Electronic Supplementary Information
for

Ratiometric hydrostatic pressure sensing in water *via* dual emissions of a water-soluble donor–acceptor–donor triad

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Experimental Section

Materials. All commercial reagents and solvents were used without further purification. The sample solutions were dissolved in spectroscopic-grade toluene, methanol (MeOH), and H_2O (Milli-Q). The target materials (**N-Boc-PTZ-DBPHZ** and **Dend-MCM**) were synthesized according to the literature.[1]

Instruments. UV/vis spectra were acquired using a JASCO V-770 spectrometer. Fluorescence spectra were acquired by using a JASCO FP-8500 spectrofluorometer. Fluorescence lifetime decays were obtained using a Hamamatsu Quantaurus-Tau single-photon counting apparatus with a light-emitting-diode light source (λ_{ex} = 405 nm). Dynamic light scattering (DLS) experiments were performed using an Otsuka ELSZ-2000 instrument.

Hydrostatic pressure spectroscopy. The spectroscopic experiments under hydrostatic pressure were conducted using a custom-built high-pressure apparatus; the details are summarized in our previous publications.[2,3] In this apparatus (Figure S1), a quartz inner cell (2 mm path length) with a Teflon tube was filled with the sample solution. The cell was set into the outer cell, which was filled with H_2O that can be hydrostatically pressurized by a hand pump. The outer cell was placed in the spectrometer, enabling acquisition of hydrostatic pressure data (range: 0.1–400 MPa) through the sapphire windows.

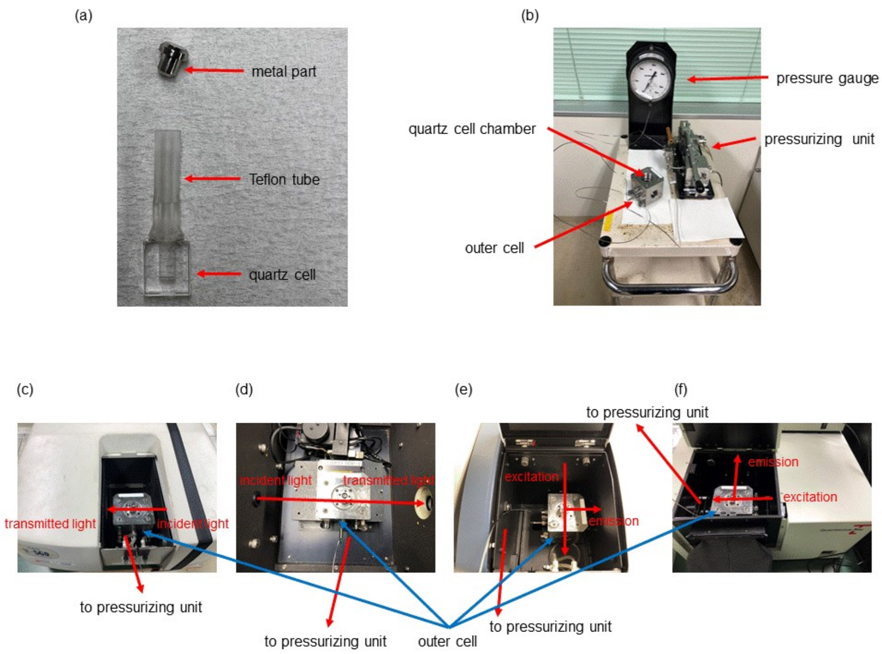

Figure S1. Photographs of (a) inner quartz cell, (b) pressurizing units, and setups for (c) UV/vis spectroscopy, (d) circular dichroism, (e) fluorescence emission, and (d) lifetime measurements. Reproduced with permission from ref. 3. Copyright 2020, John Wiley & Sons.

[1] T. Enjou, S. Goto, Q. Liu, F. Ishiwari, A. Saeki, T. Uemtasu, Y. Ikemoto, S. Watanabe, G. Matsuba, K. Ishibashi, G. Watanabe, S. Minakata, Y. Sagara and Y. Takeda, *Chem. Commun.*, 2024, **60**, 3653–3656.
[2] H. Mizuno and G. Fukuhara, *Acc. Chem. Res.* 2022, **55**, 1748–1762.
[3] H. Mizuno, M. Kitamatsu, Y. Imai and G. Fukuhara, *ChemPhotoChem* 2020, **4**, 502–507.

