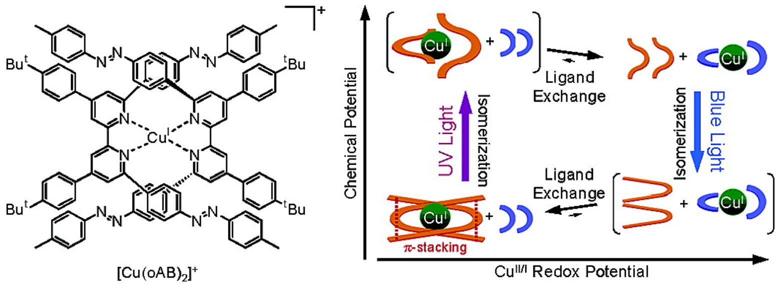
Communication

Reversible Photoelectronic Signal Conversion Based on Photoisomerization-Controlled Coordination Change of Azobenzene-bipyridine Ligands to Copper

Shoko Kume, Masaki Murata, Tomoji Ozeki, and Hiroshi Nishihara

J. Am. Chem. Soc., **2005**, 127 (2), 490-491• DOI: 10.1021/ja045093p • Publication Date (Web): 21 December 2004



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Reversible Photoelectronic Signal Conversion Based on Photoisomerization-Controlled Coordination Change of Azobenzene-bipyridine Ligands to Copper

Shoko Kume,[†] Masaki Murata,[†] Tomoji Ozeki,[‡] and Hiroshi Nishihara*,[†]

Department of Chemistry, School of Science, the University of Tokyo, 7-6-1, Hongo,
Bunkyo-ku, Tokyo 113-0033, Japan, and Department of Chemistry and Materials Science,
Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

Received August 14, 2004; E-mail: nisihara@chem.s.u-tokyo.ac.jp

The assembly of artificial molecular machines to allow precisely controlled motion that responds to light and electrons is currently a popular research topic in nanoscience.[1] However, the question of how we extract effective "output" from such motion remains to be discussed. We can find many examples of this type of motion in natural molecular machines;[2] for instance, our visual sense uses trans/cis photoisomerization of rhodopsin in the retina,[3] resulting in an electrical signal to the nervous system through a multistep chemical reaction process.[4] This natural approach—i.e. the relation of a signal receptor and a signal supplier through a reversible chemical reaction—can also be applied to the assembly of an artificial molecular machine. In the present work, we succeeded in relating the photoinduced trans/cis structural conversion of an azobenzene moiety (light receptor) and the redox reaction of a copper complex moiety (electron supplier) through a reversible ligand coordination reaction.

In our molecular design, two azobenzene moieties are substituted at the 6,6′-position of 2,2′-bipyridine, to accomplish the trans/cis structural photoconversion in the densely packed environment around the copper(I) center, which has a labile metal−ligand bond arising from its d^{10} configuration. The ligand oAB (oAB = 6,6′-bis(4″-tolylazo)-4,4′-bis(4-*tert*-butylphenyl)-2,2′-bipyridine) and its copper(I) complex $[Cu(oAB)_2]BF_4$ were synthesized and well characterized using this strategy. The ^1H NMR spectra (see Supporting Information [SI]) and the X-ray crystal structure (Figure 1) confirmed that all azo moieties in oAB and $[Cu(oAB)_2]^+$ take a completely trans form under conditions of darkness. *cis*$_2$-oAB was obtained in an almost quantitative yield of 89% by UV irradiation of a solution of *trans*$_2$-oAB, with a small amount of *trans*$_1$,*cis*$_1$-oAB formed at a photostationary state. Reaction of $[Cu(CH_3CN)_4]BF_4$ with 2 equiv of *cis*$_2$-oAB successfully yielded $[Cu(cis_2\text{-oAB})_2]^+$, which was well characterized with ^1H NMR and ^{13}C NMR spectra at 0 °C (see SI).

