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PAPER

## Energy transfer from a rhodamine antenna to a ruthenium–bipyridine center†

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The coordination of a modified rhodamine B (Rhod) to a bis-bipyridine ruthenium (II) (Ru–bpy) phototrigger complex enables a photodissociation reaction at longer wavelengths through enhanced absorption of green light (532 nm). The very high molar absorptivity of rhodamine ( $\sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and the high quantum efficiency of Förster resonance energy transfer (FRET) from rhodamine to the Ru–bpy center (0.84) result in an unusually high photosensitivity and uncaging cross-section of the Ru–bpy–rhodamine complex at longer wavelengths.

### 1. Introduction

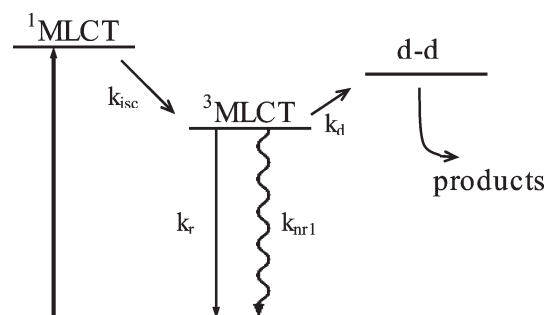
Ruthenium–bipyridine complexes, which absorb light mainly in the blue region, have been extensively investigated as light harvesting compounds.<sup>1</sup> Considerable effort has been made to shift their peak absorption bands to longer wavelengths in order to make Ru–bpy centers better collectors for solar energy conversion.<sup>2</sup>

The need to increase light absorption at longer wavelengths also arises in the design of phototriggers. In this type of device a monodentate ligand is usually released through the d–d decomposition path, and this behaviour can be used to design caged compounds.<sup>3</sup> Many molecules, including neurotransmitters and other biomolecules can be photodelivered using these complexes, which makes this one of the most promising techniques to cage drugs for photodynamic therapies, for neuroscience and for photoregulation of biological processes in general.<sup>4</sup>

The elementary photochemistry of Ru–bpy complexes, which is simple and well known, is depicted in Scheme 1: irradiation at the lowest energy MLCT (metal-to-ligand charge-transfer) band yields an excited singlet state <sup>1</sup>MLCT that decays completely to a <sup>3</sup>MLCT triplet state, which in turn can be deactivated through non-radiative pathways, radiative emission, or by thermally populating a metal centered d–d state which leads to decomposition.<sup>5</sup>

The absorption wavelength of the <sup>1</sup>MLCT band strongly depends on the basicity of the ligands. By selecting the proper ligands X and Y in a  $[\text{Ru}(\text{bpy})_2\text{XY}]^{n+}$  complex (bpy = 2,2' bipyridine) the <sup>1</sup>MLCT band can be tuned from 350 to 550 nm. Strong electron donor ligands such as aliphatic amines<sup>6</sup> yield complexes with low energy for the <sup>1</sup>MLCT band, thus leading to absorption at longer wavelengths, while strong  $\pi$  acceptors having lower  $\sigma$  basicity, such as pyridines or nitriles, shift the band towards the UV region.<sup>5</sup>

The quantum yield of photorelease ( $\Phi_{\text{pr}}$ ) is directly related to the energy of the <sup>1</sup>MLCT band and increases when this band is shifted to the UV. The position of this band is, on the other hand, closely related with the redox potential of the complex.<sup>5</sup> The rationale is simple: a high energy of the <sup>1</sup>MLCT state and its corresponding <sup>3</sup>MLCT state thermally populate the dissociative d–d state in an effective way, with high probability of yielding photoproducts. If the energy of the <sup>1</sup>MLCT band is low then the energy difference between the corresponding <sup>3</sup>MLCT band and the dissociative d–d state is large, and this thermally induced transition is less favoured. As an example,  $[\text{Ru}(\text{bpy})_2(4\text{AP})_2]^{2+}$  (4AP = 4-aminopyridine) presents its <sup>1</sup>MLCT band centered at 490 nm and a  $\Phi_{\text{pr}} = 0.03$  in aqueous solutions<sup>3</sup> while for [Ru



**Scheme 1** Jablonsky diagram of the photochemical steps leading to photodecomposition of a typical  $\text{Ru}(\text{bpy})_2\text{XY}$  complex.

