Electronic Supplementary Information

Effects of Separation Distance on the Charge Transfer Interactions in Quantum Dot-Dopamine Assemblies

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EXPERIMENTAL SECTION

Growth and Characterization of CdSe-ZnS QDs. We prepared two sets of CdSe-ZnS core-shell QDs, one yellow-emitting (with peak location at λ_{abs}= 573 nm) and one red-emitting (peak location at 610 nm). The CdSe cores were prepared in the first step via reduction of cadmium and selenium precursors at a temperature of 320-340 ^{o}C and in coordinating solvent mixture made of trioctyl phosphine (TOP), trioctyl phosphine oxide (TOPO), alkylamine and alkylphosphonic acid.[1-3] The reaction was followed by overcoating the CdSe core with 5-6 monolayers of ZnS (in a second step) using zinc and sulfur precursors, but the procedure was carried out at lower temperature (160-180°C). The nanocrystal sizes were estimated by combining data collected from three complementary techniques: small angle X-ray scattering, first absorption peak location and analysis of transmission electron microcopy (TEM) data.[4, 5] The average radius (core-plus-shell) for these two sets of nanocrystals is ~3.4 nm for the yellow- and ~4.0 nm for the red-emitting QDs.

Ligand Synthesis and Phase Transfer of the QDs. We used a total of four sets of surface ligands made of lipoic acid appended with a tunable size polyethylene glycol (LA-PEGylated) chain and a terminal amine group: LA-PEG$_{200}$-NH$_2$, LA-PEG$_{400}$-NH$_2$, LA-PEG$_{600}$-NH$_2$ and LA-

PEG_{1000}-NH_2. The above ligands have been synthesized, purified and characterized following the protocols detailed in previous protocols.[6-8] Additional data showing the Electrospray Ionization (ESI) and Matrix-assigned Laser Desorption Ionization (MALDI) Mass Spectra of LA-PEG-NH_2 ligands are provided in Figure S1.

These ligands were chemically reduced using sodium borohydride,[8] then applied to functionalize hydrophobic QDs and transfer them to buffer media. The absorption and fluorescence spectra were collected from dispersions of the QDs, before and after ligand exchange. We found that the spectral characteristics of the QDs before and after ligand exchange were essentially unchanged. Nonetheless, a loss of ~ 40% of the PL quantum yield (compared to the hydrophobic materials) has been routinely measured for the dispersions in DI water.

Assembly of the QD-Dopamine Conjugates. The above QDs were used to prepare two sets of QD-dopamine conjugates: (1) one prepared by reacting EG/amine-PEG-QDs with dopamine-modified with an isothiocyanate group (dopamine-ITC); (2) the other was prepared by reacting ZW/amine-PEG-QDs with dopamine-ITC. Briefly, 10-100 μL aliquots of dopamine-ITC pre-dissolved in DMSO (depending on the molar needed) were added to scintillation vials containing 100 μL of EG/amine-PEG-QDs or ZW/amine-PEG-QDs. DI water was further added to bring the total dispersion volume in each vial to 1 mL. The mixture was stirred for ~3.5 h in the dark, then excess free/unreacted dopamine was removed using 1 round of concentration/dilution through a membrane filtration device (Mw cutoff: 50 kDa, Millipore). The dispersions of QD-dopamine conjugates have a final QD concentration of ~0.8 μM. Aliquots (40 μL) of the QD-conjugate (stock) dispersions were mixed with 960 μL of DI water (a total volume of 1 mL and a QD concentration of 32 nM) and used to collect the fluorescence spectra. All measurements were carried out using a fixed pH (with pH 6.5, DI water). We primarily focused on the effects of varying the separation distance between the QD and dopamine using discretely controlled PEG chain length.

Absorption and Fluorescence Measurements. The absorption spectra for all samples were recorded using a UV-Vis absorption spectrophotometer (UV 2450 model from Shimadzu).

