

Synthesis of Tetrathiafulvalene-Containing Zirconium (IV) Pincers and Metallocavitands for Hosting Fullerenes

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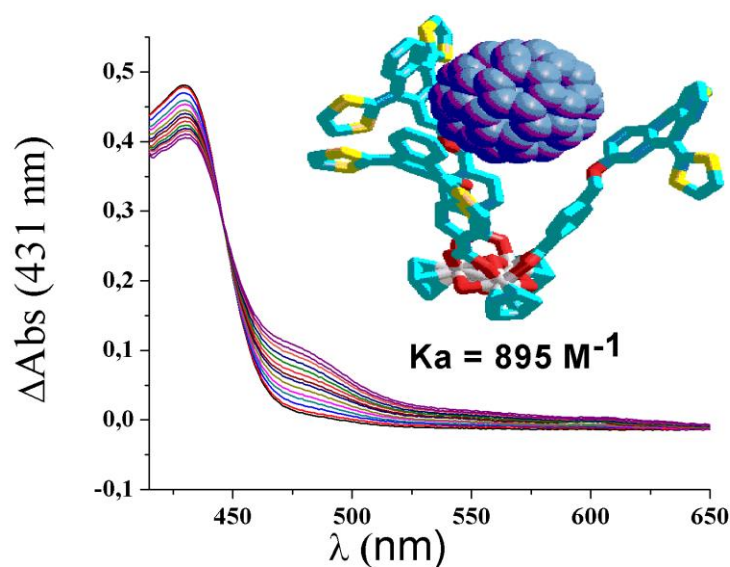
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Abstract

The synthesis and spectroscopic characterization of zirconium (IV) dicarboxylate **1** and metallocavitand **2** are described. Encapsulation studies of fullerenes C_{60} and C_{70} were performed using UV-vis spectroscopy in chlorobenzene, toluene, benzene, carbon disulfide and in a mixture of toluene/dichloromethane. UV-vis titrations have shown that the binding abilities of the hosts toward fullerene C_{70} are considerably higher than those obtained for fullerene C_{60} .

Keywords

Metallocavitands, Zirconium, Fullerenes, Host-guest, Supramolecular

Highlights

- Tripodal zirconium metallocavitands having TTF-derivatized carboxylate ligands was made.
- The solubility of the carboxylate ligands has an influence on the structure of the complexes.
- The metallocavitands can host fullerenes C_{60} and C_{70} .

Introduction

There has been a broad interest in the past few years in the chemistry of cavitands, notably for recognition properties [1-6]. By modifying the structural parameters of the cavity, a large array of guests with different size, shape and charge can be captured inside the void of the hosts. The advantages that can result from these supramolecular assemblies include the possibility of stabilizing reactive intermediates [2, 7], hosting unusual molecules within the cavity [8, 9], and controlling reaction rates, regioselectivity and yields of catalytic processes [10-15]. Although tailoring of the cavities of cavitands can be done by synthetic pathways in order to improve their performance, the multi-step functionalization can be tedious and low yielding. An alternative is the use of coordination chemistry to generate metallocavitands via self-assembly processes. Using a large array of ligands and metal precursors, it is possible to obtain interesting nanoscale architectures [16-21]. These structures may find use in a large array of applications as chemical sensors, nanoscale reaction vessels [22, 23], containers for drug delivery [24, 25], molecular switches [26-29] and memory storage devices [30]. Our research group has developed in the past few years an aggregation approach to access trimetallic conical structures with tantalum [31-33]. We focused notably on the one-step synthesis of tantalum (V) boronate metallocavitands. These metallocavitands can be prepared in good to excellent yield via the one-step reaction of Cp^*TaMe_4 with aryl boronic acids [33].

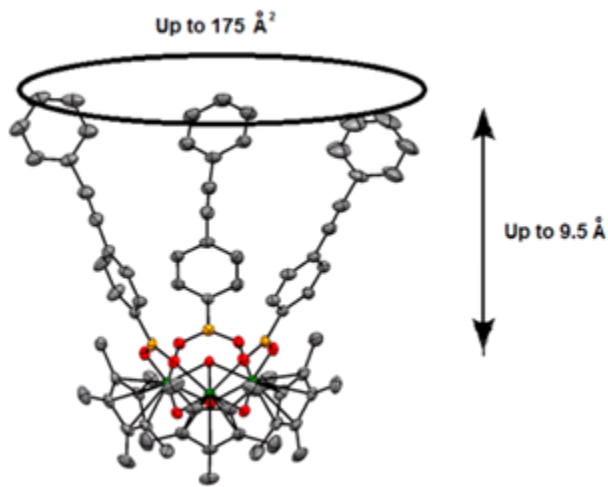


Figure 1. Example of a tantalum metallocavitand obtained by X-ray crystallography [32].

These metallocavitands possess a conic cavity similar to calix[4]arenes with a pseudo- C_3 symmetry (Figure 1). The cavity can be easily expanded to reach an upper rim area of 175 \AA^2 by the introduction of spacers on the aryl boronate moiety [31]. The tantalum metallocavitands have demonstrated hosting capabilities for Lewis bases such as acetone and tetrahydrofuran *via* hydrogen bonding and electrostatic interactions [32]. Owing to their hosting properties, high yielding synthesis and ease of manipulation, we wanted to expand this concept to the capture of fullerenes, namely C_{60} and C_{70} . The fullerenes are quite useful in modern electronics, but in order to process this material covalent functionalization is needed to increase its solubility [34]. However, the covalent functionalization modifies the π system of the fullerene cages and therefore reduces their electron accepting properties when compared to the pristine materials [35]. In the hope of keeping the exceptional electronic properties of fullerenes, a supramolecular approach is sought after to increase its solubility while keeping its electronic properties [34]. Nevertheless, since the fullerenes are known to be electron acceptors, we were concerned that the electrophilic metallic core of the tantalum metallocavitands may alter the ability of the supramolecules to host fullerenes. In order to reduce the electrophilicity of the core while keeping the C_3 -conical structure, we decided to expand our study to zirconium (IV) carboxylate complexes. By replacing the boron atoms of the boronate ligands with carbon atoms using isoelectronic carboxylate ligands, we expected for the cavity to become less electrophilic and more prone to interact with fullerenes while keeping similar structural parameters. Two pathways have been used so far for the construction of zirconium (IV) carboxylates with the desired architecture. The first method involves a sodium ethoxide mediated assembly of carboxylic acids with Cp_2ZrCl_2 [36]. Also possible is the assembly of carboxylic acids with Cp_2ZrCl_2 in aqueous dichloromethane [37].

