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Sequential Metal Ion Assembly in Cyclic Phenylazomethine

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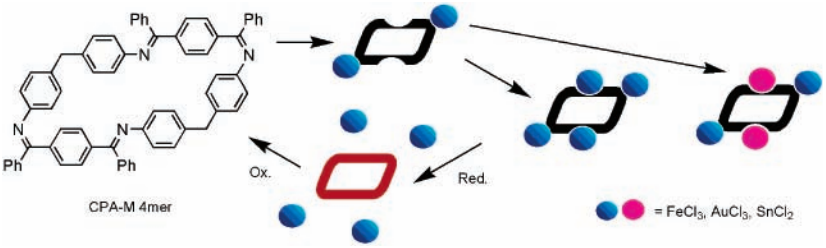
ABSTRACT

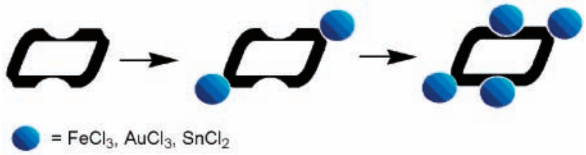


Cyclic phenylazomethines with methylene spacers (CPA-M) are obtained by dehydration of diamine with diketone. During the titration of CPA-M 4mer with FeCl$_3$, we observe two consecutive isosbestic points in the UV–vis spectra. We conclude that complexation occurs in two consecutive steps. Our analysis suggests that the stepwise metal ion assembly is caused by a difference in the basicity of the imine conformers. Metal ion binding first occurs at the *Z* imines followed by coordination to the *E* imine. Finally, metal ion assembly in this compound can be controlled electrochemically.

The assembly of metal ions in supramolecular architectures in predictable ways is a prerequisite to create novel organic−metallic hybrid nanomaterials with electronic, magnetic, or reactive functions.[1] Especially, precise control of the number and position of metal ions in organic modules is of pivotal importance for the design of functional nanostructures. In the past, we succeeded in sequential complexation of metal ions in dendritic polyphenylazomethines due to the basicity gradient along the dendrimer radius.[2] To date organic materials showing sequential self-assembly of metal ions are hardly known. Here, we report the precise control of metal ion assembly in cyclic phenylazomethines and their electrochemical switching. To the best of our knowledge this is a unique example in which the precise positioning of metal ions in an assembly is controlled by the conformation of the molecule.

Cyclic phenylazomethines with methylene spacers (CPA-M) are obtained by dehydration of diaminodiphenylmethane with dibenzoylbenzene in the presence of TiCl$_4$ and DABCO (see the Supporting Information, Scheme 1).[3] An excess of TiCl$_4$, DABCO, and diaminophenylmethane with respect to the dibenzoylbenzene is employed because it increases the

Scheme 1. Schematic Representation of Sequential Metal Ion Assembly in CPA-M 4mer[a]



[a] First the *Z* then the *E* imines are complexed.

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(1) (a) Lehn, J. M. *Science* **2002**, *295*, 2400. (b) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* (*London*) **1999**, *400*, 52. (c) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877. (d) Severin, N.; Rabe, J. P.; Kurth, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 3696. (e) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* (*London*) **2005**, *436*, 238.

(2) (a) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta M.; Chiba, H. *Nature* (*London*) **2002**, *415*, 509. (b) Higuchi, M.; Tsuruta, M.; Chiba, H.; Shiki, S.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 9988.

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overall yield in cyclic versus linear phenylazomethines, which simplifies isolation and purification of CPA-M 4mer (Figure 1), which is isolated by GPC and unambiguously identified by NMR, MS, and IR.

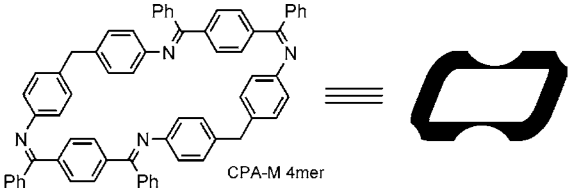

Figure 1. Structure of CPA-M 4mer.

