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Cyclophane-Based Fluorescence Tuning Induced by Hydrostatic Pressure Changes

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Abstract: In keen contrast to a usual, tedious fluorescence augment of a chloroform solution of a linear chromophore unit under high pressure, a fluorescent cyclophane solution shows a drastic fluorescence quenching under elevated pressure for which a pressure-induced increment of an intramolecular π -stacked conformation is highly likely to be responsible.

Mechanical stimuli can vary photoluminescence properties of organic materials in solution and/or solid states.^[1–18] Mechanoresponsive organic compounds are promising candidates of indicator of applied force, optical data storage and mechano-bioimaging probes for living cells. Simple and basic studies on homogeneous solutions of various fluorophores under hydrostatic pressure as one of mechanical forces have been long-term scientific subjects.^[9–18] In general, photoluminescence intensities of fluorophores in organic solvents augment under elevated pressure due to increasing viscosity of solvents used, and sometimes follow the Förster–Hoffmann equation.^[14,15] Therefore, these facts indicate that pressure-induced fluorescence-tuning, quenching of solutions is an apparently difficult task.

On the other hand, direct applications of mechanical stimuli to luminescent compounds as solid states have attracted much attention in a decade.^[1–8] Grinding, crushing and tensile deformation significantly affect the photophysical properties of molecular assembled materials.^[19–28] Of several approaches to mechanochromic luminescent materials hitherto examined, cyclic,^[29–32] dendritic,^[33–40] and mechanically-interlocked^[41] compounds, originated from particular structural features, show mechanoresponsive luminescence in the condensed states. Nevertheless, hydrostatic pressure-induced fluorescence behavior of these structurally interesting molecules has not been examined yet. In particular, fluorescent cyclophanes bearing two aromatic hydrocarbons through a flexible linker are fascinating targets since it is likely that an intramolecular interaction between two aromatic moieties in the cyclic structure may be tuned just by changing the hydrostatic pressure.

In the present study, we thus focus on an asymmetric photoluminescent cyclophane **1** (Figure 1) that shows a

contrasting fluorescence quenching behavior under hydrostatic pressure. Comparison with the results obtained from non-cyclophane **2** allows us to assess the effects of the cyclophane structure on the fluorescence responses under pressure at individual molecule level. It is still challenging to quantitatively investigate the correlation between applied mechanical grinding forces and molecular arrangement changes in crystalline or liquid-crystalline (LC) states, since crystalline particles or LC domains are divergent size and molecular assemblies. Eventually this study on the dispersed, "isolated" molecular materials under hydrostatic pressure may provide deep insights into the mechanoresponsive luminescence properties in complicate molecular assembled states.

The cyclophane **1** has 1,6-bis(phenylethynyl)pyrene^[42] and naphthalene groups, and the two aromatic hydrocarbons are bridged through hexaethylene glycol linkers.^[29] The flexible linkers can provide the cyclophane with ability to form various conformations in solution, modulating photoluminescence properties by varying hydrostatic pressure. Indeed, in the condensed states, compound **1** forms a supercooled nematic LC phase that shows a green photoluminescence and blue-emissive crystalline state at room temperature depending on a thermal treatment procedure.^[29] The green emission is ascribed to an excimer formation, on the other hand, the luminophores no longer form the excimers in the crystalline states, leading to the blue emission. Furthermore, the pyrenophane **1** shows mechanochromic luminescence in the solid state.^[29] The linear reference compound **2** has the same luminophore unit as cyclophane **1**.

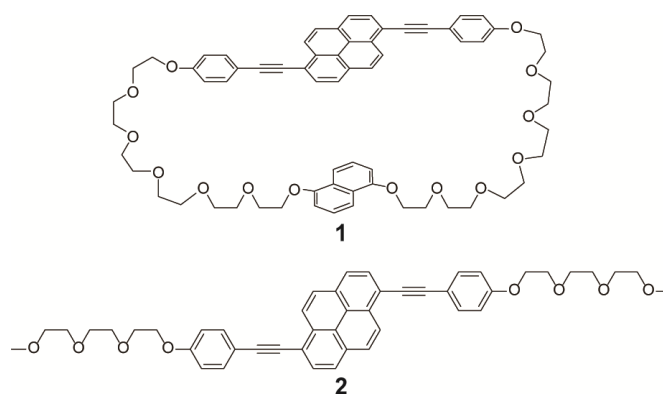


Figure 1. Chemical structures of asymmetric cyclophane **1** and the acyclic reference compound **2**.

