Supporting Information

Interestingly pH-Responsible Behavior in Benzothiadiazole-Derived Coordination Polymer Constructed via an in Situ Click Synthesis

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EXPERIMENTAL SECTION

Materials and measurements. All starting materials and reagents for synthesis were commercially available and used as received. (**Caution!** *Sodium azide salt is potentially explosive which should be carefully handled and used in small amount*.) The elemental analyses were performed with FLASH EA 1112 elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on Cu $K\alpha_1$ radiation on a PANalyticalX'Pert PRO diffractometer. Thermal analyses were carried out on a Netzsch STA 449C thermal analyzer at a heating rate of 10 °C·min^{-1} in air. The measurements of steady-state emission spectra were conducted on a JASCO FP-8300 fluorescence spectrophotometer at room temperature.

Synthesis of $[Zn_{0.5}(TBC)(H_2O)]$ (1, TBC = 4-cyano-7-(1H-tetrazol-5-yl)benzothiadiazole). **PL** (**PL** = 4,7-dicyano-benzenethiazole, 0.0186 g, 0.1 mmol), NaN_3 (0.0130 g, 0.2 mmol), $ZnSO_4·7H_2O$ (0.0288 g, 0.1 mmol) and H_2O (8 mL) were placed in a 10 mL Teflon-lined stainless-steel container. The mixture was sealed and heated at 100 °C for three days. After the mixture was cooled to ambient temperature at a rate of 5 °C/h, yellow crystals of **1** were obtained with a yield of 49%. Anal. Calcd for **1** (%): C, 34.45; H, 1.45; N, 35.15; S,11.50. Found (%): C, 34.05; H, 1.40; N, 35.61; S, 10.93. ESI-MS $(M+H)^+$: 556.86.

Synthesis of $[Cd(TBC)(N_3)(H_2O)]_n$ (2). The synthetic procedure was similar to that of **1**, except that $ZnSO_4·7H_2O$ was replaced with $Cd(NO_3)_2·4H_2O$ (0.0308 g, 0.1 mmol) and

the amount of NaN_3 was increased to 0.3 mmol. The yield of **2** was of 50%. Anal. Calcd for **2** (%): C, 23.98; H, 1.01; N, 34.96; S, 8.00. Found (%): C, 24.12; H, 1.02; N, 34.80; S, 7.55.

Crystal Data Collection and Refinement. Crystal structures of **1** (298 K) and **2** (293 K) were performed on Bruker D8 VENTURE with the X-ray source (Mo-Kα radiation, λ = 0.710 73 Å), respectively. Absorption corrections were implemented by SADABS-2016/2 (Bruker, 2016/2). An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques, based on F^2, using ShelXL. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. All the hydrogen atoms were included in the final refinement. The crystallographic data for **1** and **2** are listed in Table 1. Moreover, the selected bonds distances and bond angles are summarized in Table S1-S2, and the intermolecular hydrogen bonding are summarized in Table S3-S4. Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 1854426 and 1854427.

Table S1. Selected Bond Lengths (Å) for **1** and **2**.