These spectra were used to determine the QD concentration in the samples.[9] The steady-state fluorescence spectra were collected on a Fluorolog-3 spectrometer (HORIBA Jobin Yvon Inc., Edison, NJ) equipped with TBX PMT and air-cooled CCD camera detectors. All the steady-state PL spectra were collected using a narrow excitation line at 350 nm. The time-resolved (TR) fluorescence decay data were collected and analyzed with a TCSPC (time correlation single photon counting) system integrated into the same Fluorolog-3. A pulsed excitation signal with a repetition rate of 1 MHz at 440 nm, provided by a NanoLED-440LH (100 ps, FWHM), was used for sample excitation. The time-resolved signal was detected on the TBX detector, with allowed lifetime resolution of ~ 0.1 ns. The fluorescence decay profiles of the QD signal with time for the QD-dopamine conjugates (limited to a narrow window centered at the PL peak) were fitted to a three-exponential function of the form:

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}}. \qquad (1)$$

where t is time and A_i is a weighting parameter associated with each decay time, τ_i. An average amplitude-weighted lifetime, τ_{avg}, was extracted from the fit using Data Station software (Horiba Jovin-Yvon), with:

$$\tau_{avg} = \frac{\sum A_i \tau_i^{\,2}}{\sum A_i \tau_i}. \qquad (2)$$

The PL quenching efficiency, E, were extracted from the steady-state or time-resolved fluorescence data, using the expressions:

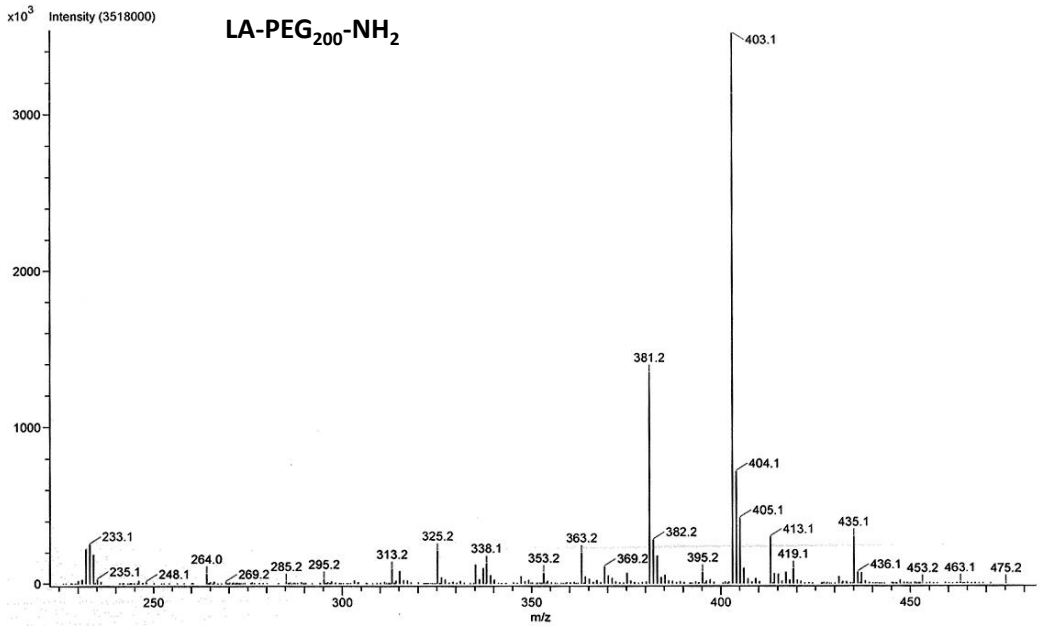
$$E = 1 - \frac{F_{DA}}{F_D}, \qquad \text{for steady-state fluorescence} \qquad (3a)$$

