

Supporting Information

Construction and Properties of the Light-Harvesting Antenna System for Phosphorescent Materials Based on Oligocardofluorenes-Tethered Pt-Porphyrins

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Experimental section

General. ^1H NMR and ^{13}C NMR spectra were measured with a JEOL EX-400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer. Coupling constants (J value) are reported in Hertz. In ^1H and ^{13}C NMR spectra, tetramethylsilane (TMS) was used as an internal standard. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and an absolute quantum yield was calculated with the integrating sphere on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in chloroform. Fluorescence lifetime analyses were carried out on a HORIBA FluoreCube spectrofluorometer system; excitation at 375 nm was carried out using a UV diode laser (NanoLED-375L).

Materials. Pyrrole and 5,10,15,20-tetraphenylporphyrin (TPP) were obtained commercially, and used without further purification. 4-(2,7-dibromo-9-(4-(octyloxy)phenyl)-9H-fluoren-9-yl)benzaldehyde (**1**), 9,9,9',9'-tetra-*n*-octyl-2,2'-bifluorenyl-7-boronic acid (**2**) and 9,9,9',9',9'',9''-hexa-*n*-octyl-2, 7';2',7''-terfluorenyl-7-boronic acid (**3**) were prepared according to the literature.^{1,2} In addition, reference molecules, 5FL and 7FL were synthesized by coupling reaction with 9,9'-dioctyl-2,7-dibromofluorene and **2** and **3**, respectively. All reaction was performed under argon atmosphere.

H2P-Br. A flask charged with 300 mL of CH_2Cl_2 was degassed with argon for 1 h, and compound **1** (2.38 g, 3.76 mmol), pyrrole (0.25 g, 3.76 mmol), and trifluoroacetic acid (TFA) (0.43 g, 3.76 mmol) was placed. After stirring for 12 h at room temperature, the solution was added 20 mL of the toluene solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (1.70 g, 7.53 mmol). After stirring for additional 5 h at room temperature, the solution was evaporated. Flash chromatography on silica gel (1 : 1 = hexane : CH_2Cl_2 , $R_f = 0.5$), provided H2P-Br (0.39 g, 0.143 mmol, 15%) as a purple powder. ^1H NMR (CDCl_3 , ppm) 8.88 (s, 8H), 8.10 (d, $J = 7.8$ Hz, 8H), 7.79 (s, 8H), 7.56 (m, 24H), 7.30 (d, $J = 8.3$ Hz, 8H), 6.87 (d, $J = 8.4$ Hz, 8H), 3.87 (t, $J = 6.3$ Hz, 8H), 1.73 (m, 8H), 1.42 (m, 8H), 1.29 (m, 32H),

0.88 (t, $J = 6.9$ Hz, 12H), -2.79 (s, 2H). ^{13}C NMR (CDCl_3 , ppm) 158.44, 153.50, 144.24, 140.95, 138.14, 136.12, 134.93, 131.08, 129.60, 129.50, 129.18, 129.01, 128.19, 126.34, 122.06, 121.73, 119.68, 114.62, 67.97, 65.11, 31.80, 29.33, 29.22, 26.06, 22.65, 14.11. HRMS (p-ESI) calcd. for $\text{C}_{152}\text{H}_{134}\text{Br}_8\text{N}_4\text{O}_4+\text{H}^+$: m/z 2721.3912; found: m/z 2721.4037.

PtP-Br. The solution containing PhCN (30 mL) was added to PtCl_2 (0.138 g, 0.52 mmol) was refluxed for 2 h, and then the solution was added compound H2P-Br (0.25 g, 0.092 mmol). After stirring for overnight at $195\text{ }^\circ\text{C}$, the solution was evaporated. After flash chromatography on silica gel (1 : 1 = hexane : CH_2Cl_2 , $R_f = 0.7$), the product (0.23 g, 0.077 mmol, 84%) was obtained as an orange powder. ^1H NMR (CDCl_3 , ppm) 8.88 (s, 8H), 8.10 (d, $J = 6.3$ Hz, 8H), 7.85 (s, 8H), 7.57 (m, 24H), 7.35 (d, $J = 8.3$ Hz, 8H), 6.89 (d, $J = 8.2$ Hz, 8H), 3.87 (t, $J = 6.1$ Hz, 8H), 1.77 (m, 8H), 1.47 (m, 8H), 1.36 (m, 32H), 0.96 (t, $J = 6.2$ Hz, 12H). ^{13}C NMR (CDCl_3 , ppm) 158.41, 153.43, 144.39, 140.77, 140.13, 138.09, 136.07, 134.16, 131.05, 130.89, 129.52, 129.14, 126.41, 122.05, 121.92, 121.69, 114.58, 67.92, 65.09, 31.80, 29.31, 29.21, 26.03, 22.65, 14.12. HRMS (p-MALDI) calcd. for $\text{C}_{152}\text{H}_{132}\text{Br}_8\text{N}_4\text{O}_4\text{Pt}$: m/z 2912.3315; found: m/z 2912.3342.

