Supporting Information

An AIE-active hemicyanine fluorogen with stimuli-responsive red/blue emission: Extending the pH sensing range by "switch + knob" effect

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Contents

Experimental Section

General Information

Materials

Solvents such as THF, chloroform, dichloromethane (DCM), and hexane were distilled under normal pressure under nitrogen immediately prior to use. Milli-Q water was used as deionized water. 4-Bromobenzaldehyde, tetrakis(triphenylphosphine)palladium(0), citric acid, and sodium hydrogen phosphate were purchased from Sigma-Adrich. Aniline was purchased from Int. Lab. All the chemicals were used as received without further purification. Compound **1**[1] and **4**[2] were prepared according to the previously published procedures.

Buffer solutions with pH 1–13 were purchased from Merk, Riedel-de Haen and Sigma-Aldrich. Buffers with pH 5.10–7.13 were prepared by citric acid and sodium hydrogen phosphate[3] and confirmed by pH meter. The aqueous mixtures of TPE-Cy for pH-responsive UV and PL tests were prepared by adding an aliquot of DMSO stock solution into aqueous buffers with specific pH values.

Instruments

pH measurements were performed on a Beckman Φ340 pH/Temp meter. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer using $CDCl_3$, DMSO-d_6, or D_2O as solvent and tetramethylsilane (TMS) as internal reference. UV absorption spectra were taken on a Milton Ray Spectronic 3000 array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Solid state quantum efficiency was measured using an integrating sphere at an excitation wavelength of 325 nm. High-resolution mass spectra (HRMS) were obtained on a GCT Premier CAB 048 mass

spectrometer operated in MALDI–TOF mode. Elemental analysis was performed with an Elementar Vario Micro Cube. Particle sizes and Zeta potential of the nanoaggregates were determined using a ZETA-Plus potential Analyzer. Morphologies of nanoaggregates were studied by a JEOL 100CX transmission electron microscope.

Suitable single crystals of TPE-Cy were grown from dichloromethane and hexane with an aliquot of ethanol at room temperature in the dark. X-ray diffraction (XRD) intensity data were collected at 173 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Processing of the intensity data was conducted using the SANT and SADABS routines, and the structure and refinement were carried out using the SHELTL suite of X-ray programs (version 6.10). The OPTEP drawing of TPE-Cy is given in Scheme 1 and its crystal data are summaried in Table S1. The powder XRD diffractogram was recorded on a Philips PW 1830 powder diffractometer using the monochromatized X-ray beam from a nickel-filtered Cu K_α radiation (λ = 1.5406 Å).

Synthesis and Characterization Data of TPE-Cy

Preparation of ***2***. Into a 100 ml round bottom flask were added **1**[1] (376 mg, 1 mmol), 4-bromobenzaldehyde (203 mg, 1.1 mmol) and tetrakis (triphenylphosphine)palladium(0) (3.5 mg, 3 μmol) were dissolved in 50 mL of degassed THF. 7.2 mL of saturated sodium carbonate solution was then added to the mixture under stirring. After reflux for 12 h, the mixture was cooled to room temperature and filtered. The solvent was removed under reduced pressure, the residue was dissolved in DCM and the solution was washed with brine and water. The organic layer was separeted and dried over magnisium sulfate. After solvent evaporation , the crude product was purified by a silica-gel column using DCM/hexane

mixture as eluent. A light yellow powder was obatined in 97% yield (422 mg, 0.967 mmol). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 10.01 (s, 1H), 7.89 (d, 2H), 7.69 (d, 2H), 7.39 (d, 2H), 7.15–7.01 (br, 17H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 191.85, 146.60, 144.16, 143.51, 143.45, 141.62, 140.11, 137.22, 134.98, 131.98, 131.34, 131.29, 131.26, 130.17, 127.79, 127.74, 127.64, 127.31, 126.62, 126.57, 126.53, 126.48. HRMS (MALDI-TOF), *m/z* 436.1609 (M^+, calcd 436.1827).

Preparation of ***3***. Into a 250 ml Two necked flask was added compound **2** (327 mg, 0.75 mmol) in 40 mL of anhydrous ethanol under nitrogen. After all the solids were completely dissolved under heating, 0.4 mL (4.5 mmol) of aniline was added. After reflux overnight, the mixture was cooled using ice water. The precipites formed were filtered out, washed twice with cold ethanol, and vacuum-dried without further purification. The product was obtained as a yellow solid in 90% yield (346 mg). ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.46 (s, 1H), 7.92 (d, 2H), 7.65 (d, 2H), 7.39 (m, 4H), 7.23 (m, 3H), 7.15–7.01 (br, 17H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 159.93, 152.08, 143.65, 163.62, 143.60, 143.51, 143.49, 141.37, 140.32, 137.82, 134.99, 131.90, 131.38, 131.31, 129.20, 129.14, 127.79, 127.71, 127.63, 127.10, 126.57, 126.52, 126.47, 126.26, 125.92, 120.89. HRMS (MALDI-TOF), *m/z* 512.1854 ($[M+H]^+$, calcd 512.2378).

Preparation of TPE-Cy. Into a 250ml flask were added compound **3** (256 mg, 0.5 mmol) and **4** (738 mg, 2.5 mmol). After vacuum-dried and refilled with nitrogen three times, 30 mL dry THF and 15 mL Ac_2O were then injected to the mixture. After refluxed overnight, the mixture was cooled to room temperature, the solvent was removed by rotary evaportaion and the residues were extracted with chloroform and water. The organic layers were combined,

further washed with brine, and dried over magnisium sulfate. After solvent evapration, the crude product was purified by silica-gel column chromatography using chloroform/methanol mixture as eluent. The product was obtained as a red solid in 73% yield (260 mg).

