Supplementary materials

Novel tetranuclear grid-like Zn(II) complexes derived from dihydrazone pyrimidine derivatives as antitumor agents

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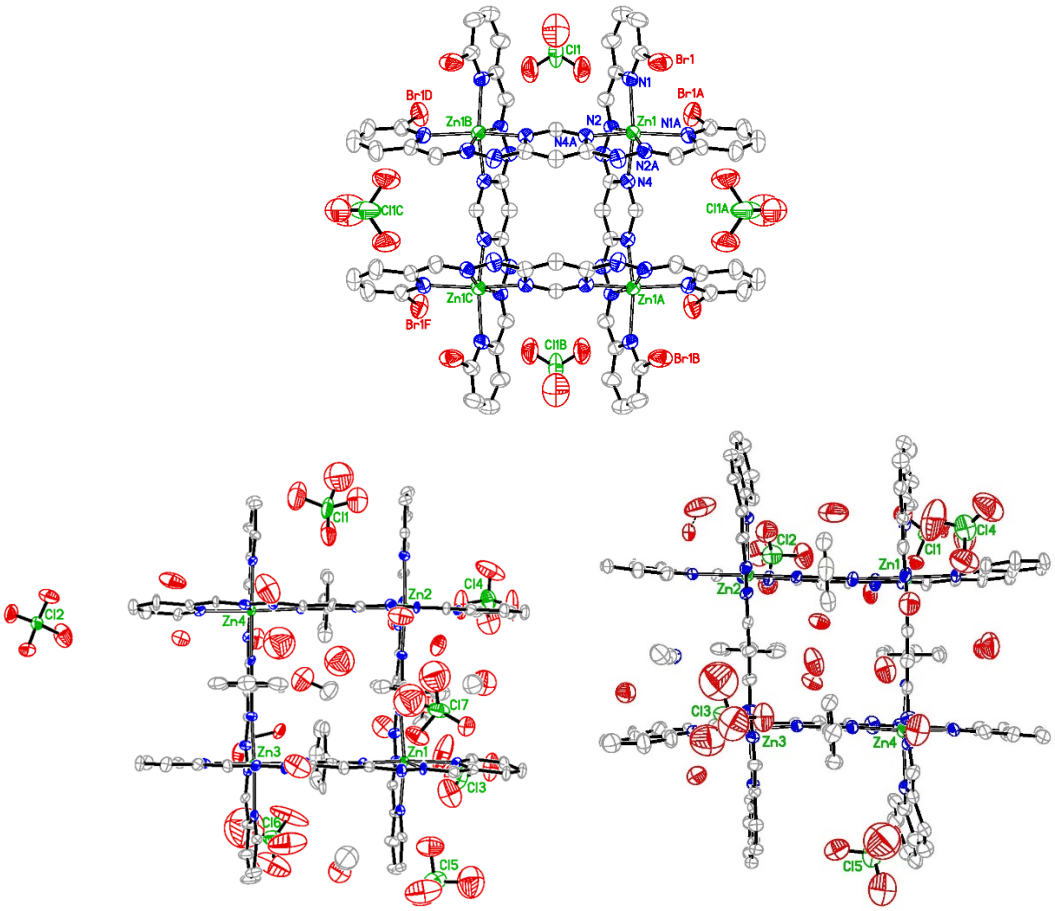
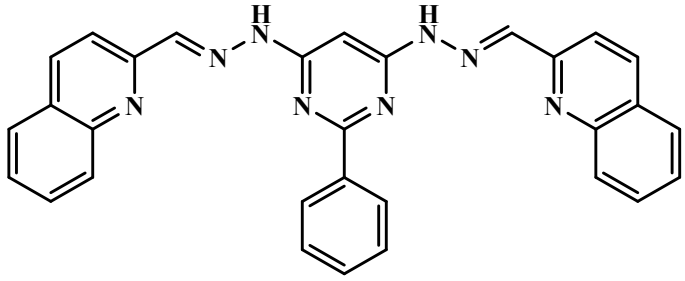


Fig. S1. The ellipsoidal diagram for the whole molecule in complexes **1**-**3**.
(hydrogen atoms are omitted for clarity.)



