

# Spectroscopic, luminescence and electrochemical studies on a pair of isomeric complexes $[(\text{bipy})_2\text{Ru}(\text{AB})\text{PtCl}_2][\text{PF}_6]_2$ and $[\text{Cl}_2\text{Pt}(\text{AB})\text{Ru}(\text{bipy})_2][\text{PF}_6]_2$ , where AB is the bis-bipyridyl bridging ligand 2,2':3',2'':6'',2''':quaterpyridine

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The positional isomers  $[(\text{bipy})_2\text{Ru}\{\text{AB}(\text{PtCl}_2)\}][\text{PF}_6]_2$  (**Ru-AB-Pt**) and  $[(\text{Cl}_2\text{Pt})\text{AB}\{\text{Ru}(\text{bipy})_2\}][\text{PF}_6]_2$  (**Pt-AB-Ru**) (bipy = 2,2'-bipyridine) were prepared by a stepwise 'complexes-as-ligands' method. Each contains  $\text{d}^6 \{\text{Ru}(\text{bipy})_2\}^{2+}$  and  $\text{d}^8 \{\text{PtCl}_2\}$  fragments coordinated to the bridging ligand 2,2':3',2'':6'',2''':quaterpyridine (AB), which contains two inequivalent bipyridyl chelating sites. Electrochemical studies show a  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  couple and four ligand-centred reductions in each case, the first two reductions being centred on the two bipyridyl fragments (A and B) of the bridging ligand, and the second two being centred on the terminal bipy ligands. The absorption and luminescence properties are consistent with the inequivalent coordination properties of sites A and B of AB. In particular, from 77 K luminescence spectra, it is seen that the Ru-based energy level is  $350 \text{ cm}^{-1}$  higher for **Ru-AB-Pt** than for **Pt-AB-Ru**. At room temperature, the Ru-based luminescence is stronger and longer-lived ( $\phi = 2.3 \times 10^{-2}$ ,  $\tau = 280 \text{ ns}$ ) for **Ru-AB-Pt** than for its isomeric counterpart ( $\phi = 7.5 \times 10^{-4}$ ,  $\tau = 13 \text{ ns}$ ).

Bridging ligands (BL) that contain two bipy-type bidentate chelating sites (bipy = 2,2'-bipyridine) are commonly used to prepare heteronuclear complexes in which a photosensitiser fragment, commonly a  $\text{Ru}^{\text{II}}$ -polypyridine group, is linked to a second metal fragment.<sup>1-3</sup> This second fragment is often a quenching group, such that intramolecular photoinduced energy or electron-transfer occurs.<sup>2,3</sup> The second fragment may, however, be a group that has other chemically useful properties than being a quencher, and in this context dinuclear complexes containing a  $\{\text{PtX}_2\}$  fragment have been of interest recently not only because of the spectroscopic and reactivity properties of the  $\text{Pt}^{\text{II}}$  centres,<sup>4-6</sup> but also because of the well-known ability of planar  $\text{Pt}^{\text{II}}$  complexes to bind to DNA.<sup>7,8</sup>

We have recently been studying the coordination chemistry of 2,2':3',2'':6'',2''':quaterpyridine,<sup>9-13</sup> a potentially binucleating bridging ligand containing two bipy-type binding sites (hereafter denoted AB, where A and B are the two inequivalent bipy sites; see Scheme 1),<sup>13</sup> and have particularly focussed on intramolecular photo-induced energy transfer between luminescent metal fragments in heteronuclear complexes.<sup>10-12</sup> One significant consequence of the asymmetry of the ligand is that the redox and luminescence properties of a particular metal fragment depend on whether it is coordinated at the less sterically hindered site A, or the more sterically hindered site B. Positional isomers  $\text{M}^1\text{-AB-M}^2$  and  $\text{M}^2\text{-AB-M}^1$  can therefore have different properties.<sup>10,11</sup> We describe here the synthesis, characterisation, and electrochemical and photophysical properties of the isomeric pair  $[(\text{bipy})_2\text{Ru}\{\text{AB}(\text{PtCl}_2)\}][\text{PF}_6]_2$  (**Ru-AB-Pt**) and  $[(\text{Cl}_2\text{Pt})\text{AB}\{\text{Ru}(\text{bipy})_2\}][\text{PF}_6]_2$  (**Pt-AB-Ru**) (Scheme 1), which show in particular how the Ru-based emission observed is strongly site-dependent.

