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## Toward the raise of new physic-chemical properties: from the bulk material to multifunctional nanoparticle arrays

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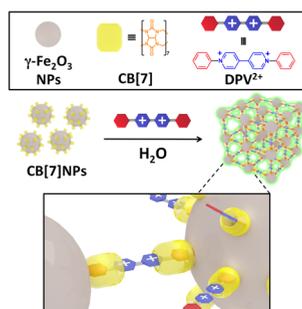
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The field of nanotechnology is increasingly leading to the elaboration of multifunctional materials for various applications (electronics, photonics, catalysis, biomedicine, sensing...). Owing to their very small size, nanoparticles (NPs) show significantly higher properties than the homologous bulk material such as optical or superparamagnetic properties among others. Additional properties can be merged through the specific surface coating with organic molecules. We decided to create a new material with novel properties, not present in either the nanoparticle or the bulk form of the material.

Here, we actively add and tune physico-chemical properties to the existing one of iron oxide nanoparticles (NPs).<sup>[1]</sup> We describe the bottom-up construction of a photoluminescent, superparamagnetic and microporous network. This array was built by threading a viologen-based ditopic ligand, diphenyl viologen, DPV<sup>2+</sup>, into the cavity of cucurbituril (CB[7]) macrocycles adsorbed on the surface of the NPs (CB[7]NPs).

The CB[7]NPs are used as building blocks to fabricate functional nanostructures via self-assembled architectures due to molecular recognition on the NP surface. Evidences for the formation of 1:2 inclusion complexes involving DPV<sup>2+</sup> and two CB[7] macrocycles was first obtained in solution by <sup>1</sup>H NMR and emission spectroscopies. The same mode of interaction between DPV<sup>2+</sup> and CB[7] occurs on the surface of CB[7]NPs and results in nanoparticle self-assembly. Samples of the DPV<sup>2+</sup> CB[7]NP network were characterized by measuring N<sub>2</sub> adsorption/desorption which established the presence of defined pores. Viologen-mediated self-assembly of CB[7]NPs did not affect the core structure (i.e. the crystallinity) of the iron-oxide nanoparticles, yet their superparamagnetic properties were enhanced. This result reflects increased aggregation and stronger random dipole-dipole interactions between the nanoparticles. Self-assembled CB[7]NPs were found to be fluorescent in solution and in the solid state as a consequence of the inclusion of the viologen ligand within the cavity of CB[7]. Fluorescence lifetime measurements of CB[7]NPs in the solid state in the absence and the presence of DPV<sup>2+</sup> support the hypothesis that DPV<sup>2+</sup> drives the self-assembly of these 3D nanoparticle arrays.

This facile supramolecular approach to NP self-assembly provides a platform for the synthesis of hybrid materials with ordered structures and properties such as superparamagnetism, luminescence and, potentially, selective porosity. This magnetic, porous and fluorescent self-assembled network can provide a useful tool to the elaboration of the next generation of nano-devices for spintronic, magnetic magneto-electronic and biomedical applications.



Scheme. Schematic representation of the supramolecular self-assembly of CB[7]-modified nanoparticles into networks upon addition of diphenyl viologen (DPV<sup>2+</sup>) bridging ligand.

Reference:

1 - Benyettou, F.; Nchimi-Nono, K.; Jouiad, M.; Lalatonne, Y.; Milosevic, I.; Motte, L.; Olsen, J.-C.; Saleh, N. i.; Trabolsi, A. *Chemistry – A European Journal* **2015**, *21*, 4607.