Switching of Photoinduced Proton Transfer from One Six Member Hydrogen Bonded Ring to Other: A Molecule of Hydrazine and pH Sensor

*VikiBhakta, Nikhil Guchhait**

Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata-700009, India

*Corresponding author. Tel.: +913323508386; fax: +913323519755

E-mail address: nguchhait@yahoo.com (N. Guchhait)

Synthesis Procedure of HBO, HBOB, HBON:

An ethanolic solution (2mmol) of 2-hydroxy-5-bromobenzaldehyde **(HB)** was treated with an equivalent amount of 2-aminophenol. Then the mixture was allowed to reflux overnight under magnetic stirrer to obtain our desire Schiff base (E)-4-bromo-2-(((2-hydroxyphenyl)imino)methyl)phenol with 82% yield. This was collected by suction filtration, washed with ethanol (20 mL) and dried in openair for 24 hours and the product is characterized by NMR spectroscopy. To a stirred solution of 5mmol of this Schiff in DCM, 9mmol of DDQ was added and allowed to stir for overnight to get 2-(benzo[d]oxazol-2-yl)-4-bromophenol **(HBO)**. Then filtrate was collected andpurified by column chromatography using ethyl acetate-hexane mixture eluent with 70% yield. **HBO** was characterized using NMR (Figure S1). The compound **HBO** (2mmol) was suspended in 20mL of glacial acetic acid and treated with 10mmol of hexamethylenetetramine (HMTA). The reaction mixture was refluxed with stirring for 20 h, after which thin-layer chromatography (TLC) analysis showed complete consumption of the starting material. The reaction mixture was then poured onto 100mL chilled 2M HCl solution, whereupon a reddish brown precipitate appeared while being stirred. The solid was filtered, washed with 50mL of water in portions, and dried for overnight in vacuum. The product3-(benzo[d]oxazol-2-yl)-5-bromo-2-hydroxybenzaldehyde (**HBOB)** was purified by column chromatography using ethyl acetate-hexane mixture eluent with 70% yield and characterized using NMR and ESI-MS (Figure S2-S4). A methanolic solution (2mmol) of **HBOB** was treated with an equivalent amount of hydrazine hydrate. Then the mixture was allowed to reflux 8 hoursunder the magnetic stirrer to obtain our desire Schiff base (E)-2-(benzo[d]oxazol-2-yl)-4-bromo-6-(hydrazonomethyl) phenol **(HBON)** with 82% yield. Thiswas collected by suction filtration, washed with ethanol (30 mL) and dried in openair for 24 hours and the product is characterized by NMR spectroscopy (Figure S7-S9).

Time Correlated Single Photon Counting (TCSPC) Measurement

The equation for fluorescence decay is the following

$$I(t) = A + \sum_{i}^{n} B_i e^{\frac{-t}{\tau_i}}$$

τ_1, τ_2, τ_3= Excited state lifetime of components

B1, B2, B3= Normalized Pre-exponential Function

$$I(t) = A + B_1 e^{\frac{-t}{\tau_1}} + B_2 e^{\frac{-t}{\tau_2}} + B_3 e^{\frac{-t}{\tau_3}}$$

$$\text{Relative Amplitude} = \frac{B_i \tau_i}{\sum_{i}^{n} B_i \tau_i}$$

Quantum Yield Measurement:

Utilizing the conventional approach, the fluorescence quantum yield of the chemical in different solvents with different polarity levels was calculated using the following equation in relation to the standard coumarin 153 molecule, whose quantum yield is known (Φ=0.95 in ethanol medium):

$$\Phi_s = \Phi_R \times \frac{A_S}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{\eta_s^2}{\eta_R^2}$$

Where, ‘A’ denotes for area under the curve of the fluorescence spectra, ‘(Abs)’ and ‘η’ denotes the absorbance value and the refractive index ofthe solvents respectively. ‘Φ’ refers

to the fluorescence quantum yield ofthe corresponding compounds. Subscripts ‘R’ and ‘S’ denote reference and sample, respectively. We have added this part in the supporting information file.

