Supporting Information

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Photocytotoxic Activity of Copper(II) and Zinc(II) Complexes of Curcumin and (Acridinyl)dipyridophenazine

Nandini Mukherjee, Abinaya Raghavan, Santosh Podder, Shamik Majumdar, Arun Kumar, Dipankar Nandi,* and Akhil R. Chakravarty*

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Experimental Section

Materials

The chemicals and reagents were procured from various commercial sources (Sigma-Aldrich, USA; S. D. Fine Chemicals, India) and used without further purification. Standard procedures from the literature were followed to purify the solvents.^[S1] Supercoiled (SC) pUC19 DNA (caesium chloride purified) was obtained from Bangalore GeNeiTM (India). FBS was procured from Gibco®. DPBS, DMEM, propidium iodide (PI), MTT, calf thymus (ct) DNA, agarose (molecular biology grade), KI, NaN₃, superoxide dismutase (SOD), catalase, TEMP, DABCO (1,4-diazabicyclo[2.2.2]octane), ethidium bromide (EB), bromophenol blue, xylene cyanol and Annexin-V-FITC/PI kit were purchased from Sigma-Aldrich, USA. DCFDA was procured from Calbiochem®, USA.

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Instrumentation

The elemental analysis was performed on a Thermo Finnigan Flash EA 1112 CHN analyzer. The infrared, absorption and fluorescence spectra were recorded using Bruker Alpha, Perkin-Elmer Spectrum 650 and HORIBA Jobin Yvon IBH TCSPC fluorimeter, respectively. The cyclic voltammograms were recorded at 298K in DMF using EG&G PAR model 253 Versastat potentiostat/galvanostat having a three electrode setup with glassy carbon as working, platinum wire as auxiliary and saturated calomel electrode as the reference electrode (SCE). The supporting electrolyte used was tetrabutylammonium perchlorate (TBAP, 0.1 M). Molar conductivity measurements were carried out on a Control Dynamics (India) conductivity meter. The magnetic susceptibility data were obtained from a Sherwood scientific magnetic susceptibility balance at 25°C. Electrospray ionization mass spectra (ESI-MS) were recorded on an Agilent 6538 Ultra high definition (UHD) accurate Mass-Q-TOF (LC-HRMS) and Micromass ESI-TOF MS instruments. ¹H NMR spectra for the ligands and diamagnetic zinc(II) complexes were obtained using a Bruker Avance 400 MHz NMR spectrometer. Flow cytometric experiments were carried out using the BD FACS-VerseTM instrument (BD Biosciences, USA). Confocal microscopic images were acquired on the Leica microscope (TCS-SP5, Germany) using water immersion objective with magnification of 63X.

Synthesis of the complexes 1-5

The copper(II) complexes **1-3** were synthesized following a general synthetic method in which copper(II) nitrate trihydrate (0.12 g, 0.5 mmol) was reacted with a methanol-acetonitrile solution (15 mL, 1:1 v/v) of curcumin (Hcur) (0.18 g for **1**, **2**; 0.5 mmol) or acetylacetone (Hacac) (0.05 g for **3**, 0.5 mmol) in presence of a base (triethylamine, 0.05 g; 0.5 mmol) for 15 min at room temperature with subsequent addition of a methanol solution (20 mL) of the dipyrrophenazine ligand (0.14 g dppz for **1**, 0.5 mmol) or a methanol-chloroform mixture (20 mL, 1:2 v/v) of acridinedipyrrophenazine ligand (0.23 g acdppz for **2**, **3**; 0.5 mmol). The filtrate was evaporated to obtain the complexes in the solid state and the solid was washed thoroughly with ice-cold methanol, acetonitrile, chloroform and finally diethyl ether and dried in vacuum over P₄O₁₀. To synthesize the zinc(II) complexes **4** and **5**, a methanol solution (10 mL) of zinc(II) nitrate hexahydrate (0.15 g, 0.5 mmol) was reacted with the phenanthroline derivative (0.14 g dppz for **4** and 0.23 g acdppz for **5**; 0.5 mmol). The reaction mixture was stirred for 15 min at room temperature. Thereafter, a methanol-acetonitrile solution (15 mL) containing deprotonated curcumin (Hcur) (0.18 g for **4**, **5**; 0.5 mmol) was added to the reaction mixture and stirred at room temperature for 1 h. The precipitate of the complexes, collected after 1 h

of stirring, was washed with ice-cold methanol, acetonitrile, chloroform and diethyl ether and dried in vacuum over P_4O_{10} .

[Cu(dppz)(cur)](NO₃) (1) (M_w = 775.23): Yield: 75%; elemental analysis calcd (%) for C₃₉H₂₉CuN₅O₉: C 60.42, H 3.77, N 9.03; found: C 59.91, H 3.80, N 8.99; ESI-MS in MeOH (m/z): 712.0559 [M – (NO₃)]⁺; Λ_M in DMF: 57 S cm² mol⁻¹ at 25°C; UV/Vis in 10% aqueous DMSO [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 455 (20,250), 415 (30,000), 380 (39,220), 360 (34,360), 279 (77,150); FT-IR [$\tilde{\nu}$ (cm⁻¹)]: 3254 (w, br), 3056 (w), 2950 (w), 1590 (m), 1506 (vs), 1453 (s), 1392 (s) (NO₃⁻), 1275 (s), 1161 (s), 1127 (m), 1075 (m), 1029 (m), 975 (m), 819 (m), 766 (m), 725 (w), 423 (w) [vs, very strong; s, strong; m, medium; w, weak; br: broad]; μ_{eff} = 2.04 μ_B at 25°C.

[Cu(acdppz)(cur)](NO₃) (2) (M_w = 952.44): Yield: 82%; elemental analysis calcd (%) for C₅₂H₃₆CuN₆O₉: C 65.58, H 3.81, N 8.82; found: C 65.23, H 4.01, N 8.75; ESI-MS in MeOH (m/z): 889.2046 [M – (NO₃)]⁺; Λ_M in DMF: 74 S cm² mol⁻¹ at 25°C; UV/Vis in 10% aqueous DMSO [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 614 (158), 459 (30,330), 433 (36,420), 388 (40,450), 364 (35,880), 279 (58,640); FT-IR [$\tilde{\nu}$ (cm⁻¹)]: 3254 (w, br), 3065 (w), 2940 (w), 1590 (m), 1505 (vs), 1445 (s), 1390 (s) (NO₃⁻), 1277 (s), 1160 (s), 1121 (s), 1075 (m), 1031 (m), 970 (m), 820 (m), 760 (m), 730 (w), 423 (w); μ_{eff} = 1.98 μ_B at 25°C.

[Cu(acdppz)(acac)](NO₃) (3) (M_w = 684.17): Yield: 80%; elemental analysis calcd (%) for C₃₆H₂₄CuN₆O₅: C 63.20, H 3.54, N 12.28; found: C 62.91, H 3.82, N 12.06; ESI-MS in MeOH (m/z): 621.1647 [M – (NO₃)]⁺; Λ_M in DMF: 50 S cm² mol⁻¹ at 25°C; UV/Vis in 10% aqueous DMSO [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 632 (90), 386 (17,920), 361 (19,100), 271 (54,340); FT-IR [$\tilde{\nu}$ (cm⁻¹)]: 3065 (w), 1573 (s), 1520 (s), 1352 (s) (NO₃⁻), 1074 (s), 1016 (w), 824 (m), 762 (m), 726 (m), 426 (m); μ_{eff} = 1.81 μ_B at 25°C.

[Zn(dppz)(cur)](NO₃) (4) (M_w = 777.07): Yield: 70%; elemental analysis calcd (%) for C₃₉H₂₉ZnN₅O₉: C 60.28, H 3.76, N 9.01; found: C 59.72, H 3.99, N 9.18; ESI-MS in MeOH (m/z): 713.1072 [M – (NO₃)]⁺; Λ_M in DMF: 65 S cm² mol⁻¹ at 25°C; UV/Vis in 10% aqueous DMSO [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 451 (28,630), 430 (31,500), 380 (22,780), 362 (19,930), 273 (85,990); FT-IR [$\tilde{\nu}$ (cm⁻¹)]: 3057 (w), 3000 (w), 1590 (m), 1502 (vs), 1386 (s), 1280 (s), 1160 (s), 1123 (m), 1030 (w), 977 (m), 838 (m), 718 (m), 556 (m), 470 (m), 440 (w); ¹H NMR (400 MHz, [D₆]DMSO, 25°C, TMS): 9.76 (s, 2H), 9.50 (s, 2H), 9.39 (s, 2H), 8.43 (s, 2H), 8.32 (s, 2H), 8.13 (s, 2H), 7.52 (2H), 7.28 (s, 2H), 7.08 (s, 2H), 6.80-6.76 (m, 4H), 5.85 (s, 1H), 3.83 (s, 6H) (s, singlet; m, multiplet).

