

**Copper(II) complexes with 4-acyl pyrazolone derivative and diimine coligands:
synthesis, structural characterization, DNA binding and antitumor activity**

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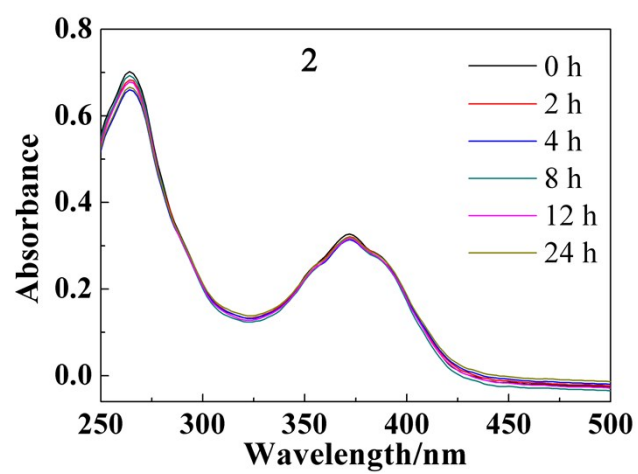
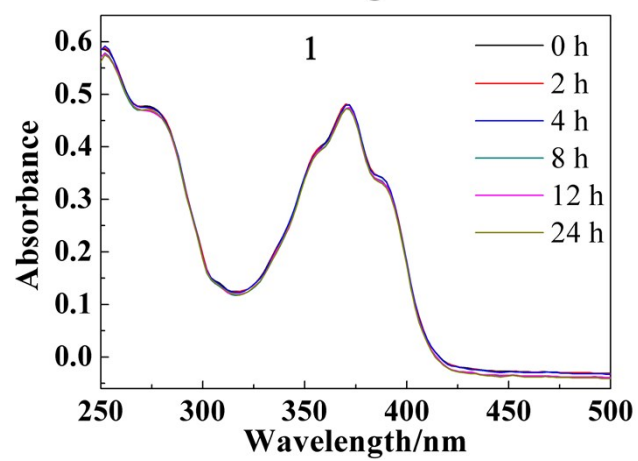
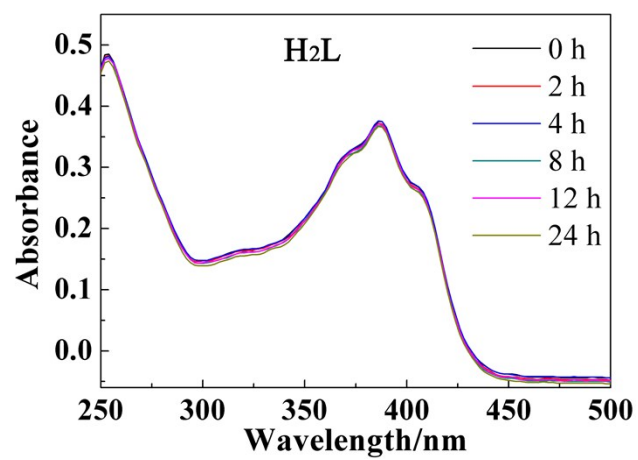
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Table S1. Selected bond lengths (Å) and angles (°) for ligand **H₂L** and complexes **1-3**.

H₂L			
O(1)-C(7)	1.3278(16)	N(3)-N(4)	1.3769(15)
O(2)-C(18)	1.2419(15)		
complexes 1			
Cu(1)-O(3)	1.945(4)	Cu(1)-N(5)	1.998(5)
Cu(1)-N(2)	1.953(5)	Cu(1)-N(6)	2.215(5)
Cu(1)-O(2)	1.983(4)		
O(3)-Cu(1)-N(2)	94.9(2)	O(2)-Cu(1)-N(5)	97.6(2)
O(3)-Cu(1)-O(2)	157.23(19)	O(3)-Cu(1)-N(6)	112.2(2)
N(2)-Cu(1)-O(2)	81.2(2)	N(2)-Cu(1)-N(6)	102.8(2)
O(3)-Cu(1)-N(5)	86.3(2)	O(2)-Cu(1)-N(6)	90.54(19)
N(2)-Cu(1)-N(5)	178.8(2)	N(5)-Cu(1)-N(6)	77.1(2)
complexes 2			
Cu(1)-N(2)	1.931(4)	Cu(1)-O(2)	1.998(4)
Cu(1)-O(3)	1.937(4)	Cu(1)-N(5)	2.256(5)
Cu(1)-N(6)	1.988(4)		
N(2)-Cu(1)-O(3)	94.6(2)	N(6)-Cu(1)-O(2)	95.65(16)
N(2)-Cu(1)-N(6)	176.8(2)	N(2)-Cu(1)-N(5)	102.25(19)
O(3)-Cu(1)-N(6)	88.07(17)	O(3)-Cu(1)-N(5)	112.16(18)
N(2)-Cu(1)-O(2)	81.26(19)	N(6)-Cu(1)-N(5)	78.26(19)
O(3)-Cu(1)-O(2)	161.56(16)	O(2)-Cu(1)-N(5)	86.27(16)

