A luminescent multicomponent species made of fullerene and Ir(III) cyclometallated subunits

by

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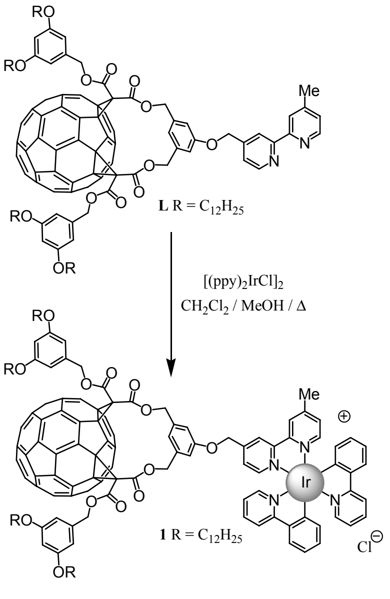
Supplementary information

Synthesis of 1

The synthesis was made as schematized in Scheme 1.



Scheme 1

1 has then been converted into its hexafluorophosphate salt before precipitation. Details are reported below.

A stirred suspension of $[Ir(ppy)_2(\mu\text{-}Cl)]_2$ (10.18 mg 0.0095 mmol) and **L** (40 mg 0.019 mmol) in CH_2Cl_2/MeOH (15 ml, 2:1 v:v) was heated to reflux. After 8 h the resulting yellow solution was cooled to room temperature and an excess of solid NH_4PF_6 was added. The precipitated solid was separated by filtration and than recrystallized from EtOH. Purification was achieved by column chromatography on neutral aluminium oxide (diameter 2.5 cm; length 20 cm) eluting with a mixture

CH_2Cl_2/MeOH 9:1 (v/v). The second band eluted (yellow-brown) contained the complex. The solution was rotary evaporated to dryness, than dissolved with a small amount of acetonitrile and precipitated by addition of diethyl ether. The yield after purification was 60%. TOF-SIMS (time-of-flight secondary ion mass spectrometry): $[M-PF_6]^+$ m/z: 2625.06. Elemental Analysis found (calculated) for $C_{171}H_{146}F_6IrN_4O_{11}P$ (%): C, 74.23 (74.14); H, 5.41 (5.31); N, 1.93 (2.02).

NMR characterization of ligand L, with a small discussion

^{1}H NMR ($CDCl_3$, 400 MHz): δ= 0.89 (t, J = 7 Hz, 12 H), 1.26 (m, 72 H), 1.72 (m, 8 H), 2.47 (s, 3 H), 3.86 (t, J = 7 Hz, 8 H), 5.05 (d, J = 13 Hz, 2 H), 5.23 (s, 2 H), 5.30 (AB, J = 12 Hz, 4 H), 5.77 (d, J = 13 Hz, 2 H), 6.37 (t, J = 2 Hz, 2 H), 6.48 (d, J = 2 Hz, 4 H), 6.88 (d, J = 1 Hz, 2 H), 7.15 (t, J = 1 Hz, 1 H), 7.18 (dd, J = 5 and 1 Hz, 1 H), 7.43 (dd, J = 5 and 1 Hz, 1 H), 8.29 (d, J = 1 Hz, 1 H), 8.49 (d, J = 1 Hz, 1 H), 8.57 (d, J = 5 Hz, 1 H), 8.72 (d, J = 5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ= 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.

In particular, the ^{1}H-NMR spectrum of **L** shows all the characteristic features of the C_s symmetrical 1,3-phenylenebis(methylene)-tethered fullerene *cis-2* bis-adduct subunit. 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.

For further details, see ref. F. Cardinali, J.-L. Gallani, S. Schergna, M. Maggini and J.-F. Nierengarten, *Tetrahedron Lett*. 2005, **46**, 2969.

