

Supporting Information

Probing the performance of imide linked micro-porous polymers for enhanced CO₂ gas adsorption applications

Narendran Rajendran, Ali Husain and Saad Makhseed*

Department of chemistry, Faculty of Science, Kuwait University, P.O. Box 5969, 13060 Safat,
Kuwait

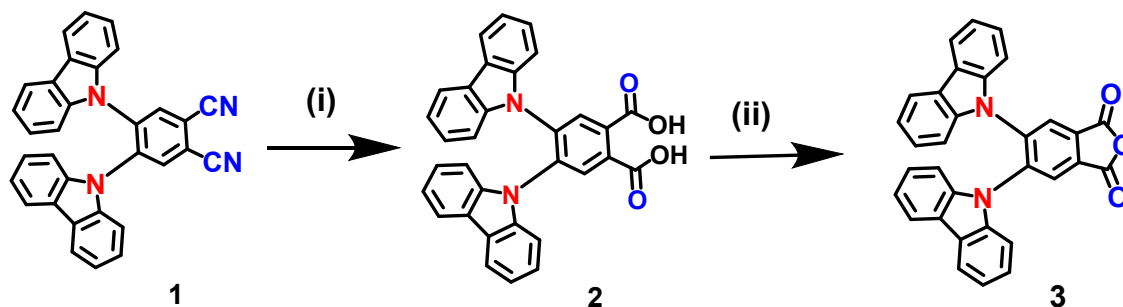
Email: saad.makhseed@ku.edu.kw

Contents

Section A. Synthesis Procedure	2
Section B. FT-IR Spectral profiles	5
Section C. NMR Profile	8
Section D. Mass analysis of monomers	12
Section E. TGA Profiles	14
Section F. DSC analysis	16
Section G. PXRD Profiles.....	18
Section H. XPS and UPS Profile.....	20
Section I. Surface morphology studies.....	22
Section J. Single Crystal X- ray diffraction studies of TM-PDA-Imide	23
Section H. CO₂/N₂ Selectivity studies.....	29
Section I. HPLC Analysis of monomers	30

Section A. Synthesis Procedure

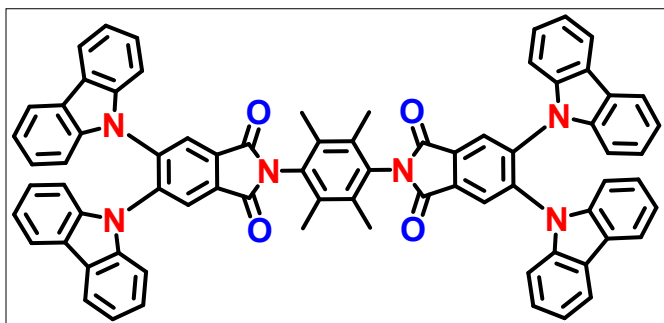
Synthesis of the monomer 5,6-di(9H-carbazol-9-yl) isobenzofuran-1,3-dione (AH)



(i) KOH, EtOH at 120°C; (ii) Ac₂O, 110°C

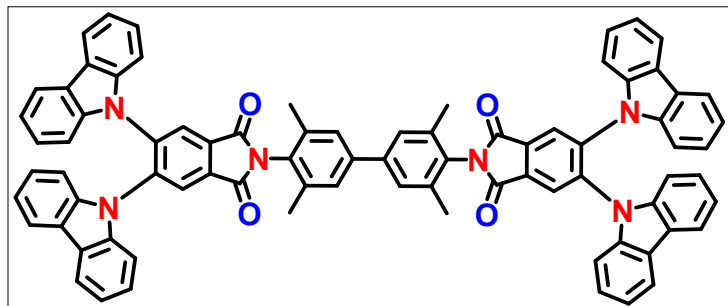
Compound 3 have been readily synthesized by the reported protocol. Initially compound 1, 4,5-di (9H-carbazol-9-yl) phthalonitrile was synthesized by nucleophilic substitution of carbazole with 4,5-dichlorophthalonitrile facilitated by cesium fluoride (CsF) [23]. The hydrolysis of 4,5-di (9H-carbazol-9-yl) phthalonitrile (1) with KOH formed 4,5-di(9H-carbazol-9-yl) phthalic acid (2). Then, dehydration of the acid with acetic anhydride produced the anhydride AH (5, 6-di (9H-carbazol-9-yl) isobenzofuran-1,3-dione) (3). Bright yellow solid; Yield 70%, m.p >300°C; IR/cm⁻¹ (KBr): 3058 (aromatic =C-H, str), 1850 (-C=O symmetric str.), 1750 (-C=O asymmetric str.), 1447 (aromatic C=C- str), 1232 (-C-N str.); ¹H-NMR (DMSO-d₆, 600MHz, δppm): 8.68 (s, 1H), 7.93-7.91 (m, 2H), 7.23-7.21 (m, 2H), 7.11-7.06 (m, 4H); ¹³C NMR (150 MHz, DMSO-d₆) δ (ppm): 167.2, 161.8, 139.9, 139, 138.7, 135.3, 133.6, 131.3, 130.4, 127.7, 125.8, 123.2, 123, 120.8, 120.4, 120.2, 109.6, 109.5; HR-MS[M+H]⁺ Calculated for (C₃₂H₁₈O₃N₂): 478.1312, obtained: 478.1310; HPLC (Purity): 99.1%.

Synthesis of the monomer – TM-PDA-imide [2,2'-(2,3,5,6-tetramethyl-1,4-phenylene) bis(5,6-di(9H-carbazol-9-yl) isoindoline-1,3-dione)]



2,3,5,6- Tetramethylphenylenediamine (80mg, 6mmol, 1 equiv.) and 5,6-di(9H-carbazol-9-yl) isobenzofuran-1,3-dione (6.4g, 13.3mmol, 2.2 equiv.) was taken in 50mL round bottom flask. Add 10mL of acetic acid, then heated the reaction to 130°C for 48 hr. Cool the reaction mixture to room temperature and filter the yellow precipitate obtained. After completion of the reaction, the yellow precipitate was filtered and washed with acetic acid and water repeatedly. The product was dried carefully and subjected to characterization. Yellow powder; Yield 60%, m.p >500°C; IR/cm⁻¹ (KBr): 3058 (aromatic =C-H, str), 1775 (-C=O symmetric str.), 1722 (-C=O asymmetric str., imide), 1449 (aromatic C=C- str); ¹H-NMR (DMSO-d₆, 600MHz, δppm): 8.51 (s, 1H), 7.95-7.93 (m, 2H), 7.41 (t, *J*=2.4Hz, 6.6Hz, 2H), 7.13-7.09 (m, 4H), 2.26 (s, 3H); ¹³C-NMR (Solid state): 166.7, 141.9, 134.2, 125, 116, 110.2, 100.6, 18.6; HR-MS[M+H]⁺ Calculated for (C₇₄H₄₈O₄N₆): 1084.3732, Found: 1084.3473; HPLC (Purity): 99.8%.

Synthesis of the monomer – TMB-PDA-imide [2,2'-(3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diyl)bis (5,6-di(9H-carbazol-9-yl) isoindoline-1,3-dione)]



3,3',5,5'-tetramethyl-[1,1'-biphenyl]-4,4'-diamine (80mg, 4.1mmol, 1 equiv.) and 5,6-di(9H-carbazol-9-yl) isobenzofuran-1,3-dione (4.3g, 9.16mol, 2.2 equiv.) was taken in 50mL round bottom flask. Add 10mL of acetic acid, then heated the reaction to 130°C for 48 hr. Cool the reaction mixture to room temperature and filter the yellow precipitate obtained. After compilation of the reaction, the yellow precipitate was filtered and washed with acetic acid and water repeatedly. The product was dried carefully and subjected to characterization. Yellow powder; Yield 80%, m.p >500°C; IR/cm⁻¹ (KBr): 3060 (aromatic =C-H, str.), 1775 (-C=O symmetric str.), 1722 (-C=O asymmetric str., imide), 1448 (aromatic C=C- str); ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.52 (s, 1H), 7.83-7.82 (m, 2H), 7.5 (s, 1H), 7.41 (t, *J*=2.4Hz, 6.6Hz, 1H), 7.25-7.24 (m, 2H), 7.14-7.09 (m, 4H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm):166, 142.2, 139.7, 139, 137.4, 131.3, 129.3, 127.9, 126.1, 126, 124, 121, 120, 109, 18.6; HR-MS (MALDI-TOF) [M+H]⁺ Calculated for (C₈₀H₅₂N₆O₄) 1160.4050, Found: 1160.4045; HPLC (Purity): 99.3%.

