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Synthesis of Fullerene Adducts with Terpyridyl- or Pyridylpyrrolidine Groups in *trans*-1 Positions

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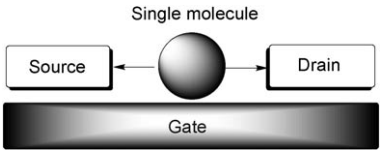
Abstract: Two C_{60} hexakis-adducts (**2** and **3**) were synthesized by using a protection–deprotection strategy. The symmetric fullerene tetrakis-adduct **8** was obtained by anthracene removal from the hexakis-adduct **7**. Reaction of **8** with terpyridylglycine or pyridylglycine afforded two hexakis-adducts, **2** and **3**. By using the retro-cyclopropanation reaction, the four malonate addends located on the equatorial belt of the hexakis-adducts were removed to afford two *trans*-1 bis-adducts, **4** and **5**, with terpyridyl- or pyridylpyrrolidine groups. The structures of **2** and **3** were confirmed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry, and ^{1}H, ^{13}C, and COSY NMR, and UV-visible spectroscopy. The cyclic voltammograms of fullerene multiadducts **2**, **3**, and **9** show irreversible reductions. Self-assembled monolayers (SAMs) of **1** and **3** were formed on gold surfaces through nitrogen adsorption. SAMs of **3** represent the first example of a fullerene hexakis-adduct formed on gold surfaces through nitrogen adsorption. Controlled potential electrolyses (CPE) were conducted to prepare *trans*-1 bis-adducts **4** and **5** modified with terpyridyl and pyridyl groups.

Keywords: electrochemistry · fullerenes · pyridyl · redox chemistry · retro-cyclopropanation

Introduction

Trapping individual or small numbers of molecules between metal electrodes to build molecular-based electronic devices has only been accomplished relatively recently (illustrated in Scheme 1), although the idea was suggested more than 30 years ago.[1] Several strategies including mechanical break junctions, metal evaporation, scanning tunneling microscopy, and conducting atomic force microscopy have been employed to place molecules between electrodes at nanometer separation.[2–4] Recent advances consist of constructing molecular devices based on carbon nanotubes,[5] C_{60},[6] and other organic molecules.[7] Building nanometer-scale electronic devices is very difficult and the process suffers from low device yield, measurement reproducibility problems, and lack of direct evidence for entrapment of molecules between metal electrodes. A frequently asked question is whether a molecule is truly present between the electrodes. Haiss et al. and Tao et al. reported the electrochemical dependence of single-molecule conductivity by incorporating redox-active molecules between the electrodes.[8,9] In a very interesting experiment, Park et al. reported a single-molecule transistor consisting of a cobalt bis(terpyridyl) complex in which the electron transport was controlled by the redox states of a single complexed Co ion.[10] The single-electron current effect has been used as the signature of single-molecule measurements.[10] The electron transport via a single molecule is affected by its structure, as reported by Mayor et al., who found that a fully conjugated pathway in the molecule significantly increases the electronic coupling between the gold electrodes and the molecule.[11]



Scheme 1. Schematic diagram of single-molecule-based transistors.

Among single molecules trapped between two electrodes, C_{60} is very attractive because of its unique electronic proper-

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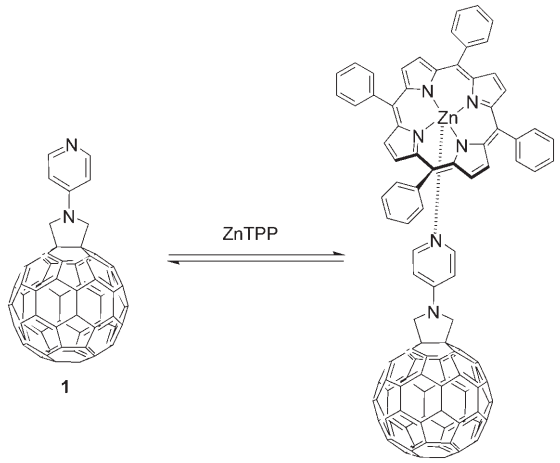
Supporting information (COSY and ^{13}C NMR spectra of terpyridylglycine, ^{1}H NMR spectrum of ^{13}C-labeled **2**, ^{1}H, ^{13}C, and COSY NMR spectra of **1**, MALDI-TOF MS of **2**, **3**, **5**, and **9**) for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

ties and its rich redox chemistry.[5] Park et al. reported the fabrication of a single-molecule transistor based on individual C_{60} molecules sandwiched between two gold electrodes.[5a] Nanomechanical oscillations of C_{60} trapped between two gold electrodes were excited by an electron current passing through the system. Ralph et al. investigated the Kondo-assisted tunneling of a single C_{60} molecule that was trapped between two ferromagnetic nickel electrodes.[12] In all of these cases, C_{60} was not connected covalently to the electrodes. The central concept behind the present work was to prepare fullerene derivatives that can be covalently attached to metal electrodes and to eventually investigate the influence of the rich redox chemistry of C_{60} on single-molecule conductivity. Selection of the appropriate adducts for covalent attachment and a strategy for regiochemical control are the focus of this article. In 2003, Wilson et al. prepared a pyridinofulleropyrroline derivative (**1**) which exhibited effective electronic coupling between the C_{60} core and the pyridyl nitrogen atom, as confirmed by ^{1}H NMR spectroscopy, molecular modeling studies, UV-visible spectroscopy, and fluorescent-quenching experiments (Scheme 2).[13] Electrochemical studies further confirmed this effective coupling between the pyridyl nitrogen atom and the fullerene core based on the fact that the first reduction of the C_{60} core was shifted by 40 mV upon complexation with a Zn–porphyrin derivative.[14]

