# Guest Exchange through Single Crystal–Single Crystal Transformations in a Flexible Hydrogen-Bonded Framework

Wenchang Xiao, Chunhua Hu, and Michael D. Ward*

Molecular Design Institute, Department of Chemistry, New York University, 100 Washington Square East, New York, New York 10003-6688, United States

S *Supporting Information*

ABSTRACT: A molecular framework based on guanidinium cations and 1,2,4,5-tetra(4-sulfonatophenyl)benzene (TSPB), an aromatic tetrasulfonate with nominal 2-fold and mirror symmetry, exhibits three crystallographically unique one-dimensional channels as a consequence of molecular symmetry and complementary hydrogen bonding between the guanidinium (G) ions and the sulfonate (S) groups of TSPB. Unlike previous GS frameworks, this new topology is sufficiently flexible to permit reversible release and adsorption of guest molecules in large single crystals through a cyclic shrinkage and expansion of the channels with retention of single crystallinity, as verified by single crystal X-ray diffraction. Moreover, the G_4TSPB framework permits guest exchange between various guest molecules through SCSCTs as well as exchange discrimination based on the size and character of the three different channels. The exchange of guest molecules during single crystal–single crystal transformations (SCSCT), a rare occurrence for hydrogen-bonded frameworks, is rather fast, with diffusivities of approximately 10^{-6} cm^2 s^{-1}. Rapid diffusion in the two channels having cross sections sufficient to accommodate two guest molecules can be explained by two-way or ring diffusion, most likely vacancy assisted. Surprisingly, rapid guest exchange also is observed in a smaller channel having a cross-section that accommodates only one guest molecule, which can only be explained by guest-assisted single-file unidirectional diffusion. Several single crystals of inclusion compounds can be realized only through guest exchange in the intact framework, suggesting an approach to the synthesis of single crystalline inclusion compounds that otherwise cannot be attained through direct crystallization methods.
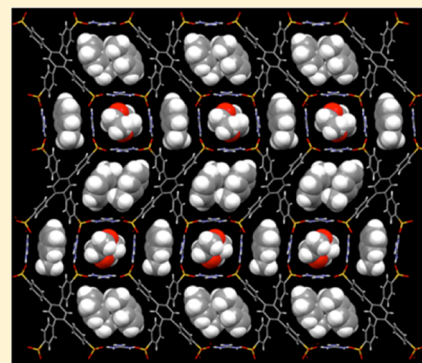
INTRODUCTION

Low-density molecular frameworks serve as platform for new materials owing to the ability to tailor the size, geometry, and chemical character of their free space through the versatility of organic synthesis. As such, molecular frameworks have been invoked as promising candidates for storage,[1] separation,[2] guest exchange,[3] and heterogeneous catalysis.[4] The utility of these frameworks, however, relies on robust architectures with predictable pore structure and control of pore characteristics. The achievement of low-density molecular frameworks with stable and permanent porosity remains a challenge, however.[5] The design and synthesis of low-density hydrogen-bonded frameworks has produced a rich variety of inclusion compounds wherein pores are occupied by guest molecules,[6] but with few exceptions[6c−f] HB frameworks typically collapse when guest molecules are removed, unlike many metal−organic frameworks (MOFs) or coordination networks, including those with intrinsic flexibility.[7] In the absence of evidence that confirms a single crystal−single crystal transformation and retention of framework single crystallinity, guest exchange often can be explained by a sequential loss of guest molecules, collapse of the framework, and nucleation and regrowth of the framework with the new guest incorporated.

Our laboratory and others have reported the design and construction of molecular frameworks built from two-dimensional quasihexagonal hydrogen-bonded networks of guanidinium (G) and sulfonate (S) groups of organomonosulfonates and disulfonates.[8−14] Through judicious selection of the organic residues attached to the sulfonate groups, the size, shape and chemical character of inclusion cavities flanked by the organosulfonate "pillars" can be adjusted in a rational manner. The inherent compliance of the 2D GS network permits the frameworks to adopt a range of architectures, from lamellar to cylindrical, depending on the particular host−guest combination.[15,16] These compounds, now more than 450 reported, demonstrate the versatility of guanidinium−sulfonate hydrogen bonds in framework design.

Herein, we report a new GS framework built from an aromatic tetrasulfonate with nominal mirror and 2-fold rotational symmetry, 1,2,4,5-tetra(4-sulfonatophenyl)benzene (TSPB). We surmised that this tetrasulfonate had the potential to produce three distinct framework architectures, lamellar, a zeolite-like framework constructed from truncated octahedra,[17] or stacks of two-dimensional grids, as illustrated schematically
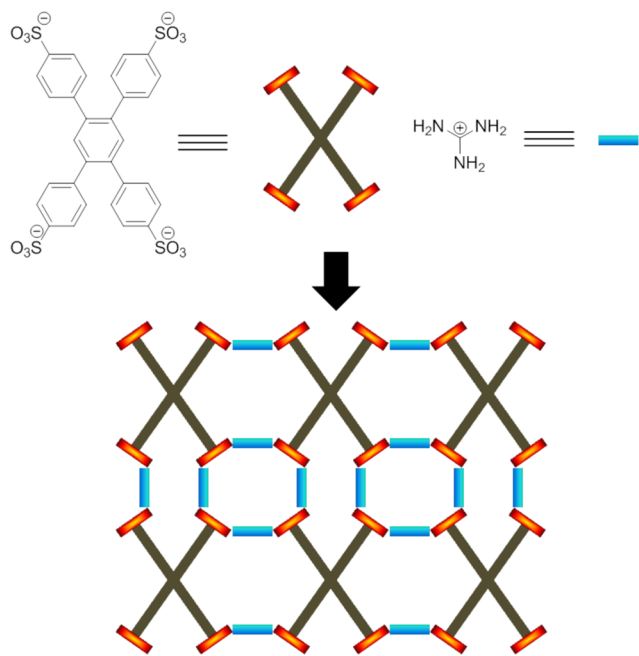
Figure 1. Schematic representation of a two-dimensional GS hydrogen bonded grid formed by guanidinium cations and TSPB anions.

