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Photoswitchable quantum dots by controlling the photoinduced electron transfers[†]

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We report photoluminescence (PL) modulation of quantum dots (QDs) by photoinduced electron transfers from acridine-1,8-dione derivative surface ligands. Reversible PL switching upon many repeated cycles was demonstrated, as alternating on and off of the UV excitation for the surface ligand has successfully resulted in the QD PL modulation.

Reversible switching of the emission from fluorescent probes can offer many emerging applications including optoelectronic devices,¹ chemical sensing,² contrast-enhanced imaging,³ and super-resolution imaging.⁴ Quantum dots (QDs) are fluorescent nanocrystals which provide distinct advantages over conventional organic dyes by the large absorption coefficient, tunable and bright photoluminescence (PL) emissions with narrow and symmetric emission profiles, and high photochemical stability.⁵ They can promise many potential applications such as probes for cellular and whole-body imaging,⁶ optical modulators,⁷ and light emitting diodes.⁸ Modulating or reversibly switching the QD emission is often crucial before QDs can be applied for such applications and outperform conventional technologies. Typically, QD emissions are modulated by energy transfers or charge transfers with molecules in proximity.^{2b,9} Spectral switching of QDs has been also demonstrated by charging/decharging type-II QDs.7b However, optically triggered modulations of QD PL have been only recently demonstrated by introducing photochromic compounds which can isomerize by light.7a,10 Optical modulations of QDs can provide unique opportunities for information processing, data storage, and next-generation imaging probes.¹¹ The photoisomerizable molecules can effectively modulate QD PL, however this is often hampered by the slow modulation dynamics (up to \sim seconds) and limited switching cycles due to the limited stability of the isomerizable molecules under continuous photoexcitations. Herein, we report reversible photo-switching of acridine-1,8-dione (AD) dye derivative functionalized QDs by photo-induced electron transfer (PET). PET has been widely used for molecule-based optical modulators especially for sensors.¹² PET-based optical modulations of QDs are not accompanied by the structural changes, and thus can guarantee the long-term stability. The electron transfer dynamics can also allow fast QD modulations. To the best of our knowledge, this is the first case reporting the PET-based QD emission modulation.

An AD disulfide derivative molecule (denoted ADD) was synthesized by modified procedures from our previous report¹³ (see ESI[†] for details). Schematic energy levels for 1.9 nm radius CdSe QD and our ADD are shown in Scheme 1. The LUMO level of the AD¹⁴ lies at a higher energy level than the conduction band of our QD.¹⁵ Electrons from the photoexcited ADDs are designed to transfer to the QD, which should result in quenching of the QD PL. 1.9 nm radius CdSe QDs (denoted b-QD) and 1.9 nm radius/1.0 nm thick shell CdSe/CdS/ZnS (core/shell/shell) overcoated QDs (denoted o-QD) were synthesized using a method previously described.¹⁶ TEM images confirm the thick CdS/ZnS shells over the b-QDs (Fig. 1c, d, and Fig. S1 for their high-resolution TEM images).

Both b-QD and o-QD show broad absorption profiles and their PL peaks at around 600 nm (Fig. 1a). PL quantum yields (QYs) of b-QD and o-QD were 4.9% and 10%, respectively. ADD shows a strong absorption at around 360 nm due to the charge transfer from the ring nitrogen to the ring carbonyl oxygen centre and emission at around 445 nm (Fig. 1b).¹⁷ The QD–ADD complex was prepared by adding a 2–100 fold molar excess of reduced form of ADDs to QDs (see ESI† for details). Two different excitation wavelengths of 365 nm and 532 nm were used. The 365 nm at UV excites both QD and ADD. The excited electrons in ADDs are expected to transfer



Scheme 1 Schematic illustration of QD photoswitching. Potential diagrams of HOMO–LUMO levels of the ADD surface molecule and 1S electron–hole levels of the CdSe QD (1.9 nm radius) are shown.