Section B. FT-IR Spectral profiles

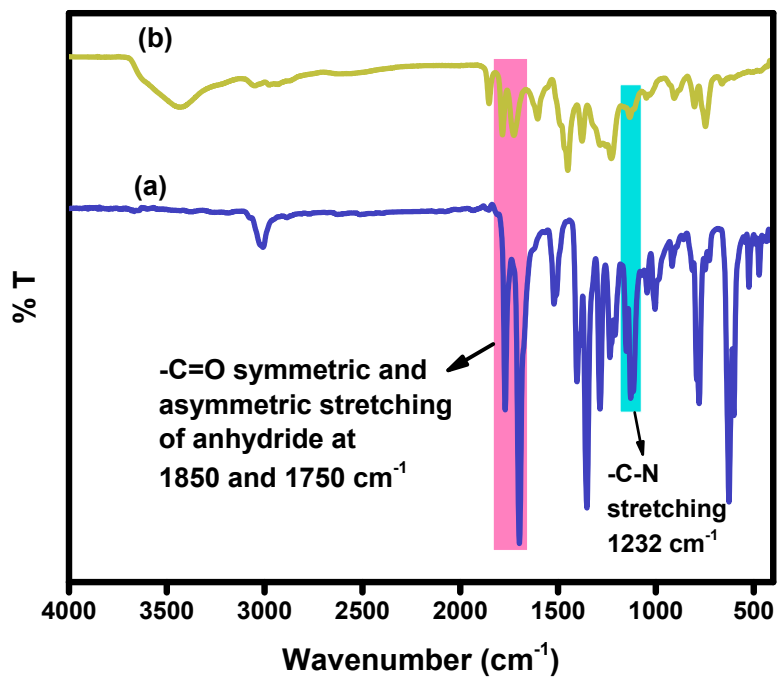


Fig. S1. FTIR spectrum of AH and AH-Poly by KBr pellet method

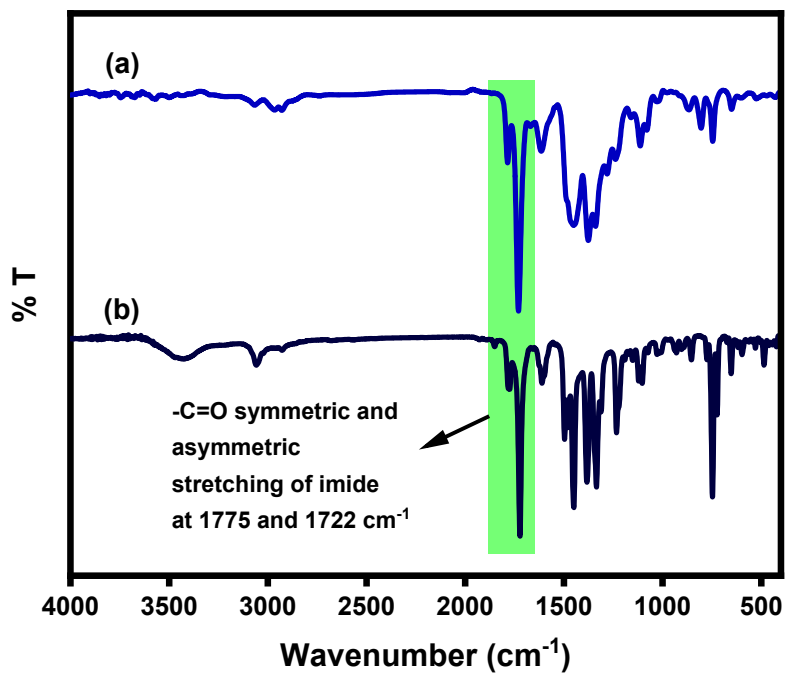


Fig. S2. FTIR spectrum of TM-PDA-imide and TM-PDA-Poly by KBr pellet method

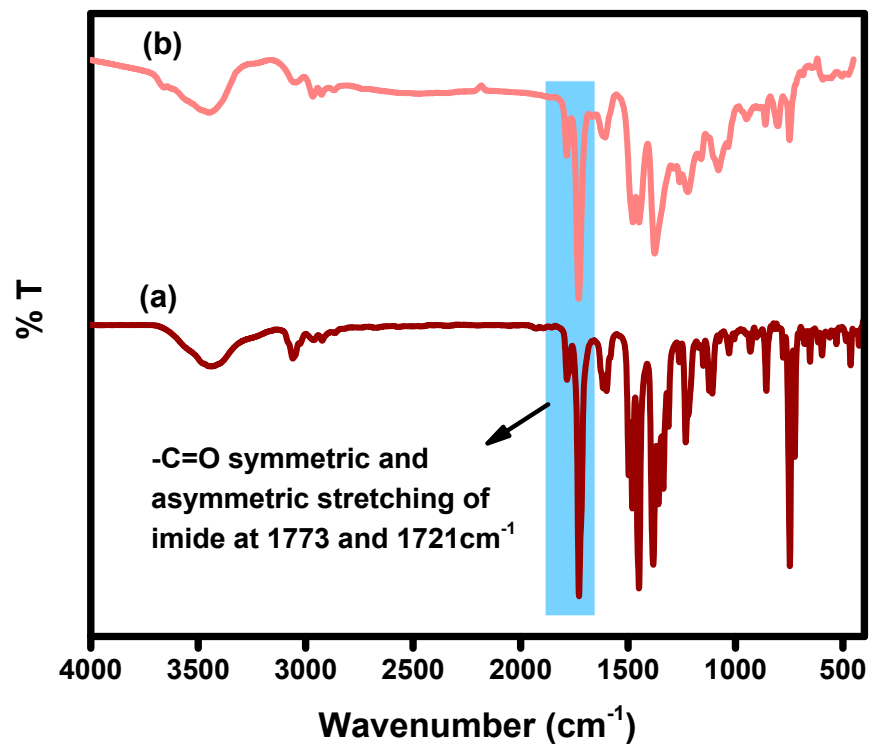


Fig. S3. FTIR spectrum of TMB-PDA-imide and TMB-PDA-Poly by KBr pellet method

Section C. NMR Profile

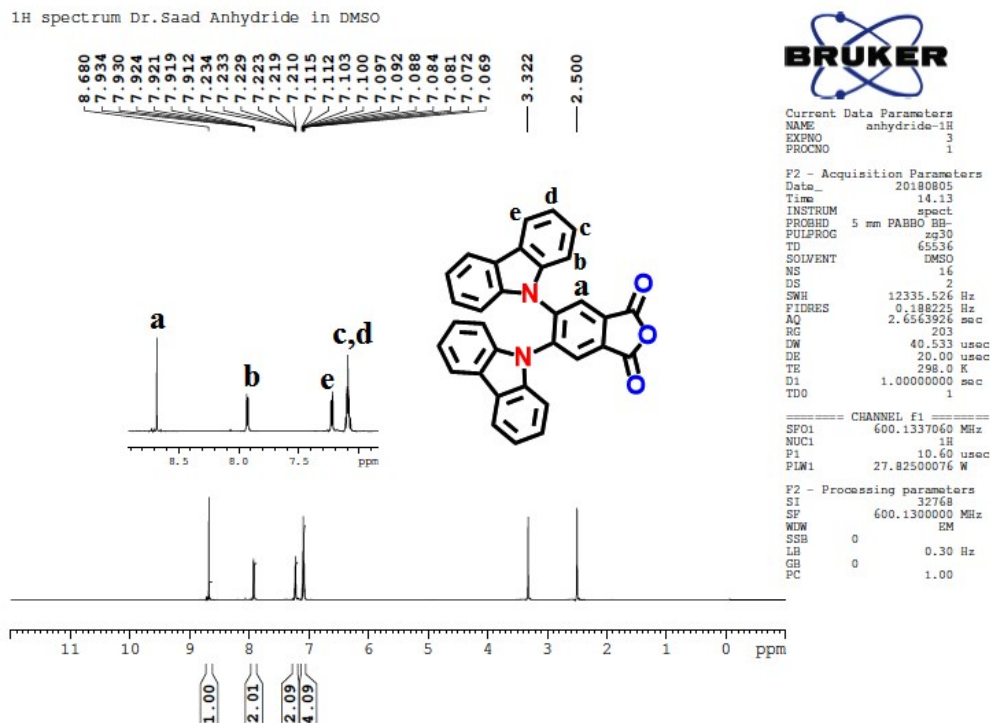


Fig. S4. ¹H-NMR of the monomer AH

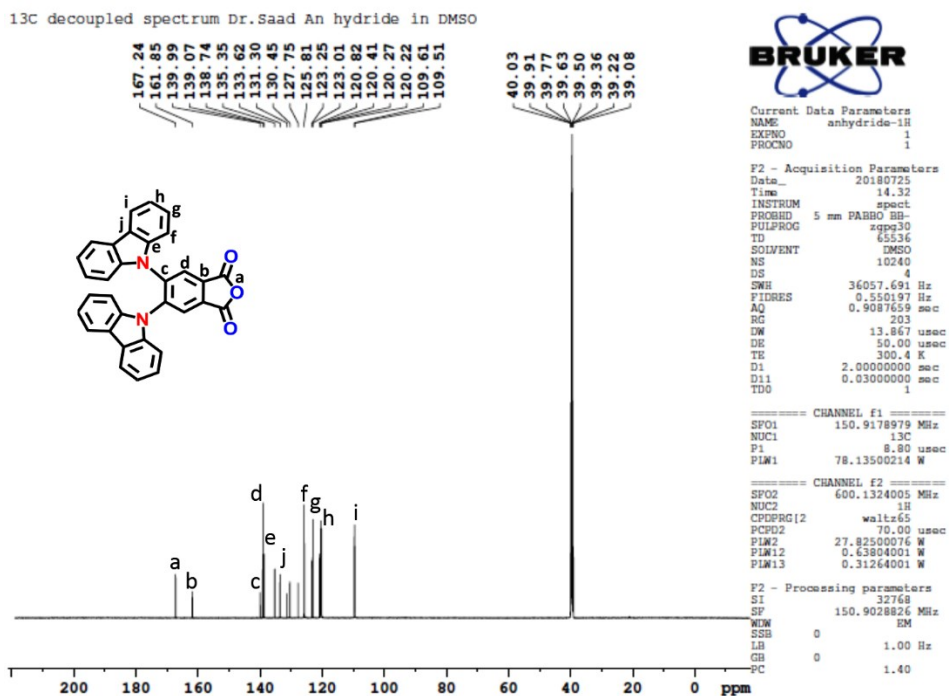


Fig. S5. ¹³C- Decoupled NMR spectrum of AH

¹H spectrum Dr.Saad Diamide 1085 in DMSO

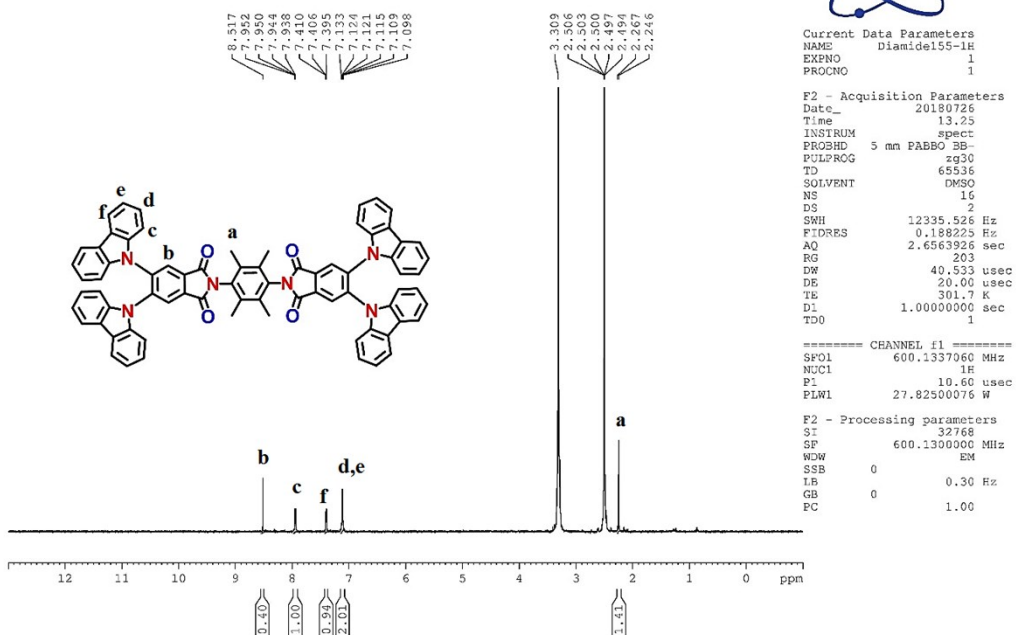


Fig. S6. ¹H-NMR of the monomer TM-PDA-imide

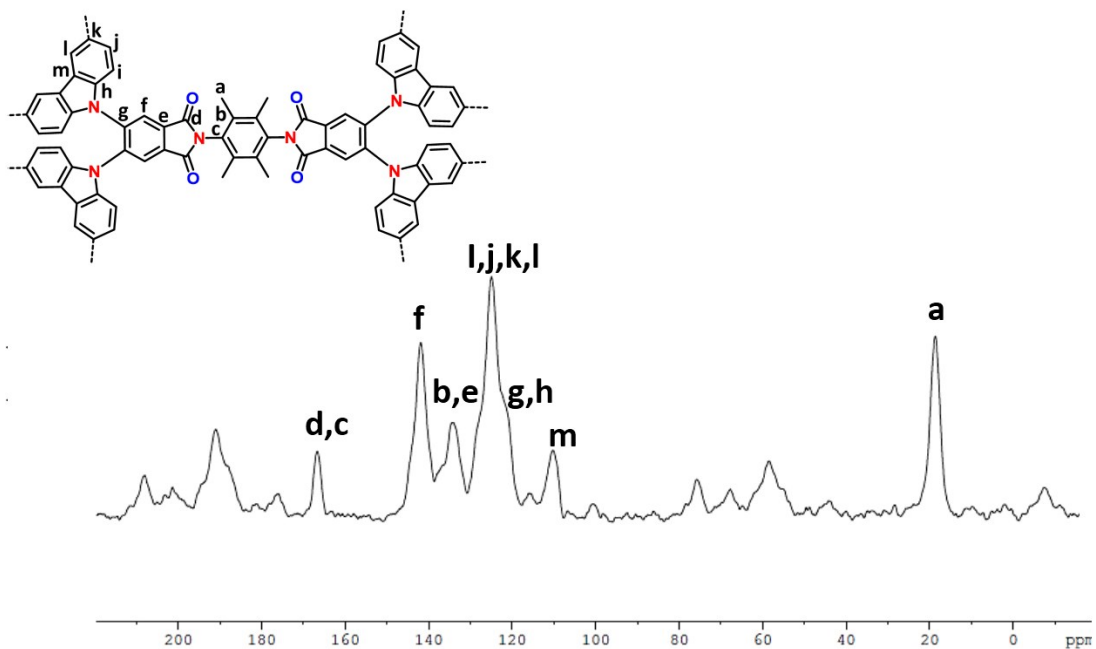


Fig. S7. Solid state ¹³C CP-MAS-spectrum of TM-PDA-Imide

Section D. Mass analysis of monomers

HRMS-Anhydride-cmass1#306 RT: 7.76 AV: 1 NL: 3.16E5
T: + c EI Full ms [449.50-500.50]

