Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Proton Transfer Triggered Proton Transfer: A Self Assisted Twin Excited State Intramolecular Proton Transfer

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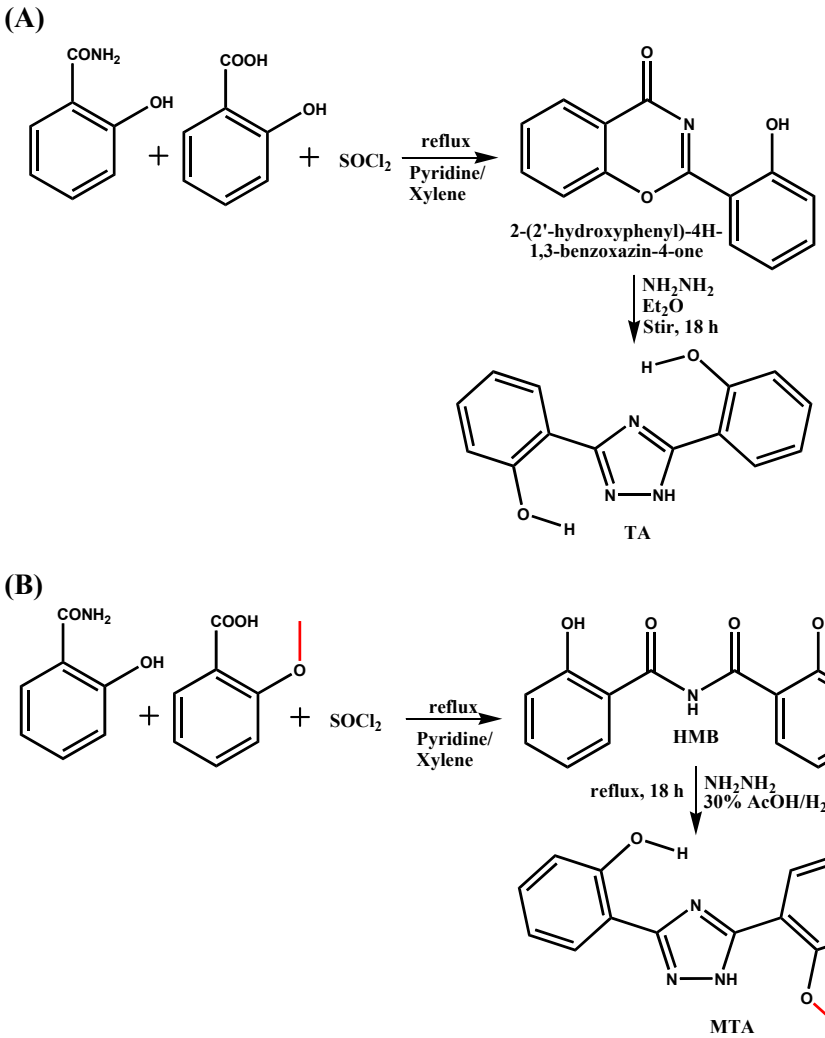
Scheme S1. Synthesis route of (A) bis-HPTA and (B) HPMTA.



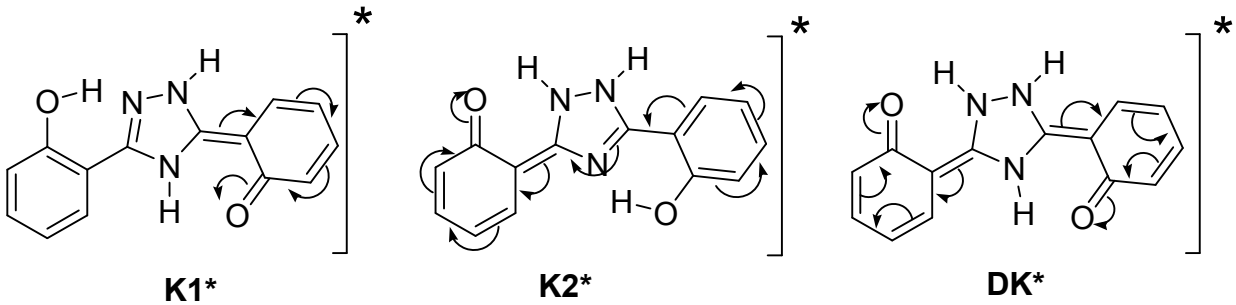


Chart S1. Extent of conjugation of the emitting unit(s) in K1*, K2*, and DK*.

