Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Visible-light Responsive Metal-Organic Framework as an Eco-friendly Photocatalyst under Ambient Air at Room Temperature

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1. X-ray Crystallography (Single-crystal diffraction) and Characterizations of Co−DCFB.

1.1 Crystal data of Co−DCFB:

$C_{30}H_{17}Cl_2N_2O_{5.5}Co_{0.5}$, Mr = 593.82, Monoclinic, space group *C2/c*, a = 23.022(3), b = 11.4407(14), c = 22.436(3) Å, α = 90.00, β = 104.889(2), γ = 90.00, V = 5710.9(12) $Å^3$, Z = 8, *D*c = 1.381 g cm^{-3}, μ(Mo-Kα) = 0.551 mm^{-1}, *T* = 200(2) K. 3954 unique reflections [R_{int} = 0.1108]. Final R_1[with $I > 2\sigma(I)$] = 0.0613, wR_2(all data) = 0.1773, GOOF = 1.010. CCDC number: 1884820.

1.2 Crystallography:

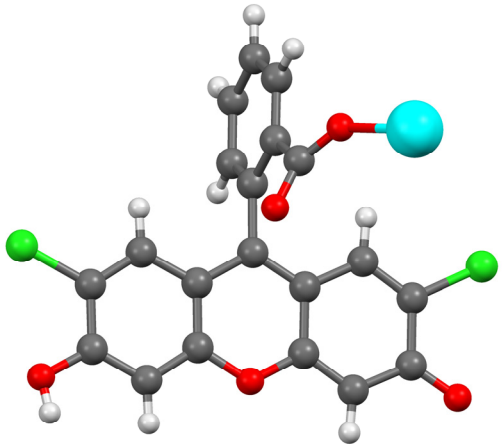
Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphitemonochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms.

1.3 Selective bond distance (Å) and angle (°) in Co−DCFB.

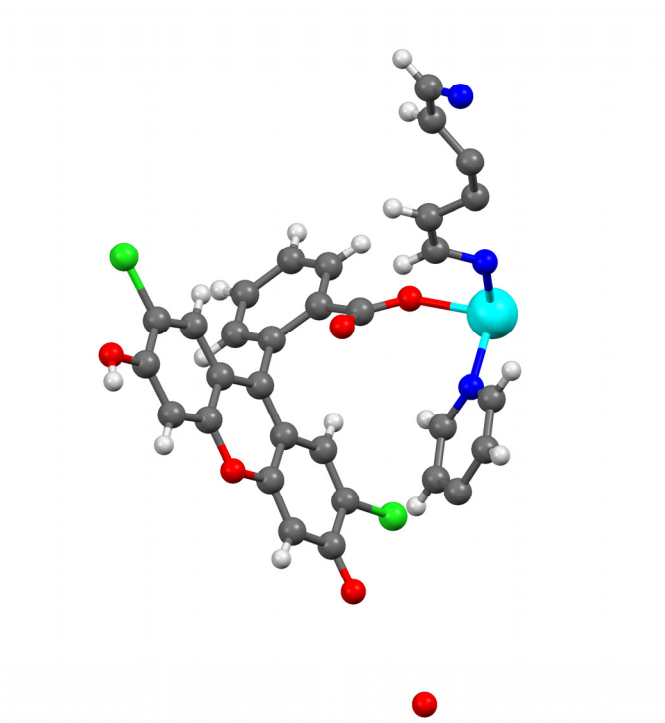
Co(1)–O(5)	2.106(2)	Co(1)–N(1)	2.121(3)
Co(1)–O(5A)	2.106(2)	Co(1)–N(1A)	2.121(3)
Co(1)–N(2)	2.151(4)	Co(1)–N(3B)	2.204(4)
O(5)–Co(1)–O(5A)	173.78(12)	O(5)–Co(1)–N(1)	93.18(9)
O(5A)–Co(1)–N(1)	86.53(9)	O(5)–Co(1)–N(1A)	86.53(9)
O(5A)–Co(1)–N(1A)	93.17(9)	O(5A)–Co(1)–N(2)	93.11(6)
N(1)–Co(1)–N(1A)	174.58(14)	O(5)–Co(1)–N(2)	93.11(6)
N(1)–Co(1)–N(2)	92.71(7)	O(5)–Co(1)–N(3B)	86.89(6)
O(5A)–Co(1)–N(3B)	86.89(6)	N(1)–Co(1)–N(3B)	87.29(7)
N(1A)–Co(1)–N(3B)	87.29(7)	N(2)–Co(1)–N(3B)	180.0

Symmetry code A: -*x*, *y*, 0.5-*z*; B: *x*, 1+*y*, *z*.

