

Supporting Information

Study of Exciton Transfer in Dense Quantum Dot Nanocomposites

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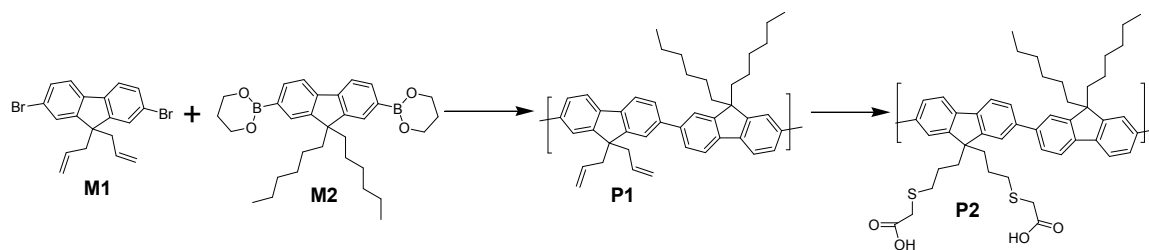


Figure S1. Synthesis of poly[(9,9-bis(propenyl)fluorenyl-2,7-diyl)-co-(9,9-dihexylfluorenyl-2,7-diyl)] (**P1**) and poly[(9,9-bis(carboxymethylsulfonyl-propyl)fluorenyl-2,7-diyl)-co-(9,9-dihexylfluorenyl-2,7-diyl)] (**P2**).

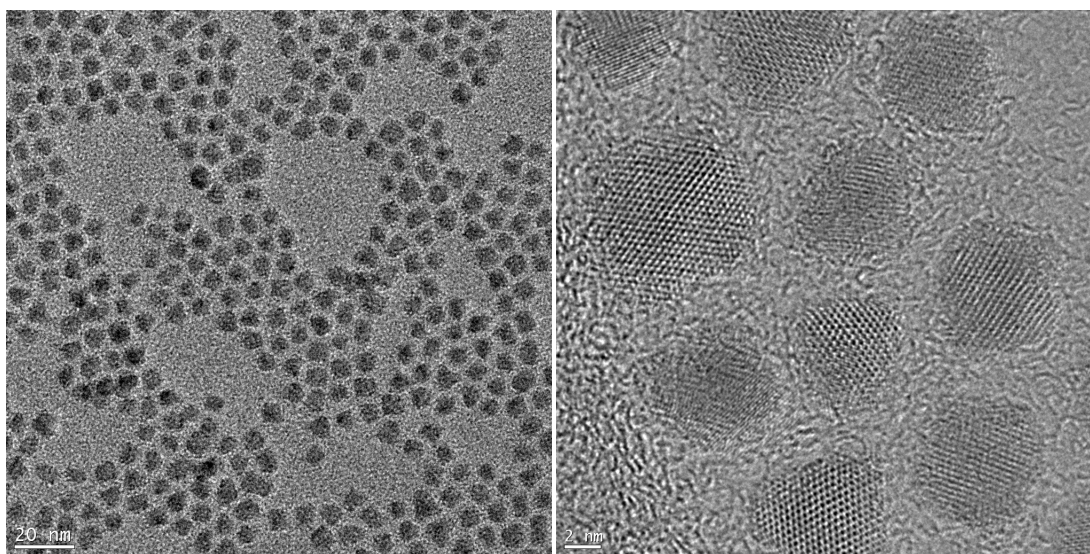


Figure S2. (Left) Transmission electron microscope image of the core/shell QDs. (Right) High resolution TEM image of the same QDs.