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† Electronic supplementary information (ESI) available: Schematics of the optical bench used for fluorescence measurements; sequence of UV-Vis absorption spectra during photolysis of RuBiMAPN; sequence of UV-Vis emission spectra during photolysis of RuBiMAPNRhod. See DOI: 10.1039/c2pp05415a

(bpy)<sub>2</sub>(py)<sub>2</sub>]<sup>2+</sup> (py = pyridine), the <sup>1</sup>MLCT band is at about 457 nm and its quantum efficiency of photorelease is almost 9 times higher ( $\Phi_{\text{pr}} = 0.26$ ).<sup>5</sup>

These considerations imply that, due to the fundamental photochemistry of the system, it is impossible to obtain a photo-trigger presenting both high absorption at longer wavelengths (~500 nm) and a high photorelease quantum yield.

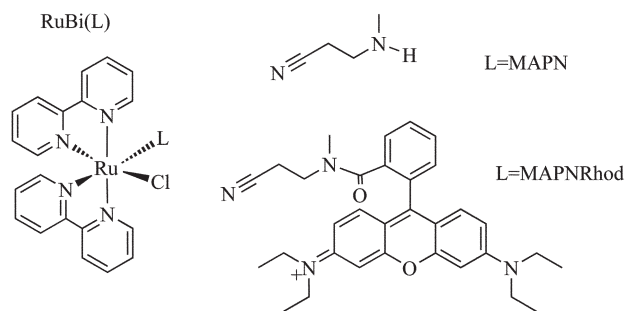
Here we propose and demonstrate a way to circumvent this restriction. A coordinated fluorescent fragment harvests long wavelength light and transfers this energy to the ruthenium center, allowing high photoactivity at long wavelengths (532 nm) with very high absorptivity and high energy transfer quantum yield.

## 2. Results and discussion

The structure of the complex [Ru(bpy)<sub>2</sub>(MAPNRhod)Cl]<sup>2+</sup>, (RuBiMAPNRhod) is depicted in Fig. 1. MAPNRhod is a fluorescent ligand obtained from rhodamine B after amidation of its carboxylic acid group using *N*-methylaminopropionitrile (MAPN), and coordinated to ruthenium through its terminal nitrile. Its synthesis and some analytical applications have been published elsewhere.<sup>7</sup>

A dilute solution of RuBiMAPNRhod presents fluorescence with an intensity of about one sixth of that of the free ligand MAPNRhod. This intensity increases after irradiation with blue light (400–473 nm), in agreement with the expected uncaging of MAPNRhod (see ESI†). The quantum yield of photorelease of the MAPNRhod ligand at 473 nm is  $\Phi_{\text{pr}} = 0.12$  at 25 °C.

Due to the presence of the highly absorbing Rhod, direct measurement of the extinction coefficient ( $\epsilon$ ) of the <sup>1</sup>MLCT band in RuBiMAPNRhod is technically challenging. However, extensive research on Ru–bpy complexes has shown that the molecular fragments situated further than one chemical bond from the Ru center have a negligible effect on the redox potential on the complexes and therefore on their MLCT absorption bands.<sup>5</sup> Thus, the analogue complex [Ru(bpy)<sub>2</sub>(MAPN)Cl]<sup>+</sup> (RuBiMAPN) in which the MAPNRhod ligand was replaced by MAPN is an excellent estimate of the <sup>1</sup>MLCT band absorptivity of the RuBiMAPNRhod complex ( $\epsilon_{\text{MAX}} = 6300 \text{ M}^{-1} \text{ cm}^{-1}$  at 469 nm in EtOH, see ESI†).



**Fig. 1** Structure of the complexes [Ru(bpy)<sub>2</sub>Cl(L)]<sup>n+</sup> for the two different ligands used in this work: RuBiMAPN, in which L = MAPN (*N*-methylaminopropionitrile) and RuBiMAPNRhod, where L = MAPNRhod.

