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Syntheses, Crystal Structure, and Photochromic Properties of Rhenium(I) Complexes Containing the Spironaphthoxazine Moiety

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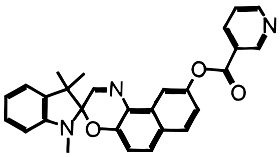
Summary: A series of novel spironaphthoxazine-containing rhenium(I) tricarbonyl diimine complexes, which show interesting photoluminescence behavior involving intramolecular photosensitization, have been synthesized and their photochromic properties studied.

The photochromic properties of spiropyrans (SP) have been extensively studied, due to their potential applications in the development of materials for ophthalmic and sunglass lenses,[1] optical filters,[2] and optical recording.[3] Spirooxazines (SO) are both structurally and functionally very similar to SP. However, it was only in the 1980s that there was a revival of interest in the study of spirooxazines, when they were recognized for their high fatigue resistance and excellent photostability.[4] Most of the studies have been confined to organic systems in which the photochromic behavior was probed by direct UV excitation. There have only been a few reports on the use of organic donors for the intermolecular photosensitization of the photochromic spironaphthoxazine moiety,[5] with almost no reports on the use of inorganic/organometallic sensitizers.[6] Herein we report the synthesis of the first series of spironaphthoxazine-containing Re(I) diimine tricarbonyl complexes and their photochromic properties. The crystal structure of one of them has also been determined.

The spironaphthoxazine-containing pyridine type ligand (SOPY; Chart 1) was synthesized by condensation[7] of 1,3,3-trimethyl-9′-hydroxyspiroindolinenaphthoxazine[8] and nicotinoyl chloride. The complexes [Re(CO)$_3$(phen)(SOPY)]ClO$_4$ (**1**), [Re(CO)$_3$(4,4′-Me$_2$-bpy)(SOPY)]ClO$_4$ (**2**), and [Re(CO)$_3$(4,4′-^{t}Bu$_2$-bpy)(SOPY)]PF$_6$ (**3**) were prepared by modification of a reported procedure for [Re(CO)$_3$(bpy)(4-Etpy)]$^+$.[9] All the compounds were characterized by ^{1}H NMR and FAB-MS and gave satisfactory elemental analyses; the structure of **3** has been determined by X-ray crystallography.[7]

Chart 1



(SOPY)

The perspective drawing of the complex cation of **3** is depicted in Figure 1. The molecule adopts a distorted-octahedral geometry with the three carbonyl groups in a facial arrangement, typical of the Re(I) diimine tricarbonyl system.[10] For the SOPY moiety, the bond distance of spiro-C(31)−O(6) is 1.51 Å, which is longer than that for a normal C−O bond. This is indicative of the weakness of the spiro-carbon−oxygen bond, typical of the spirooxazine systems.[11,12] In addition, the interplanar angle, between the indoline plane N(5)−C(31)−C(32) and the oxazine plane O(6)−C(31)−C(30), is 89.4°; these planes are thus essentially orthogonal to each other. This has also been commonly observed in other related spiropyran[11] and spirooxazine[12] systems.

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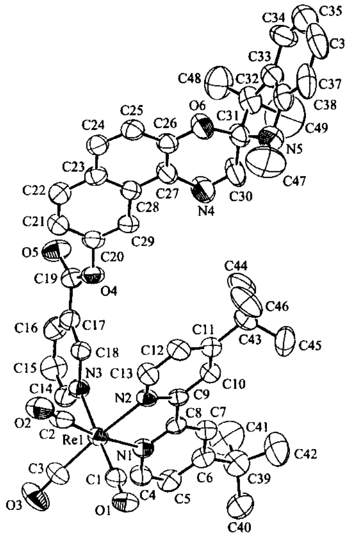
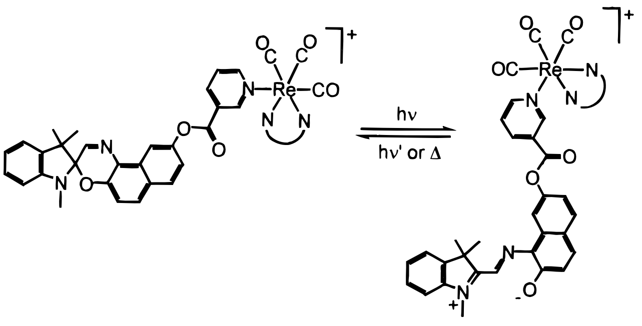


Figure 1. Perspective drawing of the complex cation of **3** with atomic numbering scheme.

