

Supplementary Materials

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1. General synthetic procedures

Azo-bridged polymers were synthesized by three different methods: (a) reductive homocoupling of aromatic nitro compounds (TNPB and TNPT) using Zn or NaBH₄ as reducing agent (AZO-B-P1 and AZO-T-P2); (b) oxidative homocoupling of aromatic amino compound (TAPT) with CuBr as an oxidizing agent (AZO-T-P3), (c) condensation reactions of various aromatic nitro compounds and various aromatic diamines under basic conditions (AZO-B-P4 – AZO-T-P14). All diamines, 1,4-phenylenediamine (PPD), benzidine (BZD), 4,4'-diaminodiphenylmethane, 4,4'-oxydianiline, 4,4'-ethylenedianiline, 4,4'-diaminobenzophenone and 4,4'-diaminodiphenyl sulfide, were purchased from the suppliers. 1,3,5-Tris(4-nitrophenyl)benzene (TNPB)¹, 2,4,6-tris(4-nitrophenyl)-1,3,5-triazine (TNPT)² and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT)² were synthesized by the procedure described in the literature.

1,3,5-Tris(4-nitrophenyl)benzene (TNPB): Yield 77 %.

IR (ATR) $\tilde{\nu}$ / cm⁻¹: 1663, 1592, 1508, 1341, 1105, 841, 748, 689.

¹³C CP/MAS NMR (400 MHz) δ / ppm: 145.7, 138.6, 129.9, 127.8, 125.8, 121.8.

2,4,6-Tris(4-nitrophenyl)-1,3,5-triazine (TNPT): Yield 85 %.

IR (ATR) $\tilde{\nu}$ / cm⁻¹: 1531, 1414, 1334, 1105, 1010, 824, 743, 684.

¹³C CP/MAS NMR (400 MHz) δ / ppm: 169.3, 149.8, 140.0, 131.0, 123.2.

2,4,6-Tris(4-aminophenyl)-1,3,5-triazine (TAPT): Yield 76 %.

IR (ATR) $\tilde{\nu}$ / cm⁻¹: 3460, 3319, 3208, 1604, 1493, 1428, 1362, 1177, 1147, 1128, 811, 722, 676.

¹H NMR (400 MHz, DMSO-d₆) δ / ppm: 8.35 (d, 6H, *J* = 8.6 Hz), 6.68 (d, 6H, *J* = 8.6 Hz), 5.90 (s, 6H).

¹³C NMR (100 MHz, DMSO-d₆) δ / ppm: 170.0, 153.4, 130.6, 123.3, 113.5.

¹ Li, G.; Wang, Z. Microporous Polyimides with Uniform Pores for Adsorption and Separation of CO₂ Gas and Organic Vapors. *Macromolecules* **2013**, *46*, 3058–3066.

² Halder, A.; Kandambeth, S.; Biswal, B.P.; Kaur, G.; Roy, N.C.; Addicoat, M.; Salunke, J.K.; Banerjee, S.; Vanka, K.; Heine, T.; Verma, S.; Banerjee, R. Decoding the Morphological Diversity in Two Dimensional Crystalline Porous Polymers by Core Planarity Modulation. *Angew. Chem. Int. Ed.* **2016**, *55*, 7806–7810.

1.1. Synthesis of AZO-B-P1 – AZO-T-P14

Synthesis of AZO-B-P1

Yield 50 %.

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3356, 1593, 1509, 1448, 1392, 1346, 841.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.9, 142.7, 127.7, 123.3.

Elemental Analysis: 69.93 %C (calc. 83.46), 10.14 %N (calc. 12.17).

Synthesis of AZO-T-P2

Yield 37 %.

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3384, 1584, 1509, 1437, 1410, 1359, 819.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 170.0, 154.3, 137.8, 122.7.

Elemental Analysis: 70.55 %C (calc. 72.40), 22.95 %N (calc. 24.12).

Synthesis of AZO-T-P3

Yield 52 %.

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3353, 1583, 1504, 1435, 1409, 1359, 816.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 170.0, 154.0, 137.9, 122.7, 114.1.

Elemental Analysis: 60.72 %C (calc. 72.40), 18.84 %N (calc. 24.12).

Synthesis of AZO-B-P4

Yield 78 %.

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3356, 1591, 1509, 1446, 1390, 1342, 1106, 841, 748, 690.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.7, 146.6, 128.0, 123.1, 115.3.

Elemental Analysis: 57.84 %C (calc. 80.16), 9.59 %N (calc. 15.58).

Synthesis of AZO-T-P5

AZO-T-P5 was synthesized by the similar procedure described in the literature.³ TNPT (500 mg, 1.13 mmol), 1,4-phenylenediamine (184 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N₂ atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (360 mg, yield 70 %).

IR (ATR) $\tilde{\nu}$ / cm⁻¹: 3376, 1583, 1492, 1406, 1356, 1336, 811.

¹³C CP/MAS NMR (600 MHz) δ / ppm: 169.0, 153.0, 149.5, 137.6, 128.6, 122.5, 115.1.

Elemental Analysis: 67.64 %C (calc. 71.67), 20.04 %N (calc. 24.76).

Synthesis of AZO-B-P6

AZO-B-P6 was synthesized by the similar procedure described in the literature.³ TNPB (500 mg, 1.13 mmol), benzidine (313 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N₂ atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (242 mg, yield 41 %).

IR (ATR) $\tilde{\nu}$ / cm⁻¹: 3361, 3030, 1590, 1513, 1441, 1388, 1342, 833.

¹³C CP/MAS NMR (400 MHz) δ / ppm: 151.5, 146.3, 141.6, 127.6, 115.5.

Elemental Analysis: 71.26 %C (calc. 82.26), 10.35 %N (calc. 13.32).

Synthesis of AZO-B-P7

AZO-B-P7 was synthesized by the similar procedure described in the literature.³ TNPB (500 mg, 1.13 mmol), 4,4'-diaminodiphenylmethane (340 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N₂ atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (175 mg, yield 29 %).

IR (ATR) $\tilde{\nu}$ / cm⁻¹: 3358, 1590, 1510, 1443, 1388, 1341, 832.

³ Patel, H.A.; Je, S.H.; Park, J.; Jung, Y.; Coskun, A.; Yavuz, C.T. Directing the Structural Features of N₂-Phobic Nanoporous Covalent Organic Polymers for CO₂ Capture and Separation. *Chem. Eur. J.* **2014**, *20*, 772–780.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.5, 146.4, 141.6, 128.5, 123.8, 115.4, 40.1.

Elemental Analysis: 71.88 %C (calc. 82.35), 10.46 %N (calc. 12.98).

Synthesis of AZO-B-P8

AZO-B-P8 was synthesized by the similar procedure described in the literature.³ TNPB (500 mg, 1.13 mmol), 4,4'-oxydianiline (343 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N_2 atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (430 mg, yield 70 %).

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3353, 1590, 1494, 1444, 1390, 1341, 827.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.9, 146.5, 142.8, 127.6, 123.3, 115.8.

Elemental Analysis: 70.55 %C (calc. 79.83), 11.12 %N (calc. 12.93).

Synthesis of AZO-B-P9

AZO-B-P9 was synthesized by the similar procedure described in the literature.³ TNPB (500 mg, 1.13 mmol), 4,4'-ethylenedianiline (361 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N_2 atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (384 mg, 61 %).

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3359, 2923, 2851, 1590, 1512, 1441, 1390, 1342, 825.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.7, 146.5, 141.2, 128.4, 123.8, 115.3, 37.0.

Elemental Analysis: 72.44% C (calc. 82.44), 10.64 %N (calc. 12.65).

Synthesis of AZO-B-P10

AZO-B-P10 was synthesized by the similar procedure described in the literature.³ TNPB (500 mg, 1.13 mmol), 4,4'-diaminobenzophenone (364 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N_2 atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (241 mg, 39 %).

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3342, 1587, 1512, 1434, 1391, 1346, 829.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 194.7, 151.9, 141.5, 129.8, 114.2.

Elemental Analysis: 74.64 %C (calc. 80.27), 11.23 %N (calc. 12.65).

Synthesis of AZO-B-P11

AZO-B-P11 was synthesized by the similar procedure described in the literature.³ TNPB (500 mg, 1.13 mmol), 4,4'-diaminodiphenyl sulfide (367 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N_2 atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (197 mg, yield 31 %).

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3364, 1590, 1510, 1444, 1391, 1341, 840.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.5, 145.9, 139.6, 127.5, 124.1, 116.3.

Elemental Analysis: 71.77 %C (calc. 77.54), 10.58 %N (calc. 12.56).