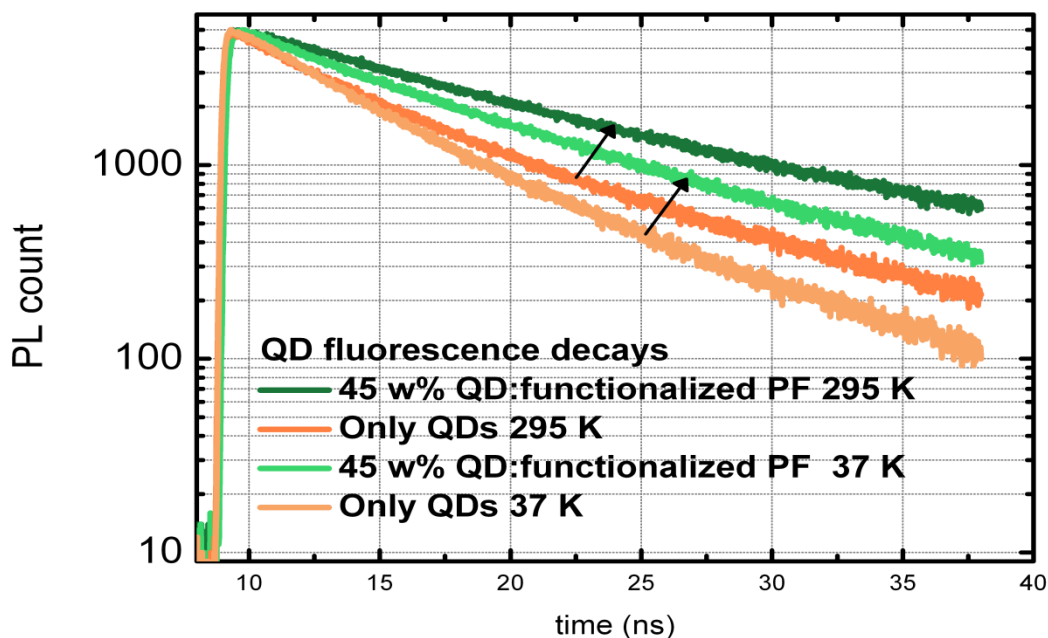


Figure S3. Enhancement of the fluorescence lifetime of the QDs in the functionalized CP-QD nanocomposite for 3 w% and 45 w% QD loading.

XPS study of the nanocomposite and blend

To understand the specific interaction between the functionalized CP and the QDs, XPS measurements were further carried out for samples of QDs alone, functionalized CP-QDs and nonfunctionalized CP-QDs. The peak binding energies of the elemental electronic states of the QDs when alone and when in polymer matrices are tabulated in Table S1. The XPS measurements indicate that the shifts in the peak binding energies are substantially greater in the case of the functionalized CP-QDs as compared to the nonfunctionalized CP-QDs. The maximum shift of ~ 0.65 eV is observed for Zn in the functionalized CP-QDs when compared to QDs alone, whereas the same peak shifts only ~ 0.12 eV for the nonfunctionalized CP-QDs. This observation suggests that there is a strong interaction between the functionalized CP and the surfaces of the QDs, since the QD surfaces are Zn-abundant. Furthermore, the Zn binding peak shifts towards higher binding energies relative to the case of only QDs. This is attributed mainly to the screening effects and high electro-negativity of the oxygen atoms of carboxyl acid moieties in the

functionalized CP.^[1] In comparison, there is no evidence for a strong interaction in the case of nonfunctional CP-QDs, since there are only small shifts in the binding peaks, which is possibly due to the change in the chemical microenvironment of the QDs.

Table S1. XPS results for chemical integration of the polymer with the QDs. Peak binding energies of the elements that constitute a QD tabulated for the cases of QDs alone, functionalized CP-QDs and nonfunctionalized CP-QDs. Shifts in the peak binding energies are also calculated for functional and nonfunctional hybrid nanostructures relative to the case of only QDs.

Elements	Only QDs (eV)	Functionalized CP-QDs (eV)	Nonfunctionalized CP-QDs (eV)	Shift in the peak (functionalized CP) (eV)	Shift in the peak (nonfunctionalized CP) (eV)
Cd	405.18	405.54	405.24	0.36	0.06
Zn	1022.03	1022.68	1022.15	0.65	0.12
Se	53.93	54.58	54.29	0.65	0.36
S	161.9	162.06	161.76	0.16	0.14
O	532.1	532.58	532.26	0.48	0.16

Theory

Loring-Anderson-Fayer (LAF) model

LAF method extends decay kinetics described by Förster theory for the three-dimensional multi-acceptor case. Donor fluorescence decay in the presence of multiple acceptors can be written as Equation S1 [2],

$$I_D(t) = I_0 \exp \left[-\frac{t}{\tau_D} - 2 \left(\frac{\gamma_{DD}}{\sqrt{2}} + \gamma_{DA} \right) \left(\frac{t}{\tau_D} \right)^{\frac{1}{2}} \right] \quad (\text{S1})$$

Where τ_D is the bare donor lifetime of the CP, γ_{DD} is the reduced donor concentration and γ_{DA} is the reduced acceptor concentration. γ_{DD} and γ_{DA} are related to the donor-donor and the donor-acceptor dipole-dipole couplings, respectively. In LAF analysis, α and β factors represent the strength factors for the donor-acceptor and the donor-donor dipole-dipole interactions, respectively.

