Electronic Supporting Information (ESI)

Red and NIR light-triggered enhancement of anticancer and antibacterial activities of dinuclear Co(II)-catecholate complexes

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Experimental details

Materials

Reagents and chemicals sourced from commercial suppliers (TCI Chemicals Pvt. Ltd., Sigma-Aldrich, U.S.A., and HiMEDIA Labs, India) and used as received. Unless specifically mentioned, all solvents used in the work were purified and dried before use by standard purification methods.[1] Phosphate buffer saline, PBS (pH = 7.2) solutions were prepared using deionized and double distilled water. $CoCl_2.6H_2O$, 1,10-phenanthroline monohydrate, Sodium azide, Dulbecco's Modified Eagle's medium (DMEM), propidium iodide, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT), 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA), 2',7'-dichlorofluorescein diacetate (DCFH-DA), and 1,3-diphenylisobenzofuran (DPBF) were procured from HiMEDIA Labs (India), SRL Life Sciences (India) and Sigma-Aldrich (U.S.A) and used as received. Annexin-V-FITC-PI kit for flow cytometry was procured from Invitrogen, U.S.A. (640914). 1,10-phenanthroline-5,6-dione and dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) was prepared from 1,10-phenanthroline (phen) according to published methods.[2] Anhydrous $CoCl_2$ was prepared by heating $CoCl_2 \cdot 6H_2O$, with the absence of H_2O confirmed by FT-IR spectroscopy through the disappearance of a broad -OH stretching band.

Measurements

The elemental (CHN) analysis was performed by using a Thermo Finnigan Flash EA 1112 analyzer. The solid-state Fourier Transform (FT) infrared (IR) spectra were recorded using a Bruker ATR FT-IR spectrometer. ^{1}H-NMR spectra were recorded at room temperature on a Bruker AVANCE 400 MHz NMR spectrometer using DMSO-d_6 as the solvent. Room temperature magnetic susceptibilities were determined by a solution NMR method using DMSO-d_6 solutions of the complexes containing 1% TMS (v/v) as the internal reference and on a Bruker AMX-400 NMR spectrometer.[3,4] The magnetic moments were calculated by the Evans method using the equation: $\mu_{eff} = 0.0618(\Delta f T/fc)$, where Δf is the observed shift in frequency of the TMS signal, T is the temperature (K), f is the operating frequency (MHz) of the NMR spectrometer, and c is the molar concentration of the complex. The UV-visible spectra of the complexes were recorded using a double-beam LABINDIA UV-visible spectrophotometer (Model: UV 3200). The solutions for the room temperature UV-visible measurements were prepared in PBS/DMF [5:1 (v/v), pH = 7.2]. Molar conductivity (Λ_M) was measured on a Labtronics, India digital conductivity meter. The fluorescence spectra for complexes **Co-2** and **Co-4** were measured on a Shimadzu RF-6000 spectrofluorometer. The solutions for the emission measurements were prepared in PBS/DMF [5:1 (v/v), pH = 7.2]. Cyclic voltammetry experiments were performed on a Biologic SP-50 Potentiostat/Galvanostat (Biologic Instruments, France) consisting of a three-electrode setup with a glassy carbon working electrode, platinum wire auxiliary electrode, and a standard calomel reference electrode (SCE). The scan speed was set at 100 mVs^{-1}. The experiments were conducted using a 2.0 mM solution of the complexes prepared in PBS /dimethylformamide (DMF, HPLC grade)

(1:9 v/v). Tetrabutylammonium perchlorate (TBAP, 0.1 M) was used as the supporting electrolyte. HRMS (ESI+) spectral data were obtained from Agilent LC/MS Q-TOF or Ultra High-Definition Accurate Mass-Q-TOF (LC-HRMS, Agilent 6538) mass spectrometers.

Computational calculations

Computational studies were performed by Density Functional Theory (DFT).[5] The B3LYP/6-31g basis set was used for C, H, N, and O atoms, while the LANL2DZ basis set was used for the Co atom as implemented in the Gaussian 16 program. Visualizations of the DFT-optimized structures and the frontier molecular orbitals (HOMOs and LUMOs) of the complexes were performed using chemcraft 1.7. To ascertain stationary points, further frequency test was performed. DMSO as the solvent was used to study the solvation effects by modeling with the integral equation formalism variant of the polarizable continuum model (IEFPCM). Time-dependent density functional theory (TD-DFT) was used to calculate electronic transitions and transition probability in DMSO.

Fluorescence quantum yield (Φ_f) determination

The fluorescence quantum yields of complexes **Co-2** and **Co-4** were measured by using coumarin-153 laser dye as a reference having a known quantum yield value of 0.56 in acetonitrile.[6] The sample for quantum yield determination was deoxygenated before spectral measurements. The sample and reference were excited at 415 nm, maintaining a low (< 0.1) but nearly equal absorbance. The integrated emission intensity was calculated using Origin 2024 software and the quantum yield was calculated using the equation $\Phi_f/\Phi_R = (A_f/A_R) \times [(OD)_R/(OD)_f] \times [(n_f)^2/(n_R)^2]$, where, Φ_f and Φ_R are the fluorescence quantum yields of the sample and reference respectively, A_f and A_R are the area under the fluorescence spectra of the sample and the reference respectively, $(OD)_S$ and $(OD)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and n_f and n_R are the respective refractive indices of the solvents used for the sample and the reference.[7]

Lipophilicity determination

The lipophilicity of the complexes was measured by determining their partition coefficients (log $P_{o/w}$) between *n*-octanol (o) and water (w) using the shake-flask method.[8] A calibration plot for the complex was constructed by determining the absorbances by varying concentrations of the complex in the aqueous medium. Then, the known concentration of the aqueous solution of the complex was mixed with an equal volume of *n*-octanol. After vortex-shaking the mixture, the two phases were allowed to separate. The remaining concentration of the complex in the aqueous phase was then determined from the calibration plot. The partition coefficient was calculated by using the equation $\log P_{o/w} = \log[C]_o/[C]_w$, where $[C]_o$ is the concentration of the complex in the *n*-octanol phase and $[C]_W$ is the concentration in the aqueous phase.

Stability and photostability experiments

UV-visible and emission spectroscopy were used to evaluate the thermodynamic stability of the complexes by recording the spectra of a solution of **Co-4** prepared in PBS/DMF (5:1 (v/v), pH = 7.2]. For dark stability, the spectral monitoring was done for 48 h. Reduced glutathione (GSH, 1.0 mM) was used as an additive for the stability assessment of complex **Co-4** in its presence. For experiments using GSH, the spectra were recorded at an interval of 8 h and up to 48 h. The photostability of the complexes was investigated by recording the UV-visible and emission spectra of a solution of **Co-4** prepared in PBS/DMF [5:1 (v/v), pH = 7.2] after irradiating the solution (every 10 min up to 1 h) with NIR diode laser light (808 nm, 450 mW, CNI Lasers, China).

Cell culture

The A549 (lung carcinoma epithelial cells) and NIH-3T3 (mouse embryonic fibroblast) cell lines were purchased from the American Type Culture Collection (ATCC, USA). Cells were maintained in DMEM supplemented with 10% FBS, 100 IU mL^{-1} of penicillin, 100 µg mL^{-1} of streptomycin, and 2.0 mM of Glutamax at 37 °C in a humidified incubator at 5% CO_2. The adherent cultures were grown as monolayers and were maintained by trypsinizing with 0.25% Trypsin-0.2 % EDTA.

Singlet oxygen quantum yield (Φ_Δ) measurement

The singlet oxygen quantum yields for **Co-2** and **Co-4** were determined through a titration experiment using 1,3-diphenylisobenzofuran (DPBF). DPBF is a well-known quencher for singlet oxygen, reacting with it to produce 1,2-dibenzoylbenzene. DPBF and complex (**Co-2** or **Co-4**) were dissolved in DMSO at a molar ratio of 60:1 and exposed to diode laser irradiation (808 nm, 450 mW, CNI Lasers, China). The photooxidation of DPBF was monitored by measuring the decrease in absorbance at 417 nm at an interval of 5 s. To determine the quantum yield, methylene blue (MB, $\Phi_\Delta = 0.52$) was employed as a standard. The decrease in intensity of the absorption maxima of DPBF at approximately 417 nm was plotted against the irradiation time. The singlet oxygen quantum yield values (Φ_Δ) were obtained by using the following equation,

$$\Phi_{\Delta c} = \Phi_{\Delta MB} \times (m_c/m_{MB}) \times (F_{MB}/F_c)$$

Where "*c*" refers to complex and "MB" refers to methylene blue, Φ_Δ is the value of singlet oxygen quantum yield, *m* is the slope of ΔOD vs. time (s) plot and *F* is the absorption correction factor, defined as $F = 1-10^{-OD}$, where OD is the optical density (absorbance) at the irradiation wavelength (ref. 15 in the manuscript)