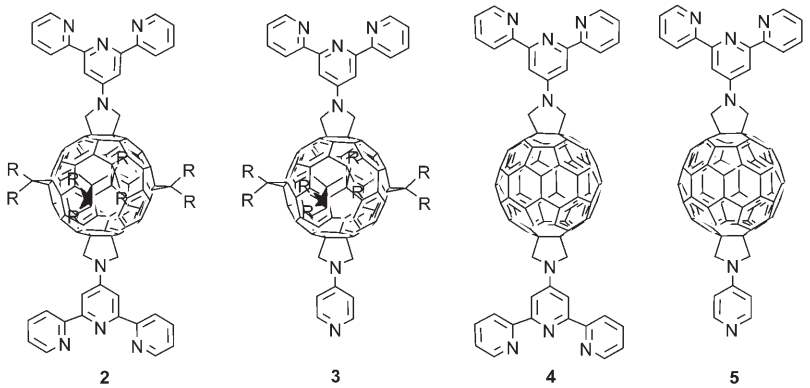


Scheme 2. Complexation of compound **1** with zinc tetraphenyl porphyrin (ZnTPP).

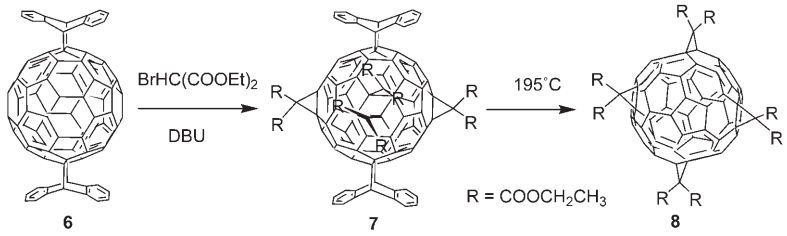
Thus C_{60} hexakis-adducts **2** and **3** with terpyridyl or pyridyl groups in the *trans*-1 positions and the corresponding *trans*-1 bis-adducts **4** and **5** (Scheme 3) were selected as the synthetic targets in the present work. Regioselective formation of *trans*-1 bis-adducts of C_{60} has been a challenging task. Relative to other bis-adduct isomers of C_{60}, the *trans*-1 arrangement is always among the least-abundant isomers, based on kinetic and electronic evidence.[15] Hirsch et al. conducted the stepwise bis-addition of diethyl malonate to C_{60} and prepared the *trans*-1 bis-adduct of C_{60} in 0.8–2% yield after tedious chromatographic separation.[16] In the case of stepwise bis-addition to C_{60} through the 1,3-dipolar cycloaddition to yield bis(*N*-methylpyrrolidine) adducts, the yield of the *trans*-1 bis-adduct was 1.5%.[17] To improve the yield of *trans*-1 bis-adducts of C_{60}, the tether-directed remote-functionalization synthetic procedure introduced by Diederich et al. has proved to be an effective alternative.[18] By using this method, they synthesized *trans*-1 bis-adducts of C_{60} in relatively high yields.[19,20] A similar tether-directed approach was developed by Rubin et al. to prepare a *trans*-1 bis-adduct of C_{60} by using the Diels–Alder reaction.[21] Surprisingly, the solid-state reaction of the monoanthracene adduct of C_{60} or the mixture of C_{60} and anthracene provided a remarkably selective synthesis of the *trans*-1 adduct, **6** (Scheme 4).[22] By reacting **6** with an excess of diethylbromomalonate, Kräutler et al. obtained the D_{2h}-symmetric hexakis-adduct **7** in 95% yield (Scheme 4).[23] Due to the thermal instability of the anthracene addends, a C_{60} tetrakis-adduct **8** with all addends located on an equatorial belt was obtained in 88% yield. Our synthetic strategy is based on this easily prepared tetrakis-adduct of C_{60} (**8**), shown in Schemes 5 and 6 (see below). Here we report the synthesis and characterization of hexakis-adducts **2** and **3** as well as *trans*-1 bis-adducts **4** and **5**.

Results and Discussion

Synthesis of the terpyridylglycine precursor: To prepare *trans*-1 bis-adducts of C_{60} with terpyridyl or pyridyl groups, the precursor, terpyridylglycine (TPG), needed to be synthesized. As far as we know, this compound has not been reported previously. Several research groups have reported the effective and convenient synthesis of 2,2′:6′,2″-terpyridine ligands by solvent-free reactions of 4′-chloro-2,2′:6′,2″-



Scheme 3. Structures of compounds **2**, **3**, **4**, and **5**.



