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Supporting Information

for

Structural Variation Determined by Length-matching Effects: Towards the Formation of Flexible Porous Molecular Crystal

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Experimental Details

General

All commercially available reagents and solvents were purchased from Adamas, General-reagent and Shanghai Lingfeng chemical reagent Co. Ltd.. The reagents used were of reagent grade, and the solvents used were of analytical grade unless otherwise stated; all reagents were directly used without further purification.^{1}H NMR were recorded on an Avance III 400 MHz NMR spectrometer (Bruker, Germany), and chemical shifts are reported in ppm (δ) using the signal of tetramethylsilane (TMS) as an internal standard. Chloroform vapour sorption was measured by IGA-100b (Hidden, U. K.)

Synthesis of the compounds:

1,1′-biphenyl-4,4′-dimethylene-bis (decyldimethylammoniumbromide) **(1)** and 1,1′-biphenyl-4,4′-dimethylene-bis (ocyldimethylammoniumbromide) **(2)** can be synthesized by a similar step. The detailed process is as follows: 4,4′-Bi(bromomethyl)biphenyl (1.73 g, 5.0 mmol; purity > 95%) was dissolved in 50 ml tetrahydrofuran (THF) in a 250 ml Erlenmeyer flask with electromagnetic stirring. N,N-Dimethylalkyledamine (10.0 mmol; purity > 97%) was diluted with 25 ml THF and added dropwise to the above solution. This solution was further stirred for six hours. After the reaction was completed, the solvent was removed under reduced pressure. The crude product was then purified by more than three recrystallizations from chloroform/acetone and then filtered to remove the remaining mechanical impurities. The target product was finally obtained by recrystallization in 62% yield. ^{1}H NMR of 10-2Ar (400 MHz, CDCl3), δ = 7.66 (d, *J* = 7.6 Hz, 4H), 7.19 (d, *J* = 7.6 Hz, 4H), 5.48 (s, 4H), 3.54 (t, *J* = 8.0 Hz, 4H), 3.23 (s, 12H), 1.83 (m, 4H), 1.26–1.37 (m, 20H), 0.87 (t, *J* = 7.2 Hz, 6H). ^{1}H NMR of 8-2Ar (400 MHz, CDCl3), δ = 7.66 (d, *J* = 7.6 Hz, 4H), 7.21 (d, *J* = 7.6 Hz, 4H), 5.47 (s, 4H), 3.53 (t, *J* = 8.0 Hz, 4H), 3.24 (s, 12H), 1.83 (m, 4H), 1.25–1.36 (m, 28H), 0.87 (t, *J* = 7.2 Hz, 6H).

Single crystal structure determination

Single-crystal X-ray diffraction experiments were performed on a Bruker Smart Apex CCD area detector diffractometer (Germany) with Cu Kα (λ = 1.54178 Å) radiation. All the calculations were done using the Bruker Smart and the BrukerShelxl program packages.

DFT calculations and noncovalent interaction analysis

The interaction energy of the complexes were computed at the M06-2x/6-311+G(d,p) level of theory by means of the Gaussian 09 package. The fragments are employed the crystallographic coordinates. These complexes were selected elaborately so that they are qualified to represent all the relevant interactions in the crystal. The interaction energy is defined as follows:

$$\Delta E = E(\text{complex}) - \sum E(\text{monomer})$$

where E(complex) is the total energy of the complex, and $\sum E$(monomer) is the sum of the total energy of the monomers.

Subsequently, in order to visualize the interaction regions as well as discriminate weak interaction types, the NCI (Noncovalent Interactions) analysis was performed by Multiwfn (A Multifunctional Wave function Analyzer) program 3.3.7. The corresponding results were processed by Visual Molecular Dynamics (VMD) software to obtain a final isosurfaces graph. Essentially, this graph is based on the process that the values of sign($\lambda 2(r)$)ρ(r) were represented by two section of gradient colors and the colors were then filled to Reduced Density Gradient (RDG) isosurfaces. In general, more blue indicates strong attraction, more green stands for van der Waals interaction and more red means strong repulsion.