1		**2**	
Zn(1)-O(1)#1	2.108(2)	Cd(1)-O(1)	2.289(2)
Zn(1)-O(1)	2.108(2)	Cd(1)-N(1)	2.291(3)
Zn(1)-N(2)#1	2.318(3)	Cd(1)-N(3)#1	2.292(3)
Zn(1)-N(2)	2.318(3)	Cd(1)-N(10)	2.314(3)
Zn(1)-N(3)#1	2.025(2)	Cd(1)-N(9)#2	2.337(3)
Zn(1)-N(3)	2.025(2)	Cd(1)-N(4)	2.451(3)
S(1)-N(1)	1.616(3)	N(1)-N(2)	1.184(4)
S(1)-N(2)	1.634(3)	N(2)-N(3)	1.169(4)
N(1)-C(8)	1.331(5)	N(3)-Cd(1)#3	2.292(3)
N(2)-C(1)	1.345(4)	N(4)-C(1)	1.345(4)
N(3)-N(4)	1.347(4)	N(4)-S(1)	1.627(3)
N(3)-C(3)	1.331(4)	N(5)-C(2)	1.335(4)
N(4)-N(5)	1.305(4)	N(5)-S(1)	1.605(3)
N(5)-N(6)	1.343(4)	N(6)-C(7)	1.128(5)
N(6)-C(3)	1.331(4)	N(7)-N(8)	1.336(4)
N(7)-C(7)	1.118(6)	N(7)-C(8)	1.341(4)
C(1)-C(2)	1.425(5)	N(8)-N(9)	1.313(4)
C(1)-C(8)	1.438(5)	N(9)-N(10)	1.346(4)
C(2)-C(3)	1.464(5)	N(9)-Cd(1)#2	2.337(3)
C(2)-C(4)	1.369(5)	N(10)-C(8)	1.331(4)
C(4)-C(5)	1.401(5)	O(1)-H(1A)	0.8500
C(5)-C(6)	1.368(5)	O(1)-H(1B)	0.8500
C(6)-C(7)	1.453(6)	C(1)-C(2)	1.426(4)
C(6)-C(8)	1.420(5)	C(1)-C(6)	1.431(4)
		C(2)-C(3)	1.428(5)
		C(3)-C(4)	1.367(5)
		C(3)-C(7)	1.446(5)
		C(4)-C(5)	1.411(5)
		C(4)-H(4)	0.9300
		C(5)-C(6)	1.380(4)

		C(5)-H(5)	0.9300
		C(6)-C(8)	1.463(4)

Symmetry code:

1: [1]1-X,1-Y,1-Z

2: [1]X,-Y+3/2,Z-1/2; [2]-X+2,-Y+1,-Z+1; [3] X,-Y+3/2,Z+1/2

Table S2. Selected Bond Angels (degree) for **1** and **2**.

1		**2**	
O(1)#1-Zn(1)-O(1)	180.0	O(1)-Cd(1)-N(1)	174.70(11)
O(1)#1-Zn(1)-N(2)#1	88.22(10)	O(1)-Cd(1)-N(3)#1	85.16(12)
O(1)-Zn(1)-N(2)#1	91.79(10)	N(1)-Cd(1)-N(3)#1	89.55(12)
O(1)-Zn(1)-N(2)	88.22(10)	O(1)-Cd(1)-N(10)	85.36(9)
O(1)#1-Zn(1)-N(2)	91.78(10)	N(1)-Cd(1)-N(10)	99.53(10)
N(2)-Zn(1)-N(2)#1	180.0	N(3)#1-Cd(1)-N(10)	158.24(11)
N(3)#1-Zn(1)-O(1)	89.31(10)	O(1)-Cd(1)-N(9)#2	89.99(10)
N(3)-Zn(1)-O(1)	89.31(10)	N(1)-Cd(1)-N(9)#2	91.27(11)
N(3)-Zn(1)-O(1)	90.69(10)	N(3)#1-Cd(1)-N(9)#2	100.61(11)
N(3)#1-Zn(1)-O(1)	90.69(10)	N(10)-Cd(1)-N(9)#2	98.93(9)
N(3)-Zn(1)-N(2)#1	96.32(10)	O(1)-Cd(1)-N(4)	87.53(10)
N(3)#1-Zn(1)-N(2)#1	83.68(10)	N(1)-Cd(1)-N(4)	91.47(11)
N(3)-Zn(1)-N(2)	83.68(10)	N(3)#1Cd(1)N(4)	82.25(10)
N(3)#1-Zn(1)-N(2)	96.31(10)	N(10)-Cd(1)-N(4)	77.82(9)
N(3)#1-Zn(1)-N(3)	180.0	N(9)#2-Cd(1)-N(4)	176.06(9)
N(1)-S(1)-N(2)	99.53(15)	N(2)-N(1)-Cd(1)	120.0(3)
C(8)-N(1)-S(1)	107.4(2)	N(3)-N(2)-N(1)	178.4(4)
S(1)-N(2)-Zn(1)	127.70(14)	N(2)-N(3)-Cd(1)#3	133.1(3)
C(1)-N(2)-Zn(1)	125.0(2)	C(1)-N(4)-S(1)	107.4(2)
C(1)-N(2)-S(1)	107.2(2)	C(1)-N(4)-Cd(1)	129.9(2)
N(4)-N(3)-Zn(1)	118.7(2)	S(1)-N(4)-Cd(1)	122.66(14)
C(3)-N(3)-Zn(1)	135.3(2)	C(2)-N(5)-S(1)	107.4(2)
C(3)-N(3)-N(4)	106.0(2)	N(8)-N(7)-C(8)	105.5(3)
N(5)-N(4)-N(3)	108.4(3)	N(9)-N(8)-N(7)	109.0(3)
N(4)-N(5)-N(6)	109.9(3)	N(8)-N(9)-N(10)	109.7(3)
C(3)-N(6)-N(5)	105.4(3)	N(8)-N(9)-Cd(1)#2	111.0(2)
N(2)-C(1)-C(2)	127.8(3)	N(10)-N(9)-Cd(1)#2	139.2(2)
N(2)-C(1)-C(8)	112.1(3)	C(8)-N(10)-N(9)	104.9(2)
C(2)-C(1)-C(8)	120.1(3)	C(8)-N(10)-Cd(1)	133.1(2)
C(1)-C(2)-C(3)	122.5(3)	N(9)-N(10)-Cd(1)	121.89(19)
C(4)-C(2)-C(1)	117.3(3)	Cd(1)-O(1)-H(1A)	120.0

