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

Unusual Fluorescent photoswitching of imidazole derivatives: Role of molecular conformation and twist angle controlled organic solid state fluorescence

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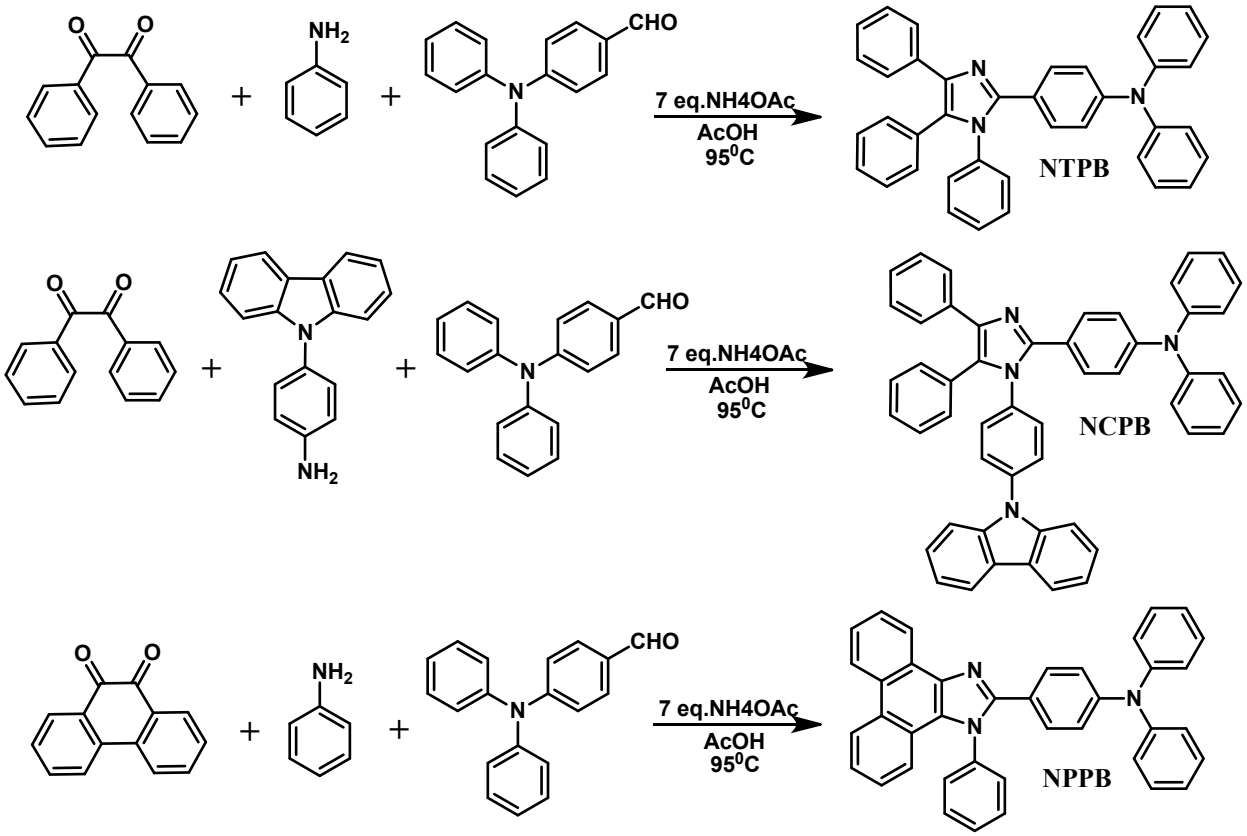
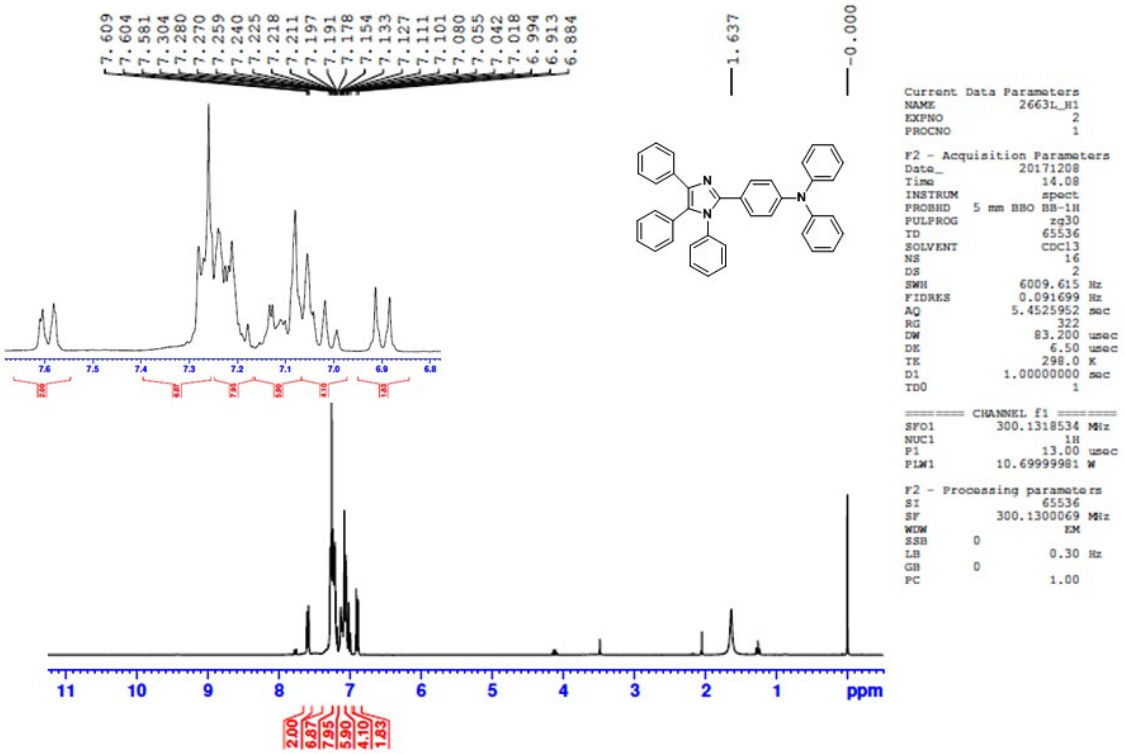
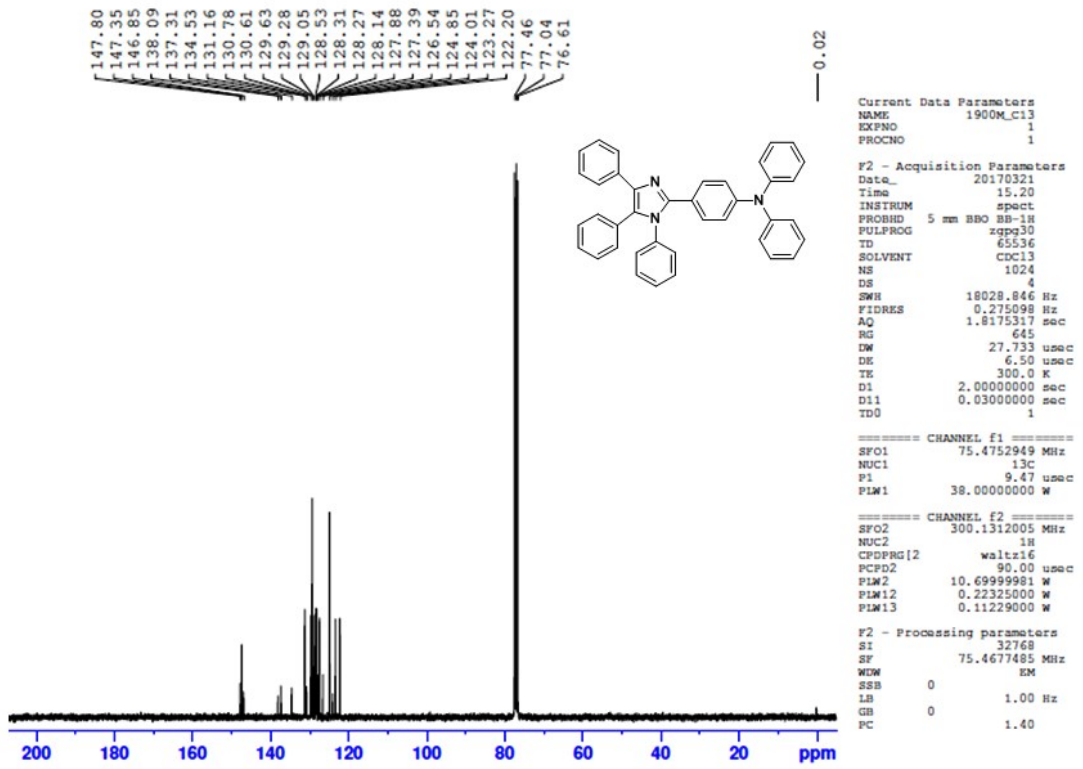
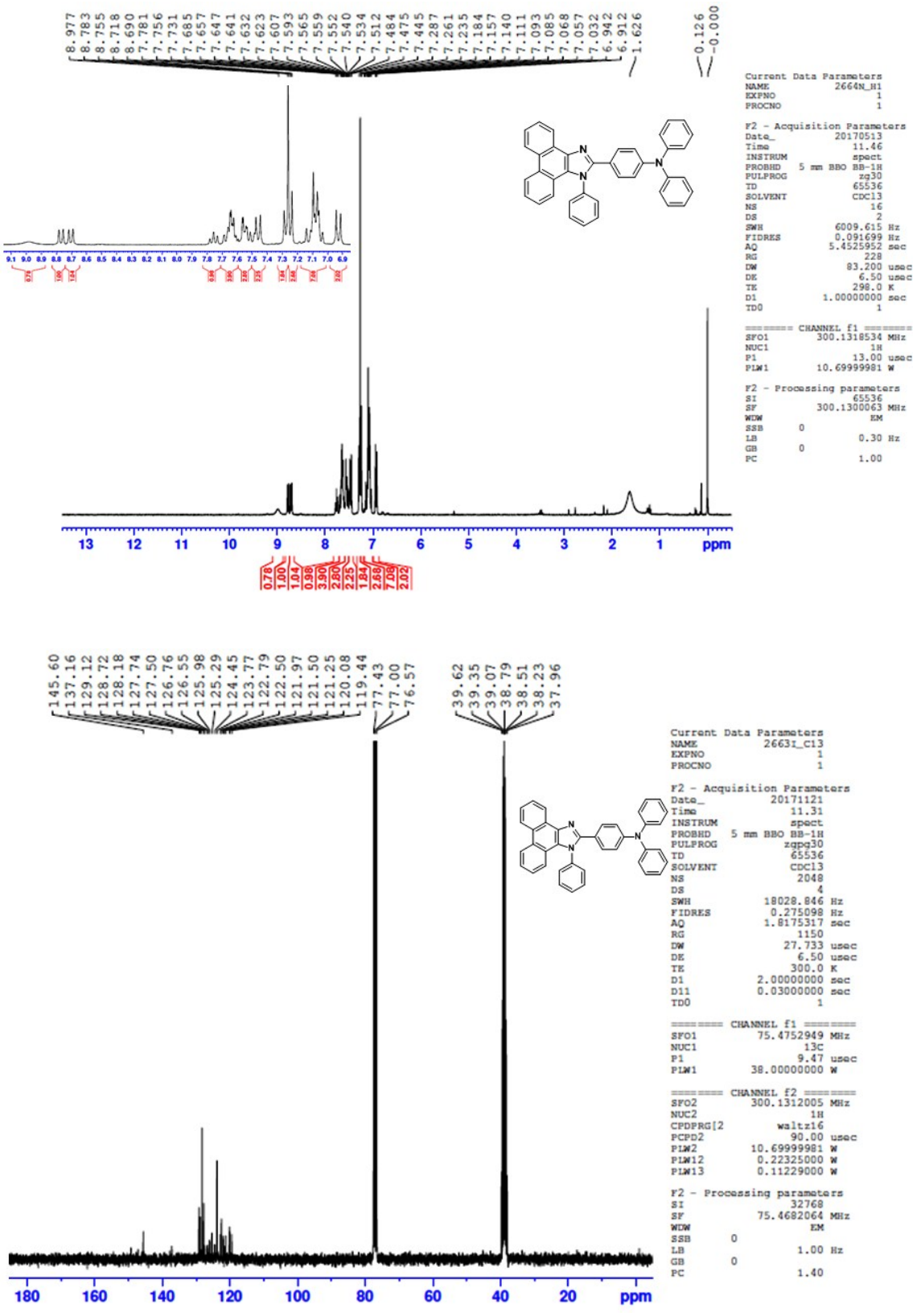


Scheme S1. Synthesis of NTPB, NPPB and NCPB.

