Supporting Information

A Novel 1,1,6,6-Tetracyano hexatriene Linked Conjugated Microporous Polymer for High Photocatalytic Hydrogen Evolution

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General:

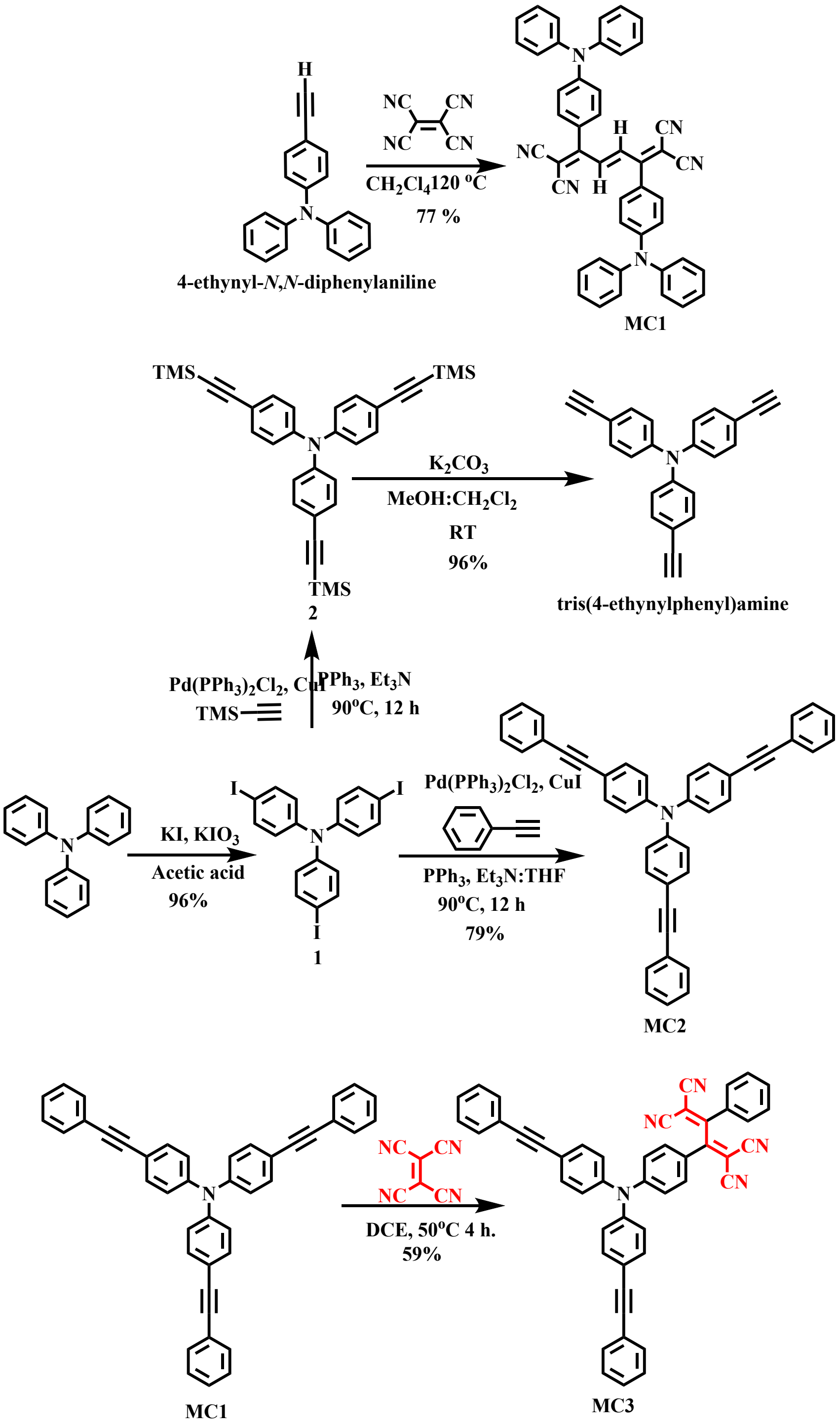
Chemicals: Triphenylamine, phenyl acetylene, tetracyanoethylene purchased from commercial suppliers (TCI, Sigma Aldrich, BLD Pharma & LOBA) and used as is without further purification. All the oxygen- or moisture-sensitive reactions were performed under a nitrogen atmosphere, and the reflux reactions were carried out in an oil bath. Anhydrous solvents are used for Sonogashira coupling reaction. Reagent-grade solvents were used for synthesis. Column chromatography was performed on silica (silica gel, particle size 100-200 mesh). TLC Spots were visualized with UV light (λ = 254 nm & 365 nm). Soxhlet extractor used to purify polymers.

Material Characterisations:

Instrumentation: ^{1}H and ^{13}C-NMR spectra were recorded on a JEOL ECZS 400 MHz and 100 MHz, respectively. Tetramethylsilane (TMS) was used as an internal standard. Coupling constant (J) values are given in Hz. Abbreviation used to designate ^{1}H multiplicities are s=singlet, d=doublet, t=triplet, m=multiplet. CPMAS NMR used for CMP. Gaussian 16 W software used for DFT calculation. UV-Vis absorption spectra were recorded on a Cary 5000

UV-Vis-NIR spectrophotometer. All the spectroscopic measurements were performed with conventional quartz cells (10 mm), and solid-state absorbance was recorded by the reflectance method with KBr as a reference. FT-IR Spectroscopy: Fourier-transform infrared spectra were recorded on a Spectrum Two FT-IR spectrometer (PerkinElmer) with UATR. X-ray Diffraction (XRD): Powder XRD patterns were collected on a Panalytical X'Pert diffractometer with Cu Kα radiation (λ = 1.5406 Å), scanning 2θ angles from 5° to 80°. Thermogravimetric Analysis (TGA): Thermal stability was assessed using an SDT Q600 V20.9 analyser, with samples heated at 10 °C min^{-1} up to 800 °C under controlled conditions. Surface Area and Porosity Analysis: N2 adsorption-desorption isotherms were obtained using a Quantachrome Nova 2200e analyser. Prior to analysis, samples were degassed at 120 °C for 12 hours. Morphological Characterisation: Field-emission scanning electron microscopy (FE-SEM) was performed on a Carl Zeiss Gemini 300 microscope to examine sample morphology. Electrochemical studies were done by using Gamry, Interface 1010E. Three electrode systems were used for studies, a Pt wire as a counter electrode, Ag/AgCl as a reference electrode and a Glassy carbon as the working electrode. Tetrabutylammonium perchlorate (TBAP) as an electrolyte and HPLC grade CH_2Cl_2 as solvent.

Experimental section:



Scheme S 1 : Synthesis of monomer & model compounds (**MC1** & **MC2**)

Synthesis:

Tetracyano ethylene (TCNE) (50 mg, 0.390 mmol) & 4-ethynyl-N, N-diphenylaniline (210 mg, 0.781 mmol) taken in tetrachloroethane. Reaction mixture heated at 120 °C for 12 h. The crude product was purified by column chromatography (DCM/hexane 80:20). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 14H), 7.22-7.16 (m, 12H), 7.07-7.04 (m, 4H) ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.8, 152.2, 145.7, 141.4, 131.1, 129.8, 126.4, 125.4, 122.5, 119.3, 113.5, 112.7, 83.7, 77.3, 77.2, 77.0, 76.7, 53.4 (ESI-TOF) m/z: $[M + H]^+$ calculated for $C_{46}H_{30}N_6$ 666.2532; found 666.2505

tris-(4-iodo-phenyl)-amine: (**1**)

Triphenylamine (2 g, 8.15 mmol) was taken in an RB flask and dissolved in 50 mL of glacial acetic acid. KI (1.45 g, 8.15 mmol) and KIO_3 were added in four portions with continuous stirring at 110 °C. The RB flask was covered in aluminium foil and stirred overnight. Poured the reaction mixture in ice water & filtered the solid and crude product, purified by silica gel chromatography (Hexane) to obtain a white solid. (96%) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (d, 2H), 7.26-7.23 (m, 4H), 7.08-7.03 (m, 6H), 6.95-6.93 (d, 2H)

tris(4-((trimethylsilyl)ethynyl)phenyl)amine (**2**):

Compound **1** (1.00 g, 1.60 mmol) and ethynyltrimethylsilane (492 mg, 4.81 mmol) in Et_3N (50 ml), $Pd(PPh_3)_2Cl_2$ (34 mg, 0.048 mmol), CuI (9.1 mg, 0.048 mmol), PPh_3 (19 mg, 0.067 mmol) stirred for 12 hours at 90 °C, after completion of the reaction, passed through silica pad and the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica, using hexane and afforded pure compounds **2** around 88 % yield. yellow solid ^{1}H-NMR (400 MHz, $CDCl_3$) 7.42- 7.39(d, J = 9.0 Hz, 6H), 7.06- 7.03(d, J = 9.0 Hz, 6H), 0.22(s, 27H), ^{13}C- NMR (300MHz, $CDCl_3$): δ 146.89, 133.29, 123.93, 117.94, 104.99, 94.07, 0.16, EI-MS found 533, 518, 252, 163, 73.

tris(4-ethynylphenyl)amine:

Compound **2** was taken in a 1:1 ratio of methanol & dichloromethane (30 ml), and K_2CO_3 was added. Stirred the reaction at RT for 4 h. After completing the reaction. Removed the solvent under reduced pressure. The crude product was washed with excess water, and the solid product was dried in a vacuum. To get quantitative yields. ^{1}H-NMR (400 MHz, $CDCl_3$) 7.38 (d, J = 7.6 Hz, 6H), 7.01 (d, J = 7.6 Hz, 6H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.0, 133.3, 123.9, 116.8, 83.4.

tris(4-(phenylethynyl) phenyl) amine (**MC2**):

