Supporting Information

Sequential Energy and Electron Transfer in a Three-component

System Aligned on a Clay Nanosheet

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Fig. S1 Fluorescence decay profiles of (AA@OAm₂¹⁶⁺−ZnTMPyP⁴⁺)∩clay, (a) excitation wavelength was set at 468 nm, (b) excitation wavelength was set at 410 nm.

Black line is the fitting curve and gray line is laser pulse, respectively.

Above black dots shows residual error (ΔR). ΔR were calculated with following

equation.

$$\Delta R = \frac{\left(y_i - Y_i\right)}{\sqrt{y_i}}$$

, where y_i is fluorescence intensity, Y_i is fitting value, respectively.



Fig. S2 Model of the adsorption distribution of (AA@OAm₂¹⁶⁺−ZnTMPyP⁴⁺)∩clay



Fig. S3 I₀/I plot of (ZnTMPyP⁴⁺-DNPV²⁺)∩clay (triangle) and

 $(AA@OAm_2^{16+}-DNPV^{2+})\cap$ clay systems(round). Horizontal axis is the loading level of DNPV²⁺. Concentration of DNPV²⁺ was changed from 0 to 4.0×10^{-6} M (corresponding

to 0 and 80% versus CEC	of the clay, respectively)
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Fig. S4 Models of the adsorption distribution of (ZnTMPyP⁴⁺−DNPV²⁺)∩clay

(a)un-uniform distribution (b) uniform distribution



Fig. S5 Fluorescence decay profiles of $(AA@OAm_2^{16+}-ZnTMPyP^{4+}-DNPV^{2+})\cap clay$, (a) excitation wavelength was set at 468 nm, (b) excitation wavelength was set at 410 nm. Black line is the fitting curve and gray line is laser pulse, respectively. Above black dots shows residual error (ΔR).

Calculation procedure for the energy transfer efficiency and the quenching efficiency

We reported that the energy transfer efficiency (η_{ET}) and the quenching efficiency (φ_q) can be quantitatively estimated by the analysis of the steady-state fluorescence spectra. The total fluorescence of $(AA@OAm_2^{16+}-ZnTMPyP^{4+})\cap$ clay complex $(F_{ET}(\nu))$ can be expressed by equation 1.

$$F_{ET}(v) = (1 - \eta_{ET} - \phi_q) \times F_D^{390}(v) + \left(1 + \frac{1 - 10^{-A_D}}{1 - 10^{-A_A}}\eta_{ET}\right) \times F_A^{390}(v) \quad (\text{eq. 1})$$

where $F_{ET}(v)$ is the fluorescence spectrum of $(AA@OAm_2^{16+}-ZnTMPyP^{4+})\cap clay$ complex, $F_D^{390}(v)$ and $F_A^{390}(v)$ are fluorescence spectra of $AA@OAm_2^{16+}\cap clay$ complex and $ZnTMPyP^{4+}\cap clay$ complex, respectively. A_D and A_A is are the absorbance of $AA@OAm_2^{16}\cap clay$ complex and $ZnTMPyP^{4+}\cap clay$ complex at 390 nm, η_{ET} is energy transfer efficiency defined in equation 2, φ_q is the quenching efficiency defined in

equation 3, respectively.

$$\eta_{ET} = \frac{k_{ET}}{k_{ET} + k_d^D + k_f^D + k_q} \text{ (eq. 2)}$$
$$\phi_q = \frac{k_q}{k_{ET} + k_d^D + k_f^D + k_q} \text{ (eq. 3)}$$

where k_d^{D} is the sum of non-radiative deactivation rate constant and intersystem crossing rate constant of AA@OAm₂¹⁶⁺, k_f^{D} is the radiative deactivation rate constant of AA@OAm₂¹⁶⁺, k_q is the quenching rate constant, and k_{ET} is energy transfer rate constant, respectively. On the basis of equation 1, the fluorescence spectrum, $F_{ET}(v)$ was simulated with the use of the respective reference fluorescence spectra, $F_D^{390}(v)$ and $F_A^{390}(v)$. Thus, parameters η_{ET} and φ_q can be obtained from the spectral simulation. However, when ZnTMPyP⁴⁺ was selectively excited by 610 nm wavelength light in $(ZnTMPyP^{4+}-AA@OAm_2^{16+})\cap$ clay system, fluorescence intensity for ZnTMPyP⁴⁺ was increased compared to ZnTMPyP⁴⁺ \cap clay due to suppression of self quenching reaction. Considering this result, $F_D^{390}(v)$, which is reference fluorescence spectrum of ZnTMPyP⁴⁺ \cap clay obtained by irradiation of the 390 nm wavelength light, also enhanced in presence of AA@OAm_2^{16+}. Compensating rate (n) for this fluorescence increase could be estimated from fluorescence intensity of ZnTMPyP⁴⁺ on the clay surface by irradiation of the 610 nm wavelength light in absence and presence of AA@OAm_2^{16+}.

