Removal of Organic Dyes from Aqueous Solution Using Novel Pyrene appended Zn(II)-based Metal-Organic Framework and its Photocatalytic Property

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Experiment details

All reagents and solvents were commercially available and used without further purification. Thermal properties were studied using a Perkin-Elmer Instrument system (STA6000) at a heating rate of 10 ˚C/min under a dinitrogen atmosphere and a flow rate of 20 mL/min. Powder XRD was recorded on Rigaku SmartLab X-ray diffractometer. UV-vis absorption spectra were recorded on a Thermo Scientific Genesys 10S UV-Vis spectrometer. Fluorescence spectra were recorded on a Horiba Scientific Fluoromax Spectrometer. Gas adsorption analysis of the MOF was conducted at 77 K using a Micromeritics ASAP 2060 instrument, following a vacuum treatment at 30 °C for 12 hours.

Crystal structure determinations

Reflection data for **$ZnSiF_6$Pyrene MOF** were collected using a Bruker APEX-II CCD-based diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The hemisphere of the reflection data was collected as ω scan frames at 0.5°/frame and an exposure time of 5 s/frame. The cell parameters were determined and refined using the APEX2 program.[1] The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using the SADABS program.[2] The compound structures were solved by direct methods and refined by full matrix least-squares using the SHELXTL program package[3] and Olex2[4] with anisotropic thermal parameters for all non-hydrogen atoms. The relevant data are summarized in Table S1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In silico studies

In silico docking studies were performed using the HEX 8.0.0 software with the following parameters: Correlation type = shape only; FFT mode = 3D; Grid dimension = 0.6; Receptor range = 180; Ligand range = 180; Twist range = 360; Distance range = 40. From the crystal strctures files, the 3D packing diagram of each coordination polymer has been saved separately as PDB (Protein Data Bank) files and the geometry optimization of Rhodamine B (RhB), Methyl Violet (MV), and Congo Red (CR) dyes has been carried out using the ChemDraw 3d software and was saved as PDB (Protein Data Bank) file. Later, the generated PDB files were used for molecular docking studies. For the visualization of non-covalent interaction between CPs and dyes, Discovery Studio 2021 software was used.

Dye adsorption/photocatalytic measurements

To evaluate the adsorption performance of **$ZnSiF_6$Pyrene MOF**, three dyes were used: Congo red (CR), methyl violet (MV), and rhodamine B (RhB). A sample of **$ZnSiF_6$Pyrene MOF** (10 mg) was added to 3 mL aqueous solutions containing each dye. The mixtures

were stirred at 1500 rpm in darkness at room temperature. UV-Vis absorption spectra of the solutions were collected at various time intervals to monitor the adsorption process. The adsorption efficiency of **$ZnSiF_6$Pyrene MOF** was calculated using the following equation:

$$\text{adsorption efficiency (\%)} = \frac{C_t - C_0}{C_0} \times 100 = \frac{A_0 - A_t}{A_0} \times 100$$

where C_o and C_t, A_o and A_t correspond to the concentration and absorbance of dyes before and after adsorption.

A finely divided sample of **$ZnSiF_6$Pyrene MOF** (10 mg) was dispersed in 3 mL of an aqueous MV dye solution (6×10^{-5} M). The photocatalytic degradation of MV was carried out under light irradiation provided by a simple LED module using two 7-W LED lamps. During the process, 1.0 mL aliquots were taken at specific time intervals, separated by centrifugation, and the characteristic electronic absorption band of the dye was recorded using a UV–visible spectrophotometer. Additionally, a control experiment was conducted under the same conditions but without the **$ZnSiF_6$Pyrene MOF** photocatalyst.

