doi:10.1246/cl.2012.122

Excitation Energy Transfer from Quantum Dots to Porphyrin J-aggregates in Hybrid Langmuir–Blodgett Multilayers

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The distance dependence of the energy-transfer efficiency from a semiconductor quantum dot (QD) layer to a porphyrin J-aggregate layer was investigated using a series of hybridized Langmuir–Blodgett multilayers, where long-range resonance energy transfer with the energy-transfer characteristic length of 13.8 ± 0.6 nm was observed.

Excitation energy transfer (ET) between energy donor–acceptor pairs is a fundamental photophysical process in life and materials science. Over the past years, this process has been very well studied for molecular systems.[1] In recent years, numerous advances have been achieved in quantum dots (QDs)-based ET investigations, regarding both fundamental theoretical analyses and biological applications, including the design of biosensors and the analysis of biomolecular conformation and interaction,[2–9] since QDs possess a variety of advantages over conventional organic dyes, such as high quantum yields, excellent photo- and chemical stability, and size dependent, tunable absorption and emission.[10] On the other hand, reports on excitation ET involving QDs and self-assembled molecular nanostructures are still limited, even though a lot of self-assembled molecular nanostructures exist in biological systems, for example, chlorophyll molecules in the light-harvesting complex.[11] In particular, excitation ET between QDs and J-aggregates[12] has not been reported except for one case,[13–16] in which cyanine dyes constituted the J-aggregates. Zhang et al. demonstrated a highly efficient ET between QDs and cyanine dye J-aggregates in layer-by-layer assembly multilayer thin films and that the direction of the energy flow can be controlled by tuning the spectral properties of the QDs.[13] Bawendi et al. reported efficient ET between QDs and associated cyanine dye J-aggregates in solution.[14–16] However, the distance dependence of ET between QDs and molecular J-aggregates has not been reported to date. In order to clarify the excitation energy transfer between the nanostructures, basic studies concerning geometric properties such as distance or alignment between energy donors and acceptors are important to determine the efficiency of the resonance ET. In this study, we have prepared a series of hybrid inorganic/organic Langmuir–Blodgett (LB) multilayers composed of QDs, polymer nanosheets, and porphyrin J-aggregates to examine the interlayer distance dependence of the resonance energy transfer between the nanostructured materials.

The structure of the LB multilayers is shown in Figure 1. An energy-donor QD monolayer was deposited on a phenyltrimethoxysilane-treated hydrophobic quartz substrate using trioctylphosphine oxide (TOPO)-capped CdSe–ZnS core–shell-structured QDs dispersed in decane by LB method.[17] Poly(*N*-dodecylacrylamide) (pDDA) was used as the spacer material between the energy donor and acceptor. The distance between the QD layer and porphyrin J-aggregate layer was controlled by changing the number of inserted pDDA layers. The thickness of a single layer of pDDA was reported to be approximately 1.7 nm,[18] which was also confirmed by our AFM measurements (Figures S1 and S2[26]). Finally, a tetraphenylporphyrin J-aggregate (TPP-J) LB film, as an energy-acceptor layer, was piled up on the top of the QD/pDDA layers using 25% aqueous sulfuric acid as a subphase by a horizontal contact method.[19]

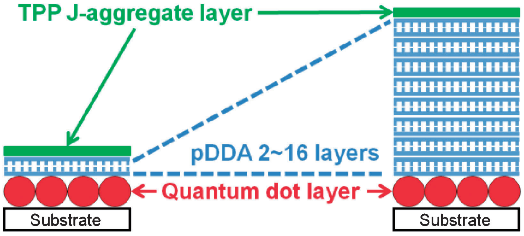

Figure 1. Structure of hybrid inorganic/organic multilayered LB films. The number of inserted pDDA layers (blue) controls the distance between the QD layer (red) and TPP J-aggregate layer (green).

