Supplementary Information

Two- & three-photon absorption and excitation phosphorescence of

oligofluorene-substituted Ir(ppy)₃

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I. Syntheses and characterizations

Chemicals were used as received unless otherwise indicated. Reagent-grade tetrahydrofuran (THF) was distilled over sodium and benzophenone and toluene was distilled over sodium. NMR spectra were recorded on Varian Mercury plus 300 or Bruker AVANCE III 400. Chemical shifts in ¹H NMR spectra are reported in parts per million (ppm) with TMS (0 ppm) as the standard. Chemical shifts in ¹³C NMR spectra are reported in parts per million (ppm) with CDCl₃ (77.0 ppm) as the standard. ESI-TOF mass spectra were recorded on a Bruker Apex IV FTMS mass spectrometer. **1-Br**^[S1] and **3-Br**^[S2] were synthesized according to the reported procedures.



Scheme S1. Syntheses of bromo-substituted cyclometalated Ir complexes

tBuppy-Br. A Schlenk tube containing 2,4-dibromopyridine (2.0)8.4 g, mmol), 4-tert-butylphenylboronic acid (0.5 g, 2.8 mmol), $Pd(PPh_3)_4$ (65 mg, 0.056 mmol), and K_2CO_3 (2.0 g, 14.5 mmol) was evacuated and backfilled with nitrogen three times. After degassed H₂O (7 mL) and toluene (14 mL) were added, the tube was sealed under nitrogen and heated at 40 °C for 15 h. The reaction mixture was then allowed to cool to room temperature before being diluted with petroleum ether (PE). After the aqueous phase was separated, the organic mixture was washed with brine and dried over anhydrous Na₂SO₄. After removal of solvents in vacuo, the residue was purified with column chromatography on silica gel, eluted with PE/DCM (dichloromethane, 4/1, v/v), to afford *t***Buppy-Br** as a white solid (0.44 g, 54%). ¹H NMR (CDCl₃, 300 MHz, ppm): 8.47 (d, 1H, J = 5.4 Hz), 7.91-7.86 (m, 3H), 7.49 (dd, 2H, $J_1 = 6.9$ Hz, $J_2 = 1.8$ Hz), 7.35 (dd, 1H, $J_1 = 5.4$ Hz, $J_2 = 1.8$ Hz), 1.35 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 158.9, 152.9, 150.3, 135.2, 133.3, 126.7, 125.8, 124.9, 123.6, 34.7, 31.2. ESI MS: Calcd. for C₁₅H₁₆BrN: 289.0. Found: 290.0 ([M+H]⁺).

ppy-Br. The synthesis of **ppy-Br** was similar to *t***Buppy-Br**, except that phenylboronic acid was used. Purification of the crude product with column chromatography on silica gel eluted with PE/EA (ethyl acetate, 10/1, v/v) afforded **ppy-Br** as a white solid (0.76 g, 40%). ¹H NMR (CDCl₃, 300 MHz ppm): δ 8.49 (d, 1H, *J* = 8.4 Hz), 7.94-7.87 (m, 3H), 7.47-7.40 (m, 3H), 7.38 (dd, 1H, *J* = 8.4, 1.2 Hz). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 155.9, 150.7, 139.3, 138.2, 129.3, 128.9, 126.7, 121.6, 119.3. ESI MS: Calcd. for C₁₁H₈BrN: 233.0. Found: 234.0 ([M+H]⁺). **5-Br.** A round-bottomed flask containing **5-dimer**^[S1] (0.20 g, 0.15 mmol), silver trifluoroacetate (0.13 g, 0.56 mmol), and **ppy-Br** (0.14 g, 0.63 mmol) was added with 2-ethoxyethanol (20 mL). The reaction mixture was heated at reflux for 5 h. After diluting with EA, the organic mixture was washed with H₂O (×3) and dried over anhydrous Na₂SO₄. After removal of solvents *in vacuo*, the residue was purified with column chromatography on silica gel (eluted with PE/EA=4/1, v/v) and afforded **5-Br** as a yellow solid (40 mg, 15%). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.98 (d, 1H, *J* = 2.1 Hz), 7.83-7.77 (m, 2H), 7.62-7.48 (m, 7H), 7.39 (d, 1H, *J* = 6.0 Hz), 6.99 (dd, 1H, *J*₁ = 6.0 Hz, *J*₂ = 2.1 Hz), 6.93-6.76 (m, 9H), 1.08 (s, 9H), 1.06 (s, 9H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 168.6, 166.8, 166.7, 162.9, 160.2, 160.1, 147.7, 146.9, 142.2, 141.0, 140.9, 137.3, 135.8, 134.4, 132.1, 130.9, 130.2, 128.8, 124.9, 124.1, 123.4, 121.8, 121.5, 121.4, 119.7, 118.5, 118.4, 117.0, 116.8, 34.4, 34.3, 31.3, 31.2. ESI MS: Calcd. for C₄₁H₃₉BrIrN₃: 845.2. Found: 846.2 ([M+H]⁺).

