Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2020

Supplementary Information

Pillar[5]arene-Based Self-Assembled Linear Supramolecular Polymer Driven by Guest Halogen-Halogen Interactions in Solid and Solution States

Talal F. Al-Azemi* and Mickey Vinodh

Chemistry Department, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait

Table of contents

* Corresponding author.
E-mail address: t.alazemi@ku.edu.kw.

Single crystal X-ray diffraction data

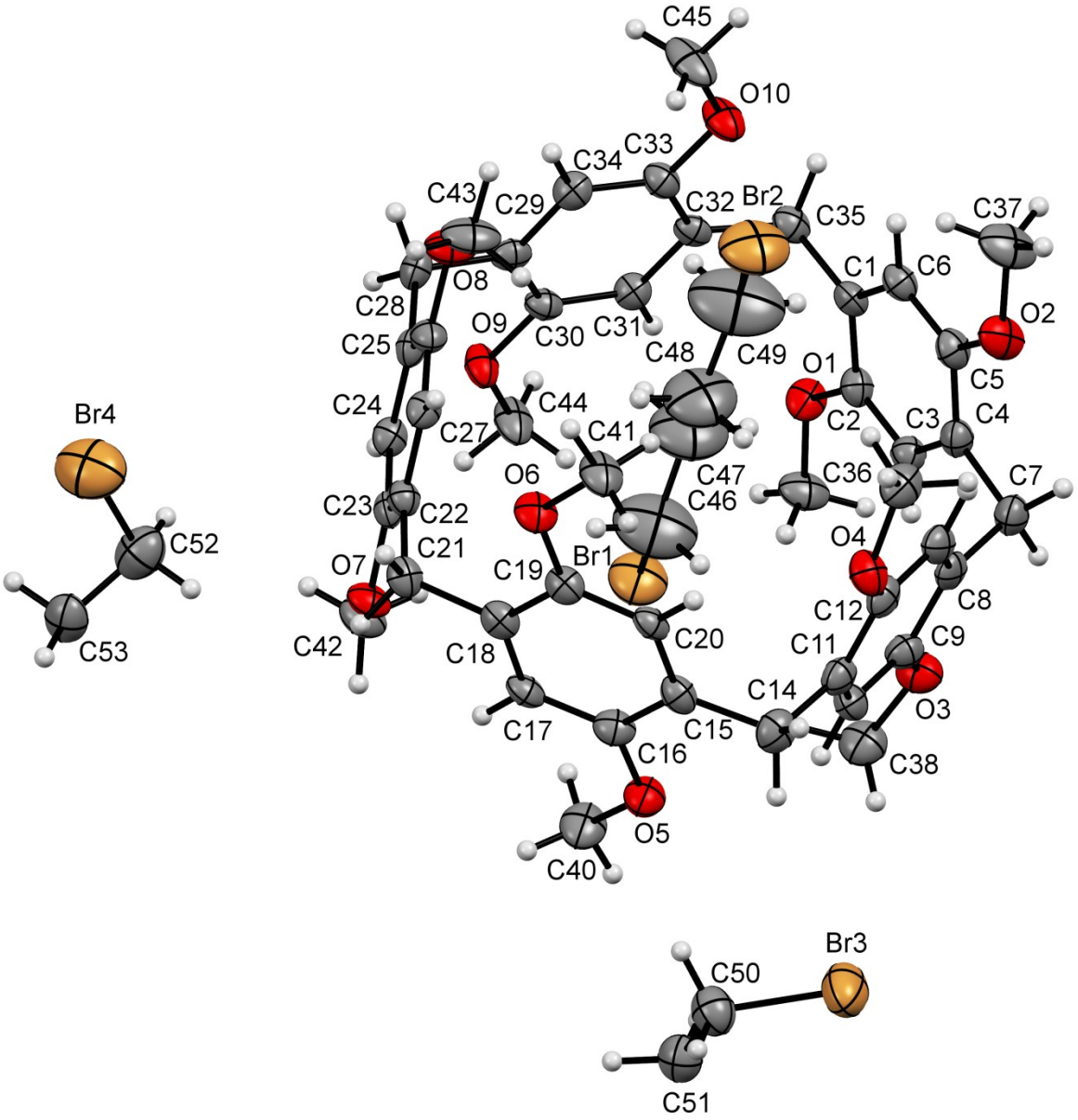

Figure S1. Thermal ellipsoid representation (50% probability) of inclusion complex [**DPM5⊃BuBr2**] asymmetric unit. Color code: gray-carbon; red-oxygen, brown-bromine and light gray-hydrogen.

Table S1. Summary on the nature and various crystallographic parameters [**DPM5⊃BuBr2**] crystals.

