

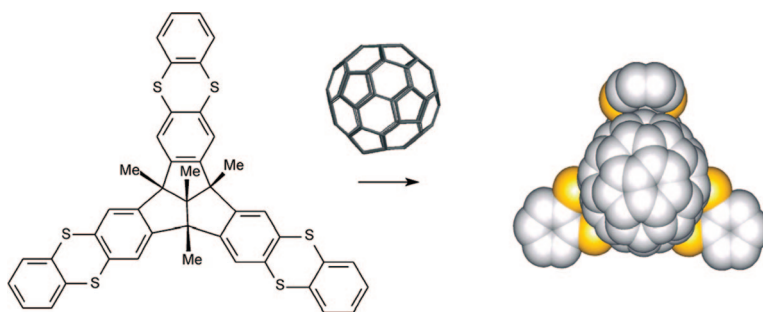
C_{3v} -Symmetrical Tribenzotriquinacenes as Hosts for C_{60} and C_{70} in Solution and in the Solid State

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Various tribenzotriquinacenes (TBTQs), most of which incorporate six functional groups at the periphery of their C_{3v} -symmetrical, rigid and convex–concave molecular framework, have been studied with respect to their ability to form supramolecular complexes with the C_{60} and C_{70} fullerenes, either in the solid state or in solution. The hexabromo derivative Br_6 -TBTQ was cocrystallized with C_{60} as $[Br_6$ -TBTQ $\cdot C_{60}$ •toluene] but, as studied by UV/vis and 1H NMR spectroscopy, aggregation in benzene, toluene, or carbon disulfide solutions was not observed. Likewise, in contrast to the related C_{5v} -symmetrical decakis(alkylthio)corannulenes, neither the parent hydrocarbon, nor a related hexamethoxy, or two hexakis(alkylthio) derivatives exhibited color, or complexation-induced chemical shift (CIS) changes with C_{60} or C_{70} . The novel tris(2,3-thianthreno)triquinacene (o - $S_2C_6H_4$)₃-TBTQ, a TBTQ derivative extended by three 1,2-benzodithiino wings, and synthesized from Br_6 -TBTQ, was found to form 1:1 complexes with C_{60} and C_{70} in both benzene and toluene solutions. Association constants were determined for the respective complexes, viz. (o - $S_2C_6H_4$)₃-TBTQ $\cdot C_{60}$ ($K_{assoc} = 977 \pm 56$) and (o - $S_2C_6H_4$)₃-TBTQ $\cdot C_{70}$ (463 ± 49 , both in benzene). The X-ray single crystal and molecular structures of the pure host and of the aggregates [(o - $S_2C_6H_4$)₃-TBTQ $\cdot C_{60}$ •2.5 chlorobenzene] were also determined.

Introduction

The design and synthesis of preorganized bowl-shaped macrocyclic hosts which can have applications in supramolecular and materials chemistry has been of considerable interest in recent years. In particular, as concerns their host–guest properties toward fullerenes C_{60} and C_{70} , such compounds have “classically” involved various functionalized derivatives of the bowl- or basket-shaped calixarenes,¹ and some calixnaphthalenes, such as **1**,² among other macrocyclic compounds (Chart 1). Most of these compounds have conformationally flexible structures that must overcome an entropic effect to efficiently

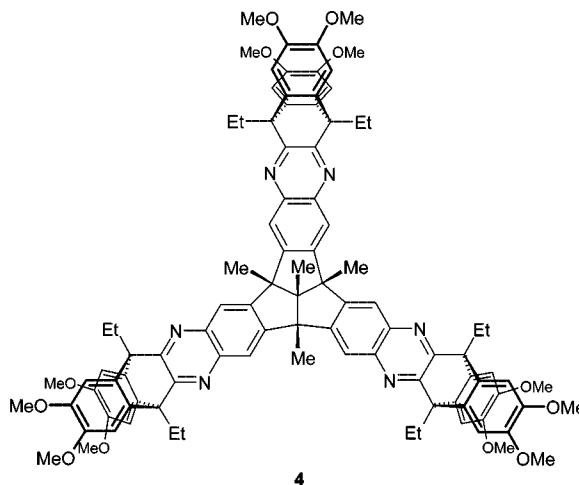
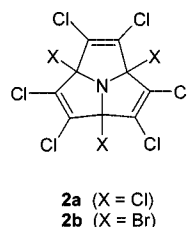
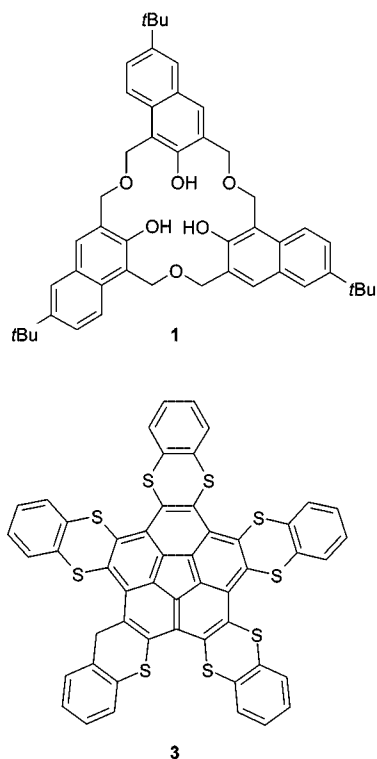
encapsulate the fullerene. Recently, some other more “exotic” and novel hosts for C_{60} have been reported, including, for

(1) For a review of fullerene–calixarene complexation studies reported up to the year 2000, see: (a) Zhong, Z.-L.; Ikeda, A.; Shinkai, S. In *Calixarenes 2001*; Asfari, Z., Böhrer, V., Harrowfield, J., Vicerns, J. Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001. (b) Makha, M.; Hardie, M. J.; Raston, C. L. *Chem. Commun.* **2002**, 1446–1447. (c) Wang, J.; Bodige, S. G.; Watson, W. H.; Gutsche, C. D. *J. Org. Chem.* **2000**, *65*, 8260–8263. (d) Ikeda, A.; Nobukuni, S.; Udzu, H.; Zhong, Z.; Shinkai, S. *Eur. J. Org. Chem.* **2000**, 3287–3293. (e) Atwood, J. L.; Barbour, L. J.; Heaven, M. W.; Raston, C. L. *Angew. Chem.* **2003**, *115*, 3376–3379; *Angew. Chem., Int. Ed.* **2003**, *42*, 3254–3257. (f) Bhattacharya, S.; Nayak, S. K.; Semwal, A.; Chattopadhyay, S.; Banerjee, M. *J. Phys. Chem. A* **2004**, *108*, 9064–9068. (g) Zhang, S.; Echegoyen, L. *J. Org. Chem.* **2005**, *70*, 9874–9881. (h) Iglesias-Sánchez, J. C.; Frago, A.; de Mendoza, J.; Prados, P. *Org. Lett.* **2006**, *8*, 2571–2574.

