Supporting information

Imination enables efficient formation of a pillararene-inspired host with endo-cavity hydrogen-bonding capability

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Experimental details

General information

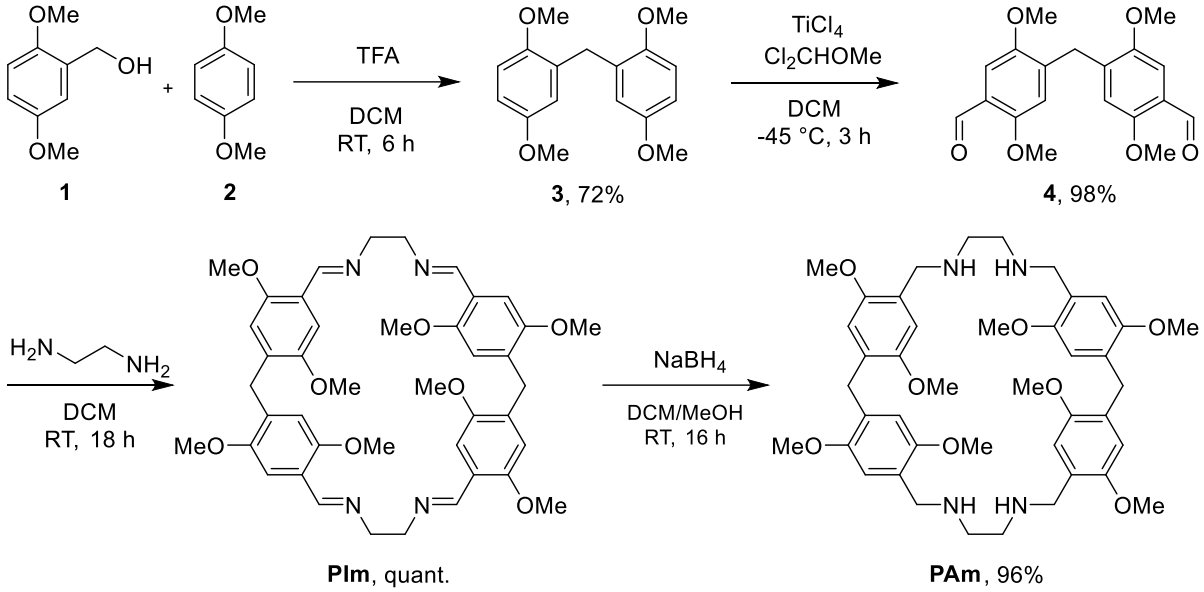
The chemicals and solvents were obtained from commercial sources (Acros Organics, Fluorochem, TCI Europe or Thermo Fischer Scientific) and used without further purification. Thin-layer chromatography (TLC) was performed on silica gel 0.20 mm 60 with fluorescent indicator UV254 (pre-coated aluminium sheets) from Merck. Compounds were visualised under visible light or UV irradiation (254 nm).

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 400 spectrometer with a Bruker Ascend™ 400 magnet system and a 5 mm PABBO BB/19F-1H/D probe with z-gradients or on a Bruker Avance II+ 600 spectrometer with a Bruker 600 UltraShield™ magnet system and a 5 mm PABBO BB-1H/D probe with z-gradients. ^{13}C-detected experiments were ^{1}H-decoupled using power-gated broadband decoupling. Variable temperature NMR was performed on a Bruker Avance Neo 600 spectrometer with an Ascend™ 600 magnet system and 5 mm PI HR-TBO (BB/F-H/F-D) probe with z-gradients. Translational diffusion measurements were performed using Bruker's 'ledbpgs2s' DOSY pulse sequence using stimulated echo and LED, bipolar gradient diffusion pulses and phase-sensitive 2-spoil pulses with a 60 ms diffusion time (D20) and 1.3 ms gradient length (P30). Data were recorded at room temperature using TopSpin 3.6.x (Bruker Avance III HD 400 and Bruker Avance II+ 600 sprectrometers) or TopSpin 4.2.x (Bruker Avance Neo 600 spectrometer). ^{1}H and ^{13}C spectra were internally calibrated using tetramethylsilane (TMS) or the deuterated solvents. The δ-values are expressed in parts per million (ppm). The following acronyms were used: s (singlet), d (doublet). The prefix app. denotes the apparent multiplicity of a signal, indicating the general shape and form of the multiplet in the spectrum, even though this is not theoretically expected based on the molecular structure of the compound and/or higher order fine structure could be observed. Coupling constants (J) are reported in Hertz (Hz).

High-resolution mass spectra were acquired on a quadrupole orthogonal acceleration time-of-flight mass spectrometer (Synapt G2 HDMS, Waters, Milford, MA). Samples were infused at 3 µL/min and spectra were obtained in positive (or: negative) ionization mode with a resolution of 15000 (FWHM) using leucine enkephalin as lock mass. Matrix-assisted laser desorption/ionization – time-of-flight (MALDI-TOF) mass spectra were recorded using a Bruker UltrafleXtreme™ MALDI-TOF/TOF system. A mixture of 10 µL 25 mg mL^{-1} trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile in chloroform and 3 µL analyte (10 mg mL^{-1} in chloroform) was prepared, after which 0.5 µL of the resulting solution was spotted onto an MTP Anchorchip 600/384 MALDI plate.

Melting points were determined on a Reichert Thermovar apparatus and are uncorrected.

Host synthesis



Scheme S1: Synthesis of host **PIm** and subsequent reduction to **PAm**.

Bis(2,5-dimethoxyphenyl)methane (**3**)

3 was prepared according to a modified literature procedure [1]. To a solution of (2,5-dimethoxyphenyl)methanol **1** (6.1 g, 36 mmol) and 1,4-dimethoxybenzene **2** (49.8 g, 360 mmol) in DCM (600 mL) was added trifluoroacetic acid (72 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. After quenching with 1 N aqueous NaOH, the organic layer was extracted three times with water, dried over $MgSO_4$, filtered and evaporated to dryness. Purification by column chromatography in DCM/PE 1/9 to 2/5 yielded the product as an off-white solid (7.5 g, 72%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.79 (app. d, J = 8.8 Hz, 2H), 6.70 (app. dd, J = 8.8, 3.1 Hz, 2H), 6.65 (app. d, J = 3.1 Hz, 2H), 3.91 (s, 2H), 3.79 (s, 6H), 3.71 (s, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ (ppm) = 153.5, 151.9, 130.3, 116.9, 111.2, 111.1, 56.1, 55.6, 30.0; **HRMS** (ESI, $[M]^+$): 288.1361 found: 288.1357; **Melting point**: 85-86 °C

^{1}H-NMR and ^{13}C-NMR data are consistent with the literature [1].

4,4'-Methylenebis(2,5-dimethoxybenzaldehyde) (**4**)

$TiCl_4$ (1 M in DCM, 17.3 mmol) was added to **3** (1.04 g, 3.6 mmol) dissolved in dry DCM (14 ml) at -45 °C. Dichloro(methoxy)methane (1.9 mL, 21.0 mmol) was added dropwise and the mixture was stirred for 3 h at -45 °C. The reaction content was poured into ice water and washed three times with water under vigorous shaking. The organic phase was directly filtered over SiO_2, which was rinsed with DCM and EtOAc, respectively. *In vacuo* removal of the solvent yielded the product as a yellow solid (1.21 g, 98%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.40 (s, 2H), 7.32 (s, 2H), 6.77 (s, 2H), 4.02 (s, 2H), 3.85 (s, 6H), 3.81 (s, 6H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ (ppm) = 189.4, 156.8, 151.8, 137.4, 123.6, 114.7, 108.4, 56.3, 56.0, 31.7; **HRMS** (ESI, $[M+H]^+$): 345.1333 found: 345.1329; **Melting point**: 154-155 °C

(4*E*,8*E*,13*E*,17*E*)-1^2,1^5,3^2,3^5,10^2,10^5,12^2,12^5-Octamethoxy-5,8,14,17-tetraaza-1,3,10,12(1,4)-tetrabenzenacyclooctadecaphane-4,8,13,17-tetraene (**PIm**)

A test tube equipped with a magnetic stirring bar was loaded with **3** (1.03 g, 3.0 mmol), ethylene diamine (200 µL, 3.0 mmol) and DCM (70 mL). The mixture was left to stir for 18 h at room temperature. *In vacuo* removal of the solvent at 25 °C yielded the product as a pale yellow solid without further purification (1.10 g, quant.).

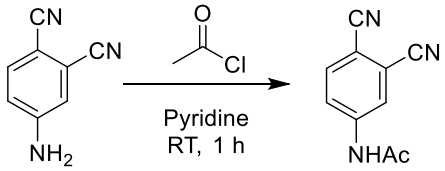
^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 4 H), 7.27 (s, 4 H), 6.80 (s, 4 H), 3.99 (s, 8 H), 3.87 (s, 4 H), 3.80 (s, 12 H), 3.57 (s, 12 H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ (ppm) = 159.1, 153.1, 151.5, 133.2, 123.2, 114.6, 108.5, 61.0, 56.1, 55.9, 30.4; **MS** (MALDI, $[M+H]^+$): Calculated: 737.354, Found: 737.375; **Melting point**: 246-247 °C

(4*E*,8*E*,13*E*,17*E*)-1^2,1^5,3^2,3^5,10^2,10^5,12^2,12^5-Octamethoxy-5,8,14,17-tetraaza-1,3,10,12(1,4)-tetrabenzenacyclooctadecaphane-4,8,13,17-tetraene (**PAm**)

To flame-dried glassware containing **PIm** (100 mg, 0.14 mmol), dry DCM (4 mL) and dry MeOH (4 mL) were added under nitrogen atmosphere. Then, $NaBH_4$ (51 mg, 1.4 mmol) was added and the reaction mixture was flushed with nitrogen. After stirring at room temperature for 16 h, the mixture was diluted with DCM and washed three times with saturated aqueous sodium carbonate. The organic phase was dried over $MgSO_4$, filtered and dried *in vacuo* to afford the product as an off-white solid (97 mg, 96%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.95 (s, 4H), 6.70 (s, 4H), 3.81 (s, 4H), 3.73 (s, 12H), 3.69 (s, 8H), 3.57 (s, 12H), 3.19 (4 H), 3.05 (s, 8H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ (ppm) = 151.5, 151.3, 128.7, 126.9, 113.6, 113.2, 56.2, 55.9, 49.4, 48.7, 30.1; **HRMS** (ESI, $[M+2H]/2^+$): Calculated: 373.2124, Found: 373.2111; **Melting point**: >300 °C

Guest synthesis



5 **G5**, 91%

Scheme S2: Synthesis of guest **G5**.

N-(3,4-Dicyanophenyl)acetamide (**G5**)

G5 was prepared according to a literature procedure [2]. 3,4-Dicyanoaniline **5** (1.0 g, 7.0 mmol) and acetyl chloride (0.66 mL, 9.3 mmol) were added to pyridine (10 mL). The mixture was left to stir for 1 h at room temperature, after which ice water (120 mL) was added. The mixture was stirred for an additional hour and subsequently filtered to yield the product as an off-white solid (1.2 g, 6.3 mmol, 91%).

^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.7 (s, 1H), 8.25 (app. d, J = 2.1 Hz, 1H), 8.04 (app. d, J = 8.7, 1H), 7.93 (app. dd, J = 8.7, 2.1 Hz, 1H), 2.12 (s, 3H); **^{13}C-NMR** (101 MHz, DMSO-d_6): δ (ppm) = 169.7, 143.7, 125.1, 122.7, 122.6, 116.2, 115.9, 115.4, 107.5, 24.2; **Mp**: 203 °C

The characterization data are in accordance with reported literature [3].

NMR characterization data

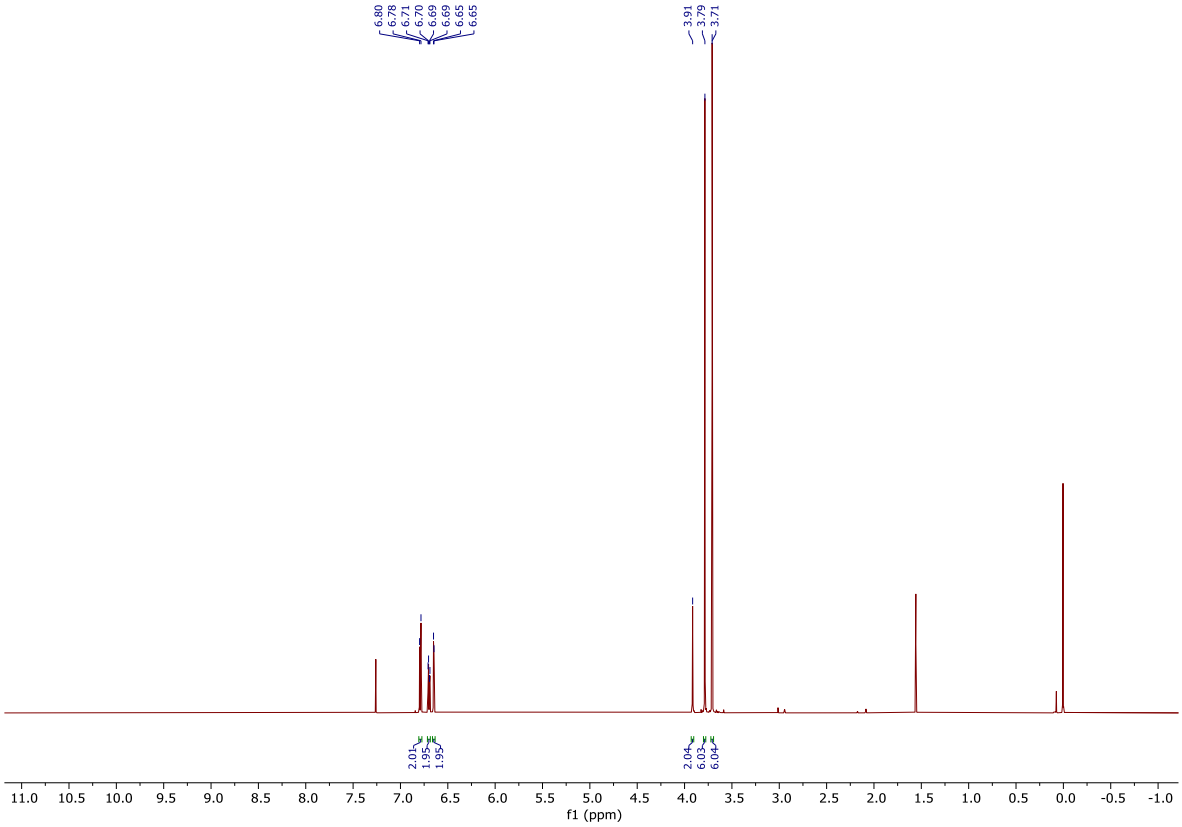


Figure S1: ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of **3**

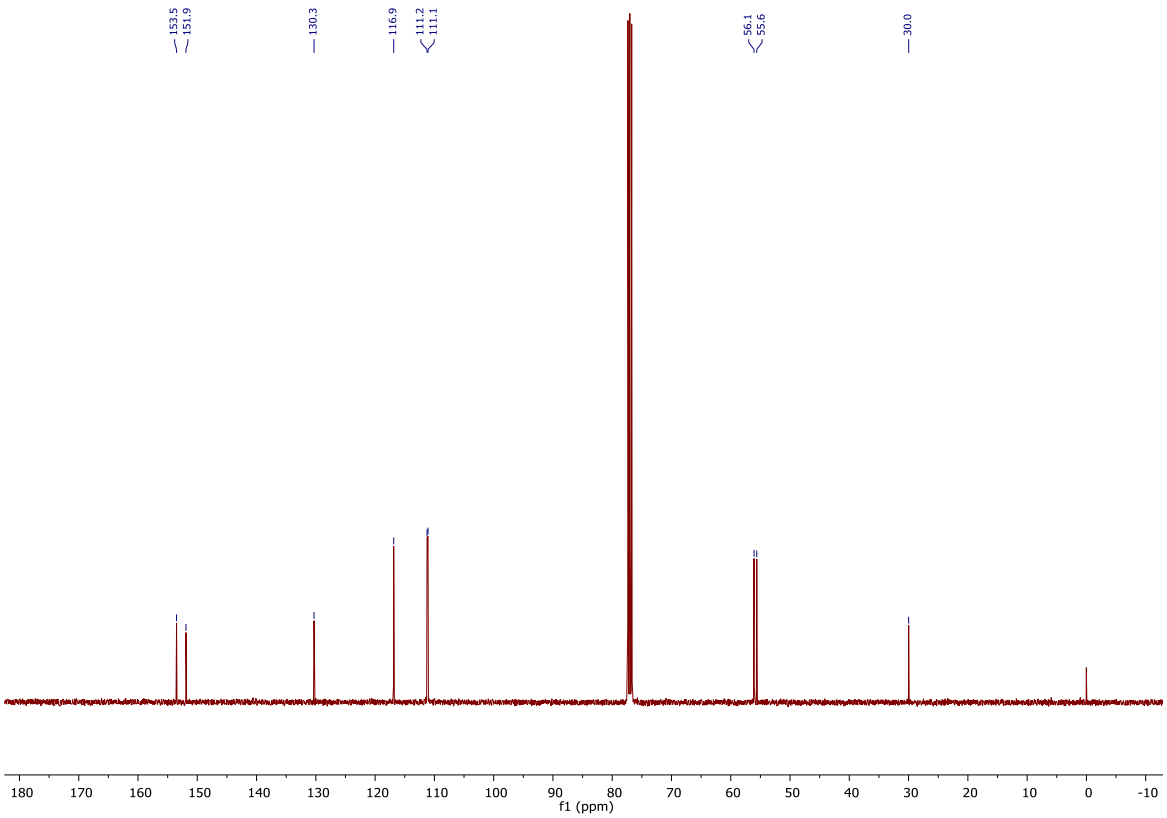


Figure S2: ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **3**

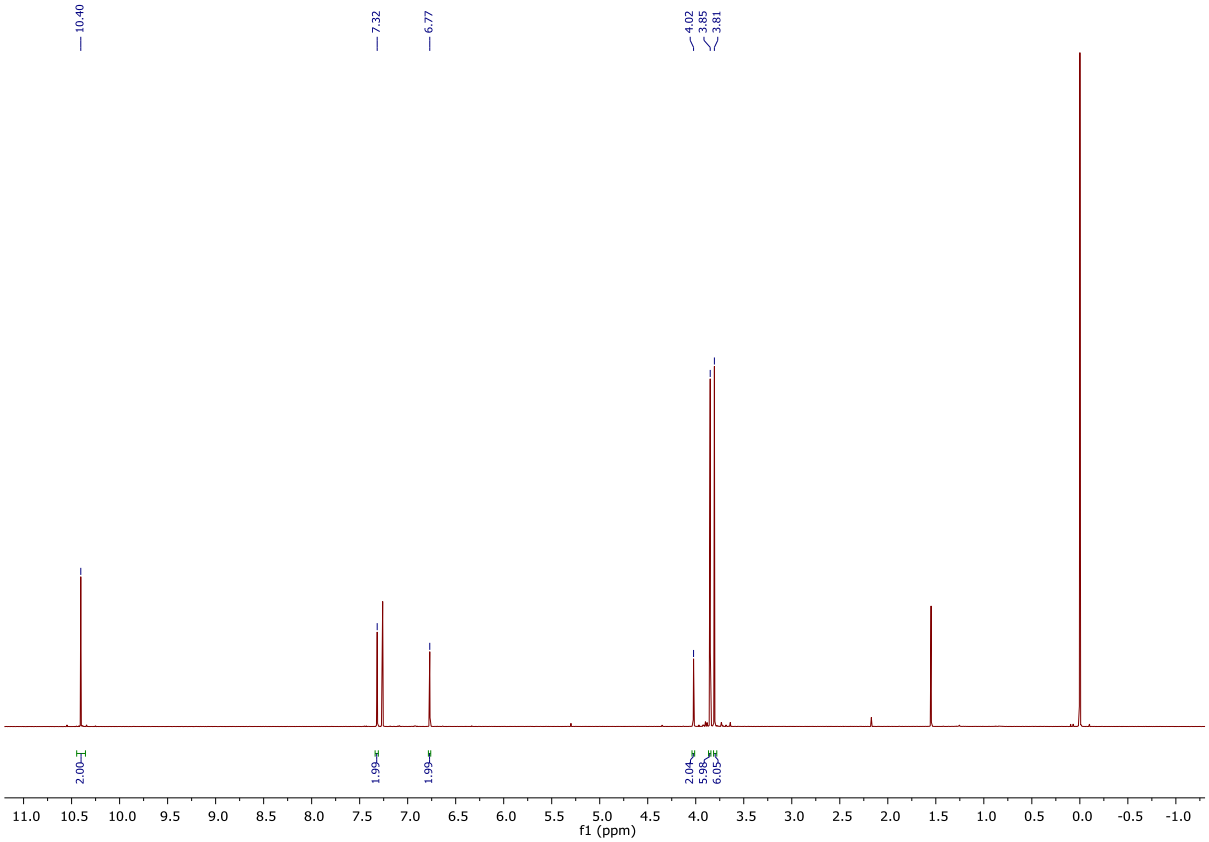


Figure S3: ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of **4**

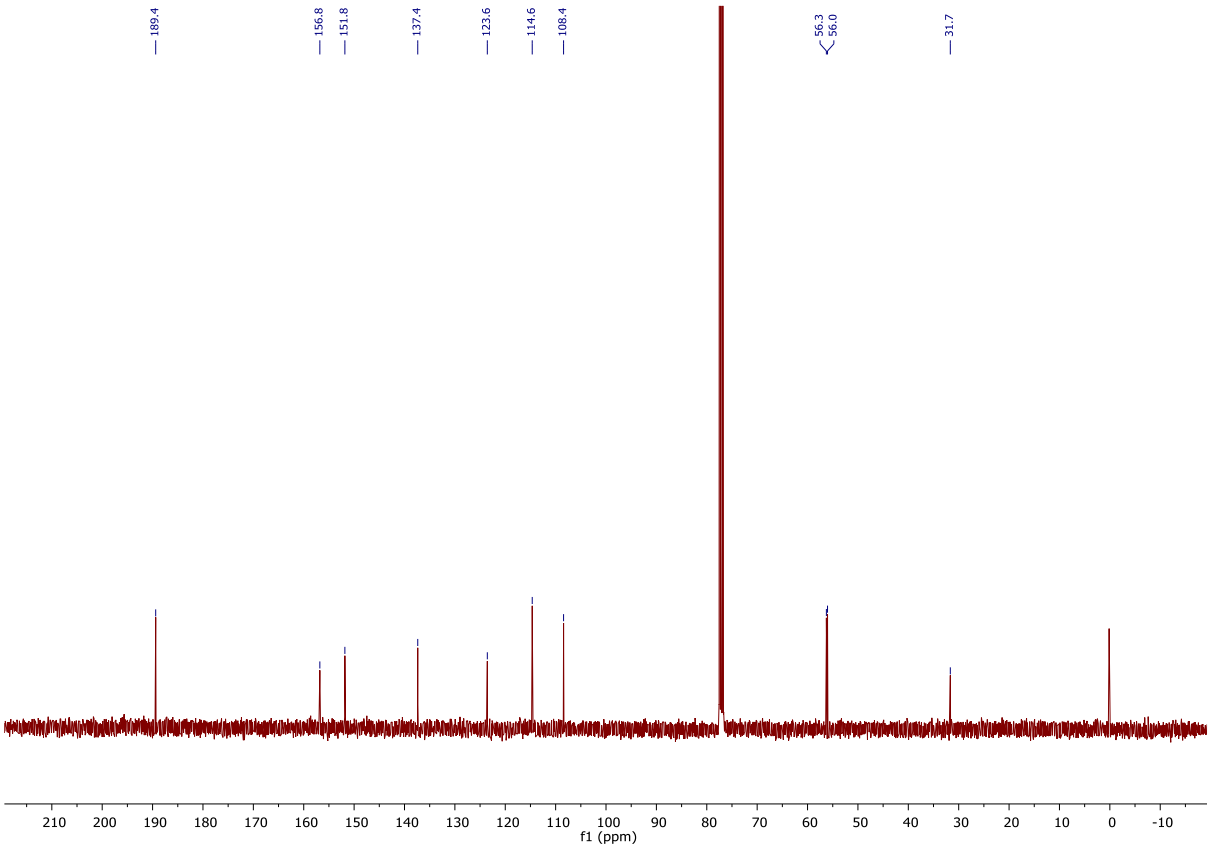


Figure S4: ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **4**

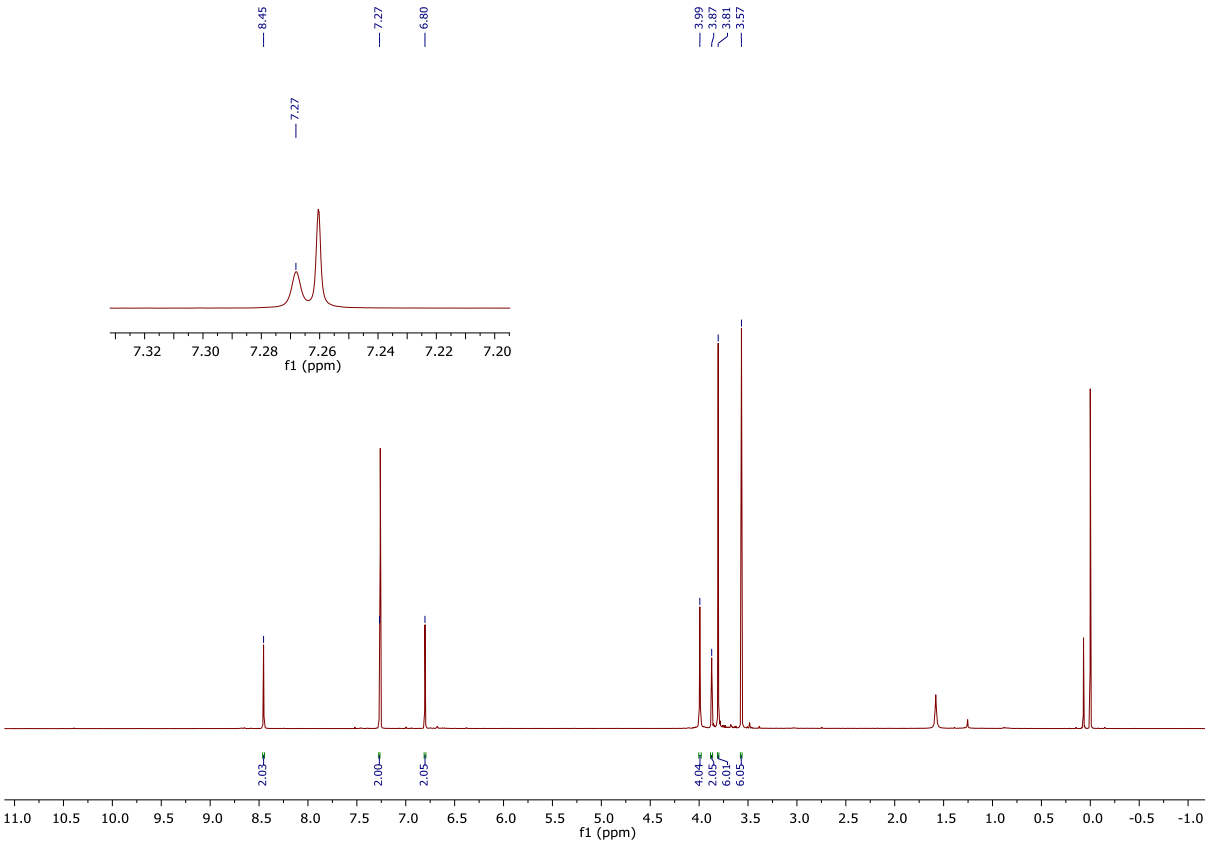


Figure S5: ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of **PIm**

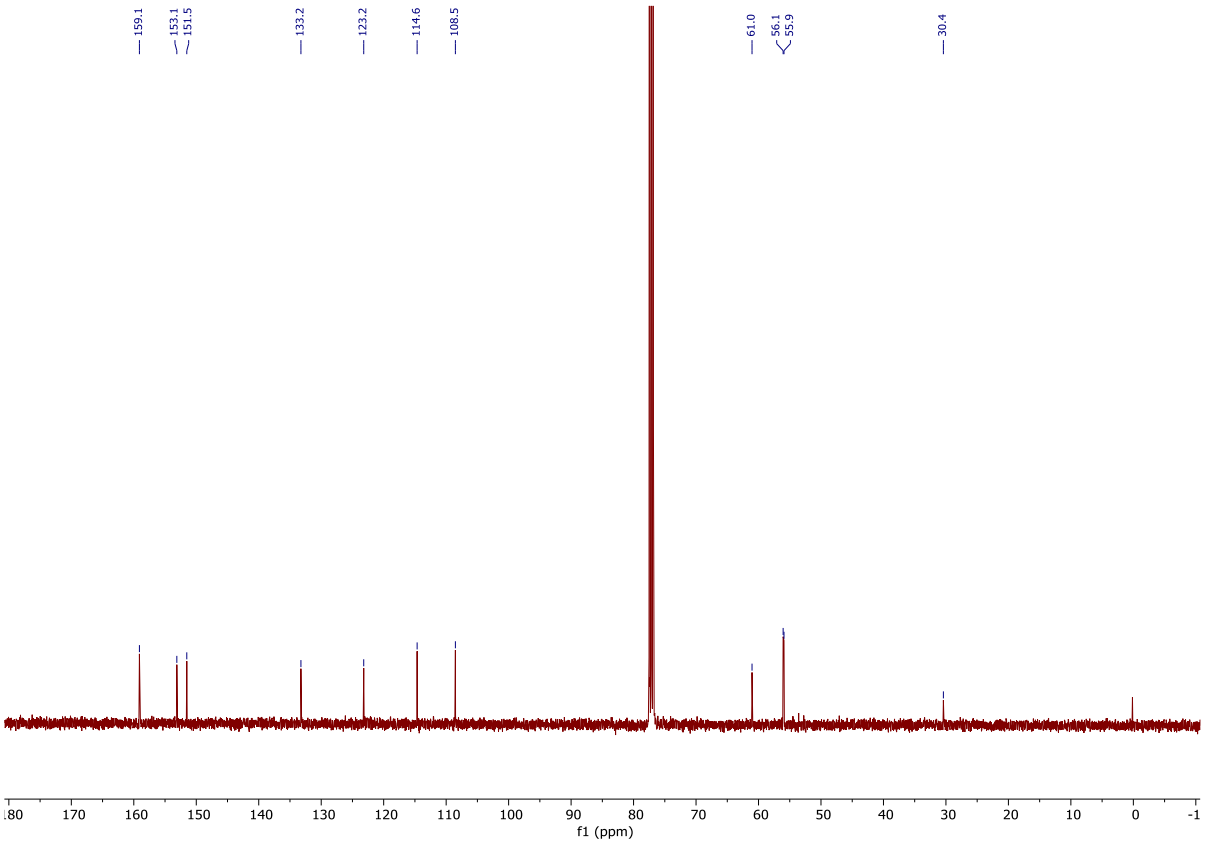


Figure S6: ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **PIm**

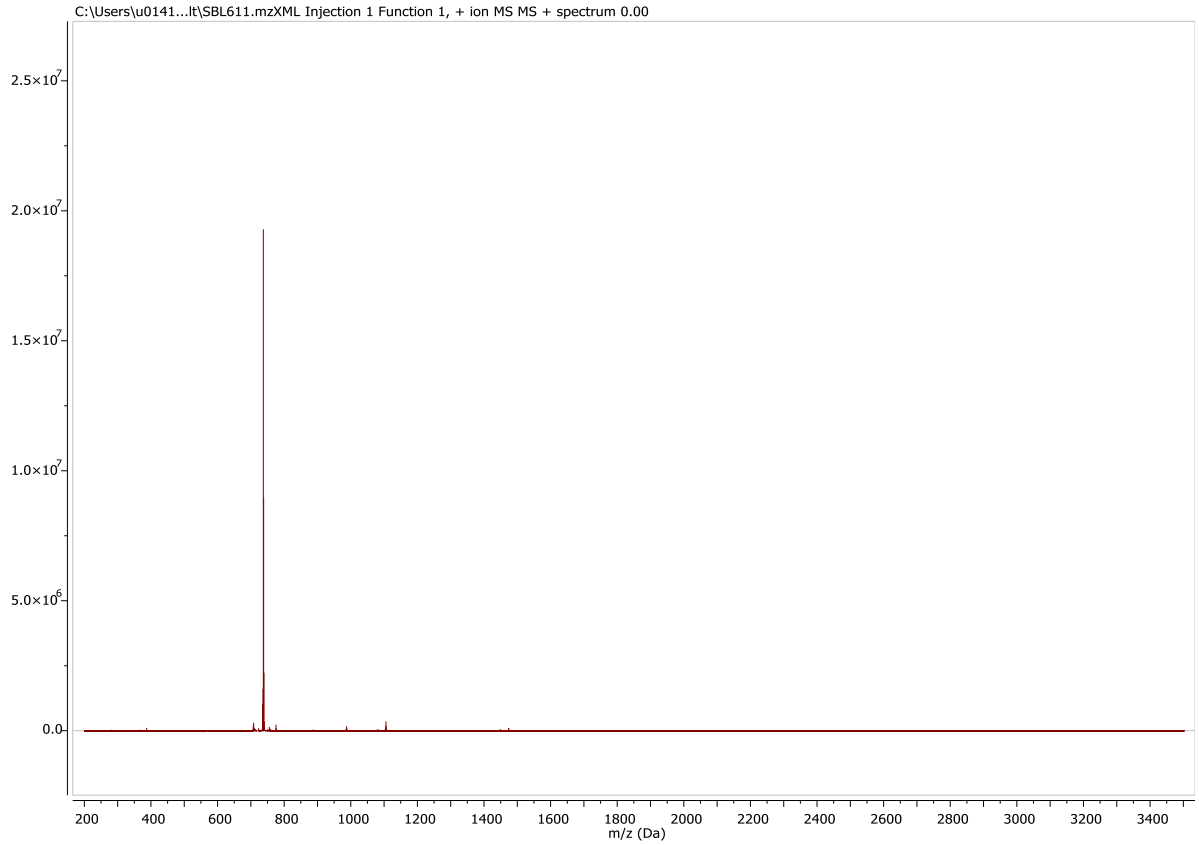


Figure S7: MALDI-TOF spectrum of (crude) **PIm** indicating the absence of oligomeric by-products