Chemical formula	$C_{53}H_{66}Br_4O_{10}$
M_r	1182.69
Crystal system, space group	Triclinic, *P*
Temperature (K)	150
a, *b*, *c* (Å)	10.3567 (8), 12.1184 (9), 22.4299 (15)
β (°)	91.283 (6), 95.977 (7), 110.754 (8)
V (Å^3)	2612.8 (3)
Z	2
μ (mm^{-1})	3.14
Crystal size (mm)	0.25 × 0.05 × 0.04
Absorption correction	Rigaku R-AXIS RAPID
	Multi-scan *ABSCOR* (Rigaku, 1995)
T_{min}, T_{max}	0.388, 0.882
No. of measured, independent & observed [$I > 2\sigma(I)$] reflections	18256, 9072, 4246
R_{int}	0.087
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.179, 0.91
No. of reflections	9072
No. of parameters	614
No. of restraints	577
H-atom treatment	Constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.16, −1.10

Table S2. Summary of weak interactions (C—H···π and C—H···O; Å, °) between **DMP5** and **BuBr2** molecule.

D—H···*A* (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C46—H46A···Cg1	2.92	3.458(10)	115
C46—H46B···Cg2	3.01	3.902(11)	151
C47—H47A···Cg3	2.80	3.703(10)	151
C47—H47B···Cg4	2.82	3.780(11)	164
C48—H48A··· O6	3.34	4.139(11)	139
C48—H48B ··· O4	3.23	4.215(11)	174
C49—H49A ···O10	2.83	3.562(12)	132
C49—H49B ··· O2	3.06	3.994(14)	158

Cg1, Cg2, Cg3 and Cg4 are the centroids of the C15–C20, C8–C13, C29–C34 and C1–C6 rings, respectively.

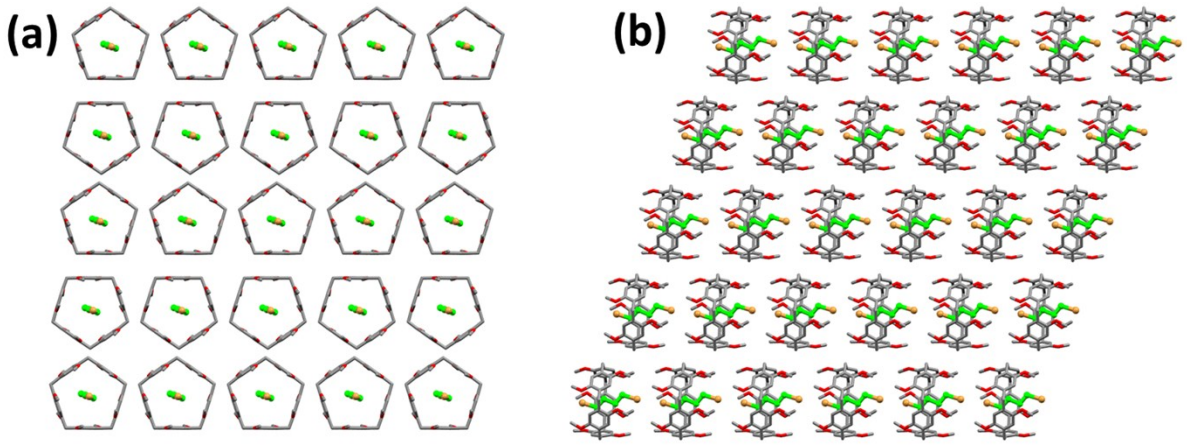

Figure 2S. Three-dimensional packing of [**DPM5⊃BuBr2**] crystals viewing along crystallographic (a) *a*-axis and (b) *c*-axis.

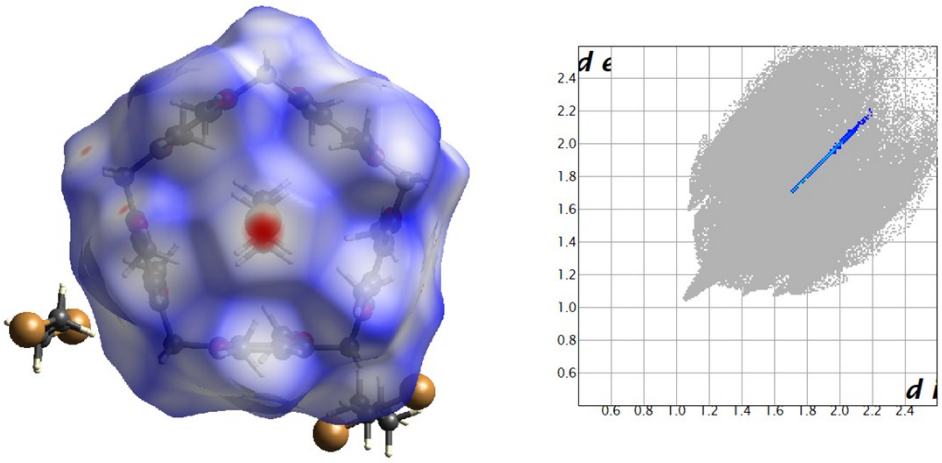

Figure S3. The Hirshfeld surface of [**DPM5⊃BuBr2**] crystal mapped with dnorm and 2D fingerprint plot for Br···Br interactions in the crystal.