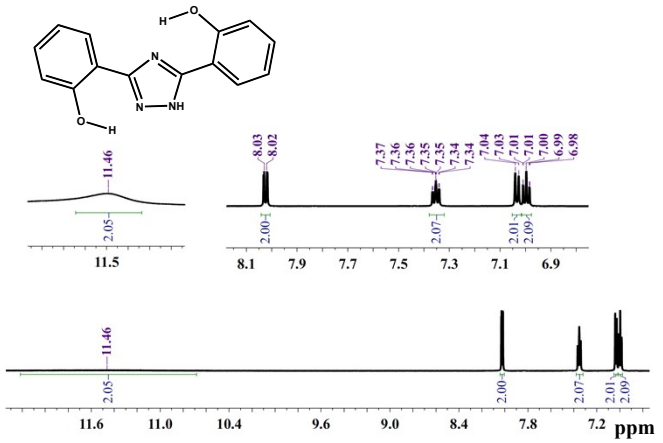


Figure S1. ^{1}H NMR of bis-HPTA (600 MHz, DMSO-d_6).

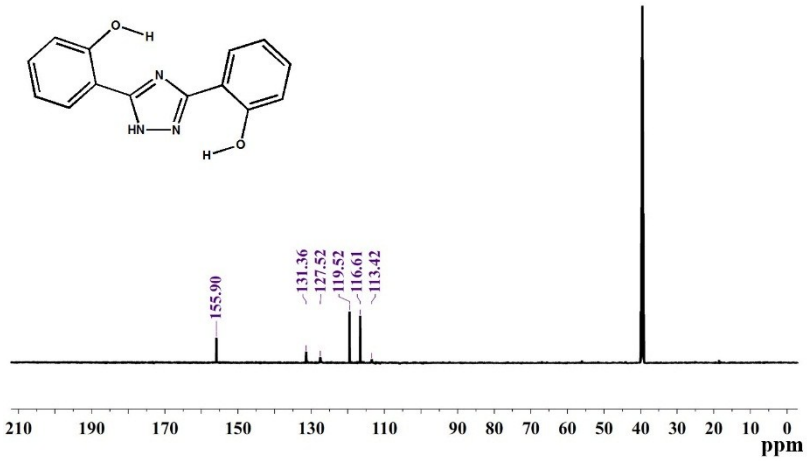


Figure S2. ^{13}C NMR of bis-HPTA (600 MHz, DMSO-d_6).

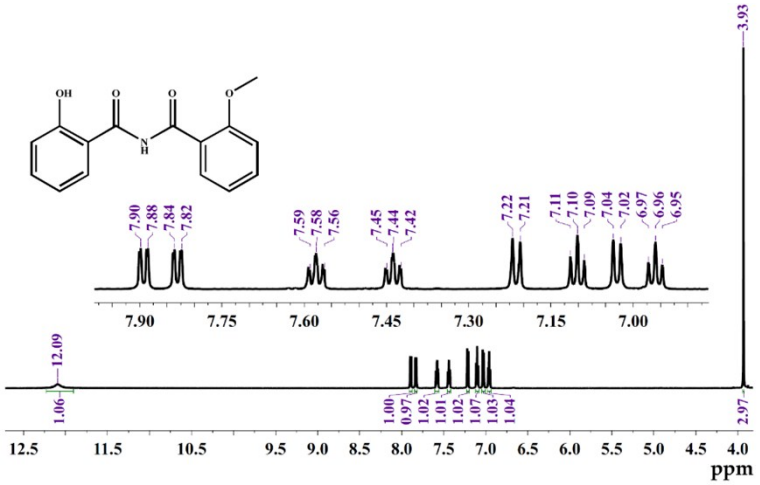


Figure S3. ^{1}H NMR of HMBB (600 MHz, DMSO-d_6).

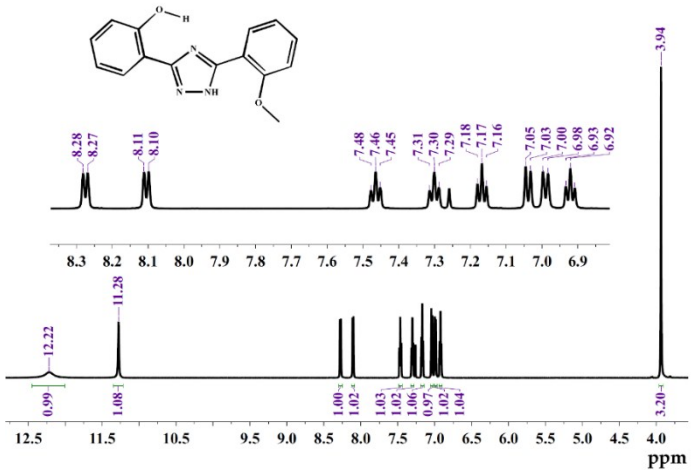


Figure S4. ^{1}H NMR of HPMTA (600 MHz, $CDCl_3$).

