Supplementary Information (SI) for RSC Advances.

Supplementary Materials

Microwave-assisted reductive homocoupling of aromatic nitro monomers: synthesis of azo-linked porous organic polymers for CO_2 capture

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Contents

1. Synthesis of nitro compounds 1–3

Nitro compound 1

Nitro compound **1** was synthesized by the procedure described in the literature.[1]

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3080; 1669; 1590; 1550; 1514; 1428; 1341; 1106; 846.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm: 8.70–8.68 (m, 3 H), 8.63 (s, 1 H), 8.48–8.41 (m, 10 H).

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 155.5; 152.2; 147.5; 143.6; 140.2; 129.3; 125.9; 121.8; 118.0.

Nitro compound 2

Nitro compound **2** was synthesized by the procedure described in the literature.[2]

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

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 169.3; 149.8; 140.0; 131.0; 123.2.

Nitro compound 3

Nitro compound **3** was synthesized by the procedure described in the literature.[3]

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3103; 3070; 1597; 1513; 1342; 1107.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm: 8.11 (d, 8H, J = 8.9 Hz); 7.37 (d, 8H, J = 8.9 Hz).

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 147.7; 143.7; 141.5; 135.6; 131.4; 124.3.

2. Optimization of microwave conditions for the synthesis of azo-linked polymers

To a 150 mg of compound 1 in 35 mL Pyrex pressure vessel, $NaBH_4$ (38,5 mg, 3 equiv.) as well as DMF (10 mL) were added. After reaction completion (Table S1) water was added (10 mL) to the reaction mixture and the resulting swelling precipitate of brown-red colour was filtered off. It was washed excessively with water and acetone first and then with DMF and THF. The product of each reaction was dried and characterized by IR. In addition, final products AZO-P-M, AZO-T-M and AZO-E-M were also characterized by solid-state ^{13}C CP/MAS NMR spectroscopy and elemental analysis.

Table S1. Optimization of microwave conditions for the synthesis of AZO-P-M from 1 (p = 300 psi, power 300 W)

entry	time / min	T / °C	m / mg	yield / %
1	30	85	-	-
2	30	120	108	92
3	15	120	109	93
4	5	120	75	64
5	5	140	110.3	94

3. Characterization of azo polymers

AZO-P-M

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1590; 1518; 1455; 1423; 1385; 1345; 1105; 1010; 833.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 153.3; 148.0; 140.9; 127.3; 122.9; 115.0.

Elemental analysis: 71.94% C (calc. 79.75); 4.60% H (calc. 4.07); 14.92% N (calc. 16.17).

AZO-T-M

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1582; 1499; 1438; 1407; 1352; 1175; 1008; 815.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 170.2; 153.9; 137.7; 129.1; 123.0; 114.6.

Elemental analysis: 63.67% C (calc. 72.40); 4.16% H (calc. 3.47); 20.47% N (calc. 24.12).

AZO-E-M

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1666; 1592; 1511; 1493; 1446; 1402; 1384; 1341; 1098; 1011; 829.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.5; 146.5; 131.6; 122.1; 114.8.

Elemental analysis: 65.45% C (calc. 81.23); 4.46% H (calc. 4.20); 11.85 %N (calc. 14.57).

4. Synthesis of AZO-P

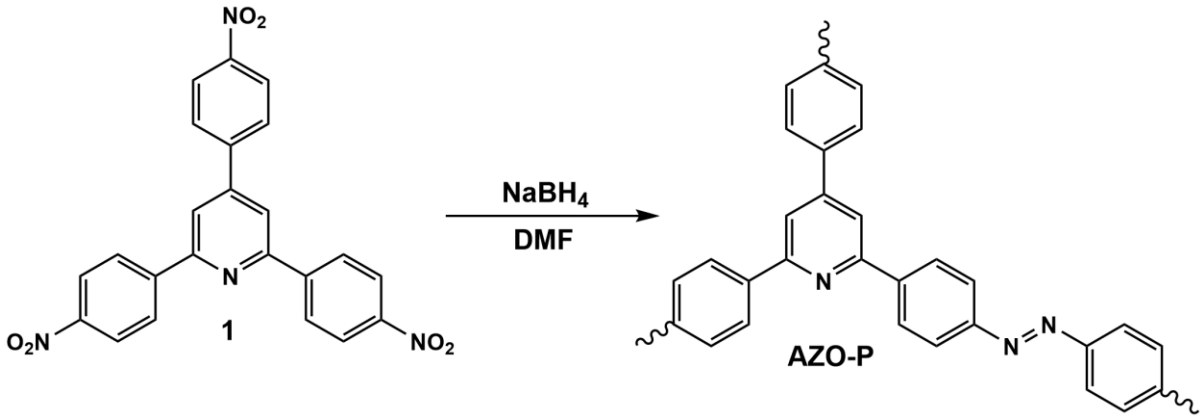


Figure S1. Synthesis of azo polymer AZO-P.

