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Thermochromic and Aggregation Properties of Bis(phenylisocyano) Rhodium(I) Diimine Complexes

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Summary: A series of bis(phenylisocyano) rhodium(I) diimine complexes with thermally mediated aggregation properties have been synthesized, and their photophysical and thermochromic properties have been studied.

The intriguing excited-state properties as well as the extraordinary properties associated with the weak metal–metal interaction of square-planar d^8 metal polypyridyl complexes[1] have attracted tremendous attention for decades. The use of the aggregation properties, controlled through the elegant design of square-planar polypyridyl Pt(II) complexes, has revealed many interesting photophysical properties, which have inspired the development of complexes that serve as chemosensors and molecular devices.[2] Despite the great successes in controlling the Rh–Rh distance by using bridging ligands with different spacers in the binuclear systems and the unique properties associated with aggregation of mononuclear Rh(I) complexes,[3] controlling and tuning the aggregation properties of mononuclear Rh complexes and polypyridyl Rh(I) complexes have been much less explored.[4] With our recent interest in designing readily tunable polypyridyl isocyano metal complexes,[5] we believe that the incorporation of isocyanide ligands into a Rh(I) diimine complex would generate square-planar d^8 metal complexes wherein the planarity, physical, aggregation, and excited-state properties would be readily tuned by altering the substituent of the isocyanide nitrogen atom. Herein, we report the synthesis, characterization, and photophysical properties of a new series of bis(phenylisocyano) Rh(I) diimine complexes with tunable aggregation properties and themochromic behavior.

The reaction of $[Rh(cod)Cl]_2$ with $AgBF_4$ in the presence of 1 equiv of diimine ligand in dichloromethane, followed by a substitution reaction with a substituted phenylisocyanide, afforded the BF_4^- salts of the desired bis(phenyisocyano) rhodium(I) diimine complexes, $[Rh(CNR)_2(N{-}N)]BF_4$, in moderate yield (Scheme 1). Complexes **1**–**5** were characterized by ^{1}H NMR, IR, and ESI-MS and gave satisfactory elemental analyses. Recrystallization of these complexes from slow diffusion of diethyl ether vapor into concentrated solutions of **1**–**5** in common organic solvents, such as acetone, acetonitrile, and THF, gave two types of solids or crystals with a red or dark green color, similar to other related square-planar d^8 transition metal complexes.[3] The solutions of these two different colored solids or crystals gave identical ^{1}H NMR and UV–vis absorption spectra. The X-ray crystal structures[6] of the two forms of **1** were also determined.

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(6) Crystal data for **green form of 1**: $[C_{32}H_{35}BF_4N_4O_{0.5}Rh]$ (**1**$\cdot$1/2Et$_2$O), M_w = 673.36, monoclinic, $C2/c$ (No. 15), a = 19.0965(4) Å, b = 20.8077(4) Å, c = 15.4552(3) Å, α = 90°, β = 96.555(2)°, γ = 90°, V = 6101.0(2) Å^3, Z = 8, D_c = 1.466 g cm^{-3}, μ(Cu–Kα) = 4.993 mm^{-1}, 6424 reflections collected, 3581 were unique (R_{int} = 0.0419) and 2681 were observed with $I \geq 2\sigma(I)$ in the ranges of $-19 \leq h \leq 20$, $-22 \leq k \leq 21$, $-15 \leq l \leq 15$ with $2\theta_{max}$ equal to 55.00°. $F(000)$ = 2760, T = 173(2) K, R_1 = 0.0468 and wR_2 = 0.1051 with a GOF on F^2 = 0.996. Data/restraints/parameters: 6424/0/391. Crystal data for **red form of 1**: $[C_{33}H_{36}BF_4N_4ORh]$ (**1**$\cdot$(CH$_3$)$_2$CO), M_w = 694.38, monoclinic, $P2_1/c$ (No. 14), a = 14.7171(5) Å, b = 13.9287(4) Å, c = 16.6506(5) Å, α = 90°, β = 109.209(3)°, γ = 90°, V = 3223.18(17) Å^3, Z = 4, D_c = 1.431 g cm^{-3}, μ(Cu–Kα) = 4.756 mm^{-1}, 9263 reflections collected, 5498 were unique (R_{int} = 0.0193) and 4669 were observed with $I \geq 2\sigma(I)$ in the ranges $-17 \leq h \leq 14$, $-16 \leq k \leq 16$, $-19 \leq l \leq 19$ with $2\theta_{max}$ equal to 67.48°. $F(000)$ = 1424, T = 293(2) K, R_1 = 0.0355 and wR_2 = 0.0942 with a GOF on F^2 = 1.045. Data/restraints/parameters: 9263/0/405. For crystallographic data in CIF and perspective drawings of these structures, see the Supporting Information.

