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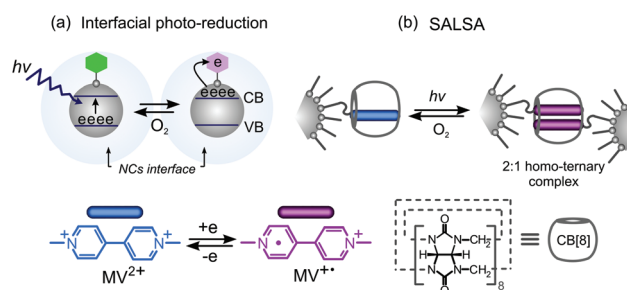
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Photo-induced interfacial electron transfer of ZnO nanocrystals to control supramolecular assembly in water†

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Herein, we show how the inherent light-induced redox properties of semiconducting nanocrystals (NCs) can be utilized for the photo-driven reversible modulation of dynamic supramolecular systems formed at their interfaces that, on their own, do not respond to light. This was achieved by the unprecedented combination of photoactive zinc oxide NCs (ZnO NCs) with a host–guest chemistry of cucurbit[8]uril (CB[8]) providing a route to the semiconductor-assisted light modulation of supramolecular assemblies (SALSA), here mediated by the photo-generation of viologen radical cations (MV^{•+}) at the NC corona and their further dimerization enhanced by CB[8] macrocycles. The reported SALSA strategy was successfully applied for light-controlled reversible assembly processes at NC interfaces enabling light-triggered release of guest molecules from surface confined discrete CB[8] host–guest complexes.

Photo-induced electron transfer (PET) plays a fundamental role in a range of chemical processes, which cover diverse biological systems, transformations of organic and inorganic species, as well as a variety of interfacial electron transfer processes.^{1–3} PET has found a wide range of applications in emerging technologies across the fields of (photo)catalysis, photovoltaics and electronics.^{1–3} Intensive development in these areas stems from the incorporation of a variety of nanoparticulate building blocks characterized by unusual physico-chemical properties and dynamic processes appearing at their highly extended surface areas. In particular, unique physico-chemical properties of semiconductor NCs that can be turned on by light, *e.g.* interfacial (solid/solution) redox processes (Scheme 1a),^{2,3} seem to be especially attractive as potential triggers to induce changes in a local chemical environment.



Scheme 1 (a) Photo-reduction of organic species at the interfaces of semiconducting NCs;³ (b) the exemplary processes to be attainable via the SALSA strategy.

While recent efforts to gain fundamental understanding of electron transfer at semiconducting interfaces have been reported,^{1–3} the implementation of semiconductor-assisted PET processes for the assembly/disassembly of molecular and supramolecular systems is immensely intriguing.

Within molecular recognition systems, one of the most promising self-assembly motifs in aqueous media relies on interactions between cucurbit[*n*]urils (CB[*n*]) and redox active derivatives of 4,4'-bipyridinium dications (viologens, MV²⁺).^{4–6} The dimerization of MV^{•+} radical cations inside the CB[8] molecular cavity as well as redox controlled stoichiometries of MV²⁺ based inclusion complexes make these systems a powerful trigger in supramolecular chemistry and dynamic nanosystems, *i.e.* molecular machines.^{4,5,7,8} However, while many chemical and electrochemical factors have been used to modulate the affinity of MV²⁺ derivatives for CB[*n*] molecular cavities,^{1,5,7} the use of light as an external stimulus to trigger changes in a completely remote and spatiotemporal manner^{9–11} is lacking for viologen-based systems.¹² Thus, semiconductor-assisted PET processes, which occur at NC interfaces, appear to be particularly attractive for the construction and modulation of dynamic supramolecular interfacial assemblies with CB[8] and MV²⁺.