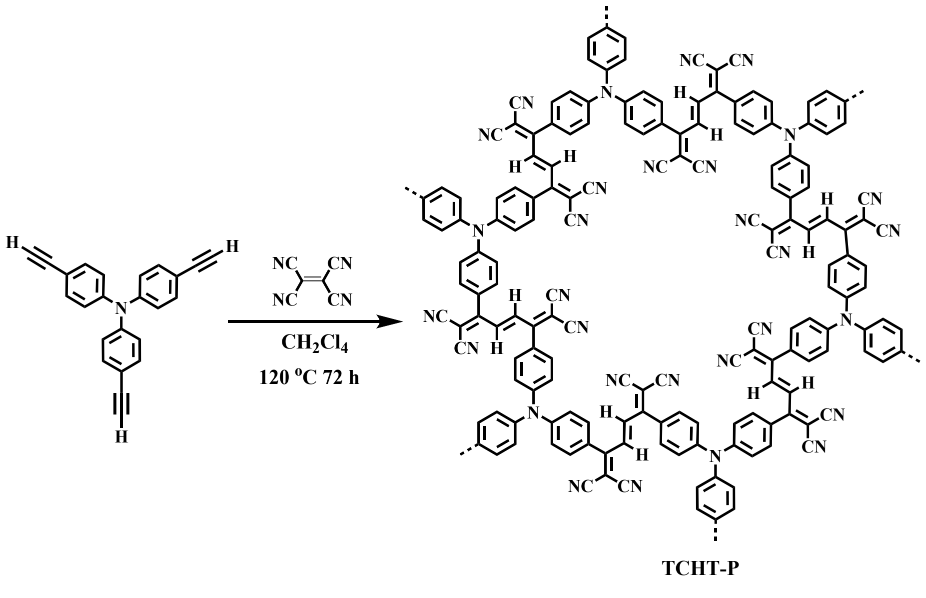
Compound **1** (1.00 g, 1.60 mmol) and phenyl acetylene (492 mg, 4.81 mmol) in dry THF (20ml), added Et_3N (20 ml), $Pd(PPh_3)_2Cl_2$ (56 mg, 0.08 mmol), CuI (21 mg, 0.08 mmol), PPh_3 (37 mg, 0.12 mmol) stirred for 12 hours at 90 °C, after completion of the reaction, passed through silica pad and the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica, using Hexane/ DCM (80:20), and afforded pure compounds **3** around 88 % yield. yellow solid (0.750 g, 72%) ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.54 (dd, *J* = 8 Hz, 6H), 7.46 (dd, *J* = 8 Hz, 6H), 7.10 (dd, *J* = 8 Hz, 6H). 13C NMR ($CDCl_3$, 100 MHz, ppm): 146.7, 132.8, 131.5, 128.4, 128.3, 124.0, 123.4, 118.0, 89.2. HRMS (ESI-TOF): m/z calculated for $C_{42}H_{27}N$ 545.2138 $[M]^+$, measured 545.2134 $[M]^+$.

2-(4-(*bis*(4-(phenylethynyl)phenyl)amino)phenyl)-3-phenylbuta-1,3-diene-1,1,4,4-tetracarbonitrile **(MC3)**:

A solution of **MC1** (0.1 g, 0.18 mmol) and TCNE (4 equivalents) in dichloroethane was stirred for 5 hours at 50 °C. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography Hexane/ DCM (60:40), to give compound **4** as a red solid (0.069 g, 59 %) ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.75-7.72 (m, 2H), 7.70-7.65 (m, 3H), 7.60-7.52 (m, 10H), 7.38-7.34 (m, 6H), 7.19-7.15 (m, 4H), 7.09-7.05 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): 168.2, 163.9, 152.7, 144.2, 134.5, 133.3, 131.6, 129.4, 128.4, 126.3, 122.9, 121.4, 119.8, 113.1, 112.3, 111.8, 111.7, 111.2, 107.8, 90.6, 88.4, 87.5, 79.9. HRMS (ESI-TOF): m/z calculated for $C_{48}H_{27}N_5$ 696.2159 $[M]^+$, measured 696.2159 $[M]^+$.

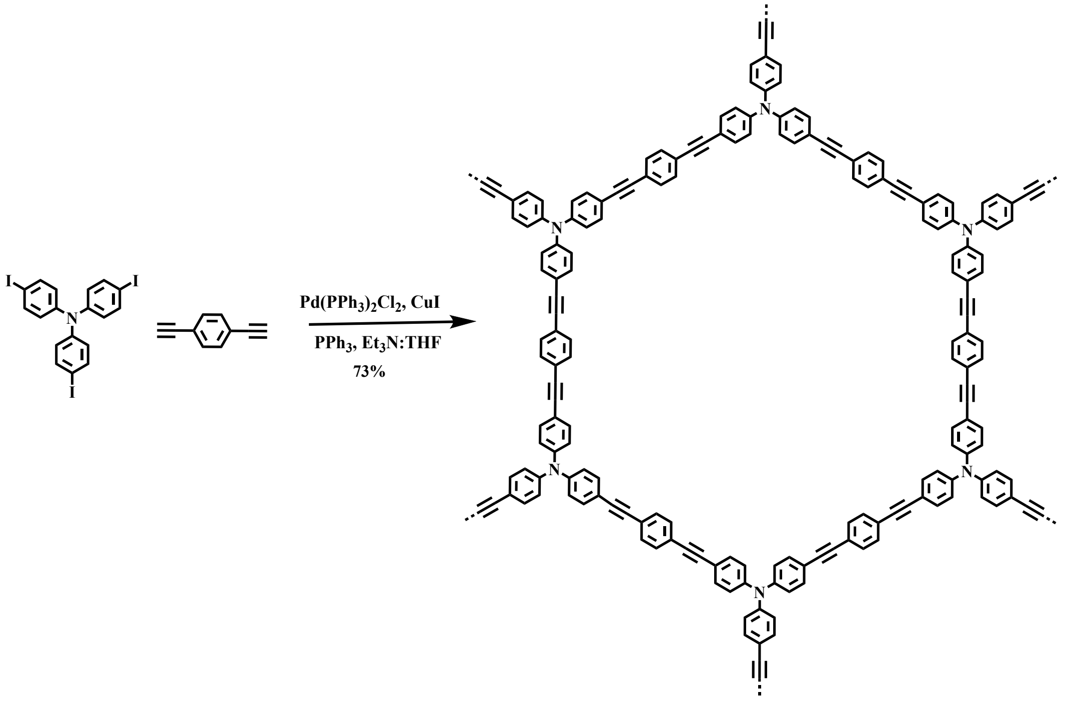
TCHT-P:

Tris(4-ethynylphenyl)amine (200 mg, 0.63 mmol) and tetracyanoethylene (TCNE, 121 mg, 0.94 mmol) were placed in a pressure vessel. Dichloromethane (CH_2Cl_4, 6 mL) was added, and the mixture was purged with nitrogen gas for 15 minutes to remove dissolved oxygen. The sealed reaction vessel was then heated at 120 °C for 72 hours. Upon completion of the reaction, the resulting solid was collected by filtration and washed sequentially with tetrahydrofuran (THF), acetone, and dimethylformamide (DMF) to remove any unreacted materials and byproducts. The crude product was further purified by Soxhlet extraction using methanol for 24 hours. Finally, the solid was dried under vacuum at 80 °C to yield a dark solid product with an 88% yield.



TCHT-P

Scheme S 2: **TCHT-P** synthesis

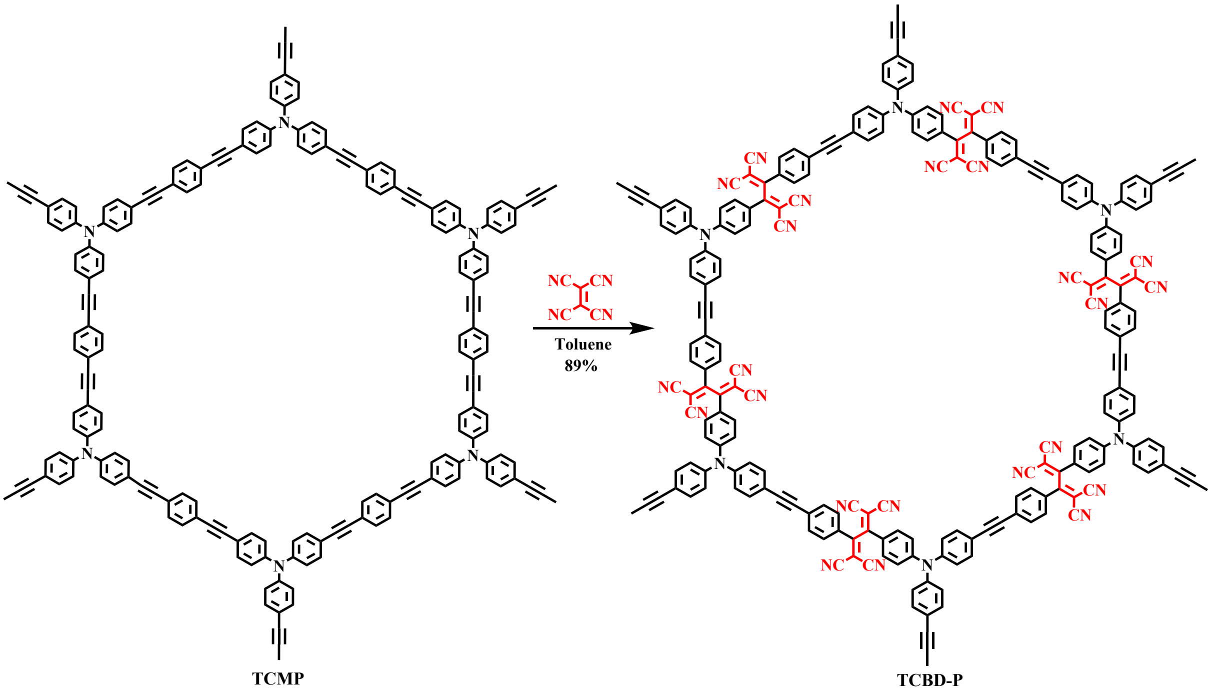


TCMP

Scheme S 3: **TCMP** synthesis

TCMP:

Compound **1** (450 mg, 0.72 mmol), *tris*(4- iodophenyl)amine (136.6 mg, 1.08 mmol), $Pd(PPh_3)_2Cl_2$ (25.4 mg, 0.0361 mmol), CuI, (7 mg, 0.0361 mmol), PPh_3 (15 mg, 0.057 mmol) were dissolved in the mixture of toluene (4 mL) and Et3N (4 mL). The reaction mixture was heated to 90 °C and stirred for 72 hours under a nitrogen atmosphere. Reaction mixture was cooled to room temperature, and the insoluble precipitated network polymer was filtered and washed 4-5 times with chloroform, DMF, methanol, water, and acetone to remove any unreacted monomers. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 48 h. The product was dried in a vacuum for 24 h at 70 °C and isolated as a fine brown powder (Yield: 73.4%).



