

Supplementary Information for:

# **Pyrene and porphyrin-based Zn metal 1-D-polymer: synthesis, molecular structure, and photocatalytic property**

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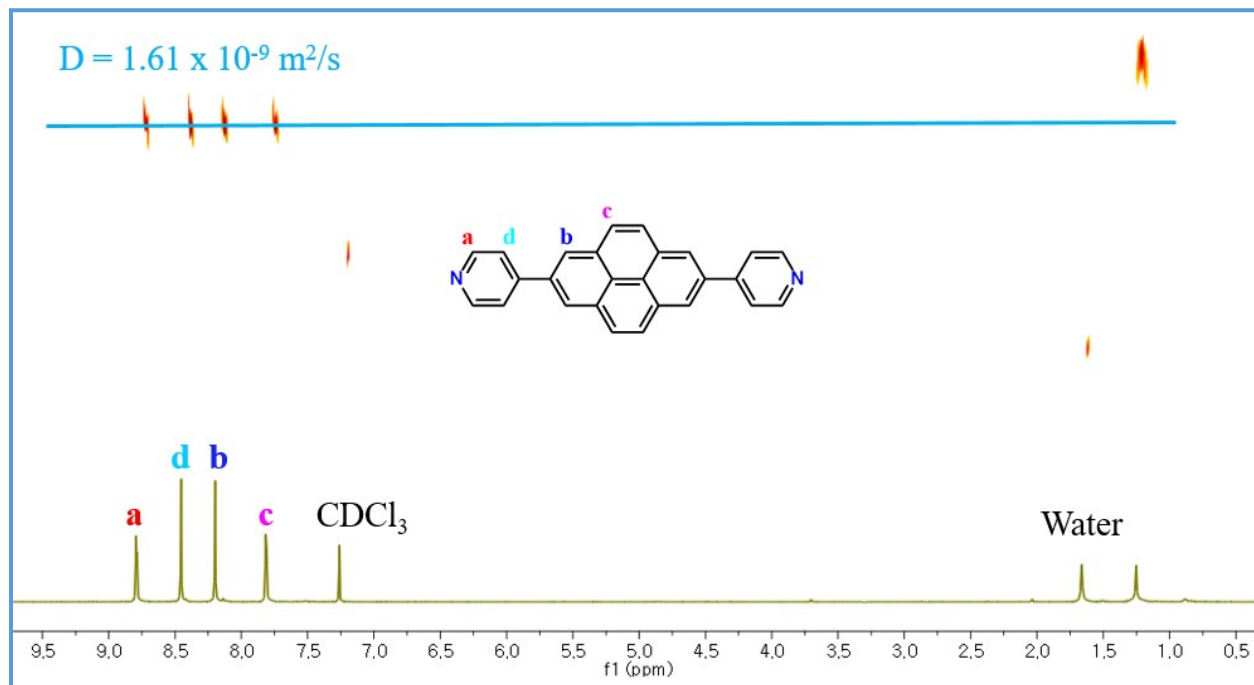
## General Information

The dipyriddy pyrene ligand **PyrPy<sub>2</sub>** was synthesized by following a procedure reported in the literature <sup>[R1]</sup> with slight modification. Our modified procedure gives pure product without the use of any column chromatography. The synthesis of **PyrPy<sub>2</sub>** is described below. The starting 2,7-dibromopyrene, pyridine-4-ylboronic acid and tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich and TCI, and used as received. Dry solvents were purchased from Aldrich and all other reagents were commercially available and used without further purification. The <sup>1</sup>H, <sup>13</sup>C (100 MHz) spectra were recorded on an Agilent 400-MR spectrometer using the residual protonated solvent as internal standard. UV-visible absorption spectra were recorded on a Thermo Scientific Genesys 10S UV-Vis spectrometer. Fluorescence spectra and fluorescence quantum yields were recorded on a Horiba Scientific Fluoromax Spectrofluorometer. Time-correlated single photon counting (TCSPC) experiments were performed on a fluorescence spectrometer (FluoTime 300, PicoQuant, Berlin, Germany). Thermogravimetric analysis (TGA) measurement was performed on a Hitachi STA7200 Thermal Analysis System. Elemental analysis was performed on an Elemental Analyzer (Elementar Analysensysteme GmbH, Germany) at Korea Basic Science Institute (KBSI), Busan center, South Korea. Powder X-ray Diffraction data was obtained by a High Resolution X-ray Diffractometer (X'Pert-PRO-MRD) at Inha University, South Korea.