C(4)-C(2)-C(3)	120.2(3)	Cd(1)-O(1)-H(1B)	120.0
N(3)-C(3)-C(2)	125.7(3)	H(1A)-O(1)-H(1B)	120.0
N(6)-C(3)-N(3)	110.4(3)	N(4)-C(1) -C(2)	111.9(3)
N(6)-C(3)-C(2)	123.9(3)	N(4)-C(1)-C(6)	127.1(3)
C(2)-C(4)-C(5)	123.2(4)	C(2)-C(1)-C(6)	121.0(3)
C(6)-C(5)-C(4)	121.0(3)	N(5)-C(2)-C(1)	113.8(3)
C(5)-C(6)-C(7)	121.6(4)	N(5)-C(2)-C(3)	126.2(3)
C(5)-C(6)-C(8)	118.8(3)	C(1)-C(2)-C(3)	120.0(3)
C(8)-C(6)-C(7)	119.5(4)	C(4)-C(3)-C(2)	118.3(3)
N(7)-C(7)-C(6)	177.1(6)	C(4)-C(3)-C(7)	121.3(3)
N(1)-C(8)-C(1)	113.8(3)	C(2)-C(3)-C(7)	120.4(3)
N(1)-C(8)-C(6)	126.6(3)	C(3)-C(4)-C(5)	121.1(3)
C(6)-C(8)-C(1)	119.6(3)	C(3)-C(4)-H(4)	119.5
		C(5)-C(4)-H(4)	119.5
		C(6)-C(5)-C(4)	123.4(3)
		C(6)-C(5)-H(5)	118.3
		C(4)-C(5)-H(5)	118.3
		C(5)-C(6)-C(1)	116.1(3)
		C(5)-C(6)-C(8)	120.0(3)
		C(1)-C(6)-C(8)	123.8(3)
		N(6)-C(7)-C(3)	177.5(5)
		N(10)-C(8)-N(7)	110.9(3)
		N(10)-C(8)-C(6)	128.1(3)
		N(7)-C(8)-C(6)	121.0(3)
		N(5)-S(1)-N(4)	99.57(15)

Symmetry code:

1: [1]1-X,1-Y,1-Z

2: [1]X,-Y+3/2,Z-1/2; [2]-X+2,-Y+1,-Z+1; [3] X,-Y+3/2,Z+1/2

Table S3. Hydrogen bonds for **1** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...N(5)	0.8689(22)	1.9734(28)	2.8362(35)	154.7
O(1)-H(1B)...N(6)	0.8684(23)	1.9518(26)	2.7645(35)	155.26

Symmetry transformations used to generate equivalent atoms: [1] -X+3/2, -Y+3/2, -Z+1; [2] X+1/2, Y-1/2, Z .

