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Thermosensitive Bucky-Bowl

Thermoresponsive Corannulene

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Abstract: We demonstrate herein that corannulene, a bowl-shaped polycyclic aromatic hydrocarbon, can assemble into larger supramolecular structures in water through a change in the solution temperature. This property is invoked through a simple five-fold symmetric substitution of the corannulene nucleus with triethylene glycol units. Interestingly, an increase in the solution temperature, which triggers the assembly process, also enhances the fluorescence emission properties of the assembled materials. Although the emission remains very weak in solution, bright green luminescence can be observed in the fibrilar form. This unexpected and interesting behavior indicates that the corannulene nucleus presents a new motif for the design of aggregation-induced emission (AIE) based luminogens. To the best of our knowledge, this is the first report of a thermoresponsive nonplanar polycyclic hydrocarbon derivative that can respond to a thermal trigger and assemble into larger emissive structures.

Introduction

Corannulene is a polycyclic aromatic hydrocarbon[1–3] with varied structural[4–6] and electronic properties.[7–13] A glance at this nonplanar molecule brings a stacking process to mind that would ultimately result in the formation of larger structures, such as a fiber, through supramolecular π–π interactions between aromatic bowls. In this context, however, only a few examples are known thus far. For example, Aida and co-workers have established two different strategies for facilitating the stacking process. One involves the substitution of the corannulene nucleus with long alkyl chains and the other is based upon hydrogen-bonding interactions between adjacent assembly precursors.[14,15] Siegel and co-workers, on the other hand, have shown that lipid modification or oligosaccharide substitution of the corannulene scaffold can render the structures prone to aggregation into larger supramolecular assemblies.[16,17] Finally, Maeda and co-workers have also substituted the corannulene unit with multiple alkyl chains to facilitate aggregation.[18] None of these systems, however, respond to a thermal stimulus. If achieved, such thermoresponsive behavior could lead to the application of corannulene in the biomedical arena.[19–21]

In this report, we show that this can be achieved through decoration of the corannulene nucleus with ethylene glycol units. These units are polar and hydrophilic. Therefore, at room temperature, they allow the molecule to dissolve in aqueous media. However, an increase in temperature results in the entropically driven removal of water molecules (an ordered state) from the appended ethylene glycol chains and an overall reduction in water solubility of the material. Above a solution temperature of 40 °C, the building block essentially becomes water-insoluble and assembles to yield larger structures. Typically, such a transition is a hallmark of thermosensitive polymers[22,23] and very few small molecular motifs are known to emulate this behavior.[24–26] Interestingly, during this work, we also observed a weak enhancement of emission in solution upon thermally triggered aggregation. In the fibrilar state, however, comparatively strong green luminescence could be seen. Therefore we report herein on the thermal responsivity of a corannulene derivative and the observation of aggregation-induced emission.[27,28] Both phenomena are of practical importance and hitherto unknown in the realm of nonplanar aromatic hydrocarbon chemistry.

Results and Discussion

To synthesize the five-fold decorated corannulene, the synthetic protocol developed by Siegel and co-workers was used.[29,30] Initially, corannulene was treated with iodine chloride to access 1,3,5,7,9-pentachlorocorannulene. Subsequent modification of this compound with thiolated triethylene glycol furnished the targeted structure **1** in an isolated yield of 38 % (Scheme 1). ^{1}H and ^{13}C NMR analyses confirmed the molecular structure (see Figures S1–S3 in the Supporting Information).

Having compound **1** in hand, first, its optical characteristics were established. As can be seen in Figure 1, in solvents such as methanol and acetonitrile, two major absorption bands located at 250 and 335 nm can be observed. The absorption coefficients (ε) of **1** at 335 nm were determined to be 34000 M^{-1} cm^{-1} in methanol and 36000 M^{-1} cm^{-1} in acetonitrile.

