Supporting Information

2,5-Thienylene-Bridged Triangular and Linear Porphyrin Trimers

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**Instrumentation and Materials**

$^1$H NMR (600 MHz) spectra were taken on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CHCl$_3$ as internal reference for $^1$H NMR ($\delta = 7.260$ ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. MALDI-TOF mass spectra were obtained with a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer without matrix. High resolution ESI-TOF mass spectra were taken on a Bruker microTOF. X-Ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

**Time-Correlated Single Photon Counting**

Time-resolved fluorescence was detected using a time-correlated single photon counting (TCSPC) technique. A home-made cavity dumped Ti:Sapphire oscillator pumped by a CW Nd-YVO$_4$ laser (Coherent, Verdi) was used as the excitation light source; this provided ultrashort pulses (100 fs at full width half maximum) and allowed for a high repetition rate (200 ~ 400 kHz). The output pulse of the oscillator was frequency-doubled with a second harmonic crystal. The TCSPC detection system consisted of a multichannel plate photomultiplier (Hamamatsu, R3809U-51) with a cooler (Hamamatsu, C4878), a TAC (time-to-amplitude converter) (EG&G Ortec, 457), two discriminators (EG&G Ortec, 584 (signal) and Canberra, 2126 (trigger)), and two wideband amplifiers (Philip Scientific (signal) and a Mini Circuit (trigger)). A personal computer with a multichannel analyzer (Canberra, PCA3) was used for data storage and processing. The overall instrumental response function was about 60 ps (fwhm). A sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection system. The decay fittings were made by using a least-squares deconvolution fitting process (LIFETIME program with an iterative nonlinear least-squares deconvolution procedure developed at the University of Pennsylvania).
Measurement of two-photon absorption cross-section ($\sigma^{(2)}$).

The TPA experiments were performed using the open-aperture Z-scan method with 120 fs pulses at a 5 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). The laser beam was divided into two parts. One was monitored by a Si photodiode (New Focus) as an intensity reference, and the other was used for the transmittance studies. After passing through an $f = 10$ cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction (z-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell is 1 mm. The transmitted laser beam from the sample cell was then probed using the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, $I_0$, ranged from 30 to 50 GW/cm. Assuming a Gaussian beam profile, the nonlinear absorption coefficient $\beta$ can be obtained by curve fitting to the observed open aperture traces with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)}$$

where $\alpha_0$ is the linear absorption coefficient, $l$ the sample length, and $z_0$ the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient $\beta$, the TPA cross-section $\sigma^{(2)}$ (in units of 1 GM = $10^{-50}$ cm$^4$ s/photon/molecule) of a single solute molecule sample can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N A d \times 10^{-3}}{h \nu}$$

where $N_A$ is the Avogadro constant, $d$ the concentration of the TPA compound in solution, $h$ is Planck’s constant, and $\nu$ is the frequency of the incident laser beam.
General Synthetic Procedure

**Synthesis of 2H and 3H:** A toluene/DMF/H$_2$O solution (2 mL/1 mL/1 drop) of 1H (50.0 mg, 0.044 mmol), 2,5-dibromothiophene (5.0 μL, 0.044 mmol), Pd$_2$(dba)$_3$ (4.0 mg, 4.4 μmol), PPh$_3$ (4.6 mg, 0.018 mmol), Cs$_2$CO$_3$ (28.6 mg, 0.088 mmol), and CsF (13.4 mg, 0.088 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 48 h. The reaction mixture was diluted with CH$_2$Cl$_2$, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC and silica-gel column chromatography (CH$_2$Cl$_2$/hexane as an eluent) and recrystallization with CH$_2$Cl$_2$/MeOH, 2H obtained as a dark red solid (12 mg, 0.063 mmol, 29% yield), while 3H was obtained as a dark green solid (4.0 mg, 0.0014 mmol, 10% yield).

**Synthesis of 2Zn and 3Zn:** Free base porphyrin 2H (20.0 mg, 0.011 mmol) or 3H (20.0 mg, 0.0070 mmol) was added to a round-bottomed 50-mL flask containing a magnetic bar, and dissolved in chloroform. Then, an excess amount of saturated zinc(II) acetate methanol solution was added. After stirring for 30 min, the complete metalation was confirmed by TLC and MALDI-TOF mass spectra. The reaction mixture was passed through a short alumina column, evaporated and recrystallized with CH$_2$Cl$_2$/MeOH. 2Zn or 3Zn was obtained quantitatively.

