

## Supporting Information 1

### Chitosan Nanocomposites with CdSe/ZnS Quantum Dots and Porphyrin

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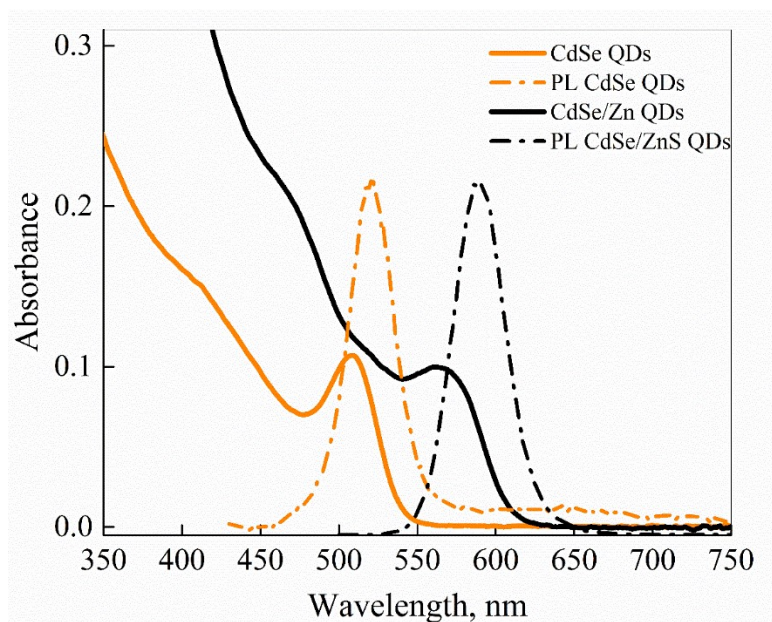


Figure S1. Absorption (solid curves) and PL (dashed curves) spectra of core CdSe QDs and core/shell CdSe/ZnS QDs in CCl<sub>4</sub>. The PL was excited at the wavelength is 417 nm.

The UV–vis absorption and PL spectra of core CdSe and core/shell CdSe/ZnS QDs, as presented in Figure S1. A significant shift in core/shell QDs spectra to longer wavelengths compared to those

of core CdSe QDs is observed. The red shift confirms the formation of shell ZnS on the Core CdSe<sup>1</sup>. The first excitonic absorption band of CdSe QDs is detected at 510 nm, and the average core diameter of CdSe QDs is estimated as  $2.7 \pm 0.3$  nm.

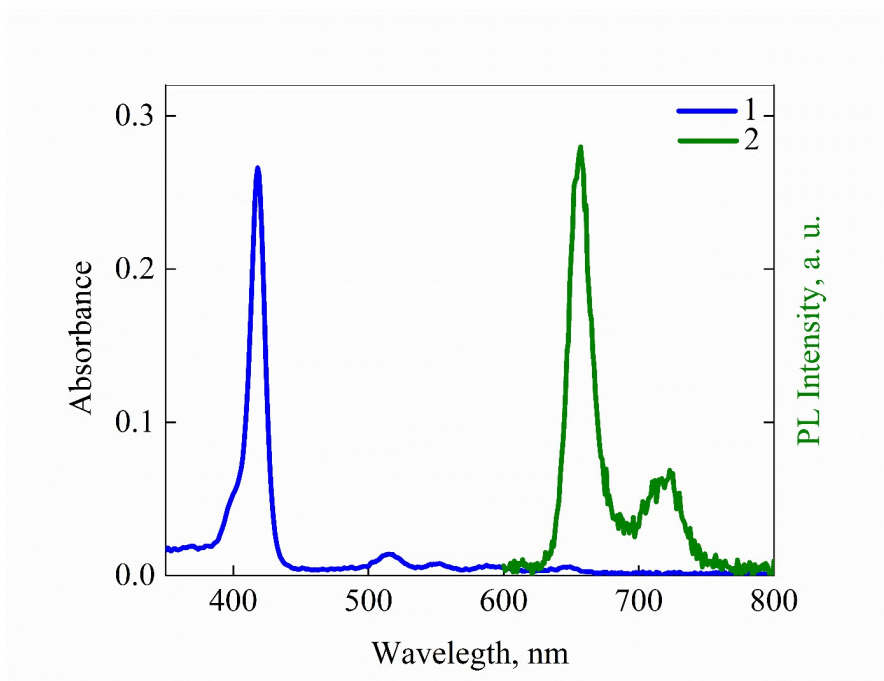


Figure S2. UV-vis (1) and PL (2) spectra of TPP molecules in  $\text{CCl}_4$ . PL excitation wavelength is 460 nm.

