

Host–Guest Systems

Fluorescent Cross-Linked Supramolecular Polymer Constructed by Orthogonal Self-Assembly of Metal–Ligand Coordination and Host–Guest Interaction

Xiaomin Qian,^[a] Weitao Gong,^{*[a]} Xiaopeng Li,^[b] Le Fang,^[a] Xiaojun Kuang,^[a] and Guiling Ning^{*[a]}

Abstract: A new host molecule consists of four terpyridine groups as the binding sites with zinc(II) ion and a copillar[5]arene incorporated in the center as a spacer to interact with guest molecule was designed and synthesized. Due to the 120° angle of the rigid aromatic segment, a cross-linked dimeric hexagonal supramolecular polymer was therefore generated as the result of the orthogonal self-assembly of metal-ligand coordination and host-guest interaction. UV/ Vis spectroscopy, ¹H NMR spectroscopy, viscosity and dynamic light-scattering techniques were employed to characterize and understand the cross-linking process with the introduction of zinc(II) ion and guest molecule. More importantly, well-defined morphology of the self-assembled supramolecular structure can be tuned by altering the adding sequence of the two components, that is, the zinc(II) ion and the guest molecule. In addition, introduction of a competitive ligand suggested the dynamic nature of the supramolecular structure.

Introduction

Supramolecular polymers, constructed from reduplicative monomeric units held together by noncovalent interactions, have gained increasing attention during the past few decades.^[1] Because of the dynamic nature of noncovalent bonds, supramolecular polymers exhibit a variety of new properties, such as stimuli-responsiveness, self-healing, reversibility, degradability, and adaptivity,^[2] which can be complementary to conventional covalently bonded polymers. Inspired by nature, like double helix DNA and the protein secondary structure, considerable effort has been devoted to constructing cross-linked supramolecular polymers since they possess intriguing functions in comparison with other topological structures. However, compared with the abundant number of linear main chain supramolecular polymers, supramolecular polymers with crosslinked topology are relatively fewer in number.^[3] Moreover, introduction of fluorescent properties into supramolecular polymers has attracted remarkable attention, and endows them

[a]	X. Qian, Dr. W. Gong, L. Fang, X. Kuang, Prof. G. Ning
	Sate Key Laboratory of Fine Chemicals, School of Chemical Engineering
	Dalian University of Technology
	No. 2, Linggong Road, High Tech Zone, Dalian (P.R. China)
	E-mail: wtgong@dlut.edu.cn
	ninggl@dlut.edu.cn
[b]	Dr. X. Li
	Department of Chemistry and Biochemistry
	Texas State University, San Marcos, Texas, 78666 (USA)
	Supporting information for this article is available on the WWW under
	http://dx.doi.org/10.1002/chem.201600561.

with potential wide-ranging applications in fluorescent sensing, photonics, electronics, and so on. $^{[3d,\,h,\,k,\,4]}$

In comparison with supramolecular polymers mainly based on one type of noncovalent interaction, orthogonal self-assembly,^[5] the introduction of different types of highly specific, noninterfering noncovalent interactions into one supramolecular system is attracting more interest because it combines the different features of each interaction, which can lead to superior architectures and specific properties. Up to now, various noncovalent interactions have been utilized orthogonally in the construction of new supramolecular polymers. Among them, metal-ligand coordination and host-guest complexation are two mainstream interactions that have been studied extensively. Metal-ligand coordination, a highly directional noncovalent interaction, has been proven to be a powerful approach for building supramolecular polymers since it allows the construction of well-defined supramolecular architectures and imparts the polymers with an increased stability compared to other noncovalent interactions. In the meantime, coordination-driven polymers have attracted great interest due to the combination of the properties of organic polymers as well as the magnetic, electronic, optical, and catalytic potential of metals.^[6] For this purpose, a variety of new ligands, such as pyridine,^[3i,j,7] 2,2'-bipyridine,^[8] 2,6-bis(1'-methylbenzimidazolyl)pyridine,^[9] porphyrin,^[10] 2,2':6'2''-terpyridine,^[11] and so forth have been extensively explored by scientists. Among them, 2,2':6',2"-terpyridine (TPY), especially for easily accessible 4'-functionalized TPY, is a versatile building block and has been studied extensively in recent years because of its generally high binding affinity towards a variety of transition as well as rare earth metal ions, due to $d\pi - p\pi^*$ back-bonding of the metal to the pyridine

Wiley Online Library



rings and the chelate effect.^[11b] Well-designed supramolecular architectures have been fulfilled based on metal–TPY building blocks, paving the ways to smart materials with the capability of being responsive to certain external changing parameters such as pH value, anion, temperature, a competitive ligand, and so on.^[12]

Host-guest complexation, which usually refers to the formation of supramolecular inclusion complexes between macrocyclic host molecules and guest molecules connected together in a highly-controlled manner, has emerged as one of the most attractive fields in supramolecular chemistry. Pillararenes, as a new class of macrocyclic hosts discovered after crown ether, calixarene, cyclodextrin, cucurbituril, and so on, have facilitated the development of supramolecular chemistry since the pioneering work reported by Ogoshi and co-workers in 2008.^[13] Host-quest chemistry based on pillararenes has also been well-established and widely explored in recent years, especially for pillar[5]arene due to its easy accessibility and versatile functionalization.^[14] Compared with the conventional hosts mentioned above, one of the most peculiar properties of pillar[5]arene is the strong binding affinities towards neutral guests in organic solvents,^[3f, i, k, 4e, g, 15] facilitating a new route for supramolecular self-assembly of neutral host-guest species in organic solvents with special physical, chemical, and optical properties.

Supramolecular systems built on the orthogonal self-assembly of metal-ligand coordination and host-quest interaction have been studied widely in the past decades.^[2e, 3h, j, 16] However, to the best of our knowledge, only two examples concerning the orthogonal self-assembly of TPY-based coordination and pillararene-based host-quest interaction have been reported so far. For example, Huang and co-workers prepared a solventdriven muscle-like metallo-supramolecular polymer from an amino-modified pillar[5]arene.^[17] The introduction of TPY moieties and the rigid structure of pillar[5]arene greatly promotes the formation of the metallo-supramolecular polymer. Yao and co-workers presented the construction of a linear supramolecular polymer with responsiveness to base stimulus and concentration-dependent fluorescence emission driven by pillararene-based host-guest molecular recognition and TPY-based metal-ligand coordination.^[4e] These two examples showed the excellent cooperation motif of TPY-based metal-ligand coordination and pillararene-based host-guest interaction under delicate design, but both with linear topology. Cross-linked supramolecular structures based on TPY and pillar[5]arene were not found as far as we know. Hence, we envisioned that it is of rather interest and importance to develop new cross-linked supramolecular polymers with TPY and pillar[5]arene moieties.

Herein, we present the design and synthesis of a new host molecule as the backbone to construct a cross-linked supramolecular polymer by the orthogonal self-assembly of metalligand coordination and host-guest interaction. As shown in Scheme 1, the host molecule mainly consists of two sectors, that is, four TPY groups decorated at the rims and a copillar[5]arene moiety incorporated in the center. First, due to the 120° internal angle of rigid bent-shaped aromatic segment and the fact that two TPY groups form a pseudo octahedral complex



Scheme 1. Schematic illustration of the metal-ligand coordination (**host** and metal ion Zn^{2+}), the host-guest interaction (**host** and guest molecule **G2**), and the orthogonal self-assembly of the three components.

with one metal ion (TPY- M^{II} -TPY),^[11a] once the complexation occurs between TPY and metal ion, a polymeric hexagonal structure was therefore formed by intermolecular coordination. Second, the copillar[5] arene works not only as a linking spacer that connects the two aromatic segments covalently, but also acts a "dynamic glue" that binds two host molecules together noncovalently through host-guest interaction. It is noteworthy that an appropriate alkyl chain of the copillar[5]arene is also quite important to keep the rigidity and avoid potential formation of monocylces.^[12a] Hence, a cross-linked dimeric supramolecular structure was anticipated after metal ion and an appropriate ditopic guest molecule was introduced into the system. Moreover, due to the rigid structure of the molecule and the introduction of metal ion and guest molecule, tunable fluorescence properties were also expected. These could serve as the rationale of our design idea.

