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Supporting Information for

Purple-to-Green Emission: Excited-State Intramolecular Proton Transfer in an Aromatic D-π-A System

Mingxia Hu[a,‡], Junxian Guo[b,c,‡], Jiaye Jin[b*], Yanrong Jia[a], Guanjun Wang[b], Teng-Teng Chen[c*], Yanying Zhao[a*]

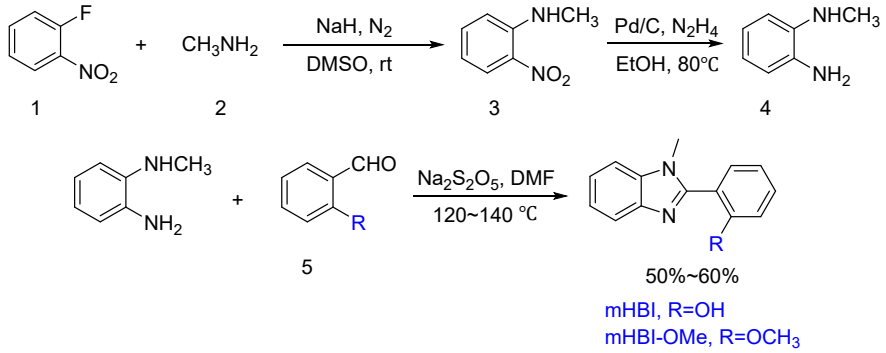
[a] *School of Materials Science and Engineering & School of Chemistry and Chemical Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China*

[b] *Department of Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200438, China*

[c] *Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China*

Corresponding author E-mail address: jyjin@fudan.edu.cn (J. Jin)
E-mail address: tengtengchen@ust.hk (T. Chen)
E-mail address: yyzhao@zstu.edu.cn (Y. Zhao)

1. *Synthesis*



Scheme S1. Synthesis route of mHBIs.

1.1 *Materials*

Unless otherwise stated, all reagents and solvents used were purchased from commercial sources and were used without further purification.

1.2 *Details*

^{1}H NMR were recorded on a Bruker AV-400 MHz, Switzerland spectrometer. We synthesize the mHBI and 1-methyl-2-(2′-methoxyphenyl)-benzimidazole (mHBI-OMe), as shown in **Scheme S1**. A mixture of 1-fluoro-2-nitrobenzene (2.4 mmol), methylamine hydrochloride (2 mmol) and sodium hydride (14 mmol) were combined in a 100 mL round-bottom flask containing 12 mL dimethyl sulfoxide (DMSO). Initially, the mixture was stirred at room temperature under a nitrogen atmosphere for 6 h. The reaction was monitored using thin-layer chromatography (TLC) with a PE:DCM ratio of 1:1. When the reaction finished, 60 mL of dichloromethane (DCM) was added. Subsequently, an amount of water was used to extract the organic layer, which was then washed, dried, and finally purified to yield **compound 3**. Next, **compound 3** was mixed with hydrazine hydrate (1:20 molar ratio) and Pd/C catalys (1:0.1 mass ratio) in 60 mL of ethanol. The mixture was stirred at 80 °C overnight, using TLC (PE:EA=3:1) to monitor. After completion, the mixture was filtered to remove Pd/C residue and extracted following the previous step. After extraction, the organic layers were spin-dried to afford **compound 4**. Finally, sodium metabisulfites **with compound 4** and **compound 5** (1:1.5:1.5 molar ratio) were combined in a round-bottom flask with 8 mL of DMF. The mixture was stirred at 120-140 °C for 6-7 h. After completion, the target product was obtained by extraction, purified, and spin-dried.

mHBI: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.29 (s, 1H), 7.76–7.67 (dd, 1H), 7.66 (dd, *J*=7.7, 6.1, 1.5 Hz, 2H), 7.42 (ddd, *J*=8.2, 7.4, 1.7 Hz, 1H), 7.36–7.26 (td, 2H), 7.08 (dd, *J*=8.3, 1.1 Hz,

1H), 7.01 (td, *J*=7.5, 1.1 Hz, 1H), 3.85 (s, 3H).

mHBI-OMe: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.82 (dd, 1H), 7.62 (dd, *J*=7.5, 1.8 Hz, 1H), 7.57–7.49 (ddd, 1H), 7.43 (dd, *J*=8.0, 1.9 Hz, 1H), 7.35 (dtd, *J*=6.6, 5.1, 1.8 Hz, 2H), 7.14 (td, *J*=7.5 Hz, 1H), 7.06 (dd, *J*=8.3 Hz, 1H), 3.85 (s, *J*=1.6 Hz, 3H), 3.69 (s, *J*=1.6 Hz, 3H).

2. *Characterization*

The steady-state spectra of mHBI ($c=5.0\times10^{-5}$ M) were obtained in acetonitrile (MeCN), dichloromethane (DCM), N, N-dimethylformamide (DMF), DMSO, ethyl acetate (EA), ethanol (EtOH), methanol (MeOH), n-hexane and tetrahydrofuran (THF), respectively. The absorption and emission and excitation spectra were recorded on UV–vis (Shimadzu UV-3600 Plus, Japan) and fluorescence (Hitachi F-4600, Japan) spectrophotometers, respectively.

Femtosecond transient absorption (fs-TA) measurements were performed using a HARPIA-TA spectrometer (Light Conversion Inc.). The excitation source was a Yb:sapphire femtosecond laser system (CARBIDE CB3-20W) operating at 1030 nm with a pulse duration of 226 fs (FWHM) and a repetition rate tunable 50 kHz. The laser output was split into pump and probe beams. The pump wavelength (210–2700 nm) was tuned via an optical parametric amplifier (ORPHEUS-HP), and the probe beam was generated by focusing the fundamental beam onto a sapphire crystal to produce a broadband supercontinuum (380–900 nm). A second harmonic generation (SHG) unit was used to generate 515 nm pump pulses. Two beams pass through the samples and the signals were then collected by the detector (pump: 315 nm,158 mw; 275 nm,120 mw). The 0.7 mM sample solutions were measured in a 2-mm path-length quartz cuvette. The subtraction of background, and chirp correction were done for all the data before analysis. The principal components were ensured by singular value decomposition (SVD), and then the global fitting was carried out with the selected principal components and exponential function using the sequential kinetics scheme based on the fs-TA spectra by CarpetView 3.0.1. The global analysis using sequential model mainly due to the stepwise interconversion of excited states.

3. *Calculations*

The geometries were optimized using density functional theory (DFT) and time-dependent density functional theory (TD-DFT). To select the appropriate functionals, we applied a series of

time-dependent density functionals, including some newly-development ones, to calculate the maximum absorption and emission bands. **Table S3** shows the completely different bands obtained using different functionals. When compared to the observed bands for mHBI, MN15 exhibited much better agreement. We employing the MN15 functional combining with def2-TZVP basis sets. Vibrational analysis was carried out to the stationary points (minimum and transition state) at the same level. The polarizable continuum model (PCM) solvent and the additional dispersion correction (DFT-D3) was accounted. All calculations were performed using the Gaussian 09 W program suite. The molecular orbital diagrams were jointly generated using Multiwfn (version 3.8(dev)) and the VMD (version 1.9.3) program.

