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## Photoinduced Ba<sup>2+</sup> release and thermal rebinding by an azacrown ether linked by an alkynyl pyridine to a (bpy)Re(CO)<sub>3</sub> group<sup>†</sup>

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A novel complex in which an azacrown ether is linked by an alkynyl pyridine to a (bpy)Re(CO)<sub>3</sub> group acts as a light-controlled ion switch:  $Ba^{2+}$  bound to the azacrown is released in *ca*. 10 ns on UV excitation, and rebinds thermally from bulk solution in *ca*. 1 µs.

The development of systems which can bind metal cations in solution and release them in response to light is relevant to the design of molecular switches, sensors, and other photodevices.1 "Caged" compounds giving irreversible cation release have been developed principally for biochemical studies.<sup>2</sup> Chromphoric crown ether compounds have been developed to act as sensors, and some also to act as reversible cation switches with designs commonly based on excited-state isomerisation or electron-transfer mechanisms which are photochemically or thermally reversible.3 Most photocontrolled ion-release systems reported to date have been all-organic,4-6 but the incorporation of a transition-metal redox centre within such systems may provide additional excited-state decay routes that bring advantages and versatility in design. We have been studying (bpy)Re(CO)<sub>3</sub>L complexes functionalised with an azacrown ether<sup>7,8</sup> to explore their potential to act as lightcontrolled ion switches based on this general design.9 Here, we report a novel switch of Ba2+ and demonstrate its effectiveness by nanosecond time-resolved UV-visible absorption (TRVIS) and emission spectroscopy.

We have prepared a novel (bpy)Re(CO)<sub>3</sub>L<sup>+</sup> complex 1, in which the ligand L contains an aza-15-crown-5 ether attached to an alkynyl pyridine.<sup>‡</sup> The rationale behind this design was that the electronic effects of Re  $\rightarrow$  bpy metal-to-ligand charge-transfer (MLCT) excitation might be communicated effectively through a C=C bond to result in a lowering of electron density at the azacrown nitrogen and, hence, in efficient cation release in the excited state. Compound 2 is a model complex with no azacrown.<sup>‡</sup>

The UV-visible absorption spectra of **1** and **2** in acetonitrile are shown in Fig. 1. For each complex, the moderately intense Re  $\rightarrow$  bpy MLCT absorption band ( $\varepsilon \approx 3500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ), which occurs at *ca*. 350 nm in similar complexes,<sup>10</sup> is obscured by intense bands due to transitions centred on the L ligand: the spectra of the free L ligands contain similar bands.



The intense band at 405 nm in the spectrum of **1** can be assigned to an intraligand charge-transfer (ILCT) transition by comparison with related complexes and ligands.<sup>11</sup>

Pulsed excitation of model complex **2** at 355 nm gave strong emission peaking at *ca*. 570 nm and the TRVIS spectrum shown in Fig. 2, both of which are characteristic of a MLCT excited state;<sup>10</sup> the transient kinetics in both cases fitted well to a single exponential decay with a lifetime of 260 ns. Thus, the observed photophysics of **2** are assigned to a Re  $\rightarrow$  bpy MLCT state.

Pulsed excitation of azacrown complex 1 at 355 nm gave very weak emission, with a lifetime of <5 ns, and no transient absorption on the nanosecond time scale. This observation indicates that any excited states created from exciting into either the ground-state MLCT absorption band, or the overlying ILCT absorption band, must decay to the ground state in <5 ns. The presence of the azacrown substituent clearly results in a MLCT state lifetime that is significantly shorter in 1 than 2. One possible explanation is that the MLCT state of 1 is quenched by ultrafast electron transfer from the azacrown nitrogen to Re, to create a ligand-to-ligand charge-transfer (LLCT) excited state, as has been observed in related complexes;<sup>8</sup> an alternative explanation could be that internal conversion creates a shortlived L ligand-centred state such as an ILCT or  ${}^3\pi\pi^*$  state.<sup>12</sup> In either case, decay to the ground state then occurs in <5 ns.

Addition of 0.1 mol dm<sup>-3</sup> Ba(ClO)<sub>4</sub> to  $\mathbf{1}$  (2 × 10<sup>-5</sup> mol dm<sup>-3</sup>) in acetonitrile resulted in a blue-shift of the intense



Fig. 1 UV-visible absorption spectra of 1, 1-Ba<sup>2+</sup> and 2 in acetonitrile.



Fig. 2 TRVIS spectrum obtained 50 ns after 355 nm excitation (5 mJ, 10 ns) of 2 in acetonitrile. Inset: TRVIS kinetic trace recorded at 380 nm.

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ground-state ILCT absorption band to 352 nm (Fig. 1), consistent with Ba<sup>2+</sup> binding to the azacrown to form **1**-Ba<sup>2+,9</sup> Pulsed excitation of **1**-Ba<sup>2+</sup> at 355 nm gave very weak emission with a lifetime of <5 ns and a TRVIS spectrum that was constant in profile at >20 ns and consisted of a bleach at 340–360 nm and an absorption band at *ca*. 410 nm (Fig. 3). The kinetics at 410 nm fitted well to a dual exponential decay with lifetimes of  $\leq$ 10 ns and 110 ns.