Azo polymer AZO-P was synthesized by the literature procedure described for similar compounds.[4] A solution of $NaBH_4$ (128 mg; 3.39 mmol) in DMF (20 mL) was added dropwise to a mixture of compound 1 (500 mg; 1.13 mmol) and DMF (30 mL). The reaction mixture was heated at 85 °C for 24 h and then filtered and washed with DMF, HCl, water and THF. After drying at 140 °C under vacuum for 5 hours, 311 mg of the red brown solid compound AZO-P was obtained with a reaction yield of 79 %.

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3366; 3036; 1591; 1517; 1454; 1422; 1386; 1356; 1225; 1179; 1010; 832.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 153.1; 148.2; 140.7; 127.6; 122.9; 115.0

Elemental analysis: 73.41 %C (calc. 79.75); 4.52 %H (calc. 4.07); 15.64 %N (calc. 16.17).

5. FT-IR spectra

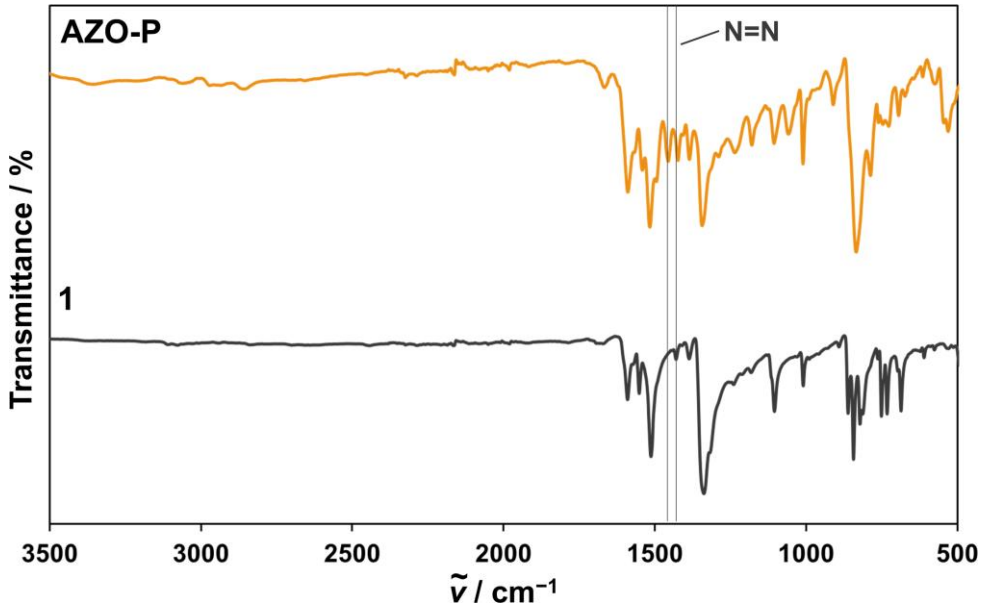
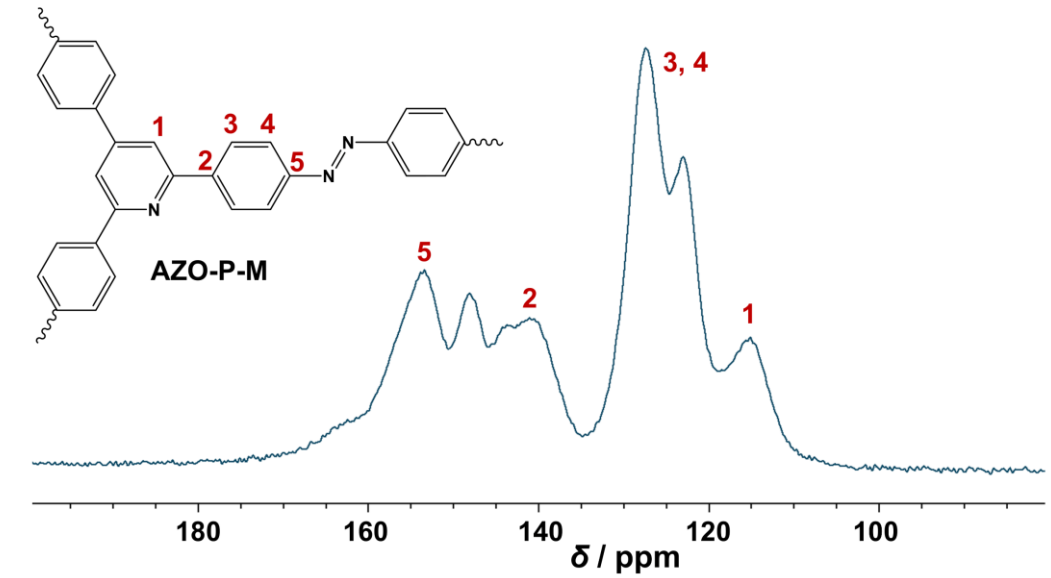