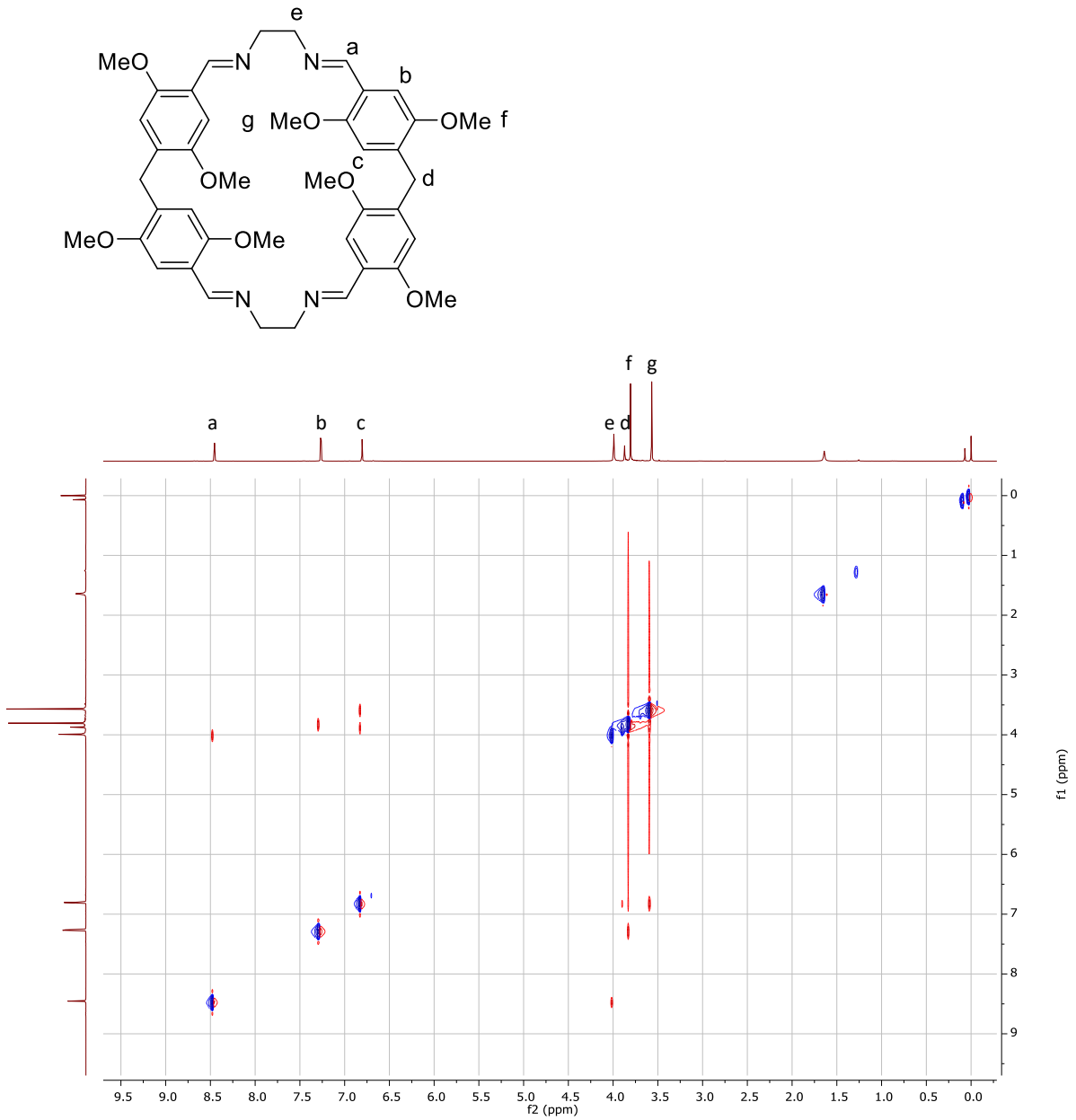


Figure S8: NOESY spectrum of **PIm** with peak allocation

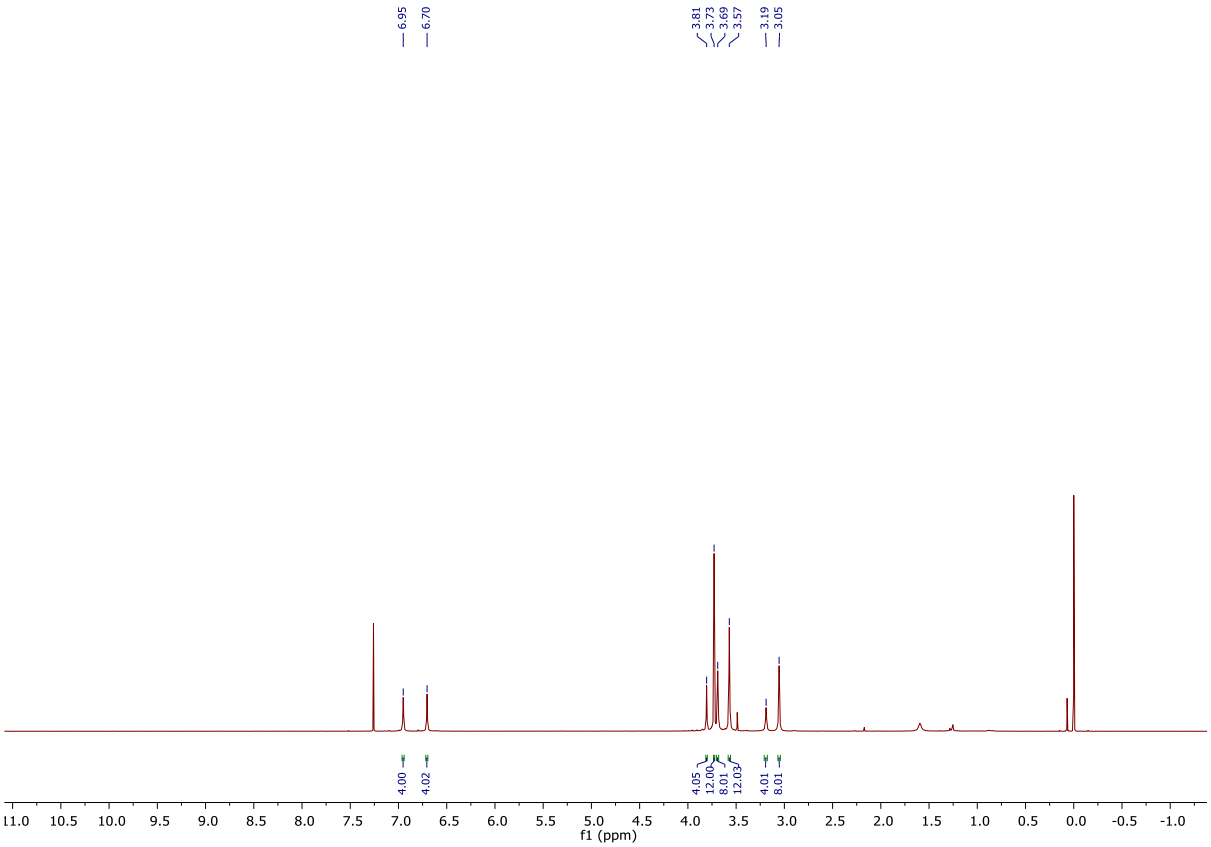


Figure S9: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **PAm**

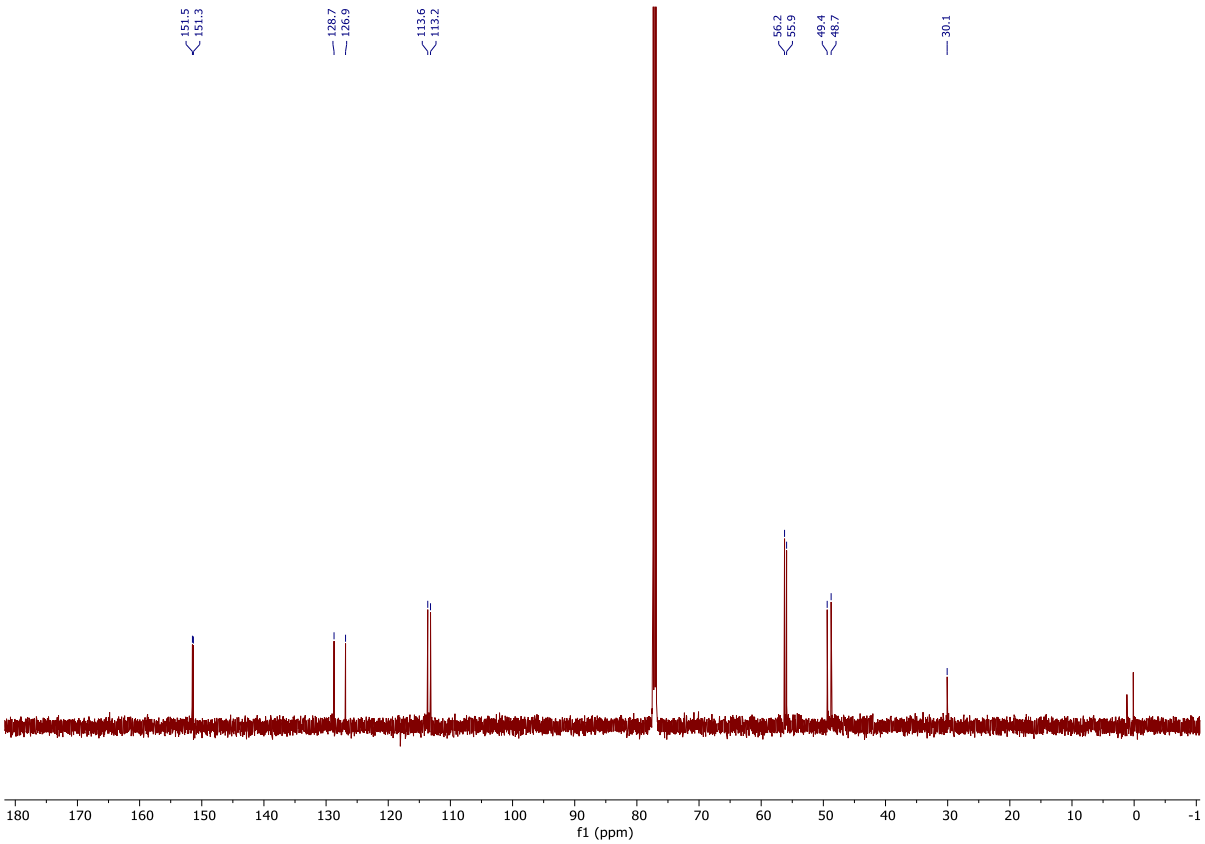


Figure S10: ^{13}C-NMR spectrum (151 MHz, $CDCl_3$) of **PAm**

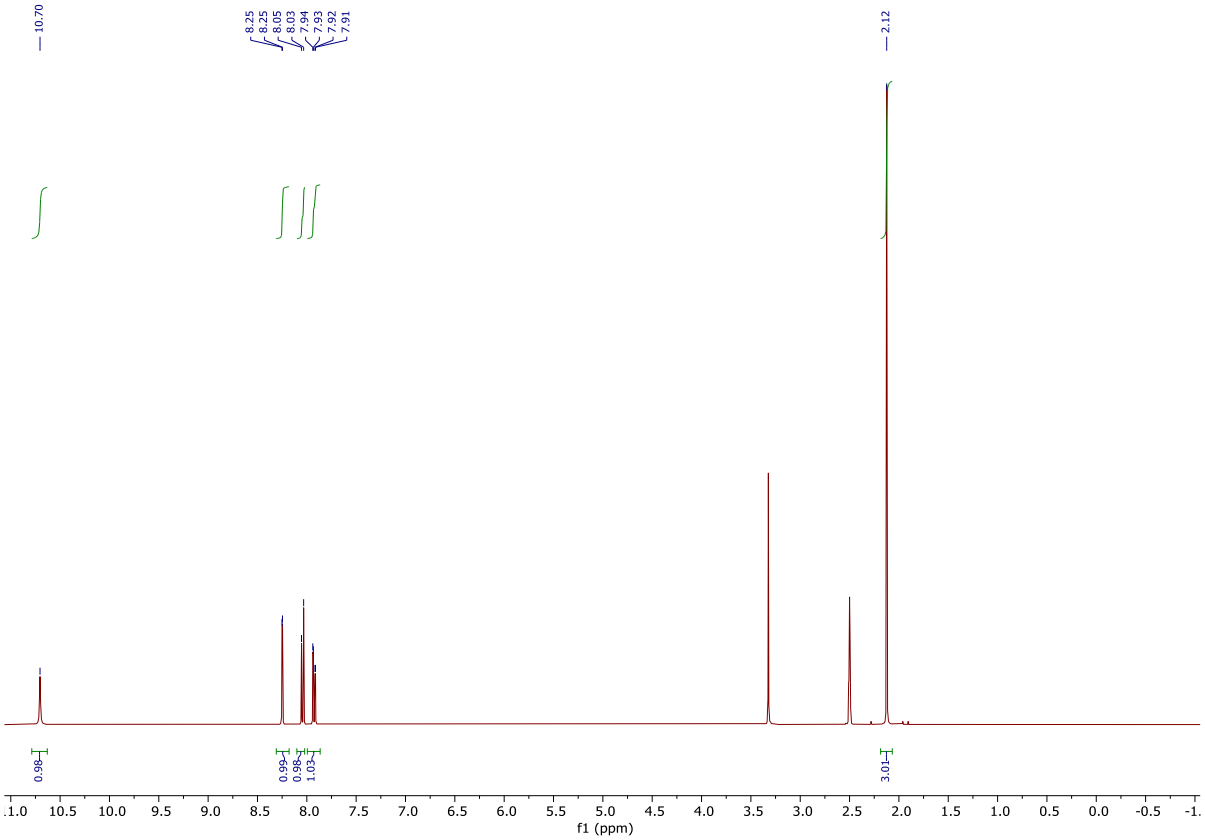


Figure S11: ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) of **G5**

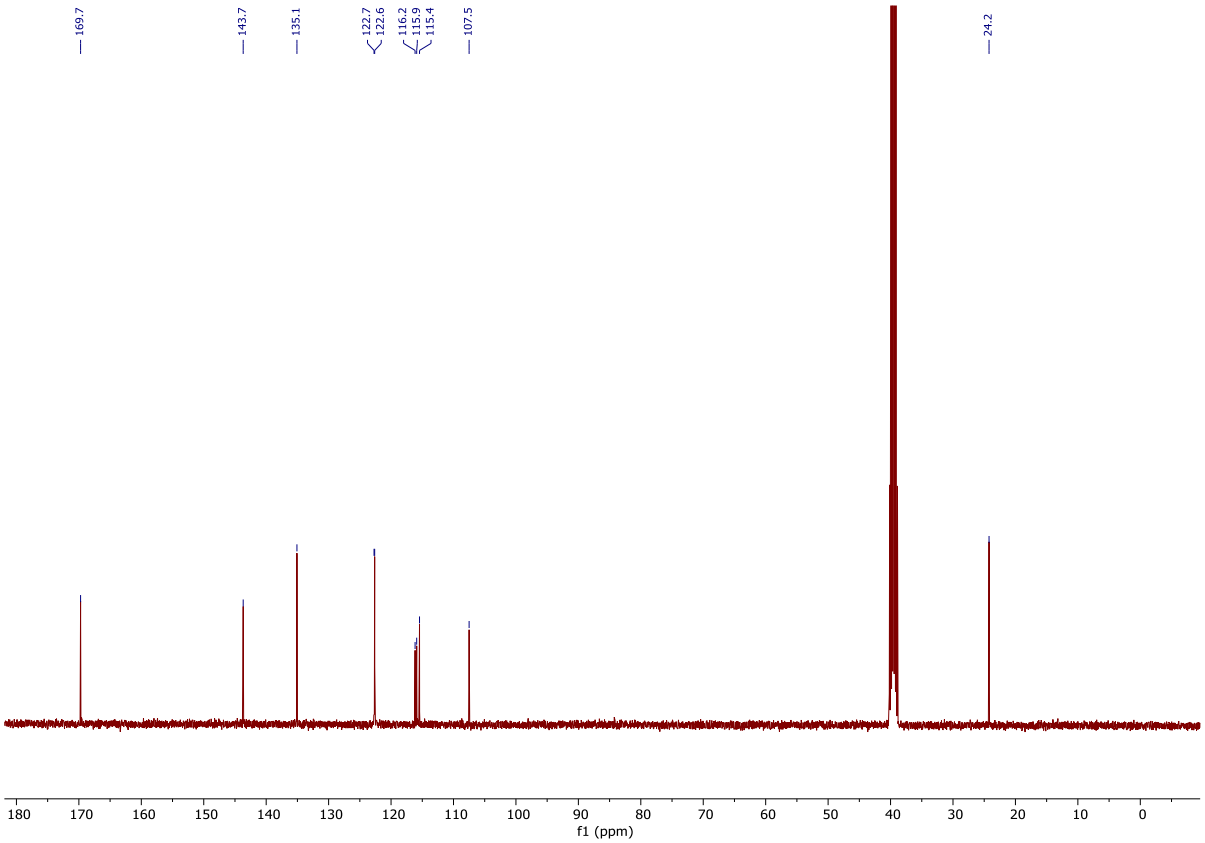


Figure S12: ^{13}C-NMR spectrum (101 MHz, DMSO-d_6) of **G5**

VT-NMR

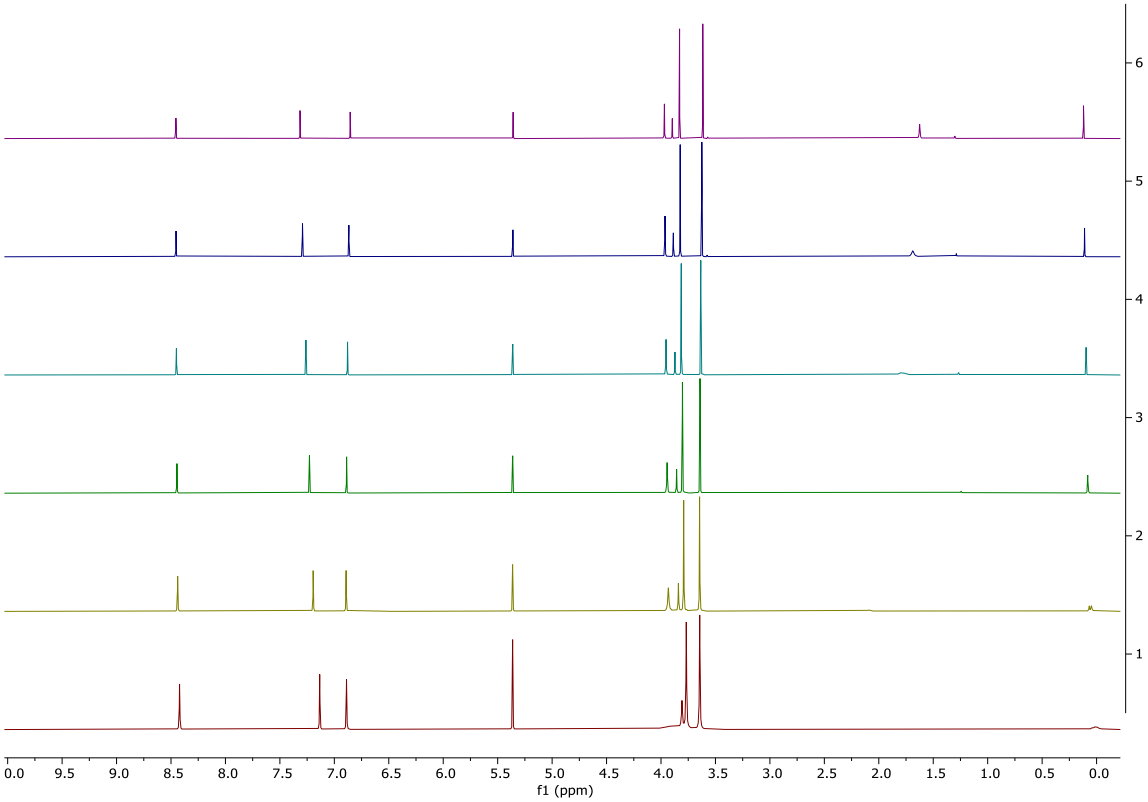


Figure S13: VT-NMR study (600 MHz, CD_2Cl_2) of **PIm**, from top to bottom: 298 K, 283 K, 263 K, 243 K, 223 K, 184 K

Crystallographic data

A single crystal of **PIm** was obtained from a DCM/heptane mixture. To the amorphous product dissolved in minimal volume of DCM, heptane was added until the cloud point. A minimal quantity of DCM was added to obtain a clear solution. The solvents were evaporated in an open air system, yielding the crystals overnight. X-ray intensity data were collected at 293(2) K on an Agilent SuperNova diffractometer with Eos CCD detector using Mo-Kα radiation (λ = 0.71073 Å). The images were interpreted and integrated with CrysAlisPRO [4] and the implemented absorption correction was applied. The structure was solved using Olex2 [5] with the ShelXT [6] structure solution program using Intrinsic Phasing and refined with the ShelXL [7] refinement package using full-matrix least-squares minimization on F^2. Non-hydrogen atoms were refined anisotropically and hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U_{eq} of the parent atoms (1.5 times U_{eq} for methyl groups). Crystal data, data collection and structure refinement details are summarized in Table **S1**. Crystallographic data for **PIm** have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 2381796.

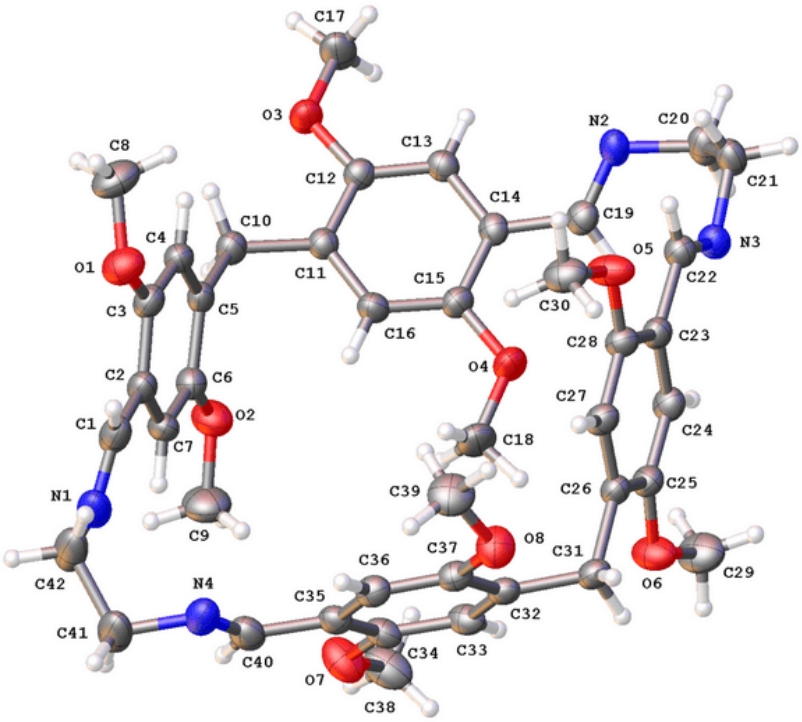


Figure S14: Molecular structure of compound **PIm** shown as atomic displacement plot drawn at 30% probability

Table S1: Crystal data and structure refinement for **PIm**

Empirical formula	$C_{42}H_{48}N_4O_8$
Formula weight	736.84
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.7079(6)
b/Å	20.9876(8)
c/Å	14.4189(6)
α/°	90
β/°	106.524(5)
γ/°	90
Volume/Å^3	3976.9(3)
Z	4
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	0.086
F(000)	1568.0
Crystal size/mm^3	0.5 × 0.15 × 0.15
Radiation	Mo Kα (λ = 0.71073 Å)
2Θ range for data collection/°	4.874 to 52.738
Index ranges	-17 ≤ h ≤ 17, -26 ≤ k ≤ 26, -18 ≤ l ≤ 17
Reflections collected	42012
Independent reflections	8112 [R_{int} = 0.0478, R_{sigma} = 0.0478]
Data/restraints/parameters	8112/0/495
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0615, wR_2 = 0.1411
Final R indexes [all data]	R_1 = 0.1113, wR_2 = 0.1654
Largest diff. peak/hole / e Å^{-3}	0.16/-0.18

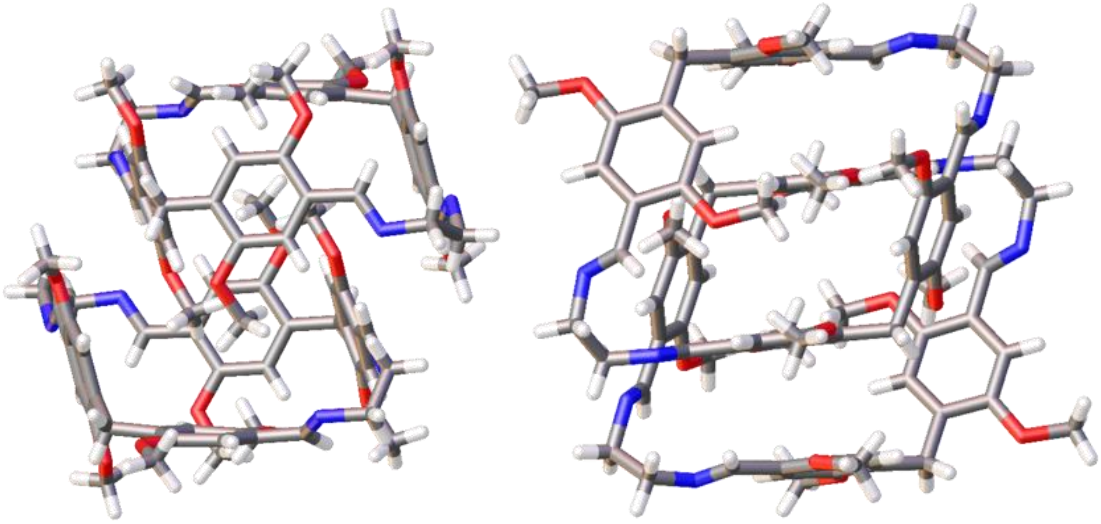


Figure S15: Side view (left) and top view (right) of the **PIm** solid-state dimers

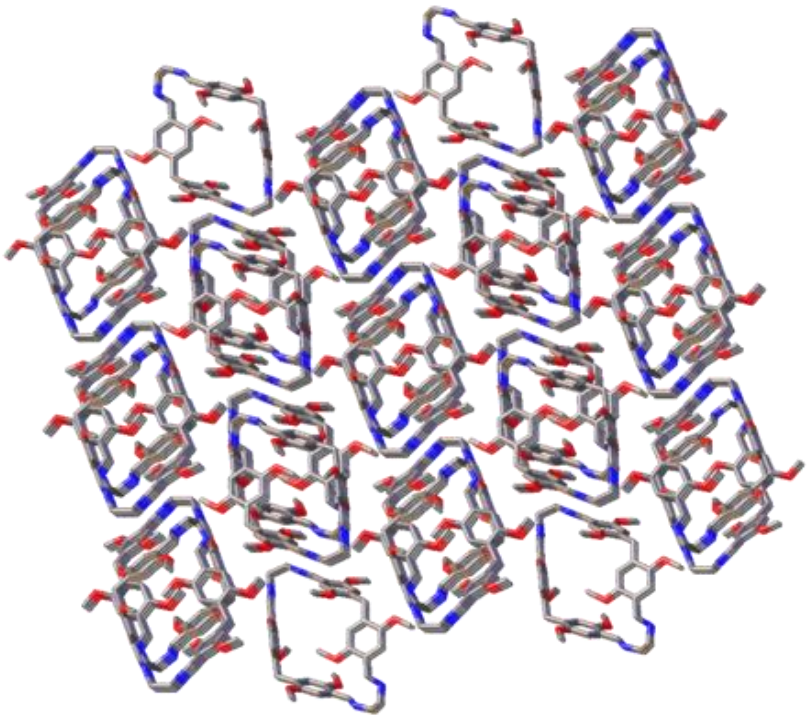


Figure S16: Packing of **PIm** showing 1D polymeric motifs along the *a*-axis. H-atoms omitted for clarity

A single crystal of **PAm** was obtained from benzene. The amorphous product was dissolved in a minimal volume of benzene and slowly evaporated in open air forming crystals containing benzene and water molecules. The latter were removed upon heating. X-ray intensity data were collected at 100(2) K on an XtaLAB Synergy-S Dualflex diffractometer equipped with monochromated CuKα radiation (λ = 1.54184 Å). The crystal was mounted on a nylon loop and coated with paratone-N oil. The images were interpreted and integrated with CrysAlisPRO [4] and the implemented absorption correction was applied. The structure was solved using Olex2 [5] with the ShelXS [6] structure solution program using Intrinsic Phasing and refined with the ShelXL [7] refinement package using full-matrix least-squares minimization on F^2. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were positioned geometrically with C–H = 0.95 Å (aromatic), C–H = 0.98 Å (methyl) and 0.99 Å (methylene) in the riding mode with isotropic temperature factors fixed at 1.2 times U_{eq} of the parent atoms (1.5 times U_{eq} for methyl groups). The H(N) atoms were located from Fourier difference maps and refined as riding, with $U_{iso}(H) = 1.2U_{eq}$ (N). The benzene molecule was found to be disordered in three distinct positions due to its location around the inversion center with occupancies of 60/20/20%. The presence of one solvent molecule per formula unit was confirmed by electron count using SQUEEZE [8]. A summary of the data collection and structure refinement parameters is provided in Table **S2**. Crystallographic data for **PAm** have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 2382390.