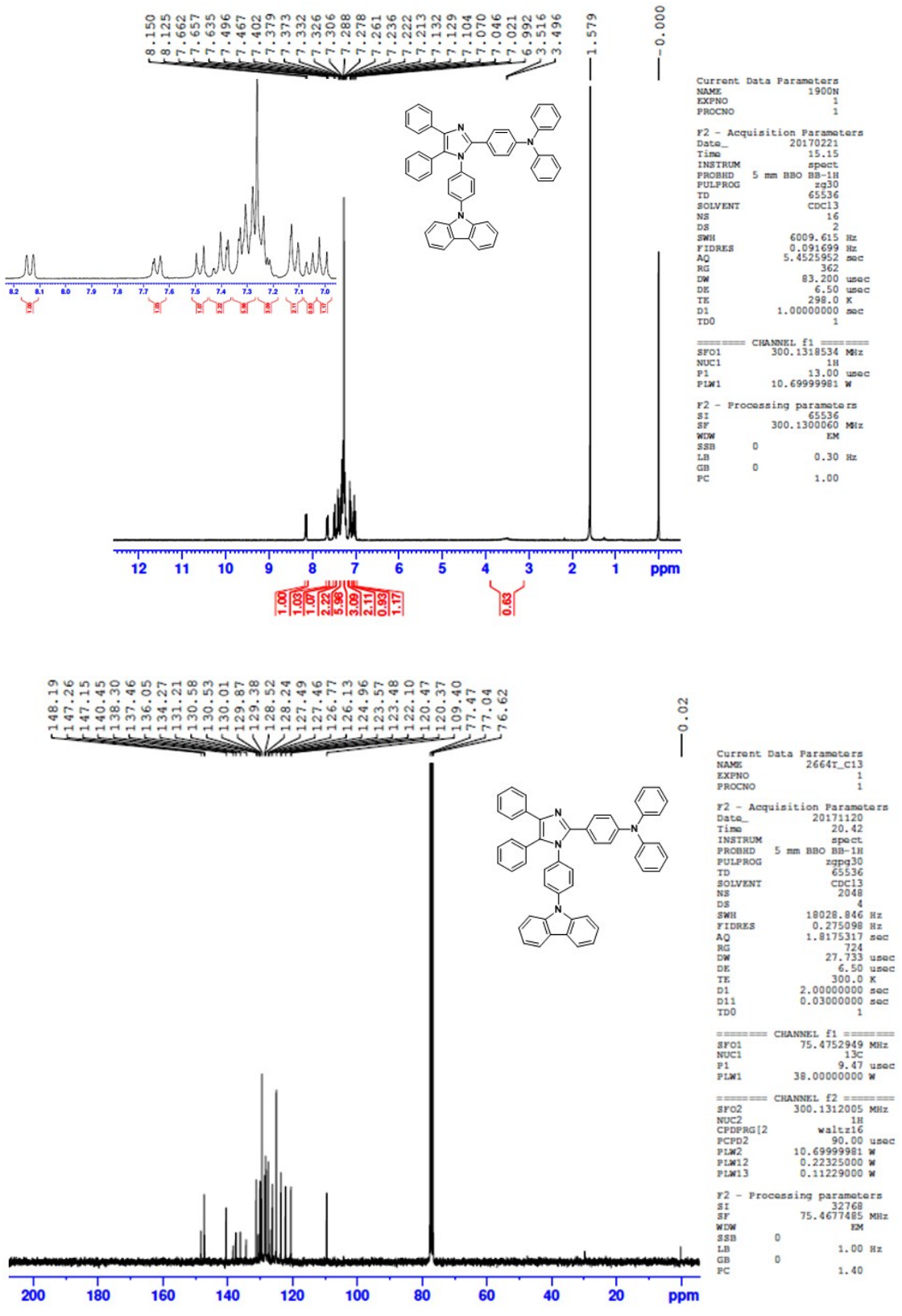




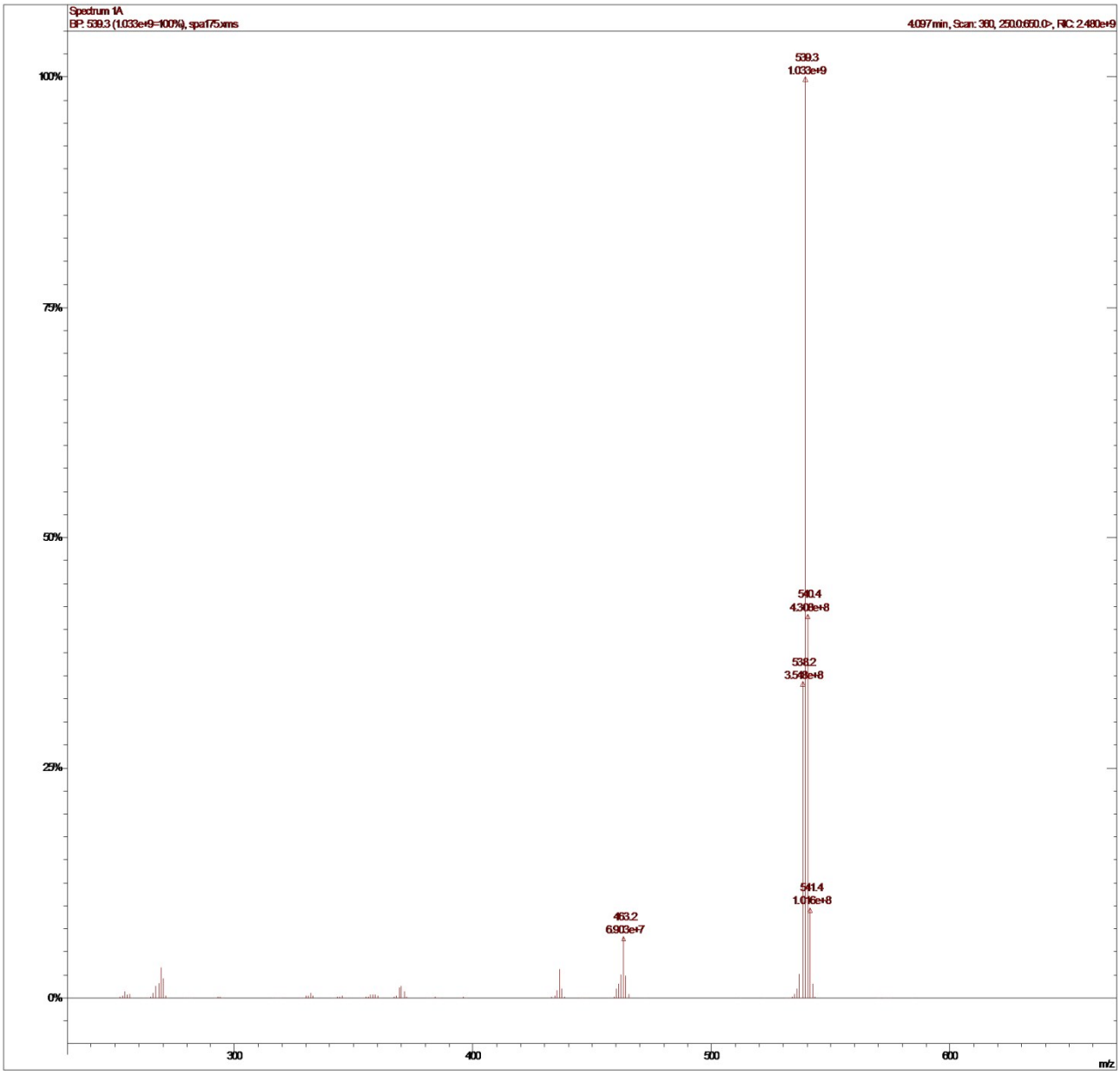
^{1}H and ^{13}C NMR of NTPB.



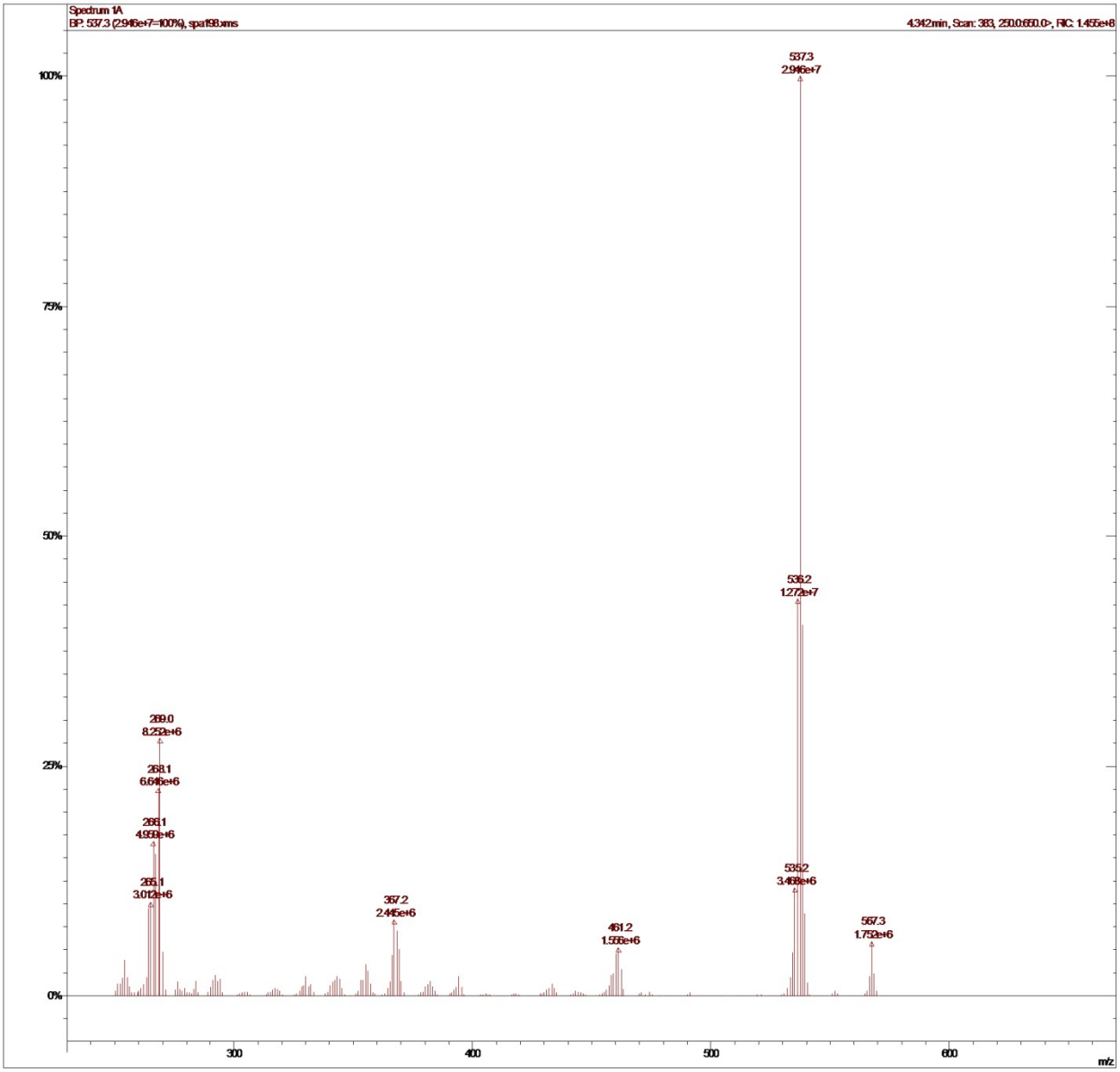
[1]H and *[13]C* NMR of NPPB.



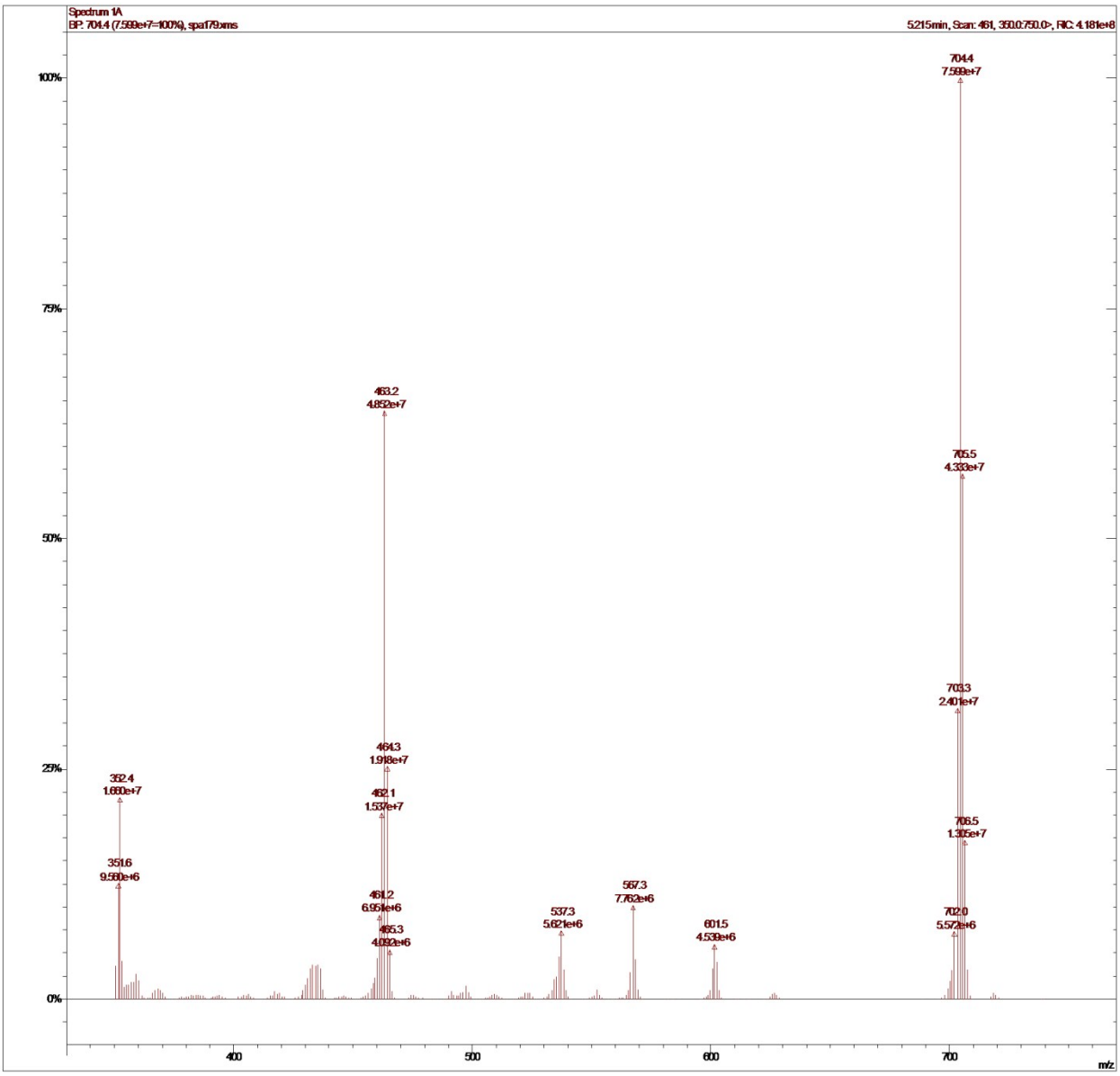
[1]H and *[13]C* NMR of NCPB.



