Molecular recognition at the liquid–liquid interface of colloidal microcapsules†

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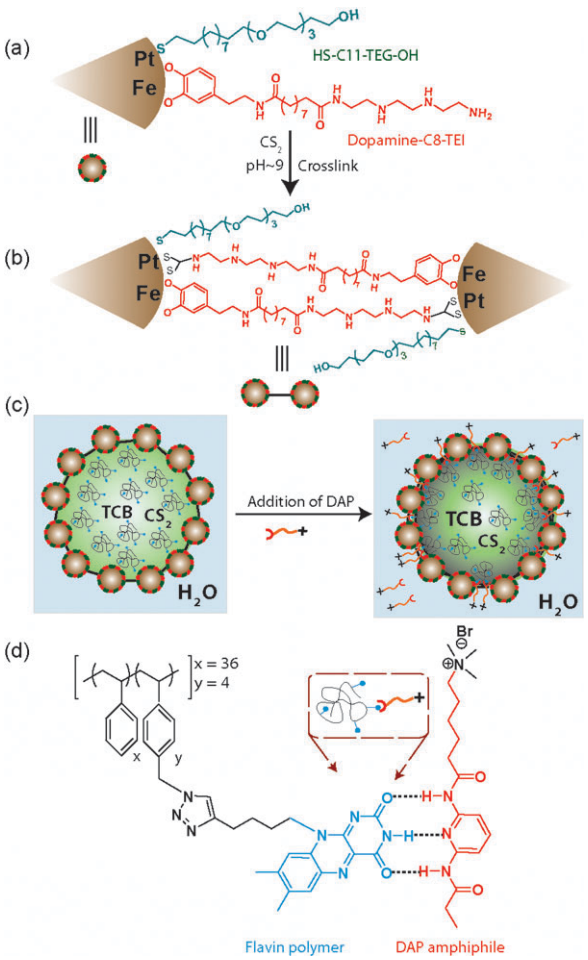
Dithiocarbamate chemistry is used as a crosslinking tool to fabricate FePt colloidal microcapsules which provide a versatile scaffold for "host–guest" recognition at the liquid–liquid interface.

Molecular recognition mediated by hydrogen bonding serves as an underlying mechanism to understand biological functions and provides a powerful toolkit to design novel functional materials.[1] Unlike biological systems, the recognition between the "host–guest" pair is mostly effective in nonaqueous media due to the high dielectric nature of water.[2] To enhance the effectiveness of hydrogen bonding in water, recent efforts have been made to create hydrophobic environment of different dimensions in the vicinity of the "host–guest" functional pair.[3]

Oil–water emulsions offer a unique microenvironment[4] where the larger interfacial area of emulsions can act as a suitable platform to localize the "host–guest" pair. To encapsulate the "host" molecule for further recognition at the interface, a stable emulsion is highly desired. Microcapsules such as polymeric microcapsules,[5] vesicles,[6] colloidal microcapsules[7] can act as a suitable candidate due to their structural stability. Amongst these, colloidal microcapsules feature great advantages due to their easy fabrication, enhanced mechanical stability and controlled permeability.[8]

Herein, we introduce an approach to fabricate stable colloidal microcapsules that are compatible with most host–guest systems. In this strategy, orthogonally functionalized FePt nanoparticles (NPs) are self-assembled at the oil–water interface and crosslinked *via* dithiocarbamate (DTC) chemistry.[9] Host–guest chemistry was demonstrated by encapsulation of the flavin polymer[10] ("host") inside the microcapsules to obtain three-point hydrogen bonding interaction at the interface with a complementary diaminopyridine (DAP, "guest") amphiphile. Host–guest interactions at the interface were then monitored by fluorescence quenching of the flavin fluorophore.[11]

For our studies we used triethylene imine (TEI) functionalized FePt NPs to fabricate colloidal microcapsules. Initially oleic acid and oleyl amine coated FePt NPs (~7 nm) were synthesized following a reported procedure.[12] Functionalization of the NPs was accomplished by place exchange reaction with HS–C_{11}–TEG–OH and dopamine–C_8–TEI ligands, respectively (Scheme 1, see also ESI†). The modified NPs were dissolved in milliQ water and pH of the solution was adjusted to ~9 by adding 0.1 M NaOH solution.



Scheme 1 (a) Orthogonal functionalization of FePt NPs. (b) Mechanism of cross-linking of FePt NPs *via* DTC chemistry to fabricate microcapsule. (c) Flavin encapsulated microcapsule and "host–guest" recognition at oil–water interface. (d) Three-point hydrogen bonding interaction between flavin and DAP.

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In the next step, 250 μL of the NPs solution were transferred to an Eppendorf tube and 10 μL of 0.5 M CS_2 in 1,2,4-trichlorobenzene (TCB) were added to it. Vigorous shaking for 10 s gave stable emulsions and emulsions were kept for 30 min prior to analysis. Excess NPs were washed two times by milliQ water and emulsions were visualized by an optical microscope (OM) (Fig. 1a, see ESI† for size distribution). This assembly strategy was further investigated by using different nonpolar solvents such as dichloromethane and hexane. Low boiling organic solvents resulted in the formation of crumbled microcapsules due to rapid evaporation of the solvent. (*e.g.* dichloromethane, inset of Fig. 1a). Microcapsules were drop casted on carbon coated copper grid for transmission electron microscope (TEM) analysis. Low-magnification image of the dried capsules shows (Fig. 1b) thin film like texture, while the high-magnification image (inset of Fig. 1b) reveals that the capsule is composed of densely packed crosslinked FePt NPs.

