

Electronic Supporting Information

Photocatalytic Activity of New Nanostructures of Ag(I) Metal-Organic Framework (Ag-MOF) for the Efficient Degradation of MCPA and 2,4-D Herbicides under Sunlight Irradiation

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Experimental

Materials and physical techniques

Starting reagents were obtained from Sigma-Aldrich and Merck company. Elemental analyses (C, H as well as N) are carried out using a rapid analyzer from Perkin Elmer, 2400 series (II) CHNO. Fourier transform infrared (FT-IR) spectra were collected as KBr pellets in the spectral range of 400-4000 cm^{-1} and Agilent company model Cary 660 FTIR. The FT-IR is fitted with an IR (from 400 to 4000 cm^{-1}) and a room temperature detector. The intensity of X-Ray data for the **1** was obtained doing graphite monochromatic $\text{MoK}\alpha$ radiation on a four-circle κ geometry KUMA KM-4 diffractometer with a 2D area CCD detector. The ω -scan method with $\Delta\omega = 1.0^\circ$ permanent picture was obtained for data collection. After every 40 images, one image was applied as a norm for tracking crystal balance and data collection as well as no modification was expected concerning the general strength parameters. The data collection was created utilizing the CrysAlis CCD technique at room temperature.³¹ Integration, scaling of the reflections, a modification for Lorentz and polarization effects and, absorption modifications were done utilizing the CrysAlis Red program³¹. The structure was solved by the primary techniques applying SHELXT and refined applying SHELXL-2014 program.³² Information on data collection variables, crystallographic data, and ultimate deal parameters are obtained in Table S1. Selected geometrical parameters are shown in Tables S2 and S3. Visualization of the structure was created with the mercury applications.³³ Powder X-Ray Diffraction (PXRD) measurements were done utilizing X'pert diffractometer made by Philips with monochromatized $\text{CuK}\alpha$ radiation.³⁴ The samples were indicated with a scanning electron microscope (SEM) (HITACHI- SU5000) in the style function of secondary electrons (SE) with a beam voltage between 10 and 20 KV. The samples were

organized by depositing a drop of substance formerly distributed ineffectively solvents on aluminum stubs followed closely by evaporation of the solvent under normal conditions. US generator used by (ultrasonic-Scientz-750F-CHINA). Melting points were determined on a 1102D device. The concentration of pollutants was measured using High-Performance Liquid Chromatography (HPLC) method by use of an Agilent 1100, Wilmington, DE, USA instrument. A Shimadzu TOC-VCSN, Japan analyzer evaluated total organic carbon (TOC). A Garmin company, model etrex 10, Taiwan, utilized the Global Positioning System (GPS) to determine the geographic location of the position of sunlight irradiation.

Photo-induced degradation of the pollutants

For degradation experiments under sunlight irradiation, 10 mL (0.5-6.5 mgL⁻¹) of every pollutant were moved into a quartz beaker, the [Ag(PHBA)₂(NO₃)_n] as photocatalyst (0.2-1.0 gL⁻¹) was added to the solution, the pH was modified (3-11), and the mixture was thirty minutes in the dark until the cycle was balanced. The solution to the degradation was agitated to a predetermined time (10-90 min). The catalyst was then detached, and the HPLC process determined the contaminant content of the solution. For having a constant illumination of sunlight, the irradiation was done at 13 o'clock each day. A Garmin company, model etrex 10, Taiwan, measured the geographic location from sea level through the Global Positioning System (GPS) including latitude, longitude and altitude of the area. The experiments on photodegradation were conducted beneath the direct sunlight irradiation under maximum sunshine. The Longitude and Latitude of the geographic location were respectively 52.13, 32.24 degrees, and the attitude was 1825 m from sea level. The amount of deterioration percentage had been estimated as:

$$\% D = [(C_o - C_t) / C_o] \times 100 \quad (1)$$

C_0 and C_t , respectively, are blank and sample concentration.

