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Highly-phosphorescent tungsten(0) carbonyl pyridyl-imidazole complexes as photosensitisers†

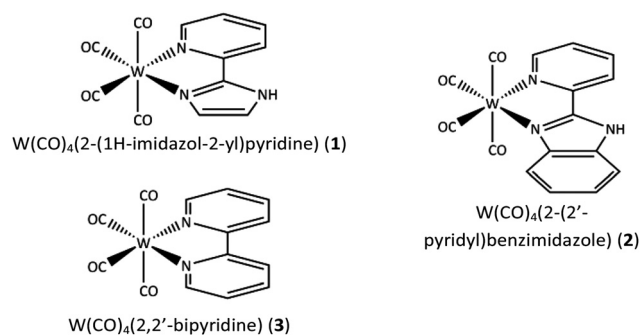
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Photoluminescence data are reported for two $W(CO)_4L$ complexes ($L = 2-(1H\text{-imidazol-2-yl})pyridine$ and $2-(2'\text{-pyridyl})benzimidazole$) in room-temperature solutions. The bidentate ligands consist of a pyridine and an imidazole moiety connected by a C–C bond. The complexes have been found to exhibit enhanced phosphorescence from the metal-to-ligand charge transfer (MLCT) excited state with quantum yields in the order of 10^{-3} , almost two orders of magnitude higher than those reported for $W(CO)_4(\text{diimine})$ complexes. One of the complexes $W(CO)_4(2-(2'\text{-pyridyl})benzimidazole)$ can serve as an efficient visible-light photosensitiser for the isomerisation of aromatic alkenes with efficiency comparable to and even exceeding that of the well-studied ruthenium tris-bipyridine complex, $Ru(bpy)Cl_2$.

Introduction

The phosphorescence of transition metal complexes such as $[Ru(bpy)_3]Cl_2$ and $Ir(ppy)_3$ in solutions has been studied in detail with their quantum yields determined to be in the order of 10^{-3} to 0.1.^{1–10} Studies^{11–17} have found that a few tungsten(0) carbonyl complexes, $W(CO)_4L$ and $W(CO)_5L$, can also exhibit phosphorescence in solutions when the lowest-lying excited state is of MLCT (metal-to-ligand charge transfer) character. In these tungsten complexes, radiative deactivation from the excited state is slow, and competing photodissociation of the ligand also has a relatively low quantum yield. Notably, Manuta and Lees¹¹ studied the photoluminescence of $W(CO)_4(\text{diimine})$ complexes (diimine = bipyridine (bpy) and its derivatives such as 4,4'-Me₂bpy, phen, 4-Me-phen, 5-Cl-phen) originating from the MLCT excited state in room-temperature solutions. The emission maxima lie between 550 and 800 nm with quantum yields in the order of 10^{-5} and emission lifetimes in the order of 10^{-7} s.

The bidentate ligands used for coordination to the tungsten centre have been mostly confined to bpy derivatives. In this work, we explore two tungsten(0) carbonyl complexes **1** and **2** comprising bidentate ligands that incorporate a pyridine and an imidazole moiety (Scheme 1). One of the goals is to continue to improve the phosphorescence quantum yields of these earth-abundant metal complexes in order to rival the



Scheme 1 Tungsten(0) carbonyl complexes studied.

likes of the more expensive ruthenium(II) and iridium(III) complexes. The luminescence properties of these ligands when coordinated to other metal centres such as Ru(II), Os(II), Pt(II) or Re(I) have been studied previously.^{5,6,18–20} Complex **3** (Scheme 1) was also prepared for comparison purposes since the spectroscopic properties of its $W(CO)_4(\text{diimine})$ family of complexes have been well-studied. We report the luminescence properties of these tungsten(0) carbonyl complexes and in particular their potential applications as photosensitisers in alkene isomerization.

