Supporting Information for

Three New Zn-based Metal-Organic Frameworks Exhibiting Selective Fluorescence Sensing and Photocatalytic Activity

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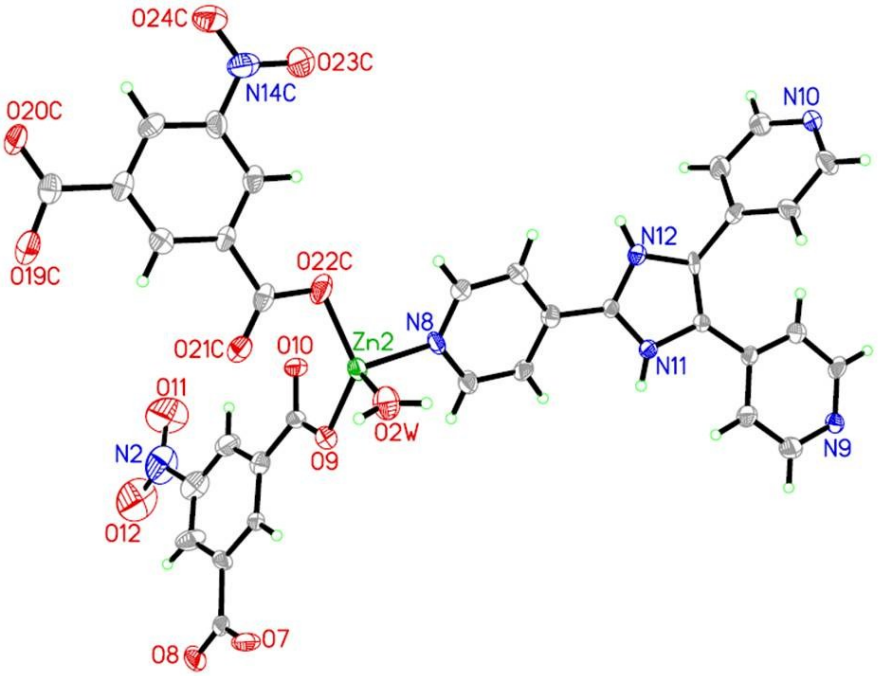
Table S1 Selected Bond Distances (Å) and Angles (°) for **1-3**[a]

		1	
Zn(1)-O(1)	1.949(6)	Zn(1)-O(7)	1.954(5)
Zn(1)-O(1W)	1.966(6)	Zn(1)-N(3)	2.048(6)
Zn(2)-O(22C)	1.935(6)	Zn(2)-O(9)	1.952(6)
Zn(2)-O(2W)	1.983(6)	Zn(2)-N(8)	2.033(6)
Zn(3)-O(13)	1.917(6)	Zn(3)-O(19)	1.956(6)
Zn(3)-O(25)	2.000(6)	Zn(3)-N(9)	2.010(6)
Zn(4)-O(3)	1.944(6)	Zn(4)-O(27)	1.959(7)
Zn(4)-N(5C)	2.022(6)	Zn(4)-O(16C)	2.031(8)
Zn(5)-O(31)	1.922(6)	Zn(5)-O(29)	1.965(7)
Zn(5)-N(4)	2.054(6)	Zn(5)-N(10D)	2.118(6)
Zn(5)-O(26E)	2.680(16)		
O(1)-Zn(1)-O(7)	134.5(3)	O(1)-Zn(1)-O(1W)	105.9(2)
O(7)-Zn(1)-O(1W)	105.3(3)	O(1)-Zn(1)-N(3)	100.7(2)
O(7)-Zn(1)-N(3)	105.6(2)	O(1W)-Zn(1)-N(3)	100.1(2)
O(22C)-Zn(2)-O(9)	131.5(2)	O(22C)-Zn(2)-O(2W)	104.8(2)
O(9)-Zn(2)-O(2W)	106.4(3)	O(22C)-Zn(2)-N(8)	100.6(2)
O(9)-Zn(2)-N(8)	108.0(2)	O(2W)-Zn(2)-N(8)	102.0(3)
O(13)-Zn(3)-O(19)	109.6(3)	O(13)-Zn(3)-O(25)	100.4(3)
O(19)-Zn(3)-O(25)	100.0(3)	O(13)-Zn(3)-N(9)	104.1(3)
O(19)-Zn(3)-N(9)	137.3(3)	O(25)-Zn(3)-N(9)	98.8(2)
O(3)-Zn(4)-O(27)	102.0(3)	O(3)-Zn(4)-N(5C)	129.6(3)
O(27)-Zn(4)-N(5C)	99.1(3)	O(3)-Zn(4)-O(16C)	100.4(3)
O(27)-Zn(4)-O(16C)	123.2(4)	N(5C)-Zn(4)-O(16C)	105.3(3)
O(31)-Zn(5)-O(29)	120.5(4)	O(31)-Zn(5)-N(4)	109.4(3)
O(29)-Zn(5)-N(4)	122.8(3)	O(31)-Zn(5)-N(10D)	99.7(3)
O(29)-Zn(5)-N(10D)	99.5(3)	N(4)-Zn(5)-N(10D)	97.6(2)
		2	
Zn(1)-O(3C)	2.0146(13)	Zn(1)-N(2)	2.0406(14)
Zn(1)-O(1)	2.0674(14)	Zn(1)-N(4D)	2.0996(14)

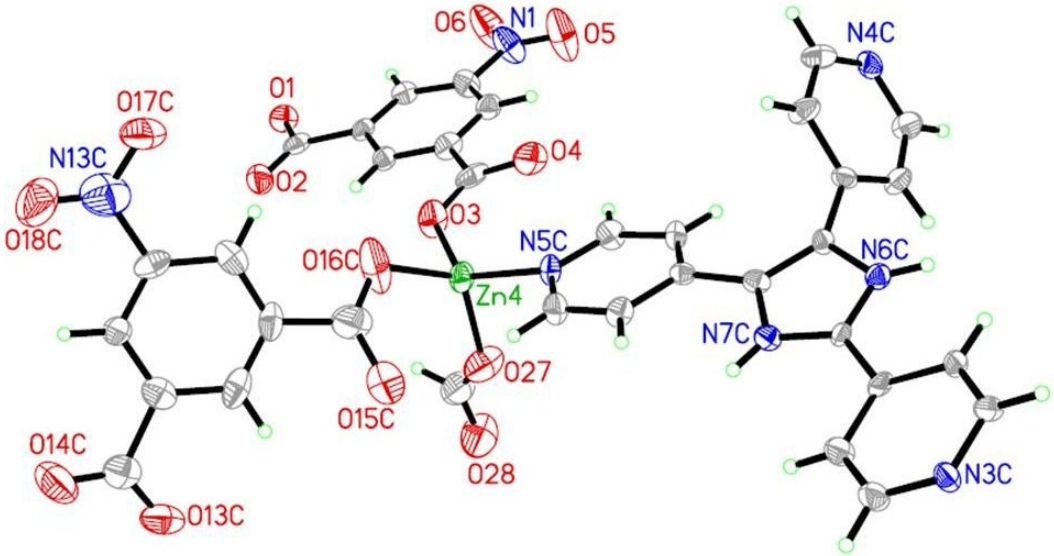
Zn(1)-O(2)	2.3323(14)		
O(3C)-Zn(1)-N(2)	142.42(6)	O(3C)-Zn(1)-O(1)	101.84(6)
N(2)-Zn(1)-O(1)	112.96(6)	O(3C)-Zn(1)-N(4D)	101.01(6)
N(2)-Zn(1)-N(4D)	91.14(5)	O(1)-Zn(1)-N(4D)	93.11(6)
O(3C)-Zn(1)-O(2)	88.63(6)	N(2)-Zn(1)-O(2)	96.88(6)
O(1)-Zn(1)-O(2)	59.36(5)	N(4D)-Zn(1)-O(2)	152.31(5)
	3		
Zn(1)-O(1)	1.9729(16)	Zn(1)-O(3D)	2.0363(17)
Zn(1)-N(1)	2.104(2)	Zn(1)-N(2E)	2.181(2)
Zn(1)-O(2C)	2.2067(19)		
O(1)-Zn(1)-O(3D)	142.63(8)	O(1)-Zn(1)-N(1)	119.89(8)
O(3D)-Zn(1)-N(1)	97.43(7)	O(1)-Zn(1)-N(2E)	87.23(7)
O(3D)-Zn(1)-N(2E)	86.30(7)	N(1)-Zn(1)-N(2E)	97.18(8)
O(1)-Zn(1)-O(2C)	92.27(7)	O(3D)-Zn(1)-O(2C)	90.25(7)
N(1)-Zn(1)-O(2C)	88.61(7)	N(2E)-Zn(1)-O(2C)	173.59(8)

[a] Symmetry codes: for **1**, C: $x-2, y, z-1$; D: $x, y+1, z$; E: $-x+2, y+1/2, -z+1$; for **2**, C: $-x+1/2, y-1/2, -z+1/2$; D: $-x+1/2, y-1/2, -z+3/2$; for **3**, D: $x, y+1, z$; E: $-x+5/2, -y+1/2, -z+2$; C: $-x+3, -y, -z+2$.

