Investigation of Excited State Intramolecular Proton Transfer and Structural Dynamics in Bis-benzimidazole Derivative (BBM)

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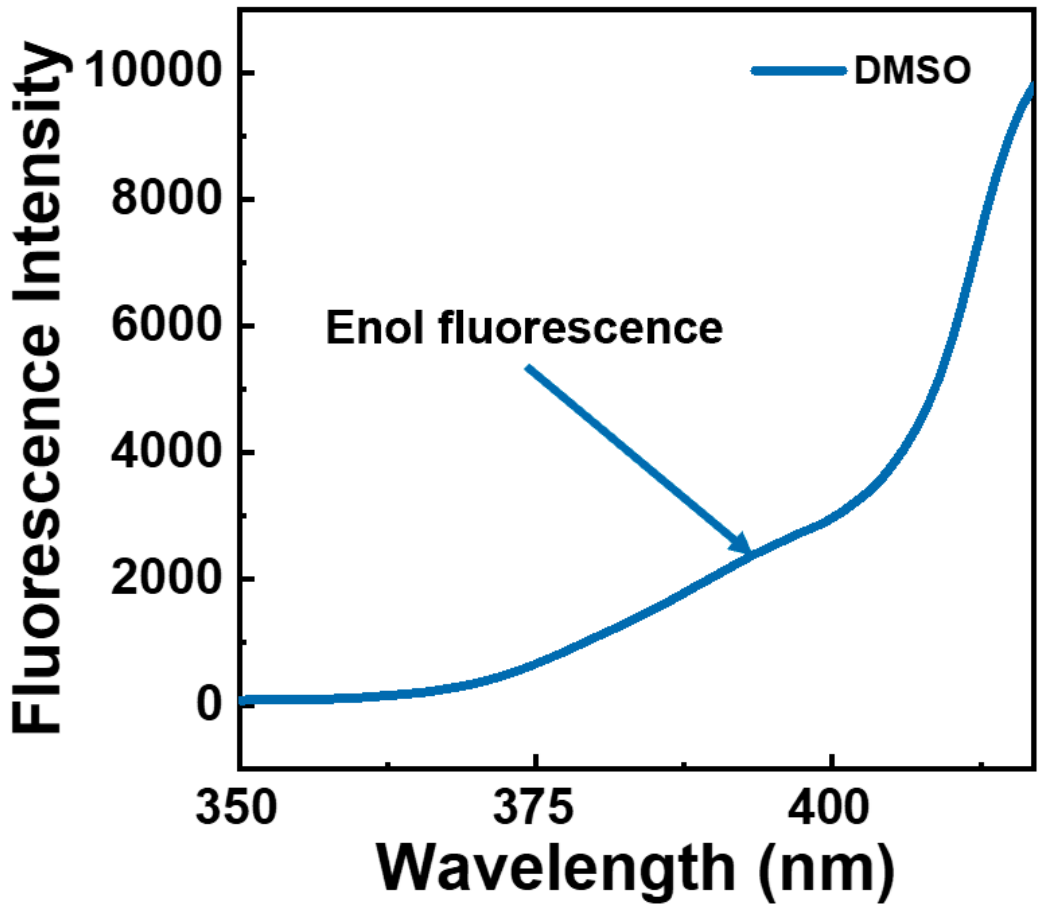


Figure S1. Steady-state fluorescence spectra of HBT in DMSO in the range of 350 to 430 nm.

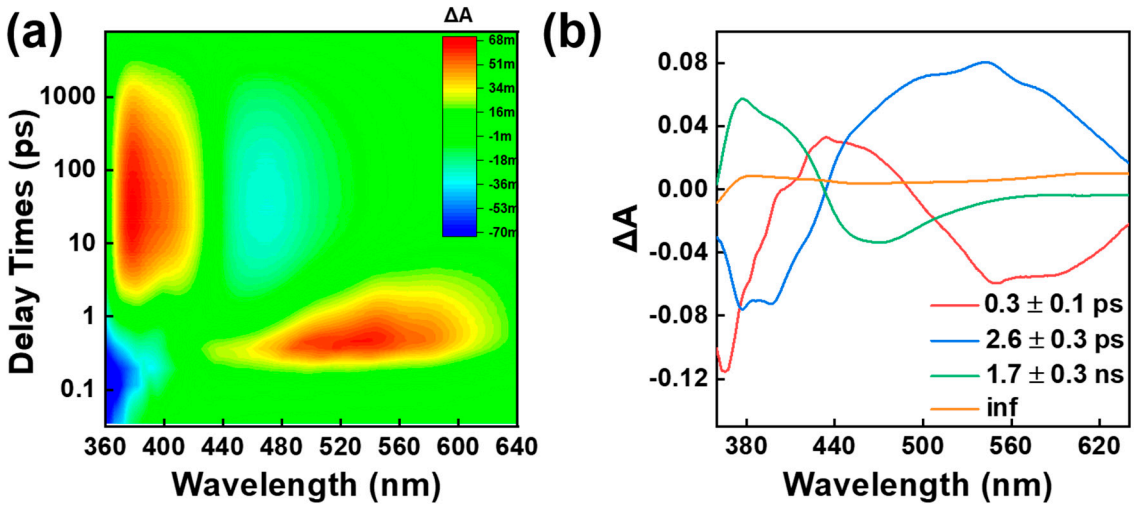


Figure S2. (a) 2D plot of TA spectrum of BBM in THF with 350 nm excitation (time delay is plotted using log scale). (b) Decay-associated difference spectra (DADS) of TA spectrum of BBM in THF.

