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Bis-calix[4]arenes Bridged by an Electroactive Tetrathiafulvalene Unit

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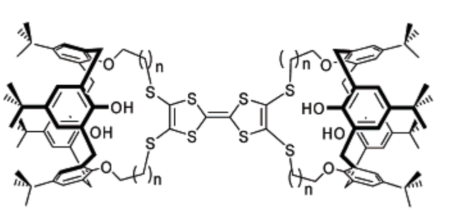

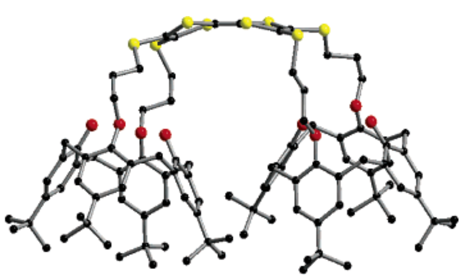

Syntheses of the first bis-calixarenes systems bridged by a tetrathiafulvalene (TTF) framework **5a**,**b** have been carried out in good yields through triethyl phosphite-mediated dechalcogenation−dimerizations of the corresponding 1,3-dithiole-2-(thi)ones **3** or **4**. X-ray structures of the calix[4]arene−TTF−calix[4]arene assembly **5b** and of the calix[4]arene−thione intermediate **3b** are analyzed and confirm the cone conformations adopted by the calix[4]arene parts, as it is also observed by ^{1}H NMR analysis of these systems. The solid-state organization in **5b** leads to alternate layers of calixarene and TTF units. The cyclic voltammograms of **5a**,**b** show as expected a two-step redox behavior but display a CV deformation for the second redox process.

Introduction

The solid-state electroconducting and magnetic properties of the tetrathiafuvalene (TTF)-based materials are well established.[1] In recent years, the tetrathiafulvalene moiety has also appeared as a redox probe in a great variety of supramolecular systems,[2] as for instance rotaxanes,[3] dendrimers,[4] and cavitands.[5]

On this ground, relevant synthetic efforts have been put forth toward the construction of the TTF framework,[6] and a wide variety of functional groups have been attached to the redox core with the common key feature that the resulting systems maintain the unique electrochemical properties encountered for the parent TTF.

On the other hand, the calix[4]arene unit has been extensively studied notably in relation with its well-established recognition properties.[7] In particular, several types of bis-calixarene derivatives covalently bridged by various functional linkers have been reported.[7]

Concomitantly, we have been interested for some years in host−guest chemistry through the designing of redox-responsive ligands based on the TTF moiety.[8]

Considering the redox properties of TTF and the scaffolding features of the calixarene moiety, we have

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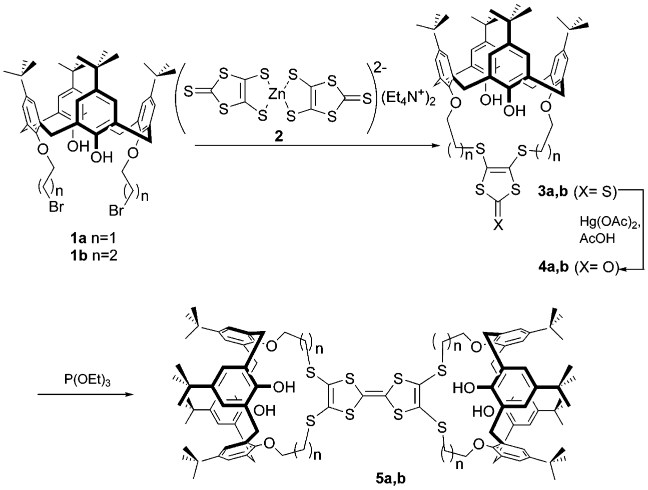
SCHEME 1



paid special attention to joining the two families in one calixarene−TTF assembly to develop new synthetic strategies to original electroactive architectures and to explore their electrochemical properties. Up to now, only one example of a calixarene−TTF assembly has been described, by Regnouf-De-Vains et al.[9] In this case, the TTF unit is grafted on the upper rim of the calixarene macrocycle.

We herein describe the synthesis, X-ray structure, and electrochemical properties of two calix[4]arene−TTF−calix[4]arene electroactive assemblies, corresponding to the first examples of double calixarenes bridged through a TTF framework.