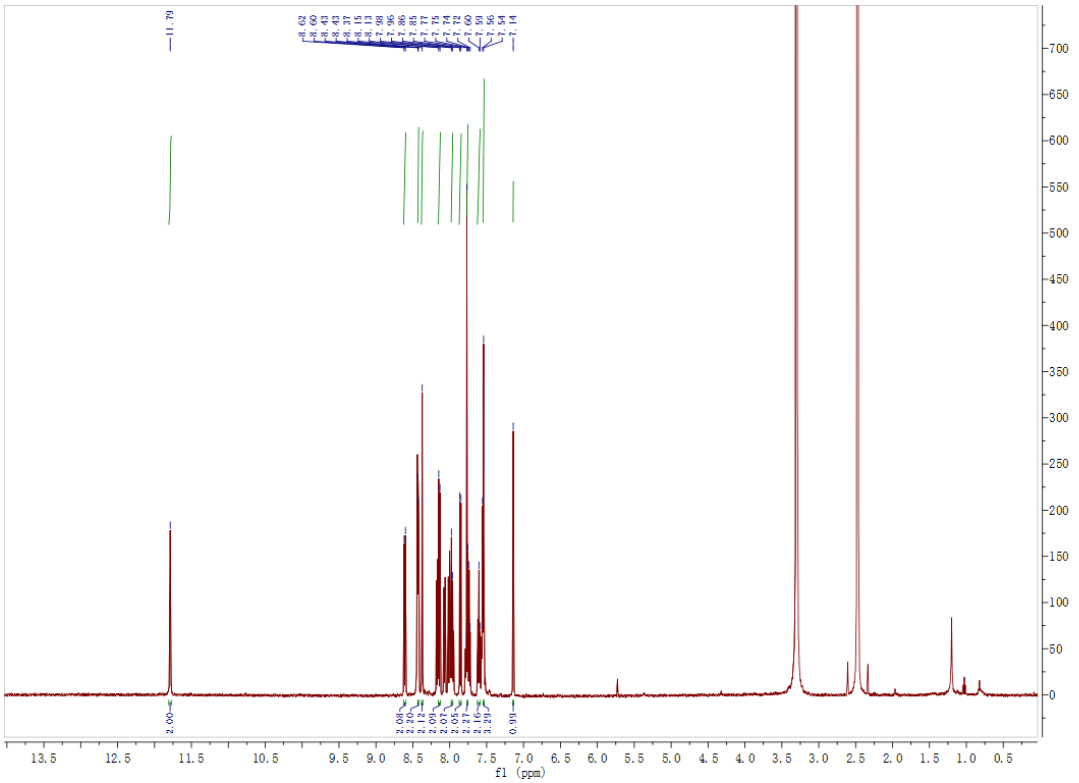


Fig. S2. ^{1}H NMR spectrum of H_2L^3.

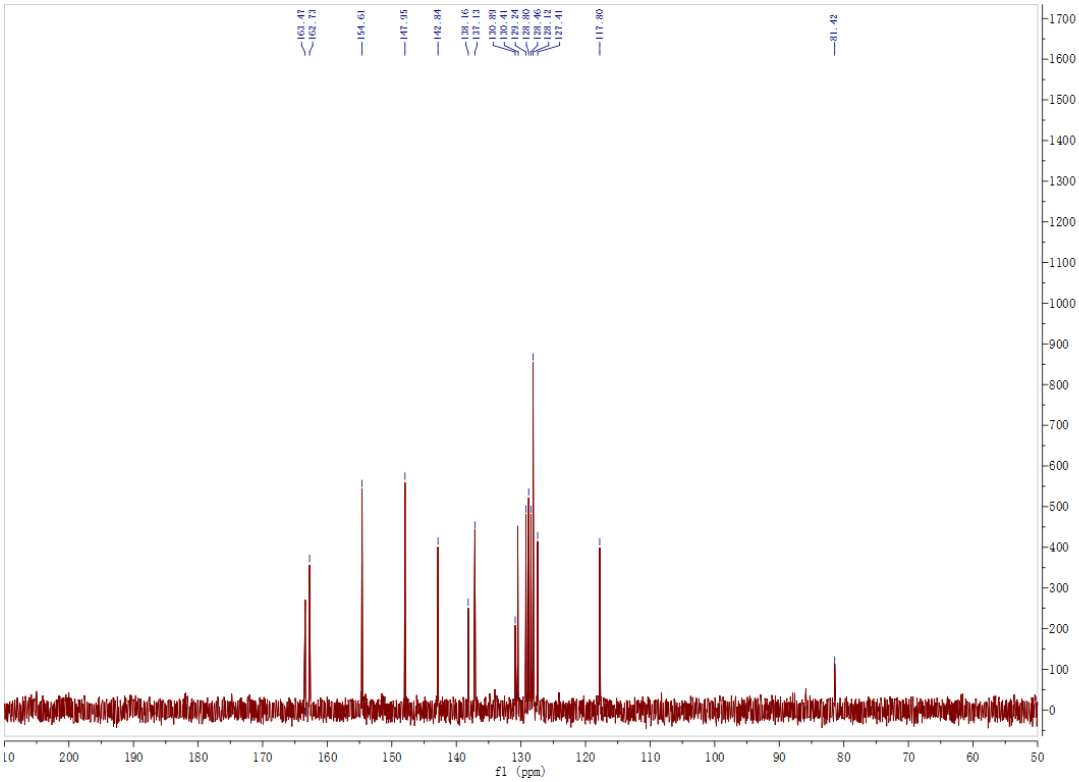


Fig. S3. ^{13}C NMR spectrum of H_2L^3.