and

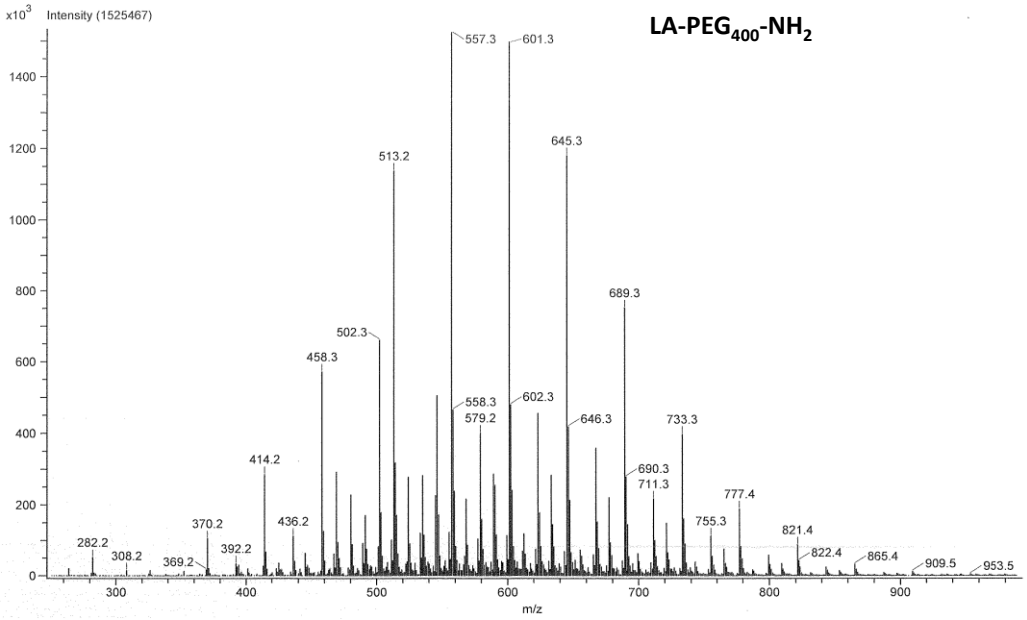
$$E = 1 - \frac{\tau_{DA}}{\tau_D}, \qquad \text{for time-resolved fluorescence} \qquad (3b)$$

where F_{DA} and F_D designate the PL intensity measured for dispersions of QD–dopamine conjugates and QDs alone (control, without dopamine complexes), respectively. Similarly, τ_{DA} and τ_D designate the exciton lifetime measured for dispersions of QD-dopamine assemblies and QDs alone, respectively.

(A)


x10^3 Intensity (3518000)
LA-PEG200-NH2
403.1
381.2
404.1
405.1
413.1
435.1
233.1
325.2
338.1
363.2
382.2
264.0
313.2
353.2
369.2
395.2
419.1
235.1
248.1
269.2
285.2
295.2
436.1
453.2
463.1
475.2
m/z

(B)


x10^3 Intensity (1525467)
LA-PEG400-NH2
557.3
601.3
645.3
513.2
689.3
502.3
458.3
558.3
602.3
579.2
646.3
733.3
414.2
690.3
711.3
777.4
370.2
436.2
755.3
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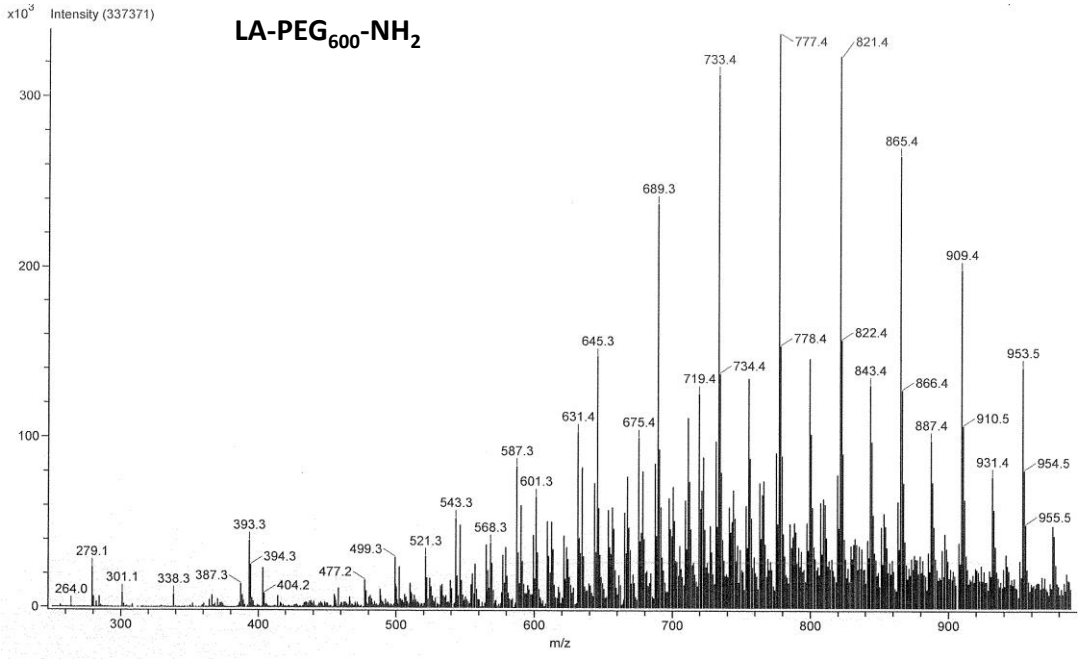
865.4
909.5
953.5
m/z