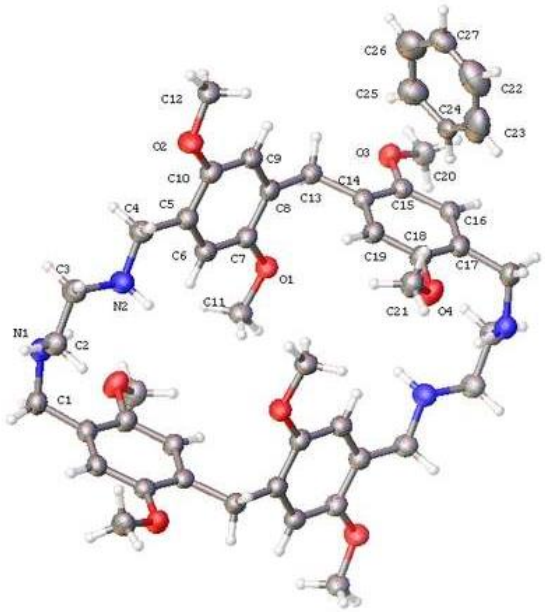


Figure S17: Molecular structure of compound **PAm** shown as atomic displacement plot drawn at 30% probability

Table S2: Crystal data and structure refinement for **PAm**

Empirical formula	$C_{48}H_{62}N_4O_8$
Formula weight	823.01
Temperature/K	100(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	9.0146(3)
b/Å	9.1779(3)
c/Å	13.5040(5)
α/°	80.713(3)
β/°	85.306(3)
γ/°	89.925(3)
Volume/Å^3	1098.83(7)
Z	1
Z'	0.5
ρ_{calc}g/cm^3	1.244
μ/mm^{-1}	0.681
F(000)	1568.0
Crystal size/mm^3	0.16×0.09×0.02
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ range for data collection/°	3.328 to 79.069
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 9, -17 ≤ l ≤ 16
Reflections collected	12432
Independent reflections	4482 [R_{int} = 0.0272, R_{sigma} = 0.0311]
Data/restraints/parameters	4482/41/335
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0501, wR_2 = 0.1403
Final R indexes [all data]	R_1 = 0.0584, wR_2 = 0.1475
Largest diff. peak/hole / e Å^{-3}	0.376/-0.24

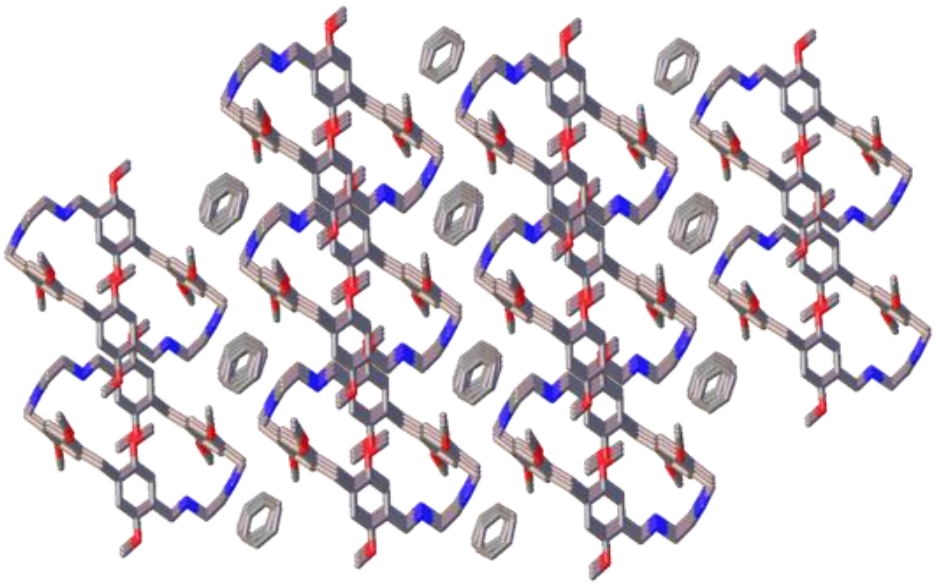


Figure S18: Packing of **PAm** showing chain formation along the *a*-axis. H-atoms omitted for clarity

Table S3: Hydrogen bonding [9] parameters for **PIm** and **PAm**

PIm				**PAm**			
D-H···A	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**	**D-H···A**	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**
Intramolecular							
C16-H16···O2	2.59	3.220(3)	125	N2-H2···O26[vi]	2.48	3.068(2)	119
C18-H18C···O6	2.89	3.792(4)	157	N2-H2···N5	2.45	2.934(2)	111
C33-H33···O6	2.92	3.545(4)	126				
C27-H27···O8	2.67	3.363(4)	132				
Intermolecular							
C9-H9A···N1[i]	2.85	3.446(4)	121	C16-H16C···O13[i]	2.23	3.501(2)	148
C4-H4···N2[ii]	2.99	3.804(4)	148	C17-H17B···O13[ii]	2.79	3.678(2)	150
C10-H10A···N2[ii]	2.99	3.919(4)	161	N5-H5···O15[iii]	2.61	3.539(2)	159
C31-H31A···N4[iii]	2.64	3.452(4)	142	C14-H14C···O15[i]	2.68	3.538(2)	147
C21-H21A···O1[iv]	2.97	3.832(4)	149	C14-H14A···O24[ii]	2.64	3.586(2)	162
C38-H38A···O3[v]	2.79	3.448(4)	127	C27-H27C···O24[iv]	2.82	3.557(2)	132
C20-H20A···O3[ii]	2.92	3.456(4)	116	C25-H25A···O26[iv]	2.67	3.352(2)	127
C39-H39A···O5[vi]	2.96	3.823(4)	150	C1-H1A···O26[v]	2.79	3.572(2)	136
C29-H29A···O7[iii]	2.92	3.684(5)	137	C16-H16A···Cg1[vii]	2.64	3.4984(19)	147
C8-H8A···O8[vii]	2.96	3.412(5)	111				
C17-H17C···Cg1[viii]	2.75	3.565(3)	143				
C30-H30B···Cg4[vi]	2.88	3.613(3)	134				
C30-H30C···Cg1[vi]	2.94	3.761(4)	144				
C39-H39B···Cg2[vi]	2.67	3.492(3)	144				

PIm: Cg1 is the centroid of phenyl ring C2-C7, Cg2 is the centroid of phenyl ring C11-C16, and Cg4 is the centroid of phenyl ring C32-C37. Symmetry codes: (i) -x,1-y,-z, (ii) x,1/2-y,-1/2+z, (iii) x,1.5-y,-1/2+z, (iv) x,y,-1+z, (v) -x,-1/2+y,1/2-z, (vi) 1-x,1-y,1-z, (vii) 1-x,-1/2+y,1/2-z (viii) x,1/2-y,1/2+z.

PAm: Cg1 is the centroid of phenyl ring C7-C12, Cg2 is the centroid of phenyl ring C18-C23, Cg3 is the centroid of phenyl ring C28-C29B, and Cg4 is the centroid of phenyl ring C28A-C33A. Symmetry codes: (i) x,-1+y,z, (ii) 1-x,2-y,1-z, (iii) 2-x,1-y,1-z, (iv) -1+x,y,z, (v) x,y,-1+z, (vi) 2-x,2-y,1-z, (vii) 1-x,1-y,1-z, (viii) 1-x,1-y,2-z.

Host-guest binding data

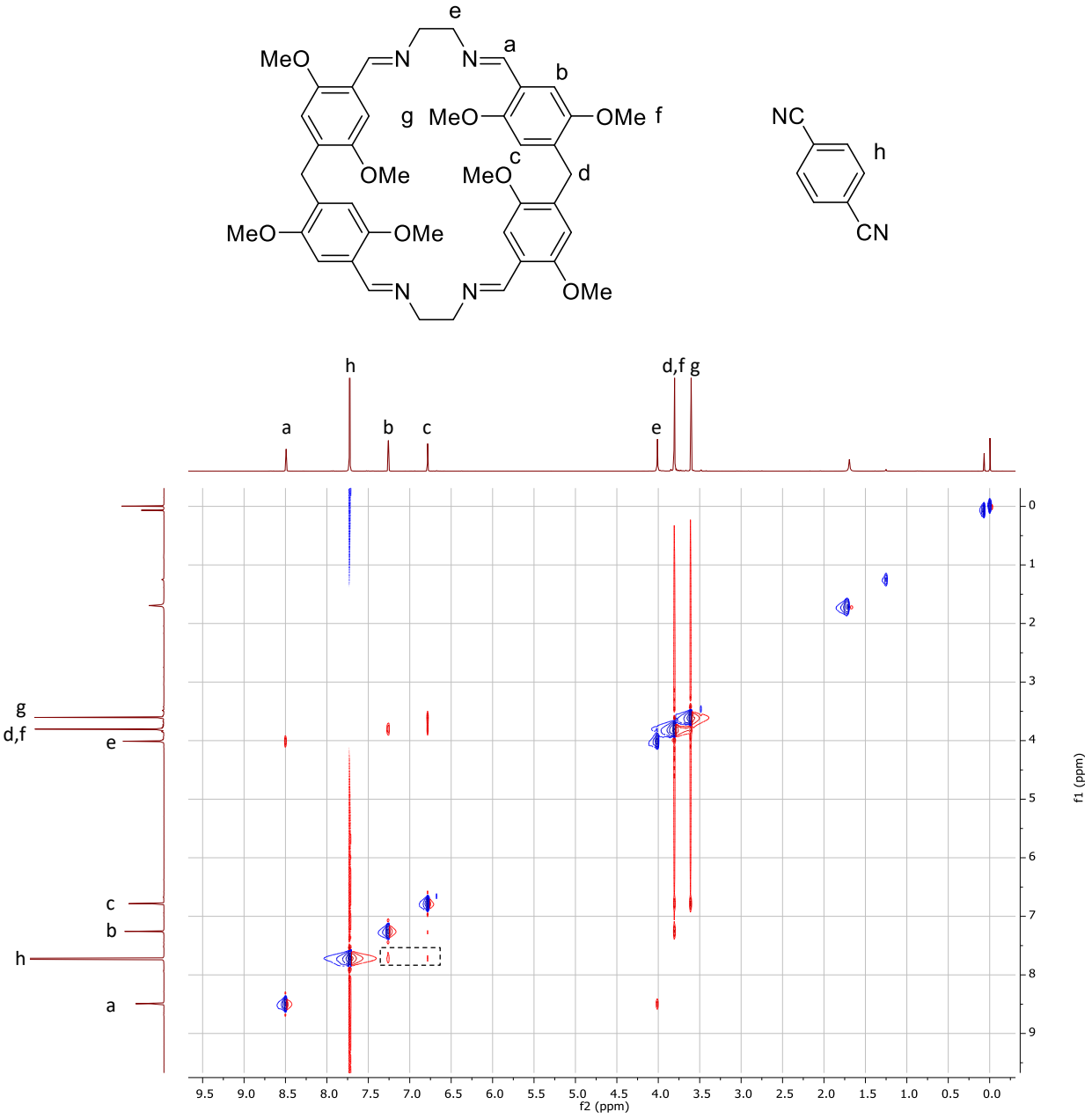


Figure S19: NOESY spectrum ($CDCl_3$, 400 MHz, 298 K) of 1:1 **PIm**:**G1** with peak allocation of **PIm** (a-g) and **G1** (h). Signals supporting host-guest binding are indicated.

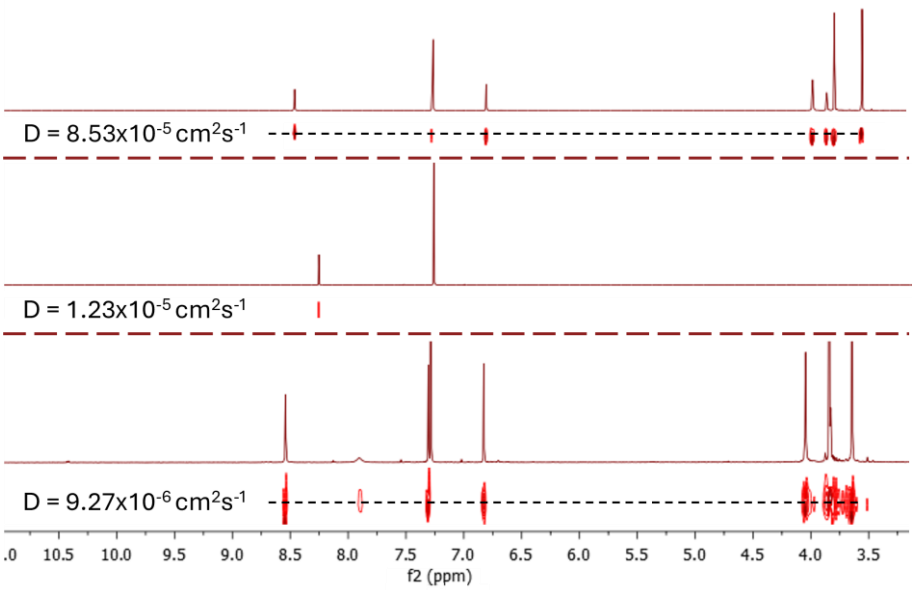


Figure S20: Partial DOSY spectra ($CDCl_3$, 400 MHz, 298 K, 2.7 mM) of **PIm** (top), **G3** (middle) and 1:1 **PIm**:**G3** (bottom)

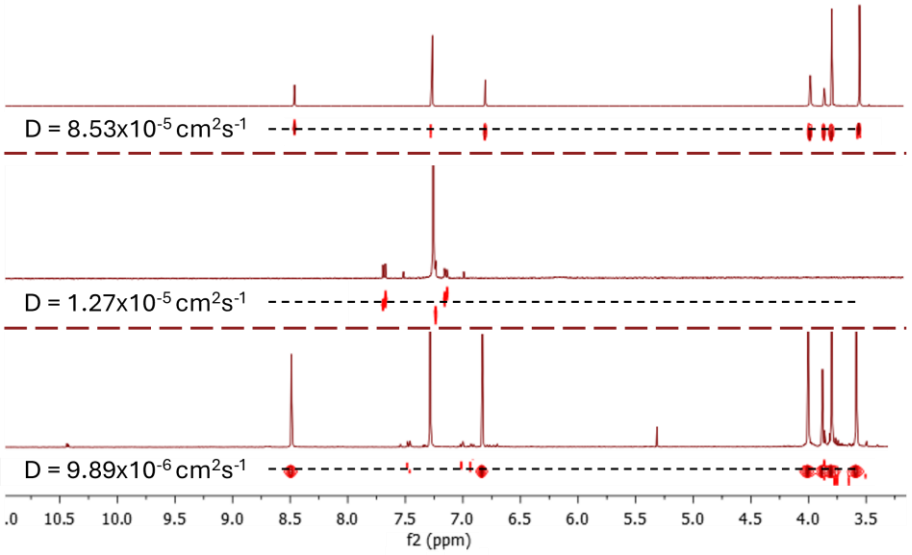


Figure S21: Partial DOSY spectra ($CDCl_3$, 400 MHz, 298 K, 2.7 mM) of **PIm** (top), **G4** (middle) and 1:1 **PIm**:**G4** (bottom)

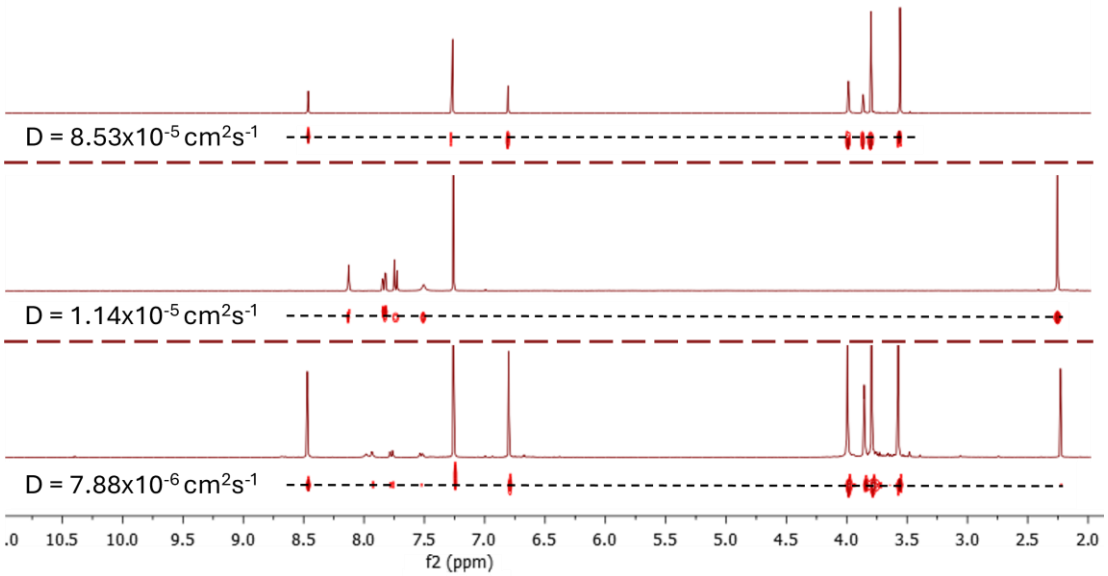


Figure S22: Partial DOSY spectra ($CDCl_3$, 400 MHz, 298 K, 2.7 mM) of **PIm** (top), **G5** (middle) and 1:1 **PIm**:**G5** (bottom)

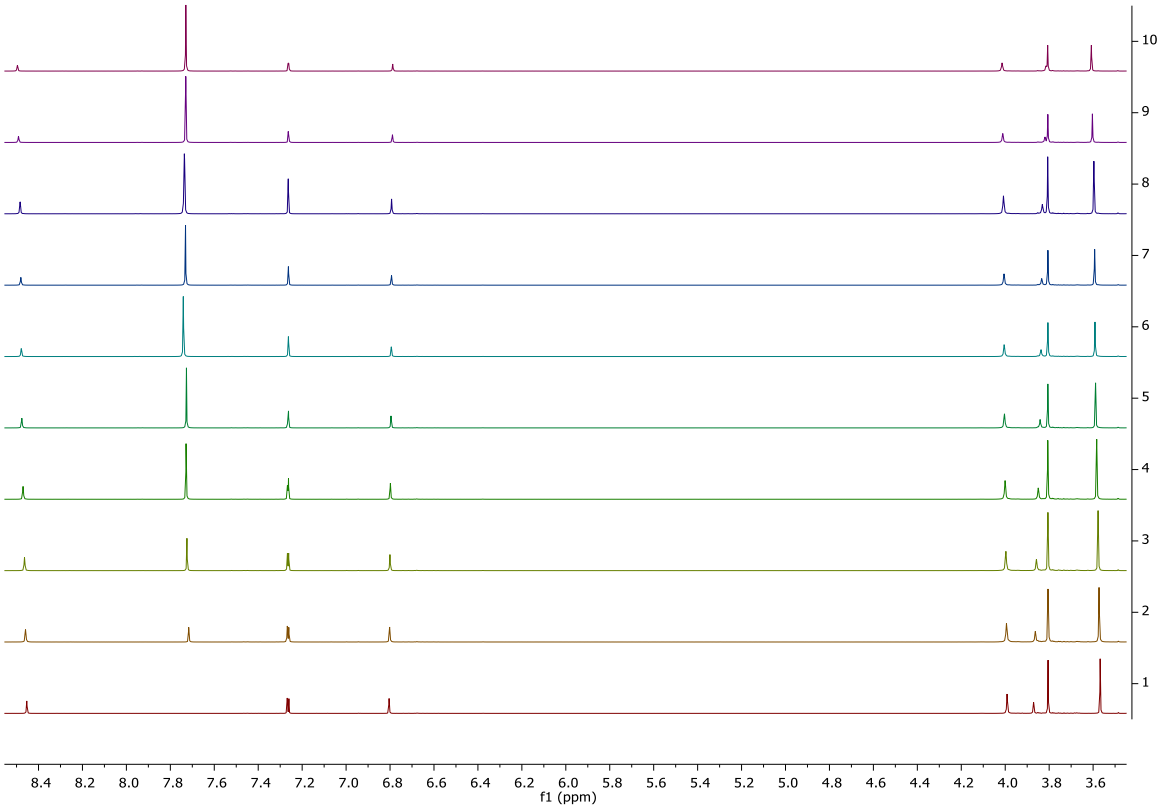


Figure S23: NMR-titration of $5.0x10^{-3}$ M **PIm** with 0-18 equiv. of **G1** in $CDCl_3$

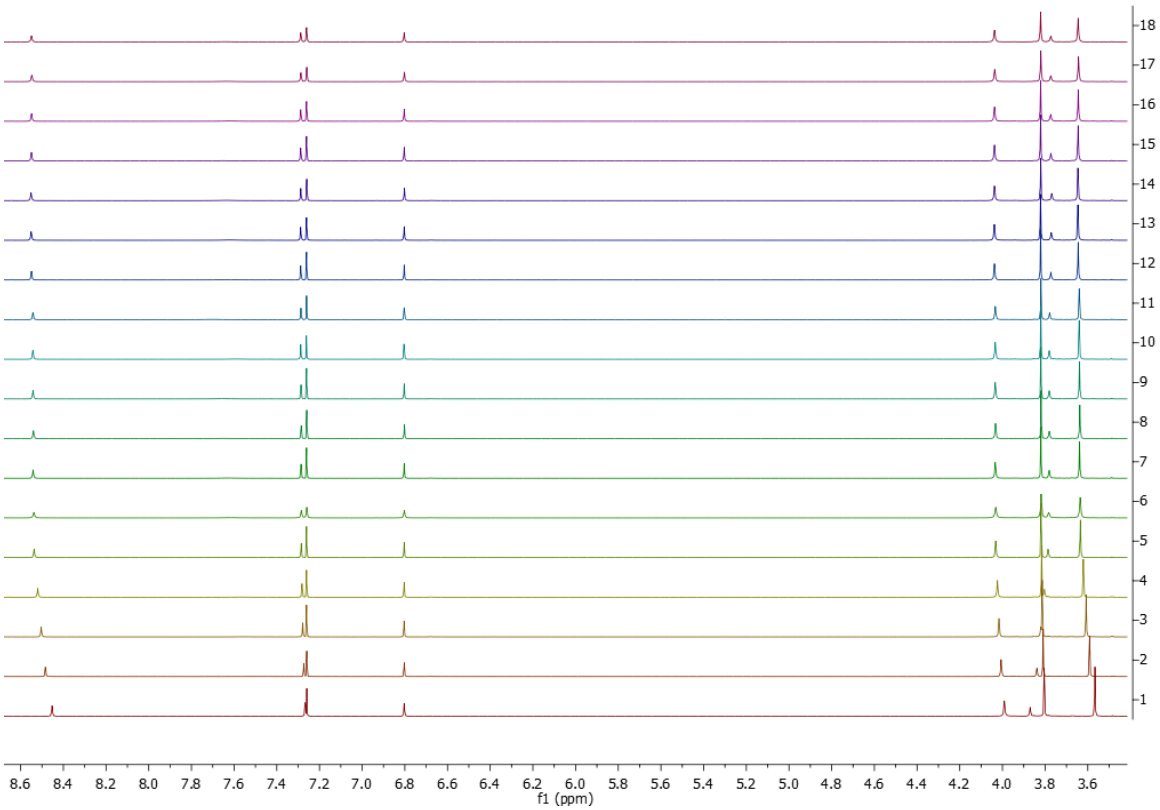


Figure S24: NMR-titration of 5.0x10^{-3} M **PIm** with 0-16 equiv. of **G3** in $CDCl_3$

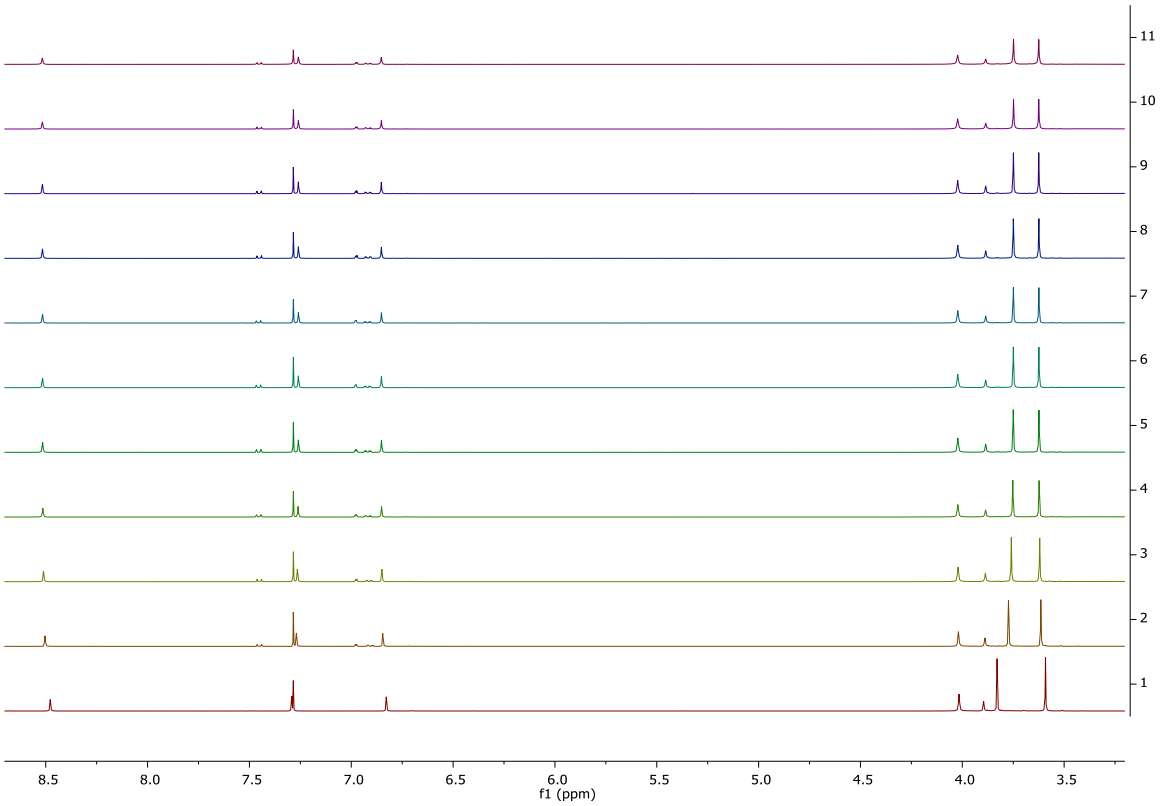


Figure S25: NMR-titration of 5.0x10^{-3} M **PIm** with 0-18 equiv. of **G4** in $CDCl_3$

