ELECTRONIC SUPPORTING INFORMATION

Sensitizer design for efficient triplet-triplet annihilation upconversion: annihilator-appended tris-cyclometalated Ir(III) complexes

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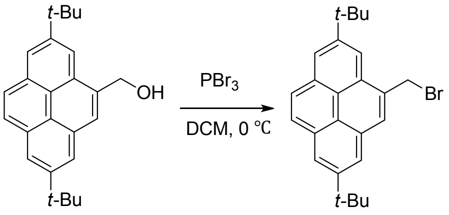
Contents

Synthetic methods and characterization data

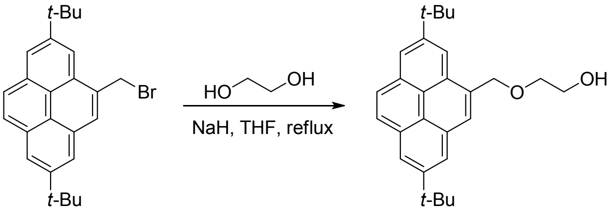
General Methods. The oxygen and moisture sensitive reactions were all performed under nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) was freshly distilled over sodium under nitrogen atmosphere prior to use. Dichloromethane (DCM) was stirred overnight with CaH_2 and then distilled. ^1H and ^{13}C NMR spectra were collected with Bruker Avance 400 (400 MHz), using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported in Hertz (Hz). ^1H and ^{13}C NMR chemical shifts were referenced to the residual solvent peak (7.26 ppm for ^1H and 77.0 ppm for ^{13}C). Electron ionization (EI) mass spectra were collected with a VG ZAB-HS mass spectrometer. Electro-spray ionization (ESI) mass spectrometry was performed using a Bruker Apex IV FTMS instrument. Elemental analyses were performed using a German Vario EL III elemental analyzer.

Synthetic procedures



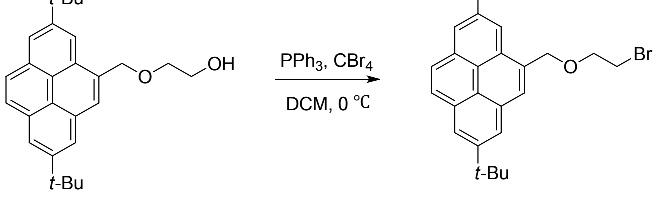
1

PBr_3 (2.2 g, 8.13 mmol) in DCM (20 mL) was added drop-wise to a stirred solution of (2,7-di-*tert*-butylpyren-4-yl)methanol (2.8 g, 8.13 mmol) in DCM (50 mL) at 0 °C. Upon completing the addition, the reaction mixture was stirred at room temperature for additional 15 min and then quenched by water before extraction with DCM. The combined organic layers were sequentially washed with aq. $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, and then concentrated *in vacuo*. The residue was purified by column chromatography with petroleum ether (PE) as the eluent to afford 4-(bromomethyl)-2,7-di-*tert*-butylpyrene **1** (3.0 g, 91%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, 1H, J = 1.6 Hz), 8.22 (d, 1H, J = 1.6 Hz), 8.21 (d, 1H, J = 1.6 Hz), 8.19 (d, 1H, J = 1.6 Hz), 8.15 (s, 1H), 8.04 (d, 1H, J = 9.2 Hz), 8.01 (d, 1H, J = 9.2 Hz), 5.20 (s, 2H), 1.62 (s, 9H), 1.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.96, 147.48, 131.40, 130.18, 129.71, 128.87, 128.20, 127.24, 126.75, 126.15, 122.40, 122.02, 121.89, 121.55, 121.54, 118.5, 34.44, 34.16, 32.03, 30.93, 30.87. MS (EI): Calcd. for $C_{25}H_{27}Br$: 406. Found: 406 (m/z). Elem. Anal.: Calcd. for $C_{25}H_{27}Br$: C, 73.71; H, 6.68; found: C, 73.90; H, 6.83.



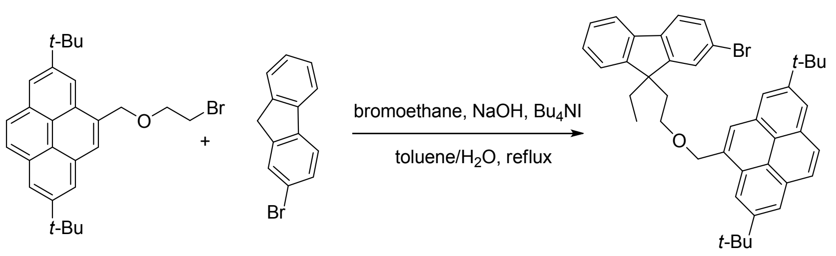
2

To a mixture of sodium hydride (91 mg, 3.79 mmol) in THF, a solution of ethylene glycol (322 mg, 5.19 mmol) in THF (3 mL) was added slowly via a syringe. After the resultant solution was stirred at ambient temperature for 1 h, a solution of **1** (470 mg, 1.15 mmol) in THF (3 mL) was slowly added to it. The reaction mixture was then stirred at reflux for 15 h and then quenched by aqueous NH_4Cl. After removal of THF *in vacuo*, the aqueous layer was extracted with ethyl acetate. The organic layer was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography using gradient PE/DCM mixtures as the eluent to give **2** (250 mg, 56%) as a white powder. ^1H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, 1H, J = 1.6 Hz), 8.21 (d, 1H, J = 1.6 Hz), 8.19 (s, 2H), 8.06 (s, 1H), 8.02 (s, 2H), 5.24 (s, 2H), 3.81-3.77 (m, 4H), 2.00 (t, 1H, J = 5.2 Hz), 1.59 (s, 9H), 1.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.78, 148.55, 132.60, 131.13, 130.71, 130.07, 129.36, 127.83, 127.71, 127.27, 123.29, 122.81, 122.43, 122.40, 122.29, 118.70, 72.63, 71.23, 62.11, 35.42, 35.23, 32.05, 31.97. MS (EI): Calcd. for $C_{27}H_{32}O_2$: 388. Found: 388 (m/z). Elem. Anal.: Calcd. for $C_{27}H_{32}O_2$: C, 83.46; H, 8.30; Found: C, 83.45; H, 8.39.