## Results and Discussion

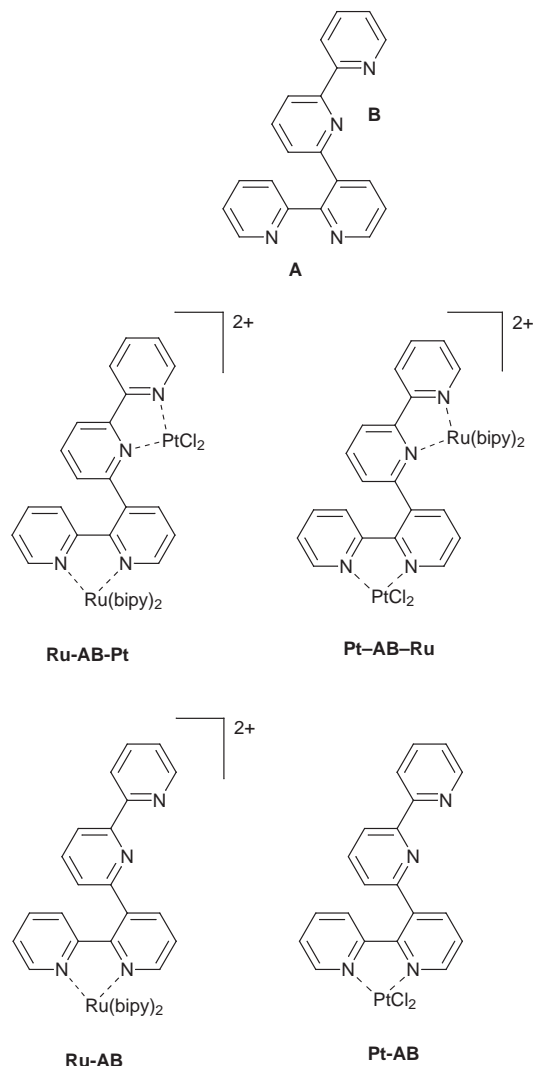
### Synthesis and characterisation of complexes

The two complexes were prepared in a stepwise manner, in

which the fragment at site A of the bridging ligand is attached first; this mononuclear complex is then reacted with the second metal fragment which coordinates at site B. An advantage of the asymmetry of the bridging ligand is that on reaction of AB with one equivalent of a metal ion M, it occupies site A uniquely to give M-AB (Scheme 1); the positional isomer AB-M, with the metal fragment coordinated at site B and site A left vacant is not observed, nor are significant amounts of the dinuclear complex M-AB-M formed.

Thus, **Ru-AB-Pt** was prepared by reaction of the mononuclear complex  $[\text{Ru}(\text{bipy})_2(\text{AB})][\text{PF}_6]_2$  (**Ru-AB**)<sup>13</sup> with  $\text{Pt}(\text{dmsO})_2\text{Cl}_2$  followed by chromatographic purification. Preparation of the positional isomer **Pt-AB-Ru** required initial preparation of the new mononuclear complex  $[\text{PtCl}_2(\text{AB})]$  (**Pt-AB**), which was isolated as an insoluble yellow solid from reaction of AB with  $[\text{Pt}(\text{dmsO})_2\text{Cl}_2]$  in a 1 : 1 ratio. Reaction of this with  $[\text{Ru}(\text{bipy})_2\text{Cl}_2]$  at high temperature then generated **Pt-AB-Ru** in good yield. The new complexes were satisfactorily characterised on the basis of elemental analyses, and electrospray (ES) mass spectrometry, in addition to giving single spots on TLC plates. It is worth noting that owing to the insolubility of **Pt-AB** an NMR spectrum could not be obtained, so initially we could not prove that it was not contaminated with the positional isomer **AB-Pt** (elemental analysis and mass spectrometry would clearly not help with this). However, the **Pt-AB-Ru** which was prepared from it was shown by luminescence studies to be clean and not contaminated with **Ru-AB-Pt**, which would inevitably have been formed from any **AB-Pt**. We can therefore be sure that reaction of AB with  $[\text{Pt}(\text{dmsO})_2\text{Cl}_2]$  gave solely the less-hindered isomer **Pt-AB**.

