Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

The Origin of Longer Wavelength Emission in 2-(4-Fluorophenylamino)-5-(2,4-dihydroxybenzeno)-1,3,4-thiadiazole and its Analogue 2-(Phenylamino)-5-(2-hydroxybenzono)-1,3,4-thiadiazole

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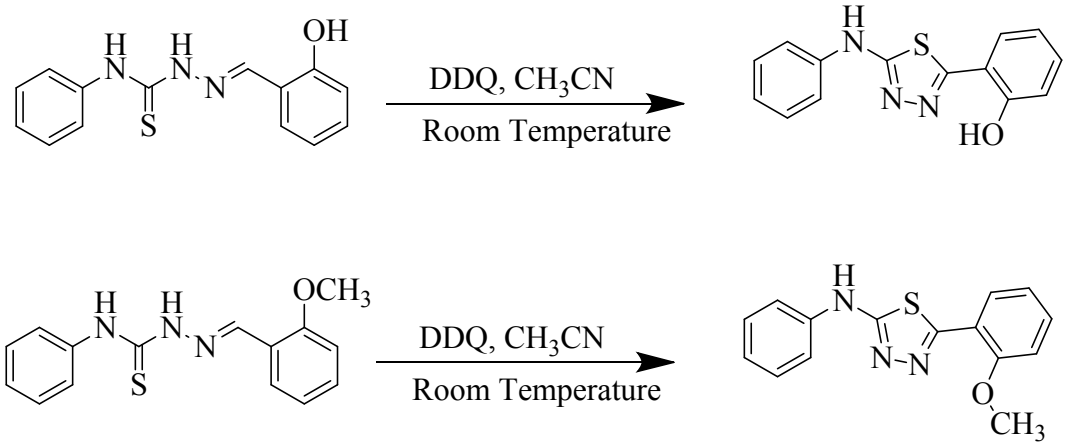

Scheme S1. Synthesis of PHBT and PMBT

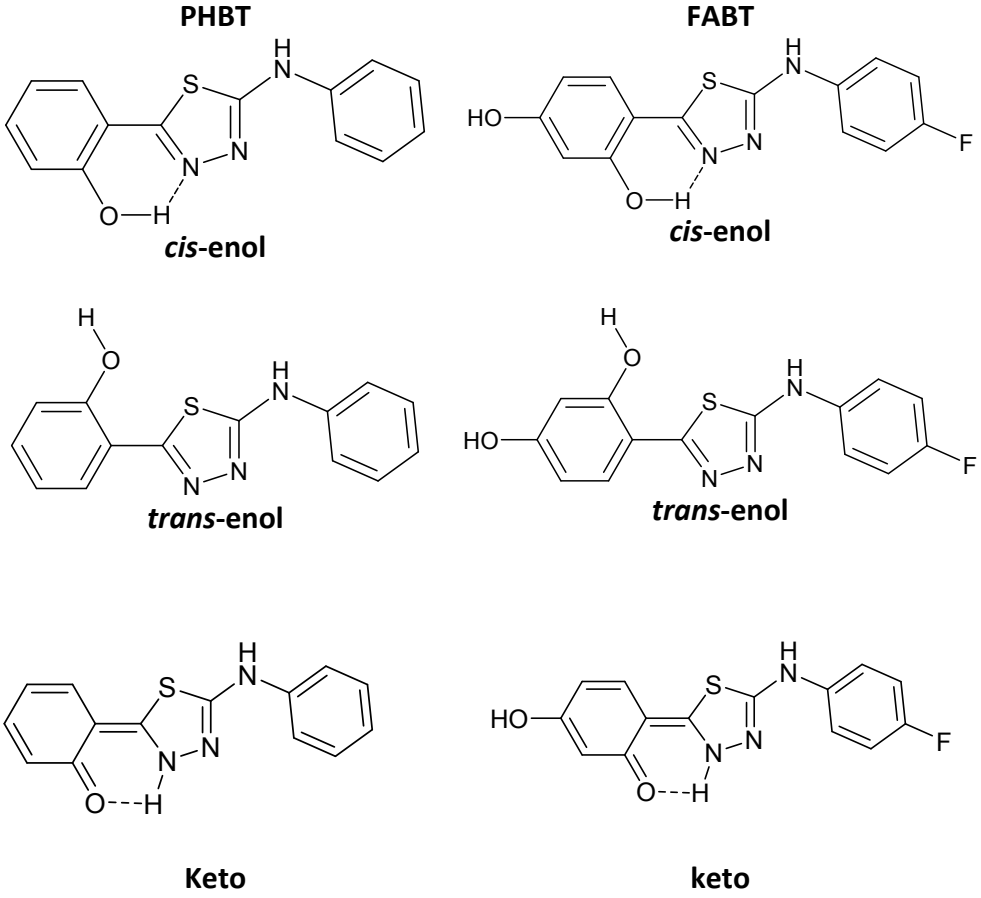

Chart S1. Different conformers and tautomers of PHBT and FABT

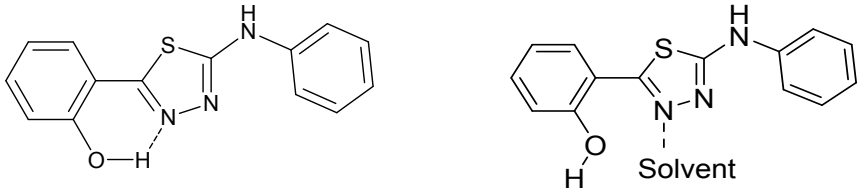

Chart S2. Cis-enol and solvated enol of PHBT

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.15 (s, 1H), 9.01 (s, 1H), 7.43 – 7.35 (m, 4H), 7.32 – 7.26 (m, 2H), 7.14 (t, J = 6.7 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H).

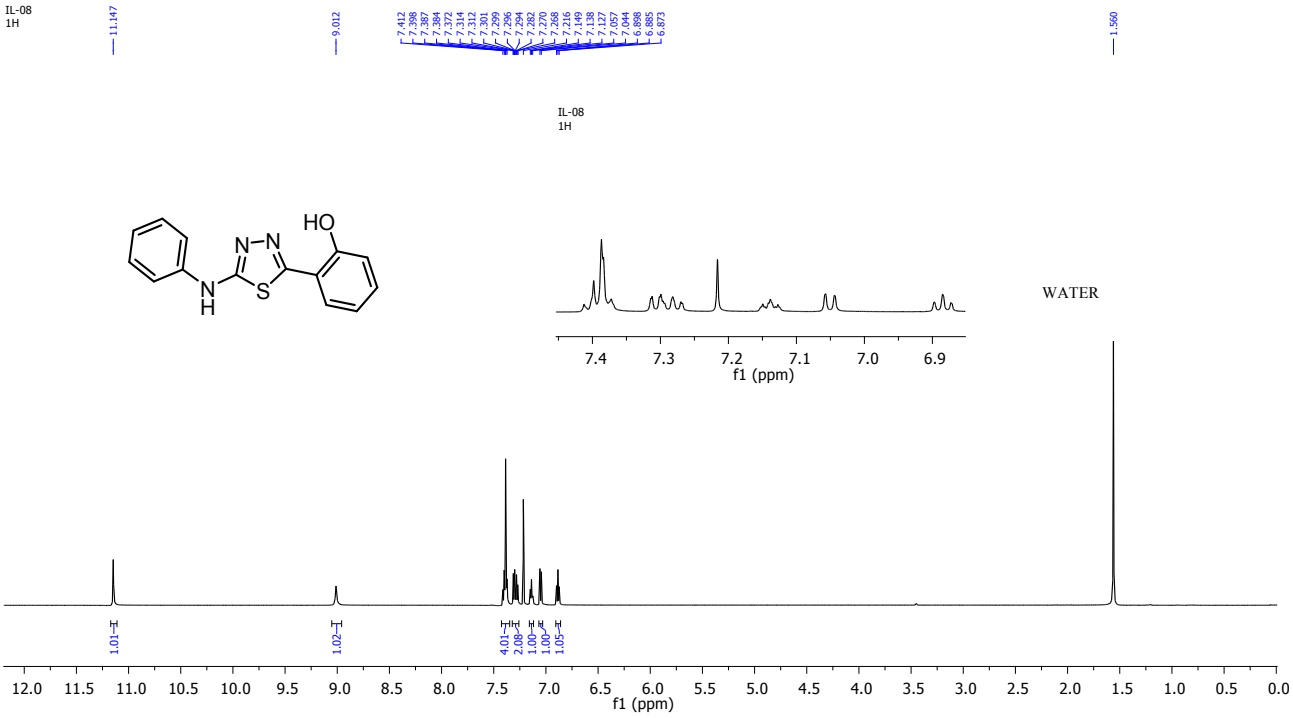

Fig. S1. ^{1}H NMR Spectrum of PHBT

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.02, 139.95, 131.70, 129.97, 128.59, 124.61, 119.88, 119.07, 117.79, 114.67.

