Electrochemistry

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# Regulating Copper-Binding Affinity with Photoisomerizable Azobenzene Ligand by Construction of a Self-Assembled Monolayer**

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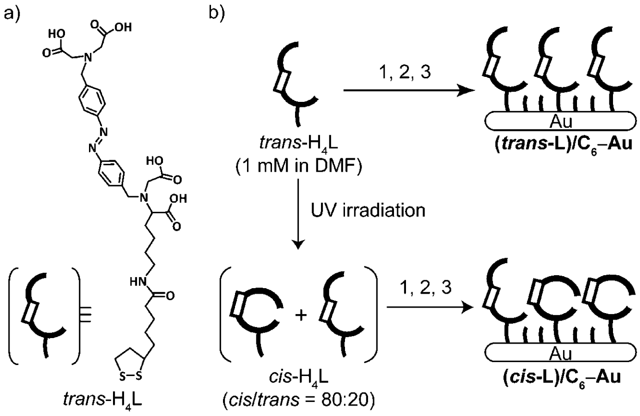
Photoactive molecules have attracted much interest because they allow molecular properties to be changed and switched dramatically.[1–5] For example, functional molecules and systems that both bind and release metal ions have been constructed by reversible structural regulation using photochromic molecules, such as spiropyran and azobenzene.[3,4] In the case of a spiropyran derivative, one of the isomers bound a transition-metal ion through its negatively charged group, whereas the other isomer did not. This photoregulated metal-binding system was useful both in solution and in a polymer matrix.[3] However, the metal-binding ability was relatively weak since the binding site was singly negatively charged, and binding sites with two or more charged groups are required for a more effectively regulated metal-binding system.

It has been reported that an azobenzene derivative containing two iminodiacetic acid moieties (azo-IDA) could strongly bind to a metal ion in aqueous solution, but the difference in the binding constants of the *trans* and *cis* isomers with the $Cu^{II}$ ion were relatively small: $K_{Cu} = 6.49 \times 10^{10}$ (*trans*) and $8.99 \times 10^{10}\,\text{M}^{-1}$ (*cis*).[4b] The *cis* ligand coordinates to a $Cu^{II}$ ion by intramolecular interaction in solution, whereas the *trans* ligand coordinates to a $Cu^{II}$ ion presumably through intermolecular interaction, although it was not discussed in detail. On a solid surface, the metal-binding behavior of a ligand is not always identical to that in solution. For example, although both isomers of an azopyridine derivative bind to transition-metal ions in solution, only one of the isomers could bind to them on an Au surface.[5] This difference in binding ability could be useful in metal-binding regulation, but it is still relatively weak ($K_{Ni} = 1.72 \times 10^4\,\text{M}^{-1}$).[6]

To construct a photoregulated system, we synthesized an asymmetrical azobenzene ligand (L) with an azo-IDA backbone and a disulfide group, and prepared its self-assembled monolayer (SAM) on an Au surface (Scheme 1). The azo-IDA backbone was designed as the strong $Cu^{II}$-binding site and the disulfide group as the surface adsorption site. SAMs have been widely studied, especially in the electrochemical evaluation of Cu ions bound to adsorbed ligands and in the photoconversion of azobenzene-modified surfaces.[7–10] In this study, the SAM of *trans*-L easily released the Cu ions, whereas that of *cis*-L did not. The binding affinity of *cis*-L, therefore, is apparently stronger than that of *trans*-L and irradiation of *cis*-L with visible light (*cis*-to-*trans* photoisomerization) led to a decrease in the number of adsorbed Cu ions. These results clearly show photoregulation of the Cu-binding affinities affixing the azobenzene ligand to the Au surface.



**Scheme 1.** a) Azobenzene ligand, *trans*-$H_4L$. b) Preparation of the SAMs of L: 1) modification of $H_4L$ to an Au surface ($H_4L$–Au), 2) modification of hexanethiol ($C_6$) to $H_4L$–Au ($H_4L/C_6$–Au), 3) deprotonation of $H_4L/C_6$–Au ($L/C_6$–Au). DMF = dimethylformamide.