We were unable to obtain X-ray quality crystals of **Ru-AB-Pt** and **Pt-AB-Ru**. However, we have previously structurally characterised two other dinuclear complexes,  $[(\text{bipy})_2\text{Os}(\text{AB})\text{Ru}(\text{bipy})_2][\text{PF}_6]_4^{11}$  and  $[\text{Cl}(\text{CO})_3\text{Re}(\text{AB})\text{Ru}(\text{bipy})_2][\text{PF}_6]_2$ ,<sup>10</sup> and in both cases the two bipy fragments A and B of the bridging ligand are mutually perpendicular for steric reasons; the same is likely to be true for these



Scheme 1

new complexes. This is in contrast to all of the other examples of Ru/Pt complexes,<sup>4–8</sup> in which the bridging ligands [bipyridimidine, 2,3-bis(2-pyridyl)pyrazine,<sup>14</sup> *etc.*] are such that the two bidentate binding sites cannot be decoupled in this way but must interact strongly across the near-planar bridge.

### Electrochemical studies

The electrochemical properties of the complexes are summarised in Table 1. Both complexes undergo one oxidation, assigned to a  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  couple, and four ligand-centred reductions. Unusually, the  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  couples are irreversible in both cases, with the return wave being appreciably less intense than the outward wave, although the wave becomes nearly symmetric at very high scan rates (*e.g.*  $5 \text{ V s}^{-1}$ ). This is indicative of decomposition occurring after oxidation. For **Pt-AB-**

**Ru** all four ligand-centred reductions were reversible, with peak-peak separations close to the theoretical ideal of 60 mV at a scan rate of  $0.2 \text{ V s}^{-1}$ . For **Ru-AB-Pt** in contrast the first two reductions are not fully reversible, with return waves less intense than the outward waves. The third reduction is symmetric but rather broad, and the fourth appears to be reversible.

There are two major points of significance in the electrochemical data. Firstly, the **Ru** fragment is more difficult to oxidise by 130 mV when in site B than in site A; *i.e.* site B stabilises the  $\text{Ru}^{\text{II}}$  state by 130 mV compared to site A. We have noticed this effect before between the positional isomers of dinuclear Ru/Re<sup>10</sup> and Ru/Os<sup>11</sup> complexes of **AB**, but the effect here is particularly large: for example in the isomeric pair of dinuclear Ru/Os complexes each metal fragment when in site B was *ca.* 40 mV harder to oxidise than when in site A.<sup>11</sup> Secondly, coordination of the electron-withdrawing  $\{\text{PtCl}_2\}$  fragment results in some of the ligand-centred reductions moving to less negative potential (*i.e.* becoming easier), and an additional reduction appears such that the dinuclear complexes both have four reductions whereas mononuclear **Ru-AB** has only three. Both of these observations are consistent with coordination of the  $\{\text{PtCl}_2\}$  fragment lowering the energy level of empty  $\pi^*$  orbitals of **AB** and facilitating reduction.<sup>4,7</sup> Thus, coordination of the  $\{\text{PtCl}_2\}$  fragment in **Ru-AB-Pt** now permits both bipy-like sites of **AB** to be reduced independently, giving two couples at  $-1.44$  and  $-1.78 \text{ V}$ . Significantly, the potentials of the two reductions of the ancillary bipy ligands on the **Ru** fragment have not changed much, as we would expect, since they are not directly affected by the  $\{\text{PtCl}_2\}$  fragment. The fact that the first two (**AB**-centred) reductions of **Ru-AB-Pt** are at similar potentials to those of the first two reductions of  $[(\text{bipy})_2\text{Ru}(\text{AB})\text{Ru}(\text{bipy})_2]^{4+}$  (**Ru-AB-Ru**)<sup>13</sup> suggests that coordination of a (neutral)  $\{\text{PtCl}_2\}$  fragment has about the same stabilising effect on the bridging ligand as does coordination of a second dipositive  $\{\text{Ru}(\text{bipy})_2\}^{2+}$  fragment.

### Spectroscopic and luminescence properties

The room-temperature ground-state absorption properties of **Ru-AB-Pt** and **Pt-AB-Ru** are collected in Table 2. Room-temperature luminescence band maxima, quantum yields and lifetimes, as obtained in acetonitrile solvent, and luminescence results obtained at 77 K in butyronitrile solvent are also listed in Table 2. For comparison purposes, data for the reference **Ru-AB** and **Pt-AB** complexes are included in the Table (because of solubility reasons, for the latter complex the solvent was  $\text{CH}_2\text{Cl}_2$ ). Fig. 1 displays absorption spectra for **Ru-AB-Pt** and **Pt-AB-Ru** in acetonitrile and for **Pt-AB** in  $\text{CH}_2\text{Cl}_2$ . Fig. 2 compares luminescence spectra as obtained at room temperature ( $\lambda_{\text{exc}} = 467 \text{ nm}$ , acetonitrile solvent) and at 77 K (butyronitrile solvent) for **Ru-AB-Pt** and **Pt-AB-Ru**. The complex **Pt-AB** was not luminescent, possibly due to chemical decomposition occurring after generation of the  $\text{Pt} \rightarrow \text{diimine}$  excited state.<sup>15,16</sup> The possible occurrence of intermolecular association in the relatively non-polar solvent required to dissolve the complex should also be taken into account: the  $\{\text{APtCl}_2\}$  fragment of **Pt-AB** will be near-planar,

