

Supporting Information

for

Photoacceleration of the Suzuki-Miyaura coupling through ligand-regulation on Ir(III)-Pd(II) bimetallic complexes

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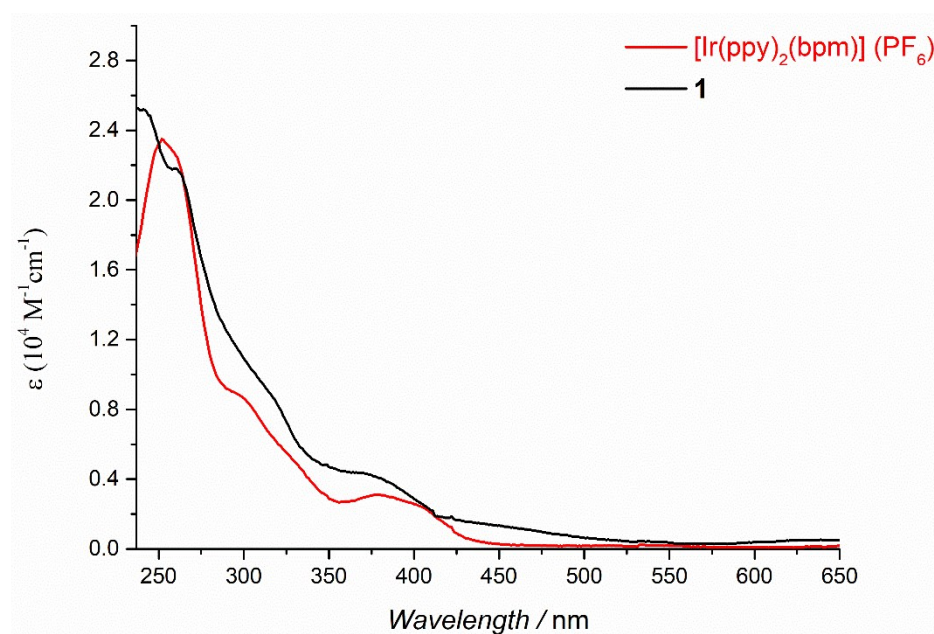


Figure S1. UV-vis spectra of $[\text{Ir}(\text{ppy})_2(\text{bpm})](\text{PF}_6)$ and **1** in DCM solution ($5 \times 10^{-5} \text{ M}$).

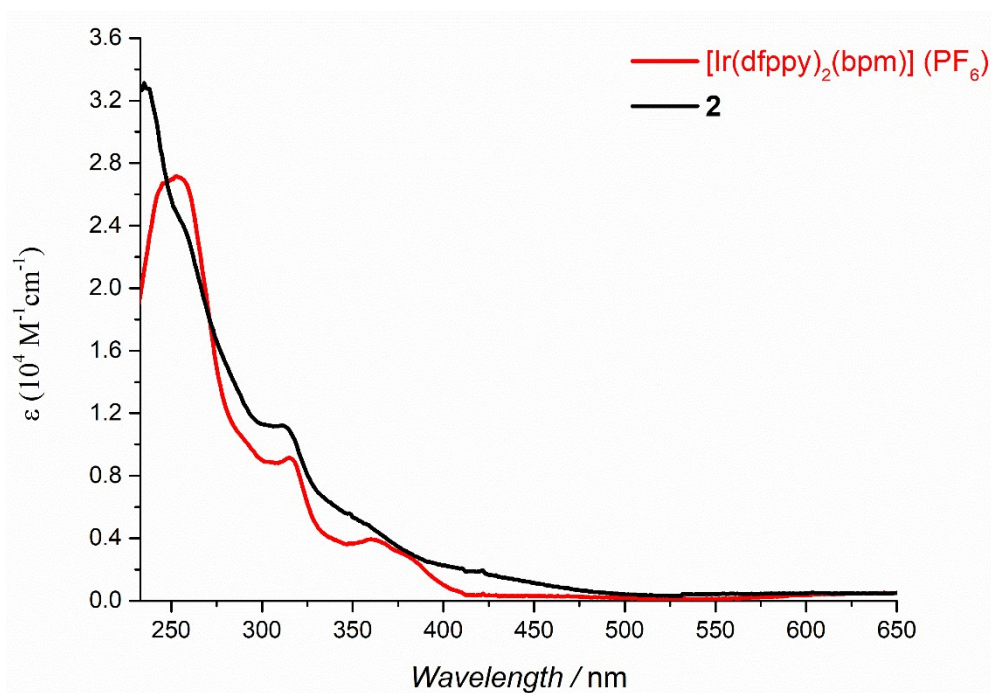


Figure S2. UV-vis spectra of $[\text{Ir}(\text{dfppy})_2(\text{bpm})](\text{PF}_6)$ and **2** in DCM solution ($5 \times 10^{-5} \text{ M}$).

