Synergistic experimental and computational investigation of azo-linked porphyrin-based porous organic polymers for CO_2 capture

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Supplementary Materials

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1. Synthesis

*Synthesis of 5,10,15,20-tetrakis(4-nitrophenyl)-21H,23H-porphyrin (**TNPPR**)*

TNPPR was synthesized by the procedures described in the literature.[1] 4-Nitrobenzaldehyde (5.5 g; 36.4 mmol) and acetic anhydride (6 mL, 63.5 mmol) were dissolved in propionic acid (150 mL). The reaction mixture was heated to reflux, and then pyrrole (2.5 mL, 36.0 mmol) was added dropwise. After refluxing for 30 min, the resulting mixture was cooled to give a residue which was collected by filtration and washed with H_2O and methanol. The resulting black powder was dissolved in pyridine (40 mL) and refluxed for 1 h. After cooling, the precipitate was collected by filtration and washed with acetone. 1.17 g of the purple powder **TNPPR** was obtained with a reaction yield of 16%.

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3321; 1594; 1557; 1514; 1474; 1400; 1343; 1107; 966; 863; 845.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm: 8.92 (s, 8H); 8.70 (d, 8H, J = 8.7 Hz); 8.53 (d, 8H, J = 8.7 Hz); −2.91 (s, 2H).

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 150.0; 147.3; 143.6; 134.2; 130.1; 119.6; 117.2.

*Synthesis of 5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphyrin (**TAPPR**)*

TAPPR was synthesized by a modified literature procedure.[1] **TNPPR** (1.0 g; 1.3 mmol) was dissolved in 122 mL of hot hydrochloric acid (70 °C), and then tin(II) chloride dihydrate (4.36 g; 19.3 mmol) was added to the mixture. The reaction mixture was heated for 3 hours at a temperature of 70 °C. At the end of the reaction, the reaction mixture was cooled to 0 °C, neutralized with concentrated ammonia and filtered. The precipitate was transferred to a Soxhlet extractor and continuously extracted using acetone. At the end of the extraction, the filtrate was evaporated under reduced pressure. 0.46 g of the dark purple powder product **TAPPR** was obtained with a reaction yield of 54%.

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3321; 3207; 2967; 1701; 1601; 1512; 1467; 1284; 1176; 965; 800.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm: 8.87 (s, 8H); 7.86 (d, 8H, J = 8.3 Hz); 7.01 (d, 8H, J = 8.3 Hz), 5,60 (s, 8H), −2.73 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6) δ / ppm: 149.0; 136.1; 129.3; 121.1; 113.3.

*Synthesis of 5,10,15,20-tetrakis(4-nitrophenyl)-21H,23H-porphyrin-Zn(II) (**TNPPR-Zn**)*

TNPPR-Zn was synthesized by a modified literature procedure.[2] The compounds **TNPPR** (0.40 g; 0.5 mmol) and zinc(II) acetate dihydrate (0.44 g; 2.0 mmol) were dissolved in a mixture of solvents: methanol (20 mL), chloroform (90 mL) and DMF (30 mL). The reaction mixture was heated to 80 °C under nitrogen atmosphere. The mixture continued to reflux for 48 hours under N_2 atmosphere. At the end of the reaction, the reaction mixture was cooled and extracted three times with 100 mL of water. The organic fractions were dried over anhydrous Na_2SO_4. After evaporation of the solvent, 0.30 g of the dark purple product **TNPPR-Zn** was obtained with a reaction yield of 69%.

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1652; 1590; 1511; 1336; 1205; 1106; 994; 846; 794; 481.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm: 8.84 (s, 8H); 8.67 (d, 8H, J = 8.7 Hz), 8.47 (d, 8H, J = 8.7 Hz).

^{13}C NMR (100 MHz, DMSO-d_6) δ / ppm: 149.7; 147.8; 132.7; 122.5; 119.4.

*Synthesis of 2,4,6-tris(4-aminophenyl)pyridine (**TAPP**)*

TAPP was synthesized by a modified literature procedure.[3] 4-Nitrobenzaldehyde (2.27 g; 0.015 mol), 4-nitroacetophenone (4.96 g; 0.03 mol) and ammonium acetate (15 g, 0.145 mol) were dissolved in 38 mL of glacial acetic acid. The reaction mixture was heated for 3 hours at a boiling temperature. At the end of the reaction, the mixture was cooled to room temperature and filtered. The precipitate was washed with acetic acid, cold ethanol and hot DMF. After drying, 3.03 g of the compound 2,4,6-tris(4-nitrophenyl)pyridine (**TNPP**) was isolated as a light yellow solid with a reaction yield of 50%.

TNPP (500 mg; 1.13 mmol) and 10% Pd/C (109 mg) were dissolved in a solvent mixture of 1,4-dioxane (14.4 mL) and ethanol (7.2 mL) and the mixture was heated to reflux under a nitrogen atmosphere. Hydrazine hydrate (2.44 mL) was added dropwise to the reaction mixture, and the mixture continued to reflux for another 18 hours. After the end of the reaction, the mixture was filtered. After evaporation of the solvent and drying of the precipitate, 349 mg of the yellow powder product **TAPP** was obtained with a reaction yield of 88%.

IR (ATR) $\tilde{\upsilon}$ / cm^{-1}: 3401; 3299; 3203; 1594; 1540.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm: 7.97 (m, 4H); 7.68 (m, 4H); 6.68 (m, 6H); 5.44 (s, 2H); 5.37 (s, 4H).

^{13}C NMR (100 MHz, DMSO-d_6) δ / ppm: 156.7; 150.3; 150.1; 149.1; 128.0; 127.4; 125.4; 114.4; 114.0; 111.6.

1.1. Synthesis of azo-linked porphyrin-based POPs APP-1–APP-8

*Synthesis of **APP-1**–**APP-6***

Azo polymers **APP-1**–**APP-6** were synthesized by a similar procedure described in the literature.[4] The syntheses were carried out according to the same general procedure, differing only in the starting amino compounds (Table 1): compound **TNPPR** (238 mg; 0.29 mmol), amino compound (0.29 mmol) and KOH (163 mg; 2.9 mmol) were dissolved in DMF (15 mL). The reaction mixture was heated to reflux in a nitrogen atmosphere and continued to reflux in an inert atmosphere for 24 hours. After cooling to room temperature, the reaction mixture was filtered and the precipitate was washed with water, DMF, acetone, THF and methanol. The precipitate was then transferred to a Soxhlet extractor and continuously washed with acetone (24 hours), chloroform (24 hours) and methanol (24 hours). The obtained solid products were dried at 140 °C under vacuum for 5 hours.

Table S1. List of starting amino compounds, masses and colors of isolated azo polymers and yields of reactions.

Azo polymer	Amino compound	Mass of Polymer (mg)	Color of polymer	Yield of reaction (%)
APP-1	4,4'-diaminodiphenylmethane	170	black	66
APP-2	4,4'-ethylenedianiline	180	black	69
APP-3	4,4-diaminodiphenyl sulfide	250	dark brown	97
APP-4	4,4'-diaminobenzophenone	233	black	92
APP-5	melamine	120	dark brown	53
APP-6	TAPP	241	dark brown	82

APP-1

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1596; 1517; 1471; 1400; 1346; 1283; 1179; 966; 859; 796; 731.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 150.9; 144.3; 130.6; 118.0; 112.8.

Elemental analysis: 69.99 %C (calc. 79.52); 4.23 %H (calc. 4.21); 15.18 %N (calc. 16.27).

APP-2

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1597; 1515; 1470; 1400; 1347; 1283; 1179; 966; 859; 796; 732.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.8; 144.6; 130.9; 118.1; 114.1.

Elemental analysis: 68.65 %C (calc. 79.61); 4.46 %H (calc. 4.38); 14.94 %N (calc.16.01).

APP-3

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3380; 3313; 1595; 1516; 1470; 1399; 1346; 1283; 1179; 965; 859; 795.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.7; 144.4; 130.3; 118.5; 112.7.

Elemental analysis: 55.04 %C (calc. 76.52); 2.99 %H (calc. 3.90); 11.64 %N (calc. 15.93).

APP-4

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3313; 1595; 1518; 1470; 1400; 1346; 1179; 966; 859; 795.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 152.0; 144.4; 130.7; 118.3; 113.6.

Elemental analysis: 87.75 %C (calc. 78.25); 4.96 %H (calc. 3.92); 18.59 %N (calc. 16.01).

APP-5

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3315; 1596; 1516; 1470; 1400; 1346; 1283; 1179; 966; 859; 795; 730.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 152.1; 144.2; 130.2; 117.5; 113.0.

Elemental analysis: 63.27 %C (calc. 71.38); 4.18 %H (calc. 3.82); 13.30 %N (calc. 24.80).

APP-6

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3316; 1598; 1515; 1470; 1400; 1347; 1283; 1179; 966; 859; 796.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 151.4; 144.4; 130.5; 118.2; 113.6.

Elemental analysis: 55.29 %C (calc. 79.43); 3.03 %H (calc. 3.98); 11.60 %N (calc. 15.59).

*Synthesis of **APP-7a***

Azo polymer **APP-7a** was synthesized by a similar procedure described in the literature.[5] **TAPPR** (0.135 g; 0.2 mmol) was dissolved in 22 mL solvent mixture of THF/toluene = 1:1. In the reaction mixture were added CuBr (19.0 mg; 0.132 mmol) and pyridine (80.7 mg; 1.02 mmol). The mixture was stirred 24 h at room temperature, 12 h at 60 °C and 12 h at 80 °C and then filtered and washed with THF and water. The solid product was soaked in 100 mL of 4M HCl for 24 h and then filtered and washed with water, 1M NaOH (200 mL), water and ethanol. After drying at 140 °C under vacuum for 5 h, 89 mg of a dark red solid was obtained (yield 67%).

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 3335; 1605; 1503; 1471; 1402; 1344; 1281; 1177; 998; 797; 714.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 150.2; 140.4; 122.7; 112.5.

Elemental analysis: 68.08 %C (calc. 77.91); 13.60 %N (calc. 18.17); 4.88 %H (calc. 3.92).

*Synthesis of **APP-7b***

Azo polymer **APP-7b** was synthesized by the literature procedure described for similar compounds.[6] A solution of $NaBH_4$ (95 mg; 2.52 mmol) in DMF (20 mL) was added dropwise

to a mixture of **TNPPR** (500 mg; 0.63 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, 250 mg of the dark purple solid compound **AZO-1** was obtained with a reaction yield of 51%

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1592; 1516; 1451; 1398; 1342; 1282; 1178; 964; 845; 793; 708.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 146.9; 131.4; 119.9.

Elemental analysis: 53.62 %C (calc. 77.91); 3.27 %H (calc. 3.92); 11.50 %N (calc. 18.17).

*Synthesis of **APP-8***

Azo polymer **APP-8** was prepared by a similar procedure described in the literature.[7] **TNPPR-Zn** (0.30, 0.35 mmol) was dissolved in a mixture of THF (7 mL) and DMF (8 mL). The solution of NaOH (0.227 g) in 1.7 mL of de-ionized water and zinc powder (0. 208 g; 3.2 mmol) were added to the reaction mixture. The reaction mixture was heated at 65 °C for 36 h. After cooling to room temperature, the mixture was poured into 100 mL of 2M HCl and stirred for 1 h. The solid was filtered off and washed with water, acetone and THF on the sinter funnel and then transferred to a Soxhlet extractor and continuously washed with water (48 h) and THF (48 h). After drying at 140 °C under vacuum for 5 h, 110 mg of a black solid product was obtained (yield 43%).

IR (ATR) $\tilde{\nu}$ / cm^{-1}: 1592; 1514; 1447; 1399; 1337; 1280; 1177; 993; 791; 715; 528.

^{13}C CP/MAS NMR (400 MHz) δ / ppm: 148.3; 131.9; 119.8.

Elemental analysis: 65.41 %C (calc. 77.37); 4.31 %H (calc. 4.81); 13.54 %N (calc. 10.02).

2. FT-IR spectra

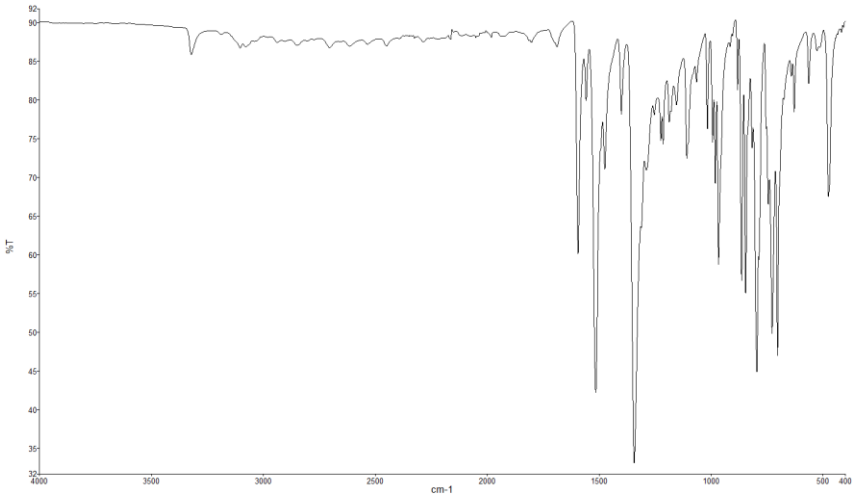


Figure S1. FT-IR spectrum of **TNPPR**.

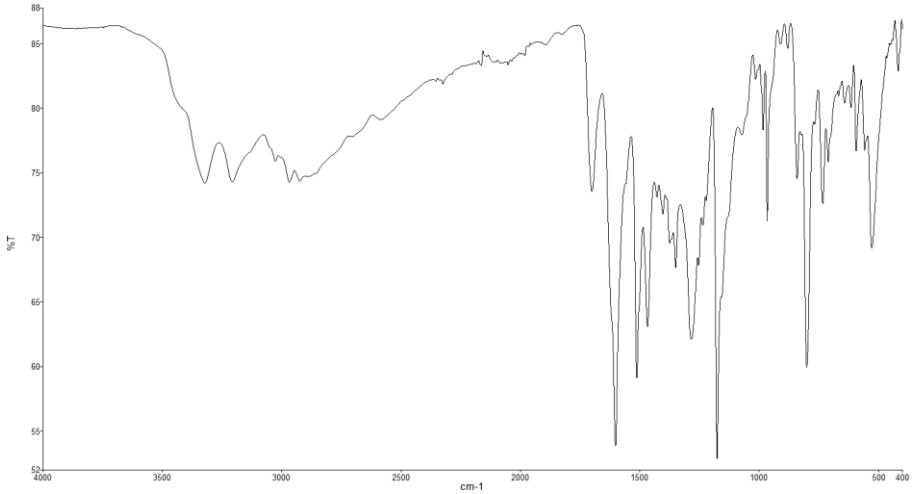


Figure S2. FT-IR spectrum of **TAPPR**.

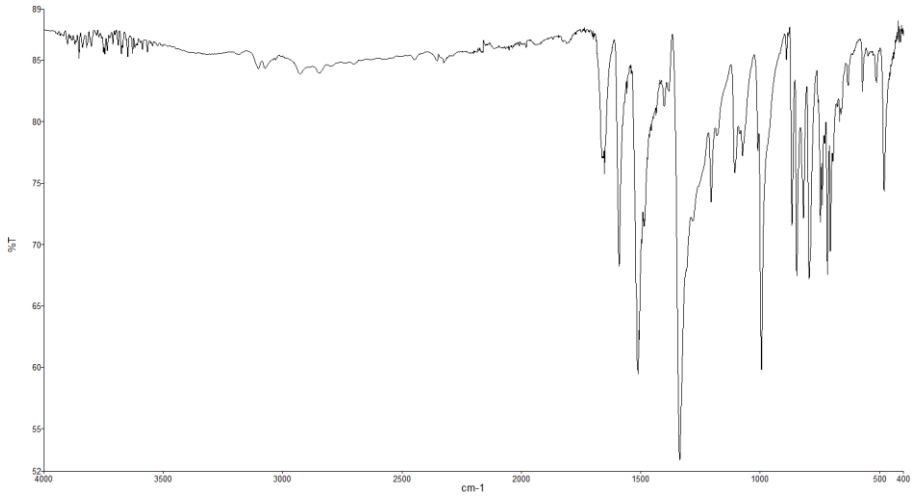


Figure S3. FT-IR spectrum of **TNPPR-Zn**.

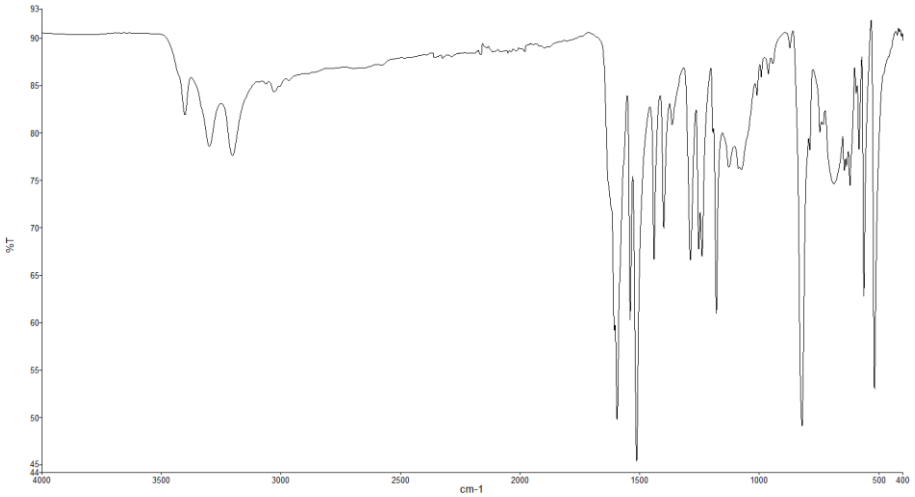


Figure S4. FT-IR spectrum of **TAPP**.

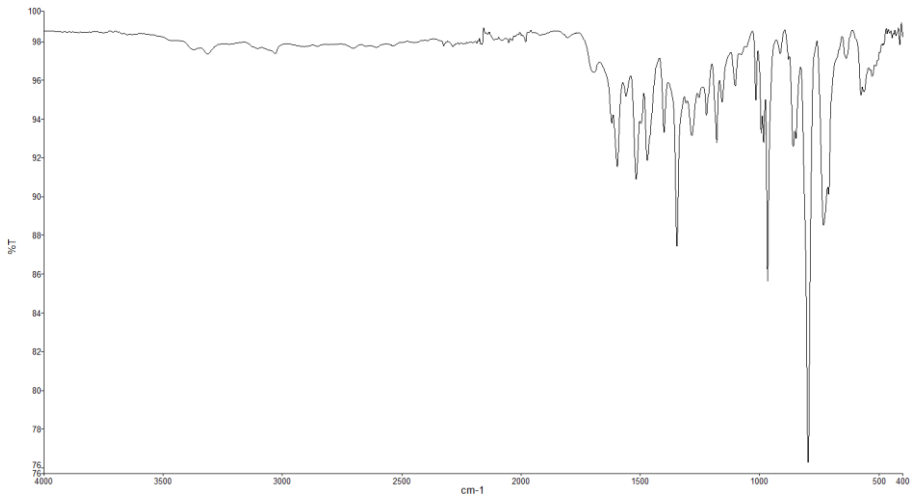


Figure S5. FT-IR spectrum of **APP-1**.

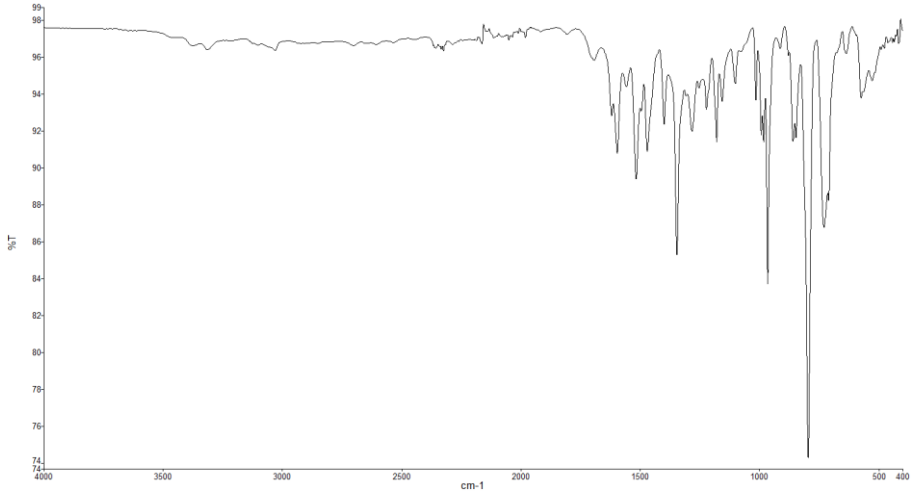


Figure S6. FT-IR spectrum of **APP-2**.

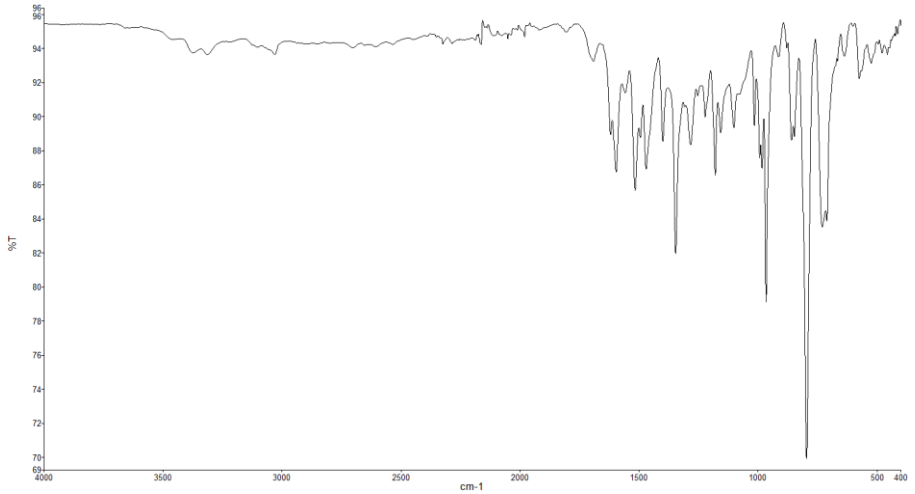


Figure S7. FT-IR spectrum of **APP-3**.

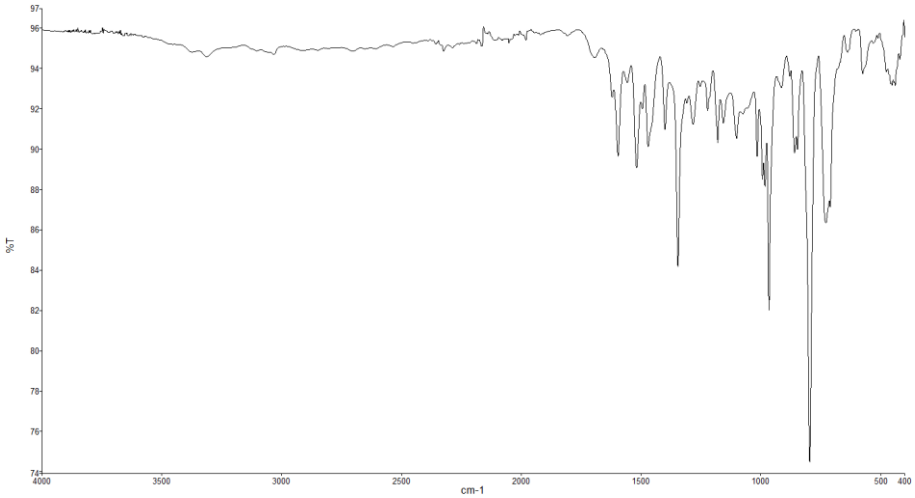


Figure S8. FT-IR spectrum of **APP-4**.

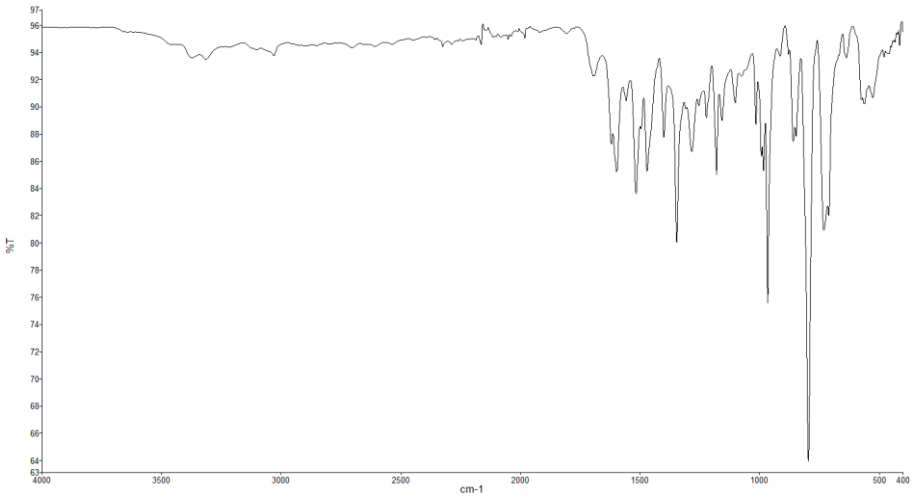


Figure S9. FT-IR spectrum of **APP-5**.