4. *Figures*

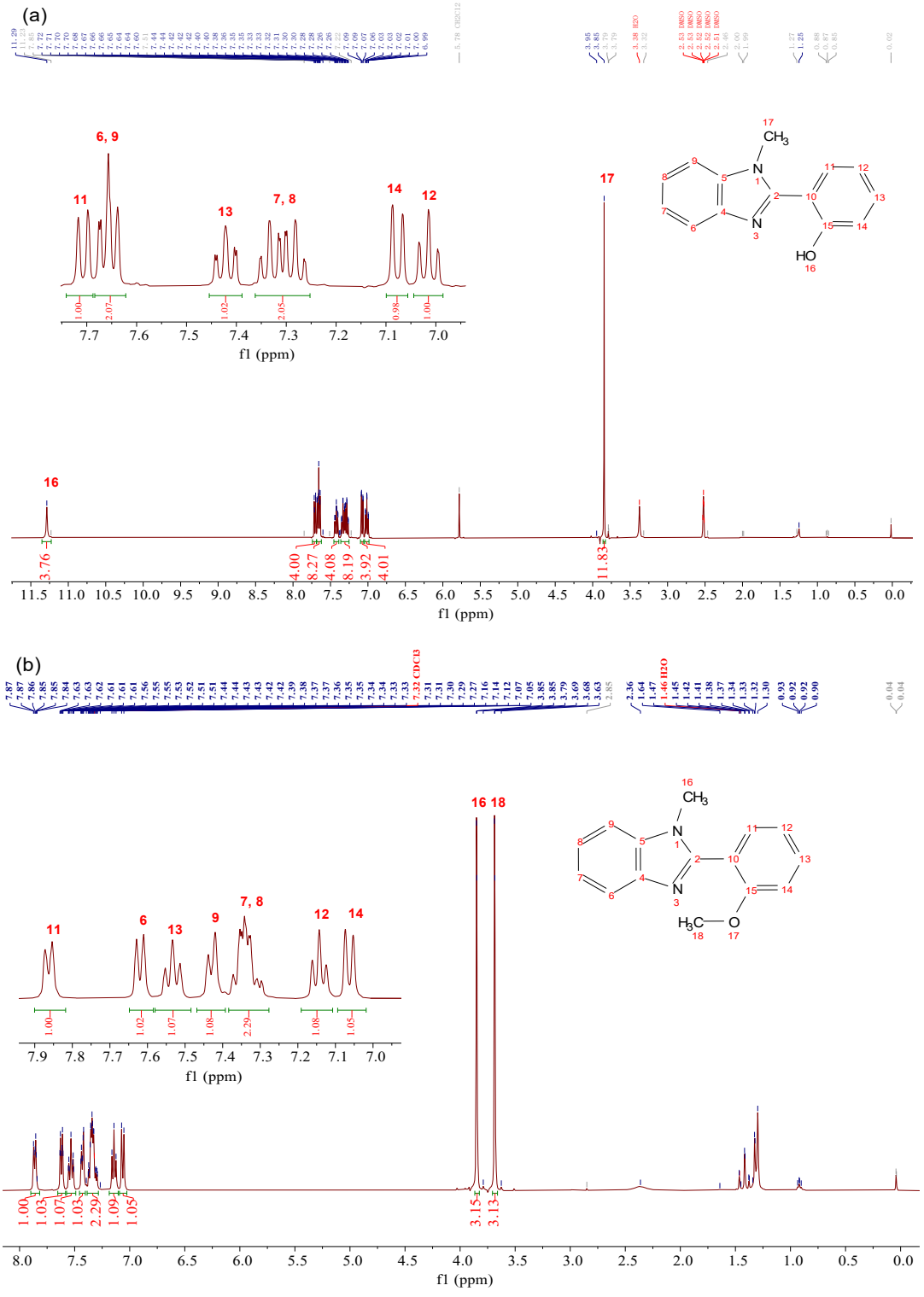


Figure S1. ^{1}H NMR of mHBI in (a) d_6-DMSO and (b) mHBI-OMe in $CDCl_3$.

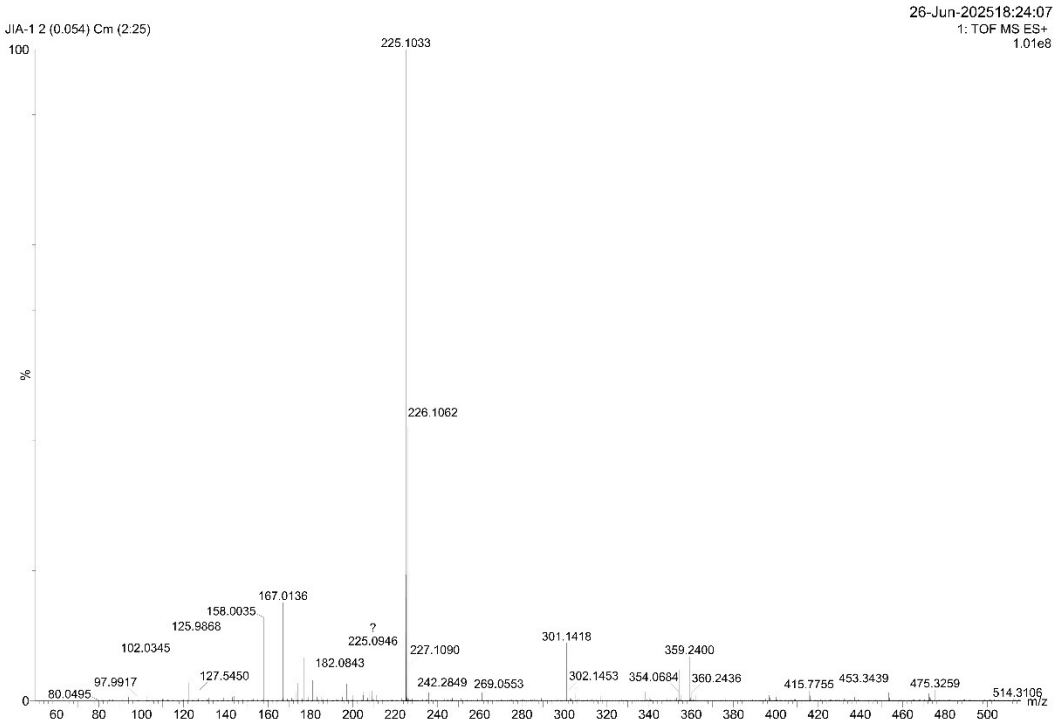


Figure S2. Time of flight mass spectrum (TOF-MS) of mHBI.

