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Decontamination of nanoparticles from aqueous samples using supramolecular gels†

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The growing use of nanomaterials and their associated risks necessitate the emergence of efficient decontamination systems. The main objective of this study is to develop a new prototype based on artificial supramolecular hydrogel capable of removing nanoparticle (NP) waste and nanomaterial by-products from aqueous suspensions. We demonstrate the high trapping efficacy of the low-molecular-weight gelators (LMWG) for very small particles (quantum dots (QDs), gold nanoparticles (AuNPs), TiO₂ nanoparticles (TiO₂-NPs), below 50 nm in diameter) from aqueous suspensions. The performance levels of removing nanoparticles from contaminated effluents could lead to a competitive alternative to filtration and dialysis devices.

Nanomaterials exhibit novel properties that offer a variety of new applications in different areas such as electronics,¹ biomedicine,^{2–4} pharmaceuticals, cosmetics, energy,⁵ environment,⁶ catalysts and materials. Owing to the potential benefits of nanotechnologies in various fields, there is a significant increase in the production and utilization of nanomaterials. The rapidly growing application of nano-products results in a potentially increased exposure of humans and environment to nanomaterials. The high reactivity of these nanomaterials may lead to adverse effects on biological systems, including human⁷ and ecological⁸ spheres. Consequently, the arrival on the market of nano-products raises crucial issues dealing with human/environment risk assessment and potentially associated contaminations.⁹ Keeping in mind the risk associated with nanomaterials, it is essential to develop efficient decontamination methods to remove or subtract

nano-particles (NPs) from contaminated wastes and environments including aqueous samples and surfaces. Surprisingly, despite the strong demand only a few types of decontamination devices (*i.e.* coagulation and flocculation of NPs by organic polymers,¹⁰ polyaluminium chloride¹¹) have been developed so far.¹²

In this context, we hypothesized that the use of the low-molecular-weight gelators (LMWGs) could serve as temporary scaffolds allowing nanoparticles to be trapped. These LMWGs offer several advantages to synthetic polymeric gels as they possess properties that are non-achievable by polymers.^{13–16} For example, water gelation by small molecules allows a rapid response of the gels to external stimuli, inherent gel-sol reversibility due to the non-covalent nature of the gel formation, and easy elimination after use thanks to the gel-to-sol transition. Our interest lies in using nucleoside-based amphiphiles capable of forming supramolecular systems. To this end, a large family of glycosylated-nucleoside-based amphiphiles featuring lipid (GNLs) have been synthesized and characterized.^{17–22} We discovered that these molecules form nanostructured hydrogels and organogels.^{17,18} In the present study, we have used a glycosylated-nucleoside fluorinated amphiphile (GNF), as a trapping scaffold to address the nano-waste issue.¹⁸ We demonstrate the ability of nanostructured supramolecular hydrogels, offered by the GNF, to entrap nanoparticles from aqueous samples (Fig. 1).

In order to evaluate the decontamination properties of a GNF, the accumulation of various NPs in the GNF hydrogel have been investigated. Initially, NPs derived from water soluble lipid-encapsulated QDs (previously synthesized in our lab), were suspended in water to prepare the contaminated samples.²³ In a typical experiment, the GNF hydrogel was prepared and incubated in the presence of the QD suspension. After allowing this mixture to settle down for 48 h in the dark, a gel along with the supernatant liquid phase was observed (Fig. 2A). The supernatant liquid was separated from the gel (Fig. 2B). As hypothesized, visualization under UV radiation ($\lambda_{\text{max}} = 312 \text{ nm}$) revealed that all the encapsulated QDs were

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