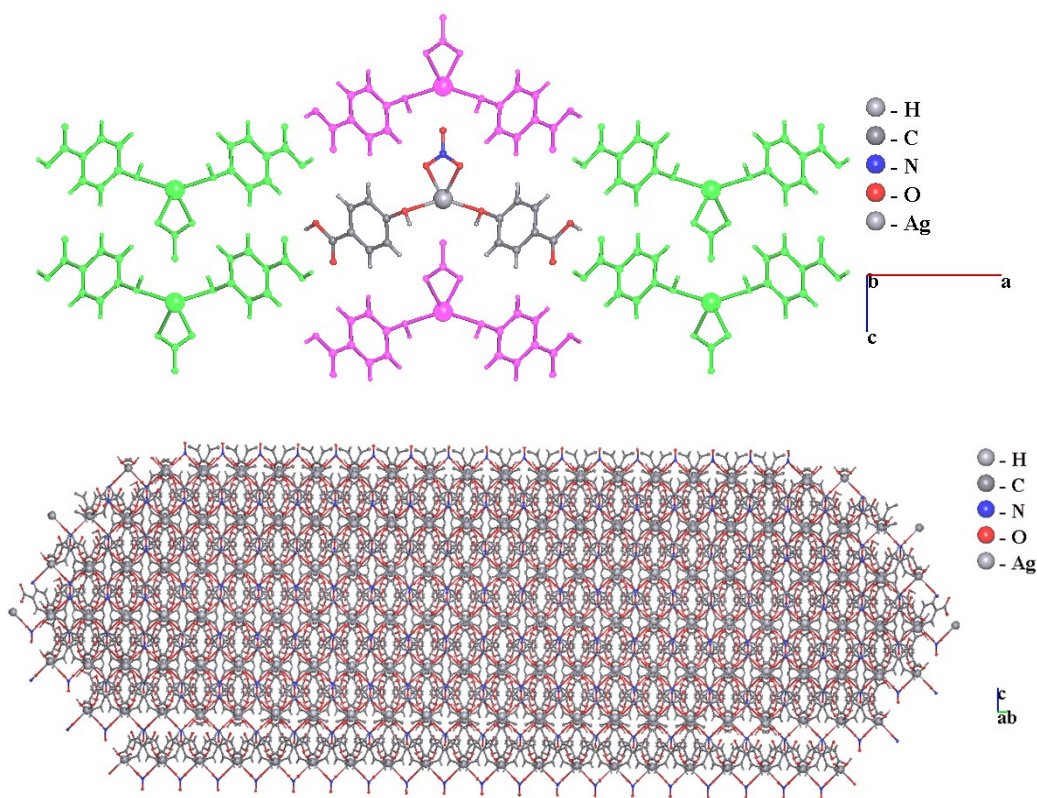


Fig.S1 Eight chains surrounding the central one (up), a fragment of the 3D framework in complex 1 (down)

