Supporting Information
for

Harnessing Excited-State Intramolecular Proton Transfer Reaction via a Series of Amino-Type Hydrogen Bonding Molecules

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Contents

Page

Detailed Synthesis and Characterizations

All reactions were carried out in oven- or flame-dried glassware under a positive pressure of argon. *N*,*N*-dimethylacetamide (DMAc), pyridine, chlorobenzene were distilled over calcium hydride. All reagents were purchased commercially and used without further purification. TLC was performed on Merck 5735 DC-plastikfolien Kieselgel 60 F254 precoated plates. Flash column chromatography was performed on silica gel (Merck 7736 Kieselgel 60H). ^{1}H-NMR (7.24 ppm for residual CHCl3 in the CDCl3 solvent as internal standard) and ^{13}C-NMR (77.0 ppm for $CDCl_3$ as internal standard) spectra were recorded on a Varian Unity-400 MHz or -600 MHz instrument. Coupling constants were reported in Hertz. IR spectra were recorded using a Bomen MB-100FT spectrometer. HRMS data was obtained from an FOEL JMS-HX110 spectrometer. Single crystal structure was determined on a Bruker AXS SMART-1000 instrument.

2-(2'-aminophenyl)benzothiazole (**PBT-NH$_2$**). To a solution of isatoic anhydride (1.0 g, 6.13 mmol) in chlorobenzene (6 mL) was added $ZnCl_2$ (297 mg, 1.84 mmol) and 2-aminothiophenol (0.85 mL, 7.97 mmol). After refluxing for 5 h, the solvent was removed under reduced pressure. The crude product was purified on silica gel to provide 943 mg (4.17 mmol, 68% yield) of **PBT-NH$_2$** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 7.95 (dd, *J* = 8.8, 0.4 Hz, 1H), 7.86 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.69 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.46-7.41 (m, 1H), 7.36-7.31 (m, 1H), 7.25-7.18 (m, 1H), 6.79-6.71 (m, 2H), 6.38 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 169.1, 153.6, 146.6, 133.1, 131.4, 130.2, 125.9, 124.7, 122.3, 121.1, 116.8, 116.7, 115.1. IR (KBr, cm^{-1}) 3466, 3290, 1612, 1596, 1582, 1555, 1493, 1454, 1250, 1223, 744, 728. HRMS (EI, m/z) calcd for $C_{13}H_{10}N_2S$, 226.0565; found, 226.0568.

2-(2'-tosylaminophenyl)benzothiazole (**PBT-NHTs**). A mixture of **PBT-NH$_2$** (80 mg, 0.35 mmol) and tosyl chloride (101 mg, 0.53 mmol) in pyridine (2.5 mL) was stirred at room temperature for 15 h. Aqueous HCl was added and the mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified on silica gel to give 128 mg (0.34 mmol, 95% yield) of **PBT-NHTs** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 12.20 (s, 1H), 8.11 (dd, *J* = 8.8, 0.4 Hz, 1H), 7.87 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.75 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.64-7.61 (m, 2H), 7.56-7.51 (m, 1H), 7.45-7.41 (m, 1H), 7.38-7.33 (m, 1H), 7.12-7.07 (m, 1H), 7.04-7.01 (m, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 167.8, 152.5, 143.5, 136.9, 136.4, 133.1, 131.7, 129.8, 129.4, 127.0, 126.7, 125.9, 123.7, 123.0, 121.2, 120.3, 120.2, 21.4. IR (KBr, cm^{-1}) 3061, 2918, 1580, 1507, 1487, 1437, 1343, 1295, 1212, 1106, 1091, 912, 813, 758. HRMS (EI, m/z) calcd for $C_{20}H_{16}N_2O_2S_2$, 380.0653; found, 380.0659.

