## One-, Two- and Three-Periodic Metal–Organic Rotaxane Frameworks (MORFs): Linking Cationic Transition-Metal Nodes with an Anionic Rotaxane Ligand

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**Abstract:** A new singly charged pyridinium axle was prepared and combined with disulfonated dibenzo[24]crown-8 ether to form a [2]pseudorotaxane. The reaction of this new, anionic ligand with  $Zn^{II}$  ions, under various crystallization conditions, resulted in the formation of three metal–organic rotaxane framework (MORF) solids; a one-

periodic ML coordination polymer and two, two-periodic  $ML_2$  square grid frameworks. The layers of square grids can be pillared to create full three-peri-

**Keywords:** metal–organic frameworks • rotaxanes • supramolecular chemistry • zinc oidic MORF structures, which have completely neutral frameworks and are porous. These three-perioidic materials represent the first examples of neutral porous MOFs in which one (or more) of the linkers is a mechanically interlocked molecule (MIM).

### Introduction

The development of new materials that have technologically important physical properties, such as nonlinear optics or ferroelectrics, is of great interest.<sup>[1]</sup> A new and relatively unexplored avenue for creating these materials is to incorporate mechanically interlocked molecules (MIMs),<sup>[2]</sup> such as catenanes or rotaxanes into metal-organic frameworks (MOFs).<sup>[3]</sup> MOFs are a well-established class of porous material consisting of inorganic metal nodes and organic bridging ligands arranged in one-, two-, or three-periodic networks.<sup>[4]</sup> The incorporation of MIMs into MOFs would allow for a unique way to manipulate the properties of materials by having control over motion at a molecular level; reminiscent of "crystalline molecular motors" first demonstrated by Garcia-Garibay.<sup>[5]</sup> Since a component of the lattice, the wheel, would be quite flexible, this new type of framework material could be thought of as a class of "soft porous crystal" as defined by Kitigawa.<sup>[6]</sup> Alternately, given the dynamic nature of the wheel in a framework pore, the concept of "robust dynamics", as recently proposed by Stoddart and Yaghi might be more appropriate.<sup>[7]</sup> By any definition, these are materials that have yet to be realized, but have significant potential and are only just beginning to be explored.

We have previously shown that combining a 1,2-bis(4,4'bipyridinium)ethane  $(1^{2+})$  axle and a dibenzo[24]crown-8 (DB24C8) wheel yields a [2]pseudorotaxane  $[1 \subset DB24C8]^{2+}$ that can act as a linker between d-block or lanthanide metals for the construction of 1-, 2-, and 3-periodic solids.<sup>[8]</sup> We have called these materials, metal–organic *rotaxane* frameworks or MORFs.<sup>[9]</sup> In order to observe molecular dynamics in the solid state, the wheel component must be able to "operate" in well-defined "space". These preliminary results, while establishing the concept of MORFs, did not meet this requirement. A primary reason was the presence of counterions in the lattice, which not only hindered any potential dynamic behavior of the wheel component, but also limited the stability of the frameworks. More recently, we have shown that by using an anionic wheel, the *anti*isomer of disulfonated dibenzo[24]crown-8, DSDB24C8<sup>2-</sup>, in conjunction with the dicationic axle  $1^{2+}$ , a neutral [2]pseudorotaxane can be generated.<sup>[10]</sup> The zwitterionic linker [1 $\subset$ DSDB24C8] was combined with neutral metal nodes, such as the classic Cu<sub>2</sub>OBn<sub>4</sub> paddlewheel, to form neutral one-periodic MORFs that were free of independent counterions.<sup>[11]</sup> However, due to the limited number of neutral metal nodes available, creating permanent porosity by increasing the periodicity of this system proved to be difficult.