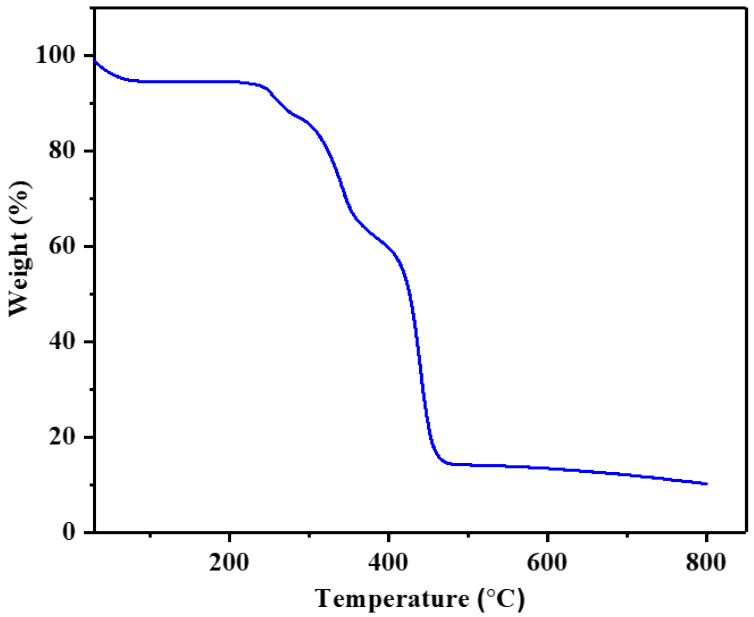

Figure S1: TGA spectra of **$ZnSiF_6$Pyrene MOF**.

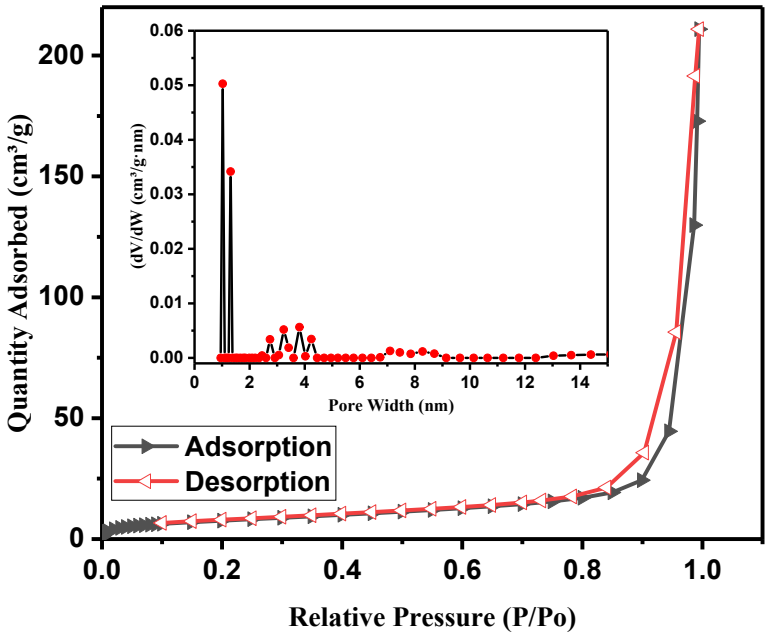

Figure S2: The N_2 adsorption isotherms of the **$ZnSiF_6$Pyrene MOF** at 77 K is shown, with solid symbols representing the adsorption curves and empty symbols indicating the desorption curves. The *inset* displays the pore size distribution of the MOF.