in Figure 1 and reported here. This new framework exhibits three crystallographically unique one-dimensional channels, with reversible release and reabsorption of dioxane molecules in one of the channels through cyclic "breathing" of the channels with retention of single crystallinity, adding to the relatively few examples of single crystal–single crystal transformations (SCSCT) in hydrogen-bonded frameworks.[18−20] Moreover, the G₄TSPB framework permits guest exchange between various guest molecules through SCSCTs as well as exchange discrimination based on the size and character of the three different channels. These observations suggest opportunities for storage of molecular compounds as well as the synthesis of crystalline inclusion compounds that cannot be attained through direct crystallization protocols.

■ MATERIALS AND METHODS

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO) and used as received.

Synthesis of Guanidinium 1,2,4,5-Tetra(4-sulfonatophenyl)-benzene (G₄TSPB). Two grams of 1,2,4,5-tetrabromo-benzene, 3.66 g of phenylboronic acid, 0.3 g of tetrakis(triphenylphosphine)-palladium and 8.3 g of K_2CO_3 were suspended in a solution comprising 30 mL of ethanol, 30 mL of water, and 60 mL of toluene. The mixture was heated at 95 °C for 18 h. After the solution cooled to room temperature, 300 mL of toluene was added and the mixture was stirred for 1 h. The organic layer was washed with 1 M NaOH twice and then dried with anhydrous $MgSO_4$. Excess toluene was removed by rotary evaporator, and the solid product was recrystallized in hexane to afford 1.2 g of an off-white solid (1,2,4,5-tetraphenylbenzene, yield = 62% based on 1,2,4,5-tetrabromo-benzene). The solid was then heated under reflux in 6 mL of 95% H_2SO_4 for 18 h, after which the hot solution was poured into 100 mL of deionized water. NaOH was added to adjust the pH to pH = 14, and then 1.7 g of N(butyl)₄Cl was added. The mixture was then extracted with CH_2Cl_2, the organic layer was dried with anhydrous $MgSO_4$, and excess solvent was removed. The resulting solid was then passed through a column packed with Amberlyst 36 ion-exchange resin. To the eluent was added 2 g of guanidinium tetrafluoroborate. The mixture was then dried with a rotary evaporator, and the resulting solid mixture was washed with hot

acetone several times and dried by allowing standing in air at room temperature, affording 1.7 g of off-white **G₄TSPB**. ¹H NMR (400M, DMSO): 7.50 (d, 8H), 7.43 (s, 2H), 7.19 (d, 8H), 6.94 (s, 24H). Elemental Anal. Calcd for $C_{34}H_{46}O_{12}S_4N_{12}$: C (43.28%), H (4.88%), N (17.82%). Found: C (43.55%), H (5.03%), N (18.35%). IR: 3417 (w), 3195 (w), 1667 (s), 1179 (w), 1127 (s), 1035 (s), 1008 (s), 1000 (s), 832 (s), 753 (s), 691 (m), 661 (s).

Preparation of G₄TSPB·(dioxane)₅. Twenty milligrams of G₄TSPB was dissolved in 0.4 mL of water, followed by diffusion of dioxane vapor into the solution, affording single crystals. Elemental Anal. Calcd for $C_{54}H_{86}O_{22}S_4N_{12}$: C (46.89%), H (6.22%), N (12.17%). Found: C (47.31%), H (6.38%), N (12.05%). IR: 3368 (w), 3194 (w), 1663 (s), 1596 (w), 1475 (m), 1187 (w), 1121 (s), 1036 (s), 1000 (m), 873 (s), 830 (s), 755 (s), 660 (m).

Preparation of G₄TSPB·(dioxane)₄. Single crystals of G₄TSPB·(dioxane)₅ were exposed to air under ambient conditions for 1 day, affording G₄TSPB·(dioxane)₄. Elemental Anal. Calcd for $C_{50}H_{78}O_{20}S_4N_{12}$: C (46.37%), H (6.03%), N (12.98%). Found: C (46.24%), H (6.11%), N (12.69%). IR: 3367 (w), 3196 (w), 1663 (s), 1596 (w), 1475 (m), 1187 (w), 1121 (s), 1036 (s), 1001 (m), 873 (s), 830 (s), 755 (s), 660 (m).

Preparation of G₄TSPB·(tetrahydrofuran)₅. Single crystals of G₄TSPB·(dioxane)₅ were immersed in tetrahydrofuran for 4 h, affording G₄TSPB·(tetrahydrofuran)₅. Elemental Anal. Calcd for $C_{54}H_{86}O_{17}S_4N_{12}$: C (49.77%), H (6.61%), N (12.90%). Found: C (49.62%), H (6.52%), N (13.17%). IR: 3421 (w), 3360 (w), 3174 (s), 1669 (s), 1187 (s), 1128 (s), 1034 (s), 1008 (s), 829 (s), 692 (s), 656 (s), 579 (s), 537 (s).