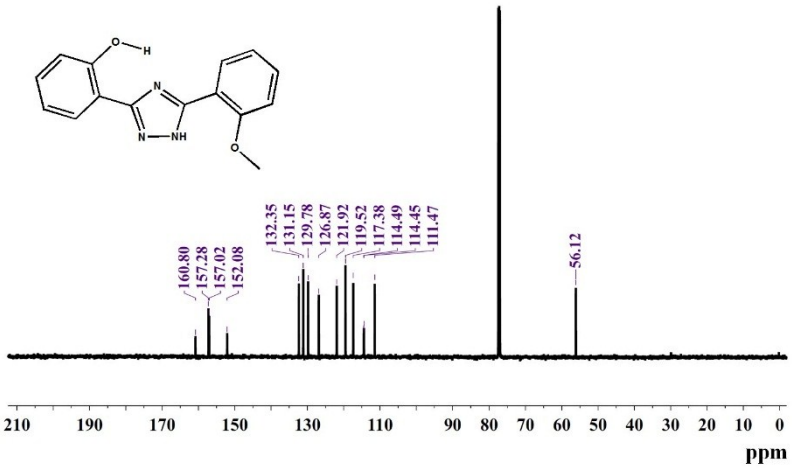


Figure S5. ^{13}C NMR of HPMPTA (600 MHz, $CDCl_3$).

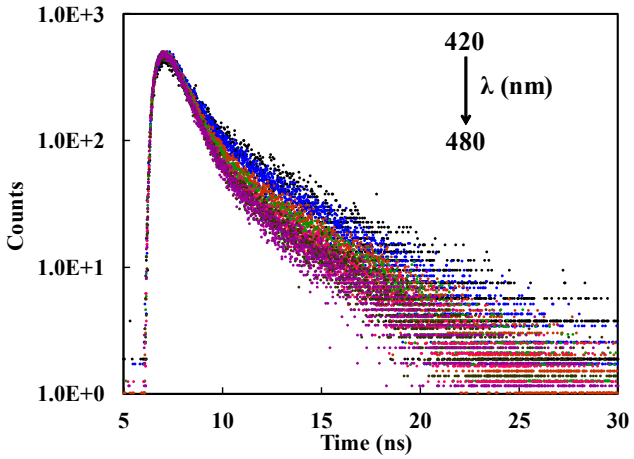


Figure S6. Fluorescence decay of bis-HPTA in dioxane recorded at different emission wavelength. (λ_{ex}= 308 nm).

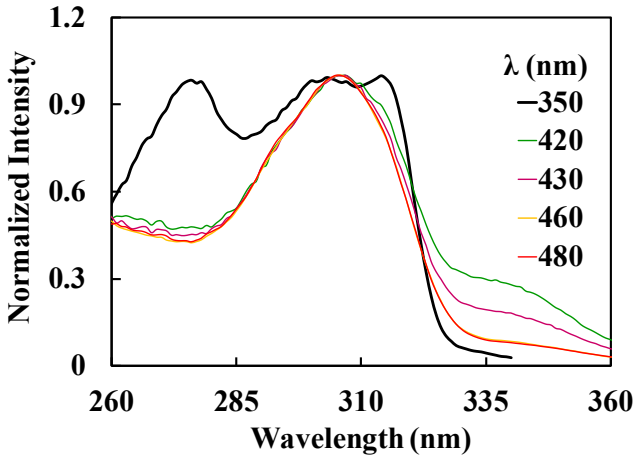


Figure S7. Normalized excitation spectra of bis-HPTA in methanol recorded at different wavelengths (λ).

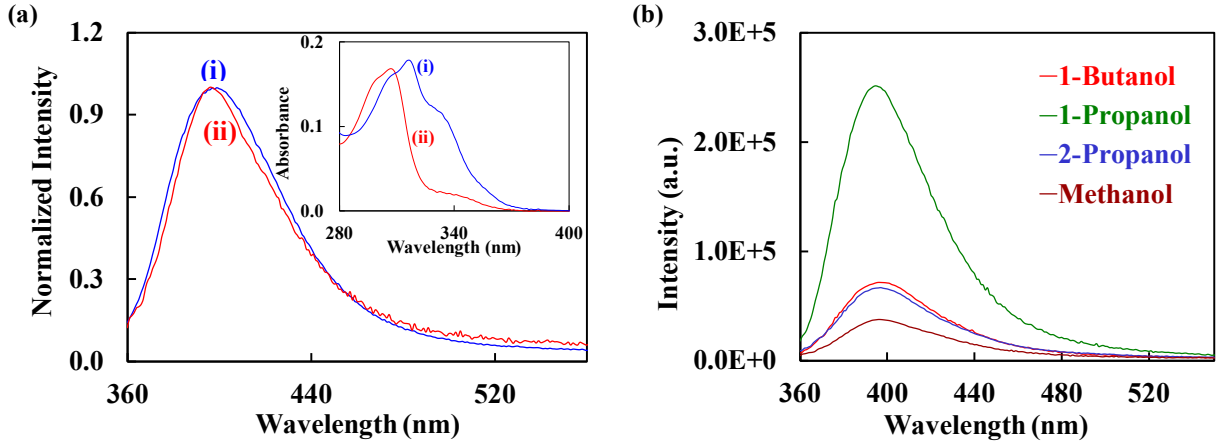


Figure S8. a) Normalized emission spectra of bis-HPTA in (i) alkaline methanol and (ii) methanol. λ_{ex}= 340 nm. The absorption spectra are shown as inset. b) Emission spectra of bis-HPTA in different polar protic solvents. λ_{ex}= 340 nm.