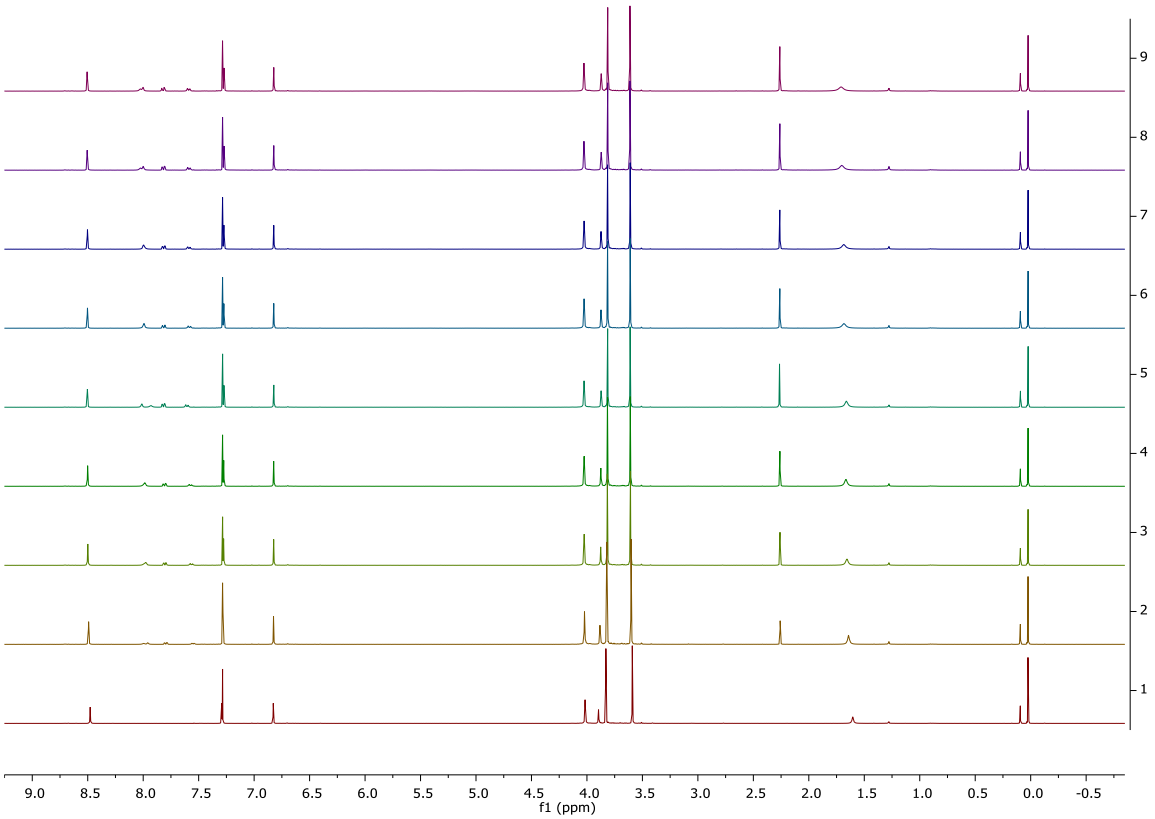


Figure S26: NMR-titration of 5.0x10^{-3} M **PIm** with 0-14 equiv. of **G5** in $CDCl_3$

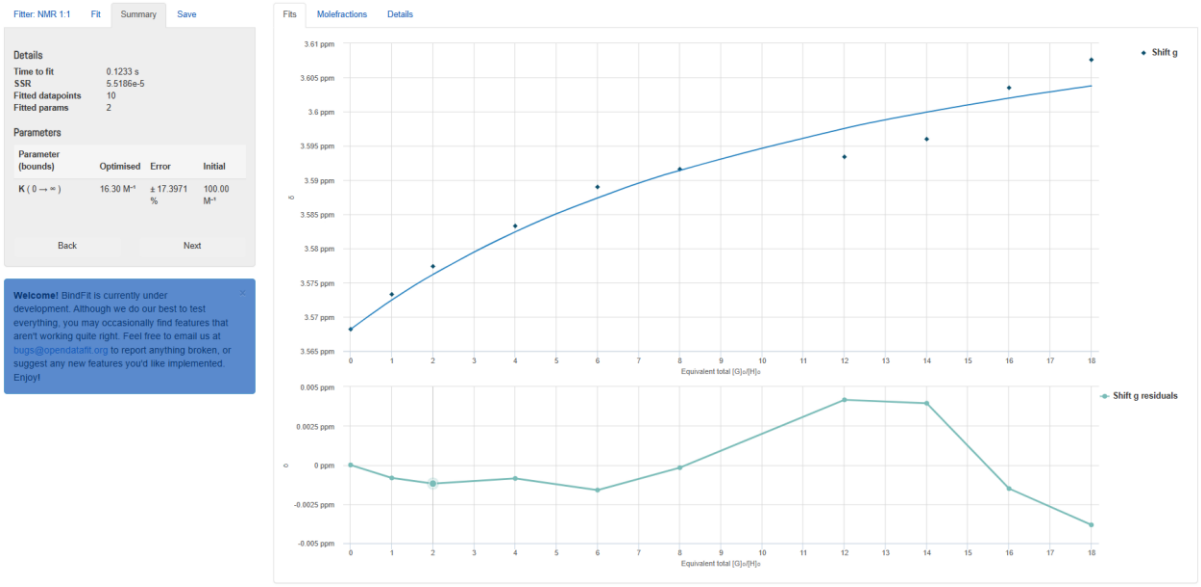


Figure S27: Non-linear 1:1 curve fitting of the NMR-titration data **G1@PIm** using BindFit [10,11] based on the shift of methyl protons **g**

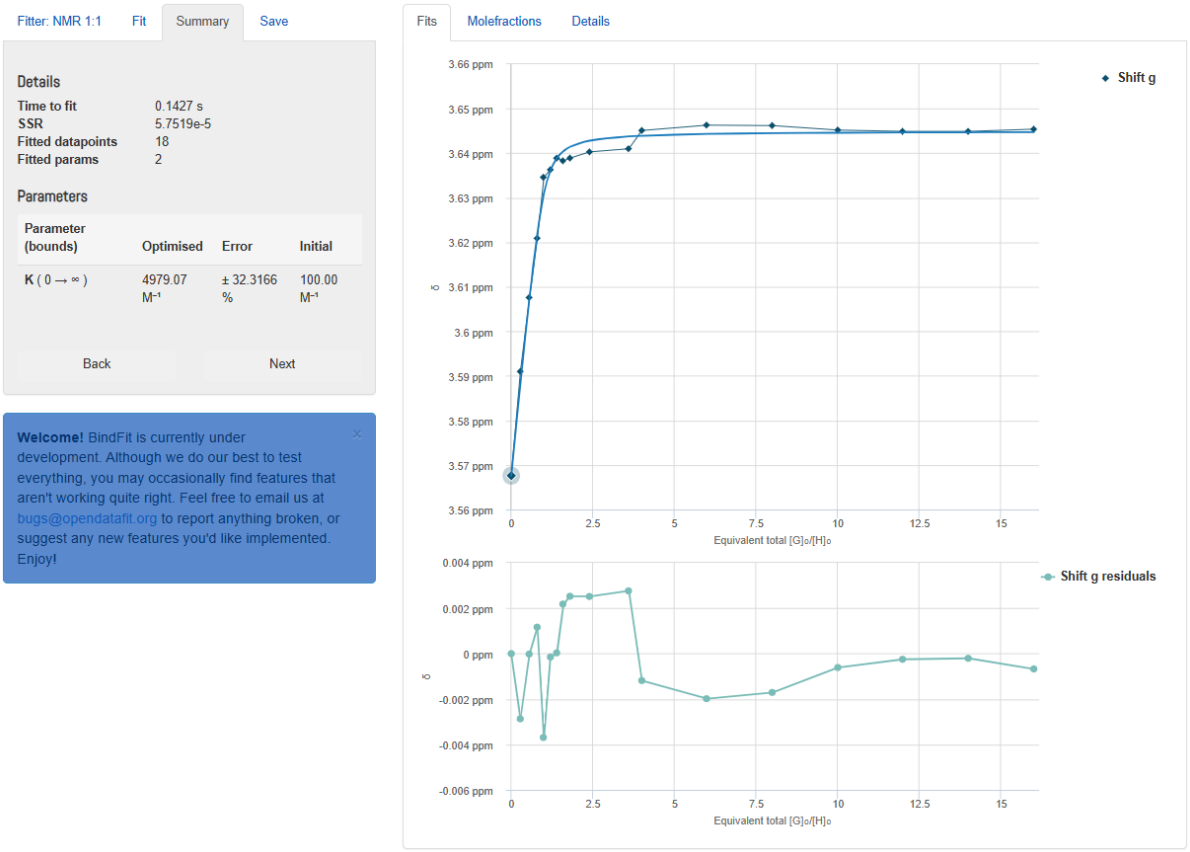


Figure S28: Non-linear 1:1 curve fitting of the NMR-titration data **G3@PIm** using BindFit [10,11] based on the shift of methyl protons **g**

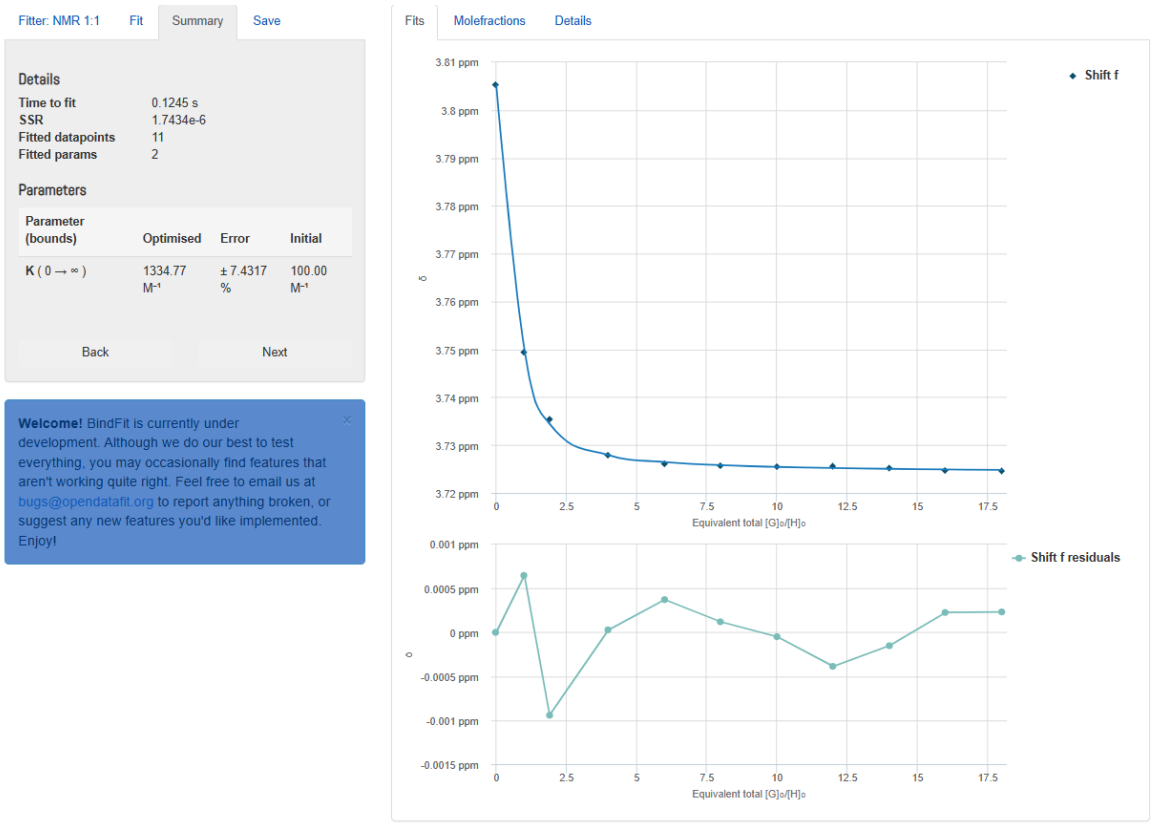


Figure S29: Non-linear 1:1 curve fitting of the NMR-titration data **G4@PIm** using BindFit [10,11] based on the shift of methyl protons **f**

Figure S30: Non-linear 1:1 curve fitting of the NMR-titration data **G5@PIm** using BindFit [10,11] based on the shift of ethylene protons **e**

Theoretical calculations

Geometry optimization and conformational analysis

Full geometry optimization at DFT level by applying the B3LYP/6-311G(2d,2p) [12,13] basis set was performed. In all cases, the effect of the solvent (chloroform) was assessed using Marenich's solvation model based on density (SMD) [14] and temperature at 296 K as implemented in Gaussian16 software [15]. The characterization of the minimum energy point was performed by Hessian matrix calculations, obtaining only positive eigenvalues.

Conformational free-energies of the **P5** and **PIm** were calculated using the same DFT model by rotating the dihedral angle of a single 1,4-dimethoxybenzene in 5° increments with respect to the methylene bridges.

Host-guest complexes

The host-guest complexes were obtained through molecular docking studies using AutoDockGPU software [16]. First, every guest was parameterized using the RESP charges as input for the docking studies. The corresponding affinity grids were generated using a 40x40x40 Å box centered in the cavity center of the previously optimized host structure to cover both *endo*-cavity as well as *exo*-wall interactions. A grid spacing of 0.375 Å was used to calculate affinity points. The molecular docking protocol performed 100 docking runs using a Lamarckian Genetic Algorithm (LGA) to sample the ligand conformational space. Docking results were filtered by extracting the lowest energy and highest cluster enrichment docking poses. Clustering of the resulting docked poses was performed using the built-in functionality of AutoDockGPU, allowing an RMSD tolerance of 2.0 Å. The obtained guest-host complexes were then submitted to a full geometry optimization at DFT level by applying the B97D3/SVP/SVPFIT basis set [17,18]. In all cases, the effect of the solvent (chloroform) was assessed using Marenich's solvation model based on density (SMD) [14] and temperature at 296 K as implemented in Gaussian16 software [15]. The characterization of the minimum energy point was performed by Hessian matrix calculations, obtaining only positive eigenvalues.

Non-covalent interaction analysis

The previously obtained minimum energy guest-host complexes were submitted to a noncovalent interaction (NCI) analysis, performed through the reduced density gradient (RDG) method [19], using Multiwfn software [20]. The visualization of the NCI gradient isosurface was depicted by VMD v.1.9 software. Blue, green and red color codes were used to describe strong interactions (hydrogen bonding), van der Waals interactions and strong repulsion (steric effects), respectively.

Molecular visualization

Visualization of the electron density maps were performed using GaussView v.6.1.1 software [21]. Snapshot visualization of the different host conformations and host-guest complexes was performed using the VMD v.1.9 software [22].

Electrostatic potential of the structures

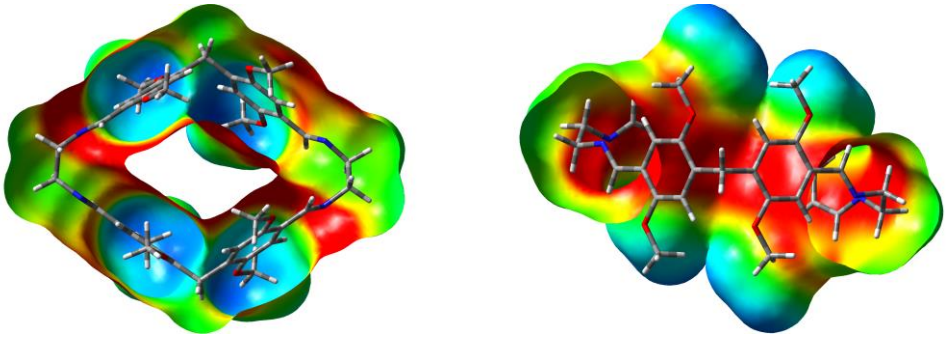


Figure S31: Electrostatic potential map of **PIm** at the B3LYP/6-311G(2d,2p) level of theory in chloroform with red representing negative and blue positive potential.

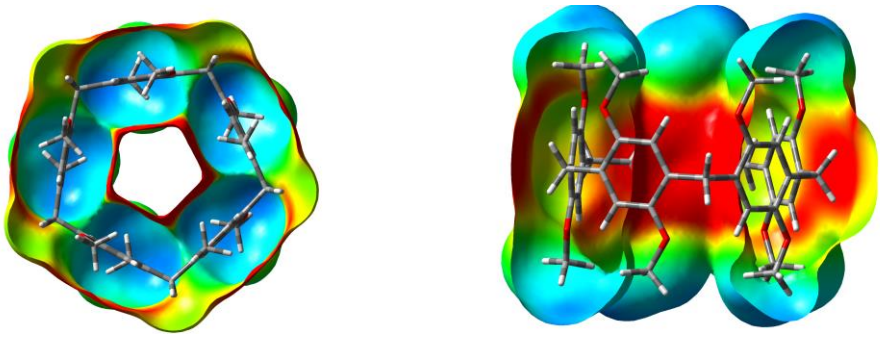


Figure S32: Electrostatic potential map of permethoxypillar[5]arene at the B3LYP/6-311G(2d,2p) level of theory in chloroform with red representing negative and blue positive potential

Cartesian coordinates of the structures

Optimized host structures

P5

Method: B3LYP/6-311G(2d,2p)

SCF Done: E(RB3LYP) = -2497.80834721 A.U. after 1 cycle

Lowest frequency: 10.3657
Zero-point correction= 0.869199 (Hartree/Particle)
Thermal correction to Energy= 0.922445
Thermal correction to Enthalpy= 0.923383
Thermal correction to Gibbs Free Energy= 0.779678
Sum of electronic and zero-point Energies= -2496.939149
Sum of electronic and thermal Energies= -2496.885902
Sum of electronic and thermal Enthalpies= -2496.884964
Sum of electronic and thermal Free Energies= -2497.028669

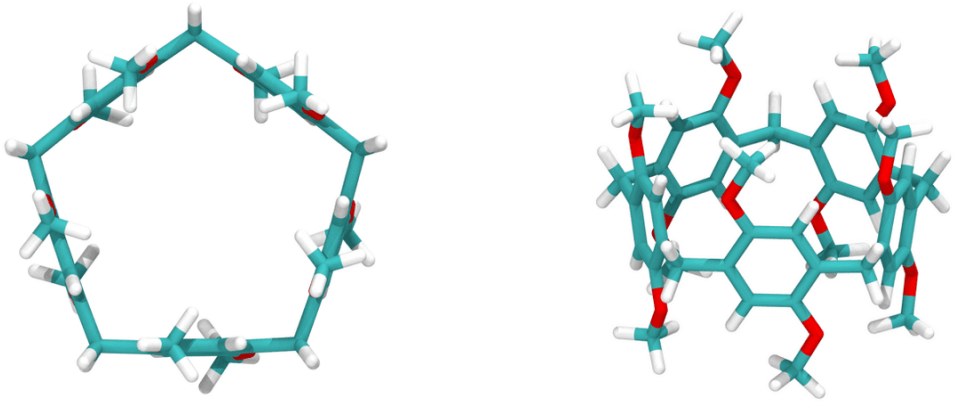


Figure S33: DFT-optimized structure of **P5**: top view (left), side view (right)

Table S4: Cartesian coordinates for the minimum energy of **P5**

1	O	6.6224220	1.1768690	20.4096580
2	O	11.6574020	2.7891910	22.0510130
3	O	8.8039730	-1.0644250	24.4937030
4	O	11.5693010	2.8956640	27.1985480
5	O	6.7610930	1.0443980	28.6960380
6	C	7.4500000	3.7250010	19.5800970
7	C	8.3249090	2.8105220	20.4216600
8	C	9.5982820	3.2155590	20.8183730
9	C	10.3993520	2.4219520	21.6375360
10	C	9.9322540	1.1794490	22.0844530
11	C	8.6713360	0.7609100	21.6624380
12	C	7.8700920	1.5547840	20.8438800
13	C	6.1489880	-0.1157800	20.7649100
14	C	12.1930900	4.0150870	21.5698840
15	C	10.7554850	0.3195220	23.0291220
16	C	10.4654410	0.6113780	24.4922620
17	C	11.1756380	1.5997050	25.1720630
18	C	10.8936130	1.9262940	26.4971580
19	C	9.8744120	1.2541450	27.1837750
20	C	9.1845150	0.2453640	26.5134090
21	C	9.4651310	-0.0796680	25.1875550
22	C	7.8229180	-1.8292830	25.1820590
23	C	12.6423210	3.5689230	26.5530160
24	C	9.5022920	1.6293180	28.6086440
25	C	8.4339150	2.7083410	28.6707010
26	C	7.0717150	2.3828490	28.6846150
27	C	8.7878050	4.0565190	28.6857660
28	C	5.3902670	0.6730770	28.7611330
29	H	6.8121460	3.1202000	18.9381220
30	H	9.9446570	4.1824160	20.4891390
31	H	8.3167060	-0.1970970	22.0087000
32	H	6.8090580	-0.9021490	20.3906730
33	H	6.0373670	-0.2206990	21.8465800
34	H	5.1737050	-0.2163510	20.2943320
35	H	11.6012950	4.8712040	21.9021050
36	H	13.1937460	4.0886430	21.9893610
37	H	12.2615200	4.0230140	20.4792710

38	H	11.8134770	0.4894910	22.8385630
39	H	10.5464230	-0.7288560	22.8245990
40	H	11.9460510	2.1277490	24.6327160
41	H	8.4010730	-0.2692360	27.0468460
42	H	8.2514050	-2.3532960	26.0399240
43	H	6.9893110	-1.2074390	25.5166240
44	H	7.4571290	-2.5604000	24.4648780
45	H	13.0436190	4.2636050	27.2872340
46	H	13.4296500	2.8737440	26.2514240
47	H	12.2990980	4.1287130	25.6798620
48	H	10.3899730	1.9817560	29.1306180
49	H	9.1450620	0.7404340	29.1253110
50	H	9.8379240	4.3021000	28.6761660
51	H	4.9119850	1.0588510	29.6647660
52	H	5.3762630	-0.4140400	28.7877270
53	H	4.8380370	1.0173960	27.8836220
54	O	8.2775830	6.2731350	20.4096490
55	O	3.2426050	4.6608230	22.0510200
56	O	6.0960310	8.5144450	24.4937060
57	O	3.3307050	4.5543460	27.1985380
58	O	8.1389060	6.4056140	28.6960550
59	C	6.5750940	4.6394840	20.4216590
60	C	5.3017210	4.2344490	20.8183750
61	C	4.5006540	5.0280600	21.6375380
62	C	4.9677540	6.2705640	22.0844500
63	C	6.2286720	6.6891000	21.6624310
64	C	7.0299130	5.8952220	20.8438740
65	C	8.7510200	7.5657840	20.7648960
66	C	2.7069140	3.4349260	21.5698980
67	C	4.1445260	7.1304950	23.0291180
68	C	4.4345670	6.8386380	24.4922590
69	C	3.7243690	5.8503080	25.1720560
70	C	4.0063920	5.5237180	26.4971510
71	C	5.0255900	6.1958680	27.1837720
72	C	5.7154870	7.2046520	26.5134090
73	C	5.4348740	7.5296840	25.1875550
74	C	7.0770820	9.2793040	25.1820670
75	C	2.2576880	3.8810840	26.5530030
76	C	5.3977070	5.8206940	28.6086420
77	C	6.4660830	4.7416700	28.6707000
78	C	7.8282840	5.0671630	28.6846230
79	C	6.1121930	3.3934930	28.6857570
80	C	9.5097310	6.7769330	28.7611610
81	H	8.0878530	4.3298000	18.9381180
82	H	4.9553450	3.2675920	20.4891460
83	H	6.5833040	7.6471070	22.0086900
84	H	8.0909510	8.3521530	20.3906580
85	H	8.8626430	7.6707060	21.8465660
86	H	9.7263020	7.6663520	20.2943170
87	H	3.2987110	2.5788100	21.9021210
88	H	1.7062600	3.3613720	21.9893790

89	H	2.6384820	3.4269940	20.4792850
90	H	3.0865330	6.9605270	22.8385590
91	H	4.3535880	8.1788720	22.8245940
92	H	2.9539590	5.3222640	24.6327060
93	H	6.4989260	7.7192520	27.0468490
94	H	6.6485910	9.8033140	26.0399310
95	H	7.9106890	8.6574610	25.5166330
96	H	7.4428710	10.0104230	24.4648880
97	H	1.8563900	3.1864010	27.2872200
98	H	1.4703580	4.5762620	26.2514100
99	H	2.6009150	3.3212960	25.6798500
100	H	4.5100240	5.4682540	29.1306120
101	H	5.7549350	6.7095770	29.1253110
102	H	5.0620750	3.1479120	28.6761500
103	H	9.9880070	6.3911550	29.6647950
104	H	9.5237350	7.8640500	28.7877610
105	H	10.0619670	6.4326190	27.8836530

PIm

Method: B3LYP/6-311G(2d,2p)

SCF Done: E(RB3LYP) = -2450.79997718 A.U. after 1 cycle

Lowest frequency: 8.2434

Zero-point correction =	0.838928 (Hartree/Particle)
Thermal correction to Energy =	0.891829
Thermal correction to Enthalpy =	0.892767
Thermal correction to Gibbs Free Energy =	0.747254
Sum of electronic and zero-point Energies =	-2449.961049
Sum of electronic and thermal Energies =	-2449.908148
Sum of electronic and thermal Enthalpies =	-2449.907210
Sum of electronic and thermal Free Energies =	-2450.052723

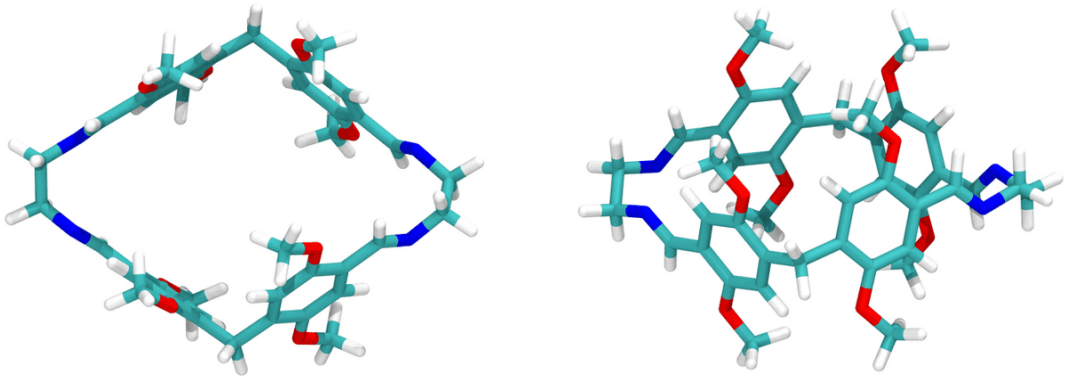


Figure S34: DFT-optimized structure of **PIm**: top view (left), side view (right)

Table S5: Cartesian coordinates for the minimum energy of **PIm**

1	O	4.2099780	7.9392330	2.2882440
2	N	2.9326100	11.2342900	0.3234230
3	C	3.3171190	10.2042240	0.9631930
4	H	4.3776300	9.9682470	1.0713210
5	O	-1.2509360	8.8219500	2.1747510
6	N	-0.4128820	7.3783370	10.1007200
7	C	2.3828010	9.2688320	1.6021170
8	O	1.1350740	5.3578780	5.5987180
9	N	1.0618820	9.6015890	11.4851080
10	C	2.8594230	8.1340540	2.2808200
11	O	-2.6296840	9.0896650	7.1844700
12	N	4.1930850	13.5919580	1.6952030
13	C	1.9536600	7.2718160	2.8998640
14	H	2.3053810	6.4022780	3.4318670
15	O	4.7976580	9.7197490	9.9436980
16	C	0.5827870	7.5061960	2.8670410
17	O	1.6983270	14.2625210	9.3357640
18	C	0.1080540	8.6392990	2.1811120
19	O	1.4480470	15.1261690	4.2356760
20	C	1.0023480	9.4969500	1.5604730
21	H	0.6637540	10.3736360	1.0321220
22	O	6.1746840	13.3078820	6.4640650
23	C	4.7344840	6.8222750	2.9992770
24	H	5.8137170	6.8793340	2.8835030
25	H	4.3785530	5.8782570	2.5807810
26	H	4.4826030	6.8704270	4.0607270
27	C	-1.7759280	9.9107500	1.4217010
28	H	-1.5057810	9.8323570	0.3662790
29	H	-1.4341910	10.8712070	1.8135290
30	H	-2.8566740	9.8470400	1.5207690
31	C	-0.3739700	6.5591950	3.5695740
32	H	0.0092340	5.5448110	3.4840490
33	H	-1.3399350	6.5951520	3.0707910
34	C	-0.5670840	6.8948580	5.0378700
35	C	0.2144660	6.2773480	6.0316720
36	C	0.0289740	6.6108420	7.3639470
37	H	0.6164960	6.1531970	8.1436280
38	C	-0.9206580	7.5624500	7.7537880
39	C	-1.7068160	8.1767370	6.7637850
40	C	-1.5194290	7.8323790	5.4245900
41	H	-2.1094210	8.3016290	4.6534030
42	C	1.8937250	4.6588980	6.5804890
43	H	2.5258350	3.9662860	6.0304010
44	H	1.2473400	4.0962730	7.2577970
45	H	2.5223070	5.3385420	7.1600390
46	C	-3.4243550	9.7554940	6.2080420
47	H	-4.0451550	9.0512820	5.6496700
48	H	-2.8066760	10.3289940	5.5137760
49	H	-4.0659190	10.4349540	6.7631310
50	C	-1.0843920	7.9230980	9.1677340
51	H	-1.8227100	8.6987960	9.3799960

52	C	-0.6484430	7.8311820	11.4595590
53	H	-0.9855410	6.9749880	12.0503380
54	H	-1.4216040	8.6077510	11.5109860
55	C	0.6413390	8.3557500	12.0999700
56	H	0.4298440	8.5506170	13.1550170
57	H	1.4167520	7.5816790	12.0441540
58	C	2.2234940	9.6472560	10.9686610
59	H	2.8896760	8.7827250	10.9962870
60	C	2.7510400	10.8428800	10.2991890
61	C	1.9615470	11.9901880	10.1584060
62	H	0.9671460	11.9573590	10.5736630
63	C	2.4328160	13.1170870	9.5040130
64	C	3.7344950	13.1257650	8.9694840
65	C	4.5250680	11.9909980	9.1198430
66	H	5.5195380	12.0085820	8.7033340
67	C	4.0544790	10.8515070	9.7736170
68	C	0.3949650	14.3117140	9.9074710
69	H	0.0084360	15.3024040	9.6813420
70	H	0.4289310	14.1774000	10.9908660
71	H	-0.2634610	13.5586400	9.4689700
72	C	6.1150250	9.6805800	9.4040750
73	H	6.1067960	9.8098280	8.3198440
74	H	6.5032950	8.6943010	9.6449950
75	H	6.7560340	10.4394280	9.8583730
76	C	4.2696370	14.3419570	8.2343220
77	H	3.7869280	15.2347530	8.6257870
78	H	5.3367770	14.4269890	8.4272610
79	C	4.0398810	14.2783910	6.7345300
80	C	2.8488500	14.7424930	6.1856410
81	H	2.1064570	15.1459820	6.8555480
82	C	2.6011890	14.6808920	4.8137370
83	C	3.5760560	14.1410930	3.9573480
84	C	4.7788670	13.6855990	4.5097910
85	H	5.5100730	13.2791810	3.8295980
86	C	5.0168950	13.7448130	5.8737210
87	C	0.4259560	15.6579990	5.0727020
88	H	-0.3881430	15.9318920	4.4066090
89	H	0.7683660	16.5476540	5.6059170
90	H	0.0703070	14.9154640	5.7900210
91	C	7.2121930	12.8180070	5.6204910
92	H	6.8952060	11.9294240	5.0702070
93	H	8.0345610	12.5566210	6.2818060
94	H	7.5467600	13.5817140	4.9149270
95	C	3.3305350	14.0451610	2.5129050
96	H	2.3508970	14.3854400	2.1715940
97	C	3.8286950	13.5273350	0.2915650
98	H	4.5279690	14.1520250	-0.2711450
99	H	2.8134890	13.9003410	0.1079030
100	C	3.9507270	12.0975750	-0.2466590
101	H	3.7967310	12.1380780	-1.3284960
102	H	4.9650310	11.7239020	-0.0595930