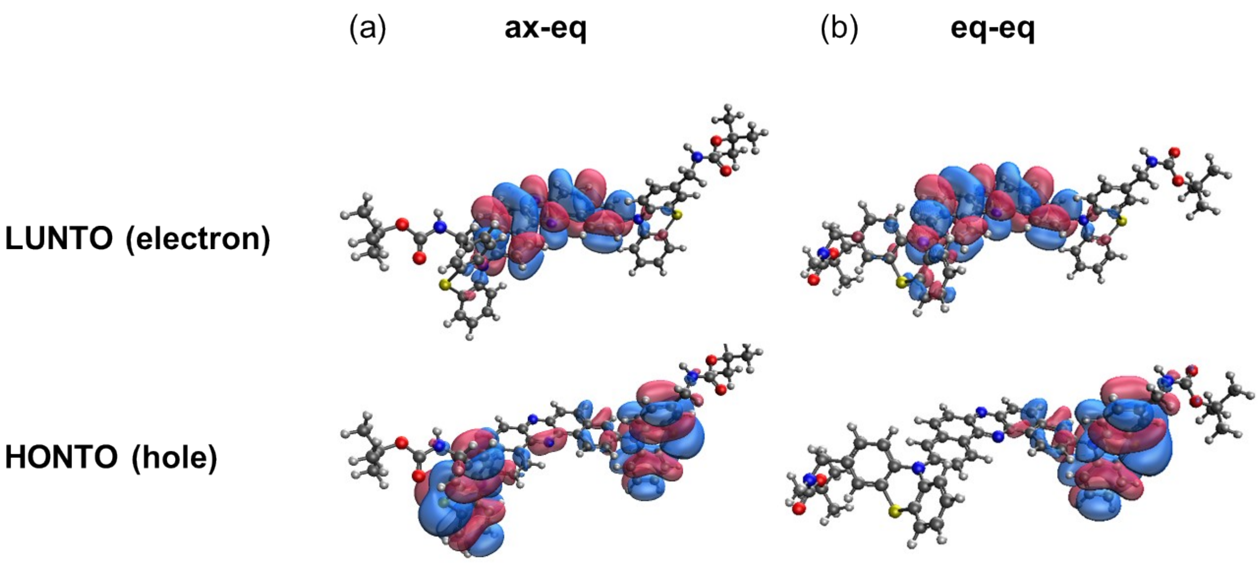

Figure S2. Hole and electron distributions of the (a) *ax–eq* and (b) *eq–eq* conformations in **N-Boc-PTZ-DBPHZ**, visualized by natural transition orbitals (NTOs). The NTOs were calculated at the TD-TDA level (LC-ωPBE/aug-cc-pVDZ) in toluene, using the ground state (S_0) optimized geometry obtained at the PBE0/6-31G(d,p) level.

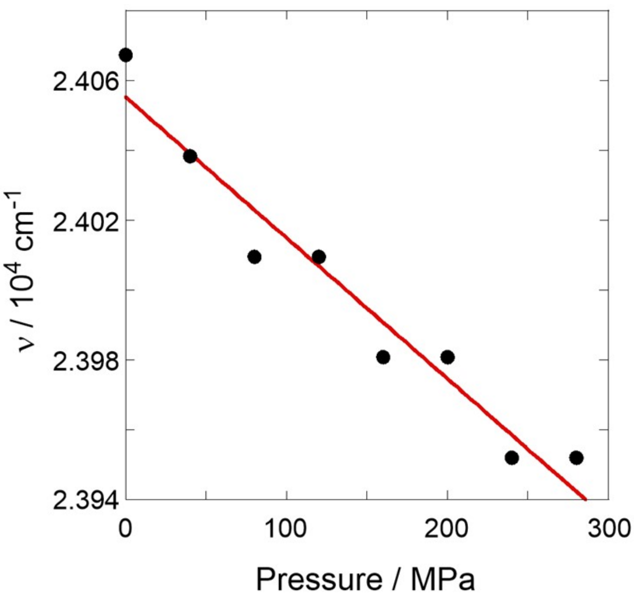

Figure S3. Plots of wavenumber changes for the pressure-induced absorption maxima of **N-Boc-PTZ-DBPHZ** in toluene (259 μM) (correlation coefficient r = 0.973, slope; −0.403 cm^{-1} MPa^{-1}).