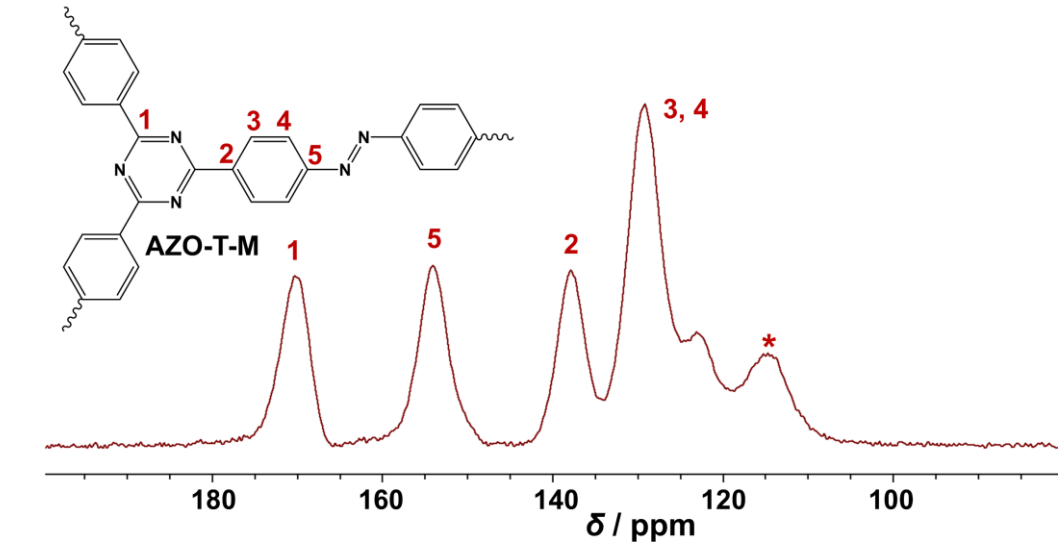
Figure S2. FT-IR spectra of azo polymer AZO-P and compound 1. Signals attributed to the stretching vibrations of the azo (–N=N–) group in polymers are marked with vertical lines.

6. ^{13}C CP/MAS NMR spectra

(a)



(b)