(C)



(D)

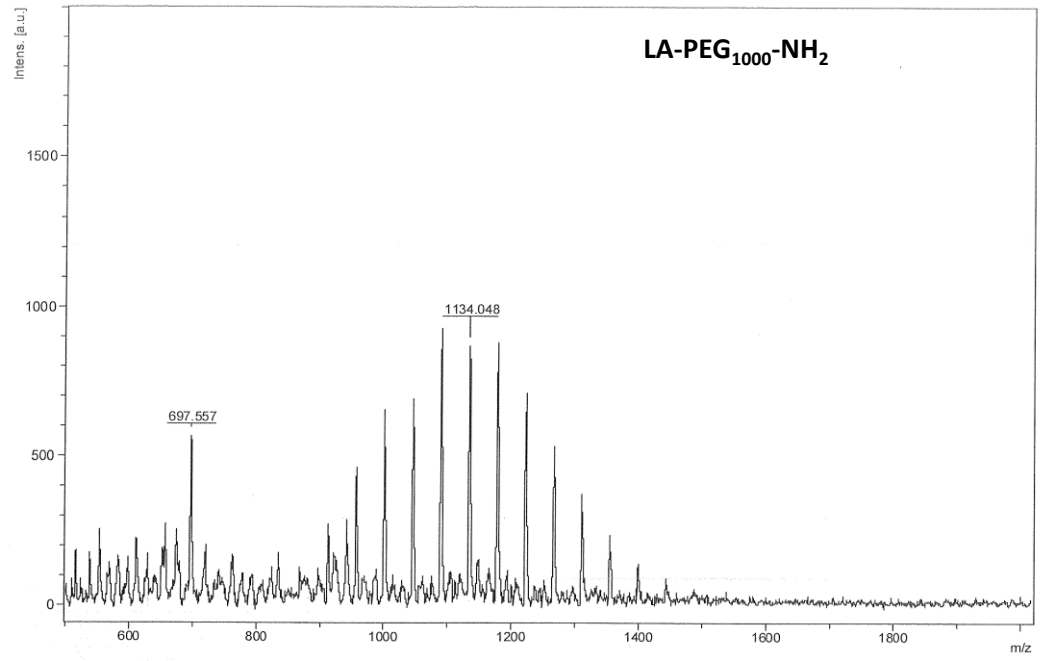


Figure S1. Electrospray Ionization (ESI) Mass Spectrum (positive mode) of LA-PEG-NH_2 with various PEG size, (A) LA-PEG_{200}-NH_2 [m/z 381.2 $(M+H)^+$, 403.1 $(M+Na)^+$], (B) LA-PEG_{400}-NH_2, [m/z 601.3 $(M+H)^+$], (C) LA-PEG_{600}-NH_2, [m/z 777.4 $(M+H)^+$] and (D) Matrix-assigned laser desorption ionization (MALDI) Mass Spectrum of LA-PEG_{1000}-NH_2 using DCTB matrix, [average m/z ~1134].

