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Synthesis and electrochemical behavior of a model redox-active thiacalix[4]arene-tetrathiafulvalene assembly

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ABSTRACT

Syntheses of the first bisthiacalix[4]arenes systems bridged by a tetrathiafulvalene (TTF) framework have been carried out through triethyl phosphite-mediated dechalcogenation dimerization of the corresponding 1,3-dithiole-2-ones. The cyclic voltammograms of the resulting bisthiacalix[4]arenes tethered by an electroactive TTF unit are provided, and exhibit an electrochemical response in the case of introduction of Ag^+.

The study of redox-active molecular receptors capable of sensing charged or neutral substrates and reporting their presence by means of an electrochemical response is an area of intense current interest.[1] Such systems incorporate a redox center presenting an electrochemically reversible behavior (e.g., ferrocene, viologen, quinone or a transition metal), which is covalently associated to a binding site. Due to remarkable electronic properties, the tetrathiafulvalene moiety (TTF) has appeared as a key building-block for switchable process in various molecular and supramolecular architectures.[2] More specifically, this system has demonstrated a good ability as a redox-probe in the topic of redox-switchable ligands.[2a–c,3] The binding unit of such redox-active receptors can involve various macrocyclic frameworks. By the virtue of their versatility and utility in supramolecular chemistry as host molecules, calixarenes have been considered as relevant structures, which mostly result from an easy access to the basic platform and a straightforward modification at the lower and upper rims.[4] Thiacalixarenes have attracted considerable interest as an alternative to 'classic' calixarenes by providing sites for functionalization not only on the aromatic rings, but also on the bridging sulfur atoms.[5] Considering the redox properties of TTF and the scaffolding features of the calixarene moiety, several groups have paid special attention in joining the two families to produce calixarene-TTF assemblies and to develop new original electroactive architectures.[6] Up to now, no example of thiacalixarene-TTF assembly has been described. Considering the fact that the occurrence of S atoms within the aromatic scaffold provides additional guest-binding properties compared to calix[4]arene analogs,[7] we herein describe the synthesis and electrochemical properties of two thiacalix[4]arene-TTF-thiacalix[4]arene electroactive architectures. These systems correspond to the first examples of thiacalix[4]arenes-TTF assemblies, and feature relevant models towards a new class of redox-active receptors. Scheme 1 shows the synthetic pathway to targeted thiacalix-TTF-thiacalix assemblies **5a** and **5b**. Alkylation at the lower rim of thiacalix[4]arene constitutes an usual procedure for constructing the thiacalixarene skeleton. Dialkylation of the *p-tert*-butylthiacalix[4]arene[5a] with an excess of methyl iodide in the presence of K_2CO_3 (1 equiv) in refluxing acetone smoothly gave the dialkylated derivative **1**.[8] This one is dialkylated with 10 equiv 1,3-dibromopropane or 1,4-dibromobutane in acetone, in the presence of K_2CO_3, to afford the expected dibromo derivatives **2a** and **2b**.[9] Thiacalixarene derivatives **2a** and **2b** are isolable in the 1,3-alternate conformation at room temperature. In principle, though four conformers are expected for thiacalix[4]arene derivatives, partial cone and 1,2-alternate conformations can be directly deduced from ^{1}H NMR resonances (*tert*-butyl and ArH protons).[10a–c] On the contrary, distinction between the cone and 1,3-alternate conformers is not straightforward in solution, because ^{1}H NMR spectra of these two conformers present the same resonance pattern for the Bu^t on the one hand and ArH protons on the other hand. Lhoták et al.[10a] reported that it was possible to distinguish between cone and 1,3-alternate isomers by ^{1}H NOE Diff experiments. Subsequently, the same

