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Incorporation of an A1/A2-Difunctionalized Pillar[5]arene into a Metal–Organic Framework

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Supporting Information

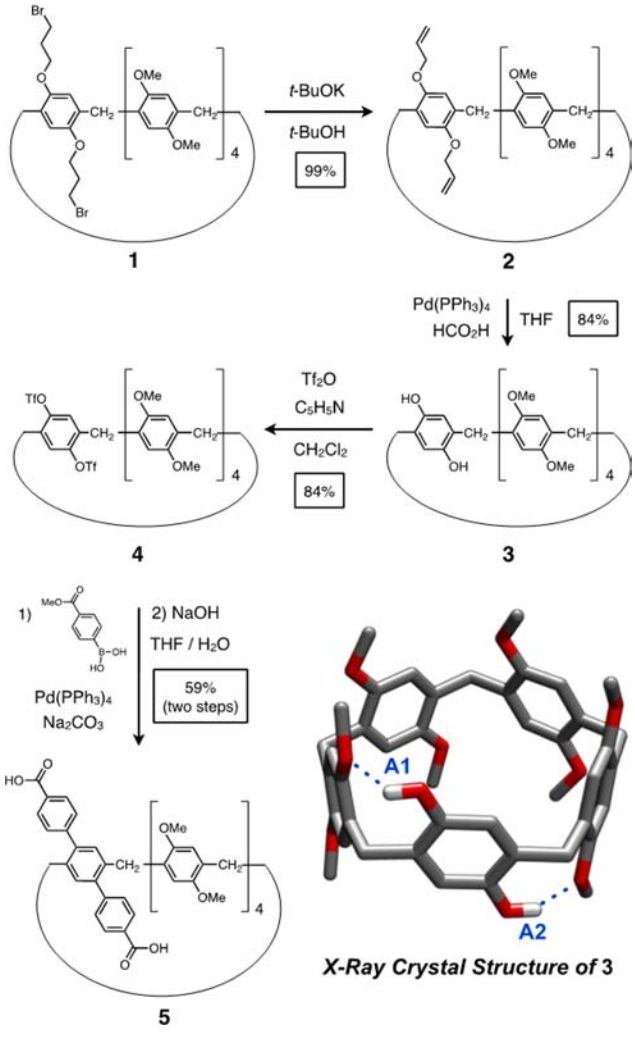
ABSTRACT: An efficient synthetic route to an A1/A2-difunctionalized pillar[5]arene containing resolvable planar chirality has been developed and the arene employed as a strut in the synthesis of **P5A-MOF-1**, which has been demonstrated by X-ray powder diffraction analysis—supported by modeling—to be isoreticular with MOF-5. This metal–organic framework has an active domain that expresses good and selective uptake of neutral and positively charged electron-poor aromatic guests, which effect color changes of the cubic crystals from faint yellow to deep orange, arising from charge transfer between the guests and active domain of **P5A-MOF-1**.

Macrocycles such as cyclodextrins,[1] crown ethers,[2] calixarenes,[3] cucurbiturils,[4] and cyclophanes[5] have become an integral part of host–guest chemistry.[6] A relatively new class of macrocycles to enter the field, the pillararenes,[7] are analogues of calixarenes composed of five, six, or seven hydroquinone rings linked through their para-positions by methylene bridges. Since pillar[5]arene was first introduced as a novel macrocycle by Ogoshi and co-workers in 2008,[7a] the chemistry of the pillararenes has been developed steadily, and they have been shown to have applications in liquid crystals,[7q] artificial transmembrane channels,[7p] nanoparticle formation,[7o] and sensing.[7j] Here we report the synthesis of an A1/A2-difunctionalized[8] pillar[5]arene that undergoes cross-coupling reactions to create a rigid strut which is then incorporated into a metal–organic framework[9] (MOF) having an active domain[10] containing docking sites for electron-poor guests.