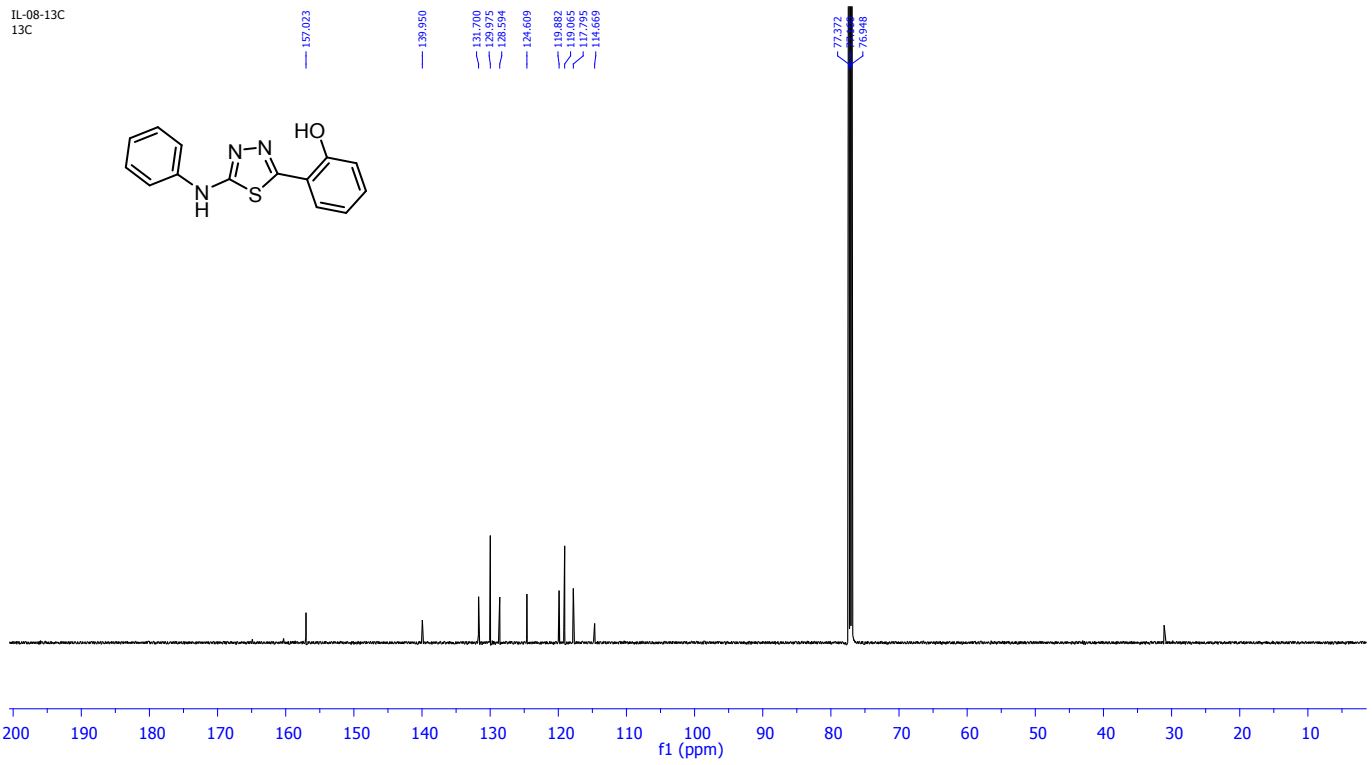

Fig. S2. ^{13}C NMR Spectrum of PHBT

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.39 (dt, *J* = 13.8, 4.9 Hz, 3H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H).

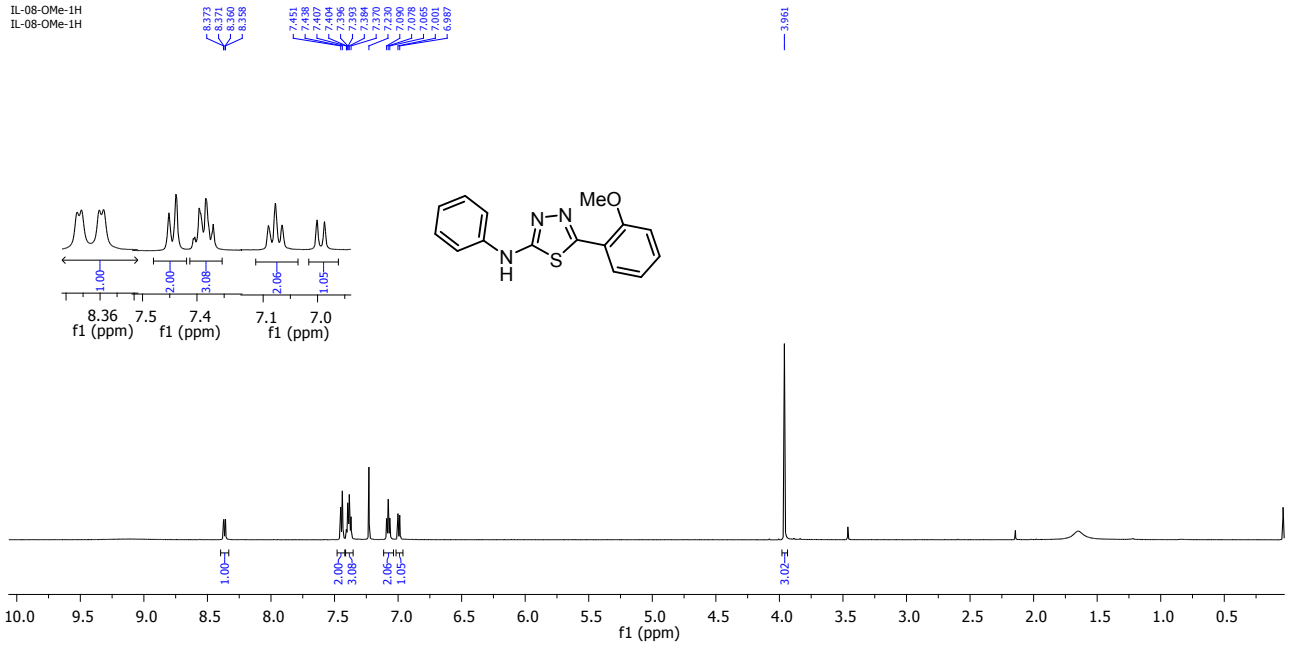

Fig. S3. ^{1}H NMR Spectrum of PMBT

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 140.6, 131.2, 129.7, 128.2, 123.2, 121.5, 119.9, 118.2, 111.5, 55.9.