The protonated azobenzene ligand in the *trans* form (*trans*-$H_4L$, Scheme 1a) was synthesized according to Scheme S1 (see the Supporting Information). Its deprotonated form (*trans*-L) was prepared by adding four equivalents of NaOH to the protonated form. The absorption spectrum of *trans*-L in aqueous solution showed three bands at 229 ($1.3 \times 10^4$), 334 ($2.1 \times 10^4$), and 420 nm ($1.6 \times 10^3\,\text{M}^{-1}\text{cm}^{-1}$, Figure S2a in the Supporting Information), which corresponded to typical $\pi$–$\pi^*$ and n–$\pi^*$ bands for a *trans*-azobenzene.[4b,9b,11] Irradiation of *trans*-L with UV light ($320 < \lambda < 400$ nm) caused *trans*-to-*cis* photoisomerization together with an absorption change (Supporting Information, Figure S2). The

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*trans*/*cis* ratio of L at the photostationary state (PSS) obtained by UV irradiation was *trans*/*cis* = 38:62,[12] which was in agreement with the value reported for azo-IDA.[4b] The calculated spectrum of *cis*-L showed three bands at 240 ($1.2\times10^4$), 295 ($6.3\times10^3$), and 430 nm ($2.1\times10^3\,\mathrm{M^{-1}cm^{-1}}$, Figure S2 a in the Supporting Information). Subsequent *cis*-to-*trans* photoisomerization was performed by irradiation with visible light (420 nm $<\lambda$), and the ratio at the new PSS was *trans*/*cis* = 80:20.

Adding one equivalent of $\mathrm{Cu^{II}}$ ions to the *trans*-L solution resulted in a blue shift of the $\pi$–$\pi^*$ band (327 nm, Figure S3 in the Supporting Information). The addition of $\mathrm{Cu^{II}}$ also affected the efficiency of photoisomerization. The ratios of $\mathrm{Cu^{II}}$ complexes for the PSSs obtained by UV and visible irradiation were *trans*/*cis* = 54:46 and 90:10, respectively. These values show that the *trans*-to-*cis* photoconversion is unfavorable in the presence of $\mathrm{Cu^{II}}$ ions, whereas the *cis*-to-*trans* conversion is favorable. It has been reported that the thermal *cis*-to-*trans* isomerization of *cis*-azo-IDA was much slower for its $\mathrm{Cu^{II}}$ complex than its unligated form, because of stabilization of the $\mathrm{Cu^{II}}$ complex.[4b] The structural similarity of L to azo-IDA suggests that the thermal stability of [$\mathrm{Cu^{II}}$(*cis*-L)] is increased by the $\mathrm{Cu^{II}}$ ion. Notably, the stabilized [$\mathrm{Cu^{II}}$(*cis*-L)] complex could be easily photoconverted to the *trans* form by irradiation with visible light, so that the bound $\mathrm{Cu^{II}}$ ions could be removed.

The absorption spectra of [$\mathrm{Cu^{II}}$(*trans*-L)] and [$\mathrm{Cu^{II}}$(*cis*-L)] showed similar d–d transition bands around 700 nm (Supporting Information, Figure S4).[13] This similarity implies that the coordination structures of [$\mathrm{Cu^{II}}$(*trans*-L)] and [$\mathrm{Cu^{II}}$(*cis*-L)] are similar to each other in aqueous solution: two *trans*-L or one *cis*-L ligand may bind to the $\mathrm{Cu^{II}}$ ion by intermolecular or intramolecular interaction, respectively. Cyclic voltammograms of both [$\mathrm{Cu^{II}}$(*trans*-L)] and [$\mathrm{Cu^{II}}$(*cis*-L)] gave similar irreversible reduction waves at about −800 mV in aqueous 0.1 M $\mathrm{NaClO_4}$ solution (Supporting Information, Figure S5).[13] Since similar reduction waves were observed in the absence of $\mathrm{Cu^{II}}$ ions for *trans*- and *cis*-L, the observed waves are attributed to the reduction from the azo to the hydrazo species ($2e^-$, $2H^+$).[9a] No redox signals of the $\mathrm{Cu^{II}}$ centers were detected in the voltammograms of [$\mathrm{Cu^{II}}$(*trans*-L)] and [$\mathrm{Cu^{II}}$(*cis*-L)], and furthermore no free $\mathrm{Cu^{II}}$ ion was observed ($\mathrm{Cu^{II}(ClO_4)_2}$: cathodic peak potential $E_{pc} = -60$ mV). These results clearly demonstrate that the $\mathrm{Cu^{II}}$ ion binds tightly to the *trans* and *cis* ligands in aqueous 0.1 M $\mathrm{NaClO_4}$ solution.