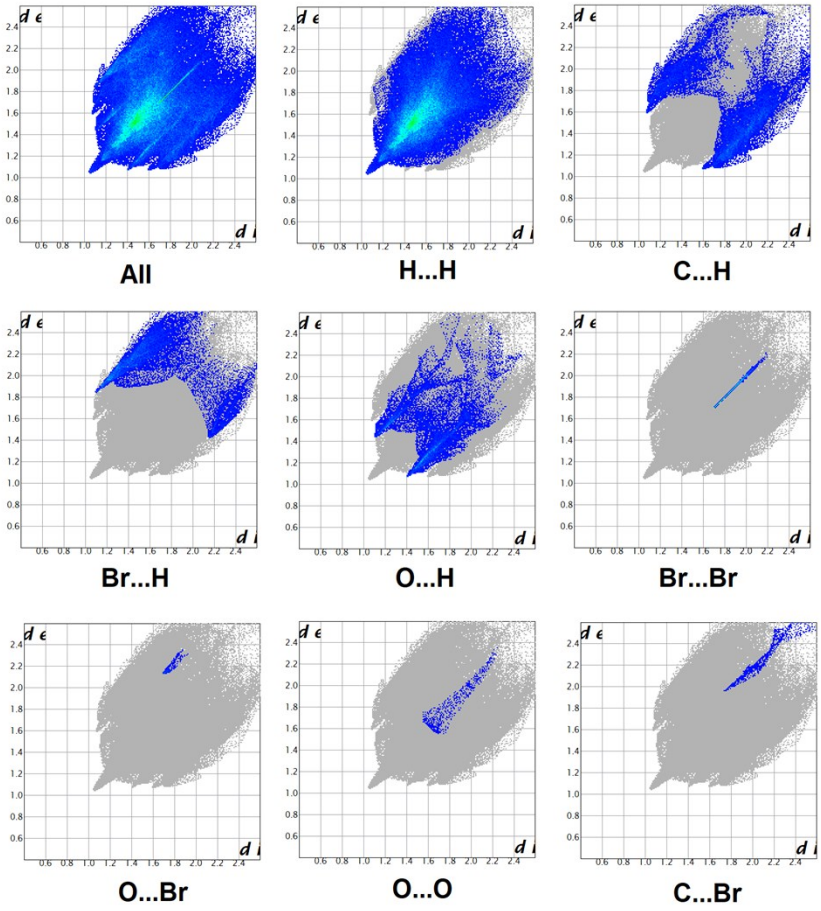

Figure S4. 2D fingerprint plot of [**DPM5⊃BuBr2**] derived from the Hirshfeld surface analysis depicting contributions from all significant intermolecular interactions (contributions from C···O and C···C interactions are too low to be considered).

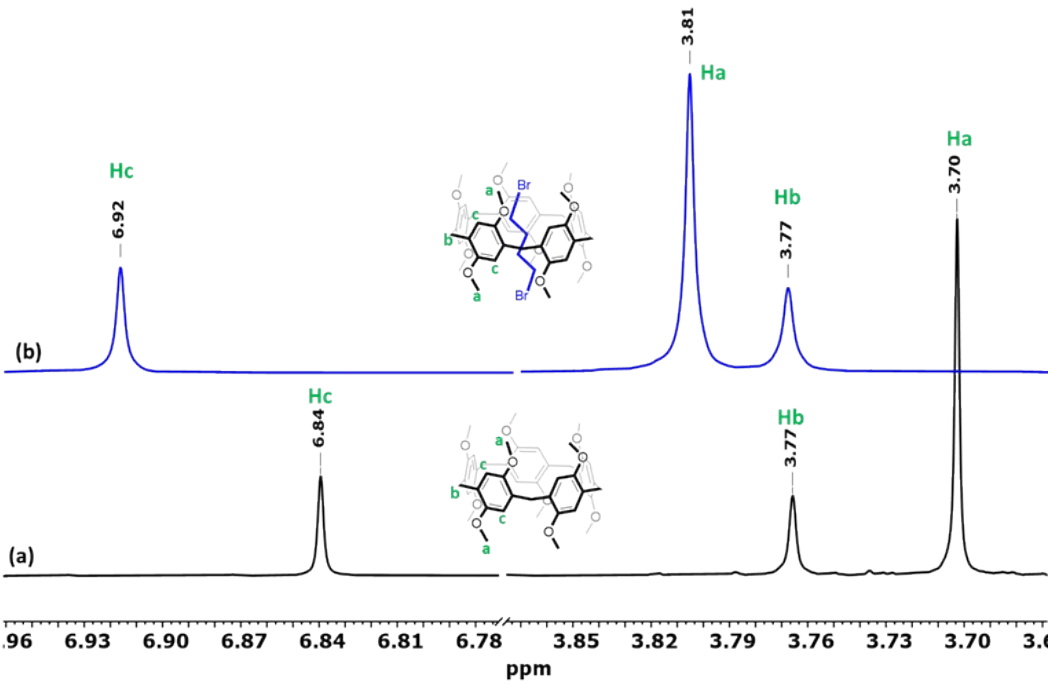

Figure S5. Pillararene region ^{1}H NMR (600 MHz, chloroform-*d*, 298 K) spectra of (a) **DMP5**, 10 mM, and (b) 10 mM of **DMP5** with equimolar 1,4-dibromobutane **BuBr2**.

