A pseudo-rotaxane based on an iridium(III)–copper(I) dyad

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The synthesis of a pseudo-rotaxane containing two metal centres has been achieved using the coordination of a ditopic organic ligand on an iridium(III) complex followed by the coordination of a copper(I) centre. Preliminary photophysical studies indicate that the excited state of the iridium is quenched by the copper unit.

Rotaxanes and catenanes are nowadays relatively common molecules1,2 whose synthesis is no longer a real challenge. They are promising precursors to intelligent organic materials in relation to molecular machines and information storage and processing at the nanometric level.3–7 Such molecular species have also been used and studied as multicomponent systems in photoinduced electron or energy transfer processes.8,9 A very special feature of mechanically linked multicomponent assemblies is that electron transfer studies can be performed between noncovalently linked electron donor and acceptor groups held together within the same molecule.10

We would now like to report a new rotaxane-like compound incorporating two different electro- and photoactive components: an iridium(III) bis-terpy complex and a copper(I) bis-phen complex (terpy = 2,2',6',2'-terpyridine; phen = 1,10-phenanthroline). Ir(terpy)2³⁺ and its derivatives have recently been shown to display interesting photochemical properties with, in particular, a long-lived excited state displaying a pronounced electron acceptor character.11 Ir(terpy)$_{2}^{3+}$ type complexes have also been used as gathering complexes and electroactive centres in porphyrinic multicomponent assemblies12 or as photoactive centres in dyads of the Ir(III)–D type13 (D = electron donor). Cu(terpy)$_{2}^{2+}$ has been used extensively in photochemistry in the course of the last 20 years (terpy = 2,9-diphenyl-1,10-phenanthroline).14

The target pseudo-rotaxane incorporating two different transition metals is shown in Scheme 1. The pseudo-tetrahedral coordination around copper(I) is provided by a macrocycle M$_{30}$ (M$_{30}$ is a phen-incorporating 30-membered ring) and a monosubstituted phenanthroline. Due to the very different coordination conditions between iridium and copper, the iridium part requiring harsher conditions has to be built first. Subsequently, the threading process using copper can be performed at room temperature.

The precursor compounds are indicated in Scheme 2 as well as the chemical reactions affording them. The ditopic ligand 4 was obtained in 49% yield using a Suzuki coupling between 4-((p-bromophenyl)-2,2'-6',2'-terpyridine and the boronic ester 2 of the corresponding starting phenanthroline (Scheme 2(a)).15 The reaction conditions for the preparation of the iridium(III) complex with a free phen site (Scheme 2(b)) were slightly changed regarding the usual chemistry of iridium bis-terpyridine complexes.11,12 Indeed, the point was to avoid the coordination of the hanging phenanthroline unit to iridium(III) and the corresponding orthometallation process. The ligand was thus used in excess (2 equiv) and the temperature carefully controlled (see Experimental for details). Using this method, a yield of 77% was obtained for 5³⁺.

The pseudo-rotaxanes I$^{4+}$ and 7$^{+}$ are readily prepared by reaction between the ring 6$^{+}$ and the corresponding thread. As already observed before, the Cu($^{II}$) cation and 1,10-phenanthroline derivatives form very stable bis-ligand pseudo-tetrahedral complexes whereas monochelates are much less stable. This has been applied in the case of I$^{4+}$ and 7$^{+}$ with unambiguous and quantitative formation of the threaded product. A solution of 5$^{3+}$ in degassed acetonitrile was added to a solution of Cu(M$_{30}$)(CH$_{3}$CN)$_{2}$ and the mixture immediately turned to a dark brown-red solution. After 2 h stirring at room
temperature, the solvents were removed to afford 1 quantitatively [Scheme 2(c)]. The various spectra acquired in acetonitrile (ES-MS, 1H-NMR 400 MHz, COSY and ROESY experiments) are in accordance with the postulated structure. Using the same method with 2-(p-anisyl)-1,10-phenanthroline instead of 5 leads to the copper-containing model 7.

The absorption spectra determined in acetonitrile for the dyad 1 and for the model components 5 and 7 (Scheme 2), are shown in Fig. 1, superimposed with the result of a simple addition of the absorption spectra of the models 7 and 5. 7 displays the typical intense bands in the UV ascribed to ligand centred (LC) transitions and a much weaker band in the visible region which is metal-to-ligand charge transfer (MLCT) in nature. 5 exhibits, in comparison with closely related Ir(terpy)2 type complexes, very similar absorption bands in the UV of LC nature but a well longer tail extending in the visible whose nature is very likely of MLCT character. For dyad 1, the good agreement between the peak positions and