The great majority of MOFs, such as those pioneered by Yaghi and co-workers, rely on organic anions to link positively charged metals or clusters,<sup>[4]</sup> so another way to create a neutral MORF would be to design an anionic [2]pseudorotaxane ligand. Since, we have previously shown that DSDB24C8<sup>2-</sup> has a high affinity for axle 1<sup>2+</sup> in MeOH<sup>[10]</sup> ( $K_a > 10^5 M^{-1}$  at 298 K), it was reasoned that it should be possible to replace one of the internal pyridinium rings of axle 1<sup>2+</sup> with a simple phenyl ring, thereby removing one of the positive charges, but still achieving significant [2]pseudorotaxane formation. A similar, singly charged pyridinium based axle has previously been reported by Quintela to form catenated structures with {Pd(diamine)} corners and various crown ether macrocycles.<sup>[12]</sup>

Herein, we present the preparation of [2]pseudorotaxanes utilizing a singly charged pyridinium axle  $2^+$  and its benzylated derivative  $3^{3+}$  with DB24C8 and DSDB24C8<sup>2-</sup> (Scheme 1). The combination of  $2^+$  and DSDB24C8<sup>2-</sup> creates a negatively charged [2]pseudorotaxane ligand  $[2 \subset DSDB24C8]^-$  that can be used to create unique one-, two- and three-periodic MORFs that are neutral and porous; significant steps towards the goal of creating a robust and porous MOF with truly dynamic components.

### **Results and Discussion**

The synthesis of  $2^+$  was accomplished by conversion of the alcohol 4-[4-( $\alpha$ -hydroxyethyl)phenyl]pyridine<sup>[13]</sup> to the corresponding bromo derivative, 4-[4-( $\alpha$ -bromoethyl)phenyl]pyri-

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Scheme 1. The pyridinium axles  $(1^{2+}, 2^+, 3^{3+})$  and crown ethers (DB24C8, DSDB24C8<sup>2</sup>) used in this study to form [2]pseudorotaxanes with varying charge.

dine, followed by alkylation with 4,4'-bipyridine and subsequent anion exchange to the triflate salt (Scheme 2). In order to investigate the extent of [2]pseudorotaxane formation, <sup>1</sup>H NMR studies were conducted using  $2^+$  as the axle and DB24C8 or DSDB24C8<sup>2-</sup> as the wheel at  $2.0 \times 10^{-3}$  M in CD<sub>3</sub>OD. There was an order of magnitude increase in asso-



Scheme 2. Reagents and conditions: i) PBr<sub>3</sub> in THF/CH<sub>2</sub>Cl<sub>2</sub>, 24 h, 0 °C; ii) 20 equiv 4,4'-bipyridine, *n*-butanol, 48 h, reflux followed by anion exchange with NaOTf in MeNO<sub>2</sub>/H<sub>2</sub>O; iii) 2 equiv benzylbromide, NaOTf, MeNO<sub>2</sub>/H<sub>2</sub>O, 80 °C, 24 h.

ciation constant between  $[\mathbf{2} \subset DB24C8]^{2+}$  and  $[\mathbf{2} \subset DSDB24C8]^{-}$  from  $3.5 \times 10^{1}$  to  $3.0 \times 10^{2} \text{ m}^{-1}$  due to the addition of increased electrostatic attraction from the sulfonate groups. Since coordination of  $[\mathbf{2} \subset DSDB24C8]^{-}$  to a Lewis acidic, transition-metal center should increase the interaction between the axle and wheel, similar to alkylation, it was also of interest to study these interactions with benzy-lated axle  $\mathbf{3}^{3+}$ . As expected, there was a substantial increase in association constant upon benzylation; from  $8.0 \times 10^{1}$  to  $2.3 \times 10^{3} \text{ m}^{-1}$  comparing DB24C8 to DSDB24C8<sup>2-</sup>. These values compare well to those observed for similar systems<sup>[14]</sup>

and verify that  $[2 \subset DSDB24C8]^-$  should be capable of acting as a pseudorotaxane linker between metal ions in a MORF.

At this point, it seems prudent to discuss the result of combining an axle such as  $2^+$ , which is unsymmetrical along its long axis (has direction), with a wheel such as DSDB24C8<sup>2–</sup>, which has a center of symmetry but no  $C_2$  primary axis. The result is two different [2]pseudorotaxanes that are cyclochiral enantiomers designated as C for clockwise and A for anticlockwise (Figure 1).



Figure 1. Enantiomers of  $[2 \subset DSDB24C8]^-$ . For enantiomer C, the sulfonate group is on the left hand side of the positively charged end of the axle. Conversely, for enantiomer A, the sulfonate group is on the right hand side.