Preparation of G₄TSPB·(toluene)₃(dioxane). Single crystals of G₄TSPB·(dioxane)₅ were immersed in toluene for 4 h, crystals affording G₄TSPB·(toluene)₃(dioxane). Elemental Anal. Calcd for $C_{59}H_{78}O_{14}S_4N_{12}$: C (54.21%), H (5.97%), N (12.86%). Found: C (53.88%), H (6.03%), N (12.96%). IR: 3419 (w), 3178 (w), 1669 (s), 1187 (s), 1128 (s), 1034 (s), 1008 (s), 828 (s), 692 (s), 659 (s), 579 (s).

Preparation of G₄TSPB·(toluene)₃(tetrahydrofuran)₀.₅. Single crystals of G₄TSPB·(tetrahydrofuran)₅ were immersed in toluene for 4 h, affording G₄TSPB·(toluene)₃(tetra-hydrofuran)₀.₅. Elemental Anal. Calcd for $C_{57}H_{74}O_{12.5}S_4N_{12}$: C (54.54%), H (5.90%), N (13.39%). Found: C (54.10%), H (6.03%), N (13.67%). IR: 3421 (w), 3360 (w), 3174 (s), 1669 (s), 1187 (s), 1128 (s), 1034 (s), 1008 (s), 828 (s), 692 (s), 656 (s), 579 (s), 537 (s).

Characterization. Infrared spectra were collected with a Magna-IR spectrometer 550. NMR data was collected under Bruker AV-400 High Performance Digital NMR Spectrometer (400 MHz). Thermal gravimetric analysis (TGA) was performed with a PerkinElmer Pyris 1. Elemental analysis was performed with a PerkinElmer Series II 2400. Single crystal X-ray diffraction data was collected on a Bruker SMART APEX II diffractometer equipped with a CCD detector and operated at 1,500W power (50KV, 30 mA) to generate Mo Kα radiation (λ = 0.71073 Å), which is graphite monochromated and MonoCap-collimated. See Supporting Information for details. Powder X-ray diffraction (PXRD) was performed with a Bruker D8 Discover Microdiffractometer with the General Area Detector Diffraction System (GADDS) equipped with a VÅNTEC-2000 2D detector. The X-ray beam was monochromated with a graphite crystal (λ Cu Kα = 1.54178 Å) and collimated with a 0.5 mm capillary collimator (MONOCAP). See Supporting Information for details.

■ RESULTS AND DISCUSSION

Slow diffusion of dioxane vapor into an aqueous solution containing 0.05 mM G₄TSPB, prepared from the acid form of TSPB and guanidinium tetrafluoroborate, afforded colorless crystals with a block-like morphology and the composition G₄TSPB·(dioxane)₅ by ¹H NMR. Single crystal X-ray diffraction afforded the best refinement for the noncentrosym-metric triclinic space group P1 (a = 16.07 Å, b = 18.33 Å, c = 35.25 Å, α = 80.34°, β = 85.48°, γ = 77.77°).

14201

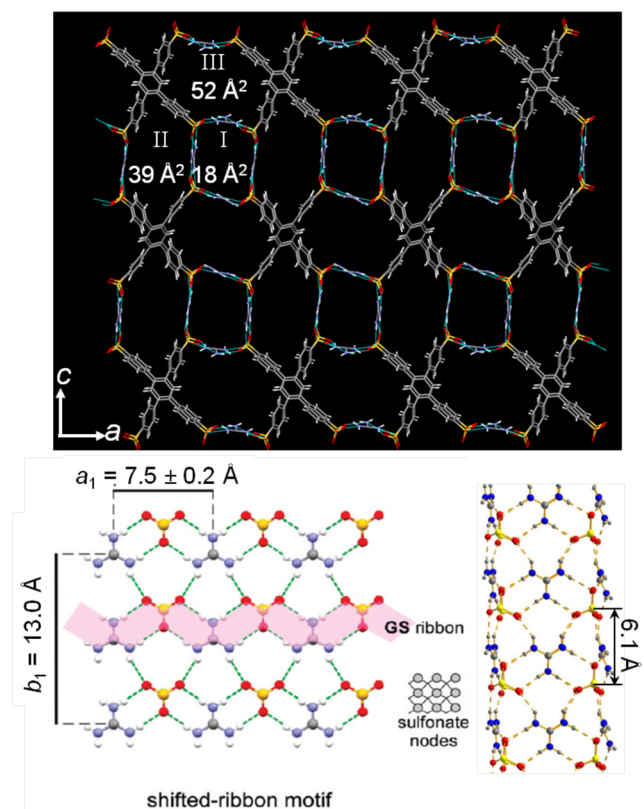dx.doi.org/10.1021/ja507689m | J. Am. Chem. Soc. 2014, 136, 14200−14206

Figure 2. (Upper panel) Crystal structure of the G_4TSPB framework in G_4TSPB·(dioxane)$_5$ as viewed along the b axis, which coincides with three crystallographically unique channels, denoted as Channels I, II, and III. The cross-section area, accounting for van der Waals radii, are denoted. (Lower panel) GS ribbons that flank the channels and form a closed cylinder corresponding to Channel I (right).

The crystal structure revealed a framework with three crystallographically unique one-dimensional channels (Figure 2), emulating the schematic representation depicted in Figure 1. The framework alone could be refined well in the centrosymmetric space group $P\bar{1}$, consistent with a reduction in symmetry by the dioxane guest molecules. The average S···S distance between the 1,2-sulfonates in each TSPB molecule is 9.0 Å, much larger than that of the typical S···S distance in GS lamellar sheets (7.2 Å). Consequently, guanidinium cations cannot bridge these sulfonate groups by hydrogen bonding,

thereby frustrating the formation of the canonical 2-D quasihexagonal GS network. Instead, these guanidinium cations form hydrogen-bonded bridges between adjacent TSPB molecules along the a and c axes to generate square-like GS hydrogen-bonded channels along the b axis (channel I) with edge lengths of approximately 6.8 Å. Channel I is surrounded by two larger crystallographically unique channels with a hexagonal-like shape created by the cleft of TSBP, one with a cross section of 9.0 Å × 15.5 Å (channel II) and the other 11.7 Å × 11.6 Å (channel III). All three channels are occupied by dioxane guest molecules: one in the channel I, two in channel II, and two in channel III. The channel walls are formed by GS ribbons, which adopt the "shifted ribbon" motif observed occasionally in GS frameworks (Figure 2).