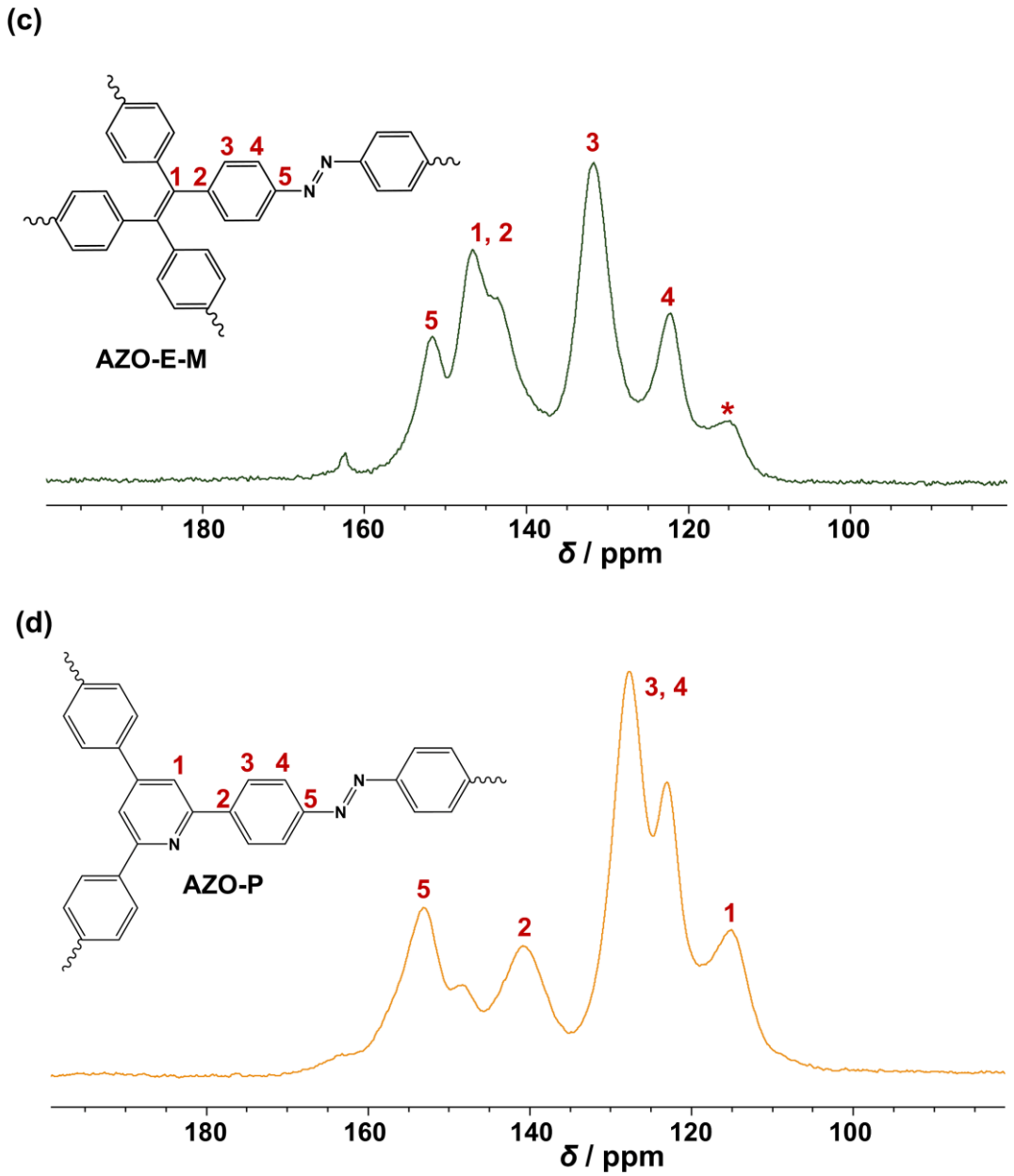


Figure S3. ^{13}C CP/MAS NMR spectra of azo polymers (a) AZO-P-M, (b) AZO-T-M, (c) AZO-E-M and (d) AZO-P.

