Aqueous self-assembly of aromatic rod building blocks

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One of the most fascinating subjects in areas such as nanoscience and biomimetic chemistry is concerned with the construction of novel supramolecular nanoscopic architectures with well defined shapes and functions. Supramolecular assemblies of aromatic rod molecules provide a facile entry into this area. Aromatic rigid rod molecules consisting of hydrophilic flexible chains, in aqueous solution can self-assemble into a variety of supramolecular structures through mutual interactions between aromatic rod molecules and water, including hydrophobic and hydrophilic interactions and π–π interaction. The supramolecular architecture in water can be manipulated by variation of the shape of the rigid segments, as well as the relative volume fraction of the flexible segment. The rigid aromatic segments have significant photonic and electronic properties. The self-assembly of aromatic rod molecules in water, therefore, can provide a strategy for the construction of well-defined and stable nanometer-size structures with chemical functionalities and physical properties as advanced materials for photonic, electronic and biological applications.

1 Introduction

The development of novel functional materials based on self-organizing systems has received a great deal of attention due to their potential in the construction of elaborately defined supramolecular nanostructures.[1,2] Self-assembling molecules in the bulk state, which include liquid crystals, block copolymers, hydrogen bonded complexes and coordination polymers, are widely studied for their great potential as advanced functional materials.[3,4] Among self-assembling systems, the construction of novel supramolecular architectures with well defined shape and size by using aromatic rod building blocks is one of the most important subjects in organic materials chemistry because they can exhibit novel electronic and photonic properties as a result of both their

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discrete dimensions and three-dimensional organizations.[5] Especially, rod–coil block molecules consisting of rigid rod and flexible coil segments are excellent candidates for creating well defined supramolecular structures *via* a process of spontaneous organization.[6] The driving force of the self-assembly is microphase separation of the rod and coil blocks into ordered periodic structures due to the mutual repulsion of the dissimilar blocks and the packing constraints imposed by the connectivity of each block. In contrast to coil–coil block molecules, rod–coil molecules can form well-ordered structures in spite of low molecular weight because the anisometric molecular shape and stiff rod-like conformation of the rod segment impart orientational organization. The energetic penalties associated with chain stretching of the coil block and interfacial energy results in self-assembly of the rod–coil molecules into a variety of supramolecular nanostructures depending on the relative volume fraction of the rod segments or temperature.[7]

Some theoretical works on rod–coil systems have predicted the phase diagram for one or two dimensions including the

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orientational interactions.[8] Recently, Glotzer and co-workers have theoretically predicted that rod–coil molecules form well-ordered structures in three dimensions in solution.[9] Their simulations demonstrated that rod–coil molecules could self-organize into well-ordered structures not predicted by available theory, such as hexagonal or tetragonal perforated layer structures, which have been observed in our experiments. Compared to coil–coil block copolymers, however, theoretical progress of rod–coil molecules is still less developed due to complex entropic interactions and orientational ordering of stiff rod segments. Keeping this in mind, we describe here a series of self-assembled structures experimentally observed in the solid state which are found to depend on the rod length.

Experimentally, rod–coil molecules with a short rod-length self-assemble into various ordered structures due to intermolecular interaction of the aromatic rods.[10] The immiscibility between the chemically distinct flexible coil and rigid rod allows the self-assembly into a layered structure at the initial stage. As the coil volume fraction or temperature increases, however, layered ordering of rod segments becomes unstable due to a large space crowding; consequently, the lamellar structure will transform into cylindrical micelles which allows more volume for coils to explore.[11] Interestingly, a bicontinuous cubic phase with $Ia3d$ symmetry is located between these two phases in contrast to the general behavior of conventional rodlike mesogens. On heating or increasing the volume fraction of the coil parts, long columns break up into smaller domains such as discrete bundles in which the rod segments are aligned parallel to each other.[12] The inner core of this supramolecular bundle is constituted by the rod bundle which has a hockey-puck shape. Subsequently, the supramolecular rod bundles self-organize into a 3-D body-centered tetragonal or body-centered cubic symmetry. On further heating, the three-dimensional lattice of the rod-bundles collapses into a disordered micellar structure with only liquid-like short range order at the aggregated center, most probably due to random thermal motion of discrete aggregates (Fig. 1(a)).[13]

In contrast, the bicontinuous cubic structure that is an intermediate structure between lamellar and columnar structure does not appear in the case of rod–coil molecules with long rod lengths although lamellar and columnar structures do exist.[14] Instead, long rods segments self-assemble into stable perforated lamellar structures with 3-D hexagonal and tetragonal symmetries (Fig. 1(b)).[15] On elongation of the aromatic rods, the strong tendency of the rods to be aligned axially with their long axes makes a greater enthalpic contribution to the free energy balance at the expense of entropic penalties associated with coil stretching. Consequently, the inter-rod interactions become stronger and the rods are strongly driven to aggregate into three-dimensional structures based on a layer structure instead of forming two interpenetrating trifunctional cylinder networks of the bicontinuous cubic structure. Increasing the length of the rod stabilizes 2D or 1D growth of the rod segments while disturbs the assembly of the rigid rod segments into discrete bundles due to larger rod-to-rod interactions.

In addition, intense research efforts have focused on self-assembly in solution, analogous to the DNA double helix, cell-membrane, α-helix and β-sheet of polypeptides in nature.[16–18] Especially, self-assembly in water has great advantages that are environmentally friendly and directly applicable for biological materials. A wide variety of morphologies including spheres, cylinders, vesicles, toroids and tubes form in aqueous solution through controlled self-assembly of incompatible molecular components such as lipid molecules, lipid–peptide, block copolymers, sugar-related molecules, dendrimers and organic–metal hybrids.[19–24] However, the prediction of the supramolecular structure is difficult due to the spatial complexity and relative weakness of the intermolecular interactions, for example, electrostatic forces, hydrogen bonding, π–π stacking and hydrophobic effects. Therefore the ability to design and arrange individual molecular building blocks into well-defined architectures in water remains a challenge. This *feature article* focuses on supramolecular assemblies of aromatic rod building blocks in aqueous solution. Introduction of a rigid segment into a self-assembling system enhances aggregation stability in water.[25]
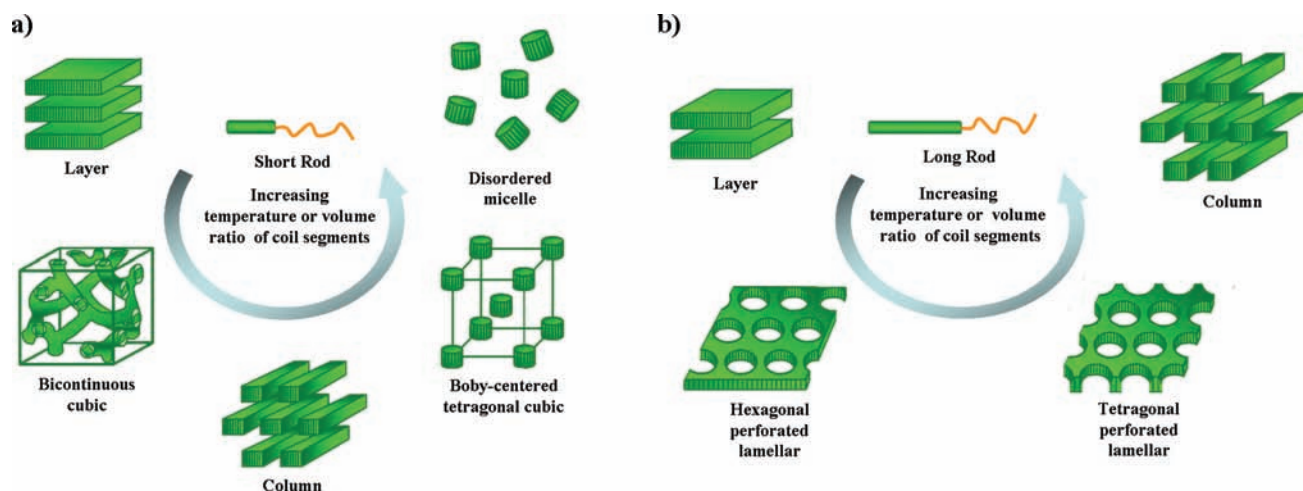
Fig. 1 Schematic representation of various supramolecular structures formed by self-assembly of rod–coil molecules with (a) short rods and (b) long rods.

