Supporting information

Heterometallic organic framework: A highly selective functional probe for carmine and TNP molecules

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X-Ray crystallography of **1**

Crystallographic data for **1** were collected on a Bruker Smart 1000 diffractometer equipped with graphite-monochromatic Cu-Kα radiation (λ = 0.71073 Å) using the ω-scan technique at the room temperature. Semiempirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods using SHELXS-2018 and was refined by full matrix least squares on $|F|^2$ using the SHELXTL-2018 program. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were geometrically generated, the hydrogen atoms of water molecules were located from difference Fourier maps and refined with the common isotropic thermal parameter. Details of the crystal parameter data collection and refinement for **1** are summarized in Table S1 in Supplementary. The selected bond lengths and angles of **1** are listed Table S2 in Supplementary. The supplementary crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Centre (CCDC), and the deposition number of CCDC is 2158949.

Table S1. The crystallographic data for compound **1**

Complex	**1**
Formula	$C_{25}H_{23}TbN_4O_{15}Zn$
Formula weight	843.76
T/K	300.69(10)
Crystal system	monoclinic
Space group	*C*2/*c*
a(Å)	24.6321(2)
b(Å)	12.56880(10)
c(Å)	18.42700(10)
α(°)	90
β(°)	104.2320(10)
γ(°)	90
V(Å^3)	5529.83(7)
Z	8
D_{calc}(g cm$^{-3)}$	2.027
μ (mm^{-1})	14.251
F(000)	3328.0
Rint	0.0179
GOOF	1.040
R_1[a] [I > 2σ(I)]	0.0222
ωR_2[b] [I > 2σ(I)]	0.0592
R_1 (all data)	0.0238
wR_2 (all data)	0.0603
largest diff. peak and hole (e Å^{-3})	0.34，-1.21

Table S2. Selected bond lengths [Å] and angles [°] for **1**

Complex **1**			
Tb(1)-O(7)	2.4535(13)	Tb(1)-O(1)	2.3156(14)
Tb(1)-O(3)	2.3511(16)	Tb(1)-O(10)	2.5060(14)
Tb(1)-O(5)	2.4178(14)	Tb(1)-O(6)	2.4953(15)
Tb(1)-O(11)	2.4661(14)	Tb(1)-O(12)	2.7389(16)
Tb(1)-O(13)	2.4364(15)	Zn(1)-O(9)	2.1127(16)
Zn(1)-O(8)	2.1142(15)	Zn(1)-N(4)	2.1211(16)
Zn(1)-N(3)	2.1896(16)	Zn(1)-N(2)	2.1126(17)
Zn(1)-N(1)	2.1663(17)		
O(7)-Tb(1)-O(10)	114.93(5)	O(7)-Tb(1)-O(6)	52.64(4)
O(7)-Tb(1)-O(11)	73.10(5)	O(7)-Tb(1)-O(12)	118.53(5)
O(1)-Tb(1)-O(7)	71.81(5)	O(1)-Tb(1)-O(3)	82.42(6)
O(1)-Tb(1)-O(10)	78.11(5)	O(1)-Tb(1)-O(5)	77.64(5)
O(1)-Tb(1)-O(6)	124.11(5)	O(1)-Tb(1)-O(11)	92.88(6)
O(1)-Tb(1)-O(12)	153.12(5)	O(1)-Tb(1)-O(13)	144.77(6)
O(3)-Tb(1)-O(7)	86.85(5)	O(3)-Tb(1)-O(10)	143.82(5)
O(3)-Tb(1)-O(5)	77.05(5)	O(3)-Tb(1)-O(6)	88.46(6)
O(3)-Tb(1)-O(11)	159.85(6)	O(3)-Tb(1)-O(12)	73.96(5)
O(3)-Tb(1)-O(13)	121.16(6)	O(10)-Tb(1)-O(12)	114.26(5)
O(5)-Tb(1)-O(7)	147.05(5)	O(5)-Tb(1)-O(10)	69.19(5)
O(5)-Tb(1)-O(6)	152.36(5)	O(5)-Tb(1)-O(11)	121.22(5)