To meet this challenge we present a new strategy for semiconductor-assisted light-modulation of supramolecular assem-

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blies, SALSA (Scheme 1b), which is based on the photo-generation of MV^{2+} radicals at the interfaces of novel zinc oxide (ZnO) NCs and their further dimerization enhanced by CB[8] macrocycles.⁷ The PET processes of SALSA were successfully applied to light-controlled assembly processes at the NC interfaces enabling light-triggered release of guest molecules from surface confined discrete CB[8] host-guest complexes. The reversibility of the reported interfacial processes was achieved both through classical chemical factors as well as by light and dioxygen. Additionally, the use of luminescent semiconductor NCs provides a striking visualization method to monitor the release and capture of NC surface-bound guest molecules.

Recently, we have provided novel water soluble ZnO nanocrystalline building blocks stabilized by using a carboxylate oligoethylene glycol shell, which exhibited ultra-long-lived photo-induced charge separation as well as a high propensity for further surface modification and were successfully applied in a hybrid nanosystem for efficient hydrogen evolution.¹³ We considered these ZnO NCs as ideal constructs for the incorporation of new chemical functionalities at their interfaces, allowing the interplay with CB[*n*] host-guest chemistry and thereby the supramolecular modulation of nanoparticulate semiconductors. Therefore, in the first step, we employed the reported synthetic approach to achieve an efficient ZnO NC surface grafting with MV^{2+} recognition sites using 1-methyl-4,4'-bipyridinium-dodecanoic acid bromide iodide, [MV^{2+} -C₁₁-COOH·Br[−]·I[−] (A); minor ligand] and 2,5,8,11-tetraoxatetradecan-14-oic acid, [MeO-dPEG(3)-COOH (B); major ligand]. This procedure afforded water-soluble ZnO@ MV^{2+} NCs (ZnO NCs 1) coated with a heterogeneous carboxylate stabilizing shell as depicted in Fig. 1a (for details see the ESI†).

ZnO NCs 1 exhibited a UV absorption band with a maximum ($\lambda_{\max}$) at 355 nm (Fig. S1†) and yellow luminescence at $\lambda_{\max}$ = 580 nm. The inorganic core of ZnO NCs 1 was roughly spherical and crystalline with a mean diameter of 7.1 ± 1.1 nm as indicated by HRTEM microscopy (6.0 ± 0.2 nm according to PXRD; Fig. S2–S4†). The average hydrodynamic diameter (D_h) was 9 ± 2 nm estimated using dynamic light

scattering (DLS; Fig. S5†). In the ¹H NMR spectrum of ZnO NCs 1 (D₂O) the signals of the MV^{2+} ligand at δ = 2.08 and δ = 1.45 ppm attributed to α -CH₂ and β -CH₂ groups, respectively, adjacent to the anchoring carboxylic functionality, are significantly shifted in comparison to the corresponding free ligand A (δ = 2.26 and δ = 1.49 ppm, respectively; Fig. S6†). This suggests that the MV^{2+} ligands are bound to Zn centers on the ZnO surface.¹⁴

For subsequent experiments on the modification of ZnO NCs 1 by surface confined supramolecular assemblies, it was crucial to demonstrate the accessibility of the interfacial MV^{2+} recognition sites of ZnO NCs 1 for CB[8] host-guest binding. In order to show that the nanocrystalline surfaces of ZnO NCs 1 can be decorated with discrete host-guest complexes, we employed naphthalene-terminated poly(ethylene glycol) chains [Np-PEG (2)] as representatives of well-established second guests for CB[8] chemistry.^{6a} The addition of CB[8] to an aqueous solution of ZnO NCs 1 and polymer 2 led to the appearance of new bands in the UV-Vis spectrum in the range of 400–600 nm, typical for charge transfer (CT) complexes (Fig. S7†).¹⁵ Moreover, the ¹H NMR spectrum in D₂O of ZnO NCs 1 and polymer 2 in the presence of CB[8] displayed characteristic upfield chemical shifts and the broadening of the viologen and naphthalene moieties' proton signals, indicating the formation of 1:1:1 hetero-ternary complexes within the ZnO@{ MV^{2+} ·Np-PEG·CB[8]} system (3) as shown in Fig. 2 and S8.†¹⁶ Notably, the upfield shift for the CB[8] protons in 3 occurred with signal broadening, in contrast to the analogous conjugates of CB[8] with ligand A and polymer 2, where the signals stemming from CB[8] remained sharp and well resolved (inset in Fig. 2).