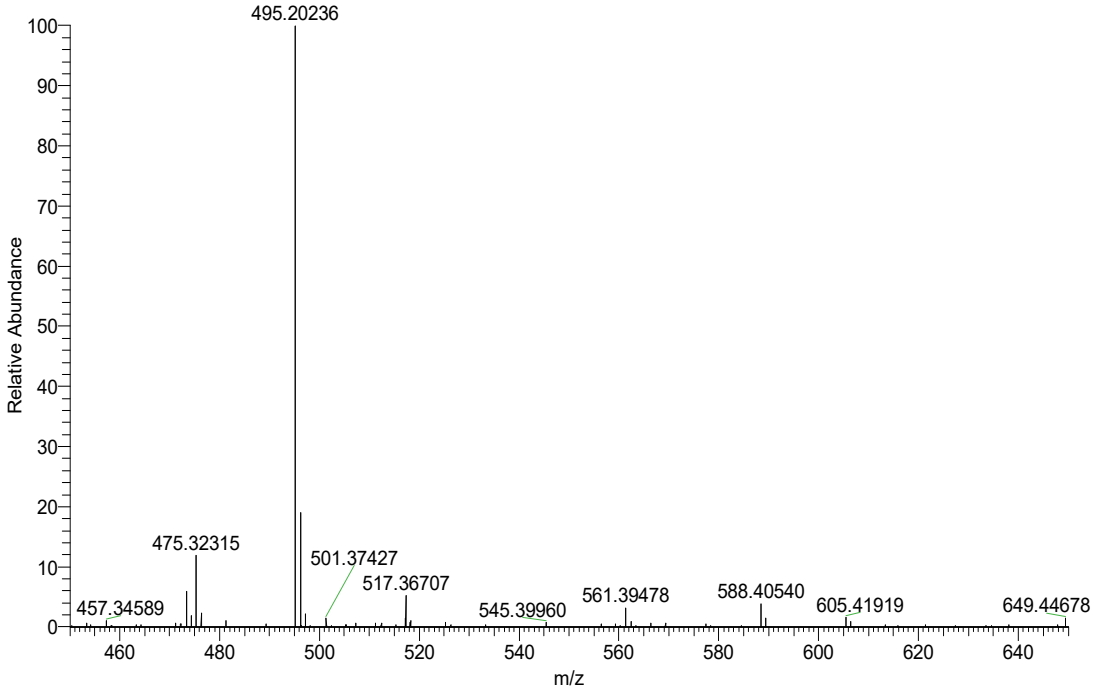


Fig. S4. ESI-HRMS of H_2L^3 at m/z 495.20236 for $C_{30}H_{22}N_8$ $[M+H]^+$.

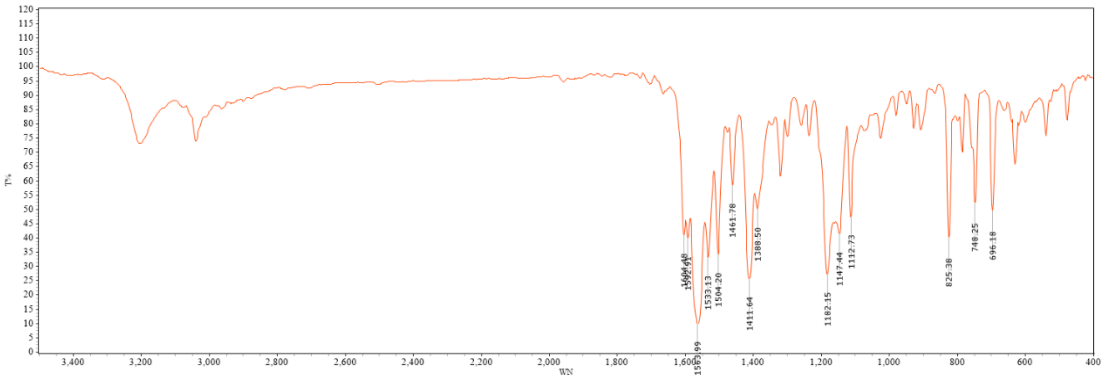


Fig. S5. IR spectrum of H_2L^3.

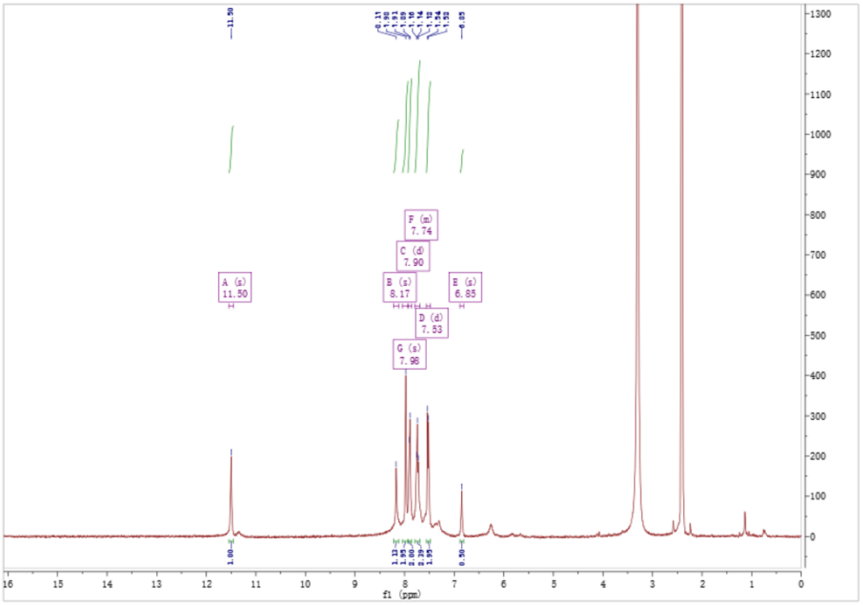


Fig. S6. [1]H NMR spectrum of complex **1**.