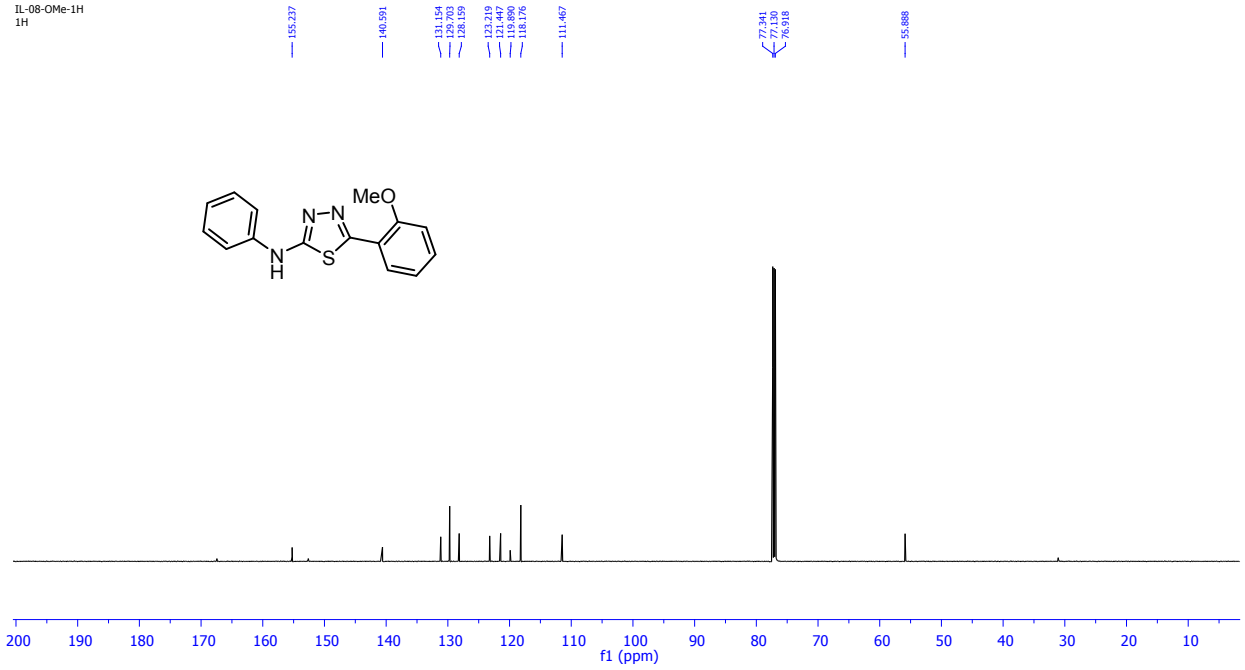

Fig. S4. ^{13}C NMR Spectrum of PMBT

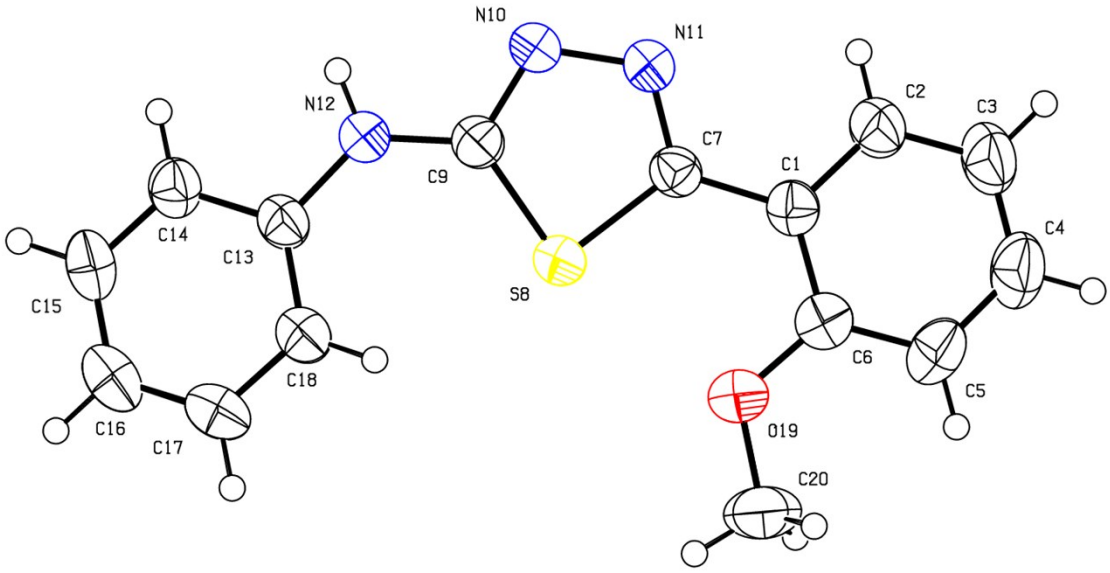

Fig. S5. Crystal structure of PMBT (Cambridge Crystallographic Data Centre (CCDC) no. 1921954-1921955)

Table S1. Experimental absorption band maxima (λ_{abs}, nm), log ε_{max}, fluorescence emission band maxima (λ_{em}, nm) and relative fluorescence yield (F) of PHBT in different solvents.

Solvent	λ_{abs} (log ε_{max})	λ_{em} (F)[a]	$\tilde{\nu}$ $\lambda_{ss}^{shorter}$ (cm^{-1})	$\tilde{\nu}$ λ_{ss}^{longer} (cm^{-1})	I_T/I_N[b]
Toluene	343 (4.30)	395 (0.0008), 531 (0.0031)	3838	10322	1.9
1,4-Dioxane	341 (4.26)	395 (0.02), 520 (0.0003)	4009	10095	0.12
Tetrahydrofuran	341 (4.26)	400 (0.02), 526 (0.0002)	4326	10168	0.17
Ethyl acetate	341 (4.48)	397 (0.03), 530 (0.0002)	4137	10458	0.13
Acetonitrile	337 (4.25)	412 (0.01)	5402		
N,N-Dimethyformamide	340 (4.39)	409 (0.25)	5081		
Dimethyl sulphoxide	338 (4.25)	416 (0.42)	5547		
1-Propanol	341 (4.58)	408 (0.11)	4816		
1-Butanol	342 (4.58)	410 (0.12)	4850		
2-Butanol	342 (4.48)	411 (0.12)	4909		
2-Propanol	340 (4.26)	408 (0.14)	4902		
Methanol	335 (4.38)	425 (0.04)	6321		

[a] *Values in parenthesis are relative fluorescence yields.*[26]

[b] I_T/I_N *represents relative intensity of the longer wavelength band with respect to the shorter wavelength band.*

Table S2. Experimental absorption band maxima (λ_{abs} (nm)), log ε_{max}, fluorescence emission band maxima (λ_{em} (nm)) and quantum yield (Φ) of PMBT in different solvents.

Solvent	λ_{abs} (log ε_{max})	λ_{em} (Φ)	$\tilde{\nu}_{ss}$(cm^{-1})
Toluene	335 (4.48)	390 (0.31)	4210
Ethyl acetate	331 (4.48)	396 (0.27)	5086
1,4-Dioxane	334 (4.26)	403 (0.33)	4877
Tetrahydrofuran	336 (4.30)	406 (0.47)	5607
Acetonitrile	332 (4.16)	415 (0.01)	6197
N,N-Dimethyformamide	339 (4.26)	418 (0.44)	5969
Dimethyl sulphoxide	340 (4.26)	416 (0.35)	5545
1-Propanol	336 (4.50)	417 (0.24)	5781
1-Butanol	336 (4.00)	418 (0.36)	5838
2-Butanol	336 (4.48)	418 (0.30)	5838
2-Propanol	335 (5.20)	418 (0.21)	5927
Methanol	331 (5.15)	426 (0.01)	6737