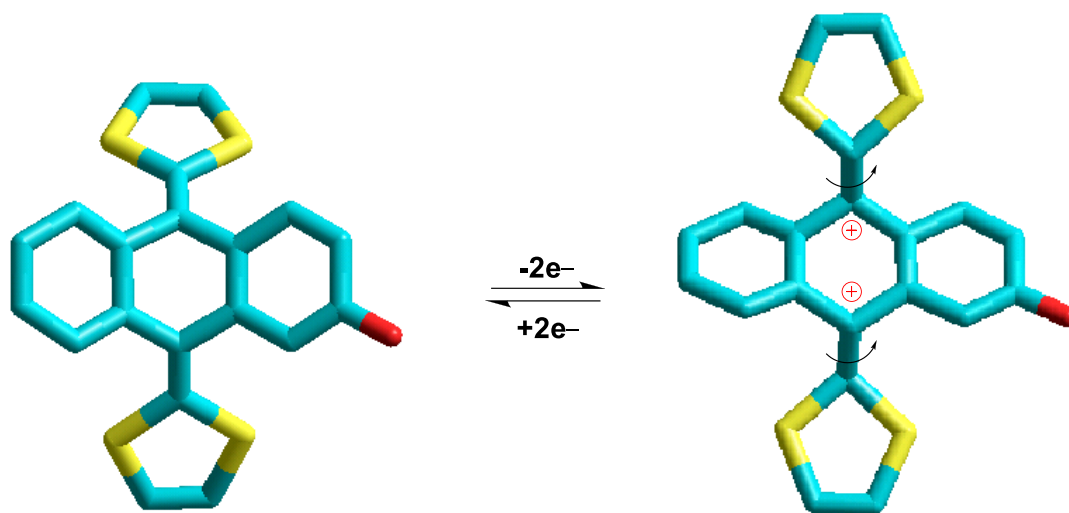


Figure 2. Structures of the neutral (left) and oxidized (right) state of tetrathiafulvalene (TTF).

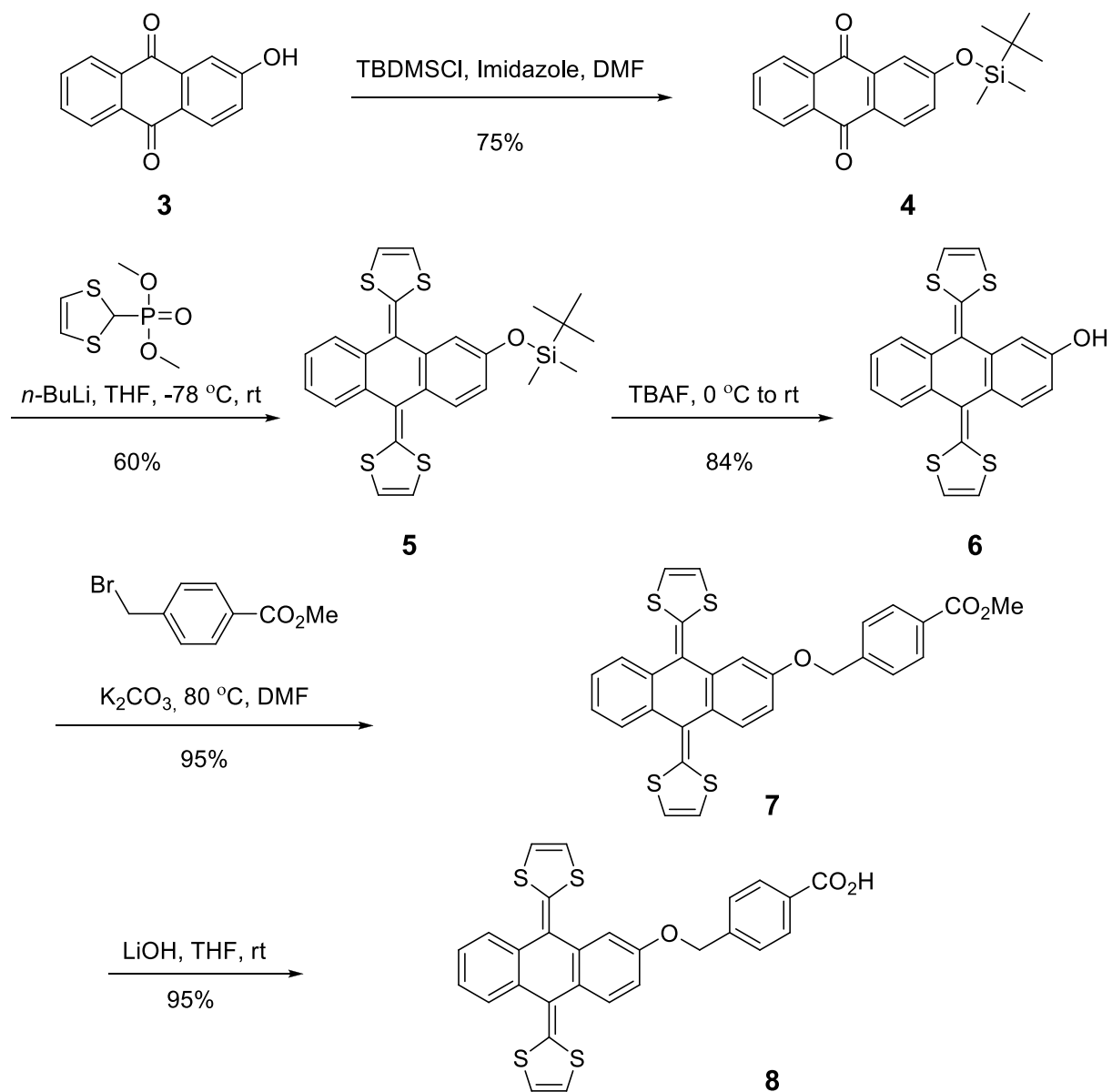
Non-covalent interactions such as π - π stacking and charge-transfer interactions are the main driving forces in fullerene host-guest chemistry [38]. From this point of view, π -extended donor systems such as the tetrathiafulvalene (TTF) are attractive molecules; they adopt a butterfly shape at the neutral state, while the corresponding dications adopt a twisted conformation that help the interaction with the spherical shape of the fullerene (Figure 2) [39]. This class of molecules has been used in the construction of hosts for fullerenes using aromatic π - π -stacking interactions between the surface of fullerenes and the extended tetrathiafulvalene (exTTF) [40-47]. Therefore, the design and investigation of new recognition molecules based on zirconium (IV) metallocavitands having TTF units will undoubtedly push forward the development of metallocavitands as hosts for fullerenes. We report herein the synthesis and the structural characterization of zirconium species containing extended cavities with exTTF carboxylate ligands and demonstrate that these metallocavitands can host C_{60} and C_{70} .