Host conformational analysis

P5 rotation

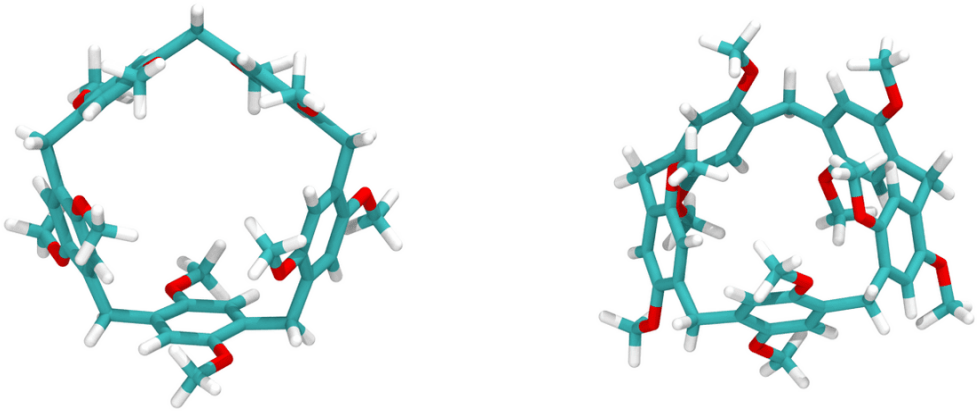


Figure S35: DFT-optimized structure of **P5** at the -90° maximum: top view (left), side view (right)

Table S6: Cartesian coordinates for **P5** at the -90° maximum

SCF Done: E(RB3LYP) = -2497.79511022 A.U. after 5 cycles

1	O	6.2954050	0.7601620	21.0519310
2	O	11.5710810	2.2851370	21.7437600
3	O	9.0612420	-1.3950730	24.8514570
4	O	11.7389450	3.0430840	26.7880610
5	O	8.4236110	3.1403360	25.9431260
6	C	7.0562290	3.1847820	19.8683040
7	C	8.0202450	2.3222100	20.6674390
8	C	9.3521980	2.7024190	20.8261520
9	C	10.2548570	1.9351760	21.5622780
10	C	9.8341550	0.7437650	22.1677690
11	C	8.5083150	0.3500870	21.9875540
12	C	7.6059760	1.1180490	21.2526760
13	C	5.8484140	-0.4834380	21.5777090
14	C	12.0595580	3.4402560	21.0735040
15	C	10.7676610	-0.0707350	23.0523200
16	C	10.6303120	0.3366610	24.5101230
17	C	11.3491270	1.4253830	25.0065790
18	C	11.1075370	1.9383050	26.2771010
19	C	10.1220880	1.3650330	27.0882920
20	C	9.4742530	0.2218190	26.6320940
21	C	9.7133200	-0.2947420	25.3588500
22	C	8.1637280	-2.0956370	25.7022410
23	C	12.7212410	3.6872370	25.9896050
24	C	9.7044420	2.0222920	28.3820360
25	C	8.6763280	3.1612500	28.3137860
26	C	8.0826760	3.6756840	27.1531590
27	C	8.2970570	3.7375890	29.5344070
28	C	7.8348940	3.6704210	24.7622100
29	H	6.3498720	2.5360940	19.3527310
30	H	9.6700910	3.6269910	20.3706460

31	H	8.1867960	-0.5666200	22.4566280
32	H	6.4145130	-1.3211620	21.1634400
33	H	5.9128800	-0.5060530	22.6679810
34	H	4.8066600	-0.5759690	21.2799330
35	H	11.5578050	4.3480670	21.4166580
36	H	13.1168690	3.5028020	21.3197770
37	H	11.9488690	3.3522400	19.9900220
38	H	11.7955080	0.0794740	22.7287650
39	H	10.5341080	-1.1276240	22.9421630
40	H	12.0586770	1.9035820	24.3496500
41	H	8.7239640	-0.2256360	27.2671250
42	H	8.6649270	-2.4593110	26.6026510
43	H	7.3103860	-1.4757690	25.9882470
44	H	7.8079840	-2.9463090	25.1256200
45	H	13.0932900	4.5175890	26.5850930
46	H	13.5517960	3.0171130	25.7525870
47	H	12.2938380	4.0752630	25.0618990
48	H	10.5890020	2.4135740	28.8872940
49	H	9.2930070	1.2529500	29.0396220
50	H	8.7533400	3.3511490	30.4347920
51	H	6.7499780	3.5437930	24.7561060
52	H	8.2626370	3.1040450	23.9406380
53	H	8.0733380	4.7284120	24.6302500
54	O	7.9968940	5.7706490	20.4098230
55	O	3.0149360	4.4896870	22.4530900
56	O	5.8898770	8.7626720	24.1699270
57	O	3.5409960	5.0438840	27.5260840
58	O	6.9746890	5.3582450	30.7982830
59	C	6.2672360	4.1920910	20.6913410
60	C	5.0091620	3.8678720	21.1971660
61	C	4.2568610	4.7771140	21.9406790
62	C	4.7556930	6.0619380	22.1927100
63	C	6.0094460	6.3908360	21.6774070
64	C	6.7643600	5.4789540	20.9399110
65	C	8.5098160	7.0862780	20.5795630
66	C	2.4354390	3.2269780	22.1485130
67	C	3.9673210	7.0710980	23.0156280
68	C	4.3242880	7.0251250	24.4920280
69	C	3.6992480	6.1118860	25.3410500
70	C	4.0932000	5.9584550	26.6690630
71	C	5.1460810	6.7278160	27.1815200
72	C	5.7231860	7.6879680	26.3527960
73	C	5.3255770	7.8474610	25.0250750
74	C	6.8612340	9.6616890	24.6910850
75	C	2.4872090	4.2188980	27.0470010
76	C	5.7525810	6.4096820	28.5273970
77	C	6.7734700	5.2770080	28.4580320
78	C	7.3687690	4.7711780	29.6223180
79	C	7.1525020	4.7127220	27.2504370
80	C	7.5289900	4.8732590	32.0135680
81	H	7.6231060	3.7210170	19.1089460

82	H	4.6279400	2.8780740	21.0018100
83	H	6.3904680	7.3812430	21.8720920
84	H	7.8510980	7.8347300	20.1326190
85	H	8.6662960	7.3244560	21.6342030
86	H	9.4673280	7.1016790	20.0645310
87	H	3.0269240	2.4036540	22.5555460
88	H	1.4549190	3.2282440	22.6185190
89	H	2.3158700	3.0897840	21.0711600
90	H	2.9039190	6.8712420	22.9000680
91	H	4.1609620	8.0693180	22.6286350
92	H	2.9252670	5.4851870	24.9265280
93	H	6.5333430	8.2811440	26.7507730
94	H	6.4558830	10.2578410	25.5120730
95	H	7.7563120	9.1359980	25.0319720
96	H	7.1276310	10.3216670	23.8690760
97	H	2.2005420	3.5866250	27.8837320
98	H	1.6235930	4.8105700	26.7330460
99	H	2.8159350	3.5880850	26.2176600
100	H	4.9770690	6.1364790	29.2428680
101	H	6.2386000	7.3004530	28.9324350
102	H	6.7038830	5.0909800	26.3489560
103	H	7.2927650	3.8177640	32.1708760
104	H	7.0734970	5.4619320	32.8062050
105	H	8.6129670	5.0097900	32.0445340

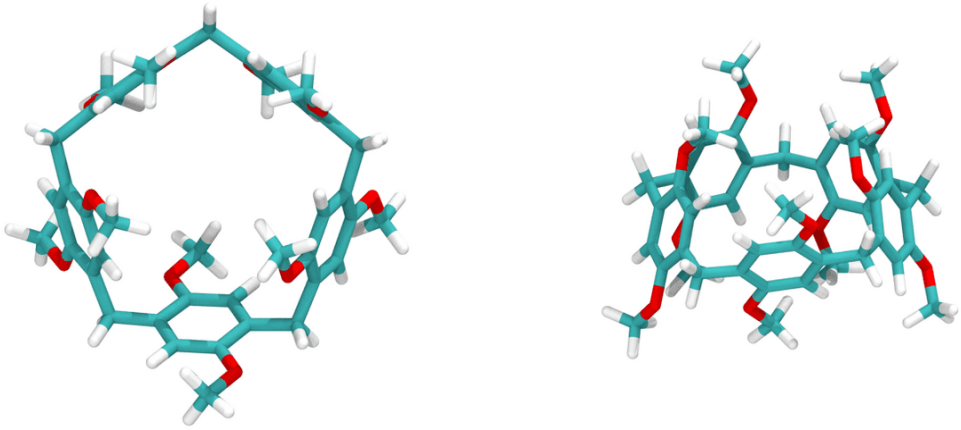


Figure S36: DFT-optimized structure of **P5** at the -70° minimum: top view (left), side view (right)

Table S7: Cartesian coordinates for **P5** at the -70° minimum

SCF Done: E(RB3LYP) = -2497.80291809 A.U. after 6 cycles

1	O	5.9276700	0.5586820	20.9361980
2	O	11.1793150	2.0175220	21.8815970
3	O	8.1995600	-0.3416100	25.2406310
4	O	12.6626500	2.6294840	26.6020560
5	O	10.3744480	5.0299280	26.8129740
6	C	6.8002080	2.9270070	19.7157920
7	C	7.7043040	2.0718650	20.5884030
8	C	9.0319810	2.4361890	20.8082460
9	C	9.8634440	1.7034600	21.6535000

10	C	9.3681370	0.5766650	22.3232650
11	C	8.0537320	0.1895620	22.0702810
12	C	7.2261820	0.9135910	21.2137600
13	C	5.4206230	-0.6405590	21.5062670
14	C	11.7242110	3.1538600	21.2244560
15	C	10.2267470	-0.1902080	23.3157540
16	C	10.3279590	0.4947760	24.6687000
17	C	11.4636750	1.2211300	25.0178120
18	C	11.5525070	1.9182920	26.2236870
19	C	10.4690540	1.9197050	27.1100710
20	C	9.3505180	1.1546900	26.7813300
21	C	9.2733070	0.4380950	25.5903130
22	C	7.0964210	-0.4068690	26.1344170
23	C	13.7680660	2.6825870	25.7127400
24	C	10.4799650	2.7507140	28.3862430
25	C	9.3248860	3.7285900	28.4637390
26	C	9.2875740	4.8511630	27.6246720
27	C	8.2635380	3.5323390	29.3436000
28	C	10.3544780	6.1038440	25.8834720
29	H	6.1029910	2.2837760	19.1814280
30	H	9.4000200	3.3228370	20.3166530
31	H	7.6785900	-0.6845910	22.5779550
32	H	6.0061230	-1.5109320	21.2001690
33	H	5.3931380	-0.5877130	22.5971680
34	H	4.4058630	-0.7446940	21.1292780
35	H	11.2104090	4.0723720	21.5172930
36	H	12.7636130	3.2110790	21.5389610
37	H	11.6857350	3.0474800	20.1374290
38	H	11.2314880	-0.3089810	22.9114470
39	H	9.8033550	-1.1862720	23.4423810
40	H	12.2770030	1.2559880	24.3105790
41	H	8.5175300	1.1498800	27.4679150
42	H	7.3874500	-0.8210080	27.1031670
43	H	6.6393650	0.5742620	26.2815270
44	H	6.3728360	-1.0716970	25.6685400
45	H	14.5194920	3.2939290	26.2070360
46	H	14.1844400	1.6895520	25.5242980
47	H	13.4985670	3.1475450	24.7611890
48	H	11.4234180	3.2878140	28.4413110
49	H	10.4340630	2.0885420	29.2534330
50	H	8.3027970	2.6798660	30.0054200
51	H	9.5223450	6.0116950	25.1817020
52	H	11.2919900	6.0408760	25.3365510
53	H	10.3000680	7.0724840	26.3875950
54	O	7.7629950	5.5055550	20.2557410
55	O	2.7874620	4.2451010	22.3304330
56	O	5.3906870	8.8138430	24.1297940
57	O	4.2254100	4.4888640	27.3784340
58	O	6.1145550	4.2433390	30.2490490
59	C	6.0081140	3.9505750	20.5134280
60	C	4.7473250	3.6353210	21.0155640

61	C	4.0235420	4.5318730	21.8001650
62	C	4.5540400	5.7931750	22.0941180
63	C	5.8030950	6.1209820	21.5673910
64	C	6.5303300	5.2219520	20.7895630
65	C	8.3101950	6.7994000	20.4752680
66	C	2.1740830	3.0109610	21.9804100
67	C	3.8187260	6.7738070	22.9915180
68	C	4.3128450	6.7336780	24.4288450
69	C	4.0043180	5.6439060	25.2446180
70	C	4.4892880	5.5420550	26.5449770
71	C	5.3045970	6.5536610	27.0725240
72	C	5.5839080	7.6573420	26.2700730
73	C	5.1082000	7.7548390	24.9600710
74	C	6.1214840	9.9119880	24.6588660
75	C	3.4235490	3.4237880	26.8867810
76	C	5.9022740	6.4197090	28.4582390
77	C	7.1041900	5.4836080	28.5008470
78	C	7.1646380	4.3966960	29.3804160
79	C	8.1846080	5.6975780	27.6444120
80	C	6.1240640	3.1340500	31.1355100
81	H	7.4100660	3.4413790	18.9753550
82	H	4.3501410	2.6561460	20.8010590
83	H	6.2065060	7.0967880	21.7925440
84	H	7.6662630	7.5824220	20.0674410
85	H	8.4826860	6.9885530	21.5373790
86	H	9.2627000	6.8132400	19.9508960
87	H	2.7533620	2.1567290	22.3385940
88	H	1.2022850	3.0124510	22.4682910
89	H	2.0328330	2.9253120	20.9002810
90	H	2.7548100	6.5447520	22.9728250
91	H	3.9441500	7.7802670	22.6002340
92	H	3.3872610	4.8616380	24.8298460
93	H	6.1976160	8.4439920	26.6831020
94	H	5.6056660	10.3670050	25.5079600
95	H	7.1296020	9.6187550	24.9624360
96	H	6.1913800	10.6393520	23.8535790
97	H	3.3507080	2.7067280	27.7008400
98	H	2.4199620	3.7646810	26.6196530
99	H	3.8839950	2.9405450	26.0218100
100	H	5.1506310	6.0524080	29.1512990
101	H	6.2058950	7.4101910	28.8046900
102	H	8.1405660	6.5374110	26.9682280
103	H	6.1267560	2.1843080	30.5944260
104	H	5.2078910	3.2086800	31.7164690
105	H	6.9800950	3.1656360	31.8145050

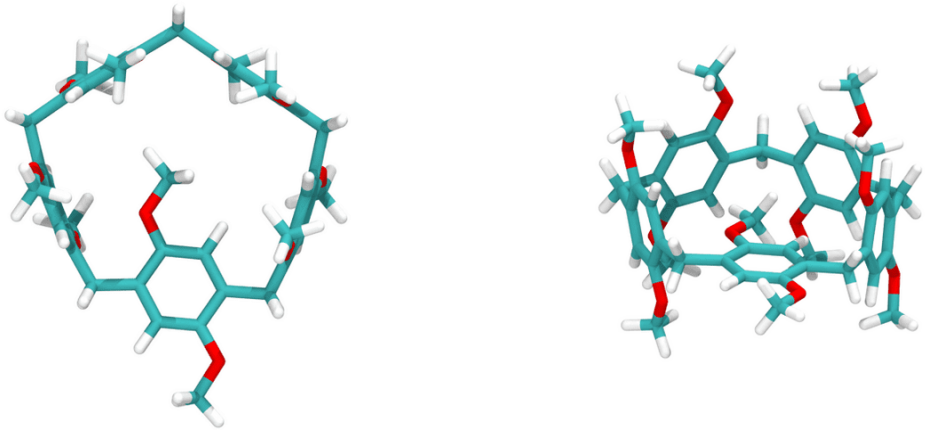


Figure S37: DFT-optimized structure of **P5** at the 0° maximum: top view (left), side view (right)

Table S8: Cartesian coordinates for **P5** at the 0° maximum

SCF Done: E(RB3LYP) = -2497.80068653 A.U. after 5 cycles

1	O	5.8363880	0.5209830	21.0965020
2	O	11.1564010	1.8698940	21.7904190
3	O	8.2492060	-0.3959990	25.3529670
4	O	12.6606900	2.7556400	26.4437320
5	O	10.5474200	5.4452820	27.1804190
6	C	6.7267900	2.8105830	19.7449310
7	C	7.6386480	1.9674940	20.6212730
8	C	8.9830580	2.3016530	20.7768550
9	C	9.8253470	1.5815980	21.6221490
10	C	9.3254970	0.4975380	22.3558560
11	C	7.9923790	0.1378970	22.1671520
12	C	7.1530430	0.8500920	21.3121180
13	C	5.3187030	-0.6377860	21.7365010
14	C	11.7070650	2.9581850	21.0604110
15	C	10.1992710	-0.2501970	23.3500470
16	C	10.3315730	0.4769600	24.6779680
17	C	11.4550840	1.2492670	24.9593740
18	C	11.5617500	1.9947400	26.1342610
19	C	10.5114250	1.9962610	27.0615400
20	C	9.4082940	1.1841000	26.8010630
21	C	9.3126730	0.4231320	25.6390340
22	C	7.1804780	-0.4630300	26.2872110
23	C	13.7238250	2.8239210	25.5048940
24	C	10.5534830	2.9009830	28.2886800
25	C	9.3513870	3.8186940	28.3903790
26	C	9.3827440	5.0947160	27.8110130
27	C	8.2114070	3.4516400	29.1025390
28	C	10.6079940	6.7013060	26.5203220
29	H	6.0051080	2.1634910	19.2489230
30	H	9.3562890	3.1564500	20.2355880
31	H	7.6129550	-0.7036260	22.7242820
32	H	5.8668950	-1.5371940	21.4454550
33	H	5.3363040	-0.5389250	22.8243850

34	H	4.2872550	-0.7271890	21.4036280
35	H	11.2294330	3.9037290	21.3271780
36	H	12.7585900	3.0001480	21.3344440
37	H	11.6254590	2.8016920	19.9818610
38	H	11.1940030	-0.3881570	22.9280010
39	H	9.7711000	-1.2380750	23.5157530
40	H	12.2416460	1.2827460	24.2226240
41	H	8.5971150	1.1791340	27.5121360
42	H	7.5171400	-0.8377170	27.2573450
43	H	6.7004830	0.5092390	26.4196320
44	H	6.4606570	-1.1624040	25.8684090
45	H	14.4700130	3.4798200	25.9471820
46	H	14.1719700	1.8426270	25.3285560
47	H	13.3944390	3.2474740	24.5529880
48	H	11.4634950	3.4892300	28.2585020
49	H	10.5954070	2.2814390	29.1882280
50	H	8.2108760	2.4960810	29.6050470
51	H	9.8712270	6.7683480	25.7161680
52	H	11.6065770	6.7657130	26.0950320
53	H	10.4628780	7.5316500	27.2165820
54	O	7.7804510	5.3606560	20.2427040
55	O	2.7616760	4.3174420	22.3317370
56	O	5.4361560	8.8456320	24.1576540
57	O	4.2049460	4.4826360	27.3291860
58	O	5.9663690	3.9611180	29.8999550
59	C	5.9721190	3.8737020	20.5268610
60	C	4.6997200	3.6139640	21.0312220
61	C	4.0094030	4.5489530	21.8011570
62	C	4.5878180	5.7923310	22.0803520
63	C	5.8484040	6.0650270	21.5499430
64	C	6.5406380	5.1291770	20.7839580
65	C	8.3793670	6.6330350	20.4532370
66	C	2.0970840	3.1084310	21.9876310
67	C	3.8905060	6.8138310	22.9620840
68	C	4.3578660	6.7591100	24.4084500
69	C	4.0333210	5.6612910	25.2061980
70	C	4.4882080	5.5459780	26.5162650
71	C	5.2888190	6.5531280	27.0742110
72	C	5.5843730	7.6650900	26.2885030
73	C	5.1390410	7.7758930	24.9688280
74	C	6.1682000	9.9312940	24.7092470
75	C	3.4170760	3.4232560	26.8057320
76	C	5.8580940	6.4115870	28.4745380
77	C	7.0881020	5.5139260	28.5185500
78	C	7.0894800	4.2811660	29.1830930
79	C	8.2547110	5.9080520	27.8634750
80	C	5.9311080	2.7206140	30.5885720
81	H	7.3270350	3.2894430	18.9731350
82	H	4.2650010	2.6479780	20.8298610
83	H	6.2893170	7.0275960	21.7612670
84	H	7.7669610	7.4385190	20.0406470

85	H	8.5606370	6.8216250	21.5138680
86	H	9.3310320	6.6054010	19.9279310
87	H	2.6364660	2.2325300	22.3556380
88	H	1.1236620	3.1559930	22.4699230
89	H	1.9581860	3.0206850	20.9073720
90	H	2.8161220	6.6400130	22.9271780
91	H	4.0731460	7.8099800	22.5676110
92	H	3.4262960	4.8829960	24.7700770
93	H	6.1853680	8.4497110	26.7232640
94	H	5.6434850	10.3828930	25.5548030
95	H	7.1688390	9.6257250	25.0252670
96	H	6.2572740	10.6661560	23.9126840
97	H	3.3264560	2.6956380	27.6086050
98	H	2.4190220	3.7653330	26.5195800
99	H	3.8978420	2.9513670	25.9454680
100	H	5.1016910	6.0087340	29.1423480
101	H	6.1261670	7.4041290	28.8412490
102	H	8.2603730	6.8671490	27.3683260
103	H	6.0135900	1.8741330	29.9018800
104	H	4.9638410	2.6819270	31.0839630
105	H	6.7199970	2.6523530	31.3423740

PIm rotation

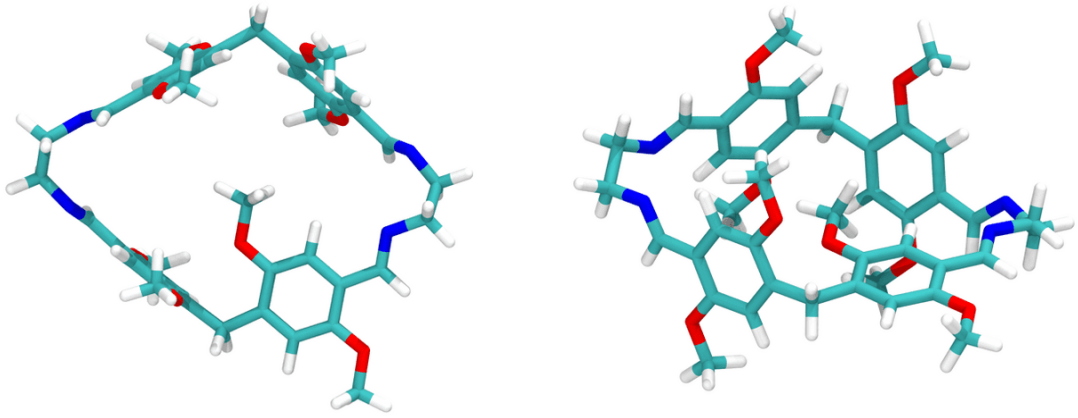


Figure S38: DFT-optimized structure of **PIm** at the -10° maximum: top view (left), side view (right)

Table S9: Cartesian coordinates for **PIm** at the -10° maximum

SCF Done: E(RB3LYP) = -2450.78907180 A.U. after 5 cycles

1	O	2.2961100	7.5230530	-0.4864730
2	N	4.2029700	10.7580940	1.0788340
3	C	3.5782660	9.7812350	0.5604020
4	H	3.6638690	9.5359560	-0.5015790
5	O	1.3758130	8.8074630	4.8188230
6	N	-0.5642390	7.4395540	10.1824690
7	C	2.6909830	8.9296390	1.3680090
8	O	1.5662270	5.6303560	5.8236200
9	N	0.6155650	9.8900580	11.4417610

10	C	2.0442600	7.8074030	0.8252760
11	O	-3.0103820	8.4454950	7.1240780
12	N	4.8150710	13.4867390	1.8167610
13	C	1.1951430	7.0544630	1.6344970
14	H	0.6926680	6.1908460	1.2241200
15	O	4.4577410	10.3105710	10.2658850
16	C	0.9541680	7.3716140	2.9731910
17	O	0.9938650	14.4191930	8.9497470
18	C	1.6114290	8.4941610	3.5126070
19	O	1.4837570	14.7313270	3.7342260
20	C	2.4599950	9.2432670	2.7083990
21	H	2.9693100	10.1074810	3.1017510
22	O	6.0003620	13.9628660	6.8367160
23	C	1.6548740	6.3971020	-1.0763550
24	H	1.9979620	6.3675790	-2.1072610
25	H	0.5676310	6.5023020	-1.0628160
26	H	1.9384040	5.4679300	-0.5770820
27	C	2.0267270	9.9425150	5.3792500
28	H	1.7452540	10.8635730	4.8639790
29	H	3.1134260	9.8349220	5.3573570
30	H	1.6924440	9.9923720	6.4120010
31	C	-0.0262950	6.4561170	3.7129440
32	H	0.3808130	5.4447670	3.6566750
33	H	-0.9501320	6.4442270	3.1312520
34	C	-0.3859070	6.7474560	5.1494590
35	C	0.4462610	6.3190890	6.1985900
36	C	0.1258210	6.6319320	7.5076420
37	H	0.7649630	6.3446740	8.3271200
38	C	-1.0242260	7.3712080	7.8192170
39	C	-1.8819930	7.7586170	6.7765370
40	C	-1.5501120	7.4380100	5.4584670
41	H	-2.1894220	7.7512380	4.6470600
42	C	2.4615230	5.2025080	6.8432910
43	H	3.2684170	4.6827760	6.3328330
44	H	1.9760610	4.5162990	7.5414420
45	H	2.8720130	6.0509290	7.3952620
46	C	-3.8757930	8.9033340	6.0906150
47	H	-4.2913680	8.0710720	5.5181930
48	H	-3.3640220	9.5924360	5.4151740
49	H	-4.6840670	9.4285800	6.5929190
50	C	-1.3006530	7.7778640	9.2016700
51	H	-2.1746920	8.4168070	9.3447560
52	C	-0.9097640	7.9499370	11.4965890
53	H	-1.1703180	7.1020530	12.1367170
54	H	-1.7705380	8.6294930	11.4650980
55	C	0.2821810	8.6622330	12.1430670
56	H	-0.0057480	8.9235410	13.1654000
57	H	1.1334390	7.9722960	12.1950930
58	C	1.8095160	10.0248040	11.0237730
59	H	2.5565780	9.2458210	11.1881590
60	C	2.2773230	11.2168170	10.3038940

61	C	1.3938960	12.2534250	9.9803180
62	H	0.3654250	12.1362170	10.2823410
63	C	1.8207650	13.3821110	9.2972510
64	C	3.1718690	13.5089450	8.9249390
65	C	4.0521700	12.4811650	9.2490310
66	H	5.0845150	12.5876300	8.9551400
67	C	3.6267170	11.3380930	9.9271900
68	C	-0.3629170	14.3666950	9.3799050
69	H	-0.8211290	15.2889690	9.0316320
70	H	-0.4342210	14.3176060	10.4686690
71	H	-0.8891600	13.5151870	8.9430530
72	C	5.8270520	10.3835400	9.8803980
73	H	5.9340460	10.4408680	8.7951870
74	H	6.2835150	9.4642140	10.2378240
75	H	6.3276600	11.2367130	10.3432700
76	C	3.6687670	14.7373260	8.1817710
77	H	3.0146320	15.5763810	8.4075500
78	H	4.6652800	14.9848190	8.5406190
79	C	3.7176940	14.5437430	6.6765030
80	C	2.5765940	14.7458720	5.9062410
81	H	1.6736310	15.0522750	6.4102460
82	C	2.5800320	14.5453320	4.5254720
83	C	3.7615670	14.1273670	3.8882530
84	C	4.9135470	13.9436960	4.6619010
85	H	5.8044170	13.6185270	4.1488110
86	C	4.9036750	14.1436610	6.0338170
87	C	0.2558240	15.1121570	4.3477230
88	H	-0.4684420	15.1807830	3.5402090
89	H	0.3393360	16.0841610	4.8386910
90	H	-0.0792620	14.3648070	5.0698850
91	C	7.2370820	13.6266460	6.2147980
92	H	7.1823270	12.6596560	5.7101590
93	H	7.9680050	13.5716140	7.0176350
94	H	7.5444080	14.3925640	5.4994860
95	C	3.7654510	13.8212070	2.4518480
96	H	2.7928430	13.8588810	1.9569540
97	C	4.6593350	13.0801770	0.4320500
98	H	5.3357030	13.6739940	-0.1881520
99	H	3.6356280	13.2373080	0.0682600
100	C	5.0403200	11.6010400	0.2538220
101	H	4.9889610	11.3422240	-0.8121670
102	H	6.0749120	11.4773400	0.5853750

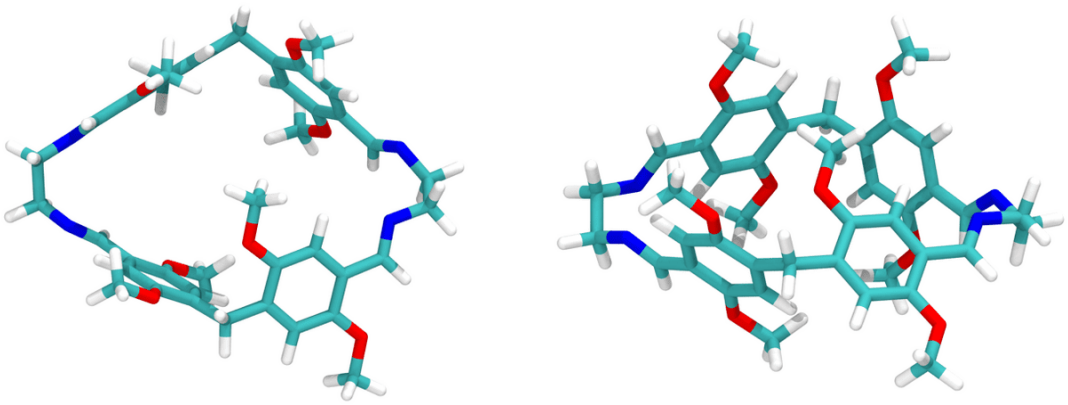


Figure S39: DFT-optimized structure of **PIm** at the -75° minimum: top view (left), side view (right)