[Zn(acdppz)(cur)](NO₃) (5) (M_w = 954.27): Yield: 63%; elemental analysis calcd (%) for C₅₂H₃₆ZnN₆O₉·CHCl₃: C 59.29, H 3.47, N 7.83; found: C 58.79, H 3.65, N 7.95; ESI-MS in MeOH (m/z): 890.1873 [M – (NO₃)]⁺; Λ_M in DMF: 58 S cm² mol⁻¹ at 25°C; UV-Vis in 10% aqueous DMSO [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 450 (41,360), 428 (47,920), 390 (42,470), 365 (33,840), 272 (65,280); FT-IR [$\tilde{\nu}$ (cm⁻¹)]: 3057 (w), 3000 (w), 1592 (m), 1495 (vs), 1445 (s), 1385 (s), 1275 (s), 1160 (s), 1123 (m), 1030 (w), 966 (m), 826 (m), 718 (m), 552 (m), 464 (m), 416 (w); ¹H NMR (400 MHz, [D₆]DMSO, 25°C, TMS): 9.81 (s, 2H), 9.50-9.36 (4H), 8.66 (s, 1H), 8.60 (d, 1H, *J* = 8 Hz), 8.39 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 2H), 8.09 (d, *J* = 8 Hz, 2H), 7.81 (2H), 7.59-7.55 (m, 4H), 7.50 (m, 2H), 7.27 (s, 2H), 7.09 (s, 2H), 6.82-6.73 (m, 4H), 5.87 (s, 1H), 3.81 (s, 6H) (d, doublet).

X-ray crystallographic and computational procedures

The crystal structure of complex **3a** was obtained by the single crystal X-ray diffraction method.^[S2-S4] Green crystals of the complex as an analogue of **3** were obtained from the reaction mixture in chloroform-methanol. A block-shaped crystal of dimensions 0.4 × 0.2 × 0.1 mm³ was mounted on a

crystal mounting loop with the help of paratone oil. The intensity data were collected at 100K using a graphite-monochromated Mo-K α X-ray source ($\lambda = 0.71073$ Å) on an automated Bruker SMART APEX-II CCD diffractometer. The structure was solved by the WinGX-software, which utilizes the SHELXL-2014 module. The perspective view of the molecule was obtained by ORTEP. Selected crystallographic data are: $C_{36}H_{26}CuN_5O_3 \cdot N_{0.5}O_{1.5} \cdot Cl_{0.5}$, Fw ($g\ M^{-1}$) = 688.89, space group *Pnna*, $a = 27.071(2)$, $b = 18.4185(17)$, $c = 16.0876(15)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 8021.5(12)$ Å³, $Z = 8$, $\rho_{calcd} = 1.141\ g\ cm^{-3}$, $T = 100(2)K$, reflections collected/unique: 248217/9304, $R(000) = 2832$, Goodness-of-fit = 1.092, $R(F_o)$ [$wR(F_o)$] = 0.1428 [0.3108] for 5180 reflections [$I > 2\sigma(I)$] and 428 parameters; R (all data) [wR (all data)] = 0.2236 [0.3756]. The CCDC deposition number is 1856304. The presence of two different lattice anions, namely, Cl^- and NO_3^- was resolved from the intensity of the associated peaks in the difference Fourier maps. Both the anions were located at special positions in the asymmetric unit thus refining with a site-occupancy of half of the chloride, one nitrogen atom and one oxygen atom of the nitrate anion. One oxygen atom of the nitrate anion was refined with site occupancy of 1.0 generating the symmetry related other oxygen atom belonging to another asymmetric unit. These anions did not show any apparent effect on the structure of the cationic complex.

The overall quality of the data was in low resolution, even when collected at 100K, which is attributed to the poor quality of the crystal. Because of this, the value of R_{int} was greater than 0.25. Several refinement cycles were performed to get a satisfactory convergence of the refinement. The level “A” alerts were due to poor diffraction quality of the crystal. The dataset contained solvent accessible voids with some amount of solvent molecule(s) used for crystallization which were not modelled properly. To avoid these voids the dataset was treated with the SQUEEZE routine in PLATON.^[S5] These solvent voids had a solvent accessible volume of 2466 Å³. The overall structure was in conformity with the expected structure of the complex. The structure obtained from this analysis was found to be suitable for molecular characterization of the complex and not for crystallographic details with low residual values.

Optimization of the geometries of the complexes **1-5** was done by density functional theory (DFT) using B3LYP level of theory and LanL2DZ basis set in Gaussian09 program (Table S3).^[S6-S8]

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Cell viability assay

MTT assay was performed to study the photocytotoxic activity of the complexes in three cancer cell lines viz. HeLa (cervical cancer), HepG2 (liver cancer) and MCF-7 (breast cancer).^[S9] Approximately 8×10^3 cells were seeded in 96 well plates in 100 μ L medium for an individual cell line. The cells were grown for 24 h at 37°C in a CO₂ incubator. The complexes were dissolved in DMSO: medium (1:99, v/v) and were added to the cells at different concentrations. Following 4 h of incubation, the medium was discarded from each well and DPBS was added. Subsequently, the cells were photo-irradiated with a broad-band visible light (400-700 nm) source for 1 h using a Luzchem Photoreactor (Model LZC-1, Ontario, Canada; light dose: 10 J cm⁻² light fluence rate: 2.4 mW cm⁻²). Next, the DPBS was removed and fresh medium was added. The medium of the control non-photo-irradiated plates was replaced with fresh medium. Both the control and the photo-irradiated plates were incubated further for 20 h in dark with subsequent addition of 25 μ L MTT (4 mg mL⁻¹) in each well and then incubated for another 3 h in dark. The culture medium was finally discarded from the plates followed by addition of 200 μ L DMSO to the wells to dissolve the purple formazan crystals and its absorbance at 570 nm was measured using a Molecular Devices Spectra Max M5 plate reader. The IC₅₀ values were calculated using a nonlinear regression analysis method (Graph Pad Prism 6).^[S10]

* To perform the cell viability assay with sparingly soluble acdppz ligand, a 200 μ M stock solution (instead of 1 or 2 mM) in DMSO was made by heating at 40 °C and this solution was used with further dilution. The assay was finally performed in 16% DMSO-cellular medium. To compare the results, the same condition was maintained for Curcumin and complexes **2** and **5**. The cell viability plots and IC₅₀ values obtained in this experimental condition are given in figures S29 and S30.

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Cell culture and cellular incorporation assay

HeLa, MCF7 and HepG2 cells were grown in 100 mm culture dishes (SPL Life sciences, Korea) in DMEM medium (supplemented with 10% FBS, 100 μ g mL⁻¹ streptomycin, and 100 U mL⁻¹ penicillin) and incubated in a humidified 5% CO₂ incubator (Sanyo, UK) at 37 °C. Approximately, 0.3×10^6 cells per well in 6-well plates were seeded and cultured for 24 h. Subsequently, the cells were treated with the complexes **2** (2 μ M, 0.2 % DMSO) or **5** (2 μ M, 0.2 % DMSO), ligands acdppz (2 μ M, 10 % DMSO), curcumin (2 μ M, 0.2% DMSO) and combination of the ligands [acdppz (2 μ M) + curcumin (2 μ M) in 10% DMSO] for 4 h in dark post which they were washed with PBS and then trypsinized. The cells were then re-suspended in PBS and acquired on the BD FACS Verse™ flow cytometer (BD Biosciences, USA). Approximately 1×10^4 cells in the singlet (forward scatter-area vs. forward scatter-height) and live gate (forward scatter-area vs. side scatter-area) were acquired for analysis. Analysis and depiction of the results as histograms were performed using the flow cytometry analysis software, FlowJo® (USA) or FCS express, version 5.

DCFDA assay for ROS detection

The cell-permeant fluorogenic dye, 2',7'-dichlorofluorescein diacetate (DCFDA, 287810, Calbiochem®, USA) was used to stain the cells for quantification of intracellular oxidative stress. The cells were seeded in 6-well plates and incubated for 24 h, post which they were treated with the copper(II) and zinc(II) complexes **2** (2 μ M, 0.2 % DMSO) or **5** (2 μ M, 0.2 % DMSO), ligands acdppz (2

μM , 10 % DMSO), curcumin (2 μM , 0.2% DMSO) and combination of the ligands [acdppz (2 μM) + curcumin (2 μM) in 10% DMSO] for 4 h, followed by photo-exposure for 1 h or the cells were incubated in dark. The cells were subsequently washed with PBS, trypsinized and enumerated by Trypan blue exclusion assay using a haemocytometer. Approximately, 0.25×10^6 cells were stained with the mentioned doses of DCFDA for 30 min at 37°C in dark. The cells were washed with PBS and $\sim 1 \times 10^4$ cells in the live singlet gate were acquired on the BD FACS Verse™ flow cytometer. The flow cytometry software, FlowJo® (USA) and FCS express, version 5 was used for analysis and depiction of the results as histograms.