A comparison of the crystal structures of $[Cu(trans_2\text{-oAB})_2]^+$ (Figure 1) and its simple analogue, $[Cu(oPh)_2]^+$ (oPh = 6,6′-diphenyl-4,4′-bis(4″-*tert*-butylphenyl)-2,2′-bipyridine) (see SI) reveals that the azobenzene group makes a significant contribution to π-conjugation and the $\pi-\pi$ stacking effects in $[Cu(trans_2\text{-oAB})_2]^+$. Four interligand $\pi-\pi$ stackings are observed between pyridine and the six phenyl rings in $[Cu(trans_2\text{-oAB})_2]^+$, and the interligand dihedral angle (between two NCuN planes) is 63°, which is lower than that for $[Cu(oPh)_2]^+$ (72°). An increment of $\pi-\pi$ stacking fairly flattens the coordination geometry around the copper center of $[Cu(trans_2\text{-oAB})_2]^+$ from the tetrahedral coordination, which is a common structure in copper(I) complexes.[5]

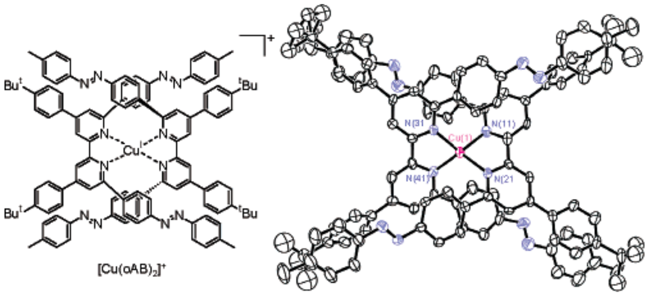


Figure 1. ORTEP drawing for $[Cu(trans_2\text{-oAB})_2]^+$ with ellipsoids drawn at the 50% probability levels. H atoms, counterions, and solvent molecules are omitted for clarity.

The *trans-cis* isomerization of the azo moiety in $[Cu(trans_2\text{-oAB})_2]^+$ is expected to change the $\pi-\pi$ stacking and coordination geometry of the copper center, because the bent structure of the *cis*-azobenzene moiety makes it difficult for this moiety to interact with the other oAB ligand. In the ^1H NMR spectra (see SI), the signals on 4-*tert*-butylphenyl moieties exhibit considerable upfield shifts (0.15−0.5 ppm) in $[Cu(trans_2\text{-oAB})_2]^+$ compared to $[Cu(oPh)_2]^+$, but almost no shifts were observed in $[Cu(cis_2\text{-oAB})_2]^+$. The upfield shifts seem to be caused by the shielding effect of opposite azo moieties of another ligand, and thus these two groups are likely far separated in $[Cu(cis_2\text{-oAB})_2]^+$, and the *cis*-azo moieties have no effect on the enhancement of $\pi-\pi$ stacking. As a result, the coordination structures of $[Cu(trans_2\text{-oAB})_2]^+$ and $[Cu(cis_2\text{-oAB})_2]^+$ are fairly different from each other with respect to the interligand π-stacking effect.

To convert the structural difference between trans and cis complexes as a driving force for electron transfer, the ligand exchange reaction can be an effective mediator, because it closely concerns both phenomena; i.e., (i) the interligand $\pi-\pi$ stacking is known to have a large stabilizing effect on formation of the α,α′-diimine bischelate copper(I) complexes,[6] and (ii) it is expected that the oxidation potential of copper(I) will change with the ligand exchange.[7] We estimated the coordination ability of these ligands by evaluating the ligand exchange equilibrium of $[Cu(bpy)_2]^+$ with *trans*$_2$-oAB or *cis*$_2$-oAB with ^1H NMR in CD_2Cl_2 (bpy = 2,2′-bipyridine). When $[Cu(bpy)_2]^+$ was added to 2 equiv of *trans*$_2$-oAB, 32% of *trans*$_2$-oAB replaced bpy and formed $[Cu(trans_2\text{-oAB})_2]^+$ to reach equilibrium within 30 min. On the other hand, almost no $[Cu(cis_2\text{-oAB})_2]^+$ formation was observed from a mixture of $[Cu(bpy)_2]^+$ and 2 equiv of *cis*$_2$-oAB. These results clearly demonstrate that the coordination stabilization of $[Cu(trans_2\text{-oAB})_2]^+$ is greater than that of $[Cu(cis_2\text{-oAB})_2]^+$, as predicted from the π-stacked structure of $[Cu(trans_2\text{-oAB})_2]^+$.

