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Anion and Cation Effects on Anion-Templated Assembly of Tetrahydroxytriptycene

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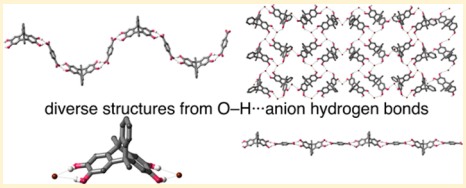
Supporting Information

ABSTRACT: A tetrahydroxytriptycene ligand **1** assembles through O–H···anion hydrogen bonds into a range of different structures. With tetrabutylammonium bromide, **1** forms a stable nanotube structure that is supported by O–H···anion hydrogen bonds, but its space is occupied by the large cation. In an effort to produce the nanotubes with different cations and anions, **1** was crystallized with different salts. The reaction of **1** with tetraethylammonium bromide gives a 2D net structure, while **1** and tetrapropylammonium bromide give a discrete 1:2 complex. Attempting to co-crystallize **1** and tetramethylammonium bromide gave crystals of an oxidized quinone form of the ligand. When **1** was crystallized with tetrabutylammonium terephthalate, two different one-dimensional anion coordination polymers were obtained, depending on the crystallization solvent: acetonitrile gave a zigzag polymer, while methanol gave a linear structure. In both cases, the tetrabutylammonium cations fill the gaps between the 1D polymers, giving a layered 2D morphology. The wide range of architectures prepared from a relatively simple ligand illustrates the potential utility of O–H···anion interactions for constructing solid-state materials.



INTRODUCTION

Research into the supramolecular chemistry of anions[1,2] has tended to focus on their behavior in solution, for example, in the study of synthetic hosts[3−7] and transmembrane transporters for these species.[8−11] Typically these solution-state systems have used hydrogen bonds to interact with the anion of interest,[12−19] although recently halogen bonding has been developed as a potent alternative to hydrogen bonding.[20−24]

O–H hydrogen-bond donors have received little attention, despite such interactions being important in biological anion recognition processes.[25−27] Nevertheless, key studies by the groups of Sessler,[28] Smith,[29] and Gale[30] have shown that aromatic or benzylic alcohols can be effective anion receptors. Recently Wang, Kass, and co-workers have demonstrated that flexible aliphatic polyols also exhibit high chloride anion binding affinities in polar organic solvents.[31−35]

In contrast to metal cations,[36] which have been employed to prepare a range of complex materials including cages,[37,38] interlocked structures,[39,40] and framework materials,[41,42] the use of anions to template the formation of self-assembled supramolecular systems remains underexplored. Pioneering studies by the groups of Wu[43,44] and Kruger and Gunnlaugsson[45] used phosphate or sulfate to form anion-templated cages. A handful of helicates[46−49] and other polymeric structures[50−57] have also been prepared using this methodology—in all cases, these structures are held together by N–H···anion hydrogen bonds. Recently, we demonstrated that O–H···anion hydrogen bonds could be used instead of N–H hydrogen bonds to assemble supramolecular polymers.[58]

We were interested in demonstrating the use of O–H···anion hydrogen bonding to form stable porous materials. We selected triptycene as a component that would help to create a porous structure, as its rigid propeller shape generates large intramolecular free volume (IMFV).[59,60] This property of triptycene has been exploited in the pursuit of porous polymers,[61−64] coordination polymers,[65−68] and porous molecules.[69−72] Using this approach, we recently reported that the triptycene-based ligand **1** containing four phenolic O–H groups[73] assembles with bromide anions to give hexagonal nanotubes with the formula $[\mathbf{1}\cdot(\mathrm{TBA{\cdot}Br})_2]_n$ via O–H···Br^- hydrogen bonding (TBA = tetrabutylammonium cation, Figure 1).[74] Using other

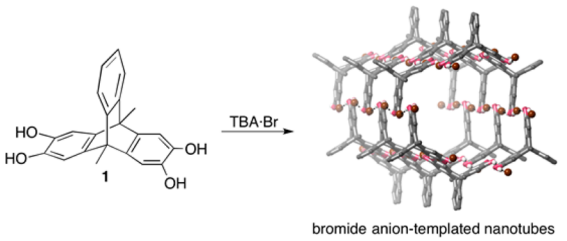


Figure 1. Assembly of **1** and TBA·Br to give solid-state hexagonal nanotubes.[74]

anions (Cl^-, I^-, NO_3^-, or HSO_4^-) did not give crystalline products. The nanotubes could be prepared in bulk, and remarkably, can withstand vacuum, heat, or water without loss of the nanotube structure.

In this work, we extend our investigation of these interesting anion-templated materials by investigating the interaction of **1** with other bromide-containing organic salts. Specifically we

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were interested to see if we can retain the nanotube structure, while reducing the size of the countercation, and in so doing increase the porosity of the anion-templated assemblies. We also study the assembly of **1** and the divalent anion, terephthalate, to form anion-templated polymers.

RESULTS AND DISCUSSION

Effect of Cations. *Background.* It is known that in certain cases, the choice of countercation can greatly affect the *apparent* anion association strength measured in solution.[75] This is particularly the case when association constants are measured in relatively nonpolar solvents such as dichloromethane or chloroform, as in these solvents tetraalkylammonium anion salts often remain ion-paired, reducing the amount of anion available for binding.[76] In other cases, the cation may genuinely affect anion association affinity, for example, by binding to the receptor and modulating the recognition in some way.[75,77]

It is well-established that changing the counteranion in a transition metal-templated system can dramatically influence the structure formed, and a number of elegant metallosupramolecular assemblies have been prepared in this manner.[78−80] In contrast, the effect of countercation on anion-templated assemblies has received almost no attention. Maeda and co-workers have elegantly demonstrated that varying the cation can affect the gross structure and properties of "charge-by-charge" assemblies consisting of a negatively charged planar anion·receptor complex and noncoordinating cations.[81,82] In these systems, while the anion···receptor interactions appear to remain unchanged on varying the countercation, the interactions between the cation and the planar anion·receptor complex as well as the ability of the cations to pack efficiently with the host−guest complex cause dramatic changes in the mesoscale properties of the system.

