Supramolecular Polymers

DOI: 10.1002/ange.200801002

Host–Guest Driven Self-Assembly of Linear and Star Supramolecular Polymers**

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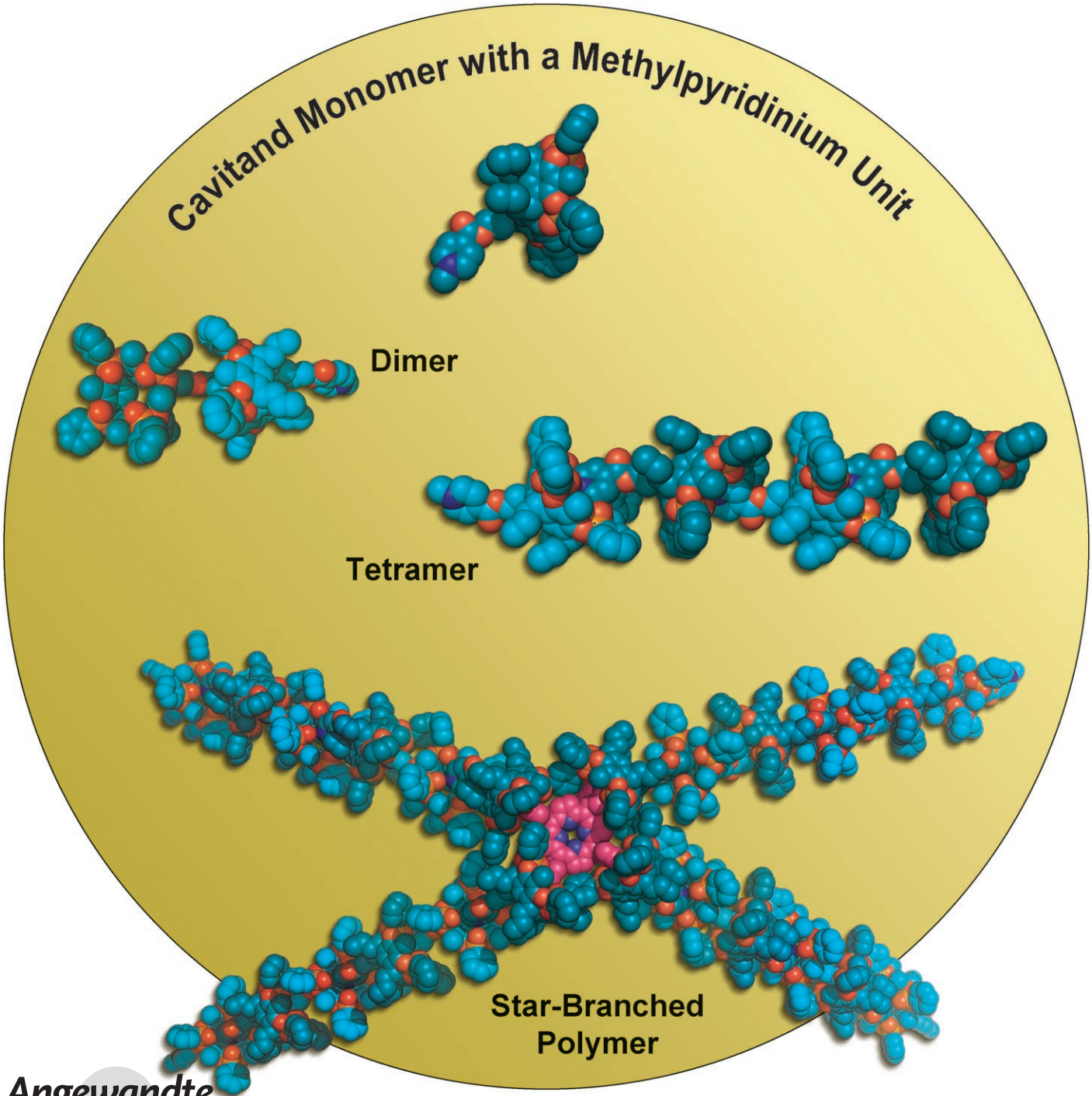

Dynamic materials[1] featuring modular components, nanoscale dimensions, and controlled responsiveness to external stimuli are among the most attractive targets in contemporary materials science. Since supramolecular polymers[2] fulfill nicely all these conditions, they are in a prominent position in the list of effective dynamic materials.