$$\alpha = \frac{1}{\tau_D} (R_{0A})^6 \quad (\text{S2})$$

$$\beta = \frac{1}{\tau_D} (R_{0D})^6 \quad (\text{S3})$$

where R_{0D} and R_{0A} are Förster radii for the donor-donor and donor-acceptor dipole couplings, respectively. If the strength factor α is much larger than β ($\alpha \gg \beta$), then LAF analysis can be used within the limit of dominant donor-acceptor coupling. Using the measured self-spectral overlap between the emission and absorption spectra of the functionalized CP, the maximum value of R_{0D} is calculated to be up to 2.3 nm. Förster radius for the donor-acceptor coupling, previous reports estimate Förster radius to be 4-7 nm for these CP-QD FRET couples.^[3, 4] Even when the smallest reported value of 4 nm is used as the Förster radius (R_{0A}), the strength of the donor-acceptor coupling is significantly larger than the

strength of donor-donor coupling ($\alpha \gg \beta$). Therefore, γ_{DD} can be neglected. In such case, the donor fluorescence decay in the presence of acceptors is given by

$$I_D = I_0 \exp \left[-\frac{t}{\tau_D} - 2\gamma_{DA} \left(\frac{t}{\tau_D} \right)^{\frac{1}{2}} \right] \quad (\text{S4})$$

Fitting the fluorescence decay curves of the CP using Equation (S4), we obtain the reduced acceptor concentration (γ_{DA}) as a function of temperature. If the donor-acceptor Förster radius ($R_{0,A}$) is given in cm and the acceptor concentration (C_A) is in M (mol/liter), the reduced acceptor concentration γ_{DA} is defined as

$$\gamma_{DA} = \frac{C_A}{C_{0,A}} = C_A \frac{2\pi^{\frac{3}{2}} N R_{0,A}^3}{3000} \quad (\text{S5})$$

where $C_{0,A}$ is the critical acceptor concentration in M (mol/liter) defined by (Ref. ^[26] main text)

$$C_{0,A} = \frac{3000}{2\pi^{\frac{3}{2}} N R_{0,A}^3} \quad (\text{S6})$$

γ_{DA} depends on the actual concentration (C_A) of the QDs, Förster radius for the donor-acceptor coupling ($R_{0,A}$) and the Avogadro's number (N). γ_{DA} can effectively change as a function of temperature since average distance between an exciton in the donor and the acceptor is shortened due to exciton diffusion in the CP. Then, FRET efficiency (η) can be calculated as follows,

$$\eta = 1 - \frac{1}{\tau_D} \int \frac{I_D(t)}{I_0} dt \quad (\text{S7})$$

After integration, the FRET efficiency is given by

$$\eta = \sqrt{\pi} \gamma_{DA} e^{\gamma_{DA}^2} (1 - \operatorname{erf}(\gamma_{DA})) \quad (\text{S8})$$

Gösele model

Gösele model^[5,6] was first developed to predict the energy transfer between chromophores in solution having translational diffusion, which is similar to our case of solid state films with conjugated polymers, where excitons could diffuse through inter- and intra-chain.

In Gösele model, the equation for the donor fluorescence decay that is modified in the presence of acceptor is given by^[7];

$$I_D(t) = I_0 \exp \left[-\frac{t}{\tau_D} - 4\pi D r_F n_A t - 2\gamma_{DA} \left(\frac{t}{\tau_D} \right)^{\frac{1}{2}} \right] \quad (\text{S9})$$

where D is the diffusion coefficient (nm^2/ns), n_A is the density of the acceptors ($\#$ of acceptors/ nm^3), τ_D is the donor fluorescence lifetime (when there is no acceptor), which is experimentally precisely known as a function of temperature, γ_{DA} is the reduced acceptor concentration, which depends on n_A , and $R_{0,A}$.

$$r_F = 0.676 \left(\frac{R_{0,A}^6}{\tau_D D} \right)^{\frac{1}{4}} \quad (\text{S10})$$

Here $R_{0,A}$ is the Förster radius. Reduced acceptor concentration (γ_{DA}) is defined as

$$\gamma_{DA} = 3.712 n_A R_{0,A}^3 \quad (\text{S11})$$

To calculate $R_{0,A}$, we employ quantum yield of the donor functionalized CP, absorbance of the QDs as measured from their thin films and comparing to the known QD concentration and estimate it as 6 nm.