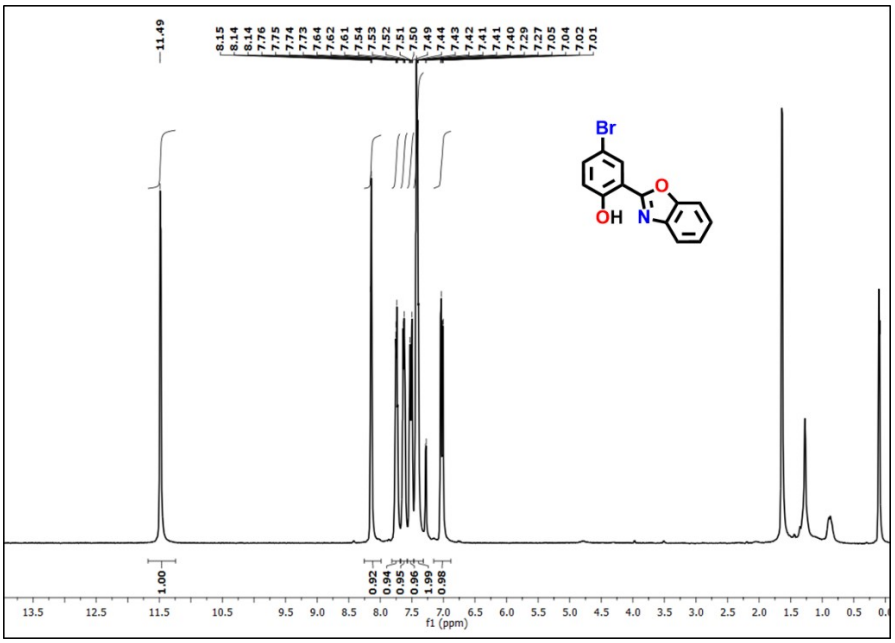

Figure S1: ^{1}H NMR spectrum of **HBO** in $CDCl_3$

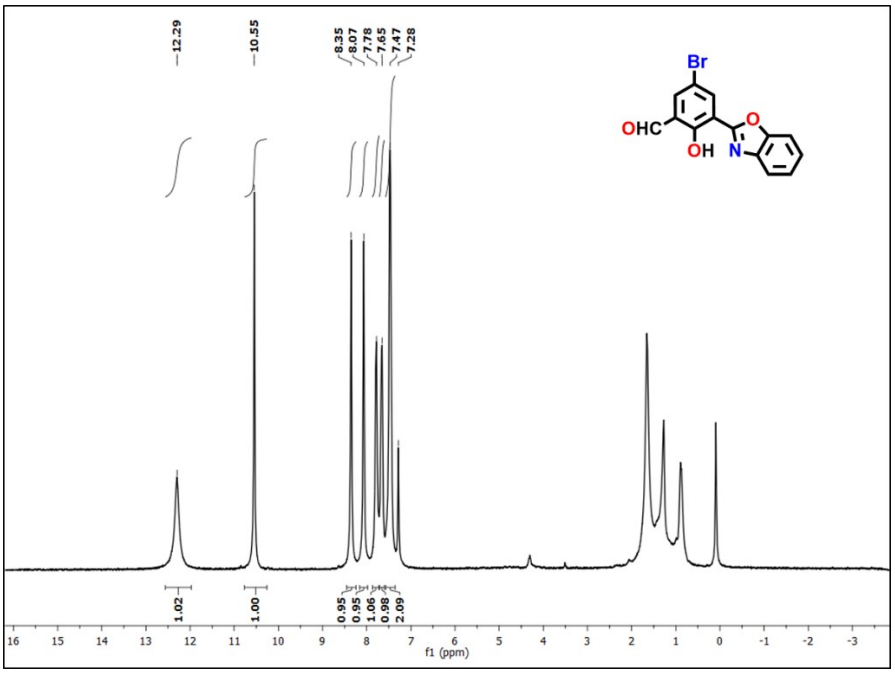

Figure S2: ^{1}H NMR spectrum of **HBOB** in $CDCl_3$

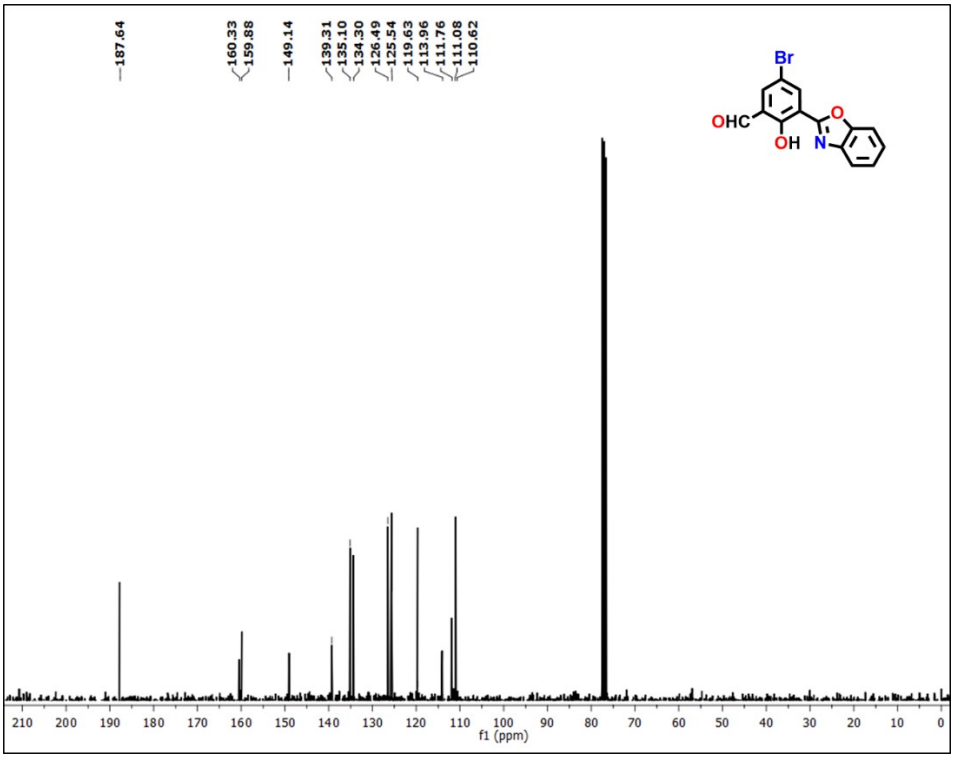

Figure S3: ^{13}C NMR spectrum of **HBOB** in $CDCl_3$

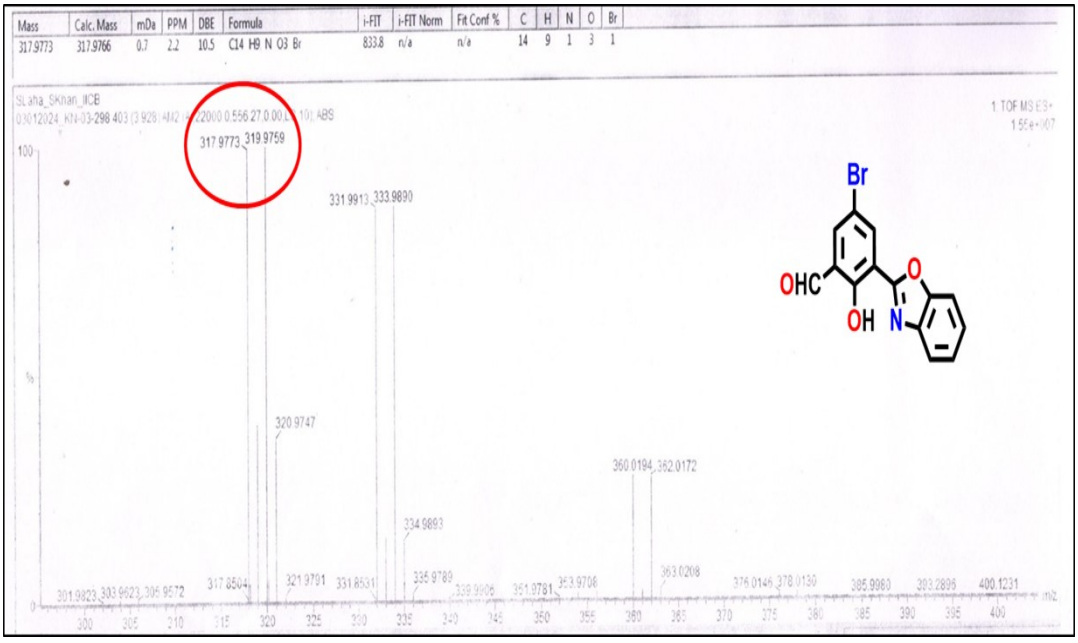

Figure S4: ESI-MS of **HBOB**

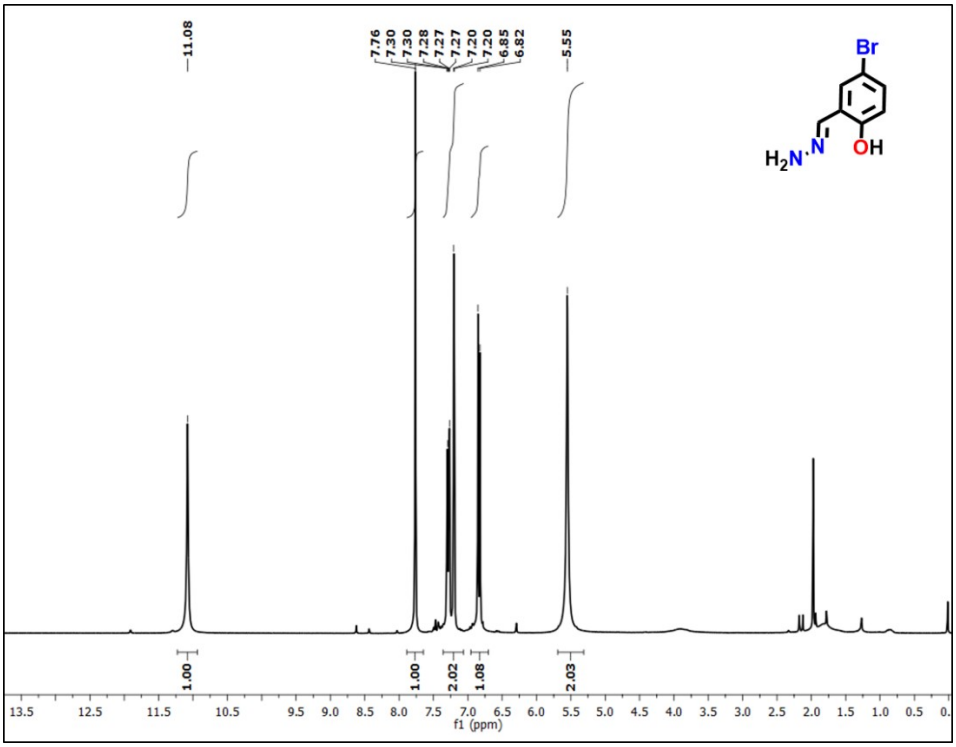

Figure S5: ^{1}H NMR spectrum of **HBN** in $CDCl_3$

