

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

# A single-molecular twin rotor: correlated motion of two pyrimidine rings coordinated to copper

†Cite this: DOI: 10.1039/x0xx00000x

Yusuke Takara,<sup>a</sup> Tetsuro Kusamoto,<sup>a</sup> Tatsuya Masui,<sup>a</sup> Michihiro Nishikawa,<sup>a,b</sup> Shoko Kume<sup>a,c</sup> and Hiroshi Nishihara\*<sup>a</sup>

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

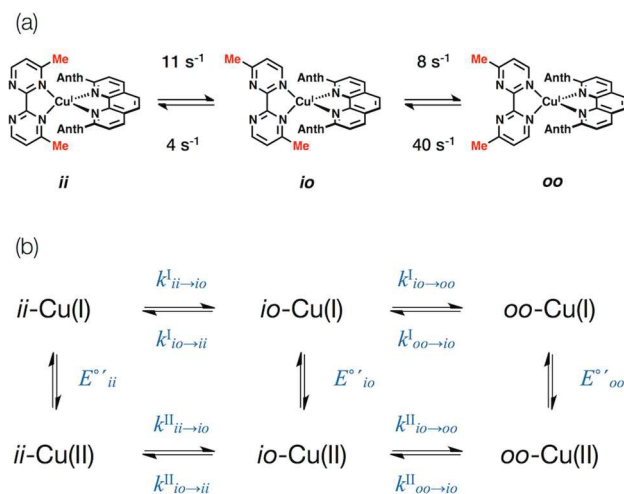
www.rsc.org/

We describe the two correlated rotational motions of pyrimidine rings in 4,4'-methyl 2,2'-bipyrimidine ligated to Cu(I). The two pyrimidine rings delimited by anthryl and phenanthroline groups rotate to afford three isomers. <sup>1</sup>H NMR measurements revealed that the two rotational processes were activated at different temperatures. Cyclic voltammetry gave the kinetic and thermodynamic parameters that provide clear evidences of the correlation between the two rotational steps.

Decades of research have been devoted to developing artificial molecular rotors to build molecular devices inspired by natural molecular machines,<sup>1–3</sup> and harnessing rotational motion is an important challenge in this field. One approach is to correlate two rotational motions, which would achieve multistability within a single molecule and enable the transmission of motion in integrated multicomponent networks.<sup>4</sup>

A pyridylpyrimidine-ligated Cu(I) molecular system capable of redox-driven motion has been reported.<sup>5–8</sup> The complexes exhibit unique isomerization behavior derived from the rotation of a coordinated pyrimidine ring. Because the 4-position of the pyrimidine ring is unsymmetrically substituted, the steric effects in the Cu coordination compound differ depending on the orientation of the substitution. The Cu(I) state preferentially adopts a tetrahedral geometry, and the Cu(II) state adopts a square planar geometry; thus, these steric effects alter the Cu(II)/Cu(I) redox characteristics. The correlation between the complex structure and the valence states of Cu allows bistability in this simple molecular design. Because we can estimate the rotational trajectory of the pyrimidine motion, the isomerization dynamics can be tuned by the steric effect around the rotor. We have previously shown that the electron-coupled rotational motion can convert an external stimulus into various outputs, such as magnetic and optical responses and

changes in rest potential, and that the rotation can be driven by light and temperature.



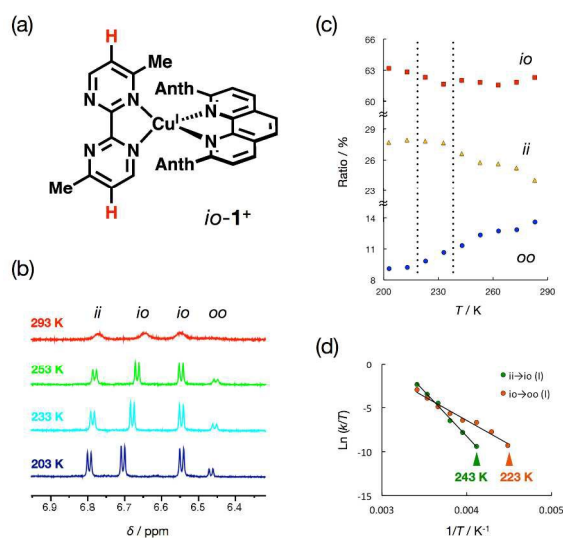
**Fig. 1** Rotational isomerization. (a) The three rotational isomers of **1**<sup>+</sup> and rotational rate constants ( $s^{-1}$ ) at 293 K. Anth = 9-anthryl. (b) Schematic of the isomerization in the Cu(I) and Cu(II) states.

