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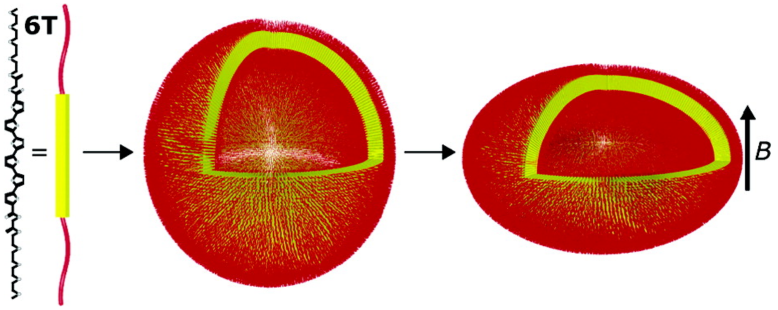

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Magnetic Deformation of Self-Assembled Sexithiophene Spherical Nanocapsules

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Nanometer-sized self-assembled architectures[1,2] are sufficiently large to be strongly affected by currently available high magnetic fields.[3] Magnetic field-induced orientation of nonspherical aggregates[4,5] arises from the magnetic torque acting on the anisotropic molecules that constitute these assemblies.[3] Three decades ago, Helfrich predicted that magnetic fields also can be used to deform spherical self-assemblies, specifically phospholipid bilayer vesicles.[6] Because of their symmetry, spheres do not align in a field, but rather deform into ellipsoids of revolution, an effect that to date has not been observed experimentally. Here we demonstrate the controlled magnetic deformation of spherical nanocapsules, assembled from bolaamphiphilic[7] sexithiophenes[8,9] into oblate spheroids. The deformed capsules can be fixed in a compatible organogel, preserving their shape outside a magnetic field.

The molecule used is a bolaamphiphile 2,5′′′′′-(*R*-2-methyl-3,6,9,12,15-pentaoxahexadecyl ester) sexithiophene (**6T**, Figure 1a). This semiconducting π-conjugated oligomer has a rigid apolar sexithiophene block substituted at both ends by polar ethylene oxide chains and forms aggregates in alcohols and water solutions and at the air/water interface.[8,9] The self-assembly behavior of **6T** molecules in 2-propanol represents a special case where the molecule/solvent combination leads to spherical architectures.[9] Aggregates of **6T** in 2-propanol (1 g/L) exhibit an absorbance spectrum (at temperatures $\leq$60 °C), which is blue-shifted with respect to the molecularly dissolved species at 80 °C.[10] The crossover from aggregates to dissolved molecules occurs within a narrow temperature window of about 20 °C, indicating a high degree of molecular order within the assemblies.[9] Dynamic light scattering (DLS) experiments reveal spherical objects with an average radius ranging from 55 nm at 20 °C to 125 nm at 60 °C, which can be visualized by scanning electron microscopy (SEM).[10] By applying a high local force with an atomic force microscope (AFM), the spheres collapse (Figure 1b) into circular objects with a typical height of 20 nm. Therefore, we conclude that the assemblies are constructed from a layer of molecules of the bola dye **6T** (Figure 1c), forming hollow spheres, that is, capsules, similar to those found for classical bolaamphiphiles[7] and thiophene-based surfactants,[11] which form vesicles in water.

6T possesses a large anisotropy in the diamagnetic susceptibility ($\Delta\chi = 8.0 \times 10^{-6}$), resulting from the six thiophene rings.[3,12] An external magnetic field ***B*** tends to orient such anisotropic molecules with their axis of lowest susceptibility (here the long axis of **6T**) along the field to minimize their magnetic energy $U_m = -\chi B^2$.[3,12] However, the spherical molecular assemblies are composed of molecules that point in all directions, and therefore the overall magnetic susceptibility is isotropic, and no magnetic alignment of the nanocapsules as a whole will occur. Instead, a magnetic field exerts a different torque on molecules that are parallel to the field (top and bottom of the sphere), compared to those perpendicular to the field (around the equator of the sphere). The sum of all these torques will deform the sphere into an oblate spheroid. The deformation leads to a decrease of the magnetic energy at the expense of an increased elastic energy. At equilibrium, the sum of the magnetic and the elastic energy is minimized, which occurs when the elastic deformation force is balanced by the magnetic force. This magnetic field-induced deformation can be detected optically as a field-induced birefringence Δn.[6] At fixed temperatures the absolute value of Δn increases with field (initially in a quadratic fashion[6]), which directly proves that there must be an appreciable magnetic deformation of the **6T** nanocapsule (Figure 1d). When the field is removed, Δn, and therefore the deformation, vanishes, which proves that the elastic deformation is a reversible process.

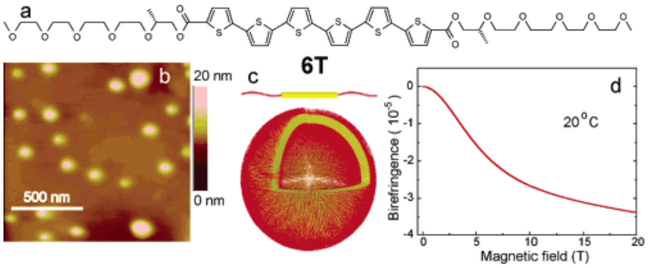

Figure 1. (a) Chemical structure of **6T**. (b) AFM image of collapsed capsules on a glass support. (c) Illustration of a **6T** nanocapsule. (d) Magnetic birefringence due to deformed nanocapsules.