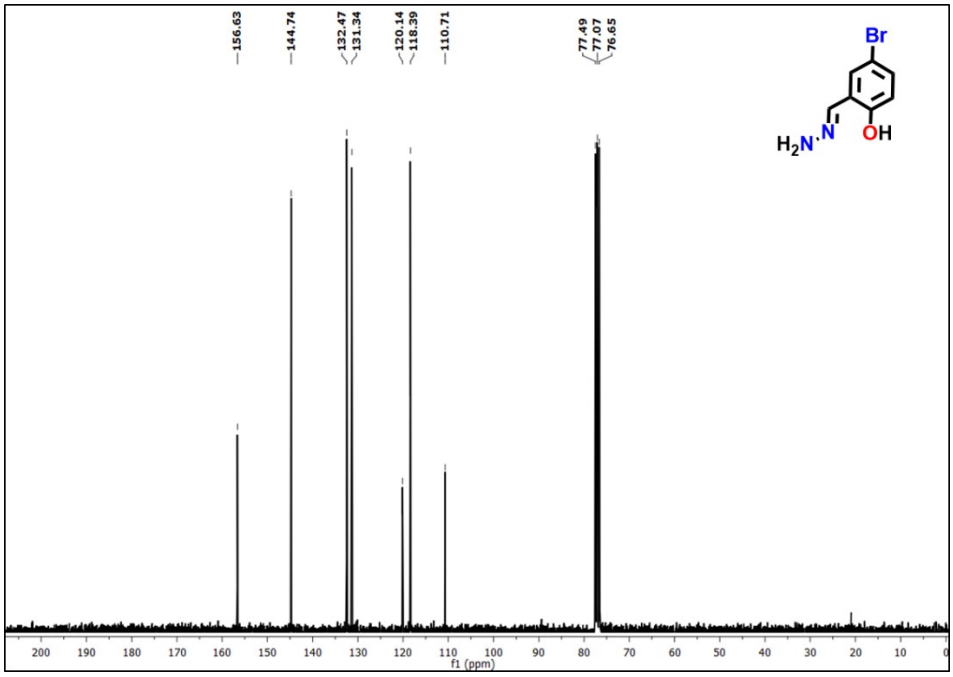

Figure S6: ^{13}C NMR spectrum of **HBN** in $CDCl_3$

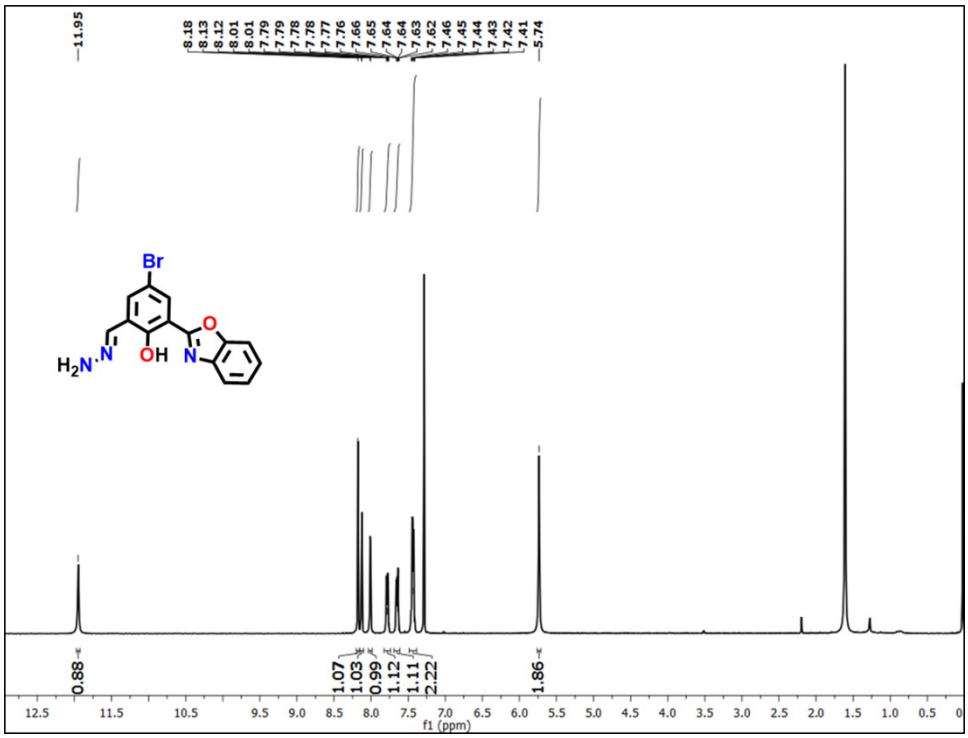

Figure S7: ^{1}H NMR spectrum of **HBON** in $CDCl_3$

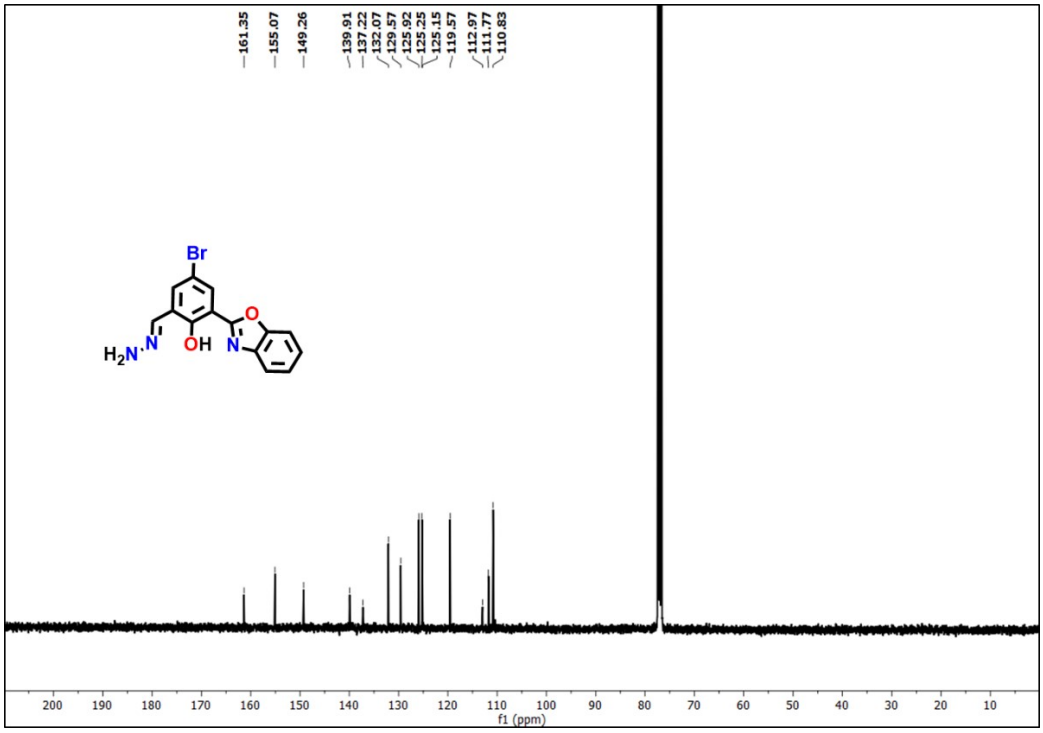

Figure S8: ^{13}C NMR spectrum of **HBON** in $CDCl_3$

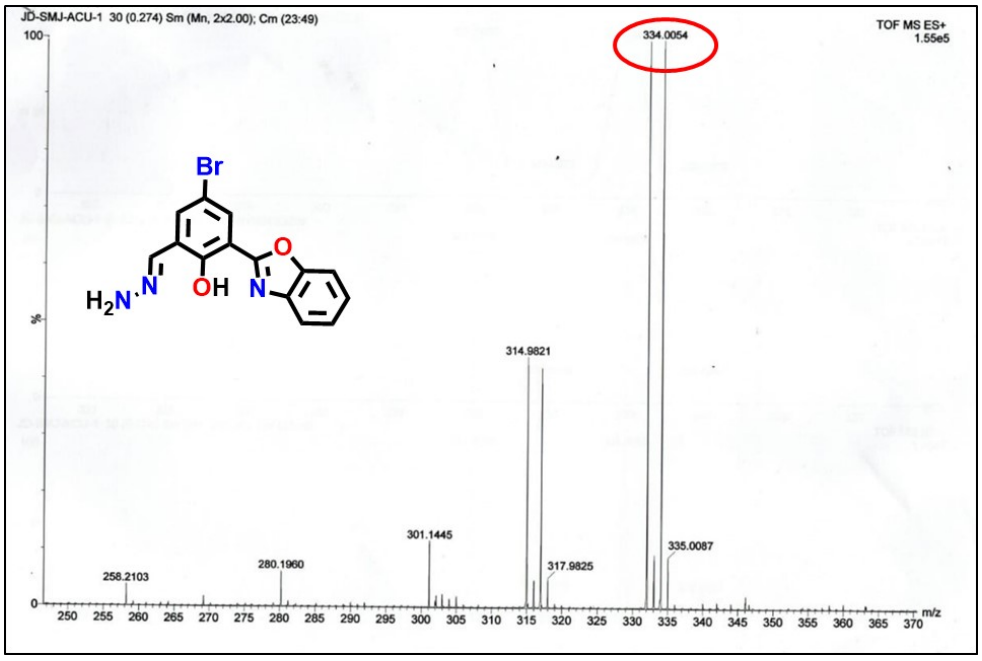

Figure S9: ESI-MS of **HBON**

Table S1. For Crystallographic Parameters of **HBOB**

Parameters	HBOB
CCDC	2351952
Formula	C14H8BrNO3
Formula Weight	318.12
Crystal System	monoclinic
Spacegroup	P $2_1/C_1$
a [Å]	4.775 (2)
b [Å]	11.0709 (5)
c [Å]	22.9812 (9)
α [°]	90
β [°]	95.654 (1)
γ[°]	90
V [Å^3]	1208.96 (9)
h, k, l (max.)	5,13,27
Z	4
D(calc) [g/cm^{-3}]	1.748
F(000)	632
Temperature (K)	273
θ Min-Max [°]	3.57, 25.724
No. of unique data	2299
R(int)	0.069
Observed data [I > 2.0 σ(I)]	675
R1, wR2	0.0348,0.0687
GOF on F^2	1.110