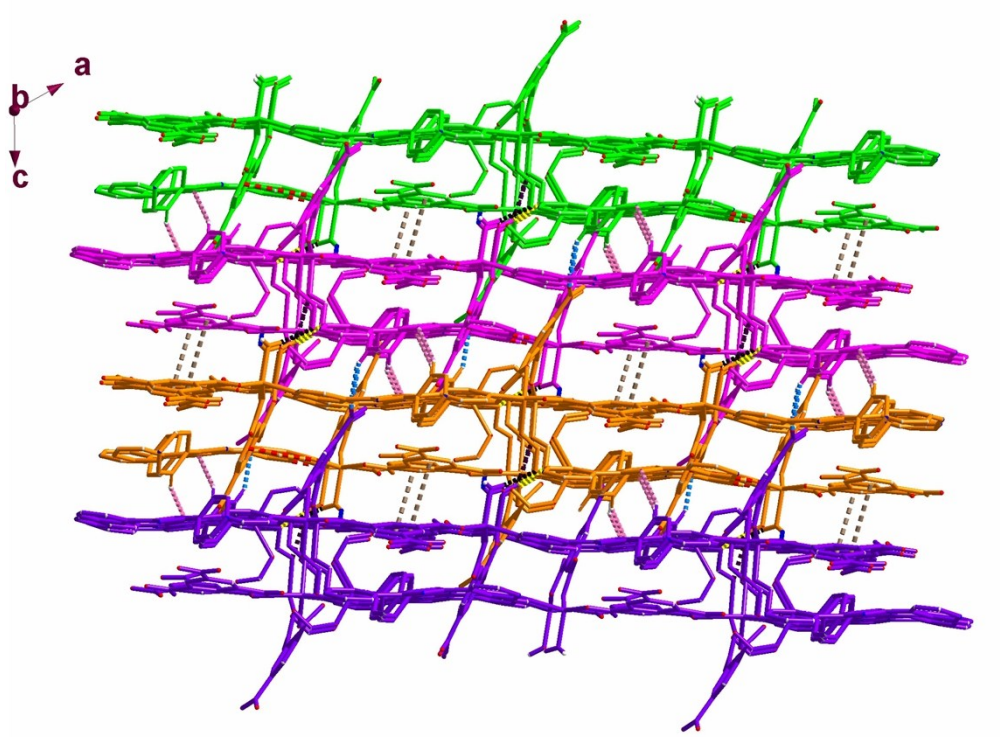
.


024C
023C
N14C
020C
019C
022C
021C
010
Zn2
N8
N12
N10
N11
N9
011
N2
012
09
02W
08
07

(a)


06
N1
05
N4C
017C
01
N13C
02
04
018C
03
N5C
016C
Zn4
N6C
N7C
027
015C
014C
028
N3C
013C

(b)



(c)

Figure S1 (a) and (b) View of the coordination environments of Zn2 and Zn4 center in **1** with labeling schemes. Symmetry codes: (C) $x - 2$, y, $z - 1$. (c) View of the 3D supramolecular structure in **1** along the *ac* plane. Partial H atoms are omitted for clarity.

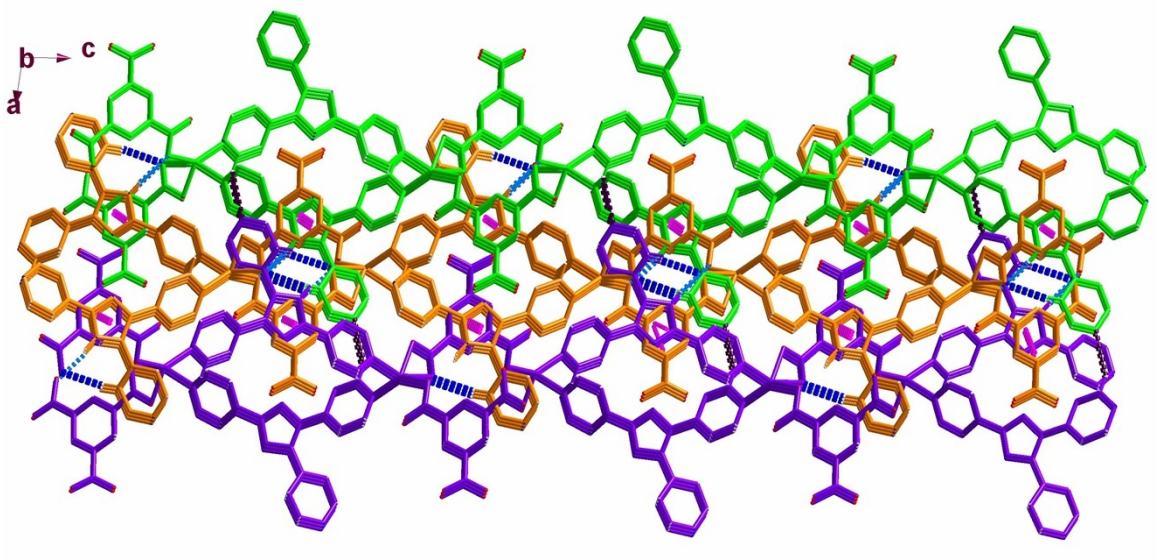


Figure S2 View of the 3D supramolecular structure in **2** along the *ac* plane. Partial H atoms are omitted for clarity.

