

Ruthenium(II) complexes with photoswitchable and photoejectable ligands

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A ruthenium(II) complex with a photoswitchable arylazopyrazole ligand is reported. Under irradiation a combination of photoisomerisation and photoejection of the ligand occurs.

Photoswitches are molecules that undergo reversible structural changes excited by light, altering properties such as polarity, conductance, rigidity, or refractive index.¹⁻⁴ Arylazopyrazoles are a very promising class of photoswitches with high thermal barriers, near quantitative photoisomerization, and properties can be easily tuned through structural modifications.⁵⁻⁸ Photoswitches have been used as ligands with metal ions,⁹⁻³³ for example in mixed-valence complexes,¹³ spin crossover systems,^{11, 12, 14} DNA binders,¹⁷ or as catalysts.^{4, 10, 19, 21-25, 27, 29, 32} Ruthenium(II) complexes have been long known to photoeject ligands.^{17, 19, 34-47} Ruthenium(II) complexes with photoswitchable ligands have also shown photoejection of a non-switchable ligand.^{17, 19} Herein, we present a ruthenium(II) complex where both photoejection and photoswitching occur on the same ligand.

Our study uses the photoswitchable pyridyl-azoarylpyrazole ligand **1**,⁸ pyridyl-pyrazole ligand **2**,⁴⁰ and 2,2'-bipyridine (bpy) to form the ruthenium(II) complexes [Ru(bpy)₂(*E*-**1**)](PF₆)₂ and [Ru(bpy)₂(**2**)](PF₆)₂.^{38, 40} (Fig. 1). Photoswitchable ligand **1** was prepared using a different method than that reported,⁸ using commercially available aniline, acetyl acetone and 2-hydrazinopyridine to give **1** in 74% yield (S1.2[†]). Spectroscopic data (S1.2.2[†]) and a single-crystal X-ray structure (CCDC: 2417092, S6.1[†]) confirmed the structure. The non-photoswitchable ligand **2** was prepared using an adaptation of literature procedures,⁴⁸ from commercially available

acetylacetone and 2-hydrazinopyridine to give **2** in a 40% yield (S1.3[†]).

The photoswitching properties of **1** were investigated using NMR and UV-vis absorption spectroscopies (S2[†]). Photostationary states (PSS) of **1** were generated by irradiating a sample of *E*-**1** in acetonitrile-*d*₃ with 365 nm, 425 nm, 470 nm, or 530 nm light for 15 minutes. Irradiation with 530 nm light gave the highest distribution of the *E* isomer (89% *E*-**1**), and irradiation with 365 nm light gave the highest distribution of the metastable *Z* isomer (98% *Z*-**1**) (Table S2[†]). These values are similar to literature values for ligand **1** in DMSO.⁸ The thermal half-life of the metastable isomer, *Z*-**1**, is 10 days at room temperature in acetonitrile (Table S5[†]).

Complexes [Ru(bpy)₂(*E*-**1**)](PF₆)₂ and [Ru(bpy)₂(**2**)](PF₆)₂ were synthesised according to previously established methods for related complexes,⁴⁹ using Ru(bpy)₂Cl₂⁵⁰ and ligand **1** or **2** in ethylene glycol in a microwave reactor. Complex [Ru(bpy)₂(*E*-**1**)](PF₆)₂ was isolated in 23% yield and characterised using NMR spectroscopy, electrospray ionisation mass spectrometry (ESI-MS) and UV-vis spectroscopy (S1.5[†]). A single-crystal X-ray structure (CCDC: 2417124, S6.2[†]) confirmed that ligand **1** was in an *E* isomer configuration. Complex [Ru(bpy)₂(**2**)](PF₆)₂ was isolated in 93% yield and similarly characterised (S1.6[†]). A single-crystal X-ray structure of the complex (CCDC: 2417094, S6.3[†]) showed that the ligand **2** is equally disordered over all three ligands positions, similar to some other [Ru(bpy)₂(L)]²⁺ complexes.^{51, 52} Complex [Ru(bpy)₂(MeCN)₂](PF₆)₂ was synthesised using a modification of literature procedures,^{53, 54} in 46% yield and was similarly characterised (S1.6[†]).

