Supplementary Information (SI) for CrystEngComm.

Phosphonated Calixarenes: Structural and Self-Assembly Behaviour Governed by the Cavity Size

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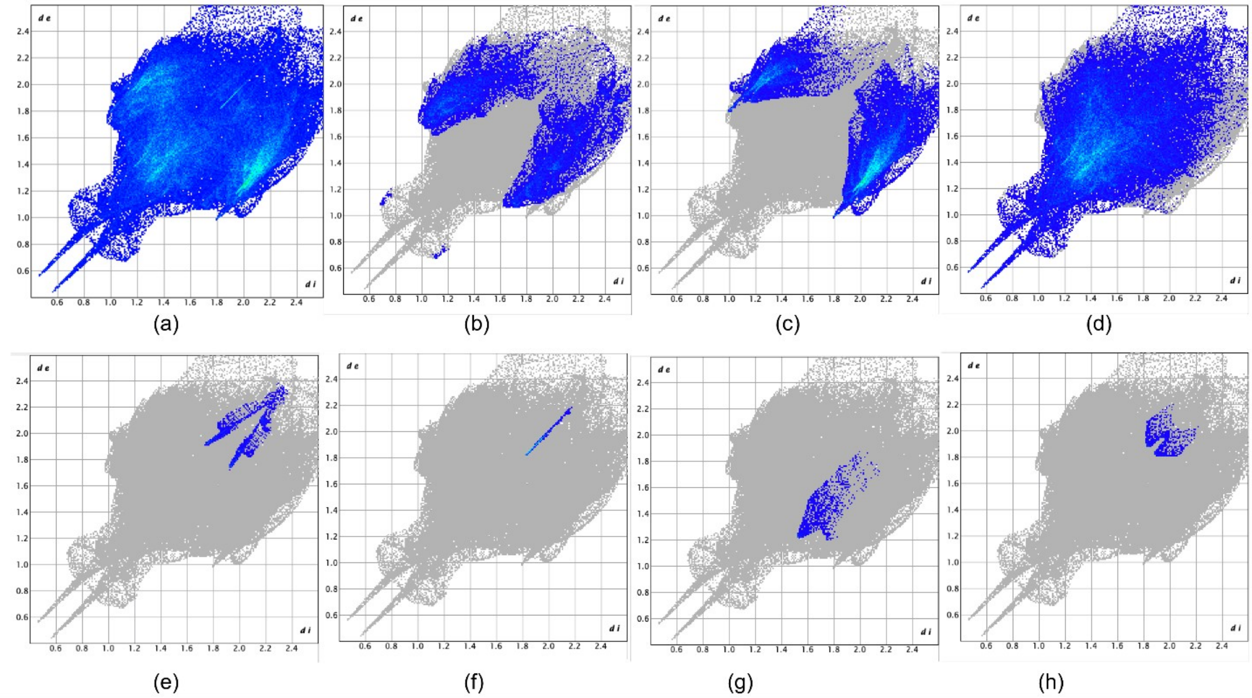
Supplementary Information

Table S1. Various contact contributions to Hirshfeld surface area in six calix[n]arene compounds.

Compound	O…H (%)	C…H (%)	C…C (%)	H…H (%)	H…Br (%)	Br…Br (%)	C…Br (%)
1	16.2	7.2	0.0	70.6	5.4	0.0	0.0
2a	0.8	15.7	0.5	56.7	24.7	0.5	1.1
2b	0.9	16.8	0	54.2	27.0	0.8	0.3
3	0.8	9.8	0.5	74.9	13.6	0.4	0.0
4	12.9	15.8	0.4	40.0	24.1	1.9	0.1
6	9.6	3.7	0.2	84.9	0.0	0.0	0.0



(a) (b) (c) (d)

(e) (f) (g) (h)

Figure S1. The full two-dimensional fingerprint plots for compound **2a**, showing (a) all interactions, and delineated into (b) C···H/H···C (15.7%), (c) Br···H/H···Br (24.7%), (d) H···H (56.7%), (e) C···Br/Br···C (1.1%), (f) Br···Br (0.5%), (g) O···H/H···O (0.8%) and (h) C···C (0.5%) interactions. Two of the three *n*-butyl chains in structure **2a** exhibit positional disorder: the chain on O1 (C10-C19, occupancies 0.67:0.33) and the chain on O3 (C30-C39, occupancies 0.50:0.50). The Hirshfeld surface analysis includes all disorder components simultaneously, resulting in short H...H contacts <1 Å (shorter than the van der Waals contact) in the fingerprint plot. These represent overlapping hydrogen positions from mutually exclusive disorder orientations and do not indicate true intermolecular contacts.