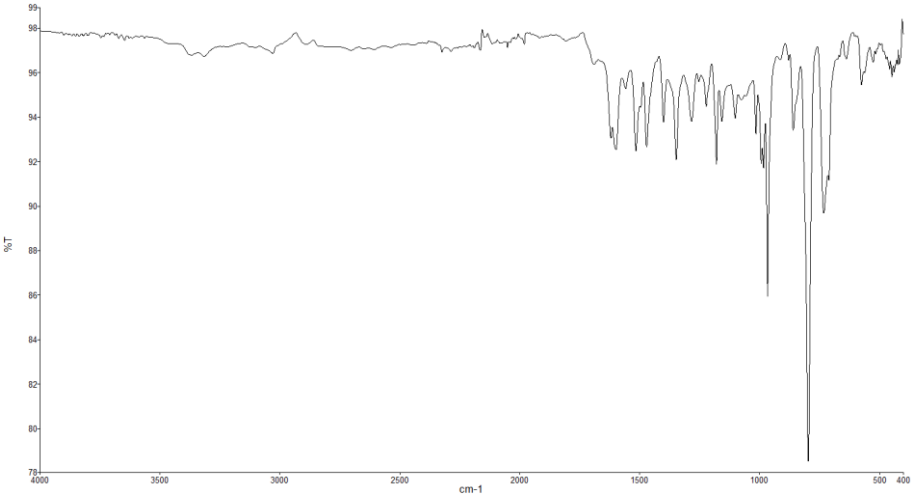


Figure S10. FT-IR spectrum of **APP-6**.

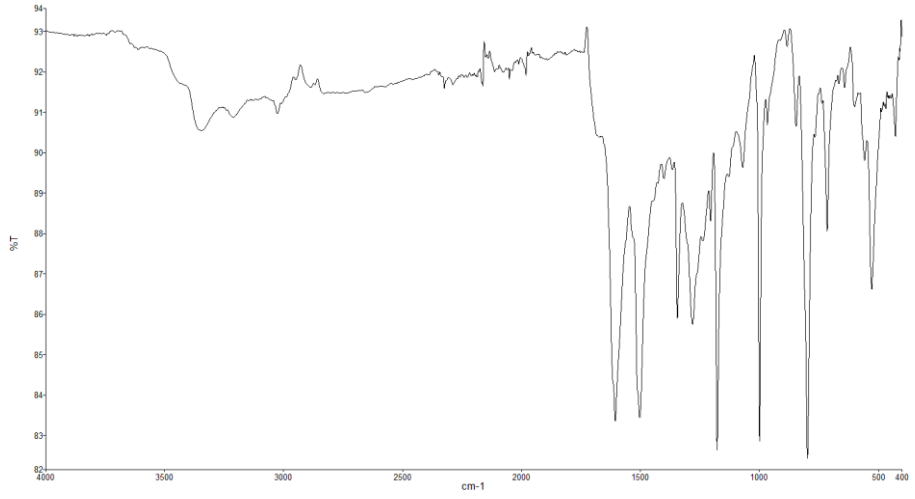


Figure S11. FT-IR spectrum of **APP-7a**.

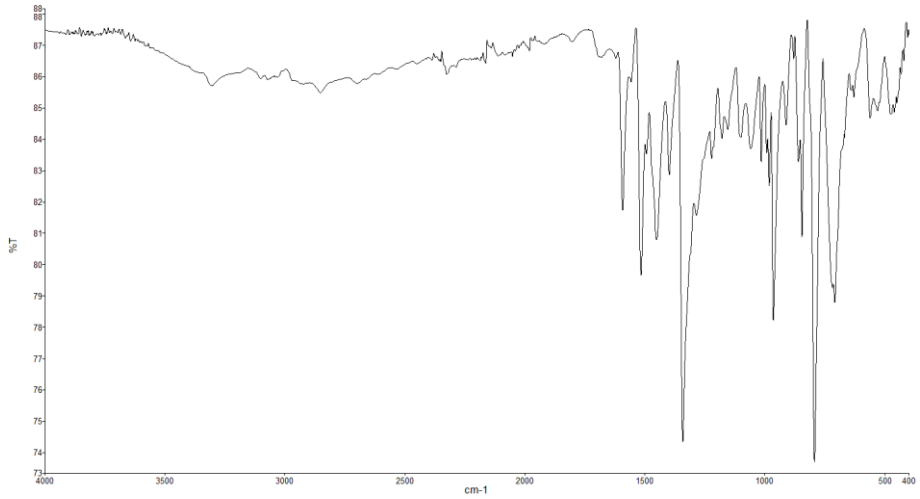


Figure S12. FT-IR spectrum of **APP-7b**.

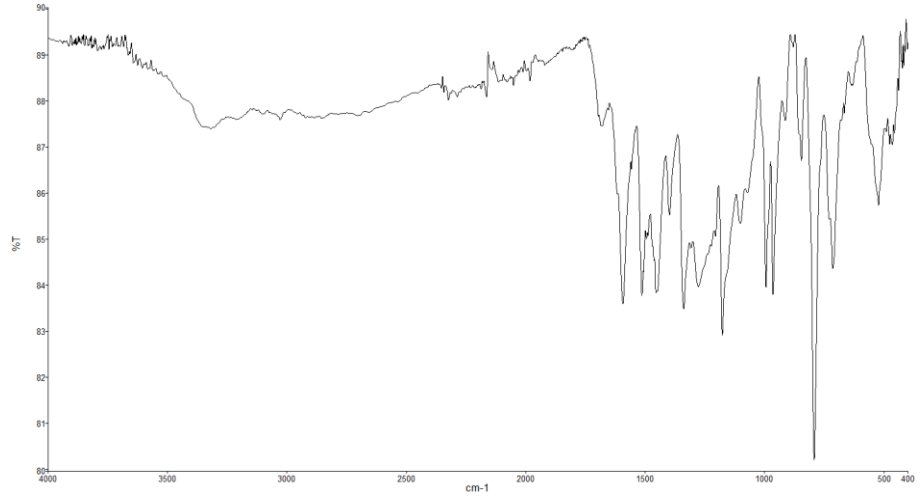


Figure S13. FT-IR spectrum of **APP-8**.

3. NMR spectra

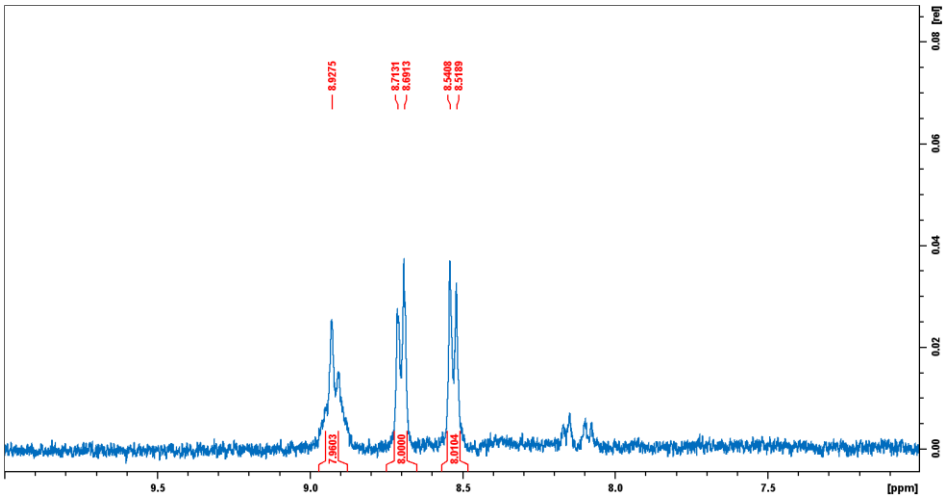


Figure S14. ^{1}H NMR spectrum of **TNPPR**.

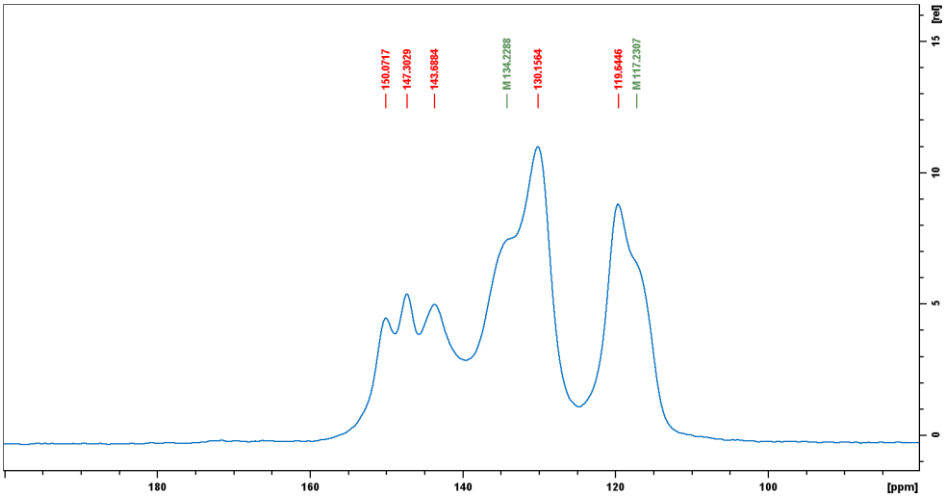


Figure S15. ^{13}C CP/MAS NMR spectrum of **TNPPR**.

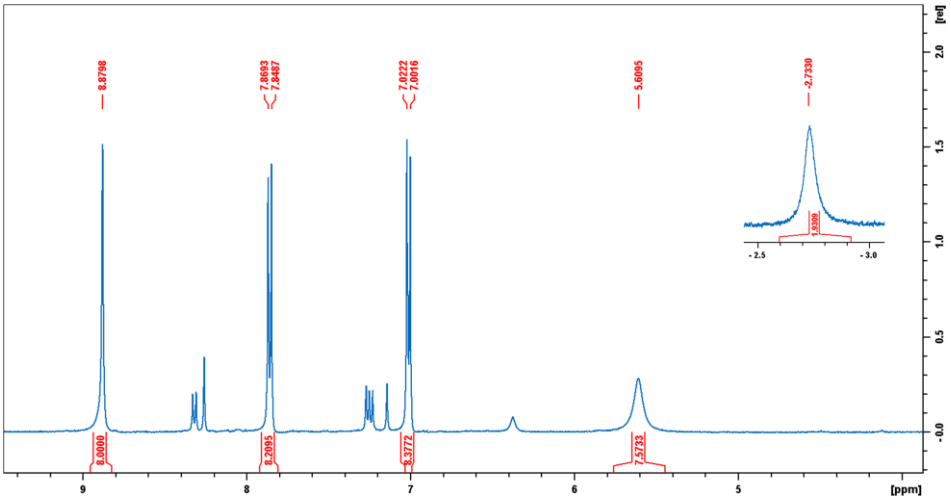


Figure S16. ^{1}H NMR spectrum of **TAPPR**.

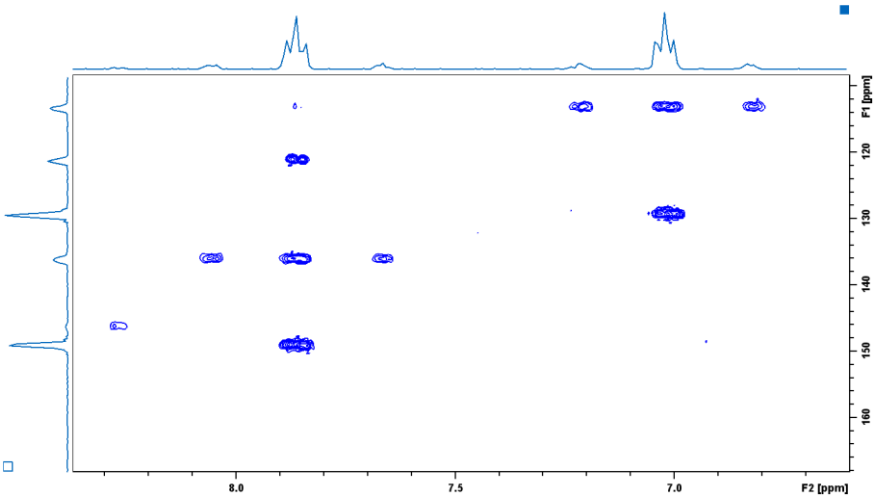


Figure S17. ^{1}H-^{13}C HMBC spectrum of **TAPPR**.

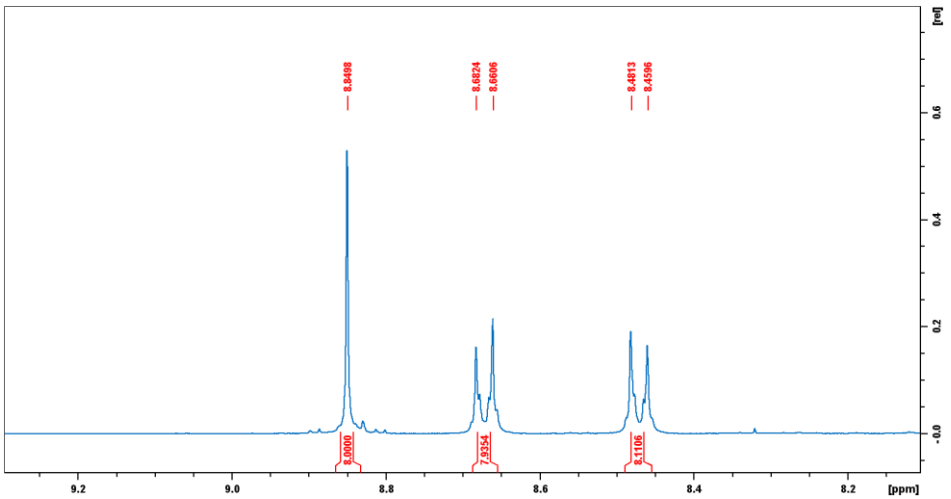


Figure S18. ^{1}H NMR spectrum of **TNPPR-Zn**.

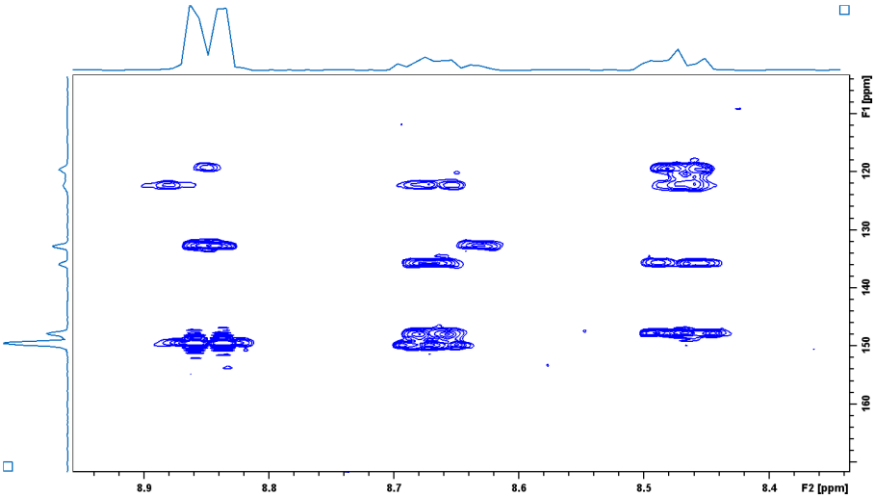


Figure S19. ^{1}H-^{13}C HMBC spectrum of **TNPPR-Zn**.

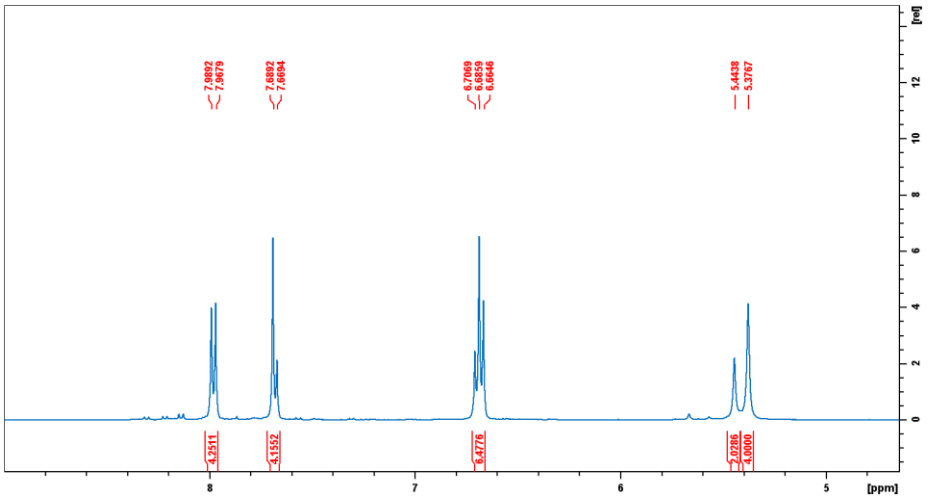


Figure S20. ^{1}H NMR spectrum of **TAPP**.

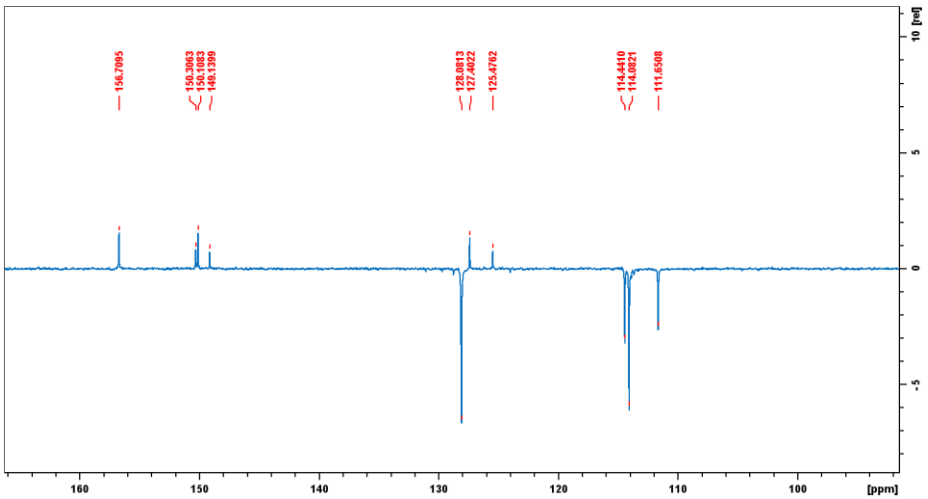


Figure S21. ^{13}C NMR spectrum of **TAPP**.

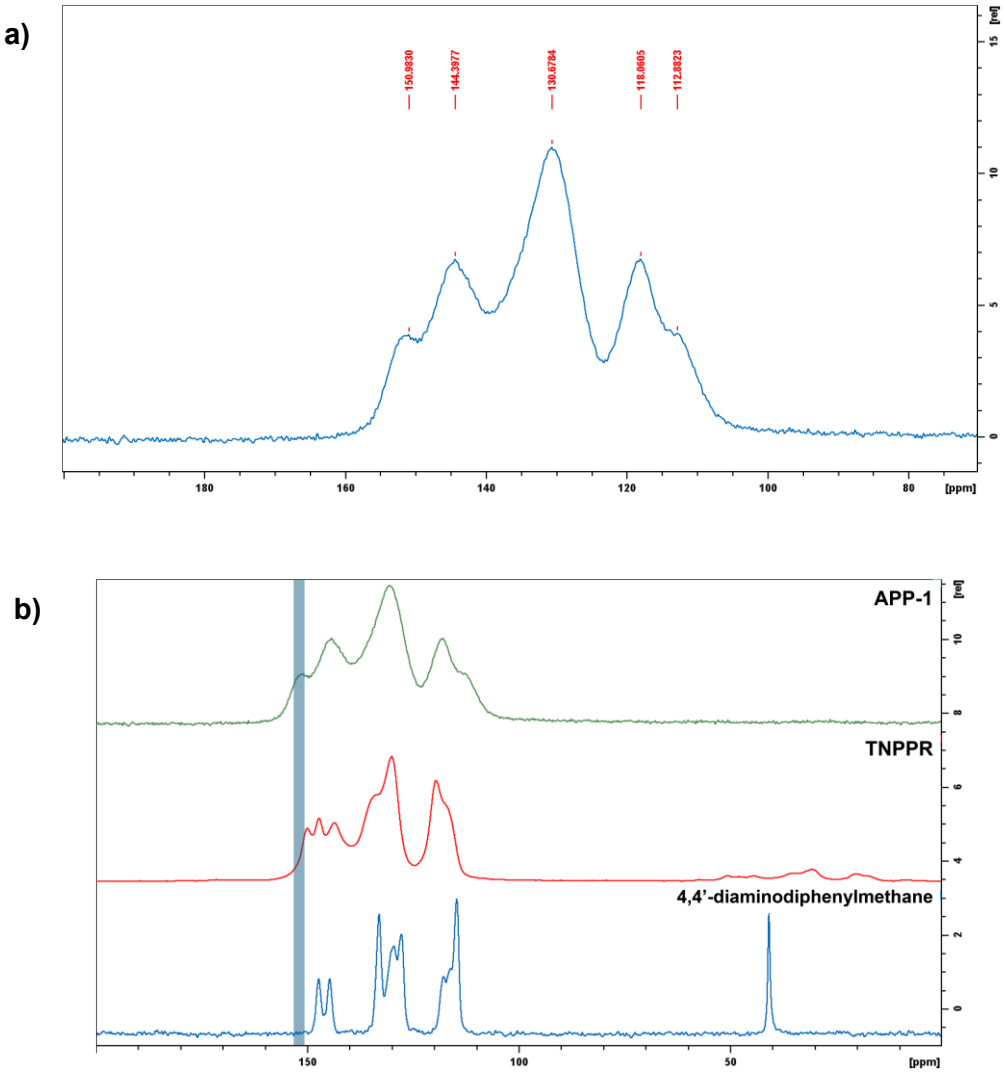
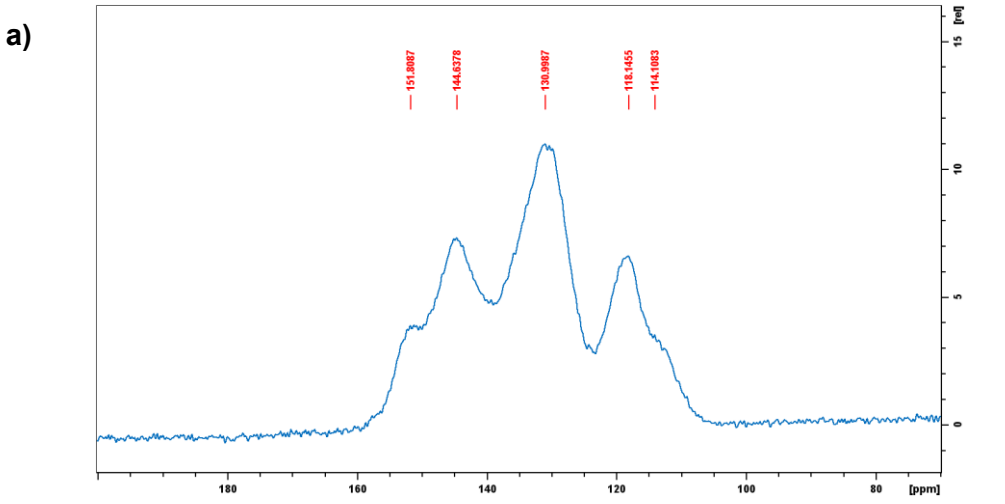


Figure S22. (a) Aromatic region of ^{13}C CP/MAS NMR spectrum of **APP-1** and (b) comparison of ^{13}C CP/MAS NMR spectra of **APP-1**, **TNPPR** and 4,4'-diaminodiphenylmethane.