2-Dimer. A round-bottomed flask containing IrCl₃ (69 mg, 0.20 mmol) and *t***Buppy-Br** (113 mg, 0.39 mmol) was added with 2-ethoxyethanol (6 mL) and H₂O (2 mL). The reaction mixture was heated at reflux for 14 h. Then H₂O (15 mL) was added to the mixture, and the yellow precipitate was filtered and washed with H₂O and MeOH/H₂O (1:1, v/v) sequentially. The obtained powder (quantitative) was used directly in the next step without further purification. ¹H NMR (CDCl₃, 300 MHz, ppm): 9.03 (d, 4H, J = 6.3 Hz), 7.96 (dd, 4H, $J_1 = 1.5$ Hz, $J_2 = 0.3$ Hz), 7.37 (d, 4H, J = 7.8 Hz), 6.96 (dd, 4H, $J_1 = 6.9$ Hz, $J_2 = 1.5$ Hz), 6.83 (dd, 4H, $J_1 = 8.1$ Hz, $J_2 = 1.5$ Hz), 6.03 (d, 4H, J = 1.5 Hz), 0.97 (s, 36H).

2-Br. The synthesis of **2-Br** was similar to **5-Br** except that **2-dimer** and *t***Buppy-Br** were used as substrates. The reaction residue was purified with column chromatography on silica gel (eluted with PE/EA=4/1, v/v) and afforded **2-Br** as a yellow solid (19 mg, 23%). ¹H NMR (CDCl₃, 300 MHz, ppm): 7.93 (d, 3H, J = 1.8 Hz), 7.50 (d, 3H, J = 8.4 Hz), 7.41 (d, 3H, J = 5.7 Hz), 7.01 (dd, 3H, $J_1 = 6.0$ Hz, $J_2 = 2.1$ Hz), 6.93 (dd, 3H, $J_1 = 8.1$ Hz, $J_2 = 2.1$ Hz), 6.78 (d, 3H, J = 2.1 Hz), 1.07 (s, 27H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 168.3, 161.7, 153.1, 147.5, 139.5, 134.3, 132.2, 124.7, 123.8, 121.7, 117.4, 34.4, 31.2. ESI MS: Calcd. for C₄₅H₄₅Br₃IrN₃: 1059.1. Found: 1060.1 ([M+H]⁺).



Scheme S2. Synthesis of carbazole-terminated trifluorenyl boronate

cz-Flu₃Br. A Schlenk tube containing carbazole (2.0 g, 8.4 mmol), dibromotrifluorene (400 mg, 0.35 mmol), $Pd_2(dba)_3$ (2 mg, 2.2×10^{-3} mmol) was evacuated and backfilled with nitrogen three times. Then $P(t-Bu)_3$ (0.5 mg, 2.5×10^{-3} mmol), *t*BuONa (35 mg, 0.36 mmol), and toluene (5 ml) were added to the tube in the glove box. The tube was sealed and heated at reflux for 18 h before the mixture was allowed to cool to room temperature and diluted with EA. The organic mixture was washed with brine and dried over anhydrous Na₂SO₄. After removal of solvents *in vacuo*, purification of the residue using column chromatography on silica gel (eluted with PE/DCM=10/1, v/v) afforded **cz-Flu₃Br** as a white solid (70

