

Electronic Supplementary Information

for

Gelation-Induced Fluorescence Enhancement of Benzoxazole-Based Organogel and Its Naked-Eye Fluoride Detection

by

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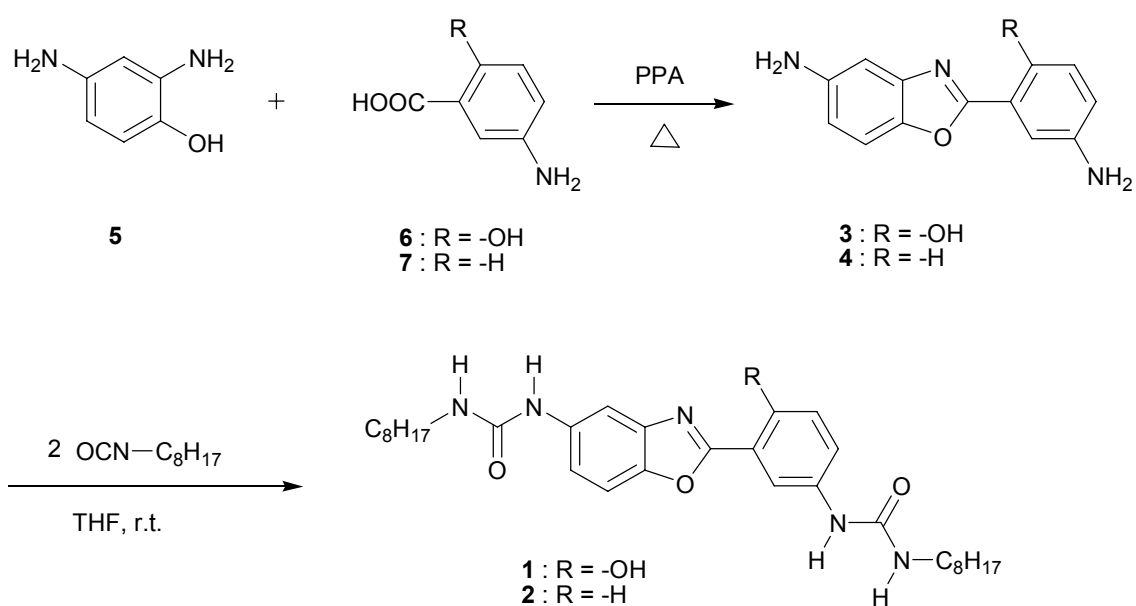
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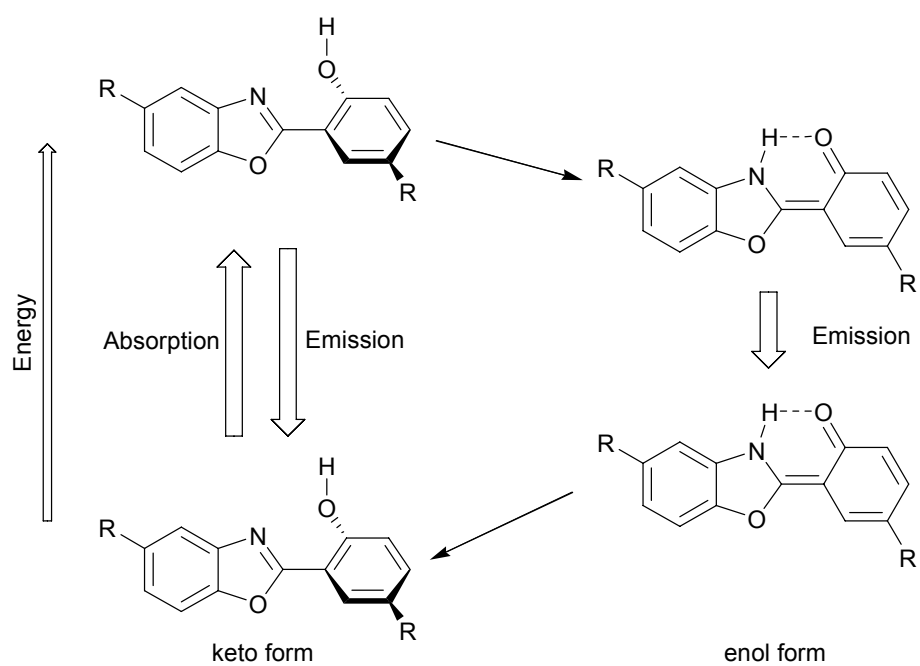
EXPERIMENTAL

