UV-Assisted Photochemical Transformation of TetranuclearCopper(II) Complex: A DFT Supported Study in β-Lactamase Inhibitory Activity Towards Antibiotic Resistance

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SUPPORTING INFORMATION

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Total number of Tables: 7

Index

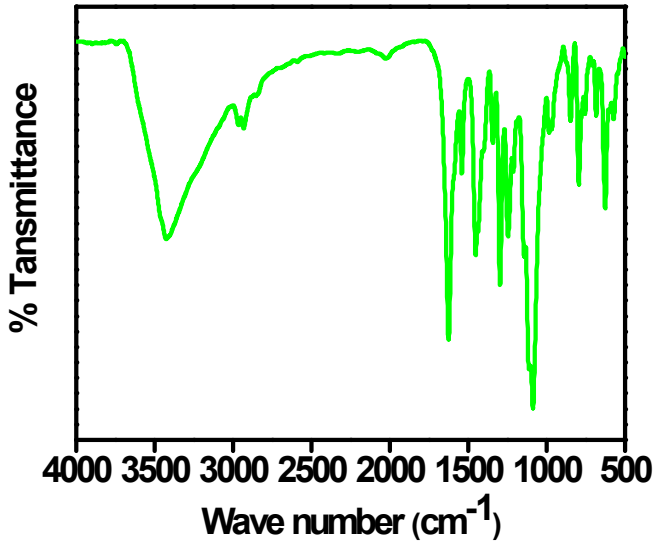

Fig S1.FT-IR spectrum of complex **1**

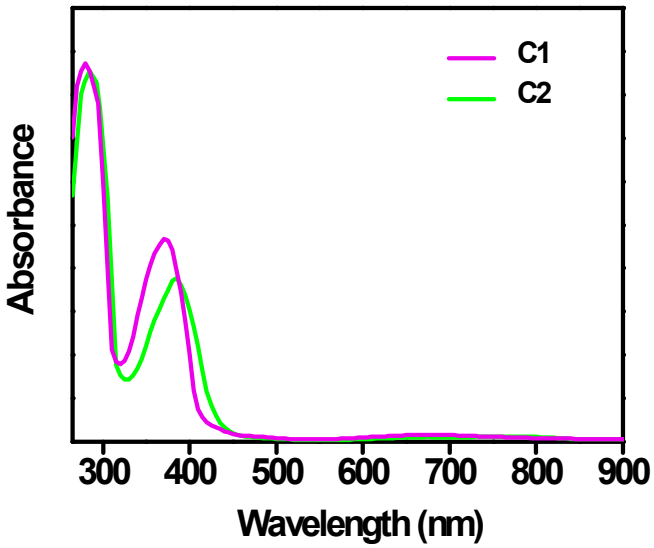

Fig S2.UV-Vis spectra of complex **1**and complex **2**

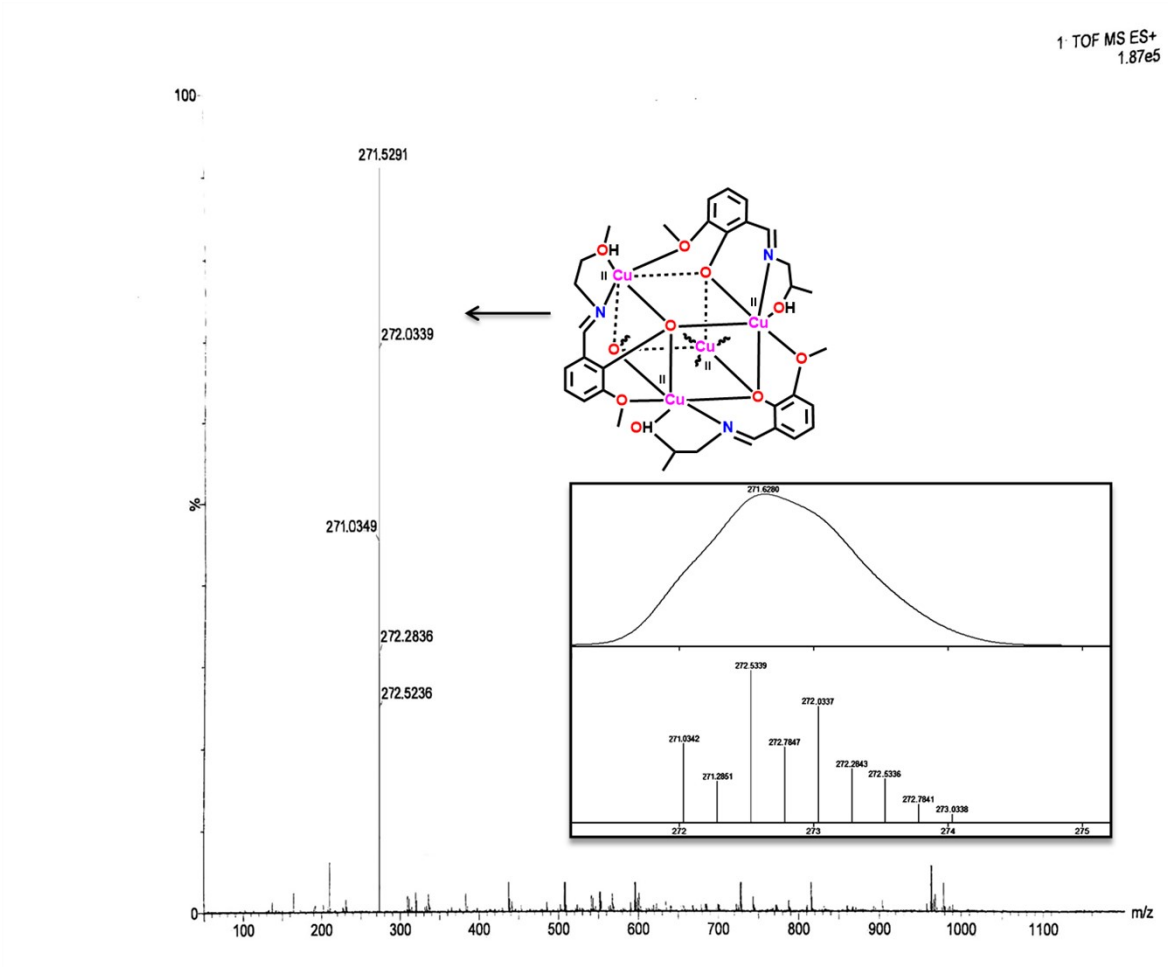

Fig S3.ESI-MS spectrum of complex **1**