Characterization Data of TPE-Cy: ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.31 (d, 1H), 8.23 (d, 2H), 8.11 (d, 1H) 7.73 (d, 2H), 7.65–7.51 (br, 4H), 7.38 (d, 2H), 7.18–7.02 (br, 17H), 4.89 (t, 2H), 3.10 (t, 2H), 2.31–2.10 (br, 4H), 1.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 181.54, 155.66, 146.42, 144.47, 143.58, 143.49, 143.26, 141.74, 140.54, 140.21, 136.91, 132.83, 132.40, 132.02, 131.39, 131.30, 129.86, 129.71, 127.87, 127.81, 127.76, 127.64, 126.78, 126.59, 126.52, 126.43, 122.54, 114.69, 112.83, 52.07, 49.42, 47.73, 27.26, 26.80, 22.45.

^{1}H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 8.39 (d, 1H), 8.22–8.11 (br, 2H), 7.89 (t, 1H), 7.86–7.76 (br, 3H), 7.67 (d, 1H), 7.59 (m, 4H), 7.18–7.04 (br, 11H), 7.03–6.92 (br, 6H), 4.64 (t, 2H), 2.61 (t, 2H), 1.97 (m, 2H), 1.81 (m, 2H), 1.75 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (TMS, ppm): 182.31, 153.96, 144.33, 143.60, 143.50, 141.80, 141.05, 140.50, 136.82, 133.91, 132.06, 131.98, 131.19, 131.12, 130.26, 129.91, 128.60, 128.54, 128.44, 127.52, 127.45, 127.34, 126.76, 123.52, 115.88, 112.82, 52.85, 50.62, 47.07, 27.56, 26.27, 22.44. HRMS (MALDI-TOF), *m/z* 714.3023 ($[M+H]^+$, calcd 714.3043). Elemental analysis calcd for $C_{48}H_{47}NO_3S$: C, 80.75; H, 6.07; N, 1.96; O, 6.72; S, 4.49. Found C, 80.05; H, 6.06; N, 1.89; S, 5.34.

TPE-Cy-OH (after addition of OH^- to TPE-Cy): ^{1}H NMR (400 MHz, DMSO-d_6/D_2O), δ (TMS, ppm): 7.53 (d, 2H), 7.46 (d, 2H), 7.39 (d, 2H), 7.13–7.03 (br, 9H), 7.02–6.88 (br, 10H), 6.77 (d, 1H), 6.58 (t, 1H), 6.39 (d, 1H), 6.31 (d, 1H), 3.00 (m, 1H), 2.88 (m, 1H), ~2.50

(overlapped with DMSO-d_6, t, 2H), 1.63 (m, 4H), 1.13 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6/D_2O), δ (TMS, ppm): 149.24, 143.90, 143.85, 143.81, 143.09, 141.56, 140.85, 139.01, 138.43, 138.11, 136.48, 132.02, 131.55, 131.45, 131.35, 131.27, 128.72, 128.66, 128.59, 127.89, 127.51, 127.44, 127.38, 126.34, 122.14, 117.85, 106.71, 100.45, 51.88, 49.04, 43.59, 28.85, 27.14, 23.30, 21.27.

Procedures for Sample Preparation in TEM, pH-Switching, and NMR Studies

Sample Preparation for TEM Study

50 μL of 0.31 mM TPE-Cy stock solution in ethanol was added dropwise to 950 μL hexane while sonicating. The resultant mixture was droped onto copper 400-mesh carrier grids covered with carbon-coated Formvar films. The solvent was removed under vacuum at room temperture.

pH-Switched Absorbtion and Emission of TPE-Cy

Experimental details are shown in Table S4. To avoid dillution effect, parallelled samples were prepared. The "Cycle no.0" means that the dye molecules are first put in deionized water without any acid and base. This aqueous mixture is prepared by adding an aliquot of concentrated DMSO stock solution of TPE-Cy into a large volume of water, in which TPE-Cy molecules are well-dispersed as nanoparticles (Figure S2). From no. 0.5 to no. 4, base and acid were added alternatively to adjust the pH. Additional water, if needed, is added to ensure that the final dye concentrations of all samples are identical.

Sample Preparation for in-situ NMR Study Shown in Figure 5 and Figure S8.

A) TPE-Cy (10 mg) in 500 μL of DMSO- d_6/D_2O (4/1 v/v).

B) KOH in D_2O (2 M, 50 μL) was added into A.

C) HCl solution (2 M, 60 μL) was added into B.

Table S1. Crystal data and structure refinement for TPE-Cy[a]

Empirical formula	C49.90 H48.60 Cl0.20 N O3.90 S	
Formula weight	763.85	
Temperature	173.00(14) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.1837(12) Å	α= 90 °.
	B = 9.1091(5) Å	β= 110.794(7) °.
	C = 23.0754(13) Å	γ = 90 °.
Volume	3966.2(4) $Å^3$	
Z	4	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	1.220 mm^{-1}	
F(000)	1622	
Crystal size	0.38 x 0.12 x 0.05 mm^3	
Theta range for data collection	5.01 to 66.99 °.	
Index ranges	-18<=h<=23, -10<=k<=10, -27<=l<=24	
Reflections collected	12802	
Independent reflections	6913 [R(int) = 0.0944]	
Completeness to theta = 66.50 °	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.86450	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6913 / 4 / 511	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0721, wR2 = 0.1321	
R indices (all data)	R1 = 0.1464, wR2 = 0.1651	
Largest diff. peak and hole	0.300 and -0.330 e.$Å^{-3}$	

[a]The single crystal contains 0.9 ethanol and 0.1 dichloromethane molecules.