SAMs of *trans*- and *cis*-L were prepared step by step (Scheme 1 b): 1) a densely packed monolayer of $\mathrm{H_4L}$ was first constructed on an Au surface ($\mathrm{H_4L}$–Au), 2) hexanethiol ($\mathrm{C_6}$) was then filled into the unmodified space on the Au surface ($\mathrm{H_4L/C_6}$–Au),[14] and finally 3) $\mathrm{H_4L}$ units were deprotonated by NaOH ($\mathrm{L/C_6}$–Au). Since *cis*-$\mathrm{H_4L}$ was immobilized by dipping it into the UV-irradiated $\mathrm{H_4L}$ solution which contained some amount of its *trans* form (*cis*/*trans* = 80:20, Figure S6 in the Supporting Information), the SAMs of *cis*-L presumably contained both the *cis* and *trans* forms.[15] The desorption waves of the *cis* and *trans* forms of $\mathrm{H_4L}$–Au were both observed at about −900 mV (Supporting Information, Figure S7), which was similar to the value obtained for the SAM of a lipoic acid.[16] The coverages of the $\mathrm{H_4L}$ units ($2e^-$/1 U) on the surface were estimated from the desorption waves as $1.6\times10^{-10}$ (*trans*) and $1.3\times10^{-10}\,\mathrm{mol\,cm^{-2}}$ (*cis*). By comparing the obtained values with the fully covered monolayers of other azobenzene derivatives ($(1–5)\times10^{-10}\,\mathrm{mol\,cm^{-2}}$),[9a,10] $\mathrm{H_4L}$–Au is estimated to be densely packed on the Au surface.

Cyclic voltammograms of (*trans*-L)/$\mathrm{C_6}$–Au before and after dipping it into $\mathrm{Cu^{II}(ClO_4)_2}$ solution were recorded in aqueous 0.1 M $\mathrm{NaClO_4}$ solution (Cu-free, Figure 1 a). The SAM after incubation of $\mathrm{Cu^{II}}$ ions ([$\mathrm{Cu^{II}}$(*trans*-L)]/$\mathrm{C_6}$–Au) gave a pair of redox waves at $E_{1/2} = +222$ mV, whereas that before incubation did not. These results indicate that the observed waves are caused by the redox reaction of $\mathrm{Cu^{I/II}}$ ($1e^-$). From the quantity of the electricity of the cathodic wave in the first cycle ($Q_{pc,0}$), the surface coverage by adsorbed Cu ions was $1.9\times10^{-10}\,\mathrm{mol\,cm^{-2}}$. Taking into account the coverage of *trans*-$\mathrm{H_4L}$ ($1.6\times10^{-10}\,\mathrm{mol\,cm^{-2}}$), about 1.2 equivalents of Cu ion was bound to *trans*-L on the surface.

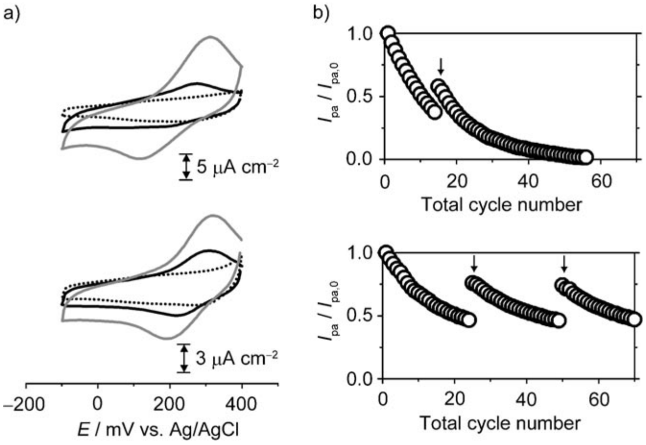

***Figure 1.*** a) Cyclic voltammograms of $\mathrm{L/C_6}$–Au (dotted line) and [$\mathrm{Cu^{II}}$(L)]/$\mathrm{C_6}$–Au (gray solid line, 1st scan; black solid line, 70th scan) in aqueous 0.1 M $\mathrm{NaClO_4}$ solution: *trans* (upper) and *cis* forms (lower). Scan rate, 50 mV s$^{-1}$. b) Plots of the relative anodic peak current ($I_{pa}/I_{pa,0}$) versus the total cycle number for [$\mathrm{Cu^{II}}$(L)]/$\mathrm{C_6}$–Au (upper, *trans* form; lower, *cis* form). The anodic peak current ($I_{pa}$) is normalized to that of the first cycle ($I_{pa,0}$). The arrows in (b) represent the first scan after an interval (10–20 s) in the consecutive scans.