7. Powder X-ray diffraction

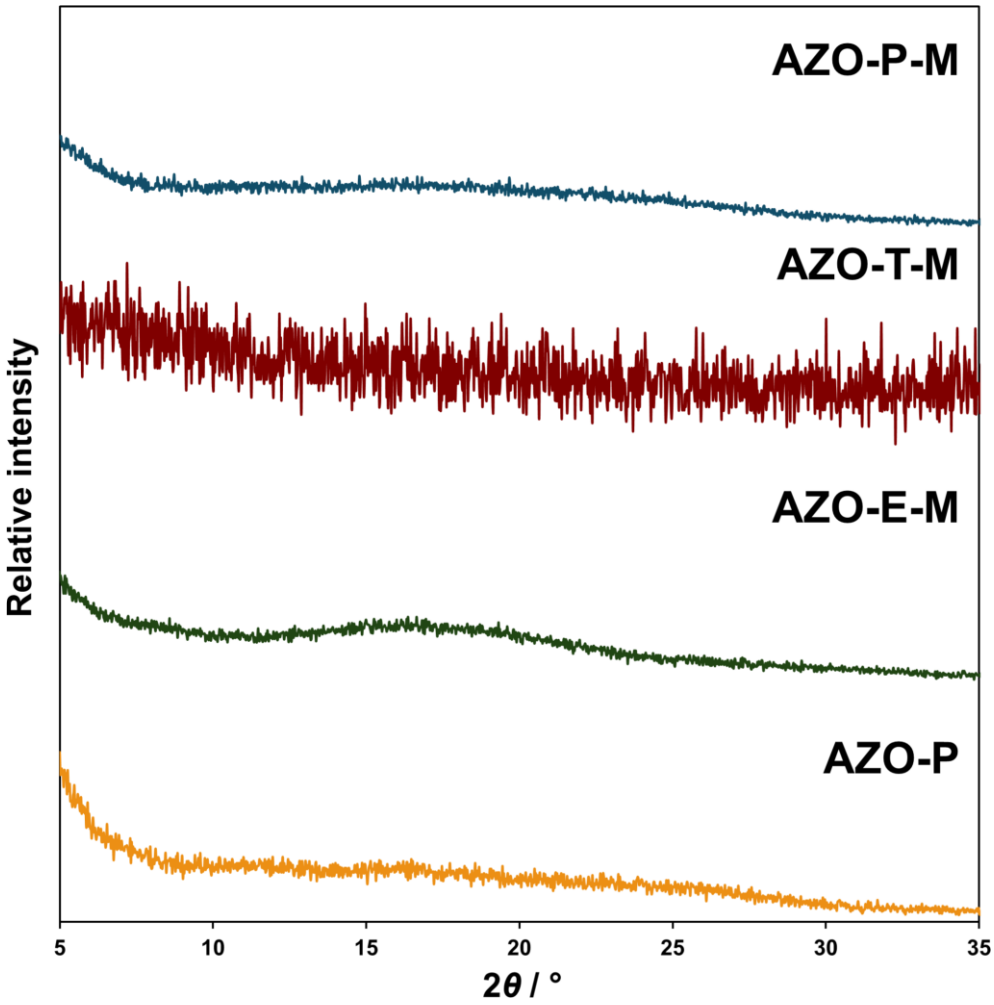
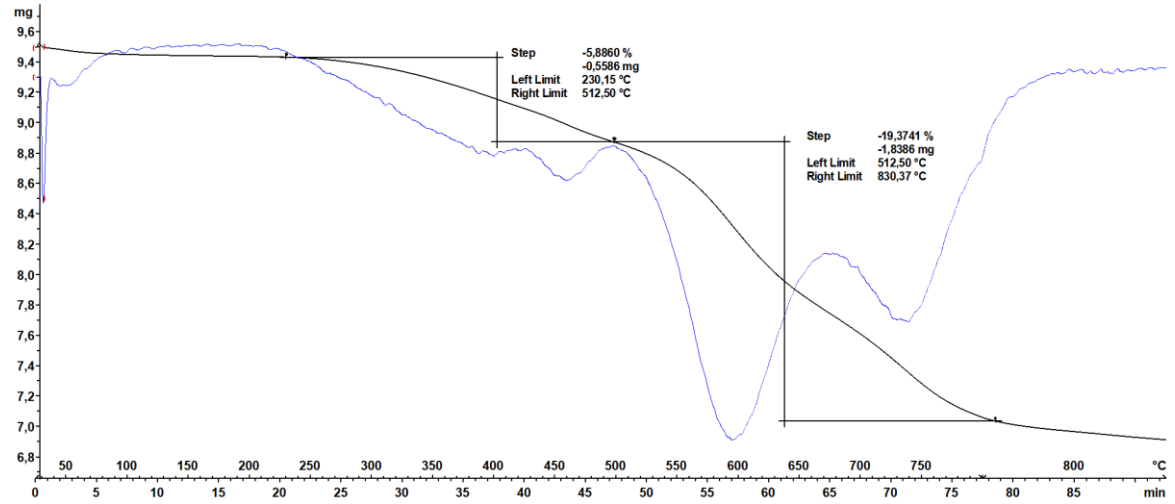
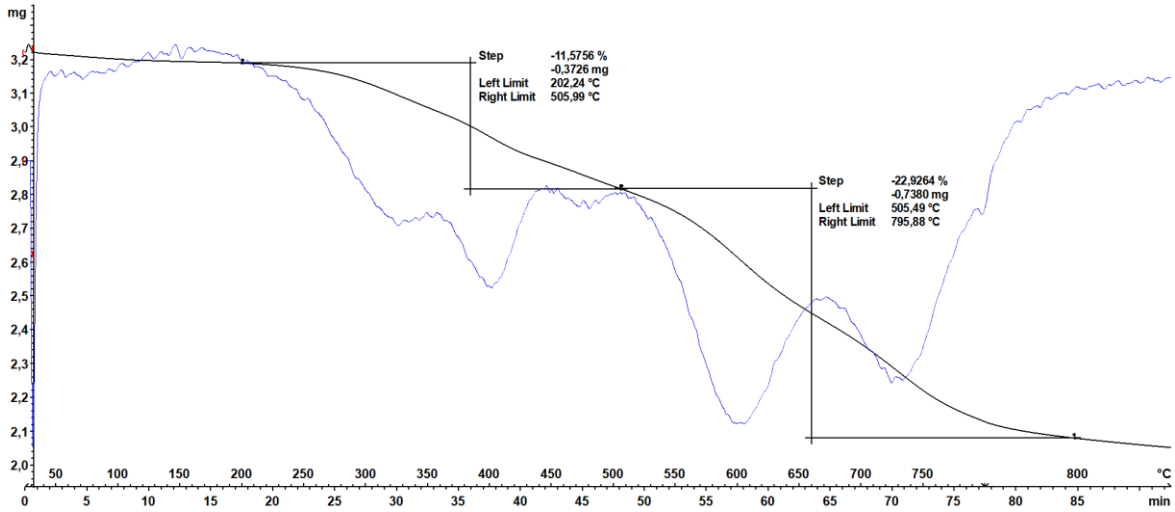


