

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

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**S** Supporting Information

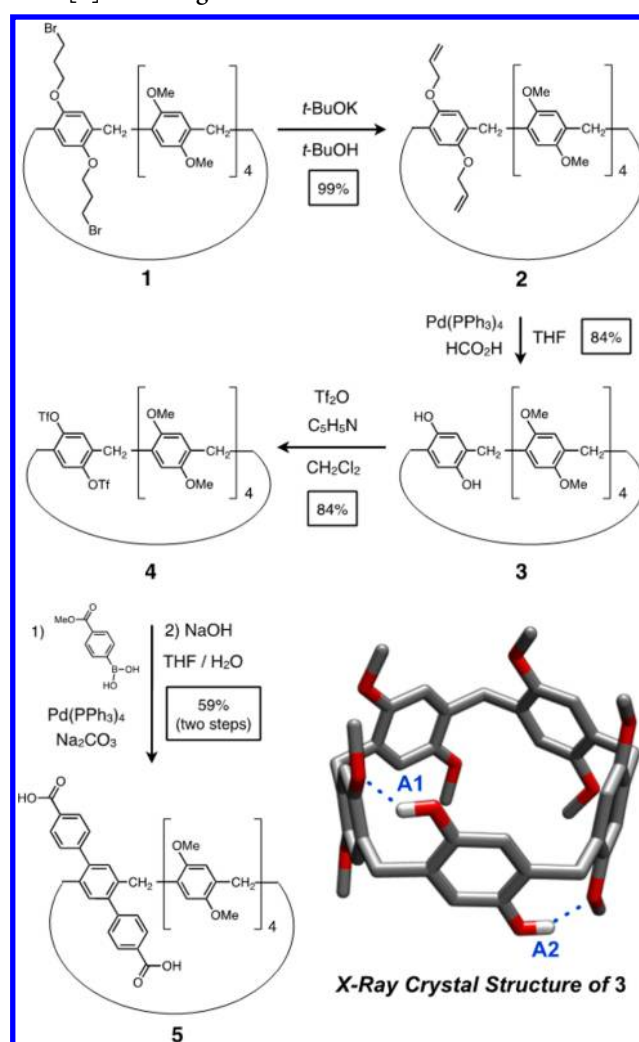
**ABSTRACT:** An efficient synthetic route to an A1/A2-difunctionalized pillar[5]arene containing resolvable planar chirality has been developed and the arene employed as a strut in the synthesis of **PSA-MOF-1**, which has been demonstrated by X-ray powder diffraction analysis—supported by modeling—to be isorecticular 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 **PSA-MOF-1**.

Macrocycles such as cyclodextrins,<sup>1</sup> crown ethers,<sup>2</sup> calixarenes,<sup>3</sup> cucurbiturils,<sup>4</sup> and cyclophanes<sup>5</sup> have become an integral part of host–guest chemistry.<sup>6</sup> A relatively new class of macrocycles to enter the field, the pillararenes,<sup>7</sup> 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,<sup>7a</sup> the chemistry of the pillararenes has been developed steadily, and they have been shown to have applications in liquid crystals,<sup>7q</sup> artificial transmembrane channels,<sup>7p</sup> nanoparticle formation,<sup>7o</sup> and sensing.<sup>7j</sup> Here we report the synthesis of an A1/A2-difunctionalized<sup>8</sup> pillar[5]arene that undergoes cross-coupling reactions to create a rigid strut which is then incorporated into a metal–organic framework<sup>9</sup> (MOF) having an active domain<sup>10</sup> containing docking sites for electron-poor guests.