Thermogravimetric analysis (TGA) revealed that the encapsulated dioxane molecules were removed completely from the framework upon heating at a rate of 10 K/min. The egress of dioxane occurred in two steps, a 6% weight loss corresponding to the loss of a single equivalent of dioxane as the temperature was raised from 298 to 423 K, followed by a second 24% weight loss, corresponding to the remaining four equivalents, as the temperature was increased from 423 to 473 K. Under ambient conditions, the first equivalent of dioxane was lost within 1 day (by TGA and ^{1}H NMR) and the remaining 4 equiv after another 20 days.

Optical microscopy revealed that single crystals did not exhibit any change in transparency or crystal integrity after the loss of the first equivalent of dioxane. This was consistent with single crystal X-ray diffraction, which revealed that this first step occurs via a single crystal-single crystal transformation (SCSCT), from the aforementioned $P1$ structure of G_4TSPB·(dioxane)$_5$ to a new crystalline phase G_4TSPB·(dioxane)$_4$ having $P2_1$ symmetry (a = 6.00 Å, b = 35.56 Å, c = 15.22 Å, β = 101.05°). The generic architecture of the framework remained unchanged, but one equivalent of dioxane was released from Channel II (one of channel II was highlighted by the white oval in Figure 3). This is somewhat surprising given the fact that pore volume and aperture of Channel II (241 Å^3 per G_4TSPB and 39 Å^2, respectively) is smaller than that of Channel III (320 Å^3 and 52 Å^2), features that would be expected to favor egress from Channel III. Instead, the selective loss of dioxane from channel II appears to reflect a greater structural compliance compared with channel III, which would be required to accommodate molecular motions during
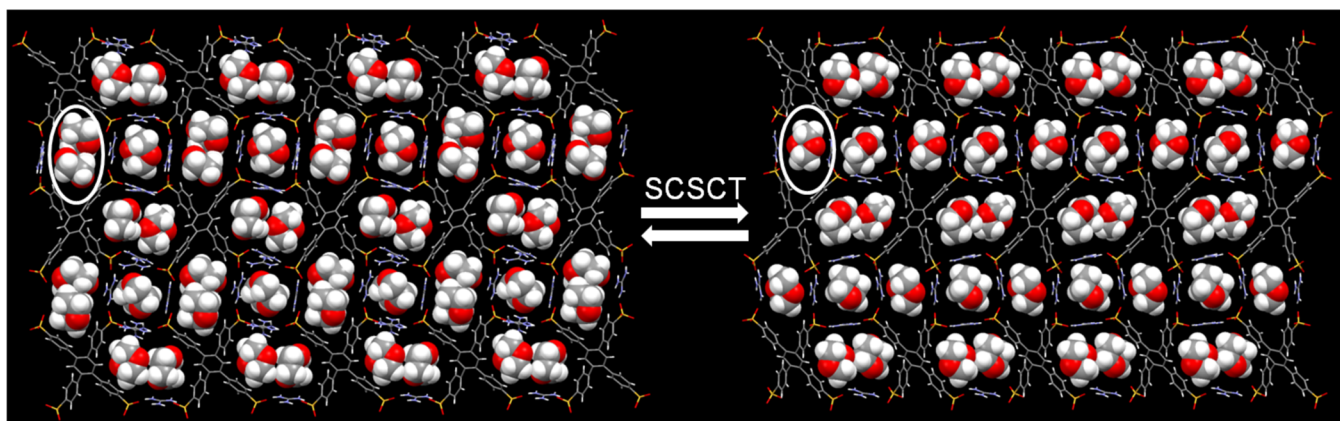

Figure 3. Reversible SCSCT of G_4TSPB framework through release and reabsorption of one equivalent of dioxane in Channel II. The orientation of the remaining dioxane in Channel II changes during the transformation.
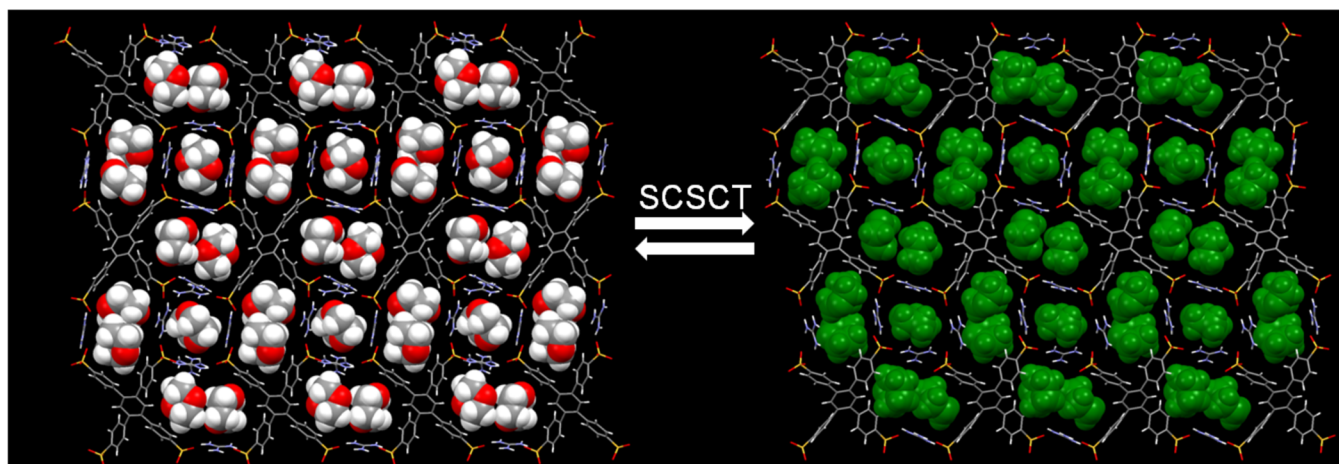
Figure 4. Reversible single crystal−single crystal transformation between $G_4TSPB \cdot (dioxane)_5$ and $G_4TSPB \cdot (tetrahydrofuran)_5$ through guest exchange. The tetrahydrofuran molecules are depicted as green to distinguish them from the dioxane molecules in $G_4TSPB \cdot (dioxane)_5$.

