Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 62 (2006) 1947–1954

Non-covalent immobilization of C_{60} on gold surfaces by SAMs of porphyrin derivatives

Sheng Zhang and Luis Echegoyen*

Department of Chemistry, Clemson University, Clemson, SC 29634, USA

Received 6 May 2005; revised 25 May 2005; accepted 27 May 2005

Available online 15 November 2005

Abstract—Three porphyrin derivatives, one containing thioctic ester groups (**3**) and the other two with thioether chains (**4** and **5**), were synthesized. The cyclic voltammograms of the porphyrin compounds exhibit two reversible reduction processes and one reversible oxidation. Stable self-assembled monolayers (SAMs) of the porphyrin compounds were formed on gold surfaces. Non-covalent immobilization of C_{60} was accomplished upon incubation of some of the porphyrin SAMs in solutions of C_{60}.

1. Introduction

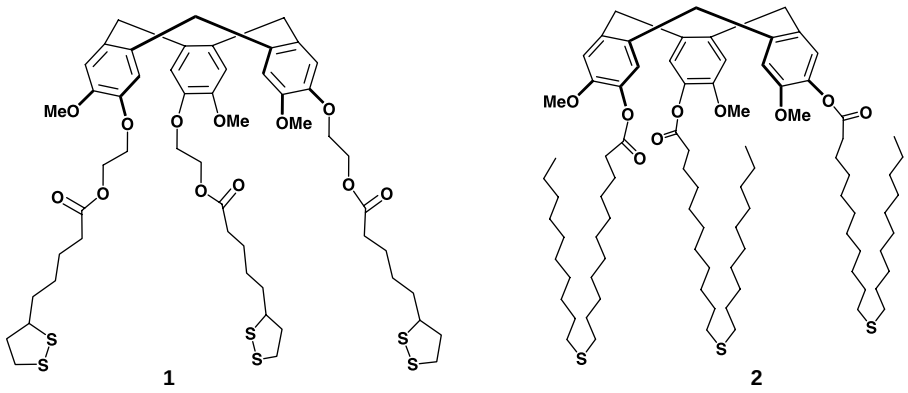
The highly symmetric three-dimensional structure and unique electronic properties of [60]fullerene make it an attractive candidate to construct novel materials.[1] While dramatic, systematic and rapid progress has been made in the covalent functionalization of C_{60},[2] supramolecular interactions with C_{60} are attracting increasing interest in recent times. [60]Fullerenesupramolecules were first detected as cocrystallized complexes with π-electron rich compounds.[3–5] Ermer first reported the supramolecular complexation of hydroquinone with C_{60} in hot benzene solution.[3] Subsequently, cocrystallizations of fullerenes with ferrocene[4] and bis(ethylenedithio)tetrathiafulvalene[5] were investigated to prepare the corresponding solid state complexes. Solid state complexes of fullerene with inorganic materials like S_8 and P_4 have also been investigated.[6] The driving force for the formation of such supramolecules is the weak charge transfer interaction between the electron deficient C_{60} and electron rich molecules.

π-Stacking enhances the weak charge transfer interaction and induces the curved surface of C_{60} prone to form convex–concave supramolecules with other interesting targets. Since covalent functionalization of C_{60} changes some of its desirable electronic properties, supramolecular complexation is attractive to orient C_{60} and yet preserve these interesting properties. The first reported inclusion complex of C_{60} was the incorporation of a single C_{60} molecule into the cavities of two γ-cyclodextrin molecules.[7] Calixarenes are organic molecules with preorganized arrays of aromatic rings. Concave–convex π-stacking interactions as well as donor–acceptor interactions play a key role in forming ball and socket complex structures of calixarenes with C_{60}. Selective complexation of crude fullerene soot with *p-tert*-butylcalix[8]arene has been utilized to purify C_{60}.[8] Evaporation of solutions of C_{60} or C_{70} in the presence of calix[6]arene yields $2C_{60}\cdot$(calix[6]arenes) or $2C_{70}\cdot$(calix[6]arenes).[9] Upon addition of calix[5]arene to C_{60} in several solvents, a color change from purple to pale yellow has been observed.[10] The complexation of a covalently linked calix[5]arene dimer shows to date the largest binding constant value for C_{60} in organic solvents ($76{,}000\ M^{-1}$).[11] However, not all calixarenes can form ball and socket structures with fullerenes. Calix[4]arenes have cavities that are too small to incorporate fullerenes.[12] Another kind of macrocyclic compound possessing the ability to complex C_{60} is cyclotriveratrylene (CTV). Addition of cyclotriveratrylene to a solution of C_{60} in toluene afforded black crystals of $1.5C_{60}\cdot$(CTV)(toluene).[13] The X-ray structure shows that C_{60} stands well above the cavity of the CTV derivative. In addition, the host–guest interaction of C_{60} with polybenzyl ether dendrimer functionalized CTV derivatives has been investigated by Nierengarten et al.[14]

Fullerenes can also interact with porphyrins and metalloporphyrins through an interaction between a curved surface and a flat surface, the so-called planar-convex interaction. This non-covalent recognition element was first confirmed by a crystal structure of a covalently linked

Keywords: Porphyrins; Fullerenes; Cyclic voltammetry; SAMs; Non-covalent immobilization.
* Corresponding author. Tel.: +1 864 656 0778; fax: +1 864 656 6613; e-mail: luis@clemson.edu

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.05.111



Scheme 1. Cyclotriveratrylene (CTV) derivatives **1** and **2**.

tetraphenylporphyrin–C_{60} dyad.[15] Following that, a series of metalloporphyrin–C_{60} supramolecules were systematically studied.[16] Favorable van der Waals attractions between the convex π-surfaces of fullerenes and the planar π-surfaces of porphyrins contribute to the supramolecular recognition. To inhibit fullerene aggregation, a porphyrin cyclic dimer[17] and a porphyrin jaw[18] were also prepared to complex C_{60}. A very selective extraction method for higher fullerenes has been developed using cyclic dimers of zinc porphyrins.[19] Very recently, the first example of 'supramolecular peapods'[20] composed of a linear Zinc porphyrin nanotube and fullerenes has been developed based on the same recognition concept.