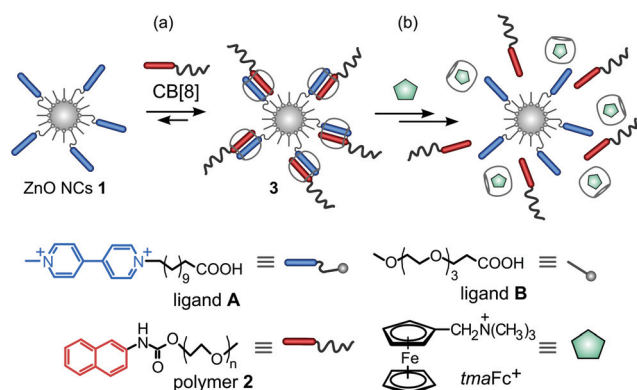


Fig. 1 Schematic representation of: (a) CB[8]-mediated interfacial functionalization of ZnO NCs 1 and (b) decomposition of the resulting interfacial supramolecular system 3 upon the addition of $tmaFc^+$. The counterions have been omitted for simplicity.

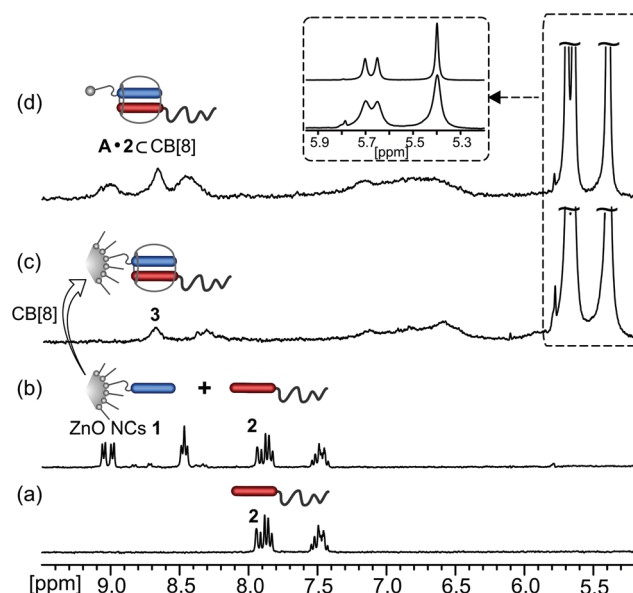


Fig. 2 ¹H NMR (300 MHz; D₂O; 298 K) spectra of: (a) polymer 2; (b) a mixture of ZnO NCs 1 and polymer 2 (MV^{2+} : Np moieties ratio 1 : 1); (c) interfacial hetero-ternary complexes of 3; and (d) the control involving an equimolar mixture of ligand A, polymer 2 and CB[8].



These observations nicely illustrate that the CB[8] host molecule was included in a larger assembly (thereby reducing its tumbling rate) as a result of the formation of the surface-localized hetero-ternary complexes of **3**.¹⁶ Notably, UV-Vis and photoluminescence (PL) measurements indicated that the photoluminescence properties of ZnO NCs **1** were preserved upon CB[8]-mediated interfacial functionalization with polymer **2** (Fig. S7 and S10†). Moreover, the resulting interfacial supramolecular system **3** can be disassembled through the use of a competitive guest, such as (ferrocenylmethyl)-trimethylammonium iodide (*tmaFc*+),¹⁷ with a concomitant release of polymer **2** and the regeneration of starting ZnO NCs **1** with photophysical properties intact, as indicated by ¹H NMR, UV-Vis and PL spectroscopy (Fig. S11–S13†).