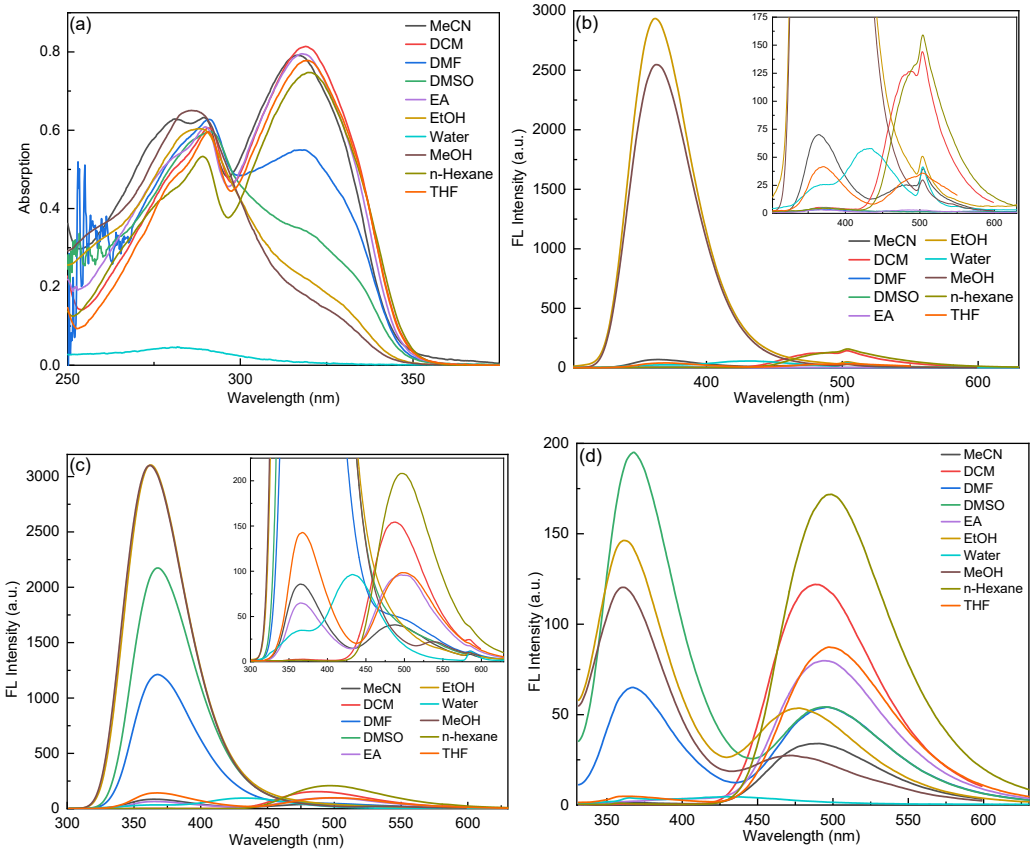


Figure S3. (a) Steady UV–Vis absorption and fluorescence spectra of mHBI (50 μM) in different solvents at λ_{ex}=(b) 250, (c) 290, and (d) 320 nm, respectively.

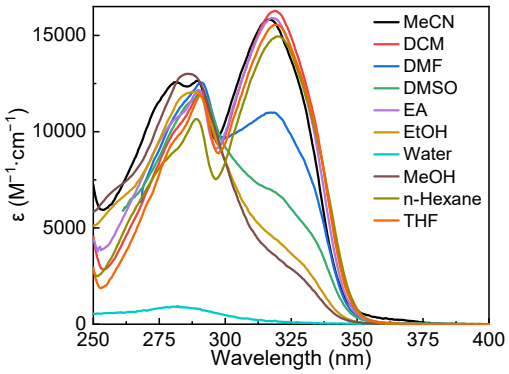


Figure S4. UV–Vis absorption spectra of mHBI in various solvents, plotted as molar extinction coefficients.

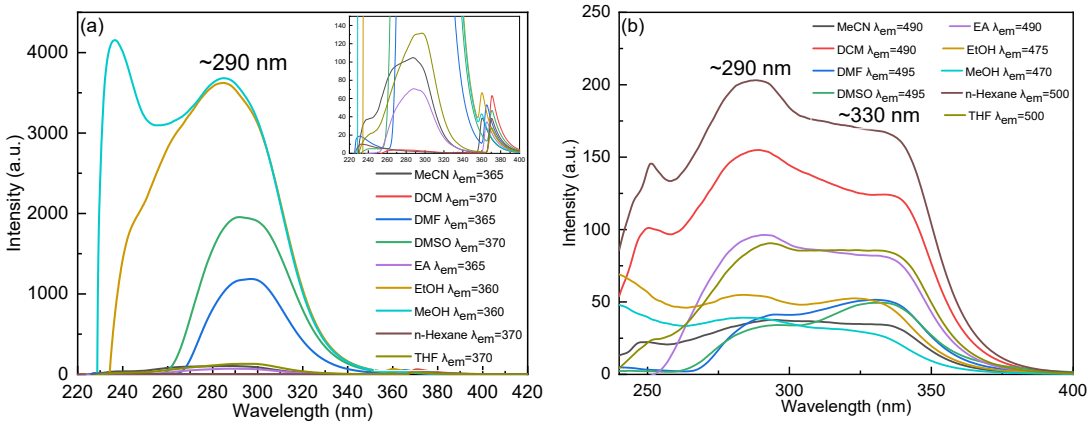


Figure S5. Excitation spectra of mHBI (50 μM) in different solvents.

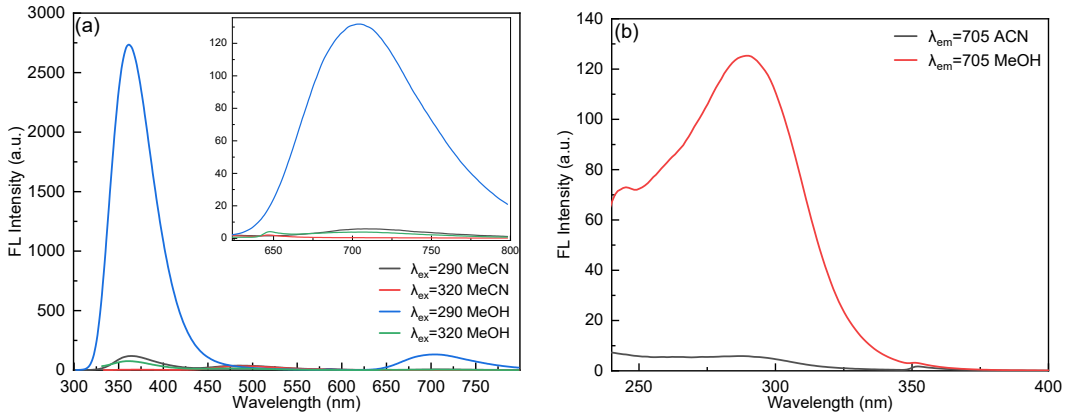


Figure S6. (a) Fluorescence and (b) excitation spectra of mHBI (50 μM).