Compelling evidence for the magnetic deformation was obtained by trapping the deformed nanocapsules, formed at high fields, in a matrix. Such a matrix should not disturb the self-assemblies of **6T**, but merely trap them in their deformed shape, even after the magnetic field is removed. To this end, we have employed 2,3-bis-*n*-decyloxyanthracene (DDOA) as a gelling agent, which is capable of gelling alcohols, including 2-propanol, via the formation of fibers.[13] The **6T**/2-propanol solution, containing DDOA molecules, is heated to 50 °C, where **6T** nanocapsules are present and the DDOA molecules are dissolved (Figure 2). The spheres are deformed by a magnetic field, and the deformation is detected by field-induced birefringence. Subsequently, with the field on, the temperature is reduced slowly, triggering the gel formation of

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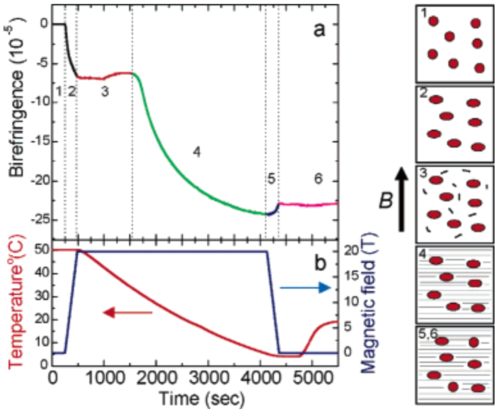

Figure 2. (a) Magnetic field-induced birefringence during the fixation of deformed nanocapsules in a DDOA organogel. (b) Temperature and magnetic field versus time. Right panel: schematic representation of the six successive phases. The **6T** solution, containing DDOA, is heated to 50 °C (1), after which the field is ramped up to 20 T (2). At 20 T, the temperature is gradually reduced, causing gelation due to formation of DDOA fibers (3). Sufficiently long gel fibers are aligned, perpendicularly to the magnetic field, yielding a further decrease of the birefringence (4). At 5 °C, the field is ramped down to zero (5). Finally, the gelled solution is heated to room temperature (6).

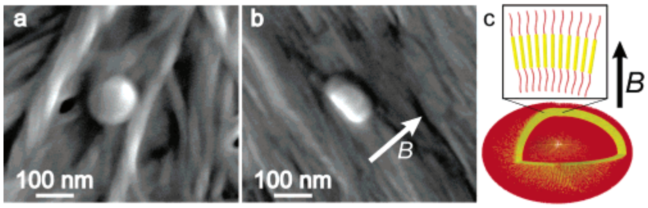

Figure 3. SEM of spherical (a: 0 T) and deformed (b: 20 T) **6T** nanocapsules in a DDOA organogel. (c) Schematic representation of the magnetically deformed nanocapsules.

DDOA. At 5 °C, the gelation is complete, the field is switched off, during which most of the birefringence is preserved, and the resulting gel sample is warmed to room temperature. Typical SEM photographs of **6T** spheres gelated without magnetic field show that (Figure 3a) they are embedded in randomly oriented DDOA fibers that constitute the organogel. In contrast, spheres gelated at 20 T are deformed into oblate spheroids contained in DDOA fibers oriented perpendicular to the magnetic field direction (Figure 3b). Apparently the gelled DDOA solution in- and outside the deformed capsules provides sufficient stability to prevent the recovery of the spherical shape after the field is switched off.

6T molecules align with their thiophene rings parallel to the magnetic field.[3,12] To maximize the number of molecules with their long axis along the field direction the capsules must deform in an oblate shape (Figure 3c), as indeed seen in the SEM images (Figure 3b). The negative sign of the birefringence (Figure 1d) implies that the molecules are aligned with their fast optical axis parallel to the magnetic field direction, that is, with the long molecular axis of **6T** along the field, consistent with the observed oblate spheroids.

The gelation method demonstrated here proves the unique opportunity to capture deformed nanocapsules, permitting further investigations and potential device applications. Furthermore, we can use the observed deformation in the SEM pictures to link the measured birefringence with the corresponding mechanical deformation from which the strength of the intermolecular interactions responsible for the elasticity of the nanocapsules can be determined. A full theoretical description is beyond the scope of this communication and is the subject of further studies.

In general, homogeneous magnetic volume forces are ideal for the simultaneous manipulation of many supramolecular assemblies in solution and can be applied in a contact-free and noninvasive manner, in contrast to other alignment techniques.[14] The method is not restricted to thiophene-based materials, and we therefore anticipate an increased use of magnetic forces as a promising tool for manipulation of supramolecular structures, such as sizable nanocontainers[11] and reactors or anisotropic photonic nanospheres.[15]

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Supporting Information Available: Detailed experimental procedures, scanning electron micrographs, dynamic light scattering, and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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