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# Materials Research Express



## PAPER

# Effect of mesogenic ligands on short and long-term spectral dynamics and stability of core-shell CdSe/ZnS quantum dots

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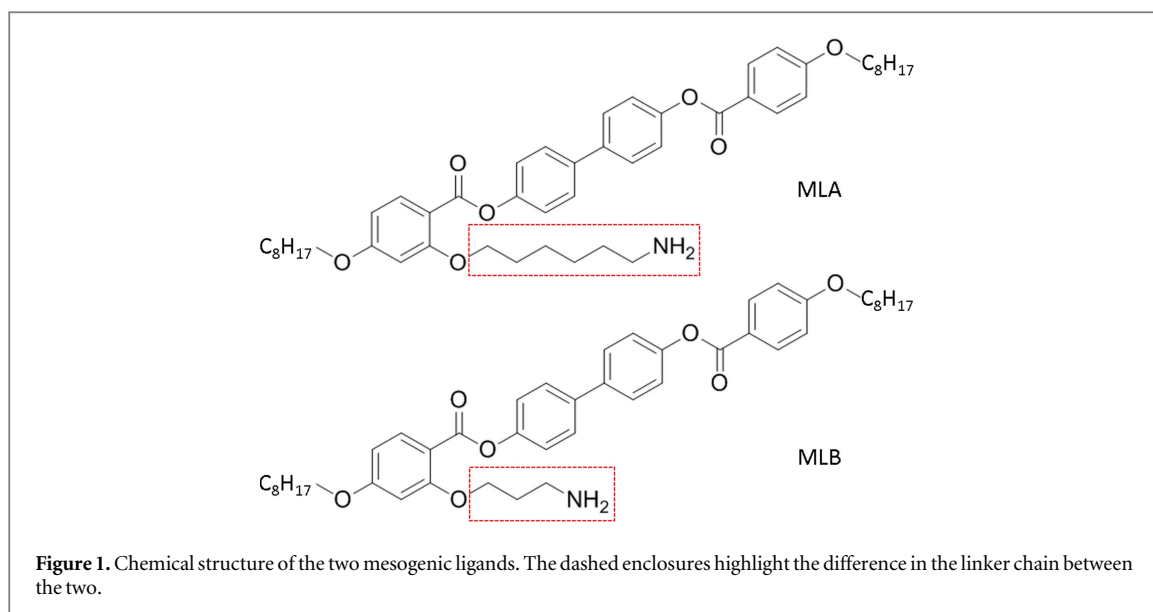
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## Abstract

Surface modification is a versatile and effective route towards improving functional and structural characteristics of chemically synthesized nanomaterials. In the specific case of semiconducting nanoparticles (quantum dots (QDs)) the photophysical properties are strongly tied to surface conditions. Therefore, a careful monitoring of photoluminescent (PL) behavior, both short and long term, is critical following alterations to their surface chemistry. We observe several noteworthy changes in the static and dynamic PL spectra of CdSe/ZnS core-shell QDs when the as-grown native ligands are exchanged with two different mesogenic ligands—rod-like molecules attached to the particle by a flexible alkyl chain. These include reduced inter-dot energy transfer, stable recombination rates and steady emission color over more than an hour of continuous photo-excitation, all effects being more prominent in the sample with the longer attachment chain. Temperature dependence of PL and recombination rates reveals further differences. Thermally activated PL recovery threshold is pushed to a higher temperature in the modified dots, while PL lifetime does not show the expected increase with decreasing temperature. Our results indicate that increased charge separation induced by the longer ligands is responsible for these effects, and this may be a route to fabricating QD films for specific applications demanding long term emission color stability.