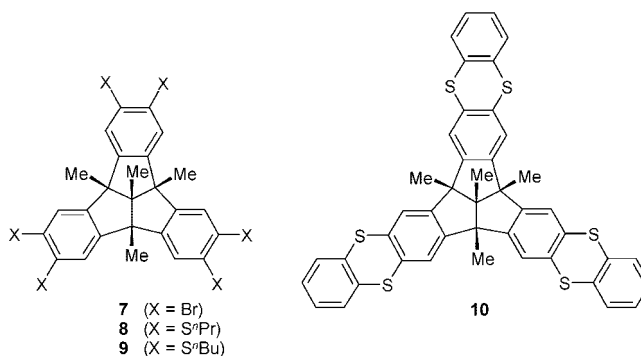
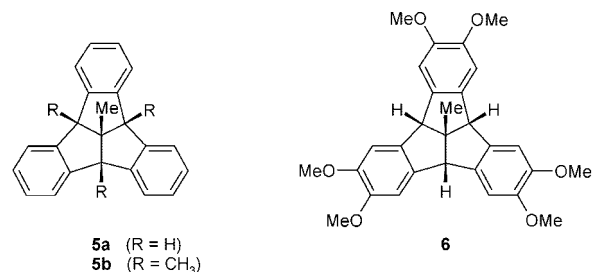
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[†] Memorial University of Newfoundland.

[‡] Bielefeld University.

CHART 1. Some Host Compounds Bearing Convex–Concave Molecular Structures That Have Been Studied with Respect to Their Association with Fullerenes in the Liquid and/or Solid State


example, the Pd₃-bisubphthalocyanine cage reported by Claessens and Torres,³ the “fly trap” corannulene derivative **3**, reported by Scott et al. and some of us,⁴ the double corannulene-containing molecular tweezer “buckycatcher” reported by Sygula et al.,⁵ as well as various other curved conjugated host molecules.⁶ Most recently, the novel tribenzotriquinacene (TBTQ)-based host **4**, as well as a close congener, were designed by Volkmer and his group, and their association with C₆₀ in solution and in the solid state was studied.⁷ All of these hosts, and others,⁸ show that a diversity of structures may be capable of binding with C₆₀ to different extents, and in various organic solvents, such as most commonly, benzene, toluene or carbon disulfide. The solubilities of C₆₀ in these solvents are sufficient enough to allow accurate and precise measurements of its association (or binding) constants with those hosts by spectroscopic titration experiments. Ideally, due to limitations which have been noted in relying solely on absorption spectroscopy,⁹ binding constants obtained only by UV–vis spectroscopy, should be confirmed by ¹H or ¹³C NMR using complexation-induced chemical shift (“CIS”) changes.¹⁰ In some cases however, C₆₀ can cocrystallize with a particular molecule in which solution complexation studies did not reveal any evidence

CHART 2. Parent Tribenzotriquinacenes **5 and Some TBTQ Derivatives (**6–10**) Studied Herein**


(3) Claessens, C. G.; Torres, T. *Chem. Commun.* **2004**, 1298–1299.

(4) (a) Georghiou, P. E.; Tran, A. H.; Mizyed, S.; Bancu, M.; Scott, L. T. *J. Org. Chem.* **2005**, *70*, 6158–6163. See also: (b) Mizyed, S.; Georghiou, P. E.; Bancu, M.; Cuadra, B.; Rai, A. K.; Cheng, P.; Scott, L. T. *J. Am. Chem. Soc.* **2001**, *123*, 12770–12774.

(5) Sygula, A.; Fronczek, F. R.; Sygula, R.; Rabideau, P. W.; Olmstead, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 3842–3843.

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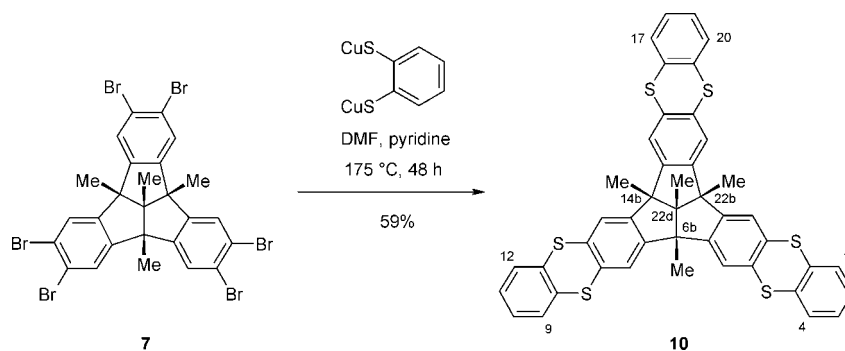
(8) Reference 7 contains a comprehensive listing of references of additional hosts for C₆₀, which have been reported by other researchers.

(9) Georghiou, P. E.; Tran, A. H.; Stroud, S. S.; Thompson, D. W. *Tetrahedron* **2006**, *62*, 2036–2044.

(10) Fielding, L. *Tetrahedron* **2000**, *56*, 6151–6170.

of supramolecular binding between the two. For example, unusual colinear coordination between the perchloroazatriquinacene **2a**^{11a} and its tribromo-hexachloro analogue **2b**^{11b} with C₆₀ (and C₇₀) have recently been reported for the solid-state by Pham et al. In the present paper, we will report on one such example and on another in which both the solution and a

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SCHEME 1. Synthesis of Tris(thianthreno)triquinacene **10** from Hexabromotribenzotriquinacene **7**

single-crystal X-ray structure provided evidence of binding between C_{60} and the particular TBTQ-based host.