O(5)-Tb(1)-O(12)	84.63(5)	O(5)-Tb(1)-O(13)	82.61(6)
O(6)-Tb(1)-O(10)	127.69(5)	O(6)-Tb(1)-O(12)	68.66(5)
O(11)-Tb(1)-O(10)	52.17(5)	O(11)-Tb(1)-O(6)	77.95(5)
O(11)-Tb(1)-O(12)	113.66(5)	O(13)-Tb(1)-O(7)	130.02(6)
O(13)-Tb(1)-O(10)	67.63(5)	O(13)-Tb(1)-O(6)	85.10(6)
O(13)-Tb(1)-O(11)	72.88(6)	O(13)-Tb(1)-O(12)	49.39(5)
O(9)-Zn(1)-O(8)	85.01(6)	O(9)-Zn(1)-N(4)	95.26(7)
O(9)-Zn(1)-N(3)	92.49(7)	O(9)-Zn(1)-N(2)	92.86(7)
O(9)-Zn(1)-N(1)	165.50(7)	O(8)-Zn(1)-N(4)	90.95(6)
O(8)-Zn(1)-N(3)	166.48(6)	O(8)-Zn(1)-N(1)	87.46(6)
N(4)-Zn(1)-N(3)	76.02(6)	N(4)-Zn(1)-N(1)	97.24(6)
N(2)-Zn(1)-O(8)	100.50(6)	N(2)-Zn(1)-N(4)	166.50(6)
N(2)-Zn(1)-N(3)	92.89(6)	N(2)-Zn(1)-N(1)	76.34(6)
Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2 #2 -x,-y,-z+2-x,-y,-z+2			

Table S3. The values of *Ksv*, Standard deviations (σ) and detection limits of compound **1** toward CM and TNP at room temperature.

Analyte	*Ksv* ($L \cdot M^{-1}$)	σ	Detection limit ($M \cdot L^{-1}$)
Carmine (CM)	6.67×10^{7}	174.83	7.76×10^{-6}
Trinitrophenyl phenol (TNP)	2.38×10^{7}	1071	1.35×10^{-4}

*Detection limits is calculated according to the formula: LOD=3σ/*Ksv*

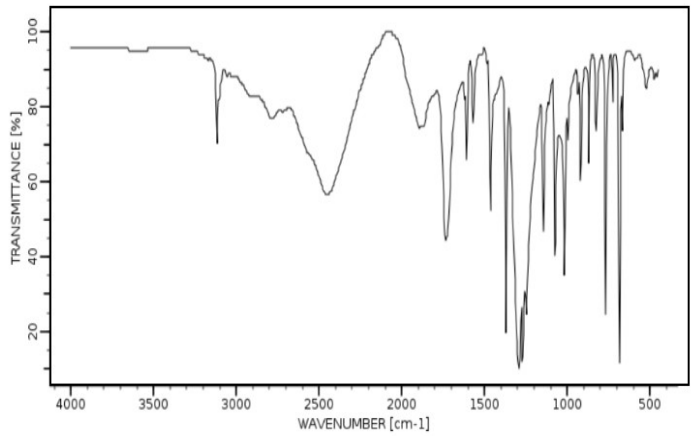

Fig S1. The IR spectrum of ligand H_2LZ.

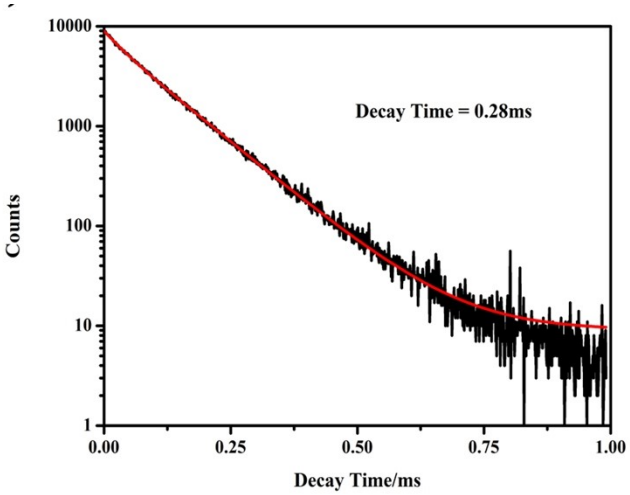

Fig S2. The fluorescence decay and fit curve for complex **1**.

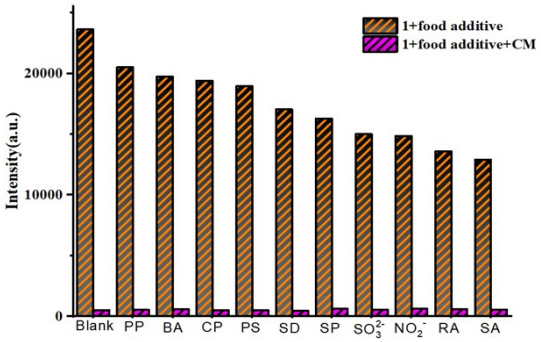

Fig S3. The responses of fluorescence of **1** towards a mixture of food additive and CM.