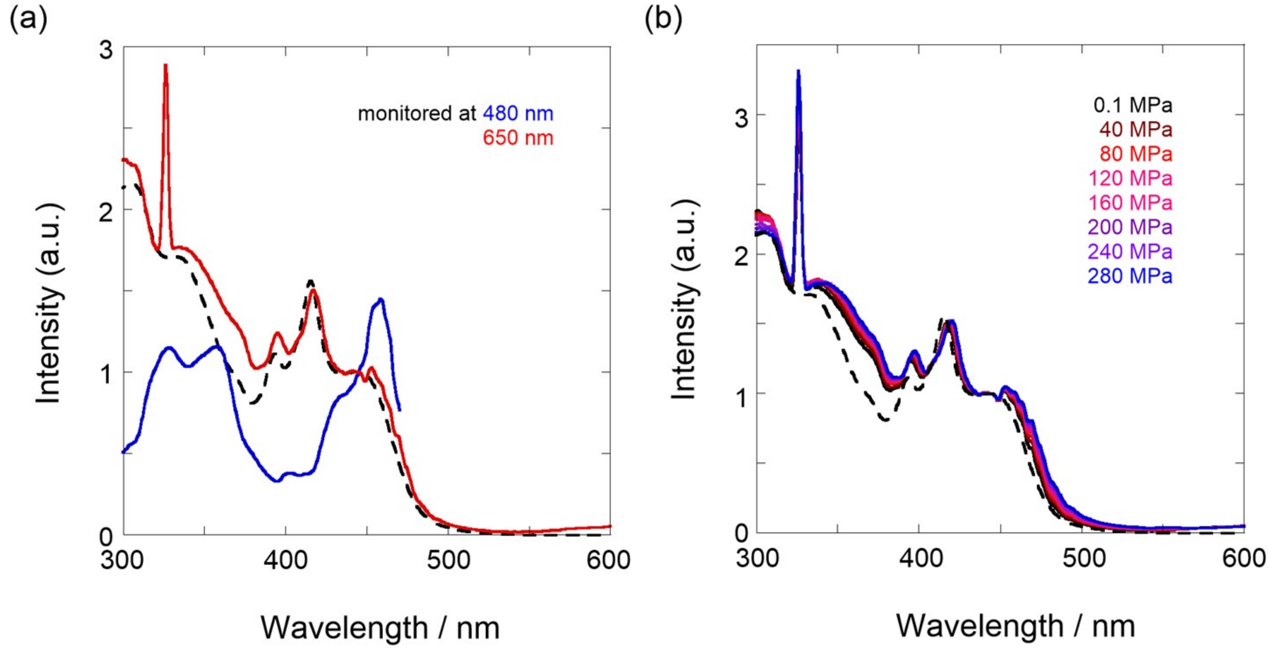

Figure S4. (a) Excitation spectra of **N-Boc-PTZ-DBPHZ** in toluene (259 μM), monitored at 480 nm (blue line) and 650 nm (red line) at room temperaturein a high-pressure cell. (b) Excitation spectra of **N-Boc-PTZ-DBPHZ** in toluene (259 μM), monitored at 650 nm at room temperature, in a high-pressure cell. Applied pressure: 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue).

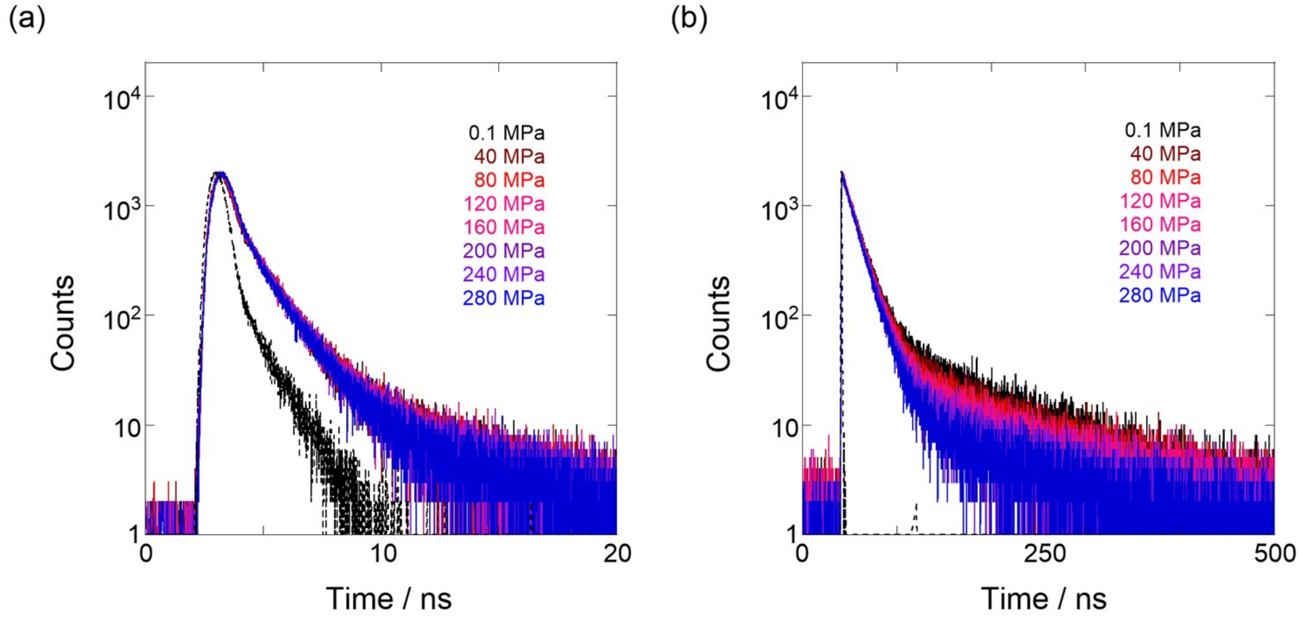

Figure S5. Time-correlated fluorescence decays (λ_{ex} = 405 nm) of **N-Boc-PTZ-DBPHZ** in toluene (a: λ_{em} = 490 nm, b: λ_{em} = 620 nm, 259 μM) at room temperature, measured in a high-pressure cell. Pressure applied: 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue). The black dotted line represents the instrument response function.

Table S1. Fluorescence lifetimes of N-Boc-PTZ-DBPHZ in toluene under hydrostatic pressures (λ_{ex} = 405 nm)[a]

Pressure/MPa	λ_{em}/nm	τ_1/ns	A_1	τ_2/ns	A_2	τ_3/ns	A_3	τ_4/ns	A_4	χ^2
0.1	470	0.1	0.46	1.2	0.54					1.3
	490	0.1	0.56	1.3	0.44					1.2
	510	0.2	0.62	1.4	0.38					1.2
	620					14.0	0.78	96.6	0.22	1.1
40	490	0.2	0.57	1.3	0.43					1.3
	620					13.8	0.82	84.9	0.18	1.2
80	490	0.2	0.58	1.3	0.42					1.2
	620					14.1	0.85	87.7	0.15	1.1
120	490	0.2	0.59	1.3	0.41					1.2
	620					13.9	0.88	80.2	0.12	1.2
160	490	0.2	0.60	1.3	0.40					1.2
	620					14.0	0.90	88.9	0.10	1.3
200	490	0.2	0.62	1.3	0.38					1.2
	620					14.1	0.92	76.7	0.08	1.1
240	490	0.3	0.64	1.3	0.36					1.1
	620					14.0	0.93	72.7	0.07	1.2
280	490	0.3	0.66	1.3	0.34					1.2
	620					14.5	1.00			1.5

[a]Fluorescence lifetime (τ_i) and relative abundance (A_i) of each excited species, determined by the hydrostatic-pressure single-photon-counting method in a non-degassed toluene solution at room temperature.

