Supramolecular Polymers

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Formation of Linear Supramolecular Polymers That Is Driven by C–H···π Interactions in Solution and in the Solid State**

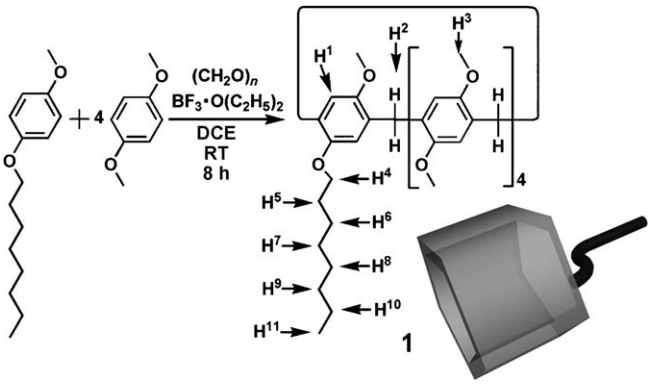
*Zibin Zhang, Yan Luo, Jianzhuang Chen, Shengyi Dong, Yihua Yu, Zhi Ma, and Feihe Huang**

C–H···π interactions are the weakest hydrogen bonds (1.5–2.5 kcal mol^{-1}), and they occur between soft acids and soft bases.[1] They are weaker than the classical hydrogen bonds between NH/O, NH/N, O/OH, and N/OH groups (3–7 kcal mol^{-1}).[1c] However, they have played significant roles in various fields of chemistry and biological systems, for example in determining the conformations of molecules,[2] crystal packing,[3] host–guest chemistry,[4] reaction selectivity,[5] and the self-assembly of molecules into organized supramolecular structures.[6] Their importance in the stabilization of conformations and structures of proteins and DNA has also been suggested in recent years.[7] On the other hand, supramolecular polymers, assembled from low molecular weight monomeric units by specific directional secondary interactions, such as hydrogen bonds, π–π interactions, hydrophobic interactions, and metal–ligand bonds, have demonstrated traditional polymeric properties and become an important part of stimuli-responsive dynamic materials.[8] Although C–H···π interactions have been used in construction of discrete supramolecular architectures,[9] supramolecular polymers driven by the C–H···π interactions have not been reported to date. Up to now, many small molecules have been used to prepare supramolecular polymers, but their preparation usually requires multiple steps and is time-consuming.[8] To find a simple way to make monomers for the preparation of supramolecular polymers is very important for future applications of supramolecular polymers. However, this still is a challenging mission for chemists.

Pillararenes are new calixarene analogues. They have shown interesting properties in host–guest chemistry.[10] Compared with traditional hosts, they have some advantages. First, they are highly symmetrical and rigid compared to crown ethers, calixarenes, and cyclodextrins, and this affords their selective binding to specially designed guests. Second, they are easier to functionalize by different substituents on the benzene rings than cucurbiturils; this enables tuning of their host–guest binding properties easily. Therefore, pillararenes are good and necessary supplements to these traditional hosts. Recently, we prepared the first copillararenes, which contain different repeating units, and found that there are four C–H···π interactions between a copillararene molecule and an included hexane molecule according to the crystal structure of their complex.[10d] Thus, we thought that if we incorporate long alkyl groups as the guest parts onto pillar[5]arenes to get A-B type monomers, we should obtain linear supramolecular polymers from self-organization in solution (Supporting Information, Scheme S1). For these supramolecular polymers, the repeating unit is a pseudorotaxane.

Using a method reported previously,[10d] a mixture of 4 equivalents of commercially available 1,4-dimethoxybenzene, 1 equivalents of 1-methoxy-4-(octyloxy)benzene, which was prepared from commercially available compounds by only one step, 5 equivalents of paraformaldehyde, and 5 equivalents of [BF_3·$O(C_2H_5)_2$] was stirred in 1,2-dichloroethane under nitrogen atmosphere at room temperature for 8 h. After purification by column chromatography, copillar[5]arene **1** was isolated in 9% yield (Scheme 1). The incorporation of the octyl group increased the solubility of **1** in most organic solvents significantly, which also increased the possibility of using it as a repeating unit for the fabrication of supramolecular polymers.

By comparison of ^{1}H NMR spectra of **1** and 1-methoxy-4-(octyloxy)benzene at 1 mM (Supporting Information, Fig-



Scheme 1. Synthesis and representation of the copillararene **1**. DCE = 1,2-dichloroethane.