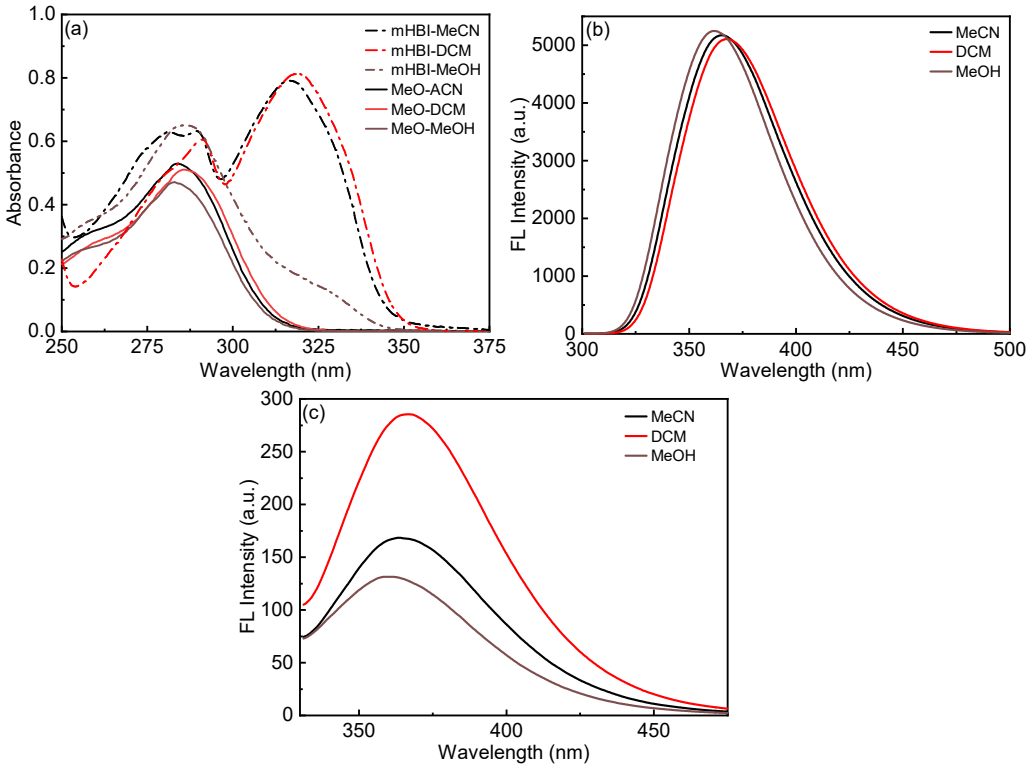
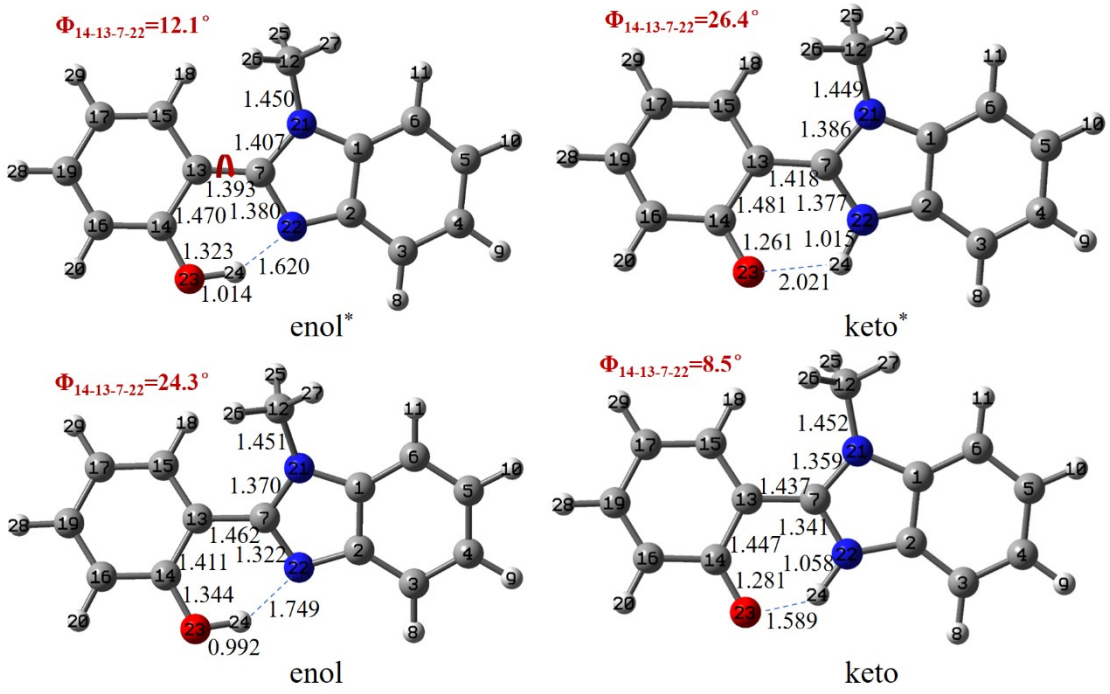
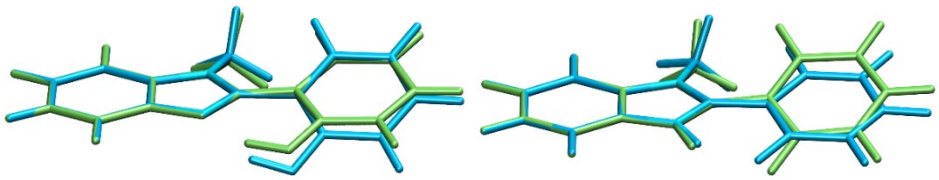


Figure S7. (a) Steady UV–Vis absorption of mHBI (50 μM) and mHBI-OMe and fluorescence spectra in different solvents under $\lambda_{ex=}$ (b) 290 and (c) 320 nm.

(a)



(b)



enol form keto form

Figure S8. (a) Optimized bond length (Å) for the enol, enol*, keto, and keto* at (TD)MN15/def2-TZVP level using (solvent=acetonitrile) model. (b) Geometry comparison of ground states (S_0 in blue) and excited states (S_1 in green).

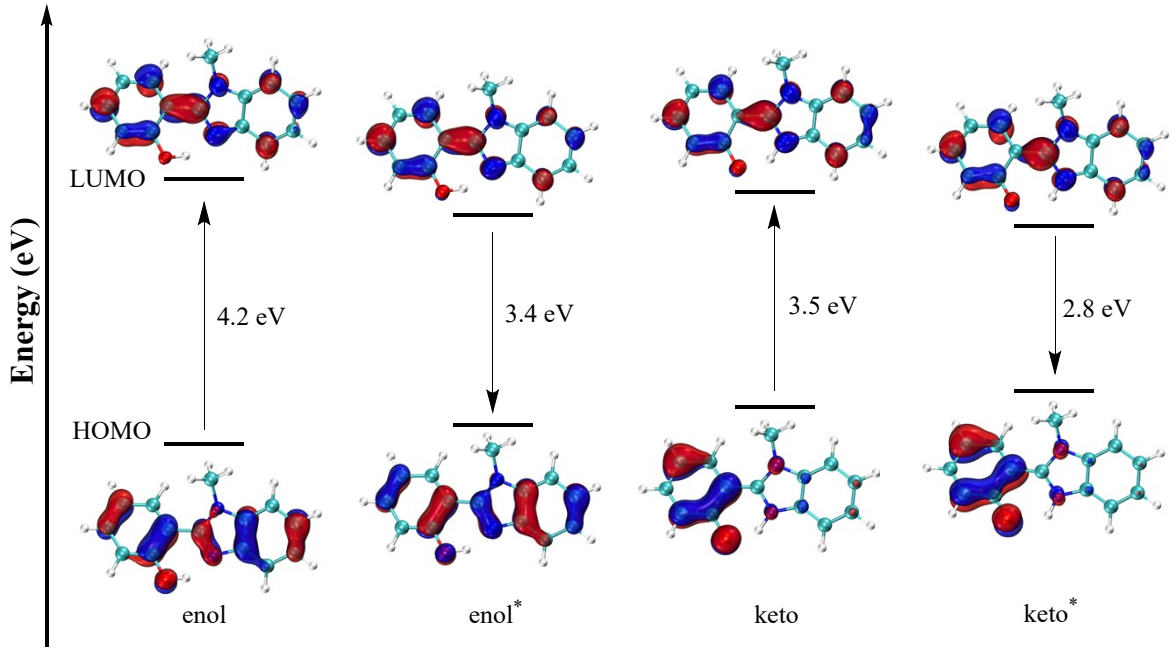


Figure S9. Frontier molecular orbitals and transition energies of mHBI calculated at MN15-TD/def2-TZVP level using PCM (solvent=acetonitrile) model.

