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Electronic Supplementary Information (ESI†)

Core Engineering within BINOL-based Porous Organic Polymers for Efficacious Sequestration of Iodine and Methyl Orange

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1. Experimental Section.

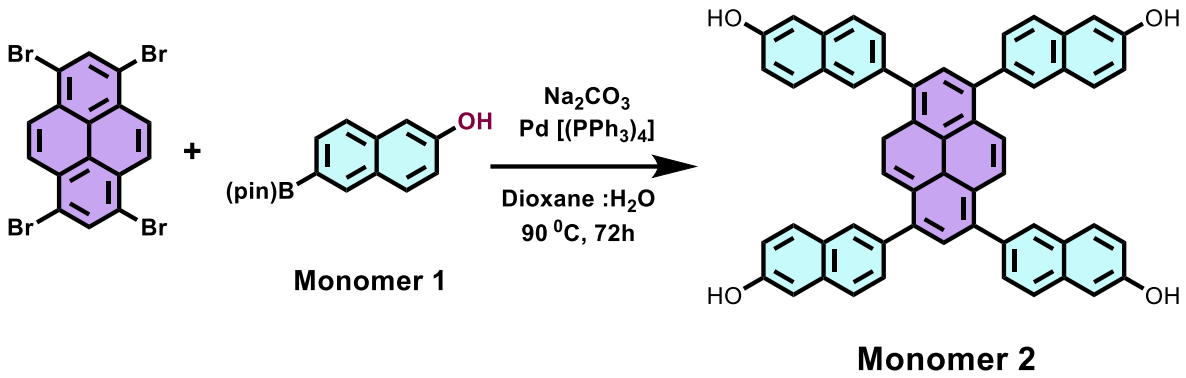
1.1. Materials and Methods. All the reagents, starting materials, and solvents were purchased from commercial suppliers and were used without further purification. Solvents were dried according to the literature procedure prior to use, as required. Thin-layer chromatography (TLC) on silica gel GF_{254} was used to determine R_f values, and visualization was performed under UV light at 254 nm. Column chromatography was performed on Merck silica gel (100-200 mesh) with chloroform as eluent. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded in a Bruker Advance III HD spectrometer in deuterated solvent at ambient temperature (300 K). Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) as the internal standard (DMSO-d_6 δ 3.6 and 2.6 ppm for ^{1}H and 39.0 ppm for ^{13}C). Solid-state ^{13}C CP/MAS NMR spectra were recorded in a Bruker Ultrashield Plus-500 NMR spectrometer. Mass spectra were recorded on an Agilent 6500 Series Q-TOF spectrometer. Fourier transform infrared spectra (FTIR, 4000-600 cm^{-1}) were performed on a Nicolet 6700 FT-IR spectrometer (Thermo Fischer) instrument; the wave numbers of recorded IR-signals are reported in cm^{-1}. Elemental analyses were carried out using a Perkin-Elmer Series-II. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond Tg Dta (PerkinElmer) instrument. The BINOL-based porous organic polymers were observed under a scanning electron microscope (SEM) model ZEISS SUPRA 40. The samples were prepared on Al stubs by adding the powder polymers and mounting them on double-sided tape. TEM measurements were carried out in a FEI Tecnai G2 20 TWIN machine operating at an accelerating voltage of 200 V. TEM samples were prepared by mounting on a carbon-coated copper grid for analysis. The particle size distribution histogram was obtained with ImageJ software. X-Ray diffraction patterns of the powder organic polymer samples were obtained using a Rigaku X diffractometer using Cu-Kα (0.15406 nm) radiation. Prior to nitrogen sorption measurements, the samples were degassed under vacuum at 120 °C for 12 h to remove residual solvent and moisture. Nitrogen adsorption–desorption isotherms were recorded at 77 K using Micrometrics 3Flex surface area analyzer. The apparent BET surface areas were calculated from the adsorption data in the relative pressure range selected according to the BET consistency criteria. XPS spectra of the samples were recorded on PHI 5000 VersaProbe III, ULVAC-PHI, INC.

1.2. Synthetic Procedures

Monomer **1** (6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) naphthalen-2-ol) and Monomer **3** were prepared following our previously published procedures.[1, 2]