We recently reported the rotational isomerization of heteroleptic Cu(I) complexes with two rotating units consisting of bipyrimidine and bis[2-(diphenylphosphino)phenyl] ether (DPEPhos),<sup>8</sup> and found that the ring rotation is restricted by the steric effect of DPEPhos to yield only the *oo*- and *io*-isomers but not the *ii*-isomer. In a dinuclear Cu(I) complex with N,N'-bis[(4-methyl-2-pyrimidinyl)-methylene]-*p*-phenylenediamine, the two pyrimidine rings rotate; however, the two rotations occur independently without any correlation.<sup>8</sup> Appropriate molecular design is important for achieving correlated ring rotations; i.e., where one rotational process affects the other.

In this study, we synthesized a new heteroleptic Cu(I) complex with bipyrimidine moieties as the dual rotating units.

The correlated rotations of the two connected rings were measured by variable-temperature  $^1\text{H}$  NMR and cyclic voltammetry.

We prepared a bipyrimidine ligand, 4,4'-dimethyl-2,2'-bipyrimidine ( $\text{Me}_2\text{bipym}$ ),<sup>9</sup> which bears two methyl groups on each ring (Fig. 1).  $[\text{Cu}(\text{Me}_2\text{bipym})(\text{L}_{\text{Anth}2})]\text{PF}_6$  ( $\mathbf{1}\cdot\text{PF}_6$ ;  $\text{L}_{\text{Anth}2}$  = 2,9-bis(9-anthracenyl)-1,10-phenanthroline<sup>10</sup>) was synthesized according to a modified literature method.<sup>5–8,10</sup> In this protocol, a tetrakis(acetonitrile)Cu(I) salt was added to a dichloromethane solution containing an  $\text{L}_{\text{Anth}2}$  and a bipyrimidyl ligand. The bulkiness of the two anthryl groups plays a key role not only in avoiding the formation of homoleptic complexes, but also in detecting rotational isomers, which generally interconvert fast without steric hindrance to the rotating rings. This complex was characterized by  $^1\text{H}$  NMR and ESI-TOF-MS.

