Supporting Information

Zn(II)-Based Metal-Organic Frameworks with Tailored Architectures: Optimizing Fluorescence Performance for Cell Imaging and Cancer Therapy

Jinglu Wang,[a#] Yutong Chen,[b#] Danian Tian,*[a] Siyi Li,[b] Peipei Cen,*[a] and Xiangyu Liu[b]

[a] *College of Public Health, Key Laboratory of Environmental Factors and Chronic Disease Control, Ningxia Medical University, Yinchuan 750004, China.*

[b] *State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China.*

[#]These authors contributed equally to this work.

***Corresponding author**

Dr. Peipei Cen
E-mail: 13895400691@163.com

***Corresponding author**

Dr. Danian Tian
E-mail: tiandanian@163.com

Contents

Table S1. Crystallographic data and refinement parameters for compound **1** and **2**.

	Compound **1**	Compound **2**
Empirical formula	$C_{22}H_{18}N_4O_6Zn$	$C_{22}H_{18}N_4O_6Zn$
Formula weight	499.77	499.79
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	*C*2/c
a(Å)	8.2605(6)	25.9395 (4)
b(Å)	10.6797(8)	10.8613(2)
c(Å)	13.5264(10)	18.3000(3)
α(°)	106.147(2)	90
β(°)	93.965(2)	121.9110(10)
γ(°)	102.238(2)	90
V(Å^3)	1109.69(14)	4376.59(13)
μ (mm^{-1})	1.153	1.169
Unique reflections	3894	4482
Observed reflections	25905	22463
R_{int}	0.0513	0.0361
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0546$ $wR_2 = 0.1368$	$R_1 = 0.0350$ $wR_2 = 0.0867$
R indices (all data)	$R_1 = 0.0738$ $wR_2 = 0.1483$	$R_1 = 0.0448$ $wR_2 = 0.0927$

Table S2. Selected bond lengths (Å) and bond angles (°) for compound **1**.

Compound **1**			
Zn(1)-O(4)	1.935(3)	O(2)-Zn(1)-N(4[1])	118.20(16)
Zn(1)-O(2)	1.979(3)	N(4[1])-Zn(1)-N(1)	111.36(16)
Zn(1)-N(4[1])	1.995(4)	C(1)-O(4)-Zn(1)	117.6(3)
Zn(1)-N(1)	2.004(4)	C(5)-O(2)-Zn(1)	116.7(3)
O(4)-Zn(1)-O(2)	96.49(14)	C(21)-N(4)-Zn(1[1)]	124.4(3)
O(4)-Zn(1)-N(4[1])	119.39(16)	C(22)-N(4)-Zn(1[1])	127.7(3)
O(4)-Zn(1)-N(1)	110.52(16)	C(11)-N(1)-Zn(1)	124.6(3)
O(2)-Zn(1)-N(4[1])	100.15(15)	C(9)-N(1)-Zn(1)	129.7(4)

[1]1-X, 1-Y, 2-Z; [2]2-X, 2-Y, 1-Z; [3]2-X, 1-Y, 2-Z

Table S3. Selected bond lengths (Å) and bond angles (°) for compound **2**.

Compound **2**			
Zn(1)-O(2)	1.9531(17)	O(4)-Zn(1)-N(1)	103.66(9)
Zn(1)-O(4)	1.9494(17)	N(1)-Zn(1)-N(4[1])	108.66(9)
Zn(1)-N(4[1])	2.005(2)	C(5)-O(2)-Zn(1)	114.84(16)
Zn(1)-N(1)	1.985(2)	C(1)-O(4)-Zn(1)	117.99(17)
O(2)-Zn(1)-N(4[1])	102.31(8)	C(20)-N(4)-Zn(1[2])	118.60(19)
O(2)-Zn(1)-N(1)	118.22(8)	C(21)-N(4)-Zn(1[2])	132.8(2)
O(4)-Zn(1)-O(2)	113.50(8)	C(10)-N(1)-Zn(1)	127.18(18)
O(4)-Zn(1)-N(4[1])	110.47(8)	C(9)-N(1)-Zn(1)	126.5(2)