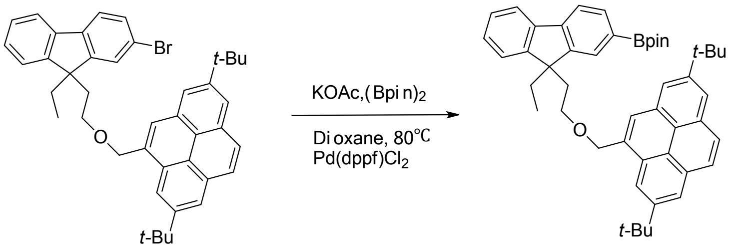
3

Triphenylphosphine (387 mg, 1.47 mmol) was added in portions to a solution of **2** (382 mg, 0.98 mmol) and carbon tetrabromide (489 mg, 1.47 mmol) in dichloromethane (15 mL) at 0 °C. The reaction mixture was stirred at room temperature for 90 min. After removal of solvents *in vacuo*, the residue was subjected to column chromatography (silica gel, PE/DCM, 2/1, v/v) to afford **3** (326 mg, 93%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.50 (d, 1H, *J* = 1.6 Hz), 8.20 (d, 1H, *J* = 1.6 Hz), 8.18 (s, 2H), 8.04 (s, 1H), 8.02 (d, 1H, *J* = 9.2 Hz), 8.00 (d, 1H, *J* = 9.2 Hz), 5.24 (s, 2H), 3.92 (t, 2H, *J* = 6 Hz), 3.51 (t, 2H, *J* = 6 Hz), 1.59 (s, 9H), 1.57 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.77, 148.59, 132.36, 131.06, 130.71, 130.04, 129.29, 127.99, 127.74, 127.21, 123.28, 122.85, 122.43, 122.42, 122.34, 119.02, 72.63, 69.83, 35.45, 35.23, 32.07, 31.97, 30.72. MS (EI): Calcd. for $C_{27}H_{31}OBr$: 450. Found: 450 (m/z). Elem. Anal.: calcd. for $C_{27}H_{31}OBr$: C, 71.83; H, 6.92; Found: C, 71.83; H, 7.22.



4

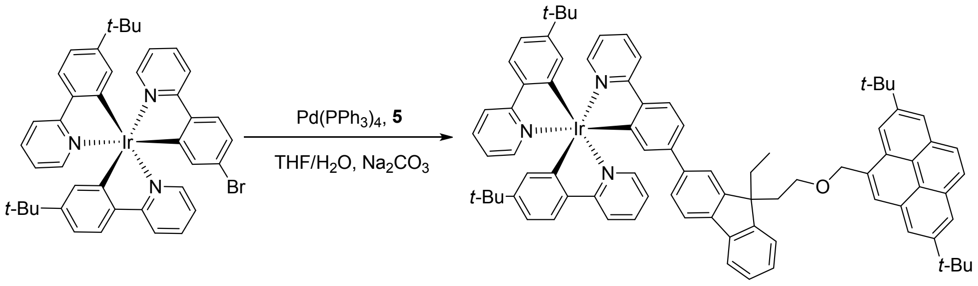
A 25 mL Schlenk tube was charged with **3** (200 mg, 0.44 mmol), 2-bromo-9*H*-fluorene (108 mg, 0.44 mmol), NaOH (531 mg, 13.28 mmol) and tetrabutylammonium iodide (8 mg, 0.022 mmol). The tube was evacuated and back-filled with nitrogen 3 times. To the mixture was added degassed toluene (1 mL) and H_2O (0.3 mL) under nitrogen atmosphere. The colorless solution turned to light red while being stirred at reflux for 11 h. To this stirred solution bromoethane (200 mg, 1.83 mmol) was added under N_2 atmosphere. The resultant solution turned back to colorless while being heated at reflux temperature for another 11 h. The reaction mixture was cooled to room temperature and diluted with DCM. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was subjected to column chromatography (silica gel, PE/DCM, 4/1, v/v) to provide **4** (66 mg, 23%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.16-8.13 (m, 4H), 7.98 (s, 2H), 7.78 (s, 1H), 7.63 (dd, 1H, *J* = 6.4 Hz, 1.6 Hz), 7.55 (d, 1H, *J* = 1.6 Hz), 7.52 (d, 1H, *J* = 8 Hz), 7.44 (dd, 1H, *J* = 8 Hz, 1.6 Hz), 7.36-7.27 (m, 3H), 4.82 (d, 1H, *J* = 12.4 Hz), 4.77 (d, 1H, *J* = 12.4 Hz), 3.15-3.06 (m, 2H), 2.50 (t, 2H, *J* = 7.6 Hz), 2.05 (q, 2H, *J* = 7.2 Hz), 1.57 (s, 9H), 1.55 (s, 9H), 0.31 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.76, 149.05, 148.55, 148.21, 140.04, 139.96, 132.85, 131.00, 130.56, 130.24, 130.18, 129.10, 127.67, 127.56, 127.26, 127.17, 126.53, 126.35, 123.10, 123.02, 122.55, 122.46, 122.02, 122.00, 121.17, 121.16, 119.88, 118.25, 71.61, 66.96, 53.92, 39.32, 35.35, 35.20, 33.45, 32.02, 31.98, 8.04. HR-MS (ESI): calcd for $C_{42}H_{43}BrO$: 642.24973; found 642.25195 (m/z), 660.28464 (m/z + NH_4^+).



