

REVIEW

# Controlling the spectroscopic properties of quantum dots via energy transfer and charge transfer interactions: Concepts and applications



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**Summary** Luminescent quantum dots (QDs) exhibit size- and composition-tunable photophysical properties that are not shared by their bulk parent materials or at the molecular scale. They have attracted considerable interest further motivated by several potential applications. A particular interest has centered on exploiting the ability of QDs to engage in both fluorescence resonance energy transfer (FRET) and charge transfer (CT) interactions with proximal fluorophores and redox active molecules/complexes, respectively. In this review, we highlight how the QD's optical and spectroscopic properties can be controlled via FRET and/or CT interactions. We first show that QDs provide a unique platform for controlling both modes of interactions. We then provide representative examples in biology which include developing sensing assemblies that report on properties such as pH changes, enzymatic activity and ligand–receptor binding. Implications in electronic devices focus on light emitting devices and photovoltaic cells, where we discuss device architecture, control over carrier injection, carrier mobility, and exciton recombination.

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## Introduction

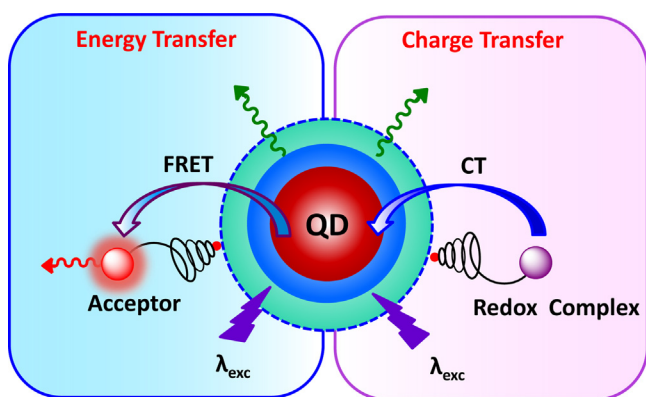
Colloidal nanoparticles including semiconductor nanocrystals, metal and metal oxide nanoparticles have generated tremendous interests in the past two decades, due to some of their unique fundamental properties and the potential they offer for a variety of applications [1–20]. These

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**Figure 1** Schematic diagrams showing QD-based energy transfer (left) and charge transfer (right) interactions.

materials possess several photophysical properties that can be tuned by size and/or composition [1,2,8,9]. Luminescent semiconductor nanocrystals (quantum dots, QDs), for example, exhibit remarkable photo stability, broad absorption profiles with large one- and two-photon cross-section, narrow tunable emission spectra and high quantum yield [1,2,21–28]. This makes them potentially useful in optical and electronic devices, such as light emitting diodes and photovoltaic devices [29–35]. These applications have been supplemented by a large potential for use as in vivo and in vitro probes in a variety of biomedical applications [3,5–7,14,16–19,36].

One very important feature of colloidal nanocrystals is their large surface-to-volume ratio, resulting in a sizable fraction of their atoms arrayed on their surfaces. As such their optical and electronic properties are highly sensitive to the nature of the surface ligands, namely, coordination interactions, lateral extension and electronic properties. The photophysical properties of the nanocrystals can also be strongly influenced by interactions with proximal redox complexes and dyes via charge transfer and/or energy transfer. This offers additional means to modulate the QD emission and carrier dynamics [20,37–41].

Fluorescence resonance energy transfer (FRET) and charge transfer (CT) interactions are two photophysical processes that are known to alter the absorption and emission properties of conventional fluorophores and they can equally affect the properties of QDs (Fig. 1). Such interactions provide a means to externally control the optical and spectroscopic properties of QDs. They have been exploited by various research groups to develop sensing platforms based on QDs that can allow the detection of target analytes, probing pH changes and accounting for ligand–receptor binding [5,16,19,20,36,42–44]. Similarly, the optical and spectroscopic properties exhibited by QDs have motivated their effective use for deep tissue imaging and as drug delivery vehicles [6,16–19,36,45–47].

There are a few parameters that can affect and control FRET and CT interactions: (1) size and shape of the nanocrystal, (2) spectral overlap between donor emission and acceptor absorption profiles, (3) the separation distance, and (4) the number of acceptors and their orientations around a single QD; the latter is particularly important for QDs because of their nanoscale dimensions.

Such interactions can also be probed using relatively simple experimental techniques, such as steady-state and time-resolved fluorescence spectroscopy [48–52]. Transient absorption (TA) and transient fluorescence spectroscopy techniques can also be used to assess electron and/or hole transfer and dynamics in these complexes [40,53–55].

In this report, we have assembled a short overview of ideas and rationales developed over the past decade for modulating the photophysical and electronic properties of quantum dots. We start by describing the fundamental concepts governing energy and charge transfer interactions. We then describe a few examples showing exquisite control over the QD fluorescence quenching using either FRET and/or CT interactions, along with implementations in biological sensing. A few examples showing the importance of charge transfer interactions between QDs and other nanomaterials with implications in light emitting devices and solar cells will also be discussed.

## Resonance energy transfer and charge transfer interactions: Background

### FRET interactions

FRET is a process that involves the non-radiative transfer of excitation energy from a photoexcited dye (donor, *D*) to a nearby ground state dye (acceptor, *A*). Such interactions manifest in a loss of the donor emission coupled with enhanced acceptor fluorescence; if the acceptor is non-fluorescent, only quenching of the donor emission is observed following interactions. FRET interactions also manifest in shortening of the donor fluorescence lifetime. Within the Förster formalism, FRET results from coupling between the donor and acceptor dipoles (developed by Förster), and as such it strongly depends on the center-to-center separation distance [39,56]. To produce efficient FRET interactions, a few key criteria must be satisfied, including: (a) close proximity between a donor and an acceptor (i.e., short separation distance, *r*, due to the nature of the dipole–dipole coupling); (b) finite (nonzero) overlap between the donor emission and acceptor absorption spectra. In addition to those two requirements, FRET also depends on the orientation between donor and acceptor dipoles, with maximum coupling measured for parallel dipoles, but no interactions measured for orthogonal dipoles.

The rate of energy transfer between a donor and an acceptor separated by a center-to-center distance *r*, is defined as [39,56]:

$$k_{\text{FRET}} = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6 \quad (1)$$

where  $\tau_D$  designates the average exciton lifetime measured for the donor in the absence of an acceptor, and the Förster radius,  $R_0$ , corresponding to a separation distance at which the FRET rate is equal to the natural decay rate,  $1/\tau_D$ ;  $R_0$  is expressed as:

$$R_0 = \left( \frac{9000 \times \ln(10) \times k_p^2 Q_D I}{128\pi^5 n_D^4 N_A} \right)^{1/6} \quad (2)$$

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