Experimental

Materials

Tungsten carbonyl ($W(CO)_6$, 99%) was purchased from Strem Chemicals. 2-(1H-Imidazol-2-yl)pyridine ($C_5H_4NC_3N_2H_3$, 97%), 2-(2'-pyridyl)benzimidazole ($C_5H_4NC_7H_5N_2$, 97%), 2,2'-bipyridyl ($(C_5H_4N)_2$, 99%), *cis*-stilbene ($C_6H_5CH=CHC_6H_5$, 96%),

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trans- α -methylstilbene ($\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CHC}_6\text{H}_5$, 99%), α -phenylcinnamionitrile ($\text{C}_6\text{H}_5\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{CN}$, 99%) and cinnamyl alcohol ($\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$, 98%) were purchased from Sigma Aldrich. Cinnamyl bromide ($\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{Br}$, predominantly *trans*, 95%) was purchased from Alfa Aesar. Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, 99.95%) was purchased from Fluka Chemicals. Acetone (CH_3COCH_3 , $\geq 99.8\%$), toluene ($\text{C}_6\text{H}_5\text{CH}_3$, $\geq 99.5\%$) and ethyl acetate ($\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$, $\geq 99.5\%$) were purchased from VWR Chemicals. Acetonitrile (CH_3CN , $\geq 99.9\%$) was purchased from Anhui Fulltime Specialised Solvents & Reagents. Deuterated Chloroform-D (CDCl_3 , 98%) was purchased from Cambridge Isotope Laboratories. All solvents and reagents were used without further purification.

Syntheses of $\text{W}(\text{CO})_4\text{L}$ complexes. $\text{W}(\text{CO})_4\text{L}$ complexes were prepared in acetone by irradiating tungsten hexacarbonyl, $\text{W}(\text{CO})_6$ and 1.5 to 2 equivalents of L for 2 hours. Freeze-pump-thaw degassing of the solution was carried out three times prior to photolysis. After reaction, acetone was removed by rotary evaporation. The remaining solid was redissolved in ethyl acetate and purified by column chromatography on silica gel. The product solution collected was then put through rotary evaporation to isolate the product.

$\text{W}(\text{CO})_4\text{-(1H-imidazol-2-yl)pyridine}$ (1): ν_{CO} = 2004 (m), 1883 (m), 1870 (sh), 1830 (s) cm^{-1} . ESI-MS (m/z): 441.7 (M^+).

^1H NMR. δ (CHCl_3): 8.9–9.1 (d, 1H), 8.1–8.3 (m, 2H), 7.66 (s, 1H), 7.45–7.55 (m, 1H), 7.38 (s, 1H).

Anal. calc. C, 32.68 H, 1.6 N, 9.53 W, 41.68. Found. C, 32.19 H, 1.99, N, 9.43 W, 42.28.

$\text{W}(\text{CO})_4\text{-(2'-pyridyl)benzimidazole}$ (2): ν_{CO} = 2005 (m), 1887 (s), 1870 (sh), 1829 (m) cm^{-1} . ESI-MS (m/z): 491.7 (M^+).

^1H NMR. δ (CHCl_3): 9.1–9.2 (d, 1H), 8.45–8.55 (d, 1H), 8.2–8.4 (t, 1H), 7.85–7.95 (m, 1H), 7.75–7.85 (m, 1H), 7.65–7.75 (t, 1H), 7.5–7.55 (m, 2H).

Anal. calc. C, 39.13 H, 1.85 N, 8.56 W, 37.43. Found. C, 38.67 H, 2.16 N, 8.57 W, 37.72.

$\text{W}(\text{CO})_4\text{(2,2'-bipyridine)}$ (3): ν_{CO} = 2007 (m), 1892 (s), 1877 (sh), 1835 (m) cm^{-1} . ESI-MS (m/z): 450.8 (M^+).

^1H NMR. δ (CHCl_3): 9.0–9.1 (d, 2H), 8.65–8.75 (d, 2H), 8.2–8.3 (m, 2H), 7.6–7.7 (m, 2H).

Anal. calc. C, 37.18 H, 1.77 N, 6.20 W, 40.69. Found. C, 37.42 H, 1.82 N, 6.17 W, 40.40.

Equipment and procedures

Photolysis experiments for the syntheses of $\text{W}(\text{CO})_4\text{L}$ complexes were conducted using a Legrand broadband lamp (200–800 nm, 11 W). Fourier Transform Infrared (FT-IR) spectra were acquired with liquid samples in CaF_2 windows cell of 0.1 mm path length using a Shimadzu IR Prestige-21 spectrometer. Electrospray Ionisation (ESI) was conducted using Finnigan MAT LCQ spectrometer. ^1H nuclear magnetic resonance (NMR) spectra were recorded with Bruker AMX 300 NMR spectrometer at room temperature, using CDCl_3 calibrated to its chemical shift.