As shown in Figure S2, the absorption spectrum of TPP (1) has the strong Soret band with the maximum at 417 nm and four Q-bands centered at 515 nm, 550 nm, 590 nm, and 650 nm, respectively; the red PL spectrum of TPP (2) has the maxima at 649 and 717 nm.

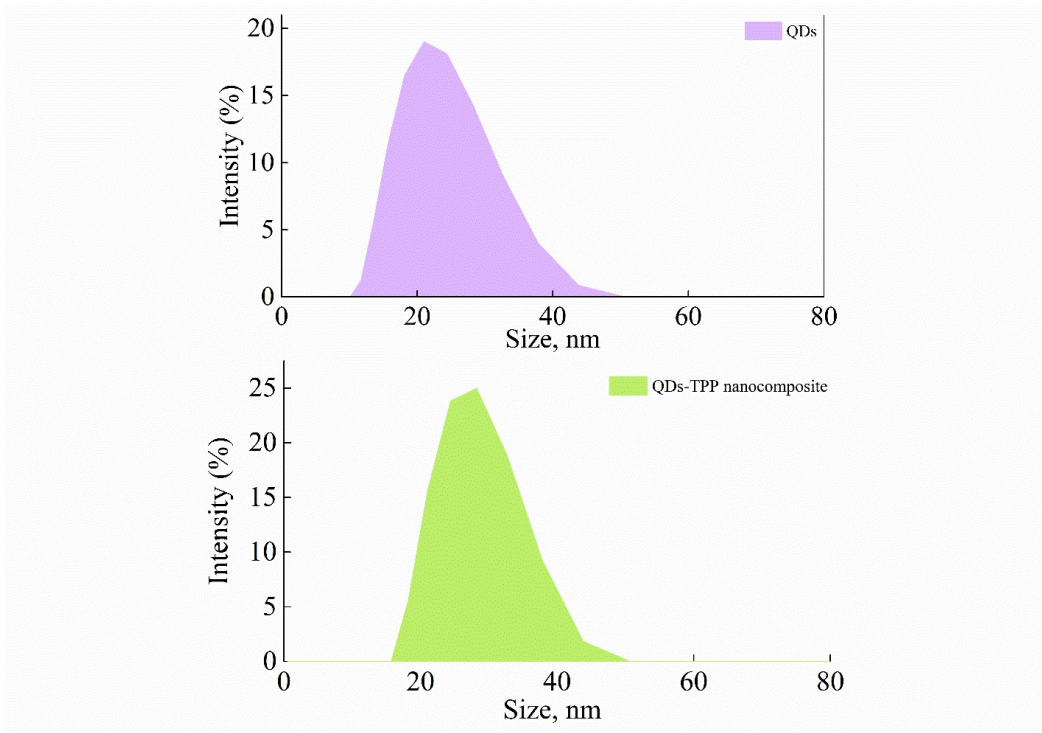


Figure S3. Size distributions measured by dynamic light scattering (DLS) for QDs and QDs-TPP nanocomposite in CS.

As shown in Figure S3, the average diameter of QDs is  $20 \pm 2$  nm, and the average diameter of the QDs-TPP nanocomposite is  $24.5 \pm 2$  nm.