Azomethines have a rich coordination chemistry and complexation is easily confirmed by the color change from yellow to orange in solution. For instance, during the titration of CPA-M 4mer with $FeCl_3$, we observe two consecutive isosbestic points in the UV−vis spectra (Figure 2). The discrete shift of the isosbestic point from 284 to 280 nm shows that complexation is not random but occurs in a stepwise fashion. This unique behavior indicates that two different binding modes occur in CPA-M 4mer during titration. The hypothesis of two distinct species is also reflected in the UV−vis spectra: The first isosbestic point at 284 nm is associated with a new absorption band at around 310 nm, while the second isosbestic point at 280 nm is associated with a new band appearing at 360 nm. Titrations of CPA-M 4mer with $SnCl_2$ and $AuCl_3$ afford similar UV−vis spectra with two isosbestic points and new absorption bands (see teh Supporting Information, Figures 1 and 2).

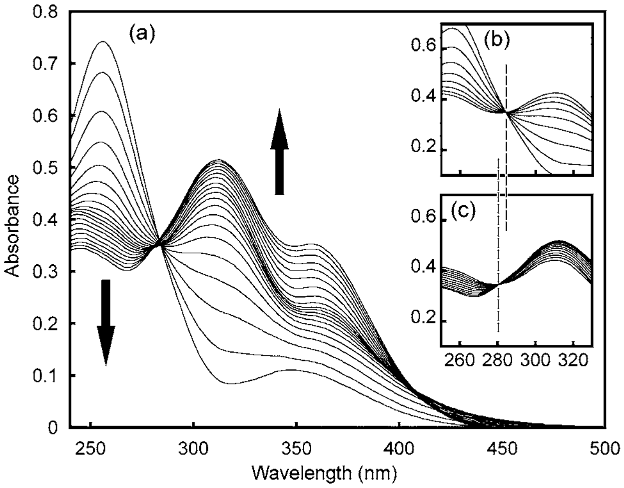

Figure 2. UV−vis spectral changes of CPA-M 4mer during addition of (a) 0−16, (b) 0−6.4, and (c) 7.2−16 equiv of $FeCl_3$. The consecutive isosbestic points occur at 284 and 280 nm as indicated by the lines in panels b and c (dichloromethane/acetonitrile = 1:1, [CPA-M 4mer] = 10 μM).

To understand the origin of sequential self-assembly, we investigated the molecular structure of CPA-M 4mer by NMR and X-ray crystallography. Analysis of single crystals by X-ray crystallography reveals a parallelogram-like structure of the CPA-M 4mer (Figure 3). In the solid, the imines of CPA-M 4mer adopt two *Z*- and *E*-conformations. We note that these two conformations are preserved in solution as indicated by room temperature NMR analysis. It is remarkable that the CPA-M 4mer exists in only one conformation, which might be caused by the bulky phenyl substituents and the limited degrees of rotation freedom.

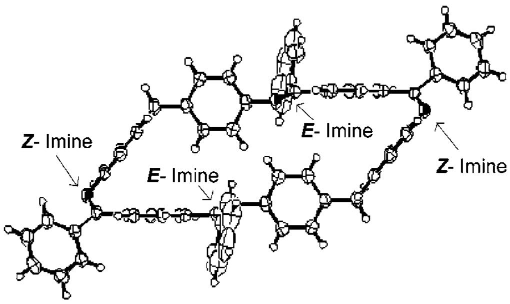

Figure 3. X-ray crystal structure of CPA-M 4mer (monoclinic, space group $P2_1/n$, $a = 14.298(3)$ Å, $b = 9.036(2)$ Å, $c = 15.77(1)$ Å, $\beta = 103.915(4)°$, $V = 3022.2(12)$ Å^3, $Z = 2$, $D_{calc} = 1.379$ g/cm^3, $\mu = 0.463$ cm^{-1}, $S = 0.991$, $R = 0.0609$, $R_w = 0.1891$).

