Electronic supplementary Information for:

Remarkable fluorescence enhancement of benzo[*g*]chromen-2-ones induced by hydrogen-bonding interactions with protic solvents

Atsushi Kobayashi,[a] ToshitadaYoshihara,[b] Kazuyuki Takehira,[b] Seiichi Uchiyama[c] and Seiji Tobita*[b]

[a]*ATEC, Gunma University, Kiryu, Gunma 376-8515, Japan*

[b]*Department of Chemistry and Chemical Biology, Gunma University, Kiryu, Gunma 376-8515, Japan*

[c]*Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Corresponding Author's Email: tobita@gunma-u.ac.jp

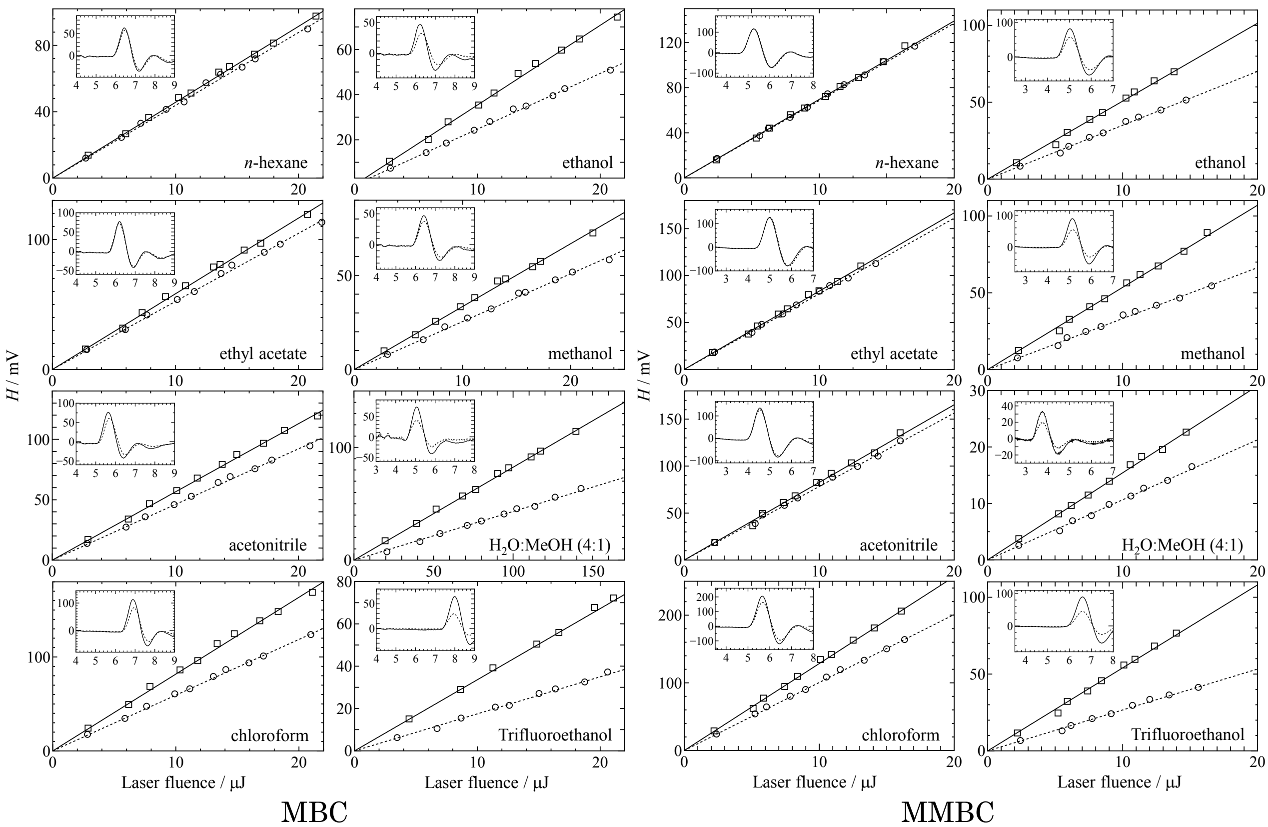

Fig. S1 Laser energy dependence of the PA signal amplitudes of MBC and MMBC in selected solvents at 293K. The PA signals are displayed in the inset.