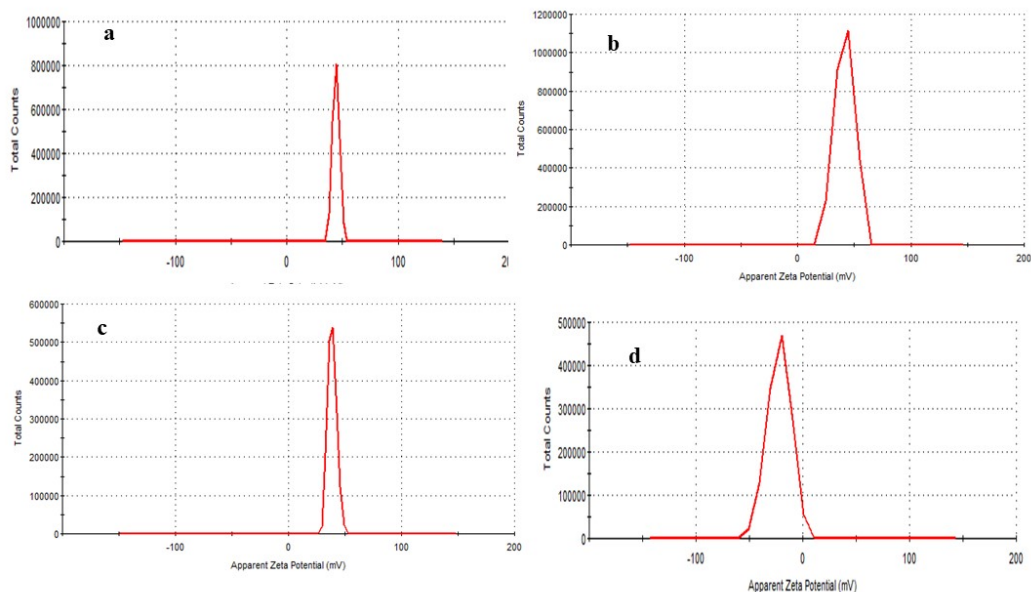


Figure S4. Zeta potential distribution graphs of (a) CS, (b) QDs, (c) QDs-TPP nanocomposite in CS and (d) QDs in water.

The zeta potential values of free CS at pH 5.5, QDs after encapsulation within CS and QDs-TPP-CS nanocomposite are +42 mV, +44 mV, and +39.8 mV, respectively, and zeta potential of free QDs in water is -25 mV, as shown in Figure S4. The zeta potential of the nanocomposite decreased due to TPP molecules aggregates in chitosan solution.

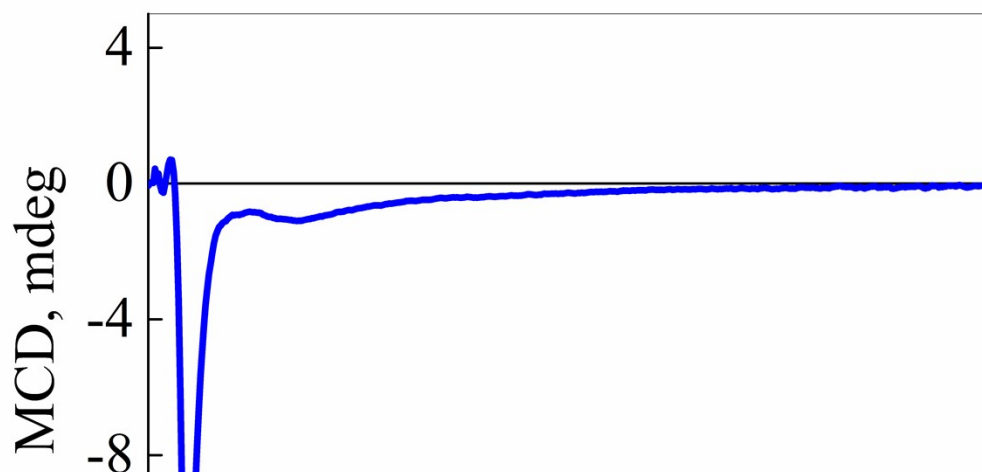


Figure S5. MCD spectrum of CS solution.

MCD spectrum of polysaccharides in an aqueous solution at pH 5.5 has a negative band at 190-250 nm as shown in FigureS5, related to  $n \rightarrow \pi^*$  transition. Therefore, MCD spectra of CS did not overlap with bands of QDs or TPP due to CS transition in the far-UV.

## References

- 1 C. B. Murray, D. J. Norris and M. G. Bawendi, Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites, *J. Am. Chem. Soc.*, 2002, **115**, 8706–8715.

## Supporting Information 2

### Chitosan Nanocomposites with CdSe/ZnS Quantum Dots and Porphyrin

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### The proposed model for the composition of QDs-TPP nanocomposite in chitosan

We demonstrate how the nanocomposites are formed based on QDs and TPP molecules in chitosan solution, as presented in Figure (S1). TPP molecules were found both in a monomeric form and in non-luminescent aggregates, where TPP aggregates lead to a decrease in the FRET efficiency.