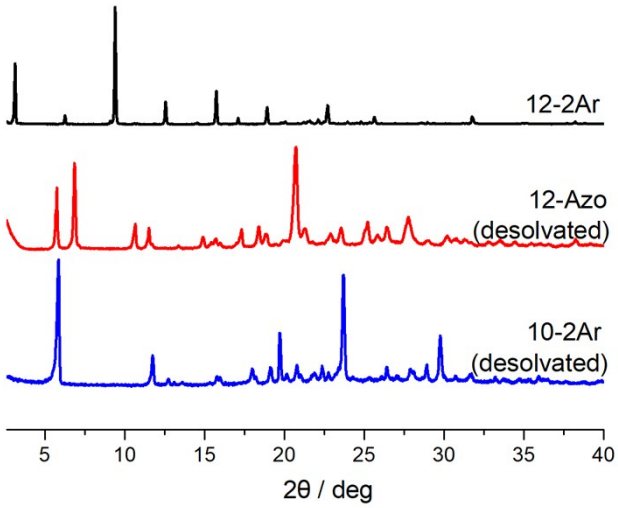


Figure S1. XRD patterns of 12-2Ar crystal, desolvated 12-Azo crystal and desolvated 10-2Ar crystal

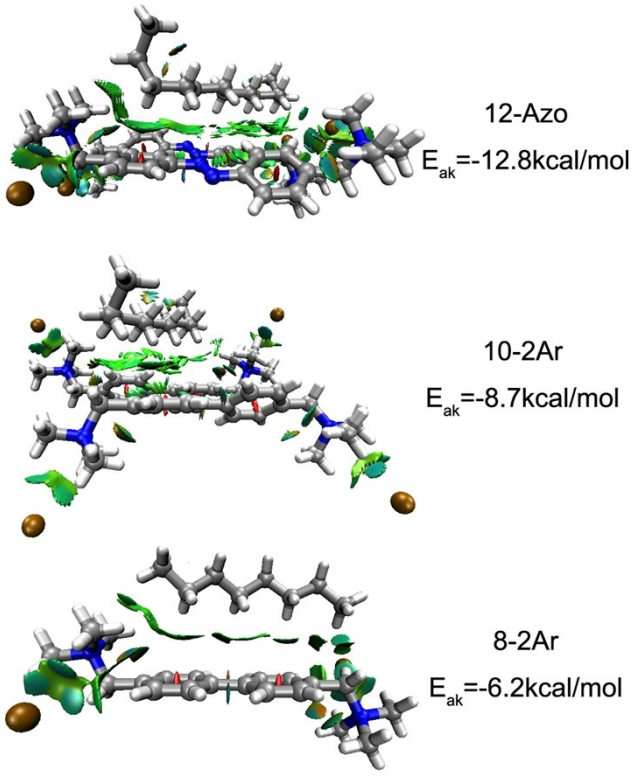


Figure S2. The calculated interaction energies of the counterparts and corresponding NCI analysis in different crystals. Color for isosurface: blue indicates polarized attraction, green means van der Waals interaction and red stands for repulsion. Color for atoms: blue, grey, and white balls denote nitrogen, carbon and hydrogen atoms, respectively, whereas olive balls represent bromide ions.

