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Tetrahedron Letters 46 (2005) 2969–2972

Tetrahedron Letters

# An amphiphilic $C_{60}$ derivative with a tris(2,2′-bipyridine)ruthenium(II) polar head group: synthesis and incorporation in Langmuir films

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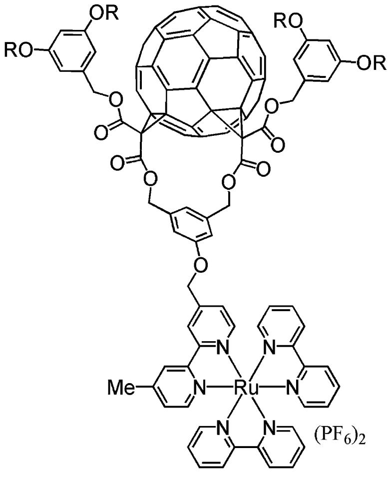
Received 1 February 2005; revised 25 February 2005; accepted 7 March 2005

**Abstract**—An amphiphilic $C_{60}$ derivative with a tris(2,2′-bipyridine)ruthenium(II) polar head group has been prepared. The Langmuir film of this compound has been characterized by its surface pressure versus molecular area ($\Pi/A$) isotherm and Brewster angle microscopy (BAM) observations.

In the last decade many covalently linked fullerene-based photoactive molecular devices have been prepared.[1] They have proven to be of great importance to gain insight into the dynamics and mechanism of intramolecular photoinduced energy and electron transfer processes.[1] Hybrid systems combining the fullerene sphere with coordination compounds of $d^6$ ($Ru^{II}$, $Re^{I}$),[2] or $d^{10}$ ($Cu^{I}$)[3] metal ions are of particular interest since the long lived metal-to-ligand charge transfer (MLCT) excited state of such complexes has a marked reducing character and is capable of starting up photoinduced electron transfer to the fullerene subunit.[2,3] Therefore such compounds appear as good candidates for the preparation of photovoltaic devices. Indeed, solar cells prepared from fullerene-substituted tris(2,2′-bipyridine)ruthenium(II) derivatives have shown promising energy conversion efficiencies.[4] Since the preparation of photovoltaic devices requires the efficient incorporation of the photoactive compound into thin films, we became interested in the synthesis of new fullerene–ruthenium(II) conjugates allowing controlled self-assembly on surfaces. In this letter, we now report the preparation of amphiphilic $C_{60}$ derivative **1** with a tris(2,2′-bipyridine)ruthenium(II) polar head group (Fig. 1) and its incorporation in Langmuir films. It is worth noticing that the molecular design of



**1** R = $C_{12}H_{25}$

**Figure 1.** Amphiphilic $C_{60}$ derivative **1** with a tris(2,2′-bipyridine)ruthenium(II) polar head group.

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*Keywords*: Fullerene; Ruthenium complexes; Langmuir films.

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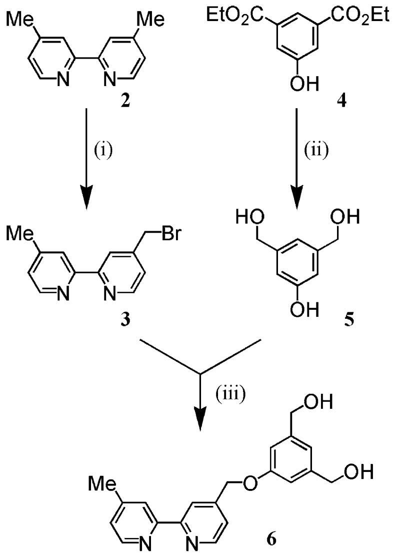
doi:10.1016/j.tetlet.2005.03.035