This joint report has resulted from previous¹² and more recent¹³ considerations on the potential use of the easily accessible tribenzotriquinacene scaffold¹⁴ and its periphery-extended congeners as host compounds in supramolecular chemistry.^{15–19} The close similarity of the TBTQ framework to that of the related cyclotrimeratrylenes,²⁰ which have been shown to be effective host compounds, has been noted.^{21,22} Its concave surface was found to exert a strong negative electrostatic potential²³ and to coordinate preferentially to tricarbonylchromium units.²⁴ Various multiple functionalizations and skeletal extensions have already been reported, including the recent construction of triquinacene-based 3-fold metacyclophanes.¹⁸ Various applications have been suggested for the use, in particular, of the mutually orthogonal orientation of the three indane wings in the TBTQ framework.^{13,15,25} In this vein, we have welcomed the recent contribution by Volkmer and his associates⁷ on their use of a particular arene-extended tribenzotriquinacene as a rigid building block for their novel "sockets"²⁶ into which fullerene C_{60} can be sequestered. That report, in particular, prompts us to disclose our own ongoing research in both the syntheses of a previously unreported 3-fold annulated tribenzotriquinacene²⁷ and the properties of such compounds with respect to their supramolecular interactions with both C_{60} and C_{70} .

Results and Discussion

Our synthetic endeavors on functionalized tribenzotriquinacenes,^{12,14–20,24} mostly based on the *centro*-methyl derivative **5a** (the so-called "methyl-hat") and the bridgehead fully methylated analogue **5b** (the "tetramethyl hat"), and our ongoing interest in the design and study of potential new hosts for C_{60} and/or C_{70} fullerenes^{2,4,9} led us to investigate their complexation behavior with several TBTQ derivatives bearing a C_{3v} -symmetrical pattern of substituents (Chart 2). Among these, the parent compound **5b**,^{17,28} the hexamethoxy "methyl hat" **6**,²¹ and the hexabromo- and hexa(alkylthio)tetramethyl hats **7–9**, which all have been described previously,^{12,17,19a} were studied. In addition, the previously unknown tris(thianthreno)triquinacene **10**,²⁷ a TBTQ derivative bearing three 1,2-benzodithiino extensions, was synthesized and its association with C_{60} and C_{70} in solution and cocrystallization in the solid state was investigated in detail.

The new "tris-flytrap" (*vide infra*) **10** was synthesized in analogy to the classic condensation procedure between dibromo-

arenes and copper(I) alkylthiolates²⁹ by heating a suspension of the hexabromotribenzotriquinacene **7** in a DMF–pyridine mixture with an excess of freshly prepared dicopper(I) benzene-1,2-dithiolate (Scheme 1). Several different attempts were performed and it was eventually found that carrying out the reaction at 175 °C for 48 h gave an acceptable yield (59%), in spite of the low solubility of the starting material. Thus, the efficiency of the 6-fold coupling of **7** with the dithiolate is comparable, but somewhat lower, than that of the 6-fold coupling of **7** with the simple copper(I) alkylthiolates in pyridine/quinoline mixtures, giving hexakis(thioethers) such as **8** and **9** in yields of 81–94%, as described previously.^{12,17} Compound **10** was obtained as a colorless solid and found to

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(24) Ceccon, A.; Gambaro, A.; Manoli, F.; Venzo, A.; Kuck, D.; Bitterwolf, T. E.; Ganis, P.; Valle, G. *J. Chem. Soc., Perkin Trans. 2* **1991**, 233–241.

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(26) Several definitions of "socket" can be found, including the following: "a receptacle where something into which an electric device can be inserted", wordnet.princeton.edu/perl/webwn.

(27) Presented at the IUPAC 3rd International Symposium on Novel Materials and Synthesis (NMS III) and 17th International Symposium on Fine Chemistry and Functional Polymers (FCFP-XVII), Shanghai, China, Oct 17–21, 2007; see: Kuck, D.; Strübe, J.; Linke, J. *J. Fudan Univ. (Nat. Sci.)* **2007**, *46*, 773–773.

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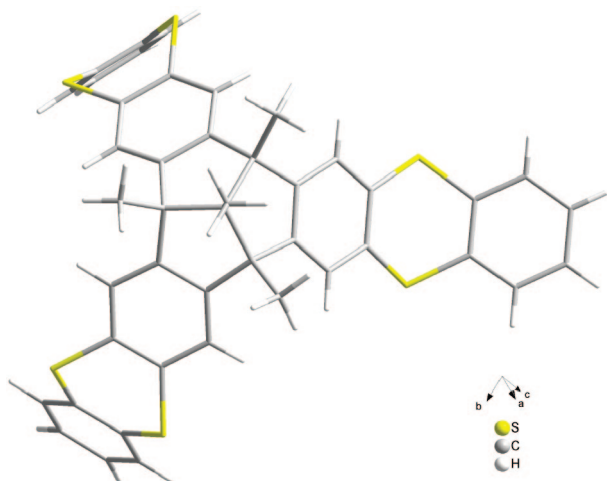


FIGURE 1. X-ray molecular structure of tris(thianthreno)triquinacene **10**, seen from the top of the convex molecular surface and illustrating the quasi- C_s -symmetrical conformation of the formally C_{3v} -symmetrical molecule.

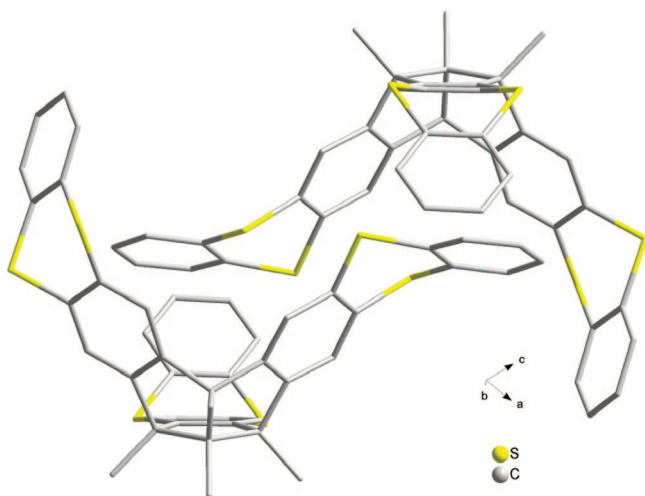


FIGURE 2. "Reciprocal" dimer of compound **10** in the crystal. The two molecules of **10** are coordinated about a center of inversion and intercalated by their *exo*-oriented thianthrene units. Hydrogen atoms have been omitted for the sake of clarity.

be soluble in normal organic solvents such as acetone, dichloromethane, benzene, and toluene.