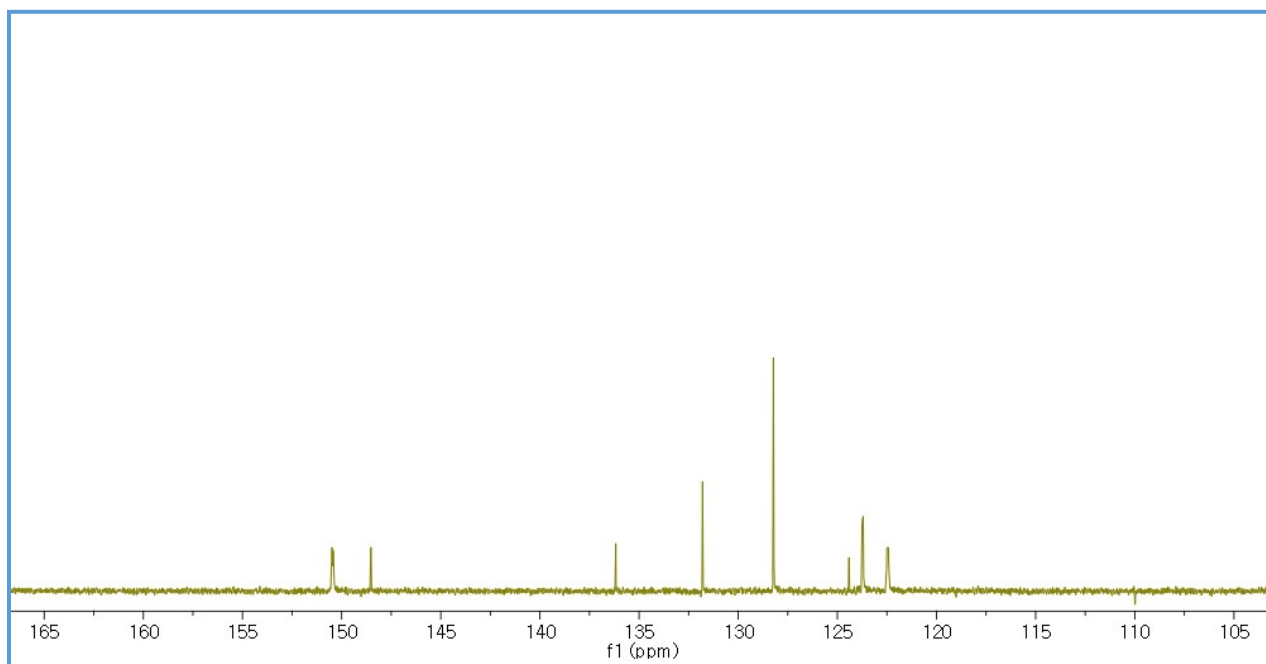
### Synthesis of ligand **PyrPy<sub>2</sub>**:

To a solution of 2,7-dibromopyrene (200 mg, 0.555 mMol) in a mixed solvent of 1,4-dioxane (8 mL) and water (2 mL), pyridine-4-ylboronic acid (150 mg, 1.22 mMol) and K<sub>2</sub>CO<sub>3</sub> (724 mg, 2.22 mMol) were added. The solution was bubbled with dry nitrogen gas for around 30 minutes. Then tetrakis(triphenylphosphine)palladium(0) (13 mg, 0.011 mMol) was added under nitrogen atmosphere. The reaction mixture was refluxed for 18 h at 115 °C or until the reaction is complete which is monitored by thin layer chromatography. The solvent was removed under reduced pressure and extracted with dichloromethane and washed several times with water. The dichloromethane extract was dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. The obtained light yellow residual was collected to get the pure product enough for further reaction.

