

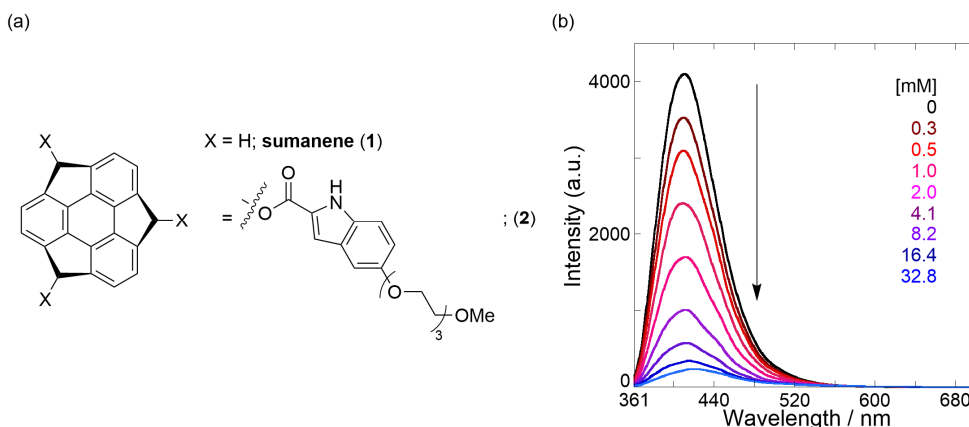
## Optical Properties and Molecular Recognition of a Sumanene-Based Chemosensor

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In this study, we chose sumanene<sup>1)</sup> (**1**) as a signal-amplification moiety and indole as a fluorescence reporter and also a molecular-recognition site, and thus conjugated each part to afford a sumanene chemosensor (**2**), shown in Fig. 1a.

The chemosensor **2** shows intriguing optical properties. The fluorescence lifetime decays of **2** gave three excited species including a rise component. This rise was not observed in a chromophoric reference compound, indicating that the indole chromophores on the sumanene scaffold intermolecularly interact on each other. Upon the gradual addition of guests examined, fluorescence intensities of **2** were quenched (see the example of benzoate in Fig. 1b). Surprisingly, a binding constant of **2** upon the complexation of benzoate was enhanced by a factor of up to 200, comparing to that obtained from the reference compound. This amplification behavior may reasonably be explained due to the sumanene scaffold; the three indole moieties cooperatively interact with benzoate.<sup>2)</sup> The results of a stack-induced amplification sensing will also be discussed.



**Figure 1.** (a) Chemical structures of sumanene (**1**) and its chemosensor (**2**). (b) Fluorescence spectra of **2** (468 μM; black) upon the gradual addition of benzoate (0.3–32.8 mM: from brown to sky blue) in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.

1) (a) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, 301, 1878. (b) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, 127, 11580. 2) Bates, G. W.; Triyanti; Light, M. E.; Albrecht, M.; Gale, P. A. *J. Org. Chem.* **2007**, 72, 8921.