Dynamically Self-Assembling Carriers Enable Guiding of Diamagnetic Particles by Weak Magnets

Olga Chovnik, Renata Balgley, Joel R. Goldman, and Rafal Klajn*

Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel

ABSTRACT: We show that diamagnetic particles can be remotely manipulated by a magnet by the reversible adsorption of dual-responsive, light-switchable/superparamagnetic nanoparticles down to their surface. Adsorption occurs upon exposure to UV light, and can be reversed thermally or by ambient light. The dynamic self-assembly of thin films of the dual-responsive nanoparticles induces attractive interactions between diamagnetic particles. We demonstrate that catalytic amounts of the dual-responsive nanoparticles are sufficient to magnetically guide and deliver the diamagnetic particles to desired locations, where they can then be released by disassembling the dynamic layers of superparamagnetic nanoparticles with visible light.

The ability to manipulate the position of small objects remotely (using an external stimulus) has widespread applications in physical and life sciences which enable goals as diverse as the transport of Bose–Einstein condensates and control of the topological state of DNA. Of particular interest is the approach involving optical trapping and manipulation; however, this technique suffers from several limitations including lack of selectivity as well as limitations associated with the high intensity of the trapping laser, such as local heating and photodamage of the trapped species. Many of these problems can be overcome by the use of a magnetic field for guiding. This strategy has enabled several interesting applications, including control of calcium signaling and magnetofection; however, only materials with high absolute values of magnetic susceptibility can be effectively guided by magnets. To overcome this limitation, and to allow random particles to be manipulated with magnetic fields, we envisaged a methodology (Figure 1) which would allow for the reversible formation of a thin paramagnetic coating on the surface of diamagnetic particles, thus rendering them responsive to magnetic fields. The resulting diamagnetic core–paramagnetic shell assemblies would be stable in the dark and could be magnetically delivered to a desired location, whereupon the diamagnetic “cargo” could be released simply by exposure to visible light, which “strips off” the thin paramagnetic shell.

In order to realize this goal, we decided to take advantage of the previously reported dual-responsive nanoparticles (NPs), which comprise superparamagnetic (SPM) Fe₃O₄ cores, ~11 nm in diameter, functionalized with monolayers of trans-azobenzene molecules (Fe₃O₄·AC in Figures 1 and 2a). Solutions of these NPs in apolar solvents are stable for prolonged periods of time (e.g., no signs of aggregation in toluene can be seen after several months in the dark) due to the hydrophobic nature of trans-azobenzene on their surfaces. Interestingly, the NPs also do not aggregate after exposure to external magnetic fields; however, only materials with high absolute values of magnetic susceptibility can be effectively guided by magnets. To overcome this limitation, and to allow random particles to be manipulated with magnetic fields, we envisaged a methodology (Figure 1) which would allow for the reversible formation of a thin paramagnetic coating on the surface of diamagnetic particles, thus rendering them responsive to magnetic fields. The resulting diamagnetic core–paramagnetic shell assemblies would be stable in the dark and could be magnetically delivered to a desired location, whereupon the diamagnetic “cargo” could be released simply by exposure to visible light, which “strips off” the thin paramagnetic shell.

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Furthermore, the addition of Fe₃O₄·AC NPs to pre-formed SiO₂@Fe₃O₄ assemblies, followed by UV irradiation, resulted in the thickening of the Fe₃O₄ shell (multilayers comprising at least four layers of Fe₃O₄ NPs were observed), and, again, no self-aggregation of Fe₃O₄ NPs was observed.¹⁸ It should be emphasized, however, that the composition of the solvent mixture played an important role in determining the outcome of the light-induced self-assembly process: when the solvent was too apolar (e.g., a 9:1 toluene–tetrahydrofuran mixture), Fe₃O₄·AC NPs, in addition to occluding the surface of silica, formed aggregates on their own (Figure S4), whereas in a much more polar 4:1 toluene–ethanol mixture, iron oxide remained in a disaggregated state, even upon exposure to UV light (due to the polar solvent’s stabilizing effect on cis-AC; Figure S6). Only in mixtures of intermediate polarity, e.g., 19:1 toluene–ethanol, Fe₃O₄·AC selectively covered the surface of SiO₂ (Figure 2b, left; also Figure S5).

To demonstrate the generality of this approach, we attempted to encapsulate small (5 nm) gold NPs inside a monolayer of Fe₃O₄·AC. Toward this end, we functionalized Au NPs with an azobenzene-terminated thiol, AT (see SI, section 2). The surface concentration of AT on Au (~3.7 azobenzene units/nm²) was intentionally higher than that of AC of Fe₃O₄ (~2.0 azobenzenes/nm²), such that the energy of interaction between two NPs would be, E_{Au−Au} > E_{Au−Fe₃O₄} > E_{Fe₃O₄−Fe₃O₄}. The higher azobenzene surface coverage on Au also led to a faster aggregation of Au·AT as compared to Fe₃O₄·AC. As a consequence, UV irradiation of a mixture of these two types of particles resulted in selective formation of Au@Fe₃O₄ core−shell assemblies (Figure 2c).¹⁹ Again, no aggregates comprising only Fe₃O₄ could be seen,¹⁸ although such aggregates formed readily (Figure 2a) in the absence of Au·AT.

