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Ruthenocene as a new donor fragment in [60]fullerene–donor dyads

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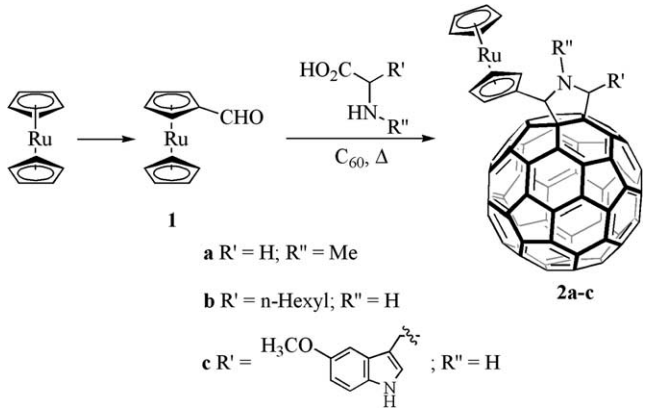
Abstract—Four novel fullerene derivatives containing ruthenocene as the donor fragment have been synthesized and their electrochemical and fluorescence properties have been studied. Steady state fluorescence studies suggest the existence of photoinduced electron transfer in these dyads.

The remarkable electronic and photophysical properties of fullerenes have attracted the interest of many groups in an effort to build donor–acceptor molecular assemblies involving C_{60} groups covalently attached to donors such as porphyrins, phthalocyanines, tetrathiafulvalenes, carotenes and ferrocene.[1] Amongst the different donors used, ferrocene derivatives have been exploited intensively in donor–acceptor (D–A) systems based on fullerene[2,3] with the aim of studying photoinduced electron-transfer processes[4] and to design new materials for molecular-based artificial photosynthesis.[5]

Ruthenocene-based D–A systems have been much less widely studied—presumably this is partly due to the irreversible redox chemistry of ruthenocene itself[6]—and, to the best of our knowledge, C_{60}–ruthenocene dyads are unknown. Recently, however, it has been found that a number of substituted derivatives undergo chemically (though not electrochemically) reversible two-electron oxidations.[7] The first ionization potentials (IPs) for ferrocene and ruthenocene are 6.86 and 7.45 eV, respectively.[8,9] Thus, ferrocene is a stronger donor in an electron-transfer sense. Nevertheless, in many D–A systems there is little evidence to distinguish between the donor strengths of ferrocene and ruthenocene and, in some cases, ruthenocene is a stronger donor.[10] The superior donor properties of ruthenocene in some D–A dyads can be attributed to the more extensive d-orbitals of ruthenium.[11] We describe here the first synthesis of new D–A dyads **2a**–**c** and **4**, which are based on C_{60} and employ ruthenocene as a donor. Preliminary investigations of their electrochemical and optical properties are also reported.

Ruthenocene carboxaldehyde (**1**) was prepared using a modification of the previously described procedure[12] by monolithiation of ruthenocene and subsequent reaction with DMF. Pyrrolidino[60]fullerene **2a** was prepared in 31% yield by 1,3-dipolar cycloaddition[13] between **1**, *N*-methylglycine and C_{60} in toluene under microwave irradiation[14] at 210 W for 45 min in a focussed microwave oven.[15] The very low solubility of this adduct led us to prepare **2b** and **2c** (Scheme 1), in which an *n*-hexyl (**2b**) and tryptophan moiety (**2c**) were incorporated into the molecule by reaction of **1**, C_{60} and the corresponding



Scheme 1.

Keywords: Ruthenocene; [60]Fullerene; Electron donor; Electron transfer.
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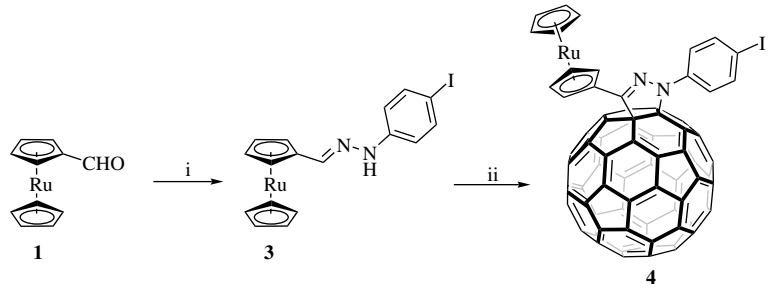

Scheme 2. Reagents and conditions: (i) 4-iodophenylhydrazine, AcOH, EtOH; (ii) NBS, Et_3N, C_{60}, 45 min, 40 °C, toluene.

amino acid. Dyads **2b–c** were obtained in 29% and 24% yield, respectively.