diffusion of the guest molecules in a size-constrained environment as well as to stabilize Channel II upon loss of half of its guests (upon loss of one equivalent of dioxane, the packing fraction of Channel II decreases from 0.73 to 0.49; whereas loss of dioxane from Channel III would decrease from 0.55 to roughly 0.28, an extremely low value). Moreover, the reduction in pore size required to achieve dense packing with a single dioxane guest is much less for Channel II. The S···S distance between the 1,2-sulfonates in $G_4TSPB \cdot (dioxane)_4$ decreased from 9.0 to 8.27 Å and the volume from 241 to 181 Å^3, such that Channel II can more effectively "shrink wrap" around the single remaining dioxane guest, which has a molecular volume of 88 Å^3. The shrinking of Channel II was accompanied by an expansion of Channel I from 111 to 160 Å^3, but the size of Channel III remained essentially unchanged. The overall unit cell volume shrinks by 71.04 Å^3 per G_4TSPB (4.27%), roughly equivalent to the volume of a dioxane molecule. This behavior is similar to breathing of pores observed in coordination and hydrogen bonding networks.[7b−d,18e]

After immersion of the single crystal of $G_4TSPB \cdot (dioxane)_4$ in dioxane for 3 h, ^{1}H NMR analysis and TGA were consistent with the complete regeneration of $G_4TSPB \cdot (dioxane)_5$ while the crystal retained its single crystallinity. Single crystal X-ray diffraction of the crystal revealed that the framework reverted back to the original $P\bar{1}$ unit cell, with the fifth dioxane molecule returning to the framework. Consequently, the SCSCT was reversible, indicating a facile pathway for egress and ingress of the fifth dioxane molecule, accompanied by a cyclic "breathing" of the framework, a rare example of a reversible SCSCT in a hydrogen bonded framework. The loss of the remaining four dioxane guest molecules, however, results in loss of crystallinity, with the crystals becoming opaque and mechanically fragile, and powder X-ray diffraction pattern revealing only several broad peaks.

Guest exchange between $G_4TSPB \cdot (dioxane)_5$ and tetrahydrofuran (80 Å^3), toluene (103 Å^3), aniline (98 Å^3) and nitrobenzene (110 Å^3), which have sizes comparable to or larger than dioxane (88 Å^3), also was observed. Immersion of a single crystal of $G_4TSPB \cdot (dioxane)_5$ in tetrahydrofuran produced a single crystal of $G_4TSPB \cdot (tetrahydrofuran)_5$ (stoichiometry by ^{1}H NMR analysis of dissolved single crystals and TGA data), that is, all five dioxane guest molecules were

replaced. Immersion of a single crystal of $G_4TSPB \cdot (dioxane)_5$ in toluene for 4 h afforded a single crystal of $G_4TSPB \cdot (toluene)_3(dioxane)$, that is, four dioxane molecules were replaced by three toluene molecules, leaving one dioxane remaining in the framework, confirmed by ^{1}H NMR and TGA data. Immersion in aniline and nitrobenzene resulted in complete replacement of the dioxane guests by 5 equiv of aniline and 1.5 equiv of nitrobenzene, respectively, consistent with ^{1}H NMR and TGA. Notably, single crystals of G_4TSPB inclusion compounds with guests other than dioxane could not be realized by direct crystallization. Attempts to crystallize $G_4TSPB \cdot (tetrahydrofuran)_5$ using conventional methods afforded an oil, whereas attempts to crystallize inclusion compounds containing toluene, aniline and nitrobenzene guests only afforded fine precipitates. Powder X-ray diffraction suggested that the toluene and nitrobenzene compounds were crystalline, but the aniline compound appeared to be highly amorphous.

The single crystals of $G_4TSPB \cdot (tetrahydrofuran)_5$ and $G_4TSPB \cdot (toluene)_3(dioxane)$ created by exchange retained their transparency, indicative of retention of single crystallinity. Powder X-ray diffraction data obtained for ground single crystals of these compounds were consistent with retention of the host framework structure in the original $G_4TSPB \cdot (dioxane)_5$. Single crystals of $G_4TSPB \cdot (dioxane)_5$ immersed in nitrobenzene and aniline, however, became opaque and mechanically fragile, and powder diffraction of the exchanged ground crystals was consistent with a reduction in crystallinity. This behavior may reflect disruption of the host framework by competitive hydrogen bonding of the amino and nitro groups.