## 1. Introduction

Surface modification of chemically synthesized semiconducting quantum dots (QDs) not only plays a critical role in determining the optical and electronic properties of the nanoparticles, but also affects the chemical stability and sample longevity [1–3]. As-synthesized QDs are coated with surface ligands primarily to prevent aggregation of the dots and to keep them suspended in the native solvent [4]. It is most common for these ligand molecules to be hydrophobic, as typical end-product solvents are non-polar. However, post-synthesis ligand exchange is often carried out for a variety of end goals. Common examples include allowing suspension of QDs in water or water-based solvents for biocompatible products [5, 6], enhancing photo-stability and prolonging shelf-life of QDs used in photo-detectors [3] and hastening charge transport by exchanging longer surface ligands for short molecules for photovoltaic applications [7]. A specific niche where QD surface chemistry plays a central role is in the development of hybrid materials, such as liquid crystal (LC)- or polymer-QD composites, where miscibility of the dots in the host medium is key to uniform dispersion [8] or to selective spatial organization [9]. Commonly used ligand molecules, such as octadecylamine, oleic acid, or trioctylphosphine oxide, result in QDs aggregating in the host, particularly when dispersed at the high concentrations needed for device development. In these cases, custom ligands are structurally similar to the host molecules are required, and for liquid crystalline media these are known as mesogenic (LC-like) ligands (MLs). Surface modification with various MLs has been attempted with the specific aim of improving the dispersions of QDs (as well as other types of nanoparticles) in LC media [10]. All ligand exchange processes alter the surface of the QDs and therefore lead to changes in spectral absorption, quantum yield [11], recombination lifetimes [12] and other related optical and electronic properties, not only in the short term post-modification, but in the long term as well. In



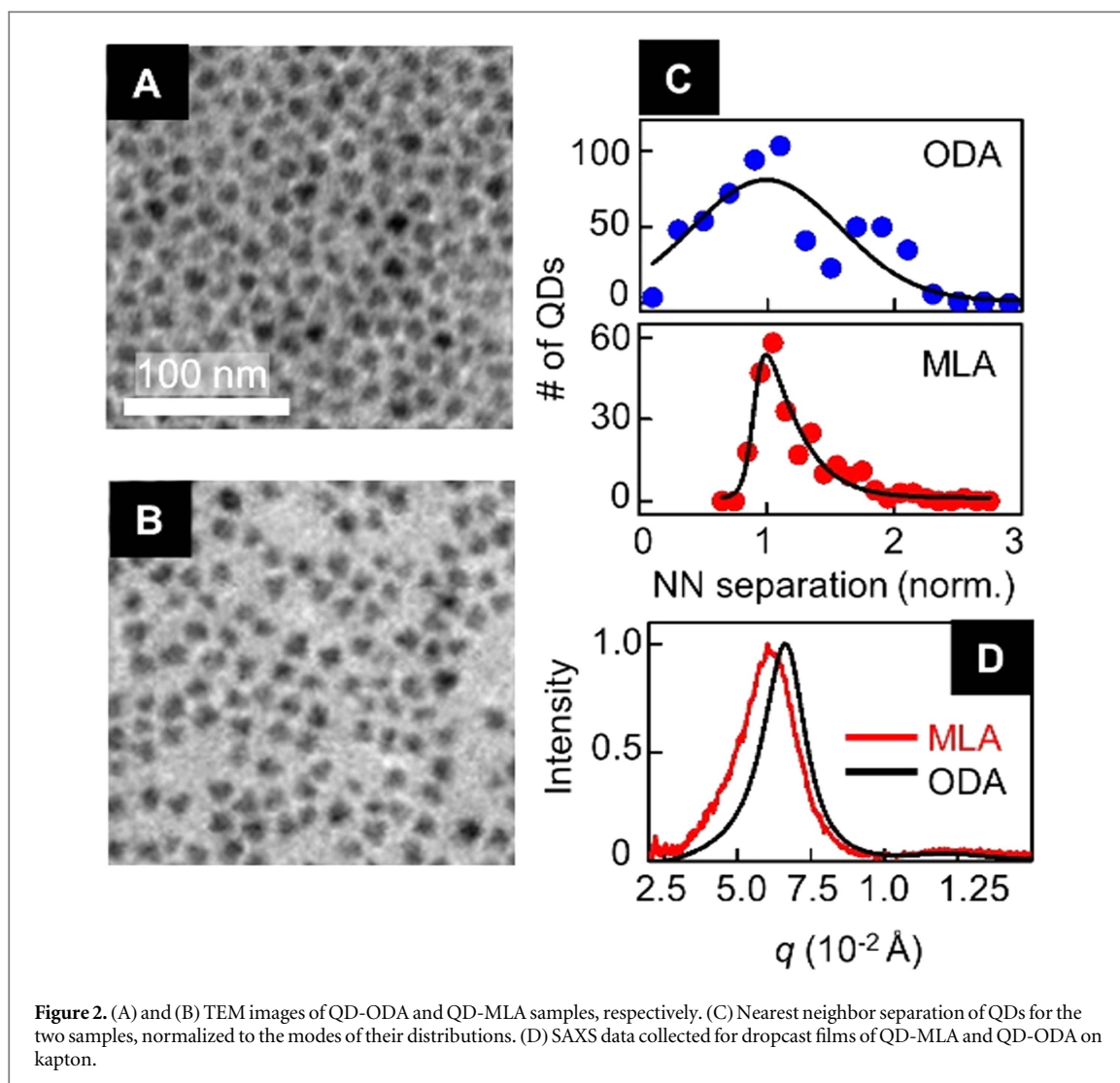
**Figure 1.** Chemical structure of the two mesogenic ligands. The dashed enclosures highlight the difference in the linker chain between the two.

