CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000880

Syntheses and Photophysical Properties of *N*-Pyridylimidazol-2-ylidene Tetracyanoruthenates(II) and Photochromic Studies of Their Dithienylethene-Containing Derivatives

Gongping Duan and Vivian Wing-Wah Yam*[a]

Abstract: A series of tetracyanoruthenate(II) with chelating pyridyl *N*-heterocyclic carbene ligands (NHC-py) was synthesized and characterized. Their photophysical and electrochemical properties as well as the photochromic behavior of their dithienylethene-containing complexes were studied. Photocyclization was found to take place upon irradiation into the metal-to-ligand charge transfer (MLCT) absorption bands of these complexes, and evidence is provided to support the triplet-sensitizing reaction pathway.

Keywords: carbenes · heterocycles · photochromism · ruthenium · triplet sensitization

Introduction

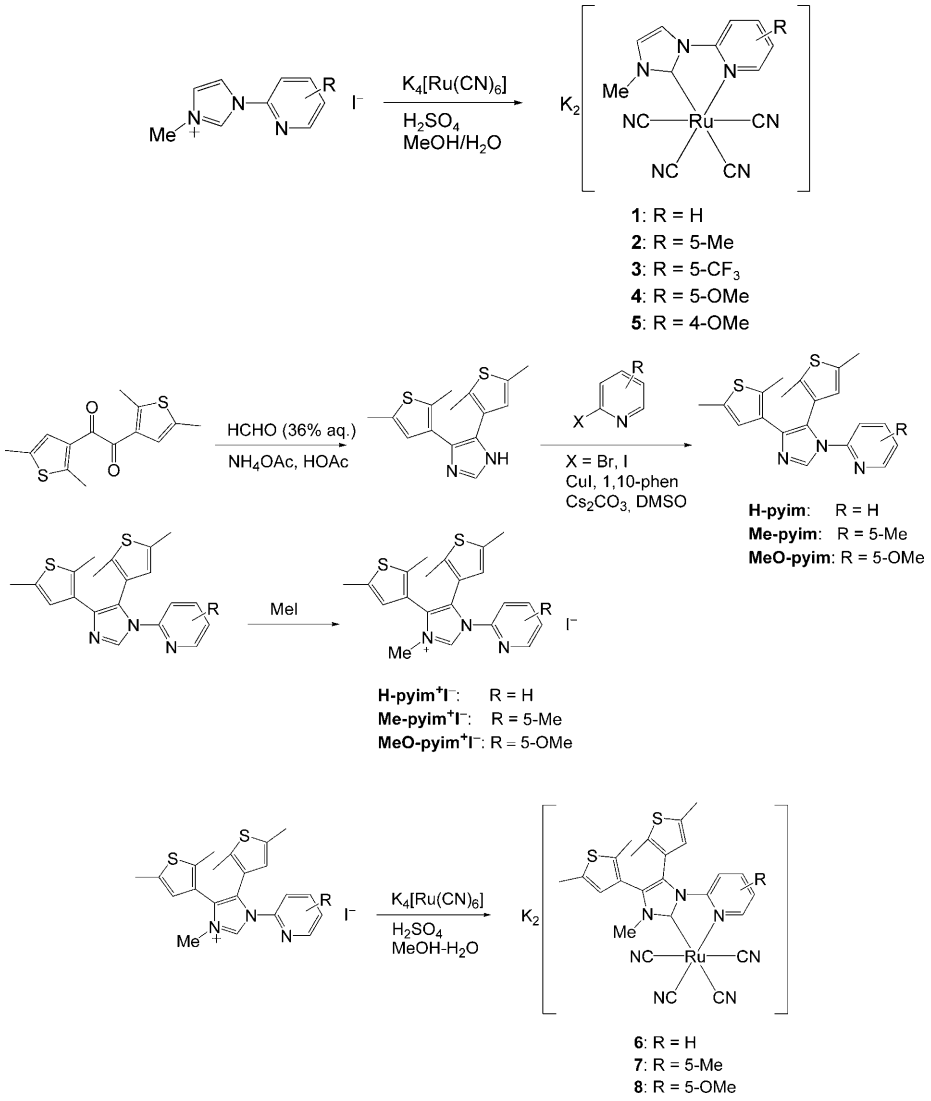
Photochromic dithienylethene compounds have drawn much attention in the past two decades due to their pronounced photochromic performance, especially their high thermal irreversibility and fatigue resistance, which may lead to their potential applications in optical data storage and molecular photoswitching.[1] In addition to the extensive studies on pure organic molecules, since the late 1990s various photochromic complexes have been generated by incorporation of metal centers into ligands that contain dithienylethene moieties,[2] which has led to the photomodulation of reactivity, luminescence, electrochemical properties and energy-transfer processes in these systems.[2–4] It was only in 2004 that Yam and co-workers reported the functionalization of the dithienylethene backbone to serve as a ligand for metal-complex formation,[4b] which is in contrast to earlier works in which the dithienylethene unit was attached as a pendant to the ligation group.[2,3a–b,4a] On the other hand, in some cases the introduction of metal centers provided a triplet-sensitizing pathway for a photocyclization reaction,[3j,4] which made the photochromic process possible upon irradiation with a longer-wavelength, less-destructive light source. Very recently, Yam and co-workers reported the photochromic studies of several Ag^{I}, Au^{I}, and Pd^{II} complexes with dithienylethene-containing monodentate *N*-heterocyclic carbene (NHC) ligands.[5] Considering the wide utilities of NHC ligands in coordination chemistry,[6] photoluminesent materials,[7] and especially catalysis,[8] this has opened new possibilities of discovering photochromic complexes with novel properties. In this paper, we report the photophysical studies of a series of tetracyanoruthenates(II) that bear chelating *N*-pyridylimidazol-2-ylidene (NHC-py) ligands, $K_2[Ru(NHC\text{-}py^R)(CN)_4]$ (R = H (**1**), 5-Me (**2**), 5-CF_3 (**3**), 5-OMe (**4**), and 4-OMe (**5**)), and the photochromic studies of their dithienylethene-containing derivatives, $K_2[Ru(NHC^T\text{-}py^R)(CN)_4]$ (T = 4,5-bis(2,5-dimethyl-3-thienyl); R = H (**6**), 5-Me (**7**), 5-OMe (**8**)). A photochromic pathway that proceeds by means of the triplet excited state was proposed and supported by experimental observations.

[a] Dr. G. Duan, Prof. Dr. V. W.-W. Yam
Centre for Carbon-Rich Molecular and
Nanoscale Metal-Based Materials Research
Department of Chemistry
HKU-CAS Joint Laboratory on New Materials
The University of Hong Kong
Pokfulam Road, Hong Kong (P.R. China)
Fax: (+852) 2857-1586
E-mail: wwyam@hku.hk

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000880.

Results and Discussion

Synthesis and characterization: Scheme 1 summarizes the synthetic routes to ligand precursors **R-pyim$^+$I$^-$** and complexes **1**–**8**. 1,2-Bis(2,5-dimethyl-3-thienyl)ethane-1,2-dione was synthesized by using modification of a reported copper(I)-mediated coupling reaction between the Grignard reagent of 3-bromo-2,5-dimethylthiophene and oxalyl chloride.[9] The diketone compound then underwent amination



Scheme 1. Synthetic routes to ligand precursors **R-pyim$^+$I$^-$** (R = H, Me, OMe) and complexes **1**–**8**.

cyclization to give 4,5-bis(2,5-dimethyl-3-thienyl)-1*H*-imidazole according to the literature procedures.[10] The ligand precursors **R-pyim$^+$I$^-$** were synthesized from Cu-catalyzed cross-coupling between the 1*H*-imidazole and various 2-halopyridine derivatives,[11] followed by the selective methylation of the imidazole ring. Tetracyanoruthenates(II) (**1**–**8**) were synthesized from $K_4[Ru(CN)_6]\cdot 3H_2O$ by using the acid-catalyzed ligand exchange reaction, similar to that of their diimine analogues.[12]

The IR spectra of all the complexes show three intense absorption bands at 2030–2060 cm^{-1} (though not all three bands were resolved in some cases) and a weaker band at around 2090 cm^{-1}, which are ascribed to the vibrational stretches of the C≡N group. Similar band shapes have also been observed in diimine tetracyanoruthenate(II) complexes,[12,13] thereby supporting their structural resemblance. In general, the stretching frequencies of the IR absorption bands of complexes **1**–**8** are found to be slightly lower (5–10 cm^{-1}) than that of the closely related diimine tetracyanoruthenates,[13b] thus suggesting a weakening of the C≡N bond, and is indicative of the poorer π-accepting as well as better σ-donating ability of the NHC-py ligands relative to that of the diimine ligands.

