Synthesis of a [60]Fullerene Derivative Covalently Linked to a Ruthenium(II) Tris(bipyridine) Complex

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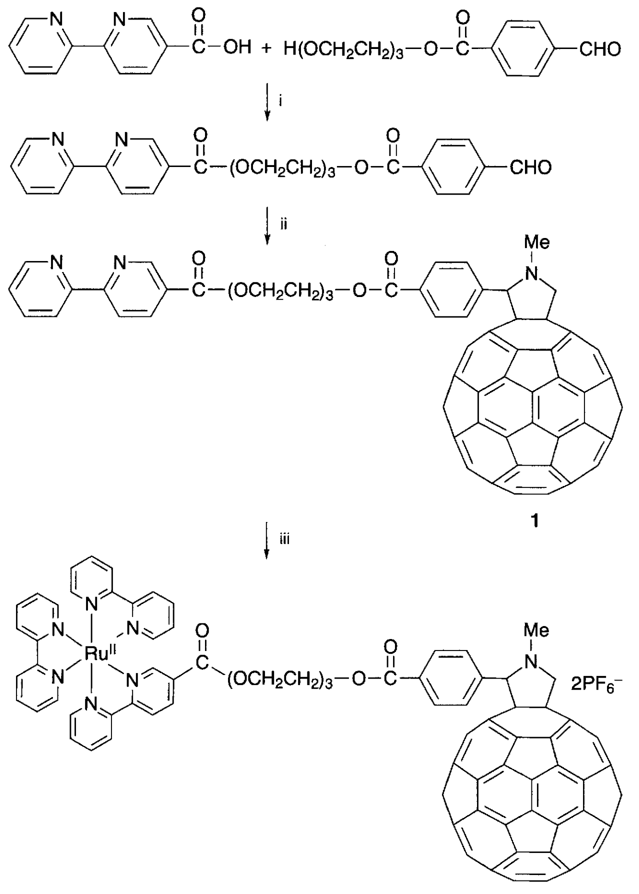
The synthesis of a [60]fullerene derivative containing the transition metal complex $Ru(bpy)_3^{2+}$ is described; its UV–VIS spectrum shows absorptions typical of the two independent chromophores.

Several recent studies on intermolecular photoinduced electron transfer between [60]fullerene and conjugated polymers or other electron donors have opened the rapidly developing area of fullerene-based photoconductors.[1–5] In this context, the possibility of linking together both donor and acceptor in a single molecule may offer new potentials in an intramolecular version of the electron-transfer process.[6,7] We report herein the synthesis of a new derivative where [60]fullerene and a transition metal complex, ruthenium(II) tris(2,2′-bipyridine), $Ru(bpy)_3^{2+}$, are covalently linked.

$Ru(bpy)_3^{2+}$ complexes constitute a thoroughly investigated class of photoactive compounds, known to give energy transfers in the excited states.[8] On the other hand, [60]fullerene has a high electron affinity[9] and is able to accept reversibly up to six electrons in solution.[10,11] The coupling of the two units would lead to an unprecedented species, particularly interesting from both the electrochemical and the photochemical points of view. For instance, systems containing two photoactive redox centres are appealing as on–off components in molecular switches.[12,13] However, although both $Ru(bpy)_3^{2+}$ complexes[8] and [60]fullerene[14,15] exhibit a rich chemistry, the covalent linking of the two moieties is not a trivial task. The two fragments have completely different solvation demands: the hydrophilic ruthe-



Scheme 1 *Reagents and conditions*: i, DCC/DMAP/CH_2Cl_2, 8 h, 70%; ii, $MeNHCH_2CO_2H$, [60]fullerene, toluene, reflux, 6 h, 48%; iii, $Ru(bpy)_2Cl_2·2H_2O$, NH_4PF_6, DCE, reflux, 3 h, 60%