Table S2. Bond lengths [Å] and angles [°] for TPE-Cy single crystal structure

S(1)-O(1)	1.432(4)	S(1)-O(2)	1.456(4)
S(1)-O(3)	1.438(4)	S(1)-C(14)	1.789(5)
N(1)-C(1)	1.329(5)	N(1)-C(8)	1.428(5)
N(1)-C(11)	1.495(5)	C(1)-C(2)	1.523(5)
C(1)-C(21)	1.432(5)	C(2)-C(3)	1.509(6)
C(2)-C(9)	1.532(5)	C(2)-C(10)	1.540(6)
C(3)-C(4)	1.377(6)	C(3)-C(8)	1.367(6)
C(4)-C(5)	1.395(7)	C(5)-C(6)	1.365(7)
C(6)-C(7)	1.381(6)	C(7)-C(8)	1.404(6)
C(11)-C(12)	1.499(6)	C(12)-C(13)	1.550(6)
C(13)-C(14)	1.497(6)	C(21)-C(22)	1.334(6)
C(22)-C(23)	1.469(5)	C(23)-C(24)	1.397(5)
C(23)-C(28)	1.385(5)	C(24)-C(25)	1.379(6)
C(25)-C(26)	1.382(5)	C(26)-C(27)	1.406(5)
C(26)-C(34)	1.475(5)	C(27)-C(28)	1.381(5)
C(30)-C(31)	1.498(5)	C(30)-C(40)	1.366(5)
C(30)-C(51)	1.504(5)	C(31)-C(32)	1.389(5)
C(31)-C(36)	1.380(5)	C(32)-C(33)	1.373(5)
C(33)-C(34)	1.412(5)	C(34)-C(35)	1.386(5)
C(35)-C(36)	1.388(5)	C(40)-C(41)	1.491(5)
C(40)-C(61)	1.490(5)	C(41)-C(42)	1.384(6)
C(41)-C(46)	1.394(5)	C(42)-C(43)	1.379(6)
C(43)-C(44)	1.383(7)	C(44)-C(45)	1.385(7)
C(45)-C(46)	1.380(6)	C(51)-C(52)	1.390(5)
C(51)-C(56)	1.392(5)	C(52)-C(53)	1.378(6)
C(53)-C(54)	1.383(6)	C(54)-C(55)	1.384(6)
C(55)-C(56)	1.388(6)	C(61)-C(62)	1.386(6)
C(61)-C(66)	1.401(6)	C(62)-C(63)	1.380(6)
C(63)-C(64)	1.396(7)	C(64)-C(65)	1.372(6)
C(65)-C(66)	1.389(6)	Cl(1S)-C(1S)	1.660(17)
Cl(2S)-C(1S)	1.746(14)	Cl(2S)-C(3S)	0.58(4)
O(2S)-C(1S)	1.477(9)	O(2S)-C(3S)	0.53(4)
O(3S)-C(1S)	1.279(15)	C(1S)-C(2S)	1.483(10)
C(1S)-C(3S)	1.592(18)	O(1)-S(1)-O(2)	110.9(3)
O(1)-S(1)-O(3)	115.2(3)	O(1)-S(1)-C(14)	105.6(2)