Results and Discussion

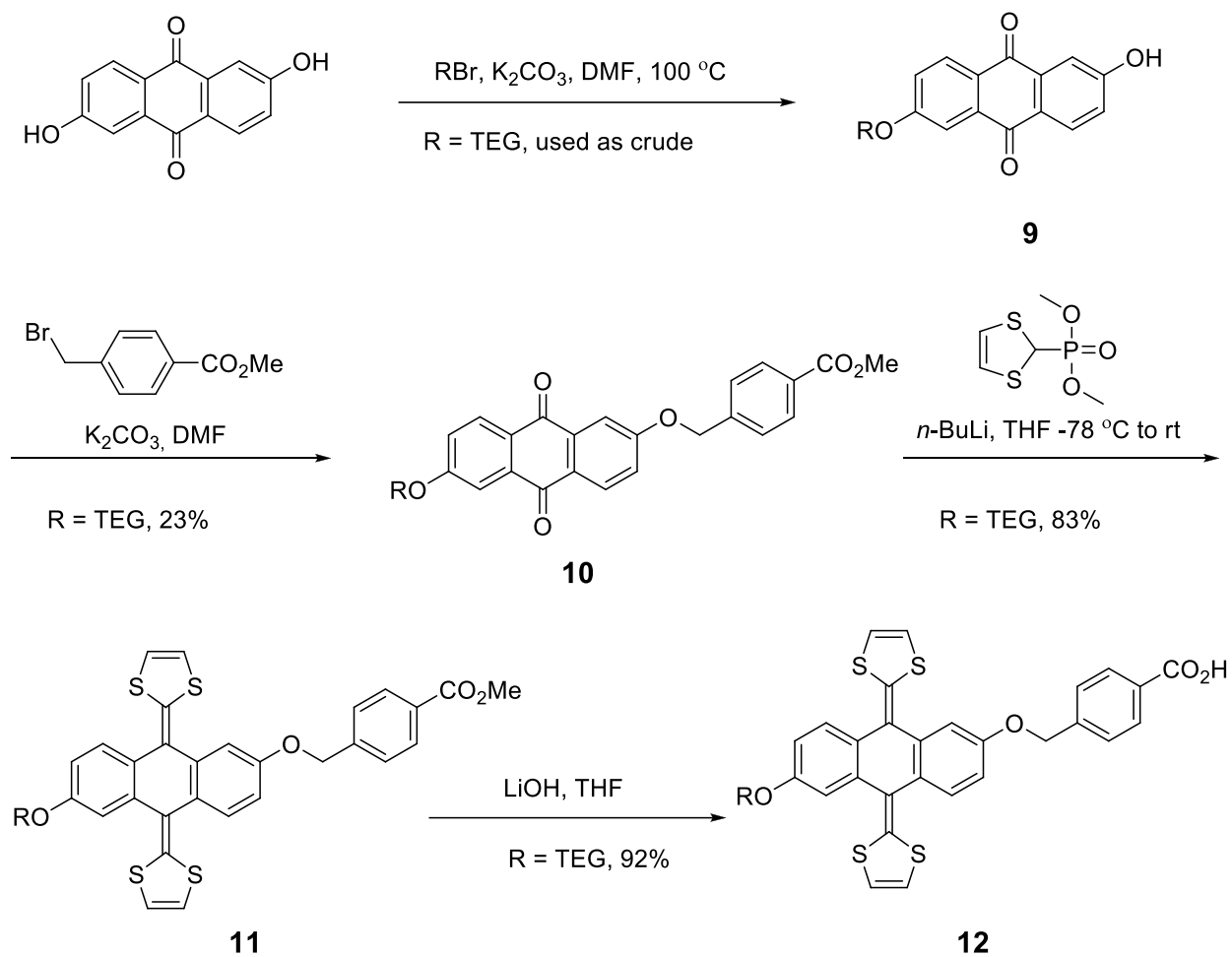
In order to generate the desired metallocavitands, the synthesis of the TTF-containing carboxylic acids **8** and **12** were carried out. Compound **8** was synthesized in five steps as described in Scheme 1. The synthesis starts by the protection of the hydroxyl group of 2-hydroxyquinone **3**

using *tert*-butyldimethylsilyl (TBS) in DMF [48]. The desired product **4** was isolated in 75% yield after purification on silica gel. The reaction of TBS-protected 2-anthraquinone **4** with 2-dimethoxyphosphinyl-1,3-dithiole using the Wittig–Horner reaction [49] in dry THF in the presence of *n*-butyllithium at -78 °C gave product **5** in 60% yield. The subsequent removal of the protecting group was accomplished by treatment of compound **5** with tetrabutylammonium fluoride (TBAF) to obtain compound **6** in 84% yield [46]. The S_N2 substitution reaction of the phenol **6** with methyl 4-(bromomethyl)benzoate yielded corresponding ester **7** in 95% yield. Hydrolysis of the latter product with lithium hydroxide followed by the acidification of the aqueous phase and by filtration provided the desired acid **8** in 95% yield after purification by precipitation.

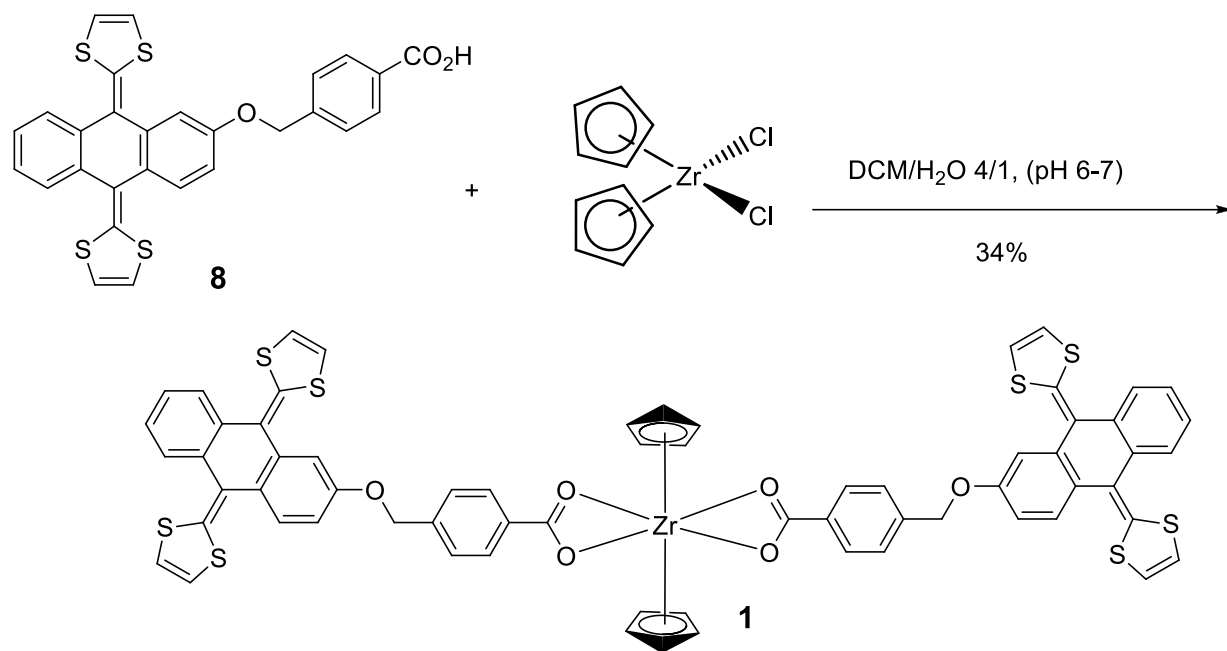
Since most of the binding studies with fullerenes are done in organic solvents, the introduction of an aliphatic chain was carried out at the 6 position to make the molecule more lipophilic which should result in an enhanced solubility. The triethylene glycol (TEG) chain was used by ease of preparation and high solubility in organic and aqueous systems [52]. It is also known that glycol chains are helpful in the preparation of fullerene receptors, since they stabilize the complex formed with fullerenes through *n*- π interaction [49-51]. Synthesis of TEG-TTF was accomplished from anthraflavic acid in a four-step procedure as outlined in Scheme 2. The first step of this synthesis was the TEGylation with triethylene glycol bromide; however, this product was used as crude material due to the difficult separation from the bis TEGylated product and unreactive glycol chains. Nucleophilic substitution of the crude material with methyl 4-(bromomethyl)benzoate yielded the crude product **10** that was purified by precipitation in methanol in 23% yield for the two-steps synthesis. The addition of 2-dimethoxyphosphinyl-1,3-dithiole to compound **10** using the Wittig–Horner [49] reaction in dry THF in the presence of *n*-butyllithium at -78 °C yielded the corresponding ester **11** in 83% yield. Hydrolysis of the ester with lithium hydroxide following by acidification with hydrochloric acid yielded the desired acid **12** in 92% yield (Scheme 3).