2-Pyrazolino[60]fullerene **4** was synthesized according to Scheme 2: ruthenocene carboxaldehyde 4-iodophenylhydrazone (**3**) was prepared in 71% yield from aldehyde **1** by a standard procedure; 1,3-dipolar cycloaddition of the nitrile imine formed in situ by reaction of **3** with NBS followed by treatment with Et_3N yielded **4** (18%).[16] Other 2-pyrazolino[60]fullerene derivatives with H, *p*-nitro or *p*-methoxy groups as substituents in the *N*-phenyl ring of the pyrazoline moiety have previously been prepared in our group;[17] the incorporation of the iodo-substituent will enable further functionalization on this side of the molecule by, for example, employing coupling reactions.

All structures were confirmed by spectroscopic analyses (NMR, FT-IR and MS). The MALDI-MS revealed molecular ion peaks in agreement with the calculated values. ^{1}H NMR spectra of **2a–c**[18] show the pyrrolidine hydrogen signals at around 4.5 and 3.5 ppm. The ruthenocene protons appear as a singlet around 4.5 ppm for the cyclopentadienyl ring without substituents and as several multiplets, between 5.0 and 4.0 ppm, for the substituted systems. Good quality ^{13}C NMR spectra of **2a** and **4** could not be recorded due to the low solubility of these compounds; for compounds **2b** and **2c**, however, the ^{13}C NMR spectra show the corresponding signals of C_{60}; the two sp^3 carbons at 89.0 and 76.0, approximately, and the rest of the carbons in the sphere between 160.0 and 140.0 ppm. In addition, the signals of the ruthenocene carbons appear between 70.0 and 72.0 ppm. The characteristic absorption of C_{60} monoadducts, at around 430 nm, is observed in the UV–vis spectra measured in CH_2Cl_2 for all new cycloadducts.

Electrochemical studies using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) at room temperature were performed to evaluate the potentials of the different redox entities of the dyads. The redox potentials are collected in Table 1, along with those of C_{60} and ruthenocene for the sake of comparison. In the reduction side, fulleropyrrolidines **2a–c** show, in the selected potential window, three quasireversible C_{60}-based reduction waves with a negative shift of around 100 mV with respect to that of pristine C_{60}. These changes are similar to those observed for other fulleropyrrolidines.[19] Nevertheless, the first reduction potential of 2-pyrazolino[60]fullerene **4** appears at

Table 1. Redox potentials (V) determined by OSWV of **2a–c**, **4** and C_{60} and ruthenocene measured in *o*-dichlorobenzene/acetonitrile (4:1)[a]

Compound	E^1_{red}	E^2_{red}	E^3_{red}	$E^{1\ b}_{ox}$
2a	−1.07	−1.48	−2.02	0.52
2b	−1.13	−1.532	−2.01	0.51
2c	−1.07	−1.48	−2.04	0.56
4	−0.97	−1.37	−1.87	0.53
C_{60}	−0.96	−1.38	−1.84	
Ruthenocene				0.57

[a] V versus $Ag/AgNO_3$; GCE as working electrode; 0.1 mol dm^{-3} TBAP; scan rate was 100 mV s^{-1}.
[b] Irreversible according to cyclic voltammetry.

0.97 V, which is hardly shifted at all with respect to C_{60}. This improved electron affinity in 2-pyrazolino[60]fullerenes has been previously observed by us.[20] Finally, in the oxidation side, the voltammogram shows the irreversible oxidation potential of the ruthenocene moiety at around 0.5 V, which is similar to those values described in the literature.[21]

The gas phase geometry and the electronic structure of **2a** and **4** were studied by density functional theory methods using the B3PW91/LanL2DZ model chemistry as implemented in the Gaussian 03 program.[22] The optimized geometry of **2a** is shown in Figure 1 and resembles that calculated for analogous ferrocene derivatives using the B3LYP/3-21G* model.[2d] The two carbon atoms in the C_{60}-pyrrolidine junction are out of the C_{60} sphere by 0.35 Å, and the ruthenocene moiety is located away from C_{60} in such a way that the distance between the C_{60} spheroid centre and the ruthenium

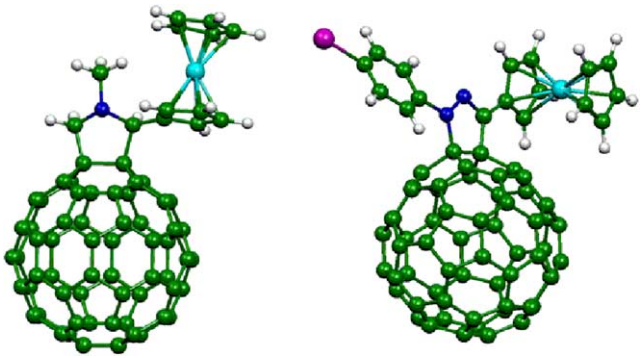

Figure 1. Optimized geometry of compounds **2a** (left) and **4** (right) calculated using B3PW91/LanL2DZ.