O(2)-S(1)-C(14)	105.2(2)	O(3)-S(1)-O(2)	112.8(3)
O(3)-S(1)-C(14)	106.3(2)	C(1)-N(1)-C(8)	110.9(4)
C(1)-N(1)-C(11)	126.1(4)	C(8)-N(1)-C(11)	122.8(4)
N(1)-C(1)-C(2)	109.5(4)	N(1)-C(1)-C(21)	121.1(4)
C(21)-C(1)-C(2)	129.4(4)	C(1)-C(2)-C(9)	112.3(4)
C(1)-C(2)-C(10)	110.0(4)	C(3)-C(2)-C(1)	101.2(3)
C(3)-C(2)-C(9)	113.2(4)	C(3)-C(2)-C(10)	108.4(4)
C(9)-C(2)-C(10)	111.3(4)	C(4)-C(3)-C(2)	130.5(4)
C(8)-C(3)-C(2)	109.5(4)	C(8)-C(3)-C(4)	120.0(4)
C(3)-C(4)-C(5)	117.7(5)	C(6)-C(5)-C(4)	121.0(5)
C(5)-C(6)-C(7)	122.9(5)	C(6)-C(7)-C(8)	114.6(5)
C(3)-C(8)-N(1)	108.7(4)	C(3)-C(8)-C(7)	123.6(4)
C(7)-C(8)-N(1)	127.8(4)	N(1)-C(11)-C(12)	109.5(4)
C(11)-C(12)-C(13)	109.3(4)	C(14)-C(13)-C(12)	118.1(4)
C(13)-C(14)-S(1)	115.8(4)	C(22)-C(21)-C(1)	123.5(4)
C(21)-C(22)-C(23)	125.7(4)	C(24)-C(23)-C(22)	117.9(4)
C(28)-C(23)-C(22)	122.7(4)	C(28)-C(23)-C(24)	119.3(4)
C(25)-C(24)-C(23)	119.8(4)	C(24)-C(25)-C(26)	122.0(4)
C(25)-C(26)-C(27)	117.5(4)	C(25)-C(26)-C(34)	122.2(4)
C(27)-C(26)-C(34)	120.3(3)	C(28)-C(27)-C(26)	121.1(4)
C(27)-C(28)-C(23)	120.2(4)	C(31)-C(30)-C(51)	112.3(3)
C(40)-C(30)-C(31)	124.3(4)	C(40)-C(30)-C(51)	123.3(4)
C(32)-C(31)-C(30)	120.7(4)	C(36)-C(31)-C(30)	120.4(4)
C(36)-C(31)-C(32)	118.6(4)	C(33)-C(32)-C(31)	120.8(4)
C(32)-C(33)-C(34)	121.3(4)	C(33)-C(34)-C(26)	121.1(4)
C(35)-C(34)-C(26)	122.0(4)	C(35)-C(34)-C(33)	116.9(4)
C(34)-C(35)-C(36)	121.6(4)	C(31)-C(36)-C(35)	120.7(4)
C(30)-C(40)-C(41)	123.1(4)	C(30)-C(40)-C(61)	121.3(4)
C(61)-C(40)-C(41)	115.3(4)	C(42)-C(41)-C(40)	119.9(4)
C(42)-C(41)-C(46)	117.1(4)	C(46)-C(41)-C(40)	122.9(4)
C(43)-C(42)-C(41)	121.6(4)	C(42)-C(43)-C(44)	120.4(5)
C(43)-C(44)-C(45)	119.2(4)	C(46)-C(45)-C(44)	119.8(5)
C(45)-C(46)-C(41)	121.9(4)	C(52)-C(51)-C(30)	119.3(4)
C(52)-C(51)-C(56)	118.2(4)	C(56)-C(51)-C(30)	122.2(4)
C(53)-C(52)-C(51)	121.2(4)	C(52)-C(53)-C(54)	120.4(4)
C(53)-C(54)-C(55)	119.1(4)	C(54)-C(55)-C(56)	120.6(4)
C(55)-C(56)-C(51)	120.4(4)	C(62)-C(61)-C(40)	121.0(4)

C(62)-C(61)-C(66)	118.0(4)	C(66)-C(61)-C(40)	120.8(4)
C(63)-C(62)-C(61)	121.9(5)	C(62)-C(63)-C(64)	119.6(4)
C(65)-C(64)-C(63)	119.3(4)	C(64)-C(65)-C(66)	121.2(5)
C(65)-C(66)-C(61)	120.1(4)	C(3S)-Cl(2S)-C(1S)	65(2)
C(3S)-O(2S)-C(1S)	93(3)	Cl(1S)-C(1S)-Cl(2S)	114.6(14)
O(2S)-C(1S)-Cl(1S)	135.7(13)	O(2S)-C(1S)-Cl(2S)	21.3(6)
O(2S)-C(1S)-C(2S)	111.5(7)	O(2S)-C(1S)-C(3S)	19.2(13)
O(3S)-C(1S)-Cl(1S)	20.9(13)	O(3S)-C(1S)-Cl(2S)	135.1(11)
O(3S)-C(1S)-O(2S)	155.7(10)	O(3S)-C(1S)-C(2S)	46.0(8)
O(3S)-C(1S)-C(3S)	146.2(18)	C(2S)-C(1S)-Cl(1S)	25.3(11)
C(2S)-C(1S)-Cl(2S)	90.2(8)	C(2S)-C(1S)-C(3S)	100.5(17)
C(3S)-C(1S)-Cl(1S)	126(2)	C(3S)-C(1S)-Cl(2S)	19.5(14)
Cl(2S)-C(3S)-C(1S)	95(3)	O(2S)-C(3S)-Cl(2S)	72(5)
O(2S)-C(3S)-C(1S)	68(2)		

Table S3. Sample preparation details for the PL measurement shown in Figure 1[a]

f_h (%)	Dye stock solution (mL)	EtOH (mL)	hexane (mL)
0	0.15	2.85	0
10	0.15	2.55	0.30
30	0.15	1.95	0.90
50	0.15	1.35	1.50
70	0.15	0.75	2.10
80	0.15	0.45	2.40
90	0.15	0.15	2.70
95	0.15	0	2.85

[a]The concentration of dye stock solution in ethanol is 0.31 mM. The calculated volume of stock solution is added to the premixed solvents of ethanol and hexane with different volume ratios under sonication or stirring.

Table S4. Sample preparation details for reversibly switching absorption and emission behaviors of TPE-Cy

Cycle no.	Dye/H_2O[a] (20 μM)	NaOH (2 M)	HCl (2 M)	NaOH (2 M)	HCl (2 M)	NaOH (2 M)	HCl (2 M)	NaOH (2 M)	HCl (2 M)	H_2O
0	1 mL									1 mL
0.5	1 mL	50 μL								950 μL
1	1 mL	50 μL	100 μL							850 μL
1.5	1 mL	50 μL	100 μL	100 μL						750 μL
2	1 mL	50 μL	100 μL	100 μL	100 μL					650 μL
2.5	1 mL	50 μL	100 μL	100 μL	100 μL	100 μL				550 μL
3	1 mL	50 μL	100 μL	100 μL	100 μL	100 μL	100 μL			450 μL
3.5	1 mL	50 μL	100 μL	100 μL	100 μL	100 μL	100 μL	100 μL		350 μL
4	1 mL	50 μL	100 μL	100 μL	100 μL	100 μL	100 μL	100 μL	100 μL	250 μL

[a]The dye molecules are well-dispersed in water as nanoparticles.