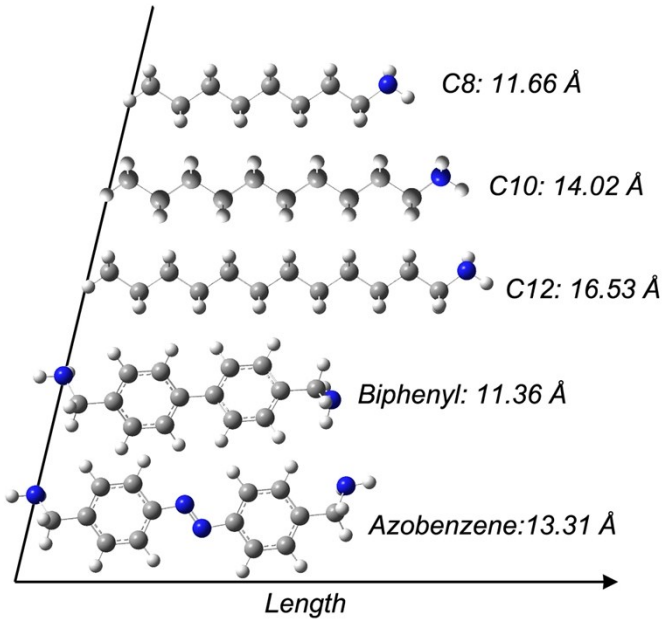
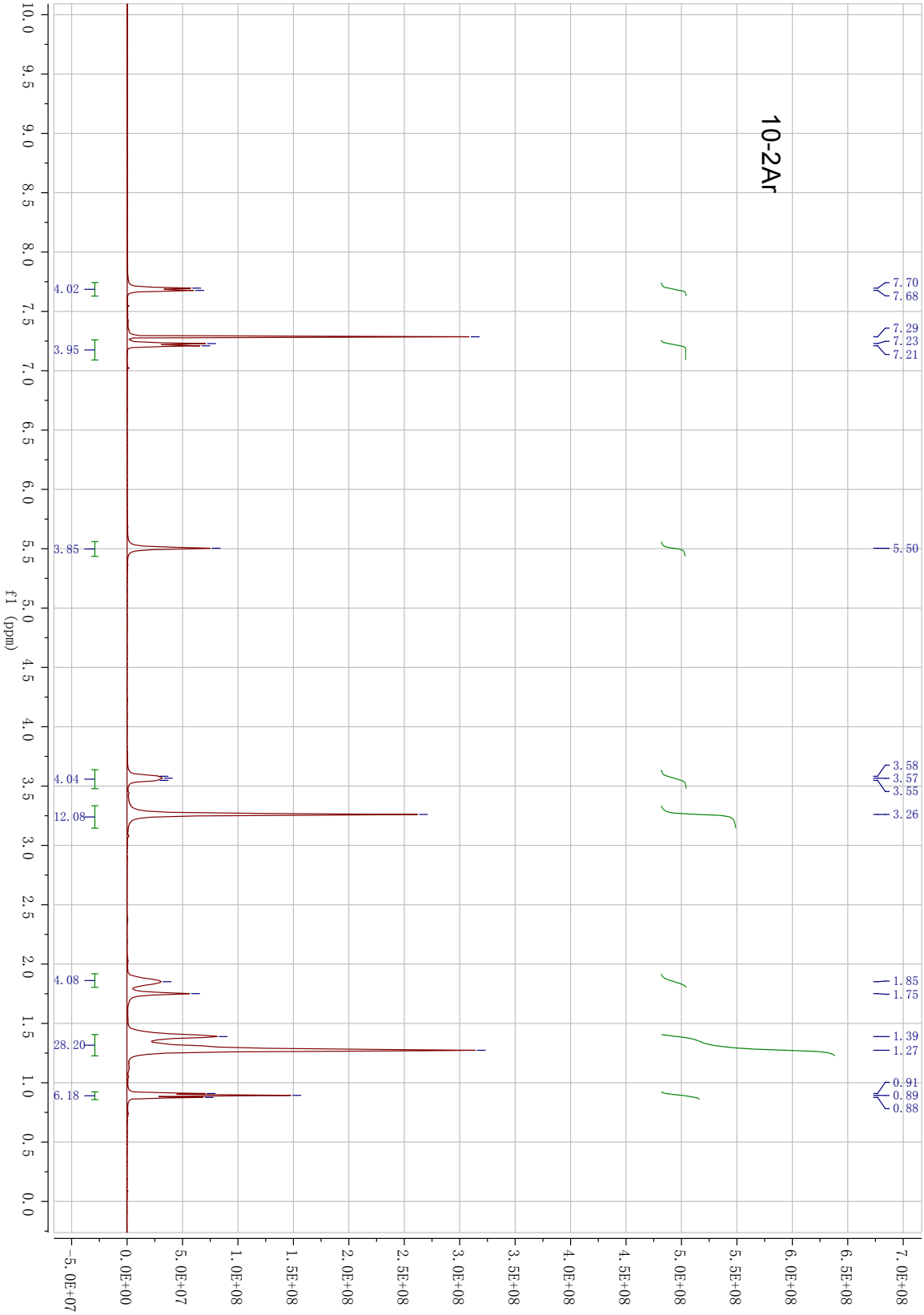
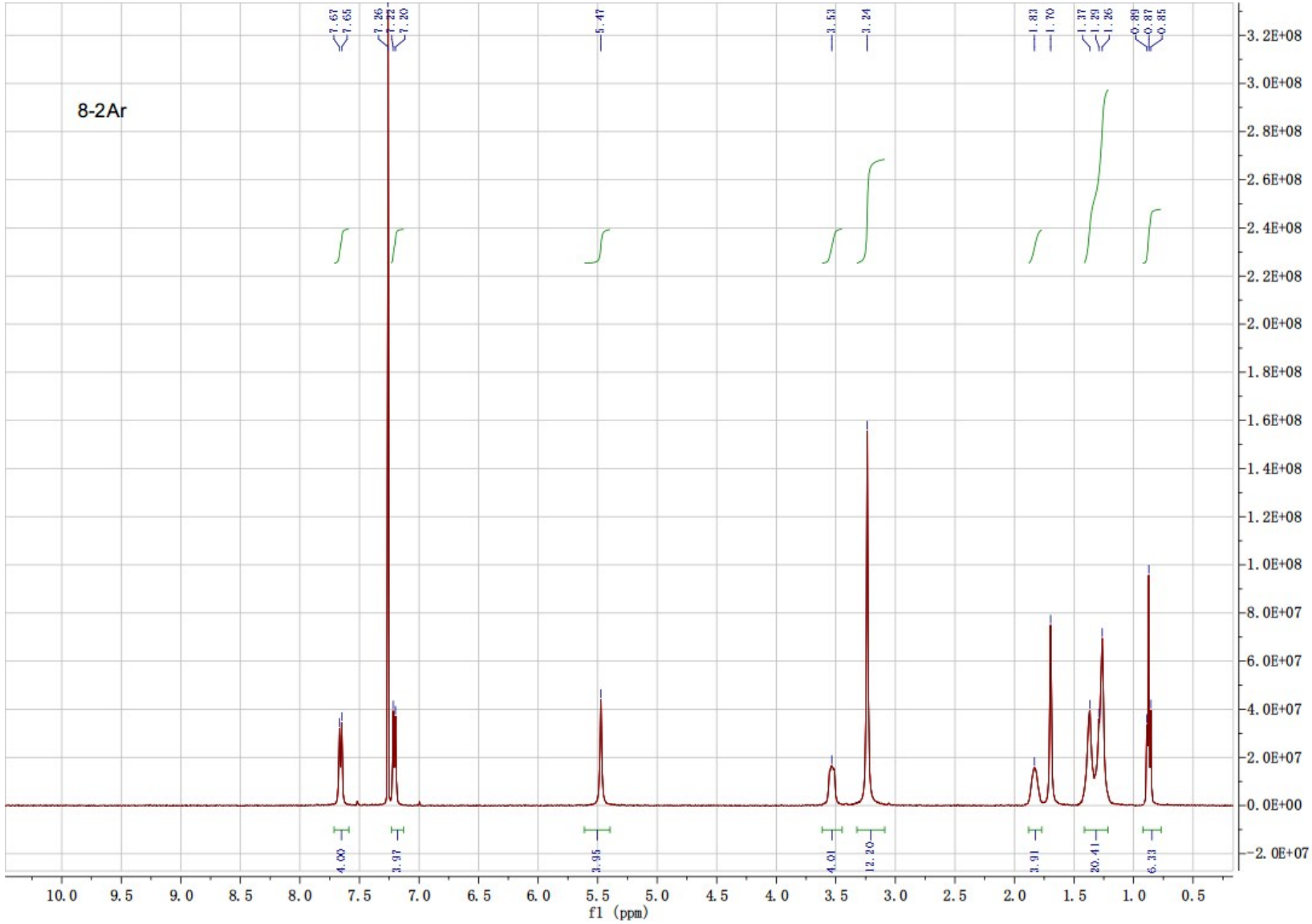


Figure S3. Simplified fragments for length evaluation. Color for atoms: grey: C; white: H; Blue: N. The fragment conformations are optimized by B3lyp/6-31+G(d,p) level of theory by means of the Gaussian 09 package.

Additional spectrums




8-2Ar
7.67
7.65
7.26
7.22
7.20
5.47
3.53
3.24
1.83
1.70
1.37
1.29
1.26
0.89
0.87
0.85
4.00
3.97
3.95
4.01
12.20
3.91
20.41
6.33
f1 (ppm)