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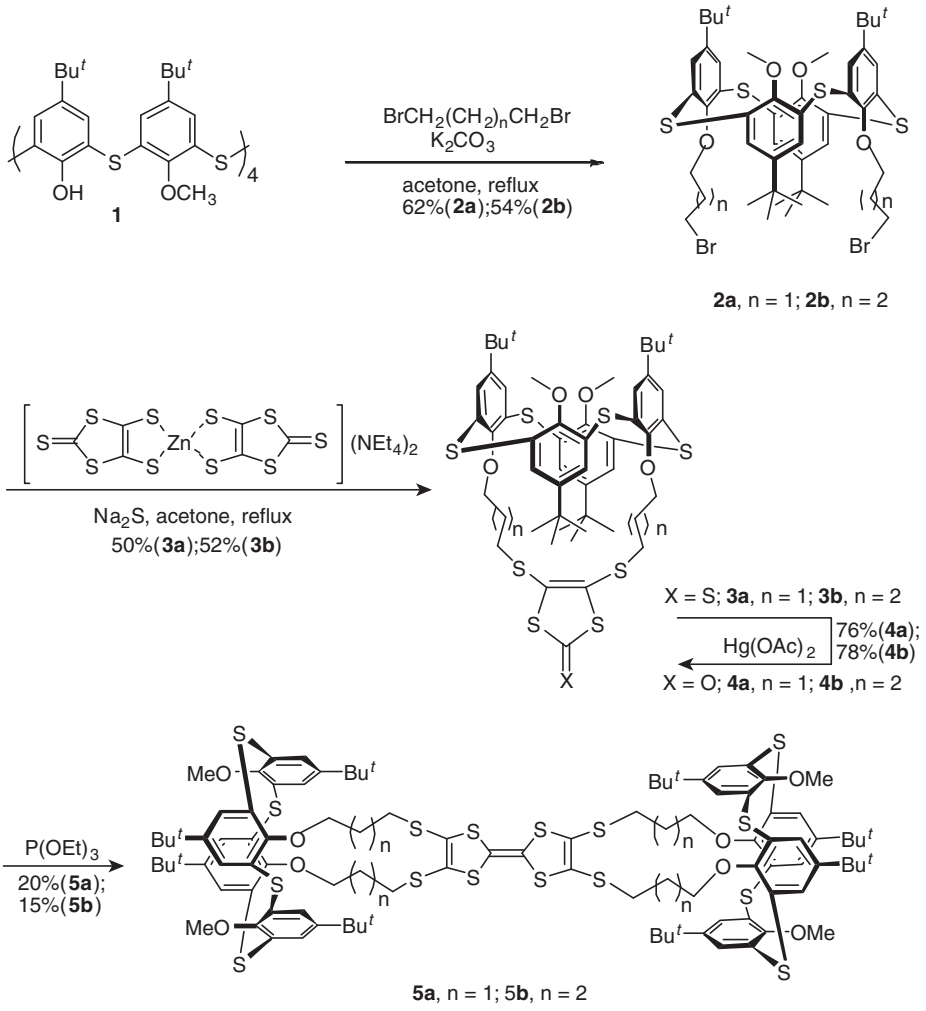

Scheme 1. Synthetic access to **5a**,**5b**.

group[10c] reported that the tetraalkylation of *p-tert*-butylthiacalix[4]arene using a bulky alkyl halide (*n*PrI) (*n*PrI/K_2CO_3 in refluxing acetone) favors formation of the 1,3-alternate conformer. Practically, alkylation of **1**, carried out using α,ω-dibromoalkyl in the presence of K_2CO_3 in refluxing acetone, leads mainly to the 1,3-alternate conformers **2a** and **2b** (Table 1). The key thiacalixarene-thione intermediates **3a** and **3b** were prepared by cyclocondensation step between bisfunctionalized dibromo-thiacalix[4]arene derivatives **2a** or **2b**, and the so-called 'zincate' salt (bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol) zincate, $TEA_2[Zn(DMIT)_2]$).[11] In both cases ($n = 1$, 2), this reaction was carried out under high-dilution conditions, and afforded the 1:1 cycloadduct in satisfactory yields (**3a**: 50%; **3b**: 52%).[12] No evidence of higher cyclocondensation products or oligomers was observed. Interestingly, we have observed that the coupling reaction between the zincate salt and compounds **2** is accelerated in the presence of Na_2S, presumably through a Zn/Na counterion exchange on the thiolate group, leading to an exaltation of its nucleophilic character. The construction of the TTF skeleton featuring the target assemblies **5a** and **5b** was achieved in low yields (<10%), by the direct self-coupling of thiacalix-thiones **3a** or **3b** mediated by triethylphosphite. Alternatively, derivatives **3a** and **3b** (X = S) were converted into their oxo analogs **4a** and **4b** (X = O) in 76-78% yields.[13] The latter afforded the target thiacalix-TTF-thiacalix systems **5a** and **5b** in 20% and 15% yields, respectively.[14] The 1,3-alternate conformation observed for the dibromo derivatives precursors **2a** and **2b** is maintained in the corresponding thiacalix-(thi)ones (**3**,**4**) and thiacalix-TTF-thiacalix derivatives (**5**). Indeed, their ^1H NMR spectra (Supplementary Figs. S1–S6) are very simple and show the presence of only one conformer under analysis conditions (Table 1).