mg, 25%). ¹H NMR (CDCl₃, 400 MHz ppm): δ 8.18 (d, 2H, J = 7.6 Hz), 7.94 (d, 1H, J = 7.6 Hz), 7.88-7.82 (m, 3H), 7.77-7.56 (m, 12H), 7.49-7.41 (m, 6H), 7.33-7.31 (m, 2H), 2.15-1.96 (m, 12H), 1.20-1.04 (m, 36H), 0.90-0.66 (m, 30H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 153.3, 152.9, 151.8, 151.5, 151.2, 151.0, 141.1, 141.0, 140.9, 140.8, 140.6, 140.5, 140.4, 140.3, 140.1, 139.9, 139.8, 139.5, 139.2, 136.3, 130.0, 128.8, 127.0, 126.8, 126.3, 126.2, 125.9, 125.8, 123.4, 122.9, 121.9, 121.5, 121.0, 120.8, 120.4, 120.1, 120.0, 119.9. 119.7, 109.8, 55.6, 55.4, 55.2, 40.3, 31.5, 41.4, 29.7, 29.6, 24.0, 23.7, 22.6, 22.5, 14.0. ESI MS: Calcd. for C₈₇H₁₀₄BrN: 1243.7. Found: 1243.7 ([M]⁺).

cz-Flu₃Bpin. A Schlenk tube containing **cz-Flu₃Br** (70mg, 0.056 mmol), (Bpin)₂, (43 mg, 0.17 mmol), Pd(dppf)Cl₂(3 mg, 4×10⁻³ mmol), KOAc (35 mg, 0.36 mmol) was evacuated and backfilled with nitrogen three times. After degassed dioxane (5 ml) was added, the tube was sealed under nitrogen atmosphere and heated at 80 °C for 23 h. The reaction mixture was then cooled to room temperature and diluted with PE. The organic mixture was washed with brine and dried over anhydrous Na₂SO₄. After removal of solvents *in vacuo*, purification of the residue using column chromatography on silica gel (eluted PE/DCM=5/1, v/v) afforded **cz-Flu₃Bpin** as a white solid (38 mg, 53%). ¹H NMR (CDCl₃, 400 MHz ppm): δ 8.18 (d, 2H, *J* = 7.6 Hz), 7.94 (d, 1H, *J* = 8.8 Hz), 7.88-7.64 (m, 15H), 7.57-7.43 (m, 6H), 7.31-7.29 (m, 2H), 2.18-2.05 (m, 12H), 1.43 (s, 12H), 1.20-1.06 (m, 36H), 0.97-0.68 (m, 30H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 152.9, 152.1, 151.8, 150.2, 143.8, 141.3, 141.0, 140.9, 140.6, 140.3, 140.2, 139.5, 136.3, 133.8, 128.9, 126.3, 126.2, 126.0, 125.9, 125.8, 123.4, 121.9, 121.6, 121.5, 120.8, 120.3, 120.1, 120.0, 119.8, 119.0, 109.8, 83.7, 67.9, 55.5, 55.3, 55.2, 40.3, 40.2, 31.5, 31.4, 29.6, 25.6, 24.9, 23.9, 23.8, 23.7, 22.5, 14.0. ESI MS: Calcd. for C₉₃H₁₁₆BNO₂: 1290.9. Found: 1290.9 ([M]⁺).