NTPB: m/z calcd for $C_{39}H_{29}N_3$ (M + H): 539.2, found: 539.3



NPPB: m/z calcd for $C_{39}H_{27}N_3$ (M + H): 537.2, found: 537.3.



NCPB: m/z calcd for $C_{51}H_{36}N_4$ (M + H): 704.2, found: 704.4.

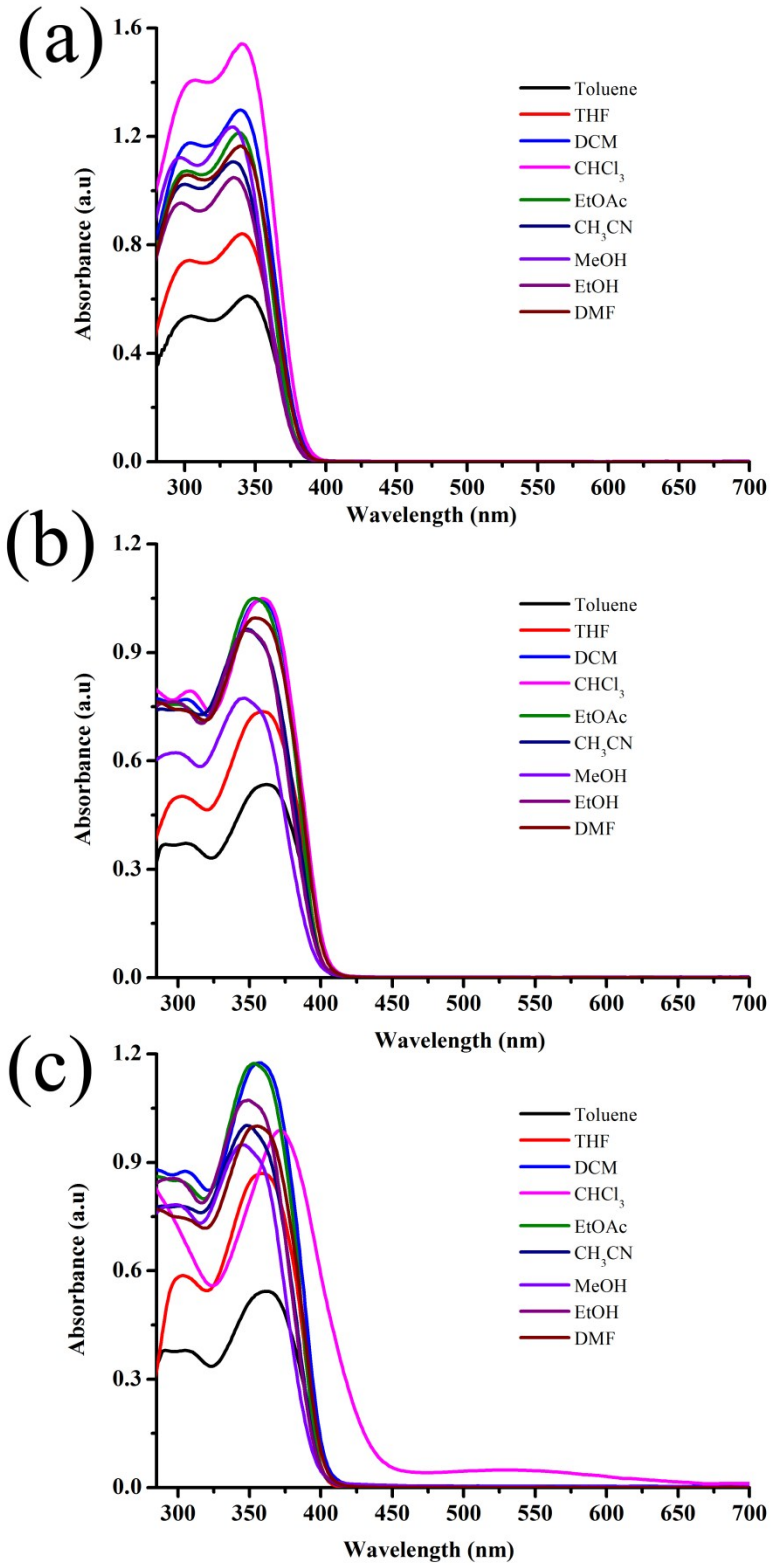


Figure S1. Absorption spectra of NTPB, NCPB and NPPB in different solvents.

Table S1. Absorption λ_{max} of NTPB, NPPB and NCPB in different solvents.

	Absorption λ_{max} (nm)								
	Toluene	**THF**	**DCM**	**$CHCl_3$**	**EtOAc**	**CH_3CN**	**CH_3OH**	**EtOH**	**DMF**
NTPB	302, 345	302, 341	302, 340	302, 340	300, 339	298, 335	295, 334	296, 335	300, 340
NPPB	302, 363	302, 360	308, 358	308, 358	355	350	298, 348	298, 350	356
NCPB	297, 340	295, 337	295, 337	296, 340	293, 337	292, 334	291, 332	292, 333	293, 337

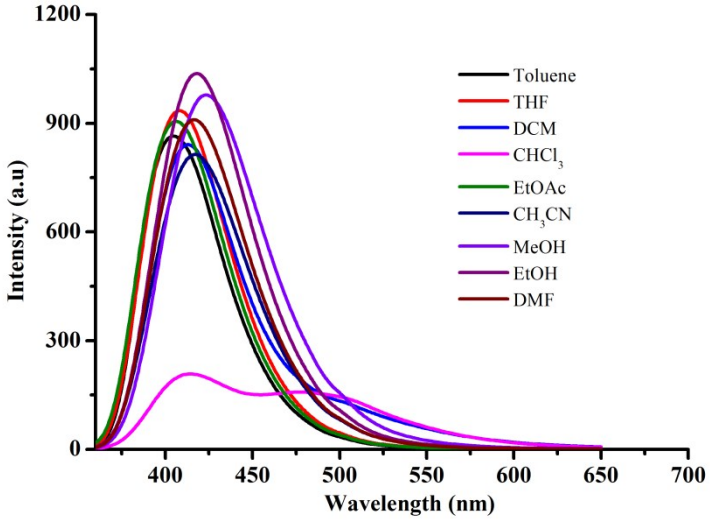


Figure S2.Fluorescence spectra of NCPB in different solvents.

Table S2.Fluorescence λ_{max} of NTPB, NPPB and NCPB in different solvents.

	Emission λ_{max} (nm)								
	Toluene	**THF**	**DCM**	**$CHCl_3$**	**EtOAc**	**CH_3CN**	**CH_3OH**	**EtOH**	**DMF**
NTPB	395	401	407	405, 472	400	410	418	412	410
NPPB	413	418	423	421	418	429	434	427	429
NCPB	405	408	413	413, 486	407	417	423	418	417

Table S3.Quantum yield of NTPB, NPPB and NCPB.

	Quantum yield (Φ_f)					
	CH_2Cl_2	Toluene	CH_3CN	EtOAc	DMF	CH_3OH
NTPB	0.951	0.563	0.737	0.833	1.000	0.920
NPPB	0.990	1.00	0.760	0.890	0.920	0.700
NCPB	0.98	0.95	0.88	0.78	0.014	0.82

Note: NTPB and NCPB with respect to quinine sulfate and NPPB with respect to 9,10-diphenylanthracene.

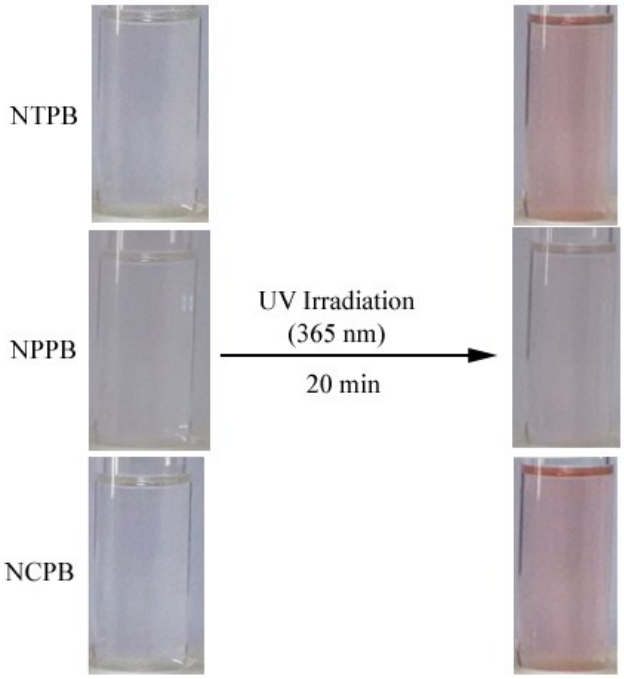


Figure S3. Digital images of NTPB, NPPB and NCPB in $CHCl_3$ before and after UV irradiation.

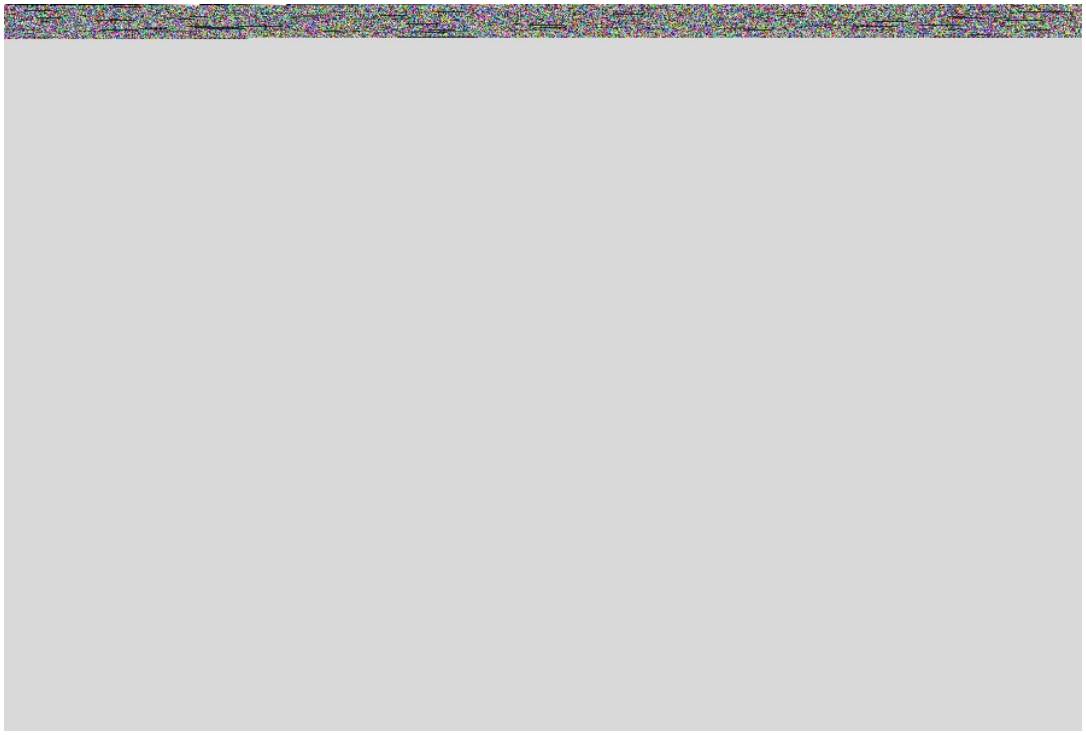


Figure S4a. ^{1}H NMR spectra of NTPB before UV irradiation.