2-(2'-acetylaminophenyl)benzothiazole (**PBT-NHAc**). A mixture of **PBT-NH$_2$** (112 mg, 0.50 mmol) and acetyl anhydride (0.11 mL, 1.0 mmol) in dichloromethane (5.0 mL) was stirred at room temperature for 40 min. The solvent was removed and the crude product was washed with ethylacetate to give 128 mg (0.48 mmol, 96% yield) of **PBT-NHAc** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 12.42 (s, 1H), 8.76 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.51-7.37 (m, 3H), 7.10 (dd, *J* = 7.6, 7.6 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 169.2, 168.7, 152.7, 138.0, 133.2, 131.9, 129.7, 126.5, 125.7, 123.0, 122.5, 121.4, 120.6, 118.7, 25.5. IR (KBr, cm^{-1}) 3060, 2850, 1697, 1592, 1492, 1443, 1303, 758. HRMS (EI, m/z) calcd for $C_{15}H_{12}N_2OS$, 268.0670; found, 268.0667.

2-(2'-methylaminophenyl)benzothiazole (**PBT-NHMe**). To a solution of *N*-methylisatoic anhydride (975 mg, 5.50 mmol) in chlorobenzene (6.0 mL) was added $ZnCl_2$ (241 mg, 1.77 mmol) and 2-aminothiophenol (0.77 mL, 7.15 mmol). After refluxing for 21 h, the solvent was removed under reduced pressure and the crude product was purified on silica gel eluting with hexane to provide 713 mg (2.97 mmol, 54% yield) of **PBT-NHMe** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 8.92 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.43-7.35 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 169.4, 153.4, 148.2, 133.0, 131.9, 130.4, 125.8, 124.6, 122.0, 120.9, 114.9, 114.5, 110.7, 29.5. IR (KBr, cm^{-1}) 3284, 3060, 2919, 2817, 1610, 1580, 1524, 1499, 1456, 1439, 1421, 1331, 1244, 1215, 956, 749, 726. HRMS (EI, m/z) calcd for $C_{14}H_{12}N_2S$, 240.0721; found, 240.0727.

2-(5'-cyano-2'-aminophenyl)benzothiazole (**CN-PBT-NH$_2$**). A mixture of 2-(5'-iodo-2'-aminophenyl)benzothiazole (168 mg, 0.48 mmol) and copper(I) cyanide (52 mg, 0.58 mmol) in DMAc (3.0 mL) was heated at 150 °C for 10 h. After removing solvent, the residual crude product was purified on silica gel to provide 72 mg (0.29 mmol, 60%) of **CN-PBT-NH$_2$** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 8.00-7.92 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.50-7.43 (m, 1H), 7.42-7.36 (m, 2H), 7.02 (brs, 2H), 6.76 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 167.0, 153.2, 149.7, 134.9, 134.0, 133.0, 126.4, 125.6, 122.7, 121.4, 119.5, 116.9, 115.1, 98.9. IR (KBr, cm^{-1}) 3412, 3286, 2924, 2852, 2216, 1624, 1599, 1510, 1438, 1314, 1252, 1175, 986, 819, 757, 724. HRMS (EI, m/z) calcd for $C_{14}H_9N_3S$, 251.0517; found, 251.0523.

2-(5'-cyano-2'- tosylaminophenyl)benzothiazole (**CN-PBT-NHTs**). A mixture of **CN-PBT-NH$_2$** (127 mg, 0.51 mmol) and tosyl chloride (145 mg, 0.76 mmol) in pyridine (3.0 mL) was stirred at room temperature for 22 h. Aqueous HCl was added and the mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to provide 203 mg (0.50 mmol, 99% yield) of **CN-PBT-NHTs** as a yellow solid. ^{1}H NMR (400

MHz, $CDCl_3$, ppm) 12.85 (s, 1H), 8.17-8.13 (m, 1H), 8.02 (d, *J* = 1.6 Hz, 1H), 7.95-7.92 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.61-7.55 (m, 2H), 7.52-7.47 (m, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 165.8, 152.2, 144.5, 140.8, 136.2, 134.5, 133.7, 133.0, 129.9, 127.3, 127.2, 126.8, 123.4, 121.5, 119.6, 118.9, 117.8, 106.4, 21.5. IR (KBr, cm^{-1}) 2923, 2862, 2229, 1506, 1499, 1458, 1437, 1398, 1347, 1300, 1260, 1220, 1164, 1090, 995, 909, 819, 759. HRMS (EI, m/z) calcd for $C_{21}H_{15}N_3O_2S_2$, 405.0606; found, 405.0610.