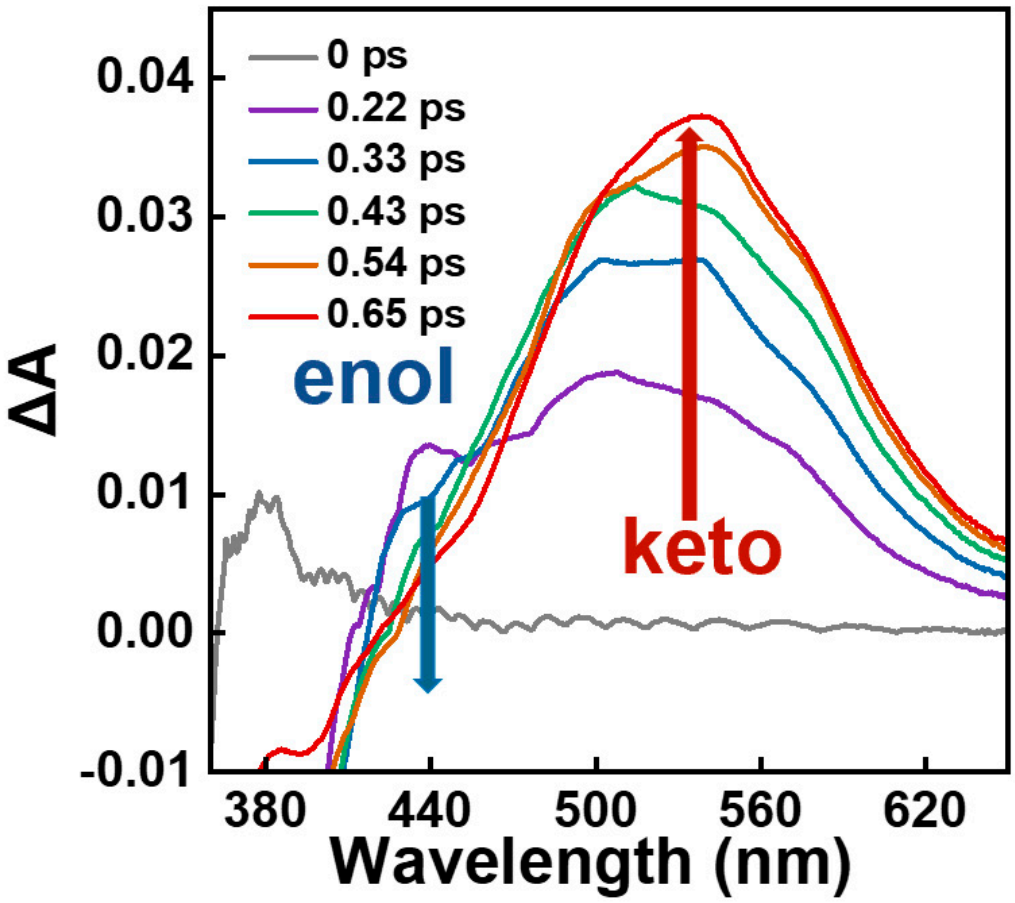


Figure S3. TA spectra of BBM in DMSO at different delay times between 0 and 0.65 ps.

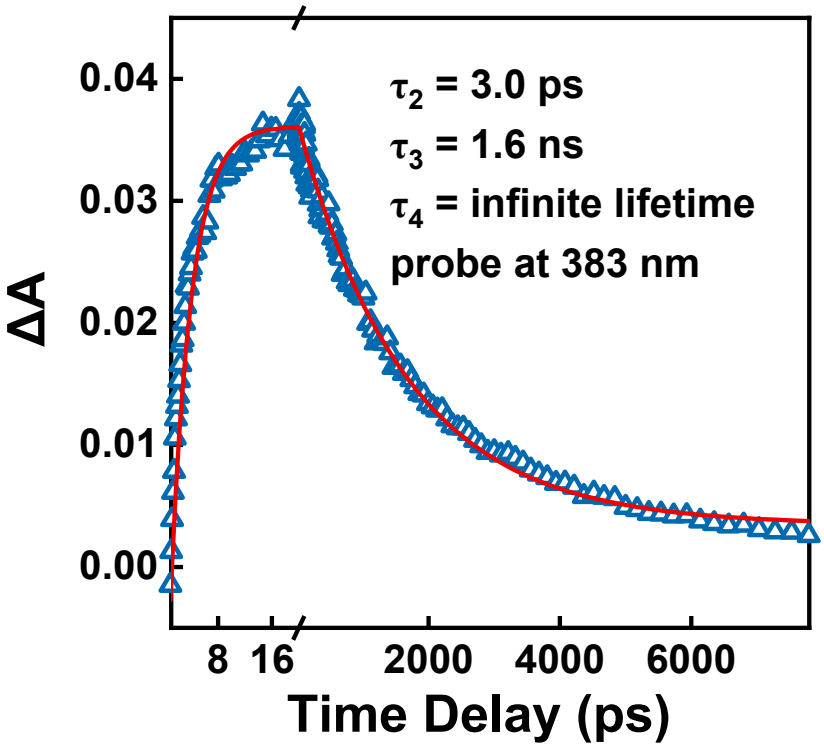


Figure S4. Transient amplitude of the TA spectra of BBM probe at 383 nm in DMSO.