[1]-1/2+X, -1/2+Y, +Z; [2]1/2+X, 1/2+Y, +Z; [3]1-X, -Y, 1-Z; [4]1/2-X, -1/2-Y, -Z

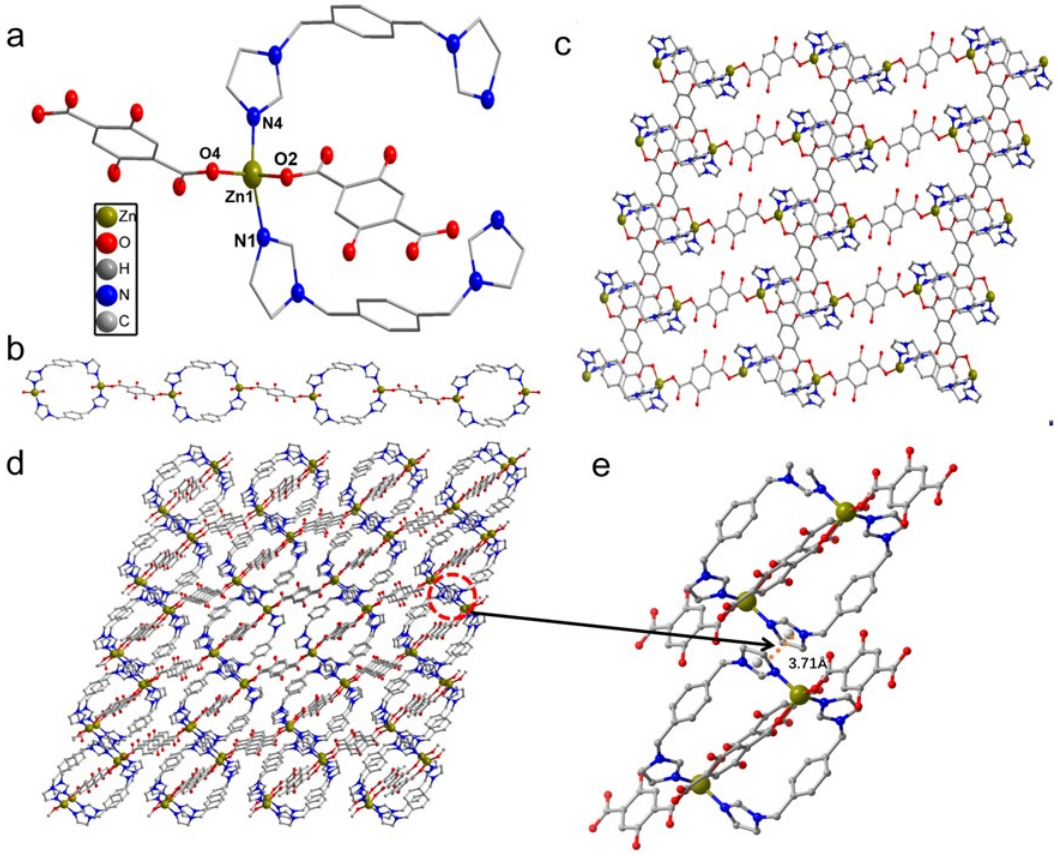

Figure S1 (a) Coordination environment and geometric configuration of Zn(II) in **1**; (b) The 1D chains of **1**; (c) The 2D layer of **1**; (d) The supramolecular 3D structure of **1**; (e) The π-π Packing diagram of **1** (the dashed line represents the interaction). All hydrogen atoms for **1** are omitted for clarity.