Because of their potential usefulness in photovoltaic cells, superconductivity and biological system, thin films of fullerene-based materials have been actively investigated. Self-assembled monolayers (SAMs) have demonstrated obvious advantages to form well defined and highly ordered fullerene arrays on surfaces. Many reports have been published describing how to covalently construct densely packed C_{60} monolayers.[21–26] Mirkin and coworkers first reported the well-ordered SAMs of a C_{60} thiol derivative on gold surfaces and SAMs of C_{60} on cysteamine modified ITO surfaces.[21] Imahori and Fukuzumi have prepared a series of self-assembled monolayers of porphyrin–fullerene dyads and triads and systematically investigated their photoelectric conversion properties.[22] Some reports have pointed out that pyridyl nitrogens, like thiol sulfurs, can strongly adsorb on gold surfaces.[23] Echegoyen et al. have reported SAMs of a fullerene derivative containing a 1,10-phenathroline adduct on gold surfaces.[24] They also prepared stable SAMs of oligothiophene–fulleropyrrolidine dyads by the spontaneous adsorption on Au (111).[25] They also described an alternative methodology to prepare thin films of fullerene derivatives by utilizing a defined molecular recognition event, the complexation between the primary ammonium cations and an 18-crown-6 moiety.[26]

Immobilization of fullerene derivatives onto surfaces can also be achieved through electrostatic interactions. The first example involving electrostatic interactions was the binding of a C_{60} modified by cationic headgroups with anionic duplex DNA.[27] Another example was the construction of photoactive ITO electrodes using a layer by layer approach. C_{60} bearing positively charged groups was deposited on ITO surfaces driven electrostatically by poly(styrene-4-sulfonate) anions.[28] In all of those cases, covalent functionalization of C_{60} was required, which partially destroys the electronic π-delocalization of the molecule due to introduction of the adduct. In addition, C_{60} has a high aggregation tendency, which affects its molecular electronic properties. To overcome both of those problems, Shinkai et al. accomplished the non-covalent incorporation of isolated C_{60} molecules by complexation with homooxacalix[3]arenes on surfaces, combining electrostatic and π-stacking.[29] The photocurrent flow of such photoactive ITO electrodes exhibited a very high quantum yield (21%) upon irradiation. In this case, C_{60} was not functionalized and presumably not self-aggregated.

In our very recent research, we reported non-covalent immobilization of C_{60} on gold surfaces by SAMs of two cyclotriveratrylene (CTV) derivatives (Shown in Scheme 1), one containing thioctic esters (**1**) and the other with thioether groups (**2**) by taking advantage of the host–guest interaction between C_{60} and the CTV derivatives.[30] Self-assembled monolayers (SAMs) of **1** and **2** were formed on gold surfaces and were characterized by CV blocking experiments, impedance spectroscopy and electrochemical reductive desorption. Non-covalent immobilization of C_{60} on gold surfaces was obtained with SAMs of the two CTV

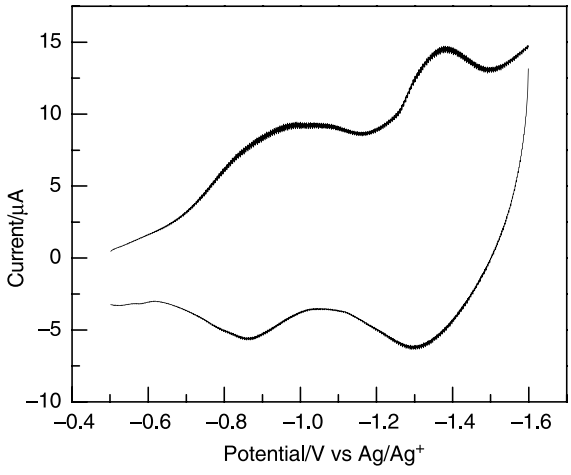


Figure 1. CV recorded in CH_3CN of SAMs of **1** after the incubation in solution of C_{60}. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 V/s.

derivatives. SAMs of **1** can bind C_{60} after they are formed or during formation. As shown in Figure 1, two well-defined reversible redox waves at $E_{1/2}=-0.93$ and -1.34 V versus Ag/Ag^+ were observed, which correspond to the first and second reduction processes of C_{60}, respectively, confirming the incorporation of C_{60} in the SAMs. However, SAMs of **2** could not incorporate C_{60} by incubation of the monolayers in solutions of C_{60}. If the mixture of **2** and C_{60} was kept for 2 weeks and then SAMs were formed from the resulting solution, C_{60} was detected in the SAMs, as shown in Figure 2. The cyclic voltammetric response recorded in CH_3CN exhibits two broad waves at $E_{1/2}=-1.06$ and -1.45 V versus Fc/Fc^+, which correspond to the first two reduction processes of C_{60}.

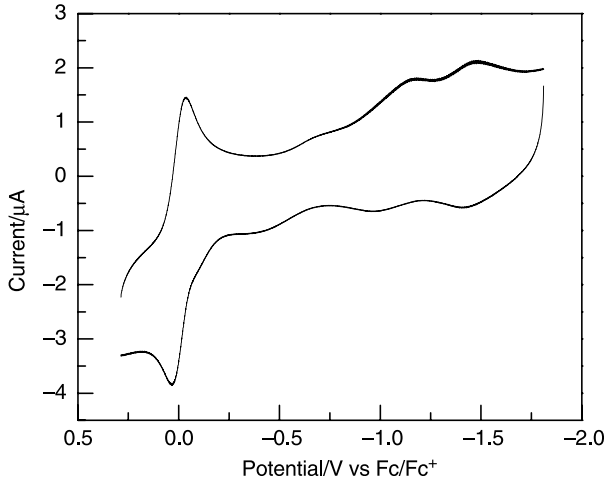


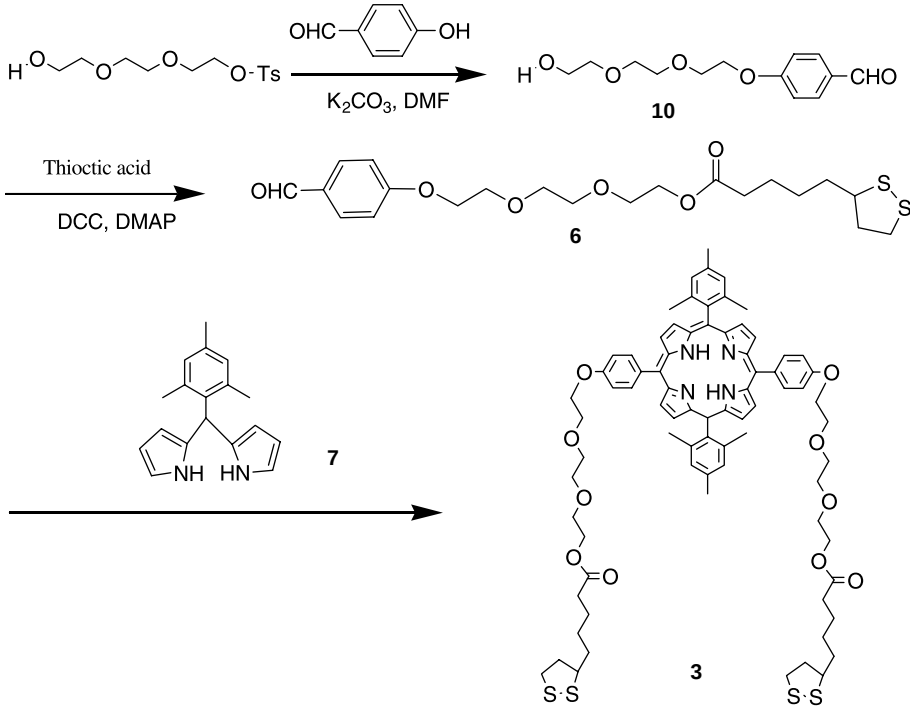
Figure 2. CV recorded in CH_3CN of SAMs grown from the mixture of C_{60} and **2** for two weeks. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 V/s.