Confocal Imaging post DCFDA-staining

The intracellular localization of the green emissive DCF-oxidized product was investigated using Leica microscope (TCS, SP8) with oil immersion lens having magnification of 63X. Approximately 5×10^4 HeLa cells were grown on glass bottom tissue culture plates in DMEM-10% FBS media and incubated for 24 h, post which they were treated with the complexes **2** (2 μM , 0.2 % DMSO) or **5** (2 μM , 0.2 % DMSO), and incubated at 37°C for 4 h. Complex untreated control cells were also incubated in identical conditions. The cells were subsequently stained with DCFDA (0.3 μM) for 30 min followed by photo-exposure for 30 min or the cells were incubated in dark. The cells were then stained with Hoechst 33342 dye (1.5 μM) for 10 min at 37°C in dark. Finally, the cells were washed with PBS to remove excess stain and subjected to live imaging. Multiple images were recorded from different parts of the plates.

Annexin-V-FITC/PI assay

The mode of cell death was determined using the Annexin-V-FITC/PI assay. The cells were seeded in 6-well plates and incubated for 24 h, post which the cells were incubated with ligands acdppz (2 μM , 10% DMSO), curcumin (2 μM , 0.2% DMSO), a combination of the ligands [acdppz (2 μM) + curcumin (2 μM) in 10 % DMSO] and 2 different concentrations of the complexes **2** and **5** [(0.4 μM , 0.1% DMSO), (2 μM , 0.2 % DMSO); vide text] for 4 h and photo-exposure was provided for 1 h (400-700 nm, light dose = 10 J cm^{-2}) in DPBS or the cells were incubated in dark. Next, the untreated, unexposed and photo-exposed cells were incubated in dark for 10 h. Subsequently, the cells were washed, trypsinized and the live cells were enumerated by Trypan blue assay using a haemocytometer. The cells were then stained with Annexin-V (conjugated to FITC) and PI, according to the manufacturer's instructions (APOAF, Sigma-Aldrich, USA). Approximately, 1×10^4 cells in the singlet gate were acquired on the BD FACS Verse™ flow cytometer. The FACS software, FACSDiva™ (BD Biosciences, USA) and FCS express, version 5 was used to construct the Annexin-V-FITC versus PI dot-plots to analyse the results.^[S10]

Confocal microscopy

The intracellular localization of the complexes was studied using a confocal microscope. Approximately, 3×10^5 HeLa cells were seeded and grown for 24 h on 35 mm polymer culture dishes. The cells were then incubated with complex **2** (15 μM , 1% DMSO) or **5** (10 μM , 1% DMSO) for 4 h in the dark at 37°C in a CO₂ incubator. Thereafter, the complex containing medium was replaced with fresh medium and live cell imaging was carried out on a Leica TCS SP5 upright confocal microscope using 63X HCX APO L U-V-I objective (NA 0.9). The complexes were excited with the laser 405 nm and emission was collected between 411–539 nm. Laser intensities and amplifier gains were adjusted to avoid pixel saturation during image acquisition.

DNA binding experiments

Binding of the complexes **1-5** to ct-DNA was studied by UV-visible absorption titration in Tris-HCl/NaCl buffer (5 mM Tris-HCl, 5 mM NaCl, pH=7.2). Purity of ct-DNA was checked from the ratio of

absorbance at 260 and 280 nm, which was approximately 1.9:1 indicating the absence of protein impurity. The concentration of DNA was measured from its absorption intensity at 260 nm with its known molar extinction coefficient (ϵ) value of $6600 \text{ M}^{-1} \text{ cm}^{-1}$. A $30 \text{ }\mu\text{M}$ DMF-solution of the complexes was used for the study. The titration experiments were performed by increasing the concentration of ct-DNA while keeping the complex concentration constant. Necessary corrections were made for absorbance of the complexes and ct-DNA itself. Each spectrum was recorded only after 5 min of ct-DNA addition to allow equilibration of the sample. The intrinsic binding constant (K_b) of the complexes to ct-DNA was calculated by non-linear curve fitting using McGhee-von Hippel (MvH) equation. The non-linear regression analysis equation was: $(\epsilon_a - \epsilon_f)/(\epsilon_b - \epsilon_f) = (b - (b^2 - 2K_b^2 C_t [DNA]_f/s)^{1/2})/2K_b C_t$, where $b = 1 + K_b C_t + K_b [DNA]_f/2s$, ϵ_a is the molar extinction coefficient of the charge transfer (CT) band at a given DNA concentration, ϵ_f is the molar extinction coefficient of DNA unbound complex, ϵ_b is molar extinction coefficient of complex when fully bound to DNA, C_t is the total complex concentration, $[DNA]_f$ is the DNA concentration, K_b is the equilibrium binding constant and s is the MvH fitting parameter.^[S11,S12] The graph plotting and non-linear least square analyses were done using Origin Lab, version 8.

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[S12] M.T. Carter, M. Rodriguez, A.J. Bard, *J. Am. Chem. Soc.* **1989**, *111*, 8901-8911.

DNA cleavage experiments

The DNA cleavage activity of the complexes was studied using supercoiled (SC) pUC19 DNA ($1 \text{ }\mu\text{L}$, $30 \text{ }\mu\text{M}$, 2686 base-pairs) in 50 mM Tris-HCl buffer containing 50 mM NaCl solution. Chemical nuclease activity of the complexes was studied using glutathione (GSH, 5 mM) as external reducing agent. For the photocleavage study, monochromatic UV-A light of 365 nm (Lamp power: 12 W , 30 min exposure) and monochromatic blue light of 446 nm (laser power: 50 mW , 45 min exposure) from a continuous-wave (CW) diode laser (Laser century make, model no. BLM442TA-100) were used. Agarose gel was used for gel electrophoresis. To determine the type of ROS generated by the complexes, mechanistic studies were carried out by adding specific radical quenching/scavenging agents (NaN_3 : 5 mM , TEMP: 5 mM , DABCO: 5 mM , D_2O : $16 \text{ }\mu\text{L}$, KI: 5 mM , DMSO: $4 \text{ }\mu\text{L}$, catalase: 4 unit , SOD: 8 unit). The samples were incubated in dark for 1 h (prior to 446 nm irradiation) or 1.5 h (prior to 365 nm UV-A light-irradiation) at 37°C . The irradiated samples and non-irradiated controls were then loaded with a dye containing 0.25% xylene cyanol, 0.25% bromophenol blue and 30% glycerol and finally casted in 1% agarose gel containing $0.5 \text{ }\mu\text{g mL}^{-1}$ ethidium bromide. Gel electrophoresis was performed in dark for $\sim 2 \text{ h}$ at 60 V in TAE (Tris Acetate EDTA) buffer. The DNA bands were visualized by UV-light and photographed. An UVITECH Gel Documentation System was used to determine the intensities of the bands, which quantify the extent of SC DNA cleavage. All the experiments were performed keeping appropriate controls.

[S13] J. Bernadou, G. Pratviel, F. Bennis, M. Giardet, B. Meunier, *Biochemistry* **1989**, *28*, 7268-7275.

Singlet oxygen generation experiment

DPBF titration experiments were performed to study singlet oxygen generation by the complexes. A $10:1$ molar ratio of DPBF and the complex was taken in air-saturated DMSO solutions and photo-irradiated with 446 nm monochromatic laser (CW Laser power: 50 mW ; CW, continuous wave). Each exposure was for 10 sec following which their absorption spectra were recorded. The absorbance of DPBF at 417 nm was monitored and from the linear plots of absorbance vs. irradiation time, the slopes were calculated. The experiments were performed with low concentration of the DPBF ($5 \text{ }\mu\text{M}$)

and the complexes (0.5 μM) in order to avoid singlet oxygen quenching by the dyes.^[S14] While calculating the absorbance decay rates, necessary corrections were made to minimize the error due to photo-degradation of DPBF alone at 446 nm irradiation. The DPBF titration experiment was also performed on the complexes irradiated with UV-A light of 365 nm light (Lamp power, 12 W; exposure, 10 s). Higher concentration of DPBF (50 μM) was used in order to minimize self-degradation of DPBF on UV light exposure.

[S14] A. Bhattacharyya, A. Dixit, S. Banerjee, B. Roy, A. Kumar, A. A. Karande, A. R. Chakravarty, *RSC Adv.*, **2016**, 6, 104474-104482.