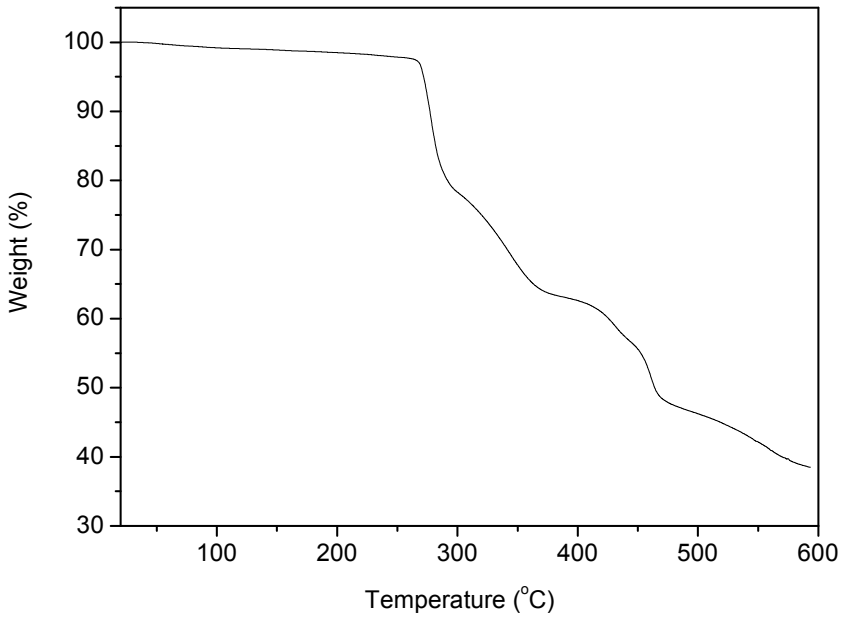
1.4 Figure S1 The coordination mode of 2',7'-dichlorofluorescein ligands in Co−DCFB. Atoms are colored as follows: Co, cyan; Cl, green; O, red; C, gray; H, white.



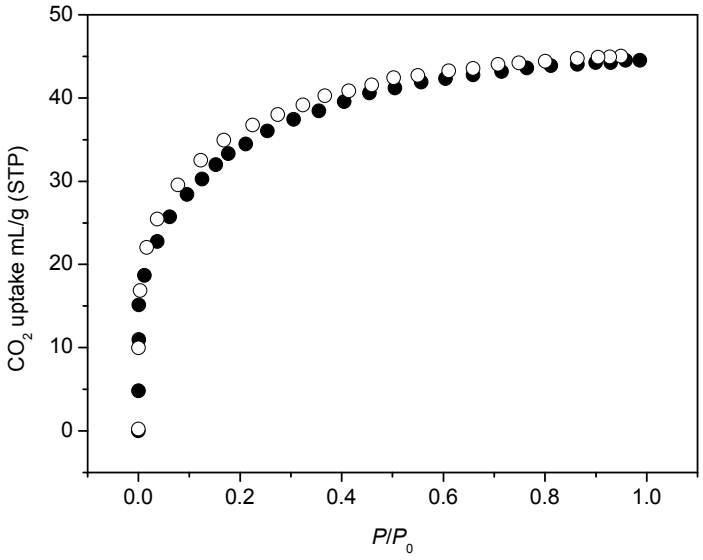
1.5 Figure S2 The asymmetric unit of Co−DCFB. Atoms are colored as follows: Co, cyan; N, blue; Cl, green; O, red; C, gray; H, white. The hydrogen atoms of free solvent molecules were omitted for clarity.



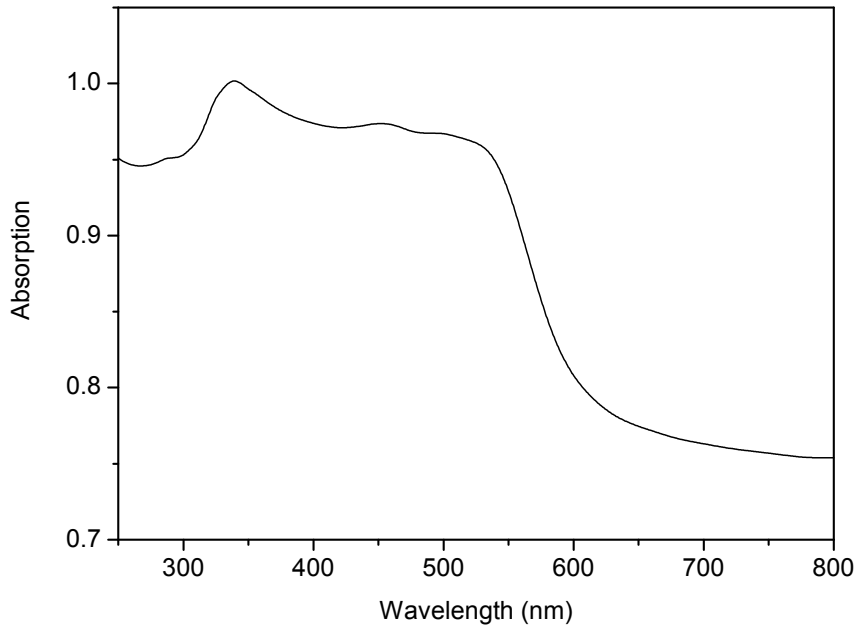
1.6 Figure S3 TGA traces of Co−DCFB ranging from room temperature to 600 °C.



