Supporting Information

Spectroscopic and Mechanistic Insights into Solvent Mediated Excited-State Proton Transfer and Aggregated Induced Emission: Introduction of Methyl Group onto 2-(o-Hydroxyphenyl)benzoxazole

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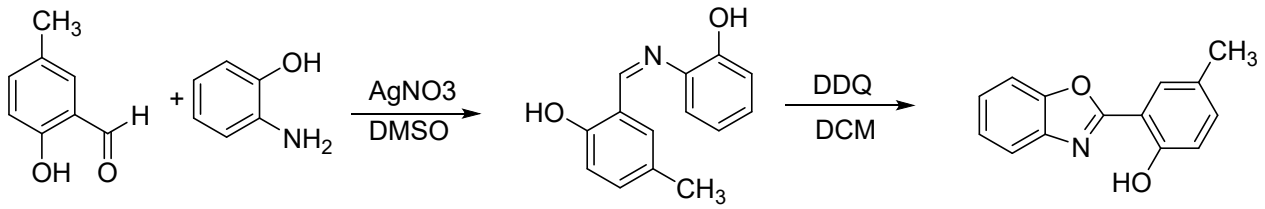
Experimental Methods and Calculation Details

Materials and general methods

Solvents were purchased from various commercial sources and used without further purification unless otherwise stated. Spectroscopic grade solvents were used in the UV/Vis and fluorescence spectroscopic measurements. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates with silica gel 60 F254 or with aluminum oxide 60 F254 neutral. Flash column chromatography was performed using silica (230-400 mesh) gel or alumina oxide (80-200 mesh) as the stationary phases. ^{1}H NMR spectra were acquired on NMR Spectrometer (Bruker, AVANCE III, 400MHz, Germanny) to confirm its structure. All chemical shifts were reported in δ units relative to tetramethylsilane. DMSO was treated with alumina gel prior to use. Electronic absorption spectra were recorded by a UV-Vis spectrophotometer (Shimadzu, 3600-Plus, Japan). Emission and excitation spectra were obtained from fluorescence spectrophotometers (HORIBA Fluoramax-4, USA and Hitachi F-7000, Japan).

Synthesis of HBO-p-CH_3 Compound.



2-Hydroxy-5-methylbenzaldehyde (4.0 mmol), 2-aminophenol (4.4 mol) and catalytic dose of silver nitrate ($AgNO_3$) were mixed in a 50 mL round-bottom flask with 20 mL dimethylsulfoxide (DMSO). Then, the mixture was stirred for 4 h in a water bath condition (35°C). The TLC template (PE:EA=3:1) was employed to monitor the progress of the reaction. The mixture was cooled to room temperature after the reaction was finished and then 60 mL dichloromethane (DCM) was added to the above room mixture, and then a large amount of saturated salt water was applied to extract the organic layer, which was span and dried to obtain the pure (Z)-2-(((2-hydroxyphenyl)imino)methyl)-4-methylphenol. Next, (Z)-2-(((2-hydroxyphenyl)imino)methyl)-4-methylphenol and 2,3-dichloro-5,6-difluoro-p-benzoquinone (DDQ) in a molar ratio of 1:1.1 were mixed in 60 mL dichloromethane. Similarly, the reaction was stirred at 40 °C for 4 h and monitored by TLC (PE:EA=5:1). Finally, by filtration the filtrate was retained and spin-dried and recrystallized with methanol to obtain the target product HBO-pCH_3. Figure S1 showed the ^{1}H NMR of HBO-pCH_3 in DMSO-d_6 (11.03(s,1H), 7.87(dt, J = 9.4, 3.1 Hz, 3H), 7.50 (m, 2H), 7.36 (dd, J = 8.4, 2.3 Hz, 1H), 7.06(d, J = 8.4 Hz, 1H), 2.36 (s, 3H).

Calculation

All the calculations are performed using the Gaussian 09W program suite[S1]. The geometries were optimized by DFT and TDDFT in the ground state and excited state, respectively, using the basis set 6-311+G(d,p) with Becke's three-parameter exchange functional accompanying the Lee-Yang-Parr nonlocal correlation functional (B3LYP)[S2-S3] and the solvent effects with the polarizable continuum model (PCM)[S4]. In addition, to avoid the misrepresentation of weak interactions, density functional theory including dispersion correction (DFT-D3)[S5-S6] was considered.