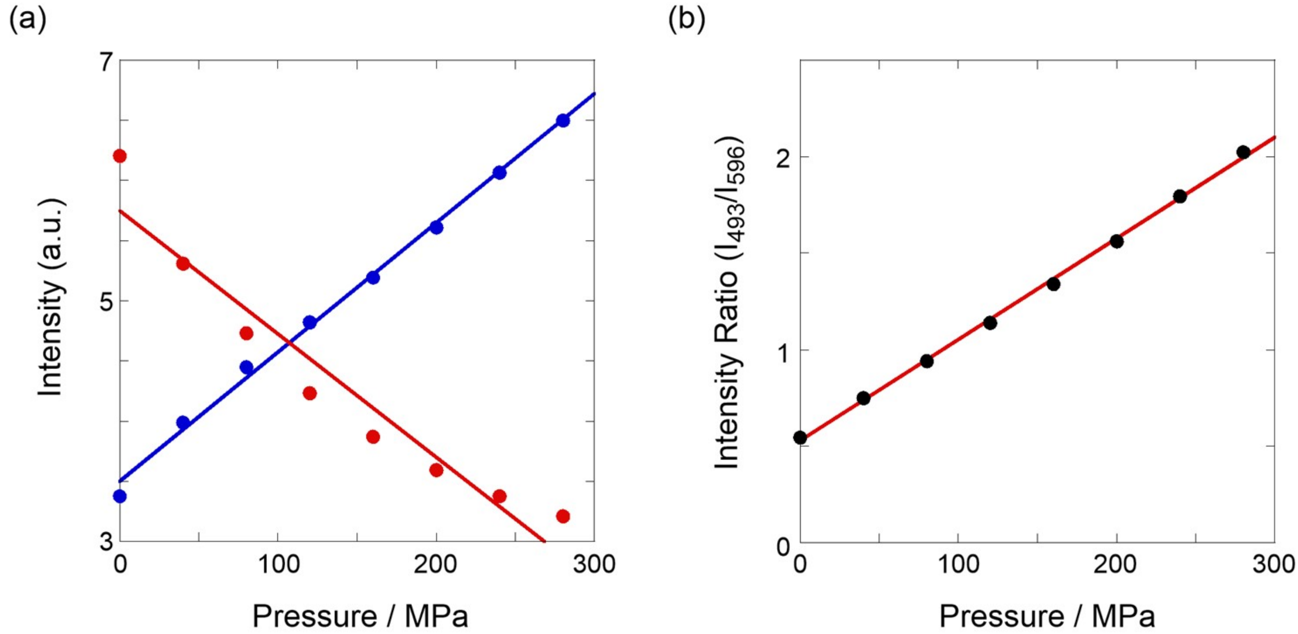

Figure S6. (a) Fluorescence changes of **N-Boc-PTZ-DBPHZ** in toluene (259 μM) at 493 nm (blue; r = 0.998, slope; 0.0107 MPa^{-1}) and 596 nm (red; r = 0.965, slope; −0.0102 MPa^{-1}) upon hydrostatic pressurization. (b) Plots of fluorescence intensity ratio changes of **N-Boc-PTZ-DBPHZ** in toluene (259 μM) upon hydrostatic pressurization (r = 0.999, slope = 0.00525 MPa^{-1}).

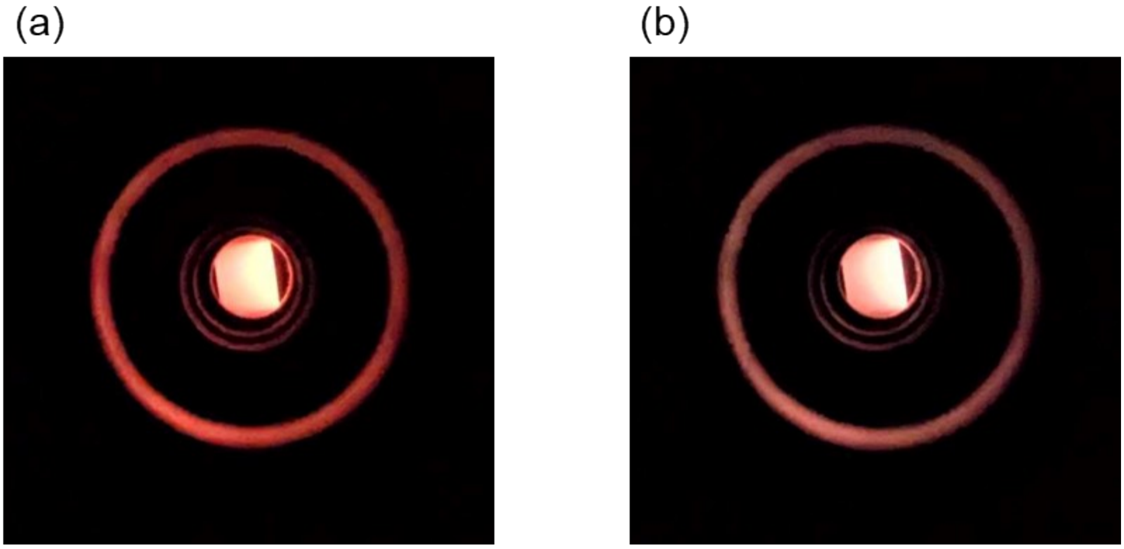

Figure S7. Photographs of the fluorescence images of **N-Boc-PTZ-DBPHZ** in toluene at (a) 0.1 MPa and (b) 280 MPa.