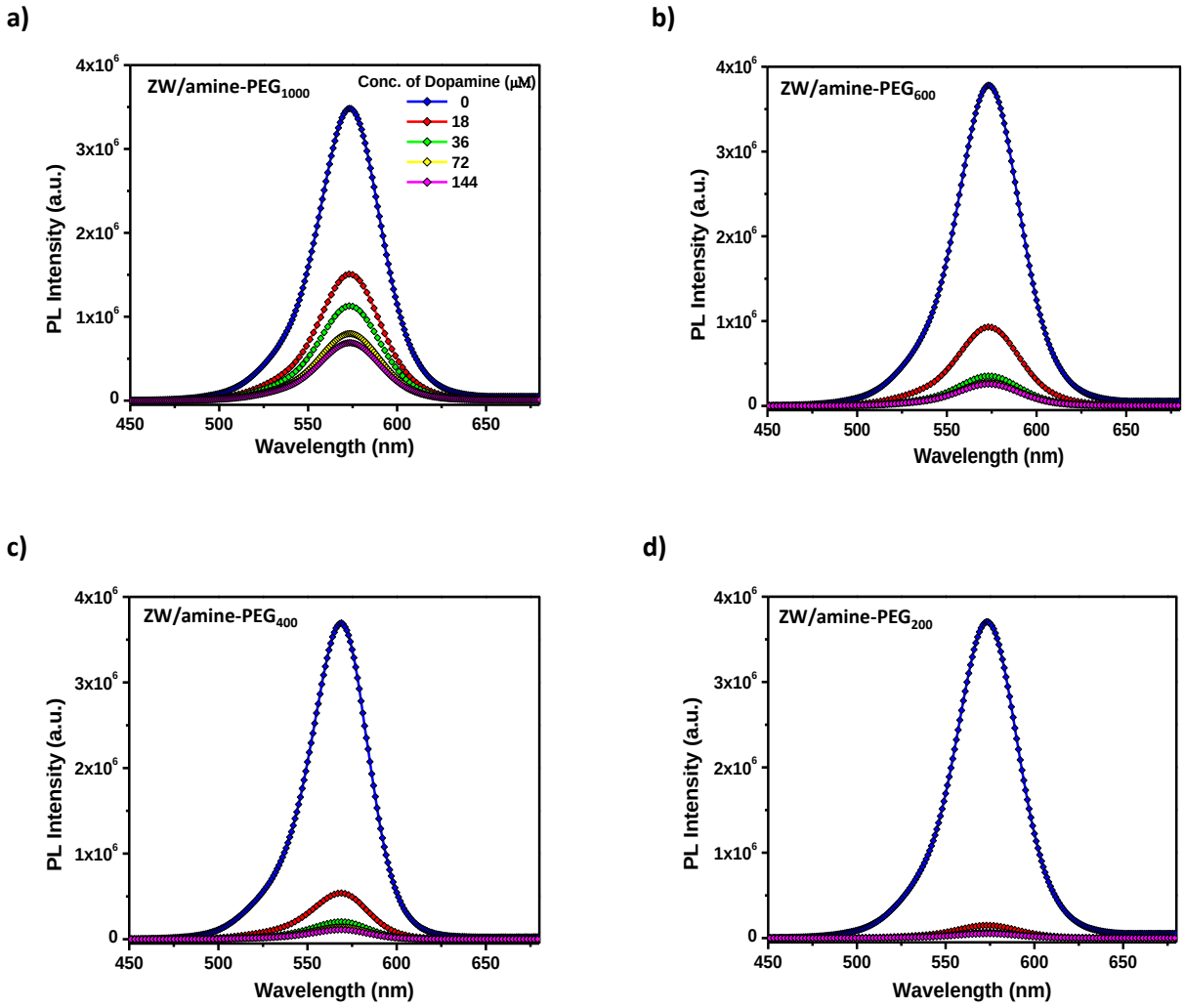


Figure S2. PL spectra collected from yellow-emitting QD-dopamine conjugates prepared using ZW/amine-PEG-QDs dispersed in DI water for increasing molar concentration of dopamine-ITC for (a) PEG_{1000}, (b) PEG_{600}, (c) PEG_{400} and (d) PEG_{200} bridge.