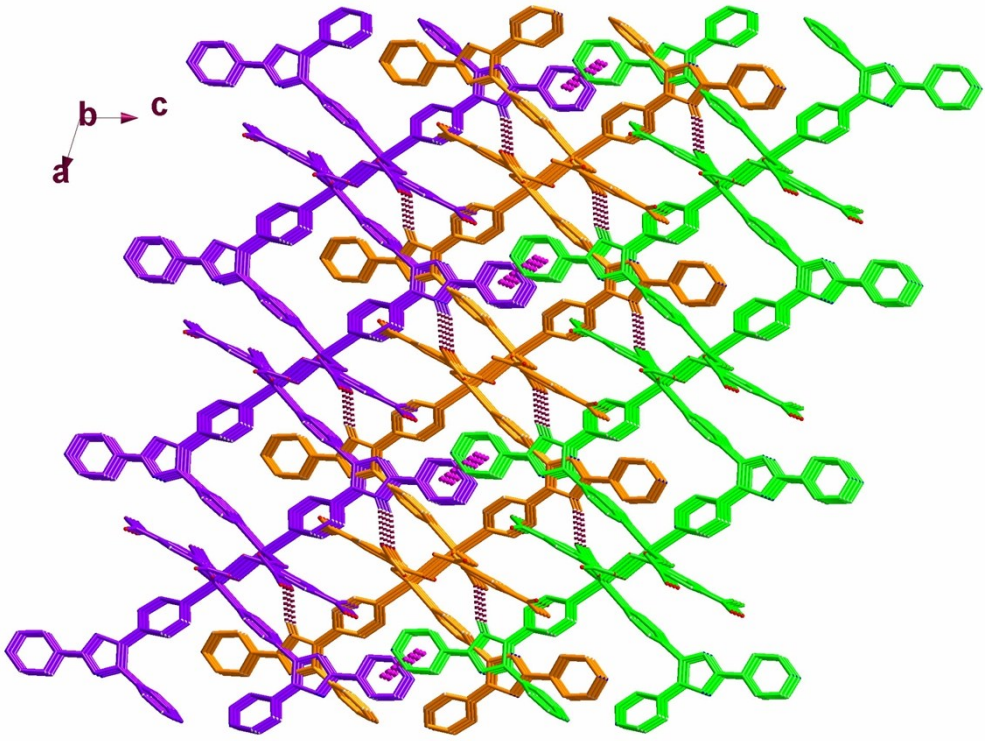
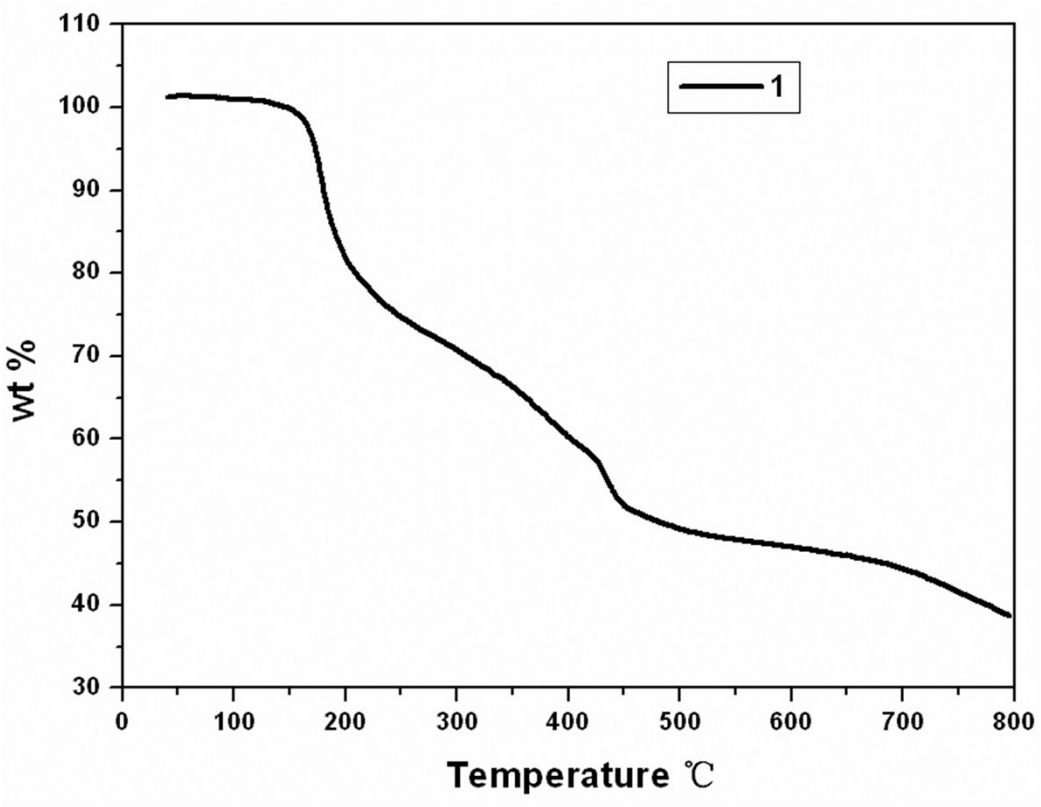
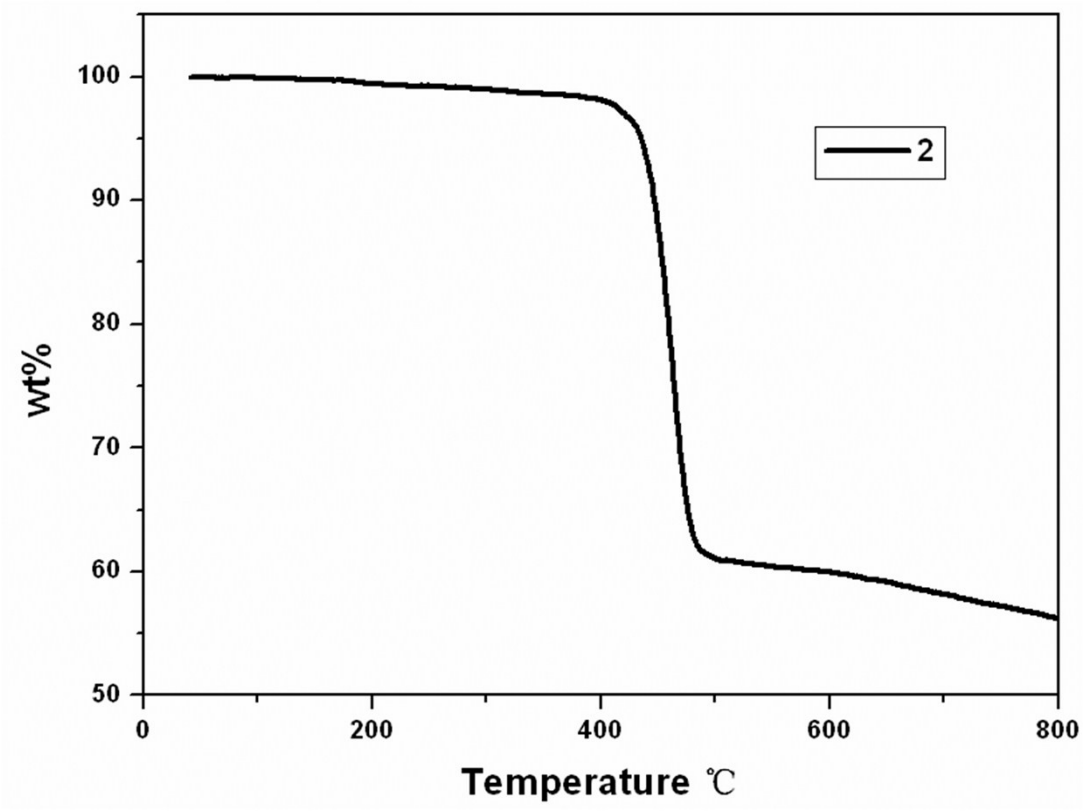


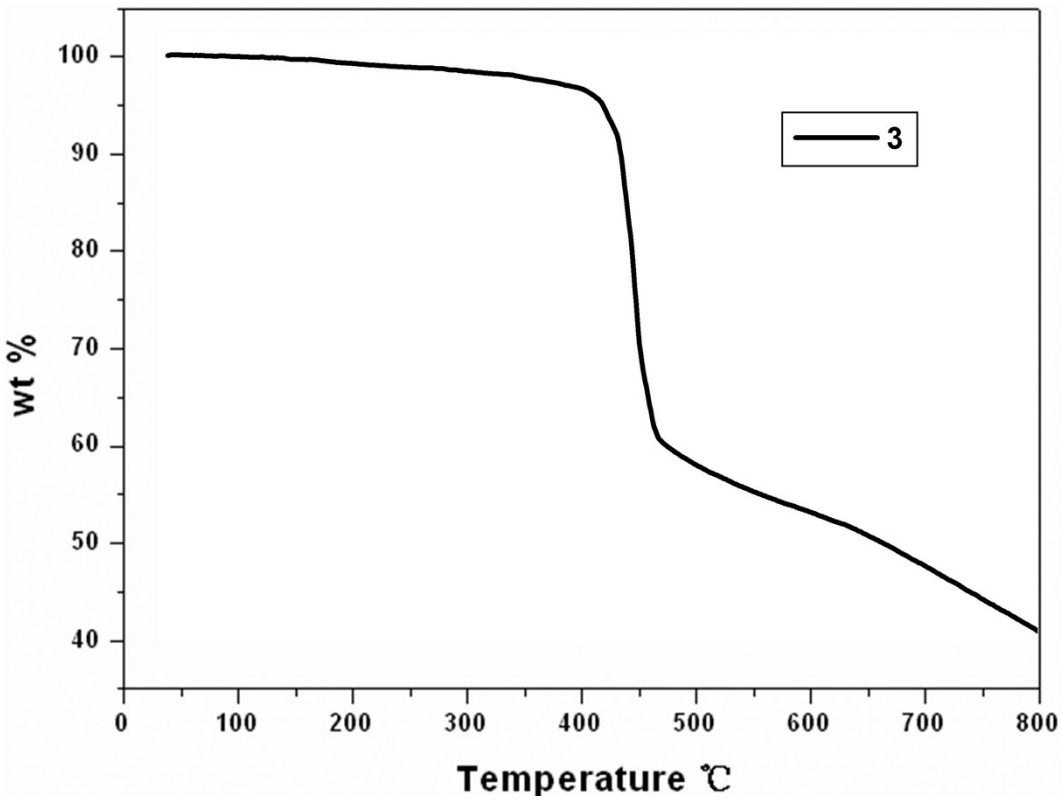
Figure S3 View of the 3D supramolecular structure in **3** along the *ac* plane. Partial H atoms are omitted for clarity.