Here we further explore the use of non-covalent interactions between porphyrin receptors and C_{60} to immobilize fullerenes on surfaces. Three porhyrin derivatives (**3**–**5**) with surface anchoring groups were prepared. All compounds were fully characterized by ^1H and ^{13}C NMR and MS spectroscopies. SAMs of these porphyrin compounds were formed on gold surfaces. Stable SAMs of these porphyrin compounds were used to supramolecularly incorporate C_{60} on gold surfaces.

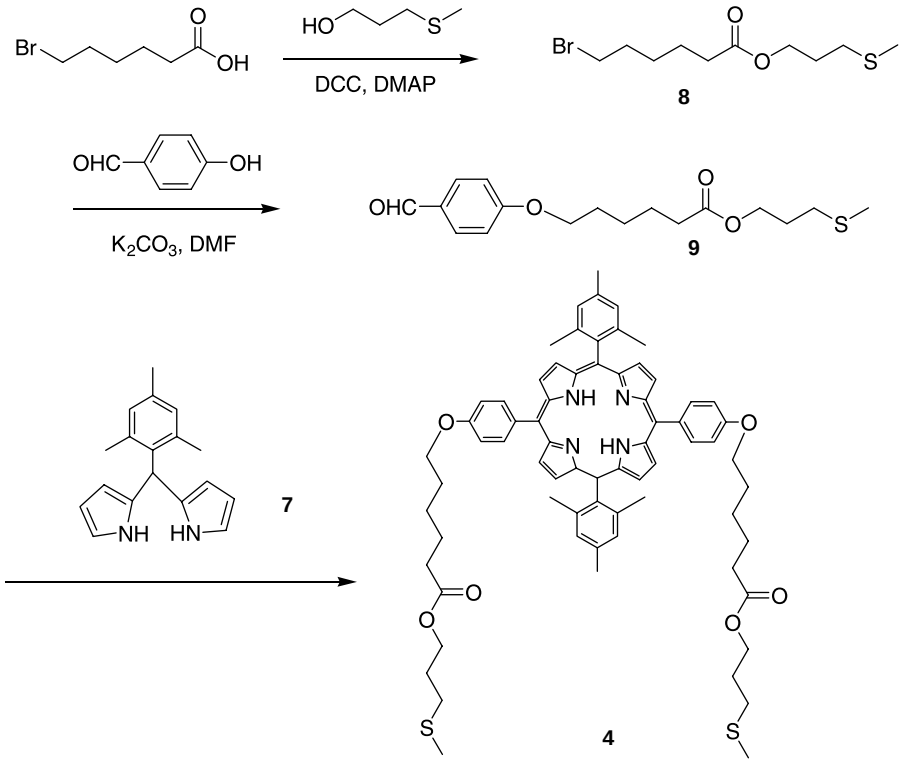
2. Results and discussions

The synthetic methods used for the preparation of porphyrin derivatives **3**–**5** are shown in Schemes 2–4. Compound **3** was obtained by the condensation of *meso*-(mesityl)dipyrromethane **7** with aldehyde **6** followed by oxidization with DDQ in anhydrous CH_2Cl_2.[31] Aldehyde **6** was prepared by coupling compound **10**[32] with thioctic acid in the presence of DCC and DMAP. Compound **10** was synthesized by the treatment of 4-hydroxybenzaldehyde with triethylene glycol monotosylate in the presence of K_2CO_3. As shown in Scheme 3, compound **8**[33] was prepared by the reaction of 6-bromohexanoic acid with 3-(methylthio)-1-propanol. Subsequent treatment of **8** with 4-hydroxybenzaldehyde afforded aldehyde **9**. Condensation of compound **9** with **7** afforded bis-thioether porphyrin derivative **4**. Treatment of **8** with tetrahydroxyphenylporphyrin in DMF using K_2CO_3 as base produced **5**.

The solution electrochemistry of compounds **3**–**5** was investigated by cyclic voltammetry in CH_2Cl_2. The cyclic voltammogram of **4** (Fig. 3) features two reversible one-electron reduction couples at -1.79 and -2.13 V versus Fc/Fc^+, respectively. The first reversible oxidation wave was observed at 0.46 V versus Fc/Fc^+. The second



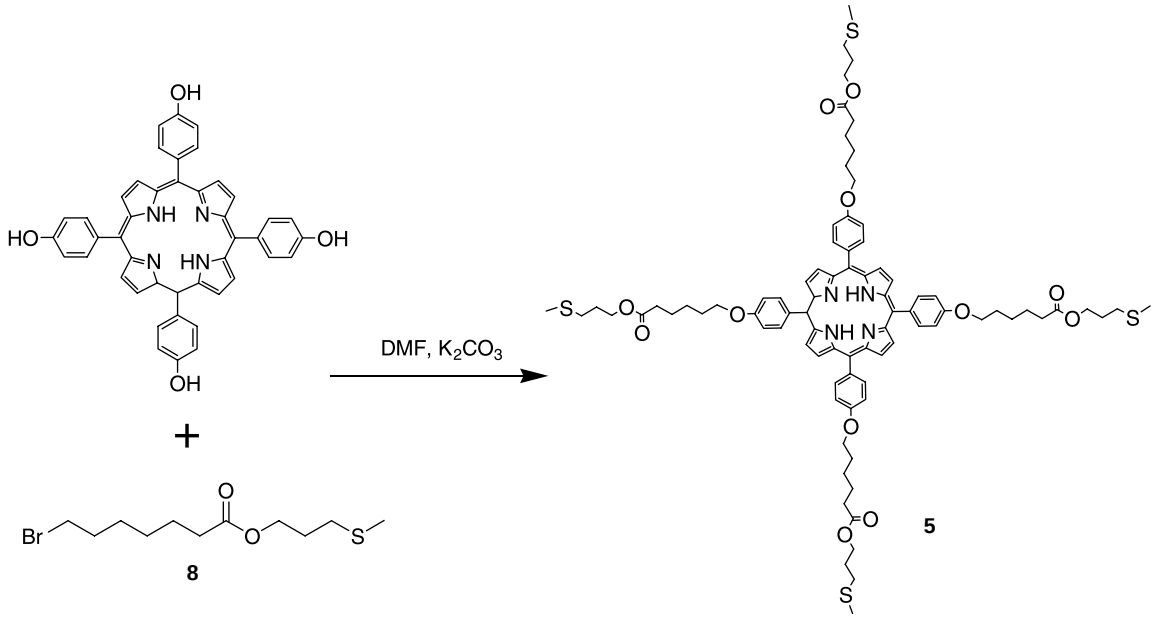
Scheme 2. Synthesis of porphyrin derivative **3**.