AFM topographical images of QD monolayer, six layers of pDDA on the QD monolayer, and hybrid QD/pDDA 6 layers/TPP-J film are shown in Supporting Information (Figure S3[26]). The morphological characteristic of the QD monolayer shows that QDs distribute homogeneously without formation of aggregative domains. The high-resolution scan and related height profile indicate that QDs are organized as a 2D monolayer and that the ruggedness of the surface of QD layer was less than 2 nm due to soft TOPO alkyl chains around QDs. Although this ruggedness might have some effect on the distance between QD layer and TPP-J layer, the nearest distance between QD centers and TPP-J layer does not change. Also, the ruggedness seems to be averaged by pDDA layers (Figure S3B[26]). Therefore, the effect of the ruggedness is disregarded in this study. However, the surface of pDDA layer is not perfectly flat, and the deviation for distance was estimated and considered in the following studies. An AFM topographical image of TPP J-aggregate layer deposited on substrate is shown in Figure S4.[26] The TPP-J layer thickness was determined to be 2.4 nm from the height profile of the AFM image, which shows good agreement with the size of porphyrin molecule, indicating that the porphyrin rings are aligned vertical to the substrate.

The absorption and emission spectra of the different LB films are shown in Figure 2. The absorption spectrum of the hybrid film QD/pDDA/TPP-J resembles the superposition of the absorption spectra of QD/pDDA and pDDA/TPP-J, which indicates that the structure of the QD layer did not suffer degradation during the deposition of the pDDA layer(s) and

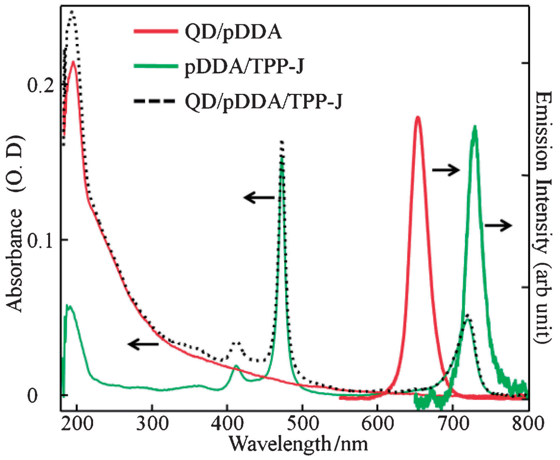

Figure 2. Absorption (thin lines) and emission spectra (thick lines) of the LB films. QDs covered with two pDDA layers (red, QD/pDDA, emission excitation wavelength: 400 nm), two pDDA layers covered with a TPP J-aggregate layer (green, pDDA/TPP-J, emission excitation wavelength: 470 nm), and inorganic/organic multilayered LB films (black broken line, QD/pDDA/TPP-J, absorption spectrum only).

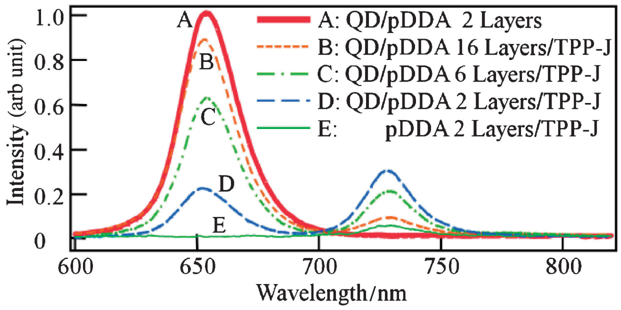

Figure 3. Emission spectra of the hybrid inorganic/organic multilayered LB films.

TPP-J layer. Spectral overlap of the QDs emission and the TPP-J absorption suggests that energy transfer should be energetically possible from QDs to TPP-J.