MOFs with organic struts incorporating macrocycles have been used recently[10] to prepare extended frameworks with active domains, which, as a result of highly favorable and specific noncovalent interactions, play host to a well-ordered distribution of guest molecules. In 2009, we described[10a] the use of a π-electron-rich BPP34C10-functionalized organic strut in the synthesis of MOF-1001 which was shown to soak up the π-electron-poor guest, methyl viologen. MOFs containing active domains show promise in the fields of chromatographic separation[11] and sensing,[12] thereby making designer organic struts containing novel macrocycles attractive synthetic targets.

We have developed a synthetic protocol (Scheme 1) to obtain an A1/A2-difunctionalized[8] pillar[5]arene organic strut, starting from **1**, which is made through the co-cyclization of 1,4-dimethoxybenzene and 1,4-bis(3-bromopropoxy)benzene, similar to our previously reported[7j] reaction for preparing monofunctionalized pillar[5]arene. Compound **1** undergoes

Scheme 1. Synthesis of A1/A2-Difunctionalized Pillar[5]arene Organic Strut[a]



[a]In the X-ray crystal structure of **3**, C is gray, O is red, H is white; alkyl H atoms are omitted for clarity.

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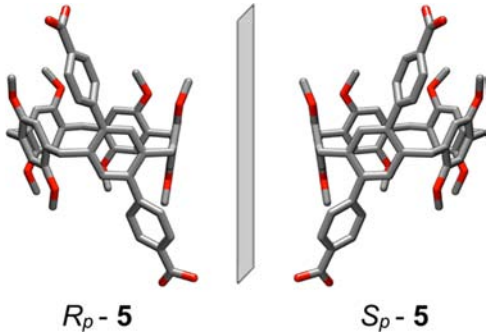

Figure 1. Solid-state structure of **5** (C is gray, O is red) which displays planar chirality and does not racemize between the R_p-**5** (left) and S_p-**5** (right) enantiomers. A DMF molecule and hydrogens have been removed from the structure to aid visual clarity.

elimination to give the diallyl ether **2**, which was deprotected using standard conditions[13] to give the A1/A2-dihydroxy-pillar[5]arene **3**. Single crystals of **3**, suitable for X-ray crystallography, were grown; the solid-state structure[14] (Scheme 1) of **3** shows that the hydroquinone unit is oriented in a direction opposite to that adopted by the 1,4-dimethoxybenzene units to support two intramolecular hydrogen bonds.

Compound **3**, when treated with triflic anhydride, affords the ditriflate **4**. Ogoshi and co-workers[7c] showed that a pertriflated pillar[5]arene can undergo 10 Pd-catalyzed cross-couplings to give a highly conjugated pillar[5]arene. In similar fashion, **4** can be converted into a rigid strut **5** by means of a Pd-catalyzed Suzuki reaction with 4-(methoxycarbonyl)phenylboronic acid, followed by saponification of the intermediate diester. The solid-state structure of **5** (Figure 1) was elucidated by single-crystal X-ray analysis[15] using crystals grown from diffusion of MeOH into a solution of **5** in DMF. The analysis indicates the presence of enantiomers in the unit cell. In keeping with its molecular C_2 symmetry, the ^{1}H NMR spectrum (see SI)[16] of **5** displays two pairs of doublets for the two homotopic pairs of constitutionally hetereotopic methylene groups—where in each case the protons are diastereotopic,[17] given the fact that **5** is conformationally rigid—and a singlet for the remaining constitutionally hetereotopic methylene group lying on the C_2 axis, which renders its methylene protons homotopic. The conformational rigidity of the pillar[5]arene-based strut **5** means that it exists as (potentially resolvable[18,19]) enantiomers, R_p and S_p (Figure 1) due to the molecule's planar chirality.[20] Compound **5** demonstrates that only two bulky monosubstituted phenyl rings are required at the A1/A2 positions on a pillar[5]arene to impart resolvable planar chirality[21] upon its constitution.