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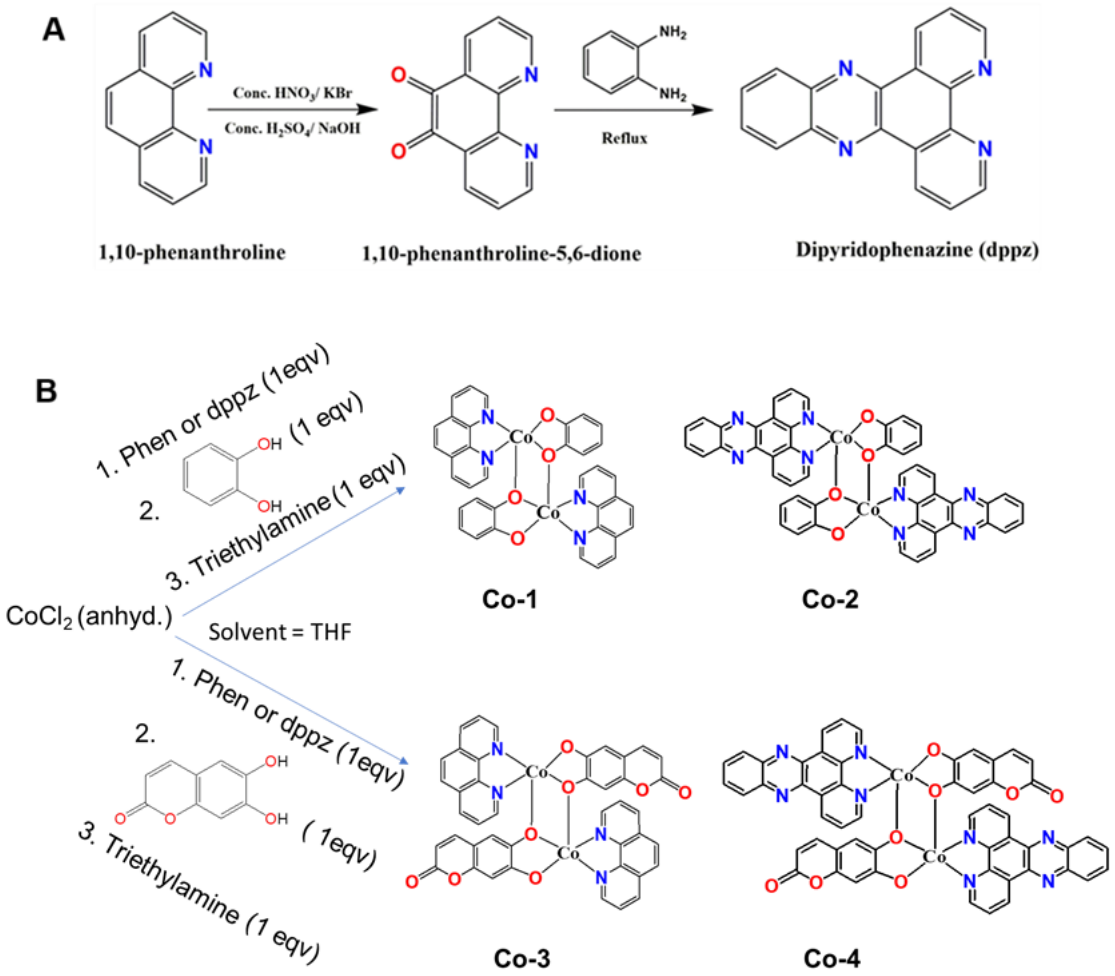

Scheme S1. (A) Synthesis of the dppz ligand from 1,10-phenanthroline. (B) Synthetic route for complexes **Co-1** to **Co-4**.

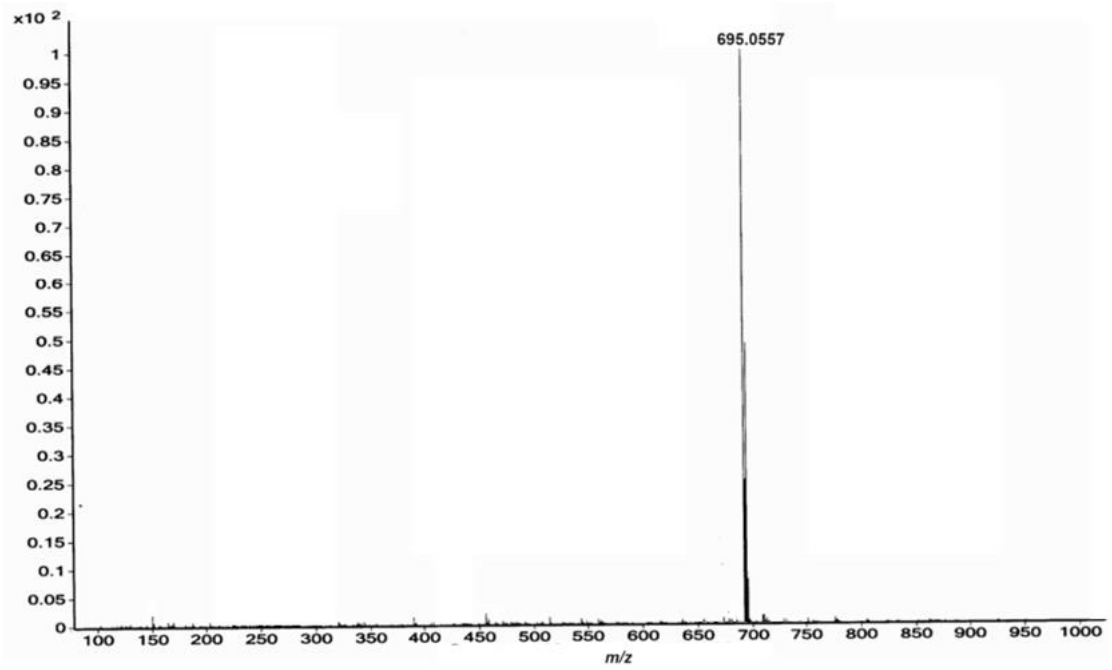

Fig. S1. HRMS (ESI+) spectrum of **Co-1** recorded in H_2O/MeOH [1:19 (v/v)] solution.

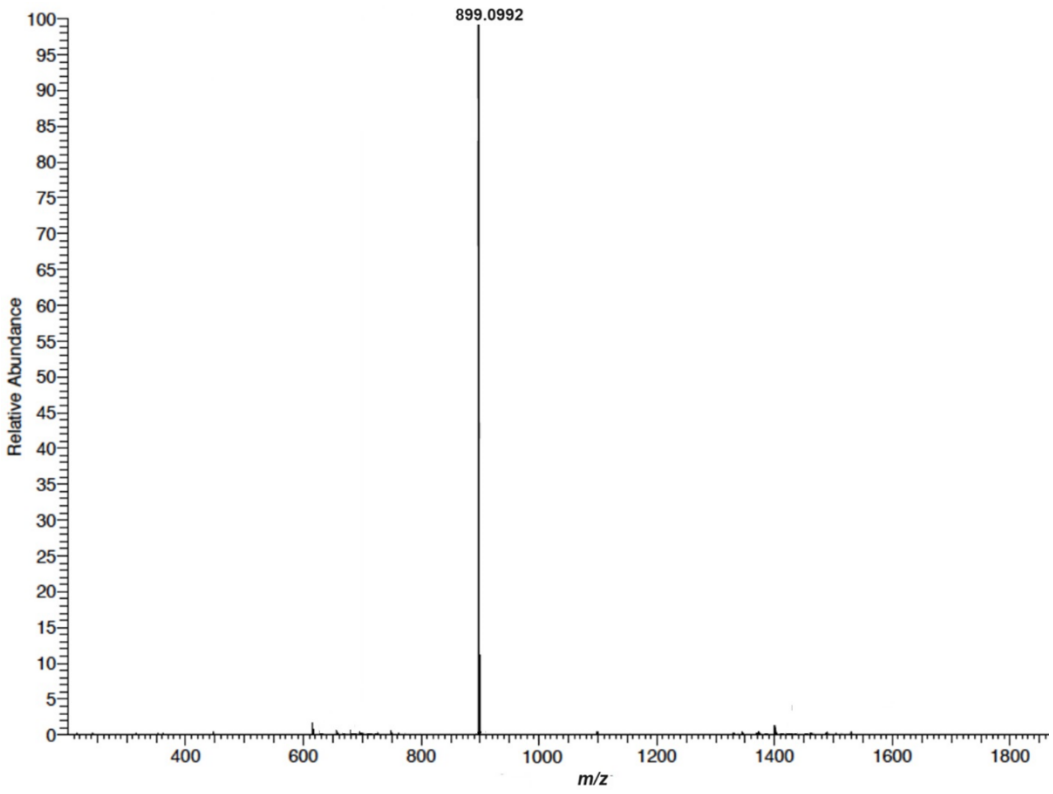

Fig. S2. HRMS (ESI+) spectrum of **Co-2** recorded in H_2O/MeOH [1:19 (v/v)] solution.

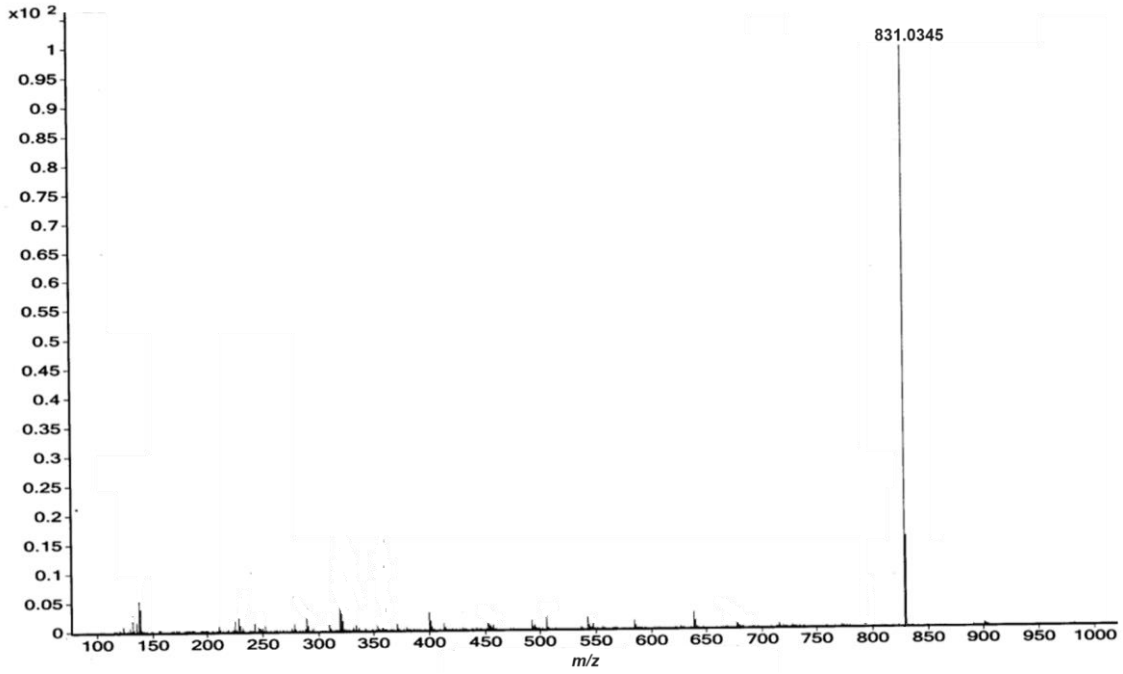

Fig. S3. HRMS (ESI+) spectrum of **Co-3** recorded in H_2O/MeOH [1:19 (v/v)] solution.