Thus, we supposed the following model, which describes the system of the QDs-TPP

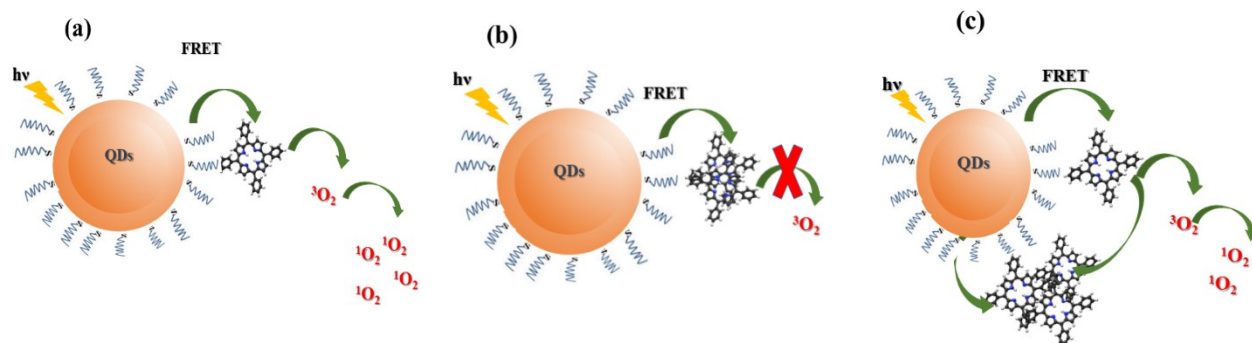


Figure S1: QD-TPP nanocomposite consists of QD with TPP monomer (a) and TPP aggregates (b) as well as with TPP both monomer and aggregates (c).

nanocomposite:

- 1- QDs-TPP nanocomposite is formed as a result of a coordination of TPP molecules on the QDs surface (thiol group of TGA). The QDs-TPP nanocomposites are formed in CS, as presented in Figure S1.
- 2- According to our system, i.e., QDs-TPP nanocomposites, TPP molecules in the nanocomposites can be presented as monomers (Figure S1a) and non-luminescent TPP aggregates. TPP aggregates are formed due to the transfer of TPP molecules from organic to aqueous medium using chitosan biopolymer. TPP aggregated cannot generate singlet oxygen, as presented in Figure S1b.
- 3- In fact, there are two energy donors and two energy acceptors in our system. Firstly, QD is the FRET donor for (i) TPP monomers and (ii) TPP aggregates. Here TPP monomers and their aggregates are FRET acceptors. Only TPP monomers can generate SO. Therefore, FRET from QDs to TPP aggregates competes with FRET from QDs to TPP monomer, leading to decreased SO concentration. Secondly, TPP monomers are FRET donors for TPP aggregates, as shown in Figure S1c.



## Estimation of the extinction coefficient and concentration of TPP aggregates in chitosan solution

Figure S2 shows absorption spectra of the TPP in CCl<sub>4</sub> and CS, which were used to estimate the extinction coefficient of the TPP molecules in CS solution. We can determine the extinction coefficient of TPP at the Soret band in CS according to the general formula (1), where we use FWHM of the Soret band of TPP in CCl<sub>4</sub> and CS. TPP extinction coefficient at the Soret band is  $4.2 \cdot 10^5 \text{ cm}^{-1} \cdot \text{M}^{-1}$  and TPP extinction coefficient in CS equals  $1.31 \cdot 10^5 \text{ cm}^{-1} \cdot \text{M}^{-1}$

$$\varepsilon_{\max}^{\text{CS}} = \varepsilon_{\max}^{\text{CCl}_4} \frac{\Delta\lambda^{\text{CCl}_4}}{\Delta\lambda^{\text{CS}}} \quad (1)$$

We can estimate the concentration of TPP monomers in CS solution using formula (2) by knowing the concentration of TPP monomers in CCl<sub>4</sub>.

