

# A new rhenium(I) tricarbonylpolypyridine donor–acceptor complex featuring a long-lived charge-separated excited state

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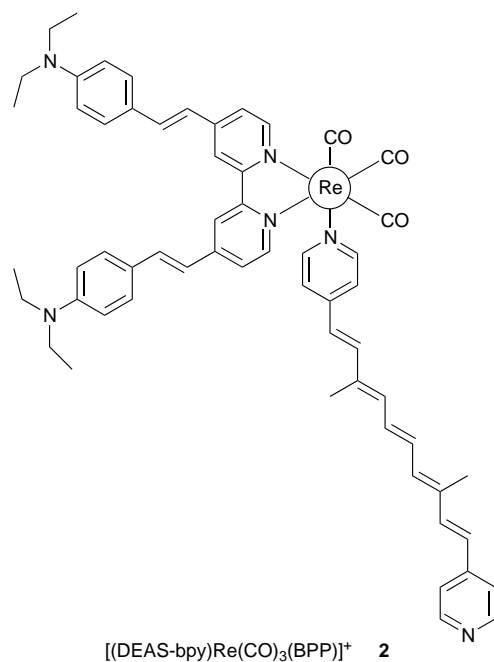
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The new mononuclear complex [(DEAS-bpy)Re(CO)<sub>3</sub>(BPP)]<sup>+</sup> is prepared {DEAS-bpy = 4,4'-bis[*p*-(diethylamino)- $\alpha$ -styryl]-2,2'-bipyridine, BPP = 1,10-bis(4-pyridyl)-3,8-dimethyl-1,3,5,7,9-decapentaene} in which electrochemical and photophysical properties clearly indicate the presence of a long-lived charge-separated excited state at room temperature upon light excitation.

Photoinduced charge separation is a pivotal process in natural photosynthesis. Archetypal examples of artificial systems include porphyrin triads and polypyridyl complexes of d<sup>6</sup> transition-metal complexes.<sup>1–10</sup> The rhenium(I) tricarbonyl complexes appear particularly interesting not only for their photophysical properties, but also because it is quite easy to synthesize species containing two different ligands connected to the same *fac*-Re<sup>I</sup>(CO)<sub>3</sub> core.

We have now prepared the new mononuclear *fac*-[(DEAS-bpy)Re(CO)<sub>3</sub>(BPP)]CF<sub>3</sub>SO<sub>3</sub> complex **2** starting from *fac*-[(DEAS-bpy)Re(CO)<sub>3</sub>Cl],<sup>11</sup> **1**, by introducing the electron-

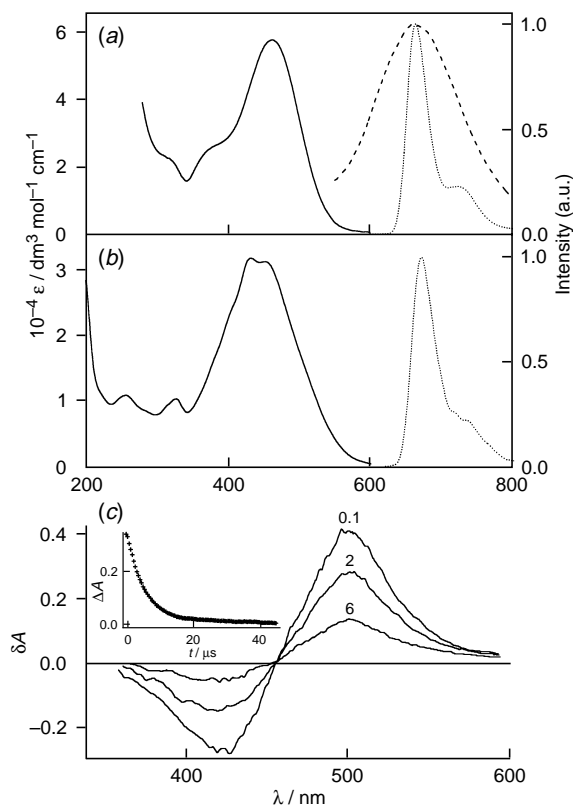


acceptor BPP ligand in the axial position.<sup>†</sup> The simultaneous coordination of BPP and DEAS-bpy on the same metal center gives rise to a very interesting donor–acceptor complex, which forms a long-lived charge-separated state upon light excitation.