**1** is based on the structure of the amphiphilic fullerene derivatives we have developed in recent years.[5] In particular, we have demonstrated that the encapsulation of the fullerene sphere in a cyclic addend surrounded by at least four long alkyl chains is an efficient strategy to prevent the irreversible aggregation resulting from the strong fullerene–fullerene interactions usually observed for amphiphilic $C_{60}$ derivatives at the air–water interface. Thus, these amphiphilic derivatives typically show good spreading characteristics and a reversible behavior upon successive compression/expansion cycles.[6]

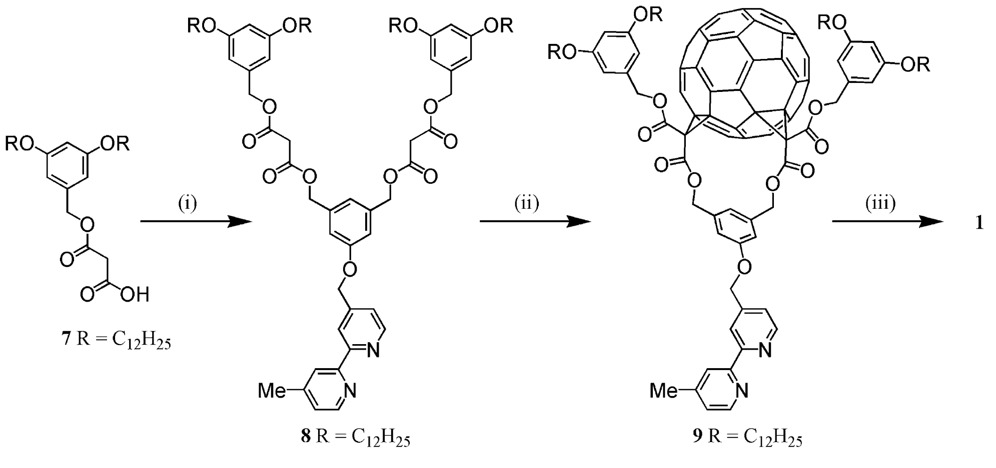
The fullerene-substituted 2,2′-bipyridine ligand used for the preparation of the ruthenium(II) complex **1** was obtained by taking advantage of the versatile regioselective reaction developed in the group of Diederich,[7] which led to $C_{60}$ bis-adducts by a cyclization reaction at the $C_{60}$ sphere with bis-malonates in a double Bingel[8] cyclopropanation. To this end, a 2,2′-bipyridine derivative substituted with a 1,3-phenylenebis(methylene)-tethered bis-malonate was prepared by an esterification reaction between diol **6** and a malonic acid monoester derivative. The synthesis of intermediate **6** is depicted in Scheme 1. Compounds **3**[9] and **5**[10] were prepared from **2** and **4**, respectively, as previously described in the literature. Reaction of bromide **3** with phenol **5** in refluxing acetone in the presence of $K_2CO_3$ afforded compound **6** in 42% yield.



**Scheme 1.** Reagents and conditions: (i) $(C_6H_5CO_2)_2O$, NBS, $CCl_4$ (30%); (ii) $LiAlH_4$, THF, Δ (77%); (iii) $K_2CO_3$, acetone, Δ (42%).

Reaction of diol **6** with malonic acid monoester **7**[5c] under esterification conditions using *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in $CH_2Cl_2$ gave bis-malonate **8** in 91% yield (Scheme 2). Treatment of **8** with $C_{60}$, $I_2$, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the desired cyclization product **9** in 49% yield. The structure and purity of all new compounds were confirmed by NMR and elemental analysis.[11] In particular, the $^1H$ NMR spectrum of **9** shows all the characteristic features of the $C_s$ symmetrical 1,3-phenylenebis(methylene)-tethered fullerene *cis*-2 bis-adduct subunit.[12] Effectively, two AB quartets are observed for the two sets of diastereotopic benzylic $CH_2$ groups and an $AX_2$ system is revealed for the aromatic protons of the 1,3,5-trisubstituted bridging phenyl ring.