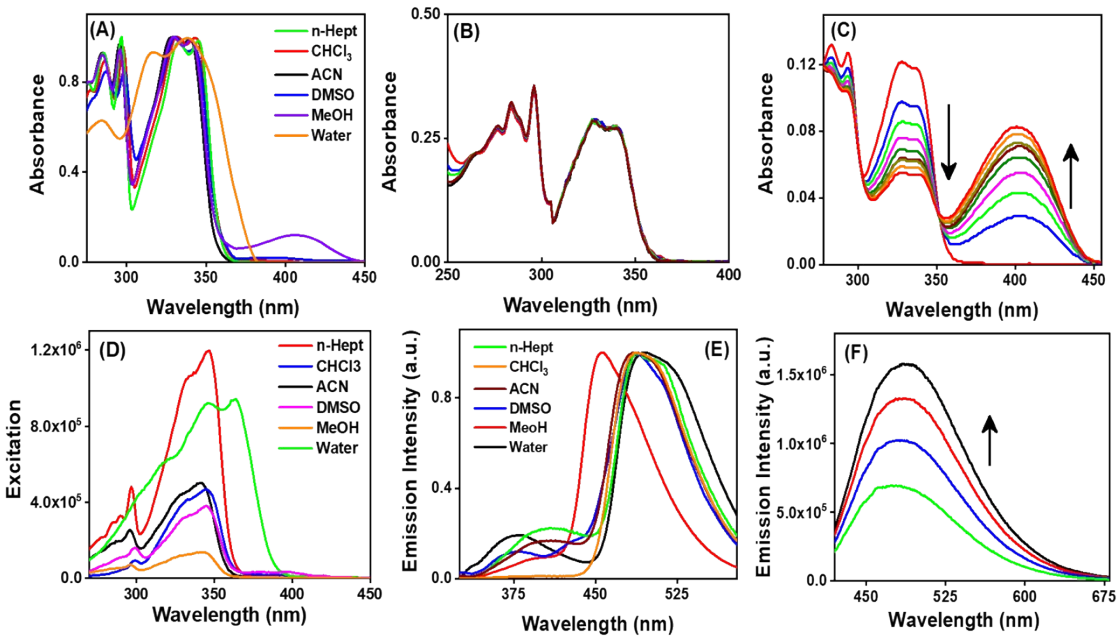

Figure S10: Absorption spectra of **HBO** in (A) different solvent, (B) presence of TFA in ACN solvent, (C) presence of TBAOH in ACN solvent, (D) Excitation spectra in different solvents, Emission spectra of **HBO** in (E) different solvents, (F) presence of TBAOH in ACN solvent.

Table S2: Table of Steady State Spectra of **HBO**

Solvents	λ^{abs}_{max}**(nm)**	λ^{abs}_{max}**(nm)**
HEPT	298, 332, 345	402,483,513
$CHCl_3$	298, 331, 343	402,485,509
ACN	298, 329, 343	399,484,504
DMSO	298, 330, 342	402,486,510
MEOH	298, 330, 342, 407	398,456,492
WATER	284, 316, 338	380,490,519
BASE	298, 330, 342, 405	487

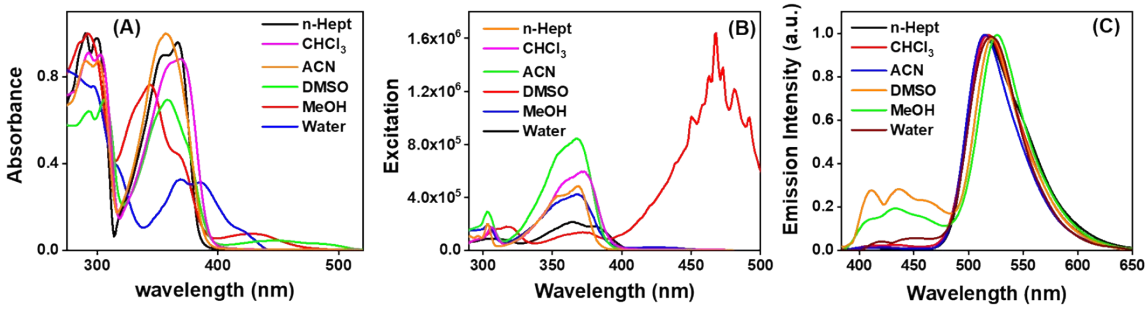

Figure S11: (A) Absorption spectra, (B) Excitation spectra, (C) Emission spectra of **HBOB** in different solvents

Table S3: Table of Steady State Spectra of **HBOB**

Solvents	λ^{abs}_{max}(nm)	λ^{abs}_{max}(nm)	Quantum yield
HEPT	298,354,365	413,518	0.22 ± 0.02
$CHCl_3$	297,360,370	432,519	0.35 ± 0.01
ACN	296,351,356	427,516	0.30 ± 0.02
DMSO	297,350,357,458	436,522	0.12 ± 0.01
MEOH	291,345,368,432	432,526	0.23 ± 0.03
WATER	295,368,386,423	440,520	0.09 ± 0.01
BASE	296,351,356,457	520	

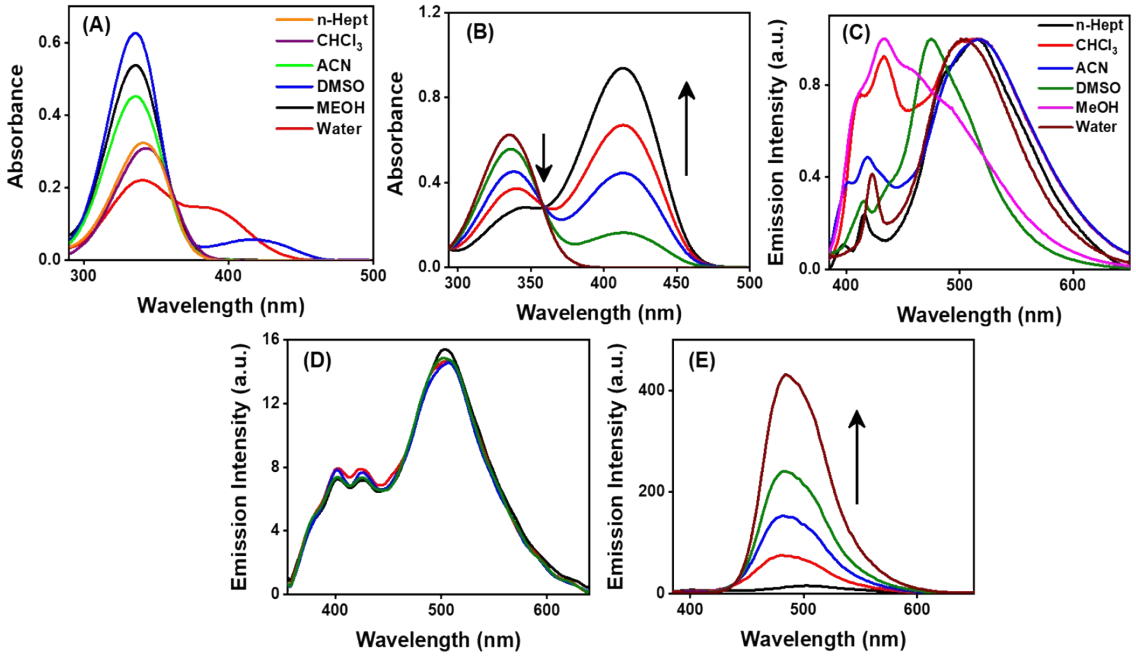

Figure S12: Absorption spectra of **HB** in (A) different solvent, (B) presence of TEA in ACN solvent, Emission spectra of **HB** in (E) different solvents, (B) presence of TFA in ACN solvent, (F) presence of TEA in ACN solvent.