References

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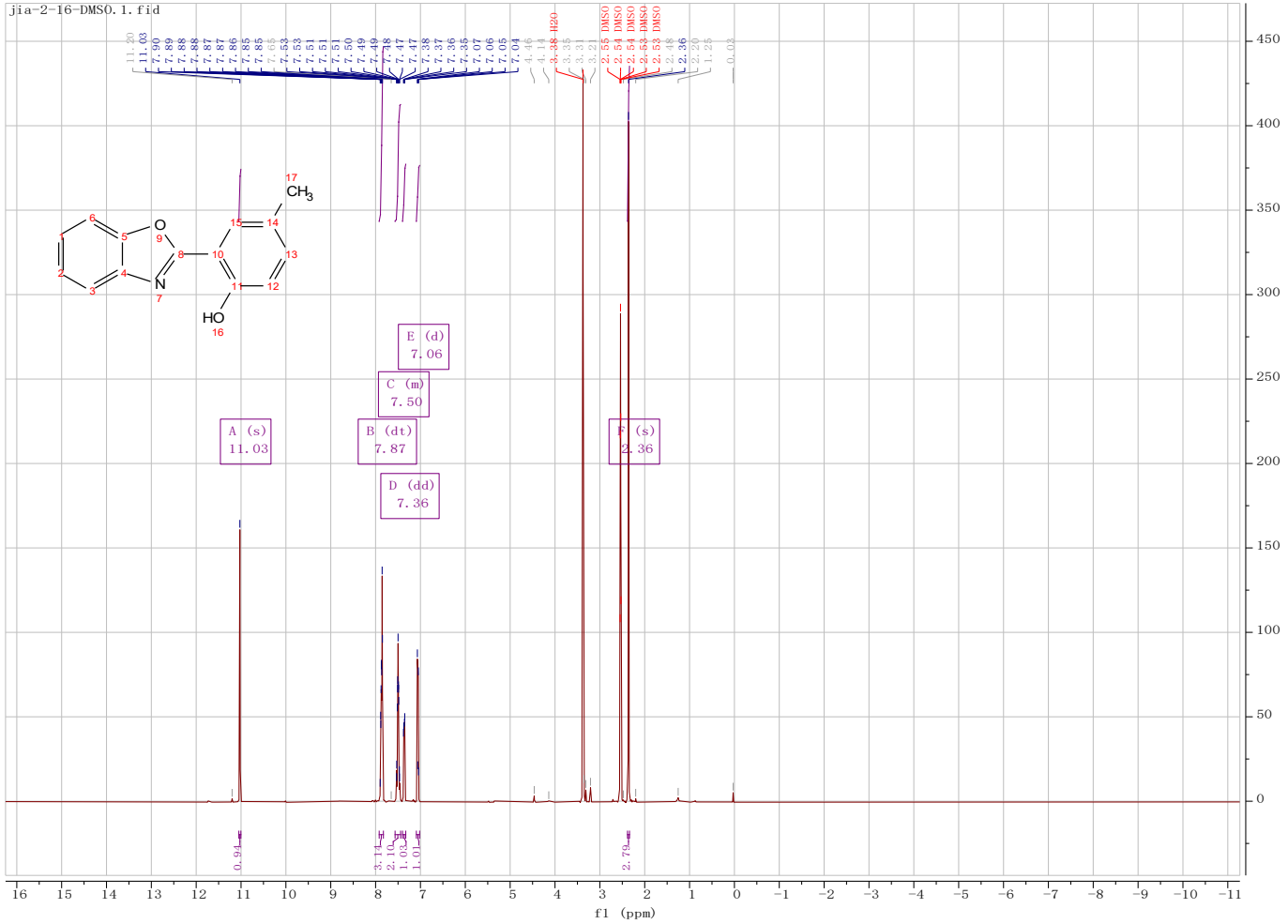
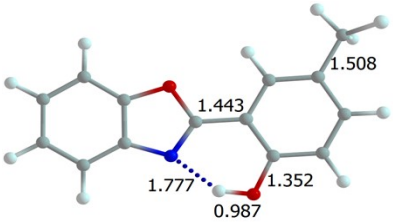