The photoswitching and photoejection behaviours of [Ru(bpy)₂(*E*-**1**)](PF₆)₂ and [Ru(bpy)₂(**2**)](PF₆)₂ in acetonitrile were studied by UV-vis absorption spectroscopy (Fig. 2). Each complex was irradiated 365 nm, 445 nm, or 530 nm light. Irradiation with 365 nm light produced the greatest change in the UV-vis spectrum for each complex (Fig. S27[†] and Fig. S28[†]).

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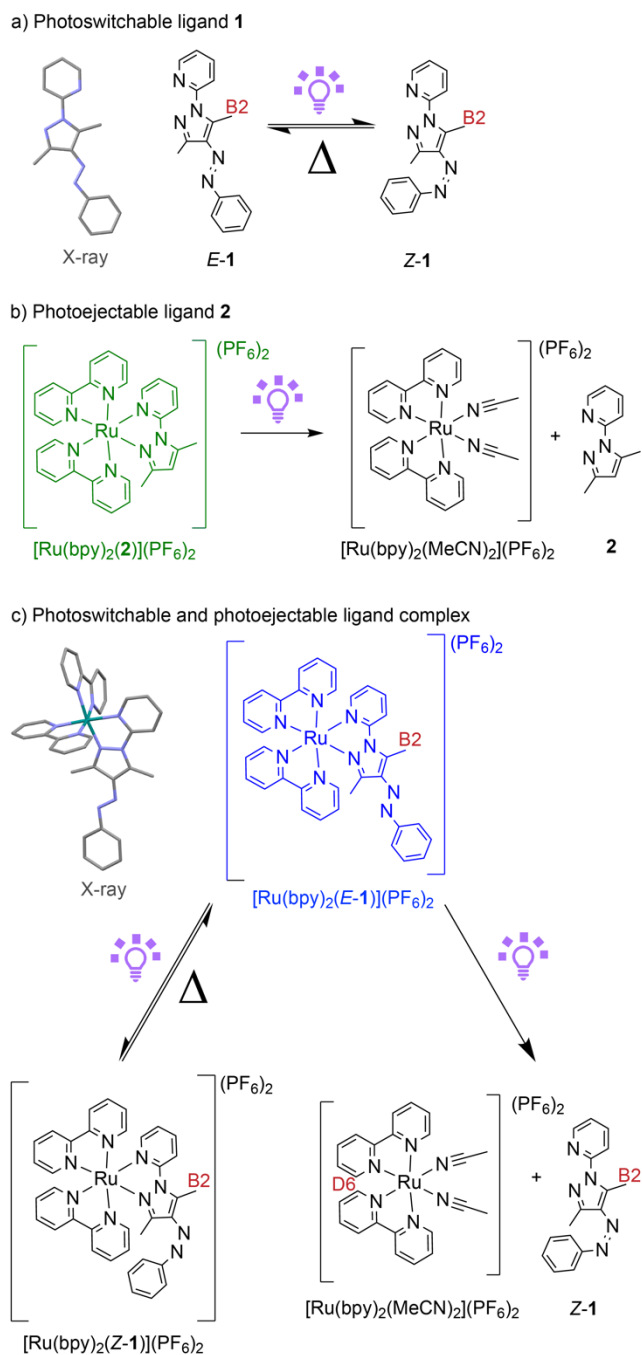


Fig. 1 a) Photoswitchable ligand, **1**, and its UV light triggered photoswitching. b) Ruthenium complex, [Ru(bpy)₂(**2**)](PF₆)₂, containing non photoswitchable ligand **2** and its photoejection triggered by UV light. c) Ruthenium complex, [Ru(bpy)₂(E-1)](PF₆)₂, containing photo switchable ligand **1** and its photoejection and photo isomerisation triggered by UV light. Chosen hydrogen environments are labelled in red.