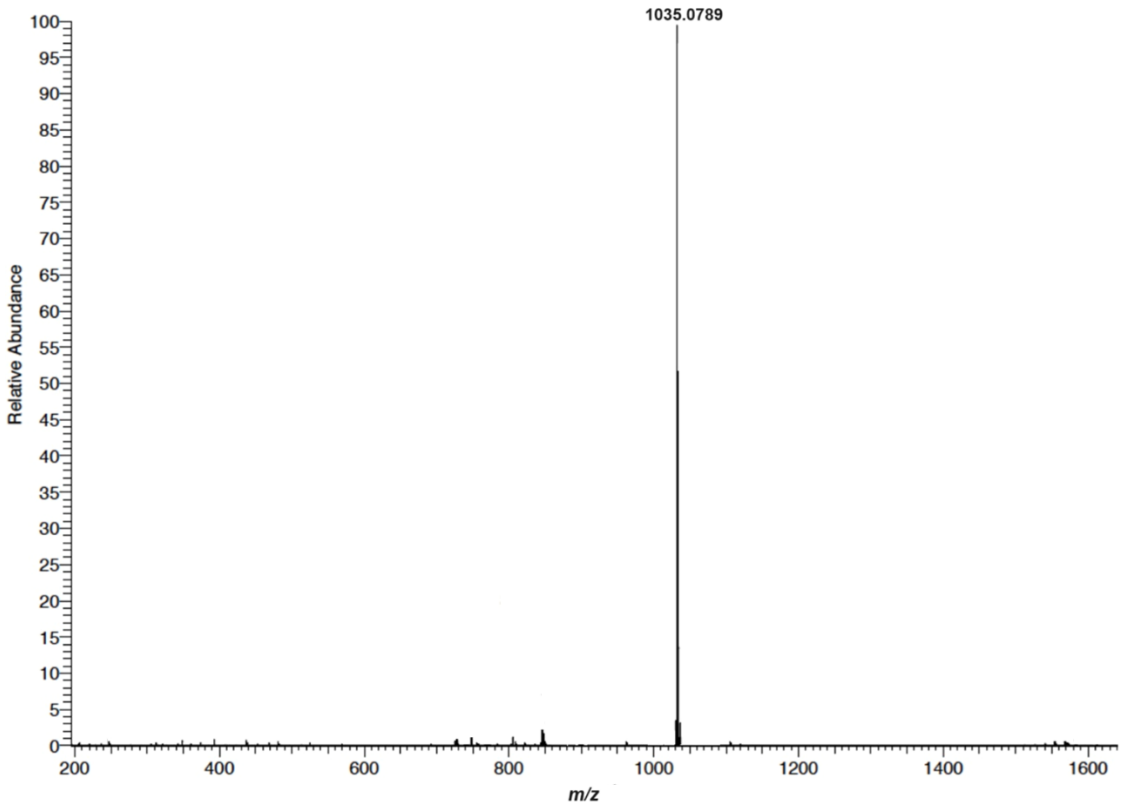

Fig. S4. HRMS (ESI+) spectrum of **Co-4** recorded in H_2O/MeOH [1:19 (v/v)] solution.

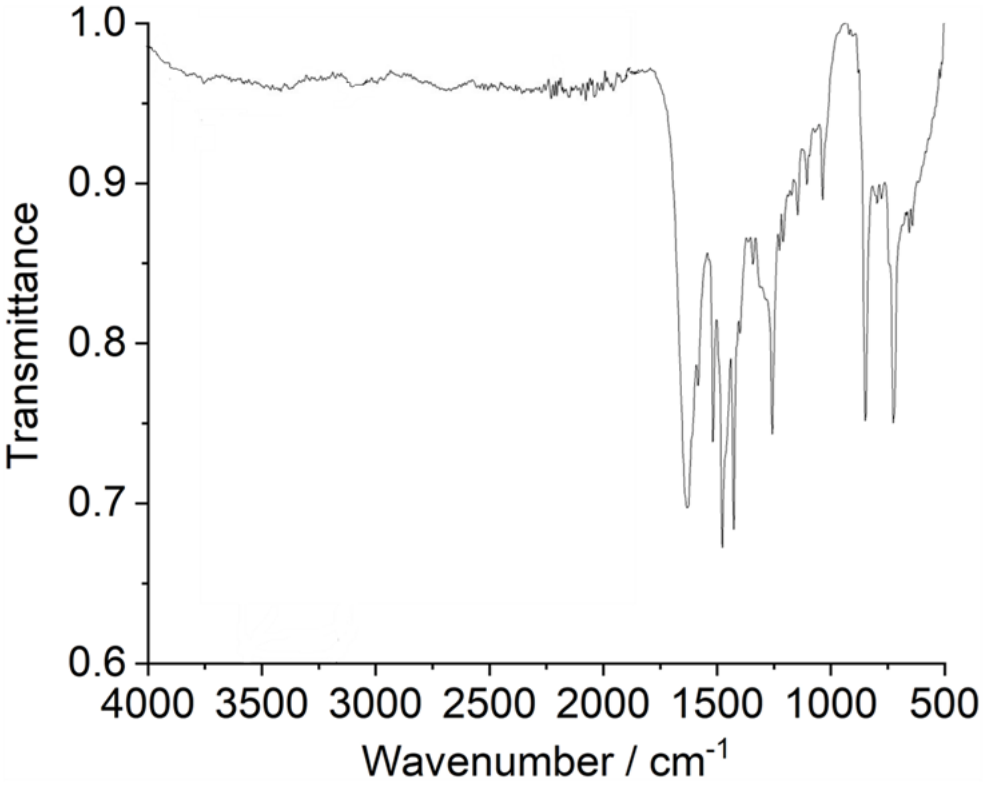

Fig. S5. The solid-state FT-IR spectrum of **Co-1**.

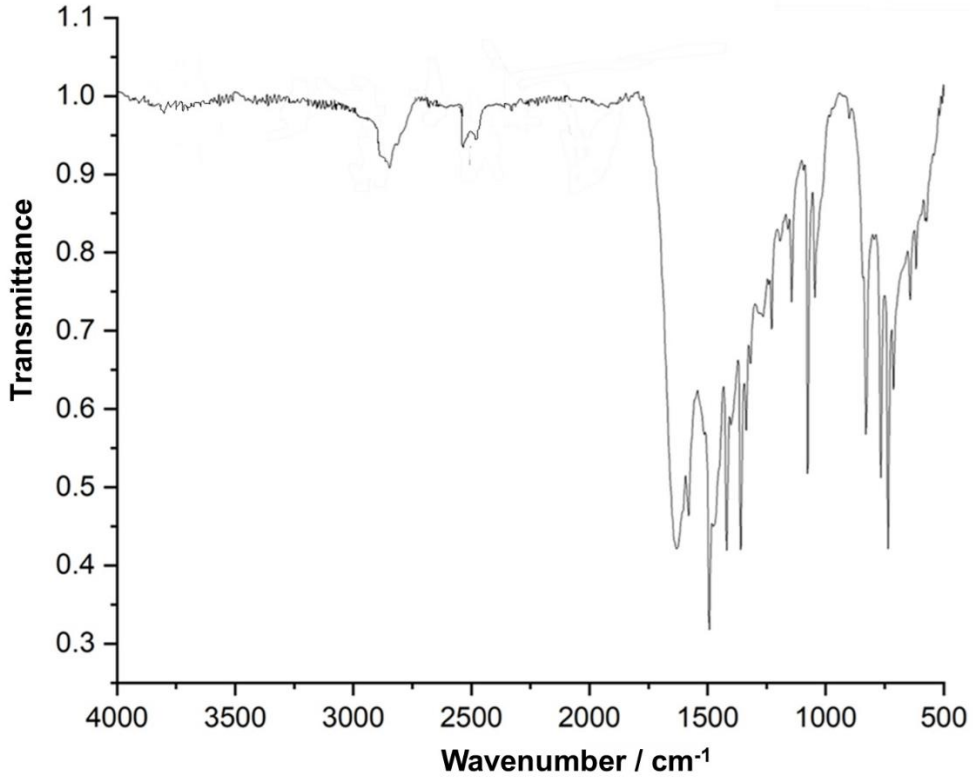

Fig. S6. The solid-state FT-IR spectrum of **Co-2**.

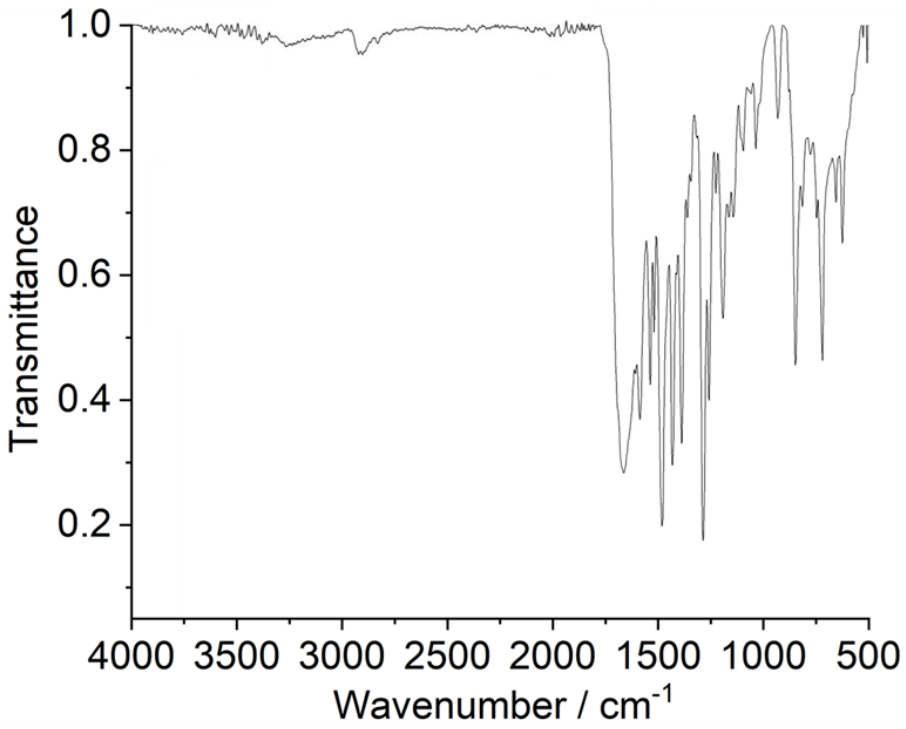

Fig. S7. The solid-state FT-IR spectrum of **Co-3**.