Scheme 4. Synthetic procedure of **8**.

terpyridine (ClTP) with aryl- or alkylamines.[25] Initially, such solvent-free reactions of ClTP with glycine or glycine *tert*-butyl ester in a sealed glass tube under vacuum were conducted. After varying the ratio of starting materials, and the reaction times and temperatures, only trace amounts of terpyridylglycine were obtained as indicated by means of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and TLC analysis. Instead, a terpyridyl dimer connected by a nitrogen atom was obtained in high yields. Reactions of 4′-amino-2,2′:6′,2″-terpyridine (ATP) with *tert*-butyl bromoacetate were carried out to synthesize terpyridyl glycine *tert*-butyl ester to afford terpyridylglycine after removal of the *tert*-butyl group. Different bases including K_2CO_3, Et_3N, and BuLi in solvents such as DMF, CH_3CN, and toluene were tried, but these did not afford terpyridylglycine either. As reported, 4-pyridylglycine was prepared in a high yield by the subsequent treatment of 4-aminopyridine with HCOH, $NaHSO_4$, and KCN.[26] The same treatment of ATP did not yield terpyridylglycine mainly due to the insolubility of ATP in water. Terpyridylglycine was eventually synthesized in 73% yield by treating ATP with ethyl glyoxylate and concentrated HCl followed by reductive hydrogenation.[27] The characterization of terpyridylglycine was established on the basis of MALDI-TOF mass spectrometry, and ^1H, ^{13}C, and COSY NMR spectroscopy (see the Supporting Information).

Synthesis of 2 and 9: The synthesis of **2** and **9** is outlined in Scheme 5. Reaction of symmetric C_{60} tetrakis-adduct **8**[23] with paraformaldehyde and terpyridylglycine in refluxing 1,2-dichlorobenzene afforded both bis- and mono(terpyridyl) C_{60} adducts **2** and **9**, respectively. It is interesting to observe that mono(terpyridyl) compound **9** was always present even after increasing the reaction time and/or by using a large excess of paraformaldehyde and terpyridylglycine. Compounds **2** and **9** were characterized by means of MALDI-TOF MS, and ^1H, ^{13}C, and COSY NMR, and UV-visible spectroscopy. Figure 1 shows the ^1H NMR spectra of compound **2**. The relatively sharp singlet at $\delta = 5.32$ ppm corresponds to the eight identical

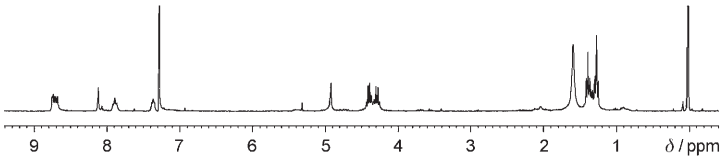
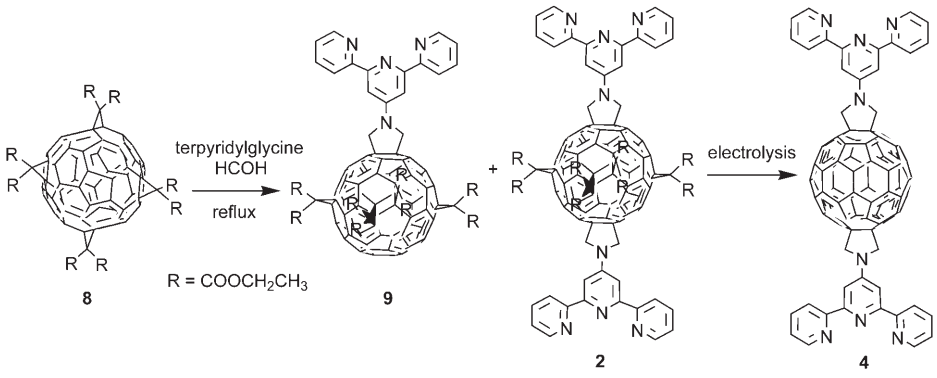


Figure 1. ^1H NMR spectrum of compound **2** in $CDCl_3$.

pyrrolidine protons. Two quartets at $\delta = 4.26$–4.33 and 4.37–4.44 ppm and two triplets at $\delta = 1.25$–1.30 and 1.37–1.41 ppm are due to the expected methylene and methyl groups on the non-equivalent malonate adducts located on the equatorial belt of C_{60}. Signals in the aromatic region were assigned to five different kinds of protons in the terpyridyl rings by using the correlation analysis. One singlet for the pyrrolidine ring protons and two different quartets and triplets for the methylene and methyl groups on the malonate belt clearly indicate a D_{2h} symmetry for compound **2**, that is, all the addends are located at octahedral positions (*trans*-1 bis(pyrrolidine) and equatorial malonate moieties). In addition, 30 sets of equivalent carbon signals in the ^{13}C NMR spectrum are consistent with the proposed D_{2h} symmetry of compound **2** (see the Supporting Information). In the case of compound **9**, three quartets with a ratio of 1:1:2 were observed at $\delta = 4.24$–4.28, 4.29–4.33, 4.34–4.37 ppm for the methylene groups of the malonate adducts, consistent with the symmetry of the compound. The triplets corresponding to the malonate methyl groups were overlapping in this case. In addition, one singlet at $\delta =$ 4.63 ppm was observed for the four equivalent pyrrolidine ring protons. To further prove the symmetry of compounds **2** and **9**, ^{13}C-enriched paraformaldehyde was used to prepare compounds labeled with ^{13}C at the pyrrolidine rings. The heteronuclear multiple quantum coherence (HMQC) NMR spectra



Scheme 5. Synthesis of fullerene derivatives with terpyridyl groups.

clearly showed the correlation between the ^{13}C label and the hydrogen atoms on the pyrrolidine rings (see the Supporting Information). MALDI-TOF MS data show molecular ion peaks (m/z) at 1900 and 1628 for bis- and mono(terpyridyl) compounds **2** and **9**, respectively (see the Supporting Information).