2 Supramolecular self-assembly dependent on molecular shape in aqueous solution

2.1 Aromatic rod–coil amphiphiles

It is well known that the connection of hydrophobic chains to hydrophilic heads at the terminals leads to amphiphilic characteristics and drives the systems to self-assemble into organized nanostructures such as micelles, cylinders and hollow vesicles in aqueous solution. However, the prediction of self-assembled morphologies from a designed amphiphile structure becomes complicated. Israelachivili proposed that self-assembled aggregates of an amphiphile consisting of hydrophobic chains and hydrophilic heads can be predicted depending on the packing parameter, $P = v/a_0 l_c$, where v is the volume of the hydrophobic chain, a_0 is the polar head surface area at the critical micellar concentration (cmc), and l_c is the chain length.[26] Amphiphiles consisting of rigid aromatic rods as a hydrophobic part and flexible poly(ethylene oxide) (PEO) chains as a hydrophilic part also show similar behavior dependent on the volume ratio of two dissimilar blocks. The rod–coil molecule (1) based on tetra-p-phenylene as a rod segment and α-D-mannopyranoside-functionalized PEO (degree of polymerization (DP) = 23) as a coil segment, for example, exhibits a micellar aggregation with 20 nm diameter in water.[27] The micelles consist of a hydrophobic inner core of rod segments encapsulated by hydrophilic PEO coils. Molecule 2, based on a short oligo(ethylene oxide) chain, assembles into spherical aggregates, but they are larger in size (approximately 40 nm).[28] The measured diameter exceeded the corresponding extended molecular length (approximately 6 nm), suggesting that these aggregates are rather vesicular entities than simple micelles, and transmission electron microscopy (TEM) images revealed that there is obvious contrast between the periphery and center in the sphere, characteristic of the projection images of hollow spheres. A more cone-shaped conformation of the long chain molecules compared to 2 leads to the formation of very small aggregates of higher curvature (Fig. 2).

In contrast, molecule 3, based on a twin-rod segment, self-assembles into cylindrical micelles with twice the diameter of the molecular length scale and lengths of up to several micrometers. This cylindrical micellar structure consists of aromatic cores surrounded by hydrophilic coil segments. The cylindrical structure of this micelle might be explained by the more tapered shape of individual molecules, compared to 1, but a second driving force might be strong π–π interactions among aromatic segments down the long axis of the cylinders.

Similar to 2, rod–coil molecule 4 based on a tetrathiophene rod and a triethylene oxide coil self-assembles into small unilamellar vesicles with a narrow size distribution of about 80 nm diameter particles.[29] Cryo-TEM images show hollow capsules with elliptical shape and this shape is proposed by anisotropic packing of the rigid tetrathiophene to maximize the rod-to-rod interactions. In contrast, Yu and co-workers reported the phase-separation behaviour of oligo[(phenylene vinylene)-co-poly(ethylene oxide)] (5) diblock copolymers which form long cylindrical micelles.[30] The diameter of the long fibers can be manipulated by controlling the repeating unit of phenylene vinylene which comprises the inner core and
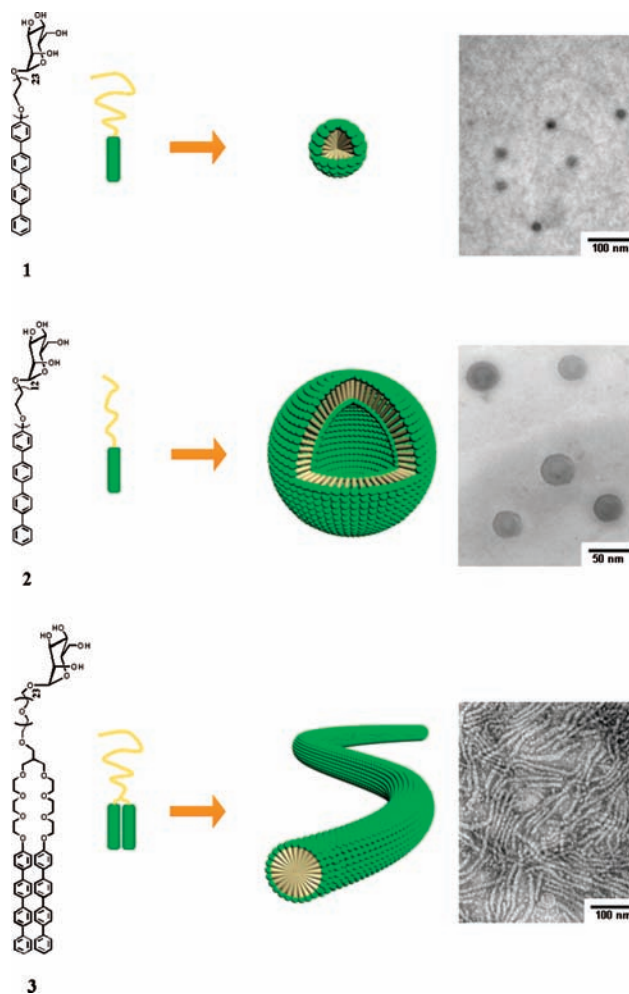

Fig. 2 Molecular structures of 1–3 and schematic representation of vesicles and spherical and cylindrical micelles and their TEM images.

these diblock polymers show interwoven fibers of several thousands nanometers in length. Compared to 1–4, the long rod length provides stronger inter-rod interactions such as hydrophobic and π–π interactions. This seems to disturb spherical aggregation of higher curvature. The authors suggest that the arrangement of the long rods inside the micelles seems to be as a result of monolayer packing with rods interdigitating each other.
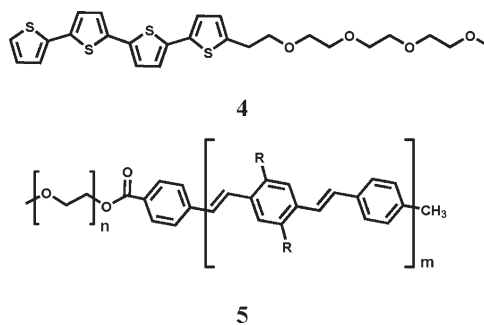

One can envision that coil–rod–coil amphiphilic molecules based on a hydrophilic PEO as a flexible chain and oligo-p-
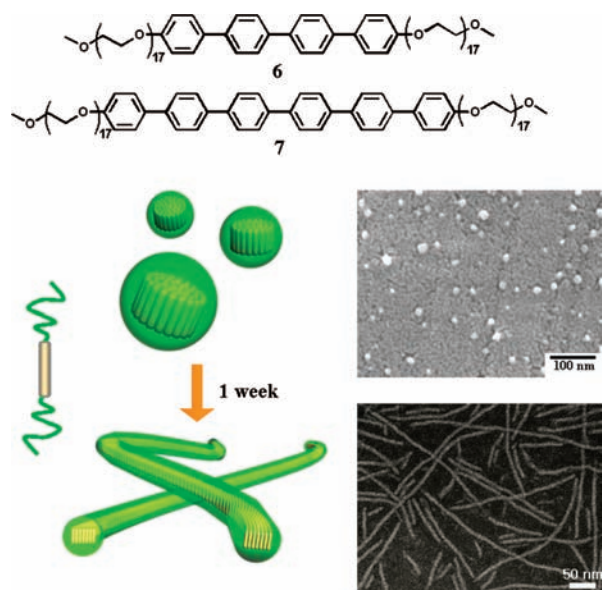
Fig. 3 Schematic representation of the spherical micelle and transformation into cylindrical micelles of the triblock rod–coil molecule (**7**) and their microscopic images.

Fig. 4 Schematic representation of the formation of (a) the barrel-like tubular structure and (b) helical tubular structure of macrocyclic rod–coil molecules and their TEM images.

phenylene as an elongated rod self-assembles into micellar aggregates in aqueous solution, in which the micelles consist of hydrophobic disklike rod bundles encapsulated by hydrophilic coils, as proposed by rod–coil theories.[31] The coil–rod–coil molecules (**6** and **7**), when dissolved in water, a selective solvent for PEO, self-assemble into discrete spherical micelles with uniform diameter of about 10 nm.[32] Considering the extended molecular length (about 10–13 nm by Corey–Pauling–Koltun (CPK) molecular models), the diameter corresponds to one molecular length indicating that the rods pack into hockey puck-like micelles similar to the rod bundles in the bulk state, as mentioned previously.[22] However, the aggregation structure of the coil–rod–coil molecule **7**, based on long rods compared to **6**, slowly changes from spherical micellar to cylindrical objects on the time scale of a week.[33] This indicates that cylindrical aggregates are a thermodynamically stable structure, consistent with diblock rod–coil molecules based on long rod length. TEM images show cylindrical aggregates with a uniform diameter of about 10 nm and lengths up to several hundreds of nanometers, indicating that the diameter of the elementary cylindrical objects corresponds to one molecular length (Fig. 3).

We reported on novel rod–coil molecules based on a hexa-*p*-phenylene rod and PEO chains that are fused together into a macrocyclic ring. In the bulk state, the rod–coil macrocyclic molecule (**8**) self-assembles into a ribbon-like ordering of the rod segments at lower temperature.[34] With increasing temperature, a flat discrete ribbon-like aggregate transforms into a curved barrel-like structure in which the rods are aligned axially with their preferred direction, and both the interior and exterior of the barrel are filled by the coil segments.[35] A ribbon-like ordering of the rod segments would confine the flexible coil segments to a flat interface, forcing a strong deformation of the flexible coils, and crowding of the coil segments due to greater thermal motion makes the system
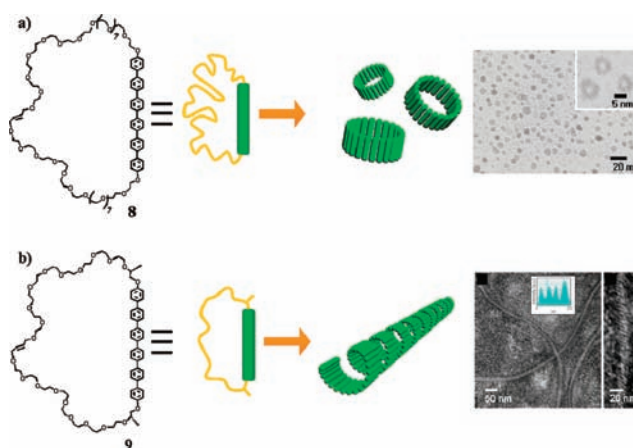
energetically unfavourable. To release this deformation without sacrificing anisotropic order of the rod segments, the flat ribbons would roll to form curved barrels. In aqueous solution, they also self-assemble into a similar barrel structure with a hydrophilic exterior and interior.[36] TEM images show that there is obvious contrast between the periphery and center in the object, indicative of a discrete barrel structure with hydrophilic channels (Fig. 4(a)).