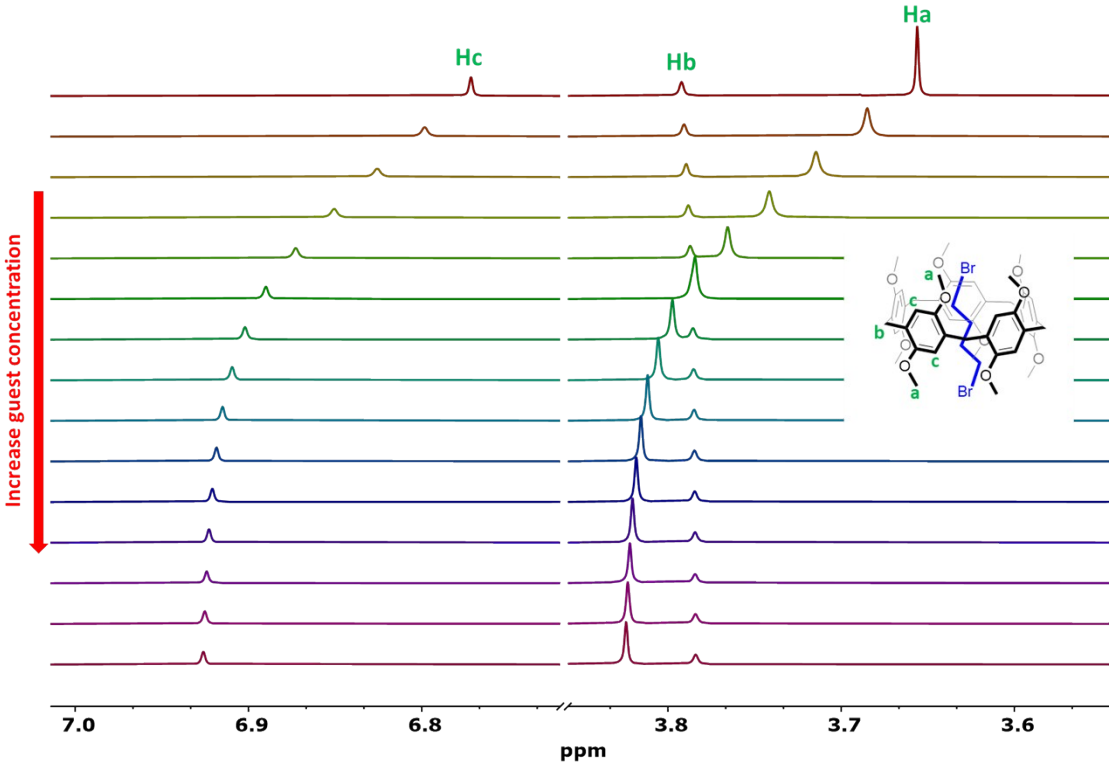

Figure S6. Partial ^{1}H NMR spectra (600 MHz, chloroform-*d*, 25 °C) of 10 mM of **DMP5** after incremental addition of 0.1 molar equivalent of the guest **BuBr2** starting from 0 to 1.4.