Results and Discussion

The synthetic route of the **host** molecule is depicted in Scheme 2. Starting from the synthesis of substituted 2, 4, 6-triphenyl pyrylium salt by an effortless condensation reaction, substituted 2, 4, 6-triphenylbenzene was obtained in an acceptable yield by a nucleophilic reaction with sodium acetate in acetic anhydride. Similar reactions had been widely utilized by Höger and co-workers in the synthesis of polycyclic aromatic hydrocarbons (PAHs).^[18] The 4'-(4-boronatophenyl)-2,2':6',2"-terpyridine was synthesized from unprotected 4-formylphenyl-



Scheme 2. Synthetic protocol of the host. (a) BF₃·OEt₂; (b) CH₃COONa, acetic anhydride; (c) 4'-(4-boronatophenyl)-2,2':6',2"-terpyridine, [Pd(PPh₃)₄], K₂CO₃, diox-ane/H₂O; (d) BBr₃, dry CH₂Cl₂; (e) K₂CO₃, KI, CH₃CN.

boronic acid by a reported method.^[19] Followed by a two-fold Pd-catalyzed Suzuki coupling reaction and a subsequent demethylation reaction, the intermediate compound **4** with two TPY units and a phenolic hydroxyl group was successfully obtained. After a Williamson-type reaction with alkyl bromidedecorated copillar[5]arene, the **host** molecule with four TPY groups at the peripheries and a copillar[5]arene moiety as the joint bridge was conveniently achieved in a satisfactory yield. The guest molecule **G2** was synthesized similarly to a reported literature.^[3k] All the known compounds were characterized by ¹H NMR, and shown to be in full agreement with data reported in the literatures. ¹H NMR, ¹³C NMR spectroscopy and HRMS were applied to characterize all the new compounds, and the data are consistent with the structures presented.

Zinc(II) ion, as one of the most favorable transition metals for TPY, was selected as the model to study the coordination process. Initially, with the aim of investigating the capacity of host to form host-Zn²⁺ complex in the presence of Zn²⁺, UV/ Vis and fluorescence titrations of **host** with Zn(OTf)₂ in a mixed solvent CHCl₃/CH₃CN (v/v, 4/1) were carried out. The monomer host showed a single broad absorption peak at 300 nm (Figure 1 a), which is attributed to the π - π * transition of the TPY group. With incremental equivalents of Zn²⁺, two isosbestic points showed up at about 294 nm and 328 nm, respectively. The two isosbestic points implied the existence of a complicated associated system. Concomitantly, the absorption peaks at 300 nm disappeared and two new absorption bands appeared at 286 nm and 342 nm, corresponding to the ligand-centered (LC) $\pi - \pi^*$ transition.^[20] No absorption peak was observed with wavelength longer than 350 nm, demonstrating the absence of metal-to-ligand charge transfer (MLCT) process. The absorption curve almost remained constant after two equivalents of Zn²⁺, indicating the maximum conversion from monomer **host**



Figure 1. (a) UV/Vis and (b) emission spectra ($\lambda_{ex} = 328$ nm) of **host** (0.01 mm) upon titration with Zn²⁺ (0 equiv, black; 2.3 equiv, green) in CHCl₃/CH₃CN (4/1, v/v). Inset of (a) shows normalized absorption changes at 342 nm () and 314 nm (); Inset of (b) shows the fluorescence color change after addition of 2.3 equivalents of Zn²⁺.



to **host-Zn**²⁺ complex was reached. The UV/Vis titration plot curve monitored at 314 and 342 nm (Figure 1a, inset) reveals a 1:2 ligand-to-metal stoichiometry, which is in accordance with our assumption as illustrated in Scheme 1. We reason that it is not feasible for two TPY units on the same molecule to coordinate with one single metal ion from a conformational consideration. Therefore, it is reasonable to deduce that every two TPY groups are linked together through one Zn²⁺ ion through an intermolecular coordination rather than intramolecular coordination, giving rise to a cross-linked hexagonal architecture. The stepwise binding constants K_1 and K_2 by UV/Vis titration are calculated to be 8152 m^{-1} and 2036 m^{-1} ($K_1 \approx 4 K_2$), which proves to be a non-cooperative process, indicating that the four TPY binding sites are truly identical and independent of each other.^[21]

In terms of fluorescence, when excited at 328 nm, monomer host showed an almost identical emission as compound 3 with a strong emission band peaking at 395 nm (the Supporting Information, Figure S1), suggesting that the incorporation of copillar[5]arene had little influence on the excited state of TPY-like molecule. After Zn²⁺ was added, the emission intensity of the monomer gradually quenched and a much broader weak band finally appeared at 458 nm after 2 equivalents of Zn^{2+} (Figure 1 b), suggesting the formation of aggregates. The fact that no TPY emission had been detected after fully coordinated with Zn²⁺ indicates that the lowest excited state of TPY units is completely guenched by coordinating with Zn²⁺ which is in agreement with the result reported previously.^[22] This new weak band can be attributed to an excited state of Zn²⁺-TPY complex. As a consequence, from a visual observation, the fluorescence color of the solution altered from violet to cyan (Figure 1 b, inset). Attempts to characterize the in situ generated host-Zn²⁺ complex by ¹H NMR spectroscopy have failed due to the poor solubility of the complex in any solvents we tried. To sum up, the spectroscopic results obtained verified the idea that the coordination occurred between host and Zn^{2+} in a molar ratio of 1:2, leading to the polymerization in which the monomers are glued together by the metal ions as presented in Scheme 1.

As mentioned before, pillararenes exhibit excellent molecular recognition towards neutral guest molecules. To link two host molecules together by host-guest complexation, a ditopic guest molecule is structurally required. Here, two ditopic neutral compounds bearing two terminal cyano groups G1^[3] and G2,^[3k] which had been reported previously to have high binding affinity with pillar[5]arene, were chosen as the models to study the slow-exchange host-guest complexation. The complexation was investigated by ¹H NMR spectroscopy first. As can be seen in Figure S2 (the Supporting Information), chemical shifts of protons on the CN-attached alkyl chain of G1 did not show any distinct movement after being added into host in deuterated chloroform. Instead, only a broadening effect of the peaks with no split was observed, which might imply that the only a small part of the protons were included into the cavity of pillar[5]arene. We speculate the length of G1 is too short to thread into the two cavities of two pillararenes. The negligible changes in the emission and absorption spectra also support the perspective that only very weak interaction existed between **host** and **G1** (the Supporting Information, Figures S3 and S4). With this idea in mind, the second ditopic triazole guest molecule with much longer alkyl chain **G2** was introduced. As shown in Figure 2, for the resulting host–guest paired complex, alkyl chain protons H_1 , H_2 , and H_3 on **G2**



Figure 2. ¹H NMR spectra (400 MHz, CDCl₃, room temperature) of **host** upon complexation with excess **G2**. (a) **host** (1 mM); (b) **host** + **G2** (3 mM); (c) **G2** (3 mM). Inset shows amplifying chemical shifts of H₄ and H₅.

showed a significant chemical shift upfield as much as $\delta =$ 3.357 ppm compared with the free **G2** ($\delta =$ 3.029 ppm for H₁, 3.357 ppm for H₂, and 2.97 ppm for H₃, respectively), supporting the formation of a complex based on host-guest interaction. Meanwhile, proton H₄ and the proton on triazole H₅ also showed a relatively small-scale upfield shift ($\delta =$ 0.015 ppm for H₄ and 0.064 ppm for H₅, respectively), which further concluded the complexation motif. Protons on the TPY moieties did not show apparent shifts, indicating the host-guest interaction without the involvement of the coordination sites.