One can easily imagine that the introduction of a chiral poly(ethylene oxide) chain into this macrocycle leads to chiral supramolecular objects. CD spectra of aqueous solutions of the macrocyclic molecule (**9**) based on a chiral coils above certain concentrations (from 0.005 wt%) show first a negative Cotton effect followed by a positive Cotton effect at higher wavelength with the CD signal passing through zero near the absorption maximum of the chromophore, indicating the formation of a helical superstructure with a preferred handedness.[37] TEM images of unstained samples show cylindrical aggregates with lengths up to several micrometers and a uniform diameter of about 20 nm. Theses fibers show obvious contrast between the wall with 3 nm thickness and center with 14 nm thickness, indicative of the projection images of tubular aggregates. Notably, TEM images of samples stained with uranyl acetate show the tubular structure with a left-handed helical arrangement with a regular pitch (4.7 nm) corresponding to the extended molecular length. Similar to achiral macrocycles mentioned above, the rod segments self-assemble into 1-D ribbon-like aggregates with a laterally stacked bilayer encapsulated by cyclic aliphatic chains in which the rod building blocks are tilted with respect to the ribbon normal in the initial state. To avoid space crowding of coil segments without sacrificing a parallel arrangement of the rod segment, these elementary strands are further coiled in a left-handed fashion to form a helical tubular structure (Fig. 4(b)).

## 2.2 Aromatic rod amphiphiles with branched chains

Aromatic rods connecting hydrophilic, flexible dendritic branches to its one end, leading to a tree-shaped molecule, can be considered as a new class of amphiphilic molecule because they consist of hydrophilic dendritic chains as a head

and a hydrophobic rod as a stem.[38] In solid states, the molecular tree (**10**) based on small branches, self-assembles into a monolayer lamellar structure in which the rod segments are fully interdigitated, similar to simple rod coil molecules. However, on increasing the number of branches, the tree molecule (**11**) self-assembles into a discrete nanostructure to release repulsive forces of crowding flexible chains maintaining the parallel arrangement of the rod segments.[17] When the molecular trees are dissolved in hydrophilic solvents, the molecules self-assemble into aggregates with interfacial curvature surrounded by the hydrophilic dendritic chains due to hydrophobic effects. In contrast to bulk states, rod segments in a selective solvent are packed in an orientationally ordered radial arrangement to maximize the contact of the hydrophilic chains with water, giving rise to a unique supramolecular structure with interfacial curvature. Consequently, the molecular trees self-assemble into capsule-like aggregates with narrow diameters. The average hydrodynamic radii of the corresponding aggregates are dependent on the size of head group (approximately 100 nm for **10** and 46 nm for **11**). This means that the molecular trees with larger flexible head groups assemble into a smaller size of aggregate to minimize the steric hindrance between crowded flexible dendritic chains. The radius of gyration of **11** is nearly identical to the hydrodynamic radius determined from dynamic light scattering, indicative of the existence of hollow spheres. As shown in Fig. 5, a field-emission scanning electron micrograph (FE-SEM) shows spherical aggregates that are approximately 80 nm in diameter. It should be noted that the capsules preserve their hollow spherical morphology even after their isolation from the solution under high vacuum as evidenced by SEM experiment, indicating that the capsules formed in THF–water are remarkably stable. This stability of shape could be attributed to self-assembly of rigid building blocks with low conformational entropy. These results demonstrate that rational design of self-assembling molecules based on a conjugated rod building block allows stable hollow nanostructures to be produced.

The introduction of a hydrophobic alkyl chain and hydrophilic dendrimer into each end of an extended rigid segment
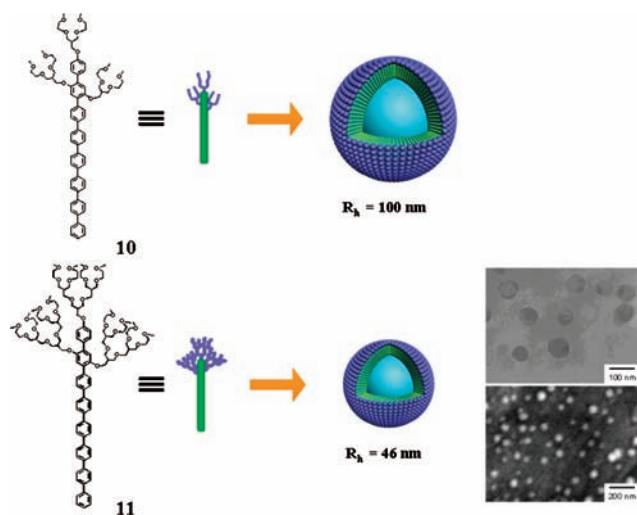
Fig. 5 Schematic representation of formation of nanocapsules of the tree molecules **11** and a TEM and FE-SEM image.
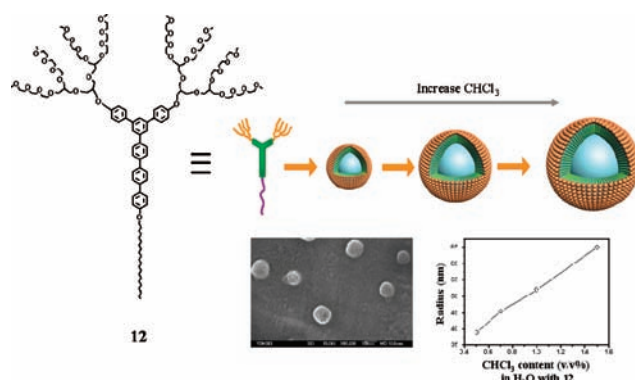
Fig. 6 Schematic representation of formation of the nanocapsule and a SEM image of **12**. The graph shows increase of diameter of the nanocapsule with increasing amount of organic solvent in water.

would give rise to a unique amphiphilic triblock system. Due to an amphiphilic characteristic, such a tree-shaped molecule (**12**) can encapsulate hydrophobic guest molecules in an aqueous environment.[39] On increasing $CHCl_3$ content as a hydrophobic guest molecule, the average hydrodynamic radii (R_H) of the corresponding aggregates increase. This molecular tree also encapsulates the hydrophobic dye Nile Red. The strong association between the guest and amphiphilic molecule, and the poor solubility of the guest molecule in water lead to the entrapment of a hydrophobic guest within the micelles. Supramolecular capsule-like aggregates and their ability to encapsulate hydrophobic guest molecules offer an attractive potential for use in a wide variety of applications ranging from controlled drug release, solubilization of hydrophobic molecules in aqueous media, to the design of nanoreactors (Fig. 6).

In contrast to molecular trees, the incorporation of a conjugated rod and bulky flexible dendrons to both ends leads to an amphiphilic dumbbell-shaped molecular architecture. When the molecular dumbbell (**13**) aggregates in aqueous solution, a parallel arrangement of the hydrophobic rod segments, commonly observed for rod–coil molecules, is prevented by bulky dendrons at both ends of the rod because of a steric repulsion between bulky dendritic segments.[40] Instead, the rod segments stack on top of each other with mutual rotation in the same direction to relieve this steric hindrance, and aggregate in one dimension with a regular helical arrangement through microphase separation between incompatible molecular components and π–π stacking interactions between the aromatic units (Fig. 7). The one-handed helical sense is induced by transfer of chiral information from the molecular to supramolecular level.