MOFs with organic struts incorporating macrocycles have been used recently<sup>10</sup> 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<sup>10a</sup> the use of a  $\pi$ -electron-rich BPP34C10-functionalized organic strut in the synthesis of MOF-1001 which was shown to soak up the  $\pi$ -electron-poor guest, methyl viologen. MOFs containing active domains show promise in the fields of chromatographic separation<sup>11</sup> and sensing,<sup>12</sup> 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<sup>8</sup> 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, sim-

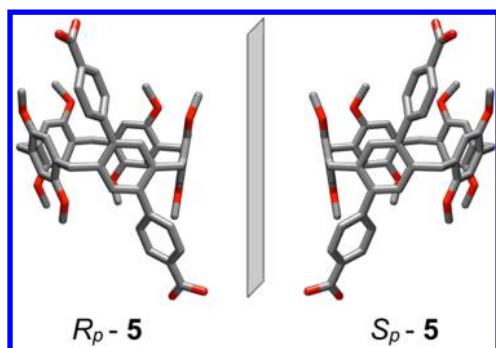
**Scheme 1. Synthesis of A1/A2-Difunctionalized Pillar[5]arene Organic Strut<sup>a</sup>**



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

ilar to our previously reported<sup>7j</sup> reaction for preparing monofunctionalized pillar[5]arene. Compound **1** undergoes

**Received:** August 20, 2012



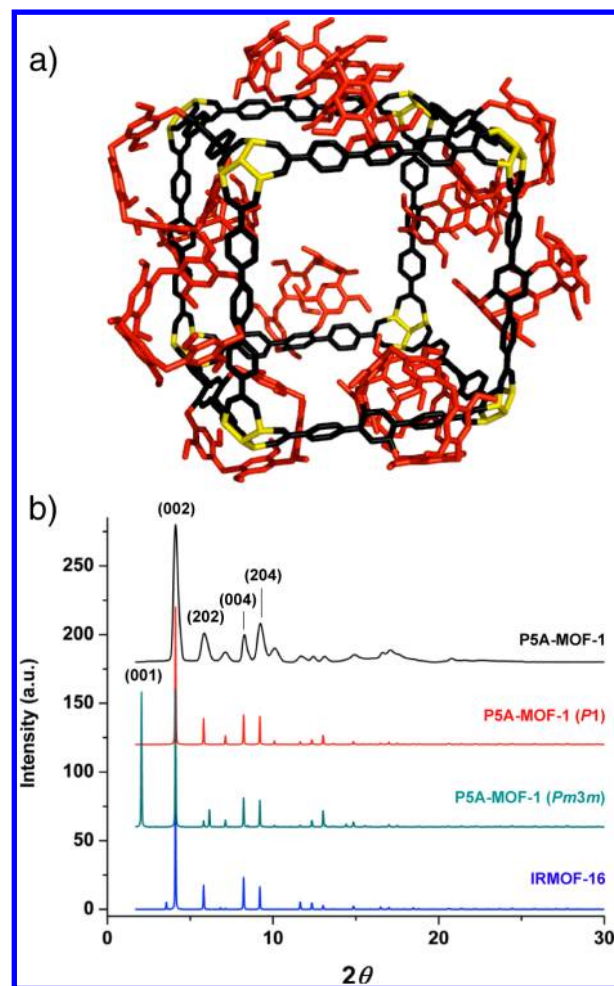
**Figure 1.** Solid-state structure of **5** (C is gray, O is red) which displays planar chirality and does not racemize between the  $R_p$ -**5** (left) and  $S_p$ -**5** (right) enantiomers. A DMF molecule and hydrogens have been removed from the structure to aid visual clarity.

elimination to give the diallyl ether **2**, which was deprotected using standard conditions<sup>13</sup> 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<sup>14</sup> (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<sup>7c</sup> 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<sup>15</sup> 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  $^1\text{H}$  NMR spectrum (see SI)<sup>16</sup> of **5** displays two pairs of doublets for the two homotopic pairs of constitutionally heterotopic methylene groups—where in each case the protons are diastereotopic,<sup>17</sup> given the fact that **5** is conformationally rigid—and a singlet for the remaining constitutionally heterotopic 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<sup>18,19</sup>) enantiomers,  $R_p$  and  $S_p$  (Figure 1) due to the molecule's planar chirality.<sup>20</sup> 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<sup>21</sup> upon its constitution.

