## Electronic Supplementary Information

# Multifunctional organic dyes: anion-sensing and light-harvesting properties of curcumin boron complexes

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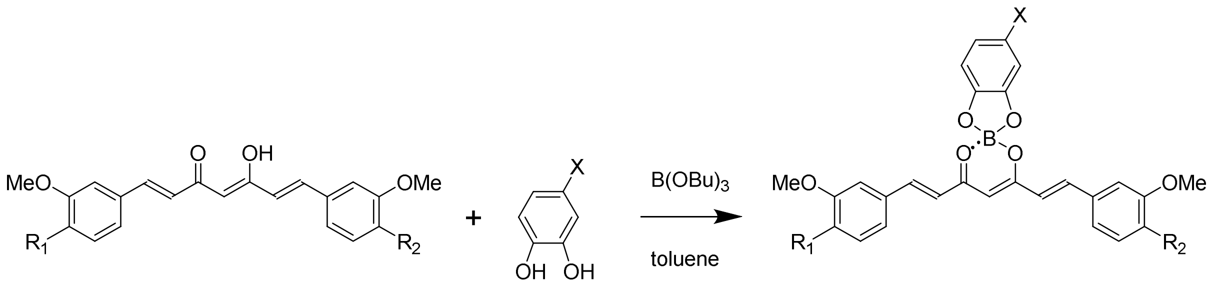
## 1. Synthesis of Dyes



**5a** $R_1 = R_2 = OH$
**5b** $R_1 = OH, R_2 = OC_8H_{17}$
**5c** $R_1 = R_2 = OC_8H_{17}$

**6a** $X = H$
**6b** $X = CO_2H$
**6c** $X = CH{=}CHCO_2H$

**CB** $R_1 = R_2 = OH, X = H$
**1** $R_1 = R_2 = OH, X = CO_2H$
**2** $R_1 = R_2 = OH, X = CH{=}CHCO_2H$
**3** $R_1 = OH, R_2 = OC_8H_{17}, X = CO_2H$
**4** $R_1 = R_2 = OC_8H_{17}, X = CO_2H$

**Scheme S1** Synthesis of curcumin boron complexes.

### General

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. $^1$H NMR (400 MHz), $^{13}$C NMR (100 MHz) and $^{11}$B NMR (128 MHz) spectra were recorded with a Bruker Avance III 400 spectrometer. IR and UV-Vis spectra were recorded with JASCO FT/IR-4200 and JASCO V-670 spectrometers, respectively. EI (70 eV) mass spectra were recorded with a Waters GCT Premier mass spectrometer, and MALDI-TOF mass spectra were measured with a JEOL JMS-S3000 mass spectrometer by using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. Elemental analyses were performed with an Elementar vario EL cube analyzer. Compounds **1–4** and **CB** were prepared by using synthetic procedures modified from the reported method of **CB**.1)

## Syntheses

**Synthesis of 5b**:$^{2)}$ A mixture of curcumin (**5a**) (0.74 g, 2.0 mmol), 1-bromooctane (0.70 mL, 4.0 mmol) and potassium *tert*-butoxide (0.90 g, 8.0 mmol) in anhydrous DMSO (40 mL) was stirred at 80 °C for 5 h under nitrogen. After cooling, cold water (10 mL) was added and the organic layer was extracted with ethyl acetate (20 mL × 3). The organic solution was dried over $Na_2SO_4$ and concentrated. The residue was purified by chromatography on silica gel (dichloromethane) and the crude product was recrystallized from *n*-hexane to afford **5b** (0.42 g, 43%) as yellow crystals. M.p. 80–81 °C; $^1$H NMR (DMSO-$d_6$): $\delta$ = 0.86 (t, $J$ = 6.8 Hz, 3H), 1.26 (m, 8H), 1.38 (m, 2H), 1.72 (m, 2H), 3.83 (s, 3H), 3.84 (s, 3H), 4.00 (t, $J$ = 6.4 Hz, 2H), 6.08 (s, 1H), 6.76 (d, $J$ = 15.6 Hz, 1H), 6.82 (d, $J$ = 16.0 Hz, 1H), 6.83 (d, $J$ = 8.4 Hz, 1H), 7.00 (d, $J$ = 8.4 Hz, 1H), 7.16 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.24 (dd, $J$ = 8.4, 2.0 Hz, 1H), 7.33 (d, $J$ = 1.6 Hz, 1H), 7.34 (d, $J$ = 2.0 Hz, 1H), 7.56 (d, $J$ = 15.6 Hz, 1H), 7.57 (d, $J$ = 16.0 Hz, 1H), 9.67 ppm (br s, 1H); $^{13}$C NMR (DMSO-$d_6$): $\delta$ = 14.00, 22.12, 25.54, 28.66, 28.70, 28.75, 31.28, 55.68, 55.72, 68.24, 100.99, 110.68, 111.37, 112.65, 115.74, 121.13, 121.97, 122.94, 123.21, 126.34, 127.51, 140.27, 140.95, 148.03, 149.19, 149.43, 150.41, 182.81, 183.67 ppm; IR (KBr): $\tilde{\nu}$ = 3375, 2925, 2853, 1626, 1586, 1509, 1463, 1423, 1262, 1135, 1033, 968 cm$^{-1}$; UV-Vis (MeCN): $\lambda_{max}$ ($\varepsilon$) = 420 nm (50900 M$^{-1}$ cm$^{-1}$); MS (EI): *m/z* (%): 480.25 (59) $[M]^+$, 462.24 (100) $[M - H_2O]^+$, 177.05 (74); elemental analysis calcd (%) for $C_{29}H_{36}O_6$: C 72.48, H 7.55; found: C 72.51, H 7.68.

**Synthesis of 5c**:$^{2)}$ A mixture of curcumin (**5a**) (0.37 g, 1.0 mmol), 1-bromooctane (0.52 mL, 3.0 mmol) and potassium *tert*-butoxide (0.56 g, 5.0 mmol) in anhydrous DMSO (20 mL) was stirred at 80 °C for 5 h under nitrogen. After cooling, cold water (10 mL) was added and the organic layer was extracted with ethyl acetate (20 mL × 3). The organic solution was dried over $Na_2SO_4$ and concentrated. The residue was purified by chromatography on silica gel (dichloromethane) and the crude product was recrystallized from *n*-hexane to afford **5c** (0.31 g, 53%) as yellow crystals. M.p. 108–109 °C; $^1$H NMR ($CDCl_3$): $\delta$ = 0.89 (t, $J$ = 6.8 Hz, 6H), 1.29–1.35 (m, 16H), 1.43 (m, 4H), 1.86 (m, 4H), 3.92 (s, 6H), 4.05 (t, $J$ = 6.8 Hz, 4H), 5.82 (s, 1H), 6.49 (d, $J$ = 15.8 Hz, 2H), 6.87 (d, $J$ = 8.3 Hz, 2H), 7.08 (d, $J$ = 1.9 Hz, 2H), 7.12 (dd, $J$ = 8.3, 1.9 Hz, 2H), 7.60 ppm (d, $J$ = 15.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$): $\delta$ = 14.08, 22.63, 25.91, 29.03, 29.19, 29.32, 31.78, 56.02, 69.04, 101.21, 110.23, 112.41, 121.86, 122.62, 127.84, 140.45, 149.52, 150.72, 183.26 ppm; IR (KBr): $\tilde{\nu}$ = 2925, 2853, 1625, 1593, 1578, 1510, 1468, 1256, 1137, 1038, 976, 850, 808 cm$^{-1}$; UV-Vis (MeCN): $\lambda_{max}$ ($\varepsilon$) = 421 nm (60600 M$^{-1}$ cm$^{-1}$); MS (EI): *m/z* (%): 592.38 (44) [*M*]$^+$, 574.37 (92), 302.20 (100), 289.19 (75), 177.06 (96), 100.09 (64); elemental analysis calcd (%) for $C_{37}H_{52}O_6$: C 74.97, H 8.84; found: C 74.84, H 9.03.

**Synthesis of 1**: A mixture of curcumin (**5a**) (0.28 g, 0.75 mmol), 3,4-dihydroxybenzoic acid (**6b**) (0.12 g, 0.75 mmol) and tributyl borate (0.20 mL, 0.75 mmol) in anhydrous toluene (20 mL) was refluxed for 3 h. After cooling, half of the solvent was removed. The precipitate was filtered and washed with chloroform. The crude product was recrystallized from acetone/acetonitrile (10:1 v/v) to afford dye **1** (0.35 g, 88%) as red crystals. M.p. 244–245 °C; $^1$H NMR (DMSO-$d_6$): $\delta$ = 3.83 (s, 6H), 6.55 (s, 1H), 6.76 (d, $J$ = 8.1 Hz, 1H), 6.86 (d, $J$ = 8.4 Hz, 2H), 7.08 (d, $J$ = 15.6 Hz, 2H), 7.21 (d, $J$ = 1.9 Hz, 1H), 7.36 (dd, $J$ = 8.4, 1.6 Hz, 2H), 7.44 (dd, $J$ = 8.1, 1.9 Hz, 1H), 7.48 (d, $J$ = 1.6 Hz, 2H), 7.91 (d, $J$ = 15.6 Hz, 2H), 10.12 (br s, 2H), 12.32 ppm (br s, 1H); $^{13}$C NMR (DMSO-$d_6$): $\delta$ = 55.74, 101.43, 108.33, 109.19, 112.72, 115.97, 117.66, 121.68, 122.69, 125.23, 126.02, 147.35, 148.13, 150.43, 151.48, 155.04, 167.60, 177.41 ppm; $^{11}$B NMR (DMSO-$d_6$): $\delta$ = 9.27 ppm; IR (KBr): $\tilde{\nu}$ = 3531, 1722, 1618, 1588, 1528, 1510, 1376, 1297, 1266, 1150, 1064, 982 cm$^{-1}$; UV-Vis (MeCN): $\lambda_{max}$ ($\varepsilon$) = 509 nm (78900 M$^{-1}$ cm$^{-1}$); MS (MALDI-TOF): *m/z*: 530.13 [*M*]$^+$; elemental analysis calcd (%) for $C_{28}H_{23}BO_{10}$: C 63.42, H 4.37; found: C 63.39, H 4.36.

**Synthesis of 2**: A mixture of curcumin (**5a**) (0.28 g, 0.75 mmol), caffeic acid (**6c**) (0.14 g, 0.75 mmol) and tributyl borate (0.20 mL, 0.75 mmol) in anhydrous toluene (20 mL) was refluxed for 3 h. After cooling, half of the solvent was removed and *n*-hexane was added. The precipitate was filtered and washed with *n*-hexane. The crude product was recrystallized from acetonitrile to afford dye **2** (0.28 g, 66%) as red crystals. M.p. > 300 °C; $^{1}$H NMR (DMSO-$d_6$): $\delta = 3.83$ (s, 6H), 6.28 (d, $J = 16.0$ Hz, 1H), 6.54 (s, 1H), 6.72 (d, $J = 8.1$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 2H), 7.01 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.08 (d, $J = 15.2$ Hz, 2H), 7.11 (d, $J = 1.7$ Hz, 1H), 7.36 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.48 (d, $J = 1.8$ Hz, 2H), 7.51 (d, $J = 16.0$ Hz, 1H), 7.91 (d, $J = 15.2$ Hz, 2H), 10.12 (br s, 2H), 12.07 ppm (br s, 1H); $^{13}$C NMR (DMSO-$d_6$): $\delta = 55.74$, 101.47, 106.87, 108.79, 112.73, 114.71, 115.98, 117.69, 122.69, 125.20, 125.94, 126.03, 145.48, 147.28, 148.14, 151.24, 151.47, 153.38, 168.12, 177.45 ppm; $^{11}$B NMR (DMSO-$d_6$): $\delta = 9.00$ ppm; IR (KBr): $\tilde{\nu} = 3481$, 1670, 1615, 1591, 1544, 1508, 1474, 1295, 1265, 1215, 1147, 1065, 998, 975 cm$^{-1}$; UV-Vis (MeCN): $\lambda_{\max}$ ($\varepsilon$) = 508 nm (73500 M$^{-1}$ cm$^{-1}$); MS (MALDI-TOF): *m/z*: 579.15 [$M$ + Na]$^{+}$, 556.16 [$M$]$^{+}$; elemental analysis calcd (%) for $C_{30}H_{25}BO_{10}$: C 64.77, H 4.53; found: C 64.57, H 4.65.

**Synthesis of 3**: A mixture of compound **5b** (0.36 g, 0.75 mmol), 3,4-dihydroxybenzoic acid (**6b**) (0.12 g, 0.75 mmol) and tributyl borate (0.20 mL, 0.75 mmol) in anhydrous toluene (10 mL) was refluxed for 3 h. After cooling, half of the solvent was removed and *n*-hexane was added. The precipitate was filtered and washed with *n*-hexane. The crude product was recrystallized from acetonitrile to afford dye **3** (0.31 g, 65%) as red crystals. M.p. 181–182 °C; $^{1}$H NMR (DMSO-$d_6$): $\delta = 0.86$ (t, $J = 6.8$ Hz, 3H), 1.26 (m, 8H), 1.40 (m, 2H), 1.72 (m, 2H), 3.82 (s, 3H), 3.83 (s, 3H), 4.03 (t, $J = 6.6$ Hz, 2H), 6.57 (s, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 7.05 (d, $J = 8.4$ Hz, 1H), 7.09 (d, $J = 15.6$ Hz, 1H), 7.14 (d, $J = 15.6$ Hz, 1H), 7.22 (d, $J = 2.0$ Hz, 1H), 7.37 (d, $J = 8.2, 1.6$ Hz, 1H), 7.42–7.47 (m, 2H), 7.48 (br s, 2H), 7.92 (d, $J$ = 15.6 Hz, 1H), 7.93 (d, $J$ = 15.6 Hz, 1H), 10.15 (br s, 1H), 12.33 ppm (br s, 1H); $^{13}$C NMR (DMSO-$d_6$): $\delta$ = 14.03, 22.14, 25.53, 28.60, 28.71, 28.75, 31.30, 55.76, 55.80, 68.42, 101.66, 108.44, 109.28, 111.71, 112.68, 112.78, 116.05, 117.65, 118.68, 121.77, 122.81, 125.10, 125.46, 126.05, 127.06, 146.83, 147.82, 148.22, 149.26, 150.48, 151.69, 152.13, 155.09, 167.69, 177.31, 177.91 ppm; $^{11}$B NMR (DMSO-$d_6$): $\delta$ = 9.13 ppm; IR (KBr): $\tilde{\nu}$ = 3498, 1669, 1615, 1589, 1545, 1508, 1473, 1295, 1265, 1216, 1146, 1065, 974, 928 cm$^{-1}$; UV-Vis (MeCN): $\lambda_{\max}$ ($\varepsilon$) = 512 nm (81700 M$^{-1}$ cm$^{-1}$); MS (MALDI-TOF): *m/z*: 665.24 [$M$ + Na]$^+$, 642.25 [$M$]$^+$; elemental analysis calcd (%) for $C_{36}H_{39}BO_{10}$: C 67.30, H 6.12; found: C 67.13, H 6.20.

**Synthesis of 4**: A mixture of compound **5c** (0.30 g, 0.50 mmol), 3,4-dihydroxybenzoic acid (**6b**) (85 mg, 0.55 mmol) and tributyl borate (0.15 mL, 0.55 mmol) in anhydrous toluene (15 mL) was refluxed for 3 h. After cooling, half of the solvent was removed and *n*-hexane was added. The precipitate was filtered and washed with *n*-hexane. The crude product was recrystallized from toluene to afford dye **4** (0.28 g, 74%) as red crystals. M.p. 215–216 °C; $^1$H NMR (DMSO-$d_6$): $\delta$ = 0.86 (t, $J$ = 6.8 Hz, 6H), 1.26 (m, 16H), 1.40 (m, 4H), 1.72 (m, 4H), 3.82 (s, 6H), 4.04 (t, $J$ = 6.6 Hz, 4H), 6.60 (s, 1H), 6.77 (d, $J$ = 8.4 Hz, 1H), 7.06 (d, $J$ = 8.8 Hz, 2H), 7.16 (d, $J$ = 15.6 Hz, 2H), 7.22 (d, $J$ = 2.0 Hz, 1H), 7.44–7.46 (m, 3H), 7.49 (d, $J$ = 1.6 Hz, 2H), 7.95 (d, $J$ = 15.6 Hz, 2H), 12.33 ppm (br s, 1H); $^{13}$C NMR (CDCl$_3$): $\delta$ = 14.30, 22.84, 26.10, 29.16, 29.39, 29.52, 31.99, 56.19, 69.31, 102.16, 109.23, 110.92, 111.05, 112.42, 117.95, 120.82, 124.67, 125.06, 127.11, 147.95, 149.79, 150.91, 152.74, 156.51, 172.45, 178.08 ppm; $^{11}$B NMR (DMSO-$d_6$): $\delta$ = 9.11 ppm; IR (KBr): $\tilde{\nu}$ = 2926, 2855, 1676, 1613, 1597, 1537, 1508, 1467, 1454, 1265, 1138, 1067, 990 cm$^{-1}$; UV-Vis (MeCN): $\lambda_{\max}$ ($\varepsilon$) = 514 nm (74700 M$^{-1}$ cm$^{-1}$); MS (MALDI-TOF): *m/z*: 777.38 [$M$ + Na]$^+$, 754.39 [$M$]$^+$, 737.38 [$M$ − OH]$^+$; elemental analysis calcd (%) for $C_{44}H_{55}BO_{10}$: C 70.02, H 7.35; found: C 69.93, H 7.46.

