

COMMUNICATION

Quenching of the Phosphorescence of Thermally Reversible Photochromic Naphthopyran Re(I) Complexes Initiated by either Visible or Ultraviolet Radiation

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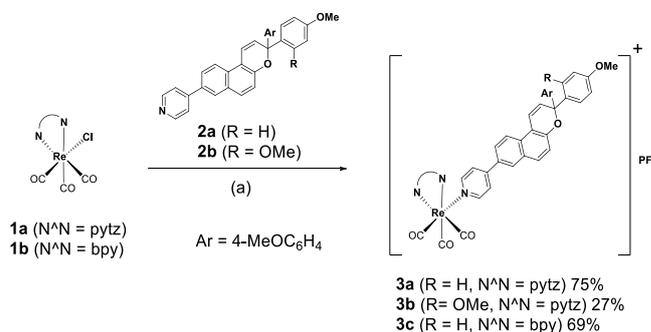
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Re(I) complexes bearing thermally reversible photochromic naphthopyran axial ligands undergo highly efficient, reversible phosphorescence quenching actuated by either visible or UV irradiation. The photoinduced quenching of the triplet metal-to-ligand charge-transfer (³MLCT) emission is interpreted based on changes in the relative energies of the excited states.

The development of transition metal (TM) complexes that incorporate photochromic ligands has received significant interest in the last two decades.¹ Incorporation of the photochromic moiety either by coordination to the metal centre or by covalently binding it to a coordinated ligand has been shown to perturb the photochromic properties.² Additionally, the photochromic reaction has been reported to modulate and/or switch the luminescence of the transition metal complexes. Photoresponsive ligands, activated by UV irradiation, employed to date include dithienylethenes,³ azobenzenes,⁴ spirooxazines,⁵ viologens⁶ and a selection of metal centres including Co,⁷ Zn,⁸ Mo,⁹ Ru,¹⁰ Rh,¹¹ Pd/Pt,¹² Ag,¹³ Cd,¹⁴ Re,¹⁵ Ir,¹⁶ Au,¹⁷ have been investigated. Thermally reversible, UV activated photochromic naphthopyrans, whilst established in ophthalmic sunlenses and variable transmission filters,¹⁸ remain unexplored as photoresponsive ligands to modulate the luminescence of TM complexes. Herein, we describe the synthesis and photophysical properties of the first Re(I) complexes containing 3*H*-naphtho[2,1-*b*]pyrans (NP) as photochromic ancillary ligands that allow the highly efficient, reversible off/on switching of the metal complex phosphorescence remarkably triggered by visible light, or more routinely by UV irradiation, leading to a dual wavelength photoswitching system.

By taking advantage of the *trans* influence, the chloride ligand of the *fac*-[Re(N[^]N)(CO)₃Cl]⁰ complexes **1a** [N[^]N = 1-benzyl-4-(2-pyridyl)-1,2,3-triazole (pytz)] and **1b** [N[^]N = 2,2'-bipyridine (bpy)] was substituted¹⁹ by the 8-(4-pyridyl)-3*H*-naphtho[2,1-*b*]pyrans **2a** and **2b**, the latter prepared by our literature protocol,²⁰ in the presence of AgPF₆, affording the *fac*-[Re(N[^]N)(CO)₃NP]⁺ complexes **3a–3c** (27–75% yield). Characterization by NMR, HRMS and FT-IR was supplemented by an X-ray crystal structure for **3c** that confirmed the approximately octahedral geometry of the rhenium centre and the *facial* configuration of the carbonyl ligands.



Scheme 1 Reagents and conditions: (a) AgPF₆, DCM, dark, N₂, rt.

Complexes **3a–3c** produced pale yellow solutions in acetonitrile with a broad absorption band centred at 346–350 nm with large $\epsilon = 1.6\text{--}3.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ (Table 1 and Fig. 1). For **3a**, the two lowest dipole-allowed transitions found in the vertical TD-DFT spectrum are located at 382 nm [$f = 0.004$] and 390 nm [$f = 0.334$], corresponding respectively to a HOMO (NP) to LUMO (pytz) transition with a small HOMO-3 (Re) to LUMO (pytz) contribution, and to a HOMO (NP) to LUMO+1 (NP/py) excitation (Fig. S56). The difference between theory (390 nm) and experiment (350 nm), ca. 0.35 eV, is quite usual for this level of theory and the selected functional. For **3c**, the two lowest dipole-allowed transitions are located at 390 nm [$f = 0.329$, HOMO (NP) to LUMO+1 (NP/bpy)] and 430 nm [$f = 0.001$, HOMO (NP) to LUMO (bpy)] (Fig. S57).