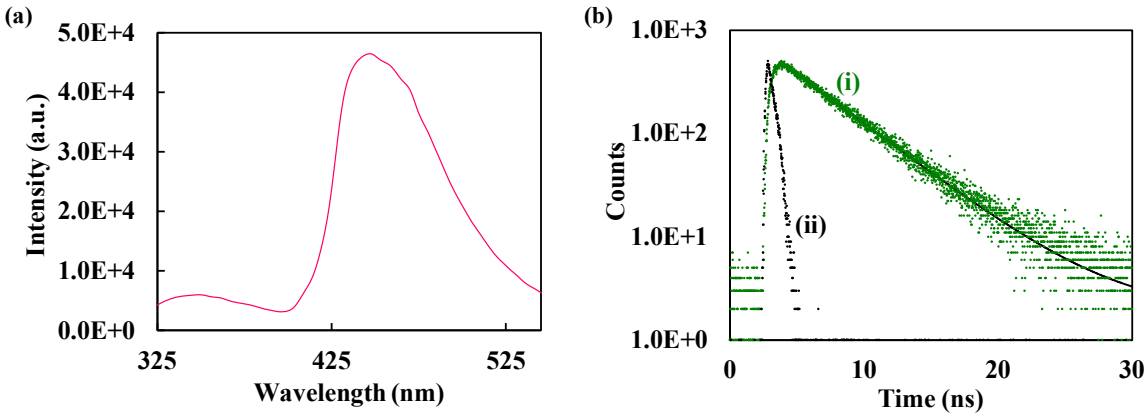
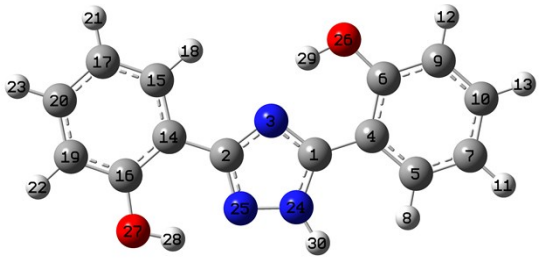


Figure S9. a) Emission spectra of HPMPTA in dioxane. (λ_{ex} = 308 nm). b) Fluorescence decay of HPMPTA in dioxane recorded at 460 nm (i). The instrument response function is shown with black dots (ii). (λ_{ex} = 308 nm).

Table S1. Fitted parameter of different fluorescence decay traces of bis-HPTA recorded at different emission wavelength (λ_{em}) in dioxane. B1 and B2 are the pre-exponential factors correspond to lifetimes, τ_1 and τ_2, respectively. χ^2 is the goodness of the fit.

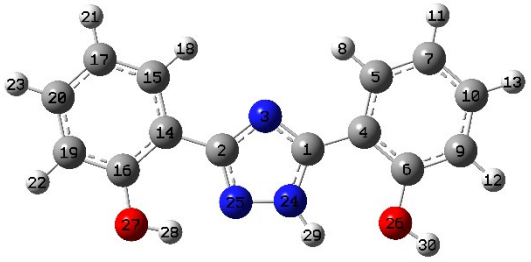
Traces λ_{em} (nm)	B1	B2	τ_1 (ns) (Relative amplitude)	τ_2 (ns) (Relative amplitude)	χ^2
420	0.0036	0.0012	0.9 (0.41)	4.0 (0.59)	1.0
430	0.0103	0.0025	0.9 (0.48)	4.0 (0.52)	1.1
440	0.0175	0.0030	0.9 (0.56)	4.1 (0.44)	1.0
450	0.0225	0.0030	0.9 (0.62)	4.1 (0.38)	1.1
460	0.0230	0.0027	0.8 (0.64)	4.0 (0.36)	1.1
470	0.0205	0.0022	0.8 (0.66)	4.0 (0.34)	1.1
480	0.0170	0.0016	0.9 (0.70)	4.0 (0.30)	1.1
490	0.0135	0.0012	0.8 (0.71)	3.8 (0.29)	1.0
500	0.0100	0.0008	0.8 (0.72)	3.8 (0.28)	0.9
510	0.0072	0.0006	0.8 (0.73)	3.8 (0.27)	0.9