PtTPP. The solution containing PhCN (200 mL) was added to PtCl_2 (1.00 g, 3.76 mmol) was refluxed for 2 h, and then the solution was added TPP (0.46 g, 0.75 mmol). After stirring for 16 h at $195\text{ }^\circ\text{C}$, the solution was evaporated. After flash chromatography on silica gel (4 : 1 = hexane : CH_2Cl_2 , $R_f = 0.3$), the product (0.36 g, 0.45 mmol, 59%) was obtained as a red powder. ^1H NMR (CDCl_3 , ppm) 8.75 (t, $J = 5.1$ Hz, 8H), 8.15 (d, $J = 7.4$ Hz, 8H), 7.74 (m, 12H).

Compound PtPF5. The solution containing tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (0.5 mg, 0.0005 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos) (1.5 mg, 0.0037 mmol), cesium carbonate (Cs_2CO_3) (0.20 g, 0.61 mmol), PtP-Br (36.4 mg, 0.0125 mmol) and **2** (82.3 mg, 0.10 mmol) in 0.5 mL of toluene and 0.5 mL of H_2O was stirred at 90 °C for 2 days under argon atmosphere. The pale orange solid (102 mg, 96%) was isolated with reprecipitation by pouring the chloroform solution of the product into 50 mL of methanol twice. ^1H NMR (CDCl_3 , ppm) 8.80 (s, 8H), 8.06 (d, $J = 7.9$ Hz, 8H), 7.96 (d, $J = 7.6$ Hz, 8H), 7.81–7.68 (m, 48H), 7.67–7.57 (m, 48H), 7.46 (d, $J = 8.3$ Hz, 8H), 7.38–7.26 (m, 32H), 6.93 (d, $J = 8.7$ Hz, 8H), 3.95 (t, $J = 6.6$ Hz, 8H), 2.02 (br, 64H), 1.76 (m, 8H), 1.43 (m, 8H), 1.25 (br, 32H), 1.03 (m, 320H), 0.77 (m, 108H), 0.66 (m, 64H). ^{13}C NMR (CDCl_3 , ppm) 158.17, 152.61, 151.80, 151.76, 151.44, 150.97, 145.52, 141.36, 140.79, 140.53, 140.47, 140.28, 140.14, 139.90, 139.77, 139.08, 138.01, 134.22, 130.77, 129.44, 126.95, 126.75, 126.27, 126.14, 126.03, 124.97, 122.91, 121.44, 121.33, 120.57, 119.97, 119.86, 119.68, 114.46, 67.95, 65.22, 55.30, 55.14, 40.35, 31.80, 31.76, 31.68, 31.65, 30.00, 29.36, 29.23, 29.17, 29.12, 26.11, 23.80, 22.55, 22.51, 22.46, 14.07, 14.02, 13.98, 13.93. LRMS (MALDI-TOF MS) calcd. for $\text{C}_{616}\text{H}_{780}\text{N}_4\text{O}_4\text{Pt}$: m/z 8500; found: m/z 8499.

PtPF7. The solution containing $\text{Pd}_2(\text{dba})_3$ (0.5 mg, 0.0005 mmol), S-Phos (1.5 mg, 0.0037 mmol), Cs_2CO_3 (0.20 g, 0.61 mmol), PtP-Br (30 mg, 0.01 mmol) and **3** (100 mg, 0.08 mmol) in 0.5 mL of toluene and 0.5 mL of H_2O was stirred at 90 °C for 2 days under argon atmosphere. The pale orange solid (110 mg, 92%) was isolated with reprecipitation by pouring the chloroform solution of the product into 50 mL of methanol twice. ^1H NMR (CDCl_3 , ppm) 8.83 (s, 8H), 8.08 (d, $J = 7.8$ Hz, 8H), 7.97 (d, $J = 7.7$ Hz, 8H), 7.78 (m, 60H), 7.65 (m, 76H), 7.48 (d, $J = 7.0$ Hz, 8H), 7.39–7.28 (m, 32H), 6.95 (d, $J = 8.4$ Hz, 8H), 3.96 (br, 8H), 2.06 (br, 96H), 1.77 (br, 8H), 1.45 (br, 8H), 1.26 (br, 32H), 1.09 (m, 480H), 0.80 (m, 188H), 0.68 (m, 64H). ^{13}C NMR (CDCl_3 , ppm) 158.19, 152.65, 151.78, 151.46, 151.01, 145.59, 141.39, 140.81, 140.49, 140.31, 140.16, 139.98, 139.10, 138.00, 134.21, 130.83, 129.48, 126.98, 126.78, 126.14, 126.03, 124.98, 122.93, 122.07, 121.47, 120.60, 119.92, 119.86, 119.70, 114.48, 67.97, 65.25,