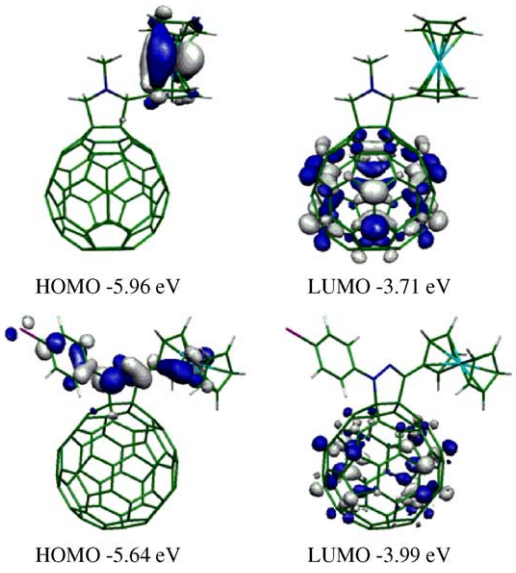

Figure 2. HOMO and LUMO molecular orbitals and their calculated energies for compounds **2a** (top) and **4** (bottom).

atom is 8.37 Å. The calculated geometry of **4** is dictated by the conjugation of the ruthenocene moiety with the pyrazoline ring, which is nearly coplanar (ca. 10°) with the cyclopentadiene ring linked to it. This geometrical arrangement reduces the distance from ruthenium to the centre of C_{60} to 7.55 Å.

The HOMO and LUMO of **2a** and **4** are shown in Figure 2 along with their calculated energies. It can be seen that for **2a** the HOMO is located over the ruthenocene moiety and the main contribution comes from ruthenium d orbitals. On the other hand, the HOMO of **4** spreads from ruthenocene to the *p*-iodophenyl ring. The LUMO in each case consists of C_{60} orbitals, which is consistent with the electrochemical results. The gas phase calculated HOMO–LUMO gap is 2.25 eV for **2a** and 1.65 eV for **4**.

As a preliminary investigation, into the photophysical properties of the newly prepared ruthenocene–C_{60} dyads **2a**–**c** and **4**, the fluorescence spectra of the materials were measured in toluene and benzonitrile as solvents. The measurements were carried out at room temperature using solutions with the same absorbance and excitation at 420 nm, at this wavelength only the C_{60} moiety is excited. In toluene solutions, **2a**–**c** emit fluorescence at around 718 nm[23] but in the more polar benzonitrile, the fluorescence is strongly quenched (Fig. 3); significant differences were not observed between the three derivatives **2a**–**c**.

On the other hand, 2-pyrazolino[60]fullerene **4** shows a different behaviour and, in both nonpolar and polar solvents, a weak emission is observed (Fig. 3) that is similar to those observed for other donor–aceptor systems based on 2-pyrazolino[60]fullerene.[17c] This quenching of the fluorescence is probably due to intramolecular electron transfer from the ruthenocene moiety to the fullerene cage, although more detailed photophysical

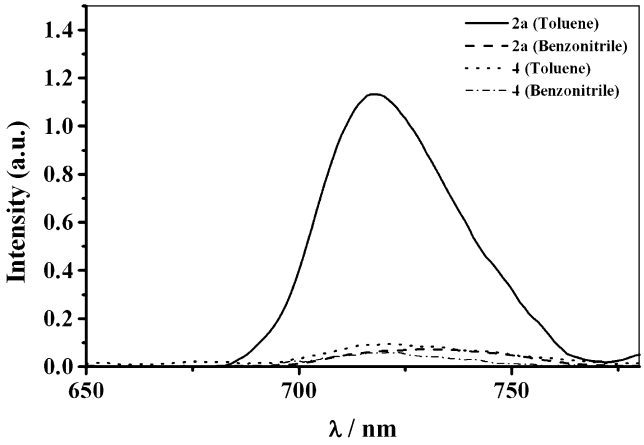

Figure 3. Relative fluorescence emission intensity of compounds **2a** and **4** in toluene (—) and benzonitrile (---).

measurements such as transient absorption spectra are necessary for a quantitative interpretation. Such investigations are now in progress.