After confirming the existence of host-guest interaction between host and G2 by ¹H NMR spectroscopy, fluorescence and UV/Vis titrations were further conducted to inspect the influence of G2 on the photophysical properties of the host, and to provide helpful information about the self-assembly mode in dilute solution. As we can see from the emission spectra in Figure 3a, with increasing equivalents of G2 added into host, the emissive peak of the host monomer centered at 395 nm showed a progressive decrease and the intensity in the longer wavelength increased slightly. G2 alone is non-emissive in solution. The inclusion of G2 apparently somehow affected arrangements of host molecules, resulting in the fluorescence change. The fluorescence color transformation is easily discernable by naked-eye under a UV light (Figure 3 a, inset). From the UV/Vis titration (Figure 3b), it is clear to see that the broad absorption band showed an apparent blue shift upon addition of 2.3 equivalents of G2 as well as an enhancement of the absorbance. The obvious absorbance change might indicate the



Figure 3. (a) Emission and (b) UV/Vis spectra (λ_{ex} = 328 nm) of host (0.01 mm) upon titration with G2 (0 equiv, black; 2.3 equiv, green) in CHCl₃/ CH₃CN (4/1, v/v). Inset of (a) shows the fluorescence color change after addition of 2.3 equivalents of G2. Inset of (b) shows the Job plot of absorption changes varying the molar ratio of host and G2 while keeping the total concentration at a constant (0.01 mm), revealing an approximate 2:1 stoichiometry.

expansion of the conjugated structure. The Job plot (Figure 3 b, inset) revealed an approximately 2:1 stoichiometry of **host** to **G2**, suggesting that every two **host** molecules interact with one **G2** molecule (Scheme 1). To have an integrative consideration, it is possible to deduce that H-aggregates were generated after **G2** was added into **host**, which involves a parallel interaction mode of the chromophores and are usually accompanied with a blueshifted absorption band as well as a relatively lower fluorescence quantum yield as reported by the literatures.^[23]

Unlike most of the reported pillararene-based supramolecular structures where pillar[5]arenes are usually decorated at the linear end or at the periphery of the molecule (in which case, the interposition of another interaction would not likely affect the host–guest interaction from a conformational consideration), here, the pillar[5]arene unit is incorporated at the center of the backbone as a spacer. We were interested to know whether these two interactions would affect each other due to the structural factor since there is no much meaning developing a supramolecular system with two main forces work in an antagonistic way. Since ¹H NMR studies were failed to conduct due to the poor solubility of the Zn²⁺-coordinated complex, fluorescence and UV/Vis tests were run to investigate the influence of the two interactions on each other. As we can see, when Zn²⁺ was added into the **host-G2** complex continuously, the fluorescence spectra showed a similar variation trend as the Zn²⁺ added into **host**: the peak at 395 nm gradually decreased and a new weak peak occurred at 458 nm (the Supporting Information, Figure S5). As for UV/Vis spectra, two peaks at 286 nm and 342 nm appeared after addition of 2.3 equivalents of Zn²⁺ (the Supporting Information, Figure S6). As we modulated the addition order of the two components, the introduction of G2 also showed a significant influence on the spectroscopic spectra of the host-Zn²⁺ complex (the Supporting Information, Figures S7 and S8), which suggest that the two interactions do not interfere with each other. That is to say, these two interactions showed an orthogonal mode.

Aggregation behavior of the supramolecular polymer with varying concentrations was investigated using Ubbelohde semi-microdilution viscometer, with host for comparison. Due to the poor solubility of the **host** and the complexes in organic solvents, we began the viscosity test at a maximum concentration of 0.25 mm. For the host alone, the specific viscosity almost remained invariant during the whole concentration range (Figure 4), indicating no obvious aggregates were formed. On the other hand, for the host-Zn²⁺ complex, the viscosity exhibited a distinct uptrend with increasing concentration, suggesting the formation of high-molecular-weight aggregates that resulted in a higher specific viscosity. It is noteworthy that as for the host-Zn²⁺-G2 complex, the specific viscosity is always higher than that of the **host-Zn**²⁺ complex. This result proves the linking function of quest molecule. The occurrence of the obvious aggregates at such a low concentration is probably due to the peculiarly cross-linked structure as well as the relatively high binding affinity of metal-ligand coordination and host-guest interaction. In general, the viscosity studies clearly support that both metal-ligand coordination and host-quest interactions are indispensable for the construction of such a supramolecular structure.



Figure 4. Specific viscosity (room temperature) of host (\square), host \bullet Zn²⁺ complex (\bullet), and host \bullet Zn²⁺ \bullet G2 complex (\blacktriangle).

www.chemeuri.ora





To further investigate the aggregation behavior during the stepwise addition of Zn^{2+} and **G2**, we have performed dynamic light scattering (DLS) experiments to monitor the dimensional changing trend during the introduction of the two interactions. As we can see from Figure 5, the DLS data of the **host** showed a hydrodynamic diameter of about 40 nm, indicative of the formation of small aggregates as confirmed by SEM and TEM in the later section. In the presence of 2 equivalents of



Figure 5. Size distribution graph of solutions of **host, hosteZn²⁺**, **hosteZn²⁺ eG2**, **hosteG2** and **hosteG2eZn²⁺** at 25 °C measured by DLS. The concentration of all the solutions is 0.1 mm.

Zn²⁺, the dimension of the nanoparticles exhibited a prominent increase up to about 600 nm, which again evidenced the efficient cross-linking by metal–ligand coordination. The dimension continued to increase to about 1100 nm as **G2** was added, indicating the successful thread of **G2** into the cavity of pillar[5]arene which, as a consequence, led to a larger average diameter distribution. However, when **G2** was first added, the DLS result indicates the formation of an aggregate with an average hydrodynamic diameter of 145 nm. Further addition of 2 equivalents of Zn²⁺ induced the dimension growth up to about 1200 nm, which is close to the result of adverse adding order. Overall, the DLS results clearly showed a growing tendency upon addition of Zn²⁺ and **G2**, suggesting that Zn²⁺ and guest molecule **G2** worked efficiently as cross-linkers that assisted the formation of aggregates with larger diameters.

Nanostructures with different morphologies obtained by supramolecular self-assembly could be of interest and prominent importance because of their potential applications in various areas.^[24] As for our system, to gain a further insight into the self-assembly behavior induced by coordination and host-guest interaction, scanning electron microscope (SEM), and transmission electron microscope (TEM) studies were conducted (Figure 6). As we can see, **host** molecules self-assembled into discrete uneven-sized spheres with an average diameter of about (50 ± 10) nm (Figure 6a). The spheres are shown to be solid, as revealed by TEM (Figure 6a, inset). The sizes of such spheres are much bigger than that of a single molecule as attained by DFT (the Supporting Information, Figure S9), in-



Figure 6. Representative SEM and TEM images showing the morphology of (a) host; (b) host a^{2+} complex; (d) host a^{2+} G2 complex; (e) host a^{2+} complex; (f) host a^{2+} complex. (c) Fluorescence microscopic image and optical microscopic (bright field, inset) image of host a^{2+} complex, both showing spherical morphologies.