Table S4. Hydrogen bonds for **2** [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...N(1)#4	0.85	2.38	3.166(4)	154.7
O(1)-H(1B)...N(7)#5	0.85	2.15	2.789(4)	132.0

Symmetry transformations used to generate equivalent atoms: [1] X,-Y+3/2,Z-1/2;[2]-X+2,-Y+1,-Z+1; [3] X,-Y+3/2,Z+1/2; [4] X,Y,Z-1; [5] X,-Y+1/2,Z-1/2.

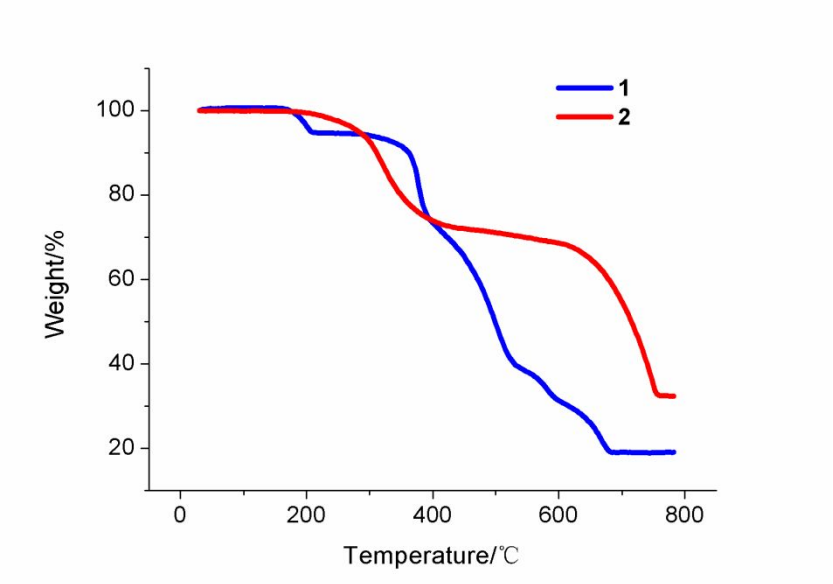

Figure S1. TGA curves of **1** (blue line) and **2** (red line).