To test the activity of these complexes under green light, irradiation experiments with a 532 nm DPSS Nd:YAG laser were performed. RuBi(L), where L = MAPN or MAPNRhod was photolyzed at 532 nm. In each case the photoproducts are [Ru(bpy)<sub>2</sub>Cl(H<sub>2</sub>O)]<sup>+</sup> and L. Results are depicted in Fig. 2.

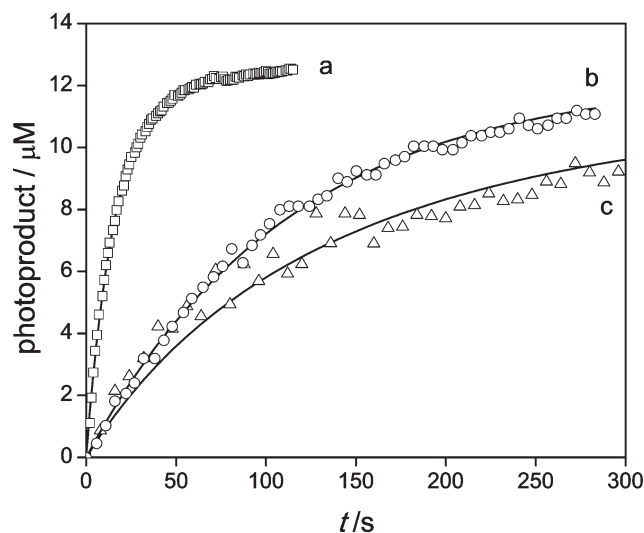
It is evident that the presence of coordinated MAPNRhod dramatically increases the rate of the photoreaction. The effect is not due to the mere presence of the dye. Indeed addition of equimolar, free MAPNRhod to a solution of RuBiMAPN decreases the rate of the photoreaction. As photolysis eventually reaches completion all reactions reach the same product concentrations.

The overall photoreaction rate depends both on the absorptivity of the reactant and on its quantum yield of photorelease. In order to obtain the quantum yield of the photoreaction, the molar absorptivity of both reactant and product must be known, because a fraction of the incident photons are absorbed by the latter, resulting in no reaction. This effect is negligible at the initial stages but becomes important after some photolysis, when the product accumulates. The presence of free, added MAPNRhod, produces a similar effect.

Given the power of the incident beam, and the volume and concentration of the complex solution, it is possible to calculate the differential amount of product as:

$$\frac{dn_{\text{P}}}{dt} = I_{\text{beam}} \times (1 - 10^{-A_{\text{T}}}) \times \frac{A_{\text{R}}}{A_{\text{T}}} \times \Phi_{\text{pr}} \quad (1)$$

where  $n_{\text{P}}$  are the moles of uncaged product,  $I_{\text{beam}}$  is the intensity of the incident light in Einsteins s<sup>-1</sup>,  $A_{\text{T}}$  and  $A_{\text{R}}$  are the solution's total absorbance and the reactant's absorbance, respectively, and  $\Phi_{\text{pr}}$  is the photoreaction quantum yield. The integration of eqn



**Fig. 2** Photoreleased ligand vs. irradiation time for the complexes RuBiMAPNRhod (a, □), RuBiMAPN (b, ○) and RuBiMAPN with added MAPNRhod (c, △), during irradiation at 532 nm in ethanol. Notice that the photoconversion is much faster for (a) than for (b) or (c), revealing the sensitization effect of the rhodamine ligand. ( $c = 12.2 \text{ μM}$ ,  $T = 24.8 \text{ °C}$ , laser power = 6.97 mW). Continuous curves are the predicted photoproduct amounts according to the integration of eqn (1), where quantum efficiencies were fitted to the experimental data (see text).