Table S2. XYZ coordinate of optimized bis-HPTA-I conformer in the ground state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.12344	-0.59373	0.00014
2	6	1.01615	-0.44056	-0.00006
3	7	-0.13039	0.30413	-0.00001
4	6	-2.54254	-0.26043	0.00024
5	6	-3.54051	-1.25547	0.00044
6	6	-2.93597	1.10366	0.00013
7	6	-4.88916	-0.92357	0.00053
8	1	-3.25768	-2.30390	0.00052
9	6	-4.30072	1.43031	0.00023
10	6	-5.26490	0.42869	0.00043
11	1	-5.64157	-1.70491	0.00068
12	1	-4.57814	2.47939	0.00015
13	1	-6.31642	0.69968	0.00050
14	6	2.37100	0.11297	-0.00020
15	6	2.56567	1.50677	-0.00030
16	6	3.50721	-0.73314	-0.00025
17	6	3.84274	2.05770	-0.00044
18	1	1.69322	2.15141	-0.00027
19	6	4.79243	-0.17336	-0.00038
20	6	4.95865	1.20873	-0.00048
21	1	3.97028	3.13530	-0.00052
22	1	5.64646	-0.84317	-0.00041
23	1	5.96132	1.62601	-0.00059
24	7	-0.57877	-1.83212	0.00018
25	7	0.77679	-1.75240	0.00006
26	8	-2.04641	2.12290	-0.00007
27	8	3.42027	-2.09012	-0.00016
28	1	2.47535	-2.36101	-0.00006
29	1	-1.12886	1.74701	-0.00012
30	1	-1.02796	-2.73684	0.00029

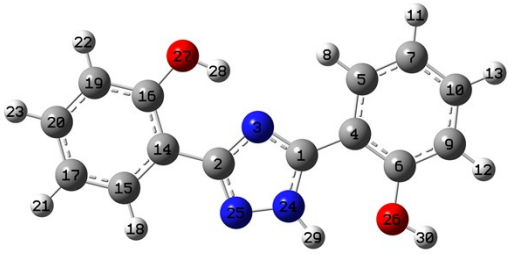
Table S3. XYZ coordinate of optimized bis-HPTA-II conformer in the ground state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.052284	-0.20469	-0.00011
2	6	-1.07614	-0.22686	0.000096
3	7	-0.00335	0.613547	0.00005
4	6	2.454758	0.218159	-0.00021
5	6	2.751599	1.593668	-0.00014
6	6	3.528889	-0.69563	-0.00038
7	6	4.066049	2.050229	-0.00024
8	1	1.924182	2.294333	-7E-06
9	6	4.850568	-0.24085	-0.00048
10	6	5.118485	1.127279	-0.00041
11	1	4.270107	3.115806	-0.00018
12	1	5.662493	-0.96335	-0.00062
13	1	6.148843	1.469169	-0.00049
14	6	-2.47562	0.209723	0.000251
15	6	-2.78705	1.581691	0.000366
16	6	-3.53743	-0.72785	0.000282
17	6	-4.10645	2.02413	0.000507
18	1	-1.96788	2.292983	0.000342
19	6	-4.86531	-0.27843	0.000425
20	6	-5.14755	1.0852	0.000536
21	1	-4.32403	3.087423	0.000593
22	1	-5.66021	-1.01758	0.000446

23	1	-6.18188	1.416783	0.000645
24	7	0.615484	-1.48717	-0.00015
25	7	-0.73642	-1.52193	-2.2E-05
26	8	3.233312	-2.03521	-0.00045
27	8	-3.33526	-2.07341	0.000175
28	1	-2.36826	-2.25877	0.000073
29	1	1.175631	-2.32956	-0.00026
30	1	4.044057	-2.56401	-0.00056

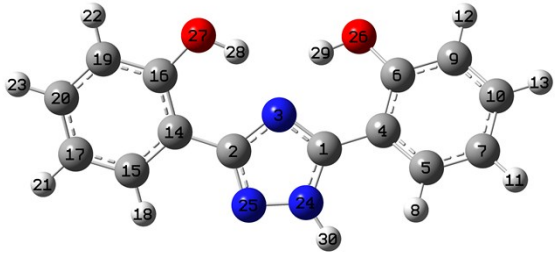
Table S4. XYZ coordinate of optimized bis-HPTA-III conformer in the ground state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	0.996608	-0.4248	-8.9E-05
2	6	-1.13565	-0.64241	0.000176
3	7	-0.13311	0.291408	0.000064
4	6	2.355582	0.117751	-0.00024
5	6	2.53752	1.513213	-0.00017
6	6	3.502358	-0.70376	-0.00044
7	6	3.809375	2.07734	-0.0003
8	1	1.658393	2.147611	-6E-06
9	6	4.781758	-0.14066	-0.00058
10	6	4.934743	1.245032	-0.00051
11	1	3.923701	3.156163	-0.00024
12	1	5.651796	-0.79232	-0.00074
13	1	5.933004	1.671494	-0.00061
14	6	-2.55489	-0.2735	0.000304
15	6	-3.55376	-1.26502	0.000269
16	6	-2.94795	1.08753	0.000411
17	6	-4.90429	-0.93182	0.000316
18	1	-3.24758	-2.30616	0.000185
19	6	-4.31139	1.418991	0.000447
20	6	-5.28003	0.419604	0.0004
21	1	-5.65785	-1.71288	0.000279
22	1	-4.58628	2.469136	0.00053