The donor fluorescence lifetime in the presence of acceptor (τ_{DA}) is estimated using the time expected value of the fluorescence decay by Gösele approach (Equation (S9)). The time expected value $\langle \tau_{DA} \rangle$ is

$$\langle \tau_{DA} \rangle = \frac{\int_0^{\infty} t \cdot I_D(t) dt}{\int_0^{\infty} I_D(t) dt} \quad (\text{S12})$$

where I_D is the donor fluorescence decay in the absence of the QDs. After integration of Equation (S12), the expected value of the donor fluorescence lifetime in the presence of the QDs is given by

$$\langle \tau_{DA} \rangle = \frac{\tau_D \left\{ (2\gamma_{DA}^2 + 3x^2)(\sqrt{\pi})\gamma_{DA} \text{Erfc} \left[\frac{\gamma_{DA}}{x} \right] - 2x(\gamma_{DA} + x^2) \exp \left[-\left(\frac{\gamma_{DA}}{x} \right)^2 \right] \right\}}{2x^4 \left\{ (\sqrt{\pi})\gamma_{DA} \text{Erfc} \left[\frac{\gamma_{DA}}{x} \right] - x \exp \left[-\left(\frac{\gamma_{DA}}{x} \right)^2 \right] \right\}} \quad (\text{S13})$$

$$x = \sqrt{1 + 4Dn_A\pi r_F\tau_D} \quad (\text{S14})$$

To cross-check the analysis performed using Gösele approach; using Equation (S12), (S13) and (S14) we calculated the time expected value ($E[\tau_{DA}]$) of the fluorescence decay of the donor functionalized CP, which gives the expected value of the fluorescence lifetime of the donor in the presence of acceptor. In Figure S4, $E[\tau_{DA}]$ is compared with the experimentally measured fluorescence lifetimes as a function of temperature for both QD densities. There is a quite good match between the model as obtained by Gösele approach and the experimental fluorescence lifetimes.

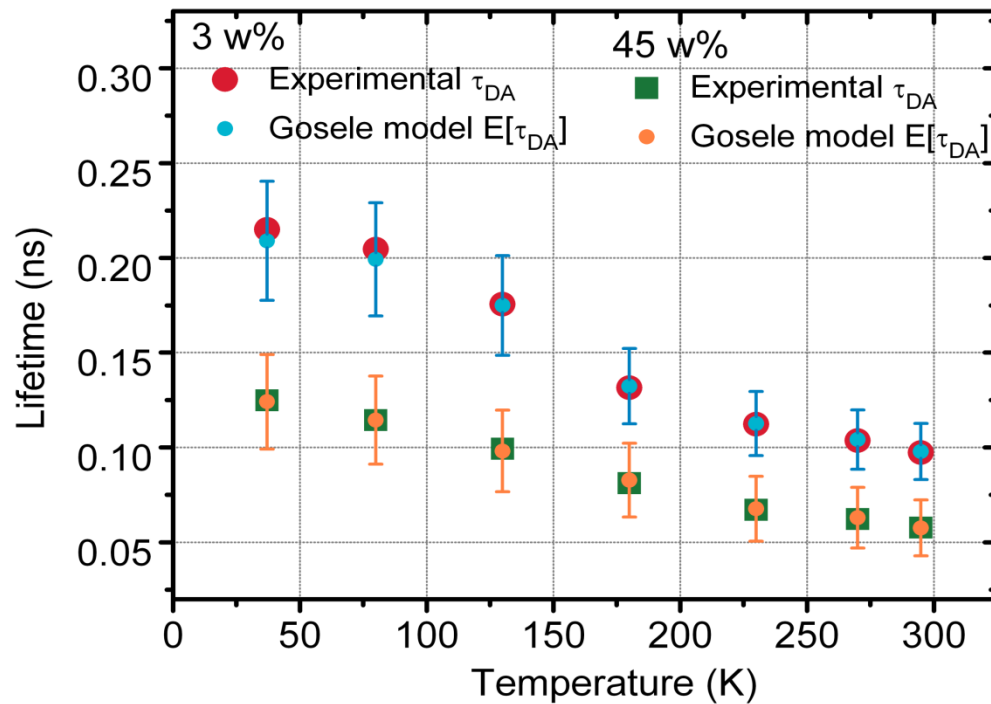
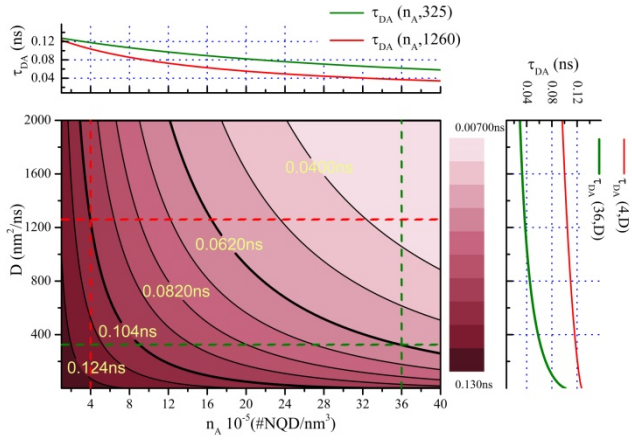
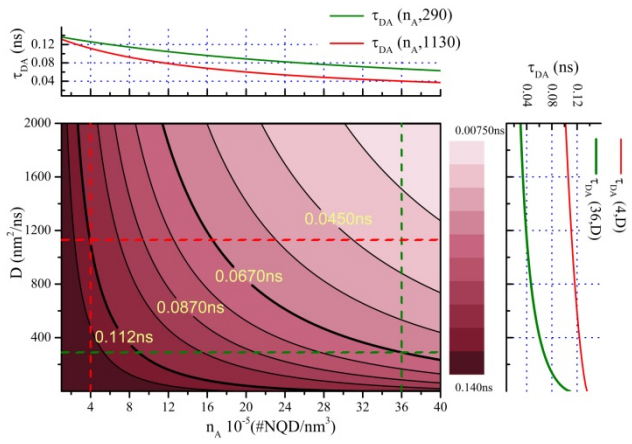