Figure S1. The ^{1}HNMR of HBO-pCH_3 in DMSO-d6



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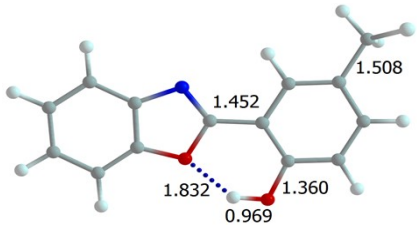
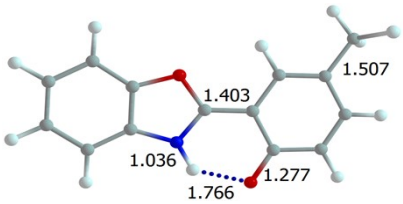
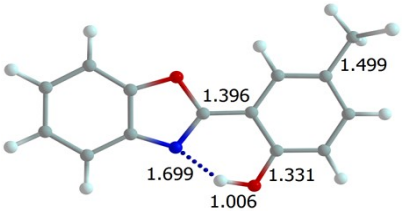


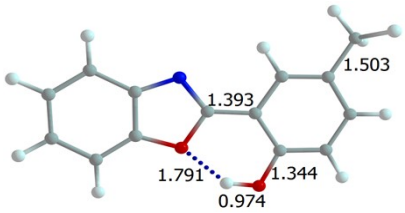
anti-enol
4.4



keto
9.2



syn-enol*
75.4



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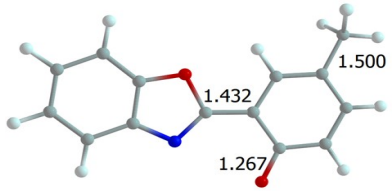

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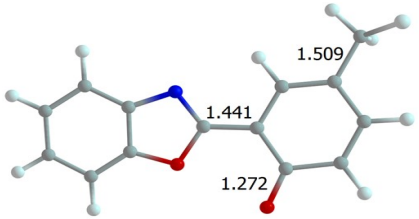
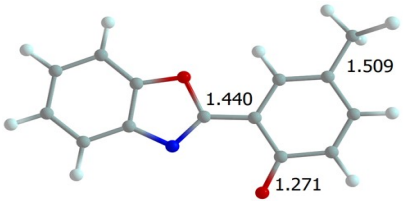
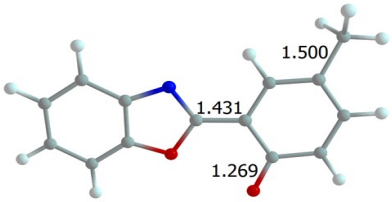


anti-anion
297.3



anion*
359.6



anti-enol*
359.1

* Minima of the corresponding first singlet excited states

Figure S2. Optimized structures and relative energy(in kcal/mol) of enol and keto HBO-pCH_3 as well as deprotonation forms in S_0 and S_1 calculated at the (TD-)B3LYP-D3(BJ)/6-311+G (d, p) level using PCM(solvent=methanol) model. Intra-molecular hydrogen bond distances are represented by dotted lines. Red: O; Withe: H; Blue: N; Gray: C.