The interplay between redox processes and molecular recognition in CB[8] chemistry has been widely studied and exploited in the design of redox-triggered dynamic supramolecular systems.^{5,7} With this in mind, we decided to investigate whether the interaction of luminescent ZnO NCs **1** with light will result in the formation of interfacial MV²⁺ radical cations,¹⁸ providing an alternative way to modulate supramolecular assemblies in water, namely SALSA. Photo-reduction of the MV²⁺ moieties on ZnO NCs **1** was studied by continuous UV-light ($\lambda = 366$ nm) irradiation of an aqueous solution of **1** in the absence of O₂. We observed a relatively fast (5 min) appearance of violet color, characteristic of MV²⁺ radical cations, that intensified upon further UV-light treatment. UV-Vis spectroscopy measurements revealed new bands at 400 nm and 600 nm indicating the formation of MV²⁺ monoradical cations (Fig. S14†).^{7,19} Subsequently, it was critical to show that photo-generated interfacial MV²⁺ species can be utilized for host-guest interactions laying the foundation for SALSA processes. CB[8] macrocycles were added to a water suspension of photo-reduced ZnO NCs **1**; this afforded the surface confined 2 : 1 inclusion complexes ZnO@{(MV²⁺)₂CB[8]} (**4**) as confirmed by the appearance of new UV-Vis absorption bands at $\lambda = 540$ and 960 nm (Fig. S14†).^{7,20} Strikingly, the photo-generation of MV²⁺ monoradical cations is accompanied by the simultaneous switching off of the ZnO luminescence (Fig. S15†).²⁰ Moreover, the formation of ZnO@MV²⁺ and subsequent dimerization within the CB[8] cavity can be reversed by the addition of O₂ to the solution.

We further envisioned that the SALSA approach could be applied for light-triggered switching between hetero- and homo-guest inclusion complexes leading to the controlled uptake and release of target molecules. To demonstrate the versatility of the SALSA approach towards light-induced redox-driven guest-exchange processes, a mixture of ZnO NCs **1** and the supramolecular system **3** with interfacial host-guest hetero ternary complexes (1 : 1; based on MV²⁺ content) in water was prepared (Fig. 3a and S19†). Continuous UV irradiation of the sample for 2 h led to the total switch off of its visible luminescence accompanied by the intensification of the magenta color and the gradual sedimentation of emerging dynamic assemblies **4** (Fig. 3b and c and S16†). The appearance of new UV-Vis absorption bands at $\lambda = 540$ and 960 nm suggested the

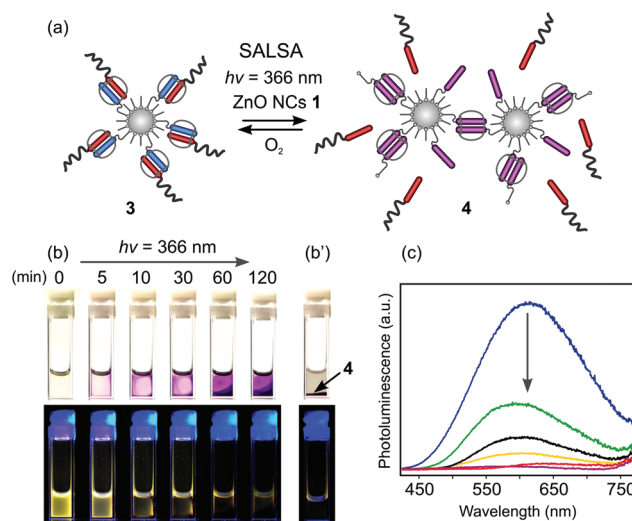


Fig. 3 (a) Schematic representation of the reversible light-triggered release of polymer **2** from the supramolecular system **3** leading to the formation of dynamic interfacial (MV²⁺)₂CB[8] inclusion complexes **4**; (b) the magenta coloration and PL quenching of the sample containing the mixture of **3** and ZnO NCs **1** upon irradiation with UV-light, (b') after 24 h the magenta precipitate consisting of large aggregates of **4** was collected; (c) PL spectra of the mixture of **3** and ZnO NCs **1** irradiated with UV-light.