In the absorption and photoluminescence studies, each sample was prepared by dissolving the complex of interest in a

desired solvent, then transferred to a quartz cell of 1 cm path length and deaerated by nitrogen purging for 10 min. UV-vis absorption spectroscopy was carried out using a Shimadzu UV-2450 spectrometer. Photoluminescence spectroscopy was conducted using a Horiba Fluoromax-4 spectrophotometer. Emission quantum yields were determined using $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as a reference standard. Time-resolved photoemission spectroscopy was recorded with a Horiba Fluorolog-3 spectrophotometer, using 374 nm, 240 ps pulses; 438 nm, 260 ps; or 483 nm, 205 ps pulses from various laser excitation sources (nanoLEDs).

For the photosensitization experiments involving isomerisation of alkenes, an alkene substrate and one of the tungsten complexes or $\text{Ru}(\text{bpy})_3\text{Cl}_2$ were stirred in a glass vial filled with 10 mL of a suitable solvent at room temperature under visible light irradiation using 24 W compact fluorescent lamp (400 nm to 800 nm) for a stipulated duration. Thereafter, ^1H NMR spectroscopy was used to analyse the resultant mixture containing both products and reactants.

Results & discussion

Photoluminescence studies

The UV-visible absorption and emission spectra of complex 1 in toluene at room temperature are illustrated in Fig. 1a. The absorbance band at $\lambda_{\text{abs,max}}$ = 460 nm is assigned to a low-lying MLCT transition as the band is found to be highly solvent-dependent; with blue-shifts up to 60 nm in more polar solvents (see Table 1). Similar solvent effects were also previously observed for the MLCT of $\text{W}(\text{CO})_4(\text{diimine})^{11,21,22}$ and $\text{W}(\text{CO})_5\text{L}^{12}$ complexes. Correspondingly, excitation at λ_{exc} = 460 nm generates an emission band with $\lambda_{\text{em,max}}$ = 590 nm. The emission lifetime (τ) of this band in toluene has also been measured to be 142 ns, which is in the same order of magnitude as the lifetimes reported for phosphorescence of $\text{W}(\text{CO})_4(\text{diimine})$ complexes^{11,23} in room-temperature solutions (Fig. 1b).

The observed emission is attributed to phosphorescence arising from the $^3\text{MLCT}$ excited state of complex 1 with the quantum yield (ϕ) estimated to be 8×10^{-3} when calibrated to the well-known standard. Similar results were also obtained for complex 2, where the phosphorescence quantum yield is 4×10^{-3} (see Table 2 and Fig. 2). In addition, both absorption and emission bands of 1 and 2 appear to consist of one component in contrast to those of $\text{W}(\text{CO})_4(\text{diimine})$ complexes which show at least two overlap components made up of the y - and z -polarized transitions respectively.¹¹ The emission spectra of the two complexes were also different in wavelength compare to those originating from their respective ligands, hence verifying that these emissions indeed arise from the complexes and not from the ligands (see ESI†).

Further observations can be made when juxtaposing the photophysical parameters of 1 and 2 with those of complex 3 (Table 2).^{11,24} First, the emission maxima in complexes 1 and 2 are red-shifted from that in complex 3. The same observation