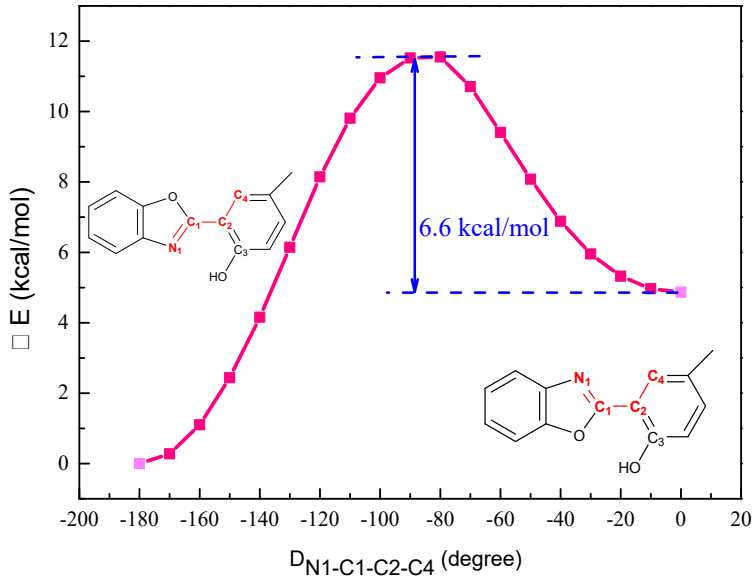
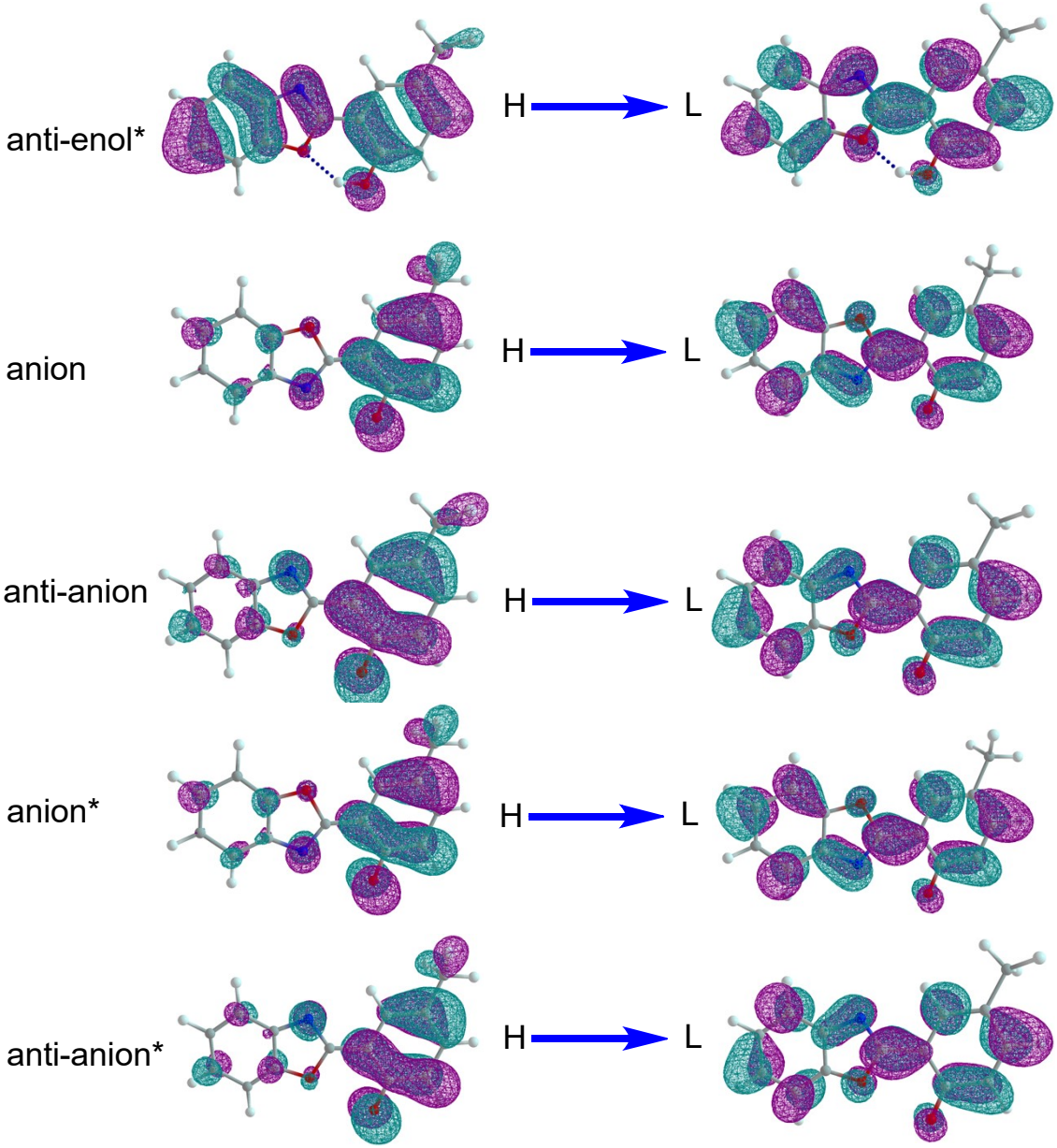


Figure S3. Potential energy curve of HBO-pCH_3 in the S_0 as a function of dehedal angle $D_{N1\text{-}C1\text{-}C2\text{-}C4}$ in methanol calculated at B3LYP-D3(BJ)/6-311+G (d, p) level using PCM(solvent=methanol) model.