formation of surface confined 2 : 1 homo-inclusion complexes of **4** with a subsequent release of polymer **2** (Fig. S17†).⁷ After 24 h, a magenta precipitate consisting of ZnO NCs **1** aggregates was collected (Fig. 3b'). In solution, after the redispersion, upon treatment in an ultrasonic bath, the resulting interparticulate assembled system **4** consists of two distinct populations of aggregates with hydrodynamic diameters of 80 ± 10 nm and 800 ± 100 nm as estimated by DLS measurements (Fig. S18†). Additionally, HRTEM measurements show that the larger assemblies of **4** form tight compact clusters, which are surrounded by open, elongated chain-like aggregates (Fig. 4 and S20†).

SALSA control over host-guest binding stoichiometry and reversibility of the processes as well as the light-induced release of polymer **2** were further investigated by NMR-tube experiments. In the ¹H NMR spectrum of a mixture of ZnO NCs **1** and the supramolecular system **3** (1 : 1; based on MV²⁺), the signals attributed to the MV²⁺ moieties of **1**, both free and bound within the CB[8] cavity, were significantly broadened (Fig. 5b and S21b). This can be explained by the complex dynamics involving two types of MV²⁺ species as well as the dynamic substitution of the Np-PEG polymer **2** between different MV²⁺CB[8] complexes present in system **3**. Upon further UV-light ($\lambda = 366$ nm; 5 min) irradiation of the sample in the absence of O₂ the ¹H NMR spectra showed a gradual disappearance of the signals attributed to MV²⁺ protons indicating the formation of paramagnetic MV²⁺ radical cations.²¹ Extended UV-light treatment ($\lambda = 366$ nm; 2 h) of the system resulted in total sample fluorescence quenching and led to the appearance of signals corresponding to the Np moieties of free



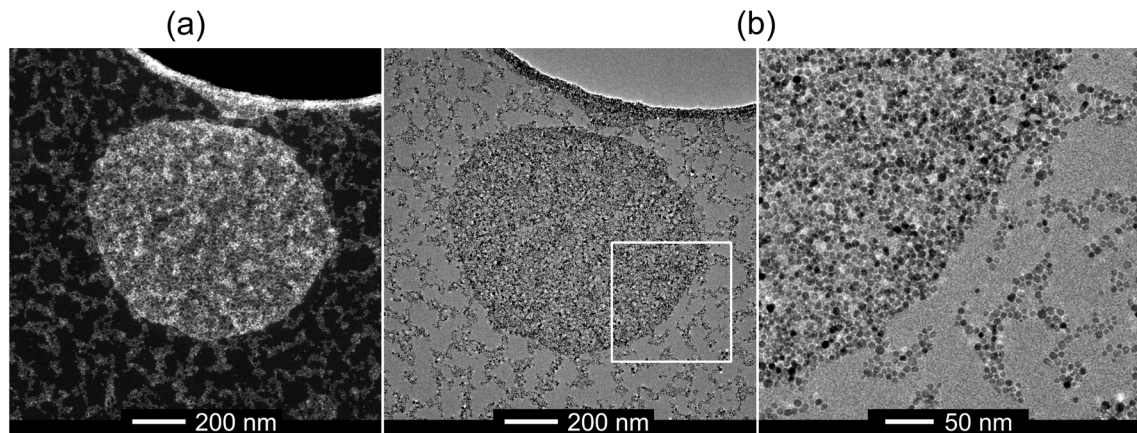


Fig. 4 The STEM (a) and HRTEM (b) images of the interparticulate system 4 in water.