[*] Z. Zhang, Y. Luo, J. Chen, S. Dong, Prof. Dr. F. Huang
Department of Chemistry, Zhejiang University Hangzhou
Zhejiang 310027 (China)
Fax: (+86) 571-8795-3189
E-mail: fhuang@zju.edu.cn
Homepage: http://www.chem.zju.edu.cn/~huangfeihe/
Assoc. Prof. Dr. Z. Ma
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences, Shanghai 200032 (China)
Prof. Dr. Y. Yu
Shanghai Key Laboratory of Magnetic Resonance
Department of Physics, East China Normal University
Shanghai 200062 (China)

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ure S4), we found that the octyl protons (especially H^{7-11}) revealed significant upfield shifts. This phenomenon clearly indicates that the flexible octyl groups tend to form intramolecular cyclic species at low concentrations. ^{1}H NMR spectra of **1** ($CDCl_3$, 400 MHz, 293 K) at concentrations in the range of 1–768 mM were monitored. As expected, the proton NMR spectra of **1** (Figure 1) are concentration-

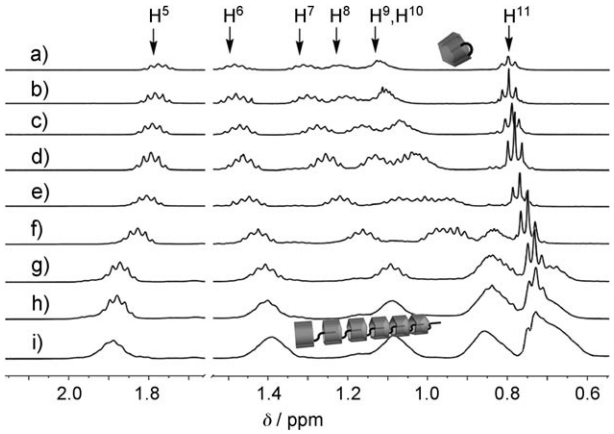

Figure 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 293 K) of **1** at different monomer concentrations: a) 1.00, b) 4.00, c) 16.0, d) 64.0, e) 128, f) 256, g) 384, h) 512, and i) 768 mM.

dependent, which reflects the involvement of fast-exchanging noncovalent interactions in solution. They revealed upfield shifts for H^{6-11} and downfield shifts for H^{1-5}. The protons H^{8-10} in particular showed relatively bigger upfield shifts. This effect is in agreement with the supramolecular polymer crystal structure (see below), which showed that protons H^{8-10} are located in the electron-rich cavity of **1**. When the concentration of **1** increased, the signals of H^{6-11} moved upfield very sharply at first (spectra a–f of Figure 1) and then slowly (spectra g–i of Figure 1), in agreement with the viscosity measurements discussed below. This result demonstrated that the percentage of complexed octyl groups increased when the concentration of **1** increased. The assignment and correlation of the protons were further validated by a NOESY NMR spectrum of **1** (Figure 2): Strong correlations

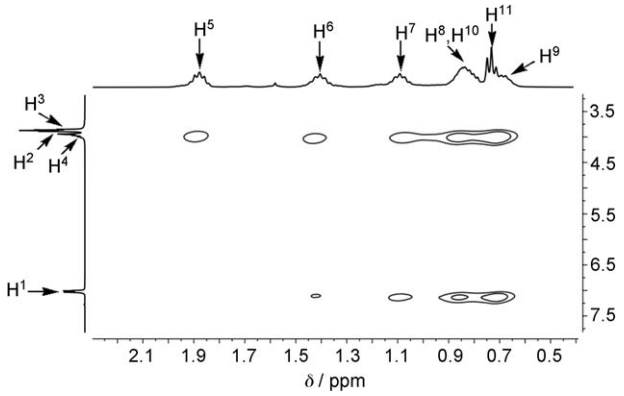

Figure 2. Partial NOESY NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **1** at a concentration of 384 mM.

were observed between the octyl protons H^{7-11} and the aromatic protons H^1 as well as the bridging methylene protons H^2 of the pillar[5]arene unit, suggesting that the octyl group was deeply threaded into the cavity of the pillararene moiety. The values of the fraction p of complexed octyl moieties at different concentrations were calculated from the chemical-shift changes of methyl protons H^{11} of the octyl group (Supporting Information, Table S1).[11] The maximum possible polymerization degree n at different concentrations were then calculated using the Carothers equation.[12] As the concentration increases, the calculated size of aggregates increases to truly large values, and linear supramolecular polymers are formed. For example, at 768 mM, $p = 97.2\,\%$ and $n = 36.8$, corresponding to a polymer with molar mass of 31.2 kDa.