2-(5'-cyano-2'-methylaminophenyl)benzothiazole (**CN-PBT-NHMe**). A mixture of 2-(5'-iodo-2'-methylaminophenyl)benzothiazole (807 mg, 2.20 mmol) and copper(I) cyanide (236 mg, 2.64 mmol) in DMAc (8 mL) was heated at 150 ^{o}C for 10 h. After removing solvent, the crude product was purified on silica gel to provide 415 mg (1.56 mmol, 71%) of **CN-PBT-NHMe** as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 9.52 (s, 1H), 8.00-7.96 (m, 2H), 7.90-7.87 (m, 1H), 7.52 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.50-7.45 (m, 1H), 7.42-7.37 (m, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 3.08 (d, *J* = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 167.2, 152.9, 150.5, 134.5, 134.4, 132.8, 126.3, 125.4, 122.4, 121.1, 119.8, 114.7, 110.1, 96.8, 29.5. IR (KBr, cm^{-1}) 3251, 2920, 2216, 1613, 1580, 1573, 1530, 1501, 1494, 1440, 1314, 1228, 1183, 986, 894, 812, 757, 726. HRMS (EI, m/z) calcd for $C_{15}H_{11}N_3S$, 265.0674; found, 265.0669.

2-(5'-amino-2'- tosylaminophenyl)benzothiazole (**NH_2-PBT-NHTs**). A mixture of **PBT-NHTs** (190 mg, 0.50 mmol), 1.5 mL of acetic acid, and 0.1 mL of nitric acid was heated at 60 °C for 4 h. Water was added and the mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to provide 180 mg of the crude nitro compound as a pale yellow solid. The crude product was then dissolved in THF (30 mL) under nitrogen and EtOH (30 mL), 10 % Pd/C (90 mg), and hydrazine monohydrate (0.4 mL) were added. The resulting solution was refluxed for 30 min and then cooled to room temperature. After removing solids by filtration, the solution was extracted with dichloromethane. The organic layer was washed with water several times and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation. The residual crude product was purified on silica gel to provide 99 mg (0.25 mmol, 50%) of **NH_2-PBT-NHTs** as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) 11.06 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.52 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.40 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 3.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.74 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.72 (brs, 2H), 2.16 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm) 167.3, 152.8, 143.7, 143.0, 135.9, 133.7, 128.9, 127.7, 126.8, 126.7, 125.7, 125.4, 123.6, 123.1, 121.1, 118.6, 115.1, 21.3. IR (KBr, cm^{-1}) 3473, 2567, 1832, 1497, 1334, 1161, 1090, 995, 910. HRMS (EI, m/z) calcd for $C_{20}H_{17}N_3O_2S_2$, 395.0762; found, 395.0765.

Table S1. Computed frontier orbitals for the titled compounds in their normal form involved in the first singlet excitation