Table S4: Table of Steady State Spectra of **HB**

Solvents	λ^{abs}_{max}(nm)	λ^{abs}_{max}(nm)
HEPT	341	403,515
$CHCl_3$	342	431,514
ACN	336	413,517
DMSO	335,420	414,476
MEOH	336	435,491
WATER	339,391	403,504
BASE	343,412	483

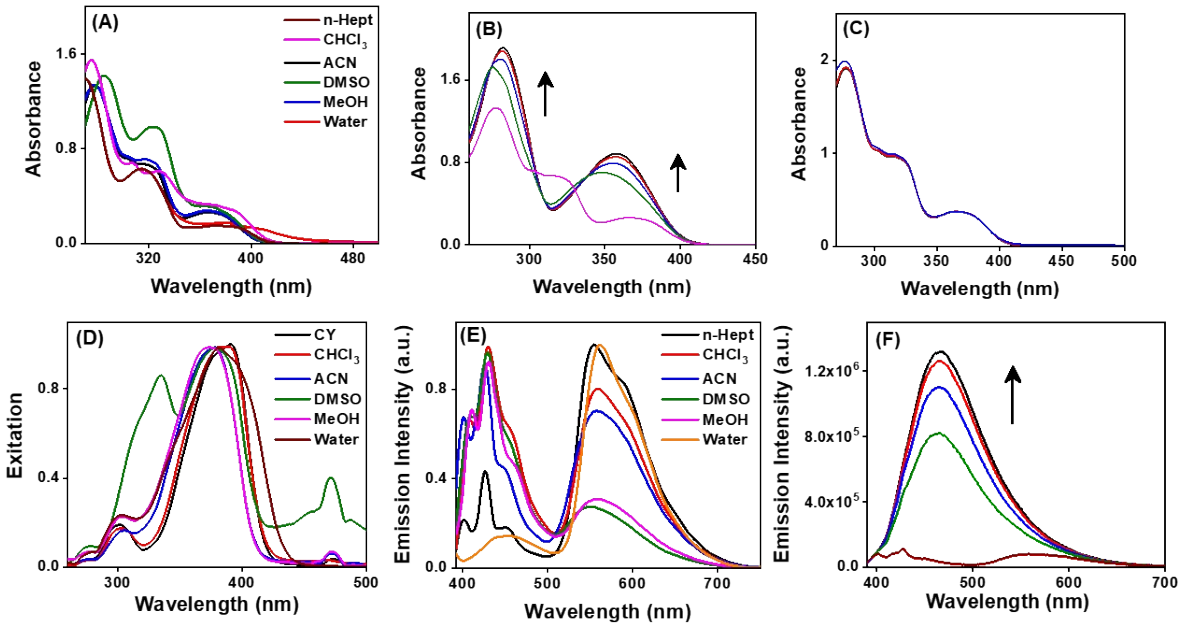

Figure S13: Absorption spectra of **HBN** in (A) different solvent, (B) presence of TEA in ACN solvent,(C) presence of TEA in ACN solvent, (D) Excitation spectra of HB, Emission spectra of HB in (E) different solvents, (F) presence of TFA in ACN solvent.

Table S5: Table of Steady State Spectra of **HBN**

Solvents	λ^{abs}_{max}(nm)	λ^{em}_{max}(nm)
HEPT	273,316,385	430,554,588
$CHCl_3$	276,327,382	430,558,587
ACN	278,319,370	429,560
DMSO	285,325,371	430,551
MEOH	378,320,370	430,557
WATE	270,314,390	452,560

R		
ACID	270,358	463

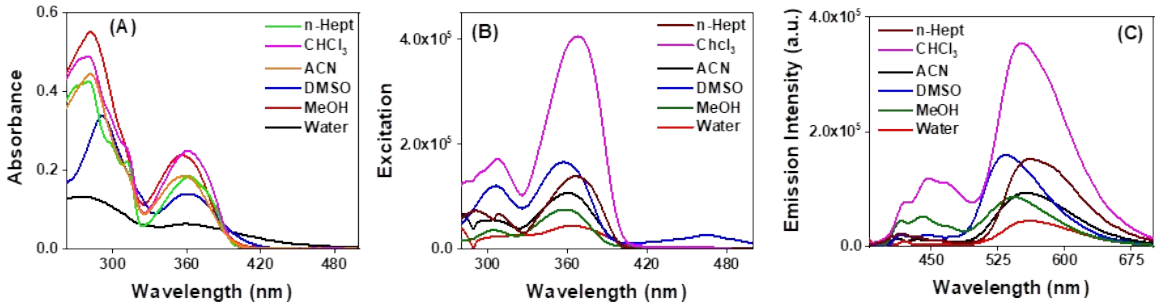

Figure S14: (A) Absorption spectra, (B) Excitation spectra, (C) Emission spectra of **HBON** in different solvents.

Table S6: Table of Steady State Spectra of **HBON**

Solvents	λ^{abs}_{max}(nm)	λ^{abs}_{max}(nm)	Quantum yield
HEPT	281,362	437,559,584	0.15 ± 0.01
$CHCl_3$	280,361	445,551	0.20 ± 0.02
ACN	282,358	438,547	0.10 ± 0.01
DMSO	291,361	440,532	0.09 ± 0.01

MEOH	292,356	441,541	0.13 ± 0.02
WATER	292,362	421,561	0.12 ± 0.01
BASE	358,440	445,500	0.22 ± 0.03
ACID	280,382	560	0.30 ± 0.02