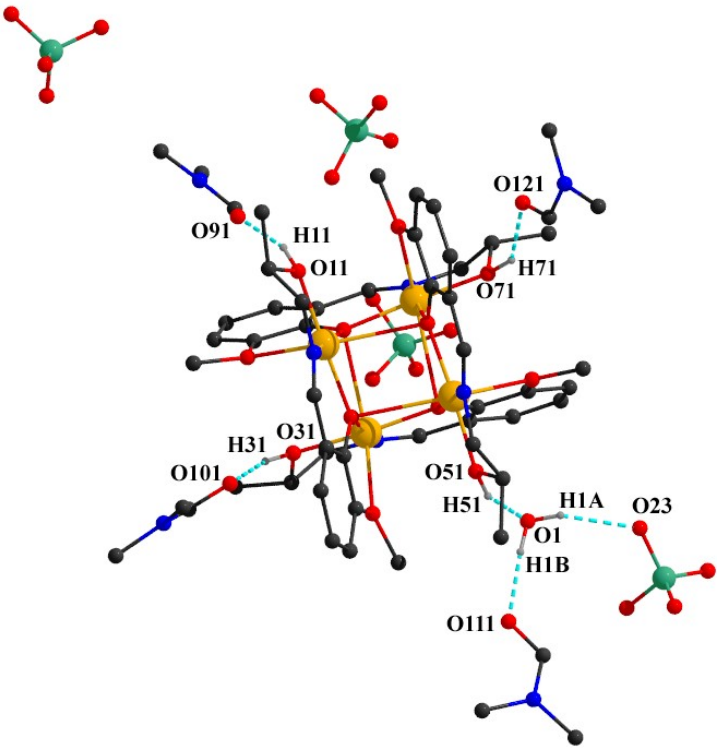

Fig S4.H-bonded structure of complex **1**. H-bonds are shown by dotted lines.

Table S1. Selected bond lengths of complex **1**

Bond lengths (Å)			
Cu1–O11	1.987(4)	Cu3–O22	2.651(4)
Cu1–O22	1.972(3)	Cu3 –O41	2.288(4)
Cu1–O62	2.673(4)	Cu3–O42	1.956(3)
Cu1–O81	2.305(4)	Cu3 –O51	1.992(5)
Cu1–O82	1.973(4)	Cu3 –O62	1.968(3)
Cu1–N14	1.922(4)	Cu3 –N54	1.905(4)
Cu2–O21	2.324(4)	Cu4 –O42	2.758(4)
Cu2–O22	1.973(3)	Cu4 –O61	2.297(5)
Cu2–O31	1.957(4)	Cu4 –O62	1.991(3)
Cu2–O42	1.947(4)	Cu4 –O71	1.963(4)
Cu2–O82	2.666(4)	Cu4–O82	1.970(4)
Cu2–N83	1.923(5)	Cu4 –N74	1.924(5)