Chem. Eur. J. 2016, 22, 6881 - 6890



dicating that numerous molecules were involved to self-assemble such a sphere. After 2 equivalents of Zn²⁺ were added, clusters of solid spheres with diameters ranging from 400 nm to 700 nm were observed (Figure 6b), which are much larger than that of the spheres obtained by host molecules. Optical microscopy also confirmed the existence of numerous solid spheres (Figure 6 c). Apparently the metal-ligand coordinationinduced assembly is responsible for the growth of the nanoparticles, which originates from small spheres that then coalesce and anneal into the observed spherical clusters. The different sizes of the large particles might depend on the numbers of small spheres involved in the aggregation process. After G2 was introduced, it is surprising to find out that enormous porous flower-like structure was formed (Figure 6 d), which is the consequence of a host-guest interaction induced self-assembly. As most of the reported orthogonal supramolecular polymers formed rodlike or fibrous networks, it is rather interesting to observe these well-organized morphological changes formed simply by adding different components, especially for the last porous flower-like structure, which might find some useful applications in catalytic area.

To inspect how the order in which Zn^{2+} and **G2** are added affects the self-assembly of the system, **G2** was first introduced this time. Surprisingly, spherical structures shown to be fully collapsed and inerratic laminar sheets with a regular width of about 650 nm were observed, which is totally different from the spherical clusters formed as Zn^{2+} was added first (Figure 6e). Apparently, host–guest interaction is the major driving force for this morphological change. An amorphous porous structure was generated upon further addition of Zn^{2+} (Figure 6 f). Though the final complexes formed by the three components were possibly the same as concluded from the spectroscopic tests, the morphologies varied depending on the introducing order of different interactions, as illustrated in Scheme 3. This might indicate that the first step plays a crucial



Scheme 3. Schematic representation of the morphological transformation during the introduction of different components.

role in the generation of the nanostructure and the morphology control. Therefore, this growth mechanism study might guide us in the fabrication of new nano-sized materials.

As aforementioned in the introduction part, compared with traditional covalently bonded polymers, one of the most fascinating properties of supramolecular polymers is their stimuli-responsiveness. In our case, the metal-ligand interaction can be manipulated by the addition of a stronger Zn^{2+} -chelating

ligand, for example, 1,4,7,10-tetrazacyclododecane (cyclen).[25] As we can see from Figure S10 (the Supporting Information), the addition of excess cyclen (4 equivalents) resulted in the fluorescence intensity enhancement as well as an emission blueshift of the system back to the original level before the addition of Zn²⁺. This result suggested that the intervention of cyclen effectively broke the cross-linked TPY-Zn²⁺ coordination bond, leading to the recovery of the fluorescence. On the contrary, the fluorescence can also be guenched and redshifted again by the further addition of 2 equivalents of Zn²⁺, indicating the re-formation of the supramolecular structure. UV/Vis studies also affirmed this invertible process. Continuous titration with cyclen led to the disappearance of the Zn²⁺-TPY peak at 342 nm, which can be restored by further addition of Zn^{2+} (the Supporting Information, Figure S11). The cleavage and formation of the competitive coordination process can be repeated several times without obvious de-amplification. Therefore, it is evident that the supramolecular polymer is capable of undergoing a reversible transition under external stimulus.

Conclusion

We have designed and synthesized a new host molecule composed of four terpyridine moieties at the four corners and a copillar[5]arene unite as the linking spacer. Owing to the wellknown coordination of terpyridine towards zinc ion and the host-guest recognition of pillar[5]arene towards neutral guest molecule G2, a cross-linked dimeric hexagonal supramolecular structure was successfully constructed. The two complexation processes were both well studied and confirmed by UV/Vis spectra, emission spectra and ¹H NMR spectroscopy and they work in an orthogonal way. Both the host and the complexes showed good but different fluorescence properties. Viscosity as well as DLS studies revealed that the metal-ligand coordination and the host-guest interaction are both indispensable for the efficient construction of such a supramolecular structure. More interestingly, changing the order in which Zn^{2+} and G2 are added led to totally different self-assembled morphologies of the complex, as observed by SEM and TEM. Finally, the stimuli responsive property of this supramolecular complex was investigated by introducing cyclen, a stronger Zn²⁺ chelating ligand, which showed good reversibility. However, due to the inherent rigid structure, the host molecule and the therefore formed supramolecular complex showed a poor solubility in any solvents that we applied, which restricted the characterizations and further applications. Further studies are being undertaken in our laboratory to design new host molecules with better solubility and, more importantly, new properties.

Experimental Section

Materials and Instruments

All the chemicals were purchased from commercial suppliers and used without further purification unless mentioned. Acetonitrile was pre-dried by shaking with type 4 Å molecular sieves, and then



distilled over calcium hydride prior to use. Dichloromethane (DCM) was refluxed with calcium hydride and distilled prior to use. Other solvents were used as received. Reactions were monitored by thinlayer chromatography (TLC) plates. Visualization of the developed plates was performed under UV light (254 nm and 365 nm). Column chromatography was performed with silica gel (100-200 mesh) using glass columns. ¹H NMR spectra were recorded on a Bruker Av400 NMR spectrometer at 400 MHz. ¹³C NMR spectra were recorded on a Bruker Av500 NMR spectrometer at 126 MHz. Chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS). High-resolution mass spectra (HRMS) were recorded on a Waters GC-TOF and LC/Q-TOF mass spectrometer. All the new compounds were characterized by ¹H NMR, ¹³C NMR spectroscopy and HRMS. For known compounds, we have cited the reported characterization data that we used to compare to our synthesized compounds and we have provided a ¹H NMR spectrum to confirm the purity of the isolated material. Fluorescence spectra were obtained from a Jasco FP-8300 spectrofluorometer. UV/Vis absorption spectra were all taken on a Hitachi UV-4100 spectrophotometer. Quartz cells with 1 cm path length were used. Measurements of the specific viscosities as a function of concentration were conducted using an Ubbelohde micro-dilution viscometer at 25 °C. To ensure the accuracy, each sample was measured for 5 times to calculate the average flowing time. Dynamic light-scattering (DLS) tests were carried out on a Malvern Zetasizer Nano ZSP and the solutions were filtered through a Teflon filter (pore size: 0.2 mm) before tests. SEM studies were carried out on a FEI Quanta 450 electron microscopy operated at 20 kV. The sample for SEM was prepared by dropcasting the solution to a freshly prepared silicon wafer and then dried in the ambient environment naturally. After that, the sample was sputtered with gold and submitted to the microscopy. TEM studies were run on a FEI Tecnai 20 electron microscopy at 200 kv. The sample for TEM was prepared by dropcasting the solution to a carbon-coated copper grid and dried in the ambient environment. Then the sample was submitted to the microscopy.

Compound 1 and 2 were prepared according to our previously reported method. $^{\ensuremath{\scriptscriptstyle 26}\xspace}$

Synthesis of 4'-(4-boronatophenyl)-2,2':6',2"-terpyridine: 4'-(4-Boronatophenyl)-2,2':6',2"-terpyridine was synthesized according to a previously reported method.^[19] ¹H NMR (400 MHz, CD₃OD): δ = 8.71–8.58 (m, 6H), 8.00 (td, *J*=7.8, 1.6 Hz, 2H), 7.83–7.68 (m, 4H), 7.50–7.45 ppm (m, 2H).The ¹H NMR data are in agreement with those found in the literature.