The mono(terpyridyl) adduct **9** was easily separated from the bis(terpyridyl) compound **2** by using column chromatography. However, no well-defined bands were observed after eluting compound **9**. Four different fractions were collected thereafter, all of which show the molecular ion peak for bis(terpyridyl) compound **2**. The resolution of the ^1H NMR spectrum is different for the different fractions. The first two fractions show well-resolved ^1H NMR spectra as shown in Figure 1. Some signal broadening was observed for the fractions that followed. These observations are probably the result of different degrees of protonation of the pyrrolidine ring and/or terpyridyl nitrogen atoms. It is worth mentioning that longer reaction times (more than 48 h) and large excesses of paraformaldehyde and terpyridylglycine result in better yields.

Synthesis of C_{60} hexakis-adduct with one terpyridyl and one pyridyl group in *trans*-1 positions: Based on the successful preparation of **2**, the synthesis of C_{60} hexakis-adduct **3** with terpyridyl and pyridyl groups located in *trans*-1 positions relative to each other was undertaken, as shown in Scheme 6. Compound **3** is interesting because it should directly attach to gold or platinum surfaces through pyridyl nitrogen adsorption. The penta-adduct **10** was prepared by refluxing **8** with paraformaldehyde and pyridylglycine in 1,2-dichlorobenzene under argon for 1 h. The ^1H NMR spectrum of **10** shows one singlet at $\delta = 4.54$ ppm for the four equivalent pyrrolidine ring protons, three quartets at $\delta = 4.33$–4.37 and 4.43–4.47 ppm, and three triplets at $\delta = 1.32$–1.35, 1.37–1.39, and 1.40–1.42 ppm for methylene and methyl groups of the malonate moieties, respectively, which is similar to that of **9**. Reacting **10** with terpyridylglycine and paraformaldehyde under the same conditions afforded the target compound **3**. The structure of **3** was confirmed by MALDI-TOF MS, and ^1H, ^{13}C, and COSY NMR, and UV-visible spectroscopy.

Figure 2 shows the COSY NMR spectrum of compound **3**. Two broad singlets around $\delta = 4.61$ and 4.93 ppm correspond to the protons in the pyrrolidine rings connected to terpyridyl and pyridyl groups, respectively. The quartets and triplets for the methylene and methyl groups in the malonates overlapped. Singlets at $\delta = 6.85$ and 8.41 ppm are correlated with each other and are ascribed to two different kinds of pyridyl protons. Other aromatic signals could be attributed to the terpyridyl protons from the COSY spectrum. In addition, the molecular ion peak (m/z) at 1746 was observed for compound **3** in the MALDI-TOF mass spectrum (see the Supporting Information).

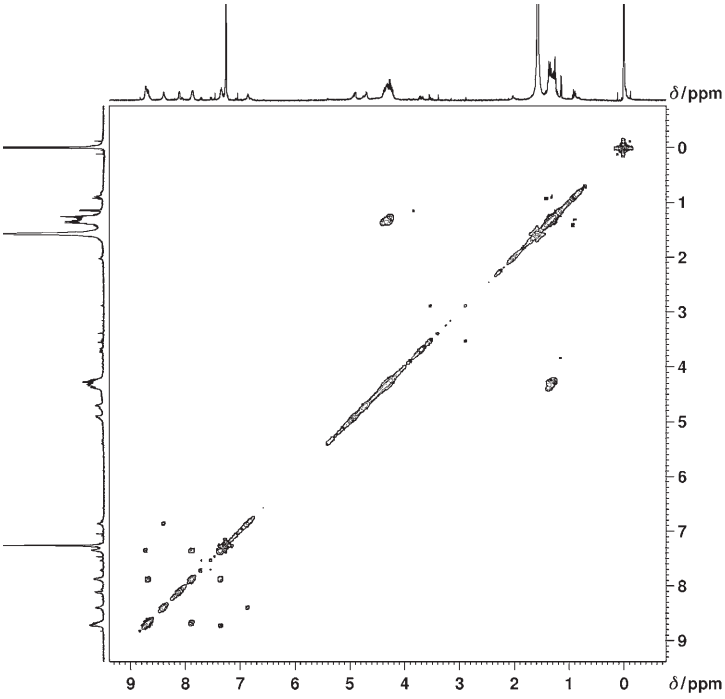
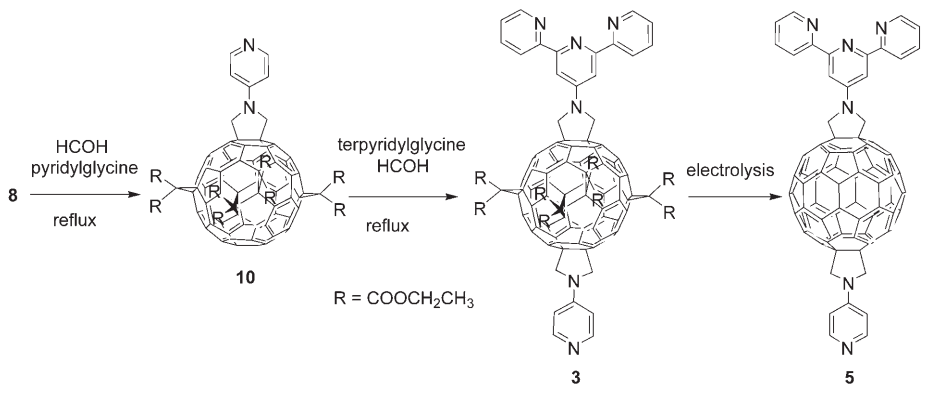


Figure 2. COSY NMR spectrum of compound **3** in $CDCl_3$.