Solution Studies. Before studying the effect of cations on the solid-state anion-templated structures formed from **1**, we were interested to see if changing the countercation had an influence on the solution binding of bromide anion to **1**. The binding of TEA·Br and TPA·Br to **1** was studied in the polar organic solvent CD_3CN, to allow comparison with previously reported data for TBA·Br. As shown in Table 1, there is very little difference between the association constants recorded for the three different salts, suggesting little cation−anion pairing in the competitive solvent used. Notably, binding is modest in all cases; the highest association constant calculated is 92 M^{-1}, which implies that only about 14% of the bromide anions in a 1:1 mixture of **1** and TBA·Br would be bound to a receptor at the concentrations used for the binding studies, 2.0 mM.

Table 1. Association Constants and Free Energies of Binding of Tetraalkylammonium Salts to 1

salt	K_a[a,b] (M^{-1})	K_a[a,c] (M^{-1})	ΔG^b (kJ mol^{-1})	ΔG^c (kJ mol^{-1})
TEA·Br	76(2)	82(2)	−10.7	−10.9
TPA·Br	68(1)	71(1)	−10.4	−10.6
TBA·Br	85(5)	92(3)	−11.0	−11.2

[a]Estimated standard errors of fitting K_a are given in parentheses. These are the errors in the fitting of the curve and are an approximate measure of the *random* error in the data. They do not account for *systematic* error (such as inaccuracies in the quantities of reagents measured out, or the temperature of the NMR spectrometer), and as such the true uncertainty is probably substantially larger. [b]Fit with WinEQNMR program.[83] [c]Fit with *fittingprogram*.[84]

Crystallization of 1 with "Large" Tetraalkylammonium Salts. Although our primary motivation for this study was to incorporate smaller cations into the nanotube architectures to make more porous structures, we also investigated the crystallization of **1** with larger tetraalkylammonium bromide salts. However, despite several attempts, we were unable to cocrystallize **1** with tetrapentylammonium, tetrahexylammonium, tetraoctylammonium, or hexadecyltrimethylammonium bromide. For each cation, diethyl ether vapor was diffused into a 1:2 stoichiometric mixture of **1** and the salt in three different solvents (dichloromethane,[85] acetone, or acetonitrile), but this gave only oils, or in the case of hexadecyltrimethylammonium bromide, crystals of the tetraalkylammonium salt.[86]

Crystallization of 1 with TPA·Br. Vapor diffusion of diethyl ether into a 1:2 mixture of **1** and TPA·Br in either dichloromethane,[85] acetone, or acetonitrile gave single crystals. In all cases, these crystals had very similar unit cells, and a full data collection was undertaken on the crystals grown from acetonitrile. The single crystal X-ray diffraction (SCXRD) data revealed that a discrete 1:2 complex was formed, $[\mathbf{1}\cdot(TPA\cdot Br)_2]$ (Figure 2). Repeating the crystallization but using a 1:1 ratio of **1** and TPA·Br gave crystals with the same unit cell as $[\mathbf{1}\cdot(TPA\cdot Br)_2]$.

Both O−H groups point toward a single Br^- and form short, linear O−H···Br^- hydrogen bonds (∠O−H···Br: 174 and 175°). H···Br^- distances are 2.35 and 2.40 Å, which is 77−78% of the sum of the van der Waals radii (%$vdW_{H,Br}$).[87,88] In the previously reported nanotube structure,[74] the O−H groups point to the sides facilitating the polymeric structure and are of comparable length (72−83%$vdW_{H,Br}$).[74]

Each bromide anion in $[\mathbf{1}\cdot(TPA\cdot Br)_2]$ is enclosed in a "pocket" composed of TPA cations, although no significant close contacts are observed between the cations and anion (closest contact, H···Br^- = 2.99 Å, 98%$vdW_{H,Br}$). Several close contacts are observed between the hydroxyl oxygen atoms of **1** and TPA cation C−H groups (H···Br: 2.59−2.95 Å, 85−96% $vdW_{H,Br}$), suggesting the presence of weak hydrogen bonds in the solid state.

Crystallization of 1 with TEA·Br. Vapor diffusion of diethyl ether into a 1:2 stoichiometric mixture of **1** and TEA·Br in acetonitrile, methanol, or a chloroform/acetone/methanol mixture gave crystals with similar unit cells.[89] A full data collection was undertaken on the crystals grown from acetonitrile, revealing the formation of a 2D net structure containing a 2:3 ratio of **1**:TEA·Br, i.e., $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]_n$ (Figure 3). Using 1.5, 2.0, or 2.5 equiv of TEA·Br all gave crystals with unit cells consistent with that of $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]_n$. The asymmetric unit cell contains one molecule of **1**, and one and a half TEA cations and bromide anions. Both TEA cations exhibit positional disorder, with one disordered over a site of symmetry. While its identity was apparent, the TEA cation on the symmetry site could not be sensibly modeled, and so PLATON-SQUEEZE was used to include this electron density in the refinement. In order to try and model powder X-ray diffraction data (PXRD, vide infra), a crude refinement of this disordered cation was attempted, but this refinement is of low quality; these refinements are discussed in more detail in the Supporting Information.

As with $[\mathbf{1}\cdot(TPA\cdot Br)_2]$, the structure of $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]_n$ is held together by O−H···Br^- hydrogen bonds, which in this structure vary significantly in length (H···Br^- = 2.36−2.76 Å, 77−90%$vdW_{H,Br}$). One end of **1** has both O−H hydrogen atoms pointing sideways, while at the other end, one O−H

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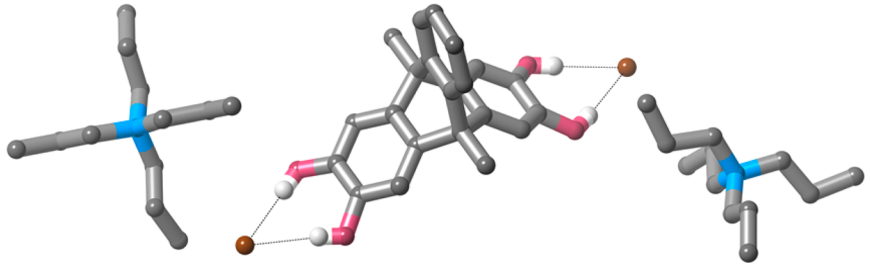

Figure 2. Structure of $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$ determined by SCXRD. Most hydrogen atoms are omitted for clarity.