Two-dimensional diffusion-ordered ^{1}H NMR spectroscopy (DOSY) experiments were performed to investigate the self-aggregation of **1** during linear supramolecular polymerization. We found that different aggregates are in fast exchange both on the ^{1}H NMR and on the DOSY timescale. As the monomer concentration increased from 16 to 512 mM, the measured weight-average diffusion coefficients decreased considerably from 6.47×10^{-10} to $1.57 \times 10^{-10}\,m^2\,s^{-1}$ (Figure 3 a), suggesting the concentration dependence of the

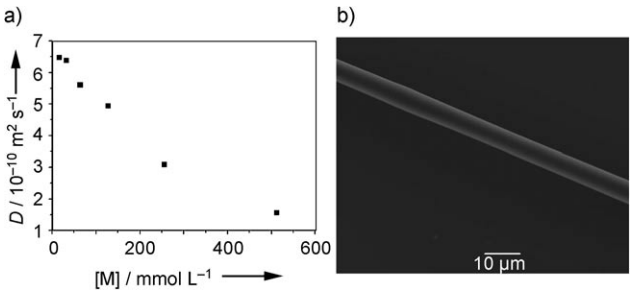

Figure 3. a) Concentration dependence of diffusion coefficient D (from ^{1}H NMR spectroscopy; 500 MHz, $CDCl_3$, 293 K) of **1**; b) Scanning electron micrograph of a gold-coated fiber drawn from a high-concentration solution of **1**.

linear supramolecular polymerization of monomer **1**. Based on previous reports, it is well-known that a high degree of polymerization for the repeating unit is necessary to observe a sharp decrease in the diffusion coefficient.[8s,13c] Thus, the current measurements clearly indicate the formation of an extended, high-molecular-weight polymeric structure. Furthermore, a rod-like fiber with a regular diameter of 9.5 μm was drawn from a high concentration solution and observed by scanning electron microscopy (Figure 3 b), providing direct evidence for the formation of a supramolecular polymer with high molecular weight.

Viscometry is a convenient method to test the propensity of monomers to self-assemble into large aggregates. Therefore, viscosity measurements were carried out in chloroform using a Cannon Ubbelohde semi-microdilution viscometer. As presented in Figure 4, the linear supramolecular polymer assembled from **1** exhibited a viscosity transition that is characterized by a change in slope in the double logarithmic

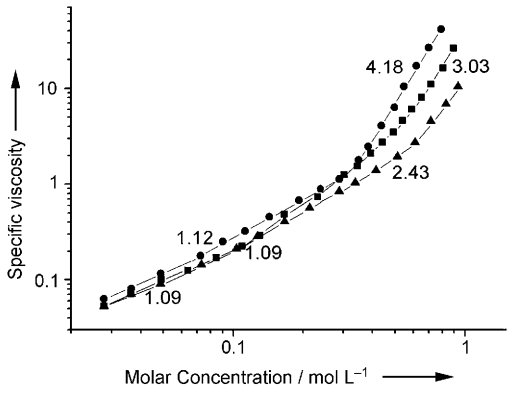

Figure 4. Specific viscosity of **1** in $CHCl_3$ (▲ 286 K; ■ 298 K; ● 310 K) versus monomer concentration at different temperatures. Values on the curves indicate the slope.

plots of specific viscosity versus concentration. In the low-concentration range, the slopes approximated unity, which is characteristic for cyclic oligomers with constant size.[8q,13,14] When the concentration exceeded the critical polymerization concentration (CPC; approximately 275 mM), a sharp rise in the viscosity was observed (slope = 3.03 at 298 K). This slope value is lower than that of the ureidopyrimidone-based self-assembling systems reported by Meijer et al. (slopes of 3–6),[8f,m] but higher than the crown-ether-based systems reported by us (slopes of 1.43–2.08),[8q,13] implying that there should be some degree of cooperativity in association between the pillar[5]arene host moieties and octyl guest units in solution, because the copillararene monomer **1** is preorganized to form a linear supramolecular polymer (Supporting Information, the caption of Scheme S1). On the other hand, the C–H···π interaction is a form of weak hydrogen bond, so it should be easily affected by the temperature. Thus we investigated how the temperature affects the aggregation of **1** in solution by viscosity measurements (Figure 4). When the concentration is below the CPC, there is no significant change for the aggregation of **1**. However, at concentrations above the CPC, when the temperature was changed from 310 K to 286 K, the slope increased from 2.43 to 4.18. This phenomenon indicated that temperature affects the aggregation of **1**; when the temperature increases, the degree of polymerization decreases. However, the CPC does not change significantly when the temperature changes. This is understandable, as we previously found that the CPC value is determined by the geometry of the monomer but not related to the interaction strength between the repeating units.[13c]