Synthesis of AZO-T-P12

AZO-T-P12 was synthesized by the similar procedure described in the literature.³ TNPT (500 mg, 1.13 mmol), benzidine (310 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N_2 atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (410 mg, yield 69 %).

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3368, 1582, 1503, 1494, 1435, 1407, 1358, 812.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 169.6, 154.0, 137.1, 128.7, 122.5, 114.9.

Elemental Analysis: 70.36 %C (calc. 74.99), 20.63 %N (calc. 21.20).

Synthesis of AZO-T-P13

AZO-T-P13 was synthesized by the similar procedure described in the literature.³ TNPT (500 mg, 1.13 mmol), 4,4'-diaminodiphenylmethane (330 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N_2 atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off

and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (321 mg, yield 52 %).

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3344, 1582, 1495, 1435, 1407, 1355, 811.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 170.1, 154.0, 145.6, 138.2, 129.6, 122.6, 115.5, 40.2.

Elemental Analysis: 67.72 %C (calc. 75.26), 16.73 %N (calc. 20.65).

Synthesis of AZO-T-P14

AZO-T-P14 was synthesized by the similar procedure described in the literature.³ TNPT (500 mg, 1.13 mmol), 4,4'-oxydianiline (340 mg, 1.70 mmol), DMF (50 mL) and KOH (634 mg, 11.3 mmol) were added in double-necked flask and heated to reflux under N_2 atmosphere. After 24 h, the reaction mixture was cooled to room temperature, poured in 300 mL of distilled water and stirred for 1 h. The reaction mixture was filtered off and washed with hot distilled water, acetone and THF. After drying at 140 °C under vacuum for 5 h, black solid was obtained (334 mg, yield 54 %).

IR (ATR) $\tilde{\nu}$ / cm^{-1} : 3384, 1601, 1493, 1409, 1336, 824.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 169.5, 150.4, 139.7, 130.2, 123.4, 116.9.

Elemental Analysis: 71.59 %C (calc. 72.78), 18.03 %N (calc. 20.58).