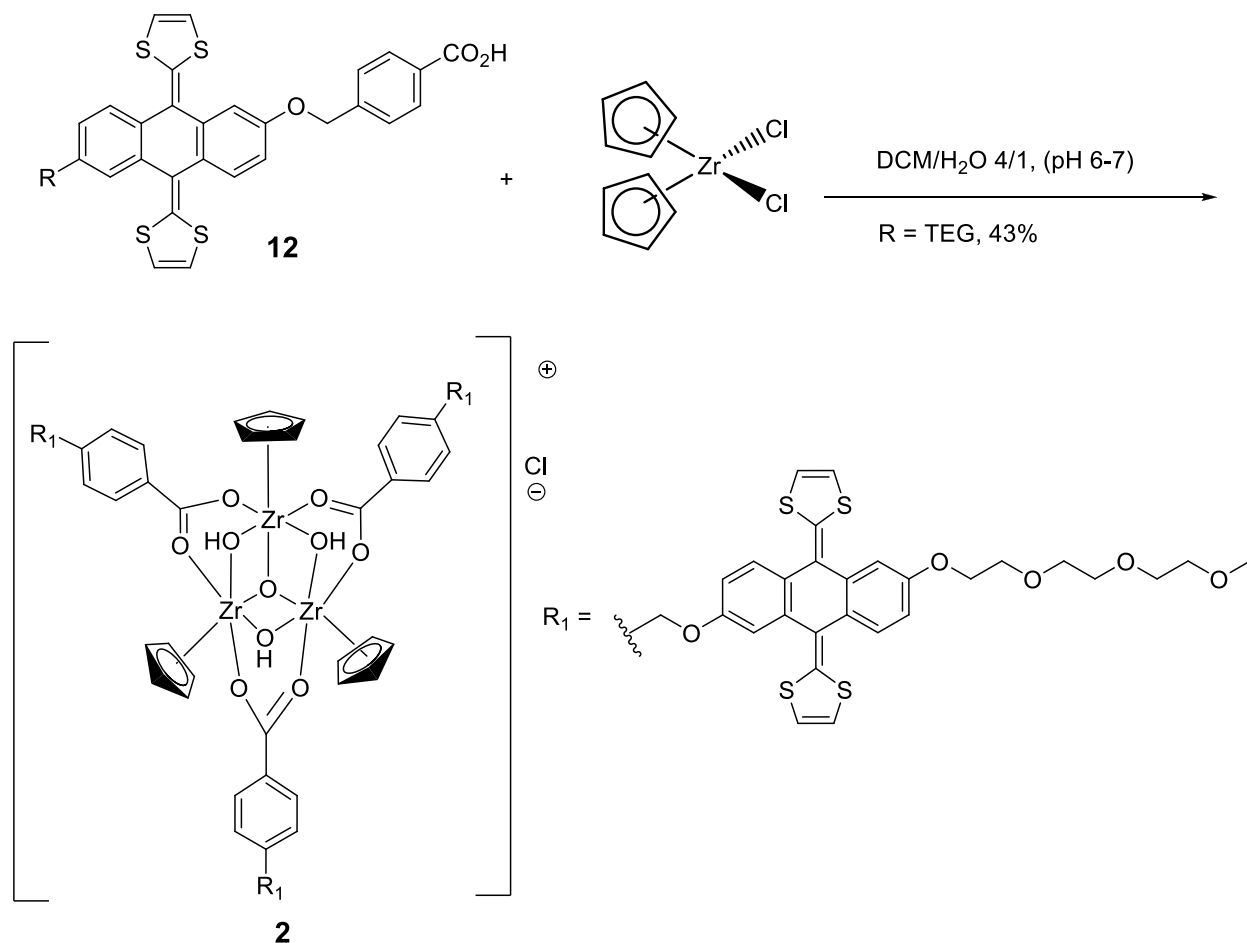
Scheme 1. Synthesis of monosubstituted TTF carboxylic acid **8**.



Scheme 2. Synthesis of bisubstituted TTF carboxylic acid **12**.



Scheme 3. Synthesis of host **1**.



Scheme 4. Synthesis of TTF zirconium (IV) metallocavitand **2**.

The synthesis of the zirconium carboxylate species **1** and **2** was accomplished according to a published procedure by reacting carboxylic acids **8** and **12**, respectively, with zirconocene dichloride in aqueous media, as described in Schemes 3 and 4 [37]. It was possible to observe by ^1H NMR spectroscopy of both solutions the disappearance of the acidic carboxylic protons, suggesting that the coordination of the carboxylate moieties had taken place. The presence of sharp singlets at $\delta = 6.31$ and 6.33 for compounds **1** and **2**, respectively, confirms the presence of the cyclopentadienyl rings. The resonances for the aromatic protons were present in the $\sim\delta 8.10$ – 6.80 region. When looking at the integration values for the proton resonances of the carboxylate ligands and of the cyclopentadienyl ligands, it is possible to observe that these two moieties are present in a 1:1 ratio in both complexes **1** and **2**. Although it was expected for compound **1** to

adopt a trimetallic structure reminiscent of analogous chemistry with arylcarboxylates [36,37], including nitrogen-containing arylcarboxylates [54], the exact MS data does not agree with such an assignment.

Indeed, a m/z of 1277.9918 was observed which correspond to a biscarboxylate biscyclopentadienyl species as illustrated in Scheme 3. Similar biscarboxylate compounds had already been described when carboxylic acids were added to zirconocene at lower pH [37]. It is probable that the low solubility of carboxylic acid **8** or of complex **1** played a role in stopping the reaction before the Cp ring could be extruded in order to generate the trimetallic species. The mass spectrometry results of species **2** suggest that with more soluble TEG-TTF derivative a metallocavitand was indeed obtained as expected from related chemistry. The formation of the trimetallic species **2** is probably made possible by a better solubility of the carboxylic acid and of the resulting complex, which allows the formation of larger molecular weight species.

Fullerenes Binding Studies

Interaction between a host and fullerenes in solution results in a decrease of the intensity of the band of the host in UV-vis spectroscopy. Addition of a solution of the fullerenes into a solution of the host **1** and of metallocavitand **2** allows measurement of the progressive decrease at the absorption maximum (λ_{\max}) of the host and therefore allows the determination of the binding constants. The association constants were obtained using the Hill equation [55] and are summarized in Table 1. As mentioned above, the addition of fullerene C_{60} to a solution of host **2** results in a decrease and a small red shift in the absorbance band. Figure 3 illustrates an example of titration of a 3 mL solution of host **2** at a concentration of 10^{-5} mol L^{-1} with a $7.2 \cdot 10^{-3}$ mol L^{-1} stock solution of fullerene C_{60} in chlorobenzene. A clear isobestic point was observed at 445 nm indicative of the formation of a 1:1 complex, as demonstrated by a Job plot (Figure S2). The number of cooperative sites was calculated using Hill equation [55] which reveals the formation of a 1:1 complex. Using the Hill equation, we estimate the binding constant (K_a) at 900 ± 210 M^{-1} , which is relatively low compare to the best TTF-based host reported to date [50].

$$\Delta\text{Abs} = \Delta\text{Abs}_{\text{max}} \frac{[\text{C}_h]^n K_a^n}{(1 + K_a^n [\text{C}_h]^n)}$$

K_a is the association constant and n the Hill coefficient and $[\text{C}_h]$ the concentration of host.