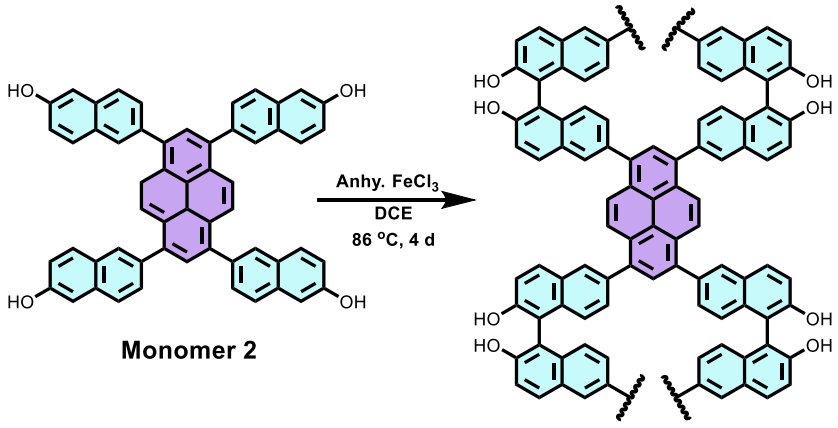
1.2.1. Procedure for synthesis of Monomer 2: 1,3,6,8-tetrabromopyrene (120 mg, 0.19 mmol) along with monomer **1** (6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) naphthalen-2-ol**;** 450 mg, 1.14 mmol), [$Pd(PPh_3)_4$] (5 mol%, 17 mg) in dioxane/H_2O (3:1) was stirred at 90 °C under argon for 72 h. Then, the reaction mixture was cooled to room temperature, quenched with water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (chloroform/methanol = 20:1) to afford compound **2** as a light green solid (68% yield). ^{1}H NMR: (DMSO-d6, 500 MHz, ppm) 9.89 (4H,s); 8.24 (4H,s); 8.15

(6H,d); 7.86-7.90(8H,m); 7.76 (4H, d); 7.25 (4H,s); 7.15-7.13 (4H,m).^{13}C NMR (DMSO-d6, 125 MHz, ppm): 156.18, 137.56, 135, 134.24, 130.64, 130.25, 129.23, 128.31, 127.83, 126.66, 126.03, 125.52,119.72, 108.97.



Scheme S1. Synthesis of monomer **2**.

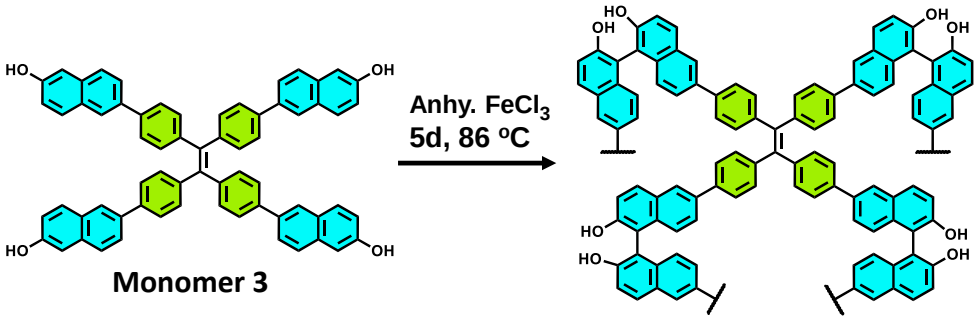
1.2.2. Procedure for the Synthesis of Polymer Pyr-BINOL-6: Monomer **2** (100 mg, 1 eqv.) dissolved in anhydrous 1,2-dichloroethane in the presence of anhydrous $FeCl_3$ (129 mg, 7 eqv.) was refluxed for 4 days. Then, the resulting precipitate was filtered and washed with dil. HCl and MeOH several times. The precipitate was again washed with $CHCl_3$, acetone, and MeOH for 48 h under Soxhlet extraction. Finally, it was dried under vacuum, and the yellow polymer **Pyr-BINOL-6** was obtained with 81% yield. Solid state ^{13}C CP/MAS NMR (ppm). 118, 123-129, 125-140, 155. TGA. 5% weight loss at 331 °C.



Scheme S2. Synthesis of polymer **Pyr-BINOL-6.**

1.2.3. Procedure for the Synthesis of TPE-BINOL-6: Monomer **3** (100 mg, 1 eqv.) dissolved in 1,2-dichloroethane in the presence of anhydrous $FeCl_3$ (135 mg, 7 eqv.) was refluxed for 5 days. Then, the resulting precipitate was filtered and washed with HCl and MeOH several times. The precipitate was again washed with $CHCl_3$, acetone, and MeOH for 48 h under Soxhlet extraction. Finally, it was dried under vacuum, and the tan polymer **TPE-BINOL-6**

was obtained with 65% yield. Solid state ^{13}C CP/MAS NMR (ppm). 108, 113-116, 123-129, 137-141, 153. FT-IR (KBr pellet, cm^{-1}). 3348, 2935, 1559, 1284, 1091. TGA. 5% weight loss at 308 °C.



Scheme S3. Synthesis of polymer **TPE-BINOL-6.**

1.3. General Process of Iodine Adsorption by Pyr-BINOL-6 and TPE-BINOL-6: The gravimetric technique was used to determine the iodine adsorption over the BINOL-based POPs at various time intervals. Specifically, 10 mg of the vacuum-dried POP sample (upon heating at 120 °C for 12 h) was placed in a pre-weighed 5 mL vial before analysis, and the vial was placed into a large sealed vial (30 mL) containing an excess amount of solid iodine and molecular sieves (5 g). The entire system was kept in an oven set to 75 °C for a certain amount of time. After the iodine-adsorbed sample was cooled to room temperature, it was weighed.

After each adsorption cycle, **Pyrene-BINOL-6** was washed with methanol several times until the washed fraction turned from yellow to colourless, and the adsorbent was dried under vacuum before further use.