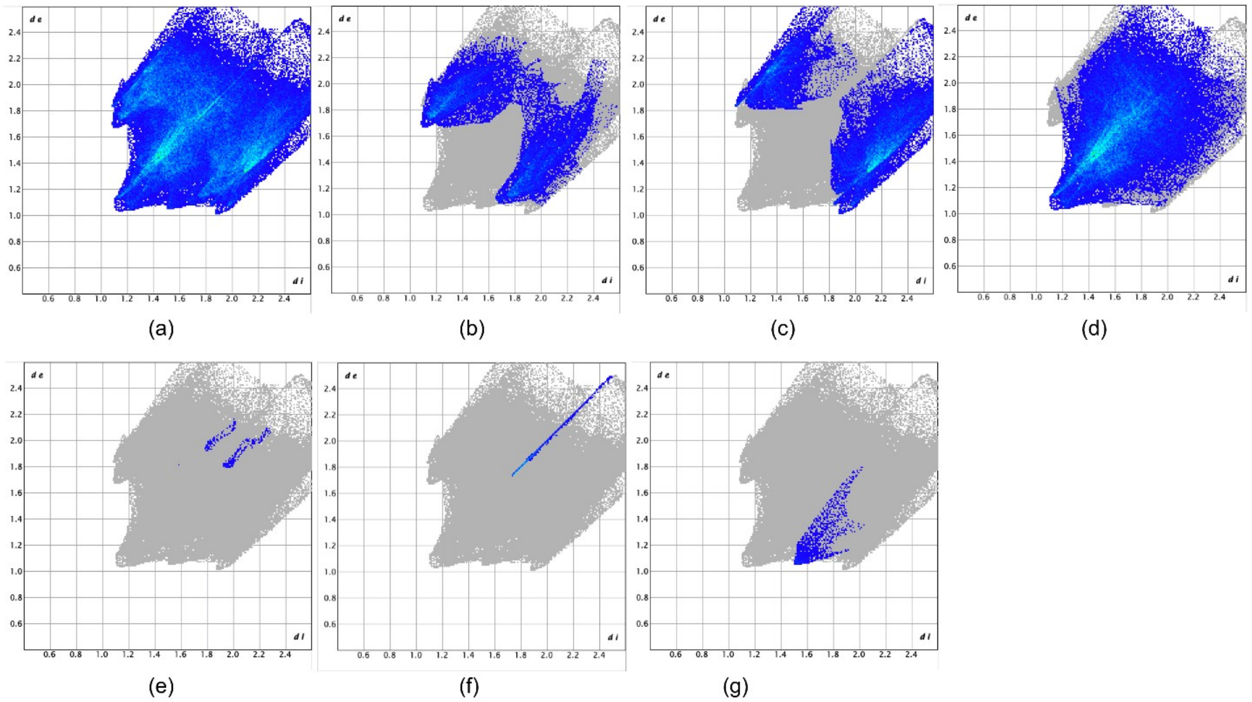


Figure S2. The full two-dimensional fingerprint plots for compound **2b**, showing (a) all interactions, and delineated into (b) C···H/H···C (16.8%), (c) Br···H/H···Br (27.0%), (d) H···H (54.2%), (e) C···Br/Br···C (0.3%), (f) Br···Br (0.8%), and (g) O···H/H···O (0.9%) interactions.

