The self-assembly of inorganic nanocrystals (NCs) into hierarchical structures on all length scales is pivotal for nanotechnology.\textsuperscript{[3]} In this context, water/oil interfaces have gained increasing attention because their fluidity may heal defects and their rich phase separation behavior may diversify the structural complexity. The study of the attachment of micrometer-sized particles at the interface has a century-long history.\textsuperscript{[2]} Nonetheless, the controlled interfacial self-assembly of NCs has been successfully realized only recently.\textsuperscript{[3–5]} The appropriate surface hydrophobicity of NCs is crucial for NCs to self-assemble at the interface because of their fairly small interfacial attachment energy. This is usually realized by the proper design of the capping ligands on the NCs.\textsuperscript{[3–4]} Herein, we demonstrate an alternative approach to render NCs interfacially active by entrapping their hydrophobic functional groups within the hydrophobic interior cavities of cyclodextrins (CDs). Furthermore, the functional groups on the hydrophobic exterior walls of CDs allow different NCs to be differentially directed from either the aqueous or organic phase to the interface, thus realizing stepwise interfacial self-assembly to form macroscopic heterogeneous multilayers of NCs over areas on the order of square centimeters.

CDs are characterized by having a hydrophilic exterior surface and a hydrophobic interior cavity that may include entirely or partially hydrophobic molecules through non-covalent interactions.\textsuperscript{[6]} This inclusion shows a strong size selectivity. α-CDs can efficiently trap long alkyl chains, and this was used to realize the phase transfer of NCs from an organic to an aqueous phase and vice versa.\textsuperscript{[9]} In contrast, β-CDs have cavities of around 7.0 Å in size, which selectively trap large molecular cages such as adamantane (7 Å in diameter).\textsuperscript{[9]} The specific inclusion of CDs and adamantane was used to grow multilayers of Au NCs on planar substrates layer by layer.\textsuperscript{[10]}

In the present study hydrophobic 6-nm-diameter CoPt\textsubscript{3} NCs capped with 1-adamantylcarboxylic acid (ACA) and hexadecylamine (HDA) were prepared as explained elsewhere.\textsuperscript{[11]} The simultaneous presence of HDA and ACA is essential for the colloidal stability of the CoPt\textsubscript{3} NCs; their partial removal leads to agglomeration of the NCs.\textsuperscript{[11]} Hence one cannot render CoPt\textsubscript{3} NCs interfacially active through ligand exchange. In our study, solutions of CoPt\textsubscript{3} NCs in toluene were brought into contact with water, in which β-CDs or their derivatives were dissolved. Since the hydrophobic cavities of β-CDs or their derivatives selectively entrap the ACA group rather than the HDA,\textsuperscript{[8,9]} their hydrophilic exterior walls convert the hydrophobic ACA domains on the CoPt\textsubscript{3} NCs into hydrophilic ones. The coexistence of hydrophobic HDAs and hydrophilic β-CDs or their derivatives may render the CoPt\textsubscript{3} NCs active at the interface, thus driving the NCs to self-assemble into a close-packed monolayer (Figure 1).

2-Hydroxypropyl-β-cyclodextrins (HPCDs) were used as models to demonstrate our concept because of their excellent water solubility.\textsuperscript{[12]} An aqueous solution of the HPCDs (10 mg mL\textsuperscript{−1}) was added to a solution of the CoPt\textsubscript{3} NCs in toluene (0.1 mg mL\textsuperscript{−1}). After gently shaking the mixture, a yellow thin film formed at the water/toluene interface (Figure 2a). In contrast, no such thin film formed in the absence of the HPCDs (see the Supporting Information). The UV/Vis spectra of the bulk phases showed little detectable absorption, thereby indicating that all the CoPt\textsubscript{3} NCs were located at the interface. This result also suggests that no phase transfer occurred. Transmission electron microscopy (TEM) imaging of these thin films, transferred from the interface, revealed a
monolayer of randomly close-packed NCs over a large area (Figure 2 b).

We prepared 6-nm- and 17-nm-diameter Fe₃O₄ NCs stabilized with oleic acid and oleylamine in toluene by the oxidation of iron(III) acetylacetonate.[13] The initial capping groups of the Fe₃O₄ NCs were quantitatively replaced with ACA by ligand exchange. Incubating the Fe₃O₄ NCs in solutions of ACA in toluene at concentrations of 2, 10, and 20 mg mL⁻¹ for two days resulted in the number of ACA groups per NC being 62, 128, and 199, as determined by ¹H NMR spectroscopy (see the Supporting Information).

Note that the maximal number of ACA groups per NC is calculated as 264. The inclusion of ACA by HPCD led to the interfacial self-assembly of the Fe₃O₄ NCs (Figure 3 a, b). We envisioned that the reduction in the absorbance of the Fe₃O₄ NCs in the toluene phase should be proportional to the number of NCs attached at the water/toluene interface.

Accordingly, we quasi-quantitatively evaluated the interfacial attachment of the Fe₃O₄ NCs at the water/toluene interface by the inclusion of ACA-capped NCs from an oil phase into CDs dissolved in water (a and b) and of the consecutive self-assembly with other hydrophilic and hydrophobic NCs into bilayers (c) or trilayers (d) based on the interaction of functional groups, such as NH₂ or SH, linked to CDs.