Table 1
Representative ^1H NMR chemical shifts (δ) for thiacalix-(thi)ones (**3**,**4**), and thiacalix-TTF-thiacalix (**5**) compounds and precursors **2**. ($CDCl_3$/TMS)

	2a	2b	3a	3b	4a	4b	5a	5b
ArH	7.44	7.41	7.51	7.50	7.51	7.51	7.51	7.51
	7.35		7.23	7.28	7.24	7.30	7.23	7.31
	$\Delta\delta = 0.11$	=0.00	=0.28	=0.22	=0.27	=0.21	=0.28	=0.20
OCH_2	4.07	3.86	3.88	3.47	3.86	3.55	3.86	3.53
OCH_3	3.39	3.49	3.22	3.39	3.20	3.40	3.20	3.40
SCH_2			2.60	2.88	2.58	2.80	2.58	2.82
t-Bu	1.31	1.30	1.29	1.30	1.28	1.30	1.28	1.29
	1.25	1.19	1.27	1.25	1.27	1.25	1.27	1.25
	$\Delta\delta = 0.06$	=0.11	=0.02	=0.05	=0.01	=0.05	=0.01	=0.04

Furthermore, the resulting 1,3-alternate cavity displays a higher symmetry in the case of the *b* series ($n = 2$) compared to the *a* series ($n = 1$), as indicated by the systematically lower $\Delta\delta$ value observed between the two different aromatic protons ($\Delta\Delta\delta$) = 0.06–0.11 ppm).

The electrochemical properties of thiacalix-TTF-thiacalix assemblies **5a** and **5b** were investigated by cyclic voltammetry (CV) in a dichloromethane-acetonitrile (1:1, v/v) mixture. TTF derivatives (e.g., the parent $TTF(SMe)_4$ system) are well-known to undergo two successive reversible one-electron redox processes leading to cation-radical and dicationic species, respectively. As

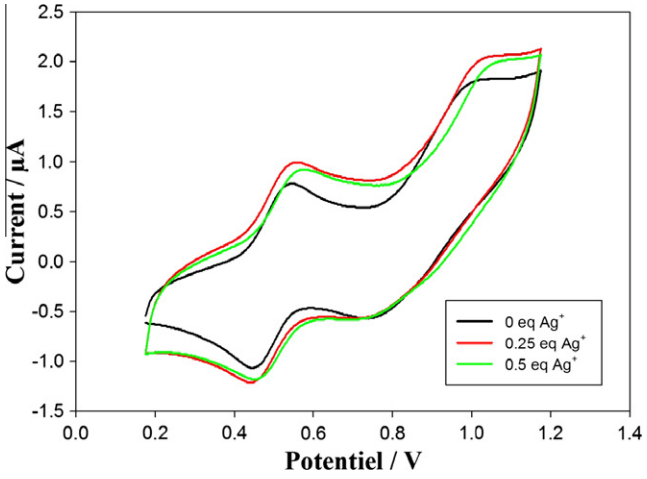

Figure 1. CV study of **5a** (10^{-3} mol L^{-1}) in the presence of increasing amounts of Ag^+. CH_2Cl_2/CH_3CN(1:1), Bu_4NPF_6 (0.1 M), v = 100 mV/s, Pt (ϕ 1 mm), versus Ag/AgCl.