The Ru(II) complex **1** was then prepared from *cis*-dichloro-bis(2,2′-bipyridine)ruthenium(II) [$Ru(bipy)_2Cl_2$] and ligand **9** under standard conditions.[3d] In a typical procedure, a mixture of [$Ru(bipy)_2Cl_2$] (61 mg, 0.12 mmol) and $AgBF_4$ (70 mg, 0.36 mmol) in acetone (30 mL) was refluxed for 3 h. After cooling and filtration, the solvent was removed and the mixture taken up in DMF (30 mL). Compound **9** (250 mg, 0.12 mmol) was then added and the resulting mixture refluxed for 3 h. After cooling, the crude product was precipitated as its $PF_6$ salt by addition of a methanolic solution of $NH_4PF_6$. The brown solid was filtered, washed with water, MeOH, and $Et_2O$. Column chromatography ($SiO_2$, $CH_2Cl_2$ containing 5% MeOH) followed by recrystallization from $CH_2Cl_2$/hexane yielded **1** (48 mg,



**Scheme 2.** Reagents and conditions: (i) **6**, DCC, DMAP, $CH_2Cl_2$, 0 °C to room temp (91%); (ii) $C_{60}$, DBU, $I_2$, toluene, room temp (49%); (iii) [$Ru(bipy)_2Cl_2$], $AgBF_4$, acetone, Δ; then filtration and evaporation; then **9**, DMF, Δ (14%).

14%) as a dark red powder.[13] The $^1$H NMR of complex **1** is consistent with the proposed structure. In addition to the signals corresponding to the $C_{60}$-substituted ligand, the resonances arising from the two unsubstituted 2,2′-bipyridine ligands are clearly observed. The structure of **1** was also confirmed by mass spectrometry. The MALDI-TOF-MS of **1** is characterized by a singly charged peak at $m/z$ 2700, which can be assigned to **1** after loss of one hexafluorophosphate counteranion. The UV–vis spectrum of **1** in $CH_2Cl_2$ solution shows the characteristic absorption features of the fullerene units as well as the diagnostic MLCT band of the tris(2,2′-bipyridine)ruthenium(II) complex at 456 nm. Interestingly, preliminary luminescence measurements in $CH_2Cl_2$ solutions ($\lambda_{\text{exc}} = 456$ nm) show a strong quenching of the tris(2,2′-bipyridine)ruthenium(II) complex emission by the fullerene moiety in **1**, indicating the occurrence of intramolecular photoinduced processes. Detailed photophysical studies are currently under investigation and will be reported in due time.

Langmuir films[14] of compound **1** have been characterized by their surface pressure versus molecular area ($\Pi/A$) isotherms and Brewster angle microscopy (BAM) observations. The $\Pi/A$ isotherm obtained with **1** is shown in Figure 2. The surface pressure rises around $A \approx 210$ Å$^2$, and the final molecular area extrapolated at zero surface pressure is $A_0 \approx 162 \pm 8$ Å$^2$, in good agreement with the value estimated by molecular modeling (Fig. 3). These films show excellent reversibility in successive compression–expansion cycles as long as the $\Pi$ is kept below the collapse pressure $\Pi_c \approx 30$ mN m$^{-1}$ (Fig. 3). The latter observation clearly indicates that the four alkyl chains are capable of efficiently preventing the aggregation due to fullerene–fullerene interactions in good agreement with our previous findings on related amphiphilic fullerene derivatives.[5]

BAM observations reveal the good quality of the films. As shown in Figure 2, the film obtained from **1** is noncontinuous at large molecular areas, with holes through which water can be seen. These domains smoothly weld together when the molecular area goes below $A \approx 200$ Å$^2$, and as long as the film does not enter the collapse regime only defectless surfaces are observed. This indicates clearly the formation of an homogeneous monomolecular layer. When the molecular area reaches $A \approx 130$ Å$^2$ ($\Pi_c \approx 30$ mN m$^{-1}$), a change of slope appears in the surface pressure curve indicating a greater compressibility of the film. At the same time, defects can be seen in the BAM pictures confirming that the film is collapsing at this point.