Table S10: Cartesian coordinates for **PIm** at the -75° minimum

SCF Done: E(RB3LYP) = -2450.79506795 A.U. after 5 cycles

1	O	1.1371920	8.2503860	-0.2965700
2	N	3.9850200	10.8612200	0.9132470
3	C	3.1875740	9.9692530	0.4850550
4	H	2.8448110	9.9524140	-0.5530020
5	O	3.3061970	7.4993070	4.7317250
6	N	-0.8934500	7.6052460	10.0104710
7	C	2.6822810	8.9035290	1.3636590
8	O	1.6491570	4.7209010	6.5639500
9	N	0.0776860	10.1745430	11.3238510
10	C	1.6470700	8.0488090	0.9540140
11	O	-1.8046690	9.0339950	6.3385140
12	N	4.2047810	13.6136340	1.7477300
13	C	1.1811320	7.0638440	1.8312090
14	H	0.3765940	6.4086360	1.5334230
15	O	3.9886560	10.2746980	10.2870330
16	C	1.7284820	6.8982460	3.0989090
17	O	0.9418550	14.7215710	9.0409070
18	C	2.7865520	7.7394890	3.4926680
19	O	1.1416260	15.0287730	3.9384410
20	C	3.2383640	8.7291860	2.6376900
21	H	4.0350670	9.3968790	2.9232620
22	O	5.7696780	13.7965600	6.7088990
23	C	0.1126790	7.3793640	-0.7653050
24	H	-0.1174910	7.7101450	-1.7747160
25	H	-0.7875260	7.4515750	-0.1509190
26	H	0.4523860	6.3418180	-0.7960210
27	C	4.3350760	8.3603730	5.2081770
28	H	3.9943460	9.3963330	5.2626240
29	H	5.2276180	8.3026650	4.5806080
30	H	4.5753520	8.0086050	6.2080520
31	C	1.2205000	5.8339970	4.0435870
32	H	2.0503920	5.2028270	4.3548090
33	H	0.5204520	5.1896060	3.5066430
34	C	0.5480390	6.3769190	5.2949880

35	C	0.8070910	5.7998640	6.5522000
36	C	0.2249670	6.3337210	7.6909470
37	H	0.4325020	5.9282410	8.6682340
38	C	-0.6422390	7.4306520	7.6240670
39	C	-0.9361800	7.9815830	6.3653390
40	C	-0.3304960	7.4522870	5.2247690
41	H	-0.5227960	7.8944290	4.2596140
42	C	1.9846760	4.1439320	7.8205150
43	H	2.6672490	3.3271280	7.5996580
44	H	1.1021490	3.7474970	8.3281120
45	H	2.4837930	4.8648890	8.4720120
46	C	-2.0845630	9.6576720	5.0892530
47	H	-2.5554070	8.9619950	4.3910110
48	H	-1.1812640	10.0735720	4.6384290
49	H	-2.7784920	10.4642700	5.3112630
50	C	-1.2074690	8.0141760	8.8471780
51	H	-1.9116980	8.8362510	8.7055110
52	C	-1.4845530	8.2767150	11.1531600
53	H	-1.9565270	7.5205570	11.7855500
54	H	-2.2498320	9.0060910	10.8604100
55	C	-0.4112710	8.9831750	11.9933050
56	H	-0.8766620	9.2909740	12.9333520
57	H	0.3925230	8.2735120	12.2246810
58	C	1.3116290	10.2293790	11.0188130
59	H	1.9922680	9.4093300	11.2555040
60	C	1.9052670	11.3843530	10.3315130
61	C	1.1279310	12.5076000	10.0260630
62	H	0.0927030	12.4863790	10.3261950
63	C	1.6621460	13.5990580	9.3605200
64	C	3.0154810	13.5938630	8.9752820
65	C	3.7929430	12.4832540	9.2882200
66	H	4.8286170	12.4879930	8.9865360
67	C	3.2609050	11.3813180	9.9603370
68	C	-0.4110580	14.7955550	9.4797020
69	H	-0.7755830	15.7674790	9.1566280
70	H	-0.4816750	14.7281040	10.5675250
71	H	-1.0227620	14.0120870	9.0270490
72	C	5.3657230	10.2321450	9.9264730
73	H	5.4975010	10.2892590	8.8439840
74	H	5.7342340	9.2735110	10.2821790
75	H	5.9299140	11.0347500	10.4066200
76	C	3.6186480	14.7661600	8.2214010
77	H	3.0892570	15.6759270	8.4971840
78	H	4.6579870	14.8807140	8.5192470
79	C	3.5477200	14.5943500	6.7137130
80	C	2.3793650	14.9120030	6.0277160
81	H	1.5469520	15.2936410	6.5969630
82	C	2.2665170	14.7267660	4.6504700
83	C	3.3558070	14.2103970	3.9278330
84	C	4.5388290	13.9141950	4.6144550
85	H	5.3588660	13.5173670	4.0374900

86	C	4.6428700	14.0939530	5.9861660
87	C	-0.0043250	15.4981210	4.6419490
88	H	-0.7735150	15.6460720	3.8883820
89	H	0.1954560	16.4484340	5.1419650
90	H	-0.3520990	14.7660420	5.3737770
91	C	6.9240710	13.3597000	5.9985600
92	H	6.7450020	12.4123060	5.4853620
93	H	7.6994560	13.2207860	6.7477770
94	H	7.2531540	14.1076650	5.2738680
95	C	3.2236860	13.9261800	2.4938060
96	H	2.2063650	13.9696160	2.0983620
97	C	3.9034960	13.2668680	0.3705490
98	H	4.3846620	13.9960000	-0.2877860
99	H	2.8244340	13.2916600	0.1702830
100	C	4.4573030	11.8827540	0.0000800
101	H	4.1901570	11.6725080	-1.0439880
102	H	5.5467160	11.9168700	0.0740950

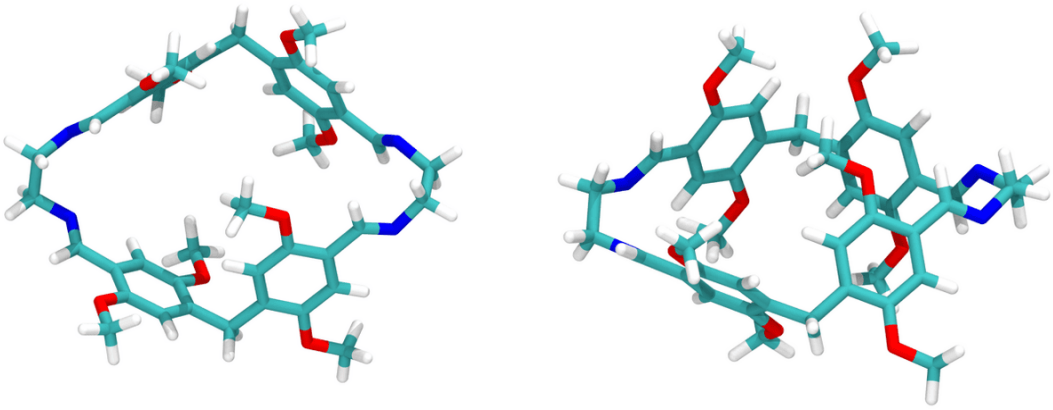


Figure S40: DFT-optimized structure of **PIm** at the -90° maximum: top view (left), side view (right)

Table S11: Cartesian coordinates for **PIm** at the -90° maximum

SCF Done: E(RB3LYP) = -2450.79407423 A.U. after 5 cycles

1	O	1.0116060	8.4150750	-0.0784960
2	N	4.0836830	10.8698790	0.8471060
3	C	3.2343830	10.0004770	0.4764500
4	H	2.7902720	10.0151660	-0.5225560
5	O	3.7479750	7.4048630	4.6174340
6	N	-0.9909580	7.5792090	10.0208390
7	C	2.7937750	8.9266700	1.3805480
8	O	1.4347600	4.5598930	6.5913710
9	N	-0.0282470	10.1591880	11.3273810
10	C	1.6603050	8.1496590	1.0932890
11	O	-1.3912090	9.3052830	6.3940220
12	N	4.1364340	13.6164390	1.6927180
13	C	1.2440440	7.1768700	2.0075640
14	H	0.3660330	6.5822010	1.8046430
15	O	3.8750200	10.2475440	10.2579350
16	C	1.9340770	6.9501390	3.1939900

17	O	0.8217490	14.6902160	9.0130430
18	C	3.0963920	7.6998310	3.4536350
19	O	1.0064950	14.8618260	3.8869220
20	C	3.5010250	8.6798180	2.5634840
21	H	4.3701150	9.2881270	2.7552380
22	O	5.6822180	13.8412710	6.6630760
23	C	-0.1223230	7.6261570	-0.4247950
24	H	-0.4530630	7.9929880	-1.3929300
25	H	-0.9310680	7.7471930	0.2994190
26	H	0.1367160	6.5685760	-0.5102460
27	C	4.9028850	8.1668290	4.9523030
28	H	4.6626860	9.2265980	5.0612360
29	H	5.6922560	8.0470860	4.2063830
30	H	5.2485270	7.7766790	5.9060760
31	C	1.4906640	5.9002920	4.1824400
32	H	2.3598700	5.3684350	4.5621770
33	H	0.8757200	5.1573970	3.6668380
34	C	0.7162730	6.4434140	5.3747150
35	C	0.7456310	5.7424560	6.5958810
36	C	0.1127830	6.2651910	7.7115980
37	H	0.1581090	5.7659720	8.6662150
38	C	-0.5936310	7.4730390	7.6507130
39	C	-0.6721080	8.1458110	6.4205910
40	C	-0.0048330	7.6292290	5.3079520
41	H	-0.0203730	8.1702210	4.3756150
42	C	1.5551130	3.8486360	7.8182420
43	H	2.1449460	2.9637900	7.5924190
44	H	0.5787390	3.5420270	8.2006620
45	H	2.0710930	4.4424420	8.5762070
46	C	-1.4407120	10.0518300	5.1820470
47	H	-1.9080550	9.4793680	4.3775390
48	H	-0.4457090	10.3760390	4.8709210
49	H	-2.0505950	10.9250210	5.3989300
50	C	-1.1982680	8.0513980	8.8574490
51	H	-1.8261550	8.9312540	8.7052700
52	C	-1.5923080	8.2650150	11.1501240
53	H	-2.0821250	7.5204660	11.7817440
54	H	-2.3426340	9.0028490	10.8410820
55	C	-0.5204620	8.9692500	11.9967620
56	H	-0.9896470	9.2783580	12.9343510
57	H	0.2808730	8.2579750	12.2314060
58	C	1.2032290	10.2081440	11.0110320
59	H	1.8825410	9.3851040	11.2408890
60	C	1.7938930	11.3600410	10.3155560
61	C	1.0155460	12.4829520	10.0117020
62	H	-0.0166730	12.4651790	10.3221700
63	C	1.5444870	13.5692460	9.3336590
64	C	2.8936960	13.5597130	8.9346310
65	C	3.6724530	12.4494110	9.2457860
66	H	4.7053680	12.4507240	8.9341780
67	C	3.1457560	11.3525220	9.9304740

68	C	-0.5232690	14.7733630	9.4738110
69	H	-0.8891580	15.7442500	9.1491620
70	H	-0.5757380	14.7146240	10.5631540
71	H	-1.1459190	13.9890250	9.0378440
72	C	5.2433060	10.1916290	9.8668790
73	H	5.3505510	10.2396260	8.7812930
74	H	5.6123280	9.2328120	10.2215000
75	H	5.8242800	10.9933360	10.3282080
76	C	3.4921720	14.7281430	8.1710630
77	H	2.9563790	15.6370110	8.4375030
78	H	4.5295360	14.8521200	8.4713540
79	C	3.4287860	14.5447590	6.6642220
80	C	2.2476320	14.8086240	5.9769590
81	H	1.3995020	15.1574070	6.5444570
82	C	2.1442050	14.6151020	4.6002320
83	C	3.2573660	14.1506850	3.8783040
84	C	4.4513120	13.9072060	4.5663050
85	H	5.2893430	13.5480680	3.9904420
86	C	4.5450900	14.0907800	5.9385180
87	C	-0.1611730	15.2766640	4.5887590
88	H	-0.9370880	15.3823620	3.8349160
89	H	-0.0093010	16.2384180	5.0836960
90	H	-0.4715790	14.5319660	5.3246200
91	C	6.8554570	13.4533580	5.9553530
92	H	6.7178630	12.4986610	5.4428850
93	H	7.6344950	13.3480370	6.7062660
94	H	7.1539340	14.2139730	5.2306040
95	C	3.1407320	13.8682980	2.4425690
96	H	2.1222320	13.8602340	2.0476820
97	C	3.8497730	13.2680950	0.3125730
98	H	4.2889780	14.0284700	-0.3396570
99	H	2.7700070	13.2384450	0.1167080
100	C	4.4712880	11.9174220	-0.0778710
101	H	4.1810830	11.6955710	-1.1130510
102	H	5.5585330	12.0104950	-0.0393070

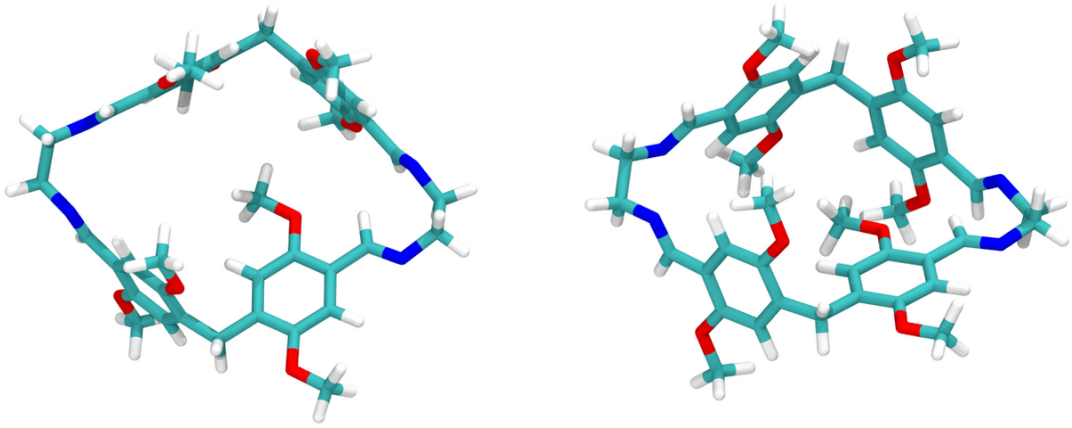


Figure S41: DFT-optimized structure of **PIm** at the 185° maximum: top view (left), side view (right)

Table S12: Cartesian coordinates for **PIm** at the 185° maximum

SCF Done: E(RB3LYP) = -2450.78938290 A.U. after 6 cycles

1	O	1.6489660	11.0509400	3.9506340
2	N	2.7992210	11.0462120	0.0967990
3	C	2.4245400	11.0088940	1.3131640
4	H	2.7401080	11.7493460	2.0387560
5	O	-0.1796910	6.8223530	0.9015160
6	N	-0.3326640	7.2467570	10.0736100
7	C	1.5590450	9.9551900	1.8576020
8	O	0.9767180	5.7425840	5.3013950
9	N	1.4185240	9.3744650	11.2888450
10	C	1.1976070	9.9951640	3.2141740
11	O	-3.2941200	8.4110240	7.5824680
12	N	4.2318350	13.5209580	1.6524460
13	C	0.4088890	8.9772210	3.7497750
14	H	0.1424160	9.0052210	4.7925270
15	O	5.0367180	9.1696020	9.5103330
16	C	-0.0411500	7.9169600	2.9755930
17	O	2.4827550	14.0728670	9.3374290
18	C	0.3081990	7.8861760	1.6113690
19	O	2.2474230	15.6815630	4.4377720
20	C	1.0978210	8.8898800	1.0717730
21	H	1.3883300	8.8781320	0.0329160
22	O	6.5622010	12.6965780	6.1890290
23	C	1.3583320	11.0873420	5.3456590
24	H	1.8365900	11.9861130	5.7232780
25	H	1.7689980	10.2182700	5.8628780
26	H	0.2831850	11.1465630	5.5284780
27	C	0.1612030	6.7245790	-0.4769910
28	H	1.2413210	6.6397970	-0.6168250
29	H	-0.2108970	7.5817380	-1.0430140
30	H	-0.3195480	5.8194530	-0.8393560
31	C	-0.9021790	6.8039870	3.5586920
32	H	-0.4615100	5.8476410	3.2774790
33	H	-1.8847450	6.8359270	3.0823300
34	C	-1.0627160	6.8865780	5.0556830

35	C	-0.0590710	6.3931650	5.9101050
36	C	-0.1405500	6.6189790	7.2750830
37	H	0.6371620	6.2899510	7.9454770
38	C	-1.2118990	7.3269450	7.8339330
39	C	-2.2473000	7.7659820	6.9911500
40	C	-2.1536690	7.5425260	5.6154150
41	H	-2.9216460	7.9110470	4.9520530
42	C	2.0290580	5.2414560	6.1190370
43	H	2.7280010	4.7594900	5.4403570
44	H	1.6609430	4.5072010	6.8393680
45	H	2.5406240	6.0470740	6.6503700
46	C	-4.3280710	8.9373050	6.7557060
47	H	-4.8405890	8.1460820	6.2044750
48	H	-3.9413400	9.6806520	6.0550960
49	H	-5.0323570	9.4144730	7.4320830
50	C	-1.2152770	7.6697840	9.2621820
51	H	-2.0114870	8.3421660	9.5890080
52	C	-0.4019190	7.7014570	11.4511620
53	H	-0.7063350	6.8554330	12.0748010
54	H	-1.1380410	8.5031960	11.5864590
55	C	0.9684580	8.1619610	11.9530690
56	H	0.8702270	8.3808720	13.0202470
57	H	1.6879940	7.3415390	11.8405930
58	C	2.5562450	9.3402440	10.7200000
59	H	3.1572730	8.4289540	10.7193770
60	C	3.1602830	10.4990020	10.0490010
61	C	2.5046300	11.7357360	10.0089550
62	H	1.5351130	11.7958050	10.4773250
63	C	3.0805090	12.8412950	9.4007110
64	C	4.3565960	12.7378880	8.8146880
65	C	5.0082810	11.5094090	8.8537030
66	H	5.9823460	11.4391240	8.3974150
67	C	4.4299150	10.3903090	9.4543830
68	C	1.2246830	14.2411870	9.9834180
69	H	0.9517810	15.2831200	9.8360650
70	H	1.2947770	14.0350820	11.0536800
71	H	0.4580660	13.6016900	9.5404160
72	C	6.3297370	9.0211910	8.9314240
73	H	6.3135990	9.2288550	7.8596100
74	H	6.6066610	7.9824060	9.0911590
75	H	7.0626150	9.6676450	9.4189980
76	C	5.0194450	13.9406610	8.1622630
77	H	4.6900070	14.8445280	8.6702440
78	H	6.0965460	13.8569160	8.2939460
79	C	4.7085150	14.0709960	6.6818230
80	C	3.6319720	14.8403790	6.2516880
81	H	3.0435300	15.3503720	6.9975090
82	C	3.2945700	14.9391290	4.9004860
83	C	4.0479830	14.2351640	3.9449200
84	C	5.1525440	13.4905710	4.3759810
85	H	5.7142410	12.9612410	3.6231750

86	C	5.4907590	13.4081650	5.7172160
87	C	1.4326710	16.3746780	5.3783120
88	H	0.6683890	16.8781270	4.7921080
89	H	2.0080460	17.1188480	5.9332880
90	H	0.9544480	15.6856520	6.0776220
91	C	7.4041740	12.0473040	5.2408250
92	H	6.8628880	11.2790800	4.6846150
93	H	8.1975670	11.5800830	5.8187440
94	H	7.8419710	12.7625520	4.5411520
95	C	3.6244330	14.2023350	2.5400710
96	H	2.7103200	14.7523080	2.3067810
97	C	3.6637030	13.4871620	0.3113210
98	H	4.2754310	14.1368480	-0.3230030
99	H	2.6385340	13.8789020	0.2887520
100	C	3.7125390	12.0998310	-0.3472810
101	H	3.5263090	12.2454780	-1.4133040
102	H	4.7327110	11.7099380	-0.2700230

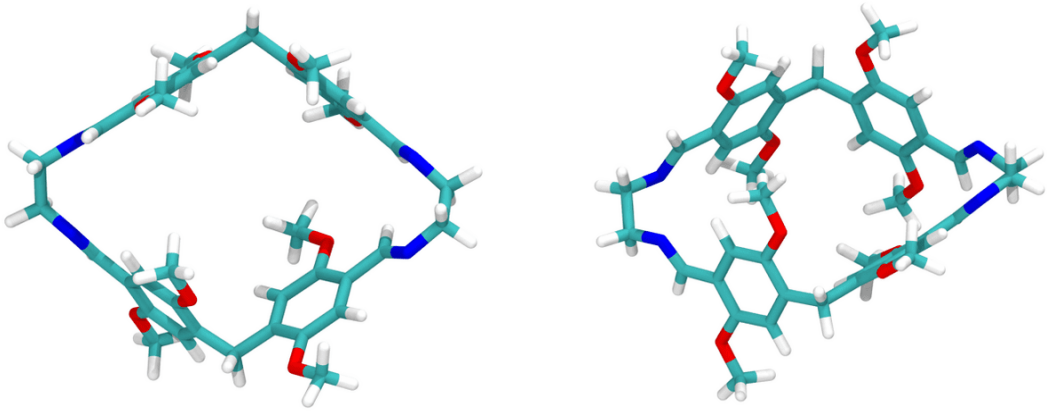


Figure S42: DFT-optimized structure of **PIm** at the 220° minimum: top view (left), side view (right)

Table S13: Cartesian coordinates for **PIm** at the 220° minimum

SCF Done: E(RB3LYP) = -2450.79141171 A.U. after 5 cycles

1	O	0.4552710	11.7428730	3.2038290
2	N	2.9543610	10.9982620	0.1495940
3	C	2.0865080	11.2257700	1.0503860
4	H	1.9196760	12.2138350	1.4665060
5	O	0.4934420	6.5594270	1.2821370
6	N	-0.2762380	7.3308830	10.0911220
7	C	1.2547020	10.1669010	1.6389210
8	O	1.1037630	6.3410470	5.1937000
9	N	1.5389820	9.2829330	11.4296960
10	C	0.4588790	10.4514600	2.7609850
11	O	-3.3946860	8.3041490	7.7365380
12	N	4.3012470	13.4102670	1.6671730
13	C	-0.2616970	9.4263770	3.3726310
14	H	-0.8441380	9.6337020	4.2559970
15	O	5.0326720	8.9226640	9.4357540
16	C	-0.2338900	8.1233970	2.8883320

17	O	2.7601220	13.9655320	9.5553280
18	C	0.5321390	7.8489900	1.7395570
19	O	2.1819870	15.2744210	4.5663490
20	C	1.2716370	8.8591100	1.1415880
21	H	1.8940660	8.6650770	0.2823450
22	O	6.7179350	12.5328840	6.1573590
23	C	-0.2549140	12.0581270	4.3968500
24	H	-0.0769370	13.1159720	4.5701070
25	H	0.1199720	11.4862720	5.2479100
26	H	-1.3276020	11.8856800	4.2821460
27	C	1.2985280	6.2208250	0.1586480
28	H	2.3590600	6.3869050	0.3611150
29	H	1.0063030	6.7869300	-0.7289410
30	H	1.1288630	5.1620630	-0.0204150
31	C	-1.0237030	7.0150500	3.5709030
32	H	-0.5650040	6.0637580	3.3117640
33	H	-2.0377600	6.9951390	3.1635260
34	C	-1.0979760	7.1518940	5.0727170
35	C	0.0160030	6.8197640	5.8664550
36	C	-0.0327940	7.0007440	7.2390910
37	H	0.8136810	6.7686040	7.8651400
38	C	-1.1728800	7.5197480	7.8653310
39	C	-2.2955630	7.8294260	7.0803340
40	C	-2.2421050	7.6374020	5.6970420
41	H	-3.0971810	7.8757580	5.0825010
42	C	2.2716070	6.0231120	5.9436900
43	H	3.0043610	5.6784040	5.2187160
44	H	2.0781540	5.2276090	6.6670530
45	H	2.6633800	6.8998640	6.4638830
46	C	-4.5440860	8.6618370	6.9759090
47	H	-4.9566290	7.8007920	6.4457270
48	H	-4.3218230	9.4585770	6.2626270
49	H	-5.2747670	9.0207800	7.6960510
50	C	-1.1753980	7.7779410	9.3118190
51	H	-1.9932990	8.3994290	9.6840980
52	C	-0.3511750	7.6928080	11.4963460
53	H	-0.6937720	6.8179680	12.0575650
54	H	-1.0614070	8.5086700	11.6766810
55	C	1.0285920	8.0682580	12.0421820
56	H	0.9231620	8.2460490	13.1159690
57	H	1.7116660	7.2212010	11.9029200
58	C	2.6413430	9.1988960	10.7997020
59	H	3.1773990	8.2506880	10.7281080
60	C	3.2796260	10.3425710	10.1363720
61	C	2.6965900	11.6147460	10.1733910
62	H	1.7636910	11.7145670	10.7049990
63	C	3.2920280	12.7017770	9.5521610
64	C	4.5145800	12.5409710	8.8738950
65	C	5.0968930	11.2780320	8.8394140
66	H	6.0293740	11.1651180	8.3097550
67	C	4.4977080	10.1780330	9.4537470

68	C	1.5668030	14.1873050	10.3001330
69	H	1.3430330	15.2459740	10.1948900
70	H	1.7070100	13.9523210	11.3575310
71	H	0.7333010	13.6017250	9.9059760
72	C	6.2759920	8.7193360	8.7707470
73	H	6.2035900	8.9546480	7.7070220
74	H	6.5042540	7.6633100	8.8893200
75	H	7.0732410	9.3124760	9.2238650
76	C	5.1880550	13.7142080	8.1825430
77	H	4.9027160	14.6353080	8.6857600
78	H	6.2663560	13.6028260	8.2734940
79	C	4.8207300	13.8221900	6.7134680
80	C	3.6854120	14.5251460	6.3237140
81	H	3.0923630	14.9951040	7.0921190
82	C	3.2980820	14.6071450	4.9860840
83	C	4.0714630	13.9707490	3.9998980
84	C	5.2246590	13.2806890	4.3915930
85	H	5.7986800	12.7997920	3.6159120
86	C	5.6026990	13.2004170	5.7224310
87	C	1.4182790	15.9951760	5.5291800
88	H	0.6088770	16.4621710	4.9740380
89	H	2.0171860	16.7699450	6.0127260
90	H	0.9987270	15.3319890	6.2883530
91	C	7.5694240	11.9439720	5.1787450
92	H	7.0537870	11.1620130	4.6173740
93	H	8.3962340	11.5039720	5.7306030
94	H	7.9573890	12.6933100	4.4853160
95	C	3.6502630	13.9896920	2.5939550
96	H	2.7140340	14.5126470	2.3871970
97	C	3.7562720	13.4575090	0.3176950
98	H	4.4025930	14.1041020	-0.2836640
99	H	2.7501040	13.8955510	0.2912090
100	C	3.7882760	12.0819320	-0.3592070
101	H	3.5412220	12.2114400	-1.4175270
102	H	4.8183620	11.7161920	-0.3383210

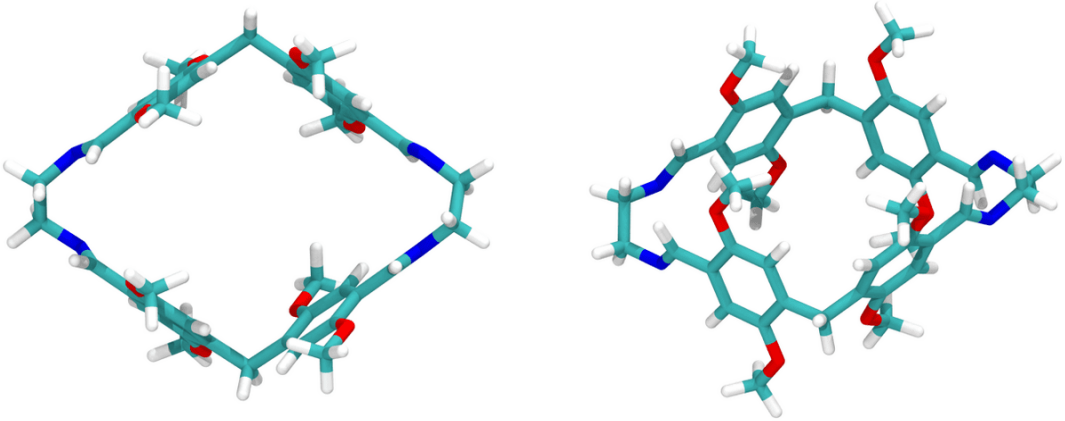


Figure S43: DFT-optimized structure of **PIm** at the 270° minimum: top view (left), side view (right)

