J|A|C|S
COMMUNICATIONS

# A “Molecular Pivot-Hinge” Based on the pH-Regulated Intramolecular Switching of Pt−Pt and $\pi-\pi$ Interactions

Chi-Kin Koo,[†] Benny Lam,[†] Sze-Kar Leung,[†] Michael Hon-Wah Lam,*,[†] and Wai-Yeung Wong[‡]

*Department of Biology & Chemistry, City University of Hong Kong, Tat Chee Avenue, Hong Kong SAR, China, and Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong SAR, China*

Received September 26, 2006; E-mail: bhmhwlam@cityu.edu.hk

The use of explicit conformational features and intra- and intermolecular interactions in specifically designed organic, coordination/organometallic, and supramolecular systems to mimic mechanical motions in the macroscopic world is of great research and applied interest.[1] Elegant molecular devices such as molecular clips, gears, hinges, ratchets, rotors, scissors, shuttles, switches, and tweezers with different supramolecular architectures have been actively explored in recent years.[1,2] Many of these devices make use of steric, electrostatic, and $\pi-\pi$ interactions as well as stimuli-induced conformational isomerization to bring about their mimetic motions. On the other hand, the metal−metal interaction has scarcely been utilized in the design of molecular devices.[3]

The dimeric $d^8$ cyclometalated systems are well-known for their intramolecular $d^8-d^8$ interactions.[4] Among the various cyclometalating ligands involved, the tridentate 6-phenyl-2,2′-bipyridine (HC^N^N) ligand (Scheme 1) is probably the most widely studied because of the special photophysical properties of its cyclometalated complexes.[4,5] We have designed and synthesized an analogous tridentate $\pi$-conjugated C,N,$N_{pyrazolyl}$ cyclometalating ligand, 2-phenyl-6-(1*H*-pyrazol-3-yl)pyridine (H**L**) (Scheme 1), that contains a $C_{phenyl}$, a $N_{pyridyl}$, and a $N_{pyrazolyl}$ donor moiety as well as a 1-pyrazolyl-NH that can still be available for further chemical interactions, such as protonation/deprotonation, after cyclometalation. Reaction of H**L** with $K_2PtCl_4$ affords the cycloplatinated complex [Pt(**L**)Cl] which further reacts with bis(diphenylphosphino)methane (dppm) to give the binuclear $\{[Pt(\mathbf{L})]_2(\mu\text{-dppm})\}(ClO_4)_2$ ($\mathbf{1}\cdot 2ClO_4$) (Figure 1).[6] Complex **1** represents a molecular “pivot-hinge” where the two [Pt(**L**)] moieties are held by the diphenylphosphino functionalities of the $\mu$-dppm with the bridging methylene as the pivot. Opening and closing of the pivot-hinge is regulated by the deprotonation/protonation of the 1-pyrazolyl-NH of the C,N,$N_{pyrazolyl}$ ligands.

Complex **1** is luminescent both in solid state and in solution at room temperature. Emission $\lambda_{max}$ of **1** in acetonitrile at 606 nm is typical of analogous binuclear cycloplatinated systems and can be attributed to the triplet metal−metal-to-ligand charge transfer ($^3$MMLCT) ($d\sigma^*(Pt) \rightarrow \pi^*(\mathbf{L})$) transition.[7,8] Addition of triethylamine leads to a dramatic change in the emission color from orange to green.[6] In aqueous DMF solutions buffered at increasing pH, the same phenomenon is also observed with a gradual shift of the emission maxima from 605 to 507 nm with a structured shoulder at 545 nm (Figure 2). Compared to the photophysical characteristics of the monomeric [Pt(**L**)Cl][6] and other similar cycloplatinated systems, the new emission peaks at high pH can be assigned the triplet metal-to-ligand charge transfer ($^3$MLCT) ($d\pi(Pt) \rightarrow \pi^*(\mathbf{L})$) transition. Spectrofluorometric titration in acetonitrile showed that the spectral response reached a plateau after 2 equiv of base was added.[6] This is consistent with the deprotonation of the 1-pyrazolyl-NH functionality on both cyclometalating ligands of **1**.