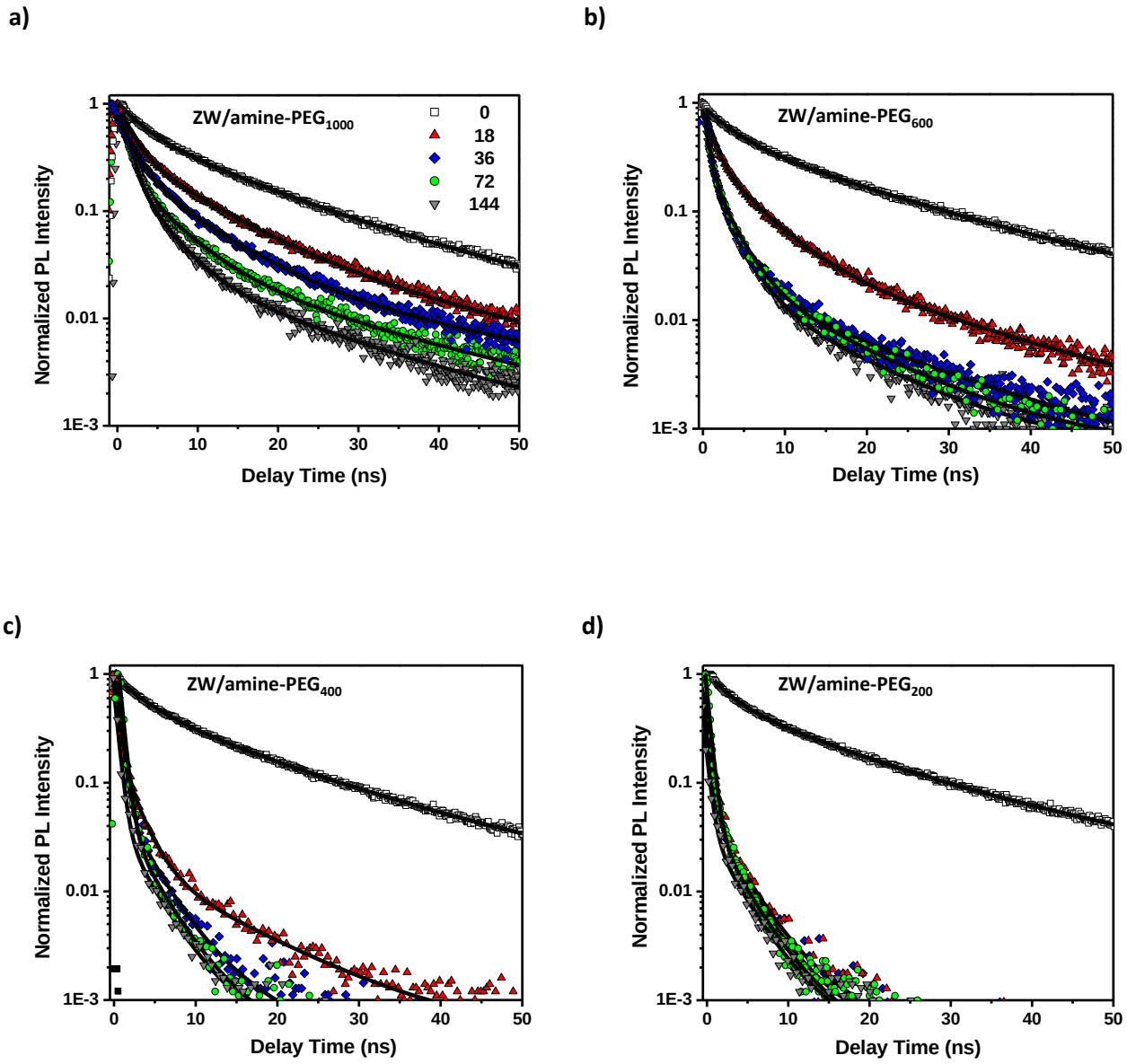


Figure S3. Normalized time-resolved PL decay profiles of yellow-emitting QD-dopamine conjugates prepared using ZW/amine-PEG-QDs dispersed in DI water with increasing the concentration of dopamine-ITC (top to bottom: 0, 18, 36, 72, 144 μM) for (a) PEG_{1000}, (b) PEG_{600}, (c) PEG_{400} and (d) PEG_{200} bridge.