**Table 1** Molar absorptivities ( $\epsilon_{532}$ ) and photoactivities ( $\epsilon_{532} \times \Phi_{\text{pr}}$ ) for RuBiMAPN and RuBiMAPNRhod phototriggers at 532 nm

Compound	$\epsilon_{532}$	$\Phi_{\text{pr}}$	$\epsilon_{532} \times \Phi_{\text{pr}}$
RuBiMAPN	1700	0.145	246
RuBiRhod	84 500	0.070	5920

(1) is easily done by a finite differences approach and the photo-release quantum yield is obtained. The values are  $\Phi_{\text{pr}} = 0.145$  for RuBiMAPN and  $\Phi_{\text{pr}} = 0.070$  for RuBiMAPNRhod, both measured in ethanol at 25 °C and 532 nm irradiation. Curves with the theoretical amount of photoreleased product vs. irradiation time according to eqn (1) are plotted in Fig. 2, along with the corresponding experimental data.

Given the quantum yield of RuBiMAPN, the much faster photoreaction of RuBiMAPNRhod compared with the analogue complex can only be explained by its very high absorptivity at 532 nm. While RuBiMAPN presents the typical absorption of this kind of Ru–bpy complexes, with  $\epsilon_{532} = 1700 \text{ M}^{-1} \text{ cm}^{-1}$ , RuBiMAPNRhod additionally shows a strong absorption band with  $\epsilon_{\text{MAX}} = 84\,500 \text{ M}^{-1} \text{ cm}^{-1}$  at 532 nm, due to its rhodamine moiety. In a low absorbance regime, typical in biological applications, the overall photorelease efficiency for a given irradiation wavelength (photoactivity) is obtained as the product  $\epsilon_{532} \times \Phi_{\text{pr}}$ . Table 1 shows that the photoactivity of the complex bearing the rhodamine ligand is 24 times higher than that of its analogue compound RuBiMAPN. The low absorptivity of the Ru–bpy MLCT band compared to that of the Rhod fragment, implies that only 2% of the absorbed photons are absorbed directly through the typical Ru–bpy pathway (see Introduction section). The high photoactivity of RuBiMAPNRhod is therefore explained if a large amount of energy captured by the rhodamine ligand is transferred to the Ru–bpy system.

Energy transfer from a coordinated dye to a Ru complex has been demonstrated before and was used to release NO through a photoredox mechanism involving nitrosyl reduction,<sup>8</sup> although in the present case a rather different release mechanism is involved. We propose that dissociative states of Ru–bpy complexes can also be populated from a coordinated excited dye molecule, leading to ligand expulsion.

Both absorption and fluorescence spectra of coordinated MAPNRhod appear to be identical in shape to those of the free dye. This suggests that the electronic–vibrational structure of MAPNRhod does not change significantly upon coordination. Although other kinds of mechanisms, such as Dexter, cannot be ruled out completely, the energy transfer from the coordinated dye can be explained through a typical Förster resonance energy transfer (FRET) mechanism. FRET is a radiationless mechanism, in which the transition dipoles of a donor (D) and an acceptor (A) establish resonance. Its efficiency depends mainly on three factors: (i) the overlap between the donor emission spectrum and the acceptor absorption spectrum; (ii) the relative orientation of their dipoles; and (iii) the distance between D and A.

FRET efficiency ( $\Phi_{\text{FRET}}$ ) can be calculated as:<sup>9</sup>

$$\Phi_{\text{FRET}} = \frac{1}{1 + (r/R_0)^6} \quad (2)$$

where  $r$  is the distance between D and A, and  $R_0$  is the characteristic distance of the D–A pair, which can be estimated using the following expression:

$$R_0^6 = 8.79 \times 10^{-5} \frac{\kappa^2 \Phi_{\text{f}}}{n^4} \int f_{\text{D}}(\lambda) \times \epsilon_{\text{A}}(\lambda) \times \lambda^4 d\lambda \quad (3)$$