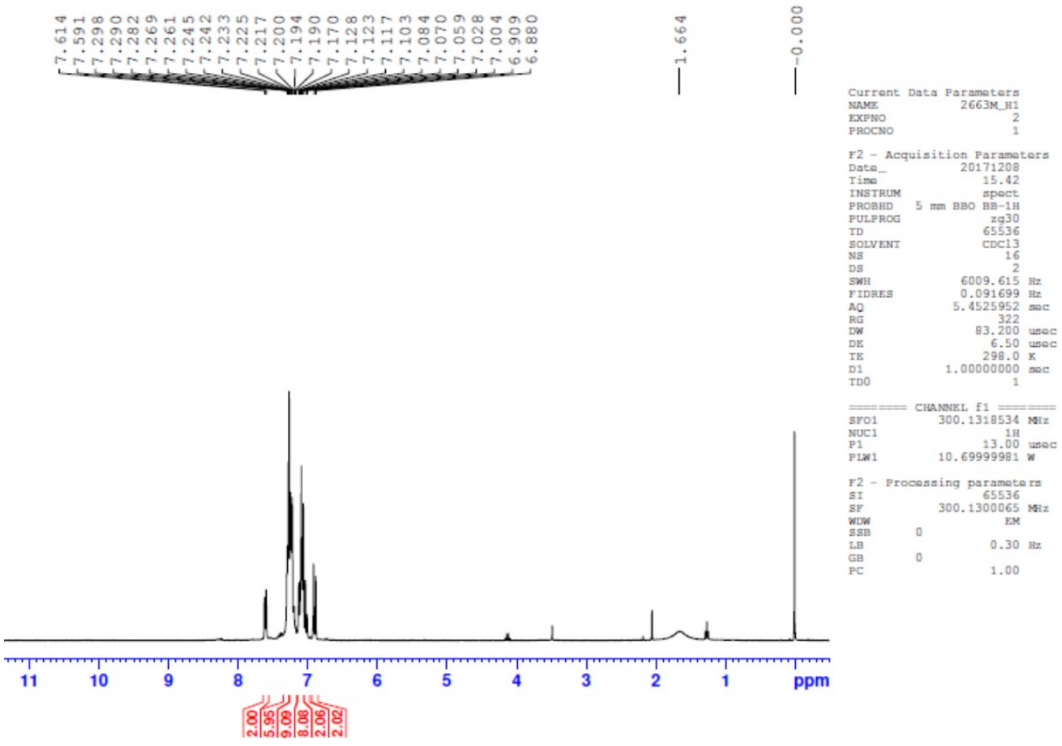


Figure S4b. ^{1}H NMR spectra of NTPB after UV irradiation.

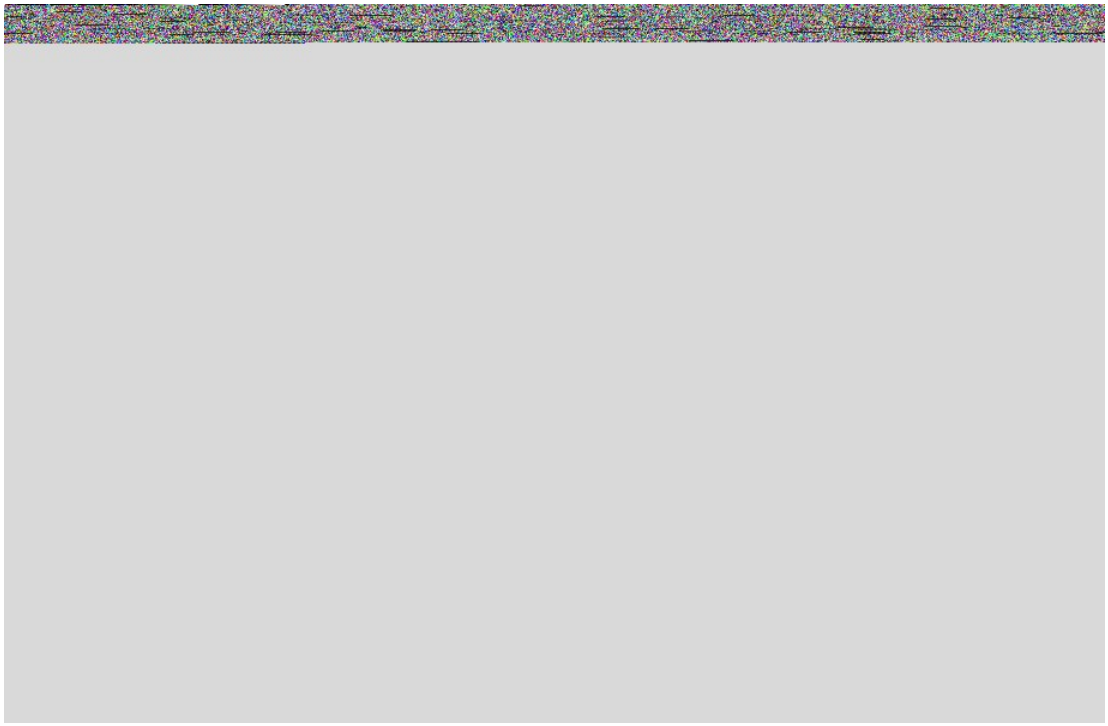


Figure S4c. *[1]H* NMR spectra of NPPB before UV irradiation.

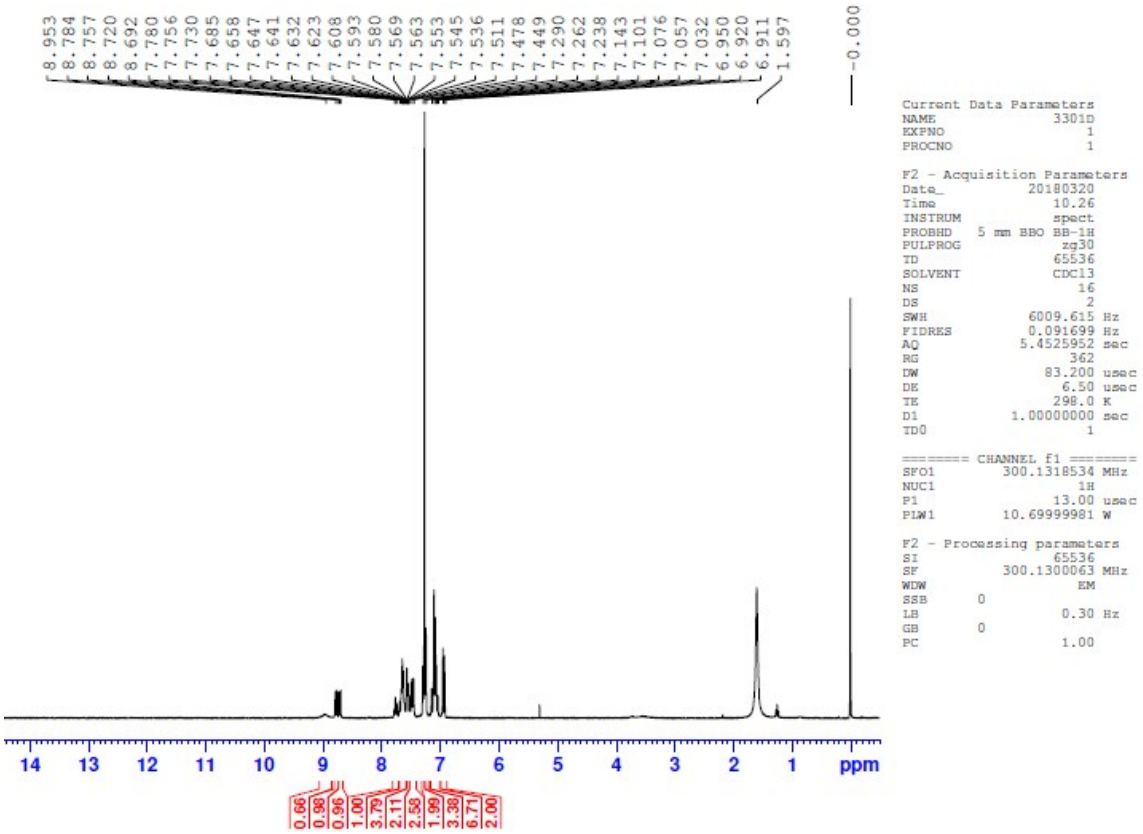
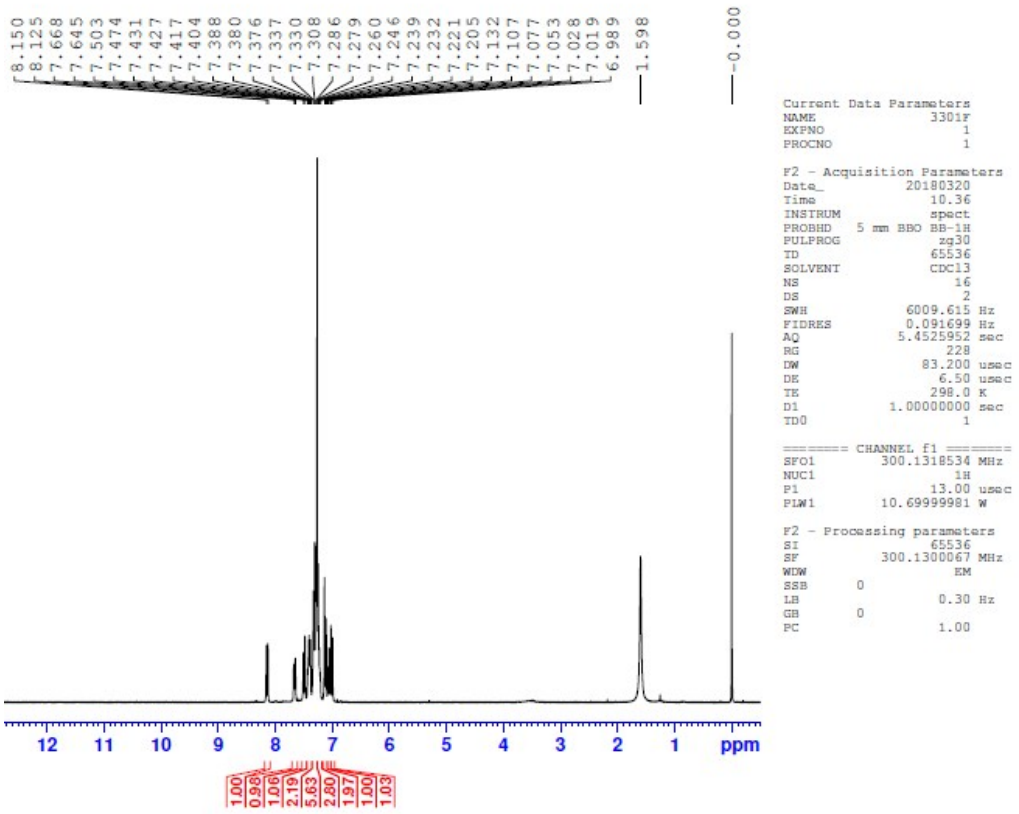


Figure S4d. *[1]H* NMR spectra of NPPB after UV irradiation.

Figure S4e. ^{1}H NMR spectra of NCPB before UV irradiation.

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FIDRES            0.091699 Hz
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Figure S4f. ^{1}H NMR spectra of NCPB after UV irradiation.

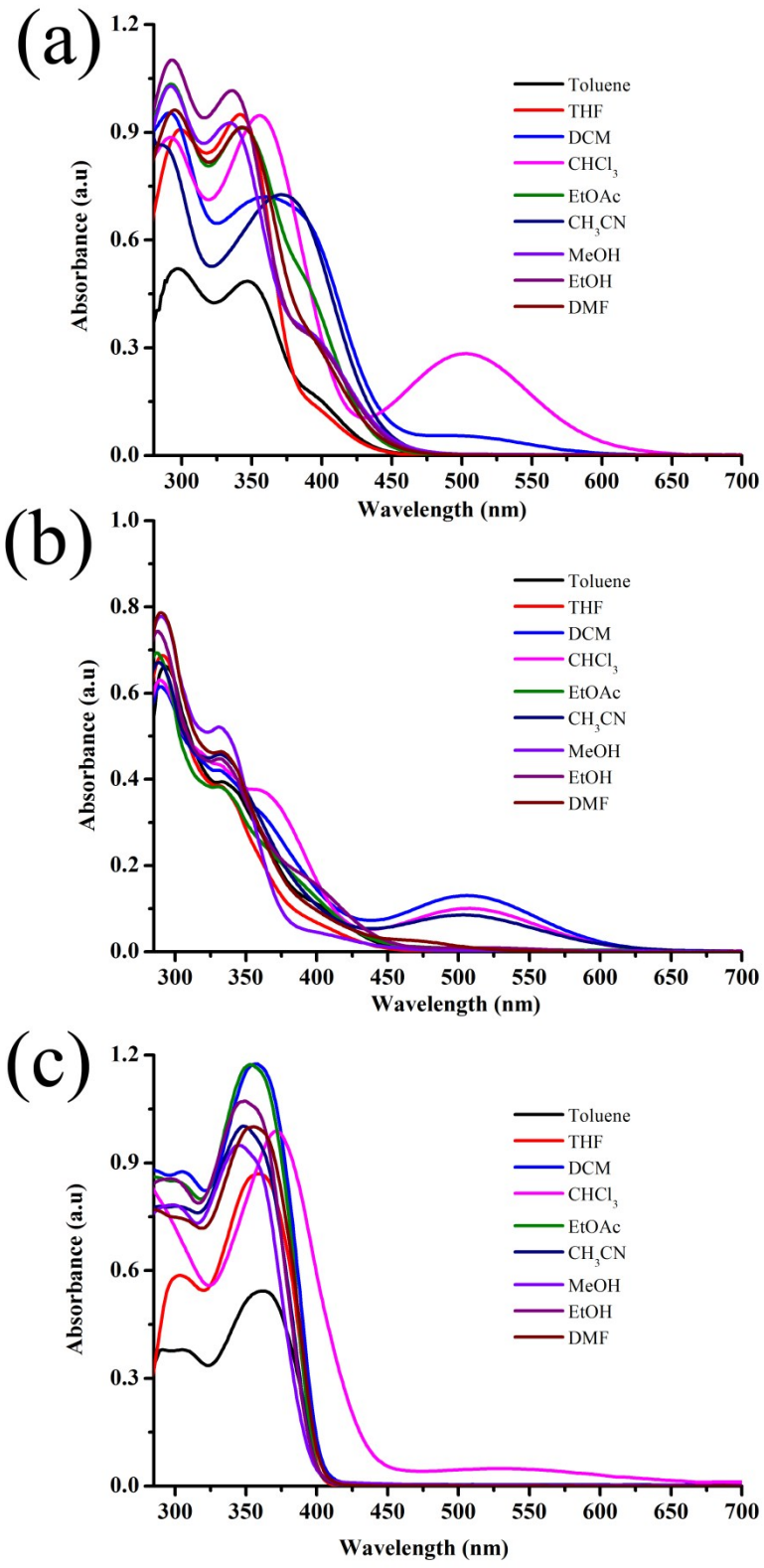
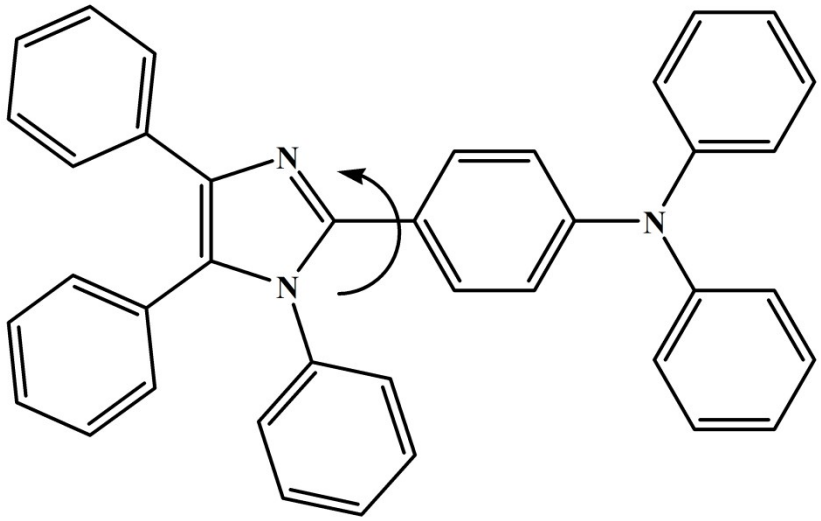


Figure S5. Absorption spectra of NTPB (a), NCPB (b) and NPPB (c) after UV irradiation in different solvents.