* Minima of the corresponding first singlet excited states

Figure S4. Optimized structures and relative energy(in kcal/mol) of enol and keto HBO-pCH_3 as well as deprotonation forms in S_0 and S_1 calculated at the (TD-)B3LYP-D3(BJ)/6-311+G (d, p) level using PCM(solvent=methanol) model. Intra-molecular hydrogen bond distances are represented by dotted lines. Red: O; Withe: H; Blue: N; Gray: C.


anti-enol*
H
L
anion
H
L
anti-anion
H
L
anion*
H
L
anti-anion*
H
L

* Minima of the corresponding first singlet excited states.

Figure S5. View of the frontier molecular orbitals (HOMO and LUMO) of HBO-pCH_3 under different condition calculated at (TD-)B3LYP-D3(BJ)/6-311+G (d, p) level using PCM(solvent=methanol) model.

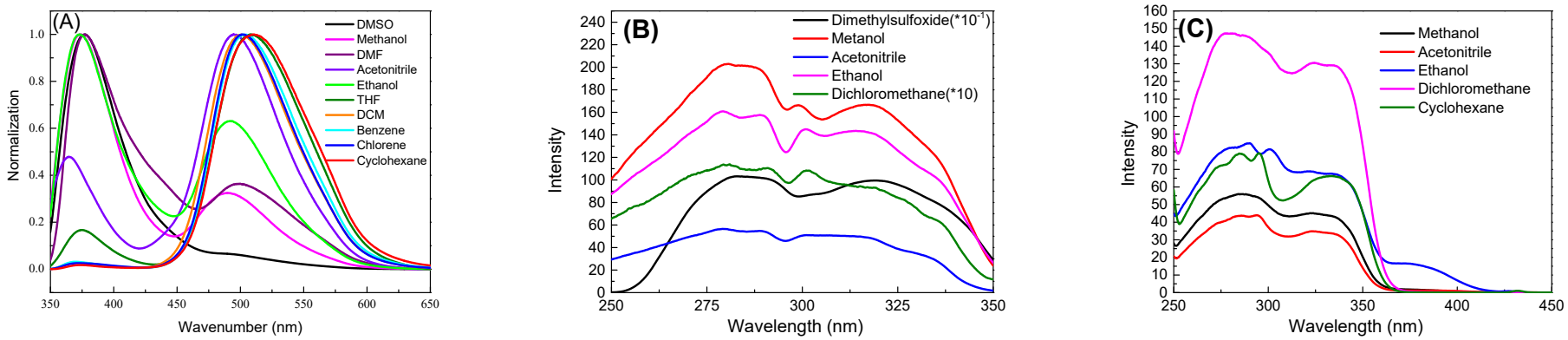


Figure S6. (A)Normalized emission spectra (λ_{ex}=330 nm), (B) excitation spectra of HBO-pCH_3 in different solvents at ~375 nm, and (C) excitation spectra of HBO-pCH_3 in different solvents at ~495 nm. Condition: The concentration of HBO-pCH_3 was ~40 μmol/L in solvents.

Table S1. Calculated emission wavelengths (λ_{em} (nm)/oscillator strengths(f) of TICTs (shown in Figure 9) at TD-B3LYP/6-311G(d,p) using PCM(solvent=methanol) model .

structure state	TICT-1 λ_{em} (nm)/f	TICT-2 λ_{em} (nm)/f	TICT-3 λ_{em} (nm)/f	TICT-4 λ_{em} (nm)/f
S_1	2036.8/0	2036.1/0	1424.9/0.0001	1426.3/0.0001
S_2	649.5/0.0112	649.5/0.0112	540.1/0.1003	540.3/0.1004
S_3	439.8/0	439.8/0	401.2/0.0002	401.3/0.0002