Table S14: Cartesian coordinates for **PIm** at the 270° minimum

SCF Done: E(RB3LYP) = -2450.79065836 A.U. after 5 cycles

1	O	-0.5912870	11.8100890	2.1554270
2	N	2.9612750	11.2065740	0.3971860
3	C	1.7460100	11.3265960	0.7505550
4	H	1.1695390	12.2361140	0.5703250
5	O	1.2679600	6.6007440	2.0300020
6	N	-0.2834850	7.4382380	10.1006770
7	C	1.0291980	10.2478370	1.4470520
8	O	1.1251670	6.4801050	5.2124270
9	N	1.6297790	9.2382000	11.5027760
10	C	-0.1504060	10.5168750	2.1608380
11	O	-3.3575560	8.5013410	7.7363700
12	N	4.2486670	13.5540030	1.7272680
13	C	-0.7871920	9.4830570	2.8448780
14	H	-1.6765050	9.6872490	3.4210960
15	O	4.9719860	8.6839420	9.3010430
16	C	-0.3018980	8.1778480	2.8230720
17	O	3.1452610	13.8850580	9.7822140
18	C	0.8580400	7.9039280	2.0759320
19	O	2.2463190	15.1861400	4.8207410
20	C	1.5135690	8.9369020	1.4184620
21	H	2.4192700	8.7587800	0.8612040
22	O	6.8391110	12.3654610	6.0704140
23	C	-1.7802890	12.1271200	2.8711060
24	H	-1.9409080	13.1916670	2.7213860
25	H	-1.6685730	11.9275340	3.9389280
26	H	-2.6405090	11.5765850	2.4830970
27	C	2.4496650	6.2920410	1.3016470
28	H	3.3206410	6.8071500	1.7133290
29	H	2.3475190	6.5431220	0.2430490
30	H	2.5882320	5.2184020	1.4021550
31	C	-1.0399390	7.0824920	3.5799400
32	H	-0.5703010	6.1283750	3.3579650
33	H	-2.0672530	7.0363400	3.2145570
34	C	-1.0776720	7.2893390	5.0810310
35	C	0.0400640	6.9742180	5.8760930
36	C	-0.0065600	7.1718600	7.2469710
37	H	0.8382680	6.9377760	7.8744200
38	C	-1.1433540	7.6990460	7.8702380
39	C	-2.2626100	8.0120350	7.0826270
40	C	-2.2155360	7.7949420	5.7031640
41	H	-3.0782330	8.0134380	5.0921840
42	C	2.2870580	6.1584210	5.9681410
43	H	3.0191190	5.8029590	5.2476500
44	H	2.0854090	5.3689430	6.6961310
45	H	2.6852340	7.0343180	6.4850930
46	C	-4.5074030	8.8547260	6.9756050
47	H	-4.9285390	7.9885570	6.4604080
48	H	-4.2831100	9.6391890	6.2493530

49	H	-5.2327700	9.2297120	7.6930330
50	C	-1.1506740	7.9416970	9.3197620
51	H	-1.9437720	8.5943220	9.6928140
52	C	-0.3556060	7.7740790	11.5125380
53	H	-0.7633070	6.9116520	12.0489580
54	H	-1.0126160	8.6311900	11.7027090
55	C	1.0393410	8.0447080	12.0825210
56	H	0.9353560	8.2015470	13.1594640
57	H	1.6666810	7.1586200	11.9251180
58	C	2.7010050	9.0930570	10.8315860
59	H	3.1598040	8.1102840	10.7079890
60	C	3.3972380	10.2095050	10.1805630
61	C	2.9274590	11.5215760	10.3101520
62	H	2.0418800	11.6715170	10.9068500
63	C	3.5689320	12.5838190	9.6925240
64	C	4.7233550	12.3545360	8.9216740
65	C	5.1960710	11.0519560	8.7979120
66	H	6.0773500	10.8883730	8.1978540
67	C	4.5497280	9.9775490	9.4095070
68	C	2.0246710	14.1684490	10.6140410
69	H	1.8843530	15.2454720	10.5668550
70	H	2.2119430	13.8749580	11.6493550
71	H	1.1216350	13.6710120	10.2535210
72	C	6.1524240	8.4118130	8.5512490
73	H	6.0358980	8.6982910	7.5040980
74	H	6.3001310	7.3368070	8.6140760
75	H	7.0213660	8.9193080	8.9757990
76	C	5.4335480	13.4951570	8.2144090
77	H	5.2376370	14.4229330	8.7471680
78	H	6.5055690	13.3142370	8.2396710
79	C	4.9871120	13.6506490	6.7714870
80	C	3.8319040	14.3653340	6.4704610
81	H	3.2857110	14.8122870	7.2860550
82	C	3.3712790	14.4918300	5.1603170
83	C	4.0884440	13.8897520	4.1118340
84	C	5.2606250	13.1876790	4.4137810
85	H	5.7903680	12.7334790	3.5917480
86	C	5.7095040	13.0589950	5.7193000
87	C	1.4662880	15.7697790	5.8595180
88	H	0.6224300	16.2433760	5.3644900
89	H	2.0318820	16.5272540	6.4065980
90	H	1.0980080	15.0138860	6.5562280
91	C	7.6313350	11.8056910	5.0273940
92	H	7.0779890	11.0507490	4.4647380
93	H	8.4805560	11.3368910	5.5182070
94	H	7.9916870	12.5766900	4.3427970
95	C	3.5896530	13.9672050	2.7341700
96	H	2.5916430	14.3950960	2.6176840
97	C	3.6074200	13.6603160	0.4286950
98	H	4.1863750	14.3561500	-0.1859470
99	H	2.5901360	14.0625960	0.5098720

100	C	3.5983150	12.3170560	-0.3160630
101	H	3.1156140	12.4696170	-1.2865740
102	H	4.6298470	12.0248270	-0.5117880

Optimized host-guest complex structures

G1@PIm

Method: B97D3/SVP/SVPFIT

SCF Done: E(RB97D3) = -2863.07100610 A.U. after 1 cycle

Lowest frequency: 8.8021

Zero-point correction=	0.922934 (Hartree/Particle)
Thermal correction to Energy=	0.985230
Thermal correction to Enthalpy=	0.986168
Thermal correction to Gibbs Free Energy=	0.823111
Sum of electronic and zero-point Energies=	-2862.148072
Sum of electronic and thermal Energies=	-2862.085776
Sum of electronic and thermal Enthalpies=	-2862.084838
Sum of electronic and thermal Free Energies=	-2862.247895

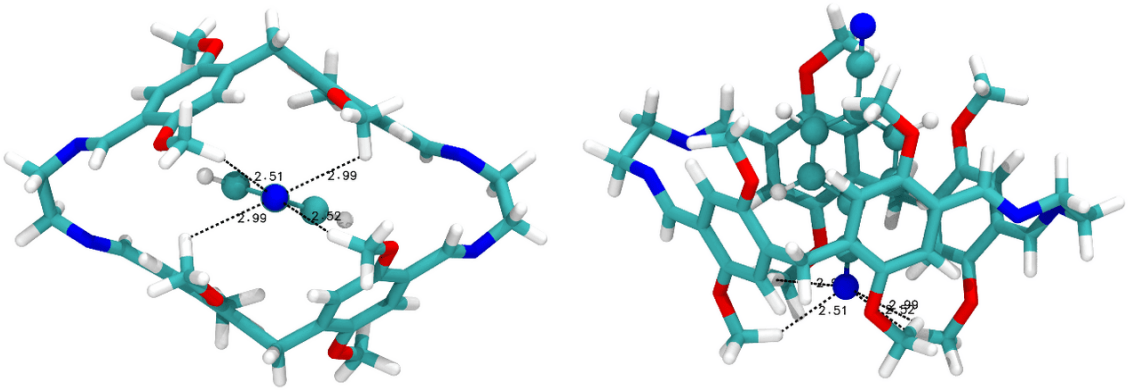


Figure S44: DFT-optimized structure of **G1@PIm**: top view (left), side view (right) with indication of C-H···N interactions with a distance cut-off of 3 Å

Table S15: Cartesian coordinates for **G1@PIm**

1	O	3.9867970	-0.0300950	-2.7838690
2	N	5.8822510	-1.5368960	0.5095970
3	C	5.2986150	-1.0509110	-0.5278140
4	H	5.3008750	-1.5830120	-1.4995500
5	O	3.6334210	2.8861830	1.9342440
6	N	-4.2241190	3.7146410	0.6498950
7	C	4.5673330	0.2214400	-0.4934310
8	O	0.1540960	3.7672300	-2.1335720
9	N	-5.8625720	1.4458730	-0.0267790
10	C	3.8986380	0.7139310	-1.6461200
11	O	-1.1345910	3.0155790	3.2115990
12	N	4.2045340	-3.8705400	0.3882840

13	C	3.1736960	1.9188830	-1.5590560
14	H	2.6344590	2.3048320	-2.4262570
15	O	-3.4785970	0.7010430	-3.2628360
16	C	3.0926120	2.6420110	-0.3617190
17	O	-3.7763780	-3.2249140	0.6597510
18	C	3.7546690	2.1416700	0.7925310
19	O	0.7634650	-3.7917350	2.5622470
20	C	4.4811140	0.9516630	0.7129700
21	H	5.0000630	0.5311380	1.5773960
22	O	0.2740970	-3.1594880	-2.9286920
23	C	3.4837520	0.5084700	-4.0043280
24	H	3.9785140	1.4686510	-4.2497620
25	H	2.3895520	0.6545870	-3.9658820
26	H	3.7244480	-0.2312290	-4.7846180
27	C	4.2275950	2.4034870	3.1304140
28	H	3.8160970	1.4169500	3.4210710
29	H	3.9866720	3.1403030	3.9136150
30	H	5.3280020	2.3204540	3.0366190
31	C	2.2771330	3.9180310	-0.2899400
32	H	2.2842330	4.4051290	-1.2760870
33	H	2.7465750	4.6023090	0.4357250
34	C	0.8381390	3.6793800	0.1351250
35	C	-0.2117670	3.6625120	-0.8220180
36	C	-1.5391520	3.5659790	-0.3866240
37	H	-2.3768880	3.6173540	-1.0854060
38	C	-1.8568690	3.3885890	0.9771270
39	C	-0.7983940	3.2780050	1.9172980
40	C	0.5263770	3.4641900	1.4852940
41	H	1.3528420	3.4433460	2.1965600
42	C	-0.8619490	3.7000060	-3.1253610
43	H	-1.4698500	2.7824560	-3.0248520
44	H	-0.3439830	3.6867780	-4.0976550
45	H	-1.5311410	4.5822110	-3.0811900
46	C	-0.1050190	2.9653800	4.1915920
47	H	0.3750230	3.9553090	4.3220060
48	H	0.6721180	2.2209100	3.9363230
49	H	-0.5902920	2.6671660	5.1339270
50	C	-3.2606430	3.3320960	1.4080640
51	H	-3.4424790	2.9525110	2.4348480
52	C	-5.5822100	3.5763440	1.1236350
53	H	-6.0375260	4.5836720	1.2104330
54	H	-5.6479260	3.0835580	2.1195930
55	C	-6.4127720	2.7766890	0.0956320
56	H	-7.4551220	2.7184970	0.4635690
57	H	-6.4116520	3.3348480	-0.8668360
58	C	-5.1277020	1.1997160	-1.0525760
59	H	-4.9960930	1.9406590	-1.8657860
60	C	-4.3896680	-0.0601170	-1.2047330
61	C	-4.4715850	-1.0494670	-0.1993970
62	H	-5.1215540	-0.8296440	0.6506830
63	C	-3.7412190	-2.2365920	-0.2857960

64	C	-2.9038580	-2.4685420	-1.4109430
65	C	-2.8178110	-1.4882750	-2.4084490
66	H	-2.1452350	-1.6727260	-3.2483920
67	C	-3.5462220	-0.2850140	-2.3256670
68	C	-4.5516760	-3.0224410	1.8322860
69	H	-5.6276160	-2.9055760	1.5970820
70	H	-4.2086330	-2.1353240	2.4000990
71	H	-4.4137900	-3.9231550	2.4519740
72	C	-2.7859050	0.4508500	-4.4835630
73	H	-2.9271010	1.3513700	-5.1024620
74	H	-3.2132140	-0.4234750	-5.0124120
75	H	-1.7061940	0.2909600	-4.3145670
76	C	-2.0866870	-3.7413930	-1.5126320
77	H	-2.6484140	-4.5649800	-1.0424910
78	H	-1.9383120	-3.9883690	-2.5742520
79	C	-0.7311540	-3.6356960	-0.8347800
80	C	-0.6226330	-3.7703210	0.5568500
81	H	-1.5436100	-3.9145020	1.1232260
82	C	0.6219680	-3.7169800	1.2088880
83	C	1.8072360	-3.6045810	0.4348970
84	C	1.6937350	-3.4317800	-0.9614120
85	H	2.6239620	-3.3222550	-1.5229570
86	C	0.4451910	-3.3947710	-1.5942180
87	C	-0.3941370	-3.9902620	3.3642980
88	H	-1.1495770	-3.1987370	3.2031720
89	H	-0.0546240	-3.9514470	4.4109870
90	H	-0.8582210	-4.9760820	3.1636510
91	C	1.4208570	-2.8568030	-3.7124090
92	H	1.9865380	-2.0045710	-3.2941590
93	H	1.0488780	-2.5888900	-4.7142420
94	H	2.0968980	-3.7308990	-3.7961240
95	C	3.1320370	-3.6749110	1.0670780
96	H	3.1533890	-3.5622680	2.1709040
97	C	5.4754570	-3.8728170	1.0757790
98	H	5.9304650	-4.8802130	0.9875280
99	H	5.3850830	-3.6319430	2.1587730
100	C	6.4343600	-2.8682200	0.3997600
101	H	7.4086690	-2.9141070	0.9230440
102	H	6.5879960	-3.1859530	-0.6553730
103	C	-0.2006960	-0.3586400	2.6253130
104	C	1.0539440	-0.5169550	1.9930650
105	C	1.1635220	-0.3339670	0.6165170
106	C	0.0204560	0.0134070	-0.1370210
107	C	-1.2328340	0.1762530	0.4935270
108	C	-1.3436990	-0.0126360	1.8691860
109	H	1.9324400	-0.7948750	2.5813130
110	H	2.1271040	-0.4578320	0.1202740
111	H	-2.1098550	0.4445690	-0.0968250
112	H	-2.3091710	0.1188600	2.3647170
113	C	-0.3145720	-0.5499360	4.0402810
114	N	-0.4077190	-0.7058990	5.1972600

115	C	0.1331110	0.1980160	-1.5523250
116	N	0.2267740	0.3447330	-2.7091770

G3@PIm

Method: B97D3/SVP/SVPFIT

SCF Done: E(RB97D3) = -3047.29127207 A.U. after 2 cycles

Lowest frequency: 18.0695

Zero-point correction =	0.921102 (Hartree/Particle)
Thermal correction to Energy =	0.986211
Thermal correction to Enthalpy =	0.987148
Thermal correction to Gibbs Free Energy =	0.822746
Sum of electronic and zero-point Energies =	-3046.370170
Sum of electronic and thermal Energies =	-3046.305062
Sum of electronic and thermal Enthalpies =	-3046.304124
Sum of electronic and thermal Free Energies =	-3046.468526

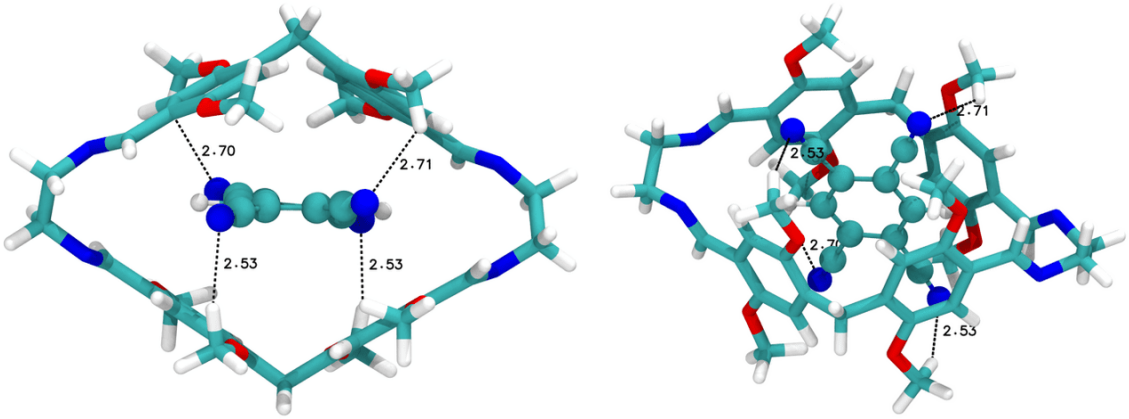


Figure S45: DFT-optimized structure of **G3@PIm**: top view (left), side view (right) with indication of C-H···N interactions with a distance cut-off of 3 Å

Table S16: Cartesian coordinates for **G3@PIm**

1	O	-3.3688130	2.5934990	3.2142280
2	N	-5.8140750	1.3773310	0.1886080
3	C	-4.9885970	1.6691030	1.1286230
4	O	-1.7439730	3.7284670	-1.9694960
5	N	5.6398260	1.4865730	-0.0505980
6	C	-3.7607460	2.4378240	0.8809270
7	O	1.5219640	3.7196080	2.1485610
8	N	5.6561700	-1.4199930	0.1280060
9	C	-2.9349820	2.8614580	1.9568180
10	O	3.1532620	2.6722610	-3.0513060
11	N	-5.7552180	-1.5282050	-0.0297370
12	C	-1.7399580	3.5542020	1.6780420
13	O	3.0410580	-2.3545850	3.1171260
14	C	-1.3586810	3.8629300	0.3656100
15	O	1.6807300	-3.9370890	-2.0319770

16	C	-2.1766330	3.4226550	-0.7107110
17	O	-3.1310700	-2.3927860	-3.0328190
18	C	-3.3642300	2.7337270	-0.4407890
19	O	-1.7318430	-3.9951210	2.0996390
20	C	-2.4970720	2.8217840	4.3150340
21	C	-2.6258740	3.5163370	-3.0667040
22	C	-0.1176170	4.6909400	0.0971580
23	C	1.1323700	3.8804350	-0.1838170
24	C	1.9575820	3.4367270	0.8854210
25	C	3.1554700	2.7699390	0.6050590
26	C	3.5542820	2.4977470	-0.7210120
27	C	2.7188210	2.9199810	-1.7898850
28	C	1.5149280	3.5926120	-1.5006380
29	C	2.4057070	3.4997560	3.2425700
30	C	2.2757180	2.9015800	-4.1471410
31	C	4.7989940	1.7612790	-0.9821040
32	C	6.7955300	0.6853670	-0.3855400
33	C	6.8032710	-0.6049530	0.4573460
34	C	4.7909350	-1.6512020	1.0490940
35	C	3.5607780	-2.4155260	0.8002370
36	C	3.2234270	-2.8070310	-0.5135520
37	C	2.0618640	-3.5395060	-0.7809640
38	C	1.2137950	-3.9273860	0.2915510
39	C	1.5342910	-3.5213020	1.5951970
40	C	2.6911790	-2.7668640	1.8684550
41	C	2.6004750	-3.7872830	-3.1096310
42	C	2.2880670	-2.8138280	4.2337220
43	C	-0.0172720	-4.7730140	0.0288230
44	C	-1.2660820	-3.9506530	-0.2238070
45	C	-1.5965090	-3.5384930	-1.5229930
46	C	-2.7700920	-2.8071330	-1.7882100
47	C	-3.6452930	-2.4836000	-0.7157960
48	C	-3.2982980	-2.8810680	0.5937110
49	C	-2.1215470	-3.5919500	0.8530790
50	C	-2.3611040	-2.8137130	-4.1529250
51	C	-2.6549410	-3.8791260	3.1786140
52	C	-4.8903220	-1.7405900	-0.9557320
53	C	-6.9209750	-0.7367600	-0.3516530
54	C	-6.9498070	0.5419590	0.5080060
55	H	-5.1505640	1.3373540	2.1732690
56	H	-1.0941790	3.8931180	2.4901980
57	H	-4.0225340	2.3885830	-1.2415650
58	H	-3.0166480	2.4281260	5.2026860
59	H	-2.2994390	3.9019360	4.4586460
60	H	-1.5357980	2.2874900	4.1935890
61	H	-2.0897500	3.8678830	-3.9626830
62	H	-3.5616170	4.0962630	-2.9453400
63	H	-2.8745570	2.4477490	-3.1984720
64	H	-0.3127360	5.3425120	-0.7695770
65	H	0.0705770	5.3312680	0.9737180
66	H	3.8214120	2.4270720	1.4005180

67	H	0.8632720	3.9329150	-2.3075100
68	H	1.8646190	3.8287510	4.1441110
69	H	3.3341910	4.0934380	3.1323450
70	H	2.6679740	2.4322670	3.3559890
71	H	2.7972670	2.5233730	-5.0403540
72	H	2.0650590	3.9808000	-4.2790220
73	H	1.3211200	2.3548940	-4.0285400
74	H	4.9622030	1.4411070	-2.0302060
75	H	7.7131890	1.2543540	-0.1345600
76	H	6.8390600	0.4190550	-1.4650530
77	H	6.8447460	-0.3337530	1.5362070
78	H	7.7268940	-1.1642290	0.2075690
79	H	4.9328610	-1.2822910	2.0853850
80	H	3.9089210	-2.5062220	-1.3085680
81	H	0.8573110	-3.8137920	2.4001710
82	H	2.1190110	-4.2480060	-3.9875120
83	H	3.5536510	-4.3108450	-2.8995050
84	H	2.8085420	-2.7240270	-3.3276170
85	H	2.7486330	-2.3550670	5.1225610
86	H	2.3363690	-3.9170860	4.3207810
87	H	1.2302870	-2.4978580	4.1790280
88	H	0.1713040	-5.4093000	-0.8499200
89	H	-0.1920560	-5.4242390	0.8994420
90	H	-0.9143230	-3.8084290	-2.3314310
91	H	-3.9891780	-2.6027440	1.3922850
92	H	-2.8321060	-2.3561590	-5.0368940
93	H	-2.3762920	-3.9165320	-4.2559400
94	H	-1.3132970	-2.4674020	-4.0894250
95	H	-2.1639420	-4.3408150	4.0506700
96	H	-3.5965980	-4.4201960	2.9611020
97	H	-2.8862870	-2.8236540	3.4105480
98	H	-5.0433910	-1.3699130	-1.9898180
99	H	-7.8309290	-1.3226120	-0.1124670
100	H	-6.9662160	-0.4529480	-1.4271100
101	H	-6.9912930	0.2608760	1.5838760
102	H	-7.8809260	1.0901640	0.2601920
103	C	1.2893410	0.0553000	0.3698210
104	C	0.8542630	0.0270250	-0.9655690
105	C	-0.5428820	0.0764870	-1.2561280
106	C	-1.4852630	0.0421990	-0.2165060
107	C	-1.0497280	0.0026080	1.1183870
108	C	0.3466080	0.0651160	1.4099570
109	C	0.7804010	0.1594850	2.7694320
110	N	1.1129370	0.2803910	3.8842890
111	C	-1.9911950	-0.1425380	2.1840040
112	N	-2.7290990	-0.3171390	3.0748140
113	C	-0.9785310	0.1831480	-2.6140700
114	N	-1.3129150	0.3148470	-3.7271240
115	C	1.7960660	-0.0918760	-2.0342220
116	N	2.5330350	-0.2433430	-2.9299900
117	H	2.3552440	0.0522280	0.5949320

118	H	-2.5509680	0.0295120	-0.4415520

G4@PIm

Method: B97D3/SVP/SVPFIT

SCF Done: E(RB97D3) = -2938.20447866 A.U. after 2 cycles

Lowest frequency: 15.5792

Zero-point correction=	0.927893 (Hartree/Particle)
Thermal correction to Energy=	0.990874
Thermal correction to Enthalpy=	0.991811
Thermal correction to Gibbs Free Energy =	0.830011
Sum of electronic and zero-point Energies =	-2937.276586
Sum of electronic and thermal Energies =	-2937.213605
Sum of electronic and thermal Enthalpies =	-2937.212668
Sum of electronic and thermal Free Energies =	-2937.374468

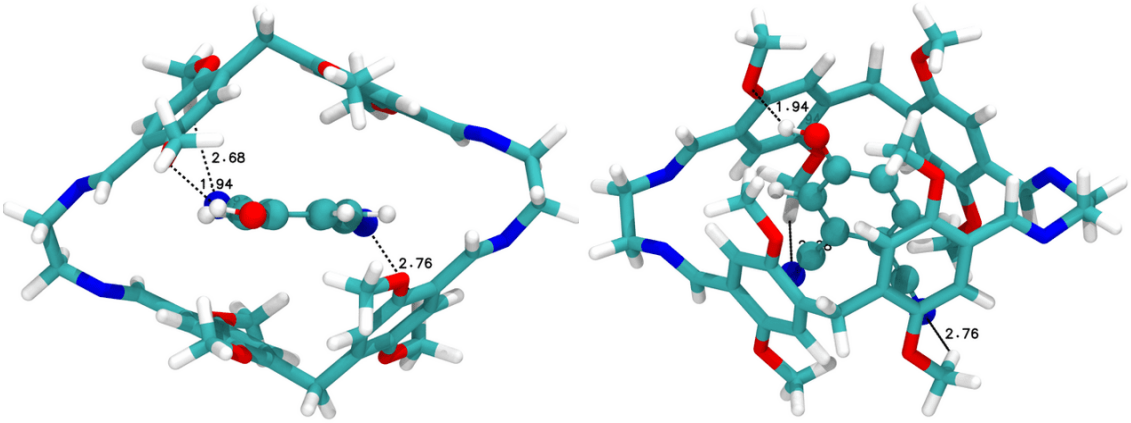


Figure S46: DFT-optimized structure of **G4@PIm**: top view (left), side view (right) with indication of C-H···N interactions and hydrogen bonds with a distance cut-off of 3 Å

Table S17: Cartesian coordinates for **G4@PIm**

1	O	-3.0533080	1.8775680	3.0066060
2	N	-5.7818670	1.4675300	-0.0304480
3	C	-4.9340400	1.6059160	0.9232070
4	O	-1.8703580	4.3170710	-1.8381160
5	N	5.5012370	1.3798470	-0.1332980
6	C	-3.7154140	2.4154560	0.7726650
7	O	1.5996920	3.8095460	2.2647680
8	N	5.6932670	-1.5494350	0.0739000
9	C	-2.8115490	2.5905550	1.8471680
10	O	2.7811530	2.4324150	-2.9834940
11	N	-5.6099930	-1.4393570	-0.3042440
12	C	-1.6717490	3.3923260	1.6837740
13	O	3.0334280	-2.1931970	3.1074880
14	C	-1.3732840	3.9898330	0.4522980
15	O	1.7849890	-4.3182880	-1.8699060
16	C	-2.2415510	3.7594560	-0.6507370
17	O	-2.9580930	-2.6666680	-3.1417750

18	C	-3.4040380	3.0019790	-0.4740830
19	O	-1.6751200	-3.7347460	2.1532630
20	C	-2.5370310	2.3969130	4.2387960
21	C	-2.7032670	4.1220610	-2.9775170
22	C	-0.1119170	4.8133470	0.2841280
23	C	1.0946850	3.9535770	-0.0471280
24	C	1.9528710	3.4833800	0.9827290
25	C	3.0923600	2.7443520	0.6502520
26	C	3.3856870	2.4059140	-0.6885310
27	C	2.4874970	2.8123950	-1.7118630
28	C	1.3657430	3.5940070	-1.3745360
29	C	2.4036260	3.3313790	3.3326200
30	C	1.8836920	2.7689520	-4.0341880
31	C	4.5990900	1.6430220	-1.0104510
32	C	6.6563790	0.6126340	-0.5432040
33	C	6.7998400	-0.6548760	0.3221340
34	C	4.8548640	-1.7586260	1.0249990
35	C	3.6469750	-2.5730870	0.8424560
36	C	3.3363090	-3.1013980	-0.4304690
37	C	2.1564010	-3.8169420	-0.6548660
38	C	1.2680680	-4.0626060	0.4269320
39	C	1.5691890	-3.5327760	1.6885250
40	C	2.7353540	-2.7778730	1.9105340
41	C	2.6424620	-4.1122040	-2.9861500
42	C	2.1126800	-2.3204840	4.1843240
43	C	-0.0047870	-4.8564630	0.2088860
44	C	-1.1949920	-3.9870470	-0.1537140
45	C	-1.4849940	-3.6937550	-1.4930640
46	C	-2.6208890	-2.9420040	-1.8551230
47	C	-3.4960760	-2.4714550	-0.8401490
48	C	-3.1805490	-2.7371850	0.5101070
49	C	-2.0389260	-3.4630810	0.8628510
50	C	-2.0117720	-2.9104810	-4.1751080
51	C	-2.4769100	-3.2251870	3.2081630
52	C	-4.7096150	-1.7160620	-1.1790450
53	C	-6.7579620	-0.6635490	-0.7168470
54	C	-6.9063700	0.5848890	0.1755870
55	H	-5.0791740	1.1193180	1.9091970
56	H	-0.9682630	3.5335530	2.5070060
57	H	-4.1031280	2.8193140	-1.2927860
58	H	-3.0001060	1.7984330	5.0394630
59	H	-2.8144350	3.4599680	4.3601450
60	H	-1.4382390	2.2906000	4.2980640
61	H	-2.2084300	4.6481460	-3.8096050
62	H	-3.7102860	4.5553420	-2.8212160
63	H	-2.8006550	3.0494900	-3.2292840
64	H	-0.2629680	5.5439280	-0.5254930
65	H	0.0833820	5.3646620	1.2167410
66	H	3.7951920	2.3949560	1.4101920
67	H	0.6737380	3.9375930	-2.1458530
68	H	1.9283900	3.6883880	4.2607830

69	H	3.4365780	3.7276750	3.2795120
70	H	2.4435510	2.2242670	3.3482110
71	H	2.2803250	2.2870130	-4.9411290
72	H	1.8384500	3.8649030	-4.1900750
73	H	0.8640160	2.3856300	-3.8421840
74	H	4.6992230	1.3134600	-2.0644040
75	H	7.5649210	1.2282620	-0.3843030
76	H	6.6239900	0.3212230	-1.6168650
77	H	6.8827720	-0.3539480	1.3908570
78	H	7.7440050	-1.1563030	0.0309790
79	H	4.9964620	-1.3159440	2.0318730
80	H	4.0465800	-2.8961310	-1.2345400
81	H	0.8525860	-3.7019610	2.4939020
82	H	2.1517570	-4.6015600	-3.8429430
83	H	3.6367740	-4.5731050	-2.8252110
84	H	2.7685020	-3.0364130	-3.2109300
85	H	2.5449170	-1.7532300	5.0243200
86	H	1.9857300	-3.3773940	4.4900020
87	H	1.1231580	-1.8943020	3.9288110
88	H	0.1606300	-5.5841150	-0.6006820
89	H	-0.2389360	-5.4125300	1.1302820
90	H	-0.8082190	-4.0804590	-2.2577690
91	H	-3.8713280	-2.3486330	1.2619940
92	H	-2.4480080	-2.4888350	-5.0944130
93	H	-1.8375560	-3.9946800	-4.3208680
94	H	-1.0461560	-2.4101070	-3.9722060
95	H	-1.9955300	-3.5491770	4.1451480
96	H	-3.5080620	-3.6279550	3.1718710
97	H	-2.5172950	-2.1195140	3.1879800
98	H	-4.8051950	-1.3994620	-2.2365620
99	H	-7.6709690	-1.2782440	-0.5812630
100	H	-6.7107410	-0.3508870	-1.7835900
101	H	-7.0122660	0.2582810	1.2345110
102	H	-7.8368790	1.1070260	-0.1213410
103	C	0.9364970	-0.1614610	1.1667520
104	C	1.4436900	-0.2763000	-0.1250910
105	C	0.5890010	-0.2131540	-1.2432940
106	C	-0.8056090	0.0047870	-1.0312400
107	C	-1.3166750	0.0874430	0.2719090
108	C	-0.4471220	0.0070740	1.3763760
109	C	-1.6811180	0.1964330	-2.1461510
110	N	-2.3801920	0.4044030	-3.0617450
111	C	1.1041470	-0.4116670	-2.5579480
112	N	1.5183250	-0.6176380	-3.6348190
113	O	-0.8904940	0.0878280	2.6500900
114	H	-1.8173000	0.4160470	2.6743930
115	H	1.6095400	-0.1963460	2.0267030
116	H	2.5134730	-0.4168160	-0.2807150
117	H	-2.3880870	0.2283400	0.4173410