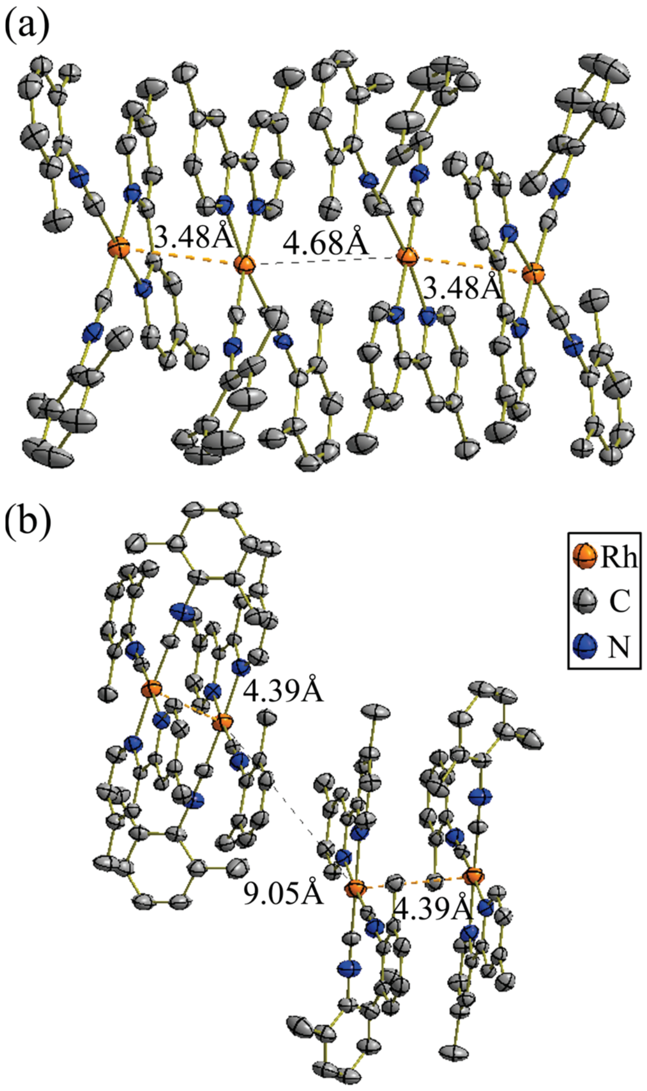
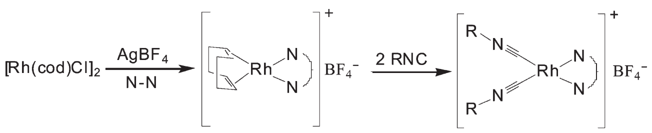


Figure 1. Thermal ellipsoid plot (40% probability level) of the crystal structures of both (a) the dark green and (b) red forms of **1**.

