Electronic supplementary information

for

Polypyridyl-based Co(III) Complexes of Vitamin B_6 Schiff base for Photoactivated Antibacterial Therapy

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Materials

Cobalt(II) chloride hexahydrate was purchased from SRL Chemicals, India. Dipicolylamine (dpa), ferrocene carboxaldehyde, and DPA (9,10-diphenyl anthracene) were purchased from TCI (Tokyo Chemical Industry Co. Ltd.,) (Japan). Triethyl amine, 2-Hydroxybenzaldehyde, and 2-aminophenol were purchased from Avra Synthesis Pvt. Ltd. (India). Benzaldehyde and 2-acetylpyridine were purchased from Merck Specialities Pvt. Ltd. Pyridoxal Hydrochloride was purchased from Sigma-Aldrich Chemicals Pvt. Ltd. Nutrient broth and agar were purchased from Himedia, India. Methanol was purchased from SDFCL (S D Fine-Chem Limited (India).

Instrumentation

For recording the UV-Vis spectrum of the complexes, Agilent Cary 60 UV-Vis spectrophotometer was used. To record the IR data, the PerkinElmer spectrum-2 FT-IR instrument was used. For the HRMS data, maXis impact 282001.00081 was used. To get SC-XRD data Bruker D8 Quest diffraction equipped with PHOTON-II CCD detector (Mo X-ray source) was used. AVH D 500AVANCE III HD 500 MHz OneBay NMR Spectrometer was used to record NMR spectra. For the incubation of microbial cultures, an incubator from Amaze Instruments, India was used. The LED panel-based light source from Veto Switchgear and cables ltd., India was used for visible light illumination.

Methods

UV- Visible spectroscopy

UV-visible studies of complexes **1**-**5** were performed using methanol as a solvent in a 1 cm quartz cuvette from 300-800 nm at ambient temperature.

$^1O_2$ generation

Generation of $^1O_2$ by the complexes was monitored in the presence of white light (0.5 J/cm^2) using the DPA (9,10-diphenyl anthracene) probe. 40 μM of Co(III) complexes (in 2:98 (v/v) DMSO/H_2O) were used in this study. The change in the absorbance of DPA in the presence of complex and light was monitored by UV-visible spectroscopy at 10-minute intervals.

Single Crystal X-ray Crystallography

Crystals for complexes **1a**, **3a**, and **4a** have been obtained by slow evaporation methods. A suitable crystal for each complex was selected and mounted in a cryo loop using a cryoprotectant paraffin oil. Complex **1a**, and **3a** were collected at 150 K temperature and complex **4a** at 104 K temperature, on a Bruker D8 quest diffractometer equipped with an incoatec microfocus source (IμS 3.0 Mo Kα, λ = 0.71073 Å) and a PHOTON-II CCD detector. X-ray diffraction intensities were collected, integrated, and scaled with APEX 4 software. Empirical absorption correction was applied to the data using a multi-scan method with SADABS programming.[1] The structure was solved by intrinsic phasing with SHELXT[2] and refined by full-matrix least-square methods on F2 using SHELXL using the ShelXle along with the Olex2 interface.[3,4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at a calculated position. They were treated as riding atoms with an isotropic displacement parameter, C-H = 0.93-0.98 Å with Uiso (H) = 1.5 Ueq for methyl groups, Uiso (H) = 1.2 Ueq (C, N) for all other C-H and N-H bonds and O—

H = 0.82 Å[Uiso(H) = 1.5Ueq(O)]. ORTEP,[5] Mercury,[6] and publCIF[7] were used for molecular graphics, validation and to prepare material for publication. Details of crystal data collections and data refinement parameters are given in **Table S1**. The complete crystallographic information files (CIF) of **1a**, **3a**, and **4a** were deposited in the Cambridge crystallographic data center (CCDC 2293658, CCDC 2293666, CCDC 2293665).

Table S1. Single crystal XRD data of **1a**, **3a**, and **4a**.

Complex	**1a**	**3a**	**4a**
a (Å)	14.4253(3)	21.4901(4)	14.9257(11)
b (Å)	14.5947(3)	15.8579(3)	25.6700(2)
c (Å)	25.4953(5)	21.6752(4)	9.3216(7)
α (°)	90	90	90
β (°)	100.006(2)	97.004(2)	121.295(2)
γ (°)	90	90	90
Crystal system	Monoclinic	Monoclinic	Monoclinic
Temperature (K)	150.00	150.00	100.00
Reported Volume (Å^3)	5285.96(19)	7331.5(2)	3051.90(4)
Space group	P121/n1	P121/n1	C 1 c 1
D_x (g cm^{-3})	1.527	1.468	1.567
Z	8	8	4
Formula Weight	$C_{26.95}H_{23}ClCoN_{5.03}O_6$	$C_{36}H_{31.50}CoF_6N_5O_{4.50}P$	$C_{36}H_{27}ClCoN_5O_6$
MW (g/mol)	607.73	810.06	720.031
μ (mm^{-1})	0.803	0.590	0.709
F (000)	2495.0	3316.0	1483.0
Reflections measured	0.1027(7464)	0.0522(10528)	0.0430(4929)
WR_2 reflections	0.2592(9312)	0.1487(12896)	0.0995(5081)

CCDC No.	2293658	2293666	2293665

Computational details

The complexes, **1**-**5** were studied in their cationic form by Density Functional Theory (DFT) using the Gaussian 16 quantum chemistry package, revision A.03.[8] We have used the LANL2DZ basis set for Co and 6-31g for all other atoms with the B3LYP function for geometry optimization in the gas phase.

Cell culture

Cell line A549 was maintained in a DMEM medium supplemented with 10% fetal bovine serum, and 1% penicillin-streptomycin solution. All cells were grown at 310 K in a humidified incubator, which provided an atmosphere of 5% CO_2/95% air (Thermo Fisher).

