36.6. UV–vis (CH_2Cl_2): λ = 229 (λ_{max}), 255, 265, 272. FT-IR (KBr, main peaks): v = 3070–3024, 2958, 2831, 1772, 1703 cm^{-1}. FAB calcd for $C_{60}H_{49}N_4O_6$ ($[M + H]^{•+}$): 921.3652. Found: 921.3681. Anal. Calcd for $C_{60}H_{48}N_4O_6$ (mol wt 921.07): C, 78.24; H, 5.25; N, 6.08. Found: C, 77.72; H, 5.21; N, 5.98.

Reaction of 1a with 2 in a Vibration Mill. A mixture of **1a** (0.1205 g, 0.232 mmol) and **2** (0.0598 g, 0.155 mmol) was shaken in a vibration mill for 1.5 h to furnish a pale yellow powder; mp 340 °C, decomp. FT-IR (KBr, main peaks): v = 3064–3026, 2954, 2918, 2854, 1772, 1699 cm^{-1}.

Reaction of 1b with 2 in a Vibration Mill. A mixture of **1b** (0.1144 g, 0.155 mmol) and **2** (0.0598 g, 0.155 mmol) was shaken in a vibration mill for 1.5 h to furnish a pale yellow powder, insoluble in all common solvents; mp 350 °C, decomp. FT-IR (KBr, main peaks): v = 3066–3024, 2952, 2926, 2852, 1772, 1701 cm^{-1}.

Reaction of 1a with 2 in Toluene (7). A suspension of **1a** (0.2062 g, 0.398 mmol) and **2** (0.1024 g, 0.265 mmol) in toluene (20 mL) was heated at reflux. After 5 min a clear yellow solution was obtained, which was heated at reflux for 24 h. The reaction mixture was allowed to cool to room temperature to furnish a clear colorless solution. The solvent was evaporated in vacuo, and the residue was dissolved in a minimum of $CHCl_3$ and applied to a SiO_2 column. The column was washed with $CHCl_3$ and eluted with $CHCl_3$/EtOAc (3:1). The eluate was filtered and concentrated in vacuo. The residue was dissolved in a minimum of $CHCl_3$ and poured into MeOH (50 mL), upon which a fine white precipitate formed. The turbid white mixture was centrifuged (3700 rpm, 30 min) to furnish a white precipitate and a clear, pale yellow solution. The precipitate was isolated by careful decantation, washed with Et_2O, and dried in vacuo to furnish a white solid. Yield: 0.175 g (57%);[10] mp 355 °C, decomp. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.44 (s, 3H), 8.28 (m, 6H), 7.98 (m, 6H), 7.39 (m, 15H), 5.48 (s, 6H), 4.70 (s, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 138.9, 131.5, 131.1, 129.0, 128.7, 128.4, 126.9, 126.2, 125.0, 124.4, 72.3, 64.3. UV–vis (CH_2Cl_2): λ = 228 (λ_{max}), 258, 272, 333, 349, 367, 387. FT-IR (KBr, main peaks): v = 3070–3025, 2956, 2856, 1772, 1703 cm^{-1}. MALDI-TOF calcd for $C_{150}H_{126}$-N_8O_{18} ($[M + 2H]^{•+}$): 2328.94. Found: 2328.92. Anal. Calcd for $C_{150}H_{126}N_8O_{18}$ (mol wt 2328.72): C, 77.37; H, 5.45; N, 4.81. Found: C, 77.19; H, 5.57; N, 4.55.

Reaction of 1b with 2 in Toluene (8). Compounds **1b** (0.6125 g, 0.829 mmol) and **2** (03201 g, 0.828 mmol) in toluene (100 mL) were allowed to react and were purified as described for **7**, above. Yield: 0.279 g (30%)[9,11] of a white powder; mp 350 °C, decomp. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.44 (s, 3H), 8.28 (m, 6H), 7.98 (m, 6H), 7.39 (m, 15H), 5.48 (s, 6H), 4.70 (s, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 138.9, 131.5, 131.1, 129.0, 128.7, 128.4, 126.9, 126.2, 125.0, 124.4, 72.3, 64.3. UV–vis (CH_2Cl_2): λ = 229 (λ_{max}), 264, 272. FT-IR (KBr, main peaks): v = 3070–3024, 2956, 2854, 1772, 1703 cm $^{-1}$. MALDI-TOF calcd for $C_{72}H_{60}N_4O_9$ ($[M]^{•+}$): 1125.28. Found: 1125.23. Anal. Calcd for $C_{72}H_{60}N_4O_9$ (mol wt 1125.30): C, 76.85; H, 5.37; N, 4.98. Found: C, 75.95; H, 5.35; N, 4.85.

Fluorescence Measurements. Dichloromethane solutions of compound **8** with, or without, addition of silver triflate were irradiated with the same excitation wavelength (272 nm) with equal optical density. The ratio of the fluorescence intensity

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(10) In two experiments, the column was "stripped" with ethyl acetate. The products obtained from this eluate comprised 30–40% of the reaction mass. MALDI-TOF spectra indicated no cyclics but dendritic products. The FTIR spectra were essentially superimposable with those of **6**.

(11) HPLC analysis of the crude reaction mixture of **8** with a Cosmosil Buckyprep column and chloroform as eluent showed a sharp peak, which was followed by a partly overlapping broad peak (approximate ratio 1:1). These peaks had short retention times (3–4 min). This column was used before in our group for the separation of spheroidal molecules, other than fullerenes. A GPC experiment vs PS with purified **8** gave a sharp peak with retention volume of 20 mL under the following conditions: concentration 1 mg per mL, eluent chloroform, 3 GPC columns in series, 1.00 mL per minute, detectors: UV and viscosity.

integral of the solution with addition of triflate to the solution without triflate is about 0.78, indicating fluorescence quenching due to the addition of the silver triflate. The fluorescence spectra of the two samples range from ∼360 to ∼520 nm with a maximum at about 425 nm.

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