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A Molecular Solomon Link**

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For over a century, mathematicians have been unraveling, investigating, and tabulating knots and links. On consulting tomes on knot theory,[1] one finds tables listing over 100 knots and links ordered by the numbers of their crossings and components. Just a handful of these knots—probably the most pleasing ones—have transcended cultural and disciplinary divides over the centuries. These popular knots or links, sought after by scholars of all persuasions, include the ubiquitous trefoil knot, the Hopf and Whitehead links, King Solomon's Knot, and the Borromean Rings (BRs). Predating the mathematical and scientific investigations of these topological constructs, many different cultures have embraced these three-dimensional knotted loops to serve as emblems of important virtues. BRs, comprising[2] three mutually interlocked rings in which no two are catenated, have surfaced to represent the inseparable union of three ideals such as the Holy Trinity and harmony between three wings of the Borromeo family. King Solomon's Knot, which also has deep historical roots,[3] is believed by many to contain all the wisdom of King Solomon. Upholding, as it does, the symbol of knowledge, it is found (Figure 1) adorning the crowns of African kings, carved into the walls of Italian abbeys, patterned in Celtic stained glass windows, and incorporated into the architectures and decors of university buildings, to name just a few instances. Although this topology holds the title of King Solomon's "Knot", it is described[1] mathematically as a "link"—or, more precisely, the 4_1^2 link, since it contains four crossings and comprises two components. Nevertheless, we will refer to this topology interchangeably as a Solomon Knot or link, in deference to its history, established eons before the mathematical cataloguing of knots and links began. Just as we have abbreviated the Borromean Rings to BRs, we will use SKs to refer to Solomon Knots.

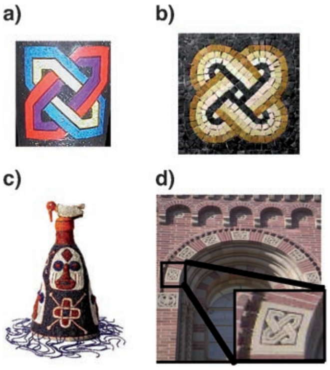

Figure 1. Solomon Knots in art and culture: a) A painting on glass from the British Isles. b) A mosaic tile from Italy, where it is known as *Il nodo di Salomone*. c) An emblem on a head-piece from Africa. Note that in some instances, the crossings of the two rings are not honored with precision by artists. d) A carving over a window to Moore Hall at the University of California, Los Angeles. The images in (b) and (c) are provided courtesy of Joel Lipton (see reference [3]).

With the advent of synthetic methodologies advancing under the umbrella of template-directed synthesis,[4] chemists began to gain access to topologically interesting molecular structures, including the trefoil knot,[5] the Hopf link (also known as a [2]catenane),[6] King Solomon's Knot (also referred to as a doubly braided, or doubled interlocked catenane, or a four-noded link)[7] and BRs.[8] Sauvage[5b–d] has produced a well-documented series of trefoil knots by allowing two threads, each composed of two bidentate 1,10-phenathroline ligands separated by a 1,3-phenylene spacer, to self-assemble around two metal-ion templates. Using this same strategy, Sauvage[7a] added an extra coordination site to the threads, and, in the presence of three metal ions, constructed an early example of a molecular Solomon Knot. Later on, Sauvage, in collaboration with Fujita, reported[7b] another molecular Solomon link by exploiting the different coordination geometries of Pd^{II} and Cu^{I}. These two metals, when combined with a 1,10-phenathroline ligand terminated with pyridyl groups, result in the formation of a Solomon Knot. Meanwhile, Puddephatt[7c] had progressed logically in his research from a macrocycle to a catenane, and finally to a molecular Solomon link by changing the constitution of the rings. Herein, we report the template-directed synthesis of a molecular Solomon link obtained from a 12-component self-assembly process that exploits dynamic covalent chemistry[9] to form eight imine bonds and 24 dative bonds associated with the coordination of two interlocked macrocycles, each