We further speculated that, since in the presence of external magnetic field the diamagnetic (=SiO₂; Au) core−paramagnetic shell assemblies interact with each other via multiple Fe₃O₄ NP dipole−dipole interactions (analogous to the interactions between all-Fe₃O₄ NP assemblies⁹), these structures could further assemble into one-dimensional aggregates. (It should be noted that the magnetic dipole interactions between assemblies comprising both diamagnetic and SPM components are maximized when the SPM components are located at their surfaces.) Indeed, application of low-intensity magnetic field to a solution of these assemblies results in the formation of linear aggregates, as shown in Figure 2b, right, and 2d. Notably, only a small, “catalytic” amount of ~11 nm Fe₃O₄ NPs (corresponding to a loose monolayer; cf. Figure 2b) is sufficient to induce further aggregation of these core−shell assemblies—for example, we have determined that assemblies comprising as little as 4% m/m of Fe₃O₄·AC NPs (96% being the Au·AT “cargo”) form larger, linear aggregates when external magnetic field is applied.

As these larger aggregates form, the magnetic force acting on them becomes large enough to overcome the Brownian force,²⁰,²¹ and the aggregates move toward the regions of maximum magnetic field, quickly concentrating near the magnets. The resulting precipitate remains attracted to a magnet and can readily be transported from one location to another in nearly quantitative yield with speeds of up to ~1 cm/s for up to 1 day in the dark, and for at least several days under UV illumination. At the same time, the formation of all of the aggregates described here is fully reversible due to their dynamic nature: both the core−shell assemblies and their linear

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**Figure 2.** (a) Light-controlled self-assembly of azobenzene-coated Fe₃O₄·AC nanoparticles. (b) UV light-induced occlusion of silica particles with Fe₃O₄·AC (left) and magnetic field-induced aggregation into linear structures (right). (c) Core−shell assemblies prepared by exposing a mixture of Au·AT and Fe₃O₄·AC NPs to UV light. (d) Linear structures obtained by exposing the core−shell assemblies to a magnetic field.
aggregates slowly disassemble in the dark due to thermal cis→trans azobenzene re-isomerization, which cancels out the attractive interactions holding NPs together within the aggregates. This re-isomerization reaction and the disassembly process can be greatly accelerated by exposing the system to visible light. Overall, the strategy described here—depicted in Figure 1a—enables us to (i) rapidly “trap” diamagnetic particles using UV light, (ii) guide them with a magnet, and (iii) release them at a desired location using visible light.

To demonstrate the proof-of-concept, we placed a UV-pre-exposed mixture comprising 88% (m/m) of gold nanoparticles (Au-AT) “cargo” and 12% Fe₃O₄·AC “carriers” at one end of a channel molded from PDMS (Figure 3a). The precipitate was then transported to the other end of the channel using a small, hand-held neodymium magnet which was moved manually underneath the channel. Subsequent exposure to intense (~1.0 mW/cm²) visible light induced quantitative disassembly of the solids and released the “cargo,” manifested by the appearance of an intense red color characteristic of gold nanoparticles. Finally, the core–shell assemblies could be re-formed and transported again upon re-exposure to UV light and the magnetic field. A movie of this procedure is available online; still shots are shown in Figure 3b.

In summary, we have demonstrated the capability to magnetically guide diamagnetic particles by reversibly coating them with a thin, dynamic paramagnetic “film”. This guiding is achieved by the simultaneous action of two external stimuli: light and a magnetic field. We envision that the methodology presented here could be extended to an “inverse” dynamic self-assembly system whereby the apolar Fe₃O₄·trans·AC NPs placed in polar solvents spontaneously aggregate due to the solvophobic effect but can be dynamically disassembled upon exposure to UV. This modified system could enable the opposite—that is, to occlude and magnetically manipulate apolar diamagnetic particles under thermally equilibrated conditions and to release them, at a desired location, with UV light. At the same time, the present study is also the first example wherein well-defined (core–shell) binary nanoparticle assemblies are generated in a single step using UV light. Current efforts are underway in our laboratories in order to extend this strategy to prepare even more complex (e.g., ternary) assemblies and to study the properties of these new materials.

**REFERENCES**


**ASSOCIATED CONTENT**

**Supporting Information**

Synthesis of nanoparticle ligands, preparation and functionalization of nanoparticles, additional nanoparticle self-assembly studies. This material is available free of charge via the Internet at http://pubs.acs.org.

**Web-Enhanced Feature**

A movie in .avi format demonstrating the assembly/disassembly process is available in the online versions.

**AUTHOR INFORMATION**

**Corresponding Author**

rafal.klajn@weizmann.ac.il

**Notes**

The authors declare no competing financial interest.

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In all experiments, we used a small NdFeB magnet (Stanford Magnets, Irvine, CA) held at a constant distance from the samples such that the particles were exposed to a magnetic field of \(\sim 0.1\) T.

This conclusion was reached by thorough inspection of the samples by means of SEM. We emphasize that whether or not Fe\(_3\)O\(_4\)·AC NPs self-aggregate depends on their concentrations relative to the concentrations of the more hydrophilic particles.

We verified by SEM that the process consists of two steps: first, Au·AT aggregates nearly quantitatively within \(\sim 30\) s of exposure to UV light, followed by a rapid (\(\sim 30-35\) s) adsorption of Fe\(_3\)O\(_4\)·AC on the Au aggregates. For comparison, pure Fe\(_3\)O\(_4\)·AC showed no signs of aggregation before 150 s of UV irradiation under the same experimental conditions.