**Synthesis of 2Ni or 3Ni:** 2H (20.0 mg, 0.011 mmol) or 3H (20.0 mg, 0.0070 mmol) was added to a round-bottomed 50-mL flask with a magnetic bar, and dissolved in toluene. Then, an excess amount of nickel(II) acetylacetonate was added. After stirring for 5 h at reflux, the reaction mixture was passed through alumina column, evaporated and recrystallized with CH$_2$Cl$_2$/MeOH. 2Ni or 3Ni was obtained quantitatively.

**Synthesis of ββ’-dithienylporphyrin zinc(II) 4Zn:** A toluene/DMF/H$_2$O solution (2 mL/1 mL/1 drop) of 1Zn (60.0 mg, 0.051 mmol), 2-bromothiophene (50 μL, 0.52 mmol), Pd$_2$(dba)$_3$ (4.6 mg, 5.0 μmol), PPh$_3$ (5.2 mg,
0.02 mmol), Cs₂CO₃ (32.8 mg, 0.10 mmol), and CsF (15.4 mg, 0.10 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 24 h. The reaction mixture was diluted with CH₂Cl₂, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH₂Cl₂/hexane as an eluent) and recrystallization with CH₂Cl₂/MeOH, 4Zn was obtained as a red solid (44.6 mg, 0.0404 mmol, 80% yield).

**Synthesis of thienylene-bridged dimer 5Zn:** A toluene/DMF/H₂O solution (2 mL/1 mL/1 drop) of 2-monoborylporphyrin (60.0 mg, 0.057 mmol), 2,5-dibromothiophene (3.18 μL, 0.028 mmol), Pd₂(dba)₃ (2.5 mg, 2.8 μmol), PPh₃ (3.0 mg, 0.012 mmol), Cs₂CO₃ (18.3 mg, 0.057 mmol), and CsF (8.6 mg, 0.057 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 24 h. The reaction mixture was diluted with CH₂Cl₂, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by silica-gel column chromatography (CH₂Cl₂/hexane as an eluent) and recrystallization with CH₂Cl₂/MeOH, 5Zn was obtained as a red solid (27.5 mg, 0.014 mmol, 50% yield).

**Synthesis of linear trimer 8Zn**

(a) **Synthesis of β,β’-bis(5-bromothien-2-yl)porphyrin zinc(II) 6Zn:** A toluene/DMF solution (2 mL/1 mL) of 1Zn (60.0 mg, 0.051 mmol), 2,5-dibromothiophene (50 μL, 0.44 mmol), Pd₂(dba)₃ (4.6 mg, 5.0 μmol), PPh₃ (5.2 mg, 0.020 mmol), Cs₂CO₃ (32.8 mg, 0.10 mmol), and CsF (15.4 mg, 0.10 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 20 h. The reaction mixture was diluted with CH₂Cl₂, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC (CHCl₃ as an eluent), and collected the last band.
After the solvent was removed under reduced pressure and recrystallization with CH₂Cl₂/MeOH, 38.0 mg of 6Zn was obtained as a red solid in 60% yield. The product is pure enough for the next reaction.

**b) Synthesis of linear trimer 8Zn:** A toluene/DMF solution (2 mL/1 mL) of β,β’-bis(5-bromothien-2-yl)porphyrin zinc(II) (6Zn, 38.0 mg, 0.03 mmol), tetraborylporphyrin (7Zn, 17.9 mg, 0.015 mmol), Pd₂(dba)₃ (2.7 mg, 3.0 μmol), PPh₃ (3.2 mg, 0.012 mmol), Cs₂CO₃ (19.5 mg, 0.060 mmol), and CsF (9.1 mg, 0.060 mmol) was degassed through three freeze-pump-thaw cycles, and the reaction flask was purged with argon. The resulting mixture was stirred at reflux for 24 h. The reaction mixture was diluted with CH₂Cl₂, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent followed by GPC column chromatography (CHCl₃ as an eluent), and collected the second eluted band. After the solvent was removed under reduced pressure and further purified with silica-gel column chromatography (CH₂Cl₂/hexane as an eluent) and recrystallization with CH₂Cl₂/MeOH, linear trimer 8Zn was obtained as a red solid (5.0 mg, 1.7 mmol, 11% yield).