$$n = \frac{I^{610}}{I_0^{610}}$$
(eq. 4)

where I_{0}^{610} and I_{0}^{610} is fluorescence intensity of ZnTMPyP⁴⁺ clay by irradiation of the 610 nm wavelength light in absence and presence of AA@OAm₂¹⁶⁺, respectively. As the result, Equation 5 was used to determine energy transfer and energy loss efficiency.

$$F_{ET}(v) = (1 - \eta_{ET} - \phi_q) \times F_D^{390}(v) + \left(1 + \frac{1 - 10^{-A_D}}{1 - 10^{-A_A}}\eta_{ET}\right) \times nF_A^{390}(v) \quad (\text{eq. 5})$$

Calculation of Gibbs free energy change(ΔG_{el}) for the electron transfer reactions Changes of Gibbs free energy (ΔG_{el}) for the two electron transfer reaction (between capsulated AA in OAm₂¹⁶⁺ and DNPV²⁺, between ZnTMPyP⁴⁺ and DNPV²⁺) could be calculated with following equation proposed by Rehm and Weller (eq. 6).

$$\Delta G_{el} \ (kcal \ mol^{-1}) = 23.06 \left[E^0 (D^+ / D) - E^0 (A / A^-) \right] - w_p - \Delta G_{00} \ (eq. 6)$$

where $E^{0}(D^{+}/D)$ is oxidation potential of electron donor, $E^{0}(A/A^{-})$ is reduction potential of DNPV²⁺(+0.02 V vs. SHE, in water), and ΔG_{00} is excitation energy, respectively. The oxidation potentials of AA and ZnTMPyP⁴⁺ are reported as +1.66 V (vs. SHE in MeCN) and +1.18 V (vs. SHE, in water), respectively. The ΔG_{00} of AA@OAm₂¹⁶⁺ and ZnTMPyP⁴⁺ are calculated as 2.94 eV and 1.91 eV from fluorescence and absorption spectra, respectively. The ΔG_{el} for both of electron transfer reaction between AA to DNPV²⁺, and between ZnTMPyP⁴⁺ to DNPV²⁺ were calculated as -127.9 and -84.1 kJ mol⁻¹, respectively. Although redox potentials of the molecules adsorbed on clay or included in cavitand would different from redox potential in solution, these ΔG_{el} are sufficiently exergonic.

Stern-Volmer analysis of (AA@OAm¹⁶⁺−DNPV²⁺)∩clay system and (ZnTMPyP⁴⁺−DNPV²⁺)∩clay system

Electron transfer rate constant could be estimated by following Stern-Volmer equation.

$$\frac{I_0}{I} = 1 + K_{SV} [Q] (eq.7)$$

where I_0 and I is fluorescence intensities in absence and presence of quencher, [Q] is

concentration of the quencher, respectively. And Ksv is the Stern-Volmer constant from which one can estimate the rate constant of quenching reaction.

$$K_{SV} = \tau_0 k_{eT} (\text{eq.8})$$

where τ_0 is the life-time of the fluorophore and k_{eT} is electron transfer rate constant, respectively. The Stern-Volmer plots in both systems were shown in Fig. S3. The slope of Stern-Volmer like plot for (AA@OAm₂¹⁶⁺–DNPV²⁺)∩clay system is almost zero. It indicated the electron transfer rate constant is very low. On the other hand, the value of I_0/I in (ZnTMPyP⁴⁺–DNPV²⁺)∩clay system was increased with increase of DNPV²⁺ concentration. However, this plot showed upward curvature, thus k_{eT} could not be estimated from the slope of this Stern-Volmer plot. We believe reason of this upward curvature is un-uniform absorption distribution of ZnTMPyP⁴⁺ and DNPV²⁺.

Calculation procedure for efficiencies of the energy transfer, electron transfer and energy loss in three components system.

Electron transfer efficiency(ϕ_{eT}) between ZnTMPyP⁴⁺ and DNPV⁴⁺ could be determined by following equation 9 and 10.

$$\phi_{eT} = 1 - m \text{ (eq. 9)}$$

 $m = \frac{I^{610'}}{I^{610}} \text{(eq. 10)}$

where I⁶¹⁰ and I⁶¹⁰, is fluorescence intensity of $(AA@OAm_2^{16+}-ZnTMPyP^{4+})\cap$ clay and $(AA@OAm_2^{16+}-ZnTMPyP^{4+}-DNPV^{2+})\cap$ clay by irradiation of the 610 nm wavelength light, respectively. Likewise, the reference fluorescence spectrum for ZnTMPyP⁴⁺ (F(v)_A³⁹⁰) must be also quenched in presence of DNPV²⁺, thus energy transfer and energy loss efficiency could be calculated by equation 11.

$$F_{ET}(v) = (1 - \eta_{ET} - \phi_q) \times F_D^{390}(v) + \left(1 + \frac{1 - 10^{-A_D}}{1 - 10^{-A_A}} \eta_{ET}\right) \times nm F_A^{390}(v) \quad (\text{eq. 11})$$