Absorption and fluorescence spectra of compounds **1** and **2** in chloroform ($c = 1.0 \times 10^{-5}$ M) under ambient condition are shown in Figure 2.^[29] Both chloroform solutions display absorption bands corresponding to 1,6-bis(phenylethynyl)pyrene between 350 and 450 nm (Figure 2a).

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Intriguingly, the two absorption bands are not superimposable, indicating that slight intramolecular, ground-state electronic interactions between 1,6-bis(phenylethynyl)pyrene and naphthalene groups are operative in the solution. The naphthalene moiety of **1** causes an increase in molar extinction coefficient between 250 and 330 nm (Figure 2a, blue line). As shown in Figure 2b, the fluorescence spectra of two solutions display well-resolved vibronic structure. Again, the fluorescence spectrum of compound **1** in chloroform does not overlap with that of a chloroform solution of **2**, which is also attributed to the ground-state interactions between the two aromatic groups.

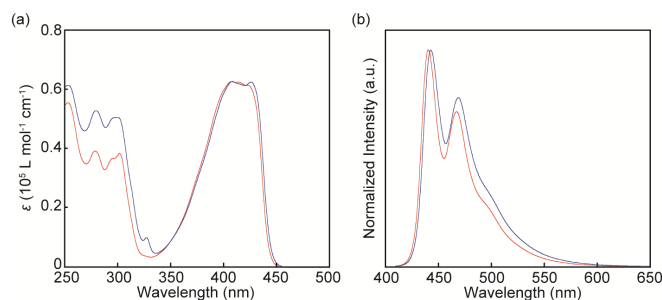


Figure 2. (a) Absorption and (b) normalized fluorescence spectra of chloroform solutions ($c = 1.0 \times 10^{-5} \text{ M}$) of **1** (blue line) and **2** (red line). All spectra were recorded under normal condition at room temperature. Emission spectra were measured with excitation light of 400 nm.

Hydrostatic pressure effects on both chloroform solutions of cyclophane **1** and the linear reference compound **2** were investigated in a custom-built high-pressure apparatus^[43] that allows us to conduct spectroscopic measurements for solutions under high pressure (see Supporting Information (SI) for detailed experimental conditions). First, photoluminescence measurements were performed for both solutions varying hydrostatic pressure (Figures 3a and b). Interestingly, the chloroform solution of **1** upon pressurized shows decreasing of the photoluminescence intensities at both main 0-0 and 0-1 bands, although the intensity around 530 nm increases slightly (*vide infra*), as shown in Figure 3a. This reduction, i.e. quenching, observed at the main bands is an opposite tendency compared to conventional aromatic hydrocarbons. Varying the pressure from 0.1 to 320 MPa, the emission intensity of the solution reduces. Concomitantly, the emission peak bathochromically shifted from 442 to 449 nm at the 0-0 band. In contrast, the linear analogue **2** in chloroform shows common response against elevated pressure. When the pressure is applied to the solution, the photoluminescence intensity exhibits gradual increase. Under 320 MPa, the emission intensity at 447 nm was enhanced by a factor of 1.6. As observed for the chloroform solution of **1**, the emission peak also showed a slight red shift from 440 to 447 nm at the 0-0 band. Under pressure applied in this study, the vibronic structures are well preserved for both solutions, suggesting that no intermolecular excimer formation between 1,6-bis(phenylethynyl)pyrene groups occurs even under high hydrostatic pressure. Under high pressure, generally intermolecular excimer formations were inhibited in solutions due to the suppressed mobility of molecules.^[9]