The exchange of dioxane guests in $G_4TSPB \cdot (dioxane)_5$ with tetrahydrofuran and toluene proceeds through a reversible SCSCT. Single crystal X-ray diffraction revealed that after 4 h in tetrahydrofuran, the $P\bar{1}$ structure of $G_4TSPB \cdot (dioxane)_5$ transformed to $P1$ with different lattice parameters (a = 12.04 Å, b = 15.89 Å, c = 34.09 Å, α = 84.67°, β = 87.39°, γ = 83.72°). The overall host framework structure remained effectively unchanged (note: the channel axes coincide with the a direction in this setting). The five dioxane guests were completely replaced by five tetrahydrofuran guests, with one tetrahydrofuran guest in Channel I and two each in Channels II and III (Figure 4). The unit cell volume decreased by 3.13%, 52.12 Å^3 less per G_4TSPB, as might be expected for the smaller
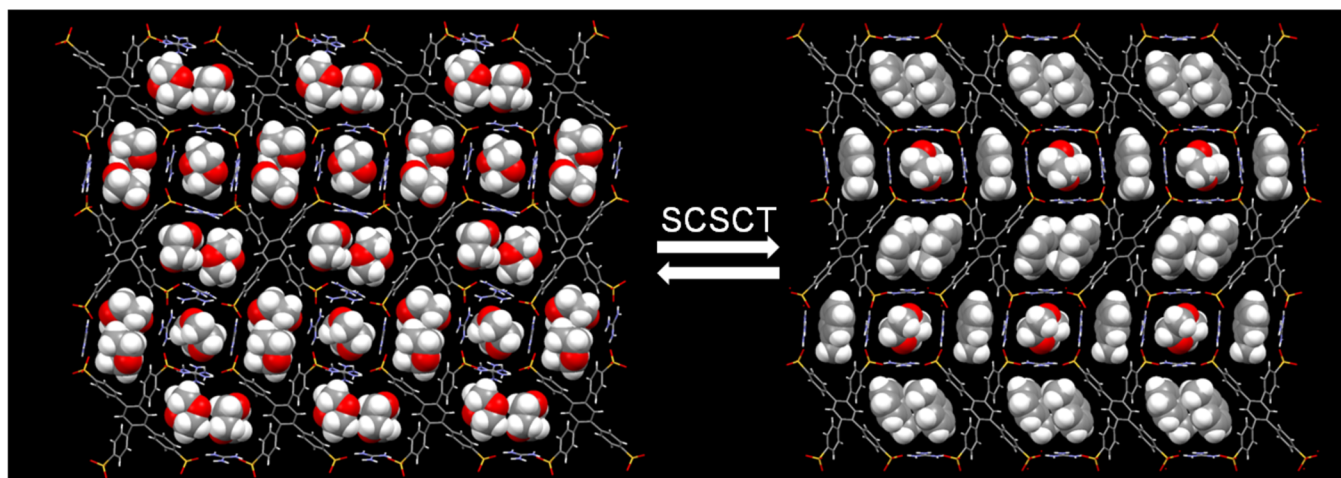
Figure 5. Reversible single crystal-single crystal transformation between G_4TSPB·(dioxane)$_5$ and G_4TSPB·(toluene)$_3$(dioxane) through guest exchange.

volume of tetrahydrofuran compared with dioxane. The S···S distance between the 1,2-sulfonates is nearly equivalent in both compounds, but the four phenyl arms of TSPB rotate slightly such that the size and shape of the channel is altered; Channel I expands from 111 to 124 Å^3, Channel II shrinks from 241 to 219 Å^3 and Channel III shrinks drastically from 320 to 231 Å^3. The 17.0% reduction in overall pore volume, as measured from Connolly surface calculations (1.2 Å sphere), is surprising when compared with the 3.13% reduction in unit cell volume. This can be attributed to the conformational flexibility of TSPB^{4-} anion, which can reduce the accessible surface area. In spite of these significant local rearrangements, the framework retains its single crystallinity, indicative of a robust character made possible by its structural compliance. Reimmersion of the same G_4TSPB·(tetrahydrofuran)$_5$ single crystal in dioxane for 4 h afforded a single crystal of G_4TSPB·(dioxane)$_5$ once again (by ^{1}H NMR and single crystal X-ray diffraction) Although the single crystal was slightly opaque, it retained its mechanical integrity and could be indexed to the original unit cell of G_4TSPB·(dioxane)$_5$. The reversible SCSCT with guest exchange could be performed for several cycles without appreciable loss of crystallinity.

The exchange of dioxane guests with toluene also occurred through a reversible SCSCT process. Single crystal X-ray diffraction revealed that after of immersion in toluene, G_4TSPB·(dioxane)$_5$ transformed from its $P\bar{1}$ structure to a single crystal of G_4TSPB·(toluene)$_3$(dioxane) in the space group $P2_1$ ($a = 6.18$ Å, $b = 35.44$ Å, $c = 15.26$ Å, $\beta = 100.52°$). The refinement of the structure actually improved, the R factor decreasing significantly from 13.02% to 9.4% because the guest molecules were ordered and could be refined well. The overall host framework architecture remained unchanged, but 1 equiv of dioxane remained in Channel I, while the other 4 equiv of dioxane in Channels II and III were replaced by 3 equiv of toluene, one in Channel II and two in Channel III (Figure 5). The long axis of the toluene guest in Channel II is perpendicular to the channel direction, and the toluene molecules in channel III organize as antiparallel face-to-face dimers, with interplanar spacing of approximately 3.6 Å. Compared with G_4TSPB·(dioxane)$_5$ framework, the overall unit cell volume of G_4TSPB·(toluene)$_3$(dioxane) shrinks by 1.34%, 22.24 Å^3 less for each G_4TSPB molecule. The S···S distance between the 1,2-sulfonates decreases from 9.0 to 8.3 Å