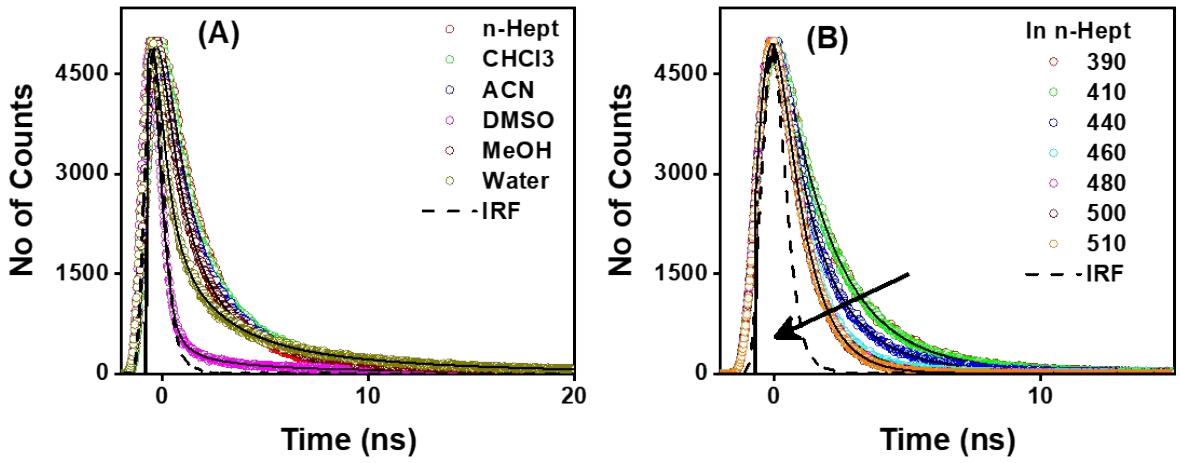

Figure S15: Emission decays of **HBO** in (λ_{ex}=314nm) (A) various solvents at 390nm (B) n-Hept at different monitoring wavelength. The dashed lines represent the IRF of the instrument. The black solid lines represent the best multiexponential fit provided to the emission decay signals.

Table S7. Excited state lifetime parameters of **HBO**

solvent	Wavelength(nm)	τ_1/α_1	τ_2/α_2	τ_3/α_3
HEPT	**390**	0.63/7	1.89/82	5/11
HEPT	**410**	0.61/5	1.87/85	4.76/10
HEPT	**440**	0.79/31	1.81/69	
HEPT	**460**	0.90/80	1.95/20	
HEPT	**500**	0.94/100		
HEPT	**510**	0.97/100		
$CHCl_3$	**390**	0.65/19	2.07/55	6.09/26
$CHCl_3$	**510**	1.12/100		
DMSO	**390**	0.148/73	2.38/11	11.65/16
DMSO	**510**	0.33/84	2.03/16	
ACN	**390**	0.35/16	1.98/59	7.14/25
ACN	**510**	0.328/98	1.48/2	
MeOH	**390**	0.58/22	1.86/48	7.19/30
MeOH	**500**	0.38/56	1.557/2	0.40/42

MeOH	**510**	0.30/91	2.48/5	0.93/4
H_2O	**390**	0.39/31	2.24/32	0.93/4
H_2O	**510**	-	1.7/6	5.96/94

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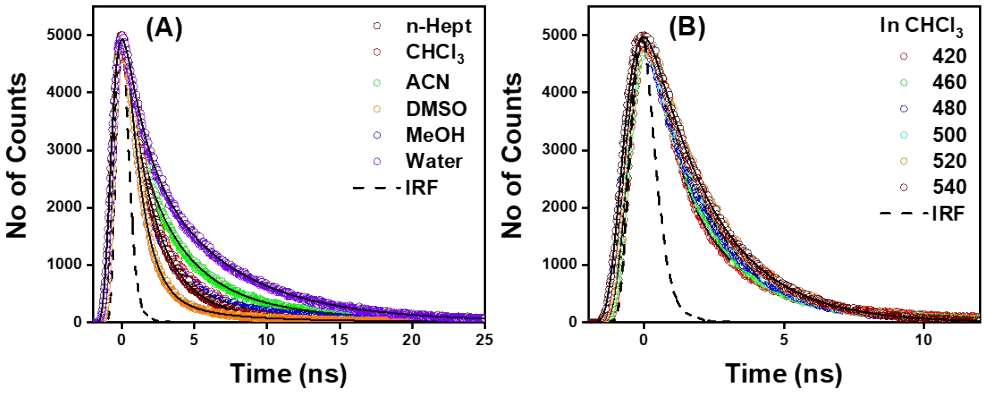

Figure S16: Emission decays of **HBOB** in (λ_{ex}=314nm) (A) various solvents at 410 nm (B) $CHCl_3$ at different monitoring wavelength. The dashed lines represent the IRF of the instrument. The black solid lines represent the best multiexponential fit provided to the emission decay signals.

Table S8. Excited state lifetime parameters of **HBOB**

solvent	**Wavelength(nm)**	**τ_1/α_1 (ns)**	**τ_2/α_2 (ns)**	**τ_3/α_3 (ns)**

HEPT	**420**	0.88/18	2.18/69	8.65/13
HEPT	**520**		2.19/100	
$CHCl_3$	**420**	0.74/24	2.3/63	9/14
$CHCl_3$	**460**	0.65/10	2.09/81	6.77/8
$CHCl_3$	**480**	0.75/12	2.17/89	
$CHCl_3$	**500**	0.87/72	2.21/93	
$CHCl_3$	**520**		2.27/100	
$CHCl_3$	**540**		2.18/100	
DMSO	**420**	0.98/71	3.34/19	12.83/10
DMSO	**520**		2.34/100	
ACN	**420**	0.54/14	3.0/57	8.86/29
ACN	**520**		2.37/100	
MeOH	**420**	0.78/29	2.54/50	8.75/21
MeOH	**520**	0.74/35	2.46/65	
H2O	**420**	1.15/16	5.46/73	13.48/11
H2O	**520**	1.13/25	2.72/75	
BASE	**520**		2.37/100	

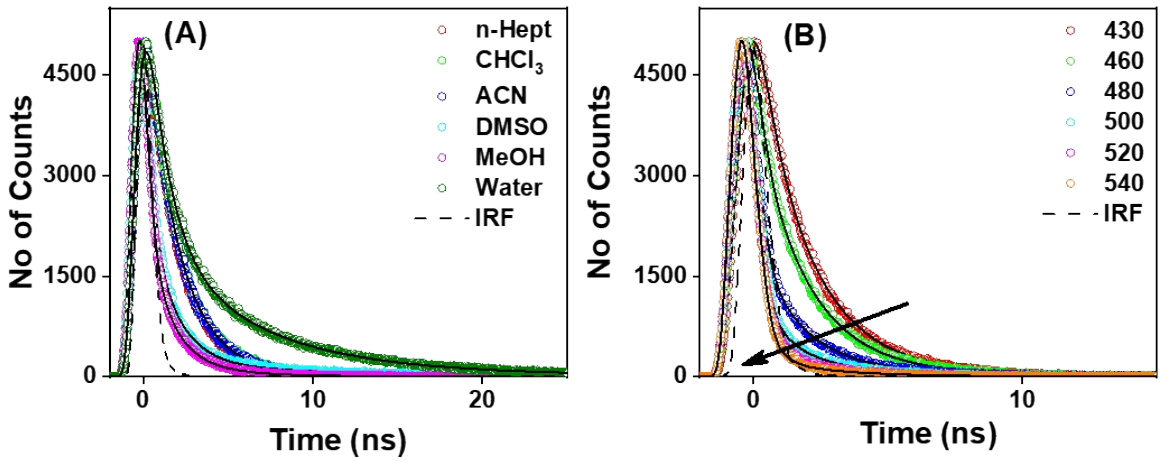

Figure S17: Emission decays of **HB** in (λ_{ex}=314nm) (A) various solvents at 410 nm (B) $CHCl_3$ at different monitoring wavelength. The dashed lines represent the IRF of the instrument. The black solid lines represent the best multiexponential fit provided to the emission decay signals.