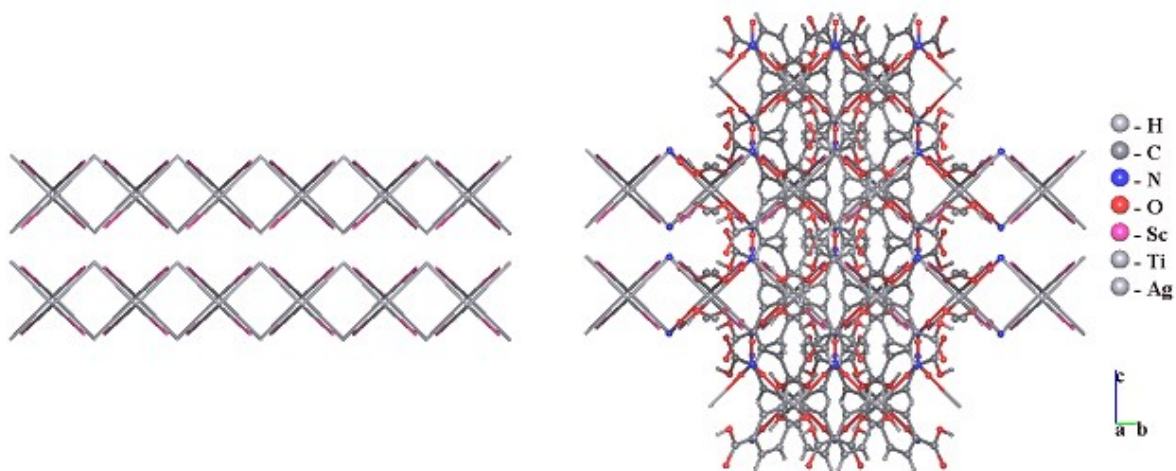


Fig.S2 Topological representation of coordination networks in complex 1

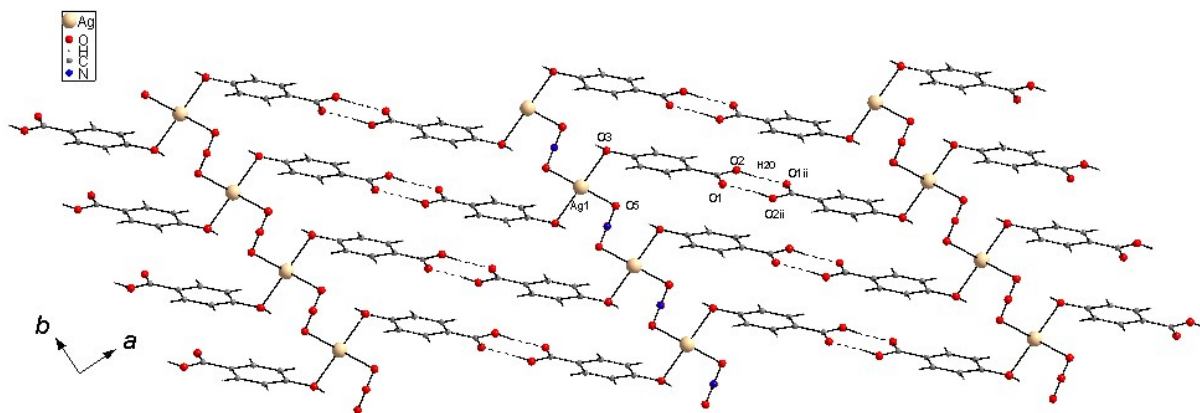
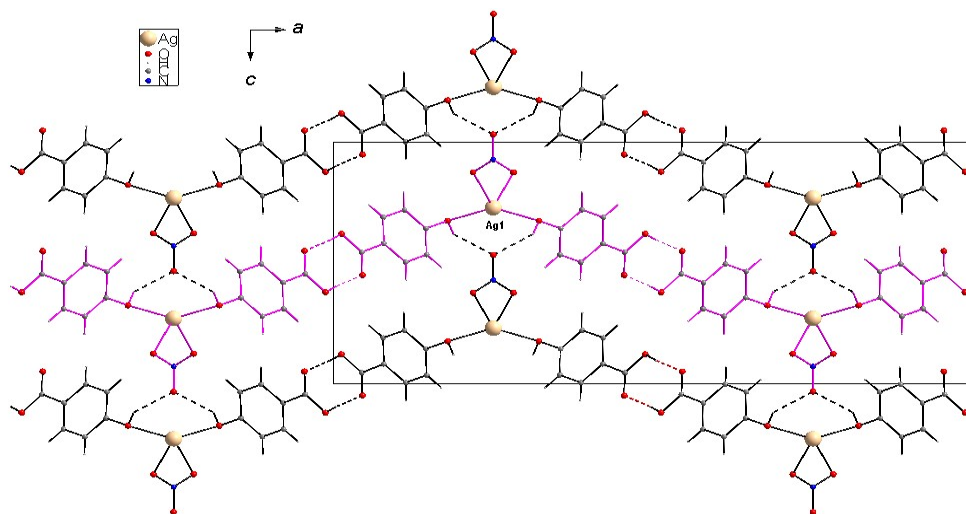
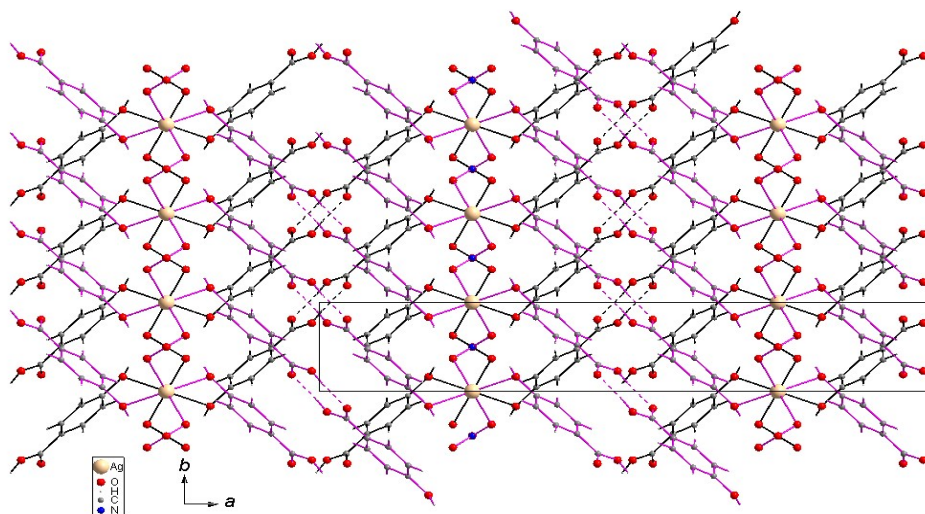


Fig.S3 View of the interacted $\{\text{Ag}(\text{p-OH-C}_6\text{H}_4\text{COO})_2(\text{NO}_3)\}_n$ polymers via O—H...O hydrogen bonds between the COOH groups with a graph of R22(8) forming layer parallel to (001) plane. Symmetry code: (ii) 1-x, -y, 1-z