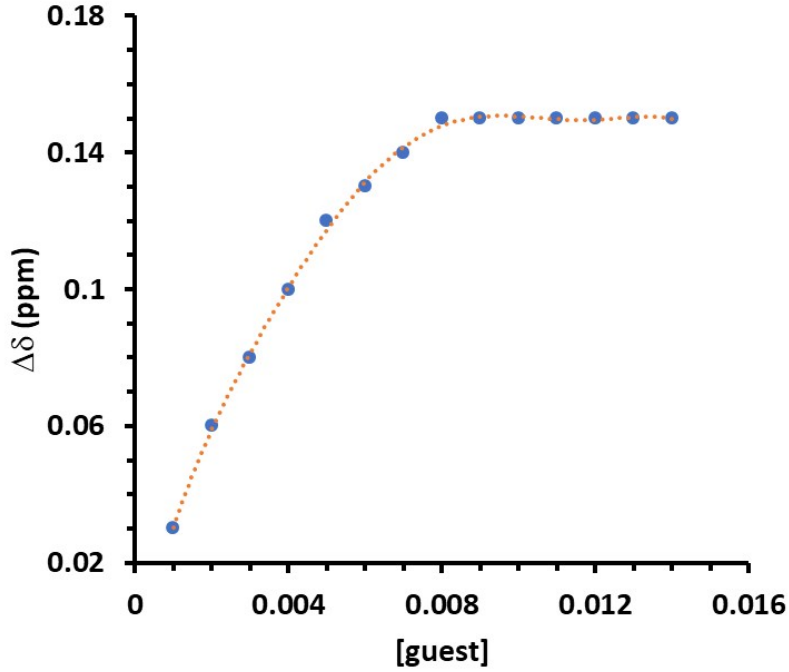

Figure S7. Plot of chemical shift (δ) changes for the host (**DMP5**) proton aromatic region as function of guest (**BuBr2**) concentration in $CDCl_3$ at 25 °C.

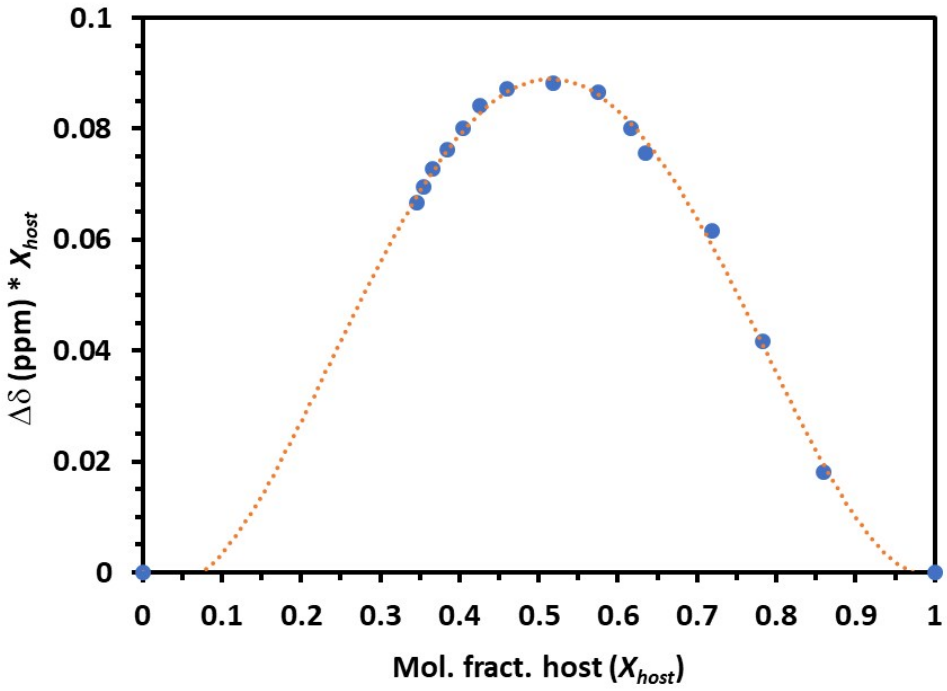

Figure S8. Job's plot for complexation of host **DMP5** with guest **BuBr2**, determined from ^{1}HNMR titration in $CDCl_3$ at 25 °C.