2. FT-IR spectra

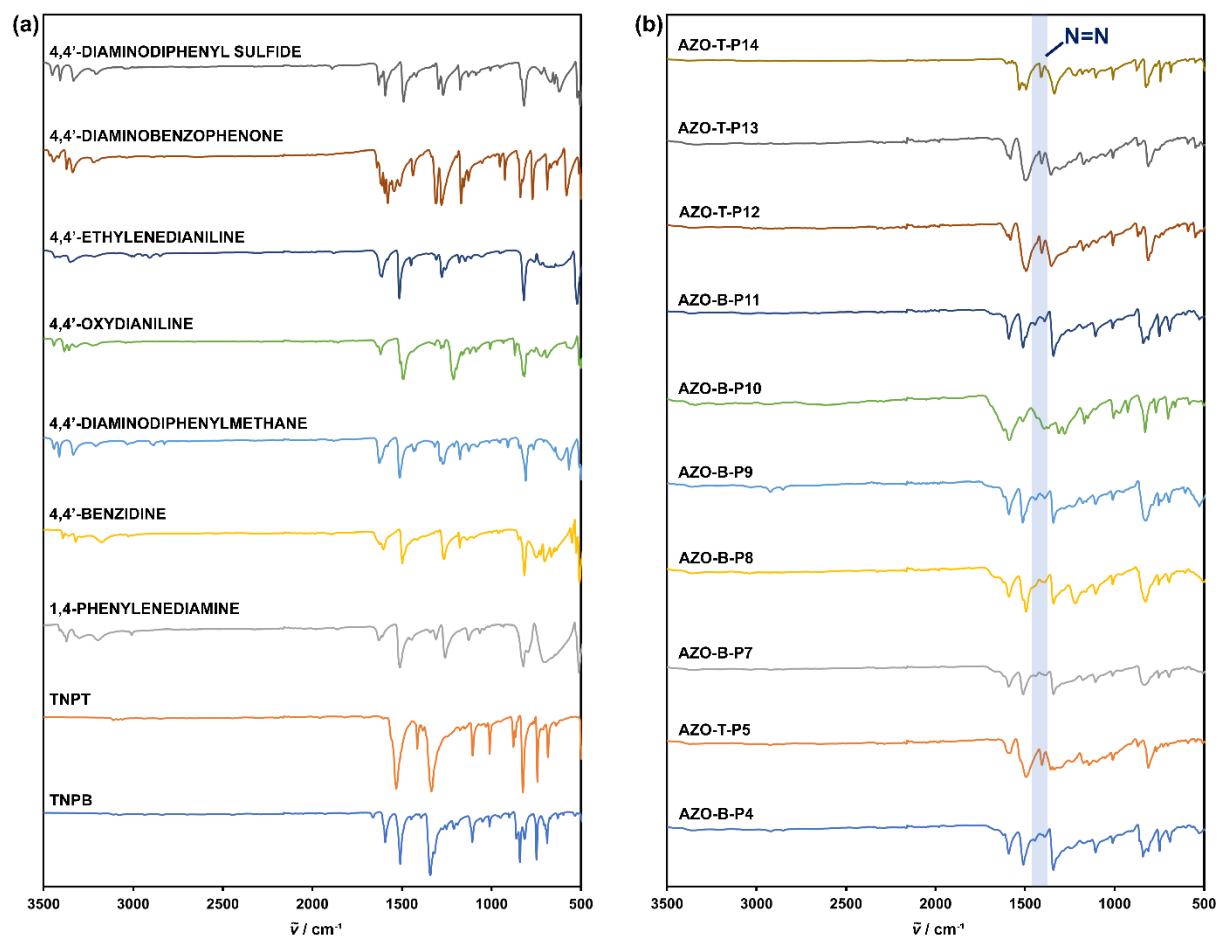
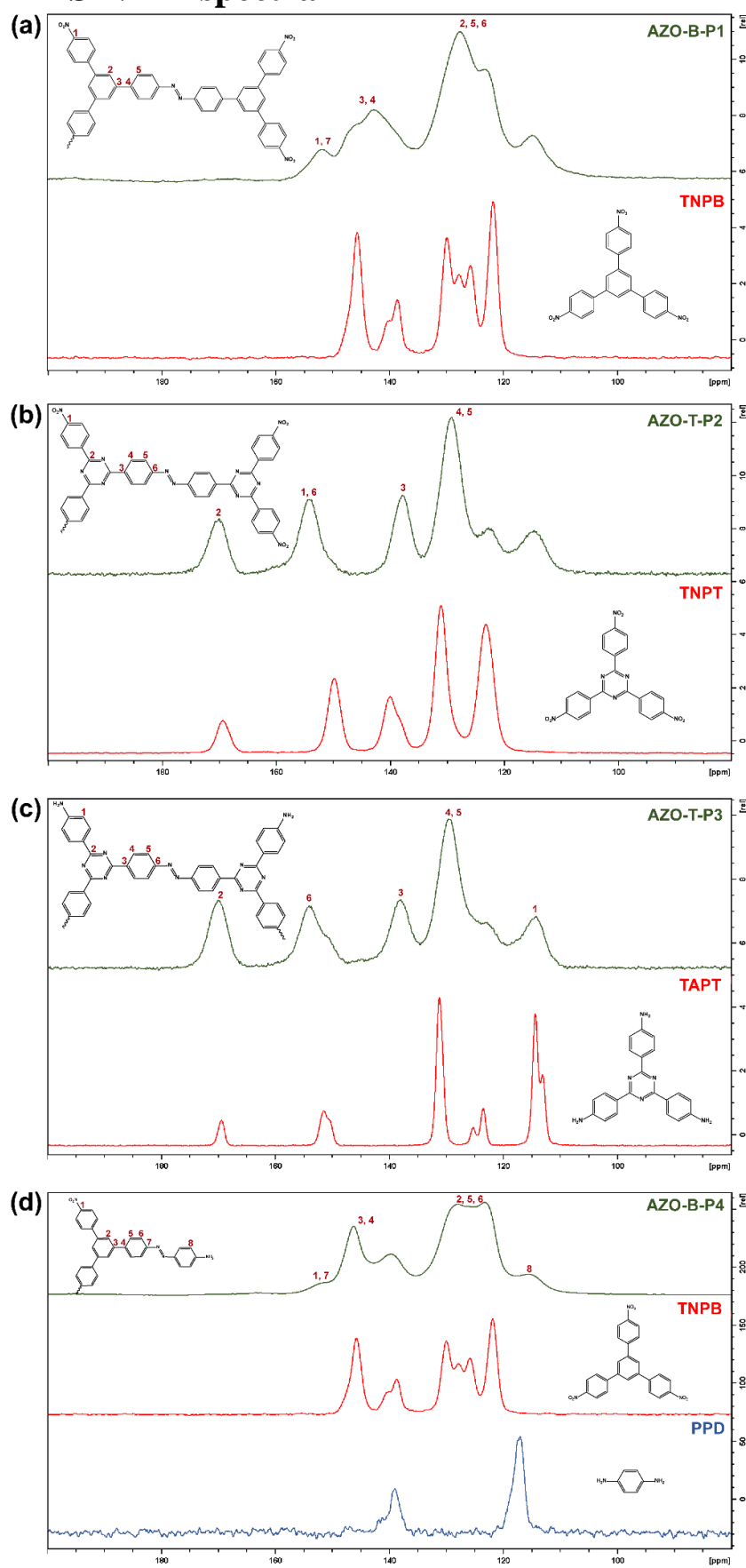
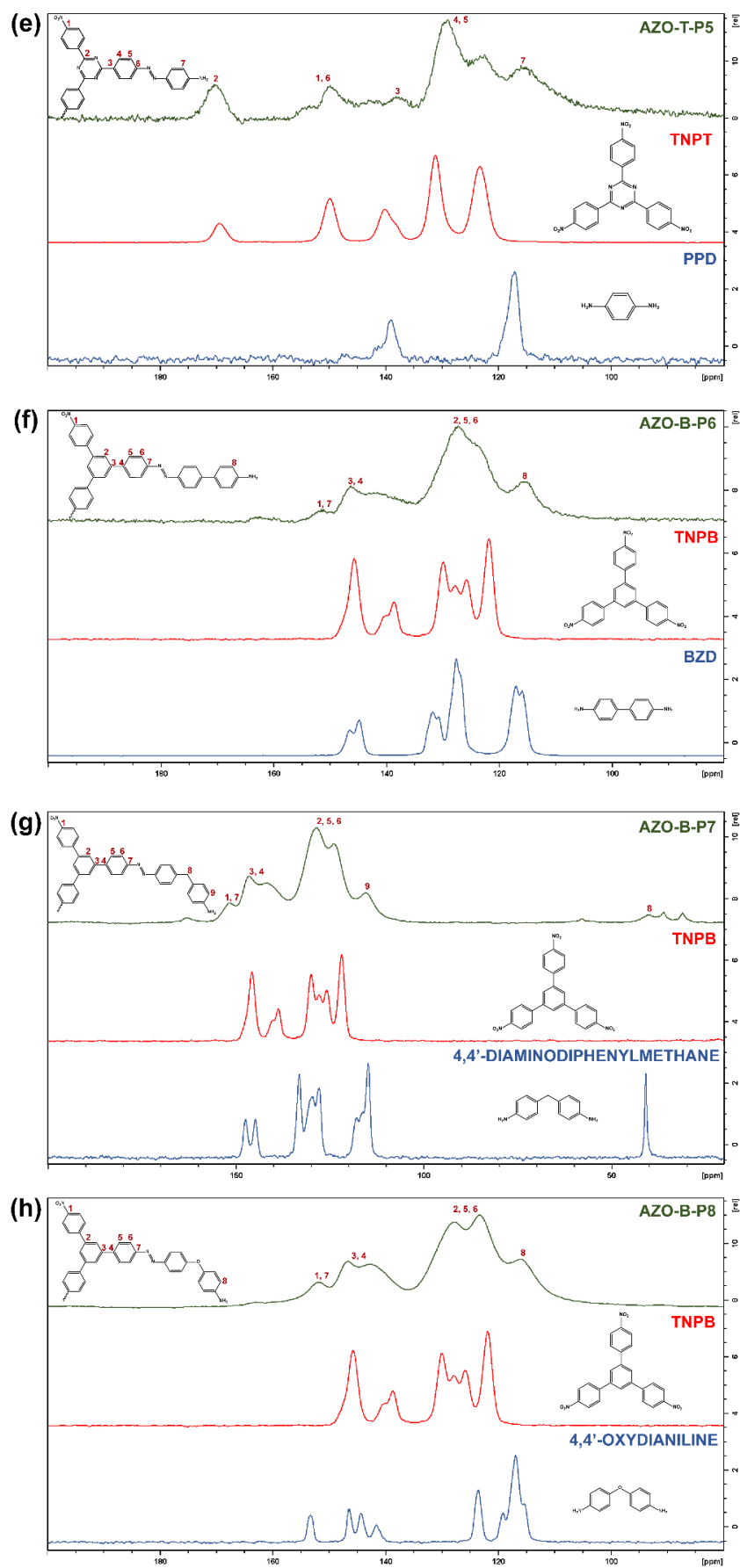
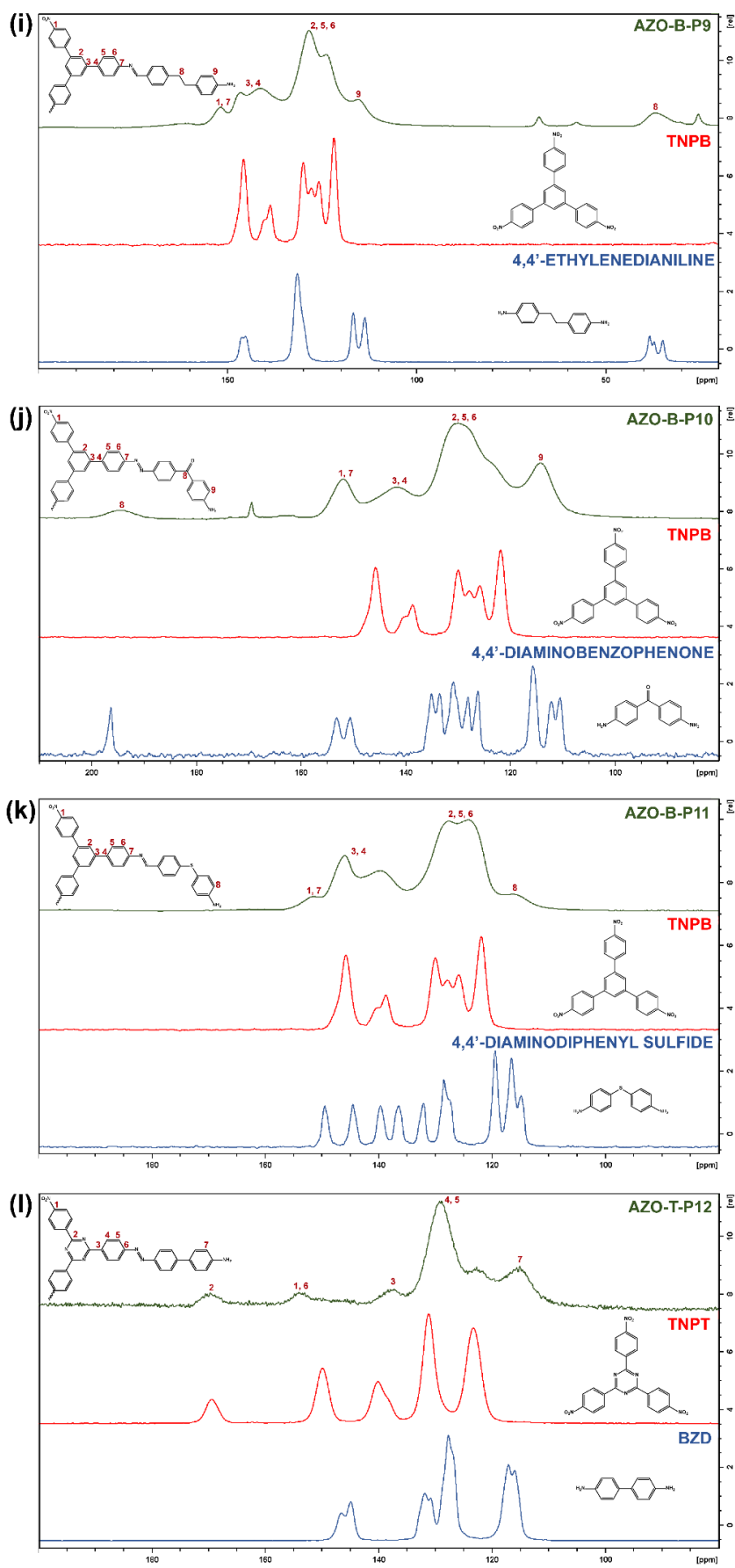


Figure S1. FT-IR spectra of (a) starting aromatic nitro and amino monomers and (b) azo-bridged polymers.