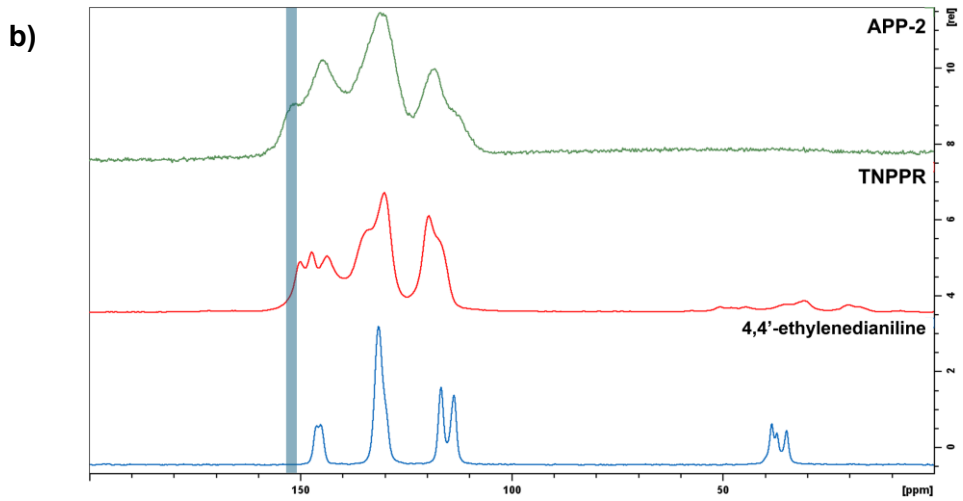


Figure S23. (a) Aromatic region of ^{13}C CP/MAS NMR spectrum of **APP-2** and (b) comparison of ^{13}C CP/MAS NMR spectra of **APP-2**, **TNPPR** and 4,4'-ethylenedianiline.

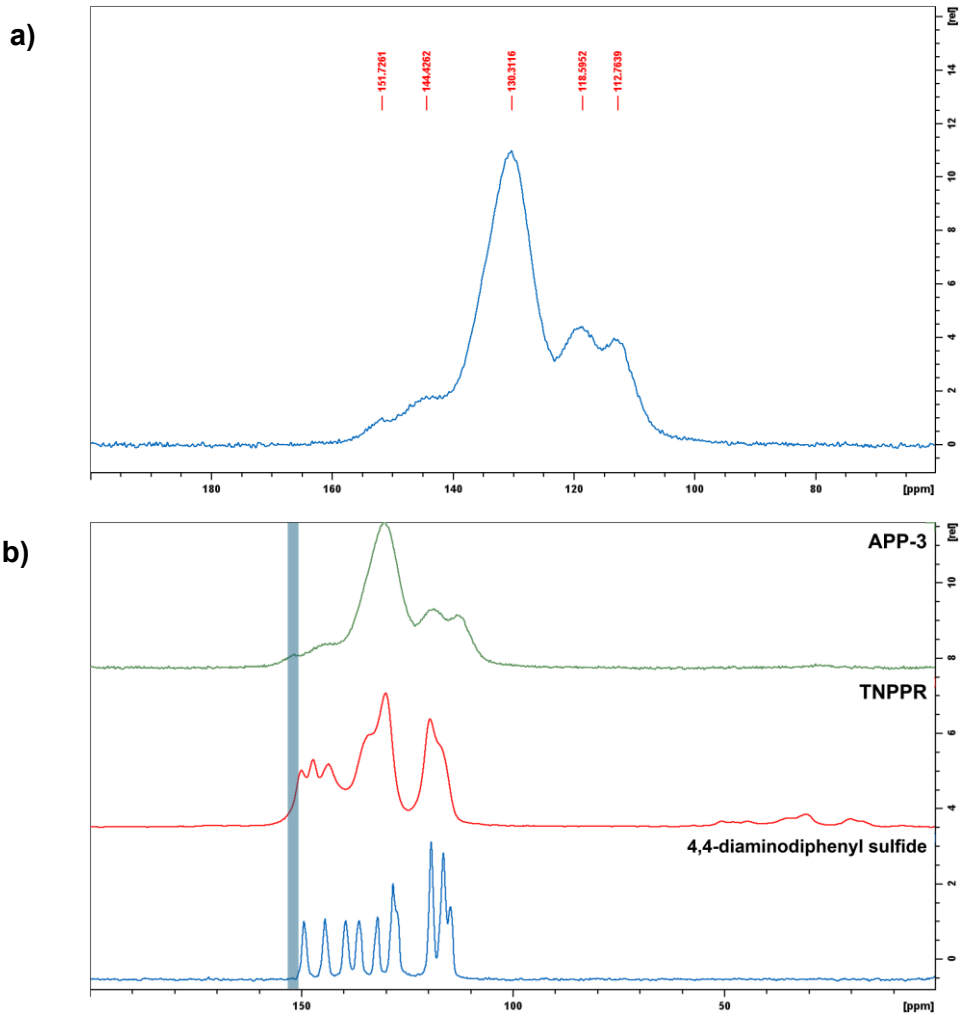


Figure S24. (a) Aromatic region of ^{13}C CP/MAS NMR spectrum of **APP-3** and (b) comparison of ^{13}C CP/MAS NMR spectra of **APP-3**, **TNPPR** and 4,4-diaminodiphenyl sulfide.

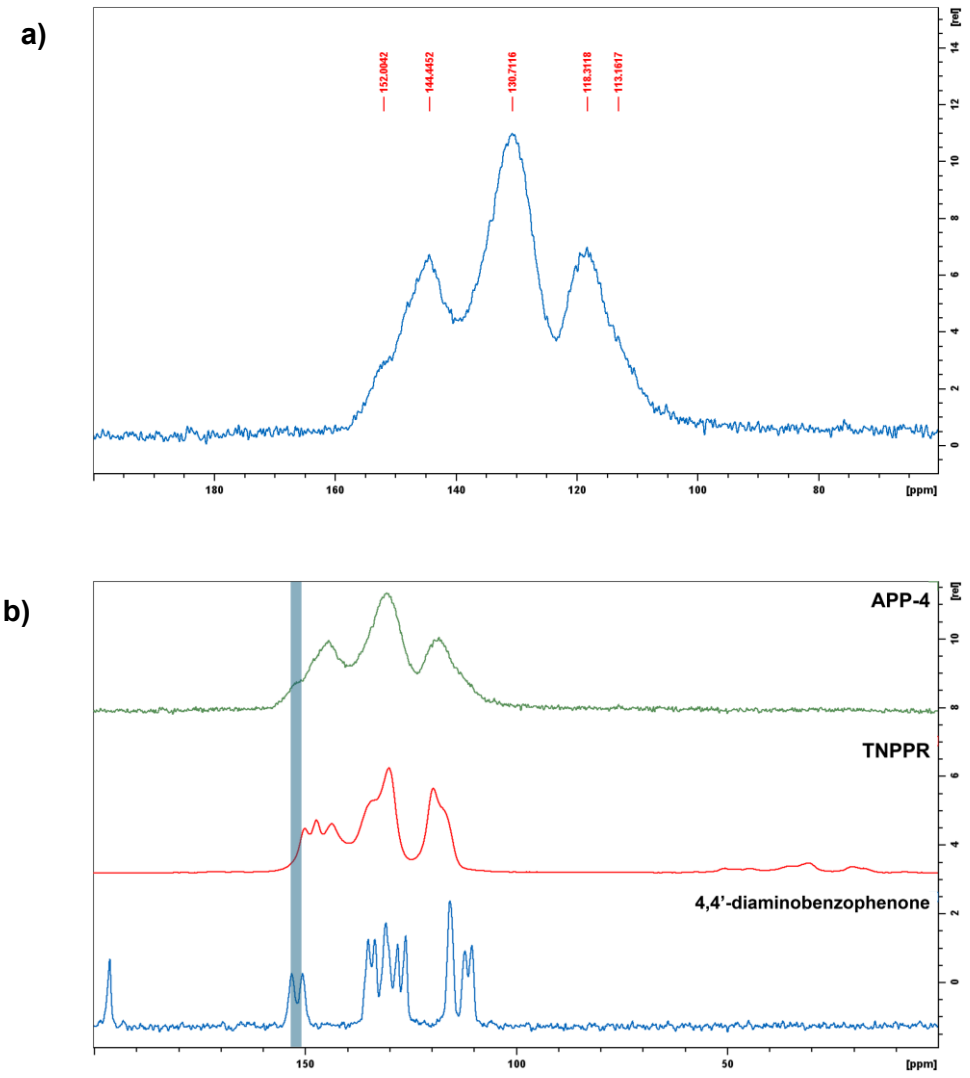
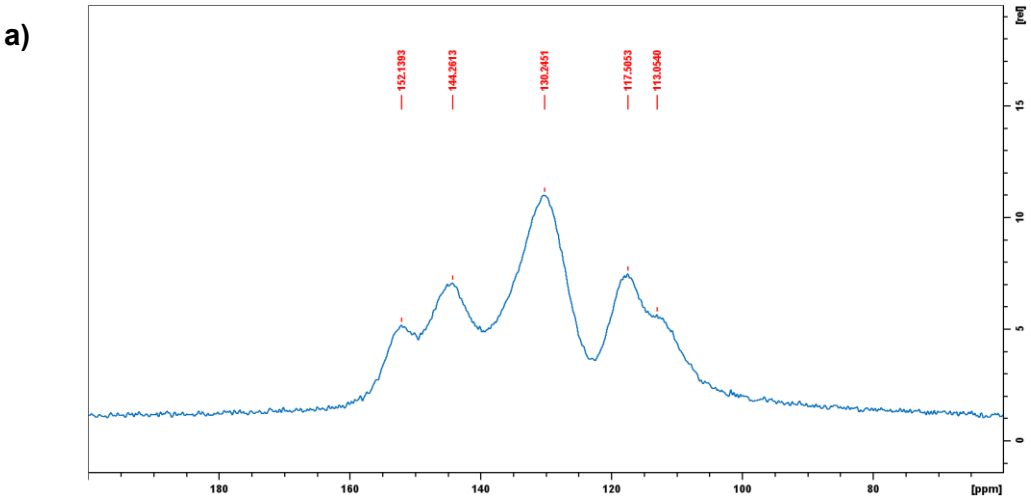


Figure S25. (a) Aromatic region of ^{13}C CP/MAS NMR spectrum of **APP-4** and (b) comparison of ^{13}C CP/MAS NMR spectra of **APP-4**, **TNPPR** and 4,4'-diaminobenzophenone.



b)

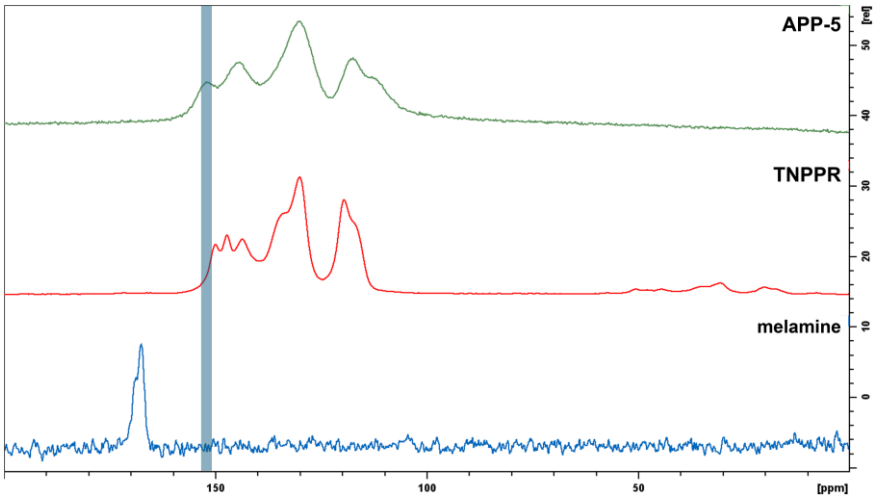
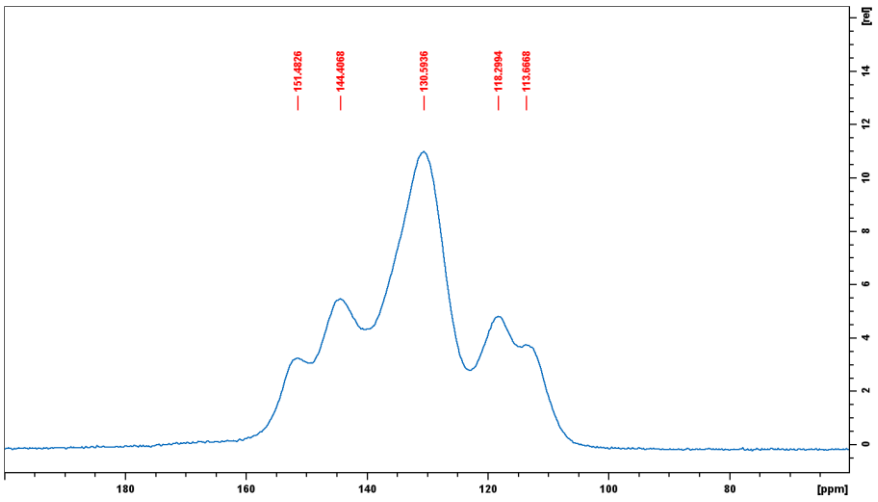


Figure S26. (a) Aromatic region of ^{13}C CP/MAS NMR spectrum of **APP-5** and (b) comparison of ^{13}C CP/MAS NMR spectra of **APP-5**, **TNPPR** and melamine.

a)



b)

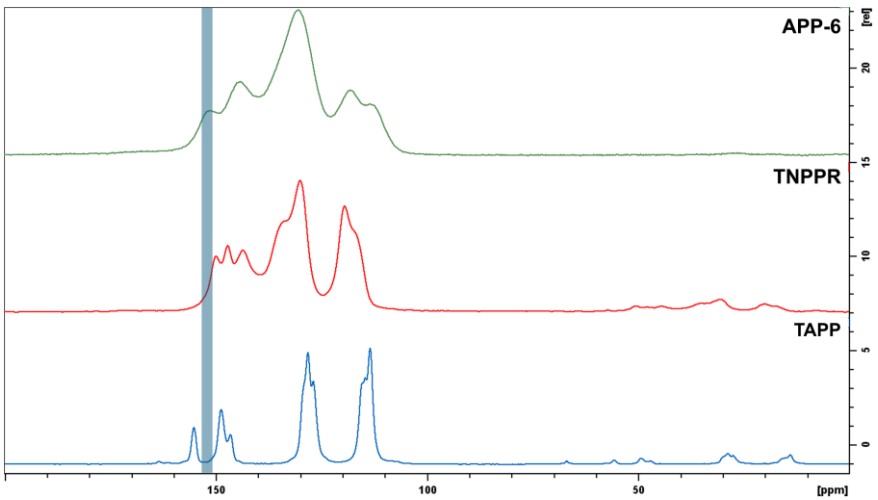


Figure S27. (a) Aromatic region of ^{13}C CP/MAS NMR spectrum of **APP-6** and (b) comparison of ^{13}C CP/MAS NMR spectra of **APP-6**, **TNPPR** and **TAPP**.

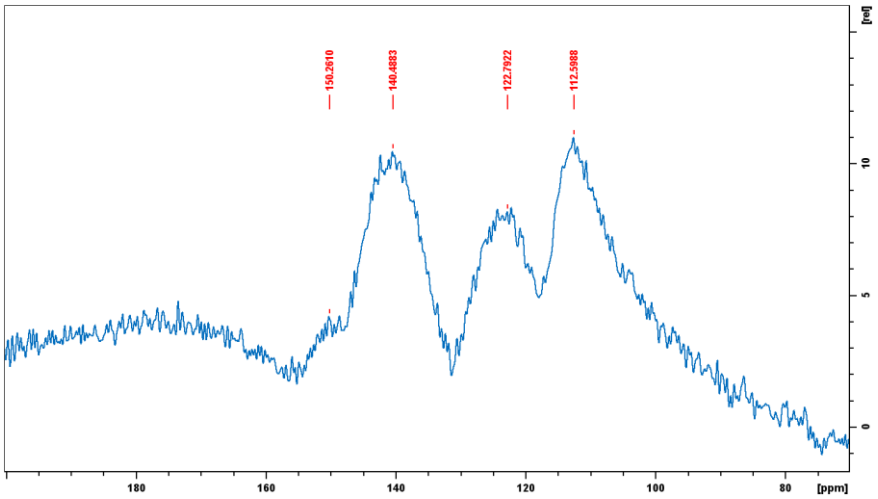


Figure S28. ^{13}C CP/MAS NMR spectrum of **APP-7a**.

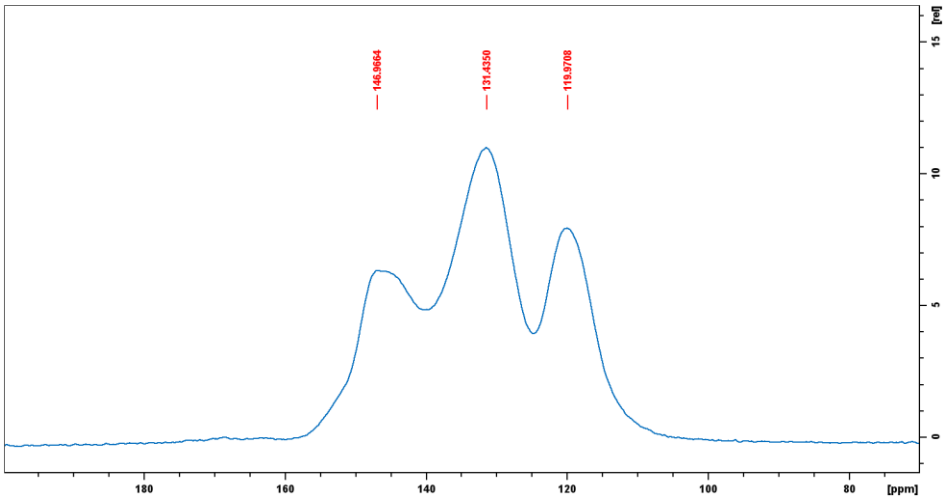


Figure S29. ^{13}C CP/MAS NMR spectrum of **APP-7b**.

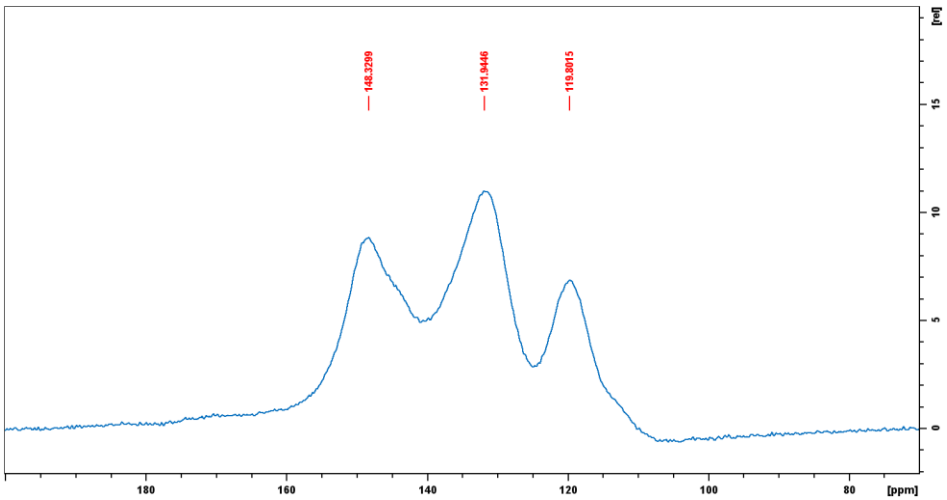


Figure S30. ^{13}C CP/MAS NMR spectrum of **APP-8**.

4. Powder X-ray diffraction

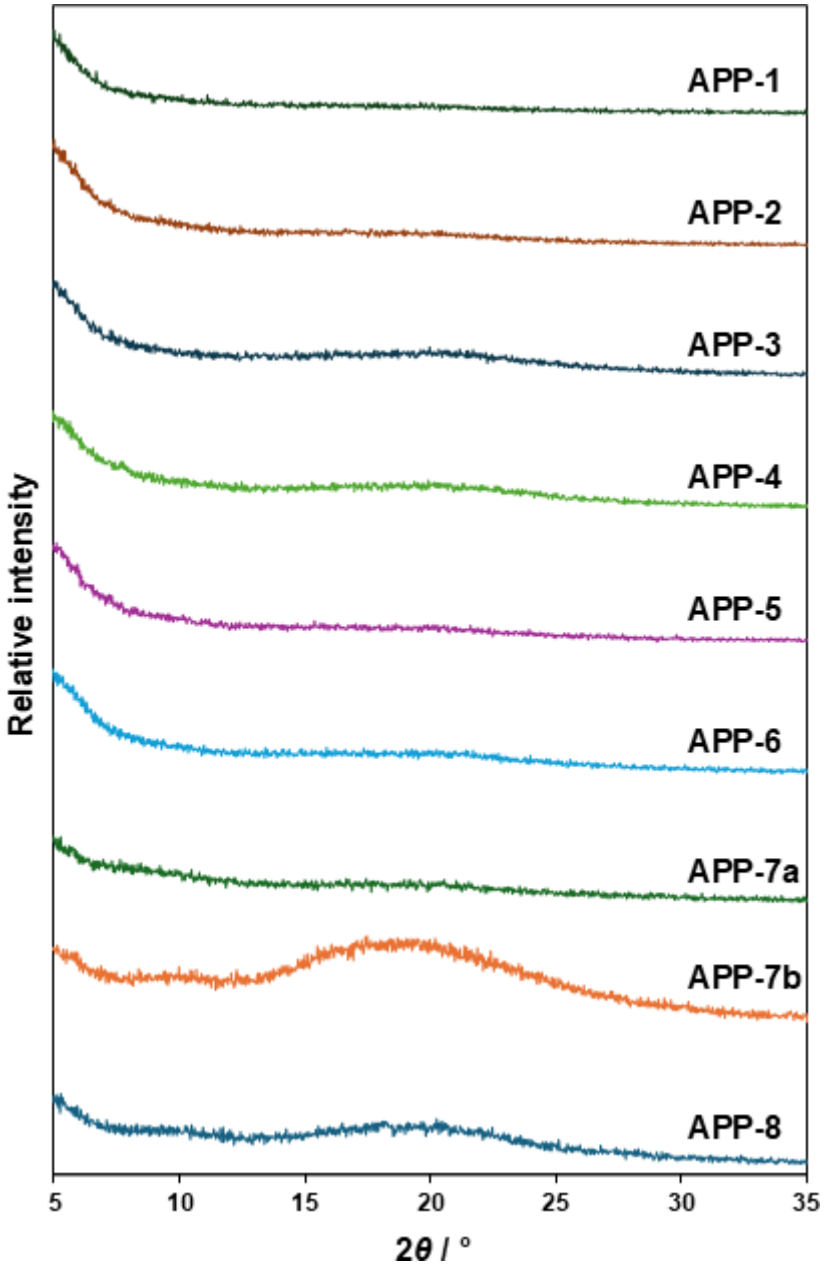


Figure S31. PXRD patterns of **APP-1** to **APP-8**.

5. Thermogravimetric analysis

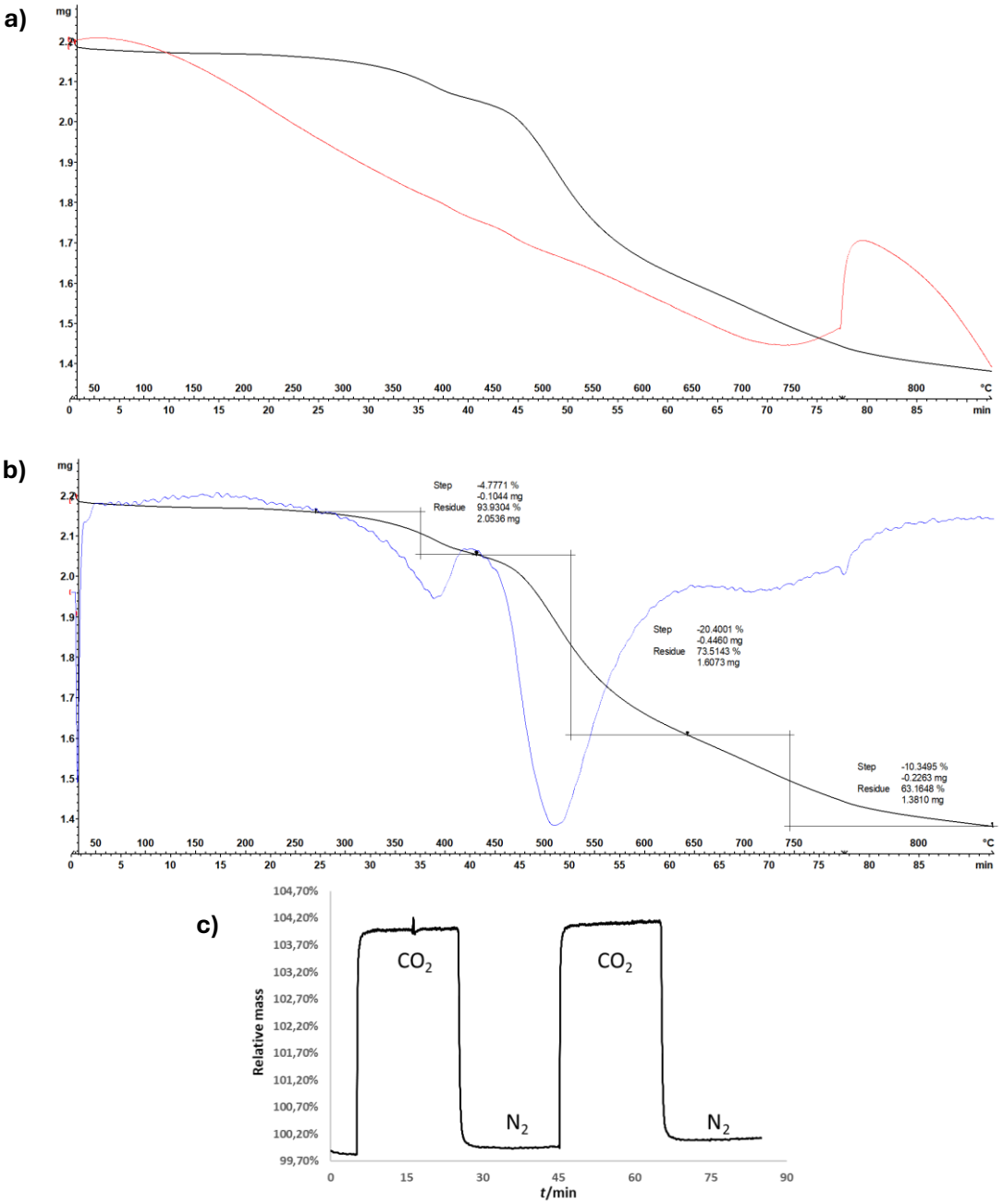


Figure S32. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-1** (a, b), and CO_2 adsorption curve (c).

