Supplementary Information

Energy Transfer in Hybrid Langmuir-Blodgett Films of Iridium Complexes and Synthetic Saponite: Dependence of Transfer Efficiency on Interlayer Distance

Hisako Sato,[a,]*Miwa Ochi,[a] Masaru Kato,[b] Kenji Tamura[c] and Akihiko Yamagishi[d]

[a] Department of Chemistry, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan, sato.hisako.my@ehime-u.ac.jp
[b]Division of Environmental Materials Science, Graduate School of Environmental Science, Hokkaido University, Sapporo, 060-0810, Japan
[c] National Institute of Materials Science, Tsukuba 305-0044, Japan
[d] Department of Chemistry, Toho University, Funabashi, Chiba 274-851,Japan

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1. The UV-visible spectra of the hybrid films and solutions

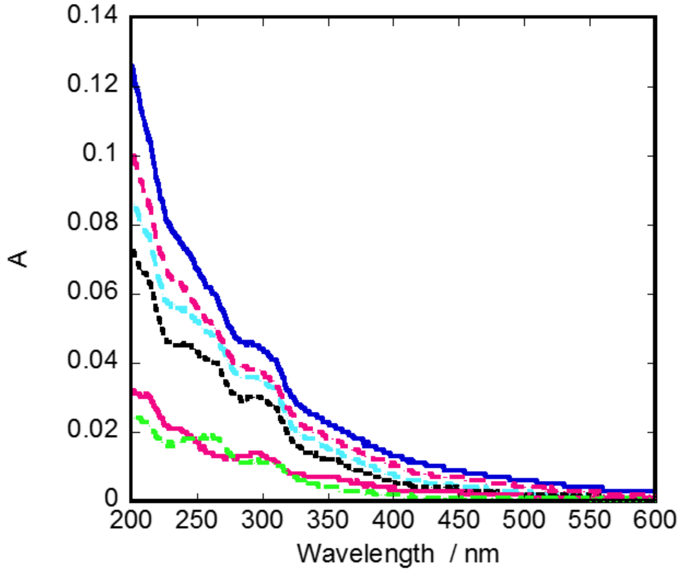


Figure S1(a). The UV-visible spectra of the hybrid LB films deposited onto quartz substrates. The film composition for each curve was following: (green) {DFPPY/SAP}, (red solid line) {PIQ/SAP}, (black) {DFPPY/SAP}/{PIQ/SAP}, (sky blue) {DFPPY/SAP}/ {SA/SAP} /{PIQ/SAP}, (red) {DFPPY/SAP}/ $\{SA/SAP\}_2$ /{PIQ/SAP} and (blue) {DFPPY/SAP}/ $\{SA/SAP\}_3$ /{PIQ/SAP}.

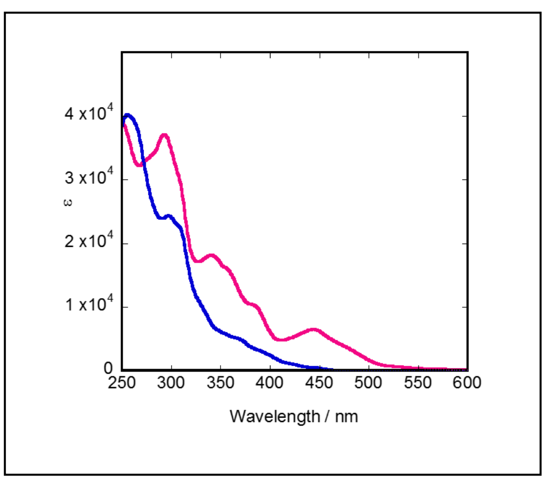


Figure S1 (b). The UV-visible spectra of $[Ir(dfppy)_2(dc9bpy)]ClO_4$ (blue) and $[Ir(piq)_2(dc9bpy)]$ ClO_4 (red) in $CHCl_3$.