23	1	-6.33111	0.693622	0.000435
24	7	0.657414	-1.73334	-7.6E-05
25	7	-0.68684	-1.89843	0.000044
26	8	3.316022	-2.06228	-0.00051
27	8	-2.05367	2.111074	0.000527
28	1	-1.13984	1.729636	0.000602
29	1	1.289106	-2.52344	-0.00018
30	1	4.165684	-2.5256	-0.00067

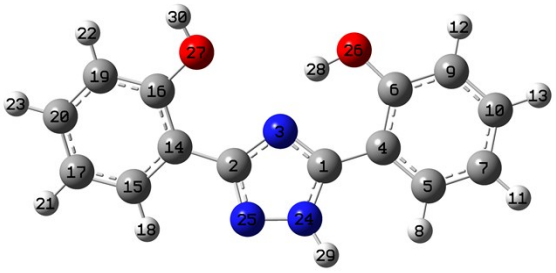
Table S5. XYZ coordinate of optimized bis-HPTA-IV conformer in the ground state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.07067	0.734051	0.034264
2	6	1.08097	0.780229	-0.02457
3	7	0.001176	-0.07241	0.018864
4	6	-2.46751	0.310659	0.050633
5	6	-3.49854	1.205863	0.400311
6	6	-2.81152	-1.01493	-0.3129
7	6	-4.83106	0.812237	0.384192
8	1	-3.25065	2.217535	0.707627
9	6	-4.15772	-1.40488	-0.33217
10	6	-5.15669	-0.50041	0.012493
11	1	-5.60856	1.515042	0.663771
12	1	-4.39459	-2.42414	-0.61924
13	1	-6.19435	-0.8197	-0.0025
14	6	2.47544	0.324056	-0.03621
15	6	3.507386	1.220068	-0.37586
16	6	2.819447	-1.00319	0.311117
17	6	4.839981	0.822636	-0.37541
18	1	3.240331	2.236632	-0.64521
19	6	4.163936	-1.4008	0.312296
20	6	5.165337	-0.49662	-0.02858
21	1	5.618365	1.528944	-0.64533
22	1	4.398245	-2.42479	0.585291

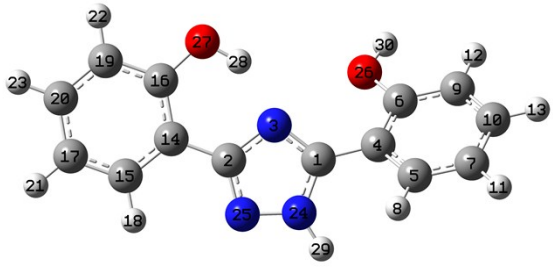
23	1	6.201868	-0.82074	-0.02618
24	7	-0.62716	2.008245	-0.00494
25	7	0.728812	2.062261	-0.03479
26	8	-1.88916	-1.94541	-0.66548
27	8	1.897531	-1.93944	0.669164
28	1	1.001884	-1.55232	0.592103
29	1	-0.99146	-1.56404	-0.56988
30	1	-1.16058	2.865745	-0.04156

Table S6. XYZ coordinate of optimized bis-HPTA-IVa conformer in the ground state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	1.10398	-0.76789	0.081198
2	6	-1.04066	-0.7558	0.097692
3	7	0.054934	0.049572	-0.05409
4	6	2.494623	-0.33709	0.001461
5	6	3.56735	-1.24185	0.12011
6	6	2.777348	1.040585	-0.19758
7	6	4.886271	-0.80991	0.045105
8	1	3.366559	-2.29858	0.270679
9	6	4.112172	1.467942	-0.27119
10	6	5.153422	0.553483	-0.1517
11	1	5.698441	-1.52315	0.137808
12	1	4.305952	2.524863	-0.42349
13	1	6.180102	0.902312	-0.21204
14	6	-2.44204	-0.31729	-0.01183
15	6	-3.42014	-1.25357	-0.39555
16	6	-2.85789	1.003712	0.262302
17	6	-4.7639	-0.90661	-0.51032
18	1	-3.10072	-2.26755	-0.61105
19	6	-4.2092	1.355292	0.141146
20	6	-5.15741	0.408732	-0.24209
21	1	-5.49382	-1.65024	-0.81326
22	1	-4.5109	2.377675	0.355993
23	1	-6.19932	0.701273	-0.33117
24	7	0.636324	-2.01754	0.302401
25	7	-0.72138	-2.0306	0.322273
26	8	1.807238	1.97524	-0.31917
27	8	-1.92725	1.92075	0.663383
28	1	0.919398	1.527136	-0.2503
29	1	1.144838	-2.87465	0.467004
30	1	-2.36315	2.764566	0.849553