Table 1 Electrochemical data<sup>a</sup>

Complex	$\text{Ru}^{2+}/\text{Ru}^{3+}$	Ligand-centred processes			
<b>Ru-AB</b> <sup>b</sup>	+0.90(70)	–1.66(60)		–1.89(80)	–2.12(70)
<b>Ru-AB-Pt</b>	+0.92 <sup>c</sup>	–1.44 <sup>c</sup>	–1.78 <sup>c</sup>	–1.95(130)	–2.12(80)
<b>Pt-AB-Ru</b>	+1.05 <sup>c</sup>	–1.38(60)	–1.73(60)	–1.95 (70)	–2.18(70)

<sup>a</sup> Potentials are in V *vs.* the ferrocene/ferrocenium couple,  $\text{Fc}/\text{Fc}^+$ ; voltammograms were recorded in acetonitrile at a Pt-bead working electrode. Peak-peak separations for chemically reversible processes (in mV) are in parentheses. The estimated error on the potential values is  $\pm 10 \text{ mV}$ .

<sup>b</sup> Data from ref. 11. <sup>c</sup> Irreversible process: the return wave was of less intensity than the outward wave (see text).

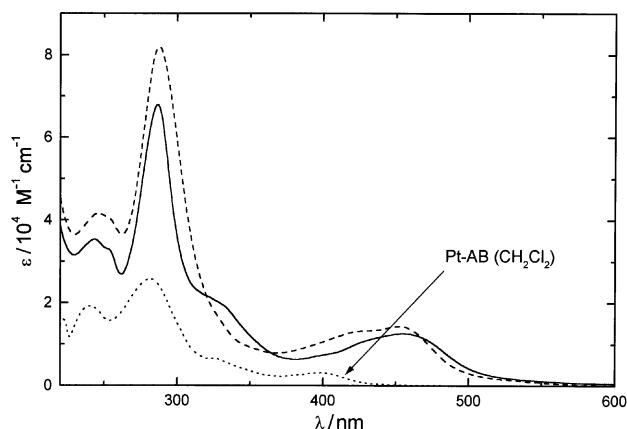
**Table 2** Spectroscopic and photophysical parameters<sup>a</sup>

	Absorption		Luminescence			
	$\lambda/\text{nm}$ ( $10^{-3} \epsilon/\text{M}^{-1} \text{cm}^{-1}$ )		293 K <sup>b</sup>			77 K <sup>c</sup>
	$\lambda/\text{nm}$	$10^{-3} \epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}^d$	$\tau/\text{ns}$	$10^3 \phi^e$	$\lambda_{\text{max}}/\text{nm}^d$
<b>Ru-AB<sup>f</sup></b>	288(74)	453(13.3)	638	190	15	588
<b>Ru-AB-Pt</b>	286(69)	455(12.4)	640	280	23.3	598
<b>Pt-AB-Ru</b>	287(83)	452(14.4)	624	13	0.75	586
<b>Pt-AB<sup>g</sup></b>	282(25)	400(0.3)	—	—	—	—

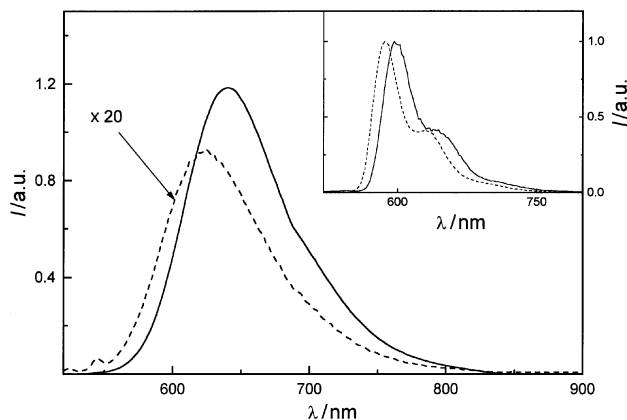
<sup>a</sup> Acetonitrile solvent unless otherwise specified. <sup>b</sup> Data for air-equilibrated solvent. <sup>c</sup> Butyronitrile solvent. <sup>d</sup> Band maxima for uncorrected spectra. <sup>e</sup> Quantum yields obtained from corrected spectra, see Experimental Section. <sup>f</sup> Data from ref. 11. <sup>g</sup>  $\text{CH}_2\text{Cl}_2$  solvent; the indicated values for the extinction coefficient are subject to a large uncertainty owing to the poor solubility of the complex (it is completely insoluble in MeCN which was used for the other complexes).