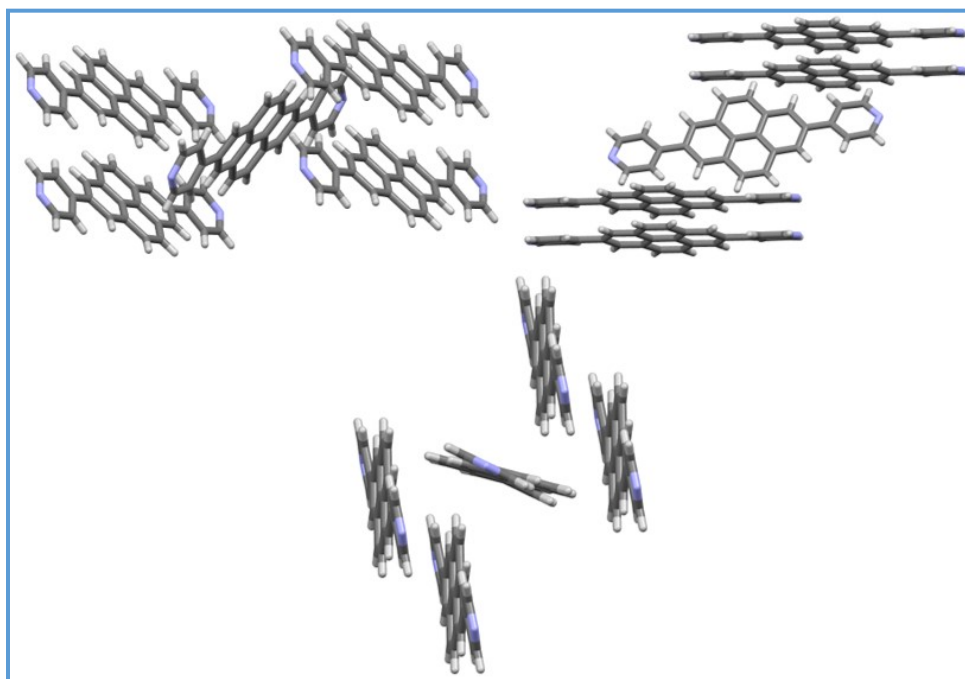
Yield: 50-55 %.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.80 (d,  $\text{H}_a$ ,  $J$  = 4Hz, 4H), 8.45 (s,  $\text{H}_d$ , 4H), 8.20 (s,  $\text{H}_b$ , 4H), 7.82 (d,  $\text{H}_c$ ,  $J$  = 4Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.49, 148.52, 136.18, 131.80, 128.22, 124.42, 123.75, 122.50 ppm. Anal. Calcd (%) for  $\text{C}_{26}\text{H}_{16}\text{N}_2$ : C, 87.62; H, 4.52; N, 7.86. Found C, 85.31; H, 3.99; N, 7.10.



**Figure S1a:**  $^1\text{H}$  NMR (down) and  $^1\text{H}$  DOSY NMR (up) of free ligand **PyrPy**<sub>2</sub> in  $\text{CDCl}_3$  at room temperature.



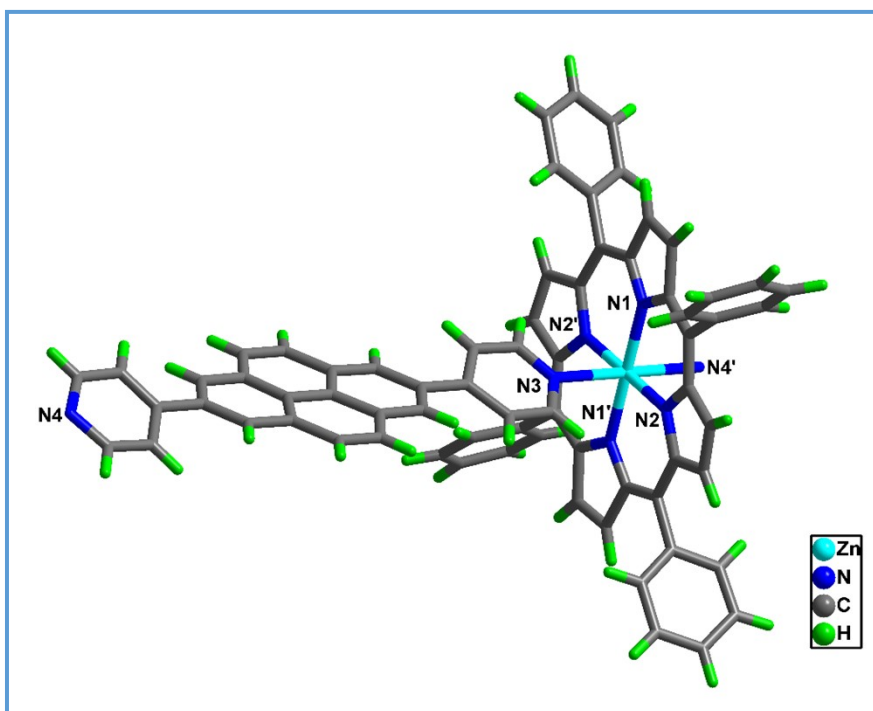
**Figure S1b:**  $^{13}\text{C}$  NMR of free ligand **PyrPy<sub>2</sub>** in  $\text{CDCl}_3$  at room temperature.