**Synthesis of CB**:1) A mixture of curcumin (**5a**) (0.37 g, 1.0 mmol), catechol (**6a**) (0.11 g, 1.0 mmol) and tributyl borate (0.27 mL, 1.0 mmol) in anhydrous toluene (20 mL) was refluxed for 3 h. After cooling, half of the solvent was removed and *n*-hexane was added. The precipitate was filtered and washed with *n*-hexane. The crude product was washed with hot chloroform and hot diethyl ether to afford **CB** (0.29 g, 60%) as red crystals. M.p. 274–275 °C; $^{1}$H NMR (DMSO-$d_6$): $\delta$ = 3.83 (s, 6H), 6.50 (s, 1H), 6.68 (m, 4H), 6.86 (d, $J$ = 8.4 Hz, 2H), 7.06 (d, $J$ = 15.6 Hz, 2H), 7.34 (dd, $J$ = 8.4, 1.6 Hz, 2H), 7.46 (d, $J$ = 1.6 Hz, 2H), 7.88 (d, $J$ = 15.6 Hz, 2H), 10.10 ppm (br s, 2H); $^{13}$C NMR (DMSO-$d_6$): $\delta$ = 55.75, 101.45, 108.86, 112.67, 115.97, 117.84, 118.91, 125.08, 126.03, 146.97, 148.14, 150.64, 151.36, 177.54 ppm; $^{11}$B NMR (DMSO-$d_6$): $\delta$ = 9.08 ppm; IR (KBr): $\tilde{\nu}$ = 3466, 1625, 1598, 1528, 1510, 1460, 1429, 1361, 1315, 1281, 1233, 1177, 1055, 955 cm$^{-1}$; UV-Vis (MeCN): $\lambda_{\max}$ ($\varepsilon$) = 503 nm (79400 M$^{-1}$ cm$^{-1}$); MS (MALDI-TOF): $m/z$: 509.13 [$M$ + Na]$^+$, 486.14 [$M$]$^+$; elemental analysis calcd (%) for $C_{27}H_{23}BO_8$: C 66.69, H 4.77; found: C 66.66, H 4.67.

## 2. Stability in Solution

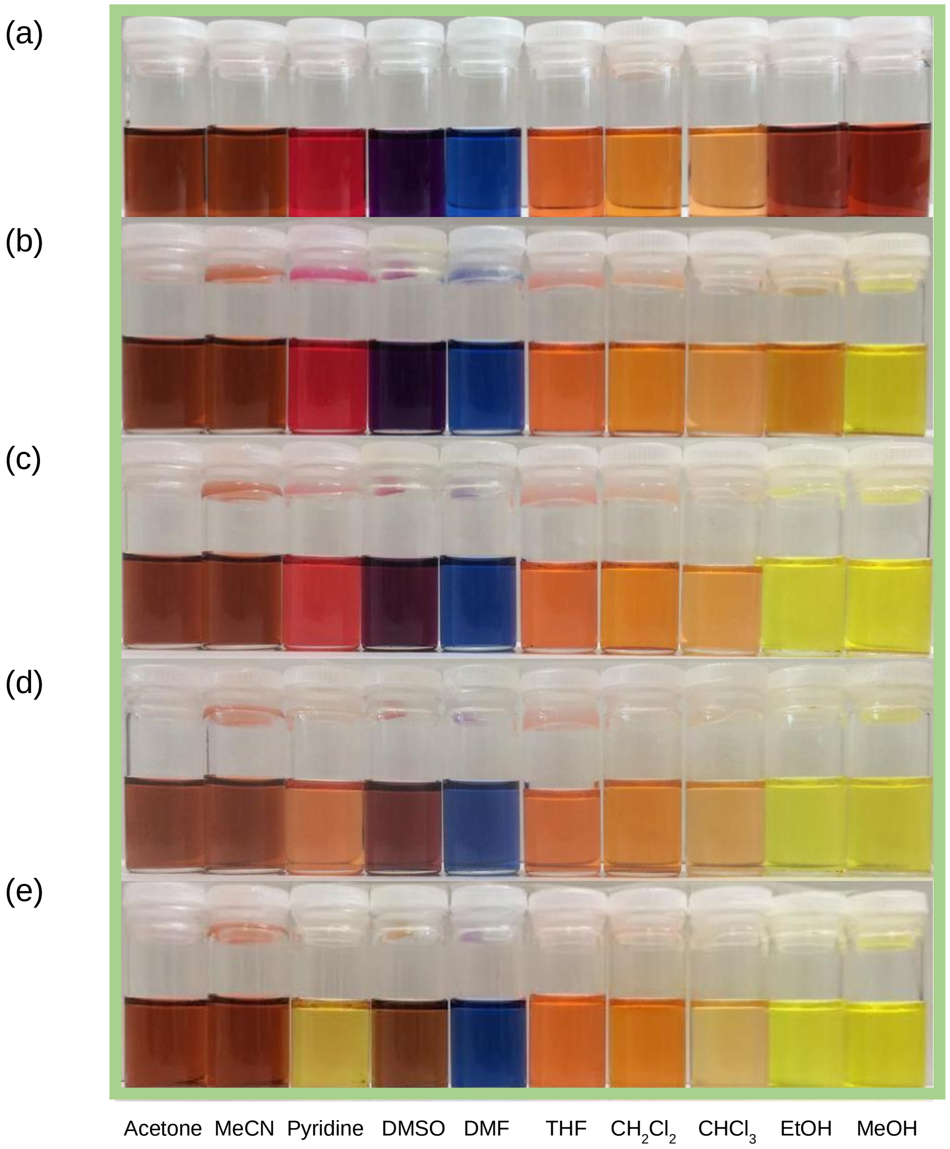


**Fig. S1** Stability of **1** in various solvents: (a) after preparation, (b) after 3 days, (c) after 1 week, (d) after 2 weeks and (e) after 4 weeks.

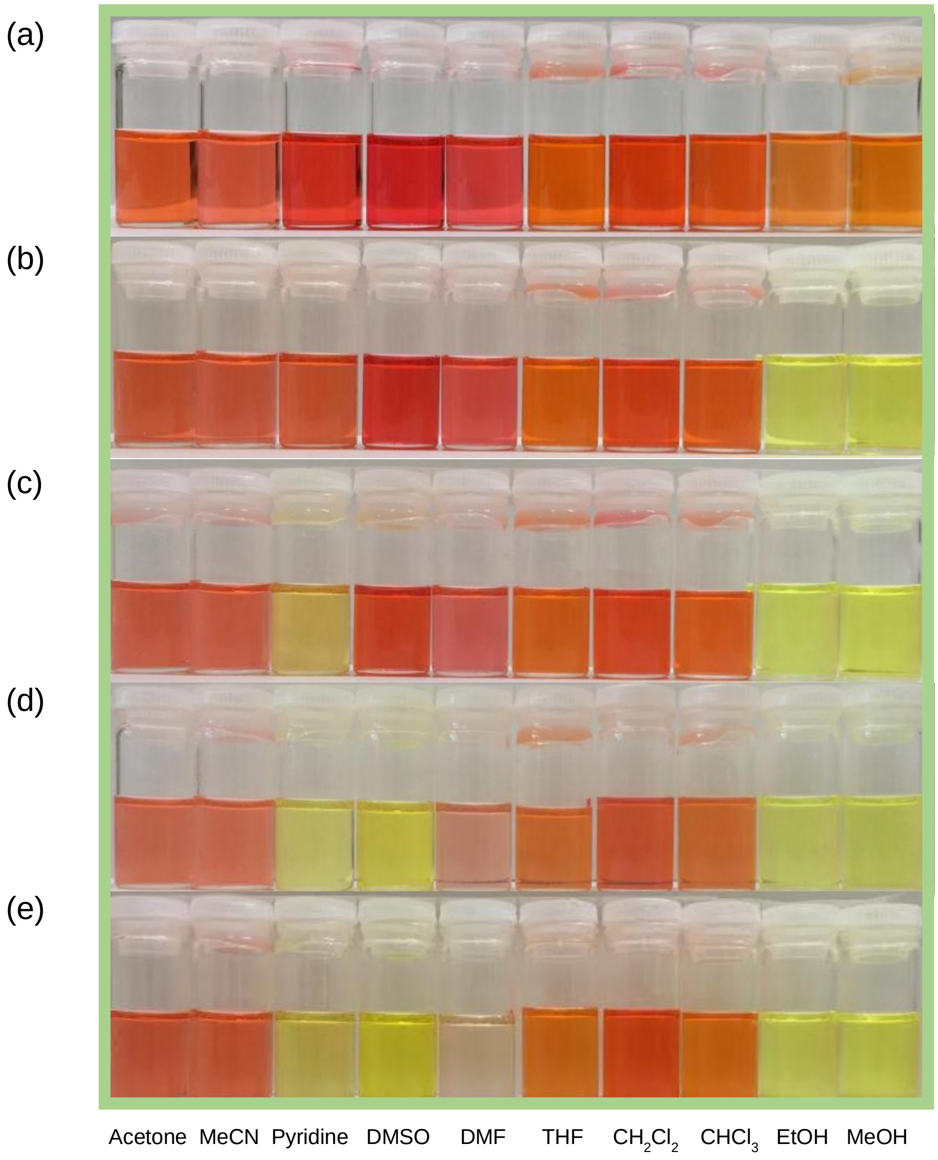


**Fig. S2** Stability of **4** in various solvents: (a) after preparation, (b) after 3 days, (c) after 1 week, (d) after 2 weeks and (e) after 4 weeks.

## 3. Solvatochromism

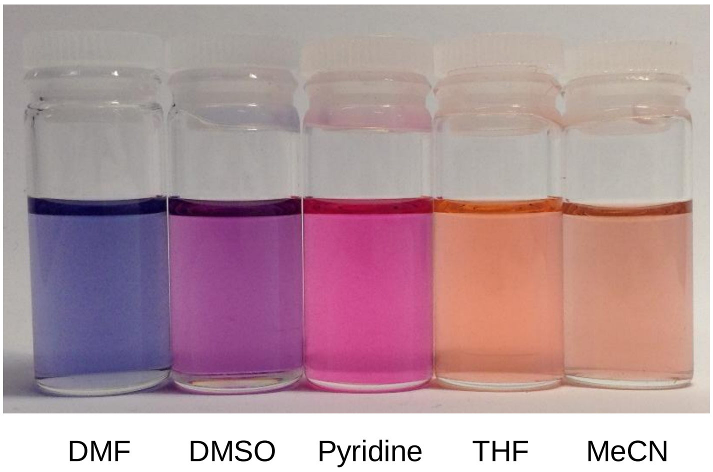


**Fig. S3** Solvatochromism of **1** (conc. 1.0 × $10^{-5}$ M) in various solvents.

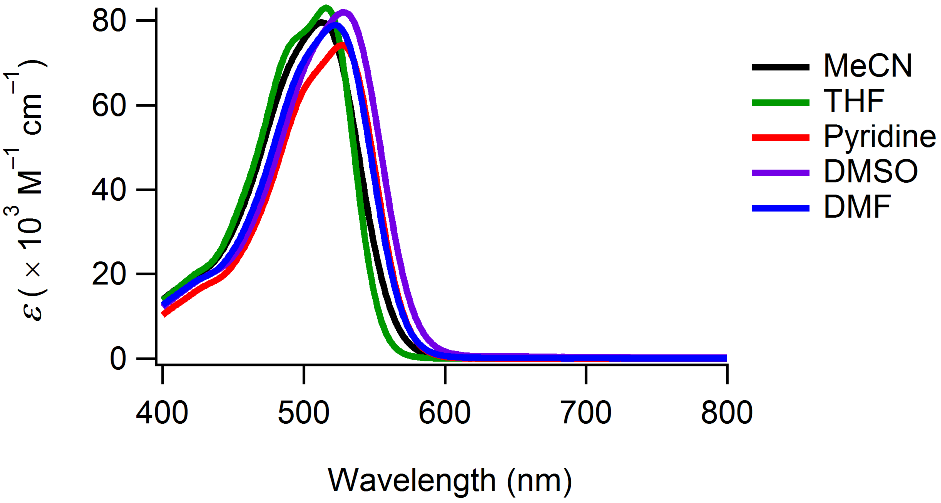


**Fig. S4** UV-Vis absorption spectra of **4** (conc. 1.0 × $10^{-5}$ M) in various solvents.

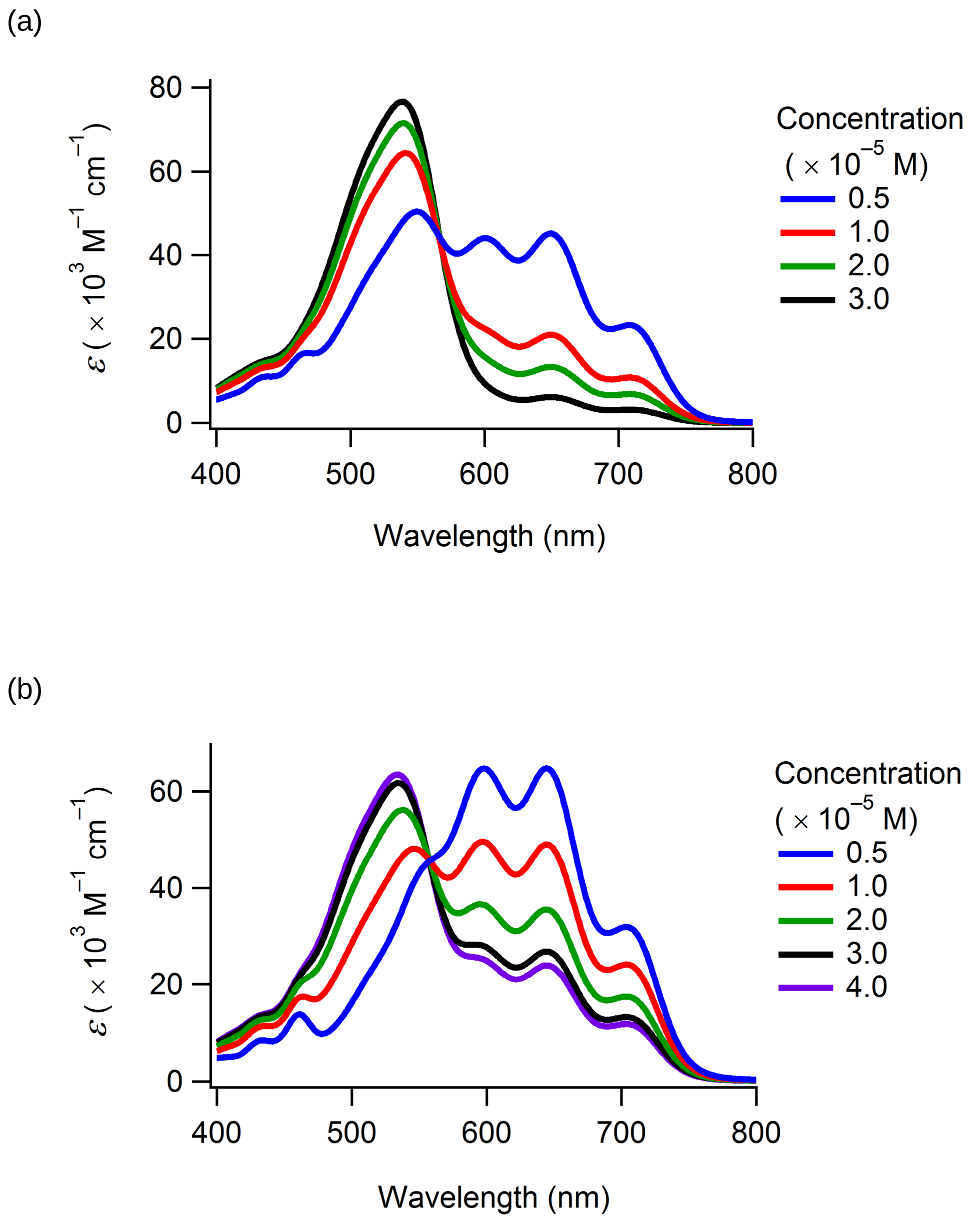


**Fig. S5** UV-Vis absorption spectra of **1** under several concentration conditions (0.5–4.0 × $10^{-5}$ M) in (a) DMSO and (b) DMF.