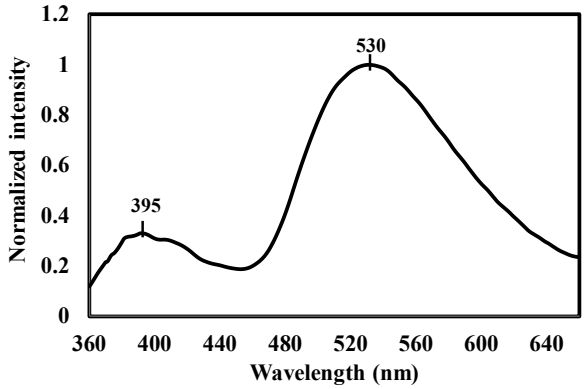

Fig. S6 (a). Emission spectrum of PHBT in toluene, λ_{ex} = 340 nm

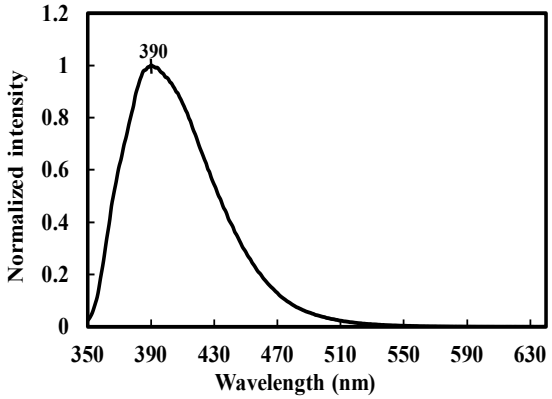

Fig. S6 (b). Emission spectrum of PMBT in toluene, λ_{ex} = 330 nm

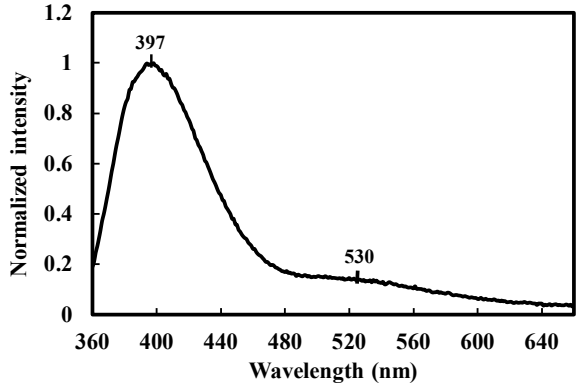

Fig. S7 (a). Emission spectrum of PHBT in ethyl acetate, λ_{ex} = 340 nm

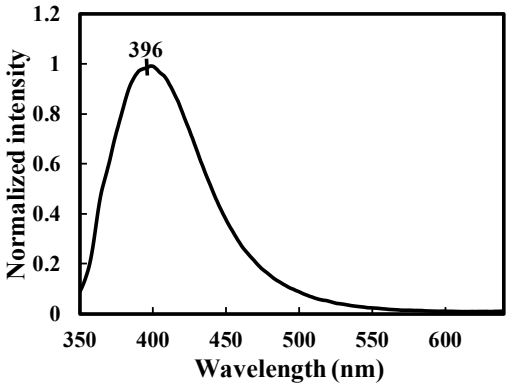

Fig. S7 (b). Emission spectrum of PMBT in ethyl acetate, λ_{ex} = 330 nm

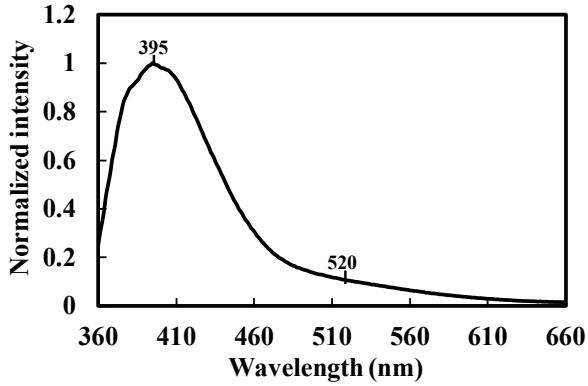

Fig. S8 (a). Emission spectrum of PHBT in dioxane, λ_{ex} = 340 nm

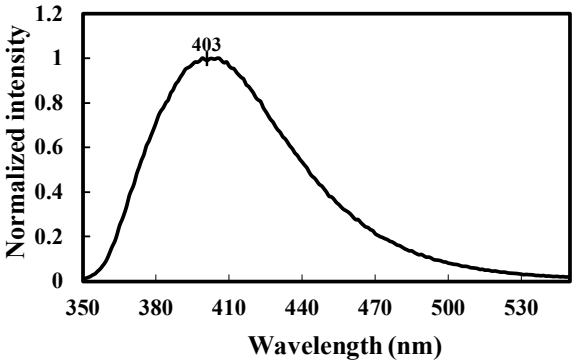

Fig. S8 (b). Emission spectrum of PMBT in dioxane, λ_{ex} = 330 nm

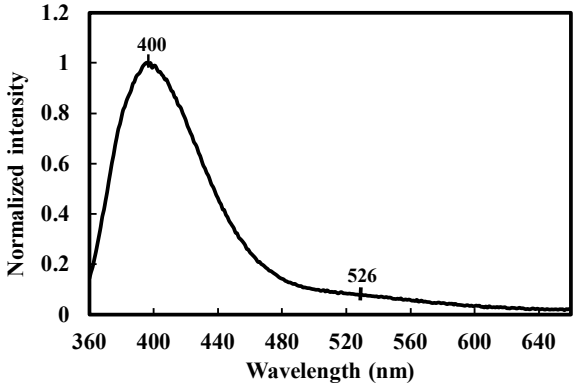

Fig. S9 (a). Emission spectrum of PHBT in THF, λ_{ex} = 340 nm

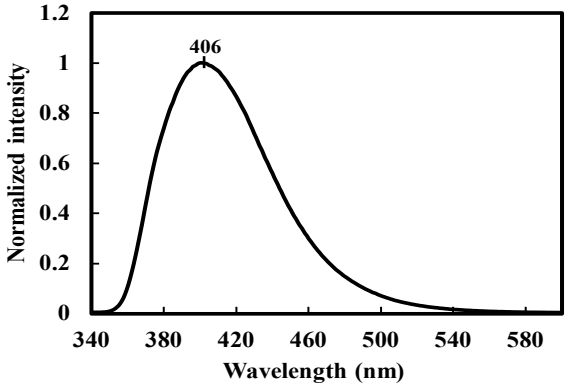

Fig. S9 (b). Emission spectrum of PMBT in THF, λ_{ex} = 330 nm

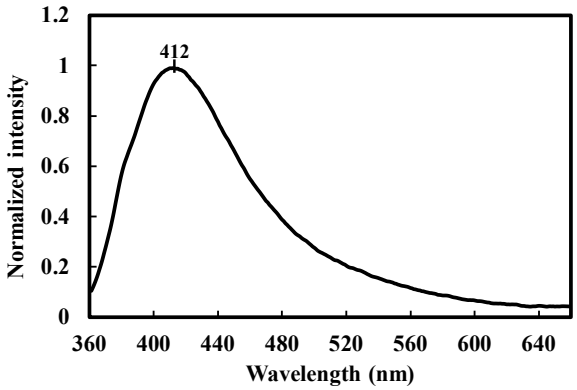

Fig. S10 (a). Emission spectrum of PHBT in acetonitrile, λ_{ex} = 340 nm

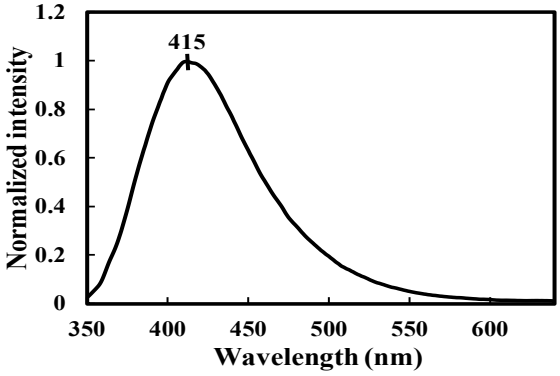

Fig. S10 (b). Emission spectrum of PMBT in acetonitrile, λ_{ex} = 330 nm

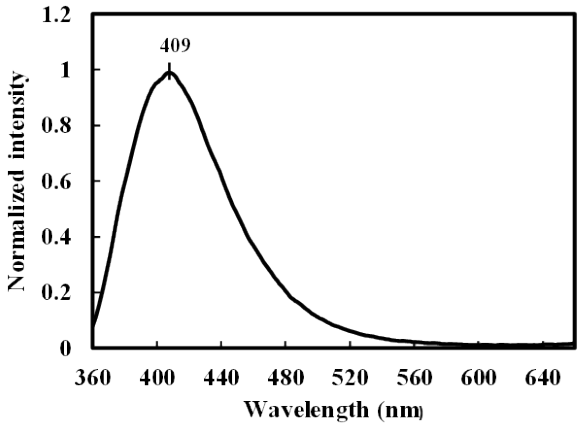

Fig. S11 (a). Emission spectrum of PHBT in DMF, λ_{ex} = 340 nm

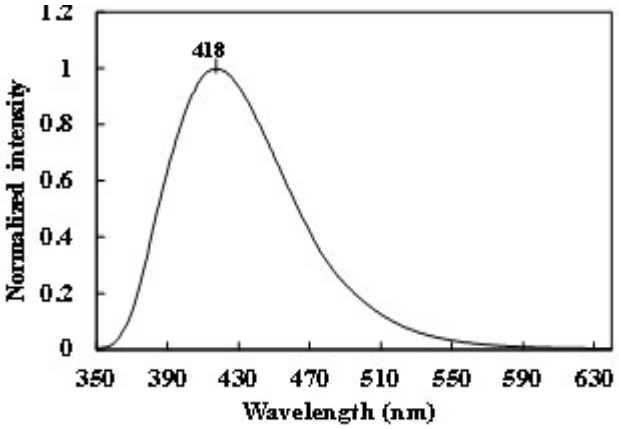

Fig. S11 (b). Emission spectrum of PMBT in DMF, λ_{ex} = 340 nm

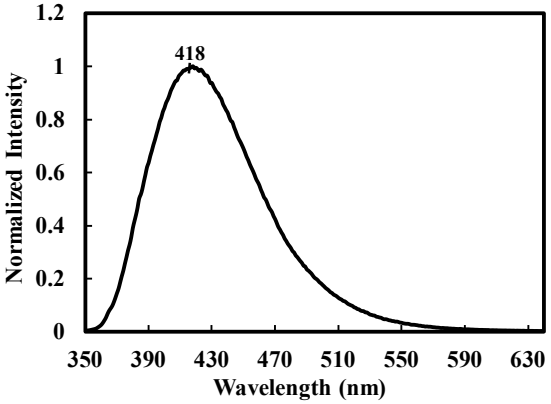

Fig. S12 (a). Emission spectrum of PHBT in DMSO, λ_{ex} = 340 nm

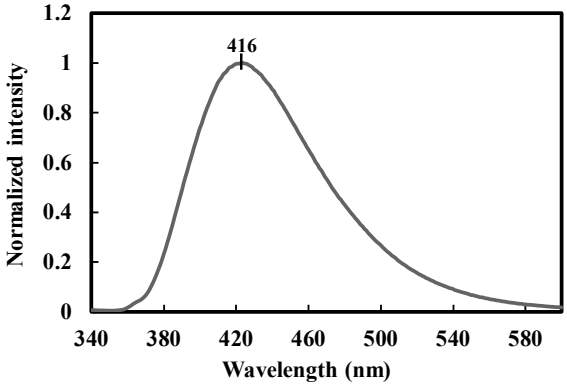

Fig. S12 (b). Emission spectrum of PMBT in DMSO, λ_{ex} = 330 nm