The initial investigation into utilizing [2CDSDB24C8]<sup>-</sup> as a linker for MORF formation involved combining equimolar amounts of [2][OTf], anti-[Me<sub>4</sub>N]<sub>2</sub>[DSDB24C8] and Zn-(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in CH<sub>3</sub>OH. The resulting solution was left to stand for three days, after which a crop of pale yellow, Xray quality crystals were isolated (50% yield). A single-crystal X-ray diffraction analysis showed the resulting material, MORF-1, to be a one-periodic solid with formula [Zn(2CDSDB24C8)(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>OH)][NO<sub>3</sub>]·2CH<sub>3</sub>OH. Figure 2a shows how two cationic [Zn(2CDSDB24C8)- $(H_2O)_2(CH_3OH)$ <sup>+</sup> units of opposite chirality are joined together in a head-to-tail fashion by coordination of a sulfonate group of one unit to the Zn<sup>II</sup> center of a neighboring unit; the closest Zn…Zn distance is 9.17 Å. The crown ethers wrap around the charged pyridinium end of the axle, which presumably optimizes the noncovalent interactions between axle and wheel. Linking cations of the same chirality through Zn-N coordination results in propagation of this dimeric unit into a racemic, double-stranded, one-periodic framework with Zn…Zn distances of 22.0 Å (Figure 2b, 2c). Although, this interesting material verified that the negatively charged rotaxane [2⊂DSDB24C8]<sup>-</sup> could be combined with a positively charged metal ion (Zn<sup>II</sup>), the resulting one-periodic framework was not neutral as non-coordinating nitrate ions were required for charge balance.

To increase the periodicity of the resulting MORF and generate a neutral framework, the amount of axle and wheel were doubled and a less coordinating solvent mixture





Figure 2. a) Two cyclochiral enantiomers joined by  $Zn^{II}$ ... $SO_3^{-}$  coordination (NO<sub>3</sub> ions and hydrogen atoms removed for clarity). b) Schematic showing how each strand consists of a single enantiomer. c) Space-filling model of MORF-1 (coordinated solvent and NO<sub>3</sub> ions omitted for clarity). Key: blue= $2^+$  axle; red=DSDB24C8<sup>2-</sup> wheel; yellow=sulfur; grey= $Zn^{II}$  ions; green=coordinated H<sub>2</sub>O and MeOH ligands.

was used; two equivalents each of [2][OTf] and *anti*- $[Me_4N]_2[DSDB24C8]$  were combined with one equivalent of  $Zn(NO_3)_2\cdot 4H_2O$  in a 1:9 CH<sub>3</sub>OH/CH<sub>3</sub>NO<sub>2</sub> solvent mixture. The resulting solution was left to stand for five days, after which a crop of pale yellow, X-ray quality crystals were isolated (64 % yield). A single-crystal X-ray diffraction analysis showed the material, MORF-2, to be neutral and two-periodic with formula  $[Zn(2 \subset DSDB24C8)_2(H_2O)_2]\cdot H_2O\cdot 21 CH_3NO_2.$ 

MORF-2 contains a neutral, square grid of  $Zn^{II}$  nodes linked by anionic [2 $\subset$ DSDB24C8]<sup>-</sup> rotaxanes with a Zn···Zn distance of 22.0 Å. Figures 3a and 3b show that each of these layers is enantiomerically pure, since each ligand adopts the same cyclochirality. These layers are stacked in an alternating AB fashion through hydrogen bonding between bridging and axially coordinated H<sub>2</sub>O molecules to yield a racemic solid (Figure 3 c). The layer spacing is 7.82 Å between closest Zn centers. The void space of the resulting channels was calculated to be 42% by PLATON and a final PLATON/SQUEEZE<sup>[15]</sup> refinement of the model accounted for 21 molecules of CH<sub>3</sub>NO<sub>2</sub> per formula unit. Unlike



Figure 3. a) Space-filling model of MORF-2 showing an enantiomerically pure square grid (solvent omitted for clarity). b) Schematic diagram of an enantiomerically pure square grid. c) Ball and stick representation of how the square grids are layered, through hydrogen-bonding (hydrogen atoms have been removed for clarity). Key: blue= $2^+$  axle; red=DSDB24C8<sup>2-</sup> wheel; yellow=sulfur; grey=Zn<sup>2+</sup>; green=H<sub>2</sub>O; hydrogen bonds=dashed black lines.

MORF-1, in which the sulfonate groups interact directly with the  $Zn^{II}$  centers, in MORF-2 the sulfonates are involved in hydrogen-bonding to the bridging H<sub>2</sub>O molecules.

