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Organogel Formation and Chromic Behavior of Hydrogen-bonding Lophine Derivatives

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A new hydrogen-bonding lophine derivative and its dimeric compound have been prepared. The monomeric compound acts as a low molecular weight gelator for several organic solvents such as benzene and tetrachloromethane, while the dimeric compound does not. However, the dimeric compound easily forms thin films by casting from solutions, and the film exhibits chromic behavior by both UV irradiation and strong shear stress.

Materials which change their colors and luminescent behavior have potential applications in a wide range of fields such as optics, sensing, and data storage. Chromic molecules often change their molecular structures along with their optical properties by applying external stimuli.[1] When such chromic molecules are introduced to self-assembled materials such as organogelators,[2] stimuli-induced structural changes on the molecular scale often lead to drastic changes in the self-assembled structure and even in the macroscopic structure of the materials due to the dynamic nature of noncovalent interactions.[3] Among chromic molecules incorporated in self-assembled materials, mechanochromic molecules remain to be developed compared with photo- and thermochromic molecules. Mechanochromic behavior is induced by mechanical stress such as pressure and shear stress.[4,5] Only a few examples of mechanochromic behavior of self-assembled materials have been reported.[6] In this study, we have focused our attention on 2,4,5-triphenylimidazole (lophine) because its dimers exhibit chromic behavior with changing their molecular structures and generating radical species induced by mechanical stress as well as photoirradiation.[5,7] Here, we report the development of hydrogen-bonding lophine derivatives as shown in Figure 1 aiming at stress-responsive organogelators.

Our new lophine derivative **1** has three (dodecylcarbamoyl)methoxy chains as self-assembling moieties attached to a lophine core. As for the molecular design of low molecular weight organogelators, introduction of hydrogen-bonding moieties with long alkyl chains to functional cores is often reported.[2d,2e] Compound **1** was prepared by the reaction of a corresponding benzil derivative and a benzaldehyde derivative with ammonium acetate in acetic acid under reflux for 24 h.[5b,8] The dimeric product **2** was prepared by oxidation of **1** with $K_3[Fe(CN)_6]$ in 10% ethanolic potassium hydroxide solution.[9]

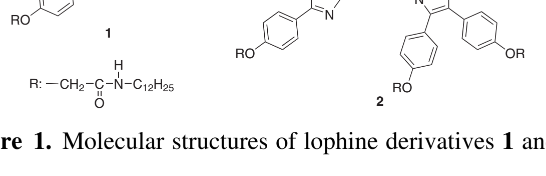

Figure 1. Molecular structures of lophine derivatives **1** and **2**.

Table 1. Gelation properties of lophine derivatives[a]

Solvent	**1**	**2**
Hexane	Gelation (9)	Solution
Acetone	Precipitation	Solution
Ethyl acetate	Viscous solution	Solution
Ethanol	Precipitation	Solution
Chloroform	Solution	Solution
Tetrachloromethane	Gelation (50)	Solution
Benzene	Gelation (25)	Solution
Toluene	Gelation (20)	Solution

[a] Minimum gel concentrations are in parentheses (given in $mg\,mL^{-1}$).

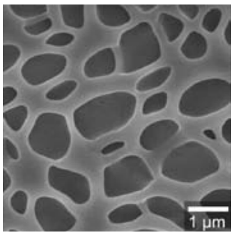

Figure 2. SEM image of xerogel of **1** formed in hexane.

The gelation properties of these lophine derivatives for common organic solvents are shown in Table 1. Monomeric compound **1** forms organogels in hexane, tetrachloromethane, and aromatic solvents. SEM observation reveals that **1** forms network-structured aggregates in solvents as shown in Figure 2. Such aggregates are believed to form through one-dimensional molecular assembly. As for the nonsubstituted lophine, single crystalline nanowires were fabricated by physical vapor deposition,[10] which indicates a lophine scaffold is suitable for one-dimensional molecular assembly. Therefore, compound **1** is expected to assemble one-dimensionally with the assistance of intermolecular hydrogen bonding and long alkyl chains without crystallization. Infrared spectra indicate the formation of hydrogen bonding, since the N–H stretching band at $3431\,cm^{-1}$ in solution shifts to $3296\,cm^{-1}$ in the gel state. On the other hand, dimeric compound **2** is readily soluble in various solvents and it does not form organogels. It seems steric hindrance of six phenyl rings in a molecule of **2** disturbs elongated one-dimensional aggregation. However, it should be noted that **2** forms thin films without crystallization by casting from solution due to the existence of long alkyl chains and amide groups. The formation of hydrogen bonding in the film of **2** is also indicated, since the N–H stretching band of infrared spectra appears at $3302\,cm^{-1}$.

