Electronic Supplementary Information (ESI)

Controlled tuning of radiative–nonradiative transition via solvent perturbation: Franck–Condon emission vs. aggregation caused quenching

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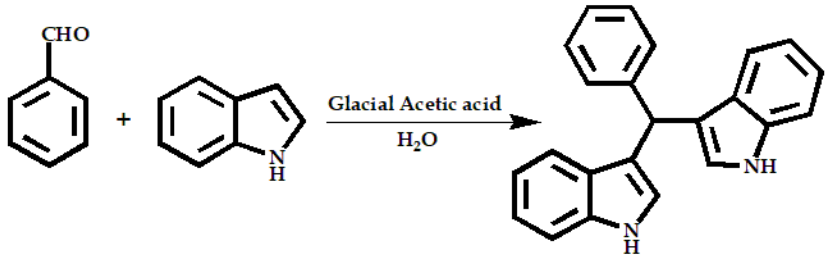
1. Synthetic outline:



Scheme S1 Synthetic outline for 3,3'-bisindolyl(phenyl)methane (BIPM).

2. ^{1}H-NMR:

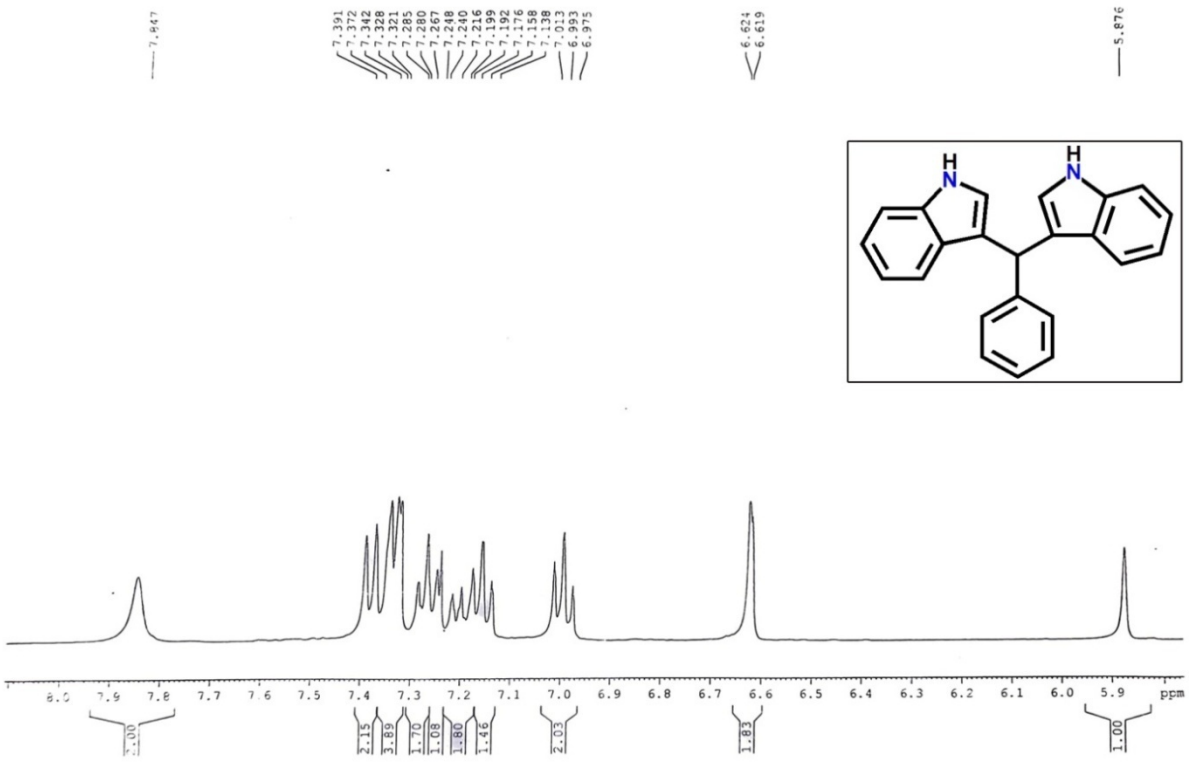


Fig. S1 ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (brs, 2H, –NH), 7.39–7.14 (m, 11H, -ArH), 6.99 (t, 2H, J=15.2 Hz, -ArH), 6.62 (d, 2H, J=2 Hz, -ArH), 5.88 (s, 1H, -CH).