Concomitant with the bpy/oAB ligand exchange reaction, the copper valence electron energy is expected to change, as the Cu^{II}/

[†] University of Tokyo.
[‡] Tokyo Institute of Technology.

10.1021/ja045093p CCC: $30.25 © 2005 American Chemical Society

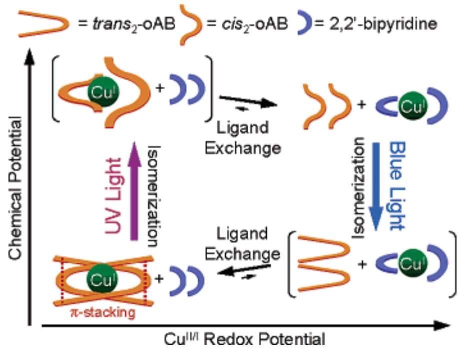


Figure 2. Schematic representation of energy migration in the mixture of oAB and $[Cu(bpy)_2]^+$.

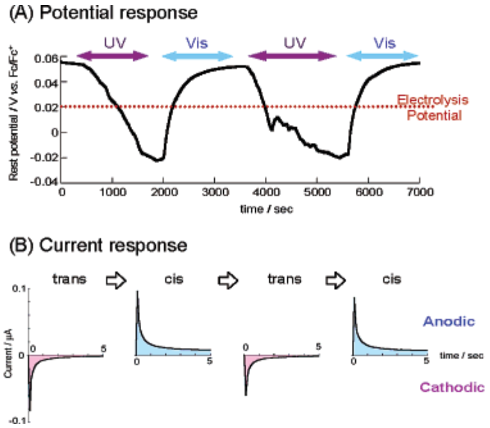


Figure 3. Time-course rest potential changes (A) and electrolysis currents (B) of a photoirradiated sample containing *trans*$_2$-oAB (1×10^{-3} M), $[Cu^I(bpy^*)_2]BF_4$ (5×10^{-5} M), and $[Cu^{II}(bpy^*)_2](BF_4)_2$ (5×10^{-4} M) in 0.1 M Bu_4NBF_4 solution (CH_2Cl_2). Sequential photoirradiation was carried out with monochromatic UV light (365 ± 30 nm) and visible light (436 ± 30 nm). The electrolysis potential applied in B was set at 0.20 V, which is the midpoint value between the trans and cis rest potentials (denoted by the red dotted line in A).

Cu^I redox potentials of $[Cu(bpy)_2]^+$ and $[Cu(\textit{trans}_2\text{-oAB})_2]^+$ differ significantly. This difference is attributed to the bulky groups at 6,6′-position of bipyridine in oAB preventing the formation of a favorable square planar structure in the Cu^{II} state.[7] In a differential pulse voltammogram of the mixture containing $[Cu(bpy)_2]^+$ and *cis*$_2$-oAB in an electrolyte solution (see SI), a Cu^{II}/Cu^I redox wave of $[Cu(bpy)_2]^+$ was observed at −0.20 V (vs ferrocenium/ferrocene), and a small redox wave of $[Cu(\textit{cis}_2\text{-oAB})_2]^+$ (0.45 V) was seen. But when *cis*$_2$-oAB was converted to *trans*$_2$-oAB with visible irradiation, a new Cu^{II}/Cu^I redox wave of $[Cu(\textit{trans}_2\text{-oAB})_2]^+$ developed at 0.45 V. This result directly exhibits that the electrochemical behavior could be controlled reversibly with UV/visible irradiation, and the reaction in this system can be described in Figure 2.