## 4. Ultrasonic-induced Chromism

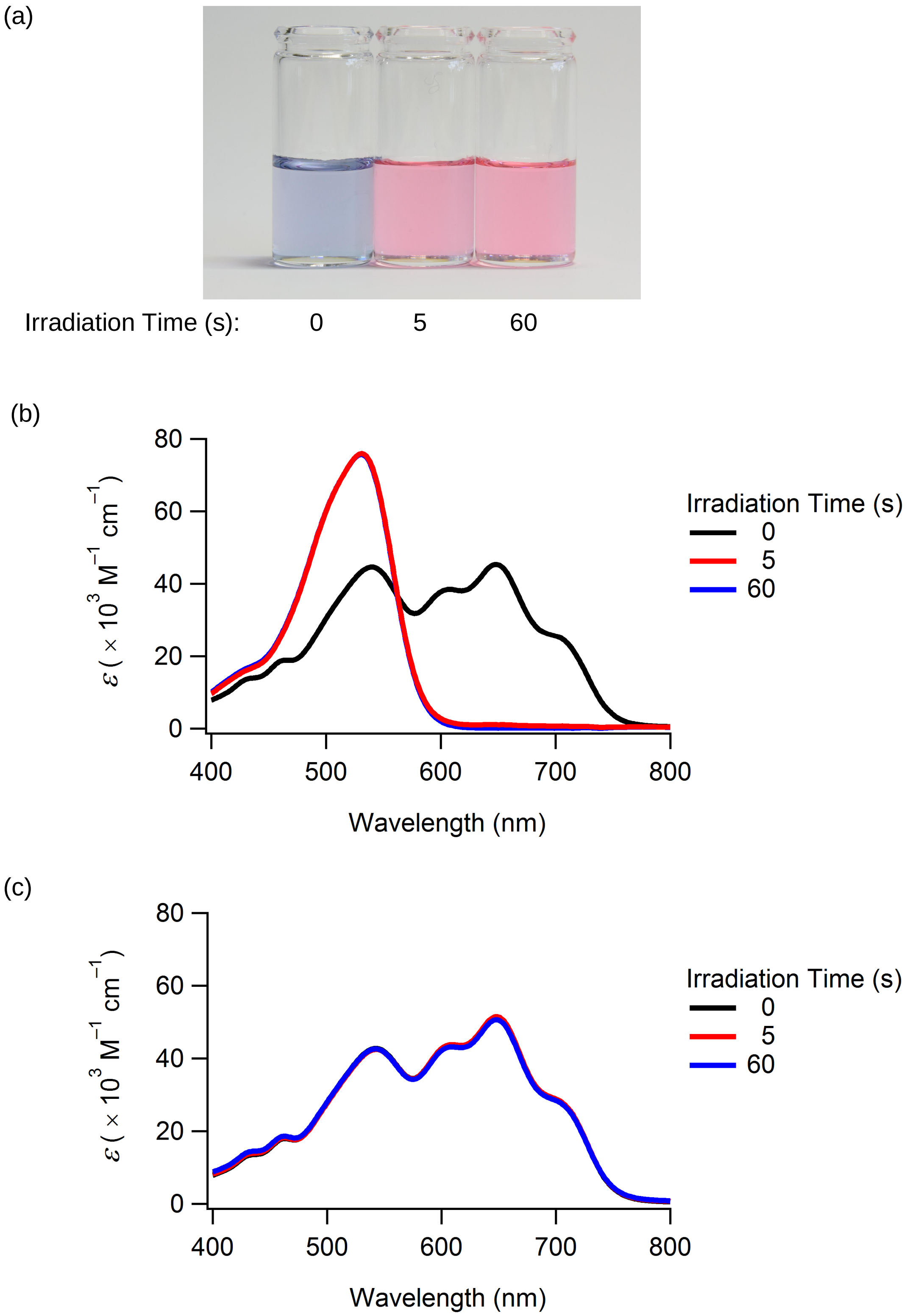


**Fig. S6** Ultrasonic treatment to a solution of **1** (conc. $5.0 \times 10^{-6}$ M) in DMSO containing 10 vol% of water: (a) solution image (see also Movie S1) and (b) time-dependent absorption spectra. Ultrasonic treatment to a buffer solution of **1** at pH = 10: (c) absorption spectra.

## 5. TEA-induced Chromism

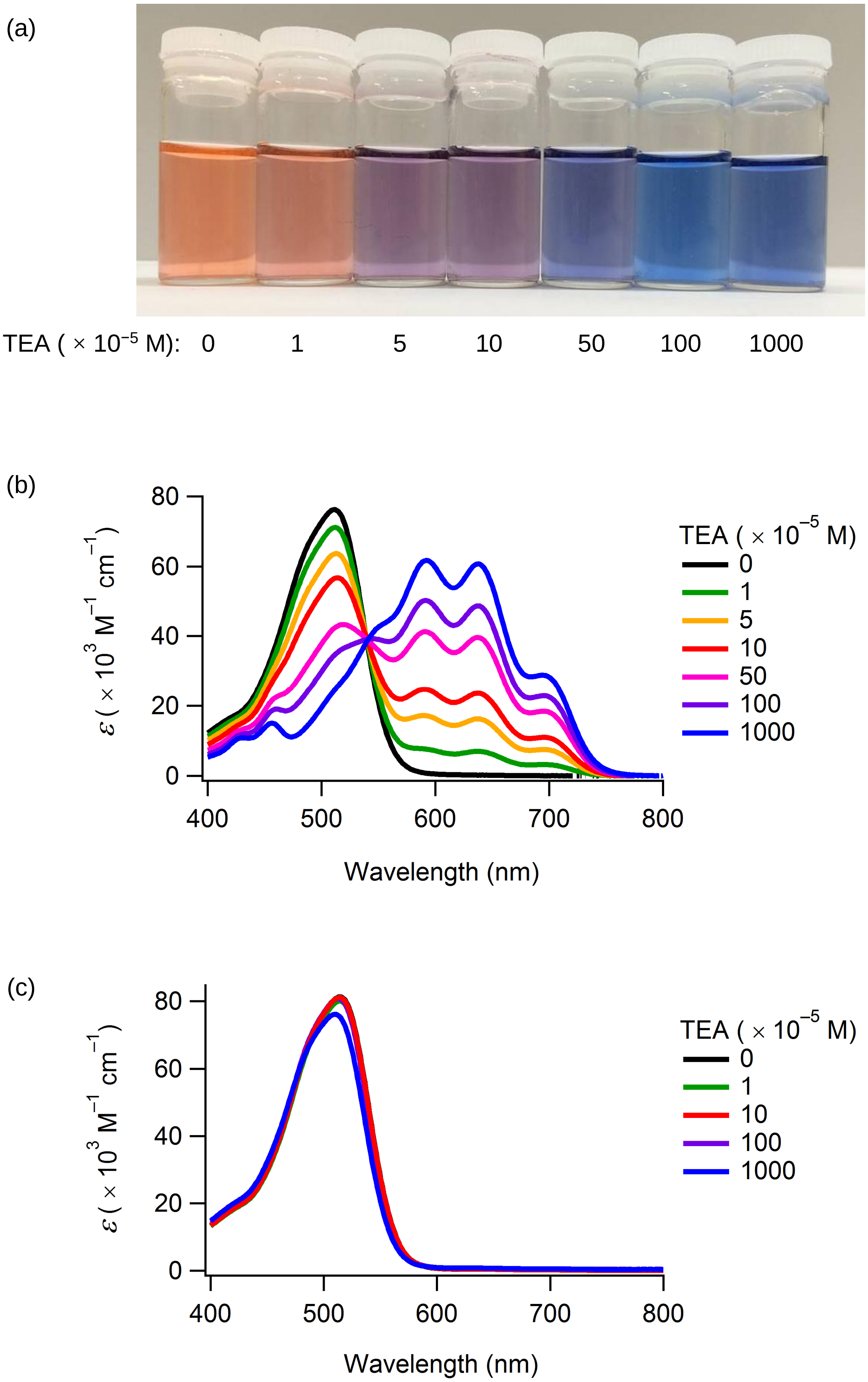
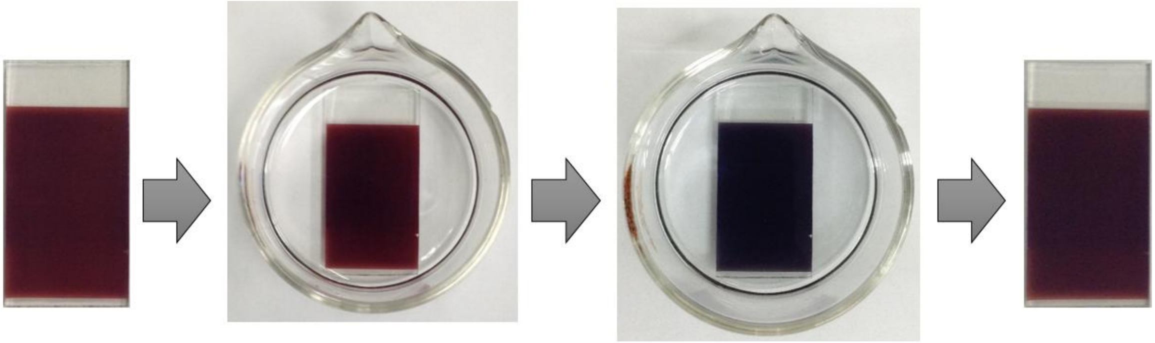


**Fig. S7** TEA-induced chromism in acetonitrile (dye conc. $1.0 \times 10^{-5}$ M): (a) solution image of dye **1** and UV-Vis absorption spectra of (b) dye **3** and (c) dye **4**.



Dye-coated $TiO_2$

In MeCN

In MeCN containing TEA (0.01 M)

In air

**Fig. S8** TEA-induced chromism of **1** on a $TiO_2$ film.

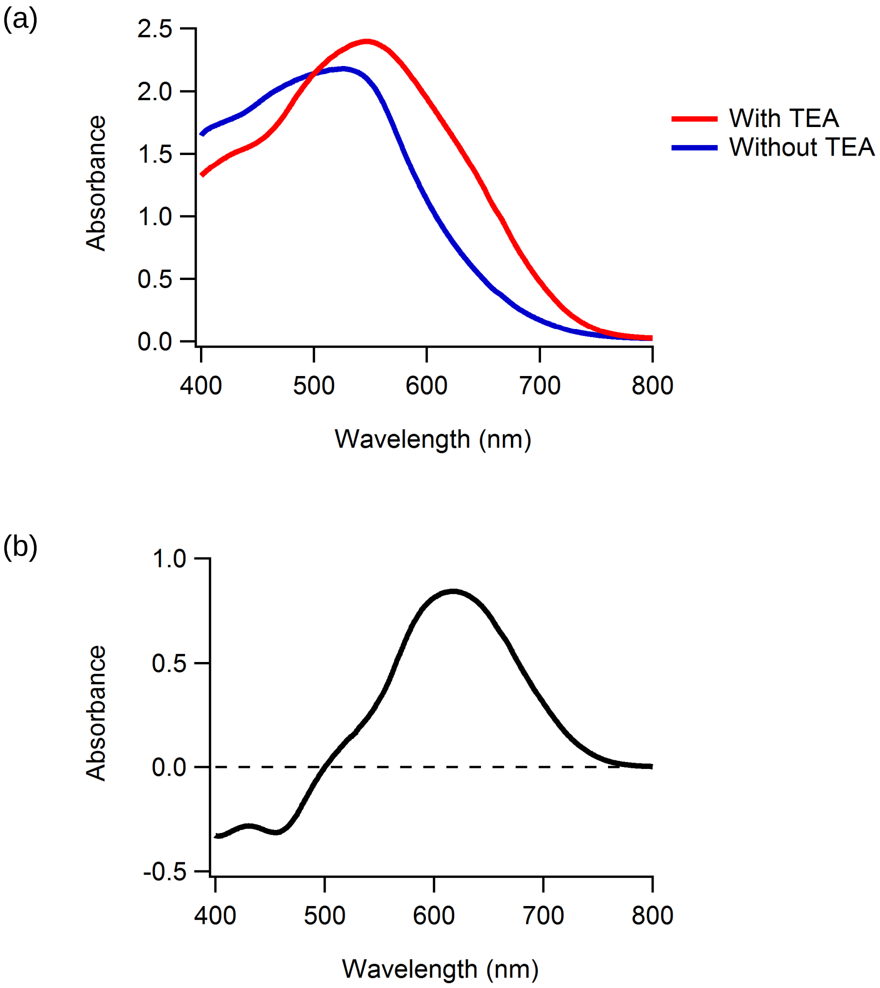


**Fig. S9** UV-Vis absorption spectra of **1** on a $TiO_2$ film by treatment with and without TEA: (a) original spectra and (b) difference spectrum.

## 6. pH-induced Chromism

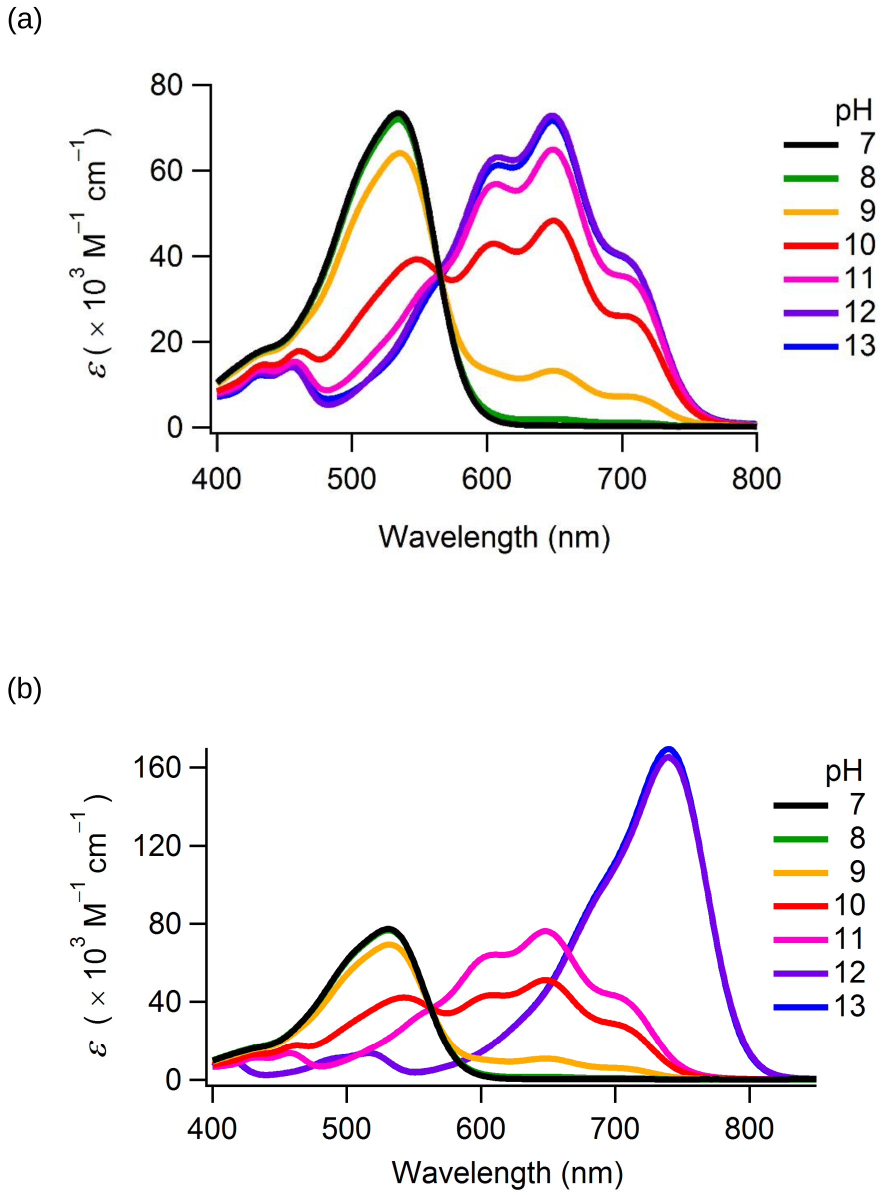


**Fig. S10** UV-Vis absorption spectra of (a) dye **3** and (b) **CB** (conc. 1.0 × $10^{-5}$ M) under several pH conditions (pH = 7–13) in DMSO containing 10 vol% of water.