and the neutrality of the complex means that there is no electrostatic barrier to association.

For **Ru-AB-Pt** and **Pt-AB-Ru**, the absorption profile in the long-wavelength region, where no absorption by the Pt centre is present (Fig. 1), is ascribed to  $\text{Ru} \rightarrow \text{AB}$  ( $^1\text{MLCT}$ ) transitions. Contributions in the same spectral region are expected from  $\text{Ru} \rightarrow \text{bipy}$  transitions,<sup>11</sup> but at slightly higher energy based on the small differences between reductions centred on the **AB** ligand and on peripheral bipy ligands, see above. From the energy position of the absorption band maximum with respect to that for **Ru-AB** in the same region, one sees that the presence of the  $\{\text{PtCl}_2\}$  centre has only a slight perturbing effect



**Fig. 1** Absorption spectra for **Ru-AB-Pt** (full line) and **Pt-AB-Ru** (dashed line) in acetonitrile, and **Pt-AB**



**Fig. 2** Luminescence spectra for **Ru-AB-Pt** (full line) and **Pt-AB-Ru** (dashed line) in acetonitrile at room temperature. The inset shows the normalized spectra at 77 K in butyronitrile

on the absorption profile. Closer examination suggests that when the Ru centre is coordinated to the A site of the **AB** ligand, the energy of the relevant  $\text{Ru} \rightarrow \text{AB}$  CT transition ( $\lambda_{\text{max}} = 455 \text{ nm}$ ) is lower than for the case of coordination to the B site ( $\text{Ru} \rightarrow \text{BA}$  charge transfer,  $\lambda_{\text{max}} = 452 \text{ nm}$ ). Exactly similar behaviour was noticed for the positional isomers obtained in the dinuclear  $\text{d}^6/\text{d}^6$  **Ru/Re**<sup>10</sup> and **Ru/Os**<sup>11</sup> complexes based on **AB**.

The luminescence results provide additional evidence of the significant differences exhibited by the two positional isomers. (i) At 77 K, the profiles of the luminescence spectra for both **Ru-AB-Pt** and **Pt-AB-Ru** are characterized by a vibrational progression of *ca.*  $1350 \text{ cm}^{-1}$  and have luminescence lifetimes of 5.9 and 4.8  $\mu\text{s}$ , respectively. Comparison of these results with those of the many members of the Ru-polypyridine family<sup>17</sup> indicates that the lowest-lying luminescent state is of  $\text{Ru} \rightarrow \text{BL}$  CT nature for both cases. From the energy position of the band peaks one sees that the  $\text{Ru} \rightarrow \text{AB}$  CT level (for **Ru-AB-Pt**) is  $350 \text{ cm}^{-1}$  lower in energy than the  $\text{Ru} \rightarrow \text{BA}$  CT level (for **Pt-AB-Ru**). For the previously explored heterodinuclear complexes with **AB**, the direct measurement of this 'positional' energy gap was possible only for the **Ru/Os** pair, where the luminescence was Os-centred both for **Ru-AB-Os** and **Os-AB-Ru**,<sup>11</sup> with an energy gap between the emission maxima of  $540 \text{ cm}^{-1}$ . For the **Ru/Re** complexes in contrast, it was found that the luminescence was Re-centred for **Re-AB-Ru** but Ru-centred for **Ru-AB-Re**, so direct comparison of the same metal emission in the two different sites was not possible.<sup>10</sup>