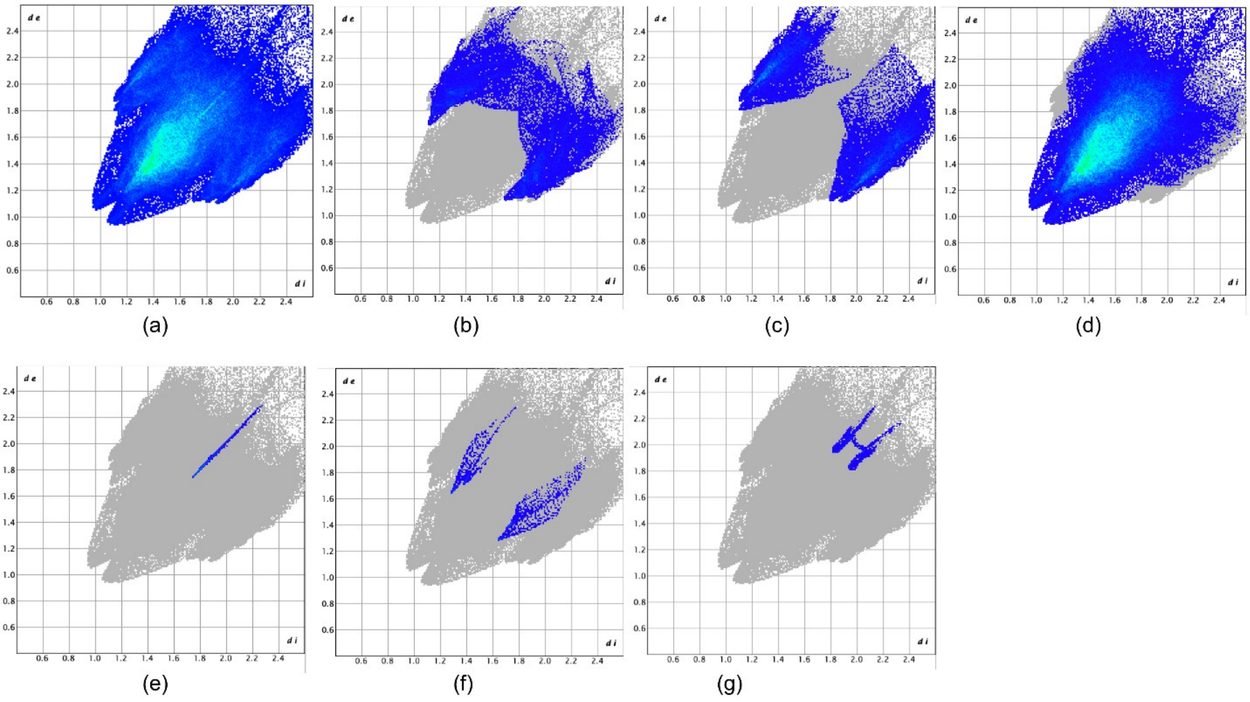
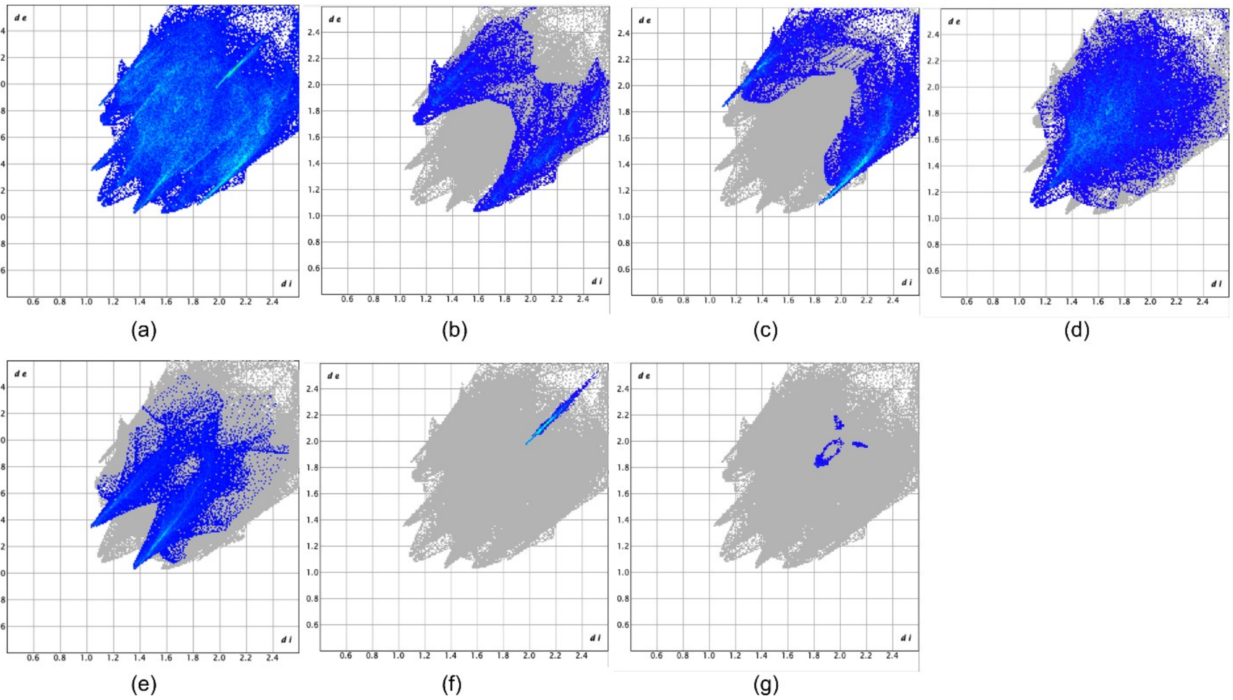