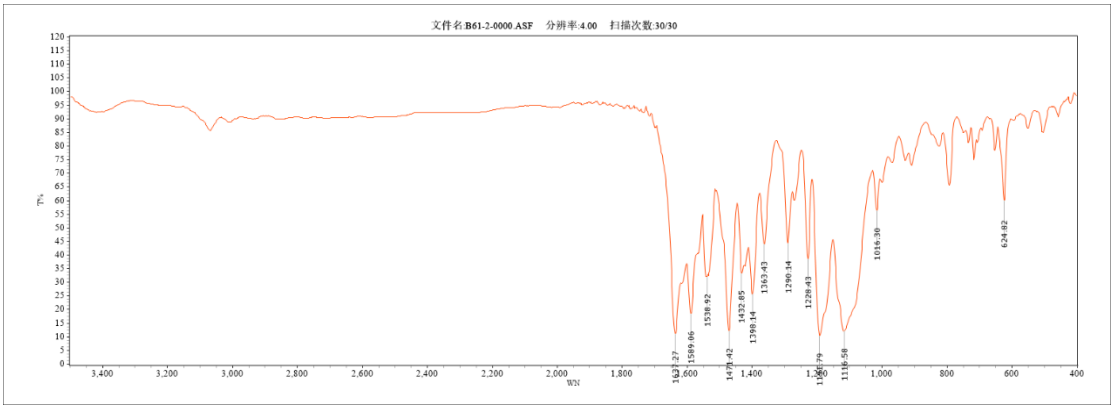


Fig. S7. IR spectrum of complex **1**.

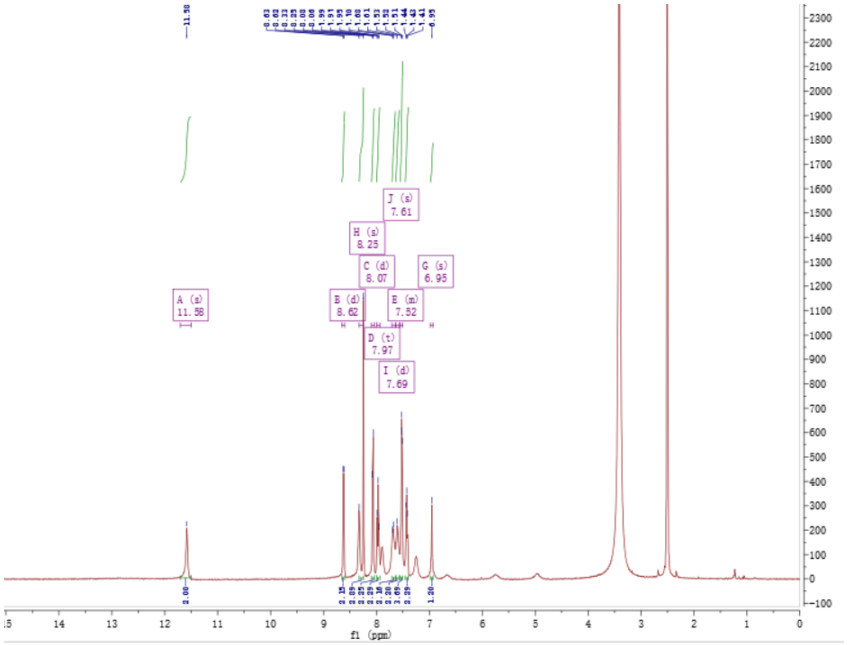


Fig. S8. [1]H NMR spectrum of complex **2**.

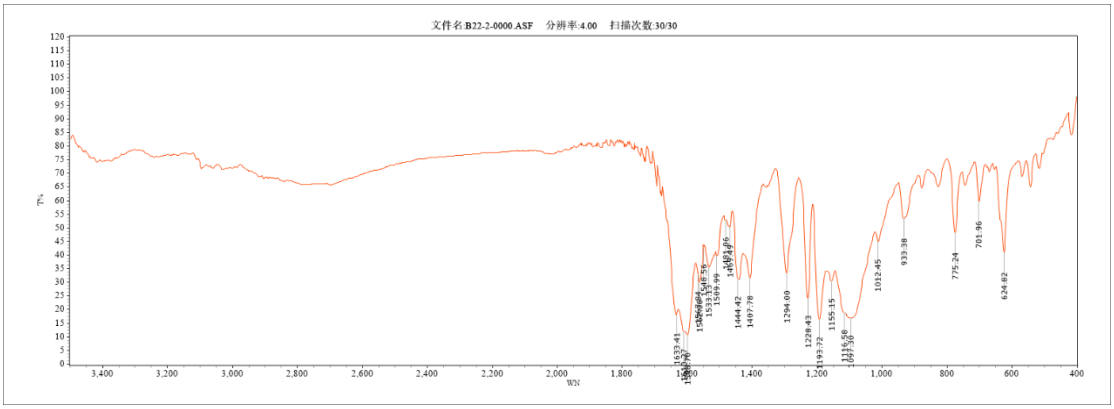


Fig. S9. IR spectrum of complex **2**.

