Investigation of the indolinyl-amide scope revealed that a diversity of functionality, including an alkylchloride-containing amide (**6**), was tolerated (Figure 1C). Particularly noteworthy is the tolerance of acidic functionality, such as terminal alkyne (**7**), ketone (**8**), and ester (**9**) functional groups, which in the sphere of α-functionalization transformations often react competitively with amides. As an additional benefit of the Maulide amide α-arylation, acyl indolines are important building blocks for further transformation: the authors demonstrated their synthetic versatility via cleavage of the amide to a carboxylic acid or aromatization to the indole oxidation state with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). These acyl indoles can then undergo catalytic reduction of the carbonyl to form an *N*-alkyl indole or transformation to a benzoxazinone or a quinazoline by ozonolysis and condensation.

In summary, Maulide and co-workers utilized trifluoromethanesulfonic anhydride, 2-I-pyridine, and pyridine *N*-oxide to transform indolinyl amides directly to α-oxytriflates with high functional-group tolerance. The authors have shown the utility of these reactive intermediates through conversion to α-bromo amides and enantioenriched α-aryl amides.

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Preview

It's a Trap! Fused Quantum Dots Are Undesired Defects in Thin-Film Solar Cells

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Electronic traps are the primary factor stifling the performance of quantum-dot (QD) solar cells to nearly half their theoretical potential. Yet, the exact origin of these traps remains largely unknown, making it difficult to address the problem. In the inaugural issue of *Matter*, Gilmore et al. employ advanced transient spectroscopy to reveal that QD dimerization can be as detrimental as unpassivated surface states in QD films.

Since their inception 30 years ago,[1,2] colloidal quantum dots (QDs) (also called semiconductor nanocrystals) have been touted as the next big thing in the world of optoelectronics.[3] Successes in the basic research of material synthesis[4] have quickly translated into utilizing the strength of QDs in multiple applications, including high-color-purity displays, lasers,[5] and low-cost solar cells.[3]

The superior light-emission performance of these nanomaterials over that of their traditional bulk counterparts, such as cadmium mercury telluride (CdHgTe) or gallium arsenide (GaAs), stems from their ability to evoke the quantum confinement effect. As suggested by the name, confining the excitons, quasiparticles made up of photoexcited electrons and holes, to a small localized region (typically a few

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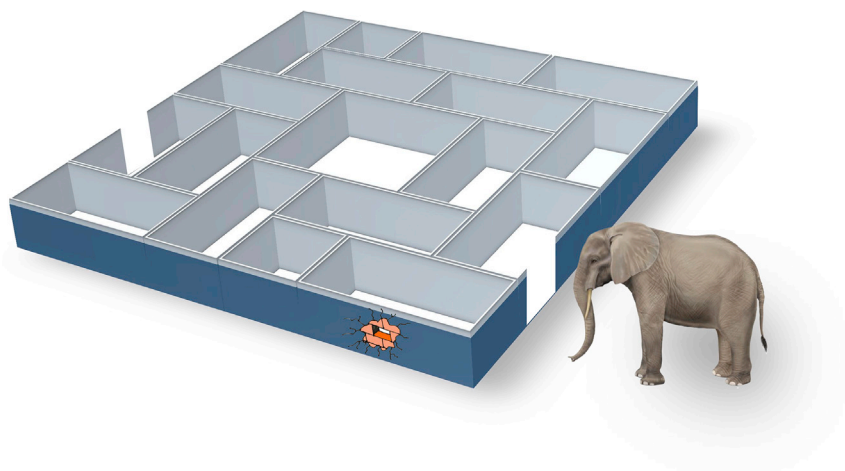
Figure 1. The Optoelectronic Performance of QD Solids Is Dependent on the Movement of Excitons (Elephant) in a Film Made of Nanocrystals (Rooms)

The poor construction of these rooms can lead to the formation of holes in the wall (poor nanocrystal surface passivation) and even the collapse of the rooms into a bigger combined room (a dimer), as shown in the center of the figure. These features grant the elephant (exciton) more space to relax and thereby serve as trap states, which facilitate irreversible recombination of the exciton, hindering the device performance.

nanometers) leads to quantum effects that produce several desirable outcomes. One such important outcome is that the electron and hole occupy the same region of space and are ready to recombine and emit a photon sooner than other potential pathways to lose the excited electron and/or hole.