expected from the electrochemical inertness of the thiacalix[4]arene platform,[15] only the TTF redox signature is observed for **5a,5b**. CV study of compounds **5a** and **5b**, which behave similarly, presents the expected two reversible redox systems, corresponding to the successive formation of the stable cation-radical and dicationic species (**5a**: Epa_1 = 0.626 V, Epa_2 = 0.912 V; **5b**: Epa_1 = 0.601 V, Epa_2 = 0.891 V) (Fig. 1, Supplementary Figs. S7 and S8). In order to evaluate the performance of this new family of compounds in cation recognition, the effect of the introduction of various metal cations ($MClO_4$) (M = Ag^+, Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}) was investigated by cyclic voltammetry. A slight anodic shift of the first oxidation potential was only observed upon progressive introduction of Ag^+ in the case of compound **5a**, a behavior which is expected for TTF-based redox-responsive ligands[2,3] (Fig. 1). Surprisingly, no additional variation could be observed for more than 0.5 equiv of cation introduced, which is presumably due to the poor binding ability of this model system. Therefore, compounds **5a**, **5b** illustrate an efficient synthetic route to a new class of thiacalixarene-TTF derivatives, and a step further to redox-responsive ligands appeals for a design optimization in order to increase their binding ability, in particular by modifying the linker fragment between TTF and the thiacalixarene subunits.

In summary, the first thiacalixarene-TTF electroactive assemblies (**5a** and **5b**), designed as parent systems for the preparation of redox-active receptors, have been prepared by high-dilution cyclocondensation and fully characterized. Preliminary electrochemical properties have been investigated by cyclic voltammetry (CV), which confirm the ability of such assemblies to generate a reversible redox behavior, a parameter of critical importance for applications as redox-switchable ligands. Electrochemical recognition studies led with various cations, demonstrate the expected anodic shift in the case of Ag^+. Extension of this work to the design of responsive receptors incorporating new binding sites is under investigation.

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Supplementary data

Supplementary data (^{1}H NMR spectra of compounds **3a**,**b**, **4a**,**b** and **5a**,**b** as well as CV of **5a**,**b**.) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.08.116.

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12. *Thiacalix[4]arene-1,3-dithiol-2-thiones* **3a** and **3b** (general procedure): A mixture of **2a** (or **2b**) (0.26 mmol), $TEA_2[Zn(DMIT)_2]$ (0.37 g, 0.52 mmol),and Na_2S (0.061 g, 0.78 mmol) in dry THF (100 mL) was refluxed under N_2 for 72 h. After the solution was cooled to room temperature, the solvent was evaporated under reduced pressure and the residue was resolved in CH_2Cl_2 (30 mL). The