Results and Discussion

Synthesis and Characterization of Calix−(Thi)-ones and Calix−TTF−Calix Derivatives. Scheme 1 outlines the synthetic pathway to the calix−TTF−calix assemblies **5a** and **5b**. The calixarene−thione intermediates **3a** and **3b** were prepared by a cyclocondensation in the key step between two bisfunctionalized precursors, i.e., the dibromo-calix[4]arene derivatives **1a** or **1b**,[10] regioselectively disubstituted on opposite phenolic rings, and the bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol) zincate **2**.[11] In both cases (n = 1, 2), this reaction was carried out in high dilution conditions and afforded the 1:1 cycloadduct in satisfactory yields (**3a**: 50%; **3b**: 55%). No evidence of higher cyclocondensation products or oligomers was observed. The construction of the TTF skeleton of the target assemblies **5a** and **5b** was achieved by the direct self-coupling of calix−thiones **3a** and **3b** mediated by triethyl phosphite, in moderate yields (28 and 30% yields, respectively). Alternatively, derivatives **3a** and **3b** (X = S) were converted to their oxo analogues **4a** and **4b** (X = O) in 70−75% yields. The latter afforded the target calix−TTF−calix systems **5a** and **5b** (55 and 72% yields, respectively) in much better yields than from **3a**,**b**.

^{1}H NMR data of calix−thiones and calix−TTF derivatives **3**−**5** (Table 1) present the expected AB splitting pattern, which corresponds to the bridging diastereotopic methylene protons ($ArCH_aH_bAr$), with a pair of doublets (J = 13 Hz) and $\Delta\delta(H_b-H_a)$ values of 0.84−0.92 ppm, which point out the cone conformation of the aromatic cavity.[12] Furthermore, this cone cavity displays a high symmetry in the case of the ***a*** series (n = 1), as indicated by the very low $\Delta\delta$ value observed between the two different aromatic protons ($\Delta\delta$ = 0.01−0.02 ppm). Conversely, the introduction of a longer bridge (***b*** series, n = 2) leads to a deformation to a pinched cone conformation for the three derivatives **3b**−**5b**, as it is shown by a higher $\Delta\delta$ value for the ArH protons (0.12−0.20 ppm). This behavior is also confirmed by the relevant separation of the *tert*-butyl resonance for derivatives of the ***b*** series. Such conformational difference may also account for the more acidic character of the phenolic proton observed in the ***a*** series (***a***: δ_{OH} = 8.22−8.28; ***b***: δ_{OH} = 7.57−7.92), for which the higher symmetry leads to stronger internal OH···O bonds between adjacent aromatic rings. Finally, the SCH_2 group is characterized by unusual low-field values in all cases (**3**−**5**) and, as expected from the deshielding effect promoted by the phenoxy rings, strongly dependent on the distance between the calixarene platform and the 1,3-dithiole ring (n = 1: 3.61−3.70 ppm; n = 2: 3.19−3.40 ppm).

X-ray Structural Studies. Single crystals of the calix−thione **3b** and the calix−TTF−calix **5b** could be grown from dichloromethane−acetonitrile mixtures, and X-ray diffraction studies were carried out (Figures 1 and 2). The cone conformation observed in solution ^{1}H NMR studies for the calixarene units of **3** and **5** is confirmed in the solid state. X-ray structures show the presence of solvent molecules beside **3b** (**3b**$(CH_3CN)_3$) and **5b** (**5b**$(CH_3CN)_5(CH_2Cl_2)$), with in particular one acetonitrile molecule pointing out from the inside of each calixarene cavity in both structures. Moreover, in the case of the calix−TTF−calix **5b**, one methylene chloride molecule is found in the additional cavity generated between calixarene units of the system. In this case, both calixarene moieties of **5b** are found on the same side of the TTF plane, with both cone axes at approximately 90° relative to the TTF plane, which is surprising if one considers the intramolecular steric pressure thus produced between the calixarene units. This value increases to ca. 120° between the calix unit and the thione part of **3b**. Such a conformation allows a specific crystallographic organiza-

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TABLE 1. Representative ^{1}H NMR Chemical Shifts (δ) for Calix−(Thi)ones and Calix−TTF−Calix Compounds 3−5 ($CDCl_3$/TMS)