Scheme 3. Synthesis of porphyrin derivative **4**.

oxidation of this porphyrin compound is not reversible, which is probably due to the introduction of long alkyl or OEG chains. Compounds **3** and **5** exhibit very similar electrochemical behavior. All the redox potentials measured for these three porphyrin derivatives are summarized in Table 1.

SAMs of compounds **3**–**5** were formed on gold surfaces by dipping gold bead electrodes into CH_2Cl_2 solutions of the target compounds. All the monolayers were characterized by cyclic voltammetry. The CV (Fig. 4) of the gold electrode modified with SAMs of **3** shows the expected two one-electron reduction processes at potentials -1.57 and -1.95 V versus Ag/Ag^+, respectively. The oxidation waves of SAMs of **3**–**5** are not reversible. The potentials were not referenced to internal Fc/Fc^+ since the SAMs blocked this compound from approaching the electrode surface. All peak potentials are proportional to the sweep rate, which was varied between 0.1 and 0.8 V/s, indicating surface-confined behavior due to the immobilization of the



Scheme 4. Synthesis of porphyrin derivative **5**.

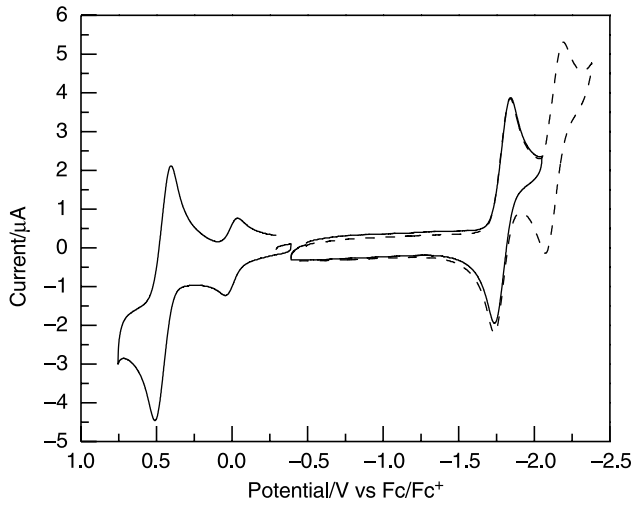


Figure 3. CV recorded in CH_2Cl_2 of **4**. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 V/s.

Table 1. Redox potentials of **3**–**5** and their SAMs

	Potentials versus Fc/Fc^+			Potentials versus Ag/Ag^+		
	$E^{1/2}_{ox.1}$	$E^{1/2}_{red.1}$	$E^{1/2}_{red.2}$		$E^{1/2}_{red.1}$	$E^{1/2}_{red.2}$
4	0.46	−1.79	−2.13	SAMs of **4**	−1.57	−1.94
3	0.46	−1.78	−2.12	SAMs of **3**	−1.57	−1.95
5	0.44	−1.78	−2.14	SAMs of **5**	−1.50	−1.85

electroactive porphyrin derivative on the surfaces. The peak-to-peak separations of the first and second reduction waves are 22 and 34 mV, respectively, indicative of electrochemically reversible processes on the surfaces.

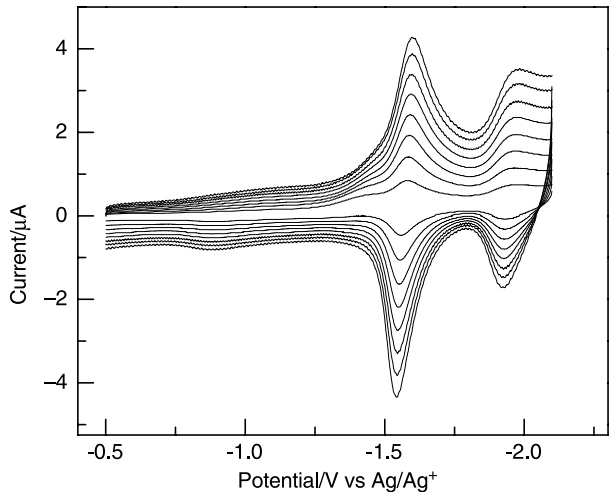


Figure 4. CV recorded in CH_3CN of SAMs grown from **3** at variable scan rates (0.1–0.8 V/s). Supporting electrolyte: 0.1 M Bu_4NPF_6.

Figure 5 shows the electrochemistry of SAMs of **4**. Two pairs of reversible reduction peaks were observed at −1.57 and −1.94 V versus Ag/Ag^+, respectively, which correspond to the first two reduction processes of **4**. The peak-to-peak separations of the first and second reduction waves are 16 and 19 mV, respectively. The electrochemical response of monolayers of **4** is also consistent with a redox system confined to the gold electrode surfaces. Compared to the second reduction, the first one is sharper, like the case of SAMs of **3**. SAMs of the four-legged porphyrin derivative **5** exhibit very similar electrochemical behavior. The redox potentials of all the monolayers are included in Table 1. It should be noted that the SAMs of **3**–**5** are very stable and their electrochemical responses remain essentially unchanged after multiple scans, which makes it possible to investigate the potential interactions with C_{60}.