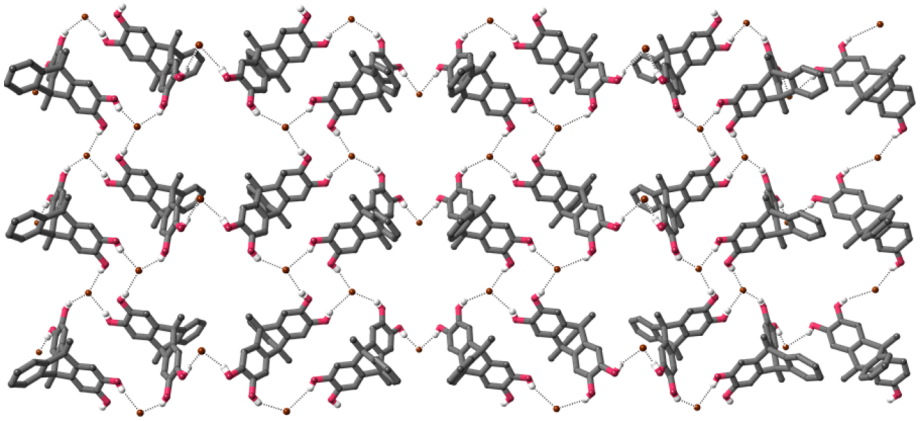

Figure 3. Structure of $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$ determined by SCXRD. TEA cations and most hydrogen atoms are omitted for clarity.

group points sideways and one forward. While analysis is complicated due to the disorder of the TEA cations, it does appear that at least one position of one of the disordered cations engages in a moderately short C−H···O hydrogen bond with a phenolic oxygen atom from **1**.

Bulk Synthesis of $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$ and $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$. The anion-templated structures $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$ and $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$ could be prepared in bulk by simply dissolving the appropriate ratio of **1** and tetraalkylammonium salt in CH_3CN and subjecting these solutions to diethyl ether vapor diffusion. After thorough drying in vacuo, this gave $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$ and $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$ as large single crystals in 62% and 72% yield, respectively. The products were characterized by ^{1}H NMR and IR spectroscopies, as well as elemental, thermogravimetric, and melting point analysis.

PXRD. PXRD was used to determine whether the structure of the bulk products was consistent with that determined by SCXRD. Figure 4 shows the recorded traces and the simulated patterns based on the SCXRD data (see the Supporting Information for further details).

In the case of $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$, there is excellent concordance between the observed PXRD trace and that calculated from the SCXRD structure. For $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$, the agreement is not as good, though the patterns are very similar. We postulate that the small differences are due to the difficulty of adequately modeling the two disordered TEA cations. While one cation could be modeled relatively well, another is disordered over a special position. It was extremely difficult to model this, and effectively this species could take any of a number of positions in this area, which would greatly affect the simulated PXRD trace. While it is not possible to exclude the existence of a different crystalline phase, this seems unlikely as by inspection under a microscope all crystals have the same habit, and several crystals gave indistinguishable unit cells. The possibility of a

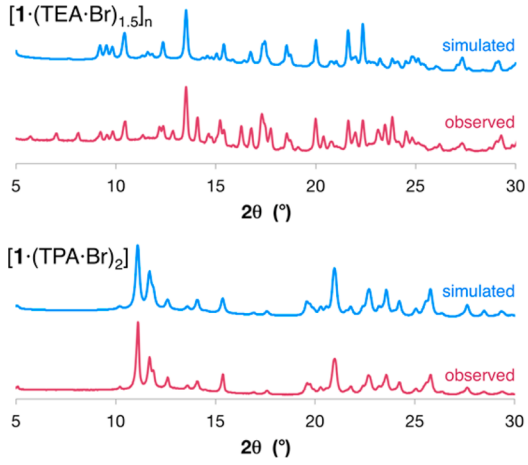

Figure 4. Comparison of observed and simulated PXRD traces for $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$ and $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$.

significant amount of impurity with a different molecular formula can be excluded on the basis of ^{1}H NMR spectroscopy and elemental analysis.

Thermogravimetric Analysis. As shown in Figure 5, both $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$ and $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$ show high thermal stability, with thermal decomposition commencing at approximately 240 °C for $[\mathbf{1}\cdot(\text{TPA}\cdot\text{Br})_2]$ and 280 °C for $[\mathbf{1}\cdot(\text{TEA}\cdot\text{Br})_{1.5}]_n$. The relatively high stability of these molecules is perhaps surprising given the weak interactions used to construct them, and suggests that anion-templated materials may be stable enough for practical applications.

*Crystallization of **1** with TMA·Br.* Diethyl ether vapor diffusion into a 1:2 stoichiometric mixture of **1** and TMA·Br gave a few dark brown crystals.[90] As shown in Figure 6, the SCXRD structure of this product does not contain any TMA·

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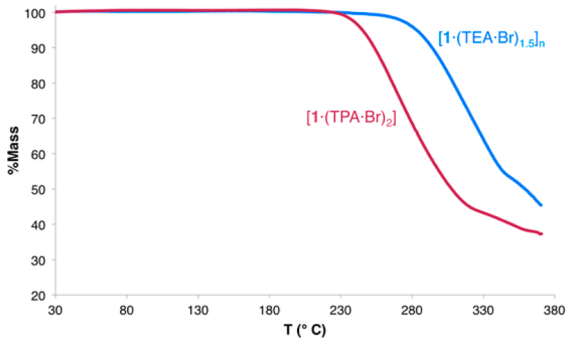

Figure 5. Thermogravimetric analyses of $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]_n$ and $[\mathbf{1}\cdot(TPA\cdot Br)_2]$ (10 °C/min under N_2).

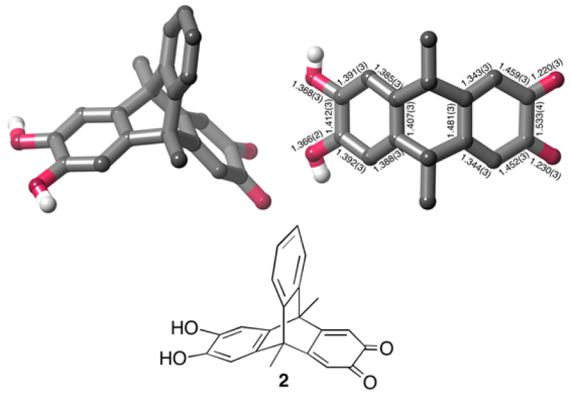

Figure 6. Structure of **2** determined by SCXRD. Most hydrogen atoms are omitted for clarity. Bond lengths are given in Å.