3. ^{13}C CP/MAS NMR spectra







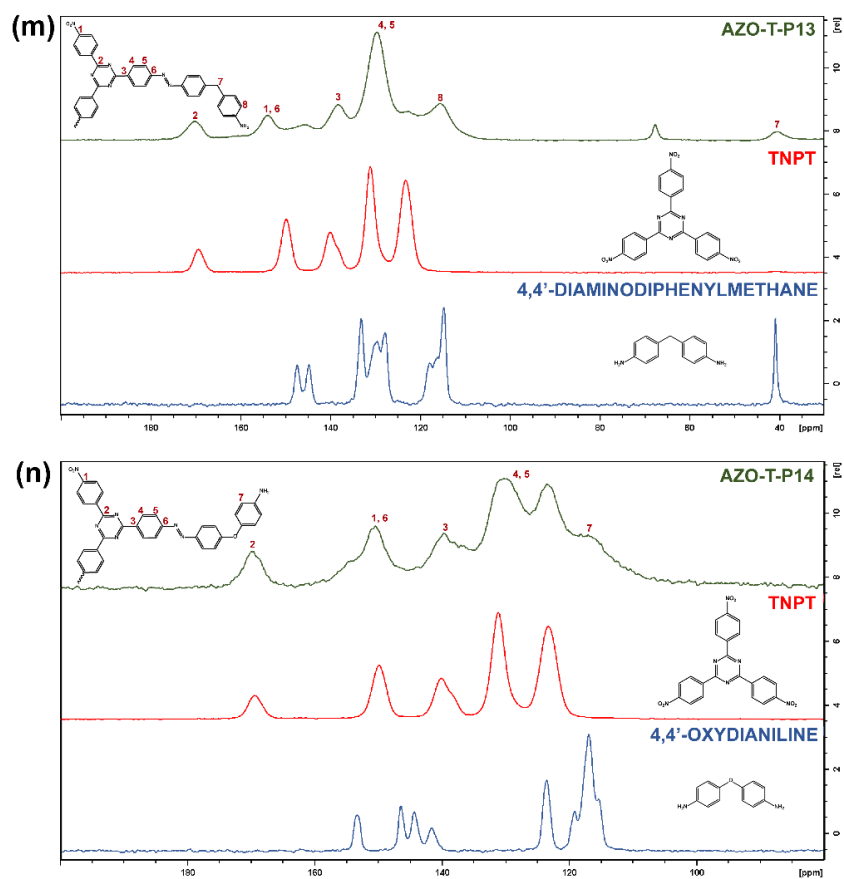


Figure S2. Comparison of ^{13}C CP/MAS NMR spectra of azo-bridged polymers and corresponding starting aromatic nitro and amino monomers.

