Supporting Information for

"Variations in Photoluminescence Intensity of a Quantum Dot Assembly Investigated by Its Adsorption on Cubic Metal–Organic Frameworks"

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Figure S1. Illustration of metal–organic framework (MOF)-5 along the (100) plane exhibiting the chemical connection points. The green, orange, and gray parts represent carbon, zinc, and oxygen atoms, respectively.



Figure S2. (a, c, e) Ultraviolet–visible (UV–Vis) and photoluminescence (PL) spectra and (b, d, f) transmission electron microscopy (TEM) images of (a, b) QD440, (c, d) QD525, and (e, f) QD612. The samples were dispersed in dimethylformamide (DMF) for the optical measurements. The excitation wavelength was 360 nm for the PL spectra, and the inset photograph of each sample was obtained under UV irradiation.



Figure S3. TEM images of the nanosized cubic MOF-5: (a) overall and (b) magnified images. The samples were synthesized by adding the MOF-5 precursors dropwise into DMF with a modulating ligand.



Figure S4. Schematic of the probable chemical interaction between quantum dots (QDs) and the nanosized cubic MOF-5. QDs can be easily adsorbed on the surface of MOF-5 via covalent bonds between the zinc atoms (QDs) and carboxylic acid (MOF-5).



Figure S5. (a) Powder XRD patterns of pristine nanosized cubic MOF-5 (blue line) and QD-supported MOF-5 (green and red lines) compared to the simulated pattern of MOF-5 (black line). (b) Magnified XRD pattern of QD-supported MOF-5 (red) and pattern of QD525 only.



Figure S6. Photographs of QD-supported MOF-5 under (a) room and (b) UV lights. The samples were prepared by adsorbing 50 µL of QDs (QD440, QD525, or QD612) on cubic MOF-5 crystals.

Calculation of scattering intensity:¹

The wavelength dependent scattering profiles were calculated by the combined model of Rayleigh scattering and Rayleigh–Gans–Debye (RGD) scattering, in which the latter describes the scattering by colloids that are slightly larger than the coverage of Rayleigh scattering. In their report, transmission of the scattering material in the absence of molecular absorption is described by

$$T = T_{\text{Ray}} \times T_{\text{RGD}} \tag{S1}$$

where T_{Ray} and T_{RGD} are the transmission by Rayleigh and RGD scatterings, respectively. Each component can be written by

$$T_{\rm Ray} = \exp\left(-K_{\rm Ray}^4 \lambda^{-4} l\right) \tag{S2}$$

$$T_{\rm RGD} = \exp\left(-K_{\rm RGD}^2 \lambda^{-2} l\right) \tag{S3}$$

by using the parameters to encode the geometry of Rayleigh and RGD scatterings (K_{Ray} and K_{RGD}), wavelength (λ), and optical path length (l). Absorbance can be described as

Abs =
$$-\log_{10} T = -\frac{\ln T}{\ln 10} = -\frac{-K_{\text{Ray}}^4 \lambda^{-4} l - K_{\text{RGD}}^2 \lambda^{-2} l}{\ln 10}$$
 (S4)

When K_{Ray} and K_{RGD} are approximated to be constant over the wavelength range of measurement, the equation can be simplified as

$$Abs = A\lambda^{-4} + B\lambda^{-2} \tag{S5}$$

by using constants A and B.

The extraction of optical absorption components from the spectra of QDs adsorbed on MOF-5 that contain intense scattering features (Figure 3a–3d, main text) was performed by predicting wavelength dependent scattering. Briefly, the three absorption profiles of different QDs (50 μ L) that were adsorbed on MOF-5 were fitted with Eq. S5 with wavelength constraints applied to exclude the range of QDs' absorption (typically 500–850 nm for QD440, 580–850 nm for QD525, and 650–850 nm for QD612). As a result, the fitting curves giving perfect matching with the experimental data in the region of constraints were obtained (Figure S7, solid blue curve). Thereafter, the curves were extrapolated down to 350 nm, which is the scattering profile calculated based on Eq. S5. The subtraction of measured curves (solid red) by calculated curves (solid blue) clearly represented the absorption features of the QDs (solid green), which revealed that the QDs were intact after they were adsorbed on MOF-5 at highest concentration.



Figure S7. (red lines) Absorption, (blue lines) calculated scattering, and (green lines) differential spectra for (a) QD440, (b) QD525, and (c) QD612 that were adsorbed on MOF-5 at 50 μ L. Wavelength dependent scattering curves were calculated by fitting absorption spectra in the spectral ranges that were irrespective of QDs with Eq. S5.