Br, and instead clearly shows that **1** has been partially oxidized to give **2**. In this molecule, one of the catechol rings of **1** has been oxidized to the quinone form. This is evidenced by short C═O bond lengths [1.220(3) and 1.230(3) Å, compared with 1.366(2) and 1.368(3) Å for the catechol O−H groups] and a wide range of C−C ring bond lengths due to the presence of both single and double bonds.

We have previously observed that a hexahydroxytriptycene is readily oxidized to the bis-catechol quinone form during crystal growth.[74] In that case, the ligand could be deliberately oxidized by stirring with base in methanol. In the case of **1**, we could achieve partial oxidation by heating **1** to reflux in the presence of base[91] (KOAc), open to the air in methanol. However, even after extended reaction times, the reaction did not proceed to completion and a mixture of **1** and **2** was obtained.

Effect of Anions. We were unable to obtain any crystalline material containing **1** when attempting to co-crystallize **1** with TBA·Cl, TBA·I, TBA·HSO_4, or TBA·NO_3 despite using a range of solvents and crystallization conditions.[74] This is in stark contrast to the nanotubes $[\mathbf{1}\cdot(TBA\cdot Br)_2]_n$, which crystallize readily from a wide range of solvents. We have now investigated the assembly of **1** with terephthalate (TP) anions, to see what the effect of using a 2^- anion would be on the self-assembled structure. We were unable to investigate the solution binding of TP, as addition of this anion to **1** caused the O−H resonance to disappear (no other resonances showed significant movement upon anion addition).

Zigzag Anion Coordination Polymer $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$. Dissolving **1** and $TBA_2\cdot TP$ in acetonitrile and leaving the mixture to stand gave a microcrystalline precipitate, which has the formula $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$. This material was isolated in 58% yield, and its identity was confirmed by ^1H NMR and IR spectroscopies. Carefully layering a solution of $TBA_2\cdot TP$ in acetonitrile with an acetonitrile solution of **1** gave single crystals suitable for SCXRD studies. The complex is a 1D anion coordination polymer with a zigzag structure that is held together by O−H···O hydrogen bonds (Figure 7).

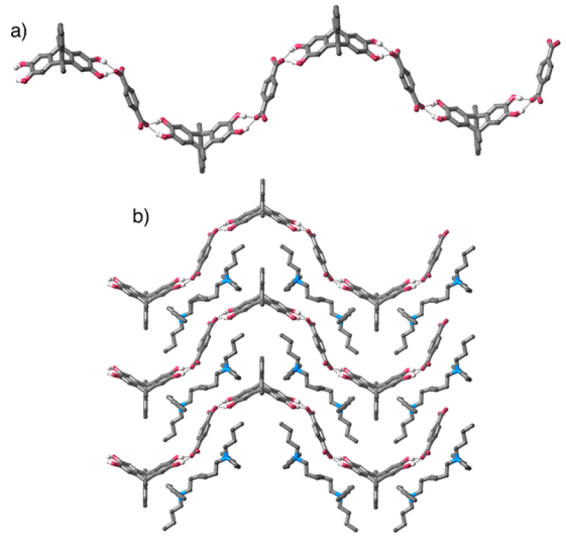

Figure 7. Solid-state structure of zigzag anion coordination polymer $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$ as determined by SCXRD: (a) image showing zigzag polymer composed of **1** and terephthalate anions; (b) image showing alternating layered structure (most hydrogen atoms and acetonitrile solvent are omitted for clarity).

The asymmetric unit cell of $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$ contains one TBA cation, half a TP anion, and half a molecule each of **1** and CH_3CN. The two crystallographically independent O−H groups form convergent hydrogen bonds to one of the carboxylate oxygen atoms. These hydrogen bonds are very short, H···O distances are 1.76 and 1.77 Å, 65% and 66% $vdW_{H,O}$ [O···O distances = 2.611(1) and 2.583(1), ∠O−H···O = 171 and 161°, respectively]. The other TP carboxylate oxygen atom is not involved in significant hydrogen bonding. The TBA cations sit between the 1D anion coordination polymers, giving an overall 2D layered structure.

Linear Anion Coordination Polymer $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$. Vapor diffusion of diethyl ether into a solution of the bulk product $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$ in methanol gave a few colorless crystals (and a very deep purple-brown solution). SCXRD showed that these are a linear 1D anion coordination polymer, $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$ (Figure 8). The asymmetric unit cell contains half a molecule of **1**, half a TP anion, and one TBA cation. A region of ill-defined diffuse electron density believed to arise from disordered solvent molecules could not be sensibly refined, and so PLATON-SQUEEZE was used to include the electron density in the refinement.

The polymer is held together by short O−H···O hydrogen bonds between the hydroxyl groups of **1**, which both point inward. The H···O distances are 1.75 and 1.78 Å, which equates to 64 and 66% $vdW_{H,O}$, respectively [O···O distances = 2.613(2) and 2.600(2), ∠O−H···O = 170 and 159°, respectively]. As was observed for the zigzag anion coordination polymer, the TBA cations sit between the 1D chains, giving an overall 2D layered structure.

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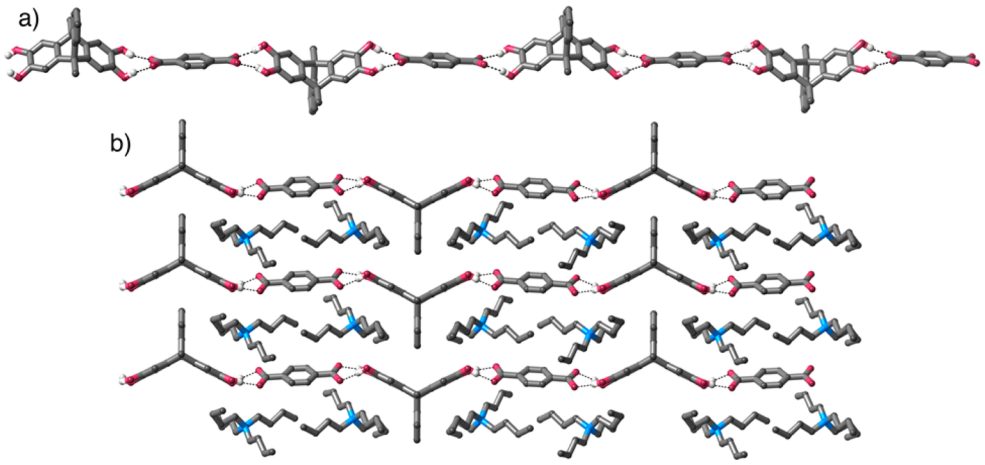

Figure 8. Solid-state structure of linear anion coordination polymer $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$ as determined by SCXRD: (a) image showing linear polymer composed of **1** and terephthalate anions; (b) image showing alternating layered structure (most hydrogen atoms omitted for clarity, PLATON-SQUEEZE has been used).