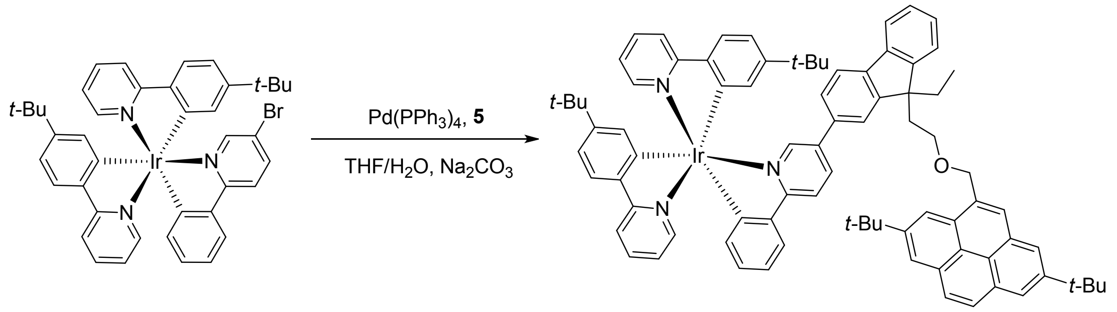
5

A 25 mL Schlenk tube was charged with **4** (50 mg, 0.078 mmol), bis(pinacolato)diboron (41 mg, 0.16 mmol), Pd(dppf)Cl_2 (2.9 mg, 0.004 mmol) and anhydrous potassium acetate (38 mg, 0.39 mmol). The tube was evacuated and back-filled with nitrogen 3 times. To the mixture was added degassed 1,4-dioxane (2 mL) under nitrogen. The mixture was stirred at 80 °C for 26 h. The reaction mixture was diluted with DCM, washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated *in vacco*. The solid residue was purified by flash column chromatography (silica gel, PE/DCM, 2/1 v/v) to give **5** (28 mg, 52%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.12 (m, 4H), 7.97 (s, 2H), 7.87 (s, 1H), 7.84 (d, 1H, J = 7.6 Hz), 7.82 (s, 1H), 7.73 (s, 1H), 7.71 (s, 1H), 7.38 (d, 1H, J = 7.2 Hz), 7.33-7.27 (m, 2H), 4.82 (d, 1H, J = 12 Hz), 4.73 (d, 1H, J = 12 Hz), 3.16-3.10 (m, 1H), 3.06-3.00 (m, 1H), 2.65-2.52 (m, 2H), 2.19-2.04 (m, 2H), 1.57 (s, 9H), 1.54 (s, 9H), 1.37 (s, 12H), 0.30 (t, 3H). HR-MS (ESI): calcd for $C_{48}H_{55}NO_3$ + NH_4^+: 708.45880; found 708.45905 (m/z + NH_4^+).

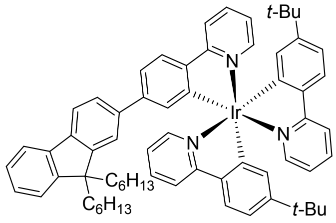
General procedures for pyrenyl-appended fluorenyl Ir(ppy)$_3$ complexes. A 25 mL Schlenk tube was charged with bromo-substituted Ir(ppy)$_3$ (0.018 mmol), **5** (1.25 eq per C-Br bond), Pd(PPh_3)$_4$ (3% mol per C-Br bond), Na_2CO_3 (0.104 mmol). The tube was evacuated and back-filled with nitrogen 3 times. Degassed H_2O (0.5 mL) and THF (2.5 mL) were added to the mixture under nitrogen atmosphere. The mixture was stirred at reflux for 18 h, and quenched with aq. NH_4Cl. The aqueous layer was then extracted by DCM. The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The solid residue was subjected to column chromatography (silica gel, PE/DCM) to get the product as a yellow solid.



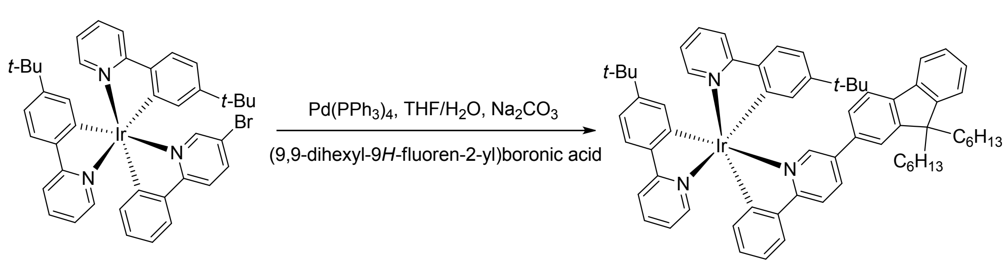
IrFppy-pyr. (20%) ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.19-7.96 (m, 6H), 7.89-7.81 (m, 3H), 7.75-7.19 (m, 19H), 7.07-7.05 (m, 1H), 6.95-6.73 (m, 6H), 4.89-4.70 (m, 2H), 3.18-2.99 (m, 2H), 2.59-2.50 (m, 2H), 2.09-1.98 (m, 2H), 1.54-1.48 (m, 18H), 1.14-1.09 (m, 18H), 0.39-0.30 (m, 3H). HR-MS (ESI): calcd for $C_{83}H_{82}IrN_3O$: 1329.60871; found 1329.61292 (m/z), 1347.64261 (m/z + NH_4^+).