55.32, 55.16, 40.37, 31.76, 31.70, 30.01, 29.19, 26.12, 23.89, 23.82, 22.57, 14.04. LRMS (MALDI-TOF

MS) calcd. for $C_{848}H_{1100}N_4O_4Pt$: m/z 11609; found: m/z 11608.

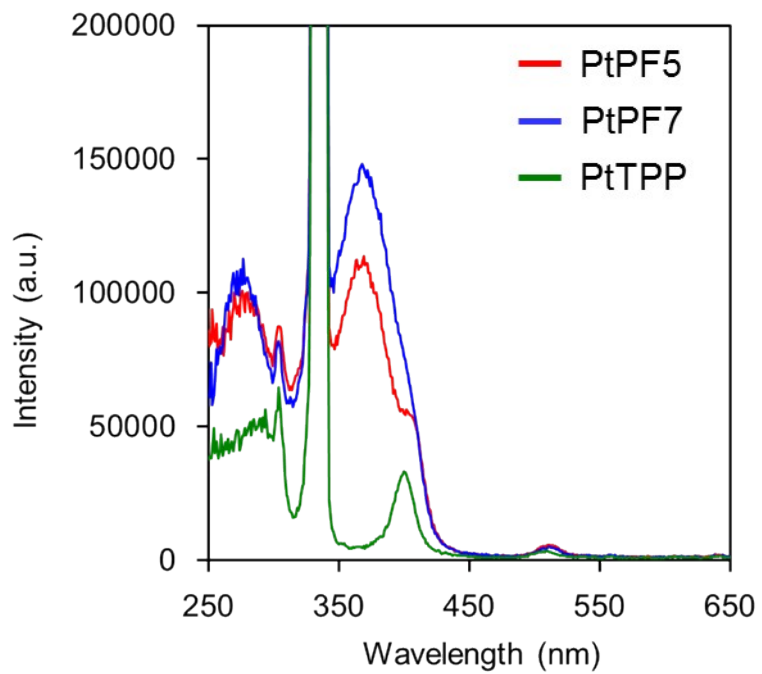


Figure S1. Excitation spectra of the LHA molecules and PtTPP (detection wavelength: 670 nm, in chloroform, 10^{-7} M).

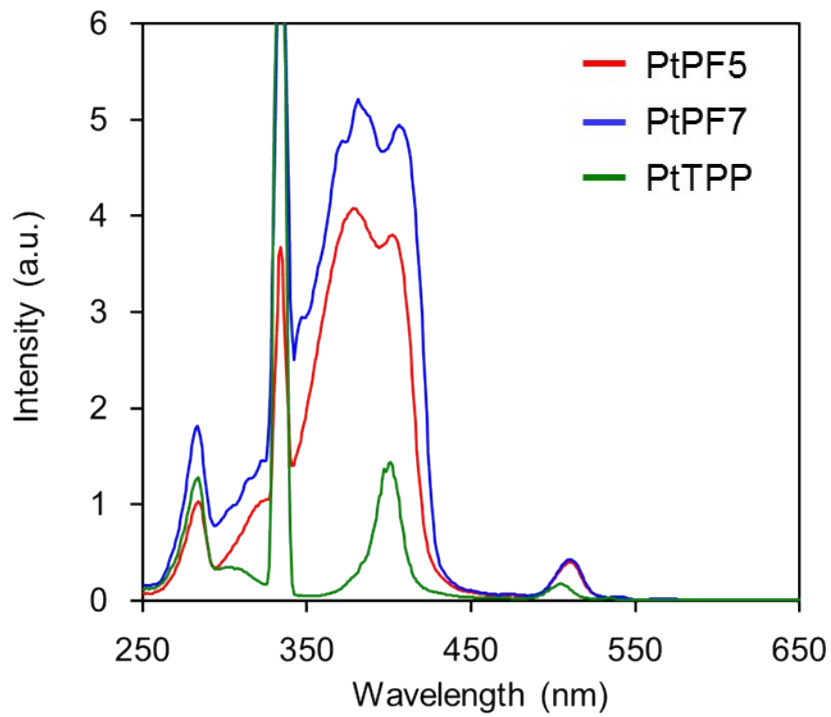


Figure S2. Excitation spectra of the LHA molecules and PtTPP (detection wavelength: 670 nm, in 2-Me-THF, 10^{-7} M and in -196 °C).

