Communication

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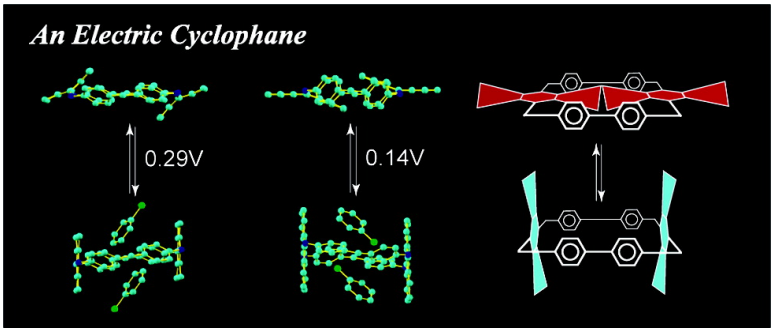

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An Electric Cyclophane: Cavity Control Based on the Rotation of a Paraphenylene by Redox Switching

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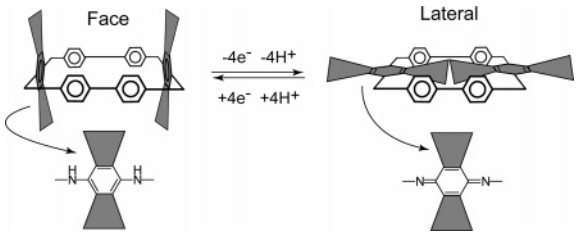
The human desire to miniaturize devices has reached to the molecular level, and much attention has been paid to molecules that produce a mechanical output on a nanometer scale. Rotation is one of the central attributes of such a mechanism. Until now, many studies related to molecular machines having a component capable of rotating in a controllable way have been done.[1] In this communication, for constructing molecular machines,[2] we propose a basic and general molecular module that fixes and releases a free rotation axis in a paraphenylene. We inserted the module into a simple molecular system (paracyclophane) and demonstrated it as to whether an active function was generated. A para-substituted aromatic (paraphenylene) ring can be regarded as a rotator using the para-rotation axis. When it is incorporated in a wider π-conjugated system, a quinoidal structure is generated and accompanied by oxidation on the substituted groups at the 1,4-position, and the axis is fixed. If the cyclic mainframe consists of the paraphenylenes, a large conformational change must occur in the entire molecule. A paraphenylenediamine is suitable for this purpose. It is the redox unit structure of polyaniline that is representative of the redox active polymer.[3] A paraphenylenediamine (benzenoid form) is converted to the paraquinonediimine (quinoidal form) by a two-electron oxidation. Furthermore, it is converted to the original form by a two-electron reduction. The conversion is reversible and stable without the formation of waste products (Scheme 1). We have recently reported the highly selective synthesis of imine macrocycles using titanium tetrachloride as the dehydration agent.[4] As the simplest cyclophane that contained paraphenylenediamine moieties, the macrocycles where a redox unit structure of polyaniline was bridged by a methylene in the para-position were designed. Hall, Jr. and co-workers have already reported a polymer possessing a quinonediimine structure that is the oxidative form of polyaniline.[5] They also confirmed using FAB-MS spectroscopy that, during the course of the polymerization, a small quantity of macrocyclic compounds was generated. The polymerization of anthraquinone (15 mM) with 4,4′-methylenedianiline (15 mM) was carried out in the presence of $TiCl_4$ (1.5 equiv) in monochlorobenzene. Many peaks attributed to the macrocyclic compound and linear oligomers were confirmed in the TOF-MS spectrum of the crude products. The entire macrocyclization was achieved by the further addition of $TiCl_4$ during the course of the polycondensation. Only peaks attributed to the paracyclophanes (AM_n, where n is the degree of polymerization) were confirmed in the TOF-MS spectrum of the crude products (Supporting Information Figure 1). High yields and the easy isolation of the cyclic oligomers resulted from the total cyclization of the linear oligomers. The AM_n products (n = 4, 6, 8, 10, 12, 14) were easily isolated in 5, 16, 10, 6, 4, and 1% yields (total: 42%), respectively, by gel permeation chromatography. A similar synthetic procedure also allowed the paracyclophanes, DM_n, during the polycondensation of duroquinone with 4,4′-methylenedianiline (Supporting Information Figure 2). The reductive AM_n (RAM_n) and DM_n (RDM_n) were easily obtained using Sn as the reductive agent.