Scheme 6. Synthesis of fullerene derivatives with terpyridyl or pyridyl groups.

Electrochemistry of penta- and hexakis-adducts of C_{60}: Cyclic voltammetry (CV) was used to evaluate the redox behavior of **2**, **3**, and **9**. As shown in Figure 3, reductions of penta- and hexakis-adducts of C_{60} are irreversible on the CV timescale at 0.1 $V s^{-1}$. For **2**, two reductions were observed at -1.40 and -1.76 V versus Fc/Fc^+. The first irreversible reduction is much smaller than the second. Compound **3** also exhibited an irreversible reduc-

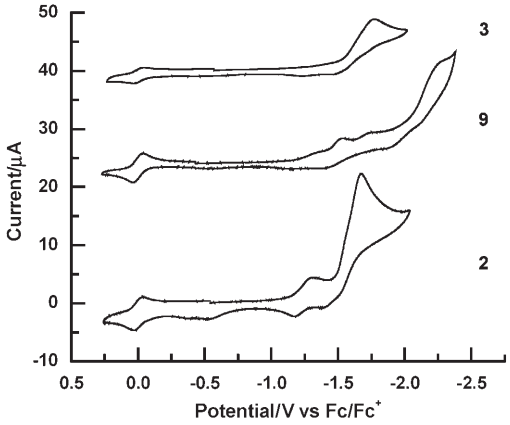


Figure 3. Cyclic voltammograms of compounds **2**, **3**, and **9** in CH_2Cl_2. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 $V s^{-1}$.

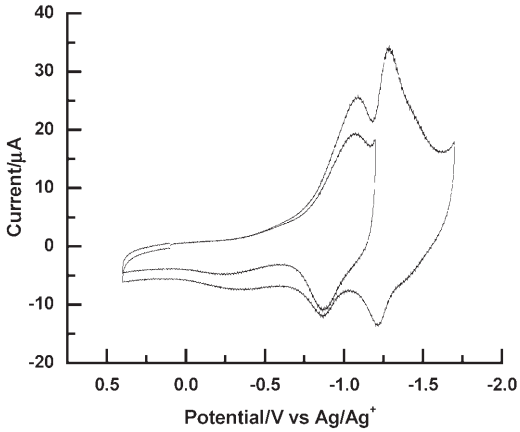


Figure 4. Cyclic voltammograms recorded in CH_3CN of SAMs of **1**. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 1 $V s^{-1}$.

tion wave at −1.77 V. In the case of **9**, three irreversible reductions were observed at −1.53, −1.75, and −2.23 V. Compared with pristine C_{60} and its lower adducts, hexakis-adducts are always difficult to reduce and the processes are irreversible.[28] As reported before, an octahedral hexakis-cyclopropanated adduct of C_{60} showed an irreversible reduction wave at −1.87 V versus Fc/Fc^+.[28] The difference of the redox behavior of **2**, **3**, and **9** can be attributed to the number of the addends added to the C_{60} cage and the geometry of the compounds. The more addends that are added to the C_{60} cage, the higher its LUMO energy level is, making it more difficult for it to accept electrons.

Self-assembled monolayers (SAMs) of fullerene derivatives 1 and 3: Due to the interesting features of fullerene-based thin-film materials, such as charge transport, biological activity, and photoconductivity, fullerenes and their derivatives have been attached to solid substrates by using techniques such as Langmuir–Blodgett (LB), supramolecular assembly, electrodeposition, spin-coating, and self-assembled monolayers (SAMs).[29,30] Among them, the self-assembling method has been preferentially employed because SAMs can afford well-defined structures spontaneously. SAMs of fullerene derivatives have been mainly obtained by the adsorption of thiol, thioether, or thioctic ester derivatives on gold surfaces.[31] Despite the fact that some reports have pointed out that pyridyl nitrogen atoms can effectively adsorb on gold and platinum surfaces in the same way as thiol sulfur atoms do, SAMs of fullerene derivatives through nitrogen adsorption on gold surfaces are largely unexplored.[32]

SAMs of **1** were formed on gold surfaces by immersing the gold beads into solutions of **1** in CS_2 for 48 h. Cyclic voltammograms of the SAMs of **1** in CH_3CN containing 0.1 M Bu_4NPF_6 show two reversible redox waves at $E_{1/2} = -0.97$ and −1.25 V versus Ag/Ag^+ corresponding to the first and second reductions of the compound, respectively (Figure 4). After conversion of those potentials versus Ag/Ag^+ to those versus Fc/Fc^+,[33] the values are −1.01 and −1.29 V. The first and second reductions are shifted anodically by 50 and 150 mV, respectively, relative to those of **1** in solution.[14] All peak potentials are proportional to the sweep rate, which was varied between 0.1 and 1 $V s^{-1}$, indicating surface-confined behavior due to the immobilization of the electroactive fullerene derivative on the gold surfaces.