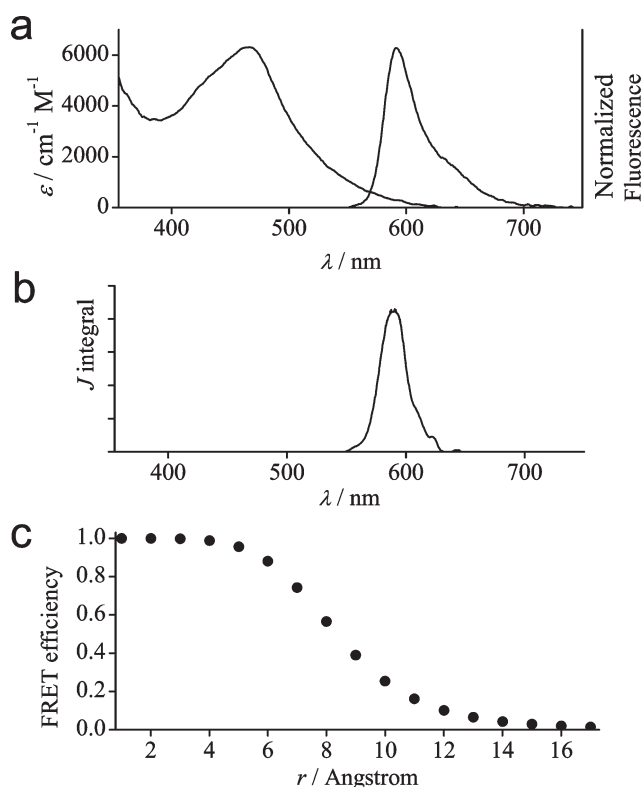
where  $\kappa^2$  is the dipole orientation factor ( $\kappa^2 = 2/3$  is often assumed),  $\Phi_{\text{f}}$  is the quantum yield of fluorescence of the donor in absence of the acceptor,  $n$  is the refractive index of the medium,  $f_{\text{D}}$  is the normalized (area = 1) donor emission spectrum,  $\epsilon_{\text{A}}$  is the acceptor molar absorptivity spectrum and  $\lambda$  the wavelength in nm. The result  $R_0^6$  is given in Å<sup>6</sup> and its sixth root represents the critical transfer distance for which excitation transfer and spontaneous deactivation of D are of equal probability.

Usually, D and A entities are chosen to allow FRET to occur at tens of nanometres. As FRET efficiency falls with the sixth power of the distance between D and A, an important overlap between their spectra that maximizes the  $J$  integral is mandatory. This is easily obtained using an acceptor with high molar absorptivity shifted somewhat to longer wavelengths relative to the donor emission. However, for shorter distances, even a small overlap can guarantee a high yield of energy transfer. This is due to the fact that  $R_0$  scales as the sixth root of the overlap integral  $J$ . In eqn (3), a 64-fold change in the overlap integral  $J$  accounts only for a 2-fold change in the characteristic distance  $R_0$ . This fact allows the election of a donor which has most of its emission spectrum at lower energies than that of the acceptor absorption, yielding only a small degree of overlap. Woolley *et al.* have referred to this effect as “reverse” FRET, and showed its occurrence between the green emitting fluorescein as donor, and the blue emitting coumarin as acceptor.<sup>10</sup>

We will assume that the xanthene fluorophore in the coordinated MAPNRhod acts as the donor (D) while the Ru–bpy center is the acceptor (A).

Fig. 3a shows the absorption band of the model complex RuBiMAPN (which we use as an estimate of the <sup>1</sup>MLCT absorption in RuBiMAPNRhod), and the emission of the MAPNRhod fragment. This fluorescence spectrum has been normalized in order to have a unitary area. The absorption of the complex extends well within the emission of rhodamine, but its molar absorptivity is low. The overlap integral can be seen in Fig. 3b. Although the overlap is effectively small, the characteristic distance  $R_0$ , where  $\Phi_{\text{FRET}} = 0.5$  corresponds to 8.36 Å (Fig. 3c). This distance is close to the typical distance between the Ru center and the xanthene moiety of MAPNRhod based on a lowest-energy conformation computed using the extended Hückel method, and which was only taken as an approximate reference value.