Acknowledgements

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16. An Ar-blanketed solution of NBS (53 mg, 0.03 mmol) and the hydrazone **3** (65.6 mg, 0.13 mmol) in dry C_6H_6 (20 mL) was stirred at room temperature for 15 min. The solvent was removed in vacuo, and a solution of C_{60} (50 mg, 0.07 mmol) and NEt_3 (7 mg, 0.07 mmol) in dry toluene (50 mL) was added to the solid. The solution was stirred for 45 min at room temperature. The solvent was removed under reduced pressure. The resulting solid was purified by silica gel flash chromatography using toluene as solvent.
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18. Selected spectroscopic data for **2a**: ^{1}H NMR (200 MHz, C_6D_6): δ 5.05 (m, 1H), 4.72 (m, 1H), 4.48 (s, 5H), 4.41 (d, 1H, J = 9.2 Hz), 4.35 (s, 1H), 4.33 (m, 1H), 4.27 (m, 1H), 3.80 (d, 1H, J = 9.2 Hz), 3.4 (br s, 1H, NH), 2.89 (s, 3H). MS (MALDI-TOF): *m/z* 1008.0 [M+1]. UV–vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 430 (3.8), 326 (4.8), 308 (4.8), 256 (5.3). IR (KBr, cm^{-1}): 3412, 2837, 1710, 1424, 1329, 1178, 997, 809, 569. Compound **2b**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.35 (s, 1H), 5.10 (m, 1H), 4.92 (m, 1H), 4.72 (s, 5H), 4.71 (m, 1H), 4.57 (m, 2H), 2.62 (m, 2H), 2.20 (m, 2H), 1.90 (m, 2H), 1.53 (m, 4H), 1.0 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.1, 153.7, 153.2, 146.8, 146.7, 146.5, 146.3, 146.1, 145.7, 145.5, 144.8, 144.3, 142.3, 141.8, 141.7, 141.6, 141.2, 139.7, 139.3, 136.8, 136.1, 135.3, 88.9, 72.3, 71.9, 71.3, 70.9, 69.4, 33.5, 32.2, 29.9, 28.8, 23.1, 14.8, 14.1. MS (MALDI-TOF): *m/z* 1078.1 [M+1]. UV–vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 430 (3.8), 328 (4.6), 307 (4.6), 256 (5.1). IR (KBr, cm^{-1}): 3409, 2328, 1426, 997, 808, 525. Compound **2c**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.05 (s, 1H, NH), 7.46 (d, 1H, J = 2.4 Hz), 7.35 (d, 1H, J = 8.8 Hz), 7.34 (s, 1H), 6.96 (dd, 1H, J = 8.8, 2.4 Hz), 5.19 (s, 1H), 4.91 (dd, 1H, J = 11.0, 2.7 Hz), 4.83 (m, 2H), 4.53 (m, 2H), 4.33 (s, 5H), 4.01 (dd, 1H, J = 11.0, 2.7 Hz), 4.00 (s, 3H), 3.61 (d, 1H, J = 11 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.2, 153.8, 153.3, 153.0, 151.1, 146.8, 146.6, 146.1, 145.7, 145.6, 145.1, 144.8, 144.0, 142.9, 142.3, 141.8, 141.7, 141.3, 139.8, 139.5, 137.4, 136.2, 131.3, 127.8, 122.8, 113.7, 112.5, 112.0, 101.2, 89.1, 75.8, 71.8, 71.7, 70.7, 70.4, 70.3, 60.2, 55.8, 29.4. MS (MALDI-TOF): *m/z* 1153.1 [M+1]. UV–vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 429 (3.8), 324 (4.8), 309 (4.8), 255 (5.3). IR (KBr, cm^{-1}): 3410, 3092, 2360, 1706, 1481, 1219, 1099, 809, 540. Compound **4**: ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.71 (d, 2H, J = 9.1 Hz), 7.65 (d, 2H, J = 9.1 Hz), 5.51 (m, 2H), 4.80 (m, 2H), 4.49 (s, 5H). MS (MALDI-TOF): *m/z* 1194.6 [M+1]. UV–vis (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 317 (4.8), 256 (5.3). IR (KBr, cm^{-1}): 3403, 1653, 1513, 1370, 1147, 826.
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