The pillar[5]arene-based strut **5** has been used to synthesize a MOF (Figure 2a) with Zn_4O secondary building units (SBUs) which is isoreticular to MOF-5.[9b] **P5A-MOF-1** was prepared in a conventional manner by heating a mixture of **5** and $Zn(NO_3)_2{\cdot}6H_2O$ in DMF at 100 °C over 24 h. The crystals (Figure 3a) of **P5A-MOF-1** are cubic and transparent. Powder X-ray diffraction (PXRD) confirmed their crystallinity (Figure 2b), while thermal gravimetric analysis (TGA) was performed to determine their thermal stability: a one-step TGA profile shows that **P5A-MOF-1** is stable to 450 °C. Crystals of **P5A-MOF-1** were activated using supercritical CO_2, and a NLDFT surface area of 300 $m^2\,g^{-1}$ was obtained from a CO_2 isotherm (see SI).

Single-crystal X-ray data obtained for **P5A-MOF-1** were not well enough resolved to discern the solid-state structure of the extended framework as a result of disorder within the MOF itself.

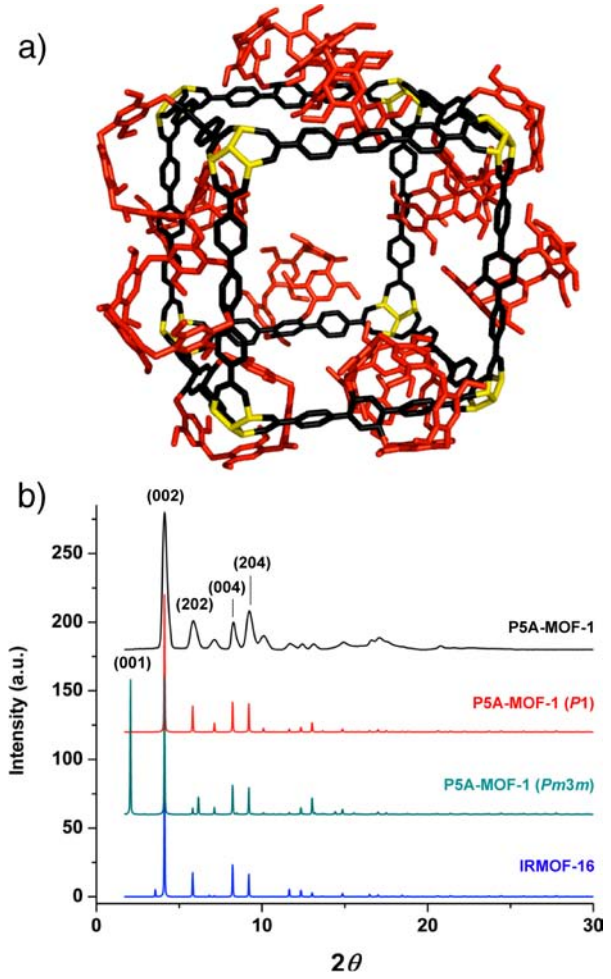

Figure 2. (a) Model of **P5A-MOF-1** (pillar[5]arene macrocycles are red, terphenylene moieties are black, zinc SBUs are yellow). (b) Experimental PXRD pattern for **P5A-MOF-1** (black), calculated PXRD patterns for **P5A-MOF-1** in a *P*1 space group (red) and a *Pm*3*m* space group (green), and PXRD pattern for IRMOF-16 (blue). See SI for full PXRD of **P5A-MOF-1**.

We believe this disorder arises principally from the rotational freedom of pillar[5]arenes around every terphenylene linker in the extended structure and a random distribution of "enantiomeric" pillar[5]arenes associated with their planar chirality.