Figures

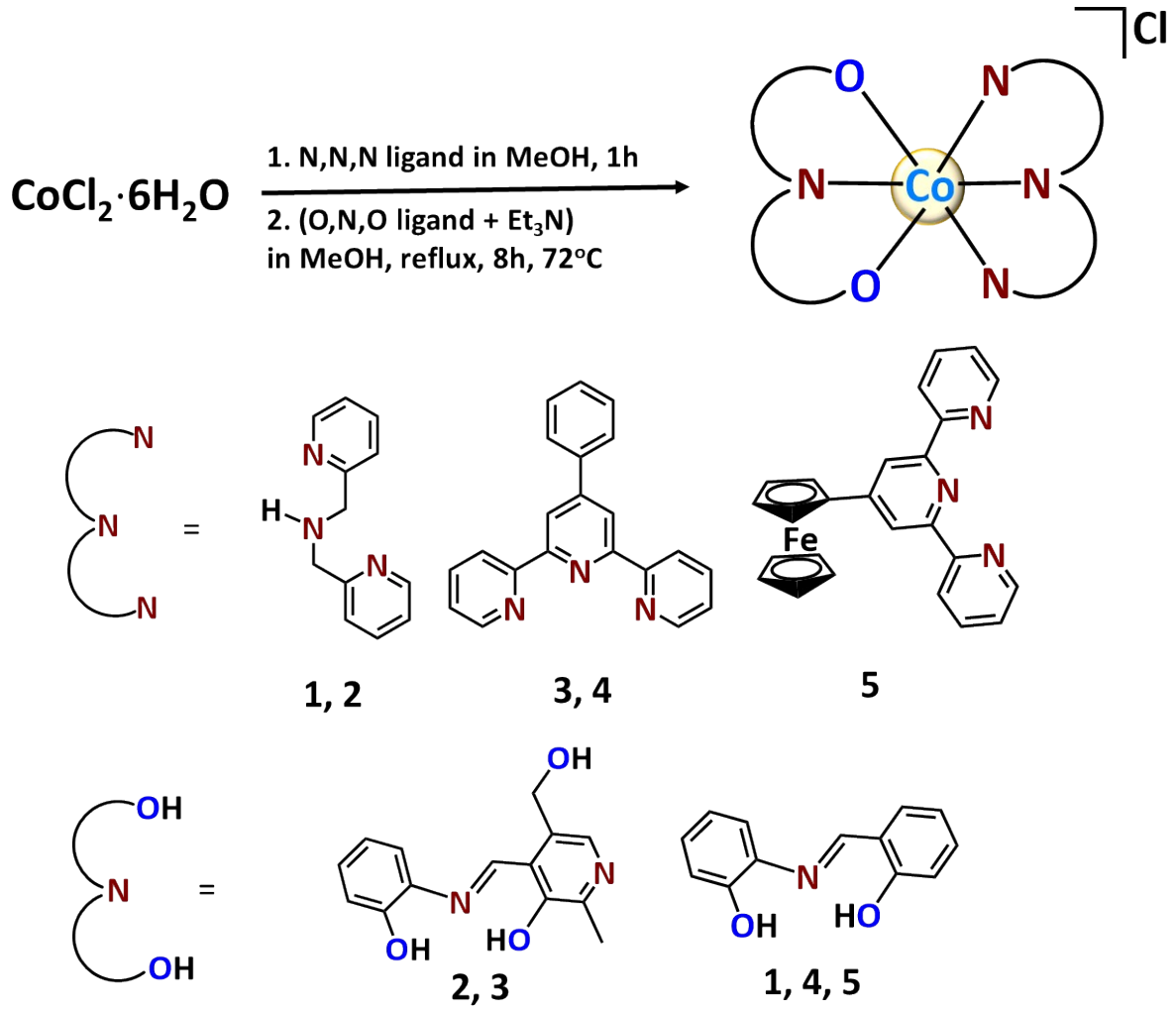

Figure S1. General Synthetic route for the synthesis of complexes **1**-**5**.