In the ^{13}C and ^1H NMR spectra, the chemical shifts of the coordinated carbene carbons are found to lie in the range of $\delta = 200$–205 ppm, as typically observed in ruthenium(II) carbene complexes.[14] Three signals that correspond to the cyano carbons are also observed, with one signal about twice the intensity of the others. This is in accordance with the C_s symmetry of the expected molecular structure. Complexes **6**–**8** showed two sets of signals in the ^1H NMR spectra at room temperature in a ratio of about 3:2. The broadening and coalescence of these signals at elevated temperature in the variable-temperature ^1H NMR spectroscopy experiments (Figure S1 in the Supporting Information) suggested that these two sets of signals could be ascribed to the slow interconversion between two conformations at room temperature, namely, the parallel and antiparallel conformations of the two thienyl groups according to previous studies on the diarylethene systems.[1b,4c] Chelation of the NHC^T-py ligand to the metal center would force the pyridine ring to be coplanar with the imidazole ring, which has led to the rotational hindrance of the thienyl groups and accounted for the above observations. The major conformer has been assigned to the antiparallel conformer based on NOESY experiments at −40 °C, at which the interconversion was almost frozen (Figure S2 in the Supporting Information).

Electronic absorption and emission studies: Complexes **1**–**8** all show intense absorptions in the range of 230–300 nm together with a low-energy band at around 300–450 nm in the electronic absorption spectra. The photophysical data of complexes **1**–**5** are summarized in Table 1. The intense high-energy absorption bands are assigned as mainly intraligand (IL) transitions, and probably with some mixing of a π(im)→π*(py) intraligand charge-transfer (ILCT) character.

Table 1. Photophysical data of complexes **1**–**5**.

Complex	Absorption[a] λ_{max} [nm] (ε [$mol^{-1}dm^3cm^{-1}$])	Medium (T [K])	Emission λ_{em} [nm] (τ_0 [μs])	ϕ_{em}[b]
1	230 (19900), 266 (7710), 332 sh (4320), 362 (5780)	MeOH (293) glass[c] (77)	549 (0.53) 475 (32.4)	0.012
2	234 (23200), 278 (8000), 328 sh (4870), 358 (6150)	MeOH (293) glass[c] (77)	547 (0.51) 475 (35.2)	0.011
3	234 (21600), 268 (9540), 390 (6200)	MeOH (293) glass[c] (77)	600 (1.97) 525 (27.0)	0.055
4	240 (22000), 288 (7580), 330 (5090), 358 (5410)	MeOH (293) glass[c] (77)	555 (0.56) 482 (47.5)	0.011
5	234 sh (20770), 252 sh (11650), 342 (7790)	MeOH (293) glass[c] (77)	509 (–[d]) 447 (12.8)	0.0017

[a] In MeOH at 293 K. [b] Excited at 365 nm. [c] EtOH/MeOH (4:1 v/v). [d] Not measured.

The lower-energy bands, which are sensitive to substituent effects on the pyridine ring, are ascribed to the $d\pi(Ru)\rightarrow\pi^*$-(NHC-py) metal-to-ligand charge-transfer (MLCT) transitions, similar to that observed in the related $[Ru(NHC\text{-}py)_3]^{2+}$ complex.[15] The substituents on the pyridine ring are found to tune the electronic absorption energy of the complexes in a trend of $CF_3 < H <$ 4-OMe, in line with the substituent effect generally observed in MLCT transitions (Figure 1a). Moreover, the low-energy band has been found to show a large blueshift upon addition of acid to methanolic solutions of the complexes, which is characteristic of a number of cyano-containing ruthenium(II) complexes,[16] and strongly suggests the MLCT nature of the transition

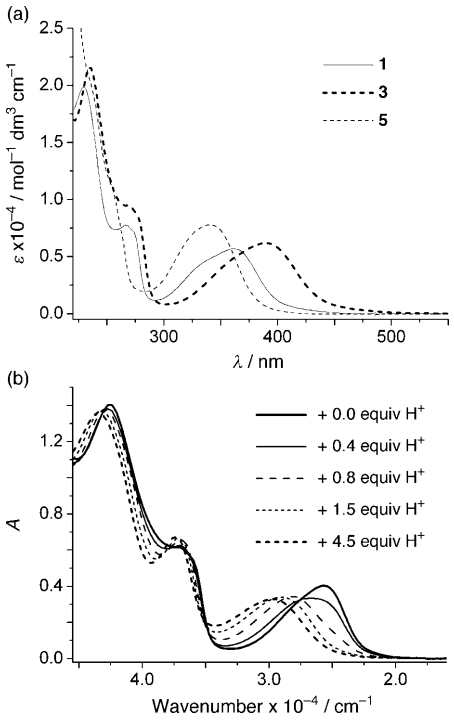


Figure 1. a) Electronic absorption spectra of complexes **1**, **3**, and **5** in methanol. b) Electronic absorption spectral changes of **3** ($c = 6.5\times10^{-5}$ mol dm^{-3}) upon addition of hydrochloric acid in methanol.

(Figure 1b). The blueshift in the absorption maxima relative to that of their diimine analogues (such as $K_2[Ru(bpy)(CN)_4]$, $\lambda_{max} = 450$ nm in methanol)[13a] has been attributed to the higher-lying π^* orbital of the NHC-py ligand given the smaller extent of its π conjugation.

Upon excitation into either the IL or MLCT absorption band, all complexes (**1**–**8**) show photoluminescence in methanol at room temperature with the maxima at around 500–600 nm. The energy of the emission follows a similar trend to that observed in the MLCT absorption band, and the lifetimes of the emissive excited states are found to lie in the range of 0.5–2 μs. Both are suggestive of a ^{3}MLCT origin for the emission. All the complexes are found to be emissive in EtOH/MeOH (4:1 v/v) glass at 77 K as well, with the emission energies (e.g., $\lambda_{em} = 475$ nm; **1**) largely hypsochromically shifted relative to that in room-temperature solution ($\lambda_{em} =$ 549 nm; **1**). The low-temperature emission energy has also been found to show a similar trend to that at room temperature, as has also been observed in the well-documented diimine counterparts,[17] which have been considered to emit from a ^{3}MLCT state at both ambient and low temperature. In the glass state, the lifetimes of all complexes are found to be 10–50 μs, which is in the range typically observed in low-temperature ^{3}MLCT emission of ruthenium(II) bipyridyl complexes while significantly shorter than the characteristic millisecond timescale of ^{3}IL emission.[18] Thus, the origin of the low-temperature glass-state luminescence has also been assigned as being derived from a ^{3}MLCT excited state. The higher-lying excited-state energy in the glass state that led to the observed blueshift has been attributed to the constraint of solvent reorganization, which would stabilize the molecule in the excited state in solution. The charge-transfer character of the excited state and the involvement of cyano solvent interactions may account for the large energy change in the solvent reorganization process.[19]

Electrochemical studies: Complexes **1**–**5** display a reversible to quasireversible oxidative couple at around +0.7 V versus the saturated calomel electrode (SCE) with ΔE_p of 60–100 mV in aqueous solution with 0.1 M KCl as supporting electrolyte. This couple is ascribed to the $Ru^{III/II}$ redox couple according to previous studies on the closely related diimine tetracyanoruthenate(II) systems (Table 2).[12,20] Substituents on the pyridine ring are found to tune the electrochemical properties of the complexes. On going from the electron-withdrawing trifluoromethyl group ($E_{1/2} = +0.82$ V vs. SCE; **3**) to the electron-donating methoxy group ($E_{1/2} = +$ 0.72 V vs. SCE; **5**), the potential for the oxidation couple becomes increasingly less positive, thereby indicating an increasing ease of oxidation due to an increase of electron density on the metal center. This trend is in accordance with the decreasing π-accepting ability as well as the increasing σ-donating ability of the ligand through the series as has been observed in the photophysical studies. When compared to the structurally related complexes that bear chelating diimine ligands ($E_{1/2} = +0.85$ V vs. SCE; $K_2[Ru(bpy)(CN)_4]$),[12] the NHC-py ligands generally would lead to less positive

Table 2. Electrochemical data for the oxidation of **1**–**5** in water (0.1 M KCl).[a]

Complex	$E_{1/2}$[b] [V] vs. SCE[c]	ΔE_p [mV][d]
1	+0.76	72
2	+0.75	85
3	+0.82	104
4	+0.76	82
5	+0.72	64

[a] Reduction potential could not be observed due to solvent window limit. [b] $E_{1/2}=0.5(E_{pa}+E_{pc})$. E_{pa} and E_{pc} are anodic and cationic peak potentials, respectively. Scan rate = 100 mV s^{-1}. [c] Data obtained using the $[Fe(CN)_6]^{3-/4-}$ couple as the reference, with $E_{1/2}$ ($[Fe(CN)_6]^{3-/4-}$) = +0.226 V versus SCE (1 M KCl, glassy carbon electrode). From ref. [25]. [d] $\Delta E_p = E_{pa} - E_{pc}$.