Scheme 1. Connection of the Active Module in an Annual Manner and Two Extreme Conformations (face and lateral) of a Paracyclophane[7]



N,*N*′-Diphenylanthraquinonediimine (AQI) and *N*,*N*′-diphenyl-2,3,5,6-tetramethyl-1,4-benzoquinonediimine (TMI) are the half-structures of AM_4 and DM_4, respectively. Nishiumi has reported that AQI and TMI show a sharp and single two-electron reversible redox couple and a one-step successive two-electron transfer in the presence of a Lewis acid.[6] AM_4 and DM_4 were also revealed to have a sharp and single two-electron (total: four electron) reversible redox couple at the potential of 0.14 and 0.29 V (vs Ag/Ag^+), respectively, in the presence of an acid. The potential peak separation (ΔE_p) between the anodic (E_{pa}) and cathodic (E_{pc}) peaks were 39 and 37 mV, respectively, for AM_4 and DM_4 (Figure 1). During the cyclic voltammetry, the redox waves were stable and reversible during 100 potential cycles. The result of the electrospectrochemical analysis of DM_4 showed, during the reduction at 0.0 V, the formation of the benzenoid structures (decreasing the absorption of the quinonediimine around 360 nm), during the oxidation at 0.35 V, the formation of quinonediimine (the increase of the absorption around 360 nm), and after the oxidation was completed, the spectrum agreed with the original spectrum of DM_4. The cycle was reversible and stable for 10 redox cycles. Furthermore, the spectrum of RDM_4 obtained from DM_4 by the chemical reduction agreed with the spectrum during the course of the reduction of DM_4 at the potential of 0.0 V (Figure 1). These results support the fact that the conversion corresponding to the redox cycle is a reversible mutual exchange of DM_4 for RDM_4. The result of the electrospectrochemical analysis of AM_4 showed the same fact for DM_4 (Supporting Information Figure 3).

To confirm the three-dimensional structural change in these cyclophanes, an X-ray crystal structure analysis was carried out. In the molecular structures of DM_4 and AM_4, the side part of the quinonediimine dropped into the cavity. Especially in AM_4, which has a larger side part than DM_4, the cavity was filled with the aromatic ring of the anthraquinone part, and the cavity was closed. On the other hand, in the structures of RAM_4 and RDM_4, the cavity was opened, and two monochlorobenzenes were included in the cavity as crystal solvents (Figure 2). An X-ray analysis revealed that the conformational change in the paracyclophane was the mutual exchange of the "face" for a "lateral" one. The ^1H NMR

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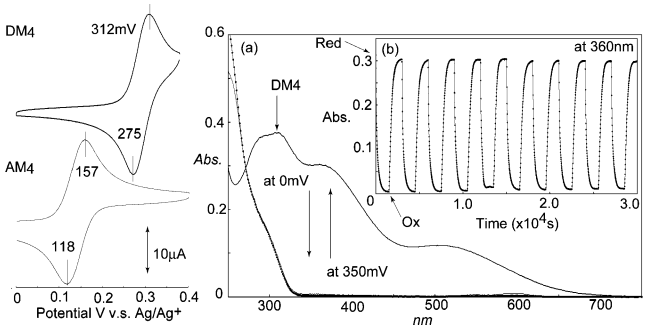

Figure 1. Cyclic voltammograms of DM_4 (0.2 mM) and AM_4 (0.2 mM) in MeCN solution containing 0.2 M $TBABF_4$ and TFA (trifluoroacetic acid). Spectroelectrochemical analysis of DM_4 in MeCN. (a) Electro UV−vis spectral changes. The applied potentials were between 0 and 0.35 V vs Ag/Ag^+. [DM_4] = 0.2 mM, [TFA] = 130 mM, [$TBABF_4$] = 0.2 M; working; Pt mesh. Path length = 1 mm. The bold line is DM_4, the normal line is after the electrochemical reduction at 0 V vs Ag/Ag^+, and the line with dots is after the chemical reduction of DM_4 by Sn drops. (b) Absorption changes recorded at intervals of 17 s monitoring at 360 nm during the 10 redox cycles.

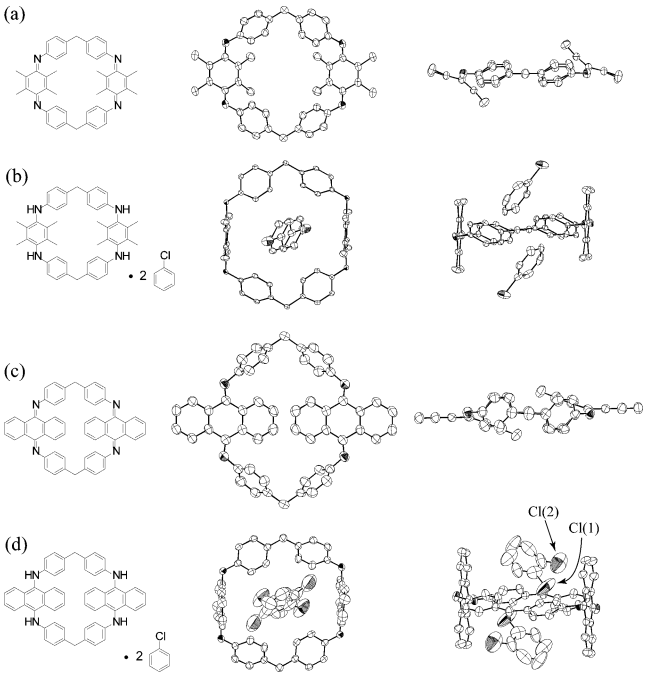

Figure 2. Molecular structures and the ORTEP diagrams of (a) DM_4, (b) RDM_4, (c) AM_4, and (d) RAM_4 with 50% probability, and the bond radius is 0.03 Å. The two crystal solvent molecules were included in the cavity of RDM_4, whereas the cavity of DM_4 was closed. Although AM_4 had no cavity space, the cavity of RAM_4 was opened, and two disordered monochlorobenzenes were included inside as crystal solvent molecules (the site occupancy factors of the chlorine atoms were Cl (1) = 0.70, and Cl (2) = 0.30, respectively). The protons were omitted for clarity.