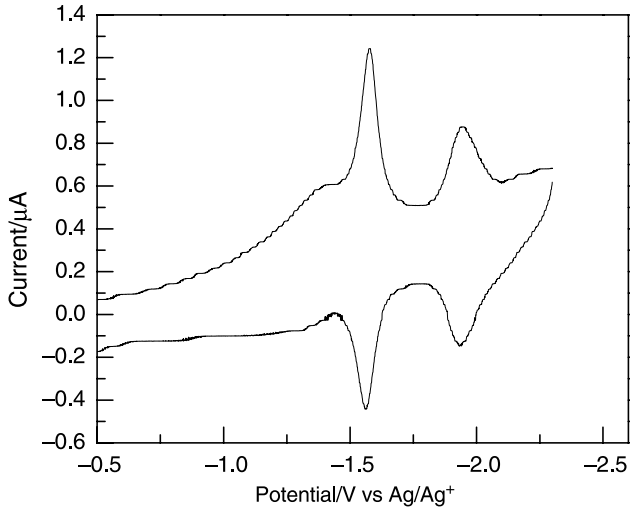


Figure 5. CV recorded in CH_3CN of SAMs of **4**.

SAMs of porphyrin compounds **3**–**5** were immersed into 1,2-dichlorobenzene solutions of C_{60} for 10 h. After washing the gold bead electrodes with copious 1,2-dichlorobenzene, toluene, and CH_2Cl_2 and drying under a flow of Argon, they were investigated by cyclic voltammetry. Figure 6 shows the electrochemistry of SAMs of **3** after the incubation in 1,2-dichlorobenzene solutions of C_{60}. In the first scan, four reduction peaks were observed at −0.94, −1.33, −1.56 and −1.93 V versus Ag/Ag^+, respectively. The first two reduction potentials are almost the same as those observed for C_{60} immobilized on gold surfaces by CTV derivatives, which correspond to the first two reduction processes of C_{60}, thus confirming the incorporation of C_{60} on gold surfaces by SAMs of **3**. The first and second reoxidation peaks are, compared to their corresponding reductions, very weak. The third and fourth redox waves are reversible redox processes with peak-to-peak separations of 31 and 33 mV, respectively, which correspond to the first and second reduction processes of the porphyrin moiety. Compared to the redox responses of free SAMs of **3**, the reduction peaks of the porhyrin after incorporation of C_{60} are broader and a shoulder peak at −1.67 V was observed. These results probably indicate formation of C_{60}–porphyrin complex on gold surfaces. Observations of additional reoxidation peaks at around −1.37 and −1.78 V versus Ag/Ag^+ also support this assumption. Unfortunately these surface-confined complexes are not very stable since the peak intensities of the first two reduction peaks keep decreasing upon successive scans and eventually only the redox responses for porphyrin group were observed after several scans.

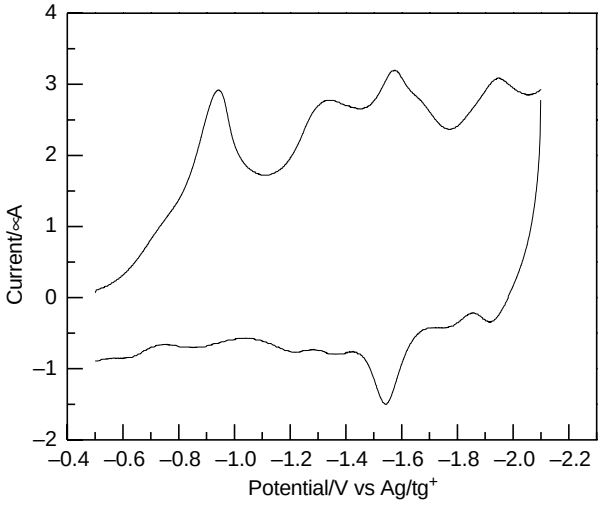


Figure 6. CV recorded in CH_3CN of SAMs of **3** after dipping into a solution of C_{60}.

Attempts to trap C_{60} on gold surfaces by SAMs of **4** were also tried. Figure 7 shows the electrochemistry of the SAMs of **4** after incubation in solutions of C_{60}. The first scan (solid line, Fig. 7) exhibits a rather complex electrochemical response with several broad peaks, probably due to the overlapping of the reductions of porphyrin and C_{60} in different complexation modes. The CV changed dramatically upon successive scans, indicating some structural rearrangement of the porphyrin–C_{60} complexes, and/or the injection of TBA^+ or release of solvent trapped during the assembly process in the SAMs. The dashed line in Figure 7 corresponds to the fourth cycle. Compared to the first scan, the peak currents of the fourth scan are drastically decreased. Four reduction peaks were observed in the fourth scan. The first and second reductions at -1.01 and -1.31 V versus Ag/Ag^+ probably correspond to the first two reduction processes of C_{60}, respectively, indicative of the incorporation of C_{60} into the SAMs of **4**. The third and fourth reductions at -1.56 and -1.93 V versus Ag/Ag^+ are reversible redox waves attributed to the first and second reduction processes of compound **4**. SAMs of

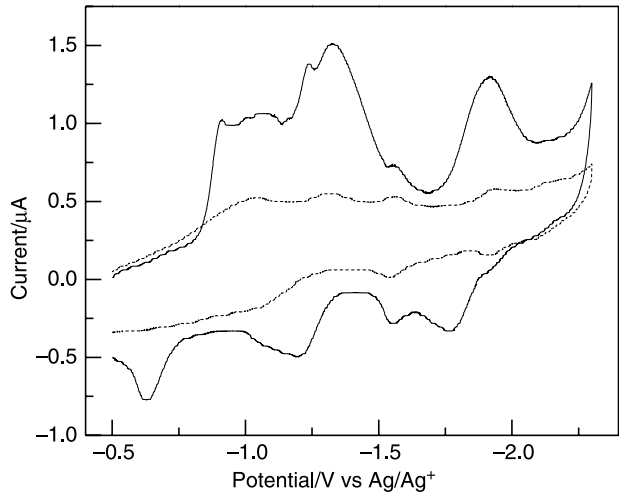


Figure 7. CV recorded in CH_3CN of SAMs of **4** after dipping into a solution of C_{60} (solid line: first scan; dashed line: fourth scan). Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 V/s.

the four-legged porphyrin derivative **5** were also tested for C_{60} binding in the same way. However, no redox response assignable to C_{60} was observed after immersing the SAMs of **5** into a 1,2-dichlorobenzene solution of C_{60}. These observations probably indicated that the four chains in the immobilized compound hinder the incorporation of C_{60} due to steric constraint.