Table S2. Selected bond angles of complex **1**

Bond angles (°)			
O11 – Cu1 – O22	175.64(15)	O22 – Cu3– O41	146.78(13)
O11 – Cu1 – O62	97.95(14)	O22 – Cu3– O42	71.77(13)
O11 – Cu1 – O81	87.11(16)	O22 – Cu3– O51	95.62(14)
O11 – Cu1 – O82	94.06(15)	O22 – Cu3– O62	81.36(13)
O11 – Cu1 – N14	83.62(18)	O22 – Cu3–N54	103.45(18)
O22 – Cu1 – O62	80.72(13)	O41– Cu3– O42	75.24(14)
O22 – Cu1 – O81	96.32(16)	O41– Cu3– O51	89.92(17)
O22 – Cu1 – O82	89.47(14)	O41– Cu3– O62	94.62(16)
O22 – Cu1 – N14	92.53(18)	O41– Cu3–N54	109.7(2)
O62 – Cu1 – O81	145.87(13)	O42– Cu3– O51	93.24(15)
O62 – Cu1 – O82	71.48(12)	O42– Cu3– O62	89.31(14)
O62 – Cu1 – N14	100.67(14)	O42– Cu3–N54	173.8(2)
O81 – Cu1 – O82	74.52(14)	O51– Cu3– O62	175.23(16)
O81 – Cu1 – N14	113.45(16)	O51– Cu3–N54	83.23(19)
O82 – Cu1 – N14	171.48(16)	O62– Cu3–N54	93.86(18)
O21 – Cu2– O22	74.48(13)	O42– Cu4– O61	143.36(12)
O21 – Cu2– O31	86.32(16)	O42– Cu4– O62	68.83(12)
O21 – Cu2– O42	99.56(14)	O42– Cu4– O71	98.57(16)
O21 – Cu2– O82	146.17(12)	O42– Cu4– O82	79.61(12)
O21 – Cu2–N34	111.83(17)	O42– Cu4–N74	103.8(2)
O22– Cu2– O31	94.39(16)	O61– Cu4– O62	74.76(14)
O22– Cu2– O42	89.46(14)	O61– Cu4– O71	88.47(17)
O22– Cu2– O82	71.77(12)	O61– Cu4– O82	95.95(14)
O22– Cu2–N34	173.11(18)	O61– Cu4–N74	112.7(2)
O31– Cu2– O42	173.67(16)	O62– Cu4– O71	95.15(16)
O31– Cu2– O82	94.02(16)	O62– Cu4– O82	88.84(14)
O31– Cu2–N34	83.49(17)	O62– Cu4–N74	172.2(2)
O42– Cu2– O82	82.41(13)	O71– Cu4– O82	174.71(17)
O42– Cu2–N34	92.11(16)	O71– Cu4–N74	83.3(2)
O82– Cu2–N34	101.79(16)	O82– Cu4–N74	92.3(2)

Table S3. Geometrical features of hydrogen bonding interactions (distances (Å) and angles (°)) in Complexes**1** and **2**

Complex	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
1	O(1) – H(1A) ··· Cl(1)	0.8500	2.3800	3.223(5)	171.00
	O(1) – H(1B) ··· Cl(3)	0.8500	2.4000	3.225(5)	163.00
	O(2) – H(2A) ··· Cl(2)	0.8800	2.3400	3.144(4)	153.00
	O(2) – H(2B) ··· Cl(1)	0.8800	2.2200	3.066(5)	161.00
	O(3) – H(3A) ··· Cl(3)	0.8800	2.5100	3.185(5)	134.00
	O(3) – H(3B) ··· Cl(1)	0.8800	2.2000	3.073(5)	175.00
	O(11) – H(11) ··· O(1)	0.86(8)	1.76(6)	2.581(7)	160(11)
2	O(1) – H(1A) ··· O(23)	0.8700	2.1600	2.885(8)	140.00
	O(1) – H(1B) ··· O(111)	0.8700	1.8100	2.656(9)	165.00
	O(11) – H(11) ··· O(91)	0.88(3)	1.73(3)	2.584(6)	161(4)
	O(31) – H(31) ··· O(101)	0.88(3)	1.78(3)	2.606(6)	156(4)
	O(51) – H(51) ··· O(1)	0.879(14)	1.77(3)	2.592(7)	155(5)
	O(71) – H(71) ··· O(121)	0.88(2)	1.78(4)	2.519(9)	140(4)

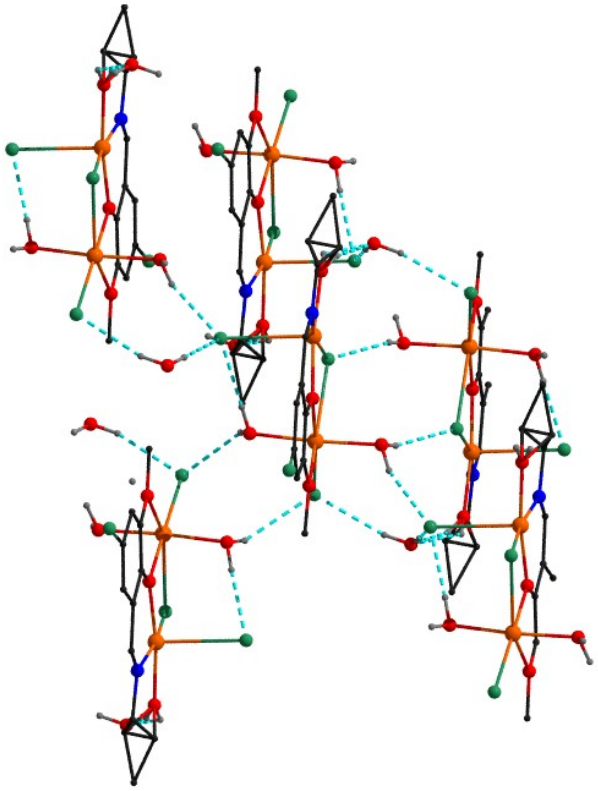

Fig S5.H-bonded structure of complex **2**. H-bonds are shown by dotted lines.