SAMs of compound **3** were prepared by immersing the clean gold beads in a 0.5 mM solution of **3** in $CHCl_3$ at 25 °C for two days.[34] The SAM-modified gold beads were then rinsed with $CHCl_3$ and dried with a stream of argon. The electrochemical behavior of SAMs of **3** was investigated by using cyclic voltammetry in CH_3CN containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. As shown in Figure 5, SAMs of **3** exhibit an irreversible redox wave at

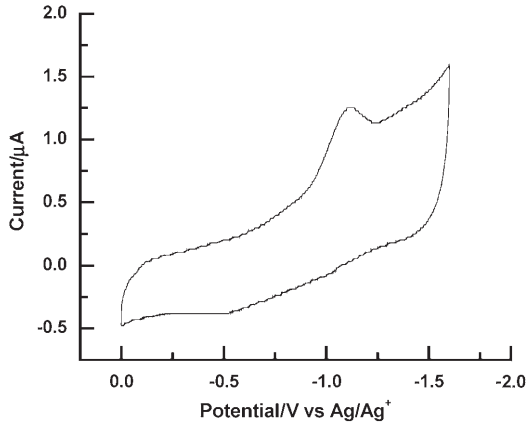


Figure 5. Cyclic voltammograms recorded in CH_3CN of SAMs of **3**. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 $V s^{-1}$.

−1.12 V versus Ag/Ag^+ (−1.16 V vs Fc/Fc^+[33]), which is assigned to the reduction of the C_{60} moiety. Although many monoadducts of C_{60} have been assembled on gold surfaces, as far as we know, immobilization of a hexakis-adduct of C_{60} on gold substrates through the pyridyl nitrogen–gold interaction has never been reported previously. After several scans the peak intensity decreased, but the redox peak in-

tensity was eventually stabilized upon successive reductive cycles, suggesting some stability of SAMs of **3**.

Electrochemical retro-cyclopropanation of fullerene multiadducts: To prepare *trans*-1 bis-adducts of C_{60} with terpyridyl or pyridyl groups (**4** and **5**), electrochemical retro-cyclopropanation reactions were conducted to remove the four malonate addends from compounds **2** and **3**. Our group has developed this reaction and used it in multiple applications.[24] All experiments were carried out by using a homemade cell as previously described.[24] Controlled potential electrolysis (CPE) was performed on samples under high vacuum in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as the supporting electrolyte. To determine the potential to be applied, the CVs of the compounds were recorded. After electrolysis, the solutions were exhaustively reoxidized at 0 V before product analysis.

Initially, the CPE of **8** was performed at −1.60 V as a control and significant voltammetric changes were observed, as illustrated in Figure 6. Compound **8** exhibited two reversible fullerene-based reductions at −0.98 and −1.36 V. The third

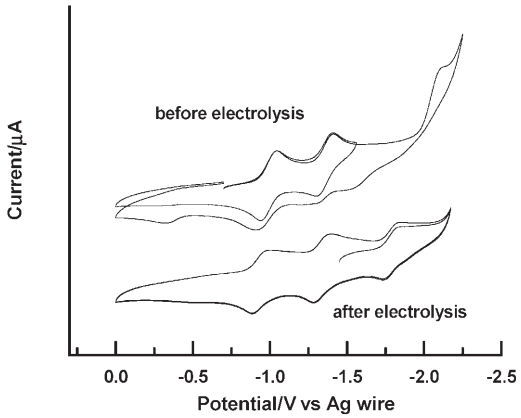


Figure 6. Cyclic voltammograms of **8** before and after electrolysis. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 V s^{-1}.

reduction is chemically irreversible, probably due to the cleavage of the cyclopropane bonds. After approximately 8 e^- per molecule were transferred, the CV showed the appearance of three reversible redox waves that match the redox behavior of C_{60} with the first reduction shifted anodically by 60 mV. After oxidation and careful chromatographic purification, C_{60} was obtained in 94% yield, clearly indicating that the four malonate addends located on the equatorial belt of C_{60} were effectively removed by this electrochemical method.

The CPE of compound **2** was carried out at −1.58 V and Figure 7 shows its electrochemical responses before and after electrolysis. The cyclic voltammogram recorded after the addition of 8 e^- per molecule clearly exhibited two reversible reduction waves at −0.87 and −1.17 V versus Ag, in sharp contrast to the CV response before electrolysis. The first reduction shifts anodically by approximately 400 mV

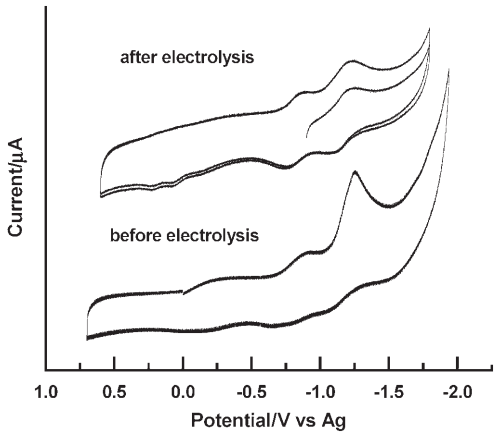


Figure 7. Cyclic voltammograms of **2** before and after electrolysis. Supporting electrolyte: 0.1 M Bu_4NPF_6. Scan rate: 0.1 V s^{-1}.

relative to the large irreversible reduction peak before electrolysis. These observations suggest that the malonate addends were removed and a new compound was formed. The MALDI-TOF MS data of the mixture after electrolysis showed the molecular ion peak for the *trans*-1 bis-adduct **4** (see the Supporting Information). CPE experiments of **2** in THF and **3** in CH_2Cl_2 gave similar results. We are currently not able to isolate compounds **4** and **5** from the electrolyte solution because of the limited amount and reduced solubility of the compounds.