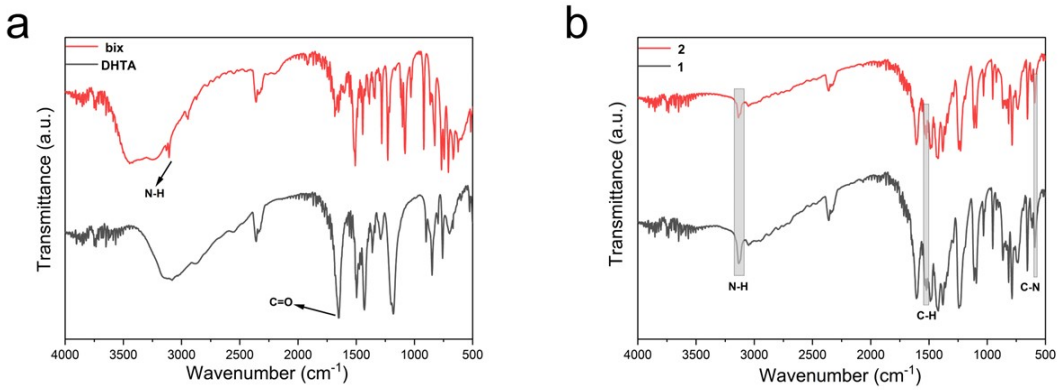

Figure S2 (a) FTIR for DHTA and bix organic ligands; (b) FTIR for **1** and **2** compounds.

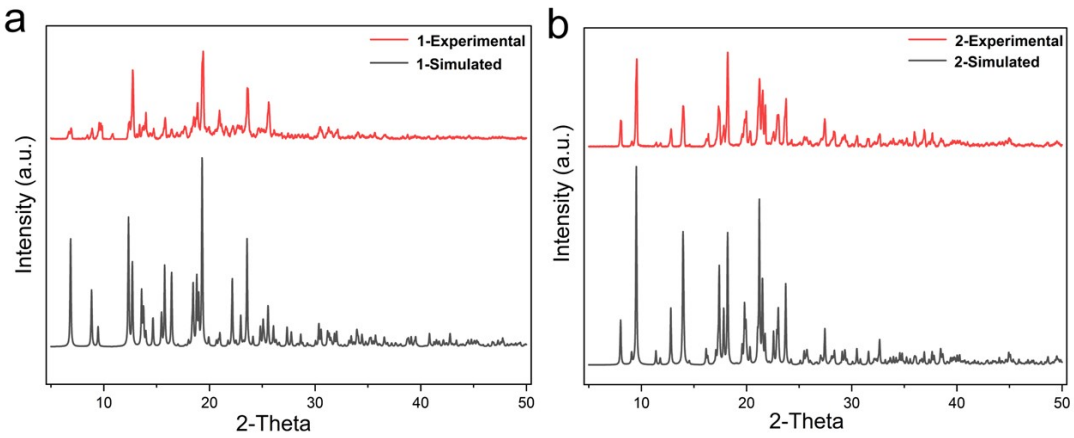

Figure S3 PXRD curves of **1** (a) and **2** (b).

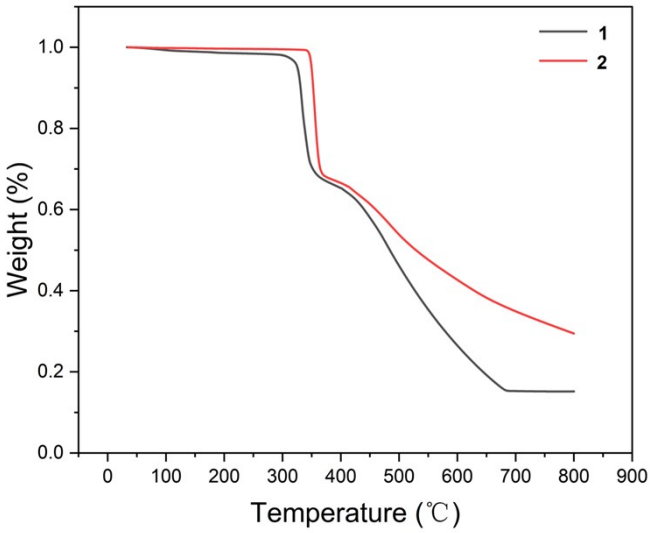

Figure S4 TGA curves of **1** and **2**.

