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## COMMUNICATION

## Reversible photochromic switching in a Ru(II) polypyridyl complex

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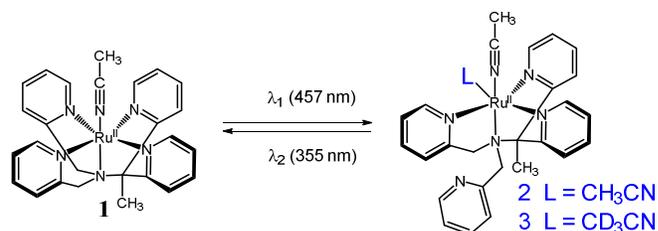
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**Abstract.** Fully reversible photoswitching of the coordination mode of the ligand MeN<sub>4</sub>Py (1,1-di(pyridin-2-yl)-N,N'-bis(pyridin-2-yl-methyl)-ethan-1-amine) in its ruthenium(II) complex with visible light is reported. Irradiation with visible light results in dissociation of a pyridyl moiety, which is reversed by irradiation at 355 nm.

The reversible photochemical switching between two distinct molecular states or structures, each having different physical properties, not least their colour, has been a cornerstone of organic photochemistry for over a century.<sup>1,2</sup> By contrast, with the exception of organic-inorganic hybrid systems,<sup>3</sup> the photochemistry of transition metal complexes has focused almost exclusively on photochemical ligand dissociation reactions, that are reversed thermally over timescales from the picosecond to the hour range.<sup>4</sup> Notable exceptions to this are hapticity changes in arene based complexes,<sup>5</sup> light induced spin state switching (LIESST) systems<sup>6</sup> and linkage isomerization<sup>7,8</sup> (e.g., with NO<sub>2</sub><sup>9</sup> and DMSO<sup>10</sup> as ligands).<sup>3,11</sup> The distinction between organic and inorganic photochemistry can largely be ascribed to the central role played by metal centred excited states, in which electron density is formally transferred from non-bonding to anti-bonding molecular orbitals (e.g., t<sub>2g</sub> → e<sub>g</sub> in octahedral complexes).<sup>12</sup> For transition metal complexes, ligand exchange involves the breaking of metal-ligand bonds. Although rare, the possibility to switch between two molecular states photochemically in transition metal complexes has been demonstrated, such as by Matsuda and co-workers<sup>13</sup> who demonstrated the reversible photochemical ligand dissociation and re-association in a Ru(II) complex containing a 2,2'-bipyridine and tris(2-pyridylmethyl)amine ligand and by Vos and co-workers<sup>14</sup> in the isomerisation of 1,2,4-triazole based Ru(II) complexes, albeit in both cases with limited photostationary states (PSS) achieved. Hence, the key challenge faced in developing inorganic photoswitchable systems that match contemporary organic photochromes such as

dithienylethenes<sup>2</sup> and overcrowded alkene based molecular rotary motors,<sup>15</sup> are i) to achieve a substantial difference in absorption, preferably with a complete loss of absorbance at a particular wavelength (λ<sub>1</sub>) to enable a photostationary state (PSS) of 100% to be achieved, and to be able to revert to the original state as completely as possible by irradiation at a different wavelength (λ<sub>2</sub>) (Scheme 1) and ii) that both forms are thermally stable under the conditions of irradiation to prevent spontaneous reversion.

Herein, we report the reversible photochemical switching of the coordination state of the ligand MeN<sub>4</sub>Py in its Ru(II) complex (Scheme 1). We show that irradiation with visible light (> 420 nm) results in dissociation of one of the pyridine moieties of the MeN<sub>4</sub>Py ligand and coordination of an acetonitrile ligand to yield a stable complex **2**. Unusually complex **2** can be reverted to **1** again by irradiation with near-UV light (e.g., 355 nm) and the process repeated over multiple switching cycles (Fig. 1).