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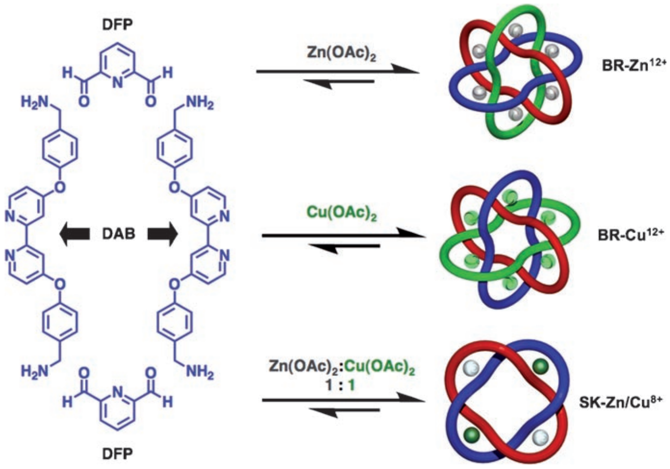
tetranucleating and decadentate overall, to a total of two Zn^II^ and two Cu^II^ ions. The two macrocycles provide, diagonally in pairs, four *exo*-bidentate bipyridyl and four *endo*-diiminopyridyl ligands to the four metal ions. This unexpected topology was obtained by altering the conditions of our molecular BR synthesis[8] templated by Zn^II^ ions. For reasons we can only speculate about at this stage, in the presence of *equimolar amounts* of Zn^II^ and Cu^II^ ions, the molecular Solomon link becomes one of the thermodynamic products in solution.

Our synthesis[8] of molecular BRs relies upon using six Zn^II^ ions as metal templates to preorganize six *endo* diformylpyridine (DFP) and six *exo* diaminobipyridine (DAB) fragments such that they undergo an 18-component self-assembly process (Scheme 1). Under appropriate conditions ($Zn(OAc)_2$, *i*PrOH, 70 °C, 24 h), BR-Zn·12 TFA can be isolated in yields of 95 %, even when the reaction is conducted[10] on a gram scale (TFA = trifluoroacetate). Zn^II^ was chosen as the metal template for two reasons, namely, 1) it is kinetically labile and so can accommodate octahedral geometry provided this arrangement is favorable for the orthogonal alignment of the ligands, thus assisting in BR formation, and 2) it is diamagnetic, which makes it possible to monitor the reaction by ^1H NMR spectroscopy. Subsequently, we synthesized a range of Borromeates[11] [e.g., BR-Cu·12 TFA (85 %), BR-Ni·12 TFA (82 %), BR-Cd·12 TFA (80 %), BR-Mn·12 TFA(70 %), and BR-Co·12 TFA (36 %)] using other transition-metal ions as templates. The dependence of the percentage yields (given in parentheses) of the Borromeates on the choice of metal ion intrigued us so much that we wondered what the outcome would be if we mixed the metal templates (e.g., Zn^II^ and Cu^II^). In many cases, mixed-metal templates[12] have resulted in metallo-organic architectures different from those that are templated by their homometal analogues. Thus, using otherwise the same conditions as those employed in the making of BR-Zn·12 TFA, we mixed $Zn(OAc)_2$ and $Cu(OAc)_2$ with DAB-H_n·*n* TFA and DFP in a 1:1:2:2 ratio. The reaction mixture afforded a pale-blue powder, which was crystallized over two weeks from MeOH/Et_2O by vapor diffusion to give green, rhomboid-shaped, single crystals (Figure 2) suitable for X-ray crystallography.



Scheme 1. Whereas the addition of $Zn(OAc)_2$ or $Cu(OAc)_2$ to a solution of DAB and DFP in *i*PrOH leads eventually to the near-quantitative formation of crystals of BR-Zn·12TFA and BR-Cu·12TFA, respectively, the addition of the two diacetates in a 1:1 molar ratio leads to the production of single crystals of SK-Zn/Cu·8TFA under kinetic control.