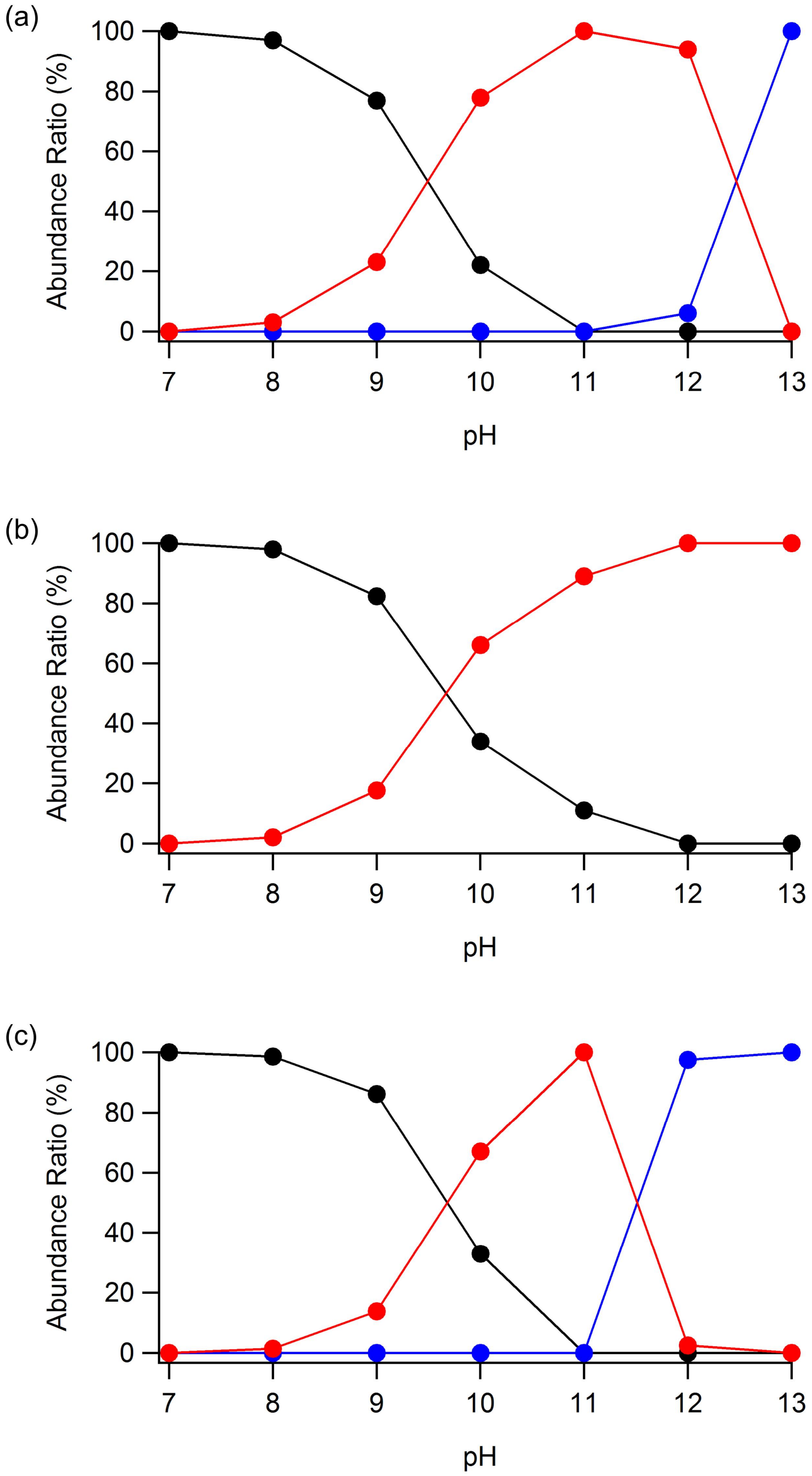


**Fig. S11** Abundance ratios among neutral species (●), phenoxide monoanion (●) and dianion (●) under several pH conditions (pH = 7–13): (a) dye **1** ($\mathrm{p}K_{\mathrm{a1}}$ = 9.5, $\mathrm{p}K_{\mathrm{a2}}$ = 12.5), (b) dye **3** ($\mathrm{p}K_{\mathrm{a}}$ = 9.7) and (c) **CB** ($\mathrm{p}K_{\mathrm{a1}}$ = 9.7, $\mathrm{p}K_{\mathrm{a2}}$ = 11.5).

## 7. Theoretical Calculations

Density functional theory (DFT) calculations were performed on the neutral molecule, monoanion and dianion of **CB** at the B3LYP/6-31G(d) level.3) The UV-Vis absorption spectra of these species in DMSO were simulated by using time-dependent DFT (TDDFT) calculations (Fig. S12).

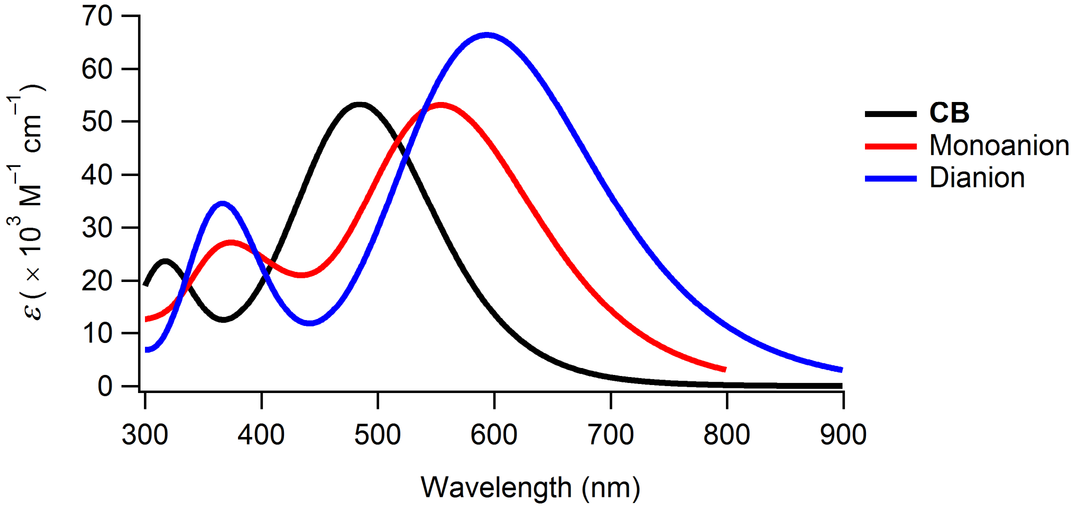


**Fig. S12** UV-Vis absorption spectra of **CB** and its monoanion and dianion species simulated by using TDDFT calculations at the B3LYP/6-31G(d) level.

## 8. Anion-sensing Properties

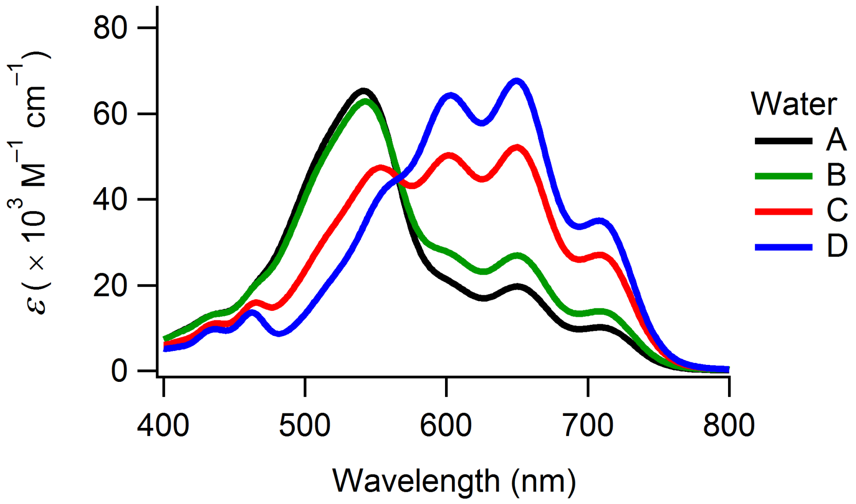


**Fig. S13** UV-Vis absorption spectra of **1** (conc. 1.0 × $10^{-5}$ M) in DMSO containing 0.1 vol% of water (hardness (mg $L^{-1}$), pH): **A** (0, 5.6), **B** (60, 7.6), **C** (300, 7.6) and **D** (1500, 7.4).

**Table S1** Chromism of **CB** solutions[a] upon addition of inorganic salts[b]

| | $Na^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $NH_4^+$ |
|---|---|---|---|---|
| $Cl^-$ | × | × | × | × |
| $SO_4^{2-}$ | ○ | ○ | ○ | ○ |
| $CO_3^{2-}$ | ○ | ○ | ○ | ○ |

[a] Conc. 3.0 × $10^{-5}$ M in DMSO containing 10 vol% of water. [b] Observed (○) and not observed ( × ).

**Table S2** Chromism of **CB** solutions[a] upon addition of sodium salts

| Anion | Formula | p$K_b$ [b] | Colour Change[c] |
|---|---|---|---|
| Hydroxide | $OH^-$ | | ○ |
| Phosphate | $PO_4^{3-}$ | 1.7 | ○ |
| Carbonate | $CO_3^{2-}$ | 3.7 | ○ |
| Hydrogenphosphate | $HPO_4^{2-}$ | 6.8 | ○ |
| Hydrogencarbonate | $HCO_3^-$ | 7.6 | ○ |
| Acetate | $CH_3CO_2^-$ | 9.2 | ○ |
| Fluoride | $F^-$ | 10.8 | ○ |
| Dihydrogenphosphate | $H_2PO_4^-$ | 11.9 | × |
| Sulfate | $SO_4^{2-}$ | 12.0 | ○ |
| Tetrafluoroborate | $BF_4^-$ | 13.5 | × |
| Nitrate | $NO_3^-$ | 15.4 | × |
| Perchlorate | $ClO_4^-$ | 15.6 | × |
| Chloride | $Cl^-$ | 20.2 | × |
| Hydrogensulfate | $HSO_4^-$ | | × |

[a] Conc. $3.0 \times 10^{-5}$ M in DMSO containing 10 vol% of water. [b] Values in water (25 °C), Ref. 4. [c] Observed (○) and not observed ( × ).

## 9. Photovoltaic Fabrication

Titanium oxide ($TiO_2$) paste (Sumitomo Osaka Cement Co., Ltd.) was printed onto a F-doped $SnO_2$ (FTO) glass (Nippon Sheet Glass Co., Japan) by using a screen-printing method. The resulting film was composed of a transparent layer 11 μm thick and a scattering layer 6 μm thick (area: 0.25 $cm^2$). The film was sintered at 525 °C for 1 h and was cooled to 120 °C and then room temperature. The films were coated with dyes **1–4** by dipping in dye acetonic solutions (0.2 mM) at 25 °C for 22 h in the dark. Each FTO-supported dye-coated $TiO_2$ film was incorporated into a thin-layer sandwich-type cell comprising a platinum counter-electrode, a polypropylene film spacer (thickness: 60 μm) and an organic electrolyte solution. The electrolyte solution consisted of 0.60 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.05 M iodine ($I_2$) and 0.10 M lithium iodide (LiI) solutions in acetonitrile. A Wacom WXS-80C-2 solar simulator was used to give an irradiation of 100 mW $cm^{-2}$ at the surface of solar cells (AM 1.5 solar light). Current density–voltage characteristics were measured by using an Advantest R6243 source meter. Photocurrent density for incident photo-to-current conversion efficiency (IPCE) spectra was measured with an Eko Seiki SPM-005B equipped with halogen and xenon lamps.

## 10. Electrochemical Potentials

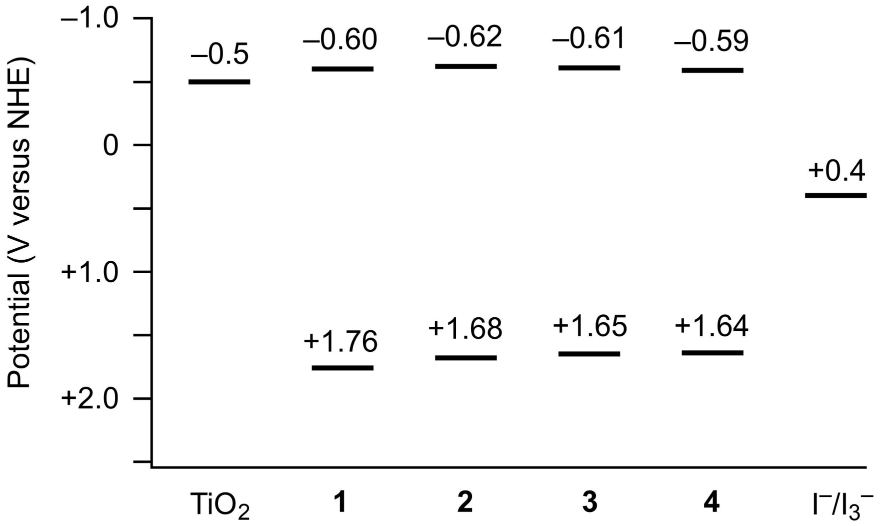


**Fig. S14** Electrochemical potential diagram of dyes **1–4** in volts versus NHE: oxidation potentials of ground states versus iodine redox potential and oxidation potentials of excited states versus the $TiO_2$ conduction band.