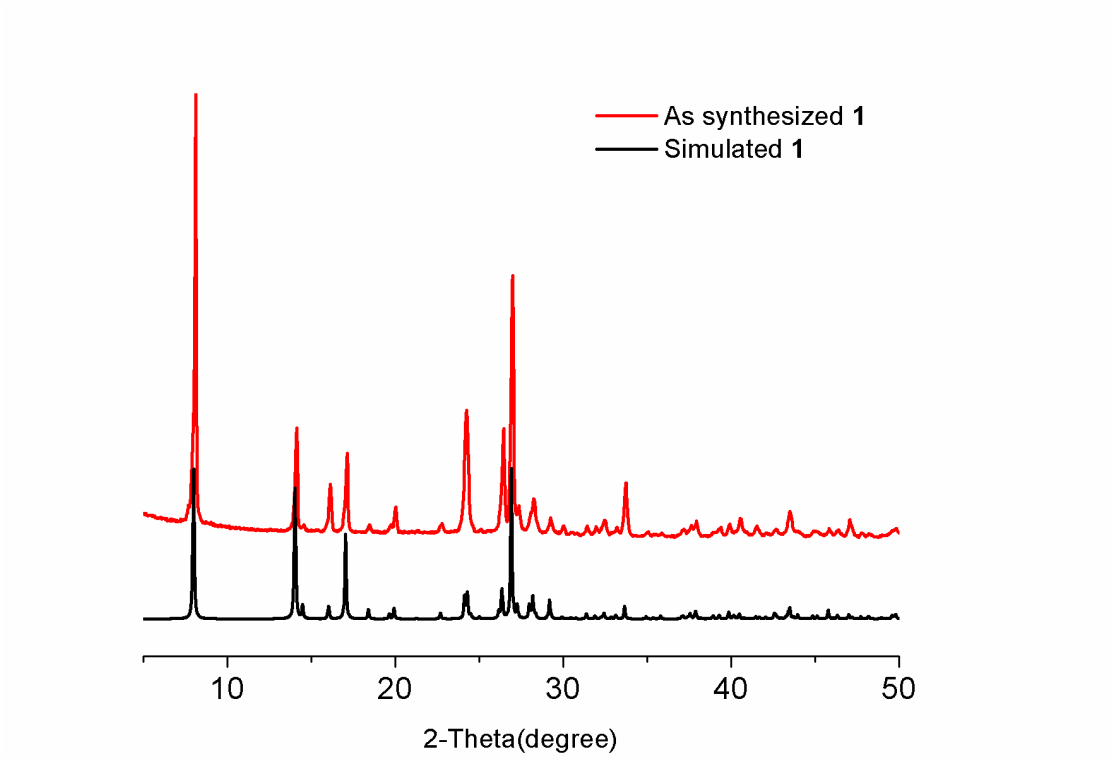

Figure S2. PXRD patterns of **1**. (Simulated: black, sample: red).

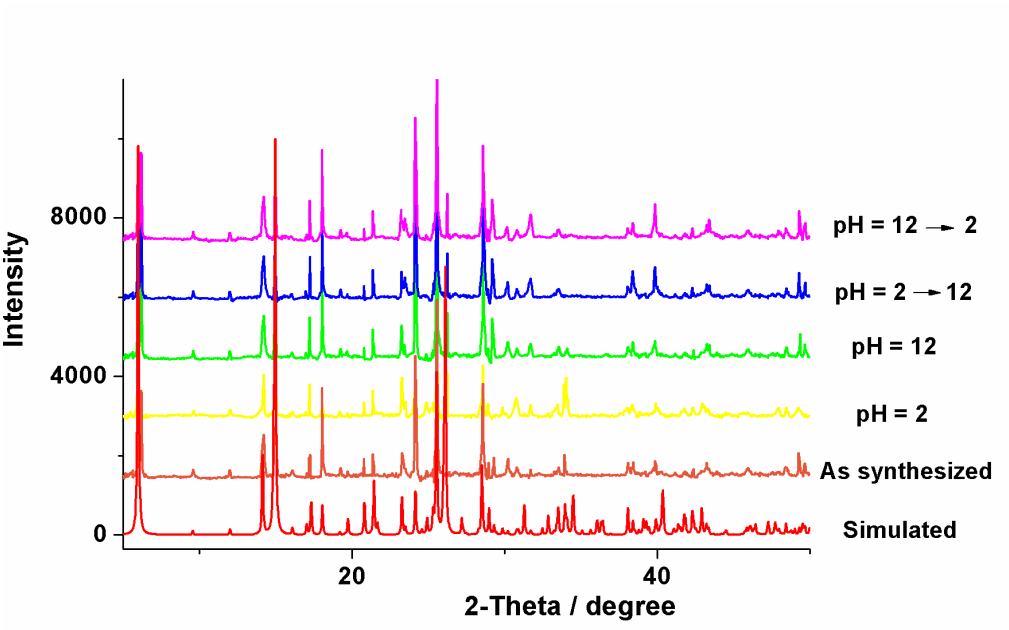

Figure S3. The simulated (black) and experimental (red), soaked in buffer solution (pH = 2, yellow), and soaked in buffer solution (pH = 12, green), soaked in buffer solution (the pH value was modulated from 2 to 12, blue), and soaked in buffer

solution (the pH value was modulated from 12 to 2, matanga) PXRD patterns for complex **2**.