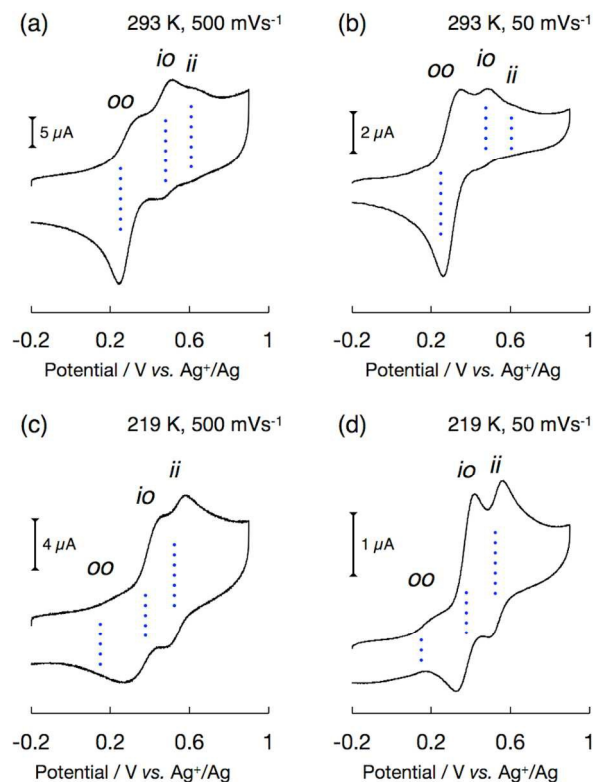


**Fig. 2** Variable-temperature  $^1\text{H}$  NMR measurements of  $\mathbf{1}\cdot\text{PF}_6$  in acetone- $d_6$ . (a) *io*-isomer of  $\mathbf{1}^+$ . (b)  $^1\text{H}$  NMR spectra of protons labeled red in (a) taken at different temperatures. (c) Ratio of the isomers calculated from the integrated value of signals at different temperatures. Dotted lines indicate the temperatures at which rotation occurs. (d) Eyring plots of the *ii*  $\rightarrow$  *io* rotation and *io*  $\rightarrow$  *oo* rotation based on the rate constants estimated by simulative analysis on  $^1\text{H}$  NMR.

Variable-temperature  $^1\text{H}$  NMR measurements were conducted by cooling the sample solution to 203 K, and then heating it gradually. The  $^1\text{H}$  NMR spectra of  $\mathbf{1}\cdot\text{PF}_6$  at 203 K showed three peaks (Fig. 2b) that were assigned to the protons at the 5-position of the *oo*-, *io*-, and *ii*-isomers, considering the shielding effect of the Cu(I) center.<sup>5</sup> The ratios of the three isomers calculated from the integrated values of the peaks were *oo*:*io*:*ii* = 1:6:3 at 203 K. The signal splitting that emerged upon heating indicates that the interconversion rate of the isomers competed with the timescale of the NMR measurements.

Characteristic behavior was observed in the plot of the ratios of isomers versus temperatures (Fig. 2c). Below 223 K, the ratio of the isomers was almost constant, indicating that the rotations were frozen. From 223 to 243 K, the ratio of the *oo*-isomer increased and that of the *io*-isomer decreased. The ratio of the *ii*-isomer remained constant in this region. These results

suggest that only the rotation between the *oo*- and *io*-isomers occurred. Above 243 K, the rotation between *io*- and *ii*-isomers was observed, indicating two-step rotational behavior. The simulative analysis on the broadening signals also revealed the difference in temperature-dependence of the rotation rates; the *ii*  $\rightarrow$  *io* rotation freezes at higher temperature than *io*  $\rightarrow$  *oo* rotation (Fig. 2d).



**Fig. 3** Cyclic voltammograms of  $\mathbf{1}^+$  (0.5 mM) in 0.1 M  $n\text{Bu}_4\text{NPF}_6$ -acetone at various temperatures and scan rates. (a) 293 K and  $500\text{ mVs}^{-1}$ , (b) 293 K and  $50\text{ mVs}^{-1}$ , (c) 219 K and  $500\text{ mVs}^{-1}$ , and (d) 219 K and  $50\text{ mVs}^{-1}$ . All voltammograms are for the first cycle.

Cyclic voltammograms of  $\mathbf{1}\cdot\text{PF}_6$  at 293 K (Fig. 3a, b) show three redox signals, which were assigned to the redox reactions of the *oo*-, *io*-, and *ii*-isomers, respectively, from the negative to the positive potential, based on the electrochemistry of Cu complexes.<sup>11</sup> The rotational behaviour was observed as the peak currents changed, particularly in the cathodic sweep. The reduction current was larger than the oxidation current for the *oo*-isomer, whereas it was smaller than the oxidation current for the *ii*- and *io*-isomers, suggesting that the *ii*- and *io*-isomers were converted to the *oo*-isomer in the Cu(II) state. This is consistent with our previous results for one pyrimidine rotation. In the Cu(II) equilibrium state, a rotor strongly prefers the outer form to the inner form because of the increase in steric hindrance owing to the conformational distortion arising from the conversion from the tetrahedral geometry of Cu(I) to the square planar geometry of Cu(II). The conversion was more obvious at the slower scan rate where the rotation took place before the reduction (Fig. 3b). Cyclic voltammetry at 219 K showed negligible differences between the anodic and the

cathodic waves, even at a rate of  $50 \text{ mV s}^{-1}$  (Fig. 3c, d), indicating that rotation was frozen at 219 K within the time scale of cyclic voltammetry.