the case of surface modification using MLs, while basic spectral properties such as quantum yield are usually documented following ligand exchange, the focus is largely on studying the dispersion of the QDs within the host phase with the goal of understanding guest–host interactions, rather than long-term QD behavior. It is important to characterize and understand these long-term changes, to allow rational design for improved functional and structural stability.

We present a study of the effects of surface modification in 6.2 nm diameter CdSe/ZnS core–shell QDs (with 5% size inhomogeneity in a typical ensemble). When the original octadecylamine (ODA) ligands are substituted with mesogenic ligands, we find several spectral changes that result from our surface modification, especially with respect to how the QD ensembles behave under continuous and prolonged photo-excitation. The most striking result is that the emission color is stabilized considerably, in effect arresting photo-oxidation completely.

## 2. Experimental details

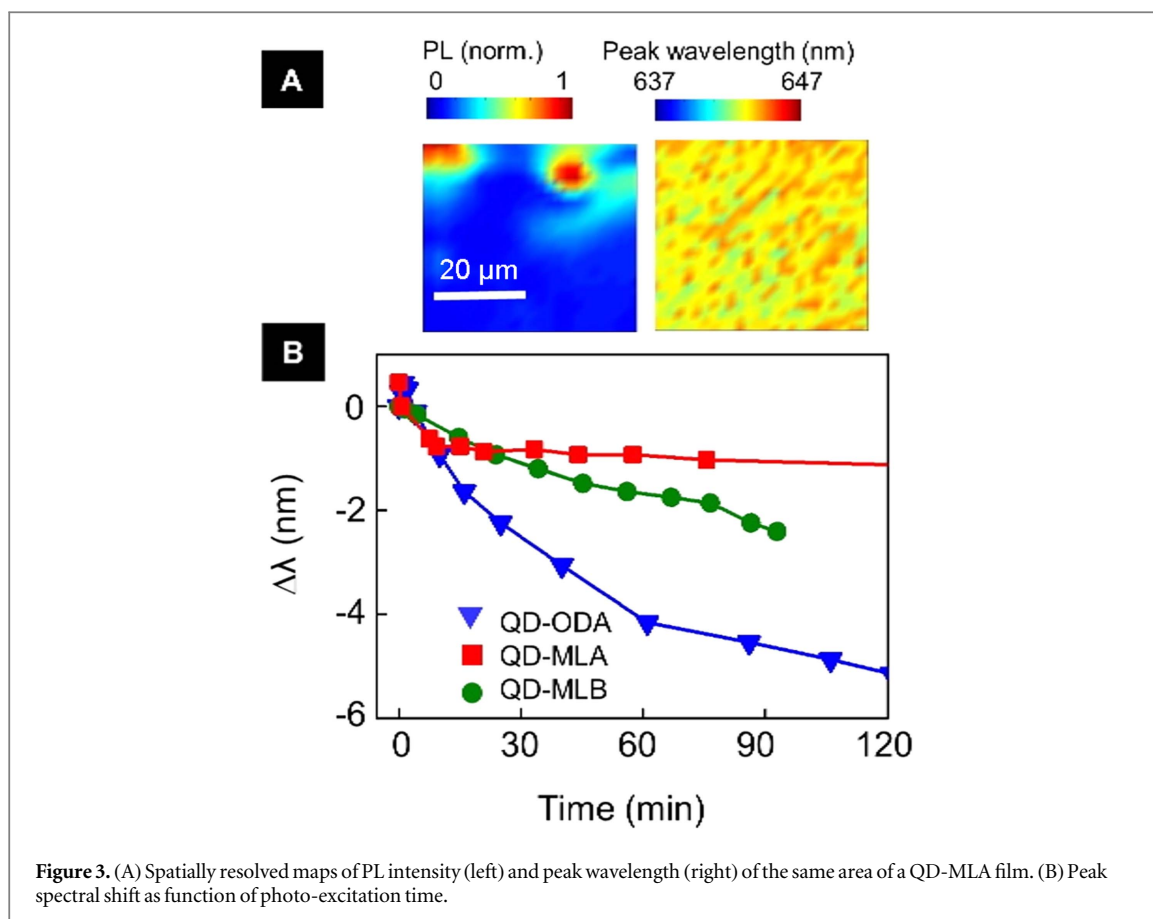
The two MLs used in this work are shown in figure 1. They consist of a rigid aromatic core, designed to couple to the QD surface via a flexible amine-terminated alkyl chain linkage (3 or 6 carbons long) highlighted in dashed boxes. ODA simply consists of a linear 18 C-atom long alkyl-terminated chain. The ligand exchange process follows the precipitation-redispersion scheme outlined in detail in [10]. For optical measurements, drop-cast films of QDs with ODA (QD-ODA) and with mesogenic ligands (QD-MLA/B) are prepared by allowing slow drying of QDs deposited on clean substrates, following [13]. For static spectral measurements, a Coherent CUBE laser excites the samples at 409 nm with excitation power of 28  $\mu W$  and the data is collected by an Acton 300i spectrometer dispersed onto a thermo-electrically cooled CCD (resolution  $\sim 0.18$  nm). For time-correlated measurements, an ultrafast tunable Ti:Sapphire laser is used as the optical excitation source, frequency-doubled to 409 nm with an excitation power of 30  $\mu W$ . The detector is a single photon avalanche diode coupled to a time-correlated single photon counting system (PicoHarp 300) with an instrument response function of 12 ps, positioned after a monochromator. All room temperature measurements are conducted in ambient conditions using a Nikon 100X objective with a diffraction limited resolution of  $\sim 500$  nm. For