Remarkably, the helical strands of molecular dumbbell (**14**) transform into nanocages triggered by the addition of aromatic guest molecules.[41] In aqueous media, aromatic guest molecules are intercalated between the rod segments via intermolecular interactions, including hydrophobic and π–π interactions. This intercalation of the guest molecules puts some distance between the adjacent molecular dumbbells to remove the steric repulsion between bulky dendritic segments at both ends of a rod and subsequently drives the twisted packing arrangement of the rod segments into a parallel arrangement.
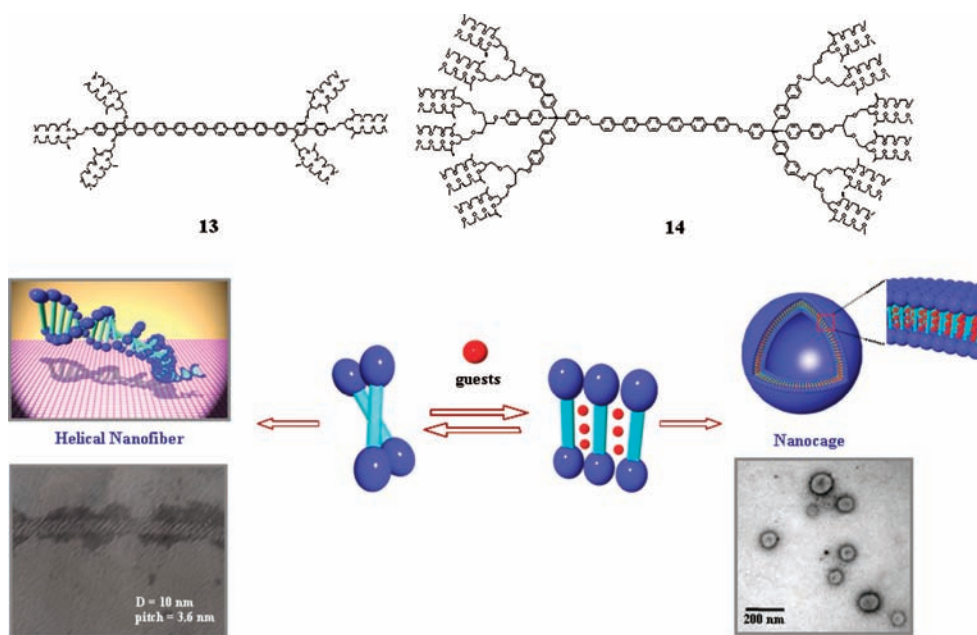
Fig. 7 Molecular structure of molecular dumbbells and representation of the reversible transformation of helical fibers into a spherical capsule of the dumbbell-shaped molecule **14**.

This parallel arrangement of the rod segments leads to the formation of a cagelike structure. Upon removal of the guest molecule by simple extraction by using organic solvents, the hollow capsules transform again into helical fibers (Fig. 7). This dynamic structural variation triggered by external stimuli may find useful application in the development of responsive supramolecular materials.

Recently, Meijer and co-workers reported an interesting spherical aggregate, a hollow vesicle which has supramolecular chirality.[42] The dumbbell-shaped molecule (**15**) consisting of oligo(*p*-phenylene vinylene) (OPV) as a hydrophobic rod and two hydrophilic tris[tetra(ethylene oxide)]benzene wedges at both ends self-assembles into hollow capsules while most of optically active OPV molecules self-assemble into 1-D helical fibers, indicating that OPV molecules in vesicle layer assemble with chirality at the molecular level (Fig. 8). On heating at 90 °C, the Cotton effect gradually disappears while maintaining the aggregates as confirmed by dynamic light scattering (DLS). This indicates that the chiral aggregates at the molecular level are broken, while strong hydrophobic forces hamper vesicle disruption at the microscopic level.

Würthner and co-workers reported the shape dependent organization of perylene bisimides (PBI) amphiphiles.[43] The wedge-shaped PBI (**16**) self-assembles into small micellar aggregates in aqueous solution due to larger hydrophilic head group, similarly to general surfactants. However, the dumbbell-shaped PBI (**17**) forms nanorod aggregates similar to molecular dumbbells (**13** and **14**) described above. Interestingly, the mixture of the wedge-shaped PBI (**16**) and another dumbbell-shaped PBI (**18**) consisting of a hydrophilic bulky chain on one side and hydrophobic bulky chain on the other forms hollow vesicles with a diameter of 94 nm and a wall thickness of 7–8 nm, which is approximately twice the length of PBIs, indicative of bilayer packing (Fig. 9). The insertion of

dumbbell-shaped PBI in the micelle formed by the wedge-shaped PBI increases the hydrophobic parts and subsequently the curvature of the micelles changes from a curved interface to a more flat one. This change of the interface curvature due to the co-assembly leads to the transformation from micelles into vesicles.

2.3 Aromatic disk-shaped amphiphiles

The construction of disk-shaped molecules with rigid aromatic cores opens a way to novel supramolecular aggregates, which have attracted great interest in molecular and supramolecular materials.[44] Rigid disk-shaped molecular architectures containing flexible chains on their periphery have proven to self-
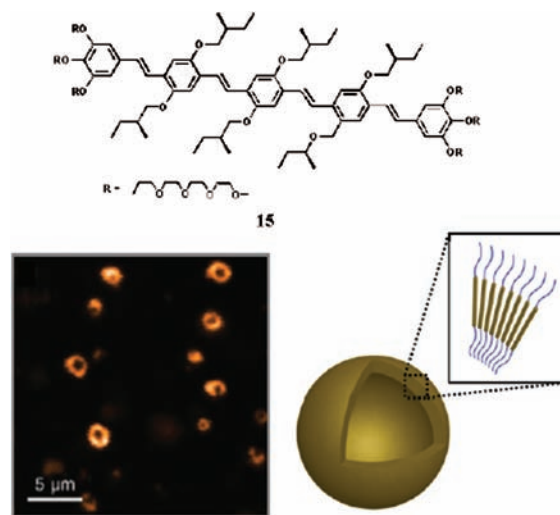

Fig. 8 Chemical structure, scanning confocal microscopy image, and schematic representation of the vesicles of OPV **15**.[42]
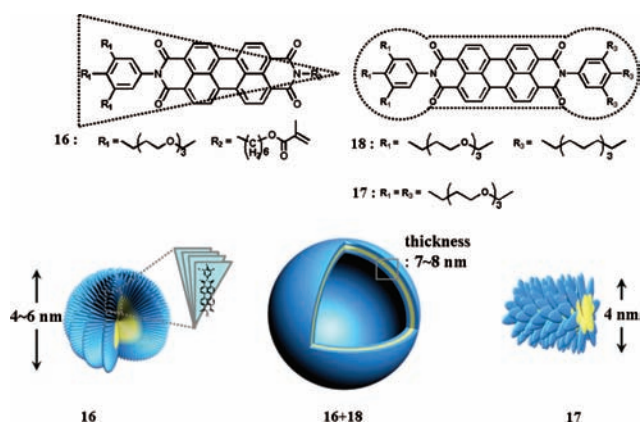
Fig. 9 Chemical structures and schematic illustration for the formation of micelles from **16**, bilayer vesicles from the co-assembly of **16** and **18**, and rod aggregates from **17**.

assemble into a large variety of organized supramolecular columns. In particular, amphiphilic disk-shaped molecules containing hydrophilic chains self-organize into a well-defined supramolecular structure in aqueous solution. Aida and co-workers have reported that amphiphilic hexa-*peri*-hexabenzo-coronene (HBC) molecules with two dodecyl chains on one side and two triethylene glycol chains on the other form discrete nanotubular graphite through strong π–π interactions between HBCs in polar organic solution.[45] This nanotube consists of a graphitic wall formed from numerous molecular graphene sheets stacked parallel to the longer axis of the tube. End-functionalization of triethylene glycol chains on one side of HBC with isothiouronium ion leads to a water-dispersible nanotubular graphitic assembly.[46] Isothiouronium ion-appended HBC amphiphile (**19**) self-assembles into well-dispersible nanotubes due to their electrostatic repulsion of the positively charged surface while other non-ionic HBC amphiphiles tend to form thick bundles (Fig. 10).

Incorporation of a rigid macrocycle and hydrophilic chains into discotic amphiphiles would lead to another class of self-assembling systems that self-assemble into hollow tubular aggregates. The amphiphilic rigid macrocycle (**20**) with hydrophilic dendritic chains shows a unique example of tubules in
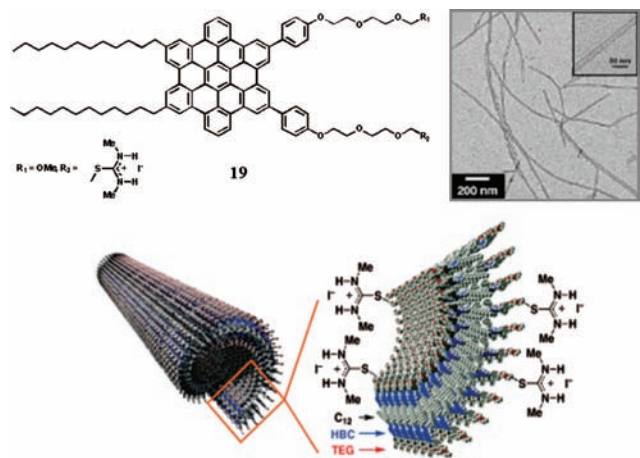
Fig. 10 Chemical structure and schematic illustrations of the graphitic nanotube and TEM image of HBC **19**.[45]
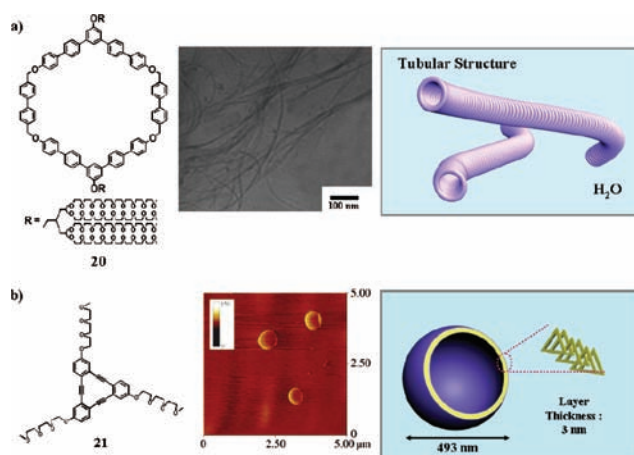
Fig. 11 Schematic representation of (a) tubular structure and TEM image of macrocyclic molecule **20** and (b) hollow vesicle and AFM image of macrocyclic molecule **21**.[48]