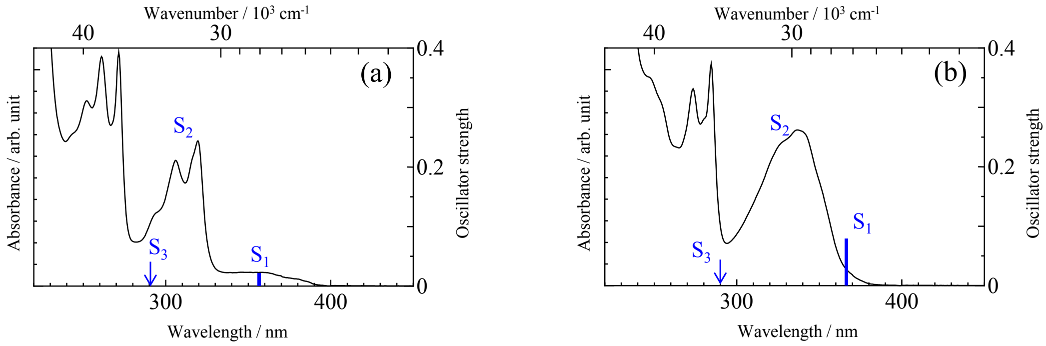

Fig. S2 Absorption spectra of (a) MBC and (b) MMBC in *n*-hexane and wavelengths and oscillator strengths (blue line) of S_1, S_2 and S_3 states calculated with the TD-B3LYP // B3LYP method using the 6-31G (d,p) basis set. Arrows in figures show the calculated wavelengths for the S_3 (n,π*) state.

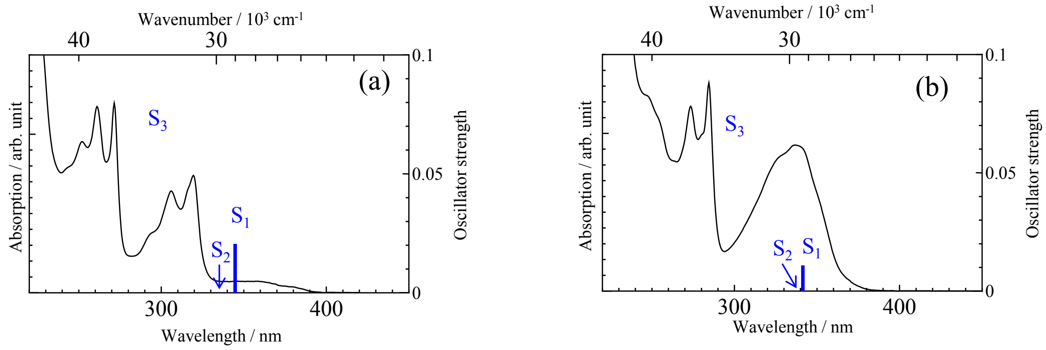

Fig. S3 Absorption spectra of (a) MBC and (b) MMBC in *n*-hexane and wavelengths and oscillator strengths (blue line) of S_1, S_2 and S_3 states calculated with the INDO/S-CI method. Arrows in figures show the calculated wavelength for the S_2 (n,π*) state.