IrpFpy-pyr. (68%) ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16-8.13 (m, 3H), 8.11-8.06 (m, 1H), 7.99 (s, 1H), 7.94 (d, 1H, J = 1.2 Hz), 7.84-7.26 (m, 19H), 7.15-7.13 (m, 1H), 7.05-7.01 (m, 1H), 6.95-6.72 (m, 8H), 4.85-4.76 (m, 2H), 3.09-2.98 (m, 2H), 2.57-2.38 (m, 2H), 2.12-1.89 (m, 2H), 1.56-1.51 (m, 18H), 1.12-1.08 (m, 18H), 0.32-0.20 (m, 3H). HR-MS (ESI): calcd for $C_{83}H_{82}IrN_3O$: 1329.60871; found 1329.60734 (m/z).



IrFppy. This compound was previously reported in the literature[1].



IrpFpy. (82%) Similar procedures for preparing IrpFpy-pyr are followed, except using (9,9-dyhexyl-9H-fluoren-2-yl)boronic acid for Suzuki coupling reagent. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.91-7.80 (m, 5H), 7.68-7.49 (m, 9H), 7.34-7.30 (m, 4H), 7.09 (d, 1H, J = 1.2 Hz), 7.05 (d, 1H, J = 2.0 Hz), 6.96-6.82 (m, 8H), 2.00-1.91 (m, 2H), 1.85-1.78 (m, 2H), 1.12 (s, 9H), 1.10 (s, 9H), 1.08-1.00 (m, 12H), 0.77-0.73 (m, 6H), 0.59-0.49 (m, 4H). HR-MS (ESI): calcd for $C_{66}H_{72}IrN_3$: 1099.53555; found 1099.53316 (m/z).

Photophysical Measurements

Steady state spectroscopy and quantum yield measurements. All the measurements were carried out using freshly distilled DCM or toluene as solvents. UV-vis absorption spectra were recorded using a Hitachi U-4100 spectrophotometer with a 1-cm quartz cell. Photoluminescence spectra were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer with right-angle geometry, using 1-cm quartz cuvettes. The excitation wavelength in the quantum yield measurements was 380 nm. The phosphorescence spectra at 77 K were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer with right-angle geometry using quartz tube in MeTHF matrix at liquid nitrogen temperature.

1. *Phosphorescence spectra*

The phosphorescence spectra of 2,7-di-*tert*-butylpyrene (DBP), IrFppy-pyr and IrpFpy-pyr are presented in Figures S1 and S2. Only very weak DBP singlet emission was observed, indicating efficient energy transfer from singlet excited [DBP] to [IrFppy] or [IrpFpy], including in the frozen MeTHF matrix (Fig. S2a). As shown in Fig. S2b, phosphorescence emissions from [IrFppy] or [IrpFpy] and appended DBP could be observed in spectra with certain delay time. The emission peak wavelengths at 77 K and corresponding energy levels are summarized in Table S1.

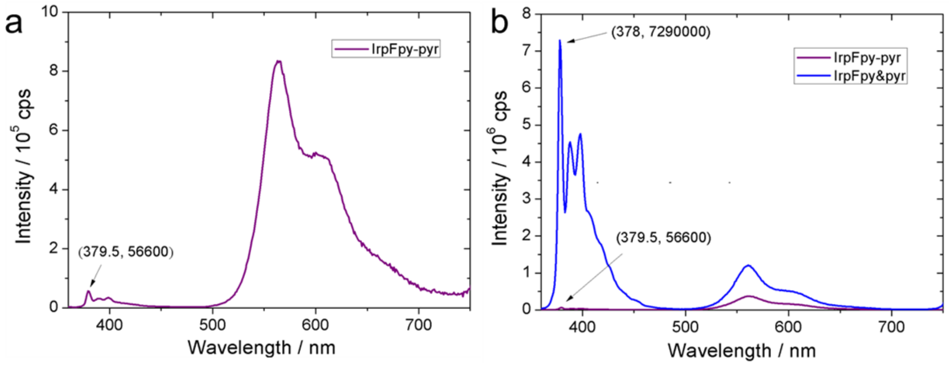


Fig. S1 Emission spectra of (a) IrpFpy-pyr and (b) IrpFpy-pyr (purple) in comparison with mixture of IrpFpy and DBP at the same concentration (measured in deaerated toluene excited at 340 nm with O.D. of 0.1 at r.t.).