aqueous solution (Fig. 11(a)).[47] TEM images show long cylindrical aggregates with a diameter of approximately 10 nm, which is consistent with the molecular dimension (about 9 nm). This indicates that the rigid macrocyclic segments stack directly on top of each other to form a 1D tubular aggregate that is composed of a hydrophobic, stiff interior with a hydrophobic internal cavity and a hydrophilic, flexible exterior. The decrease of the void volume of the macrocyclic molecules *via* the design of the small macrocyclic ring, can lead to interesting aggregates in solution. Discotic macrocyclic molecule (**21**) consisting of a rigid hydrophobic *ortho*-phenylene ethylene macrocycle and polar flexible triethylene glycol displays vesicular self-assembly behaviour in aqueous solution.[48,49] In chloroform–water (1 : 1) solution, the macrocyclic amphiphiles form stable hollow capsules which do not collapse after solvent evaporation, while discotic macrocycles generally self-organize into 1-D cylinders in solution (Fig. 11(b)). TEM images show that the wall thickness of the vesicle is 3 nm, indicating that the macrocycle packs into a bilayer of the phenylene ethylene macrocycle encapsulated by more polar triethylene glycol chains.

## 3 Reversible gelation of supramolecular nanocylinders

Among the nanostructures formed by self-assembly of designed aromatic rod molecules in aqueous solution, a 1D fibrillar assembly has proved to be particularly interesting for applications such as nanowires and biomimetic macromolecules.[50] The hierarchical assembly of such 1D structures could result in the formation of three-dimensional, elastic networks whose void spaces are filled with water through interconnecting the extended micelles. As mentioned above, the coil–rod–coil molecule (**7**) forms discrete cylindrical micelles as thermodynamically stable objects in water.[33] Remarkably, the addition of a small amount of rod–coil–rod (**22**) molecules into the solution of **7** drives the isotropic solution of the cylindrical micelles to the anisotropic, nematic gel state in which the fibers are aligned parallel to each other to form rigid bundles. This formation of large bundles is the result of the

bridging of the individual cylindrical micelles through co-assembly with **22**. The aromatic moieties of rod–coil–rod molecule **22** would co-assemble into the aromatic cores of the cylindrical micelles of **7** through hydrophobic and π–π interactions, which interconnects between the individual cylindrical micelles to form an anisotropic 3D network. In great contrast, the addition of **23**, based on short hydrophilic poly(ethylene oxide) chains, in the cylindrical micelle solution does not induce gelation because the chain length of **23** is too short to interconnect the supramolecular cylinders, while that of **22** is sufficiently long to interconnect adjacent cylindrical micelles (Fig. 12). This interesting dynamic bridging of supra-molecular cylinders in aqueous solution can provide a useful strategy to construct one-dimensional nematic structure with three-dimensional elastic properties.

The 1D structures with stimulus-responsive features are likely to further enhance their scope as intelligent materials.[51] Aromatic amphiphiles based on oligo(ethylene oxide) den-drons can lead to the formation of thermoresponsive nanofibers, because ethylene oxide chains become dehydrated with increasing temperature. The T-shaped aromatic amphiphiles (**24** and **25**) self-assemble into a fibrillar structure consisting of aromatic cores in which the T-shaped aromatic segments are stacked with dimeric association to maximize π–π interactions and hydrophilic dendritic corona that are exposed to the aqueous environment.[52] The T-shaped molecule (**25**) based on the tetrabranched oligoether dendron forms longer fibrillar aggregates than **24** based on dibranched ones because a dendritic architecture with a higher generation exhibits a more hydrophobic nature due to the dendritic effect. This long fibrillar structure of T-shaped amphiphile (**25**) with a hydro-philic oligoether dendritic exterior has temperature-dependent solution behaviour which with increasing temperature induces a reversible phase transition from the fluid state to a gel. On heating, the hydrophobicity of the oligoether dendron in-creases because of the break-up of hydrogen bonds between the ethylene oxide chains and water molecules, which results in enhanced hydrophobic interactions between adjacent fibrils to form a 3D network (Fig. 13). In addition, the gel is trans-formed into a fluid solution by addition of hydrophobic guest molecules because the breakup of long fibrils into discrete micelles arises from the packing frustration of the T-shaped aromatic segments by intercalation of the guest molecules. These stimulus-responsive features of the fibrils show a
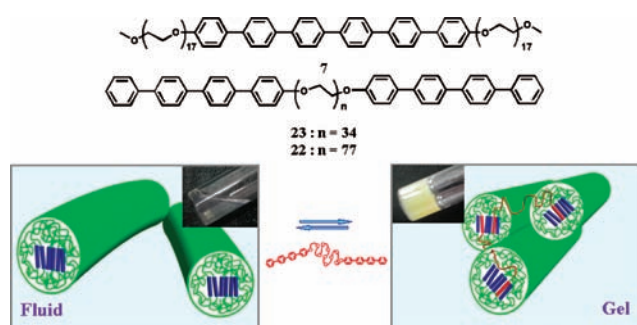
Fig. 12 Chemical structures of triblock rod–coil molecules and schematic representation of reversible gelation of **7** with **22**.
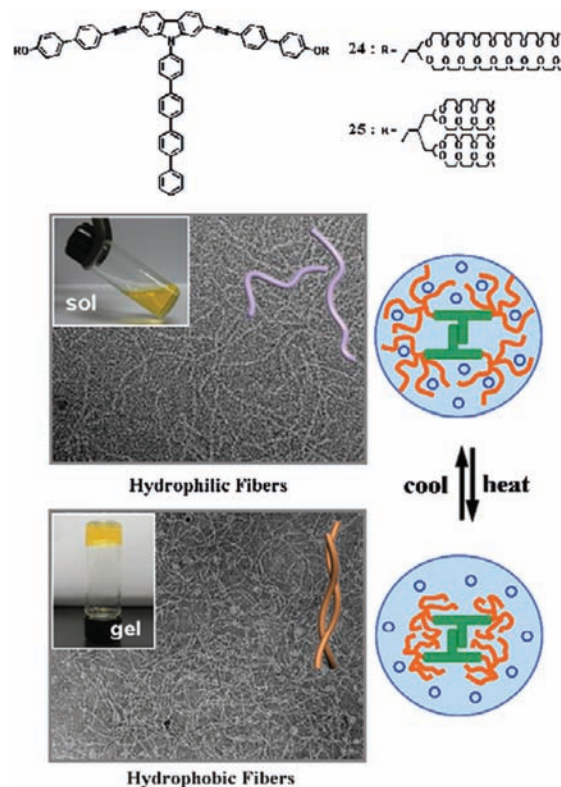

Fig. 13 Chemical structures of T-shaped molecules and schematic illustration of reversible gelation upon increasing the temperature.

remarkable contrast to conventional fibrillar gels that dissolve upon heating.

4 Carbohydrate-coated nanostructures

The self-assembly of amphiphilic molecules containing carbo-hydrate moieties is known to play a role in efficient multivalent ligands toward receptor proteins and the specific assembly formed by their molecular architecture can affect their biolo-gical activities.[53] As mentioned above, the rod–coil amphi-philes **1–3**, which have a conjugated mannose unit at the end of poly(ethylene oxide) chains show significant size and struc-tural changes from vesicles to cylindrical micelles to spherical micelles, with only small variation in molecular architec-ture.[27,28] After these supramolecular objects coated by carbo-hydrate are added to lectin concanavalin A (Con A) solution that selectively recognizes mannose, TEM observations show that the each object, such as micelles, cylinders and vesicles, is surrounded by lectin proteins through multivalent interactions (Fig. 14). Hemagglutination inhibition assay with Con A, that is to inhibit Con A-promoted erythrocyte agglutination, shows that the supramolecular architecture has a significant effect on the binding activity. All of the objects showed high inhibitory potencies in the hemagglutination assay. The relative potencies of vesicle (**2**) and cylinder (**3**) show 800- and 1000-fold increases, respectively, over methyl mannose, while small micelle (**1**) shows a 1800-fold increase, suggesting that the spherical micellar objects with higher curvature are more efficient inhibitors than the vesicular and cylindrical objects.
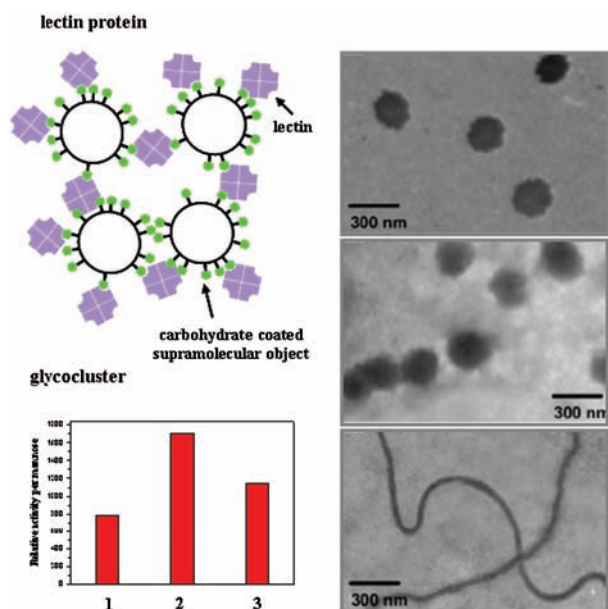
Fig. 14 Schematic illustration of binding Con A and supramolecular structures, and relative activity of Con A-induced hemagglutination inhibition based on the minimum inhibitory concentration (MIC) of **1–3**, and TEM images of **1–3** with Con A.