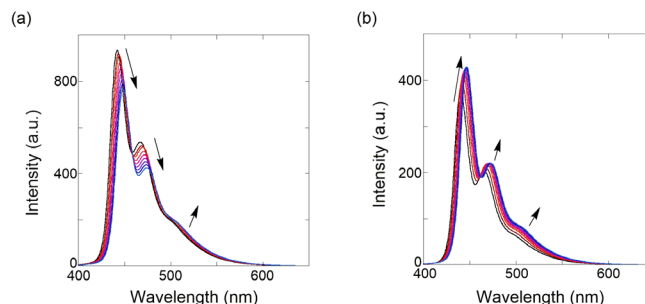


Figure 3. Fluorescence spectra of chloroform solutions of (a) **1** (6 μM) and (b) **2** (6 μM) at 0.1, 40, 80, 120, 160, 200, 240, 280, and 320 MPa (from black to light blue) at room temperature in a high-pressure cell. Spectra were measured with excitation light of (a) 365 nm and (b) 330 nm, where all solutions showed the almost identical absorbances.

We next carried out absorption spectroscopic measurements under pressure for both chloroform solutions of **1** and **2**. As shown in Figure 4, the absorption spectra display gradual red shifts under increasing pressure. It is well known that absorption bands of aromatic hydrocarbons commonly show red shifts under hydrostatic pressure in solution.^[44] Similar gradual red shifts were also observed for the excitation spectra of both solutions (Figure S1 in the SI). The absorbances of **1** and **2** gradually increase for both cases since these effective concentrations at elevated pressure become higher by compress.

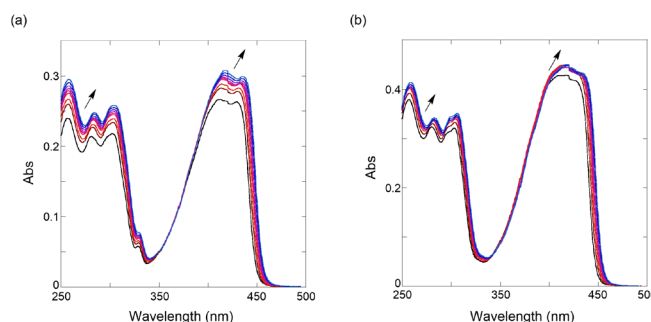


Figure 4. Absorption spectra of chloroform solutions of (a) **1** (61 μM) and (b) **2** (55 μM) at 0.1, 40, 80, 120, 160, 200, 240, 280, and 320 MPa (from black to light blue) at room temperature in a high-pressure cell.

To further elucidate the factors that control such contrasting fluorescence switching behaviors, we analyzed the data extracted from the spectroscopic measurements described above. Figures 5a and b show a correlation between emission intensities and hydrostatic pressure. The plots of emission intensities at 442, 467, and 530 nm for **1** as a function of pressure show linear decreases (the first two) and slight increase (latter) in Figure 5a. Conversely, although the same fluorophore was introduced in the molecular structure, compound **2** shows non-linear increases in emission intensities, data of which were subjected to the Förster-Hoffmann equation. Thus, the common logarithm of the fluorescence intensities was plotted against the common logarithm of pressure-dependent

viscosities in Figure 5c. The data points obtained in high pressure fall on a single straight line, indicating operation of the same fluorescence augment mechanism over the pressure range studied. This result thus suggests that the acyclic linear analogue **2** exhibits a fluorophore susceptible to viscosity changes as were the cases with viscosity sensors previously reported.^[14,15]