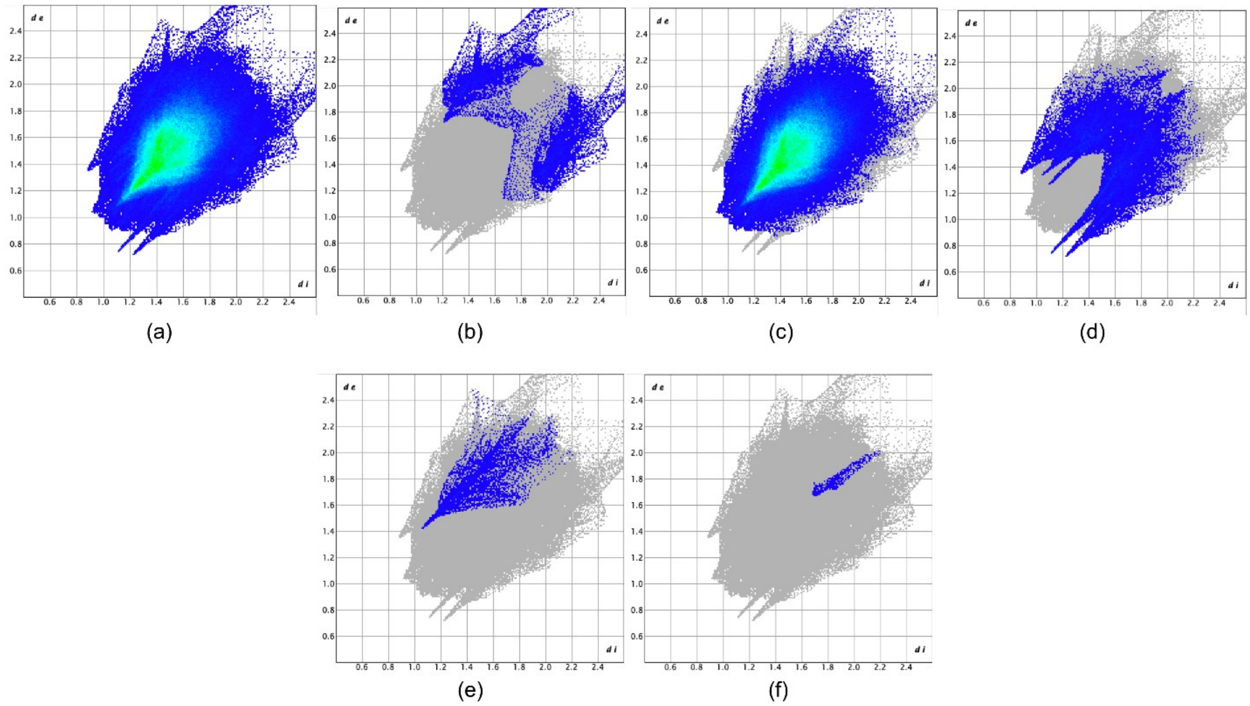
Figure S3. The full two-dimensional fingerprint plots for compound **3**, showing (a) all interactions, and delineated into (b) C···H/H···C (9.8%), (c) Br···H/H···Br (13.6%), (d) H···H (74.9%), (e) Br···Br (0.4%), (f) O···H/H···O (0.8%) and (g) C···C (0.5%) interactions.



(a) (b) (c) (d)

(e) (f) (g)

Figure S4. The full two-dimensional fingerprint plots for compound **4**, showing (a) all interactions, and delineated into (b) C···H/H···C (15.8%), (c) Br···H/H···Br (24.1%), (d) H···H (40.0%), (e) O···H/H···O (12.9%) (f) Br···Br (1.9%), and (g) C···C (0.4%) interactions.