Fig. 4 shows the complete Jablonsky diagram for RuBiMAPNRhod, in which the photons can be absorbed both by the <sup>1</sup>MLCT Ru–bpy band and by the Rhod. If a high energy (blue) photon causes a <sup>1</sup>MLCT transition, the subsequent evolution of the system will be the classical Ru–bpy photochemistry. The rhodamine ligand can also absorb low energy (green) photons, making a transition to the excited state MAPNRhod\*. This excited state can decay through radiative (fluorescence) or non-radiative paths or it might transfer its energy to the Ru center



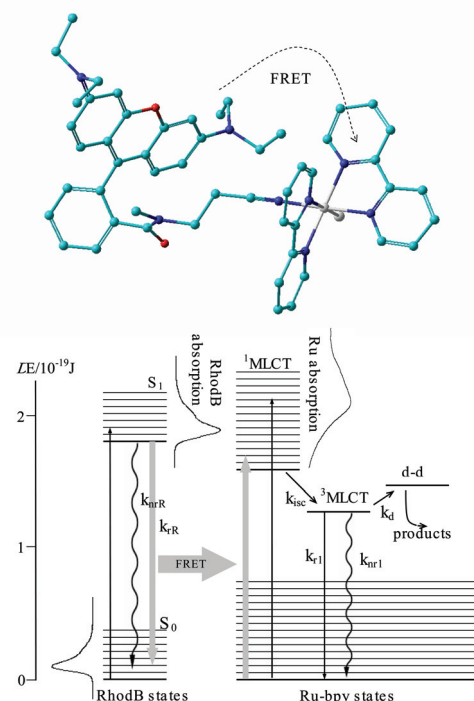
**Fig. 3** (a) Left: absorption of RuBiMAPN, right: fluorescence of MAPNRhod, area normalized to unity (b) overlap  $J$  integral of curves in a. (c) FRET efficiency vs. distance obtained from the data in a and b.

through FRET, populating its excited states and eventually releasing the ligand which in this case is MAPNRhod itself.

Under these assumptions, some quantitative estimates can be done. The modified MAPNRhod ligand presents an emission quantum yield of  $\Phi_{\text{MAPNRhod}} = 0.51$  measured in ethanol. This is somewhat lower than the value reported for Rhod ( $\Phi_{\text{Rhod}} = 0.70$ )<sup>11</sup> possibly due to the increased non-radiative decay through vibrational excitation of the  $\text{CH}_2\text{-CH}_2\text{-CN}$  tail. This value corresponds to the ratio  $k_{\text{r}}/(k_{\text{r}} + k_{\text{nr}})$  where  $k_{\text{r}}$  and  $k_{\text{nr}}$  are the radiative and non-radiative rate constants, respectively.

After coordination to the acceptor Ru center, the emission of MAPNRhod decreases dramatically to  $\Phi_{\text{RuBiMAPNRhod}} = 0.08$ . This decrease in fluorescence can be ascribed to additional non-radiative relaxation (a higher  $k_{\text{nr}}$ ) and to FRET ( $k_{\text{FRET}}$ ). If we assume that the non-radiative relaxation probability does not change significantly upon coordination, then  $\Phi_{\text{FRET}} = k_{\text{FRET}}/(k_{\text{FRET}} + k_{\text{nr}} + k_{\text{r}})$  can be calculated as  $1 - (\Phi_{\text{RuBiMAPNRhod}}/\Phi_{\text{MAPNRhod}}) = 0.84$ . This FRET efficiency corresponds to a distance  $r = 6.2 \text{ \AA}$ , within 15% of the estimated Ru–xanthene separation.