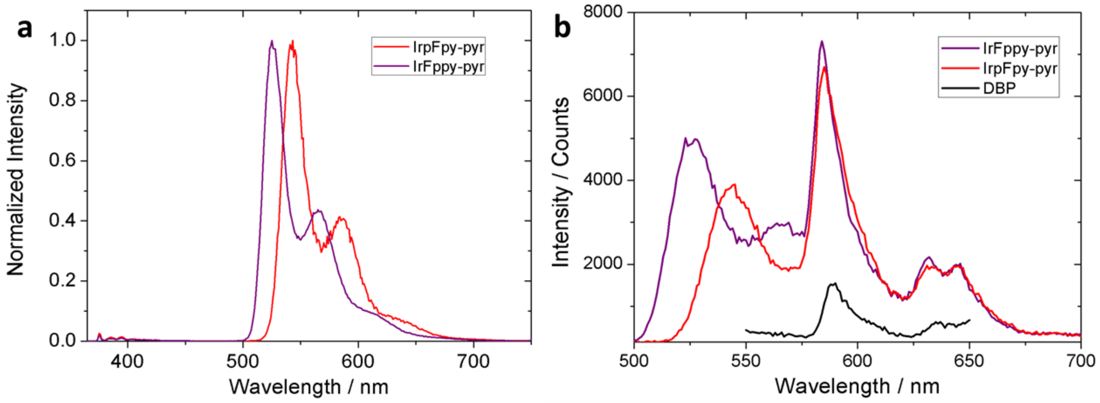


Fig. S2 Phosphorescence spectra of IrFppy-pyr and IrpFpy-pyr (at 3×10^{-5} M in MeTHF at 77 K, excited at 340 nm): (a) steady-state emissions and (b) spectra collected with a certain delay time. Samples were excited by a pulsed Xe lamp. The phosphorescence spectra of unattached **DBP** is also presented for comparison (b, black line).

Table S1 Phosphorescence emission maxima of IrFppy-pyr, IrpFpy-pyr and appended [DBP] at 77 K in MeTHF with calculated triplet energy levels

	λ_{em}/nm (MeTHF, 77 K)	Energy level (eV)
IrFppy-pyr	525	2.36
IrpFpy-pyr	543	2.28
DBP	585	2.12

2. *Concentration dependence of luminescence quantum yields*

The concentration dependent quantum yields of IrFppy-pyr and IrpFpy-pyr were systematically investigated in deaerated toluene at 20 °C. The data were summarized in Fig. S3. Both compounds showed a slight decrease of quantum yields as the concentration was increased.[2] The quantum yields of IrpFpy-pyr and IrFppy-pyr at the lowest examined concentration were still far below the quantum yields of model IrpFpy and IrFppy, suggesting that intermolecular self-quenching was not the main reason for the drop off of quantum yields upon [DBP] attachment.

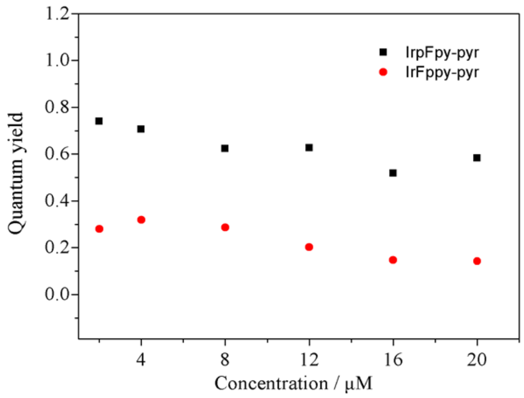


Fig. S3 Concentration dependence of emission quantum yields of IrFppy-pyr and IrpFpy-pyr measured in deaerated toluene solutions excited at 450 nm by Xenon lamp with Ir(ppy)$_3$ as quantum yield standard.[3]

Lifetime measurement. Photoluminescence decay curves were collected on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer. Samples for phosphorescence lifetime measurements were prepared in freshly distilled toluene. The solutions were degassed by three cycles of freeze-pump-thaw and re-filled with nitrogen. Lifetimes shorter than 1 microsecond were measured with TCSPC using a LifeSpec-Red spectrofluorometer with 372 nm laser source (Edinburgh). Lifetimes between 1 to 20 microseconds were measured with TCSPC using a FluoroMax-4P spectrofluorometer with NanoLED of 369 nm as the excitation source. Lifetimes longer than 20 microseconds were measured using a FluoroMax-4P spectrofluorometer with a pulsed Xenon flash lamp as the excitation source and excited at 425 nm. Phosphorescence lifetimes were fitted with single exponential decay without deconvolution. The exponential fits were performed using Horiba Jobin Yvon DAS6 software or origin 8.0. The long triplet lifetimes of IrFppy-pyr and IrpFpy-pyr were extremely sensitive to oxygen, as shown by the great fluctuations in obtained data. Thus, larger error bars occur with these long lifetime data.

A bi-exponential decay was observed for longer lifetime component of IrpFpy-pyr, which corresponds to 1.57 ms (42%) and 0.77 ms (58%). The averaged lifetime value was used in Table 1. We suspect that this bi-exponential decay was related to the fact that the structure of IrpFpy-pyr represented two pairs of diastereomeric enantiomers (one of the chiral centers was the *fac*-Ir and the other was the 9-position of fluorene). The diastereomers likely exhibit slightly different lifetimes. Moreover, these varied lifetimes in different diastereomer structures probably have differed susceptibility to various quenching processes, such as intermolecular self-quenching, residual oxygen quenching, etc., which further complicated the apparent lifetime values. The same situation should occur to diastereomers of IrFppy-pyr as well, but those diastereomers may just happen to display nearly identical behaviors with negligible differences in lifetimes, undetectable by the instruments.

Time-resolved phosphorescence decay profiles of IrFppy-pyr and IrpFpy-pyr were recorded in the time range up to 200 ns (Fig. S4). Both compounds were excited by 372 nm laser pulses with repetition frequency of 100 Hz (the low repetition frequency was applied to ensure the complete decay of the millisecond excited state). The contribution of the shorter lifetime component to the steady state intensity (known as lifetime-weighted quantum yield[4]) was very small, being about 0.05% for IrFppy-pyr and 0.04% for IrpFpy-pyr, which were estimated by comparing the magnitude of intensity decay over the first 100 ns with the residual intensity beyond 100 ns (presumably the shorter nanosecond lifetime component was fully decayed in about 100 ns).