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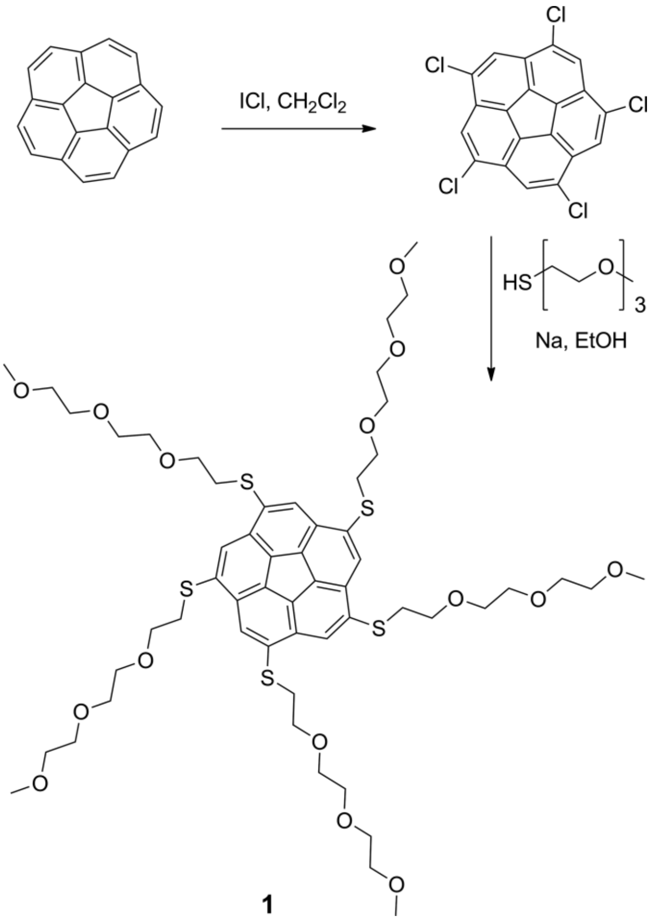


Scheme 1. Synthesis of corannulene **1**.

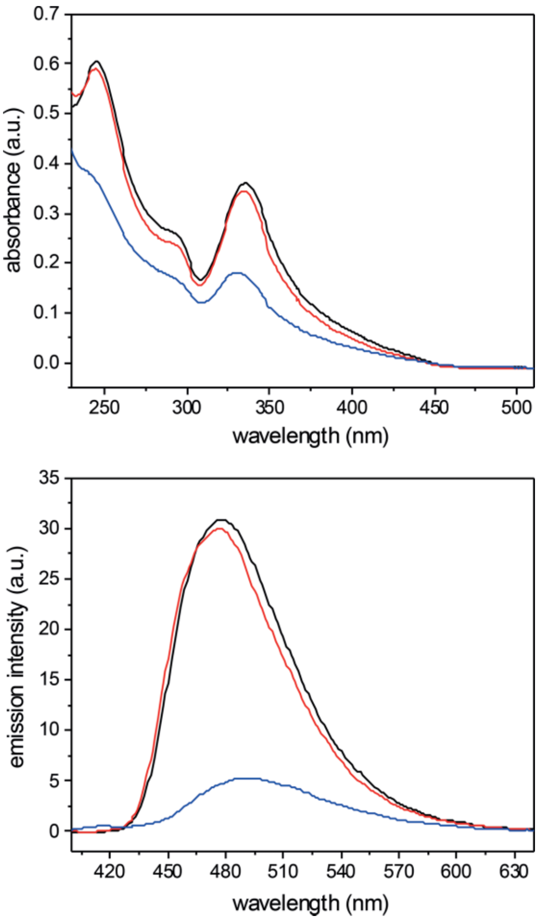


Figure 1. Absorption (top) and emission (bottom) spectra of **1** in water (blue line), methanol (red line), and acetonitrile (black line) at room temperature.

In water, these absorption bands exhibit a significant decrease in intensity ($\varepsilon = 17000\ \text{M}^{-1}\ \text{cm}^{-1}$). The emission spectrum of **1** upon excitation at 335 nm exhibits a similar trend; moderate emission intensities are observed in methanol and acetonitrile, whereas in water, a significant reduction in intensity is seen.

Next, dynamic light scattering (DLS) measurements were carried out in water at room temperature (see Figure S4 in the Supporting Information). The study showed that structures of very small sizes (<5 nm) are present in the solution. This indicates that intermolecular interactions at room temperature must be limited to an oligomeric level (supramolecular dimers, trimers, tetramers, etc. of **1**). Moore and co-workers observed similar behavior in the case of ethylene glycol appended phenylacetylene macrocycles when dissolved in polar solvents.[31]

During the course of this study, we observed that heating, originally intended to obtain a perfectly clear solution by assisting the solubilization, as is common in synthetic laboratories, had the opposite effect as the aqueous solution turned turbid (Figure 2 and Figure S5 in the Supporting Information). This observation revealed the sensitivity of the ethylene glycol appended corannulene **1** to changes in solution temperature. To confirm this, temperature-dependent transmittance measurements were carried out (Figure 3). At room temperature, the aqueous solution remained clear. However, raising the temperature led to a loss of the optical clarity of the aqueous solution, and above 40 °C the transmittance dropped suddenly as the solution became opaque. Cooling the solution to room temperature restored the optical clarity. Heating and cooling cycles could be repeated many times, thereby indicating the reversibility of the thermally triggered assembly process (Figure 3).