The as-synthesized samples of MORF-2 readily lose  $CH_3NO_2$  at room temperature and immersion of the crystalline material in  $CHCl_3$  followed by treatment under mild vacuum at room temperature yielded a solvent-free sample. Thermal gravimetric analysis (TGA) and variable-temperature powder X-ray diffraction (VT-PXRD) studies showed the sample to be moderately stable with loss of bridging and coordinated  $H_2O$  molecules in the range 80–100 °C, followed by decomposition of the metal–ligand network above 225 °C. The PXRD patterns recorded below 80 °C matched well with that predicted from the single-crystal data and at 100 °C were consistent with formation of a new layered structure, presumably due to loss of the weak interlayer hydrogen-bonding, but retention of the much stronger square

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grid structure. Attempts to perform standard BET measurements were unsuccessful as the conditions required for full evacuation of the pores also resulted in collapse of the pillaring hydrogen bonds.

During the initial preparations of MORF-2, we were able to isolate a small amount ( $\approx 10\%$ ) of another crystalline material. Single-crystal X-ray diffraction analysis showed this colorless material, MORF-3, to be neutral and three-periodic with formula [Zn(2 $\subset$ DSDB24C8)<sub>2</sub>][{Zn(CH<sub>3</sub>OH)<sub>2</sub>-(H<sub>2</sub>O)<sub>2</sub>(SO<sub>4</sub>)]<sub>2</sub>]·42 CH<sub>3</sub>NO<sub>2</sub>. MORF-3 contains the same neutral, square grid of Zn<sup>II</sup> nodes and [2 $\subset$ DSDB24C8]<sup>-</sup> rotaxanes as MORF-2 (Figure 4a), but the pillaring groups are very different. In place of the simple coordinated and hydrogen-bonded H<sub>2</sub>O molecules is a much more robust fragment made of two {Zn(CH<sub>3</sub>OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>} centers bridged by two



Figure 4. a) Space-filling model of MORF-3 showing a racemic square grid (solvent omitted for clarity). b) Schematic diagram of a racemic square grid. c) Ball and stick representation of how the square grids are pillared by  $[Zn(H_2O)_4(SO_4)]_2$  clusters (hydrogen atoms have been removed for clarity). Key: blue=2<sup>+</sup> axle; red=DSDB24C8<sup>2-</sup> wheel; yellow=sulfur; grey=Zn<sup>2+</sup>.

 $SO_4^{2-}$  ions. Pillaring with this  $[{Zn(CH_3OH)_2(H_2O)_2(SO_4)}_2]$ cluster results in a much larger layer spacing of 11.0 Å between Zn centers of the square grids. Figure 4b illustrates another difference between MORF-2 and MORF-3; the arrangement of cyclochiral linkers is such that each layer is comprised of an identical racemic mixture with adjacent C and A linkers in the same grid rather than the alternating, enantiomeric layers observed for MORF-2.

The void space of the resulting channels in MORF-3 was calculated to be 55% by PLATON and a final PLATON/ SQUEEZE<sup>[15]</sup> refinement of the model accounted for 42 molecules of  $CH_3NO_2$  per formula unit. Unlike MORF-2, which is pillared with weak, noncovalent hydrogen bonding, the direct coordination of bridging  $SO_4^{2-}$  ions between the two different types of  $Zn^{II}$  ions leads to a truly three-period-ic coordination polymer with increased stability between layers.

Unfortunately, it was not possible to synthesize and isolate MORF-3 free from contamination with MORF-2. In the synthesis of these materials, MORF-2 is by far the dominant species. It was determined that the source of the  $SO_4^{2^-}$ ions for creating MORF-3 was contamination of samples of the crown ether salt  $[Me_4N]_2[DSDB24C8]$  with  $[Me_4N]_2$ - $[SO_4]$ , as the synthesis involves treatment of DB24C8 with excess  $H_2SO_4$  and neutralization with  $[Me_4N][OH]$ . Elimination of the  $[Me_4N]_2[SO_4]$  contaminate resulted in only MORF-2 being produced. Attempts to purposefully produce MORF-3 by the addition  $SO_4^{2^-}$  ions were successful, but these samples were always mixtures of MORF-2 and MORF-3. To date no successful method for separation and isolation of bulk samples of pure MORF-3 has been devised.