$Ru^{III/II}$ potentials ($E_{1/2}$ = +0.76 V vs. SCE; **1**), which could be ascribed to the poorer π-accepting ability as well as the better σ-donating ability of the NHC ligand relative to the bipyridine ligand.

Photochromic studies: Upon excitation into the IL or MLCT absorption bands, complexes **6**–**8** undergo photocyclization to generate the closed form of the complexes (Scheme 2) with the appearance of new bands and a drop in the absorbance of the original bands. ^{1}H NMR spectra of the irradiated samples also show appearance of new signals that belong to the closed forms of the complexes (Table S1 in the Supporting Information). The closed forms of the complexes are found to absorb in the long-wavelength region, at around 500 nm, which could be attributed to the generation of a more extended π-conjugated system. Based on previous studies on other metal-coordinated dithienylethene systems,[4b,5] the origin of the lowest-energy absorption band in the closed form of the complex is tentatively assigned as a spin-allowed IL transition, whereas the 370 nm band may be attributed to an admixture of the IL and MLCT transitions (Figure 2a). Upon the addition of acid, the electronic absorption band at 508 nm of the closed form of **8** shows little change—in fact, it is even slightly redshifted to 514 nm—upon protonation of the cyano groups, whereas the band at around 370 nm shows a blueshift (Figure S3 in the Supporting Information). These observations are not in favor of a possible assignment of the low-energy 508 nm band as a MLCT transition, which usually occurs in this region, and are supportive of the assignment of a mixed IL/MLCT character of the 370 nm band. Table 3 lists the photophysical data of the open and closed forms of **6**–**8**.

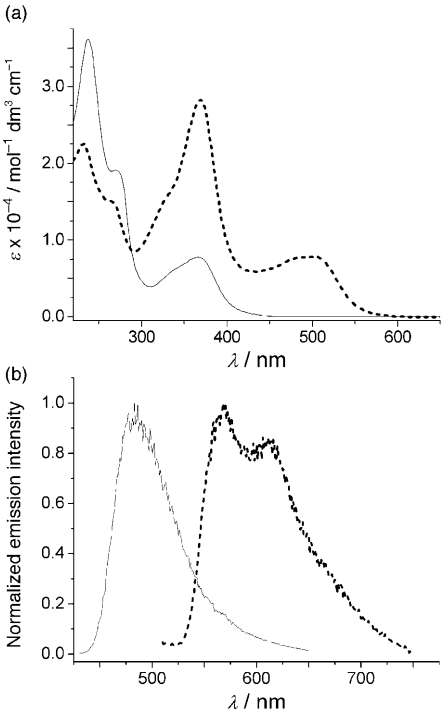
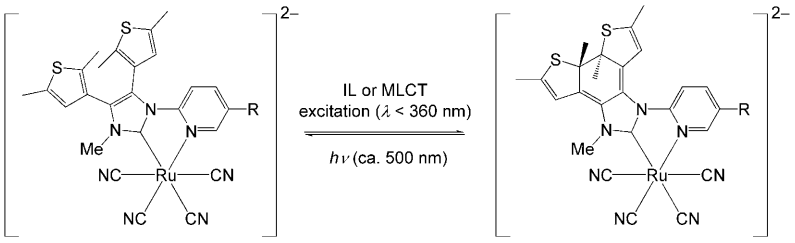


Figure 2. a) Electronic absorption spectra of the open (solid line) and closed (dashed line) forms of **6** in methanol. b) Normalized corrected emission spectra of the open (solid line) and closed forms (dashed line) of **6** in EtOH/MeOH (4:1 v/v) glass at 77 K.

Upon irradiation into the lowest-energy bands of the closed form of the complexes, photocycloreversion takes place, which leads to the recovery of the open forms. Under the same irradiation, the closed forms of complexes **6**–**8** also show a weak emission at 580–590 nm in MeOH at room temperature (Table 3). Unlike the ^{3}MLCT emission of the open form (vide supra), this emission shows only a slight blueshift in alcoholic glass at low temperature relative to that in room-temperature solution (Table 3), thereby suggesting a smaller solvent reorganization upon excitation. Given the IL character of the lowest-energy absorption, this emission might originate from an IL excited state. The closed forms also emit at 77 K. The emission spectra show well-resolved vibronic structures with vibrational progressional spacings of around 1250 cm^{-1} (Figure 2b), and appear to be the mirror image of the low-energy region of the excitation spectra (Figure S4a in the Supporting Information). With reference to studies of the glass-state photoluminescence in the absence and presence of acid at 77 K, the origin of the low-temperature emission of the closed form has been tentatively assigned as being derived from an excited state of IL character (Figure S4 in the Supporting Information).[21]



Scheme 2. Photochromic reaction of complexes **6**–**8**.

Table 3. Photophysical data of the open and closed forms of complexes **6–8**.

Complex	Absorption[a] λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}])	Medium (T [K])	Emission λ_{em} [nm] (τ_0 [μs])	ϕ_{em}
6 (open form)	238 (36100), 270 (19100), 338 (6120), 366 (7780)	MeOH (293)	580 (0.15)	0.0023[b]
		glass[c] (77)	484 (25.0)	
6 (closed form)	232 (22500), 266 sh (15000), 328 sh (15300), 368 (28200), 478 sh (7550), 502 (7830)	MeOH (293)	585 (–[d])	–[d]
		glass[c] (77)	568 (<0.1)	
7 (open form)	238 (36000), 274 (14800), 332 sh (5290), 362 (6650)	MeOH (293)	568 (0.13)	0.0021[b]
		glass[c] (77)	478 (26.6)	
7 (closed form)	232 (19800), 270 (11000), 326 sh (14800), 368 (27400), 482 sh (7870), 502 (8190)	MeOH (293)	591 (–[d])	0.0003[e]
		glass[c] (77)	565 (<0.1)	
8 (open form)	242 (36100), 286 (13400), 334 (6120), 360 (5950)	MeOH (293)	572 (0.13)	0.0018[b]
		glass[c] (77)	484 (36.9)	
8 (closed form)	238 (20000), 280 (12600), 330 sh (17400), 366 (28100), 480 sh (7960), 508 (8610)	MeOH (293)	591 (–[d])	0.0005[e]
		glass[c] (77)	565 (<0.1)	

[a] In MeOH at 293 K. [b] Excited at 365 nm. [c] EtOH/MeOH (4:1 v/v). [d] Not measured. [e] Excited at 480 nm. Due to the photocycloreversion upon irradiation, the data were obtained with larger uncertainty, estimated to be ±40%.

Complexes **6–8** have been found to show moderate quantum yields of photocyclization (Φ = 0.4–0.6, Table 4) upon irradiation into both the IL and MLCT bands, whereas the photochemical quantum yields of the reverse reaction are significantly lower ($\Phi \approx 0.09$), as commonly observed in dithienylethene compounds.[1b] In the presence of oxygen, the photocyclization quantum yields at both excitation wavelengths are found to drop remarkably (Table 4), thus suggesting that the photochemical reaction may take place through a triplet excited state in both cases.[4a,d] On the other hand, the excited-state lifetimes of the complexes that bear the photochromic moiety (i.e., **6**, **7**, and **8**) are found to be remarkably shorter than that of their corresponding analogues without the photochromic part (i.e., **1**, **2**, and **4**), respectively, in both room-temperature solution and the low-temperature glass state, although their electronic absorption and emission spectra are almost identical. The luminescence quantum yields of the photochromic complexes are found to decrease to the same extent as that of the lifetimes when compared to those without the photochromic unit (e.g., τ_0 = 0.53 μs, ϕ_{em} = 0.012, **1**; τ_0 = 0.15 μs, ϕ_{em} = 0.0023, **6**), and thus indicates the existence of a competing deactivation pathway for the emissive ^{3}MLCT excited state in these complexes. Based on these observations, it would be reasonable to propose a triplet-sensitizing pathway for the photocyclization reaction through the ^{3}MLCT excited state in this system. Similar mechanisms have been suggested previously in other metal-containing photochromic systems.[4a,c,d]

Table 4. Photochemical quantum yields (Φ)[a] of complexes **6–8** in MeOH at 293 K.