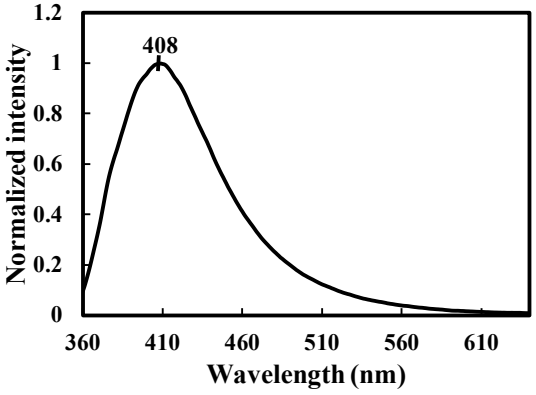

Fig. S13 (a). Emission spectrum of PHBT in 1-propanol, λ_{ex} = 340 nm

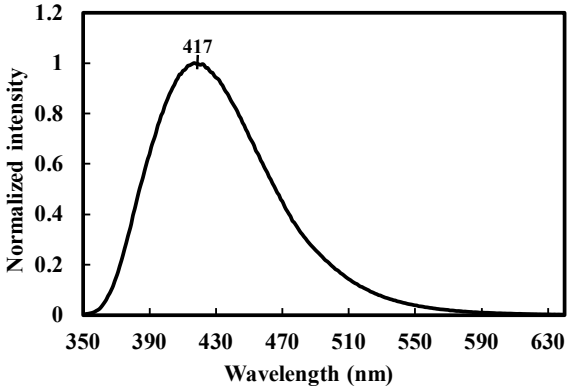

Fig. S13 (b). Emission spectrum of PMBT in 1-propanol, λ_{ex} = 330 nm

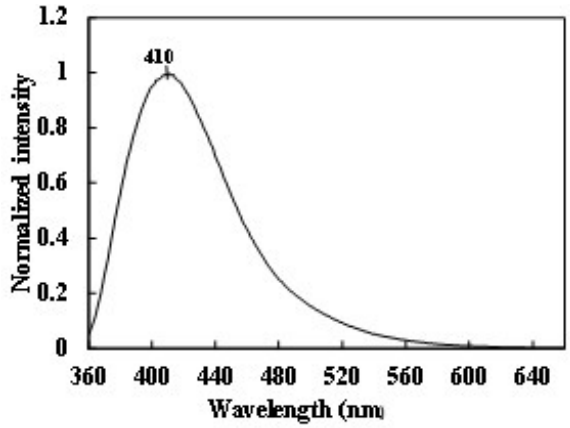

Fig. S14 (a). Emission spectrum of PHBT in 1-butanol, λ_{ex} = 330 nm

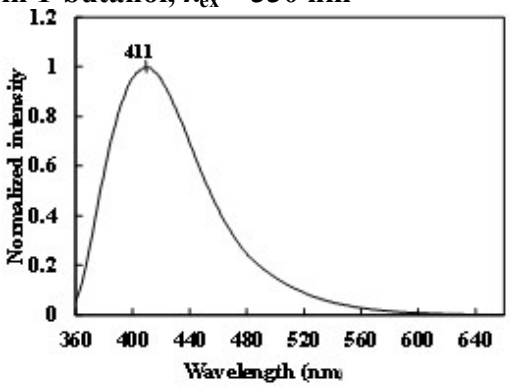

Fig. S15 (a). Emission spectrum of PHBT in 2-butanol, λ_{ex} = 340 nm

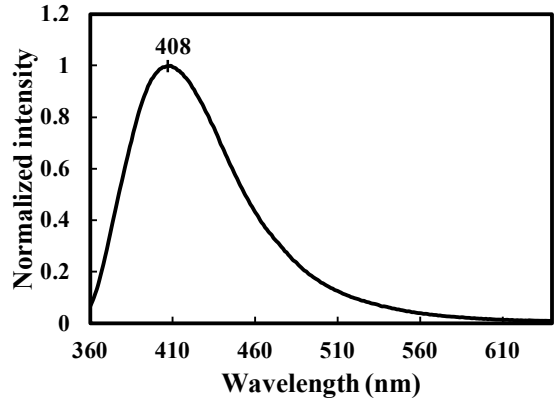

Fig. S16 (a). Emission spectrum of PHBT in 2-propanol, λ_{ex} = 340 nm

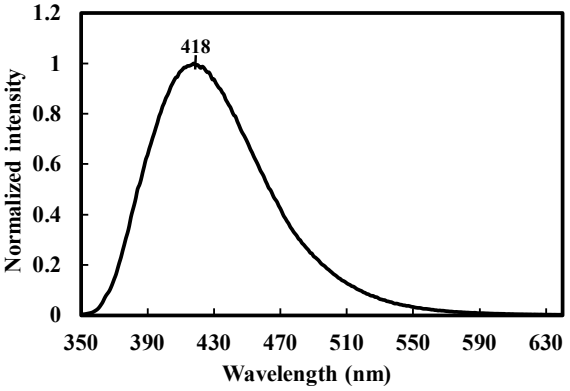

Fig. S14 (b). Emission spectrum of PMBT in 1-butanol, λ_{ex} = 330 nm

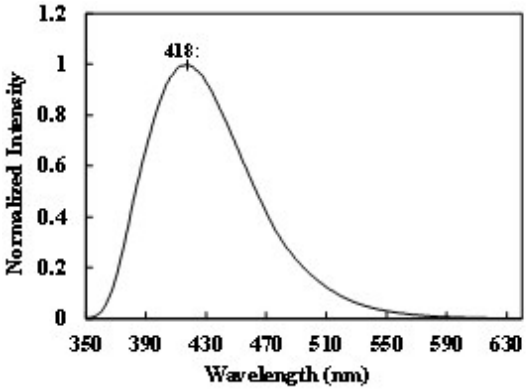

Fig. S15 (a). Emission spectrum of PMBT in 2-butanol, λ_{ex} = 330 nm

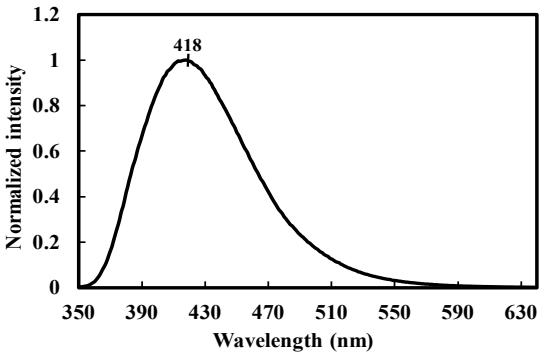

Fig. S16 (b). Emission spectrum of PMBT in 2-propanol, λ_{ex} = 330 nm

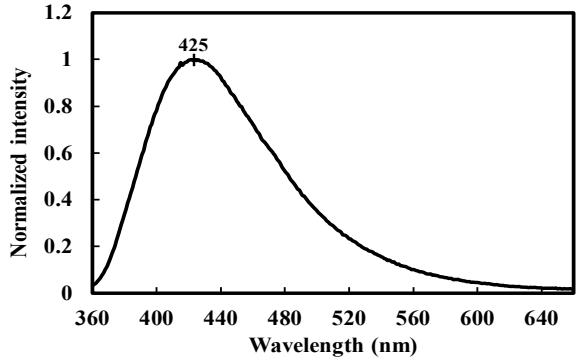

Fig. S17 (a). Emission spectrum of PHBT in methanol, λ_{ex} = 340 nm

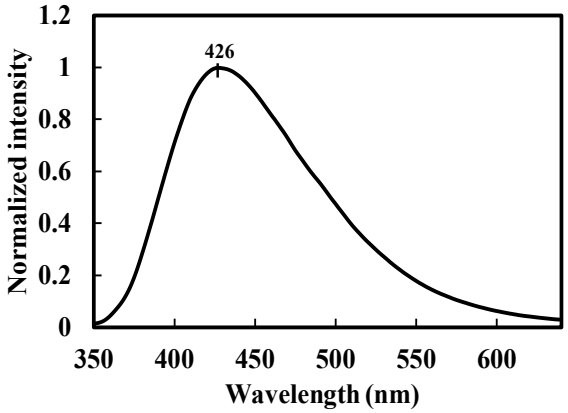

Fig. S17 (b). Emission spectrum of PMBT in methanol, λ_{ex} = 330 nm

Table S3. Theoretically calculated emission wavelength maximum for enol and keto species of PHBT in few selected solvents

Solvent	λ_{em}^{enol} (nm)	λ_{em}^{keto} (nm)
Cyclohexane	350	486
Toluene	350	471
THF	422	441
Methanol	416	

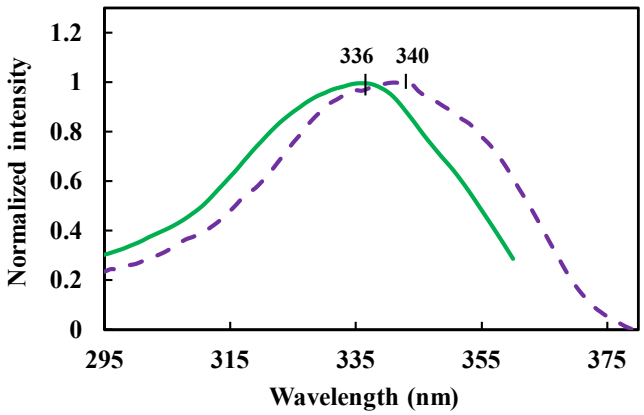

Fig. S18. Normalized excitation spectra of PHBT in ethyl acetate at λ_{em} = 380 nm (solid line) and 520 nm (dashed line).