Schemes and Figures

Scheme S1. Synthesis of the copper(II) complexes 1-3.

Scheme S2. Synthesis of the zinc(II) complexes 4 and 5.

Figure S1. The ESI-MS of complex **1** showing the $[M-NO_3]^+$ peak at 712.0559 (m/z) in methanol (top) and the isotopic distribution pattern observed (bottom).

Figure S2. The ESI-MS of complex **2** showing the $[M-NO_3]^+$ peak at 889.2046 (m/z) in methanol (top) and the isotopic distribution pattern observed (bottom).

Figure S3. The ESI-MS of complex **3** showing the $[M-NO_3]^+$ peak at 621.1647 (m/z) in methanol (top) and the isotopic distribution pattern observed (bottom).

Figure S4. The ESI-MS of complex **4** showing the $[M-NO_3]^+$ peak at 713.1072 (m/z) in methanol (top) and the isotopic distribution pattern observed (bottom).

Figure S5. The ESI-MS of complex **5** showing the $[M-NO_3]^+$ peak at 890.1873 (m/z) in methanol (top) and the isotopic distribution pattern observed (bottom).

Figure S6. IR spectrum of complex 1 in the solid phase.

Figure S7. IR spectrum of complex 2 in the solid phase.

Figure S8. IR spectrum of complex **3** in the solid phase.

Figure S9. IR spectrum of complex **4** in the solid phase.

Figure S10. IR spectrum of complex **5** in the solid phase.

Figure S11. ^1H NMR spectrum of paramagnetic copper(II) complex $[\text{Cu}(\text{dppz})(\text{cur})]\text{NO}_3$ (**1**) in DMSO-d_6 .

Figure S12. ^1H NMR spectrum of paramagnetic Cu(II) complex $[\text{Cu}(\text{acdppz})(\text{cur})]\text{NO}_3$ (2) in $\text{DMSO}-\text{d}_6$.

Figure S13. ^1H NMR spectrum of Zn(II) complex $[\text{Zn}(\text{dppz})(\text{cur})]\text{NO}_3$ (4) in $\text{DMSO}-\text{d}_6$.

Figure S14. 1H NMR spectrum of complex $[Zn(acdppz)(cur)]NO_3$ (5) in $DMSO-d_6$.

Figure S15. (a) Absorption and (b) emission spectra ($\lambda_{ex} = 430$ nm) of the complexes 1-5 in 1:1 (v/v) $DMSO:DPBS$.

Figure S16. Cyclic voltammograms of complex **1** showing cathodic (a), anodic (b), and small scan (c, d) in 0.1 M TBAP-DMF at a scan rate of 100 mV s⁻¹.

Figure S17. Cyclic voltammograms of complex **2** showing cathodic (a), anodic (b), and small scan (c, d) in 0.1 M TBAP-DMF at a scan rate of 100 mV s⁻¹.

Figure S18. Cyclic voltammograms of complex **3** showing cathodic (a), anodic (b), and small scan (c, d) in 0.1 M TBAP-DMF at a scan rate of 100 mV s^{-1} .

Figure S19. Cyclic voltammograms of complexes **4** and **5** showing cathodic [(a), **4**; (c), **5**] and anodic [(b), **4**; (d), **5**] scans in 0.1 M TBAP-DMF at a scan rate of 100 mV s⁻¹.

Figure S20. IR spectrum of complex **3a** in crystalline form.

Figure S21. (a) The unit cell packing diagram of complex **3a** with eight complex molecules in the unit cell with colour codes: C, grey; N, green; O, blue; Cl, violet; and Cu, red. **(b)** The unit cell packing diagram of complex **3a** showing π - π stacking interactions (sky blue dashed line) involving planar dppz and acridine moieties.

Figure S22. Energy optimized structures of the complexes **1** and **4** along with the corresponding HOMO and LUMO. Colour codes: C, black; N, green; O, dark blue; Cu, red; and Zn, light blue.

Figure S23. The time-dependent UV-visible spectra of free curcumin and the curcumin complexes **1**, **2**, **4** and **5** in 1:9 (v/v) DMSO: cellular medium (10% FBS in DMEM) in dark at 37°C [(a), Curcumin; (b), **1**; (c), **2**; (d), **4**; (e), **5**].

Figure S24. Absorption spectra of complexes **1**, **2**, **4** and **5** following 1 h of photoirradiation 1:1 (v/v) DMSO:DPBS (red) and prior to photo-irradiation (black).

Figure S25. Mass spectra of complexes **1-3** in methanol following 1 h of photoirradiation (400-700 nm) 1:1 (v/v) DMSO:DPBS [(a), **1**; (b), **2**; (c), **3**].

Figure S26. Photocytotoxicity of complexes 1-5 in HeLa cells upon irradiation with visible light (400-700 nm, 10 J cm^{-2} , red symbol) and in dark (black symbol) post 4 h of incubation with the complexes: [(a), 1; (b), 2; (c), 3; (d), 4; (e), 5].

Figure S27. Photocytotoxicity of complexes 1-5 in MCF-7 cells upon irradiation with visible light (400-700 nm, 10 J cm^{-2} , red symbol) and in dark (black symbol) post 4 h of incubation with the complexes: [(a), 1; (b), 2; (c), 3; (d), 4; (e), 5].

Figure S28. Photocytotoxicity of complexes **1-5** in HepG2 cells upon irradiation with visible light (400-700 nm, 10 J cm^{-2} , red symbol) and in dark (black symbol) post 4 h of incubation with the complexes: [(a), **1**; (b), **2**; (c), **3**; (d), **4**; (e), **5**].

Figure S29. Photocytotoxicity of ligands acridinyldipyridophenazine (Acdppz) (a), curcumin (Hcur) (b), Complex **2** (c) and Complex **5** (d) in HeLa cells upon irradiation with visible light (400-700 nm, 10 J cm^{-2} , red symbol) and in dark (black symbol) post 4 h of incubation with the compounds (16% DMSO-cellular medium).

Figure S30. Bar diagrams showing cytotoxicity of complexes and ligands on HeLa cells upon irradiation with visible light (400-700 nm, 10 J cm^{-2} , red symbol) and in dark (black symbol) post 4 h of incubation with the compounds (16% DMSO-cellular medium). The * sign indicates the data at the 50 μM as the highest concentration used. Respective IC₅₀ values are given in green.

Figure S31. Histograms showing cellular uptake of complexes **2** and **5** in HeLa cells after 4 h of incubation in dark at 37°C.

Figure S32. (a) Histograms showing cellular uptake of complexes **2** (2 μ M), **5** (2 μ M), Hcur (2 μ M), Acdppz (2 μ M), and a combination of Hcur (2 μ M) + Acdppz (2 μ M) in HeLa cells after 4 h of incubation in dark at 37°C. (b) Bar diagram showing corresponding percent cell positivity upon treatment with the complexes, ligands and combination of ligands in HeLa cells after 4 h of incubation in dark at 37°C. The experiment was performed in 0.2% DMSO-cellular medium except where Acdppz (10% DMSO-cellular medium) was used.

Figure S33. Histograms showing the photo-induced ROS generation by the complexes **2** (2 μ M) (a) and **5** (2 μ M) (b), Hcur (2 μ M) (c), Acdppz (2 μ M) (d), and a combination of Hcur (2 μ M) + Acdppz (2 μ M) (e) in HeLa cells [Color codes: cells alone, black; cells + DCFDA (1 μ M), blue; cells + DCFDA (1 μ M) + complex (2 μ M) in dark, green; and cells + DCFDA (1 μ M) + complex (2 μ M) after photo-irradiation (400-700 nm, 10 $J\text{ cm}^{-2}$), red]. The experiments were performed in 0.2% DMSO-cellular medium except where Acdppz (10% DMSO-cellular medium) was used.

Figure S34. Histograms showing the photo-induced ROS generation by the complexes **2** (2 μM) (a) and **5** (2 μM) (b), Hcur (2 μM) (c), Acdppz (2 μM) (d), and a combination of Hcur (2 μM) + Acdppz (2 μM) (e) in HeLa cells [Color codes: cells alone, black; cells + DCFDA (10 μM), blue; cells + DCFDA (10 μM) + complex (2 μM) in dark, green; and cells + DCFDA (10 μM) + complex (2 μM) after photo-irradiation (400-700 nm, 10 J cm^{-2}), red]. The experiments were performed in 0.2% DMSO-cellular medium except where Acdppz (10% DMSO-cellular medium) was used.

Figure S35. Bar diagram showing the photo-induced ROS generation by the complexes **2** (2 μM) and **5** (2 μM), Hcur (2 μM), Acdppz (2 μM), and a combination of Hcur (2 μM) + Acdppz (2 μM) in HeLa cells in dark and on photo-irradiation (400-700 nm, 10 $J\text{ cm}^{-2}$). The experiments were performed in 0.2% DMSO-cellular medium except where Acdppz (10% DMSO-cellular medium) was used.