The intensities of the observed redox peaks of [$\mathrm{Cu^{II}}$(*trans*-L)]/$\mathrm{C_6}$–Au were gradually decreased by performing redox cycles (Figure 1 b). Isopotential points were observed at +164 and +286 mV during the process (Supporting Information, Figure S8), which suggests that the initial Cu-bound state changes.[17] The intensities of the redox peaks increased again after an interval in consecutive scans (the arrows in Figure 1 b). These two observations indicated that the decrease in the intensities of the redox peaks was not a result of the desorption of *trans*-L but of the Cu ions: the Cu-bound state ([$\mathrm{Cu^{II}}$(*trans*-L)]/$\mathrm{C_6}$–Au) was converted to the Cu-free one ((*trans*-L)/$\mathrm{C_6}$–Au). In addition, the redox waves of $\mathrm{Cu^{I/II}}$ were almost completely diminished in the 70th cycle (Figure 1). Decreases in the intensities of the redox peaks of the Cu ions have been observed in relatively weak binding of Cu ions to adsorbed molecules.[8f] Therefore, the Cu-binding affinity to the immobilized *trans*-L is relatively weak and the bound Cu ions may be easily desorbed from $[Cu^{II}(trans\text{-}L)]/C_6$–Au.

The redox wave of $Cu^{I/II}$ was observed at $E_{1/2} = +280$ mV in the cyclic voltammograms of $[Cu^{II}(cis\text{-}L)]/C_6$–Au (Figure 1 a), and about 0.9 equivalents of Cu ion was bound to each ligand L, judging by the coverage of the Cu ions ($1.2 \times 10^{-10}$ mol cm$^{-2}$). The intensities of the peak currents decreased as in $[Cu^{II}(trans\text{-}L)]/C_6$–Au, but the decrease stopped around $I_{pa}/I_{pa,0} \approx 0.5$ (Figure 1 b). The (*cis*-L)/$C_6$–Au was presumably a mixed monolayer composed of *cis*- and *trans*-L (and $C_6$),[15] and the Cu ions bound to *trans*-L were easily desorbed as stated above. The desorption of the Cu ions in $[Cu^{II}(cis\text{-}L)]/C_6$–Au is attributed to the coexisting *trans*-L adsorbed on the Au surface, and desorption of the Cu ions from immobilized *cis*-L was somewhat slower (or did not occur) compared to that from *trans*-L. These results suggest that the Cu-binding affinity of *cis*-L is stronger than that of *trans*-L on the Au surface. The difference is likely to be induced by the surface modification,[5] which makes it difficult for the adsorbed *trans*-L to bind to a $Cu^{II}$ ion by intermolecular interaction.

To investigate the photoconversion from a stronger binding state to a weaker one, $[Cu^{II}(cis\text{-}L)]/C_6$–Au was irradiated with visible light after 70 cycles of scans. Cyclic voltammograms were recorded after the electrolyte solution was renewed to avoid rebinding of the Cu ions. Interestingly, the intensities of the redox peaks of $Cu^{I/II}$ were gradually decreased by increasing the irradiation time and finally diminished after 270 min of irradiation (Figure 2). Two isopotential points (+78 and +333 mV) were detected during the decrease in intensity, and the intensities of the redox peaks of the bound Cu ions increased again after incubation in the Cu solution. The change in the cyclic voltammograms indicates that $[Cu^{II}(cis\text{-}L)]$ (the stronger binding state) was converted to *trans*-L (Cu-free state) probably through $[Cu^{II}(trans\text{-}L)]$ (the weaker binding state) and the Cu-binding affinity was regulated by irradiation of light.

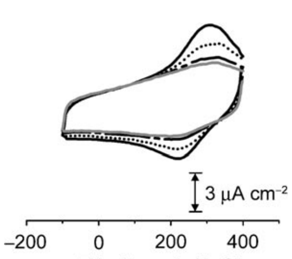

***Figure 2.*** Cyclic voltammograms of $[Cu^{II}(cis\text{-}L)]/C_6$–Au before (black solid line) and after irradiation with visible light for 90 min (dotted line), 180 min (hashed solid line), and 270 min (gray solid line). The SAM before light irradiation corresponds to that after 70 scans in Figure 1. The modified Au surface was irradiated with visible light in aqueous 0.1 M $NaClO_4$ solution. After irradiation, the electrolyte solutions were renewed before the cyclic voltammograms were measured.