3. Conclusion

Three porphyrin derivatives with sulfur anchoring groups were synthesized. Cyclic voltammograms of these target compounds exhibit two reversible reduction processes and one reversible oxidation peaks for **3**–**5**. The second oxidation of these compounds is not reversible. SAMs of **3**–**5** were formed on gold surfaces and investigated by cyclic voltammetry. SAMs of **3** and **4** can trap C_{60} on gold surfaces, as detected by observing the first two reduction processes of C_{60}. SAMs of **5**, however, were not effectively at trapping C_{60} on gold surfaces in the same way. Electrochemical studies also show that such surface complexes of C_{60} are not stable upon successive reductive scans, probably due to the weak binding interaction.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer. Mass spectroscopy was recorded with an Omni Flex MALDI-TOF spectrometer. Elemental analyses were performed using a Carlo Erba EA 1106. Deionized water was prepared with a nanopure infinity ultrapure water system. The gold beads were prepared and electrochemically cleaned as reported previously.[34] Monolayers on gold were prepared by the immersion of freshly prepared gold beads in 1 mM solutions of compounds **3**–**5** in CH_2Cl_2. All electrochemical measurements were performed with the CHI 660 Electrochemical Workstation. 0.1 M tetrabutylammonium hexafluorophosphate in CH_2Cl_2 (redistilled) was used as the supporting electrolyte (degassed with Argon). Platinum wire was employed as the counter electrode. An Ag/Ag^+ electrode or Ag wire was used as the reference for the monolayer and solution electrochemistry, respectively. In the case of solution electrochemistry, Ferrocene (Fc) was added as an internal reference and the potentials were referenced relative to the Fc/Fc^+ couple. The potentials of monolayer electrochemistry were referenced relative to the Ag/Ag^+ couple. A glassy carbon electrode, polished with aluminum paste and ultrasonicated in deionized water and CH_2Cl_2 bath, was used as the working electrode for the solution electrochemistry. SAM modified gold bead electrodes were used as working electrodes for monolayer electrochemistry.

4.1.1. Synthesis of 10. 4-Hydroxybenzaldehyde (0.86 g, 7.04 mmol), triethylene glycol monotosylate (1.46 g, 4.8 mmol), K_2CO_3 (5.40 g, 39.1 mmol) and DMF (20 ml) were refluxed under Ar for 48 h. After removing the solvent, the brownish residue was treated with 10% aqueous HCl and dichloromethane. The organic layer was washed three times

with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude residue was chromatographed on silica gel using 20% AcOEt/CH_2Cl_2 as eluent to give a pale yellow oil **10**. Yield: 78%. ^{1}H NMR ($CDCl_3$, ppm): 9.18 (s, 1H), 7.79–7.59 (d, 2H, J=8.6 Hz), 6.99–6.96 (d, 2H, J=8.6 Hz), 4.18–4.15 (t, 2H, J=4.8 Hz), 3.86–3.83 (t, 2H, J=4.8 Hz), 3.69–3.61 (m, 6H), 3.57–3.54 (t, 2H, J=4.8 Hz), 2.99 (s, 1H). ^{13}C NMR ($CDCl_3$, ppm): 190.69, 163.59, 131.78, 129.84, 114.68, 72.33, 70.65, 70.11, 69.22, 67.48, 61.45.

4.1.2. Synthesis of 6. Thioctic acid (1.04 g, 5.04 mmol) and **10** (0.86 g, 3.38 mmol) were dissolved in CH_2Cl_2 (30 ml). The mixture was stirred for 30 min at 0 °C under Ar. Then 1,3-dicyclohexylcarbodiimide (DCC) (1.04 g, 5.03 mmol) and 4-(dimethylamino)-pyridine (DMAP) (0.13 g, 1.06 mmol) were added, and the mixture was stirred for another 30 min at 0 °C. The cooling bath was then removed and the solution allowed to warm to room temperature. After being stirred for 48 h under Ar, the reaction mixture was filtered through a fine glass frit to afford a clear filtrate and the insoluble urea byproduct as a white solid. The filtrate was washed three times with water and dried over $MgSO_4$. After filtration and evaporation, the residue was chromatographed on silica gel using 20% AcOEt/CH_2Cl_2 as eluent to give a pale yellow oil **6** (1.29 g, 86%). ^{1}H NMR ($CDCl_3$, ppm): 9.72 (s, 1H), 7.68–7.65 (d, 2H, J=8.6 Hz), 6.88–6.86 (d, 2H, J=8.6 Hz), 4.09–4.06 (m, 4H), 3.75–3.71 (t, 2H, J=4.8 Hz), 3.59–3.55 (m, 6H), 3.42–3.38 (m, 1H), 3.00–2.92 (m, 2H), 2.29–2.26 (m, 1H), 2.20–2.15 (t, 2H, J=7.4 Hz), 1.89–1.27 (m, 7H). ^{13}C NMR ($CDCl_3$, ppm): 190.14, 172.72, 163.26, 131.35, 129.44, 114.34, 70.26, 69.98, 68.90, 68.60, 67.25, 62.82, 55.76, 39.65, 37.93, 33.99, 33.33, 28.12, 24.04.

4.1.3. Synthesis of 3. 5-Mesityldipyrromethane **7** (0.13 g, 0.50 mmol) and **6** (0.22 g, 0.50 mmol) were dissolved in CH_2Cl_2 (10 ml) and then TFA (0.10 g, 0.89 mmol) was added slowly over 30 s. The mixture was stirred at room temperature for 30 min. DDQ (0.11 g, 0.50 mmol) was added and the mixture was stirred at room temperature for another hour. The complete reaction mixture was poured onto a pad of alumina and eluted with a mixture of AcOEt/CH_2Cl_2 from 0 to 50% until the eluting solution was pale brown. The solvent was removed under vacuum to give a dark purple solid, which was dissolved in toluene and heated under reflux for 1 h in the presence of DDQ (0.11 g, 0.50 mmol) to oxidize any remaining chlorine. After cooling to room temperature, the reaction mixture was purified by column chromatography (SiO_2, 10% AcOEt/CH_2Cl_2) to afford compound **3** (0.23 g, 32%). ^{1}H NMR ($CDCl_3$, ppm): 8.82–8.81 (d, 4H, J=4.8 Hz), 8.70–8.69 (d, 4H, J=4.8 Hz), 8.13–8.12 (d, 4H, J=8.3 Hz), 7.31–7.30 (d, 4H, J=8.3 Hz), 7.28 (s, 4H), 4.43 (t, 4H, J=4.8 Hz), 4.31 (t, 4H, J=4.8 Hz), 4.06 (t, 4H, J=4.8 Hz), 3.87 (t, 4H, J=4.8 Hz), 3.80 (m, 8H), 3.62–3.48 (m, 2H), 3.18–3.05 (m, 4H), 2.63 (s, 6H), 2.40–2.39 (m, 6H), 1.84 (s, 12H), 1.83–1.27 (m, 14H). ^{13}C NMR ($CDCl_3$, ppm): 173.61, 158.66, 139.50, 138.62, 137.78, 135.58, 134.69, 127.84, 119.11, 118.24, 112.93, 71.09, 70.84, 70.11, 69.42, 67.80, 63.62, 56.42, 40.29, 38.55, 34.70, 34.09, 28.85, 24.75, 21.75, 21.59. m/z (MALDI): 1371 (M^++H). Anal. Calcd for $C_{78}H_{90}O_{10}N_4S_4$: C, 68.29; H, 6.62. Found: C, 68.87; H, 6.21.