Because the inspiration of our present work came from the complex crystal structure of a copillararene and a hexane molecule,[10d] we believed that we could obtain the crystal structure of **1**. In fact, when we obtained the structure of a single crystal formed from the slow evaporation of a solution of **1** in a chloroform/methanol mixture by X-ray analysis (Figure 5), we were surprised. Quite a few reported A-B monomers assemble in the self-inclusion monomeric or dimeric style in the solid state.[15] However, in this crystal structure, the octyl group of a copillararene penetrates deeply

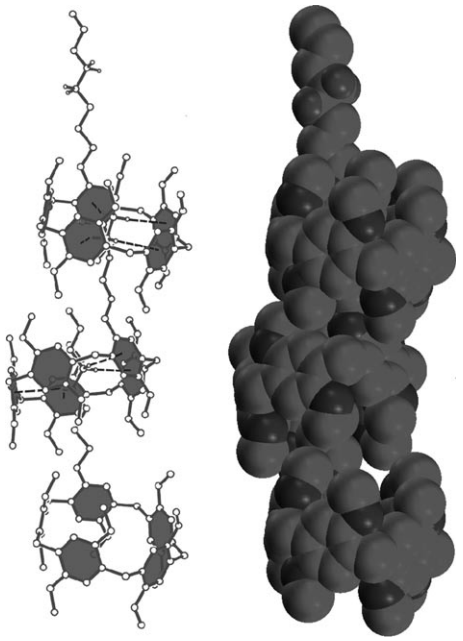

Figure 5. Two views of the one-dimensional arrangement of **1**. Only hydrogen atoms related to the C–H···π interactions (indicated by dotted lines) are shown; other hydrogen atoms are omitted for clarity.

into the electron-rich cavity of another adjacent copillararene monomer and the monomers align along an axis to form a head-to-tail linear supramolecular polymer throughout the entire crystal. There are four hydrogen atoms on the included octyl group with C–H···π plane distances of 2.82–2.99 Å, which are shorter than 3.05 Å (the longest interatomic distance for the existence of a C–H···π interaction), thus implying the existence of C–H···π interactions between the copillararene monomers.[1a] These are the main enthalpic (ΔH) driving forces for the inclusion of the octyl group in the copillararene cavity of the adjacent monomer. Although the C–H···π interaction is the weakest hydrogen bond, quadruple C–H···π interactions are strong enough to hold an electroneutral alkyl chain in the electron-rich cavity of a copillar[5]arene in the solid state. In chloroform, the positive entropy term (ΔS) resulting from exclusion of the solvent from the cavity should also augment the binding by reducing the free energy of the system (ΔG) (Supporting Information, Scheme S1 caption).[16]

In conclusion, based on easily available copillararene monomers, linear supramolecular polymers can be efficiently constructed driven by quadruple C–H···π interactions. Only two steps were required to prepare copillararene monomer **1** from commerically available compounds. By combination of various techniques, including ^{1}H NMR, DOSY, NOESY, and viscometry at different temperatures, it was demonstrated that the formation of the supramolecular polymer is highly dependent on the temperature and monomer concentration. Moreover, rodlike fibers were drawn from a high-concentration solution and observed by SEM, thus directly providing evidence for the formation of a supramolecular polymer with a high-molecular weight. The crystal structure of **1** revealed that the aggregation of copillararene monomer **1** to form a

linear supramolecular polymer was driven by the quadruple C–H···π interactions coupled with the entropic effect of desolvation of the host cavity. The present study affords the first example of a supramolecular polymer driven by C–H···π interactions. Furthermore, for the first time, the host–guest chemistry of pillararenes was used in the preparation of a supramolecular polymer. Considering the easy availability of copillararene monomers and the stimuli-responsiveness of the resultant supramolecular polymers, the present study provides a new and simple way to fabricate stimuli-responsive supramolecular polymeric materials.