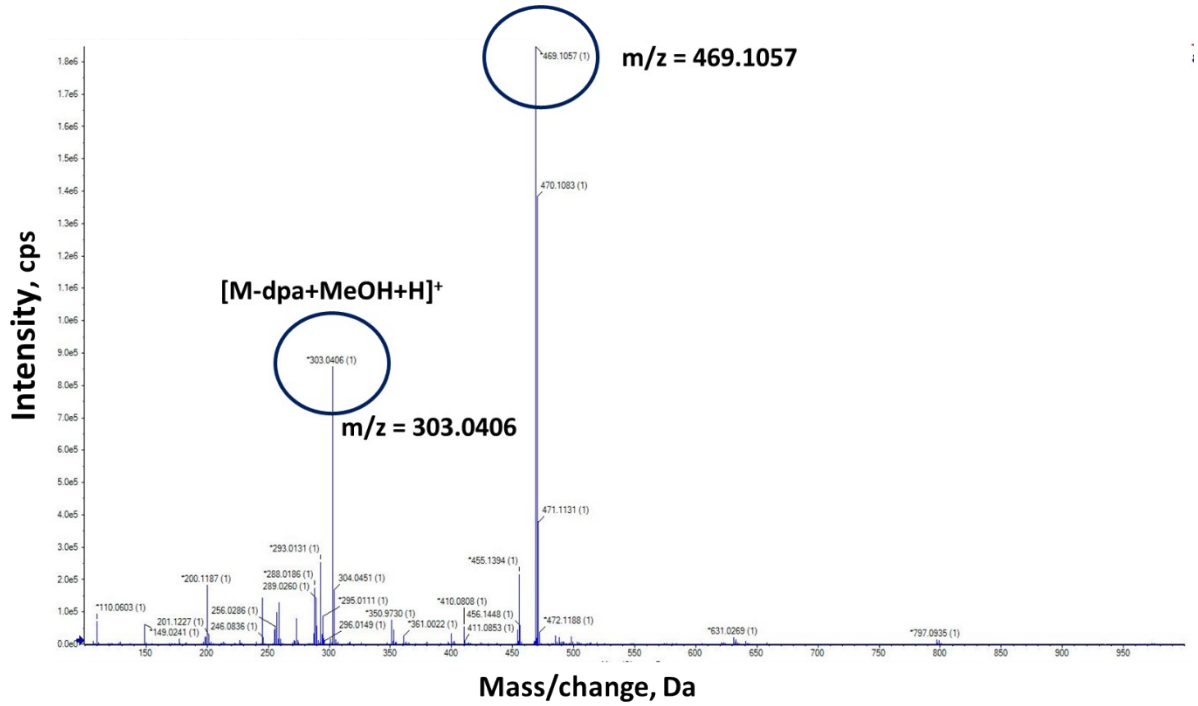

Figure S2. The HR-MS (High resolution mass spectrometry) spectrum of complex **1** in MeOH. The calculated m/z value is 469.10.

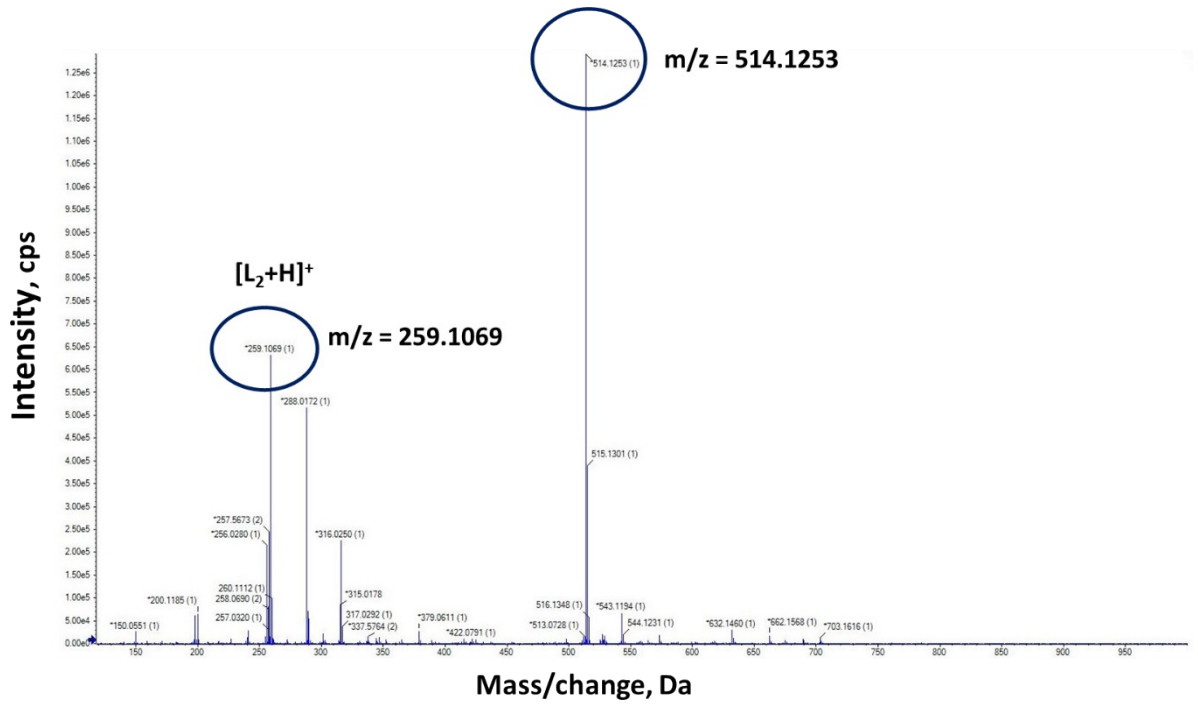

Figure S3. The HR-MS spectrum (High resolution mass spectrometry) of complex **2** in MeOH. The calculated m/z value is 514.12.