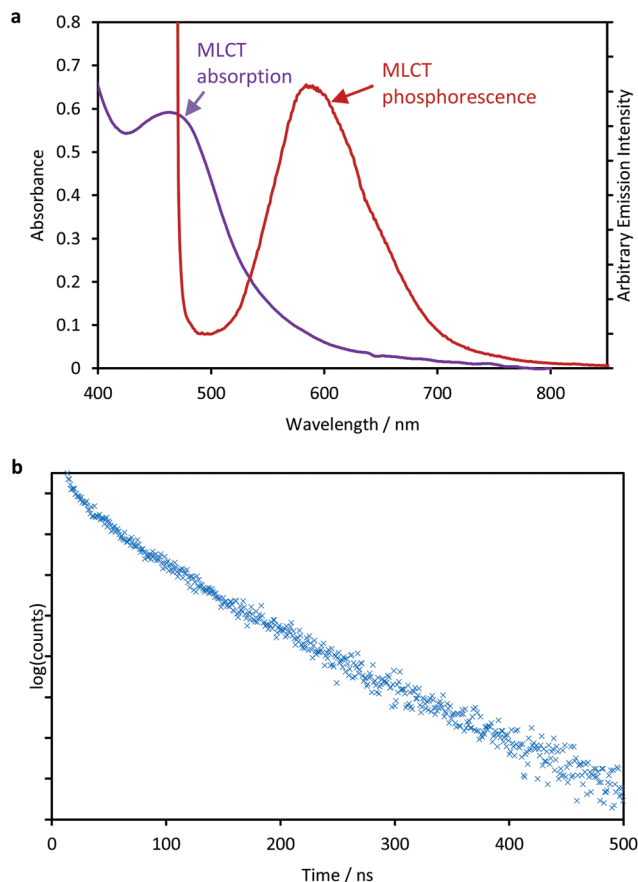


Fig. 1 (a) Absorption (—) and emission (—, $\lambda_{\text{ex}} = 460$ nm) spectra, and (b) emission decay (in log scale) of complex **1** in toluene at 298 K. The emission curve fits to a biexponential function with two lifetimes, 3.7 ns and 142 ns of relative amplitudes 0.13. The former lifetime corresponds to the lifetime of the excitation beam.

Table 1 MLCT absorption maxima of complexes **1** to **3** in various solvents at 298 K (ϵ = dielectric constant)

| Complex | Solvent | | | |
|----------|---------------------------------------|----------------------------------|--|----------------------------------|
| | Acetonitrile ($\epsilon = 37.5$) | Acetone ($\epsilon = 20.7$) | Dichloromethane ($\epsilon = 8.93$) | Toluene ($\epsilon = 2.38$) |
| 1 | 405 | 426 | 446 | 463 |
| 2 | 450 | 462 | 478 | 484 |
| 3 | 452 | 465 | 481 | 514 |

has previously been made between $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_2\text{L}]^{2+}$ where L is a pyridyl-imidazole derivative.^{5,18} Second and more significantly, the quantum yields of **1** and **2** are two orders of magnitude higher than that of complex **3**. Fig. 2 compares the intensity of the emission spectra of complexes **1**, **2** and **3**, where that of complex **3** has to be multiplied by a factor of 50 to be visible on the same scale.

The rate of intersystem crossing (ISC) between the singlet and triplet manifold within each complex also plays an important role. The non-radiative transition is largely driven by

Table 2 Photophysical parameters for complexes **1** to **3** in toluene at 298 K (ϵ = molar absorption coefficient $\text{M}^{-1} \text{cm}^{-1}$)

| Complex | MLCT | | | |
|----------|---|-------------------------------------|------------------|------------------|
| | $\lambda_{\text{abs,max}}/\text{nm}$ (ϵ) | $\lambda_{\text{em,max}}/\text{nm}$ | τ/ns | $\phi^a/10^{-3}$ |
| 1 | 463 (6800) | 590 | 142 ^b | 8 |
| 2 | 484 (7500) | 650 | 215 ^c | 4 |
| 3 | 514 (6200) | 560, 790 | 348 ^d | 0.05 |

^a Estimated relative to the emission of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. ^b Excited with 438 nm, 260 ps pulses. ^c Excited with 483 nm, 205 ps pulses. ^d Reported lifetime of $\text{W}(\text{CO})_4(4\text{-Me-Phen})$.¹⁰

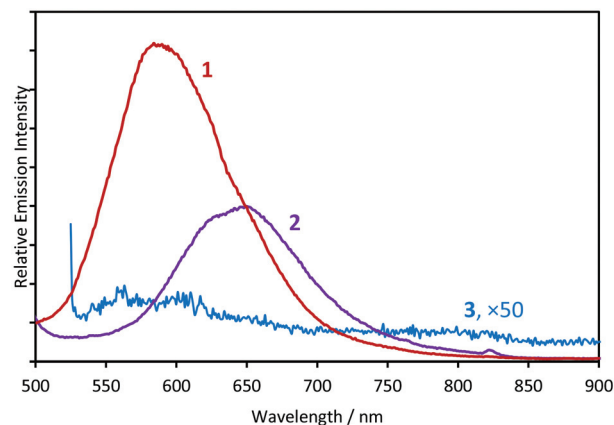


Fig. 2 Emission spectra of complexes **1** (—, $\lambda_{\text{ex}} = 460$ nm), **2** (—, $\lambda_{\text{ex}} = 480$ nm) and **3** (—, multiplied by factor of 50, $\lambda_{\text{ex}} = 515$ nm) in toluene at 298 K.

spin-orbit coupling (SOC), which is enhanced by the heavy tungsten atom. We posit that the rate of ISC could be much faster in **1** and **2** due to higher contributions of W in the MLCT states. In addition, SOC is expected to be more effective when orbitals involved in the electronic transition (*i.e.*, d orbitals on W and π orbitals on the ligand) are overlapping and spatially close. Compared to complex **2**, the ligand π orbitals in **1** are relatively more localized and stronger SOC effects could result in a higher rate of ISC and a subsequently higher quantum yield of emission. The explanation is also consistent with the observation of only very weak phosphorescence from **3** as its bipyridine ligands are expected to be most delocalised amongst the three complexes.