Scheme 2 Synthesis of the pseudo-rotaxane 1 and of the models 5 and 7.
intensities of the spectrum resulting from the superposition of the absorption of components compared to the experimental one, indicates a negligible coupling between the components. In the inset of Fig. 1, the emission spectrum of the model 5\textsuperscript{2+} is compared to that of the dyad 1\textsuperscript{2+} following excitation at 390 nm for solutions with concentrations adjusted to provide the same absorption of photons by the Ir\textsuperscript{3+} complex unit. The emission of the iridium(III) complex component in the dyad 1\textsuperscript{2+} is almost completely quenched. In agreement, time-resolved luminescence determinations indicate that the lifetime of the Ir\textsuperscript{3+} chromophore, which is 730 ns in the model component 5\textsuperscript{2+}, is reduced in the dyad 1\textsuperscript{2+} to less than the apparatus resolution time of 0.5 ns.

Upon excitation in either the UV or visible spectral range, no emission from the copper(I) component could be detected, neither in the model 7\textsuperscript{2+} nor in the dyad. This has to be assigned to the virtually zero emission yield in acetonitrile of copper( I) bis-phenanthroline derivatives unsubstituted or monosubstituted at the 2 or 9 positions.\textsuperscript{10} The luminescence properties at 298 K and 77 K for the model 5\textsuperscript{2+} and the dyad 1\textsuperscript{2+} are collected in Table 1. Iridium(III) complex 5\textsuperscript{2+} displays a low emission quantum yield, a broad spectral shape and a remarkable shift to higher energy in band maxima upon passing from fluid solutions to rigid matrix at 77 K, indicating an excited state with predominant MLCT character. This is different from the assignment of previously studied iridium(III) bis-terpy type complexes exhibiting a \( \text{d} \) nature.\textsuperscript{11}

In principle, the detected excited state quenching of the iridium(III) component in 1\textsuperscript{2+} could be due either to electron and/or to energy transfer. Iridium(III) bis-terpy type complexes are in fact rather good electron acceptors in their ground states, ca. \(-0.7\) V vs. SCE,\textsuperscript{11} whereas copper(I) phen type complexes can easily oxidize to copper(II) at a potential of ca. \(+0.6\) V vs. SCE.\textsuperscript{14,18} The energy of the excited state localized on the iridium complex in 1\textsuperscript{2+}, \(2.4\) eV (Table 1), could easily provide the energy for the electron transfer from the iridium to the copper units with a \( \Delta G \) of reaction of ca. \(-1\) eV, that is strongly exothermic. On the other hand, the same excited state could transfer energy to the copper unit, whose excited state is reported to have an energy of ca. \(1.7\) eV, with an highly favorable \( \Delta G \) of ca. \(-0.7\) eV.\textsuperscript{14,18} The present data do not allow us to draw a conclusive interpretation about the quenching mechanism and we are presently working on modification of the copper ligand in order to prepare a luminescent copper(I) bis-phenanthroline derivative. This, without changing the thermodynamic parameters of the system, could provide a powerful tool to investigate the nature of the photoinduced processes.

In conclusion, a new pseudo-rotaxane has been prepared, which contains an unusual combination of transition metals, Ir(III) and Cu(I). In future work, the real rotaxane will be prepared by attaching an organic stopper on the phen nucleus. Efficient luminescence quenching of the iridium(III) component by the copper(I) part has been observed. Further studies on the present complex, 1\textsuperscript{2+}, as well as on other related systems will be required in order to establish whether the quenching mechanism involves energy or electron transfer.

**Experimental**

The following chemicals were prepared according to literature procedures: 2-(1-m-bromophenyl)phenanthroline,\textsuperscript{19,20} 4-((p-bromophenyl)terpyridine,\textsuperscript{20} ButpyIrCl\textsubscript{3},\textsuperscript{11} Cu(M30)(CH\textsubscript{3}CN)\textsubscript{2}PF\textsubscript{6},\textsuperscript{16} and 2-(p-anisyl)-1,10-phenanthroline.\textsuperscript{18} All other chemicals were commercially available and used without further purification. \(^1\)H-NMR spectra were acquired on either a Bruker AC300 or a Bruker AM400 spectrometer, using the deuterated solvent as the lock and residual solvent as the internal reference. Mass spectra were obtained by using a VG ZAB-HF spectrometer (FAB), a Fisons VG Platform (ES), or a Fisons VG Trio 2000 (EI) spectrometer.