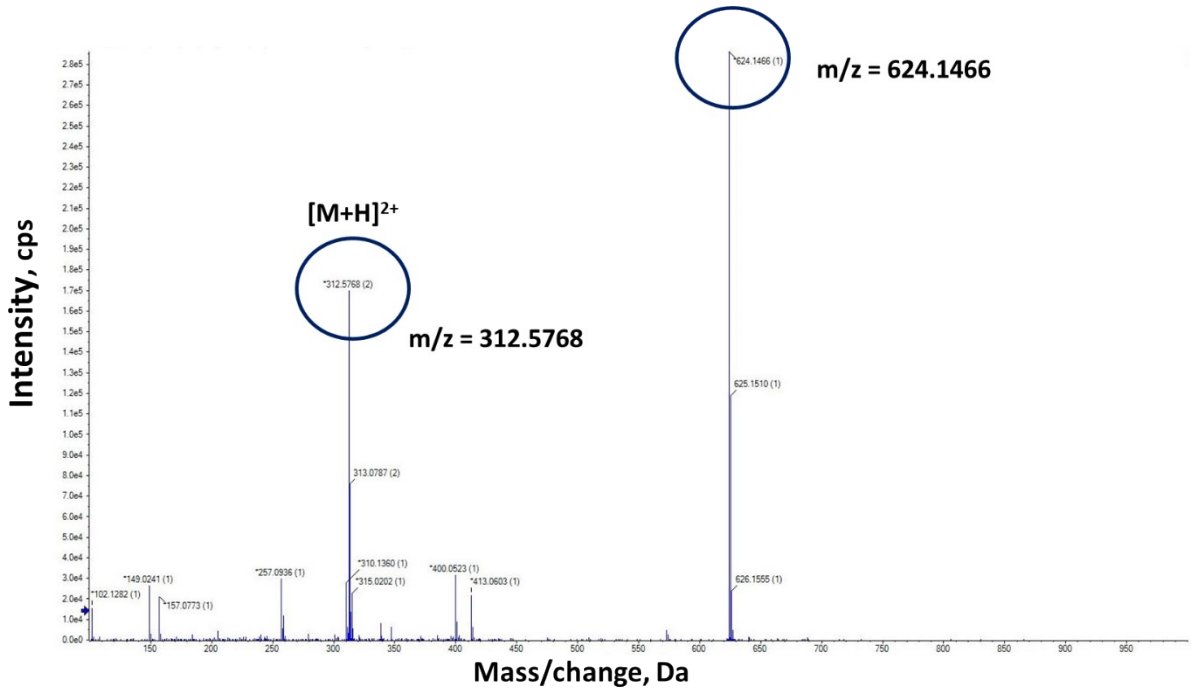

Figure S4. The HR-MS spectrum (High-resolution mass spectrometry) of complex **3** in MeOH. The calculated m/z value is 624.14.

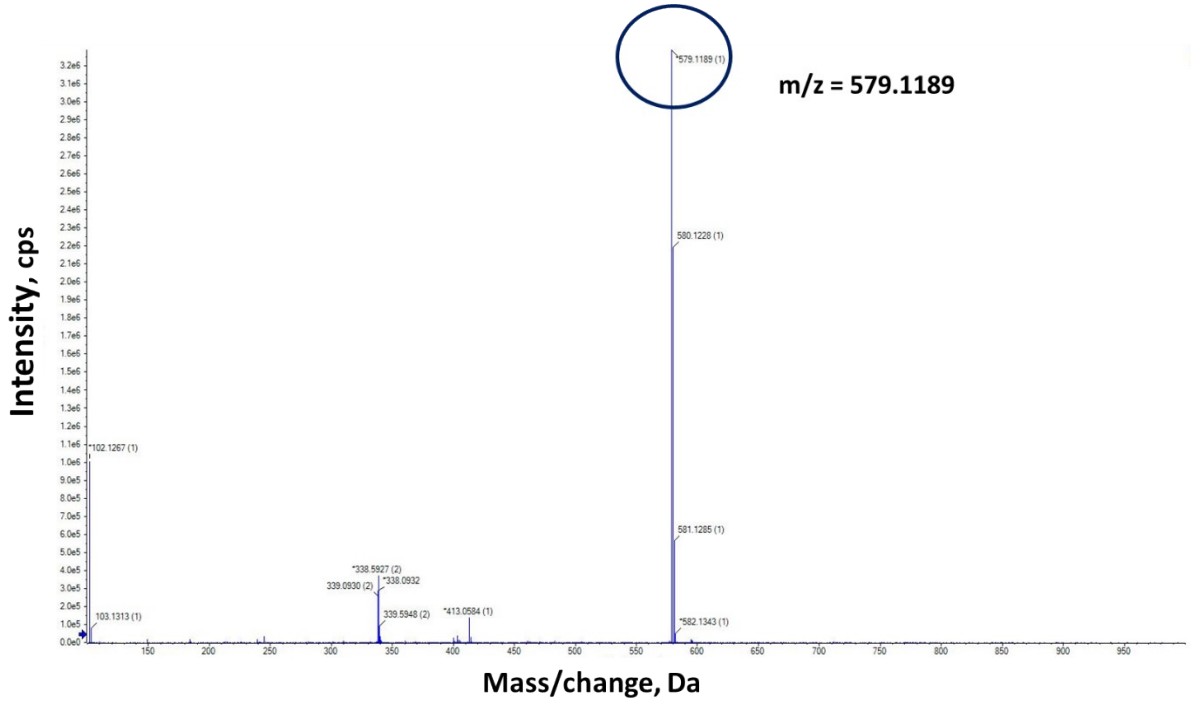

Figure S5. The HR-MS (High-resolution mass spectrometry) spectrum of complex **4** in MeOH. The calculated m/z value is 579.12.