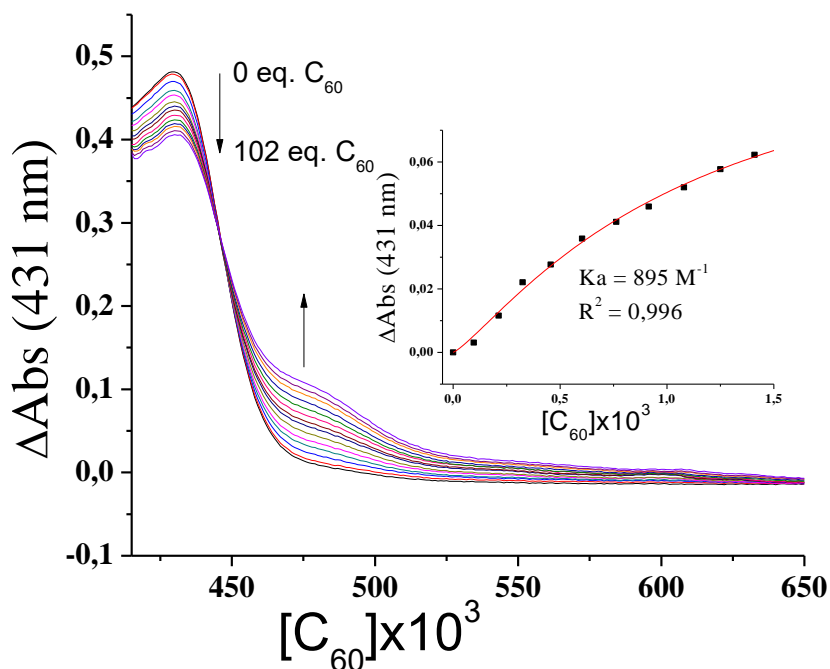


Figure 3. (a) UV-vis spectral changes of **2** ($1.0 \cdot 10^{-5} \text{ M}$) upon addition of stock solution of C_{60} ($7.3 \cdot 10^{-3} \text{ M}$) in chlorobenzene at 298 K. Inset: Plot of the UV-vis changes at 431 nm.

Table 1 Binding constant K_a (M^{-1}) and selectivity factor ($K_{a,\text{C}_{70}}/K_{a,\text{C}_{60}}$) for complexation of C_{60} and C_{70} with hosts **1** and **2** in four different solvents.

Host	Solvent ^a	$K_a \text{ C}_{60}^b$ (M^{-1})	$K_a \text{ C}_{70}^b$ (M^{-1})	$K_{a,\text{C}_{70}}/K_{a,\text{C}_{60}}$

1	Chlorobenzene	640 ± 150	-	-
2	Chlorobenzene	900 ± 210	3380 ± 1290	3.8
	Toluene/DCM 2:1	2730 ± 610	-	-
	CS ₂	820 ± 170	-	-

a DCM = dichloromethane. **b** UV-vis (298 °K). The K_a values were calculated using Hill equation.

C₆₀ is less soluble in toluene so we thought that decreasing fullerene solubility could increase the binding interactions between the fullerene and the metallocavitand. However, toluene did not improve the affinity, probably due to the low solubility of our guest in toluene and no association constant was measured. Nevertheless, when a 2:1 mixture of toluene/DCM was used, a four fold increase of the binding constant was observed compared to chlorobenzene. Correspondingly to what was observed with chlorobenzene, the band at 440 nm for host **2** in toluene/DCM decreases upon addition of C₆₀ while a new band at (λ_{max}) 490 nm appeared, forming a clear isobestic point at 460 nm, which points to the formation of a 1:1 complex in this solvent. A binding constant of $2730 \pm 610 \text{ M}^{-1}$ was estimated using Hill equation, with a Hill coefficient of 1, which is a clear indication of the formation of a 1:1 complex (Figure S5). As a model for the binding between C₆₀ and host **1**, energy-minimized structure of **1**-C₆₀ was obtained (Figure 4). The model is consistent with the data mentioned above which suggest the formation of 1:1 complex.

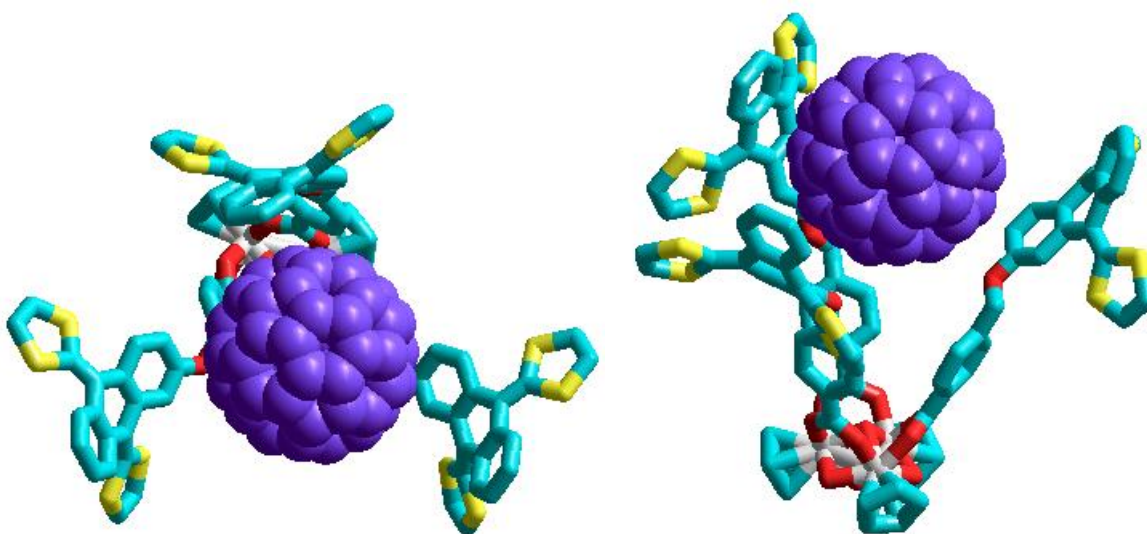


Figure 4. Energy-minimized structure of the self-assembled metallocavitand **2** with fullerene C₆₀ obtained with amber field force using HyperChem™ (TEG chains were removed for clarity).

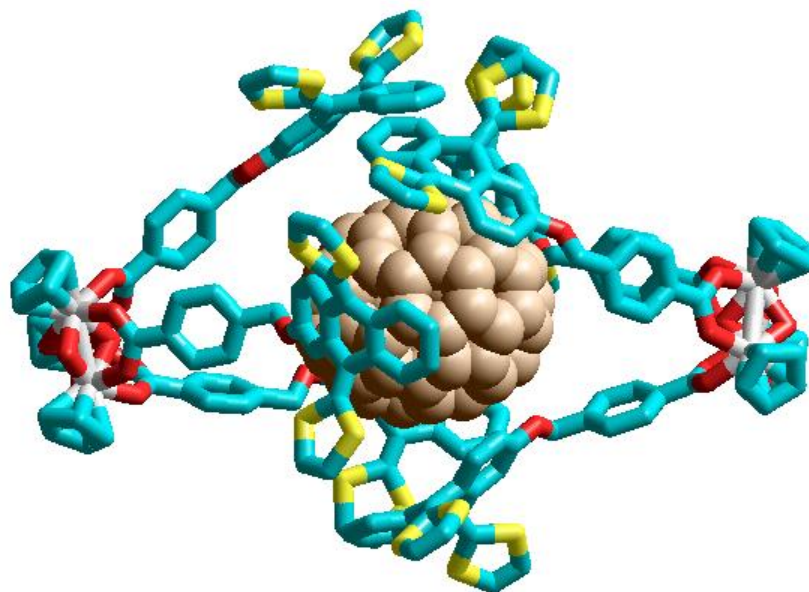


Figure 5. Energy-minimized structure of the self-assembled metallocavitand **2** with fullerene C₇₀ obtained with amber field force using HyperChem™ (TEG chains were removed for clarity).