after SCSCT. As a result, the size of channel II shrinks significantly from 241 to 182 Å^3, while channel I expands from 111 to 143 Å^3 and channel III expands slightly from 320 to 331 Å^3. Even after significantly longer exchange time (9 days), the structure and composition remained unchanged, and Channel I was still occupied by dioxane alone, most likely reflecting the aversion of the nonpolar toluene molecule for the polar environment of Channel I. Immersion of a single crystal of G_4TSPB·(toluene)$_3$(dioxane) crystals in dioxane reverted to G_4TSPB·(dioxane)$_5$ after 4 h (by ^{1}H NMR and single crystal X-ray diffraction), with no appreciable loss of single crystallinity even after five cycles of exchange between these two compounds.

Notably, replacement of dioxane with tetrahydrofuran in a single crystal of G_4TSPB·(dioxane)$_5$ with a width of 1 mm along the b-axis (the direction of the channels) was complete within approximately 3 h (by ^{1}H NMR), indicating a diffusion coefficient of approximately 10^{-6} cm^2/s, in the range observed for alkanes and small molecules in microporous zeolites.[21,22] Rapid diffusion in channels II and III, which have cross sections sufficient to accommodate two guest molecules, can be explained by two-way or ring diffusion,[23] most likely vacancy assisted. The rapid guest exchange in Channel I, however, is surprising as its cross section can only support single-file diffusion.[24] Inspection of the crystal structure reveals that these channels are polar, with the half of the channels having a polarity opposite the other half, as expected for the $P\bar{1}$ pseudosymmetry of the framework. The polar nature of the channels may play a role in supporting unidirectional single-file diffusion, wherein incoming guests enter one end of the channel, while the outgoing guests exit at the opposite end. The observation that dioxane guests do not exit Channel I when immersed in toluene, even though these guests are highly soluble in toluene, argues that new guests play a crucial in promoting the diffusion and egress of guests from the channel, provided they are not sterically prohibited from inclusion in the channel.

Exchange between tetrahydrofuran and toluene in the G_4TSPB also can be achieved through a SCSCT process. Surprisingly, immersion of a single crystal of G_4TSPB·(tetrahydrofuran)$_5$ crystals in toluene produced G_4TSPB·(toluene)$_3$(tetrahydrofuran)$_{0.5}$ (confirmed by TGA and ^{1}H NMR. The crystal quality after exchange was not sufficient for a
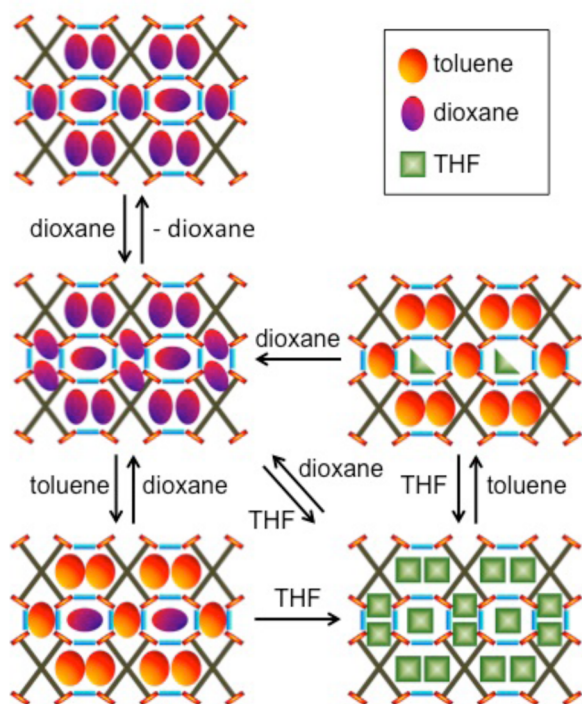
Figure 6. Schematic illustration of reversible single crystal−single crystal transformations based on G₄TSPB framework.

complete single crystal structure solution, but the unit cell was indexed (Supporting Information). Reimmersion of the same G₄TSPB·(toluene)₃(tetrahydrofuran)₀.₅ crystal in tetrahydrofuran for 4 h afforded a single crystal of G₄TSPB·(tetrahydrofuran)₅ once again (by ^{1}H NMR and single crystal unit cell characterization).

SUMMARY

In summary, a high symmetry tetrasulfonate with structural characteristics that favor the formation of a 2D hydrogen-bonded grid-like network produces a unique hydrogen-bonded framework with three crystallographically unique channels with different physicochemical characteristics. This new framework is sufficiently compliant to permit reversible release and adsorption of various guest molecules through a cyclic shrinkage and expansion of the channels with retention of single crystallinity, adding to the growing, yet small, family of single crystal−single crystal transformations (SCSCT) in hydrogen-bonding frameworks. Moreover, the different channels discriminate between exchanging guests (Figure 6), most likely based on size and polarity of guest molecules, and several single crystals of inclusion compounds that cannot be obtained through direct crystallization can be synthesized by guest exchange in the single crystals. Although the exchange processes described here are limited to simple guest molecules, these observations suggest an approach to the synthesis of new materials based on functional guests in hydrogen-bonded frameworks.

ASSOCIATED CONTENT

⑤ Supporting Information

Experimental details and characterization, including ^{1}H NMR, TGA, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
mdw3@nyu.edu

Notes
The authors declare no competing financial interest.