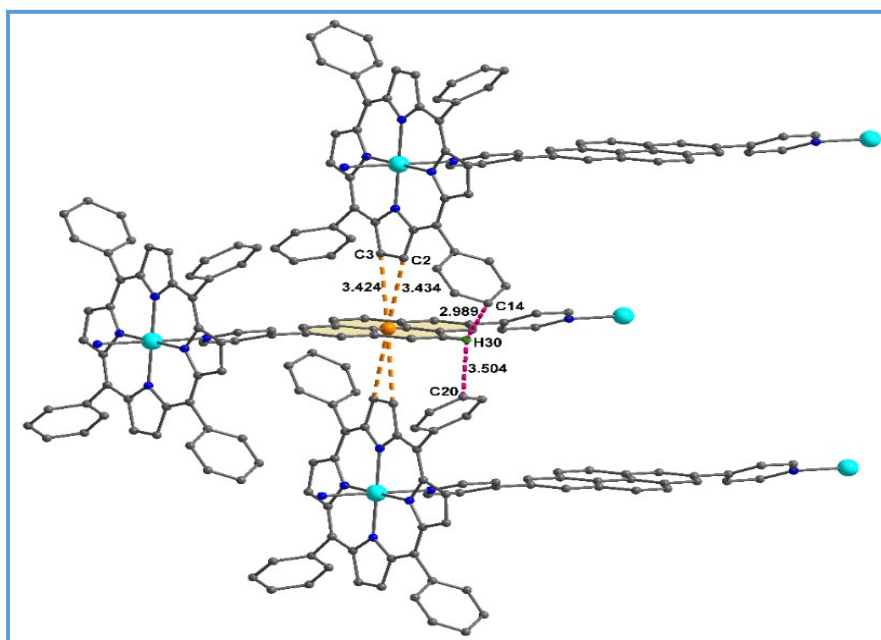
**Figure S2:** Different views of the packing structure seen in single crystal structure of ligand **PyrPy<sub>2</sub>**.

**Synthesis of polymer ZnPyrPorp.** Ligands tetraphenylporphyrin (TPP, 8 mg, 0.013 mMol),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (5.8 mg, 0.0195 mMol) and  $\text{PyrPy}_2$  (4.64 mg, 0.013 mMol) were added in a 4 mL vial. Then DMF (1.5 mL) and ethanol (0.5 mL) were added to the vial. The mixture was sonicated for 5-10 minutes. Then 30  $\mu\text{L}$  of nitric acid (1M in ethanol) was added to the solution and heated for 18 h in a preheated oven maintained at 85  $^\circ\text{C}$ . After cooling, the purple crystals were washed with ethanol for several times until the washing solution becomes almost colourless. Identical reactions were carried out in five vials to obtain large amount of the crystals.