1.4. Procedure for VB XPS.

The valence-band onsets (VBxps) for **Pyr-BINOL-6** and **TPE-BINOL-6** are 0.84 eV and 0.35 eV, respectively. The electron work function (Φ) of the analyzer was 4.85 eV. Using these values in equation S1, the valence band potential could be obtained

$E_{VB} = \Phi + VB_{xps} - 4.44$ …….(S1)

The E_g value, i.e., optical band gap, was calculated from the Tauc plot (equation S2).

$E_{CB} = E_{VB} - E_g$…….(S2)

1.5. General procedure for the dye degradation.

In a glass vial, 2 mg of powdered catalysts were dispersed in the aqueous solutions containing the dyes, and the resulting suspension was stirred in the dark for 1 h with prior ultrasonication to achieve adsorption-desorption equilibrium, followed by exposure of the mixture to 50W blue

LED light. Then, the solutions were tested with UV-vis spectroscopy, after discerning their visual color change under the naked eye. The degradation efficiency was calculated using equation S3,

$$\% \text{ Degradation} = [(C_0-C_t)/C_0] \times 100 \ldots\ldots \text{(S3)}$$

1.6. General procedure for the kinetic study.

The time-dependent measurements were performed with a 50 ppm initial dye concentration in water in the presence of 2 mg of the catalysts. After certain time intervals, 0.5 mL of an aliquot from the test solution was withdrawn using a 0.22 µm syringe filter and tested for UV-vis spectroscopy. The concentration was determined with the help of Lambert-Beer's law. The results fitted well with the pseudo-first-order rate equation S4,

$$\ln (A/A_0) = -kt \qquad \ldots\ldots\ldots \text{(S4)}$$

1.7. General Process of recycling for Pyr-BINOL-6: After each cycle, the polymer was washed with vigorous stirring for 4 h in methanol and water, and was recovered through centrifugation. Thereafter, it was put through the next run with prior vacuum drying.

2. Characterization

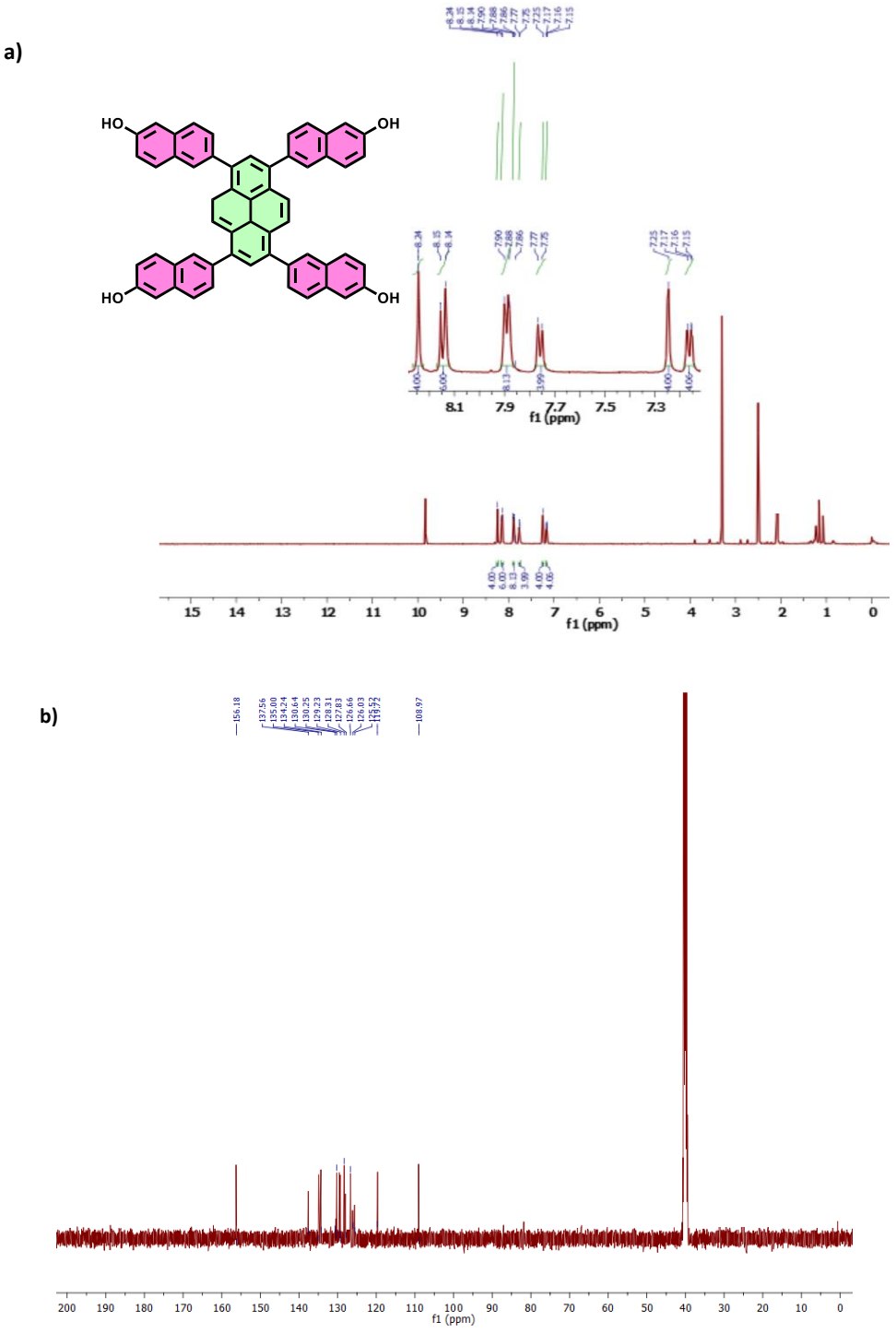


Fig. S1. a) ^{1}H and b) ^{13}C NMR spectra for monomer **2** in DMSO-d_6.

