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Synthesis and self-assembly of a triphenylene-containing amphiphilic conjugated macrocycle

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ABSTRACT

A new amphiphilic π-conjugated system containing a shape-persistent conjugated macrocycle with two triphenylene chromophores as the anchoring units has been successfully synthesized. The amphiphilic macrocycle has been found to self-assemble into robust and uniform microspheres, presumably due to the strong π−π stacking interaction between triphenylene chromophores.

1. Introduction

Amphiphilic or in a broader term dual-character molecules (including block copolymers) self-organize into a variety of structures such as spheres, vesicles, cylinders, and lamellars.[1] These nano-objects may be rendered electrically and optically active if a π-conjugated component is built into the self-assembling molecule.[2,3] Indeed, amphiphilic conjugated systems have drawn tremendous attention in recent years.[4] Such systems can be realized by having a rigid π-conjugated segment as the core, asymmetrically flanked with hydrophilic chains on one end and hydrophobic tails on the other, as shown schematically in Figure 1. Indeed, a number of such systems have been reported, where the π-conjugated component is either a rigid rod (linear π-conjugated oligomers, model A)[2,3,5] or a planar disk (polycyclic aromatic systems, model B).[6] One elegant representative example for each type is shown in Figure 1. Interestingly, a π-conjugated amphiphile with a rigid π-conjugated cyclic core has not yet been realized (model C in Fig. 1). Such amphiphilic rigid macrocycles with their unique molecular geometry may self-assemble to new interesting nano-objects.

Shape-persistent macrocycles based on phenylene ethynylenes have been actively studied in recent years.[7] There are also reports of amphiphilic rigid macrocycles.[8,9] However, the reported amphiphilic macrocycles either have the cyclic component itself as the hydrophobic component[9] or have both hydrophilic and hydrophobic chains laterally attached to rotatable phenyl rings in the frame

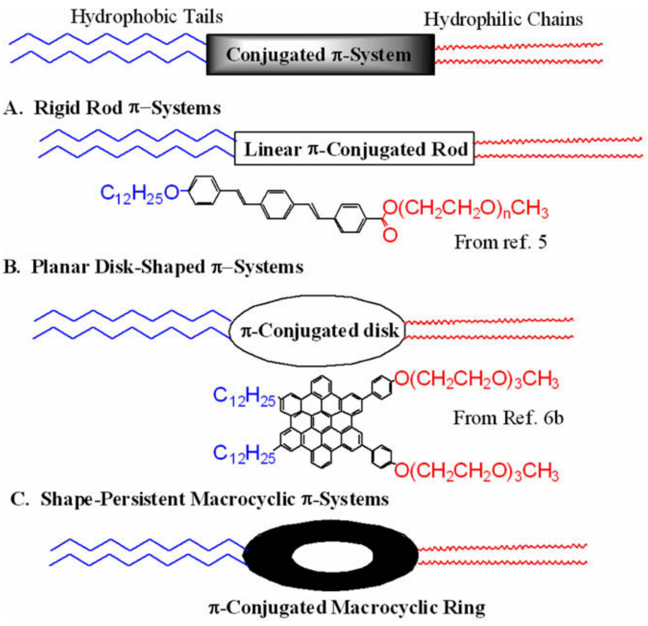

Figure 1. Schematic models of amphiphilic π-conjugated systems.

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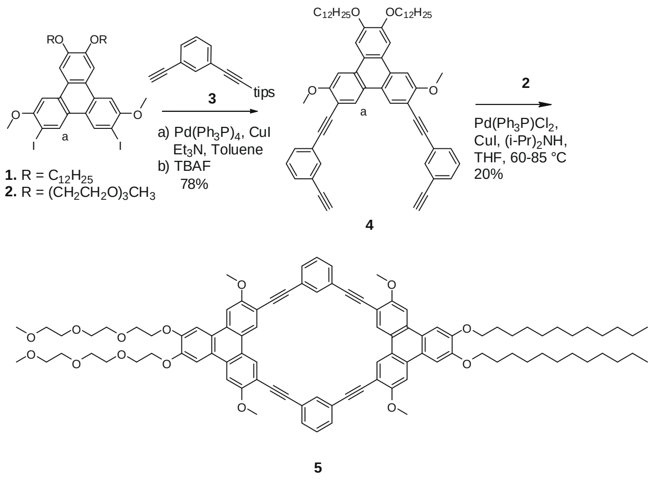
of the macrocycle.[8] Such macrocycles were designed to possess switchable interior environments. The new amphiphilic rigid macrocycles as shown in model C of Figure 1 have a hydrophilic head and a hydrophobic tail and thus represent a new class of conjugated amphiphiles. In this Letter, we report the synthesis of the first such shape-persistent amphiphiles.