In conclusion, we have demonstrated that the Cu-binding affinity of immobilized *trans*-L on an Au surface was weaker than that of *cis*-L. Moreover, irradiation of the stronger $Cu^{II}$-binding state, $[Cu^{II}(cis\text{-}L)]/C_6$–Au, with UV light led to removal of the bound Cu ions. These results indicate that the Cu-binding state can be photoregulated, although the binding affinity of the ligand is potentially high. Since the coordination sites, the target metal ions, and the substrate materials of the ligand could be changed systematically, this type of azobenzene ligand could be useful to construct not only a functional molecular unit, but also a novel reversible metal-ion-binding system.

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[1] a) G. C. R. Ellis-Davies, J. H. Kaplan, *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 187–191; b) G. A. Woolley, *Acc. Chem. Res.* **2005**, *38*, 486–493; c) C. Renner, L. Moroder, *ChemBioChem* **2006**, *7*, 868–878; d) K. L. Ciesienski, K. L. Haas, M. G. Dickens, Y. T. Tesema, K. J. Franz, *J. Am. Chem. Soc.* **2008**, *130*, 12246–12247.

[2] a) S. Hirota, Y. Fujimoto, J. Choi, N. Baden, N. Katagiri, M. Akiyama, R. Hulsker, M. Ubbink, T. Okajima, T. Takabe, N. Funasaki, Y. Watanabe, M. Terazima, *J. Am. Chem. Soc.* **2006**, *128*, 7551–7558; b) H. Prakash, A. Shodai, H. Yasui, H. Sakurai, S. Hirota, *Inorg. Chem.* **2008**, *47*, 5045–5047; c) I. Takahashi S. Kuroiwa, H. E. Lindofors, L. A. Ndamba, Y. Hiruma, T. Yajima, N. Okishio, M. Ubbink, S. Hirota, *J. Pept. Sci.* **2009**, *15*, 411–416.

[3] a) G. E. Collins, L.-S. Choi, K. J. Ewing, V. Michelet, C. M. Bowen, J. D. Winkler, *Chem. Commun.* **1999**, 321–322; b) T. Suzuki, Y. Kawata, S. Kahata, T. Kato, *Chem. Commun.* **2003**, 2004–2005.

[4] a) M. Blank, L. M. Soo, N. H. Wassermann, B. F. Erlanger, *Science* **1981**, *214*, 70–72; b) S. Shinkai, S. Nakamura, M. Nakashima, O. Manabe, M. Iwamoto, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2340–2347; c) A. Momotake, T. Arai, *Tetrahedron Lett.* **2003**, *44*, 7277–7280; d) M. Nanasawa, Y. Horikago, M. Hirai, *Polym. Bull.* **1995**, *35*, 103–108.

[5] Z. Wang, M. J. Cook, A.-M. Nygård, D. A. Russell, *Langmuir* **2003**, *19*, 3779–3784.

[6] I. M. Klotz, W.-C. Loh Ming, *J. Am. Chem. Soc.* **1953**, *75*, 4159–4162.

[7] For examples, see: a) K. Ataka, J. Heberle, *J. Am. Chem. Soc.* **2003**, *125*, 4986–4987; b) M. Abe, T. Michi, A. Sato, T. Kondo, W. Zhou, S. Ye, K. Uosaki, Y. Sasaki, *Angew. Chem.* **2003**, *115*, 3018–3021; *Angew. Chem. Int. Ed.* **2003**, *42*, 2912–2915; c) J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1169; d) I. Takahashi, T. Inomata, Y. Funahashi, T. Ozawa, K. Jitsukawa, H. Masuda, *Chem. Commun.* **2005**, 471–473; e) S. Zhang, C. M. Cardona, L. Echegoyen, *Chem. Commun.* **2006**, 4461–4473; f) I. Takahashi, T. Inomata, Y. Funahashi, T. Ozawa, H. Masuda, *Chem. Eur. J.* **2007**, *13*, 8007–8017; g) T. Inomata, K. Shinozaki, Y. Hayashi, H. Arii, Y. Funahashi, T. Ozawa, H. Masuda, *Chem. Commun.* **2008**, 392–394; h) C. Amatore, D. Genovese, E. Maisonhaute, N. Raouafi, B. Schöllhorn, *Angew. Chem.* **2008**, *120*, 5289–5292; *Angew. Chem. Int. Ed.* **2008**, *47*, 5211–5214; i) S. H. Choi, B.-S. Kim, C. D. Frisbie, *Science* **2008**, *320*, 1482–1486.