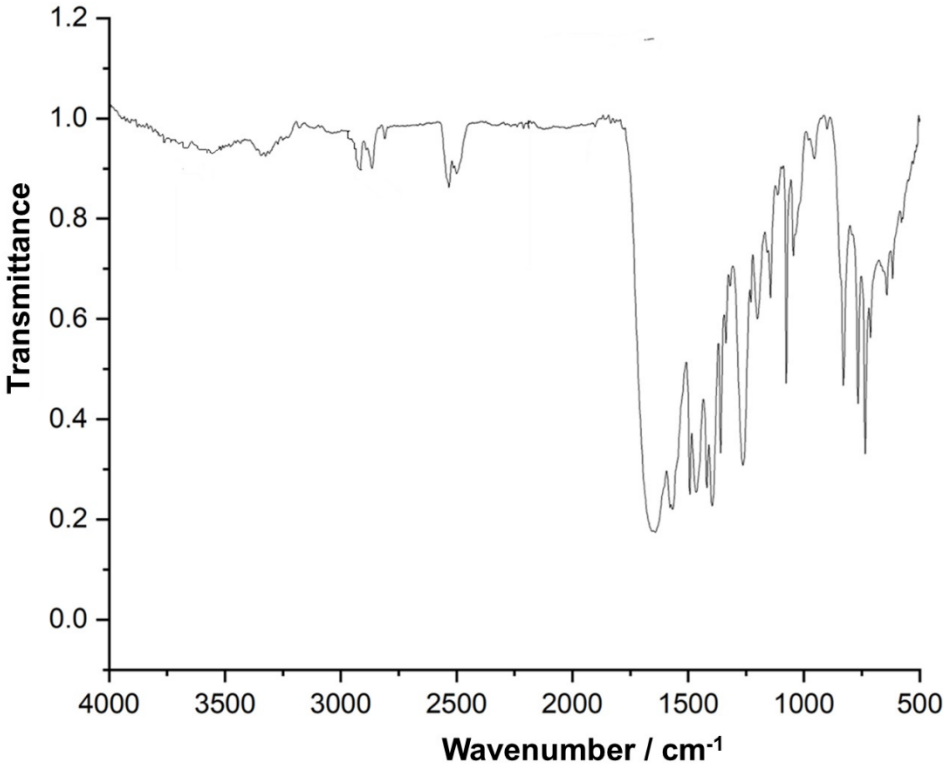

Fig. S8. The solid-state FT-IR spectrum of **Co-4**.

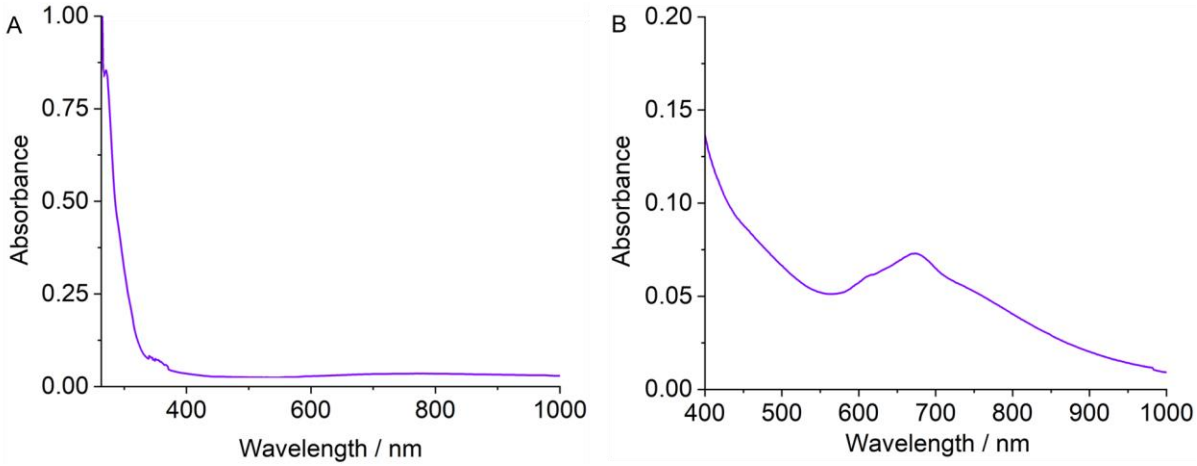

Fig. S9. (A) Room temperature UV-visible spectrum of **Co-1** (11 μM) recorded in DMF/PBS (1:5 v/v, pH = 7.2) solution. (B) Room temperature UV-visible spectrum of **Co-1** (70 μM) recorded in DMF/PBS (1:5 v/v, pH = 7.2) solution highlighting the (M+L)L' charge transfer transition.

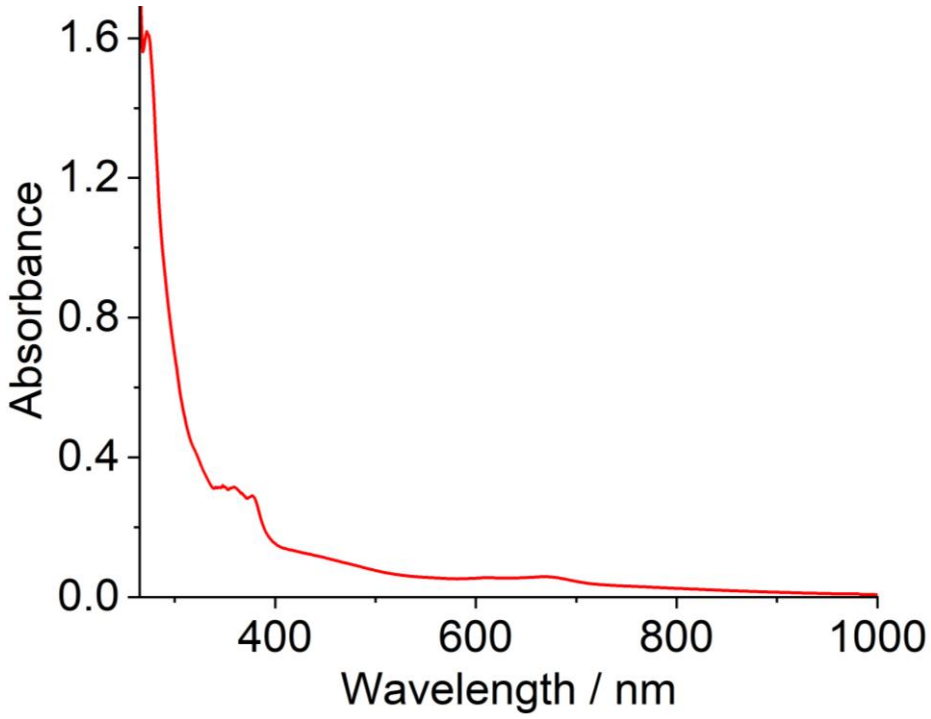

Fig. S10. Room temperature UV-visible spectrum of **Co-2** (11 μM) recorded in DMF/PBS (1:5 v/v, pH = 7.2) solution.

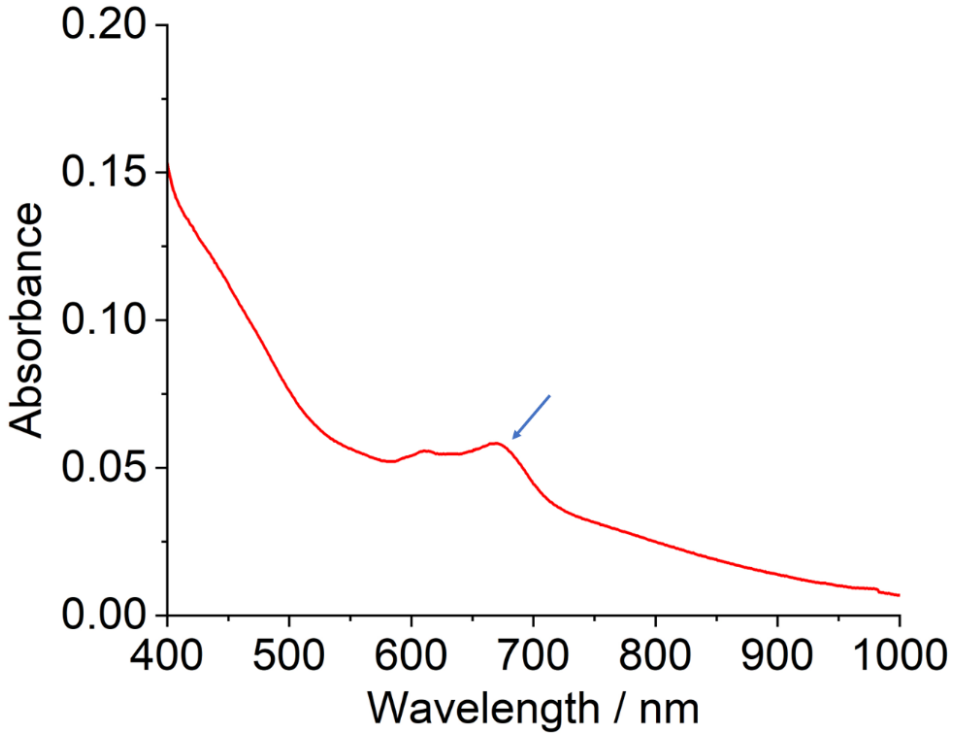

Fig. S11. A magnified view of the UV-visible spectrum of **Co-2** (presented in Fig. S10) highlighting the (M+L)L' charge transfer transition.

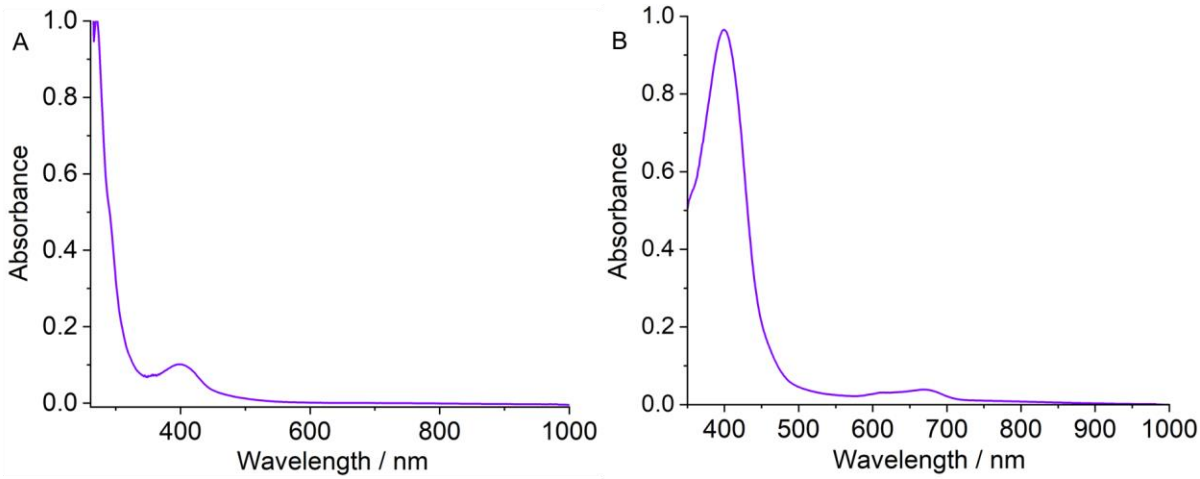

Fig. S12. (A) UV-visible spectrum of **Co-3** (11 μM) recorded in DMF/PBS (1:5 v/v, pH = 7.2) solution. (B) UV-visible spectrum of **Co-3** (70 μM) recorded in DMF/PBS (1:5 v/v, pH = 7.2) solution highlighting the (M+L)L' charge transfer transition.