Table 1 collects the electrochemical, absorption, and luminescence data of **1** and **2**, and of the free DEAS-bpy and BPP ligands. Electrochemical characterization of complex **2** indicates that the first reduction process occurs at  $-0.88$  V. This

process can be assigned to BPP reduction by comparison with the reduction potentials of the two free DEAS-bpy and BPP ligands. The first oxidation process observed for complex **2** ( $+0.75$  V) is bielectronic and irreversible, indicating that this process involves DEAS-bpy amine oxidation as indeed found in the free DEAS-bpy ligand (bielectronic irreversible wave at  $+0.66$  V). On the other hand, it is known that the coordinated bpy unit is oxidized only at very high potential ( $E > 2$  V),<sup>13</sup> and oxidation of the free ligand BPP features a monoelectronic process at  $+1.00$  V.

Fig. 1 illustrates absorption and emission spectra of complexes **1** and **2**. The photophysical properties of **2** in a rigid matrix at 77 K are very similar to those shown by **1**. Indeed, the two complexes show emission spectra almost identical in position and shape, and with similar lifetime values (Table 1). As in **1** the 77 K emission is known to originate from a DEAS-



**Fig. 1** Absorption spectrum (—), and uncorrected luminescence spectra at room temp. (---) and at 77 K (dotted line) for complexes **1** (a) and **2** (b); solvents are DMF at room temperature and DMF–CH<sub>2</sub>Cl<sub>2</sub> (9 : 1 v/v) were used at 293 and 77 K, respectively. (c) Transient absorption spectra at room temp. in deaerated acetonitrile solution for **2**,  $\lambda_{\text{exc}}$  355 nm. The spectra were acquired with a delay of 0.1, 2 or 6  $\mu$ s after the pulse, and a width of 0.5  $\mu$ s. Inset: decay of the transient signal, monitored at 510 nm.

**Table 1** Electrochemical, absorption and emission data

Compound	Electrochemistry <sup>a</sup>		Absorption <sup>b</sup> $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	Luminescence <sup>c</sup>	
	$E_{\text{red}}/\text{V}$	$E_{\text{ox}}/\text{V}$		$\lambda_{\text{max}}$ (298 K)/ nm ( $\tau/\text{ns}$ )	$\lambda_{\text{max}}$ (77 K)/nm ( $\tau/\mu\text{s}$ )
<b>1</b> <sup>d</sup>	-1.27	+0.69 <sup>e</sup>	455 (57100) <sup>e</sup>	674 (33) <sup>e</sup>	665 (630) <sup>f</sup>
<b>2</b>	-0.88 [1]	+0.75 i <sup>g</sup> [2]	454 (31100)	—	675 (360)
DEAS-bpy	-2.00 [4]	+0.66 i <sup>g</sup> [2]	394 (53200)	516 (<1)	632 ( $\approx 2000$ ) <sup>h</sup>
BPP	-0.86 [3]	+1.00 i <sup>g</sup> [1]	428 (52500) <sup>i</sup>	557 (<1)	490 (0.028) 490 (<0.001)

<sup>a</sup> Argon-purged acetonitrile solution containing 0.05 M  $\text{NEt}_4\text{PF}_6$ , room temp.; potentials vs. SCE; unless otherwise noted, the waves are reversible or quasi-reversible; number of exchanged electrons in square brackets. <sup>b</sup> Room temp., in MeCN solution, unless otherwise stated. <sup>c</sup> Emission maxima and luminescence lifetimes in deaerated acetonitrile solution at room temp. and in MeOH-EtOH (4:1, v/v) rigid matrix at 77 K, unless otherwise noted. <sup>d</sup> Ref. 11. <sup>e</sup> In DMF. <sup>f</sup> DMF- $\text{CH}_2\text{Cl}_2$  (9:1, v/v). <sup>g</sup> i = Irreversible. <sup>h</sup> In  $\text{C}_3\text{H}_7\text{I}$  glass. <sup>i</sup>  $\epsilon$  value in EtOH, from ref. 12.

