Inorg. Chem. **2008**, 47, 7447−7449

Inorganic Chemistry
Communication

A New Class of Isocyanide-Containing Rhenium(I) Bipyridyl Luminophore with Readily Tunable and Highly Environmentally Sensitive Excited-State Properties

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Received May 18, 2008

A new class of readily tunable and highly environmentally sensitive luminescent rhenium(I) tetra(isocyano)bipyridyl complexes has been synthesized and characterized, and their luminescent properties have been investigated. Preliminary studies showed that the metal-to-ligand charge-transfer $[d\pi(\mathrm{Re}) \rightarrow \pi^*(\mathrm{bpy})]$ absorption and emission are extremely sensitive to the nature of the solvent and the rigidity of the environment.

Rhenium(I) bipyridylcarbonyl complexes have received considerable attention not only because of their rich excited-state chemistry but also because of the luminescence properties associated with the metal-to-ligand charge-transfer (MLCT) excited state.[1] These compounds are also widely used as building blocks for many different applications,[2–4] such as photosensitizers,[2] photocatalysts,[3] solar energy converters,[3] and luminescent sensors and probes.[4] While rhenium(I) carbonylbipyridyl complexes have been extensively investigated, the isoelectronic rhenium(I) isocyanobipyridyl complexes have not been explored. It is hypothesized that replacing the carbonyl ligands with isocyanide ligands would provide an additional means of tuning the excited-state properties of the metal complex system because the electronic and steric properties of an isocyanide are readily tuned by the substituents attached to its N atom. Another advantage of isocyanides is the possible extension of the rhenium bipyridine luminophore toward the construction of highly functionalized molecular systems of widely diverse solubility and property by simply altering the substituent group on the isocyanide ligands. Herein, we report the synthesis, characterization, and photophysical properties of a new class of luminescent rhenium(I) tetra(isocyano)bipyridyl complexes that show readily tunable and highly environmentally sensitive excited-state properties.

The reaction of $[\mathrm{Re(CNR)_5I}]$[5] with AgOTf in tetrahydrofuran (THF), followed by a substitution reaction with bipyridyl ligands and a metathesis reaction using $\mathrm{NH_4PF_6}$, afforded the $\mathrm{PF_6^-}$ salts of the desired rhenium(I) tetra(isocyano)bipyridyl complexes,

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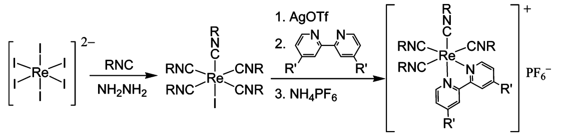
10.1021/ic800906x CCC: $40.75

Scheme 1. Synthetic Route to Rhenium(I) Tetra(isocyano)bipyridyl Complexes



1 R = C_6H_4Cl-*4*; R' = OMe **2** R = C_6H_4Cl-*4*; R' = ^tBu **3** R = C_6H_4Cl-*4*; R' = H **4** R = C_6H_4F-*4*; R' = H **5** R = $C_6H_3(CH_3)_2$-*2,6*; R' = H

$[Re(CNR)_4(R'_2bpy)]PF_6$, in moderate yield (Scheme 1). Compounds **1**−**5** were characterized by ^1H NMR, IR, electrospray ionization mass spectrometry, and satisfactory elemental analysis. The X-ray crystal structure[6] of **5** was also determined.

The Re atom in **5** adopted a distorted octahedral geometry (Figure 1). The angle subtended by the N atoms of bipyridine at the Re center, N(1)−Re(1)−N(2), was 74.2°, which is much smaller than the ideal angle of 90° in octahedral geometry. This deviation is due to the steric requirement of the chelating ligand.[4] The *trans*-isocyanide ligands show longer Re−C (2.03 vs 1.95 Å) and shorter C≡N (1.16 vs 1.18 Å) distances than the *cis*-isocyanide ligands. These observations are likely attributed to competition between the two *trans*-isocyanide ligands for the π back-bonding and the large trans influence of isocyanide.