	Photocyclization				Photocycloreversion	
	Φ_{280}		Φ_{360}		Φ_{500}	
	deaerated	aerobic	deaerated	aerobic	deaerated	aerobic
6	0.52	–[b]	0.58	–[b]	0.096	–[b]
7	0.53	0.40	0.47	0.40	0.092	0.092
8	0.45	0.26	0.42	0.32	0.089	–[b]

[a] Not corrected for the percentage of photoactive antiparallel conformation. [b] Not measured.

Conclusion

In summary, the synthesis of a series of chelating *N*-pyridylimidazol-2-ylidene tetracyanoruthenates(II) has been achieved through the use of the pyridylimidazolium ligand precursors under acidic condition. The lowest-energy excited state of these complexes has been assigned as the ^{3}MLCT state in both room-temperature solution and the low-temperature glass state. The *N*-heterocyclic carbene ligands are found to be more σ-donating and less π-accepting than their bipyridyl analogues, as revealed by photophysical and electrochemical studies. Substituents on the pyridine ring have been found to affect the electronic absorption and emission spectra of the complexes remarkably, whereas introduction of the dithienylethene moiety on the imidazolium ring had little effect on the energy of the transitions but would offer an additional competing pathway for the deactivation of the ^{3}MLCT excited state. With the incorporation of the metal center, the photochromic reaction has been accomplished by means of a sensitizing mechanism that involves the triplet excited state, which would extend the excitation source to lower-energy visible light. Such incorporation of a metal center has led to the tuning of the photochromic properties of this class of compounds.

Experimental Section

Materials: 2-Bromo-5-methylpyridine (98%) was obtained from Lancaster Synthesis Ltd. 2-Chloro-5-trifluoromethylpyridine (97%), 2-bromopyridine (99%), and 1,10-phenanthroline (anhydrous, 99%) were obtained from Alfa Aesar. Cesium carbonate (99%) was obtained from Aldrich Chemical Company. Ruthenium(III) chloride hydrate (40–43% Ru, w/w) was obtained from Strem Chemicals, Inc. All other reagents and solvents were of analytical grade and were used as received unless specifically mentioned. Methanol for measurements was distilled over magnesium. 2-Iodo-5-methoxypyridine was synthesized according to literature methods.[22] $K_4[Ru(CN)_6]\cdot 3H_2O$ was prepared according to a literature method.[23] Caution! Potassium cyanide is very toxic and should be handled with care.

Syntheses: All reactions were performed under nitrogen using Schlenk techniques.

4,5-Bis(2,5-dimethyl-3-thienyl)-1*H*-imidazole: A mixture of ammonium acetate (2.26 g, 29 mmol), 1,2-bis(2,5-dimethyl-3-thienyl)ethane-1,2-dione (1.12 g, 4.0 mmol), and formaldehyde (35 wt% aqueous solution, 0.57 g,

6.6 mmol) in glacial acetic acid (25 mL) was heated to gentle reflux for 10 h. After cooling, the majority of the solvent was removed under reduced pressure. Water was added to the residue, and the mixture was neutralized carefully with aqueous NaOH solution. White precipitate formed during the process. The mixture was then extracted with isopropanol/chloroform mixture (1:3 v/v, 4×20 mL), and the organic extracts were combined. After solvent removal, the resulting solid was boiled with diethyl ether for a while. Filtration gave the desired product as an off-white crystalline solid. Yield: 1.01 g, 3.5 mmol, 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (brs, 6H; 2-Me), 2.39 (s, 6H; 5-Me), 6.59 (brs, 2H; thienyl), 7.68 (s, 1H; imidazolyl 2-H), 8.95 ppm (brs, 1H; NH); elemental analysis calcd (%) for $C_{15}H_{16}N_2S_2{\cdot}0.25H_2O$: C 61.50, H 5.68, N 9.56; found: C 61.27, H 5.56, N 9.24.

2-[4,5-Bis(2,5-dimethyl-3-thienyl)-1*H*-imidazol-1-yl]pyridine (H-pyim): A mixture of 4,5-bis(2,5-dimethyl-3-thienyl)-1*H*-imidazole (0.81 g, 2.8 mmol), cesium carbonate (1.5 g, 4.6 mmol), copper(I) iodide (0.11 g, 0.58 mmol), and 1,10-phenanthroline (0.11 g, 0.59 mmol) were placed in a two-necked round-bottom flask charged with a reflux condenser. Degassed DMSO (30 mL) was added to the flask, followed by 2-bromopyridine (0.55 g, 3.5 mmol). The resulting mixture was heated to 130–140 °C under nitrogen, and the reaction was monitored by TLC. After cooling to room temperature, ethyl acetate (30 mL), Na_2EDTA, water (30 mL), and aqueous NH_4Cl solution (saturated, 5 mL) were added to the reaction mixture. The mixture was allowed to stir in open air for about 30 min. The resulting mixture was extracted with ethyl acetate (3×20 mL), and the combined organic extracts were washed with water (4×20 mL) and brine. After solvent removal, the residue was purified by flash column chromatography on silica gel (pretreated with 1% triethylamine in hexane) using ethyl acetate/petroleum ether (1:2 v/v) as eluent. The desired product was obtained as an off-white solid. Yield: 0.83 g, 2.3 mmol, 65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (s, 3H; 2-Me), 2.22 (s, 3H; 2-Me), 2.35 (s, 6H; 2×5-Me), 6.31 (s, 1H; thienyl), 6.49 (s, 1H; thienyl), 6.75 (d, J = 8.2 Hz, 1H; pyridyl 3-H), 7.23 (dd, J = 7.4, 5.0 Hz, 1H; pyridyl 5-H), 7.61 (td, J = 7.8, 1.9 Hz, 1H; pyridyl 4-H), 8.27 (s, 1H; imidazolyl 2-H), 8.51–8.53 ppm (m, 1H; pyridyl 6-H); MS (EI$^+$): m/z: 365 $[M]^+$, 350 $[M-Me]^+$, 273 $[M-Me-C_5H_3N]^+$; elemental analysis calcd (%) for $C_{20}H_{19}N_3S_2{\cdot}0.33H_2O$: C 64.66, H 5.34, N 11.31; found: C 64.55, H 5.20, N 11.00.

2-[4,5-Bis(2,5-dimethyl-3-thienyl)-1*H*-imidazol-1-yl]-5-methylpyridine (Me-pyim): **Me-pyim** was synthesized using a method similar to that for **H-pyim**, except 2-bromo-5-methylpyridine (0.62 g, 3.6 mmol) was used in place of 2-bromopyridine. Purification by flash column chromatography on silica gel (pretreated with 1% triethylamine in hexane) using ethyl acetate/petroleum ether (1:1 v/v) as eluent gave the desired product as a pale yellow solid after solvent removal. Yield: 0.59 g, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (s, 3H; 2-Me), 2.21 (s, 3H; 2-Me), 2.35 (s, 9H; 2×5-Me and pyridyl 5-methyl), 6.30 (s, 1H; thienyl), 6.50 (s, 1H; thienyl), 6.64 (d, J = 8.6 Hz, 1H; pyridyl 3-H), 7.40 (dd, J = 8.6, 2.3 Hz, 1H; pyridyl 4-H), 8.20 (s, 1H; imidazolyl 2-H), 8.32–8.33 ppm (m, 1H; pyridyl 6-H); MS (EI$^+$): m/z: 379 $[M]^+$, 364 $[M-Me]^+$, 273 $[M-Me-C_6H_5N]^+$; elemental analysis calcd (%) for $C_{21}H_{21}N_3S_2$: C 66.47, H 5.58, N 11.07; found: C 66.20, H 5.70, N 10.67.