1.7 Figure S4 CO_2 adsorption/desorption isotherms of Co−DCFB at 195 K.

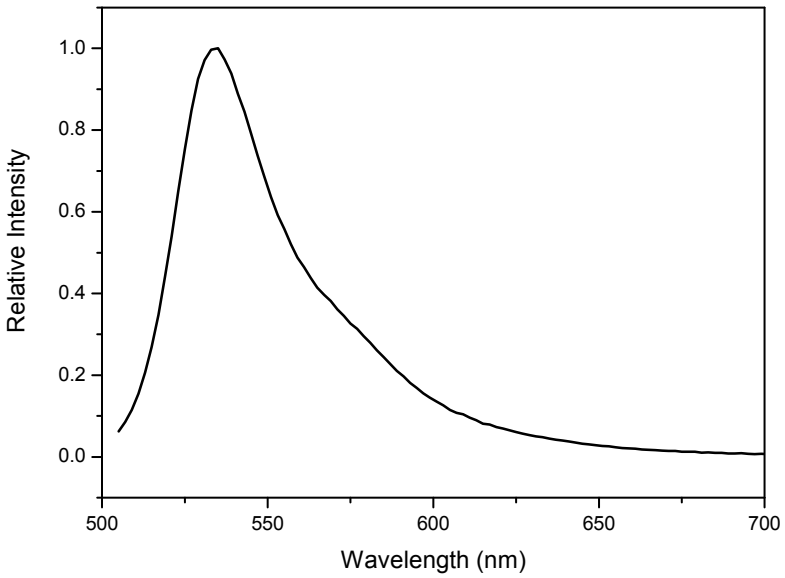


1.8 Figure S5 The UV/vis absorption spectra for solid Co−DCFB.

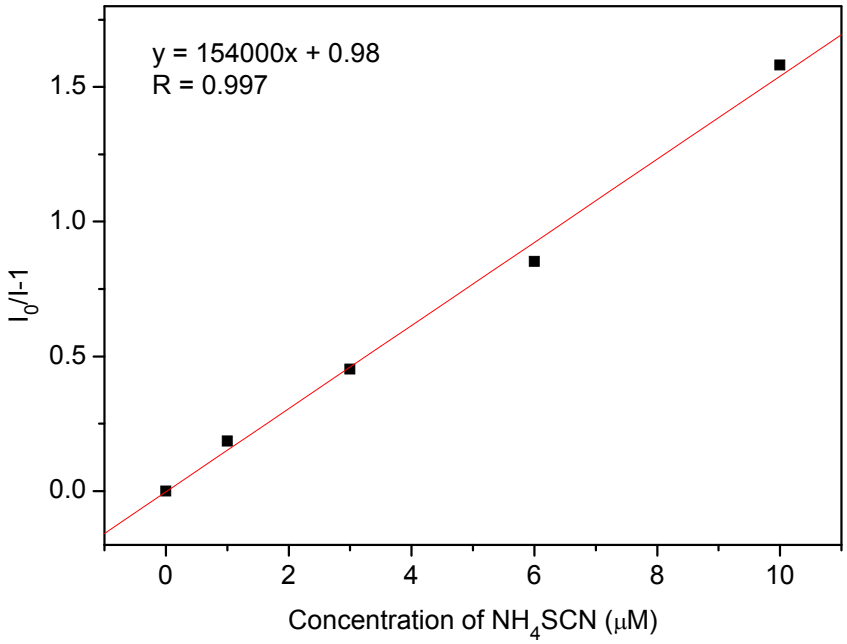


2. Photocatalysis and mechanism discussion.

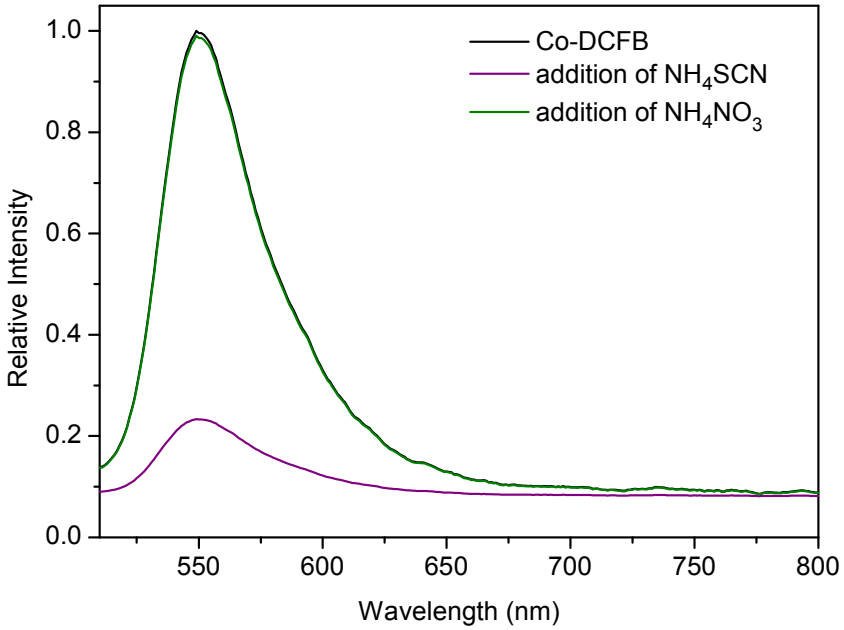
2.1 Figure S6 The emission spectrum of 0.1 mM 2',7'-dichlorofluorescein in acetonitrile solution when excited at 490 nm.



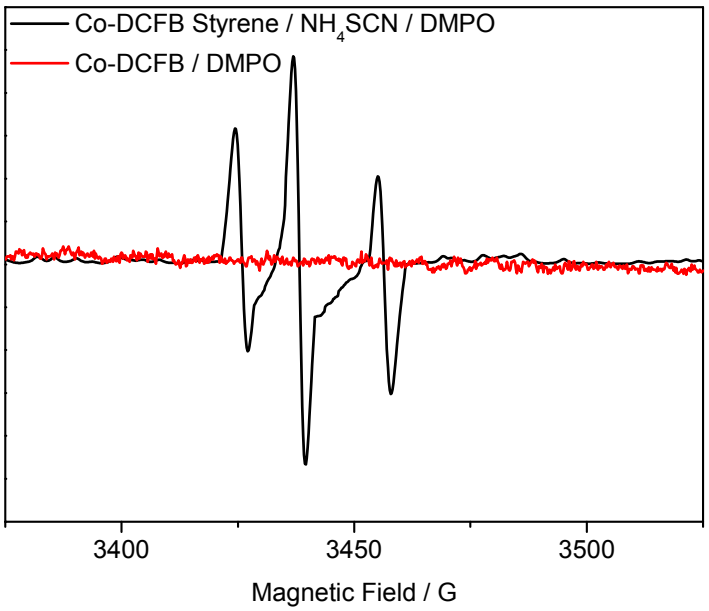
2.2 Figure S7 The Stern−Volmer plot of Co−DCFB quenched by NH_4SCN acetonitrile solution, where I_0 and I are the fluorescence intensity before and after NH_4SCN incorporation, respectively.



2.3 Figure S8 Family of emission spectra of Co−DCFB suspension upon addition of compound NH_4SCN and NH_4NO_3 up to 1.4 μM, respectively.



2.4 Figure S9 EPR spectra of Co−DCFB after 3 hours of visible light irradiation in aerated CH_3CN containing 50 mM DMPO (red line) and 50 mM DMPO, 60 mM NH_4SCN and 50 mM styrene (black line).



3. X-ray Crystallography of DCF−bpy.

3.1 Crystal data of DCF−bpy:

$C_{52}H_{28}Cl_4N_2O_{12}$, Mr = 1014.56, Triclinic, space group *P-1*, a = 7.8397(9), b = 13.2138(16), c = 22.211(3) Å, α =89.955(3), β = 89.125(3), γ = 75.659(3), V =2229.0(5) $Å^3$, Z = 2, *D*c = 1.512 g cm^{-3}, μ(Mo-Kα) = 0.71073 mm^{-1}, *T* = 200(2) K. 5223 unique reflections [R_{int} = 0.0946]. Final R_1[with $I > 2\sigma(I)$] = 0.0811, wR_2(all data) = 0.1911, GOOF = 1.064. CCDC number: 1884819.

3.2 Figure S10 The asymmetric unit of **DCF−bpy**. Atoms are colored as follows: Cl, green; O, red; C, gray; N, blue; H, white.