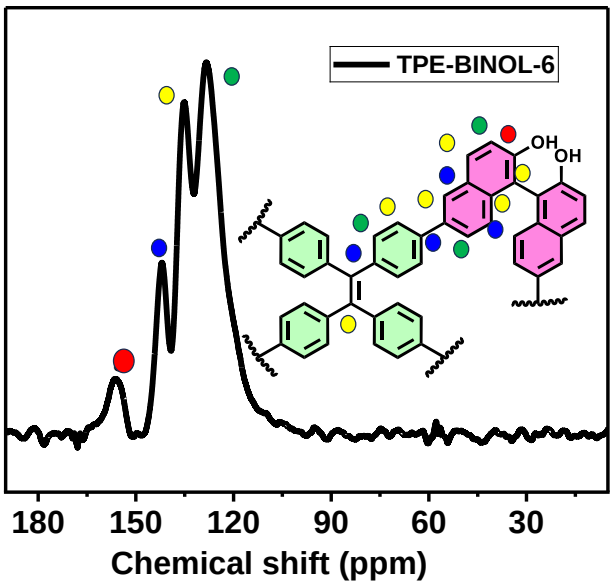


Fig. S2. Solid-state ^{13}C NMR spectrum of **TPE-BINOL-6**.

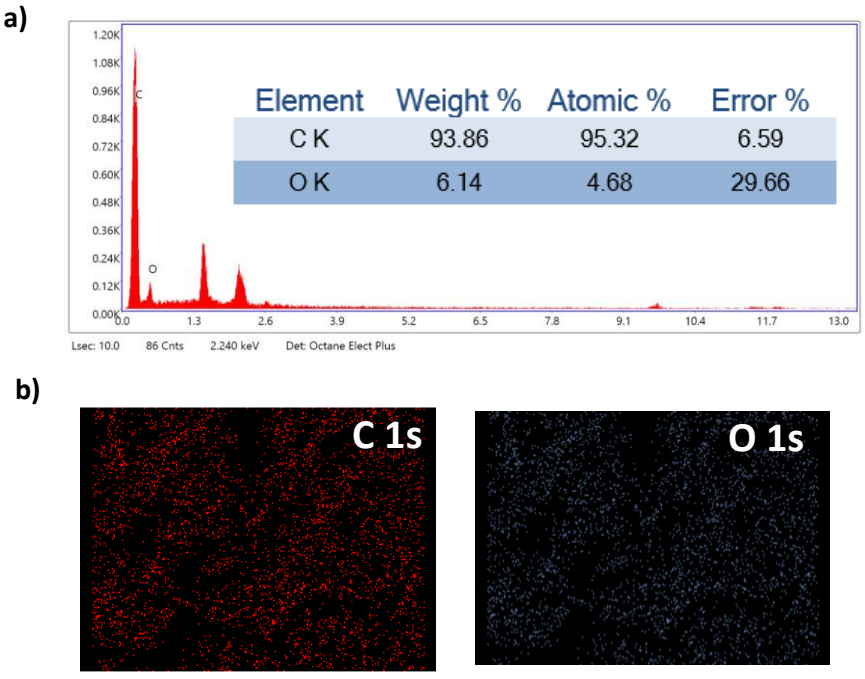


Fig. S3. EDAX pattern and elemental mapping for **Pyr-BINOL-6**.

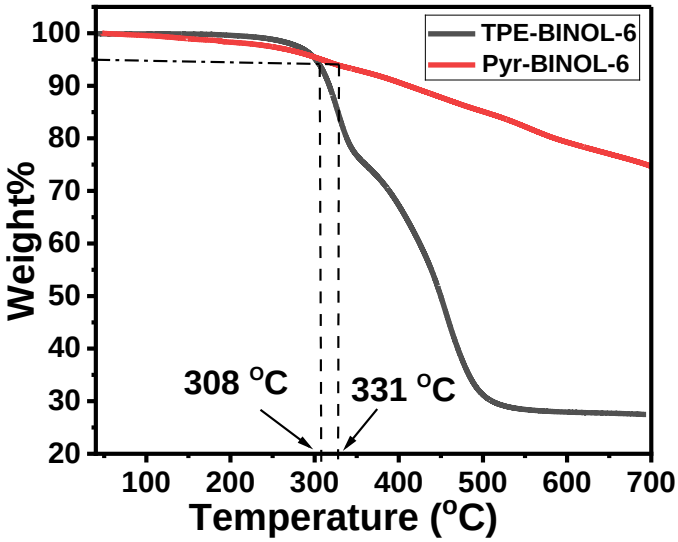


Fig. S4. TGA curve of **TPE-BINOL-6** and **Pyr-BINOL-6** under argon atmosphere.