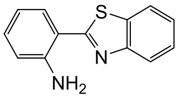
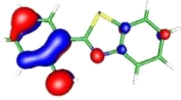
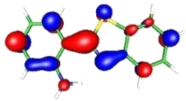
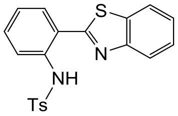
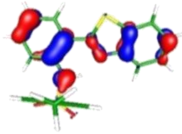
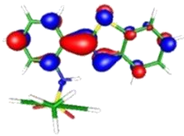
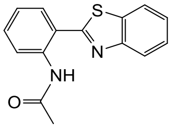
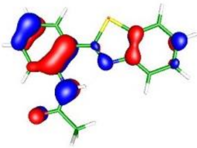
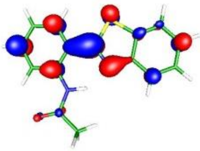
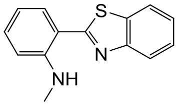
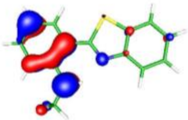
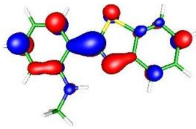
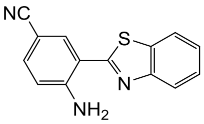
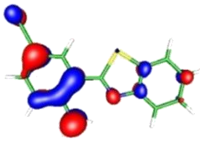
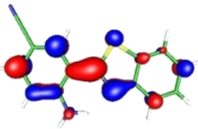
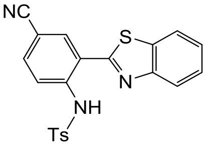
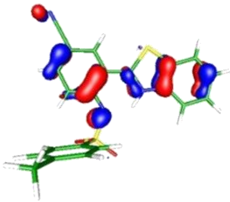
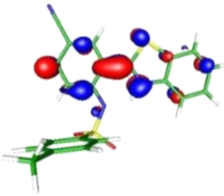
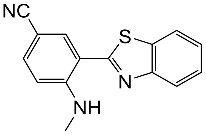
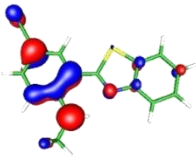
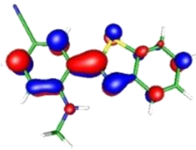
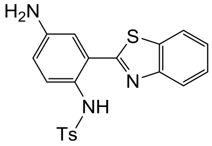
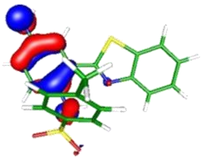
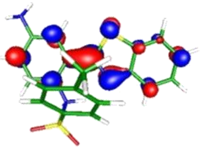
Compound	Structure	HOMO	LUMO
PBT-NH_2			
PBT-NHTs			
PBT-NHAc			
PBT-NHMe			
CN-PBT-NH_2			
CN-PBT-NHTs			
CN-PBT-NHMe			
NH_2-PBT-NHTs			

Table S2. The computed corresponding energy differences (ΔE and ΔE*, in kcal/mol) between the normal form and tautomer form species in the ground (S_0) and the lowest excited state (S_1) for the titled compounds. The energies reported here correspond to optimized structures, for which the calculation showed no negative frequency.

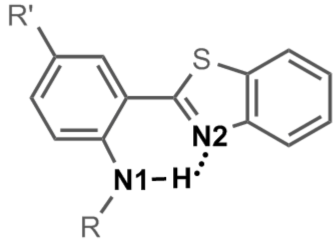
S_0			
Compound	Normal Form (hartree)	Tautomer Form (hartree)	Computed ΔE (kcal/mol)
PBT-NHMe	-1048.625519	[#]	
PBT-NH_2	-1009.310541	[#]	
CN-PBT-NHMe	-1140.897520	[#]	
CN-PBT-NH_2	-1101.581979	[#]	
PBT-NHAc	-1162.014385	[#]	
NH_2-PBT-NHTs	-1883.759131	-1883.738587	12.89
PBT-NHTs	-1828.382105	-1828.364342	11.15
CN-PBT-NHTs	-1920.649640	-1920.634068	9.77

S_1			
Compound	Normal Form (hartree)	Tautomer Form (hartree)	Computed ΔE* (kcal/mol)
PBT-NHMe	-1048.514415	-1048.502811	7.28
PBT-NH_2	-1009.193656	-1009.184634	5.66
CN-PBT-NHMe	-1140.783744	-1140.777227	4.09
CN-PBT-NH_2	-1101.462950	-1101.458814	2.60
PBT-NHAc	-1161.891171	-1161.889206	1.23
NH_2-PBT-NHTs	-1883.657267	-1883.659209	-1.22
PBT-NHTs	-1828.259033	-1828.268849	-6.16
CN-PBT-NHTs	-1920.526496	-1920.538078	-7.27

[#] These computations did not converge after optimization.