REFERENCES

(1) (a) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238. (b) Kitaura, R.; Kitagawa, S.; Kubota, Y.; Kobayashi, T.; Kindo, L.; Mita, Y.; Matsuo, A.; Kobayashi, M.; Chang, H.-C.; Ozawa, T.; Suzuki, M.; Sakata, M.; Takata, M. *Science* **2002**, *298*, 2358. (c) Xiao, W.; Hu, C.; Ward, M. D. *Cryst. Growth Des.* **2013**, *13*, 3197.

(2) (a) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J. H.; Go, Y. B.; Eddaoudi, M.; Matzger, A. J.; O'Keefe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523. (b) Yaghi, O. M.; Li, G. M.; Li, H. L. *Nature* **1995**, *378*, 703. (c) Pivovar, A. M.; Holman, K. T.; Ward, M. D. *Chem. Mater.* **2001**, *13*, 3018.

(3) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Saied, O.; Maris, T.; Wuest, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 14956.

(4) (a) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. (b) Endo, K.; Koike, T.; Sawaki, T.; Hayashida, O.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4117.

(5) (a) McKeown, N. B. *J. Mater. Chem.* **2010**, *20*, 10588. (b) Holst, J. R.; Trewin, A.; Cooper, A. I. *Nat. Chem.* **2010**, *2*, 915. (c) Sozzani, P.; Bracco, S.; Comotti, A.; Ferretti, L.; Simonutti, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1816.

(6) (a) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D. In *Inclusion Compounds*; Academic Press: London, 1991; Vol. 1, p 5. (b) Hollingsworth, M. D.; Brown, M. E.; Hillier, A. C.; Santarsiero, B. D.; Chaney, J. D. *Science* **1996**, *273*, 1355. (c) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737. (d) Comotti, A.; Bracco, S.; Yamamoto, A.; Beretta, M.; Hirukawa, T.; Tohnai, N.; Miyata, M.; Sozzani, P. *J. Am. Chem. Soc.* **2014**, *136*, 618. (e) Comotti, A.; Bracco, S.; Yamamoto, A.; Beretta, M.; Hirukawa, T.; Tohnai, N.; Miyata, M.; Sozzani, P. *J. Am. Chem. Soc.* **2014**, *136*, 618. (f) Mastalerz, M. *Chem.—Eur. J.* **2012**, *18*, 10082.

(7) (a) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782. (b) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273. (c) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109. (d) Ferey, G.; Serre, C. *Chem. Soc. Rev.* **2009**, *38*, 1380.

(8) Russell, V. A.; Etter, M. C.; Ward, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 1941.

(9) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575.

(10) Swift, J. A.; Reynolds, A. M.; Ward, M. D. *Chem. Mater.* **1998**, *10*, 4159.

(11) Evans, C. C.; Sukarto, L.; Ward, M. D. *J. Am. Chem. Soc.* **1999**, *121*, 320.

(12) Holman, K. T.; Pivovar, A. M.; Swift, J. A.; Ward, M. D. *Acc. Chem. Res.* **2001**, *34*, 107.

(13) Burke, N. J.; Burrows, A. D.; Mahon, M. F.; Teat, S. J. *CrystEngComm* **2004**, *6*, 429.

(14) Dumitrescu, D.; Legrand, Y.-M.; Dumitrascu, F.; Barboiu, M.; van der Lee, A. *Cryst. Growth Des.* **2012**, *12*, 4258.

(15) Horner, M. J.; Holman, K. T.; Ward, M. D. *Angew. Chem., Int. Ed.* **2001**, *40*, 4045.

(16) Comotti, A.; Bracco, S.; Sozzani, P.; Hawxwell, S. M.; Hu, C. H.; Ward, M. D. *Cryst. Growth Des.* **2009**, *9*, 2999.

(17) Liu, Y.; Hu, C.; Comotti, A.; Ward, M. D. *Science* **2011**, *333*, 436.

(18) (a) Biradha, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3392. (b) Wu, C.-D.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 1958. (c) Zhang, J.-P.; Lin, Y.-Y.; Zhang, W.-X.; Chen, X.-M. *J. Am. Chem. Soc.* **2005**, *127*, 14162. (d) Ghosh, S. K.; Kaneko, W.; Kiriya, D.; Ohba, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 8843. (e) Deiters, E.; Bulach, V.; Hosseini, M. W. *Chem. Commun.* **2005**, 3906. (f) Wahl, H.; Haynes, D. A.; Roex, T. *Chem. Commun.* **2012**, 1775.

(19) (a) Fur, E. L.; Demers, E.; Marris, T.; Wuest, J. D. *Chem. Commun.* **2003**, 2966. (b) Dechambenoit, P.; Ferlay, S.; Kyritsakas, N.; Hosseini, M. W. *J. Am. Chem. Soc.* **2008**, *130*, 17106.

(20) Liu, Y.; Ward, M. D. *Cryst. Growth Des.* **2009**, *9*, 3859.

(21) Jobic, H.; Méthivier, A.; Ehlers, G.; Farago, B.; Haeussler, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 364.

(22) Krishna, R. *Chem. Soc. Rev.* **2012**, *41*, 3099.

(23) Glicksman, M. E. *Diffusion in Solids*; John Wiley & Sons, Inc.: New York, 2000.

(24) (a) Sholl, D. S.; Fichthorn, K. A. *Phys. Rev. Lett.* **1997**, *79*, 3569. (b) Meersmann, T.; Logan, J. W.; Simonutti, R.; Caldarelli, S.; Comotti, A.; Sozzani, P.; Kaiser, L. G.; Pines, A. *J. Phys. Chem. A* **2000**, *104*, 11665.

14206

dx.doi.org/10.1021/ja507689m | *J. Am. Chem. Soc.* 2014, 136, 14200−14206