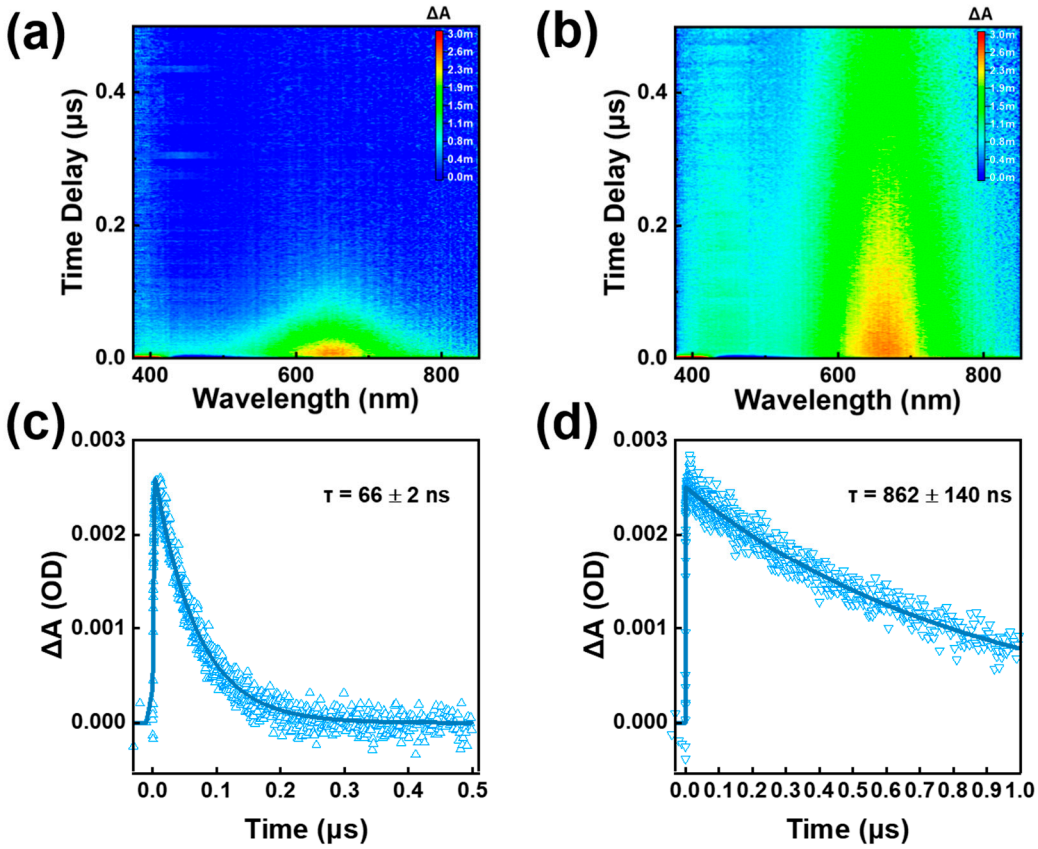


Figure S5. 2D plot of EOS-TA of BBM in (a) DMSO, and (b) THF, transient amplitude of the EOS-TA spectra of BBM probe at 667 nm in (c) DMSO, and (d) THF.

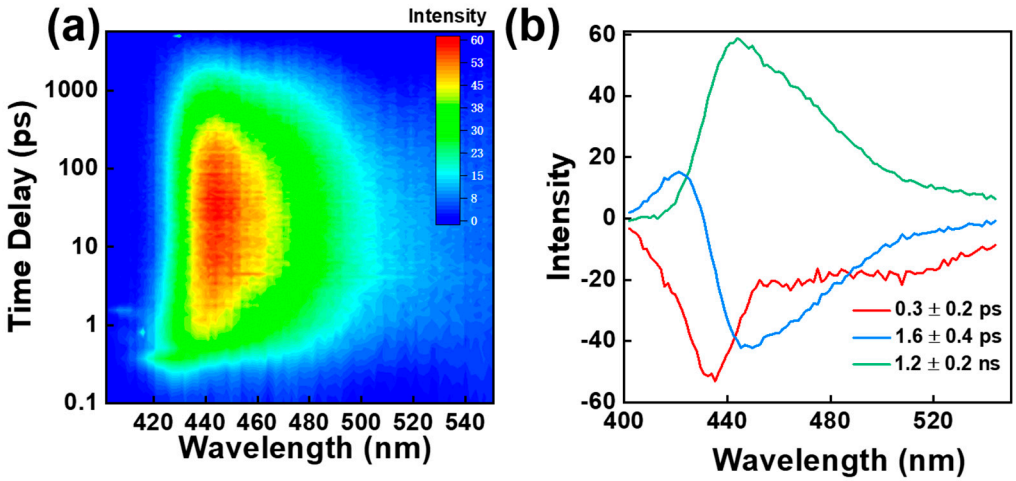


Figure S6. (a) 2D plot of fs fluorescence up-conversion spectra of BBM under 350 nm excitation in THF (time delay is plotted using log scale); (b) DADS of fs fluorescence up-conversion spectra of BBM in THF.