**Compound Data**

2H: ¹H NMR (CDCl₃): δ 12.58 (s, 2H, meso), 9.16 (s, 4H, pyrrole-β), 8.91 (d, J = 4.6 Hz, 4H, pyrrole-β), 8.87 (d, J = 4.6 Hz, 4H, pyrrole-β), 8.17 (d, J = 1.8 Hz, 8H, di-tert-butylphenyl-ortho), 8.07 (d, J = 1.8 Hz, 4H, di-tert-butylphenyl-ortho), 8.05 (s, 4H, thiophene), 7.86 (m, 4H, di-tert-butylphenyl-para), 7.80 (m, 2H, di-tert-butylphenyl-para), 7.60 (s, 72H, tert-butyl), 1.53 (s, 36H, tert-butyl), –2.37 (s, 4H, NH) ppm; UV/Vis (CH₂Cl₂): λmax (ε [M⁻¹ cm⁻¹]) = 426 (313000), 525 (55000), 605 (19000), 659 (4000) nm; HR-MS (ESI-TOF-MS): m/z = 1911.1378, calcld for (C₁₃₂H₁₄₉N₈S₂)+ = 1911.1373 ([M + H]+). Fluorescence (CH₂Cl₂, λex = 426 nm): λmax = 663 nm, Φₚ = 0.005.
**2Zn**: $^1$H NMR (CDCl$_3$): $\delta$ 12.73 (s, 2H, meso), 9.25 (s, 4H, pyrrole-$\beta$), 9.01 (d, $J = 4.6$ Hz, 4H, pyrrole-$\beta$), 8.98 (d, $J = 4.6$ Hz, 4H, pyrrole-$\beta$), 8.18 (m, 4H, di-tert-butylphenyl-ortho), 8.18 (d, $J = 1.8$ Hz, 8H, di-tert-butylphenyl-ortho), 8.09 (d, $J = 1.8$ Hz, 4H, di-tert-butylphenyl-ortho), 8.05 (s, 4H, thiophene), 7.86 (m, 4H, di-tert-butylphenyl-para), 7.79 (m, 2H, di-tert-butylphenyl-para), 1.59 (s, 72H, tert-butyl), 1.53 (s, 36H, tert-butyl) ppm; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$ [M$^{-1}$ cm$^{-1}$]) = 429 (309000), 557 (40000) nm; HR-MS (ESI-TOF-MS): $m/z = 2037.9623$, calcd for (C$_{132}$H$_{145}$N$_8$S$_2$Zn$_2$)$^+ = 2037.9615$ ([M$+$H$]^+$); Fluorescence (CH$_2$Cl$_2$, $\lambda_{\text{ex}} = 429$ nm): $\lambda_{\text{max}} = 691$ nm, $\Phi_f = 0.008$.

**2Ni**: $^1$H NMR (CDCl$_3$): $\delta$ 12.16 (s, 2H, meso), 9.06 (s, 4H, pyrrole-$\beta$), 8.78 (s, 8H, pyrrole-$\beta$), 7.95 (d, $J = 1.8$ Hz, 8H, di-tert-butylphenyl-ortho), 7.90 (s, 4H, thiophene), 7.87 (d, $J = 1.8$ Hz, 4H, di-tert-butylphenyl-ortho), 7.78 (m, 4H, di-tert-butylphenyl-para), 7.71 (m, 2H, di-tert-butylphenyl-para), 7.49 (m, 2H, pyridyl), 1.53 (s, 72H, tert-butyl), 1.50 (s, 36H, tert-butyl) ppm; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$ [M$^{-1}$ cm$^{-1}$]) = 424 (273000), 536 (45000) nm; HR-MS (ESI-TOF-MS): $m/z = 2023.9758$, (C$_{132}$H$_{145}$N$_8$S$_2$Ni$_2$)$^+ = 2023.9751$ ([M$+$H$]^+$).