An X-ray structure analysis was performed with a single crystal of **10** obtained from chloroform. The crystals were found to contain two solvent molecules per molecule of **10**, one of which was ordered and the other of which was disordered. Surprisingly, only two of the three thianthreno wings of **10** are oriented such that they extend the concavity of the triquinacene core, the third wing being bent outward (Figure 1). To a first approximation, this generates a C_s -symmetrical structure bearing a rather deep bowl that is nevertheless accessible laterally. Interestingly, the thianthreno unit which is bent outward partially fills the interior concavity of an adjacent molecule of **10** aligned antiparallel and coconcave to the first one, such that its own outward thianthreno unit protrudes into the bowl of the first one. Hence, a "reciprocal" dimer of two molecules of **10** is formed in which the *exo*-oriented thianthrene wings are mutually associated with the bowl of the partner molecule (Figure 2).

Thus, the intercalation of two molecules of **10** generates dimers, having roughly globular shapes, which are packed in a

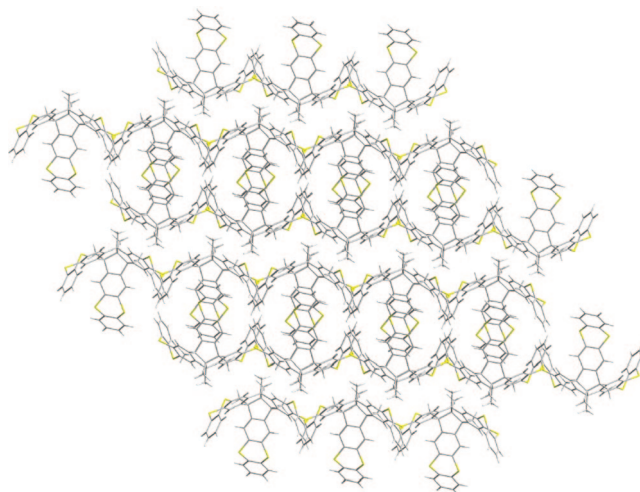


FIGURE 3. Crystal structure of **10** consisting of layers of dimers.

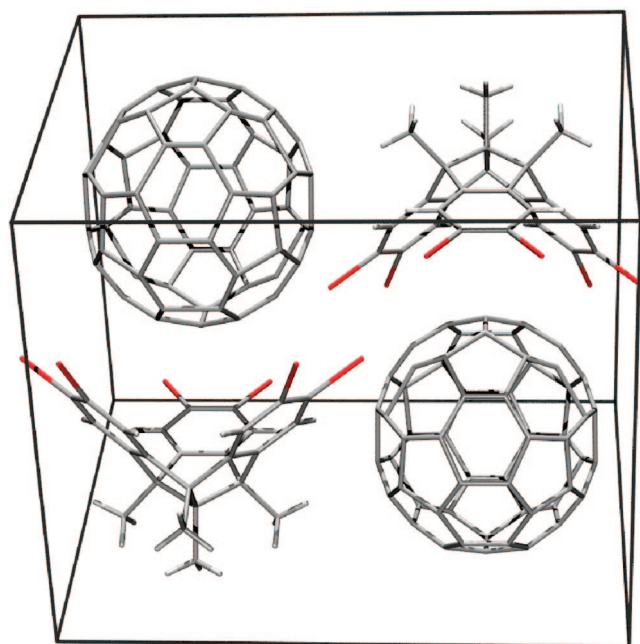


FIGURE 4. X-ray unit cell structure of the solid-state complex [7C₆₀•toluene]. The toluene molecules are disordered and have been omitted for the sake of clarity.

highly regular crystal lattice (Figure 3). The dimers are arranged in layers such that the convex sides of the extended tribenzotriquinacene frameworks of adjacent sheets of dimers face each other in corrugated packings.

The tris(thianthreno)triquinacene **10** represents a C_{3v} -symmetrical analogue of the corannulene-based, C_{5v} -symmetrical and, likewise, rigid and bowl-shaped flytrap **3**, which was shown to associate with C₆₀ in solution.⁴ We had postulated that the regular concavity and rigid symmetry of our tribenzotriquinacenes would make them similarly suitable candidates for supramolecular complexation with C₆₀ and also with C₇₀. Molecular mechanics modeling³⁰ appeared to support that initial postulate. Disappointingly, none of the three compounds **5b–7** showed any experimental evidence for complexation when each

(30) Molecular modeling was conducted using Spartan'06 (Windows version) Molecular Modeling Software. Molecular mechanics (MMFF94) calculations were conducted on the optimized geometry of the host and/or complexes.

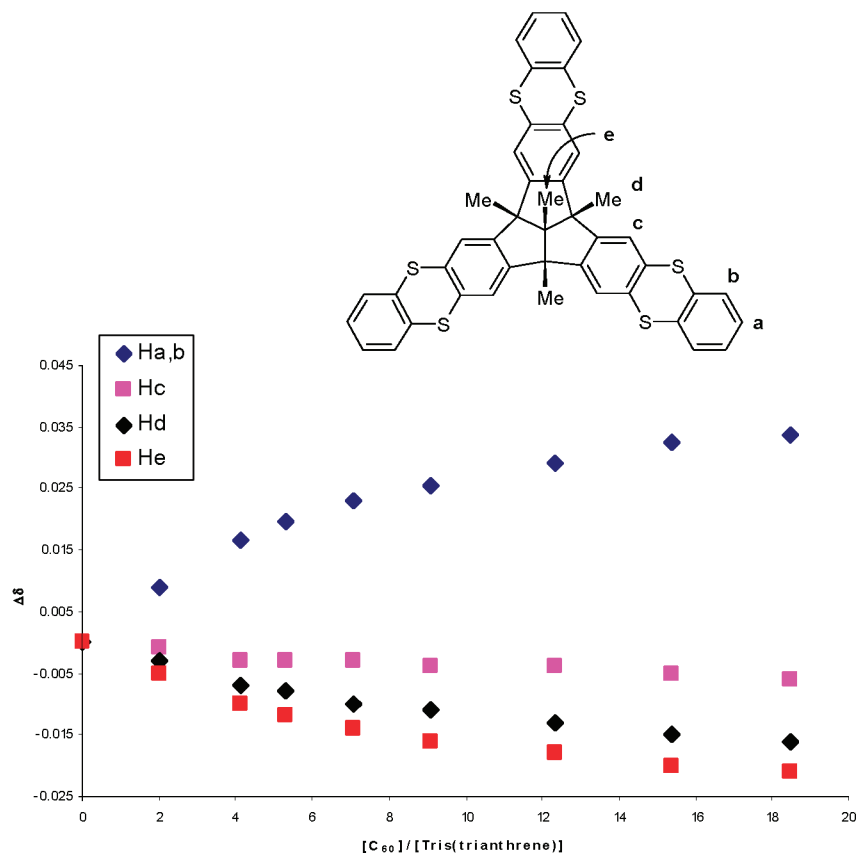


FIGURE 5. Complexation-induced chemical shift (CIS) changes for protons on tris(thianthrene)triquinacene **10** from titrations of C₆₀ in benzene-d₆.