Scheme 1. Synthetic Route to Bis(phenylisocyano) Rhodium(I) Diimine Complexes



1 N-N = 4,4'-Me$_2$bpy; R = C$_6$H$_3$Me$_2$-*2,6*
2 N-N = bpy; R = C$_6$H$_3$Me$_2$-*2,6*
3 N-N = 5,6-Br$_2$phen; R = C$_6$H$_3$Me$_2$-*2,6*
4 N-N = bpy; R = C$_6$H$_4$Cl-*4*
5 N-N = bpy; R = C$_6$H$_2$Br$_3$-*2,4,6*

The Rh atom in both forms of **1** adopted a square-planar geometry with the phenyl ring of one of the isocyanide ligands twisted at an interplanar angle of ca. 51° with respect to the plane of the complexes. One crystallographic asymmetric unit of the red form consists of **1** and an acetone, whereas that of the green form consists of **1** and half a diethyl ether. The [Rh(CNR)$_2$(bpy)]$^+$ units in the crystal of the dark green material are stacked with their orientations alternately rotated by 90° and 180° with respect to the adjacent units. The 90° and 180° rotations correspond to the shorter Rh−Rh distances (3.48 Å) and the longer Rh−Rh distances (4.68 Å), respectively (Figure 1a). The observation of the relatively short Rh−Rh distance in the range of 3.2−3.9 Å, which is only slightly longer than the formal Rh−Rh bond distance of 2.8−3.2 Å, between two adjacent [Rh(CNR)$_2$(bpy)]$^+$ units is suggestive of a weak metal−metal interaction. In the red crystalline material, the shortest distance between two neighboring [Rh(CNR)$_2$(bpy)]$^+$ units is 4.39 Å, which is much longer than the typical Rh−Rh distances of 3.2−3.9 Å in stacked Rh$^{\mathrm{I}}$ complexes with significant metal−metal interactions.[3] Therefore, the green and the red crystals can be considered as dimeric and monomeric forms of the complex. The dimeric nature of the units in the green crystal was further supported by π−π interactions between the bipyridyl units of neighboring complexes. Although different solvent molecules were found in the X-ray crystal structures of the red form and the green form, the significant difference in the color of these forms is not the result of the interaction between the complex and the specific solvent molecule since the red- and green-colored solids could also be obtained by the recrystallization of these complexes in other solvent systems. As with other chelating diimine ligands,[5] the angles subtended by the nitrogen atoms of the bipyridine at the Rh center, N−Rh−N, were about 78.2° in both forms, which is much smaller than the ideal angle of 90° in the square-planar geometry.

The two forms of the solids or crystals of **1**−**5** dissolved in acetone to give yellow to orange solutions with identical absorption spectra. A moderately intense absorption shoulder at 455−490 nm (Table 1), with the absorption energy following the trend of **1** (462 nm) > **2** (475 nm) > **3** (490 nm) for the same 2,6-dimethylphenyl isocyanide ligands and **5** (455 nm) > **4** (470 nm) > **2** (475 nm) for the same bipyridine ligands, was also observed. This absorption energy trend is suggestive of the metal-to-ligand charge transfer (MLCT) transition of [dπ(Rh) → π*(N−N)], but it probably includes some mixing from metal-centered and ligand-to-ligand charge transfer (LLCT) [π(RNC) → π*(N−N)] transitions. In general, the presence of electron-donating substituents on the diimine ligand should raise the π* orbital energies of the ligand, whereas a better stabilized dπ(Rh) orbital should result in the presence of better π-accepting isocyanide ligands, both of which would lead to a higher MLCT energy. Consequently, using the same bipyridine ligand, the absorption energy of this absorption shoulder is in line with the different π-accepting abilities of the isocyanide ligands: Br$_3$−C$_6$H$_2$NC > Cl−C$_6$H$_4$NC > (CH$_3$)$_2$C$_6$H$_3$NC.[5]