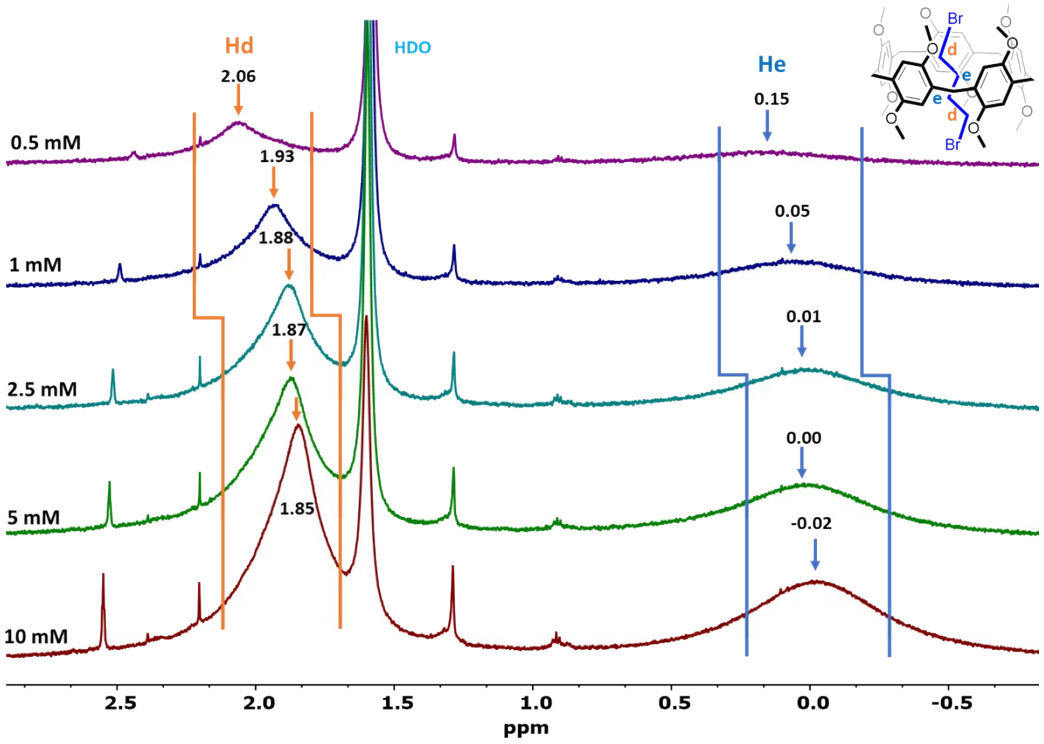

Figure S9. Partial ^{1}H NMR (600 MHz, chloroform-*d*, 298 K) spectra of [**DPM5⊃BuBr2**] inclusion complex at different concentrations.

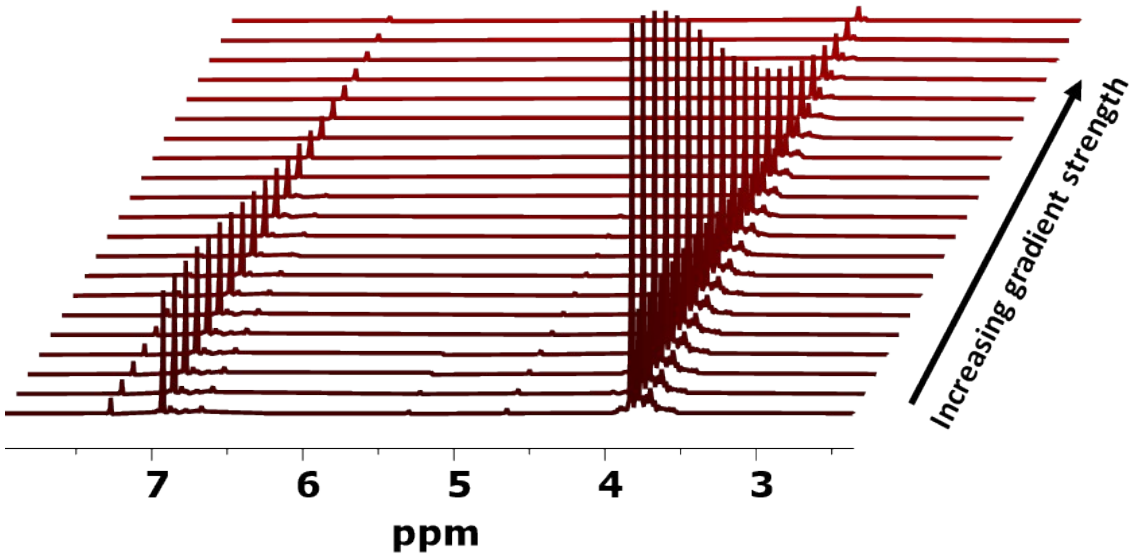

Figure S10. Experimental 1D ^{1}H Diffusion traces (600 MHz, $CDCl_3$) a progressive intensity decay as a function of gradient strength for the complex [**DMP5 ⊃ BuBr2**].