A sample of [Ru(bpy)₂(**2**)](PF₆)₂ (10 μM, acetonitrile, 298 K) was irradiated with 365 nm light and the absorbance was monitored over 75 minutes (Fig. 2a). The MLCT band ($\lambda_{\text{max}} = 449$ nm) is blue-shifted by 23 nm to 426 nm, characteristic of [Ru(bpy)₂(MeCN)₂](PF₆)₂. The absorption spectrum from 300–500 nm after irradiation is the same as that of [Ru(bpy)₂(MeCN)₂](PF₆)₂. This data is consistent with the formation of [Ru(bpy)₂(MeCN)₂](PF₆)₂ and free ligand **2** which has no absorption over 300 nm. ESI-MS (Fig. S42[†]) data showed

that signals characteristic of [Ru(bpy)₂(**2**)]²⁺ disappeared after irradiation, and peaks characteristic of [Ru(bpy)₂(MeCN)₂]²⁺ and [**2**+H]⁺ were formed. A solution of [Ru(bpy)₂(**2**)](PF₆)₂ in acetonitrile-*d*₃ (Fig. S35[†]) was irradiated with 365 nm light for 30 mins, and the ¹H NMR spectrum was also consistent with the quantitative formation of [Ru(bpy)₂(MeCN)₂](PF₆) and **2**. Our studies show that **2** is an effective photoejectable ligand as the complex quantitatively undergoes photoejection, in line with previous reports.³⁸

The photoswitchable complex, [Ru(bpy)₂(E-1)](PF₆)₂ (13 μM, acetonitrile, 298 K), was irradiated at 365 nm and the UV-vis absorbance from 250–550 nm was monitored over 75 minutes (Fig. 2b). After irradiation, the MLCT band does not match that of [Ru(bpy)₂(MeCN)₂](PF₆)₂. The spectrum of [Ru(bpy)₂(E-1)](PF₆)₂ after irradiation is also not any combination of the spectra of E-1, Z-1 and [Ru(bpy)₂(MeCN)₂](PF₆)₂, suggesting the formation of a new species, presumably [Ru(bpy)₂(Z-1)](PF₆)₂. We used NMR spectroscopy to analyse the new species that were formed. A sample of [Ru(bpy)₂(E-1)](PF₆)₂ in acetonitrile-*d*₃ was irradiated with 365 nm light for 2.5 hours. A series of new ¹H NMR peaks are formed. To determine the composition of the mixture we used the signal intensity of the methyl protons associated with E-1 and Z-1 (H^{B2}, see Fig. 1 for labelling, S1.2.2[†] for data), the methyl protons of [Ru(bpy)₂(E-1)](PF₆)₂ (H^{B2}, S1.5.2[†]), the protons corresponding to [Ru(bpy)₂(MeCN)₂](PF₆)₂ (H^{D6}, S1.7.2[†]), and the peak at 2.85 ppm which was assigned to the methyl protons of [Ru(bpy)₂(Z-1)](PF₆)₂ (H^{B2}). These peaks were chosen as they are well separated, and their signal intensities were normalised for the number of protons in each case. Using these signals [Ru(bpy)₂(MeCN)₂](PF₆)₂ and free ligand **1** make up just 5% of the total mixture, indicating that photoejection occurs for [Ru(bpy)₂(E-1)](PF₆)₂, as discussed above for [Ru(bpy)₂(**2**)](PF₆)₂. However, the photoejection of ligand **1** does not occur quantitatively as was observed for ligand **2**, which is surprising as the binding motifs of the pyridyl-pyrazole are the same for both **1** and **2**. Other ¹H NMR peaks with a relative abundance of 16% of this mixture are also formed (Fig. 3, highlighted in yellow), which we assign to [Ru(bpy)₂(Z-1)](PF₆)₂. The NMR sample was then heated at 75 °C for 5 hours (Fig. 3). The peaks characteristic of [Ru(bpy)₂(MeCN)₂](PF₆)₂ and ligand **1** do not change in signal intensity and remain as 5% of the mixture. However, the peaks assigned to [Ru(bpy)₂(Z-1)](PF₆)₂ decrease in intensity to become less than 2% of the mixture and the peaks of [Ru(bpy)₂(E-1)](PF₆)₂ increase in intensity to form 93% of the mixture. This change is consistent with the thermal isomerisation from the metastable isomer [Ru(bpy)₂(Z-1)](PF₆)₂ to the stable [Ru(bpy)₂(E-1)](PF₆)₂ isomer. The new species formed could also be a partially ejected complex with either the pyridyl nitrogen or pyrazolyl nitrogen substituted by solvent to form [Ru(bpy)₂(**1**)(MeCN)](PF₆)₂. However, no such complex was observed via ESI-MS (S5.1[†]). The species formed by irradiation could not be separated from [Ru(bpy)₂(E-1)](PF₆)₂ via TLC or column chromatography, indicating that this new species has a similar polarity to [Ru(bpy)₂(E-1)](PF₆)₂. The measured diffusion coefficient⁵⁵ of the new species (Table S6[†]) is similar to that of [Ru(bpy)₂(E-1)](PF₆)₂, implying that the new species