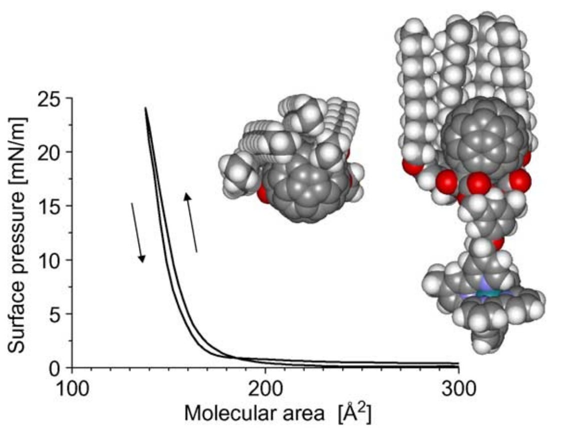


**Figure 3.** A successive compression/expansion cycle with a monolayer of **1** showing the reversibility of the process. Top view (left) and side view (right) of the calculated structure of **1** (molecular modeling performed with *Spartan*) used to estimate the molecular area.

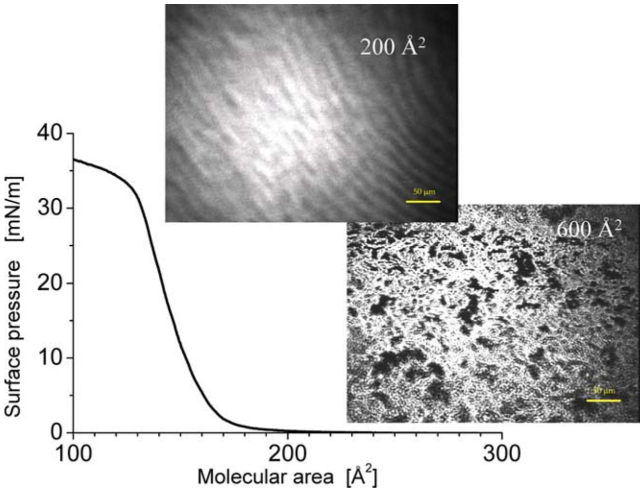


**Figure 2.** Pressure–area isotherm for **1** and Brewster angle microscopy images at $A = 600$ Å$^2$ ($\Pi = 0 \pm 0.1$ mN m$^{-1}$) and 200 Å$^2$ ($\Pi = 0.25 \pm 0.1$ mN m$^{-1}$).

In conclusion, we have shown that $C_{60}$ derivative **1** with a tris(2,2′-bipyridine)ruthenium(II) polar head group is a suitable amphiphilic derivative for the preparation of stable Langmuir films. We are currently investigating the physical properties of the Langmuir–Blodgett films made from this molecule, and more specifically their behavior in photoelectrochemical cells for solar energy conversion.

## Acknowledgements

This research was supported by a fellowship from the CNRS and the Région Alsace to F.C. We further thank L. Oswald for technical help and M. Schmitt for recording the high field NMR spectra. M.M. wish to thank MIUR (contracts 2004035502 and RBAU017S8R) for financial support.