Scheme S2. NTPB rotation between TPA and imidazole ring under UV irradiation.

Table S4. Dihedral angle of NPPB and NTPB.

Structure	Dihedral angle	Exp. (nm)	Theory (nm)
NPPB	0	495	495
	12		489
	30		472
	90		396
NTPB	0	480	479
	15		469
	29		455
	90		402

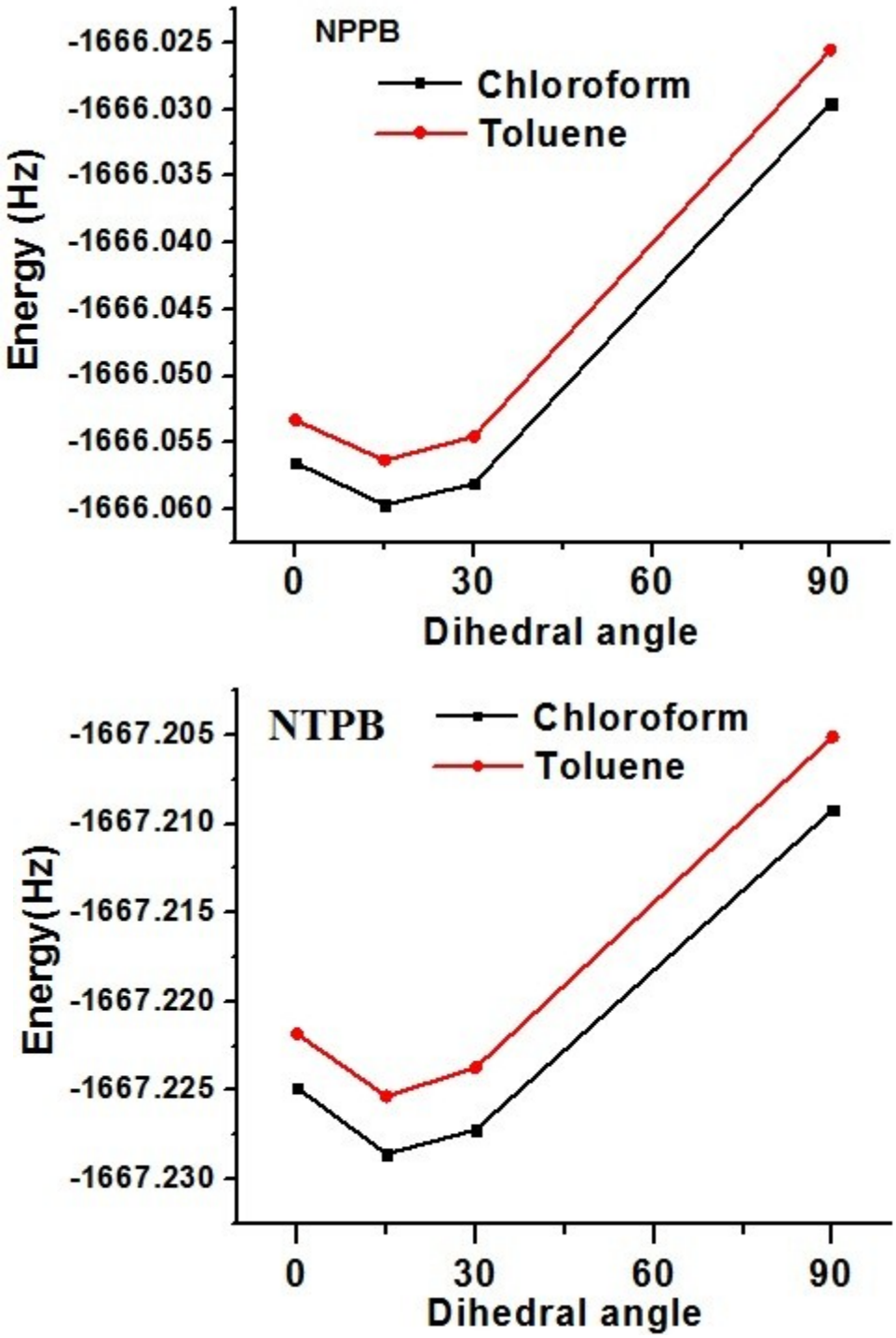


Fig. S6. Energy Vs dihedral twist angle of NPPB and NTPB in $CHCl_3$ and toluene

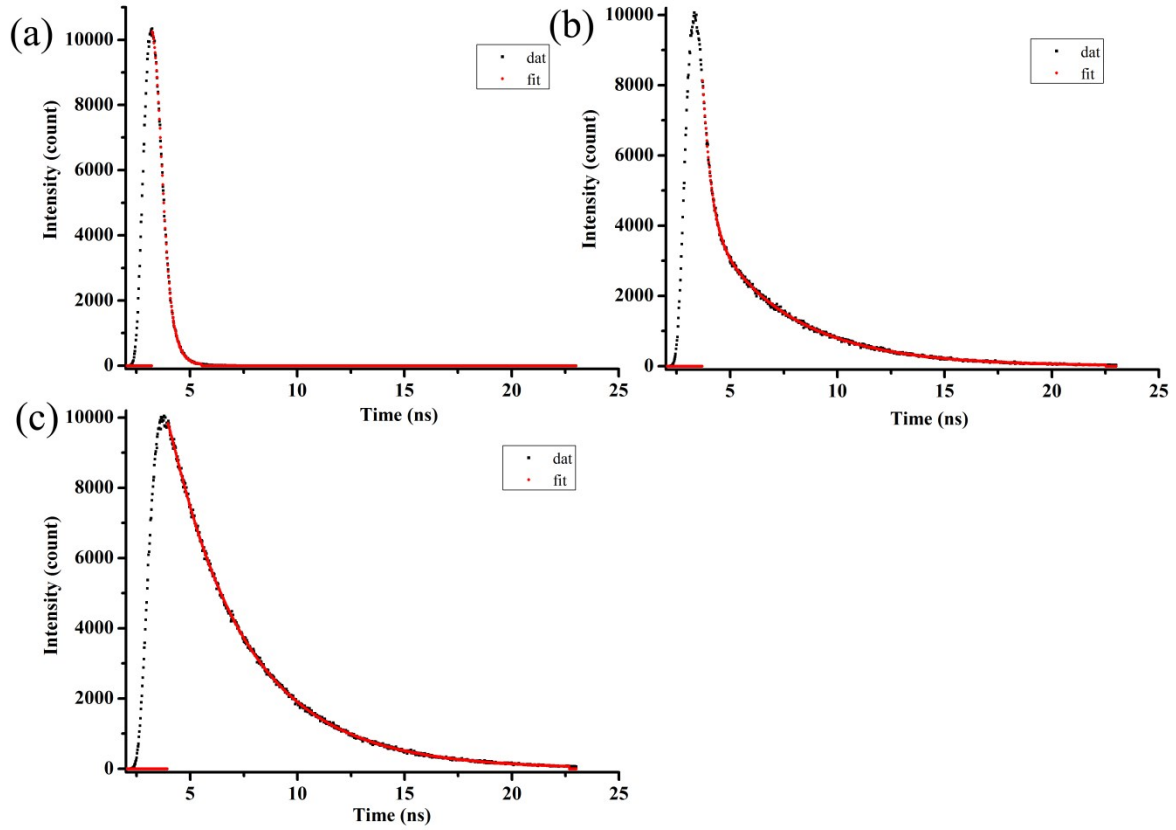


Figure S7. Excited state lifetime of NTPB measured at (a) 404 and (b) 477 nm before UV irradiation and (c) 486 nm after UV irradiation.

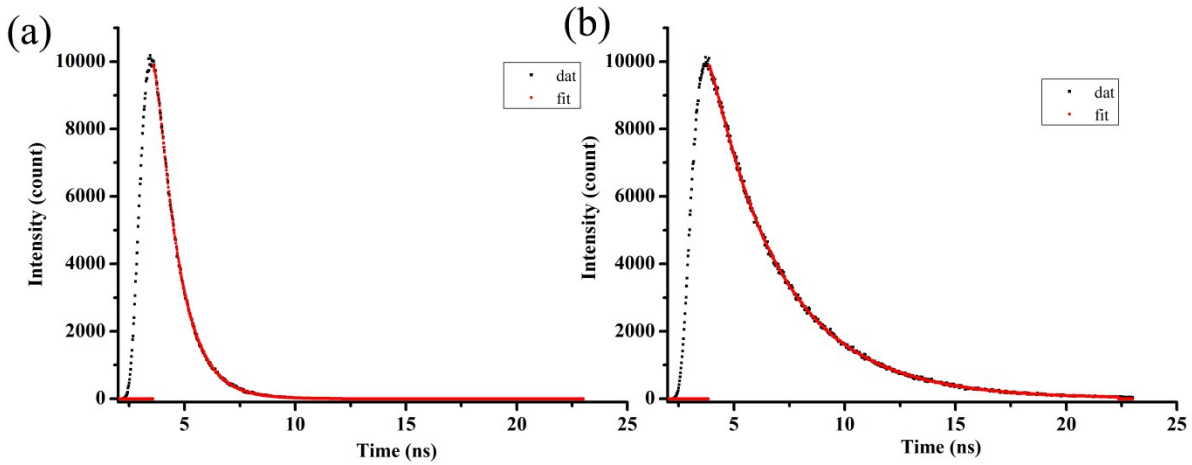


Figure S8. Excited state lifetime of NPPB measured at (a) 404 nm before UV irradiation and (b) 496 nm after UV irradiation.

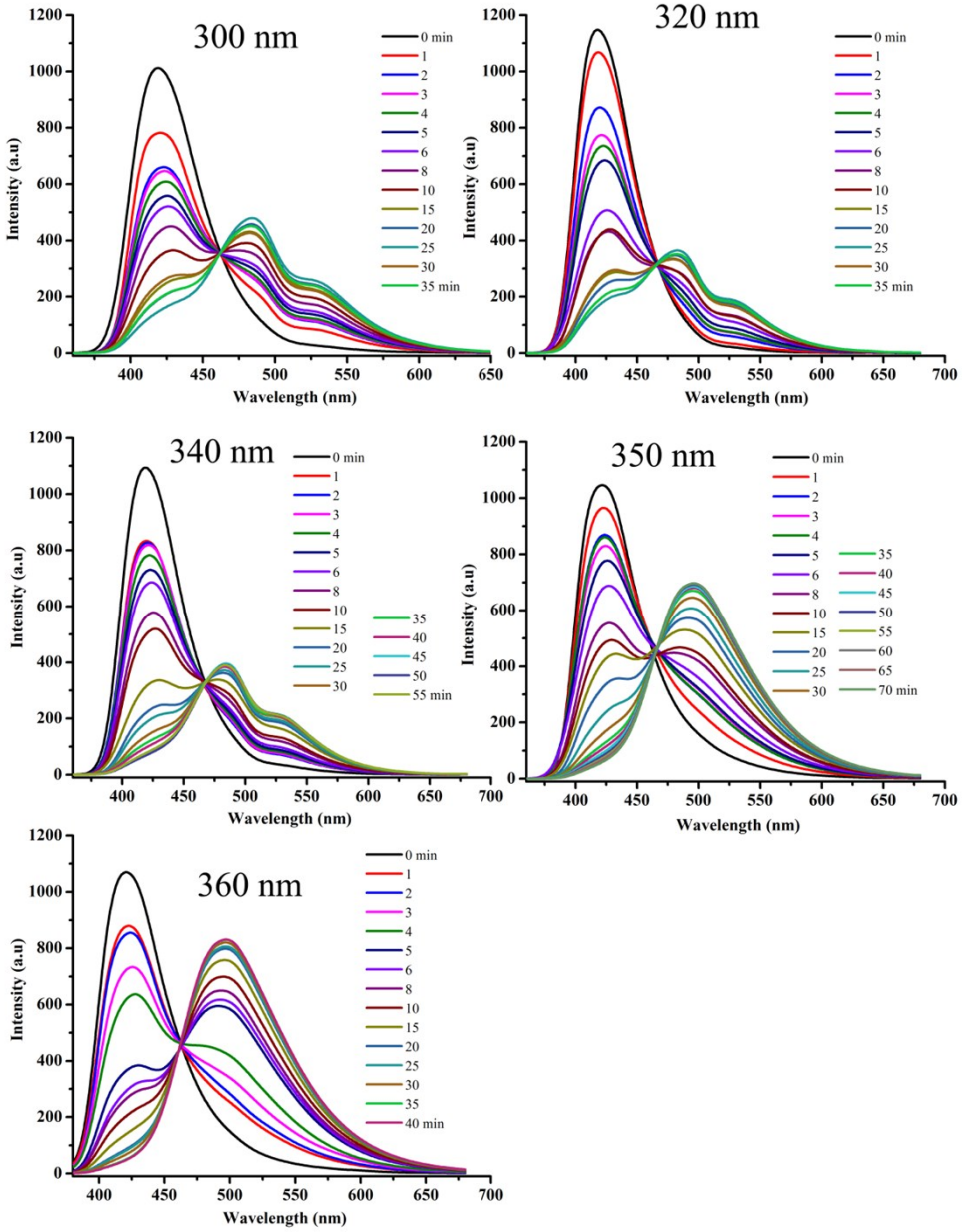


Figure S9. Excitation wavelength dependent photoswitching of NPPB in $CHCl_3$.