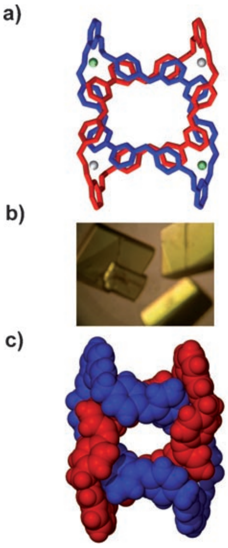


Figure 2. a) Tubular representation of the solid-state structure of SK-Zn/Cu^{8+} viewed down one of its three C_2 axes. The TFA ions coordinated to the metal dications have been omitted for clarity. b) The large green, rhomboid-shaped, single crystals of SK-Zn/Cu·8 TFA. c) Space-filling representation of the solid-state structure of SK-Zn/Cu^{8+}.

Ten random single crystals were analyzed independently. In all 10 cases, it was revealed that the molecular structure was not that of a BR in the crystalline state. Instead, it is clear that the same ligands that are present in the BRs assemble in pairs to give another type of molecular link, namely, the SK shown in Figure 2. As the distribution of Zn^II^ and Cu^II^ was indistinguishable from an analysis of the X-ray crystallographic data,[13,14] a species that contains two Zn^{2+} ions and two Cu^{2+} ions is illustrated in Figure 2, although six different species—ignoring chirality—are possible: two homometal species, Zn_4 and Cu_4, and four heterometal species, Zn_3Cu, Zn_2Cu_2 (as both *cis* and *trans* isomers), and $ZnCu_3$. The solid-state structure (Figure 2 a,c) of SK-Zn/Cu·8 TFA (Scheme 1) reveals a molecular structure with approximately D_2 symmetry. Each of the two equivalent macrocyclic ligands adopts a twisted chairlike conformation, and the SK-Zn/Cu^{8+} octacation is symmetry-related from half of one of the macrocyclic ligands, which is 24.4 Å long from the tip of one pyridyl unit to the tip of the other. Molecular recognition is manifest in a mutually compatible manner. The two equivalent macrocyclic ligands are held together by four metal ions (M), positioned 16.2 and 16.3 Å apart in the same ligand, with adjacent distances in different ligands ranging from 11.3 to 11.8 Å. The macrocyclic ligands are coordinated at each end in a slightly distorted octahedral geometry to five N atoms (M−N bond lengths ranging from 1.8 to 2.3 Å with the *cis* N−M−N bond angles ranging from 69.6 to 120.6°), with the sixth coordination site occupied by an O atom (M–O bond lengths of 2.0 to 2.1 Å and *cis* O–M–N bond angles ranging from 88.2 to 95.9°) belonging to a TFA ion with a disordered trifluoromethyl group. The four equivalent bipyridyl ligands are sandwiched unsymmetrically between four pairs of benzyloxy rings, such that the π–π-stacking distances are between 3.2 and 3.5 Å. The SK-Zn/Cu^{8+} octacation contains an inner cavity that is embraced with eight O atoms that are pointing inwards in a distorted cubelike array (Figure 3). The adjacent O⋯O distance in the twisted upper and lower faces of the distorted cube range from 5.7 to 5.8 Å and the O⋯O separations between these planes vary between 4.3 and 4.5 Å.

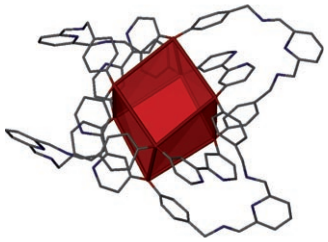


Figure 3. A stick representation of the solid-state structure of SK-Zn/Cu^{8+} upon which is superimposed the distorted cube connecting the eight O atoms.