	3a	**4a**	**5a**	**3b**	**4b**	**5b**
OH	8.22	8.28	8.25	7.57	7.71	7.92
ArH	7.03; 7.02	7.04; 7.03	7.01; 6.99	7.05; 6.85	7.04; 6.87	7.02; 6.90
	(Δ = 0.01)	(Δ = 0.01)	(Δ = 0.02)	(Δ = 0.20)	(Δ = 0.17)	(Δ = 0.12)
$ArCH_2Ar$	4.24; 3.38	4.26; 3.39	4.25; 3.35	4.17; 3.33	4.18; 3.33	4.24; 3.32
	(Δ = 0.86)	(Δ = 0.87)	(Δ = 0.90)	(Δ = 0.84)	(Δ = 0.85)	(Δ = 0.92)
t-Bu	1.23; 1.14	1.24; 1.16	1.22; 1.14	1.27; 0.99	1.27; 1.01	1.26; 1.04
	(Δ = 0.09)	(Δ = 0.08)	(Δ = 0.08)	(Δ = 0.28)	(Δ = 0.26)	(Δ = 0.22)
SCH_2	3.70	3.68	3.61	3.40	3.37	3.19

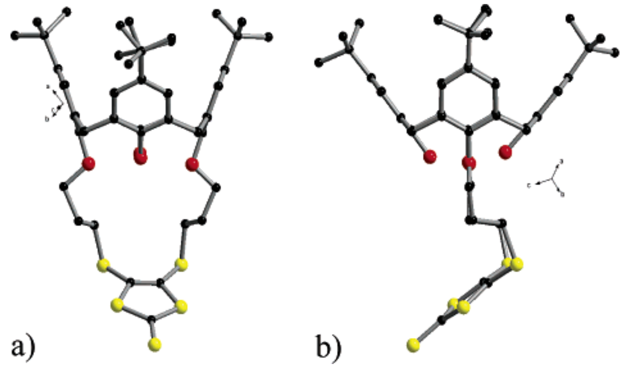

FIGURE 1. X-ray crystal structure of **3b**$(CH_3CN)_3$ (acetonitrile molecules omitted).

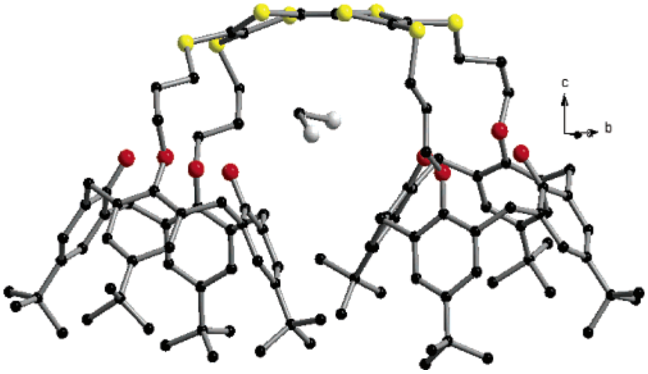

FIGURE 2. X-ray crystal structure of **5b**$(CH_3CN)_5(CH_2Cl_2)$ (acetonitrile molecules omitted).

tion in **5b**, where hydrocarbon layers involving the calixarene pockets alternate along the *c*-axis with layers enriched by O and S atoms (see Supporting Information).

Cyclic Voltammetry Studies. The electrochemical properties of calix−TTF−calix assemblies **5a** and **b** were investigated by cyclic voltammetry (CV) in a dichloromethane−acetonitrile (1/1, v/v) mixture (Figure 3). The TTF derivatives (e.g., the parent $TTF(SMe)_4$ system) are well-known to undergo two successive reversible one-electron redox processes leading, respectively, to cation−radical and dicationic species. It appears from the preliminary CV study that compounds **5a** and **5b**, which behave similarly despite the above-mentioned conformational difference between **5a** and **5b** in solution, present the expected two successive redox systems. The first one corresponds to the reversible oxidation to the stable cation−radical ($E^{1/2}{}_1 = 0.43$ V), and the second one ($E_2{}^{ox} = 1.07$ V) is distorted and assigned to the oxidation to the dicationic species. No convincing explanation could be given until now to justify this distortion.