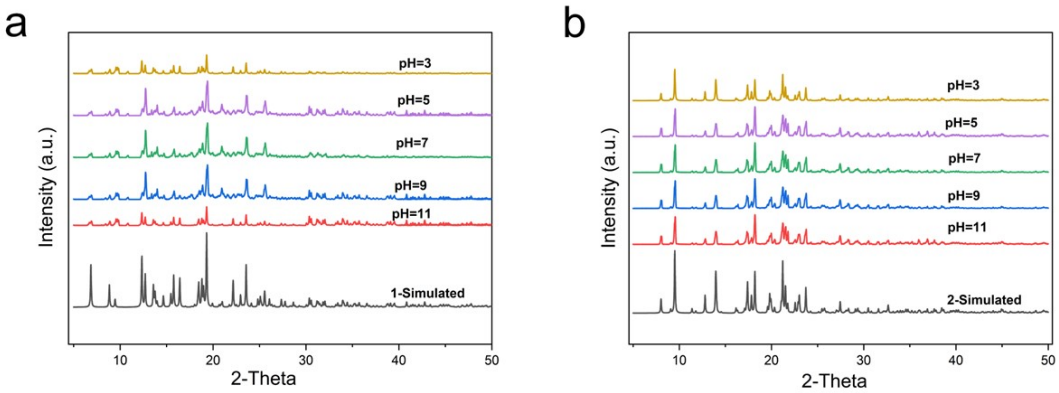

Figure S5 The pH stability of **1** (a) and **2** (b).