$$C_{\text{CS}}^{\text{TPP}} = \frac{\tau_{\text{CS}}^{\text{TPP}} \cdot I_{\text{CS}}^{\text{TPP}} \cdot C_{\text{CCl}_4}^{\text{TPP}}}{\tau_{\text{CCl}_4}^{\text{TPP}} \cdot I_{\text{CCl}_4}^{\text{TPP}}} \quad (2)$$

where  $\tau_{\text{CCl}_4}^{\text{TPP}}$  are PL decay time of the TPP in CCl<sub>4</sub> (8 ns) and  $\tau_{\text{CS}}^{\text{TPP}}$  PL decay time of TPP in CS (5.7 ns), as shown in Figure S3.  $I_{\text{CS}}^{\text{TPP}}$  and  $I_{\text{CCl}_4}^{\text{TPP}}$  are integrated TPP PL intensities in CS, and CCl<sub>4</sub> and  $C_{\text{CCl}_4}^{\text{TPP}}$  is TPP concentration in CCl<sub>4</sub>. The concentration of TPP aggregates can be estimated using formula (3).

$$C_{\text{aggregates}}^{\text{TPP}} = C_{\text{total}}^{\text{TPP}} - C_{\text{monomers}}^{\text{TPP}} \quad (3)$$

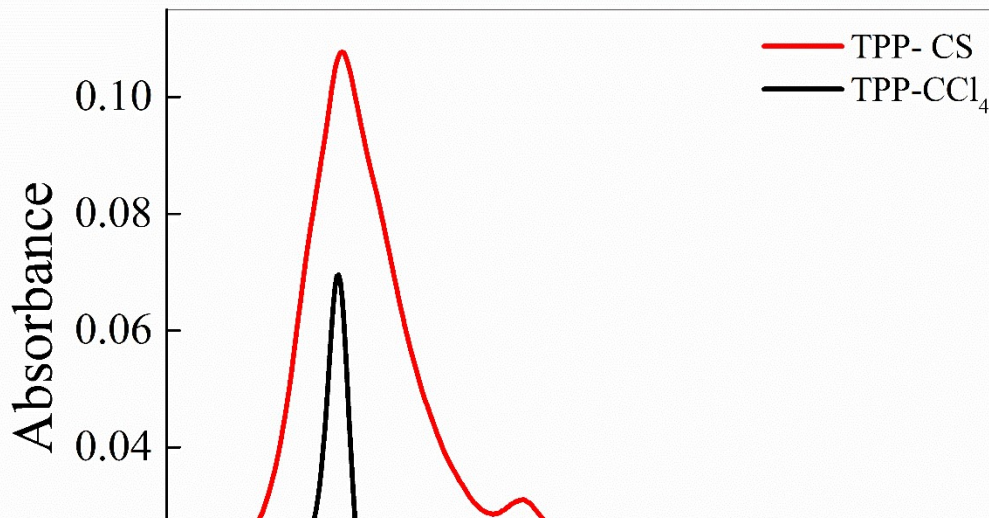


Figure S2. Absorption spectra of TPP in chitosan (CS) solution and  $\text{CCl}_4$ .