(a) (b) (c) (d)

(e) (f)

Figure S5. The full two-dimensional fingerprint plots for compound **6**, showing (a) all interactions, and delineated into (b) C···H/H···C (3.7%), (c) H···H (84.9%), (d) O···H/H···O (9.6%), (e) N···H/H···N (1.5%), and (f) C···C (0.2%) interactions.

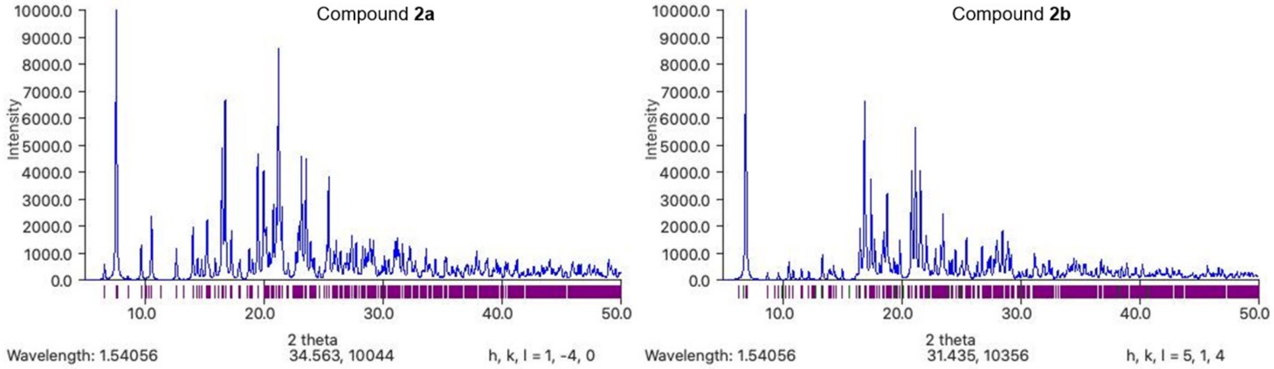


Figure S6. Calculated powder X-ray diffraction (PXRD) patterns of compounds **2a** and **2b** generated from single crystal structure data using Mercury software, confirming distinct crystal structures.

Crystallographic Refinement Details

Crystallographic refinement of the studied compounds encountered several challenges, which resulted in elevated *R*1 values (from 0.0488 to 0.2104). The primary issues encountered were:

a) Disorder: Significant positional and/or orientational disorder was observed in phosphonic acid groups, *n*-alkyl chains and solvent molecules. This disorder was modeled using PART/FVAR instructions in SHELXL. The disordered components were refined with distance (DFIX/SADI) and displacement parameter (SIMU in compound **7**) restraints to maintain chemical reasonableness. Residual electron density in the crystals of compounds **5** and **7** that could not be interpreted as chemically reasonable moieties was effectively removed using the SQUEEZE[1] program.

b) Weak diffraction: The weakest intensities of the X-ray data processing program CrysAlisPro[2] are reported for compound **7** - the diffraction limit of 1.48 Å.

c) Quality of measured intensities:

- Compound **3**: Averaged mosaicity (eigenvectors in degrees) – 16 runs, e1=1.76, e2=0.64, e3=5.08
- Compound **5**: Averaged mosaicity (eigenvectors in degrees) – 22 runs, e1=1.53, e2=0.69, e3=1.41
- Compound **7**: Averaged mosaicity (eigenvectors in degrees) – 61 runs, e1=0.67, e2=0.75, e3=1.09

The elevated R-factor values for compounds **3** and **5** are primarily attributed to sample quality issues, while for compound **7**, disorder is the dominant factor. To improve chemical plausibility and reasonable geometries, some constraints/restrictions were employed using SHELXTL instructions.

Despite the elevated *R*1 values, the molecular connectivity, bond lengths, and angles are chemically reasonable and consistent with expected values for phosphonated calix[n]arenes. The structures were validated using checkCIF software, and significant alerts have been addressed in the deposited CIF validation reports. While these *R*1 values are higher than those typically observed for small molecule structures, they are acceptable given the challenges described above and the chemical significance of the structural determinations.

References:

1 A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9-18.

2 Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.