Scheme S 4: **TCBD-P** synthesis

TCBD-P:

In the 15 ml pressure vessel, TCMP (50 mg) was taken in anhydrous toluene and sonicated for 5 min. To the above mixture, an equal amount of tetracyanoethylene was added, and the reaction mixture was heated at 100-120 °C for 24 hours. Reaction mixture filtered, the solid washed with methanol, water, DMF and Acetone. Further purification of the polymer was carried out by Soxhlet extraction with methanol and $CHCl_3$ for 48 h. The product was dried in a vacuum for 24 h at 70 °C and isolated as a fine black powder (Yield: 73.4%).

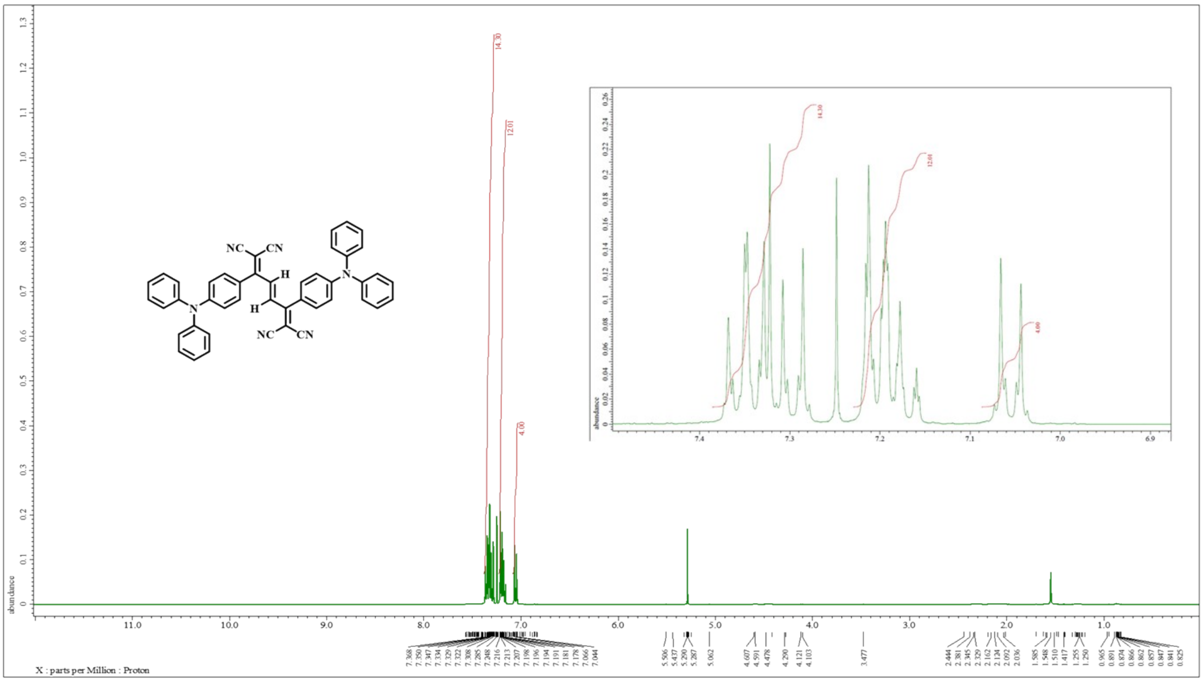


Figure S 1: ^{1}H NMR spectrum of **MC1**

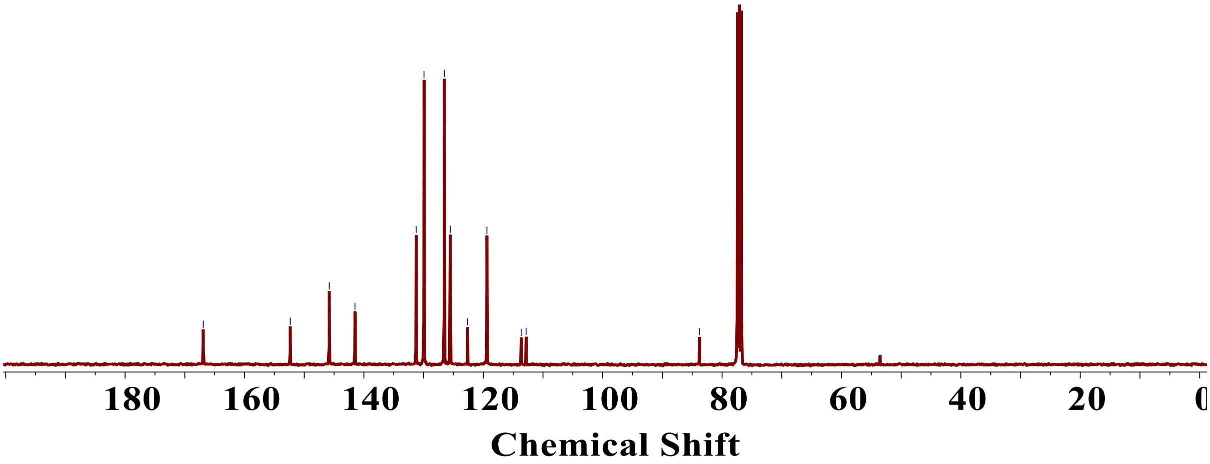


Figure S 2: ^{13}C NMR spectrum of **MC1**

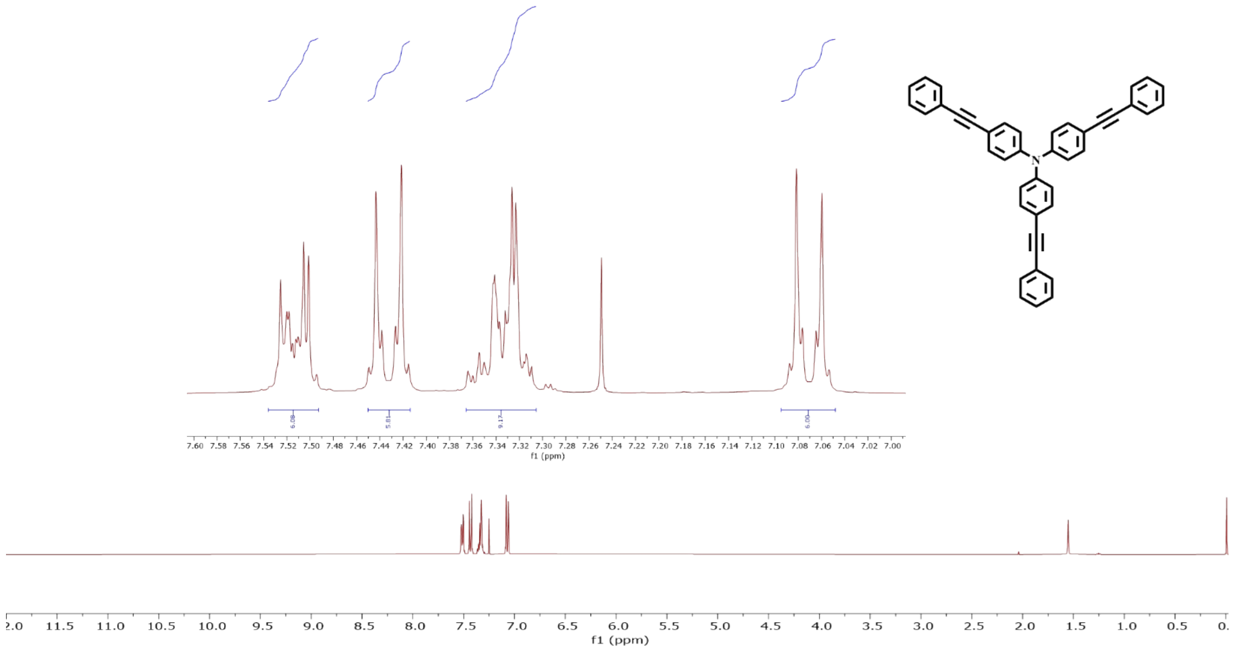


Figure S 3: ^{1}H NMR spectrum of **MC2**

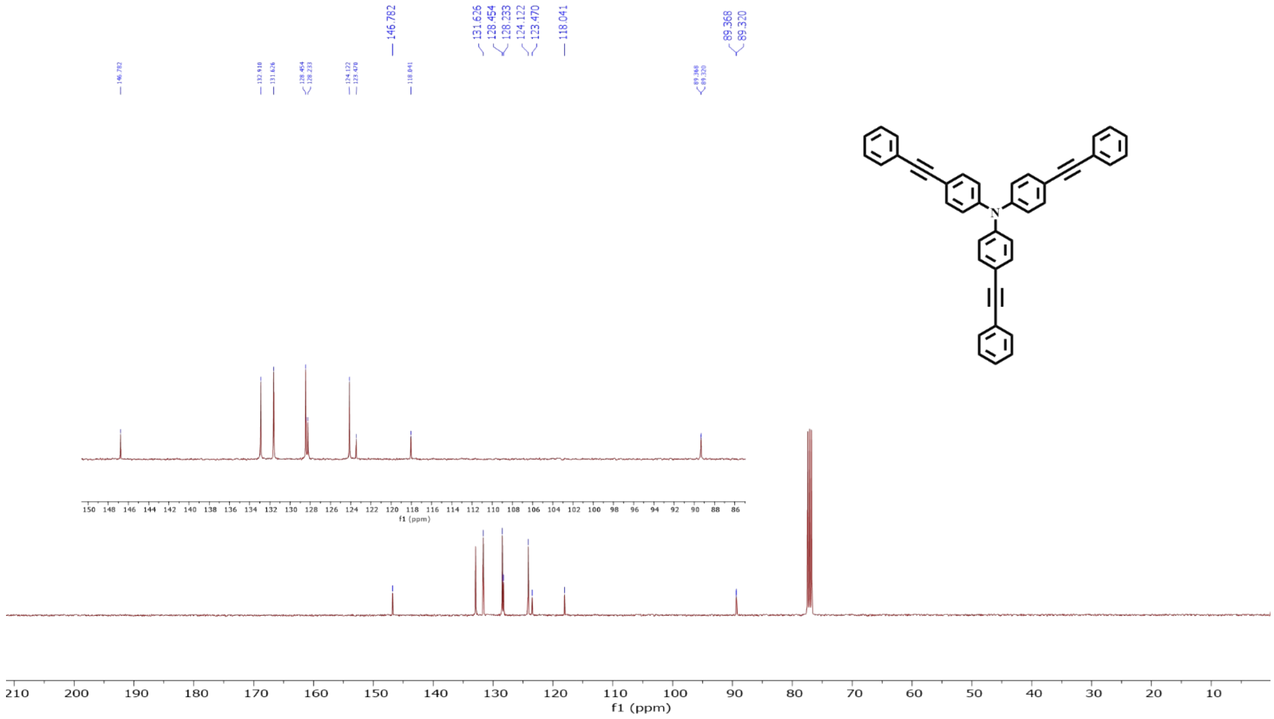


Figure S 4: ^{13}C NMR spectrum of **MC2**

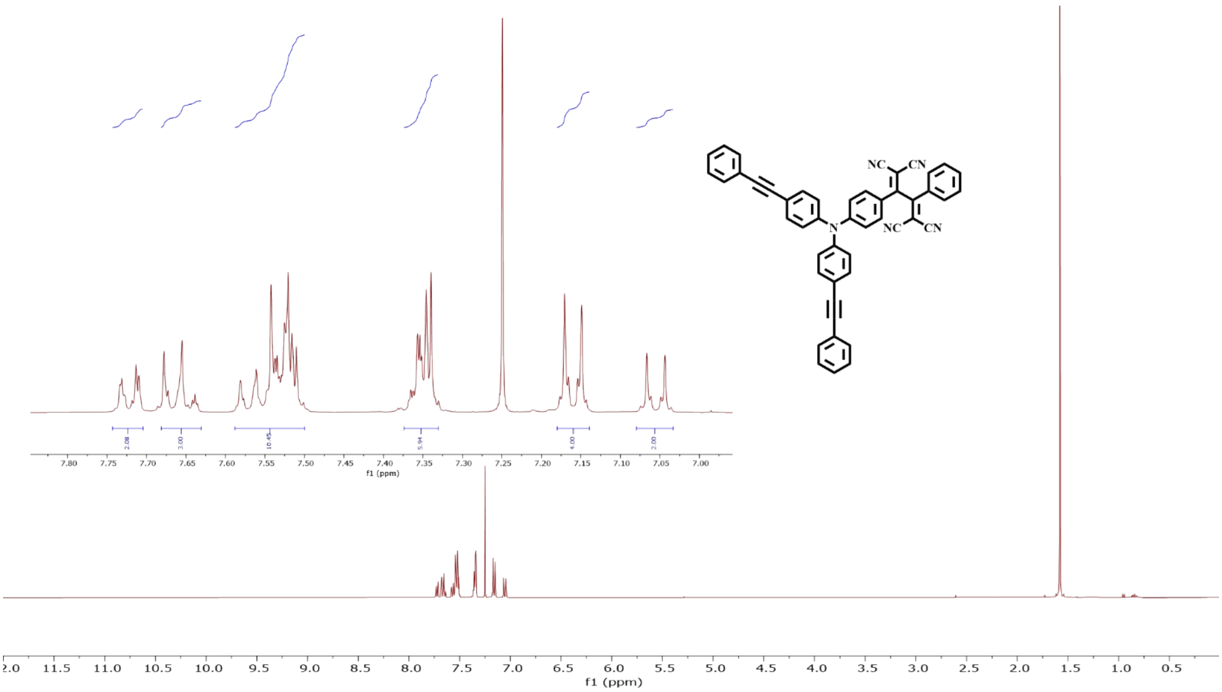


Figure S 5: 1H NMR spectrum of **MC3**

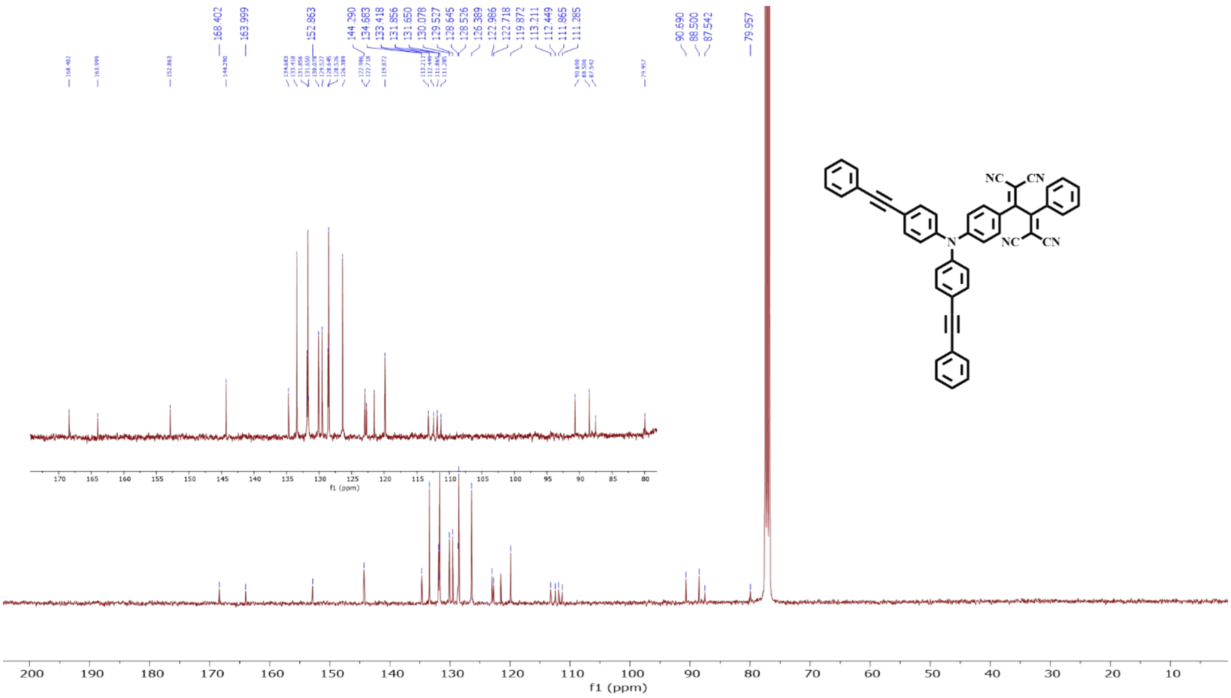


Figure S 6: ^{13}C NMR spectrum of **MC3**

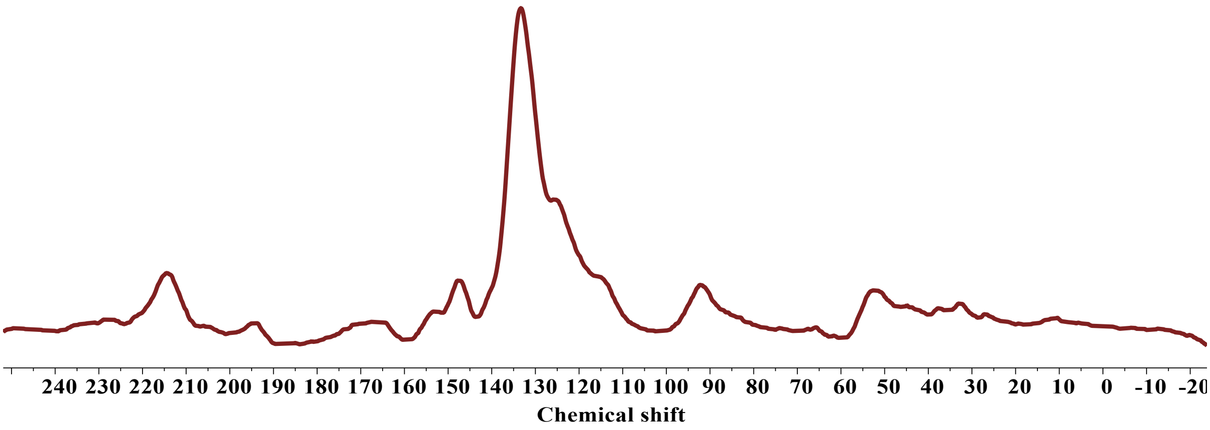


Figure S 7: ^{13}C CPMAS NMR spectrum of **TCHT-P**