Conclusion

We have reported the synthesis of two hexakis-adducts of C_{60} with terpyridyl or pyridyl groups in a *trans*-1 position and the electrochemical retro-cyclopropanation reaction to prepare their corresponding *trans*-1 bis-adducts. Two hexakis-adducts and one penta-adduct of C_{60} were prepared and characterized by MALDI-TOF mass spectrometry, and ^1H, ^{13}C, COSY NMR, and UV-visible spectroscopy, and cyclic voltammetry analyses. Electrochemical studies show that SAMs of compounds **1** and **3** form spontaneously on gold surfaces. SAMs of **3** represent the first example of a hexakis-adduct of C_{60} on gold surfaces through nitrogen adsorption. Controlled potential electrolyses of multiadducts of C_{60} revealed that it is possible to prepare *trans*-1 bis-1,3-dipolar cycloadducts of C_{60}, which are extremely difficult to synthesize by statistical bis-addition procedures. Future work will include the purification of *trans*-1 bis-adducts of C_{60} with terpyridyl and pyridyl groups, construction of supramolecules on solid substrates, and fabrication of fullerene-based single-molecule transistors.

Experimental Section

General method: Reagents were purchased from commercial suppliers and used without further purification. Compound **8** was prepared as de-

scribed in a published procedure.[23] Gold wire (99.999%) was obtained commercially. NMR spectra were recorded on a Bruker Ac 300 or 500 spectrometer. UV/Vis spectroscopy was recorded on a Shimadzu 2101PC spectrophotometer. Mass spectroscopy was recorded with an Omni Flex MALDI-TOF spectrometer. Deionized water was prepared with a nanopure infinity ultrapure water system.

Monolayer preparation: The gold beads were prepared as previously described[33] and cleaned by electrolysis in 0.1 M $HClO_4$ at a potential of 2.3 V for 5 min and dipped into 0.1 M HCl for 20 min. The gold beads were then washed with water and then methanol. Monolayers of **3** and **1** were self-assembled by immersing the gold beads into a deaerated solution of **3** in $CHCl_3$ and a solution of **1** in CS_2 for 48 h. The SAM-modified gold beads were rinsed with suitable solvents and dried in a stream of argon.

Electrochemical measurements: All electrochemical measurements were performed in redistilled CH_2Cl_2 (degassed with argon) with 0.1 M nBu$_4$NPF$_6$ as the supporting electrolyte on a CHI 660 Electrochemical Workstation (CH Instruments Inc, Austin, Texas). A platinum wire was employed as the counter electrode. A silver wire was used as the reference. Ferrocene (Fc) was added as an internal reference and all the potentials were referenced relative to the Fc/Fc$^+$ couple. A glassy carbon electrode (CHI, 3 mm in diameter), polished with 0.3 μm aluminum paste and ultrasonicated in a deionized water bath, was used as the working electrode. Bulk electrolysis was performed by using a homemade electrochemical cell. A 2–4 mg sample of fullerene derivatives **2**, **3**, or **8** was used for each experiment, and 600 mg of the supporting electrolyte ($TBAPF_6$) was added to the electrolysis cell. The cell was degassed and pumped to a pressure of 10^{-6} torr. The solvent (dichloromethane or THF), which had also been degassed and pumped to the same pressure in the presence of calcium hydride, was then vapor-transferred into the cell. Prior to controlled potential electrolysis (CPE), cyclic voltammetry was performed by using a glassy carbon electrode to obtain the reduction potential versus an Ag wire pseudoreference electrode. The latter was separated from the bulk solution by using a Vycor tip. CPE at 293 K was performed on a Pt-mesh (100 mesh, 6.5 cm^2) working electrode. After reductive electrolysis, the solution was reoxidized at 0 V.

Synthesis of terpyridylglycine: A solution of 4′-amino-2,2′:6′,2″-terpyridine (0.40 g, 1.61 mmol), ethyl glyoxylate (50% in toluene, 0.36 g, 1.78 mmol), 95% ethanol (8 mL), and concentrated HCl (12 mL) was allowed to stand at room temperature for 1 h in a hydrogenation bottle. The catalyst (0.30 g of 5% Pd on carbon) was added, and the mixture was hydrogenated by using a Parr low-pressure reaction apparatus charged initially at 48 psi until no further absorption of hydrogen was evident. Distilled water (20 mL) was added, and the mixture was heated on a water bath to dissolve the pale yellow precipitate that formed during the reaction. Removal of the catalyst by filtration of the warm mixture and evaporation of the filtrate gave the terpyridylglycine hydrochloride as a light yellow-green solid. Concentrated HCl was added, and the mixture was heated at 100 °C for 1 h, cooled to 25 °C, and allowed to stand for a week. Collection of the solid by vacuum filtration gave a pale yellow-green solid (0.38 g, 76%). ^{1}H NMR (D_2O, 300 MHz): δ = 8.53–8.54 (d, J = 5.2 Hz, 2H), 8.35–8.40 (t, J = 7.6 Hz, 2H), 8.22–8.25 (d, J = 7.8 Hz, 2H), 7.81–7.85 (t, J = 6.4 Hz, 2H), 7.05 (s, 2H), 3.88 ppm (s, 2H); ^{13}C NMR (D_2O, 75 MHz): δ = 172.70, 156.50, 147.26, 145.55, 142.15, 127.85, 123.70, 108.93, 43.60 ppm; MS (MALDI): m/z: 307 [M^++1], 306 [M^+].