Table S4. Selected bond parameters of complex **2**

Bond lengths (Å)			
Cu1 –Cl1	2.7550(18)	Cu2 –Cl2	2.691(2)
Cu1 –Cl2	2.2603(18)	Cu2 –Cl3	2.262(3)
Cu1 – O11	1.985(6)	Cu2 – O2	1.970(3)
Cu1 – O22	1.941(5)	Cu2 – O3	1.961(3)
Cu1 – N14	1.923(6)	Cu2 – O21	2.329(4)
		Cu2 – O22	2.023(5)
Bond angles (°)			
Cl1 –Cu1–Cl2	95.80(6)	Cl2 –Cu2 – O21	149.18(15)
Cl1 –Cu1– O11	97.05(14)	Cl2 –Cu2 – O22	76.45(14)
Cl1 –Cu1– O22	89.48(11)	Cl3 –Cu2 – O2	94.21(14)
Cl1 –Cu1– N14	94.21(14)	Cl3 –Cu2 – O3	91.20(16)

Cl2 –Cu1– O11	94.03(13)	Cl3 –Cu2 – O21	100.70(15)
Cl2 –Cu1– O22	89.41(13)	Cl3 –Cu2 – O22	173.05(15)
Cl2 –Cu1– N14	169.66(17)	O2 –Cu2 – O3	174.6(2)
O11 –Cu1– O22	172.27(17)	O2–Cu2 – O21	86.72(16)
O11 –Cu1– N14	82.2(3)	O2 –Cu2 – O22	88.59(16)
O22 –Cu1– N14	93.3(2)	O3–Cu2 – O21	91.82(18)
Cl2 –Cu2 –Cl3	109.96(7)	O3 –Cu2 – O22	85.98(17)
Cl2 –Cu2 – O2	88.00(15)	O21 –Cu2 – O22	73.08(19)
Cl2 –Cu2 – O3	90.60(16)		

Table S5. Bond valence sum (BVS) calculations for complexes **1** and **2**

Complex	atom	Calculated BVS*
1	Cu1	2.035
	Cu2	2.089
	Cu3	2.092
	Cu4	2.044
2	Cu1	2.108
	Cu2	2.021

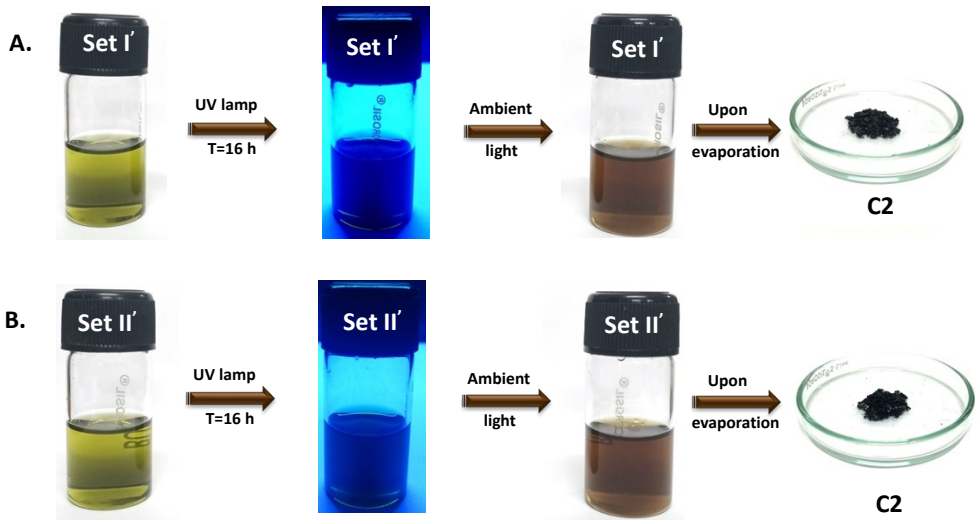

Fig S6. Pictorial representation for transformation of **(A)** Set I' (**C1** only) and **(B)**Set II' (**C1** + nitrocefin) in methanol-H_2O into crystalline **C2** under UV lamp.