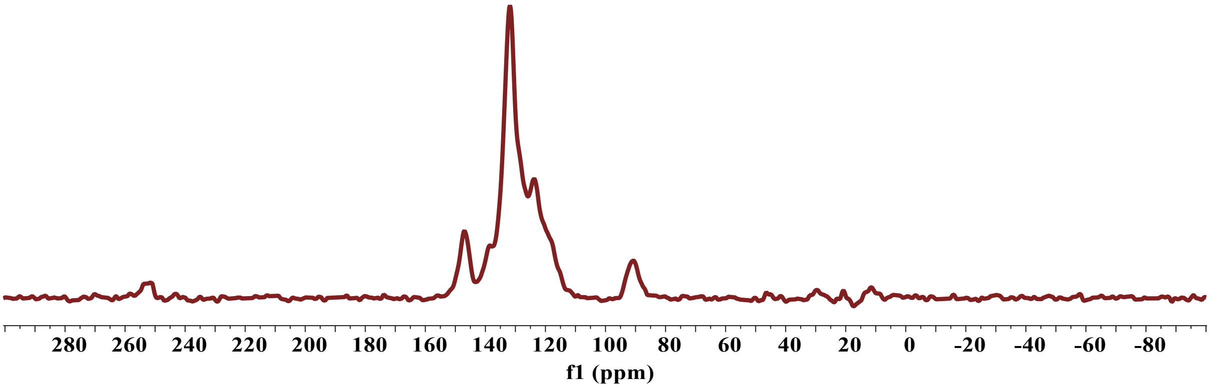


Figure S 8: ^{13}C CPMAS NMR spectrum of **TCMP**

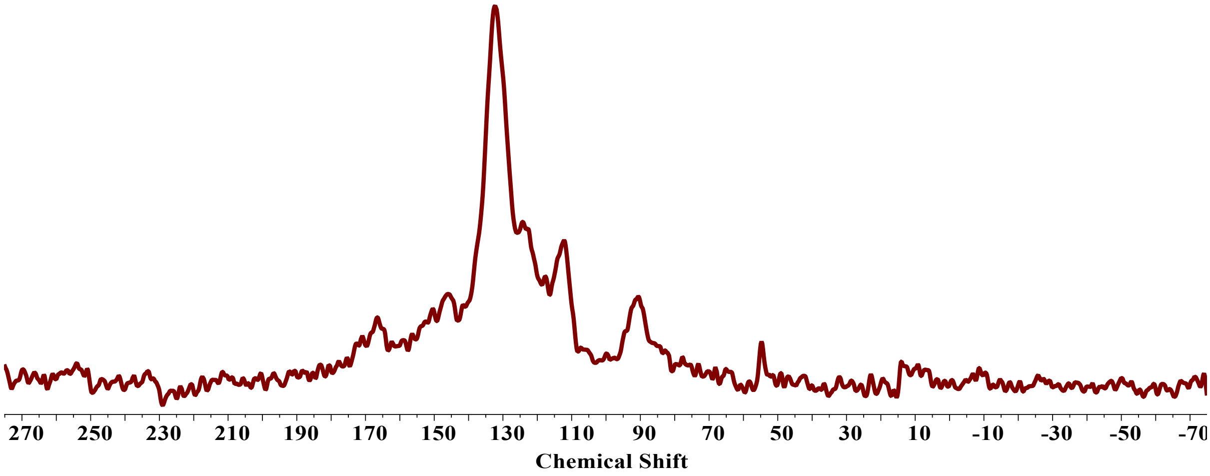


Figure S 9: ^{13}C CPMAS NMR spectrum of **TCBD-P**

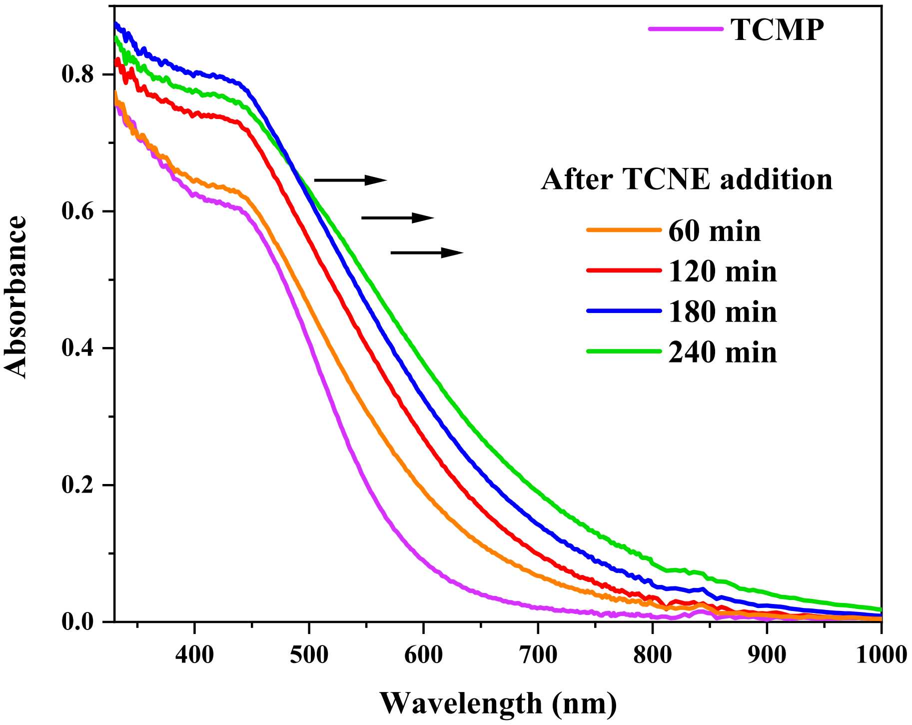


Figure S 10: Absorption spectrum of **TPA CMP** recorded with reaction of TCNE at different time interval

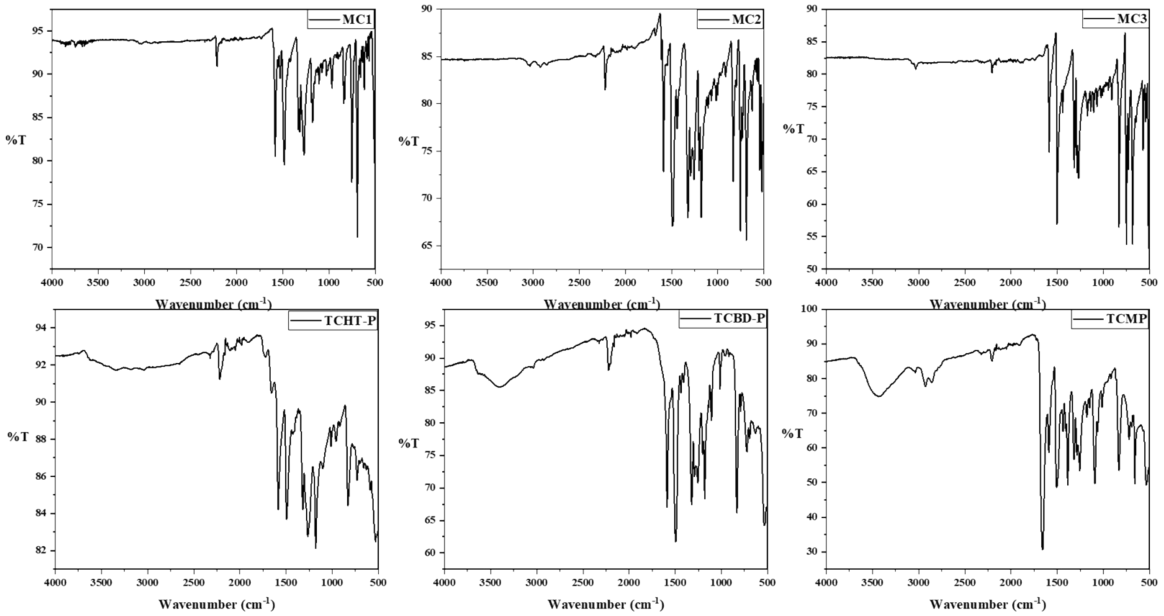


Figure S 11: FTIR spectrum of model compounds & CMPs

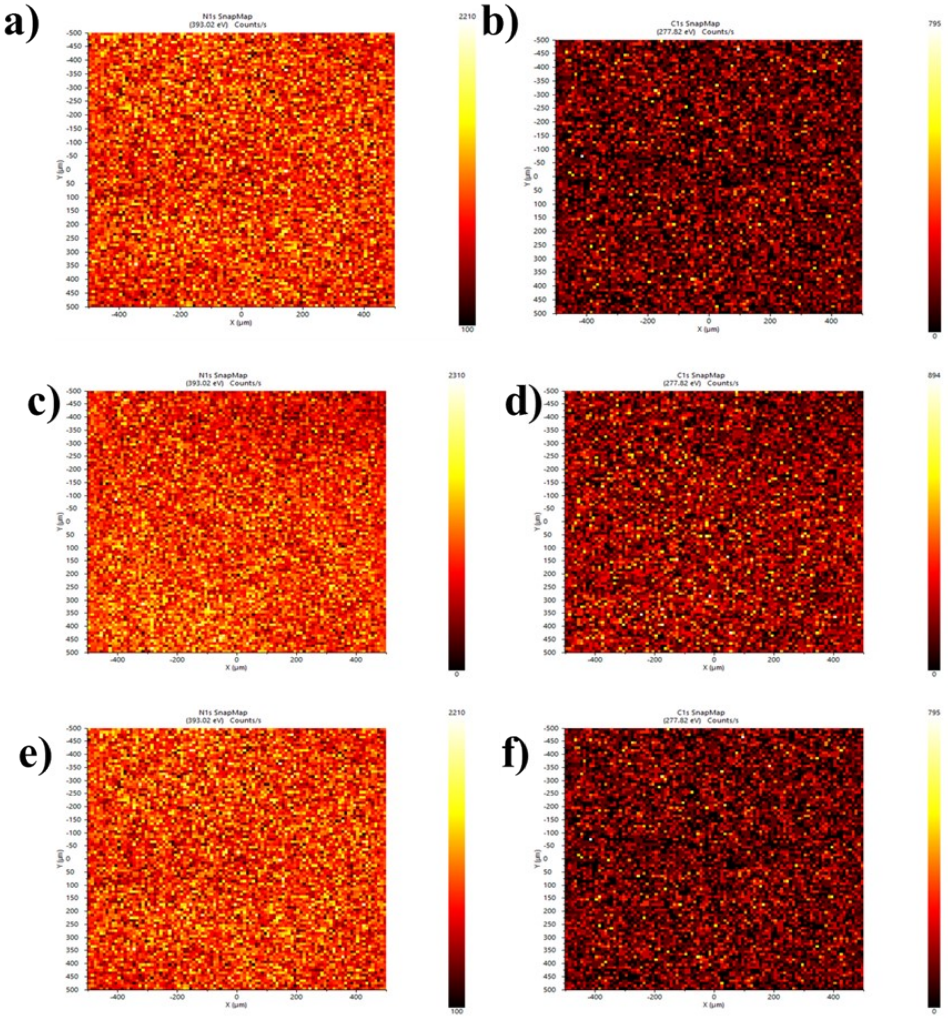


Figure S 12: High-resolution C 1s and N 1s spectra of **TCHT-P** (a, b), **TCMP** (c,d), **TCBD-P** (e, f)