While the self-assembly of supramolecular polymers driven by hydrogen bonding[3] and metal coordination[4] has undergone explosive development, the host–guest route is by far less traveled, despite the many different options potentially available. As very high association constants are required for the self-assembly of truly polymeric materials,[5] the number of possibilities is greatly reduced. So far, most of the research has been centered on solvophobic interactions using cyclodextrins as hosts,[6] and, to a lesser extent, on pseudorotaxane threading with alkylammonium guests.[7] More recently calixarenes,[8] cavitands,[9] and donor–acceptor molecules[10] have been used as monomers, leading to the formation of oligomeric materials.

In this paper we report a new class of supramolecular polymers whose self-assembly is driven by the outstanding complexation properties of tetraphosphonate cavitands toward methylpyridinium guests. Phosphonate cavitands are resorcinarene-based molecular receptors presenting one or more P^V moieties as bridging units.[11] Tetraphosphonate cavitands in their all-inward configuration[12] are able to complex positively charged species, such as ammonium salts or inorganic cations with very high association constants ($K_{ass} = 10^7$–$10^9\,M^{-1}$).[13]

The target cavitand monomers **1a**,**b** (Figure 1), which present four inward-facing phosphonate bridges at the upper rim and a single methylpyridinium unit at the lower rim, were synthesized in four steps starting from a monofunctionalized resorcinarene[14] (see the Supporting Information). The four methyl groups in the apical positions were introduced to deepen the cavity and to strengthen CH–π interactions. The structurally related tetrathiophosphonate analogues **2a**,**b** were also prepared to be used as chain stoppers. In fact, **2** retains its monomeric form both in solution (Figure 6a) and in the solid state as shown by the crystal structure of **2a** (see the Supporting Information). The P=O/P=S exchange completely suppresses methylpyridinium complexation, which is mainly driven by cation–dipole interactions.

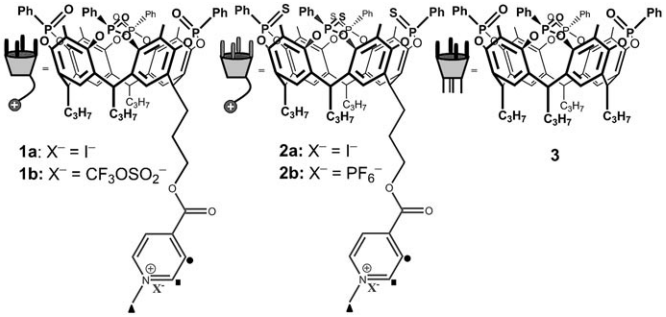

Figure 1. Monomers **1a**,**b**, chain stoppers **2a**,**b**, and model cavitand **3**. In structures **1** and **2** the labels on the pyridinium ring correspond to diagnostic ^{1}H NMR resonances shown in Figure 6.

The complexation properties of tetraphosphonate cavitands toward methylpyridinium guests were studied by isothermal titration calorimetry (ITC) using derivative **3** as the host. The formation of **2a**·**3** and **2b**·**3** dimers represents a suitable model of a single polymerization step. In both cases the measured K_{ass} values exceed $10^7\,M^{-1}$ in dichloromethane (Table 1).

Table 1: Thermodynamic parameters deduced from ITC experiments for the host–guest dimers at 298 K.[a]

Entry	ΔH [kJ mol^{-1}]	$T\Delta S$ [kJ mol^{-1}]	ΔG [kJ mol^{-1}]	K_{ass} [M^{-1}]
2b·**3**[b]	-11.9 ± 0.4	16.1 ± 0.5	-28.0 ± 0.2	$(8.2\pm0.7)10^4$
2b·**3**[c]	-30.0 ± 0.1	13.4 ± 0.5	-43.6 ± 0.5	$(4.0\pm0.1)10^7$
2a·**3**[c]	-26.1 ± 0.2	15.2 ± 0.9	-41.4 ± 0.8	$(1.9\pm0.6)10^7$
2b·**3**[b] + competitive guest[d]	-99.7 ± 12.6	-77.9 ± 13.6	-21.8 ± 0.6	$(6.0\pm1.4)10^3$

[a] All reported values are the average of three independent measurements. [b] In methanol. [c] In dichloromethane. [d] Competitive guest is *N*-butylmethylammonium chloride.