Characterization

All starting materials were obtained from commercial supplies and used as received. 2,4-Diaminophenol dihydrochloride and octyl isocyanate were purchased from Aldrich. 5-Aminosalicylic acid and polyphosphoric acid were purchased from TCI and Acros, respectively. Other chemicals were purchased from Duksan. Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on Bruker Biospin DRX300 (Korea Basic Science Institute). UV-Vis spectra were recorded on Lambda 35 (PerkinElmer) and fluorescent spectra were measured on Cary Eclipse (Varian). FE-SEM images of the xerogels were obtained using a JEOL JSM-7000F with an accelerating voltage of 5.0 kV.



Scheme S1. Synthetic route of **1** and **2**.



Scheme S2. ESIPT mechanism of HPB unit.

Synthesis

3¹ : 6.34 g (32.7 mmol) of 2,4-diaminophenol dihydrochloride and 5.00 g (32.7 mmol) of 5-aminosalicylic acid were mixed with 150 ml of polyphosphoric acid (PPA). The reaction mixture was heated to 150 °C under ambient condition and stirred for 12 h. The resulting mixture was cooled to room temperature and poured into ice-water with vigorous stirring. The solution was neutralized by addition of sodium bicarbonate. The crude product was collected by filtration, followed by recrystallization in ethanol. Further purification was carried out with column chromatography with ethyl acetate-toluene mixture. After evaporation, the product was dried in *vacuo* (yield: 2.09 g, 27 %). ¹H NMR (300 MHz, DMSO-*d*₆): δ=10.56 (s, OH, 1H), 7.44 (d, *J*=8.70 Hz, Ar-H, 1H), 7.17 (d, *J*=2.40 Hz, Ar-H, 1H), 6.86 (d, *J*=2.10 Hz, Ar-H, 1H), 6.75-6.83 (m, Ar-H, 2H), 6.69 (d, *J*=10.80 Hz, Ar-H, 1H), 5.18 (s, NH, 2H), 4.87 (s, NH, 2H).

4 : 6.43 g (32.7 mmol) of 5-aminosalicylic acid and 4.48 g (32.7 mmol) of 3-aminobenzoic acid were mixed with PPA (150 ml). Further experimental procedure was the same with the synthetic method for **3**. (yield: 4.84 g, 67 %). ¹H NMR (300 MHz, DMSO-*d*₆): δ=7.38 (d, *J*=6.36 Hz, Ar-H, 2H), 7.26 (d, *J*=5.67 Hz, Ar-H, 1H), 7.19 (t, *J*=11.7 Hz, Ar-H, 1H), 6.84 (d, *J*=1.26 Hz, Ar-H, 1H), 6.74 (d, *J*=5.85 Hz, Ar-H, 1H), 6.64 (q, *J*=6.39 Hz, Ar-H, 1H), 5.41 (s, NH, 2H), 5.07 (s, NH, 2H).

1² : 0.50 g (2.07 mmol) of **3** in 10 ml of THF was added into a mixture of 2.25 g (14.5 mmol) of octyl isocyanate and 45 ml of THF with stirring. The reaction mixture was stirred

at room temperature for 24 h. The gel-like yellow product was filtered and washed with THF for several times. Without further purification, a product was dried in *vacuo* (yield: 0.38 g, 33 %). M.p. 121 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ=10.80 (s, OH, 1H), 8.60 (s, NH, 1H), 8.41 (s, NH, 1H), 8.26 (d, *J*=2.7 Hz, Ar-H, 1H), 7.96 (d, *J*=2.1 Hz, Ar-H, 1H), 7.68 (d, *J*=8.7 Hz, Ar-H, 1H), 7.32 (d, *J*=11.1 Hz, Ar-H, 2H), 7.00 (d, *J*=8.7 Hz, Ar-H, 1H), 6.15 (t, *J*=11.1 Hz, NH, 1H), 6.07 (t, *J*=11.1 Hz, NH, 1H), 3.09 (quintet, *J*=23.4 Hz, 4H), 1.28-1.44 (m, 24H), 0.86 (t, *J*=13.2 Hz, 6H); Anal. Calcd (%) for C₃₁H₄₅N₅O₄: C 67.49, H 8.22, N 12.69; Found: C 67.64, H 8.20, N 12.67.