The redox potential change generated through photoisomerization can be externally retrieved as an electrode potential response, when we employ an equilibrium of Cu^{II}/Cu^I in solution. In an oAB−$[Cu^I(bpy^*)_2]^+$−$[Cu^{II}(bpy^*)_2]^{2+}$ (bpy* = 4,4′-di-*tert*-butyl-2,2′-bpy) ternary system, a reversible potential response was obtained with alternate photoirradiation of UV/visible light (Figure 3A). The response first exhibited a negative potential shift ($\Delta E = 75$ mV) with *trans*-to-*cis* photoisomerization (UV irradiation). The potential shift was maintained in the dark and was restored to its initial value by visible irradiation, which caused cis-to-trans back isomerization. The potential change was reproducible in multiple sequences following reversible trans/cis photoisomerization. In addition, the electric current response induced by closing the electronic circuit was also measured with the bias potential maintained at the midpoint between the cis and trans redox potentials (at 0.02 V). The current was cathodic in the trans form, but it was inverted to anodic when UV irradiation isomerized the azobenzene moiety to the *cis* form (Figure 3B). The response also could be repeated continuously, and it is worth noting that the system completely recovered its initial state in a sequential procedure, because the charge migration was canceled out through the cathodic and anodic current.

The photoelectric conversion was also attained using a simple solid polymer electrolyte cell, ITO/oAB, $[Cu^I(bpy^*)_2]^+$, $[Cu^{II}(bpy^*)_2]^{2+}$(PEO-Li$^+$)/ITO (see SI). The voltage between the two ITO electrodes changed positively and negatively with multiple sequences responding to UV and visible light irradiation, respectively. The potential difference between the two ITOs may be caused by the temporal gradient of the trans/cis ratio through the light path.

In conclusion, a molecular machine-based photoelectric conversion system was demonstrated in this study. The coordination chemistry of copper plays a key role in converting the photoinduced mechanical work of azobenzene to electronic work, and thereby creating a reversible and charge-storable system. The combination of a redox reaction with trans/cis conversion of azobenzene has been reported by several groups thus far,[8] but electrons were used as input stimuli to induce isomerization. The catenation of individual reversible reactions to make an input/output path is a completely new approach that affords a molecular system working purely with light energy and supplying electrical signals to outside of the molecule.

Acknowledgment. The synchrotron radiation experiment was performed at the BL04B2 in the SPring-8 with the approval of the JASRI (Proposal No. 2003A0454-CD1-np). This work was supported by Grants-in-Aid for Scientific Research (Nos. 15033215 (area 417) and 14204066), and by a grant from The 21st Century COE Program for Frontiers in Fundamental Chemistry from MEXT, Japan.

Supporting Information Available: Mateirals and methods, crystal structures of $[Cu(\textit{trans}_2\text{-oAB})_2]BF_4$ and $[Cu(oPh)_2]BF_4$, ^{1}H NMR data of Cu complexes, DPV data, and data for a polymer electrolyte system. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Special issues on molecular machines can be found in *Acc. Chem. Res.* **2001**, *34*. (b) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3349−3391. (c) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152−155. (d) Stanier, C. A.; Alderman, S. J.; Claridge, T. D. W.; Andreson, H. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 1769−1772. (e) Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133−137. (f) Armaroli, N. Balzani, V. Sauvage, J.-P. Ventura, B. *J. Am. Chem. Soc.* **1999**, *121*, 4397−4408. (g) Nishihara, H. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 407−428.

(2) Mehta, A. D.; Rief, M.; Spudich, J. A.; Smith, D. A.; Simmons, R. M. *Science* **1999**, *283*, 1689−1695.

(3) Wald, G. *Science* **1968**, *162*, 230−239.

(4) Stavenga, D. G.; DeGrip, W. J.; Pugh, E. N. *Molecular Mechanism in Visual Transduction*; Elsevier: Amsterdam, 2000.

(5) Munakata, M.; Kitagawa, S.; Asahara, A.; Masuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1927−1929.

(6) Meyer, M.; Albrecht-Gary, A.-M.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *Inorg. Chem.* **1999**, *38*, 2279−2287.

(7) (a) Federlin, P.; Kern, J.-M.; Rastegar, A. *New. J. Chem.* **1990**, *14*, 9−12. (b) Kume, S.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **2003**, *42*, 2194−2196.

(8) (a) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658−660. (b) Kondo, T.; Kanai, T.; Uosaki, K. *Langmuir* **2001**, *17*, 6317−6324.

JA045093P