Figure S8. (a, d) Normalized PL spectra of QD440, (b, e) QD525, and (c, f) QD612 that were (a, b, c) densely supported on cubic MOF-5 crystals and (d, e, f) spin-coated on glasses. The dotted lines in each figure show the PL spectrum of the sample that was dispersed in DMF. The excitation wavelength was 390 nm for the PL spectra.

Sample	QD amount	PL peak	A_1	$ au_{ m l}$	A_2	$ au_2$	<7>	2
	(µL)	(nm)		(ns)		(ns)	(ns)	χ
QD440	10	440	0.49	3.28	0.51	11.43	9.66	1.10
	30	440	0.60	4.19	0.40	13.58	10.57	1.18
	50	440	0.62	4.60	0.38	13.93	10.62	1.19
QD525	10	525	0.60	1.08	0.40	8.21	7.00	1.14
	30	525	0.65	1.12	0.35	7.55	6.15	1.02
	50	525	0.74	0.76	0.26	6.14	4.75	1.10
QD612	10	612	0.38	3.02	0.62	18.46	17.06	1.13
	30	613	0.31	3.65	0.69	19.10	17.86	0.99
	50	612	0.33	6.00	0.67	18.82	17.08	1.06

Table S1. Fitting parameters for the PL decay curves of several quantum dots (QDs) (QD440, QD525, and QD612) that were adsorbed on the surface of the cubic metal–organic framework (MOF)-5 crystals shown in Figures 5a–c

Förster resonance energy transfer (FRET) Analysis:²

The Förster distance (R_0) is described by Eq. S1:

$$R_{\rm o} = \left(\frac{9(\ln 10)\kappa^2 \eta_{\rm D}}{N_{\rm A} 128\pi^5 n^4} J\right)^{1/6},\tag{S6}$$

where, κ , η_D , N_A , and n are the relative orientation of the dipoles between the donor and acceptor, the PL QY of the donor, the Avogadro number (mol⁻¹), and the refractive index of the medium (DMF in this case), respectively. $\kappa^2 = 2/3$ was used since the positional relationship between the donor and the acceptor was random. J is the factor that represents the magnitude of the spectral overlap between the PL of the donor and the absorption by the acceptor, which is generally described with M⁻¹cm⁻¹nm⁴ unit. When the Avogadro number and J (M⁻¹cm⁻¹nm⁴) = 10¹⁷ × J(mol⁻¹nm⁶) were applied, Eq. S1 could be simplified as follows:

$$R_0 = 0.0211 (\kappa^2 \eta_D n^{-4} J)^{1/6} [\text{nm}].$$
(S7)

The essence of *J* is as follows:

$$J = \int_0^\infty f_{\rm D}(\lambda) \varepsilon_{\rm A}(\lambda) \lambda^4 d\lambda \,, \tag{S8}$$

where, $f_D(\lambda) \text{ [nm}^{-1]}$ is the normalized emission spectrum of the donor as a function of λ , which is described as $f_D = F_D(\lambda) / \int F_D(\lambda) d\lambda$ utilizing the PL spectrum, $F_D(\lambda)$. $\varepsilon_A(\lambda) \text{ [M}^{-1}\text{cm}^{-1]}$ is the molar absorption coefficient of the acceptor as a function of λ [nm]. $\varepsilon_A(\lambda)$ of QDs was calculated by treating one core/shell QD as a large molecule.

Homo-FRET of quantum dot system:

According to the theory of homo-FRET (homotransfer) established by T. Förster^{3, 4}, the occurrence of homo-FRET is undetectable with both PL decay and PL quantum yield measurements, and only the loss of fluorescence anisotropy is observed for specific fluorophores.⁵ However, it has recently been revealed (as well as in this paper) that homo-FRET changes PL intensity of quantum dot clusters due to an energy migration to dark particles. Herein, the variations of PL decay curve and quantum yield are discussed under the assumptions that there is homotransfer between particles and there are dark particles that is nonluminescent, only-absorbing particles.



Figure S9. Four model cases depicting the configuration of QD ensemble. (Case I) Isolated particles are pulse excited, (Case II) two particles make pairs in ensemble and one of the two particles are pulse excited, (Case III) one bright particle and one dark particle form pairs in ensemble and bright particles are pulse excited, and (Case IV) two bright and one dark particles are aligned in close and the bright particle at end is pulse excited. Initial exciton number is N(0).