Table S9. Excited state lifetime parameters of **HB**

Solvent	**Wavelength(nm)**	**τ_1(ns)/α_1**	**τ_2(ns)/α_2**	**τ_3(ns)/α_3**

Heptane	**430**	1.28/62%	2.7/37%	-
Heptane	**500**	0.08/79%	1.9/20%	-
$CHCl_3$	**430**	0.5/14.8%	1.9/80%	5.8/4.3%
$CHCl_3$	**460**	0.1/26.3%	1.8/65.6%	4.9/8%
$CHCl_3$	**480**	0.1/54%	1.7/38%	4.6/7%
$CHCl_3$	**500**	0.1/72%	1.7/22%	4.6/5%
$CHCl_3$	**520**	0.1/84%	2.4/15%	-
$CHCl_3$	**540**	0.1/88%	2.6/11%	-
DMSO	**430**	0.2/37%	1.6/44%	10/19%
DMSO	**490**	0.17/23%	2.9/65%	11/11%
MeOH	**430**	0.15/51%	1.4/39%	4.2/10%
MeOH	**490**	0.1/51.4%	1.3/36%	3.6/11%
H_2O	**430**	1.14/31%	5.5/54%	14/15%
H_2O	**490**	0.7/37%	3.1/35%	10/28%
Base	**490**	0.35/27	2.9/73	

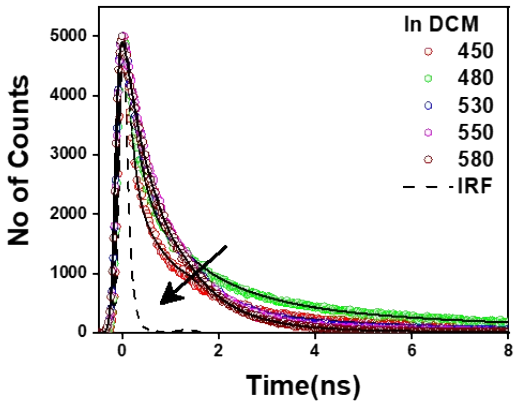

Figure S18: Emission decays of **HBON** in (λ_{ex}=403nm) DCM at different monitoring wavelength. The dashed lines represent the IRF of the instrument. The black solid lines represent the best multiexponential fit provided to the emission decay signals

Table S10. Excited state lifetime parameters of **HBON**

solvent	Wavelength(nm)	τ_1	α_1	τ_2	α_1	τ_3	α_3	χ^2
HEPT	**550**			0.722	92.24%	2.197	7.76%	1.13
HEPT	**530**	0.084	10.84%	0.811	79.63%	4.480	9.53%	1.02
HEPT	**480**	0.062	23.25%	1.264	28.04%	5.195	48.71%	1.05

$CHCl_3$	**550**	0.114	11.69%	1.180	76.25%	5.394	12.07%	1.02
DCM	**580**	0.092	6.39%	0.876	87.5%	4.727	6.11%	1.10
DCM	**550**	0.097	6.68%	0.886	83.25%	5.186	10.07%	0.93
DCM	**530**	0.129	7.17%	0.886	76.46%	5.568	16.37%	1.04
DCM	**480**	0.224	16.62%	1.321	36.6%	6.397	46.78%	1.02
DMSO	**480**	0.135	16.46%	0.731	38.83%	3.150	44.71%	1.00
DMSO	**550**	0.187	40.68%	0.723	37.09%	2.408	22.23%	1.00
ACN	**480**	0.055	29.4%	0.636	51.02%	3.781	19.59%	1.23
ACN	**550**			0.399	79.85%	0.849	20.15%	1.20
MeOH	**480**	0.0866	39.94%	0.747	41.02%	2.537	19.04%	1.15
MeOH	**550**	0.1273	48.42%	0.586	41.69%	2.50	9.89%	0.95
H_2O	**550**	0.037	18.05%	0.723	22.43%	1.731	59.52%	1.16
ACID	**550**	0.089	2.82%	2.059	97.18%			0.99
ACID	**480**	0.094	6.07%	0.6777	66.0%	3.762	27.93%	1.01
BASE	**450**	0.0745	7.4%	1.35	61.17%	3.50	31.43%	0.95

BASE	**500**	0.88	28.57%	1.53	71.34%	1.02

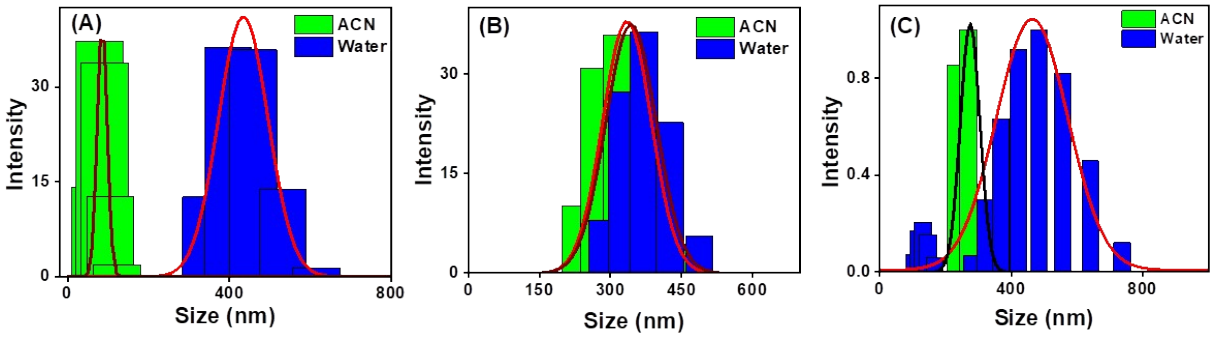

Figure S19: Dynamic Light Scattering spectra of (A) **HBO**, (B) **HBOB**, (C) **HBON**

Solvent abbreviation Index

Abbreviation	**Solvent name**
H	Heptane
$CHCl_3$	Chloroform
DCM	Dichloromethane
ACN	Acetonitrile
DMSO	DimethylSulfoxide
MeOH	Methanol
W	Water

THF	Tetrahydrofuran
TFA	Trifluroacetic Acid
TEA	Triethylamine
TBAOH	Tetrabutylammonium Hydroxide