Although this problem precluded a complete analysis of the stability and thermal properties of MORF-3, some general observations could be made. Crystals of MORF-3 readily lose CH<sub>3</sub>NO<sub>2</sub> at room temperature and could be washed with CHCl<sub>3</sub> and evacuated under mild vacuum with no evident change in structure; similar to the behavior of MORF-2 under the same conditions. Similar to MORF-2, TGA of mixtures of MORF-2 and MORF-3 lost coordinated solvents in the range 80-100 °C and decomposed above 225 °C. Although it is reasonable to speculate that, even with the loss of coordinated solvents, the moderately strong coordination bonds of the square grid and pillar would be sufficient to maintain a three-periodic structure, it was not possible to unambiguously determine whether the structure observed by single-crystal X-ray analysis was retained above 100°C.

Finally, although MORF-2 and MORF-3 both contain a neutral, square grid as designed, there are some interesting structural differences in addition to the pillaring groups and ligand cyclochirality. In MORF-2, the axle and wheel are  $\pi$ -stacked (see Figure 3 c) in a fashion similar to that observed for almost every other X-ray structure determined for this type of rotaxane<sup>[9c,10]</sup> and charge transfer between these components give rise to the yellow color of the material.<sup>[14a]</sup> In stark contrast, the axle in MORF-3 is rotated  $\approx 90^{\circ}$  and is

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better described as being involved in a CH··· $\pi$  interaction with the crown ether aromatic ring. This perpendicular orientation negates any charge transfer interaction and this material is colorless. This very subtle difference in orientation of the aromatic rings in MORF-2 and MORF-3 begs the question; is it possible for these orientations to interconvert in the solid state, that is, display robust dynamics. Although an unambiguous answer to this question will have to wait for more detailed experiments, it should be noted that gentle heating of the colorless crystals of MORF-3 produced a yellow material, which we believe could be the result of reorientation of the MIM components from a perpendicular CH– $\pi$  to a  $\pi$ -stacked rotaxane.

#### Conclusion

In conclusion, we have prepared and characterized the first examples of neutral porous MOF materials containing a component that is only linked to the MOF framework by virtue of a mechanical bond (a MIM). In addition, we have shown that although the two-periodic nature of the square grid reported herein limits the stability of the MORF, this strategy has the potential to make the realization of robust, three-periodic MOFs containing dynamic MIM components a reality. Work towards this goal is ongoing.

#### **Experimental Section**

General comments: 4-Pyridineboronic acid, 4-bromophenethyl alcohol, tetrakis(triphenylphosphine)palladium(0), phosphorus tribromide, 4,4'-bipyridine, sodium trifluoromethanesulfonate, benzylbromide and DB24C8 were purchased from Aldrich and used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and used as received. Solvents were dried using an Innovative Technologies Solvent Purification System. Thin-layer chromatography (TLC) was performed using Teledyne Silica gel 60 F<sub>254</sub> plates and viewed under UV light. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230-400 mesh). Flash column chromatography was performed using Teledyne Ultra Pure Silica/RP-C<sub>18</sub> Silica Gel (230-400 mesh) on a Teledyne Isco Combiflash R<sub>f</sub>. <sup>1</sup>H NMR 1D and 2D experiments were performed on a Brüker Avance 500 instrument, with working frequency of 500.13 MHz. Chemical shifts are quoted in ppm relative to tetramethylsilane, using the residual solvent peak as a reference standard. 2D NMR analysis (1H-1H COSY) were used to assign all 1H NMR peaks. High-resolution mass spectrometry (HR-MS) experiments were performed on a Micromass LCT electrospray ionization (ESI) time-of-flight (ToF) mass spectrometer. Solutions with concentrations of  $1.0 \times 10^{-3}$  M were prepared in methanol, and injected for analysis at a rate of 5 µLmin<sup>-1</sup> by using a syringe pump. 4-[4-( $\alpha$ -Hydroxyethyl)phenyl]pyridine was prepared by the literature method;<sup>[13]</sup> m.p. 105 °C, no m.p. data were cited in the literature. The <sup>1</sup>H NMR spectral data were consistent with the formulation and subsequent conversion to the bromo species (below) verified the successful preparation of this compound.

