Copper Sensor

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Turn-On and Selective Luminescence Sensing of Copper Ions by a Water-Soluble $Cd_{10}S_{16}$ Molecular Cluster**

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The detection of trace amounts of copper(I) ion is of increasing importance in light of its environmental and biomedical implications. One convenient detection tool is the luminescent chemosensor, whereby the major challenge is to construct sensing systems that exhibit positive responses with high selectivity and sensitivity in water.[1] A variety of fluorescence sensors have been designed by combining an organic fluorophore and a metal-binding chelate,[2] but few examples of "turn-on" sensors that function in aqueous solutions have been reported.

Recently, cadmium chalcogenide nanomaterials have emerged as a novel class of luminescent probes as a result of their unusual photoluminescence properties.[3] These materials are potentially useful for metal-ion sensing, as metal ions, including copper ions, are expected to interact with surface heteroatoms (S, Se, Te) to affect the optical properties of the material. Although the effects of metal ions on photoluminescence properties have been investigated for several nanoclusters and nanorods, only quenching effects have been reported for copper ions.[4,5] Herein, we demonstrate a unique turn-on response of the water-soluble CdS cluster molecule **2** towards copper ions, and highlight its selectivity and sensitivity.

The CdS cluster that we used in this study is a defined and neutral molecule with the general formula $[Cd_{10}S_4(SR)_{12}]$ which has a truncated tetrahedral $Cd_{10}S_{16}$ core and twelve surface substituents (R) attached to the sulfur atoms.[6] We reported recently that clusters capped by lipophilic groups (R = simple alkyl or aryl, such as **1**) show surface-mediated emission at around 600 nm in organic solvents at ambient temperature.[7] To explore the properties of such molecular clusters in aqueous systems, we appended oligo(ethylene glycol) (OEG, $-(OC_2H_4)_nOCH_3$, $n \approx 6$) units to the surface phenyl groups of the phenyl-capped precursor **1** by the thiolate exchange reaction to give **2**. In contrast to **1**, the OEG-modified cluster **2** showed high solubility in water and in organic solvents such as acetonitrile and chloroform.

In HEPES buffer (100 mM, pH 7.0) at 25 °C, **2** (6.7 μM) showed an emission band at 600 nm upon excitation of the cluster at 350 nm. The titration of this solution with $[Cu^I(CH_3CN)_4]PF_6$ resulted in a notable enhancement of photoluminescence along with a slight red shift of the emission maximum to 620 nm (Figure 1 a).[8,9] For example, when **2** was mixed with one molar equivalent of Cu^I ion, the intensity at 620 nm and the integrated band area increased by factors of 9.1 and 7.4, respectively. As shown in Figure 1 b, the emission intensities at 620 nm increased upon the addition of Cu^I to reach a plateau at $[Cu^I]_0/[\mathbf{2}]_0 \approx 2.0$ with $I/I_0 \approx 12.5$.[10] The nearly linear correlation observed up to $[Cu^I]_0/[\mathbf{2}]_0 = 1.0$ allowed easy detection of Cu^I at nanomolar to micromolar concentrations. Under these conditions the dynamic range and the detection limit were estimated to reach 10 μM and approximately 0.07 μM ($\approx$4 ppb), respectively.

This sharp positive response that was observed was found to be highly specific to Cu^I. As summarized in Figure 2 a, no

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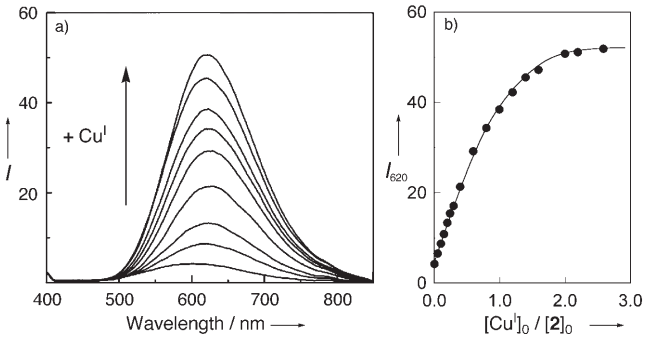

Figure 1. a) Photoluminescence response (λ_{ex} = 350 nm) of **2** (6.7 μM) upon the addition of Cu^{I} (from bottom to top: 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, and 2.0 equiv) in HEPES buffer (*N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid, 100 mM) containing MeCN (2 vol%) at 25 °C; b) plot of the photoluminescence intensity at 620 nm.