Scheme S3. Syntheses of oligofluorene-substituted Ir(ppy)₃ complexes

General procedures for oligofluorenyl Ir complexes. A Schlenk tube containing bromo-substituted Ir complex, ^[S1,S2] oligofluorenyl boronic acid^[S3] or boronate (1.1 eq. per C-Br bond), Pd(PPh₃)₄ (0.03 eq per C-Br bond), and K₂CO₃ (1 mmol) was evacuated and backfilled with nitrogen three times. After the addition of degassed THF (2 mL) and H₂O (0.5 mL), the tube was sealed under nitrogen atmosphere and heated at reflux overnight. The mixture was then diluted with PE, and the aqueous layer was separated. After washing with brine, the organic layer was dried over anhydrous Na₂SO₄. Upon removal of solvents *in vacuo*, the residue was subjected to flash column chromatography on silica gel (eluted with PE/DCM) to afford the oligofluorenyl iridium complexes as yellow solids.

5. (18 mg, 78%). ¹H NMR (CDCl₃, 300 MHz ppm): δ 8.16-8.13 (m, 1H), 7.83-7.36 (m, 27H), 7.42-7.29 (m, 5H), 7.19 (dd, 1H, J_1 = 6.0 Hz, J_2 = 1.5 Hz), 6.98-6.85 (m, 6H), 2.20-1.85 (m, 12H), 1.30-0.70 (m, 84H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 167.0, 166.9, 161.9, 152.4, 152.1, 152.0, 151.9, 151.8, 151.4, 151.0, 147.1, 143.8, 141.2, 141.5, 140.9, 140.6, 140.4, 140.3, 139.9, 139.4, 137.3, 136.0, 135.6, 134.6, 134.5, 134.4, 132.2, 129.6, 126.8, 126.1, 126.0, 123.6, 123.1, 122.9, 121.5, 121.4, 121.3, 120.3, 120.2, 120.0, 119.9, 118.7, 118.4, 118.3, 116.8, 116.1, 92.9, 55.5, 55.4, 55.3, 55.1, 40.3, 40.1, 34.4, 34.3, 31.5, 31.4, 31.3, 31.2, 29.7, 29.6, 29.5, 23.8, 23.6, 22.5, 14.0. ESI-TOF HRMS: Calcd. for C₁₁₆H₁₃₇IrN₃: 1766.0475 ([M+H]⁺). Found: 1766.0452.

1a. (14 mg, 79%). ¹H NMR (CDCl₃, 300 MHz ppm): δ 8.09 (d, 3H, *J* = 1.6 Hz), 7.92 (dd, 3H, *J*₁ = 8.4 Hz, *J*₂ = 1.6 Hz), 7.88 (d, 3H, *J* = 8.4 Hz), 7.60-7.55 (m, 9H), 7.38 (d, 3H, 8.0 Hz), 7.32 (s, 3H), 7.26-7.23 (m, 9H), 7.15 (d, 3H, *J* = 1.6 Hz), 6.97 (dd, 3H, *J*₁ = 8.0 Hz, *J*₂ = 1.6 Hz), 2.01-1.97 (m, 12H), 1.16 (s, 27H), 1.04-0.94 (m, 12H), 0.90-0.86 (m, 12H), 0.64 (t, 18H, *J* = 7.2 Hz), 0.53-0.41 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.7, 161.0, 152.2, 151.8, 150.7, 145.1, 141.1, 140.9, 140.3, 135.6, 134.6, 134.5, 133.9, 127.2, 126.7, 124.7, 123.2, 122.8, 120.3, 120.2, 119.7, 118.4, 117.1, 55.1, 40.4, 40.3, 34.4, 31.7, 31.4, 29.8, 29.7, 26.9, 23.8, 23.7, 22.6, 22.5, 14.0, 13.9. ESI-TOF HRMS: Calcd. for C₁₂₀H₁₄₅IrN₃: 1822.1101 ([M+H]⁺). Found: 1822.1142.