## 11. Copy of Spectra

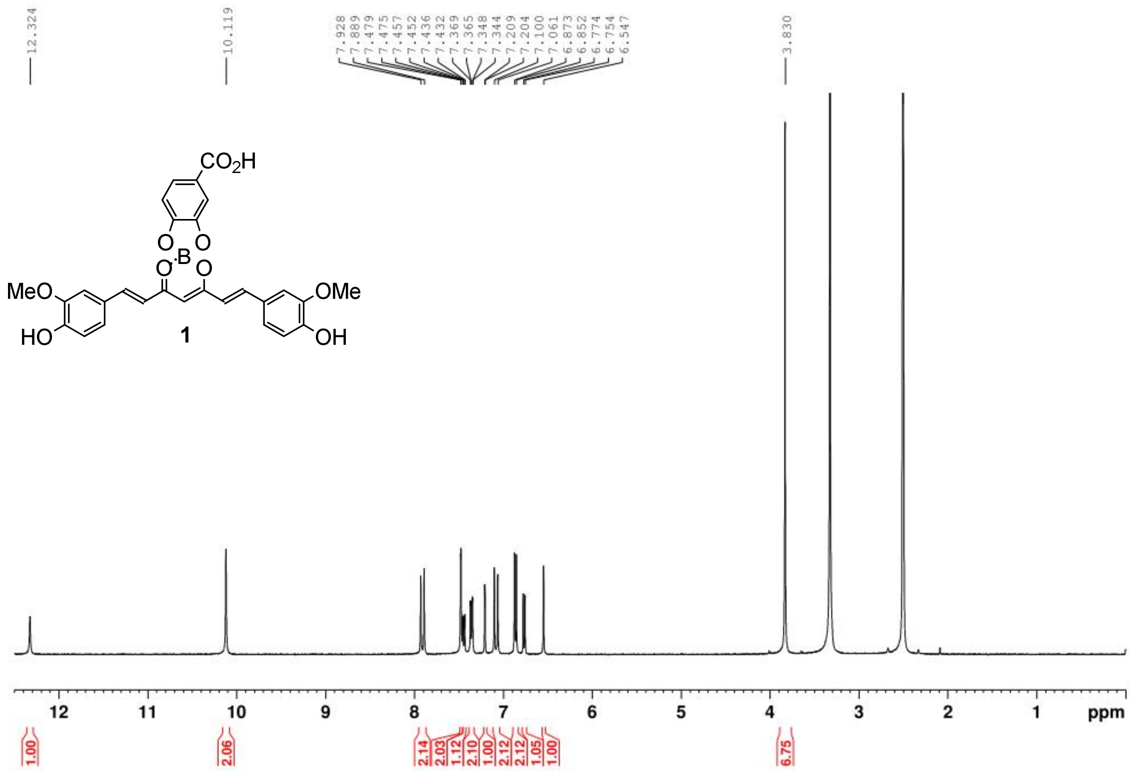


**Fig. S15** $^1$H NMR spectrum of **1** in DMSO-$d_6$.

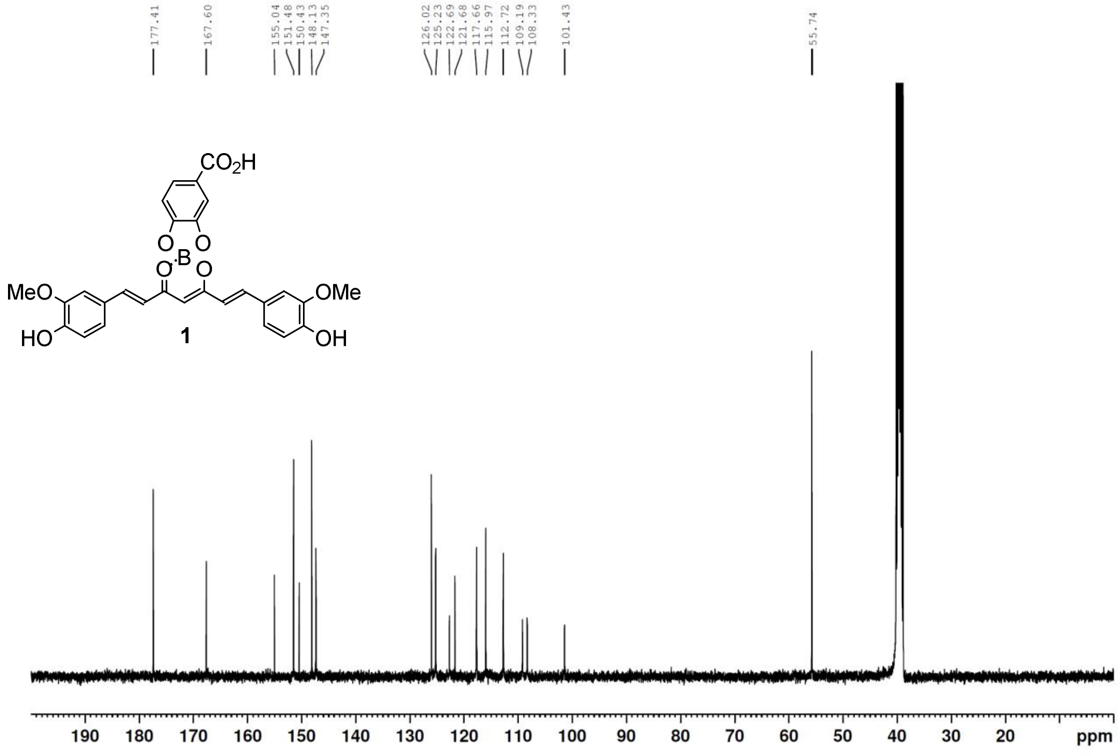


**Fig. S16** $^{13}$C NMR spectrum of **1** in DMSO-$d_6$.

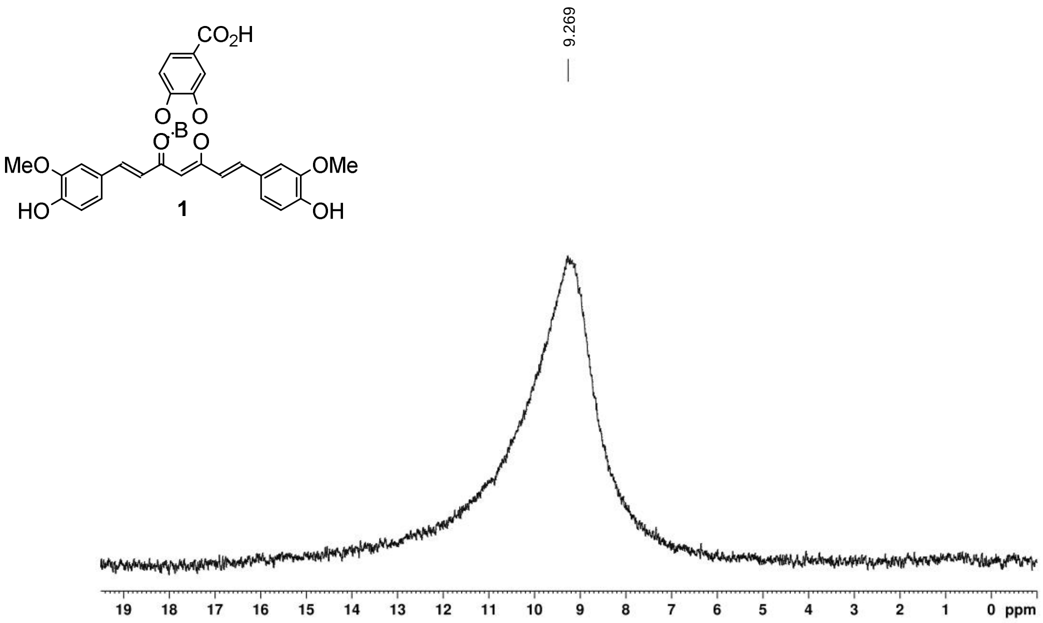


**Fig. S17** $^{11}$B NMR spectrum of **1** in DMSO-$d_6$.

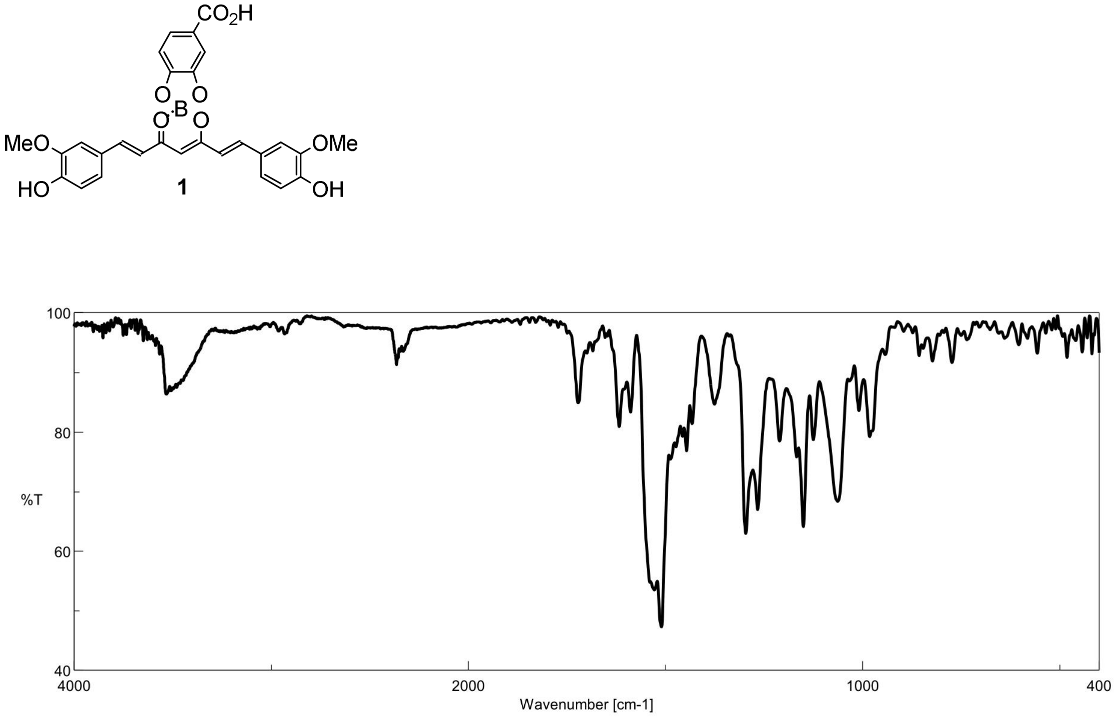


**Fig. S18** IR spectrum of **1**.

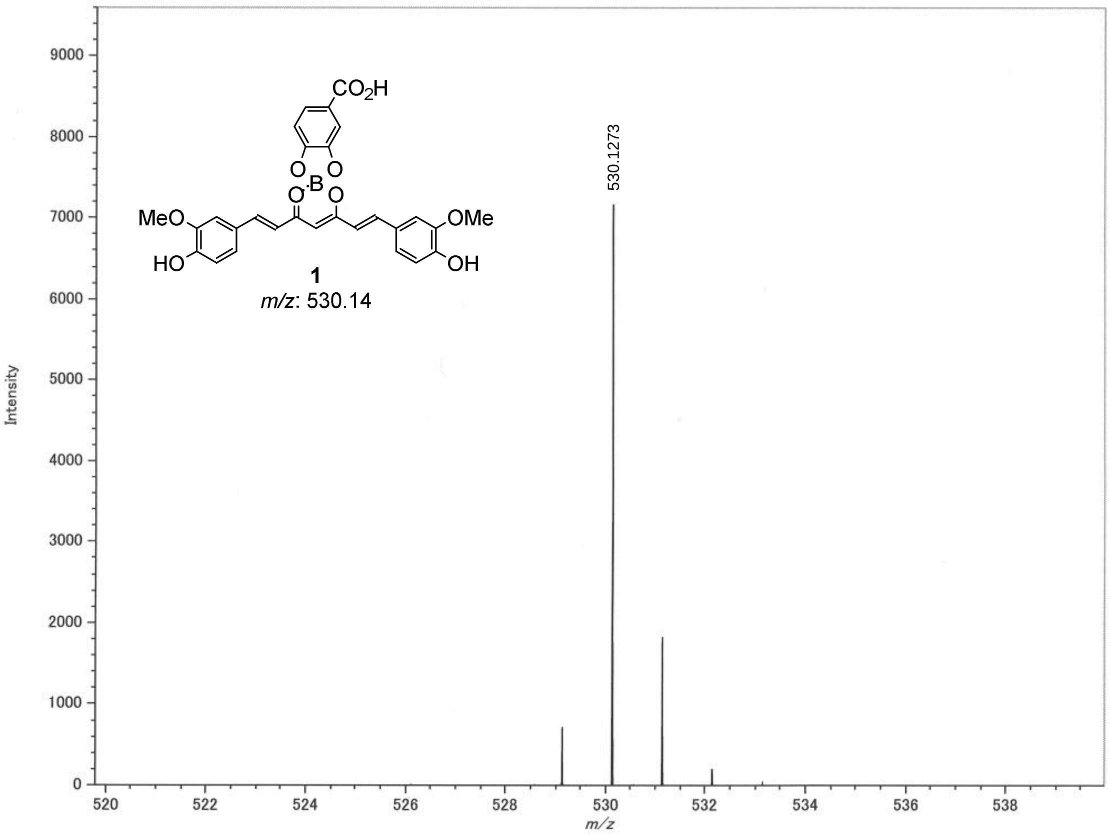


**Fig. S19** MALDI-TOF MS spectrum of **1**.

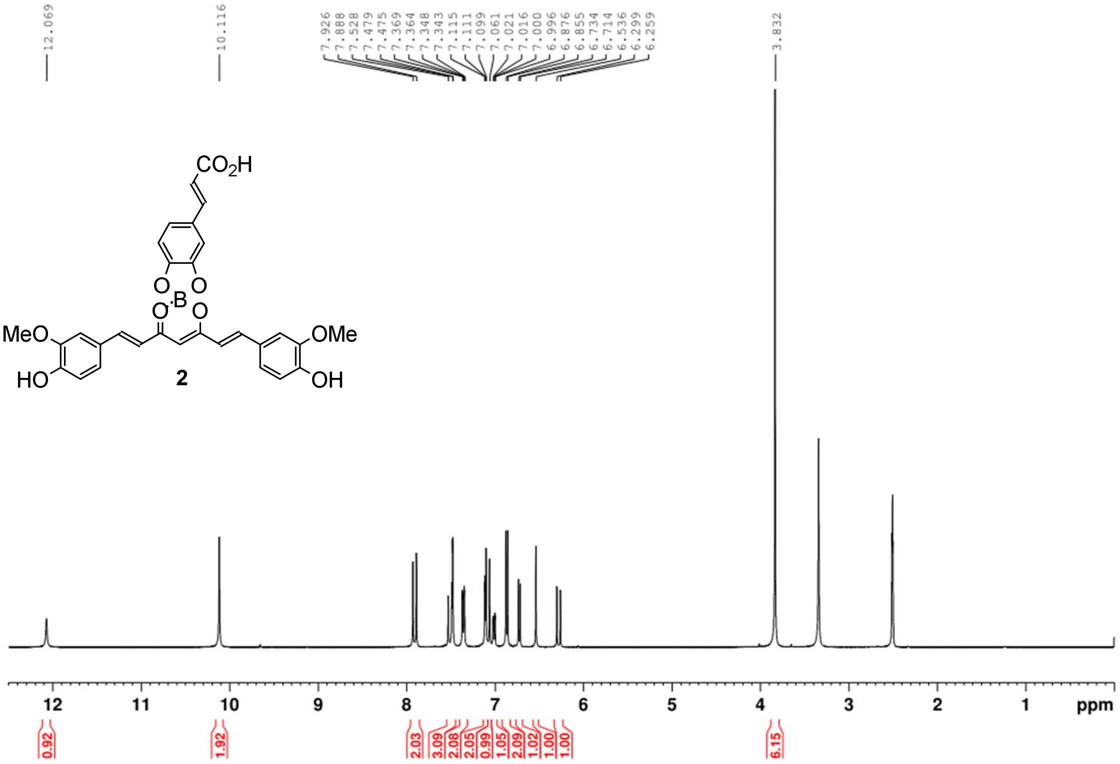


**Fig. S20** $^1$H NMR spectrum of **2** in DMSO-$d_6$.

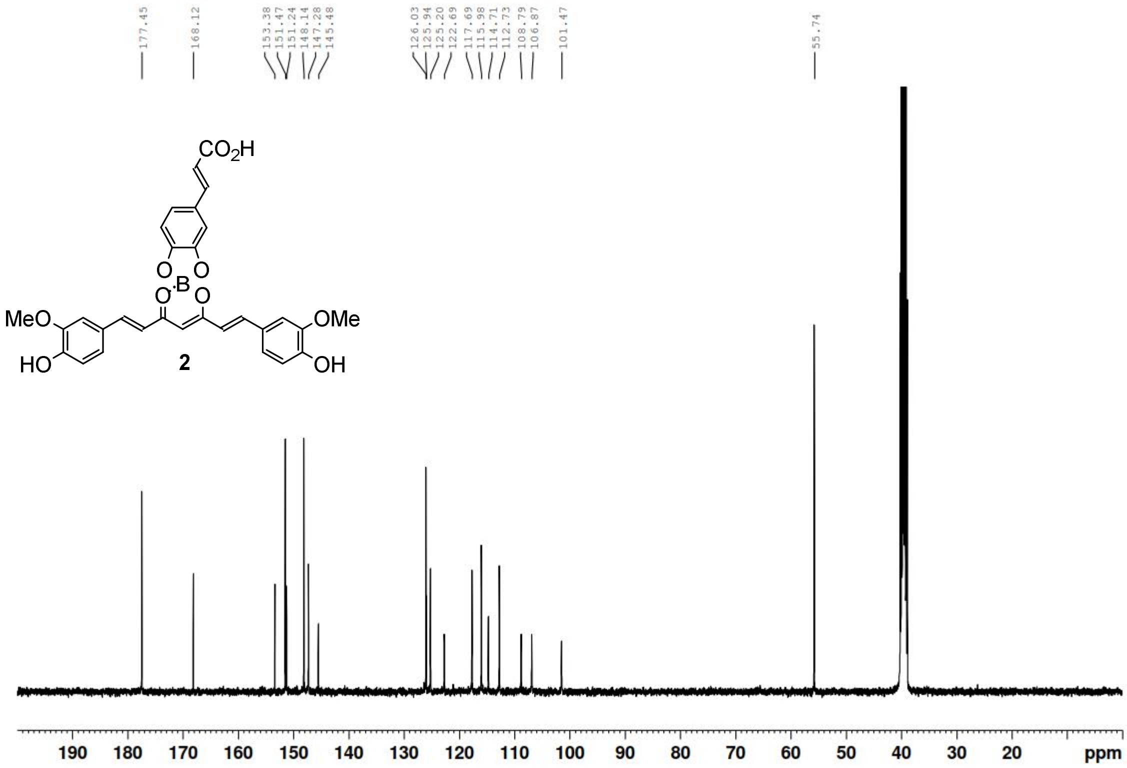