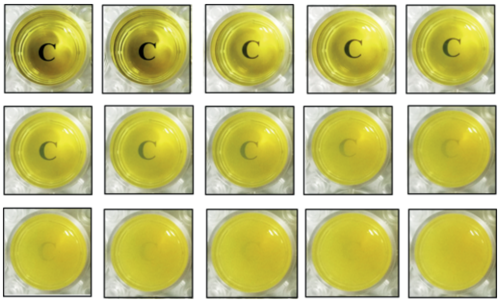


Figure 2. Digital pictures showing gradual changes in transmittance of an aqueous solution (1 mM) of **1** upon slowly increasing the temperature on a hotplate.

The transmittance studies indicated conformational changes of the molecule and the associated assembly process upon thermal activation. This further motivated us to investigate the concomitant changes in the absorption and emission proper-

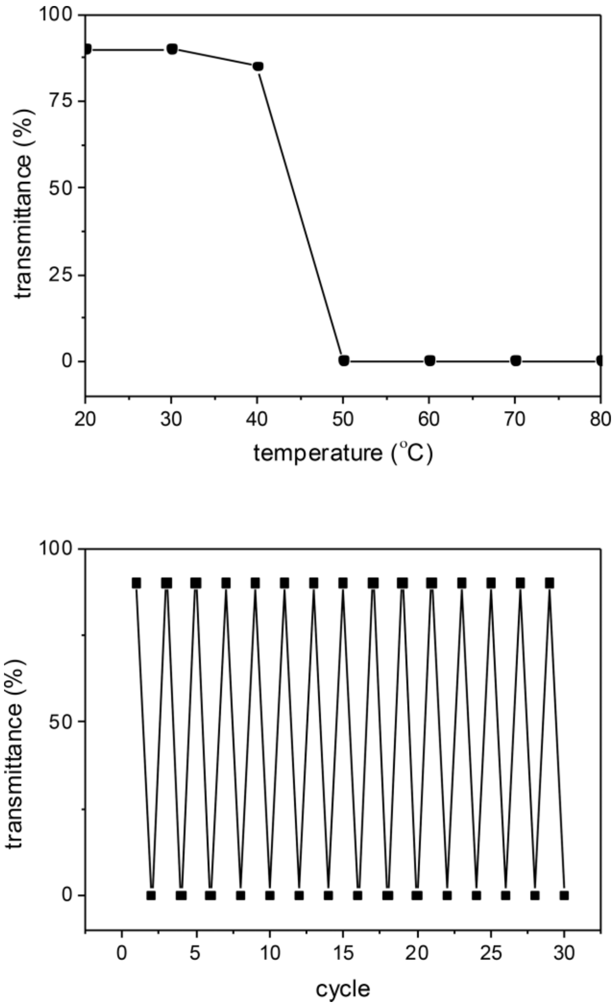


Figure 3. Temperature-dependent transmittance of an aqueous solution of **1** at 800 nm (top) and upon subjecting this solution to repeated heating and cooling treatment (bottom).

ties as a function of temperature. Interestingly, the UV/Vis absorption spectrum remained unchanged upon increasing the temperature of the aqueous solution of **1** (see Figure S6 in the Supporting Information). However, changes were observed in the emission spectra. Namely, the emission intensity increased with increasing temperature (Figure 4). The quantum yields for the fluorescence (φ_f) of **1** at 20 and 70 °C were calculated to be 0.4 and 1.2 %, respectively. This result suggests that the thermally triggered stacking of the corannulene nucleus restricts molecular motion and leads to enhanced emission, as is known for thermoresponsive polymers capable of aggregation-induced emission.[32–36] Although the emission remained very weak, we believe that the underlying concept can be harnessed to develop better emitters in solution. Nonetheless, inspired by these observations, we dropcast an aqueous solution of **1** onto a glass slide and maintained the temperature at 50 °C (Figure 5). Evaporation of the solvent left a solid network of fibers that emitted strongly when excited at 400 nm. This suggests that although in solution the enhancement of emission is limited, a significant response can be achieved in the solid state. In light of this, we believe that corannulene derivatives can be investigated in the future as new aggregation-induced emission probes.