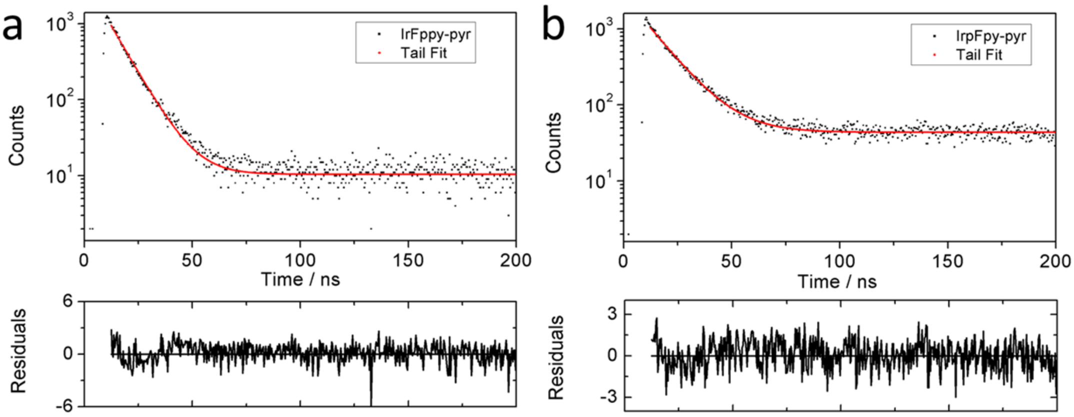


Fig. S4 Time-resolved phosphorescence decays of (a) IrFppy-pyr and (b) IrpFpy-pyr in deaerated toluene (1×10^{-5} M) excited by 372 nm laser pulse at repetition rate of 100 Hz.

Nanosecond Transient Absorption. Nanosecond transient absorption measurements were performed on a LP-920 laser flash photolysis setup (Edinburgh). Excitation at 410 nm with a from a computer-controlled Nd:YAG laser/OPO system from Opotek (Vibrant 355 II) operating at 10 Hz was directed to the samples with O.D. of ~0.12 at the excitation wavelength.

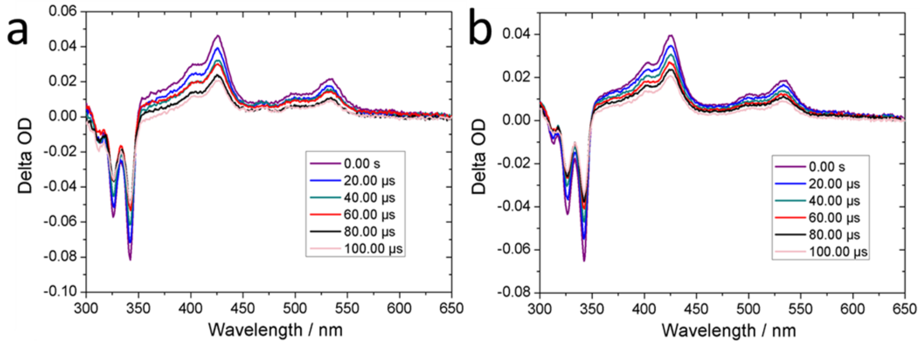


Fig. S5 Transient absorption difference spectra of (a) IrFppy-pyr and (b) IrpFpy-pyr at 10 μM in deaerated toluene recorded at 20 °C, excited with 410 nm pulsed laser (~10 mJ/pulse, FWHM = 8 ns).

Upconversion measurement. The upconversion spectra were recorded by a FluoroMax-4P spectrofluorometer using a Xenon lamp as the excitation source (the light intensity was c.a. 7 mW/cm^2). The samples were excited at 450±5 nm. A 400 nm long-pass filter was placed between the lamp and sample to avoid shorter-wavelength light interferences. Freshly distilled toluene was used as the solvent. Each of sample solution was degassed by three freeze-pump-thaw cycles and then sealed under vacuum. Ir(ppy)$_3$ (Φ_p =0.97) was used as quantum yield standard for upconversion measurements.[3]

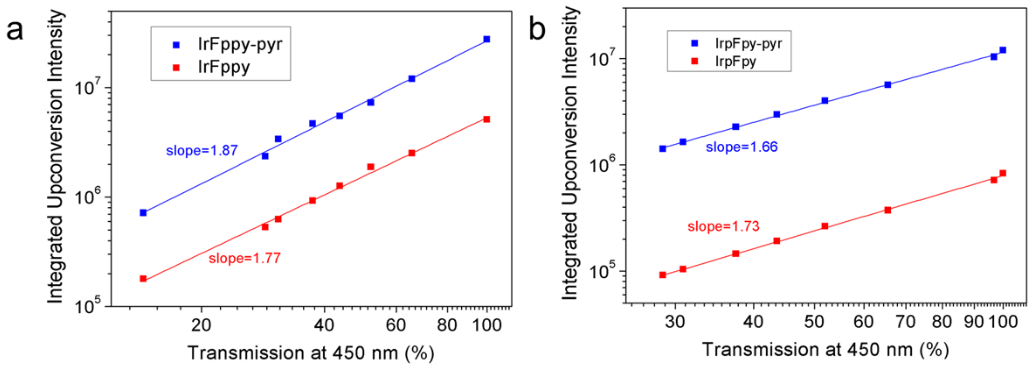


Fig. S6 Integrated upconversion emission intensity (sensitizer at 1×10^{-5} M) as a function of transmission percentage of neutral density filters[5] at 450 nm (measured in deaerated toluene with annihilator concentration of 6×10^{-5} M). The deviation from a quadratic relationship may be due to the disturbance of strong phosphorescence from the high quantum yield sensitizers.