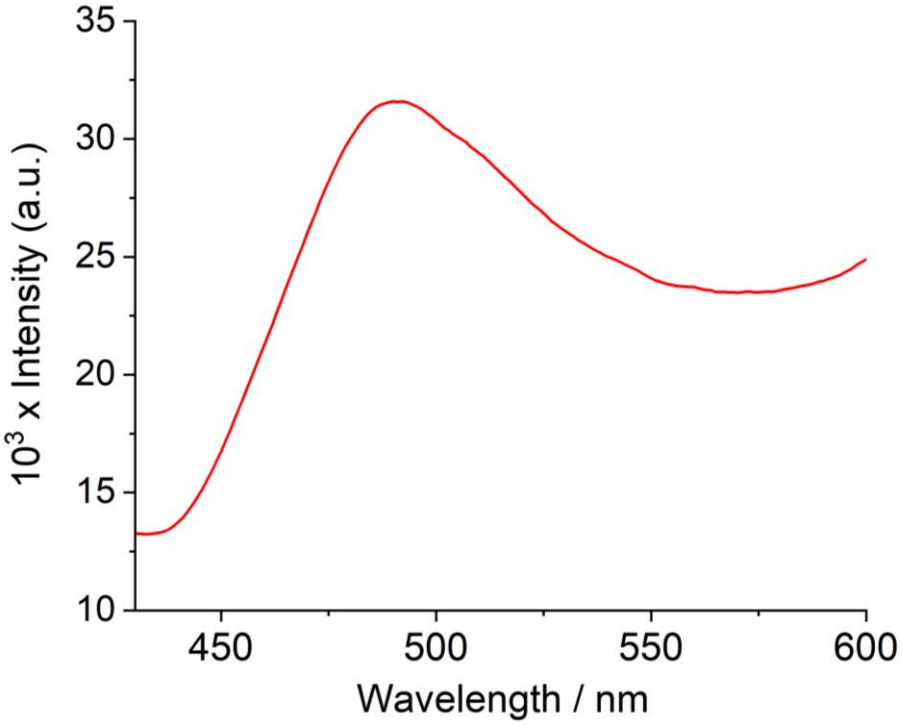

Fig. S13. The emission spectra of **Co-3** (11 μM) in PBS/DMF (5:1 v/v, pH = 7.2). λ_{ex} = 410 nm.

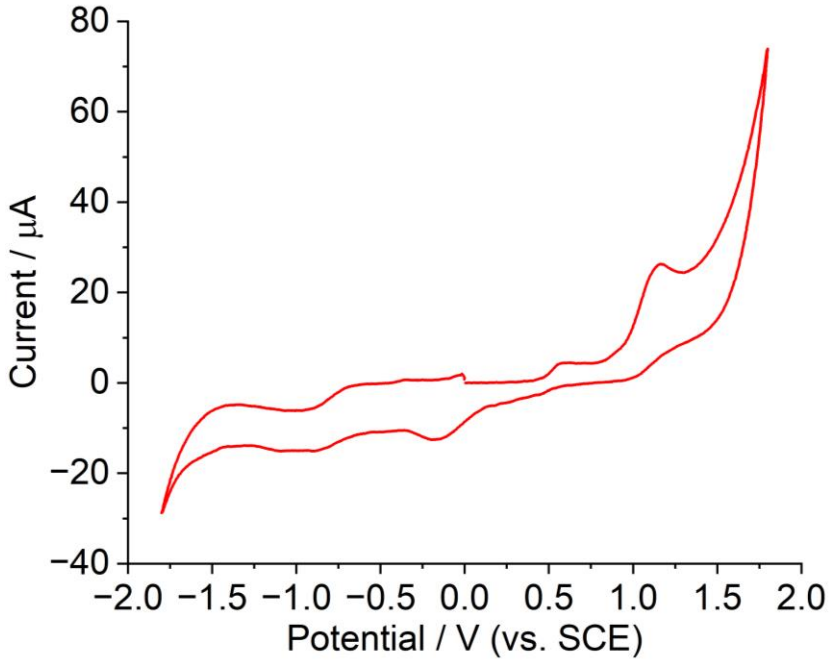

Fig. S14. Cyclic voltammogram of **Co-1** in 1:9 v/v PBS/DMF.

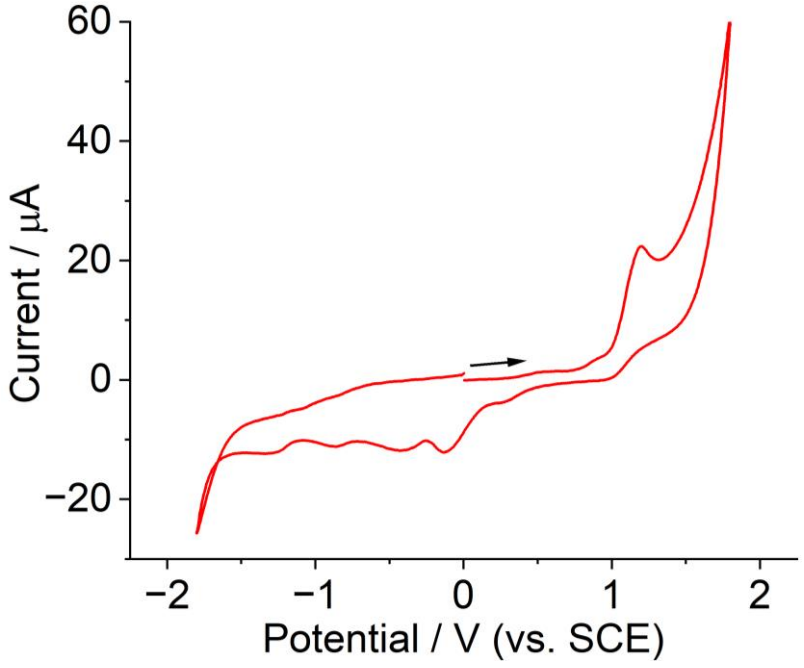

Fig. S15. Cyclic voltammogram of **Co-2** in 1:9 v/v PBS/DMF.

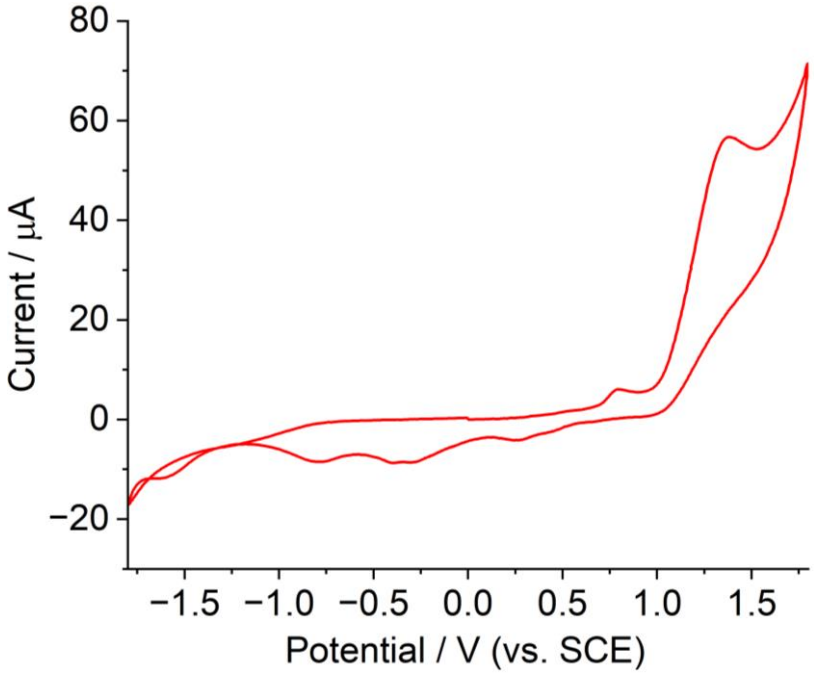

Fig. S16. Cyclic voltammogram of **Co-3** in 1:9 v/v PBS/DMF.

Table S1. DFT-optimized coordinates for complex **Co-1**.

C	-3.9990510000	-3.4203820000	-1.1741320000
C	-5.1548960000	-2.7122820000	-0.8595590000
C	-5.0527880000	-1.5011850000	-0.1397610000
C	-3.7522230000	-1.0771750000	0.2073360000
C	-2.7387520000	-2.9337030000	-0.7892360000
C	-6.1544450000	-0.6725650000	0.2811740000
C	-3.5411220000	0.1051580000	0.9568010000
C	-4.6263750000	0.8953640000	1.3862280000
C	-5.9502570000	0.4681720000	1.0086290000
C	-4.3149980000	2.0371430000	2.1579790000
H	-5.1069960000	2.6838080000	2.5114950000
C	-2.9866120000	2.3159050000	2.4553990000
C	-1.9581930000	1.4809230000	1.9877550000
H	-7.1590410000	-0.9745690000	0.0148450000
H	-4.0577990000	-4.3540920000	-1.7140070000
H	-6.1265520000	-3.0856790000	-1.1546740000
H	-1.8133190000	-3.4519470000	-0.9862110000
H	-6.7937000000	1.0714260000	1.3186600000
H	-2.7262190000	3.1849210000	3.0413030000
H	-0.9150030000	1.6666810000	2.1785290000
N	-2.6189250000	-1.7795700000	-0.1137410000
N	-2.2305700000	0.3918400000	1.2483410000
C	1.1626850000	-2.4202440000	1.0416950000
C	2.0372640000	-3.4915110000	1.2799520000
C	3.1543390000	-3.3043330000	2.0996540000
C	3.4176420000	-2.0543560000	2.6811050000
C	2.5633610000	-0.9724680000	2.4342810000
C	1.4458570000	-1.1594860000	1.6225260000
H	1.8181590000	-4.4532780000	0.8354970000
H	2.7412020000	-0.0006930000	2.8754200000
O	0.5500940000	-0.1434110000	1.3092390000
O	0.0302970000	-2.5058680000	0.2959050000
Co	-0.9979500000	-0.9018050000	0.4665730000
C	2.9864450000	-2.3156950000	-2.4560450000
C	4.3147850000	-2.0373820000	-2.1580670000
C	4.6262270000	-0.8958160000	-1.3860060000
C	3.5410450000	-0.1054080000	-0.9568050000
C	1.9580860000	-1.4804930000	-1.9886240000
C	5.9501020000	-0.4690600000	-1.0078990000

