

Electronic supplementary information for
Selective MeCN/EtCN sorption and preferential inclusion of
substituted benzenes in a cage structure with
arylsulfonamide-armed anthraquinones

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1. ORTEP drawings of 1-4

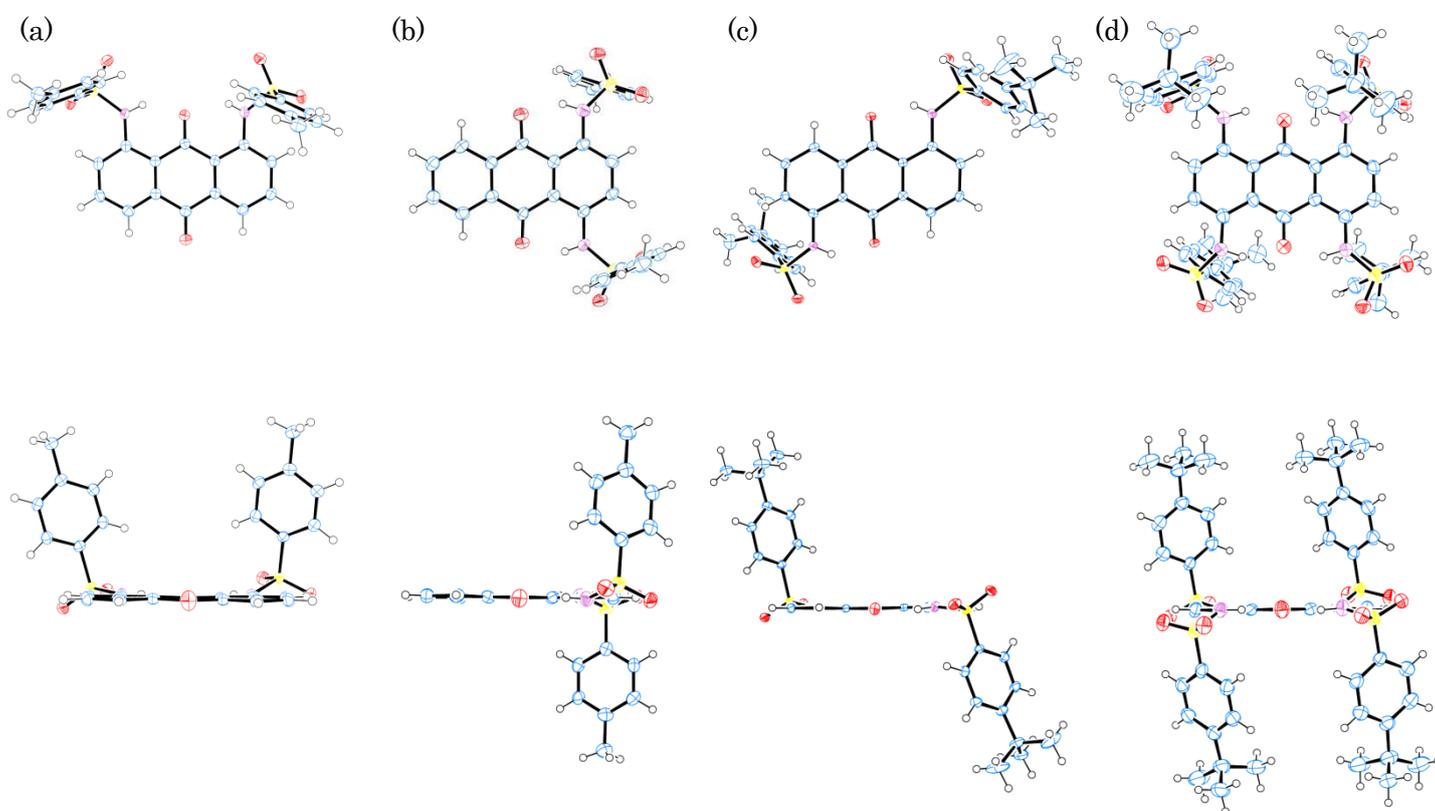


Figure S1 Top view (top) and side view (bottom) of X-ray structures of (a) **1**, (b) **2**, (c) **3**, and (d) **4**. Displacement ellipsoids are drawn at the 50% probability level. Solvate molecules are omitted for clarity. Crystal data of **1**•(MeCN) and **4**•(toluene) were used to draw the corresponding ORTEP.