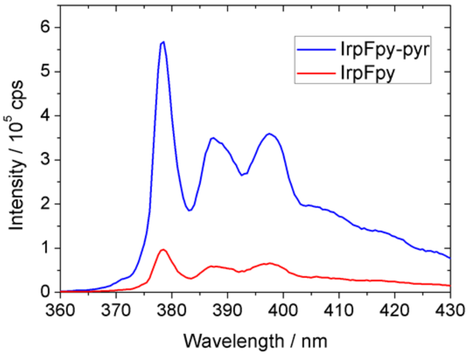


Fig. S7 Comparison of up-converted emissions from deaerated toluene solutions of IrpFpy-pyr or IrpFpy (both at 1×10^{-5} M) in the presence of DBP (annihilator concentration at 6×10^{-5} M), excited at 450 nm by a Xenon lamp.

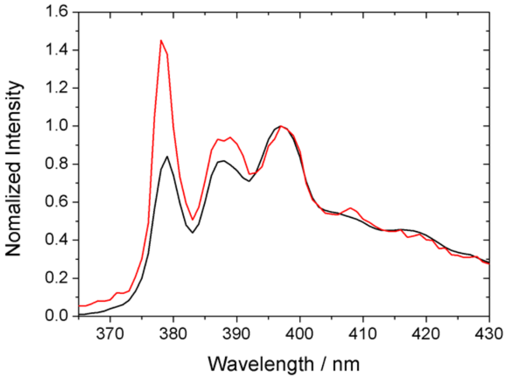


Fig. S8 Up-converted emission profiles measured in deaerated toluene solutions of IrFppy (1×10^{-5} M) and DBP (1×10^{-3} M, black line; 6×10^{-5} M, red line), normalized at 397 nm.

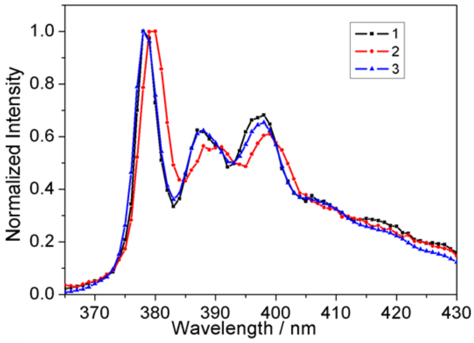
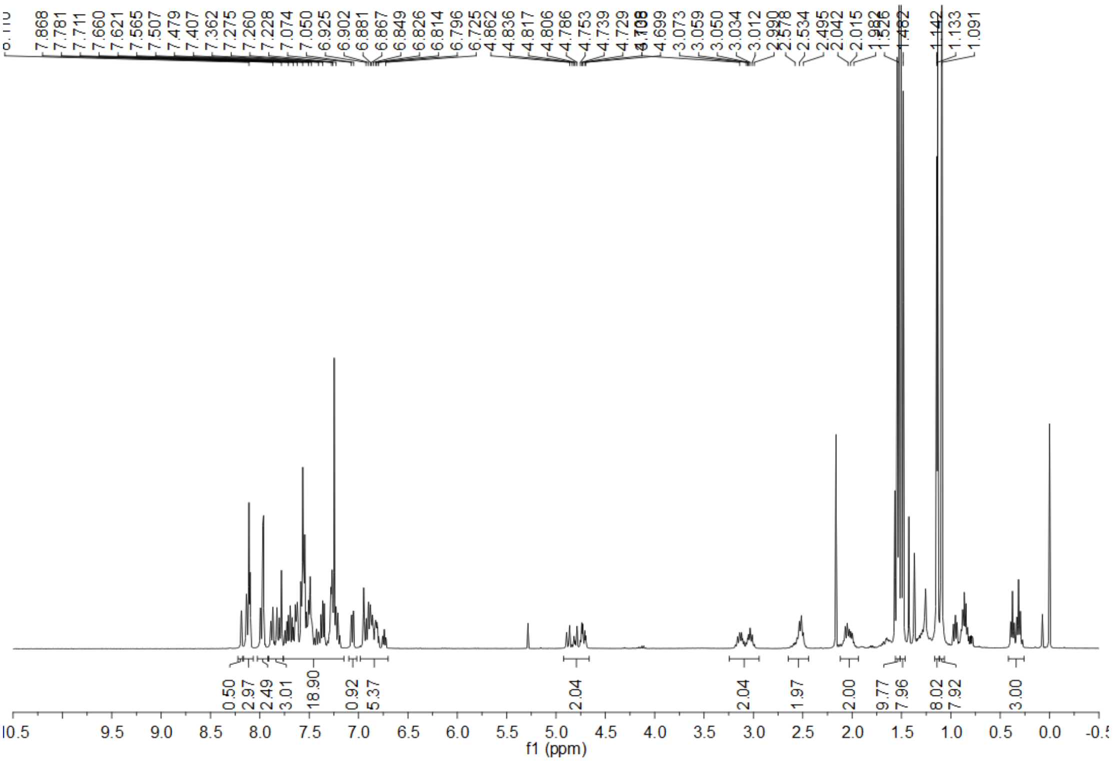
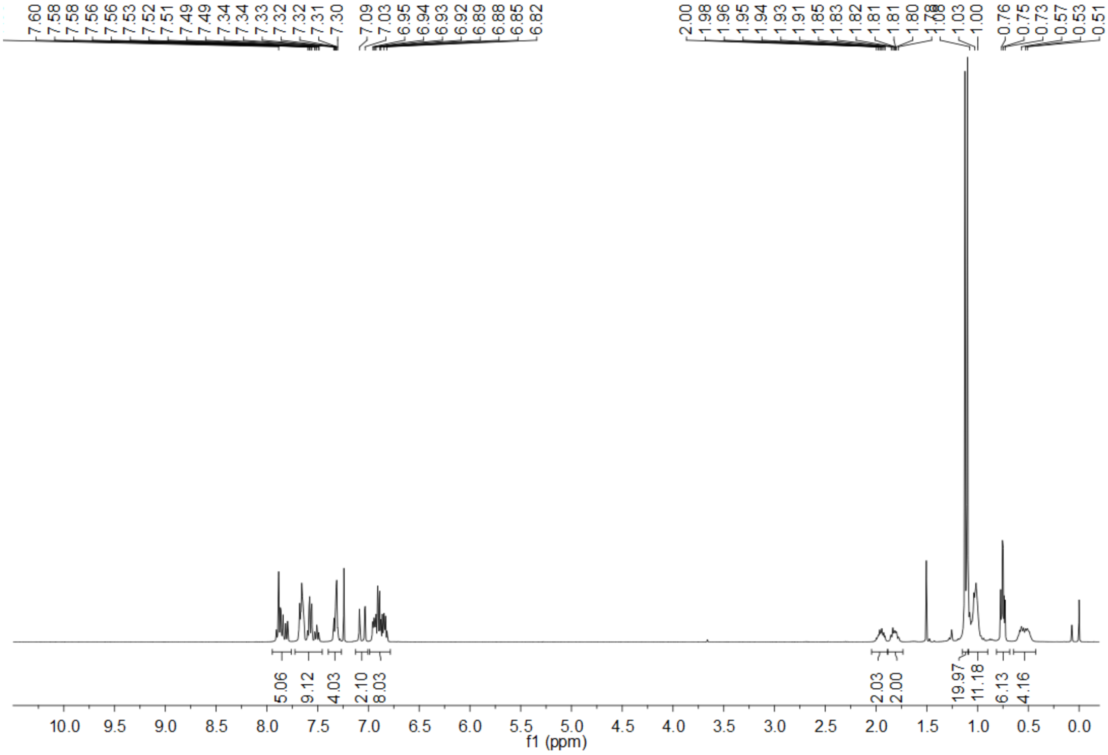