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[1] a) H. Suezawa, T. Yoshida, M. Hirota, H. Takahashi, Y. Umezawa, K. Honda, S. Tsuboyama, M. Nishio, *J. Chem. Soc. Perkin Trans. 2* **2001**, 2053 – 2058; b) M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, *CrystEngComm* **2009**, *11*, 1757 – 1788; c) O. Takahashi, Y. Kohno, M. Nishio, *Chem. Rev.* **2010**, *110*, 6049 – 6076.

[2] a) T. Morimoto, H. Uno, H. Furuta, *Angew. Chem.* **2007**, *119*, 3746 – 3749; *Angew. Chem. Int. Ed.* **2007**, *46*, 3672 – 3675; b) H. Miyake, H. Kamon, I. Miyahara, H. Sugimoto, H. Tsukube, *J. Am. Chem. Soc.* **2008**, *130*, 792 – 793; c) M. Kaufmann, M. Gisler, C. J. Leumann, *Angew. Chem.* **2009**, *121*, 3868 – 3871; *Angew. Chem. Int. Ed.* **2009**, *48*, 3810 – 3813.

[3] a) K. Sada, K. Inoue, T. Tanaka, A. Tanaka, A. Epergyes, S. Nagahama, A. Matsumoto, M. Miyata, *J. Am. Chem. Soc.* **2004**, *126*, 1764 – 1771; b) Z. Q. Xie, B. Yang, F. Li, G. Cheng, L. L. Liu, G. D. Yang, H. Xu, L. Ye, M. Hanif, S. Y. Liu, D. G. Ma, Y. G. Ma, *J. Am. Chem. Soc.* **2005**, *127*, 14152 – 14153; c) K. Dziubek, M. Podsiadlo, A. Katrusiak, *J. Am. Chem. Soc.* **2007**, *129*, 12620 – 12621.

[4] a) S. Tartaggia, A. Scarso, P. Padovan, O. De Lucchi, F. Fabris, *Org. Lett.* **2009**, *11*, 3926 – 3929; b) R. Carrillo, M. Lopez-Rodriguez, V. S. Martin, T. Martin, *Angew. Chem.* **2009**, *121*, 7943 – 7948; *Angew. Chem. Int. Ed.* **2009**, *48*, 7803 – 7808; c) N. P. Barwell, M. P. Crump, A. P. Davis, *Angew. Chem.* **2009**, *121*, 7809 – 7812; *Angew. Chem. Int. Ed.* **2009**, *48*, 7673 – 7676; d) J. P. Collin, F. Durola, J. Frey, V. Heitz, F. Reviriego, J. P. Sauvage, Y. Trolez, K. Rissanen, *J. Am. Chem. Soc.* **2010**, *132*, 6840 – 6850.

[5] M. Nishio, *Tetrahedron* **2005**, *61*, 6923 – 6950.

[6] V. R. Thalladi, T. Smolka, A. Gehrke, R. Boese, R. Sustmann, *New J. Chem.* **2000**, *24*, 143 – 148.

[7] a) T. Shibata, T. Nishinaka, T. Mikawa, H. Aihara, H. Kurumizaka, S. Yokoyama, Y. Ito, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 8425 – 8432; b) S. H. Chou, K. H. Chin, F. M. Chen, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 6625 – 6630; c) M. Harigai, M. Kataoka, Y. Imamoto, *J. Am. Chem. Soc.* **2006**, *128*, 10646 – 10647; d) Y. Yamaguchi, W. Jin, K. Matsunaga, S. Ikemizu, Y. Yamagata, J. I. Wachino, N. Shibata, Y. Arakawa, H. Kurosaki, *J. Med. Chem.* **2007**, *50*, 6647 – 6653; e) R. P. Saha, R. Bhattacharyya, P. Chakrabarti, *Proteins* **2007**, *67*, 84 – 97; f) M. Cohen, D. Reichmann, H. Neuvirth, G. Schreiber, *Proteins* **2008**, *72*, 741 – 753; g) K. Kar, S. Ibrar, V. Nanda, T. M. Getz, S. P. Kunapuli, B. Brodsky, *Biochemistry* **2009**, *48*, 7959 – 7968; h) M. J. Plevin, D. L. Bryce, J. Boisbouvier, *Nat. Chem.* **2010**, *2*, 466 – 471.