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Table 1 Summary of photophysical data of the *fac*-[Re(N[^]N)(CO)₃NP]⁺ complexes **3a–3c** in degassed acetonitrile.

	$\lambda_{\max}^{[a]}/\text{nm}$ ($\epsilon^{[b]}/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{em}}^{[c]}/\text{nm}$ ($\lambda_{\text{exc}}^{[d]}/\text{nm}$)	$\Phi_{\text{em}}^{[e]}/\%$ (τ/ns)	$\lambda_{\text{PSS}}^{[f]}/\text{nm}$	$\Delta A_{\text{Conc}}^{[g]}/\text{M}^{-1}$	$k_{\Delta}^{[h]}/\text{s}^{-1}$ (Amplitude/%)	$t_{1/2}^{[i]}/\text{s}$	EQ ^[j] /%
3a	350 (3.3×10^4)	490 (392)	0.8 (4, 71, 551)	490	2.7×10^4	3.6×10^{-1} (2) 1.3×10^{-4} (98)	5531	85 ^[l]
3b	346 (1.6×10^4)	500 (382)	0.6 (5, 74, 469)	490	1.4×10^4	5.7×10^{-1} (36) 3.0×10^{-4} (64)	1165	87 ^[k] 79 ^[l]
3c	350 (1.6×10^4)	603 (394)	0.2 (7, 36, 280)	490	1.0×10^4	7.4×10^{-1} (3) 3.2×10^{-4} (97)	2034	12 ^[k]

[a] λ_{\max} = maximum wavelength of absorption. [b] ϵ = molar attenuation coefficient. [c] λ_{em} = maximum wavelength of emission. [d] λ_{exc} = excitation wavelength. [e] Φ_{em} = quantum yield of emission. [f] λ_{PSS} = maximum wavelength of absorption at the PSS. [g] ΔA_{Conc} = colour generated at the photostationary state after continuous UV irradiation of 1 molar of a given photochrome in solution, calculated as $\Delta A/\text{Concentration}$, ΔA being the induced optical density at λ_{PSS} . [h] k_{Δ} = thermal bleaching rate constant. [i] $t_{1/2}$ = thermal bleaching half-life. [j] EQ = emission quench (%) calculated as the ratio of the intensity of emission at λ_{em} of the PSS and closed-form. [k] after UV irradiation (365 nm, P_{lamp} 8 W, 1 min). [l] after visible light irradiation (405 nm, P_{lamp} 1 mW, 1 min).

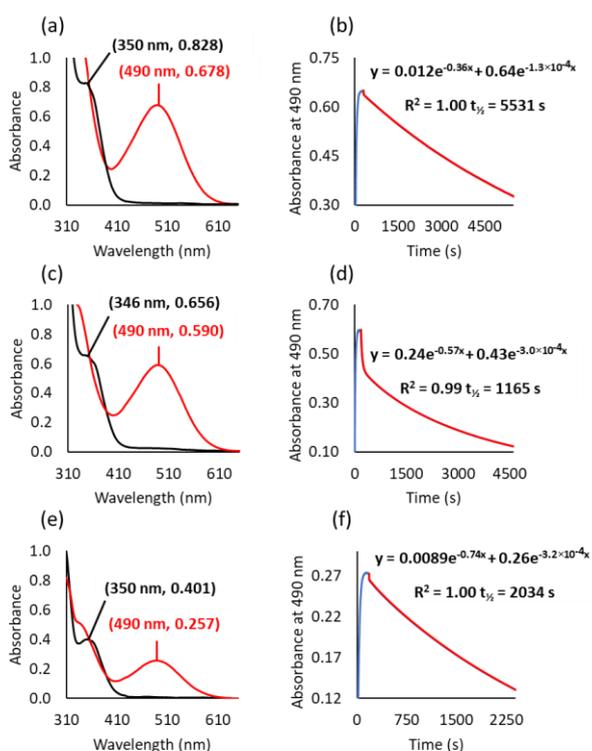


Fig. 1 (a) UV-Vis absorption spectra of **3a** (black, 0.025 mM) and corresponding PSS (red, λ_{irr} 325 nm, P_{lamp} 150 W, 5 min). (b) Bi-exponential fit of absorbance of PSS from **3a** at 490 nm in the dark = $f(t)$. (c) UV-Vis absorption spectra of **3b** (black, 0.042 mM) and corresponding PSS (red, λ_{irr} 325 nm, P_{lamp} 150 W, 3 min). (d) Bi-exponential fit of absorbance of PSS from **3b** at 490 nm in the dark = $f(t)$. (e) UV-Vis absorption spectra of **3c** (black, 0.025 mM) and corresponding PSS (red, λ_{irr} 325 nm, P_{lamp} 150 W, 3 min). (f) Bi-exponential fit of absorbance of PSS from **3c** at 490 nm in the dark = $f(t)$. All in degassed acetonitrile.