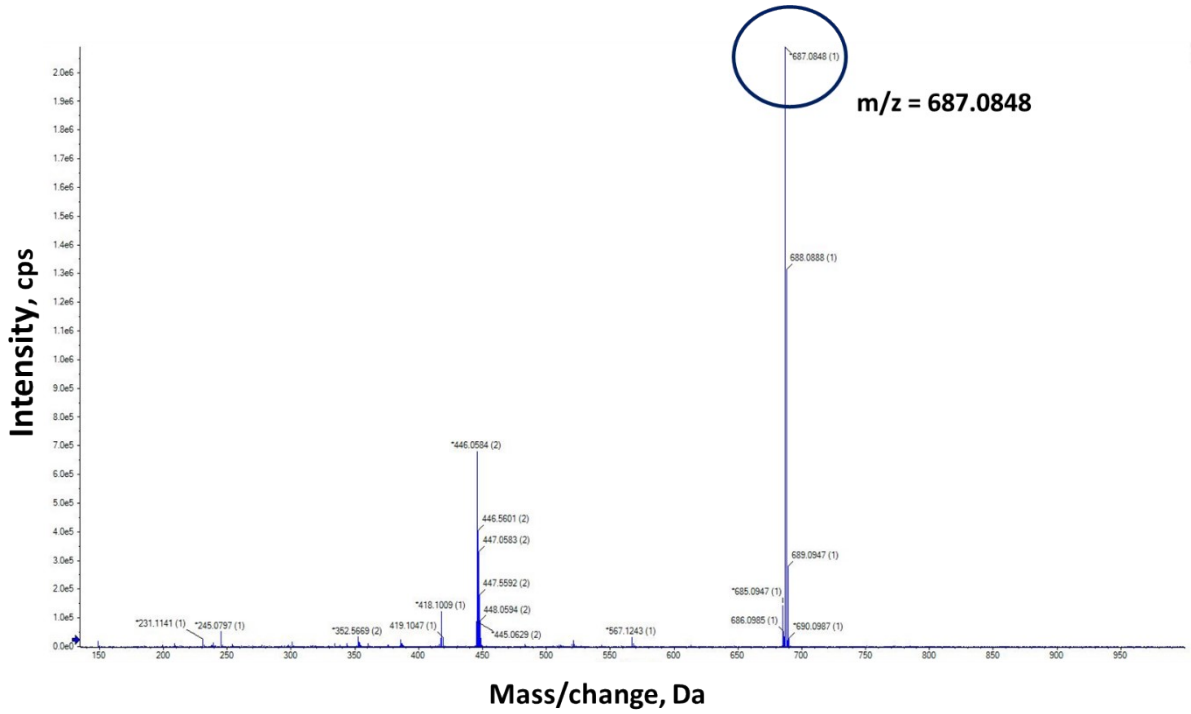

Figure S6. The HR-MS (High-resolution mass spectrometry) spectrum of complex **5** in MeOH. The calculated m/z value is 687.08.

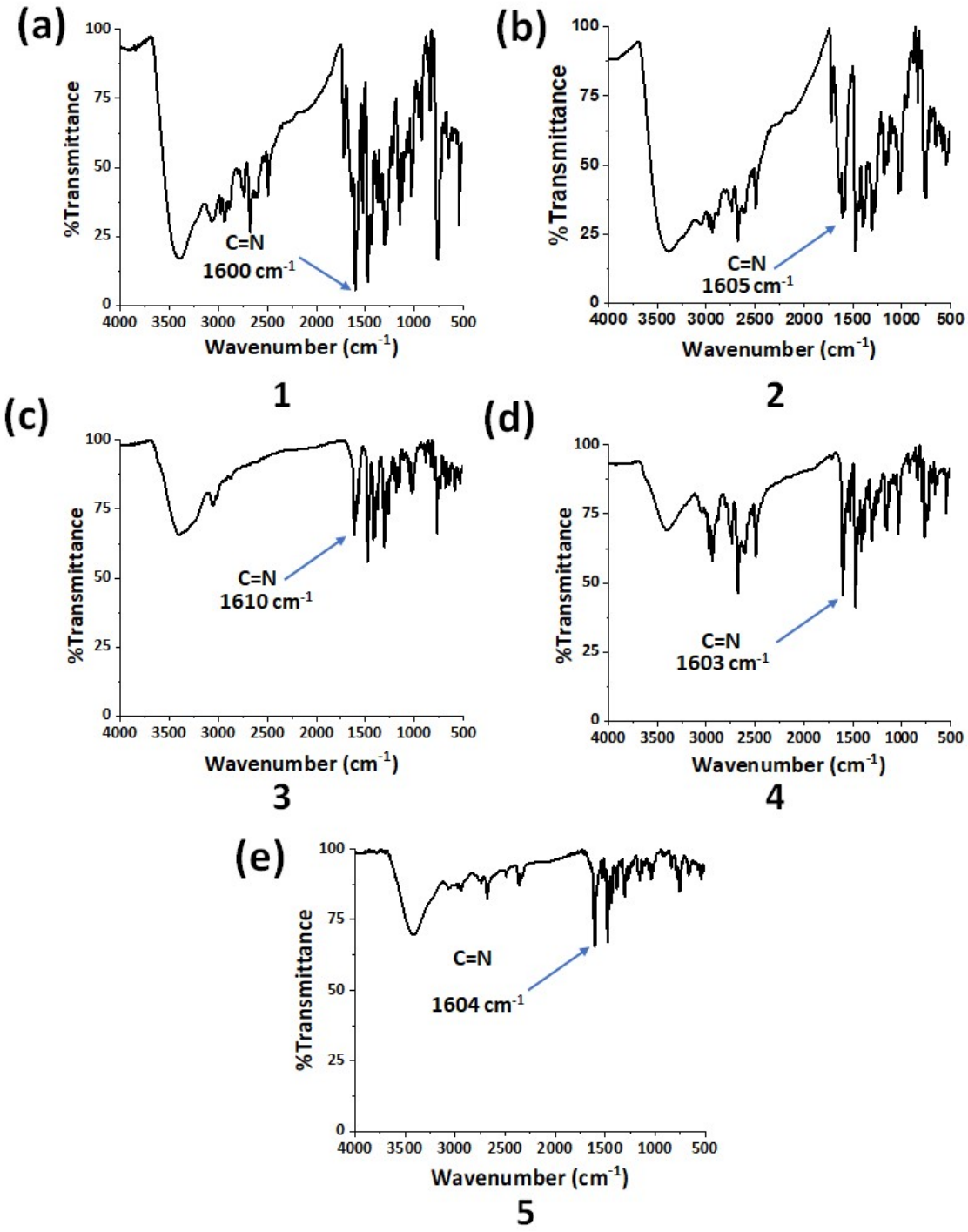

Figure S7: (a-e) FTIR data of complexes **1**-**5** in solid phase.