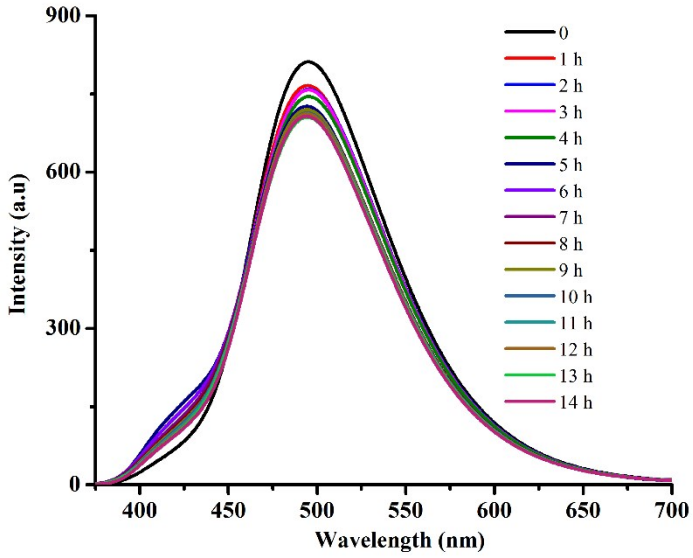


Figure S10. Reverse kinetics of NPPB under dark condition.

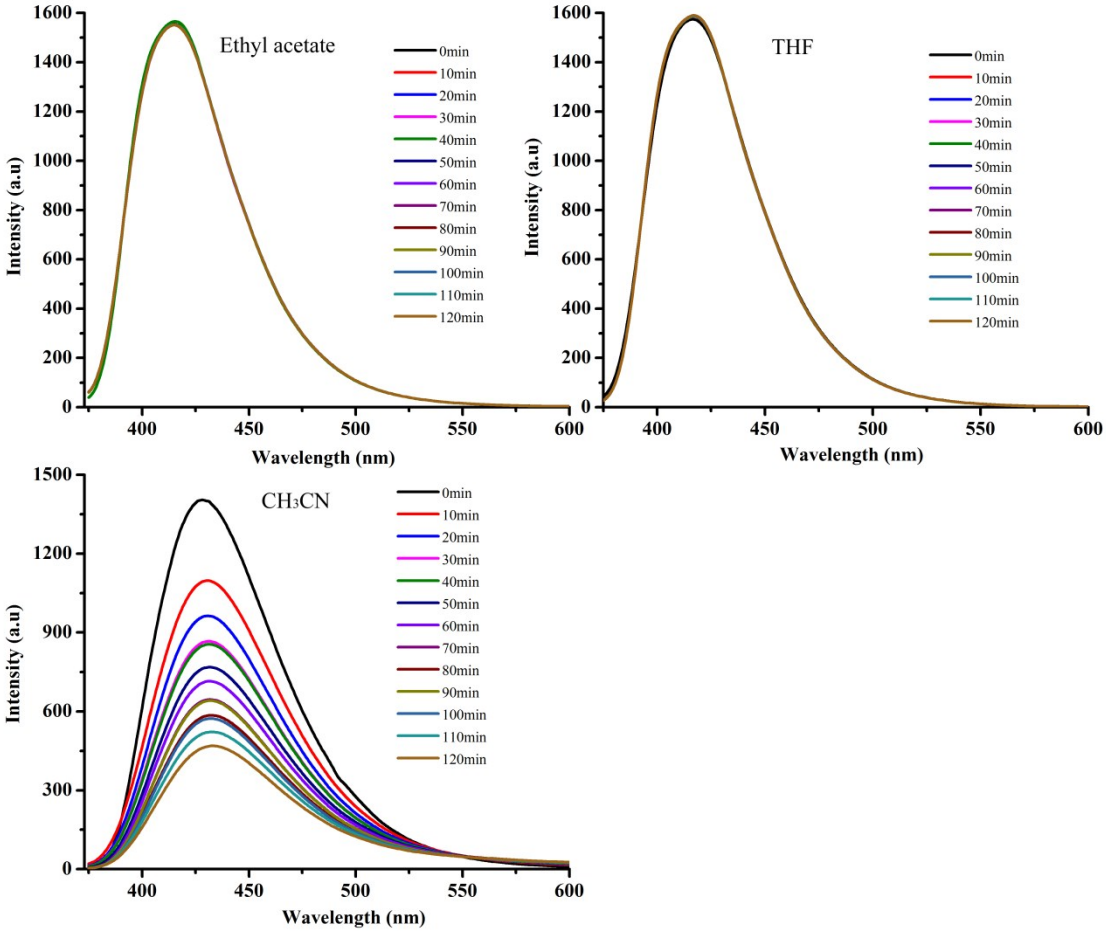


Figure S11. Fluorescence spectra showing photostability of NPPB in ethyl acetate, THF and CH_3CN solvents.

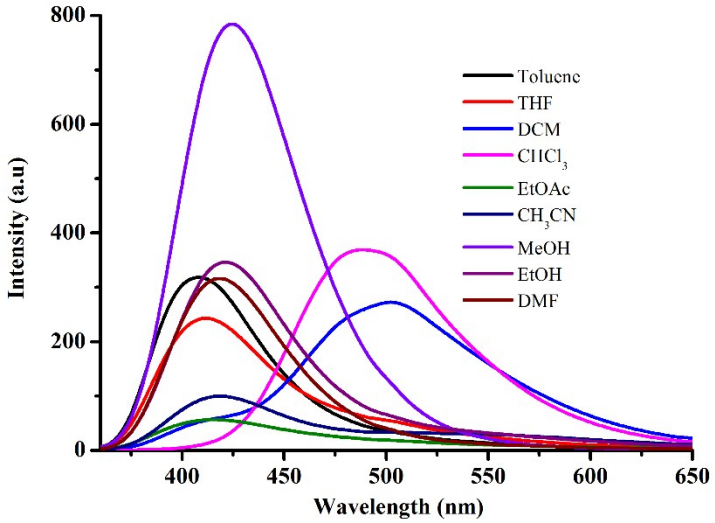


Figure S12.Fluorescence spectra of NCPB after UV irradiation in different solvents.

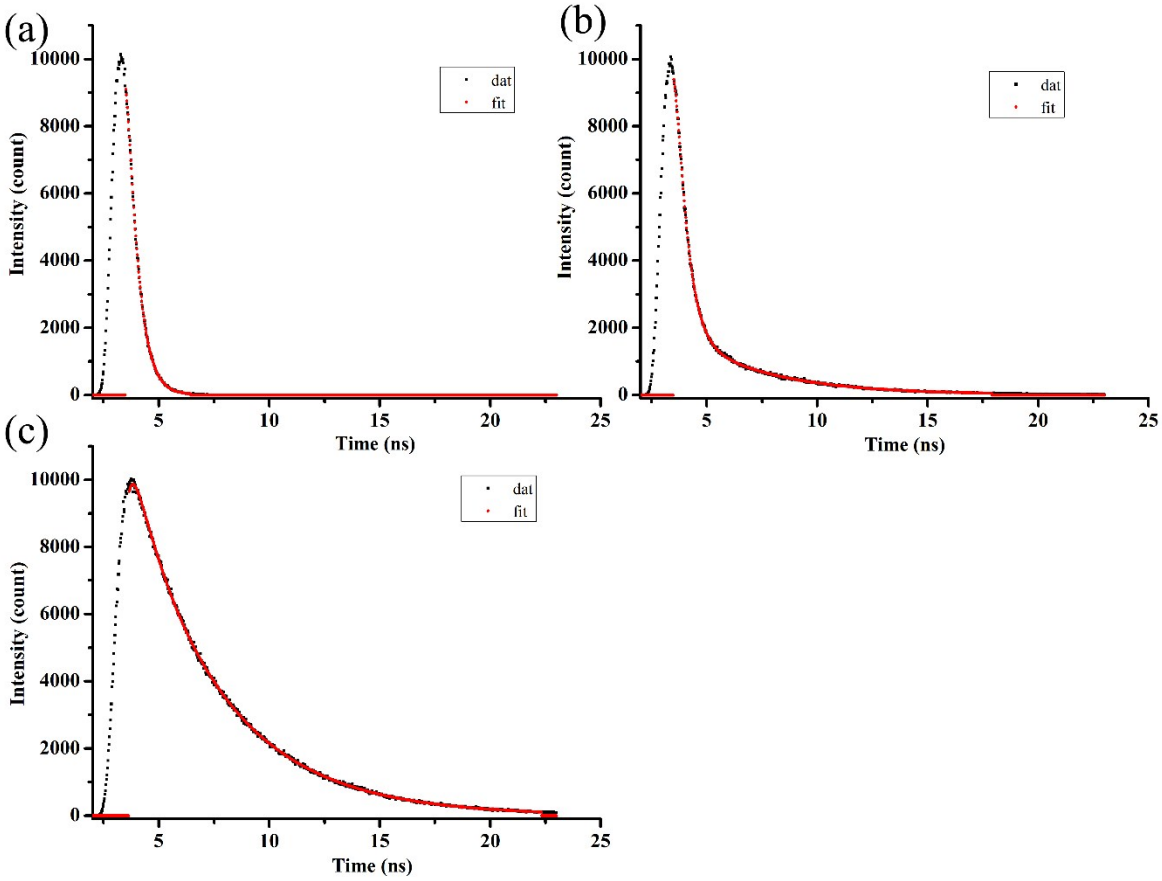


Figure S13. Excited state lifetime of NCPB measured at (a) 413 and (b) 486 nm before UV irradiation and (c) 492 nm after UV irradiation in $CHCl_3$.

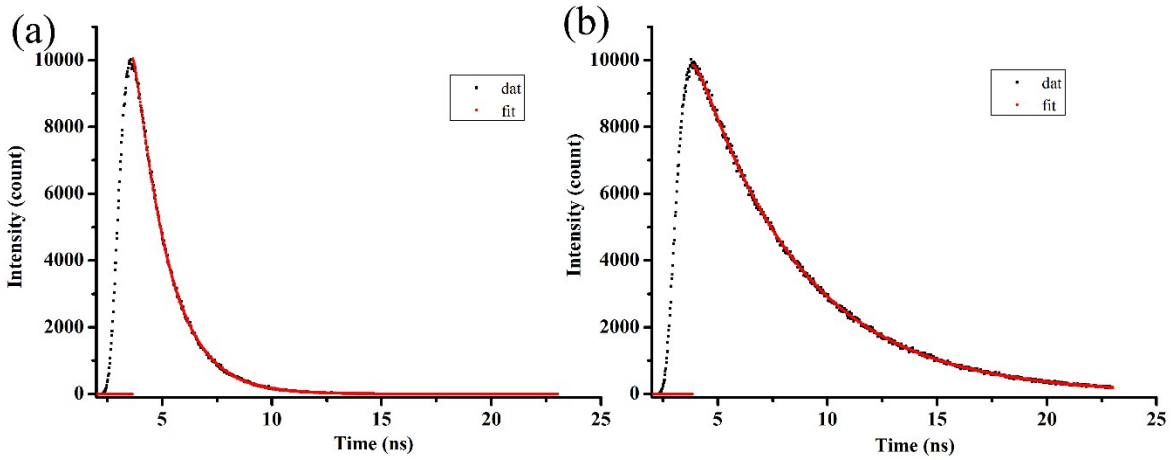


Figure S14. Excited state lifetime of NCPB measured at (a) 413 nm before UV irradiation and (b) 503 nm after UV irradiation in CH_2Cl_2.

Table S5. Crystal data and structure refinement for NTPB-1 (CCDC No. 1854516).

Identification code	NTPB-1	
Empirical formula	C39 H29 N3	
Formula weight	539.65	
Temperature	173(2) K	
Wavelength	0.610 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.931(4) Å	α= 90°.
	b = 12.546(3) Å	β= 107.66(3)°.
	c = 27.155(5) Å	γ = 90°.
Volume	5821(2) $Å^3$	
Z	8	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.054 mm^{-1}	
F(000)	2272	
Crystal size	0.095 x 0.084 x 0.074 mm^3	
Theta range for data collection	1.728 to 24.998°.	
Index ranges	-23<=h<=23, -17<=k<=17, -37<=l<=37	
Reflections collected	27101	
Independent reflections	7750 [R(int) = 0.0384]	
Completeness to theta = 21.469°	97.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.966	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7750 / 12 / 380	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1321	
R indices (all data)	R1 = 0.0595, wR2 = 0.1392	
Extinction coefficient	0.0114(9)	
Largest diff. peak and hole	0.310 and -0.263 $e.Å^{-3}$	

Table S6. Crystal data and structure refinement for NTPB-2 (CCDC No. 1854517).