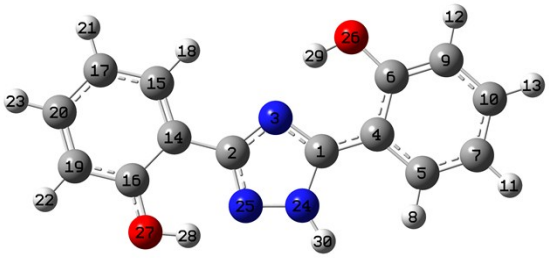
Table S7. XYZ coordinate of optimized bis-HPTA-IVb conformer in the ground state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.02332	-0.66636	0.101482
2	6	1.11601	-0.76704	0.130102
3	7	0.061715	0.084775	-0.08273
4	6	-2.43421	-0.28776	-0.04133
5	6	-3.34152	-1.19285	-0.62198
6	6	-2.91745	0.963911	0.398574
7	6	-4.69091	-0.87832	-0.76591
8	1	-2.97305	-2.146	-0.98959
9	6	-4.27324	1.280807	0.249612
10	6	-5.15343	0.366516	-0.32764
11	1	-5.36938	-1.58945	-1.2249
12	1	-4.63414	2.246338	0.594498
13	1	-6.20076	0.631106	-0.43624
14	6	2.509193	-0.32492	0.018317
15	6	3.569082	-1.22703	0.226623
16	6	2.813321	1.021961	-0.30102
17	6	4.89553	-0.82057	0.125711
18	1	3.330183	-2.25729	0.47012
19	6	4.15346	1.426654	-0.40147
20	6	5.183891	0.515331	-0.19051

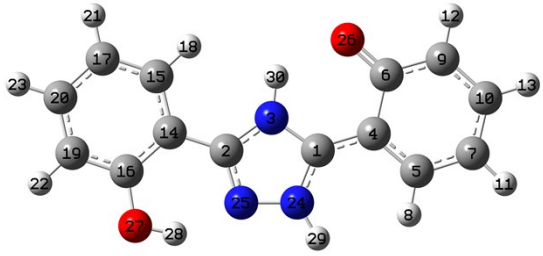
21	1	5.697571	-1.53296	0.290487
22	1	4.360845	2.463584	-0.64674
23	1	6.21532	0.845959	-0.27245
24	7	-0.61394	-1.91832	0.413403
25	7	0.738789	-2.00743	0.439485
26	8	-2.03948	1.82745	0.982397
27	8	1.857254	1.962167	-0.5184
28	1	0.966204	1.537743	-0.41778
29	1	-1.17755	-2.72047	0.660648
30	1	-2.50191	2.629335	1.265501

Table S8. XYZ coordinate of optimized bis-HPTA-I conformer in the excited state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-1.1463	-0.51813	0.000036
2	6	0.99895	-0.33724	-5.7E-05
3	7	-0.11678	0.401797	-8.1E-05
4	6	-2.52528	-0.24583	0.000162
5	6	-3.52014	-1.28786	0.00048
6	6	-3.0117	1.114789	0.000053
7	6	-4.87828	-0.9893	0.000695
8	1	-3.20699	-2.32788	0.00057
9	6	-4.36757	1.387383	0.000289
10	6	-5.32341	0.341017	0.00061
11	1	-5.59963	-1.80271	0.00094
12	1	-4.68121	2.427519	0.000197
13	1	-6.3832	0.573212	0.00078
14	6	2.369593	0.174172	-0.00016
15	6	2.65709	1.528624	-0.00019
16	6	3.483582	-0.76269	-0.00024
17	6	3.987013	1.977704	-0.00029
18	1	1.840487	2.240308	-0.00014
19	6	4.83216	-0.28757	-0.00033
20	6	5.073965	1.063156	-0.00036
21	1	4.187641	3.042818	-0.00032
22	1	5.628588	-1.02207	-0.00039
23	1	6.090566	1.438393	-0.00044
24	7	-0.54986	-1.78837	0.000045
25	7	0.811994	-1.66003	-4E-06
26	8	-2.13447	2.170962	-0.00036
27	8	3.290413	-2.05434	-0.00022
28	1	2.269616	-2.23952	-0.00014
29	1	-1.21514	1.815487	-0.00067
30	1	-0.97378	-2.70178	0.000361

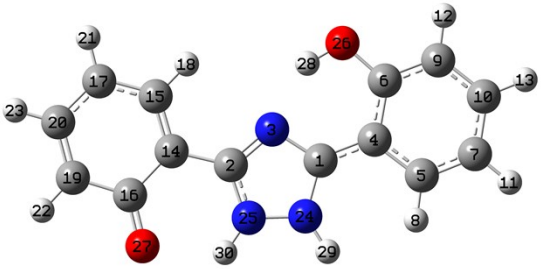
Table S9. XYZ coordinate of optimized K1 tautomer in the excited state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	1.17699	-0.57055	-0.00011
2	6	-1.05432	-0.41410	0.00015
3	7	0.10691	0.30432	0.00002
4	6	2.57337	-0.26075	-0.00024
5	6	3.55817	-1.25023	-0.00031
6	6	2.99456	1.15238	-0.00029
7	6	4.94949	-0.91464	-0.00041
8	1	3.28768	-2.30206	-0.00028
9	6	4.38727	1.43833	-0.00039
10	6	5.36108	0.41092	-0.00045
11	1	5.67799	-1.71924	-0.00046
12	1	4.67650	2.48491	-0.00042
13	1	6.41712	0.66068	-0.00052
14	6	-2.40481	0.13011	0.00030
15	6	-2.62455	1.52289	0.00058
16	6	-3.52747	-0.73876	0.00014
17	6	-3.91038	2.04889	0.00067
18	1	-1.77736	2.20120	0.00074
19	6	-4.82127	-0.19923	0.00023