[2]Pseudorotaxane formation and measurement of association constants: A <sup>1</sup>H NMR spectrum of an equimolar solution  $(2.0 \times 10^{-3} \text{ M})$  of pyridinium axle (as the triflate salt) and disulfonated dibenzo[24]crown-8 ether (as the Me<sub>4</sub>N<sup>+</sup> salt) was recorded in CD<sub>3</sub>OD at 298 K for each axle. Since these equilibria were slow on the NMR timescale, the concentrations of all species at equilibrium were determined using the initial crown and axle concentrations and integration of the aromatic NCH resonance

for free and complexed axle. These concentration values were then used to calculate an association constant with an estimated error of 10%.

Synthesis of 4-[4-(a-bromoethyl)phenyl]pyridine: 4-[4-(a-Hydroxyethyl)phenyl]pyridine (3.50 g, 0.0176 mol) was dissolved in a 1:1 mixture of THF/CH<sub>2</sub>Cl<sub>2</sub> (200 mL) under a nitrogen atmosphere and placed on ice. Phosphorustribromide (13.4 mL of a 1.0 M solution, 0.0132 mol) was added to the reaction vessel by syringe and the reaction left to stir for 24 h. The reaction was then quenched with H<sub>2</sub>O, and the solvent removed via a rotary evaporator. A separation was performed with H<sub>2</sub>O/CHCl<sub>3</sub> and the solution basified with Na2CO3 to pH 10. The organic layer was washed with H<sub>2</sub>O (3×20 mL), dried over MgSO<sub>4</sub>, and the solvent removed to yield a yellow oil; crude yield by NMR analysis was 75%. The product was purified by flash column chromatography using Teledyne Ultra Pure Silica/RP-C<sub>18</sub> Silica Gel, with a solvent gradient of hexanes with 0-70% EtOAc. The product was isolated as a white crystalline solid. Yield, 2.51 g, 60%; m.p. 180–182°C (decomp); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 8.66$  (d,  ${}^{3}J = 4.4$  Hz, 2H), 7.62 (d,  ${}^{3}J = 8.0$  Hz, 2H), 7.51 (d,  ${}^{3}J = 4.4$  Hz, 2H), 7.35 (d,  ${}^{3}J = 8.0$  Hz, 2H), 3.62 (t,  ${}^{3}J = 7.4$  Hz, 2H), 3.24 ppm (t,  ${}^{3}J =$ 7.4 Hz, 2H); ESI-MS: m/z calcd for  $[M+H]^+$ : 262.0226; found: 262.0225.

**Synthesis of 2[OTf**]: 4-[4-(α-Bromoethyl)phenyl]pyridine (1.00 g, 0.00379 mol) was dissolved in n-butanol (250 mL) and slowly added over 24 h through a syringe pump, to a solution of 20 equivalents of 4.4'-bipyridine (11.9 g, 0.0763 mol) in n-butanol (200 mL). The solution was refluxed for 48 h, cooled to room temperature and placed in the freezer for 2 h to allow for precipitation of the product. The precipitate was filtered by vacuum filtration, dried and stirred in CHCl3 to remove any excess 4,4'-bipyridine. (the product is approx. 95% pure at this point with a 5% impurity from the reaction of 4-[4-(a-bromoethyl)phenyl]pyridine with itself. The crude product was further purified by column chromatography on silica gel using a 7:1:2 mixture of MeOH/2 M NH<sub>4</sub>Cl(aq)/MeNO<sub>2</sub>. The product was isolated as an off-white solid (yield: 1.00 g, 63 %). The product was anion exchanged from the bromide salt to the OTf- salt by way of a two-layer NaOTf (aq)/MeNO<sub>2</sub> extraction. Yield, 0.902 g, 90%; m.p. >200 °C (decomp); <sup>1</sup>H NMR (CD<sub>3</sub>OD):  $\delta = 8.99$  (d, 2 H, <sup>3</sup>J = 6.5 Hz), 8.79 (d,  ${}^{3}J=5.4$  Hz, 2H), 8.68 (d,  ${}^{3}J=5.4$  Hz, 2H), 8.46 (d,  ${}^{3}J=6.5$  Hz, 2H), 8.00 (d,  ${}^{3}J=5.4$  Hz, 2H), 7.95 (d,  ${}^{3}J=5.4$  Hz, 2H), 7.83 (d,  ${}^{3}J=$ 8.0 Hz, 2H), 7.45 (d,  ${}^{3}J$  = 8.0 Hz, 2H), 4.99 (t,  ${}^{3}J$  = 7.1 Hz, 2H), 3.48 ppm (t,  ${}^{3}J=7.1$  Hz, 2H); ESI-MS: m/z calcd for [2]<sup>+</sup>: 338.1652; found: 338.1658.