We were not able to isolate this material in bulk, as a significant amount of **1** appears to be oxidized when it is dissolved in methanol. A methanol solution of **1** containing $TBA_2\cdot TP$ rapidly turns purple, and if the bulk product $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$ is dissolved in CD_3OD or DMSO-d_6, new peaks become visible in the ^1H NMR spectrum within a few minutes, which appear to correspond to the partially oxidized form, **2**. Interestingly, while oxidation begins within minutes, even after 2 weeks in CD_3OD, complete conversion of **1** to **2** is not observed.

DISCUSSION

While crystallizing **1** with smaller tetraalkylammonium bromide salts did not allow us to isolate the desired porous nanotube architectures, we were able to prepare other robust bulk materials via anion-templation. Changing from TBA to TPA to TEA results in nanotube,[74] discrete, and net-like architectures, respectively. It is surprising that varying the tetraalkylammonium cation has such a profound effect on the structure and hydrogen-bonding arrangement of the anion-templated materials.

As previously discussed, Maeda and co-workers have elegantly demonstrated that varying the cation can affect the gross structure and properties of "charge-by-charge" assemblies.[81,82] However, in their systems, the structural changes are thought to arise from packing of the anion and cation rather than the anion···receptor hydrogen-bonding arrangement. In contrast, in the complexes containing **1**, the coordination between the host and receptor is disrupted by varying the cation.

The solution binding data (vide supra) indicate that the cation has a negligible influence on the solution behavior of these systems, as would be expected for these "non-coordinating" cations. However, on crystallization, a dramatic structure-directing effect is observed.

These systems bear an interesting resemblance to counter-anion-templated transition metal complexes[78−80] as a significantly weaker force (interactions between the alkylammonium cations and **1** in our case, interactions between ligand and anions in the case of counteranion templation) has a major influence on product structure. This occurs even in the presence of a stronger structure-directing synthon (O−H···Br hydrogen bonding in our system, metal···ligand coordination in the case of counteranion templation.)

In the case of the anion coordination polymers prepared from **1** and $(TBA)_2\cdot TP$, changing solvent caused a significant change in the architecture of the supramolecular polymer. A change in the hydrogen-bonding arrangement was also observed. Notably, in both cases, the hydrogen bonds are short.

Two different effects can be considered when trying to rationalize the formation of the various different anion-templated products in this work: either maximizing the various weak intermolecular forces present, or trying to form a close-packed product. In the bromide-templated materials, there appear to be some relatively close contacts between the alkylammonium cations and **1**; however, the disorder present in the cations of the TEA and TBA-containing structures means that we cannot draw firm conclusions about the impact of these short contacts on the nature of the product formed.

The close-packing argument may explain why we were unable to obtain crystalline material containing alkylammonium cations larger than TBA. However, the nanotube structure of $[\mathbf{1}\cdot(TBA\cdot Br)_2]_n$ contains significant void space, yet still forms reproducibly.

Taken together, we suggest that a mixture of several factors determines the architecture of these anion-templated systems. These factors include satisfying the O−H···anion hydrogen bonding requirements of the ligand and anion, achieving reasonably efficient crystal packing (minimizing void space), and "secondary" hydrogen-bonding interactions between the alkylammonium cation and the ligand.

CONCLUSIONS

Several anion-templated structures have been assembled using O−H···Br^- or O−H···terephthalate hydrogen bonds. In the case of the bromide anion-templated architectures $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]_n$ and $[\mathbf{1}\cdot(TPA\cdot Br)_2]$, these materials can be prepared in bulk in good yields and display high thermal stability. When **1** was crystallized in the presence of TMA·Br in methanol, crystals of an oxidized form of **1** were obtained. We also observed partial oxidation of **1** beginning almost immediately when it was dissolved in CD_3OD or DMSO-d_6 in the presence of $TBA_2\cdot TP$. Despite this, single crystals of two different forms of 1D anion coordination polymers could be obtained by

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growing the crystals from two different solvents, and one of these could be prepared in bulk in good yield.

All of the various anion-templated structures reported in this paper (discrete complex, 2D net, different 1D anion coordination polymers) are obtained from a relatively simple tetrahydroxytriptycene ligand. We suggest that design and synthesis of more complex ligands will allow the preparation of practically useful anion-templated materials. Work toward this goal is underway.

EXPERIMENTAL SECTION

General Remarks. Dimethyltetrahydroxytriptycene **1** was prepared as previously described.[92] Tetrapentylammonium bromide was prepared from tetrapentylammonium iodide by washing a CH_2Cl_2 solution of this compound repeatedly with $NH_4Br_{(aq)}$. Tetrabutylammonium terephthalate was prepared from terephthalic acid and tetrabutylammonium hydroxide in methanol/water as previously described.[93] All other reagents were bought from commercial suppliers and used as received. Details of instrumentation are given in the Supporting Information.

Synthesis of $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]_n$. Dimethyltetrahydroxytriptycene **1** (35 mg, 0.10 mmol) and TEA·Br (32 mg, 0.15 mmol) were dissolved in acetonitrile (5 mL) and subjected to diethyl ether vapor diffusion. Over 2−4 days, large pale brown crystals developed; these were isolated by filtration, washed with copious diethyl ether, and thoroughly dried in vacuo to give $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]_n$ as pale brown single crystals. Yield: 41 mg (0.062 mmol, 62%).

^{1}H NMR (CD_3CN, 5.0 mM, 300 MHz): 7.25−7.31 (m, 2H), 6.96−7.02 (m, 2H), 6.85 (s, 4H), 6.72* (br. s, 4H), 3.14 (q, J = 7.3 Hz, 12H), 2.21 (s, 6H), 1.19 (apparent tt, J = 7.3 Hz, 1.8 Hz, 18H) ppm.