2. Dimer structures and packing arrangements of 2 and 3

Well-defined molecular scaffolding of disubstituted **1-3** induced formation of the significant dimer structure. Figure S2 shows the dimer structures of **2** and **3** in the crystal. Anthraquinone overlapped in a slip-stack fashion to form the respective dimers. Slip-stacking of anthraquinone in **2** and **3**, observed in the crystalline state, is energetically favoured due to charge-transfer interaction between the donor and acceptor parts of anthraquinone. Arylsulfone units faced outward and were arranged perpendicular to the anthraquinone plane in the dimer structures. Steric hindrance between bulky arylsulfone units could be avoided by rotation/inversion of the molecules. As a result, a rigid, defined, dimensional dimer was formed.

A critical difference between the dimer structures of **2** and **3** could be found in the arrangement of four arylsulfone units in the respective dimers. While all four arylsulfone units in dimer of **2** are

directed outward in four directions, two arylsulfone units overlap each other in that of **3**, where only two arylsulfone units are available for intermolecular interaction. If we consider the rigid molecular structure in the solid state and similar thermodynamically stable π dimer formation of anthraquinone in **2** and **3**, the difference could be accounted for simply by the difference in the nature of substitution and molecular symmetry.

The difference in the dimer structures induced significantly different packing arrangements. In the case of 1,4-disubstituted derivative **2**, the dimers were stacked in a slip-stack fashion to form a one-dimensional column along the *a*-axis. Short π - π contacts of anthraquinone moieties were observed in the column, and the columns were connected by $C_{Ar}-H\cdots O=S$ interactions. On the other hand, the dimers were arranged in a zig-zag fashion in crystals of 1,5-disubstituted derivative **3**. While $C_{Ar}-H\cdots O=S$ and $C_{tBu}-H\cdots O=S$ interactions were also observed between the dimers in **3**, there is no π stacking between the dimers, in contrast to **2**. If we consider the significant $C-H\cdots O=S$ interaction in the crystal structures of **2** and **3**, the origin of significantly different packing arrangements from structurally similar arylsulfonamide-armed anthraquinone was the number of available sulfonamide groups to connect the dimer. While the packing in crystal **3** was sparse, it did not adsorb or include gas or solvent molecules (Figure S8).

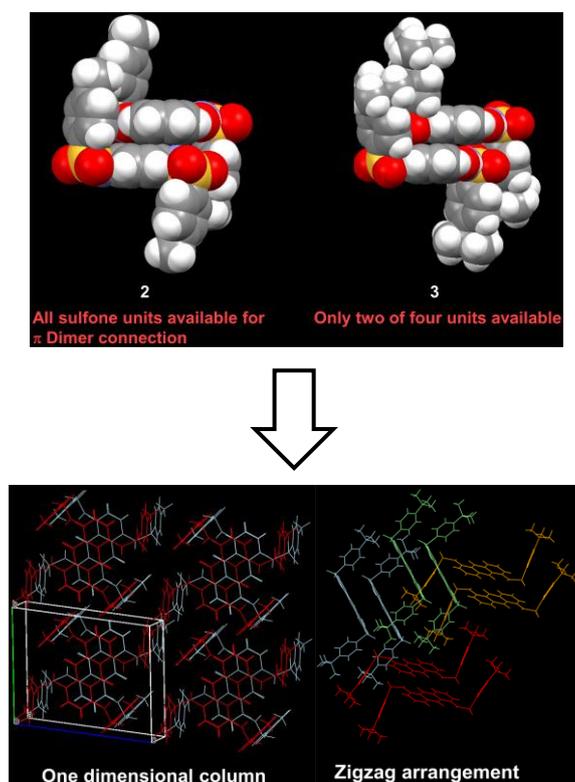


Figure S2 Dimer structures (top) and packing arrangements (bottom) of 1,4- and 1,5-bis(sulfonamide)-armed anthraquinones **2** (left) and **3** (right).