Upon cooling, the yellow solutions of **1**−**5** changed to a green color with the evolution of a new absorption band at ca. 629−678 nm, which grew in intensity and showed a slight red shift as temperature decreased (Figure 2a). The close resemblance of this absorption band with the green crystal's absorption (Figure S5, Supporting Information) suggested that this new absorption band be ascribed to the absorption of the dimeric form of the complex, [Rh(CNR)$_2$(N−N)]$_2^{2+}$. The assignment is further supported by the linear relationship between $[\mathbf{5}]_{\mathrm{T}}/(A_{655})^{1/2}$ and $(A_{655})^{1/2}$ (Figure 2a, inset) at a constant temperature,[3d,7] where $[\mathbf{5}]_{\mathrm{T}}$ is the total concentration of **5** and A_{655} is the absorbance at $\lambda_{\max}$ of the new absorption band. At a concentration of 0.97 mM in acetone solution, this new absorption of **4** and **5** evolved at ca. 253 K, whereas for **1**, **2**, and **3**, it evolved at ca. 203 K. This may be attributed to the more sterically demanding nature of the

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(7) See the Supporting Information for the equation used in equilibrium analysis.

Table 1. Photophysical Data for Complexes 1−5

complex	emission^a λ_{em}/ nm (τ_o/μs)	T/K	absorption^b λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})
1	574 (0.51, 1.52)	298	369 (10 760), 462 (975)
		183	629^c
2	580 (0.48, 1.61)	298	375 (10 055), 475 (840)
		183	654^c
3	588 (0.52, 1.74)	298	362 (10 200), 388 (10 365), 490 (880)
		183	670^c
4	570 (0.55, 1.87)	298	372 (11 550), 470 (960)
		183	678^c
5	565 (0.82, 2.30)	298	366 (11 285), 455 (850)
		183	655^c

^{a} Measured in EtOH/MeOH (4:1 v/v) glass at 77 K upon excitation at 460 nm. Emission maxima are uncorrected values. ^{b} In acetone. ^{c} Absorption of the dimeric unit of the complexes $[Rh(CNR)_2(N-N)]_2^{2+}$.

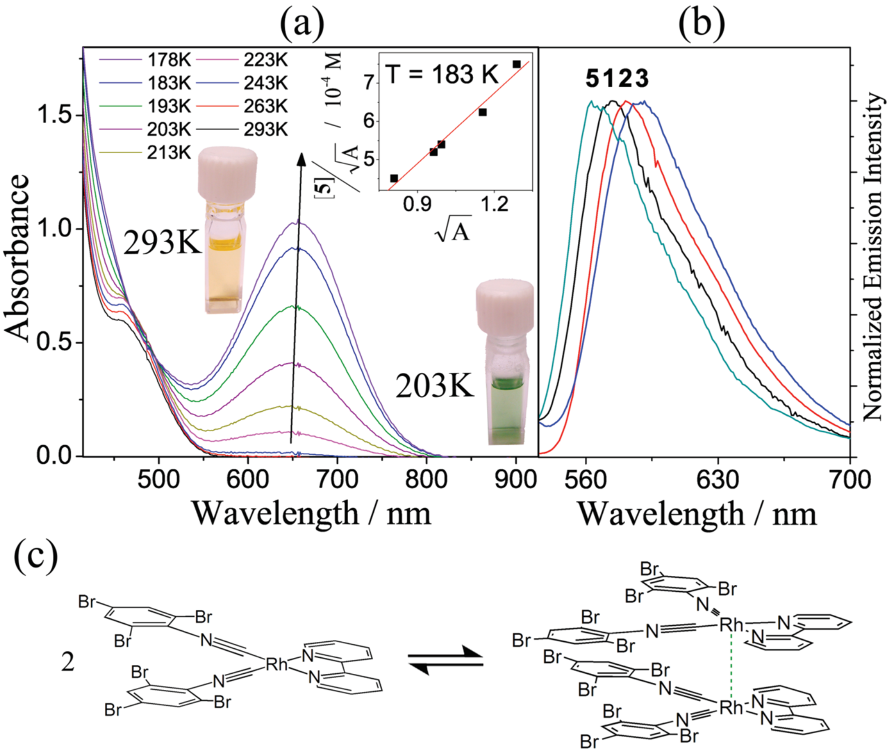

Figure 2. (a) UV−vis absorption spectral changes of a 0.97 mM acetone solution of **5** at different temperatures. The inset shows the plot of $[\mathbf{5}]_T/(A_{655})^{1/2}$ vs $(A_{655})^{1/2}$. (b) Overlaid uncorrected emission spectra of **1**−**3** and **5** in EtOH/MeOH 4:1 (v/v) glass at 77 K. (c) Dimerization of **5**.