One of the important issues regarding the preparation of the self-assembling systems is their capability to respond to external stimuli such as pH, temperature, and interaction with guest molecules and biological receptors.[54] The new carbohydrate conjugate aromatic molecule (**26**) self-assembles into mannose-coated cylindrical micellar objects with a uniform diameter and a length of several hundred nanometers.[55] Remarkably, these cylindrical objects transform into spherical micellar objects on addition of small guest molecules. The aromatic guest molecules would intercalate within the aromatic cores of the cylindrical micelles through hydrophobic and π–π interactions. This intercalation causes the packing of

the aromatic segments within the core to be loose. As a result, the cylindrical micelles might break up into spherical micelles. Upon removal of the guest molecule by simple extraction, the original cylindrical objects are fully recovered, thus indicating that this structural transformation is reversible in response to the external-stimuli (Fig. 15). Both cylindrical and spherical micelles appear to specifically bind to the multiple mannose binding proteins (MBPs) of bacterial pili in *Escherichia coli* (ORN 178), demonstrating that the mannose-coated objects are excellent multivalent ligands toward specific receptors on the cell surface. TEM images show that a number of nanoobjects are located along the long bacterial pili; maintenance of the shape and size of the objects even after binding to the bacterial pili indicates high stability of the supramolecular objects. Interestingly, after addition of carbohydrate-coated objects, the motility of the *E. coli* strain immediately decreases. However, the degree of disruption of *E. coli* motility of both nanoobjects is quite different. The cylindrical objects inhibit motility of the *E. coil* much more than the spherical micelles formed by addition of guest molecules. It seems that multivalent interactions between the mannoses on the nanostructures and the MBPs cause intra-bacterial pili aggregations and the resulting aggregates might inhibit the bacterial motility. The spherical micelles are too short to cross-link the pili, whereas long cylinders are able to crosslink the pili. As a result, the degree of motility inhibition of *E. coli* can be manipulated by controlling the shape of the nanostructures. Consequently, the ability to control and systematically alter the features of supramolecular materials with molecular design can provide a novel opportunity to investigate the widespread roles of multivalent binding in biological systems.

5 Aqueous aggregates as nanoreactores

As mentioned above, coil–rod–coil molecules (**6** and **7**) self-assemble into micellar aggregates in aqueous environments. The resulting hydrophobic aromatic core of the micelles would
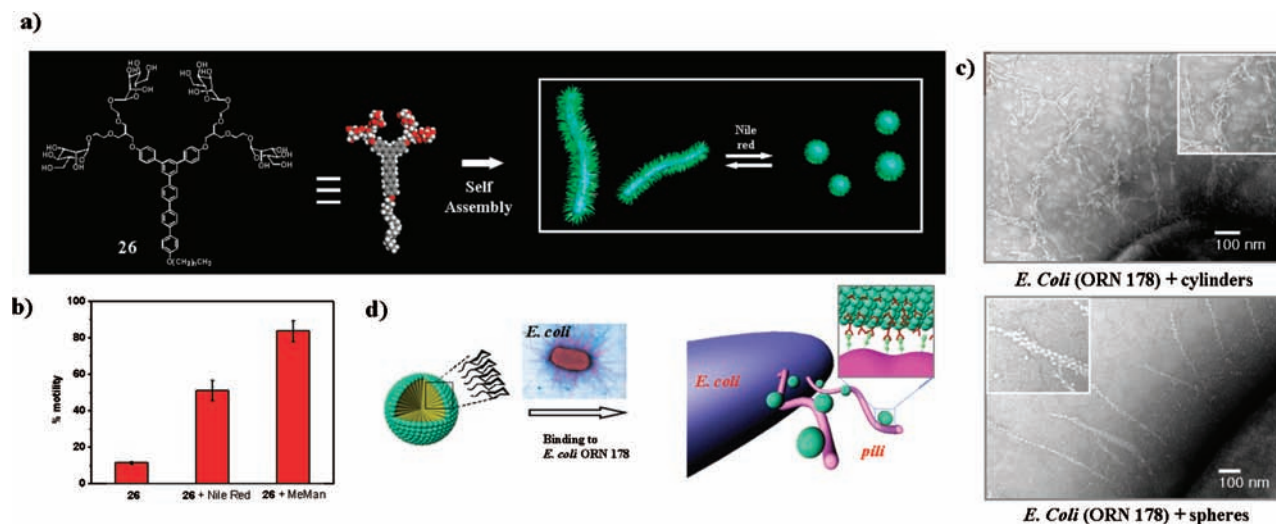
Fig. 15 (a) Chemical structure and schematic illustration of reversible transformation from nanofibers to spherical micelles upon addition of guest molecule (Nile Red). (b) Bacterial motility inhibition assay. (c) TEM images with negative staining of a sectioned area of pili of the *E. coli* ORN 178 strain bound with cylindrical (**26**) and spherical micelles (**26** + Nile Red). (d) Schematic representation of multivalent binding of carbohydrate-coated supramolecular objects.
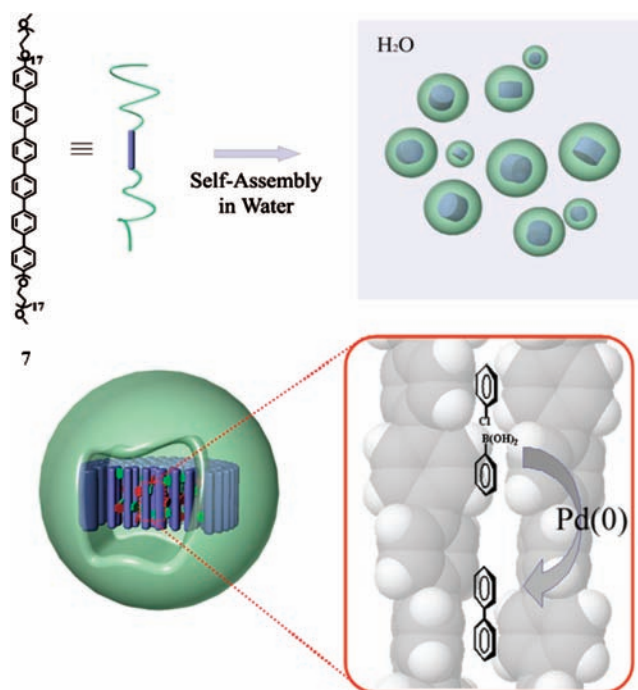
Fig. 16 Schematic representation of a supramolecular reactor.[48]

provide a nanoenvironment suitable for the confinement of hydrophobic aromatic guest molecules *via* hydrophobic interactions and π–π interaction. Subsequently, these aromatic bundles of the micelles could be used as a supramolecular reactor for aromatic coupling reactions in aqueous media.[48] In the case of amphiphile **7**, the coupling reactions of a wide range of bromobenzenes including electron-rich and electron-deficient substrates occur smoothly with a quantitative conversion at room temperature. Remarkably, even the cross-coupling reaction of aryl chloride, which is generally unreactive in the same condition, takes place with reasonable yields. The confinement of the aromatic substrate between aromatic segments in the micelle enforces their close proximity to provide a highly concentrated reaction site that lowers the energy barrier for the aromatic coupling reaction (Fig. 16). This indicates that the packing of aromatic segments within aggregates in water plays a key role in this reaction. Actually, rod–coil amphiphile **6**, consisting of tetra-*p*-phenylene, which is believed to have fewer inter-rod interactions than **7** based on hexa-*p*-phenylene rods, shows a low yield for the aromatic coupling reaction. This supramolecular approach to a reactor in water provides economically and environmentally friendly systems for organic synthesis.

6   Conclusions

A variety of different supramolecular structures including small spherical micelles, vesicles, long cylindrical micelles, barrels, helical fibers and helical tubes, can be formed by self-assembly of aromatic building blocks with attached oligoether chains in aqueous solution (Fig. 17). These unique structures seem to originate from a combination of organizing forces by amphiphilic characteristics that show the tendency of their liphophilic and liphophobic parts to segregate in space
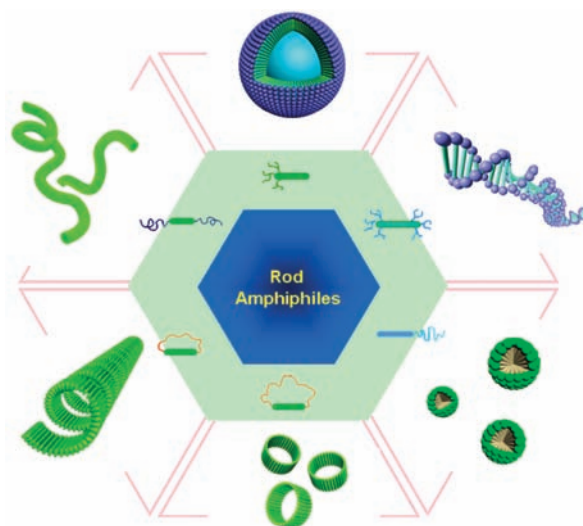

Fig. 17 Schematic representation of various supramolecular structures formed by self-assembly of aromatic rod molecules in aqueous solution.

into distinct microdomains, π-stacking of the aromatic building blocks, and the molecular architectures.