2. The FTIR spectra of the hybrid LB films

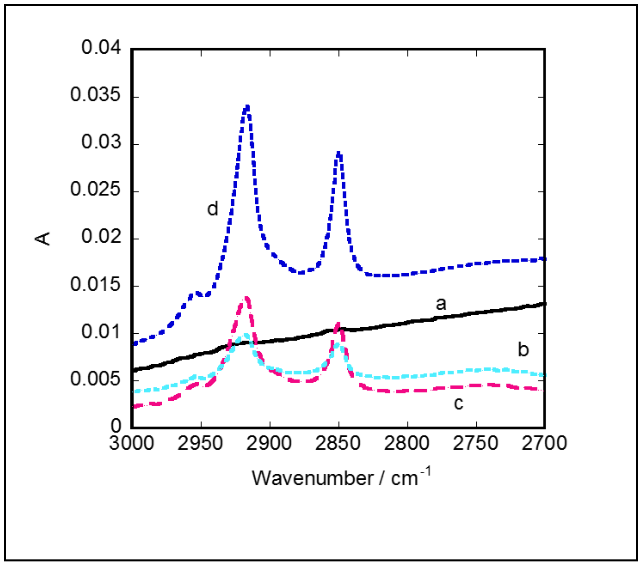


Figure S2. The FTIR spectra of the hybrid LB films deposited onto quartz substrates. The film composition for each curve was following: (black) {DFPPY/SAP}/{PIQ/SAP}, (sky blue) {DFPPY/SAP}/{SA/SAP}/{PIQ/SAP}, (red) {DFPPY/SAP}/$\{SA/SAP\}_2$/{PIQ/SAP} and (blue) {DFPPY/SAP}/ $\{SA/SAP\}_3$ /{PIQ/SAP}.

3. **Dynamic emission properties of the hybrid films**

Table S1. The lifetime analyses for the emission at 490 nm according to eq. (1) in the text

Hybrid LB film	lifetime (μs)			
	Fast(τ_1)	Slow(τ_2)	F1(fast)	F2(slow)
{DFPPY/SAP}	0.65	1.52	0.020	0.008
{DFPPY/SAP}/{PIQ/ SAP}	0.11	0.57	0.013	0.012
{DFPPY/SAP}/$\{SA/SAP\}_1$/{PIQ/SAP}	0.18	0.68	0.011	0.009
{DFPPY/SAP}/$\{SA/SAP\}_2$/{PIQ/SAP}	0.26	0.90	0.007	0.007
{DFPPY/SAP}/$\{SA/SAP\}_3$/{PIQ/SAP}	0.37	1.11	0.009	0.007
{DFPPY/SAP}/$\{SA/SAP\}_4$/{PIQ/SAP}	0.55	1.44	0.010	0.006

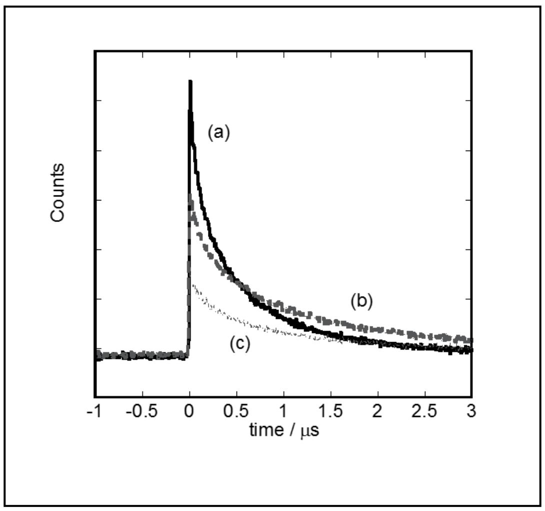


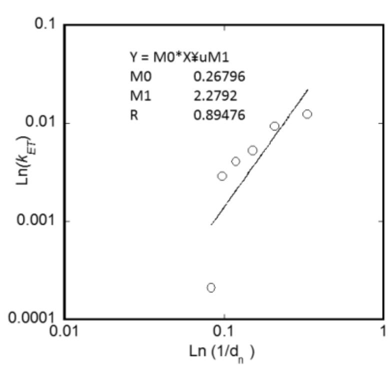
Figure S3. The lifetime of emission at 590 nm from multi-layered hybrid LB films. The film composition for each curve was following: (a) {DFPPY/SAP}/{PIQ/SAP}, (b) {DFPPY/SAP}/{SA/SAP}/{PIQ/SAP} and (c) {DFPPY/SAP}/$\{SA/SAP\}_2$/{PIQ/SAP}.