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Fig. 1 UV-vis spectra (closed circles) and normalized PL spectra (open circles) of (a) b-QD (black) and o-QD (red), and (b) ADD in THF solvent. TEM images of (c) the b-QD, and (d) the o-QD.

from the LUMO to conduction bands of QDs, which should result in negatively charged QDs of which PL can be effectively quenched by fast Auger processes.^{7b,18} Whereas, the 532 nm at visible was chosen to selectively excite QDs. Fig. 2 shows the emission spectra of the b-QD-ADD complex (denoted b-QD-ADD) and the overcoated counterpart of the o-QD-ADD complex (denoted o-QD-ADD) excited either by the UV or visible light. The complex between QD and ADD was set at a 1:2 molar ratio. As complexing with ADDs, the b-QD-ADD showed significantly reduced PL intensity. Under UV, the PL quenched to 6% before the ADD surface functionalization. This quenching is attributed to the efficient PET from ADD to b-QD with no inorganic shell layer. PL quenching by the inner filter effect from the absorption of the ADDs should be insignificant because the molar extinction coefficient of the QD^{19} is more than 100-fold higher than that of ADD^{20} at the excitation wavelength. The b-QD-ADD also showed significant quenching (PL intensity down to 37%) when excited by visible light. This quenching is thought to originate from charge transfer as ADD functions as an electron acceptor. In contrast, o-QD-ADD showed more dramatic PL changes by the excitation wavelengths. When excited by UV, o-QD-ADD showed the guenched PL down to 17%. The guenching efficiency is slightly smaller than that of b-QD-ADD, yet it is remarkably



Fig. 2 (a, b, d, and e) PL spectra of QD samples before the ADD functionalization (red) and after the QD–ADD complexation by 1 : 2 molar ratio (black). (a) b-QD/365, (b) b-QD/532, (d) o-QD/365, and (e) o-QD/532 (sample/excitation wavelength nm). (c and f) Fluorescence decay profiles of (c) b-QD-ADD (black) and b-QD-DHLA (red), and (f) o-QD-ADD (black) and o-QD-DHLA (red). All the complexes were prepared by 1 : 50 molar ratio for the decay profiles and were excited at 375 nm.

efficient quenching considering the inorganic double shell layers of CdS and ZnS which form 1.0 nm thickness. This efficient PL quenching via PET can be obtained because of the energy level cascades from ADD LUMO to the conduction band of CdSe via 1S electron levels of CdS and ZnS shell lavers.^{14,21} In addition, the efficient quenching of o-OD-ADD suggests that the PET electrons should occupy delocalized states of the QD in the conduction band rather than surface states because the protective CdS and ZnS shell layers should better passivate the surface defect sites than the bare QD counterpart. When o-QD-ADD was excited by the visible light, the complex retained the PL as high as 84% of that of QD before surface modification. This makes a sharp contrast to the case of b-QD-ADD. The CdS and ZnS shell layers seem to effectively block the charge transfer quenching mechanism. The quenched PL of o-QD-ADD under 365 nm excitation can be partially restored by intentional exposure of the sample to air, which is similar to the case of charged QDs via chemical electron injection (Fig. S6a, ESI[†]).^{7b,22} The photoexcited electrons in ADD can transfer to QD in o-QD-ADD, and as a result the ADD emission was efficiently suppressed (Fig. S6b, ESI[†]). As a control, a physical mixture of identical QDs with disulfide form of ADD which cannot anchor on QD surfaces was used. The control sample showed more than 5 times brighter ADD emission, which confirms the inability to efficiently interact with QDs by the lack of anchoring unit (Fig. S6b, ESI⁺). Fig. 2c and f show time-resolved PL measurements for b-QD-ADD and o-QD-ADD under the UV excitation (Table S1, ESI⁺). Both b-OD-ADD and o-OD-ADD showed significantly shortened PL lifetimes, from 1.4 ns to 0.64 ns and from 5.5 ns to 3.0 ns, respectively, when compared with b-QD and o-OD control samples. For the controls, a surface molecule that lacks the ADD chromophore but has the identical anchoring unit, dihydrolipoic acid (DHLA), was used for the surface functionalization. The faster PL decays confirm the efficient PET from the ADD to QD in the QD-ADD complex.