3. ^{13}C-NMR:

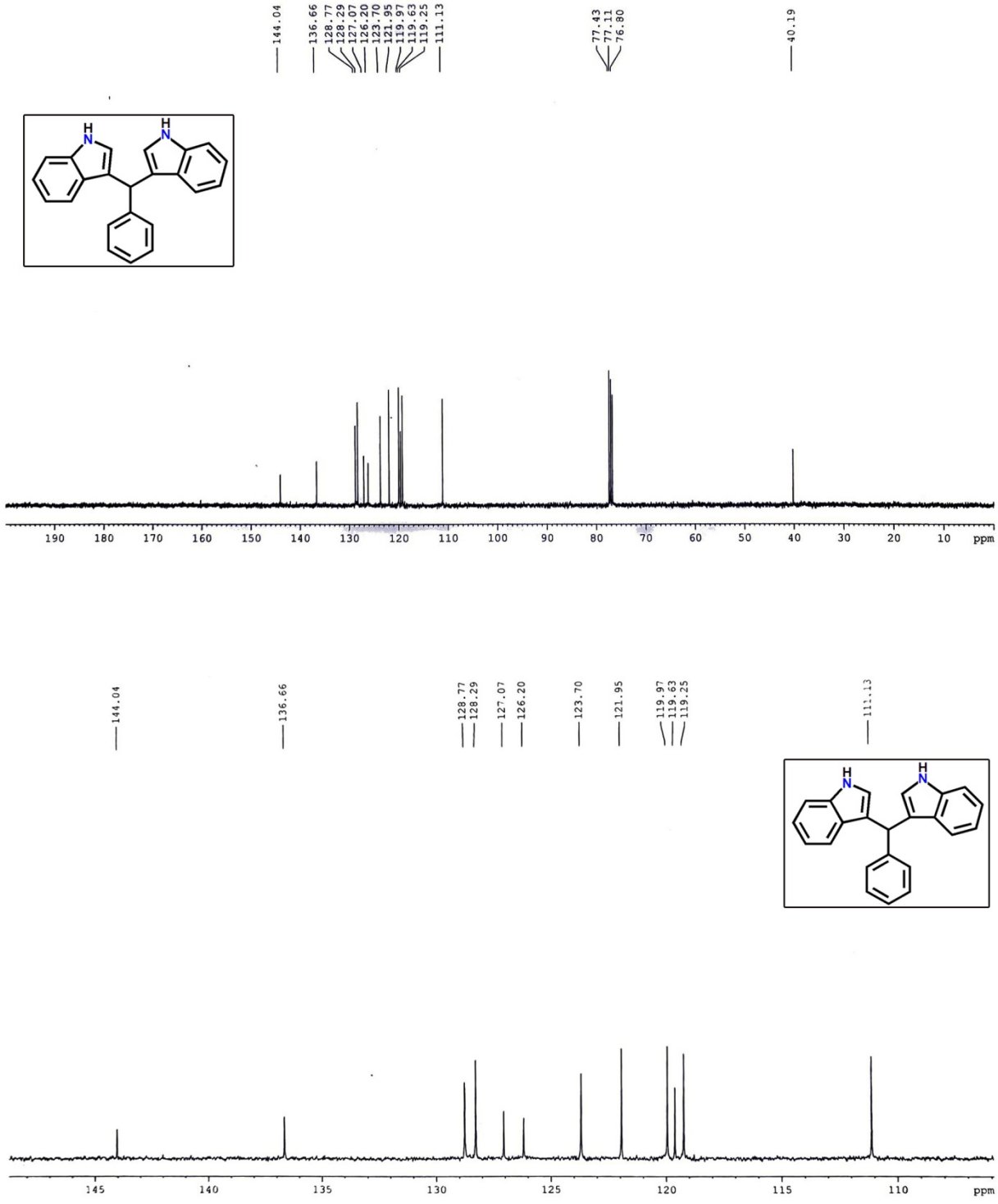


Fig. S2 ^{13}C-NMR of BIPM (100 MHz, $CDCl_3$): δ (ppm) 144.0, 136.7, 128.8, 128.3, 127.1, 126.2, 123.7, 122.0, 120.0, 119.6, 119.3, 111.1, 40.2.