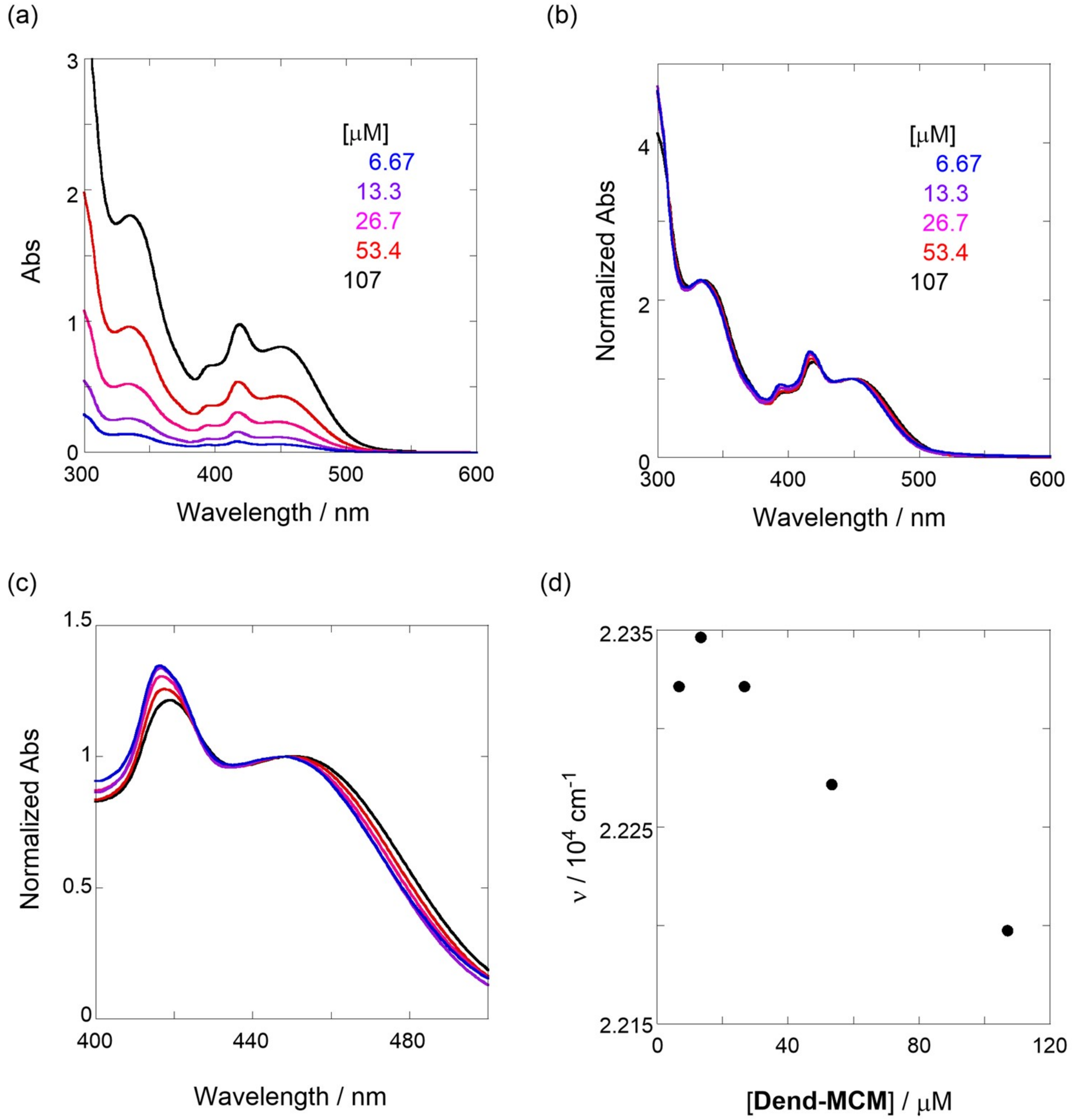

Figure S8. (a) Original and (b) normalized UV/vis absorption spectra of **Dend-MCM** in MeOH (6.67, 13.3, 26.7, 53.4, and 107 μM, from blue to black) at room temperature, measured in a 1 cm cell. (c) Magnification of **Figure S8b**. (d) Plots of concentration-dependent wavenumber changes for the absorption maxima of **Dend-MCM** in MeOH.

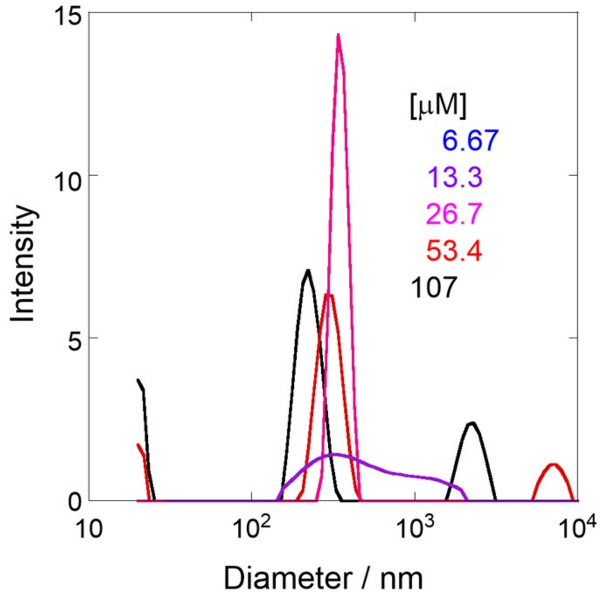

Figure S9. DLS profiles of **Dend-MCM** in MeOH (6.67, 13.3, 26.7, 53.4, and 107 μM, from blue to black) at room temperature, measured in a 1 cm cell.