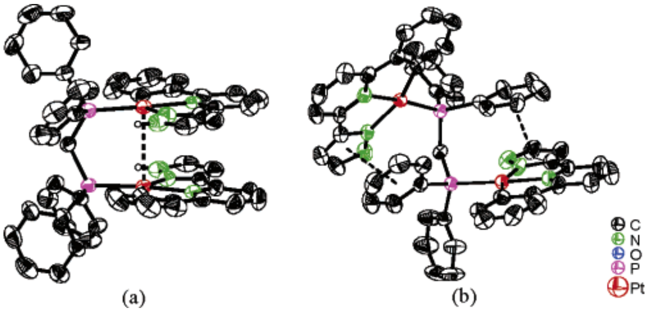


***Figure 1.*** ORTEP plots of **1** before (a) and after (b) deprotonation of the 1-pyrazolyl-NH on the C,N,$N_{pyrazolyl}$ ligands. Hydrogen atoms, except the 1-pyrazolyl-NH, are omitted for clarity.

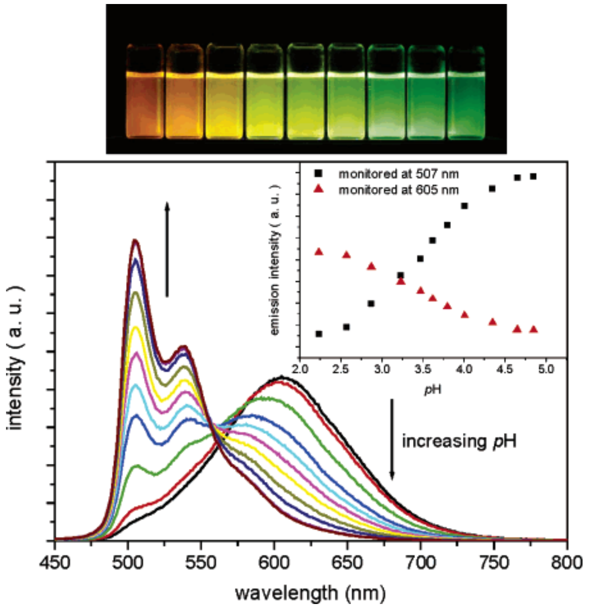


***Figure 2.*** (Top) Photograph showing the dramatic change in the luminescent responses of **1** (concentration = 2.5 × $10^{-5}$ M) in 2:1 (v/v) DMF: aqueous buffer of different pH (left to right): 2.23, 2.57, 2.87, 3.47, 3.62, 3.80, 4.35, 4.65, and 4.85. (Bottom) Spectral traces of the spectrofluorometric titration of **1**. The inset shows the plot of relative emission intensity at 507 (■) and 605 (▲) nm against pH. Excitation $\lambda$ = 355 nm.

The origin of such a spectrofluorometric response of **1** is revealed by X-ray crystallography. Figure 1a shows the crystal structure of **1** which is comparable to its analogous $\{[Pt(C\text{\^{}}N\text{\^{}}N)]_2(\mu\text{-dppm})\}^{2+}$, where the two cycloplatinated [Pt(**L**)] moieties are parallel to each other with Pt−Pt separation of 3.193(2) Å, indicating the presence of $d^8-d^8$ interaction.[7]

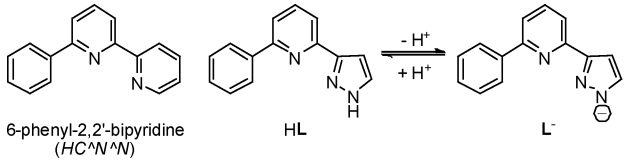
Figure 1b shows the crystal structure of deprotonated **1** obtained by slow evaporation of its acetone solution in the presence of excess

---

[†] City University of Hong Kong.
[‡] Hong Kong Baptist University.