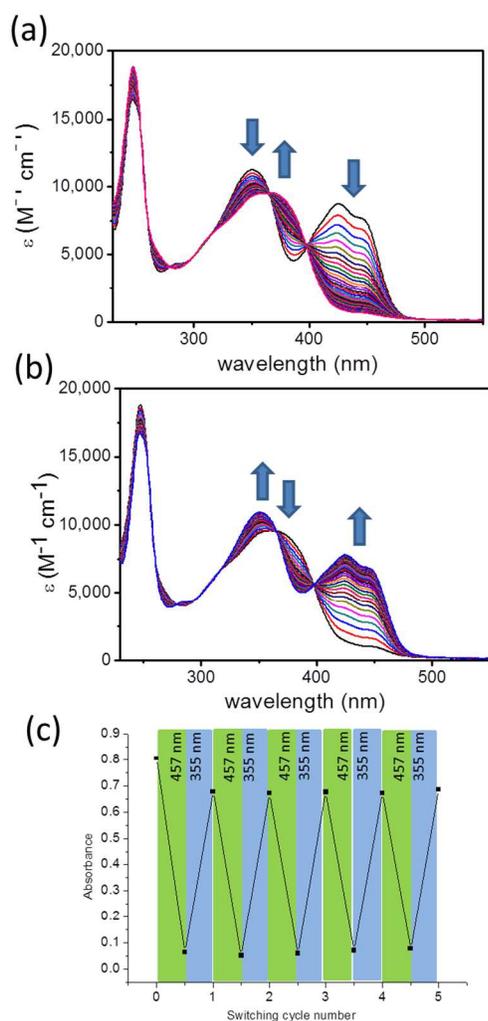
**Scheme 1** Reversible Photochromic Switching

Complex **1** was prepared from RuCl<sub>3</sub> and the ligand MeN<sub>4</sub>Py (see SSI for details). The UV/Vis absorption spectrum of **1** in CH<sub>3</sub>CN shows absorption bands at 247, 350, 425 and 445 nm (log<sub>10</sub> ε<sub>425</sub> = 3.9). The band at 247 nm is assigned as a π-π\* transition of the pyridine units,

whereas the three visible absorption bands are assigned to metal to ligand charge transfer (<sup>1</sup>MLCT) transitions.<sup>16</sup>

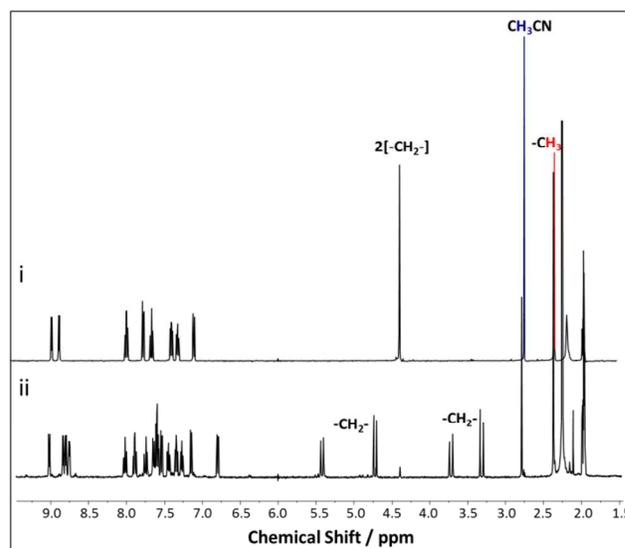
Irradiation (at 457 nm) of **1** in CH<sub>3</sub>CN results in a near complete loss in visible absorption at 445 nm (photostationary state, PSS > 95%, *vide infra*) and a change to the absorption band at ca. 350 nm with isosbestic points maintained at 365 and 398 nm (Fig. 1a). Notably thermal reversion to **1** does not occur at ambient conditions and prolonged heating above 50 °C is required to recover the initial spectrum. Remarkably subsequent irradiation at 355 nm results in a near complete restoration of the original UV/vis absorption spectrum (Fig. 1b). The photochromic switching can be repeated over multiple cycles without loss in performance (Fig. 1c).<sup>17</sup>

That the changes in visible absorption upon irradiation at 457 nm are due to dissociation of one of the pyridyl rings together with coordination of an additional acetonitrile was confirmed by <sup>1</sup>H NMR spectroscopy and ESI-MS.



**Fig. 1** Changes to the UV/Vis absorption spectrum of **1** in CH<sub>3</sub>CN upon irradiation at a) 457 nm b) 355 nm and c) Absorbance at 425 nm after successive irradiation at 457 nm and 355 nm over five cycles.

Irradiation of **1** in CD<sub>3</sub>CN at 457 nm results in a complete change in its <sup>1</sup>H-NMR spectrum (Fig. 2). **1** is a symmetrical complex with a single resonance at 4.37 ppm for the four methylene hydrogens of the MeN<sub>4</sub>Py ligand.<sup>18</sup> After irradiation four doublets (at 3.31, 3.72, 4.72 and 5.42 ppm, with the former pair corresponding to the methylene unit of the dissociated pyridine unit and the latter pair to the other methylene unit see SOI for DQF-COSY NMR spectra) are observed reflecting the complete loss in symmetry upon pyridyl dissociation together with a doubling in the number of resonances in the aromatic region. The residual signals of **1** indicate that the photostationary state achieved is >95% in favour of **3** (Scheme 1).