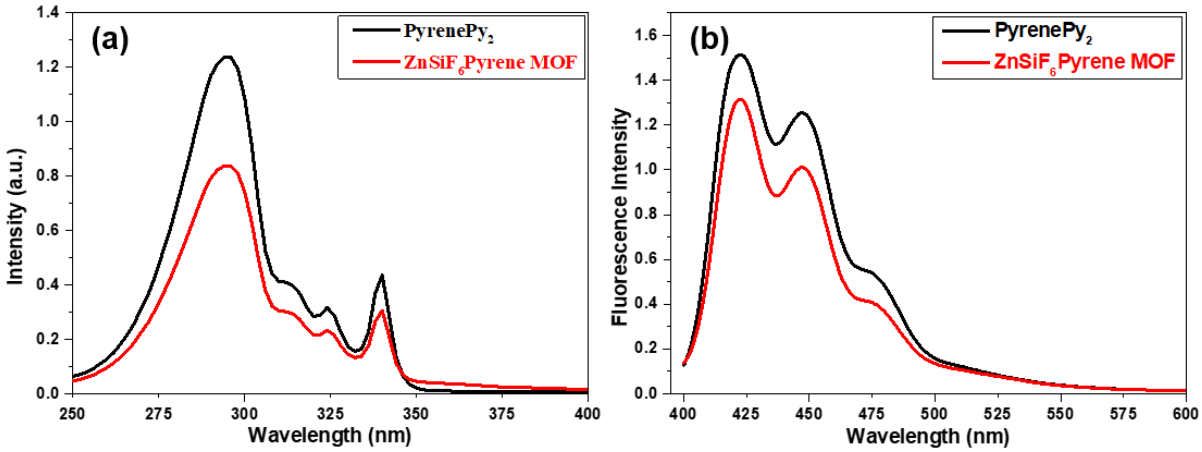

Figure S3: UV-Vis (a) and PL (b) spectra in ethanol (dispersed) at 1 x10^{-5} Molar concentration (excitation wavelength for PL is 385 nm).

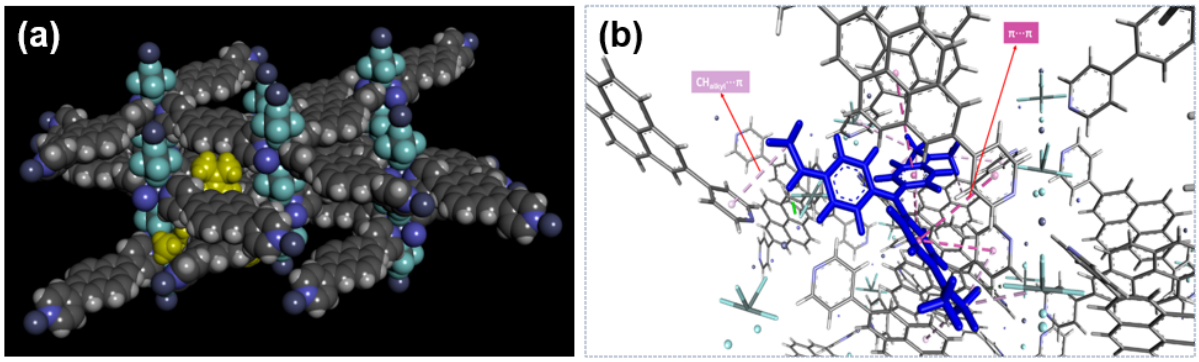

Figure S4. (a) Space filled docked structure (color code: MOF, black; MV, yellow) and (b) non-covalent interactions between **$ZnSiF_6$Pyrene MOF** and CR (color code: MOF, black; MV, blue).

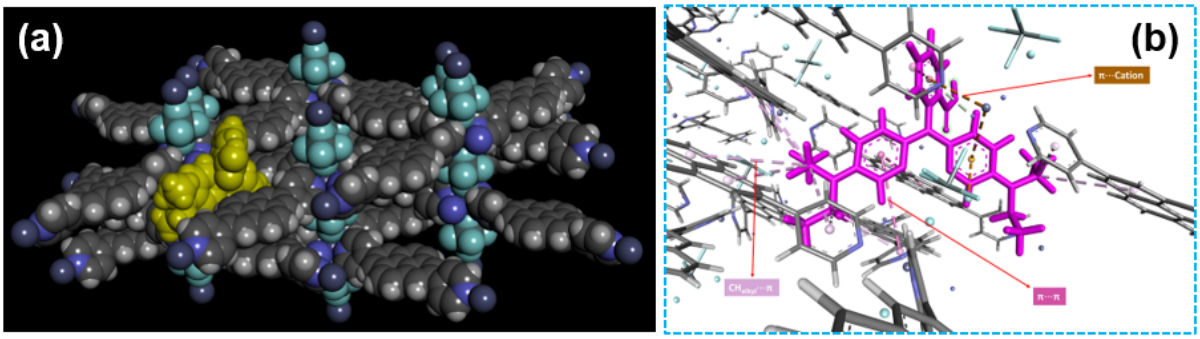

Figure S5. (a) Space filled docked structure (color code: MOF, black; RhB, yellow) and (b) non-covalent interactions between **$ZnSiF_6$Pyrene MOF** and RhB (color code: MOF, black; RhB, dark pink).