Figure S36. Confocal microscopic images showing photoinduced ROS generation by the complexes **2** (2 μ M) and **5** (2 μ M) in HeLa cells [panels (a)-(d): untreated control; panels (e)-(h) complex **2** treated HeLa cells in dark; panels (i)-(l) complex **2** treated HeLa cells in light; panels: (m)-(p) complex **5** treated HeLa cells in dark; panels: (q)-(t) complex **5** treated HeLa cells in light. Panels (a), (e), (i), (m) and (q) showing the transmitted light images; panels (b), (f), (j), (n) and (r) showing the fluorescence of Hoechst; panel (c) displaying fluorescence of DCFDA in untreated control cells; panel (g) displaying fluorescence of DCFDA in complex **2** treated cells in dark; panel (k) displaying fluorescence of DCFDA in complex **2** treated cells in light; panel (o) displaying fluorescence of DCFDA in complex **5** treated cells in dark; panel (s) displaying fluorescence of DCFDA in complex **5** treated cells in light and panels (d), (h), (l), (p), (t) showing the merged images of Hoechst and DCFDA]. The scale bar for all panels is 20 μ m.

Figure S37. FACS analysis for Annexin-V-FITC/PI assay shows the percent population of HeLa cells undergoing early apoptosis (lower right quadrant, stained by Annexin-V-FITC alone), late apoptosis (upper right quadrant, stained by both Annexin-V-FITC and PI), and necrosis (upper left quadrant, stained by PI alone) upon treatment with the copper(II) complex **2** (2 μ M), zinc(II) complex **5** (2 μ M), Hcur (2 μ M), Acdppz (2 μ M) and a combination of Hcur (2 μ M) + Acdppz (2 μ M) in the dark and photo-irradiated (400-700 nm) conditions. The experiments were performed in 0.2% DMSO-cellular medium except where Acdppz (10% DMSO-cellular medium) was used. FACS analysis was performed after 10h post-incubation. Significant lowering in the number of viable cells (while recording

the fluorescence) in case of complex **5** (in light) indicates its high photocytotoxic potential. Number of viable cells was less in case of complex **2** and Acdppz ligand (in light) as well.

Figure S38. Absorption spectral traces of complex **1** in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta\epsilon_{af}/\Delta\epsilon_{bf}$ vs. [DNA].

Figure S39. Absorption spectral traces of complex **2** in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta\epsilon_{af}/\Delta\epsilon_{bf}$ vs. [DNA].

Figure S40. Absorption spectral traces of complex **3** in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta\epsilon_{af}/\Delta\epsilon_{bf}$ vs. [DNA].

Figure S41. Absorption spectral traces of complex **4** in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta\epsilon_{af}/\Delta\epsilon_{bf}$ vs. [DNA].

Figure S42. Absorption spectral traces of complex **5** in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta\epsilon_{\text{af}}/\Delta\epsilon_{\text{bf}}$ vs. [DNA].

Figure S43. (a)-(n) Gel diagrams showing the cleavage of pUC19 DNA (0.2 μ g, 30 μ M base pair) by the complexes **1–5**, ligands dppz, acdppz and Hcur in dark, in monochromatic blue laser light (446 nm, 50 mW, 45 min exposure), in monochromatic UV lamp exposure (365 nm, 12W, 30 min exposure) and in presence of GSH (5 mM). The gel diagrams include the mechanistic aspects of photonuclease activity of complexes **1** and **2** in the presence of various singlet oxygen quenchers and hydroxyl radical scavengers in monochromatic light of 446 nm, where [complex] = 30 μ M, incubation time: 1 h, exposure time: 45 min. Detail experimental conditions are given below in tabular form.

Lane No.	Experimental Condition	% NC	Lane No.	Experimental condition	% NC
Gel- (a)					
1	DNA control in dark	3	5	DNA+ 2 (30 μ M)+ KI in 446 nm	42
2	DNA+ 1 (30 μ M) in 446 nm	66	6*	DNA+ 2 (30 μ M)+ D ₂ O in 446 nm	84
3*	DNA+ 2 (30 μ M)+ D ₂ O in 446 nm	94	7*	DNA+ 1 (30 μ M)+ DMSO in 446 nm	20
4	DNA+ 1 (30 μ M)+ KI in 446 nm	22			

Gel-(b)					
8	DNA control in 446 nm	6	11	DNA+ 1 (30 μ M) + TEMP in 446 nm	60
9	DNA+ 1 (30 μ M)+ Catalase in 446 nm	25	12*	DNA+ 1 (30 μ M)+ DMSO in 446 nm	20
10	DNA+ 1 (30 μ M)+ KI in 446 nm	22			
Gel-(c)					
13	DNA control in 365 nm	4	16	DNA+ 2 (50 μ M) in 365 nm	90
14	DNA+ 1 (50 μ M) in 365 nm	83	17*	DNA+ dppz (50 μ M) in 365 nm	13
15	DNA+ 3 (50 μ M) in 365 nm	70			
Gel-(d)					
18	DNA control in dark	5	20*	DNA+ 1 (30 μ M) in 446 nm	67
19	DNA+ 1 (50 μ M) in dark	6	21	DNA+ 1 (30 μ M)+ DMSO in 446 nm	30
Gel-(e)					
22	DNA control in dark	3	24	DNA+ 2 (30 μ M)+ DABCO in 446 nm	74
23	DNA+ 2 (30 μ M) in dark	9			
Gel-(f)					
25	DNA+ Hcur (30 μ M) in dark	10	28	DNA+ 5 (30 μ M) in 446 nm	40
26	DNA+ 2 (30 μ M) + GSH in dark	35	29	DNA+ Hcur (30 μ M) in 446 nm	13
27	DNA control in 446 nm	7	30	DNA+ 3 (30 μ M) in 446 nm	54
Gel-(g)					
31	DNA control in 446 nm	10	33	DNA+ 1 (30 μ M) + DABCO in 446 nm	60
32	DNA+ 1 (30 μ M) + SOD in 446 nm	23	34	DNA+ 1 (30 μ M) in dark	11
Gel-(h)					
35	DNA control in 365 nm	5	39	DNA+ 5 (50 μ M) in 365 nm	63
36	DNA+ 2 (50 μ M) in 365 nm	80	40	DNA+ dppz (50 μ M) in 365 nm	4
37	DNA+ 2 (50 μ M) in dark	9	41	DNA+ acdppz (50 μ M) in 365 nm	6
38	DNA+ 5 (50 μ M) in dark	15			
Gel-(i)					
42	DNA control in 446 nm	4	45	DNA+ 2 (30 μ M)+ DMSO in 446 nm	33
43*	DNA+ 2 (30 μ M) in 446 nm	84	46*	DNA+ 2 (30 μ M)+ TEMP in 446 nm	71

44*	DNA+ 2 (30 μ M)+ SOD in 446 nm	54	47	DNA+ 2 (30 μ M)+ Catalase in 446 nm	42
Gel-(j)					
48	DNA control in dark	6	52	DNA+ 4 (50 μ M) in 365 nm	53
49	DNA+ Hcur (30 μ M) in 446 nm	8	53	DNA+ acdppz (50 μ M) in 365 nm	20
50	DNA+ 4 (30 μ M) in 446 nm	36	54	DNA+ Hcur (30 μ M) in 446 nm	17
51	DNA+ 4 (50 μ M) in dark	11			
Gel-(k)					
55	DNA control in dark	3	58	DNA+ dppz (50 μ M) in dark	3
56	DNA+ 1 (50 μ M) in dark	6	59	DNA+ 3 (50 μ M) in dark	11
57	DNA+ acdppz (50 μ M) in dark	4			
Gel-(l)					
60	DNA control in dark	2	63	DNA+ 2 (30 μ M) in 446 nm	83
61*	DNA+ 1 (30 μ M) in 446 nm	67	64	DNA+ 4 (30 μ M) + GSH in dark	15
62	DNA+ 2 (30 μ M) in 446 nm	90	65	DNA+ 5 (30 μ M) + GSH in dark	9
Gel-(m)					
66	DNA+ GSH in dark	10	68*	DNA+ 1 (30 μ M) + GSH in dark	40
67*	DNA+ 3 (30 μ M) + GSH in dark	42	69*	DNA+ 1 (30 μ M) + GSH in dark	62
Gel-(n)					
70	DNA control in dark	3	73	DNA+ 1 (30 μ M) + D ₂ O in 446 nm	63
71	DNA+ 1 (30 μ M) + NaN ₃ in 446 nm	56	74	DNA+ 2 (30 μ M) + NaN ₃ in 446 nm	76
72	DNA+ 1 (30 μ M) + DMSO in 446 nm	20	75	DNA+ 2 (30 μ M) + D ₂ O in 446 nm	95

*Some linear form of DNA was also observed along with the NC form.