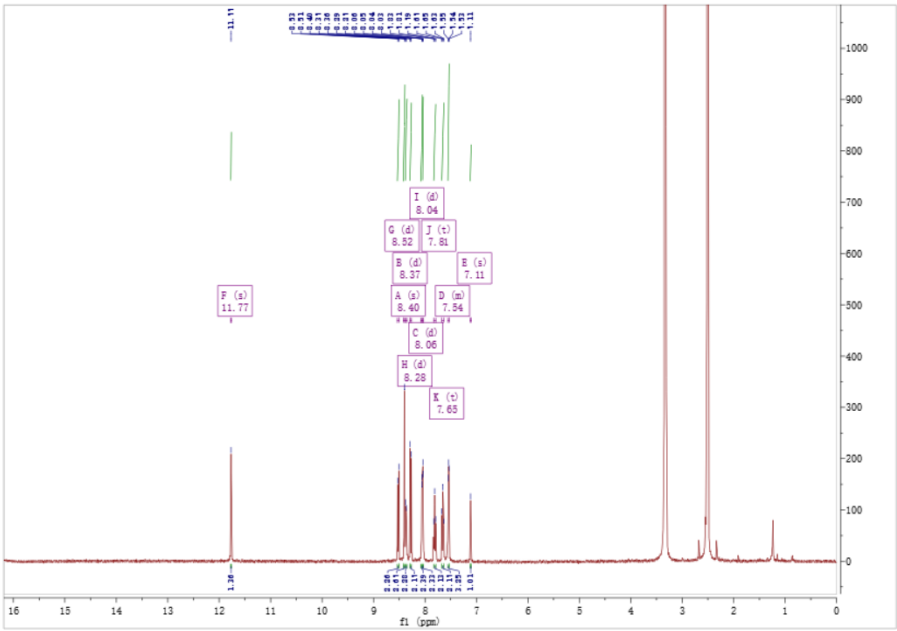


Fig. S10. ^{1}H NMR spectrum of complex **3**.

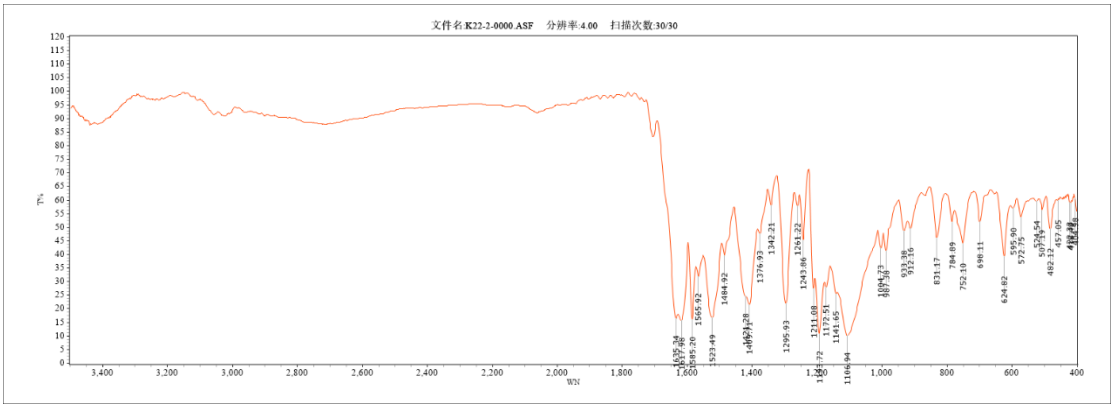


Fig. S11. IR spectrum of complex **3**.

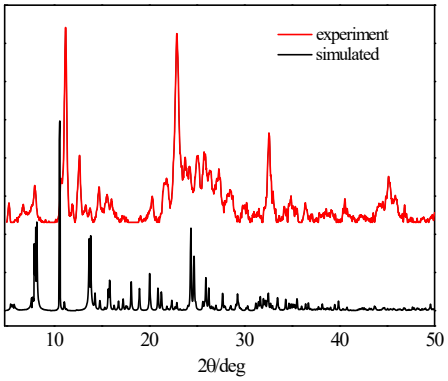


Fig. S12. XRD patterns of simulated compound and experimental sample of complex **1**.