[8] a) C. Fouquey, J.-M. Lehn, A.-M. Levelut, *Adv. Mater.* **1990**, *2*, 254 – 257; b) N. Yamaguchi, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 2518 – 2520; *Angew. Chem. Int. Ed.* **1998**, *37*, 2361 – 2364; c) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* **2001**, *101*, 4071 – 4098; d) H. W. Gibson, N. Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.* **2003**, *125*, 3522 – 3533; e) M. Miyauchi, Y. Kawaguchi, A. Harada, *J. Inclusion Phenom. Macrocyclic Chem.* **2004**, *50*, 57 – 62; f) A. T. ten Cate, H. Kooijman, A. L. Spek, R. P. Sijbesma, E. W. Meijer, *J. Am. Chem. Soc.* **2004**, *126*, 3801 – 3808; g) F. Huang, H. W. Gibson, *J. Am. Chem. Soc.* **2004**, *126*, 14738 – 14739; h) F. Huang, H. W. Gibson, *Chem. Commun.* **2005**, 1696 – 1698; i) F. Huang, D. S. Nagvekar, C. Slebodnick, H. W. Gibson, *J. Am. Chem. Soc.* **2005**, *127*, 484 – 485; j) T. Park, S. C. Zimmerman, *J. Am. Chem. Soc.* **2006**, *128*, 11582 – 11590; k) T. Park, S. C. Zimmerman, *J. Am. Chem. Soc.* **2006**, *128*, 13986 – 13987; l) E. Kolomiets, E. Buhler, S. J. Candau, J. M. Lehn, *Macromolecules* **2006**, *39*, 1173 – 1181; m) O. A. Scherman, G. B. W. L. Ligthart, R. P. Sijbesma, E. W. Meijer, *Angew. Chem.* **2006**, *118*, 2126 – 2130; *Angew. Chem. Int. Ed.* **2006**, *45*, 2072 – 2076; n) W. Weng, J. B. Beck, A. M. Jamieson, S. J. Rowan, *J. Am. Chem. Soc.* **2006**, *128*, 11663 – 11672; o) J. Gao, Y. He, H. Xu, B. Song, X. Zhang, Z. Wang, X. Wang, *Chem. Mater.* **2007**, *19*, 14 – 17; p) B. Song, H. Wei, Z. Wang, X. Zhang, M. Smet, W. Dehaen, *Adv. Mater.* **2007**, *19*, 416 – 420; q) F. Huang, D. S. Nagvekar, X. Zhou, H. W. Gibson, *Macromolecules* **2007**, *40*, 3561 – 3567; r) E. M. Todd, S. C. Zimmerman, *Tetrahedron* **2008**, *64*, 8558 – 8570; s) T. F. A. Greef, G. Ercolani, G. B. W. L. Ligthart, E. W. Meijer, R. P. Sijbesma, *J. Am. Chem. Soc.* **2008**, *130*, 13755 – 13764; t) R. M. Yebeutchou, F. Tancini, N. Demitri, S. Geremia, R. Mendichi, E. Dalcanale, *Angew. Chem.* **2008**, *120*, 4580 – 4584; *Angew. Chem. Int. Ed.* **2008**, *47*, 4504 – 4508; u) T. F. A. Greef, E. W. Meijer, *Nature* **2008**, *453*, 171 – 173; v) Z. Ge, J. Hu, F. Huang, S. Liu, *Angew. Chem.* **2009**, *121*, 1830 – 1834; *Angew. Chem. Int. Ed.* **2009**, *48*, 1798 – 1802; w) A. Ciesielski, G. Schaeffer, A. Petitjean, J.-M. Lehn, P. Samorì, *Angew. Chem.* **2009**, *121*, 2073 – 2077; *Angew. Chem. Int. Ed.* **2009**, *48*, 2039 – 2043; x) T. F. A. Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687 – 5754; y) Y. Liu, Y. Yu, J. Gao, Z. Wang, X, Zhang, *Angew. Chem.* **2010**, *122*, 6726 – 6729; *Angew. Chem. Int. Ed.* **2010**, *49*, 6576 – 6579.

