



A porous coordination architecture assembled by silver triflate and 9,10-bis(3,5-dicyano-1-phenyl)anthracene and its gas adsorption profile

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ABSTRACT

We report a crystal structure and guest uptake measurements of a 2D coordination polymer, **3**·2(AgOTf)·2(acetone) which has been assembled by silver triflate and 9,10-bis(3,5-dicyano-1-phenyl)anthracene (**3**). When the as-prepared sample was evacuated, the **3**·2(AgOTf) framework retains its original structure with a void space into which guest molecules such as acetone and benzene can be restored.

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Self-assembly of metal ions and bridging ligands has gained much attention because of the production of many interesting porous solids which can entrap guest molecule.¹ In the heart of this synthetic approach, the design and use of pertinent organic linkers play a key role because they are essential in preparing a variety of supramolecular assemblies with metal ions. Among many possible functional groups such as pyridyl, carboxylate, sulfide, and phosphates, the –CN on the aromatic ring has proved to be especially versatile for the self-assembly of Ag-supramolecular architectures.² Once the cyano group is chosen as a metal-binding group, the next step is to determine a suitable aromatic motif to which the cyano group is introduced. We have targeted a bis(resorcinol) derivative of anthracene (**1**), which can form a 2D network through hydrogen bonds between terminal hydroxyl groups of the bis(resorcinol) groups.³ The large aromatic spacer of **1** acts as a part of the framework wall in the de novo building block in making new coordination architecture which has huge cavities capable of binding many guest molecules. The guest incorporation capability of **1** can be enlarged if other phenyl units are inserted into the main skeleton of **1** as demonstrated recently by us.⁴

If the resorcinol groups are replaced by other groups, the organic linker can be used as a building block in making new coordination architecture instead of hydrogen bond networks. One example is a coordination polymer assembled by Cd²⁺ and 5-(9-anthracenyl)pyrimidine, which was reported by Aoyama and co-workers a long time ago.⁵ The produced network was 1D coordination polymer because the pyrimidyl group was introduced at one side of

the anthracene nucleus. In this contribution, we report a self-assembly system of Ag(I)-coordination supramolecular architecture based on 9,10-bis(3,5-dicyano-1-phenyl)anthracene (**3**). This new ligand has two dicyanophenyl groups at both sides of an anthracene moiety, and hence acts as a four connector when combined with silver triflate (AgOTf) to produce a two-dimensional extended network, **3**·2(AgOTf).

The phenylcyanol anthracene derivative (**3**) was made by treating **2** with KCN in the presence of tris(dibenzylideneacetone)dipalladium(0) chloroform (Pd₂(dba)₃(CHCl₃)) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) adducts (Scheme 1).^{6,7} The metal complex **3**·2(AgOTf) was obtained in mixing of acetone containing **3** and silver trifluoromethane sulfonate by light shielding for 1 week. The obtained crystal is yellow and very stable in a couple of organic solvents such as benzene, acetone, and ethyl acetate (orthorhombic, space group P2₁2₁2₁).⁸ Figure 1 shows the X-ray crystal structure of **3**·2(AgOTf)·2(acetone), where anthracene unit made orthogonal crossed structure with adjacent benzene ring, which can catch silver metal cation by coordination bond through cyano groups of anthracene. It means that the fundamental structure of cyano–silver–cyano unit (–CN·Ag·NC–) was formed. It was recognized that four units of **3**·2(AgOTf)·2(acetone) assembled together, which resulted in a formation of big cavity. The longitudinal and lateral direction sizes of the cavity are 17.214 and 16.828 Å, respectively. It was shown that two acetone molecules and two triflate anions were captured in the cavity. The distance between oxygen of acetone and silver was 3.100 and 3.176 Å and the oxygen of triflate and silver was 2.594 and 2.659 Å, respectively. As shown in Figure 2, it was recognized that cancellous sheet with two dimensions was formed, where these sheets get lined up back and forth. It was also indicated that these sheets take