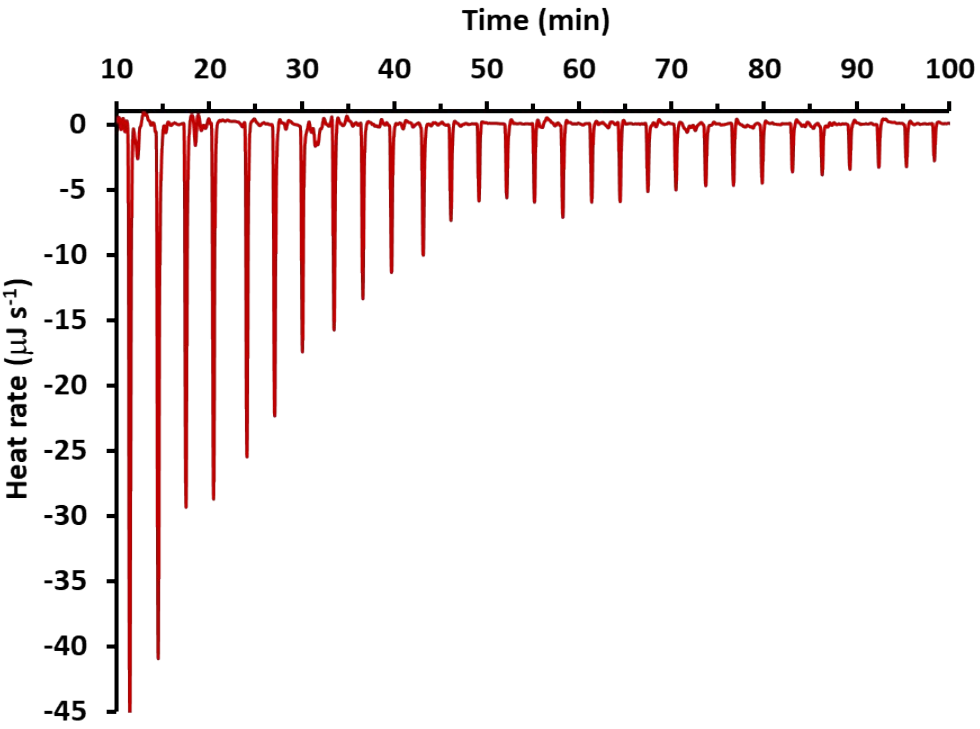

Figure S11. Host-guest complexation ITC experiment raw heats for sequential injections in chloroform of **DMP5** with **BuBr2** at 25 °C.

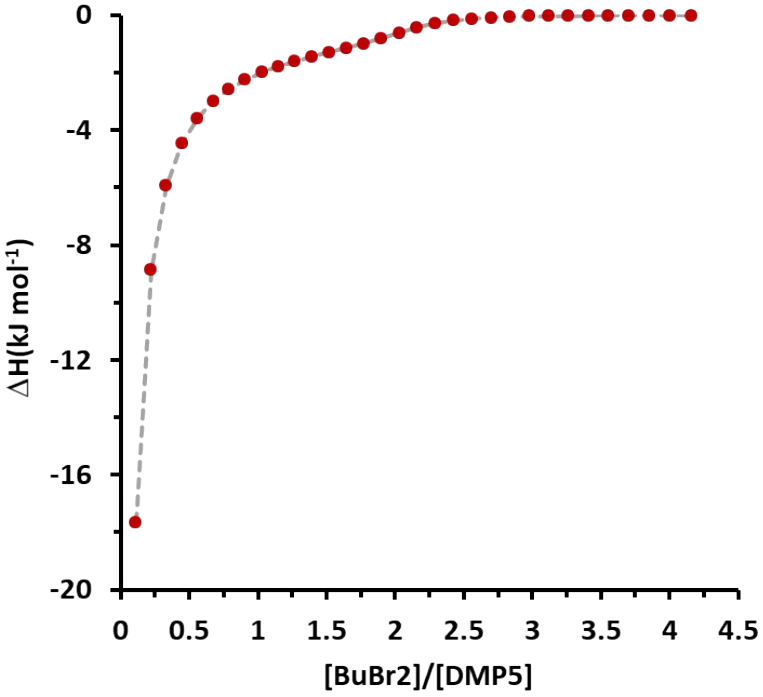

Figure S12. Net heat of complexation of 10 mM solution of **DMP5** with **BuBr2** as a function of molar ratio after subtracting heat of dilution.