Using RuBiMAPN parameters for an estimation of photorelease quantum efficiency of the Ru–bpy center, the maximum expected quantum yield of ligand photorelease from MAPNRhod photon capture is  $\Phi_{\text{pr}} = \Phi_{\text{FRET}} \times \Phi_{\text{pr}}(\text{RuBiMAPN}) = 0.84 \times 0.145 = 0.122$ . The experimental value is  $\Phi_{\text{pr}} = 0.070$ , indicating that some other processes are needed to account for the extra energy decay in the Ru–bpy center. It is very common that big ligands (such as MAPNRhod) increase the non-radiative



**Fig. 4** Top: a molecular diagram showing the excited MAPNRhod inducing a Ru–bpy MLCT transition. Bottom: Scheme of states of RuBiMAPNRhod. A photon absorbed by the MAPNRhod ligand yields its singlet excited state. This energy is transferred to the main Ru–bpy photochemical pathway, leading to photodecomposition. “FRET” refers to Förster-type energy coupling between the two parts of the molecule.

relaxation in the excited Ru–bpy states by allowing extra vibrational modes and increased interaction with the solvent. It is also possible that MAPNRhod is recaptured more efficiently than MAPN, as the latter is probably more efficiently solvated.

### 3. Experimental

All reagents were purchased from Sigma-Aldrich and were used as received.  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  was synthesized according to the literature using water as solvent.<sup>12</sup>

#### 3.1 Photochemical, UV-Vis spectra and quantum yield measurements

The optical bench has a spectrophotometer for absorbance measurements, together with light sources mounted in a conventional configuration for fluorescence measurements (see ESI†). Absorption and emission spectra were measured with an Ocean Optics PC2000 diode-array spectrometer running OOChem software, recording both reaction kinetics at single absorption wavelengths and complete absorption or emission spectra. Quantum yield measurements were performed using a stirred, temperature stabilized (25 °C) four-faced cuvette. Rhodamine B was used as a fluorescence standard to calibrate emission quantum yield measurements ( $\Phi_{\text{r}} = 0.31$  in aqueous solutions). The fluorescence quantum yield of the complex was obtained directly from the ratio of the spectral areas, which present the

same shape. The photo-uncaging quantum yield measurements were performed with a Nd : YAG diode pumped solid state laser doubled to 532 nm with a constant power of 6.97 mW. Irradiation light was collimated and sent through a stirred, fluorescence glass cuvette with a 1 cm optical path perpendicular to the light collector path. Total irradiation energy was measured using a Coherent Fieldmaster FM light meter with a visible light photodiode model SR45. For a typical photolysis measurement, lab lights were dimmed, and the reactants solution was allowed to reach thermal equilibrium for 10 min while stirring inside the air-tight cuvette in the dark. Spectra were recorded usually once per second before, during, and after laser irradiation. Reaction progress was calculated by reconstructing each measured absorption spectrum as a linear combination of the absorption spectra of the reactants and of the products (for RuBiMAPN) and by the ratio of the measured emission spectral area to the expected emission spectral area (for RuBiMAPNRhod). UV-Vis spectra were acquired with a HP8453 diode-array spectrophotometer. Fluorescence emission measurements were made with a PTI Quantamaster spectrofluorometer, corrected for the instruments response function. NMR spectra were obtained with a 500 MHz Bruker AM-500.

### 3.2 Syntheses

Rhodamine B-methylaminopropionitrileamide (MAPNRhod) and  $[\text{Ru}(\text{bpy})_2(\text{L}_1)\text{Cl}]\text{PF}_6$ , ( $\text{L}_1 = \text{MAPNRhod}$ ) were synthesized according to the literature.<sup>7</sup> The analogue complex  $[\text{Ru}(\text{bpy})_2(\text{L}_2)\text{Cl}]\text{PF}_6$ , ( $\text{L}_2 = \text{MAPN}$ ) was synthesized as described<sup>7</sup> using MAPN instead of VACN.

## 4. Conclusions

In brief, this new mechanism found in a rhodamine-enhanced ruthenium phototrigger opens a full set of possibilities for designing Ru-bpy sensitizers, based in rhodamine and possibly other fluorescent dyes (fluoresceins, rhodols, etc.) The coordination of the fluorophore through a photoinert group (*i.e.* a phosphine) as auxiliary ligand may extend the spectral range of photorelease of other molecules to longer wavelengths.

As the photochemistry of uncaging is the same as that of energy conversion, it is expected that harvesting light through a rhodamine or similar center could also be used to extend the wavelengths at which Ru-based dye sensitized solar cells (DSSC) are effective. Further research in these topics is under development.

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