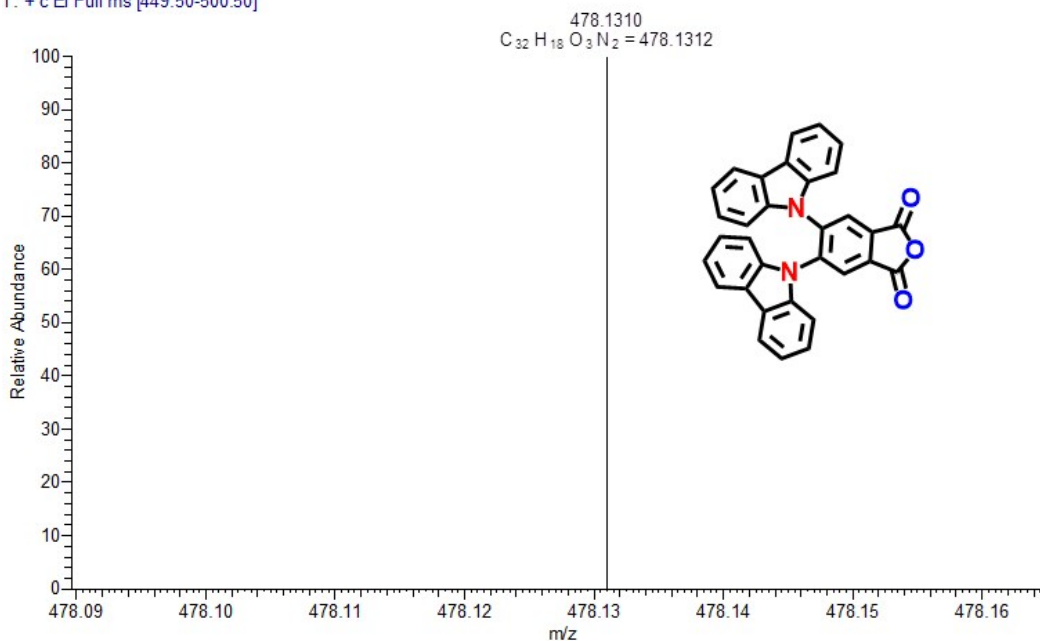


Fig. S10. HR-MS analysis of the monomer AH

DCI-HRMS-M3-re 181016131313-cmass2 #20 RT: 1.26 AV: 1 NL: 1.11E4
T: + c EI Full ms [899.50-1200.50]

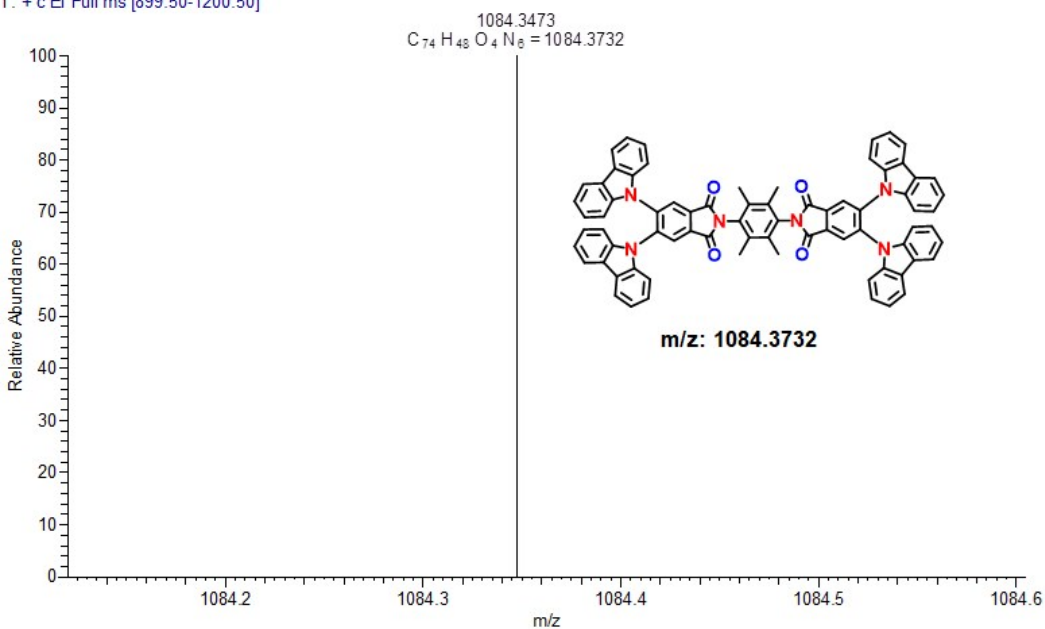


Fig. S11. HR-MS analysis of the monomer TM-PDA-imide

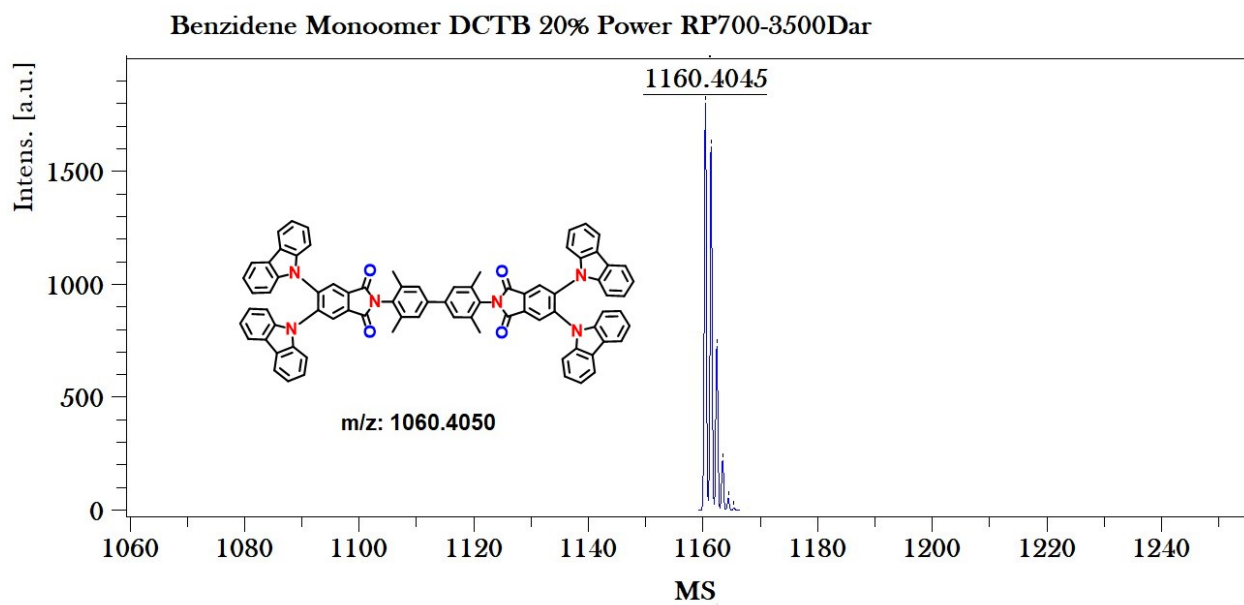


Fig. S12. MALDI-MS analysis of the monomer TMB-PDA-imide

Section E. TGA Profiles

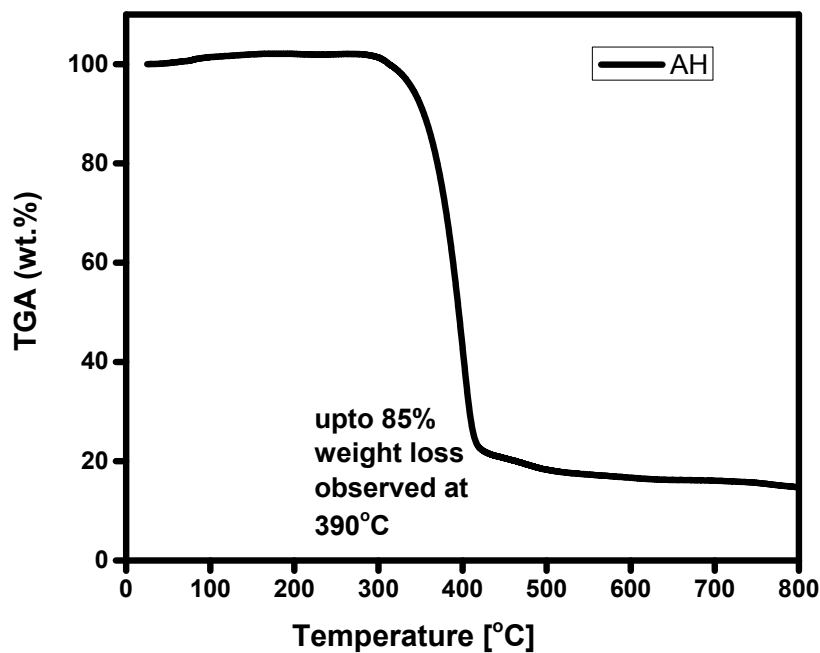


Fig. S13. TGA Profiles of AH at a heating rate of 10 °C/min in Nitrogen atmosphere

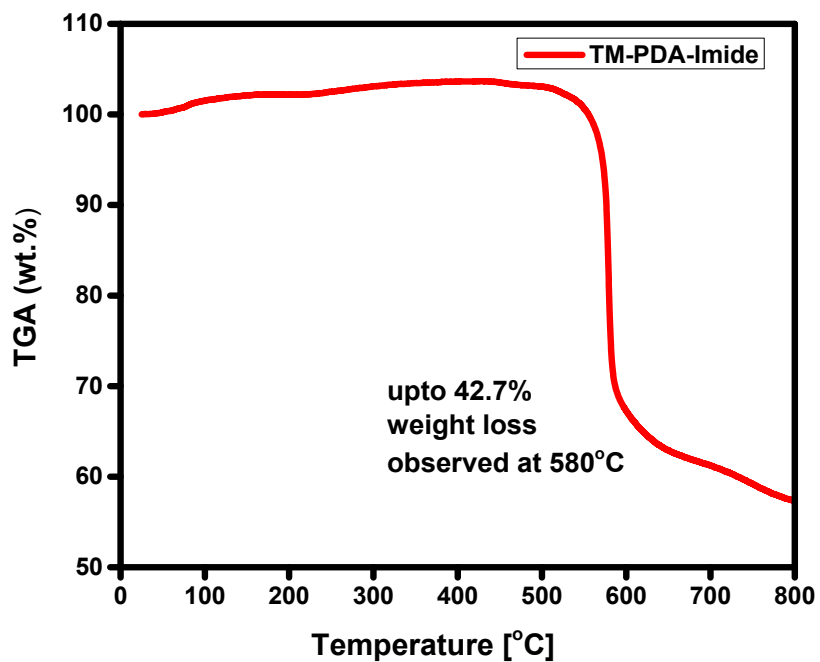


Fig. S14. TGA Profiles of TM-PDA-imide at a heating rate of 10 °C/min in Nitrogen atmosphere