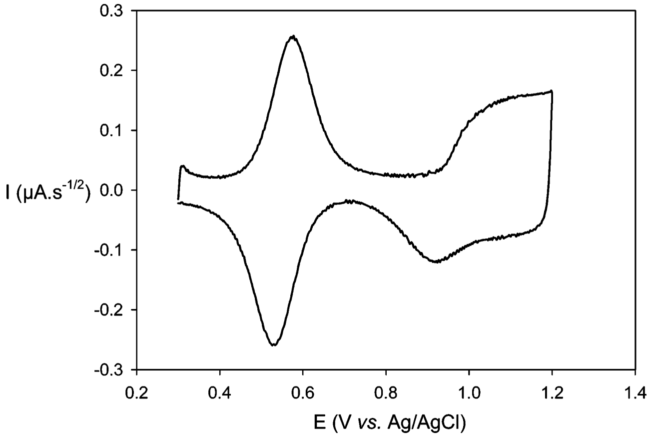

FIGURE 3. Deconvoluted CV of **5b** (0.5×10^{-3} M) in CH_2Cl_2/CH_3CN, Bu_4NPF_6 (0.2 M), v = 0.1 V/s, Pt (ϕ 1×10^{-3} m), vs Ag/AgCl.

Conclusion

In conclusion, calix−TTF−calix electroactive assemblies have been prepared by high-dilution cyclocondensations. Their X-ray structures show the expected cone conformation of the calix[4]arene, arranged around the tetrasubstituted TTF plane. Such architectures constitute a suitable model to study the multielectron redox activity of such assemblies. Extension of this work to design new responsive receptors is under investigation.

Experimental Section

Instruments. ^{1}H NMR (500.13 MHz) and ^{13}C NMR (125.75 MHz) spectra were recorded on a 500 MHz spectrometer. Chemical shifts (δ are expressed in parts per million and related to the tetramethylsilane (TMS) signal). Mass spectra were achieved on two different spectrometers, with MALDI-TOF or ESI sources. X-ray crystallographic data were collected on a IPDS diffractometer, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A cryostream device has been used for low-temperature measurements. Cyclic voltammetry experiments were carried out on a potentiostat−galvanostat with solvents and electrolyte of electrochemical grades. CV experiments were carried out at 298 K in a conventional three-electrode cell equipped with a Pt disk working electrode (diameter: 1 mm), a Pt wire counter electrode, and a Ag, AgCl reference electrode.

X-ray Structural Data: Crystal Data for 3b,3CH$_3$CN: $C_{59}H_{75}N_3O_4S_5$, M = 1050.23, monoclinic, a = 12.5015(8) Å, b = 35.409(2) Å, c = 14.217(1) Å, β = 110.70(1)°, V = 5887(1) Å^3, space group $P2_1/a$, Z = 4, calculated density 1.18, crystal dimensions (mm^3): 0.2 × 0.2 × 0.1, T = 200 K, μ = 0.243 mm^{-1}, $2\theta_{max}$ = 48°, 30 355 measured reflections of which 9099 were unique ($R_{(int)}$ = 0.199) and 3788 had $I/\sigma(I) > 2$. The structure was solved and refined using the SHELXL97 package. A statistical disorder affects one *tert*-butyl group. The hydrogen atoms were treated with a riding model. The refinements of positions of the non-H atoms and anisotropic thermal motion parameters of sulfur, oxygen, and carbon (except those of solvent molecules and *tert*-butyl groups) atoms converge to $R(F) = 0.092$ (3788 reflections, 561 parameters), $wR_2(F^2) = 0.249$ (all data), GOF on F^2 0.88, $\Delta\rho_{\max} = 0.49$ e Å^{-3}.

Crystal Data for 5b,5CH_3CN,CH_2Cl_2: $C_{117}H_{149}Cl_2N_5O_8S_8$, M =2080.44, orthorhombic, $a = 12.9144(9)$ Å, $b = 23.419(1)$ Å, $c = 38.574(3)$ Å, $V = 11\,666(1)$ Å^3, space group $P2_12_12_1$, $Z = 4$, calculated density 1.185, crystal dimensions (mm^3): 0.6 × 0.3 × 0.05, $T = 293$ K, $\mu = 0.251$ mm^{-1}, $2\theta_{\max} = 48°$, 46 334 measured reflections of which 17 179 were unique ($R_{(\text{int})} = 0.077$) and 10 483 had $I/\sigma(I) > 2$. The structure was solved and refined using the SHELXL97 package. A statistical disorder affects one acetonitrile molecule and two *tert*-butyl groups of the calix−TTF−calix molecule. The hydrogen atoms were treated with a riding model. The refinements of positions of the non-H atoms and anisotropic thermal motion parameters of sulfur atoms converge to $R(F) = 0.077$ (10 483 reflections, 638 parameters), $wR_2(F^2) = 0.201$ (all data), Flack parameter 0.03 (9), GOF on F^2 0.95, $\Delta\rho_{\max} = 0.74$ e Å^{-3}.