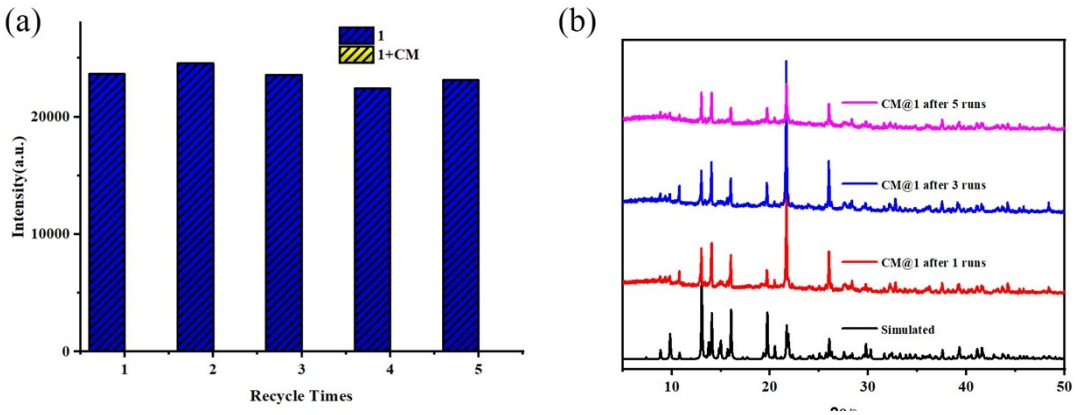

Fig S4. (a) Recyclability of complex **1** immerses in CM; (b) PXRD patterns of CM@**1** after five times.

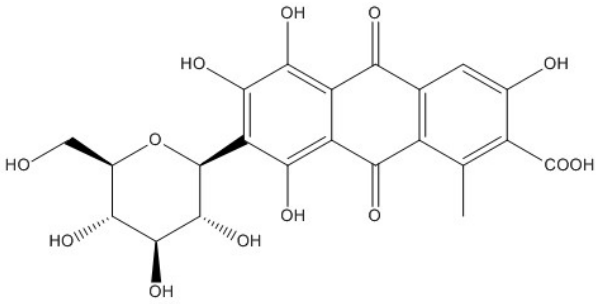

Fig S5. The structure of carmine.

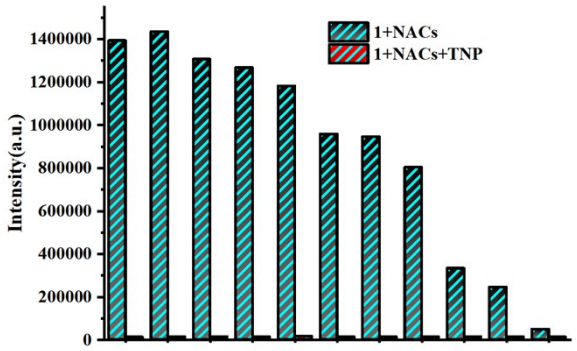

Fig S6. The responses of fluorescence system towards a mixture of NACs and TNP.

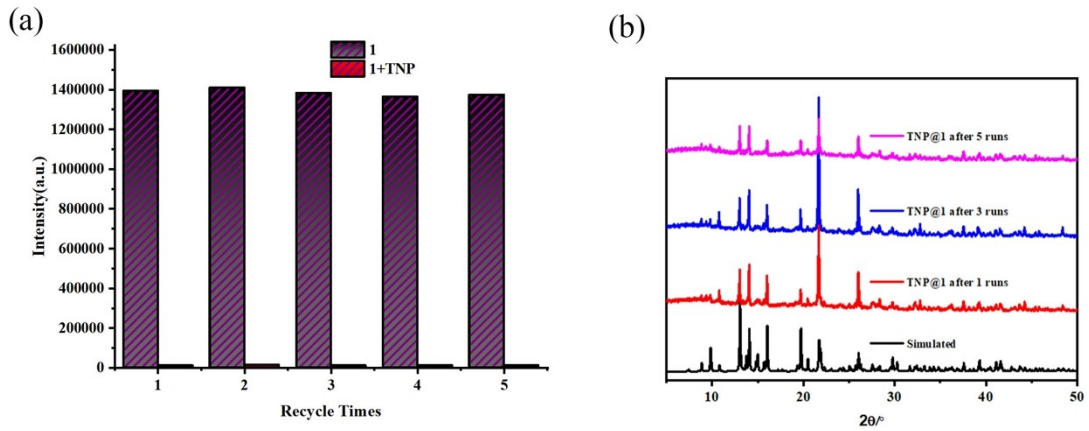

Fig S7. (a) Recyclability of complex **1** immerses in TNP; (b) PXRD patterns of complex **1** after sensing five times.