10.1021/ja066914o CCC: $33.50

*Scheme 1*



triethylamine. The two [Pt($\mathbf{L}^-$)] moieties are not parallel to each other anymore, and the Pt−Pt separation has increased to 5.555(2) Å. Instead of intramolecular $d^8$−$d^8$ interaction, the deprotonated **1** possesses a pair of intramolecular $\pi$−$\pi$ interactions between the two deprotonated pyrazolyl rings on the cyclometalating ligands and two phenyl rings of the $\mu$-dppm. Interplanar distances between the interacting aromatic rings are 3.54−3.75 Å. It seems that, upon deprotonation of the 1-pyrazolyl-NH on C,N,$\mathrm{N_{pyrazolyl}}$, Coulombic repulsion between the negatively charged cyclometalating ligands, together with the compensation from the establishment of the two intramolecular $\pi$−$\pi$ interactions between the pyrazolyl rings and the phosphino phenyl rings, cleaves the Pt−Pt interaction between the two [Pt($\mathbf{L}^-$)] moieties. Such a cleavage diminishes the $^3$MMLCT emission and enhances the $^3$MLCT emissions from the two noninteracting [Pt($\mathbf{L}^-$)] units.

The switching from the lower energy $^3$MMLCT emission to the higher energy $^3$MLCT emission via the cleavage of the Pt−Pt interaction can be reversed by the addition of acid (Figure 3). Such a switching process can be repeated without observable loss in fidelity. In essence, the pH-regulated formation and cleavage of the Pt−Pt $d^8$−$d^8$ interaction in **1** mimics the mechanical motions of a pivot-hinge (Figure 4). The methylene bridge of the $\mu$-dppm acts as the pivot upon which the two cyclometalated [Pt(**L**)] units can be swung toward opposing directions. The pivot-hinge is closed under the Pt−Pt $d^8$−$d^8$ interaction, holding the two [Pt(**L**)] units together when the 1-pyrazolyl-NH functionality of the C,N,$\mathrm{N_{pyrazolyl}}$ ligands is protonated. Upon deprotonation of the 1-pyrazolyl-NH, the Pt−Pt interaction is cleaved with the two [Pt($\mathbf{L}^-$)] units swinging away from each other, and thus, the pivot-hinge is open. The parted [Pt($\mathbf{L}^-$)] units are held in position by the intramolecular $\pi$−$\pi$ interactions between the negatively charged pyrazolyl ring on the cyclometalating ligands and the phenyl rings on the $\mu$-dppm bridge.

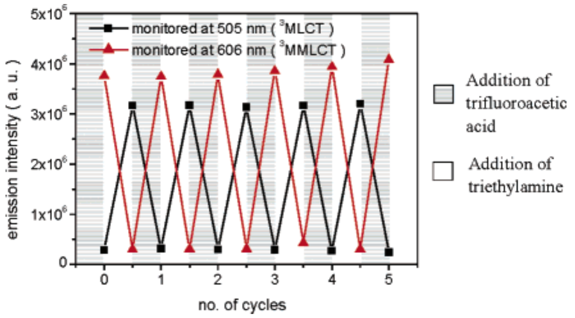


***Figure 3.*** Reversible switching between $^3$MMLCT (at 606 nm, ▲) and $^3$MLCT (at 505 nm, ■) emission of **1** (concentration = $5 \times 10^{-5}$ M) in acetonitrile (with 0.05 M of $^t\mathrm{Bu_4NPF_6}$) by alternate addition of triethylamine and trifluoroacetic acid for five repeating cycles. Excitation $\lambda$ = 355 nm.

To conclude, we have demonstrated the reversible manipulation of the cleavage and re-establishment of Pt−Pt and intramolecular $\pi$−$\pi$ interactions in both organic and aqueous organic media using the binuclear cycloplatinated complex **1** with the new C,N,$\mathrm{N_{pyrazolyl}}$ ligand. The dynamic actions involved resemble mechanical motions of a pivot-hinge and are unambiguously captured by X-ray crystallography.