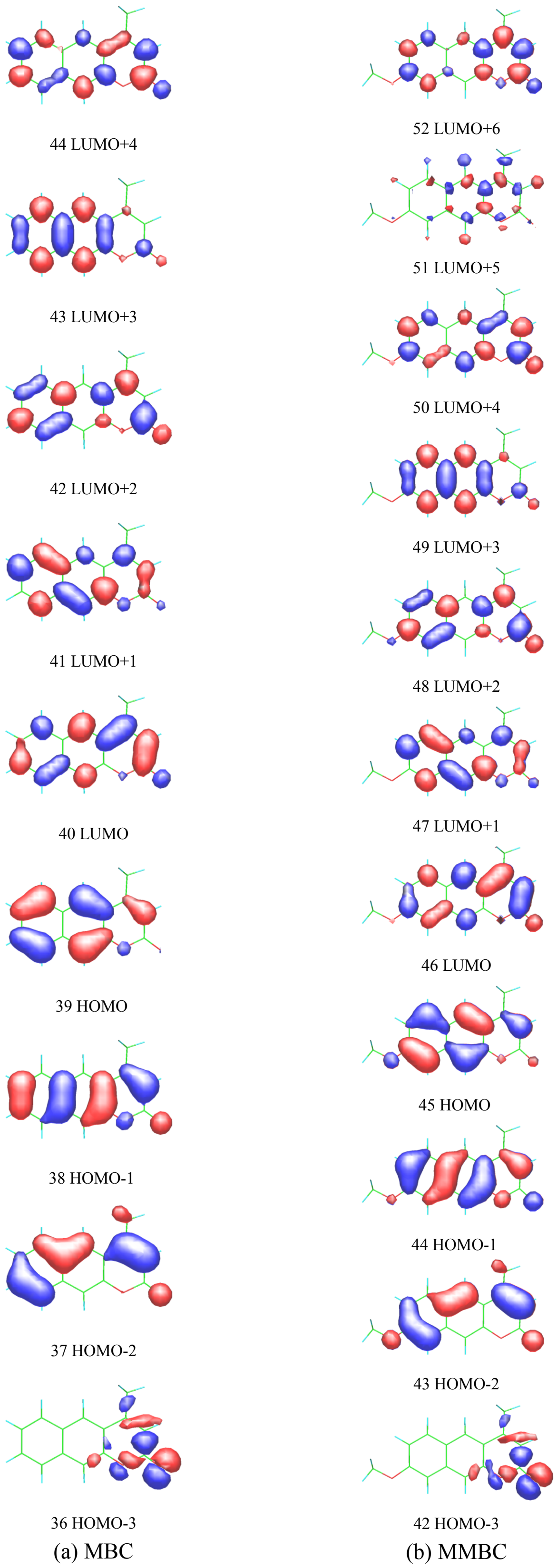

Fig. S4 HOMO and LUMO orbitals for (a) MBC and (b) MMBC calculated with the INDO/S-CI method.

Table S1 Excitation energies (ΔE), wavelengths (λ), and oscillator strengths (f) of MBC and MMBCcalculated with TD-BLYP/6-31G (d,p)//B3LYP/6-31G (d,p) basis set.

Compound	State	ΔE (kJ mol^{-1})	λ (nm)	f	Transition	
MBC	S_1	290.5	411.7	0.0124	55 → 56	0.6795
					55 → 57	-0.1150
	S_2	329.2	363.2	0.0000	53 → 56	0.7063
	S_3	353.7	338.1	0.1997	52 → 56	-0.1002
					54 → 56	0.6275
					55 → 57	-0.1693
					55 → 58	-0.2272
MMBC	S_1	274.0	436.5	0.0398	62 → 64	-0.1509
					63 → 64	0.6682
					63 → 65	-0.1088
	S_2	306.5	390.2	0.0004	61 → 64	0.7050
	S_3	324.7	368.3	0.2043	60 → 64	-0.1235
					62 → 64	0.6266
					63 → 64	0.1441
					63 → 65	0.2023
					63 → 66	0.1482

Synthesis of 6,7,8,9-tetrahydro-4-methyl-2H-benzo[*g*]chromen-2-one

4,5,6,7-Tetrahydro-2-naphthol (4.5 g, 30 mmol) and ethyl acetoacetate (6 ml, 40 mmol) were mixed and H_2SO_4 (Conc. 30 ml) was dropped slowly to the mixture at room temperature. The mixture was stirred for 17h. Then, the reaction mixture was poured into water (300 ml) and the reaction products were precipitated. The products were filtrated and recrystallized from ethanol. The residue was chromatographed on a silica gel using ethyl acetate as an eluent to afford 6,7,8,9-tetrahydro-4-methyl-2*H*-benzo[*g*]chromen-2-one (4.5 g, 21 mmol, 70%) ; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.45 (s,1H), 7.09 (s,1H), 6.23 (s, 1H), 2.82-2.80 (m, 4H), 2.40 (s, 4H), 1.77-1.73 (quin, 4H, J = 3 Hz).

Synthesis of 4-methyl-2*H*-benzo[*g*]chromen-2-one (MBC)

6,7,8,9-Tetrahydro-4-methyl-2*H*-benzo[*g*]chromen-2-one (2.14 g, 10 mmol), benzoyl peroxide (2.0 g, 8.3 mmol) and *N*-bromosuccinimide (3.8 g, 21 mmol) were dissolved in CCl_4 (150 ml) at 20 °C. After 1h, potassium acetate (30 g, 0.3 mol) and glacial acetic acid (10 g, 0.1 mol) were add into the solution, and stirred for 5h. Then, the reaction mixture was poured into water (200 ml) and the reaction products were extracted with $CHCl_3$ (150 ml). The organic layer was washed with water (100 ml), dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel using acetyl acetate as an eluent to afford 4-methyl-2*H*-benzo[*g*]chromen-2-one (510 mg, 2.5 mmol, 25%) ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.96-7.93 (d, 1H, J = 9 Hz), 7.89-7.86 (d, 1H, J = 9 Hz), 7.72 (s, 1H), 7.60-7.55 (t, 1H, J = 7.5 Hz), 7.52-7.47 (t, 1H, J = 7.5 Hz), 6.36 (s, 1H), 2.57 (s, 3H).