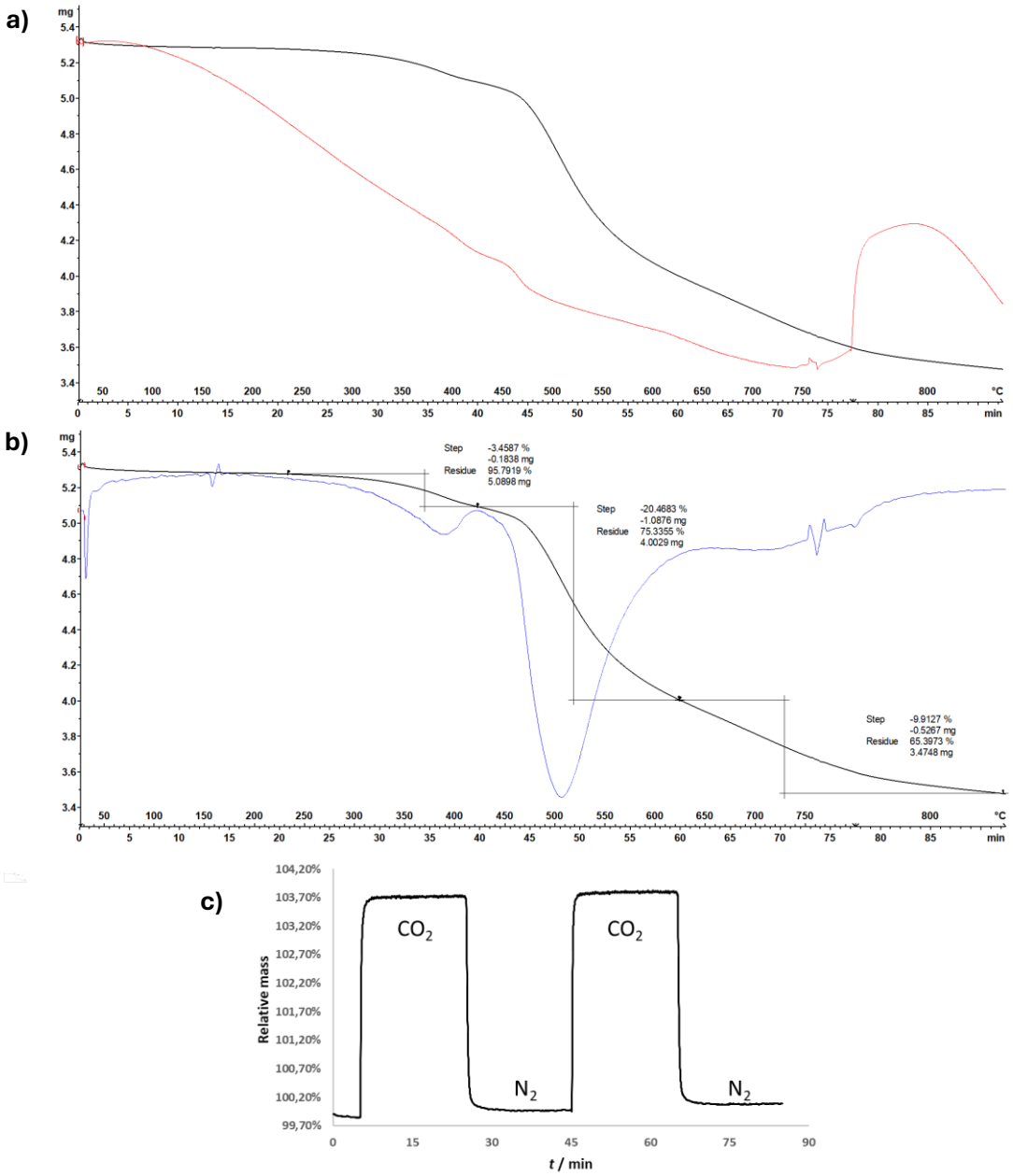


Figure S33. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-2** (a, b), and CO_2 adsorption curve (c).

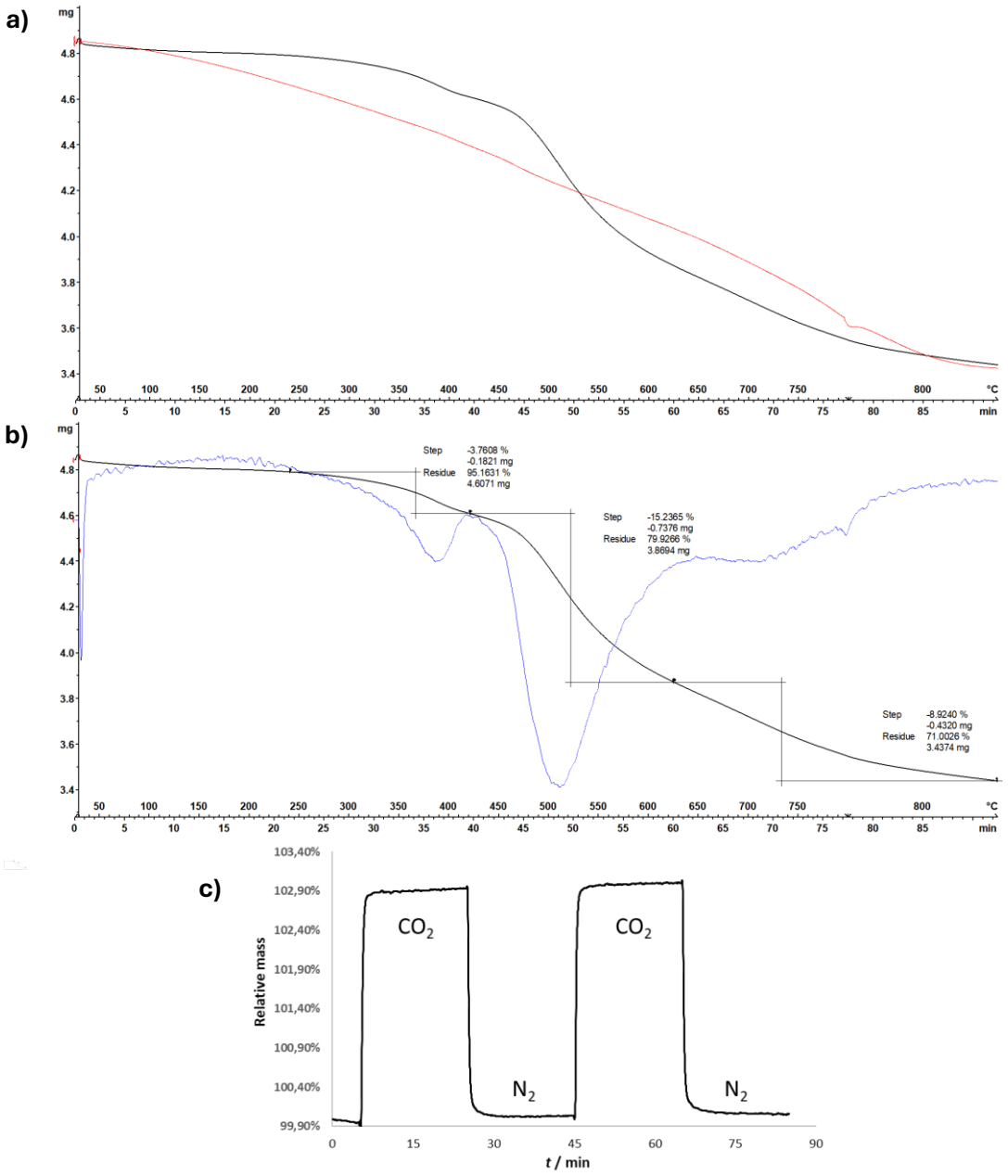


Figure S34. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-3** (a, b), and CO_2 adsorption curve (c).

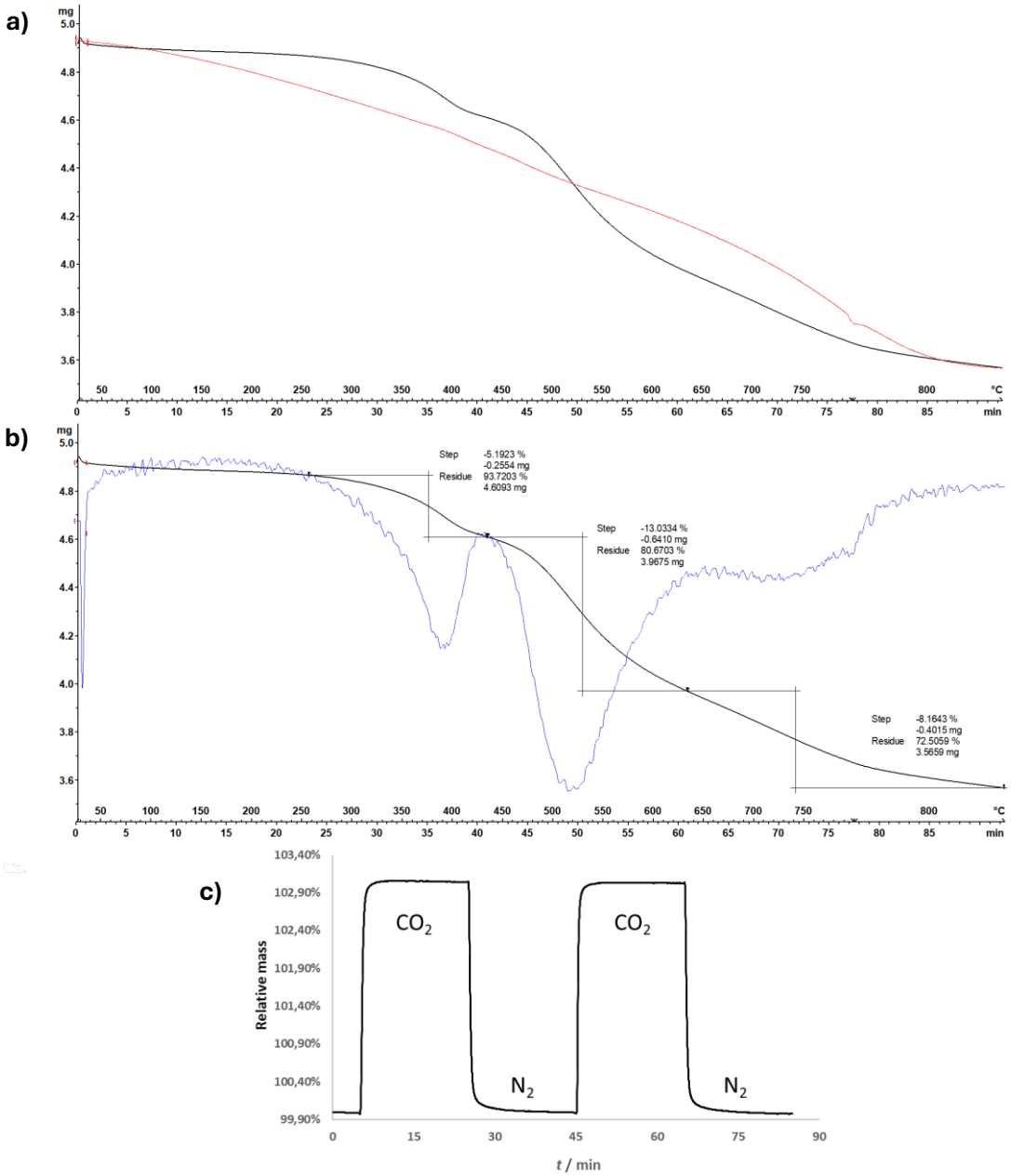


Figure S35. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-4** (a, b), and CO_2 adsorption curve (c).

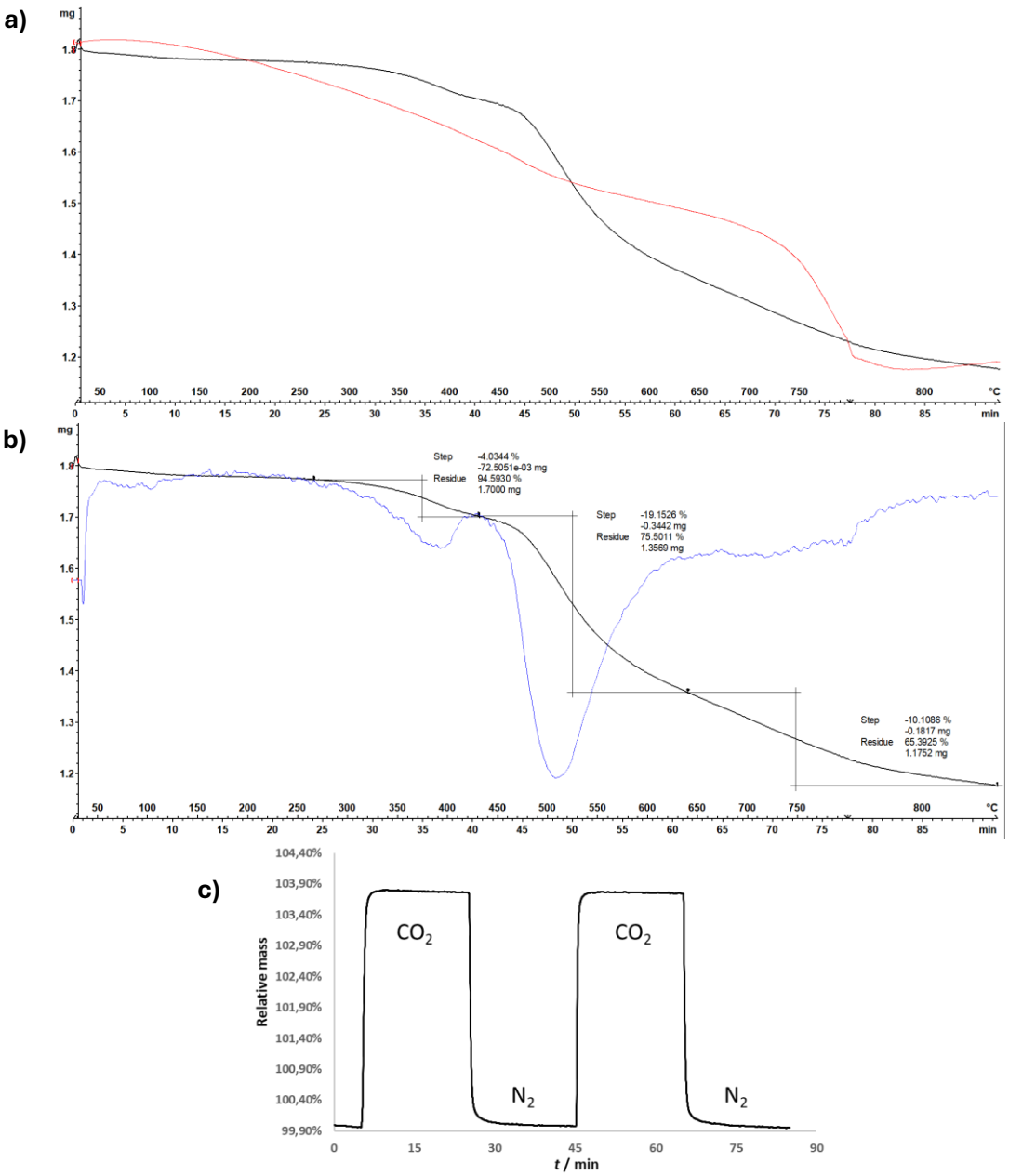


Figure S36. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-5** (a, b), and CO_2 adsorption curve (c).

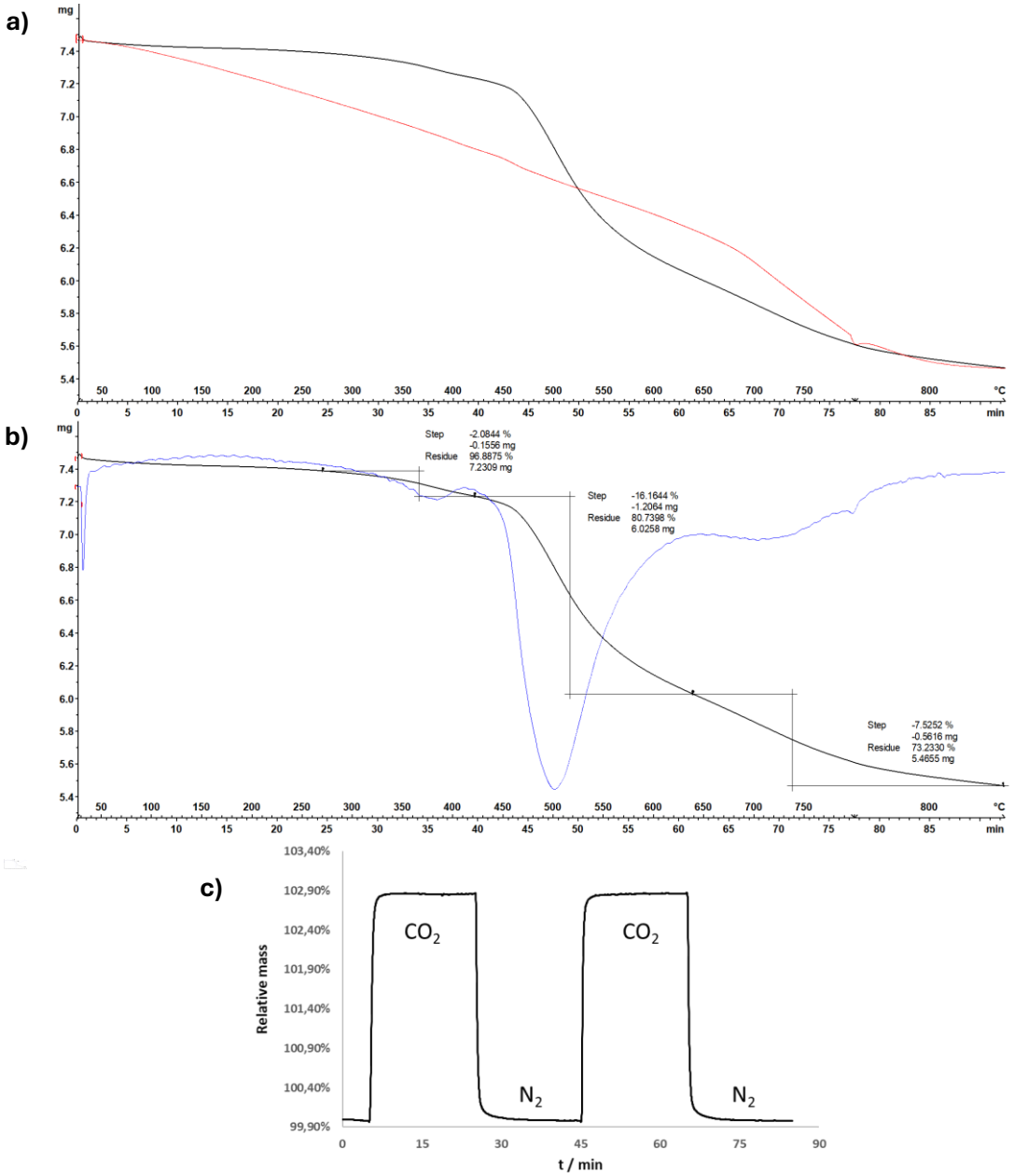


Figure S37. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-6** (a, b), and CO_2 adsorption curve (c).

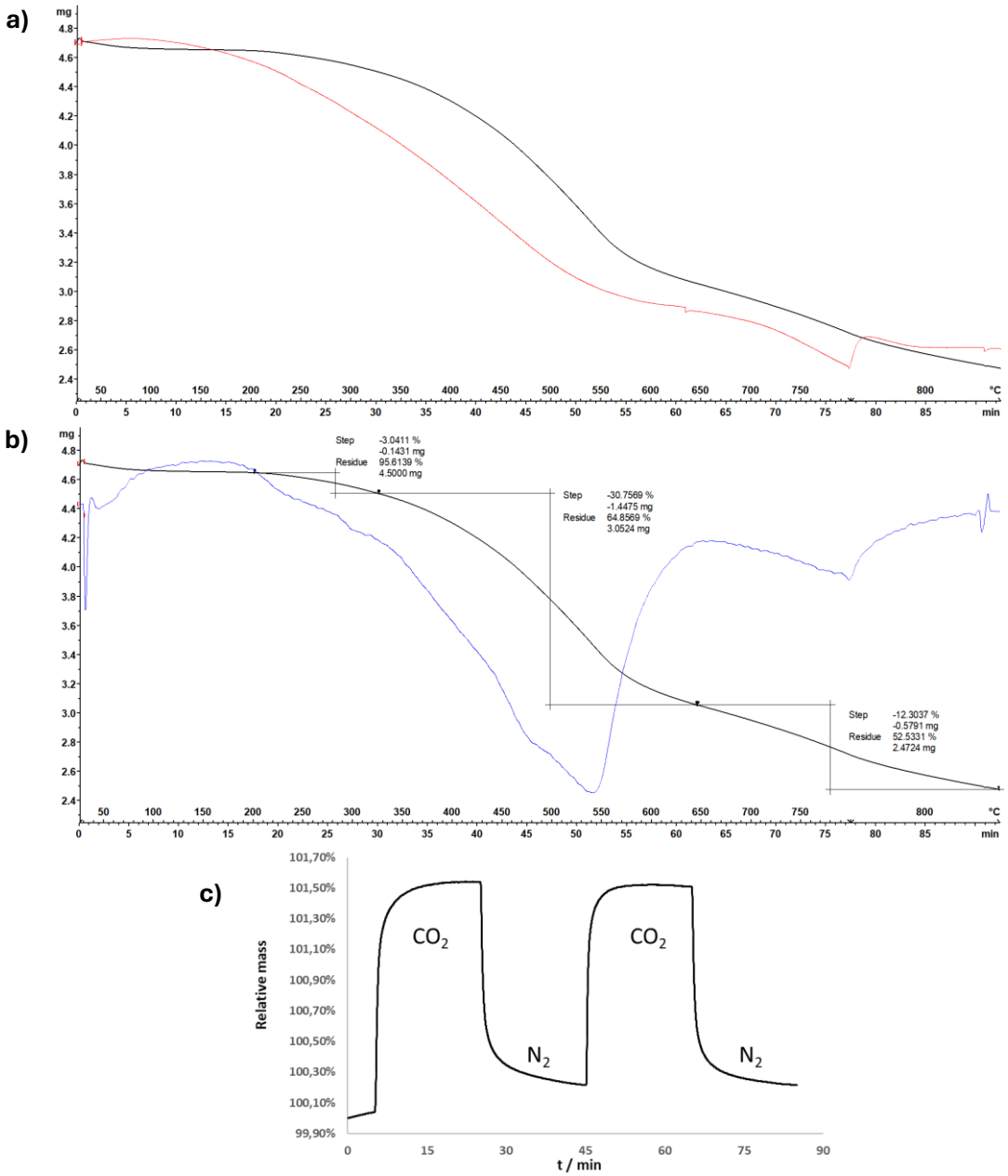


Figure S38. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-7a** (a, b), and CO_2 adsorption curve (c).