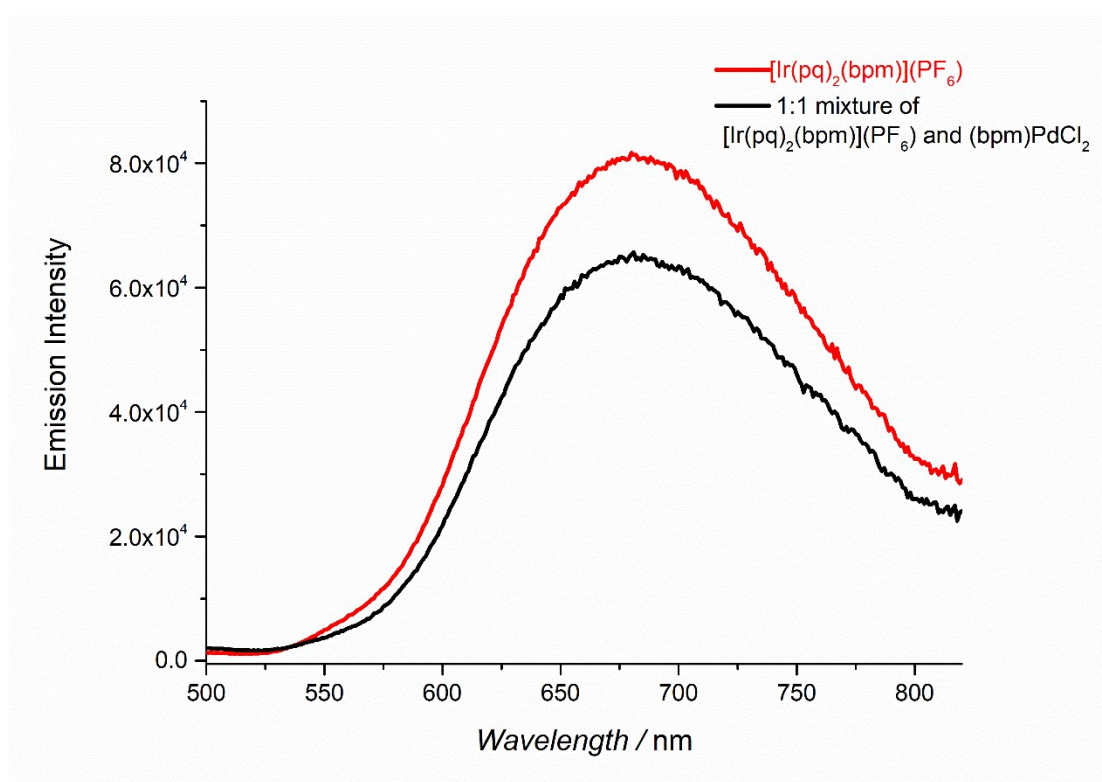


Figure S3. Emission spectra of a mixture of $[\text{Ir}(\text{pq})_2(\text{bpm})](\text{PF}_6)$ and $(\text{bpm})\text{PdCl}_2$ (1:1, $2 \times 10^{-4} \text{ M}$, DCM solution). Excitation wavelength: 405 nm.