[9] a) A. Scarso, L. Trembleau, J. Rebek, Jr., *Angew. Chem. Int. Ed.* **2003**, *115*, 5657 – 5660; *Angew. Chem.* **2003**, *115*, 5657 – 5660; *Angew. Chem. Int. Ed.* **2003**, *42*, 5499 – 5502; b) A. M.-P. Pederson, R. C. Vetor, M. A. Rouser, F. Huang, C. Slebodnick, D. V. Schoonover, H. W. Gibson, *J. Org. Chem.* **2008**, *73*, 5570 – 5573; c) M. Liu, S. Li, M. Zhang, Q. Zhou, F. Wang, M. Hu, F. R. Fronczek, N. Li, F. Huang, *Org. Biomol. Chem.* **2009**, *7*, 1288 – 1291; d) D. Ajami, J. Rebek, Jr., *Nat. Chem.* **2009**, *1*, 87 – 90.

[10] a) T. Ogoshi, S. Kanai, S. Fujinami, T. A. Yamagishi, Y. Nakamoto, *J. Am. Chem. Soc.* **2008**, *130*, 5022 – 5023; b) D. R. Cao, Y. H. Kou, J. Q. Liang, Z. Z. Chen, L. Y. Wang, H. Meier, *Angew. Chem.* **2009**, *121*, 9901 – 9903; *Angew. Chem. Int. Ed.* **2009**, *48*, 9721 – 9723; c) C. Li, Q. Xu, J. Li, F. Yao, X. Jia, *Org. Biomol. Chem.* **2010**, *8*, 1568 – 1576; d) Z. Zhang, B. Xia, C. Han, Y. Yu, F. Huang, *Org. Lett.* **2010**, *12*, 3285 – 3287; e) C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu, F. Huang, *Org. Lett.* **2010**, *12*, 4360 – 4363.

[11] K. A. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley, New York, **1987**.

[12] C. H. Carothers, *Trans. Faraday Soc.* **1936**, *32*, 39 – 53.

[13] a) F. Wang, C. Y. Han, C. L. He, Q. Z. Zhou, J. Q. Zhang, C. Wang, N. Li, F. H. Huang, *J. Am. Chem. Soc.* **2008**, *130*, 11254 – 11255; b) F. Wang, B. Zheng, K. Zhu, Q. Zhou, C. Zhai, S. Li, N. Li, F. Huang, *Chem. Commun.* **2009**, 4375 – 4377; c) F. Wang, J. Q. Zhang, X. Ding, S. Y. Dong, M. Liu, B. Zheng, S. J. Li, L. Wu, Y. H. Yu, H. W. Gibson, F. H. Huang, *Angew. Chem.* **2010**, *122*, 1108 – 1112; *Angew. Chem. Int. Ed.* **2010**, *49*, 1090 – 1094.

[14] A. Einstein, *Ann. Phys.* **1906**, *19*, 289 – 306.

[15] a) R. Corradini, A. Dossena, R. Marchelli, A. Panagia, G. Sartor, M. Saviano, A. Lombardi, V. Pavone, *Chem. Eur. J.* **1996**, *2*, 373 – 381; b) R. Corradini, A. Dossena, G. Galaverna, R. Marchelli, A. Panagia, G. Sartor, *J. Org. Chem.* **1997**, *62*, 6283 – 6289; c) H. F. M. Nelissen, F. Venema, R. M. Uittenbogaard, M. C. Feiters, R. J. M. Nolte, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2045 – 2053; d) J. W. Park, S. Y. Lee, H. J. Song, K. K. Park, *J. Org. Chem.* **2005**, *70*, 9505 – 9513; e) Y. Han, K. Cheng, K. A. Simon, Y. Lan, P. Sejwal, Y.-Y. Luk, *J. Am. Chem. Soc.* **2006**, *128*, 13913 – 13920; f) X. Ma, D. Qu, F. Ji, Q. Wang, L. Zhu, Y. Xu, H. Tian, *Chem. Commun.* **2007**, 1409 – 1411.

[16] T. Taira, Y. Suzaki, K. Osakada, *Chem. Eur. J.* **2010**, *16*, 6518 – 6529; J. Cui, V. D. Uzunova, D.-S. Guo, K. Wang, W. M. Nau, Y. Liu, *Eur. J. Org. Chem.* **2010**, 1704 – 1710; M. Yanase, M. Matsuoka, Y. Tatsumi, M. Suzuki, H. Iwamoto, T. Haino, Y. Fukazawa, *Tetrahedron Lett.* **2000**, *41*, 493 – 497; K. Datta, M. Banerjee, A. K. Mukherjee, *J. Phys. Chem. B* **2004**, *108*, 16100 – 16106.