fullerene was tested in either benzene, toluene or carbon disulphide solutions; no color or ¹H NMR CIS changes could be discerned using various host-to-guest ratios. However, slow evaporation of the toluene solutions of **5b** or **7**, each of which contained equimolar amounts of C₆₀, afforded dark red-brown crystals. Whereas the single crystals obtained with the parent hydrocarbon were not suitable for X-ray analysis, an X-ray structure of a single crystal derived from the hexabromo compound **7** was successfully determined and solved, showing that the unit cell consisted of two 1:1:1 complexes of **7**, C₆₀, and toluene (Figure 4).

The X-ray structural analysis of **7**C₆₀ revealed that the dark-red prisms crystallized in the monoclinic crystal system, in the *P*2₁/*m* (#11) space group and with lattice constants of *a* = 12.3490(14) Å, *b* = 17.1710(18) Å, *c* = 13.4281(15) Å, and β = 91.906(3)°. The toluene molecules were found to be completely disordered, and there is one hydrogen atom missing from the toluene in the model. The characteristic C_{3v}-symmetry of the TBTQ component **7** within the crystalline compound [**7**C₆₀•toluene] is retained as was also found for **7**, determined recently.^{19a}

More interestingly, the mutual orientation of the tribenzo-triquinacene units in [**7**C₆₀•toluene] resembles only to a very small extent that reported by Pham et al. for perchloro-10-azatriquinacene (**2a**) in their X-ray crystal structure of **2a**C₆₀,^{11a} and for the tribromo-hexachloro-10-azaquinacene **2b** in their X-ray crystal structure of **2b**C₆₀.^{11b} In **7**C₆₀, the molecules are arranged in antiparallel columns, whereas in Pham's X-ray structures, they are arranged in parallel columns. In the X-ray structure of [**7**C₆₀•toluene] the shortest average contact Br...C distances between **7** and the fullerene pointing

to the concave surface of the "bowl" of **7** are 3.36 Å, and those between the same atoms of **7** and the neighboring fullerene are slightly shorter, at 3.31 Å. The intermolecular Br...Br contacts between neighboring molecules of **7** are 3.47 Å and the shortest Br...C distance between **7** and a carbon atom in a toluene molecule is 3.55 Å. The shortest average contact Br...C distances in this structure are very similar to the corresponding values in **2a**C₆₀, for which the shortest average contact Cl...C distances are 3.31 Å,^{11a} and to those in **2b**C₆₀, for which the close contact Cl...C distances range from 3.25 to 3.44 Å, and in which there are Br...C distances of 3.43 and 3.46 Å.^{11b} The C₆₀ molecule is not orientationally disordered, which is in agreement with the observed results of Pham and co-workers. It should also be noted that these authors did not describe any binding studies with **2a** or **2b** and C₆₀ or C₇₀, which presumably implies that they did not see any solution complexation either. However, whereas these authors also reported the X-ray structures of 1:1 complexes of these two halogenated azatriquinacenes with C₇₀,¹¹ all of our attempts at forming similar single-crystal C₇₀ complexes with **7** were unsuccessful.

Although no evidence could be found for the complexation of C₆₀ or C₇₀ in solution with any of the compounds **5b**–**7**, we hypothesized that, by analogy with our previous experience with the fullerene complexation behavior of the alkylthiocorannulene derivatives,⁴ the corresponding C_{3v}-symmetrical hexakis(alkylthio)tribenzotriquinacenes **8** and **9**^{12,17} and the newly designed tris(thianthrene)triquinacene **10**²⁷ could be better hosts for these fullerenes. Again, molecular modeling (see Figure 9, below) suggested that this hypothesis was reasonable. In fact, it turned

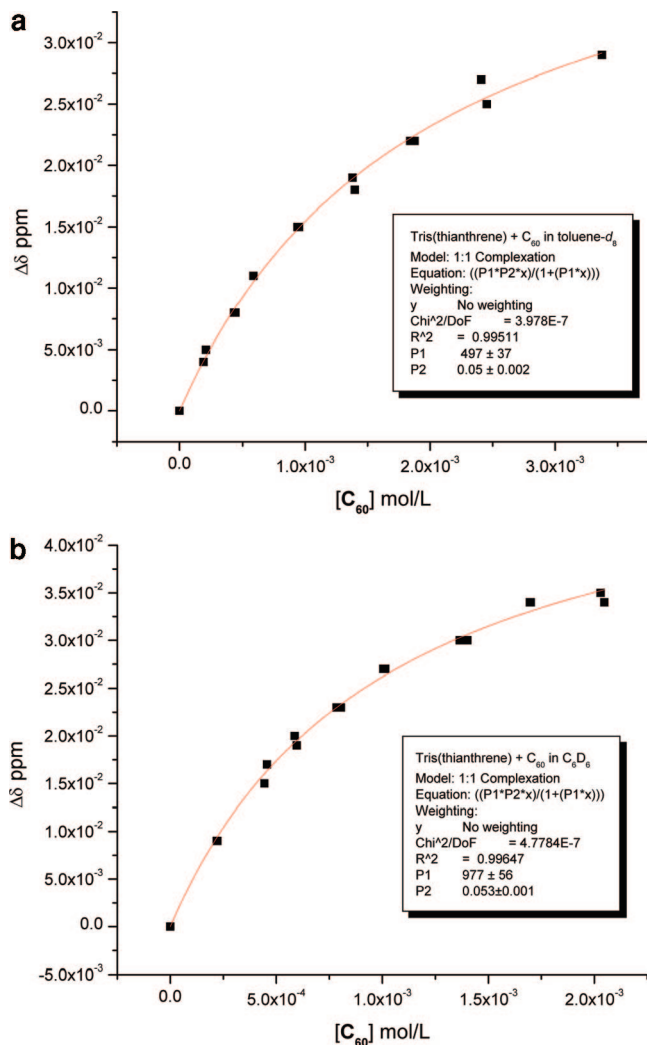


FIGURE 6. Nonlinear curve fitting of CIS changes from the titration of tris(thianthreno)triquinacene **10** with C₆₀ (a) in benzene-*d*₆ and (b) in toluene-*d*₈.

out that only in the case of **10** was there any experimentally demonstrable evidence for such complexation with the fullerenes tested.