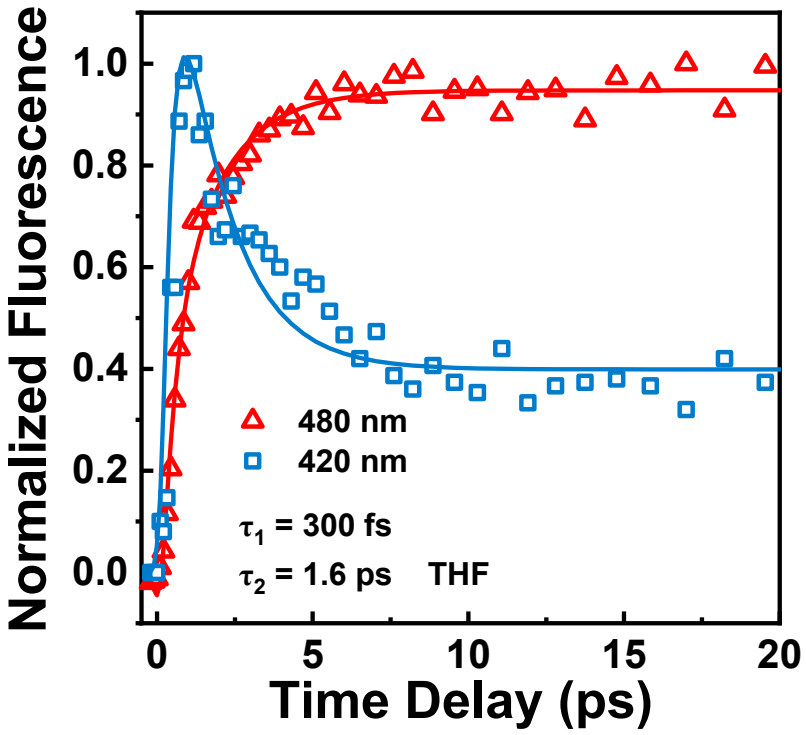


Figure S7. Transient amplitude of BBM-keto* fluorescence probe at 420 nm and 480 nm in THF，τ_1 and τ_2 are retrieved from global analysis.

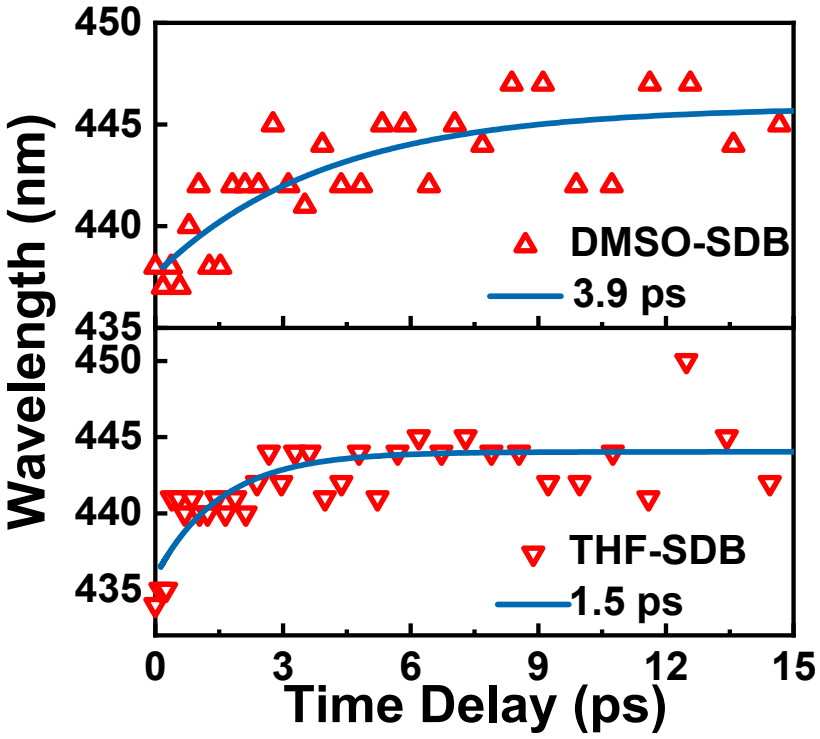


Figure S8. Transient fluorescence frequency shift of BBM-keto* in DMSO and THF.

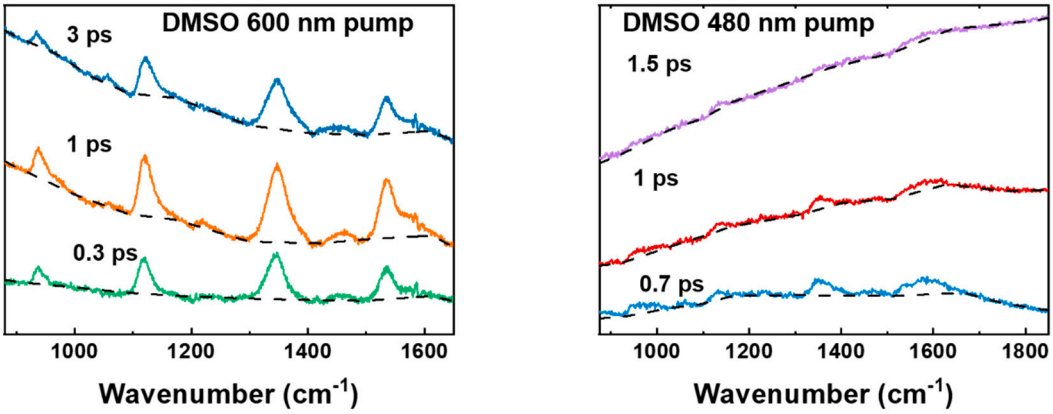


Figure S9. Excited state stimulated Raman data of BBM at different time delays with the baseline drawn (dash line).