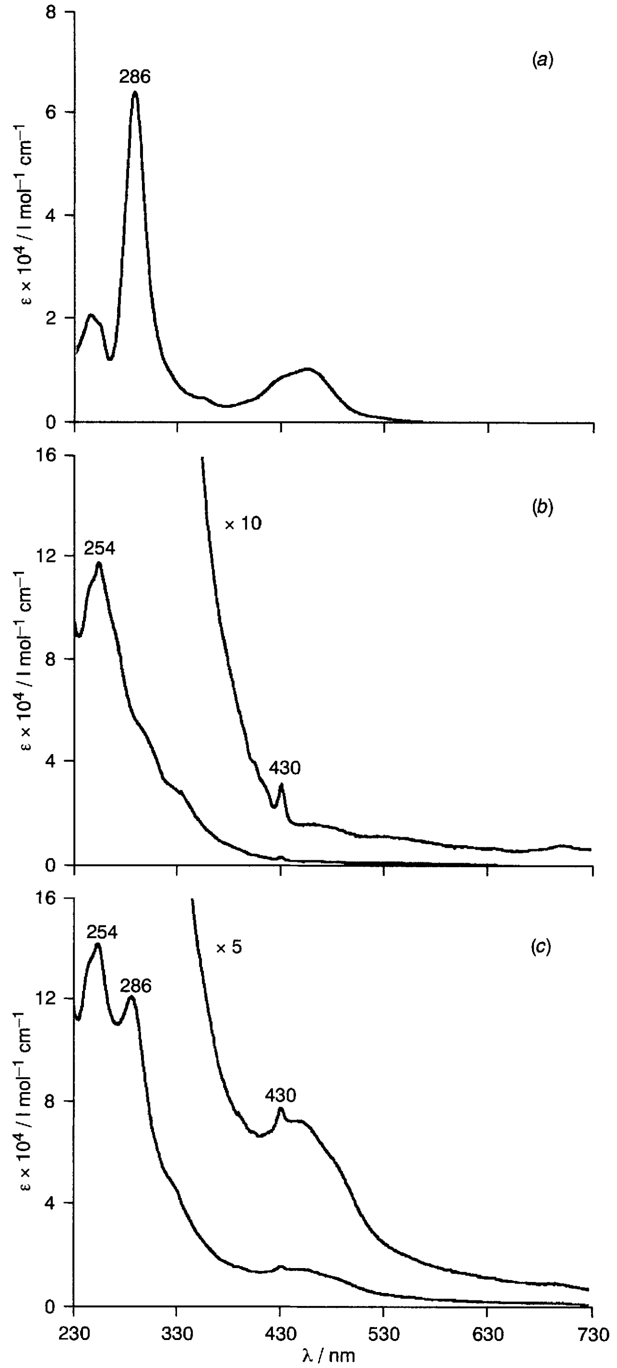


Fig. 1 UV–VIS spectra of (*a*) $Ru(bpy)_2(bpy\text{-}5\text{-}CO_2H)(PF_6)_2$ in MeOH, (*b*) **1** in CH_2Cl_2 and (*c*) **2** in CH_2Cl_2

nium salt requires solvents that usually do not help dissolve the hydrophobic fullerene sphere. As a matter of fact, from the beginning of our studies, we have been coping with a major experimental problem: the insolubility of the final product in any solvent. This was the case, for instance, in the coupling based on a simple amide bond formation. The reaction between Ru(bpy)$_2$(bpy-5-COCl)(PF$_6$)$_2$ and the parent N–H fulleropyrrolidine[16] gave a stone-like material, resistant to any further investigation. Any other synthetic strategies involving the coupling between a suitable ruthenium salt and a modified fullerene resulted in the formation of a brownish precipitate, insoluble in all the solvents, thus preventing any possibility of structural characterization.

Eventually, it was decided to prepare a fullerene derivative soluble in polar solvents and to form the ruthenium complex in the final stage. [60]Fullerene was functionalised *via* our recently reported azomethine ylide cycloaddition.[16] The fulleropyrrolidine **1** containing a bipyridyl group was thus synthesized according to Scheme 1 and fully characterised (^{1}H and ^{13}C NMR, FTIR, MALDI-MS, UV–VIS). Ligand **1** was allowed to react with Ru(bpy)$_2$Cl$_2$·2H$_2$O in refluxing 1,2-dichloroethane in the presence of an excess of NH$_4$PF$_6$. The reaction was monitored by TLC (CH$_2$Cl$_2$–MeOH), following the disappearance of **1**. After filtration, the solution was concentrated at reduced pressure and the brownish solid washed with toluene, methanol and water. The product was then dissolved in THF, filtered and after evaporation of the solvent, dried *in vacuo*. Compound **2** is reasonably soluble in methylene chloride, 1,2-dichloroethane, acetonitrile and insoluble in toluene.

The MALDI spectrum shows a cluster of signals with a maximum at *m/z* 1770, corresponding to the loss of a PF$_6$ fragment from the parent ion, and a cluster with a maximum at 1625 (loss of two PF$_6$ fragments). The proton NMR spectrum (CD$_3$CN) exhibits four sets of aromatic signals, a typical pattern for Ru(bpy)$_3^{2+}$ complexes, as well as complex multiplets corresponding to the triethylene glycol chain, a singlet and a doublet (J = 9.5 Hz) at δ 5.1 and 5.0 ppm, respectively, which account for the pyrrolidine ring protons (the doublet of the other proton of the pyrrolidine ring is hidden under the ethylene chain signal) and a singlet at δ 2.7 (N–CH$_3$). The ^{13}C NMR spectrum shows a host of signals in the aromatic region (58 peaks are expected for the fullerene sphere together with 30 peaks for the pyridine rings and 4 peaks for the phenyl ring) and also a crowded δ 45–75 region (11 peaks expected). C, H, N combustion analysis of **2** is in agreement with the assigned structure.

Most interestingly, the UV–VIS spectrum of **2** displays strong absorptions due to both the ruthenium complex and the fullerene moieties. Fig. 1 shows the UV–VIS spectrum of **2** together with those of the ligand **1** and the acid Ru(bpy)$_2$(bipy-5-CO$_2$H)(PF$_6$)$_2$ for comparison. The electronic spectrum of **2** is the virtual superimposition of the two independent chromophores present in the molecule.

Compound **2** is currently being investigated as a model for the study of long-lived charge separated states and will be compared to compounds with conventional rigid spacers[7] less flexible than the triethylene glycol chain.

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