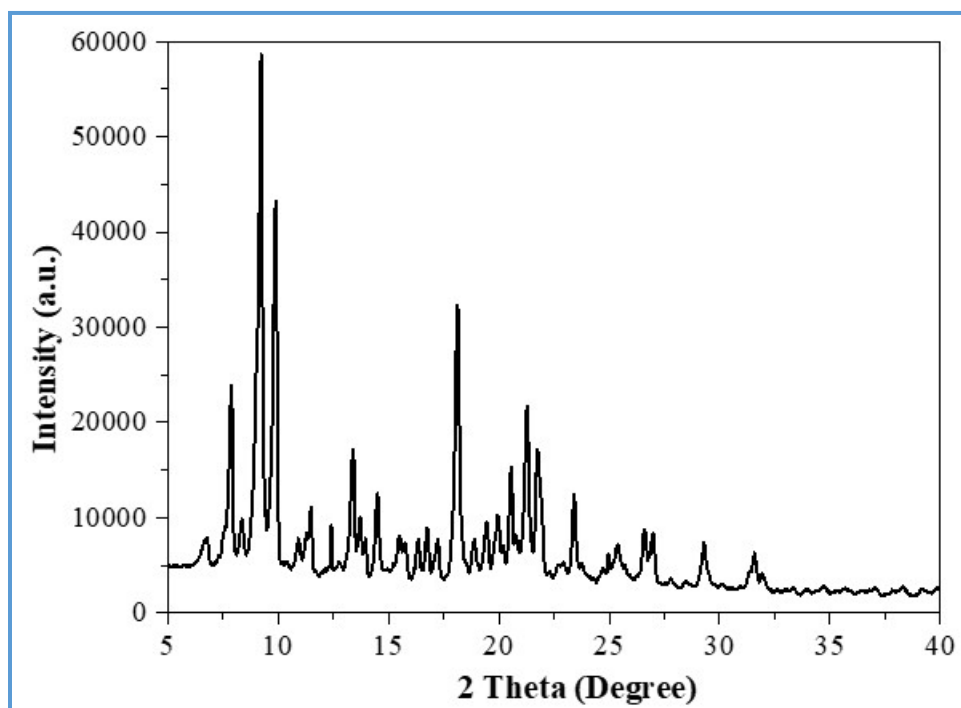
Yield: 40-45 mg. Anal. Calcd (%) for  $\text{C}_{26}\text{H}_{16}\text{N}_2$ : C, 81.27; H, 4.29; N, 8.12. Found C, 81.75; H, 4.29; N, 8.23.



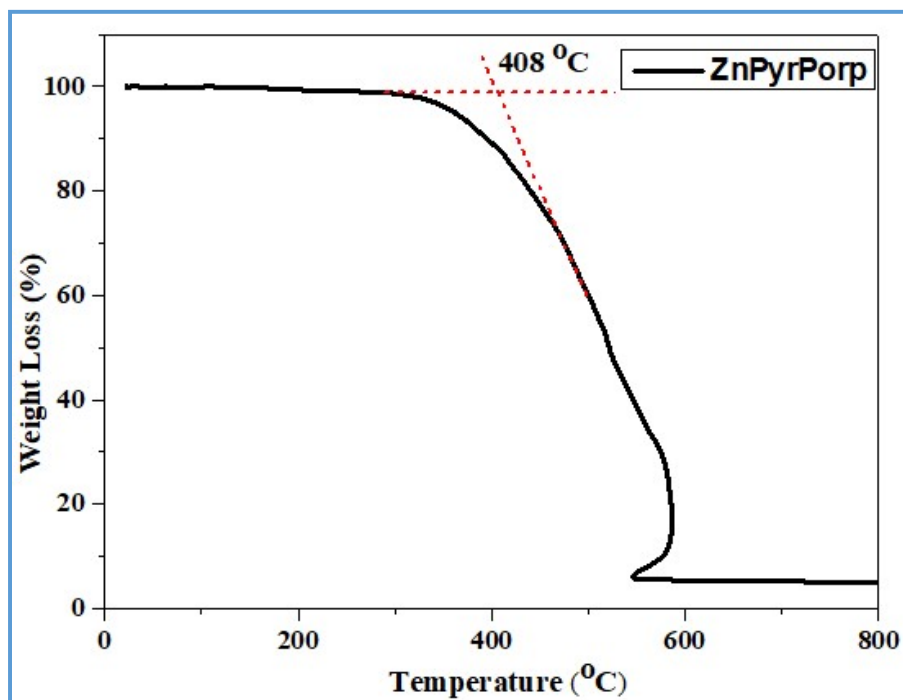
**Figure S3:** Monomeric structure of polymer **ZnPyrPorp**.