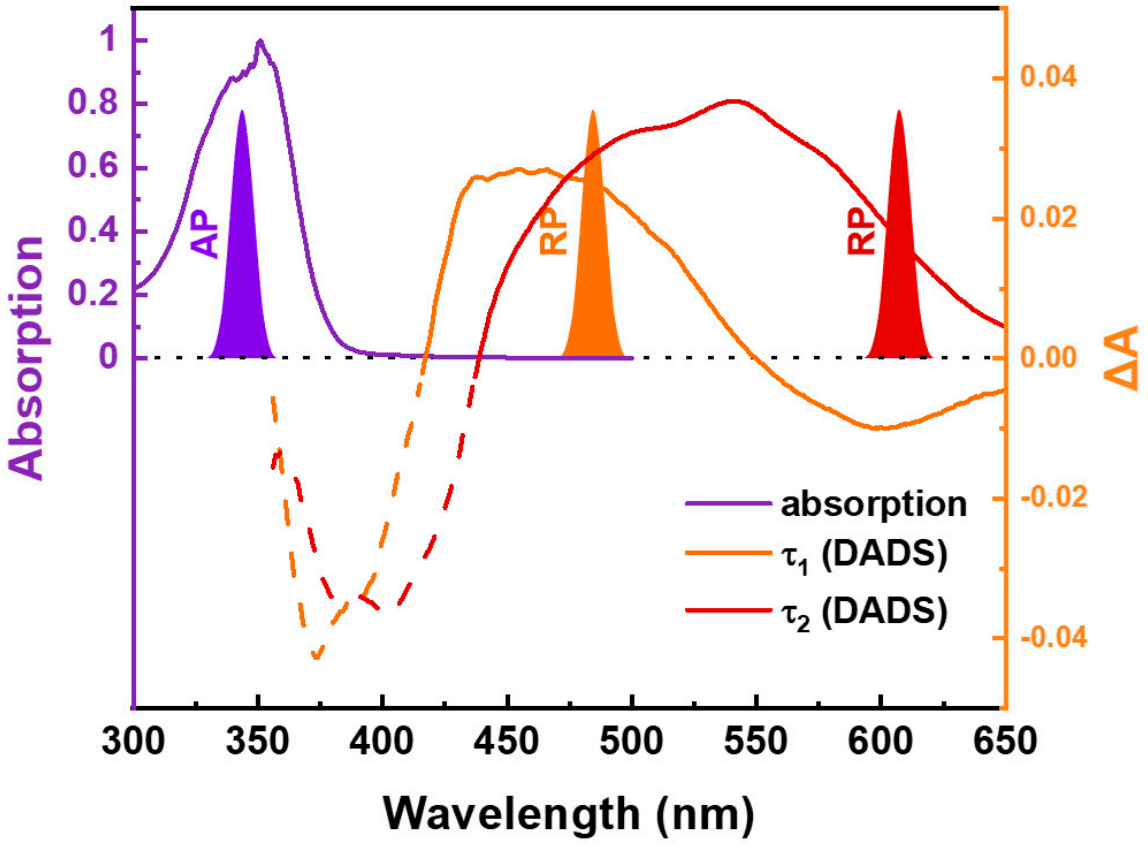
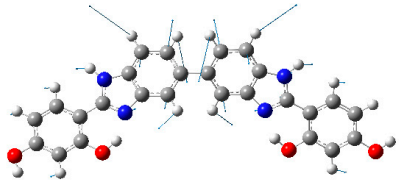
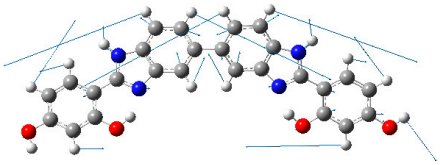


Figure S10. Steady-state absorption spectrum and DADS spectrum of τ_1 and τ_2 in TA. The actinic pump (AP) at 350 nm and Raman pump (RP) at 480 and 600 nm are depicted by colored spikes.

Enol



Mode (I)



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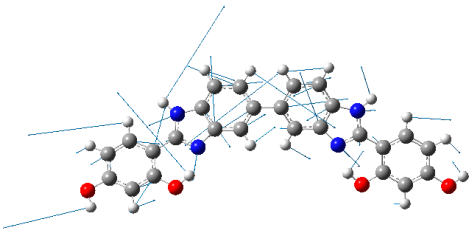

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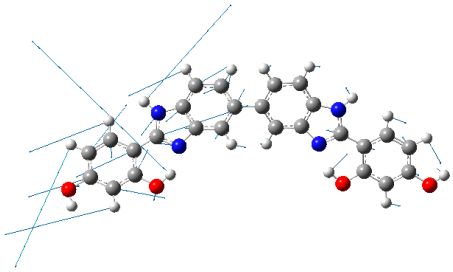

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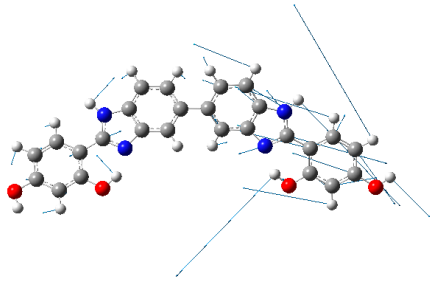
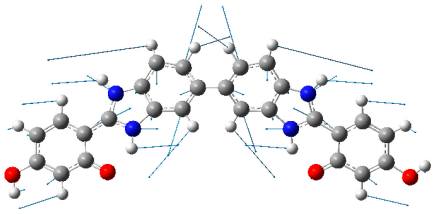


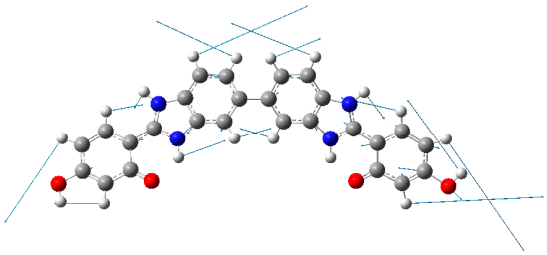
Mode (V)

Figure S11. DFT calculation of BBM-Enol form showing optimized structure and Raman modes (I-V).