4. Experimental and computational results:

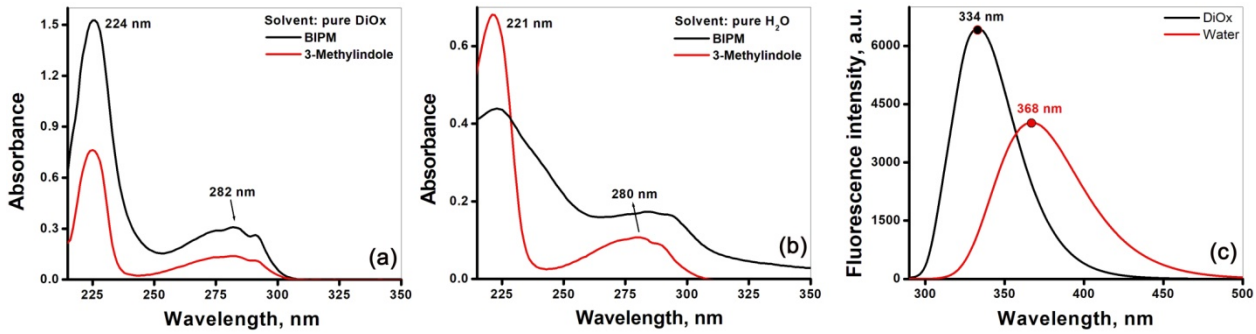


Fig. S3 Comparisons of the absorption spectra of BIPM and 3-methylindole in pure (a) DiOx and (b) H_2O; (c) fluorescence spectra of 3-methylindole in pure DiOx and H_2O. λ_{ex} = 280 nm, [BIPM] = 22.4 µM and [3-methylindole] = 22.4, Temp. 298 K.

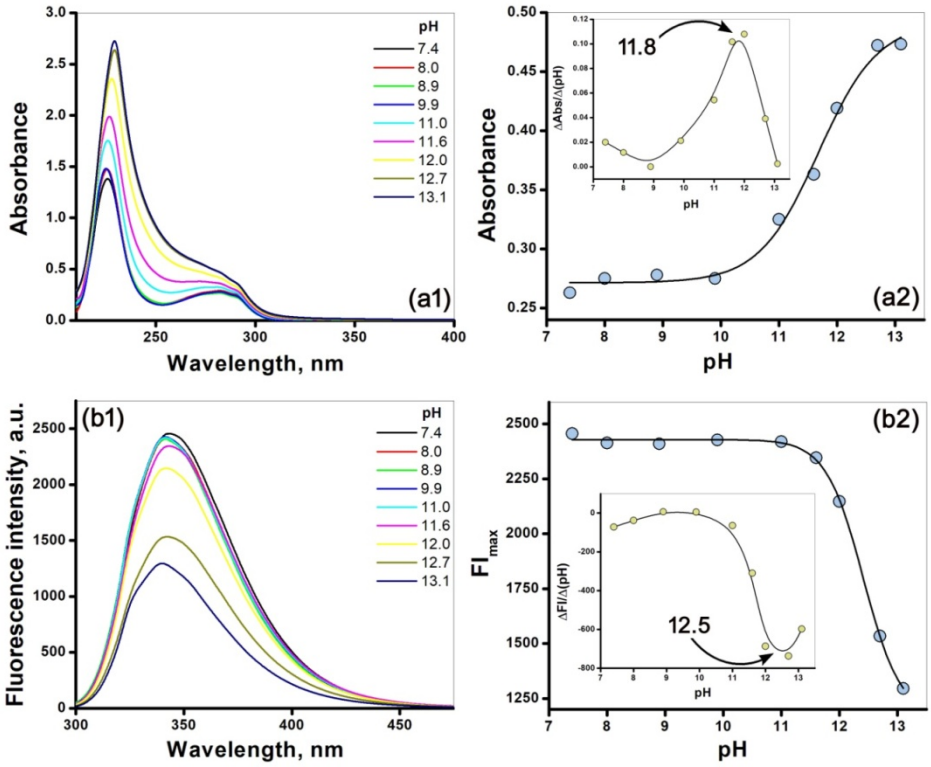


Fig. S4 (a1) Absorption and (b1) fluorescence pH titration curves for BIPM at 40% f_w; plots (a2) and (b2) show the sigmoidal changes in the absorbance value at 282 nm and fluorescence intensity at emission maxima with pH (corresponding derivative plots in the insets), respectively. λ_{ex} = 280 nm, [BIPM] = 22.44 µM, Temp. 298 K.