**Peak disappears on addition of D_2O.*

IR: ∼ 3150 cm^{-1} (broad, O−H stretch). EA: C 61.7, H 7.5, N 3.5%; calc. for $[\mathbf{1}\cdot(TEA\cdot Br)_{1.5}]$, $C_{34}H_{48}N_{1.5}O_4Br_{1.5}$: C 61.7, H 7.3, N 3.2%. mp 218.5−219.5 °C.

Synthesis of $[\mathbf{1}\cdot(TPA\cdot Br)_2]$. Dimethyltetrahydroxytriptycene **1** (35 mg, 0.10 mmol) and TPA·Br (53 mg, 0.20 mmol) were dissolved in acetonitrile (5 mL) and subjected to diethyl ether vapor diffusion. Over 2−4 days, large pale brown crystals developed; these were isolated by filtration, washed with copious diethyl ether, and thoroughly dried in vacuo to give $[\mathbf{1}\cdot(TPA\cdot Br)_2]$ as pale brown single crystals. Yield: 67 mg (0.072 mmol, 72%).

^{1}H NMR (CD_3CN, 5.0 mM, 300 MHz): 7.25−7.30 (m, 2H), 6.96−7.01 (m, 2H), 6.86* (br. s, 8H), 3.01−3.07 (m, 16H), 2.21 (s, 6H), 1.58−1.71 (m, 16H), 0.94 (t, J = 7.3 Hz, 24H) ppm.

**Peak intensity reduces on addition of D_2O.*

IR: ∼ 3190 cm^{-1} (broad, O−H stretch). EA: C 62.8, H 8.7, N 3.3%; calc. for $[\mathbf{1}\cdot(TPA\cdot Br)_2]$, $C_{46}H_{74}N_2O_4Br_2$: C 62.9, H 8.5, N 3.2%. mp 180.0−181.0 °C.

Synthesis of $[\mathbf{1}\cdot TP\cdot(TBA)_2]_n$. A solution of TBA_2·TP (26 mg, 0.040 mmol) in CH_3CN (2 mL) was added to a solution of **1** in CH_3CN (14 mg, 0.040 mmol) in a vial. The solution was stirred briefly, then the vial was sealed and left to stand overnight giving a sandy-colored microcrystalline precipitate. This was isolated by filtration, washed with CH_3CN (3 × 1 mL) and CH_2Cl_2 (3 × 1 mL) and dried in vacuo to give $[\mathbf{1}\cdot TP\cdot(TBA)_2]$. Yield: 23 mg (0.023 mmol, 58%).

^{1}H NMR (CD_3OD, 300 MHz): 7.95 (s, 4H), 6.77 (s, 4H), 7.20−7.26 (m, 2H), 6.92−6.98 (m, 2H), 3.19 (t, J = 8.4 Hz, 16 H), 2.20 (s, 6H), 1.58−1.68 (m, 16H), 1.34−1.46 (m, 16H), 1.01 (J = 7.3 Hz, 24H). IR: ∼ 3000 (broad, obscured, O−H stretch), 1736 (C−O stretch), 1366 (C−O stretch), 1229 (C−O stretch), 1217 (C−O stretch). mp. ∼ 230 °C (dec.).

X-ray Crystallography. SCXRD data were collected on a Bruker APEX DUO diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54178 Å). All data were collected at 90 K to a resolution of 0.77 Å. Raw frame data (including data reduction, interframe scaling, unit cell refinement, and absorption corrections) for all structures were processed using APEX2.[94] Structures were solved using SUPERFLIP[95] and refined using full-matrix least-squares on F^2 within the CRYSTALS suite.[96] Unless otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generally visible in the Fourier difference map and were initially refined with restraints on bond lengths and angles, after which the positions were used as the basis for a riding model.[97] Individual structures are discussed in more detail in the Supporting Information. Full crystallographic data in CIF format are provided as Supporting Information [CCDC Numbers: 1400478−1400480 and 1418005−1418007].

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b01342.

Details of instrumentation, NMR spectra and photographs of new compounds, details of SCXRD and PXRD, and solution anion binding studies (PDF)

Full crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Evans, N. H.; Beer, P. D. *Angew. Chem., Int. Ed.* **2014**, *53*, 11716−11754.

(2) Busschaert, N.; Caltagirone, C.; Van Rossom, W.; Gale, P. A. *Chem. Rev.* **2015**, *115*, 8038−8155.

(3) Custelcean, R. *Chem. Soc. Rev.* **2014**, *43*, 1813−1824.

(4) Cai, J.; Sessler, J. L. *Chem. Soc. Rev.* **2014**, *43*, 6198−6213.

(5) Gale, P. A.; Caltagirone, C. *Chem. Soc. Rev.* **2015**, *44*, 4212−4227.

(6) Elmes, R. B. P.; Jolliffe, K. A. *Chem. Commun.* **2015**, *51*, 4951−4968.

(7) Dutta, R.; Ghosh, P. *Chem. Commun.* **2015**, *51*, 9070−9084.

(8) Davis, J. T.; Gale, P. A.; Okunola, O. A.; Prados, P.; Iglesias-Sánchez, J. C.; Torroba, T.; Quesada, R. *Nat. Chem.* **2009**, *1*, 138−144.

(9) Busschaert, N.; Gale, P. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 1374−1382.

(10) Ko, S.-K.; Kim, S. K.; Share, A.; Lynch, V. M.; Park, J.; Namkung, W.; van Rossom, W.; Busschaert, N.; Gale, P. A.; Sessler, J. L.; Shin, I. *Nat. Chem.* **2014**, *6*, 885−892.

(11) Lisbjerg, M.; Valkenier, H.; Jessen, B. M.; Al-Kerdi, H.; Davis, A. P.; Pittelkow, M. *J. Am. Chem. Soc.* **2015**, *137*, 4948−4951.

(12) Gale, P. A. *Chem. Commun.* **2008**, 4525−4540.

(13) Kubik, S. *Chem. Soc. Rev.* **2009**, *38*, 585−605.

(14) Li, A.-F.; Wang, J.-H.; Wang, F.; Jiang, Y.-B. *Chem. Soc. Rev.* **2010**, *39*, 3729−3745.

(15) Amendola, V.; Fabbrizzi, L.; Mosca, L. *Chem. Soc. Rev.* **2010**, *39*, 3889−3915.

(16) Cai, J.; Sessler, J. L. *Chem. Soc. Rev.* **2014**, *43*, 6198−6213.