1b. (19 mg, 81%). ¹H NMR (CDCl₃, 300 MHz ppm): δ 8.14 (d, 3H, J = 1.6 Hz), 7.96 (dd, 3H, $J_1 = 8.4$ Hz, $J_2 = 1.6$ Hz), 7.91 (d, 3H, J = 8.4 Hz), 7.74-7.53 (m, 27H), 7.43 (d, 3H, J = 8.4 Hz), 7.37-7.27 (m, 12H), 7.16 (d, 3H, J = 1.6 Hz), 6.99 (dd, 3H, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz), 2.05-1.82 (m, 24H), 1.17 (s, 27H), 1.10-0.92 (m, 48H), 0.78-0.55 (m, 84H) ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.7, 161.0, 152.2, 152.1, 151.5, 151.4, 150.9, 145.1, 140.9, 140.8, 140.7, 140.4, 139.4, 135.6, 134.7, 134.6, 133.9, 126.9, 126.7, 126.1, 126.0, 124.9, 123.3, 122.9, 121.4, 121.3, 120.4, 120.3, 120.0, 119.8, 119.6, 118.4, 55.3, 55.1, 40.3, 34.5, 31.6, 31.4, 31.3, 19.8, 19.7, 29.6, 23.7, 23.6, 22.6, 22.5, 14.0, 13.9. ESI-TOF HRMS: Calcd. for C₁₉₅H₂₄₁IrN₃: 2819.8647 ([M+H]⁺). Found: 2819.8610.

2. (11 mg, 51%). ¹H NMR (CDCl₃, 300 MHz ppm): δ 8.15-8.11 (m, 3H), 7.90-7.58 (m, 54H), 7.46-7.30 (m, 12H), 7.17 (m, 3H), 7.10-7.12 (m, 3H), 2.15-2.01 (m, 36H), 1.20-1.01 (m, 135H), 0.90-0.65 (m, 90H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 165.7, 161.1, 152.1, 151.7, 151.5, 151.4, 150.9, 145.1, 140.9, 140.8, 140.7, 140.5, 140.4, 140.3, 140.2, 139.8, 139.4, 135.6, 134.7, 134.6, 134.0, 126.9, 126.7, 126.1, 124.8, 123.3, 122.9, 121.4, 121.3, 120.4, 120.3, 120.0, 119.9, 119.8, 119.6, 118.4, 117.1, 55.3, 55.2, 55.1, 40.3, 24.4, 31.6, 31.4, 31.3, 29.6, 29.5, 23.7, 22.7, 22.5, 14.0. ESI-TOF HRMS: Calcd. for C₂₇₀H₃₃₇IrN₃: 3816.6159 ([M+H]⁺). Found: 3816.6130.

3. (8 mg, 37%). ¹H NMR (CDCl₃, 300 MHz ppm): δ 8.10 (d, 3H, J = 8.4 Hz), 8.05-8.03 (m, 3H), 7.83-7.61 (m, 54H), 7.38-7.29 (m, 12H), 7.13 (d, 3H, J = 7.8 Hz), 6.98 (t, 3H, J = 6.3 Hz), 2.16-1.92 (m, 36H), 1.20-0.91 (m, 108H), 0.90-0.60 (m, 90H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 164.7, 160.0, 151.8, 151.2, 151.1, 150.7, 150.5, 140.0, 139.9, 139.8, 139.3, 139.0, 138.5, 138.4, 135.2, 134.7, 133.6, 133.0, 125.2, 125.1, 124.8, 124.7, 123.9, 122.3, 120.8, 120.4, 120.3, 119.8, 119.4, 119.3, 119.1, 118.9, 118.8, 117.4, 108.7, 54.5, 54.3, 39.4, 39.3, 33.4, 30.6, 30.4, 30.3, 28.8, 28.7, 28.6, 25.9, 22.9, 22.7, 21.7, 21.6, 21.5, 13.2, 13.0. ESI-TOF HRMS: Calcd. for C₂₅₈H₃₁₃IrN₃: 3648.4281. ([M+H]⁺) Found: 3648.4268.