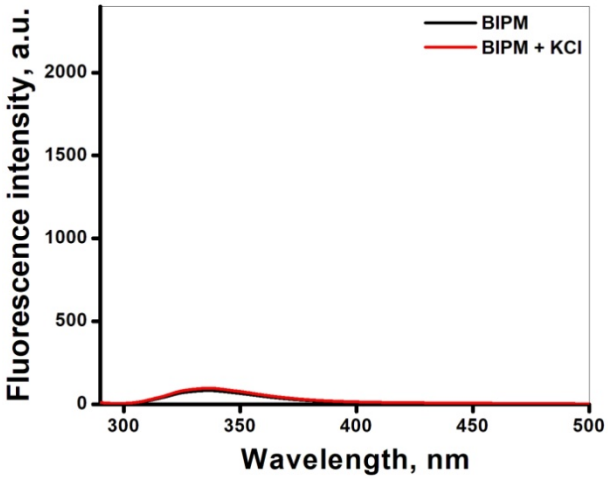


Fig. S5 Fluorescence spectra of BIPM in presence and absence of KCl at 13.1 pH in the solvent system of 100% f_w. λ_{ex} = 280 nm, [BIPM] = 22.44 µM, Temp. 298 K.

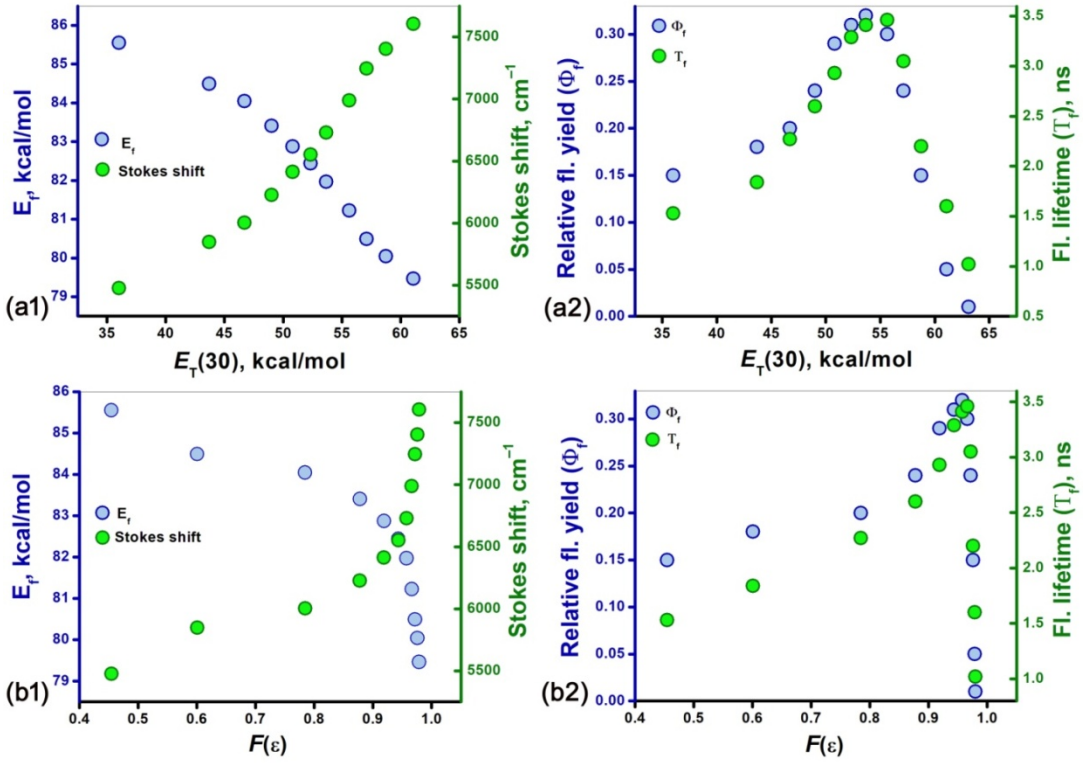


Fig. S6 Plots of energy of fluorescence, Stokes shift, relative fluorescence yield and fluorescence lifetime against the (a) Reichardt's solvent polarity parameter, $E_T(30)$ and (b) Onsager's solvation function, $F(\epsilon)$.

		Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm): 248.4	Peak 1:	279.7	99.1	111.3
PdI: 0.176	Peak 2:	5110	0.9	539.2
Intercept: 0.938	Peak 3:	0.000	0.0	0.000
Result quality : Good				

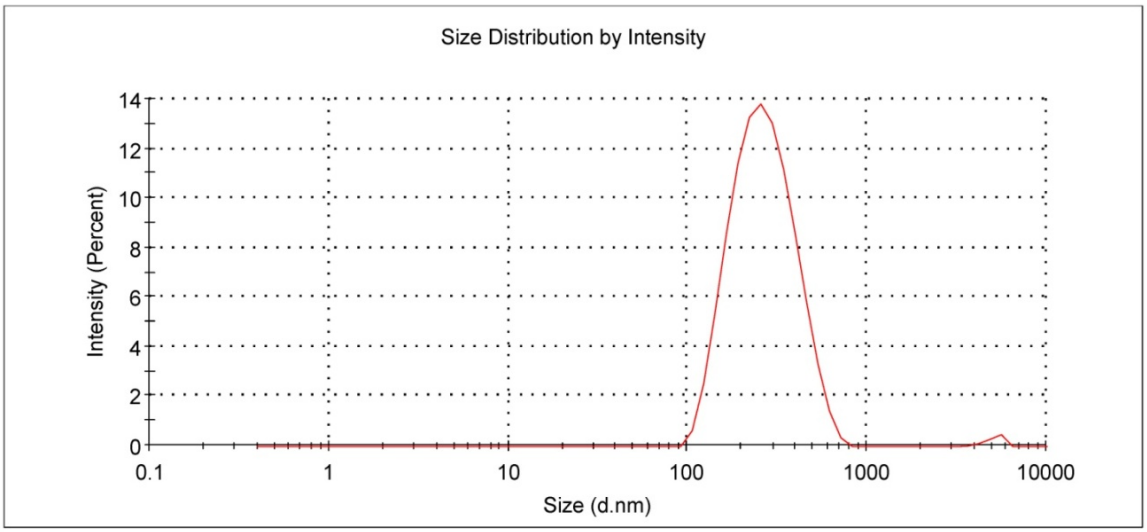


Fig. S7 Particle size distribution of BIPM-aggregates in pure H_2O from DLS measurement. [BIPM] = 22.44 µM; Temp. 298 K.

Table S1 Optimized energies of S_0 and S_1-states of BIPM in pure DiOx and pure H_2O.

Solvent	S_0 (au)	S_1 (au)	S_0-S_1 (kJ mol^{-1})	µ (S_0), Debye	µ (S_1), Debye
DiOx	-996.77926002	-996.62491282	405.1614	3.67	3.50
H_2O	-996.78882239	-996.64103655	388.0117	4.61	5.78