crude mixture was washed with water (2 × 100 mL) and the organic layer was dried with Na_2SO_4 and evaporated to dryness under reduced pressure. Upon purification by a silicagel column chromatography (V(CH_2Cl_2)/V(petroleum ether) = 1:20), pure compounds were obtained as yellow solid in 50% (**3a**) and 52% (**3b**) yields. Compound **3a**: mp >270 °C. ^{1}H NMR($CDCl_3$, 400 MHz): δ 7.51 (s, 4H, ArH), 7.23 (s, 4H, ArH), 3.88 (t, J = 5.87 Hz, 4H, –O$CH_2$$CH_2$–), 3.22 (s, 6H, –O$CH_3$), 2.60 (t, J = 7.48 Hz, 4H, –$CH_2$$CH_2$S–), 1.78–1.74 (m, 4H, –$CH_2$$CH_2$$CH_2$), 1.29 (s, 18H,C($CH_3$)$_3$), 1.27 (s, 18H, C($CH_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 212.1, 158.0, 156.2, 146.7, 146.0, 139.5, 131.3, 129.7, 127.3, 125.8, 70.0, 56.7, 34.4, 34.2, 31.3, 31.2, 30.7; IR(KBr, cm^{-1}): 2961, 2867, 1634, 1459, 1413, 1379, 1263, 1067, 1009, 877, 800, 761; MS-ESI: m/z calculated: 1026; found: 1049 (M+Na)$^+$. Anal. Calcd for $C_{51}H_{62}O_4S_9$: C, 59.64; H, 6.09; S, 28.04. Found: C, 59.72; H, 6.15; S, 28.08. Compound **3b**: mp = 261.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (s, 4H, ArH), 7.28 (s, 4H, ArH), 3.47 (s, br, 4H, –O$CH_2$$CH_2$–), 3.39 (s, 6H, –$OCH_3$), 2.88 (s, br, 4H, –$CH_2$$CH_2$S–), 1.52 (s, br, 8H, –$CH_2$$CH_2$$CH_2$$CH_2$–), 1.30 (s, 18H, C($CH_3$)$_3$), 1.25 (s, 18H, C($CH_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 210.8, 157.9, 156.4, 146.0, 145.2, 135.8, 132.0, 130.1, 127.1, 126.5, 71.2, 56.4, 37.2, 34.0, 33.8, 31.1, 31.0, 29.2, 29.0, 25.4; IR (KBr, cm^{-1}): 2961, 2868, 1634, 1579, 1460, 1411, 1381, 1262, 1070, 1009, 879, 765, 647; MS-ESI: m/z calculated: 1054; found: 1093 (M+K)$^+$. Anal. Calcd for $C_{53}H_{66}O_4S_9$: C, 60.33; H, 6.31; S, 27.29. Found: C, 60.36; H, 6.38; S, 27.30.