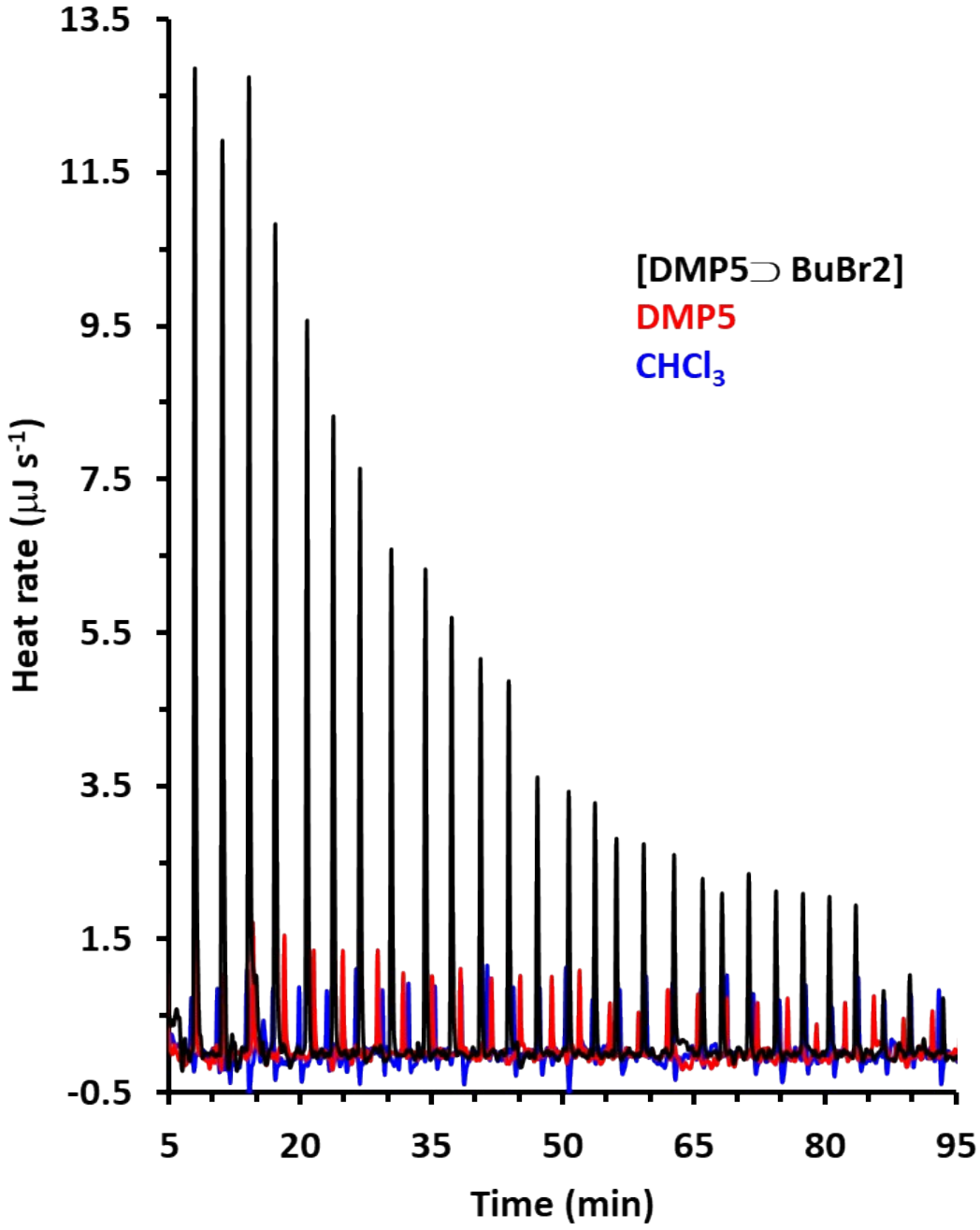

Figure S13. Overlay ITC dilution raw heats for sequential injections of complex [**DMP5** ⊃ **BuBr2**], **DMP5** and **$CHCl_3$** in chloroform at 25 °C.

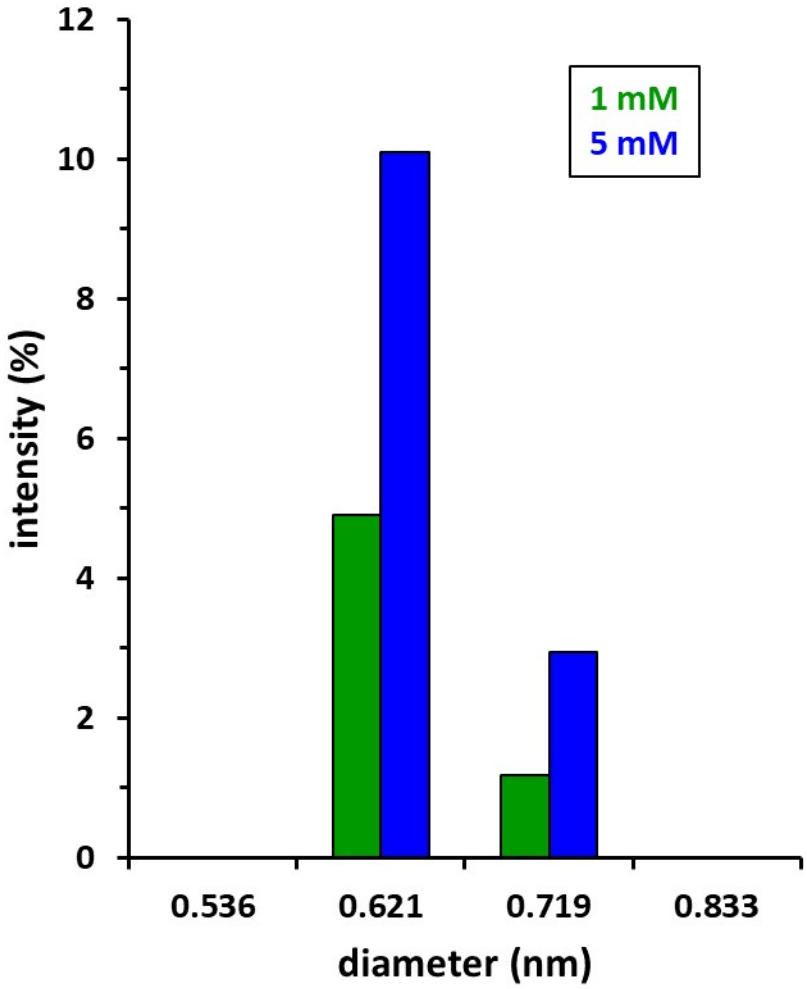

Figure S14. Hydrodynamic diameter (D_h) of 0.621 and 0.719 nm corresponding to the host **DMP5** observed at 1 mM and 5 mM concentration.