**Fig. S21** $^{13}$C NMR spectrum of **2** in DMSO-$d_6$.

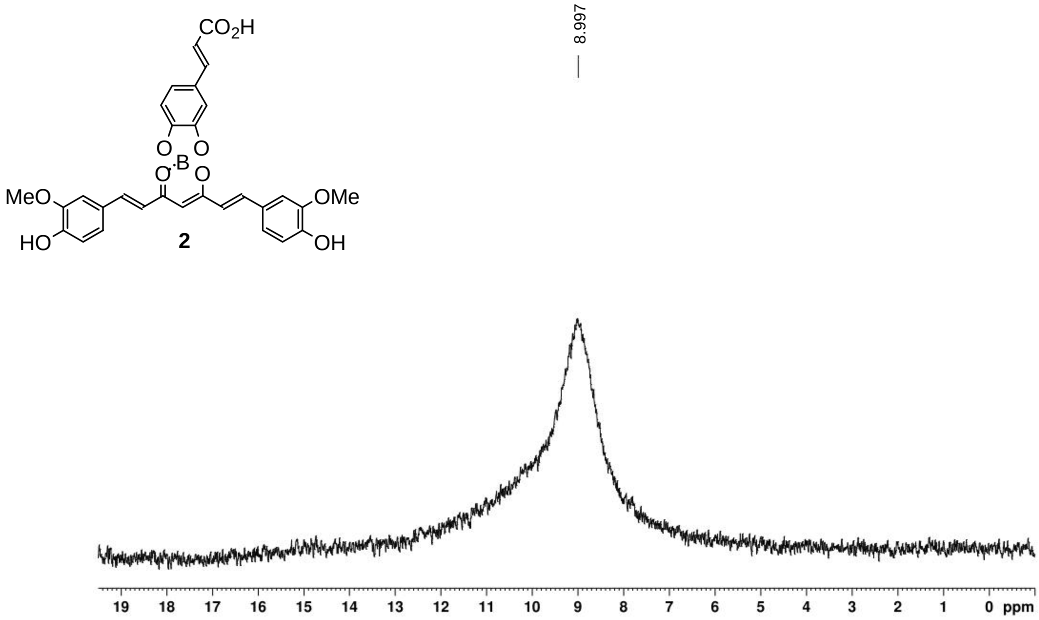


**Fig. S22** $^{11}$B NMR spectrum of **2** in DMSO-$d_6$.

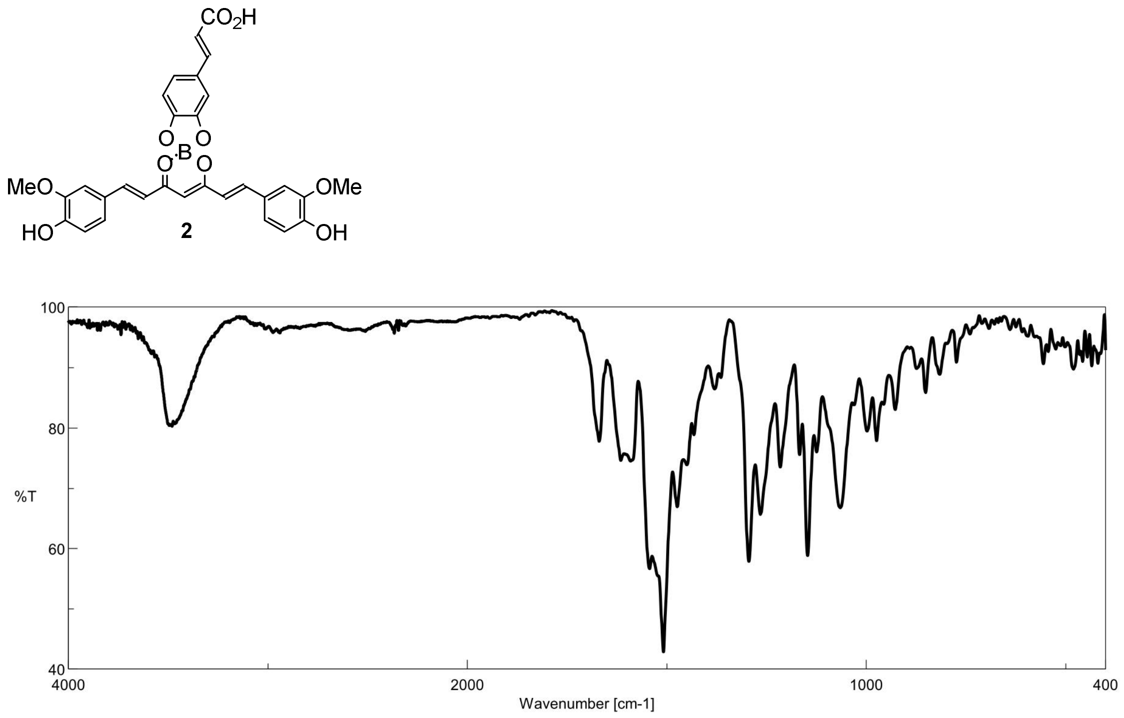


**Fig. S23** IR spectrum of **2**.

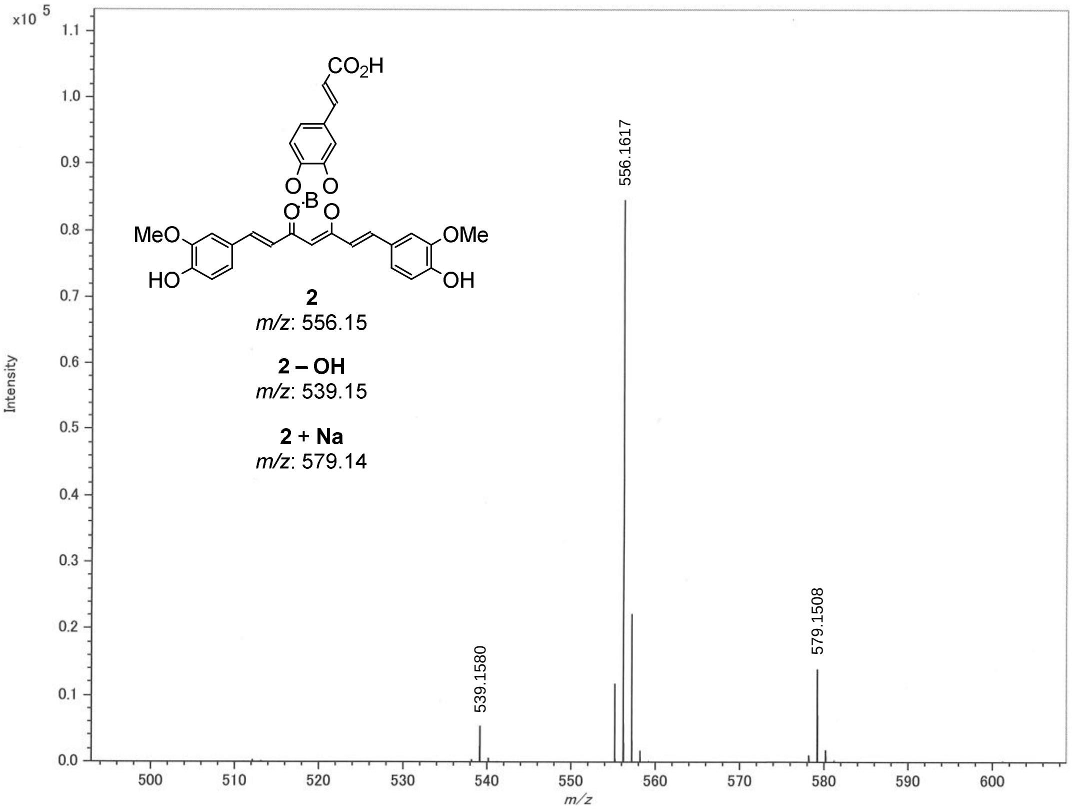


**Fig. S24** MALDI-TOF MS spectrum of **2**.

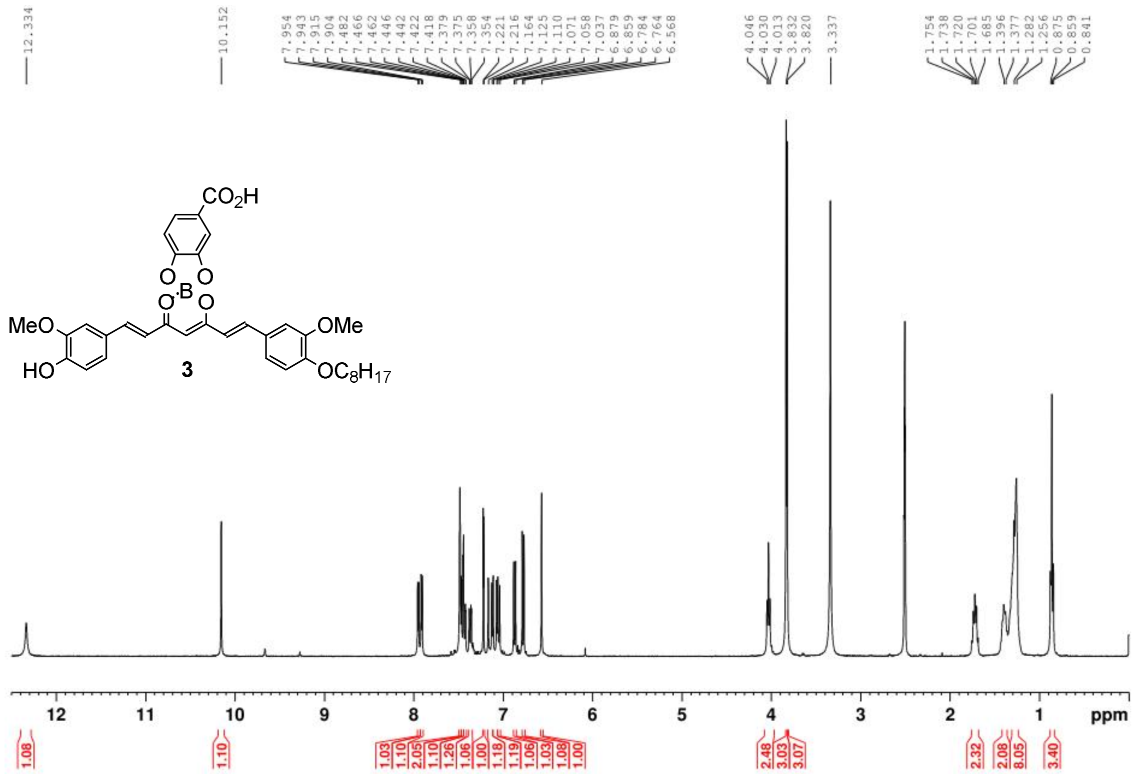


**Fig. S25** $^1$H NMR spectrum of **3** in DMSO-$d_6$.

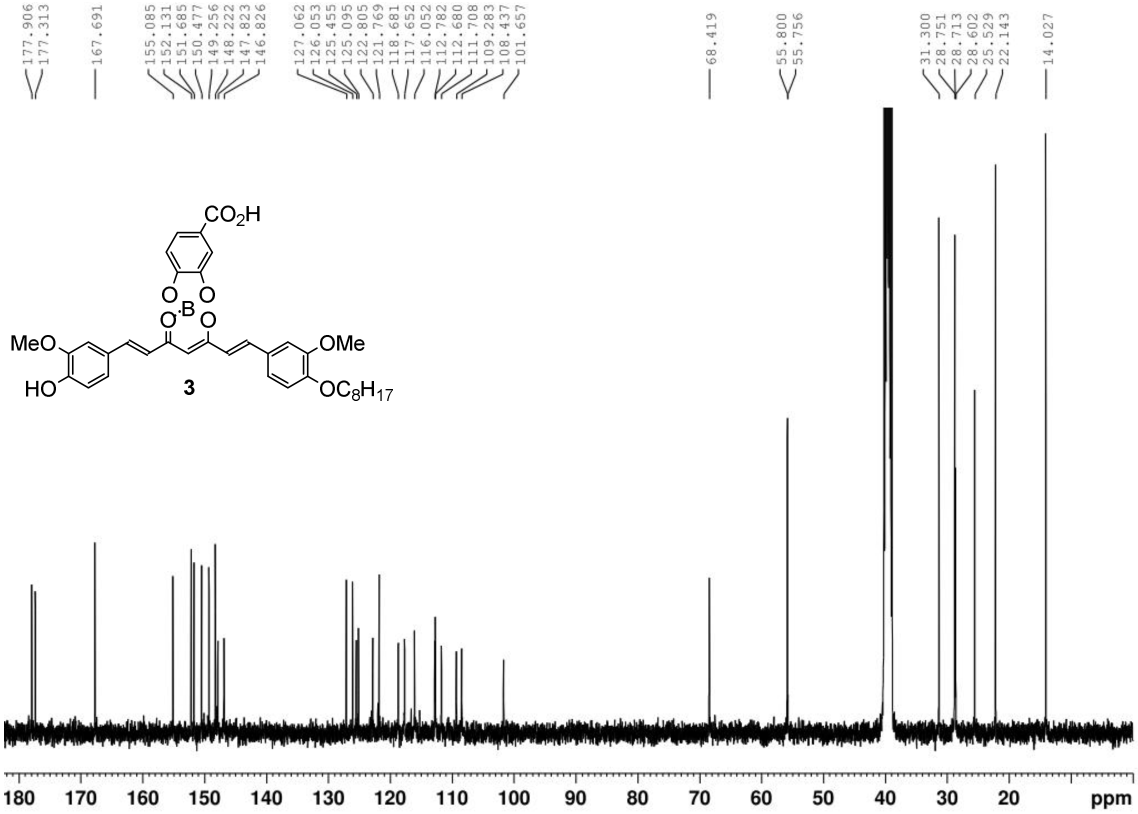


**Fig. S26** $^{13}$C NMR spectrum of **3** in DMSO-$d_6$.

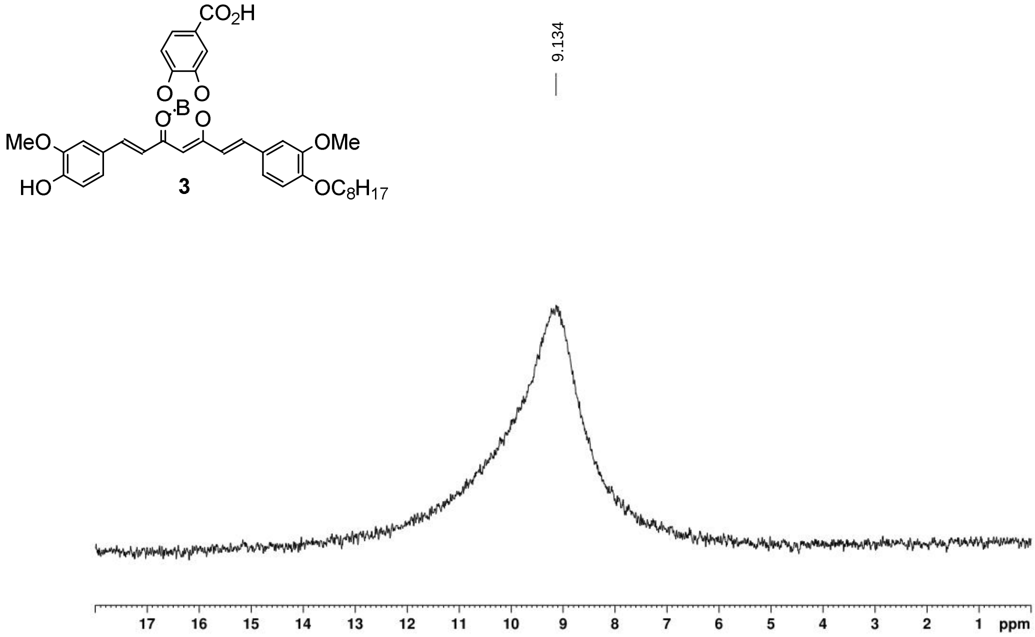