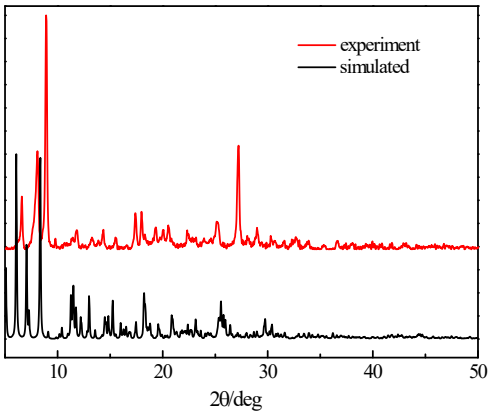


Fig. S13. XRD patterns of simulated compound and experimental sample of complex **2**.

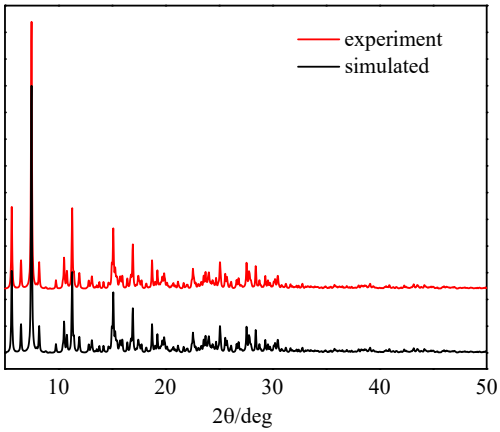


Fig. S14. XRD patterns of simulated compound and experimental sample of complex **3**.

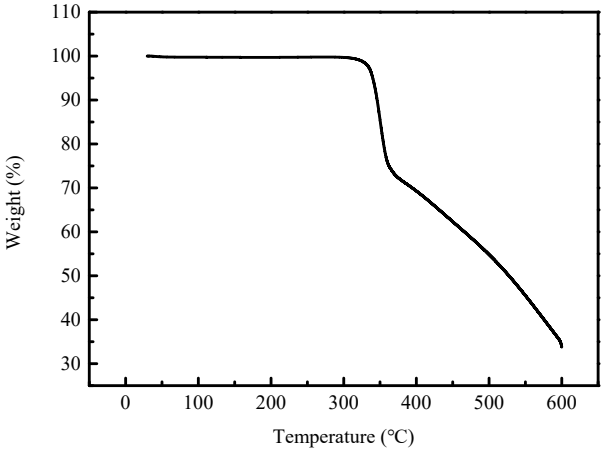


Fig. S15. TG analysis of complex **1**.

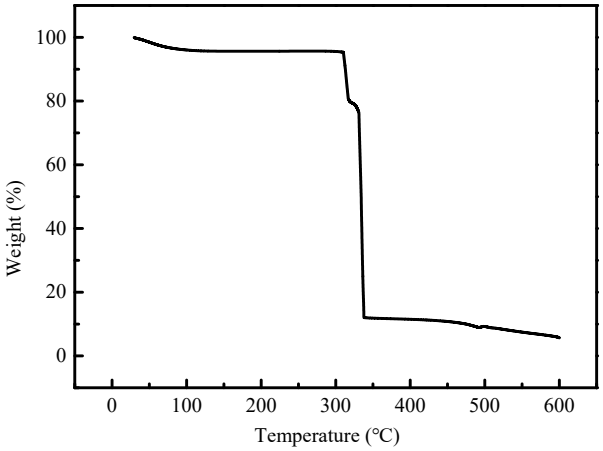


Fig. S16. TG analysis of complex **2**.

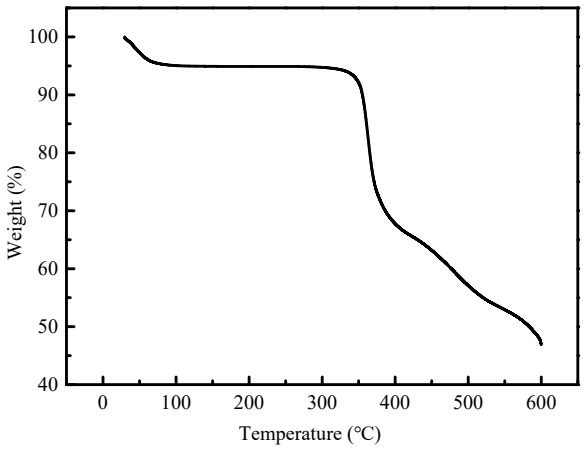


Fig. S17. TG analysis of complex **3**.