Not surprisingly, host **2** preferentially binds to C₇₀ in comparison to C₆₀ as the average selectivity for C₇₀ over C₆₀ is 3.8. Such a stabilization of the C₇₀⊂**2** supramolecular complex can be attributed to the presence of additional π - π interactions between the curved surface of C₇₀, which has a flatter surface than C₆₀ (better π -contact), and the curved π -region of host. The slightly lower solubility of C₇₀ compare to C₆₀ can also play a role. Surprisingly, host **2** formed a 2:1 complex with C₇₀ (Figure 5) as determined with the Job's plot (Figure S3), suggesting that host **2** is too tight to accommodate the bigger C₇₀. To the best of our knowledge, this is one of the rare cases in which such difference in the binding mode between C₆₀ and C₇₀ is observed. Similarly to host **1**, the energy-minimized structure of host **2** and C₇₀ suggested the formation of 2:1 complex (Figure 5).

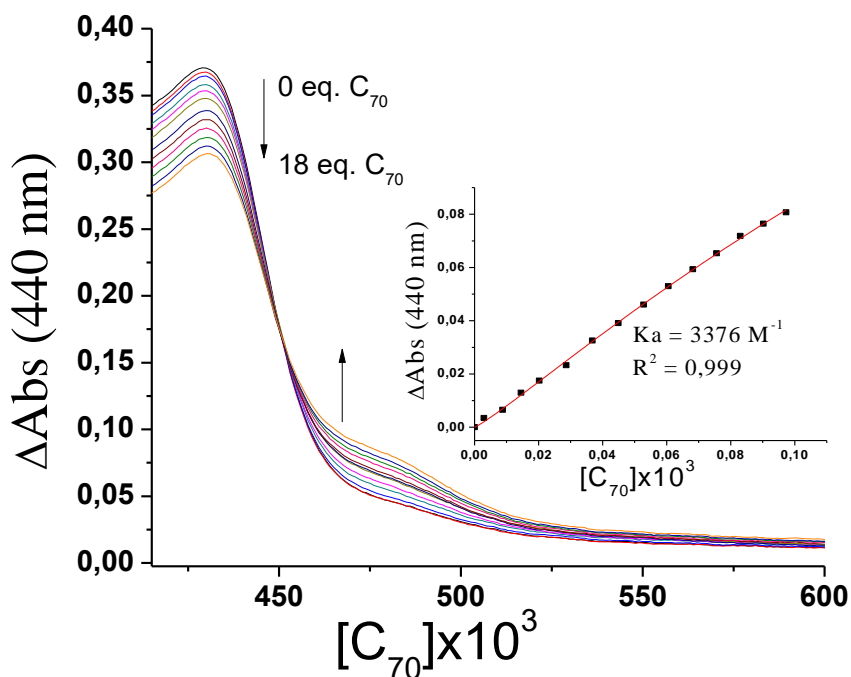


Figure 6. (a) UV-vis spectral changes of **2** ($0.6 \cdot 10^{-5} \text{ M}$) upon addition of stock solution of C_{70} ($9 \cdot 10^{-4} \text{ M}$) in chlorobenzene at 298 K. Inset: Plot of the UV-vis changes at 430 nm.

Finally, UV-vis spectrophotometric titrations were investigated using host **1**. The titration of fullerene C_{60} into a solution of host **1** results in a decrease and a red shift of the absorption at λ_{max} . A clear isobestic point can be observed at 447 nm. A binding constant of 642 M^{-1} was measured in chlorobenzene using the Hill equation (Table 1). It is worth mentioning that the values measured for host **1** are not accurate because of the presence of traces of impurities that could not be removed.

Conclusions

In summary we have synthesized two new TTF containing zirconium complexes as hosts for fullerene. In presence of the carboxylic acid **8**, host **1**, having two carboxylate ligands, was formed rather than the expected metallocavitands, probably because of the lower solubility of the

precursors. The addition of a triethyleneglycol chain to the carboxylic acid increases significantly the solubility and allows the formation of metallocavitand **2**. The latter species has shown low binding affinity toward C₆₀ and the Job's plot suggests the formation of a 1:1 complex between the fullerene C₆₀ and host **2**. A small improvement was observed toward C₇₀ capture due to the ellipsoidal form, hence increasing the contact between host and guest. Interestingly, in the latter case, a 2:1 complex was formed.

Experimental section

General Procedure

General: All solvents (ACS grade) were distilled and put through a Vacuum Atmosphere Company (CA, USA) solvent purification system. All the reagents were purchased from Sigma Aldrich Co., TCI America or Oakwood Products and used as received. All reactions were carried out under an atmosphere of argon with freshly distilled solvents, unless otherwise noted. NMR spectra were recorded at 25 °C on Bruker 400 and 500 MHz instruments and calibrated with tetramethylsilane (TMS) as an internal reference. Mass spectra were performed by the Mass Spectrometry Facilities at Laval University. UV-vis spectra were measured on Varian Cary 500 Scan spectrophotometer.

Synthesis of Compounds

[(Cp₂Zr(μ₂-O',O''C-C₆H₄-4-CH₂O-TTF)₂] (**1**):

In a 100 mL round-bottom flask compound **8** (0.133 g, 0.25 mmol) was dissolved in water (1.5 mL) and sodium hydroxide NaOH (1 mmol) was then added. The pH of the solution was adjusted to pH 6-7 by addition of hydrochloric acid, until a precipitate was formed. This suspension was then added dropwise via pipette to a solution of zirconocene dichloride (0.073 g, 0.25 mmol) in dichloromethane (6 mL) under vigorous stirring. The reaction mixture was stirred for 30 min at room temperature, and then the two-phase system was allowed to separate. The

aqueous phase was extracted with CH₂Cl₂ (10 ml), the organic layers were combined, dried over anhydrous MgSO₄, filtered, and the solvent was removed under reduced pressure. Compound **1** was purified by precipitation in acetone followed by trituration with acetone (yellow solid, 34%). ¹H NMR (400 MHz, CDCl₃) δ = ppm 8.08 (d, *J* = 7.3 Hz, 4H), 7.71-7.64 (m, 4H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 4H), 7.27 (m, 6H), 6.88 (m, 2H), 6.31 (s, 10H), 6.31 (d, *J* = 4.0 Hz, 8H), 5.20 (s, 4H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 156.4, 136.9, 136.2, 135.4, 135.2, 133.9, 130.1, 129.1, 127.0, 126.2, 125.9, 125.9, 125.0, 124.9, 121.9, 117.3, 117.2, 117.1, 117.0, 116.0, 114.8, 114.0, 112.5, 111.3, 76.7, 69.5. HRMS (ESI); *m/z*: [M]^{*+} calcd for C₆₆H₄₄O₆S₈Zr 1277.9945, found 1277.9918.