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β-CD (1 mM). We found that incubation at high temperature favored the formation of monolayers of NCs at the water/toluene interface: heating may weaken the intra- and intermolecular hydrogen bonding between the β-CD and the inclusion of ACA\(^{[13]}\) (see the Supporting Information). In comparison to HPCD, β-CDs enhanced the stability of the emulsions. By staining with aqueous solutions of CdTe NCs, we found that the emulsions obtained were of the oil-in-water type (see the Supporting Information).

After the ACA functional groups on the CoPt\(_3\) or Fe\(_3\)O\(_4\) NCs had been inserted within the hydrophobic cavities of the β-CDs, the hydrophobic exterior walls of the latter were envisioned not only to result in the NCs becoming hydrophilic but also to provide flexibility for the further modification and conjugation with other materials. This encouraged us to utilize β-CDs with functional groups on the exterior walls to absorb different nanosized objects onto macroscopic monolayers of close-packed CoPt\(_3\) or Fe\(_3\)O\(_4\) NCs. Thus, heterogeneous multilayers composed of different NCs may be generated, which should be of great importance for microelectronics applications.\(^{[16]}\) β-CDs functionalized with one SH or NH\(_2\) group on the exterior walls, namely, mono(6-deoxy-6-[(mercaptohexamethylene)thio])-β-cyclodextrin (SH-β-CD)\(^{[17]}\) and 6-monodeoxy-6-monoamino-β-cyclodextrin (NH\(_2\)-β-CDs) were recruited as new functional groups to direct different NCs to consecutively self-assemble at the water/oil interface (Figure 1). Similar to HPCDs, the NH\(_2\)-β-CDs and SH-β-CDs were able to direct ACA-capped NCs (CoPt\(_3\) and Fe\(_3\)O\(_4\)) to self-assemble into randomly close-packing monolayers through the inclusion of ACA into the CD (see the Supporting Information). After the aqueous solution of SH-β-CDs was replaced by pure water, hydrophilic 6-nm-diameter Ag NCs stabilized with oleic acid were introduced into the toluene phase. The strong interaction between the SH groups on the β-CDs and the Ag NCs led to the interfacial attachment of the Ag NCs on the monolayers of the 6-nm-diameter Fe\(_3\)O\(_4\) NCs (Figure 4a), accompanied by the appearance of a stronger metallic luster to the film and the disappearance of the dark-yellow color in the toluene phase (Figure 3a). TEM imaging demonstrated the formation of bilayers of close-packed NCs, but it was hard to distinguish the chemical nature of these two NCs because of their similar size and electron contrast (see the Supporting Information).

Similarly, bilayers composed of 6-nm-diameter CoPt\(_3\) and 12-nm-diameter Au NCs were formed at the interface by absorbing citrate-stabilized Au NCs from the aqueous phase using NH\(_2\) groups attached to β-CDs (see the Supporting Information). The resulting Ag/Fe\(_3\)O\(_4\) NC bilayers are envisaged to have a hydrophobic surface in contact with the toluene, because of the free oleic acid capping the Ag NCs, and a slightly hydrophilic lower surface in contact with the water, as a result of free SH-β-CDs capping the Fe\(_3\)O\(_4\) NCs. The free SH groups on the Fe\(_3\)O\(_4\) NCs may be employed to attach other hydrophilic NCs from the aqueous phase (Figure 1). In the current study, 12-nm-diameter citrate-stabilized Au NCs were introduced into the aqueous phase. Figure 4b shows that after gentle shaking, the Ag/Fe\(_3\)O\(_4\) NC bilayer films located at the interface appear purple when viewed in the transmittance mode and golden in the reflectance mode, thus suggesting the interfacial attachment of 12-nm-diameter Au NCs. TEM imaging of broken areas of the resulting thin films revealed a trilayer structure (see the Supporting Information). The existence of different NCs was demonstrated by energy-dispersive X-ray spectroscopy (EDX) and EDX mapping (see the Supporting Information). The thickness of the trilayers was nearly 25–30 nm, which is consistent with the formation of an Ag/Fe\(_3\)O\(_4\)/Au NC trilayer (see the Supporting Information). Note that both the bilayers and trilayers remain magnetic because of the existence of magnetic NCs (see the Supporting Information).

In summary, we have demonstrated that the use of the specific inclusion of adamantane by CD can direct hydrophobic ACA-capped NCs to self-assemble into macroscopic randomly close-packing monolayers at water/oil interfaces. By introducing functional groups, such as NH\(_2\) or SH, onto the exterior surfaces of CDs, we succeeded in directing different hydrophobic and hydrophilic NCs to self-assemble in a stepwise manner at the water/oil interface, thereby generating macroscopic heterogeneous multilayers. This result demonstrates the unique amphoteric character of the water/oil interface—being able to conjugate both hydrophilic and hydrophobic NCs from water and oil phases. Since the success of our approach relies on the molecular structure of CDs, it should pave a versatile and efficient way to the stepwise self-assembly of NCs with different chemical natures and surface wettability into macroscopic lamellar superlattices of NCs based on well-established host–guest chemistry. The trilayer films of Ag/Fe\(_3\)O\(_4\)/Au NCs, which is a magnetic NC monolayer sandwiched between two metallic NC ones, should hold immense promise in technical applications, such as magnetic information storage and processing.

**Experimental Section**

Aqueous solutions (0.2 mL) of β-CD or its derivatives were brought into contact with solutions of NCs in toluene (0.2 mL). The gentle shaking led to a thin film being formed at the interface and the
Communications

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/C23 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Keywords:
host–guest systems · interfaces · multilayers ·
nanostructures · self-assembly