Simulative analysis was performed on the cyclic voltammograms taken at 219, 253, 273, and 293 K to obtain the kinetic and thermodynamic parameters for the rotational isomerization. The simulated curves reproduced the voltammograms well by assuming that the two-step interconversion mechanism is dominant and the direct conversion between *oo*- and *ii*-isomers is negligible. The voltammograms taken at 219 K could be simulated by assuming that rotation was frozen. The three overlapped redox waves were deconvoluted into three waves:  $E^{\circ}_{oo} = 0.28 \text{ V}$ ,  $E^{\circ}_{io} = 0.48 \text{ V}$ , and  $E^{\circ}_{ii} = 0.61 \text{ V}$  vs  $\text{Ag}^+/\text{Ag}$ . By simply increasing the number of rotors, we achieved a larger potential shift for isomerization within a single molecule compared with our previous Cu complexes consisting of just one rotor. The redox potential shifts for each rotational step were different:  $E^{\circ}_{io} - E^{\circ}_{oo} = 0.20 \text{ V}$  and  $E^{\circ}_{ii} - E^{\circ}_{io} = 0.13 \text{ V}$ . This means that the molecule requires different energies for each ring rotation. The rate constants were also estimated by the simulative analysis (Fig. 1a).

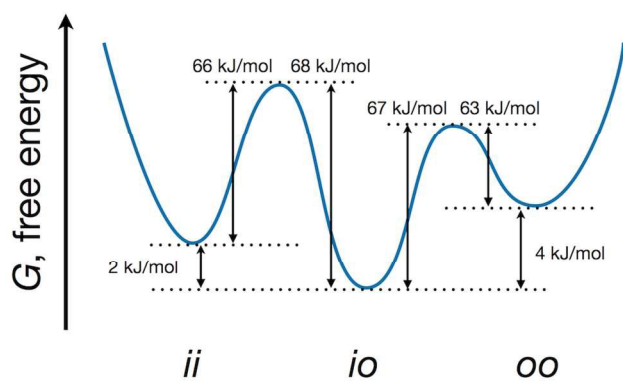


Fig. 4 Free-energy diagram of the three isomers with the values of  $\Delta G^{\circ}$  and  $\Delta G^{\ddagger}$ .

Note that a comparison of the rotation rate constants in the Cu(I) state ( $k_{oo \rightarrow io} > k_{io \rightarrow ii}$  and  $k_{ii \rightarrow io} > k_{io \rightarrow oo}$ ) reveals that the rate of *ii*  $\rightarrow$  *io* (or *oo*  $\rightarrow$  *io*) rotation is faster than that of the subsequent *io*  $\rightarrow$  *oo* (or *io*  $\rightarrow$  *ii*) rotation. This implies that **1**·**PF**<sub>6</sub> shows unique behaviour, where the first ring rotation decelerates the second.

Eyring plots and van 't Hoff plots (Fig. S1 and S2) gave the standard Gibbs free energies ( $\Delta G^{\circ}$ ) and activation Gibbs free energies ( $\Delta G^{\ddagger}$ ) (Table S2). The free energy diagram shown in Fig. 4 summarizes these values. The *ii*-isomer is thermodynamically more stable than the *oo*-isomer; however, the *ii*-isomer is less stable than the *io*-isomer due to the balance of the electronic and steric effects of the methyl groups at the inner position.<sup>5,6</sup> The diagram confirms that the *ii*  $\rightarrow$  *io* rotation is kinetically favoured compared with the subsequent *io*  $\rightarrow$  *oo* rotation. The deceleration of the second rotation is more obvious in the *oo*-isomer rotations; the  $\Delta G^{\ddagger}$  value for the *oo*  $\rightarrow$  *io* rotation is substantially lower than the  $\Delta G^{\ddagger}$  value for the subsequent *io*  $\rightarrow$  *ii* rotation.