Another positive effect of quantum confinement is band-gap tuning. Imagine trying to squeeze an elephant (exciton) into a small room (nanocrystal): the smaller the room, the greater the stress on the elephant (Figure 1). As a result, for an exciton, the energy difference between the electron and hole energy levels, called the optical band gap, becomes dependent on the size of the QD.[1,2] This is important because the bandgap is responsible for the color of light that a QD can absorb or emit; blue-emitting materials have larger band gaps than red-emitting ones. Therefore, simply changing the size of the QD allows one to tune the emission color over a broad range by using the same material composition as opposed to

needing to find a new material or composition for each required emission color.

In addition to quantum confinement effects, colloidal QDs also offer solution-based processing, reducing the cost of material synthesis and device fabrication.[3]

Unfortunately, quantum confinement serves as a double-edged sword. Smaller rooms (nanocrystals) mean that there are more walls (nanocrystal surfaces) to maintain. The performance of QD devices is thus plagued by the occurrence of sub-band-gap states that act as "traps" for the excitons in the device. Holding to the elephant analogy, these trap states can be thought of as damage or even holes in the walls, which make the room slightly more comfortable for the elephant by providing extra space for the elephant's tail or trunk (Figure 1). Therefore, such trap states act as local energy minima and hence draw the exciton, delaying it on its path to the extracting electrodes and increasing the chances of electron-hole recombination, i.e., their

irreversible loss, which lowers the device efficiency.

Current major efforts in improving QD device performance have mostly focused on repairing the walls (passivating the nanocrystal surfaces). In this approach, the trap states are considered a manifestation of surface imperfections and thus are attempted to be repaired by switching to new ligands or changing the ligand density,[6] sort of like adding new cement and bricks to the wall of the room. Although effective, this approach does not appear to completely resolve the issue, indicating that other fundamental mechanisms are at play, demanding further investigation.

In the inaugural issue of *Matter*, Gilmore et al.[7] present a radically new interpretation of the origin of trap states. The authors use transient absorption spectroscopy to describe the manifestation of trap states generated via the epitaxial dimerization of lead sulfide (PbS) QDs. Under the elephant analogy, this new class of traps can be thought of as a fusion of two rooms (nanocrystals), providing lots more space for the elephant (exciton) to dwell in this comfortable room for longer periods of time (Figure 1), thus increasing its chances of never reaching the exit (recombining).

According to this model, the poor construction of the walls for two adjacent rooms can lead to the collapse of the walls and therefore a fusion of the two rooms into one larger room rather than the formation of a hole in the wall. In other words, the poor surface passivation thought to traditionally induce surface defects might simply be facilitating the dimerization of nanocrystals, leading to electronic coupling and hence the formation of the observed trap states. This hypothesis helps to reconcile literature observations: for example, cadmium

sulfide (CdS) shells are found to reduce the trap-state density and improve the performance of PbS QDs.[8] According to this new model, the large CdS shells reinforce the walls and serve to prevent dimerization of the PbS QDs in addition to passivating surface defects.

The authors also demonstrate that this new class of optically active trap states can undergo de-trapping of the sequestered excitons upon exposure to the appropriate energy. This de-trapping process was observed to occur via two different mechanisms. A fast light-intensity-dependent de-trapping mechanism was observed to occur on a timescale of about 35 ps. The kinetic behavior of such temperature-independent de-trapping was found to be reminiscent of Auger-assisted recombination (recombination involving three or more charge carriers).[5,9] That is to say, the increase in light intensity was thought to generate two excitons per trap, the recombination of one of which could then supply the energy for the escape of the other. In other words, the elephant is pushed back to the smaller room by another elephant in the same room, even if this room is bigger. The second, slower de-trapping mechanism was found to be independent of the light intensity and dependent on the temperature. This thermally assisted process occurred at a timescale of about 500 ps and can essentially be thought of as the elephant having some rest

from lingering in the bigger room and deciding to move to the smaller room on its own accord.

The systematic study showed that even relatively scarce dimers (1 in 2,500 QDs) are sufficient to negatively affect the performance of the material. Therefore, even accidental formation of an odd dimer during the synthesis of QDs can turn out to be detrimental for the performance of the material. In fact, the authors found that these trap states manifested themselves even prior to the ligand exchange process, traditionally thought to be the key source of nanocrystal surface damage and deterioration of surface passivation. The density of dimers was found to further increase after the ligand exchange process, supporting the notion that inadequate surface passivation generated by the ligand exchange process can further facilitate dimerization as well.

This enlightening work sheds light on the importance of developing synthetic methods and ligand exchange procedures that eliminate the occurrence of dimers during QD synthesis, which will provide much-needed insight and enable further progress in the development of trap-free high-performance QD materials. That being said, one must not discredit the occurrence of surface defects as another important contributor to trap states and should aim to synthesize QD materials free of both surface defects and dimers in order to

truly minimize or eliminate the trap states.

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