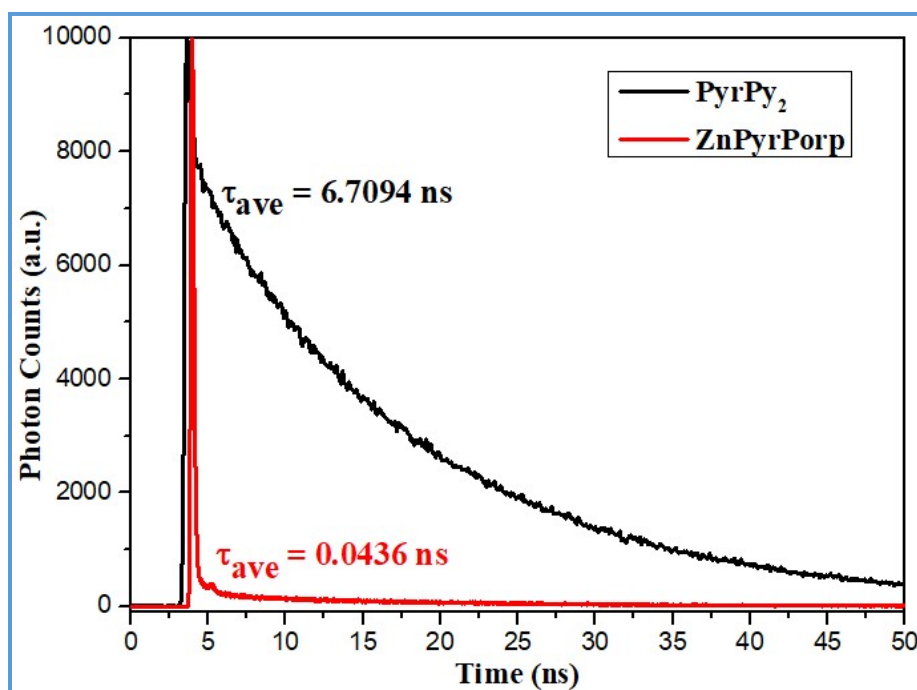
**Figure S4:** Representation showing the weak  $\pi$ --- $\pi$  and C-H--- $\pi$  intermolecular interaction in polymer **ZnPyrPorp**.



**Figure S5:** Powder X-ray Diffraction (PXRD) spectrum of polymer **ZnPyrPorp**.



**Figure S6:** Thermogravimetric analysis (TGA) spectrum of polymer **ZnPyrPorp**.



**Figure S7:** Average fluorescence time decay profile for **PyrPy<sub>2</sub>** and polymer **ZnPyrPorp** monitored at pyrene region upon excitation at 405 nm.

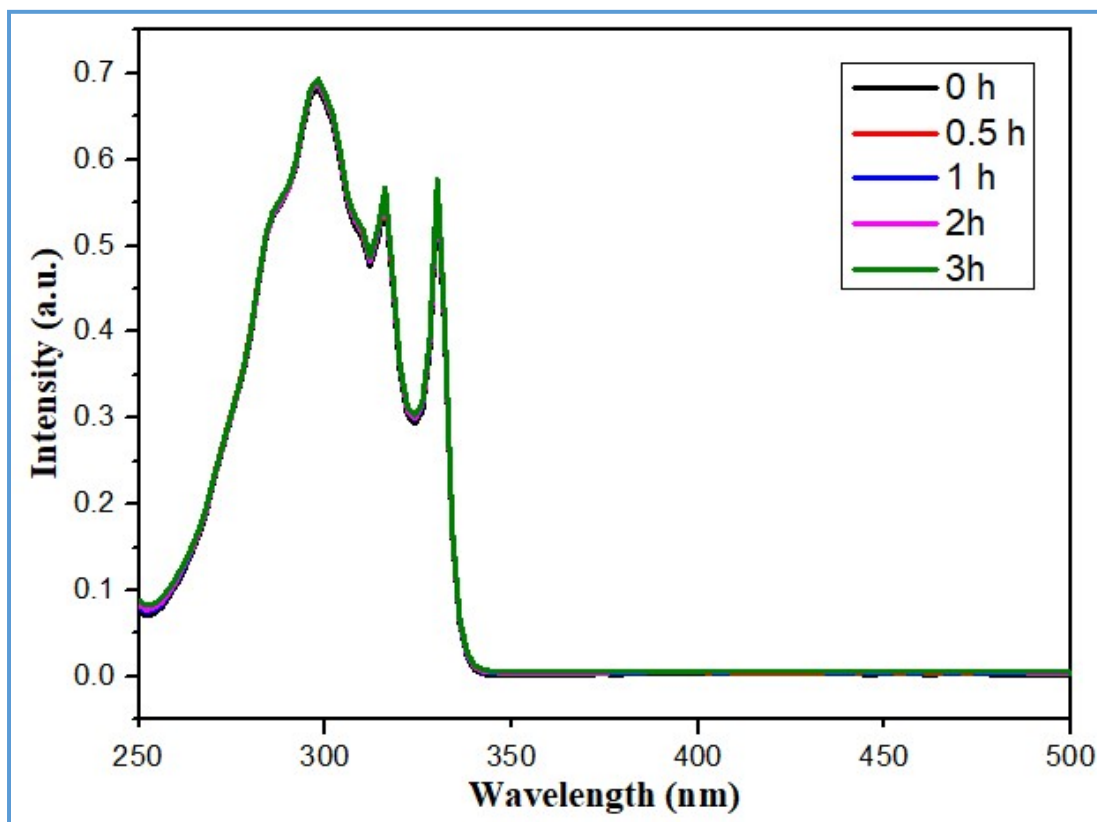
### **Photocatalytic performance measurement:**

