Pergamon

Tetrahedron Letters 44 (2003) 2673–2676

TETRAHEDRON
LETTERS

Synthesis of a new C_{60}-substituted tris(2,2′-bipyridine)ruthenium(II) complex

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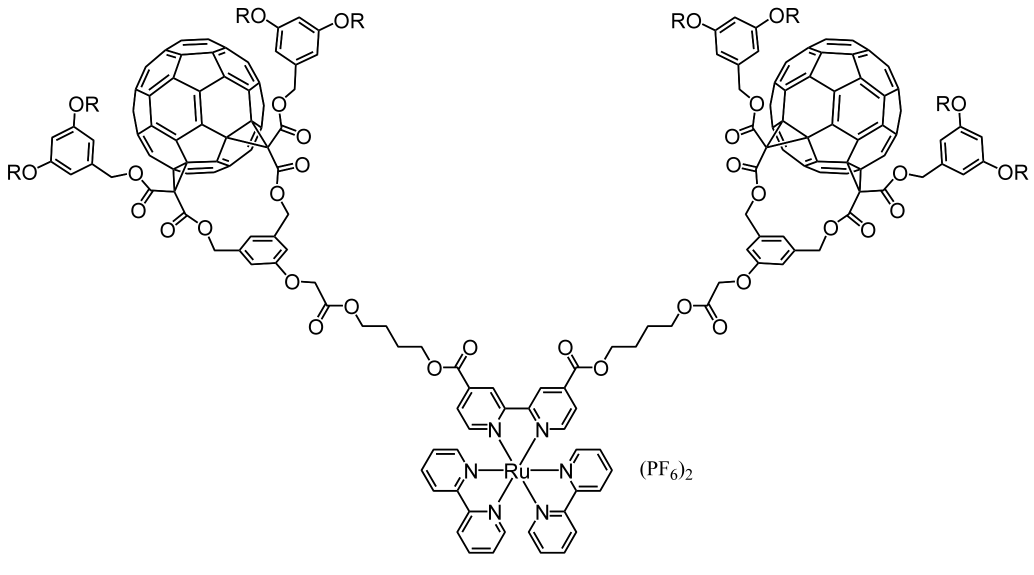
Received 31 January 2003; revised 5 February 2003; accepted 6 February 2003

Abstract—A new tris(2,2′-bipyridine)ruthenium(II) complex substituted with two fullerene subunits has been prepared starting from a fullerene carboxylic acid derivative and a 2,2′-bipyridine ligand bearing two alcohol functions. © 2003 Elsevier Science Ltd. All rights reserved.

The unique electronic properties of C_{60} have generated a significant research effort focused on its use as the electron acceptor in photochemical molecular devices.[1] When compared to equivalent systems with acceptors of smaller size such as benzoquinone, accelerated charge separation and decelerated charge recombination are typically observed for fullerene-based acceptor–donor systems.[1] The smaller reorganization energy of C_{60} positions the photoinduced charge separation rate upward along the normal region of the Marcus curve, while forcing the charge recombination rate downward in the inverted region, thus leading to the photogeneration of long lived charge-separated states.[1] Of particular interest is the combination of the carbon sphere with transition metal complexes such as tris(2,2′-bipyridine)ruthenium(II). Effectively, the long lived metal-to-ligand charge transfer (MLCT) excited state of these complexes has a marked reducing character mak-



1 R = C_8H_{17}

Figure 1. Compound **1**.

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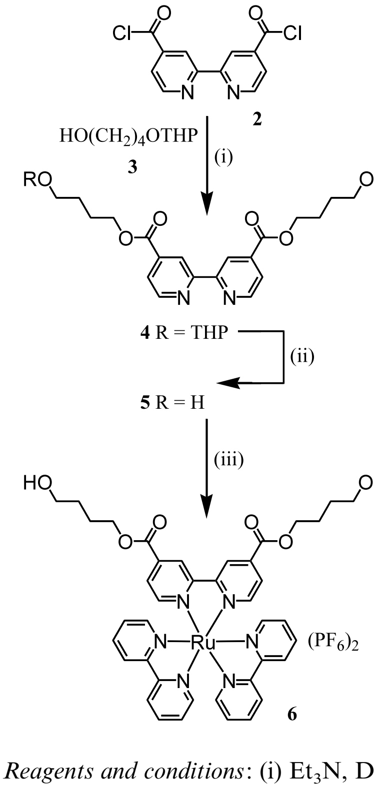
doi:10.1016/S0040-4039(03)00342-3