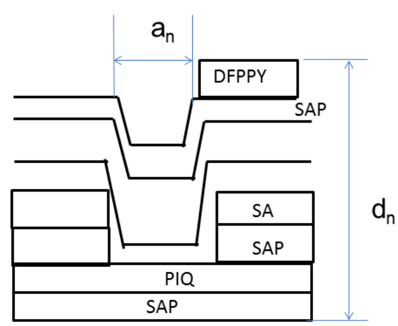
4. The model calculation of energy transfer rates in hybrid films with holes

(i) The relative value of energy transfer rate (k_{ET}) was calculated for the model multi-layered hybrid films. In each film, it was assumed that the nth intervening layer of {SA/SAP} possesses a hole with the width a_n and the depth of one layer thickness (see a drawing below the plot). The interlayer distance, d_n (denoted as R_d in the text) was assumed to be 3.0 + 1.81n in nm for n=0 ~5.

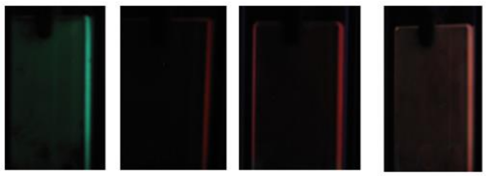
Number of inserted [SA/clay] layers (n)	d_n /nm	Hole size/ nm (a_n)	Formula for calculating k_{ET} values	k_{ET}(relative value)
0	3	0	$1/d_0^4$	0.01235
1	4.81	1	$1/d_0^4 - 1/(d_0 + a_1)^4 + 1/(d_1 + a_1)^4$	0.00932
2	6.62	0.4	$1/d_1^4 - 1/(d_1 + a_2)^4 + 1/(d_2 + a_2)^4$	0.00527
3	8.43	0.3	$1/d_2^4 - 1/(d_2 + a_3)^4 + 1/(d_3 + a_3)^4$	0.00409
4	10.24	0.2	$1/d_3^4 - 1/(d_3 + a_4)^4 + 1/(d_4 + a_4)^4$	0.00289
5	12.05	0.01	$1/d_4^4 - 1/(d_4 + a_5)^4 + 1/(d_5 + a_5)^4$	0.00021

(ii) The plot of the calculated k_{ET} versus the inverse of the interlayer distance (d_n) between {DFPPY/SAP} and {PIQ/SAP}. The right figure shows the drawing of a model film with holes.





5. The photographic images of the quartz substrates covered with single- and multi-layered hybrid films



(a) (b) (c) (d)

Figure S4. The emission in vacuum under the irradiation of UV-light: (a) {DFPPY/SAP}, (b) {PIQ/SAP}, (c) {DFPPY/SAP}/{PIQ/SAP} and (d) {DFPPY/SAP}/{SA/SAP}$_5$/{PIQ/SAP}

6. Calculation of spectral overlap integral (J) and Förster radius (R_0)

The rate constant of Förster-type energy transfer (k_{ET}) is expressed by the following equation:

$$k_{ET} = \frac{9000\ Ln10\ \ k^2\ \ \Phi}{128\pi^5 n^4 N\tau_D R^6} J(\lambda) \qquad \text{(S1)}$$

in which τ_D, R_0 , R and J (λ) denote the excited life time of a donor in the absence of an acceptor, Förster radius, the donor/acceptor distance and the spectral overlap integral, respectively. R_o is given by:

$$R_0 = 9.78 \times 10^{-5} (\kappa^2 \phi n^{-4} J(\lambda))^{\frac{1}{6}}$$

(in cm) (S2)

J (λ) is given by:

$$\mathrm{J}(\lambda) = \frac{\int F_d(\lambda)\varepsilon(\lambda)\lambda^4 d\lambda}{\int F_d(\lambda) d\lambda} \qquad \text{(S3)}$$

$$k_{ET} = \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6 \qquad \text{(S4)}$$

$$\eta_{ET} = k_{ET} / (k_{ET} + k_{NR}) \qquad \text{(S5)}$$

As for other parameters in equations (S2) and (S3), κ is the orientation factor, ϕ the quantum yield of donor, n the refractive index of the medium, N the Avogadro constant, λ the wavelength, ε_a the extinction coefficient of the acceptor and F_d the normalized emission intensity of the donor. η_{ET} denotes the energy transfer efficiency and k_{NR} represented the decay constant in the absence of an acceptor. $J(\lambda)$ was calculated to be 1.14 x 10^{-14} $M^{-1}cm^3$ from the emission and absorption spectra of the present donor-acceptor pairs. Assuming $\kappa^2 = 2/3$ (random orientation), n = 1.3 and ϕ=0.14, R_o was obtained to be 2.62 nm. Inserting this value and τ_D = 0.65 μs (experimentally obtained), k_{ET} was calculated to be 6.85x10^5 s^{-1} at R= 3.0 nm from eq. (S4).