complexes **3**

Cu(1)-O(1)	1.9340(19)	Cu(1)-N(5)	2.236(2)
Cu(1)-O(2)	1.9529(19)	Cu(1)-N(6)	2.044(2)
Cu(1)-N(3)	1.957(2)		
O(1)-Cu(1)-O(2)	167.32(9)	O(2)-Cu(1)-N(3)	81.19(9)
O(1)-Cu(1)-N(3)	94.95(9)	O(2)-Cu(1)-N(5)	91.73(8)
O(1)-Cu(1)-N(5)	100.94(8)	O(2)-Cu(1)-N(6)	90.97(9)
O(1)-Cu(1)-N(6)	92.31(9)	N(3)-Cu(1)-N(5)	103.94(9)
N(3)-Cu(1)-N(6)	171.93(9)	N(6)-Cu(1)-N(5)	78.07(9)



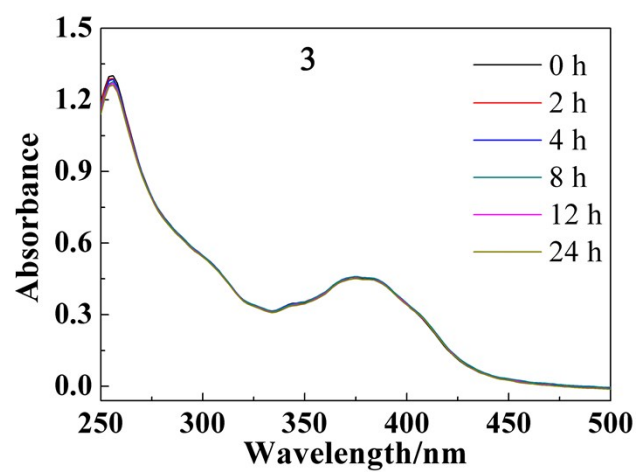
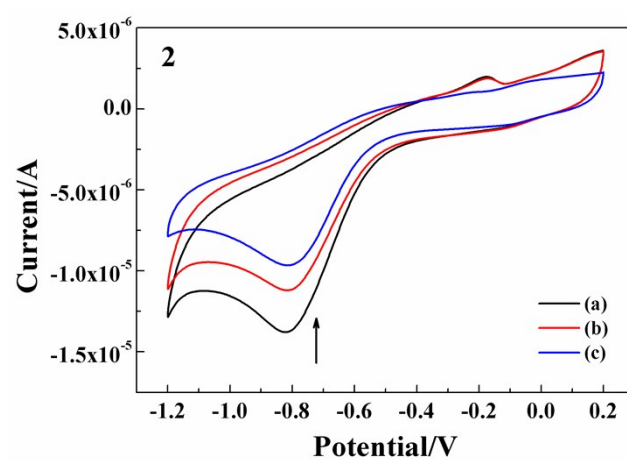
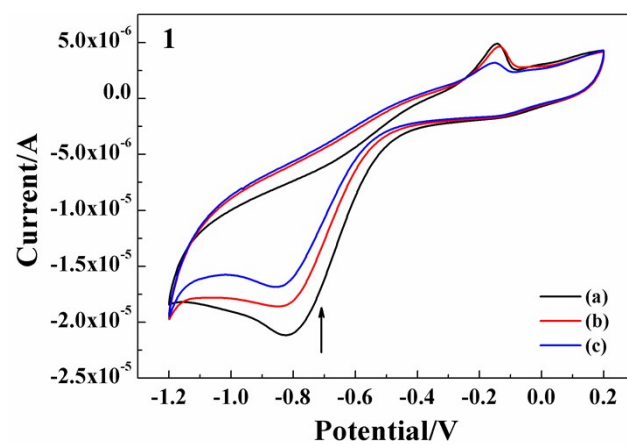
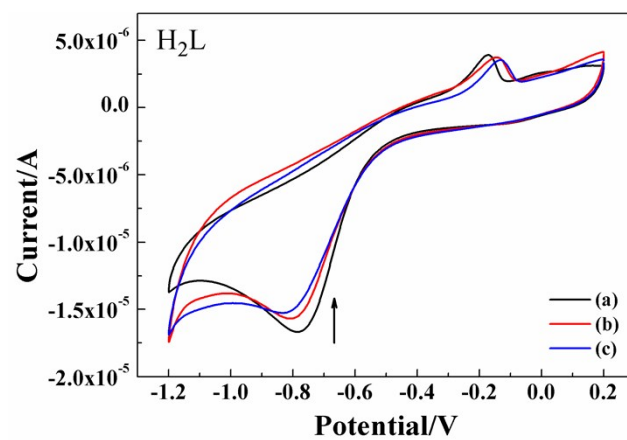


Fig. S1 Stability of the **H₂L** ligand and complexes **1-3** in PBS at different times.