1-cz: (12 mg, 69%). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.19-8.16 (m, 9H), 7.99-7.78 (m, 22H), 7.78-7.55 (m, 40H), 7.55-7.31 (m, 19H), 7.17 (s, 3H), 7.00 (d, 3H, J = 7.2 Hz), 2.15-1.88 (m, 36H), 1.20-1.00 (m, 135H), 0.90-0.58 (m, 90H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 167.3, 161.7, 152.8, 152.1, 152.0, 151.9, 151.8, 148.3, 147.2, 141.9, 141.2, 141.1, 141.0, 140.4, 140.1, 139.5, 136.9, 136.3, 134.6, 126.3, 126.2, 126.0, 125.9, 125.8, 123.3, 123.1, 121.8, 121.4, 121.3, 120.8, 120.3, 120.1, 120.0, 119.8, 116.8, 115.9, 109.8, 55.5, 55.4, 55.3, 53.4, 40.4, 40.3, 34.4, 31.5, 31.4, 29.7, 29.6, 23.9, 23.8, 22.6, 22.5, 14.0. ESI-TOF HRMS: Calcd. for C₃₀₆H₃₅₈IrN₆: 4312.7928 ([M+H]⁺). Found: 4312.7910.

2-cz. (11 mg, 83%). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.19 (d, 6H, *J* = 8.0 Hz), 8.15-8.13 (m, 3H), 7.95 (d, 3H, *J* = 8.4 Hz), 7.88-7.83 (m, 15H), 7.74-7.66 (m, 30H), 7.57-7.42 (m, 24H), 7.33-7.28 (m, 9H), 7.05-6.99 (m, 6H), 2.18-2.02 (m, 36H), 1.19-1.09 (m, 135H), 0.91-0.74 (m, 90H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 167.4, 161.8, 152.9, 152.1, 152.0, 151.8, 148.2, 147.3, 142.0, 141.2, 141.1, 140.9, 140.3, 140.1, 139.5, 137.0, 136.3, 134.6, 126.3, 126.2, 126.1, 125.9, 125.8, 123.4, 123.3, 121.9, 121.5, 121.3, 120.8, 120.3, 120.1, 119.8, 116.8, 115.9, 109.8, 55.6, 55.5, 55.4, 40.4, 40.3, 34.4, 31.5, 31.4, 31.3, 29.7, 29.6, 23.9, 23.8, 22.5, 14.0. ESI-TOF HRMS: Calcd. for C₃₀₆H₃₅₈IrN₆: 4312.7928 ([M+H]⁺). Found: 4312.7998.

II. Linear photophysical characterizations

Steady-state UV-Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer using the absorption mode in 1-cm quartz cells for solution samples. Photoluminescence spectra of iridium complexes were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer with the right-angle geometry, using 1-cm quartz cuvettes for solution samples. The emission spectra were corrected for the wavelength dependency of the detector sensitivity and monochromator gratings. Ir(ppy)₃ was used as the linear excitation emission quantum yield standard (Φ_p =0.97 in toluene),^[S4] and the absorbance of solutions used for quantum yield measurements was 0.05-0.1 at the excitation wavelength. Solutions for quantum yield measurements were deoxygenated by bubbling N₂ for eight minutes before the emission intensity measurements, and the variations in measured quantum yields were less than 5% upon repetition. Lifetimes measurements were performed by time-correlated single-photon counting using a Horiba Jobin Yvon FluoroHub-B instrument, with NanoLED of 370 nm as the excitation source, while lifetimes >20 µs were measured by pulsed xenon lamp. Samples were subjected to at the least three freeze-pump-thaw cycles before lifetime measurements.



Fig. S1 UV-Vis absorptions and normalized photoluminescence spectra of iridium complexes in deoxygenated THF solutions.

III. Density functional theory calculations

Density functional theory (DFT) calculations were carried out using the Gaussian 09 suite of programs.^[S5] Molecular geometry optimization and MO energies were calculated using the B3LYP hybrid functional with 6-31G* basis set for C, H, and N atoms and the "double- ζ " quality LANL2DZ basis set for Ir atoms. In the calculations the hexyl groups at the 9-position of fluorene units were replaced with methyl groups for saving the calculation time.