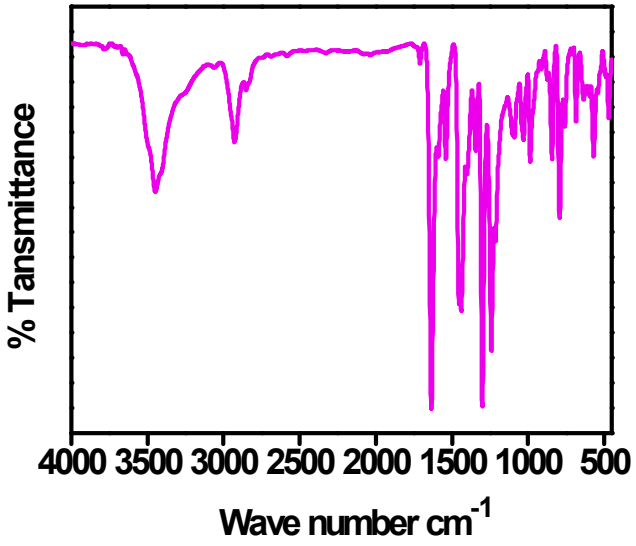

Fig S7.FT-IR spectrum of complex **2**

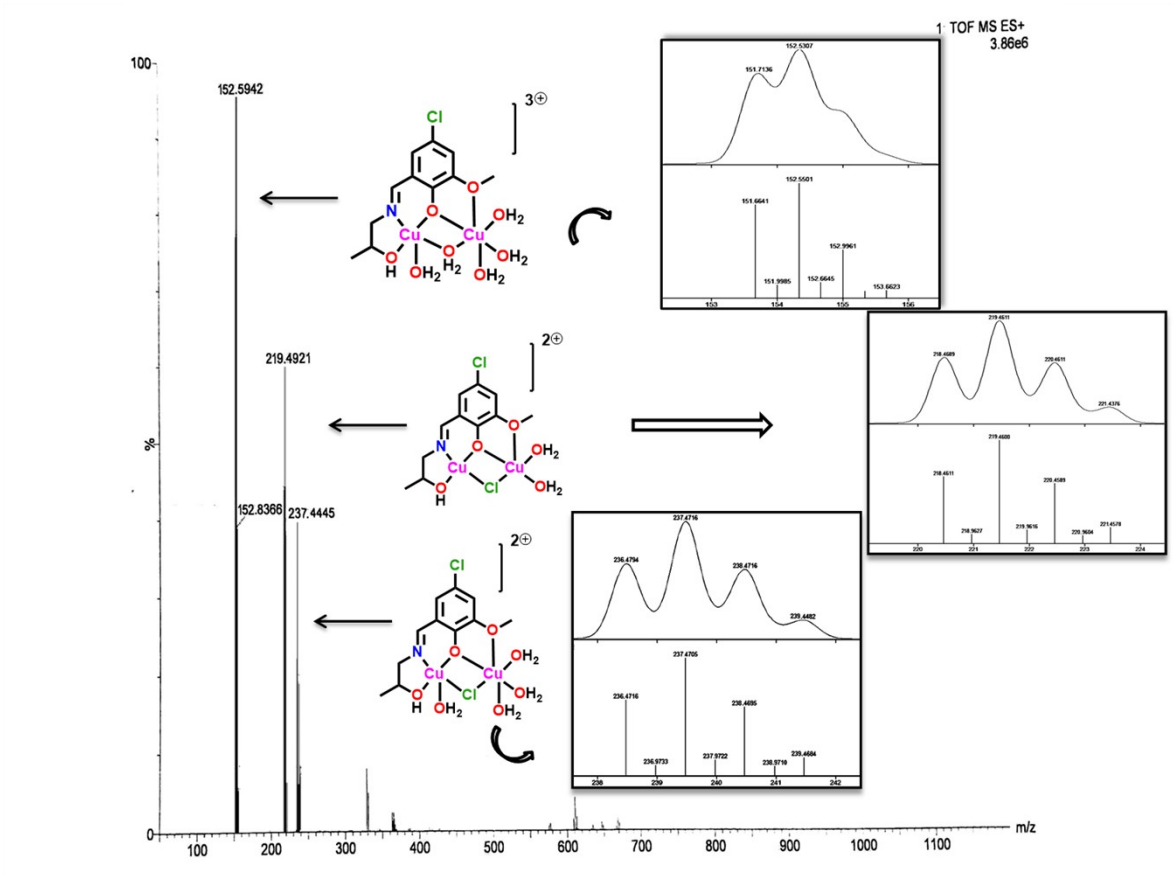

Fig S8.ESI-MS spectrum of complex **2**

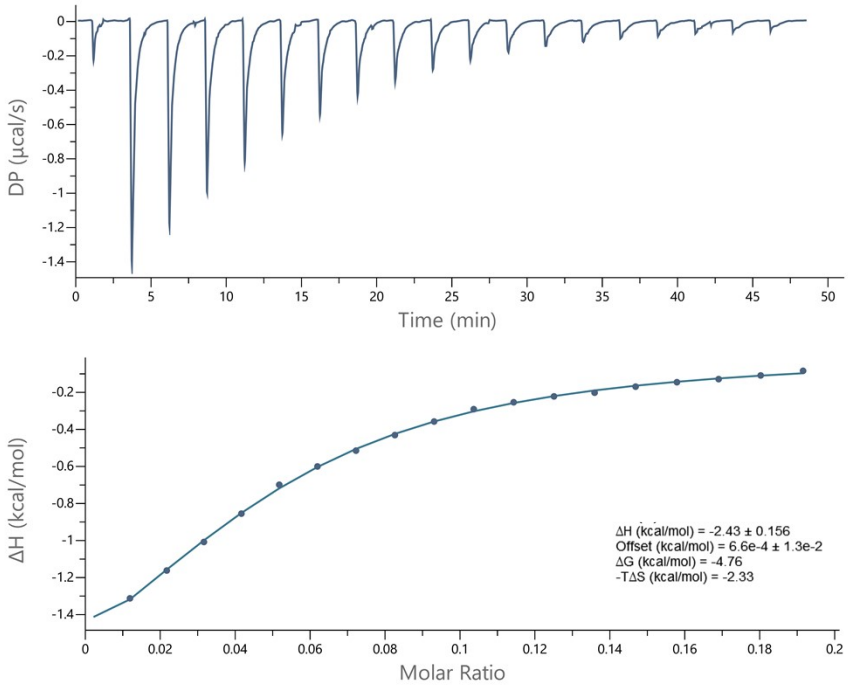

Fig S9. Isothermal titration calorimetry profiles for **C2** binding to chloride ion. Top panel: heat effects against time for the titration of **C2** (3 μM) with chloride ion (4.5 μM) in 70:30 methanol-water medium at 25 °C. Bottom panel: the integrated heat effects after correction of the heat of dilution against the molar ratio of chloride.