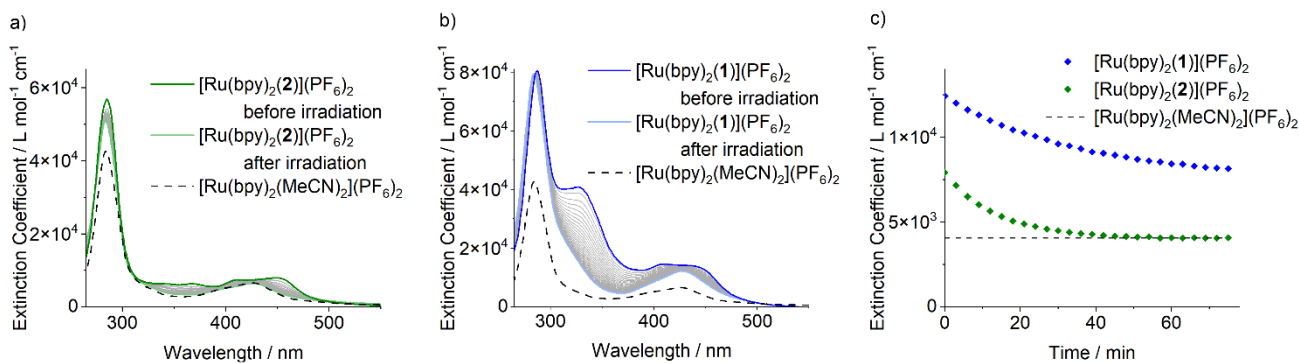


Fig. 2 a) UV-vis absorption (10 μM , acetonitrile, 298 K) spectra of $[\text{Ru}(\text{bpy})_2(\mathbf{2})](\text{PF}_6)_2$ after irradiation at 365 nm for 75 minutes. From 0 minutes (dark green) to 75 minutes (light green). UV-vis absorption spectra of $[\text{Ru}(\text{bpy})_2(\text{MeCN})_2](\text{PF}_6)_2$ is shown through a dashed line. b) UV-vis absorption spectra of $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ (13 μM , acetonitrile, 298 K) after irradiation at 365 nm for 75 minutes. From 0 minutes (dark blue) to 75 minutes (light blue). UV-vis absorption spectra of $[\text{Ru}(\text{bpy})_2(\text{MeCN})_2](\text{PF}_6)_2$ is shown through a dashed line. c) Extinction coefficient at 450 nm of $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ and $[\text{Ru}(\text{bpy})_2(\mathbf{2})](\text{PF}_6)_2$ (acetonitrile, 298 K) during irradiation with 365 nm light for 75 minutes. $[\text{Ru}(\text{bpy})_2(\text{MeCN})_2](\text{PF}_6)_2$ is shown through a dashed line.

and $[\text{Ru}(\text{bpy})_2(\mathbf{E-1})](\text{PF}_6)_2$ are also similar in size.