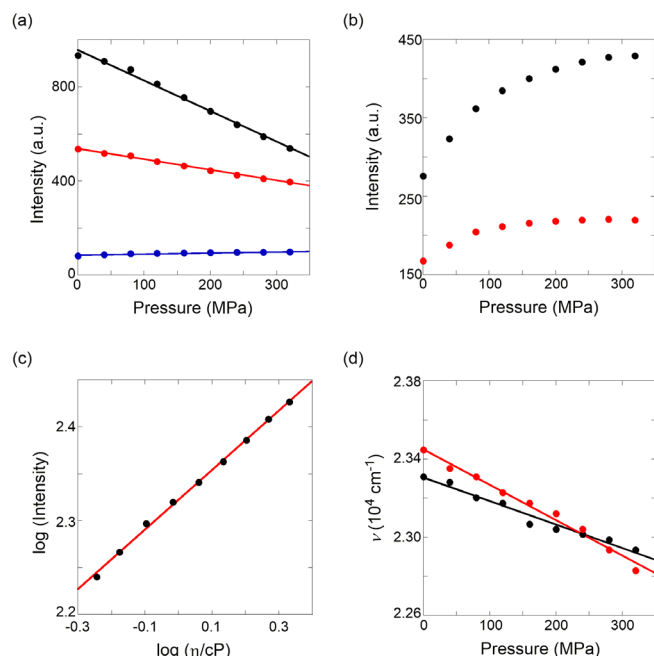


Figure 5. Plots of fluorescence intensities of chloroform solutions of (a) **1** at 442 nm (black; correlation coefficient $r = 0.996$), 467 nm (red; correlation coefficient $r = 0.998$), and 530 nm (blue; correlation coefficient $r = 0.941$) and (b) **2** at 447 nm (black) and 473 nm (red) as a function of pressure. (c) Plot of fluorescence intensity data according to the Förster-Hoffmann equation for **2** (correlation coefficient $r = 0.999$); pressure-dependent viscosities (η) were estimated by the data described in the literature.^[45] (d) Plots of wavenumber for 0-0 absorption maxima for **1** (black; correlation coefficient $r = 0.986$, slope; $-1.20 \text{ cm}^{-1}/\text{MPa}$) and **2** (red; correlation coefficient $r = 0.993$, slope; $-1.82 \text{ cm}^{-1}/\text{MPa}$) as a function of pressure in chloroform.

The significant difference in the emission modulation under pressure between **1** and **2** is attributed to the naphthalene group of cyclic compound **1**. Under pressure, cyclic compound **1** easily forms an intramolecularly π -stacked conformation that shows a lower fluorescence quantum efficiency at a longer wavelength, which leads to the decrease in emission intensity at the main bands and the slight development in intensity at longer wavelength for **1**, due to a general aggregation-caused quenching (ACQ). Indeed, compound **1** shows a lower quantum yield in the crystalline state ($\Phi = 0.15$) or the supercooled nematic phase ($\Phi = 0.54$) compared to that in solution ($\Phi = 0.95$).^[29] This is also supported by the closer inspection for both absorption spectra. Compound **2**, which is considered to show the “common” red shift of absorption band under pressure, gave a slope of $-1.82 \text{ cm}^{-1}/\text{MPa}$ when wavenumbers of absorption peaks corresponding to the 0-0 transition were plotted as a function of pressure (Figure 5d, red line). In contrast, the observed slope of **1** is $-1.20 \text{ cm}^{-1}/\text{MPa}$, thus indicating a smaller

red shift of the 0-0 absorption band comparing to that obtained from the acyclic compound **2**. This is an obvious evidence confirming that a non-negligible amount of ground-state interaction between the 1,6-bis(phenylethynyl)pyrene and naphthalene chromophore units increases in the pressurized solution, and eventually the intramolecular interaction gives different UV/vis spectral shifts and opposite, fluorescence quenching responses. It should be noted that plots for wavenumbers of emission peaks ascribed to 0-0 and 0-1 bands as a function of pressure gave all linear relationships (Figure S2 in the SI). Cyclophane **1** displays slopes of -0.981 and $-0.946 \text{ cm}^{-1}/\text{MPa}$ for 0-0 and 0-1 transitions, respectively, while those obtained from acyclic compound **2** are -1.07 and $-1.09 \text{ cm}^{-1}/\text{MPa}$, indicating slight suppression of bathochromic shifts in the fluorescence changes of **1** under pressure. These different shifts of fluorescence changes further reinforces the existence of the intramolecular stack conformation. To directly elucidate this quenching behavior of **1** upon pressurized, we performed the quenching experiment of **2** upon addition of the naphthalene chromophore unit at an atmospheric pressure (Figure S3 in the SI). In the quenching experiment of **2**, the same quenching at the main bands and the slight development at the longer wavelength were observed, strongly indicating that the hydrostatic pressure-induced quenching of the pyrene chromophore in the structure of **1** can be caused by the naphthalene unit through the flexible hexaethyleneglycol linkers.