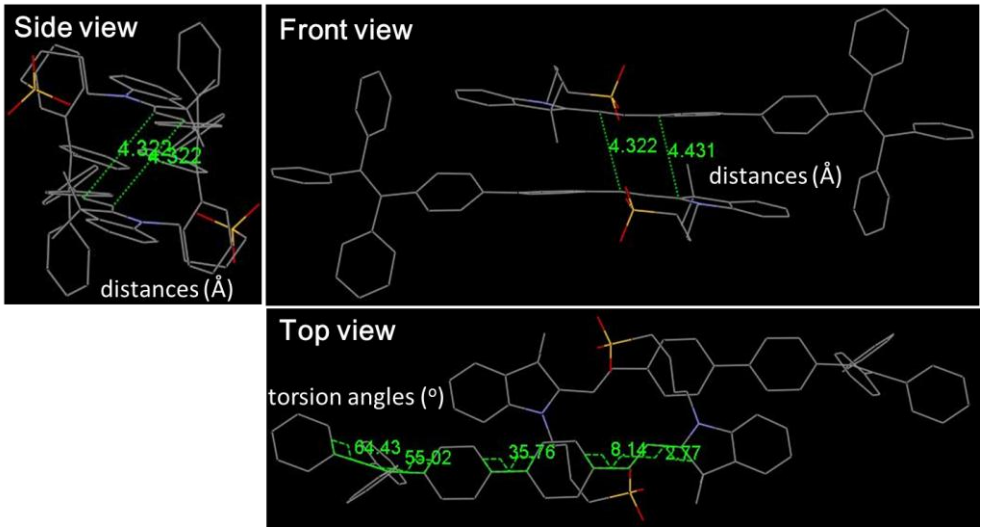

Figure S1. Different packing views of two adjacent TPE-Cy's in the single crystal structure.

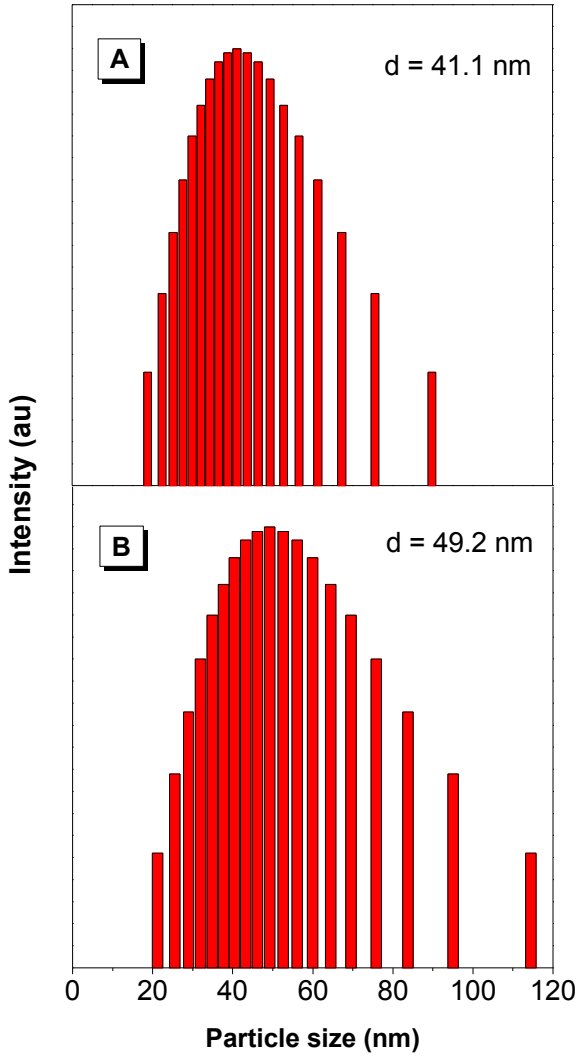

Figure S2. Particle size distribution of TPE-Cy in water. (A) Fresh sample. (B) Sample kept at room temperature for seven days. The fresh sample is prepared by adding a small volume of concentrated DMSO stock solution of TPE-Cy into a large volume of water.

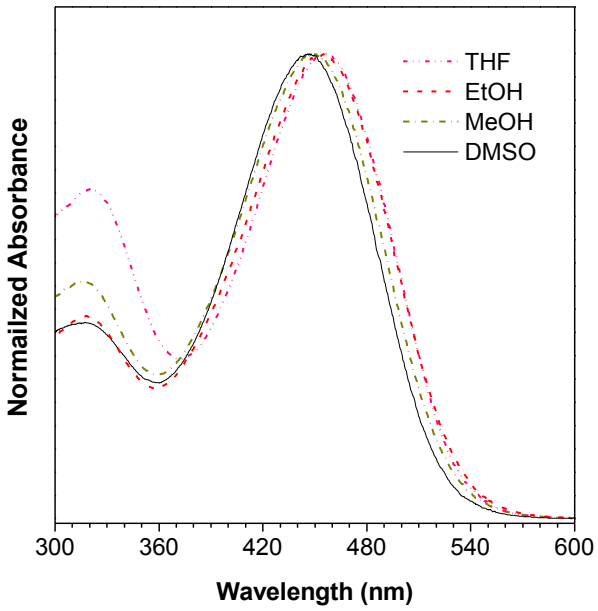

Figure S3. Normalized absorption spectra of TPE-Cy in different solvents.