2-[4,5-Bis(2,5-dimethyl-3-thienyl)-1*H*-imidazol-1-yl]-5-methoxypyridine (MeO-pyim): **MeO-pyim** was synthesized using a method similar to that for **H-pyim**, except 2-iodo-5-methoxypyridine (0.86 g, 3.6 mmol) was used in place of 2-bromopyridine. Purification by flash column chromatography on silica gel (pretreated with 1% triethylamine in hexane) using ethyl acetate/petroleum ether (1:1 to 3:1 v/v) as eluent gave the desired product as a very pale yellow solid after removal of the solvent. Yield: 0.85 g, 2.1 mmol, 59%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.88 (s, 3H; 2-Me), 2.20 (s, 3H; 2-Me), 2.35 (s, 6H; 2×5-Me), 3.88 (s, 3H; OMe), 6.29 (s, 1H; thienyl), 6.51 (s, 1H; thienyl), 6.70 (d, J = 8.9 Hz, 1H; pyridyl 3-H), 7.13 (dd, J = 8.9, 3.0 Hz, 1H; pyridyl 4-H), 8.12 (s, 1H; imidazolyl 2-H), 8.18 ppm (d, J = 3.0 Hz, 1H; pyridyl 6-H); MS (EI$^+$): m/z: 395 $[M]^+$, 380 $[M-Me]^+$, 273 $[M-Me-C_6H_5NO]^+$; elemental analysis calcd (%) for $C_{21}H_{21}N_3S_2O{\cdot}0.25H_2O$: C 63.05, H 5.42, N 10.50; found: C 63.24, H 5.42, N 10.31.

4,5-Bis(2,5-dimethyl-3-thienyl)-3-methyl-1-(pyridin-2-yl)-1*H*-imidazolium iodide (H-pyim$^+$I$^-$): Iodomethane (0.2 mL, 3 mmol) was added to a solution of **H-pyim** (190 mg, 0.50 mmol) in toluene (8 mL) and the mixture was stirred at 50–60 °C. White precipitate was formed after several hours. After 24 h, more iodomethane (0.2 mL, 3 mmol) was added and the mixture was further stirred for one day. The imidazolium iodide was collected by filtration and washed with toluene and diethyl ether. Yield: 240 mg, 0.46 mmol, 93%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95 (s, 3H; 2-Me), 2.05 (brs, 3H; 2-Me), 2.28 (s, 3H; 5-Me), 2.45 (s, 3H; 5-Me), 3.99 (s, 3H; NMe), 6.24 (s, 1H; thienyl), 6.76 (s, 1H; thienyl), 7.45 (dd, J = 7.5, 4.9 Hz, 1H; pyridyl 5-H), 7.57 (d, J = 8.1 Hz, 1H; pyridyl 3-H), 7.84 (td, J = 7.8, 1.7 Hz, 1H; pyridyl 4-H), 9.91 (s, 1H; imidazolyl 2-H), 8.52–8.54 ppm (m, 1H; pyridyl 6-H); MS (FAB$^+$): m/z: 380 $[M-I]^+$; elemental analysis calcd (%) for $C_{21}H_{22}N_3S_2I{\cdot}0.5H_2O$: C 48.84, H 4.49, N 8.14; found: C 48.99, H 4.37, N 7.81.

4,5-Bis(2,5-dimethyl-3-thienyl)-3-methyl-1-(5-methylpyridin-2-yl)-1*H*-imidazolium iodide (Me-pyim$^+$I$^-$): **Me-pyim$^+$I$^-$** was synthesized using a method similar to that for **H-pyim$^+$I$^-$**, except **Me-pyim** was used in place of **H-pyim**. Yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 3H; 2-Me), 2.04 (brs, 3H; 2-Me), 2.29 (s, 3H; 5-Me), 2.40 (s, 3H; pyridyl 5-Me), 2.45 (s, 3H; 5-Me), 3.98 (s, 3H; NMe), 6.24 (s, 1H; thienyl), 6.75 (s, 1H; thienyl), 7.42 (d, J = 8.2 Hz, 1H; pyridyl 3-H), 7.62 (dd, J = 8.2, 2.2 Hz, 1H; pyridyl 4-H), 8.32–8.33 (m, 1H; pyridyl 6-H), 9.90 ppm (s, 1H; imidazolyl 2-H); MS (FAB$^+$): m/z: 394 $[M-I]^+$; elemental analysis calcd (%) for $C_{22}H_{24}N_3S_2I{\cdot}0.5H_2O$: C 49.81, H 4.75, N 7.92; found: C 49.48, H 4.71, N 7.65.

4,5-Bis(2,5-dimethyl-3-thienyl)-3-methyl-1-(5-methoxypyridin-2-yl)-1*H*-imidazolium iodide (MeO-pyim$^+$I$^-$): **MeO-pyim$^+$I$^-$** was synthesized using a method similar to that for **H-pyim$^+$I$^-$**, except **MeO-pyim** was used in place of **H-pyim**. Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 3H; 2-Me), 2.04 (brs, 3H; 2-Me), 2.29 (s, 3H; 5-Me), 2.45 (s, 3H; 5-Me), 3.90 (s, 3H; OMe), 3.97 (s, 3H; NMe), 6.24 (s, 1H; thienyl), 6.74 (s, 1H; thienyl), 7.29 (dd, J = 8.8, 3.0 Hz, 1H; pyridyl 4-H), 7.58 (d, J = 8.8 Hz, 1H; pyridyl 3-H), 8.14 (d, J = 3.0 Hz, 1H; pyridyl 6-H), 9.86 ppm (s, 1H; imidazolyl 2-H); MS (FAB$^+$): m/z: 411 $[M+H-I]^+$; elemental analysis calcd (%) for $C_{22}H_{24}ON_3S_2I{\cdot}H_2O$: C 47.57, H 4.72, N 7.56; found: C 47.89, H 4.69, N 7.31.

K_2[Ru(NHC-py)(CN)$_4$] (1): A mixture of $K_4[Ru(CN)_6]{\cdot}3H_2O$ (95 mg, 0.20 mmol) and 1-methyl-3-(2-pyridyl)-1*H*-imidazolium iodide (64 mg, 0.22 mmol) was placed in a two-necked round-bottomed flask charged with a reflux condenser. The flask was flushed three times with nitrogen by the pump–fill method. A mixture of water and methanol (1:1 v/v, 20 mL) that contained sulfuric acid (0.10 mmol) was degassed by purging with nitrogen for 10 min and then added to the flask. The resulting solution was heated to reflux under nitrogen for 60–70 h. The solution gradually turned greenish yellow upon heating, and appeared slightly turbid. The solvent was removed under reduced pressure to give a yellowish solid. The solid was redissolved in deionized water and carefully neutralized with aqueous KOH solution to pH 7. The resulting solution was centrifuged at 6000 rpm for 10 min, and the clear supernatant was evaporated to dryness under reduced pressure. The resulting yellow solid was redissolved in water (1 mL) and methanol (10 mL) was added to this solution. Precipitation occurred and the solid was removed by filtration. The filtrate was evaporated under reduced pressure. The resulting solid was again dissolved in water (1 mL) and acetone (10 mL) was added slowly. The mixture was allowed to stand overnight. The yellow precipitate that formed was collected by filtration and dried under vacuum at room temperature. Analytically pure product was obtained as a greenish yellow crystalline solid by slow vapor diffusion of acetone to an aqueous solution of the product. Yield: 56 mg, 0.11 mmol, 55%; ^{1}H NMR (400 MHz, [D$_4$]MeOH): δ = 4.15 (s, 3H; NMe), 7.18–7.22 (m, 2H; imidazolyl and pyridyl 5-H), 7.70 (d, J = 8.3 Hz, 1H; pyridyl 3-H), 7.88 (ddd, J = 8.3, 7.5, 1.7 Hz, 1H; pyridyl 4-H), 7.92 (d, J = 2.2 Hz, 1H; imidazolyl), 9.22 ppm (ddd, J = 4.9, 1.7, 0.7 Hz, 1H; pyridyl 6-H); IR (KBr): $\tilde{\nu}$ = 2093 (m), 2060 (s), 2052 (s), 2039 cm^{-1} (m) (C≡N); MS (FAB$^-$): m/z: 433 $[M]^-$, 404 $[M-K]^-$, 365 $[M-2K]^-$; elemental analysis calcd (%) for $C_{13}H_9N_7RuK_2{\cdot}2.5H_2O$: C 32.02, H 2.89, N 20.11; found: C 31.93, H 2.71, N 19.95.