In common with the trefoil knot,[15,16] the SK is unconditionally topologically chiral (Figure 4a), and molecules can be assigned the descriptor *P* or *M*, according to their absolute chiralities, by using the skew-line system (Figure 4b).[17] It transpires that SK-Zn/Cu·8TFA crystallizes as a racemic modification of the *P* and *M* enantiomers, as indicated by the centrosymmetric space group and the enantiomeric pair of molecules present in the unit cell (Figure 4c). At the supramolecular level, the enantiomeric SK-Zn/Cu^{8+} octacations are stabilized by pairs of intermolecular C–H⋯π interactions, each involving a methylene group hydrogen atom and the π face of a benzyloxy function in a neighboring enantiomeric molecule (C⋯π 3.41, H⋯π 2.53 Å). These noncovalent interactions help to sustain the layered superstructures shown in Figure 5a. The elliptically shaped channels, which traverse the crystal in a manner that is approximately mutually orthogonal, are filled with disordered TFA counterions and solvent molecules, which may not be entirely innocent when it comes to the growth of single crystals composed of mixed-metal SKs. This supposition is supported by high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) performed on single crystals dissolved in MeOH prior to their analysis. HR-ESI-MS reveals (Figure 6) not only a set of three peaks at *m/z* 1440.2345 $[M_{SK}-3\,TFA+Cu/Zn]^{2+}$, 1052.1702 $[M_{SK}]^{3+}$, and 818.9403 $[M_{SK}+TFA]^{4+}$, but also a set of three peaks at *m/z* 1463.2198 $[M_{BR}-3\,TFA]^{3+}$, 1069.4266 $[M_{BR}-4\,TFA]^{4+}$, and 832.7438 $[M_{BR}-5\,TFA]^{5+}$ that apparently show[18] the presence of BRs containing six metal ions. It follows that the SK-Zn/Cu^{8+} species are most likely interconverting with BR-Zn/Cu^{12+} species in the methanolic solution. We are, therefore, led to the conclusion that the reason we obtain single crystals containing only the SK-Zn/Cu^{8+} species is that they are formed under kinetic control from a dynamic library containing BR-Zn/Cu^{12+} and SK-Zn/Cu^{8+} species. For the time being, at least, we are assuming that the kinetically controlled crystallization process[19–21] is orchestrated by 1) the mixed-metal dications and/or 2) the TFA ions, plus perhaps solvent molecules.

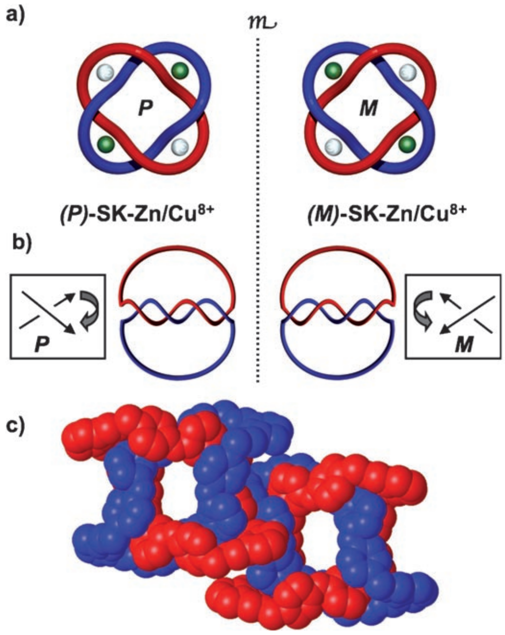


Figure 4. a) Graphical representations of the *P* and *M* enantiomers of SK-Zn/Cu^{8+}. b) The enantiomeric octacations depicted as a braided [2]catenane whereby the helical chiralities are assigned by using the skew-line system. The convention established for two-braided links with four or more crossings involves first of all orienting the two rings in parallel. This perspective reveals the double helix that results from the four crossings observed in this particular braided presentation. The skew-line system can be applied by orienting two arrows down each strand of the helix such that they are both pointing in the same direction. The arrow head of the bottom arrow is traversed back to overlap with the arrow head of the top arrow. If this pathway traces a clockwise direction, then the crossing is assigned the plus (*P*) descriptor, and if it traces a counterclockwise direction, then the crossing is assigned the minus (*M*) descriptor. c) Space-filling representation of the centrosymmetrically related *(P)*-SK-Zn/Cu^{8+} and *(M)*-SK-Zn/Cu^{8+} enantiomers in the solid state.

