



## Quantized Electronic Doping towards Atomically-Controlled ‘Charge Engineered’ Semiconductor Nanocrystals

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### Introduction

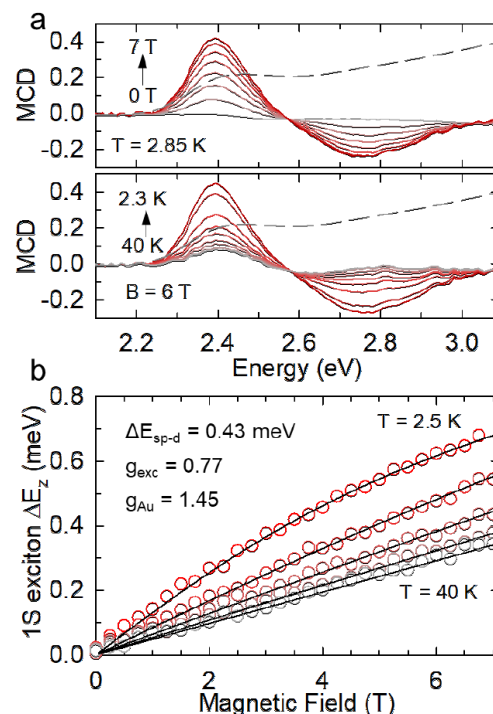
‘Charge engineering’ of semiconductor nanocrystals (NCs) through so-called electronic impurity doping is a long-lasting challenge in colloidal chemistry and holds promise for ground-breaking advancements in many optoelectronic, photonic and spin-based nanotechnologies. To date, our knowledge is limited to a few paradigmatic studies on a small number of model compounds and doping conditions, with important electronic dopants still unexplored in nanoscale systems. Equally importantly, fine tuning of charge engineered NCs is hampered by the statistical limitations of traditional approaches. The resulting intrinsic doping inhomogeneity restricts fundamental studies to statistically averaged behaviours and complicates the realization of advanced device concepts based on their advantageous functionalities. Here we aim to address these issues by realizing the first example of II-VI NCs electronically doped with an exact number of heterovalent gold atoms, a known *p*-type acceptor impurity in bulk chalcogenides. Single-dopant accuracy across entire NC ensembles is obtained through a novel non-injection synthesis employing ligand-exchanged gold clusters as ‘quantized’ dopant sources to seed the nucleation of CdSe NCs in organic media. Structural, spectroscopic and magneto-optical investigations trace a comprehensive picture of the physical processes resulting from the exact doping level of the NCs. Gold atoms, doped here for the first time into II-VI NCs, are found to incorporate as nonmagnetic  $\text{Au}^+$  species activating intense size-tuneable intragap photoluminescence and artificially offsetting the hole occupancy of valence band states. Fundamentally, the transient conversion of  $\text{Au}^+$  to paramagnetic  $\text{Au}^{2+}$  ( $5d^9$  configuration) under optical excitation results in strong photoinduced magnetism and diluted magnetic semiconductor behaviour revealing the contribution of individual paramagnetic impurities to the macroscopic magnetism of the NCs. Altogether, our results demonstrate a new chemical approach towards NCs with physical functionalities tailored to the single impurity level and offer a versatile platform for future investigations and device exploitation of individual and collective impurity processes in quantum confined structures.

### Results and Discussion

We make significant progress by realizing, for the first time, CdSe NCs electronically doped with gold atoms through a new quantized-doping route using magic-sized gold clusters in organic media as nucleation seeds. The obtained Au:CdSe NCs are the first example of II-VI NCs incorporating gold dopants produced by any known route. Structural and analytical characterization, combined with spectroscopic measurements and chemical etching experiments, indicate that the clusters consist of seven gold atoms and that they seed the nucleation of CdSe NC containing an equivalent number of gold impurities preferentially located in the particle core. magnetic circular dichroism (MCD) measurements reveal that the transient change of the oxidation state from  $\text{Au}^+$  (with nonmagnetic  $5d^{10}$  electronic configuration) to  $\text{Au}^{2+}$  (with paramagnetic  $5d^9$  electronic configuration) during the multistep exciton recombination process results in strong photo-induced paramagnetism. Fundamentally, such a photo-triggered diluted magnetic semiconductor (DMS) behaviour follows a step-like trend with the illumination intensity revealing the contribution of individual paramagnetic impurities to the macroscopic magnetism of the NCs. The process is formalized through a phenomenological dynamic model, indicating that the maximum paramagnetic response is obtained when all gold impurities in the NCs are photo-converted from their native non-magnetic  $\text{Au}^+$  state into the paramagnetic  $\text{Au}^{2+}$ .

### References

[1] Capitani, C. *et al.*, *Nano Letters*, *accepted and in press* (2019).



**Figure: Magnetic properties of Au:CdSe NCs.** (a) MCD spectra of Au:CdSe NCs, from which the Zeeman splitting of the 1S exciton can be inferred. Top panel: MCD spectra are shown at 2.85 K in different magnetic fields from 0 to 7 T. Bottom panel: MCD spectra at 6 T, at temperatures from 40 to 2.3 K. The linear absorption spectrum is reported as a dashed grey line in a and b. (b) Enhanced Zeeman splitting of the 1S band-edge exciton versus magnetic field, at various temperatures. The high field saturation and strong temperature dependence indicate the existence of *sp*-*d* exchange coupling between the conduction/valence bands of the semiconductor host and paramagnetic dopants in the NCs. This species is consistent with  $\text{Au}^{2+}$  dopants excited by fast localization (capture) of the VB hole. Lines are fits to a Brillouin function using a single set of parameters.