The extended structure of **P5A-MOF-1** was modeled (see SI) using non-interpenetrated IRMOF-16[9e] as the backbone and incorporating pillar[5]arenes with randomly distributed chiralities and orientations with respect to the terphenylene linkers. The geometry of the predicted structure was optimized to give a cubic unit cell with dimensions of $a = b = c = 42.980$ Å and a space group of *P*1. The simulated PXRD pattern of the modeled structure matches closely with the experimental one for **P5A-MOF-1** (Figure 2b). An alternative approach to modeling the extended structure with a *Pm*3*m* space group was also pursued to determine if a model with higher symmetry might also fit the experimental MOF data. In this alternative model, each organic strut, ordered throughout the 3D framework, contains four pillar[5]arene rings in the shape of both "enantiomers" in two different orientations, each with a 0.25 occupancy disorder. Although the cubic cell dimensions of the model are identical with those of the first model, the simulated PXRD pattern presents extra peaks (Figure 2b), including a sharp 001 reflection.

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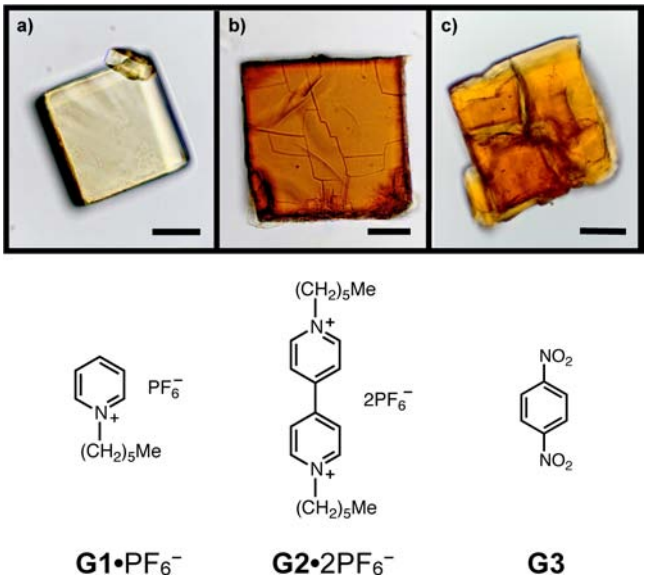

Figure 3. (Top) Optical microscopy images of **P5A-MOF-1** (a) with no guest (scale bar, 200 μm), (b) after uptake of **G2**·2PF$_6$ (scale bar, 100 μm, and (c) after uptake of **G3** (scale bar, 100 μm). (Bottom) Electron-poor compounds used in guest uptake studies with **P5A-MOF-1**: *N*-hexylpyridinium cation (**G1**$^+$), *N*,*N*′-dihexyl-4,4-bipyridinium dication (**G2**$^{2+}$), and 1,4-dinitrobenzene (**G3**).

Thus, it seems that the lower symmetry model provides a better match with the experimental data.

We investigated the ability of **P5A-MOF-1** to take up guests (Figure 3). At the outset, however, we evaluated the ability of the strut **5** to form complexes with three guests:[22] the PF_6^- salts of *N*-hexylpyridinium cation (**G1**$^+$) and *N*,*N*′-dihexyl-4,4-bipyridinium dication (**G2**$^{2+}$), as well as the neutral 1,4-dinitrobenzene (**G3**). ^{1}H NMR titrations in CD_3COCD_3 revealed association constants (K_a) between **5** and **G1**·PF$_6$, **G2**·2PF$_6$, and **G3** of 43.2 ± 2.9, 170 ± 50, and 66.2 ± 1.9 M^{-1}, respectively.