Synthesis of 2 and 9: A mixture of **8** (10 mg, 0.0074 mmol), paraformaldehyde (2 mg, 0.07 mmol), and terpyridylglycine (9 mg, 0.03 mmol) was placed under reflux in 1,2-dichlorobenzene (6 mL) under argon. The reaction was monitored by TLC analysis. After stirring under reflux for 15 h, another 1 mg of paraformaldehyde and 4 mg of terpyridylglycine were added to the reaction mixture and stirred under reflux for a further 30 h. The solution was washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel). 1–2% MeOH/CH_2Cl_2 eluted mono(terpyridyl) compound **9** as a brown solid (1.8 mg, 15%) and 3–6% MeOH/CH_2Cl_2 eluted different fractions of compound **2** (6.6 mg, total yield = 47%).

Compound ***2***: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.68–8.75 (m, 8H), 8.12 (s, 4H), 7.87–7.92 (t, J = 7.8 Hz, 4H), 7.36–7.39 (t, J = 6.0 Hz, 4H), 4.93 (s, 8H), 4.39–4.44 (q, 8H), 4.26–4.33 (q, 8H), 1.37–1.41 (t, J = 7.2 Hz, 12H), 1.25–1.30 ppm (t, J = 7.2 Hz, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 163.80, 163.51, 156.41, 156.14, 154.60, 152.41, 148.94, 146.90, 145.46, 143.94, 140.32, 139.77, 136.81, 123.74, 121.41, 107.14, 70.87, 68.18, 66.93, 66.22, 62.79, 59.89, 46.12, 44.84, 29.69, 14.15, 14.01 ppm; UV/Vis ($CHCl_3$): λ_{max} = 265, 378, 487, 523 nm; MS (MALDI): m/z: 1900 [M^++1], 1754, 1681, 1594, 1440.

Compound ***9***: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.67 (m, 4H), 7.93 (s, 2H), 7.78 (br s, 2H), 7.29 (br s, 2H), 4.63 (s, 4H), 4.34–4.37 (q, 4H), 4.29–4.32 (q, 4H), 4.22–4.25 (q, 8H), 1.18–1.35 ppm (m, 24H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 163.65, 154.87, 154.12, 152.81, 147.16, 146.45, 146.21, 145.95, 145.33, 144.25, 143.48, 143.09, 142.29, 138.68, 138.05, 136.67, 126.78, 124.34, 121.35, 113.55, 70.61, 69.21, 67.45, 62.90, 60.16, 36.74, 36.23, 30.56, 14.16, 14.05 ppm; UV/Vis ($CHCl_3$): λ_{max} = 265, 344, 478, 544 nm; MS (MALDI): m/z: 1628 [M^++1], 1555, 1484, 1411, 1340.

Synthesis of 10: A mixture of **8** (15 mg, 0.01 mmol), paraformaldehyde (15 mg, 0.49 mmol), and *N*-pyridylglycine (25 mg, 0.16 mmol) was placed under reflux in 1,2-dichlorobenzene (10 mL) under argon for 1 h. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica (eluent dichloromethane, then dichloromethane/methanol 100:3). This afforded **10** (4 mg, 28%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.33–8.34 (d, J = 6.5 Hz, 2H), 6.81–6.82 (d, 2H), 4.56 (s, 4H), 4.43–4.47 (q, 4H), 4.31–4.39 (m, 12H), 1.40–1.42 (t, J = 7.0 Hz, 6H), 1.36–1.39 (t, J = 7.0 Hz, 6H), 1.32–1.35 ppm (t, J = 7.0 Hz, 12H); UV/Vis ($CHCl_3$): λ_{max} = 247, 285, 473, 540 nm; MALDI-TOF: m/z: 1472.

Synthesis of C_{60} derivative 3: A mixture of **10** (6 mg, 0.004 mmol), paraformaldehyde (1.4 mg, 0.05 mmol), and terpyridylglycine (4 mg, 0.013 mmol) was refluxed in 1,2-dichlorobenzene (4 mL) under argon. After 15 h, another 1 mg of paraformaldehyde and 2 mg of terpyridylglycine were added to the reaction mixture, which was stirred under reflux for another 20 h. The solution was washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel). Unreacted **10** (1.4 mg) and compound **3** (2.8 mg, 52% based on consumed **10**) were eluted with 2 and 4% MeOH/CH_2Cl_2, respectively. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.62 (m, 4H), 8.32 (s, 2H), 8.03 (s, 2H), 7.71 (br s, 2H), 7.28 (br s, 2H), 6.82 (s, 2H), 4.93 (s, 4H), 4.64 (s, 4H), 4.22–4.38 (m, 16H), 1.21–1.39 ppm (m, 24H); UV/Vis ($CHCl_3$): λ_{max} = 265, 382, 488, 523 nm; MS (MALDI): m/z: 1747 [M^++1], 1746 [M^+], 1674, 1602, 1531, 995.

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