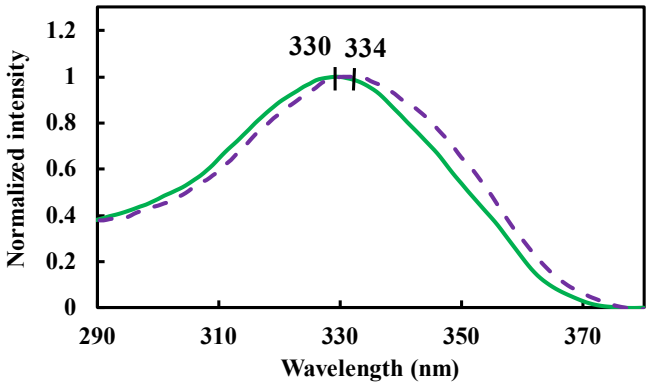

Fig. S19. Normalized excitation spectra of PHBT in acetonitrile at λ_{em} = 400 nm (solid line) and 500 nm (dashed line).

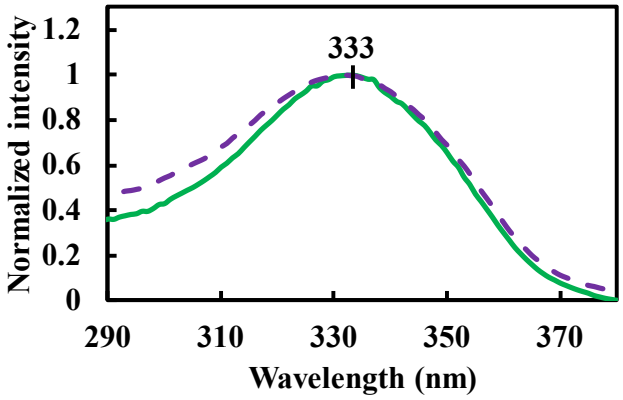

Fig. S20. Normalized excitation spectra of PHBT in methanol at λ_{em} = 420 nm (solid line) and 500 nm (dashed line).

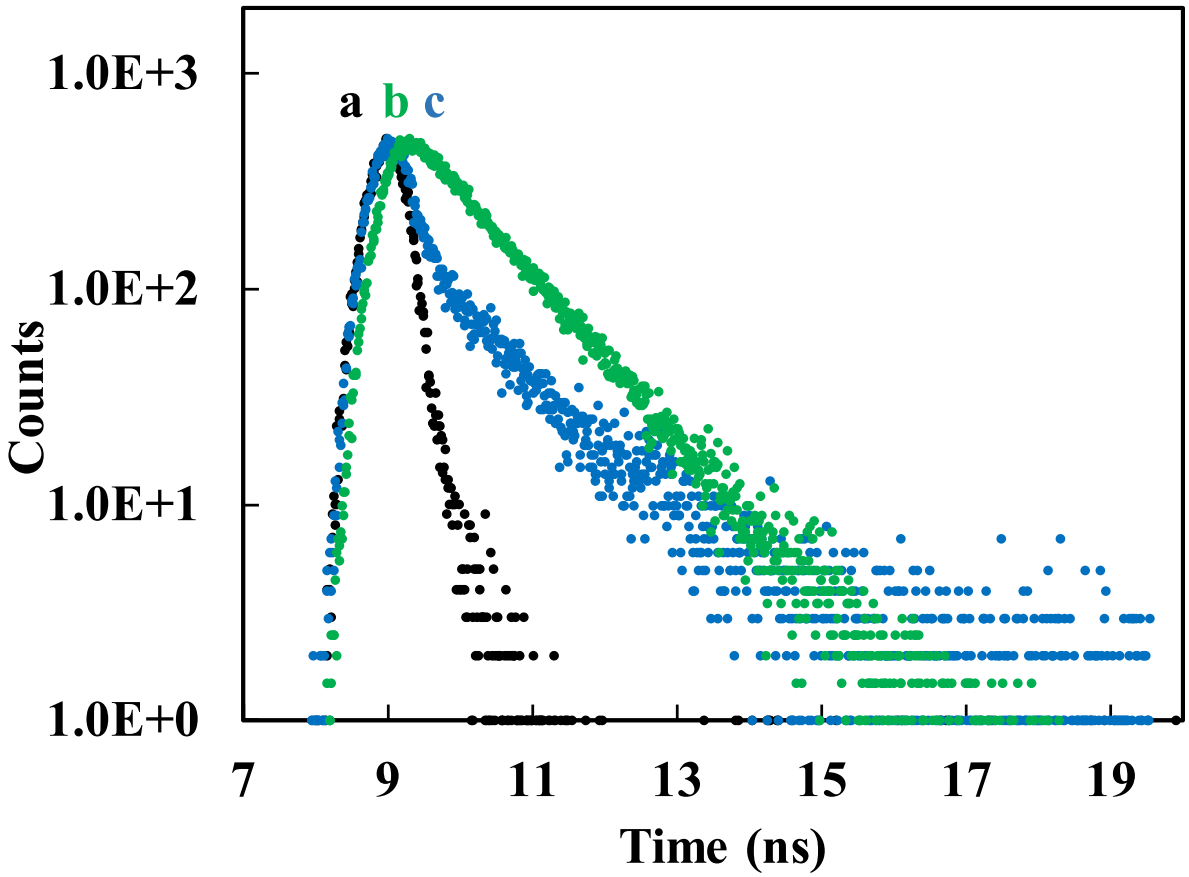

Fig. S21. (a) Instrument response function, (b) fluorescence decay of PHBT monitored at λ_{em} = 395 nm and (c) fluorescence decay of PHBT monitored at λ_{em} = 520 nm in 1,4-dioxane, λ_{ex} = 336 nm.