Samples of **P5A-MOF-1** were suspended in Me_2CO prior to guest uptake experiments to remove excess of DMF from within the framework. The samples were then introduced into saturated solutions of **G1**·PF$_6$, **G2**·2PF$_6$, and **G3** in Me_2CO. With **G2**·2PF$_6$ and **G3**, the crystals underwent an immediate color change (Figure 3b,c) from faint yellow to deep orange upon addition of the guests, most likely because of charge-transfer interactions between the guests and **P5A-MOF-1**. The MOF samples were allowed to take up guests for 12 h before they were washed with Me_2CO and dissolved in DMSO-d_6/TFA-d and their ^{1}H NMR spectra recorded. Integration of appropriate probe protons led to quantification of the uptake of guests by the MOF (Table 1). **IRMOF-16-OPX**, prepared from an oligo-*p*-xylene (OPX) derivative[23] (**S3** in SI) of *p*-terphenyl-4,4″-dicarboxylic acid,[24] was used as a control. Although both **P5A-MOF-1** and **IRMOF-16-OPX** are isoreticular with IRMOF-16, the latter does not have an active domain. The guest uptake experiments were performed under identical conditions for both MOFs.

P5A-MOF-1 takes up **G1**·PF$_6$, **G2**·2PF$_6$, and **G3** from their saturated solutions in Me_2CO in moderate to high amounts. Table 1 lists the mole ratios of the guest to the organic strut found in the MOF. The fact that, under identical conditions, **P5A-MOF-1** takes up a significantly larger amount of each guest than does **IRMOF-16-OPX** suggests the active domain of **P5A-MOF-1** is able to interact with guest molecules through favorable noncovalent bonding interactions. Uptake of adamantane, which has been shown[7a] to be too large to reside inside the cavity of pillar[5]arene, but small enough to pass through the pores of either MOF, was similar for both **P5A-MOF-1** and **IRMOF-16-OPX** (see SI).

Table 1. Mole Ratio of Guest to Organic Strut in P5A-MOF-1 and IRMOF-16-OPX, Obtained from ^{1}H NMR Spectra after Guest Uptake and Digestion of MOF[a]

	P5A-MOF-1	IRMOF-16-OPX
	Single-Guest Uptake Experiments	
G1$^+$	0.755	0.121
G2^{2+}	0.366	0.125
G3	0.293	0.084
	Two-Guest Uptake Experiments	
G1$^+$ + **G2**$^{2+}$	0.091 **G1**$^+$/0.176 **G2**$^{2+}$	0.089 **G1**$^+$/0.069 **G2**$^{2+}$
G1$^+$ + **G3**	0.090 **G1**$^+$/0.127 **G3**	0.027 **G1**$^+$/0.032 **G3**
G2^{2+} + **G3**	0.310 **G2**$^{2+}$/0.100 **G3**	0.068 **G2**$^{2+}$/0.014 **G3**

[a]Uptake with a single guest was performed with a saturated solution of the guest in Me_2CO. Uptake with two guests was performed in a Me_2CO solution with each guest at 40.0 mM. K_a values of guest with **5** determined by ^{1}H NMR titration in CD_3COCD_3: **G1**$^+$, 43.2 ± 2.9 M^{-1}; **G2**$^{2+}$, 170 ± 50 M^{-1}; **G3**, 66.2 ± 1.9 M^{-1}.

In a final experiment, **P5A-MOF-1** was suspended in Me_2CO with equimolar concentrations (40.0 mM) of two different guests to determine if there is preferential uptake of one guest over the other. While we envisioned that the observed guest-to-MOF ratios would depend to some extent on the K_a values of the guests with **5** in solution, other factors, including the sizes and diffusion rates of the guests, might also be significant. **P5A-MOF-1** showed almost twice the uptake of **G2**·2PF$_6$ compared to **G1**·PF$_6$ (Table 1), reflecting the larger K_a value for the former than the latter in binding **5**. Under identical conditions, the uptake by **IRMOF-16-OPX** of these two guests is very similar, as expected. Comparable results, which reflect ratios of K_a values, can be observed when **P5A-MOF-1** is exposed to equimolar combinations of the other guests (Table 1).