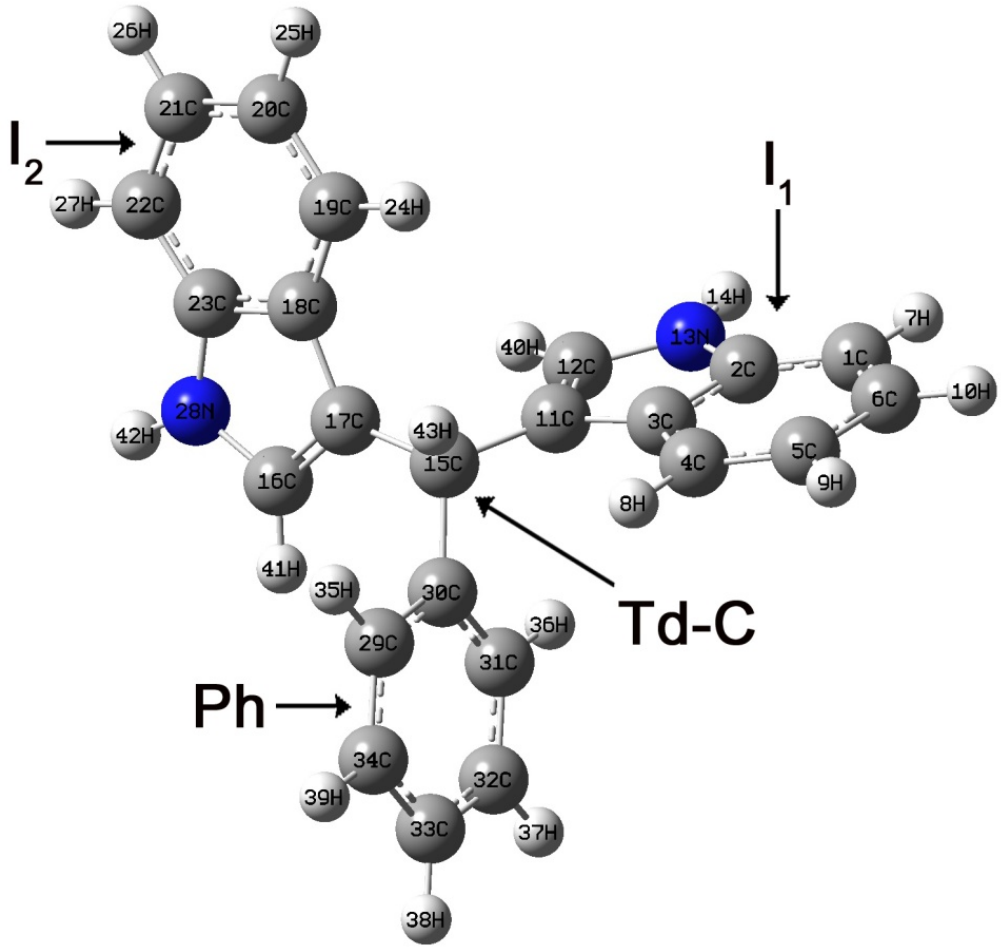


Fig. S8 Optimized geometry of BIPM (S_0) showing the atom numbers.

Table S2 Atomic and group NBO charges of the S_0 and S_1 states of BIPM in pure DiOx. The atom numbers and the groups were according to Fig. S8.

DiOx (S_0)							
I-1		**I-2**		**Ph**		**Td-C**	
Atom no.	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**
H8	+0.210	H24	+0.212	H36	+0.215	H43	+0.222
H9	+0.203	H25	+0.204	H37	+0.205	C15	-0.265
H10	+0.203	H26	+0.203	H38	+0.204		
H7	+0.209	H27	+0.209	H39	+0.205		
H14	+0.411	H43	+0.411	H35	+0.206		
H40	+0.220	H41	+0.220	C30	-0.002		
C11	-0.086	C17	-0.082	C31	-0.214		
C3	-0.090	C18	-0.092	C32	-0.198		
C4	-0.193	C19	-0.194	C33	-0.211		
C5	-0.228	C20	-0.229	C34	-0.200		
C6	-0.209	C21	-0.209	C29	-0.206		
C1	-0.240	C22	-0.240				
C2	+0.156	C23	+0.155				
N13	-0.548	N28	-0.542				
C12	-0.003	C16	-0.005				
Total gr. charge = +0.015			**+0.021**		**+0.004**		**-0.043**
DiOx (S_1)							
I-1		**I-2**		**Ph**		**Td-C**	
Atom no.	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**
H8	+0.213	H24	+0.216	H36	+0.216	H43	+0.218
H9	+0.203	H25	+0.205	H37	+0.205	C15	-0.269
H10	+0.201	H26	+0.205	H38	+0.204		
H7	+0.210	H27	+0.210	H39	+0.205		
H14	+0.411	H43	+0.409	H35	+0.206		
H40	+0.225	H41	+0.224	C30	-0.004		
C11	-0.089	C17	-0.081	C31	-0.212		
C3	-0.099	C18	-0.104	C32	-0.198		
C4	-0.194	C19	-0.192	C33	-0.211		
C5	-0.226	C20	-0.235	C34	-0.199		
C6	-0.216	C21	-0.212	C29	-0.208		
C1	-0.237	C22	-0.231				
C2	+0.150	C23	+0.151				
N13	-0.534	N28	-0.544				
C12	-0.007	C16	-0.001				
Total gr. Charge = +0.011			**+0.020**		**+0.004**		**-0.051**

Table S3 Atomic and group NBO charges of the S_0 and S_1 states of BIPM in pure H_2O. The atom numbers and the groups were according to Fig. S8.