temperature dependent studies the samples are mounted in an advanced research system cryo-free system capable of temperature control in the range 300–10 K. Transmission electron microscopy (TEM) images are obtained with a JEOL-2010 TEM equipped with a LaB<sub>6</sub> filament and operated at 200 kV in the Imaging and Microscopy Facility, UC Merced. TEM samples are prepared by placing 0.2  $\mu l$  of solution diluted to 10% of original concentration on a TEM copper grid with carbon film, wicking excess solvent, and placed in a vacuum oven for  $\sim 4$  h to remove residual solvent. Small angle x-ray scattering (SAXS) measurements are carried out at the stanford synchrotron radiation lightsource, beamline 4–2 at 11 keV. SAXS transmission experiments were carried out on thin film samples dropcast in toluene and deposited on Kapton® film using a 1 mm  $\times$  300  $\mu m$  beam profile. Data was collected using a CCD detector and analyzed using custom SasTool software available at the beamline.



### 3. Results and discussion

QDs with ODA, when densely packed, tend to be highly close-packed as the flexible ODA ligands interdigitate to some extent. By contrast, the MLs are much more rigid due to the aromatic cores and there is some evidence that the ligands associate with these cores arranged laterally, stabilizing NP packing with an increased particle separation compared to ODA [14]. TEM images of QD-ODA and QD-MLA films are shown in figures 2(A) and (B), respectively. The distributions of nearest neighbor (NN) distances between the dots averaged over a  $1 \mu\text{m}^2$  region in these images are shown in figure 2(C), calculated using ImageJ software [15]. The data is normalized to the mode of the distributions as a  $\pm 2$  nm error in the image analysis renders the actual separation values inaccurate. However, comparison of the plots reveals a tighter NN separation within the QD-MLA film despite the overall packing fraction being smaller compared to QD-ODA. The characteristic inter-dot separation in the films is derived from the SAXS data shown in figure 2(D). The positions of the scattering peaks are determined by subtracting a baseline from the raw data, producing inter-dot separations of 9.4 nm for QD-ODA, and 10.4 nm for QD-MLA. The QD-MLB films were expected to have a particle spacing intermediate to these values, given the shorter linker length (figure 1), but in these SAXS measurements we observed an average dot separation similar to QD-MLA.