QD PL quenching efficiency *via* PET from ADD is expected to increase as a large number of ADDs exist on the QD surface.²³ The ADD/QD molar ratio was varied as 2, 20, or 100 for o-QD-ADD, and the PL properties were studied. As the ADD ratio increased, PL intensity of the o-QD-ADD decreased accordingly (Fig. 3a). To remove the inner filter effect and obtain the PET-induced quenching efficiencies, control samples were prepared using physical mixtures of ADDs in their disulfide form with as-prepared QDs (Fig. S7, ESI†). The PET-induced PL quenching efficiency was estimated using $1 - (I_{S,365}/I_{R,532})$, where I_{365} and I_{532} are the QD PL intensities



Fig. 3 (a) PL spectra of o-QD-ADDs prepared by different QD/ADD molar ratios of 1 : 2 (red), 1 : 20 (blue), and 1 : 100 (green). QD sample before the ADD functionalization was measured for a control (black). Excitation at 365 nm. (b) PET induced QD PL quenching efficiencies of the o-QD-ADDs.



Fig. 4 QD PL switching upon many repeated cycles for (a) o-QD-ADD (1 : 50 molar ratio), (b) and CdTe/CdSe type-II QD-ADD (1 : 50 molar ratio) with alternating on–off cycles of UV light under continuous visible light illumination. Red and gray squares denote relative PL intensities at their QD PL on and off status, respectively. Relative PL intensity is defined as [QD–ADD complex PL intensity]/[non-surface modified QD PL intensity]. The excitation power is 2.2 mW cm⁻² for the 532 nm and 0.18 mW cm⁻² for the 365 nm, respectively.

when excited by 365 nm and 532 nm, respectively. $I^{\rm S}$ represents the intensity of o-QD-ADD, and $I^{\rm R}$ the mixture control. The PET-induced PL quenching efficiencies of 82%, 87%, and 98% were obtained by increasing the ADD ratio from 2, 20 to 100 (Fig. 3b). This result indicates that a large number of electron donors (ADDs) per QD can efficiently quench the QD PL when excited at 365 nm. However, the quenching efficiencies for the cases of 20 and 100 ADD ratios were actually lower than expected. The actual numbers of ADDs on QD surfaces do not seem to reach the nominal amounts presumably because of the limited surface derivatization sites on QDs and increasing steric and electrostatic repulsions for the additional ADD anchoring.

Fig. 4a showcases the reversible PL switching capability of the o-QD-ADD sample (1 : 50 QD : ADD ratio) by repeated UV excitation on-off modulation under continuous illumination by 532 nm light. Additional UV irradiation suppressed the QD PL intensity, and this was reversibly switched back by turning off the UV excitation. The o-QD-ADD was at its 'on' status when the UV excitation was 'off' and vice versa. We speculate that the injected spectator electrons at QDs can transfer back to oxidized ADDs, which should result in the charge neutralization and may facilitate the reversible PL switching. This can be a prototype for QD PL modulation by external light triggering. The average QD PL quenching efficiency up to four repeated cycles was 24%. CdTe/CdSe (core/shell) type-II QDs were prepared to test the PL modulation capability by introducing ADD (see ESI[†] for the synthetic procedures and Fig. S2 for their optical properties and TEM images). The QD PL modulation experiment was repeated using the type-II QDs (1: 50 QD : ADD ratio) (Fig. 4b). The average QD PL quenching efficiency was 40%. The type-II QDs have unique exciton characteristics, where the electrons and holes are spatially separated. The electrons reside mostly in the shells, while the holes stay in the cores. The quenching efficiency was enhanced for the type-II QD case presumably because of the enhanced overlap between the shell-localized excitonic electrons and the ADD originated electrons. Besides, the long lifetime of type-II QD excitons^{7b,24} may have also contributed to enhanced interactions between excitons and PET electrons. For both o-QD-ADD and type-II QD-ADD samples, the PL modulations were stably reversible over numerous times of switching cycles.

In summary, we have demonstrated a unique optical modulation of QD PL by controlling the PET using our ADD surface ligands. The switching response was faster than the milli-second scale, which calls for further time-resolved spectroscopy studies to elucidate the dynamics of the turn on and off processes. This external light triggered PL modulation capability can open a new window for many applications.

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