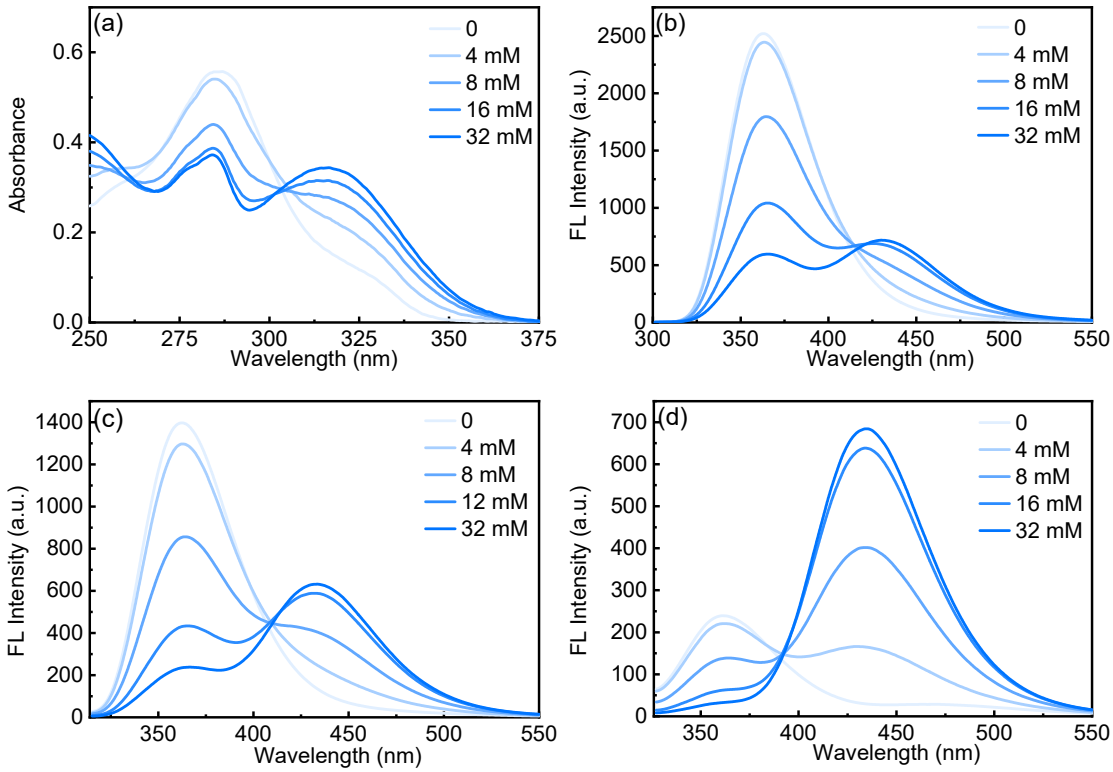


Figure S10. (a) Steady UV–Vis absorption and fluorescence spectra in mHBI(50 μM)/MeOH doped with the different concentrations of TBAOH under excitation at (b) 290, (c) 304, and (d) 316 nm.

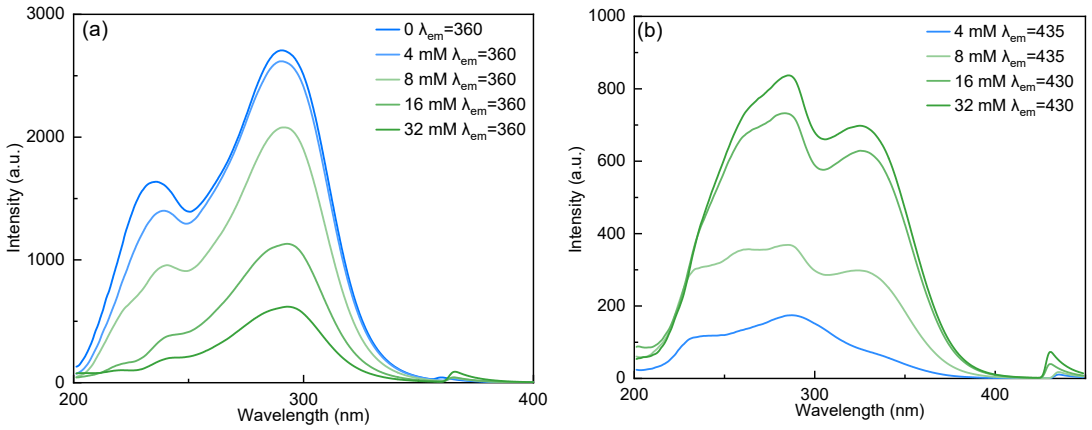


Figure S11. Excitation spectra of mHBI in MeOH doped with different concentrations of TBAOH.

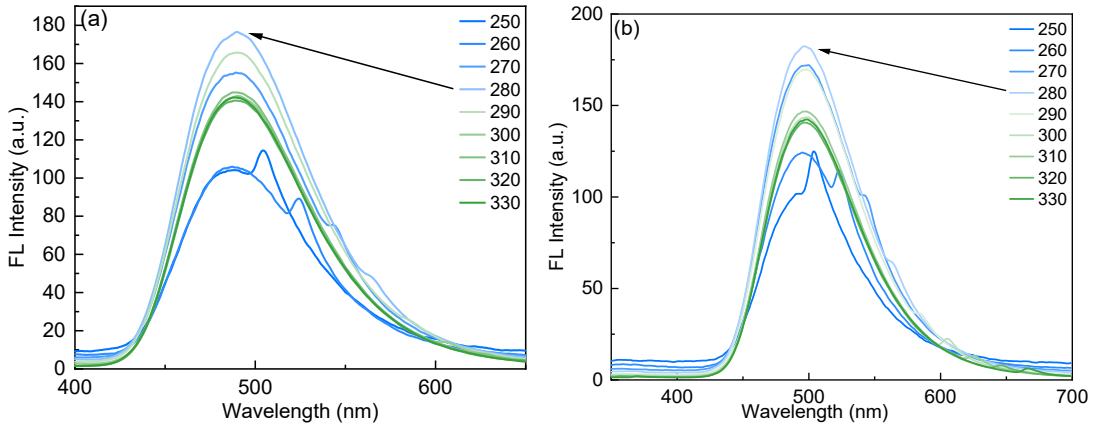


Figure S12. Fluorescence spectra of mHBI(50 μM) under different excitation wavelengths in (a) DCM and (b) n-Hexane.