(ii) At room temperature, the profile and maximum of the luminescence bands are as expected for a Ru-based emission<sup>17</sup> both for **Ru-AB-Pt** and **Pt-AB-Ru**, see Fig. 2. However, the luminescence lifetimes  $\tau$  are 280 and 13 ns, respectively, with luminescence quantum yields  $\phi = 2.3 \times 10^{-2}$  and  $7.5 \times 10^{-4}$ , respectively. These data are consistent with a reduced ligand strength for the Ru-based moiety of **Pt-AB-Ru** arising from the inherent steric hindrance of the B site. This would cause a reduced Ru-centred d-d orbital splitting, resulting in the presence of relatively low-lying Ru-centred MC excited states, which are thermally accessible from the luminescent  $^3\text{MLCT}$  levels and which undergo very fast radiationless deactivation, thereby providing an efficient quenching pathway.<sup>17</sup> The very significant reduction in the emission lifetime and quantum yield from the Ru fragment coordinated to the B site of **Pt-AB-Ru** is entirely consistent with this. In contrast no such marked difference was noticed for the Os-based luminescence at the two different sites in the positional isomers **Ru-AB-Os** ( $\phi = 3.2 \times 10^{-3}$ ,  $\tau = 41 \text{ ns}$ ) and **Os-AB-Ru** ( $\phi = 1.3 \times 10^{-3}$ ,  $\tau = 26 \text{ ns}$ ),<sup>11</sup> which may be accounted for on the basis of the intrinsic stronger ligand field at the Os centre with respect to the Ru centre: a modest reduction in the ligand-field strength arising from the steric hindrance at site B is not sufficient to make the Os-based MC levels thermally accessible, so this deactivation pathway does not operate for **Os**<sup>11</sup>.

In conclusion, the inequivalence of the coordination sites A and B of the bridging ligand **AB** results in electrochemical and spectroscopic properties that are markedly different for the positional isomers **Ru-AB-Pt** and **Pt-AB-Ru**. Thus, for the former case the Ru-centred oxidation is less positive, the lowest-lying MLCT absorption maximum and the Ru-based luminescence band maximum correspond to energy levels that are lower, with respect to the same properties exhibited by the isomeric counterpart. Remarkably, the room-temperature Ru-based luminescence is stronger and longer-lived (by more than one order of magnitude, Table 2) for **Ru-AB-Pt** than for its isomeric counterpart. This behaviour represents a distinctive feature within the families of dinuclear complexes of the Ru/Os, Ru/Re and Ru/Pt couples.<sup>1,4,6,18</sup>

## Experimental

### General details

The bridging ligand **AB**,<sup>13</sup> the mononuclear precursor **Ru-AB**,<sup>13</sup> [Pt(dmsO)<sub>2</sub>Cl<sub>2</sub>],<sup>19</sup> and [Ru(bipy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O,<sup>20</sup> were all prepared according to the published methods. Instrumentation used for electrochemical and mass spectroscopic studies has been described previously.<sup>10–12</sup>

Absorption spectra were recorded with a Perkin Elmer Lambda 9 spectrophotometer in dilute (10<sup>–5</sup> M) acetonitrile solution. Luminescence experiments were performed (i) in air-equilibrated acetonitrile solution at room temperature in 1 cm cuvettes, (ii) in butyronitrile rigid matrix at 77 K (liquid-nitrogen temperature) by using samples contained in capillary tubes immersed in a quartz finger.

Luminescence spectra were obtained from a Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928 phototube. Uncorrected luminescence band maxima are used throughout the text unless otherwise stated. In order to determine luminescence quantum yields we employed corrected luminescence spectra on an energy scale (cm<sup>–1</sup>). The corrected spectra were obtained either by using a correction curve provided by the firm or by employing a calibrated 45 W quartz-halogen tungsten filament lamp by Optronic Laboratories as a standard for the correction of the phototube response. Luminescence quantum yields  $\phi_s$  were computed according to the following equation

$$\frac{\phi_s}{\phi_r} = \frac{A_r n_s^2(\text{area})_s}{A_s n_r^2(\text{area})_r}$$

where s and r stand for sample and reference standard, respectively, *A* is the absorbance (taken  $\leq 0.1$ ) at the selected excitation wavelength, and *n* is the refractive index of the solvent. [Ru(bipy)<sub>3</sub>]Cl<sub>2</sub> was chosen as a reference standard ( $\Phi = 2.8 \times 10^{-2}$  in air-equilibrated water).<sup>21</sup> The experimental uncertainty in the band maximum for absorption and luminescence spectra is 2 nm; that for luminescence quantum yield is 20%. Luminescence lifetimes were obtained with an IBH single-photon-counting apparatus (N<sub>2</sub> lamp, excitation at 337 nm). The uncertainty in the evaluated lifetimes is 8%.