[(CpZr)₃(μ₂,O',O''C-C₆H₄-4-OCH₂-(TTF-6-TEG))₃(μ₃-O)(μ₂-OH)₃]-HCl (2): In a 100 mL round-bottom flask compound **12** (0.139 g, 0.25 mmol) was dissolved in water (1.5 mL) and sodium hydroxide NaOH (1 mmol) was then added. The pH of the solution was adjusted to pH 6-7 by addition of hydrochloric acid, until a precipitate was formed. This suspension was added dropwise via pipette to a solution of zirconocene dichloride (0.073 g, 0.25 mmol) in dichloromethane (6 mL) under vigorous stirring. The reaction mixture was stirred for 30 min at room temperature, and then the two-phase system was allowed to separate. The aqueous phase was extracted with CH₂Cl₂ (10 ml), the organic layers were combined, dried over anhydrous MgSO₄, filtered, and the solvent was removed under reduced pressure. Compound **2** was purified by precipitation in acetone followed by trituration with acetone (yellow solid, 43%). ¹H NMR (500 MHz, CDCl₃) δ ppm 8.09 (m, 6H), 7.62-7.53 (m, 12H), 7.27-7.21 (m, 6H), 6.89 (m, 6H), 6.84 (m, 6H), 6.33 (s, 15H), 6.29 (m, 12H), 5.22 (s, 6H), 4.23-4.18 (m, 6H), 3.91-3.87 (m, 6H), 3.78-3.74 (m, 6H), 3.72-3.65 (m, 14H), 3.57-3.54 (m, 6H), 3.38 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃): 156.8, 156.3, 137.1, 136.9, 134.2, 134.1, 130.1, 128.5, 126.9, 126.2, 126.0, 121.8, 121.7, 117.2, 117.1, 114.8, 114.3, 112.3, 112.2, 111.3, 111.0, 71.9, 70.9, 70.7, 70.6, 69.7, 67.7, 59.1. HRMS (ESI); *m/z*: [M]^{*+} calcd for C₁₂₀H₁₁₁O₂₅S₁₂Zr₃ 2605.1199, found 2605.0969.

2-tert-butyldimethylsilyl-2-hydroxyanthraquinone (4): To a solution of 2-hydroxyanthraquinone (2.5 g, 11.2 mmol) in DMF (10 mL) was added *tert*-butyldimethylsilyl chloride (2.51 g, 16.7 mmol) followed by imidazole (1.14 g, 16.7 mmol) and the reaction was sonicated under nitrogen at 20 °C for 1 h. DMF was removed under reduced pressure, the residue was dissolved in dichloromethane, washed with water, and dried over MgSO₄. The solvent

removed under reduced pressure and the crude material was purified by column chromatography on silica gel using hexanes/EtOAc (95: 5 v/v) afforded compound **4** (2.83 g, 75%) as a white solid. ^1H NMR (400 MHz, CDCl_3) δ ppm 8.30-8.25 (m, 2H), 8.22 (d, $J = 8.5$ Hz, 1H), 7.79-7.75 (m, 2H), 7.66 (d, $J = 2.6$ Hz, 1H), 7.19 (dd, $J = 8.5, 2.6$ Hz, 1H), 1.01 (s, 9H), 0.29 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) $\delta = 183.2, 182.20, 161.3, 135.5, 134.1, 133.7, 129.9, 127.1, 127.1, 125.9, 117.4, 25.5, 18.6, -4.34$. m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{Si}$ 339.1411, found 339.1431.

(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-6-yloxy)(tert-butyl)dimethylsilane

(5): To a solution of dimethyl 1,3-dithiol-2-yl-2-phosphonate (3.18 g, 15 mmol) in dry THF (15 ml) at -78 °C under argon atmosphere, *n*-BuLi (1.6M, 15.0 mmol) was added over a period of 10 min. After 0.5 h at -78 °C, the corresponding anthraquinone (1.97 g, 6.0 mmol), suspended in dry THF (15 ml), was added dropwise into the solution of the phosphonate. The mixture was stirred for an additional hour at -78 °C, then allowed to warm to 20 °C, and then left to stand overnight at room temperature. The THF was evaporated under reduced pressure and water (75 ml) was added. The residue was extracted with CH_2Cl_2 , (3 x 50 ml) and the combined organic layers were dried over MgSO_4 , filtered and the solvent was removed under reduced pressure. Chromatography of the crude reaction mixture was done on a short silica gel column using hexanes/EtOAc (95:5 v/v) as eluent, to afford compound **5** (1.82 g, 60%) as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ ppm 7.68 (m, 2H), 7.57-7.51 (m, 1H), 7.30-7.26 (m, 2H), 7.15 (d, $J = 2.4$ Hz, 1H), 6.76 (dd, $J = 8.4, 2.5$ Hz, 1H), 6.31-6.26 (m, 2H), 6.27-6.25 (m, 2H), 1.02 (m, 9H), 0.27 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) $\delta = 153.7, 136.8, 135.6, 135.5, 135.3, 133.5, 129.0, 126.1, 125.9, 125.8, 124.9, 122.2, 117.4, 117.2, 117.1, 116.2, 25.7, 18.2, -4.29, -4.20$. m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{27}\text{OS}_4\text{Si}$ 511.0709, found 511.0731.

9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-2-ol (6): To a solution of compound **5** (1.75 g, 3.42 mmol) in dry THF, tetrabutylammonium fluoride (4.1 mmol, 4.1 ml) was added and the reaction mixture was stirred at room temperature for 12 h. The solvent was removed in under reduced pressure and methanol was added before the resulting solution was sonicated for 5 min. The precipitate was filtered, washed with methanol and dried under high vacuum to yield the desired product (1.14 g, 84%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ ppm 9.84 (s,

1H), 7.66-7.55 (m, 2H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.32 (m, 2H), 7.06 (d, $J = 2.4$ Hz, 1H), 6.76-6.69 (m, 3H), 6.67 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) $\delta = 156.0, 136.6, 136.6, 135.3, 135.0, 133.6, 126.7, 126.5, 126.4, 126.4, 125.1, 125.0, 121.4, 121.3, 118.6, 118.4, 118.3, 118.2, 113.3, 111.9$. m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{13}\text{OS}_4$ 396.9844, found 396.9865.

Methyl 4-((9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-6-yloxy)methyl)benzoate

(7): In a 25 mL round-bottom flask potassium hydroxide (0.76 g, 5.5 mmol) was added to dry DMF (9 mL) at room temperature. After stirring for 5 min, anthraquinone (0.73 g, 1.83 mmol) was added, followed by methyl 4-(bromomethyl)benzoate (460 mg, 2.0 mmol). The reaction mixture was heated to 80 °C and the stirring was continued for 12 h, after which time the mixture was poured into 50 mL of cold water. The precipitate was filtered, washed with water, methanol and dried under reduced pressure to give the desired product (0.95 mg, 95%) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ ppm 8.09-8.02 (m, 2H), 7.70-7.63 (m, 2H), 7.60 (d, $J = 8.5$ Hz, 1H), 7.53 (d, $J = 8.5$ Hz, 2H), 7.29-7.26 (m, 3H), 6.88 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.29-6.22 (m, 4H), 5.19 (d, $J = 3.5$ Hz, 2H), 3.93 (d, $J = 3.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) $\delta = 166.9, 156.4, 142.3, 136.9, 136.1, 135.4, 135.2, 133.8, 129.9, 129.6, 129.0, 126.9, 126.2, 125.9, 125.9, 124.9, 124.8, 121.9, 117.2, 117.1, 117.1, 117.0, 112.5, 111.2, 69.5, 52.2$. m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{21}\text{O}_3\text{S}_4$ 545.0368, found 545.0351.