The photocatalytic properties of the polymer were evaluated by the conversion of dihydroxynaphthalene (DHN) to Juglone under UV-Vis light irradiation provided by a 150 W halogen lamp (KL 1500: SCHOTT, Mainz, Germany). 1.6 mg of DHN was added into 100 ml of acetonitrile solvent in a quartz reactor. Then oxygen gas was purged into the solution for around 8-10 mins in the absence of light. Then 2 mg of the **ZnPyrPorp** polymer was added into the solution. The solution was irradiated with light from a distance of 10 cm with continuous stirring. 2 mL of the reaction solution was extracted at regular intervals for 2h and the measurement was performed. Once the conversion is complete, the solution was filtered and **ZnPyrPorp** polymer was collected and used for the second run to check its recyclability. Similar reaction was also performed in the absence of the polymer. The absorption peaks at approximately  $\lambda = 298$  and 330, and 427 nm were continuously monitored.

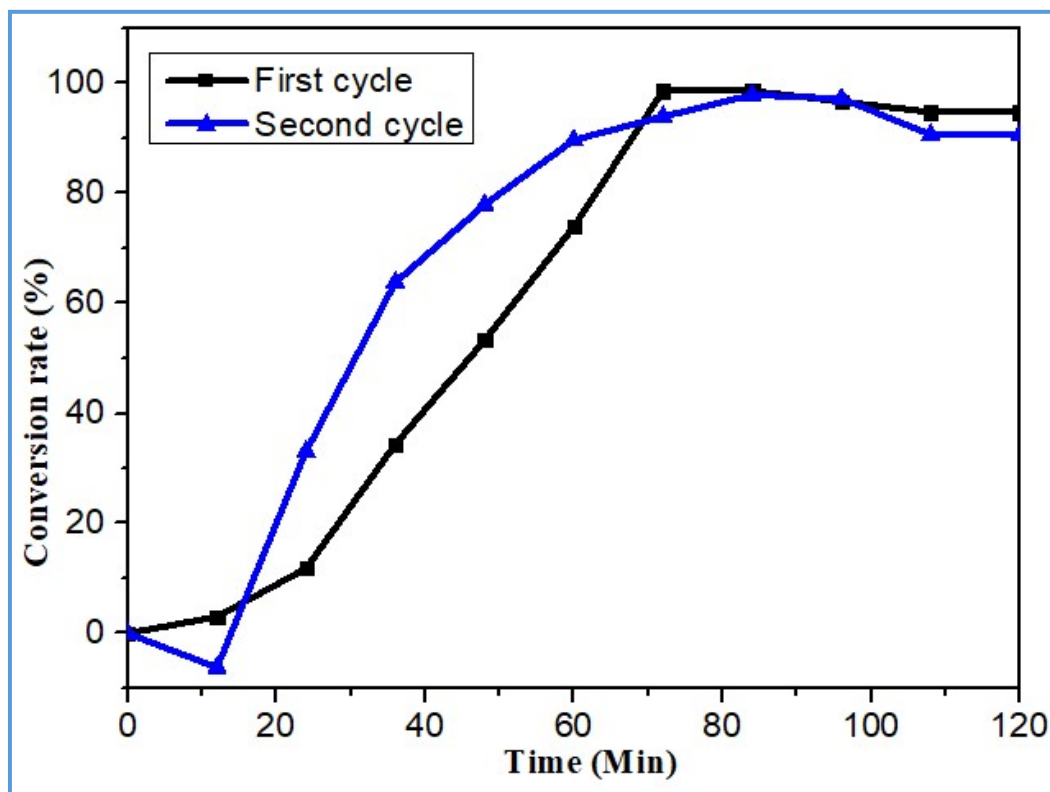
### **Confocal laser scanning microscope (CLSM) of PyrPy<sub>2</sub> and ZnPyrPorp:**