**Synthesis of 3[OTf]**<sub>3</sub>: Compound **2**[OTf] (100 mg, 0.205 mmol), benzylbromide (140 mg, 0.821 mmol), and NaOTf (140 mg 0.820 mmol) were dissolved in a 1:1 mixture of MeNO<sub>2</sub>/H<sub>2</sub>O (50 mL) and heated at 80 °C for 24 h. Solvent was removed by a rotary evaporator and a two-layer extraction was performed using MeNO<sub>2</sub> and H<sub>2</sub>O. The MeNO<sub>2</sub> layer was isolated, and the solvent removed. The resulting material was then stirred in EtOAc overnight to precipitate the product and remove excess benzylbromide. The product was isolated as an off-white solid. Yield: 80 mg, 40%; m.p. > 200 °C (decomp); <sup>1</sup>H NMR (CD<sub>3</sub>OD):  $\delta$ =9.29 (d, <sup>3</sup>J = 6.4 Hz, 2H), 9.16 (d, <sup>3</sup>J = 6.2 Hz, 2H), 8.99 (d, <sup>3</sup>J = 6.4 Hz, 2H), 8.62 (d, <sup>3</sup>J = 6.4 Hz, 2H), 8.60 (d, <sup>3</sup>J = 6.2 Hz, 2H), 7.56-7.47 (m, 10H), 5.94 (s, 2H), 5.80 (s, 2H), 5.03 (t, <sup>3</sup>J = 7.0 Hz, 2H), 7.51 ppm (t, <sup>3</sup>J = 7.0 H, 2Hz). ESI-MS: *m*/z calcd for [**3**(OTf)<sub>2</sub>]<sup>+</sup>: 818.1793; found: 818.1805.

**X-ray diffraction analysis:** Single crystals were frozen in paratone oil inside a cryoloop. Reflection data were integrated from frame data obtained from hemisphere scans on a Bruker APEX diffractometer with a CCD detector. Decay was monitored by 50 standard data frames measured at the beginning and end of each data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined using full-matrix least-squares methods against  $|F^2|$  data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison). The SHELXTL library<sup>[16]</sup> of programs was used for X-ray solutions

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and figures were drawn with DIAMOND software.<sup>[17]</sup> CCDC-786890 (MORF-1), 7868921 (MORF-2) and 786892 (MORF-3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Synthesis of MORF-1: Compound 2[OTf] (10.0 mg, 0.0205 mmol), anti- $[Me_4N]_2[DSDB24C8]$  (15.8 mg, 0.0205 mmol), and  $Zn(NO_3)_2$ ·4 H<sub>2</sub>O (5.4 mg, 0.0205 mmol) were dissolved in CH<sub>3</sub>OH (3 mL). The resulting solution was partially covered and left to stand for three days after which a crop of pale yellow, X-ray quality crystals with formula  $[Zn(2 \subset DSDB24C8)(H_2O)_2(CH_3OH)][NO_3] \cdot 2CH_3OH$ were isolated (12.5 mg, 50% yield). X-ray data:  $C_{50}H_{65}N_4O_{22}S_2Zn$ ,  $M_r = 1203.55$ , pale yellow prisms  $(0.32 \times 0.26 \times 0.14 \text{ mm})$ , triclinic,  $P\overline{1}$ , a=11.353(2), b=10.353(2)15.891(2), c = 17.369(3) Å,  $\alpha = 111.098(2)$ ,  $\beta = 97.685(2)$ ,  $\gamma = 104.313(2)^{\circ}$ ,  $V = 2745.5(7) \text{ Å}^3, Z = 2, \rho_{\text{calcd}} = 1.456 \text{ g cm}^{-3}, \mu = 0.607 \text{ mm}^{-1}, \text{min/max}$ transmission = 0.8931, Mo<sub>Ka</sub>  $\lambda$  = 0.71073 Å, T = 173.0(2) K, 26089 total reflections (R(int) = 0.1180), R1 = 0.0987, wR2 = 0.2281 [ $I > 2\sigma(I)$ ], R1 =0.1784, wR2 = 0.2842 [all data], GoF( $F^2$ ) = 1.009, data/variables/restraints = 9623/713/16.