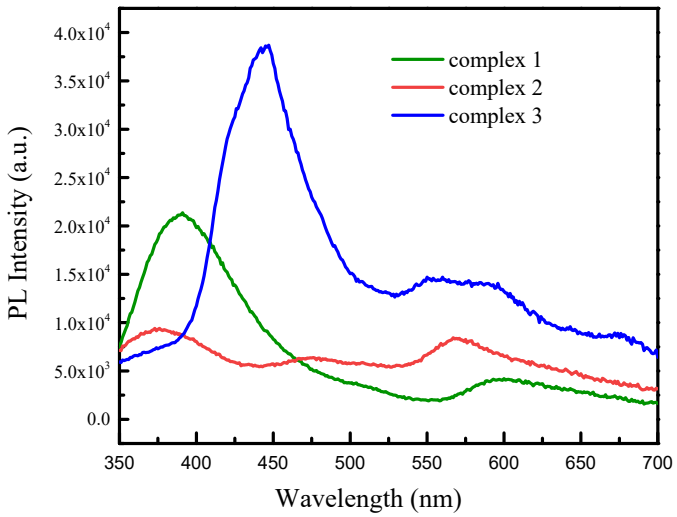


Fig. S18. Fluorescence spectra of complexes **1-3** (10 μM) in Tris-HCl-NaCl (pH=7.4). λ_{ex} = 300 nm.

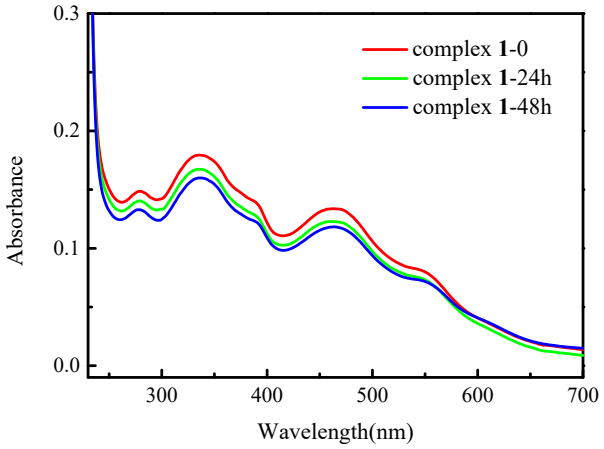


Fig. S19. UV-Vis spectra of complex **1**.

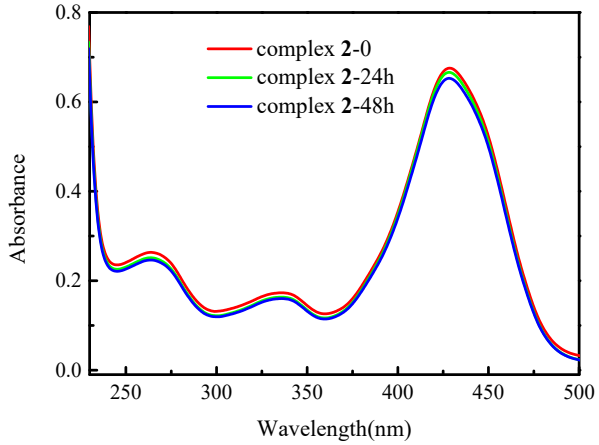


Fig. S20. UV-Vis spectra of complex **2**.

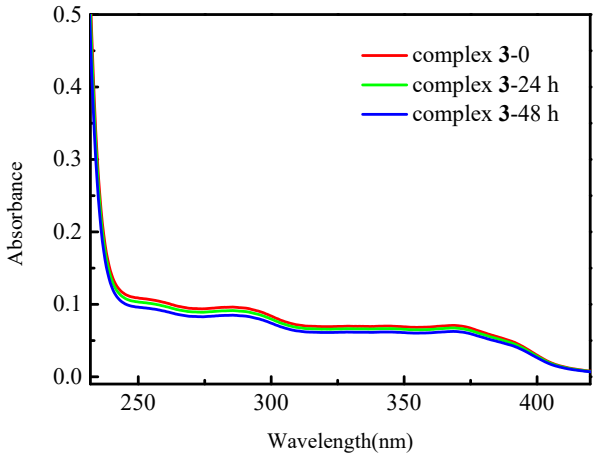


Fig. S21. UV-Vis spectra of complex **3**.

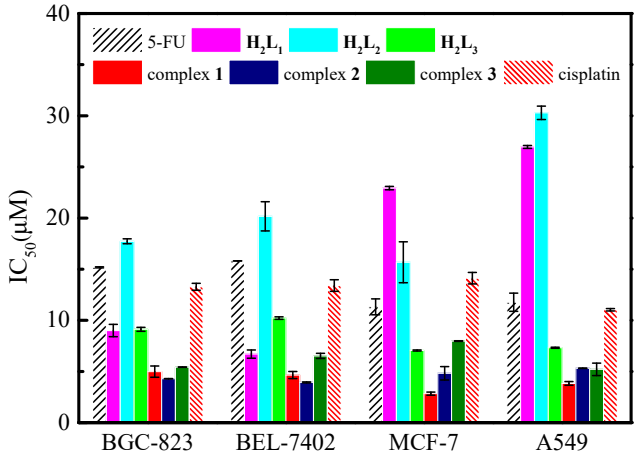


Fig. S22. IC_{50} values of H_2L^1-H_2L^3 and complexes **1**-**3** against BGC-823, BEL-7402, MCF-7 and A549 cells for 48 h.