**Fig. S27** $^{11}$B NMR spectrum of **3** in DMSO-$d_6$.

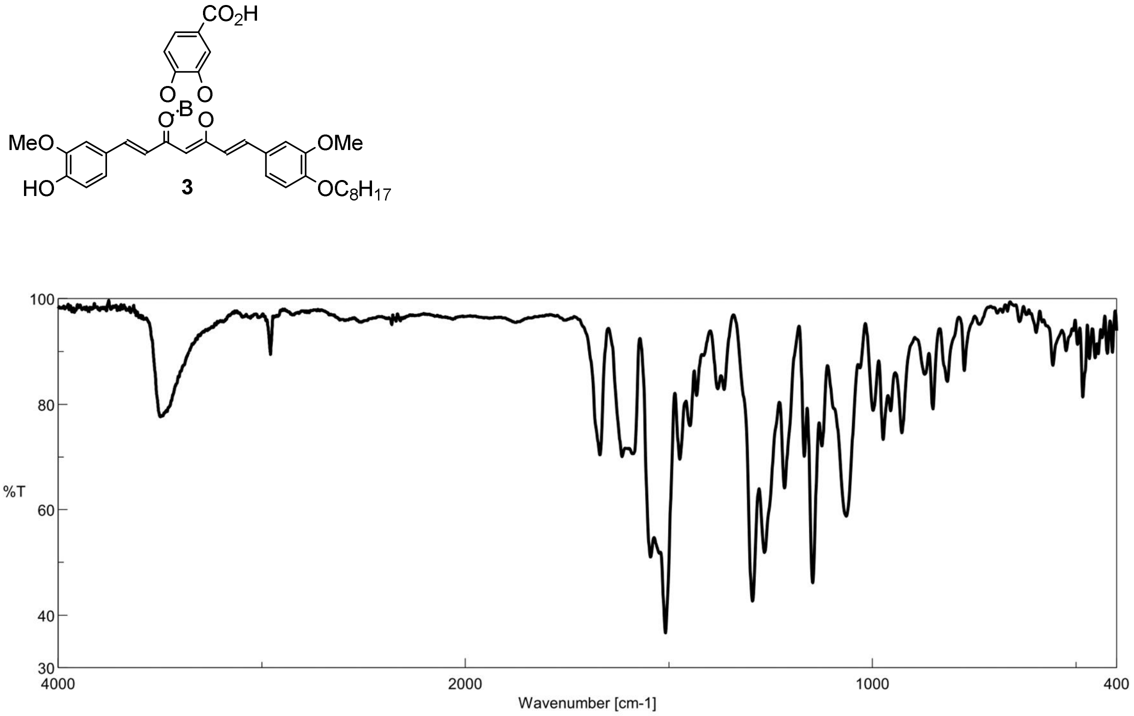


**Fig. S28** IR spectrum of **3**.

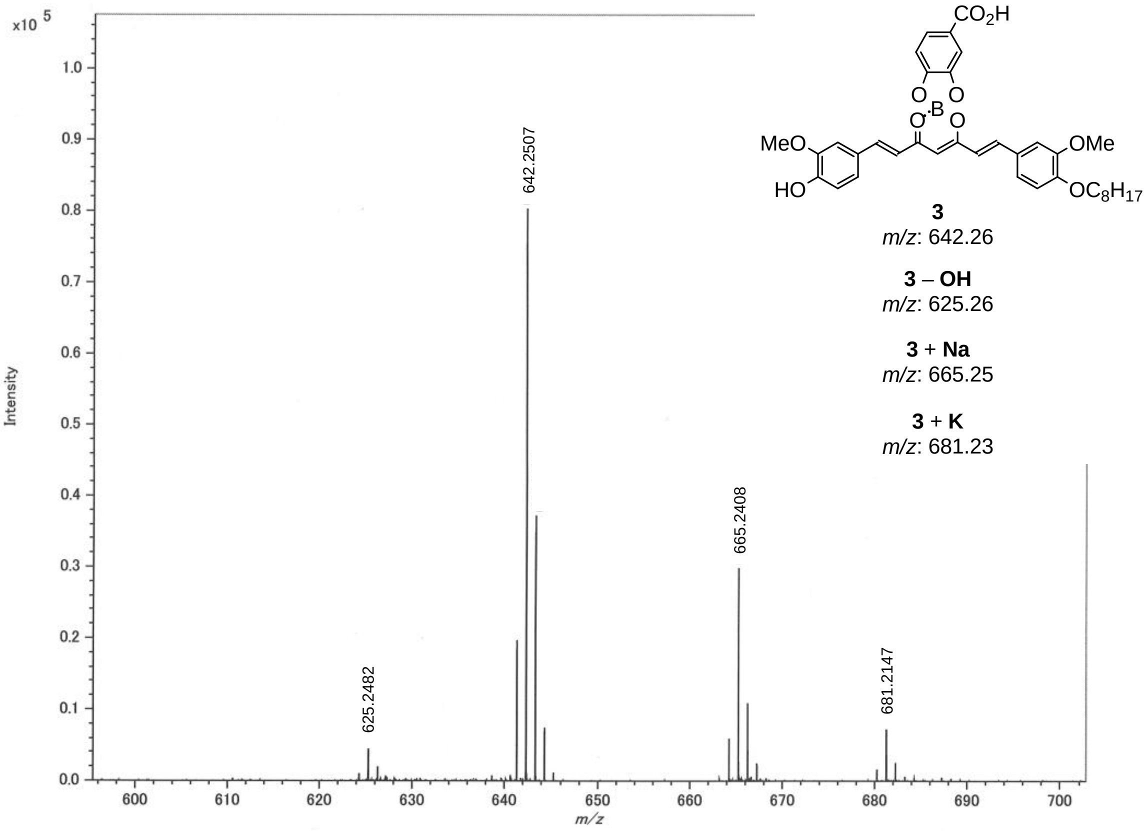


**Fig. S29** MALDI-TOF MS spectrum of **3**.

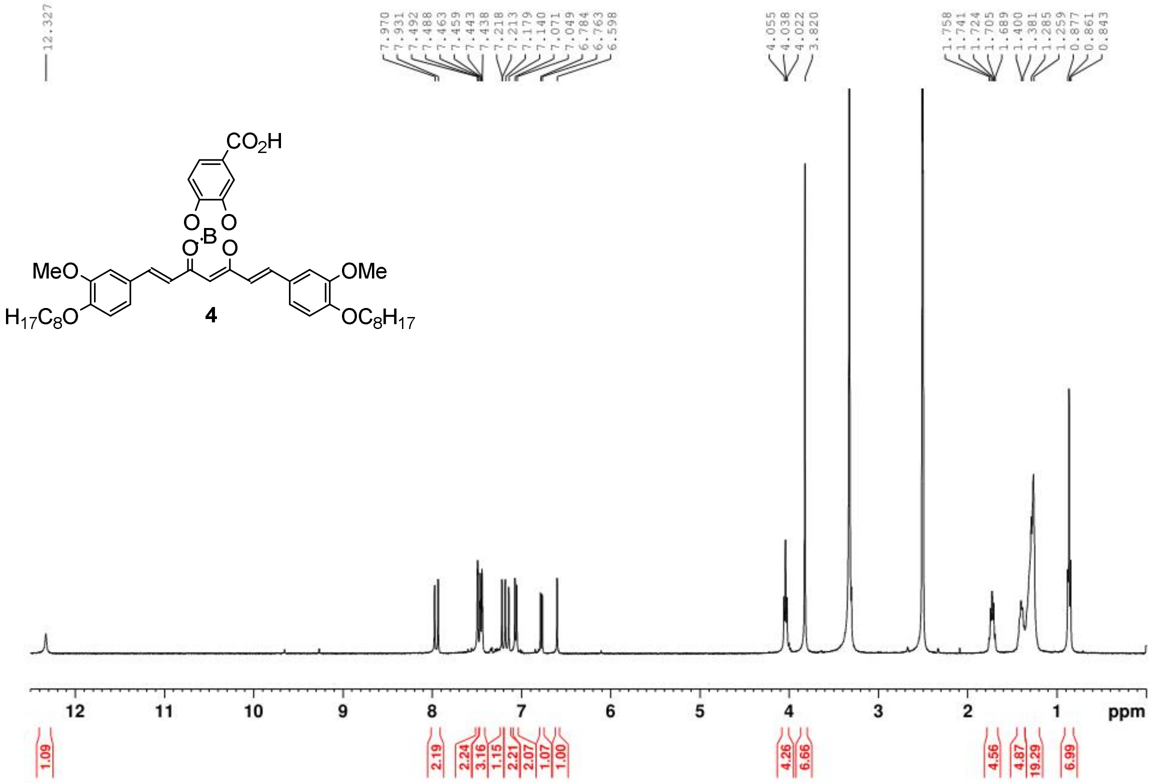


**Fig. S30** $^1$H NMR spectrum of **4** in DMSO-$d_6$.

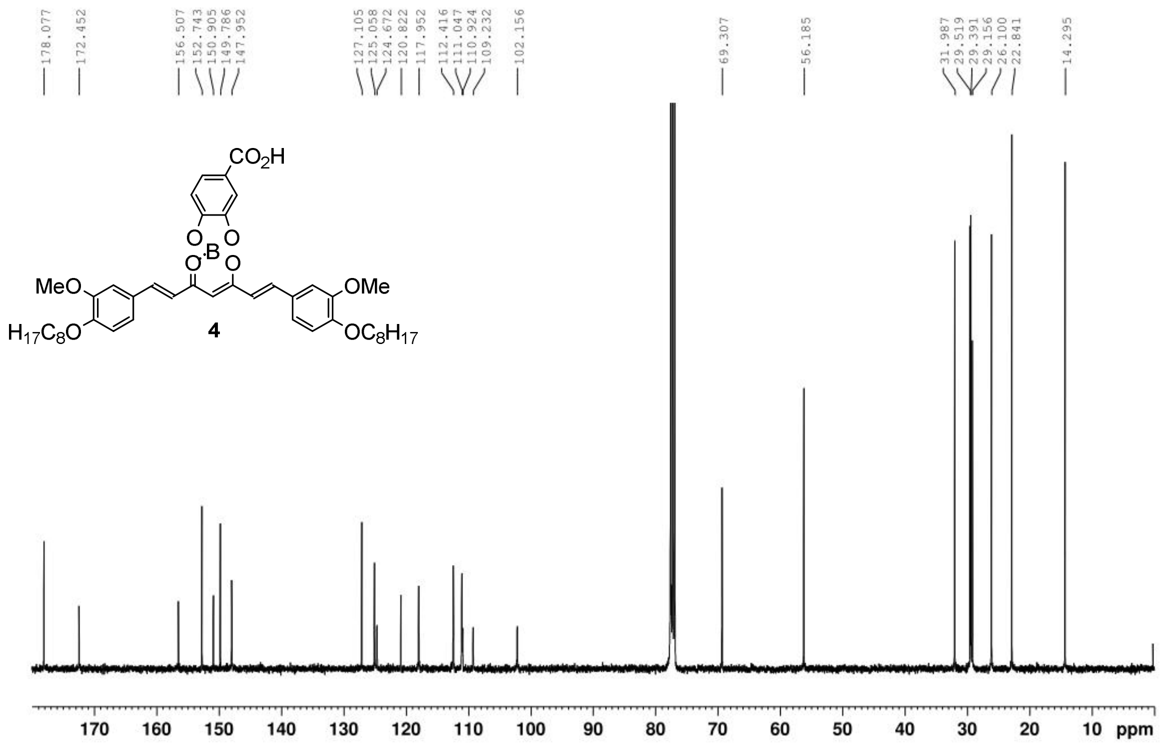


**Fig. S31** $^{13}$C NMR spectrum of **4** in $CDCl_3$.

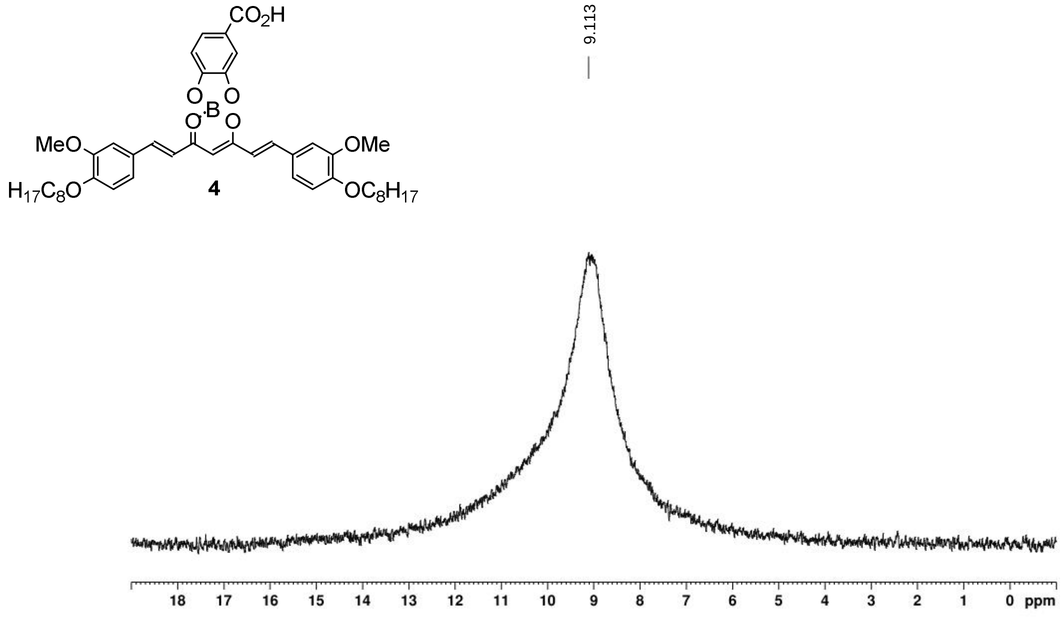


**Fig. S32** $^{11}$B NMR spectrum of **4** in DMSO-$d_6$.

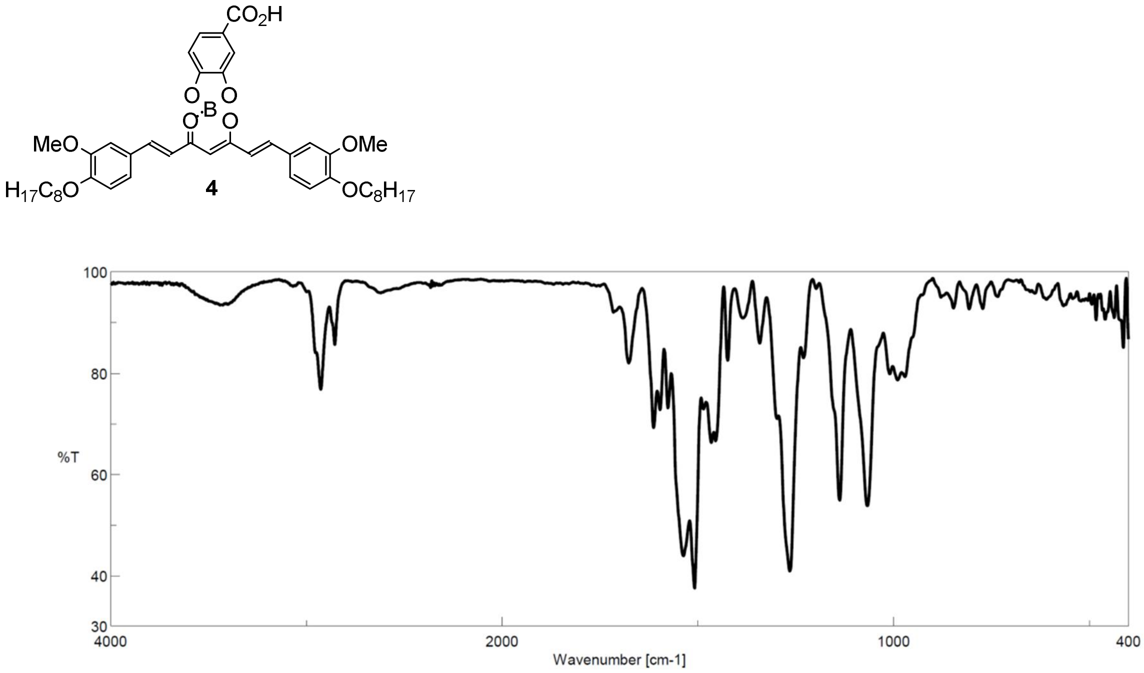


**Fig. S33** IR spectrum of **4**.

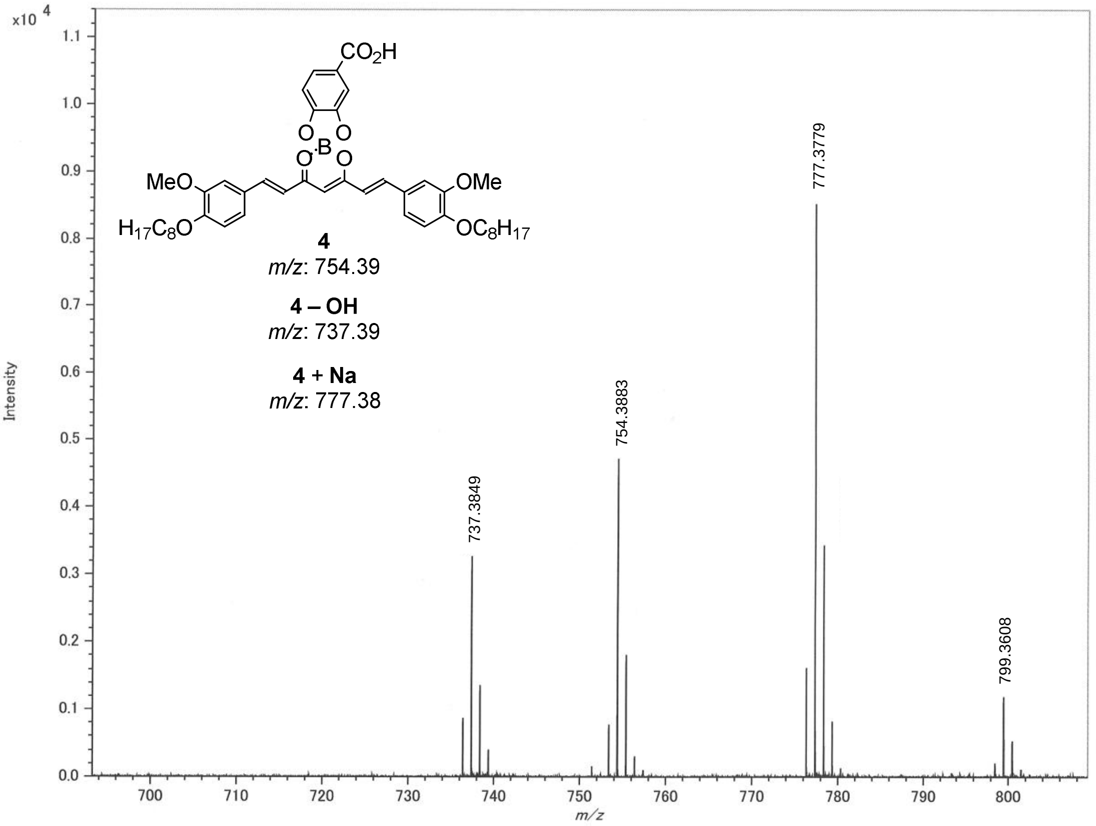