	HOMO (eV)	LUMO (eV)		HOMO (eV)	LUMO (eV)
1	-4.73	-1.62	1a	-4.75	-1.49
1-cz	-4.79	-1.68	1b	-4.75	-1.58
2	-4.70	-1.65	4	-4.80	-1.62
2-cz	-4.71	-1.66	5	-4.76	-1.68
3	-4.81	-1.38	6	-4.76	-1.33

Table S1. Ground-state frontier molecular orbital energy levels from DFT calculations



Fig. S2 DFT calculated ground-state HOMOs and LUMOs at the optimized geometry



Fig. S3 DFT calculated ground-state HOMO and LUMO of 4-6 at optimized geometry

IV. Two- and three-photon absorptions and excitation phosphorescence

For two- and three-photon excitation phosphorescence measurements, a femtosecond laser system composed of a Spectra-Physics TOPAS optical parametric amplifier (OPA) pumped by a Spfire ACE-F-1KXP Ti:sapphire amplifier (<120 fs, 1 KHz) was used. The OPA had signal and idler wavelength tuning ranges of 1100-1600 nm and 1600-2600 nm, respectively. The 2PA cross section measurements were carried out at a number of wavelengths in the range 650-1200 nm. To obtain these wavelengths, the second harmonic of the signal or idler was used in the range of 650-800 nm or 800-1100 nm, and the signal wavelength was used at 1100-1200 nm. The pulse from the OPA was focused by lens with the focal length of 50 cm, and the distance of the sample cell (1×1 cm) to the lens was 40 cm. To minimize the effects of re-absorption, the excitation beam was moved close to the quartz cell wall facing the slit of the imaging spectrograph. The emission was detected in a direction perpendicular to the pump beam. The two-photon cross sections were determined by comparative measurements using Rhodamine B in methanol as the reference.

Three-photon cross section at 1064 nm was firstly obtained by ps open-aperture Z-scan measurements.^[S6] A 1064 nm Nd:YAG laser (PL2143B, EKSPLA, Lithuania) was used as the light source. The laser pulse width was 25 ps (fwhm), and the repetition rate was adjusted to 10 Hz. The spatial profile of the laser beam was a nearly Gaussian distribution. The beam was focused by plano-convex lens with a focal length of 20 cm. The three-photon absorption coefficient α_3 was obtained by fitting the T-(z) curve using the 3PA theoretical equation 1:

$$T(z) = \frac{1}{\sqrt{2\pi\alpha_3 L \left(\frac{I_0 w_0^2}{w^2(z)}\right)^2}} \int_0^1 \frac{R(x)}{x\sqrt{-\ln x}} dx,$$

where $R(x) = \ln\left(\sqrt{1 + 2\alpha_3 L \left(\frac{I_0 w_0^2}{w^2(z)}\right)^2 x^2} + \sqrt{2\alpha_3 L \left(\frac{I_0 w_0^2}{w^2(z)}\right)^2 x^2}\right)$ (1)

The absolute 3PA cross sections at 1064 nm were calculated according to the following equation:

$$\sigma_{3PA} = \frac{\alpha_3 (hv)^2}{N_0} \tag{2}$$

where hv is one photon energy; N_0 is the number of absorbing species per cm³.

The three-photon absorption cross sections at alternative wavelengths were estimated by comparing the phosphorescence intensity excited by fs laser at corresponding wavelength and calibrate it to that from excitation at 1064 nm at the same power density.^[S7]



Fig. S4 Two- and three-photon excitation spectra collected from deoxygenated THF solutions



Fig. S5 Emission spectra of **1** (upper) and **1-cz** (lower) in deoxygenated THF solutions upon excitation at two different wavelengths with varied excitation power (laser frequency: 1 kHz)