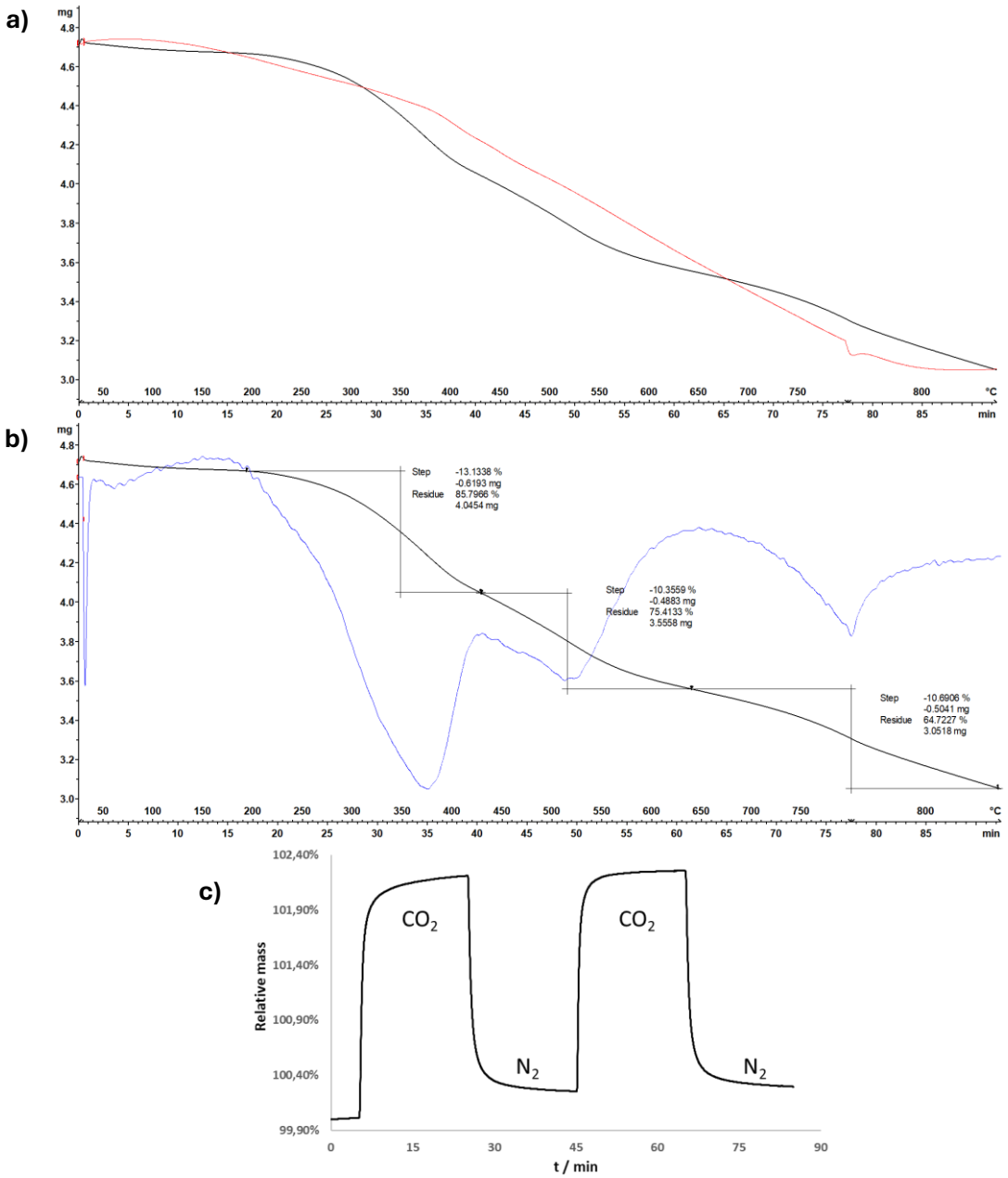


Figure S39. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-7b** (a, b), and CO_2 adsorption curve (c).

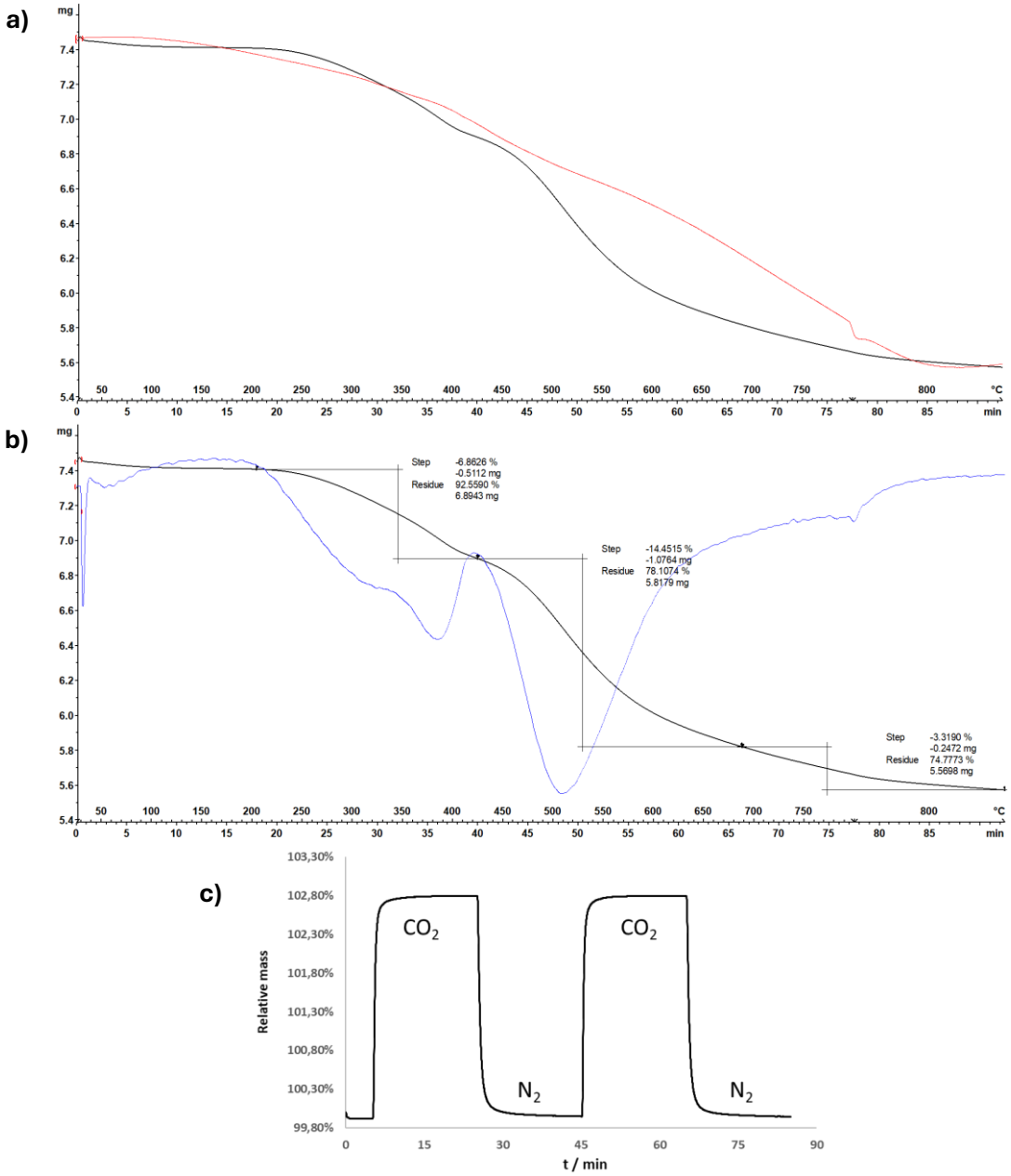


Figure S40. TGA (black), DSC (red) and 1st derivative of weight (blue) curves of **APP-8** (a, b), and CO_2 adsorption curve (c).

6. N_2 adsorption-desorption analysis

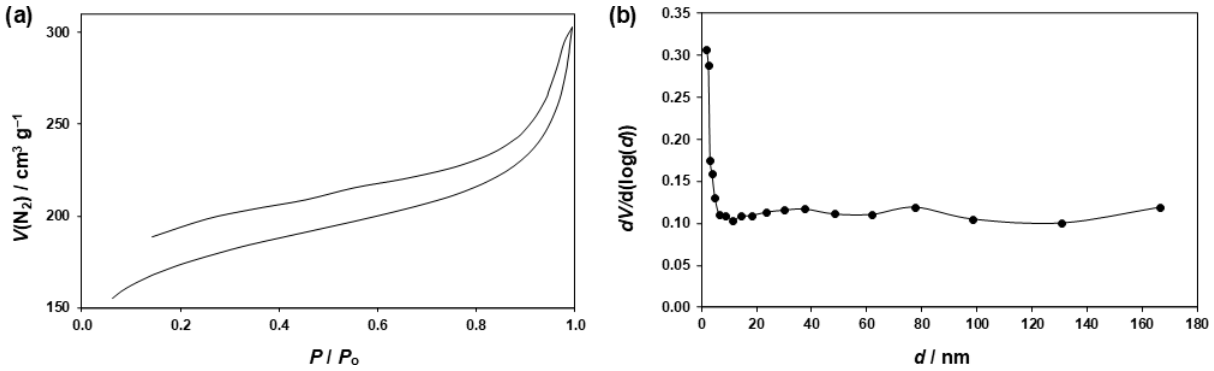


Figure S41. (a) N_2 adsorption-desorption isotherms of **APP-1** measured at 77 K and (b) pore size distributions of **APP-1**.

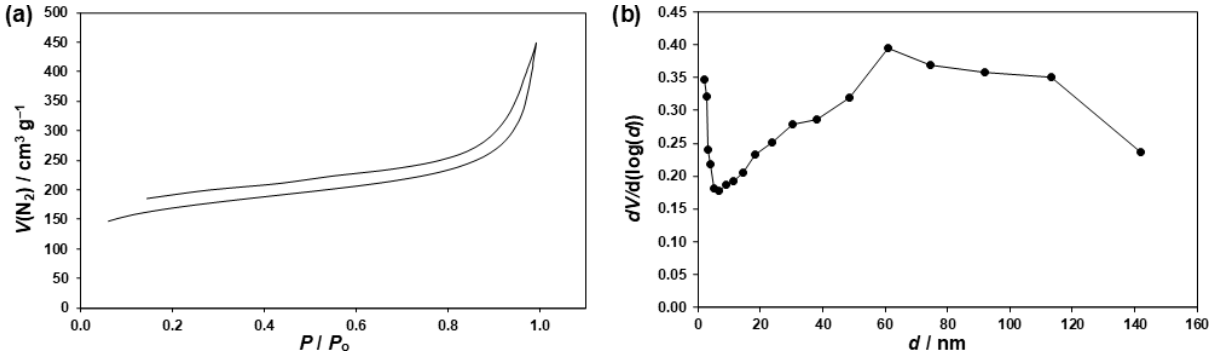


Figure S42. (a) N_2 adsorption-desorption isotherms of **APP-3** measured at 77 K and (b) pore size distributions of **APP-3**.

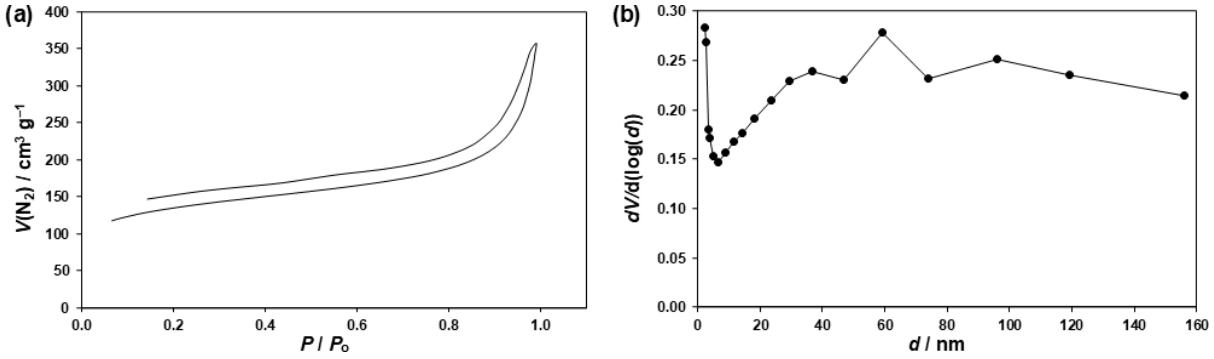


Figure S43. (a) N_2 adsorption-desorption isotherms of **APP-4** measured at 77 K and (b) pore size distributions of **APP-4**.

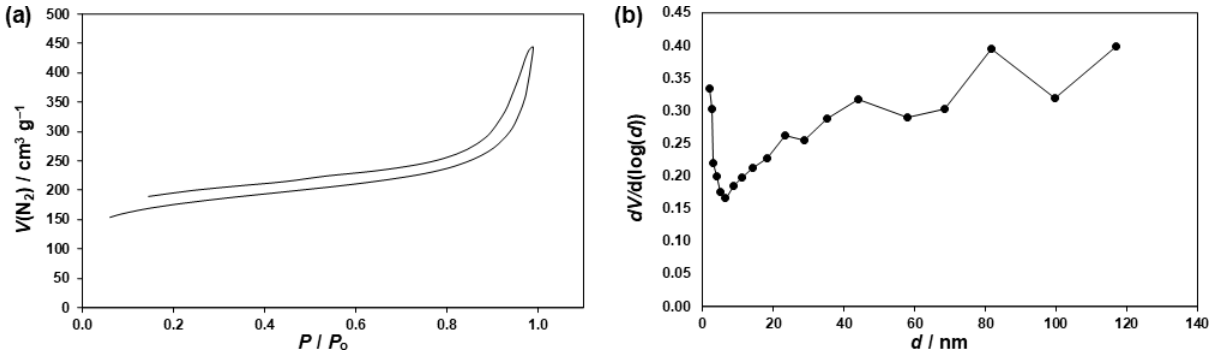


Figure S44. (a) N_2 adsorption-desorption isotherms of **APP-5** measured at 77 K and (b) pore size distributions of **APP-5**.

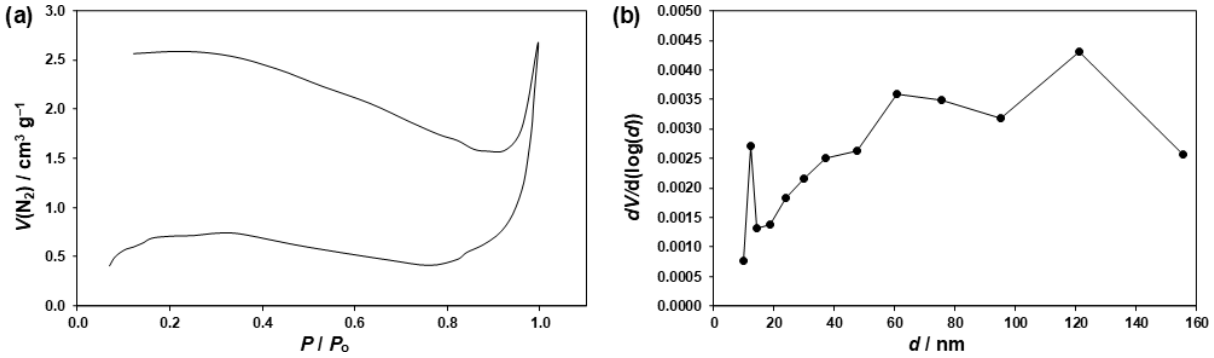


Figure S45. (a) N_2 adsorption-desorption isotherms of **APP-8** measured at 77 K and (b) pore size distributions of **APP-8**.

Table S2. The correlation coefficient (R^2) for the BET linear fit.

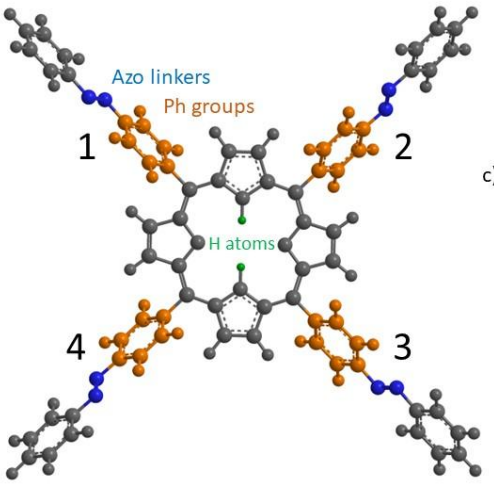
Sample	Correlation coefficient (R^2)
APP-1	0.9996
APP-2	0.9995
APP-3	0.9997
APP-4	0.9997
APP-5	0.9997
APP-6	0.9997
APP-7a	0.9999
APP-7b	0.9884
APP-8	0.9877

7. Computational studies of generated structures

7.1. APP-7 conformational analysis

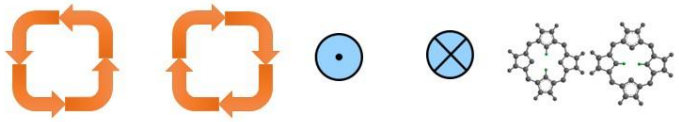
First, to get better insight into the relative orientation of phenyl rings and azo groups, conformational analysis was performed on APP-7 fragments. Geometries were generated in GaussView program. Fifteen geometries were proposed by rotating dihedral angles around nitrogen-nitrogen linkages and benzene units (Figure S46.). After optimization, fragments were connected into 2D layers using Chem3D and GaussView (PBC tools). Finally, optimized 2D layers were converted into 3D structures using GaussView (PBC tools). To find the most stable geometry of APP-7, a comparison of energies relative to the smallest energy for each conformation was performed for 0D fragments, 2D layers, and 3D crystal structures. The most stable conformation of 3D crystal structures (P12) was picked for further modification and generation of other 2D layered compounds with rhombohedral (APP-2 and APP-8) and rectangular-like pores (APP-1, APP-3 and APP-4). More computational details about the programs and methodology can be found in the Experimental section of the manuscript.

a)



b)

Ph groups		Azo linkers		H atoms	
A (counterclockwise)	B (clockwise)	A (inwards)	B (outwards)	A	B



c)

		Ph-group orientation				
		$A_1A_2A_3A_4$	$B_1A_2A_3A_4$	$B_1A_2B_3A_4$	H atoms A $B_1B_2A_3A_4$	H atoms B $B_1B_2A_3A_4$
Azo-linker orientation	$A_1A_2A_3A_4$	P1	P2	P3	P4	P13
	$B_1A_2B_3A_4$	P5	P6	P7	P8	P14
	$A_1A_2B_3B_4$	P9	P10	P11	P12	P15

Figure S46. Schematic representation of an APP-7 0D fragment with colored units whose dihedral angle and relative orientation of building units were changed based on schematic representation listed in Table b). c) Labelling scheme for APP-7 0D conformers P1–P15 investigated in this paper.

Table S3. Unit cell parameters (*a*, *b*, *c*, α, β and γ) of the optimized geometries of proposed APP-7 2D layers and 3D structures. The labels of the layer group and space groups used in the CRYSTAL17.

	PORF-COF conformation	Space Group	CRYSTAL17 label	a/Å	b/Å	c/Å	α / °	β/ °	γ/ °
2D layers	P1	*P* 2*	2	26.9191	26.7706				90
	P2	*P* 1*	1	26.5473	27.1425				90
	P3	*P* 2*	2	27.8318	25.7647				90
	P4	*P* 1*	1	26.7403	26.9012				90
	P5	*P*ban*	46	26.3626	27.3843				90
	P6	*P* 1*	1	26.6854	27.0578				89.9
	P7	*P* 1*	1	27.0581	27.0581				89.9
	P8	*P* 1*	1	27.1083	26.6417				90
	P9	*P* 1*	1	26.9365	26.7949				90
	P10	*P* 1*	1	26.4605	27.2442				90
	P11	*P* 1*	1	26.7237	26.9924				90
	P12	*P* 1*	1	26.2896	27.3982				90
	P13	*P* 1	1	26.5932	27.0632				90
	P14	*P* 1	1	26.8980	26.8469				90
	P15	*P* 1	1	26.4359	27.2933				90
3D structures	P1	*P* 2/n	13	26.2727	26.4842	4.0639	90	90	90.1
	P2	*P* $\bar{1}$	2	26.9136	26.8126	4.0569	110.4	100.5	89.6
	P3	*P* m m n	59	26.0773	27.4860	3.7513	90	90	90
	P4	*P* 21/m	11	25.0244	27.3250	3.8918	90	87.2	90
	P5	*P*ban	50	26.4851	27.4302	3.9683	90	90	90
	P6	*P* $\bar{1}$	2	27.2635	26.5329	4.0316	101.1	77.2	90.3
	P7	*P* 2/n	13	26.9194	26.3399	3.9511	90	90	90.2
	P8	*P* 2/c	13	28.1675	25.5790	4.0158	90	109.9	90
	P9	*P* 2/c	13	27.7176	26.1629	4.1557	90	72.0	90
	P10	*P* $\bar{1}$	2	26.9136	26.8126	4.0569	110.4	100.5	100.5
	P11	*P* 21/m	11	26.9093	26.6191	3.9400	90	78.1	90
	P12	*P* 21/m	11	25.0325	27.2964	3.8922	90	87.0	90

* The corresponding layer group number, according to the International Tables for Crystallography.

Table S4. Relative energies of the optimized geometries of modeled APP-7 0D conformers and 2D layers.

	PORF-COF conformation	Space Group	CRYSTAL17 label	E kJ mol^{-1}
2D layers	P1	*P* 2*	2	12.35
	P2	*P* 1*	1	7.03
	P3	*P* 2*	2	0.00
	P4	*P* 1*	1	8.14
	P5	*P*ban*	46	12.53
	P6	*P* *	1	7.61
	P7	*P* 1*	1	0.64
	P8	*P* 1*	1	8.35
	P9	*P* 1*	1	13.37
	P10	*P* 1*	1	6.27
	P11	*P* 1*	1	2.13
	P12	*P* 1*	1	5.81
	P13	*P* 1*	1	7.92
	P14	*P* 1*	1	8.84
	P15	*P* 1*	1	5.87

* The corresponding molecule/layer group number, according to the International Tables for Crystallography.

Table S5. Relative energies of the optimized geometries of modeled APP-7 3D structures

	PORF-COF conformation	Space Group	CRYSTAL17 label	E kJ mol^{-1}
3D structures	P1	*P* 2/n	13	187.82
	P2	*P* $\bar{1}$	2	43.47
	P3	*P* m m n	59	14.63
	P4	*P* 21/m	11	10.62
	P5	*P*ban	50	177.67
	P6	*P* $\bar{1}$	2	53.45
	P7	*P* 2/n	13	53.53
	P8	*P* 2/c	13	26.17
	P9	*P* 2/c	13	182.68
	P10	*P* $\bar{1}$	2	35.46
	P11	*P* 21/m	11	43.71
	P12	*P* 21/m	11	0.00

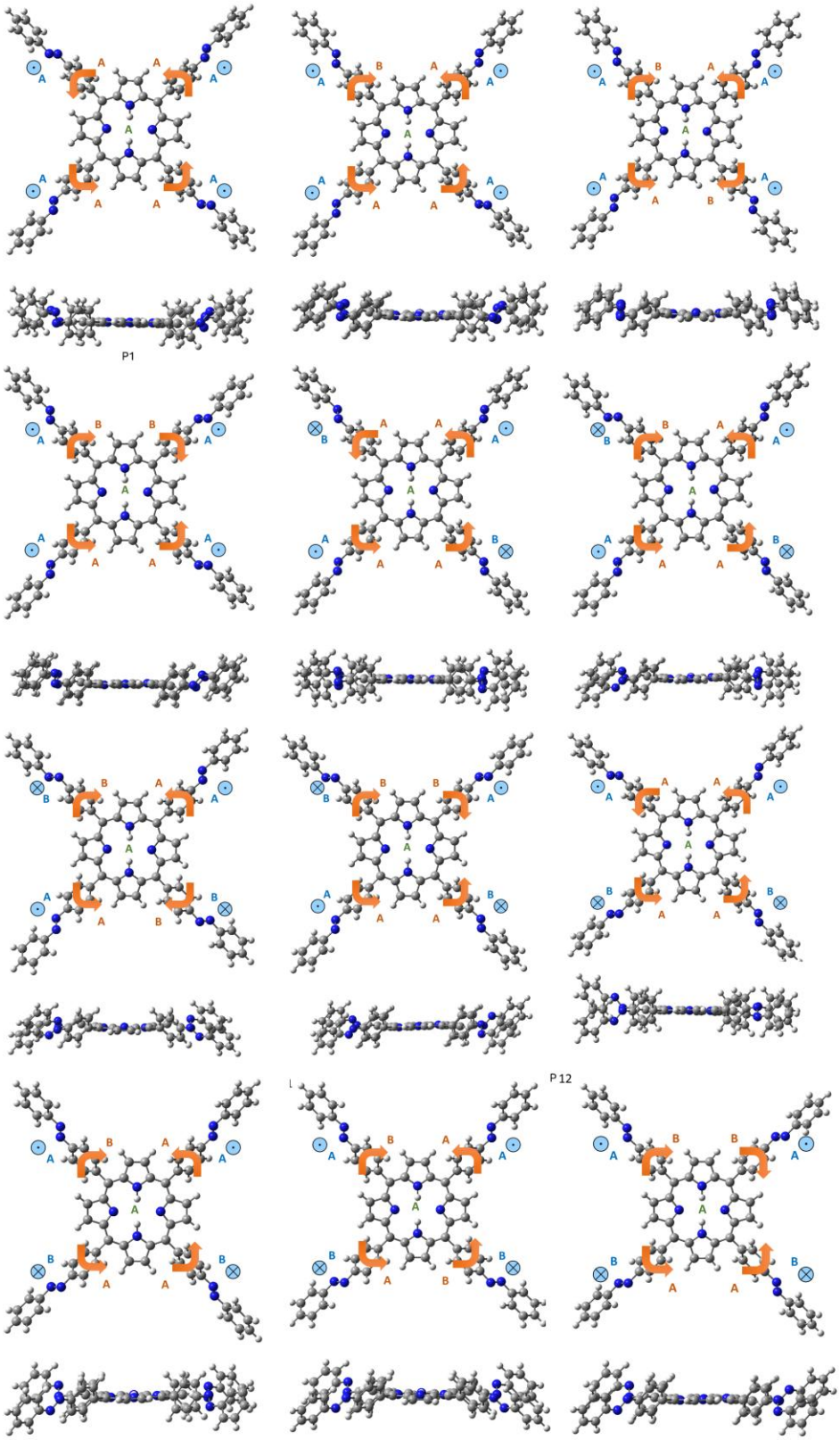


Figure S47. Optimized geometries of APP-7 0D conformers P1–P12 seen from top and side-view. Optimization was performed at the PBE-D3/pob-TZVP-rev2 level of theory.