The rigid stereochemistry associated with the planar chirality of the strut **5** means that it should be possible, after resolving **5**, to prepare "enantiomeric" **P5A-MOF-1** samples without fear of **5** racemizing during the synthesis (at 100 °C) of the MOF. The prospect of being able to prepare chiral, enantiomerically pure, pillar[5]arene-containing MOFs to separate racemic mixtures of appropriate analytes is being pursued in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, modeling, and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Crystal data for **3**: $C_{43}H_{46}O_{10}$, red prism, 0.070 × 0.207 × 0.219 mm^3; monoclinic, space group *C*2; a = 21.2730(3), b = 11.9713(2), and c = 17.7886(2) Å; β = 99.5880(10)°; V = 4466.8(6) $Å^3$; T = 100(2) K, Z = 4, ρ_{calc} = 1.075 g cm^{-3}, μ(Cu Kα) = 0.621 mm^{-1}, F(000) = 1536.0; independent measured reflections, 24 167; $R1$ = 0.0645 and wR_2 = 0.2036 for 7579 independent observed reflections [$2\theta \leq 124°$, $I > 2\sigma(I)$]. CCDC 896923.

(15) Crystal data for **5**: $C_{57}H_{54}O_{12}(C_3H_7NO)$, colorless column, 0.074 × 0.130 × 0.430 mm^3, monoclinic, space group $P2_1/c$; a = 14.5211(2), b = 34.3107(4), and c = 11.87650(10) Å; β = 97.2640(10)°; V = 5869.73(12) $Å^3$; T = 100(2) K, Z = 4, ρ_{calc} = 1.069 g cm^{-3}, μ(Cu Kα) = 0.612 mm^{-1}, F(000) = 2128; independent measured reflections, 39 135; $R1$ = 0.0669 and wR_2 = 0.1648 for 10 348 independent observed reflections [$2\theta \leq 124°$, $I > 2\sigma(I)$]. CCDC 896924.

(16) Two-dimensional NOESY was employed in the assignment of the 1-D ^{1}H NMR spectrum (see SI).

(17) Even at elevated temperatures (100 °C) exchange between the diastereotopic methylene protons is not observed, indicating that the two benzoic acid substituents of **5** render the strut too large to be able to pass through the middle of the annulus which constitutes pillar[5]arene, implying that the inversion between the R_p and S_p enantiomers (Figure 1) does not occur on the NMR time scale, or indeed it would appear, on the laboratory time scale.

(18) At room temperature, the ^{1}H NMR spectra (see SI) for **1**−**4** all display three singlets corresponding to the constiutionally heterotopic methylene groups, indicating that the enantiomeric pairs of these pillar[5]arene derivatives are inverting rapidly on the ^{1}H NMR time scale.

(19) Further proof that the R_p and S_p enantiomers of **5** are resolvable comes from its ^{1}H NMR spectrum (see SI) after addition of a resolving agent—the alkaloid (−)-cinchonidine—revealing multiple resonances for protons, diastereotopic by external comparison, present in the diastereoisomeric acid−base pair (salts).

(20) Further discussion on the planar chirality of pillar[5]arene: Ogoshi, T.; Masaki, K.; Shiga, R.; Kitajima, K.; Yamagishi, T.-a. *Org. Lett.* **2011**, *13*, 1264.

(21) The ^{1}H NMR spectrum of the dimethyl ester (**S1** in SI) of **5** indicates that it is also, as expected, conformationally rigid and so exists as resolvable enantiomers which, in this instance, have been separated (resolved) by chiral HPLC.

(22) Guests similar to $\mathbf{G1}^+$ and $\mathbf{G2}^{2+}$ have previously been reported to bind inside the cavity of pillar[5]arene and the electron/poor nature of **G3** also makes it a suitable guest for **5**. See: Ogoshi, T. *J. Incl. Phenom. Macro.* **2012**, *72*, 247.

(23) The four methyl groups present in **S3** enhance its solubility in organic solvents.

(24) Grunder, S.; Stoddart, J. F. *Chem. Commun.* **2012**, *48*, 3158.