Synthesis of MORF-2: Compound 2[OTf] (20.0 mg, 0.0410 mmol), anti-[Me<sub>4</sub>N]<sub>2</sub>[DSDB24C8] (31.6 mg, 0.0410 mmol), and Zn(NO<sub>3</sub>)<sub>2</sub>·4 H<sub>2</sub>O (5.4 mg, 0.0205 mmol) were dissolved in a 1:9 CH<sub>3</sub>OH/CH<sub>3</sub>NO<sub>2</sub> solvent mixture (3 mL). The resulting solution was left partially covered to stand for five days after which a crop of pale vellow. X-ray quality crystals with formula  $[Zn(2 \subset DSDB24C8)_2(H_2O)_2] \cdot H_2O \cdot 21 CH_3NO_2$  were isolated (43.6 mg, 64% yield). X-ray data:  $C_{115}H_{169}N_{27}O_{74}S_4Zn$ ,  $M_r = 3307.38$ , yellow prisms ( $0.34 \times 0.30 \times 0.22$  mm), monoclinic, C2/c, a=28.756(3), b= 33.394(4), c = 15.572(2) Å,  $\beta = 98.303(2)^{\circ}$ , V = 14796(3) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} =$  $1.485 \text{ g cm}^{-3}, \ \mu = 0.334 \text{ mm}^{-1}, \ \text{min/max} \ \text{transmission} = 0.7459, \ \text{Mo}_{K\alpha} \ \lambda =$ 0.71073 Å, T = 173.0(2) K, 67226 total reflections (R(int) = 0.0833). The unit cell included a large region of disordered CH3NO2 solvent molecules in addition to the single hydrogen-bonded water molecule which connects the layers. The water was located and refined, but the CH<sub>3</sub>NO<sub>2</sub> molecules were severely disordered and could not be modeled. We therefore employed the program SQUEEZE<sup>[15]</sup> to calculate the diffraction contribution of the solvent molecules and produce a data set with solvent-free diffraction intensities. With no solvent contribution, before SQUEEZE:  $R1 = 0.2066, wR2 = 0.5118 [I > 2\sigma(I)], R1 = 0.2564, wR2 = 0.5427$  (all data),  $GoF(F^2) = 1.633$ , data/variables/restraints = 13022/654/145. After SQUEEZE; R1 = 0.0736, wR2 = 0.1850 [ $I > 2\sigma(I)$ ], R1 = 0.1133, wR2 =0.2044 (all data),  $GoF(F^2) = 0.985$ , data/variables/restraints = 13029/654/ 104.

Synthesis of MORF-3: During the crystallization of MORF-2, as described above but with SO<sub>4</sub><sup>2-</sup> impurities (see text for explanation), a small crop of colorless crystals with formula [Zn(2CDSDB24C8)2][{Zn- $(CH_3OH)_2(H_2O)_2(SO_4)_2]$ ·42  $CH_3NO_2$  were also isolated ( $\approx 10\%$  yield). X-ray data:  $C_{140}H_{250}N_{48}O_{128}S_6Zn_3$ ,  $M_r = 5042.35$ , colorless prisms (0.38×  $0.14 \times 0.12$  mm), orthorhombic,  $Cmc2_1$ , a = 35.882(6), b = 24.607(4), c = 10.000021.956(4) Å, V = 19386(5) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.728 \text{ g cm}^{-3}$ ,  $\mu = 0.570 \text{ mm}^{-1}$ , min/max transmission = 0.5789, Mo<sub>Ka</sub>  $\lambda$  = 0.71073 Å, T=173.0(2) K, 61667 total reflections (R(int)=0.1675). The unit cell included a very large region of severely disordered CH<sub>3</sub>NO<sub>2</sub> molecules which could not be modeled. We therefore employed the program SQUEEZE<sup>[15]</sup> to calculate the diffraction contribution of the solvent molecules and produce a data set with solvent-free diffraction intensities. With no solvent contribution, before SQUEEZE: R1=0.2030, wR2=0.4679 [I>2o(I)], R1= 0.2957, wR2 = 0.5078 (all data),  $GoF(F^2) = 2.593$ , data/variables/restraints = 10313/258/17. After SQUEEZE; R1 = 0.0853, wR2 = 0.2037 [I>  $2\sigma(I)$ ], R1 = 0.1376, wR2 = 0.2304 (all data),  $GoF(F^2) = 0.962$ , data/variables/restraints = 10311/694/506.

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