The pillar[5]arene-based strut **5** has been used to synthesize a MOF (Figure 2a) with  $\text{Zn}_4\text{O}$  secondary building units (SBUs) which is isoreticular to MOF-5.<sup>9b</sup> **PSA-MOF-1** was prepared in a conventional manner by heating a mixture of **5** and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in DMF at 100 °C over 24 h. The crystals (Figure 3a) of **PSA-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 **PSA-MOF-1** is stable to 450 °C. Crystals of **PSA-MOF-1** were activated using supercritical  $\text{CO}_2$ , and a NLDFT surface area of 300  $\text{m}^2 \text{g}^{-1}$  was obtained from a  $\text{CO}_2$  isotherm (see SI).

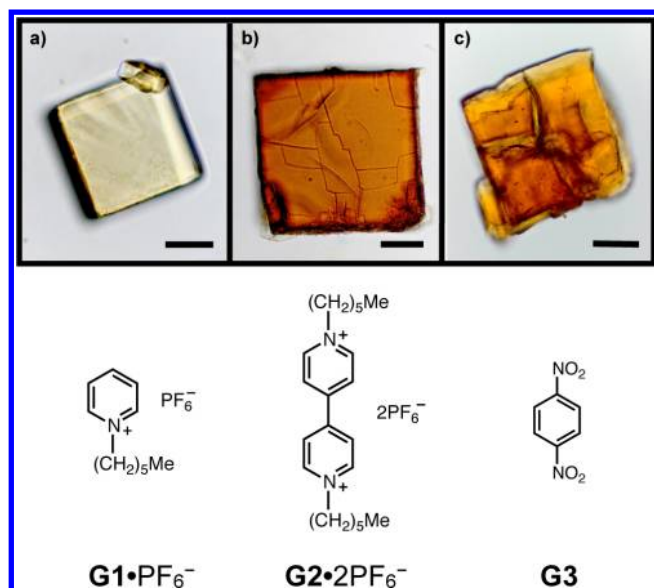
Single-crystal X-ray data obtained for **PSA-MOF-1** were not well enough resolved to discern the solid-state structure of the extended framework as a result of disorder within the MOF itself.



**Figure 2.** (a) Model of **PSA-MOF-1** (pillar[5]arene macrocycles are red, terphenylene moieties are black, zinc SBUs are yellow). (b) Experimental PXRD pattern for **PSA-MOF-1** (black), calculated PXRD patterns for **PSA-MOF-1** in a  $P1$  space group (red) and a  $Pm3m$  space group (green), and PXRD pattern for IRMOF-16 (blue). See SI for full PXRD of **PSA-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 **PSA-MOF-1** was modeled (see SI) using non-interpenetrated IRMOF-16<sup>9e</sup> 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  $a = b = c = 42.980 \text{ \AA}$  and a space group of  $P1$ . The simulated PXRD pattern of the modeled structure matches closely with the experimental one for **PSA-MOF-1** (Figure 2b). An alternative approach to modeling the extended structure with a  $Pm3m$  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.



**Figure 3.** (Top) Optical microscopy images of **PSA-MOF-1** (a) with no guest (scale bar, 200  $\mu\text{m}$ ), (b) after uptake of **G2·2PF<sub>6</sub>** (scale bar, 100  $\mu\text{m}$ ), and (c) after uptake of **G3** (scale bar, 100  $\mu\text{m}$ ). (Bottom) Electron-poor compounds used in guest uptake studies with **PSA-MOF-1**: *N*-hexylpyridinium cation (**G1<sup>+</sup>**), *N,N'*-dihexyl-4,4'-bipyridinium dication (**G2<sup>2+</sup>**), 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 **PSA-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:<sup>22</sup> the  $\text{PF}_6^-$  salts of *N*-hexylpyridinium cation (**G1<sup>+</sup>**) and *N,N'*-dihexyl-4,4'-bipyridinium dication (**G2<sup>2+</sup>**), as well as the neutral 1,4-dinitrobenzene (**G3**). <sup>1</sup>H NMR titrations in  $\text{CD}_3\text{COCD}_3$  revealed association constants ( $K_a$ ) between **5** and **G1·PF<sub>6</sub>**, **G2·2PF<sub>6</sub>**, and **G3** of  $43.2 \pm 2.9$ ,  $170 \pm 50$ , and  $66.2 \pm 1.9 \text{ M}^{-1}$ , respectively.