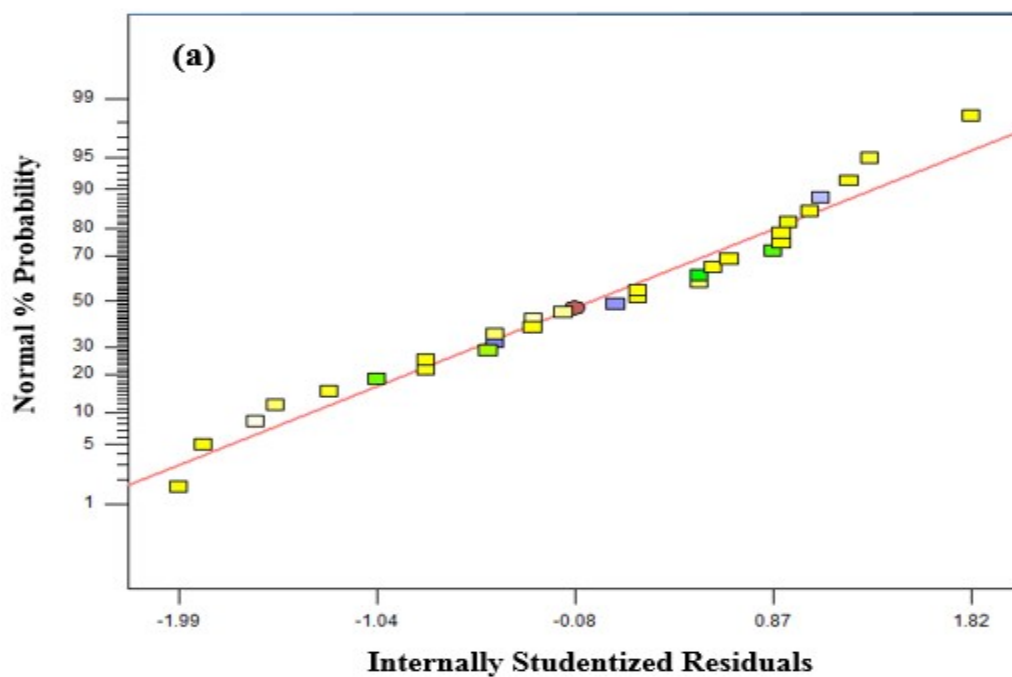


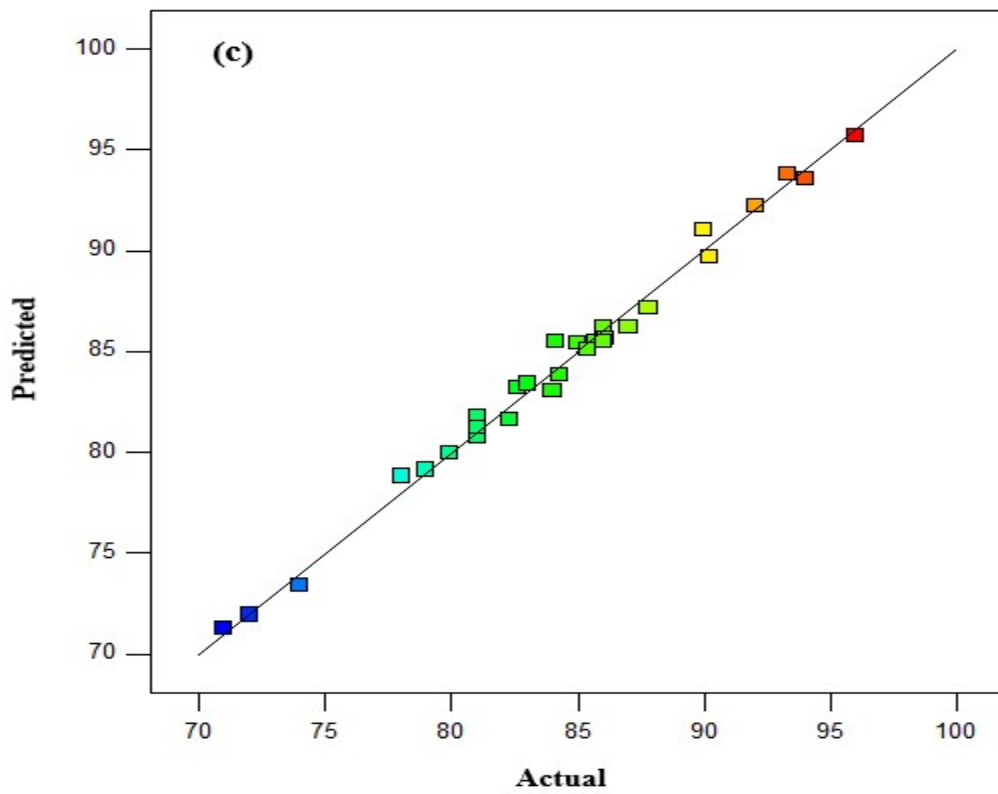