The evidence from the UV-vis, ESI-MS and NMR data all suggests that the new species formed is $[\text{Ru}(\text{bpy})_2(\mathbf{Z-1})](\text{PF}_6)_2$. The mechanism of formation could be that $\text{Ru}(\text{bpy})_2(\mathbf{E-1})(\text{PF}_6)_2$ first undergoes photoejection to form $[\text{Ru}(\text{bpy})_2(\text{MeCN})_2](\text{PF}_6)_2$ and $\mathbf{E-1}$, then the free ligand photoisomerises to form $\mathbf{Z-1}$, and finally re-coordinates to the ruthenium centre to form $[\text{Ru}(\text{bpy})_2(\mathbf{Z-1})](\text{PF}_6)_2$. Heating $[\text{Ru}(\text{bpy})_2(\text{MeCN})_2](\text{PF}_6)_2$ and $\mathbf{E-1}$ or $\mathbf{Z-1}$ in acetonitrile- d_3 at 50 degrees and monitoring by NMR showed that under these conditions the ligand did not coordinate to the ruthenium centre and the solution remains as free $\mathbf{1}$ and $[\text{Ru}(\text{bpy})_2(\text{MeCN})_2](\text{PF}_6)_2$ (Fig. S37[†] and Fig. S38[†]). This suggests that the photoisomerisation of the ligand $\mathbf{1}$ occurs while coordinated to the ruthenium centre. The relative NMR signals of $[\text{Ru}(\text{bpy})_2(\mathbf{E-1})](\text{PF}_6)_2$ after irradiation with 365 nm light for 2.5h showed 80% of the $[\text{Ru}(\text{bpy})_2(\mathbf{E-1})](\text{PF}_6)_2$ remains as $[\text{Ru}(\text{bpy})_2(\mathbf{E-1})](\text{PF}_6)_2$ while 5% undergoes photoejection to form $[\text{Ru}(\text{bpy})_2(\text{MeCN})_2](\text{PF}_6)_2$, and 15% isomerises to form $[\text{Ru}(\text{bpy})_2(\mathbf{Z-1})](\text{PF}_6)_2$. The composition of $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ in the mixture is 16% of the metastable $[\text{Ru}(\text{bpy})_2(\mathbf{Z-1})](\text{PF}_6)_2$ and 84% of the stable $[\text{Ru}(\text{bpy})_2(\mathbf{E-1})](\text{PF}_6)_2$ complex. This ratio is significantly lower than the distribution of the metastable isomer of $\mathbf{1}$ alone under identical irradiation conditions (98% $\mathbf{Z-1}$ and 2% $\mathbf{E-1}$) (Table S2[†]). The ratio is also lower than the PSS of $\mathbf{1}$ in a 1:1 molar solution of $\mathbf{1}$ and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (48% $\mathbf{Z-1}$ and 52% $\mathbf{E-1}$) (S2.4[†]), indicating that the difference is not simply due to the ruthenium complex acting as an inner filter for the available light. This data is consistent with photoisomerisation being inhibited upon coordination to the ruthenium metal centre.

This example shows that three different ruthenium complexes can be accessed when irradiating with the same wavelength of light. Each complex will have different photophysical properties and could influence catalytic performance. While the selectivity of this first example is not ideal, it does demonstrate a pathway for developing photoswitchable complexes with more than two configurations.

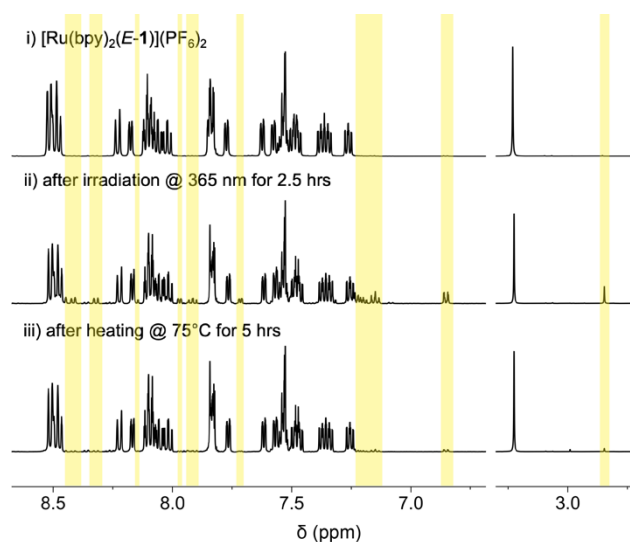


Fig. 3 ^1H (500 MHz, 298 K, $\text{MeCN-}d_3$) NMR spectra of $[\text{Ru}(\text{bpy})_2(\mathbf{E-1})](\text{PF}_6)_2$ after i) irradiation for 3.5 hours ii) heating at 75°C for 5 hours. Peaks corresponding to the proposed $[\text{Ru}(\text{bpy})_2(\mathbf{Z-1})](\text{PF}_6)_2$ complex are highlighted.

Author contributions

KAS performed all synthesis and characterisation, IAM performed NMR diffusion measurements, KAS, MHC and MB collected and refined crystallographic data, JPV collected and analysed ESI-MS data, and JEB oversaw the project. All authors wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Data availability

The data supporting this article have been included as part of the supplementary information. Crystallographic data⁵⁶⁻⁶⁰ has been deposited at the CCDC (2417092, 2417124, 2417094).

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