The highest lying MO of strong M character is HOMO-3 that plays a minor role in the 430 nm band (<10 %) but dominates in a weak band at 389 nm [$f = 0.002$] likely underneath the main 390 nm absorption. Evidently, excitation at the broad

absorption band centred at ca. 350 nm of Re(I) complexes **3a–3c** directly triggers a strong intra-ligand (IL) transition that has a CT character from the NP core to the pyridine moiety, besides a weak transition of metal-ligand-to-ligand charge-transfer (MLL'CT) character²¹ in which the electron density is displaced from the π system of the whole Re(CO)₃NP to the π^* system of the electron-accepting bidentate ligand (N[^]N).

Upon excitation at 382–394 nm, structureless and broad emission bands centred at 490 nm (**3a**), 500 nm (**3b**) and 603 nm (**3c**) are observed in degassed acetonitrile, with Φ_{em} of 0.8, 0.6 and 0.2%, respectively (Table 1 and Fig. 2a). The decay of emission was fitted to a triexponential model with lifetimes $\tau_1 = 4\text{--}7$ ns, $\tau_2 = 36\text{--}74$ ns and $\tau_3 = 280\text{--}551$ ns (Table 1 and Fig. S43). Furthermore, the emission bands undergo a significant bathochromic shift with increasing solvent dielectric constant (Fig. 2b). Considering, the sensitivity of the emission energies to the electronic nature of the bidentate ligands, the moderately long emission lifetimes²² and the pronounced emission solvatochromism,²³ the emission bands of **3a** and **3b** were assigned as being triplet metal-to-ligand charge-transfer (³MLCT) [$d\pi(\text{Re}) \rightarrow \pi^*(\text{pytz})$] phosphorescence.²⁴ In both **3a** and **3c**, vertical TD-DFT returns three triplets below the lowest singlet at the FC geometry, so intersystem crossing (ISC) is possible to those three states. Nevertheless, for **3a** only one triplet state could be located and minimized with U-DFT (Fig. S58). This triplet presents a 0-0 wavelength at 650 nm, and exhibit a dominant IL character. The observed emission is therefore arising from a higher triplet of MLCT character, the emission being ineffective consistent with the poor Φ_{em} , as compared to other *fac*-[Re(pytz)(CO)₃L]⁺ complexes,²⁵ which is a consequence of internal conversion (IC) to the lower-lying IL triplet state. The tailing of the recorded emission bands to lower energy, particularly notable for **3b**, may be attributed to weak mixed emission arising from triplets of IL character. This claim is supported by (i) the multiexponential fit of the emission decay suggesting the existence of multiple emissive events, including long-lived phosphorescent emission from triplets of MLCT and IL character, and short-lived fluorescent emission from the singlet excited state and (ii) by the excitation profiles recorded

for **3a** and **3b** (Fig. 2c and 2d). Thus, the emission centred at 490–500 nm derives from an excitation band centred at 358–362 nm, matching closely with the theoretical MLL'CT transition at 382 nm. While the emission at 650 nm derives from a bathochromic-shifted excitation band centred at 383–390 nm, assigned as the IL transition (390 nm according to theory). For **3c**, two triplet states could be located and minimized with U-DFT, the first of ligand-to-ligand charge transfer (LLCT) character and the second of IL character (Fig. S59). For the former a 0-0 phosphorescence wavelength of 587 nm was computed. For the latter, the corresponding value is 653 nm. Considering the position of emission maximum at lower energy, it is predicted that the emission band of **3c** centred at 603 nm (see Fig. 2a) to be highly mixed and derived from emission of triplets of MLCT, LLCT and IL character.