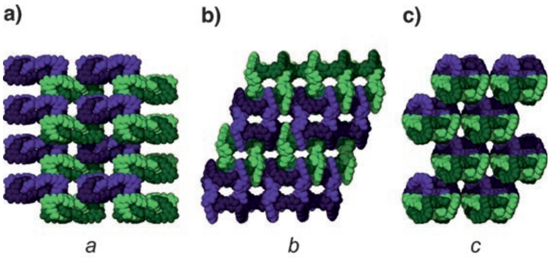


Figure 5. Space-filling representation of the packing of *(P)*-SK-Zn/Cu^{8+} (purple) with respect to *(M)*-SK-Zn/Cu^{8+} (green) in the solid-state superstructure looking down the a) *a* axis, b) *b* axis, and c) *c* axis.

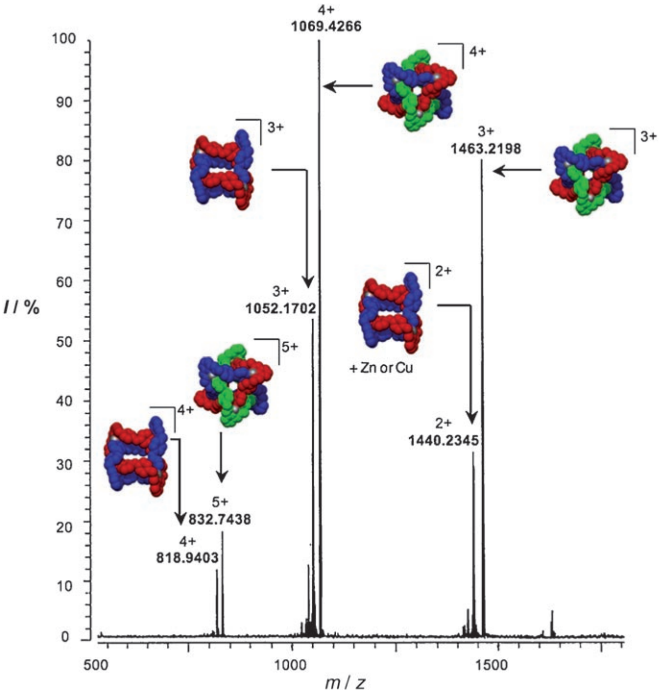


Figure 6. The HR-ESI mass spectrum obtained from a methanolic solution of a single crystal of SK-Zn/Cu·8TFA.

The fact that dynamic chemistry—involving not just noncovalent and coordinative (dative) bonds, but also reversible covalent bonds[9]—along with a phase change from solution to the solid state, results in the formation of a molecular Solomon Knot[22] in the crystalline state is a situation that merits further investigation. Presently, we are trying to obtain better X-ray crystallographic data to see if we can unravel the nature of this kinetically controlled crystallization process. In a wider context, the finding described herein is significant because it suggests that, in these dynamic mechanically interlocked systems, there is present, under the appropriate conditions, a dynamic combinatorial library from which it is possible, during a crystallization process that is kinetically controlled, to amplify one of the members of the library. What does all this control at a supramolecular level mean for covalent chemistry? It means, for example, that synthetic chemistry is ready to make substantial inroads into the synthesis of some really exotic molecular links.