ing them good candidates for the construction of donor-fullerene arrays which might undergo photoinduced electron transfer. A few examples of such arrays have been reported to date and photoinduced electron transfer has been effectively observed.[2,3] In line with this research, we became interested in the synthesis of new C_{60}-substituted tris(2,2′-bipyridine)ruthenium(II) complexes by using the fullerene carboxylic acid building blocks we have developed in recent years.[4] To this end, we have prepared a 2,2′-bipyridine ligand bearing two hydroxy groups allowing the attachment of two fullerene carboxylic acid units via an esterification reaction. The new Ru(II) complex described in this paper is depicted in Figure 1.

The synthesis of the 2,2′-bipyridine derivative bearing two alcohol functions **5** is depicted in Scheme 1. Reaction of bis(acid chloride) **2**[5] with 4-(3,4,5,6-tetrahydro-2*H*-pyran-2-yloxy)butanol **3** in the presence of Et_3N and 4-dimethylaminopyridine (DMAP) in toluene afforded compound **4** as a mixture of diastereomers in 61% yield. The removal of the 3,4,5,6-tetrahydro-2*H*-pyranyl (THP) protecting groups in **4** was carried out by treatment with an excess of *p*-toluenesulfonic acid (TsOH) in refluxing ethanol. The desired 2,2′-bipyridine derivative **5** was thus obtained in 90% yield. The Ru(II) complex **6** was then prepared in 48% yield from $[Ru(bipy)_2Cl_2]$ and ligand **5** under standard conditions.[3] The esterification of **6** with carboxylic acid **7**[6] was performed in CH_2Cl_2 using *N*,*N*′-dicyclohexylcarbodiimide (DCC), DMAP and 1-hydroxybenzotriazole (HOBt) (Scheme 2). The desired C_{60}-substituted tris(2,2′-bipyridine)ruthenium(II) complex **1** was subsequently isolated in 41% yield after a tedious chromatographic purification. Actually, the separation of complex **1** from the 1,3-dicyclohexylurea (DCU) by-product was found to be particularly difficult. Alternatively, compound **1** was also prepared following another route: DCC-mediated esterification of ligand **5** with **7** afforded **8** which was metalated to give **1**. This second strategy for the preparation of **1** was much more convenient. Effectively, in this case, the product obtained from the esterification step was less polar and could be easily purified.