[8] a) I. Rubinstein, S. Steinberg, Y. Tor, A. Shanzer, J. Sagiv, *Nature* **1988**, *332*, 426–429; b) D. W. M. Arrigan, L. L. Bihan, *Analyst* **1999**, *124*, 1645–1649; c) W. Yang, D. Jaramillo, J. J. Gooding,

D. B. Hibbert, R. Zhang, G. D. Willett, K. J. Fisher, *Chem. Commun.* **2001**, 1982–1983; d) W. Yang, J. J. Gooding, D. B. Hibbert, *J. Electroanal. Chem.* **2001**, *516*, 10–16; e) R. K. Shervedani, A. Farahbakhsh, M. Bagherzadeh, *Anal. Chim. Acta* **2007**, *587*, 254–262; f) A. M. Etorki, A. R. Hillman, K. S. Ryder, A. Glidle, *J. Electroanal. Chem.* **2007**, *599*, 275–287; g) V. Ganesh, M. P. C. Sanz, J. C. Mareque-Rivas, *Chem. Commun.* **2007**, 804–806; h) I. Szymańska, M. Stobiecka, C. Orlewska, T. Rohand, D. Janssen, W. Dehaen, H. Radecka, *Langmuir* **2008**, *24*, 11239–11245.

[9] a) B. R. Herr, C. A. Mirkin, *J. Am. Chem. Soc.* **1994**, *116*, 1157–1158; b) T. Weidner, F. Bretthauer, N. Ballav, H. Motschmann, H. Orendi, C. Bruhn, U. Siemeling, M. Zharnikov, *Langmuir* **2008**, *24*, 11691–11700.

[10] a) Y.-Q. Wang, H.-Z. Yu, J.-Z. Cheng, J.-W. Zhao, S.-M. Cai, Z.-F. Liu, *Langmuir* **1996**, *12*, 5466–5471; b) H. Z. Yu, H. B. Shao, Y. Luo, H. L. Zhang, Z. F. Liu, *Langmuir* **1997**, *13*, 5774–5778; c) W.-W. Zhang, H.-F. Li, L. Liu, J.-L. Xie, C.-S. Lu, Y. Zhou, X.-M. Ren, Q.-J. Meng, *J. Colloid Interface Sci.* **2003**, *261*, 82–87.

[11] N. Tamai, H. Miyasaka, *Chem. Rev.* **2000**, *100*, 1875–1890.

[12] The *trans*/*cis* ratios were calculated from the intensities of the $\pi$–$\pi^*$ transition bands (334 (L) and 327 nm ([$Cu^{II}$(L)])): *trans* (%) $= A_{PSS}/A_{trans} \times 100$; $A_{PSS}$, absorbance of the PSS; $A_{trans}$, absorbance of the 100% *trans* form (Ref. [4b]). The actual ratios of the PSSs were *trans*/*cis* = 32:68 (UV irradiation) and 80:20 (visible-light irradiation) by estimation from the $^1$H NMR spectra of L (Supporting Information, Figure S2b).

[13] As the *trans*-to-*cis* photoconversion was unfavorable in the presence of $Cu^{II}$ ions, [$Cu^{II}$(*cis*-L)] was prepared by addition of one equivalent of $Cu^{II}$ ion after irradiation of *trans*-L with UV light.

[14] We used hexanethiol to decrease the background currents in the cyclic voltammograms (Refs. [7d] and [7f]) and to prevent reactions of the $Cu^{II}$ ions with the adsorbed sulfur atoms (Ref. [8d]).

[15] When an Au surface is dipped into a solution with two different molecules, the ratio of the molecules adsorbed on the surface is not generally the same as that in the solution. For examples, see: a) S. Imabayashi, T. Mita, T. Kakiuchi, *Langmuir* **2005**, *21*, 1470–1474; b) F. von Wrochem, F. Scholz, A. Schreiber, H.-G. Nothofer, W. E. Ford, P. Morf, T. Jung, A. Yasuda, J. M. Wessels, *Langmuir* **2008**, *24*, 6910–6917.

[16] a) J. Madoz, B. A. Kuznetzov, F. J. Medrano, J. L. Garcia, V. M. Fernandez, *J. Am. Chem. Soc.* **1997**, *119*, 1043–1051; b) Y. Dong, S. Abaci, C. Shannon, M. J. Bozack, *Langmuir* **2003**, *19*, 8922–8926.

[17] J. G. Gaudiello, T. C. Wright, R. A. Jones, A. J. Bard, *J. Am. Chem. Soc.* **1985**, *107*, 888–897.