2 : 0.50 g (2.22 mmol) of **4** in 45 ml of THF was added into a mixture of 2.41 g (15.5 mmol) of octyl isocyanate and 45 ml of THF with stirring. The reaction mixture was stirred at ambient condition for 48 h. The resulting precipitate was filtered and washed with THF for several times. Without further purification, a product was dried under vacuum (yield: 0.68 g, 57 %). M.p. 115 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ=8.71 (s, NH, 1H), 8.54 (s, NH, 1H), 8.42 (s, Ar-H, 1H), 7.91 (d, *J*=2.1 Hz, Ar-H, 1H), 7.69 (d, *J*=10.2 Hz, Ar-H, 1H), 7.62 (d, *J*=8.7 Hz, Ar-H, 1H), 7.40-7.50 (m, Ar-H, 2H), 7.31 (d, *J*=8.4 Hz, Ar-H, 1H), 6.19 (t, *J*=11.4 Hz, NH, 1H), 6.12 (t, *J*=11.1 Hz, NH, 1H), 3.08-3.14 (m, 4H), 1.29 (br s, 24H), 0.86 (t, *J*=13.2 Hz, 6H); Anal. Calcd (%) for C₃₁H₄₅N₅O₃ : C 69.50, H 8.47, N 13.07; Found: C 69.71, H 8.54, N 13.25.

Gelation test : A mixture of a weighed gelator **1** in DMF in a screw-capped vial was heated around boiling point until a clear solution appeared. After clear solution was

obtained, cold toluene was added into the vial, immediately. Strong greenish fluorescent gel was confirmed by the inversion of a test vial method.

Anion Sensing : Anion sensing studies were carried out in a 10 mm quartz cuvette. The UV-Vis and fluorescence spectral changes of **1** and **2** (7.50×10^{-6} M) in the presence of each anion were recorded in DMSO. For the naked-eye anion detections of gel **1**, 100 equiv. of anion was dropped on the top of the gel **1** (0.5wt%, DMF:toluene = 1:9 (v/v)), respectively. After 5 min, the vial was inversed and color change and gel-to-sol transition was monitored. Tetrabutylammonium fluoride (TBAF) was used as fluoride anion and other anions (Cl^- , Br^- , I^- , CH_3COO^- and H_2PO_4^-) were also used in the form of their tetrabutylammonium salt.