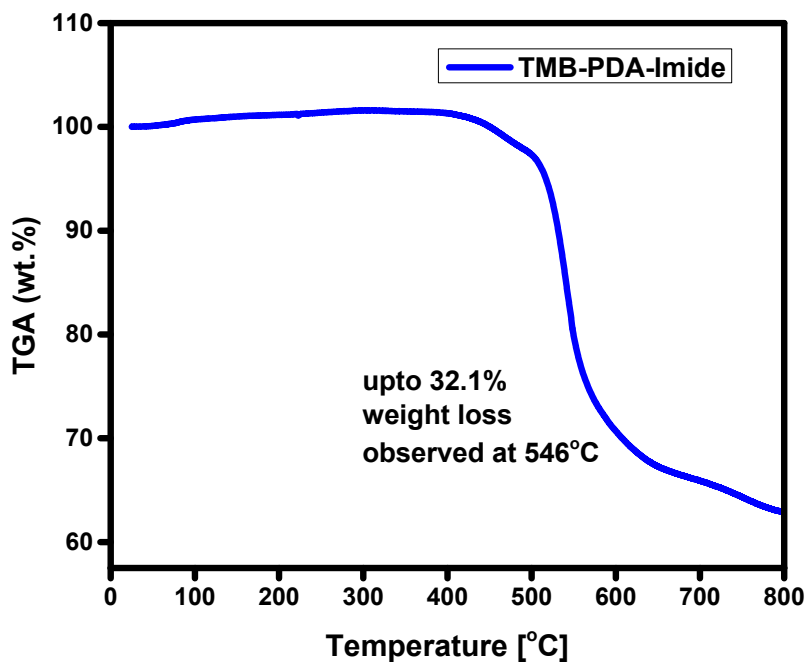


Fig. S15. TGA Profiles of TMB-PDA-imide at a heating rate of 10 °C/min in Nitrogen atmosphere

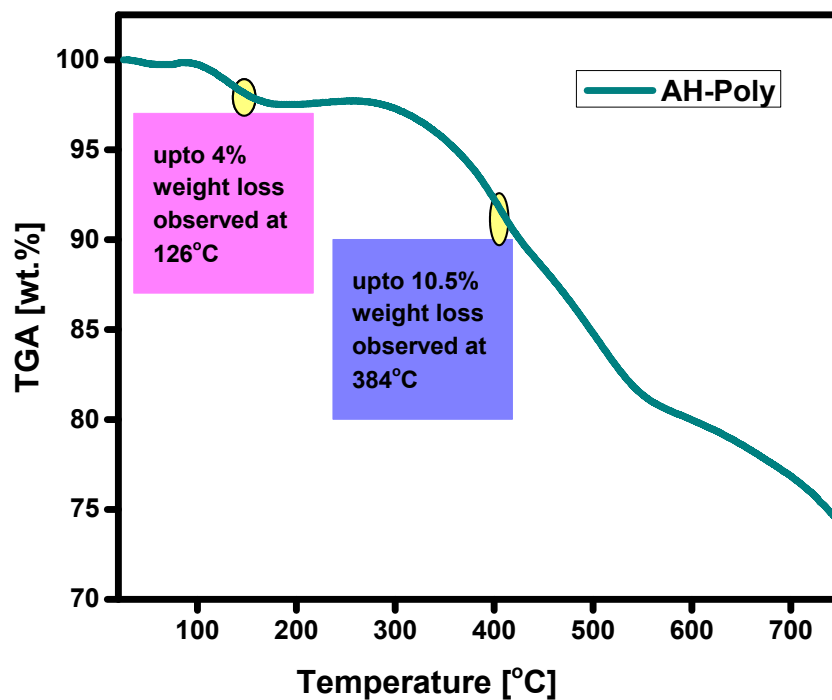


Fig. S16. TGA Profiles of AH-Poly at a heating rate of 10 °C/min in Nitrogen atmosphere

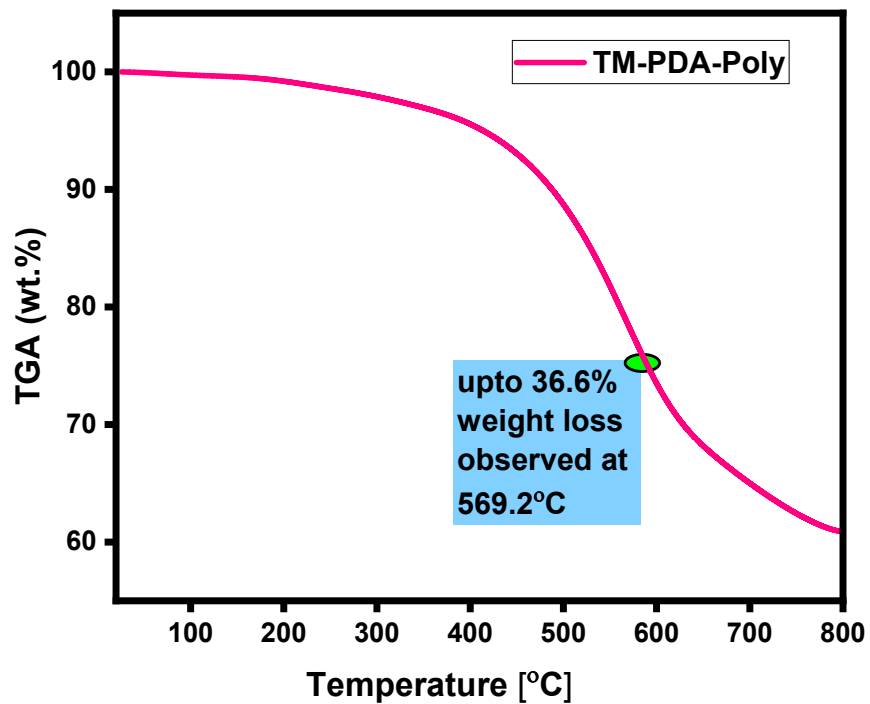


Fig. S17. TGA Profiles of TM-PDA-Poly at a heating rate of 10 °C/min in Nitrogen atmosphere

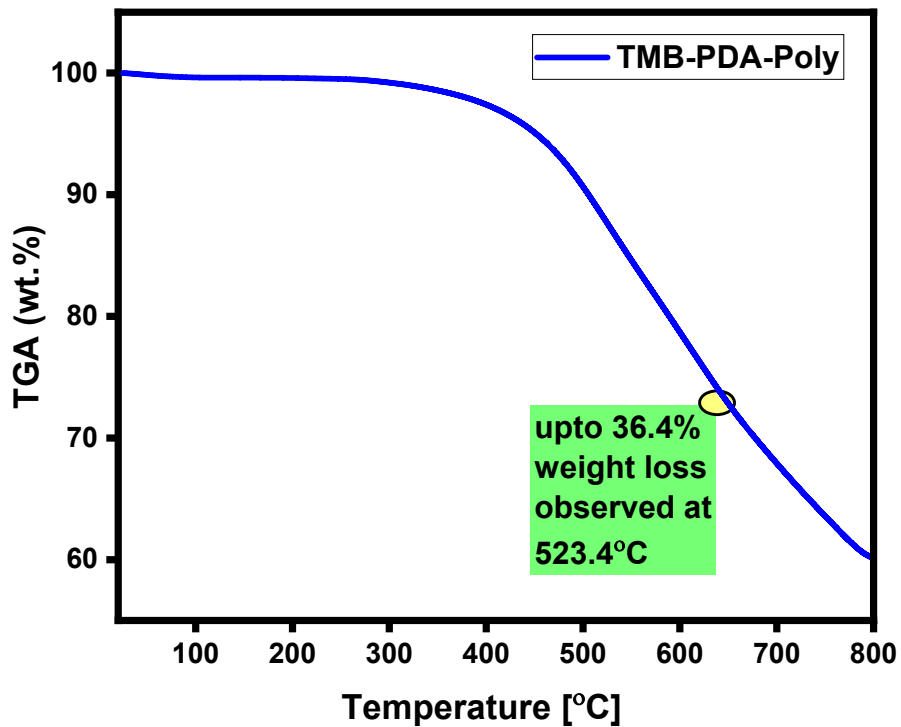


Fig. S18. TGA Profiles of TMB-PDA-Poly at a heating rate of 10 °C/min in Nitrogen atmosphere