Figure S4. Time expected value of donor functionalized CP fluorescence lifetime in the presence of acceptor (τ_{DA}) is compared with the experimental donor fluorescence lifetime in the presence of low (3 w%) and high (45 w%) QD densities.

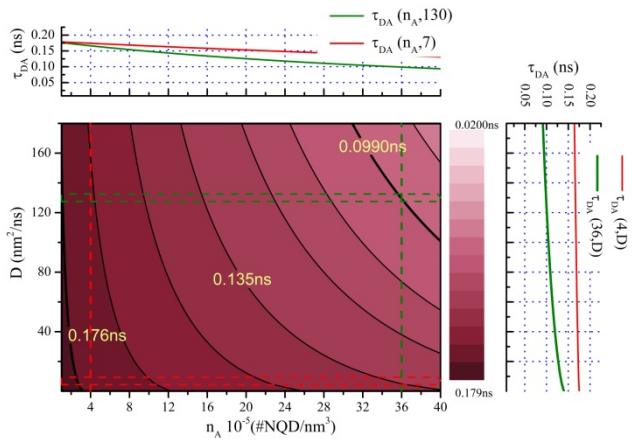
Iso-donor-fluorescence lifetime plots by Gösele model



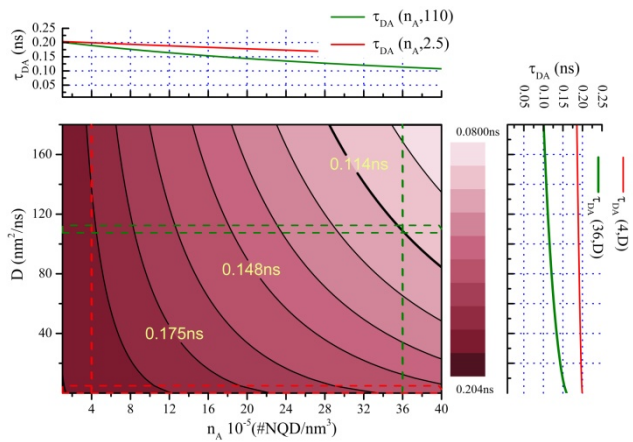
270 K



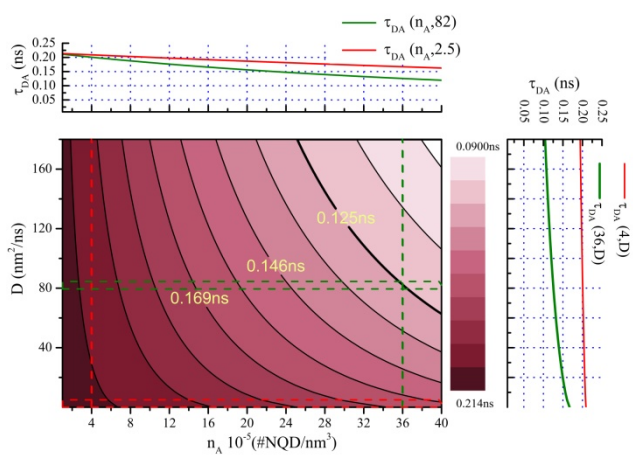
230 K



130 K



80K



37K

Figure S5. Iso- τ_{DA} curves at 270, 230, 130, 80 and 37 K, which were not demonstrated in the main manuscript due to space consideration.

Temperature dependent steady state PL dynamics

At room temperature, both polymer alone and 3 w% loaded hybrid sample exhibits quite broad polymer emission with strong second vibronic emission peak along with the defect emission in the 480-550 nm. However, for the case of high loading of 45 w%, the defect state emission, which appears as a shoulder at 480 and 530 nm is significantly