Scheme 1 shows the structure of the macrocyclic amphiphile. Two planar polycyclic aromatic hydrocarbon structures (triphenylene), one with hydrophilic chains and the other with hydrophobic tails, are used as corner units, which not only enhance inter-ring π−π interactions, but also act as anchors to direct the positioning of the approaching rings during self-assembly.

The synthesis of the new amphiphilic system is shown in Scheme 1 as well. Diiodo-functionalized triphenylenes **1** and **2** were synthesized according to an approach reported previously.[10] Sonogashira coupling of **1** with **3**, followed by desilylation, gave compound **4** in 78% overall yield. Subsequent coupling of **4** with compound **2** resulted in amphiphilic macrocycle **5**. To improve the yield of the cyclized product, the reaction system was kept at high-dilution condition by dropping the two reactants (**2** and **4**) into the catalyst solution over days (see Supplementary data for detailed experimental procedures). Even so, a yield of only 20% is obtained, presumably due to the formation of oligomers and their corresponding larger macrocycles. The ^{1}H NMR spectra of **5** in $CDCl_3$ show an extremely broad hump from 6.6 to 8.2 ppm (see Supplementary data for the spectra) in the aromatic region, indicating strong inter-ring π-stacking. Sitting on this broad hump, one can identify five discernible peaks. There is also one well-isolated aromatic signal appearing at 8.7 ppm. The complete disappearance of signals corresponding to proton *a* in **4** and proton *a* in **2** (see Scheme 1 for proton labeling and Fig. S3 of Supplementary data for the ^{1}H NMR spectra of **2**, **4**, and **5**)), coupled with the observation of the expected 6 aromatic signals in the ^{1}H NMR spectrum of **5** supports, albeit not conclusively, the macrocycle structure of **5**. MALDI-TOF measurements show a sharp dominant peak at *m/z* 1514.12 (100%), corresponding to the molecular ion (*m/z* = 1513.81) and a less intense peak at 1622.00 (30%) which is attributed to (M+Ag$^+$). The purity of **5** is also confirmed by the elemental analysis.



Scheme 1. Synthesis of triphenylene-based shape-persistent macrocycles.

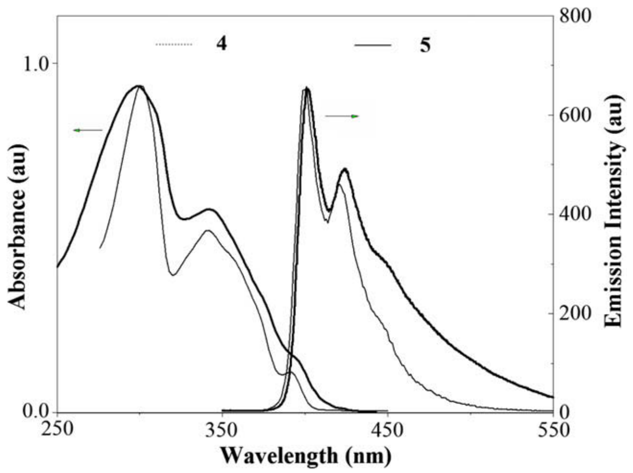


Figure 2. UV–vis absorption and fluorescence emission spectra of compound **4** and macrocycle **5** in chloroform solutions.

Figure 2 shows the UV/Vis absorption and fluorescence emission spectra of compound **4** and macrocycle **5** in chloroform. As expected by the *meta* linkage of the phenyl ring which breaks π-conjugation, macrocycle **5** shows absorption and emission spectra similar to those of compound **4**. For example, both compounds show absorption bands at around 300 and 340 nm and emission peaks at 400 and 422 nm. It is noted however that macrocycle **5** has a slightly red-shifted (by 4 nm) band edge in its absorption spectrum and a clear emission tail extending to much longer wavelengths. These observations may indicate the formation of some inter-ring aggregates in the solution of **5**.