Synthesis of compound 3: To a 250 mL round bottom flask, 2 (0.492 g, 1 mmol), 4'-(4-boronatophenyl)-2,2':6',2"-terpyridine (0.847 g, 2.4 mmol) and K₂CO₃ (10 mmol, 1.382 g) were suspended in a mixture of dioxane (60 mL) and water (20 mL). After bubbling with N_2 for 10 min, [Pd(PPh_3)_4] (0.04 mmol, 46.24 mg) was added immediately. The mixture was heated at 88 $^\circ\text{C}$ under N₂ atmosphere for 36 h. After cooling to room temperature, the solvent was evaporated and DCM (100 mL) was added. The red solution was washed three times with water and the organic phase was collected and dried over anhydrous MgSO₄. After the solvent was evaporated in vacuum, compound 3 (0.55 g, 58%) was obtained as a white powder after purification by column chromatography with a mixture eluent of DCM and CH₃OH (100:1, v/v). ¹H NMR (400 MHz, CDCl₃): $\delta = 8.87$ (s, 4H), 8.78 (d, J = 4.0 Hz, 4H), 8.73 (d, J=7.9 Hz, 4H), 8.08 (d, J=8.3 Hz, 4H), 7.94 (t, J=7.0 Hz, 4H), 7.88-7.81 (m, 15 H), 7.72–7.66 (m, 2 H), 7.41 (dd, J=6.8, 5.2 Hz, 4 H), 7.06 (d, J = 8.8 Hz, 2 H), 3.90 ppm (s, 3 H); ¹³C NMR (126 MHz, CDCl₃): $\delta =$ 159.38, 156.17, 155.89, 149.64, 149.09, 142.06, 141.76, 141.18, 140.38, 139.49, 137.29, 136.90, 133.53, 128.40, 127.78, 127.76, 127.52, 127.47, 124.77, 124.32, 123.85, 121.38, 118.65, 114.31, 55.38 ppm; TOF-LD-MS calcd for $C_{67}H_{47}N_6O$: 951.3811 $[M+H]^+$; found: 951.3788.

Synthesis of compound 4: Under N₂ atmosphere, compound 3 (0.475 g, 0.5 mmol) was dissolved in dry DCM (30 mL). Then the solution was cooled to -78 °C and BBr₃ (0.46 mL, 3 mmol) was added in one portion. The solution turned brown immediately and was allowed to obtain room temperature overnight, then quenched slowly with a few drops of water until no gas was observed. The precipitate was filtered and washed with DCM and CH₃OH repeatedly, which gave 4 (0.42 g, 89.7%) as a yellow powder. ¹H NMR (400 MHz, [D_6]DMSO): $\delta\!=\!8.98$ (d, J $\!=\!8.1$ Hz, 4H), 8.94–8.91 (m, 8H), 8.36 (t, J=7.8 Hz, 4H), 8.19 (d, J=8.3 Hz, 4H), 8.08-8.02 (m, 9H), 7.97-7.92 (m, 6H), 7.82-7.78 (m, 4H), 7.75 (d, J=8.5 Hz, 2H), 6.94 ppm (d, J=8.7 Hz, 2 H); ¹³C NMR (126 MHz, [D₆]DMSO): $\delta =$ 152.10, 152.05, 152.03, 150.85, 150.84, 150.82, 150.78, 150.15, 150.13, 146.40, 146.39, 146.35, 146.31, 142.28, 142.27, 142.25, 142.23, 142.22, 142.21, 142.19, 141.22, 139.86, 138.27, 135.22, 135.20, 128.27, 127.97, 127.87, 127.84, 127.80, 127.57, 127.56, 127.54, 127.30, 126.32, 126.31, 123.43, 120.16, 115.76 ppm; TOF-LD-MS calcd for C₆₆H₄₅N₆O: 937.3655 [*M*+H]⁺; found: 937.3638.

Synthesis of 1,4-bis(4-bromobutoxy)benzene: 1,4-Bis(4-bromobutoxy)benzene was synthesized similarly according to a previously published procedure.^[27] ¹H NMR (400 MHz, CDCl₃): δ =6.83 (s, 4 H), 3.96 (t, *J*=6.1 Hz, 4H), 3.51 (t, *J*=6.7 Hz, 4H), 2.13–2.04 (m, 4H), 1.94 ppm (dt, *J*=12.6, 6.2 Hz, 4 H). The ¹H NMR data are in agreement with those found in the literature.

Synthesis of copillar[5]arene: To a 250 mL three-neck round 1,4-bis(4-bromobutoxy)benzene bottom flask, (1.564 g, 4.116 mmol), 1,4-dimethoxybenzene (5.687 g, 41.16 mmol) and paraformaldehyde (3.391 g, 113.045 mmol) were added. Then, 1,2-dichloroethane (100 mL) was added and the solution was degassed with N₂ for 10 min. Boron trifluoride diethyl etherate (5.7 mL, 45.22 mmol) was injected into the flask under N₂ atmosphere and the mixture was stirred at room temperature. After 30 min, methanol (60 mL) was added to quench the reaction. The solvent was evaporated under vacuum and the residue was dissolved in DCM (50 mL) and washed with saturated NaHCO3 aqueous solution for three times. After that, the organic phase was dried over anhydrous MgSO₄ and crude product was obtained as a white powder. Recrystallization from a mixture of ethanol and DCM (3:1, v: v) gave pure copillar[5]arene (1.3 g, 32.3%) as white crystals. ¹H NMR (400 MHz, CDCl₃): δ = 6.81 (s, 2 H), 6.79 (d, J=3.5 Hz, 4 H), 6.76 (s, 2H), 6.72 (s, 2H), 3.84-3.75 (m, 14H), 3.70-3.63 (m, 24H), 3.21 (s, 4 H), 1.78 ppm (d, J = 18.6 Hz, 8 H); ¹³C NMR (126 MHz, CDCl₃): $\delta =$ 150.67, 150.61, 150.55, 150.43, 149.71, 128.42, 128.26, 128.24, 128.13, 128.05, 114.63, 113.97, 113.96, 113.70, 113.49, 67.23, 55.91, 55.70, 55.64, 33.38, 29.65, 29.35, 29.14, 28.32 ppm; TOF-LD-MS calcd for C₅₁H₆₀O₁₀Br₂: 990.2553 [*M*]⁺; found: 990.2544.

Synthesis of host molecule: Copillar[5]arene (59.4 mg, 0.06 mmol), compound 4 (56.2 mg, 0.06 mmol), K₂CO₃ (82.9 mg, 0.6 mmol) and a catalytic amount of Kl (5 mg) were placed in a 100 mL round bottom flask. Dry CH₃CN (50 mL) were added and the suspension was heated at reflux at 82 °C under N₂ atmosphere for 3 days. After cooling to room temperature, the pale precipitate was filtered off and washed with deionized water and CH₃CN repeatedly. After drying in vacuum, host was obtained as a white powder which was used without further purification. ¹H NMR (400 MHz, CDCl₃): δ =8.81 (s, 8H), 8.76 (d, *J*=3.9 Hz, 8H), 8.70 (d, *J*=8.1 Hz, 8H), 8.02 (d, *J*=8.2 Hz, 8H), 7.88 (dd, *J*=23.4, 15.9 Hz, 39H), 7.65 (d, *J*=7.3 Hz, 4H), 7.40–7.35 (m, 8H), 7.01 (d, *J*=9.1 Hz, 4H), 6.88–6.67 (m, 10H), 4.26–3.52 (m, 42H), 2.04 ppm (s, 8H); ¹³C NMR (126 MHz, [D₈]THF): δ =155.89, 154.27, 154.20, 148.56, 147.52, 147.21, 139.80,

Chem. Eur. J. **2016**, 22, 6881 – 6890



139.54, 138.78, 137.45, 135.63, 134.66, 126.22, 125.73, 125.59, 125.52, 125.37, 122.32, 121.86, 118.85, 116.27, 113.67, 53.06, 52.91, 52.88, 26.40, 25.11, 24.70 ppm; TOF-LD-MS calcd for $C_{183}H_{147}N_{12}O_{12}$: 2704.1261 $[M + H]^+$; found: 2704.1147.

