Summary of Research

Photomechanical motion of aromatic diimide molecules

Materials that are capable of change their shape and size, or of actuation by physical stimuli are of particular importance as media for conversion energy to mechanical work. Such mechanically responsive or actuating materials are promising candidates as dynamically active elements providing a wide range of applications: e.g., artificial muscles, actuators, and electromechanical devices. These mechanical responses are based on local chemical changes triggered by molecular motions, which transferred to distortion of macroscopic shape of bulk material. When physical stimulus is photo-irradiation, mechanical response materials are classified into three mechanisms. One is cis-trans isomerization, the others are ring opening and closure reactions, and cycloaddition reactions.

We recently found the photochemical reaction of naphthalene diimides having alkylamino side chains in the solid states. Upon irradiation of light (λ = 370 nm), the compound of **1** showed color change from yellow to black (Fig.1ab). After standing in dark, the color of **1** recovered to be yellow. This came from the formation of radical anion of **1** as evidenced by UV-Vis-Nir spectroscopy. Furthermore, the crystal **1** showed photomechanical motion (Fig.1c). Based on the magnetic susceptibility and the theoretical calculation, the mechanical motion of **1** was accounted for electronic repulsions among $\mathbf{1}$-$\mathbf{1}^{\bullet-}$, $(\mathbf{1})_2^{\bullet-}$, and $\mathbf{1}$-$\mathbf{1}^{-}$. Therefore our observed photomechanical motion was found to be a novel mechanism based on the radical formation by photo-irradiation. Currently we are trying to develop to a practical application for photo-actuator as an environmental device.

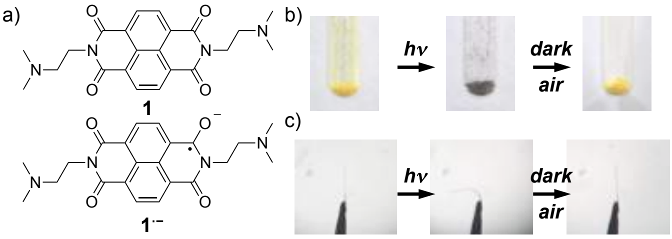

Fig.1 a)-Chemical structure of **1** and $\mathbf{1}^{\cdot-}$-b) Color change of **1** upon irradiation -λ=370nm-c) Mechanical motion of **1**

Molecular recognition by nanoscaled macrocyclic molecules

A) *Nanotube as chemo-sensor*

Pyromellitic diimide is known to be an electron acceptor. We synthesized various kinds of nanoscaled macrocyle consiting of pyromellitic diimide (PDI). Because of the electron-poor cavity, these macrocycles act as the host for the electron-donor molecules, which are recognized by the charge transfer (CT) interaction. The most revealing property is that **2** formed gel by complexation with *N*,*N*-dimethylaniline. After treatment from gel to xerogel, the resulting structure was found to be the formation of nanoscaled porous tube (Fig.2ab). This porous nanotube have a function as chemo-sensor: the nanotube **2** showed color change from pale yellow to purple red by changing guest adsorbates. With increasing of the donor ability of the guest molecule, the absorption bond was shifted to red due to increasing CT interaction (Fig.2c). Thus, our observed molecular sensing based on the CT interaction considerably reflects the guest property.

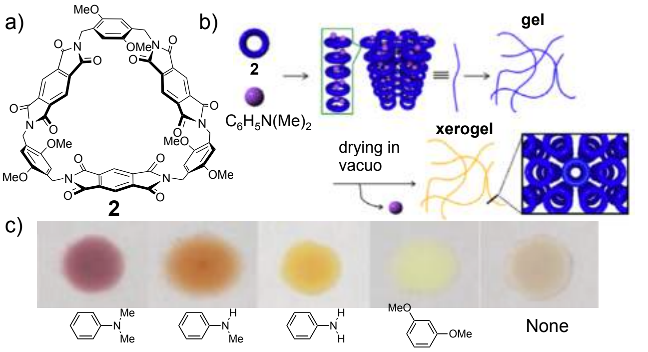

Fig.2 a) Macrocycle containing of PDI-**2**-b) Gelation induced by the complex with $C_6H_5N(Me)_2$, and formation of nanoscaled porous tube c) Color change of tubular **2** by adsorption of guest