	TCHT-P		TCMP		TCBD	
	Expected Atomic %	**XPS survey Atomic %**	**Expected Atomic %**	**XPS survey Atomic %**	**Expected Atomic %**	**XPS survey Atomic %**
C	82	78	92	88	85	80
N	12	9	3	1	10	7

Table S 1: Atomic concentrations of carbon and nitrogen in **TCHT-P, TCMP & TCBD-P**

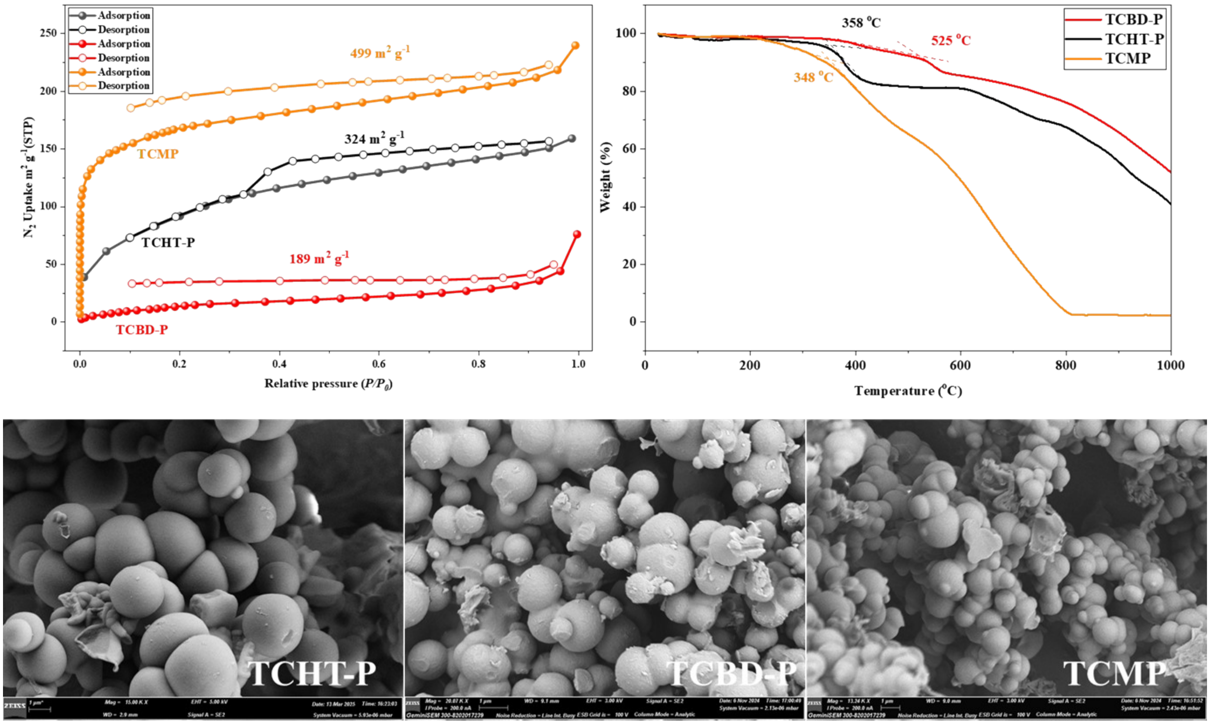


Figure S 13: BET adsorption isotherms a) Thermogravimetric analysis trace under a nitrogen atmosphere with a heating rate of 20 °C min^{-1} b) and FESEM images c) of **TCHT-P, TCBD-P & TCMP**.

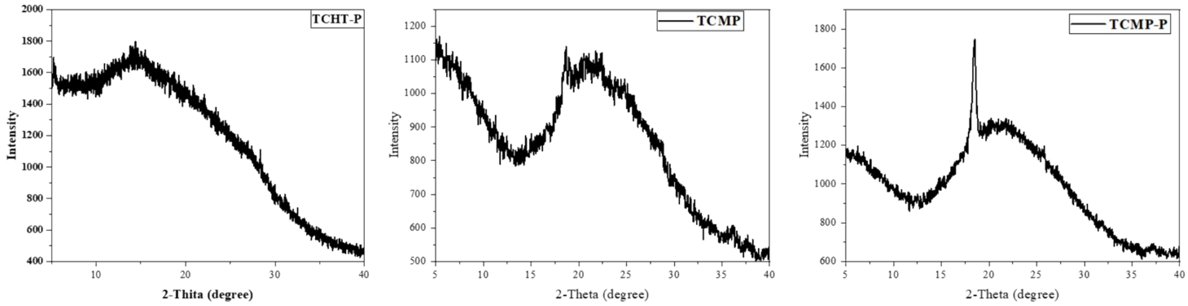


Figure S 14: PXRD of **CMPs**

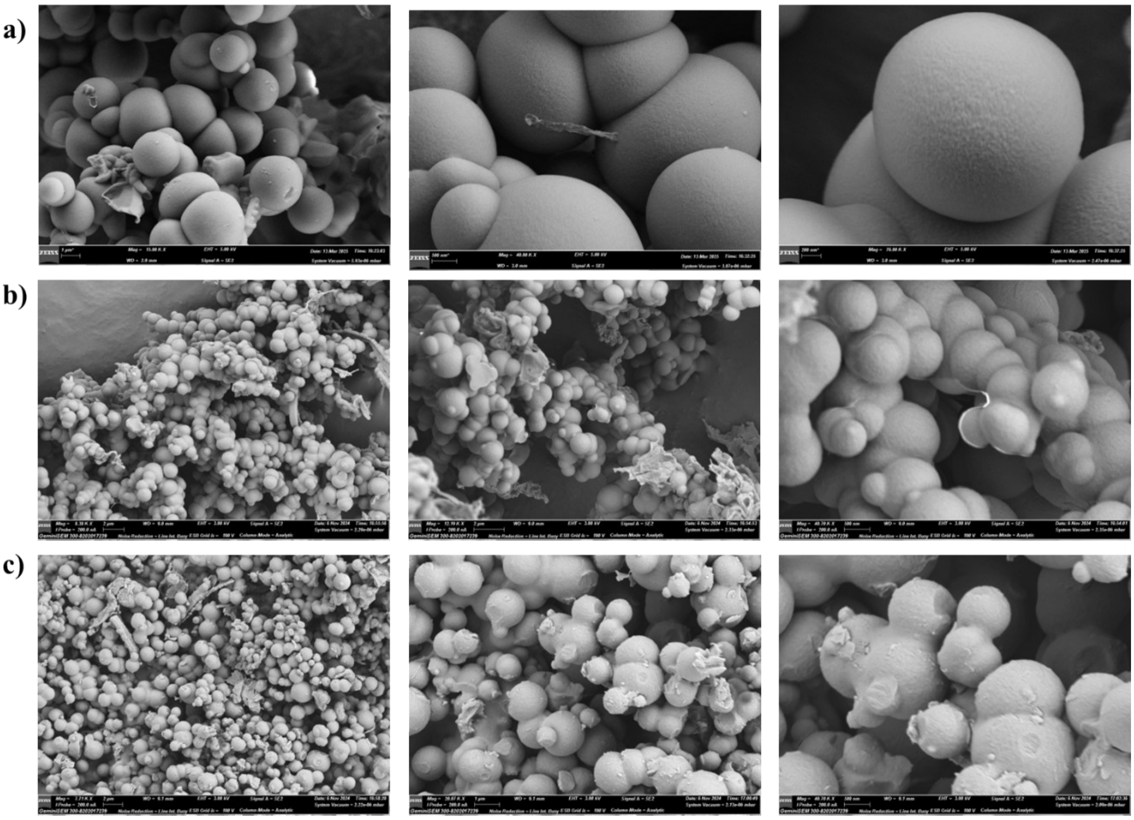


Figure S 15: FE-SEM images of **TCHT-P** (a); **TCMP** (b) & **TCBD-P** (c)

DFT study:

All density functional theory (DFT) calculations were performed using the Gaussian 16 program package. Geometry optimizations of the molecular model compounds were carried out in the ground state using the hybrid B3LYP functional, in conjunction with the 6-31G(d,p) basis set. The optimized structures were confirmed to be true minima by the absence of imaginary frequencies.

For polymeric model systems, geometry optimizations were performed using the PBE functional (PBEPBE) with the 6-31G(d,p) basis set. These calculations were employed to analyse qualitative trends in the electronic structure and frontier orbital distributions of the polymeric frameworks.