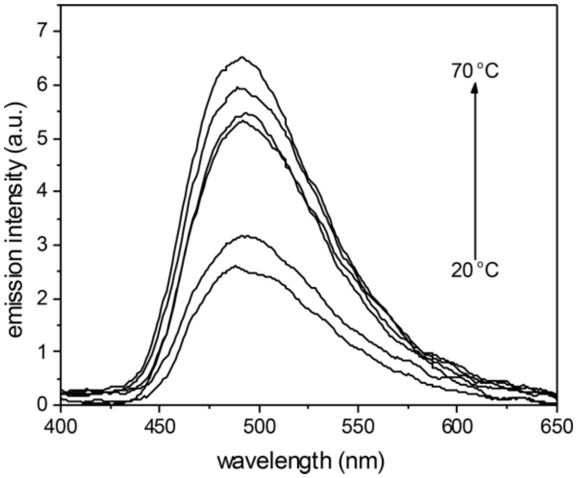


Figure 4. Emission spectra of **1** in water in the temperature range 20–70 °C.

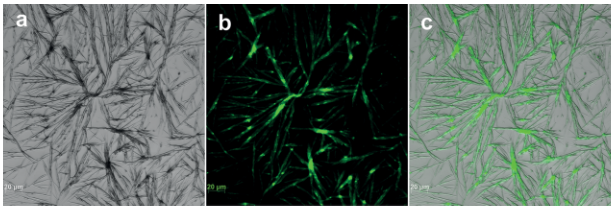


Figure 5. a) Bright-field, b) fluorescence excitation at 400 nm and collection at 480–580 nm, and c) overlay of a and b confocal fluorescence microscopy images (200 × 200 μm) obtained upon dropcasting an aqueous solution of **1** (10 mM) maintained at 50 °C on a glass slide.

The aforementioned optical microscopy observation then motivated us to investigate the morphology of the assembled architectures. Initially, atomic force microscopy in tapping mode was employed to avoid any contact between the probe tip and the material. This study indicated that the heights of the fibers are in the range of 10–100 nm, while their lengths are in the micrometer range (see Figure S7 in the Supporting Information). Encouraged by these results, we studied a sample of **1** by scanning electron microscopy (SEM) in low-energy ionization (LEI) mode. The aqueous solution used for the SEM experiments were deliberately made higher in concentration (20 mM) than used so far and a slow evaporation of water was ensured so as to facilitate the aggregation process and observation of longer structures. This change in experimental conditions indeed resulted in the formation of uninterrupted supramolecular fibers of hundreds of micrometers in length. The high density of these fibers can be seen in Figure 6. Such a large fibrilar structure, formed upon thermal assembly of a nonplanar polycyclic aromatic hydrocarbon derivative, is truly unprecedented. The chemical composition of the fibers was then confirmed by using energy-dispersive X-ray spectroscopy, which revealed the presence of carbon, hydrogen, and sulfur atoms in the assem-