C	3.7522220000	1.0766880000	-0.2069580000
C	5.0527860000	1.5002430000	0.1406800000
C	6.1543620000	0.6714540000	-0.2801140000
C	5.1549720000	2.7110870000	0.8609050000
H	6.1266340000	3.0841270000	1.1564520000
C	3.9992320000	3.4193880000	1.1753500000
C	2.7389220000	2.9331690000	0.7898590000
H	6.7934800000	-1.0724740000	-1.3177910000
H	2.7260150000	-3.1845220000	-3.0422110000
H	5.1067260000	-2.6842090000	-2.5114160000
H	0.9149160000	-1.6658700000	-2.1798460000
H	7.1589520000	0.9731300000	-0.0133940000
H	4.0580520000	4.3528920000	1.7155680000
H	1.8135610000	3.4515940000	0.9866990000
N	2.2305320000	-0.3916650000	-1.2488930000
N	2.6190420000	1.7793030000	0.1139710000
C	-1.4457950000	1.1600960000	-1.6229850000
C	-2.5637260000	0.9730650000	-2.4341870000
C	-3.4180930000	2.0549620000	-2.6806450000
C	-3.1545420000	3.3049570000	-2.0993170000
C	-2.0370710000	3.4921750000	-1.2801830000
C	-1.1624620000	2.4208790000	-1.0423270000
H	-2.7418180000	0.0012770000	-2.8751950000
H	-1.8177470000	4.4539390000	-0.8358350000
O	-0.0296380000	2.5065060000	-0.2970550000
O	-0.5498820000	0.1441580000	-1.3100670000
Co	0.9979670000	0.9021090000	-0.4670950000
H	-3.8173440000	4.1385030000	-2.2956460000
H	-4.2790610000	1.9262950000	-3.3235380000
H	4.2782750000	-1.9257050000	3.3244350000
H	3.8170470000	-4.1378960000	2.2962770000

Table S2. DFT-optimized coordinates for complex **Co-2**.

C	1.2422440000	-2.2137000000	1.3659830000
C	2.1610010000	-3.2002470000	1.7551440000
C	3.2401450000	-2.8560550000	2.5746470000
C	3.4212750000	-1.5330610000	3.0074350000
C	2.5209690000	-0.5363230000	2.6112140000
C	1.4413500000	-0.8793900000	1.7985450000
H	2.0063380000	-4.2184430000	1.4240330000
H	2.6338450000	0.4890920000	2.9375410000
O	0.5076550000	0.0416810000	1.3384370000
O	0.1447140000	-2.4467180000	0.5997290000
Co	-0.9657070000	-0.8906540000	0.5417130000
C	-1.4412440000	0.8804970000	-1.7994330000
C	-2.5212110000	0.5375640000	-2.6117080000
C	-3.4215260000	1.5344320000	-3.0075170000
C	-3.2401520000	2.8573970000	-2.5747500000
C	-2.1606740000	3.2014240000	-1.7555920000
C	-1.2419040000	2.2147550000	-1.3668300000
H	-2.6343520000	-0.4878210000	-2.9380260000
H	-2.0057970000	4.2195800000	-1.4244530000
O	-0.1440440000	2.4475510000	-0.6009400000
O	-0.5074310000	-0.0406410000	-1.3398050000
Co	0.9657580000	0.8912950000	-0.5424570000
C	3.1514390000	-2.4428130000	-2.0558200000
C	4.4566120000	-2.0870570000	-1.7195970000
C	4.6824460000	-0.8629730000	-1.0694820000
C	3.5667510000	-0.0640430000	-0.7851820000
C	2.0818530000	-1.5982870000	-1.7386830000
C	5.9982940000	-0.3646170000	-0.6717960000
C	3.6938070000	1.2197780000	-0.1662380000
C	4.9388550000	1.7483660000	0.2058300000
C	6.1254530000	0.9283940000	-0.0349920000

C	4.9580670000	3.0323050000	0.7720240000
H	5.9025080000	3.4625720000	1.0690210000
C	3.7550730000	3.7238600000	0.9263710000
C	2.5483830000	3.1377240000	0.5300410000
H	2.9502820000	-3.3787450000	-2.5554030000
H	5.2967070000	-2.7256090000	-1.9463800000
H	1.0544700000	-1.8301240000	-1.9612840000
H	3.7451620000	4.7182720000	1.3476280000
H	1.5897850000	3.6271870000	0.6029670000
N	2.2872940000	-0.4227260000	-1.1095710000
N	2.5199920000	1.9007800000	-0.0048750000
C	8.4256030000	0.6328570000	0.0967470000
C	8.3007400000	-0.6465140000	-0.5375930000
C	9.4641540000	-1.4239270000	-0.7749990000
C	10.6970350000	-0.9450050000	-0.3944280000
C	10.8207590000	0.3255800000	0.2362590000
C	9.7098520000	1.1010940000	0.4781550000
H	9.3404430000	-2.3842090000	-1.2542450000
H	11.5853820000	-1.5351820000	-0.5729440000
H	11.8009270000	0.6788370000	0.5257420000
H	9.7739180000	2.0685920000	0.9546470000
N	7.3205180000	1.4007420000	0.3331330000
N	7.0752230000	-1.1194790000	-0.9130550000
C	-3.7545560000	-3.7239300000	-0.9263650000
C	-4.9577170000	-3.0327100000	-0.7717210000
C	-4.9387120000	-1.7487640000	-0.2055570000
C	-3.6937150000	-1.2198190000	0.1661930000
C	-2.5479320000	-3.1374590000	-0.5303710000
C	-6.1254620000	-0.9290880000	0.0355410000
C	-3.5668180000	0.0640400000	0.7850650000
C	-4.6826510000	0.8627270000	1.0695790000
C	-5.9984720000	0.3639930000	0.6722460000

C	-4.4569780000	2.0869170000	1.7195110000
H	-5.2971610000	2.7252890000	1.9464680000
C	-3.1517830000	2.4430400000	2.0553420000
C	-2.0820820000	1.5987700000	1.7380370000
H	-3.7444840000	-4.7183460000	-1.3476070000
H	-5.9021080000	-3.4632590000	-1.0684680000
H	-1.5892160000	-3.6266530000	-0.6035420000
H	-2.9507450000	3.3790990000	2.5547400000
H	-1.0547050000	1.8308780000	1.9603800000
N	-2.5197330000	-1.9004800000	0.0045310000
N	-2.2873450000	0.4230400000	1.1091080000
C	-8.3010260000	0.6452970000	0.5386070000
C	-8.4257220000	-0.6341310000	-0.0956420000
C	-9.7099450000	-1.1027070000	-0.4767190000
C	-10.8209880000	-0.3274570000	-0.2345910000
C	-10.6974290000	0.9431850000	0.3960100000
C	-9.4645740000	1.4224320000	0.7762610000
H	-9.7738840000	-2.0702440000	-0.9531490000
H	-11.8011380000	-0.6809720000	-0.5238220000
H	-11.5858800000	1.5331490000	0.5747150000
H	-9.3409860000	2.3827670000	1.2554330000
N	-7.0755320000	1.1185880000	0.9137390000
N	-7.3205010000	-1.4017500000	-0.3322650000
H	-3.9383590000	3.6239300000	-2.8864300000
H	-4.2526650000	1.2842570000	-3.6537400000
H	4.2521370000	-1.2827770000	3.6539770000
H	3.9382920000	-3.6225190000	2.8866180000

Table S3. DFT-optimized coordinates for complex **Co-3**.

C	-2.8972710000	4.0419000000	1.8893720000
C	-4.0956070000	3.9636160000	1.1906700000
C	-4.1876490000	3.1195710000	0.0604560000
C	-3.0320000000	2.3854590000	-0.2771790000
C	-1.7864280000	3.2801400000	1.4854110000
C	-5.3499670000	2.9523290000	-0.7741750000
C	-3.0128010000	1.5259550000	-1.4043350000
C	-4.1447020000	1.3938690000	-2.2329950000
C	-5.3276930000	2.1326270000	-1.8692410000
C	-4.0142750000	0.5425630000	-3.3547300000
H	-4.8512810000	0.4007630000	-4.0250670000
C	-2.8062550000	-0.1024950000	-3.5835250000
C	-1.7240000000	0.0735460000	-2.7035520000
H	-6.2516410000	3.4922290000	-0.5181460000
H	-2.8047450000	4.6874830000	2.7500280000
H	-4.9534390000	4.5436850000	1.5027460000
H	-0.8292020000	3.3171680000	1.9813090000
H	-6.2117290000	2.0256610000	-2.4837050000
H	-2.6852520000	-0.7557820000	-4.4348080000
H	-0.7751930000	-0.4192860000	-2.8303260000
N	-1.8576030000	2.4628140000	0.4243230000
N	-1.8272520000	0.8723710000	-1.6289170000
C	2.1079640000	1.9042190000	0.1256380000
C	3.3027690000	2.5503200000	0.4719640000
C	4.4665710000	2.2091270000	-0.2056010000
C	4.4922340000	1.2350930000	-1.2346020000
C	3.2842570000	0.5707850000	-1.5584200000
C	2.1215530000	0.8942810000	-0.8877530000
H	3.3193920000	3.3121310000	1.2358450000
C	5.7435720000	0.9854240000	-1.8842530000
H	3.2655380000	-0.1803190000	-2.3371260000
C	6.8838630000	1.6384270000	-1.5270950000
C	6.9008850000	2.6198570000	-0.4681020000
H	5.7703160000	0.2540530000	-2.6836160000
H	7.8293300000	1.4558050000	-2.0132050000
O	5.6406720000	2.8714390000	0.1593350000
O	7.8737390000	3.2500750000	-0.0520700000
O	0.9022430000	0.2721910000	-1.1176710000
O	0.9154440000	2.1737280000	0.6845210000