Calculation of the driving forces of the electron and energy transfer processes

(i) Driving force of the energy transfer from the Ir-based MLCT state to the $^1C_{60}$ state:

ΔG = energy of $^1C_{60}$ (approximated at the maximum of the fullerene fluorescence spectrum, 1.76 eV) – energy of MLCT state (approximated at the maximum of its model species at 77 K, 2.31 eV) = -0.55 eV.

(ii) Driving force of the energy transfer from the Ir-based ^{3}MLCT state to the $^3C_{60}$ state:

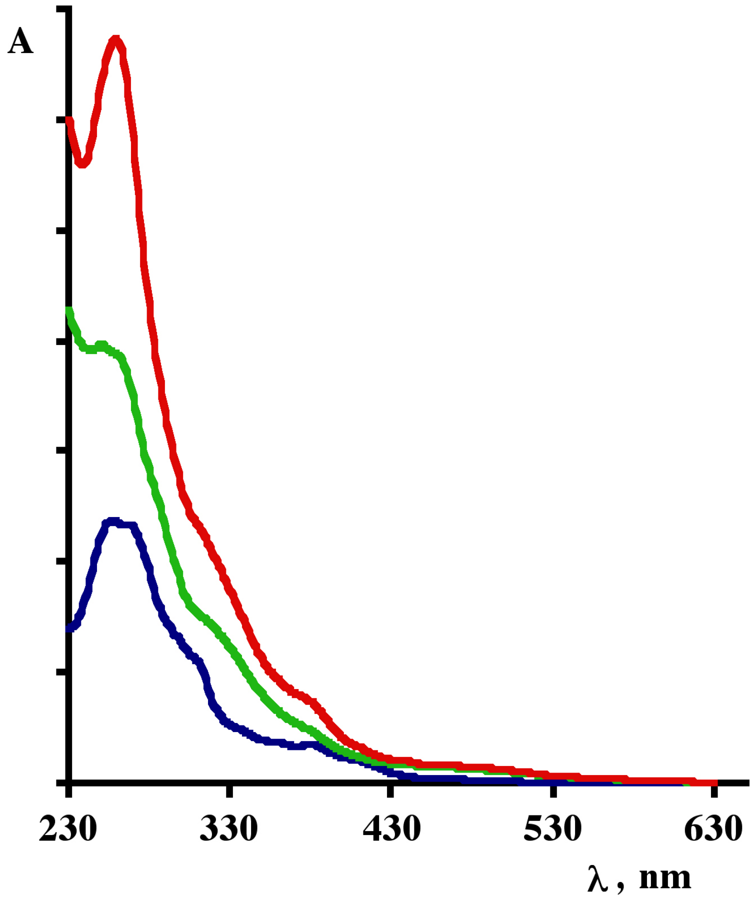
ΔG = energy of $^3C_{60}$ (from the 77 K emission spectrum of **1**, 1.50 eV) – energy of ^{3}MLCT state (approximated at the maximum of its model species at 77 K, 2.31 eV) = -0.81 eV.

(iii) Driving force of the electron transfer from the Ir-based ^{3}MLCT state to the fullerene subunit:

$\Delta G = e[{}^*E_{ox}$ (Ir-subunit) – E_{red} (fullerene)] = -0.40 eV.

In the former equation, the excited state oxidation potential of the Ir-based MLCT triplet state (-1.08 V) is obtained from the oxidation potential of the ground state (+1.23 V) and the MLCT excited state energy (2.31 eV), in the usual manner. The reduction potential of the fullerene subunit is the first reduction of **1** (-0.68 V). In the electron transfer driving force calculation, the work term is neglected.

Absorption spectrum of 1



The Figure shows the absorption spectrum of **1** (red), and of its individual components, [Ir(ppy)$_2$(bpy)](PF$_6$) (blue) and the C$_{60}$-containing free ligand **L** (green), reported for comparison. Compounds are equimolar. The spectra are in dichloromethane, since **L** was unsoluble in acetonitrile. As one can see, the absorption spectra of the Ir(III)-based subunit and the fullerene species overlap significantly, however at wavelength longer than 430 nm the fullerene-based absorption predominates.