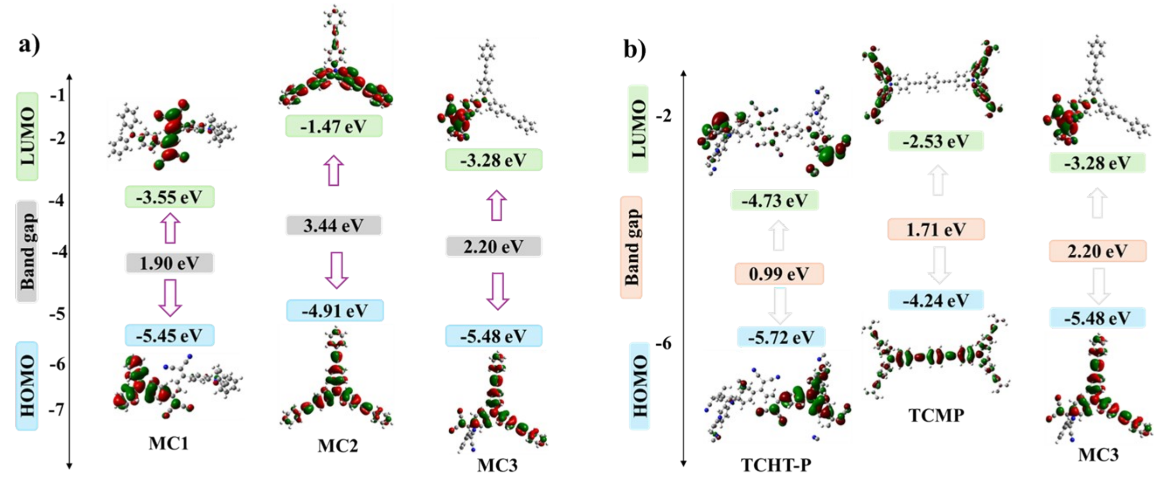
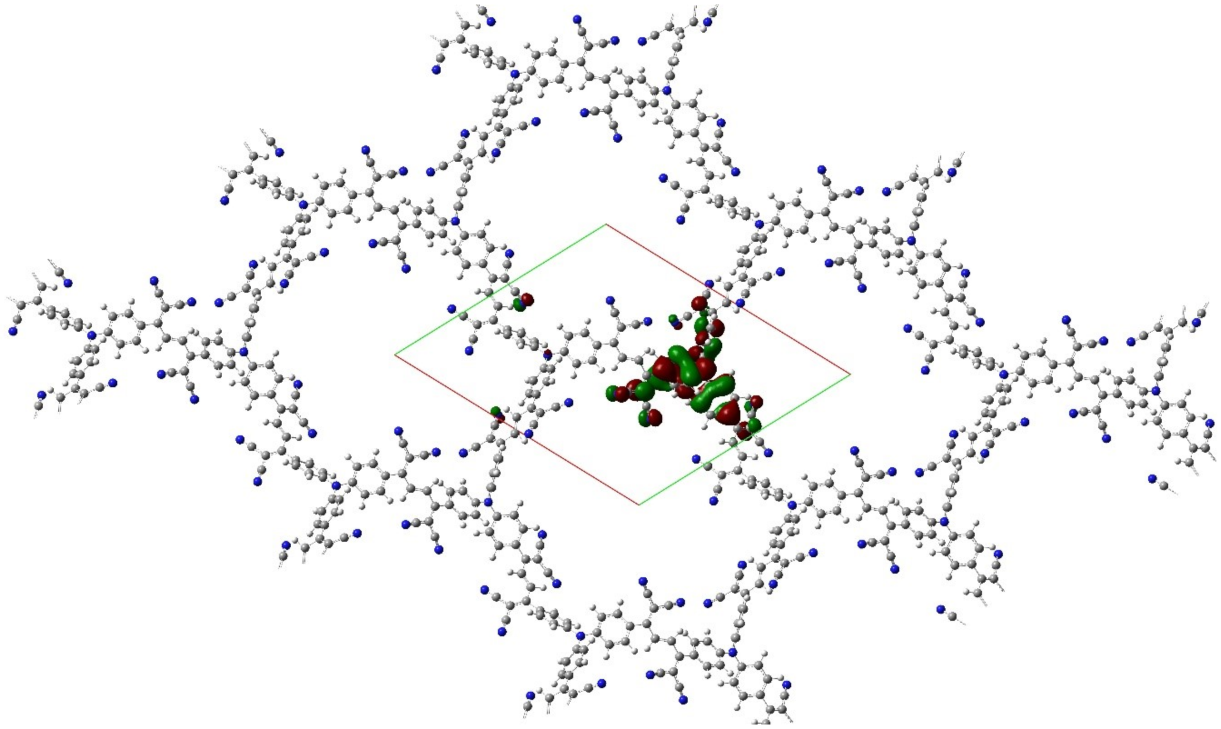


Figure S 16: Comparison of frontier molecular orbitals and band gaps of model molecules (**MC1-MC3**) & Polymers (**TCHT-P & TCMP & TCBD-P**)



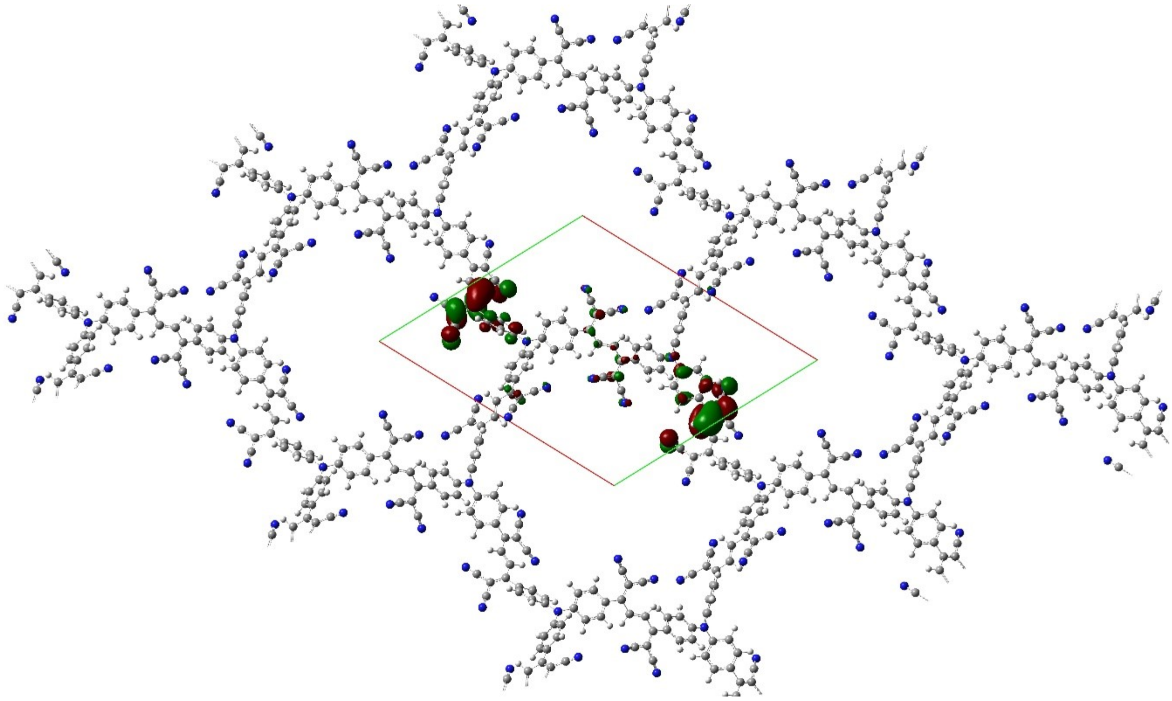


Figure S 17 Degenerated HOMO = -5.72 eV (top) and degenerated LUMO = -4.74 eV (bottom) of TCHT-P and Band gap = 0.99 eV

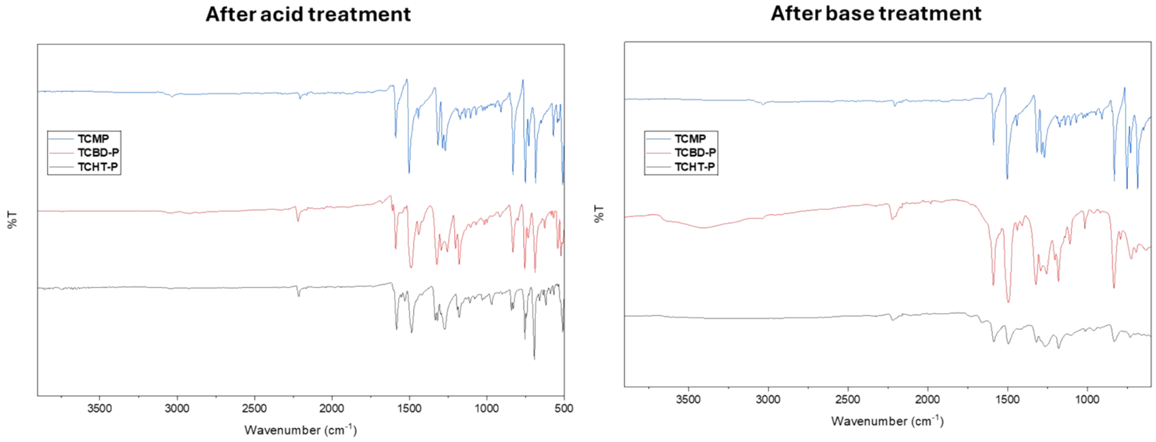


Figure S18: Polymer stability study by FT-IR

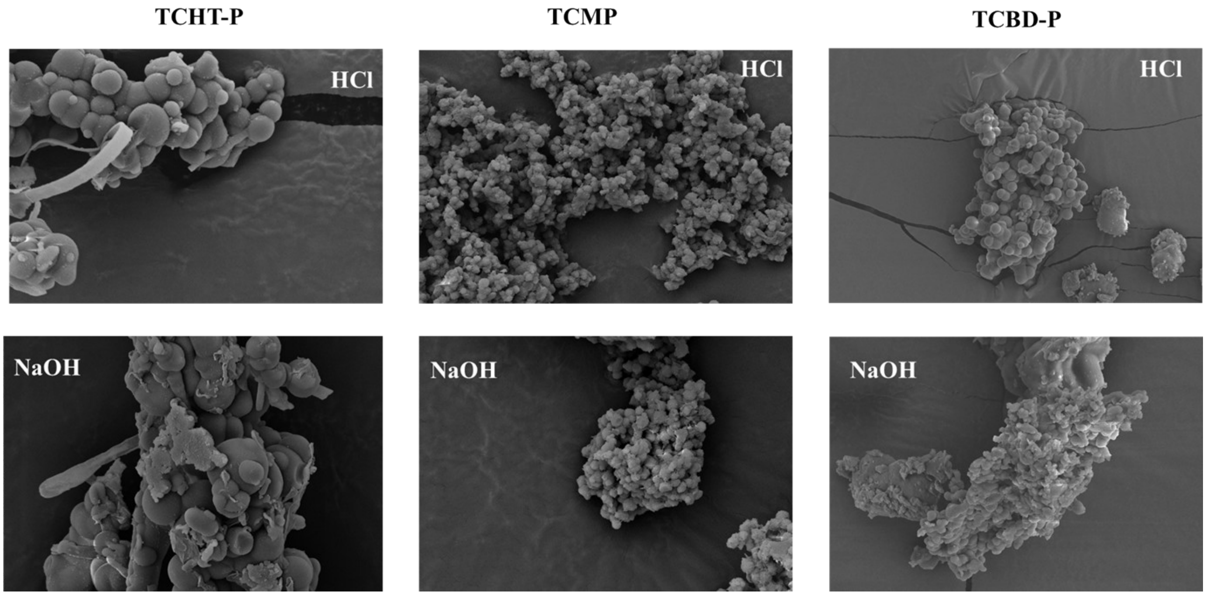


Figure S19**:** Stability of **TCMP**, **TCBD-P** and **TCHT-P** in aq HCl and NaOH