4.1.4. Synthesis of 8. 6-Bromohexanoic acid (2.56 g, 13.12 mmol) and 3-(methylthio)-1-propanol (1.16 g, 10.92 mmol) were dissolved in CH_2Cl_2 (40 ml). Then 1,3-dicyclohexylcarbodiimide (DCC) (3.39 g, 16.43 mmol) and 4-(dimethylamino)-pyridine (DMAP) (0.40 g, 3.27 mmol) were added, and the mixture was stirred at 0 °C for 30 min. The cooling bath was then removed and the solution allowed to warm to room temperature. After being stirred for 48 h under Ar, the reaction mixture was filtered through a fine glass frit to afford a clear filtrate and the insoluble urea byproduct as a white solid. The filtrate was washed three times with water, and dried over $MgSO_4$. After filtration and evaporation, the residue was chromatographed on silica gel using CH_2Cl_2 as eluent to give a pale yellow oil **8** (2.60 g, 84%). ^{1}H NMR ($CDCl_3$, ppm): 4.11–4.09 (t, 2H, J=6.8 Hz), 3.35–3.33 (t, 2H, J=6.8 Hz), 2.51–2.48 (t, 2H, J=6.8 Hz), 2.28–2.25 (t, 2H, J=6.8 Hz), 2.04 (s, 3H), 1.87–1.85 (m, 4H), 1.62–1.59 (m, 2H), 1.45–1.42 (m, 2H). ^{13}C NMR ($CDCl_3$, ppm): 173.44, 63.00, 34.08, 33.60, 32.45, 30.68, 28.25, 27.70, 24.14, 15.58.

4.1.5. Synthesis of 9. 4-Hydroxybenzaldehyde (0.55 g, 4.50 mmol), **8** (1.06 g, 3.74 mmol), K_2CO_3 (4.15 g, 30 mmol) and DMF (30 ml) were refluxed under Ar for 48 h. After removing the solvent, the brownish residue was treated with 5% aqueous HCl and dichloromethane. The organic layer was washed three times with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude residue was chromatographed on silica gel using 3% AcOEt/CH_2Cl_2 as eluent to give a pale yellow oil **9** (1.04 g, 86%). ^{1}H NMR ($CDCl_3$, ppm): 9.90 (s, 1H), 7.86–7.83 (d, 2H, J=8.6 Hz), 7.02–6.99 (d, 2H, J=8.6 Hz), 4.21–4.18 (t, 2H, J=6.0 Hz), 4.10–4.06 (t, 2H, J=7.2 Hz), 2.59–2.57 (t, 2H, J=6.0 Hz), 2.39–2.35 (t, 2H, J=7.2 Hz), 2.12 (s, 3H), 1.96–1.74 (m, 6H), 1.59–1.54 (m, 2H). ^{13}C NMR ($CDCl_3$, ppm): 190.73, 173.25, 163.28, 131.95, 130.33, 114.71, 68.01, 62.88, 34.07, 30.57, 28.72, 28.16, 25.55, 24.60, 15.46.

4.1.6. Synthesis of 4. Condensation of 5-mesityldipyrromethane **7** (0.14 g, 0.52 mmol) and **9** (0.17 g, 0.52 mmol) in CH_2Cl_2 (10 ml) with TFA (0.11 g, 0.96 mmol) by following the procedure described for **3** afforded a purple solid **4** (180 mg, 30%). ^{1}H NMR ($CDCl_3$, ppm): 8.85–8.84 (d, 4H, J=4.8 Hz), 8.71–8.69 (d, 4H, J=4.8 Hz), 8.15–8.12 (d, 4H, J=8.4 Hz), 7.30 (s, 4H), 7.29–7.27 (d, 4H, J=8.4 Hz), 4.30–4.24 (m, 8H), 2.65 (s, 6H), 2.64–2.61 (m, 4H), 2.50–2.45 (t, 4H, J=7.5 Hz), 2.16 (s, 6H), 2.07–1.99 (m, 12H), 1.89 (s, 12H), 1.86–1.84 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): 173.77, 158.91, 139.52, 139.41, 138.39, 135.62, 135.06, 127.83, 119.79, 118.67, 112.78, 68.00, 63.07, 34.39, 30.77, 29.31, 28.36, 25.99, 24.96, 21.74, 21.59, 15.66. m/z (MALDI): 1134 (M^+). Anal. Calcd for $C_{70}H_{78}O_6N_4S_2$: C, 74.04; H, 6.93. Found: C, 74.67; H, 6.45.

4.1.7. Synthesis of 5. Tetra-(*p*-hydroxyphenyl)porphyrin (50 mg, 0.074 mmol), **8** (0.40 g, 1.41 mmol), K_2CO_3 (0.31 g, 2.24 mmol) and DMF (freshly distilled over CaH_2, 30 ml) were refluxed under Ar for 3 days. After removing the solvent, the residue was treated with water and dichloromethane. The organic layer was washed three times with water and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude residue was chromatographed on

silica gel using 5–7% AcOEt/CH_2Cl_2 containing 0.3% Et_3N as eluent to yield purple solid **5** (60 mg, 55%). ^1H NMR ($CDCl_3$, ppm): 8.79 (s, 8H), 8.04–8.02 (d, 8H, $J=8.4$ Hz), 7.19–7.17 (d, 8H, $J=8.6$ Hz), 4.16–4.13 (m, 16H), 2.53–2.50 (t, 8H, $J=7.4$ Hz), 2.39–2.36 (t, 8H, $J=7.4$ Hz), 2.04 (s, 12H), 1.93–1.53 (m, 32H). ^{13}C NMR ($CDCl_3$, ppm): 178.01, 173.75, 158.92, 135.90, 135.70, 132.44, 130.52, 119.86, 112.76, 69.40, 63.04, 34.67, 34.38, 30.74, 29.79, 29.39, 29.29, 29.08, 28.33, 25.98, 24.94, 23.02, 15.63. *m/z* (MALDI): 1134 (M^+). Anal. Calcd for $C_{84}H_{102}O_{12}N_4S_4$: C, 67.80; H, 6.91. Found: C, 67.01; H, 6.02.

Acknowledgements

Financial support from the National Science Foundation, (Grant no. CHE-0135786) is greatly appreciated.