The electronic absorption spectrum of the free ligand (SOPY) shows an absorption peak at 320 nm and a shoulder at 342 nm, which are most likely the $\pi \rightarrow \pi^*$ transitions of the naphthoxazine moiety. The observation of a very weak band at ca. 604 nm is attributed to the presence of a trace amount of the photomerocyanine (PMC) form which is in equilibrium with the close form, as is typically found in these systems.[4a,13] An additional low-energy absorption shoulder at ca. 380−400 nm is observed in the absorption spectra of complexes **1**−**3**, which is absent in the free SOPY ligand. This absorption shoulder with an extinction coefficient on the order of 10^3 is ascribed to the MLCT ($d\pi \rightarrow \pi^*$(diimine)) transition, typical of rhenium(I) diimine systems.[9,10b−f,14] Upon irradiation at 366 nm, the free ligand (SOPY) and complexes **1**−**3** show photochromism, with the formation of the absorption band peaking at ca. 604 nm corresponding to the generation of the photomerocyanine form. After the irradiation, the absorbance at 604 nm returns to its original value, indicative of the reversible nature of the photochromic reaction. Excitation of **1**−**3** into the MLCT band at 420 nm also gave rise to the photochromic reaction. No spectral changes were observed for the free ligand SOPY with 420 nm excitation. The observation of PMC formation upon MLCT excitation is indicative of an efficient intramolecular photosensitization reaction of the SOPY moiety by the MLCT excited state, which shifts the excitation energy to a lower energy visible region (Scheme 1).

Scheme 1



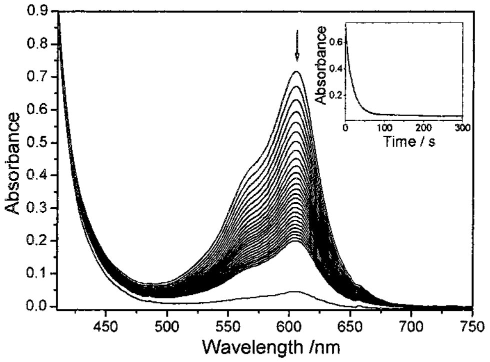


Figure 2. UV−vis absorption spectral changes of **1** in MeOH after excitation at 420 nm at times of 0−34 s with intervals of 1 s and at $t = \infty$. The insert shows the decay trace of the absorbance at 604 nm with time.

Table 1. Summary of Decoloration Rate Constants under Various Conditions[a]

	k_{dc}/s^{-1}				
	CH_2Cl_2	MeOH	MeOH[b]	MeOH (0.1 M $^nBu_4NClO_4$)	3×10^{-3} M $ZnCl_2$ in MeOH (0.1 M $^nBu_4NClO_4$)
SOPY	0.25	0.049	0.073	0.041	0.036
1	0.22	0.057	0.12	0.047	0.042
2	0.21	0.054	0.12	0.046	0.041
3	0.21	0.059	0.11	0.049	0.043

[a] The temperature was 15 °C, except where noted. [b] At 20 °C.

The spectral change after the excitation at 420 nm of **1** representing the bleaching of the absorption at 604 nm in MeOH at 15 °C is shown in Figure 2. The insert shows the decay trace of this absorbance with time, which is found to follow a first-order kinetics. The thermal decoloration rate constant, k_{dc}, has been obtained from the plot of $\ln(A_t - A_\infty/A_0 - A_\infty)$ vs time in different solvent systems, at different temperatures, and in the presence of various concentrations of Zn^{2+}. The results are summarized in Table 1. The k_{dc} value is found to strongly depend on temperature, with an approximately 2-fold increase upon increasing the temperature from 15 to 20 °C in MeOH solution. Of the three solvent systems studied, CH_2Cl_2 gave the largest k_{dc} value, whereas MeOH (0.1 M $^nBu_4NClO_4$) gave the smallest. This parallels the order of an increasing solvent polarity from CH_2Cl_2 to MeOH to 0.1 M $^nBu_4NClO_4$ in MeOH and is in line with the zwitterionic nature of the PMC form, which would be more stabilized in polar solvents than in nonpolar solvents.

The decoloration rate constants, k_{dc}, are also found to decrease upon the addition of $ZnCl_2$, with a linear dependence on the amount of $ZnCl_2$ added, which could be attributed to the stabilization of the PMC form by complex formation with the Zn^{2+} ion. Similar findings have also been reported.[13c,15] However, unlike the other spiropyran and spirooxazine systems studied, in which a dramatic decrease of the decoloration rate occurs upon