The observed increase in inter-dot spacing due to the mesogenic ligands is expected to reduce energy transfer (ET) in QD-MLA/B films, as ET in QDs is dipole-mediated, scaling as  $1/r^6$ , where  $r$  is the inter-dot separation [16]. This decreased ET can be seen in figure 3(A), which shows spatially resolved maps of PL intensity and the corresponding peak wavelength of a  $50 \mu\text{m}^2$  area of a QD-MLA film (solution emission centered on 636 nm). The intensity map (left) is largely homogenous with the exception of two bright spots at the top, corresponding to regions of high QD density. Typically in such crowded spots ET is very efficient and the emission is shifted to longer wavelengths (red shift). The map of the peak wavelength (right) for the same region varies between

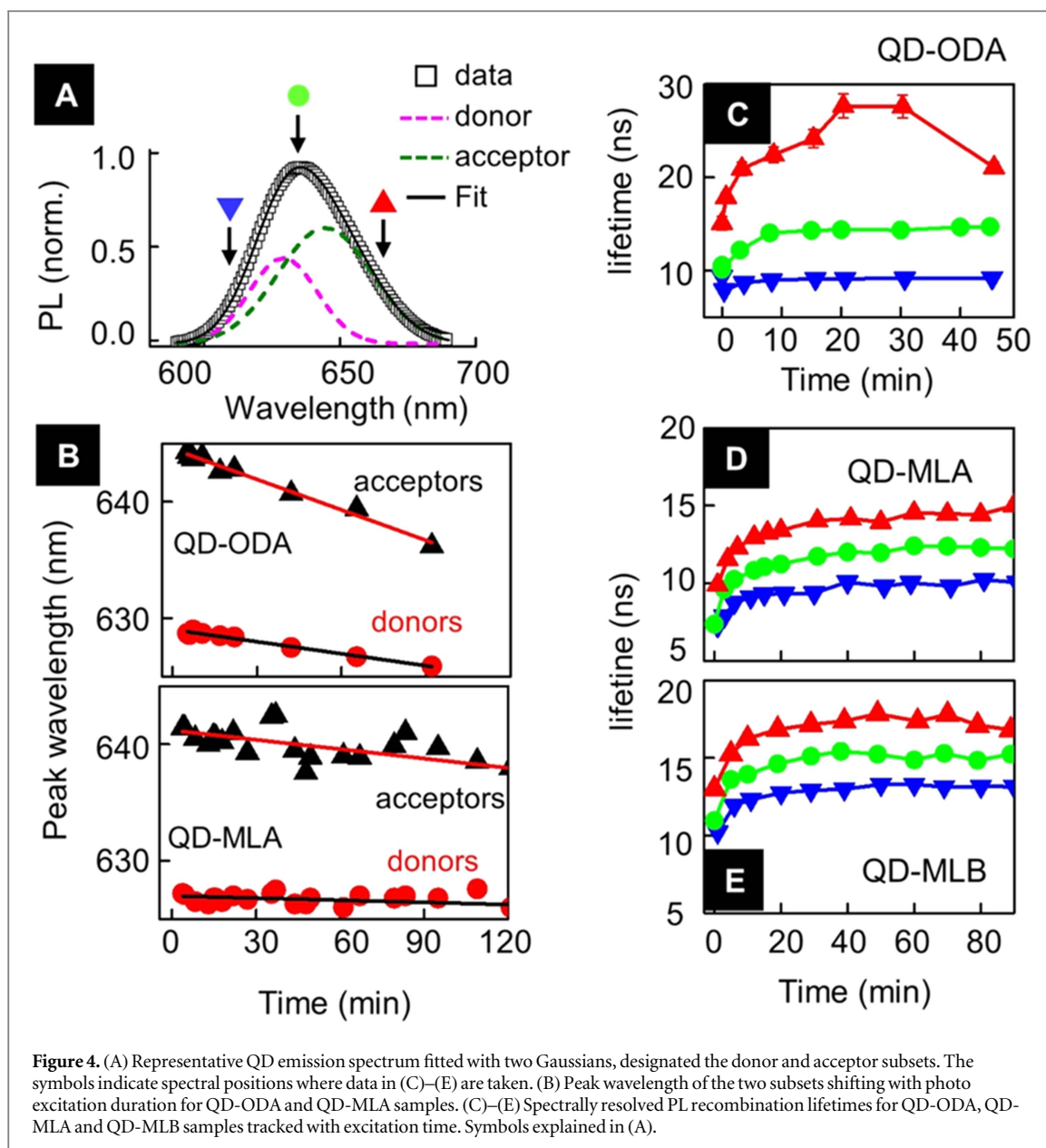


**Figure 3.** (A) Spatially resolved maps of PL intensity (left) and peak wavelength (right) of the same area of a QD-MLA film. (B) Peak spectral shift as function of photo-excitation time.