Identification code	NTPB-2	
Empirical formula	C40 H33 N3 O	
Formula weight	571.69	
Temperature	173(2) K	
Wavelength	0.610 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.602(2) Å	α= 90°.
	b = 16.393(3) Å	β= 102.46(3)°.
	c = 18.032(4) Å	γ = 90°.
Volume	3060.1(11) $Å^3$	
Z	4	
Density (calculated)	1.241 Mg/m^3	
Absorption coefficient	0.056 mm^{-1}	
F(000)	1208	
Crystal size	0.105 x 0.095 x 0.084 mm^3	
Theta range for data collection	1.457 to 25.000°.	
Index ranges	-14<=h<=14, -22<=k<=22, -24<=l<=24	
Reflections collected	30756	
Independent reflections	8516 [R(int) = 0.0680]	
Completeness to theta = 21.469°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.959	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8516 / 0 / 399	
Goodness-of-fit on F^2	0.921	
Final R indices [I>2sigma(I)]	R1 = 0.0508, wR2 = 0.1202	
R indices (all data)	R1 = 0.0901, wR2 = 0.1318	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.208 and -0.316 $e.Å^{-3}$	

Table S7. Crystal data and structure refinement for NTPB-3 (CCDC No. 1854519).

Identification code	NTPB-3	
Empirical formula	$C_{39}H_{29}N_3$	
Formula weight	539.65	
Temperature	173(2) K	
Wavelength	0.600 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.4670(19) Å	α= 84.16(3)°.
	b = 10.183(2) Å	β= 76.29(3)°.
	c = 15.829(3) Å	γ = 75.31(3)°.
Volume	1432.6(6) $Å^3$	
Z	2	
Density (calculated)	1.251 Mg/m^3	
Absorption coefficient	0.053 mm^{-1}	
F(000)	568	
Crystal size	0.150 x 0.144 x 0.025 mm^3	
Theta range for data collection	1.747 to 24.999°.	
Index ranges	-13<=h<=13, -14<=k<=14, -22<=l<=22	
Reflections collected	16739	
Independent reflections	8394 [R(int) = 0.0274]	
Completeness to theta = 21.100°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.908	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8394 / 0 / 380	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0458, wR2 = 0.1233	
R indices (all data)	R1 = 0.0634, wR2 = 0.1306	
Extinction coefficient	0.059(5)	
Largest diff. peak and hole	0.387 and -0.256 $e.Å^{-3}$	

Table S8. Crystal data and structure refinement for NCPB (CCDC No. 1854520).

Identification code	NCPB	
Empirical formula	C51 H36 N4	
Formula weight	704.84	
Temperature	173(2) K	
Wavelength	0.610 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.552(3) Å	α= 90°.
	b = 14.684(3) Å	β= 91.92(3)°.
	c = 17.328(4) Å	γ = 90°.
Volume	3700.6(13) $Å^3$	
Z	4	
Density (calculated)	1.265 Mg/m^3	
Absorption coefficient	0.055 mm^{-1}	
F(000)	1480	
Crystal size	0.078 x 0.075 x 0.065 mm^3	
Theta range for data collection	1.560 to 24.999°.	
Index ranges	-20<=h<=20, -19<=k<=20, -24<=l<=24	
Reflections collected	36888	
Independent reflections	10201 [R(int) = 0.0464]	
Completeness to theta = 21.469°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.937	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10201 / 0 / 496	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1162	
R indices (all data)	R1 = 0.0621, wR2 = 0.1234	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.327 and -0.355 e.$Å^{-3}$	

Table S9. Crystal data and structure refinement for NPPB (CCDC No. 1854519).

Identification code	NPPB	
Empirical formula	C39 H27 N3	
Formula weight	537.63	
Temperature	100(2) K	
Wavelength	0.700 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.587(4) Å	α= 90°.
	b = 7.7400(15) Å	β= 105.94(3)°.
	c = 21.032(4) Å	γ = 90°.
Volume	2752.8(10) $Å^3$	
Z	4	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	1128	
Crystal size	0.110 x 0.010 x 0.009 mm^3	
Theta range for data collection	2.012 to 28.000°.	
Index ranges	-23<=h<=23, -10<=k<=10, -28<=l<=28	
Reflections collected	23783	
Independent reflections	6767 [R(int) = 0.0788]	
Completeness to theta = 24.835°	97.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.802	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6767 / 0 / 380	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0628, wR2 = 0.1646	
R indices (all data)	R1 = 0.0892, wR2 = 0.1795	
Extinction coefficient	0.029(3)	
Largest diff. peak and hole	0.506 and -0.330 $e.Å^{-3}$	

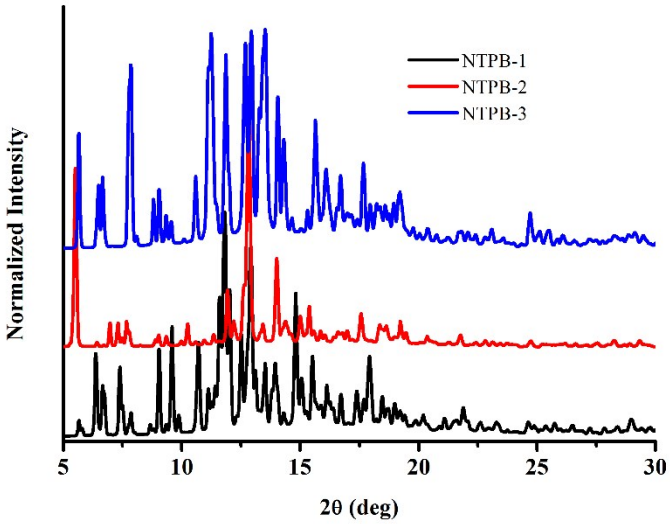


Figure S15. PXRD for all three polymorphs of NTPB.

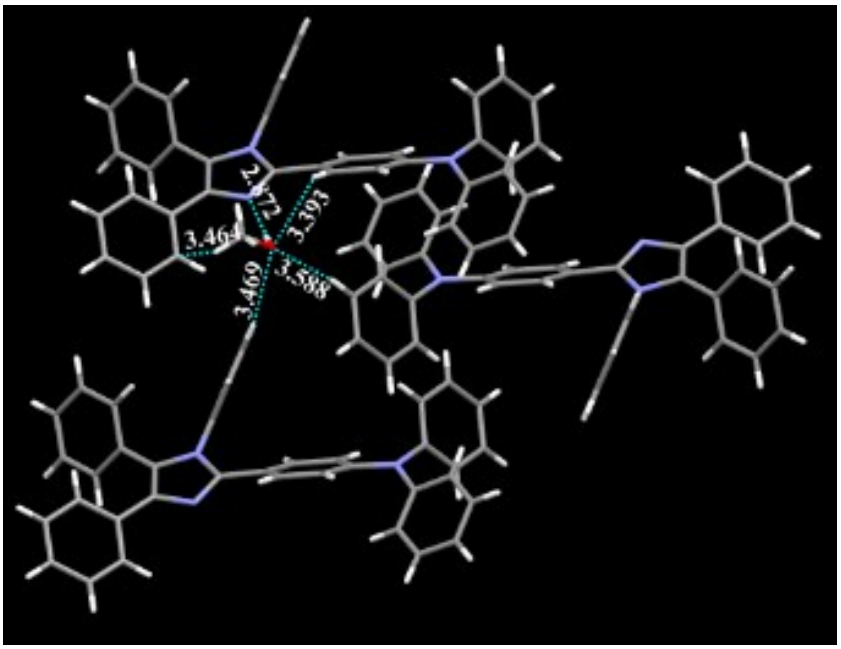


Figure S16. NTPB-2 H-bonding.

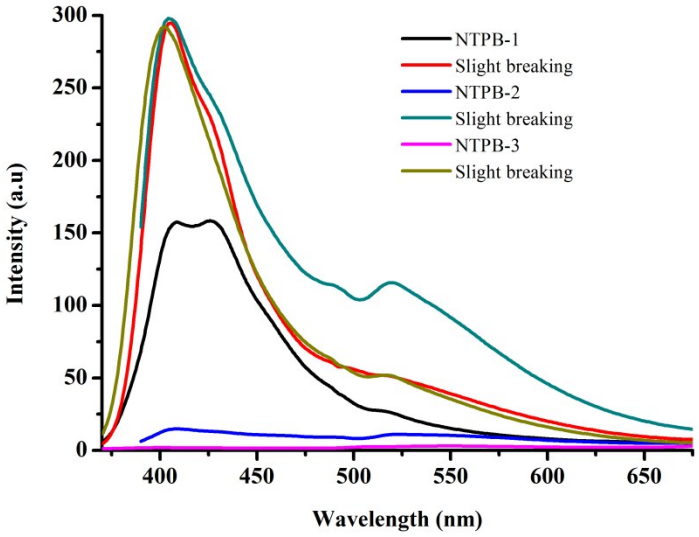


Figure S17. Solid state fluorescence of NTPB-1, NTPB-2 and NTPB-3.

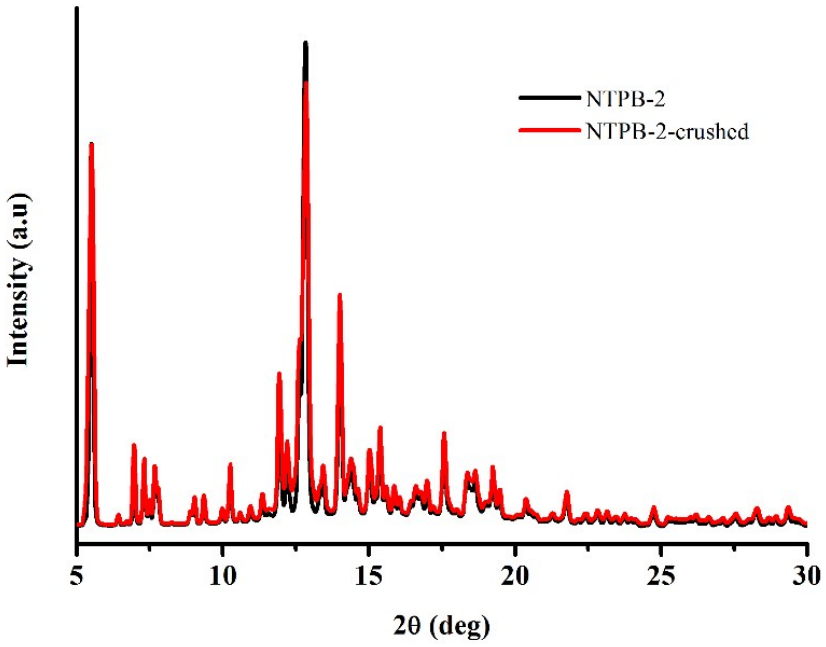


Figure S18. PXRD pattern of NTPB-2 before and after crushing.

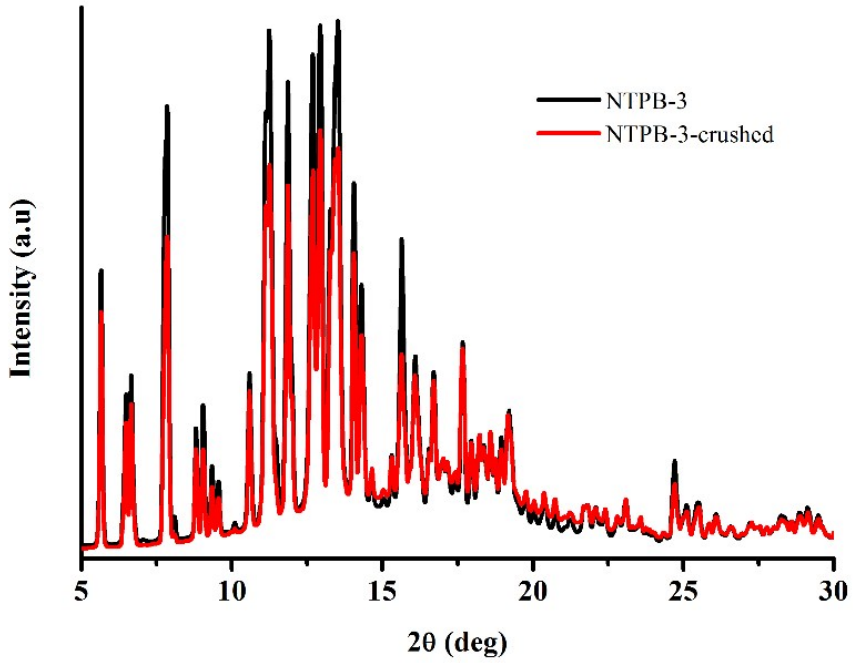


Figure S19. PXRD pattern of NTPB-3 before and after crushing.