110
100
90
80
70
60
50
40
30
wt %
0
100
200
300
400
500
600
700
800
Temperature ℃
1

(a)


100
90
80
70
60
50
wt%
0
200
400
600
800
Temperature ℃
2

(b)



(c)

Figure S4 Thermogravimetric analyses (TGA) patterns of (a) for **1**, (b) for **2**, and (c) for **3** measured from room temperature to 800 °C, respectively.

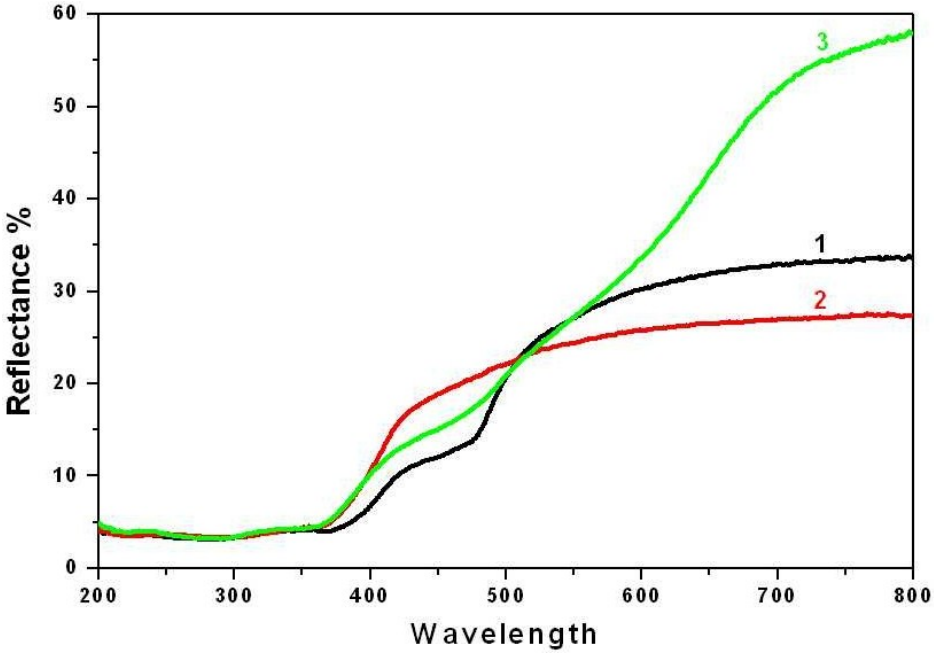
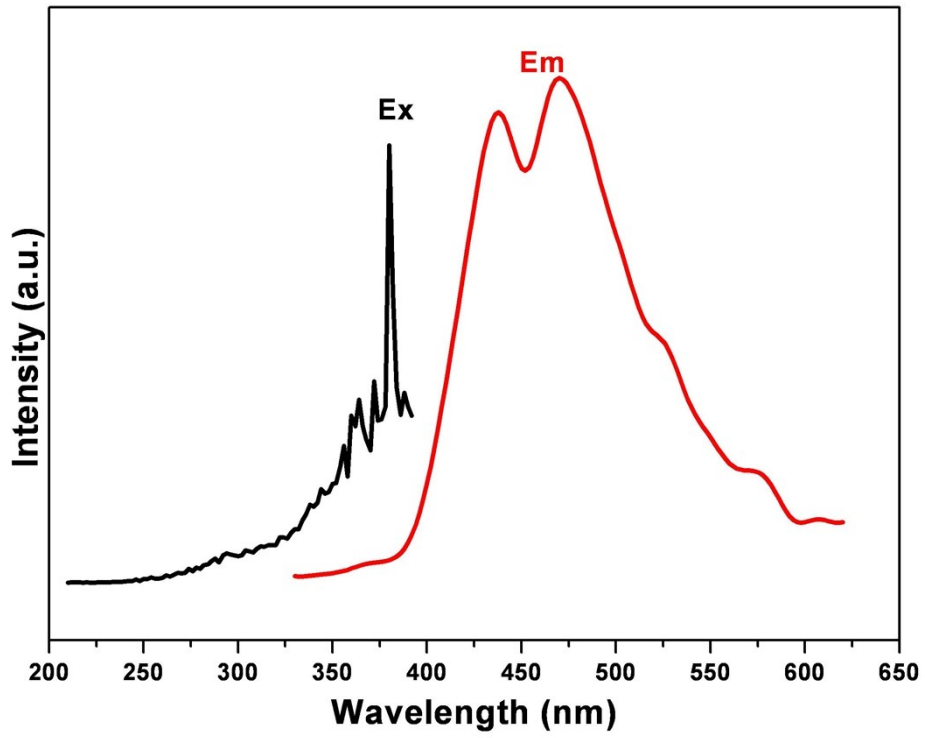
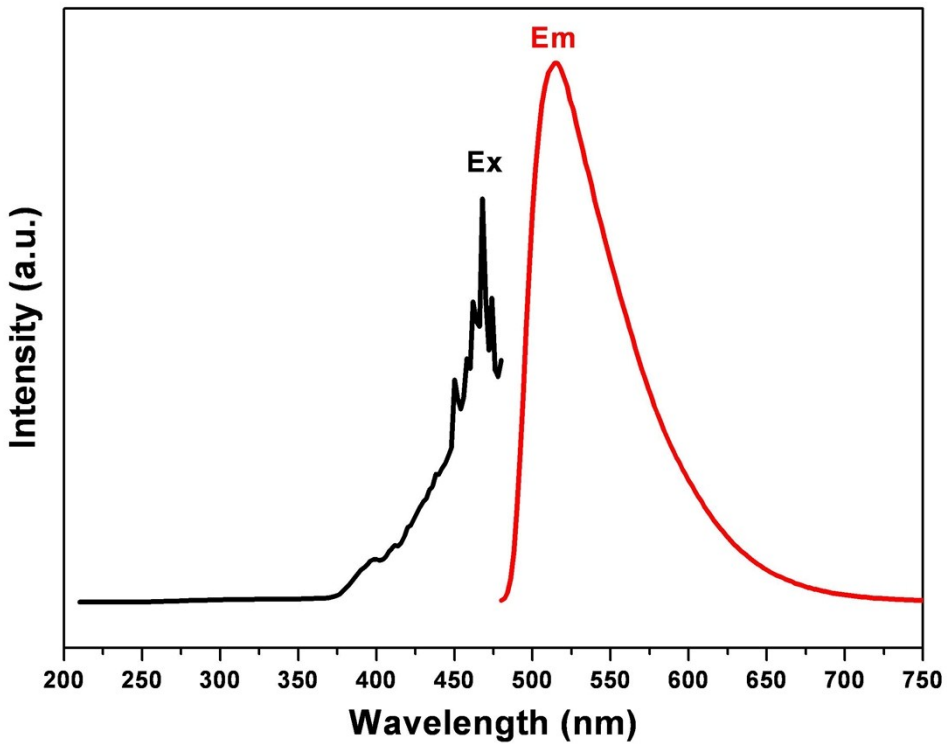


Figure S5 The diffuse-reflectance spectroscopy of solid UV-vis absorption properties of **1**–**3.**

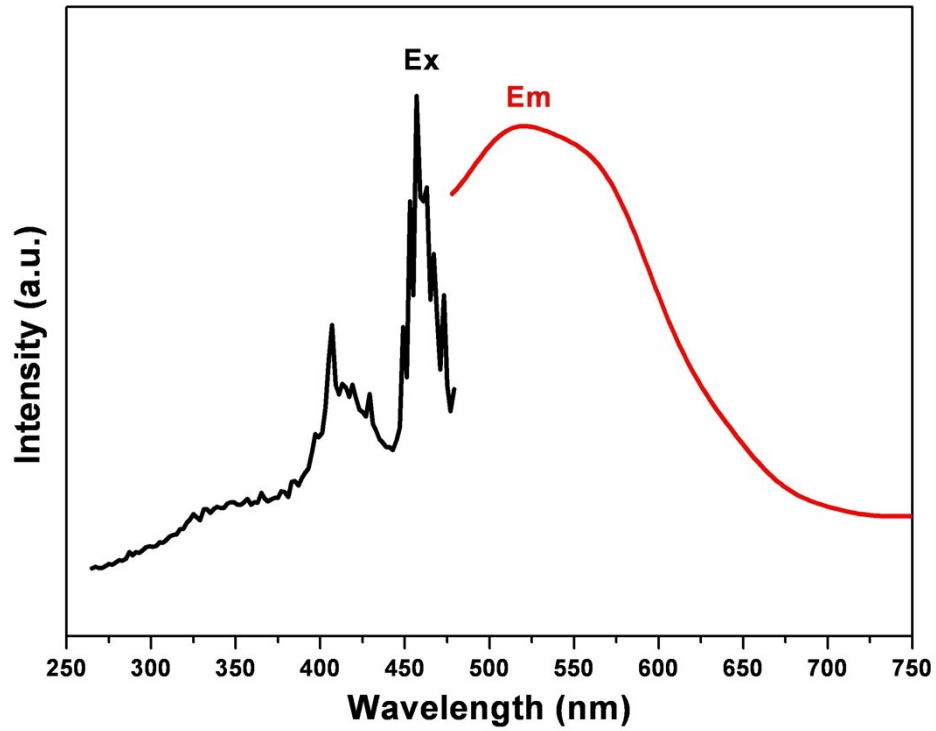


(a)