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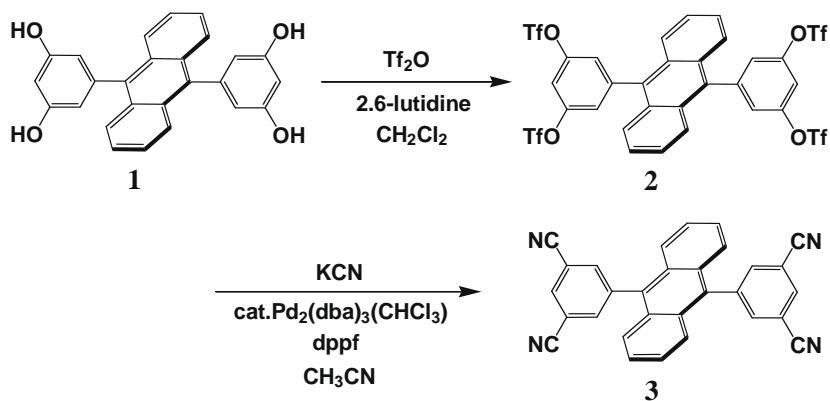
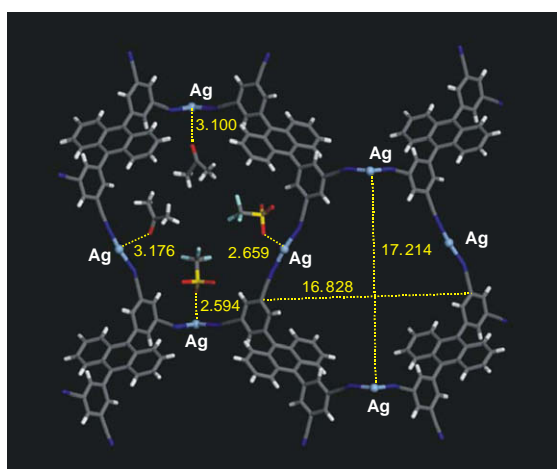
Scheme 1. Preparations of **2** and **3** from **1**.

Figure 1. The fragment of one **3**·2(AgOTf)·2(acetone) layer is drawn using a stick model. Two OTf anions and two acetone molecules reside in the cavity provided by four Ag ions and four **3** ligands.

place with doing a one-eighty, which resulted in the formation of a deep vacant cavity. During the formation of sheets, π - π interactions (edge to edge) were observed at the benzene ring in **3**, of which the distance was 3.513 Å. The side and top views show two sheets lay on running parallel and dogleg shapes of two dimensional sheet structure, respectively. On investigation a

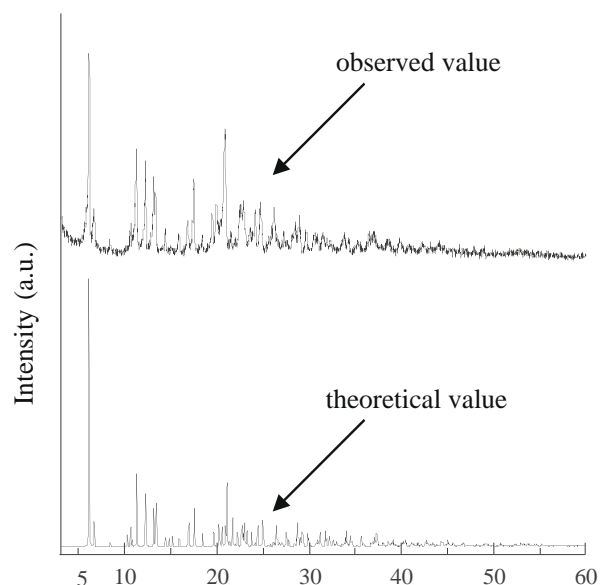


Figure 3. Two XRD patterns for the simulated and evacuated samples are presented and compared.

different nature between **1** and **3**·2(AgOTf)·2(acetone) crystals was observed, and it was recognized that **3**·2(AgOTf)·2(acetone) crystal might be staunch because it was made from $-\text{CN}\cdots\text{Ag}\cdots\text{NC}-$ coordination bonded architecture.