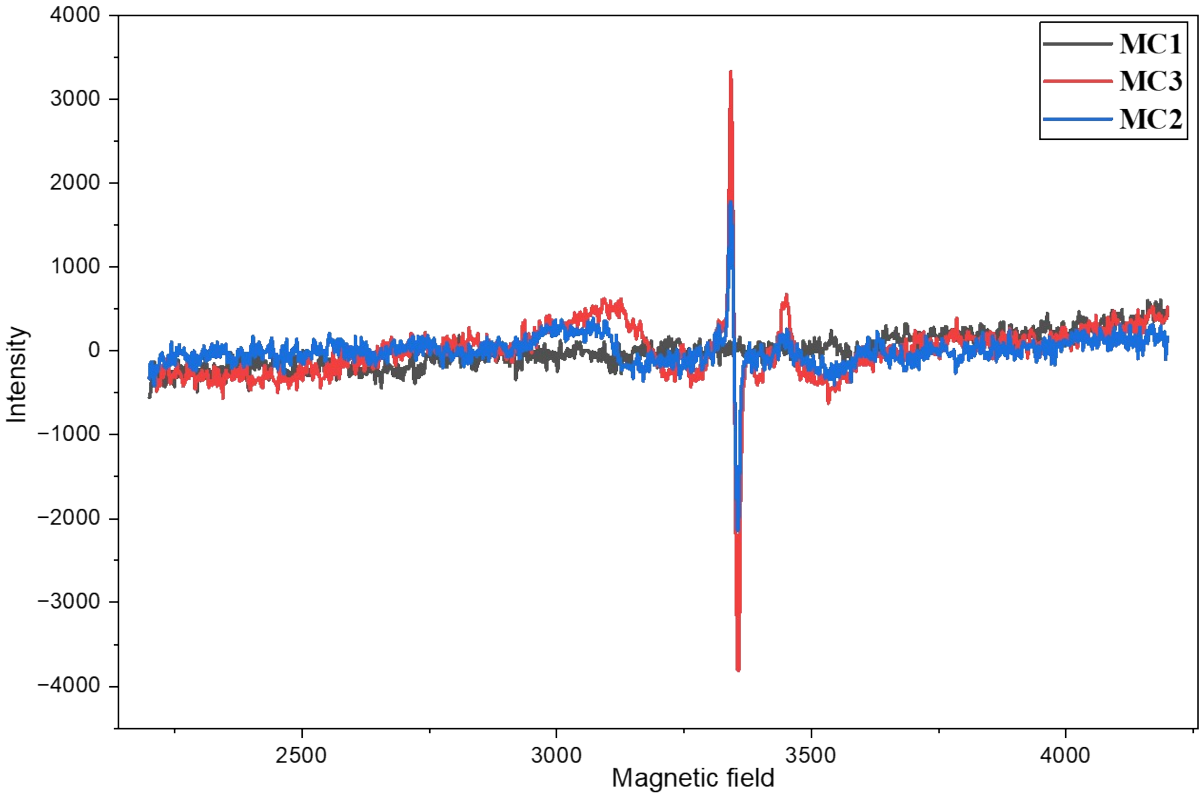
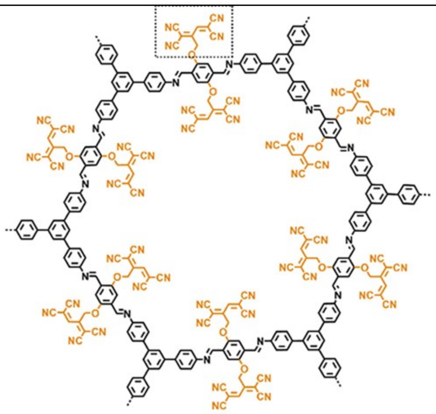
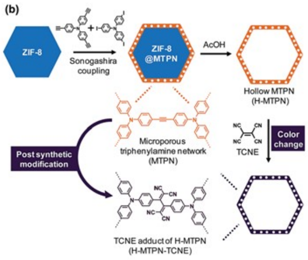
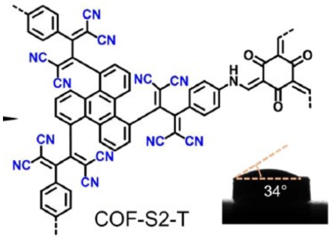
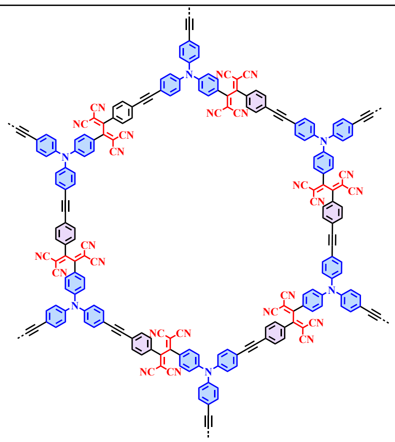


Figure S20**:** EPR spectrum of model compounds

Sr. No.	Polymer	Name	Application	Reference
1		GT-COF 3[1]	Photothermal conversion and solar-driven water evaporation	CCS Chem. 2021, 3, 2926–2937
2		H-MTPN-TCNE[2]	Cathode material	Chem. Commun., 2017, 53, 8778--8781
3		COF-S2-T[3]	Photothermal conversion and solar-driven water evaporation	*JACS Au* 2023, 3, 1711−1722
4		**TCBD-P**	Heterogeneous catalysis for H_2 production	This work

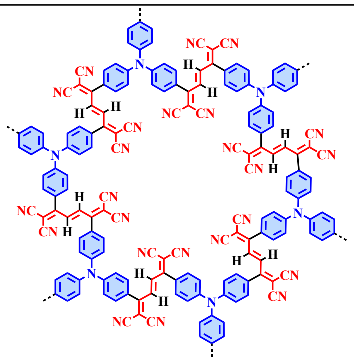
5		**TCHT-P**	Heterogeneous catalysis for H_2 production	This work

Table S 2: Various reported TCBD-based 2D polymers for different applications

Cyclic voltammetry (CV) experiment:

The electrochemical measurements were conducted using a potentiostat (Interface 1010E, 31184) in a three-electrode configuration with a scan rate of 10 mV/s. The experiments were carried out in anhydrous acetonitrile, using tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The setup consisted of a platinum wire as the auxiliary electrode, a silver/silver chloride (Ag/AgCl) electrode as the reference electrode, and a glassy carbon electrode as the working electrode. Ferrocene was employed for internal calibration prior to each measurement.

Experimental procedure:

The experiments for photocatalytic H_2 production with full solar light irradiation have been performed using a 15 mL cylindrical quartz vial with a 300 W xenon lamp having a total intensity of 110 mW cm^{-2}. Firstly, 2 mg of the solid sample (**TCHT-P**/ **TCBD-P**/**TCMP**) is taken in the quartz vial with subsequent addition of 10 mL of Milli-Q water and 100 µL of 4-methoxybenzyl alcohol (4-MBA) as a sacrificial electron donor. Then, 3 wt% of co-catalyst platinum (II) chloride (H_2PtCl_4) aqueous solution is added. Next, an airtight rubber septum is used to seal the quartz vial and the air is evacuated by high-purity Ar gas purging for 10 min. The quartz vial has been set up at a specific distance in front of the xenon light source with continuous stirring over a magnetic stirrer, to achieve the desired light intensity. A water-cooling system maintained the temperature of the quartz vial at room temperature.

Gas chromatography (Shimadzu GC-2030, thermal conductivity detector TCD, Ar carrier gas flow) was utilized for quantitative determination of the generated H_2 gas. Regular time intervals of 2h are maintained for analysing the generated H_2 gas. The gas is collected from the empty headspace (free volume of 5.4 mL) of the quartz vial by a 100 μL syringe and rapidly injected into the TCD detector. This experiment is run for a prolonged 12 h to get a proper estimate of the H_2 gas produced.

The solar-to-hydrogen efficiency was calculated using the following equation[4]:

$$STH = \frac{(r_{H_2}) \times (237 kJ/mol)}{P_{total}(mW/cm^2) \times area\ (cm^2)}$$

STH is defined as the chemical energy produced divided by the solar energy input. The chemical energy produced is the rate of hydrogen production multiplied by the Gibbs free energy per mole of H_2 (at 25°C, DG = 237 kJ/mol). The solar energy input is incident illumination power intensity (P_{total} in mW cm^{-2}) multiplied by the illuminated effective area (cm^2).

References

1 X. Tang, Z. Chen, Q. Xu, Y. Su, H. Xu, S. Horike, H. Zhang, Y. Li, C. Gu, *CCS Chemistry* **2021**, *4*, 2842–2853.

2 J. Choi, E. Soon Kim, J. Hong Ko, S. Moon Lee, H. Jin Kim, Y.-J. Ko, S. Uk Son, *Chem. Commun.* **2017**, *53*, 8778–8781.

3 Z. Lin, Y.-H. Zhong, L. Zhong, X. Ye, L.-H. Chung, X. Hu, Z. Xu, L. Yu, J. He, *JACS Au* **2023**, *3*, 1711–1722.

4 Y. Qi, Y. Zhao, Y. Gao, D. Li, Z. Li, F. Zhang, C. Li, *Joule* **2018**, *2*, 2393–2402.