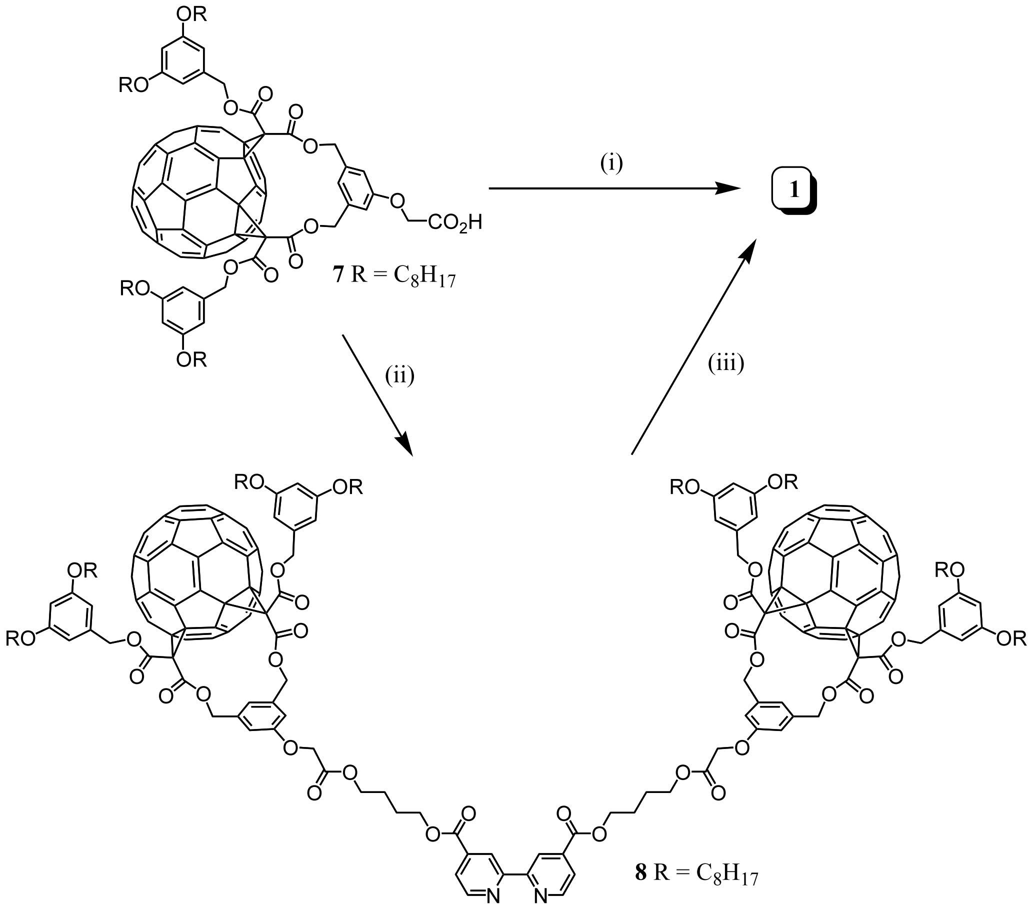


Scheme 1. *Reagents and conditions*: (i) Et_3N, DMAP, toluene, rt (61%); (ii) TsOH, EtOH, Δ (90%); (iii) $[Ru(bipy)_2Cl_2]$, $AgBF_4$, acetone, Δ; then filtration and evaporation; then **5**, DMF, Δ (48%).

The structure and purity of all new compounds were confirmed by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.[7] The ^1H NMR spectra of **1** and **8** are depicted in Figure 2. For both compounds, unambiguous assignments were achieved on the basis of 2D-COSY and NOESY spectra recorded at room temperature in $CDCl_3$.

The spectrum of **8** shows all the characteristic features of the C_s symmetrical 1,3-phenylenebis(methylene)-tethered fullerene *cis*-2 bis-adduct substituent.[4] Effectively, two sets of AB quartets are observed for the diastereotopic benzylic CH_2 groups ($H_{A–B}$ and $H_{C–D}$) and an AX_2 system is revealed for the aromatic protons of the 1,3,5-trisubstituted bridging phenyl ring (H_c and H_d). The spectrum is also characterized by three sets of aromatic signals in a typical pattern for a 4,4′-disubstituted 2,2′-bipyridine (H_e, H_f and H_g). The ^1H NMR of complex **1** is also consistent with the proposed structure. In addition to the signals corresponding to the fullerene-functionalized ligand, the resonances arising from the two unsubstituted 2,2′-bipyridine ligands are clearly observed. It can be noted that compound **1** is C_2 symmetric and therefore chiral. As a result, the two equivalent fullerene *cis*-2 bis-adduct moieties have lost their plane of symmetry. For this reason, the two protons H_d that were equivalent in ligand **8** are not equivalent any longer in the complex and give rise to two sets of signals (in theory, the same effect should also be seen for protons H_A, H_B, H_C and H_D but it is not observed). The structures of **1** and **8** were also confirmed by mass spectrometry as they show the expected molecular ion peak.[7]

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. Actually, the absorption spectrum of **1** matches the profile obtained by summing the spectra of the component units (**6** and **7**), indicating that there are no significant ground state interactions between the chromophores. Preliminary luminescence measurements in CH_2Cl_2 solutions show a substantial quenching of the tris(2,2′-bipyridine)ruthenium(II) complex emission by the fullerene moieties in **1**, indicating the occurrence of



Scheme 2. *Reagents and conditions*: (i) **6**, DCC, DMAP, HOBt, CH_2Cl_2, 0°C to rt (41%); (ii) **5**, DCC, DMAP, HOBt, CH_2Cl_2, 0°C to rt (66%); [Ru(bipy)$_2$Cl$_2$], $AgBF_4$, acetone, Δ; then filtration and evaporation; then **8**, DMF, Δ (55%).