Section F. DSC analysis

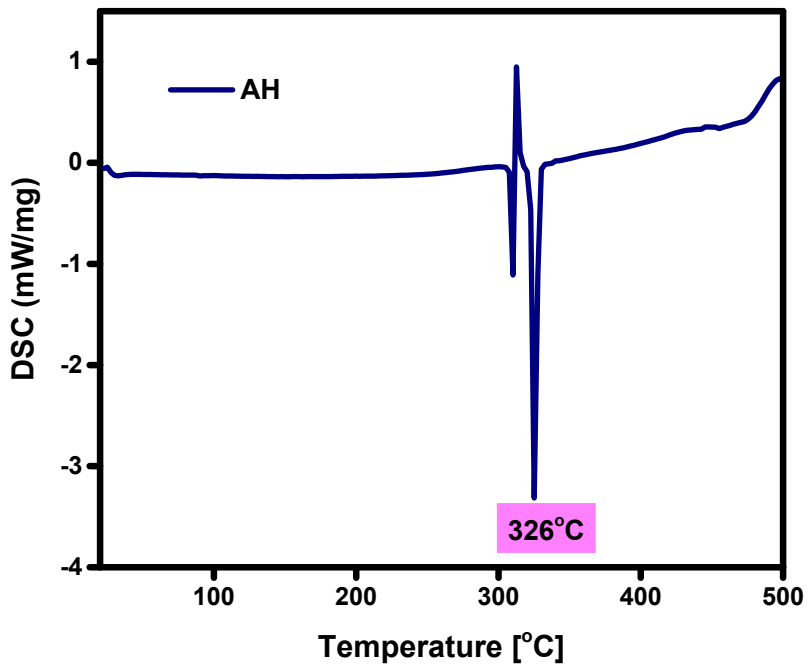


Fig. S19. DSC analysis of the monomer AH was recorded at 10°C/min

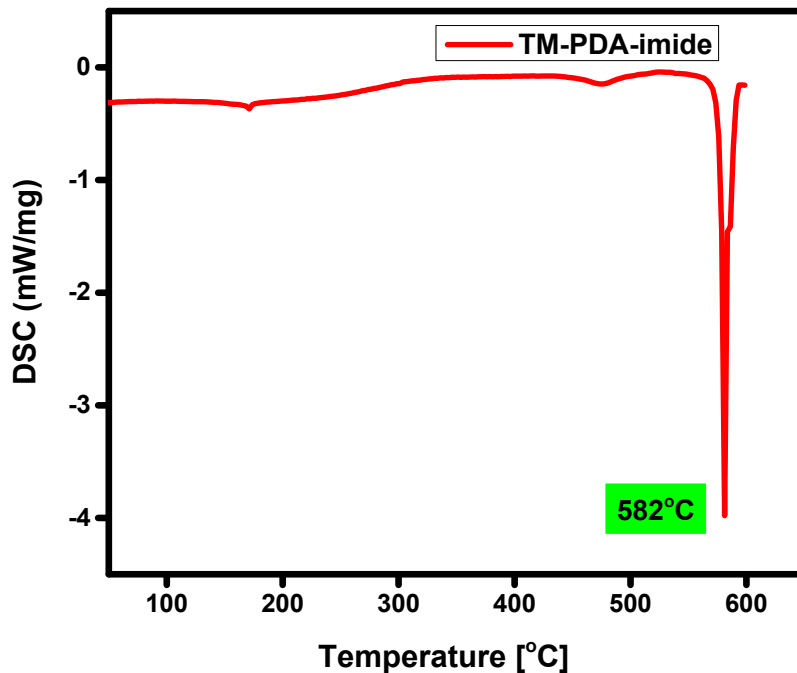


Fig. S20. DSC analysis of the monomer TM-PDA-imide was recorded at 10°C/min

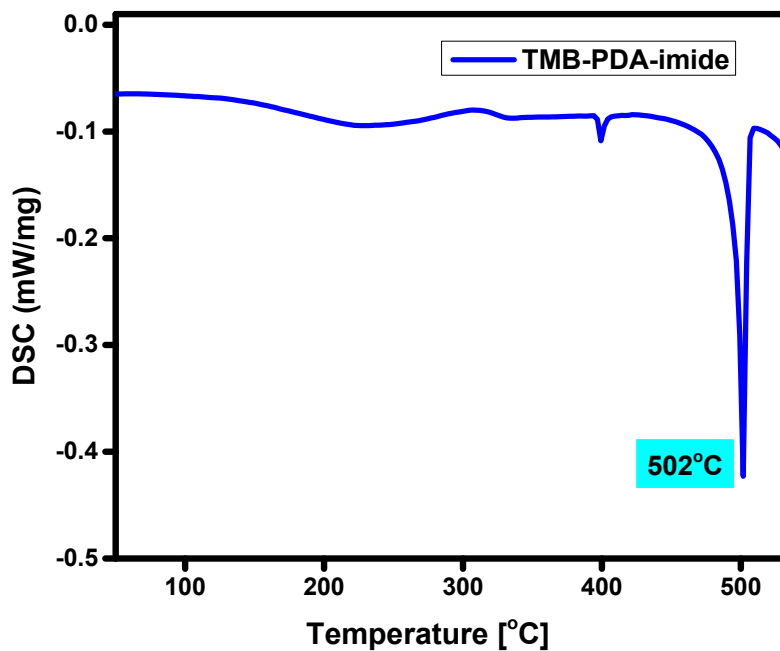


Fig. S21. DSC analysis of the monomer TMB-PDA-imide was recorded at 10°C/min

Table S1 Thermal studies of the prepared monomers and the polymers

Material	T _g , °C	T _d , °C	Weight loss in %
AH	-	390	85.3
TM-PDA-Imide	-	580	42.7
TMB-PDA-Imide	-	546	32.1
AH-Poly	126	384	10.5
TM-PDA-Poly		569	36.5
TMB-PDA-Poly		523	36.4