Experimental Section

SK-Zn/Cu·8TFA: Boc-protected DAB (108.2 mg, 0.18 mmol) was dissolved in neat CF_3CO_2H (5 mL) and stirred at room temperature for 30 min (Boc = *tert*-butyloxycarbonyl). The excess of TFA was removed under reduced pressure, followed by subsequent additions and removals of MeOH (3 × 5 mL), leaving DAB-H_n·nTFA as a pink tar. $Zn(OAc)_2$ (16.5 mg, 0.09 mmol) and $Cu(OAc)_2$ (16.4 mg, 0.09 mmol) were added simultaneously with stirring to an *i*PrOH solution (5 mL) containing the freshly deprotected DAB, followed by the addition of DFP (24.6 mg, 0.18 mmol). The reaction mixture was heated at 70 °C for 24 h to produce a pale-yellow solution, along with a light-blue precipitate. The mixture was allowed to cool down to room temperature, and the precipitate was removed by filtration, washed with *i*PrOH (3 × 2 mL) and Et_2O (3 × 2 mL), and dried to yield a pale-blue powder (91.1 mg). Elemental analysis (%) of the pale-blue powder, calcd: Zn 5.82, Cu 5.66; found: Zn 5.91, Cu 4.05. An EPR spectrum, recorded on the pale-blue powder, confirmed the presence of copper with a hyperfine coupling constant (A) of 140 and the following g factors: $g_x = 2.08$, $g_y = 2.25$, and $g_z = 2.25$. The ^1H NMR spectrum of a single crystal recorded in CD_3OD is very broad, which indicates the presence of paramagnetic Cu^{II} ions. Crystals suitable for X-ray crystallography were grown by vapor diffusion of Et_2O into a solution of the pale-blue powder dissolved in MeOH. X-ray crystallography on 10 single crystals showed that all were SK-Zn/Cu·8TFA.

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[13] Crystal data for $[(C_{62}H_{46}N_{10}O_4)_2(ZnO_2CCF_3)_2(CuO_2CCF_3)_2]$-$(CF_3CO_2)_4\cdot 6.4\,CH_3OH$-$\cdot 8.2\,H_2O$, monoclinic, $a = 23.002(4)$, $b = 28.703(5)$, $c = 28.946(5)$ Å, $\beta = 113.164(6)°$, $V = 17570(5)$ Å^3, space group $C2/c$, $Z = 4$, $\rho_{calcd} = 1.148\,g\,cm^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $F(000) = 6235$, $T = 120(2)$ K, 13601 unique reflections ($2\theta_{max} = 51.1°$), of which 6095 were observed $[I_o > 2\sigma(I)]$. Final R factors: $R_1 = 0.1908$, $wR_2 = 0.3591$ for 775 parameters.

[14] Single crystals of SK-Zn/Cu·8TFA, suitable for X-ray crystallography, were obtained by vapor diffusion of Et_2O into a methanolic solution of the compound over a period of two weeks. A single green crystal ($0.52 \times 0.28 \times 0.22\,mm^3$) was attached, for example, with oil to a thin glass fiber. As solvent loss is evident immediately after the crystal has been removed from the mother liquor, suitable crystals were extremely difficult to mount. Data were collected on a Bruker-Nonius FR591 rotating anode diffractometer with $Mo_{K\alpha}$ radiation by using the φ and ω scan modes (210-s exposure per frame). Data were corrected for absorption by using the SADABS program, and structural solution and refinement were performed with the SHELX-97 software package. All non-hydrogen atoms of SK-Zn/Cu·8TFA were refined anisotropically, whereas the hydrogen atoms were included at geometrically calculated positions and allowed to ride on their parent atoms. CCDC-617801 contains 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.

[15] Molecules with intertwined and interlocked structures, such as the SKs, have nonplanar graphs and so can exhibit topological chirality. See: a) C. Liang, K. Mislow, *J. Math. Chem.* **1995**, *16*, 27–34; b) C. Liang, K. Mislow, *J. Math. Chem.* **1995**, *18*, 1–24; c) K. Mislow, *Top. Stereochem.* **1999**, *22*, 1–82; d) J.-C. Chambron, C. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, *Chirality* **1998**, *10*, 125–133.