Table S10. Energy levels, energy gaps, calculated absorption and emission maximum of SPA175, SPA179, SPA188, SPA198 and SPA231 calculated by the TD-DFT, B3PW91/6-31G(d, p), Gaussian 09 program.[a]

	HOMO (eV)		LUMO (eV)		Energy gap (eV)		λ_{abs} (nm)	λ_{em} (nm)
	GS	ES	GS	ES	GS	ES		
SPA175 NTPB-2:	-5.11	-4.72	-1.04	-1.45	-4.07	-3.28	339	430
SPA179 NCPB:	-5.19	-4.73	-1.33	-1.43	-3.86	-3.30	363	367
SPA188 NTPB-1	-5.11	-4.52	-0.96	-1.32	-4.15	-3.20	329	394
SPA198 NPBB:	-5.08	-4.86	-1.27	-1.50	-3.81	-3.36	363	422
SPA231 NTPB-3	-5.00	-4.53	-0.96	-1.33	-4.04	-3.19	344	396

[a]Abbreviation: HOMO = highest occupied molecular orbitals, LUMO = lowest unoccupied molecular orbitals, GS = ground state, ES = excited state, λ_{abs} = absorption maximum, λ_{em} = emission maximum.

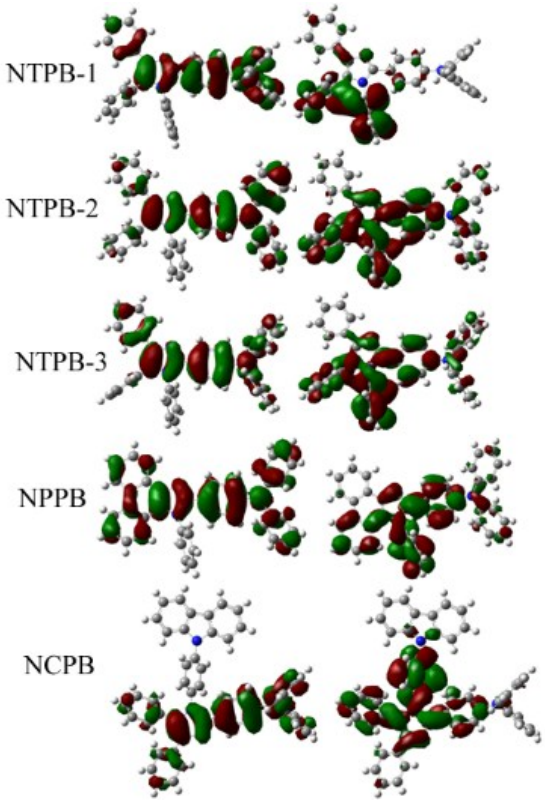


Figure S20. Molecular orbital plots of the HUMOs and LUMOs of NTPB, NPPB and NCPB.

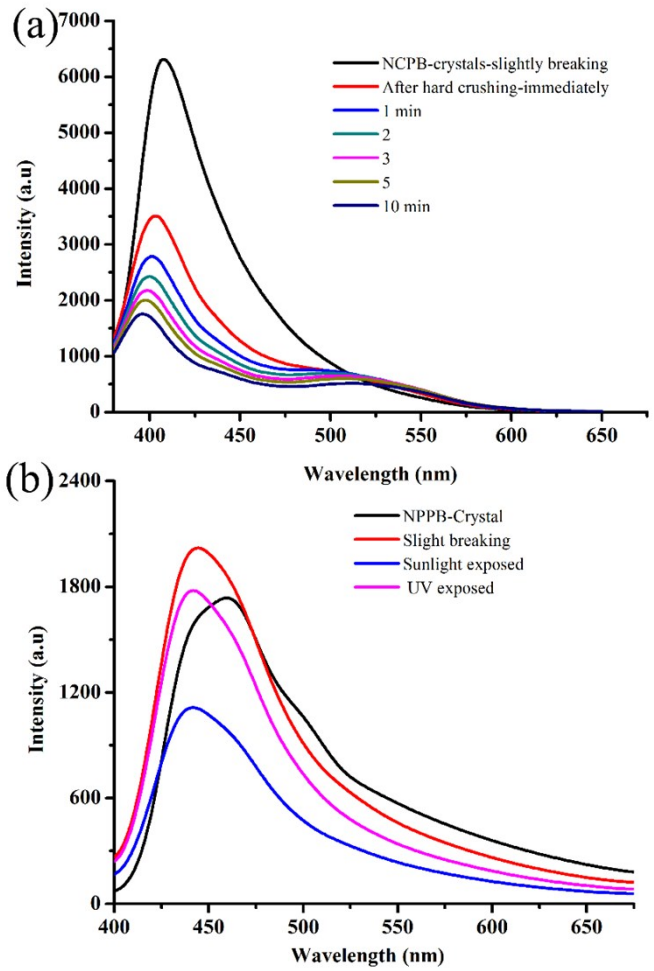


Figure S21. Photoresponsive fluorescence switching of NCPB (a) and NPPB (b).

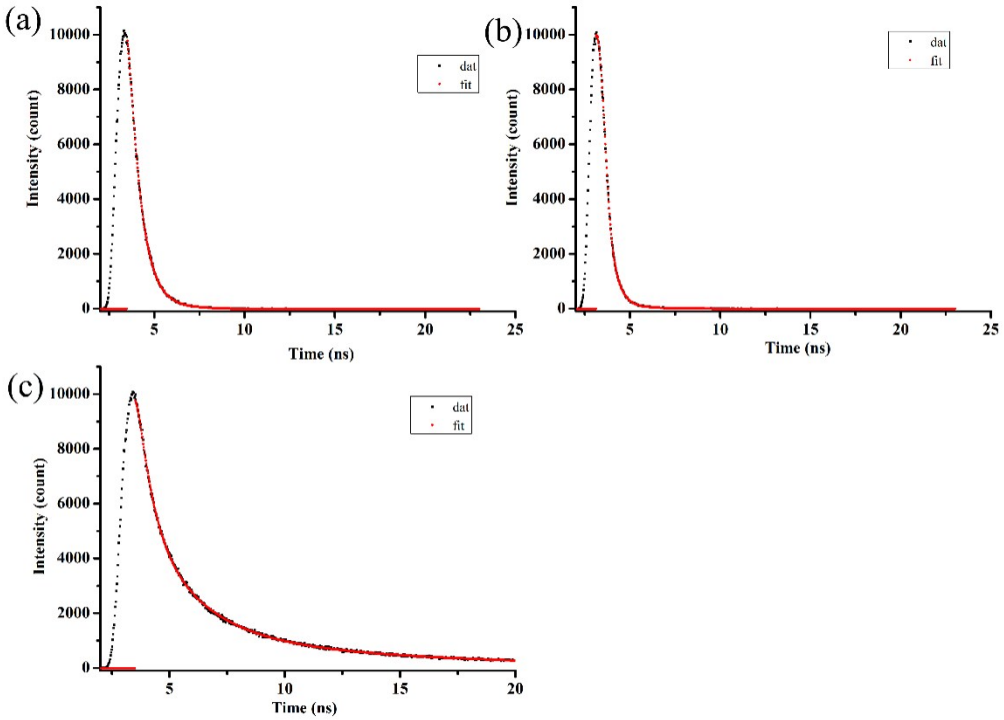


Figure S22. Excited state lifetime of NTPB solids measured at (a) 405 nm before UV irradiation and (b) 405 nm and (c) 508 nm after UV irradiation.

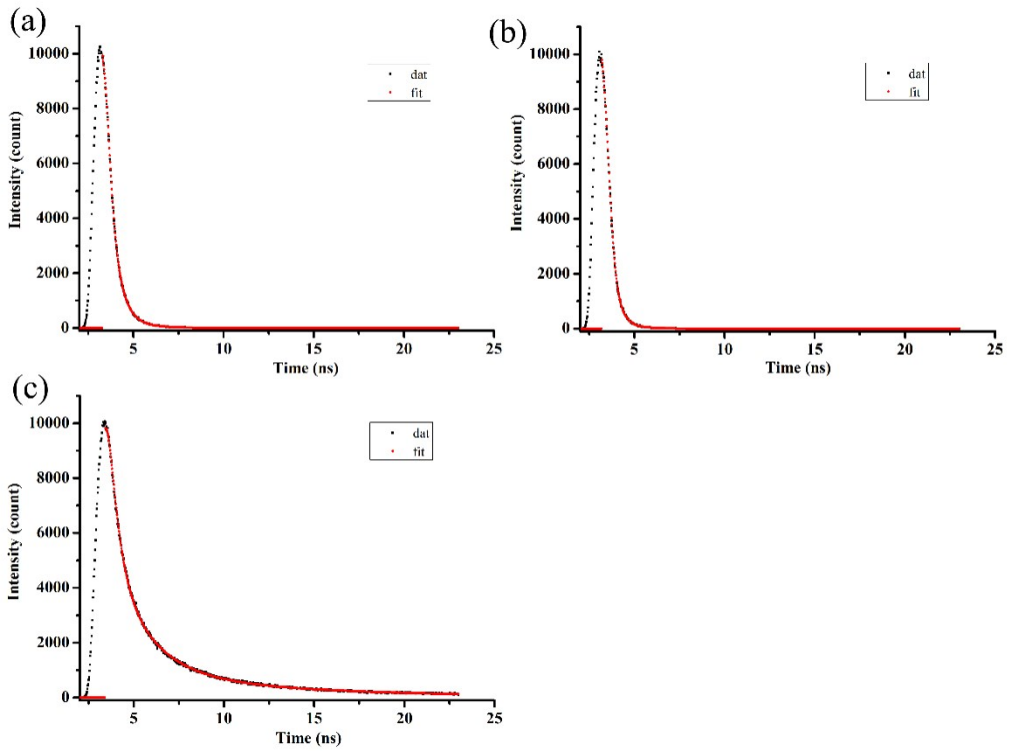


Figure S23. Excited state lifetime of NCPB solids measured at (a) 403 nm before UV irradiation and (b) 396 nm and (c) 513 nm after UV irradiation.

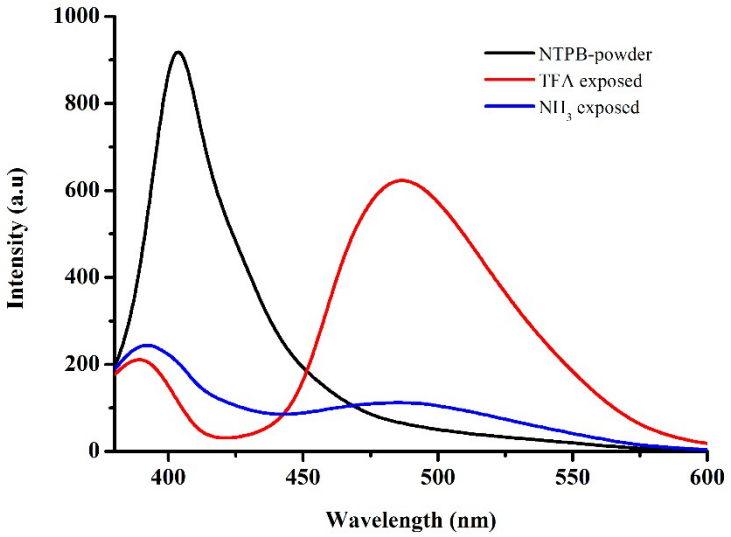


Figure S24. Halochromic behavior of NTPB.

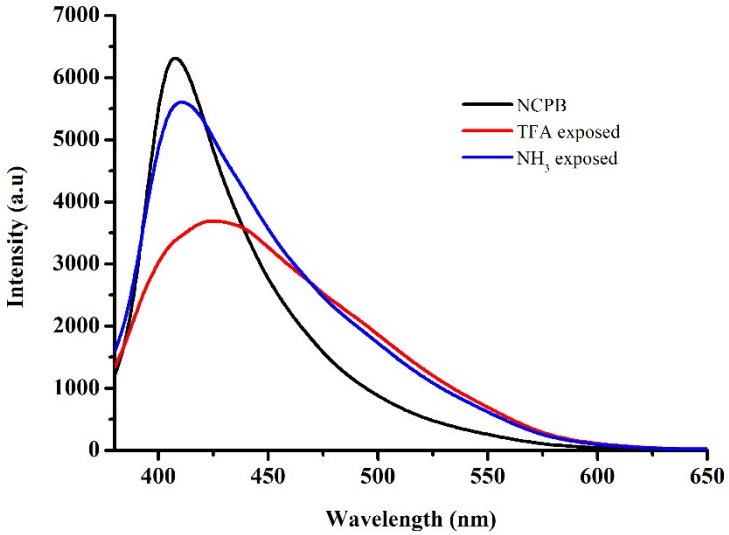


Figure S25. Halochromic behavior of NCPB.

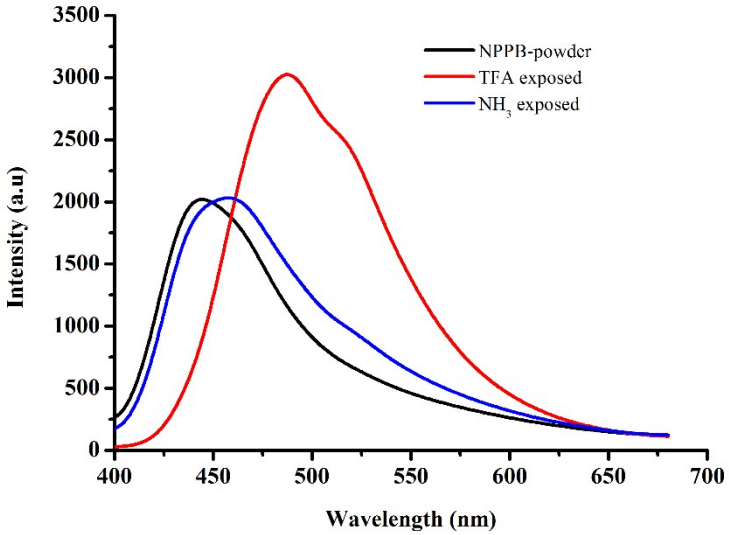


Figure S26. Halochromic behavior of NPPB.