Table S3. Computed energy differences (ΔE*), experimental ^{1}H NMR chemical shifts of the N−H hydrogens in $CDCl_3$, and computed N−H bond distances in the S_0 and S_1 states for the titled compounds

Compound	ΔE* (kcal/mol)	N1−H Chemical Shift (ppm)	N1−H at S_0 (Å)	N2−H at S_0 (Å)	N1−H at S_1 (Å)	N2−H at S_1 (Å)
PBT-NHMe	7.28	8.94	1.01442	1.91258	1.03578	1.79051
PBT-NH$_2$	5.66	6.38	1.01289	1.96668	1.03156	1.83942
CN-PBT-NHMe	4.09	9.52	1.01654	1.89660	1.03762	1.77906
CN-PBT-NH$_2$	2.60	7.02	1.01434	1.94545	1.03197	1.83687
PBT-NHAc	1.23	12.42	1.02082	1.84862	1.04078	1.75759
NH$_2$-PBT-NHTs	-1.22	11.06	1.02465	1.92103	1.04992	1.73211
PBT-NHTs	-6.16	12.20	1.02757	1.85687	1.05050	1.73591
CN-PBT-NHTs	-7.27	12.85	1.02936	1.8316	1.05052	1.73125



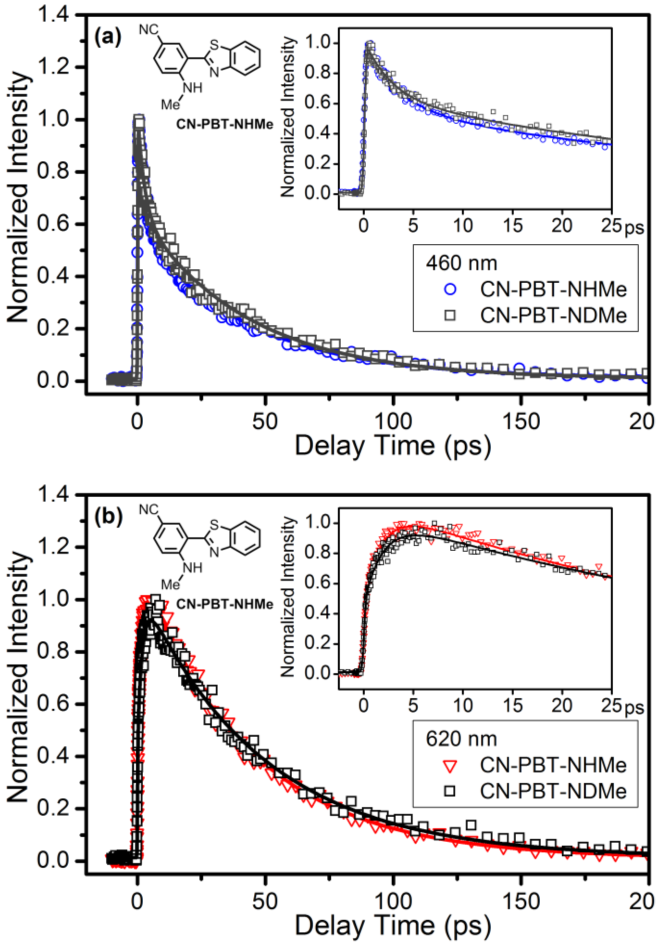


Figure S1. Comparisons between the uPL kinetic traces of **CN-PBT-NHMe** and **CN-PBT-NDMe** in dry CH_2Cl_2. The sample was excited at 400 nm and emission kinetic data were collected at (a) 460 nm for the normal emission and (b) 620 nm for the tautomer emissions. Solid lines depict the best fits using eq. 3 in the text. The fitting data are summarized in Table S4. Insets: The enlargement of kinetic traces from 0 to 25 ps.