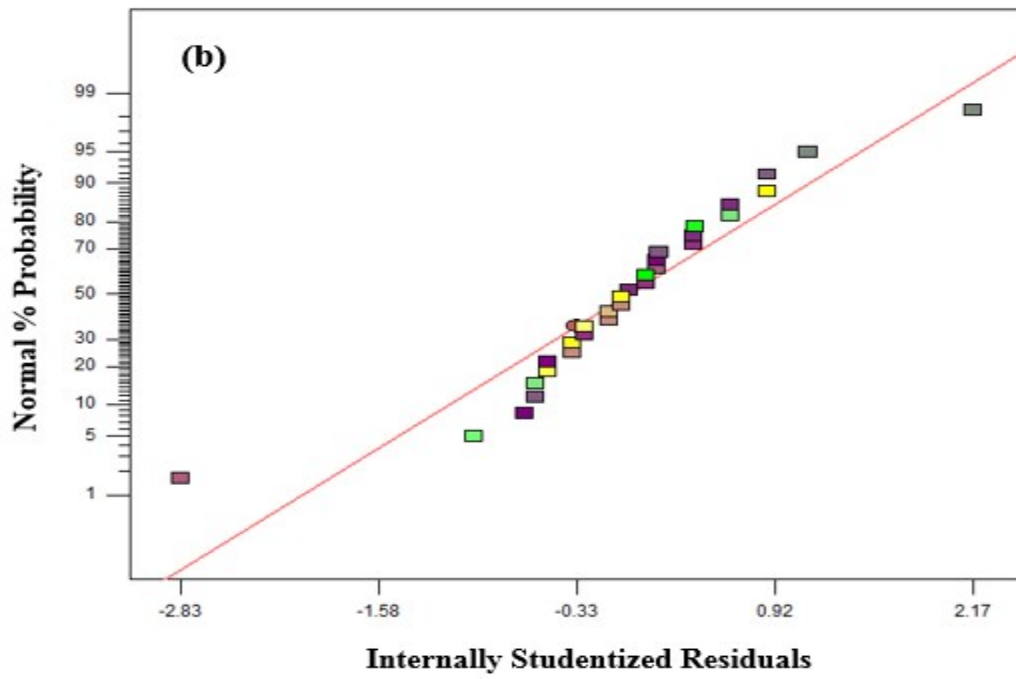
(a)