**Fig. 2.** <sup>1</sup>H-NMR (400 MHz) spectrum i) **1** ii) **2** (formed by irradiation of **1** at 457 nm) in CD<sub>3</sub>CN.

Notably although the irradiation was carried out in CD<sub>3</sub>CN, the signal from the CH<sub>3</sub>CN ligand (2.72 ppm) undergoes only a partial decrease in integration and a minor downfield shift, indicating that it is slow to exchange. Indeed, while the ESI-MS spectrum of a solution of **1** irradiated at 457 nm shows a base peak at *m/z* 282 corresponding to **2** ([Ru<sup>II</sup>(CH<sub>3</sub>CN)<sub>2</sub>(MeN<sub>4</sub>Py)]<sup>2+</sup>), when irradiated in CD<sub>3</sub>CN the base peak is [Ru<sup>II</sup>(CH<sub>3</sub>CN)(CD<sub>3</sub>CN)(MeN<sub>4</sub>Py)]<sup>2+</sup> (*m/z* 285), and subsequent irradiation at 355 nm results in the reappearance of the peak at *m/z* 262 corresponding to **1** ([Ru<sup>II</sup>(CH<sub>3</sub>CN)<sub>2</sub>(MeN<sub>4</sub>Py)]<sup>2+</sup>) as well as at 263.5 corresponding to [Ru<sup>II</sup>(CD<sub>3</sub>CN)<sub>2</sub>(MeN<sub>4</sub>Py)]<sup>2+</sup>. The limited exchange of the acetonitrile ligand is confirmed by Raman and FTIR spectroscopy also (see SOI).

The photochemistry of **1** is identical in both air equilibrated and argon purged acetonitrile and is unaffected by the presence of 1% water (see SOI Figs S17-20 for details). Taken together with the absence of emission, suggests that ligand dissociation occurs rapidly following absorption of a photon and does not involve water or oxygen. Indeed in other solvents such as DMSO, acetone and water, complex **1** shows photochemical dissociation of a pyridyl ring upon irradiation at 457 nm, however, the changes are not reversed upon irradiation at 355 nm and it is apparent from the absorption spectra that DMSO and water coordinates to the complex followed by loss of the acetonitrile ligand. Notably however in the case of water, although irradiation results in the formation of [Ru<sup>II</sup>(H<sub>2</sub>O)(MeN<sub>4</sub>Py)]<sup>2+</sup>, subsequent addition of CH<sub>3</sub>CN

(5% v/v) results in a slow thermal recovery (2.5 h) of complex **1**, which is accelerated (15 min) by irradiation at 355 nm. These data show that the complex  $[\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{MeN}_4\text{Py})]^{2+}$  is also photochemically active towards dissociation of a pyridyl ring but that the  $\text{CH}_3\text{CN}$  ligand is needed in order to trap complexes of the type **2**.

## Conclusions

In conclusion, we show that bi-directional photoswitching of a coordination complex between two thermally stable states can be achieved and circumvent the need to incorporate organic photoswitches as ligands. The forward reaction involves dissociation of a pyridine moiety of the ligand, while the reverse reaction involves photo-dissociation of the solvent molecule that filled the vacant coordination site. The dissociation of the pyridyl moiety and not the  $\text{CH}_3\text{CN}$  ligand is ascribed to a *trans*-effect of the amine of the  $\text{MeN}_4\text{Py}$  ligand. The role of solvent in terms of coordination places an important limitation in the current system in comparison with organic chromophores in regard to solid state applications; however it is envisaged that careful ligand design in which a coordinating nitrile group is appended to the ligand may broaden the solvent scope and allow for application of this photochromic switching system in a wider range of solvents and in polymer matrices. The ability to switch between two distinct molecular states with visible and UV light opens up opportunities to develop new classes of photoswitches based on coordination complexes.

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## Notes and references

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- 17 The quantum yields for the forward and reverse processes have been estimated at 0.1% and 1.5 %, respectively based on rate of change of absorbance and fractional absorption of light at the wavelength of irradiation. The ratio is consistent with the photostationary states reached.
- 18 It should be noted that the apparent singlet observed for the methylene hydrogens of **1** is due to their accidentally identical chemical shift