Using the crystallographic data of CPA-M 4mer, we compute the energy of the molecular orbitals (MO) (CAChe software). We notice a distinct difference in the energies of the MOs of the *Z* and *E* imines: HOMO and HOMO-1, the MOs of highest energy, are located at the *Z* imines, while HOMO-2 and HOMO-3 are found at the *E* imines (see the Supporting Information, Figure 3). It is reasonable to assume that the basicity of the imines follows the same trend as the energies of the HOMOs.[4] We, therefore, propose that the difference in basicity is responsible for the stepwise assembly process in the CPA-M 4mer. Complexation would therefore first occur at the *Z*- and then at the *E*-imine (Scheme 1). In addition, electrostatic repulsion and/or steric hindrance may also affect metal ion coordination to CPA-M 4mer. Further evidence for stepwise complexation is provided from the UV spectra: Due to the smaller conjugation length of the *Z*-imine the absorption band (310 nm) of the first complexation step occurs at lower wavelength than the consecutive complex-

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(3) For polyphenylazomethines see: (a) Volpe, A. A.; Carson, J. C., Jr.; Kaufman, L. G. *Thermochim. Acta* **1971**, *2*, 175. (b) Kaufman, L. G.; Funke, P. T.; Volpe, A. A. *Polym. Prepr.* (*Am. Chem. Soc.*, *Div. Polym. Chem.*) **1970**, *11*, 250. (c) Taylor, L. T.; Vergez, S. C.; Busch, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 3170. (d) Williams, P. A.; Ellzey, K. A.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1993**, *26*, 5820. For cyclic phenylazomethines see: (e) Higuchi, M.; Kanazawa, H.; Yamamoto, K. *Org. Lett.* **2003**, *5*, 345.

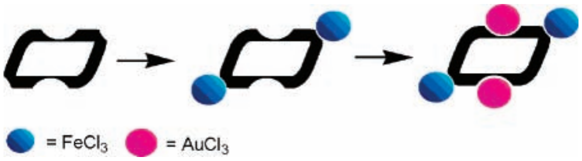
(4) (a) Shen, J.; Shao, J.; Ou, Z.; E, W.; Koszarna, B.; Gryko, D. T.; Kadish, K. M. *Inorg. Chem.* **2006**, *45*, 2251. (b) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Thompson, A. M. W. C. *Inorg. Chem.* **1995**, *34*, 2759.

ation of the *E*-imine (360 nm).[5] This is the first example to control the sequence of self-assembly of metal ions through the conformation of a molecule.

We determine the binding constants (log *K*) by simulating the spectral changes during titration (see the Supporting Information, Figure 4). The log *K* values of the first binding step (*Z*-imines) of $FeCl_3$, $AuCl_3$, and $SnCl_2$ are estimated to be 5.2, 4.5, and 4.2, respectively. The binding constants in the second binding step are more than 10 times smaller. The large difference of binding constants between cis and trans imines explains the stepwise assembly of metal ions.

In this series of metal ion chlorides, log *K* of $FeCl_3$ is higher than that of $AuCl_3$ and $SnCl_2$. This observation prompted us to explore self-assembly with different metal ions (Scheme 2). When we add $FeCl_3$ at first, and then $AuCl_3$, we observe again two consecutive isosbestic points (Supporting Information, Figure 5), which confirms heterocomplexation as shown in Scheme 2. On the other hand, if we first add $AuCl_3$, we do not observe an isosbestic point during addition of $FeCl_3$ (Supporting Information, Figure 6). The absence of an isosbestic point indicates metal ion exchange, because log *K* of $FeCl_3$ is higher than that of $AuCl_3$.

Scheme 2. Schematic Representation of Heterometal Ion Assembly in CPA-M 4mer



Generally, metal ion coordinated polyphenylazomethines including dendritic ones do not show a reversible electrochemistry, because the reduced imines are not stable and easily undergo side reactions. In contrast, CPA-M 4mer exhibits a reversible electrochemistry if complexed or protonated. For instance, the tin complex shows a single redox wave at -0.5 V (Figure 4). Initially, in the absence of metal ions there is no redox process of CPA-M 4mer as indicated by the absence of any current in the potential window. Upon addition of tin chloride, we note a redox peak at -0.5 V, which shifts to more oxidative potential with increasing concentration. The peak separation is smaller than 60 mV, indicating a one-step successive two-electron transfer process. The concentration-dependent redox potential obeys the Nernst equation (inset in Figure 4; slope: 60 mV/log-[$SnCl_2$]). We conclude that as the metal ions bind to CPA-M 4mer two electrons per phenyldiimine unit are transferred, which is a total of four metal ions and four electrons per molecule[6]