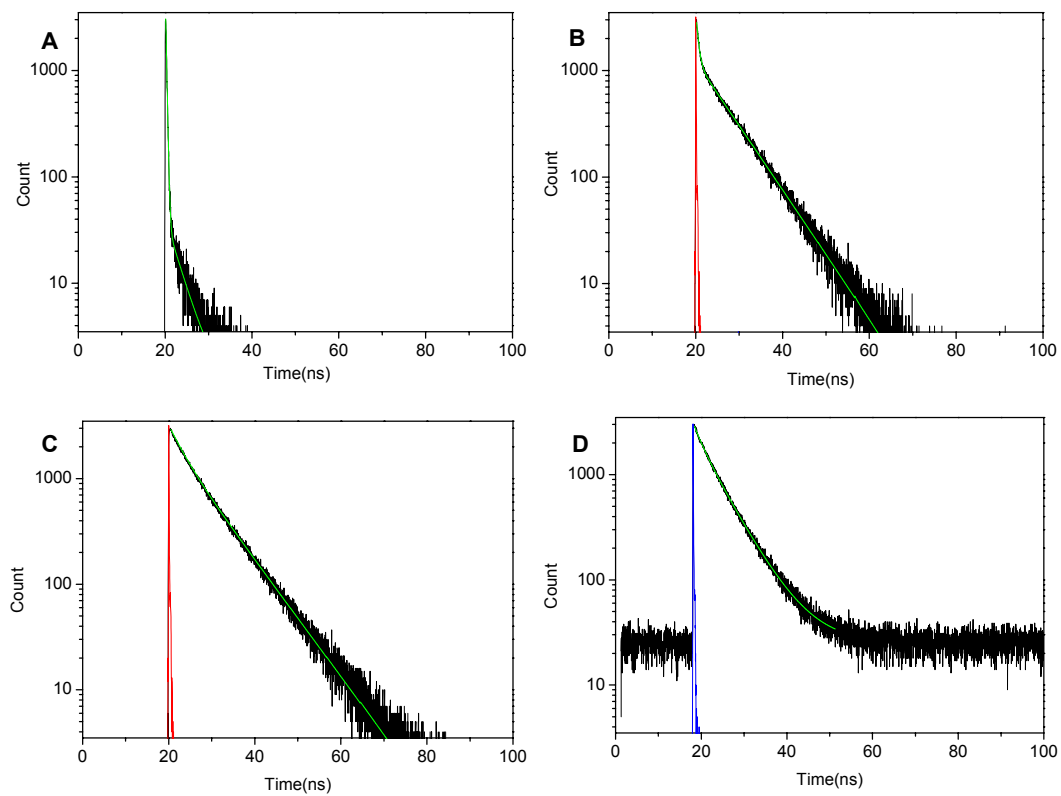


Fig. S1. Time-resolved fluorescence spectroscopic analysis of (A) **1** solution in DMF (at 541 nm), (B) wet-gel **1** in DMF/toluene (at 519 nm), (C) xerogel **1** (at 519 nm) and (D) wet-gel **1** in DMF/toluene upon addition of 100 equiv. fluoride anion (506 nm).

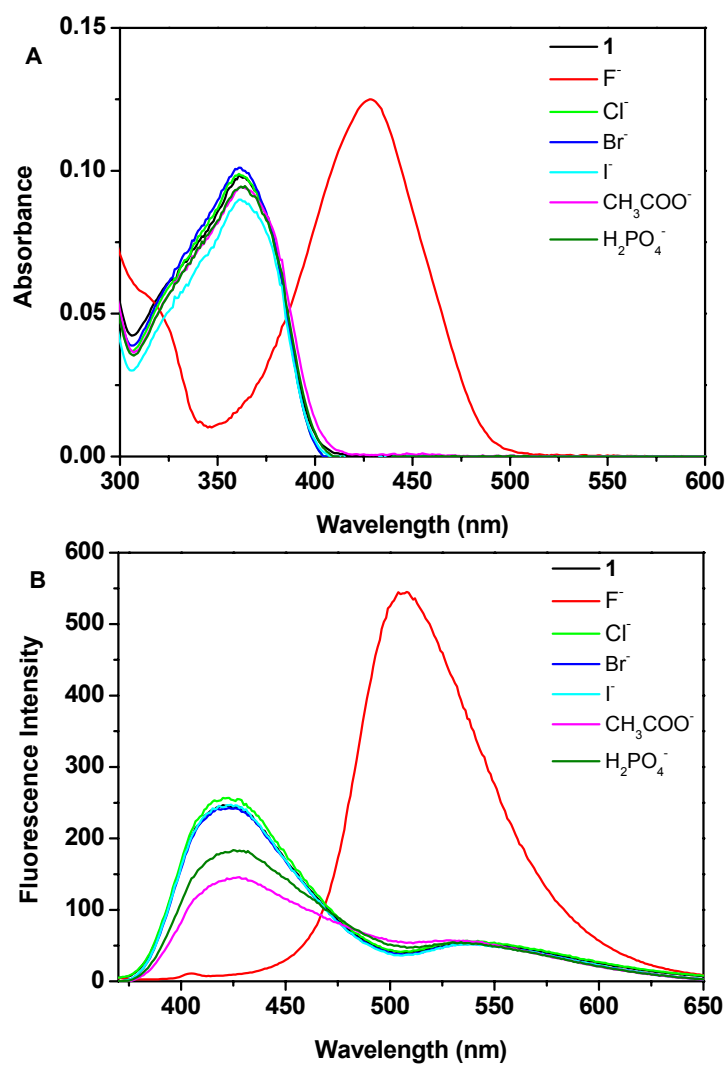


Fig. S2. (A) UV-Vis absorption and (B) fluorescence changes in **1** in DMSO (7.50×10^{-6} M) upon addition of 100 equiv. anion in DMSO.