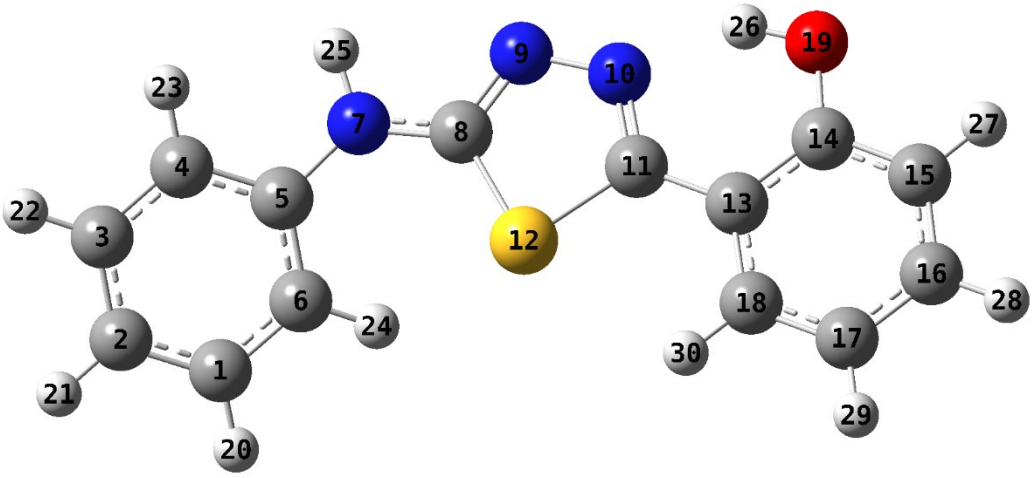

Fig. S22. Ground state optimized geometry of PHBT *cis*-enol

Table S4. Ground state optimized Parameters of PHBT *cis*-enol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.3942	1.7079	0.642138
2	6	0	-5.59938	1.303279	0.065096
3	6	0	-5.68107	0.038284	-0.52697
4	6	0	-4.56932	-0.80061	-0.55756
5	6	0	-3.35474	-0.38994	0.019114
6	6	0	-3.27692	0.868556	0.634265
7	7	0	-2.27559	-1.29419	-0.02181
8	6	0	-0.93016	-1.07818	0.047564
9	7	0	-0.09542	-2.08636	0.173021
10	7	0	1.204662	-1.68701	0.121211
11	6	0	1.392413	-0.39813	-0.02282
12	16	0	-0.13807	0.487485	-0.13006
13	6	0	2.708843	0.225506	-0.06348
14	6	0	3.874834	-0.57544	0.0887
15	6	0	5.139827	0.030821	0.056969
16	6	0	5.261861	1.403804	-0.12526
17	6	0	4.120967	2.205369	-0.28048
18	6	0	2.864581	1.614031	-0.24942
19	8	0	3.824626	-1.91258	0.265938
20	1	0	-4.31863	2.679523	1.121262
21	1	0	-6.4638	1.959295	0.081044
22	1	0	-6.61125	-0.2955	-0.977
23	1	0	-4.63377	-1.77527	-1.03386
24	1	0	-2.36898	1.188528	1.131318
25	1	0	-2.50758	-2.27395	-0.13358
26	1	0	2.877013	-2.20299	0.25991
27	1	0	6.012154	-0.60325	0.17705
28	1	0	6.249781	1.854221	-0.14845
29	1	0	4.214699	3.276505	-0.42535
30	1	0	1.981649	2.235239	-0.37305

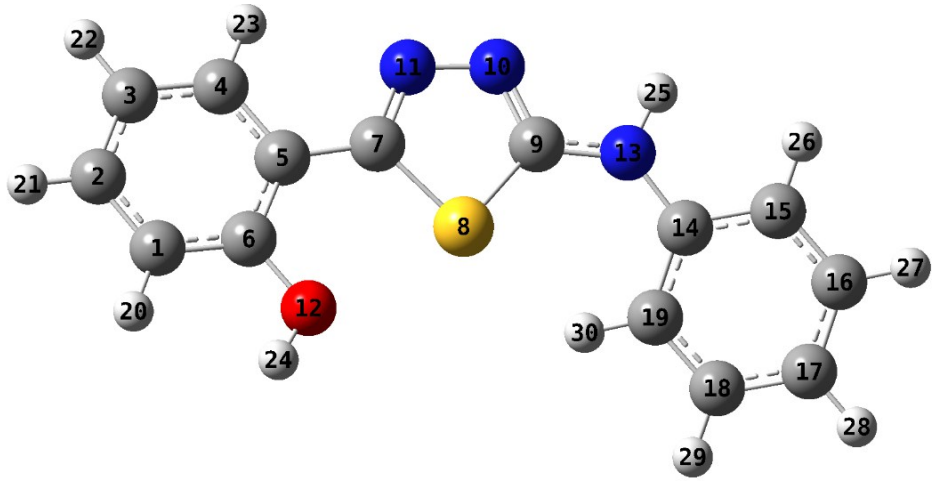

Fig. S23. Ground state optimized geometry of PHBT *trans*-enol

Table S5. Ground state optimized parameters of PHBT *trans*-enol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.47877	1.592418	-0.15943
2	6	0	-5.51506	0.669195	-0.03847
3	6	0	-5.22197	-0.69203	0.104582
4	6	0	-3.8973	-1.1147	0.124997
5	6	0	-2.8292	-0.20217	0.003798
6	6	0	-3.14743	1.163733	-0.13852
7	6	0	-1.45315	-0.71494	0.025536
8	16	0	0.013399	0.284129	-0.05742
9	6	0	0.910741	-1.21699	0.064535
10	7	0	0.146412	-2.28811	0.152488
11	7	0	-1.17869	-1.98969	0.123818
12	8	0	-2.10972	2.051026	-0.25529
13	7	0	2.27053	-1.35858	0.005019
14	6	0	3.308683	-0.41383	0.025925
15	6	0	4.57159	-0.83168	-0.43468
16	6	0	5.652852	0.04545	-0.42519
17	6	0	5.498768	1.358521	0.033493
18	6	0	4.248094	1.771679	0.495516
19	6	0	3.157508	0.897612	0.503611
20	1	0	-4.69544	2.652253	-0.27142
21	1	0	-6.54475	1.013026	-0.05523
22	1	0	-6.02225	-1.41871	0.200448

23	1	0	-3.65608	-2.16553	0.235415
24	1	0	-2.44393	2.952815	-0.35516
25	1	0	2.547705	-2.32818	-0.09239
26	1	0	4.696656	-1.8457	-0.80554
27	1	0	6.617997	-0.29791	-0.78588
28	1	0	6.340242	2.043942	0.033897
29	1	0	4.112121	2.78265	0.868461
30	1	0	2.21118	1.238175	0.904995

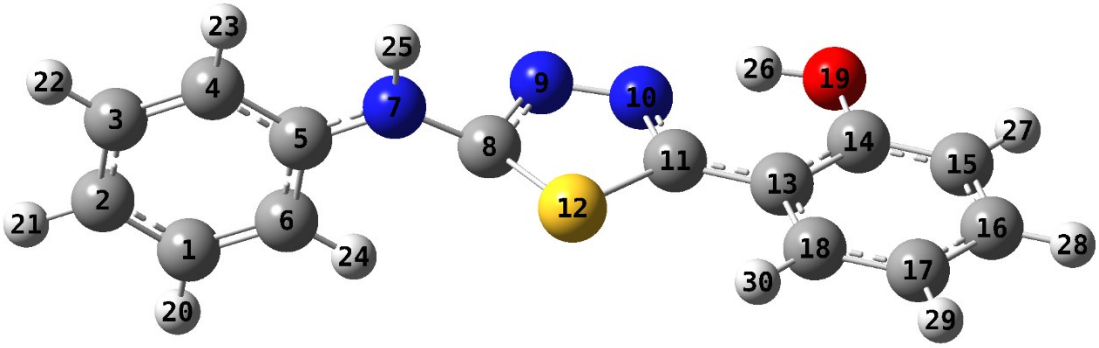

Fig. S24. Excited state optimized geometry of PHBT *cis*-enol

Table S6. Excited state optimized parameters of PHBT *cis*-enol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.3942	1.7079	0.642138
2	6	0	-5.59938	1.303279	0.065096
3	6	0	-5.68107	0.038284	-0.52697
4	6	0	-4.56932	-0.80061	-0.55756
5	6	0	-3.35474	-0.38994	0.019114
6	6	0	-3.27692	0.868556	0.634265
7	7	0	-2.27559	-1.29419	-0.02181
8	6	0	-0.93016	-1.07818	0.047564
9	7	0	-0.09542	-2.08636	0.173021
10	7	0	1.204662	-1.68701	0.121211
11	6	0	1.392413	-0.39813	-0.02282
12	16	0	-0.13807	0.487485	-0.13006
13	6	0	2.708843	0.225506	-0.06348
14	6	0	3.874834	-0.57544	0.0887

15	6	0	5.139827	0.030821	0.056969
16	6	0	5.261861	1.403804	-0.12526
17	6	0	4.120967	2.205369	-0.28048
18	6	0	2.864581	1.614031	-0.24942
19	8	0	3.824626	-1.91258	0.265938
20	1	0	-4.31863	2.679523	1.121262
21	1	0	-6.4638	1.959295	0.081044
22	1	0	-6.61125	-0.2955	-0.977
23	1	0	-4.63377	-1.77527	-1.03386
24	1	0	-2.36898	1.188528	1.131318
25	1	0	-2.50758	-2.27395	-0.13358
26	1	0	2.877013	-2.20299	0.25991
27	1	0	6.012154	-0.60325	0.17705
28	1	0	6.249781	1.854221	-0.14845
29	1	0	4.214699	3.276505	-0.42535
30	1	0	1.981649	2.235239	-0.37305