Table S1. Selected bond distances (Å) and bond angles (°) in complex **1**

Complex **1**	bond distances (Å) / bond angles (°)
Zn(1)-N(1)	2.213(3)
Zn(1)-N(2)	2.119(3)
Zn(1)-N(4)	2.147(3)
N(2)-Zn(1)-N(1)	118.78(12)
N(2)-Zn(1)-N(2)	162.01(16)
N(4)-Zn(1)-N(1)	147.26(11)

Table S2. Selected bond distances (Å) and bond angles (°) in complex **2** and **3**

Complex **2**		Complex **3**	
Zn(1)-N(2)	2.225(9)	Zn(1)-N(1)	2.266(11)

Zn(1)-N(12)	2.189(9)	Zn(1)-N(2)	2.056(12)
Zn(1)-N(1)	2.208(11)	Zn(1)-N(4)	2.339(10)
Zn(1)-N(9)	2.200(11)	Zn(1)-N(17)	2.290(12)
Zn(1)-N(30)	2.078(10)	Zn(1)-N(18)	2.054(12)
Zn(1)-N(10)	2.106(11)	Zn(1)-N(20)	2.283(11)
Zn(2)-N(20)	2.203(12)	Zn(2)-N(5)	2.219(12)
Zn(2)-N(8)	2.212(10)	Zn(2)-N(7)	2.044(11)
Zn(2)-N(18)	2.101(11)	Zn(2)-N(8)	2.397(9)
Zn(2)-N(7)	2.092(11)	Zn(2)-N(29)	2.186(10)
Zn(2)-N(17)	2.175(10)	Zn(2)-N(31)	2.023(10)
Zn(2)-N(5)	2.218(9)	Zn(2)-N(32)	2.409(10)
Zn(3)-N(13)	2.230(9)	Zn(3)-N(9)	2.387(12)
Zn(3)-N(15)	2.100(14)	Zn(3)-N(10)	2.026(12)
Zn(3)-N(25)	2.184(11)	Zn(3)-N(12)	2.225(10)
Zn(3)-N(26)	2.120(12)	Zn(3)-N(25)	2.326(10)
Zn(3)-N(36)	2.179(14)	Zn(3)-N(26)	2.112(12)
Zn(3)-N(28)	2.218(10)	Zn(3)-N(28)	2.249(10)
Zn(4)-N(29)	2.188(10)	Zn(4)-N(13)	2.238(9)
Zn(4)-N(31)	2.095(11)	Zn(4)-N(15)	2.042(14)
Zn(4)-N(21)	2.231(9)	Zn(4)-N(16)	2.305(10)
Zn(4)-N(24)	2.199(13)	Zn(4)-N(21)	2.180(10)
Zn(4)-N(32)	2.184(11)	Zn(4)-N(23)	2.068(14)
Zn(4)-N(23)	2.117(13)	Zn(4)-N(24)	2.416(14)
N(12)-Zn(1)-N(9)	148.5(4)	N(1)-Zn(1)-N(4)	147.3(5)
N(1)-Zn(1)-N(2)	148.1(4)	N(18)-Zn(1)-N(2)	174.4(4)
N(30)-Zn(1)-N(10)	166.4(4)	N(20)-Zn(1)-N(17)	148.8(5)
N(8)-Zn(2)-N(5)	148.1(4)	N(5)-Zn(2)-N(9)	147.8(4)
N(7)-Zn(2)-N(18)	166.8(4)	N(29)-Zn(2)-N(32)	151.2(4)
N(17)-Zn(2)-N(20)	148.7(4)	N(31)-Zn(2)-N(7)	168.7(4)

N(15)-Zn(3)-N(26)	168.8(5)	N(10)-Zn(3)-N(15)	175.0(4)
N(25)-Zn(3)-N(28)	147.8(5)	N(28)-Zn(3)-N(26)	174.7(4)
N(36)-Zn(3)-N(13)	147.8(5)	N(12)-Zn(3)-N(9)	149.2(5)
N(31)-Zn(4)-N(23)	168.0(4)	N(15)-Zn(4)-N(23)	171.3(5)
N(24)-Zn(4)-N(21)	148.7(5)	N(21)-Zn(4)-N(24)	150.1(5)
N(32)-Zn(4)-N(29)	147.8(5)	N(13)-Zn(4)-N(16)	149.3(5)

Table S3. ^{1}H NMR and IR signals for complexes **1-3** and their assignments.

Complex	Amide −NH−		Imine −CH=N−		ClO_4^-	Zn−N
	^{1}H NMR δ	IR cm^{-1}	^{1}H NMR δ	IR cm^{-1}	IR cm^{-1}	IR cm^{-1}
Complex **1**	11.50	3029	7.98	1637	1116, 624	500
Complex **2**	11.58	3095	8.25	1598	1116, 624	520
Complex **3**	11.77	3056	8.40	1617	1106, 624	482

Table S4. log$P_{o/w}$ of complexes **1-3** between octanol and phosphate buffer.

Complexes	C_o/μg·ml^{-1}	C_w/μg·ml^{-1}	**log*P***
1	2.06	1.03	0.30
2	1.24	1.45	-0.07
3	0.81	0.61	0.12