	$\lambda_{\rm ex} = 780 \ \rm nm$	$I (GW/cm^2)^a$	$\lambda_{\rm ex} = 1060 \ {\rm nm}$	$I (GW/cm^2)^a$
1 a	2.09±0.07	6.1~24	3.08±0.07	16~54
1b	2.13±0.04	6.4~26	2.90±0.03	16~66
1	2.01 ±0.04	4.8~26	3.00±0.07	48~140
1-cz	2.07±0.04	5.0~29	3.05±0.04	23~93
2	2.04 ±0.03	2.9~19	2.95±0.08	60~220
2-cz	2.04 ±0.05	2.8~20	2.86±0.05	55~260
3	2.09±0.03	8.4~53	2.97±0.02	21~73
4	2.09±0.02	23~85	2.88±0.07	21~114
5	2.03±0.06	2.9~16	3.04±0.05	32~149
6	2.09±0.03	11~44	3.03±0.05	48~128

Table S2. Slopes of linear fitting in double-log plots and excitation power density data

^a peak power density



Fig. S6 Emission spectra of **2** (upper) and **2-cz** (lower) in deoxygenated THF solutions upon excitation at two different wavelengths with varied excitation power (laser frequency: 1 kHz)



Fig. S7 Plots of emission intensity of **3** vs. excitation power at different excitation wavelengths and the emission spectra at different excitation power in deoxygenated THF at 10^{-5} M (laser frequency: 1 kHz)



Fig. S8 Log-log plots of emission intensity vs. excitation power with linear fitting at different excitation wavelengths and emission spectra at different excitation power in deoxygenated THF (top: 4; middle: 5; bottom: 6; laser frequency: 1 kHz, concentration= 10^{-5} M)



Fig. S9 Plots of emission intensity vs. excitation power with linear fitting and emission spectra at different excitation power in deoxygenated THF at 10^{-5} M (top: **1a**; bottom: **1b**; laser frequency: 1 kHz)



Fig. S10 Normalized emission spectra of **1** upon excitation at indicated wavelengths in deoxygenated THF, via one-, two- and three-photon excitations, respectively.



Fig. S11 Open aperture Z-scan data of **1-cz** (left), **2** (middle) and **2-cz** (right) at 1064 nm (the solid line represents the best fitting to 3PA).



Fig. S12 Open aperture Z-scan data of **3** (left), **1a** (middle) and **1b** (right) at 1064 nm (the solid line represents the best fitting to 3PA).



Fig. S13 Open aperture Z-scan data of **4** (left), **5** (middle) and **6** (right) at 1064 nm (the solid line represents the best fitting to 3PA).

	N_0^{a}/cm^{-3}	$I_0^{b} / (W^* cm^{-2})$	$\alpha_3^{c/(cm^3/W^2)}$	$\sigma^{d}/(10^{-78} \text{ cm}^{6} \text{ s}^{2} \text{ photon}^{-2})$
1	$1.8*10^{18}$	$1.0*10^{11}$	1.96*10 ⁻²¹	38.0
1-cz	$1.6*10^{18}$	$1.0*10^{11}$	$2.44*10^{-21}$	53.2
2	$3.0*10^{18}$	$1.0*10^{11}$	4.24*10 ⁻²¹	49.3
2-cz	5.2*10 ¹⁸	$1.1*10^{11}$	$1.12*10^{-20}$	75.1
3	$1.8*10^{18}$	$1.2*10^{11}$	$1.70*10^{-21}$	32.9
1 a	$3.0*10^{18}$	$1.6*10^{11}$	5.80*10 ⁻²²	6.8
1b	$3.0*10^{18}$	$1.4*10^{11}$	$1.50*10^{-21}$	17.5
4	$9.0*10^{18}$	$1.2*10^{11}$	1.95*10 ⁻²¹	7.6
5	$9.0*10^{18}$	$1.0*10^{11}$	2.05*10 ⁻²¹	8.0
6	$9.0*10^{18}$	$1.4*10^{11}$	1.61*10 ⁻²¹	6.2

 Table S3. Three-photon nonlinear absorption coefficients and absolute cross-sections by ps open aperture Z-scan method at 1064 nm.

^{*a*} number of absorbing species per cm³; ^{*b*} peak power density at z=0; ^{*c*} three-photon absorption coefficients; ^{*d*} three-photon absorption cross-sections (laser pause FHWM = 25 ps).

V. Reference

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Copies of ¹H NMR spectra