Samples of **PSA-MOF-1** were suspended in  $\text{Me}_2\text{CO}$  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<sub>6</sub>**, **G2·2PF<sub>6</sub>**, and **G3** in  $\text{Me}_2\text{CO}$ . With **G2·2PF<sub>6</sub>** 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 **PSA-MOF-1**. The MOF samples were allowed to take up guests for 12 h before they were washed with  $\text{Me}_2\text{CO}$  and dissolved in  $\text{DMSO-}d_6/\text{TFA-}d$  and their <sup>1</sup>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<sup>23</sup> (**S3** in SI) of *p*-terphenyl-4,4''-dicarboxylic acid,<sup>24</sup> was used as a control. Although both **PSA-MOF-1** and **IRMOF-16-OPX** are isorecticular with **IRMOF-16**, the latter does not have an active domain. The guest uptake experiments were performed under identical conditions for both MOFs.

**PSA-MOF-1** takes up **G1·PF<sub>6</sub>**, **G2·2PF<sub>6</sub>**, and **G3** from their saturated solutions in  $\text{Me}_2\text{CO}$  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, **PSA-MOF-1** takes up a significantly larger amount of each guest than does **IRMOF-16-OPX** suggests the active domain of **PSA-MOF-1** is able to interact with guest molecules through favorable noncovalent bonding interactions. Uptake of adamantane, which

**Table 1.** Mole Ratio of Guest to Organic Strut in **PSA-MOF-1** and **IRMOF-16-OPX**, Obtained from <sup>1</sup>H NMR Spectra after Guest Uptake and Digestion of MOF<sup>a</sup>

	<b>PSA-MOF-1</b>	<b>IRMOF-16-OPX</b>
Single-Guest Uptake Experiments		
<b>G1<sup>+</sup></b>	0.755	0.121
<b>G2<sup>2+</sup></b>	0.366	0.125
<b>G3</b>	0.293	0.084
Two-Guest Uptake Experiments		
<b>G1<sup>+</sup> + G2<sup>2+</sup></b>	0.091 <b>G1<sup>+</sup></b> /0.176 <b>G2<sup>2+</sup></b>	0.089 <b>G1<sup>+</sup></b> /0.069 <b>G2<sup>2+</sup></b>
<b>G1<sup>+</sup> + G3</b>	0.090 <b>G1<sup>+</sup></b> /0.127 <b>G3</b>	0.027 <b>G1<sup>+</sup></b> /0.032 <b>G3</b>
<b>G2<sup>2+</sup> + G3</b>	0.310 <b>G2<sup>2+</sup></b> /0.100 <b>G3</b>	0.068 <b>G2<sup>2+</sup></b> /0.014 <b>G3</b>

<sup>a</sup>Uptake with a single guest was performed with a saturated solution of the guest in  $\text{Me}_2\text{CO}$ . Uptake with two guests was performed in a  $\text{Me}_2\text{CO}$  solution with each guest at 40.0 mM.  $K_a$  values of guest with **5** determined by <sup>1</sup>H NMR titration in  $\text{CD}_3\text{COCD}_3$ : **G1<sup>+</sup>**,  $43.2 \pm 2.9 \text{ M}^{-1}$ ; **G2<sup>2+</sup>**,  $170 \pm 50 \text{ M}^{-1}$ ; **G3**,  $66.2 \pm 1.9 \text{ M}^{-1}$ .

has been shown<sup>7a</sup> 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 **PSA-MOF-1** and **IRMOF-16-OPX** (see SI).