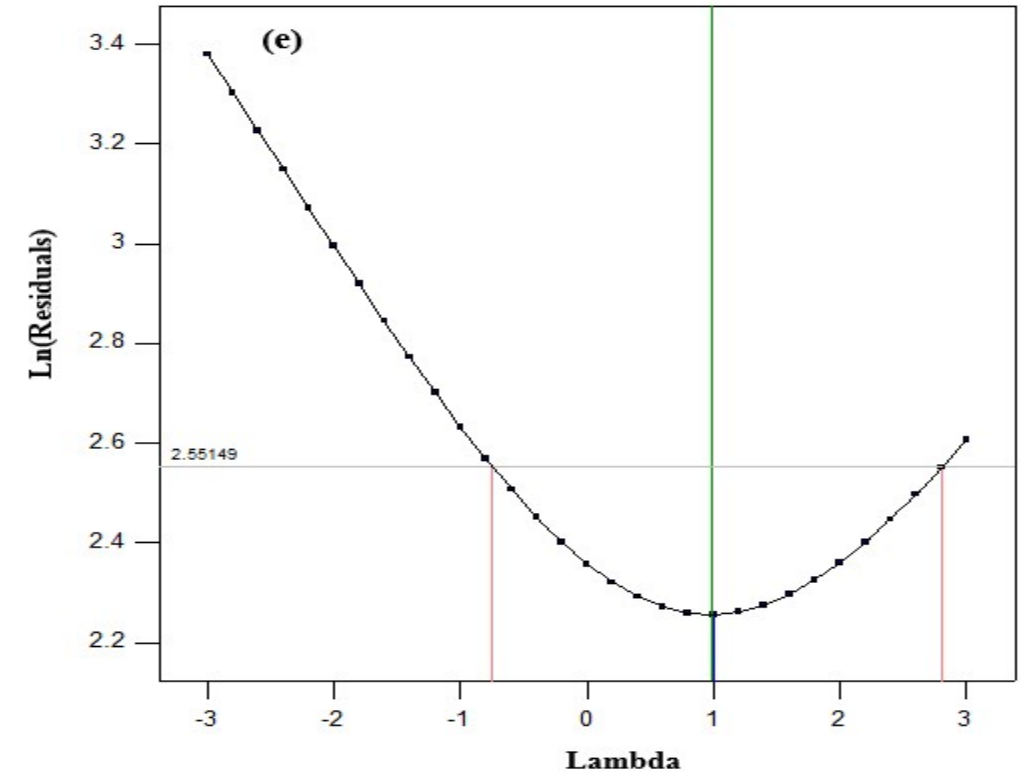
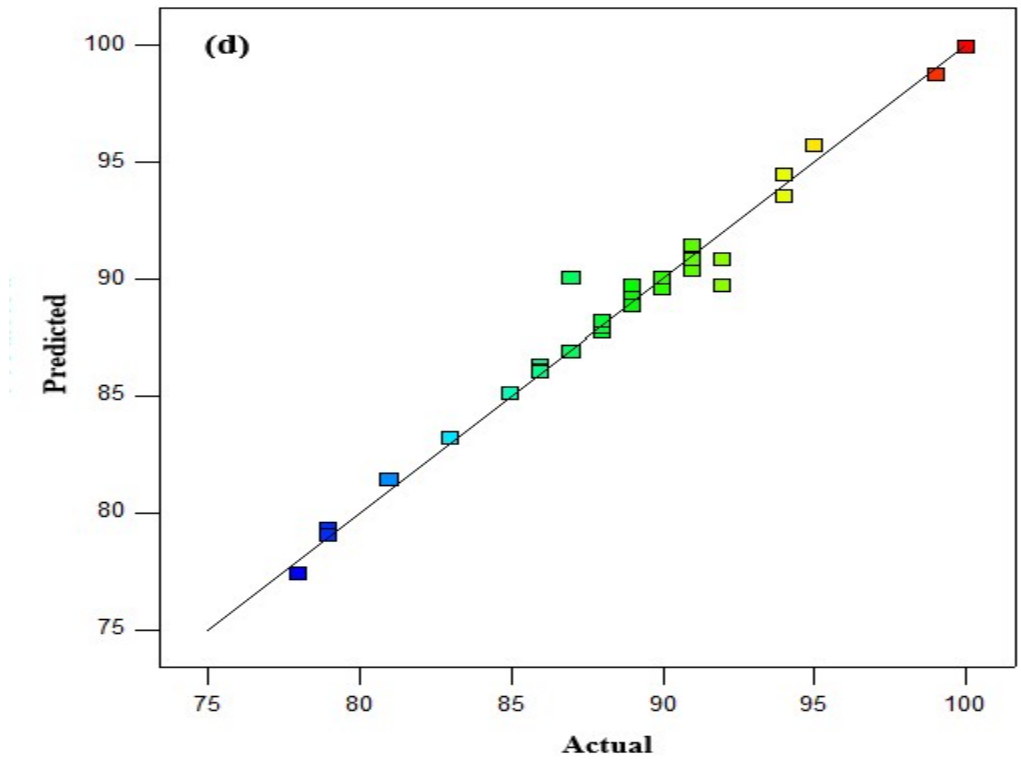


(b)

Fig.S4 Arrangement of neighbouring 2D-coordinating polymer viewed along b-axis (a) and c-axis (b). The layers are marked with different colour (black and pink)