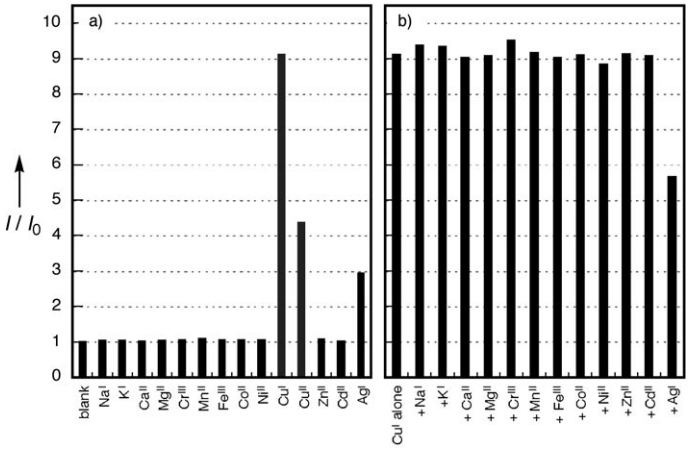

Figure 2. a) Photoluminescence response (λ_{ex} = 350 nm) of **2** (6.7 μM) monitored at 620 nm upon the addition of chloride or nitrate salts of metal ions (1.0 mM for Na^{I}, K^{I}, Ca^{II}, Mg^{II} and 6.7 μM for the other cations); b) emission response of Cu^{I} (6.7 μM) in the presence of equimolar amounts of other cations in HEPES buffer (100 mM) containing MeCN (2 vol%) at 25 °C.

emission enhancements were observed for alkaline (Na, K), alkaline-earth (Mg, Ca), or most other environmentally and biologically relevant metal ions (e.g., Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}). The excellent selectivity for Cu^{I} was further demonstrated by the observation that the emission response to Cu^{I} was not affected by the presence of the above transition-metal ions or of millimolar concentrations of NaCl, KCl, $CaCl_2$, and $MgCl_2$ (Figure 2b). Among the metal ions examined, Ag^{I}, which has the electronic structure $4d^{10}$, induced a less prominent but definite increase in emission intensity ($I/I_0 = 2.9$ at $[Ag^{I}]_0/[\mathbf{2}]_0 = 1.0$; Figure 2a). This result suggests that the positive response is specific to the Group 11 d^{10} metal ions.

A positive response was also observed for Cu^{II}, thus revealing the unique ability of **2** to respond to either Cu^{I} or Cu^{II}. It has been reported that the interaction of Cu^{II} with a colloidal CdS results in its reduction to Cu^{I}.[4a,b] A similar redox process appears to occur in the present system. In the ^{1}H NMR spectrum of a mixture of **2** and 1.0 equivalent of $Cu(NO_3)_2$, no paramagnetic features attributable to d^9 Cu^{II} were observed, and the cluster signals were very similar to those of the mixture with diamagnetic Cu^{I}.[11,12] Therefore, the positive emission response to Cu^{II} arises from in situ reduction to Cu^{I}, which again indicates the specificity for monovalent d^{10} ions of the Group 11 elements.

In contrast to the strong increase in emission intensity upon the addition of Cu^{I}, negligible changes were observed in the absorption spectrum of **2**.[11] Isarov and Chrysochoos reported that the metal-displacement reaction of surface Cd by Cu in a colloidal system leads to the emergence of a new absorption band tailing the red region as a result of the formation of Cu_xS species.[4a] In the present case, the absorption onsets were observed at ca. 420 nm and no tailing to the red region was observed throughout the titration. Therefore, as suggested by the results for our colloidal system at low copper-ion concentrations, it is likely that isolated Cu^{I} ions bind to surface sulfur atoms of **2** through simple Cu–S coordination bonds.

To obtain further insight into the adduct between **2** and Cu^{I}, we investigated the complexation stoichiometry by the Job method. As shown in Figure 3, a plot of the amount of the

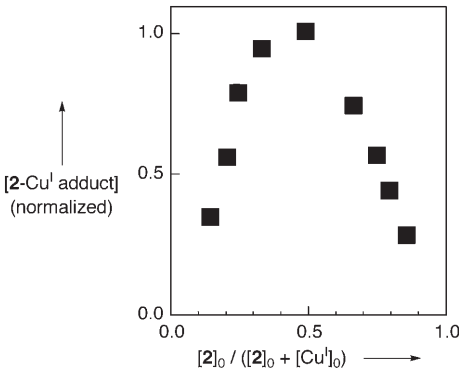

Figure 3. Job plot for the formation of the **2**–Cu^{I} adduct estimated from the emission intensity at 620 nm with $[\mathbf{2}]_0 + [Cu^{I}]_0$ maintained at 20 μM.

adduct, as estimated from the emission intensity, versus $[\mathbf{2}]_0/([\mathbf{2}]_0 + [Cu^{I}]_0)$ gave a maximum at 0.5, thus indicating 1:1 complexation. However, the simplest one-to-one adduct does not seem to be a major product. Size-exclusion chromatography (SEC) of **2** showed a significant shift of the elution peak towards a higher-molecular-weight region upon the addition of Cu^{I} (Figure 4a,b). Therefore, if the general preference of Group 11 d^{10} ions to form a two-coordinate complex with linear geometry is also considered, **2** and Cu^{I} are likely to assemble through S–Cu–S bridges to form a multicluster/nuclear network with a 1:1 composition $(\mathbf{2}\cdot Cu^{I})_m$, as illustrated schematically in Figure 5.