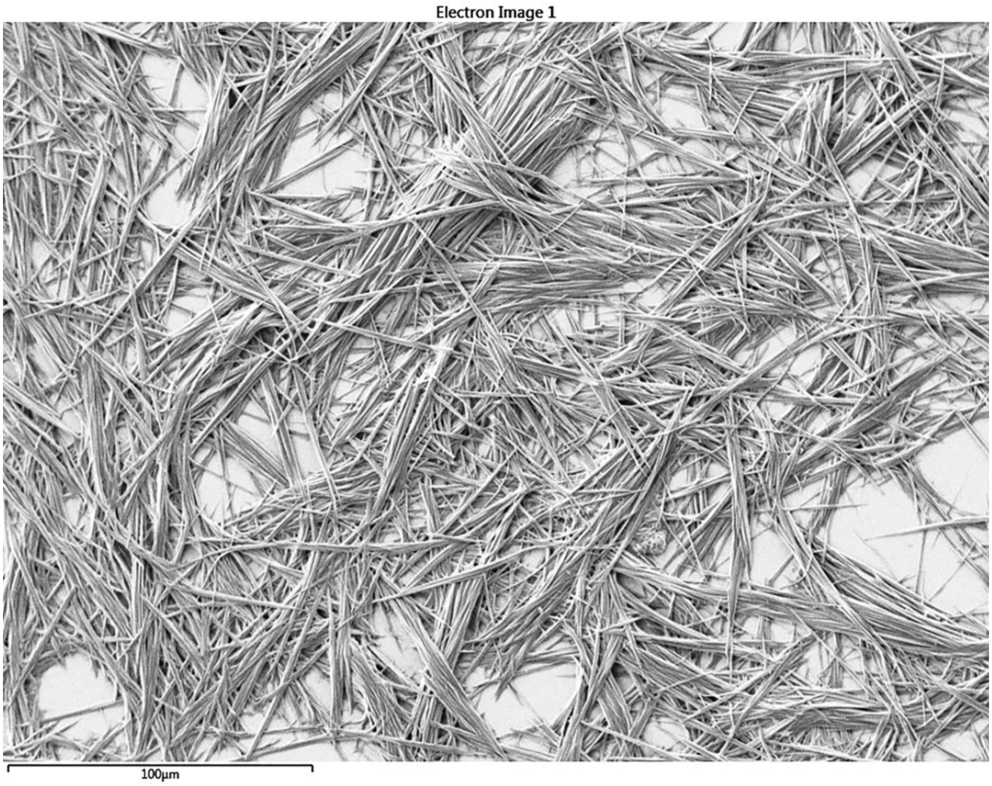


Figure 6. SEM image of the self-assembled fibres from a thermoreponsive assembly of **1** (scale bar = 100 μm).

bled structure in a ratio of 7.6:1.7:0.6, which is in agreement with the theoretically calculated ratio of 7.3:2:0.6 (see Figure S8 in the Supporting Information).

To further investigate the assembly process, variable-temperature ^{1}H NMR spectroscopy was employed using deuteriated water as the solvent. At room temperature, the signal arising from the corannulene nucleus can be seen at 6.7 ppm and those of the ethylene oxide units can be seen in the region of 3–3.8 ppm. Upon increasing the temperature, the signals arising from the aromatic and aliphatic protons broaden and move downfield (Figure 7). The most pronounced shift appears above the solution temperature of 40 °C. This suggests the thermally triggered formation of larger supramolecular structures in which the building block loses its mobility and is frozen. This is in perfect agreement with previous studies on ethylene glycol based thermoresponsive polymeric systems[36] and reflects the thermal behavior, discussed in the previous sections, of the present system. In deuteriated acetonitrile, a solvent in which the thermally triggered assembly process cannot occur, minor changes were observed in the peak positions and the signals remained sharp upon changing the solution temperature (see Figure S9 in the Supporting Information).

It is known that increasing the degree of polymerization can modulate thermal behavior. To examine whether this strategy is valid for the corannulene-based ethylene glycol system, new derivatives **2** and **3** were synthesized in isolated yields of 43 and 52 %, respectively. The ethylene glycol segments in **2** and **3** each carry 7 and 16 units, respectively (Figure 8 and Figures S10–S21 in the Supporting Information). Upon heating, however, no turbidity was observed in aqueous samples of **2** or **3** (Figure 9). In these systems, small oligomeric aggregates may exist, however, overall, the material remains soluble in water in the investigated temperature range of 10–100 °C.