**Fig. S34** MALDI-TOF MS spectrum of **4**.

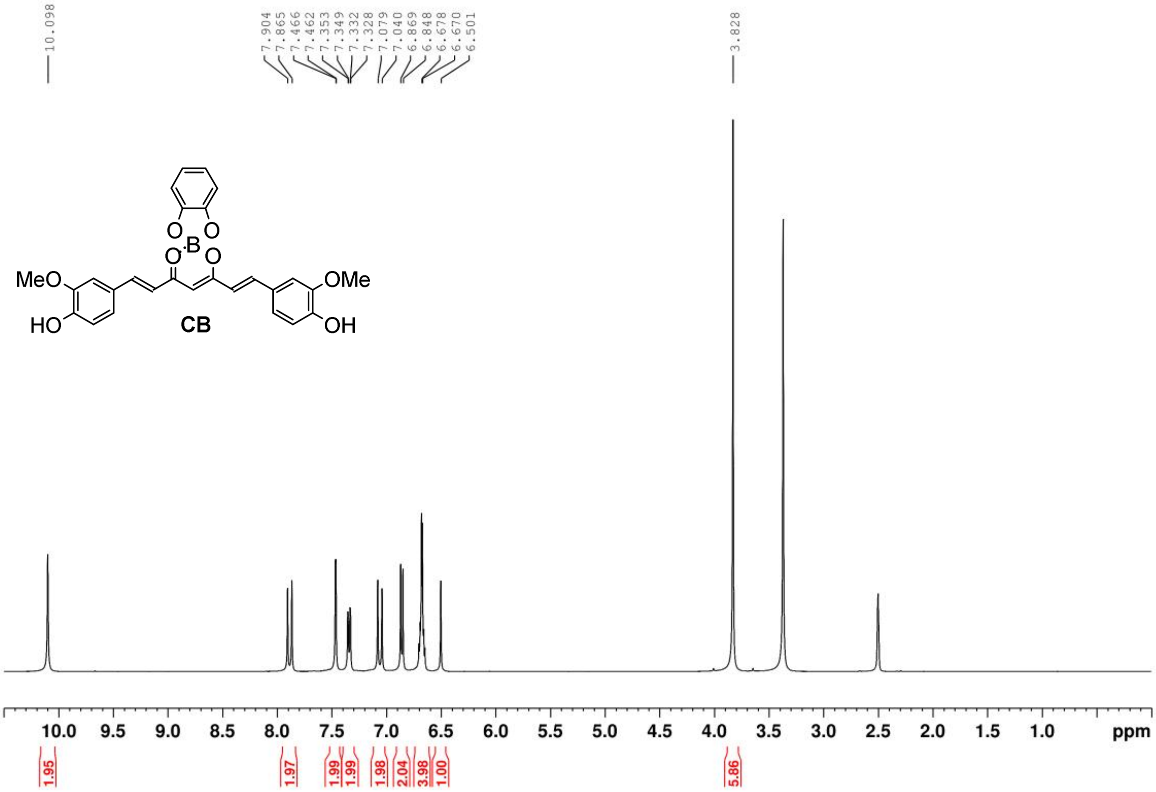


**Fig. S35** ${}^{1}$H NMR spectrum of **CB** in DMSO-$d_6$.

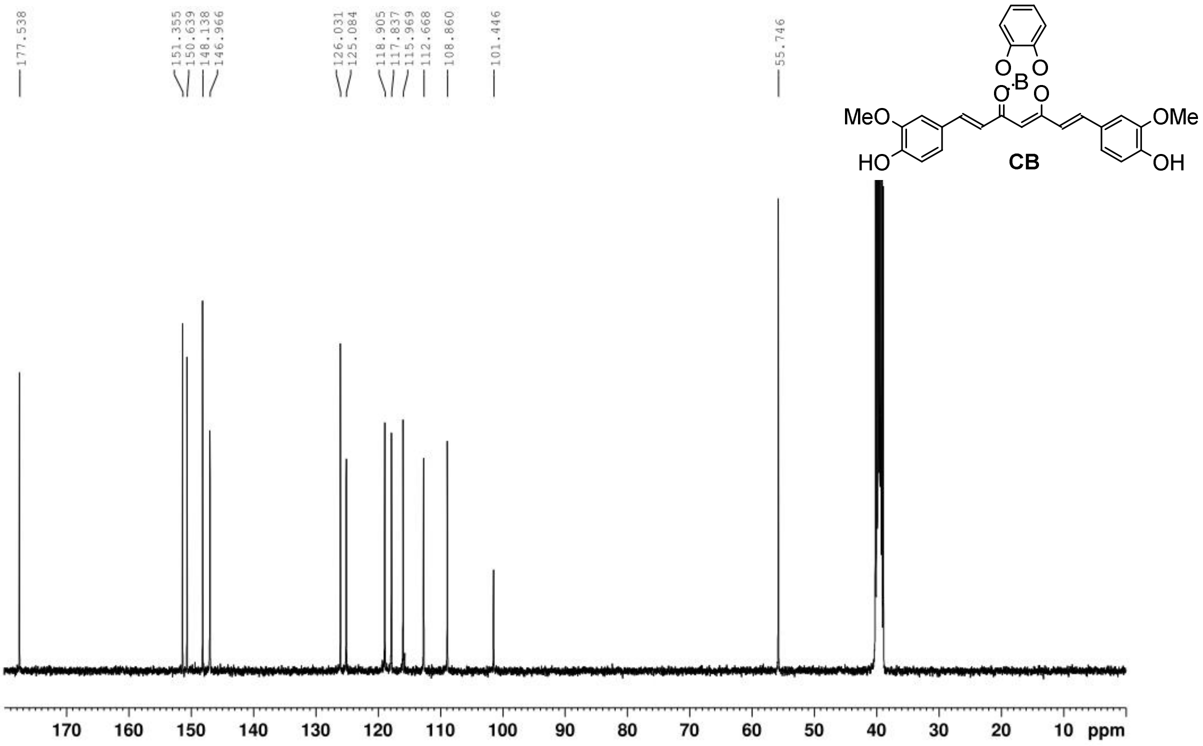


**Fig. S36** ${}^{13}$C NMR spectrum of **CB** in DMSO-$d_6$.

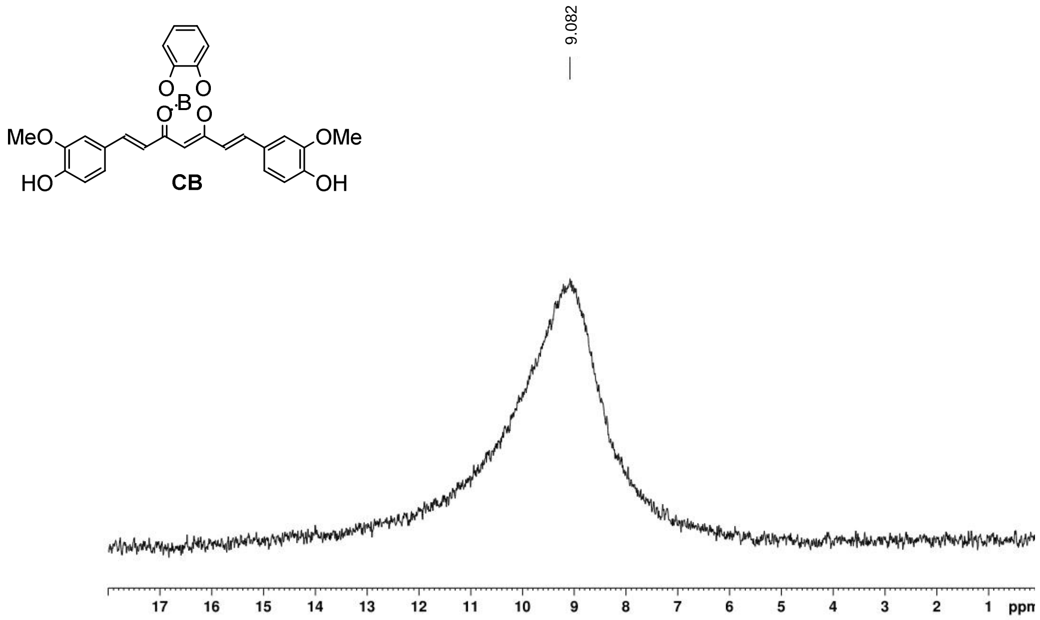


**Fig. S37** $^{11}$B NMR spectrum of **CB** in DMSO-$d_6$.

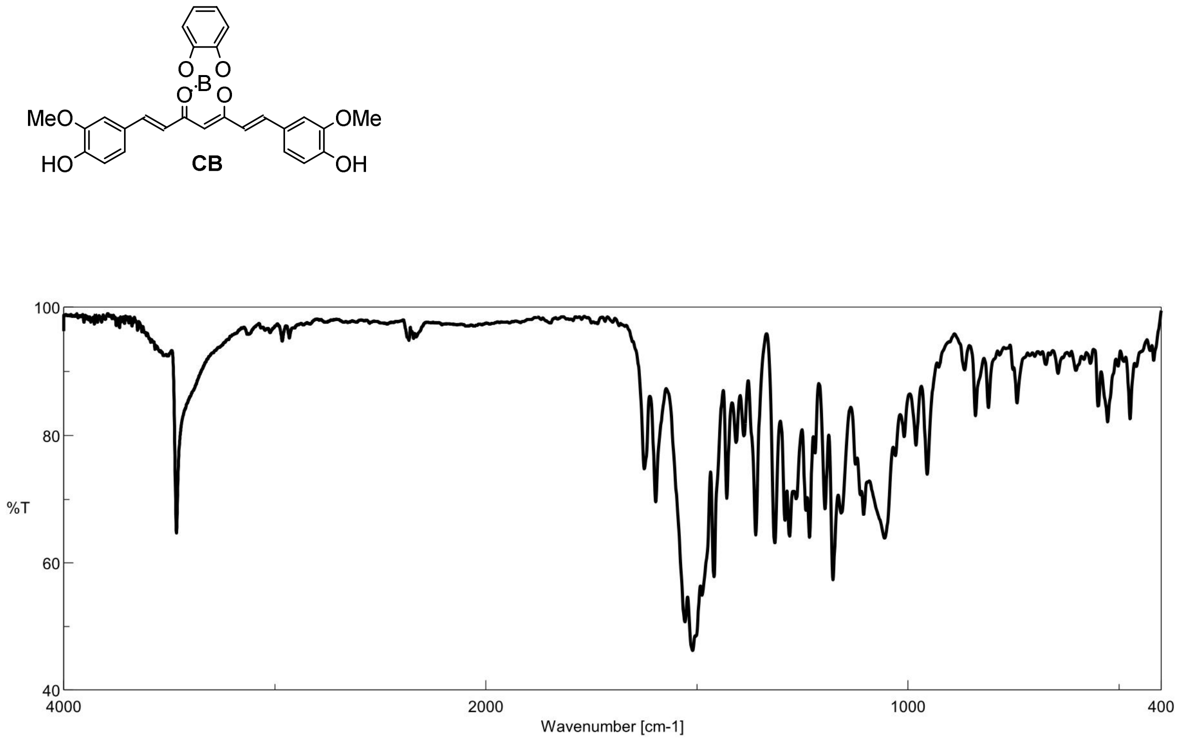


**Fig. S38** IR spectrum of **CB**.

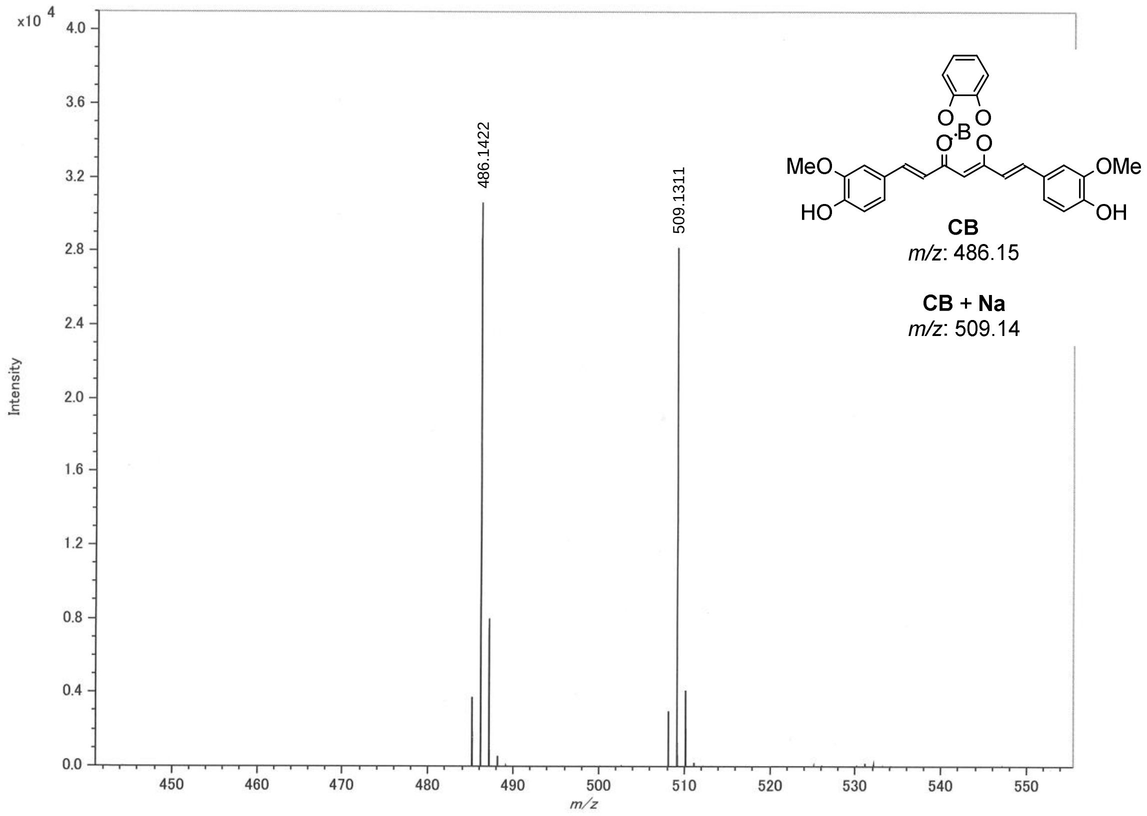


**Fig. S39** MALDI-TOF MS spectrum of **CB**.

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