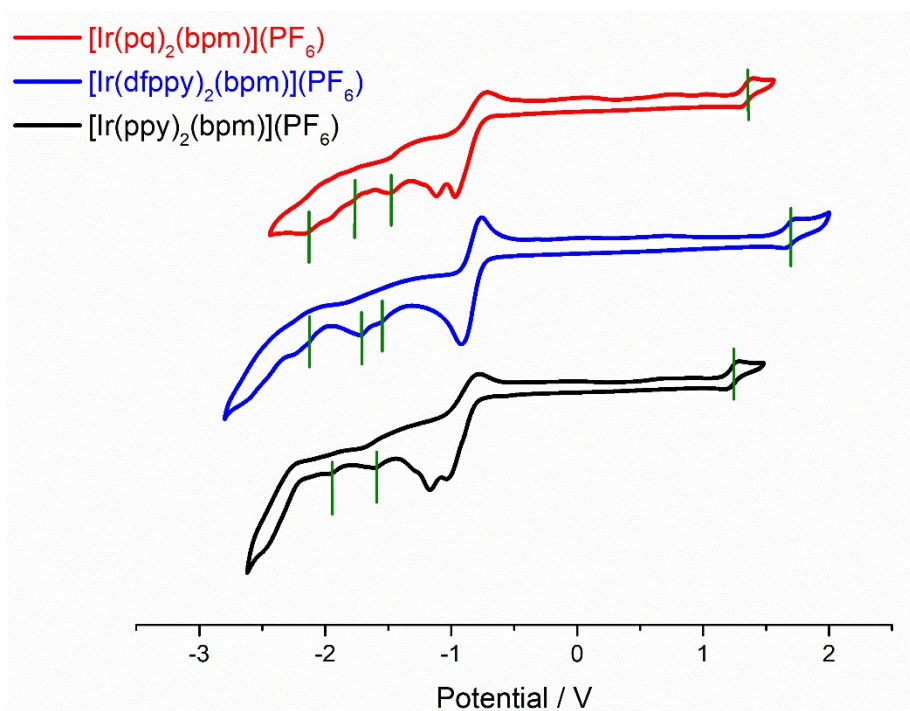


Figure S4. Cyclic voltammograms of mononuclear Ir(III) complexes.

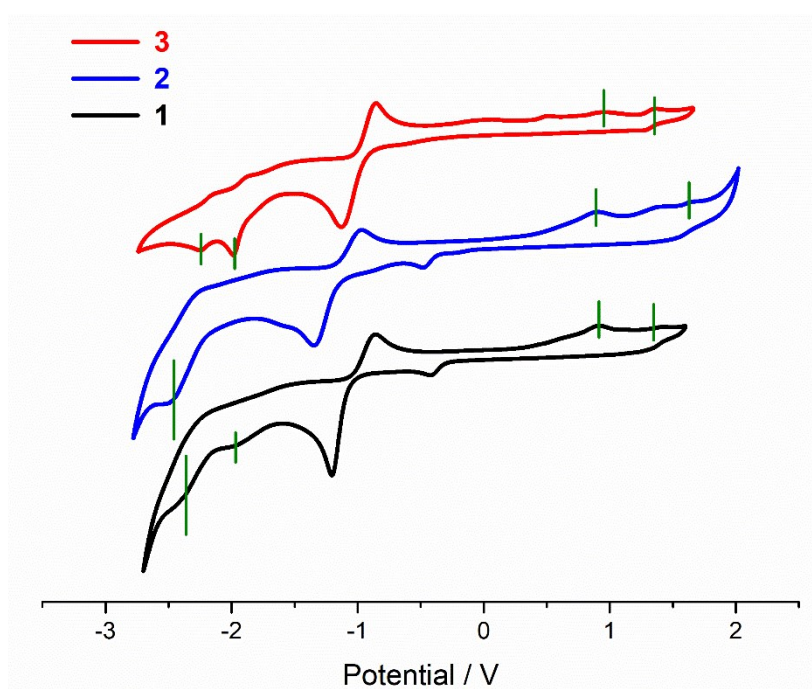


Figure S5. Cyclic voltammograms of Ir-Pd complexes.