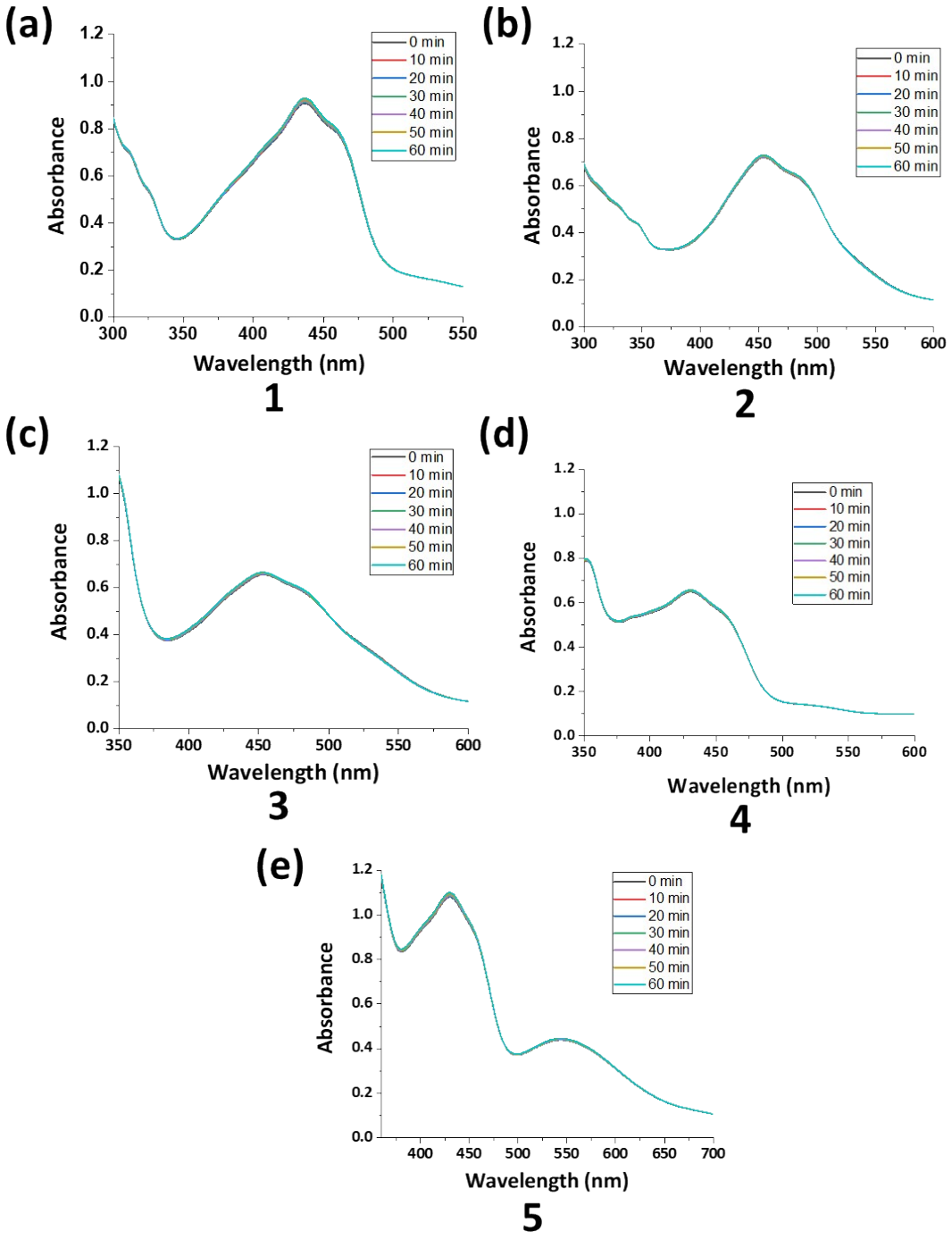

Figure S8. Photo-stability of complexes **1**-**5** in MeOH up to 1 h.

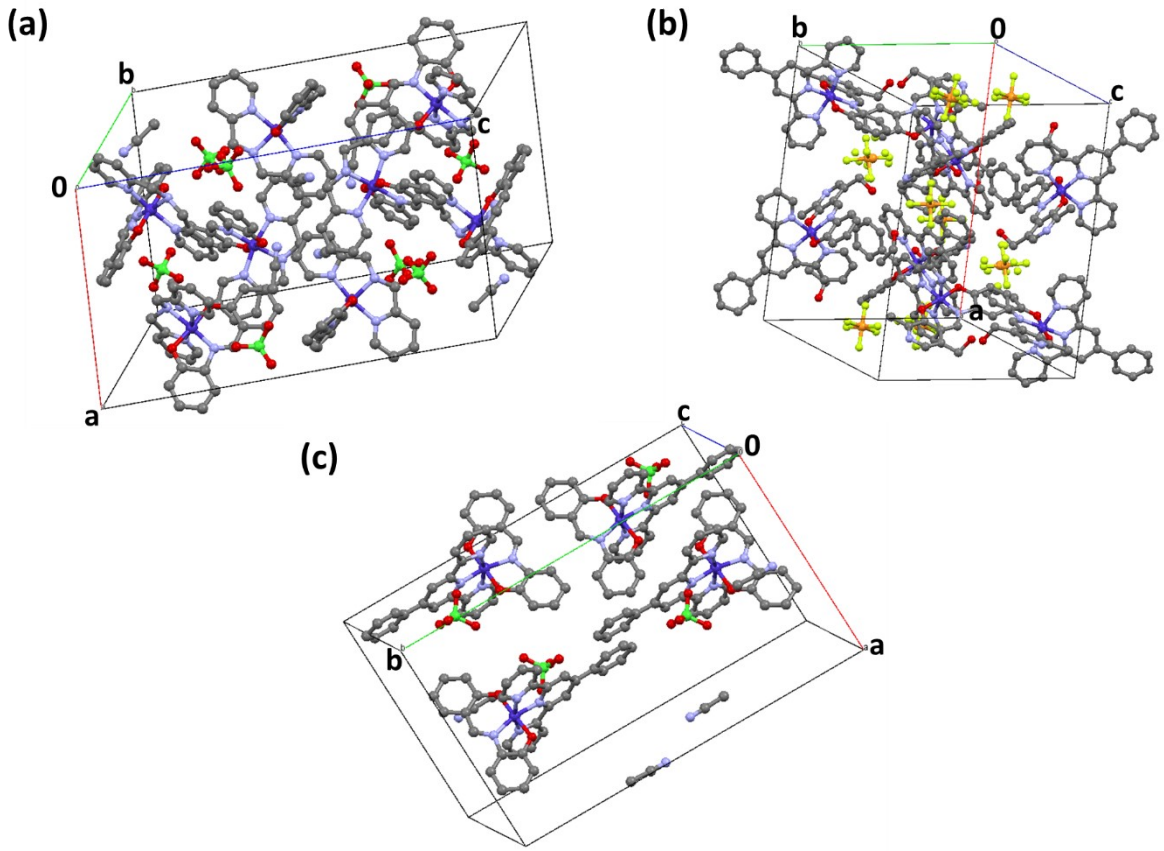

Figure S9. Unit cell packing of **1a** (a), **3a** (b), and **4a** (c). The pictures were made using Mercury 3.8 software.[9]