4. Powder X-ray diffraction

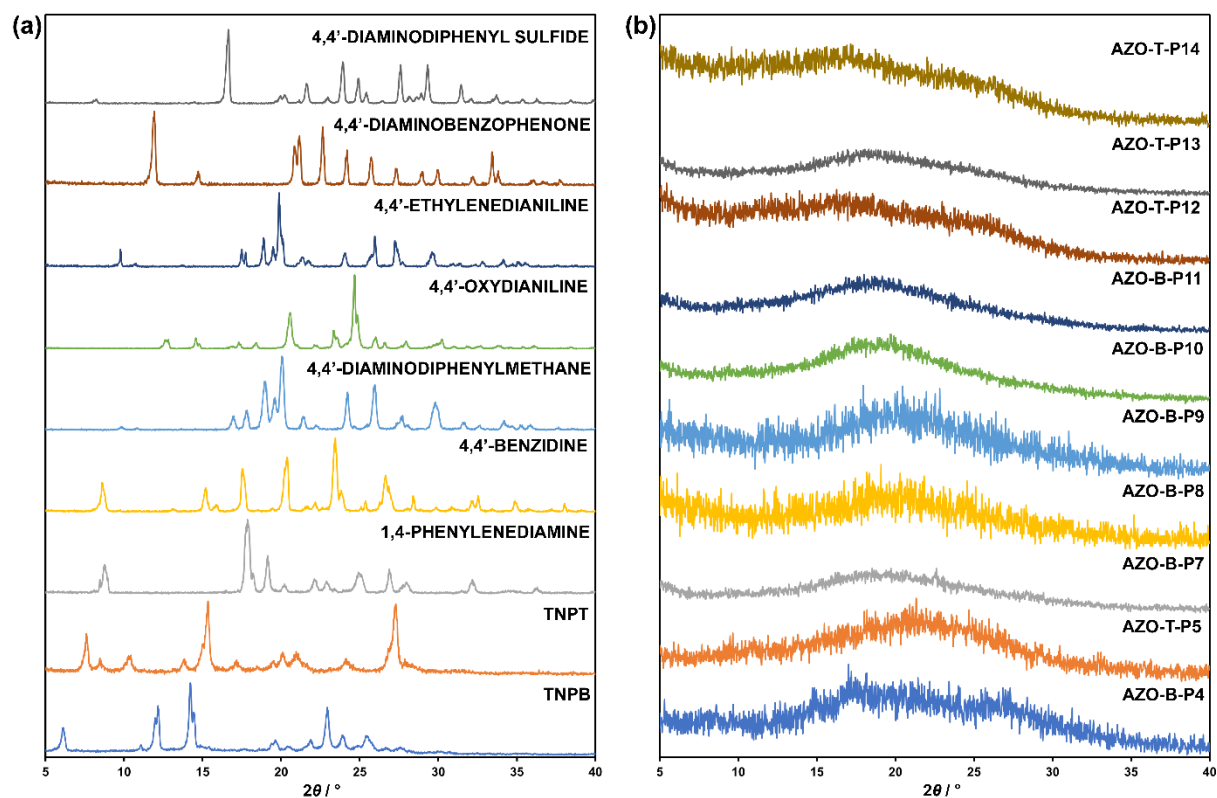
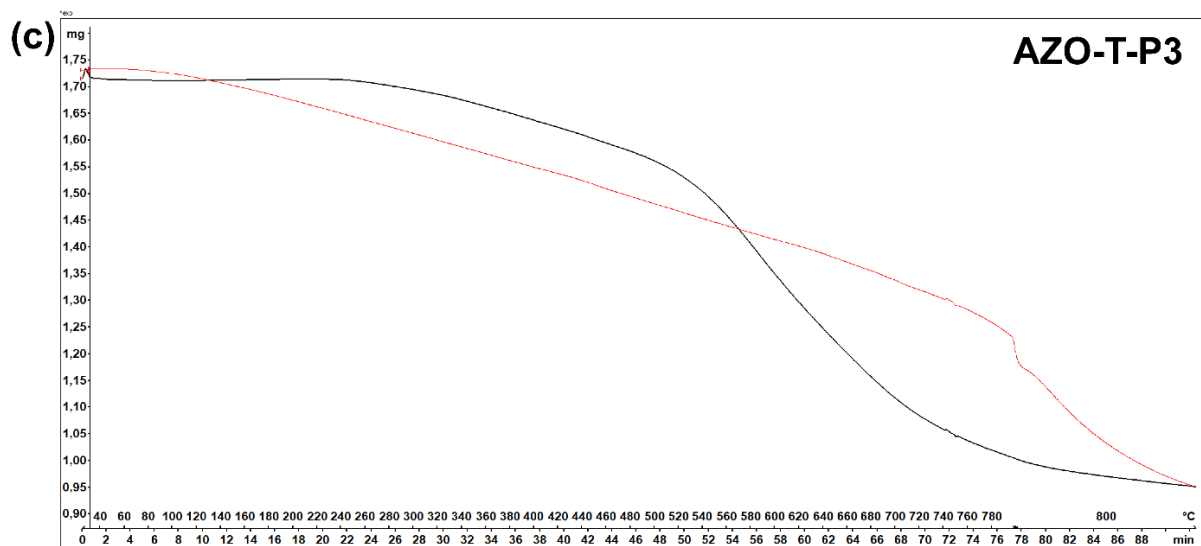
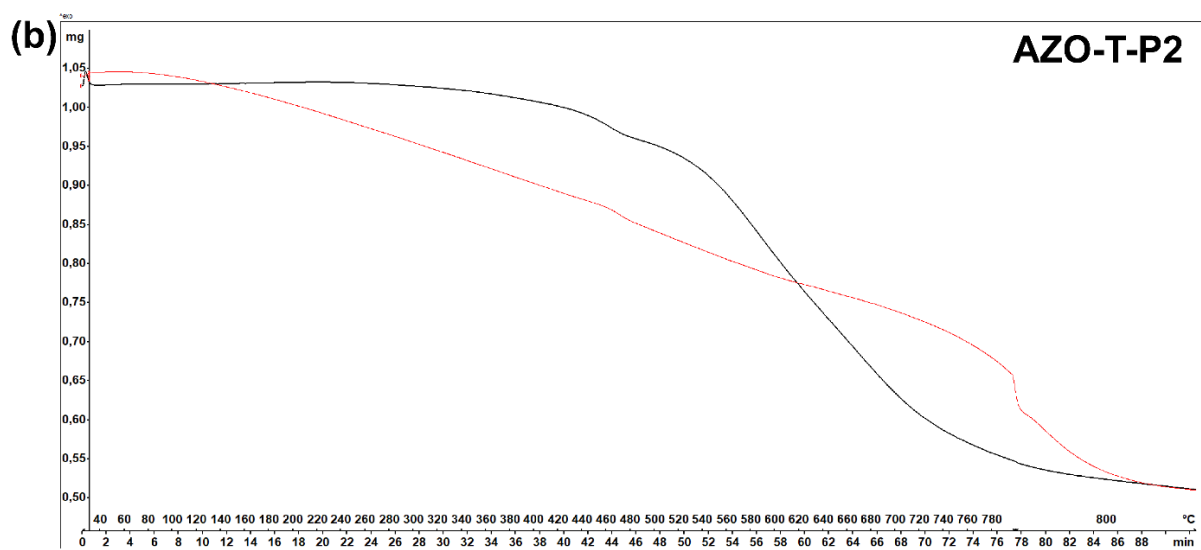
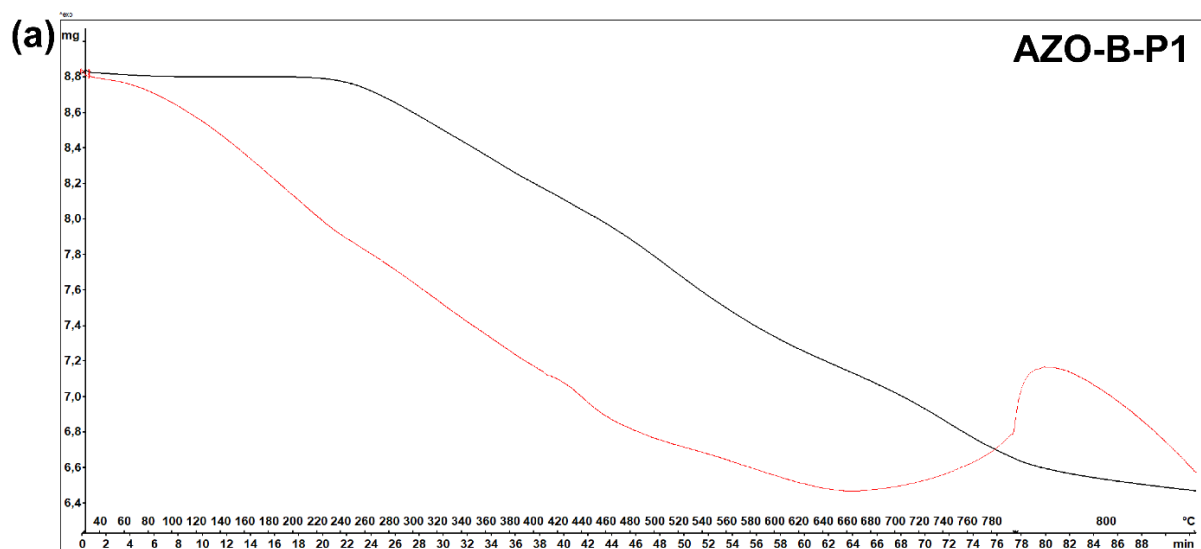
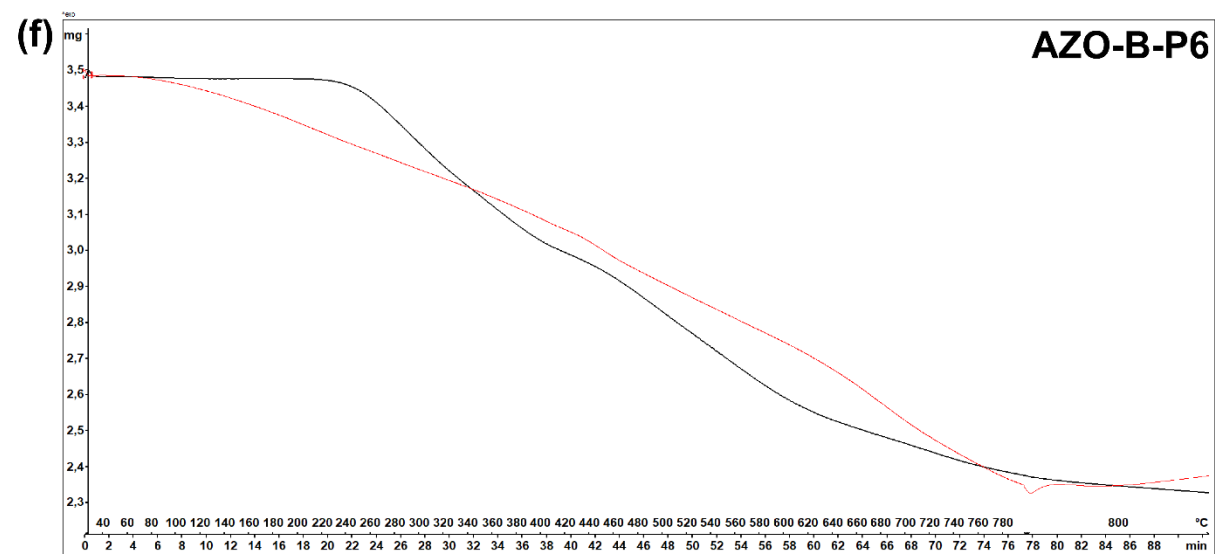
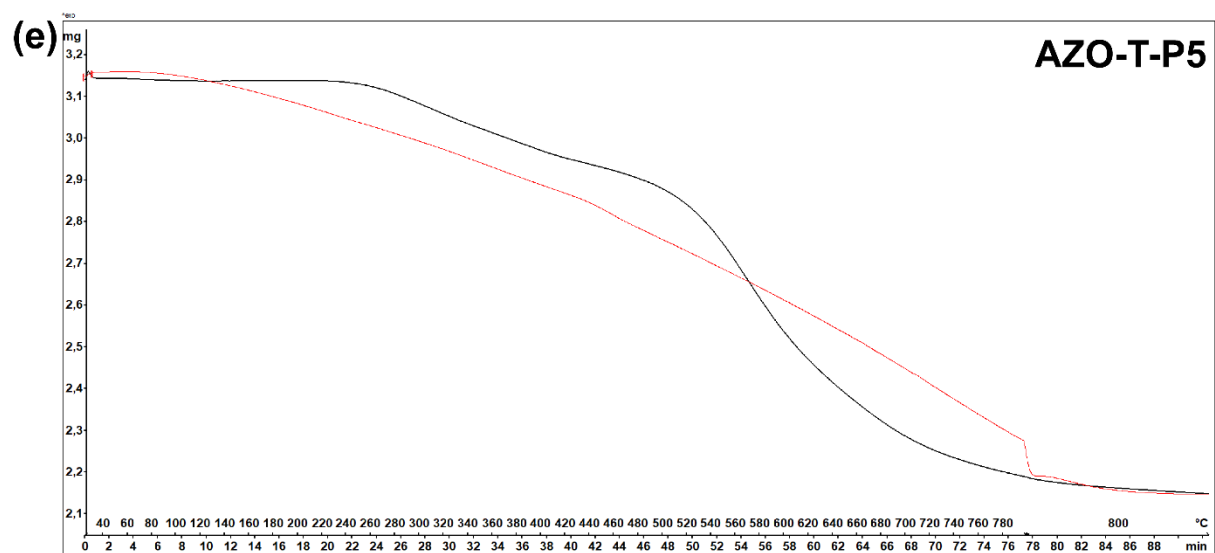
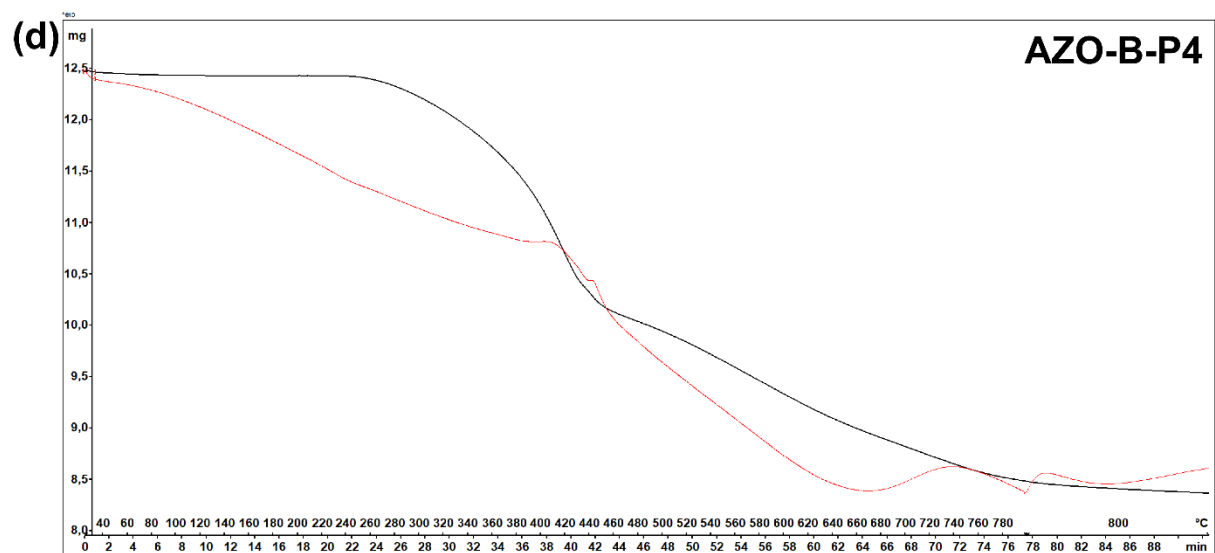
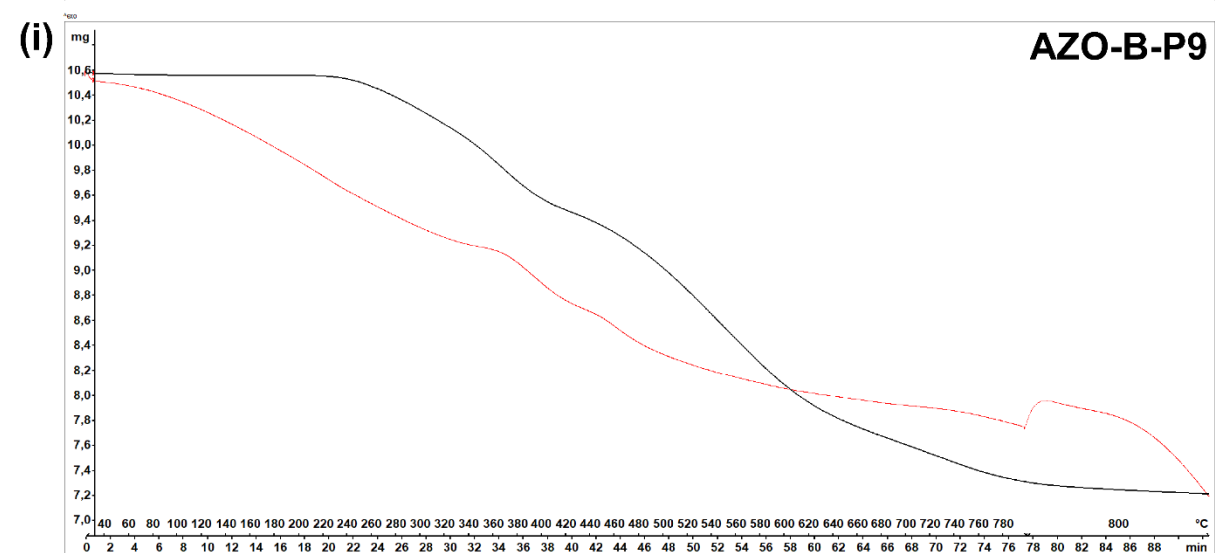
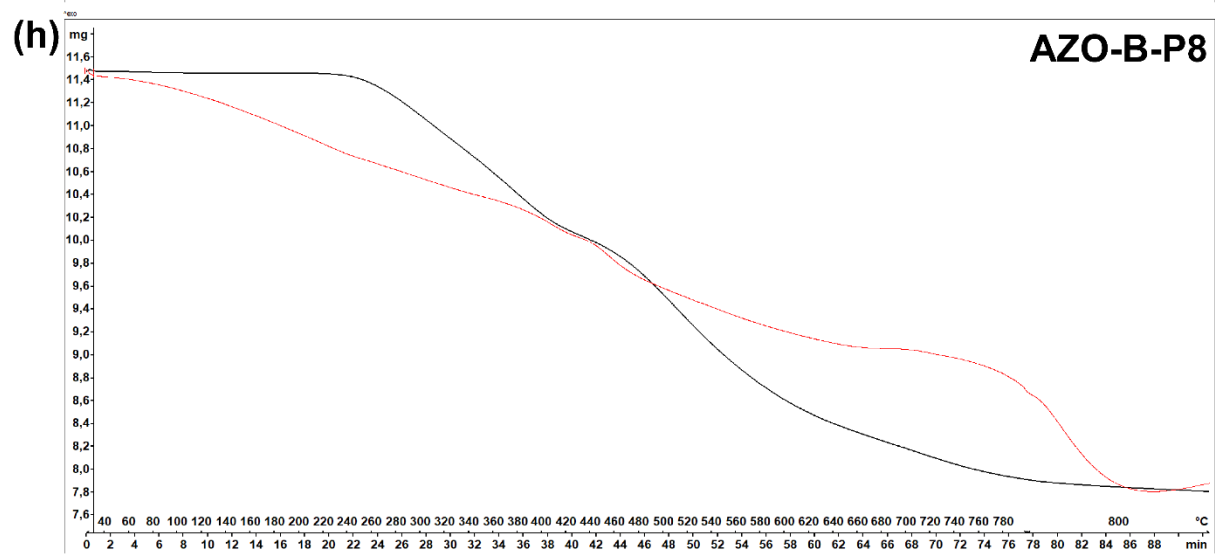
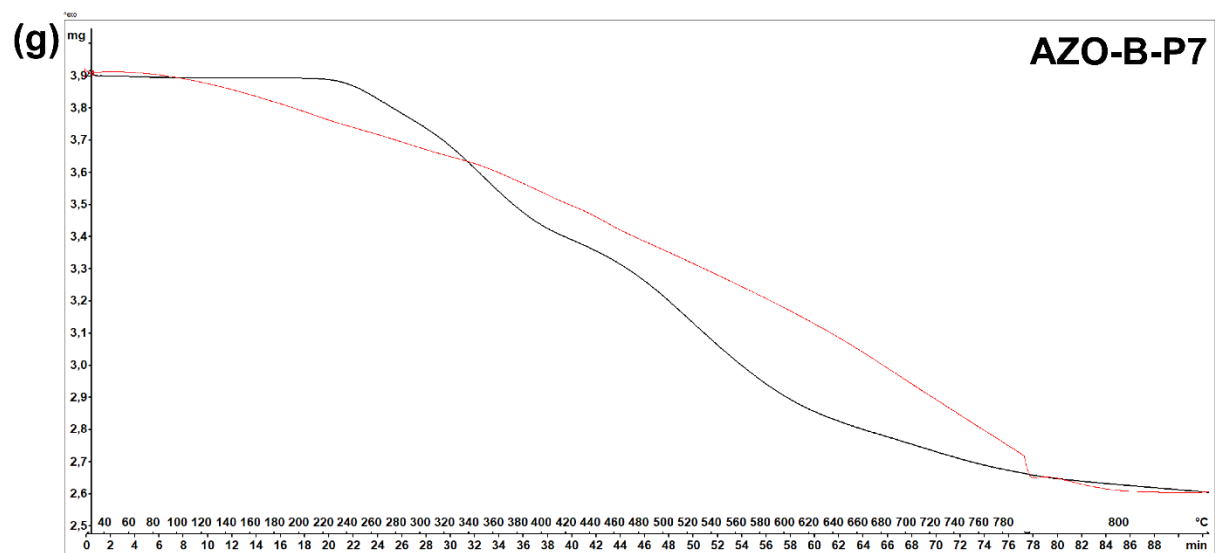