Keto-pt2



Mode(I)



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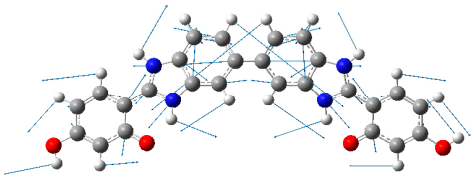

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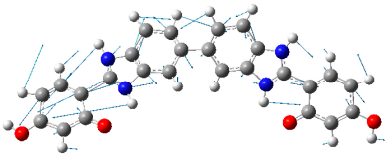

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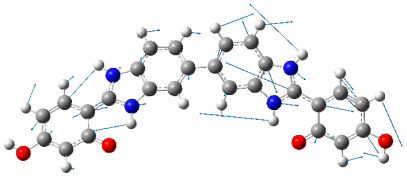
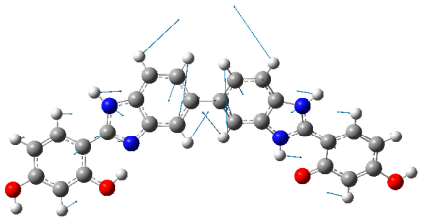


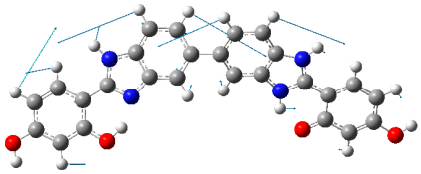
Mode(V)

Figure S12. DFT calculation BBM-Keto form (ESIPT occurs in both HBI halves) showing optimized structure and Raman modes (I-V).

Keto-pt1



Mode(I)



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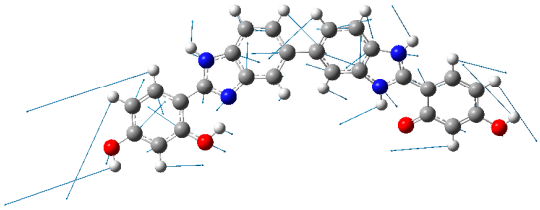

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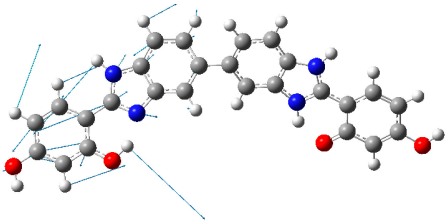

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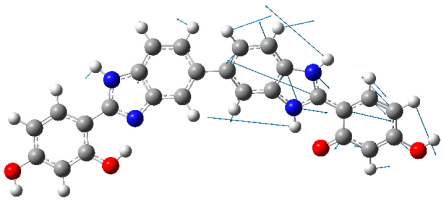


Mode(V)

Figure S13. DFT calculation (ESIPT occurs in one HBI halve) showing optimized structure and Raman modes (I-V).

Table S1. Detailed description of Raman modes was achieved through experiment (exp) and DFT calculations (theo).

		enol	**keto-pt2[a]**	**keto-pt1[b]**	**Vibrational mode assignment**
(I)	theo.	960	959	973	C-H bending out of plane
	exp.	953		939	
(II)	theo.	1160	1166	1163	C-H waging in plane
	exp.	1130		1122	
(III)	theo.	1335	1343	1369	Benzene and imidazole rings stretching and C-H in plane waging
	exp.	1358		1348	
(IV)	theo.	1566	1601	1595	C-C stretching
	exp.	1565		1534	
(V)	theo.	1570	1604	1633	C-C stretching
	exp.	1587		1568	

[a] DFT results for ESIPT occurred in one HBI half of BBM-keto form

[b] DFT results for ESIPT occurred in two HBI halves of BBM-keto form

Table S2. Atomic coordinates of Enol Keto-pt2 and Keto-pt1 by DFT calculation.

Enol

Tag	Symbol	X	Y	Z
1	C	-2.87443	0.722347	-0.00211
2	C	-3.49094	1.883843	-0.51372
3	C	-2.75829	3.026157	-0.82667
4	C	-1.38525	2.975014	-0.61233
5	C	-0.73776	1.824311	-0.09883
6	C	-1.49484	0.68923	0.209934
7	C	-5.0009	0.290679	-0.13694
8	H	-3.22829	3.915454	-1.22875
9	H	-0.78818	3.841873	-0.86866
10	H	-1.02984	-0.19646	0.625857
11	H	-5.56566	2.193726	-0.91548
12	C	0.737179	1.822852	0.103209
13	C	1.387176	2.972867	0.615159
14	C	1.491895	0.685998	-0.20475
15	H	0.791869	3.841108	0.870924
16	C	2.871748	0.716848	0.006131
17	H	1.025001	-0.19921	-0.61956
18	C	3.490759	1.877859	0.515759
19	C	2.760427	3.021792	0.828338
20	H	3.232357	3.910713	1.228992
21	C	4.997625	0.282072	0.137978
22	H	5.566324	2.185258	0.913785
23	C	6.263923	-0.4275	0.052882
24	C	8.684112	-0.52939	0.345805
25	C	7.493278	-2.45998	-0.51352
26	C	8.681608	-1.84816	-0.13032
27	H	9.611587	-0.05406	0.643799
28	H	7.496814	-3.47864	-0.88074
29	C	-6.26768	-0.4177	-0.05481
30	C	-6.29046	-1.75367	0.425871
31	C	-7.48907	0.166099	-0.43673
32	C	-7.49968	-2.44925	0.507515
33	C	-8.68737	-0.51929	-0.35766
34	H	-7.50809	1.184238	-0.80707
35	C	-8.68658	-1.83802	0.11817
36	H	-7.49	-3.46816	0.878121
37	H	-9.61931	-0.05682	-0.65602
38	O	-9.88876	-2.47837	0.178245
39	H	-9.77461	-3.37629	0.513524
40	O	-5.17235	-2.39827	0.816274
41	H	-4.40238	-1.77422	0.698158
42	O	9.824684	-2.5839	-0.23969
43	H	10.58393	-2.06453	0.051968
44	O	5.165138	-2.40907	-0.81308