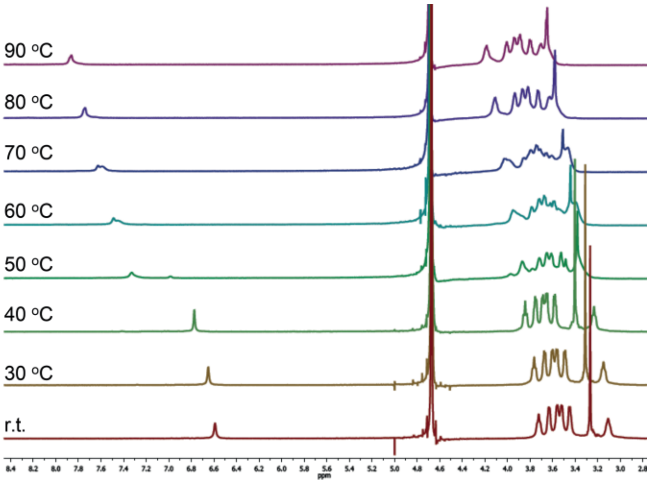
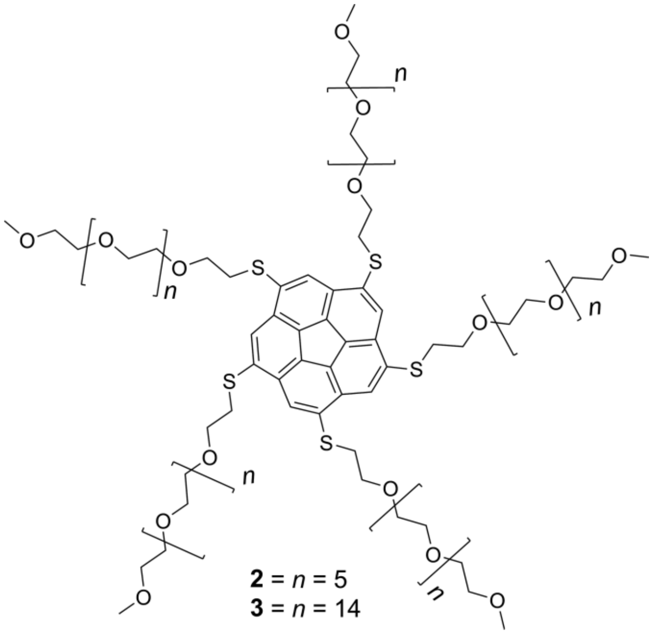


Figure 7. ^{1}H NMR spectra of **1** in deuteriated water at different temperatures. The range 3–4 ppm shows signals from protons of the ethylene glycol based side-chains, and the signal in the range 6.6–8 ppm arises from the corannulene core.



2 = n = 5
3 = n = 14

Figure 8. Chemical structures of corannulene derivatives **2** and **3** with longer ethylene glycol segments attached to the corannulene core.

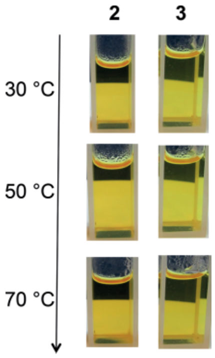


Figure 9. Digital pictures showing aqueous solutions of **2** (left) and **3** (right) at different temperatures.

Conclusions

Corannulene, when modified with chemically polar triethylene glycol units, is soluble in water at room temperature. However, increasing the temperature to above 40 °C causes turbidity and assembly of the building blocks into larger structures. The assembly process is completely reversible and can be carried out a number of times with no negative effects on the properties of the corannulene. Scanning electron and atomic force microscopy analyses indicate that the thermally triggered assembly process produces large fibrilar structures of micrometer length. Interestingly, the assembly process enhances the emission capability of the corannulene derivative. These results are remarkable because corannulene and its derivatives typically show little tendency to aggregate to form larger supramolecular structures or to emit light. The triggering of structural and property changes in a biologically pertinent temperature range along with its emissive characteristics indicate the potential utility of the presented nonplanar aromatic building block in biologically relevant thermoresponsive materials.

Experimental Section

Synthesis of 1: Sodium pieces (231 mg, 10.03 mmol) in absolute ethanol (5 mL) were stirred for 40 min and then 2-[2-(2-methoxyethoxy)ethoxy]ethane-1-thiol (1.80 g, 10.03 mmol) was added dropwise and the reaction mixture stirred at room temperature. After 2 h, the volatiles were removed under reduced pressure and the crude dried under vacuum for 2 h. The obtained salt was dissolved in *N*,*N*′-dimethylethyleneurea (DMEU; 2 mL), and then 1,3,5,7,9-pentachlorocorannulene (265 mg, 0.627 mmol) was added in one portion and the reaction mixture stirred further at room temperature. After 10 d, the reaction mixture was diluted with toluene (300 mL), washed with water (3 × 200 mL), and the organic layer was washed once with brine (100 mL), dried with Na_2SO_4, and concentrated. SiO_2 column chromatography of the obtained crude mixture using 50 % EtOAc in hexane and then 10 % MeOH in EtOAc as eluents afforded the corannulene pentasulfide **1** (272 mg, 0.238 mmol, 38 %) as a brown solid. M.p. 48–49 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 5 H), 3.79 (t, J = 6.7 Hz, 10 H), 3.60–3.65 (m), 3.49–3.51 (m), 3.33–3.36 (m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1, 134.8, 131.4, 125.7, 71.9, 70.5, 70.5, 70.4, 69.7, 59.0, 34.5 ppm. IR (neat): $\tilde{\nu}_{max}$ = 3055, 2985, 2306, 1423, 1265 cm^{-1}. HRMS (ESI): calcd. for $C_{55}H_{81}O_{15}S_5$ $[M + H]^+$ 1141.4179; found 1141.4246.

