# Supplementary Information

# **Dual Emitting Langmuir-Blodgett Films of Cationic Iridium Complexes and Montmorillonite Clay for Oxygen Sensing**

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# 1. The <sup>1</sup>H NMR data and Mass spectroscopy data of iridium(III) complexes

1) [Ir(dfppy)<sub>2</sub>(dc9bpy)]ClO<sub>4</sub>: <sup>1</sup>H NMR (chloroform-d, 400MHz, 25 °C)

 $\delta$  9.43 (s, 2H), 8.30 (d, *J* = 8.8 Hz, 2H), 7.81 (dd, *J* = 6.0, 6.0 Hz, 2H), 7.71 (d, *J* = 6.0 Hz, 2H), 7.50 (d, *J* = 5.7 Hz, 2H), 7.23 (d, *J* = 5.7 Hz, 2H), 7.09 (dd, *J* = 6.0, 6.0 Hz, 2H), 6.55 (ddd, *J* = 9.3, 9.3, 2.5 Hz, 2H), 5.68 (dd, *J* = 6.0, 2.0 Hz, 2H), 2.99 (t, J = 7.7 Hz, 4H), 1.71 (tt, J = 7.7, 7.7 Hz, 4H), 1.42-1.20 (overlapped, 24H), 0.86 (t, J = 6.8 Hz, 6H)

MS (m/z; FAB): 981.41 (calculated for  $[Ir(dfppy)_2(dc9bpy)]^+$  C<sub>50</sub>H<sub>56</sub>F<sub>4</sub>IrN<sub>4</sub>), 980 (experimentally obtained).

2) [Ir(ppy)<sub>2</sub>(dc9bpy)]ClO<sub>4</sub>: <sup>1</sup>H NMR (chloroform-d, 400 MHz, 25 °C)

δ 8.76 (s, 2H), 7.89 (d, J = 7.9 Hz, 2H), 7.78-7.72 (overlapped, 4H), 7.66 (d, J = 7.9, 0.9 Hz, 2H), 7.54 (d, J = 5.8 Hz, 2H), 7.17 (dd, J = 5.8, 1.5 Hz, 2H), 7.06-6.98 (overlapped, 4H), 6.90 (dd, J = 7.5, 7.5 Hz, 2H), 6.29 (d, J = 7.9, 0.9 Hz, 2H), 2.90 (t, J = 7.7 Hz, 4H), 1.70 (tt, J = 7.7, 7.7, 4H), 1.42-1.20 (overlapped, 24H), 0.87 (t, J = 6.7 Hz, 6H)

MS (m/z; FAB): 909.44 (calculated for  $[Ir(ppy)_2(dc9bpy)]^+ C_{50}H_{60}IrN_4$ ), 910 (experimentally obtained).

# 2. The electronic absorption spectra of iridium(III) complexes in methanol



Figure S1. The UV-visible spectra of  $[Ir(ppy)_2(dc9bpy)]ClO_4$  (black) and  $[Ir(dfppy)_2(dc9bpy)]ClO_4$ (blue) in methanol, respectively.

## 3. The $\pi$ -A curves of the floating films of iridium(III) complexes



Figure S2. The  $\pi$ -A curves of  $[Ir(ppy)_2(dc9bpy)]ClO_4$  (green) and  $[Ir(dfppy)_2(dc9bpy)]ClO_4$ (blue) when a subphase was an aqueous suspension of sodium montmorillonite (10 mgL<sup>-1</sup>)(solid line) or pure water (dotted line).

4. The AFM images of the hybrid films deposited onto glass substrates



(a)

(b)



(c)

(d)

Figure S3. The AFM images of the hybrid films deposited onto a glass substrate at 10 mNm<sup>-1</sup>; (a) {DFPPY/clay}, (b) {PPY/clay}, (c) {PPY/clay/DFPPY/clay} and (d) {DFPPY/clay/PPY/clay}.

#### 5. The XRD diffraction pattern of the multi-layered hybrid film deposited on a glass substrate



Figure S4. Powder XRD pattern of a multi-layered film, {PPY/clay}<sub>n</sub> (n=20).

The peak at  $2\theta = 2.6$  deg corresponded to ca 3.3 nm. The right figure shows the possible structure in which a complex molecule,  $[Ir(ppy)_2(dc9bpy)]^+$ , with the height of ca 2.0 nm is adsorbed onto a single layer of montmorillonite clay whose thickness is ca 1.0 nm.