45	H	4.396646	-1.78431	-0.69362
46	N	-3.83857	-0.24578	0.223194
47	N	-4.83818	1.576661	-0.58892
48	N	4.83754	1.568681	0.589269
49	N	3.834092	-0.253	-0.21962
50	C	6.286175	-1.76567	-0.42767
51	C	7.484358	0.156721	0.429872
52	H	7.505886	1.174817	0.799962

Keto-pt2

Tag	Symbol	X	Y	Z
1	C	-2.86143	0.71999	-0.00235
2	C	-3.48992	1.868822	-0.51168
3	C	-2.75852	3.008485	-0.82501
4	C	-1.38392	2.959773	-0.61137
5	C	-0.7363	1.813634	-0.09855
6	C	-1.49013	0.673428	0.213043
7	C	-5.0629	0.299366	-0.15038
8	H	-3.23151	3.895216	-1.22747
9	H	-0.7896	3.827326	-0.86997
10	H	-1.02644	-0.21148	0.629677
11	H	-5.56413	2.197932	-0.91966
12	C	0.736979	1.812515	0.104014
13	C	1.386748	2.958508	0.614791
14	C	1.488796	0.670837	-0.20653
15	H	0.793849	3.82724	0.87268
16	C	2.860489	0.715819	0.007253
17	H	1.023505	-0.21395	-0.62161
18	C	3.49107	1.86471	0.513989
19	C	2.761537	3.005767	0.826846
20	H	3.236134	3.892499	1.22741
21	C	5.061139	0.293391	0.151511
22	H	5.566479	2.192135	0.917457
23	C	6.284304	-0.42873	0.054039
24	C	8.700628	-0.54223	0.34341
25	C	7.494828	-2.47735	-0.52359
26	C	8.673525	-1.87243	-0.14198
27	H	9.637952	-0.08416	0.637488
28	H	7.504757	-3.4966	-0.89172
29	C	-6.28712	-0.41991	-0.0566
30	C	-6.24877	-1.78614	0.448644
31	C	-7.51783	0.160918	-0.442
32	C	-7.50607	-2.46413	0.517308
33	C	-8.70375	-0.5279	-0.35898
34	H	-7.54163	1.17885	-0.816
35	C	-8.68153	-1.85693	0.127716

36	H	-7.50739	-3.4836	0.889754
37	H	-9.64362	-0.08079	-0.65519
38	O	-9.88949	-2.49287	0.185953
39	H	-9.77393	-3.3895	0.524729
40	O	-5.16193	-2.35584	0.812142
41	H	-3.87642	-1.18563	0.56101
42	O	9.825342	-2.60166	-0.24746
43	H	10.57764	-2.07493	0.048359
44	O	5.149647	-2.36268	-0.80654
45	H	3.875421	-1.19274	-0.55509
46	N	-3.86499	-0.21369	0.206483
47	N	-4.84664	1.570188	-0.5908
48	N	4.847628	1.5647	0.590927
49	N	3.862602	-0.21919	-0.20194
50	C	6.241764	-1.79679	-0.44968
51	C	7.515662	0.150527	0.432405
52	H	7.5447	1.168756	0.805034

Keto-pt1

Tag	Symbol	X	Y	Z
1	C	2.858132	0.719015	0.001202
2	C	3.473547	1.880377	0.504553
3	C	2.745465	3.022936	0.81335
4	C	1.376253	2.971291	0.6019
5	C	0.732277	1.820818	0.097014
6	C	1.481703	0.684932	-0.20712
7	C	4.97386	0.294335	0.1359
8	H	3.217719	3.914047	1.21112
9	H	0.777005	3.839098	0.855879
10	H	1.013256	-0.20254	-0.61891
11	H	5.54122	2.192467	0.900671
12	C	-0.73541	1.820458	-0.10175
13	C	-1.3846	2.966829	-0.60165
14	C	-1.4825	0.679295	0.200836
15	H	-0.78945	3.837687	-0.85357
16	C	-2.85162	0.724418	-0.01149
17	H	-1.01334	-0.20804	0.609624
18	C	-3.48175	1.874462	-0.50688
19	C	-2.75564	3.016451	-0.81098
20	H	-3.23206	3.90685	-1.20407
21	C	-5.03752	0.308278	-0.15561
22	H	-5.55144	2.203566	-0.90427
23	C	-6.25161	-0.42402	-0.05674
24	C	-8.65976	-0.56768	-0.32708
25	C	-7.41969	-2.48438	0.516152
26	C	-8.60942	-1.89638	0.148683

27	H	-9.60695	-0.12088	-0.61105
28	H	-7.41281	-3.50682	0.878648
29	C	6.23352	-0.41505	0.055085
30	C	6.242652	-1.74938	-0.41888
31	C	7.454503	0.162773	0.430727
32	C	7.445527	-2.45006	-0.49945
33	C	8.645226	-0.52802	0.352493
34	H	7.479798	1.183807	0.7968
35	C	8.634802	-1.84659	-0.11626
36	H	7.428683	-3.47175	-0.86565
37	H	9.582028	-0.07043	0.646827
38	O	9.822398	-2.49057	-0.17549
39	H	9.696932	-3.38636	-0.5044
40	O	5.126029	-2.37885	-0.79946
41	H	4.365488	-1.74098	-0.67799
42	O	-9.74007	-2.6372	0.258515
43	H	-10.4975	-2.11773	-0.02774
44	N	3.816682	-0.24499	-0.21956
45	N	4.813243	1.574995	0.578761
46	N	-4.83121	1.576093	-0.58382
47	C	-6.18254	-1.78745	0.435899
48	C	-7.48747	0.140597	-0.42085
49	H	-7.53192	1.162159	-0.78673
50	N	-3.84738	-0.20769	0.190822
51	H	-3.88779	-1.19295	0.53584
52	O	-5.0816	-2.33582	0.779076