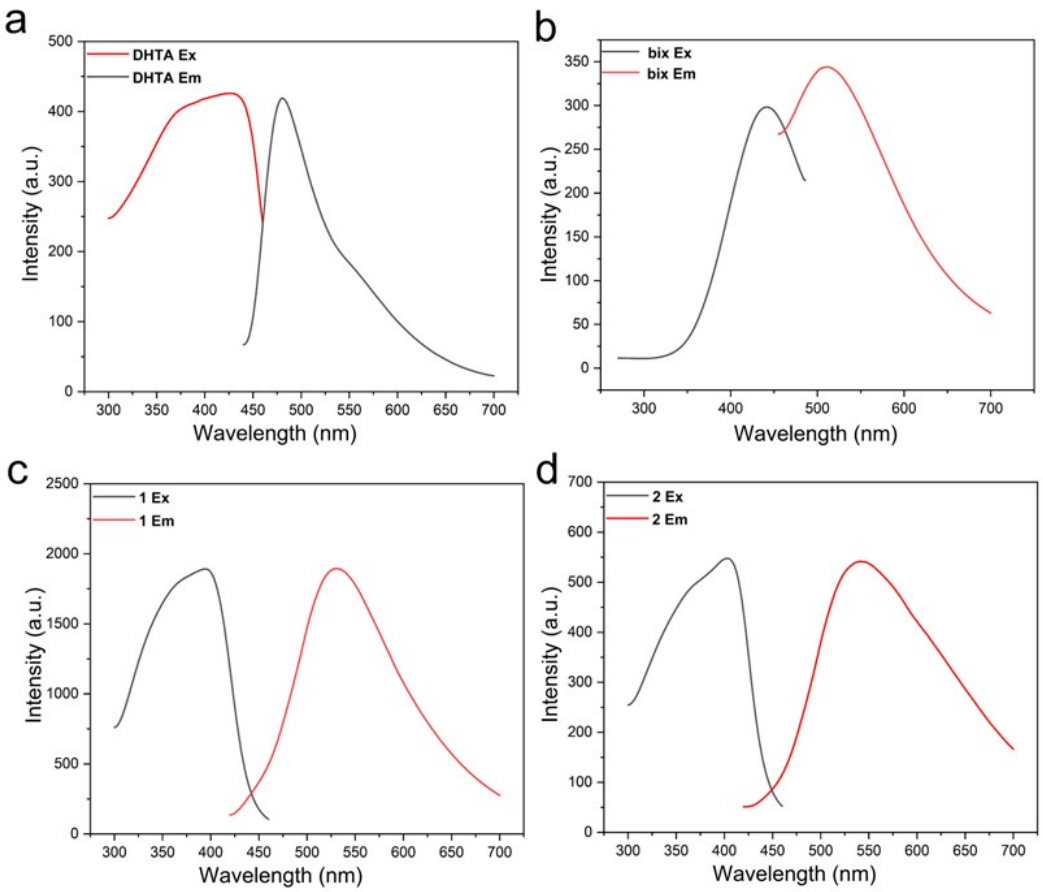

Figure S6 Solid-state Fluorescence excitation and emission spectra of ligands DHTA (a), bix (b), **1** (c) and **2** (d). (Temperature = 23 °C, E_{xDHTA} = 425 nm, E_{xbix} = 440 nm, E_{x1} = 394 nm, E_{x2} = 402 nm.)

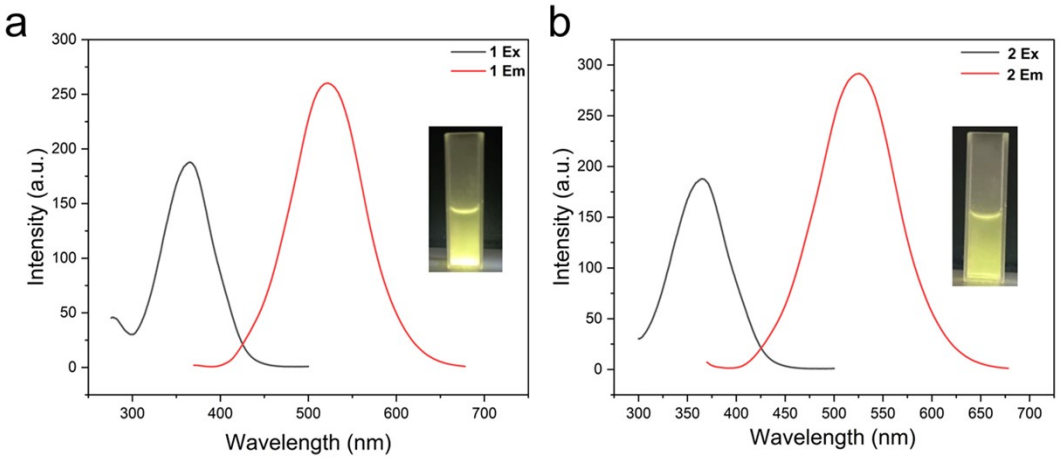

Figure S7 Liquid fluorescence pattern of **1** (a) and **2** (b). (The solvent is ultrapure water, pH = 7.0, temperature = 23 °C, E_{x1} = 365 nm, E_{x2} = 370 nm)

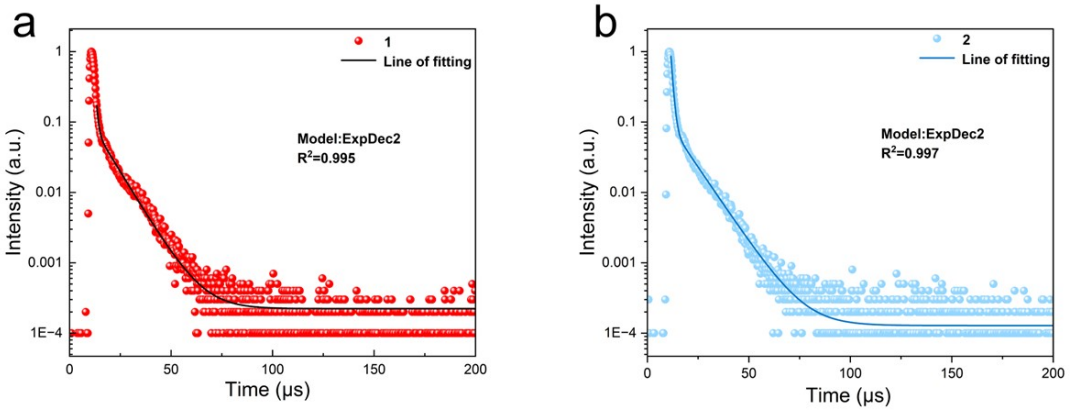

Figure S8 The luminescence decay curves of **1** (a) and **2** (b).

