A New Twist in the World of Magic-Sized Clusters

The origin of the giant magnetic moments in Mn^{2+}-doped CdSe nanoclusters was elucidated through synchrotron X-ray diffraction and EXAFS spectroscopy.

In the evolving field of nanoscience, "magic-sized clusters" (MSC) occupy a fascinating niche between molecules and bulk solids. These ultra-small aggregates, typically less than two nanometers in diameter, exhibit discrete energy levels and unique quantum properties that cannot be explained by classical semiconductor physics. Among them, $(CdSe)_{13}$ nanoclusters have become a model system for understanding how atomic-scale surface chemistry dictates optoelectronic behavior. A collaborative team led by Elise Yu-Tzu Li and Yi-Hsin Liu from National Taiwan Normal University uncovered an unexpected phenomenon: Mn^{2+}-doped $(CdSe)_{13}$ nanoclusters exhibit an extraordinary magnetic moment exceeding 40 μB at 180 K, which is nearly an order of magnitude larger than expected for such diluted magnetic systems.[1]

One of the most challenging questions in nanotechnology is how dopant atoms integrate into nanoclusters. In bulk or even quantum-dot materials, doping mechanisms can often be modeled statistically. However, in MSCs, where each cluster contains only a few dozen atoms, every dopant counts. The local environment of a single Mn^{2+} ion can drastically alter the entire system's electronic and magnetic responses depending on its coordination number, bonding partners, and surrounding ligands. Synchrotron-based extended X-ray absorption fine structure (EXAFS) at the Cd K-edge and Mn K-edge provided crucial insights. By analyzing the oscillations in X-ray absorption beyond the edge, EXAFS allowed the researchers to quantitatively determine interatomic distances, coordination numbers, and the presence of specific bonding shells (Cd–Se, Cd–N, Cd–O, Mn–O, and Mn–N) with sub-angstrom precision. The EXAFS measurements performed at **TLS 01C2** and **TLS 17C1** revealed that clusters synthesized from two different selenium precursors exhibited strikingly different coordination environments, as shown in **Fig. 1**. In Se–urea-derived clusters, Cd atoms were coordinated mainly by Se and N atoms (Cd–Se ≈ 2.62 Å, Cd–N ≈ 2.36 Å). By contrast, Se–$NaBH_4$-derived clusters required an additional Cd–O shell at 2.35 Å to fit the EXAFS data accurately. This subtle but crucial difference signaled that oxygen atoms from acetate ligands were directly bonded to Cd, forming mixed Cd–O and Cd–N coordination networks. X-ray diffraction (XRD) measurements performed at **TPS 09A** and **TLS 01C1** further reveal that Mn^{2+} doping is markedly more efficient in the Se–$NaBH_4$–derived $(CdSe)_{13}$ nanoclusters, which contain Cd–O and Mn–O coordination, than in those prepared from Se–urea, where Cd–O bonding is absent. The Se–$NaBH_4$ route yields dopant concentrations nearly an order of magnitude higher, demonstrating a substantially enhanced incorporation of Mn^{2+}. Such bonding motifs could not be inferred from optical or NMR data alone; they emerged clearly only through synchrotron EXAFS analysis. The presence of Cd–O bonding turned out to be the missing piece of the puzzle. In Se–$NaBH_4$-derived clusters, acetate ligands introduced oxygen atoms capable of forming strong Cd–O and Mn–O bonds, thus stabilizing the tetrahedral Mn^{2+} coordination within the cluster core. This chemical environment dramatically enhanced the dopant incorporation efficiency, raising Mn^{2+} substitution levels to over 12%, compared to just 1.3% in Se–urea-derived samples that lacked Cd–O interactions.

With the structure clarified, the researchers could now interpret the unexpected magnetic and optical phenomena. Mn^{2+}-doped $(CdSe)_{13}$ clusters synthesized *via* the Se–$NaBH_4$ route exhibited a fivefold increase in photoluminescence (PL) intensity, along with prolonged emission lifetimes and field-dependent blue shifts in PL spectra under magnetic fields up to 0.5 T. These magneto-optical effects originated from spin–spin coupling between Mn^{2+} ions and photoexcited carriers within the quantum-