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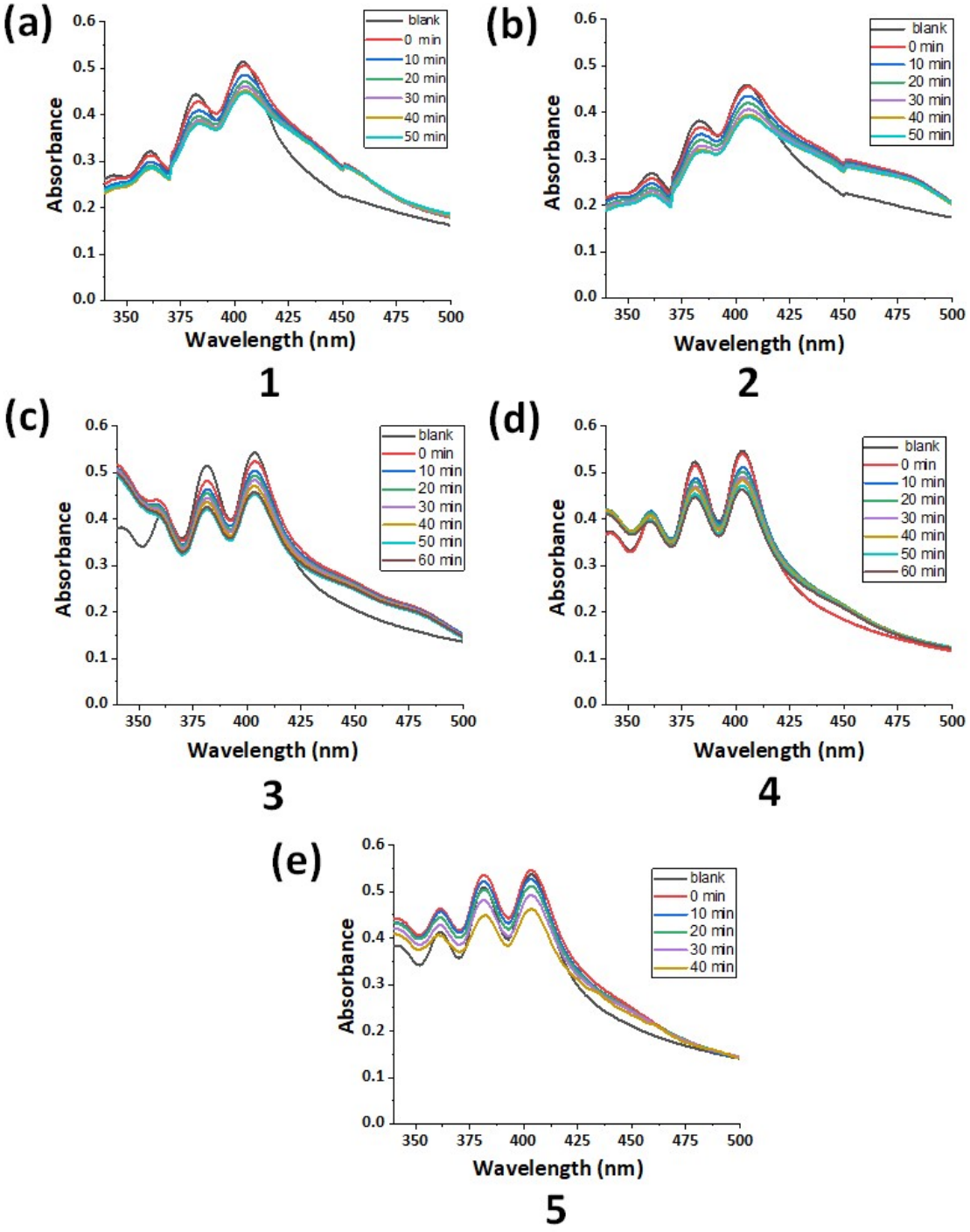

Figure S10. (a-e) Change in the intensity of the DPA-based absorption bands in the presence of complex **1**-**5** upon light exposure.

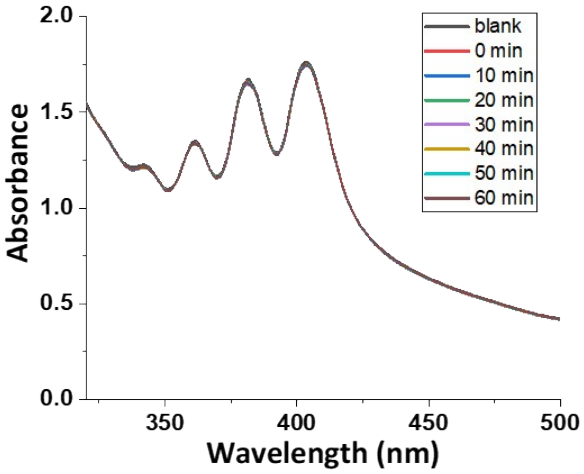

Figure S11. Change in the intensity of the DPA-based absorption bands in the presence of CoF_3 (40 μM) upon light exposure.