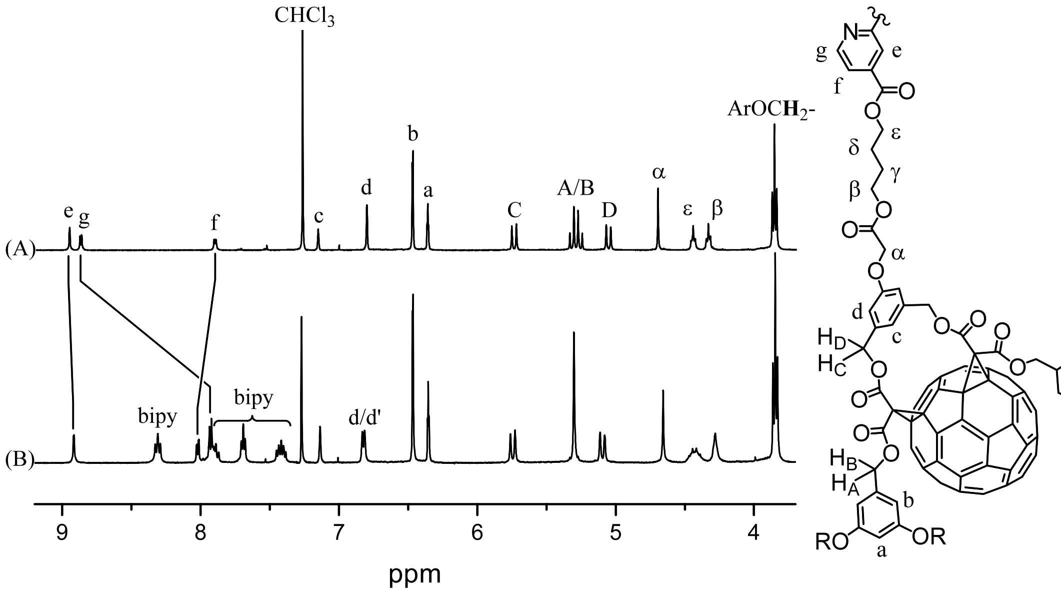


Figure 2. ^{1}H NMR spectra (CDCl$_3$, 400 MHz) of **8** (A) and **1** (B).

intramolecular photo-induced processes. Detailed photophysical studies are currently under investigation and will be reported in due time.

Acknowledgements

This research was supported by the French Ministry of Research (ACI Jeunes Chercheurs) and 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.

References

1. (a) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527–2547; (b) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445–2457; (c) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48.
2. (a) Maggini, M.; Dono, A.; Scorrano, G.; Prato, M. *Chem. Commun.* **1995**, 845–846; (b) Maggini, M.; Guldi, D. M.; Mondini, S.; Scorrano, G.; Paolucci, F.; Ceroni, P.; Roffia, S. *Chem. Eur. J.* **1998**, *4*, 1992–2000; (c) Polese, A.; Mondini, S.; Bianco, A.; Toniolo, C.; Scorrano, G.; Guldi, D. M.; Maggini, M. *J. Am. Chem. Soc.* **1999**, *121*, 3446–3452; (d) Armaroli, N.; Accorsi, G.; Felder, D.; Nierengarten, J.-F. *Chem. Eur. J.* **2002**, *8*, 2314–2323.
3. Armspach, D.; Constable, E. C.; Diederich, F.; Housecroft, C. E.; Nierengarten, J.-F. *Chem. Eur. J.* **1998**, *4*, 723–733.
4. (a) Felder, D.; Gutiérrez Nava, M.; del Pilar Carreon, M.; Eckert, J.-F.; Luccisano, M.; Schall, C.; Masson, P.; Gallani, J.-L.; Heinrich, B.; Guillon, D.; Nierengarten, J.-F. *Helv. Chim. Acta* **2002**, *85*, 288–319; (b) Nierengarten, J.-F.; Felder, D.; Nicoud, J.-F. *Tetrahedron Lett.* **1999**, *40*, 269–272; (c) Nierengarten, J.-F. *Chem. Eur. J.* **2000**, *6*, 3667–3670; (d) Nierengarten, J.-F.; Eckert, J.-F.; Rio, Y.; Carreon, M. P.; Gallani, J.-L.; Guillon, D. *J. Am. Chem. Soc.* **2001**, *123*, 9743–9748.
5. Garelli, N.; Vierling, P. *J. Org. Chem.* **1992**, *57*, 3046–3051.
6. Compound **7** was prepared in eleven steps according to the procedure described in Ref. 4a.
7. Compound **8**: ESMS: *m*/*z* 3941.1 ([M+H]$^+$, calcd *m*/*z* 3941.4). Anal. calcd for $C_{264}H_{196}N_2O_{34}$: C, 80.47; H, 5.01. Found: C, 80.19; H, 5.15%.
   Compound **1**: ESMS: *m*/*z* 2176.9 ([M−2PF$_6$]$^{2+}$, calcd *m*/*z* 2176.9. Anal. calcd for $C_{284}H_{212}F_{12}N_6O_{34}P_2Ru$: C, 73.46; H, 4.60. Found: C, 73.19; H, 4.95%.