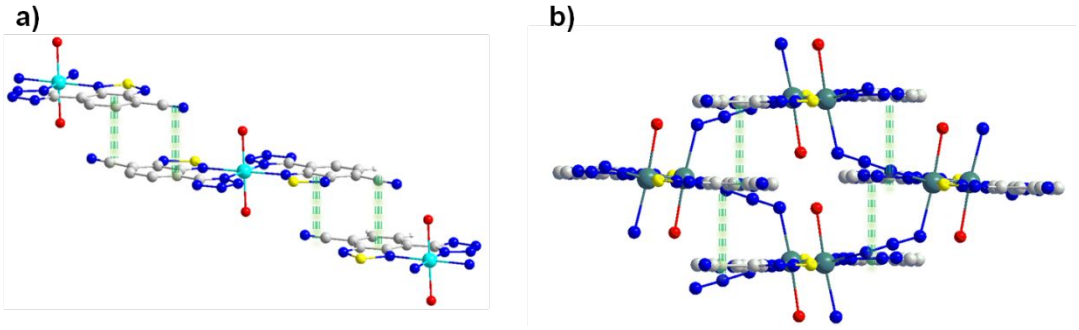

Figure S4. a) Schematic representation of BTD *syn*-dimer in complex **1**. b) Schematic representation of BTD *anti*-dimer in complex **2**.

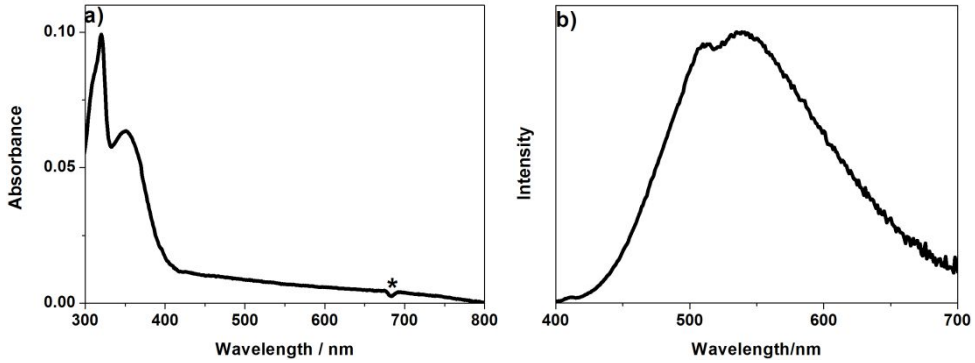

Figure 5. UV-vis absorption (a, * instrumental error) and emission (b, excited at 360 nm) spectra of **1** in water at room temperature.

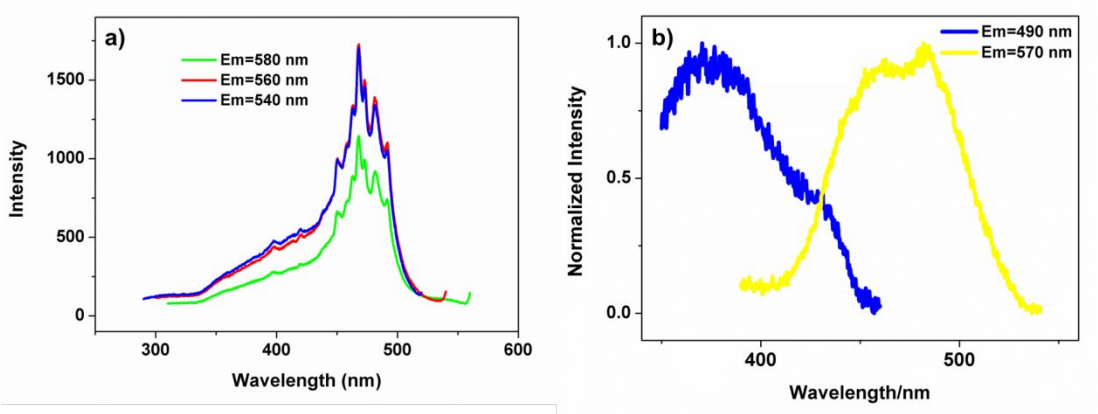

Figure S6. Excitation spectra of **1** (a) and **2** (b) in the solid state at room temperature.