Supramolecular Complexation Behavior of Hexakis(thioalkyl)tribenzotriquinacenes 8–10 with C₆₀ and C₇₀.^{1H}

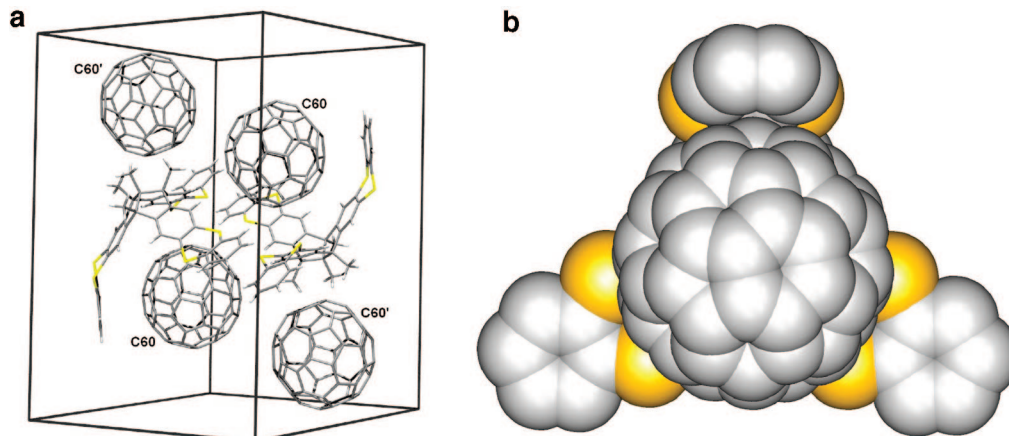


FIGURE 7. X-ray unit cell structure of the 2:1 complex of C₆₀ complex with tris(thianthreno)triquinacene **10**. (a) Chlorobenzene molecules have been omitted for clarity, and (b) top view onto the molecule of C₆₀ which is nested within **10**, showing the C_{2v} symmetry of the host within the solid-state complex.

NMR titration experiments were conducted using each of compounds **8**, **9**, and **10** with either C₆₀ or C₇₀ in each of the same three solvents already used for compounds **5b–7**, as described above. However, only tris(thianthreno)triquinacene **10** was found to exhibit any CIS changes in its ¹H NMR signals observed with both of the fullerenes. Figure 5 shows the changes observed, in benzene-*d*₆, for the chemical shifts of the different protons in **10** as a function of the concentration, in this case, of added C₆₀. The relatively largest absolute chemical shift changes observed were for the high-field aromatic protons, for example, 1-H and 2-H (≡ H^a and H^b) and these values were used for the subsequent quantitative determination of the association constants.

Job and mole-ratio plots indicated that 1:1 supramolecular complexes formed under the conditions examined. This was confirmed when the determinations of *K*_{assoc} values were determined in benzene-*d*₆ and toluene-*d*₈ using nonlinear curve fitting plots for the 1:1 binding isotherm as described by Connors.³¹ For C₆₀ in benzene-*d*₆ and toluene-*d*₈, *K*_{assoc} values of 977 (±56) and 497 (±37) were obtained (Figure 6a and b), and for C₇₀ in the same solvents, *K*_{assoc} were found to be 463 (±49) and 233 (±42), respectively. Surprisingly, and in contrast to the “fly trap” corannulene **3** that was reported earlier by some of us,⁴ no complexation was observed when the tris(thianthreno) analogue **10** was tested in carbon disulfide with either C₆₀ or C₇₀. On the other hand, it should be noted that in a different solution complexation study of C₆₀ and C₇₀ conducted with the calixnaphthalene **1**, a similar phenomenon was observed: In that case, *K*_{assoc} values could be determined when benzene-*d*₆ and toluene-*d*₈ were used as solvents, but not when CS₂ was used.⁹ It is less surprising that no complexation could be detected between **10** and C₆₀ or C₇₀ when carbon tetrachloride^{1f} was used since the solubilities of the fullerenes are very low in that solvent, thus precluding the observation of any significant CIS in the NMR titrations.

X-Ray Structural Analysis of 10C₆₀. Characteristic red crystals formed upon slow evaporation of the solutions containing equimolar amounts of **10** and C₆₀ or C₇₀ in benzene or toluene, but these crystals proved to not be suitable for X-ray structural determinations. Gratifyingly, however, crystals also formed from a chlorobenzene solution of **10** and C₆₀, which enabled the determination of the X-ray structure (Figure 7). A red platelet having the empirical formula C₁₇₉H₄₃Cl_{2.50}S₆, hence corresponding to [10C(C₆₀)₂·2.5 chlorobenzene], crystallized in the primitive monoclinic crystal system, in the *P*2₁/*n* (#14)

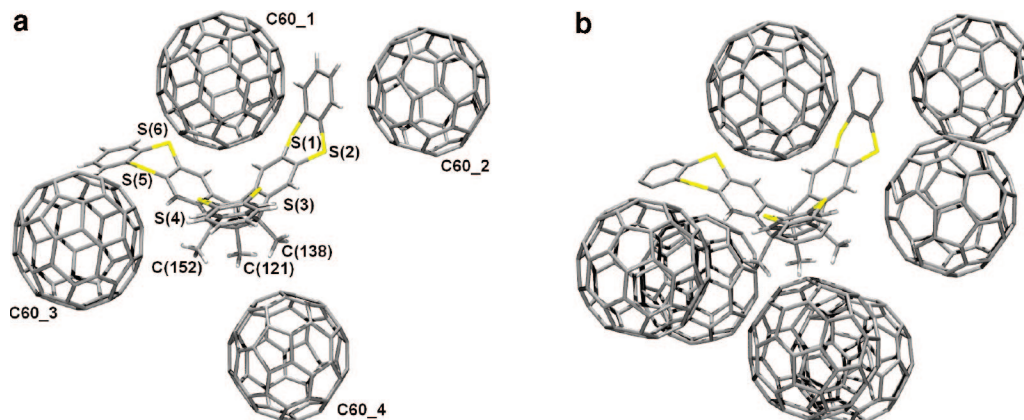


FIGURE 8. (a) X-ray structure showing the orientation of closest van der Waals contacts between: (i) C_{60} molecules nested in the central "bowl" of tris(thianthreno)triquinacene **10**, that is, " C_{60_1} "; (ii) within the "partial bowl" of **10**, that is, " C_{60_3} "; and (iii) outside, that is, " C_{60_2} " and " C_{60_4} ". (b) X-ray structure showing the orientation of closest van der Waals contacts between **10** and up to seven C_{60} molecules.