Materials. Unless otherwise noted, solvents and starting products were commercially available and used without further purification. Calix[4]arene dibromide **1a**,**b**[10] and zincate salt **2**[11] were prepared according to the reported procedures.

Calix[4]arene-1,3-dithiol-2-thiones 3a,b. A mixture of a dibromo calix[4]arene derivative **1a** or **1b** (3 mmol) and bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol) zincate **2** (2.1 mmol) was refluxed for 20 h in acetonitrile (300 mL). The solvent was removed in vacuo, and the residue was dissolved in methylene chloride (100 mL), washed with water (3 × 100 mL), and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to a silica gel column chromatography using a gradient polarity (eluent: CH_2Cl_2/petroleum ether, 1/2 to 1/1). Thione **3a** or **3b** was obtained as orange powders after solvent evaporation, in 50 (**3a**) and 55% (**3b**) yields.

3a: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.22 (s, 2 H), 7.03 (s, 4 H), 7.02 (s, 4 H), 4.25 (t, $J = 5.8$ Hz, 4 H), 4.24 (d, $J = 12.8$ Hz, 4 H), 3.70 (t, $J = 5.8$ Hz, 4 H), 3.38 (d, $J = 12.8$ Hz, 4 H), 1.23 (s, 18 H), 1.14 (s, 18 H); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ 211.7, 150.8, 149.3, 147.7, 141.7, 138.7, 133.1, 127.3, 126.1, 125.3, 71.9, 38.5, 34.2, 33.8, 32.5, 31.7, 31.2; FT-IR (KBr, cm^{-1}) 3410.3 (OH), 1486.5 (C=S); HR-ESI-MS (*m/z*) $C_{51}H_{62}O_4S_5Na$ calcd 921.3149, found 921.3146 (M + Na)$^+$.

3b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (s, 2 H), 7.05 (s, 4 H), 6.85 (s, 4 H), 4.17 (d, $J = 13$ Hz, 4 H), 4.04 (t, $J = 5.8$ Hz, 4 H), 3.40 (t, $J = 5.8$ Hz, 4 H), 3.33 (d, $J = 13$ Hz, 4 H), 2.38 (m, 4 H), 1.27 (s, 18 H), 0.99 (s, 18 H); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ 211.7, 150.6, 149.1, 147.4, 141.8, 139.8, 132.6, 127.6, 125.7, 125.2, 74.7, 53.4, 35.0, 34.0, 33.8, 31.8, 31.7, 31.0, 30.8; FT-IR (KBr, cm^{-1}) 3405.3 (OH), 1485.1 (C=S); ESI-MS (*m/z*) 927.3 (M$^+$).

Calix[4]arene-1,3-dithiol-2-ones 4a,b. A mixture of calix−thione **3a** or **3b** (0.65 mmol) and mercury acetate (2.1 mmol) in 20 mL of a chloroform−acetic acid mixture (3:1) was stirred under N_2 at room temperature for 20 h. The resulting white precipitate was filtered off using Celite and washed thoroughly with $CHCl_3$. The combined organic phases were washed with a dilute $NaHCO_3$ solution and then water and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by silicagel chromatography (eluent dichloromethane) to afford the corresponding 1,3-dithiol-2-one derivative in 70 (**4a**) and 75% (**4b**) yields.

4a: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.28 (s, 2 H), 7.04 (s, 4 H), 7.03 (s, 4 H), 4.26 (d, $J = 12.8$ Hz, 4 H), 4.25 (t, $J = 4.8$ Hz, 4 H), 3.68 (t, $J = 4.8$ Hz, 4 H), 3.39 (d, $J = 12.8$ Hz, 4 H), 1.24 (s, 18 H), 1.16 (s, 18 H); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ 189.8, 150.8, 149.4, 147.6, 141.7, 133.1, 129.4, 127.4, 126.0, 125.3, 72.0, 38.3, 34.2, 33.8, 32.5, 31.7, 31.1; FT-IR (KBr, cm^{-1}) 3412.9 (OH), 1673.0 (C=O).