20	6	-5.01082	1.17904	0.00049
21	1	-4.05690	3.12367	0.00089
22	1	-5.66306	-0.88395	0.00010
23	1	-6.02022	1.57913	0.00055
24	7	0.57567	-1.80776	-0.00006
25	7	-0.78901	-1.71180	0.00011
26	8	2.10522	2.07955	-0.00026
27	8	-3.41955	-2.08990	-0.00010
28	1	-2.47068	-2.34922	-0.00010
29	1	1.00975	-2.71753	-0.00013
30	1	0.29490	1.30601	-0.00005

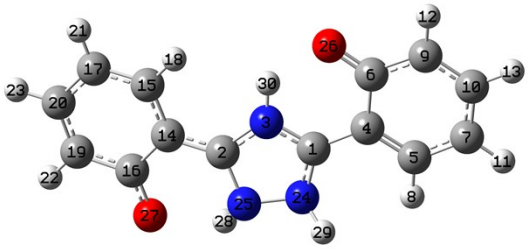
Table S10. XYZ coordinate of optimized K2 tautomer in the excited state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.15963	-0.57829	0.00013
2	6	1.01389	-0.40003	-0.00005
3	7	-0.09194	0.31740	-0.00004
4	6	-2.52715	-0.25097	0.00023
5	6	-3.55244	-1.25473	0.00037
6	6	-2.96084	1.12428	0.00017
7	6	-4.89948	-0.91441	0.00046
8	1	-3.27379	-2.30448	0.00040
9	6	-4.31042	1.44025	0.00027
10	6	-5.29522	0.43128	0.00041
11	1	-5.64747	-1.70241	0.00056
12	1	-4.58900	2.49002	0.00022
13	1	-6.34627	0.70014	0.00048
14	6	2.39792	0.11878	-0.00021
15	6	2.60946	1.47936	-0.00034
16	6	3.53811	-0.79670	-0.00024
17	6	3.91991	2.01908	-0.00049
18	1	1.75781	2.15053	-0.00031
19	6	4.85992	-0.19969	-0.00040

20	6	5.03757	1.17116	-0.00052
21	1	4.04948	3.09524	-0.00059
22	1	5.70171	-0.88359	-0.00041
23	1	6.03717	1.59291	-0.00064
24	7	-0.61596	-1.86050	0.00019
25	7	0.75132	-1.71705	0.00011
26	8	-2.05862	2.15543	0.00003
27	8	3.40052	-2.05457	-0.00013
28	1	-1.14851	1.78293	-0.00003
29	1	-1.04300	-2.77265	0.00046
30	1	1.43331	-2.47073	0.00010

Table S11. XYZ coordinate of optimized DK tautomer in the excited state. (Optimized geometry is shown below).



Atom Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.13739	-0.61293	0.10012
2	6	-1.08731	-0.39558	0.23625
3	7	0.12497	0.25051	0.16445
4	6	2.54313	-0.25339	-0.00293
5	6	3.52537	-1.21911	-0.13186
6	6	2.91317	1.16236	0.02141
7	6	4.89872	-0.86308	-0.21793
8	1	3.26501	-2.27182	-0.18040
9	6	4.31434	1.47574	-0.06264
10	6	5.28117	0.47875	-0.17845
11	1	5.64137	-1.64664	-0.31559
12	1	4.58470	2.52615	-0.04069
13	1	6.33077	0.74593	-0.24354
14	6	-2.38428	0.14337	0.11495
15	6	-2.62892	1.54305	0.14218
16	6	-3.48902	-0.79537	-0.10281
17	6	-3.91057	2.04796	-0.01471
18	1	-1.80355	2.23258	0.30291
19	6	-4.78710	-0.21399	-0.24876

20	6	-4.99140	1.15843	-0.20589
21	1	-4.08012	3.11964	0.01616
22	1	-5.61789	-0.89595	-0.40792
23	1	-5.99676	1.55476	-0.32381
24	7	0.61290	-1.87838	0.07804
25	7	-0.77396	-1.75111	0.39574
26	8	2.03193	2.07595	0.10552
27	8	-3.28677	-2.06462	-0.17967
28	1	-1.45567	-2.36811	-0.07445
29	1	1.07763	-2.62371	0.58857
30	1	0.33764	1.25221	0.11081