This conclusion strongly suggests that the formation of Cu^{I}-containing multicluster species $(\mathbf{2}\cdot Cu^{I})_m$ is responsible for the sharp emission response to Cu^{I}. The similarity of the excitation spectral patterns ($\lambda_{em} = 610$ nm) before and after the addition of Cu^{I} indicates that the original S-to-Cd transition associated with the emission at 620 nm is almost completely retained after the complexation with Cu^{I}. This

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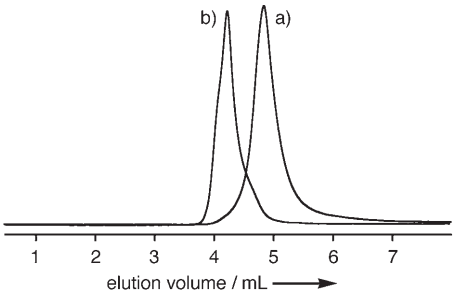

Figure 4. SEC profiles of a) **2** and b) **2**/$[Cu^{I}(CH_3CN)_4]PF_6$ (1:4 molar ratio) monitored at 340 nm with a Shodex OHpak SB802.5HQ instrument with $MeCN/H_2O$ (60/40 v/v) as the eluent.

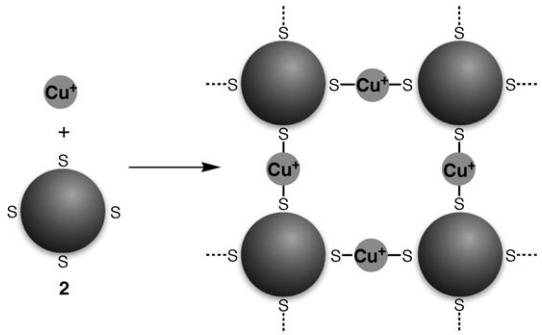

Figure 5. Schematic illustration of a possible network structure of the **2**–Cu^{I} aggregate: $(\mathbf{2}\cdot Cu^{I})_m$. The large spheres represent the clusters.

notion is supported by the above-mentioned absorption profiles, in which no substantial changes were observed upon complexation. Therefore, the observed emission enhancement corresponds to the increase in the quantum yield, which may result from the generation of a new and efficient radiative path involving the bound Cu^{I} ion and/or from the suppression of a nonradiative process. With respect to the latter possibility, we proposed recently that the cluster emission is enhanced when the free motion (rotation) of the surface substituents is suppressed.[7a] A similar mechanism may be involved in the present case, as the formation of S–Cu–S bridges should require the mutual interpenetration of surface aryl units on neighboring clusters, thereby restricting their motion.

In conclusion, we have demonstrated the first CdS-based photoluminescence sensor that shows a turn-on response to copper ions in aqueous solution. Studies on the structures of the aggregate species $(\mathbf{2}\cdot Cu^{I})_m$ as well as their photoluminescence properties are currently underway. Applications for turn-on sensing of small biorelevant molecules are worth further investigation.

Experimental Section

Cluster **2** was prepared by the ligand-exchange reaction of **1**[7] with 4-OEG-modified thiophenol ($HSC_6H_4(OC_2H_4)_nOCH_3$), which was prepared by coupling 4,4′-dihydroxydiphenyl disulfide[13] with the tosylate ester of poly(ethylene glycol) methyl ether ($M_n \approx 350$) followed by $NaBH_4$ reduction. The thiol (2.4 mmol) was added to a solution of **1** (50 mg) in MeCN (0.020 mmol/20 mL), and the mixture was heated at 60 °C for 6 h. After removal of the solvent, the residue was washed copiously with ether to give **2** as a tan solid (113 mg, 95 %). IR spectroscopy showed the complete disappearance of the absorption bands due to the phenyl groups of **1**. From the ^1H NMR spectrum, the average number of ethylene glycol units was estimated to be six. Elemental analysis calcd (%) for $C_{228}H_{372}Cd_{10}S_{16}O_{84}S_{16}$ ($Cd_{10}S_4(SC_6H_4(OC_2H_4)_6OCH_3)_{12}$): C 44.93, H 6.15, S 8.42; found: C 45.04, H 6.09, S 8.61; no nitrogen was found.