643–644 nm (red-shift of 7–8 nm), including the spots of high density. In QD-ODA films similar measurements routinely show spectral red-shifts of 10–12 nm.

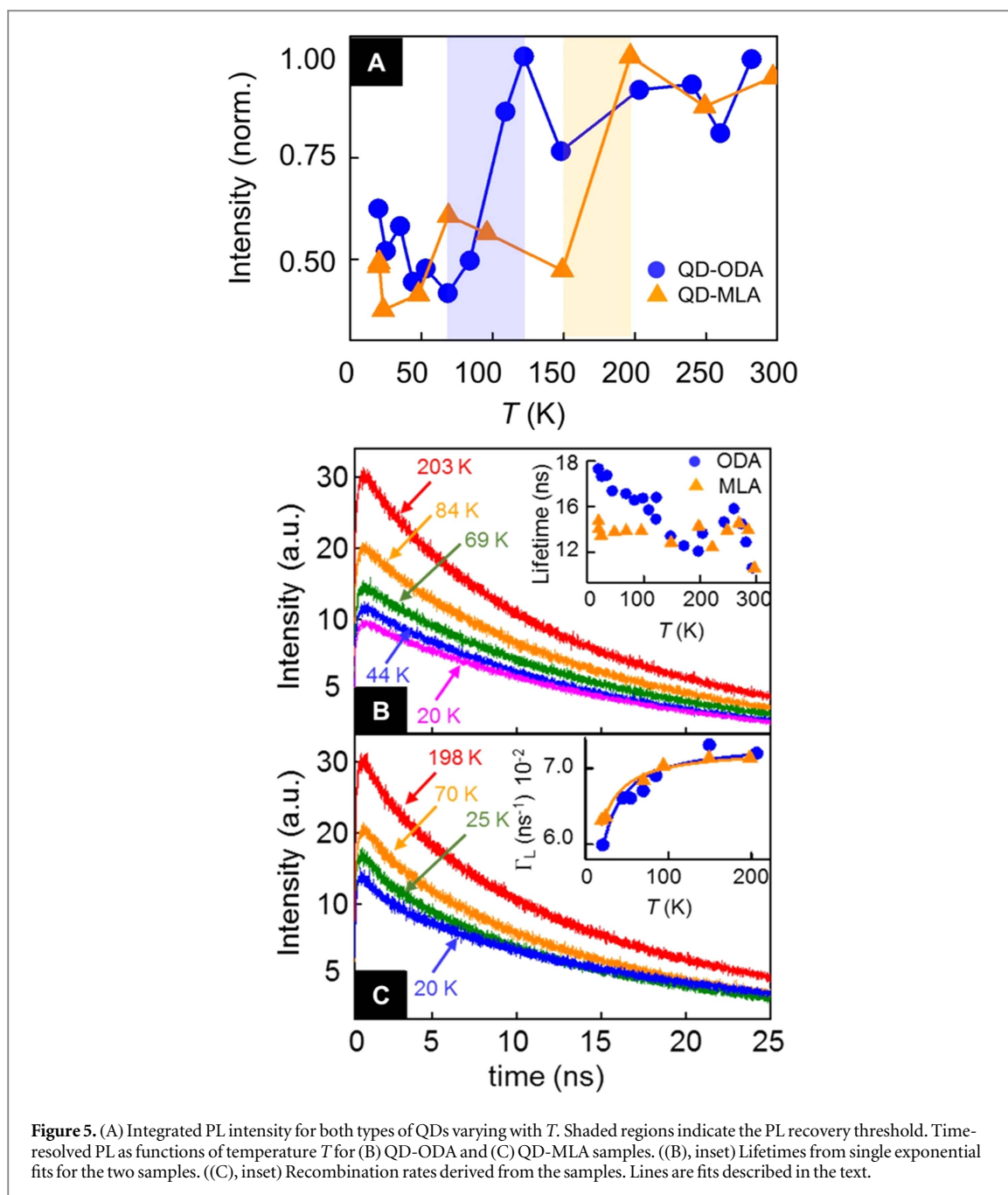
In our earlier work we established that ET increases photo-darkening rates in larger dots within an ensemble, even in a nominally single color collection. Therefore, reducing in the QD-MLA films should be advantageous to the QD ensemble in terms of photo-stability. To investigate this, we monitor the PL of QD films over a period of 120 min under continuous excitation, and plot the peak emission shift,  $\Delta\lambda$ , in figure 3(B).  $\Delta\lambda$  is measured from the peak emission at the start of photo-excitation (designated ‘0’ on the time axis). QD-ODA blue shifts rapidly by 4 nm in the first 60 min and then slowly by another 2 nm in the next 60 min QD-MLB performs better, exhibiting approximately a 3 nm shift over the entire 100 min period. QD-MLA is noticeably better than both, shifting only by 1 nm in the first 10 min and then stabilizing completely beyond that. Spectral blue shift is indicative of oxidation of the QD core, which reduces the core diameter and results in increased quantum confinement. Lack of an observed significant blue shift is therefore a very encouraging sign. We analyze this further and de-convolute the inhomogeneously broadened spectrum into two subsets by fitting it as a cumulative of two Gaussian distribution. These represent the smaller dots (donors) and the larger dots (acceptors) that participate in intra-ensemble ET. We show one example in figure 4(A), noting that while in reality the ensemble spectrum is a superposition of more than two distributions, this simple model allows us insight into how the spectral weight redistributes with photo-excitation. In figure 4(B) we track the peak positions of each of these subsets with time for QD-ODA (top) and QD-MLA (bottom) films. In both types of QD films each subset blue shifts linearly with time, although with varying rates. QD-ODA film has stronger intra-ensemble ET than QD-MLA, confirmed by the longer wavelength peak positions of the subsets at the start of photo-excitation. As a result, the acceptors blue-shift faster than the donors, as has been observed in close-packed QD films [13]. By comparison QD-MLA shows that the blue-shift rate for the acceptors and the donor spectral emission is far smaller over the entire time.