$K_2[Ru(NHC\text{-}py^{5\text{-}Me})(CN)_4]$ (2): Complex **2** was synthesized using a method similar to that for **1** except 1-methyl-3-[2-(5-methyl-pyridyl)]-1*H*-imidazolium iodide (33 mg, 0.11 mmol) was used as the ligand precursor in place of 1-methyl-3-(2-pyridyl)-1*H*-imidazolium iodide to react with $K_4[Ru(CN)_6]\cdot 3H_2O$ (41 mg, 0.10 mmol). Analytically pure product was obtained as a pale yellow crystalline solid. Yield: 33 mg, 0.085 mmol, 70%; ^{1}H NMR (300 MHz, [D$_4$]MeOH): $\delta = 2.38$ (s, 3H; Me), 4.14 (s, 3H; NMe), 7.17 (d, $J = 2.2$ Hz, 1H; imidazolyl), 7.57 (d, $J = 8.4$ Hz, 1H; pyridyl 3-H), 7.69 (dd, $J = 8.4$, 2.1 Hz, 1H; pyridyl 4-H), 7.86 (d, $J = 2.2$ Hz, 1H; imidazolyl), 9.07–9.12 ppm (m, 1H; pyridyl 6-H); MS (FAB$^-$): *m*/*z*: 418 [*M*−K]$^-$, 379 [*M*−2K]$^-$; IR (KBr): $\tilde{\nu} = 2093$ (m), 2056 (s), 2035 cm^{-1} (s) (C≡N); elemental analysis calcd (%) for $C_{14}H_{11}N_7RuK_2\cdot 3H_2O$: C 32.93, H 3.36, N 19.20; found: C 32.64, H 3.20, N 18.95.

$K_2[Ru(NHC\text{-}py^{5\text{-}CF_3})(CN)_4]$ (3): Complex **3** was synthesized using a method similar to that for **1** except 1-methyl-3-[2-(5-trifluoromethyl-pyridyl)]-1*H*-imidazolium iodide (36 mg, 0.10 mmol) was used as the ligand precursor in place of 1-methyl-3-(2-pyridyl)-1*H*-imidazolium iodide to react with $K_4[Ru(CN)_6]\cdot 3H_2O$ (43 mg, 0.10 mmol), and the reaction time was reduced to about 40 h. Analytically pure product was obtained as a bright yellow crystalline solid. Yield: 38 mg, 0.070 mmol, 65%; ^{1}H NMR (400 MHz, [D$_4$]MeOH): $\delta = 4.17$ (s, 3H; NMe), 7.26 (d, $J = 2.2$ Hz, 1H; imidazolyl), 7.89 (d, $J = 8.7$ Hz, 1H; pyridyl 3-H), 8.00 (d, $J = 2.3$ Hz, 1H; imidazolyl), 8.16 (dd, $J = 8.7$, 2.0 Hz, 1H; pyridyl 4-H), 9.58–9.60 ppm (m, 1H; pyridyl 6-H); IR (KBr): $\tilde{\nu} = 2093$ (m), 2058 (s), 2046 cm^{-1} (m) (C≡N); MS (FAB$^-$): *m*/*z*: 472 [*M*−K]$^-$, 433 [*M*−2K]$^-$, 407 [*M*−2K−CN]$^-$; elemental analysis calcd (%) for $C_{14}H_8N_7F_3RuK_2\cdot 4H_2O$: C 28.86, H 2.77, N 16.83; found: C 29.03, H 2.55, N 16.59.

$K_2[Ru(NHC\text{-}py^{5\text{-}OMe})(CN)_4]$ (4): Complex **4** was synthesized using a method similar to that for **1** except 1-methyl-3-[2-(5-methoxypyridyl)]-1*H*-imidazolium iodide (31 mg, 0.10 mmol) was used as the ligand precursor in place of 1-methyl-3-(2-pyridyl)-1*H*-imidazolium iodide to react with $K_4[Ru(CN)_6]\cdot 3H_2O$ (42 mg, 0.10 mmol). Analytically pure product was obtained as a greenish yellow crystalline solid. Yield: 26 mg, 0.050 mmol, 50%; ^{1}H NMR (300 MHz, [D$_4$]MeOH): $\delta = 3.94$ (s, 3H; OMe), 4.14 (s, 3H; NMe), 7.16 (d, $J = 2.2$ Hz, 1H; imidazolyl), 7.47 (dd, $J = 9.0$, 2.8 Hz, 1H; pyridyl 4-H), 7.62 (d, $J = 9.0$ Hz, 1H; pyridyl 3-H), 7.83 (d, $J = 2.2$ Hz, 1H; imidazolyl), 9.00 ppm (d, $J = 2.8$ Hz, 1H; pyridyl 6-H); IR (KBr): $\tilde{\nu} = 2091$ (m), 2058 (s), 2048 (s), 2037 cm^{-1} (s) (C≡N); MS (ESI$^-$): *m*/*z*: 396 [*M*+H−2K]$^-$, 369 [*M*−2K−CN]$^-$, 342 [*M*−2K−CN−HCN]$^-$; elemental analysis calcd (%) for $C_{14}H_{11}N_7ORuK_2\cdot 2.5H_2O$: C 32.49, H 3.12, N 18.94; found: C 32.58, H 2.90, N 18.44.

$K_2[Ru(NHC\text{-}py^{4\text{-}OMe})(CN)_4]$ (5): Complex **5** was synthesized using a method similar to that for **1** except 1-(4-methoxypyridin-2-yl)-3-methyl-1*H*-imidazol-3-ium iodide (31 mg, 0.10 mmol) was used as ligand precursor in place of 1-methyl-3-(2-pyridyl)-1*H*-imidazolium iodide to react with $K_4[Ru(CN)_6]\cdot 3H_2O$ (51 mg, 0.12 mmol). Analytically pure product was obtained as a pale yellow crystalline solid. Yield: 39 mg, 0.070 mmol, 70%; ^{1}H NMR (300 MHz, [D$_4$]MeOH): $\delta = 3.96$ (s, 3H; OMe), 4.14 (s, 3H; NMe), 6.81 (dd, $J = 6.5$, 2.3 Hz, 1H; pyridyl 5-H), 7.16 (d, $J = 2.1$ Hz, 1H; imidazolyl), 7.28 (d, $J = 2.3$ Hz, 1H; pyridyl 3-H), 7.94 (d, $J = 2.1$ Hz, 1H; imidazolyl), 8.95 ppm (d, $J = 6.5$ Hz, 1H; pyridyl 6-H); IR (KBr): $\tilde{\nu} = 2087$ (m), 2054 (s), 2035 cm^{-1} (s) (C≡N); MS (ESI$^-$): *m*/*z*: 434 [*M*−K]$^-$, 395 [*M*−2K]$^-$, 342 [*M*−2K−CN−HCN]$^-$; elemental analysis calcd (%) for $C_{14}H_{11}N_7ORuK_2\cdot 3H_2O$: C 31.93, H 3.25, N 18.62; found: C 31.46, H 3.18, N 18.61.

$K_2[Ru(NHC^T\text{-}py)(CN)_4]$ (6): Complex **6** was synthesized using a method similar to that for **1** except **H-pyim$^+$I$^-$** (50 mg, 0.10 mmol) was used as the ligand precursor in place of 1-methyl-3-(2-pyridyl)-1*H*-imidazolium iodide to react with $K_4[Ru(CN)_6]\cdot 3H_2O$ (41 mg, 0.10 mmol). The reaction and workup were all conducted in the absence of light. Analytically pure product was obtained as a yellow crystalline solid. Yield: 37 mg, 0.050 mmol, 50%; ^{1}H NMR (400 MHz, [D$_4$]MeOH): $\delta = 2.03$ (s, 1.8H; 2-Me), 2.06–2.10 (m, 3H; 2-Me), 2.24 (s, 1.2H; 2-Me), 2.40 (s, 1.2H; 5-Me), 2.42 (s, 4.8H; 5-Me), 3.97 (s, 3H, NMe), 6.48 (s, 0.4H; thienyl, parallel conformation), 6.53 (s, 0.4H; thienyl, parallel conformation), 6.66 (s, 0.6H; thienyl, antiparallel conformation), 6.68 (s, 0.6H; thienyl, antiparallel conformation), 6.84 (d, $J = 8.4$ Hz, 1H; pyridyl 3-H), 7.12 (t, $J = 6.4$ Hz, 1H; pyridyl 5-H), 7.58 (t, $J = 8.0$ Hz, 1H; pyridyl 4-H), 9.32 ppm (dd, $J = 5.6$, 1.1 Hz, 1H; pyridyl 6-H); IR (KBr): $\tilde{\nu} = 2093$ (m), 2054 (s), 2046 cm^{-1} (s) (C≡N); MS (FAB$^-$): *m*/*z*: 624 [*M*−K]$^-$, 597 [*M*−K−HCN]$^-$, 585 [M−2K]$^-$, 532 [*M*−2K−CN−HCN]$^-$; elemental analysis calcd (%) for $C_{25}H_{21}N_7S_2RuK_2\cdot 2.5H_2O$: C 42.42, H 3.70, N 13.85; found: C 42.29, H 3.61, N 13.49.