measurements allow us to investigate the conformation of these cyclophanes in solution (see the results of ^1H NMR measurement in Supporting Information Figures 4−6).[7] In AM_4 and DM_4, they take a lateral conformation in solution. On the other hand, RAM_4 and RDM_4 are considered to take a face conformation more predominantly in solution. These results prove that the switching process is as follows. In an oxidative state, the cyclophanes take a lateral conformation, and the cavity is closed. On the contrary, in a reductive state, they take a face conformation, and the cavity is opened. The process occurs stably and reversibly. The intermediate structures of these cyclophanes were also confirmed by X-ray analyses (Supporting Information Figure 7).

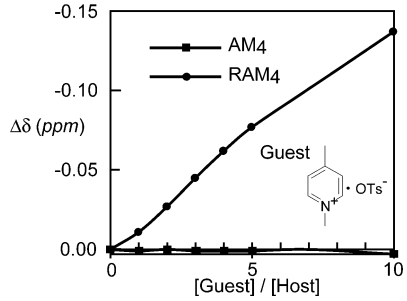

Figure 3. The changes in the chemical shift value of the methylene groups of the cyclophanes during the ^1H NMR titration with a aromatic cationic guest (1,4-dimethylpyridinium-*p*-toluenesulfonate).

In conclusion, AM_4 and DM_4 can reversibly open and close their cavities in the redox process. A paraphenylenediamine is the simplest and most basic molecular module to fix and release the free rotation in paraphenylene and has a general purpose. Thus, a paraphenylenediamine provides a basic unit for the molecular actuation unit available not only for a specific limited molecular system but also for many kinds of molecular systems. To open and close the cavity is the most direct approach to switch molecular recognition in cyclophane inclusion chemistry. Actually, the complexation with a guest molecule was switched by these conformational switches (Figure 3 and Supporting Information Figure 8).[8] Attempts to further develop the redox-driven molecular machine system containing paraphenylenediamine moieties are now in progress.

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Supporting Information Available: Synthesis and characterization data, ^1H and ^{13}C NMR, CIF files, and electrochemical analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Hawthorne, M. F.; Zink, J. I.; Skelton, J. M.; Bayer, M. J.; Liu, C.; Livshits, E.; Baer, R.; Neuhauser, D. *Science* **2004**, *303*, 1849. (b) Hernández, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532. (c) Koumura, N.; Zijlstra, R. W. J.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152. (d) Shima, T.; Hampel, F.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5537.

(2) (a) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines: A Journey into the Nanoworld*; Wiley-VCH: Weinheim, Germany, 2003. (b) Gleiter, R.; Hopf, H. *Modern Cyclophane Chemistry*; Wiley-VHC: Weinheim, Germany, 2004.

(3) Boyer, M. I.; Quillard, S.; Louarn, G.; Froyer, G.; Lefrant, S. *J. Phys. Chem. B* **2000**, *104*, 8952.

(4) (a) Higuchi, M.; Kanazawa, H.; Tsuruta, M.; Yamamoto, K. *Macromolecules* **2001**, *34*, 8847. (b) Higuchi, M.; Kanazawa, H.; Yamamoto, K. *Org. Lett.* **2003**, *5*, 345. (c) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, *415*, 509.

(5) (a) Williams, P. A.; Ellzey, K. A.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1993**, *26*, 5820. (b) Hall, H. K., Jr.; Padias, A. B.; Williams, P. A.; Gosau, J.-M.; Boone, H. W.; Park, D.-K. *Macromolecules* **1995**, *28*, 1.

(6) Nishiumi, T.; Chimoto, Y.; Hagiwara, Y.; Higuchi, M.; Yamamamo, K. *Macromolecules* **2004**, *37*, 2661.

(7) (a) Tabushi, I.; Yamada, H.; Kuroda, Y. *J. Org. Chem.* **1975**, *40*, 1946. (b) Keehn, P. M.; Rosenfeld, S. M. *Cyclophane II*; Academic Press: New York, 1983.

(8) (a) Deans, R.; Niemz, A.; Breinlinger, E. C.; Rotello, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 10863. (b) Kaifer, A. E. *Acc. Chem. Res.* **1999**, *32*, 62. (c) Nabeshima, T.; Furusawa, H.; Yano, Y. *Angew. Chem., Int. Ed.* **1994**, *33*, 1750. (d) Liu, Y.; Flood, A. H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 9150. (e) Ariga, K.; Terasaka, Y.; Sakai, D.; Tsuji, H.; Kikuchi, J. *J. Am. Chem. Soc.* **2000**, *122*, 7835.

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