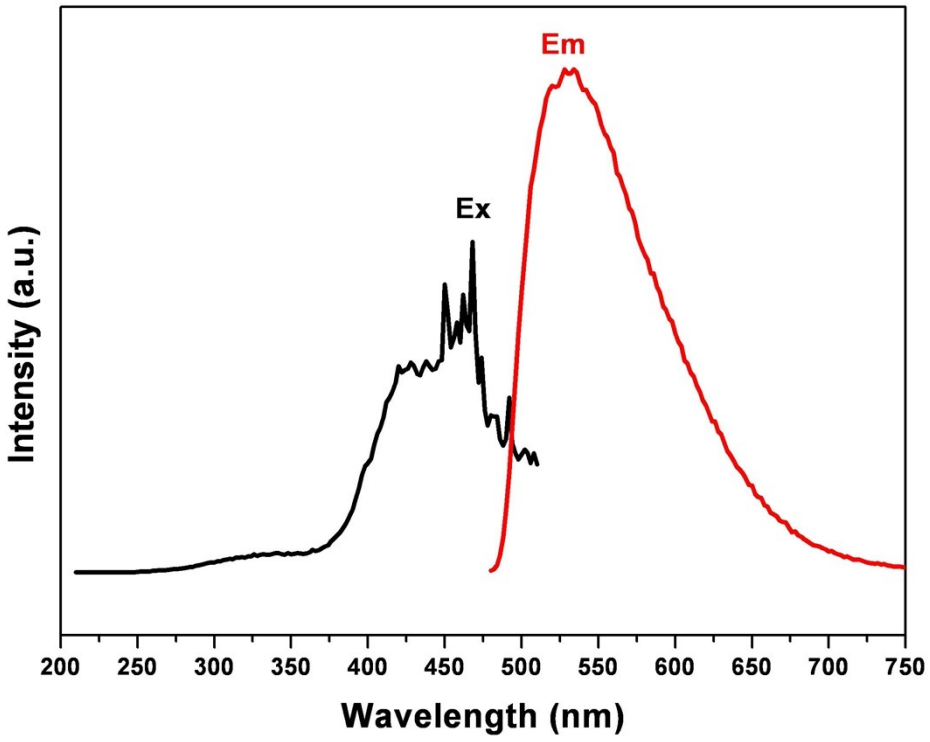


(b)

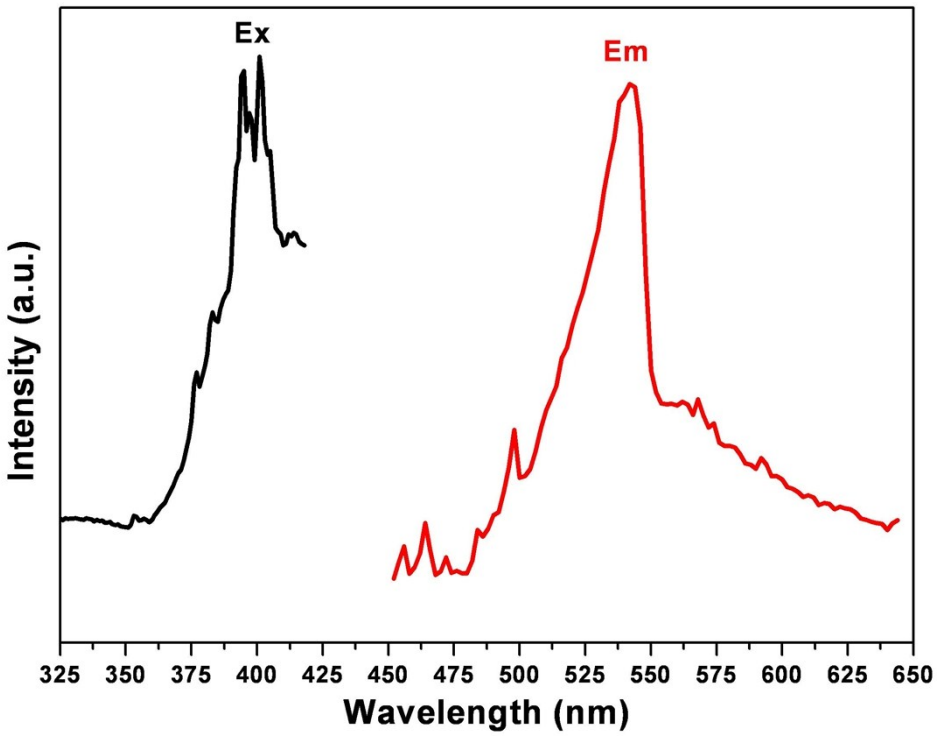
Figure S6 Excitation and emission spectra of the free ligands in the solid state at room temperature: (a) for H_2**L** and (b) Htpim.


Ex
Em
Intensity (a.u.)
250
300
350
400
450
500
550
600
650
700
750
Wavelength (nm)

(a)

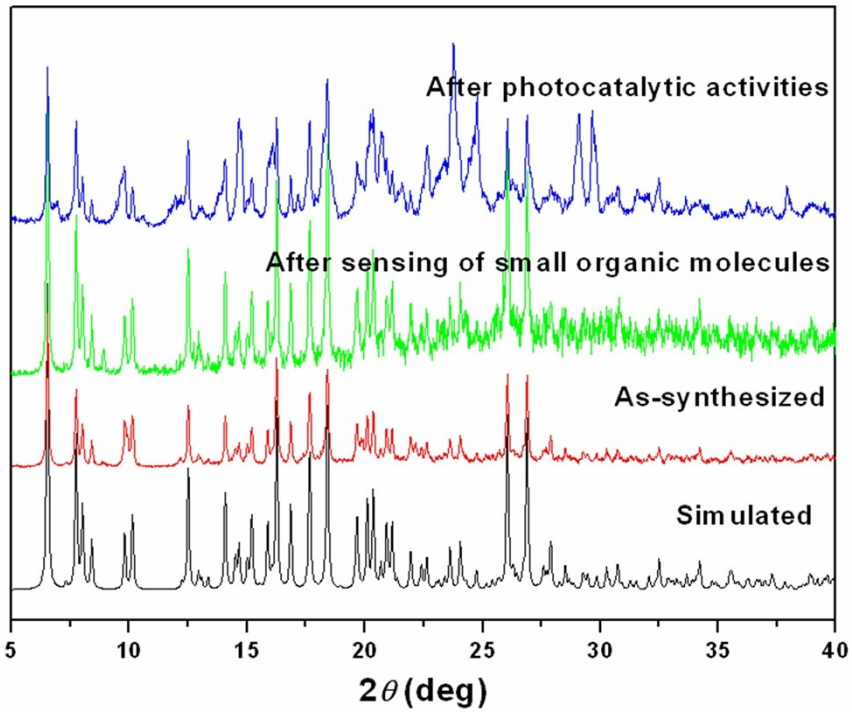

Em
Ex
Intensity (a.u.)
200
250
300
350
400
450
500
550
600
650
700
750
Wavelength (nm)

(b)