B) *A giant macrocycle*

The condensation reaction of aldehyde with cyclic urea and/or with amine spontaneously proceeds, and then gives thermodynamically stable product. By changing the reaction condition such as acidity of media or use of rigid substrate, we can choose the size and the number of the units of the component of the macrocycle at will. The condensation reaction of formalin with ethylene urea gave 6-membered macrocycle at 6*N* HCl condition, while a large 12-membered ring was obtained at weak acidic condition. On the other hands, the reaction between the rigid di-aldehyde and the tri-amine gave a giant tetrahedral macrocycle **3** (Fig.3a). Noteworthy is the fact that the size of **3** is 23 Å. This macrocycle **3** was found to have the property to increase in volume in solution by complexation with guest solvent molecules. In the crystalline state, **3** formed mesoporous structure (Fig.3b). The lipophilic pores of **3** uniformly formed in an ordered array, and contribute to the selective adsorption of 1-BuOH among the isomers of butanol (Fig.3c).

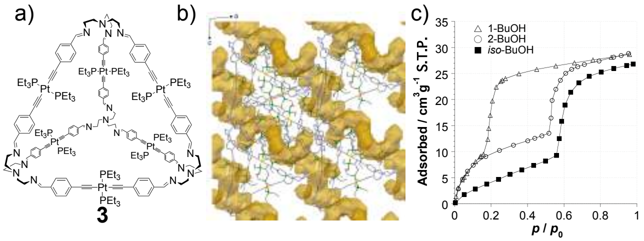

Fig.3 a) Giant macrocycle **3** b) A uniformly ordered array of lipophilic mesopores of **3** c) BuOH isotherm of **3**. Selectivity of 1-BuOH as high as 4.3 among the isomers at p/p_0=0.3.

Molecular assembly: Exciton interaction in small π-electronic molecular aggregate

A simple streptopolymethine merocyanine is composed of electron donating nitrogen and electron accepting oxygen, linked by a conjugated odd number of methine carbons. Due to the asymmetrical structure, merocyanines are peculiar in their optical and photophysical properties. Although theoretical studies of a streptopolymethine merocyanine predict that exciton interaction is present among its aggregates, very little experimental evidence has been reported so far. We have addressed this issue by using 4-amino-6-oxopyrimidine derivatives. Since the parent **4a** contains the simple merocyanine structure in the molcular skelton with several hydrogen bonding sites, self-association of **4a** forms an ordered aggregate structure (Fig.4a). The absorption and fluorescence spectral properties of **4a** clearly showed that the molecule **4a** formed the aggregate, and showed an exciton band, appearing at an absorption of 350 nm due to the red-shifted HOMO–LUMO transition. Upon light irradiation of the exciton band, a fluorescence band at 398 nm (Φ_{FL} = 0.10) was observed. Based on these spectral features, the aggregated **4a** was fond to form J-type aggregation (Fig.4bc). Next, the simple isobutyl group at the 4 position of the amino group can change the mode of the self-assembly of **4c** from the linear tape structure to the novel hexameric ball-like supramolecular structures by the interplay of hydrophobic and H-bonding interactions (Fig.4d). The hexameric ball was found to be stable than the tape by comparison of solubility curves the polymorphic crystal of **4c**.

In the crystal of **4a** and **4a**·1.5H_2O, **4a** formed supramolecular structure as an infinite double H-bonded ribbon. Since the observed molecular arrangements are rarely found in the literature, IR spectral analysis and theoretical calculation were studied, and revealed that the cooperativity of the hydrogen bonding ranged up to 9-mer of **4a**.

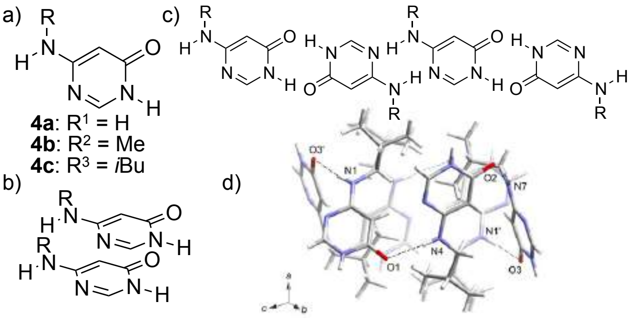

Fig.4 Chemical structure of 4-amino-6-oxopyrimidines (a) and their supramolecular structures; b) linear tape c) π-π stacking d) hexameric bowl (**4c**)