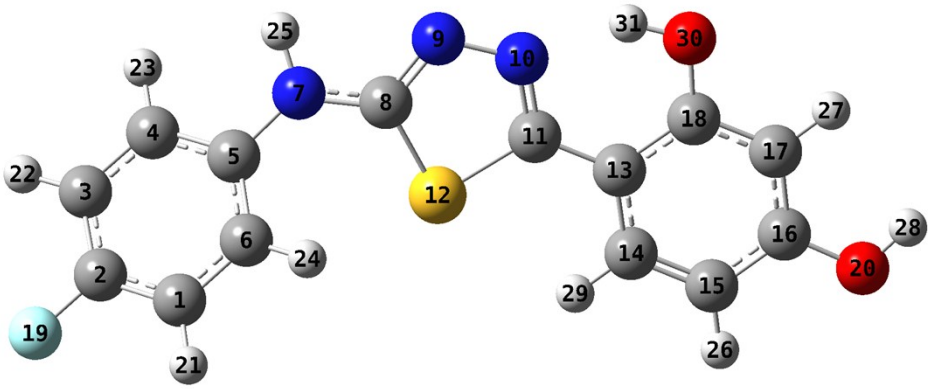

Fig. S25. Ground state optimized geometry of FABT *cis*-enol

Table S7. Ground state optimized parameters of FABT *cis*-enol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.37768	-1.40214	0.791563
2	6	0	-5.51362	-1.0792	0.062577
3	6	0	-5.60309	0.085325	-0.69059
4	6	0	-4.50444	0.942196	-0.7281
5	6	0	-3.33928	0.644382	-0.00182
6	6	0	-3.29021	-0.52603	0.770587

7	7	0	-2.27101	1.564778	-0.04997
8	6	0	-0.92711	1.337917	0.038838
9	7	0	-0.07908	2.327185	0.189711
10	7	0	1.217407	1.906016	0.142162
11	6	0	1.383562	0.615367	-0.01977
12	16	0	-0.16181	-0.24211	-0.15595
13	6	0	2.686146	-0.02843	-0.05485
14	6	0	2.833615	-1.41504	-0.26275
15	6	0	4.074889	-2.0291	-0.2877
16	6	0	5.224451	-1.24292	-0.10226
17	6	0	5.121598	0.13136	0.102098
18	6	0	3.864958	0.748949	0.126382
19	9	0	-6.57839	-1.92842	0.089873
20	8	0	6.428453	-1.88628	-0.13435
21	1	0	-4.35149	-2.31076	1.382985
22	1	0	-6.50762	0.305941	-1.24656
23	1	0	-4.54735	1.844785	-1.33048
24	1	0	-2.42038	-0.75101	1.376592
25	1	0	-2.50421	2.54265	-0.17127
26	1	0	4.175272	-3.09623	-0.44867
27	1	0	6.003321	0.749371	0.244107
28	1	0	7.148983	-1.25606	0.005127
29	1	0	1.947898	-2.02655	-0.40995
30	8	0	3.83271	2.081474	0.326153
31	1	0	2.886809	2.384128	0.311453

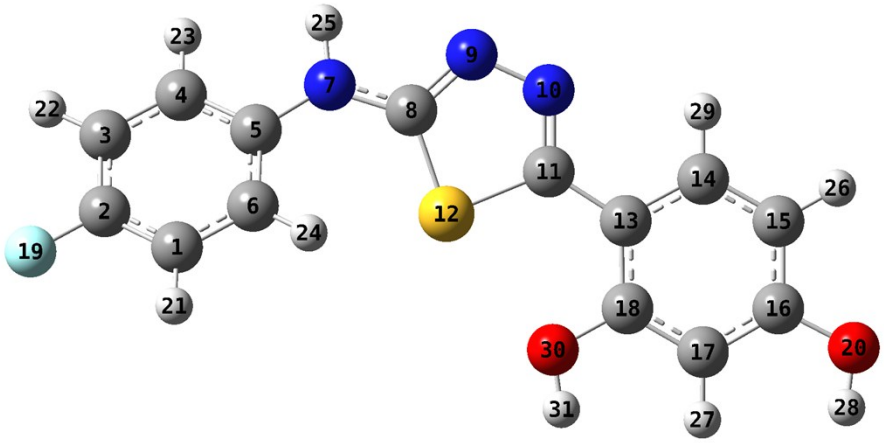

Fig. S26. Ground state optimized geometry of FABT *trans*-enol

Table S8. Ground state optimized parameters of FABT *trans*-enol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.282674	-1.46055	-0.61679
2	6	0	5.484731	-1.0498	-0.06035
3	6	0	5.638502	0.205972	0.514849
4	6	0	4.542886	1.065613	0.545057
5	6	0	3.307526	0.680825	-0.00814
6	6	0	3.192501	-0.58666	-0.60122
7	7	0	2.255391	1.610845	0.035112
8	6	0	0.899302	1.43496	-0.05082
9	7	0	0.106385	2.477933	-0.17249
10	7	0	-1.21255	2.141007	-0.1485
11	6	0	-1.44945	0.861206	-0.02375
12	16	0	0.046347	-0.09195	0.100121
13	6	0	-2.80575	0.304623	-0.01333
14	6	0	-3.90351	1.172817	-0.19544
15	6	0	-5.21408	0.721448	-0.18872
16	6	0	-5.46797	-0.64336	0.004786
17	6	0	-4.4084	-1.53343	0.188303
18	6	0	-3.09182	-1.06091	0.178163
19	9	0	6.549927	-1.902	-0.0803
20	8	0	-6.77288	-1.04733	0.002485
21	1	0	4.20176	-2.44178	-1.07165
22	1	0	6.592698	0.497857	0.939644
23	1	0	4.642947	2.043785	1.006608
24	1	0	2.268992	-0.89617	-1.07446
25	1	0	2.512688	2.584255	0.144096
26	1	0	-6.04444	1.403742	-0.33187
27	1	0	-4.59862	-2.59388	0.341052
28	1	0	-6.83428	-2.00289	0.137119
29	1	0	-3.69596	2.226017	-0.3447
30	8	0	-2.03689	-1.91461	0.354419
31	1	0	-2.34593	-2.82122	0.48513

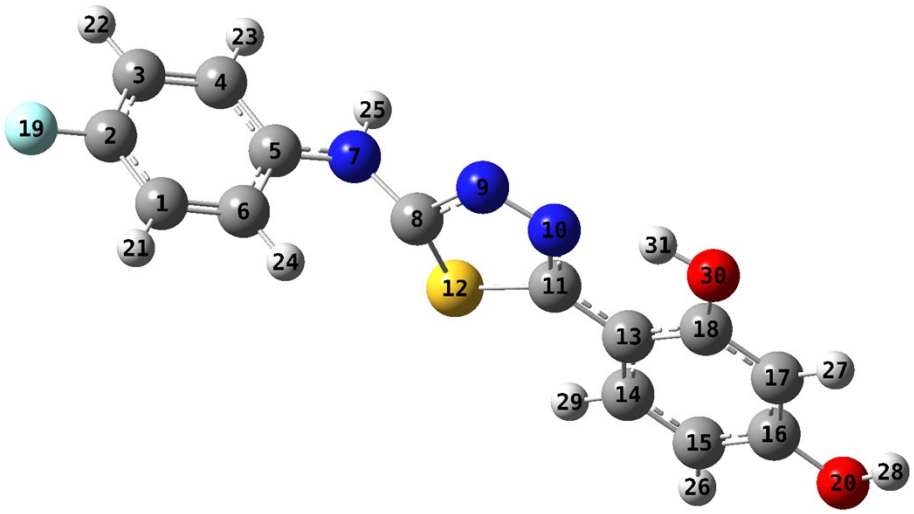

Fig. S27. Excited state optimized geometry of FABT *cis*-enol

Table S9. Excited state optimized parameters of FABT *cis*-enol

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.93869	-0.01388	1.434593
2	6	0	-5.99973	-0.13459	0.523093
3	6	0	-5.8136	-0.20268	-0.86864
4	6	0	-4.53209	-0.14844	-1.36052
5	6	0	-3.41526	-0.0249	-0.4631
6	6	0	-3.65219	0.040975	0.952417
7	7	0	-2.17574	0.027714	-0.96245
8	6	0	-0.97429	0.208501	-0.19393
9	7	0	-0.38684	1.44077	-0.32975
10	7	0	0.924742	1.376093	-0.18868
11	6	0	1.465903	0.157488	-0.13458
12	16	0	0.233996	-1.13314	-0.30315
13	6	0	2.884924	-0.07749	-0.00309
14	6	0	3.434946	-1.37725	0.025884
15	6	0	4.801854	-1.60559	0.144402
16	6	0	5.66704	-0.51054	0.242502
17	6	0	5.165332	0.79277	0.219084
18	6	0	3.79193	1.019965	0.098312
19	9	0	-7.24836	-0.18622	0.999274
20	8	0	7.011669	-0.77037	0.362082
21	1	0	-5.15015	0.03555	2.496192
22	1	0	-6.67428	-0.2943	-1.52043
23	1	0	-4.35066	-0.1955	-2.42878

24	1	0	-2.80076	0.139948	1.611143
25	1	0	-2.09701	0.005373	-1.98209
26	1	0	5.203924	-2.61238	0.166261
27	1	0	5.826086	1.65231	0.29088
28	1	0	7.499725	0.061074	0.43224
29	1	0	2.767191	-2.23116	-0.04144
30	8	0	3.3681	2.305738	0.078372
31	1	0	2.377575	2.304203	-0.02327