**Photophysical determinations**

Absorption and luminescence spectra were measured in air-equilibrated spectrophotometric grade solvents with a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer and a Spex Fluorolog II spectrofluorimeter, respectively. Luminescence quantum yields (\( \Phi_{\text{em}} \)) were evaluated, after correction for the photomultiplier response, with reference to air-equilibrated Ir(Butpy)\textsubscript{2}(PF\textsubscript{6})\textsubscript{3} in acetonitrile as a standard (\( \Phi_{\text{em}} = 0.022 \)).\textsuperscript{17} Luminescence lifetimes (\( \tau \)) were obtained with an IBH single photon counting apparatus with pulse diode excitation at 375 nm and 0.5 ns resolution. The experimental uncertainty on the absorption and luminescence maxima is 2 nm, while that for the \( \Phi_{\text{em}} \) and \( \tau \) values is 10%.

**Syntheses**

Table 1 Luminescence properties of the model 5\textsuperscript{2+} and dyad 1\textsuperscript{2+} in nitriles

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<th>298 K\textsuperscript{a}</th>
<th>77 K\textsuperscript{b}</th>
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<tr>
<td>( \lambda_{\text{max}}/\text{nm} )</td>
<td>( \tau/\text{ns} )</td>
<td>( \phi_{\text{em}} )</td>
</tr>
<tr>
<td>5\textsuperscript{2+}</td>
<td>550</td>
<td>732</td>
</tr>
<tr>
<td>1\textsuperscript{2+}</td>
<td>548</td>
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\( \text{a} \) In acetonitrile. \( \text{b} \) In butyronitrile rigid glass. \( \text{c} \) Air-equilibrated solutions. \( \text{d} \) Excitation at 390 nm for steady state, 375 nm for time-resolved determinations. \( \text{e} \) Energy levels of the excited states, from the maxima of the emission bands at 77 K.\textsuperscript{4} A very weak emission could be fitted by two exponential decays of 2.5 ns (95%) and ca. 700 ns (5%), ascribable to traces of strongly luminescent phenanthroline and 5\textsuperscript{2+} components, respectively. \( \text{f} \) Luminescence quantum yields calculated on the basis of the photons absorbed by the Ir\textsuperscript{3+} component.

were removed under reduced pressure and the complex dried under vacuum and used without further purification. 1H-NMR (CD3CN, 300 MHz): δ 8.70 (d, 1H, H8p; J = 8.5 Hz); 8.60 (d, 2H, H7, J = 8.2 Hz); 8.40–8.26 (m, 4H, H2, H3, H4, H5); 8.11–8.09 (m, 3H, H4pH5p); 7.98 (d, 2H, H1, J = 8.2 Hz); 7.28 (d, 1H, H3, J = 8.5 Hz); 7.71 (d, 1H, H2, J = 8.5 Hz); 7.39 (d, 4H, H6, J = 8.2 Hz); 7.24 (d, 2H, H7, J = 8.2 Hz); 6.00–5.95 (m, 6H, H4pH5pH6pH7pH8pH9p); 3.83–3.40 (m, 23H, H3pH4pH5pH6pH7pH8pH9p).

Ir-Cu dyad 4b. A solution of Cu(CH3CN)2(PF6)2 (4.3 mg, 0.011 mmol) in degassed MeCN (2.6 mL) was transferred through a canula to a stirred solution of macrocycle M30 (6.6 mg, 0.011 mmol) in CH2Cl2 (3 mL) under argon. The resulting yellow-orange solution of 6146 was stirred at room temperature for 30 min. Then a degassed solution of 5147 (18 mg, 0.011 mmol) in MeCN (2 mL) was transferred through a canula into it, resulting in the immediate formation of a brown-red solution that was stirred at room temperature under argon for 2 h. The solvents were removed under reduced pressure and the complex dried under vacuum and used without further purification. 1H-NMR (CD3CN, 300 MHz): δ 7.07 (s, 1H, H8p; J = 8.5 Hz); 8.46 (d, 2H, H7, J = 8.2 Hz); 8.37–8.5 (m, 8H, H4pH5pH6pH7pH8pH9p); 8.06 (d, 1H, H2, J = 8.5 Hz); 8.01–7.97 (m, 6H, H3pH4pH5pH6pH7pH8); 7.93 (d, 1H, H1, J = 8.4 Hz); 7.87 (t, 1H, H2, J = 1.6 Hz); 7.81 (dd, 2H, H7, J = 8.5 Hz, J = 0.8 Hz); 7.76 (dd, 2H, H6, J = 4.5 Hz, J = 1.2 Hz). 13C-NMR (CD3CN, 75 MHz): δ 157.7, 156.5, 156.2, 150.6, 149.3, 144.6, 144.2, 141.2, 140.6, 137.6, 137.1, 137.0, 136.2, 129.5, 129.3, 128.7, 128.6, 128.3, 128.1, 127.9, 127.8, 126.9, 126.6, 126.5, 124.0, 123.1, 121.6, 121.1, 120.7, 118.9, 116.5.

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