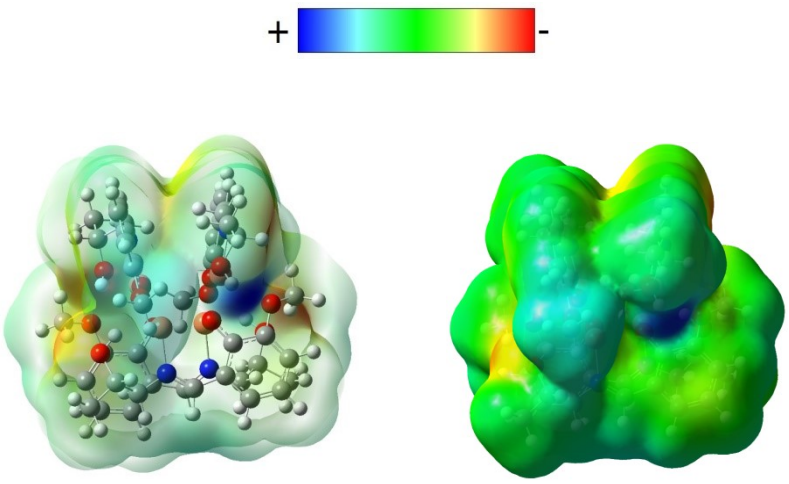

Fig S10. The molecular electrostatic potential analysis (MEP) diagram of **C1**

Table S6: Calculated HOMO-LUMO energy gaps of complex 1 in the solvent phase; Gas phase values are also mentioned in the parenthesis.

System	E & ΔE (all in eV)	DFT Functionals		
		B3LYP	TPSSH	BP86
1	E_{HOMO}	-4.81 (-4.44)	**-4.22** (-3.82)	-4.00 (-3.65)
	E_{LUMO}	-1.43 (-1.17)	**-1.76** (-1.44)	-2.33 (-2.02)
	ΔE	3.38 (3.27)	**2.46** (2.38)	1.67 (1.63)

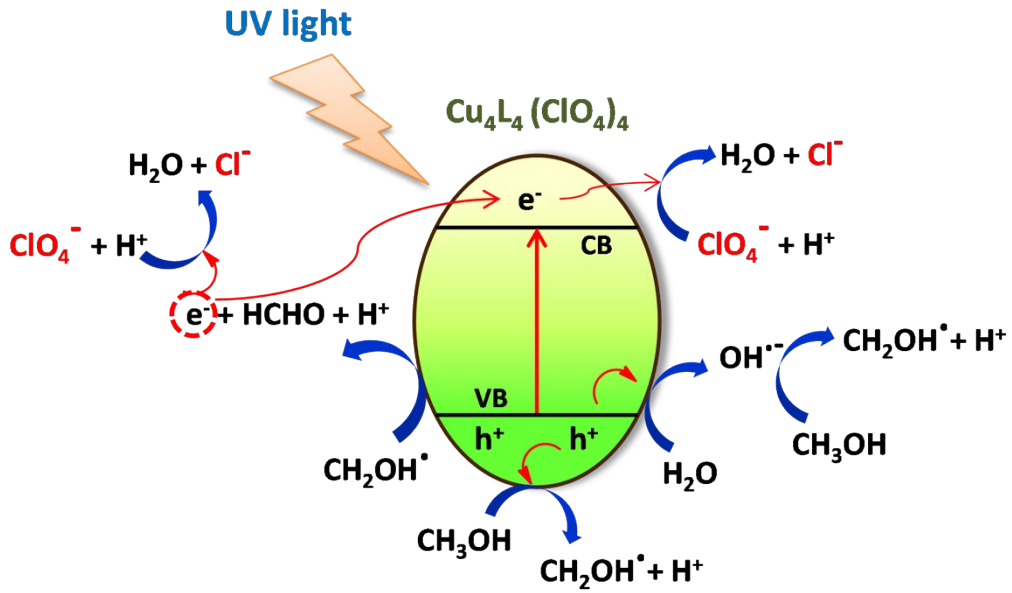

Fig S11. Schematic representation of photocatalytic mechanism of chlorate reduction in presence of **C1**in 70:30 v/v MeOH-water medium.CB and VB present conduction and valence bands, respectively.