Figure S4. PXRD patterns of AZO-P-M, AZO-T-M, AZO-E-M and AZO-P.

8. Thermogravimetric analysis



(AZO-P)



(AZO-P-M)

Figure S5. TGA (black) and 1st derivative of weight (blue) curves of azo polymers AZO-P and AZO-P-M.

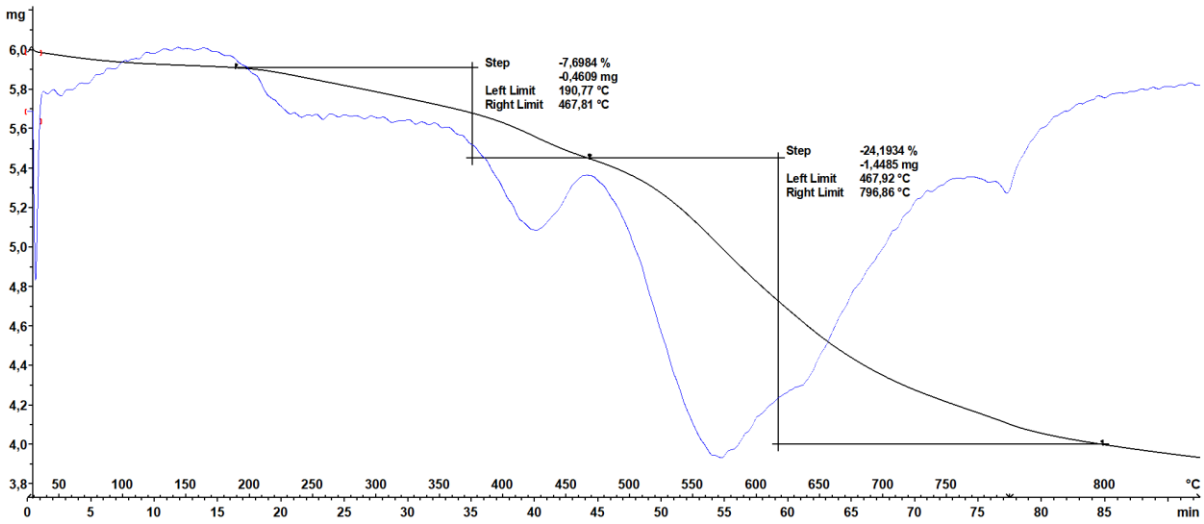


Figure S6. TGA (black) and 1st derivative of weight (blue) curves of azo polymer AZO-T-M.