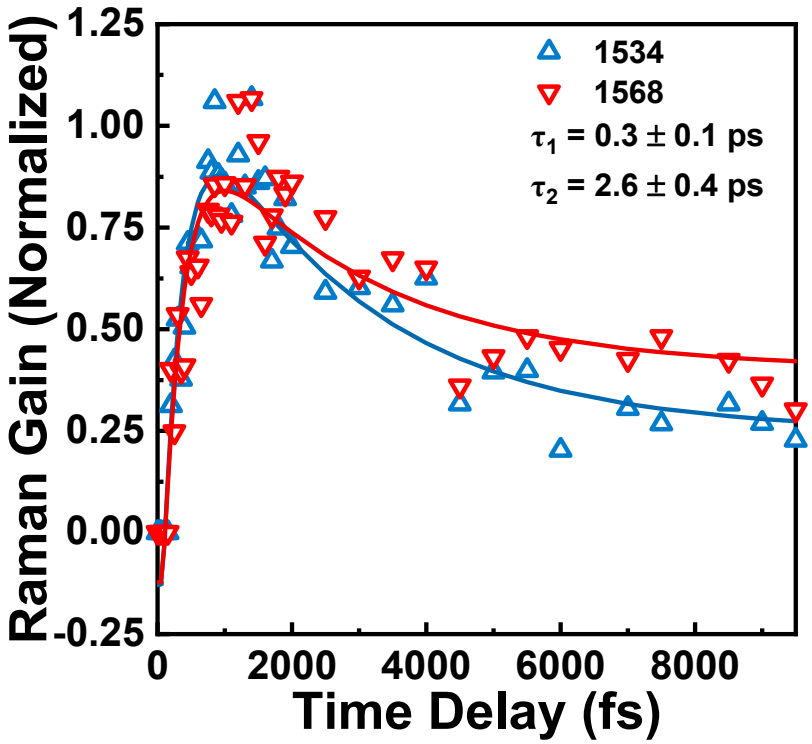


Figure S14. Transient amplitude Raman modes IV and V of BBM-keto* in THF with 600 nm Raman pump excitation.

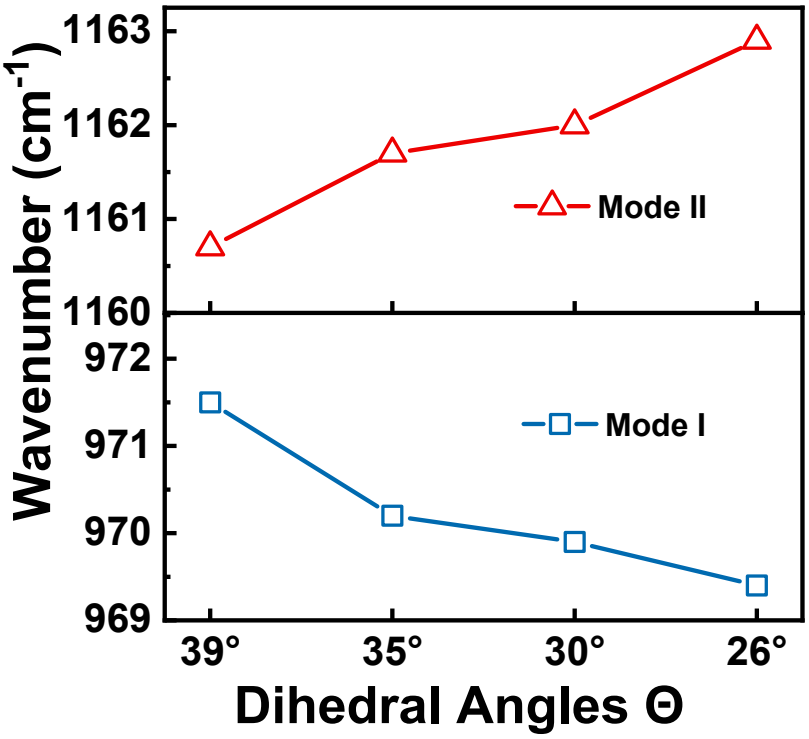
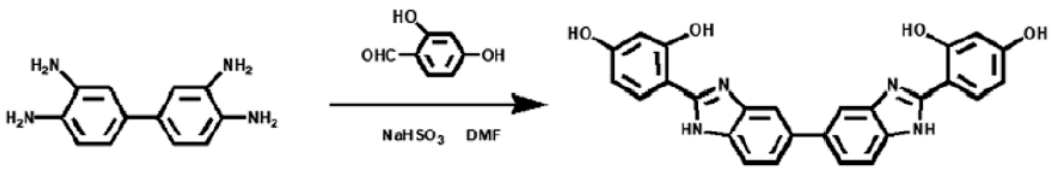


Figure S15. Transient frequency shift of BBM-keto* in TD-DFT calculation.

Table S3. TD-DFT calculation of emission wavelength and oscillator strength of BBM-keto* at Θ = 35°, 30°, and 26°.

Θ	35°	30°	26°
Emission wavelength (nm)	419	420	421
Oscillator strength	0.97	1.01	1.05



Scheme S1. Synthetic route of bis-benzimidazole derivative [26].