4b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.71 (s, 2 H), 7.04 (s, 4 H), 6.87 (s, 4 H), 4.18 (d, $J = 12.9$ Hz, 4 H), 4.05 (t, $J = 5.9$ Hz, 4 H), 3.37 (t, $J = 5.9$ Hz, 4 H), 3.33 (d, $J = 12.9$ Hz, 4 H), 2.39 (m, 4 H,), 1.27 (s, 18 H), 1.01 (s, 18 H); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ 189.5, 150.6, 149.2, 147.4, 141.8, 132.7, 130.9, 127.6, 125.7, 125.2, 74.7, 53.3, 34.7, 34.0, 33.8, 31.9, 31.7, 31.0, 30.4; FT-IR (KBr, cm^{-1}) 3392.3 (OH), 1676.0 (C=O); HR-ESI-MS (*m/z*) $C_{53}H_{66}O_5S_4Na$ calcd 933.3691, found 933.3688 (M + Na)$^+$.

Calix[4]arene−TTF−Calix[4]arene Derivatives 5a,b. A suspension of calix[4]arene-1,3-dithiol-2-one **4a** or **4b** (0.108 mmol) in freshly distilled triethyl phosphite (1 mL) was heated at 130 °C for 6 h, under an N_2 atmosphere. After warming to rt, cold methanol (50 mL) was added, which afforded a yellow precipitate. This precipitate was thoroughly washed with methanol to give analytically pure bis-calixarene system **5a** or **5b** as an orange powder in 55 and 72% yields, respectively. (The same procedure was used starting from thiones **3a**,**b** instead of **4a**,**b** and afforded the target systems **5a**,**b** in 28 and 30% yields, respectively.)

5a: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.25 (s, 2 H), 7.01 (s, 4 H), 6.99 (s, 4 H), 4.25 (d, $J = 12.8$ Hz, 4 H), 4.21 (t, $J = 4.6$ Hz, 4 H), 3.61 (t, $J = 4.6$ Hz, 4 H), 3.35 (d, $J = 12.8$ Hz, 4 H), 1.22 (s, 18 H), 1.14 (s, 18 H); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ 150.9, 149.5, 147.3, 141.4, 137.4, 133.0, 129.4, 127.3, 125.9, 125.1, 111.8, 72.0, 38.0, 34.1, 33.7, 32.8, 32.5, 31.6, 31.1; FT-IR (KBr, cm^{-1}) 3422.0 (OH); ESI-MS 1756.8 (M$^+$ + Na, 40); HR-ESI-MS (*m/z*) $C_{102}H_{124}O_8S_8Na$ calcd 1755.6960, found 1755.6943 (M + Na)$^+$.

5b: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (s, 2 H), 7.02 (s, 4 H), 6.90 (s, 4 H), 4.24 (d, $J = 13$ Hz, 4 H), 4.02 (t, $J = 6.3$ Hz, 4 H), 3.32 (d, $J = 13$ Hz, 4 H), 3.19 (t, $J = 6.3$ Hz, 4 H), 2.40 (m, 4 H), 1.26 (s, 18 H), 1.04 (s, 18 H); ^{13}C NMR ($CDCl_3$, 125.75 MHz) δ 150.6, 149.4, 147.3, 141.6, 133.0, 130.8, 127.7, 125.7, 125.2, 110.2, 74.9, 34.0, 33.8, 33.5, 32.0, 31.7, 31.1, 30.5; FT-IR (KBr, cm^{-1}) 3401.5 (OH); HR-ESI-MS (*m/z*) $C_{106}H_{132}O_8S_8$ calcd 1788.7688, found 1788.7705 (M $^+$).

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Supporting Information Available: X-ray crystallographic data of compounds **3b**$(CH_3CN)_3$ and **5b**$(CH_3CN)_5(CH_2Cl_2)$ (CIF), as well as a view of the packing mode in the crystallographic network, and ^{1}H NMR and ^{13}C NMR spectra for compounds **3a**,**b**, **4a**,**b**, and **5a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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