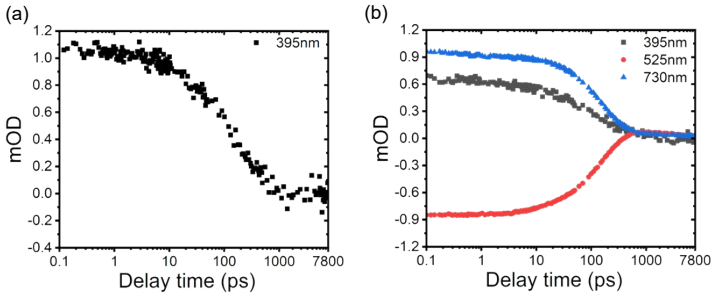


Figure S13. kinetic traces of mHBI in MeCN with (a) 275 and (b) 315 nm excitation at different wavelengths.

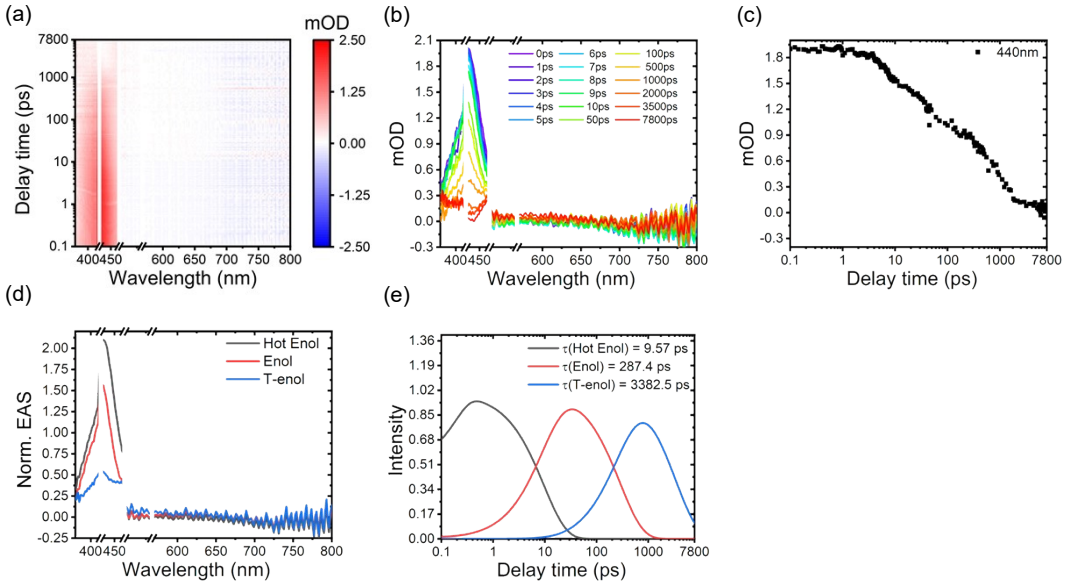


Figure S14. (a) 2D fs-TA spectra, (b) time-resolved fs-TA spectra at selected delays, (c) kinetic traces at 440 nm, (d) EAS feature and (e) evolution traces of EAS species from the global analysis for the fs-TA spectra of mHBI in MeOH with 275 nm excitation.

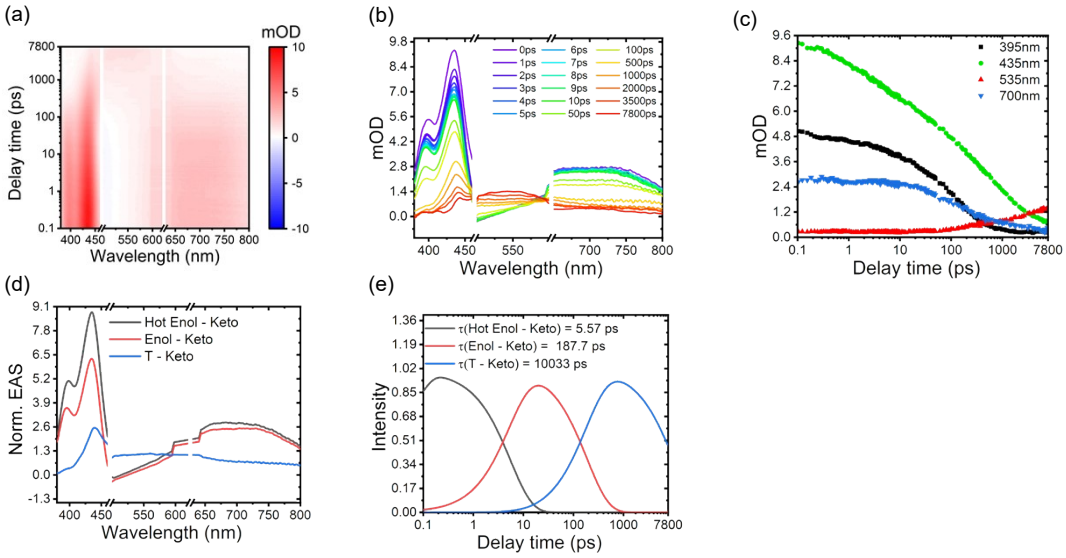


Figure S15 (a) 2D fs-TA spectra, (b) time-resolved fs-TA spectra at selected delays, (c) kinetic traces at different wavelengths, (d) EAS feature and (e) evolution traces of EAS species from the global analysis for the fs-TA spectra of mHBI in MeOH with 315 nm excitation.

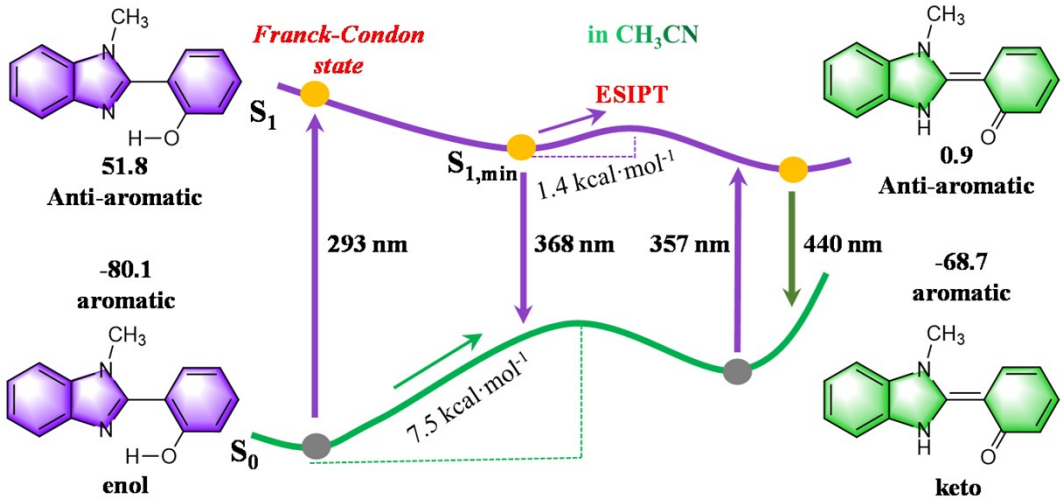
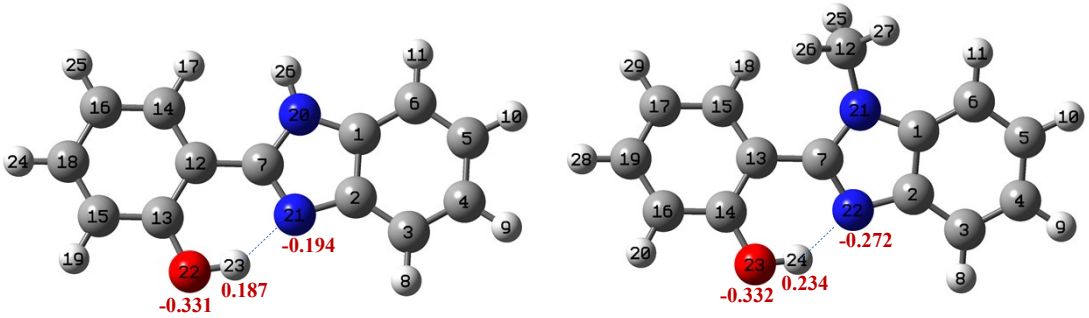