Synthesis of guest molecule G1: To a 100 mL round bottom flask, hydroquinone (1.1 g, 0.01 mol), 5-bromovaleronitrile (4.86 g, 0.03 mol) and K₂CO₃ (13.82 g, 0.1 mol) were added in one portion. Then, 50 mL dry acetonitrile was added and the suspension was heated at reflux at 82 °C for 24 h under N₂ atmosphere. After cooling to room temperature, acetonitrile was evaporated and 100 mL DCM was added. The solution was washed 3 times with water and the organic phase was dried over anhydrous MgSO₄. The guest molecule was obtained as a white powder (1.5 g, 55.1%) after purification by column chromatography with DCM as the eluent. ¹H NMR (400 MHz, CDCl₃) δ = 6.81 (s, 4H), 3.96 (t, *J*=5.5 Hz, 4H), 2.45 (t, *J*=6.8 Hz, 4H), 1.96–1.84 ppm (m, 8H); ¹³C NMR (126 MHz, CDCl₃): δ = 152.96, 119.59, 115.34, 67.21, 28.24, 17.00 ppm; TOF-El-MS calcd for C₁₆H₂₀N₂O₂: 272.1525 [*M*]⁺; found 272.1532.

Synthesis of 1,1'-[1,4-butanediylbis(oxy)]bis[4-(2-propyn-1-yloxy)]benzene: 1,1'-[1,4-Butanediylbis(oxy)]bis[4-(2-propyn-1-yloxy)]benzene was synthesized according to a reported literature with some modifications.^[4e] 4-(Propargyloxy)phenol (4.44 g, 0.03 mol), 1,4-dibromo butane (6.48 g, 0.03 mol) and K_2CO_3 (12.44 g, 0.12 mol) were added to a 250 mL round-bottom flask. CH₃CN (100 mL) was added and the suspension was heated at reflux at 82 °C for 8-12 h (monitored by TLC). The mixture was cooled to room temperature and CH₃CN was evaporated and the residue was dissolved in DCM. After being washed three times with water, the organic phrase was collected and dried over anhydrous MgSO₄. 1,1'-[1,4butanediylbis(oxy)]bis[4-(2-propyn-1-yloxy)]benzene (2.44 g, 46.5%) was obtained as a yellowish powder after purifying by column chromatography with a mixture of hexane/ethyl acetate (10: 1, v/v) as the eluent. ¹H NMR (400 MHz, CDCl₃): $\delta = 6.92$ (d, J = 9.2 Hz, 4H), 6.84 (d, J=9.1 Hz, 4 H), 4.64 (d, J=2.4 Hz, 4 H), 3.98 (t, J=5.5 Hz, 4H), 2.50 (t, J=2.4 Hz, 2H), 1.95 ppm (dt, J=5.6, 2.9 Hz, 4H). The ¹H NMR data are in agreement with those found in the literature. Synthesis of guest molecule G2: Compound G2 was synthesized according to a reported literature with some modifications.^[4e] Sodium ascorbate (0.99 g, 5 mmol) and CuSO₄·5 H₂O (0.62 g, 2.5 mmol) were added to a solution of 1,1'-[1,4-butanediylbis(oxy)]-

2.5 mmol) were added to a solution of 1, 1–[1,4-butanediylos(0x)]bis[4-(2-propyn-1-yloxy)]benzene (1.75 g, 5 mmol) and 5-azidopentanenitrile (1.86 g, 15 mmol) in DMF(4 mL), and the mixture was heated at 90 °C for 12 h. After cooling to room temperature, the brown solution was poured into 100 mL brine and a light-yellow precipitate was formed. The precipitate was collected and dissolved in DCM. The solution was washed three times with water and the organic phase was dried over anhydrous Na₂SO₄. **G2** (2.48 g, 82.9%) was obtained as a white solid after DCM was removed by a rotary evaporator and used without further purification. ¹H NMR (400 MHz, CDCl₃): δ =7.62 (s, 2H), 6.92 (d, *J*=8.7 Hz, 4H), 6.83 (d, *J*=8.7 Hz, 4H), 5.17 (s, 4H), 4.44 (s, 4H), 3.98 (s, 4H), 2.41 (t, *J*=6.9 Hz, 4H), 2.16–2.05 (m, 4H), 1.94 (s, 4H), 1.66 ppm (s, 4H). The ¹H NMR data are in agreement with those found in the literature.

Acknowledgements

The authors are grateful for financial support from the National Natural Science Foundation of China(No. 21206016) and the Fundamental Research Funds for the Central Universities (DUT14LK08).

Keywords: fluorescence · host-guest systems · morphology · self-assembly · supramolecular chemistry