The effect of reduced ET and arrested photo-oxidation in QD-MLA/B extends to dynamic PL aspects as well. Figures 4(C)–(E) plot spectrally resolved PL recombination lifetimes of the three types of QD films. The spectral positions where the time-resolved data are taken are indicated in figure 4(A) with symbols (downward triangle, circles, and upward triangles) commensurate with those used in the plots. The time-resolved traces are mono-exponential, a sign of weak inter-dot interactions. We extract the lifetime  $\tau$  from these traces with  $I(t) = I_0 e^{-t/\tau}$  and comparing the three, note that lifetimes  $\tau$  increase with emission wavelength, a consequence of



ET. At the start, the difference between the lifetimes of the blue to red emitting dots is greater in the QD-ODA films than the others, as also expected from the reduced ET in QD-MLA/B samples. The actual lifetimes seem to scale inversely with the ligand length, from longest in ODA to shortest in MLA functionalized dots. The trend exhibited by the lifetimes changing with photo excitation time is also strikingly different: the QD-ODA shows a steep increase at the longer wavelengths in the first 60 min, followed by a decrease. The lifetimes at other wavelengths show little (at peak of emission) to no changes (at blue end). This trend is characteristic of close-packed QD films with typical ligands and at even longer times, the curves have been seen to actually converge. Incidentally, the first 60 min is also when the spectrum undergoes the rapid blue-shift shown figure 3(B) and the increasing lifetime of the larger dots is a direct consequence of this. As some of the acceptor dots oxidize, they also go dark and do not contribute to the ensemble PL. The QD-MLA and QD-MLB films both show a 2–5 ns increase over the entire time window, while the difference between lifetimes at different wavelengths is unchanged. This long time stability of recombination lifetimes is highly unusual in dense QD films and is a testament to the lack of photo-induced damage in these dots.