All of the complexes showed four N≡C stretches in the 1850−2140 cm^{-1} region, which is what one would have expected for a molecule of C_{2v} symmetry.[7] Using the descriptions of the vibrational modes for the related rhenium(I) tetracarbonylbipyridyl systems,[7b–d] the four stretches at 1860−1940, 2000−2030, 2040−2060, and 2120−2140 cm^{-1} were assigned to the respective A_1, B_1, A_1, and B_2 modes. The high-frequency vibration at ca. 2130 cm^{-1} was very close to that of the free isocyanide ligand N≡C stretch (~2140 cm^{-1}), indicating that there was only a weak π-back-bonding interaction between the Re metal and one or more isocyanide ligands. This is in accordance with the shorter C≡N distances in the *trans*-isocyanide ligands, as is observed in the crystal structure of **5**.

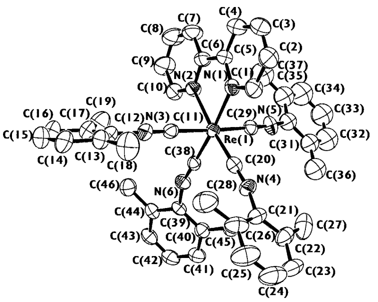


Figure 1. Perspective drawing of the complex cation of **5**. H atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): Re(1)−N(1), 2.160(5); Re(1)−N(2), 2.179(5); Re(1)−C(11), 2.027(7); Re(1)−C(20), 1.948(6); Re(1)−C(29), 2.035(6); Re(1)−C(38), 1.949(5); C(11)−N(3), 1.163(8); C(20)−N(4), 1.185(8); C(29)−N(5), 1.160(8); C(38)−N(6), 1.181(7); N(1)−Re(1)−N(2), 74.22(19); N(3)−C(11)−Re(1), 177.3(6); N(4)−C(20)−Re(1), 178.3(5); N(5)−C(29)−Re(1), 177.2(6); N(6)−C(38)−Re(1), 178.6(5).

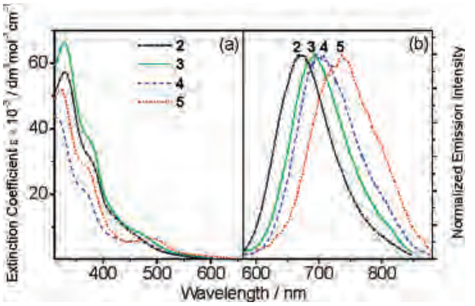


Figure 2. (a) Electronic absorption spectra. (b) Overlaid uncorrected emission spectra of **2**−**5** in dichloromethane at 298 K.

The electronic absorption spectra of **1**−**5** showed intense absorptions at 240−320 nm, with molar extinction coefficients on the order of 10^4 dm^3 mol^{-1} cm^{-1} (Table S1 in the Supporting Information). These absorptions were assigned to intraligand ($\pi \rightarrow \pi^*$) transitions of the arylisocyanide and bipyridine moieties. One to two additional moderately intense absorption shoulders (Figure 2a), with molar extinction coefficients on the order of 10^3 dm^3 mol^{-1} cm^{-1}, were ascribed to an admixture of MLCT transitions of $d\pi(Re) \rightarrow \pi^*(RNC)$ and $d\pi(Re) \rightarrow \pi^*(bpy)$, with some mixing of a ligand-to-ligand charge-transfer (LLCT) $[\pi(RNC) \rightarrow \pi^*(bpy)]$ transition. The lowest-energy absorption shoulders were found to follow the order **1** (412 nm) ≈ **2** (412 nm) > **3** (456 nm) > **4** (471 nm) > **5** (492 nm), which was sensitive to changes in the bipyridine and isocyanide ligands and in agreement with the assignment of a predominant MLCT $[d\pi(Re) \rightarrow \pi^*(bpy)]$ transition. In general, the presence of electron-donating substituents on the bipyridine ligand would raise the π^*-orbital energies of the ligand, leading to a higher MLCT energy. With the same bipyridine ligand, the absorption energies of this lowest-energy absorption are in line with the π-accepting abilities of the isocyanide ligands: $Cl-C_6H_4NC$ > $F-C_6H_4NC$ > $(CH_3)_2C_6H_3NC$, where the better π-accepting $Cl-C_6H_4NC$ would better stabilize the $d\pi(Re)$ orbital, giving rise to the highest-energy MLCT $[d\pi(Re) \rightarrow \pi^*(bpy)]$ transition. The higher-energy bands at ca. 400 nm in **3**−**5** were tentatively assigned to the MLCT $[d\pi(Re) \rightarrow \pi^*(RNC)]$ transition because the π^* orbital of arylisocyanide was expected to be higher-lying in energy than that of the bipyridine ligands.[8,9] The lack of an obvious separate band in this region and the unusually large molar extinction coefficient for the 412-nm band in **1** and