References and notes

1. Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic: San Diego, 1996.
2. (a) Hirsch, A. *The chemistry of the Fullerenes*; Thieme: Stuttgart, 1994. (b) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317.
3. Ermer, O. *Helv. Chim. Acta* **1991**, *74*, 1339.
4. Crane, J. D.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1746.
5. Izuoka, A.; Tachikawa, T.; Sugawara, T.; Suzuki, Y.; Konno, M.; Saito, Y.; Shinohara, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1472.
6. (a) Burgi, H. B.; Venugopalan, P.; Schwarzenbach, D.; Diederich, F.; Thigen, C. *Helv. Chim. Acta* **1993**, *76*, 2115. (b) Douthwaite, R. E.; Green, M. L. H.; Heyes, S. J.; Rosseinsky, M. J.; Turner, J. F. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1367.
7. (a) Anderson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerstrom, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604. (b) Yoshida, Z.; Takekuma, H.; Takekuma, S.-I.; Matsubara, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1597.
8. Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229.
9. Raston, C. L.; Atwood, J. L.; Nichols, P. J.; Sudria, I. B. N. *Chem. Commun.* **1996**, 2615.
10. Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed.* **1997**, *36*, 259.
11. Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 997.
12. Ikeda, A.; Yoshimura, M.; Shinkai, S. *Tetrahedron Lett.* **1997**, *38*, 2107.
13. (a) Steed, J. W.; Junk, P. C.; Atwood, J. L.; Barnes, M. J.; Raston, C. L.; Burkhalter, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 10346. (b) Atwood, J. L.; Barnes, M. J.; Gardiner, M. G.; Raston, C. L. *Chem. Commun.* **1996**, 1449.
14. (a) Nierengarten, J.-F.; Oswald, L.; Eckert, J.-F.; Nicoud, J.-F.; Armaroli, N. *Tetrahedron Lett.* **1999**, *40*, 5681. (b) Felder, D.; Heinrich, B.; Guillon, D.; Nicoud, J.-F.; Nierengarten, J.-F. *Chem. Eur. J.* **2000**, *6*, 3501. (c) Rio, Y.; Nierengarten, J.-F. *Tetrahedron Lett.* **2002**, *43*, 4321.
15. Sun, Y.; Drovetskaya, T.; Bolskar, R. D.; Bau, R.; Boyd, P. D. W.; Reed, C. A. *J. Org. Chem.* **1997**, *62*, 3642.
16. (a) Evans, D. R.; Fackler, N. L. P.; Xie, Z.; Richard, C. E. F.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 8466. (b) Olmstead, M. M.; Costa, D. A.; Maitra, K.; Noll, B. C.; Phillips, S. L.; van Calcar, P. M.; Balch, A. L. *J. Am. Chem. Soc.* **1999**, *121*, 7090. (c) Boyd, P. D. W.; Hodgson, M. C.; Richard, C. E. F.; Oliver, A. G.; Chaker, L.; Brothers, P. J.; Bolskar, R. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 10487. (d) Ishii, T.; Aizawa, N.; Yamashita, M.; Matsuzaka, H.; Kodama, T.; Kikuchi, K.; Ikemoto, I.; Iwasa, Y. *J. Chem. Soc., Dalton Trans.* **2000**, 4407.
17. Tashiro, K.; Aida, T.; Zheng, J.-Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 9477.
18. Sun, D. Y.; Tham, F. S.; Reed, C. A.; Chaker, L.; Burgess, M.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2000**, *122*, 10704.
19. Shoji, Y.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2004**, *126*, 6570.
20. Yamaguchi, T.; Ishii, N.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 13934.
21. (a) Chen, K.; Caldwell, W. B.; Mirkin, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 1193. (b) Shi, X.; Caldwell, W. B.; Chen, K.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 11598.
22. (a) Imahori, H.; Fukuzumi, S. *Adv. Funct. Mater.* **2004**, *14*, 525. (b) Imahori, H.; Azuma, T.; Ozawa, S.; Yamada, H.; Ushida, K.; Ajavakom, A.; Norieda, H.; Sakata, Y. *Chem. Commun.* **1999**, 557. (c) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 2099.
23. (a) Hudson, J. E.; Abruna, H. D. *J. Phys. Chem.* **1996**, *100*, 1036. (b) Cunha, F.; Tao, N. J.; Wang, X. W.; Jin, Q.; Duong, B.; D'Agnese, J. *Langmuir* **1996**, *12*, 6410. (c) Zhang, S.; Dong, D.; Gan, L.-B.; Liu, Z. F.; Huang, C. H. *New J. Chem.* **2001**, *25*, 606.
24. Dominguez, O.; Echegoyen, L.; Cunha, F.; Tao, N. J. *Langmuir* **1998**, *14*, 821.
25. Liu, S.-G.; Marineau, C.; Raimundo, J.-M.; Roncali, J.; Echegoyen, L. *Chem. Commun.* **2001**, 913.
26. Arias, F.; Godinez, L. A.; Wilson, S. R.; Kaifer, A. E.; Echegoyen, L. *J. Am. Chem. Soc.* **1996**, *118*, 6086.
27. (a) Cassel, A. M.; Scrivens, W. A.; Tour, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1528. (b) Takenaka, S.; Yamsshita, K.; Takagi, M.; Hatta, T.; Tanaka, A.; Tsuge, O. *Chem. Lett.* **1999**, 319.
28. Luo, C.; Guldi, D. M.; Maggini, M.; Menna, E.; Mondini, S.; Kotov, N. A.; Prato, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3905.
29. (a) Hatano, T.; Ikeda, A.; Akiyama, T.; Yamada, S.; Sano, M.; Kanekiyo, Y.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2* **2000**, 909. (b) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855.
30. Zhang, S.; Palkar, A.; Fragoso, A.; Prados, P.; de Mendoza, J.; Echegoyen, L. *Chem. Mater.* **2005**, *17*, 2063.
31. (a) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864. (b) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391. (c) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827. (d) Lee, C.-L.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427.
32. Davidson, R. S.; Palmer, S. J.; Pratt, J. E.; Wilson, S. P. WO 9733202, 1997, CAN 127:301279.
33. Zhang, M. J.; Vedantham, P.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2004**, *69*, 8340.
34. (a) Zhang, S.; Echegoyen, L. *J. Am. Chem. Soc*. **2005**, 127, 2006. (b) Zhang, S.; Echegoyen, L. *Org. Lett*. **2004**, 6, 791. (c) Zhang, S.; Song, F.; Echegoyen, L. *Eur. J. Org. Chem*. **2004**, 2936.