T_g – glass transition temperature

T_d – decomposition temperature

Section G. PXRD Profiles

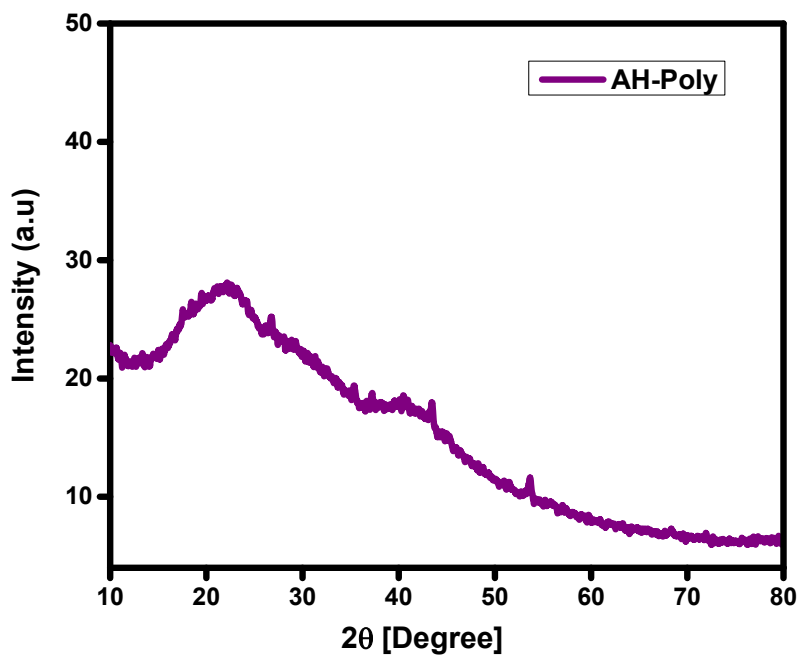


Fig. S22. Powder XRD Pattern of AH-Poly

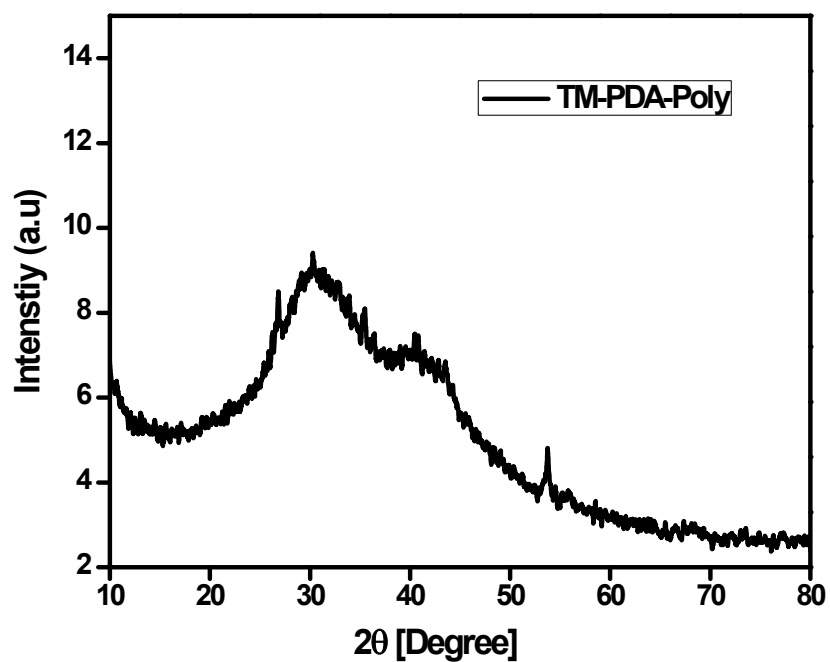


Fig. S23. Powder XRD Pattern of TM-PDA-Poly

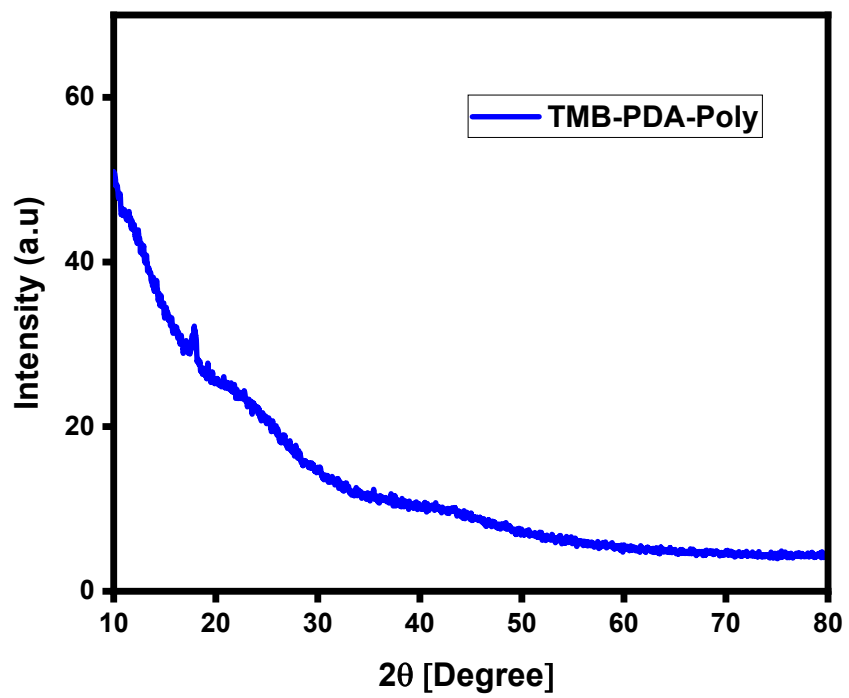


Fig. S24. Powder XRD Pattern of TMB-PDA-Poly

Section H. XPS and UPS Profile

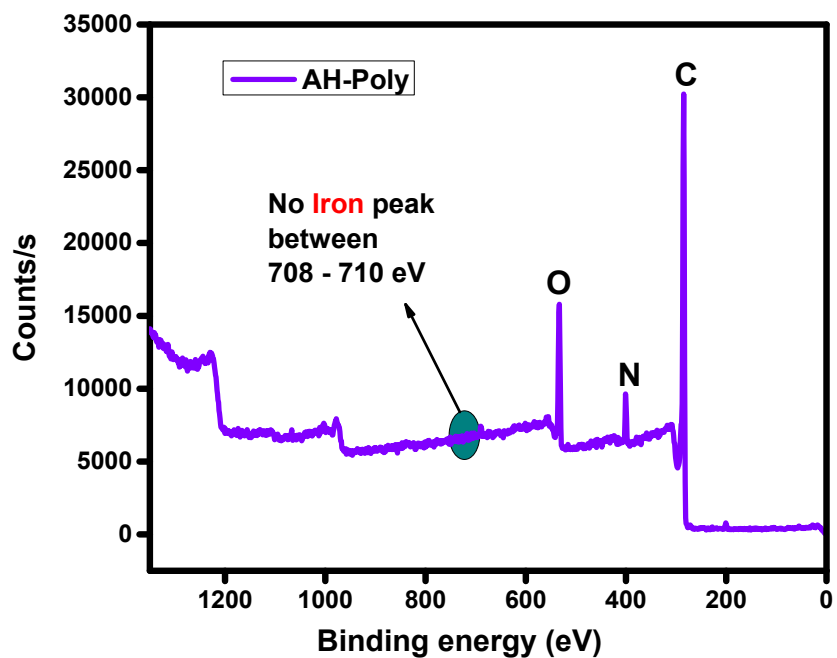


Fig. S25. XPS Survey scan of AH-Poly by using ESCALAB

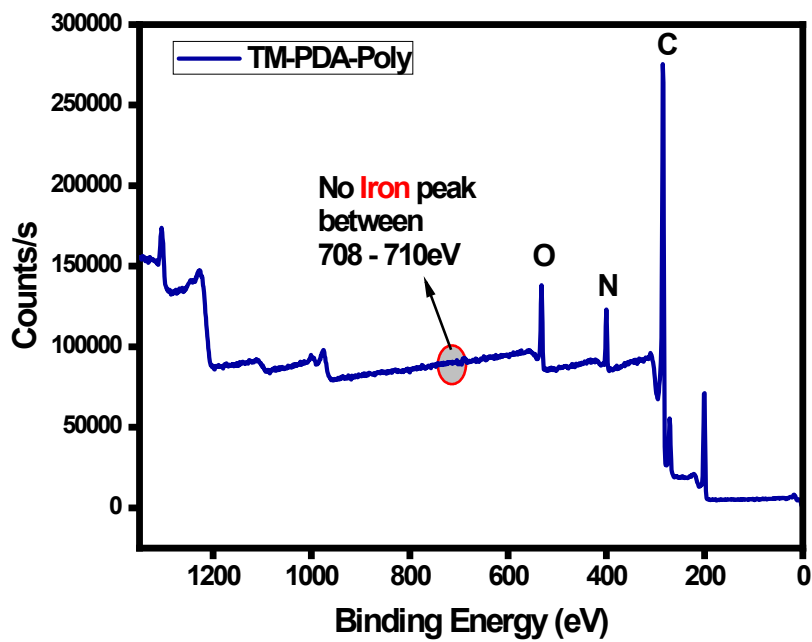


Fig. S26. XPS Survey scan of TM-PDA-Poly by using ESCALAB

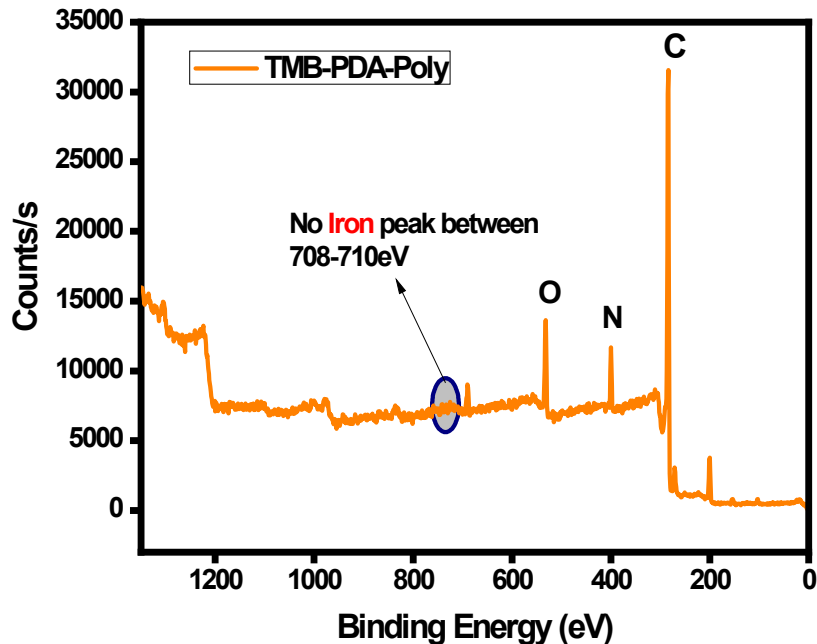


Fig. S27. XPS Survey scan of TMB-PDA-Poly by using ESCALAB

Table S2 Elemental analysis of TM-PDA-Poly and TMB-PDA-Poly by XPS

Sample	Carbon		Oxygen		Nitrogen		Chloride	
	Peak BE (eV)	Atomic %	Peak BE (eV)	Atomic %	Peak BE (eV)	Atomic %	Peak BE (eV)	Atomic %
AH-Poly	284.6	83.8	533	12	400.3	4.1	-	-
TM-PDA-Poly	284.5	79.5	531.5	6.8	399.9	5.5	200.1	8.1
TMB-PDA-Poly	284.6	80.8	531.3	8.2	400.4	5.3	200.5	3.74

Section I. Surface morphology studies

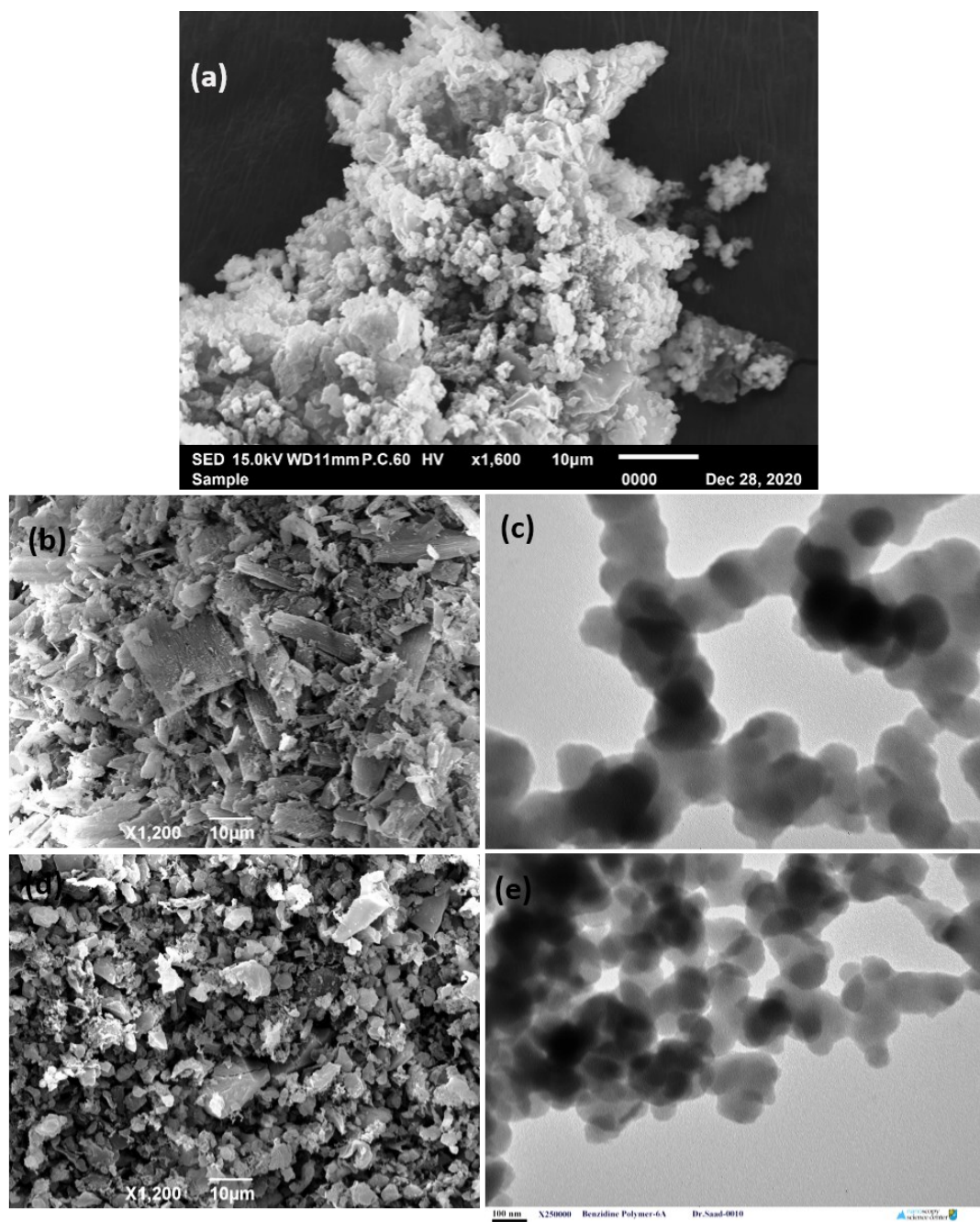


Fig. S28. SEM and TEM images of AH-Poly (a), TM-PDA-Poly (b), (c) and TMB-PDA-Poly (d) and (e)

Section J. Single Crystal X- ray diffraction studies of TM-PDA-Imide

Experimental

The single crystals of TM-PDA-Imide suitable for diffraction analysis were grown from its dichloromethane solution by solvent evaporation. The X-ray data collection of this crystal was made by Rigaku R-AXIS RAPID diffractometer using filtered Mo-K α radiation. The structure was then solved by direct methods and expanded using Fourier techniques. All calculations were performed using the ‘CrystalStructure’ crystallographic software package except for refinement, which was performed using SHELXL-2017/1. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using the riding model.

Discussion on crystal data

The various crystallographic data including crystal nature and refinement parameters of TM-PDA-Imide are summarized in the **Table S3**.

Table S3. Summary on the nature of the crystals and various crystallographic parameters of TM-PDA-Imide

Crystal sample	TM-PDA-Imide
Chemical formula	C ₇₈ H ₅₆ Cl ₈ N ₆ O ₄
M_r	1424.88
Crystal system, space group	Triclinic, P-1
Temperature (K)	150
a, b, c (Å)	9.979 (2), 12.736 (3), 16.016 (4)
α, β, γ (°)	111.967 (8), 102.448 (7), 93.928 (7)
V (Å ³)	1818.2 (8)
Z	1
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.36
Crystal size (mm)	0.20 × 0.20 × 0.20
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan

	<i>ABSCOR</i> (Rigaku, 1995)
T_{\min}, T_{\max}	0.920, 0.940
No. of measured, independent & observed [$I > 2\sigma(I)$] reflections	14627, 6384, 2038
R_{int}	0.163
$(\sin \theta/\lambda)_{\max}$ (\AA^{-1})	0.595
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.080, 0.220, 0.85
No. of reflections	6384
No. of parameters	435
H-atom treatment	Constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ($e \text{\AA}^{-3}$)	0.38, -0.37

The molecular structure of TM-PDA-Imide obtained from diffraction analysis is given **Figure S29 & S30**. The asymmetric unit of these crystals contain only half fragment of TM-PDA-Imide structure and the whole molecules could be generated by appropriate symmetry expansion. Two molecules of CH_2Cl_2 molecules are also co-crystalized along with this macromolecule as the interstitial solvents.

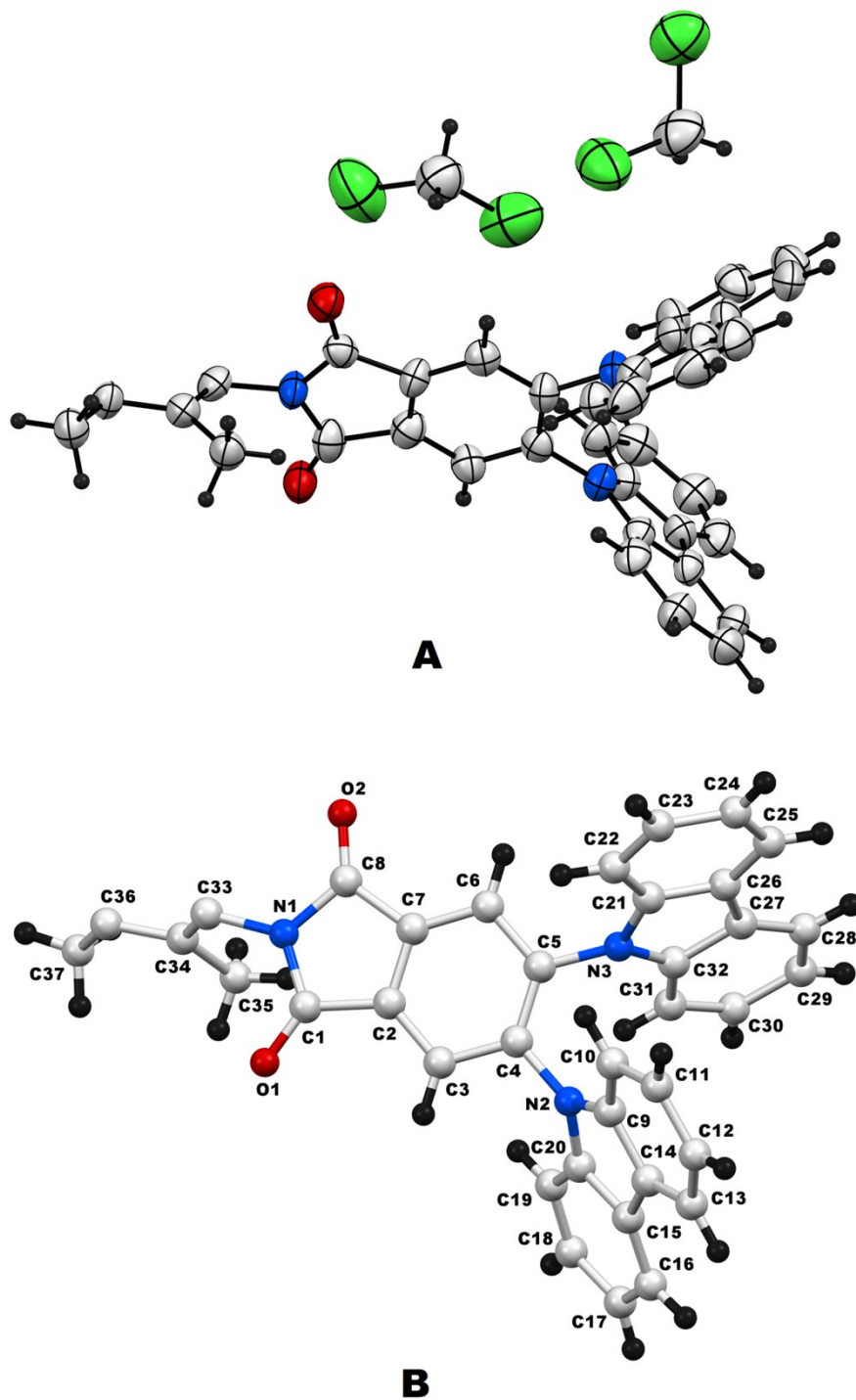


Figure S29. (A) Thermal ellipsoid representation of the asymmetric unit of TM-PDA-Imide along with solvent molecules; (B) asymmetric unit of TM-PDA-Imide showing atom numbers used in the study. Color code: blue- nitrogen; gray- carbon; red oxygen; green- chlorine and black- hydrogen.