Table S7:Comparing the kinetic parameters with other analogous zinc or copper complexes for hydrolysis of nitrocefin

Metal-based catalysts for hydrolysis of nitrocefin	K_{cat}(S^{-1} or min^{-1}) or V_{max}(mol L^{-1} S^{-1})	pH	solvent	λ_{max} ofhydrol. pdt(nm)	Year[ref]
$[Cu_2L2(H_2O)_2Cl_3](H_2O)$ [HL2=4-chloro-2 ((2hydroxypropyl)imino)methyl)-6-methoxyphenol]	**5×10^3 min^{-1}**	**7.5**	**MeOH-water/tricine**	**486**	**This article**
$[Cu_2L_2CH_3COO)_2]$ L=saldman	**0.35×10^{-8} mol L^{-1} S^{-1}**	**7**	**DMSO-phosphate buffer**	**496**	**2017[1]**
$[CuZnL_2CH_3COO)_2]$ L=saldman	**0.48×10^{-8} mol L^{-1} S^{-1}**	**7**	**DMSO-phosphate buffer**	**496**	**2017[1]**
$Cu_2(H_2pat^1)(OH)^+$	**11.34×10^{-3} S^{-1}**	**11.5**	**ACN-HEPES**	**390**	**2016[2]**
$[Zn_2$**L1**$(\mu\text{-}OAc)(OAc)_2(H_2O)]$ HL1=2-((diethylamino)methyl)-6-((dimethylamino)methyl)-4-methyl phenol	**4.12×10^{-6} mol L^{-1} min^{-1}**	**7.5**	**DMSO-HEPES**	**oxacillin at 254 nm**	**2011[3]**
$[Zn_2$**L1**$(\mu\text{-}NO_3)(NO_3)_2]$ **L1**=*N*,*N*′-bis(6-methyl-2-pyridylmethyl)-*N*,*N*′-bis(2-pyridylmethyl)-*N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine	**0.21 min^{-1}**	**7**	**DMSO-MOPS**	**496**	**2001[4]**
$[Zn_2($**BPAN**$)(\mu\text{-}OH)(\mu\text{-}O_2PPh_2)](ClO_4)_2$ **BPAN=**2,7-bis[2-(2-pyridylethyl)aminomethyl]-1,8-naphthyridine	**0.075 min^{-1}**	**7**	**DMSO-MOPS**	**496**	**2001[4]**
$[Zn_2$**L1**$(i\text{-}NO_3)(NO_3)_2]$ [**HL1**= 2,6-bis{[*N*-(2-dimethylaminoethyl)-*N*-methyl] aminomethyl}-4-methylphenol]	**6×10^3 min^{-1}**	**7.5**	**DMSO-HEPES**	**486**	**2000[5]**
$[Zn_2$**L1**$(i\text{-}OMe)(NO_3)_2]$ [**HL1**=2,6-bis{[*N*-(2-dimethylaminoethyl)-*N*-methyl] aminomethyl}-4-methylphenol]	**4.2×10^3 min^{-1}**	**7.5**	**DMSO-HEPES**	**486**	**2000[5]**
$[Zn_2$**L1**$(i\text{-}OH)(NO_3)_2]$ [**HL1**=2,6-bis{[*N*-(2-dimethylaminoethyl)-*N*-methyl] aminomethyl}-4-methylphenol]	**3.1×10^3 min^{-1}**	**7.5**	**DMSO-HEPES**	**486**	**2000[5]**
$[Zn_2L2(NO_3)_3]$ [**HL2=***N*,*N*-bis(2-pyridylmethyl)-*tert*butylamine (bpta)]	**13.7×10^3 min^{-1}**	**7.5**	**DMSO-HEPES**	**486**	**2000[5]**
$Zn(cyclen)(NO_3)_2$	**2.8×10^3 min^{-1}**	**7.5**	**DMSO-**	**486**	**2000[5]**

			HEPES		
$Zn(bpta)(NO_3)_2$	**7.2×10^3 min^{-1}**	**7.5**	**DMSO-HEPES**	**486**	**2000[5]**
$[Cd_4(CO_2EtH_2\mathbf{L1})_2(CH_3COO)_{3.75}C_{l0.25}(H_2O)_2](PF_6)_2$ [CO_2EtH_2**L1**=Ethyl 4-Hydroxy-3,5-bis(((2-methoxyethyl)-(pyridin-2-ylmethyl)amino) Methyl)Benzoate)]	**9.4×10^{-3} S^{-1}**	**8**	**ACN-HEPES**	**510**	**2012[6]**
$[Cd_2(CO_2Et\mathbf{L2})(CH_3COO)_2](PF_6)$ [CO_2Et**L2=**Ethyl 4-Hydroxy-3,5-bis(((2-methoxyethyl)-(pyridin-2-ylmethyl)amino) Methyl)Benzoate]	**9.7×10^{-3} S^{-1}**	**8**	**ACN-HEPES**	**510**	**2012[6]**

Cartesian Co-ordinate of **1** (**TPSSH optimized**)

0 1

Cu	-0.90676800	1.95537500	-0.04380000
Cu	-0.90233300	-1.95734800	0.03840300
Cu	0.91053000	-0.03996500	-1.95228800
Cu	0.89843200	0.04196200	1.95758900
O	0.88693900	-1.84152800	-0.77629800
O	-0.87747900	0.77898300	-1.84505600
O	-0.88656300	-0.78221800	1.84092400
O	0.87765500	1.84385000	0.78227700
O	0.52864600	3.88000000	-0.91682300
O	-1.49260600	4.60194100	1.29935300
H	-0.88594700	4.31218400	0.59727800
O	1.49587600	1.30712900	-4.59702500
H	0.89150500	0.60251300	-4.30865300
O	-1.47360400	-4.60580200	-1.30850900