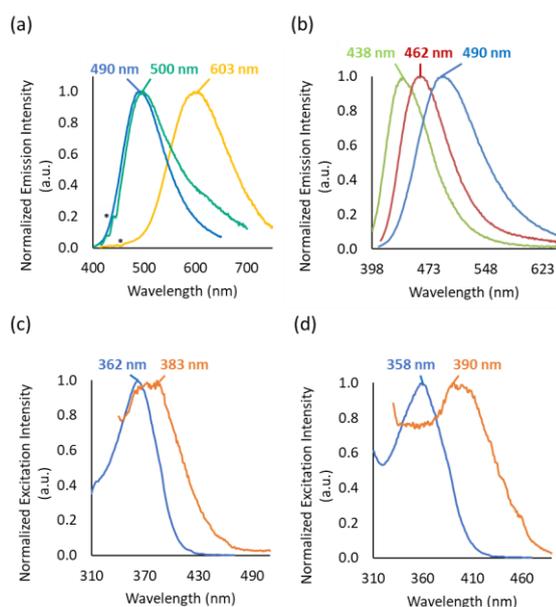
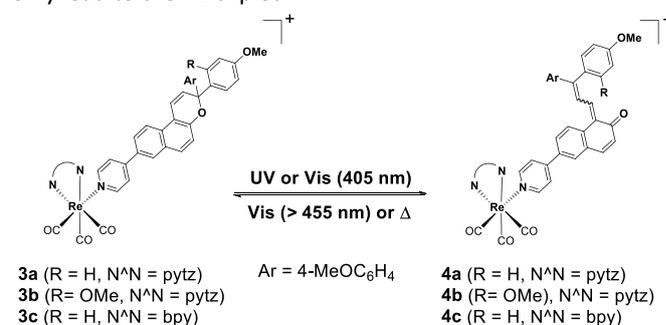


Fig. 2 (a) Normalized corrected emission spectra of **3a** (blue, 0.019 mM, λ_{exc} 392 nm), **3b** (cyan, 0.013 mM, λ_{exc} 382 nm) and **3c** (yellow, 0.023 mM, λ_{exc} 394 nm) in degassed acetonitrile. (b) Normalized corrected emission spectra of **3a** (green, 0.034 mM in degassed toluene, λ_{exc} 388 nm), **3a** (red, 0.016 mM in a degassed mixture of dichloromethane:toluene (1:1), λ_{exc} 394 nm) and **3a** (blue, 0.019 mM in degassed acetonitrile, λ_{exc} 392 nm). (c) Normalized corrected excitation spectra of **3a** (0.025 mM in degassed acetonitrile) for emission at 490 nm (blue) and for emission at 650 nm (orange). (d) Normalized corrected excitation spectra of **3b** (0.042 mM in degassed acetonitrile) for emission at 490 nm (blue) and for emission at 650 nm (orange). *Raman scattering.

The Re(I) complexes **3a–3c** exhibit UV-triggered photochromism affording red coloured solutions as a consequence of electrocyclic ring-opening of the pyran moiety (Fig. 1, Scheme 2). A photostationary state (PSS) could be established after only 20 s of continuous UV irradiation (λ_{irr} 365 nm, P_{lamp} 8 W). Unlike the typical phototochromism of naphthopyrans, including **2a,b** which exhibit photochromism when activated by UV radiation only;²⁶ it is remarkable that the photochromic process of the complexes **3a–3c** can be triggered by irradiation with visible

light (λ_{irr} 400–450 nm). This phenomenon is justified by the perturbation of the IL transition by coordination to the metal centre,²⁷ which led to a bathochromic shift of the absorption band that tailed into the visible region. The photochromic reactions were accompanied by the evolution of intense and broad absorption bands centred at 490 nm. The coloured PSS faded to the original colourless state either thermally or by assisted visible light irradiation ($\lambda_{irr} > 455$ nm). Bleaching in the dark followed a bi-exponential decay, typical of naphthopyran systems,²⁸ with a first and second thermal bleaching rate constants in the order of $10^{-1} s^{-1}$ and $10^{-4} s^{-1}$, respectively (Fig. 1 and Table 1). For **4a** and **4c**, theory predicts the existence of a strong absorption band in the visible centred at 528 nm [$f = 1.024$] and 532 nm [$f = 1.031$], respectively, of pure HOMO (NP) to LUMO (NP) character, correlating well with the experimental data (Fig. S60 and S61). In the vertical excitation spectra, only one lower triplet of the same 3IL character can be found below the lowest singlet, i.e., triplet states of other character are higher than the lowest singlet in **4a** and **4c**, meaning that ISC will only lead to the 3IL triplet.



Scheme 2 Photoisomerization of Re(I) complexes **3a–3c**.