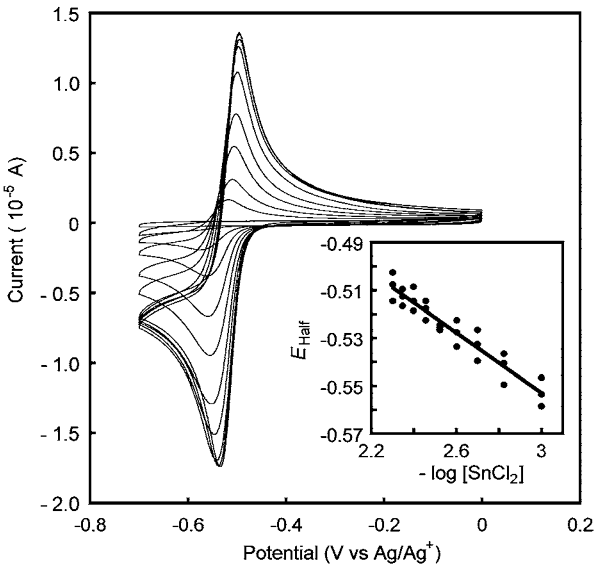
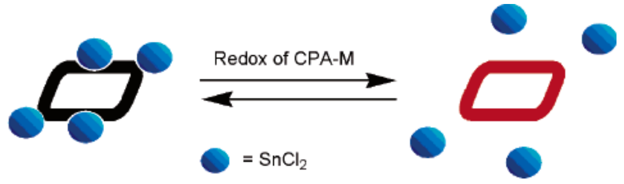


Figure 4. Cyclic voltammograms of CPA-M 4mer (0.25 mM) in 0.2 M $TBABF_4$/acetonitrile in the presence of $SnCl_2$ (0$-$5.0 mM) (scan rate: 100 mV/s; electrode: carbn disk). Inset: Concentration-dependent potential (slope: -60 mV/$-$log[$SnCl_2$]).

Furthermore, we notice that under in situ spectroelectrochemical conditions we observe the release of the assembled metal ions upon reduction due to the structural and electronic changes of the reduced species.[7] The release of metal ions is confirmed by a decrease of the corresponding absorption bands in UV$-$vis spectra at the reduction potential (Supporting Information, Figure 7). This result means that metal ion assembly in this compound can be controlled electrochemically (Scheme 3).

Scheme 3. Schematic Representation of Releasing Assembled Metal Ions after the Reduction



In conclusion, we present the unique sequential complexation behavior of a cyclic phenylazomethine with metal ions as well as their electrochemical properties. By controlling the conformation through the molecular structure we can program the self-assembly algorithm of these compounds.

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[5] For the difference in the absorption band maximum between *E* and *Z* imines, see: (a) Higuchi, M.; Kimoto, A.; Shiki, S.; Yamamoto, K. *J. Org. Chem.* **2000**, *65*, 5680. (b) Higuchi, M.; Yamamoto, K. *Org. Lett.* **1999**, *1*, 1881.

[6] For one-step successive two-electron transfers see: (a) Evans, D. H.; Hu, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3983. (b) Hu, K.; Evans, D. H. *J. Electroanal. Chem.* **1997**, *423*, 29. (c) Hapiot, P. F.; Kispert, L. D.; Konovalov, V. V.; Saveant, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6669. (d) Nishiumi, T.; Chimoto, Y.; Hagiwara, Y.; Higuchi, M.; Yamamoto, K. *Macromolecules* **2004**, *37*, 2661.

[7] (a) Liu, Y.; Flood, A. H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 9150. (b) Deans, R.; Niemz, A.; Breinlinger, E. C.; Rotello, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 10863. (c) Nabeshima, T.; Furusawa, H.; Yano, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1750.

This approach is relevant for the construction and exploitation of metalloorganic nanostructures and devices.

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Supporting Information Available: Additional data of metal ion assembly and CIF of CPA-M 4mer. This material is available free of charge via the Internet at http://pubs.acs.org.

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