Case I

When a QD ensemble in which each of them is electrically isolated is irradiated and N(0) particles are moved to the excited state (single exciton for each particle), the number of the excited QDs after the time t, N(t), can be written as

$$\frac{dN(t)}{dt} = -N(t)(k_{\rm f} + k_{\rm nr}) \tag{S9}$$

where $k_{\rm f}$ and $k_{\rm nr}$ are the rates for radiative and non-radiative recombination, respectively. The solution of the differential equation, Eq. S9, is

$$N(t) = N(0)\exp\{-(k_{\rm f} + k_{\rm nr})t\}$$
(S10)

By introducing PL lifetime $\tau = (k_{\rm f} + k_{\rm nr})^{-1}$, the Eq. S10 can be recast as

$$N(t) = N(0)\exp\left(-\frac{t}{\tau}\right)$$
(S11)

Therefore, the PL decay curve of this QD is

$$I_1(t) = k_f N(t) = k_f N(0) \exp\left(-\frac{t}{\tau}\right)$$
(S12)

PL intensity is

$$F_{1} = \int_{0}^{\infty} I_{0}(t)dt = \int_{0}^{\infty} k_{f} N(0) \exp\left(-\frac{t}{\tau}\right) dt = k_{f} N(0)\tau = \frac{k_{f}}{k_{f} + k_{nr}} N(0)$$
(S13)

Since N(0) is the initial number of photoexcited QDs, $\frac{k_f}{k_f + k_{nr}}$ is regarded as PL quantum yield.

<u>Case II</u>

When two identical QDs that are expedientially labeled as j and k form pairs in an ensemble, and if only the particle labeled as j in the pairs are photoexcited to generate N(0) particles in excited state, two differential equations are generated.

$$\frac{dN_j(t)}{dt} = -\frac{N_j(t)}{\tau} - k_{\rm ret}N_j(t) + k_{\rm ret}N_k(t)$$
(S14)

$$\frac{dN_k(t)}{dt} = -\frac{N_k(t)}{\tau} - k_{\rm ret}N_k(t) + k_{\rm ret}N_j(t)$$
(S15)

where $N_j(t)$ and $N_k(t)$ are the number of excited QDs at time t for the directly photoexcited particle (j)and the nearby particle (k), k_{ret} is the rate for Förster energy transfer. Note that k_{ret} is identical for forward and backward energy transfer due to the nature of homotransfer. When the boundary conditions of $N_j(0) =$ N(0) and $N_k(0) = 0$ are applied, the solution of the simultaneous differential equations, Eq. S14 and Eq. S15 becomes

$$N_{j}(t) = \frac{N(0)}{2} \exp\left(-\frac{t}{\tau}\right) \{1 + \exp(-2k_{\text{ret}}t)\}$$
(S16)

$$N_k(t) = \frac{N(0)}{2} \exp\left(-\frac{t}{\tau}\right) \{1 - \exp(-2k_{\rm ret}t)\}$$
(S17)

Therefore, the PL decay curves for the QDs labeled with *j* and *k* becomes

$$I_{j}(t) = k_{\rm f} N_{j}(t) = \frac{k_{\rm f} N(0)}{2} \exp\left(-\frac{t}{\tau}\right) \{1 + \exp(-2k_{\rm ret}t)\}$$
(S18)

$$I_k(t) = k_f N_k(t) = \frac{k_f N(0)}{2} \exp\left(-\frac{t}{\tau}\right) \{1 - \exp(-2k_{\text{ret}}t)\}$$
(S19)

The summation of Eq. S18 and Eq. S19 gives

$$I_{2}(t) = I_{j}(t) + I_{k}(t) = k_{f}N(0)\exp\left(-\frac{t}{\tau}\right)$$
(S20)

that is completely consistent with Eq. S12, which is the decay curve expected for the isolated QDs. Photoluminescence quantum yield is given same as Eq. S13. Dimensionless PL decay curves were shown in Figure S10 as examples.



Figure S10. Dimensionless PL decay curves calculated following Eqs. S12, S18, S19, and S20 with parameters of $k_f = k_{nr} = k_{ret} = 0.05$ and N(0) = 20.