$K_2[Ru(NHC^T\text{-}py^{5\text{-}Me})(CN)_4]$ (7): Complex **7** was synthesized using a method similar to that for **6** except **Me-pyim$^+$I$^-$** (53 mg, 0.10 mmol) was used as the ligand precursor in place of **H-pyim$^+$I$^-$** to react with $K_4[Ru(CN)_6]\cdot 3H_2O$ (51 mg, 0.12 mmol). Analytically pure product was obtained as a pale yellow crystalline solid. Yield: 42 mg, 0.058 mmol, 58%; ^{1}H NMR (400 MHz, [D$_4$]MeOH): $\delta = 2.02$ (brs, 1.8H; 2-Me), 2.07 (brs, 3H; 2-Me), 2.23 (brs, 1.2H; 2-Me), 2.32 (s, 3H; pyridyl 5-Me), 2.39 (brs, 1.2H; 5-Me), 2.42 (brs, 4.8H; 5-Me), 3.96 (s, 3H, NMe), 6.47 (s, 0.4H; thienyl, parallel conformation), 6.51 (s, 0.4H; thienyl, parallel conformation), 6.64 (s, 0.6H; thienyl, antiparallel conformation), 6.67 (s, 0.6H; thienyl, antiparallel conformation), 6.73 (d, $J = 8.6$ Hz, 1H; pyridyl 3-H), 7.42 (d, $J = 8.6$ Hz, 1H; pyridyl 4-H), 9.18 ppm (s, 1H; pyridyl 6-H); IR (KBr): $\tilde{\nu} = 2093$ (m), 2060 (s), 2044 cm^{-1} (s) (C≡N); MS (FAB$^-$): *m*/*z*: 638 [*M*−K]$^-$, 599 [*M*−2K]$^-$, 573 [*M*−2K−CN]$^-$, 546 [*M*−2K−CN−HCN]$^-$; elemental analysis calcd (%) for $C_{26}H_{23}N_7S_2RuK_2\cdot 3H_2O$: C 42.72, H 4.00, N 13.41; found: C 42.95, H 3.73, N 13.46.

$K_2[Ru(NHC^T\text{-}py^{5\text{-}OMe})(CN)_4]$ (8): Complex **8** was synthesized using a method similar to that for **6** except **MeO-pyim$^+$I$^-$** (50 mg, 0.09 mmol) was used as the ligand precursor in place of **H-pyim$^+$I$^-$** to react with $K_4[Ru(CN)_6]\cdot 3H_2O$ (58 mg, 0.14 mmol). Analytically pure product was obtained as a pale yellow crystalline solid. Yield: 41 mg, 0.055 mmol, 60%; ^{1}H NMR (400 MHz, [D$_4$]MeOH): $\delta = 2.02$ (brs, 1.8H; 2-Me), 2.07 (brs, 3H; 2-Me), 2.23 (brs, 1.2H; 2-Me), 2.42 (brs, 6H; 5-Me), 3.89 (s, 3H; OMe), 3.95 (s, 3H, NMe), 6.47 (s, 0.4H; thienyl, parallel conformation), 6.51 (s, 0.4H; thienyl, parallel conformation), 6.64 (s, 0.6H; thienyl, antiparallel conformation), 6.67 (s, 0.6H; thienyl, antiparallel conformation), 6.75 (d, $J = 9.3$ Hz, 1H; pyridyl 3-H), 7.22 (dd, $J = 9.3$, 3.0 Hz, 1H; pyridyl 4-H), 9.06 ppm (d, $J = 3.0$ Hz, 1H; pyridyl 6-H); IR (KBr): $\tilde{\nu} = 2091$ (m), 2054 cm^{-1} (s) (C≡N); MS (FAB$^-$): *m*/*z*: 654 [*M*−K]$^-$, 615 [*M*−2K]$^-$; elemental analysis calcd (%) for $C_{26}H_{23}N_7OS_2RuK_2\cdot 3.5H_2O$: C 41.31, H 4.00, N 12.97; found: C 41.37, H 3.88, N 12.79.

Physical measurements and instrumentation: NMR spectra were recorded using either a Bruker DPX 300 (300 MHz) or a Bruker AVANCE 400 (400 MHz) FT-NMR spectrometer. Variable-temperature ^{1}H NMR spectra and NOESY spectra at −40 °C were recorded using a Bruker DPX 500 (500 MHz) FT-NMR spectrometer equipped with a Bruker BVT 2000 temperature controller. Chemical shifts (δ) were reported in ppm relative to tetramethylsilane (Me_4Si). Electron-impact (EI) and fast-atom-bombardment (FAB) mass spectra were recorded using a Finnigan MAT 95 mass spectrometer. Negative-ion electrospray-ionization (ESI) mass spectra were recorded using a Finnigan LCQ spectrometer. All infrared (IR) spectra were recorded as KBr disks using a Bio-Rad FTS-7 Fourier Transform IR spectrometer (4000–400 cm^{-1}). Elemental analyses of ligands and metal complexes were performed using a Flash EA 1112 elemental analyzer by the Institute of Chemistry at the Chinese Academy of Sciences in Beijing. UV/Vis absorption spectra were recorded using a Hewlett–Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra were recorded using a Spex Fluorolog-2 Model F111 fluorescence spectrometer with or without corning filters. Excited-state lifetimes of the samples in solution and in the glass state were measured from the luminescence decay profile. The excitation source was a 355 nm output (third harmonic, 8 ns) of a Spectra-Physics Quantum-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay signals at a selected wavelength were detected using a Hamamatsu R928 photomultiplier tube connected to a 50 Ω load resistor and the voltage signal recorded using a Tektronix Model TDS 620A digital oscilloscope. The lifetime (τ_0) was determined by nonlinear fitting of the luminescence decay traces using the first-order exponential decay model, $I(t) = I_0\exp(-t/\tau_0)$. Solution samples for measurements of steady-state luminescence, lifetime, photochemical, and photoluminescence quantum yield were thoroughly degassed with no less than four freeze–

pump–thaw cycles prior to the measurements. Photoluminescence quantum yields of the open forms of the complexes were determined with excitation at 365 nm using an aqueous solution of quinine bisulfate as reference ($\phi_{365}=0.546$);[24a] whereas that of the closed forms of the complexes were determined with excitation at 480 nm using a methanolic solution of $[Ru(bpy)_3]Cl_2$ as reference ($\phi_{480}=0.045$).[24b,c] Cyclic voltammetric measurements were performed using a CH Instruments, Inc. model CHI 620 electrochemical analyzer. Measurements were performed in aqueous solution with 0.1 M KCl as supporting electrolyte. AgCl/Ag electrode was used as the reference electrode, and glassy carbon electrode (CH Instruments, Inc.) was used as the working electrode with a platinum wire as the counterelectrode. Glassy carbon electrode was polished with 1 μm and 0.3 μm α-alumina slurry (Linde) on a microcloth (Buehler Co.) successively, and then sonicated and rinsed thoroughly with deionized water.

Acknowledgements

V.W.-W.Y. acknowledges the support from The University of Hong Kong under the Distinguished Research Achievement Award Scheme and the URC Strategic Research Theme on Molecular Materials. This work has been supported by a General Research Fund (GRF) grant from the Research Grants Council of Hong Kong Special Administrative Region, P.R. China (HKU 7057/06P). G.D. acknowledges the receipt of a postgraduate studentship, administrated by The University of Hong Kong.

[1] a) R. M. Kellogg, M. B. Greon, H. Wynberg, *J. Org. Chem.* **1967**, *32*, 3093–3100; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; c) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.* **2005**, *34*, 327–336; d) H. Tian, S. Wang, *Chem. Commun.* **2007**, 781–792.

[2] a) M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, K. Furuichi, *J. Am. Chem. Soc.* **1996**, *118*, 3305; b) A. Fernández-Acebes, J. M. Lehn, *Adv. Mater.* **1998**, *10*, 1519–1522.