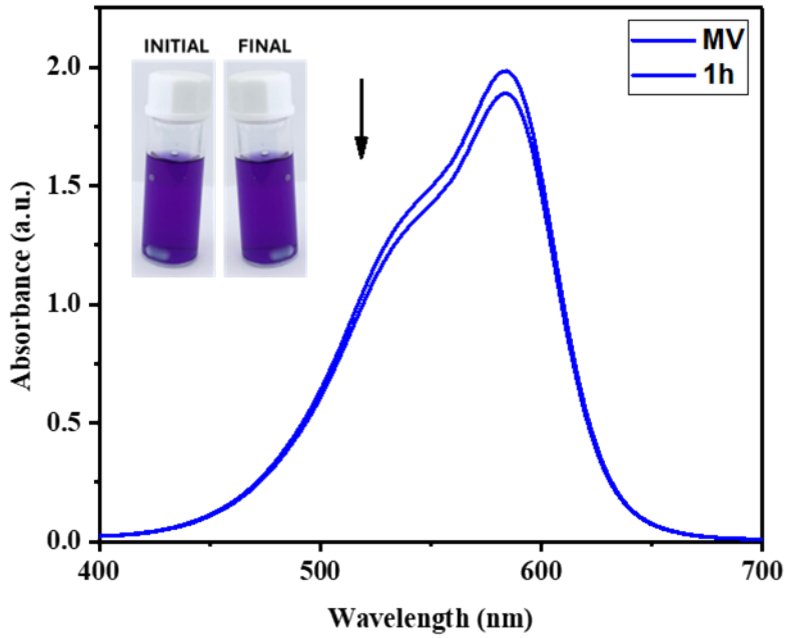

Figure S6: UV-visible absorption spectra of MV dye before and after 1h of light irradiation using two 7-W LED lamps.

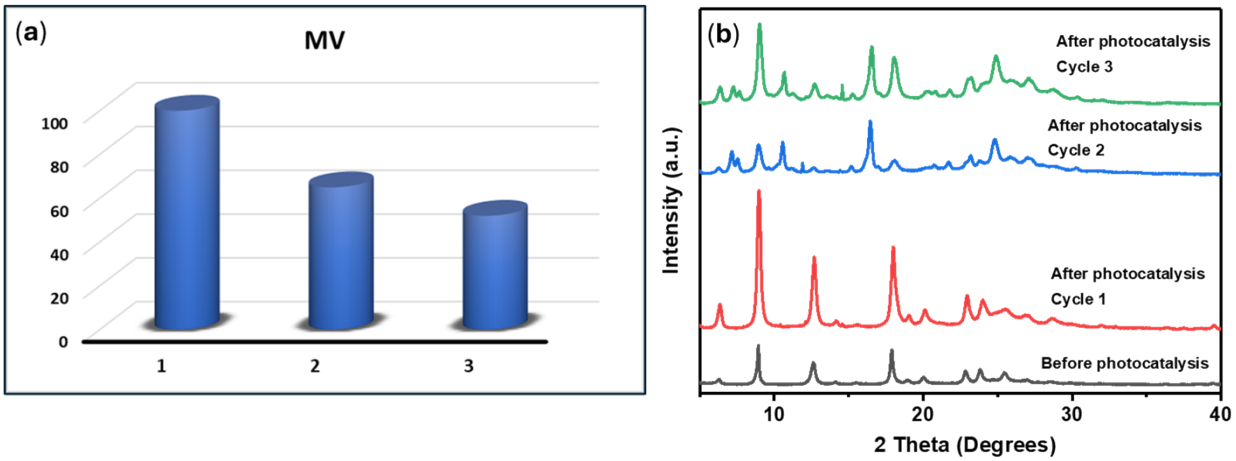

Figure S7: (a) The recyclability of the **$ZnSiF_6$Pyrene MOF** for the photocatalytic degradation of methyl violet (MV) was assessed across three consecutive cycles and (b) PXRD of **$ZnSiF_6$Pyrene MOF** recorded before and after photocatalysis.