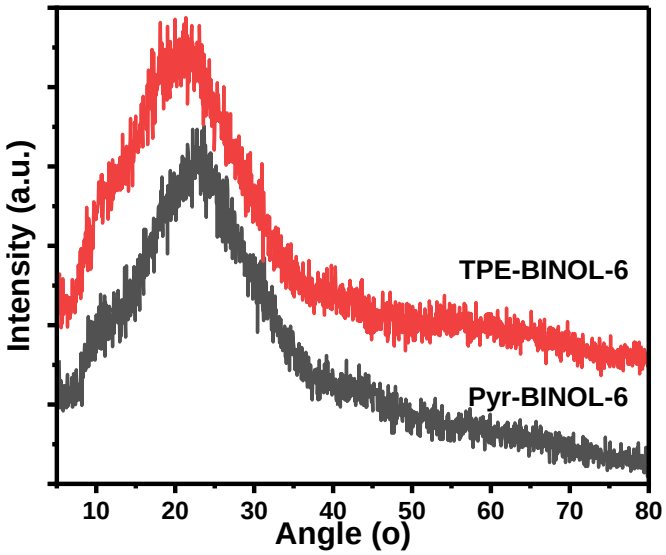


Fig. S5. PXRD profile for **Pyr-BINOL-6** and **TPE-BINOL-6**.

Table S1. Comparison of iodine uptake for our as-synthesized POP with previously reported adsorbents

Adsorbents	Surface area (m^2/g)	Iodine uptake (g/g)	References
HPOP-4	89.86	6.25	*ACS Appl. Polym. Mater.* 2023**, 5**, 5349−5359.
TTDP-1	12	5.36	*ACS Appl. Polym. Mater*. 2020, **2**, 5121-5128.
TPE-TPDA-CMP	634	4.68	*ACS Appl. Mater. Interfaces* 2023, **15**, 46408−46416.
CTAPA	8.3	3.96	*Chem. Eng. J.* 2024**, 484**, 149739.
POP-2	41	3.82	*J. Hazard. Mater.* 2017, **338**, 224–232.
Pyr-BINOL-6	**438**	**3.71**	**This work**
CMPNH2	6.44	2.83	*J. Mater. Chem. A* 2020, **8**, 1966-1974.
BDP-CPP-1	635	2.83	*J. Mater. Chem. A* 2017, **5**, 6622-6629.
C-POP3	19.0	2.22	*ACS Appl. Mater. Interfaces* 2025, **17**, 17783−17793.
TPE-BINOL-6	**112**	**2.15**	**This work**
CMP-4	9.5	2.08	*Angew. Chem. Int. Ed.* 2021, **60**, 8967-8975.
CMPN-3	1368	2.08	*J. Mater. Chem. A* 2015, **3**, 87-91.
NAPOP-1	657	2.06	*J. Polym. Sci., Part A: Polym. Chem.* 2016, **54**, 1724−1730.
NOP-54	1178	2.02	*Chem. Eng. J.* 2018, **334**, 900-906.
NiP-CMP	2600	2.02	*Chem. Commun.* 2014, **50**, 8495-8498.
ZIF-8	1551	2.0	*ACS Appl. Mater. Interfaces* 2023, **15**, 54702-54710
PCN-222-CF3	1482	1.97	*Chem. Eng. J.* 2023, **461**, 142058
Zn-MOF-2	921.45	1.96	*ACS Appl. Mater. Interfaces* 2023, **15**, 35082-35091
NRPP-1	**1579**	**1.92**	*ACS Appl. Mater. Interfaces* 2018, **10**, 16049-16058
TTPT	315.5	1.77	*Polym. Chem.* 2018, **9**, 777-784.
CMP-2	20.2	1.77	*Angew. Chem. Int. Ed.* 2021, **60**, 8967-8975