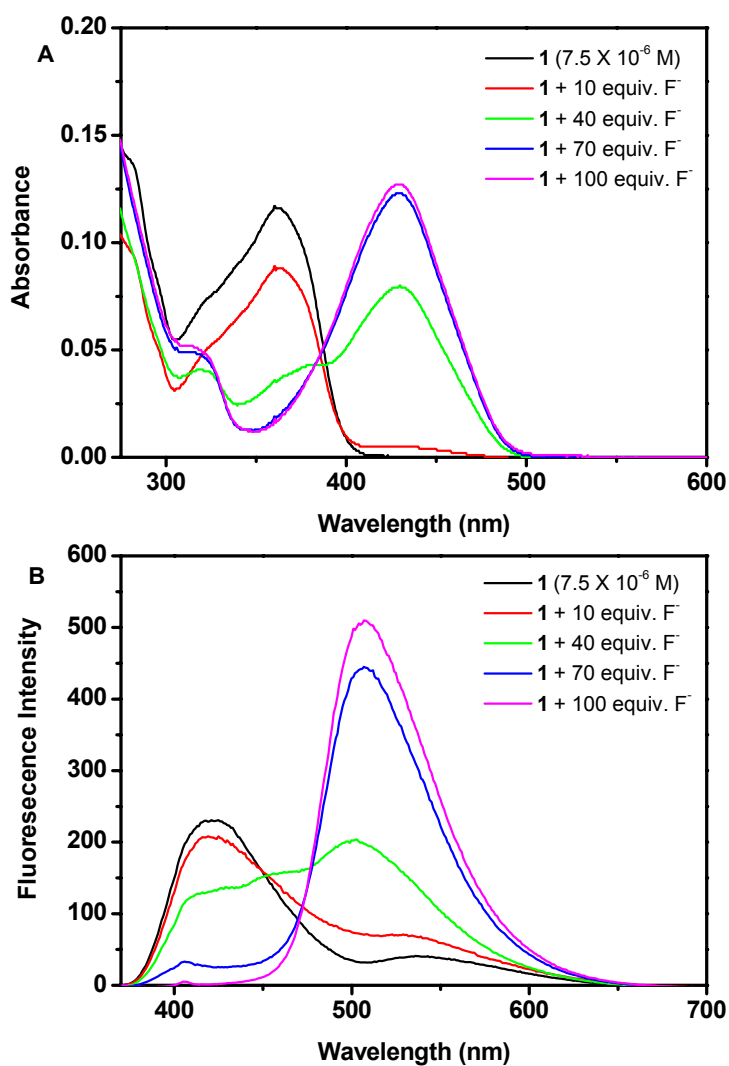


Fig. S3. (A) UV-Vis absorption and (B) fluorescence changes in **1** in DMSO (7.50×10^{-6} M) upon addition of fluoride anion.