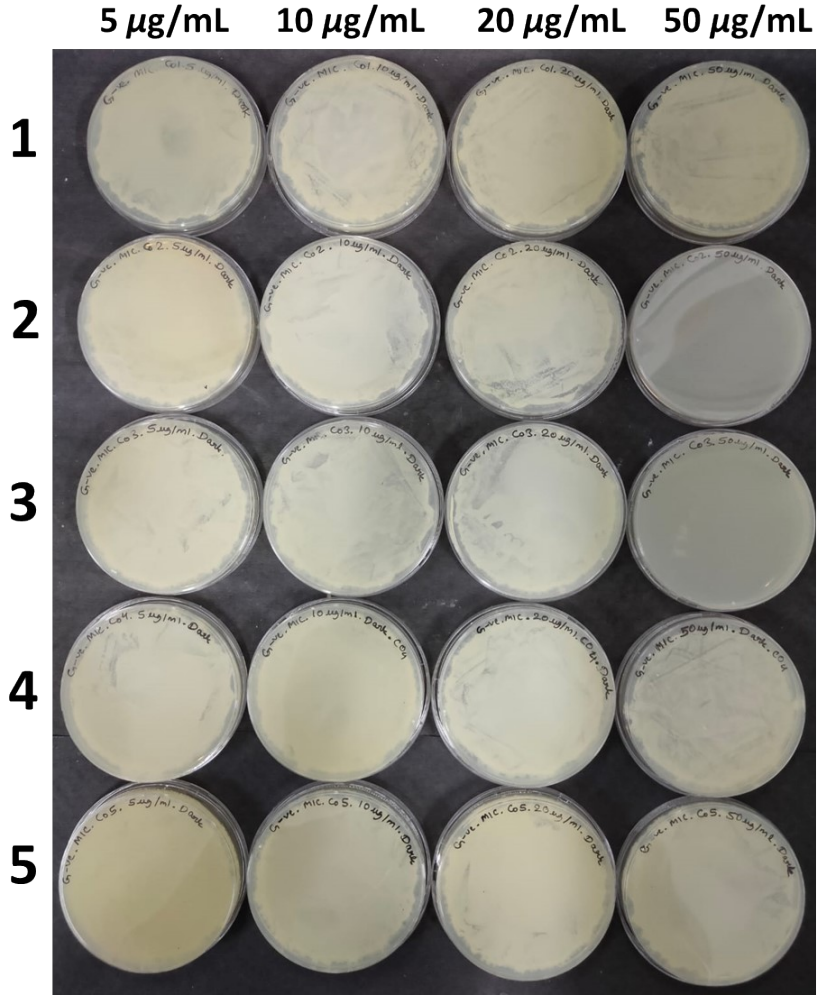

Figure S12. Antibacterial activity of complexes **1**-**5** against *E. coli* under dark.

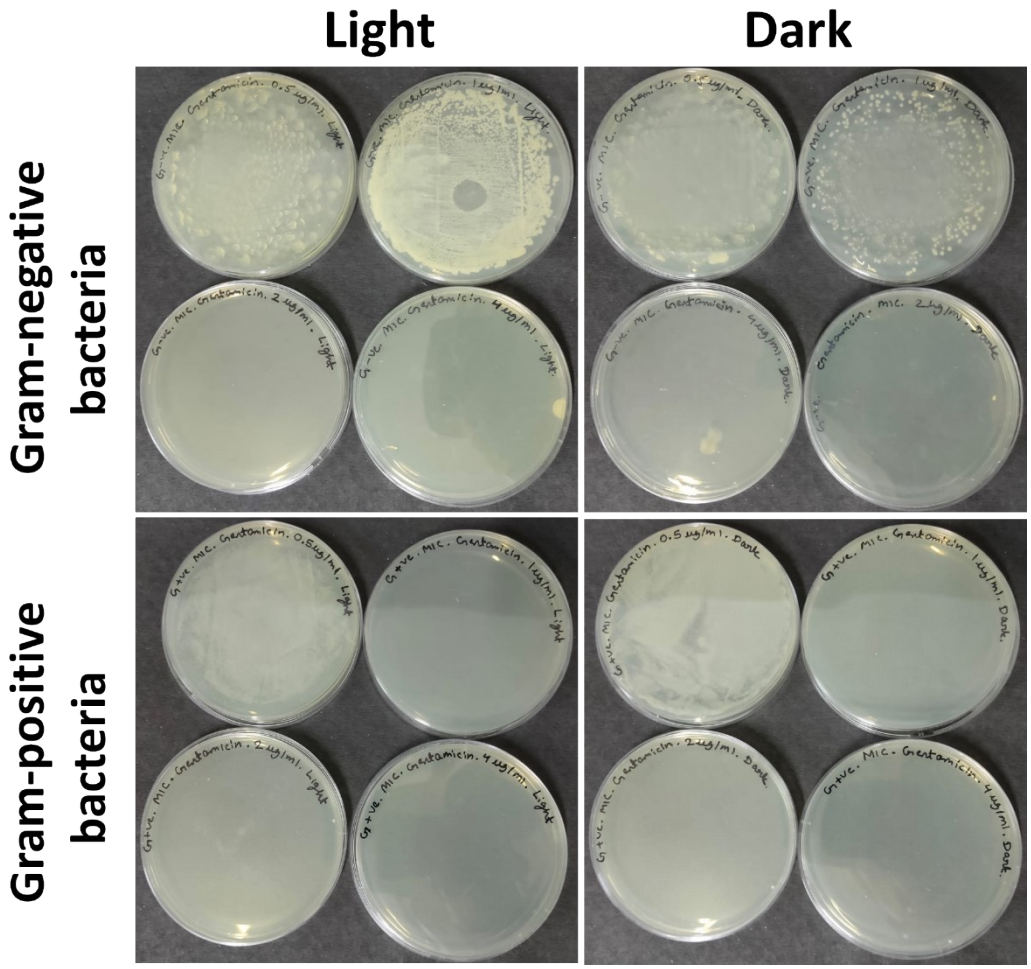

Figure S13. Inhibition activity of gentamicin against *S. aureus* (gram-positive) and *E. coli* bacteria (gram-negative) upon light exposure.

References:

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