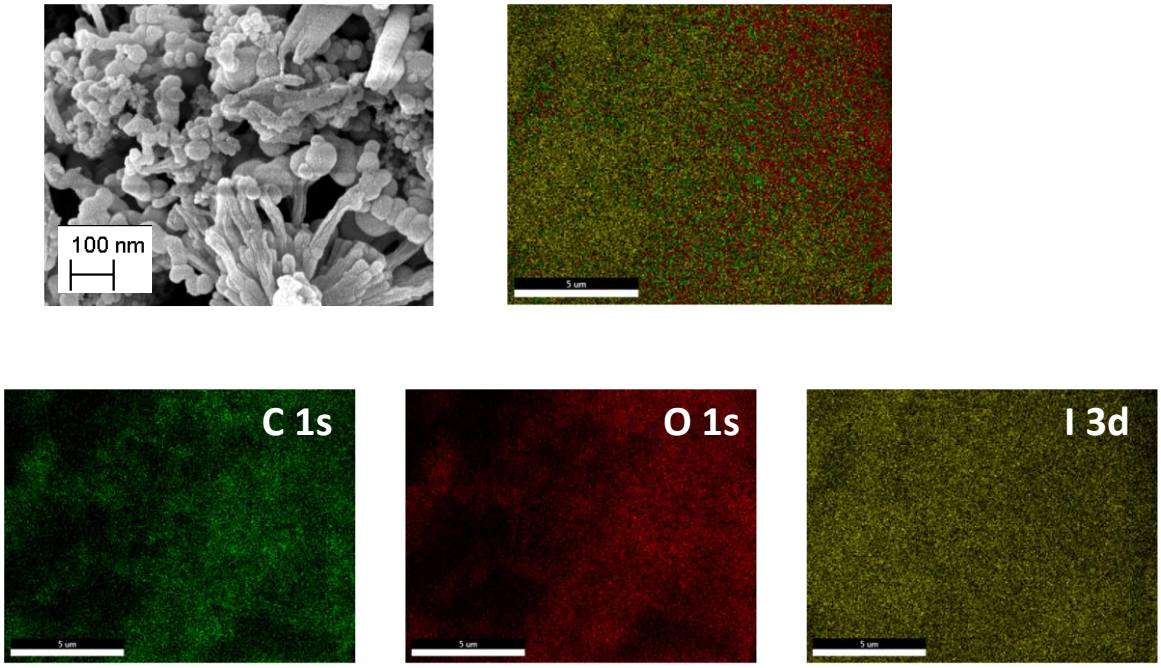


Fig. S6. FESEM image and elemental mapping for **I_2@Pyr6**.

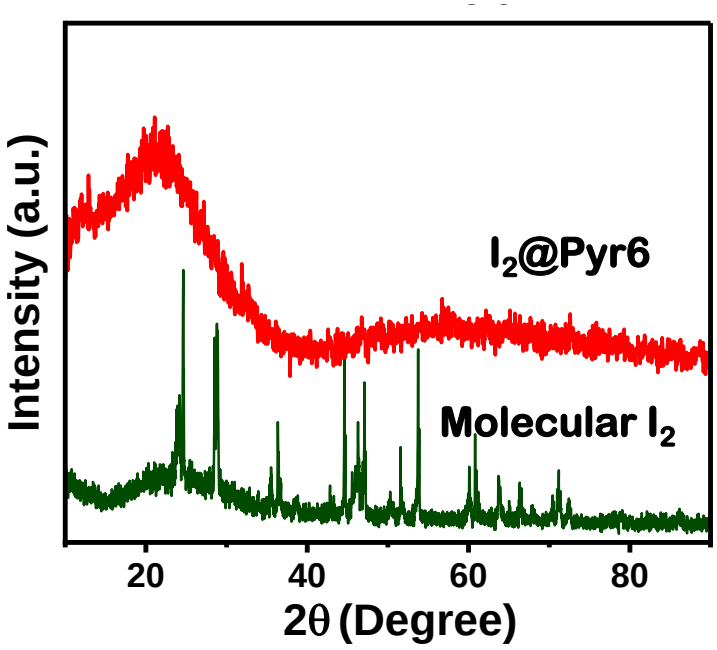


Fig. S7. PXRD pattern for **I_2@Pyr6** (red) and molecular iodine (green)**.**

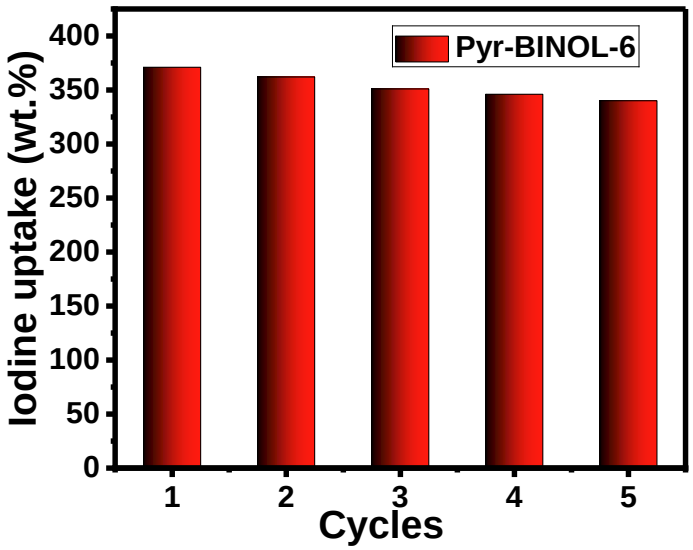


Fig. S8. Recyclability profile for iodine uptake with **Pyr-BINOL-6** up to five consecutive cycles.