In a final experiment, **PSA-MOF-1** was suspended in  $\text{Me}_2\text{CO}$  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. **PSA-MOF-1** showed almost twice the uptake of **G2·2PF<sub>6</sub>** compared to **G1·PF<sub>6</sub>** (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 **PSA-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” **PSA-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.

## ■ ACKNOWLEDGMENTS

The authors thank Benjamin Moritz for performing the chiral HPLC studies, Dr. Amy Sarjeant and Dr. Charlotte Stern for performing the PXRDs and single-crystal X-ray crystallography data collection, and Dr. Saman Shafie for performing the mass spectrometry experiments. This work was supported by the Non-



Equilibrium Energy Research Center, which is an Energy Frontier Research Center funded by the U.S. Department of Energy, Offices of Basic Energy Sciences, under Award No. DE-SC0000989. R.Q.S. acknowledges support from the Defense Threat Reduction Agency (HDTRA1-10-1-0023) J.T.H. and O.K.F. gratefully acknowledge financial support from the Defense Threat Reduction Agency (grant No. HDTRA1-09-1-0007). N.L.S. thanks the National Science Foundation for a Graduate Research Fellowship.

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- (14) Crystal data for **3**: C<sub>43</sub>H<sub>46</sub>O<sub>10</sub>, red prism, 0.070 × 0.207 × 0.219 mm<sup>3</sup>; monoclinic, space group C2<sub>1</sub>; *a* = 21.2730(3), *b* = 11.9713(2), and *c* = 17.7886(2) Å;  $\beta$  = 99.5880(10)°; *V* = 4466.8(6) Å<sup>3</sup>; *T* = 100(2) K, *Z* = 4,  $\rho_{\text{calc}}$  = 1.075 g cm<sup>-3</sup>,  $\mu(\text{Cu K}\alpha)$  = 0.621 mm<sup>-1</sup>, *F*(000) = 1536.0; independent measured reflections, 24 167; *R*<sub>1</sub> = 0.0645 and *wR*<sub>2</sub> = 0.2036 for 7579 independent observed reflections [ $2\theta \leq 124^\circ$ , *I* > 2 $\sigma$ (*I*)]. CCDC 896923.
- (15) Crystal data for **5**: C<sub>57</sub>H<sub>54</sub>O<sub>12</sub>(C<sub>3</sub>H<sub>7</sub>NO), colorless column, 0.074 × 0.130 × 0.430 mm<sup>3</sup>, monoclinic, space group P2<sub>1</sub>/c; *a* = 14.5211(2), *b* = 34.3107(4), and *c* = 11.87650(10) Å;  $\beta$  = 97.2640(10)°; *V* = 5869.73(12) Å<sup>3</sup>; *T* = 100(2) K, *Z* = 4,  $\rho_{\text{calc}}$  = 1.069 g cm<sup>-3</sup>,  $\mu(\text{Cu K}\alpha)$  = 0.612 mm<sup>-1</sup>, *F*(000) = 2128; independent measured reflections, 39 135; *R*<sub>1</sub> = 0.0669 and *wR*<sub>2</sub> = 0.1648 for 10 348 independent observed reflections [ $2\theta \leq 124^\circ$ , *I* > 2 $\sigma$ (*I*)]. CCDC 896924.
- (16) Two-dimensional NOESY was employed in the assignment of the 1-D <sup>1</sup>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<sub>p</sub> and S<sub>p</sub> 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 <sup>1</sup>H NMR spectra (see SI) for **1–4** all display three singlets corresponding to the constitutionally heterotopic methylene groups, indicating that the enantiomeric pairs of these pillar[5]arene derivatives are inverting rapidly on the <sup>1</sup>H NMR time scale.
- (19) Further proof that the R<sub>p</sub> and S<sub>p</sub> enantiomers of **5** are resolvable comes from its <sup>1</sup>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 <sup>1</sup>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 G1<sup>+</sup> and G2<sup>2+</sup> 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.