An environment-sensitive fluorophore methoxybenzocoumarin emitting in protic environments

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Environment-sensitive fluorophores change their photophysical properties (e.g., fluorescence quantum yield (Φ_f), maximum emission wavelength and fluorescence lifetime) depending on the surrounding environment. These environment-sensitive fluorophores were utilized for the development of fluorescent sensors by combining stimulus-responsive macromolecules such as proteins and synthetic polymers. Herein, we synthesized a new fluorescent compound 8-methoxy-4-methyl-2*H*-benzo[*g*]chromen-2-one (MBC, Fig. 1a) as an unusual environment-sensitive fluorophore. MBC is almost non-fluorescent in aprotic solvents (e.g., $\Phi_f < 0.001$ in *n*-hexane), whereas it strongly fluoresces in protic solvents (e.g., $\Phi_f = 0.37$ in methanol) (Fig. 1b and 1c). Time-resolved photoacoustic measurements revealed that the extremely fast non-radiative processes of MBC in non-polar solvents are attributed predominantly to internal conversion. The photophysical properties of MBC examined in selected solvents with different polarities and hydrogen-bond donating abilities indicate that the internal conversion rate is greatly reduced by hydrogen-bonding interactions with protic solvents. The fast internal conversion in MBC in aprotic solvents can be explained in terms of the proximity effect between energetically close $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ states.

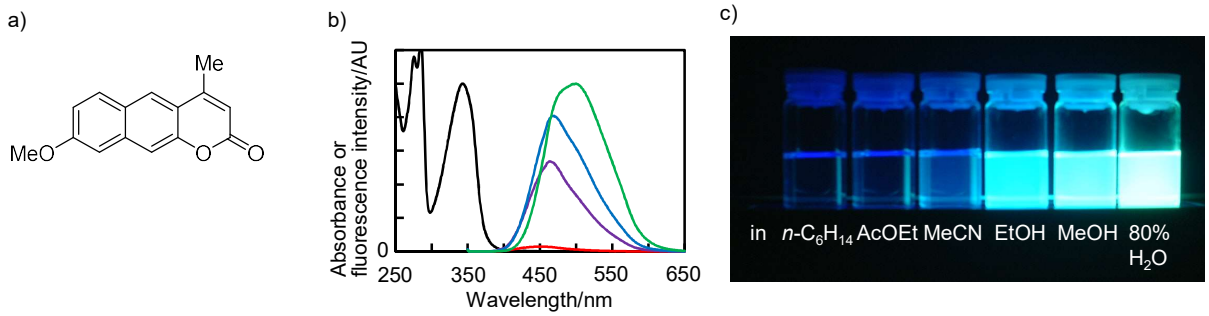

Figure 1. An environment-sensitive fluorophore MBC: a) Chemical structure, b) Representative absorption (black) and fluorescence (colored) spectra of MBC (10 μM) in acetonitrile (red), ethanol (purple), methanol (black and blue) and water-methanol (4:1, v/v) (green). Samples were excited at λ_{abs}. c) Visual images of the fluorescence in solutions.

Next, we synthesized a new fluorescent acrylamide-type monomer *N*-((8-methoxy-2-oxo-2*H*-benzo[*g*]chromen-4-yl)methyl)-*N*-methylacrylamide (MBC-AA, Fig. 2a) bearing the MBC structure. A fluorescent polymeric thermometer was prepared from *N*-isopropylacrylamide and MBC-AA, and it showed good functionality in aqueous solution (e.g., high sensitivity to temperature change and high chemical stability) (Fig. 2b and 2c), indicating the applicability of the new environment-sensitive fluorophore MBC for use in fluorescent sensors.

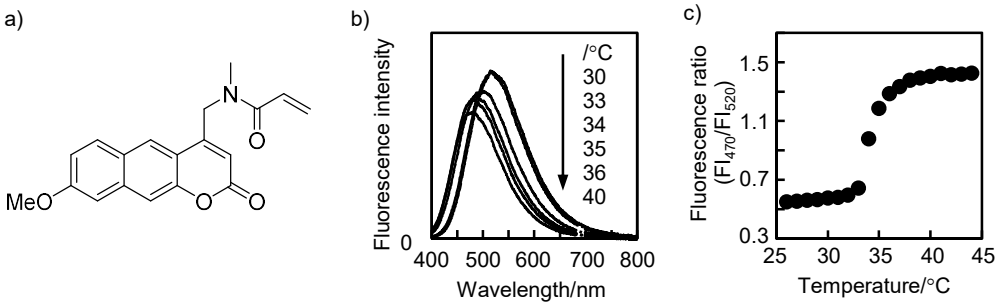

Figure 2. A fluorescent polymeric thermometer prepared from MBC-AA and *N*-isopropylacrylamide: a) Chemical structure of MBC-AA, b) Representative fluorescence spectra of the polymeric thermometer in water with increasing temperature. The polymer sample (0.01 w/v%) was excited at 345 nm. c) Change in the fluorescence intensity ratio of the polymeric thermometer at 470 nm and 520 nm (FI_{470}/FI_{520}).

Funding: The Sumitomo Foundation, The Japan Science and Technology Agency (the Development of Advanced Measurement and Analysis System program), The Japan Society for the Promotion of Science (Grant-in-Aid for Challenging Exploratory Research 16K14002), The Spanish Ministry for Economy and Competitiveness (grants CTQ2008-06777-C02-02 and CTQ2014-54729-C2-1-P, PhD fellowship BES-2009-012264, travel grant EEBB-I-13-07155)

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[2] MBC is now commercially available.
See http://www.tcichemicals.com/eshop/en/gb/commodity/M1862/.

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