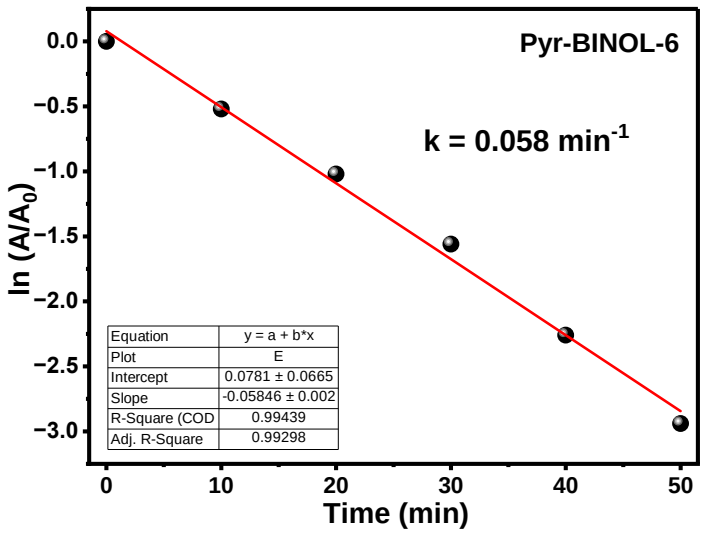


Fig. S9. Pseudo first-order fitting for **Pyr-BINOL-6** in the case of MO degradation.

Table S2. Comparison of our as-synthesized POP with previously reported inorganic and organic photocatalysts towards the degradation of methyl orange.

Photocatalyst	Degradation Efficiency (%)	Time (min)	Reference
Pyr-BINOL-6	> 99	50	**This work**
PDA-COP-1	92	120	*J. Phys. Chem. C*, 2018, **122**, 274-284.
CMP-13	99.99%	60	*J. Mater. Sci.* 2024, **59**, 4072-4085
Ag-TiO_2/PP	81.4	180	*Surf. Interfaces*, 2021, **26**, 101318
PT-13	90.4	540	*Mater. Sci. Semicond. Process.*, 2017, **57**, 157-165
POP-1	90	135	*Appl. Catal. B: Environ.*, 2018, **227**, 102-113
PES/ZnO	95	540	*Catalysts*, 2017, **7**, 313
Co_3O_4-ZnO	> 99	120	*Mater. Lett.*, 2021, **284**, 128902
$ZnIn_2SO_4$	51.3	90	*RSC Adv.* 2017, **7**, 12292

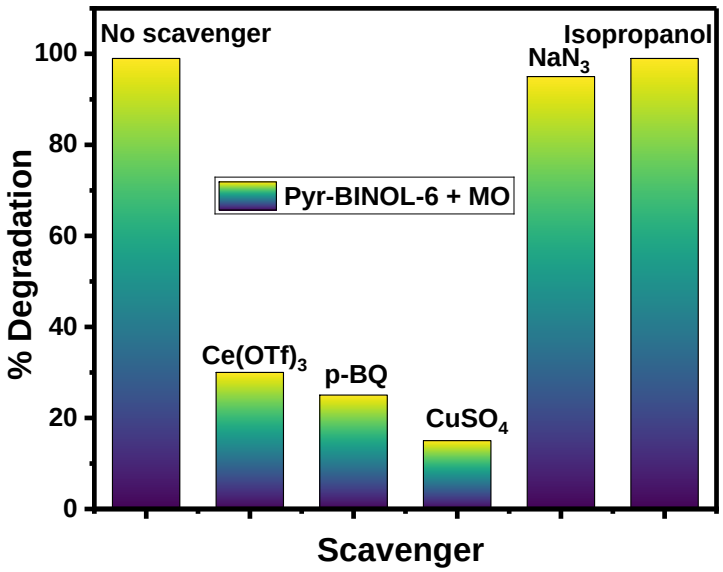


Fig. S10. Scavenger control study for **Pyr-BINOL-6** in case of MO degradation.