3. Crystal structure of **1**•(EtCN)

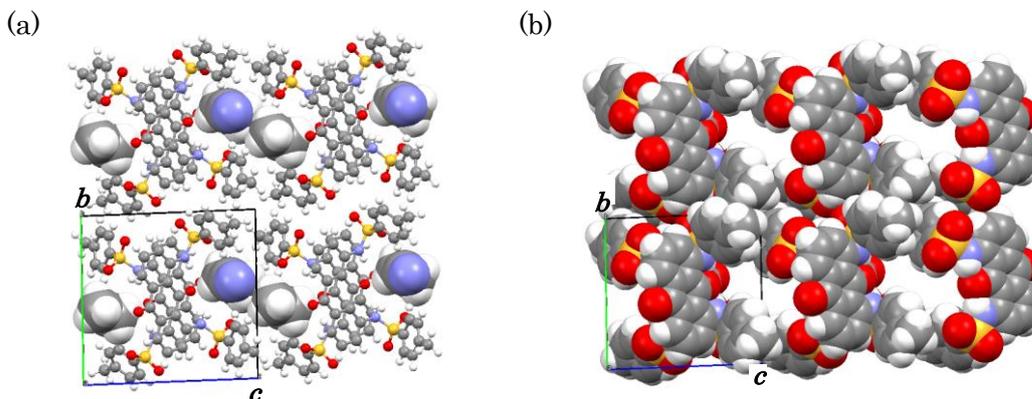


Figure S3 Crystal structure of **1**•(EtCN). a) Unit cell viewed along the *a*-axis. EtCN molecules are shown in a CPK model. b) CPK drawing of the packing structure and the 1D channel along the *a*-axis in the absence of EtCN.

4. Thermogravimetry curve of **1**•(MeCN) crystal

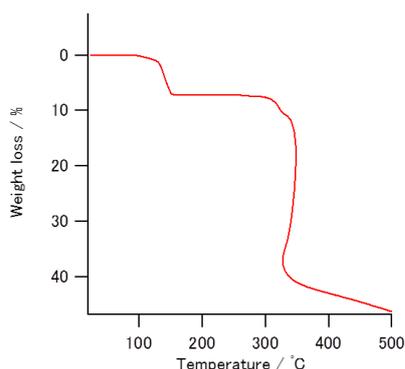


Figure S4 Thermogravimetry curve of **1**•(MeCN) crystal. The weight loss observed at 160 °C corresponds to the quantitative loss of CH₃CN from the crystal.

5. DFT energy calculation of **1**•MeCN and **1**•EtCN

We performed DFT (B3LYP/6-31G*) energy calculation of **1**•(MeCN) and **1**•(EtCN) with the molecular geometry of each crystals to discuss selective MeCN/EtCN sorption behavior of the crystal **1**. The energy differences between the host-guest complex **1**•(solvent) (E_{HG}) and the sum of isolated host **1** (E_H) and solvent (E_G) were calculated. The solvent association energies $\Delta E = -[E_{HG} - (E_H + E_G)]$ for **1**•(MeCN) and **1**•(EtCN) were 9.17 and 8.27 kcal/mol, respectively, which shows affirmative MeCN/EtCN adsorption of **1**.