The confocal laser scanning microscope (CLSM) study were performed under a DMI-8 fluorescence microscope (Leica, Wetzlar, Germany) with a DFC-7000T CCD camera (Leica, Wetzlar, Germany) of Leica Microsystems (Wetzlar, Germany). Crystals of samples under measurement were kept on top of a thin glass slide and CLSM images were collected upon excitation at different wavelengths. Obtained images were converted into TIFF format with image software from Leica Microsystems.





**Figure S8:** UV-Visible absorption spectra of DHN solution without polymer **ZnPyrPorp**. No change is observed even after 3 h of irradiation.



**Figure S9:** Photooxidation of DHN to Juglone in the presence of catalyst **ZnPyrPorp**. It shows a conversion rate of 95% and 92% in the first and second cycles respectively.

**Table1.** Crystal Data and structure refinement for **PyrPy<sub>2</sub>** and **ZnPyrPorp**.

	<b>PyrPy<sub>2</sub></b>	<b>ZnPyrPorp</b>
CCDC #	<b>2051912</b>	<b>2051913</b>
Empirical formula	C <sub>26</sub> H <sub>16</sub> N <sub>2</sub>	C <sub>152</sub> H <sub>102</sub> N <sub>16</sub> O <sub>4</sub> Zn <sub>2</sub>
Formula weight	356.41	2347.27
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	P21/c	C2/c
a/Å	11.0306(6)	15.2278(13)
b/Å	5.4848(3)	20.3428(14)
c/Å	13.9759(7)	20.3837(19)
α/°	90	90
β/°	91.922(3)	110.889(6)
γ/°	90	90
Volume/Å <sup>3</sup>	845.07(8)	5899.4(9)
Z	2	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.401	1.321
μ/mm <sup>-1</sup>	0.082	0.474
F(000)	372.0	2436.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	7.982 to 51.362	4.004 to 53.38
Index ranges	-13 ≤ h ≤ 13, -6 ≤ k ≤ 6, -17 ≤ l ≤ 17	-19 ≤ h ≤ 19, -25 ≤ k ≤ 25, -25 ≤ l ≤ 25
Reflections collected	10964	38331
Independent reflections	1599 [Rint = 0.0408, Rsigma = 0.0279]	6068 [Rint = 0.0848, Rsigma = 0.0716]
Data/restraints/parameters	1599/0/127	6068/109/480
Goodness-of-fit on F <sup>2</sup>	1.037	1.081
Final R indexes [I ≥ 2σ (I)]	<sup>a</sup> R <sub>1</sub> = 0.0417 <sup>b</sup> wR <sub>2</sub> = 0.1132	<sup>a</sup> R <sub>1</sub> = 0.1412, <sup>b</sup> wR <sub>2</sub> = 0.3535
Final R indexes [all data]	<sup>a</sup> R <sub>1</sub> = 0.0624 <sup>b</sup> wR <sub>2</sub> = 0.1282	<sup>a</sup> R <sub>1</sub> = 0.1720 <sup>b</sup> wR <sub>2</sub> = 0.3713
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.31	3.07/-1.90

$$^a R_1 = \sum ||F_o| - |F_c| / \sum |F_o|. \quad ^b wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}.$$

## REFERENCES:

R1. H. L. Ozores, M. Amorín and J. R. Granja, *J. Am. Chem. Soc.*, 2017, **139**, 776-784.