4-((9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-6-yloxy)methyl)benzoic acid (8): A solution of compound **7** (0.82 g, 1.5 mmol) was dissolved in THF (20 mL) and treated with a solution of LiOH (2 mL, 6.0 mmol), the reaction mixture was heated at 60 °C for 5 h (reaction was monitored by TLC). After reaction completion, the reaction mixture was poured into 100 mL of brine/water (1/1 v/v) mixture. The precipitate was filtered, washed with water, methanol, and then dried under reduced pressure to afford the desired product (0.75 g, 95%) as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ ppm 7.93-7.90 (m, 2H), 7.64-7.60 (m, 2H), 7.55 (m, 1H), 7.47 (m, 2H), 7.35-7.31 (m, 2H), 7.21 (d, $J = 2.6$ Hz, 1H), 7.00 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.75-6.67 (m, 4H), 5.22 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) $\delta = 168.7, 156.7, 140.4, 137.5, 136.6, 135.3, 135.0, 134.9, 129.8, 128.5, 127.4, 126.6, 126.6, 126.4, 125.12, 125.1, 121.0, 120.9, 118.6, 118.6, 118.4, 112.9, 111.6, 69.6$. m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{19}\text{O}_3\text{S}_4$ 531.0212, found 531.0240.

methyl 4-((2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-9,10-dihydro-9,10-dioxoanthracen-6-yloxy)methyl)benzoate (10): In a 50 ml round-bottom flask compound **9** was dissolved in dry DMF, methyl 4-(bromomethyl) benzoate (1.145g, 5 mmol) and potassium carbonate (1.38g, 10 mmol) were added. The reaction mixture was heated at 60 °C and stirred at the same temperature for further 12 hours. The mixture was poured in 100 mL of water and extracted with dichloromethane (3 x 50 ml). The organic layers were combined and washed with brine (3x100 ml), dried over MgSO₄, and evaporated under reduced pressure. Addition of methanol to the crude product produced a precipitate that was filtered-off and dried under reduced pressure to yield compound **10** as off-white- solid. That was used directly in the next step of synthesis without further purification (23% yield for the two steps of synthesis). ¹H NMR (500 MHz, CDCl₃) δ ppm 8.20 (t, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.72 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.26 (m, 2H), 5.27 (s, 2H), 3.92 (s, 5H), 4.30 (s, 2H), 3.76 (m, 2H), 3.67 (m, 4H), 3.55 (m, 2H), 3.37 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): 181.9, 181.9, 166.6, 163.6, 163.1, 140.7, 135.7, 135.6, 130.0, 129.94, 129.7, 129.6, 127.4, 127.1, 127.0, 121.08, 121.03, 110.8, 110.9, 71.9, 70.6, 70.1, 69.35, 68.1, 59.0, 52.1. *m/z* [M+H]⁺ calcd for C₃₀H₃₁O₉ 535.1963 found 535.1986.

Methyl 4-((2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-6-yloxy)methyl)benzoate (11): To a solution of dimethyl 1,3-dithiol-2-yl-2-phosphonate (5.2 mmol) in dry THF (15 ml) at - 78 °C and under argon atmosphere, *n*-BuLi (1.6M, 5.44 mmol) was added. After 0.5 h. at - 78 °C, the corresponding quinone **10** (1.5 mmol) suspended in dry THF (15 ml), was added dropwise into the phosphonate solution. The mixture was stirred for 1 h at -78 °C, then allowed to warm at room temperature, and left to stand overnight. The THF was evaporated under reduced pressure, water (75 ml) added, and the residue extracted with CH₂Cl₂, (3 x 50 ml). The combined organic layers were dried over MgSO₄, filtered and the solvent was removed under reduced pressure. Purification of the product was achieved by column chromatography on silica gel with 20% EtOAc/DCM as eluent to yield the desired product as a yellow solid (83%, 0.88 g). ¹H NMR (500 MHz, CDCl₃) δ ppm 8.07 (d, *J* = 7.7 Hz, 2H), 7.58 (m, 2H), 7.53 (m, 2H), 7.24 (m, 2H), 6.85 (m, 2H), 6.30-6.21 (m, 4H), 5.24-5.15 (m, 2H), 4.20 (m, 2H), 3.93 (s, 3H), 3.89 (m, 2H), 3.76 (m, 2H), 3.72-3.65 (m, 4H), 3.56 (d, *J* = 3.45 Hz, 2H), 3.38 (s, 3H). ¹³C{¹H} NMR (125 MHz, CDCl₃): 166.8, 156.8, 156.3,

142.3, 137.0, 136.9, 134.2, 134.1, 129.9, 129.6, 128.9, 128.5, 126.9, 126.1, 126.0, 121.8, 121.7, 117.2, 112.3, 112.2, 71.9, 70.8, 70.6, 70.6, 69.7, 69.51, 67.6, 59.01, 52.1. m/z $[M+H]^+$ calcd for $C_{36}H_{35}O_7S_4$ 707.126, found 707.1297.

4-((2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-9,10-di(1,3-dithiol-2-ylidene)-9,10-

dihydroanthracen-6-yloxy)methyl)benzoic acid (12): In a 50 mL round-bottom flask compound **11** (0.707 g, 1 mmol) was dissolved in THF (20 mL) and treated with a solution of LiOH (2ml, 3.0 mmol). The resulting mixture was heated at 60 °C for 12 h. After reaction completion, the solvent was removed under reduced pressure, followed by addition of HCl (1 M solution in water) until pH ~ 2. The aqueous layer was extracted with CH_2Cl_2 (3x10 ml) and the organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to afford the desired product **12** (0.64 g, 92%) as a yellow solid. 1H NMR (500 MHz, $CDCl_3$) δ ppm 8.13 (d, $J = 7.5$ Hz, 2H), 7.61-7.52 (m, 4H), 7.22 (m, 2H), 6.85 (m, 2H), 6.25 (m, 4H), 5.20 (m, 2H), 4.19 (s, 2H), 3.92-3.87 (m, 2H), 3.77 (m, 2H), 3.73-3.66 (m, 4H), 3.57 (m, 2H), 3.39 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 171.3, 156.7, 156.2, 143.2, 137.0, 136.8, 134.2, 129.0, 128.8, 128.5, 126.1, 126.0, 121.7, 121.6, 117.2, 117.1, 117.0, 112.3, 112.12, 111.1, 110.9, 71.9, 70.8, 70.6, 70.5, 69.7, 69.4, 67.6, 59.0. m/z $[M+H]^+$ calcd for $C_{35}H_{33}O_7S_4$ 693.1104, found 693.1128.

General method for UV-vis titrations

UV-vis titrations were recorded on a Varian Carry 500 scan spectrophotometer. Analytical grade solvents were used for all the titrations. UV-vis titration experiments were carried out with solutions of cavitands (0.6 μM to 1.0 μM) in chlorobenzene, toluene, and carbon disulfide or in toluene/DCM 2:1 (3 mL) in a quartz cuvette. 3 mL of solvent was added to the second cuvette which was used as a reference solution. An aliquot of C_{60} or C_{70} from a stock solution of fullerenes containing the host with the same concentration to the host in the cuvette was added while another aliquot from solution of C_{60} or C_{70} with the same volume and concentration was added to the reference cuvette. The absorption maximum (λ_{max}) of the host was recorded after each addition and a plot of ΔA versus the concentration of fullerene [fullerene] was plotted. The binding constant (Ka) was evaluated by non-linear curve fitting with OriginPro 8.0 (OriginLab)

using the equation 1. In all the solvent, the binding constant was estimated using Hill equation (Eq. 1).

$$\Delta\text{Abs} = \Delta\text{Abs}_{\text{max}} \frac{[\text{C}_h]^n K_a^n}{(1 + K_a^n [\text{C}_h]^n)} \quad (1)$$

Where K_a is the association constant and n the Hill coefficient and $[\text{C}_h]$ the concentration of host.

Supporting Information Available: NMR spectra of species and UV-titration experiments are available.

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