Interestingly, the complexation is driven not only by enthalpy but also by entropy, indicating that solvation plays a significant role in the process. In fact, the K_{ass} values are strongly influenced by the solvent for both guests, increasing by two orders of magnitude in moving from methanol to methylene chloride. In contrast the role of the counterion is limited, with a small preference for PF_6^- over iodide.

The crystal structure of the **2b**·**3** dimer (Figure 2) gives evidence of the two major interactions responsible for the complexation: a multiple ion–dipole interaction between the inward-facing P=O groups and the positively charged methylpyridinium moiety, and directional hydrogen bonds involving the acidic methyl group with the π-basic cavity (CH_3–π interaction) and the *ortho* H-pyridinum atoms with two opposite P=O groups.

The same interactions responsible for dimer formation are observed in the homopolymer crystal structure of **1b**, where each linear polymeric chain packs against other four antiparallel chains (Figure 3). The charges of the monomers

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[**] This work was supported by NoE MAGMANet (E.D. and R.M.Y.) and PRIN 2006034018 (S.G.). We thank Prof. J. de Mendoza and his team at ICIQ for the use of ITC.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

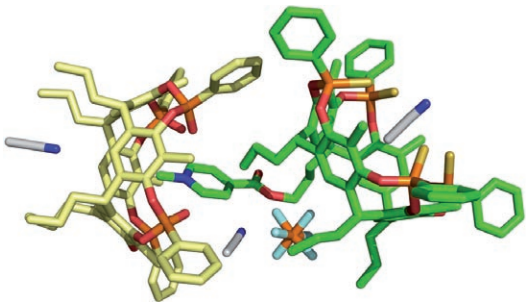

Figure 2. Crystal structure of dimer **2b**·**3**.

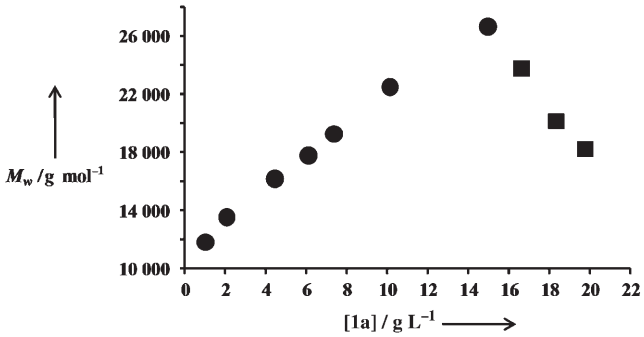

Figure 4. SLS measurements of M_w versus concentration for the homopolymer **1a** alone (black circles) and along with added chain stopper **2a** (black squares), see the Supporting Information.

bearing the guest functionality are counterbalanced by triflate anions located in between the lower-rim alkyl chains, close to the methylpyridinium cations. In the crystal the polymer assumes a straight and extended (all-*trans* pyridinium linker) conformation, by alternately bending the cavity mouth of each monomer of about ±45° with respect to the chain-growth direction.

The weight-average molecular weight M_w of polymer **1a** was experimentally determined at different concentrations in chloroform by static (elastic) light scattering (SLS, Figure 4) in batch off-line mode. The M_w of the polymer increases linearly with the concentration in the range of 1.04–15.0 g L^{-1} and reaches an upper value of 26300 g mol^{-1}, which corresponds to an average degree of polymerization $\langle N_W \rangle$ of 18 units. Beyond this concentration the SLS signal was saturated as it is dependent on both concentration and molecular weight.[5,15] Stepwise addition of stopper **2a** led to a progressive linear decrease of M_w (Figure 4). In contrast, the presence of 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrintetra(*p*-toluene sulfonate) (**4**) as a template led to a substantial increase in M_w (Table 2). The porphyrin acts as nucleation unit for the formation of a star-branched polymer through its four *meso* pyridinium groups (Figure 5).[16] Porphyrin **4** is insoluble in pure chloroform, and it is driven into solution by complexation with the end cavities of the polymer chains. The solubility of **4** in solutions of **1a** depends on the concentration of the latter; the maximum **4**/**1a** ratio is 2.5% molar in a solution containing 1.04 g L^{-1} **1a** (Table 2), in which the concentration of end cavities is higher. In this way the M_w of the polymer can be dramatically increased without changing the monomer concentration.