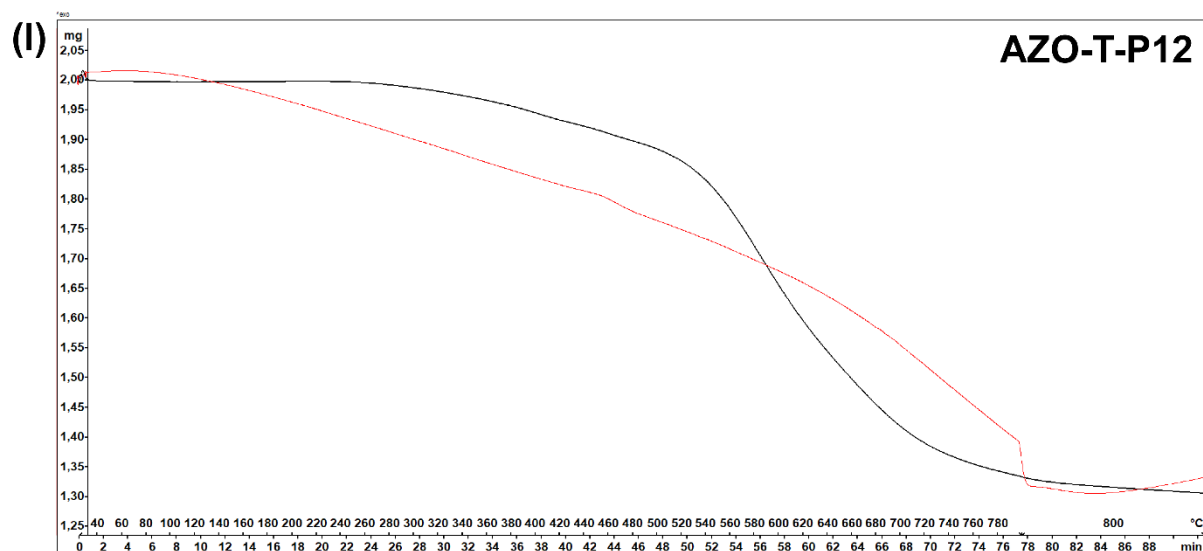
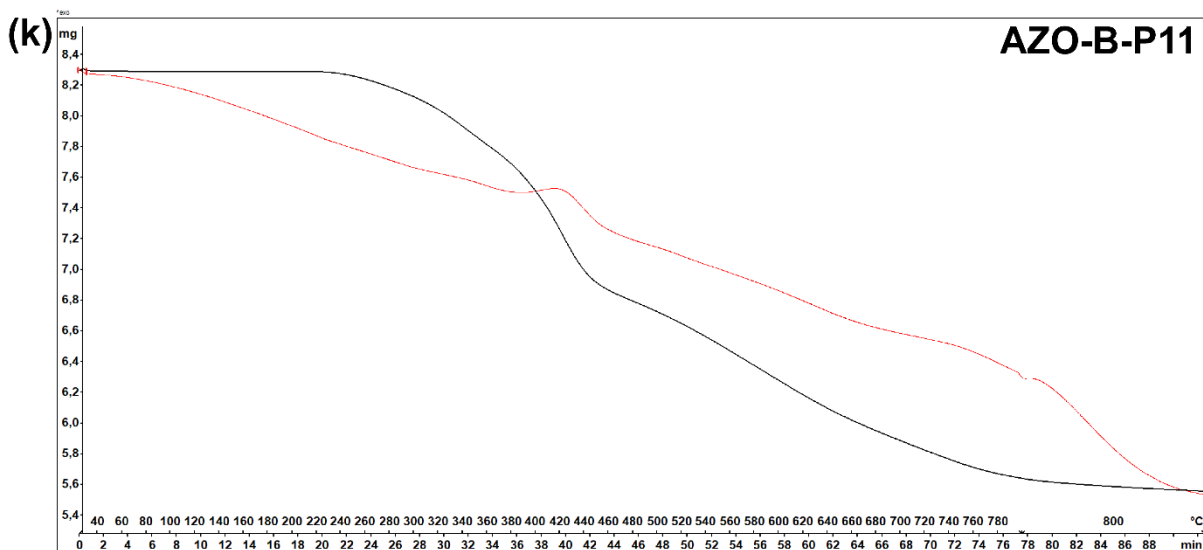
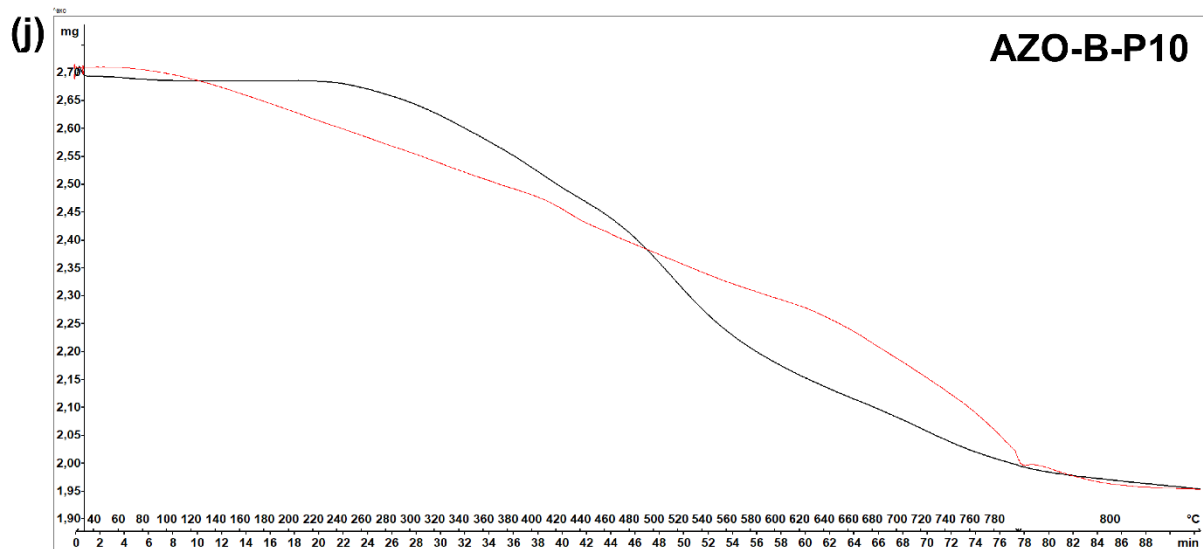
Figure S3. PXRD diffractograms of (a) starting aromatic nitro and amino monomers and (b) azo-bridged polymers.