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(6) Crystal data for **5**: $[C_{50}H_{54}F_6N_6OPRe]$, $M = 1086.16$, triclinic, $P\bar{1}$ (No. 2), $a = 12.515(2)$ Å, $b = 14.369(2)$ Å, $c = 16.693(3)$ Å, $\alpha = 83.00(2)°$, $\beta = 72.52(2)°$, $\gamma = 68.00(2)°$, $V = 2654.6(7)$ Å^3, $Z = 2$, $D_c = 1.359$ g cm^{-3}, μ(Mo Kα) = 2.379 mm^{-1}, 15 754 reflections collected, 9873 were unique ($R_{int} = 0.0209$), and 8122 were observed with $I \geq 2\sigma(I)$ in the ranges of $-15 \leq h \leq 14$, $-17 \leq k \leq 17$, $-20 \leq l \leq 17$ with $2\theta_{max}$ equal to 51.36°. $F(000) = 1096$, $T = 301$ K. R1 = 0.0447 and wR2 = 0.1231 with a GOF on F^2 = 1.007. Data/restraints/parameters: 9873/3/517. The C atoms [C(30)−C(37)] on the dimethylphenyl groups in one of the dimethylphenylisocyanide ligands were refined isotropically because of their relatively high thermal parameters. For crystallographic data in CIF, see the Supporting Information.

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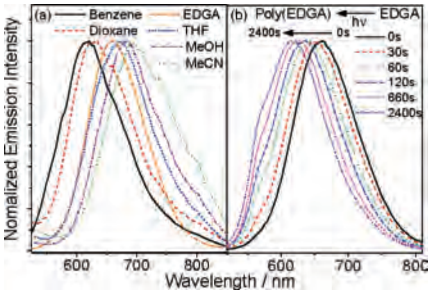

Figure 3. Normalized uncorrected emission spectra of **1** (a) in different solvents at 298 K and (b) in photopolymerizable EGDA in the presence of 1% DMPA photosensitizer as a function of the irradiation time.

2 suggest that the dπ(Re) → π^*(bpy) and dπ(Re) → π^*(RNC) MLCT transitions were not resolved as a result of their closeness in energy.

Upon excitation at $\lambda > 350$ nm, **1**−**5** in a dichloromethane solution displayed red luminescence with emission maxima in the range of 670−740 nm (Figure 2b). It is likely that the emission originated from the lowest-energy ^{3}MLCT state derived from the excitation of a dπ(Re) → π^*(bpy) transition. These emission bands were of much lower energy than the ^{3}MLCT phosphorescence of [Re(CO)$_3$(bpy)Cl] (612 nm)[1e] and the structured ligand-centered phosphorescence of [Re(CO)$_4$(bpy)]OTf (448 nm).[7b] This can be rationalized by the higher basicity of arylisocyanide ligands compared to carbonyl ligands, which results in the formation of a higher-lying dπ(Re) orbital and thus lower MLCT energy. The emission energies (E_{em}), as reflected from the emission maxima, were on the order of **2** (671 nm) > **1** (681 nm) and **3** (690 nm) > **4** (698 nm) > **5** (738 nm), which are suggestive of an assignment of a ^{3}MLCT [dπ(Re) → π^*(bpy)]origin. This emission showed an energy dependence similar to that on the properties of the bipyridine and isocyanide ligands observed for the lowest-energy absorption bands. On the basis of this energy dependence, however, an assignment of this emission to an LLCT [π(RNC) → π^*(bpy)] origin cannot be excluded because both MLCT [dπ(Re) → π^*(bpy)] and LLCT [π(RNC) → π^*(bpy)] emissions would produce the same energy trend.