Notably, the photochromic reaction led to efficient reversible photoquenching of the 3MLCT [$d\pi(Re) \rightarrow \pi^*(N^{\wedge}N)$] phosphorescence. This phenomenon was particularly evident for **3a** and **3b** in which 85% (λ_{em} 490 nm) and 87% (λ_{em} 500 nm) of the 3MLCT [$d\pi(Re) \rightarrow \pi^*(pytz)$] phosphorescence was quenched after generation of the PSS with UV irradiation (λ_{irr} 365 nm) (Table 1, Fig. 3). For **3c** (Table 1, Fig. S51), the photoquenching of the vertical emission at 603 nm was comparatively smaller (12%), likely a result of the highly mixed triplet character of the emission band. Remarkably, the quenching of the 3MLCT [$d\pi(Re) \rightarrow \pi^*(pytz)$] phosphorescence could also be achieved by visible light irradiation (λ_{irr} 400–450 nm), exemplified for **3b** which displayed a vertical quench of emission at 500 nm of 79%. In the photomerocyanines, T_1 is strictly located on the ligand and it is very low in energy according to theory (ca. 1.4 eV). It is also the only triplet below the lowest singlet (S_1). This contrasts with the naphthopyrans, in which three triplets (including the emissive 3MLCT excited state) can be found below S_1 (*vide supra*). In the naphthopyrans, ISC can first populate higher energy emissive triplet states (T_3 , T_2) that could then either emit a photon or IC to the dominant T_1 . In the photomerocyanines, emission quenching is achieved by fast population of S_1 by IC followed by ISC to the only and dominant non-emissive (*energy gap law*) T_1 . Remarkably, for **3b** the original cyan luminescence is absent in solution at the PSS (Fig. 3 cuvette images), being replaced by a very

faint red luminescence which may be derived from an inefficient ISC between a higher S_n and a higher T_n of the photomerocyanine **4b**. Bleaching of the colour of the solutions of the PSS either thermally or with visible light, is accompanied by the regeneration of **3a–3c**, and restoration of the initial luminescence. Moreover, these absorbance and emission changes are reversible over at least ten photochromic cycles under degassed conditions (Fig. S32, S35, S48 and S50).

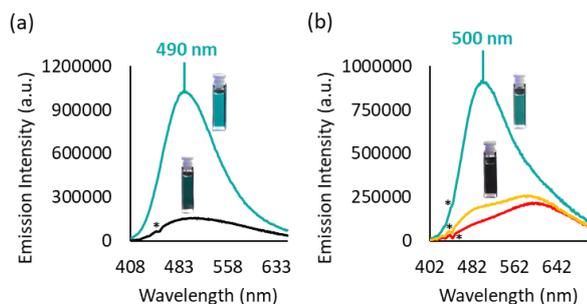


Fig. 3 (a) Corrected emission spectra of **3a** (cyan, 0.019 mM) and the PSS (black), λ_{exc} 392 nm – PSS reached after UV irradiation (λ_{irr} 365 nm, P_{lamp} 8 W, 1 min). (b) Corrected emission spectra of **3b** (cyan, 0.042 mM) and the PSS, λ_{exc} 382 nm – Yellow, PSS after visible light irradiation (λ_{irr} 405 nm, P_{lamp} 1 mW, 1 min); Red, PSS after UV irradiation (λ_{irr} 365 nm, P_{lamp} 2 W, 1 min). All in degassed acetonitrile. *Raman scattering.

In summary, we have shown that the emission from the novel *fac*-[Re(N^{^N})(CO)₃NP]⁺ complexes **3a–3c** arises from a ³MLCT excited state mixed in variable extent with emission from triplets of other characters. Complexes **3a–3c** exhibit photochromism at room temperature initiated by either visible light irradiation (λ_{irr} 400–450 nm) or by UV irradiation; such dual wavelength actuation of a naphthopyran system is both unique and remarkable. Of note is the ability to affect the bleaching both thermally and photochemically, the latter taken with visible light actuation, instead of higher energy UV,²⁹ provides an advantageous example of a low energy switching system. The UV or visible light generated PSS are accompanied by up to 87% quenching of the ³MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$] phosphorescence. The absorbance and emission changes exhibit fatigue resistance over at least ten cycles under degassed conditions. The novel *fac*-[Re(N^{^N})(CO)₃NP]⁺ complexes constitute a unique example of thermally reversible photochromes applied to the photoquenching of phosphorescence operational by either visible light or UV actuation.

Author Contributions

All authors contributed equally to this work. O. De Azevedo thanks the University of Huddersfield for funding this project and Thomas Broadbent for the acquisition of the photographs. D. Jacquemin is indebted to the CCIPL computational centre installed in Nantes for generous allocation of computational resources.

Conflicts of interest

There are no conflicts to declare.

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