5. Thermogravimetric analysis









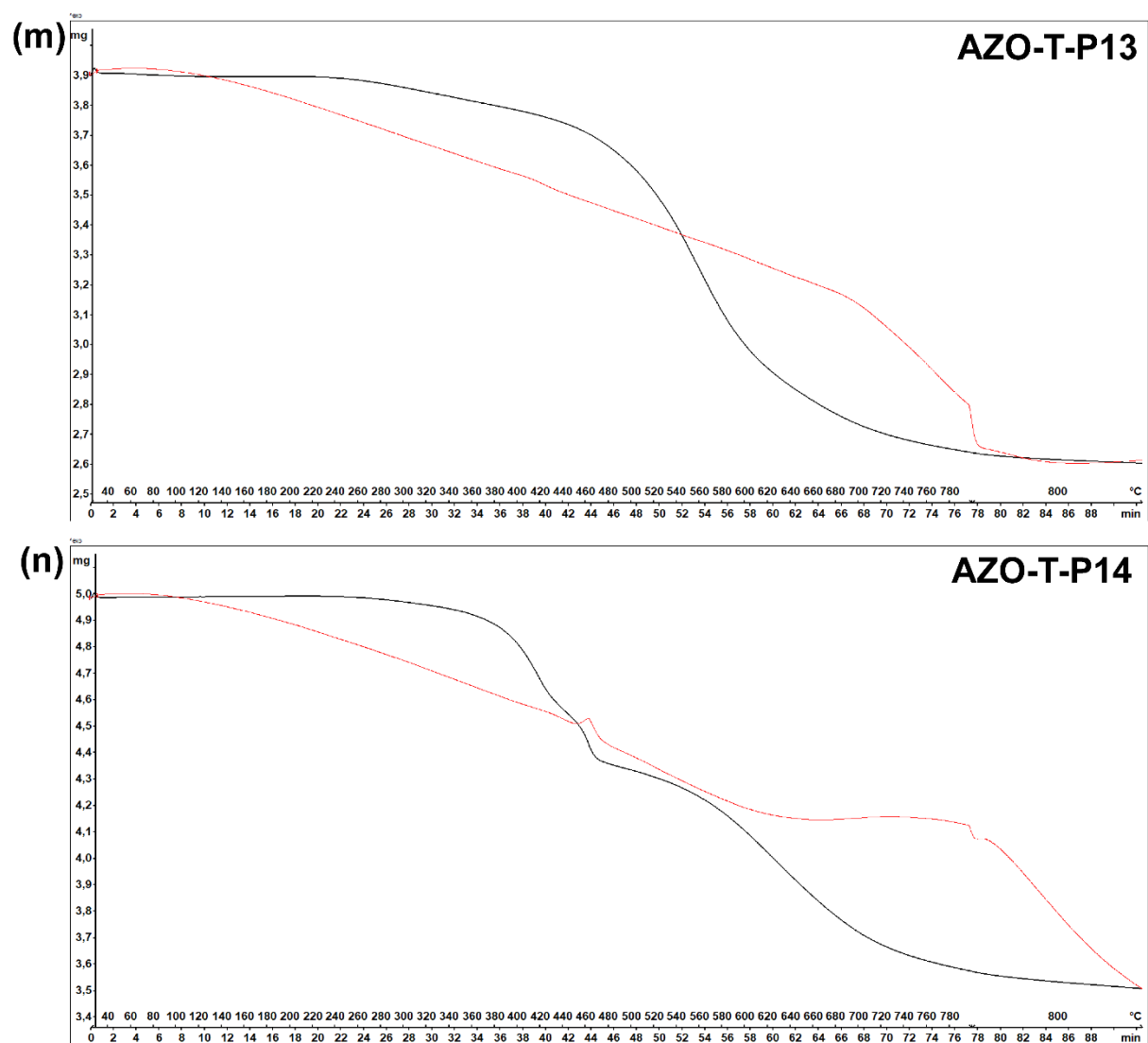


Figure S4. TGA (black) and DSC (red) curves of azo-bridged polymers.