The emissions of these complexes were extremely sensitive to the solvent medium and the rigidity of their environment. The emission of **1** was found to show a significant blue shift with ΔE_{em} of ca. 1800 cm^{-1} from an acetonitrile solution to a benzene solution (Figure 3a), which is comparable to the most significant solvatochromic MLCT emissive systems, such as [Ru(CN)$_4$(bpy)] and [W(CO)$_4$(bpy)].[10] The emission maxima were found to show a red shift with an increase in the dielectric constant of the solvent from benzene to MeCN: benzene (619 nm) > dioxane (630 nm) > THF (673 nm) > MeOH (683 nm) > MeCN (698 nm). This may be attributed to the significant increase in the dipole moment of the excited state, which is more stabilized in a polar solvent medium, relative to its ground state. A similar emission energy dependence with a much smaller ΔE_{em} of ca. 800 cm^{-1} was also observed for **5** (Figure S1 in the Supporting Information). Except for emission data obtained in methanol, the emission energy was well-correlated with Dimroth's solvent parameter[11] (Figure S2 in the Supporting Information). The deviation of the emission in methanol from the correlation may be due to the significant hydrogen-bonding factor, which is not important in this system, in the derivation of Dimroth's parameter.[11] The lowest-energy absorption also displayed positive solvatochromism (Figure S3 in the Supporting Information); however, the absorption energy of this band is difficult to determine because there is a significant overlap of different electronic transitions.

The emission energy of **1** was also found to be highly dependent on the rigidity of the medium. The emission of **1** in ethylene glycol dimethacrylate (EGDA) containing 1% by weight of Irgacure 651 (DMPA) photoinitiator shows a blue shift from 660 to 610 nm ($\Delta E_{\text{em}} \approx 1240$ cm^{-1}) as well as an increase in the emission intensity during the course of photopolymerization (Figure 3b). This could be rationalized by an increase in the rigidity of the medium, in which the solvent dipoles could not reorient themselves around the complex to stabilize the excited state and thus resulted in an energetically high-lying excited state.

All complexes also displayed intense photoluminescence in 4:1 (v/v) EtOH/MeOH glass at 77 K (Table S1 in the Supporting Information). A similar emission energy dependence and a blue shift in emission energies relative to those in the solution state were also observed. These emissions were also tentatively assigned to be derived from the ^{3}MLCT [dπ(Ru) → π^*(bpy)] excited-state origin. The extended, submicrosecond excited-state lifetime observed in a glass medium at 77 K is also supportive of its triplet parentage.

The electrochemical properties of the complexes were investigated by cyclic voltammetry (Table S2 in the Supporting Information). All complexes displayed a quasi-reversible oxidation couple at $E_{1/2} \approx +0.7$ V vs SCE and an irreversible oxidation wave at $E_{\text{pa}} \approx +1.4$ V vs SCE, both of which are dependent on the electron richness of the metal center and therefore tentatively assigned to successive metal-centered oxidations. One quasi-reversible couple at $E_{1/2} \approx -1.5$ V vs SCE and three irreversible reduction waves at E_{pc} in the ranges of −1.72 to −2.03, −2.16 to −2.54, and −2.29 to −2.72 V vs SCE were observed. In view of the relative sensitivity of these reductions to the bipyridine and isocyanide ligands, the reversible reduction couple is assigned to the reduction of the bipyridine ligand and the first two irreversible reduction waves are assigned to successive reductions of the isocyanide ligands. The third reduction wave, which shows a significant dependence on the nature of both isocyanide and bipyridine ligands, is assigned to metal-centered reduction.

Acknowledgment. The work described in this paper was supported by a grant from City University of Hong Kong (7002307). Prof. Vivian W.-W. Yam is gratefully acknowledged for her helpful comments and discussions.

Supporting Information Available: Synthetic procedure, characterization, photophysical, and electrochemical data for **1**−**5** and [Re(CNR)$_5$I], a CIF file giving crystal data for **5**, a plot of emission energy versus Dimroth's parameter for **1** and **5**, absorption and emission spectra of **5** in different solvents, and Tables S1−S7. This material is available free of charge via the Internet at http://pub.acs.org.

IC800906X