Figure S16. Calculated relative energy, transition energy (nm) and NICS(1)_ZZ values (ppm) of different structures at (TD)MN15/def2-TZVP level using (solvent=acetonitrile) model.



HBI mHBI

Figure S17. Calculated atomic dipolemoment corrected Hirshfeld charges of enol tautomer at MN15/def2-TZVP level using PCM (solvent=acetonitrile) model. (Other charge of atoms are shown in Table S8.)

5. *Tables*

Table S1. The maximum absorption, fluorescence emission and excitation bands (nm) of mHBI in different solvents.

	λ_{abs}^{max}	λ_{em}^{max}		λ_{ex}^{max}	
Solvent	–	$\lambda_{ex=290}$ [a]	$\lambda_{ex=320}$ [a]	$\lambda_{em,1}$ [b]	$\lambda_{em,2}$ [c]
MeCN	**289, 317**	**365, 488**	**491**	**287**	**294, 333**
DCM	291, 319	488	489	–	290, 336
DMF	291, 318	368 [d]	367, 496	298	296, 331
DMSO	291, 318	368 [d]	368, 495	292	296, 333
EA	290, 318	366, 496	495	288	291, 333
EtOH	288 [d]	363 [d]	362, 478	285	284, 323
H_2O	280 [d]	367, 433	430	–	–
MeOH	**286 [d]**	**362 [d]**	**361, 473**	**285**	**281, 328**
n-Hexane	289, 321	498	499	–	289, 332
THF	291, 320	368, 501	498	297	294, 333
Cal. [e]	293, 357	368	440	–	–

[a] Excited wavelength. [b] Derived from Figure S3 (a). [c] Derived from Figure S3 (b). [d] There is an additional shoulder peak. [e] Calculated at the TD-MN15/def2-TZVP levelusing PCM (solvent=acetonitrile) model.

Table S2. The absorbance at 316 nm (A_{316}) for mHBI in various solvents, along with the hydrogen-donating ability (α), hydrogen-accepting ability (β), and polarity of the various solvents.

Solvent	A_{316}	**α***	**β***	**α+β**
MeOH	0.19	0.43	0.47	0.90
EtOH	0.24	0.37	0.48	0.85
DMSO	0.35	0.00	0.88	0.88
DMF	0.55	0.00	0.74	0.74
THF	0.76	0.00	0.48	0.48
MeCN	0.79	0.07	0.32	0.39

* Data from reference 37, 38.

Table S3. Experimental and calculated maximum absorption and emission bands of mHBI at different TDDFT/def2-TZVP levels using PCM(solvent=acetonitrile) model.

TD-DFT	λ_{abs}^{max} [a]		λ_{em}^{max} [a]	
	enol	keto	enol	keto
B3LYP	313.8	377.1	379.8	477.3
CAM-B3LYP	284.8	340.4	358.5	417.1
M06-2X	280.4	- [b]	355.7	422.2
MN15	**293.4**	**356.6**	**368.3**	**440.4**
PBE0	305.7	- [b]	368.5	446.7
WB97X-D	281.7	342.2	355.7	416.5
Exp.	289.4	316.8	365.2	491.0

[a] Maximum absorption and emission peak.

[b] This structure was not obtained.

Table S4. The structural parameters of enol, enol*, keto and keto* in mHBI calculated at (TD)MN15/def2-TZVP levels using PCM (solvent=acetonitrile) model.

	enol	**enol***	**keto**	**keto***
O23–H24[a]	**0.992**	**1.014**	**1.589**	**2.021**
N22–H24	**1.749**	**1.620**	**1.058**	**1.015**
C14–O23	1.344	1.323	1.281	1.261
C13–C14	1.411	1.470	1.447	1.481
C7–C13	1.462	1.939	1.437	1.418
N21–C7	1.370	1.407	1.359	1.386
N22–C7	1.322	1.380	1.058	1.377
N21–C12	1.451	1.450	1.452	1.449
$\Phi_{14\text{-}13\text{-}7\text{-}22}$ [b]	**24.3**	**12.1**	**8.5**	**26.4**

[a] Bond distances in Å

[b] Dihedral angles in degrees.

Table S5. The fitted parameters of Figure 2.

I_{316}	y=-0.11251x+1.04498, R^2=0.98084
I_{365} λ_{ex}=290 nm	y=0.10659x, R^2=0.99499
I_{365} λ_{ex}=320 nm	y=0.12930x-0.31019, R^2=0.99572
I_{max}	y=-0.52235x+491.82353, R^2=0.96908

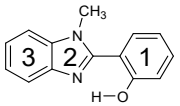
Table S6. The fitted parameters of Figure 3.

I_{365} in methanol	y=38.075x-99257.23, R^2=0.99219; y=-61.468x+20068.57, R^2=0.86498
I_{365} in acetonitrile	y=1.16894x-281.8902, R^2=0.98965; y=-1.37245x+446.461, R^2=0.65363
I_{490}	y=0.59158x-145.44242, R^2=0.99460

Table S7. The time constant of global analysis results of mHBI under 275 and 315 nm excitations in MeCN and MeOH.

Solvent	λ_{exc}/nm	τ_{01}/ps	τ_{12}/ps	τ_{23}/ps
MeCN	275	12.1	261.8	-
	315	6.6	145.6	6149.5
MeOH	275	9.6	287.4	3382.5
	315	5.6	187.7	10033.0

Table S8. Calculated NICS(1)_ZZ values and barrier (ΔE) from enol to keto in the S_0 and S_1 states at (TD)MN15/def2-TZVP level using PCM (solvent=acetonitrile) model.

Structure	NICS(1)_ZZ/ppm					$\Delta E(S_0)$ [a]	$\Delta E(S_1)$ [a]
	Form	1	2	3	total		
	enol	-25.1	-24.7	-30.2	-80.1	7.5	1.4
	enol*	63.7	-2.9	-9.0	51.8		
	keto	-18.7	-19.9	-30.1	-68.7		
	keto*	29.4	-8.0	-20.5	0.9		

[a] Energy barrier of IPT reaction, unit: kcal·mol^{-1}.