Co	-0.4940490000	1.2701440000	-0.2614430000
C	2.8147180000	0.0168670000	3.4854180000
C	4.0222670000	-0.6279700000	3.2579720000
C	4.1492830000	-1.4890820000	2.1431720000
C	3.0179130000	-1.6227170000	1.3143320000
C	1.7301650000	-0.1666930000	2.6088760000
C	5.3279610000	-2.2396880000	1.7902940000
C	3.0353880000	-2.4903840000	0.1929400000
C	4.1854650000	-3.2401060000	-0.1313130000
C	5.3461010000	-3.0744270000	0.7064210000
C	4.0876060000	-4.0995090000	-1.2498300000
H	4.9382610000	-4.6983820000	-1.5466040000
C	2.8911080000	-4.1744720000	-1.9527620000
C	1.7867230000	-3.3960590000	-1.5630560000
H	6.2103530000	-2.1327600000	2.4070380000
H	2.6960860000	0.6780870000	4.3305620000
H	4.8616710000	-0.4774010000	3.9230340000
H	0.7812950000	0.3255220000	2.7367790000
H	6.2419010000	-3.6309280000	0.4646570000
H	2.7939080000	-4.8337540000	-2.8026100000
H	0.8287910000	-3.4312200000	-2.0578200000
N	1.8334960000	-0.9677490000	1.5366290000
N	1.8632030000	-2.5668690000	-0.5119400000
C	-2.1151560000	-0.9985690000	0.8015970000
C	-3.2889290000	-0.6256170000	1.4517250000
C	-4.4667080000	-1.2822320000	1.1096230000
C	-4.4989020000	-2.3040130000	0.1320680000
C	-3.2966630000	-2.6638070000	-0.5179190000
C	-2.1046430000	-2.0244760000	-0.1910630000
H	-3.2913400000	0.1425740000	2.2094470000
C	-5.7679010000	-2.9224590000	-0.1347040000
H	-3.2922950000	-3.4459540000	-1.2654110000
C	-6.9035420000	-2.5364870000	0.5054860000
C	-6.9064750000	-1.4787920000	1.4923170000
H	-5.8065110000	-3.7180760000	-0.8692050000
H	-7.8597110000	-2.9961340000	0.3097280000
O	-5.6384560000	-0.8890830000	1.7646880000
O	-7.8806870000	-1.0414740000	2.1068500000
O	-0.8972610000	-2.3132090000	-0.7411460000
O	-0.9031800000	-0.3903160000	1.0367150000

Co	0.4965560000	-1.3753840000	0.1684330000

Table S4. DFT-optimized coordinates for complex **Co-4**.

C	-1.5514210000	2.3582700000	-0.2828500000
C	-2.5762300000	3.2513600000	-0.6237870000
C	-3.6841400000	3.3453010000	0.2095570000
C	-3.8191440000	2.5723440000	1.3895260000
C	-2.7881950000	1.6563450000	1.7117040000
C	-1.6827880000	1.5512570000	0.8909650000
H	-2.5022550000	3.8705670000	-1.5042450000
C	-4.9941860000	2.7694490000	2.1844870000
H	-2.8555650000	1.0500420000	2.6054490000
C	-5.9660230000	3.6531010000	1.8262900000
C	-5.8701690000	4.4465950000	0.6233270000
H	-5.1007480000	2.1923720000	3.0956370000
H	-6.8534840000	3.8058560000	2.4200600000
O	-4.6845840000	4.2490210000	-0.1521440000
O	-6.6913870000	5.2607260000	0.2007470000
O	-0.6404190000	0.6625060000	1.1150510000
O	-0.4179110000	2.2031830000	-0.9895070000
Co	0.8354500000	1.1096300000	-0.0239540000
C	1.6693640000	-1.6473800000	-0.8162350000
C	2.7927100000	-1.7207450000	-1.6357620000
C	3.7906400000	-2.6314450000	-1.3019480000
C	3.6942720000	-3.4654060000	-0.1639220000
C	2.5503200000	-3.3658200000	0.6599590000
C	1.5344210000	-2.4694290000	0.3427050000
H	2.8857120000	-1.1067560000	-2.5182670000
C	4.7752600000	-4.3810130000	0.0769960000
H	2.4491620000	-3.9966870000	1.5330080000
C	5.8579210000	-4.4449220000	-0.7423400000
C	5.9932510000	-3.5934650000	-1.9040010000

H	4.7115880000	-5.0345450000	0.9387540000
H	6.6720740000	-5.1309540000	-0.5683050000
O	4.9102510000	-2.6963970000	-2.1373410000
O	6.9365590000	-3.5638920000	-2.6952590000
O	0.3842150000	-2.3213340000	1.0504800000
O	0.6340370000	-0.7685550000	-1.0418360000
Co	-0.8395040000	-1.1963940000	0.1084420000
C	-3.1250660000	0.2481390000	-3.1978280000
C	-4.4223760000	-0.0040270000	-2.7597530000
C	-4.6129540000	-0.6107670000	-1.5061930000
C	-3.4715540000	-0.9187230000	-0.7553630000
C	-2.0277740000	-0.0863910000	-2.3943740000
C	-5.9185760000	-0.9420420000	-0.9366580000
C	-3.5590230000	-1.5700270000	0.5189210000
C	-4.7898060000	-1.9230200000	1.0902550000
C	-6.0071400000	-1.5879870000	0.3521140000
C	-4.7652310000	-2.5858900000	2.3285810000
H	-5.6988110000	-2.8680090000	2.7913930000
C	-3.5359290000	-2.8721500000	2.9213350000
C	-2.3439710000	-2.4954770000	2.2906520000
H	-2.9509790000	0.7136860000	-4.1561720000
H	-5.2845430000	0.2534090000	-3.3557320000
H	-1.0063280000	0.0989870000	-2.6792110000
H	-3.4909900000	-3.3919510000	3.8668200000
H	-1.3629340000	-2.7090930000	2.6849190000
N	-2.2009310000	-0.6581630000	-1.1862810000
N	-2.3603460000	-1.8498870000	1.1092290000
C	-8.3232610000	-1.5908960000	0.1885720000
C	-8.2355050000	-0.9505050000	-1.0925640000
C	-9.4252530000	-0.6375940000	-1.8000050000
C	-10.6479330000	-0.9513310000	-1.2525280000
C	-10.7350610000	-1.5886470000	0.0182490000

C	-9.5985150000	-1.9031880000	0.7271860000
H	-9.3297470000	-0.1506900000	-2.7594020000
H	-11.5569260000	-0.7116150000	-1.7865240000
H	-11.7088310000	-1.8232030000	0.4254340000
H	-9.6358630000	-2.3846490000	1.6935140000
N	-7.1915480000	-1.9005160000	0.8876630000
N	-7.0199140000	-0.6411930000	-1.6319570000
C	3.5232630000	2.8180030000	-2.8287800000
C	4.7533290000	2.5455950000	-2.2320250000
C	4.7799080000	1.8846070000	-0.9929750000
C	3.5513920000	1.5169180000	-0.4271290000
C	2.3330680000	2.4295040000	-2.2020890000
C	5.9978950000	1.5630100000	-0.2506350000
C	3.4667820000	0.8580950000	0.8431940000
C	4.6089230000	0.5583950000	1.5966200000
C	5.9129220000	0.9076060000	1.0334640000
C	4.4205490000	-0.0550320000	2.8469340000
H	5.2837150000	-0.2991040000	3.4472530000
C	3.1242630000	-0.3278180000	3.2773520000
C	2.0265780000	-0.0042470000	2.4709100000
H	3.4760430000	3.3331070000	-3.7765900000
H	5.6854810000	2.8328050000	-2.6941780000
H	1.3525490000	2.6325050000	-2.6028910000
H	2.9517610000	-0.7977170000	4.2341220000
H	1.0061480000	-0.2041890000	2.7495780000
N	2.3508870000	1.7837890000	-1.0202320000
N	2.1968540000	0.5797340000	1.2675390000
C	8.2287220000	0.9456280000	1.1992610000
C	8.3124940000	1.5965840000	-0.0766840000
C	9.5852190000	1.9289470000	-0.6092450000
C	10.7234720000	1.6253380000	0.1013270000
C	10.6404510000	0.9802920000	1.3684690000

C	9.4203080000	0.6459080000	1.9093390000
H	9.6188140000	2.4136080000	-1.5739530000
H	11.6953250000	1.8735780000	-0.3021760000
H	11.5509060000	0.7512250000	1.9048540000
H	9.3283540000	0.1538410000	2.8665990000
N	7.0151720000	0.6157060000	1.7316270000
N	7.1799570000	1.8972290000	-0.7772910000

Table S5. TD-DFT predicted electronic transitions and oscillator strength (*f*) for **Co-4**.

Complex, HOMO, LUMO	**Energy (eV)**	**Wavelength (nm) calculated**	**Orbitals involved in transitions**	**Oscillator strength (*f*)**
HOMO=253 LUMO=254	0.9671	1282.05	250→254 250→256 253→254 253→256 253→258	0.0723
	1.9659	631	251→255 252→254 252→256	0.0835
	2.1164	586	247→254 251→255 252→254 252→256 253→261 253→262	0.1020

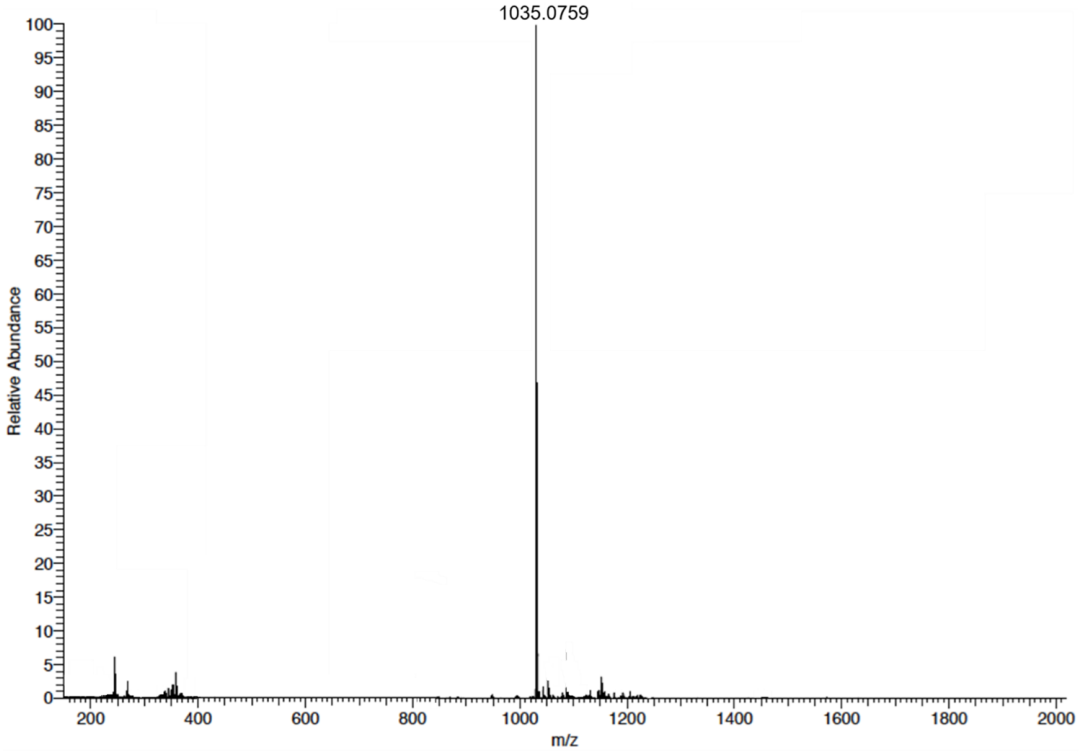

Fig. S17. HRMS (ESI+) spectrum of **Co-4** recorded in H_2O/MeOH [1:19 (v/v)] solution after 48 h of incubation showing the retention of the dimeric identity of the complex.