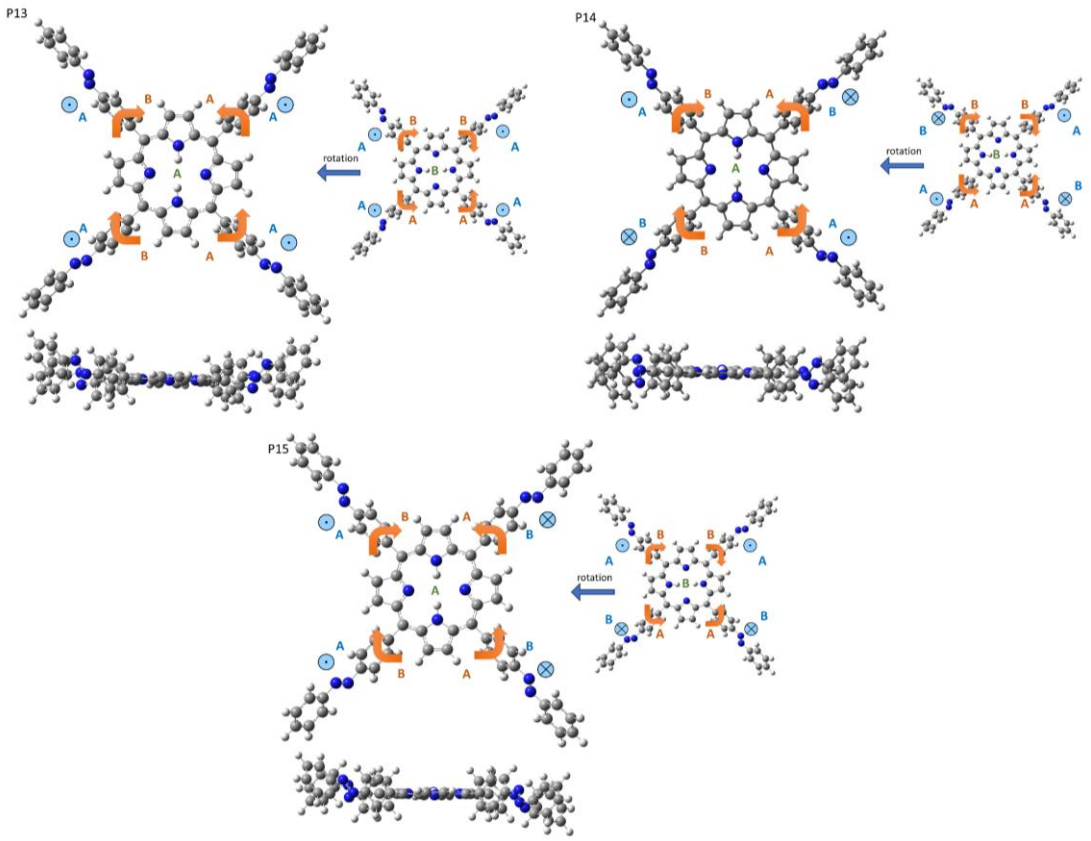


Figure S48. Optimized geometries of APP-7 0D conformers P13–P15 seen from top and side-view. Optimization was performed at the PBE-D3/pob-TZVP-rev2 level of theory.

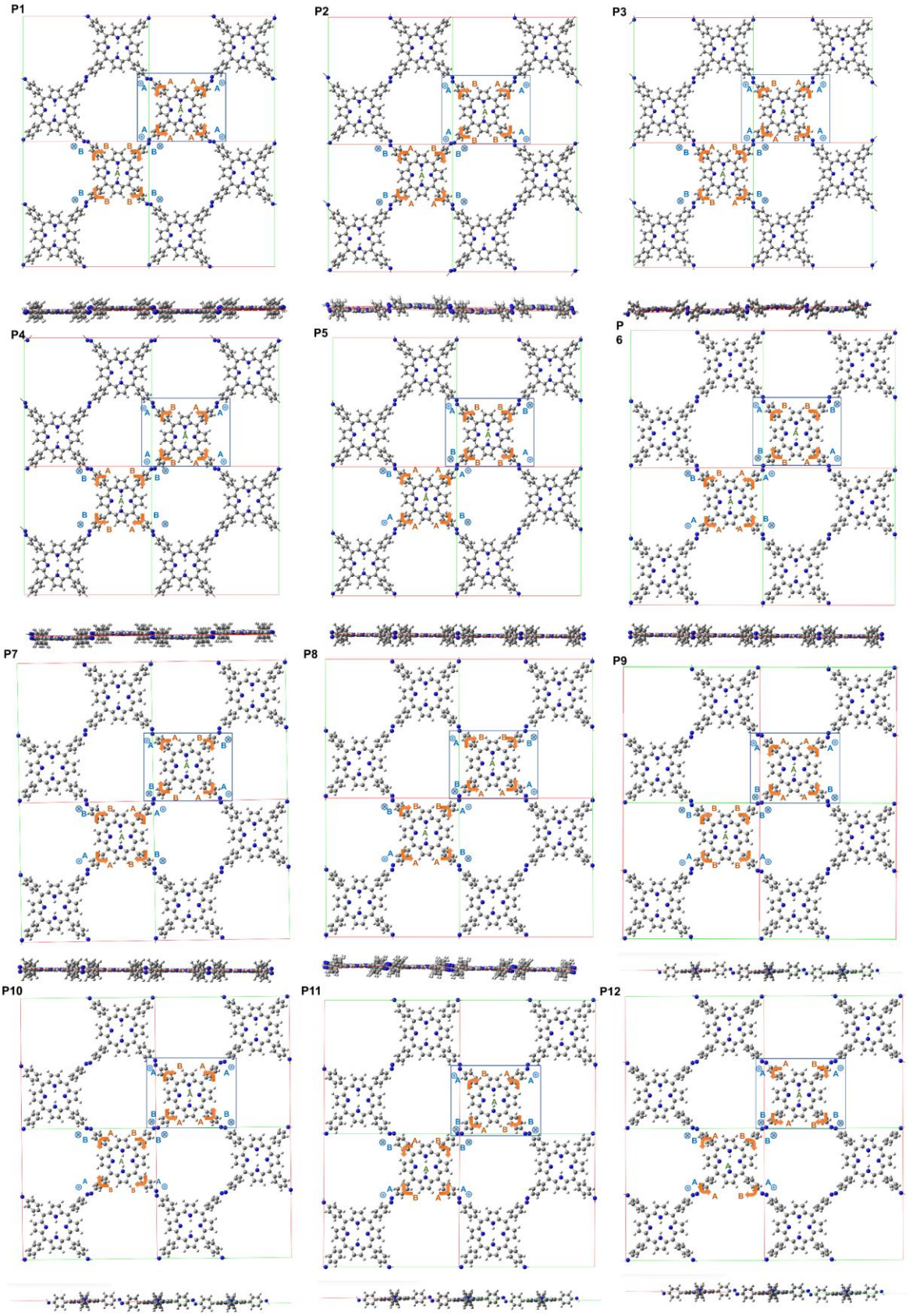


Figure S49. Optimized geometries of APP-7 2D layers P1–P12 seen from top and side-view. Optimization was performed at the PBE-D3/pob-TZVP-rev2 level of theory.

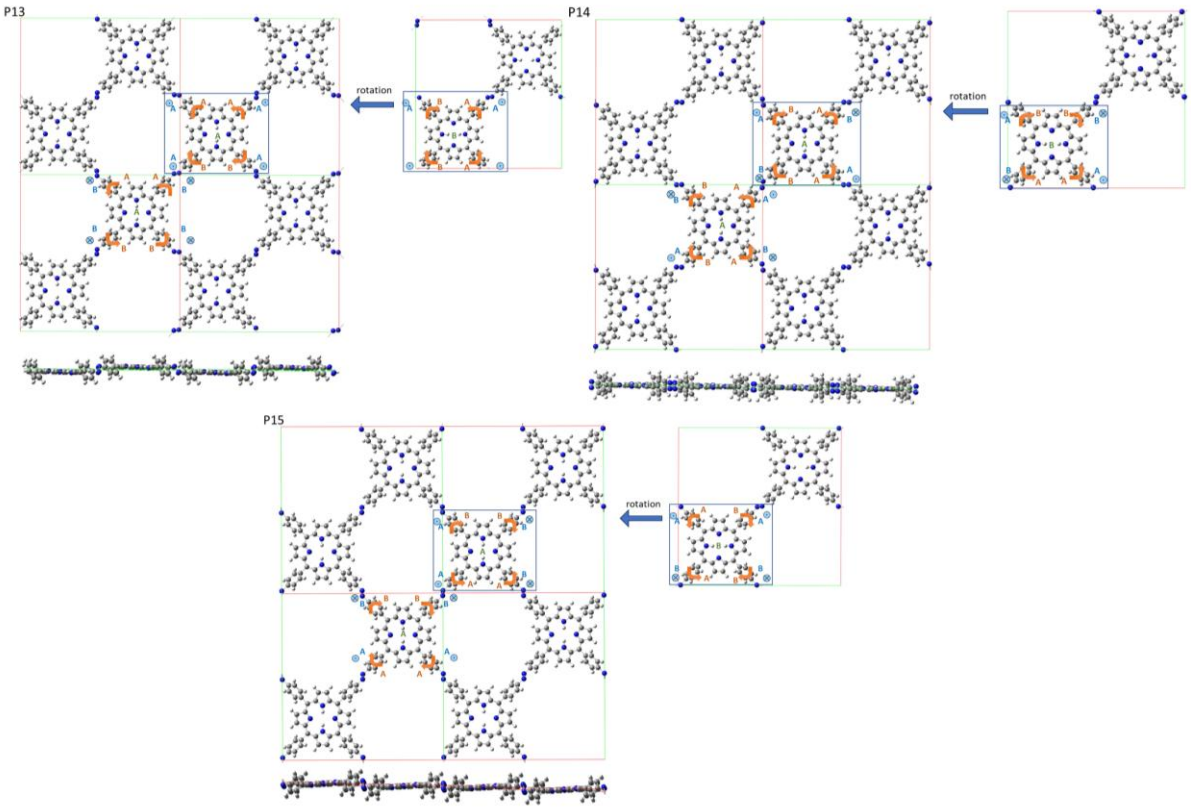


Figure S50. Optimized geometries of APP-7 2D layers P13–P15 seen from top and side-view. Optimization was performed at the PBE-D3/pob-TZVP-rev2 level of theory.

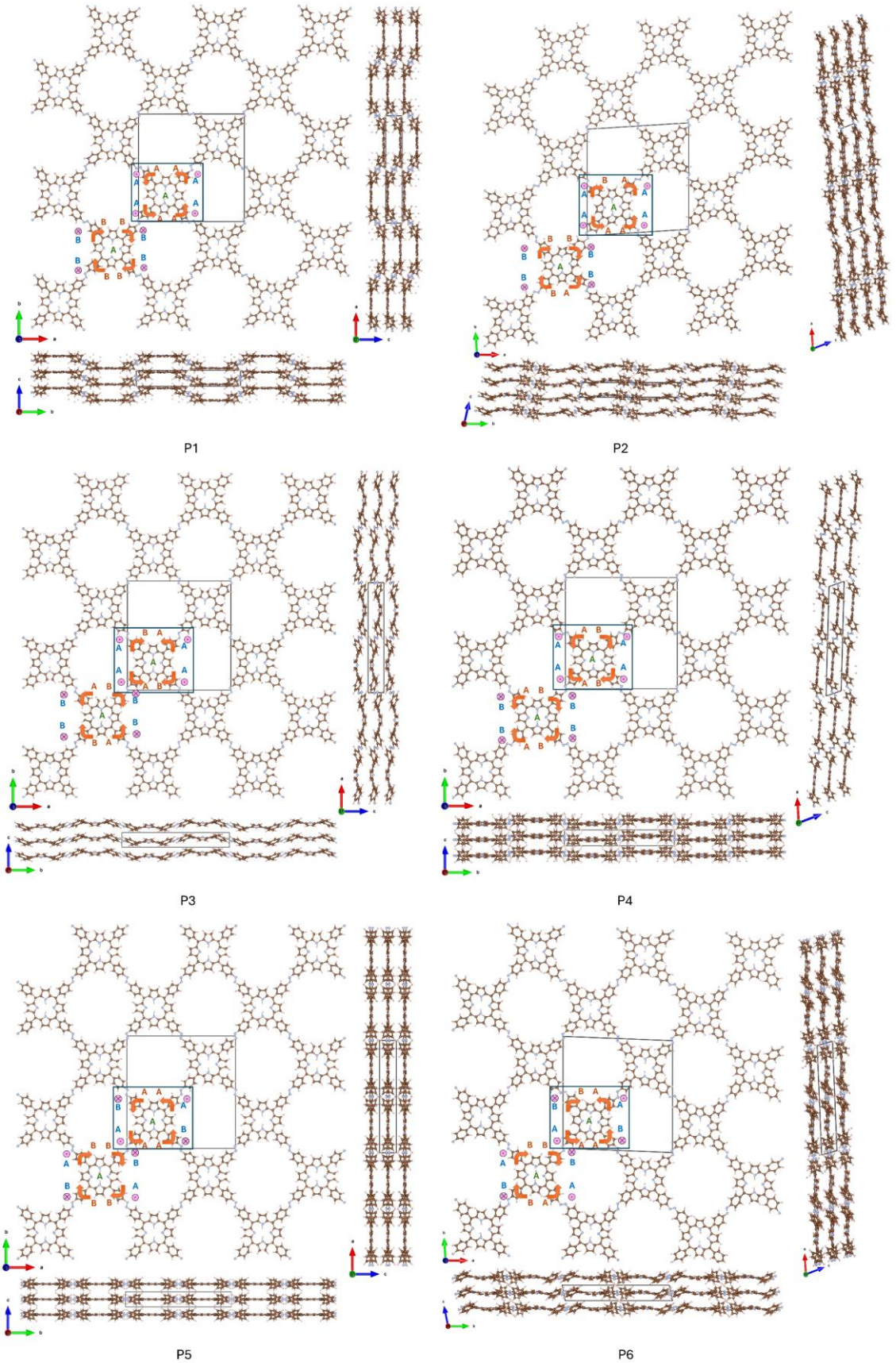


Figure S51. Optimized geometries of APP-7 3D structures P1–P6 shown along cell vectors *a*, *b* and *c*. Optimization was performed at the PBE-D3/pob-TZVP-rev2 level of theory.

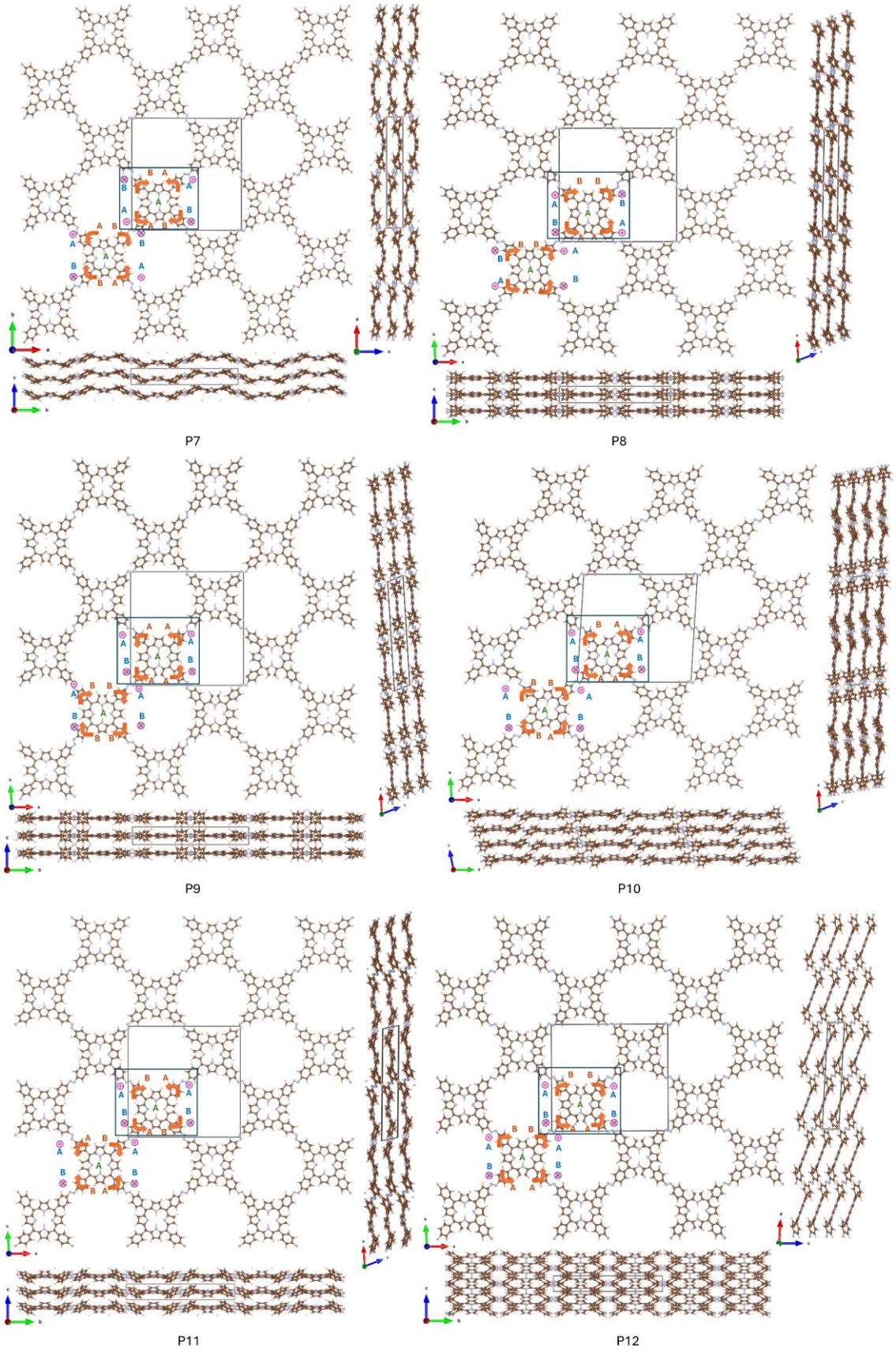


Figure S52. Optimized geometries of APP-7 3D structures P7–P12 shown along cell vectors *a*, *b* and *c*. Optimization was performed at the PBE-D3/pob-TZVP-rev2 level of theory.

7.2. 3D geometries of APPs

Table S6. Unit cell parameters (*a*, *b*, *c*, α, β and γ) of the optimized APPs 3D geometries (PBE-D3/pob-TZVP-rev2). The labels of the layer group and space groups used in the CRYSTAL17.

Compound	Space Group	CRYSTAL17 label	a/Å	b/Å	c/Å	α / °	β/ °	γ/ °
APP-1	*P* 21/c	14	37.3301	40.6363	3.9711	90	89.0	90
APP-2	*C* 2/m	12	45.7682	44.5117	4.4251	90	118.9	90
APP-3	*P* 21/c	14	36.2838	39.7894	3.9724	90	90	90
APP-4	*P* 21/c	14	39.0383	40.6331	3.9260	90	83.9	90
APP-5	P m m m	47	35.3823	35.3734	35.3613	90	90	90
APP-6	*P* m m m	47	46.7044	47.9558	48.4064	90	90	90
APP-7	*P* 21/m	11	25.0325	27.2964	3.8922	90	87	90
APP-8	*P* 21/m	11	25.0244	27.3250	3.8918	90	87.2	90
APP-2 (AB staggered)	*C* 2/m	12	11.7105	48.3794	8.7957	90	84.3	90

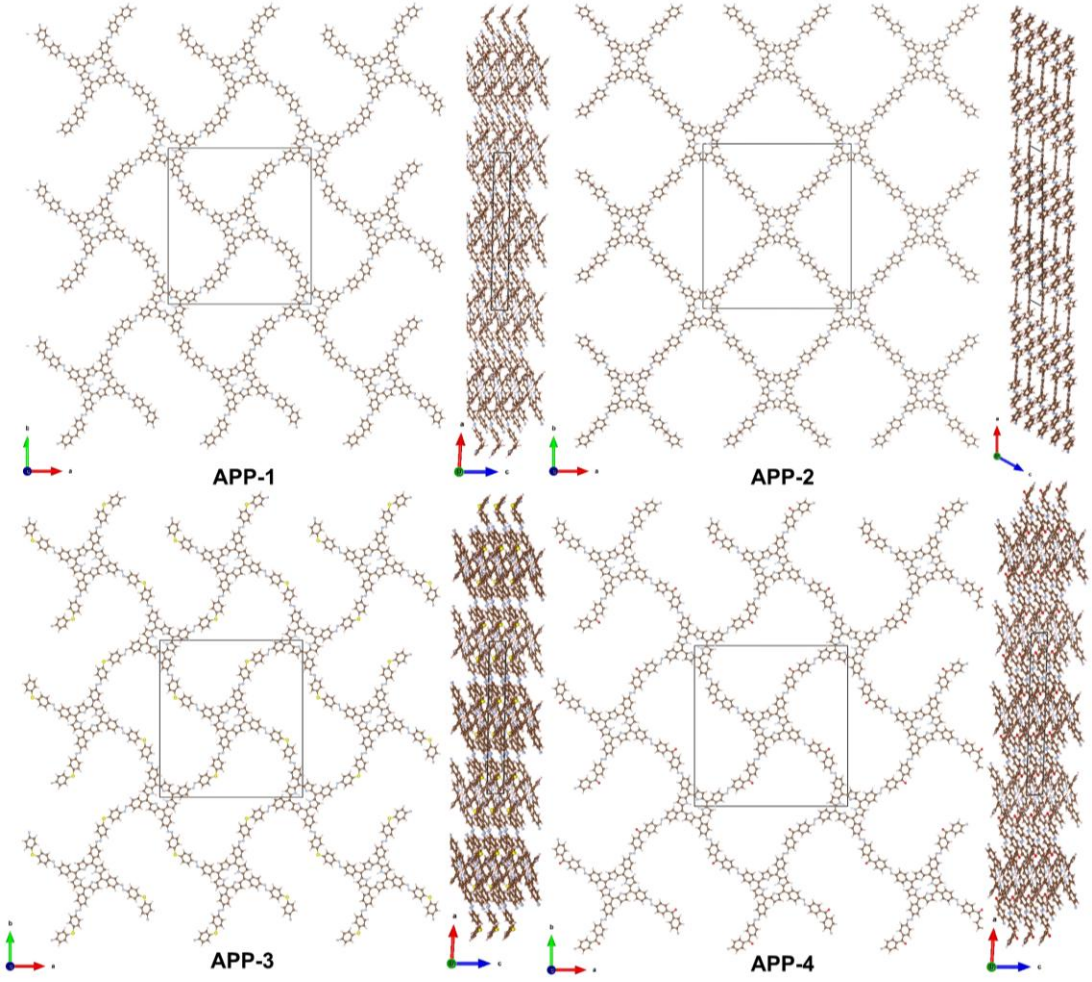


Figure S53. Optimized 3D geometries (PBE-D3/pob2-TZVP-rev2) of APP-1–4 with eclipsed (AA-stacked) 2D layers shown along the *c* and *b* unit cell vectors.