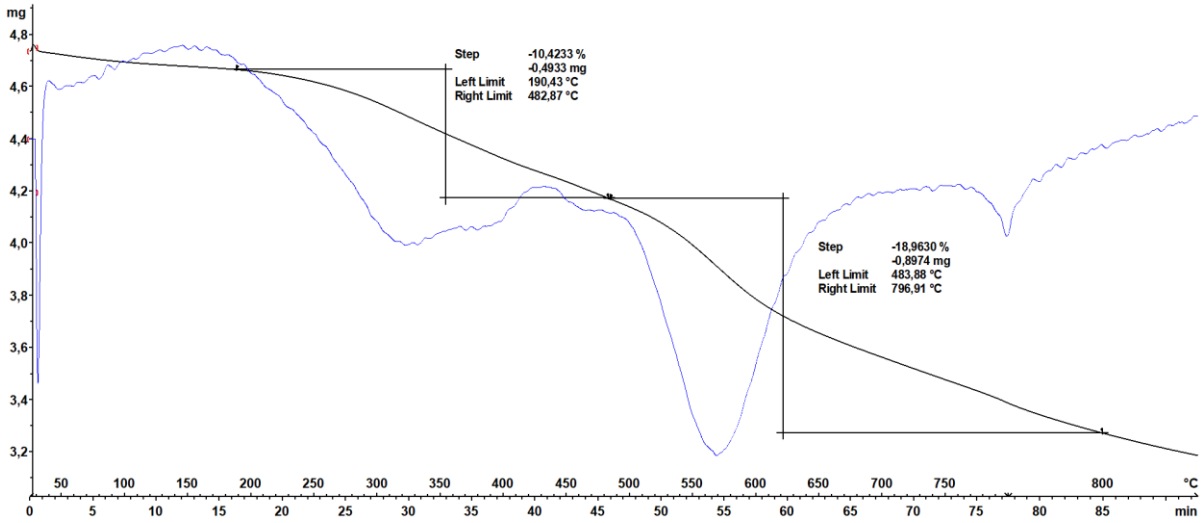


Figure S7. TGA (black) and 1st derivative of weight (blue) curves of azo polymer AZO-E-M.

9. N_2 adsorption-desorption analysis

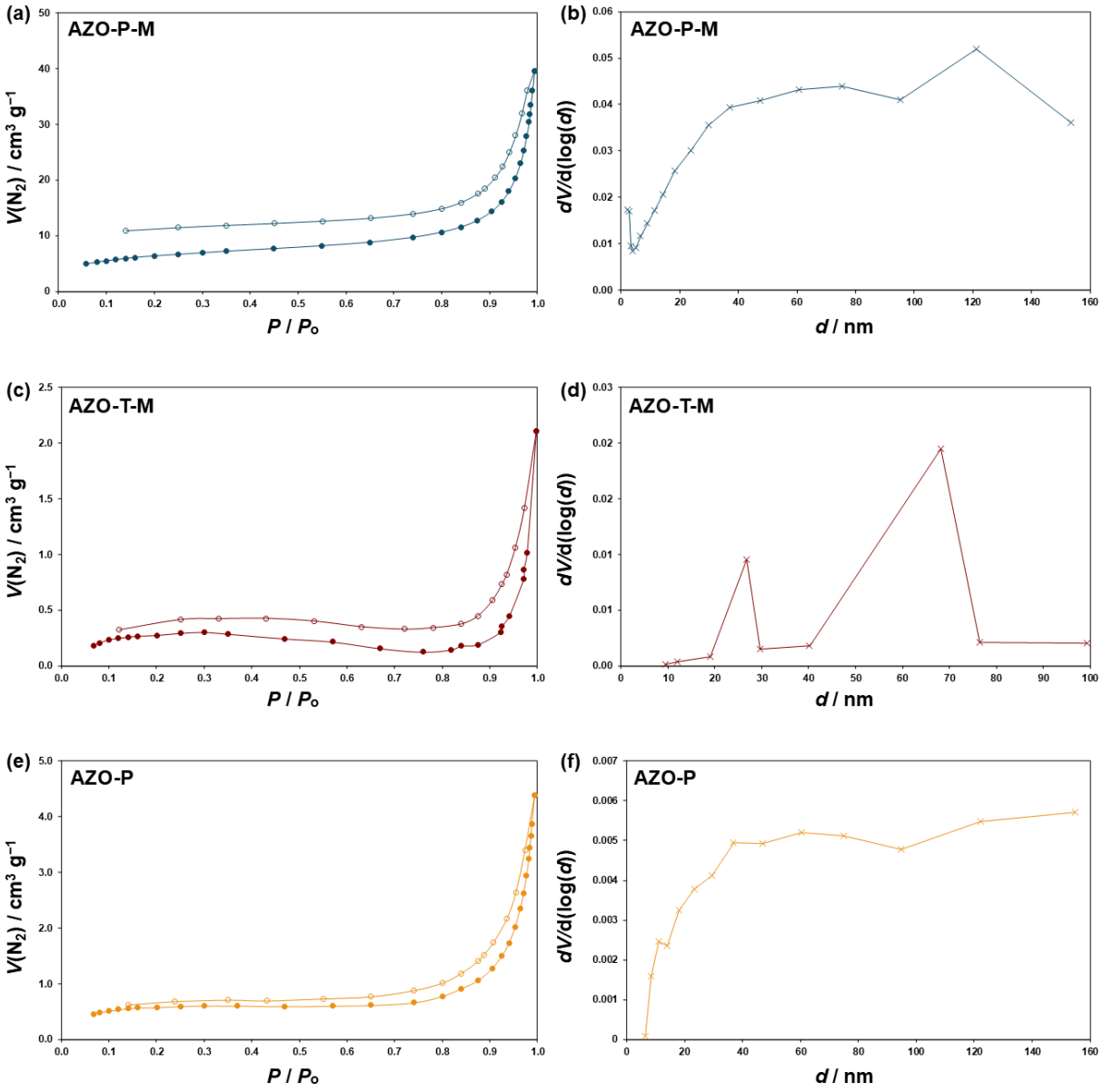


Figure S8. N_2 adsorption-desorption isotherms of (a) AZO-P-M, (c) AZO-T-M and (e) AZO-P measured at 77 K and pore size distributions of (b) AZO-P-M, (d) AZO-T-M and (f) AZO-P.