The UV-visible signature for ion release is obtained by subtracting the steady-state UV-visible spectrum of  $1-Ba^{2+}$  from that of 1 (Fig. 3). The TRVIS spectrum obtained at > 20 ns after excitation of  $1-Ba^{2+}$  matches this difference spectrum (Fig. 3), demonstrating that  $Ba^{2+}$  has been released and the ground-state of 1 has been formed in < 20 ns. This TRVIS spectrum then decays to the baseline, indicating that  $Ba^{2+}$  rebinds to 1 to form  $1-Ba^{2+}$  again, restoring the starting equilibrium.

The dependence of the kinetics on metal cation concentration were studied by repeating the TRVIS experiment on **1**-Ba<sup>2+</sup> at  $[Ba^{2+}] = 0.10-0.0018 \text{ mol dm}^{-3}$  (Fig. 4). The kinetics recorded at every concentration fitted well to a dual exponential decay, with the lifetime of the longer-lived component showing a strong dependence on Ba<sup>2+</sup> concentration and increasing to 1.8  $\mu$ s at  $[Ba^{2+}] = 1.8 \times 10^{-3} \text{ mol dm}^{-3}$ . Both the time scale and concentration dependence indicate that the cation rebinds from bulk solution, rather than geminately, and thereby that excitation of **1**-Ba<sup>2+</sup> releases Ba<sup>2+</sup> into bulk solution. A plot of the rate constant for the longer-lived component ( $k_2$ ) versus Ba<sup>2+</sup> concentration (Fig. 4) gave a slope of  $9.3 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for the observed second-order rate constant for rebinding of Ba<sup>2+</sup> to **1**; it is comparable to that of  $4 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ 



Fig. 3 Top: TRVIS spectra obtained at 4, 18, 30, 50 and 100 ns after 355 nm excitation of  $1-Ba^{2+}$  in acetonitrile. Bottom: TRVIS spectrum at 100 ns overlaid with the difference spectrum (red trace) obtained by subtracting the steady-state UV-visible spectrum of  $1-Ba^{2+}$  from that of 1 (scaled to 410 nm).



**Fig. 4** Selected TRVIS kinetics recorded at 410 nm after 355 nm excitation of **1**-Ba<sup>2+</sup> in acetonitrile at Ba<sup>2+</sup> concentrations of (purple)  $7.5 \times 10^{-3}$ , (green) 0.020, (red) 0.040, and (blue) 0.10 mol dm<sup>-3</sup>. Inset: Plot of  $k_2$  (see text) *versus* Ba<sup>2+</sup> concentration, with a linear regression fit.

obtained for binding of  $Ba^{2+}$  to a benzothia zolium styryl aza-15-crown-5 dye in acetonitrile.<sup>6</sup>

The mechanism of photorelease from 1-Ba<sup>2+</sup> is not revealed by the present study, although the short-time data provide some information about the MLCT and ILCT states populated on excitation. The short-lived emission from 1-Ba2+ indicates that its MLCT state lifetime is similar to that of 1, and shorter than that of 2, suggesting that the ground-state azacrown-Ba<sup>2+</sup> interaction may be lost in < 5 ns in the MLCT state. The shorttime TRVIS spectrum shows strong bleaching at ca. 350 nm and absorption at ca. 400 nm, indicating that the ground-state ILCT band is bleached and suggesting that an ILCT state is observed; the short-time kinetics suggest that this ILCT state then decays in  $\leq 10$  ns. The lifetime of this ILCT state is longer for **1**-Ba<sup>2+</sup> than for 1, for which no nanosecond transient spectrum was observed, suggesting that Ba2+ may remain associated with 1 on the nanosecond time scale. Studies of all-organic azacrown dyes have shown that an azacrown nitrogen-cation bond can break in < 10 ps on excitation to produce a longer-lived species in which the cation is more loosely bound to the azacrown.5 The shortlived features reported here may arise from such a species, present before full release of Ba<sup>2+</sup> from the azacrown; this process requires large structural rearrangement of the azacrown and full solvation of the cation.

In summary, we report a (bpy)Re(CO)<sub>3</sub>L<sup>+</sup> complex which binds Ba<sup>2+</sup>, releases it on excitation, and rebinds it thermally on a time scale of 0.1–2  $\mu$ s depending on the metal cation concentration. This work contributes to the rational design of efficient light-controlled ion switches and their potential applications; further work will concentrate on the detailed nature of the cation release mechanism and will extend the present studies to other metal cations.

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## Notes and references

‡ (4,7,10,13-tetraoxa-1-azacyclopentadecyl)benzene (phenylaza-15-crown-5) was formylated at the 4-position according to ref. 13 to yield (4,7,10,13-tetraoxa-1-azacyclopentadecyl)benzaldehyde, from which 4-ethynyl(4,7,10,13-tetraoxa-1-azacyclopentadecyl)benzene was prepared by a method based on refs 14 and 15 and used to synthesise ligand L **1** according to ref 16. Ligand L **2** was synthesised identically, starting from benzaldehyde. (bpy)Re(CO)<sub>3</sub>L+PF<sub>6</sub><sup>-</sup> complexes **1** and **2** were prepared from the respective ligands L **1** and L **2**, respectively, according to ref. 7; analytical data are given as electronic supplementary information.

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