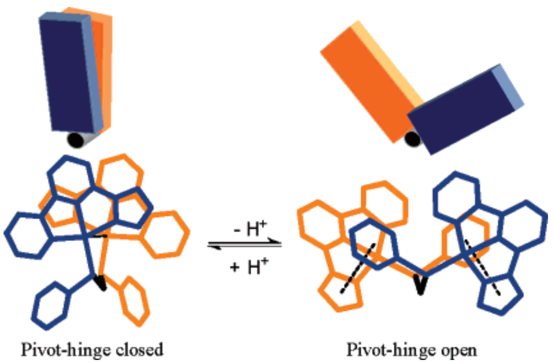


***Figure 4.*** Crystal structures showing the opening and closing of the molecular pivot-hinge by the protonation and deprotonation of the 1-pyrazolyl-NH of the C,N,$\mathrm{N_{pyrazolyl}}$ ligands of the binuclear cycloplatinated complex **1**. One phosphino phenyl ring on each side of the $\mu$-dppm bridge is omitted for clarity.

**Acknowledgment.** The work described in this paper was funded by the Research Grants Council of Hong Kong SAR, China (CityU 1108/02P).

**Supporting Information Available:** Experimental details and characterizations of $\mathbf{1}\cdot(\mathrm{ClO_4})_2$, X-ray crystallographic data of **1** (protonated and deprotonated forms), and spectroscopic/spectrofluorometric titrations of **1**. This material is available free of charge via Internet at http://pubs.acs.org.

## References

(1) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (b) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines: A Journey into the Nanoworld*; Wiley-VCH: Weinheim, Germany, 2004.

(2) (a) Klärner, F.-G.; Kahlert, B.; Boses, R.; Bläser, D.; Juris, A.; Marchioni, F. *Chem.—Eur. J.* **2005**, *11*, 3363−3374. (b) Cheng, P.-N.; Chiang, P.-T.; Chiu, S.-H. *Chem. Commun.* **2005**, 1285−1287. (c) Klärner, F.-G.; Kahlert, B.; Nellesen, A.; Zienau, J.; Ochsenfeld, C.; Schrader, T. *J. Am. Chem. Soc.* **2006**, *128*, 4831−4841. (d) Kottas, G. S.; Clarke, L. I.; Horinek, D.; Michl, J. *Chem. Rev.* **2005**, *105*, 1281−1376. (e) Romeo, R.; Carnabuci, S.; Fenech, L.; Plutino, M. R.; Albinati, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 4494−4498. (f) Norikane, Y.; Tamaoki, N. *Org. Lett.* **2004**, *6*, 2595−2598. (g) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 5612−5613. (h) Vicario, J.; Katsonis, N.; Ramon, B. S.; Bastiaansen, C. W. M.; Broer, D. J.; Feringa, B. L. *Nature* **2006**, *440*, 163.

(3) (a) Yam, V. W.-W.; Li, C.-K.; Chan, C.-L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2857−2859. (b) Li, C.-K.; Lu, X.-X.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *Inorg. Chem.* **2004**, *43*, 7421−7430.

(4) (a) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1991**, *30*, 4446. (b) Lu, W.; Chan, M. C.-W.; Cheung, K.-K.; Che, C.-M. *Organometallics* **2001**, *20*, 2477−2486. (c) Siu, P. K.-M.; Ma, D.-L.; Che, C.-M. *Chem. Commun.* **2005**, 1025−1027.

(5) (a) Wong, K.-H.; Chan, M. C.-W.; Che, C.-M. *Chem.—Eur. J.* **1999**, *5*, 2845−2849. (b) Kui, S. C.-F.; Chui, S. S.-Y.; Che, C.-M.; Zhu, N. *J. Am. Chem. Soc.* **2006**, *128*, 8297−8309.

(6) Refer to the Supporting Information.

(7) Cheung, T.-C.; Cheung, K.-K.; Peng, S.-M.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1996**, 1645−1651.

(8) Lai, S.-W.; Chan, M. C.-W.; Cheung, T.-C.; Peng, S.-M.; Che, C.-M. *Inorg. Chem.* **1999**, *38*, 4046−4055.

JA066914O