Figure S44. (a)-(i) Gel diagrams showing the mechanistic aspects of photonuclease activity of complexes **1**, **2** and **5** in the presence of various singlet oxygen quenchers and hydroxyl radical scavengers in monochromatic UV light of 365 nm, where [complex] = 50 μ M, incubation time: 1.5 h, exposure time: 30 min. Detail experimental conditions are given below in tabular form.

Lane No.	Experimental Condition	% NC	Lane No.	Experimental condition	% NC
Gel- (a)					
1	DNA control in dark	3	3	DNA+ 2 (50 μ M)+ Argon in 365 nm	4
2	DNA+ 1 (50 μ M)+ Argon in 365 nm	6	4	DNA+ 5 (50 μ M)+ Argon in 365 nm	10
Gel-(b)					
5	DNA+ 1 (50 μ M)+ KI in 365 nm	31	8	DNA+ 2 (50 μ M)+ D ₂ O in 365 nm	94
6	DNA+ 5 (50 μ M)+ KI in 365 nm	28	9	DNA+ 2 (50 μ M) in 365 nm	86
7	DNA+ 1 (50 μ M)+ DMSO in 365 nm	44	10	DNA+ 2 (50 μ M)+ KI in 365 nm	61
Gel-(c)					
11	DNA control in 365 nm	4	14	DNA+ 5 (50 μ M)+ Argon in 365 nm	15
12	DNA+ 5 (50 μ M)+ Catalase in 365 nm	30	15	DNA+ 5 (50 μ M)+ TEMP in 365 nm	40
13	DNA+ 5 (50 μ M)+ DMSO in 365 nm	26	16	DNA+ 5 (50 μ M)+ NaN ₃ in 365 nm	46
Gel-(d)					
17	DNA control in dark	7	21	DNA+ 2 (50 μ M) in 365 nm	88
18*	DNA+ 2 (50 μ M)+ D ₂ O in 365 nm	98	22	DNA+ 2 (50 μ M) in dark	10
19*	DNA+ 2 (50 μ M)+ TEMP in 365 nm	58	23	DNA+ 2 (50 μ M)+ Argon in 365 nm	4
20*	DNA+ 2 (50 μ M)+ NaN ₃ in 365 nm	65	24	DNA+ 5 (50 μ M)+ Argon in 365 nm	10
Gel-(e)					
25	DNA+ 5 (50 μ M)+ DMSO in 365 nm	26	28	DNA+ 5 (50 μ M)+ DMSO in 365 nm	23
26*	DNA+ 5 (50 μ M)+ D ₂ O in 365 nm	70	29	DNA+ 5 (50 μ M)+ DABCO in 365 nm	42
27	DNA+ 5 (50 μ M)+ D ₂ O in 365 nm	90			
Gel-(f)					
30	DNA control in 365 nm	4	34	DNA+ 1 (50 μ M) in 365 nm	85
31	DNA+ 2 (50 μ M)+ NaN ₃ in 365 nm	75	35	DNA+ 2 (50 μ M) in 365 nm	90

32	DNA+ 1 (50 μ M)+ TEMP in 365 nm	66	36	DNA+ 2 (50 μ M)+ Catalase in 365 nm	60
33	DNA+ 2 (50 μ M)+ DABCO in 365 nm	61	37	DNA+ 2 (50 μ M)+ DMSO in 365 nm	61
Gel-(g)					
38	DNA control in 365 nm	10	42*	DNA+ 1 (50 μ M)+ D ₂ O in 365 nm	80
39	DNA+ 1 (50 μ M)+ D ₂ O in 365 nm	87	43*	DNA+ 2 (50 μ M)+ D ₂ O in 365 nm	97
40	DNA+ 1 (50 μ M) + D ₂ O in 365 nm	86	44*	DNA+ 1 (50 μ M)+ DABCO in 365 nm	81
41	DNA+ 2 (50 μ M)+ D ₂ O in 365 nm	90	45*	DNA+ 1 (50 μ M) in 365 nm	81
Gel-(h)					
46	DNA control in dark	2	47	DNA+ 1 (50 μ M)+ Catalase in 365 nm	26
Gel-(i)					
48	DNA control in dark	3	50	DNA+ 5 (50 μ M)+ Catalase in 365 nm	33
49*	DNA+ 5 (50 μ M) in 365 nm	63			

*Some linear form of DNA was also observed along with the NC form.

Figure S45. Plot shows the change in DPBF absorbance at 417 nm with time on photo exposure (446 nm, power = 50 mW, 10 sec) in presence of the complexes **1-5**.

Figure S46. Absorption spectral traces of DPBF (50 μM) in presence of **1-5** (5 μM) in DMSO solutions, after each photoexposure of 10 s (365 nm, 12W).

Table S1. Selected crystallographic parameters

Empirical Formula	$\text{C}_{36} \text{H}_{26} \text{Cl}_{0.5} \text{Cu}_1 \text{N}_{5.5} \text{O}_{4.5}$
Fw/ gM^{-1}	688.89
Crystal system	orthorhombic
Space group	P n n a
$a/\text{\AA}$	27.071(2)
$b/\text{\AA}$	18.4185(17)
$c/\text{\AA}$	16.0876(15)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$U/\text{\AA}^3$	8021.5(12)
Z	8
$2\theta_{\text{max}}/^\circ$	55.25
T, K	100
h, k, l_{max}	35, 24, 20
$\rho_{\text{calcd}} / \text{g cm}^{-3}$	1.141
$\lambda / \text{\AA} (\text{Mo-K}\alpha)$	0.71073
μ / mm^{-1}	0.619
Restraints / parameters	2 / 428
$F(000)$	2832
Goodness-of-fit	1.092
$R(F_o)^a, I > 2\sigma(I) [wR(F_o)]^b$	0.1428 [0.3108]
$R(\text{all data})[wR(\text{all data})]$	0.2236[0.3756]

$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $^b wR = \{\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)]\}^{1/2}$, $w = [\sigma (F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$

Table S2. Selected bond distances (Å) and angles (°) for complex **3a**

bond	bond length
Cu(1)-N(1)	2.008(6)
Cu(1)-N(2)	2.005(7)
Cu(1)-O(1)	1.891(6)
Cu(1)-O(2)	1.912(5)
Cu(1)-O(3)	2.274(6)
bond	bond angle
N(1)-Cu(1)- N(2)	81.7(3)
O(1)-Cu(1)- O(2)	95.1(2)
O(1)-Cu(1)- O(3)	93.2(2)
O(2)-Cu(1)- O(3)	92.8(2)
N(1)-Cu(1)- O(2)	168.2(2)
N(1)-Cu(1)- O(3)	97.7(2)
N(2)-Cu(1)- O(2)	92.0(3)
N(2)-Cu(1)- O(3)	95.5(2)
N(1)-Cu(1)- O(1)	89.7(2)
N(2)-Cu(1)- O(1)	168.5(3)
Cu(1)-O(1)- C(33)	122.8(6)
Cu(1)-N(2)- C(1)	113.8(5)
Cu(1)-N(1)- C(2)	112.5(5)
Cu(1)-O(2)- C(31)	122.1(6)

Table S3. Optimized coordinates of complexes **1-5** as obtained from DFT calculations using B3LYP/LANL2DZ level of theory

Complex 1				
Atomic		Coordinates (Angstroms)		
Number	X	Y	Z	
6	1.909103000	-5.793921000	1.230311000	
6	0.562551000	-5.335951000	1.146856000	
6	0.320000000	-3.965535000	0.983098000	

6	1.383839000	-3.023093000	0.901804000
6	2.713464000	-3.500961000	0.987748000
6	2.966614000	-4.868461000	1.149262000
6	1.053418000	-1.611815000	0.730673000
6	1.923111000	-0.558755000	0.673494000
6	2.288167000	3.220763000	0.347646000
6	3.445688000	4.112844000	0.371616000
6	3.358648000	5.457026000	0.145494000
6	4.444198000	6.433706000	0.154110000
8	0.206864000	1.080862000	0.324378000
8	1.082762000	3.765101000	0.178590000
6	4.147379000	7.776885000	-0.186386000
6	5.124210000	8.782838000	-0.193912000
6	6.453895000	8.438970000	0.166642000
6	6.769452000	7.101972000	0.491141000
6	5.785117000	6.109986000	0.488636000
6	-2.770703000	0.720099000	-0.162698000
7	-2.442311000	2.025810000	-0.115706000
6	-3.418595000	2.975855000	-0.221418000
6	-4.781595000	2.651728000	-0.376593000
6	-5.125090000	1.277302000	-0.426288000
6	-4.115773000	0.312673000	-0.320482000
6	-2.976824000	4.358523000	-0.164187000
6	-3.896303000	5.422507000	-0.258207000
6	-5.322084000	5.117076000	-0.417830000
6	-5.763056000	3.737155000	-0.476900000
7	-1.633418000	4.555918000	-0.013693000
6	-1.144285000	5.809566000	0.052041000
6	-2.001367000	6.931590000	-0.033271000
6	-3.379573000	6.741125000	-0.189495000
7	-6.197524000	6.134289000	-0.505907000