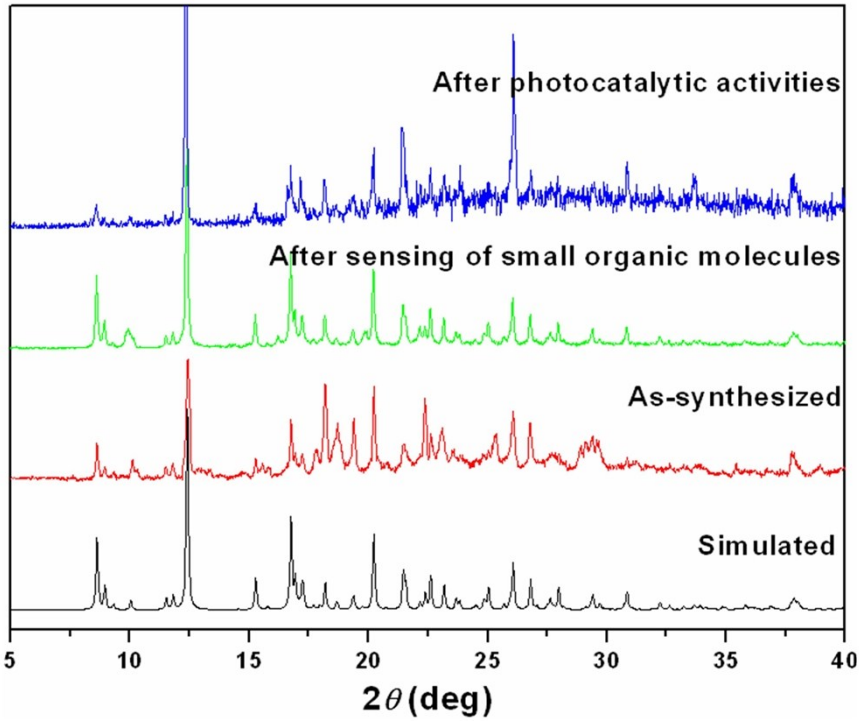


(c)

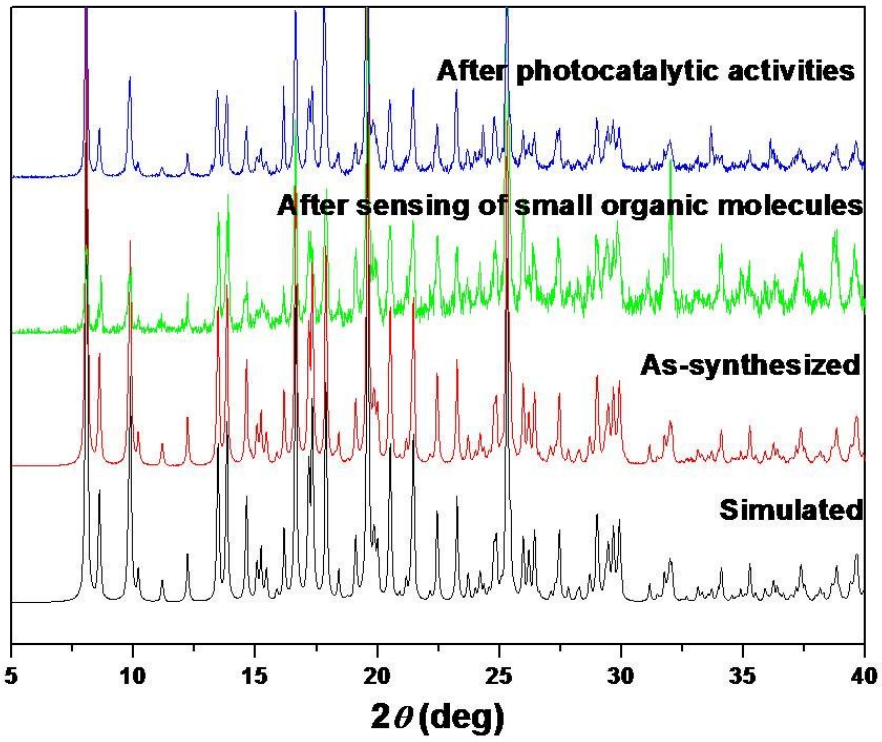
Figure S7 Excitation and emission spectra of **1–3** in the solid state at room temperature: (a) for **1**, (b) for **2**, and (c) for **3.**


After photocatalytic activities
After sensing of small organic molecules
As-synthesized
Simulated
5
10
15
20
25
30
35
40
2θ (deg)

(a)


After photocatalytic activities
After sensing of small organic molecules
As-synthesized
Simulated
5
10
15
20
25
30
35
40
2θ (deg)

(b)



(c)

Figure S8 X-ray powder diffraction (XRPD) patterns of simulated, as-synthesized, after sensing of small organic molecules, and after photocatalytic activities measured in air, respectively: (a) for **1**, (b) for **2**, and (c) for **3**.

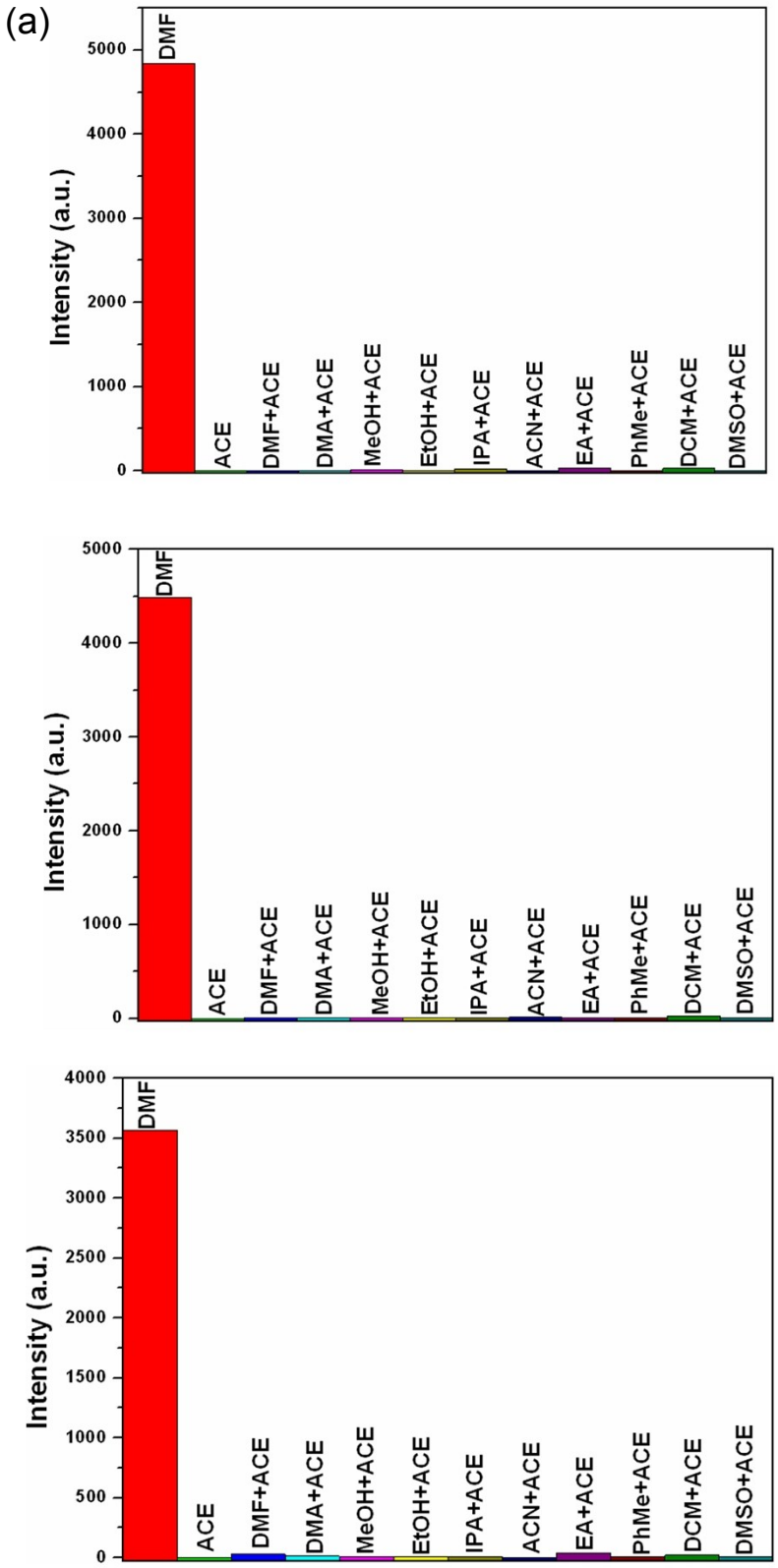


Figure S9 Emission intensities of **1** (a), **2** (b) and **3** (c) in DMF solutions of mixed organic solvents.