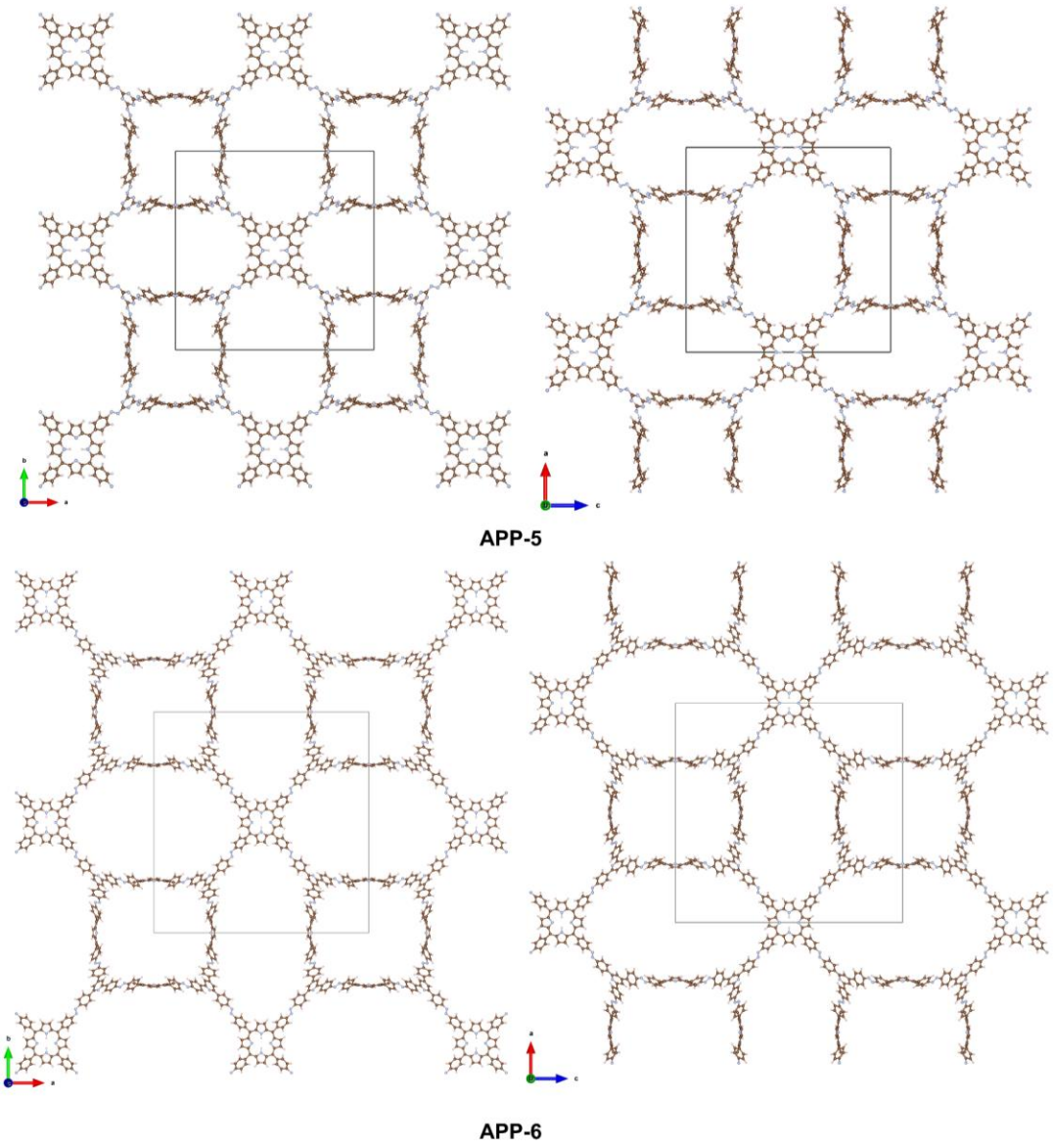


Figure S54. Optimized 3D geometries (PBE-D3/pob2-TZVP-rev2) of compounds APP-5 and APP-6 shown along the *c* and *b* unit cell vectors.

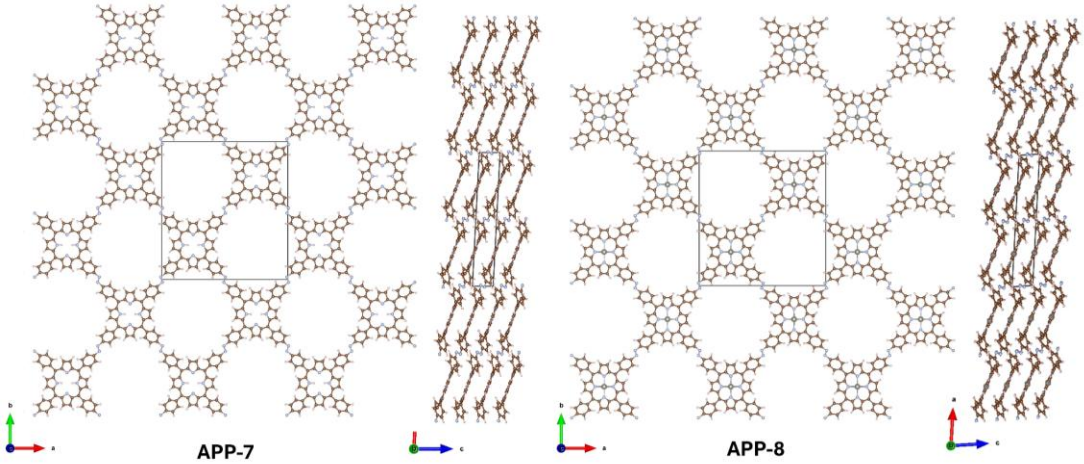


Figure S55. Optimized 3D geometries (PBE-D3/pob2-TZVP-rev2) of APP-7 and APP-8 with eclipsed (AA-stacked) 2D layers shown along the *c* and *b* unit cell vectors.

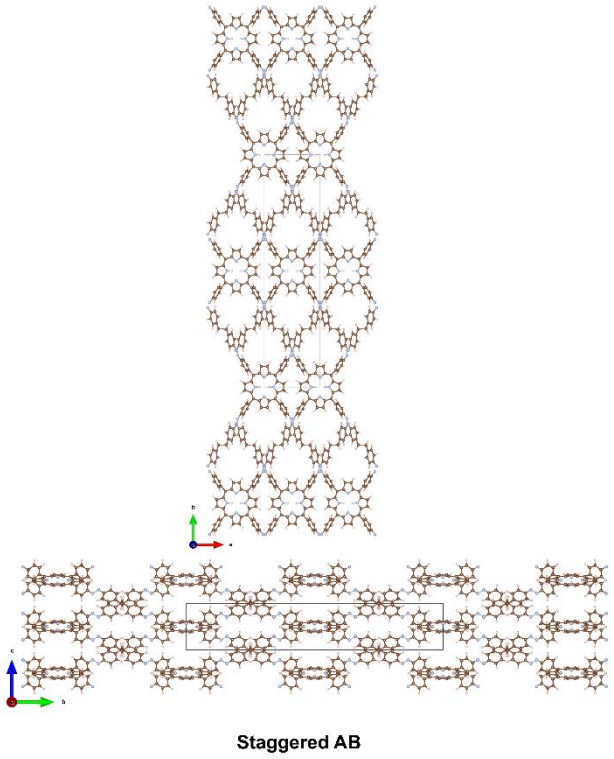


Figure S56. Optimized 3D geometry (PBE-D3/pob2-TZVP-rev2) of APP-2 with staggered (AB-stacked) 2D layers shown along the *c* unit cell vector.

8. Computational studies of adsorption isotherms

Table S7. Calculated framework properties of APPs (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
APP-1	2x2x8	0.582	1.056	1968.57
APP-2	2x2x8	0.228	1.504	2246.36
APP-3	2x2x8	0.632	0.942	1930.97
APP-4	2x2x8	0.581	1.071	1934.17
APP-5	2x2x8	0.186	4.920	6777.37
APP-6	2x2x8	0.104	9.167	7567.13
APP-7	2x2x8	0.834	0.568	1332.12
APP-8	2x2x8	0.922	0.510	1195.06
APP-2 (AB staggered)	3x2x4	0.726	0.783	2387.81

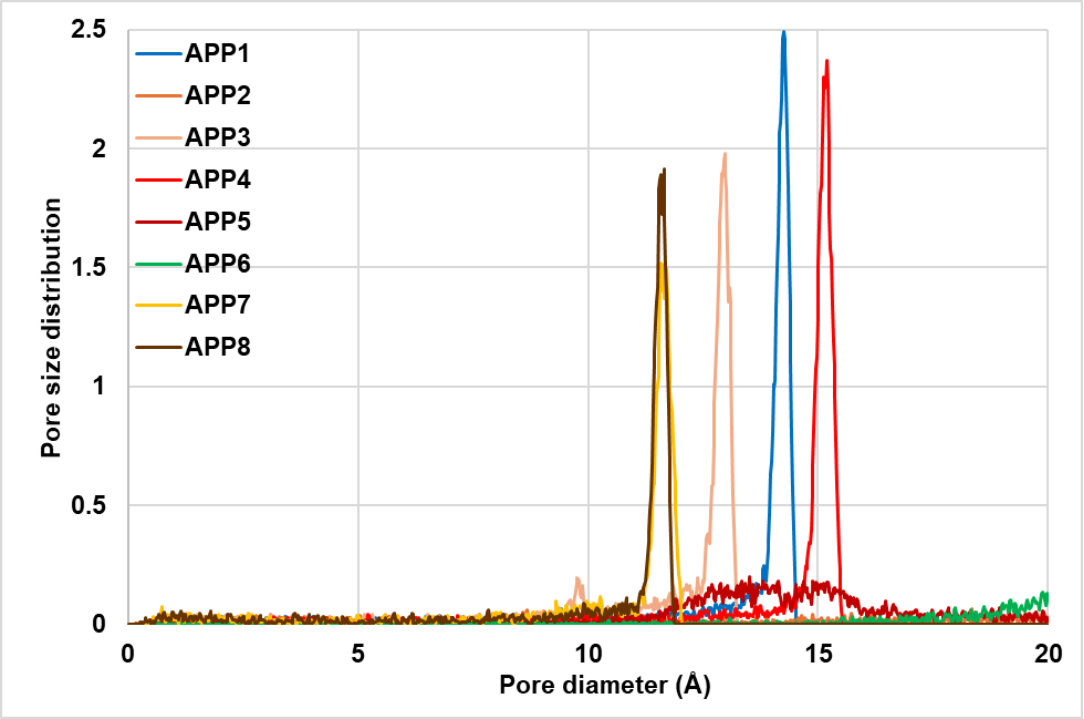


Figure S57. Pores size distribution of model compounds AAPs.

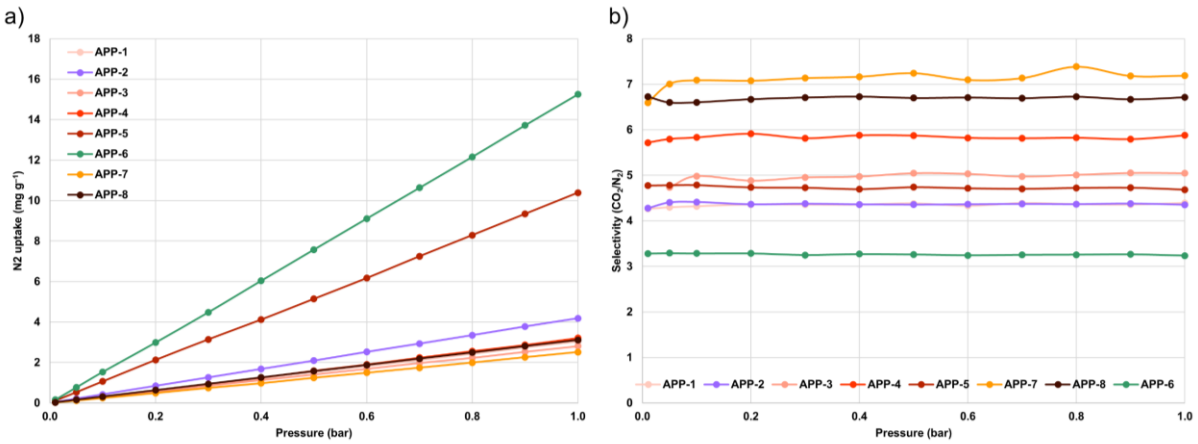


Figure S58. a) N_2 adsorption isotherms of model compounds at 298 K. b) CO_2/N_2 selectivities of APP-1–8 for binary mixtures (15 : 85 molar ratio) at 298 K.

Table S8. Calculated adsorption uptake of N_2 molecules at pressure of 1 bar and 298 K and average CO_2/N_2 selectivities of APP-1–8 for binary mixtures (15 : 85 molar ratio) at 298 K.

Compound	N_2 uptake (mg g^{-1})	Selectivity CO_2/N_2
APP-1	3.04	4.36
APP-2	4.19	4.37
APP-3	2.81	5.03
APP-4	3.21	5.88
APP-5	10.39	4.74
APP-6	15.3	3.26
APP-7	2.52	7.11
APP-8	3.11	6.68
APP-2 (AB staggered)	14.20	21.92

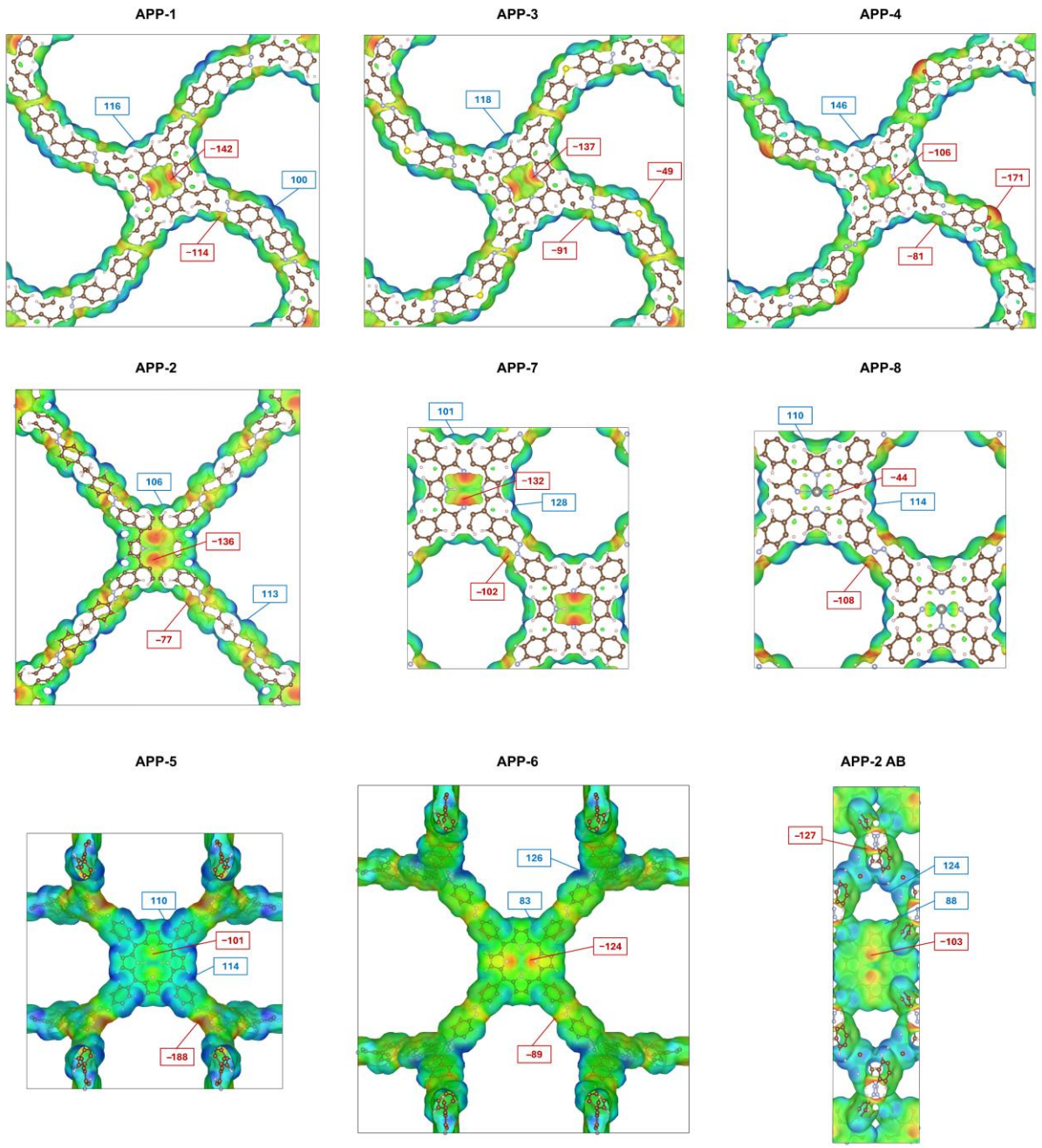


Figure S59. ESP maps of the selected unit cells of APP-1–8. Geometries optimized at the PBE-D3/pob-TZVP-rev2 level of theory The calculated ESP values are expressed in kJ mol^{-1} e^{-1}.

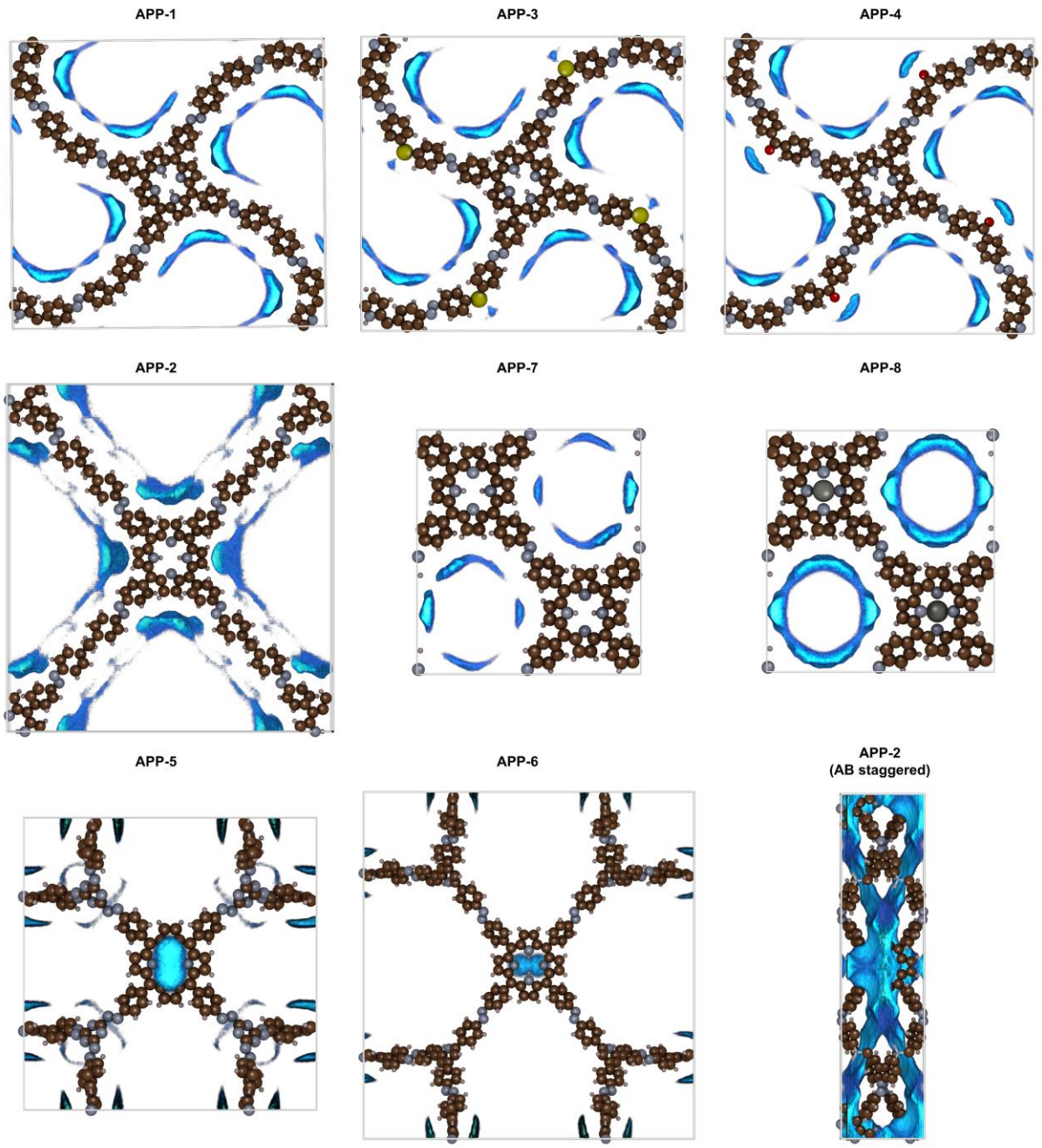


Figure S60. Density plots showing the average distribution of adsorbed CO2 molecules on APP-1–8 calculated at 298 K and 1 bar.

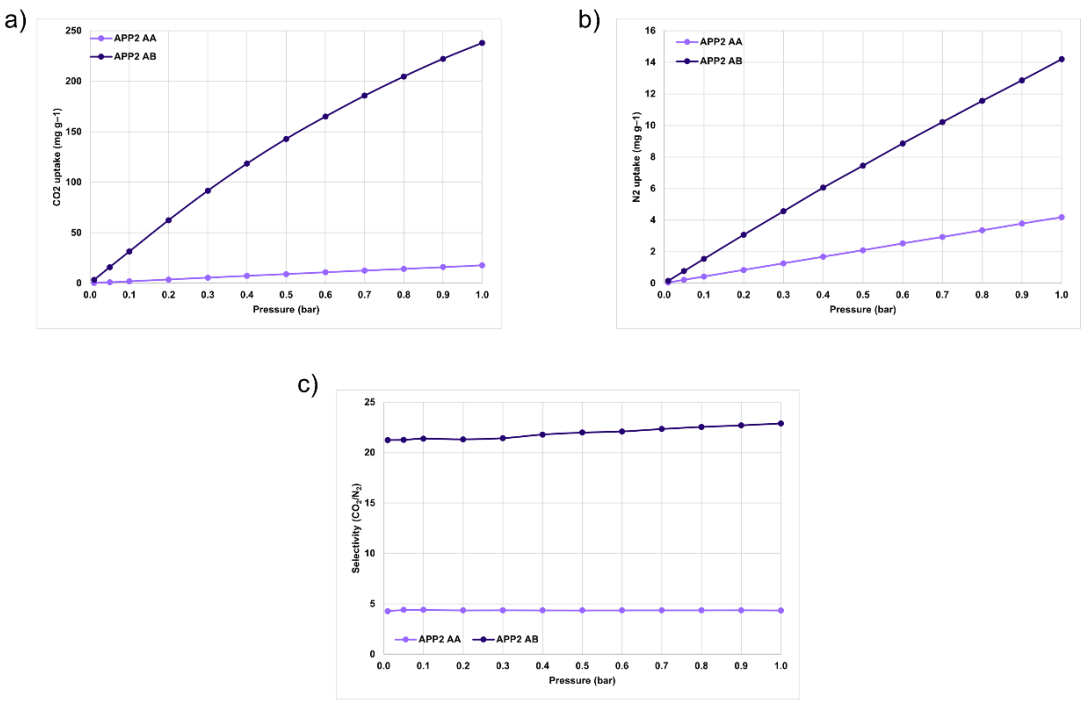


Figure S61. Comparison of a) CO_2 adsorption and b) N_2 adsorption isotherms at 298 K for AA (eclipsed) and AB (staggered) configurations of APP-2. c) CO_2/N_2 selectivities of AA (eclipsed) and AB (staggered) configurations of APP-2 for binary mixtures (15 : 85 molar ratio) at 298 K.

9. Fractional atomic coordinates and unit cell parameters.

Table S9. Fractional atomic coordinates for the unit cell of APP-1.