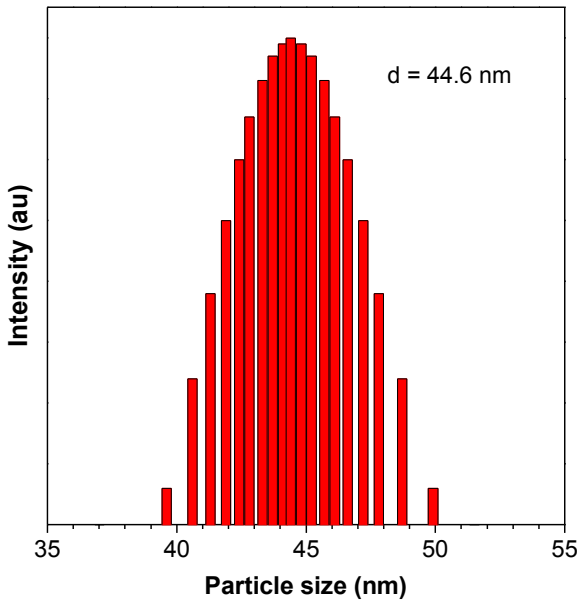

Figure S4. Particle size distribution of TPE-Cy in ethanol/hexane (v/v 5/95) mixture.

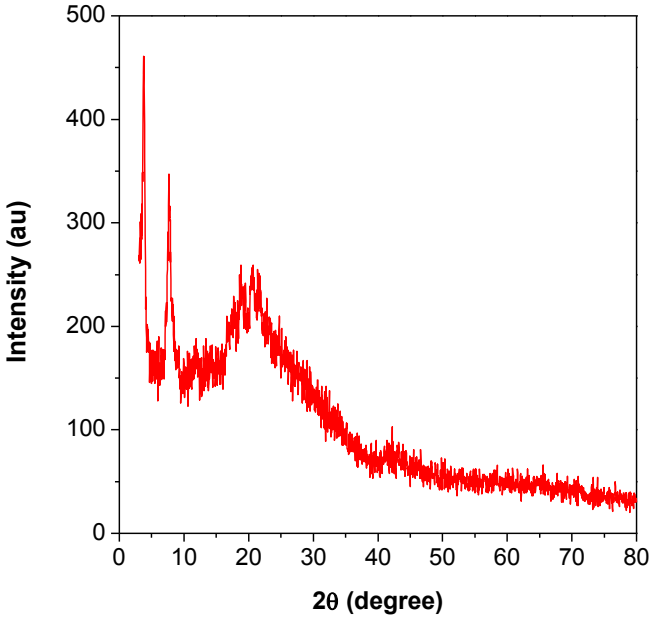

Figure S5. XRD diffractogram of TPE-Cy powder prepared form natural evaporation of its solution.

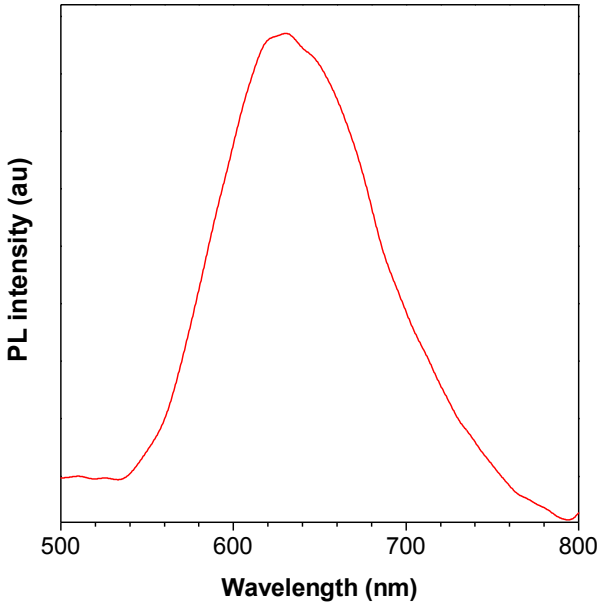

Figure S6. PL spectrum of TPE-Cy in solid powder state.

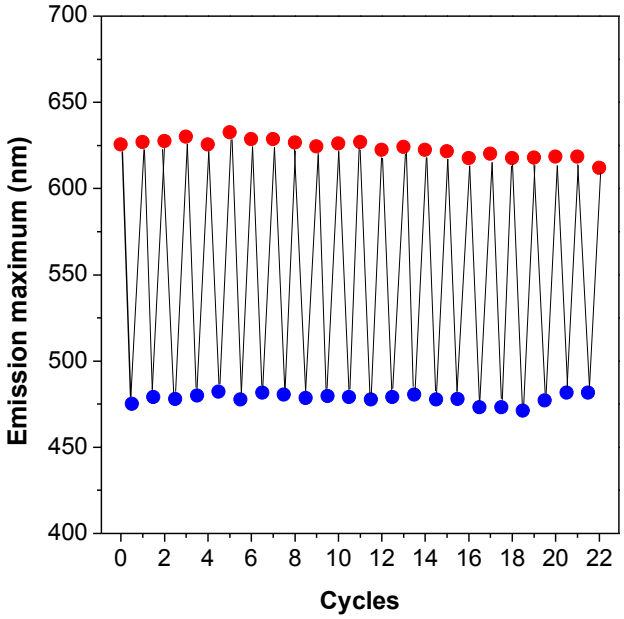

Figure S7. Emission maximum versus switching cycles.