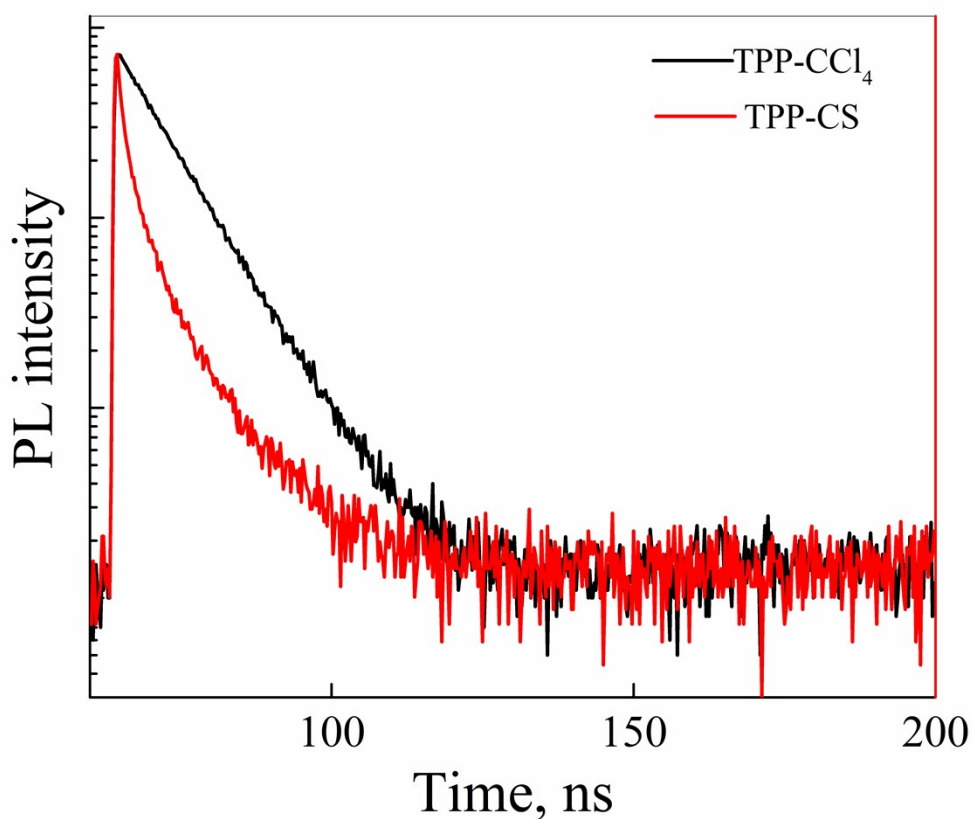


Figure S3. PL decay curves of TPP in  $\text{CCl}_4$  and CS solutions.

Figure S4 shows the PL excitation spectra (PLE) of TPP in  $\text{CCl}_4$  and CS, and we can compare the first absorption band of TPP in both solvents. Also, the FWHM of the first absorption band of TPP (Q band) located at 650 nm in  $\text{CCl}_4$  and CS, was found almost equal in  $\text{CCl}_4$  and CS: about 19 and 20 nm, respectively. It may confirm that the radiative rate doesn't change when transferring



TPP from CCl<sub>4</sub> to CS. In this case, the shortening of TPP PL decay time may indicate the increase in the nonradiative transition rate when TPP is transferring from CCl<sub>4</sub> to CS, as shown in Figure S3.