Case III

If one of the QD pair that were defined in case II is a dark particle, energy transfer practically occurs oneway as mentioned below, since these particles are nonluminescent while remaining optical absorption unchanged. Therefore, the dark particles can be mathematically treated as $k_{nr} \gg 1$, which is reasonable when Auger recombination $\tau \sim 1-10$ ps and/or a very efficient surface defect levels $\tau < 100$ ps are regarded as the cause of nonluminescence. Other variables are basically same as the case II. When the dark particles are labeled as k, the lifetime for the particle k becomes very small ($\tau_k \ll 1$). Therefore, Eq. S17 is approximated to be

$$N_k(t) = \frac{N(0)}{2} \exp\left(-\frac{t}{\tau}\right) \{1 - \exp(-2k_{\text{ret}}t)\} \cong 0$$
 (S21)

By using Eq. S21, Eq. S14 can be simplified as

$$\frac{dN_j(t)}{dt} = -\frac{N_j(t)}{\tau} - k_{\rm ret}N_j(t)$$
(S22)

keeping the boundary condition for *j* as $N_j(0) = N(0)$. The solution of Eq. S22 gives

$$N_j(t) = N(0) \exp\left\{-t\left(\frac{1}{\tau} + k_{\rm ret}\right)\right\}$$
(S23)

PL decay curve becomes

$$I_{3}(t) = I_{j}(t) = k_{f}N_{j}(t) = k_{f}N(0)\exp\left\{-t\left(\frac{1}{\tau} + k_{ret}\right)\right\}$$
(S24)

PL intensity is described by

$$F_{3} = \int_{0}^{\infty} I_{3}(t)dt = \int_{0}^{\infty} k_{f}N(0)\exp\left\{-t\left(\frac{1}{\tau} + k_{ret}\right)\right\}dt = k_{f}N(0)\left(\frac{\tau}{1 + k_{ret}\tau}\right) = \frac{k_{f}N(0)}{k_{f} + k_{nr} + k_{ret}}$$
(S25)

Dimensionless PL decay curves were shown in Figure S11 as examples.



Figure S11. Dimensionless PL decay curves calculated following Eqs. S12, S20, and S24 with parameters of $k_{\rm f} = k_{\rm nr} = k_{\rm ret} = 0.05$ and N(0) = 20.

Case IV

In case three QDs are aligned linearly and the right end QD (labeled as l) is a dark particle, when the QD j is pulse photoexcited, the differential equations can be written as

$$\frac{dN_j(t)}{dt} = -\frac{N_j(t)}{\tau} - k_{\rm ret}N_j(t) + k_{\rm ret}N_k(t)$$
(S26)

$$\frac{dN_k(t)}{dt} = -\frac{N_k(t)}{\tau} - 2k_{\rm ret}N_k(t) + k_{\rm ret}N_j(t) + k_{\rm ret}N_l(t)$$
(S27)

$$N_l(t) \cong 0 \tag{S28}$$

with boundary conditions of $N_j(0) = N(0)$ and $N_k(0) = 0$. The solutions for the particles *j* and *k* are given

by

$$N_{j}(t) = \frac{N(0)}{2} \left\{ \left(1 - \frac{1}{\sqrt{5}}\right) \exp\left(\frac{-2 - \left(3 + \sqrt{5}\right)k_{\text{ret}}\tau}{2\tau}t\right) + \left(1 + \frac{1}{\sqrt{5}}\right) \exp\left(\frac{-2 - \left(3 - \sqrt{5}\right)k_{\text{ret}}\tau}{2\tau}t\right) \right\} (S29)$$

$$N_{k}(t) = \frac{N(0)}{\sqrt{5}} \left\{ -\exp\left(\frac{-2 - (3 + \sqrt{5})k_{\text{ret}}\tau}{2\tau}t\right) + \exp\left(\frac{-2 - (3 - \sqrt{5})k_{\text{ret}}\tau}{2\tau}t\right) \right\}$$
(S30)

PL decay curves for these particles are

$$I_{j}(t) = \frac{k_{\rm f}N(0)}{2} \left\{ \left(1 - \frac{1}{\sqrt{5}}\right) \exp\left(\frac{-2 - \left(3 + \sqrt{5}\right)k_{\rm ret}\tau}{2\tau}t\right) + \left(1 + \frac{1}{\sqrt{5}}\right) \exp\left(\frac{-2 - \left(3 - \sqrt{5}\right)k_{\rm ret}\tau}{2\tau}t\right) \right\} (S31)$$
$$I_{k}(t) = \frac{k_{\rm f}N(0)}{\sqrt{5}} \left\{ -\exp\left(\frac{-2 - \left(3 + \sqrt{5}\right)k_{\rm ret}\tau}{2\tau}t\right) + \exp\left(\frac{-2 - \left(3 - \sqrt{5}\right)k_{\rm ret}\tau}{2\tau}t\right) \right\} (S32)$$