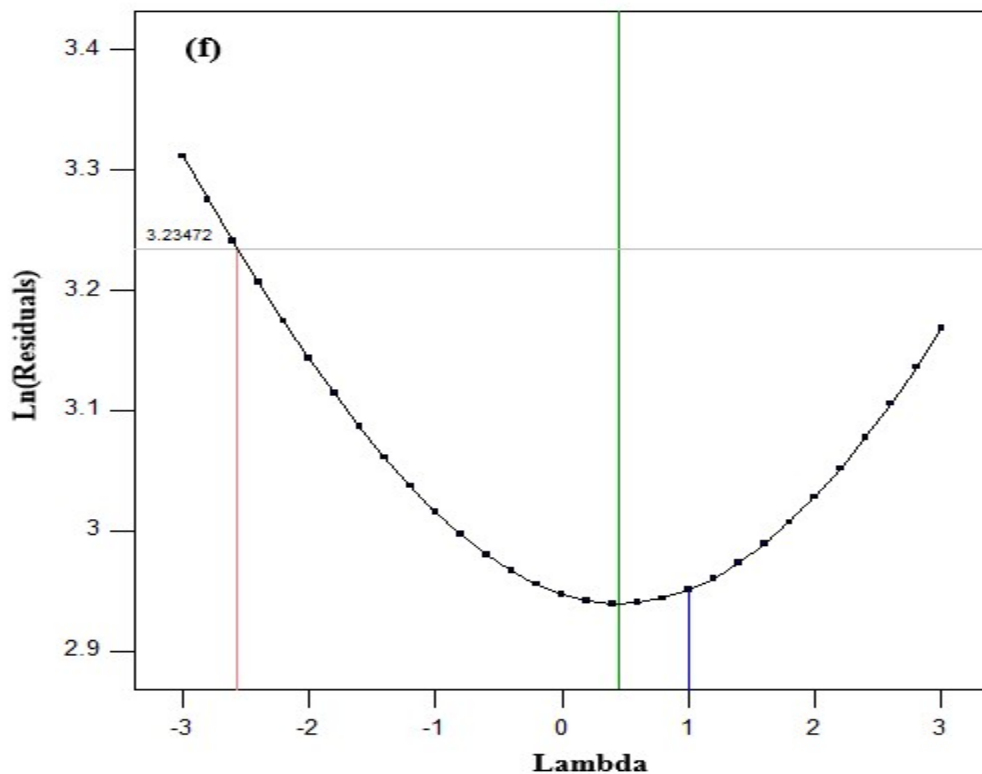
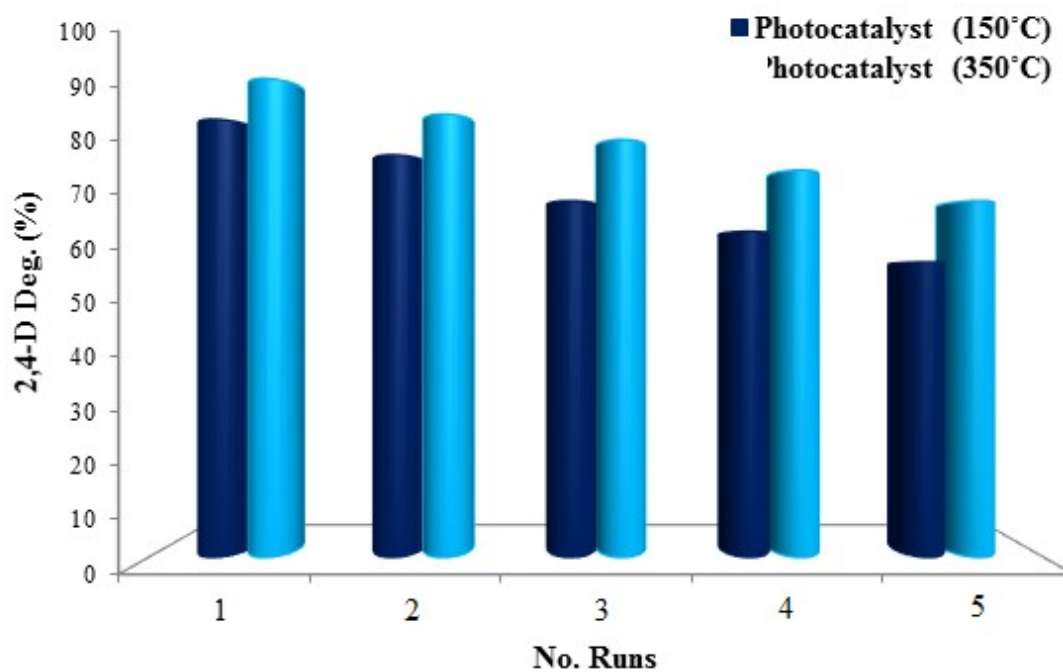


Fig.S5 Normal probability plot of residuals (a and b); Plot of actual vs predicted values (c and d) and Box-Cox plot (e and f) for 2,4-D and MCPA respectively in degradation of mixture of 2,4-D and MCPA