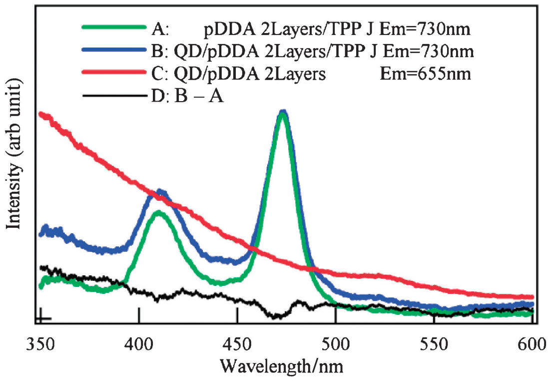

Figure 4. Emission excitation spectra of the LB films: QDs covered with two pDDA layers (red, QD/pDDA), two pDDA layers covered with a TPP J-aggregate layer (green, pDDA/TPP-J), hybridized multilayered LB films (blue, QD/pDDA/TPP-J), and difference spectrum between A and B (black, B − A).

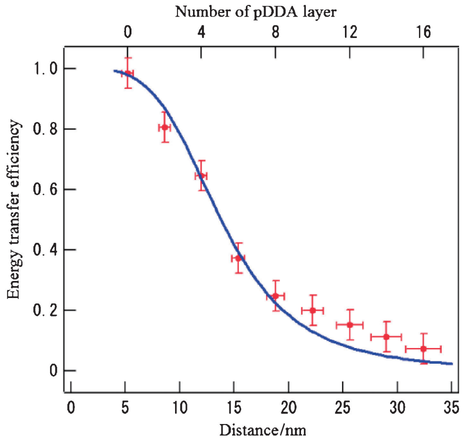

Figure 5. Energy-transfer efficiency plotted against the number of inserted pDDA layers and the distance between the center of QD and TPP J-aggregate layer. Each data point corresponds to an average data of four samples. The error bars for distance were calculated from AFM topographs of pDDA films. The calculated curve (blue line) was obtained from eq 1 with $d_0 = 13.8$ nm.

The emission spectra (excitation wavelength: 350 nm) of the monolayer of QDs covered with two layers of pDDA, several hybrid QD/pDDA n-layers/TPP-J films, and two layers of pDDA covered with a TPP-J layer are shown in Figure 3. In the hybrid film with the double-layered pDDA spacer (Figure 3D), the emission of QDs was quenched by almost 80% relative to that of pDDA/QD (Figure 3A), and the J-aggregate emission around 730 nm became six times higher than that of the pDDA/TPP-J (Figure 3E). This indicates that efficient excitation energy transfer occurs from the QD layer to the TPP-J layer. The intensity of the emission peak (655 nm) originating from the QD layer decreases with decreasing number of pDDA spacer layers. The emission excitation spectra of the monolayer of QDs covered with two layers of pDDA, hybrid QD/pDDA/TPP-J film, and two layers of pDDA covered with a TPP-J layer are shown in Figure 4. The difference spectrum (Figure 4D) between the excitation spectra of QD/pDDA/TPP-J film (Figure 4B) and that of pDDA/TPP-J layers (Figure 4A), which was obtained by monitoring the emission intensity at 730 nm, is similar to the excitation spectra of the QDs (Figure 4C, monitoring the emission intensity at 655 nm). This fact confirms that the energy transfer indeed occurs from the QD layer to the TPP J-aggregates layer in the hybrid LB films. In the case of layer-by-layer assembly,[13] the near-field dipole–dipole coupling between QD and J-aggregate was attributed as the primary mechanism for the excitation energy transfer.

Figure 5 shows plots of energy-transfer efficiency, $\Phi_{\mathrm{ET}} = 1 - I_d/I_0$, versus the estimated distance, d, between the center of the QD and TPP-J layers, where I_d and I_0 are the QDs emission intensities at 655 nm in the presence and absence of the TPP-J layer, respectively. The estimated distance d was calculated by $d = [4.0 + (N_{\mathrm{pDDA}} \times 1.7) + 1.2]$ nm: the radius of CdSe–ZnS/TOPO QDs is 4.0 nm, where the radius of core (CdSe), the thickness of ZnS shell and TOPO are estimated to be 3.0, 0.3, and 0.7 nm, respectively.[20] N_{pDDA} is the number of inserted pDDA layers, and 1.7 is the thickness of one pDDA layer. The middle of the TPP-J layer was thought as the center of acceptor layer, 1.2 nm is the distance from the edge of TPP-J layer to the middle of the layer. The efficiency (Φ_{ET}) values decrease with increasing the number of inserted pDDA spacer layers and the estimated distance (d). Kuhn et al. reported excitation energy-transfer efficiency between two kinds of cyanine dyes,[21] and discussed the efficiency dependence on the donor–acceptor interlayer distance by using a model of a single dipole of donor in the proximity of a thin acceptor layer.[22] In the case wherein the acceptor layer interacts only with the polarization electric-field component oscillating in the plane of the layer, the interlayer distance dependence of energy-transfer efficiency is given by eq 1:

$$\Phi_{\mathrm{ET}} = 1 - I_d/I_0 = 1/(1 + (d/d_0)^4) \qquad (1)$$

In this system, Φ_{ET} is the averaged energy-transfer efficiency from the QDs to the porphyrin J-aggregate layer, d is the separation distance between the center of the QD and J-aggregate layers, and d_0 is the energy-transfer characteristic length, defined by eq 2:[13,22]

$$(d_0)^4 = (4\pi)^{-4}(3/2)^3 n^{-4} q^{\mathrm{QD}} \int \lambda^4 A^{\mathrm{J}}(\lambda) f^{\mathrm{QD}}(\lambda)\mathrm{d}\lambda \qquad (2)$$

in which n is the refractive index of the media (pDDA LB film), q^{QD} is the emission quantum yield of QDs, $A^{\mathrm{J}}(\lambda)$ is the absorption spectrum of the porphyrin J-aggregate acceptor layer upon normal incidence, $f^{\mathrm{QD}}(\lambda)$ is the normalized emission spectrum of QDs. By assuming $n = 1.5$ and $q^{\mathrm{QD}} = 0.75$,[23] the value of d_0 is calculated to be 12 nm for the present case. Also d_0 is defined as the distance which yields 50% probability of energy transfer; that is, $I_d/I_0 = 0.5$. The experimental energy-transfer characteristic length value d_0 in the present system was 13.8 ± 0.6 nm, which is longer than the calculated value of 12 nm. As shown in Figure 5, the blue curve was obtained from eq 1, which contains experimental energy-transfer characteristic length 13.8 nm as d_0, the experimental data (red dots) correlates well with the calculated curve (blue curve). To make the relationship more clear, the distance dependence of energy-transfer efficiency between QD and porphyrin J-aggregate layer is plotted in the form of $\ln(\Phi_{\mathrm{ET}}^{-1} - 1)$ versus $\ln(d)$ (Figure S5).[24,26] The experimentally observed distance dependence of the transfer efficiency is in agreement with the negative four power dependence predicted by Kuhn in the layer-to-layer donor–acceptor system. We found that the energy transfer between the QD layer and the TPP J-aggregate took place over longer distances than previously reported for two cyanine dyes,[21] in which the d_0 was less than 8.5 nm. Referring to eq 2, a large absorption coefficient of TPP J-aggregate and the relatively higher emission quantum yield of QDs cause a longer interlayer energy-transfer characteristic length between QD and TPP-J layers. However, eq 2 is described with a point–dipole approximation, donor in the proximity of a thin acceptor layer, and disregarding the coherent interaction between donor and acceptor. In nanostructured systems, such approximation has a potential of large error,[9] derived from large dipole moment of the QDs[25] or exciton delocalization of the J-aggregates.[12] The long-range resonance energy transfer from the QD layer to the TPP J-aggregates layer in the hybrid LB films indicates such possibility.

In summary, the distance between QDs and J-aggregates in the hybrid LB films was controlled by changing the number of inserted pDDA nanosheet layers. Highly efficient energy transfer between QD and TPP-J layers has been accomplished where long-range resonance energy transfer with the energy-transfer characteristic length of 13.8 ± 0.6 nm was observed. The distance is much longer than those observed for molecule-base systems.

This work was supported by "Post-silicon Solar Cells for Ultra-high Efficiencies," by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

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