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11. Compound **9**: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 0.89$ (t, $J = 7$ Hz, 12H), 1.26 (m, 72H), 1.72 (m, 8H), 2.47 (s, 3H), 3.86 (t, $J = 7$ Hz, 8H), 5.05 (d, $J = 13$ Hz, 2H), 5.23 (s, 2H), 5.30 (AB, $J = 12$ Hz, 4H), 5.77 (d, $J = 13$ Hz, 2H), 6.37 (t, $J = 2$ Hz, 2H), 6.48 (d, $J = 2$ Hz, 4H), 6.88 (d, $J = 1$ Hz, 2H), 7.15 (t, $J = 1$ Hz, 1H), 7.18 (dd, $J = 5$ and 1 Hz, 1H), 7.43 (dd, $J = 5$ and 1 Hz, 1H), 8.29 (d, $J = 1$ Hz, 1H), 8.49 (d, $J = 1$ Hz, 1H), 8.57 (d, $J = 5$ Hz, 1H), 8.72 (d, $J = 5$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta = 14.1$, 21.2, 22.7, 26.1, 29.2, 29.3, 29.4, 29.6, 31.9, 48.9, 66.8, 67.2, 68.1, 68.5, 68.7, 70.5, 76.4, 101.6, 107.1, 112.7, 116.0, 118.9, 121.4, 122.0, 124.9, 134.3, 135.7, 136.1, 137.8, 138.3, 140.0, 141.0, 141.1, 142.2, 142.7, 142.8, 143.1, 143.6, 143.7, 143.9, 144.1, 144.3, 144.5, 144.9, 145.0, 145.1, 145.3, 145.5, 145.7, 146.0, 146.7, 147.3, 147.4, 148.2, 148.5, 149.0, 149.5, 155.5, 156.6, 158.3, 160.3, 162.5, 162.6; Anal. Calcd for $C_{148}H_{128}O_{13}N_2$. $H_2O$: C 82.27, H 6.06, N 1.30. Found C 82.48, H 6.10, N 1.28.
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13. Compound **1**: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 0.89$ (t, $J = 7$ Hz, 12H), 1.27 (m, 72H), 1.71 (m, 8H), 2.56 (s, 3H), 3.84 (t, $J = 7$ Hz, 8H), 5.15 (d, $J = 14$ Hz, 2H), 5.29 (br s, 2H), 5.31 (AB, $J = 12$ Hz, 2H), 5.32 (AB, $J = 12$ Hz, 2H), 5.69 (d, $J = 14$ Hz, 2H), 6.34 (br s, 2H), 6.45 (d, $J = 2$ Hz, 4H), 6.87 (d, $J = 10$ Hz, 2H), 7.17 (s, 1H), 7.24 (d, $J = 6$ Hz, 1H), 7.49 (m, 6H), 7.64 (d, $J = 6$ Hz, 1H), 7.74 (m, 4H), 7.93 (m, 4H), 8.34 (m, 5H), 8.50 (s, 1H); $^{13}$C NMR (CDCl$_3$, 50 MHz): $\delta = 14.1$, 21.2, 22.6, 26.1, 29.2, 29.3, 29.4, 29.6, 31.9, 48.9, 53.4, 66.7, 67.3, 68.0, 68.8, 70.6, 101.6, 107.2, 112.5, 115.1, 121.7, 124.0, 125.4, 128.2, 129.2, 134.3, 135.6, 135.9, 136.4, 137.6, 137.8, 138.9, 139.8, 141.0, 141.1, 141.9, 142.6, 143.1, 143.4, 143.6, 144.8, 144.1, 144.5, 144.8, 144.9, 145.2, 145.5, 145.6, 145.7, 145.9, 147.3, 147.4, 148.7, 149.2, 150.8, 151.3, 155.9, 156.4, 156.5, 156.6, 157.8, 160.3, 162.5; UV/vis (CH$_2$Cl$_2$) $\lambda_{max}$ ($\varepsilon$): 456 (19,600), 286 (136,000), 250 (126,00); MALDI-TOF-MS: *m*/*z*: 2700 ($[M-PF_6]^+$ calcd for $RuC_{168}H_{144}O_{13}N_6PF_6$: 2699.95).
14. Langmuir monolayers of **1** were formed on pure water by spreading in the order of 50 μL drops of a 0.005 M solution of **1** in CHCl$_3$ with a gas-chromatography syringe; for a detailed description of the setup used for the preparation and the studies of the Langmuir films, see Ref. 5c.