### Preparation of Ru-AB-Pt

A mixture of **Ru-AB** (0.075 g, 0.074 mmol) and [Pt(dmsO)<sub>2</sub>Cl<sub>2</sub>] (0.156 g, 0.36 mmol) was dissolved in a mixture of dry, degassed MeOH (20 cm<sup>3</sup>) and MeCN (10 cm<sup>3</sup>) under N<sub>2</sub>. After heating to reflux for 18 h in the dark the reaction mixture was concentrated *in vacuo* and the product precipitated by addition of further MeOH. The solid was filtered off and dried, and was then purified by chromatography (alumina, MeCN). The main orange band was collected, evaporated to dryness and the resultant solid was recrystallised from MeCN/Et<sub>2</sub>O to give clean **Ru-AB-Pt** in 30% yield. ES-MS: *m/z* 1135 {*M* – PF<sub>6</sub>}<sup>+</sup>, 476 {*M* – 2PF<sub>6</sub> – Cl}<sup>2+</sup>. Found: C, 37.2; H, 2.4; N, 8.7. Required for [(bipy)<sub>2</sub>Ru]AB(PtCl<sub>2</sub>)[PF<sub>6</sub>]<sub>2</sub>, C: 37.5; H, 2.4; N, 8.8%.

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### Preparation of Pt-AB

A mixture of the ligand **AB** (0.200 g, 0.65 mmol) and [Pt(dmsO)<sub>2</sub>Cl<sub>2</sub>] (0.272 g, 0.64 mmol) in distilled MeOH (50 cm<sup>3</sup>) under N<sub>2</sub> was heated to reflux in the dark for 12 h. After it had been cooled, the yellow precipitate was collected by filtration, washed with MeOH and CH<sub>2</sub>Cl<sub>2</sub>, and dried to give clean **Pt-AB** in 77% yield. ES-MS: *m/z* 540 {*M* – Cl}<sup>+</sup>.

### Preparation of Pt-AB-Ru

A mixture of **Pt-AB** (0.100 g, 0.17 mmol) and [Ru(bipy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O (0.101 g, 0.19 mmol) in ethylene glycol (50 cm<sup>3</sup>) under N<sub>2</sub> was heated to 160 °C for 30 min. After the mixture had been cooled, addition of an aqueous solution of KPF<sub>6</sub> precipitated the product which was filtered off, dried and recrystallised from MeCN/Et<sub>2</sub>O to give clean **Pt-AB-Ru** in 70% yield. ES-MS: *m/z* 1135 {*M*<sup>+</sup> – PF<sub>6</sub>}<sup>+</sup>, 495 {*M*<sup>+</sup> – 2PF<sub>6</sub>}<sup>2+</sup>, 476 {*M* – 2PF<sub>6</sub> – Cl}<sup>2+</sup>. Found: C, 36.9; H, 2.5; N, 8.6. Required for [(Cl<sub>2</sub>Pt)AB{Ru(bipy)<sub>2</sub>}] [PF<sub>6</sub>]<sub>2</sub>, C: 37.5; H, 2.4; N, 8.8%.