(17) Ramabhadran, R. O.; Liu, Y.; Hua, Y.; Ciardi, M.; Flood, A. H.; Raghavachari, K. *J. Am. Chem. Soc.* **2014**, *136*, 5078−5089.

(18) Edwards, S. J.; Valkenier, H.; Busschaert, N.; Gale, P. A.; Davis, A. P. *Angew. Chem., Int. Ed.* **2015**, *54*, 4592−4596.

DOI: 10.1021/acs.cgd.5b01342
Cryst. Growth Des. XXXX, XXX, XXX−XXX

(19) Qiao, B.; Sengupta, A.; Liu, Y.; McDonald, K. P.; Pink, M.; Anderson, J. R.; Raghavachari, K.; Flood, A. H. *J. Am. Chem. Soc.* **2015**, *137*, 9746−9757.
(20) Beale, T. M.; Chudzinski, M. G.; Sarwar, M. G.; Taylor, M. S. *Chem. Soc. Rev.* **2013**, *42*, 1667−1680.
(21) Sarwar, M. G.; Dragisić, B.; Dimitrijević, E.; Taylor, M. S. *Chem. - Eur. J.* **2013**, *19*, 2050−2058.
(22) Langton, M. J.; Robinson, S. R.; Marques, I.; Félix, V.; Beer, P. D. *Nat. Chem.* **2014**, *6*, 1039−1043.
(23) Robinson, S. R.; Mustoe, C.; White, N. G.; Brown, A.; Thompson, A. L.; Kennepohl, P.; Beer, P. D. *J. Am. Chem. Soc.* **2015**, *137*, 499−507.
(24) Gilday, L. C.; Robinson, S. W.; Barendt, T. A.; Langton, M. J.; Mullaney, B. R.; Beer, P. D. *Chem. Rev.* **2015**, *115*, 7118−7195.
(25) Pflugrath, J. W.; Quiocho, F. A. *Nature* **1985**, *314*, 257−260.
(26) Luecke, H.; Quiocho, F. A. *Nature* **1990**, *347*, 402−406.
(27) Dutzler, R.; Campbell, E. B.; Cadene, M.; Chait, B. T.; MacKinnon, R. *Nature* **2002**, *415*, 287−294.
(28) Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154−157.
(29) Smith, D. K. *Org. Biomol. Chem.* **2003**, *1*, 3874−3877. Winstanley, K. J.; Sayer, A. M.; Smith, D. K. *Org. Biomol. Chem.* **2006**, *4*, 1760−1767.
(30) Busschaert, N.; Jaramillo-Garcia, J.; Light, M. E.; Herniman, J.; Langley, G. J.; Gale, P. A. *RSC Adv.* **2014**, *4*, 5389−5393.
(31) Shokri, A.; Schmidt, J.; Wang, X.-B.; Kass, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 2094−2099.
(32) Shokri, A.; Schmidt, J.; Wang, X.-B.; Kass, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 16944−16947.
(33) Shokri, A.; Wang, X.-B.; Kass, S. R. *J. Am. Chem. Soc.* **2013**, *135*, 9525−9530.
(34) Shokri, A.; Kass, S. R. *Chem. Commun.* **2013**, *49*, 11674−11676.
(35) The same authors have also recently reported a preorganized tripodal alcohol-based anion receptor that displays strong anion recognition through O−H···anion hydrogen bonds: Shokri, A.; Deng, S. H. M.; Wang, X.-B.; Kass, S. R. *Org. Chem. Front.* **2014**, *1*, 54−61.
(36) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734−777.
(37) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418−3438.
(38) Ronson, T. K.; Zarra, S.; Black, S. P.; Nitschke, J. R. *Chem. Commun.* **2013**, *49*, 2476−2490.
(39) Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Kintzinger, J.-P. *Tetrahedron Lett.* **1983**, *24*, 5095−5098.
(40) Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurney, R. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 9260−9327.
(41) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 5962−5964.
(42) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 974−987.
(43) Wu, B.; Cui, F.; Lei, Y.; Li, S.; de Sousa Amadeu, N.; Janiak, C.; Lin, Y.-J.; Weng, L.-H; Wang, Y.-Y.; Yang, X.-J. *Angew. Chem., Int. Ed.* **2013**, *52*, 5096−5100.
(44) Yang, D.; Zhao, J.; Zhao, Y.; Lei, Y.; Cao, L.; Yang, X.-J.; Davi, M.; de Sousa Amadeu, N.; Janiak, C.; Zhang, Z.; Wang, Y.-Y.; Wu, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 8658−8661.
(45) Pandurangan, K.; Kitchen, J. A.; Blasco, S.; Boyle, E. M.; Fitzpatrick, B.; Feeney, M.; Kruger, P. E.; Gunnlaugsson, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 4566−4570.
(46) Sánchez-Quesada, J.; Seel, C.; Prados, P.; de Mendoza, J. *J. Am. Chem. Soc.* **1996**, *118*, 277−278.
(47) Haketa, Y.; Maeda, H. *Chem. - Eur. J.* **2011**, *17*, 1485−1492.
(48) Li, S.; Jia, C.; Wu, B.; Luo, Q.; Huang, X.; Yang, Z.; Li, Q.-S.; Yang, X.-J. *Angew. Chem., Int. Ed.* **2011**, *50*, 5721−5724.
(49) Schneebeli, S. T.; Frasconi, M.; Liu, Z.; Wu, Y.; Gardner, D. M.; Strutt, N. L.; Cheng, C.; Carmieli, R.; Wasielewski, M. R.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2013**, *52*, 13100−13104.
(50) Hosseini, M. W.; Ruppert, R.; Schaeffer, P.; De Cian, A.; Kyritsakas, N.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2135−2136.
(51) Brooks, S. J.; Gale, P. A.; Light, M. E. *CrystEngComm* **2005**, *7*, 586−591.
(52) Chifotides, H.; Schottel, B. L.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 7202−7207.
(53) Wang, T.; Yan, X.-P. *Chem. - Eur. J.* **2010**, *16*, 4639−4649.
(54) Zhang, Z.; Kim, D. S.; Lin, C.-Y.; Zhang, H.; Lammer, A. D.; Lynch, V. M.; Popov, I.; Miljanić, O. M.; Anslyn, E. V.; Sessler, J. L. *J. Am. Chem. Soc.* **2015**, *137*, 7769−7774.
(55) Gong, H.-Y.; Rambo, B. M.; Karnas, E.; Lynch, V. M.; Sessler, J. L. *Nat. Chem.* **2010**, *2*, 406−409.
(56) Gong, H.-Y.; Rambo, B. M.; Lynch, V. M.; Keller, K. M.; Sessler, J. L. *J. Am. Chem. Soc.* **2013**, *135*, 6330−6337.
(57) Wang, J.; Li, S.; Yang, P.; Huang, X.; Yang, X.-J.; Wu, B. *CrystEngComm* **2013**, *15*, 4540−4548.
(58) White, N. G.; Carta, V.; MacLachlan, M. J. *Cryst. Growth Des.* **2015**, *15*, 1540−1545.
(59) Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301−3315.
(60) Ma, Y.-X.; Meng, Z.; Chen, C.-F. *Synlett* **2014**, *26*, 6−30.
(61) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864−11873.
(62) Gulam Rabbani, M.; Reich, T. E.; Kassab, R. M.; Jackson, K. T.; El-Kaderi, H. M. *Chem. Commun.* **2012**, *48*, 1141−1143.
(63) Sekizkardes, A. K.; Islamoglu, T.; Kahveci, Z.; El-Kaderi, H. M. *J. Mater. Chem. A* **2014**, *2*, 12492−12500.
(64) Sekizkardes, A. K.; Altarawneh, S.; Kahveci, Z.; Islamoglu, T.; El-Kaderi, H. M. *Macromolecules* **2014**, *47*, 8328−8334.
(65) Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2006**, *45*, 1442−1444.
(66) Vagin, S.; Ott, A.; Weiss, H.-C.; Karbach, A.; Volkmer, D.; Rieger, B. *Eur. J. Inorg. Chem.* **2008**, *2008*, 2601−2609.
(67) Vagin, S. I.; Ott, A. K.; Hoffmann, S. D.; Lanzinger, D.; Rieger, B. *Chem. - Eur. J.* **2009**, *15*, 5845−5853.
(68) Crane, A. K.; Patrick, B. O.; MacLachlan, M. J. *Dalton Trans.* **2013**, *42*, 8026−8033.
(69) Chong, J. H.; Ardakani, S. J.; Smith, K. J.; MacLachlan, M. J. *Chem. - Eur. J.* **2009**, *15*, 11824−11828.
(70) Mastalerz, M.; Oppel, I. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 5252−5255.
(71) Zhang, G.; Mastalerz, M. *Chem. Soc. Rev.* **2014**, *43*, 1934−1947 and references therein.
(72) Taylor, R. G. D.; Carta, M.; Bezzu, C. G.; Walker, J.; Msayib, K. J.; Kariuki, B. M.; McKeown, N. B. *Org. Lett.* **2014**, *16*, 1848−1851.
(73) Chen and co-workers have reported studies on the solid-state assembly of hydroxy-substituted triptycenes through intermolecular hydrogen bonding, and through hydrogen bonding to neutral 4,4′-bipyridine: Zhang, C.; Chen, C.-F. *CrystEngComm* **2010**, *12*, 3255−3261. Han, Y.; Jiang, Y.; Chen, C.-F. *Chin. Chem. Lett.* **2013**, *24*, 475−478.
(74) White, N. G; MacLachlan, M. J. *Chem. Sci.* **2015**, *6*, 6245−6249.
(75) Sessler, J. L.; Gross, D. E.; Cho, W.-S.; Lynch, V. M.; Schmidtchen, F. P.; Bates, G. W.; Light, M. E.; Gale, P. A. *J. Am. Chem. Soc.* **2006**, *128*, 12281−12288.
(76) Alunni, S.; Pero, A.; Reichenbach, G. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1747−1750.
(77) Hua, Y.; Ramabhadran, R. O.; Karty, J. A.; Raghavachari, K.; Flood, A. H. *Chem. Commun.* **2011**, *47*, 5979−5981.
(78) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1838−1840.
(79) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Dupont-Gervais, A.; Van Dorsselaer, A.; Kneisel, B.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 10956−10962.
(80) Chifotides, H. T.; Dunbar, K. R. *Acc. Chem. Res.* **2013**, *46*, 894−906.