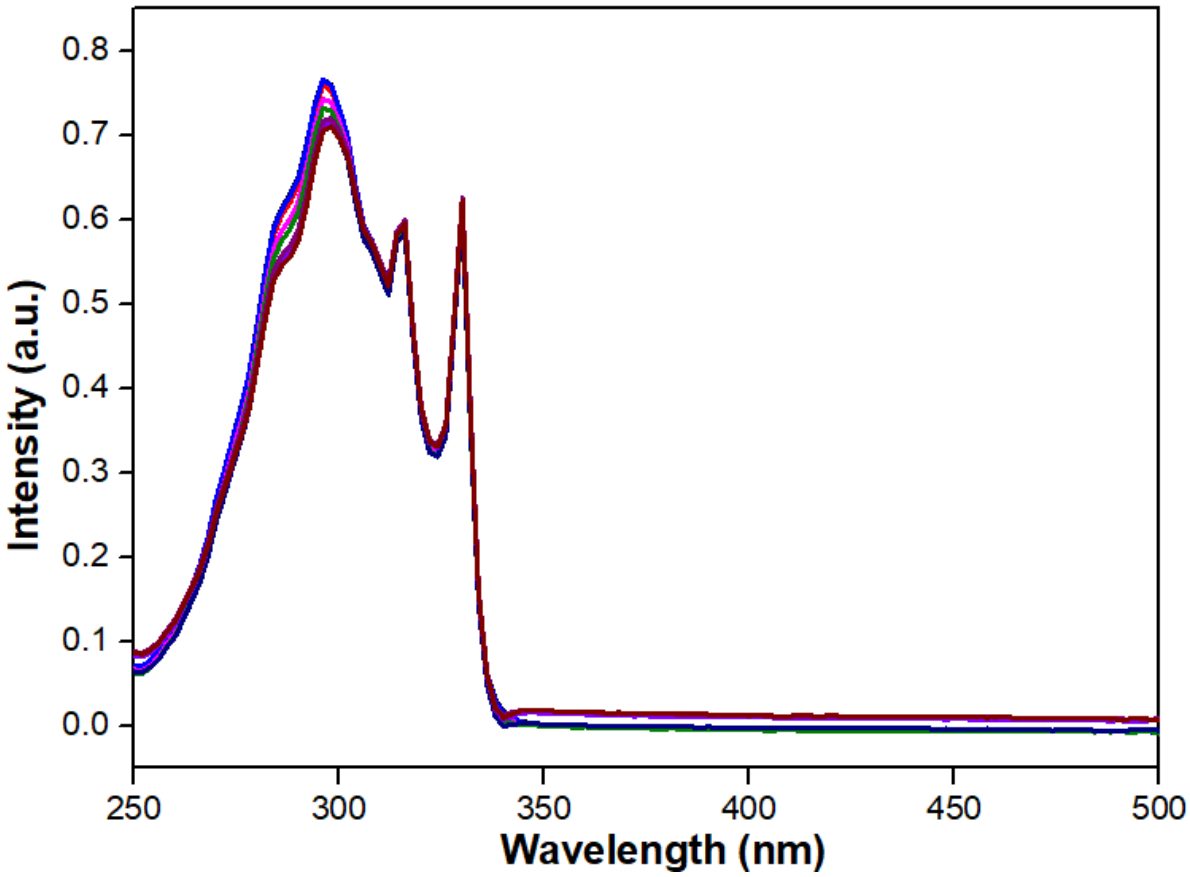

Figure S8: UV-visible absorption spectra that occurred due to the photooxidation of DHN in the absence of **$ZnSiF_6$Pyrene MOF** catalyst. No reaction took place in the absence of the catalyst studied for over 5 h.

References:

[1] Bruker-AXS (2014). APEX2. Version 2014.11-0. Madison, Wisconsin, USA.

[2] L. Krause, R. Herbst-Irmer, G. M. Seldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3-10.

[3] G. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8.

[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.