When methanol vapor was diffused into a chloroform solution of **5**, the clear solution became opaque and eventually precipitates were formed. Scanning electron microscopy (SEM) indicated that the precipitates are composed of microspheres with remarkable size uniformity (Fig. 3a). The average size of the microspheres

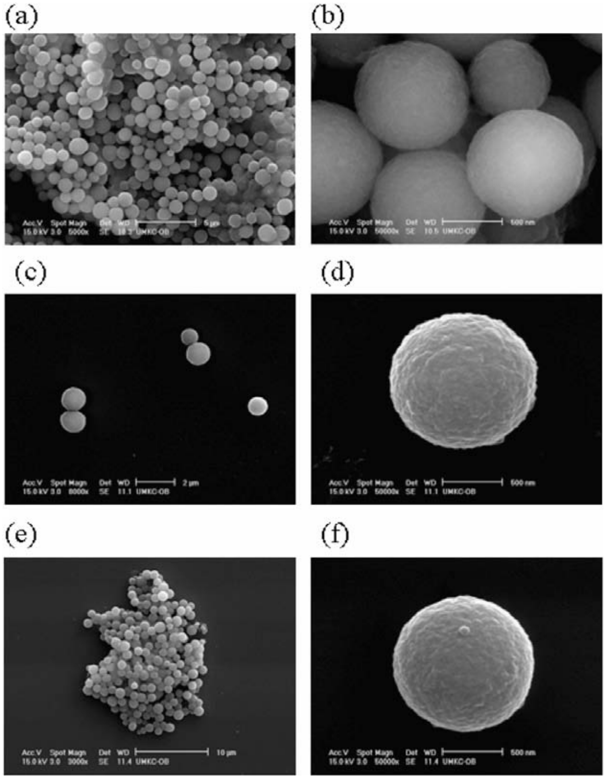


Figure 3. SEM images of microspheres prepared by vapor diffusion of methanol to a chloroform solution of **5**: (a) sample on tape with Pt-coating (b) sample on tape without Pt-coating; (c) and (d) sample on mica, after dispersion in methanol; (e) and (f) sample on mica after heating at 60 °C for 1 h.

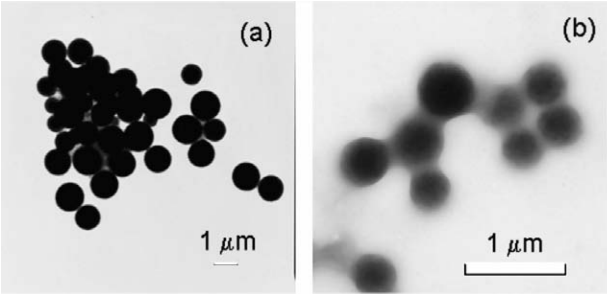


Figure 4. TEM images of microspheres prepared by vapor diffusion of methanol to a chloroform solution of **5**.

was found to be 1.1 ± 0.2 μm. The contact edge between adjacent balls is clearly visible (Fig. 3b). The microsphere aggregates can be dispersed by diluting with methanol (Fig. 3c and d). The microspheres exhibit excellent stability as no change was observed in regard to their size and shape after they were heated at 60 °C for an hour and subjected to high-vacuum environments (Fig. 3e and f).

To figure out whether the microspheres are solid balls or vesicles, methanol-dispersed microspheres were subjected to transmission electron microscopy (TEM). As shown in Figure 4a, microspheres without staining appeared as a dark disk. When images of some of the smallest spheres were visualized, darker cores and lighter edges were noticed (Fig. 4b), indicating that they are solid balls. The preference for microsphere formation may indicate that the rigid macrocyclic core of **5** does not have a truly planar geometry. Molecular modeling indeed showed that the ring system in **5**, when interacting with methanol, exhibits a certain curvature with the two triphenylene rings both bending upward (see Supplementary data). One intriguing question has to do with how the cyclic cores stack to form the microspheres: do they stack concentrically or radially with the macrocyclic plane either perpendicular or parallel to the spherical surface. Preliminary studies using polarized microscopy on those microspheres were not successful due to limited instrument resolution. To realize other self-assembled nano- and micro-objects, such as coiled nanotubes, macrocyclic amphiphiles with more planar π-conjugated cyclic cores may be needed. The amphiphilicity of the system may also need to be enhanced. In particular, the hydrophilicity of the system needs to be improved so that a balanced amphiphilicity can be achieved. We are currently synthesizing such systems.

In conclusion, a new type of shape-persistent macrocyclic amphiphile has been successfully prepared. Such a new amphiphile self-assembles into robust and uniformly sized microspheres.

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Supplementary data

Synthetic details, ^{1}H NMR spectra, MALDI-TOF mass spectra, additional SEM and TEM micrographs, and diameter histogram are available. Supplementary data associated with this Letter can be found, in the online version, at doi:10.1016/j.tetlet.2009.02.177.

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