[3] a) E. Murguly, T. B. Norsten, N. R. Branda, *Angew. Chem.* **2001**, *113*, 1802–1805; *Angew. Chem. Int. Ed.* **2001**, *40*, 1752–1755; b) A. Fernández-Acebes, J. M. Lehn, *Chem. Eur. J.* **1999**, *5*, 3285–3292; c) J. K. W. Lee, C. C. Ko, K. M. C. Wong, N. Zhu, V. W. W. Yam, *Organometallics* **2007**, *26*, 12–15; d) J. Kühni, V. Adamo, P. Belser, *Chimica* **2006**, *60*, 207–211; e) T. W. Ngan, C. C. Ko, N. Zhu, V. W. W. Yam, *Inorg. Chem.* **2007**, *46*, 1144–1152; f) P. H. M. Lee, C. C. Ko, N. Zhu, V. W. W. Yam, *J. Am. Chem. Soc.* **2007**, *129*, 6058–6059; g) W. Tan, Q. Zhang, J. Zhang, H. Tian, *Org. Lett.* **2009**, *11*, 161–164; h) R. T. F. Jukes, V. Adamo, F. Hartl, P. Belser, L. De Cola, *Coord. Chem. Rev.* **2005**, *249*, 1327–1335; i) M. N. Roberts, J. K. Nagle, J. G. Finden, N. R. Branda, M. O. Wolf, *Inorg. Chem.* **2009**, *48*, 19–21; j) M. N. Roberts, C. J. Carling, J. K. Nagle, N. R. Branda, M. O. Wolf, *J. Am. Chem. Soc.* **2009**, *131*, 16644–16645.

[4] a) R. T. F. Jukes, V. Adamo, F. Hartl, P. Belser, L. De Cola, *Inorg. Chem.* **2004**, *43*, 2779–2792; b) V. W. W. Yam, C. C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 12734–12735; c) C. C. Ko, W. M. Kwok, V. W. W. Yam, D. L. Phillips, *Chem. Eur. J.* **2006**, *12*, 5840–5848; d) M. T. Indelli, S. Carli, M. Ghirotti, C. Chiorboli, M. Ravaglia, M. Garavelli, F. Scandola, *J. Am. Chem. Soc.* **2008**, *130*, 7286–7299.

[5] V. W. W. Yam, J. K. W. Lee, C. C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2009**, *131*, 912–913.

[6] a) H. M. Lee, C. C. Lee, P. Y. Cheng, *Curr. Org. Chem.* **2007**, *11*, 1491–1524; b) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561–3598.

[7] a) C. F. Chang, Y. M. Cheng, Y. Chi, Y. C. Chiu, C. C. Lin, G. H. Lee, P. T. Chou, C. C. Chen, C. H. Chang, C. C. Wu, *Angew. Chem.* **2008**, *120*, 4618–4621; *Angew. Chem. Int. Ed.* **2008**, *47*, 4542–4545; b) V. K. M. Au, K. M. C. Wong, N. Zhu, V. W. W. Yam, *J. Am. Chem. Soc.* **2009**, *131*, 9076–9085.

[8] a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; b) M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* **2009**, *109*, 3677–3707.

[9] F. Babudri, V. Fiandanese, G. Marchese, A. Punzi, *Tetrahedron Lett.* **1995**, *36*, 7305–7308.

[10] a) C. W. Huffman, *J. Org. Chem.* **1958**, *23*, 727–729; b) D. Davidson, M. Weiss, M. Jelling, *J. Org. Chem.* **1937**, *2*, 319–327; c) M. R. Grimmett in *Imidazole and Benzimidazole Synthesis*, Academic Press, London, **1997**, p. 151; d) M. M. Krayushkin, S. N. Ivanov, A. Yu. Martynkin, B. V. Lichitsky, A. A. Dudinov, B. M. Uzhinov, *Russ. Chem. Bull.* **2001**, *50*, 116–121.

[11] a) J. Rosevear, J. F. K. Wilshire, *Aust. J. Chem.* **1991**, *44*, 1097–1114; b) R. A. Altman, E. D. Koval, S. L. Buchwald, *J. Org. Chem.* **2007**, *72*, 6190–6199.

[12] H. Adams, W. Z. Alsinid, G. M. Davies, M. B. Duriska, T. L. Easun, H. E. Fenton, J. M. Herrera, M. W. George, K. L. Ronayne, X. Z. Sun, M. Towrie, M. D. Ward, *Dalton Trans.* **2006**, 39–50.

[13] a) C. J. Timpson, C. A. Bignozzi, B. P. Sullivan, E. M. Kober, T. J. Meyer, *J. Phys. Chem.* **1996**, *100*, 2915–2925; b) M. Kovács, A. Horváth, *Inorg. Chim. Acta* **2002**, *335*, 69–76.

[14] a) J. A. Wright, A. A. Danopoulos, W. B. Motherwell, R. J. Carroll, S. Ellwood, *J. Organomet. Chem.* **2006**, *691*, 5204–5210; b) F. Zeng, Z. Yu, *Organometallics* **2008**, *27*, 6025–6028; c) O. Kaufhold, F. E. Hahn, T. Pape, A. Hepp, *J. Organomet. Chem.* **2008**, *693*, 3435–3440.

[15] S. U. Son, K. H. Park, Y. S. Lee, B. Y. Kim, C. H. Choi, M. S. Lah, Y. H. Jang, D. J. Jang, Y. K. Chung, *Inorg. Chem.* **2004**, *43*, 6896–6898.

[16] a) M. T. Indelli, C. A. Bignozzi, A. Marconi, F. Scandola in *Photochemistry and Photophysics of Coordination Compounds* (Eds.: H. Yersin, A. Vogler), Springer, Berlin, **1987**, p. 159; b) F. Scandola, M. T. Indelli, *Pure Appl. Chem.* **1988**, *60*, 973–980.

[17] A. A. Abdel-Shafi, M. D. Ward, R. Schmidt, *Dalton Trans.* **2007**, 2517–2527.

[18] G. A. Crosby, *Acc. Chem. Res.* **1975**, *8*, 231–238.

[19] a) A. Juris, F. Barigelletti, V. Balzani, P. Belser, A. von Zelewsky, *J. Chem. Soc. Faraday Trans. 2* **1987**, *83*, 2295–2306; b) N. R. M. Simpson, M. D. Ward, A. F. Morales, F. Barigelletti, *J. Chem. Soc. Dalton Trans.* **2002**, 2449–2454.

[20] C. A. Bignozzi, C. Chiorboli, M. T. Indelli, M. A. Rampi Scandola, G. Varani, F. Scandola, *J. Am. Chem. Soc.* **1986**, *108*, 7872–7873.

[21] Upon acid addition, the changes of the excitation spectra are quite similar to that of the electronic absorption spectra (Figure S4c in the Supporting Information). The emission spectra also appear as mirror images of the lower-energy region of the excitation spectra (Figure S4b). These suggest that the band at 450–550 nm may be due to an IL origin as in the UV/Vis spectra, and the emissions in both cases are also derived from such an IL origin. Moreover, as shown in Figure S4d, upon protonation of the cyano groups, the emission of the open form of **8** shows a blueshift from 484 to 466 nm, which is typical of a MLCT origin (although the shift is not as pronounced as in the absorption or excitation spectra due to the weaker basicity of the cyano groups in the excited state and the fast protonation equilibrium),[16b] whereas the emission of the closed form is shifted to a lesser extent in the reverse direction from 567 to 572 nm. This is also supportive of the above assignment, and thus the emission in the glass state at 77 K is tentatively assigned as an origin of intraligand nature, probably with a singlet character given the short lifetimes (Table 3).

[22] a) A. Lützen, M. Hapke, H. Staats, J. Bunzen, *Eur. J. Org. Chem.* **2003**, 3948–3957; b) Y. Hama, Y. Nobuhara, Y. Aso, T. Otsubo, F. Ogura, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1683–1686; c) J. J. Song, N. K. Yee, Z. Tan, J. Xu, S. R. Kapadia, C. H. Senanayake, *Org. Lett.* **2004**, *6*, 4905–4907.

[23] R. A. Krause, C. Violette, *Inorg. Chim. Acta* **1986**, *113*, 161–162.

[24] a) J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024; b) K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1639–1640; c) J. N. Demas, G. A. Crosby, *J. Am. Chem. Soc.* **1971**, *93*, 2841–2847.

[25] D. C. Thornton, K. T. Corby, V. A. Spendel, J. Jordan, *Anal. Chem.* **1985**, *57*, 150–155.

Received: April 8, 2010
Published online: September 21, 2010