Synthesis of PEG-Thiol (Total Number of Ethyleneoxy Units = 7): Et_3N (15.9 mL, 114.28 mmol) and DMAP (140 mg, 1.14 mmol) were added to a stirred solution of poly(ethylene glycol) monomethyl ether 350 (20 g, 57.14 mmol) in anhydrous CH_2Cl_2 (200 mL) at room temp. The reaction mixture was then cooled to 0 °C and *p*-toluenesulfonyl chloride (13.07 g, 68.57 mmol) was added portionwise and then the reaction mixture was warmed to room temp. After 48 h, the volatiles were evaporated under reduced pressure and the obtained crude was purified by SiO_2 column chromatography to afford the viscous tosylate in a yield of 92 % (26.5 g, 52.55 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.2 Hz, 2 H), 7.30 (d, J = 8.2 Hz, 2 H), 4.11 (br. t, J = 4.8 Hz, 2 H), 3.48–3.65 (m), 3.32 (s, 3 H, OMe), 2.40 (s, 3 H, Ar-Me) ppm. The obtained tosylate (26.5 g, 52.45 mmol) was dissolved in absolute EtOH (190 mL) and treated with thiourea (4.79 g, 62.94 mmol) for 10 h at 100 °C. Then the reaction mixture was brought to room temp. and the volatiles evaporated under reduced pressure. Aqueous NaOH solution (20 wt.-%, 200 mL) was added to the obtained liquid and the reaction mixture heated at reflux for 5 h. Then the reaction mixture was cooled with ice-cold water and acidified with 15 % HCl to pH ≈ 2. The solution was extracted with EtOAc (300 mL), the aqueous layer was saturated with NaCl and extracted further with EtOAc (2 × 200 mL), the combined organic layers were washed once with brine, dried with Na_2SO_4, and the solvent evaporated under reduced pressure. The obtained crude was purified by SiO_2 column chromatography with 50 % EtOAc in hexane (v/v) to 10 % MeOH in EtOAc as eluents to afford MeO-(ethyleneoxy)$_n$-SH (10.8 g, 29.5 mmol, 52 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.48–3.59 (m), 3.27–3.32 (m, 3 H), 2.62–2.66 (m, 2 H), 1.51–1.56 (m, 1 H, -SH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.6, 71.6, 70.3, 70.2, 69.9, 58.7, 24.0 ppm. IR (neat): $\tilde{\nu}_{max}$ = 3529, 2870, 2553, 1967, 1639, 1458, 1350, 1249, 1103 cm^{-1}.

Synthesis of PEG-Thiol (Total Number of Ethyleneoxy Units = 16): Poly(ethylene glycol) monomethyl ether 750 (20 g, 26.66 mmol) was treated with Et_3N (5.39 g, 32.0 mmol), DMAP (65 mg, 0.533 mmol), and *p*-toluenesulfonyl chloride (6.1 g, 32 mmol) for 3 d to afford a crude tosylate. Then the crude mixture was purified by SiO_2 column chromatography with 1:1 hexane/toluene and then 1:3 (v/v) MeOH/toluene as eluents to afford the pure tosylate (21.69 g, 23.99 mmol, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz), 4.09 (br. t, *J* = 4.8 Hz, 2 H), 3.47–3.63 (m, OMe), 3.31 (s, 3 H), 2.39 (s, 3 H, Ar-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 132.8, 129.6, 127.7, 71.7, 70.5, 70.3, 70.2, 69.0, 68.4, 58.8, 21.4 ppm. IR (neat): $\tilde{\nu}_{max}$ = 2873, 2746, 2349, 1647, 1597, 1454, 1350, 1249, 1172, 1103 cm^{-1}. The obtained tosylate (21.6 g, 23.88 mmol) was dissolved in absolute EtOH (120 mL) and treated with thiourea (2.18 g, 28.65 mmol) for 8 h at 100 °C. Then the reaction mixture was cooled to room temp. and the solvent removed under reduced pressure. An aqueous NaOH solution (20 wt.-%, 120 mL) was added to the obtained liquid and the reaction mixture heated at reflux for 5 h. Then the reaction mixture was cooled with ice-cold water and acidified with 15 % HCl to pH ≈ 2. The solution was extracted with EtOAc (250 mL), the aqueous layer was saturated with NaCl and extracted further with EtOAc (2 × 250 mL). The combined organic layers were washed once with brine, dried with Na_2SO_4, and the solvent removed under reduced pressure. The obtained crude was purified by SiO_2 column chromatography with 100 % toluene to 50 % EtOH in toluene as eluents to afford MeO-(ethyleneoxy)$_n$-SH (12.5 g, 16.31 mmol, 61 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.59–3.64 (m), 3.52–3.54 (m, 2 H), 3.36 (s, 3 H, OMe), 2.66–2.70 (m, 2 H), 1.58 (t, *J* = 8.2 Hz, 1 H, SH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 72.4, 71.4, 70.2, 70.1, 70.0, 69.7, 58.5, 23.8 ppm. IR (neat): $\tilde{\nu}_{max}$ = 3564, 2870, 2553, 1641, 1458, 1350, 1296, 1249, 1199, 1170 cm^{-1}.