APP-1, Space group : *P* 21/c			
a = 37.3301 Å, b=40.6363 Å, c=3.9711 Å			
α = *γ* = 90˚,β = 89.0˚			
Atom	x	y	z
N1	0.72328	0.42598	0.84457
N2	0.72810	0.39451	0.87869
N3	0.52186	0.45829	0.31456
N4	0.89796	0.21116	0.74929
N5	0.92521	0.20780	0.94551
N6	0.55162	0.52229	0.49335
C7	0.56054	0.42222	0.03037
C8	0.58602	0.47502	0.25453
C9	0.55687	0.45335	0.20927
C10	0.67978	0.46875	0.87215
C11	0.64634	0.48109	0.96367
C12	0.50382	0.43032	0.21808
C13	0.52772	0.40794	0.03631
C14	0.68996	0.43709	0.97304
C15	0.66675	0.41866	0.18200
C16	0.63379	0.43154	0.27828
C17	0.62229	0.46271	0.16407
C18	0.76085	0.38306	0.74003
C19	0.76923	0.35020	0.80947
C20	0.78454	0.40202	0.54029
C21	0.80103	0.33648	0.68596
C22	0.81600	0.38809	0.41798
C23	0.82501	0.35518	0.49061
C24	0.85978	0.34154	0.34591
C25	0.87035	0.30760	0.45647
C26	0.90075	0.30267	0.65362
C27	0.85064	0.27995	0.35705
C28	0.91110	0.27144	0.75456
C29	0.86075	0.24854	0.45561
C30	0.89088	0.24402	0.65655
C31	0.93249	0.17481	0.03092
C32	0.91309	0.14749	0.91584
C33	0.96235	0.16970	0.23379
C34	0.92412	0.11604	0.99742
C35	0.97315	0.13801	0.31455
C36	0.95459	0.11035	0.19388
C37	0.58288	0.50731	0.38059
C38	0.61087	0.53098	0.42143
C39	0.55839	0.55405	0.60061

C40	0.59605	0.55926	0.55120
C41	0.46707	0.42335	0.27256
H42	0.52687	0.51126	0.49621
H43	0.58475	0.41302	0.90855
H44	0.63768	0.50478	0.86683
H45	0.52010	0.38489	0.92043
H46	0.67562	0.39468	0.27099
H47	0.61618	0.41761	0.44763
H48	0.75058	0.33607	0.96722
H49	0.80741	0.31088	0.74194
H50	0.91633	0.32407	0.73110
H51	0.93423	0.26756	0.91331
H52	0.89046	0.15175	0.75167
H53	0.97641	0.19123	0.32876
H54	0.91013	0.09485	0.89549
H55	0.63885	0.52681	0.35850
H56	0.61000	0.58189	0.60895
H57	0.99609	0.13426	0.47604
H58	0.85737	0.34166	0.06820
H59	0.88151	0.35901	0.40174
H60	0.84605	0.22674	0.37671
H61	0.82739	0.28323	0.19756
H62	0.83397	0.40253	0.25534
H63	0.77714	0.42727	0.48085
H64	0.69796	0.48243	0.70549

Table S10. Fractional atomic coordinates for the unit cell of APP-2.

APP-2, Space group : *C* 2/m			
a = 45.7682 Å, b=44.5117 Å, c=4.4251 Å			
α = *γ* = 90˚,β = 118.9˚			
Atom	x	y	z
N1	0.15473	0.13961	0.17235
N2	0.04845	0.00000	0.06103
N3	0.14582	0.16065	0.94113
N4	0.00000	0.04595	0.00000
C5	0.05564	0.05548	0.05065
C6	0.02481	0.06470	0.01924
C7	0.01541	0.09607	0.01250
C8	0.09411	0.01541	0.03359
C9	0.06536	0.02547	0.05367
C10	0.17231	0.17971	0.98599
C11	0.16315	0.20517	0.77244
C12	0.18689	0.22674	0.81744
C13	0.22034	0.22311	0.07081
C14	0.09556	0.12204	0.85506
C15	0.07201	0.10140	0.83439
C16	0.24544	0.24771	0.14258
C17	0.12842	0.12047	0.12982
C18	0.13688	0.09824	0.38361
C19	0.11316	0.07755	0.36031
C20	0.08036	0.07852	0.08287
C21	0.20600	0.17511	0.22948
C22	0.22951	0.19647	0.26604
H23	0.11188	0.03025	0.01330
H24	0.02626	0.00000	0.06532
H25	0.03047	0.11542	0.02696
H26	0.13696	0.20772	0.57875
H27	0.17935	0.24695	0.65704
H28	0.08959	0.13913	0.65715
H29	0.04676	0.10193	0.61647
H30	0.23547	0.26913	0.17845
H31	0.26841	0.24326	0.38517
H32	0.16230	0.09802	0.59924
H33	0.11965	0.06051	0.56000
H34	0.21272	0.15503	0.39014
H35	0.25572	0.19302	0.45673

Table S11. Fractional atomic coordinates for the unit cell of APP-3.

APP-3, Space group : *P* 21/c			
a = 36.2838 Å, b=39.7894 Å, c=3.9724 Å			
$\alpha = \beta = \gamma = 90^{\circ}$			
Atom	x	y	z
S1	0.89204	0.36481	0.30787
N2	0.52614	0.45923	0.30869
N3	0.73602	0.44130	0.81036
N4	0.74458	0.41000	0.86158
N5	0.91500	0.22279	0.75681
N6	0.94270	0.21710	0.94728
N7	0.55094	0.52666	0.48513
C8	0.56253	0.45690	0.19676
C9	0.56915	0.42552	0.01601
C10	0.59050	0.48114	0.23795
C11	0.68742	0.48150	0.84053
C12	0.65199	0.49167	0.93735
C13	0.51022	0.42937	0.21448
C14	0.53681	0.40845	0.02757
C15	0.70071	0.45013	0.94183
C16	0.67838	0.42977	0.15467
C17	0.64333	0.44044	0.25454
C18	0.62884	0.47129	0.14182
C19	0.77924	0.40061	0.72248
C20	0.79154	0.36848	0.81102
C21	0.80151	0.42077	0.50618
C22	0.82564	0.35667	0.69254
C23	0.83521	0.40890	0.38292
C24	0.84765	0.37680	0.47775
C25	0.89785	0.32255	0.45480
C26	0.92891	0.31531	0.64193
C27	0.87390	0.29668	0.36504
C28	0.93581	0.28263	0.74393
C29	0.88067	0.26400	0.46937
C30	0.91147	0.25671	0.65999
C31	0.94687	0.18306	0.03461
C32	0.92435	0.15675	0.92502
C33	0.97703	0.17554	0.23240
C34	0.93270	0.12390	0.00625
C35	0.98509	0.14247	0.31314
C36	0.96344	0.11576	0.19734
C37	0.58436	0.51375	0.36595
C38	0.61097	0.53992	0.40270
C39	0.55506	0.55946	0.59266
C40	0.59325	0.56760	0.53656
C41	0.47313	0.41948	0.27503
H42	0.64109	0.51512	0.84144

H43	0.79117	0.44530	0.43223
H44	0.68953	0.40607	0.24314
H45	0.85028	0.30230	0.21307
H46	0.77407	0.35353	0.98331
H47	0.83534	0.33197	0.76697
H48	0.94716	0.33581	0.71022
H49	0.95931	0.27653	0.89564
H50	0.90154	0.16280	0.76470
H51	0.99353	0.19635	0.32309
H52	0.91640	0.10341	0.90769
H53	0.64005	0.53775	0.33413
H54	0.60557	0.59166	0.59255
H55	0.00825	0.13686	0.47064
H56	0.52649	0.51363	0.49209
H57	0.70490	0.49667	0.67038
H58	0.86279	0.24323	0.40120
H59	0.85195	0.42398	0.20535
H60	0.53112	0.38440	0.91236
H61	0.62638	0.42498	0.42602
H62	0.59486	0.41807	0.88951

Table S12. Fractional atomic coordinates for the unit cell of APP-4.

APP-4, Space group : *P* 21/c			
a = 39.0383 Å, b=40.6331 Å, c=3.9260 Å			
$\alpha = \gamma = 90^{\circ}, \beta = 83.9^{\circ}$			
Atom	x	y	z
O1	0.87748	0.35542	0.32911
N2	0.51890	0.45740	0.29667
N3	0.71425	0.41786	0.75777
N4	0.72027	0.38804	0.85500
N5	0.89294	0.20774	0.84003
N6	0.91910	0.20507	0.01737
N7	0.55060	0.52025	0.45318
C8	0.55246	0.45092	0.16714
C9	0.55483	0.41945	0.98892
C10	0.58142	0.47140	0.18881
C11	0.67269	0.46075	0.75928
C12	0.64052	0.47430	0.85748
C13	0.50041	0.43009	0.21514
C14	0.52262	0.40659	0.01790
C15	0.68115	0.42950	0.87722
C16	0.65686	0.41222	0.09933
C17	0.62502	0.42613	0.19859
C18	0.61585	0.45740	0.07815
C19	0.75364	0.37656	0.74048
C20	0.76178	0.34545	0.86425
C21	0.77834	0.39416	0.52475
C22	0.79435	0.33219	0.77876
C23	0.81057	0.38067	0.43793
C24	0.81914	0.34956	0.56437
C25	0.86422	0.30345	0.57921
C26	0.89483	0.29918	0.73392
C27	0.84480	0.27581	0.50468
C28	0.90507	0.26813	0.82673
C29	0.85564	0.24447	0.58659
C30	0.88539	0.24047	0.75363
C31	0.92727	0.17232	0.09474
C32	0.90969	0.14438	0.99280
C33	0.95625	0.16817	0.27312
C34	0.92167	0.11330	0.06159
C35	0.96795	0.13685	0.34202
C36	0.95127	0.10860	0.23267
C37	0.57992	0.50387	0.31537
C38	0.60798	0.52626	0.33357
C39	0.55868	0.55166	0.55489
C40	0.59513	0.55518	0.47494
C41	0.46474	0.42463	0.29848
C42	0.85489	0.33739	0.47816

H43	0.63355	0.49787	0.75288
H44	0.77128	0.41810	0.42840
H45	0.66403	0.38836	0.19674
H46	0.82168	0.27886	0.37397
H47	0.74235	0.33278	0.03676
H48	0.80097	0.30857	0.88589
H49	0.90952	0.32101	0.78935
H50	0.92791	0.26447	0.95934
H51	0.88767	0.14789	0.84748
H52	0.96893	0.19014	0.35883
H53	0.90910	0.09171	0.96757
H54	0.63467	0.52090	0.24706
H55	0.60968	0.57715	0.52087
H56	0.99013	0.13385	0.48587
H57	0.52622	0.51046	0.47640
H58	0.69157	0.47339	0.58028
H59	0.84162	0.22246	0.52344
H60	0.83026	0.39358	0.27037
H61	0.51448	0.38371	0.90961
H62	0.60651	0.41312	0.37763
H63	0.57792	0.40899	0.85324

Table S13. Fractional atomic coordinates for the unit cell of APP-5.

APP-5, Space group : *P m m m*			
a = 35.3823 Å, b=35.3734 Å, c=35.3613 Å			
$\alpha = \beta = \gamma = 90^{\circ}$			
Atom	x	y	z
N1	0.24208	0.21137	0.18020
N2	-0.50000	0.44286	0.23000
N3	0.22632	0.17908	0.18706
N4	0.22993	0.05970	0.00000
N5	0.18019	0.25807	0.28864
N6	0.18701	0.27388	0.32093
N7	0.00000	0.27029	0.44028
N8	0.28868	0.31987	0.24202
N9	0.32100	0.31298	0.22633
N10	0.44032	-0.50000	0.22990
N11	0.23615	0.28943	0.26600
N12	0.21068	0.23405	0.23613
N13	0.26606	0.26390	0.21067
N14	0.05713	0.27022	-0.50000
N15	0.23000	0.00000	0.05717
C16	0.22951	0.09822	0.09951
C17	0.21687	0.11904	0.01942
C18	0.23007	0.06906	0.06956
C19	0.25279	0.13061	0.09702
C20	0.20601	0.09402	0.13138
C21	0.25234	0.15802	0.12494
C22	0.20598	0.12100	0.15987
C23	0.22870	0.15337	0.15661
C24	0.23927	0.23696	0.21106
C25	0.21107	0.26086	0.26307
C26	0.26311	0.28900	0.23922
C27	0.23485	0.03092	0.08040
C28	0.24518	0.01921	0.11851
C29	0.15655	0.27152	0.34662
C30	0.15978	0.29427	0.37898
C31	0.13129	0.29424	0.40595
C32	0.09700	0.24741	0.36937
C33	0.09946	0.27072	0.40175
C34	0.06952	0.27014	0.43091
C35	0.08035	0.26538	0.46907
C36	0.03204	0.27448	0.41835
C37	0.11845	0.25507	0.48079
C38	0.01941	0.28331	0.38091
C39	0.12492	0.24786	0.34196
C40	0.34669	0.34343	0.22870
C41	0.37908	0.34015	0.20601
C42	0.34201	0.37511	0.25231

C43	0.40604	0.36863	0.20603
C44	0.36941	0.40303	0.25275
C45	0.40181	0.40053	0.22950
C46	0.43096	0.43047	0.23007
C47	0.46909	0.41964	0.23487
C48	0.41841	0.46795	0.22568
C49	0.48080	0.38155	0.24525
C50	0.38101	0.48058	0.21679
C51	0.22572	0.08162	0.03206
H52	0.00000	0.26670	0.46903
H53	0.36671	0.42709	0.27188
H54	0.46905	-0.50000	0.23353
H55	0.27194	0.13328	0.07298
H56	0.23353	0.03096	0.00000
H57	0.27052	0.18288	0.12364
H58	0.18803	0.11831	0.18481
H59	0.25252	0.03796	0.14169
H60	0.18470	0.31224	0.38168
H61	0.13309	0.31268	0.43061
H62	0.07298	0.22824	0.36669
H63	0.14162	0.24774	0.46203
H64	0.03798	0.28958	0.35731
H65	0.38180	0.31519	0.18808
H66	0.31714	0.37643	0.27046
H67	0.43072	0.36679	0.18763
H68	0.46205	0.35838	0.25262
H69	0.35743	0.46201	0.21049
H70	0.12365	0.22966	0.31711
H71	0.21059	0.14263	0.03800
H72	0.18759	0.06936	0.13321

Table S14. Fractional atomic coordinates for the unit cell of APP-6.

APP-6, Space group : *P m m m*			
a = 46.7044 Å, b=47.9558 Å, c=48.4064 Å			
$\alpha = \beta = \gamma = 90^{\circ}$			
Atom	x	y	z
N1	0.15811	0.24580	0.36502
N2	0.04527	0.23669	-0.50000
N3	0.13655	0.22865	0.36422
N4	0.25940	0.25952	0.27728
N5	0.36399	0.34517	0.26203
N6	0.35990	0.36602	0.27880
N7	0.50000	0.45613	0.28342
N8	0.45655	-0.50000	0.28366
N9	0.00000	0.23586	0.45821
N10	0.25218	0.13750	0.14981
N11	0.27228	0.13746	0.13121
N12	0.26696	0.00000	0.04360
N13	0.26695	0.04191	0.00000
C14	0.05235	0.23592	0.44916
C15	0.01454	0.24374	0.41274
C16	0.02342	0.23827	0.44107
C17	0.06198	0.23412	0.47658
C18	0.07449	0.23477	0.42732
C19	0.09061	0.22898	0.48582
C20	0.07257	0.21494	0.40600
C21	0.09795	0.25333	0.42737
C22	0.09345	0.21358	0.38565
C23	0.11884	0.25209	0.40710
C24	0.11679	0.23202	0.38601
C25	0.17759	0.24229	0.34298
C26	0.17460	0.22243	0.32172
C27	0.20120	0.26048	0.34277
C28	0.19470	0.22122	0.30078
C29	0.22137	0.25907	0.32176
C30	0.21849	0.23947	0.30030
C31	0.23972	0.23881	0.27765
C32	0.25845	0.21925	0.23503
C33	0.27869	0.26048	0.25648
C34	0.30030	0.28292	0.25776
C35	0.29571	0.30634	0.27480
C36	0.32600	0.28124	0.24274
C37	0.31592	0.32733	0.27678
C38	0.34641	0.30213	0.24468
C39	0.34163	0.32537	0.26169
C40	0.38246	0.38570	0.27863
C41	0.40640	0.38453	0.26103
C42	0.37989	0.40776	0.29753

C43	0.42719	0.40502	0.26257
C44	0.40087	0.42824	0.29901
C45	0.42493	0.42725	0.28158
C46	0.44734	0.44904	0.28274
C47	0.47573	0.43983	0.28570
C48	0.43893	0.47718	0.28018
C49	0.48529	0.41195	0.29089
C50	0.40994	0.48583	0.27319
C51	0.25740	0.19837	0.21267
C52	0.23170	0.18440	0.20640
C53	0.28206	0.19172	0.19717
C54	0.23077	0.16433	0.18579
C55	0.28116	0.17220	0.17609
C56	0.25541	0.15825	0.17025
C57	0.26994	0.11539	0.11203
C58	0.28553	0.11840	0.08746
C59	0.25382	0.09103	0.11651
C60	0.28443	0.09781	0.06733
C61	0.25325	0.07032	0.09661
C62	0.26830	0.07332	0.07151
C63	0.26740	0.05127	0.05032
C64	0.27203	0.02362	0.05914
C65	0.26237	0.05884	0.02258
C66	0.28180	0.01434	0.08562
C67	0.25278	0.08636	0.01404
C68	0.23951	0.21789	0.25741
C69	0.27803	0.24135	0.23457
H70	0.02343	0.23851	-0.50000
H71	0.50000	0.47737	0.28132
H72	0.26324	0.00000	0.02270
H73	0.02882	0.24768	0.39547
H74	0.10865	0.22519	0.47221
H75	0.05464	0.20037	0.40594
H76	0.09917	0.26910	0.44359
H77	0.09245	0.19818	0.36908
H78	0.13686	0.26651	0.40685
H79	0.15617	0.20844	0.32209
H80	0.20304	0.27572	0.35947
H81	0.19163	0.20599	0.28423
H82	0.23973	0.27316	0.32132
H83	0.27571	0.30734	0.28638
H84	0.33042	0.26304	0.22998
H85	0.31248	0.34557	0.28981
H86	0.36667	0.30099	0.23342
H87	0.40786	0.36747	0.24622
H88	0.36116	0.40816	0.31102
H89	0.44553	0.40452	0.24860

H90	0.39904	0.44522	0.31393
H91	0.47120	0.39436	0.29474
H92	0.39235	0.47198	0.26811
H93	0.21209	0.18982	0.21752
H94	0.30240	0.20166	0.20239
H95	0.21101	0.15324	0.18084
H96	0.30020	0.16684	0.16419
H97	0.29825	0.13727	0.08467
H98	0.24195	0.08903	0.13578
H99	0.29654	0.10017	0.04820
H100	0.24046	0.05159	0.09982
H101	0.28857	0.02813	0.10219
H102	0.24618	0.10306	0.02776
H103	0.22500	0.20019	0.25915
H104	0.29220	0.24407	0.21687

Table S15. Fractional atomic coordinates for the unit cell of APP-7.

APP-7, Space group : *P* 21/m			
a = 25.0325 Å, b=27.2964 Å, c=3.8922 Å			
α = *γ* = 90˚,β = 87.0˚			
Atom	x	y	z
N1	0.74996	0.17482	0.00081
N2	0.50632	0.51898	0.40551
N3	0.67101	0.25000	0.84484
N4	0.82890	0.25000	0.15686
N5	0.00630	0.01899	0.40557
H6	0.56432	0.20093	0.52167
H7	0.79984	0.06132	0.09971
H8	0.55525	0.15818	0.06948
H9	0.51523	0.59596	0.03537
H10	0.94463	0.15822	0.93159
H11	0.29991	0.56132	0.09836
H12	0.83288	0.07646	0.58092
H13	0.40286	0.51350	0.67209
H14	0.90288	0.01349	0.67290
H15	0.01514	0.09600	0.03577
H16	0.93563	0.20093	0.47951
H17	0.70777	0.25000	0.94884
H18	0.66711	0.07648	0.42051
H19	0.79212	0.25000	0.05299
C20	0.87241	0.07994	0.45280
C21	0.41111	0.54497	0.50522
C22	0.91109	0.04496	0.50606
C23	0.61657	0.12182	0.75285
C24	0.88337	0.12183	0.24840
C25	0.56433	0.12701	0.90161
C26	0.93558	0.12703	0.09936
C27	0.52505	0.09245	0.84600
C28	0.97488	0.09247	0.15461
C29	0.53681	0.05104	0.64209
C30	0.96315	0.05105	0.35841
C31	0.35748	0.70841	0.23330
C32	0.85740	0.20841	0.23487
C33	0.59444	0.22489	0.61998
C34	0.90549	0.22489	0.38139
C35	0.65796	0.15929	0.81225
C36	0.84196	0.15929	0.18926
C37	0.72447	0.09318	0.94928
C38	0.79110	0.14426	0.08708
C39	0.77546	0.09318	0.05212
C40	0.70882	0.14426	0.91446
C41	0.62755	0.07994	0.54840

Table S16. Fractional atomic coordinates for the unit cell of APP-8.

APP-8, Space group : *P* 21/m			
a = 25.1881 Å, b=26.5767 Å, c=3.9530 Å			
$\alpha = \beta = \gamma = 90^{\circ}$			
Atom	x	y	z
ZN1	0.74996	0.75000	0.00062
N2	0.49421	0.51843	0.60601
N3	0.74996	0.67240	0.00067
N4	0.00579	0.51846	0.39419
N5	0.82266	0.75000	0.17899
N6	0.67725	0.75000	0.82241
C7	0.77465	0.58951	0.05593
C8	0.79010	0.64131	0.09346
C9	0.70982	0.64131	0.90777
C10	0.72529	0.58951	0.94502
C11	0.83894	0.65744	0.19954
C12	0.66098	0.65744	0.80170
C13	0.89977	0.72435	0.39269
C14	0.60015	0.72435	0.60859
C15	0.85227	0.70815	0.25190
C16	0.64765	0.70815	0.74943
C17	0.96177	0.54932	0.34602
C18	0.53820	0.54931	0.65443
C19	0.97289	0.59122	0.13424
C20	0.52705	0.59118	0.86637
C21	0.93298	0.62566	0.08576
C22	0.56694	0.62563	0.91512
C23	0.88061	0.61942	0.24675
C24	0.61932	0.61942	0.75425
C25	0.90937	0.54183	0.50154
C26	0.59062	0.54184	0.49906
C27	0.86989	0.57628	0.45009
C28	0.63008	0.57630	0.55076
H29	0.70175	0.55688	0.89218
H30	0.92922	0.69962	0.48434
H31	0.57070	0.69962	0.51684
H32	0.48656	0.59549	0.99330
H33	0.94192	0.65788	0.91856
H34	0.55799	0.65783	0.08246
H35	0.90137	0.50964	0.67048
H36	0.59864	0.50966	0.33000
H37	0.82982	0.57157	0.58084
H38	0.67016	0.57161	0.42011
H39	0.01338	0.59554	0.00721
H40	0.79820	0.55688	0.10872

Table S17. Fractional atomic coordinates for the unit cell of APP-2 (AB staggered configuration).

APP-2 (staggered, AB), Space group : *C* 2/m			
a = 11.7105 Å, b=48.3794 Å, c=8.7957 Å			
α = *γ* = 90˚,β = 84.3˚			
N1	0.00000	0.04196	-0.50000
N2	-0.47941	0.13572	0.21468
N3	-0.16686	0.00000	0.42823
N4	-0.48797	0.15858	0.29279
C5	-0.34518	0.01420	0.38822
C6	-0.19477	0.05094	0.42106
C7	-0.08681	0.05931	0.46341
C8	-0.23207	0.02343	0.41195
C9	-0.18404	-0.25145	-0.00969
C10	0.44872	0.17926	0.22522
C11	0.46053	0.20609	0.28194
C12	0.41535	0.22850	0.20879
C13	0.35773	0.22455	0.07823
C14	-0.37418	0.11638	0.42421
C15	-0.30788	0.09506	0.47317
C16	-0.31593	0.07140	0.23171
C17	-0.41286	0.11519	0.27785
C18	-0.38500	0.09231	0.18340
C19	0.34058	0.19738	0.02822
C20	-0.27481	0.07256	0.37665
C21	0.38487	0.17489	0.10001
C22	-0.05292	0.08814	0.47486
H23	-0.48882	0.20880	0.37858
H24	-0.08255	0.00000	0.45054
H25	-0.41741	0.02781	0.37600
H26	0.42815	0.24950	0.24981
H27	-0.29008	0.05417	0.15598
H28	-0.39792	0.13411	0.49713
H29	-0.28022	0.09553	-0.41190
H30	-0.14499	-0.23209	0.02604
H31	0.34422	0.24581	-0.13215
H32	0.37728	0.15396	0.05617
H33	0.29585	0.19408	-0.07368
H34	-0.41546	0.09207	0.07001
H35	-0.10331	0.10601	0.44823

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