Summarizing our results so far, the mesogenic ligands appear advantageous in several respects, including emission color and lifetime stability, with the slightly longer MLA performing the best. The one detrimental aspect is the slightly reduced PL lifetimes compared to QD-ODA dots. For further insight into this we look at temperature dependent static and dynamic PL. QD properties are strongly modulated by thermal changes, and these studies highlight any subtle changes in surface properties and energetics resulting from ligand exchange. In figure 5(A) we plot the integrated PL intensity with temperature  $T$  in the range of 300–20 K for QD-ODA and



QD-MLA films. Both types of QDs show similar trends, where the intensity is quenched at low  $T$  followed by a recovery (anti-quenching) and saturation at higher  $T$ . The recovery threshold is almost 100 K higher in the QD-MLA film. Anti-quenching is symptomatic of suppression of non-radiative recombination channels brought about by thermally induced carrier activation [17–19]. Prior studies have demonstrated that with increasing ligand length, the PL recovery is pushed to higher  $T$ , a result of the surface states moving farther from the core of the QDs and not due to worsened surface quality [20]. Spectrally integrated time-resolved PL data in figures 5(B) and (C) in the same temperature range are all single-exponential, confirming lack of significant non-radiative recombination. The inset in figure 5(B) plots the lifetimes obtained from fits to the time-resolved traces with temperature. Neither sample shows any significant changes with  $T$ , but QD-ODA lifetime appears to begin a sharp rise around 100 K, while QD-MLA lifetime remains fairly constant. PL recombination in QDs above 20 K is governed by the thermal equilibration between the allowed ('bright') and forbidden ('dark') states that are separated by a few meV. Following analysis in [21] we plot the recombination rate  $\Gamma_L$  (inverse of lifetime) versus  $T$  in figure 5(C) inset. The data is fit to:



$$\Gamma_L = \frac{\Gamma_A + \Gamma_F}{2} - \frac{\Gamma_A - \Gamma_F}{2} \tanh\left(\frac{\Delta E}{2k_B T}\right),$$

where  $\Gamma_A$  and  $\Gamma_F$  are the recombination rates of the allowed and forbidden states and  $\Delta E$  is the energy splitting between the two. For QD-ODA we obtain  $\Delta E = 2.9$  meV and  $\Gamma_A = 0.087$  ns<sup>-1</sup>; QD-MLA fit returns marginally different values of  $\Delta E = 2.6$  meV and  $\Gamma_A = 0.095$  ns<sup>-1</sup>. The mesogenic ligands have aromatic benzene rings where the  $\pi$  electrons serve as efficient conduits for charge transfer when stacked closely, by capturing the photogenerated holes. Functionalizing QDs with similar ‘hole accepting’ ligands has been reported to cause PL quenching and faster recombination [22]. We observe a reduced lifetime for both mesogenic ligands in figure 4 and an increased  $\Gamma_L$  in figure 5(B). The unchanging lifetime at  $T < 100$  K for QD-MLA in figure 5(A) is likely also a consequence of exciton dissociation via charge transfer. The decreased energy splitting between the bright and dark states is an additional indicator of reduced electron–hole overlap. Neither of these changes are very great, implying the surface modification does not affect the dynamic properties of the dots to any significant extent. The room temperature spectrally integrated lifetime of the QD films  $\tau_F$  in the inset of figure 5(A) can give us an estimate of the ET efficiency  $\eta$ , using  $\eta = 1 - \tau_F/\tau_S$ , where  $\tau_S$  is the recombination lifetime of isolated dots in solution. We calculate an efficiency of 20% for QD-ODA and 9% for QD-MLA, which is in agreement with our previous observation that ET is reduced following functionalization with the mesogenic ligands.

## 4. Conclusion

The use of these liquid crystalline molecules to functionalize nanoparticles was motivated by the drive to develop hybrid materials with added functionalities. In the case of QDs, this modification allows better dispersion in LQ hosts [10], templated assembly into three-dimensional architectures [14] and possibly novel photonics applications [23]. We have demonstrated that these surface modifications are sustainable where long-term QD properties are concerned and in some aspects, lead to improved optical performance in close-packed films, such as stabilization of both emission wavelength and recombination dynamics. There is considerable effort invested in developing photo-stable QDs, particularly for photovoltaic applications where long-term exposure to high photon flux is unavoidable. The most successful of these are the ‘giant’ QDs, so named because of a thick shell that removes surface states from proximity to the core [24]. Achieving stability via surface modification is a more general route that could lead to improved performance by all QDs, allowing for more widespread usages.

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