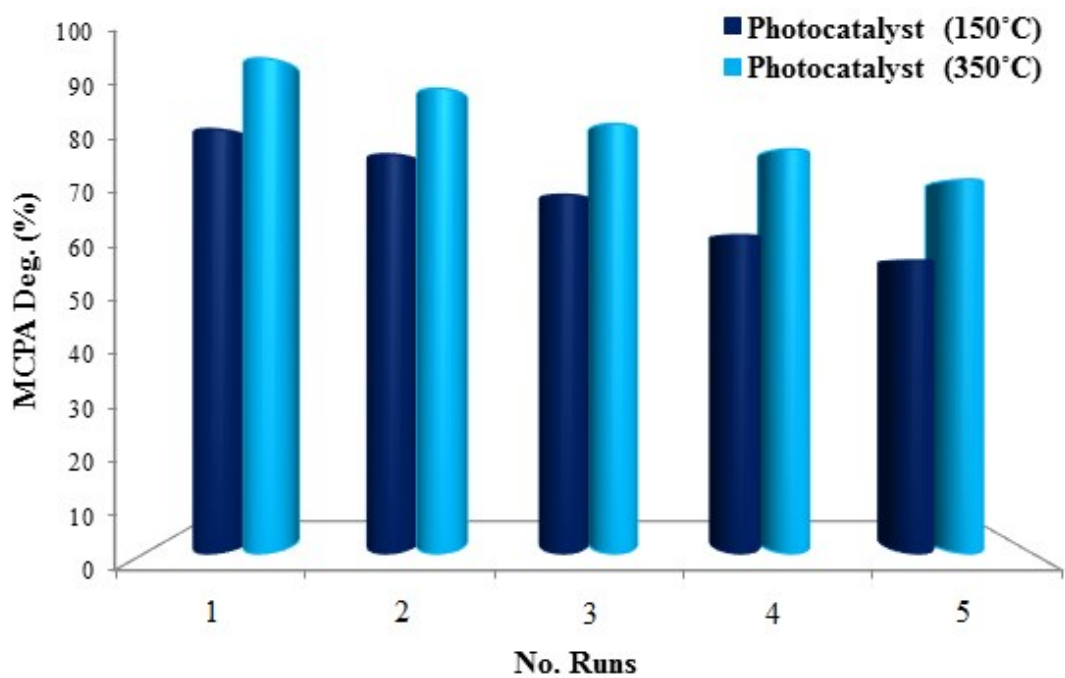


Fig.S6 Reusability of photocatalyst in photocatalytic degradation of (a) 2,4-D (150 °C, 350 °C), and (b) MCPA (150 °C, 350 °C)

Table S1. Crystallographic data for [Ag(*p*-OH-C₆H₄COO)₂(NO₃)₂]_n **1**

Empirical formula	C ₁₄ H ₁₂ NO ₉ Ag
Formula weight (g·mol ⁻¹)	446.12
Crystal system, space group	orthorhombic, <i>Pcca</i> (No. 54)
Temperature (K)	295(2)
<i>a</i> (Å)	28.094(4)
<i>b</i> (Å)	4.5817(4)
<i>c</i> (Å)	11.7941(8)
<i>V</i> (Å ³)	1518.1(3)
<i>Z</i>	4
<i>D</i> _{calc} (g·cm ⁻³)	1.952
μ (mm ⁻¹)	1.381
<i>F</i> (000)	888
Crystal size (mm)	0.29 × 0.25 × 0.22
Radiation type, wavelength, λ (Å)	Mo <i>K</i> α , 0.71073
θ range(°)	2.773 ÷ 28.066
Absorption correction	multi-scan
<i>T</i> _{min} / <i>T</i> _{max}	0.82665 / 1.000
Reflections collected / unique / observed	19217 / 1752 / 1473
<i>R</i> _{int}	0.018
Refinement on	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.031
<i>wR</i> (<i>F</i> ² all reflections)	0.088
Goodness-of-fit, <i>S</i>	1.002
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	+0.581, -0.754

$$wR = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma wF_o^4 \}^{1/2}; w^{-1} = \sigma^2(F_o^2) + (0.0471P)^2 + 2.0814P \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

Table S2. Selected geometrical parameters (Å, °) for {Ag(*p*-OH-C₆H₄COO)₂(NO₃)₂]_n complex

Ag1—O3	x2	2.238(2)	Ag1—O5	x2	2.583(3)
O3—Ag1—O5		96.09(8)	O3—Ag1—O3 ^{<i>i</i>}		146.83(13)
O5—Ag1—O5 ^{<i>i</i>}		95.76(17)	O3—Ag1—O5 ^{<i>i</i>}		106.07(9)

Symmetry code: (*i*) $-x + 1/2, -y + 2, z$;

Table S3. Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O \cdots O4 ⁱ	0.86(1)	2.28(2)	3.028(3)	147(4)
O2—H2O \cdots O1 ⁱⁱ	0.85(1)	1.81(1)	2.654(3)	175(4)

Symmetr code: (i) x, -y+2, z+1/2; (ii) -x+1, -y, -z+1

Effective variables	symbol	Real values of coded levels				
	X _i	-2(-a)	-1	0	1	+2(+a)
pH	X ₁	3	5	7	9	11
pollutant concentration (mgL ⁻¹)	X ₂	0.5	2.0	3.5	5.0	6.5
Catalyst dosage (gL ⁻¹)	X ₃	0.2	0.4	0.6	0.8	1.0
Irradiation time (min)	X ₄	10	30	50	70	90

Table S4. Coded and actual levels of the experimental variables