

PHOTOLUMINESCENCE

Nanocrystals play hot potato

“Generating delayed photoluminescence in nanocrystals may be valuable in solid-state lighting and background-free time-resolved imaging”

Semiconductor nanocrystals not only absorb and emit light at well-defined energies, but do so in high quantum yields that makes them desirable for optoelectronic or solar energy applications. Devices based on these valuable materials rely on energy transfer between nanocrystals and other components, such as luminescent molecules. For example, a photo-excited polycyclic aromatic hydrocarbon, such as tetracene, can transfer a triplet exciton to a PbS nanoparticle. Energy can also flow the other way — exciting a CdSe nanocrystal transfers a triplet exciton to the appended pyrene or anthracene groups. These studies notwithstanding, there is much to learn about how hybrid materials absorb, juggle and release energy. Addressing this in *Nature Chemistry*, Felix Castellano and colleagues describe photochemistry of pyrene-decorated CdSe nanocrystals of varying sizes, and uncover an excited-state equilibrium between the nanocrystals and the pyrenes.

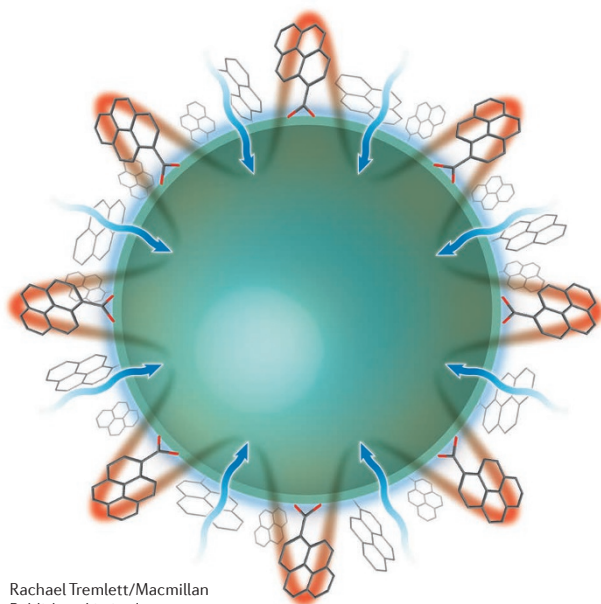
Exciting a semiconductor often yields a triplet exciton, which can be transferred to a nearby chromophore through a Dexter process, whereby an electron in the conduction band hops to the chromophore's LUMO, and an electron in the chromophore's HOMO hops to the valence band. This exchange-induced energy transfer is reversible as the exciton can be transferred back and forth, provided the gaps between the respective frontier orbitals or bands are comparable. Castellano's team further developed the pyrene–CdSe system by preparing differently sized monodisperse CdSe nanocrystals and treating them with 1-pyrenecarboxylic acid. Irradiating a sample containing small (2.4 nm) nanocrystals affords a high-energy first exciton ($\lambda = 488$ nm), whose transfer to the pyrene groups is so far downhill (0.51 eV) that the reverse transfer is not observed. Indeed, the pyrenes behave as they would in solution, either phosphorescing over the course of 50 ms or transferring energy to molecules in a process applicable to catalysis or photodynamic therapy.

The team's key finding came when they used larger nanocrystals (4.6 nm), the first exciton energy of which ($\lambda = 600$ nm) exceeds that of the pyrenes by only 0.07 eV. The excited-state lifetime of the appended pyrenes decreased, and it became clear that, with a little thermal energy, “the pyrene chromophores were repopulating the CdSe excited state with kinetics that depended on the temperature and energy gap between the CdSe and pyrene excited states”, explains Castellano. His hunch was confirmed when studying the pyrene–CdSe system by time-resolved photoluminescence, which revealed that the characteristic CdSe emission was delayed and had a lifetime

matching that determined from the pyrene transient absorption kinetics at room temperature. Thus, systems with larger CdSe nanocrystals are in a fine exciton-juggling equilibrium, emitting light that is characteristic of CdSe but with a time delay.

One might wonder why Castellano and co-workers go to the lengths of preparing functionalized nanocrystals when certain transition metal centres, which have similar electronic structures and narrow optical bands, are also triplet sensitizers. The advantages of nanocrystals lie in their superior photophysics — they have smaller singlet–triplet gaps and are more efficient absorbers and emitters. Nevertheless, the pyrene-functionalized 4.6 nm CdSe nanocrystals exhibit luminescence quantum efficiencies of only 13%. Despite the unfunctionalized CdSe crystals being nearly defect free, once covered with carboxylate ligands, the oscillator strength of the crystal decreases. Thus, before functionalizing the nanocrystal, the team is considering protecting it with a coating thick enough to shield it but thin enough to allow Dexter energy transfer. Higher quantum efficiencies would also make it easier to characterize the triplets using magnetic resonance spectroscopy. Once optimized, thermally activated delayed photoluminescence abounds with applications. “Generating delayed photoluminescence in nanocrystals may be valuable in solid-state lighting and background-free time-resolved imaging,” predicts Castellano.

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