Photosensitisation

We are interested in finding potential applications for the synthesised tungsten complexes. There has been much research carried out on photoredox catalysis using iridium and ruthenium pyridine complexes.^{25–28} However non-redox photoprocesses such as alkene isomerization *via* excited triplet state energy transfer are less investigated. Fabry and co-workers²⁹ have used phosphorescent metal complexes such as $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as visible-light photosensitisers to isomerise alkenes into

Table 3 Isomerisation reactions of *trans*- and *cis*-stilbene with visible light irradiation

| Entry | Catalyst ^a | Substrate ^b | Solvent | Duration/h | Conversion ^c /% | TON ^d |
|-------|-----------------------|------------------------|--------------|------------|----------------------------|------------------|
| 1 | [Ru] | <i>trans</i> - | Acetonitrile | 18 | 94 | 6.3 |
| 2 | [Ru] | <i>cis</i> - | Acetonitrile | 18 | 4 | <1 |
| 3 | 1 | <i>trans</i> - | Toluene | 18 | 11 | <1 |
| 4 | 1 | <i>cis</i> - | Toluene | 18 | 9 | <1 |
| 5 | 2 | <i>trans</i> - | Toluene | 18 | 49 | 3.3 |
| 6 | 2 | <i>cis</i> - | Toluene | 18 | 31 | 2.1 |
| 7 | 2 | <i>trans</i> - | Toluene | 48 | 74 | 4.9 |
| 8 | 2 | <i>cis</i> - | Toluene | 48 | 26 | 1.7 |
| 9 | 2 | <i>trans</i> - | Acetonitrile | 18 | 78 | 5.2 |
| 10 | 2 | <i>cis</i> - | Acetonitrile | 18 | 21 | 1.4 |
| 11 | 3 | <i>trans</i> - | Toluene | 18 | 0 | — |
| 12 | 3 | <i>cis</i> - | Toluene | 18 | 0 | — |

^a 15 mol% catalyst loading. ^b 0.1 mmol substrate. ^c Conversion is calculated by comparing the integrations of peaks corresponding to alkenyl H.

^d Turnover number (TON) is calculated by dividing the conversion by the mol% catalyst loading.

their corresponding geometric isomers. With their enhanced phosphorescence, we reason that complexes **1** and **2** could be developed into novel and cheaper visible-light photosensitisers for such isomerisation reactions.

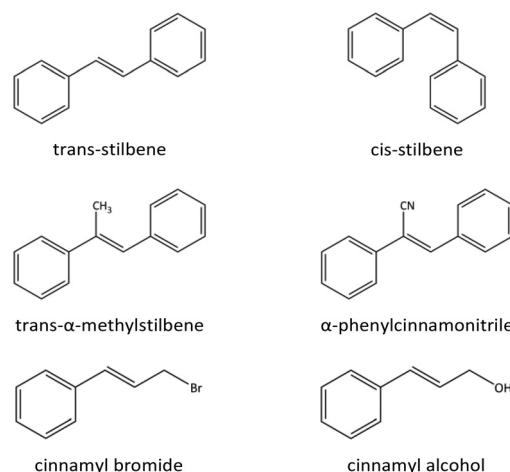
The efficiency of the tungsten complexes as photosensitisers is compared with the commonly-used [Ru(bpy)₃]Cl₂. Using stilbenes as the test case, we first verify that [Ru(bpy)₃]Cl₂ is able to photosensitise *trans*- to *cis*-stilbene isomerization. Indeed, irradiating *trans*-stilbene in the presence of a catalytic amount of the ruthenium complex in acetonitrile resulted in 94% conversion to *cis*-stilbene (Table 3, entry 1). On the other hand, only 4% conversion of *cis*-stilbene to *trans*-stilbene was achieved under the same conditions (Table 3, entry 2), which agrees with the previous report that the *trans*-to-*cis* stilbene isomerisation is largely one-directional in the presence of [Ru(bpy)₃]Cl₂.

Under the same conditions but in toluene, *trans*-to-*cis* stilbene conversion of 11% and *cis*-to-*trans* conversion of 9% (Table 3, entries 3 and 4) were achieved using **1** as the photosensitiser. As increasing the reaction time also did not improve the conversion rate, complex **1** has limited use as an efficient photosensitiser.