Compound	E_{HG} (a.u.)	E_H (a.u.)	E_G (a.u.)	ΔE (kcal/mol)
1 •(MeCN)	-2569.68917	-132.72300	-2436.95155	9.17
1 •(EtCN)	-2609.05504	-172.01937	-2437.02249	8.27

6. Packing arrangements of crystals $4 \cdot (\text{xylene})_2$ and $4 \cdot (\text{anisole})_2$

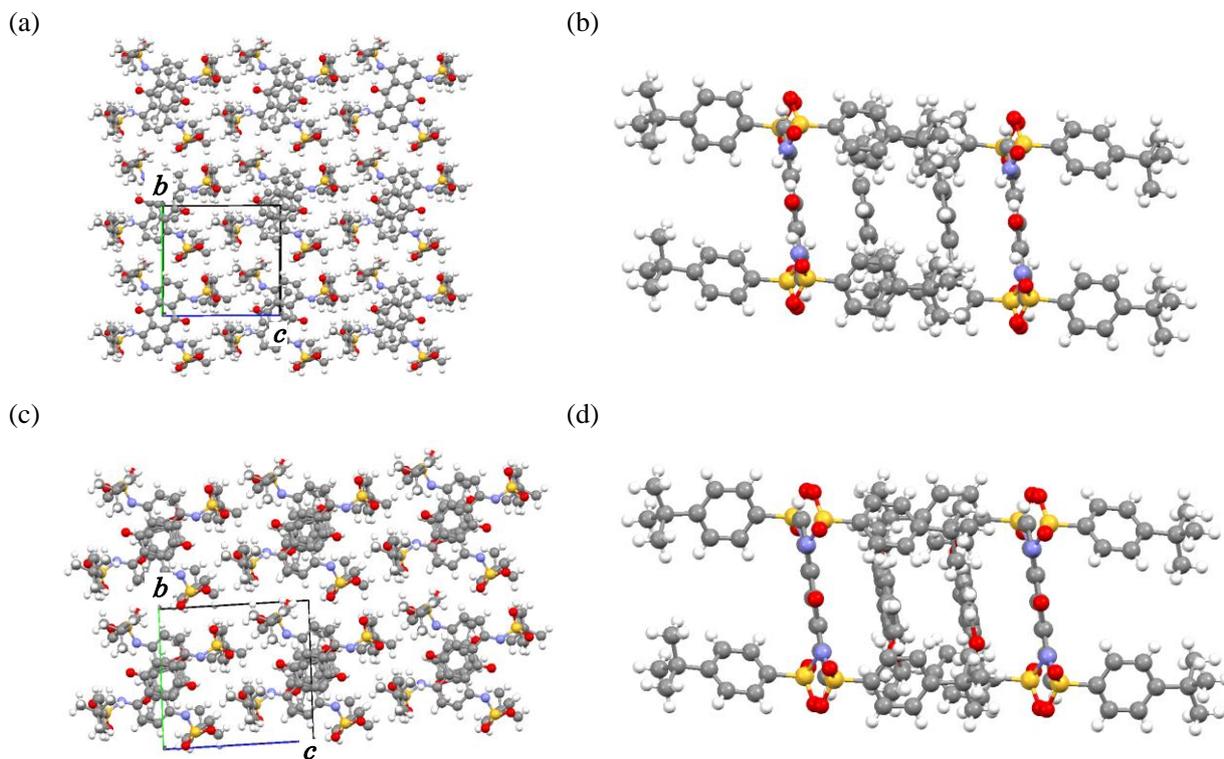
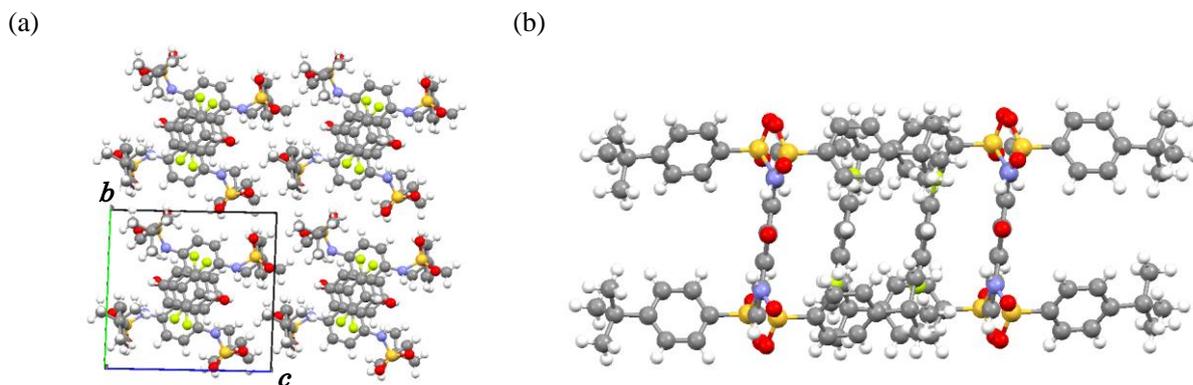