Nonsubstituted lophine dimers are known to respond to both photoirradiation and mechanical stress as mentioned above.[5,7] As for dimeric compound **2**, it exhibits photochromic behavior from yellow to green both in solutions and a solid state by UV

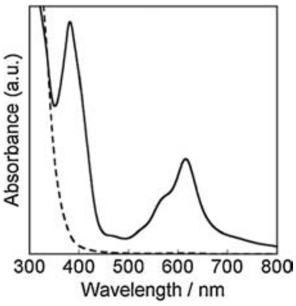

Figure 3. Comparison of absorption spectra of **2** in benzene before (dashed line) and after (solid line) UV irradiation.

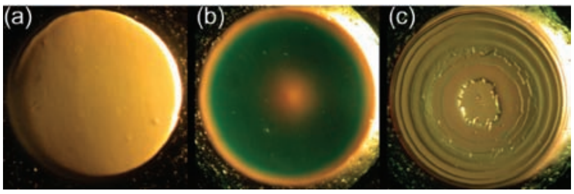

Figure 4. Photographs of the thin film of **2** (a) at ambient pressure, (b) under shear stress, and (c) at ambient pressure after releasing the stress.

irradiation. Figure 3 shows spectral changes on UV irradiation. New absorption bands around 380 and 630 nm appear on UV irradiation. These bands gradually decrease in the dark. Preliminary ESR measurements of **2** in solid states indicate the generation of radical species along with photochromic behavior.

It should be noted that dimeric compound **2** also exhibits mechanochromic behavior. As for mechanochromic behavior of a nonsubstituted lophine dimer, it changes its color only by grinding in a mortar.[5] Though no color change was observed for **2** with a mortar, a thin cast film of **2** exhibits reversible color changes by applying strong shear stress with a sapphire anvil cell[11] as shown in Figure 4. A vertically pressured thin film between two sapphire anvils is sheared by the rotation of the lower anvil and immediately the color of the film changes from yellow to green. The color returns to yellow by releasing the stress. These color changes are almost the same as those induced by photoirradiation. Therefore, compound **2** is expected to be cleaved to radical species by strong shear stress. As for the nonsubstituted lophine, it has been reported that molecular structures of the photochromic dimer and the mechanochromic dimer are slightly different in the way of connection of two lophine units.[5] However, both dimers are cleaved to the same radical species on photoirradiation or mechanical stress. In our studies, an individual dimeric compound **2** exhibits both photo- and mechanochromic behavior. It is still unclear whether our results can be explained by the effects of the introduction of self-assembling moieties to lophine molecules. One possible reason is the strength of mechanical stress. Our apparatus can generate shear stress equivalent to more than 1 GPa of hydrostatic pressure,[11b,11c] which is much larger than the stress generated by grinding with a mortar. Moreover, we have recently reported chromic behavior of photochromic spiropyran induced by shear stress with our apparatus.[11b,12]

In conclusion, we have demonstrated emerging uses of lophine-based compounds as organogelators and multistimuli responsive materials by the introduction of hydrogen-bonding moieties. The existence of hydrogen-bonding moieties enables the formation of organogels and thin films without crystallization. Though efficient use of structural changes along with chromic behavior for the modulation of molecular assemblies has not been achieved so far, we are now exploring better molecular designs serving our purpose.

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8 ^{1}H NMR (d_6-DMSO, 270 MHz): δ 12.43 (br, 1H), 8.03 (t, $J = 3.6$ Hz, 3H), 7.99 (d, $J = 8.9$ Hz, 2H), 7.43 (d, $J = 8.6$ Hz, 4H), 7.04 (d, $J = 8.9$ Hz, 2H), 6.95 (d, $J = 8.6$ Hz, 4H), 4.52 (s, 2H), 4.47 (s, 4H), 3.12 (q, $J = 6.5$ Hz, 6H), 1.44–1.40 (m, 6H), 1.28–1.21 (m, 54H), 0.83 (t, $J = 6.8$ Hz, 9H).

9 ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.09–8.02 (m, 6H), 7.98 (d, $J = 8.8$ Hz, 4H), 7.45 (d, $J = 8.3$ Hz, 4H), 7.39 (d, $J = 8.8$ Hz, 4H), 7.03 (d, $J = 8.8$ Hz, 4H), 7.00 (d, $J = 9.3$ Hz, 4H), 6.88 (d, $J = 8.3$ Hz, 4H), 4.51 (s, 8H), 4.44 (s, 4H), 3.14–3.09 (m, 12H), 1.42–1.39 (m, 12H), 1.24–1.21 (m, 108H), 0.83 (t, $J = 6.6$ Hz, 18H).

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12 Our preliminary experiments indicate a nonsubstituted photochromic lophine dimer can also change its color by applying strong shear stress with our apparatus.