Water (S_0)							
I-1		**I-2**		**Ph**		**Td-C**	
Atom no.	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**
H8	+0.212	H24	+0.213	H36	+0.217	H43	+0.224
H9	+0.207	H25	+0.208	H37	+0.210	C15	-0.267
H10	+0.208	H26	+0.208	H38	+0.210		
H7	+0.218	H27	+0.218	H39	+0.211		
H14	+0.424	H43	+0.424	H35	+0.210		
H40	+0.224	H41	+0.224	C30	-0.002		
C11	-0.090	C17	-0.087	C31	-0.220		
C3	-0.097	C18	-0.097	C32	-0.201		
C4	-0.205	C19	-0.203	C33	-0.216		
C5	-0.235	C20	-0.235	C34	-0.202		
C6	-0.218	C21	-0.218	C29	-0.212		
C1	-0.240	C22	-0.240				
C2	0.152	C23	+0.151				
N13	-0.540	N28	-0.539				
C12	-0.002	C16	-0.005				
Total gr. Charge = +0.018			**+0.022**		**+0.005**		**-0.043**
Water (S_1)							
I-1		**I-2**		**Ph**		**Td-C**	
Atom no.	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**	**Atom no.**	**Charge**
H8	+0.210	H24	+0.210	H36	0.218	H43	+0.233
H9	+0.208	H25	+0.208	H37	0.210	C15	-0.279
H10	+0.208	H26	+0.208	H38	0.210		
H7	+0.219	H27	+0.219	H39	0.210		
H14	+0.423	H43	+0.423	H35	0.218		
H40	+0.222	H41	+0.222	C30	-0.008		
C11	-0.080	C17	-0.080	C31	-0.214		
C3	-0.108	C18	-0.108	C32	-0.203		
C4	-0.202	C19	-0.202	C33	-0.215		
C5	-0.236	C20	-0.237	C34	-0.203		
C6	-0.227	C21	-0.227	C29	-0.214		
C1	-0.233	C22	-0.233				
C2	+0.145	C23	+0.145				
N13	-0.533	N28	-0.533				
C12	-0.003	C16	-0.005				
Total gr. charge = + 0.013			**+0.010**		**+0.009**		**-0.046**

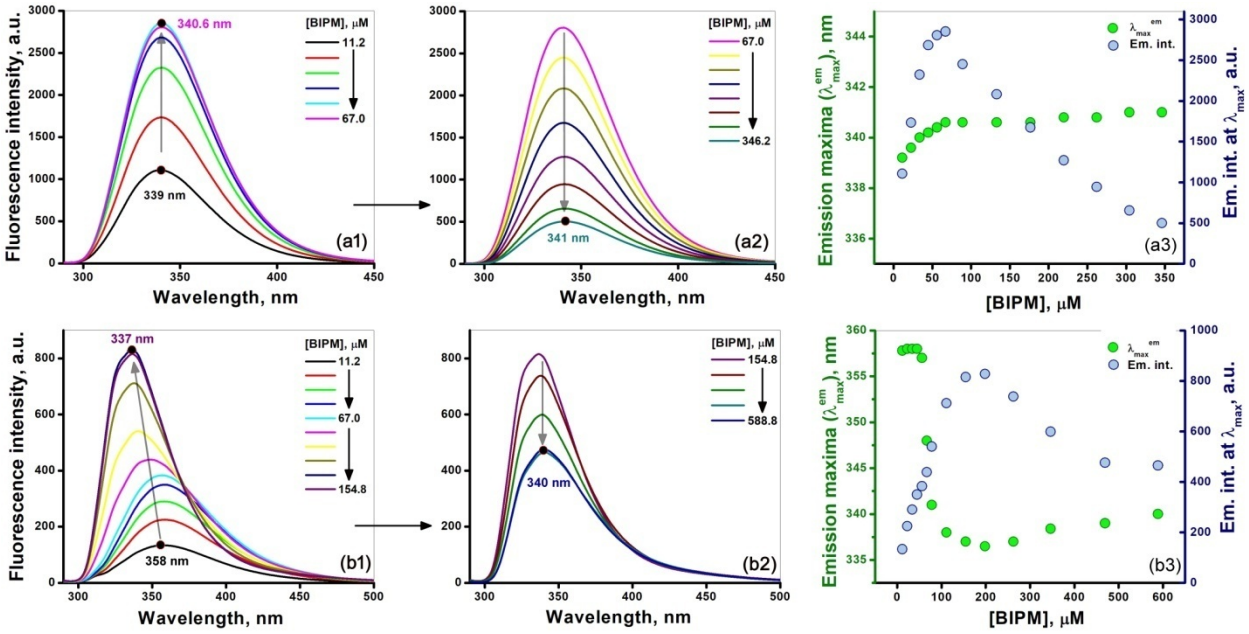


Fig. S9 Changes in the fluorescence response of BIPM upon gradual increase in its concentration in the solvent systems with (a) 10% and (b) 90% f_w. λ_{ex} = 280 nm, Temp. 298 K.