H	-0.87150800	-4.31501300	-0.60293400
O	-0.54332400	0.91815800	3.87668400
O	1.47037000	-1.30226800	4.60723200
H	0.86622400	-0.59941800	4.31412500
O	-0.51739400	-0.91831800	-3.88052100
O	0.53209900	-3.87998400	0.91909600
N	2.82242500	-0.23561500	-2.34611100
N	-2.81257900	-2.35989100	0.23109800
N	-2.81700400	2.35269100	-0.24749600
N	2.80733000	0.24240100	2.36370100
C	1.93260500	2.52375000	0.43847600
C	1.94119200	-2.51958900	-0.42687900
C	-1.92971500	0.43069600	-2.52687300
C	1.81714500	3.61492800	-0.48798900
C	-1.94391200	-0.43547400	2.51557400
C	-1.80822900	-0.49520300	-3.61789000
C	-3.57803900	-1.84122400	1.14016100
H	-4.64529800	-2.10101000	1.09793800
C	3.58396100	-1.14647500	-1.82484100
H	4.65240800	-1.10606700	-2.07999500
C	-3.57569100	1.83211500	-1.16111900
H	-4.64384300	2.08915900	-1.12527400
C	-3.24499000	0.92604100	-2.24209000

C	3.24519600	2.23657500	0.93952000
C	1.82251700	-3.61171500	0.49805700
C	3.56992200	1.15492600	1.84694700
H	4.63682700	1.11725600	2.10888900
C	-3.45608000	3.22867700	0.73529300
H	-3.35202800	2.77031200	1.72592800
H	-4.53055100	3.33245300	0.51670800
C	4.35346100	-3.01810000	-0.48734000
H	5.34141000	-2.78123400	-0.87559800
C	3.25612600	-2.22940000	-0.92006200
C	-3.25623500	-0.93390000	2.22275900
C	-2.82263800	4.63343100	0.79362000
H	-2.83059800	5.05411800	-0.22523800
C	-2.90016400	-0.90007800	-4.36274000
H	-2.76562000	-1.59894600	-5.18215600
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C	2.91219200	4.35777700	-0.88811500

H	2.78216800	5.17741500	-1.58758300
C	4.34345900	3.02719700	0.51269000
H	5.32958600	2.79260000	0.90690800
C	-2.80635700	-4.64062200	-0.81018300
H	-2.81897600	-5.06133200	0.20861200
C	-3.44358800	-3.23742100	-0.75548800
H	-3.33470900	-2.77876300	-1.74546800
H	-4.51909300	-3.34382400	-0.54333800
C	4.19466700	4.06400500	-0.38527300
H	5.04854500	4.65491400	-0.69946700
C	3.45902700	0.75029200	-3.22039100
H	4.53459600	0.53624000	-3.32222300
H	3.34993300	1.74026900	-2.76179100
C	4.20149800	-4.05598400	0.40885400
H	5.05470500	-4.64548600	0.72748200
C	-4.18536500	-0.40284100	-4.07125800
H	-5.03678600	-0.72071800	-4.66374000
C	-4.33995400	0.49441900	-3.03471100
H	-5.32820400	0.88437900	-2.80194700
C	-0.33458300	-2.28285900	-4.27804700
H	0.74004700	-2.46577400	-4.23110100
H	-0.68169000	-2.45107900	-5.30399500
H	-0.84881500	-2.95795000	-3.58634900

C	-3.60470000	-5.55423700	-1.73598300
H	-3.62002400	-5.14449100	-2.75162500
H	-4.63732600	-5.66664700	-1.39065200
H	-3.13890800	-6.54202400	-1.77598400
C	3.44075000	-0.74155400	3.24244500
H	3.33683600	-1.73198300	2.78360400
H	4.51516600	-0.52496500	3.35090200
C	2.82801500	0.80680400	-4.62632200
H	2.84093500	-0.21175300	-5.04760500
C	-0.36616800	2.28314900	4.27505700
H	-0.71978500	2.45069800	5.29889300
H	-0.87787600	2.95690500	3.58018100
H	0.70828900	2.46857500	4.23445400
C	-4.21124900	0.39447700	4.04468900
H	-5.06714600	0.71098800	4.63142700
C	3.63171500	1.73195500	-5.53588000
H	3.17028300	1.77327000	-6.52565800
H	4.66429300	1.38512500	-5.64401300
H	3.64679400	2.74731600	-5.12543200
C	-2.92906300	0.89495800	4.34386700
H	-2.80138200	1.59502000	5.16335800
C	-4.35720100	-0.50411100	3.00804800
H	-5.34307100	-0.89648500	2.76932300

C	-3.62841900	5.54507000	1.71491500
H	-3.64834100	5.13532700	2.73047900
H	-4.65939400	5.65482700	1.36384800
H	-3.16537400	6.53404200	1.75744000
C	3.60132600	-1.72147600	5.55955600
H	3.13382700	-1.76333200	6.54645900
H	4.63236500	-1.37207300	5.67392200
H	3.62142500	-2.73703800	5.14982000
C	0.34856100	-4.27502800	2.28434500
H	0.85768000	-3.57895000	2.95879600
H	0.70072900	-5.29870000	2.45583900
H	-0.72668800	-4.23333000	2.46488700
C	2.80110200	-0.79879000	4.64445200
H	2.80899000	0.22006300	5.06515600

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