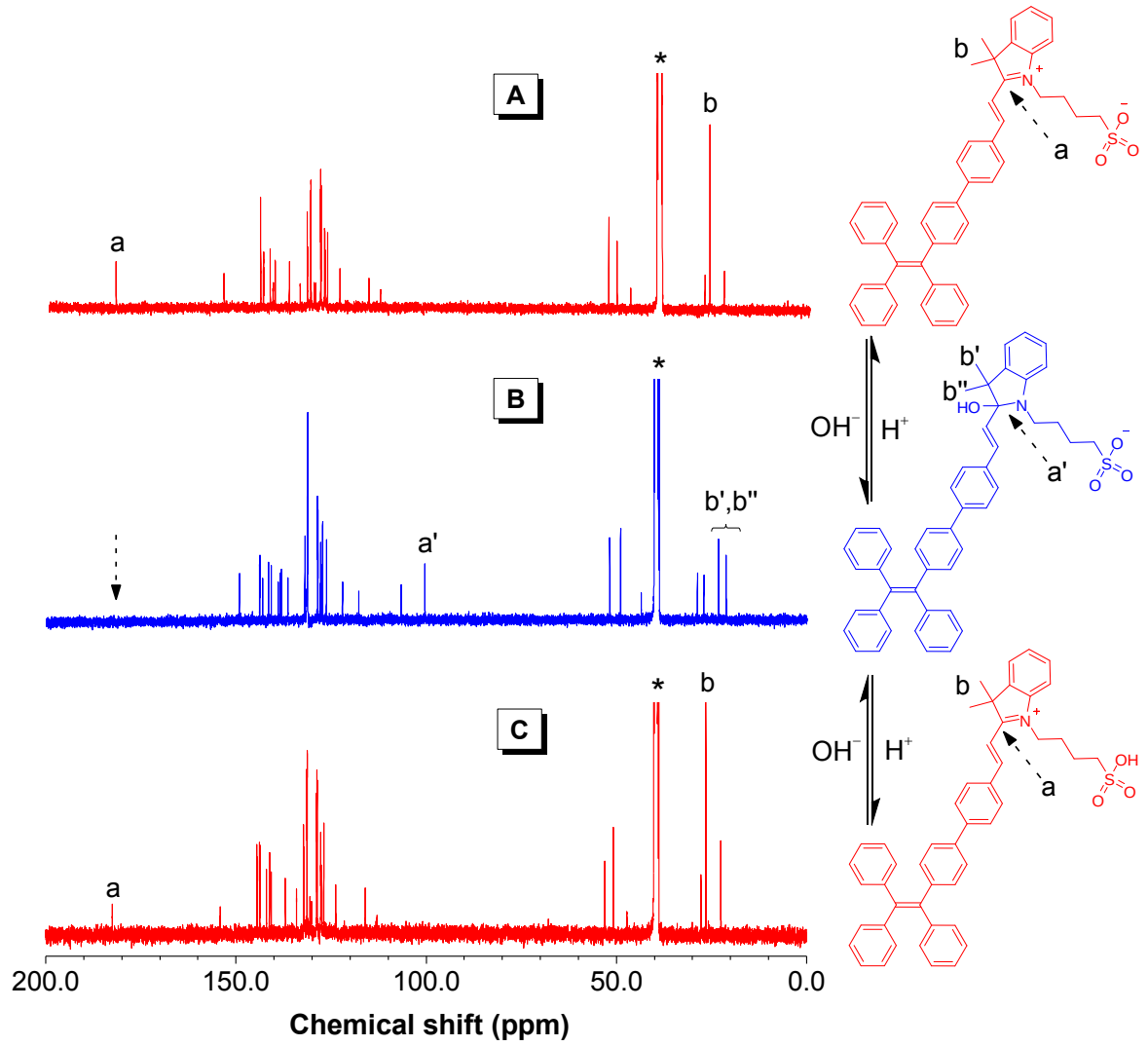

Figure S8. ^{13}C NMR spectra of TPE-Cy in 0.5 mL of (A) DMSO-d_6/D_2O (4/1 v/v), (B) followed by addition of 0.05 mL 2 M KOH in D_2O, and (C) further by addition of 0.06 mL 2 M HCl in H_2O. The water peaks are marked with asterisks.