DOI: 10.1021/acs.cgd.5b01342
Cryst. Growth Des. XXXX, XXX, XXX−XXX

(81) Haketa, Y.; Sasaki, S.; Ohta, N.; Masunaga, H.; Ogawa, H.; Mizuno, N.; Araoka, F.; Takezoe, H.; Maeda, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 10079−10083.
(82) Dong, B.; Terashima, Y.; Haketa, Y.; Maeda, H. *Chem. - Eur. J.* **2012**, *18*, 3460−3463.
(83) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311−312.
(84) Thordarson, P. *Chem. Soc. Rev.* **2011**, *40*, 1305−1323.
(85) **1** is not soluble in dichloromethane, so **1** and tetraalkylammonium bromide salts were combined in acetone, evaporated to dryness under reduced pressure, and the resulting oil dissolved in dichloromethane.
(86) Crystals gave a unit cell that matched a previously-determined structure of trimethylhexadecylammonium bromide: Prukala, W.; Marciniec, B.; Kubicki, M. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2007**, *E63*, o1464−o1466.
(87) Alvarez, S. *Dalton Trans.* **2013**, *42*, 8617−8636.
(88) For a more detailed explanation of the advantages and disadvantages of using %vdWH,X to describe hydrogen bonding parameters, see: White, N. G.; Serpell, C. J.; Beer, P. D. *Cryst. Growth Des.* **2014**, *14*, 3472−3479.
(89) TEA·Br is not soluble in chlorinated solvents or acetone, so we could not use these solvents (as we had for TPA·Br or TBA·Br).
(90) TMA·Br is not sufficiently soluble in chlorinated solvents, acetone or acetonitrile to allow their use.
(91) Deprotonation of catechol is known to increase its tendency to oxidize: Dei, A.; Sorace, L. *Dalton Trans.* **2003**, 3382−3386.
(92) Zong, Q.-S.; Chen, C.-F. *Org. Lett.* **2006**, *8*, 211−214.
(93) Campanelli, A. R.; Scaramuzza, L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1986**, *C42*, 1380−1383.
(94) *APEX2*, 2007; Bruker AXS Inc., Madison, Wisconsin, USA.
(95) Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786−790.
(96) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.
(97) Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Crystallogr.* **2010**, *43*, 1100−1107.

DOI: 10.1021/acs.cgd.5b01342
Cryst. Growth Des. XXXX, XXX, XXX−XXX