

Solvent-directed, pressure-controllable chemosensor: A case of helical anthracene dimer

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The exploration of a pressure-responsive chemosensor is of particular significance in current multidisciplinary chemistry from the viewpoints of mechanoscience. So far, we have developed such chemosensors that are susceptible to hydrostatic pressure in solutions.¹ Of these, an anthracene-fused helicene, **[4]HA** (Fig. 1a), shows ratiometric pressure-responsive fluorescence changes upon the hydrostatic pressurization. The ratiometry in **[4]HA** is caused by the [4+4] photocyclodimerization of the intramolecularly π - π stacked anthracenes.² In this study, we focused on a pseudo-helicene dimer, **[2]HA₂** (Fig 1b) that is linked with two fused anthracene skeletons (**[2]HA**) via a single bond, which is believed to

exhibit a solvation-dependent pressure sensitivity. Interestingly, as shown in Fig. 1c, **[2]HA₂** showed a distinctive pressure-induced fluorescence response. The fluorescence responses in some solvents are strongly dependent on solvent polarity estimated by E_T value; the response sign (ΔI) inverted at the border of E_T as 40 kcal mol⁻¹, shown in Fig. 1d. The excited-state dynamics (k_f and k_{nr}) of **[2]HA₂** under hydrostatic pressures supports the origins controlling pressure-induced solvation-driven transition states. It should be therefore noted that such interesting chemosensory responses are originated from the excited-state dynamics greatly involving pressure-induced microenvironmental polarities.

1) Mizuno, H.; Fukuhara, G. *Acc. Chem. Res.* **2022**, 55, 1748–1762. 2) Kinoshita, T.; Fujise, K.; Tsurumaki, E.; Toyota, S.; Fukuhara, G. *Chem. Commun.* **2022**, 58, 3290–3293.

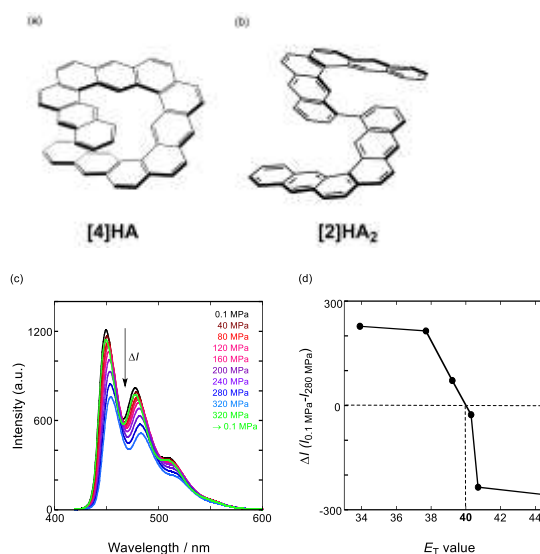


Figure 1. Chemical structures of helical anthracenes ((a) **[4]HA** and (b) **[2]HA₂**). (c) Fluorescence spectra of **[2]HA₂** in dichloromethane (λ_{ex} 412 nm, 57 μ M) at room temperature, measured in a high-pressure cell. (d) Hydrostatic pressure-induced ΔI ($I_{0.1\text{MPa}} - I_{280\text{MPa}}$).