repressed. Moreover, the first vibronic emission peak becomes dominant. This observation indicates the suppression of the exciton diffusion in the highly loaded case at room temperature since the over-population of the defect states and lower energy vibronic emission levels is assisted with the exciton diffusion. At low temperature cases, high energy vibronic peak dominates the spectrum. For the case of high QD loading, the dominant of the high energy vibronic peak is more pronounced.

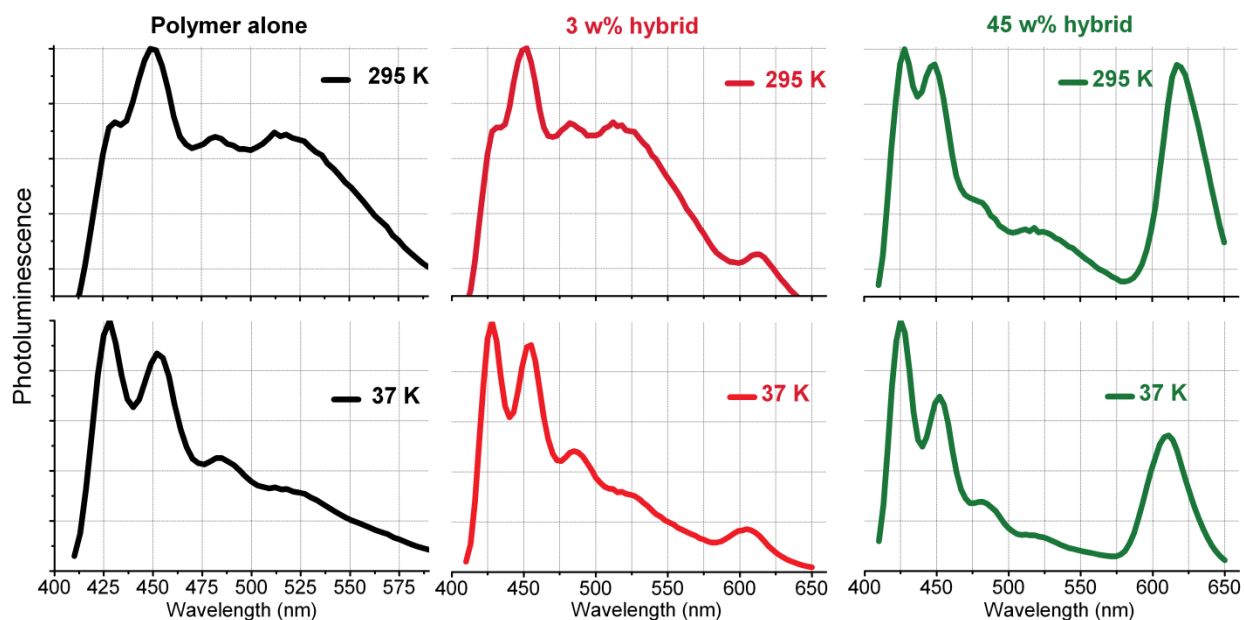


Figure S6. Steady state PLs of the solid state films of functionalized CP alone, 3 w% and 45 w% hybrid at 295 K and 37 K. The changes of the vibronic peaks in the PL spectrum of this polymer indicate the evolution of the exciton diffusion as a function of QD loading. High energy vibronic emission becomes dominant as the QD loading is increased due to the suppression of the exciton diffusion.

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