10. CO_2 sorption

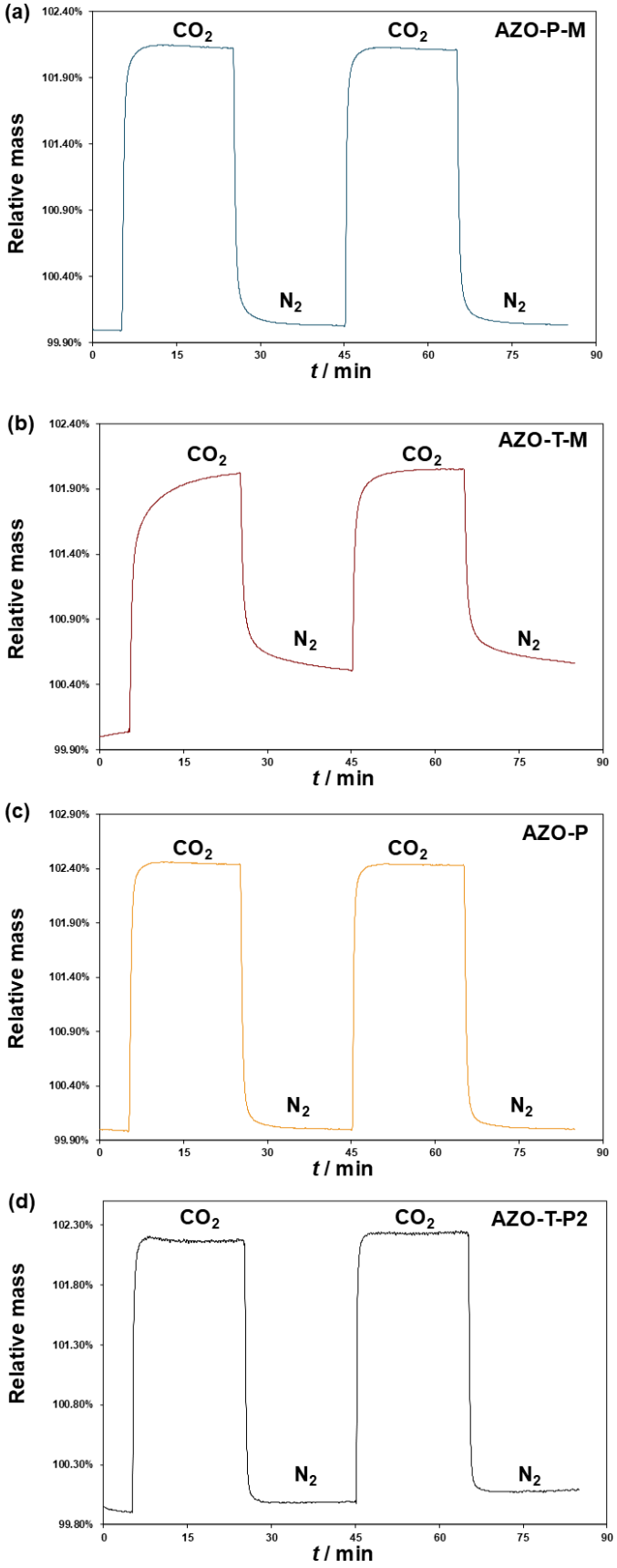


Figure S9. CO_2 adsorption curves of (a) AZO-P-M, (b) AZO-T-M, (c) AZO-P and (d) AZO-T-P2.

11. References

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3 S. A. Ceballos, S. Gil and A. M. Costero, *RSC Adv.*, 2017, **7**, 14279–14282.

4 J. X. Zhou, X. S. Luo, X. Liu, Y. Qiao, P. Wang, D. Mecerreyes, N. Bogliotti, S. L. Chen and M. H. Huang, *J. Mater. Chem. A*, 2018, **6**, 5608–5612.