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## Self-Assembly and Cross-linking of FePt Nanoparticles at Planar and Colloidal Liquid–Liquid Interfaces

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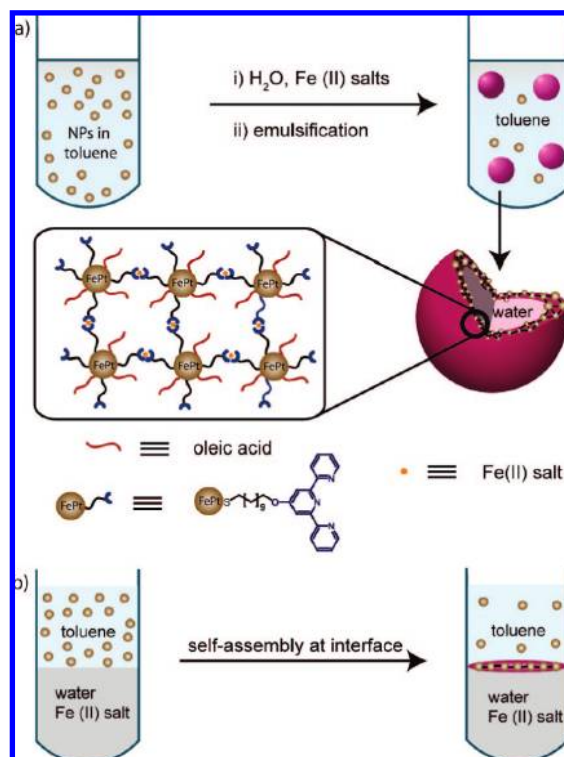
Self-assembly of nanoparticles (NPs) provides access to multi-scale nanocomposite systems.<sup>1</sup> The optical, electronic, and magnetic properties of such structures are different from their isolated counterparts and have applications in such diverse areas as biosensing,<sup>2</sup> electronic devices,<sup>3</sup> and drug delivery vehicles.<sup>4</sup> Self-assembly at the liquid–liquid interface offers a straightforward pathway for the production of organized nanostructures.<sup>5</sup> In this approach, colloidal particles localize at the interface to minimize the Helmholtz free energy.<sup>6</sup> A range of microporous capsules (colloidosomes) and membranes with controlled pore sizes and pore size distribution have been created using this strategy.<sup>7</sup>

Despite the versatility of interfacial assembly strategies, the creation of stable membranes and capsules remains a challenge.<sup>8</sup> The competition between the interfacial energy and spatial fluctuations resulting from NP thermal energy causes instability in as-formed membranes and capsules. Two approaches have been recently developed to fabricate stable membranes and colloidosomes using NPs of various sizes.<sup>9</sup> Lin et al., has fabricated a stable ultrathin CdSe membrane at the interface by cross-linking the ligands of CdSe NPs<sup>9a</sup> while Duan et al. prepared stable magnetic colloidosomes at the interface of water-in-oil droplets using agrose gelled water phase.<sup>9b</sup> In both cases the initially formed membrane and colloidosomes were subjected to thermal treatment ( $\geq 60$  °C) to afford stability, and also the cross-linking of the NPs at the interfaces was slow ( $\sim 8$  h). Both, time and temperature of thermal treatment can limit the tunability and applicability of these methods.

Here, we report an alternate route to fabricate stable colloidal shells and membranes by cross-linking NPs at the liquid–liquid interface using coordination chemistry. In this strategy, terpyridine thiol (Terpy-SH) functionalized FePt NPs are self-assembled at water–toluene interfaces and cross-linked through complexation of terpyridine with Fe(II) metal ions.<sup>10</sup> The major advantage of this assembly process is the essentially instantaneous formation of robust cross-linked structures under ambient condition.

Oleic acid and oleyl amine stabilized FePt magnetic NPs ( $7.0 \pm 1$  nm) were synthesized following a literature procedure<sup>11</sup> and then functionalized with Terpy-SH ligand<sup>12</sup> via place-exchange reaction (see Supporting Information). Aqueous Fe(II) tetrafluoroborate hexahydrate (1 M) droplets were then added to a toluene dispersion of the functionalized FePt magnetic NPs. Vigorous mixing for several seconds resulted in the formation of stable emulsions (Scheme 1a). The colloidal shells formed by this technique were  $35\text{--}60$   $\mu\text{m}$  (Figure 1a). The appearance of pink colored ( $\lambda_{\text{max}} = 540$  nm) NP shells (Figure 1a, inset) confirms metal to ligand charge transfer (MLCT) complex formation<sup>13</sup> (see Supporting Information for detailed experimental procedure) and subsequent self-assembly of FePt NPs at the liquid interface. Transmission electron microscopy (TEM) image of the dried shells reveals that the wall of the colloidal shells is composed of FePt NPs in a network structure. (Figure 1b)