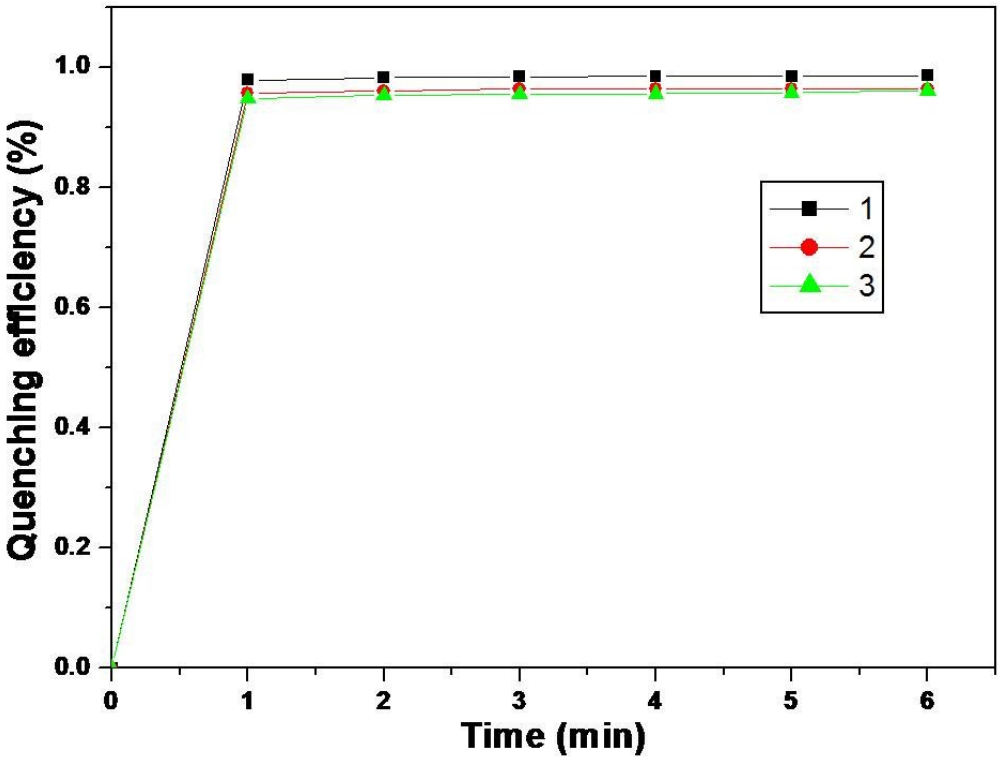
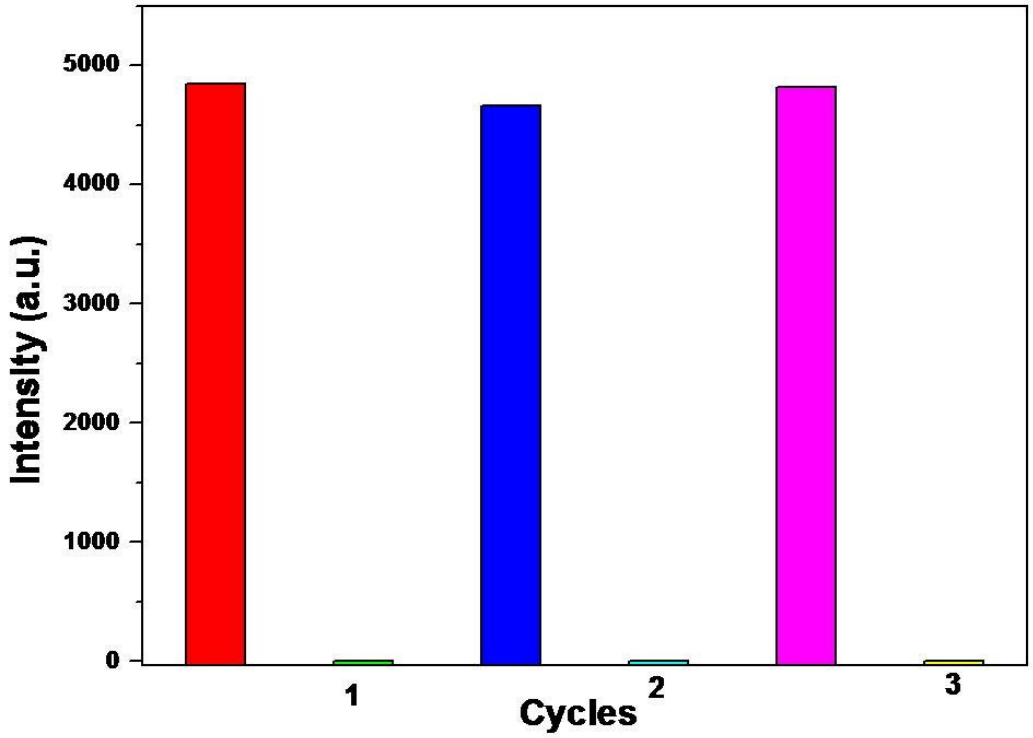
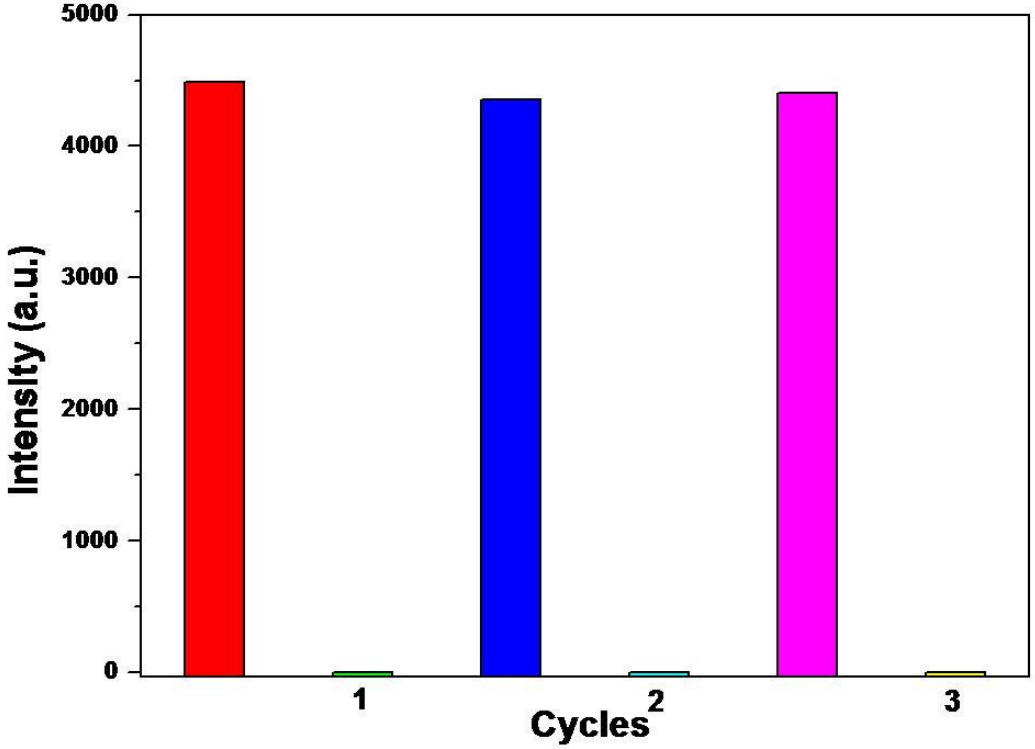