The reversible disassembly of the homopolymer could be triggered by addition of a competitive guest, *N*-butylmethylammonium iodide. The K_{ass} of the complex between this guest and **3** could not be measured by ITC, since its value exceeds 10^8 M^{-1}, which is the upper limit of reliable K_{ass} determination by this method.[17] Therefore the affinity of this competitive guest for **3** was evaluated by ITC by means of guest-exchange experiments with complex **2b**·**3** and *N*-butylmethylammonium chloride in methanol (Table 1). The recorded ΔG value indicates a large preference for complexation of the *N*-butylmethylammonium ion and indicates complete guest exchange at close to the stoichiometric ratio.

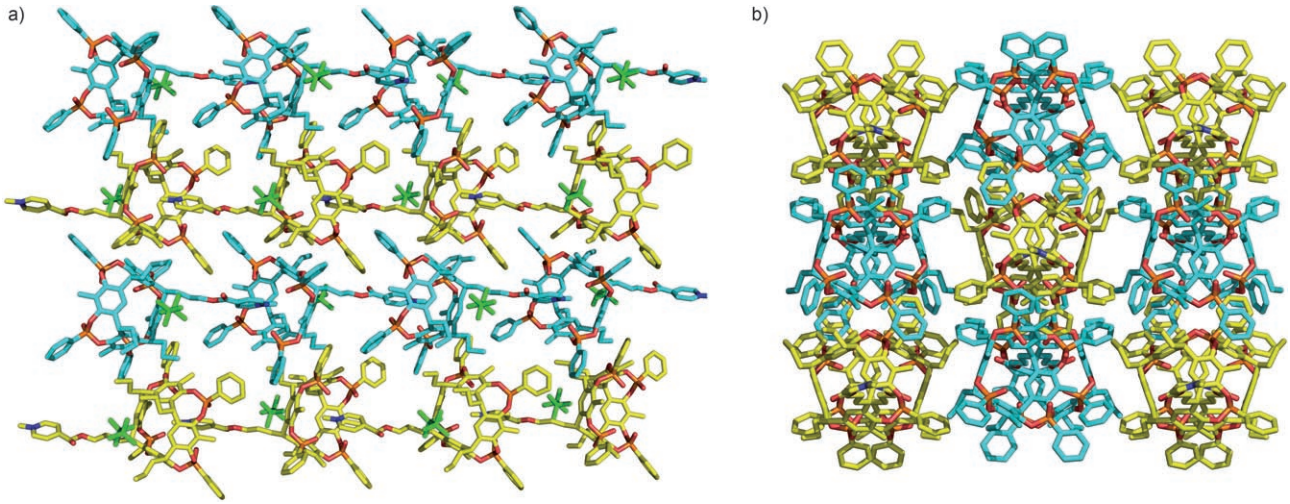

Figure 3. Views of the crystal packing of the **1b** homopolymer perpendicular (a) and parallel (b) to the linear polymeric chains. Two crystallographically independent monomer molecules are present in the cell, each of which gives rise to a similar chain that grows antiparallel (yellow and light blue chains) (a). Each chain interacts with other four antiparallel chains giving a checkerboard pattern when viewed along the chain (b).

Table 2: SLS measurements of the weight-average molecular weight of the star-branched polymer.

Conc. [g L^{-1}]	Molar ratio **4**/**1a** [%]	M_w^0 **1a** linear polymer[a]	M_w **1a** star polymer[b]
1.04	2.5	11850 ± 150	46210 ± 580
2.05	2.0	13490 ± 230	41600 ± 180
4.10	2.0	15940 ± 90	49700 ± 180

[a] M_w^0 before addition of the template. [b] M_w after addition of template **4**.

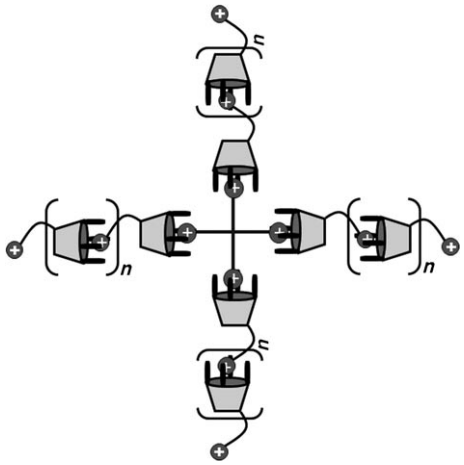

Figure 5. Template-induced formation of a host–guest star-branched polymer.