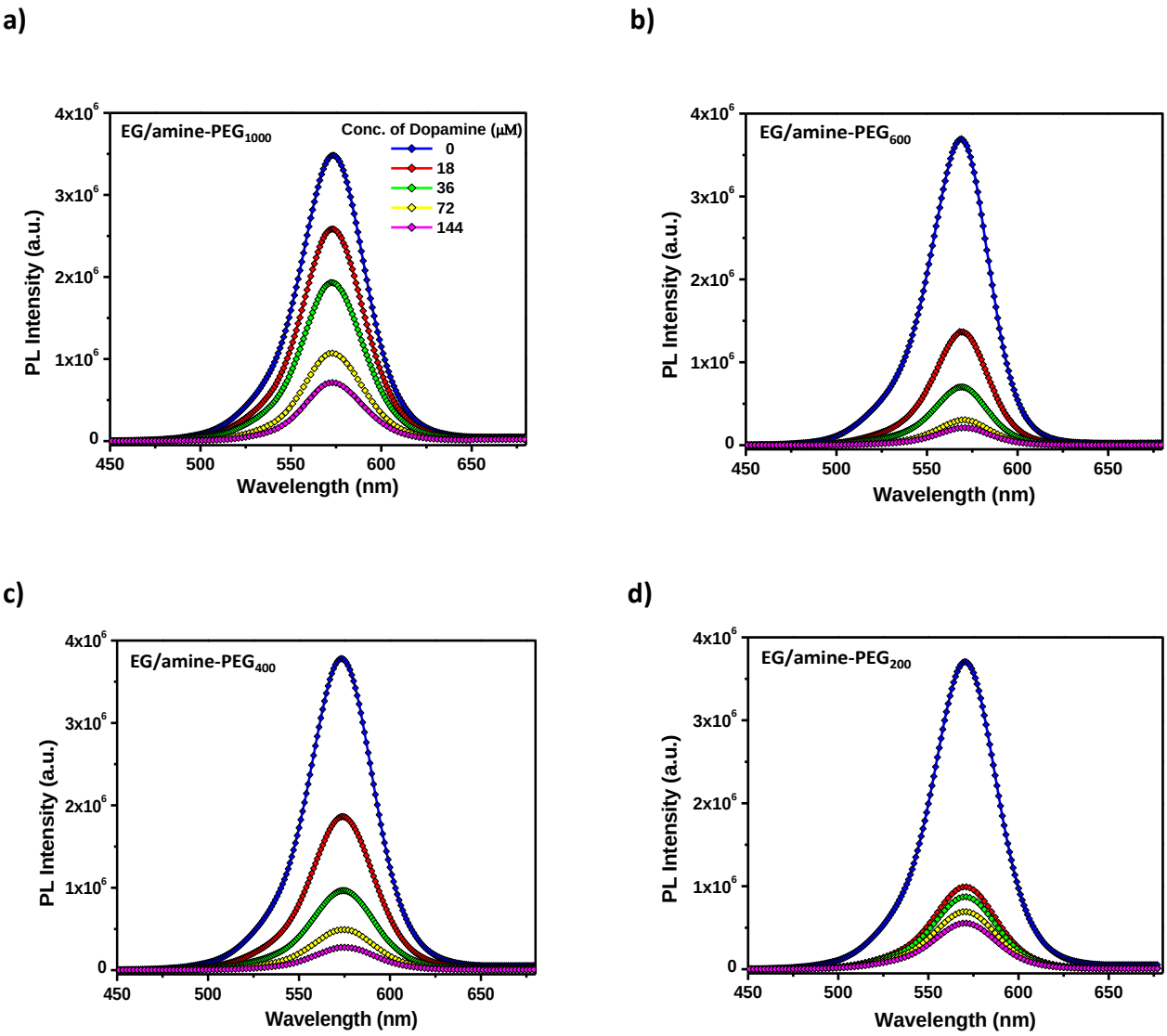


Figure S4. PL spectra collected from yellow-emitting QD-dopamine conjugates prepared using EG/amine-PEG-QDs dispersed in DI water for increasing molar concentration of dopamine-ITC for (a) PEG_{1000}, (b) PEG_{600}, (c) PEG_{400} and (d) PEG_{200} bridge.