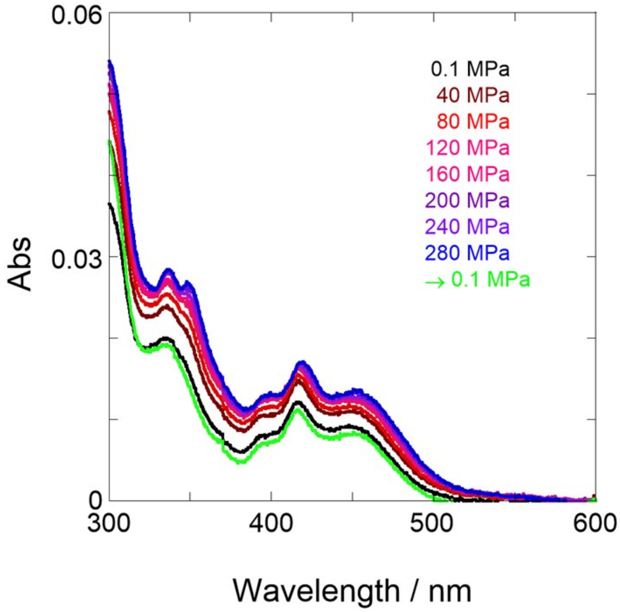

Figure S10. UV/vis absorption spectra of **Dend-MCM** in MeOH (4.89 μM) at room temperature, measured in a high-pressure cell. Applied pressure: 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue). The green line shows the spectrum at 0.1 MPa depressurized from 280 MPa.

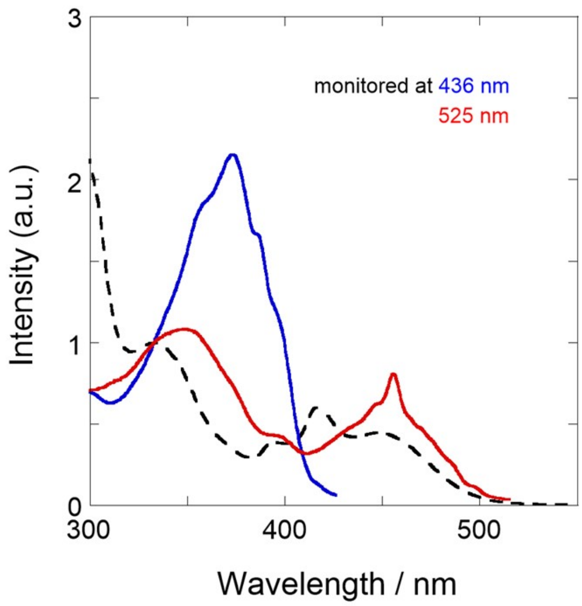

Figure S11. Excitation spectra of **Dend-MCM** in MeOH (5.02 μM), monitored at 436 nm (blue line) and 525 nm (red line) at room temperature, measured in a 1 cm cell.

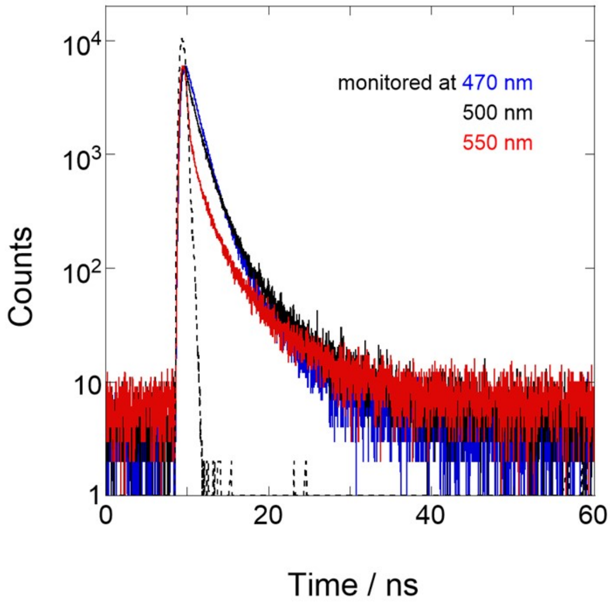

Figure S12. Time-correlated fluorescence decays (λ_{ex} = 405 nm, 5.02 μM) of **Dend-MCM** in MeOH, monitored at 470 (blue), 500 (black), and 550 nm (red) at room temperature, measured in a 1 cm cell. The black dotted line represents the instrument response function.

Table S2. Fluorescence lifetimes of Dend-MCM in MeOH (λ_{ex} = 405 nm, 5.02 μM)[a]

λ_{em}/nm	τ_1/ns	A_1	τ_2/ns	A_2	τ_3/ns	A_3	χ^2
470	<0.1	0.10	1.4	0.76	4.1	0.14	1.0
500	0.1	0.21	1.4	0.57	4.1	0.22	1.1
550	<0.1	0.56	1.3	0.26	4.6	0.18	1.1

[a]Fluorescence lifetime (τ_i) and relative abundance (A_i) of each excited species, determined using the single-photon counting method in a non-degassed MeOH solution at room temperature.