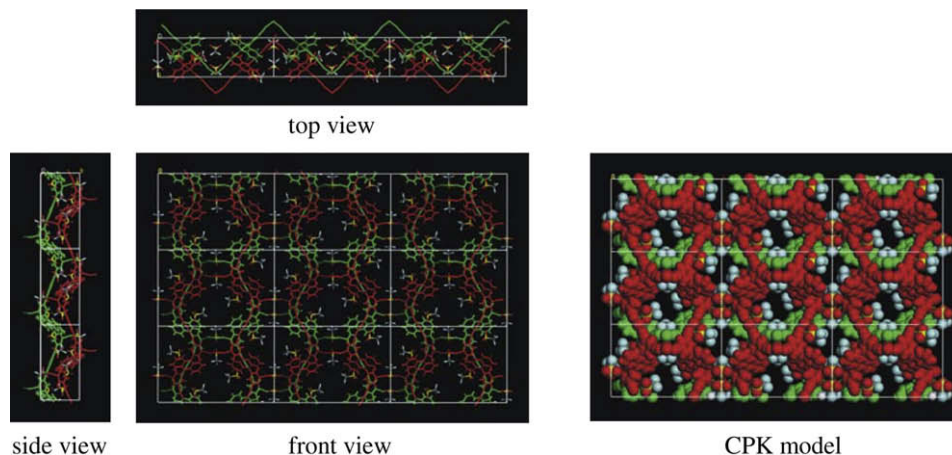


Figure 2. Two **3**·2(Ag) layers are drawn with green and red colors, while the OTf anions are depicted with the default atomic colors. The included acetone molecules have been omitted in order to show the void space clearly.

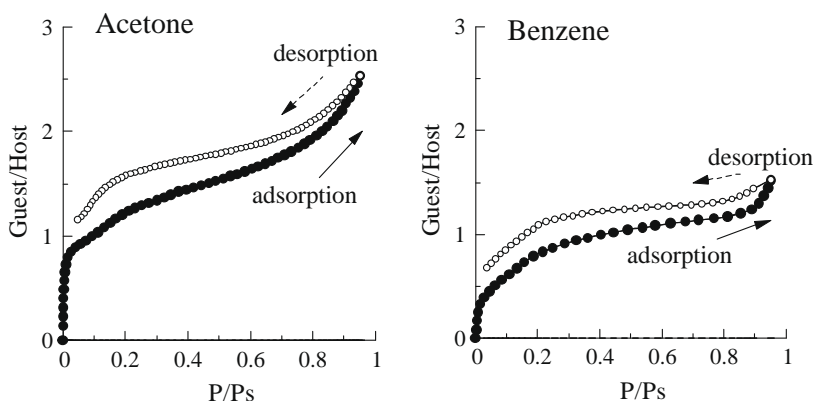


Figure 4. Acetone and benzene adsorption isotherms measured up to a respective vapor pressure, Ps at 298 K. The as-prepared sample, **3**(2AgOTf)·2(acetone) was fully evacuated to remove the occluded acetone molecules before the measurements.

In order to examine whether the crystal cavity exists or not when the guest molecules are excluded, a powder X-ray structure analysis was done. Single crystal of **3**·2(AgOTf)·2(acetone) was dried to remove the acetone at 60 °C in vacuo to give acetone-free apohost **3**·2(AgOTf). As shown in Figure 3, it was recognized that the existence of the same peaks of theoretical figures were confirmed. It means that the structure of **3**·2(AgOTf) was rigid because the cavity remained in existence when guests were excluded. To investigate the capability of adsorption for guest molecules, vapor adsorption analysis for apohost was done. The isotherm measurements for acetone or benzene were performed at 298 K by using an automatic volumetric adsorption apparatus (BELSORP 18SP-V; BEL Inc). It was recognized that 50 mL of acetone and 30 mL of benzene were absorbed per 1.0 g of apohost, respectively. It means that apohost adsorbed 2 acetone molecules and 1 benzene molecule per apohost complex, respectively. It was suggested that the difference of adsorption behavior between acetone and benzene was dependent on these molecular sizes. At the first stage of an absorption near the 0 of P/Ps, it shows that the 1 acetone molecule and 0.5 benzene molecule were captured in the cavity of the apohost, as shown in Figure 4. The curve of absorption isotherm indicates that the cavity of apohost continued to exist under the guest-free situation. It means that apohost has the same size cavity under all conditions.