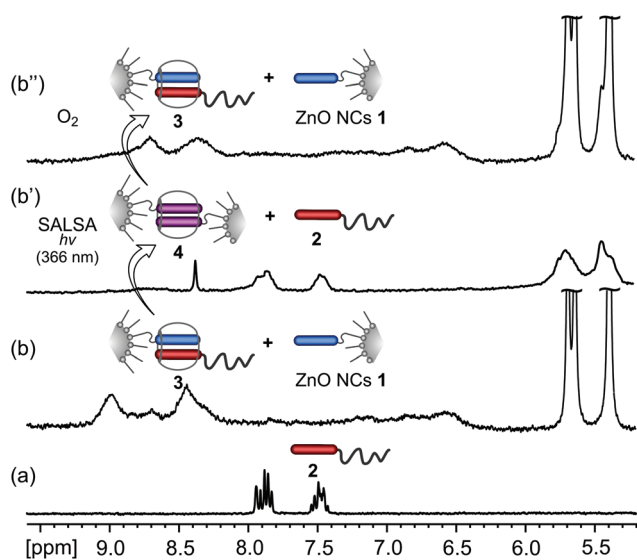


Fig. 5 ^1H NMR (300 MHz; D_2O ; 298 K) spectra of: (a) polymer 2; (b) a mixture of the supramolecular system 3 and ZnO NCs 1 (1 : 1 based on MV^{2+}), (b') after 2 h of UV irradiation in the absence of O_2 and (b'') upon further exposure to O_2 .

polymer 2 (Fig. 5b' and S21c'†). Additionally, the broadening of the ^1H NMR signals attributed to CB[8] protons was observed indicating the formation of 2 : 1 inclusion complexes 4 mediated by the dimerization of interfacial MV^{2+} radical cation species in the CB[8] molecular cavities. Exposing the resultant system 4 to O_2 led to the recovery of its luminescence properties together with the uptake of polymer 2 regenerating the starting surface-localized hetero-ternary complexes of 3, as indicated by ^1H NMR and PL (Fig. 5b'', S16 and S21c''†).²²

In conclusion, we have demonstrated, for the first time, that photoactive ZnO NCs can serve as photo-switchable nanoparticulate building blocks for the rich host-guest chemistry of CB[8]. Water-soluble MV^{2+} -functionalized ZnO NCs were successfully modified in a controllable manner through the use of CB[8] as a binding motif resulting in interfacial supra-

molecular nanosystems, whose assembly can be controlled either by classical chemical factors or through favorable interaction with UV light. In the systems presented, light is a clean, effective and remote stimulus that can readily modulate interfacial host-guest interactions, thus enabling the photo-controlled release of guest molecules as well as the light-induced assembly of more complex supramolecular systems. Through SALSA, the modification and construction of nanomaterial interfaces is driven by the photo-generation of MV^{2+} radical cations on the interface of ZnO NC coronas, followed by the formation of $\{(\text{MV}^{2+})_2\text{CB}[8]\}$ binding motifs. SALSA is entirely reversible and the target guest molecules can be further complexed by NCs upon exposure of the system to oxygen. Finally, it was shown that the luminescent semiconductor NCs provided an illuminating possibility to visually monitor the capture and release of guest molecules from surface-bound CB[8] based assemblies. We believe that the reported system paves the way for the development of new, colloidal, multifunctional semiconducting nanostructures for optoelectronics, photovoltaics and catalysis as well as unique photoluminescent tools for biological imaging and sensing in aqueous environments.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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- 22 We note that the interfacial photo-generation of MV⁺ radical species followed by SALSA processes are completely reversible towards O₂ treatment at every stage of the described *in situ* experiments. However, once **4** precipitates from solution, its further re-dispersion is difficult, which is more likely an effect of other forces emerging in the system during aggregate formation, *i.e.* cooperative weak interactions between stabilizing ligand chains of the adjacent NCs.