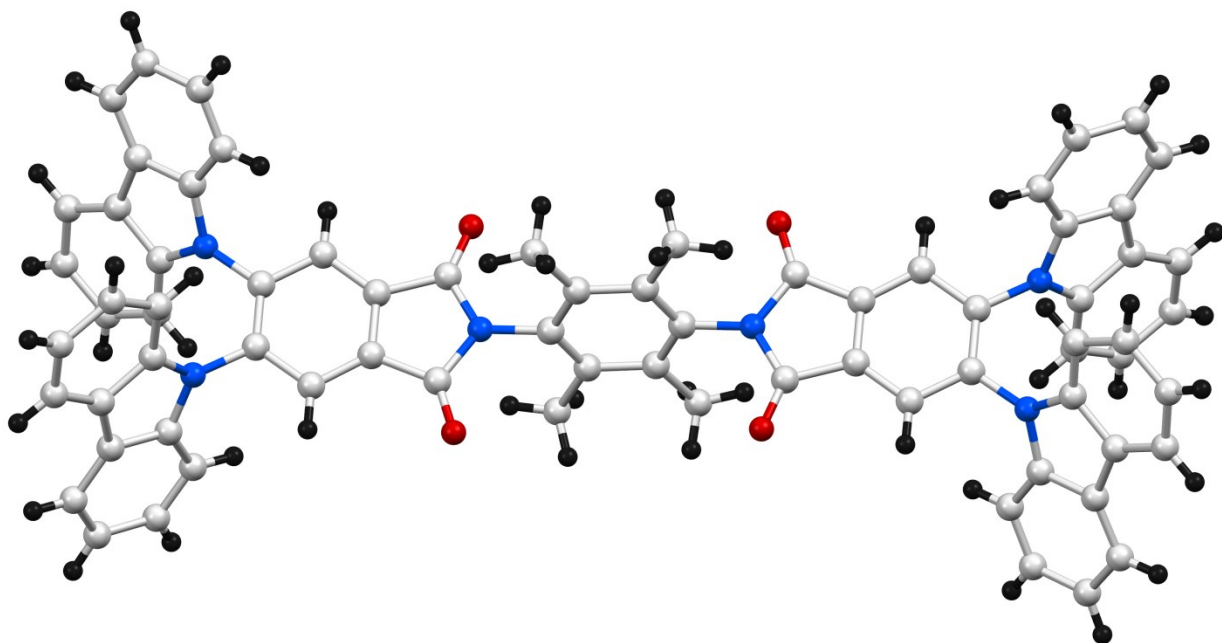


Figure S30. Crystal structure of TM-PDA-Imide obtained from X- ray diffraction analysis after symmetry expansion. Color code: blue- nitrogen; gray- carbon, red- oxygen and black hydrogen.

From The crystal structure it is clear that the orientation carbazole groups are around 55- 70 degree twisted with respect to the plane of phthalimide moiety and the mutual orientations of carbazole groups in the molecule are as wide as around 70°. At the same time the tetramethyl substituted phenyl moiety at the center of the molecule is twisted about 68° with respect to the phthalimide plane. The quantitative details of the torsion angles correspond to the carbazole moieties/ tetramethyl substituted phenyl ring with respect to the phthalimide ring in TM-PDA-Imide are provided in **Table S4**.

Table S4. Tortion angles correspond to the carbazole moieties/ tetramethyl substituted phenyl ring with respect to the phthalimide ring in TM-PDA-Imide.

Constituent atoms	Torsion angle	Constituent atoms	Torsion angle
C3 C4 N2 C20	55.3 (8)	C4 C5 N3 C32	71.3 (8)
C3 C4 N2 C9	-115.6(7)	C4 C5 N3 C21	-120.1(7)

C5	C4	N2	C9	64.4 (9)	C6	C5	N3	C21	60.7 (8)
C5	C4	N2	C20	-124.7(7)	C6	C5	N3	C32	-107.9(7)
C1	N1	C33	C34	-68.3.(8)	C8	N1	C33	C34	-107.3(7)

The carbazole moieties are positioned sufficiently wide so that adjacent carbazoles in the TM-PDA-Imide crystals are propagate as interlocked network as demonstrated in the **Figure S31**. It is also observed that appreciable intermolecular bondings are present between these interlocked carbazole moieties via C-H... π and π ... π interactions. The crystal network is also characterized by multiple intermolecular C-H... O interactions between adjacent TM-PDA-Imide molecules as depicted in **Figure S32**.

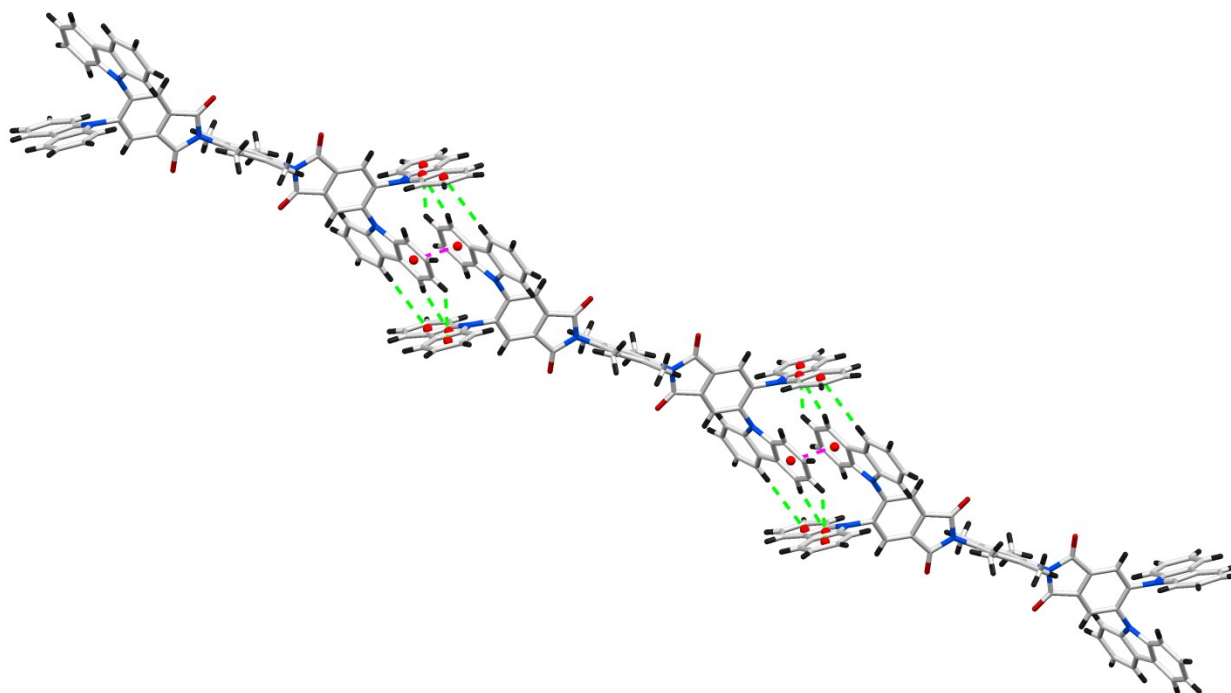


Figure S31. Crystal structure of TM-PDA-Imide showing intermolecular carbazole-carbazole interactions through C-H... π and π ... π interactions.

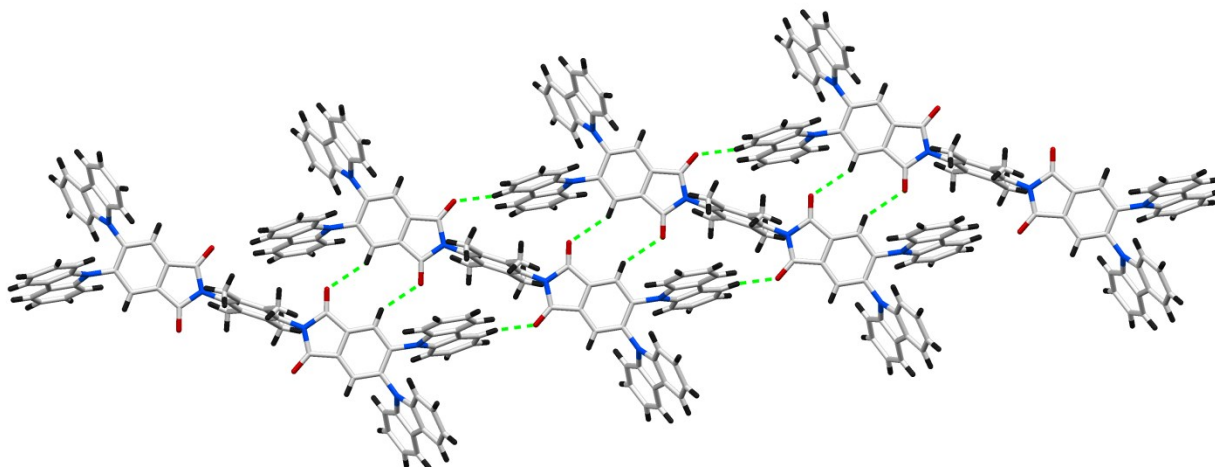


Figure S32. Crystal structure of TM-PDA imide showing intermolecular bonding through C-H...O interactions.

The crystal packing of Pz_CAR viewing from a-, b- and c- directions are depicted in **Figure S33** and it is seen that the interlocked carbazole- carbazole interactions enabled them to pack as liner manner with plenty of void space available in the network which could be occupied by solvent molecules. The solvent molecules which occupied in the vacant spaces of the crystal are also contribute to the stability of these crystals.

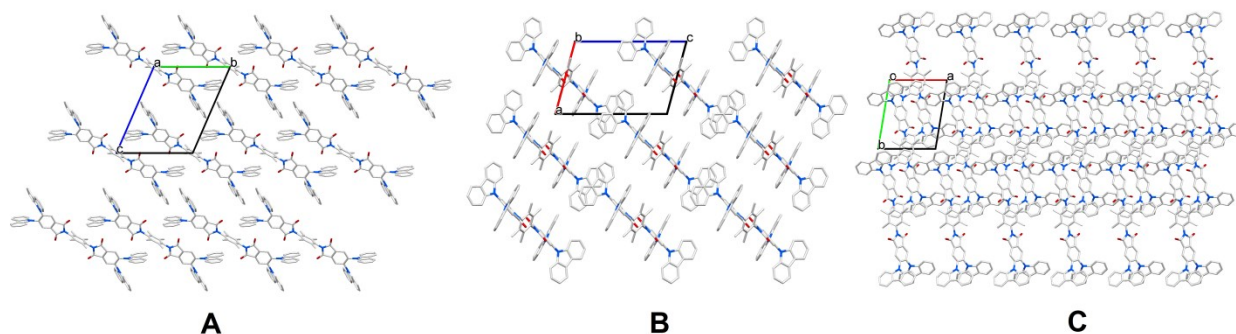


Figure S33. Packing pattern of TM-PDA-Imide molecules (A) in a- direction; (B) in b- direction and (C) in c- direction. Hydrogen atoms and solvent molecules are omitted for clarity.