In addition, the self-assembled supramolecular structures have an availability of various applications as nanoreactors, encapsulation of hydrophobic guest molecules, gelation reagents and biological materials. It is also expected that many more rigid aromatic systems which can assemble into novel supramolecular structures in aqueous solution such as giant vesicles or artificial cells will be developed in the near future for possible applications as diverse as self-assembled materials for nanotechnology, periodic porous materials, biomimetic materials and optoelectronic nanomaterials.

References

1 (*a*) J.-M. Lehn, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4763; (*b*) S. Förster and T. Plantenberg, *Angew. Chem., Int. Ed.*, 2002, **41**, 688; (*c*) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491; (*d*) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte and N. A. J. M. Sommerdijk, *Chem. Rev.*, 2001, **101**, 4039.
2 (*a*) A. Ajayaghosh, C. Vijayakumar, R. Varghese and S. J. George, *Angew. Chem., Int. Ed.*, 2006, **45**, 1141; (*b*) M. Lee, B.-K. Cho and W.-C. Zin, *Chem. Rev.*, 2001, **101**, 3869.
3 (*a*) S. Föster and M. Antonietti, *Adv. Mater.*, 1998, **10**, 195; (*b*) F. Zeng and S. C. Zimmerman, *Chem. Rev.*, 1997, **97**, 1681.
4 (*a*) L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071; (*b*) T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; (*c*) C. Kaes,

M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. H. White, *Angew. Chem., Int. Ed.*, 1998, **37**, 920; (*d*) Y. Cui, S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 6014.

5 (*a*) C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485; (*b*) A. J. Berresheim, B. Müller and K. Müllen, *Chem. Rev.*, 1999, **99**, 1747; (*c*) W. Steffen, B. Köhler, M. Altmann, U. Scherf, K. Stitzer, H.-C. Loye and U. H. F. Bunz, *Chem.–Eur. J.*, 2001, **7**, 117; (*d*) S. A. Jeneckhe and X. L. Chen, *Science*, 1999, **283**, 372.

6 (*a*) M. Lee and Y.-S. Yoo, *J. Mater. Chem.*, 2002, **12**, 2161; (*b*) S. I. Stupp, *Curr. Opin. Colloid Interface Sci.*, 1998, **3**, 20; (*c*) J.-H. Ryu, B.-K. Cho and M. Lee, *Bull. Korean Chem. Soc.*, 2006, **27**, 1270.

7 (*a*) A. N. Semenov, *Mol. Cryst. Liq. Cryst.*, 1991, **209**, 191; (*b*) D. R. M. Williams and G. H. Fredrickson, *Macromolecules*, 1992, **25**, 3561; (*c*) A. Halperin, *Macromolecules*, 1990, **23**, 2724.

8 V. Pryamitsyn and V. Ganesan, *J. Chem. Phys.*, 2004, **120**, 5824.

9 (*a*) M. A. Horsch, Z. Zhang and S. C. Glotzer, *Phys. Rev. Lett.*, 2005, **95**, 056105; (*b*) Z. Zhang, M. A. Horsch, M. H. Lamm and S. C. Glotzer, *Nano Lett.*, 2003, **3**, 1341.

10 (*a*) M. Lee M and N.-K. Oh, *J. Mater. Chem.*, 1996, **6**, 1079; (*b*) M. Lee, N.-K. Oh and M.-G. Choi, *Polym. Bull.*, 1996, **37**, 511; (*c*) M. Lee, N.-K. Oh and W.-C. Zin, *Chem. Commun.*, 1996, 1787.

11 (*a*) M. Lee, B.-K. Cho, H. Kim and W.-C. Zin, *Angew. Chem., Int. Ed.*, 1998, **37**, 638; (*b*) M. Lee, B.-K. Cho, H. Kim, J.-Y. Yoon and W.-C. Zin, *J. Am. Chem. Soc.*, 1998, **120**, 9168.

12 (*a*) M. Lee, B.-K. Cho, Y.-G. Jang and W.-C. Zin, *J. Am. Chem. Soc.*, 2000, **122**, 7449; (*b*) E. Lee, J.-H. Ryu, M.-H. Park, M. Lee, K.-H. Han, Y.-W. Chung and B.-K. Cho, *Chem. Commun.*, 2007, 2920.

13 M. Lee, D.-W. Lee, B.-K. Cho, J.-Y. Yoon and W.-C. Zin, *J. Am. Chem. Soc.*, 1998, **120**, 13258.

14 (*a*) J.-H. Ryu, N.-K. Oh, W.-C. Zin and M. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 3551; (*b*) N.-K. Oh, W.-C. Zin, J.-H. Im, J.-H. Ryu and M. Lee, *Chem. Commun.*, 2004, 1092.

15 (*a*) M. Lee, B.-K. Cho, K. J. Ihn, W.-K. Lee, N.-K. Oh and W.-C. Zin, *J. Am. Chem. Soc.*, 2001, **123**, 4647; (*b*) B.-K. Cho, M. Lee, N.-K. Oh and W.-C. Zin, *J. Am. Chem. Soc.*, 2001, **123**, 9667.

16 (*a*) V. Percec, A. E. Dulcey, M. Peterca, P. Adelman, R. Samant, V. S. K. Balagurusamy and P. A. Heiney, *J. Am. Chem. Soc.*, 2007, **129**, 5992; (*b*) J. H. K. Ky Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma and E. W. Meijer, *Nature*, 2000, **407**, 167; (*c*) R. S. Johnson, T. Yamazaki, A. Kovalenko and H. Fenniri, *J. Am. Chem. Soc.*, 2007, **129**, 5735.

17 (*a*) F. Vera, R. M. Tejedor, P. Romero, J. Barberá, M. B. Ros, J. L. Serrano and T. Sierra, *Angew. Chem., Int. Ed.*, 2007, **46**, 1873; (*b*) T. Kato, T. Matsuoka, N. Masayuki, Y. Kamikawa, K. Kanie, T. Nishimura, E. Yashima and S. Ujiie, *Angew. Chem., Int. Ed.*, 2004, **43**, 1969; (*c*) A. Ajayaghosh, C. Vijayakumar, R. Varghese and S. J. George, *Angew. Chem., Int. Ed.*, 2006, **45**, 456.

18 (*a*) J. C. Nelson, J. G. Saven, J. S. Moore and P. G. Wolynes, *Science*, 1997, **277**, 1793; (*b*) R. B. Prince, L. Brunsveld, E. W. Meijer and J. S. Moore, *Angew. Chem., Int. Ed.*, 2000, **39**, 228; (*c*) K. Kishikawa, S. Furusawa, T. Yamaki, S. Kohmoto, M. Yamamoto and K. Yamaguchi, *J. Am. Chem. Soc.*, 2002, **124**, 1597–1605.

19 (*a*) K. Nørgaard and T. Bjørnholm, *Chem. Commun.*, 2005, 1812; (*b*) G. V. Oshovsky, D. N. Reinhoudt and W. Verboom, *Angew. Chem., Int. Ed.*, 2007, **46**, 2366; (*c*) J.-H. Fuhrhop and T. Wang, *Chem. Rev.*, 2004, **104**, 2901; (*d*) J.-H. Fuhrhop, U. Bindig and U. Siggel, *J.Chem. Soc., Chem. Commun.*, 1994, 1583.

20 (*a*) X. Wang, Y. Shen, Y. Pan and Y. Liang, *Langmuir*, 2001, **17**, 3162; (*b*) H. Kobayashi, K. Koumoto, J. H. Jung and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, 2002, 1930; (*c*) H. Kobayashi, M. Amaike, J. H. Jung, A. Friggeri, S. Shinkai and D. N. Reinhoudt, *Chem. Commun.*, 2001, 1038.

21 (*a*) T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1401; (*b*) M. Masud, T. Hanada, K. Yase and T. Shimizu, *Macromolecules*, 1998, **31**, 9403; (*c*) T. Shimizu, R. Iwaura, M. Masuda, T. Hanada and K. Yase, *J. Am. Chem. Soc.*, 2001, **123**, 5947; (*d*) J. H. Jung, S. Shinkai and T. Shimizu, *Chem.–Eur. J.*, 2002, **8**, 2684; (*e*) S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura and H. Shirai, *Chem. Mater.*, 2000, **12**, 1523.