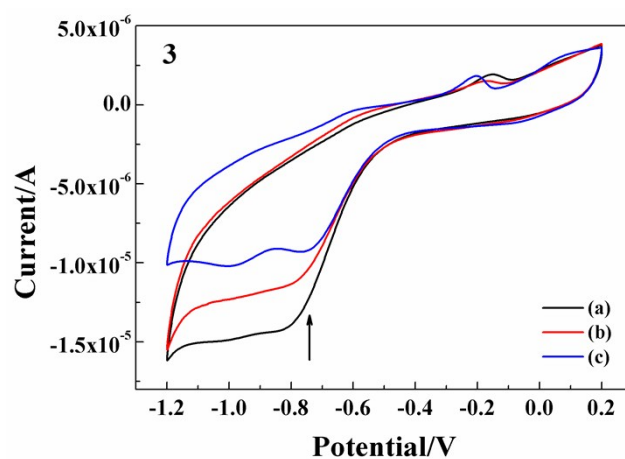


Fig. S2 Cyclic voltammograms of the **H₂L** ligand and complexes **1-3** (50 μ M) in the absence (a) and presence of HS-DNA. [DNA]= 200 μ M (b) and 400 μ M (c), scan rate was 100 mV $\cdot$ s⁻¹. The arrows show the changes upon addition of the DNA.

Table S2 The properties of **H₂L** and complexes **1-3** bound to DNA.

Compound	$\lambda_{\max}$ (nm)	$\Delta\epsilon$ (%)
H₂L	249 ^a , 385 ^b	18.49 ^a , 19.49 ^b
1	247 ^a , 369 ^b	20.98 ^a , 23.58 ^b
2	264 ^a , 372 ^b	51.49 ^a , 54.45 ^b
3	254 ^a , 370 ^b	69.76 ^a , 63.20 ^b

^a LMCT, ^b $\pi \rightarrow \pi^*$.

Table S3 IC₅₀^a values of complex **3** and DDP toward NCTC-1469, RAW 264.7 and Eca-109 cells.

IC ₅₀ values (μ M) ^a			
Compound	NCTC-1469	RAW 264.7	Eca-109
3	3.53 $\pm$ 0.67	4.18 $\pm$ 0.64	3.68 $\pm$ 0.14
DDP	39.00 $\pm$ 8.92	9.99 $\pm$ 1.32	47.66 $\pm$ 3.49

^a IC₅₀ values are presented as the mean $\pm$ SD (n=3).

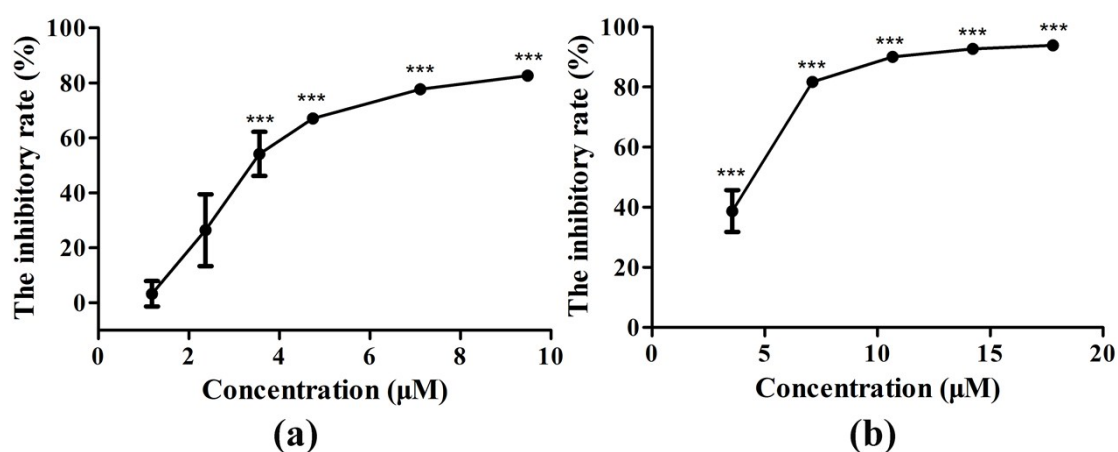


Fig. S3 The inhibitory activities of complex **3** against NCTC-1469 (a) and RAW 264.7 cells (b) for 24 h.