Fig. S9 Comparison of normalized emission spectra of (1) UC emission signal (reproduced from blue line in Fig. S7), (2) [DBP] singlet emission, and (3) unattached DBP singlet emission (reproduced from Fig. S1).

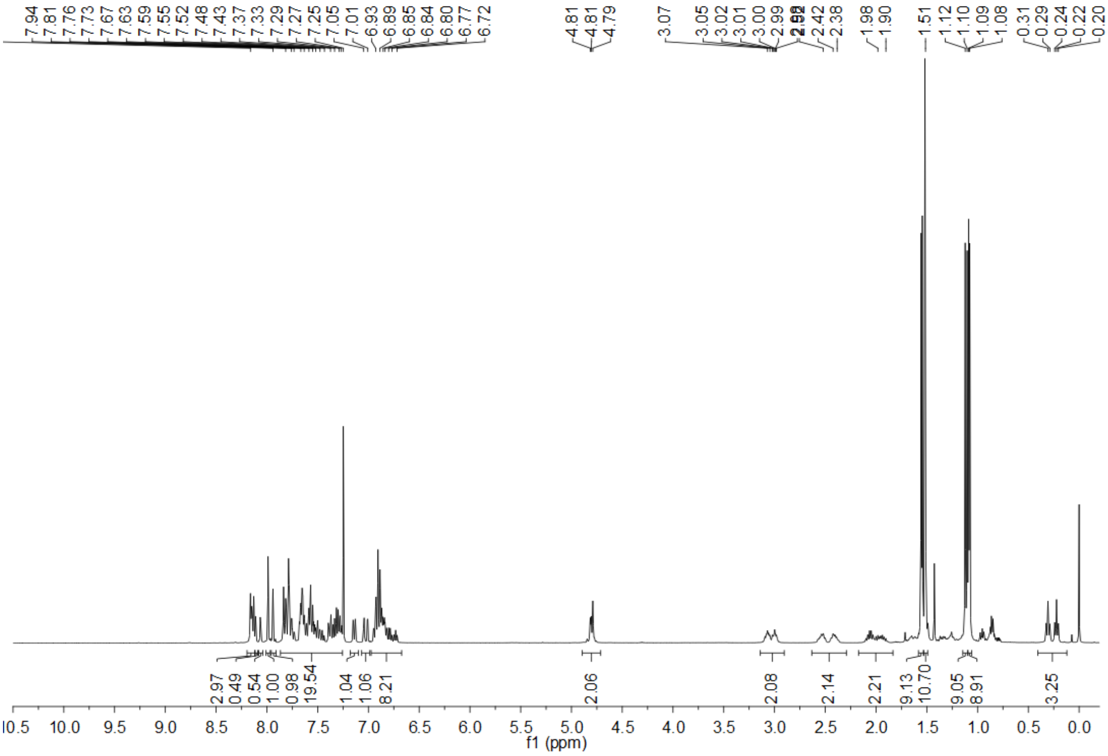
^{1}H NMR Spectra of new iridium sensitizers



IrFppy-pyr



IrpFpy



IrpFpy-pyr

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