In this study, tetraphenylcyano derivative of anthracene (**3**) has been successfully prepared by the reaction of tetra triflates of bis(resorcinol) derivative of anthracene (**2**) treated with KCN. In the complex, **3**·2(AgOTf)·2(acetone) system gets 2D cancellous structure, where cyano groups make coordination linkage with Ag (I) resulting in making a hole structure. On investigation by using X-ray powder diffraction and vapor adsorption analysis, it was recognized that apohost is keeping whole structure even on the guest-free situation. The hole size is capable to adsorb 2 acetone molecules per **3**·2(AgOTf) complex.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.10.044.

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- Preparation of triflate derivative of 9,10-bis(3,5-dihydroxy-1-phenyl)anthracene (**2**): To a CH₂Cl₂ solution (300 mL) containing **1** (3.24 g, 8.25 mmol) cooled in ice bath, 2,6-lutidine (19.06 mL, 80.25 mmol) and trifluoromethane sulfonic anhydride (14.7 mL, 80.25 mmol) were added and stirred for 6 h. at room temperature. The reaction mixture was concentrated in vacuo, and the obtained residue was extracted with chloroform. The chloroform layer was washed with water, saturated copper sulfate solution, water, and saturated saline. The organic layer was dried over Na₂SO₄, and filtered, evaporated to crude product, which was then washed with ethanol and filtered to give a triflate derivative 9,10-bis(3,5-dihydroxy-1-phenyl)anthracene (6.77 g, 89% yield). ¹H NMR (300 MHz, DMSO-*d*₆/CDCl₃): δ 8.260 (s, 2H, phenyl-H), 7.825–7.833 (d, 4H, phenyl-H), 7.519 (m, 8H, anthracene-H).
- Preparation of cyano derivative of 9,10-bis(3,5-dihydroxy-1-phenyl)anthracene (**3**): To a solution of 50 mL of CH₃CN containing **2** (4.32 g, 4.70 mmol), tris(dibenzylideneacetone)-dipalladium(0)chloroform adduct (0.389 g, 0.380 mmol), 1,1'-bis(diphenylphosphino)ferrocene (0.844 g, 1.50 mmol), KCN (2.59 g, 40.0 mmol) were added. The reaction mixture was stirred at 50 °C for 24 h. Then, the reaction mixture was concentrated to remove organic solvents and extracted with chloroform. The organic layer was concentrated under reduced pressure to give oily residue, which was treated with activated carbon filtration, and then purified with alumina flash column chromatography. Elution with chloroform gave fractions containing corresponding product, which was concentrate to remove solvents and the resulting product was treated with a *p*-xylene to give **3** (1.85 g, 92.2% yield) as precipitates. ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.54 (s, 8H, phenyl-H), 8.34 (d, 4H, phenyl-H), 8.74 (s, 2H, anthracene-H). ¹³C NMR (75 MHz, DMSO-*d*₆/CDCl₃): δ 113.9(s), 117.3(s), 126.2(s), 126.9(s), 129.2(s), 133.8(s), 139.0(s), 140.6(s). IR (KBr): 2234 cm⁻¹ (–CN).
- Crystal data: C₃₈H₂₆Ag₂F₆N₄O₈S₂, *M* = 1060.49, colorless, crystal dimensions 0.20 × 0.20 × 0.20 mm, orthorhombic, space group P2₁2₁2₁, *a* = 26.3733(8), *b* = 8.75662(2), *c* = 17.2143(6) Å, *V* = 39755.5(5) Å³, *Z* = 4, Mo *K*α radiation *D*_{calc} = 1.772 g cm⁻³, *T* = 163.2 K, numerical absorption correction, μ(Mo *K*α) = 1.173 cm⁻¹, data collections using Rigaku RAXIS-RAPID imaging plate diffractometer, 44260 measured reflections, 30980 unique reflections (*R*_{int} = 0.059), 4950 observed reflections (*I* > 2.00σ (*I*)), 522 parameters, *R* = 0.0809, w*R* = 0.1623, refined against |*F*|, GOF = 1.6947. All crystallographic data of these crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC No. 690241. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).