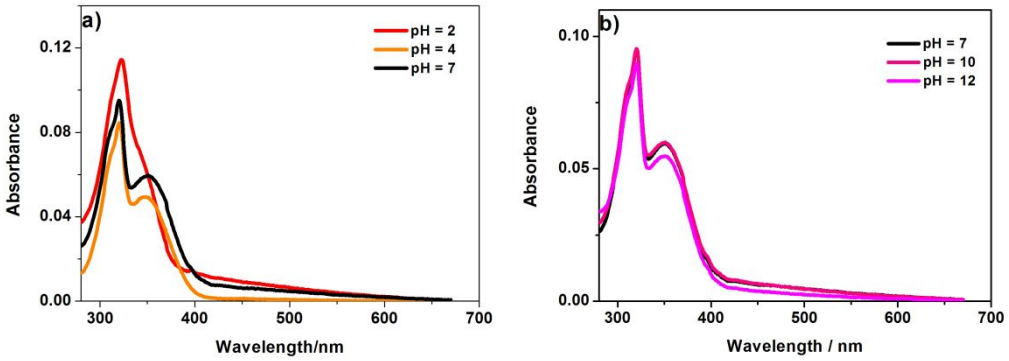

Figure S7. Absorption spectra of **1** toward different pH values (a, pH ≤ 7； b, pH ≥ 7) in Britton-Robinson buffer solution.

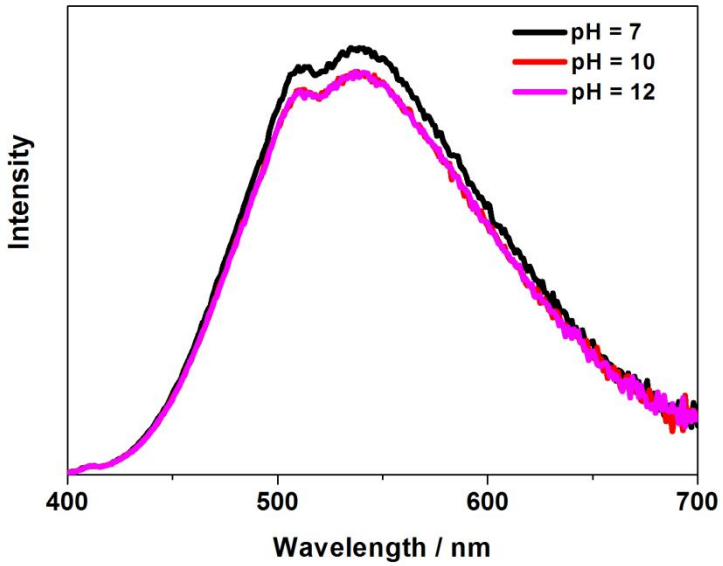

Figure S8. Emission spectra of **1** toward different pH values (pH ⩾ 7) in Britton-Robinson buffer solution.

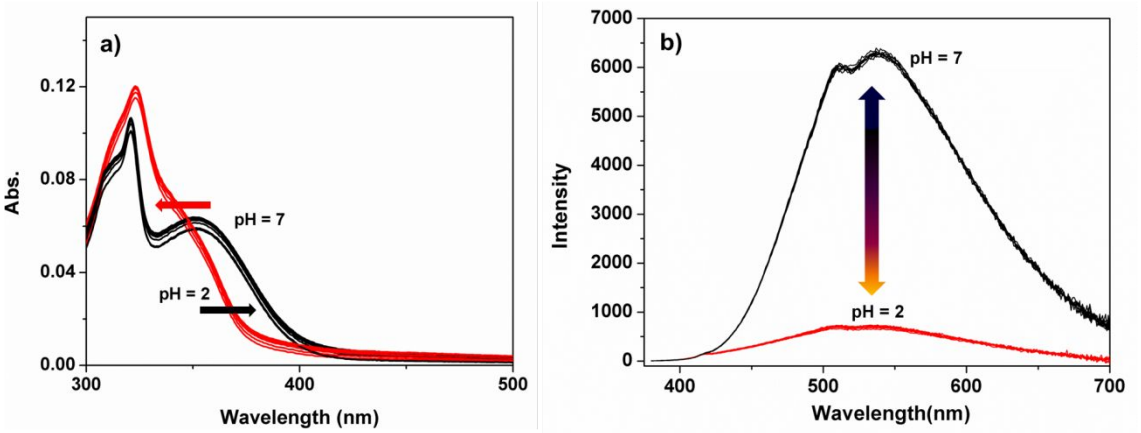

Figure S9. Absorption (a) and emission (b) spectra of **1** under 8 cycles of external pH stimulus in Britton-Robinson buffer solution.