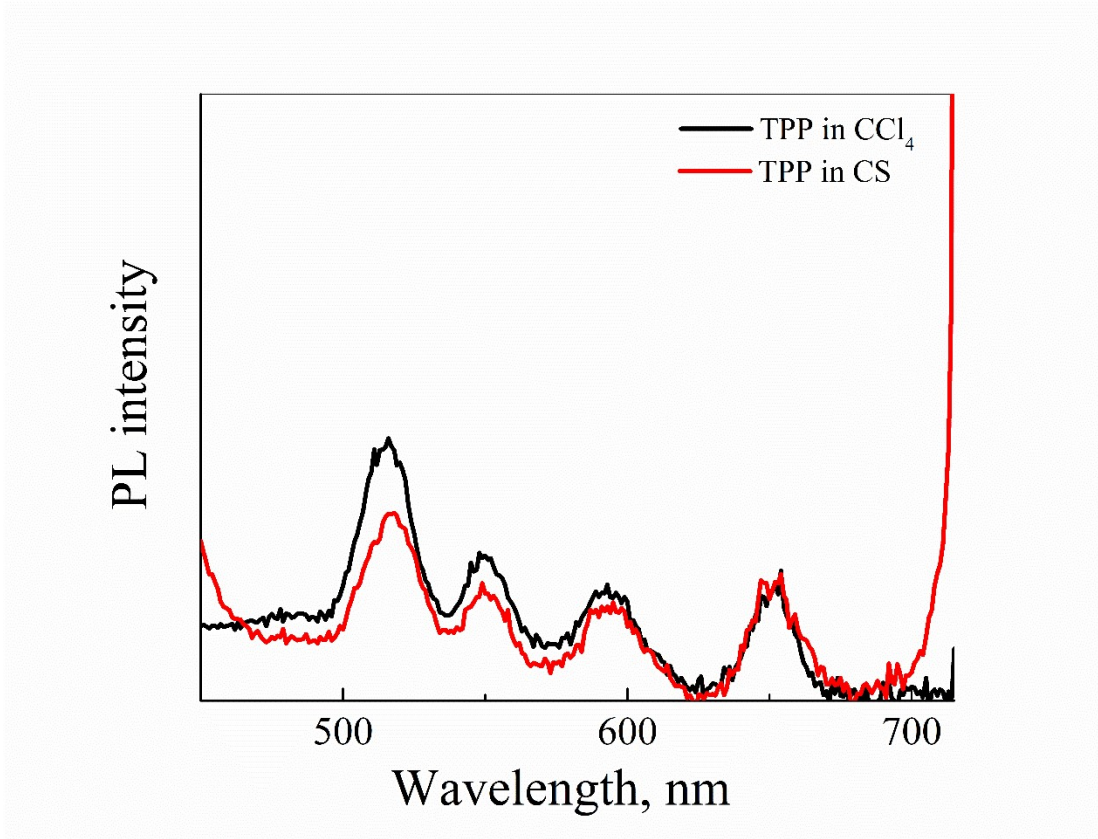


Figure S4. PLE spectra of TPP in CCl<sub>4</sub> and CS. PL registration wavelength is 725 nm.

#### Estimation of FRET efficiency using PL quenching of QDs with TPP in nanocomposites

FRET efficiency can be correctly estimated by experimental data using the following equation:

$$E_{FRET} = \frac{I_{TPP}^{sens} \cdot D_{TPP}^{free}}{D_{QD} \cdot I_{TPP}^{free} \cdot f} \cdot 100\% \quad (4)$$

where  $I_{TPP}^{sens}$  and  $I_{TPP}^{free}$  are the PL intensities of the TPP sensitized in nanocomposite and free TPP, respectively.  $D_{QD}$ ,  $D_{TPP}^{free}$  are the optical densities of donors (QDs) and free acceptors at the PL excitation wavelength (460 nm) and  $f$  is the fraction of QDs associated with TPP monomers. TPP monomers ( $\sim 40\%$  TPP monomers) concentration ( $1.98 \cdot 10^{-7}$  M) and QDs concentration ( $3.1 \cdot 10^{-7}$  M) with  $n \sim 0.5$

The FRET formula (4) was utilized to estimate the energy transfer efficiency in nanocomposites. The FRET efficiency from QDs to TPP is approximately 45 % at the lowest TPP concentration in the samples with  $n = 0.5$ . An increase in the TPP concentration in nanocomposites led to a sharp decrease in FRET efficiency from 45 % to 17%.

### **Estimation of FRET efficiency by indirect way using PL of singlet oxygen generation by QDs-TPP nanocomposite in chitosan solution**

To monitor SO generation, the samples of CS with free TPP and QDs-TPP nanocomposites with a molar ratio of 0.5 and with the same TPP concentration were irradiated with visible light (460 nm) at room temperature, and SOSG PL spectra were measured after each portion of irradiation. FRET efficiency was estimated by PL of SO generation from nanocomposite and free TPP in CS solution. SO is generated only by TPP monomers. Wherefore, we should determine the TPP monomer concentration from total concentration in nanocomposite with QDs. Average FRET efficiency for QD-TPP monomer conjugate in CS estimated with PL intensity of SOSG = **25 %** using the formula (5). The molar ratio ( $n = C_{TPP\ mono}/C_{QDs}$ ) equals 0.5, TPP monomer concentration  $\sim 40\%$  ( $1.98 \cdot 10^{-7}$  M) and QDs concentration ( $3.1 \cdot 10^{-7}$  M), where aggregates TPP concentration  $\sim 60\%$ , indicates that TPP molecules exist in more aggregates than monomers in nanocomposites.

$$E_{FRET} = \frac{\Delta I_{SO}^{sens} \cdot C_{TPP} \cdot \varepsilon_{TPP}}{\Delta I_{SO}^{direct} \cdot C_{QDs} \cdot \varepsilon_{QDs} \cdot f} \quad (5)$$

where  $\varepsilon_{QDs}$ ,  $\varepsilon_{TPP}$  are the extinction coefficients of QDs and TPP, and  $C_{QDs}$ ,  $C_{TPP}$  are the concentrations of QDs and TPP monomer and  $E_{FRET}$  is the FRET efficiency from QDs to TPP.

$\frac{\Delta I_{SO}^{sens}}{\Delta I_{SO}^{direct}}$  is the change in SOSG PL intensity at 530 nm when SO interacts with SOSG sensor.

The FRET efficiency value estimated from QDs PL quenching is twice that estimated from SOSG PL intensity. It means that only TPP monomers can generate SO, and we have energy dissipation in our system.