Successful encapsulation of the host flavin polymer inside the microcapsules during their formation was confirmed by fluorescence of the microcapsules in aqueous medium (Fig. 2a). To study the recognition process inside the microcapsule, an excess of the guest DAP amphiphile was added to the aqueous solution. Concomitant quenching of fluorescence (Fig. 2b) from the microcapsule was observed due to three-point hydrogen bonding interaction between "host–guest" at the oil–water interface. Semiquantitative assessment of the binding constant between flavin and complementary DAP was obtained by monitoring the fluorescence intensity of a single microcapsule. Fluorescence titration of flavin in the presence of increasing DAP equivalents yielded a $K_a \approx 250\ M^{-1}$ (Fig. 3) which is comparable to their solution study. Titration of excess DAP amphiphile into microcapsules containing the fluorescent *N*(3)-methylated polymer (Fig. 2c) failed to display significant quenching (Fig. 2d and 3), suggesting that three-point hydrogen bonding interactions were responsible for fluorescence quenching.

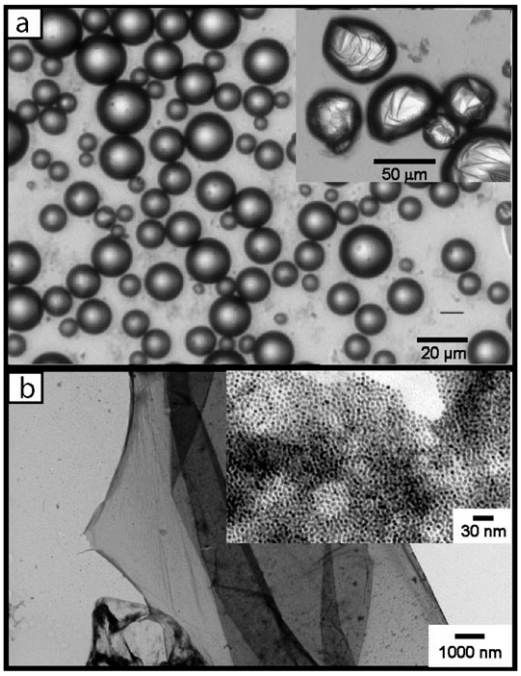

Fig. 1 OM micrographs of (a) FePt microcapsules at oil-in-water interface using DTC crosslinking strategy. Inset shows crumbled microcapsules. (b) Low-magnification TEM images of dried microcapsules showing film like texture. Inset represents higher-magnification TEM image.

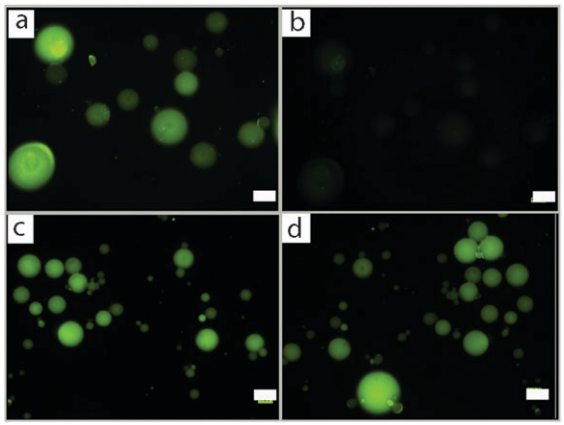

Fig. 2 Fluorescence microscopy images of (a) flavin encapsulated microcapsule (b) after addition of excess DAP. Similarly, fluorescence images of (c) *N*-methyl flavin encapsulated micro capsule (d) after addition of excess DAP. All scale bars represent 40 μm of length.

The fact that DAP–flavin recognition quenched fluorescence prevented direct determination of the localization of the host–guest complexes within the microsphere. Localization can be inferred, however, from the experiments performed using a planar interface. In this experiment the fluorescence of flavin polymer was recorded in TCB. In the next step, an aqueous solution of excess DAP was added to the organic phase. No fluorescence quenching was observed after agitation, indicating that DAP and flavin polymers are soluble only in water and oil, respectively (for details see ESI† Fig. S1), and recognition can occur only at the interface, *i.e.* in the proximity of the particle shell.

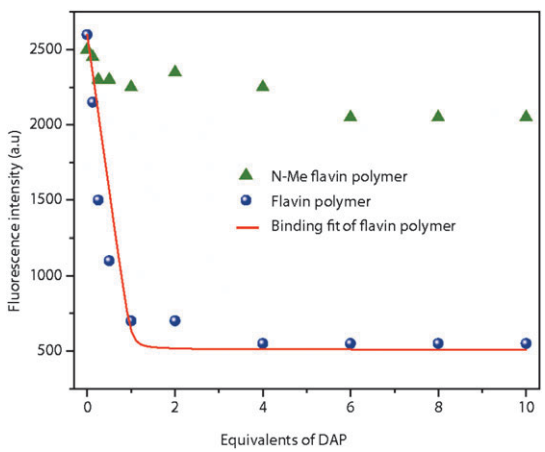

Fig. 3 Binding plot shows dramatic quenching of flavin polymer fluorescence upon addition of DAP ($K_a \approx 250\ M^{-1}$) whereas control *N*-methylated flavin does not show any fluorescence quenching.

In summary, we have developed a simple and mild way to fabricate stable colloidal microcapsules at the oil–water interface based on orthogonal functionalization of FePt NPs followed by DTC mediated crosslinking. Furthermore, we have shown using fluorescence experiments that these capsules provide a suitable macroscopic platform to confine host–guest pairs at their liquid–liquid interface.

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