Therefore, PL decay curve for the three QD system is given by the sum of Eqs. S31 and S32.

$$I_4(t) = \frac{k_{\rm f}N(0)}{2} \left\{ \left(1 - \frac{3}{\sqrt{5}}\right) \exp\left(\frac{-2 - \left(3 + \sqrt{5}\right)k_{\rm ret}\tau}{2\tau}t\right) + \left(1 + \frac{3}{\sqrt{5}}\right) \exp\left(\frac{-2 - \left(3 - \sqrt{5}\right)k_{\rm ret}\tau}{2\tau}t\right) \right\} (S33)$$

Thereby, PL intensity is given by

$$F_4(t) = \int_0^\infty I_4(t)dt = \frac{k_f N(0)\tau(1+3k_{\rm ret}\tau)}{1+k_{\rm ret}\tau(3+k_{\rm ret}\tau)} = \frac{k_f N(0)\{1+3k_{\rm ret}/(k_f+k_{\rm nr})\}}{k_f+k_{\rm nr}+k_{\rm ret}\{3+k_{\rm ret}/(k_f+k_{\rm nr})\}}$$
(S34)

In summary, the value of PL quantum yield (as well as decay curves) is identical to individual particle (Case I) no matter how much homotransfer occurs (Case II). However, PL quantum yield decreases when the particle that is adjacent to the dark particle is excited (Case III). The PL quantum yield also decreases when the particle that is two particles away from the dark particle is photoexcited, because an excitation energy is partly transferred to the dark particle (Case IV). The equations describing PL quantum yield expected for the cases I–IV are summarized in **Table S2** as well as examples of values when $k_f = k_{nr} = k_{ret}$ and $k_f = k_{nr} = 0.5k_{ret}$ are assumed. These results indicated that decrease in PL intensity of bright particles only occur in the presence of both homotransfer and dark particles. Experimentally, homo-FRET between QDs

occurred more significantly at higher loading amount on MOF-5, and only QD525 showed the PL intensity plateau due to the presence of dark particles.

Alignment	PL quantum yield	Value examples of PL quantum yield in case $k_{\rm f} = k_{\rm nr} = k_{\rm ret}$	Value examples of PL quantum yield in case $k_{\rm f} = k_{\rm nr} =$ $0.5k_{\rm ret}$
Case I	$\frac{k_{\rm f}}{k_{\rm f} + k_{\rm nr}}$	0.5	0.5
Case II	$\frac{k_{\rm f}}{k_{\rm f}+k_{\rm nr}}$	0.5	0.5
Case III	$\frac{k_{\rm f}}{k_{\rm f} + k_{\rm nr} + k_{\rm ret}}$	0.33	0.25
Case IV	$\frac{k_{\rm f}\{1+3k_{\rm ret}/(k_{\rm f}+k_{\rm nr})\}}{k_{\rm f}+k_{\rm nr}+k_{\rm ret}\{3+k_{\rm ret}/(k_{\rm f}+k_{\rm nr})\}}$	0.45	0.4

Table S2. Equations and values of PL quantum yield expected for the cases I–IV

References

1. Shachar, M. H.; Uahengo, G.; Penilla, E. H.; Kodera, Y.; Garay, J. E. Modeling the effects of scattering and absorption on the transmission of light in polycrystalline materials. *J. Appl. Phys.* **2020**, *128* (8), 083103.

2. Chou, K. F.; Dennis, A. M. Forster Resonance Energy Transfer between Quantum Dot Donors and Quantum Dot Acceptors. *Sensors* **2015**, *15* (6), 13288-13325.

3. Förster, T. Zwischenmolekulare Energiewanderung und Fluoreszenz. *Ann. Phys.* **1948**, *437*, 55-75.

4. Förster, T. Intermolecule energy migration and fluorescence. In *Biological Physics*, Mielczarek, E. V., Knox, R.S., Greenbaum, E., Ed. Springer: New York, 1993; pp 148-160.

5. Runnels, L. W.; Scarlata, S. F. Theory and application of fluorescence homotransfer to melittin oligomerization. *Biophys. J.* **1995**, *69* (4), 1569-1583.