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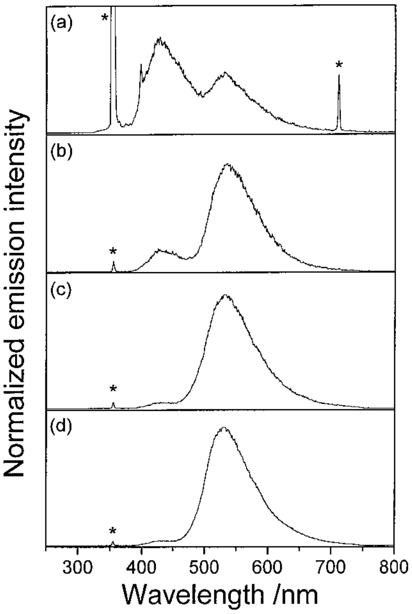

Figure 3. Emission spectra of (a) the free ligand SOPY, (b) **1**, (c) **2**, and (d) **3** in degassed CH_2Cl_2 solution at room temperature. The asterisks denote artifacts which are due to laser scattering and its harmonics.

addition of transition-metal ions, the decrease in k_{dc} occurs to a smaller extent. This could be ascribed to the absence of an additional chelating substituent group (−OR) at the position ortho to the O atom in the oxazine ring which, if present, would form a stable complex with the metal ions in a chelating manner.

Complexes **1**−**3** have also been shown to exhibit strong luminescence, while the free ligand SOPY shows only very weak luminescence upon 355 nm laser pulse excitation at room temperature in CH_2Cl_2 solution (Figure 3). Two emission bands are observed at 426 and 535 nm in all cases, with the low-energy band being more prominent relative to that of the high-energy band in the complexes. In view of the close resemblance between the emission spectrum of the ligand and those of the complexes, both the high-energy and low-energy emission bands were assigned to the ligand-centered (LC) fluorescence and phosphorescence, respectively. Although the ^{3}MLCT emission of rhenium(I) tricarbonyl diimine systems[14] also occurs at energies similar to that of the low-energy band, an assignment of the low-energy emission as MLCT phosphorescence is not favored. This has been rationalized by the observation of the same low-energy band in the ligand emission spectrum as well as supported by the fact that the emission energies are insensitive to the diimine ligands, irrespective of their different π^* orbital energies. No ^{3}MLCT emission typical of rhenium(I) tricarbonyl diimine systems were observed, even upon excitation into the MLCT absorption band at $\lambda > 400$ nm. Only the ligand-centered emission typical of the SOPY ligand was observed. These observations, together with that of photomerocyanine formation upon excitation at the MLCT band, are suggestive of an efficient photosensitization of the SOPY by the MLCT excited state. It is likely that an intramolecular energy transfer from ^{3}MLCT to the SOPY moiety occurs to give the ^{3}SOPY state, which would either return back to the ground state with emission of light or, upon prolonged irradiation, undergo the ring-opening process to give the colored PMC form. The triplet state energy of ^{3}SOPY (~225 kJ mol^{-1}), estimated from the LC phosphorescence peak maximum at ca. 530 nm, is similar to those reported for other spironaphthoxazines.[5] The postulation of an energy transfer step could further be supported by energetic considerations. A ^{3}MLCT triplet state energy, estimated from the MLCT phosphorescence of the control complex $[Re(CO)_3(4,4'\text{-}Me_2\text{-}bpy)(2\text{-naphthanylnicotinate})]ClO_4$, which peaks at ca. 520 nm, is sufficient for the energy to be transferred to the ^{3}SOPY state, which acts as the energy acceptor.

It is also interesting to note that the relative intensities of the two emission bands vary for different complexes and for the ligand. In the complexes, the LC phosphorescence becomes predominant, whereas in the free ligand the LC fluorescence is the predominant band. The higher relative emission intensities of the low-energy band in the complexes relative to that of the ligand are indicative of a much more efficient intersystem crossing from the singlet excited state to the triplet in the complexes. This is in agreement with the larger spin−orbit coupling due to the presence of the heavy Re atom in the complexes. Besides, the presence of an efficient photosensitization pathway, as a result of intramolecular energy transfer from the ^{3}MLCT state to the ^{3}SOPY state, would also lead to the enhancement of the low-energy phosphorescence.

A close scrutiny of the emission spectra of the complexes shows that the relative intensity of the low-energy emission band compared to the high-energy one increases as one goes from **1** to **2** to **3.** This trend is suggestive of an increase in the efficiency of energy transfer from the ^{3}MLCT to the ^{3}SOPY state as the diimine is changed from phen to Me_2bpy to $^tBu_2$bpy, which is in line with the ^{3}MLCT donor energy of the $^tBu_2$bpy and Me_2bpy complexes being higher than that of the phen complex. Thus, **3**, with the highest ^{3}MLCT donor energy, would give rise to the most efficient energy transfer and, hence, the highest intensity ratio of the low-energy to high-energy emission.

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Supporting Information Available: Text giving details of the syntheses and characterization data, including the complete crystal data for **3** and ^{1}H NMR, IR, and elemental analyses for SOPY and complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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