Note: NICS(1)_ZZ more negative, more aromaticity; positive signs represent antiaromaticity.

Table S8. Calculated atomic dipolemoment corrected Hirshfeld charges of enol tautomer at MN15/def2-TZVP level using PCM (solvent=acetonitrile) model. (The atom numbers are shown in Figure S15.)

HBI		**mHBI**	
C1	0.010035	C1	-0.08103
C2	-0.01655	C2	-0.04811
C3	-0.13183	C3	-0.09802
C4	-0.14162	C4	-0.13752
C5	-0.14175	C5	-0.15221
C6	-0.13374	C6	-0.02846
C7	0.109784	C7	0.09076
H8	0.13912	H8	0.137902
H9	0.131451	H9	0.131178
H10	0.133187	H10	0.131971
H11	0.147844	H11	0.090396
C12	-0.05326	C12	-0.19419
C13	0.095939	C13	-0.04073
C14	-0.12401	C14	0.062865
C15	-0.15674	C15	-0.09821
C16	-0.14503	C16	-0.12393
H17	0.138673	C17	-0.15857
C18	-0.1151	H18	0.111259
H19	0.132061	C19	-0.115
N20	-0.09924	H20	0.123658
N21	**-0.1937**	N21	0.116454
O22	**-0.3314**	**N22**	**-0.2715**
H23	**0.18667**	**O23**	**-0.3322**
H24	0.14372	**H24**	**0.23435**
H25	0.136405	H25	0.120141
H26	0.279091	H26	0.114011
		H27	0.133569
		H28	0.139231

H29	0.141935

Table S9. Cartesian coordinates of enol, enol*, keto, and keto* optimized at (TD)MN15/def2-TZVP levels using PCM (solvent=acetonitrile) model.

enol				**enol***			
C	1.982075	0.580792	0.036801	C	1.981205	0.598749	-0.01419
C	1.850254	-0.79823	-0.18503	C	1.813259	-0.8269	-0.06221
C	2.983629	-1.60541	-0.29356	C	2.951601	-1.66401	-0.12466
C	4.220783	-0.99596	-0.17365	C	4.192126	-1.05738	-0.12619
C	4.338237	0.386261	0.049738	C	4.338189	0.345933	-0.07236
C	3.222387	1.200557	0.159294	C	3.236203	1.197367	-0.01558
C	-0.14694	0.0173	-0.09156	C	-0.18469	0.061215	0.021807
H	2.890619	-2.67013	-0.46531	H	2.839059	-2.73925	-0.16198
H	5.119987	-1.59333	-0.2542	H	5.084439	-1.66919	-0.17031
H	5.324045	0.825076	0.135264	H	5.334222	0.769735	-0.07969
H	3.31842	2.26619	0.323176	H	3.357735	2.271934	0.011126
C	0.383031	2.438333	0.508635	C	0.47569	2.513277	0.411688
C	-1.60797	0.077617	-0.10645	C	-1.5748	0.12205	-0.04315
C	-2.33962	-1.08615	0.213923	C	-2.34933	-1.11932	0.100965
C	-2.31415	1.23204	-0.46532	C	-2.34106	1.313388	-0.27358
C	-3.7325	-1.03765	0.251006	C	-3.73873	-1.09993	0.086685
C	-3.69764	1.267584	-0.45018	C	-3.71424	1.290459	-0.28531
H	-1.76903	2.107805	-0.78945	H	-1.83275	2.242854	-0.47764
C	-4.40485	0.128475	-0.07179	C	-4.43311	0.09159	-0.08749
H	-4.26715	-1.93977	0.52018	H	-4.25253	-2.04453	0.214045
N	0.695496	1.079187	0.10726	N	0.727887	1.1311	0.054589
N	0.512091	-1.11692	-0.25777	N	0.514731	-1.12778	-0.02729
O	-1.74244	-2.25762	0.491986	O	-1.73754	-2.27945	0.274225
H	-0.78112	-2.17301	0.263913	H	-0.73862	-2.13167	0.184914
H	0.266816	3.097244	-0.35156	H	0.236622	3.124274	-0.45896
H	-0.52852	2.449101	1.100917	H	-0.33996	2.567078	1.129296
H	1.19896	2.807722	1.126691	H	1.370931	2.914041	0.883809
H	-5.48716	0.144343	-0.047	H	-5.515	0.097703	-0.0925
H	-4.21991	2.170463	-0.73615	H	-4.2561	2.210431	-0.46572

keto				**keto***			
C	1.984917	0.585893	0.00387	C	1.98354	0.568385	0.016323
C	1.839358	-0.80275	-0.05968	C	1.885929	-0.82886	-0.13999
C	2.939417	-1.65057	-0.09328	C	3.02088	-1.62281	-0.25696
C	4.191313	-1.05582	-0.06322	C	4.2553	-0.9759	-0.21358
C	4.337606	0.336401	-0.00347	C	4.351899	0.407807	-0.05543
C	3.239044	1.183041	0.030754	C	3.214914	1.208295	0.065557

C	-0.19323	0.11039	-0.02941	C	-0.19957	0.014214	0.04264
H	2.819625	-2.72411	-0.14174	H	2.945525	-2.69561	-0.37036
H	5.075496	-1.67895	-0.08923	H	5.160861	-1.56221	-0.30232
H	5.331806	0.762961	0.013985	H	5.329486	0.871288	-0.02737
H	3.364559	2.256604	0.068286	H	3.291446	2.281251	0.181284
C	0.448066	2.544353	0.240716	C	0.421513	2.409873	0.583103
C	-1.63026	0.114655	-0.03776	C	-1.61183	0.087841	-0.05697
C	-2.29109	-1.16675	0.087963	C	-2.40197	-1.13425	0.220435
C	-2.39598	1.287828	-0.20513	C	-2.30553	1.239176	-0.44104
C	-3.71734	-1.13208	0.126148	C	-3.82091	-1.05127	0.142116
C	-3.76988	1.264126	-0.19429	C	-3.70951	1.272235	-0.4677
H	-1.90212	2.232339	-0.37781	H	-1.76278	2.12443	-0.74271
C	-4.42652	0.033937	-0.00989	C	-4.47013	0.137501	-0.17367
H	-4.22305	-2.083	0.247571	H	-4.37112	-1.95622	0.371306
N	0.703091	1.129212	0.036664	N	0.701922	1.063076	0.126603
N	0.484325	-1.04628	-0.08004	N	0.552341	-1.12581	-0.13216
O	-1.66572	-2.28199	0.158153	O	-1.80935	-2.20291	0.531237
H	-0.13508	-1.90218	-0.03398	H	0.098763	-2.03409	-0.11214
H	0.142287	3.032046	-0.68339	H	0.32619	3.10872	-0.24856
H	-0.31527	2.679129	1.003226	H	-0.49653	2.413759	1.165423
H	1.366924	3.004564	0.592702	H	1.239833	2.735816	1.224393
H	-5.50998	0.003688	0.011621	H	-5.55064	0.184441	-0.20264
H	-4.33397	2.176344	-0.33278	H	-4.20329	2.197443	-0.73639