In order to estimate the generality of the observed “opposite” fluorescence behavior, we performed similar experiments using acetonitrile, toluene, and acetone for a wide range of solvent polarities (Figures S4-S9 in the SI and Table 1). All the solutions of the cyclophane **1** and the linear analogue **2** show similar behaviors observed in the chloroform solution, i.e., the compound **1** in the three solvents upon pressurized shows the quenching, whereas the compound **2** in these solutions shows the gradual fluorescence augment under elevating hydrostatic pressure. As listed in Table 1, all the hydrostatic pressure-induced slopes for absorption and emission bands clearly suggested that the observed behavior is not solvent-specific. Thus, the cyclophane **1** in the solutions gave gentler slopes than those obtained from the compound **2** in the solutions. Again, these solvent-dependent results indicate the non-negligible interaction between the two aromatic units.

Table 1. Hydrostatic pressure-induced shifts for absorption and emission maxima in different solvents.							
Solvent	$E_a^{[a]}/\text{kcal mol}^{-1}$	Slope for pressure-induced absorption maxima at the 0-0 band/ $\text{cm}^{-1} \text{ MPa}^{-1}$	Slope for pressure-induced absorption maxima at the 0-0 band/ $\text{cm}^{-1} \text{ MPa}^{-1}$	Slope for pressure-induced emission maxima at the 0-0 band/ $\text{cm}^{-1} \text{ MPa}^{-1}$	Slope for pressure-induced emission maxima at the 0-1 band/ $\text{cm}^{-1} \text{ MPa}^{-1}$	Slope for pressure-induced emission maxima at the 0-1 band/ $\text{cm}^{-1} \text{ MPa}^{-1}$	Slope for pressure-induced emission maxima at the 0-1 band/ $\text{cm}^{-1} \text{ MPa}^{-1}$
		1	2	1	2	1	2
toluene	33.9	-1.10	-1.23	-0.993	-1.04	-0.958	-1.10
chloroform	39.1	-1.20	-1.82	-0.981	-1.07	-0.946	-1.09
acetone	42.2	-0.985	-1.11	-0.946	-1.00	-0.916	-0.987
acetonitrile	45.6	-0.871	-0.934	-0.850	-0.905	-0.958	-1.01

[a] Reichardt's solvent polarity parameter^[46].

In conclusion, we have revealed for the first time that the asymmetric cyclophane **1** shows the gradual fluorescence quenching at elevated pressure in solution, in sharp contrast to the general pressure-induced fluorescence enhancement caused by the linear analogue **2** which follows the Förster-Hoffmann equation. The naphthalene moiety via the flexible linkers introduced to **1**, i.e. cyclophane structure, plays a pivotal role in the observed unconventional, fluorescence quenching behavior. Under elevated hydrostatic pressure, two aromatic groups accelerate formation of the π -stacked conformation with low quantum efficiency.

The mechanoresponsive luminescence properties at individual molecular level in solution state could provide us with important and complementary information when the mechanoresponsive luminescence behavior is discussed for the condensed states. Furthermore, unconventional mechanoresponsive luminescence behavior that has never been achieved by simple aromatic hydrocarbons may be observed for complicated molecular structures. Therefore, similar investigation for other topological molecules are underway in our group.

Acknowledgements

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Conflicts of interest

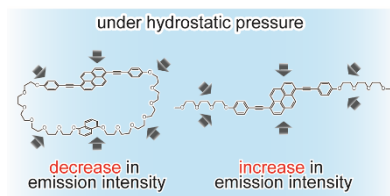
There are no conflicts to declare.

Keywords: fluorescence • hydrostatic pressure • cyclophane • supramolecular chemistry • mechanoresponsive luminescence

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COMMUNICATION

A fluorescent cyclophane solution shows a drastic fluorescence quenching under elevated pressure for which a pressure-induced increment of an intramolecular π -stacked conformation is highly likely to be responsible.



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