Synthesis of 2: Sodium pieces (169 mg, 7.34 mmol) in absolute ethanol (2.5 mL) were stirred for 40 min and then poly(ethylene glycol) methyl ether thiol (ethyleneoxy units = 7; 2.68 g, 7.34 mmol) was added dropwise and the solution stirred at room temperature. After 2 h, the volatiles were removed under reduced pressure and the residue dried under vacuum for 2 h. The obtained sodium salt was dissolved in DMEU (1.5 mL), and then 1,3,5,7,9-pentachlorocorannulene (194 mg, 0.459 mmol) was added in one portion and the reaction mixture stirred further at room temperature. After 10 d, the reaction mixture was diluted with EtOAc (200 mL), water (200 mL) was added, and the aqueous layer was saturated with NaCl and further extracted with EtOAc (2 × 200 mL). The combined organic layers were washed once with brine (100 mL), dried with Na_2SO_4, and concentrated. SiO_2 column chromatography of the obtained crude mixture with 1:1 (v/v) toluene/acetone to 4:1 (v/v) toluene/MeOH as eluents afforded the corannulene pentasulfide **2** as a brown liquid 400 mg, 0.197 mmol, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 5 H), 3.79 (t, *J* = 6.8 Hz, 10 H), 3.59–3.65 (m), 3.52–3.55 (m, 16 H), 3.32–3.37 (m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.03, 134.7, 131.2, 125.5, 71.7, 70.4, 70.3, 69.6, 58.8, 34.3 ppm.

Synthesis of 3: Sodium pieces (109 mg, 4.73 mmol) in absolute ethanol (2.0 mL) were stirred for 40 min and then poly(ethylene glycol) methyl ether thiol (ethyleneoxy units = 16; 3.62 g, 4.73 mmol) in absolute ethanol (2 mL) was added dropwise and the solution stirred at room temperature. After 2 h, the volatiles were removed under reduced pressure and the residue dried under vacuum for 2 h. The obtained sodium salt was dissolved in DMEU (2.0 mL) and then 1,3,5,7,9-pentachlorocorannulene (125 mg, 0.295 mmol) was added in one portion and the reaction mixture stirred further at room temperature. After 10 d, the reaction mixture was diluted with EtOAc (200 mL), water (200 mL) was added, and the aqueous layer was saturated with NaCl and further extracted with EtOAc (3 × 150 mL). The combined organic layers were washed once with brine (100 mL), dried with Na_2SO_4, and concentrated. SiO_2 column chromatography of the obtained crude mixture with 1:1 (v/v) $CHCl_3$/acetone and then with 2:2:1 (v/v/v) $CHCl_3$/MeOH/acetone as eluents afforded the corannulene pentasulfide **3** as a brown viscous liquid (620 mg, 0.152 mmol, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (s, 5 H), 3.75 (t, *J* = 6.8 Hz, 10 H), 3.49–3.66 (m), 3.28–3.33 (m) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1, 134.7, 131.3, 125.6, 71.8, 70.4, 70.3, 69.6, 58.8, 34.4 ppm.

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Keywords: Fused-ring systems · Corannulene · Aggregation · Supramolecular chemistry · Self-assembly · Thermosensitivity

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