space group with lattice constants of $a = 21.171(4)$ Å, $b = 18.745(3)$ Å, $c = 25.119(4)$ Å, and $\beta = 91.987(4)^\circ$. The asymmetric unit contains one-half-occupancy disordered chlorobenzene generated by a symmetry expansion. Cl(3) represents a chlorine atom in one orientation of the molecule and represents a carbon atom in the other orientation. The occupancy of this chlorine atom was adjusted to reflect this disorder. The fullerenes are completely ordered, as was also reported by Pham et al.¹¹ in their structures of $2aC_{60}$ and $2bC_{60}$ but in contrast with the X-ray structure of $C_{60}C1$ reported by some of us previously.²

One of the two C_{60} molecules (labeled as " C_{60} ") is clearly nested within the cavity of the tris(thianthreno)triquinacene **10** which, in this partial structure, has C_{2v} -symmetry (Figure 7). The distance between the centroid of the C_{60} and the bridgehead carbon atom of the apex of **10** (C-22d) is 8.30 Å. Notably, this value is shorter by ~ 0.30 Å than the corresponding distance seen with the $7C_{60}$ (8.60 Å), implying that, in the latter case, the fullerene is not as deeply embedded or nested within the bowl as it is in $10C_{60}$. In turn, using this criterion, tris(thianthreno)triquinacene $10C_{60}$ is very similar to Volkmer's compound, the related complex $4C_{60}$, the X-ray structure analysis of which showed that the centroid of C_{60} is 8.308 Å apart from the central bridgehead.⁷ Thus, from the geometrical point of view, the two tribenzotriquinacene-based cavities **4** and **10** host C_{60} with very similar degree of tightness, notwithstanding the fact that two of the benzodithiino wings of **10** are bent outside in the solid state, whereas the framework of Volkmer's host necessarily preserves the 3-fold, all-concave orientation of its three "walls". By way of contrast, the distance within the bowl of the C_3 -symmetrical hexahomotrioxacalix[3]naphthalene **1**, within the complex 1_2C_{60} , from the C_{60} centroid to that generated around the narrow-rim hydroxyl groups is 7.32 Å.²

Closer analysis of the X-ray structure of $10C_{60}$ (Figure 8a) suggests possible additional reasons as to why CIS changes could be observed in the titration experiments of C_{60} (and presumably with C_{70}) with **10** but not with **7**. The closest contacts between the "bowl" and the associated C_{60} and the neighboring C_{60} molecules, as shown in (Figure 8b), are listed in Table 1.

The data presented in Table 1 indicate (ignoring the possible role of the chlorobenzene) that there are multiple close contacts between both the sulfur atoms and the methyl groups of **10** with up to seven C_{60} molecules. Significant parts of these close

TABLE 1. List of Closest van der Waals Contacts, As Obtained from the X-Ray Structural Analysis of the Complex $[10C_{60}]_2 \cdot 2.5 C_6H_5Cl$ Shown in Figure 8

Closest contacts between the "bowl" of tris(thianthreno)triquinacene 10 and C_{60_1} (defined by C(61)–C(120))	
S(3)···C(91)	3.467(7) Å
S(4)···C(79)	3.398(7) Å
S(5)···C(65)	3.845(8) Å
S(6)···C(65)	3.702(9) Å
Closest contacts between the "bowl" of 10 and C_{60_2} (defined by C(61 ₂)–C(120 ₂))	
C(132)···C(88 ₂)	3.458(11) Å
Closest contacts between the "bowl" of 10 and C_{60_3} (defined by C(61 ₃)–C(120 ₃))	
S(4)···C(196 ₃)	3.662(10) Å
S(5)···C(61 ₃)	3.378(8) Å
Closest contacts between the "bowl" of 10 and C_{60_4} (defined by C(61 ₄)–C(120 ₄))	
C(121)H(1)···C(116 ₄)	3.0802 Å
C(138)H(13)···C(116 ₄)	3.8513 Å
Closest contacts between the "partial bowl" arm of 10 and C_{60' (defined by C(61)–C(120))	
C(121)H(2)···C(16)	2.8895 Å
C(124)H(6)···C(16)	2.7791 Å
C(152)H(23)···C(16)	2.9610 Å
Closest contacts between the "partial bowl" arm of 10 and $C_{60'_2}$ (defined by C(61)–C(120))	
C(121)H(3)···C(24 ₂)	3.2761 Å
C(138)H(14)···C(24 ₂)	3.1345 Å
C(152)H(22)···C(24 ₂)	2.9291 Å

contacts, together with the nesting of a C_{60} deep into the "bowl" of **10**, which also would enhance any π – π interactions between the electron-rich aromatic rings of the TBTO scaffold, may offer insights as to why **10** formed a complex with C_{60} in solution whereas the other C_{3v} -symmetrical tribenzotriquinacenes that were tested in this study did not. Since X-ray structures could not be obtained with the simpler hexakis(alkylthio)tribenzotriquinacenes **8** and **9**, supramolecular C_{60} "complexes" with each of the analogues **8**–**10** were subjected to molecular mechanics modeling and the distances from the centroids of the C_{60} molecules to the apex (C-12d in **8** and **9**, C-22d in **10**) of each of these three hosts were determined (Figure 9). Values of 10.59, 11.12, and 8.71 Å were calculated from these structures

(31) Connors, A. *Binding Constants*; Wiley, New York, 1987.