In conclusion, we reported the two correlated rotational motions in Cu(I) complexes. <sup>1</sup>H NMR measurements have revealed that three isomers coexist and interconvert in solution. Furthermore, the two rotational processes are activated at different temperatures, indicating the correlation of the two motions. The kinetic and thermodynamic parameters obtained from the quantitative analysis of the cyclic voltammograms also support the conclusion that first ring rotation decelerates the second rotation.

## Notes and references

<sup>a</sup> Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

<sup>b</sup> Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1, Kichijoji-kitamachi, Musashino, Tokyo, 180-8633, Japan

<sup>c</sup> Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8536, Japan.

Electronic Supplementary Information (ESI) available: Synthetic procedures and details of electrochemistry and simulation analysis.

See DOI: 10.1039/c000000x/

- 1 J. Michl and E. C. H. Sykes, *ACS Nano*, 2009, **3**, 1042–1048; W. R. Browne and B. L. Feringa, *Nature Nanotech*, 2006, **1**, 25–35.
- 2 T. Kudernac, N. Ruangsupapichat, M. Parschau, B. Maciá, N. Katsonis, S. R. Harutyunyan, K.-H. Ernst, and B. L. Feringa, *Nature*, 2011, **479**, 208–211; S. P. Fletcher, F. Dumur, M. M. Pollard, and B. L. Feringa, *Science*, 2005, **310**, 80–82.
- 3 C. Manzano, W. H. Soe, H. S. Wong, F. Ample, A. Gourdon, N. Chandrasekhar, and C. Joachim, *Nature Mater*, 2009, **8**, 576–579; G. Vives, A. Carella, J.-P. Launay, and G. Rapenne, *Coordination Chemistry Reviews*, 2008, **252**, 1451–1459.
- 4 S. Hiraoka, E. Okuno, T. Tanaka, M. Shiro, and M. Shionoya, *J. Am. Chem. Soc.*, 2008, **130**, 9089–9098; C.-Y. Kao, Y.-T. Hsu, H.-F. Lu, I. Chao, S.-L. Huang, Y.-C. Lin, W.-T. Sun, and J.-S. Yang, *J. Org. Chem.*, 2011, **76**, 5782–5792.
- 5 K. Nomoto, S. Kume, and H. Nishihara, *J. Am. Chem. Soc.*, 2009, **131**, 3830–3831; S. Kume, K. Nomoto, T. Kusamoto, and H. Nishihara, *J. Am. Chem. Soc.*, 2009, **131**, 14198–14199.
- 6 S. Kume and H. Nishihara, *Dalton Trans*, 2011, **40**, 2299–2305.
- 7 M. Nishikawa, K. Nomoto, S. Kume, and H. Nishihara, *J. Am. Chem. Soc.*, 2012, **134**, 10543–10553.Y.
- 8 Hattori, M. Nishikawa, T. Kusamoto, S. Kume, and H. Nishihara, *Inorg. Chem.*, 2014, **53**, 2831–2840; Y. Hattori, M. Nishikawa, T. Kusamoto, S. Kume, and H. Nishihara, *Chem. Lett.*, 2014, **43**, 1037–1039.
- 9 J. Nasielski, A. Standaert, and R. Nasielski-Hinkens, *Synthetic Communications*, 1991, **21**, 901–906.
- 10 M. Schmittel, U. Lüning, M. Meder, A. Ganz, C. Michel, and M. Herderich, *Heterocyclic Communications*, 1997, **3**, 493–498; M. Schmittel, C. Michel, S.-X. Liu, D. Schildbach, and D. Fenske, *Eur. J. Inorg. Chem.*, 2001, 1155–1166.
- 11 P. Federlin, J. M. Kern, A. Rastegar, C. Dietrichbuecker, P. A. Marnot, and J. P. Sauvage, *New J. Chem.*, 1990, **14**, 9–12; S. Kume, M. Kurihara, and H. Nishihara, *Inorg. Chem.*, 2003, **42**, 2194–2196.