13. *Thiacalix[4]arene-1,3-dithiol-2-ones* **4a** and **4b** (general procedure): A mixture of thiacalix-thione **3a** (or **3b**) (0.4 mmol) and mercury acetate (1.2 mmol) in 12 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, water, and dried over $MgSO_4$. The solvent was removed in vacuo, and the crude product was purified by silica gel chromatography (V(ethyl acetate)/V(petroleum ether) = 1:10) to afford the corresponding 1,3-dithiol-2-one derivative in 76% (**4a**) and 78% yield (**4b**). Compound **4a**: mp >270 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (s, 4H, ArH), 7.24 (s, 4H, ArH), 3.86 (t, J = 5.95 Hz, 4H, –O$CH_2$$CH_2$–), 3.20 (s, 6 H, –$OCH_3$), 2.58 (t, J = 7.85 Hz, 4H, –$CH_2$$CH_2$S–), 1.77–1.71 (m, 4H, –$CH_2$$CH_2$$CH_2$–), 1.28 (s, 18H, C($CH_3$)$_3$); 1.27 (s, 18H, C($CH_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.1, 158.0, 156.2, 146.6, 145.9, 131.2, 130.4, 129.6, 127.4, 125.9, 70.1, 56.8, 34.4, 34.2, 33.9, 31.4, 31.2, 30.6; IR (KBr, cm^{-1}): 2961, 2867, 1755, 1674, 1641, 1416, 1378, 1267, 1089, 1007, 879, 734, 648; MS-ESI: m/z calculated: 1010; found: 1033 (M+Na)$^+$. Anal. Calcd for $C_{51}H_{62}O_5S_8$: C, 60.58; H, 6.19; S, 25.32. Found: C, 60.60; H, 6.21; S, 25.36. Compound **4b**: mp = 264.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (s, 4H, ArH), 7.30 (s, 4H, ArH), 3.55 (s, br, 4H, –O$CH_2$$CH_2$–), 3.40 (s, 6H, –$OCH_3$), 2.80 (s, br, 4H, –$CH_2$$CH_2$S–), 1.53 (s, br, 8H, –$OCH_2$$CH_2$$CH_2$$CH_2$S), 1.30 (s, 18H, C($CH_3$)$_3$), 1.25 (s, 18H, C($CH_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.3, 158.2, 156.8, 146.3, 145.5, 132.2, 130.3, 127.5, 127.0, 126.8, 71.5, 56.8, 37.3, 34.4, 34.1, 31.4, 31.2, 29.7, 29.4, 25.5; IR (KBr, cm^{-1}): 2961, 2867, 1716, 1672, 1461, 1413, 1381, 1268, 1088, 1008, 881, 760, 647; MS-ESI: m/z calculated: 1038; found 1061 (M+Na)$^+$. Anal. Calcd for $C_{53}H_{66}O_5S_8$: C, 61.26; H, 6.41; S, 24.63. Found: C, 61.31; H, 6.45; S, 24.61.
14. *Bis(thiacalix[4]arene)-TTF derivatives* **5a** and **5b** (general procedure): A suspension of thiacalix[4]arene-1,3-dithiol-2-one **4a** or **4b** (0.112 mmol) in freshly distilled triethylphosphite (2 mL) and dry toluene (2 mL) was heated at 130 °C for 6 h, under an N_2 atmosphere. After cooling to rt, cold methanol (50 mL) was added and afforded a crude material which was purified by silicagel column chromatography ((V($C_{H2}C_{l2}$)/V(petroleum ether = 1:30). The pure compounds were obtained as deep yellow solids in 20% (**5a**), and 15% (**5b**) yields. Compound **5a**: mp >270 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (s, 8H, ArH); 7.23 (s, 8 H, ArH); 3.86 (t, J = 5.58 Hz, 8H, –O$CH_2$$CH_2$–), 3.20 (s, 12H, –$OCH_3$), 2.58 (t, J = 7.65 Hz, 8H, –$CH_2$$CH_2$S–), 1.76–1.73 (m, 8H, –$CH_2$$CH_2$$CH_2$–), 1.28 (s, 36H, C($CH_3$)$_3$), 1.27 (s, 36H, C($CH_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.9, 156.1, 146.6, 145.9, 131.2, 130.4, 129.6, 127.4, 126.0, 70.1, 34.5, 34.4, 34.2, 33.9, 31.4, 31.2, 30.6, 29.7; IR (KBr, cm^{-1}): 2963, 2906, 2870, 1634, 1454, 1408, 1375, 1262, 1091, 1020, 801, 706; MS-ESI: m/z calculated: 1991; found: 1034 (M+2 K)$^{2+}$, 2001 (M+NH_4−1)$^+$; Anal. Calcd for $C_{102}H_{124}O_8S_{16}$: C, 61.53; H, 6.28; S, 25.76. Found: C, 61.12; H, 6.36; S, 25.86. Compound **5b**: mp >270 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (s, 8H, ArH), 7.31 (s, 8H, ArH), 3.53 (s, br, 8H, –O$CH_2$$CH_2$–), 3.40 (s, 12H, –$OCH_3$), 2.82 (s, br, 8H, –$CH_2$$CH_2$S–), 1.55–1.45 (m, 16H, –$CH_2$$CH_2$$CH_2$$CH_2$–), 1.29 (s, 36H, C($CH_3$)$_3$), 1.25 (s, 36H, C($CH_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.3, 155.9, 145.4, 144.5, 131.2, 129.3, 126.7, 126.0, 70.7, 56.0, 33.4, 33.1, 30.5, 30.2, 28.5; IR (KBr, cm^{-1}): 2961, 2902, 2868, 1687,1454, 1383, 1268, 1089, 1010, 935, 707; MS-ESI: m/z calculated: 2047; found: 1046 (M+2Na)$^{2+}$, 2069 (M+Na)$^+$; Anal. Calcd for $C_{106}H_{132}O_8S_{16}$: C, 62.21; H, 6.51; S, 25.02. Found: C, 62.20; H, 6.08; S, 24.80.
15. Iki, N.; Ogawa, S.; Matsue, T.; Miyano, S. *J. Electroanal. Chem.* **2007**, *610*, 90–95.