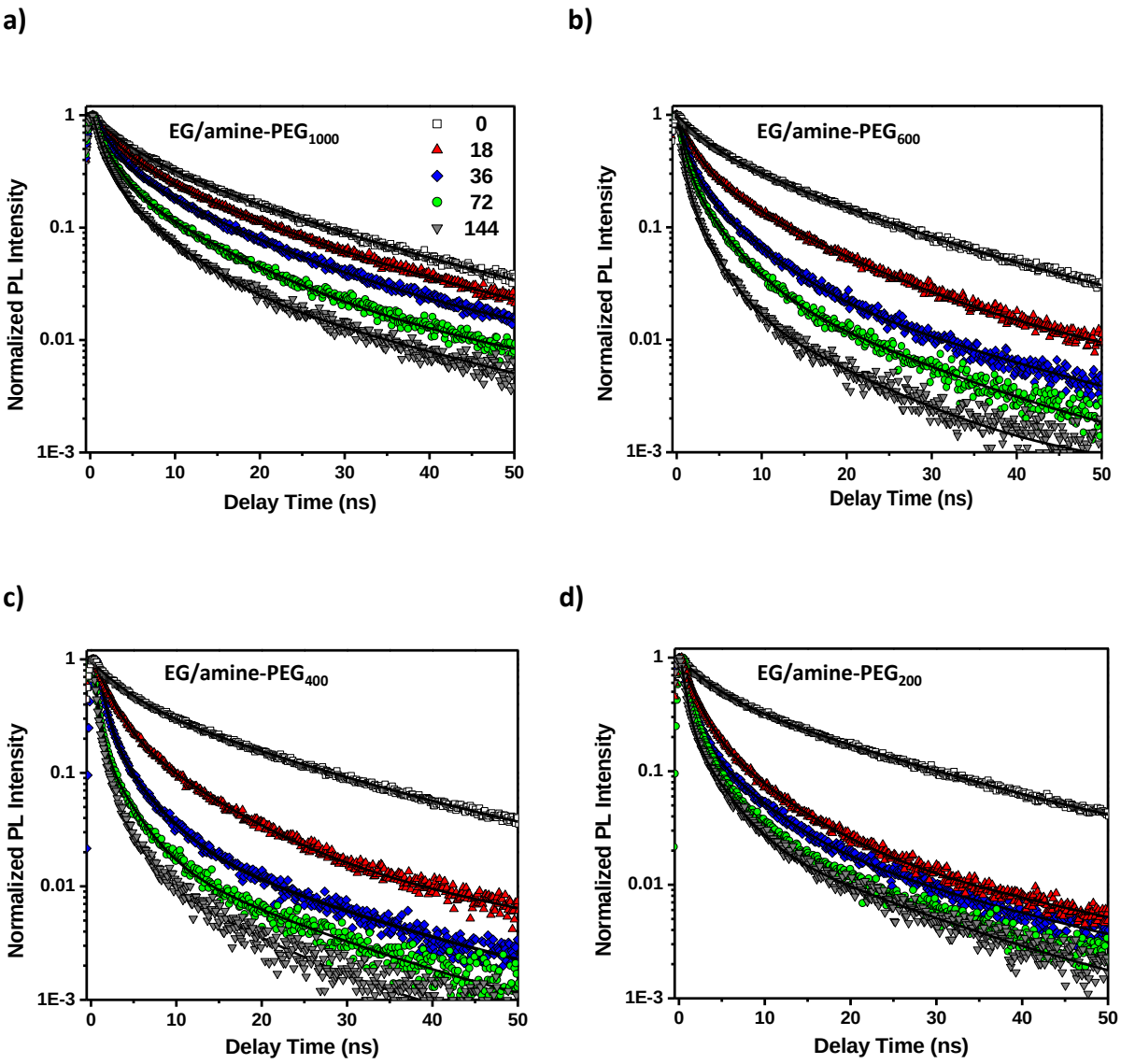


Figure S5. Normalized time-resolved PL decays of yellow-emitting QD-dopamine conjugates prepared using EG/amine-PEG-QDs dispersed in DI water with increasing the concentration of dopamine-ITC (top to bottom: 0, 18, 36, 72, 144 μM) for (a) PEG_{1000}, (b) PEG_{600}, (c) PEG_{400} and (d) PEG_{200} bridge.

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