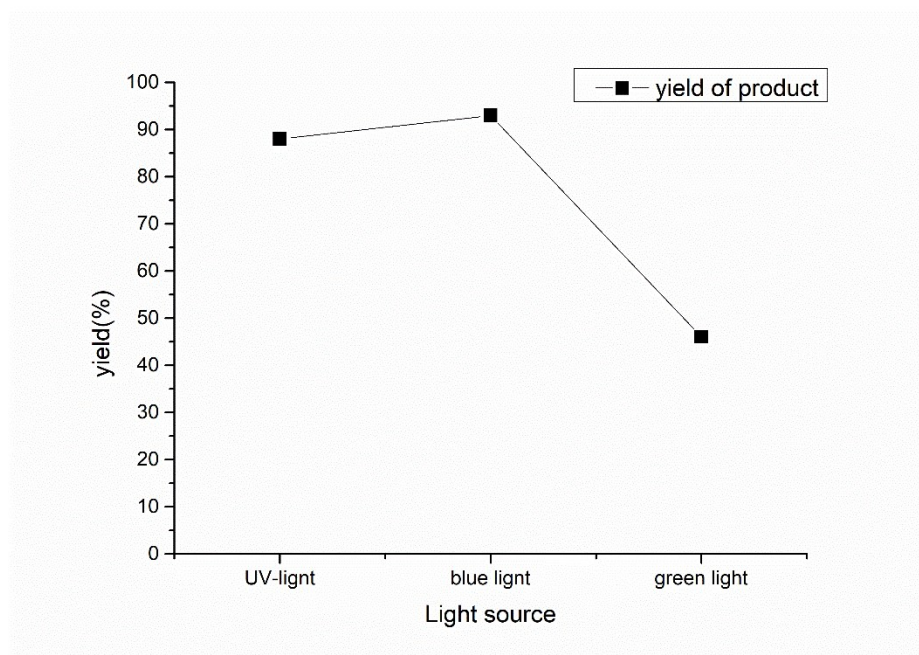
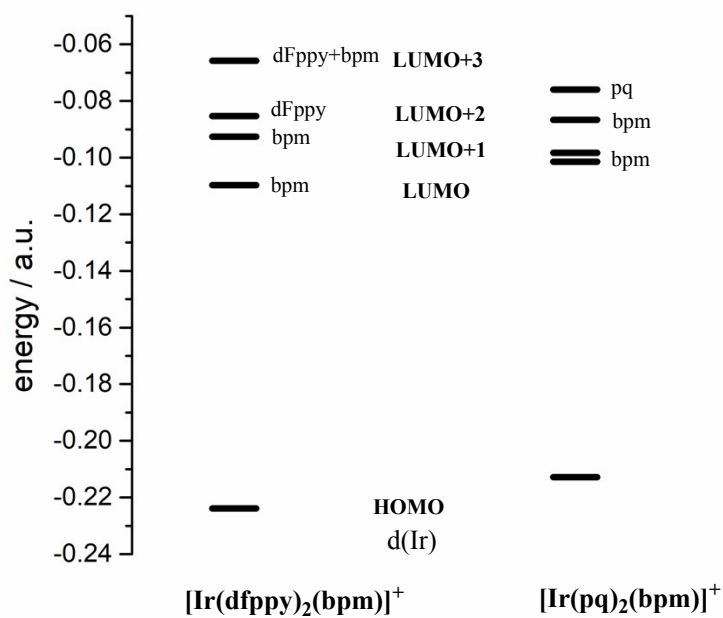


Figure S6. Action spectrum of complex **3**.

Computational Details: DFT calculations were performed using the Gaussian 09W software.¹ Optimization of ground-state structures was performed by using DFT with the B3LYP functional. The LanL2DZ^{2a-c} and 6-31G(d,p)^{2d,e} basis sets were used to treat iridium and all other atoms, respectively.



Scheme S1. The energy levels of the frontier orbitals for [Ir(dfppy)₂(bpm)]⁺ and [Ir(pq)₂(bpm)]⁺.

¹H NMR of catalytical product.

4-Methylbiphenyl: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.47 (t, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 2.44 (s, 3H).

1-(Biphenyl-4-yl)ethanone: ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.50 (t, 2H), 7.43 (t, 1H), 2.67 (s, 3H).

2-Methylbiphenyl: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 (t, 2H), 7.40 – 7.35 (m, 3H), 7.29 (dd, *J* = 7.3, 3.3 Hz, 4H), 2.31 (s, 3H).

3-Methylbiphenyl: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.1 Hz, 2H), 7.46 (q, *J* = 9.0, 8.1 Hz, 4H), 7.41 – 7.35 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 2.47 (s, 3H).

4-Fluoro-4'-methylbiphenyl: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.14 (t, 2H), 2.43 (s, 3H).

4-(*p*-Methoxyphenyl)toluene: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H).

2-Methoxy-1,1'-binaphthyl: ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.99 (d, $J = 4.1$ Hz, 1H), 7.93 (d, $J = 8.2$ Hz, 1H), 7.68 (t, 1H), 7.50 (d, $J = 8.5$ Hz, 3H), 7.42 – 7.20 (m, 5H), 3.81 (s, 3H).

3,5-Dimethyl-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.3$ Hz, 2H), 7.52 – 7.43 (m, 2H), 7.42 – 7.34 (m, 1H), 7.26 (d, $J = 1.6$ Hz, 2H), 7.09 (s, 1H), 2.43 (s, 6H).

2-Methyl-1-phenyl-naphthalene: ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.5$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.53 (t, $J = 7.3$ Hz, 2H), 7.49 – 7.40 (m, 4H), 7.38 – 7.29 (m, 3H), 2.27 (s, 3H).

2-Methyl-1-(3,5-dimethyl-phenyl)-naphthalene: ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.52 – 7.33 (m, 4H), 7.10 (s, 1H), 6.92 (s, 2H), 2.42 (s, 6H), 2.29 (s, 3H).

1-Phenylnaphthalene: ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.2$ Hz, 2H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.59 – 7.42 (m, 9H).

2-Methyl-1,1'-binaphthalene: ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.46 (m, 2H), 7.40 (t, 2H), 7.33 – 7.14 (m, 4H), 2.13 (s, 3H).

- 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo,

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