- [1] a) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev.* 2001, 101, 4071–4097; b) T. F. A. de Greef, E. W. Meijer, *Nature* 2008, 453, 171–173; c) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li, F. Huang, *J. Am. Chem. Soc.* 2008, 130, 11254–11255; d) T. F. A. de Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* 2009, 109, 5687–5754; e) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson, F. Huang, *Angew. Chem. Int. Ed.* 2010, 49, 1090–1094; *Angew. Chem.* 2010, 122, 1108–1112; f) T. Aida, E. W. Meijer, S. I. Stupp, *Science* 2012, 335, 813–817; g) L. Yang, X. Tan, Z. Wang, X. Zhang, *Chem. Rev.* 2015, 115, 7196–7239.
- [2] a) B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt, E. W. Meijer, Adv. Mater. 2000, 12, 874–878; b) S. Burattini, B. W. Greenland, D. H. Merino, W. Weng, J. Seppala, H. M. Colquhoun, W. Hayes, M. E. Mackay, I. W. Hamley, S. J. Rowan, J. Am. Chem. Soc. 2010, 132, 12051–12058; c) R. J. Wojtecki, M. A. Meador, S. J. Rowan, Nat. Mater. 2011, 10, 14–27; d) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma, F. Huang, Angew. Chem. Int. Ed. 2011, 50, 1397–1401; Angew. Chem. 2011, 123, 1433–1437; e) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, Angew. Chem. Int. Ed. 2011, 50, 1905–1909; Angew. Chem. 2011, 123, 1945–1949; f) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng, F. Huang, Angew. Chem. Int. Ed. 2012, 51, 7011–7015; Angew. Chem. 2012, 124, 7117–7121; g) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu, F. Huang, Adv. Mater. 2012, 24, 362–369; h) X. Yan, F. Wang, B. Zheng, F. Huang, Chem. Soc. Rev. 2012, 41, 6042–6065.
- [3] a) E. A. Parrilla, P. R. Cabrer, W. A. Soufi, F. Meijide, E. R. Núñez, J. V. Tato, Angew. Chem. Int. Ed. 2000, 39, 2856-2858; Angew. Chem. 2000, 112, 2978 – 2980; b) V. H. Soto Tellini, A. Jover, J. C. García, L. Galantini, F. Meijide, J. V. Tato, J. Am. Chem. Soc. 2006, 128, 5728-5734; c) R. Dong, Y. Liu, Y. Zhou, D. Yan, X. Zhu, Polym. Chem. 2011, 2, 2771-2774; d) X. Ji, Y. Yao, J. Li, X. Yan, F. Huang, J. Am. Chem. Soc. 2013, 135, 74-77; e) R. Fang, Y. Liu, Z. Wang, X. Zhang, Polym. Chem. 2013, 4, 900-903; f) C. Li, K. Han, J. Li, Y. Zhang, W. Chen, Y. Yu, X. Jia, Chem. Eur. J. 2013, 19, 11892-11897; g) B. Yu, B. Wang, S. Guo, Q. Zhang, X. Zheng, H. Lei, W. Liu, W. Bu, Y. Zhang, X. Chen, Chem. Eur. J. 2013, 19, 4922-4930; h) L. He, J. Liang, Y. Cong, X. Chen, W. Bu, Chem. Commun. 2014, 50, 10841 -10844; i) Z. Y. Li, Y. Zhang, C. W. Zhang, L. J. Chen, C. Wang, H. Tan, Y. Yu, X. Li, H. B. Yang, J. Am. Chem. Soc. 2014, 136, 8577-8589; j) X. Yan, T. R. Cook, J. B. Pollock, P. Wei, Y. Zhang, Y. Yu, F. Huang, P. J. Stang, J. Am. Chem. Soc. 2014, 136, 4460-4463; k) N. Song, D. X. Chen, Y. C. Qiu, X. Y. Yang, B. Xu, W. Tian, Y. W. Yang, Chem. Commun. 2014, 50, 8231-8234.
- [4] a) T. E. Kaiser, H. Wang, V. Stepanenko, F. Würthner, Angew. Chem. Int. Ed. 2007, 46, 5541–5544; Angew. Chem. 2007, 119, 5637–5640; b) K. Wang, C. Y. Wang, Y. Zhang, S. X. A. Zhang, B. Yang, Y. W. Yang, Chem. Commun. 2014, 50, 9458–9461; c) D. Chen, J. Zhan, M. Zhang, J. Zhang, J. Tao, D. Tang, A. Shen, H. Qiu, S. Yin, Polym. Chem. 2015, 6, 25–29; d) P. Wang, H. Xing, D. Xia, X. Ji, Chem. Commun. 2015, 51, 17431–17434; e) B. Shi, K. Jie, Y. Zhou, D. Xia, Y. Yao, Chem. Commun. 2015, 51, 4503–4506; f) L. B. Meng, D. Li, S. Xiong, X. Y. Hu, L. Wang, G. Li, Chem. Commun. 2015, 51, 4643–4646; g) N. Song, D. X. Chen, M. C. Xia, X. L. Qiu, K. Ma, B. Xu, W. Tian, Y. W. Yang, Chem. Commun. 2015, 51, 5526–5529.
- [5] a) H. Hofmeier, U. S. Schubert, *Chem. Commun.* 2005, 2423–2432;
 b) S. L. Li, T. Xiao, C. Lin, L. Wang, *Chem. Soc. Rev.* 2012, *41*, 5950–5968;
 c) M. L. Saha, S. De, S. Pramanik, M. Schmittel, *Chem. Soc. Rev.* 2013, *42*, 6860–6909;
 d) C. H. Wong, S. C. Zimmerman, *Chem. Commun.* 2013, *49*, 1679–1695;
 e) X. Y. Hu, T. Xiao, C. Lin, F. Huang, L. Wang, *Acc. Chem. Res.* 2014, *47*, 2041–2051.
- [6] a) D. Kanpton, M. Burnworth, S. J. Rowan, C. Weder, Angew. Chem. Int. Ed. 2006, 45, 5825-5829; Angew. Chem. 2006, 118, 5957-5961; b) F. S. Han, M. Higuchi, D. G. Kurth, Adv. Mater. Adv. Matter. 2007, 19, 3928-3931; c) D. Asil, J. A. Foster, A. Patra, X. de Hatten, J. del Barrio, O. A. Scherman, J. R. Nitschke, R. H. Friend, Angew. Chem. Int. Ed. 2014, 53, 8388-8391; Angew. Chem. 2014, 126, 8528-8531; d) A. J. McConnell,

Chem. Eur. J. **2016**, 22, 6881 – 6890

C. S. Wood, P. P. Neelakandan, J. R. Nitschke, *Chem. Rev.* 2015, *115*, 7729–7793.

- [7] a) H. J. Kim, W. C. Zin, M. Lee, J. Am. Chem. Soc. 2004, 126, 7009–7014;
 b) K. Chen, L. Tang, Y. Xia, Y. Wang, Langmuir 2008, 24, 13838–13841;
 c) H. J. Kim, J. K. Kim, M. Lee, Chem. Commun. 2010, 46, 1458–1460;
 d) M. J. Mayoral, C. Rest, V. Stepanenko, J. Schellheimer, R. Q. Albuquerque, G. Fernández, J. Am. Chem. Soc. 2013, 135, 2148–2151; e) M. Chen,
 C. Wei, J. Tao, X. Wu, N. Huang, G. Zhang, L. Li, Chem. Eur. J. 2014, 20, 2812–2818; f) C. Rest, M. J. Mayoral, K. Fucke, J. Schellheimer, V. Stepanenko, G. Fernández, Angew. Chem. Int. Ed. 2014, 53, 700–705; Angew. Chem. 2014, 126, 716–722; g) M. Chen, C. Wei, X. Wu, M. Khan, N. Huang, G. Zhang, L. Li, Chem. Eur. J. 2015, 21, 4213–4217.
- [8] a) C. Kaes, A. Katz, M. W. Hosseini, Chem. Rev. 2000, 100, 3553-3590;
 b) S. Kawano, N. Fujita, S. Shinkai, J. Am. Chem. Soc. 2004, 126, 8592-8593;
 c) Y. Li, A. Y. Y. Tam, K. M. C. Wong, W. Li, L. Wu, V. W. W. Yam, Chem. Eur. J. 2011, 17, 8048-8059;
 d) T. Tu, W. Fang, X. Bao, X. Li, K. H. Dötz, Angew. Chem. Int. Ed. 2011, 50, 6601-6605; Angew. Chem. 2011, 123, 6731-6735.
- [9] a) J. B. Beck, S. J. Rowan, J. Am. Chem. Soc. 2003, 125, 13922-13923;
 b) M. Burnworth, J. D. Mendez, M. Schroeter, S. J. Rowan, C. Weder, Macromolecules 2008, 41, 2157-2163; c) W. Weng, Z. Li, A. M. Jamieson, S. J. Rowan, Soft Matter 2009, 5, 4647-4657; d) J. R. Kumpfer, J. Jin, S. J. Rowan, J. Mater. Chem. 2010, 20, 145-151; e) M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, Nature 2011, 472, 334-338; f) J. R. Kumpfer, J. J. Wie, J. P. Swanson, F. L. Beyer, M. E. Mackay, S. J. Rowan, Macromolecules 2012, 45, 473-480;
 g) C. Heinzmann, S. Coulibaly, A. Roulin, G. L. Fiore, C. Weder, ACS Appl. Mater. Interfaces 2014, 6, 4713-4719.
- [10] a) K. Ogawa, Y. Kobuke, Angew. Chem. Int. Ed. 2000, 39, 4070–4073; Angew. Chem. 2000, 112, 4236–4239; b) U. Michelsen, C. A. Hunter, Angew. Chem. Int. Ed. 2000, 39, 764–767; Angew. Chem. 2000, 112, 780– 783; c) Q. Zha, X. Rui, T. Wei, Y. Xie, CrystEngComm 2014, 16, 7371– 7384; d) N. U. Day, C. C. Wamser, M. G. Walter, Polym. Int. 2015, 64, 833– 857; e) H. Lee, Y. H. Jeong, J. H. Kim, I. Kim, E. Lee, W. D. Jang, J. Am. Chem. Soc. 2015, 137, 12394–12399; f) D. V. Kondratuk, L. M. A. Perdigão, A. M. S. Esmail, J. N. O'Shea, P. H. Beton, H. L. Anderson, Nat. Chem. 2015, 7, 317–322.
- [11] a) H. Hofmeier, U. S. Schubert, *Chem. Soc. Rev.* 2004, *33*, 373–399;
 b) P. R. Andres, U. S. Schubert, *Adv. Mater.* 2004, *16*, 1043–1068; c) R. Shunmugam, G. J. Gabriel, K. A. Aamer, G. N. Tew, *Macromol. Rapid Commun.* 2010, *31*, 784–793; d) A. Wild, A. Winter, F. Schlütter, U. S. Schubert, *Chem. Soc. Rev.* 2011, *40*, 1459–1511; e) T. Bauer, Z. Zheng, A. Renn, R. Enning, A. Stemmer, J. Sakamoto, A. D. Schlüter, *Angew. Chem. Int. Ed.* 2011, *50*, 7879–7884; *Angew. Chem.* 2011, *123*, 8025–8030; f) A. Fermi, G. Bergamini, M. Roy, M. Gingras, P. Ceroni, *J. Am. Chem. Soc.* 2014, *136*, 6395–6400; g) Z. Zheng, L. Opilik, F. Schiffmann, W. Liu, G. Bergamini, P. Ceroni, L. T. Lee, A. Schütz, J. Sakamoto, R. Zenobi, J. VandeVondele, A. D. Schlüter, *J. Am. Chem. Soc.* 2014, *136*, 6103–6110.
- [12] a) S. Schmatloch, M. F. González, U. S. Schubert, *Macromol. Rapid Commun.* 2002, 23, 957–961; b) A. Y. Y. Tam, K. M. C. Wong, G. Wang, V. W. W. Yam, *Chem. Commun.* 2007, 2028–2030; c) M. Chiper, D. Fournier, R. Hoogenboom, U. S. Schubert, *Macromol. Rapid Commun.* 2008, 29, 1640–1647; d) M. Yan, S. K. P. Velu, M. Maréchal, G. Royal, J. Galvez, P. Terech, *Soft Matter* 2013, 9, 4428–4436; e) C. Y. S. Chuang, V. W. W. Yam, *Chem. Eur. J.* 2014, 20, 13016–13027.
- [13] T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi, Y. Nakamoto, J. Am. Chem. Soc. 2008, 130, 5022-5023.