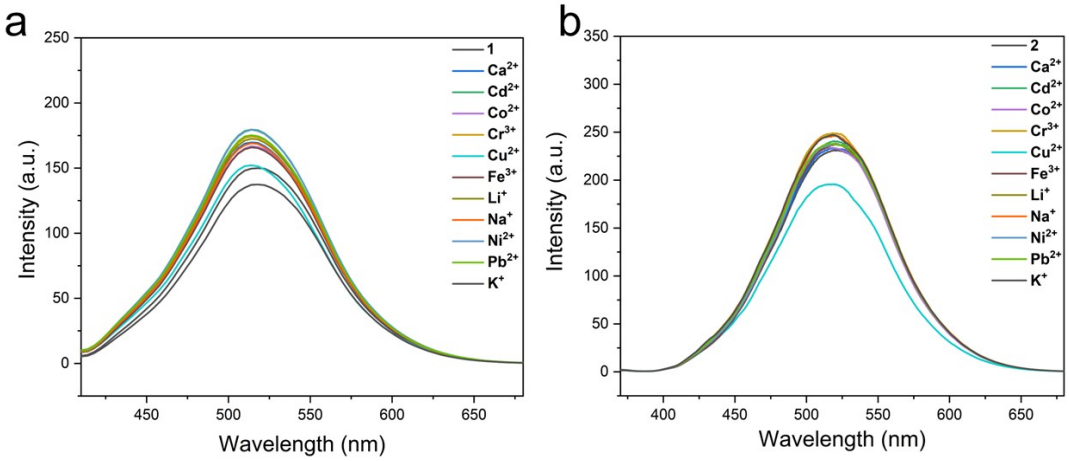

Figure S9 Fluorescence intensity of **1** (a) and **2** (b) upon addition of different metal cations (20 μL) in aqueous solutions. (The solvent is ultrapure water, pH = 7.0, temperature = 23 °C, E_{x1} = 365 nm, E_{x2} = 370 nm)

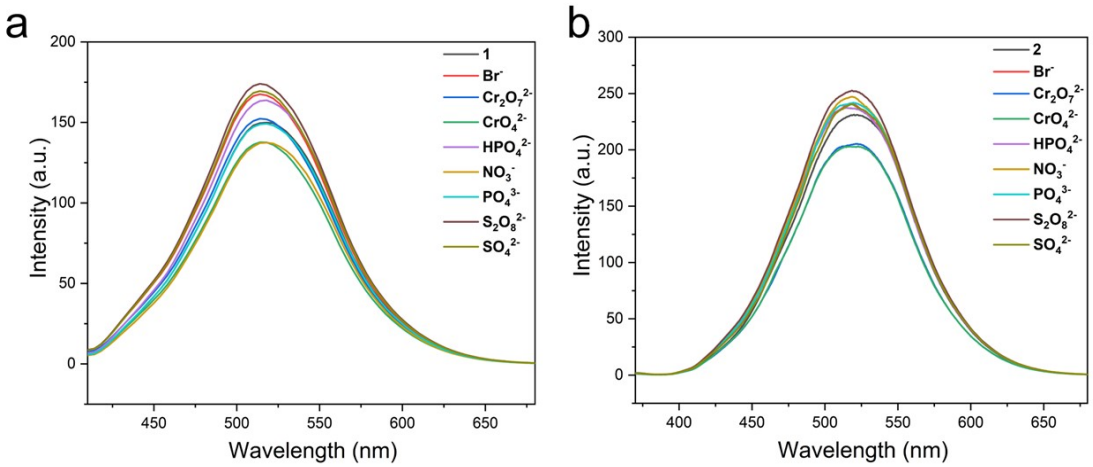

Figure S10 Fluorescence intensity of **1** (a) and **2** (b) with the addition of different anions (20 μL) in aqueous solutions. (The solvent is ultrapure water, pH = 7.0, temperature = 23°C, E_{x1} = 365 nm, E_{x2} = 370 nm)