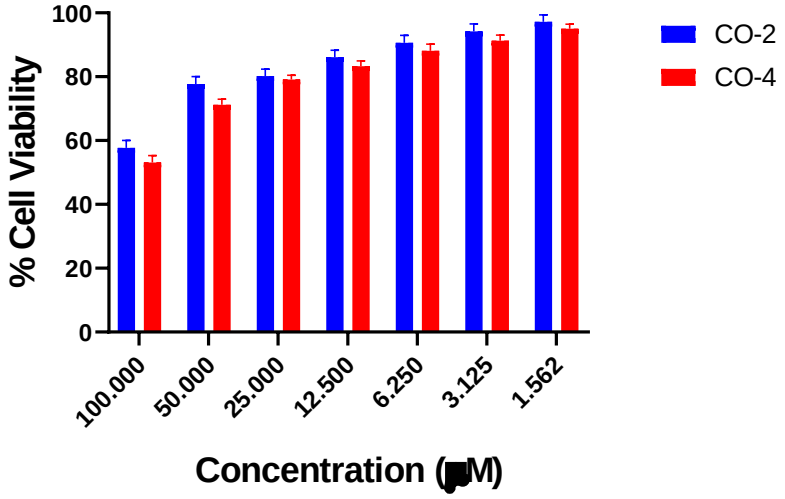

Fig. S18. Bar graph representing the % cell viability conducted for NIH-3T3 normal embryonic fibroblast cell line treated with complexes **Co-2** and **Co-4**.

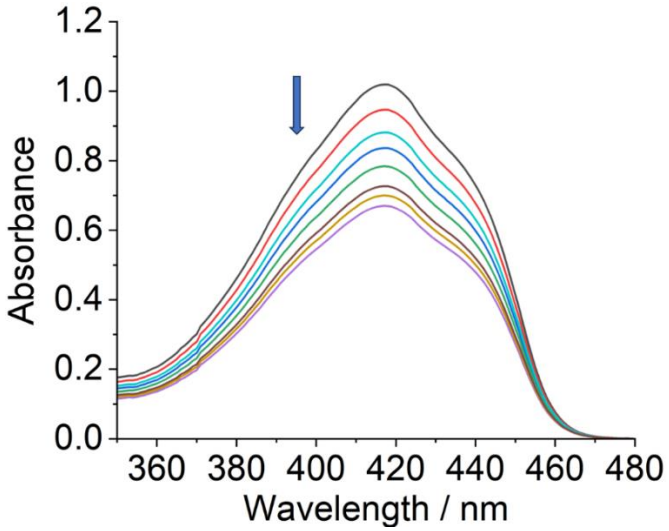

Fig. S19. The gradual drop in the absorbance of DPBF treated with **Co-4** (15 μM) under 808 nm (450 mW) light irradiated conditions.

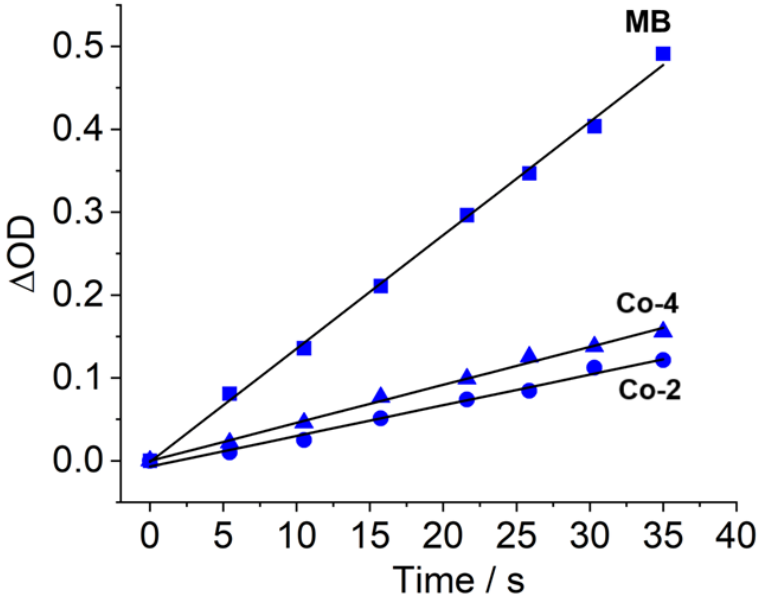

Fig. S20. Plots of ΔOD vs. time to calculate singlet oxygen quantum yield (ϕ_Δ) for **Co-2** (circle) and **Co-4** (triangle). Methylene blue (MB, square) was used as a reference. All experiments used light of 808 nm (450 mW) for irradiation.

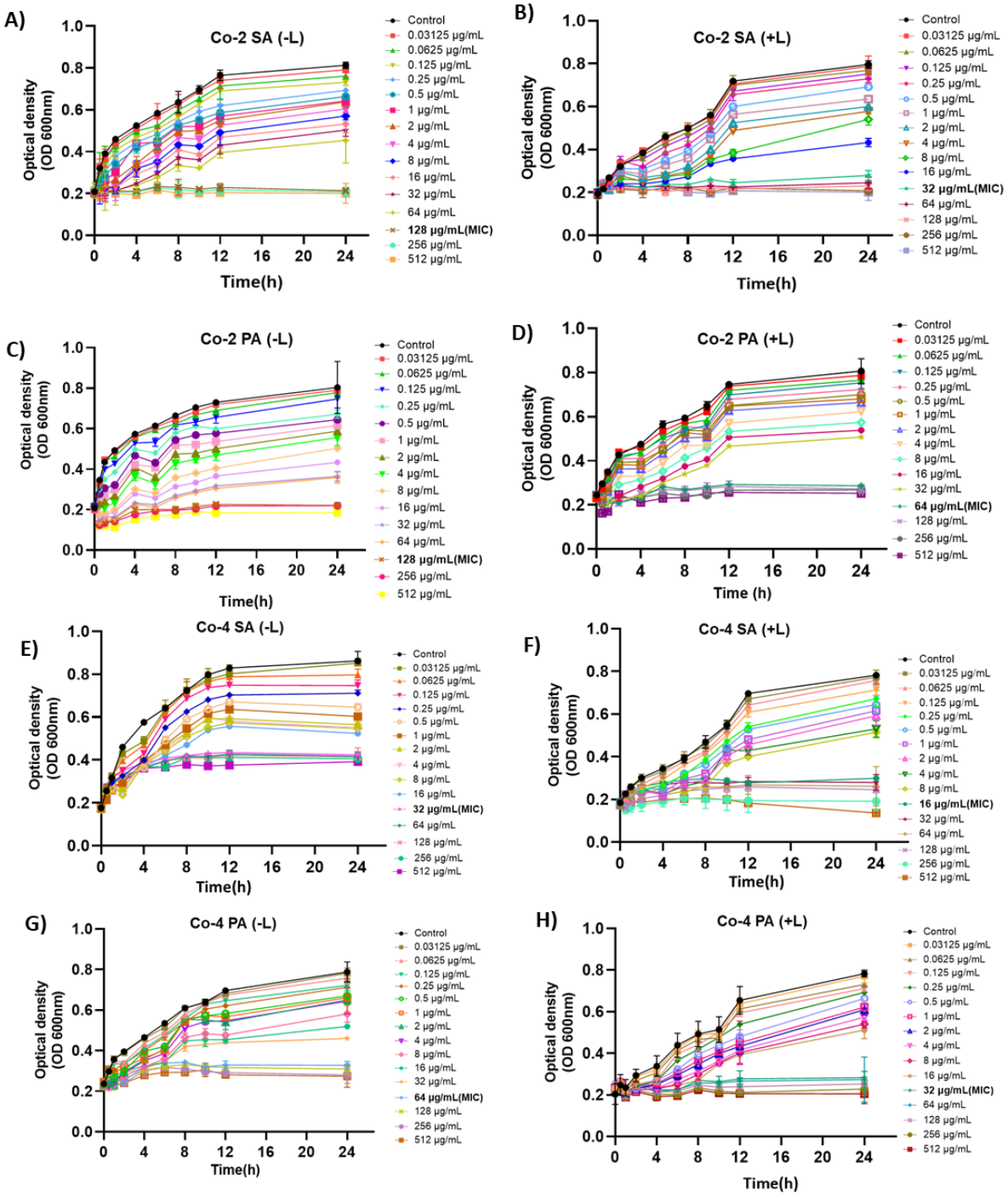

Fig. 21. Determination of minimum inhibitory concentration by broth microdilution method. Growth inhibition curves (A to D) of *P. aeruginosa* (*PA*) and *S. aureus* after treatment with **Co-2** with and without laser irradiation. **Co-2** (dark, in A) and **Co-2** (+ 808 nm light, in B) against *SA;* **Co-2** (dark, in C) and **Co-2** (+ 808 nm light, in D) against *PA*. Growth inhibition curves (E to H) of *P. aeruginosa* (*PA*) and *S. aureus* after treatment with **Co-4** with and without laser irradiation. **Co-4** (dark, in E) and **Co-4** (+ 808 nm light, in F) against *SA;* **Co-4** (dark, in G) and **Co-4** (+ 808 nm light, in H) against *PA*. –L signifies dark while + L signifies light irradiation.

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