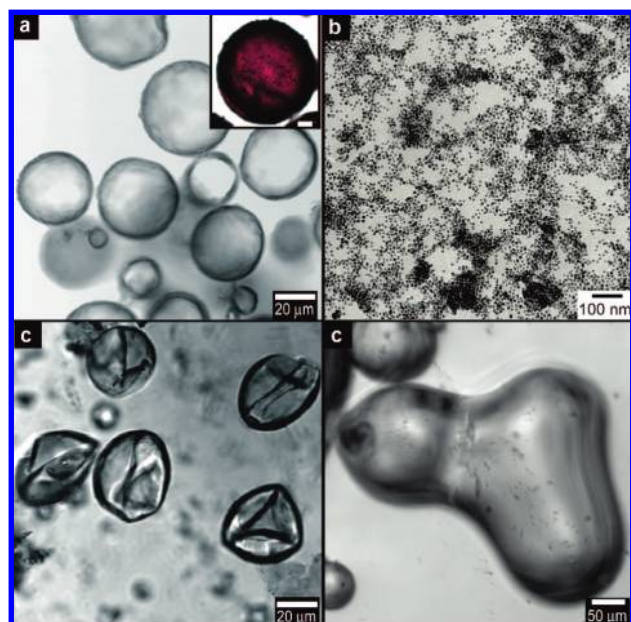
Scheme 1. FePt NP<sup>a</sup>



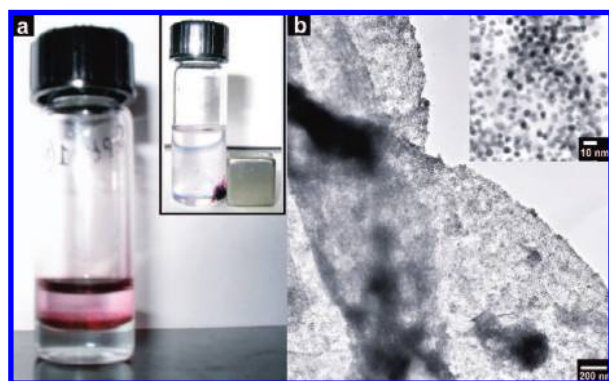
<sup>a</sup> Illustration shows (a) FePt NP colloidal shells formation at water-in-toluene interface. Cross-sectional view of the colloidal shells represents NP network formed by complexation of the Terpy ligand with Fe(II) tetrafluoroborate hexahydrate salt; (b) FePt NP membrane formation at water-toluene interface.

The NP-stabilized colloidal shells are very stable; evaporation of water over a 5 day period resulted in crumpled but still intact colloidal shells (Figure 1c). Also when subjected to heat at 50 °C the shells crumple after 2 min but remain discrete. (see Supporting Information). On the other hand, stabilization of emulsion without Fe(II) salt resulted in formation of unstable structures Figure 1d, as did assembly using reduced ( $> 1$  M) concentrations of Fe(II) salts.

A similar strategy was used to prepare FePt membranes at the water–toluene interface. Toluene dispersions of FePt NPs were allowed to stand over an aqueous solution containing 1 M Fe(II) tetrafluoroborate hexahydrate. The dark toluene solution became colorless with a concomitant formation of a pink membrane (Figure 2a). TEM analysis of the dried membrane (Figure 2b) shows the thin-film morphology, while the high magnification image (inset) clearly reveals that the membrane is composed of densely packed FePt nanoparticles.



**Figure 1.** (a) Optical micrographs (OMs) of FePt NP colloidal shells fabricated at water-in-oil interface with complexation agent, Fe(II) metal salt. Inset: Pink-colored shell around water droplets indicates NP network formation [concn of Fe(II) salt  $\approx 100 \mu\text{M}$ , scale bar  $50 \mu\text{m}$ ]. (b) TEM image of the colloidal shell; (c) OM of the crumbled colloidal shells after partial drying; (d) OM of FePt NP colloidal shells fabricated at water-in-oil interface without Fe(II) salt.



**Figure 2.** (a) Photograph of the FePt membrane at water-oil interface. Inset: Membrane in toluene subjected to magnetic field. (b) TEM micrographs of the membrane. Inset: High magnification image of the membrane shows close-packed FePt NPs.

Preliminary experiment indicates that this membrane can be manipulated using external magnetic fields. In this study, the biphasic system was homogenized by the addition of methanol. The free-floating membrane could then be moved through application of a magnetic field using a permanent magnet (Figure 2a inset). The fabrication of NPs membrane by this technique is general and can be extended to other nanoparticulate systems; Terpy-SH functionalized  $2 \pm 1 \text{ nm}$  Au NPs provided essentially identical membranes (see Supporting Information).

In summary, we have developed a simple strategy for the creation of highly stable NP self-assemblies at liquid-liquid interfaces.

Stable water-in-oil colloidal shells and membranes were prepared using Terpy-SH functionalized FePt NPs, with cross-linking effected at room-temperature through Fe(II) metal ion complexation. These systems could be manipulated using external magnetic fields, providing a convenient and gentle means of positioning these materials. Tuning of the assembly process and application of this methodology to the creation of functional devices is underway and will be reported in due course.

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**Supporting Information Available:** Experimental procedures, optical micrographs of (a) FePt colloidal shells at  $50 \text{ }^\circ\text{C}$ ; (b) FePt colloidal shells at varying salt concentration. Digital photograph of Au NP membrane at water-toluene interface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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