6	-7.525761000	5.832099000	-0.653165000
6	-7.967502000	4.449859000	-0.711708000
7	-7.063199000	3.424480000	-0.621354000
6	-8.488026000	6.881469000	-0.749594000
6	-9.831480000	6.569773000	-0.896910000
6	-10.267866000	5.204398000	-0.954317000
6	-9.356954000	4.162389000	-0.864104000
29	-0.579601000	2.816892000	0.103889000
8	2.101143000	-7.155444000	1.388949000
8	7.405690000	9.456392000	0.205167000
8	-0.411505000	-6.316466000	1.237805000
6	-1.812727000	-5.924999000	1.165943000
8	4.687216000	10.073331000	-0.473389000
6	5.470883000	10.940377000	-1.371841000
1	-0.702642000	-3.604478000	0.919826000
1	3.552320000	-2.815212000	0.924903000
1	3.992690000	-5.227033000	1.212091000
1	-0.006684000	-1.372768000	0.644943000
1	2.994307000	-0.715284000	0.769782000
1	4.402750000	3.637668000	0.571227000
1	2.366926000	5.850178000	-0.076250000
1	3.135463000	8.069772000	-0.454335000
1	7.793813000	6.849303000	0.761666000
1	6.059336000	5.094300000	0.756104000
1	-1.946449000	0.021979000	-0.072587000
1	-6.167554000	1.002741000	-0.546471000
1	-4.350551000	-0.745439000	-0.357949000
1	-0.070656000	5.893195000	0.173582000
1	-1.578865000	7.928743000	0.024425000
1	-4.067222000	7.577114000	-0.258653000
1	-8.136484000	7.907162000	-0.703957000

1	-11.326985000	4.992134000	-1.070129000
1	-9.665430000	3.122735000	-0.905337000
1	3.049343000	-7.398057000	1.438099000
1	8.281271000	9.141500000	0.510730000
1	-10.568839000	7.364199000	-0.970437000
1	-2.371685000	-6.856654000	1.264409000
1	-2.078072000	-5.245383000	1.988125000
1	-2.044416000	-5.454873000	0.199597000
1	4.852051000	11.830090000	-1.504384000
1	6.431935000	11.198340000	-0.923412000
1	5.625739000	10.443612000	-2.338980000
6	1.505758000	0.828503000	0.493880000
6	2.502656000	1.832858000	0.505798000
1	3.527482000	1.506441000	0.644696000

Complex 2

Atomic		Coordinates (Angstroms)		
Number	X	Y	Z	
6	1.841032000	-5.765170000	1.501480000	
6	0.499015000	-5.290203000	1.443976000	
6	0.270265000	-3.924691000	1.227710000	
6	1.343906000	-3.003641000	1.067979000	
6	2.668809000	-3.498239000	1.128496000	
6	2.908068000	-4.861093000	1.342097000	
6	1.027864000	-1.595792000	0.848130000	
6	1.910006000	-0.558781000	0.725017000	
6	2.308445000	3.205695000	0.282823000	

6	3.474251000	4.086668000	0.249248000
6	3.391904000	5.422151000	-0.025586000
6	4.484159000	6.389829000	-0.079467000
8	0.206717000	1.086957000	0.346299000
8	1.104271000	3.758850000	0.135145000
6	4.188713000	7.721247000	-0.464814000
6	5.171961000	8.718514000	-0.532865000
6	6.507144000	8.378651000	-0.189240000
6	6.821079000	7.052739000	0.179254000
6	5.830147000	6.068957000	0.236865000
6	-2.768714000	0.747162000	-0.216128000
7	-2.433103000	2.049433000	-0.136555000
6	-3.402597000	3.007823000	-0.229560000
6	-4.766242000	2.696080000	-0.405241000
6	-5.117201000	1.324940000	-0.489954000
6	-4.114804000	0.351948000	-0.396362000
6	-2.953144000	4.386009000	-0.137227000
6	-3.865901000	5.457270000	-0.211457000
6	-5.291701000	5.164539000	-0.392695000
6	-5.739318000	3.789250000	-0.490990000
7	-1.609509000	4.572249000	0.025251000
6	-1.113737000	5.821085000	0.124573000
6	-1.964374000	6.949686000	0.063889000
6	-3.342563000	6.770932000	-0.105751000
7	-6.158626000	6.190274000	-0.467277000
6	-7.487185000	5.900585000	-0.639993000
6	-7.933801000	4.523174000	-0.738342000
7	-7.040560000	3.489211000	-0.661450000
6	-8.436926000	6.958561000	-0.726525000
6	-9.789851000	6.684484000	-0.901196000
6	-10.221723000	5.311046000	-0.994896000

6	-9.324364000	4.259535000	-0.920085000
29	-0.567020000	2.825262000	0.104621000
8	2.019229000	-7.121198000	1.714450000
8	7.466117000	9.389720000	-0.211589000
6	-10.799059000	7.783500000	-1.005422000
6	-11.811360000	7.923230000	-0.014351000
6	-12.782135000	8.995640000	-0.168147000
7	-12.751801000	9.873055000	-1.205625000
6	-11.779952000	9.742726000	-2.146261000
6	-10.768241000	8.696719000	-2.097850000
6	-11.773892000	10.681594000	-3.234456000
6	-10.831725000	10.590444000	-4.240058000
6	-9.847691000	9.545215000	-4.211978000
6	-9.817167000	8.628744000	-3.177178000
6	-11.912200000	7.082685000	1.150310000
6	-12.920174000	7.270963000	2.078487000
6	-13.890563000	8.315041000	1.907594000
6	-13.817902000	9.156754000	0.814654000
8	-0.484968000	-6.250455000	1.611549000
6	-1.882272000	-5.840896000	1.568964000
8	4.738860000	10.001460000	-0.851247000
6	5.501945000	10.819649000	-1.811209000
1	-0.748739000	-3.550625000	1.184992000
1	3.514492000	-2.829275000	1.005301000
1	3.930517000	-5.232741000	1.384764000
1	-0.030953000	-1.343970000	0.784938000
1	2.981219000	-0.726320000	0.800343000
1	4.431897000	3.610220000	0.442927000
1	2.398080000	5.813931000	-0.240659000
1	3.172987000	8.011187000	-0.721342000
1	7.849589000	6.802759000	0.436177000

1	6.103473000	5.062048000	0.536582000
1	-1.949959000	0.041424000	-0.134260000
1	-6.159897000	1.059428000	-0.627252000
1	-4.355382000	-0.703562000	-0.460991000
1	-0.040043000	5.896213000	0.252013000
1	-1.536864000	7.942654000	0.150001000
1	-4.025297000	7.612162000	-0.158034000
1	-8.074686000	7.977956000	-0.642904000
1	-11.279110000	5.111805000	-1.143998000
1	-9.646481000	3.226320000	-0.999845000
1	2.965064000	-7.376179000	1.741800000
1	8.345886000	9.081012000	0.088193000
1	-12.541310000	11.449152000	-3.227741000
1	-10.834405000	11.300848000	-5.062415000
1	-9.124884000	9.474351000	-5.020973000
1	-9.073524000	7.838220000	-3.183791000
1	-11.176958000	6.300046000	1.311790000
1	-12.979360000	6.628534000	2.953488000
1	-14.674973000	8.442488000	2.648797000
1	-14.525186000	9.965209000	0.658775000
1	-2.450518000	-6.758660000	1.726797000
1	-2.110435000	-5.122057000	2.368603000
1	-2.139769000	-5.409799000	0.591009000
1	4.894744000	11.715904000	-1.952960000
1	6.484455000	11.075209000	-1.410276000
1	5.608964000	10.284485000	-2.764283000
6	1.505331000	0.826519000	0.505960000
6	2.512655000	1.820044000	0.471385000
1	3.536832000	1.486422000	0.597551000