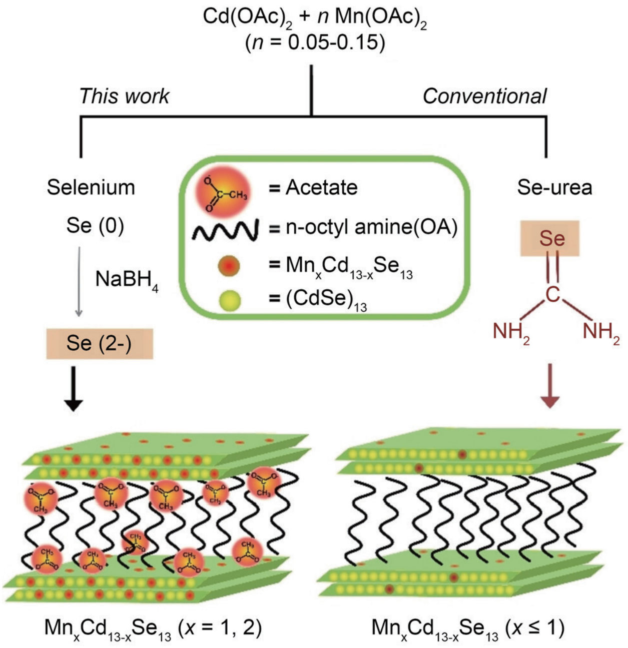

Fig. 1: Schematic representation of synthetic processes with the two selenium-based precursors, Se-$NaBH_4$ and Se-urea, employed in this study. [Reproduced from Ref. 1]

confined clusters. Density functional theory calculations revealed that transitions between ferromagnetic and antiferromagnetic states correspond to energies around 1.9–2.0 eV, which match the experimental PL emission near 600 nm. Interestingly, at low dopant levels (< 1%), the PL blue-shifted under magnetic fields, implying magnetic-field-induced destabilization of spin-coupled excitonic recombination. At higher dopant concentrations (~6–7%), excessive spin–spin coupling quenched PL, owing to nonradiative recombination *via* dark exciton states. These results paint a complex but coherent picture: surface ligand chemistry dictates local coordination of the dopant, which in turn governs spin exchange, exciton dynamics, and magneto-optical behavior.

Magnetic measurements performed using a superconducting quantum interference device magnetometer revealed that Mn^{2+}-doped $(CdSe)_{13}$ nanoclusters display paramagnetism with a hint of ferromagnetic hysteresis at 2 K. More astonishingly, the effective magnetic moment reached over 40 μB per cluster at 180 K, vastly exceeding the theoretical spin-only contribution (5.5 μB) of isolated Mn^{2+} ions. The researchers proposed a mechanism involving charge redistribution and spin fluctuations at the Se-rich cluster surfaces. Mulliken population analyses indicated electron transfer from the amine ligands to Se atoms through Cd, creating localized charge imbalances and unpaired spins. These surface states could couple with the Mn^{2+} spins to form magnetic polarons, where charge carriers and localized spins align collectively under internal magnetic fields up to 30 T. Such dynamic spin alignment and electron precession within the clusters explain the enhanced magnetic susceptibility and the emergence of giant magnetic moments. The interplay of ligand chemistry, spin–orbit coupling, and magnetic polaron formation defines a new paradigm for magnetically active nanomaterials that function even at relatively high temperatures. (Reported by Yu-Jong Wu)

This report features the work of Elise Yu-Tzu Li, Yi-Hsin Liu and their collaborators published in Angew. Chem. Int. Ed. ***64****, e202420257 (2025).*

TPS 09A Temporally Coherent X-ray Diffraction
TLS 01C2 X-ray Powder Diffraction

- XRD
- Materials science

TLS 01C1 EXAFS
TLS 17C1 EXAFS

- EXAFS
- Materials sciences

Reference

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Atomic-Level Recycling of a Controversial Herbicide

Through combined experimental and synchrotron analyses, this work reveals the mechanism by which MOF-808 degrades glyphosate and converts it into non-toxic species.

Glyphosate (N-phosphonomethyl glycine; GPh), one of the most widely used herbicides globally, has faced increasing scrutiny for its persistence in ecosystems and potential health impacts. Traditional remediation strategies, such as microbial degradation or oxidation, often transform GPh into equally problematic byproducts like aminomethyl phosphonic acid (AMPA) or phosphoric acid, both of which can be toxic or contribute to eutrophication. The pressing challenge has been to develop a catalytic process that decomposes GPh into truly benign products under mild, environmentally friendly conditions.

A recent study by a collaborative team from the University of New South Wales (Australia), Universidad Nacional de Córdoba (Argentina), Colorado School of Mines (USA), and the NSRRC discovered that Zr-based metal–organic framework nanocrystals (nMOF-808) can completely degrade GPh at room temperature, producing N-formyl glycine and hydroxymethyl phosphonate with very low toxicity.[1] Most remarkably, the reaction proceeds without external energy input and leaves no harmful residues in solution, as the phosphonate byproduct remains bound to the catalyst framework.

MOF-808 is a zirconium-based porous framework consisting of $Zr_6O_4(OH)_4$ clusters connected by benzene-1,3,5-tricarboxylate linkers. Its high stability in water and tunable coordination environment make it ideal for catalytic reactions involving polar molecules. The research team synthesized MOF-808 in two crystal sizes to examine the role of surface defects