Figure S5 (a) Packing arrangement of the xylene-solvated crystal of **4**. (b) Arrangement of xylene molecules in a cage formed by two molecules of **4**. (c) Packing arrangement of the anisole-solvated crystal of **4**. (d) Arrangement of anisole molecules in a cage formed by two molecules of **4**.

7. Packing arrangements of crystals $4 \cdot (\text{fluorobenzene})_2$ and $4 \cdot (\text{benzonitrile})_2$



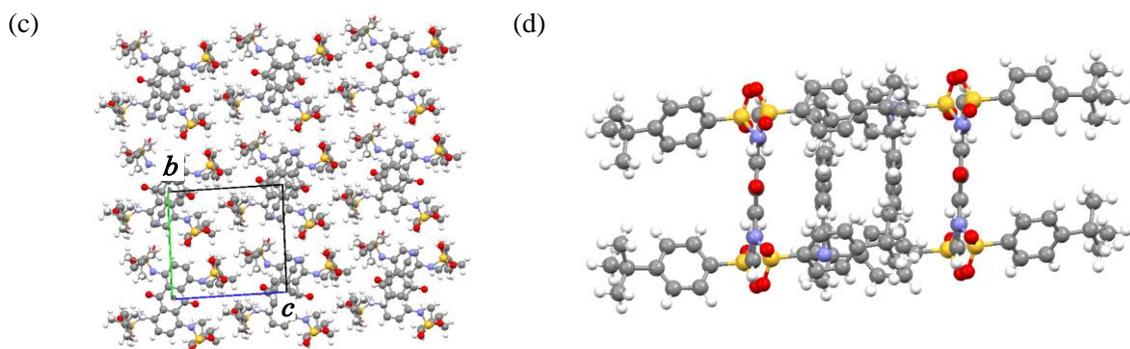


Figure S6 (a) Packing arrangement of the fluorobenzene-solvated crystal of **4**. (b) Arrangement of toluene molecules in a cage formed by two molecules of **4**. (c) Packing arrangement of the benzonitrile-solvated crystal of **4**. (d) Arrangement of benzonitrile molecules in a cage formed by two molecules of **4**.