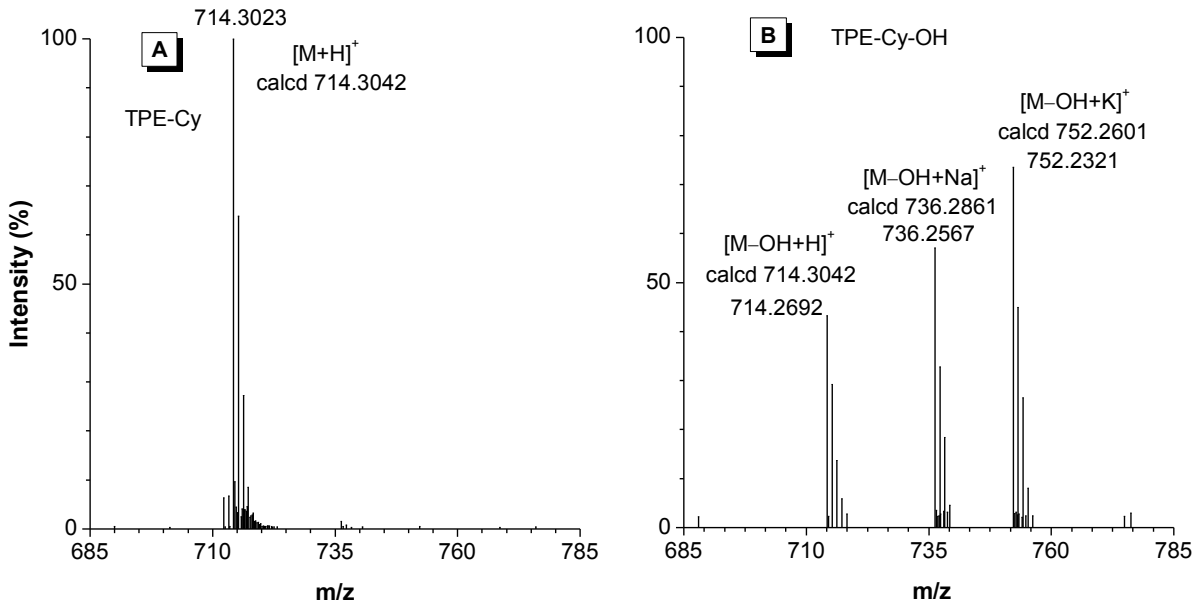

Figure S9. High resolution mass spectra of TPE-Cy (A) before and (B) after addition of aqueous KOH solution.

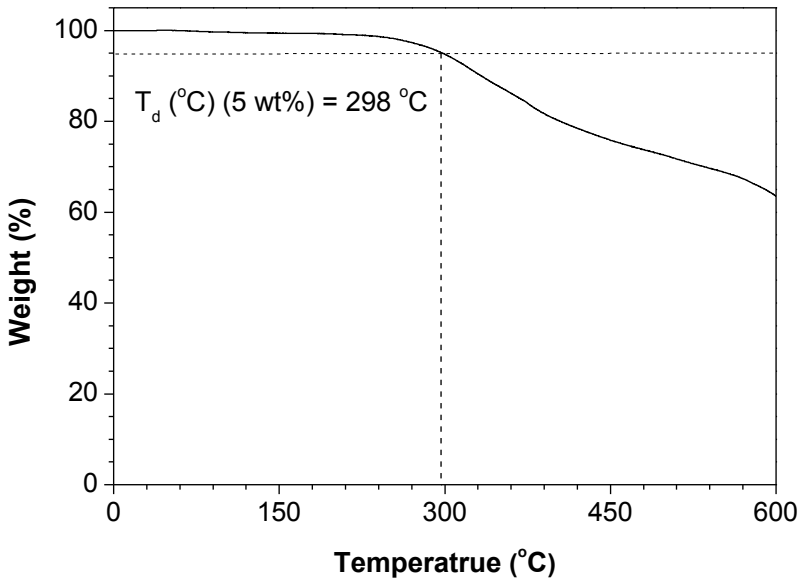

Figure S10. TGA thermogram of TPE-Cy recorded under nitrogen at a heating rate of 10 ^{o}C/min

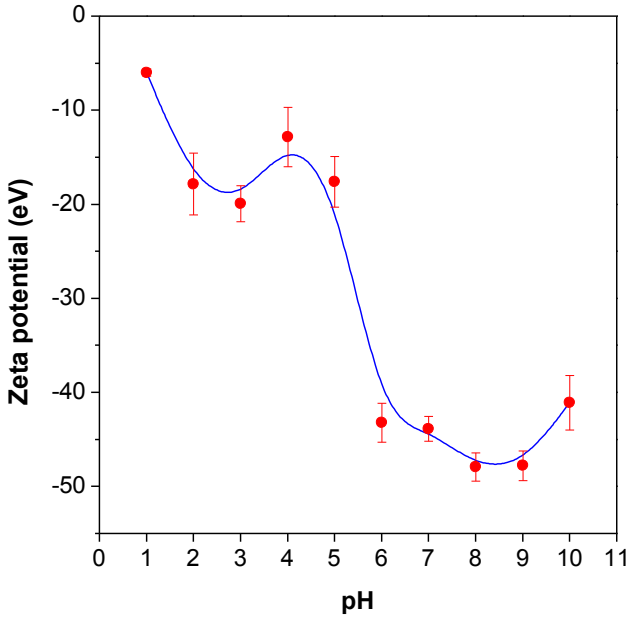

Figure S11. Zeta Potential of TPE-Cy in buffer solutions with different pH values.

References

1. Yuan, W. Z.; Lu, P.; Chen, S.; Lam, J. W. Y.; Wang, Z.; Liu, Y.; Kwok, G. S.; Ma, Y.; Tang, B. Z. *Adv. Mater*. **2010**, *22*, 2159–2163.
2. N. Narayanan, G. Patonay. *J. Org. Chem*, **1995**, *60*, 2391–2395.
3. Dawson, R. M. C.; Elliot, D. C.; Elliot, W. H.; Jones, K. M. *Data for Biochemical Research;* 3rd ed., Oxford Science Publ., 1986.