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## References

- 1 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759; V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.
- 2 Some representative recent examples: L. De Cola, V. Balzani, F. Barigelletti, L. Flamigni, P. Belser, A. von Zelewsky, M. Frank and F. Vögtle, *Inorg. Chem.*, 1993, **32**, 5228; F. Vögtle, M. Frank, M. Nieger, P. Belser, A. von Zelewsky, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1643; S. van Wallendaal, M. W. Perkovic and D. P. Rillema, *Inorg. Chim. Acta*, 1993, **32**, 1643; M. T. Indelli, C. A. Bignozzi, A. Harriman, J. R. Schoonover and F. Scandola, *J. Am. Chem. Soc.*, 1994, **116**, 3768; P. Belser, R. Dux, M. Baak, L. De Cola and V. Balzani, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 595; G. F. Strouse, J. R. Schoonover, R. Duesing and T. J. Meyer, *Inorg. Chem.*, 1995, **34**, 2725; J. R. Shaw, G. S. Sadler, W. F. Wacholtz, C. K. Ryu and R. H. Schmehl, *New J. Chem.*, 1996, **20**, 749; M. Frank, M. Nieger, F. Vögtle, P. Belser, A. von Zelewsky, L. De Cola, V. Balzani, F. Barigelletti and L. Flamigni, *Inorg. Chim. Acta*, 1996, **242**, 281; J. Otsuki, M. Tsujino, T. Iizaki, K. Araki, M. Seno, K. Takatera and T. Watanabe, *J. Am. Chem. Soc.*, 1997, **119**, 7895; L. Sun, H. Berglund, R. Davydov, T. Norrby, L. Hammarström, P. Korall, A. Börje, C. Philouze, K. Berg, A. Tran, M. Andersson, G. Stenhausen, J. Mårtensson, M. Almgren, S. Styring and B. Åkermark, *J. Am. Chem. Soc.*, 1997, **119**, 6996.
- 3 High-nuclearity dendrimeric complexes: S. Campagna, A. Gianetto, S. Serroni, G. Denti, S. Trusso, F. Mallamace and N. Micali, *J. Am. Chem. Soc.*, 1995, **117**, 1755; S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto and V. Balzani, *Chem. Eur. J.*, 1995, **1**, 211; V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Acc. Chem. Res.*, 1998, **31**, 26.
- 4 V. W.-W. Yam, V. W.-M. Lee and K.-K. Cheung, *J. Chem. Soc., Chem. Commun.*, 1994, 2075; V. W.-W. Yam, V. W.-M. Lee and K.-K. Cheung, *Organometallics*, 1997, **16**, 2833.
- 5 Y.-Y. Ng, C.-M. Che and S.-M. Peng, *New J. Chem.*, 1996, **20**, 781.
- 6 R. Sahai and D. P. Rillema, *Inorg. Chim. Acta*, 1986, **118**, L35; R. Sahai and D. P. Rillema, *J. Chem. Soc., Chem. Commun.*, 1986, 1133.
- 7 M. Milkevitch, E. Brauns and K. J. Brewer, *Inorg. Chem.*, 1996, **35**, 1737.

- 8 M. Milkevitch, B. W. Shirley and K. J. Brewer, *Inorg. Chim. Acta*, 1997, **264**, 249; M. Milkevitch, H. Storrie, E. Brauns, K. J. Brewer and B. W. Shirley, *Inorg. Chem.*, 1997, **36**, 4534.
- 9 R. L. Cleary, D. A. Bardwell, M. Murray, J. C. Jeffery and M. D. Ward, *J. Chem. Soc., Perkin Trans. 2*, 1997, 2179; M. Guardigli, L. Flamigni, F. Barigelletti, C. S. W. Richards and M. D. Ward, *J. Phys. Chem.*, 1996, **100**, 10620; M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1994, 3095.
- 10 D. A. Bardwell, F. Barigelletti, R. L. Cleary, L. Flamigni, M. Guardigli, J. C. Jeffery and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 2438.
- 11 V. Balzani, D. A. Bardwell, F. Barigelletti, R. L. Cleary, M. Guardigli, J. C. Jeffery, T. Sovrani and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1995, 3601.
- 12 R. L. Cleary, K. J. Byrom, D. A. Bardwell, J. C. Jeffery, M. D. Ward, G. Calogero, N. Armaroli, L. Flamigni and F. Barigelletti, *Inorg. Chem.*, 1997, **36**, 2601; J. R. Schoonover, A. Shreve, R. B. Dyer, R. L. Cleary, M. D. Ward and C. A. Bignozzi, *Inorg. Chem.*, 1998, **37**, 2598.
- 13 M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1993, 1321.
- 14 L. De Cola and F. Barigelletti, *Gazz. Chim. Ital.*, 1988, **118**, 417.
- 15 O. Horváth and K. L. Stevenson, *Charge Transfer Photochemistry of Coordination Compounds*, VCH, New York, Weinheim, Cambridge, 1993, ch. 13; A. Vogler and H. Kunkely, *Angew. Chem.*, 1982, **94**, 217.
- 16 Pt<sup>II</sup> complexes may be luminescent; this usually happens when the involved excited state is not of Pt → diimine nature. See for instance: C. B. Blanton, Z. Murtaza, R. J. Shaver and D. P. Rillema, *Inorg. Chem.*, 1992, **31**, 3230; W. B. Connick and H. B. Gray, *J. Am. Chem. Soc.*, 1997, **119**, 11627.
- 17 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrine Complexes*, Academic Press, London, 1991.
- 18 R. Ziessel, *J. Chem. Educ.*, 1997, **74**, 673; F. Scandola, R. Argazzi, C. A. Bignozzi and M. T. Indelli, *J. Photochem. Photobiol. A: Chem.*, 1994, **82**, 191.
- 19 J. H. Price, A. N. Williamson, R. F. Schramm and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280.
- 20 B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334.
- 21 K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697.

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