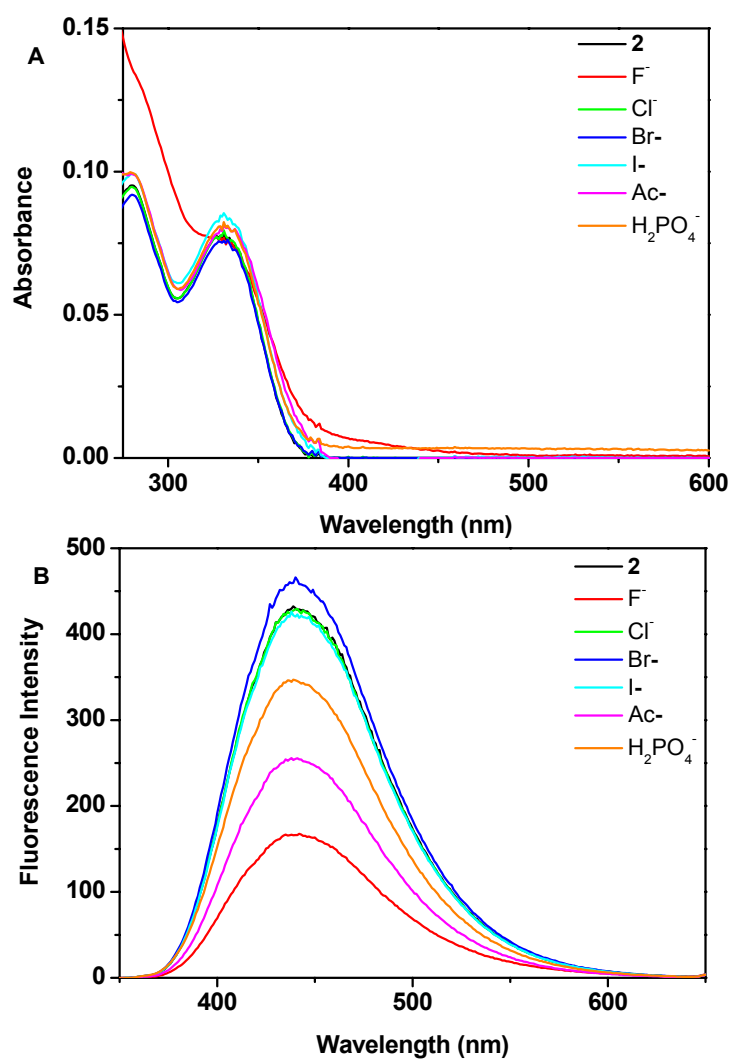


Fig. S4. ((A) UV-Vis absorption and (B) fluorescence changes in **2** in DMSO (7.50×10^{-6} M) upon addition of 100 equiv. anion in DMSO.

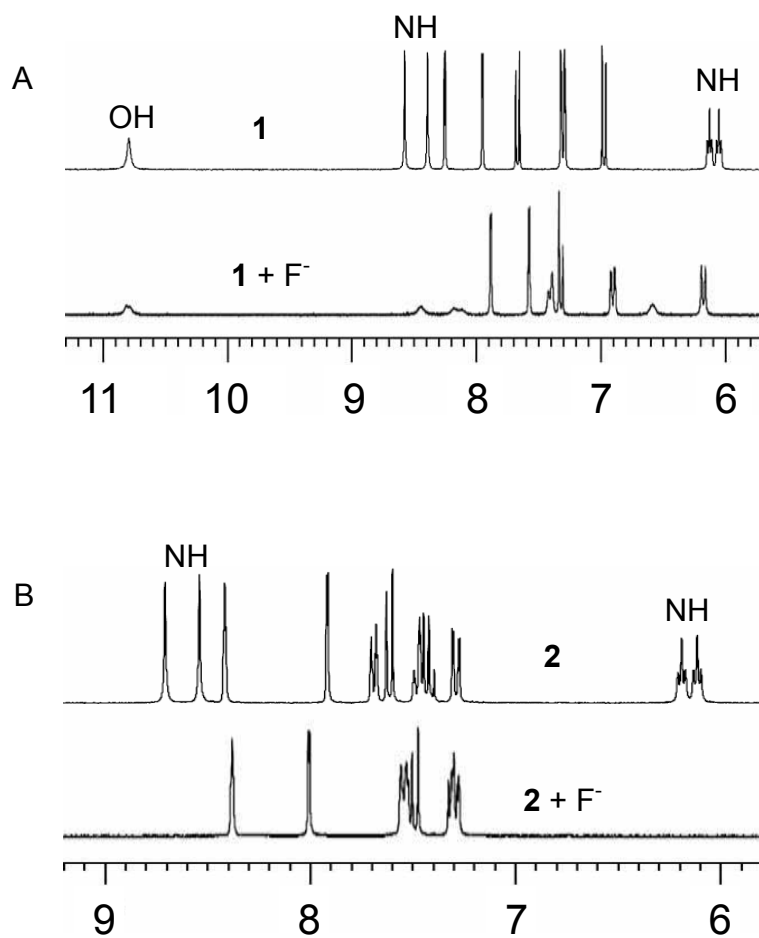


Fig. S5. Partial ¹H NMR spectra of (A) **1** and (B) **2** in DMSO-*d*₆ in the absence and in the presence of 10 equiv. of TBAF.

References

- 1 (a) A. Pla-Dalmau, *J. Org. Chem.*, 1995, **60**, 5468; (b) T. H. Kim, G. Li, W. H. Park and T.S. Lee, *Mol. Cryst. Liq. Cryst.*, 2006, **445**, 185.
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