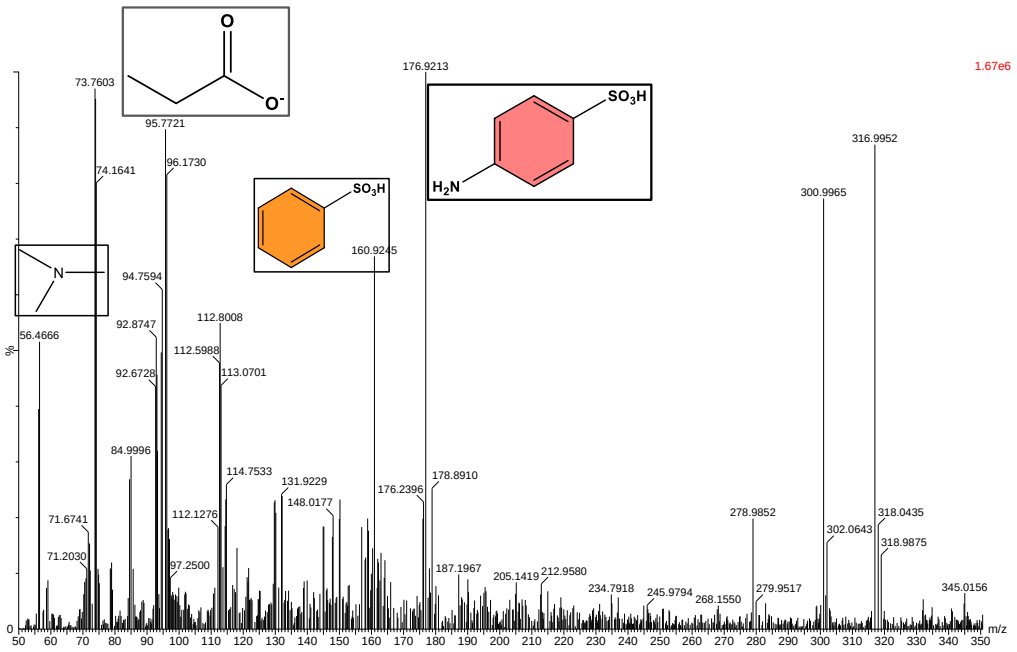


Fig. S11. Degradation fragments analysis for MO with **Pyr-BINOL-6** with LC-MS profile.

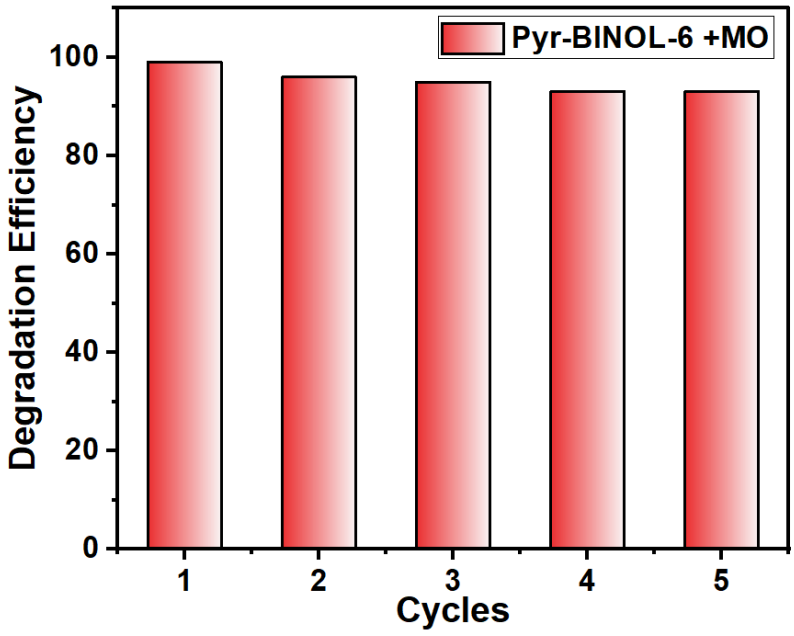


Fig. S12. Recyclability profile for **Pyr-BINOL-6** after methyl orange degradation**.**

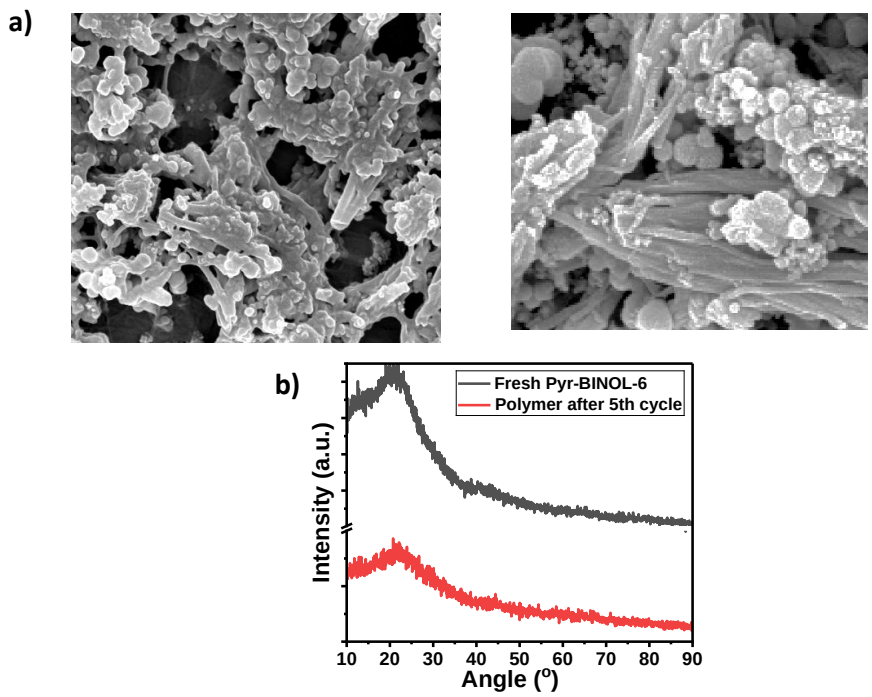


Figure S13. a) SEM images and b) PXRD pattern for fresh (left) and recycled **Pyr-BINOL-6** after MO degradation up to 5th cycle (right).

References

1. F. Banerjee, S. Bera, T. Nath and S. K. Samanta, *Nanoscale*, 2024, **16**, 11999-12006.
2. S. Karmakar, S. Bera, F. Banerjee, S. Sau and S. K. Samanta, *Sep. Purif. Technol.*, 2026, **385**, 136472.