6. The change of emission intensity from the hybrid films on introducing and evacuationg oxygen gas



Figure S5. The change of emission intensity from {PPY/clay} and {DFPPY/clay}, when oxygen gas was introduced and evacuated. The excitation and emission wavelengths were 430 nm and 500 nm and 550 nm, respectively. The films were prepared for an aqueous dispersion containing 10 mg  $L^{-1}$  of sodium montmorillonite as a subphase.

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#### 7. Emission lifetime measurements

Table S1. Emission lifetimes in the singly deposited hybrid LB films in vacuum

Single-layer	$ au_1$	$\tau_2$
{DFPPY/clay}	29 ns	465 ns
{PPY/clay}	21 ns	294 ns

Emission lifetime measurements were performed with a time-resolved near-infrared fluorescence spectrophotometer (Hamamatsu C-7990-01) using an Nd-YAG laser (CryLas FTSS355Q, THG: 355 nm, 14 kHz, FWHM 1 ns) as an excitation light source. The emission lifetimes ( $\tau_1$  and  $\tau_2$ ) were estimated by fitting the decay curves under the assumption of double-exponential curves.

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#### 8. The emission spectra of the homogenous hybrid films



Figure S6. Emission spectra from (a)  $\{DFPPY/clay\}_2$  and (b)  $\{PPY/clay\}_2$ , respectively. The solid and dotted curves were the spectra measured in vacuum and under air, respectively. The excitation wavelength was 430 nm. The films were prepared for an aqueous dispersion containing 10 mg L<sup>-1</sup> of sodium montmorillonite.

9. The UV-vis spectra of single- and heterogeneous hybrid films



Figure S7. The UV-visible spectra of {DFPPY/clay} (blue) and {PPY/clay} (black), respectively (left) and the UV-visible spectra of {PPY/clay/DFPPY/clay} (black) and {DFPPY/clay/PPY/clay} (blue), respectively (right).

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#### 10. The reconstruction of emission spectra from the heterogeneous hybrid films



Figure S8. The emission spectra from the hybrid double-layered films were reconstructed in terms of the sum of emitting components. The films are {PPY/clay/DFPPY/clay} for (a) ~ (d) and {DFPPY/clay/PPY/clay} for (e) ~ (h). The followings are assumed as an emitting component: {DFPPY/clay} (solid and dotted sky blue curves for the observed and calculated spectra, respectively), {PPY/clay} (solid and dotted green curves for the observed and calculated spectra, respectively) and {PPY/clay/DFPPY/clay}, {DFPPY/clay/PPY/clay} (black solid and pink dotted curves for the observed and calculated spectra, respectively). And (and calculated spectra, respectively). Oxygen pressure was (a) 0, (b) 1, (c) 4, (d) 11, (e) 0, (f) 1, (g) 4 and (h) 11 kPa, respectively. The simulation was done according to equation (2) in the text.

11. The analyses of the emission spectra from a single-layered hybrid film of a mixture of PPY and DFPPY: an evidence for energy transfer



Figure S9. The emission spectrum from a single-layered hybrid film of a mixture of PPY and DFPPY at 1:1 ratio, or {DFPPY + PPY/clay}, was reconstructed in terms of the sum of emitting components of {DFPPY/clay} and {PPY/clay} in vacuum: {DFPPY + PPY/clay} (black solid and pink solid curves for the observed and calculated spectra, {DFPPY/clay} (solid and dotted sky blue curves for the observed and calculated spectra, respectively ) and {PPY/clay} (solid and dotted green curves for the observed and calculated spectra, respectively). The observed spectrum of the emission from {DFPPY + PPY/clay} was well reproduced by assuming the occurrence of energy transfer from DFPPY to PPY. The parameters of  $\eta_{ET}$ ,  $\phi$  and  $\phi$  are calculated to be 0.35, 0.18 and 0.18 in equation (2) in the text, respectively.

### 12. The schematic model for dual-emitting oxygen-sensing films

The following schemes show how the efficiency of energy transfer depends on the deposition order in heterogeneous hybrid films: (a), (c){PPY/clay/DFPPY/clay}, in which energy transfer occurs to an appreciable extent so that the emission is mainly from PPY, and (b), (d) {DFPPY/clay/PPY/clay}, in which energy transfer does occur so that the total emission spectrum depends on the pressure of oxygen gas.