G5@PIm

Method: B97D3/SVP/SVPFIT

SCF Done: E(RB97D3) = -3070.83871581 A.U. after 2 cycles

Lowest frequency: 9.2017

Zero-point correction =	0.977313 (Hartree/Particle)
Thermal correction to Energy =	1.043799
Thermal correction to Enthalpy =	1.044737
Thermal correction to Gibbs Free Energy =	0.875250
Sum of electronic and zero-point Energies =	-3069.861402
Sum of electronic and thermal Energies =	-3069.794916
Sum of electronic and thermal Enthalpies =	-3069.793979
Sum of electronic and thermal Free Energies =	-3069.963466

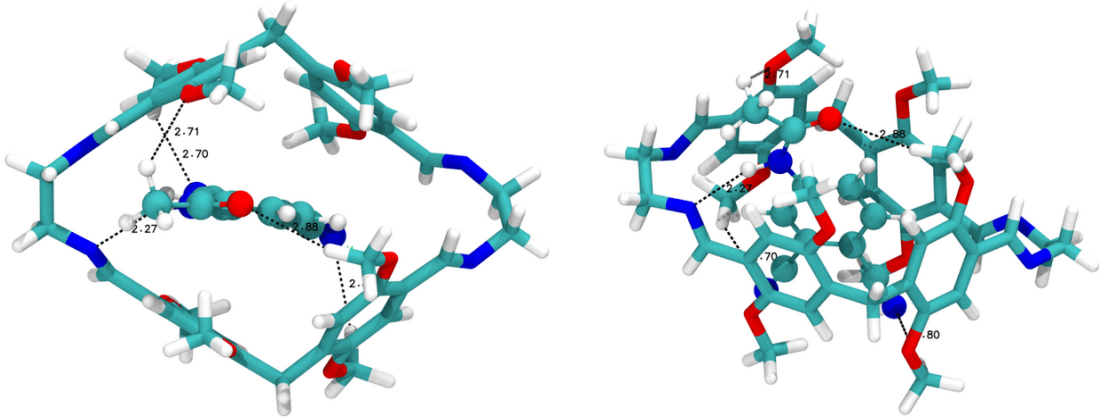


Figure S47: DFT-optimized structure of **G5@PIm**: top view (left), side view (right) with indication of C-H···N interactions and hydrogen bonds with a distance cut-off of 3 Å

Table S18: Cartesian coordinates for **G5@PIm**

1	O	-2.7115990	2.2836350	2.7307120
2	N	-5.2833840	1.2918220	-0.2083110
3	C	-4.5868940	1.8282460	0.7341790
4	O	-1.7086620	4.5311610	-2.2472860
5	N	5.7277120	1.5998420	-0.0947530
6	C	-3.3995100	2.6498590	0.4896790
7	O	1.8999100	4.4243840	1.8705390
8	N	5.6734390	-1.3081800	0.2842140
9	C	-2.4689690	2.8894640	1.5379160
10	O	2.9022690	2.0168410	-3.0332440
11	N	-5.4503260	-1.6207640	-0.1756710
12	C	-1.3439160	3.6949880	1.2900060
13	O	3.1714830	-2.6640880	3.1849180
14	C	-1.1046380	4.2459010	0.0235370
15	O	1.7479770	-3.6620650	-2.0892290
16	C	-2.0149880	3.9797230	-1.0339910
17	O	-2.9083000	-2.6258530	-3.1807660
18	C	-3.1526340	3.2047250	-0.7862730
19	O	-1.5965430	-4.3888090	1.9229330

20	C	-1.8508610	2.5535300	3.8338260
21	C	-2.5826050	4.3091730	-3.3442730
22	C	0.1486230	5.0610760	-0.2236130
23	C	1.3513610	4.1576370	-0.4211180
24	C	2.2230440	3.8706550	0.6624720
25	C	3.3447280	3.0643280	0.4489960
26	C	3.6022950	2.4779630	-0.8090180
27	C	2.6756390	2.6846770	-1.8665260
28	C	1.5794930	3.5437850	-1.6616580
29	C	2.7340220	4.1477930	2.9901120
30	C	2.0252340	2.2301010	-4.1338710
31	C	4.8162250	1.6705840	-0.9971560
32	C	6.8628840	0.7375510	-0.3225560
33	C	6.7994500	-0.4729150	0.6302510
34	C	4.7883740	-1.5650530	1.1788540
35	C	3.5957810	-2.3684900	0.8717910
36	C	3.2416610	-2.6114320	-0.4722890
37	C	2.1398480	-3.4054040	-0.8034640
38	C	1.3775730	-4.0169830	0.2276440
39	C	1.7011730	-3.7430740	1.5643580
40	C	2.7968460	-2.9247240	1.9051150
41	C	2.3719590	-2.9447820	-3.1442240
42	C	2.2845810	-2.9927960	4.2460430
43	C	0.2335810	-4.9531690	-0.1170110
44	C	-1.0684180	-4.2240280	-0.3800330
45	C	-1.3861320	-3.7852710	-1.6722240
46	C	-2.5814360	-3.0974990	-1.9439890
47	C	-3.4959930	-2.8511200	-0.8867270
48	C	-3.1736910	-3.2922550	0.4160830
49	C	-1.9731380	-3.9575090	0.6831850
50	C	-1.9642670	-2.7553790	-4.2382580
51	C	-2.5228280	-4.2785730	2.9964820
52	C	-4.7145100	-2.0753960	-1.1271440
53	C	-6.5794890	-0.7906640	-0.5338750
54	C	-6.4837880	0.5680550	0.1747700
55	H	-4.8588390	1.6804680	1.7986140
56	H	-0.6095450	3.8869420	2.0748500
57	H	-3.8886260	3.0092250	-1.5679950
58	H	-2.2349090	1.9549230	4.6736230
59	H	-1.8699440	3.6272420	4.1037280
60	H	-0.8086680	2.2489600	3.6246900
61	H	-2.1583780	4.8682280	-4.1937920
62	H	-3.6042080	4.6850100	-3.1388590
63	H	-2.6325880	3.2372590	-3.6095350
64	H	0.0095490	5.6845610	-1.1193940
65	H	0.3292340	5.7223360	0.6375310
66	H	4.0612830	2.8489770	1.2444420
67	H	0.8651530	3.7375170	-2.4650920
68	H	2.2782730	4.6695550	3.8471940
69	H	3.7614830	4.5320300	2.8369700
70	H	2.7798030	3.0630700	3.2048880

71	H	2.4047130	1.5980650	-4.9528620
72	H	2.0334220	3.2884910	-4.4601450
73	H	0.9860160	1.9299220	-3.9002720
74	H	4.9090300	1.1380740	-1.9656070
75	H	7.7927220	1.2977260	-0.1015320
76	H	6.9223080	0.3631750	-1.3693450
77	H	6.7719140	-0.1133090	1.6830730
78	H	7.7321680	-1.0563970	0.4914080
79	H	4.8810100	-1.2019230	2.2220390
80	H	3.8746560	-2.1568290	-1.2377790
81	H	1.0847990	-4.1971400	2.3432120
82	H	1.8542170	-3.2434810	-4.0702300
83	H	3.4465110	-3.1978100	-3.2367130
84	H	2.2707570	-1.8497540	-3.0061820
85	H	2.7300750	-2.5688030	5.1600220
86	H	2.1832240	-4.0892850	4.3688670
87	H	1.2822930	-2.5492880	4.0944510
88	H	0.5044780	-5.5300900	-1.0160360
89	H	0.0897270	-5.6591520	0.7155100
90	H	-0.6633640	-3.9805630	-2.4648620
91	H	-3.8944040	-3.0705750	1.2065060
92	H	-2.4095660	-2.2532830	-5.1111150
93	H	-1.7773290	-3.8182900	-4.4865350
94	H	-1.0078720	-2.2603160	-3.9877720
95	H	-2.0248280	-4.7148410	3.8772200
96	H	-3.4529430	-4.8422910	2.7850860
97	H	-2.7761850	-3.2255320	3.2174020
98	H	-4.9530540	-1.8653270	-2.1882210
99	H	-7.5137910	-1.2789130	-0.1906830
100	H	-6.6662360	-0.6357970	-1.6332510
101	H	-6.5456900	0.4172230	1.2746910
102	H	-7.3653240	1.1691870	-0.1284910
103	C	-1.5366390	0.1162110	-0.7931300
104	C	-1.8524010	-0.2344100	0.5391960
105	C	-0.8533370	-0.2856710	1.5177920
106	C	0.4983170	0.0316290	1.1824340
107	C	0.8094410	0.3050740	-0.1628370
108	C	-0.1838740	0.3378020	-1.1421760
109	C	1.4933380	0.1493820	2.1986020
110	N	2.2881270	0.3164560	3.0432650
111	C	-1.1927440	-0.6581740	2.8563150
112	N	-1.4559190	-0.9838600	3.9496740
113	N	-2.6009910	0.2572210	-1.6786230
114	C	-2.5751920	0.4830010	-3.0421620
115	C	-3.9530360	0.5909100	-3.6664770
116	O	-1.5407070	0.5638510	-3.7014260
117	H	-3.5286350	0.2886120	-1.2437710
118	H	-2.8857760	-0.4563160	0.8118170
119	H	1.8434840	0.5301030	-0.4312600
120	H	0.0726500	0.5716780	-2.1740390
121	H	-3.8951570	1.2251950	-4.5644960

122	H	-4.7076560	0.9823360	-2.9647700
123	H	-4.2694680	-0.4194380	-3.9817100

NCI analysis of the structures

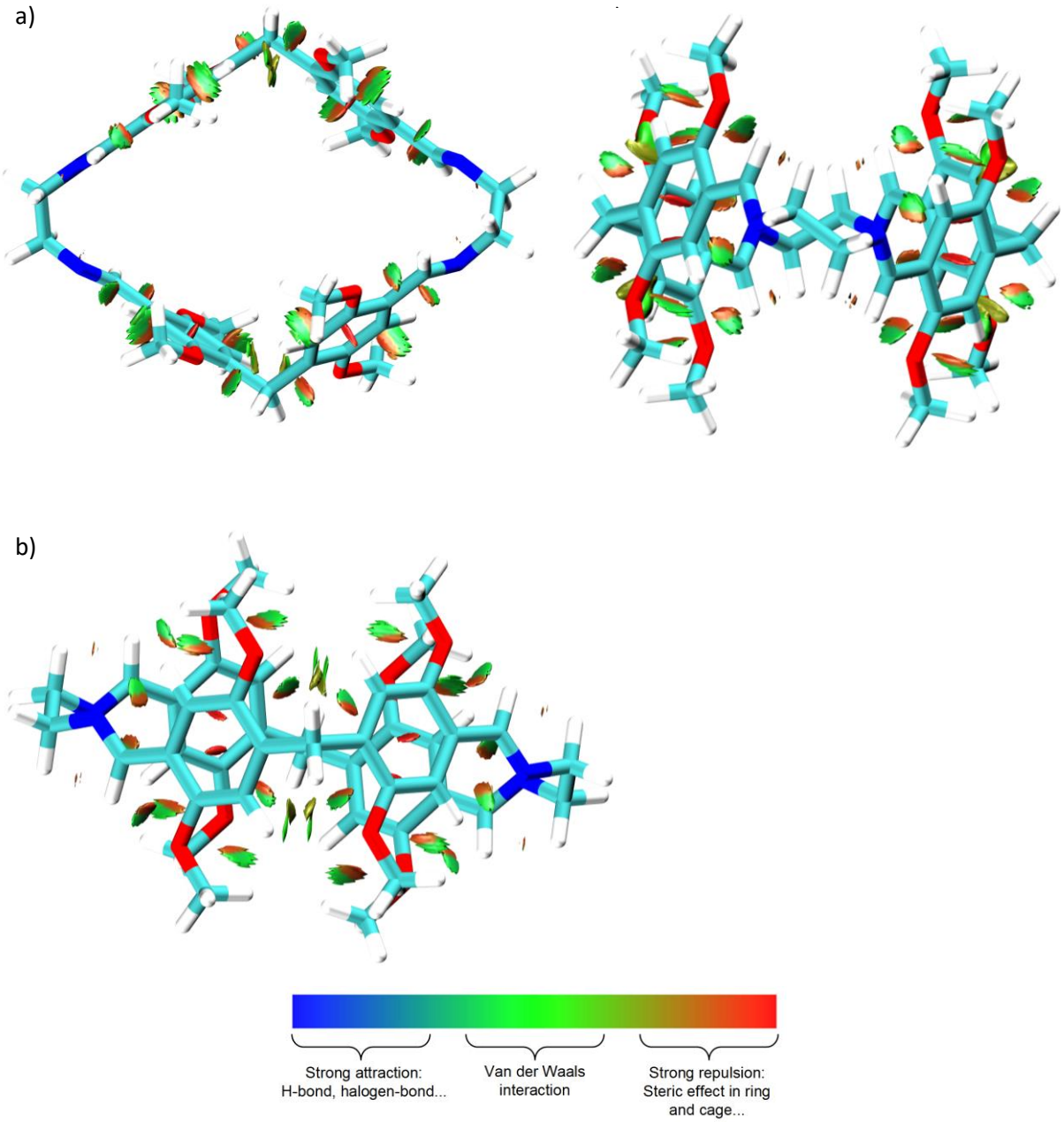


Figure S48: Colored RDG-based NCI isosurfaces of **PIm**: a) top view, b) side view through the methylene bridges, c) side view through the ethylenediamine units

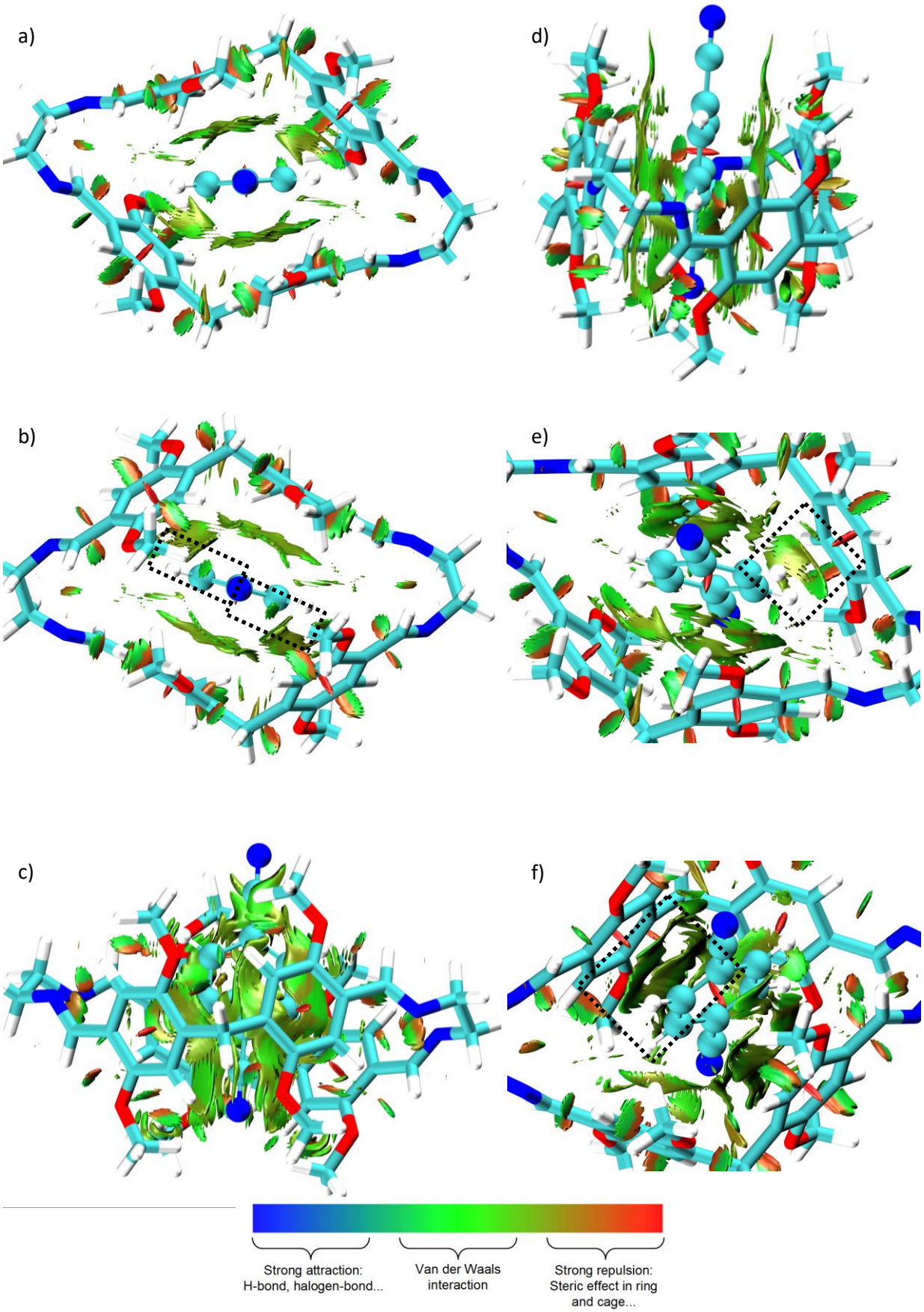


Figure S49: Colored RDG-based NCI isosurfaces of **G1@PIm**: a) top view, b) bottom view with indication of C-H···N interactions, c) side view through the methylene bridges, d) side view through the ethylenediamine units, e) zoom with indication of C-H···π interactions, f) zoom with indication of π···π interactions

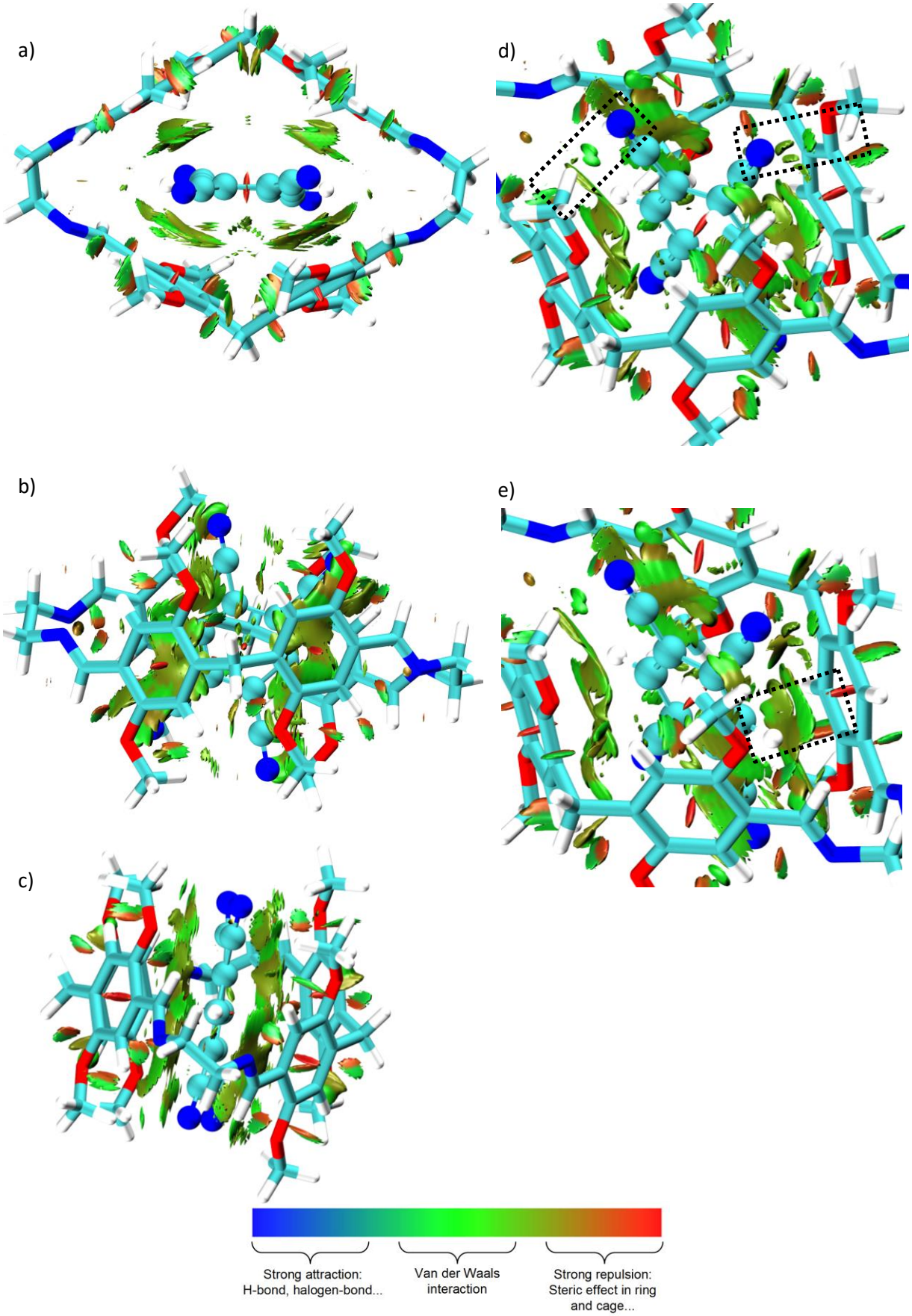


Figure S50: Colored RDG-based NCI isosurfaces of **G3@PIm**: a) top view, b) side view through the methylene bridges, c) side view through the ethylenediamine units, d) zoom with indication of C-H···π interactions, e) zoom with indication of π···π interactions

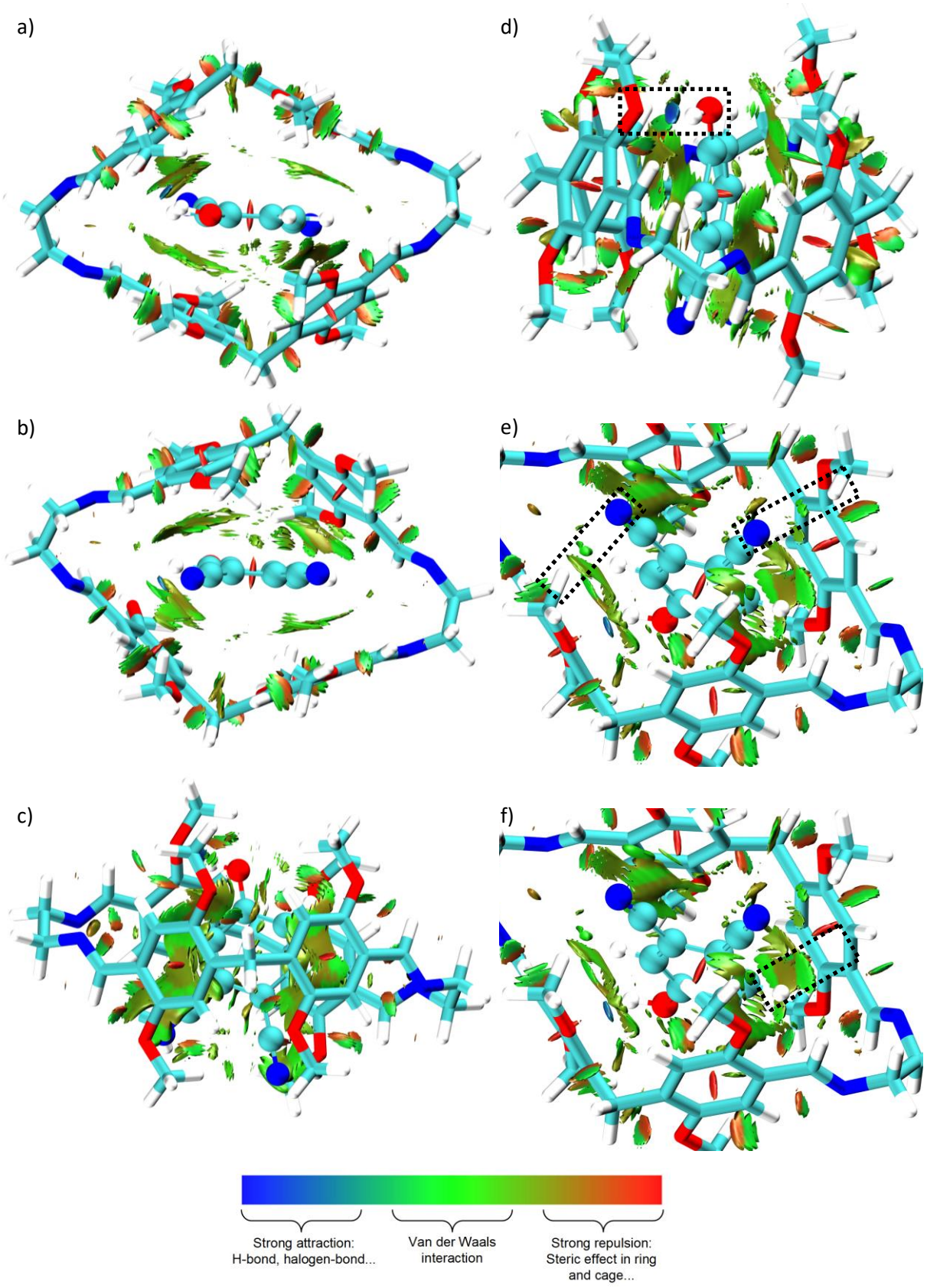


Figure S51: Colored RDG-based NCI isosurfaces for **G4@PIm**: a) top view, b) bottom view, c) side view through the methylene bridges, d) side view through the ethylenediamine units with indication of the O-H···O hydrogen bond, e) zoom with indication of C-H···N interactions, f) zoom with indication of C-H··· π interactions

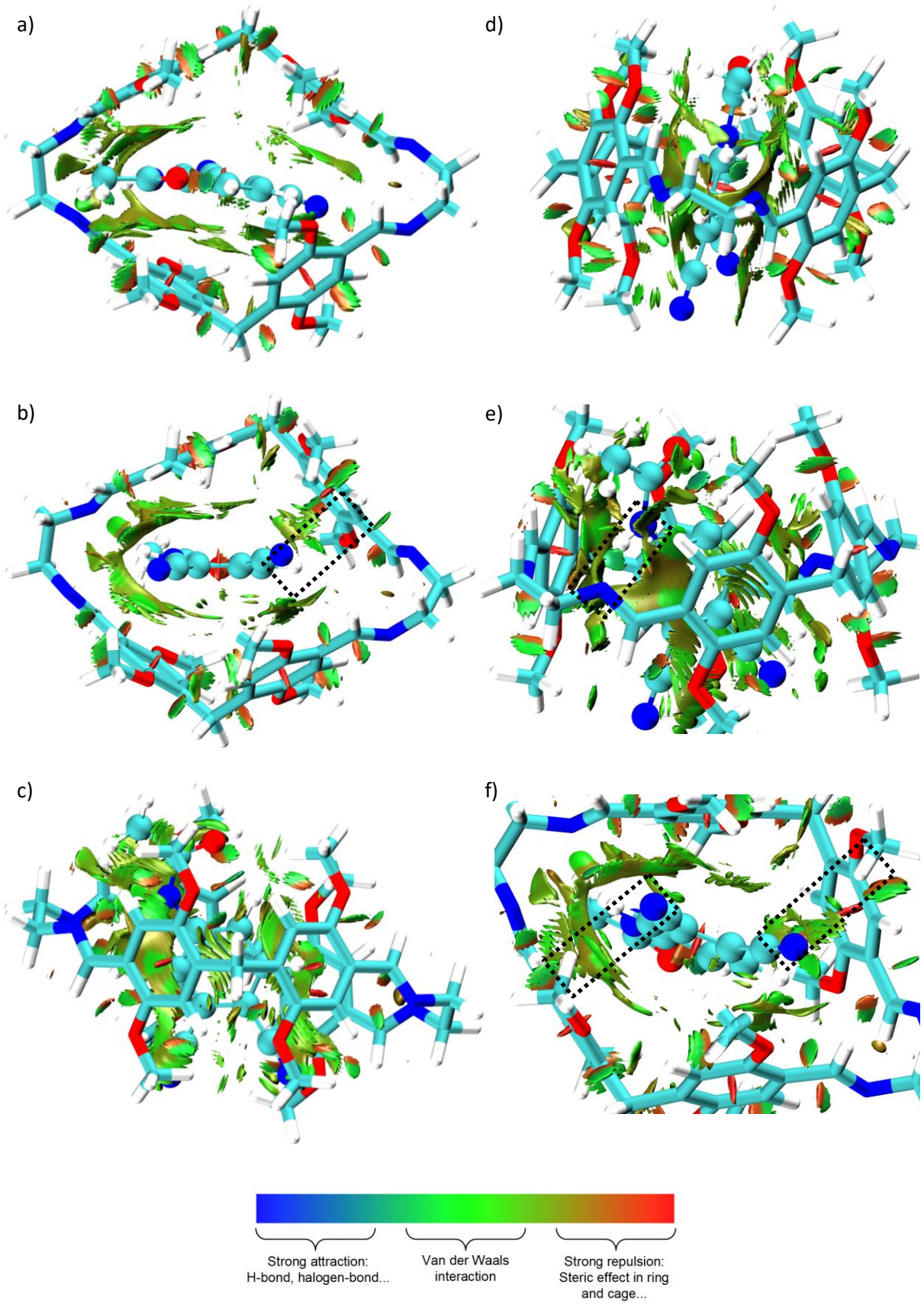


Figure S52: Colored RDG-based NCI isosurfaces for **G4@PIm**: a) top view, b) bottom view with indication of C-H···N interactions, c) side view through the methylene bridges, d) side view through the ethylenediamine units, e) zoom with indication of the N-H···N hydrogen bond, e) zoom with indication of, f) zoom with indication of C-H··· π interactions

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