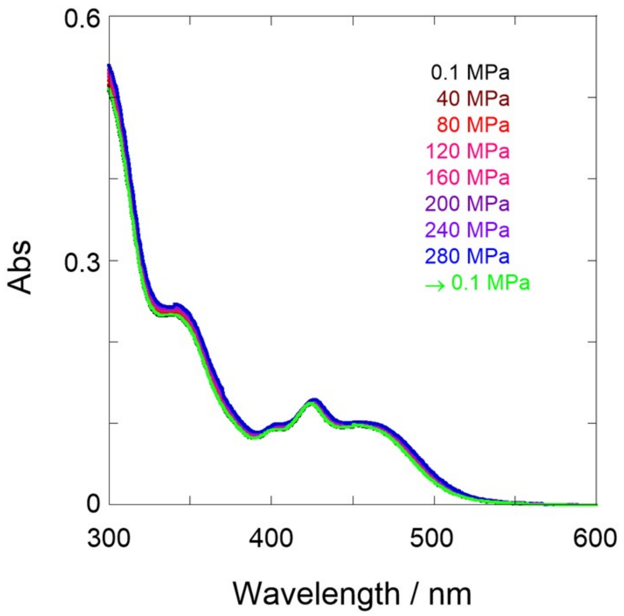

Figure S13. UV/vis absorption spectra of **Dend-MCM** in H_2O (62.3 μM) at room temperature, measured in a high-pressure cell. Applied pressure: 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue). The green line shows the spectrum at 0.1 MPa, depressurized from 280 MPa.

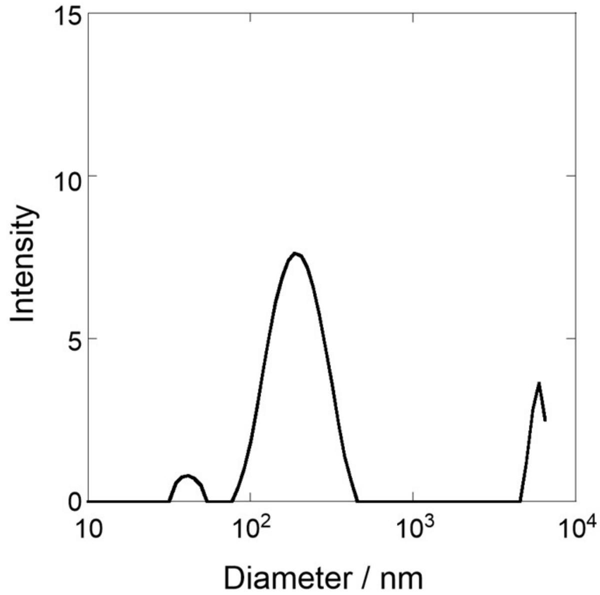

Figure S14. DLS of **Dend-MCM** in H_2O (4.66 μM) at room temperature, measured in a 1 cm cell.

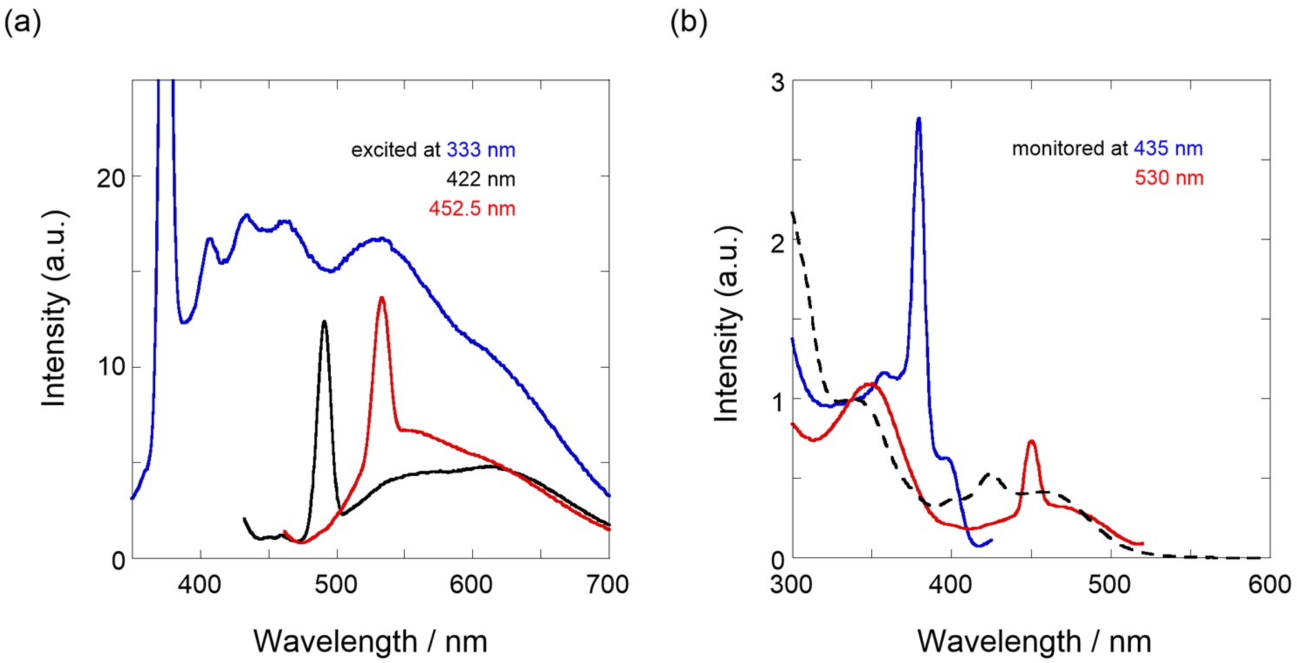

Figure S15. (a) Fluorescence spectra of **Dend-MCM** in H_2O (4.66 μM), excited at 333 nm (blue), 422 nm (black), and 452.5 nm (red) at room temperature, measured in a 1 cm cell. (b) Excitation spectra of **Dend-MCM** in H_2O (4.66 μM), monitored at 435 nm (blue) and 530 nm (red) at room temperature, measured in a 1 cm cell.