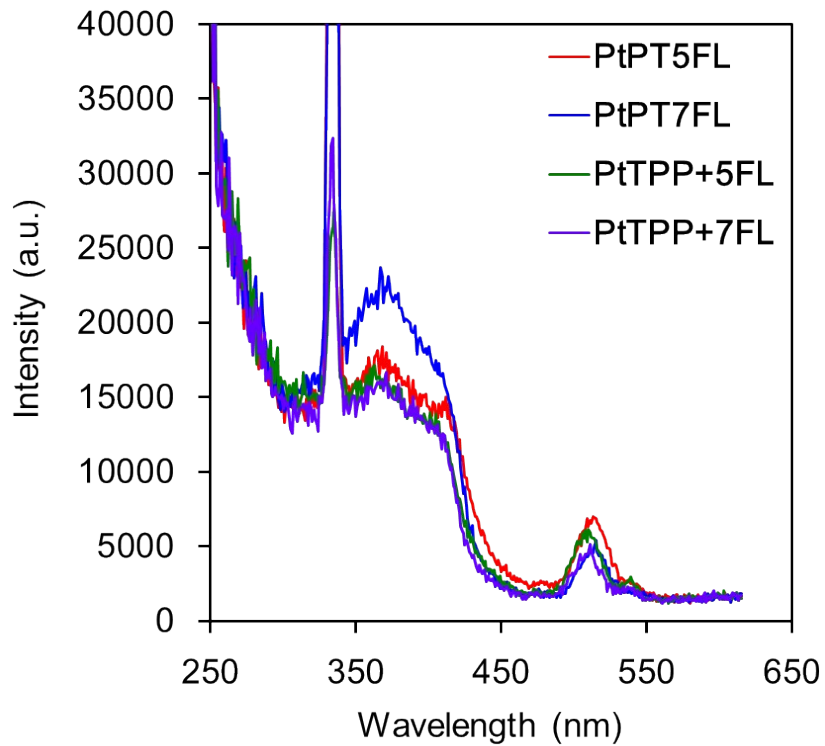


Figure S3. Excitation spectra of the LHA molecules and the composites (detection wavelength: 670 nm, in film states).

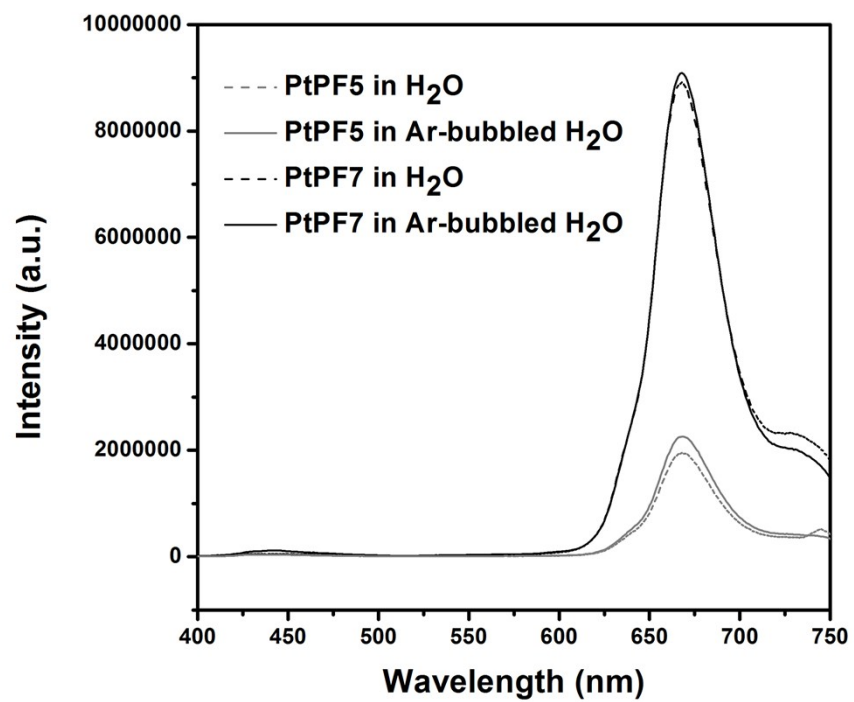


Figure S4. PL spectra of the LHA molecules in the film state (excitation wavelength: 373 nm, solid line: in Ar-bubbled H₂O, dotted line: in H₂O).

References

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