Photoluminescence and excitation spectra were recorded with a JASCO FP-6500 spectrofluorometer equipped with a Hamamatsu Photonics R928 photomultiplier tube detector. An optical filter was mounted in front of the detector window to block out light of wavelengths below 360 nm and thus avoid second-order effects of the excitation light.

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[1] a) R. Krämer, *Angew. Chem.* **1998**, *110*, 804; *Angew. Chem. Int. Ed.* **1998**, *37*, 772; b) N. Shao, Y. Zhang, S. Cheung, R. Yang, W. Chan, T. Mo, K. Li, F. Liu, *Anal. Chem.* **2005**, *77*, 7294; c) R. Méallet-Renault, R. Pansu, S. Amigoni-Gerbier, C. Larpent, *Chem. Commun.* **2004**, 2344; d) S. Kaur, S. Kumar, *Chem. Commun.* **2002**, 2840; e) K. Rurack, M. Kollmannsberger, U. Resch-Genger, J. Daub, *J. Am. Chem. Soc.* **2000**, *122*, 968; f) A. Torrado, G. K. Walkup, B. Imperiali, *J. Am. Chem. Soc.* **1998**, *120*, 609.

[2] a) L. Yang, R. McRae, M. M. Henary, R. Patel, B. Lai, S. Vogt, C. J. Fahrni, *Proc. Natl. Adac. Sci. USA* **2005**, *102*, 11179; b) M. Royzen, Z. Dai, J. W. Canary, *J. Am. Chem. Soc.* **2005**, *127*, 1612; c) Z. Xu, Y. Xiao, X. Qian, J. Cui, D. Cui, *Org. Lett.* **2005**, *7*, 889; d) P. Chen, C. He, *J. Am. Chem. Soc.* **2004**, *126*, 728.

[3] A. L. Rogach, D. V. Talapin, H. Weller in *Colloids and Colloid Assemblies* (Ed.: F. Caruso), Wiley-VCH, Weinheim, **2004**, chap. 2.

[4] a) A. V. Isarov, J. Chrysochoos, *Langmuir* **1997**, *13*, 3142; b) Y. Chen, Z. Rosenzweig, *Anal. Chem.* **2002**, *74*, 5132; c) K. M. Gattás-Asfura, R. M. Leblanc, *Chem. Commun.* **2003**, 2684; d) B. Tang, J. Niu, C. Yu, L. Zhuo, J. Ge, *Chem. Commun.* **2005**, 4184; e) M. T. Fernández-Argüelles, W. J. Jin, J. M. Costa-Fernández, R. Pereiro, A. Sanz-Medel, *Anal. Chim. Acta* **2005**, *549*, 20.

[5] Positive responses have been reported for other metal ions: for Zn^{2+}, see ref. [4b]; for Ag^{+}, see: A. Kumar, S. Kumar, *Chem. Lett.* **1996**, 711; L. Spanhel, H. Weller, A. Fojtik, A. Henglein, *Ber. Bunsen-Ges.* **1987**, *91*, 88.

[6] a) R. D. Adams, B. Zhang, C. J. Murphy, L. K. Yeung, *Chem. Commun.* **1999**, 383; b) F. E. Osterloh, D. P. Hewitt, *Chem. Commun.* **2003**, 1700.

[7] a) T. Hiratani, K. Konishi, *Angew. Chem.* **2004**, *116*, 6069; *Angew. Chem. Int. Ed.* **2004**, *43*, 5943; b) K. Konishi, T. Hiratani, *Chem. Lett.* **2006**, 184.

[8] To prevent disproportionation of Cu^{I}, the titration experiments were conducted in the presence of CH_3CN (2 vol %); see: P. Kanau, R. B. Jordan, *Inorg. Chem.* **2001**, *40*, 3879, and ref. [2a].

[9] Similar red shifts upon interaction with copper(I) ion have been reported for CdS colloids (refs. [4a,b]), for which the generation of a new energy level involving copper is suggested.

[10] The strong complexation did not allow determination of the association constant from the titration profiles, but it is estimated to be larger than $10^7\,M^{-1}$.

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[11] See the Supporting Information.
[12] The reduction of Cu^{II} was further supported by the appearance of new ^{1}H NMR signals due to disulfide formed by the oxidative coupling of the surface thiolates.
[13] R. S. Sengar, V. N. Nemykin, P. Basu, *New J. Chem.* **2003**, *27*, 1115.

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