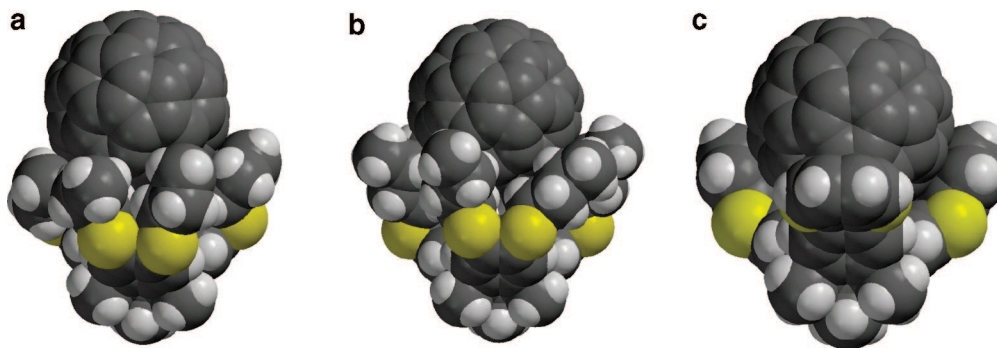


FIGURE 9. Space-filling models of the supramolecular complexes of C₆₀ with (a) hexakis(*n*-propylthio)-TBTQ **8**, (b) hexakis(*n*-butylthio)-TBTQ **9** and, (c) tris(thianthreno)triquinacene **10**, as generated by Spartan'06-MMFF98.

of **8**C₆₀, **9**C₆₀, and **10**C₆₀, respectively. These values are supportive of the hypothesis that, in the molecules studied and reported herein, the depth of the nesting of C₆₀ into the concave surface of a TBTQ host molecule is an important predictive criterion. This is presumably also consistent with the finding that the depth of solid-state nesting of C₆₀ reported for **4**C₆₀⁷ and found for **10**C₆₀ in the present work are identical.

Conclusions

Tribenzotriquinacenes bearing extended multifunctionalized arene peripheries can be suitable C_{3v}-symmetrical hosts for supramolecular association with C₆₀ and C₇₀ not only in the solid state but also in solution. In this respect, the present work describes a particular and relatively easily accessible TBTQ derivative, the tris(thianthreno)triquinacene **10**, in an interesting parallel to the recently reported TBTQ derivative **4**,⁷ to the C_{5v}-symmetrical 10-fold alkylthio-substituted corannulenes, and to the most closely corannulene-based flytrap **3**, in particular. In view of the number and orientation of the structural components of the hosts **3**, **4**, and **10**, the association constants with C₆₀, determined under comparable conditions so far, appear to reflect the hosts individual architectures: $K_{\text{assoc}}(\mathbf{10}) < K_{\text{assoc}}(\mathbf{3}) < K_{\text{assoc}}(\mathbf{4})$. A similar rationale seems to emerge for the solid state, in that the hexabromotribenzotriquinacene **7** enables a significantly less efficient nesting of C₆₀ into the tribenzotriquinacene cavity ("bowl") than do the TBTQ hosts **10** and **4** bearing extended aromatic peripheries. This corresponds to the lack of any association with C₆₀ and C₇₀ in the liquid phase and the identical depth of nesting in solid-state **10**C₆₀ and **4**C₆₀ (8.30 and 8.31 Å, respectively). We may expect that the increasing interest in tribenzotriquinacene derivatives bearing various mutually orthogonally oriented polycyclic extensions will render the host-guest chemistry of these compounds also to be of interest in their supramolecular chemistry. The noteworthy parallel of the development of tris(thianthreno)triquinacene **10**²⁷ from the present collaborative effort and Volkmer's TBTQ-based hosts⁷ and also further recent fruitful collaborative studies into extended tribenzotriquinacenes with the groups of Cao¹⁸ and Langhals²⁵ provide us with a promising and enjoyable proof of this trend.

Experimental Section

6b,14b,22b,22d-Tetramethyl-[6b,14b,22b,22d]tetrahydro-[1,4]benzodithino-[2',3':5',6']indeno[1',2',3':3,4]thianthreno-[2',3':5,6]pentaleno[1,2-*b*]thianthrene [Tris(thianthreno)triquinacene, **10].** (1) A mixture of copper(I) oxide (859 mg, 6.00 mmol), benzene-1,2-dithiol (852 mg, 6.00 mmol), and ethanol (10 mL) was heated to reflux for 48 h. After that period, the red color had vanished and a milky-white suspension of dicopper(I) benzene-1,2-dithiolate had formed. The product was filtered by suction, washed with a few mL of ethanol, and dried in vacuo to give a colorless solid (1.60 g, quantitative yield).

(2) A suspension of hexabromotetramethyltribenzotriquinacene **7**^{12,17} (200 mg, 247 μmol) in dimethylformamide (5.0 mL) and pyridine (1.5 mL) was stirred while dicopper(I) benzene-1,2-dithiolate (250 mg, 933 μmol) was added. The mixture was heated to 175 °C for 48 h. After cooling to ambient temperature, the deep-brown product mixture was poured onto ice (100 g) and hydrochloric acid (35%, 30 mL). The resulting mixture was extracted with diethyl ether and washed with hydrochloric acid (10%), water, aqueous ammonia, and again with water. The solution was dried over sodium sulfate, and the solvent was removed under reduced pressure. The solid residue was subjected to chromatography on silica gel (*n*-hexane/trichloromethane 2:1) to give the tris(thianthreno) **10** (110 mg, 59%) as a colorless solid, mp > 380 °C, which was crystallized from chloroform. ¹H NMR (500 MHz, CDCl₃): δ = 7.44 (m, 6 H), 7.39 (s, 6 H), 7.18 (m, 6 H), 1.55 (s, 9 H, CH₃), 1.24 (s, 3 H, CH₃). ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 148.4 (C), 135.67 (C), 135.3 (C), 128.7 (CH), 127.6 (CH), 123.1 (CH), 71.4 (C), 62.0 (C), 25.8 (CH₃), 16.1 (CH₃). IR (cm⁻¹): 3049.8, 2963.9, 1443.5, 1427.6, 1374.5, 1353.9, 1251.7; MS (DEI, 70 eV): *m/z* (%): 750 (50) [M⁺], 735 (16), 375 (7). Accurate mass (EI-MS): C₄₄H₃₀S₆ calcd 750.06718 found: 750.06773.

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Supporting Information Available: NMR (¹H and ¹³C), MS, and IR spectra and cif files for the single crystal X-ray structures of [7C₆₀•toluene] **10** and [10C(C₆₀)₂•2.5 chlorobenzene]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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