Complex 3

Atomic		Coordinates (Angstroms)		
Number		X	Y	Z
29	12.420109000	7.048200000	7.494422000	
7	18.322874000	9.713598000	6.634814000	
8	12.070316000	5.888952000	8.992912000	
7	12.968196000	8.282097000	5.987136000	
7	14.342261000	7.331152000	8.059828000	
6	16.377832000	8.495870000	7.404045000	
7	16.857534000	10.723097000	4.410803000	
7	25.082046000	12.947205000	5.439836000	
8	10.624375000	6.891199000	6.814967000	
6	14.274766000	8.675008000	6.078604000	
6	15.024007000	8.156744000	7.209198000	
6	14.967272000	6.808077000	9.133801000	
1	14.369959000	6.161986000	9.767490000	
6	16.325759000	7.100610000	9.397356000	
1	16.802948000	6.665333000	10.268443000	
6	17.034309000	7.944828000	8.533875000	
1	18.076856000	8.191279000	8.704219000	
6	17.031682000	9.389390000	6.442061000	
6	18.920691000	10.547482000	5.726085000	
6	20.285798000	10.917043000	5.894907000	
1	20.821928000	10.517276000	6.749329000	
6	20.911426000	11.756028000	4.977980000	
6	20.158740000	12.250965000	3.850815000	
1	20.657095000	12.913113000	3.148497000	
6	18.827902000	11.919315000	3.662157000	
1	18.257530000	12.299966000	2.821121000	
6	18.171910000	11.057736000	4.591300000	

6	16.284223000	9.904116000	5.312504000
6	14.876734000	9.534105000	5.137217000
6	14.072007000	9.993681000	4.063515000
1	14.512771000	10.655717000	3.325896000
6	12.735609000	9.584837000	3.981028000
1	12.097951000	9.921306000	3.170980000
6	12.204329000	8.719988000	4.966160000
1	11.177725000	8.371199000	4.952286000
6	22.341766000	12.161057000	5.144162000
6	22.743865000	12.971755000	6.243630000
6	21.839021000	13.481931000	7.241121000
1	20.780489000	13.252577000	7.168669000
6	22.296402000	14.272428000	8.279285000
1	21.597510000	14.653323000	9.019852000
6	23.688007000	14.608278000	8.390317000
1	24.024240000	15.229157000	9.216358000
6	24.587446000	14.153975000	7.445983000
1	25.644350000	14.397378000	7.488885000
6	24.149467000	13.336918000	6.347780000
6	24.693171000	12.178656000	4.388656000
6	25.699146000	11.777369000	3.444518000
1	26.711316000	12.126425000	3.622793000
6	25.375318000	10.976541000	2.366481000
1	26.140203000	10.674733000	1.656081000
6	24.024283000	10.527050000	2.183024000
1	23.788724000	9.883150000	1.339367000
6	23.028594000	10.896781000	3.068977000
1	22.017801000	10.528037000	2.922174000
6	23.317844000	11.746225000	4.194918000
6	9.639548000	6.186674000	7.337039000
6	9.754084000	5.412853000	8.512026000

1	8.876710000	4.874696000	8.846914000
6	10.931204000	5.290721000	9.281526000
6	10.956050000	4.435700000	10.527413000
1	11.718136000	3.653128000	10.422620000
1	9.988700000	3.967294000	10.723117000
1	11.237721000	5.050674000	11.391439000
6	8.333042000	6.255954000	6.580563000
1	7.995304000	7.298404000	6.522240000
1	7.552892000	5.654521000	7.052927000
1	8.482929000	5.904316000	5.551982000

Complex 4

Atomic		Coordinates (Angstroms)		
Number		X	Y	Z
6	1.887460000	-5.786061000	1.539074000	
6	0.653144000	-5.406052000	0.939033000	
6	0.419790000	-4.051369000	0.665296000	
6	1.386318000	-3.050975000	0.966690000	
6	2.605031000	-3.452044000	1.563252000	
6	2.846256000	-4.802566000	1.844160000	
6	1.073434000	-1.660813000	0.644268000	
6	1.886032000	-0.571649000	0.784064000	
6	2.241832000	3.184536000	0.188169000	
6	3.373782000	4.100335000	0.353915000	
6	3.303147000	5.433138000	0.068281000	
6	4.362095000	6.431384000	0.203043000	
8	0.231491000	0.976417000	-0.003834000	
8	1.098683000	3.675942000	-0.268235000	
6	4.080592000	7.769717000	-0.167841000	
6	5.031969000	8.794592000	-0.061356000	

6	6.318709000	8.475840000	0.447877000
6	6.621309000	7.143539000	0.802914000
6	5.662407000	6.132688000	0.686520000
6	-2.827014000	0.762530000	0.269642000
7	-2.467802000	2.007053000	-0.095502000
6	-3.422347000	2.966576000	-0.270473000
6	-4.797460000	2.712948000	-0.082114000
6	-5.174408000	1.401281000	0.299119000
6	-4.185323000	0.426117000	0.475699000
6	-2.948348000	4.288994000	-0.642168000
6	-3.847885000	5.357634000	-0.833272000
6	-5.284752000	5.119122000	-0.662378000
6	-5.756976000	3.802981000	-0.281600000
7	-1.597052000	4.432144000	-0.774829000
6	-1.080591000	5.634910000	-1.091347000
6	-1.915758000	6.756597000	-1.305498000
6	-3.303019000	6.619891000	-1.178248000
7	-6.138535000	6.139118000	-0.862333000
6	-7.477764000	5.903065000	-0.688246000
6	-7.947986000	4.588378000	-0.294948000
7	-7.068011000	3.557211000	-0.102967000
6	-8.415328000	6.956287000	-0.893096000
6	-9.776246000	6.738263000	-0.706967000
6	-10.231368000	5.429953000	-0.305634000
6	-9.347817000	4.381836000	-0.109946000
30	-0.575101000	2.697010000	-0.456550000
8	2.073843000	-7.134926000	1.793781000
8	7.240186000	9.511572000	0.595431000
8	-0.230372000	-6.439625000	0.673410000
6	-1.506624000	-6.128830000	0.043480000
8	4.605203000	10.078668000	-0.386453000

6	5.469478000	10.957923000	-1.194012000
1	-0.517408000	-3.749655000	0.205998000
1	3.363776000	-2.718296000	1.816078000
1	3.785666000	-5.101718000	2.306045000
1	0.080170000	-1.475315000	0.233983000
1	2.899041000	-0.673959000	1.164944000
1	4.291979000	3.653965000	0.727615000
1	2.345855000	5.800373000	-0.300908000
1	3.098909000	8.044878000	-0.544884000
1	7.613881000	6.908829000	1.185330000
1	5.926320000	5.120472000	0.976750000
1	-2.016021000	0.055276000	0.400935000
1	-6.225668000	1.181807000	0.451368000
1	-4.446367000	-0.583573000	0.773622000
1	0.000187000	5.683485000	-1.160247000
1	-1.469880000	7.711838000	-1.560842000
1	-3.975712000	7.457029000	-1.330870000
1	-8.035518000	7.930173000	-1.184618000
1	-11.297940000	5.273744000	-0.170054000
1	-9.688121000	3.393771000	0.182721000
1	2.942587000	-7.322405000	2.206517000
1	8.079551000	9.211480000	1.001056000
1	-10.408074000	7.345098000	0.056869000
1	-2.008771000	-7.090931000	-0.067672000
1	-2.112546000	-5.466574000	0.678101000
1	-1.360769000	-5.670834000	-0.944991000
1	4.855967000	11.838497000	-1.395140000
1	6.370674000	11.231456000	-0.642027000
1	5.738570000	10.464303000	-2.137284000
6	1.480389000	0.787099000	0.420317000
6	2.439297000	1.820548000	0.523834000

1 3.423263000 1.543473000 0.887123000

Complex 5

Atomic Number	Coordinates (Angstroms)		
	X	Y	Z
6	1.521623000	-5.626574000	-1.236143000
6	0.214887000	-5.061671000	-1.202014000
6	0.074503000	-3.689181000	-0.954963000
6	1.203062000	-2.850022000	-0.736892000
6	2.492036000	-3.433067000	-0.774828000
6	2.643057000	-4.803414000	-1.021822000
6	0.973336000	-1.430035000	-0.486421000
6	1.910682000	-0.464476000	-0.246475000
6	2.469502000	3.256747000	0.483694000
6	3.683247000	4.038281000	0.716803000
6	3.647895000	5.380148000	0.970362000
6	4.779341000	6.268176000	1.227377000
8	0.260033000	1.259306000	-0.035078000
8	1.300324000	3.897192000	0.522531000
6	4.519719000	7.639742000	1.471380000
6	5.542920000	8.560098000	1.742068000
6	6.882862000	8.093320000	1.779735000
6	7.160133000	6.734651000	1.517005000
6	6.129329000	5.830238000	1.246594000
6	-1.982433000	3.243788000	2.960395000
7	-1.971123000	3.446054000	1.625548000
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