- [14] a) M. Xue, Y. Yang, X. Chi, Z. Zhang, F. Huang, Acc. Chem. Res. 2012, 45, 1294–1308; b) P. J. Cragg, K. Sharma, Chem. Soc. Rev. 2012, 41, 597–607; c) T. Ogoshi, T. A. Yamagishi, Eur. J. Org. Chem. 2013, 2961–2975; d) H. Zhang, Y. Zhao, Chem. Eur. J. 2013, 19, 16862–16879; e) C. Li, Chem. Commun. 2014, 50, 12420–12433.
- [15] a) L. Liu, D. Cao, Y. Lin, H. Tao, Y. Kou, H. Meier, *Org. Biomol. Chem.* 2011, 9, 7007–7010; b) C. Li, S. Chen, J. Li, K. Han, M. Xu, B. Hu, Y. Yu, X. Jia, *Chem. Commun.* 2011, 47, 11294–11296; c) X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia, C. Li, *Chem. Commun.* 2012, 48, 2967–2969; d) X. Shu, J. Fan, J. Li, X. Wang, W. Chen, X. Jia, C. Li, *Org. Biomol. Chem.* 2012, 10, 3393–3397; e) C. Li, J. Ma, L. Zhao, Y. Zhang, Y. Yu, X. Shu, J. Li, X. Jia, *Chem.* 2013, 49, 1924–1926.
- [16] a) D. Whang, Y. M. Jeon, J. Heo, K. Kim, J. Am. Chem. Soc. 1996, 118, 11333 11334; b) Y. Liu, Y. L. Zhao, H. Y. Zhang, H. B. Song, Angew. Chem. Int. Ed. 2003, 42, 3260 3263; Angew. Chem. 2003, 115, 3382 3385; c) Y. Liu, Z. Huang, X. Tan, Z. Wang, X. Zhang, Chem. Commun. 2013, 49, 5766 5768; d) Y. Ding, P. Wang, Y. K. Tian, Y. J. Tian, F. Wang, Chem. Commun. 2013, 49, 5951 5953; e) H. Masai, J. Terao, S. Seki, S. Nakashima, M. Kiguchi, K. Okoshi, T. Fujihara, Y. Tsuji, J. Am. Chem. Soc. 2014, 136, 1742 1745; f) H. Xing, P. Wei, X. Yan, Org. Lett. 2015, 44, 815 832; h) Y. Gong, S. Zhang, Y. Geng, C. Niu, S. Yin, Q. Zeng, M. Li, Langmuir 2015, 31, 11525 11531; j) K. Jie, Y. Zhou, B. Shi, Y. Yao, Chem. Commun. 2015, 51, 8461 8464.
- [17] L. Gao, Z. Zhang, B. Zheng, F. Huang, Polym. Chem. 2014, 5, 5734-5739.
- [18] a) S. Höger, S. Rosselli, A. D. Ramminger, V. Enkelmann, Org. Lett. 2002,
 4, 4269–4272; b) X. H. Cheng, S. Höger, D. Fenske, Org. Lett. 2003, 5,
 2587–2589; c) C. Mahler, U. Müller, W. M. Müller, V. Enkelmann, C. Moon, G. Brunklaus, H. Zimmermann, S. Höger, Chem. Commun. 2008,
 4816–4818; d) G. Ohlendorf, C. W. Mahler, S. S. Jester, G. Schnakenburg,
 S. Grimme, S. Höger, Angew. Chem. Int. Ed. 2013, 52, 12086–12090;
 Angew. Chem. 2013, 125, 12308–12312.
- [19] A. Schultz, X. Li, B. Barkakaty, C. N. Moorefield, C. Wesdemiotis, G. R. Newkome, J. Am. Chem. Soc. 2012, 134, 7672-7675.
- [20] A. Anthonysamy, S. Balasubramanian, V. Shanmugaiah, N. Mathivanan, Dalton Trans. 2008, 2136–2143.
- [21] a) B. Perlmutter-Hayman, Acc. Chem. Res. 1986, 19, 90–96; b) P. Thordarson, Chem. Soc. Rev. 2011, 40, 1305–1323.
- [22] A. Fermi, P. Ceroni, M. Roy, M. Gingras, G. Bergamini, Chem. Eur. J. 2014, 20, 10661 – 10668.
- [23] a) H. Yao, K. Domoto, T. Isohashi, K. Kimura, *Langmuir* 2005, 21, 1067– 1073; b) K. C. Hannah, B. A. Armitage, *Acc. Chem. Res.* 2004, 37, 845– 853.
- [24] a) B. Rybtchinski, ACS Nano 2011, 5, 6791–6818; b) E. Busseron, Y. Ruff,
 E. Moulin, N. Giuseppone, Nanoscale 2013, 5, 7098–7140; c) L. Zhang,
 L. Qin, X. Wang, H. Cao, M. Liu, Adv. Mater. 2014, 26, 6559–6964; d) L.
 Zhang, X. Wang, T. Wang, M. Liu, Small 2015, 11, 1025–1038.
- [25] B. Gruber, E. Kataev, J. Aschenbrenner, S. Stadlbauer, B. König, J. Am. Chem. Soc. 2011, 133, 20704–20707.
- [26] X. Qian, W. Gong, M. K. Dhinakaran, P. Gao, D. Na, G. Ning, Soft Matter 2015, 11, 9179–9187.
- [27] Y. Chang, K. Yang, P. Wei, S. Huang, Y. Pei, W. Zhao, Z. Pei, Angew. Chem. Int. Ed. 2014, 53, 13126–13130; Angew. Chem. 2014, 126, 13342–13346.

Received: February 5, 2016 Published online on April 8, 2016