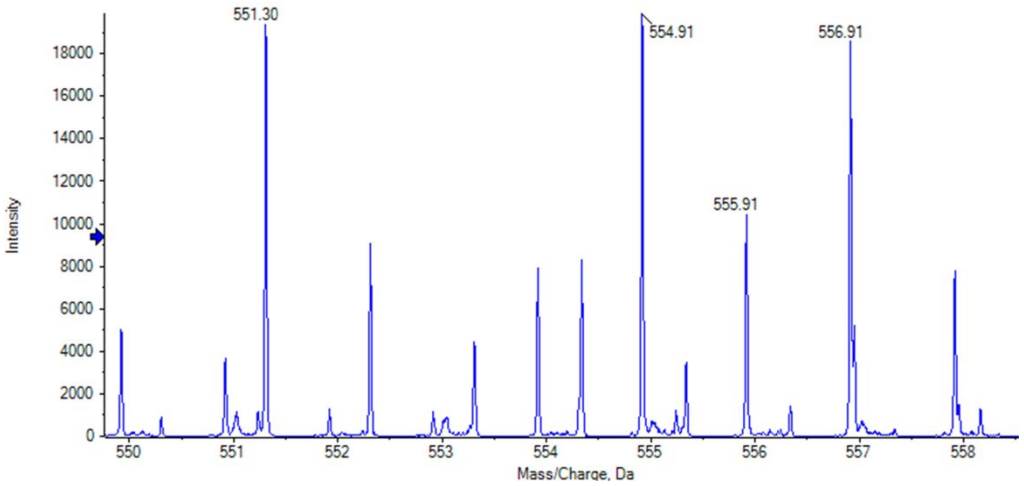

Figure S10. The ESI-MS of **1** after 8 cycles of external pH stimulus.

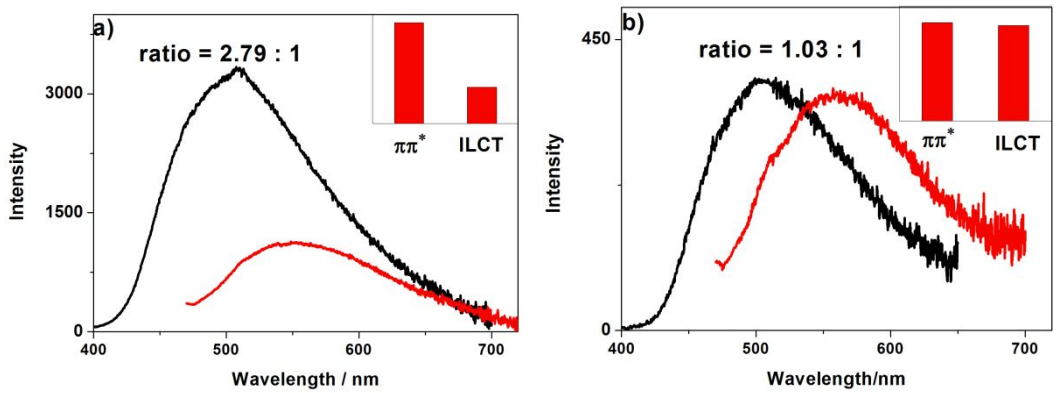

Figure S11. a) After complex **2** was separated from the B-R buffer solution (pH = 2), emission spectra of **2** that was dispersed again in another Britton-Robinson buffer solution (pH = 12). b) After complex **2** was separated from the B-R buffer solution (pH = 12), emission spectra of **2** that was dispersed again in another Britton-Robinson buffer solution (pH = 2).