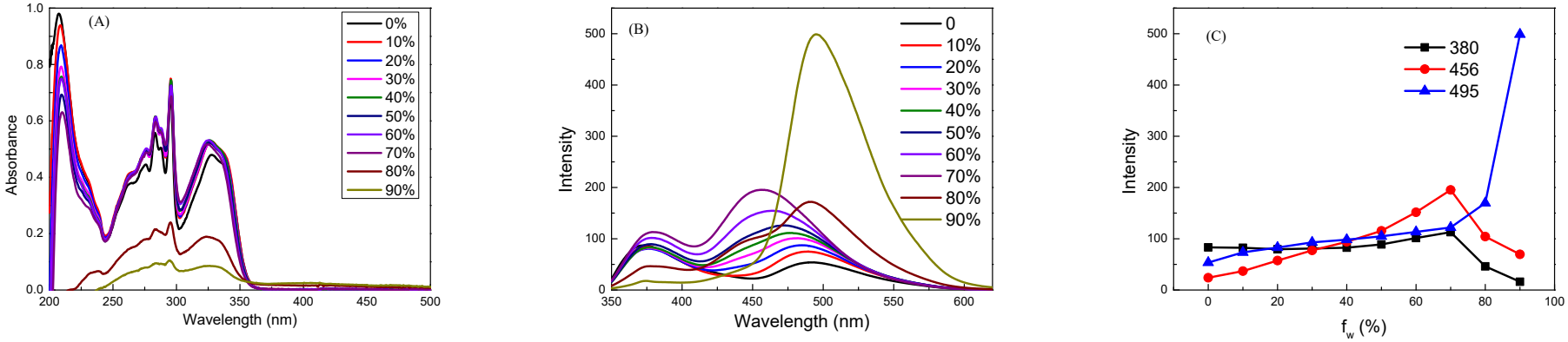


Figure S7. (A) Absorption spectra and (B) Emission spectra in water/ ethanol mixtures with different water fraction(f_w). (C) Emission intensities at 380, 456, and 495 nm as functions of f_w. Conditions: Concentration of HBO-pCH_3 was ~40 μmol/L, excitation was at 330 nm.

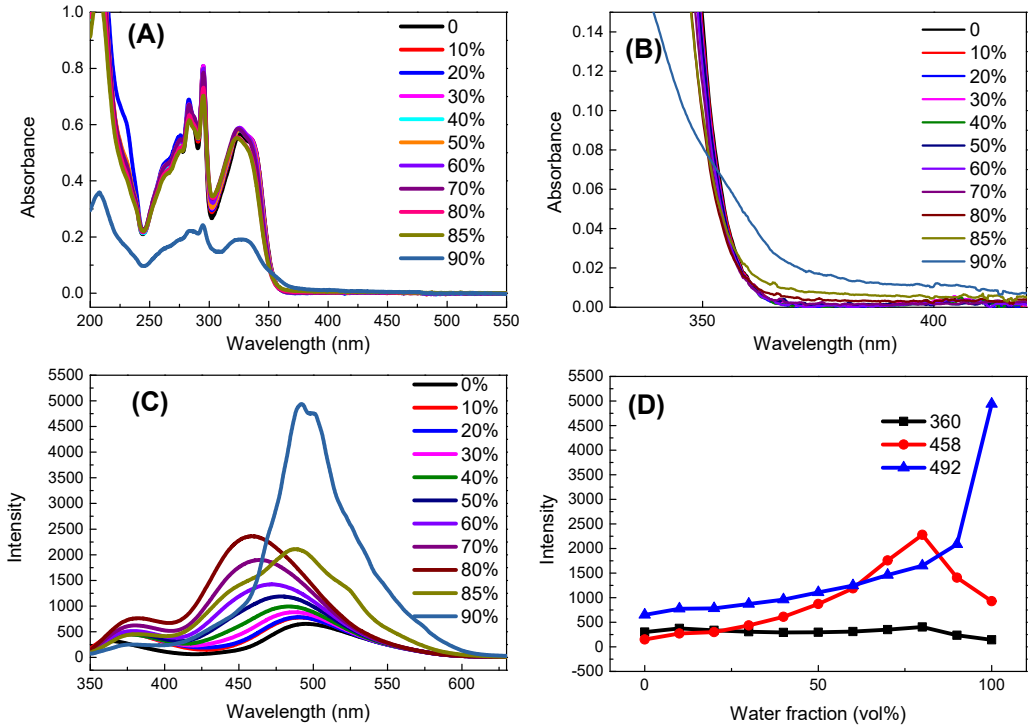


Figure S8. (A) Absorption spectra and (B) local enlargement of A); (C) emission spectra of HBO-pCH_3 in water/ acetonitrile mixtures with different water fraction (f_w); (D) emissions at 360, 458, and 496 nm as functions of f_w. Conditions: Concentration of HBO-pCH_3 was ~40 μmol/L, excitation was at 330 nm.