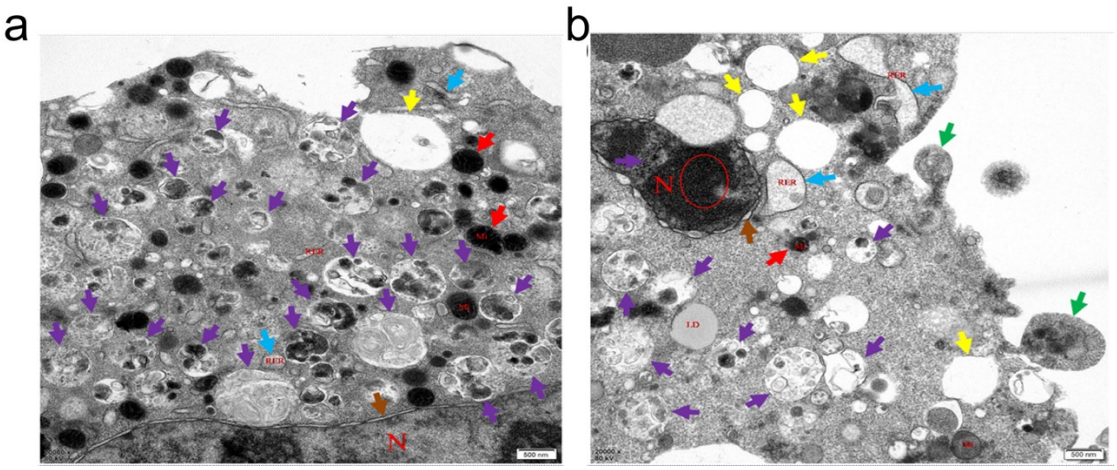

Figure S11 (a) and (b) belong to the transmission electron microscopy image of compound **1** in HeLa cells. Nucleus (N), mitochondria (Mi), rough endoplasmic reticulum (RER), lipid droplets (LD); nuclear shrinkage and widening of perinuclear space (↑), chromatin agglutination (□), mitochondrial shrinkage (↑), rough endoplasmic reticulum expansion (↑), apoptotic bodies (↑), vacuoles (↑), autophagy (↑).

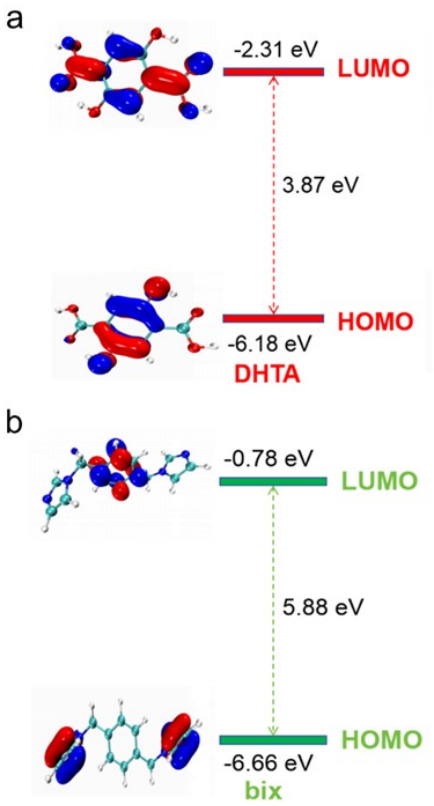

Figure S12 Energy level diagram of DHTA (a) and bix (b).