However, complex **2** performs better with much higher *trans*-to-*cis* and *cis*-to-*trans* conversion rates respectively (Table 3, entries 5 and 6). To ascertain whether the isomerisation has reached its photostationary state, the reaction time was increased to 48 hours. About 74% of initial *trans*-isomer was converted to the *cis*-isomer (Table 3, entry 7), while 26% of the *cis*-isomer was converted to the *trans*-isomer (Table 3, entry 8), leading to a *trans*- to *cis*-isomer ratio of 1 : 3 in toluene. The isomerisation also proceeds in acetonitrile with a comparable ratio of 1 : 4 (Table 3, entries 9 and 10). It is worth noting that the isomerization is proceeding in a catalytic manner although with small turnover numbers.

As further controls, we note that conversion in either direction was not observed when complex **3** was used (Table 3, entries 11 and 12). In addition, the W(CO)₆ precursor and the ligands themselves also do not function as visible-light photosensitisers.

To expand the substrate scope, complex **2** was used to photosensitise the isomerisation of other *trans*-alkenes (Scheme 2 and Table 4). Interestingly the isomerisation of three of the *trans*-alkenes is more efficient when complex **2** is used instead of [Ru(bpy)₃]Cl₂. On the other hand, *trans*-cinnamyl

**Scheme 2** Substrate scope of the alkene isomerisation reactions.**Table 4** Isomerisation reactions of other *trans*-alkenes with visible light irradiation for 18 hours

| Substrate ^a | Conversion ^b /%, TON ^c for the catalyst ^d | |
|--------------------------------|--|----------------------|
| | 2 in toluene | [Ru] in acetonitrile |
| <i>trans</i> -α-Methylstilbene | 65, 4.3 | 23, 1.5 |
| α-Phenylcinnamionitrile | 32, 2.1 | 0 |
| Cinnamyl bromide | 0 | 22, 1.5 |
| Cinnamyl alcohol | 19, 1.3 | 0 |

^a 15 mol% catalyst loading. ^b Conversion is calculated by comparing the integrations of peaks corresponding to alkenyl H. ^c TON is calculated by dividing the conversion by the mol% catalyst loading.

^d 0.1 mmol substrate.

bromide can only be converted to its *cis*-isomer by the ruthenium complex.

The isomerisation of alkenes is believed to be initiated by the transfer of energy from the triplet state of the photosensitizer donor.²⁹ For example, the ³MLCT state of [Ru(bpy)₃]Cl₂ is generated during irradiation and lies at 2.12 eV (ref. 1) which is very close to the triplet state of *trans*-stilbene (2.1 eV) but lower than that of *cis*-stilbene (2.6 eV).³⁰ Thus, upon collisional energy transfer in the solution phase, *trans*-stilbene can act as the more efficient triplet energy acceptor and undergoes isomerisation. However, if the energy difference is the only criterion, one expects α -phenylcinnamonnitrile, which has lower lying excited singlet and triplet states due to the electron-withdrawing resonance effect of the –CN group, to undergo isomerisation.³¹ In contrast cinnamyl bromide and cinnamyl alcohol would remain resistant to isomerisation by virtue of their higher-lying triplet states.

The results in Table 4 clearly cannot be rationalized using only differences in energy levels between the donor and acceptor. Within Dexter's framework for describing triplet energy transfer, which involves a concerted two-electron exchange, a good spectral overlap is necessary between the pair of excited donor (D*) and acceptor (A), as well as effective molecular orbital overlaps on D* and A that participate in the electron exchange. Furthermore, it is known that solvent molecules are capable of acting as non-resonant bridges for superexchange interactions³² between photosensitizers and acceptors. Their intervening roles in the mediating the transfer of triplet excitons may account for the unexpected conversion yields. At present, we are carrying out more detailed mechanistic study of the process in order to understand the photosensitisation process.

Conclusions

We have shown that W(CO)₄L complexes where L is a bidentate ligand carrying pyridine-imidazole moieties exhibit enhanced phosphorescence from the MLCT excited state, with quantum yields up to two orders of magnitude higher than those previously reported for W(CO)₄(diimine) complexes. Interestingly complex 2 can also function as an efficient photosensitizer for the geometric isomerisation of aromatic alkenes. Investigations of the reaction mechanism are underway to provide more insights into the process.

Acknowledgements

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