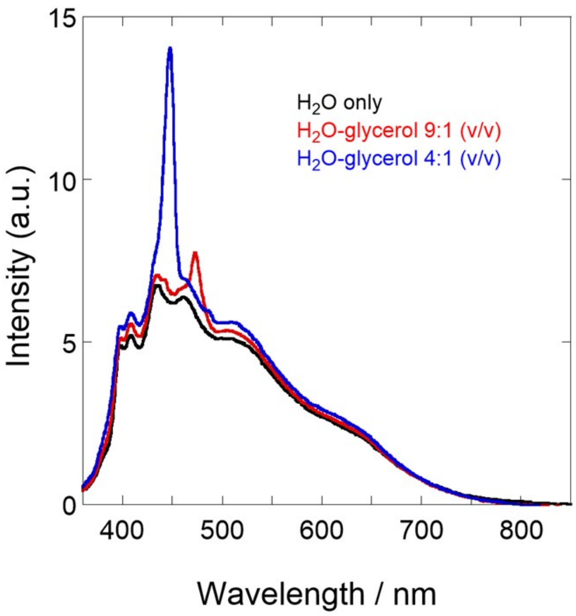

Figure S16. Fluorescence spectra (λ_{ex} 350 nm) of **Dend-MCM** in H_2O (27.7 μM, black line), H_2O-glycerol 9:1 (v/v) (27.7 μM, red line), and H_2O-glycerol 4:1 (v/v) (27.7 μM, blue line) at 0.1 MPa, measured in a 1 cm cell.

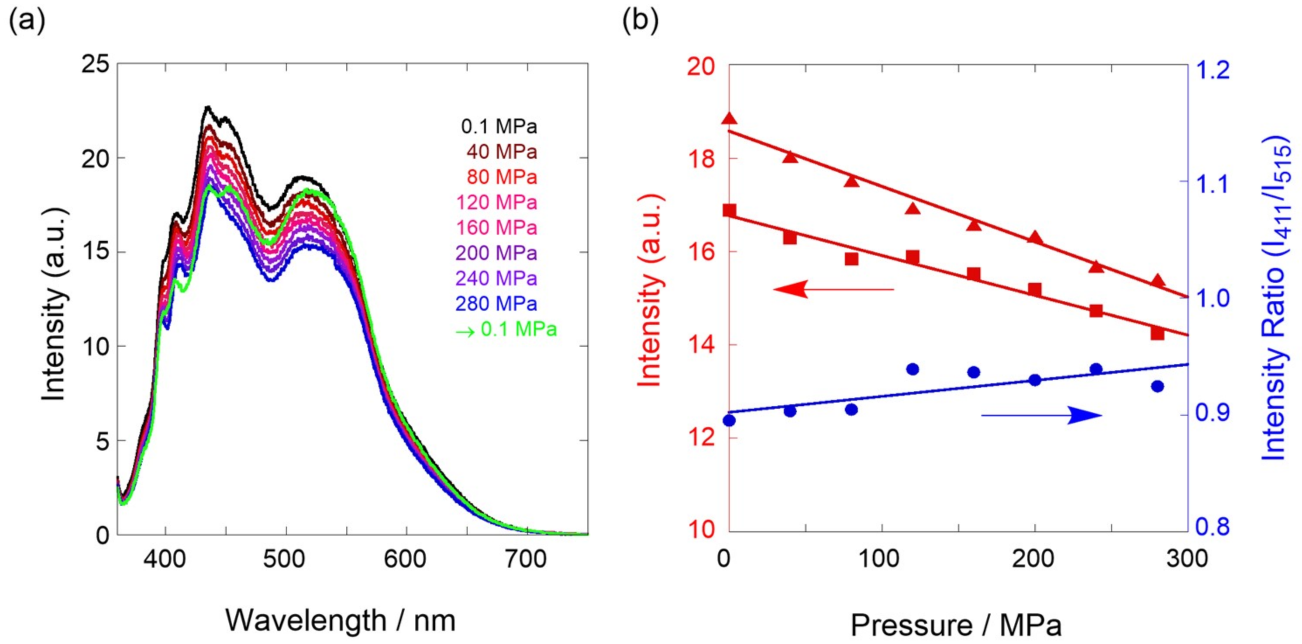

Figure S17. Fluorescence spectra (λ_{ex} 350 nm) of **Dend-MCM** in PBS (46.5 μM) at 0.1, 40, 80, 120, 160, 200, 240, and 280 MPa (from black to blue) at room temperature, measured in a high-pressure cell. The green line shows the spectrum at 0.1 MPa depressurized from 280 MPa. (b) Fluorescence intensity changes of **Dend-MCM** in PBS (46.5 μM) at 411 nm (red square; r = 0.983, slope; −0.00852 MPa^{-1}) and 515 nm (red triangle; r = 0.989, slope; −0.0119 MPa^{-1}), and plots illustrating the fluorescence intensity ratio changes between the emissions at 411 nm and 515 nm (blue circle; r = 0.747, slope; 0.000137 MPa^{-1}).