Table S4. Observed emission lifetimes (τ_{obs}) by uPL for **CN-PBT-NHMe** and **CN-PBT-NDMe** in CH_2Cl_2 at room temperature.

	τ_{obs} by uPL (pre-exp. factor)	
$\lambda_{monitor}$ / nm	**CN-PBT-NHMe**	**CN-PBT-NDMe**
460	2.31 ps (0.44)	2.69 ps (0.37)
	43.0 ps (0.56)	42.6 ps (0.63)
620	2.10 ps (-0.39) [a]	1.88 ps (-0.37) [a]
	43.8 ps (0.61)	48.0 ps (0.63)

[a] Rise kinetics.

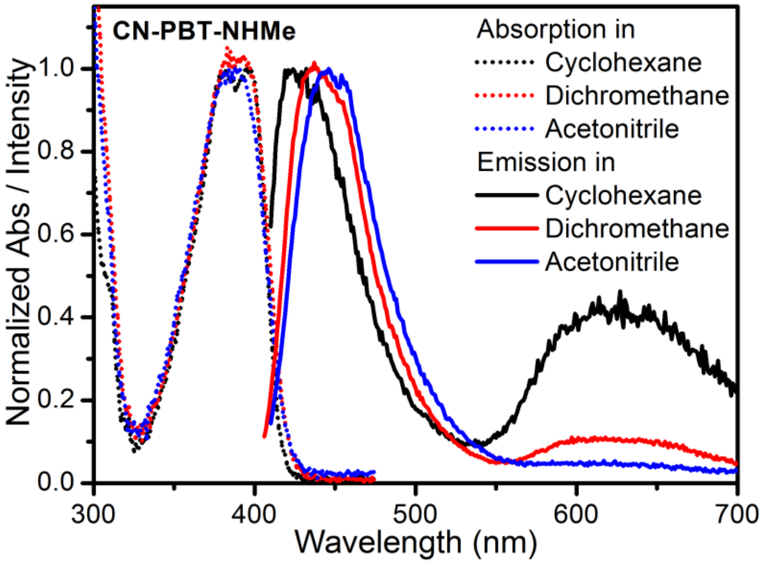


Figure S2. Normalized steady-state absorption and emission spectra for **CN-PBT-NHMe** in aprotic solvents at room temperature.

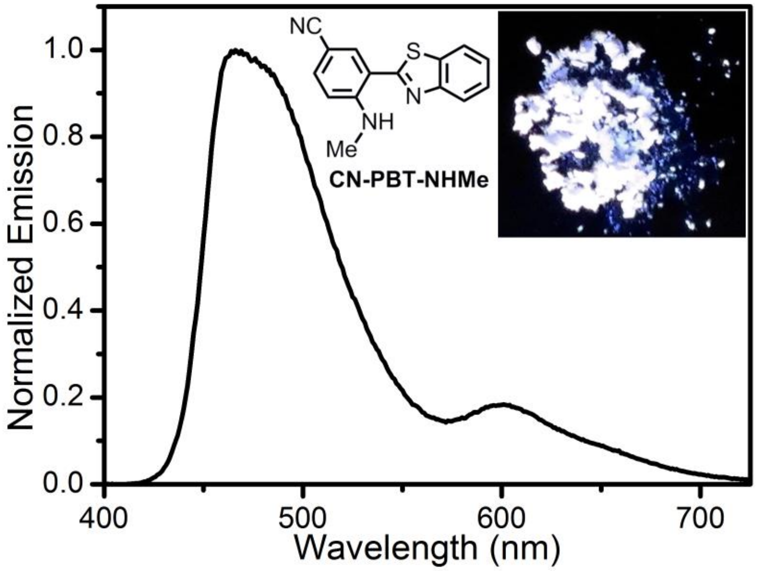


Figure S3. Steady-state emission spectrum for the powder of **CN-PBT-NHMe** excited at 380 nm. Inset: Emission hue from the **CN-PBT-NHMe** powder under the illumination of 365-nm light from a UV lamp.