6. Computational studies of azo-bridged polymers

Table S1. Unit cell parameters (a , b , c , α , β and γ) of the optimized geometries (PBE-D3/pob-TZVP-rev2) of benzene-based (AZO-B) and triazine-based (AZO-T) model compounds.

	Compound	Space group	CRYSTAL17 label	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	$\alpha / ^\circ$	$\beta / ^\circ$	$\gamma / ^\circ$
AA stacking	AZO-B	$P \bar{3}$	147	25.6247	25.6247	3.5830	90	90	120
	AZO-B-PPD	$P \bar{3}$	147	36.1836	36.1836	3.5759	90	90	120
	AZO-B-BZD	$P \bar{3}$	143	43.3587	43.3587	3.5786	90	90	120
	AZO-T	$P \bar{3}$	147	25.2081	25.2081	3.5170	90	90	120
	AZO-T-PPD	$P \bar{3}$	147	35.6570	35.6570	3.5265	90	90	120
	AZO-T-BZD	$P \bar{3}$	143	42.7213	42.7213	3.5440	90	90	120

Table S2. Calculated framework properties of the AA stacked 2D layered compounds (framework density, available pore volume and average surface area) and the size of the simulation box used in the GCMC calculations.

	Compound	GCMC simulation box	Framework density, g/cm ³	Available pore volume, cm ³ /g	Average surface area, m ² /g
AA stacking	AZO-B	2×2×8	0.563	1.140	1957
	AZO-B-PPD	2×2×8	0.411	1.794	2237
	AZO-B-BZD	2×2×8	0.351	2.203	2306
	AZO-T	2×2×8	0.598	1.031	1828
	AZO-T-PPD	2×2×8	0.431	1.671	2127
	AZO-T-BZD	2×2×8	0.367	2.075	2207

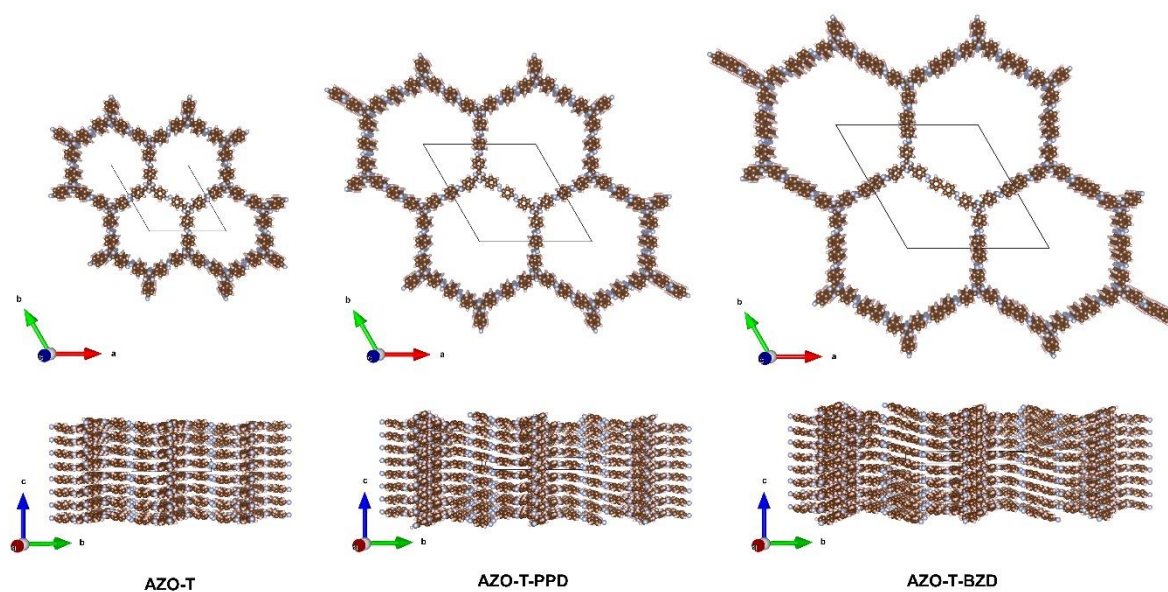


Figure S5. Optimized geometries (PBE-D3/pob2-TZVP-rev2) of AZO-T, AZO-T-PPD and AZO-T-BZD with eclipsed (AA-stacked) geometries of 2D layers shown along the c and a unit cell vectors). Unit cells are represented by grey lines.

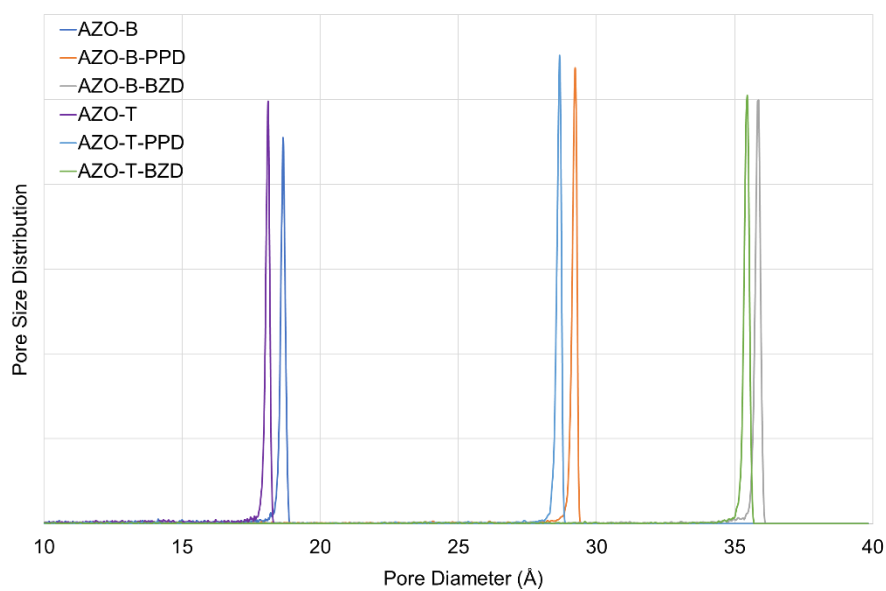


Figure S6. Pores size distribution of AA stacked configurations.

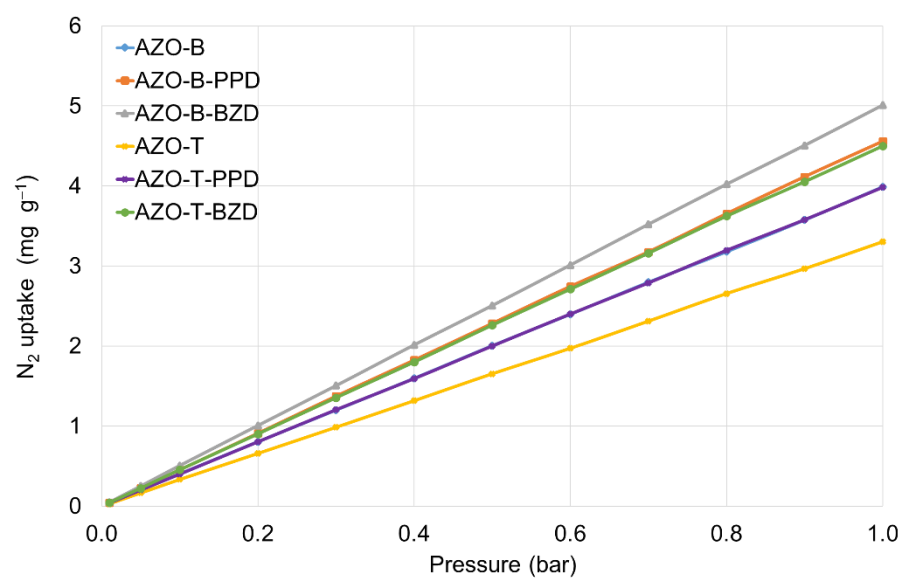


Figure S7. N_2 adsorption isotherms simulated at 298 K.