Section H. CO₂/N₂ Selectivity studies

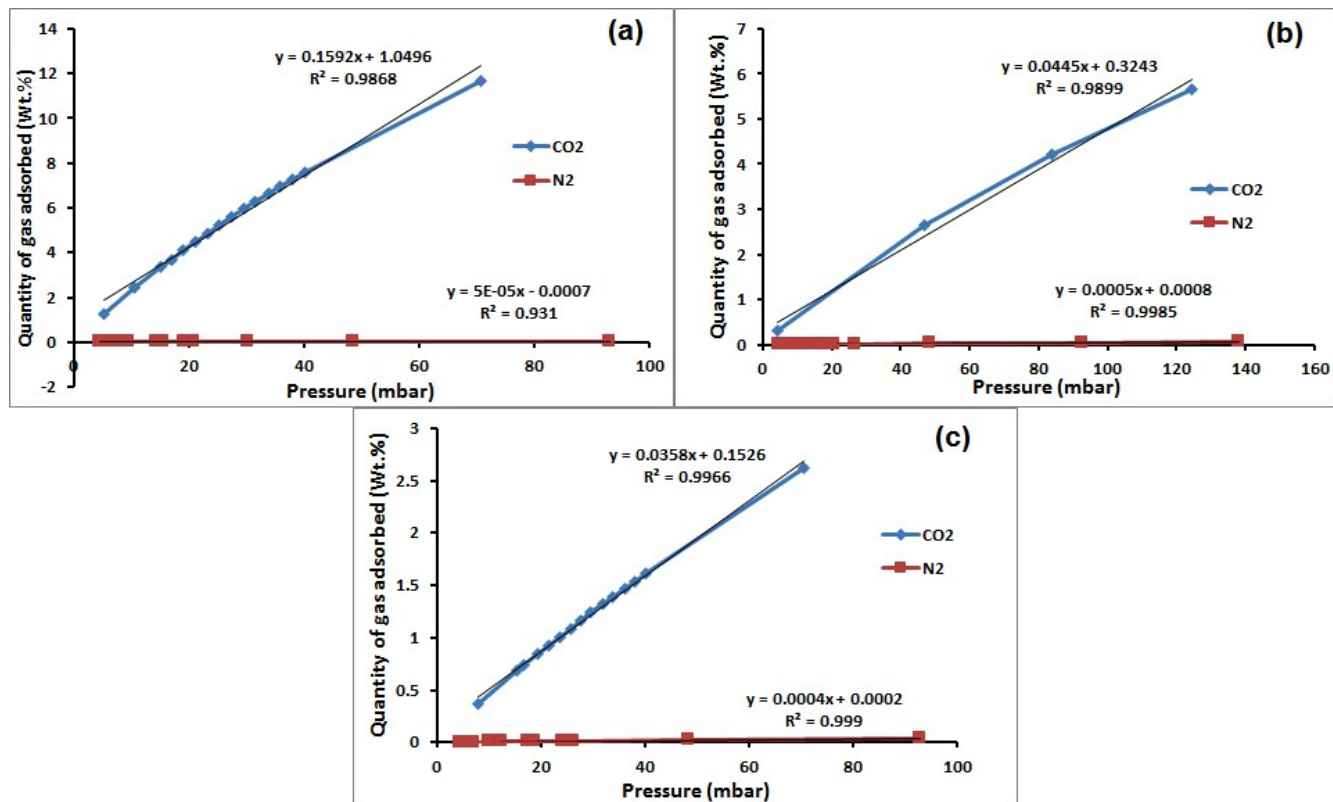
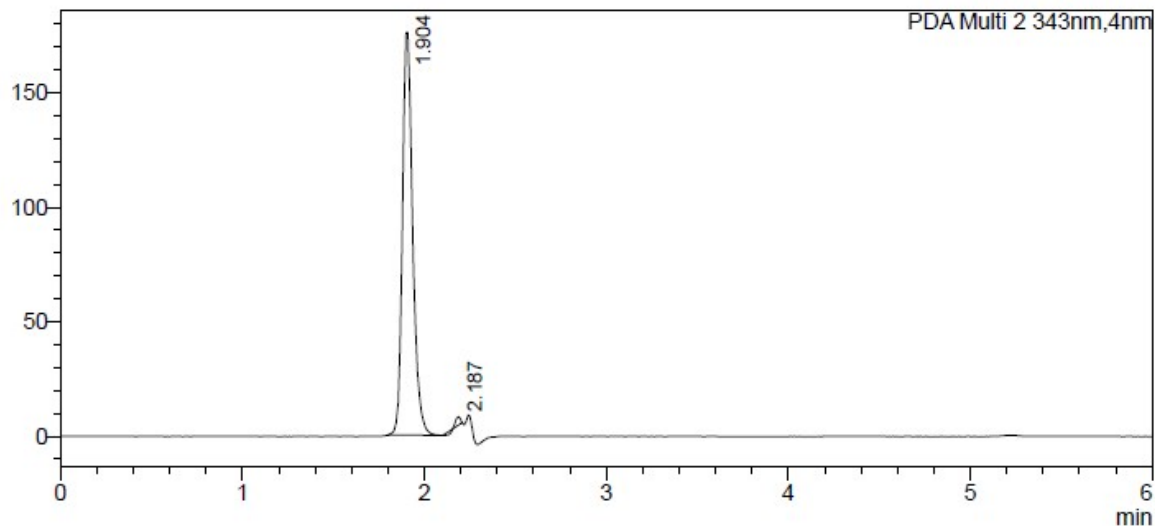


Figure S34. Adsorption selectivity CO₂/N₂ of (a) AH-Poly, (b) TM-PDA-Poly and (c) TMB-PDA-Poly calculated using Henry's law initial slope method at 273K

Section I. HPLC Analysis of monomers

<Chromatogram>

mAU



Peak Table

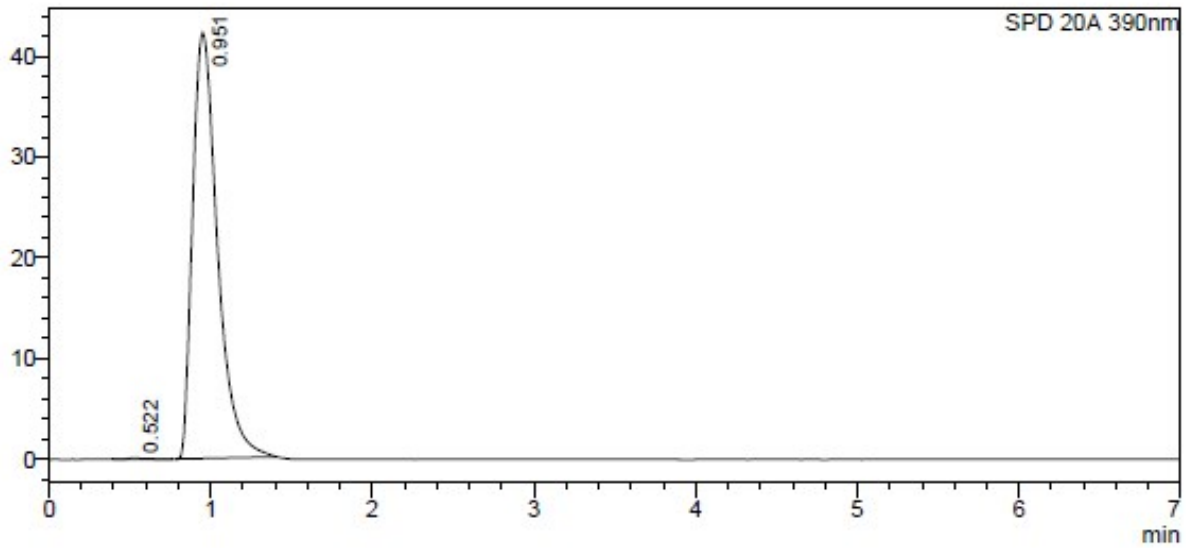
PDA Ch2 343nm

Peak#	Ret. Time	Area	Area%
1	1.904	688625	99.149
2	2.187	5910	0.851
Total		694535	100.000

Figure S35. HPLC chromatogram of AH monomer [Condition: column- Thermofisher C8 150x4.6mm, 5um; flow rate- 0.8mL/min; mobile phase- CH₂Cl₂ in 1%pyridine; run time 6 min]

<Chromatogram>

mV



Peak Table

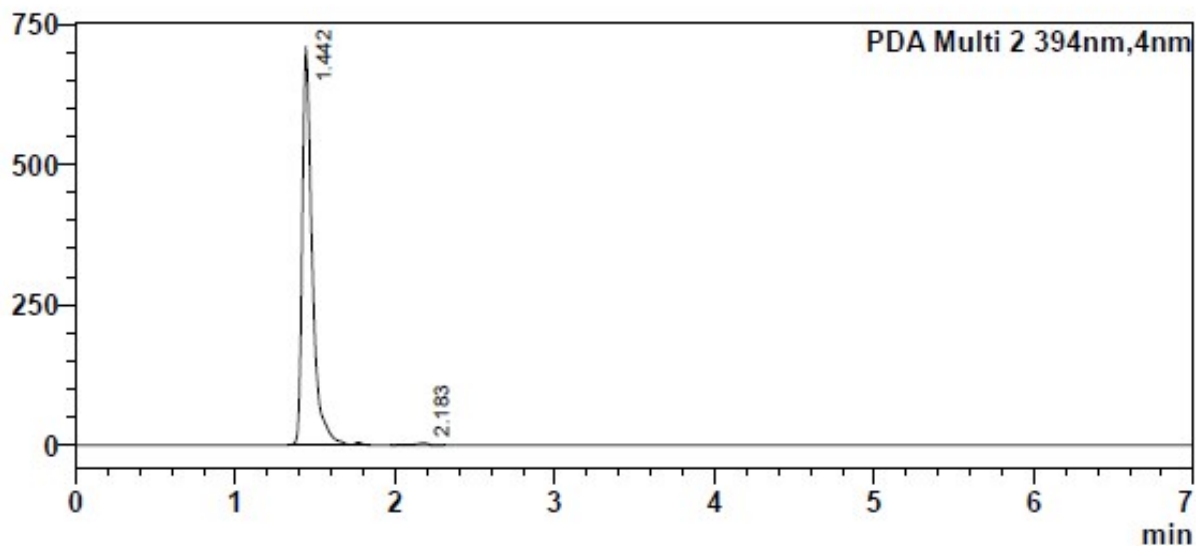
SPD 20A 390nm

Ret. Time	Area	Area%
0.522	852	0.189
0.951	451337	99.811
	452189	100.000

Figure S36. HPLC chromatogram TM-PDA-imide monomer [Condition: column- Thermofisher C8 150x4.6mm, 5um; flow rate- 0.8mL/min; mobile phase- CH₂Cl₂ in 1%pyridine; run time 7 min]

<Chromatogram>

mAU



Peak Table

PDA Ch2 394nm

Peak#	Ret. Time	Area	Area%
1	1.442	3097180	99.331
2	2.183	20861	0.669
Total		3118041	100.000

Figure S37. HPLC chromatogram TMB-PDA-imide monomer [Condition: column- Thermofisher C8 150x4.6mm, 5um; flow rate- 0.8mL/min; mobile phase- CH₂Cl₂ in 1%pyridine; run time 6 min]