22 (*a*) H. A. Behanna, J. J. J. M. Donners, A. C. Gordon and S. I. Stupp, *J. Am. Chem. Soc.*, 2005, **127**, 1193; (*b*) S. R. Bull, M. O. Guler, R. E. Bras, T. J. Meade and S. I. Stupp, *Nano Lett.*, 2005, **5**, 1; (*c*) M. O. Guler, R. C. Claussen and S. I. Stupp, *J. Mater. Chem.*, 2005, **15**, 4507; (*d*) R. C. Claussen, B. M. Rabatic and S. I. Stupp, *J. Am. Chem. Soc.*, 2003, **125**, 12680; (*e*) S. Ray, A. K. Das, M. G. B. Drewb and A. Banerjee, *Chem. Commun.*, 2006, 4230.

23 (*a*) N. Chebotareva, P. H. H. Bomans, P. M. Frederik, N. A. J. M. Sommerdijka and R. P. Sijbesma, *Chem. Commun.*, 2005, 4967; (*b*) J. T. Davis and G. P. Spada, *Chem. Soc. Rev.*, 2007, **36**, 296; (*c*) Y. Geng, D. E. Discher, J. Justynska and H. Schlaad, *Angew. Chem., Int. Ed.*, 2006, **45**, 7578; (*d*) H. M. König, T. Gorelik, U. Kolb and A. F. M. Kilbinger, *J. Am. Chem. Soc.*, 2007, **129**, 704; (*e*) A. E. Ghzaoui, F. Gauffre, A.-M. Caminade, J.-P. Majoral and H. Lannibois-Drean, *Langmuir*, 2004, **20**, 9348.

24 (*a*) E. R. Zubarev, J. Xu, A. Sayyad and J. D. Gibson, *J. Am. Chem. Soc.*, 2006, **128**, 15098; (*b*) E. R. Zubarev, J. Xu, A. Sayyad and J. D. Gibson, *J. Am. Chem. Soc.*, 2006, **128**, 4958; (*c*) K. L. Genson, J. Holzmueller, C. Jiang, J. Xu, J. D. Gibson, E. R. Zubarev and V. V. Tsukruk, *Langmuir*, 2006, **22**, 7011.

25 (*a*) B. M. Discher, Y. Y. Won, D. S. Ege, J. C. M. Lee, F. S. Bates, D. E. Discher and D. A. Hammer, *Science*, 1999, **284**, 1143; (*b*) H. Kukula, H. Schlaad, M. Antoniett and S. Föster, *J. Am. Chem. Soc.*, 2002, **124**, 1658; (*c*) J.-F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, B. Decamps, E. Leroy, S. Boileau and U. S. Schubert, *Macromolecules*, 2002, **35**, 9748.

26 J. N. Israelachivili, *Intermolecular and Surface Forces*, Academic Press, New York, 1985.

27 B.-S. Kim, D.-J. Hong, J. Bae and M. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 16333.

28 B.-S. Kim, W.-Y. Yang, J.-H. Ryu, Y.-S. Yoo and M. Lee, *Chem. Commun.*, 2005, 2035.

29 L. Jiang, R. C. Hughes and D. Y. Sasaki, *Chem. Commun.*, 2004, 1028.

30 (*a*) H. Wang, H. H. Wang, V. S. Urban, K. C. Littrell, P. Thiyagarajan and L. Yu, *J. Am. Chem. Soc.*, 2000, **122**, 6855; (*b*) H. Wang, W. You, P. Jiang, L. Yu and H. H. Wang, *Chem.–Eur. J.*, 2004, **10**, 986.

31 D. R. M. Williams and G. H. Fredrickson, *Macromolecules*, 1992, **25**, 3561.

32 (*a*) M. Lee, C.-J. Jang and J.-H. Ryu, *J. Am. Chem. Soc.*, 2004, **126**, 8082; (*b*) J.-H. Ryu, C.-J. Jang, Y.-S. Yoo, S.-G. Lim and M. Lee, *J. Org. Chem.*, 2005, **70**, 8956.

33 J.-H. Ryu and M. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 14170.

34 W.-Y. Yang, J.- H. Ahn, Y.-S. Yoo, N.-K. Oh and M. Lee, *Nat. Mater.*, 2005, **4**, 399.

35 M. In, O. Aguerre-Chariol and R. Zana, *J. Phys. Chem. B*, 1999, **103**, 7747.

36 D. T. Bong, T. D. Clark, J. R. Granja and M. R. Ghadiri, *Angew. Chem., Int. Ed.*, 2001, **40**, 988.

37 W.-Y. Yang, E. Lee and M. Lee, *J. Am. Chem. Soc.*, 2006, **128**, 3484.

38 Y.-S. Yoo, J.-H. Choi, J.-H. Song, N.-K. Oh, W.-C. Zin, S. Park, T. Chang and M. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 6294.

39 C.-J. Jang, J.-H. Ryu, J.-D. Lee, D. Sohn and M. Lee, *Chem. Mater.*, 2004, **16**, 4226.

40 J. Bae, J.-H. Choi, Y.-S. Yoo, N.-K. Oh, B.-S. Kim and M. Lee, *J. Am. Chem. Soc.*, 2005, **127**, 9668.

41 J.-H. Ryu, H.-J. Kim, Z. Huang, E. Lee and M. Lee, *Angew. Chem., Int. Ed.*, 2006, **45**, 5304.

42 F. J. M. Hoeben, I. O. Shklyarevskiy, M. J. Pouderoijen, H. Engelkamp, A. P. H. J. Schenning, P. C. M. Christianen, J. C. Maann and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2006, **45**, 1232.

43 X. Zhang, Z. Chen and F. Würthner, *J. Am. Chem. Soc.*, 2007, **129**, 4886.

44 (*a*) M. D. Watson, A. Fechtenkötter and K. Müllen, *Chem. Rev.*, 2001, **101**, 1267; (*b*) J. J. van Gorp, J. A. J. M. Vekemans and E. W. Meijer, *J. Am. Chem. Soc.*, 2002, **124**, 14759; (*c*) D. Wu, L. Zhi, G. J. Bodwell, G. Cui, N. Tsao and K. Müllen, *Angew. Chem., Int. Ed.*, 2007, **46**, 5417.

45 (*a*) J. P. Hill, W. Jin, A. Kosaka, T. Fukushima, H. Ichihara, T. Shimomura, K. Ito, T. Hashizume, N. Ishii and T. Aida, *Science*, 2004, **304**, 1481; (*b*) W. Jin, T. Fukushima, A. Kosaka, M. Niki, N. Ishii and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 8284.

46 G. Zhang, W. Jin, T. Fukushima, A. Kosaka, N. Ishii and T. Aida, *J. Am. Chem. Soc.*, 2007, **129**, 719.

47 J.-H. Ryu, N.-K. Oh and M. Lee, *Chem. Commun.*, 2005, 1770.

48 S. H. Seo, J. Y. Chang and G. N. Tew, *Angew. Chem., Int. Ed.*, 2006, **45**, 7526.

49 (*a*) F. Hof and J. Rebek Jr., *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4775; (*b*) J. Kang and J. Rebek Jr, *Nature*, 1997, **385**, 3650; (*c*) J. M. Heemstra and J. S. Moore, *J. Am. Chem. Soc.*, 2004, **126**, 1648.

50 (*a*) J. D. Hartgerink, E. Beniash and S. I. Stupp, *Science*, 2001, **294**, 1684; (*b*) A. Aggeli, I. A. Nyrkova, M. Bell, R. Harding, L. Carrick, T. C. B. McLeish, A. N. Semenov and N. Boden, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**(11), 857; (*c*) H. G. Börner and H. Schlaad, *Soft Matter*, 2007, **3**, 394.

51 (*a*) M. Barboiu and J.-M. Lehn, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5201; (*b*) K. Kuroiwa, T. Shibata, A. Takada, N. Nemoto and N. Kimizuka, *J. Am. Chem. Soc.*, 2004, **126**, 2016.

52 (*a*) K.-S. Moon, H.-J. Kim, E. Lee and M. Lee, *Angew. Chem., Int. Ed.*, 2007, **46**, 6807; (*b*) E. E. Dormidontova, *Macromolecules*, 2002, **35**, 987; (*c*) Y. Haba, C. Kojima, A. Harada and K. Kono, *Angew. Chem., Int. Ed.*, 2007, **119**, 238.

53 (*a*) G. Thoma, A. G. Katopodis, N. Voelcker, R. O. Duthaler and M. B. Streiff, *Angew. Chem., Int. Ed.*, 2002, **41**, 3195; (*b*) Y. Aoyama, T. Kanamori, T. Nakai, T. Sasaki, S. Horiuchi, S. Sando and T. Niidome, *J. Am. Chem. Soc.*, 2003, **125**, 3455.

54 (*a*) X. Guo and F. C. Szoka, *Acc. Chem. Res.*, 2003, **36**, 335; (*b*) M. Johnsson, A. Wagenaar and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 2003, **125**, 757; (*c*) F. Chécot, S. Lecommandoux, Y. Gnanou and H.-A. Klok, *Angew. Chem., Int. Ed.*, 2002, **41**, 1339; (*d*) M. Lee, S.-J. Lee and L.-H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 12724; (*e*) A. Ajayaghosh, P. Chithra and R. Varghese, *Angew. Chem., Int. Ed.*, 2007, **46**, 230.

55 J.-H. Ryu, E. Lee, Y.-b. Lim and M. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 4808.