8. Packing arrangements of $4 \cdot (\text{trimethylbenzenes})_2$

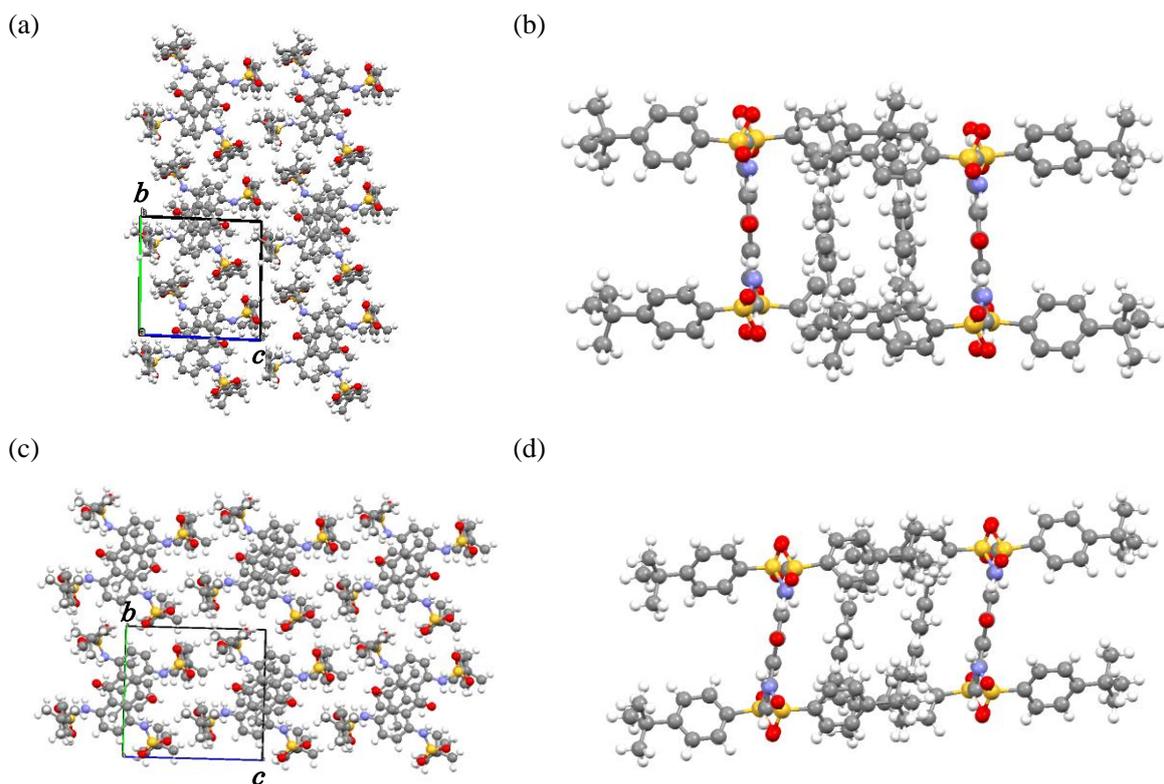


Figure S7 (a) Packing arrangement of the 1,2,4-trimethylbenzene solvated crystal of **4**. (b) Arrangement of 1,2,4-trimethylbenzene molecules in a cage formed by two molecules of **4**. (c) Packing arrangement of the 1,2,3-trimethylbenzene solvated crystal of **4**. (d) Arrangement of 1,2,3-trimethylbenzene molecules in a cage formed by two molecules of **4**.

9. Gas adsorption experiment with crystals 1 and 3

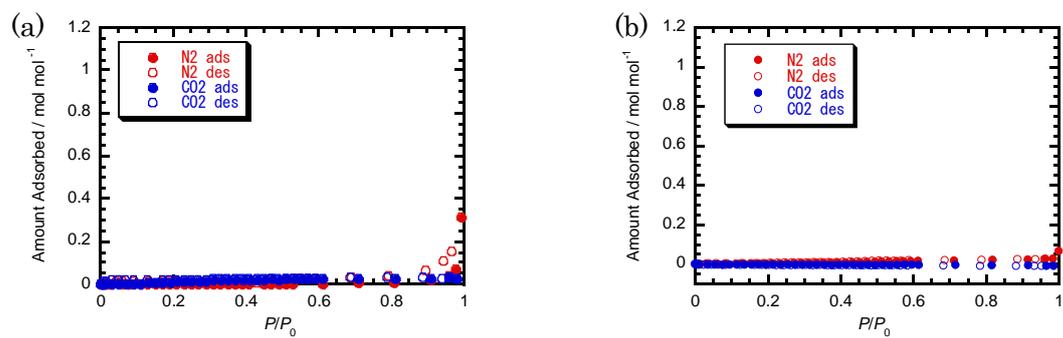


Figure S8 N₂ and CO₂ adsorption isotherms of crystals **1**(left) and **3**(right). No gas adsorption was observed.