The polymer disassembly, monitored by ^{1}H NMR spectroscopy in $CDCl_3$,[18] is recorded in Figure 6. Addition of two equivalents of *N*-butylmethylammonium iodide to **1a** led to the complete disassembly of the polymer (Figure 6d). The chemical shifts of pyridine aromatic and N-CH_3 protons are comparable to those of the stopper **2a** (Figure 6a), while the NH and N-CH_3 peaks of the ammonium salt undergo large upfield shifts. These changes prove that the competitive guest replaced the methylpyridinium moiety inside the cavity, inducing the depolymerization. Finally, addition of two equivalents of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) restored the original polymer quantitatively (Figure 6e). DBU breaks the ammonium–cavitand complex by deprotonating the guest. Since DBU is a bulky base, it cannot enter the cavity; therefore the affinity of its protonated form for **1a** is very low.

The same protocol can be followed visually by suspending the **1a** polymer in acetonitrile, where it is insoluble (see vials in Figure 6). Addition of one equivalent of *N*-butylmethylammonium iodide to the suspension was sufficient to obtain a perfectly homogeneous solution, as expected for disassembled small oligomeric and monomeric species. The solution became again heterogeneous after addition of one equivalent of DBU, owing to the presence of the reassembled polymer.

In conclusion, a new family of host–guest supramolecular polymers has been designed, prepared, and characterized. The self-association mode leading to the polymer formation has been clarified both in solution and in the solid state. The degree of polymerization can be finely tuned by addition of a chain stopper, in the form of structurally related but complexation-inefficient tetrathiophosphonate cavitand **2**. The remarkable plasticity of the system is proven by the guest-triggered reversible assembly–disassembly and by the template-driven switch from the linear to star-branched polymer.

Received: March 1, 2008
Published online: May 5, 2008

Keywords: host–guest chemistry · phosphonate cavitands · self-assembly · supramolecular chemistry · supramolecular polymers

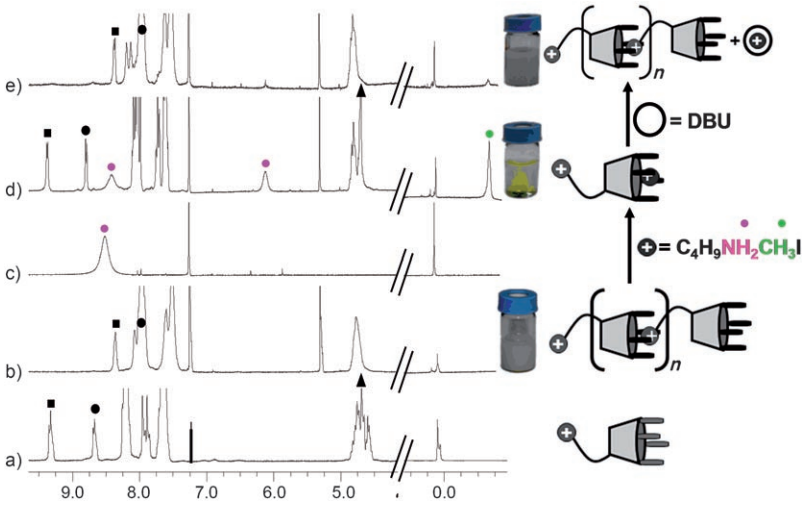

Figure 6. Section of the ^{1}H NMR spectra (300 MHz, solvent $CDCl_3$) showing the guest-triggered assembly–disassembly of the homopolymer **1a** (see Figure 1 for assignment of diagnostic ^{1}H NMR resonances in **1a**/**2a**): a) **2a**, b) homopolymer **1a**, c) *N*-butylmethylammonium iodide, d) **1a**·*N*-butylmethylammonium iodide complex, e) restored homopolymer **1a**.

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[18] The disassembly–reassembly sequence can be traced also by ^{31}P NMR spectroscopy under the same conditions (see Figure S2 in the Supporting Information).