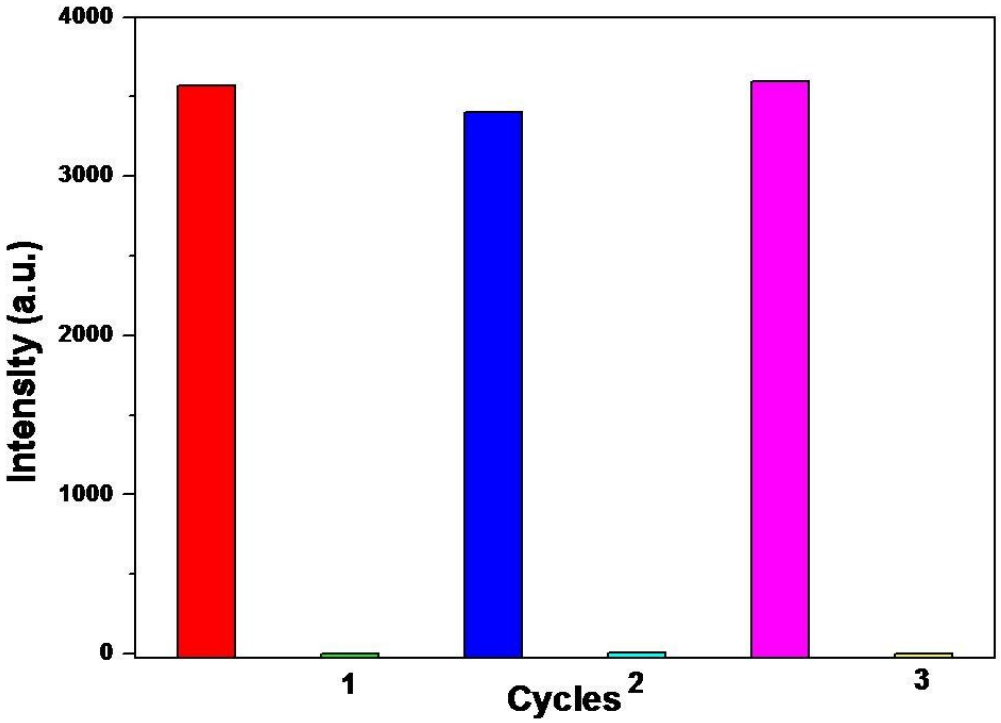
Figure S10 The time-dependent fluorescence quenching of **1–3** upon exposure to NB.


5000
4000
3000
2000
1000
0
Intenslty (a.u.)
1
2
3
Cycles

(a)

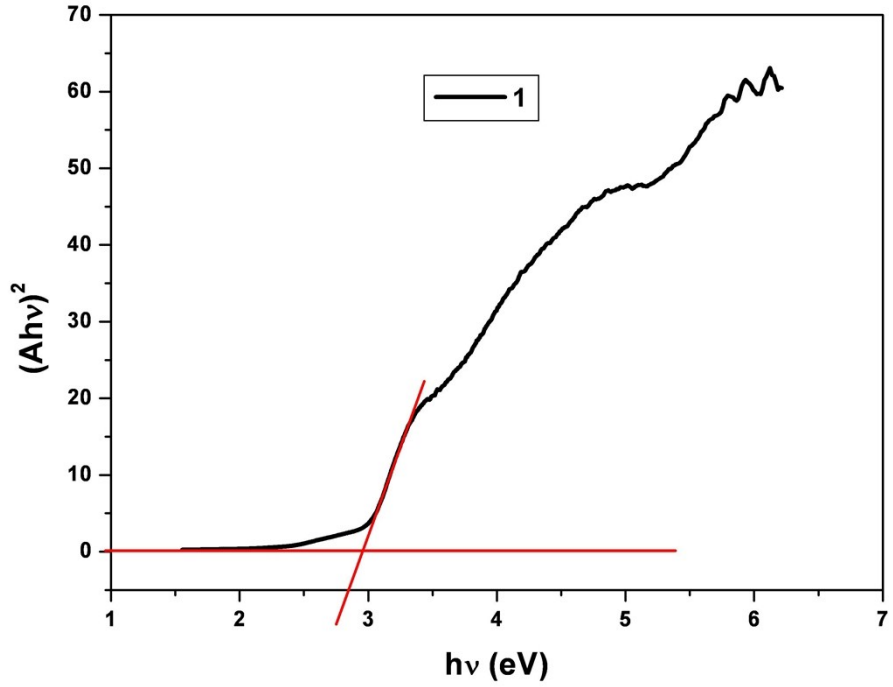

5000
4000
3000
2000
1000
0
Intenslty (a.u.)
1
2
3
Cycles

(b)

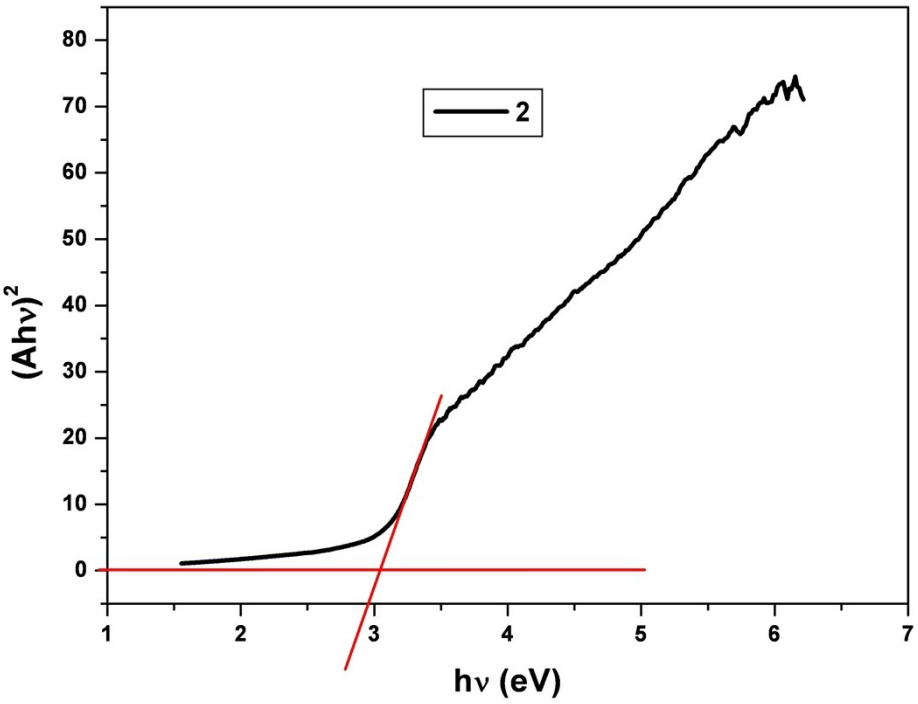


(c)

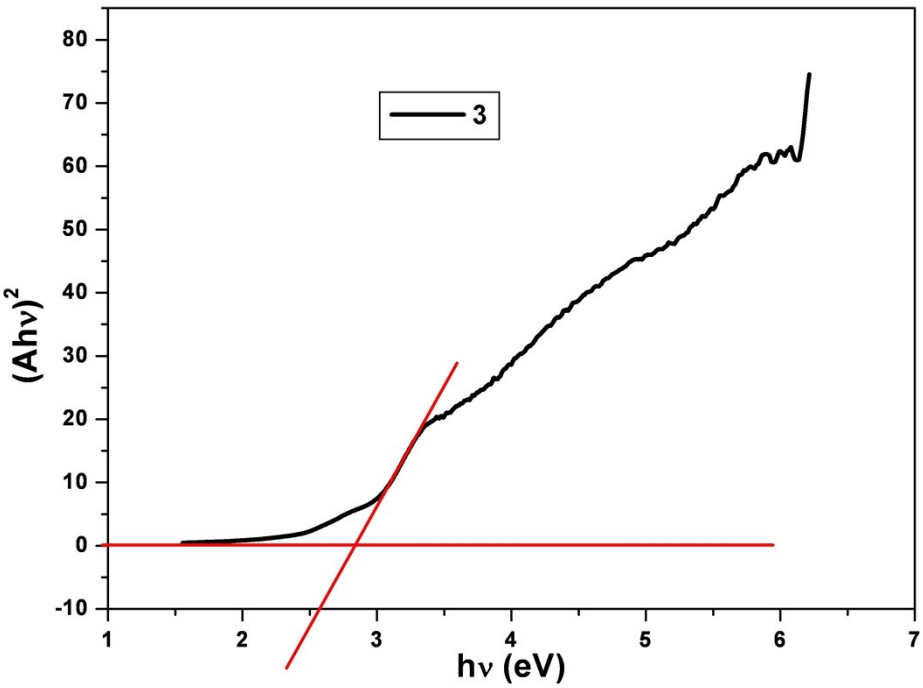
Fig. S11 Recycling test of **1** (a), **2** (b) and **3** (c) as chemical sensors in sensing of ACE with 3 times.


1
(Ahν)²
hν (eV)
0
10
20
30
40
50
60
70
1
2
3
4
5
6
7

(a)


2
(Ahν)²
hν (eV)
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7

(b)



(c)

Figure S12 The $(Ahν)^2$ vs hν curve of **1** (a), **2** (b) and **3** (c).