bpy ligand centered (LC) phosphorescence emission, the same should hold also for **2**. The photophysical properties at room temp. in fluid solution are, on the contrary, completely different. Complex **1** features an emission band again due to a DEAS-bpy LC phosphorescence emission, whereas **2** does not show any luminescence emission.<sup>‡</sup>

Further experiments at room temp. showed that in **2** a transient species is formed following laser flash excitation in deaerated acetonitrile (Fig. 1). An absorption band with  $\lambda_{\text{max}}$  ca. 520 nm is observed arising from the new transient species formed, together with the bleaching of the ground-state absorption around 430 nm. The kinetic of the back reaction to the ground state was followed both at 510 nm (decay of the transient species) and at 430 nm (ground state recovery), obtaining in both cases a good first-order fit, with the same kinetic constant within experimental error ( $k = 0.23 \times 10^6 \text{ s}^{-1}$ ). No sign of decomposition was observed.

In an additional experiment, absorption of the triplet state of the free BPP ligand was measured populating it by energy transfer using anthracene as the triplet donor. The spectrum measured 2  $\mu\text{s}$  after the excitation pulse features a single absorption band at 640 nm. This excludes that the transient spectrum observed in complex **2** may arise from triplet energy transfer to the BPP subunit.

The photophysical behavior of complex **2** can be rationalized by considering the energy position of the relevant states that can be reached after light excitation.

At room temp., the energy of the DEAS-bpy LC phosphorescence can be taken from the 77 K emission (corresponding to  $E = 1.83 \text{ eV}$ ), by considering that the energy of a LC state is essentially temperature independent. Electrochemical data (Table 1) indicate that the simultaneous presence of DEAS-bpy and BPP modules, which are both electroactive units, gives rise to a redox-separated state, corresponding to BPP reduction and DEAS-bpy oxidation, with  $E = 0.88 + 0.75 = 1.63 \text{ eV}$ . Given the relative energy position of these two states, at room temp., **2** is not emissive because of the presence of this redox-separated state as the lowest excited state, thus deactivating the LC state. The transient observed for complex **2** in laser flash experiments is assigned to this redox-separated species.

At 77 K, complex **2** features emission from the lowest-lying LC state, as the level corresponding to the charge-separated state moves to higher energy. Indeed it is known that in rigid media, charge-separated states are normally trapped in a non-equilibrium condition, so that their energy content is higher with respect to the room temp. situation.<sup>14</sup>

The simultaneous coordination of the bidentate DEAS-bpy and the monodentate BPP ligands to a *fac*- $\text{Re}^{\text{I}}(\text{CO})_3$  center leads to a donor-acceptor complex which at room temp. gives rise to

a 4.3  $\mu\text{s}$  charge-separated state upon light excitation. It is worth noting that this charge-separated state is noticeably long-lived compared to those observed in other donor-acceptor complexes in homogeneous solution.<sup>4,5,9,10</sup> The slowness of the intramolecular back-electron-transfer reaction to the ground state can be justified by considering that its energy content (1.63 eV) places it in the so called 'Marcus inverted region'.<sup>15</sup>

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## Footnotes and References

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† Complex **2** has been prepared by reacting **1** with  $\text{AgCF}_3\text{SO}_3$  followed by subsequent addition of the BPP ligand. The deep-red crude product was then purified by chromatography and recrystallization. Elemental analysis, IR, NMR, and FAB<sup>+</sup> spectra were performed with satisfactory results.

‡ Note that, whereas MLCT states are usually important to determine the spectroscopic properties of  $\text{Re}^{\text{I}}(\text{CO})_3$  complexes, in **1** and **2** the behavior is dominated by LC states.

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