2,6-dimethylphenylisocyanide ligands, in which at least one of the phenyl moieties is twisted with respect to the plane of the Rh complexes and exerts a steric repulsion on the other monomer in the dimeric form, rendering the dimeric unit less stable. In light of previous spectroscopic work on binuclear Rh(I) complexes with bridging isocyanide ligands,[3b−3f,3h] this absorption is tentatively assigned to the transition from $d\sigma^*[d_{z^2}*(Rh)]$ to $p\sigma[p_z(Rh)]$ mixed with some $\pi^*(N-N)$ character from the dimeric complex $[Rh(CNR)_2(N-N)]_2^{2+}$. Thus, the absorption energy of this new absorption band is sensitive to both the steric effects from the phenylisocyanide ligands and the π-accepting ability of the diimine ligands. Consequently, among complexes with the same isocyanide ligands, this new absorption for **3** (678 nm) is significantly red-shifted relative to **2** (654 nm), as the diimine ligand of **3** (5,6-Br_2phen) has a better π-accepting ability. On the other hand, the absorption energy of this band also showed significant dependence on the steric factors from the isocyanide ligands. With the same bipyridine ligand, the new absorption of **4** (670 nm) is red-shifted compared to those of **2** (654 nm) and **5** (655 nm). This may be attributed to the decreased steric bulk of the isocyanide ligands in **4** (Cl–C_6H_4NC), rendering it easier to achieve the shorter Rh−Rh distance in the dimeric unit and resulting in a red-shifted absorption energy.[3a−3h] Similarly, a slight red shift of this absorption band with decreasing temperature may be ascribed to the possible shortening of the Rh−Rh distance in the dimer units as the temperature decreased.

The solids and solutions of these complexes are nonemissive at room temperature, but they become strongly luminescent with emission maximum of 565−588 nm (Figure 2b, Table 1) upon excitation into the absorption shoulder at ca. 460 nm in EtOH/MeOH 4:1 (v/v) glass at 77 K. This emission was attributed to the emission of the monomeric complex, as the emission energy is higher than the lowest-energy absorption of the dimeric form. This emission showed an energy dependence similar to the lowest-energy absorption shoulder in the acetone solution, in which the emission maximum is consistent with the π-accepting ability of the diimine ligand and is in the reverse order of the π-accepting ability of the isocyanide ligands. Thus, these emissions were also tentatively assigned to originate from the ^{3}MLCT [dπ(Rh) → π^*(N−N)] excited-state origin. The extended, submicrosecond excited-state lifetime observed in glass medium at 77 K also supports its triplet origin.

In summary, a series of bis(phenylisocyano) rhodium(I) diimine complexes with thermally mediated aggregation properties have been synthesized, and their photophysical and thermochromic properties have been studied. By varying the substituent on the nitrogen atom of the isocyanide ligands, the electronic and steric nature of the isocyanide ligands and the subsequent photophysical, thermochromic, and aggregation properties of the complexes could be readily tuned. These studies will be useful in designing Rh(I) polypyridyl complexes for thermally responsive molecular devices and Rh(I) complexes with controllable aggregation properties. Further modifications of this system to elucidate the aggregation and photophysical properties and to design functional molecular devices are now in progress.

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Supporting Information Available: Synthetic procedures and characterization for **1**−**5**, derivation of equation for equilibrium analysis, solid-state reflectance spectrum of **5**, decay analysis of TCSPC data, Ortep drawings, and CIF files giving crystal data for both forms of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.