[16] Although the classic example is the trefoil knot, [2]catenanes can also display topological chirality, provided that both rings encompass constitutional directionality. By contrast, the BRs remain achiral even after ring orientation. See reference [15c].

[17] D. M. Walba, *Tetrahedron*, **1985**, *41*, 3161–3212.

[18] Zn^{II} and Cu^{II} are only two atomic mass units apart and also have overlapping isotope distributions. Calculations of the theoretical peaks centered at m/z 1068.88 and associated with a statistical distribution of all 10 possible BR species produce patterns which resemble closely the peak centered at m/z 1069.1723 in the HR-ESI mass spectrum (Figure 6). Coincidentally, the theoretical peak for the BR species with three Zn^{II} and three Cu^{II} ions also matches well with the experimentally observed spectrum.

[19] In the area of crown ether/dialkylammonium ion recognition, we have observed previously the PF_6^- anion-assisted formation in the solid state of discrete supermolecules with pseudorotaxane geometries which are stabilized by complementary C–H···F hydrogen bond interactions. See: a) P. R. Ashton, M. C. T. Fyfe, P. T. Glink, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1997**, *119*, 12514–12524; b) P. R. Ashton, M. C. T. Fyfe, S. K. Hickingbottom, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 577–589; c) P. R. Ashton, M. C. T. Fyfe, M.-V. Martínez-Díaz, S. Menzer, J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1998**, *4*, 1523–1534; d) M. C. T. Fyfe, J. F. Stoddart, D. J. Williams, *Struct. Chem.* **1999**, *9*, 243–259; e) D. G. Amirsakis, M. A. Garcia-Garibay, S. J. Rowan, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **2001**, *113*, 4386–4391; *Angew. Chem. Int. Ed.* **2001**, *40*, 4256–4261.

[20] A dramatic example of a kinetically controlled self-assembly process was witnessed when, on crystallization from the appropriate solvent mix, tetrabenzo[24]crown-8 and dibenzylammonium hexafluorophosphate form an array of [2]pseudorotaxanes stabilized by C–H···F hydrogen bonds to a highly ordered, interstitially located PF_6^- anions. When the crystals of the [2]pseudorotaxane are dissolved in CD_3COCD_3, the 1:1 complex disassembles spontaneously at 25 °C with a half-life of 15.5 days, that is, $\Delta G^{\neq} = 26\,kcal\,mol^{-1}$. See: a) P. R. Ashton, S. J. Cantrill, J. A. Preece, J. F. Stoddart, Z.-H. Wang, A. J. P. White, D. J. Williams, *Org. Lett.* **1999**, *1*, 1917–1920; b) S. J. Cantrill, J. A. Preece, J. F. Stoddart, Z.-H. Wang, A. J. P. White, D. J. Williams, *Tetrahedron* **2000**, *56*, 6675–6681.

[21] The kinetically controlled self-assembly of two different donor–acceptor pseudorotaxanes on crystallization was reported recently: B. H. Northrop, S. I. Khan, J. F. Stoddart, *Org. Lett.* **2006**, *8*, 2159–2162.

[22] Molecular SKs are prevalent in nature. For example, the product of site-specific recombination on circular unknotted DNA can show topological selectivity toward the formation of a DNA-based SK. See: a) S. D. Colloms, J. Bath, D. J. Sherratt, *Cell* **1997**, *88*, 855–864; b) N. Sträter, D. J. Sherratt, S. D. Colloms, *EMBO J.* **1999**, *18*, 4513–4522; c) I. Grainge, D. Buck, M. Jayaram, *J. Mol. Biol.* **2000**, *298*, 749–764; d) S. Pathania, M. Jayaram, R. M. Harshey, *Cell* **2002**, *109*, 425–436; e) M. Vazquez, S. D. Colloms, D. W. Sumners, *J. Mol. Biol.* **2005**, *346*, 493–504.