**3H**: $^1$H NMR (CDCl$_3$): $\delta$ 11.46 (s, 3H, meso), 9.28 (s, 6H, pyrrole-$\beta$), 8.97 (br, 12H, 6H for thiophene and 6H for pyrrole-$\beta$), 8.92 (d, $J = 4.6$ Hz, 6H, pyrrole-$\beta$), 8.24 (d, $J = 1.8$ Hz, 12H, di-tert-butylphenyl-ortho), 8.10 (d, $J = 1.8$ Hz, 6H, di-tert-butylphenyl-ortho), 7.96 (m, 6H, di-tert-butylphenyl-para), 7.81 (m, 3H, di-tert-butylphenyl-para), 1.68 (s, 108H, tert-butyl), 1.56 (s, 54H, tert-butyl), –2.34 (s, 6H, NH) ppm; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ ($\varepsilon$ [M$^{-1}$ cm$^{-1}$]) = 429 (230000), 479 (186000), 529 (89000), 574 (41000), 608 (19000), 661 (6000) nm; HR-MS (ESI-TOF-MS): $m/z = 2866.6962$, calcd for (C$_{198}$H$_{223}$N$_{12}$S$_3$)$^+ = 2866.7034$ ([M$+$H$]^+$); Fluorescence (CH$_2$Cl$_2$, $\lambda_{\text{ex}} = 429$ nm): $\lambda_{\text{max}} = 672$ nm, $\Phi_f = 0.051$.

**3Zn**: $^1$H NMR (CDCl$_3$): $\delta$ 11.62 (s, 3H, meso), 9.41 (s, 6H, pyrrole-$\beta$), 9.10 (d, $J = 4.6$ Hz, 6H, pyrrole-$\beta$), 9.05 (d, $J = 4.6$ Hz, 6H, pyrrole-$\beta$), 9.04 (s, 6H, thiophene), 8.27 (d, $J = 1.8$ Hz, 12H, di-tert-butylphenyl-ortho), 8.12 (d, $J = 1.8$ Hz, 6H, di-tert-butylphenyl-ortho), 7.98 (m, 6H, di-tert-butylphenyl-para), 7.82 (m, 3H,
di-tert-butylphenyl-para), 1.68 (s, 108H, tert-butyl), 1.55 (s, 54H, tert-butyl) ppm; UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} (\varepsilon [\text{M}^{-1} \text{cm}^{-1}]) = 427 (210000), 462 (195000), 494 (230000), 570 (68000), 601 (6000) \text{ nm}; \) HR-MS (ESI-TOF-MS): \( m/z = 3056.4399, \text{ calcd for (C}_{198}\text{H}_217\text{N}_{12}\text{S}_{3}\text{Zn}_{3})^+ = 3056.4394 ([M + H]^+); \) Fluorescence (CH₂Cl₂, \( \lambda_{\text{ex}} = 427 \text{ nm})): \( \lambda_{\text{max}} = 646 \text{ nm}, \Phi_\text{F} = 0.056. \)

3Ni: \(^1\text{H} \text{NMR (CDCl}_3\)): \( \delta 10.99 (s, 3\text{H}, \text{meso}), 9.08 (s, 6\text{H}, \text{pyrrole-}\beta), 8.85 (d, J = 4.6 \text{ Hz, 6H, pyrrole-}\beta), 8.81 \) (d, \( J = 4.6 \text{ Hz, 6H, pyrrole-}\beta), 8.51 (s, 6H, thiophene), 8.00 (d, \( J = 1.8 \text{ Hz, 12H, di-tert-butylphenyl-ortho}, 7.89 \) (d, \( J = 1.8 \text{ Hz, 6H, di-tert-butylphenyl-ortho}), 7.85 (m, 6H, di-tert-butylphenyl-para), 7.73 (m, 3H, di-tert-butylphenyl-para), 1.58 (s, 108H, tert-butyl), 1.48 (s, 54H, tert-butyl) ppm; UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} (\varepsilon [\text{M}^{-1} \text{cm}^{-1}]) = 438 (262000), 536 (74000), 586 (81000) \text{ nm}; \) HR-MS (ESI-TOF-MS): \( m/z = 3036.4557, \text{ calcd for (C}_{198}\text{H}_217\text{N}_{12}\text{S}_{3}\text{Ni}_{3})^+ = 3036.4591 ([M + H]^+). \)

4Zn: \(^1\text{H} \text{NMR (CDCl}_3\)): \( \delta 11.04 (s, 1\text{H}, \text{meso}), 9.15 (s, 2\text{H}, \text{pyrrole-}\beta), 9.0 (d, J = 4.6 \text{ Hz, 2H, pyrrole-}\beta), 8.99 \) (d, \( J = 4.6 \text{ Hz, 2H, pyrrole-}\beta), 9.04(s, 6H, thiophene), 8.13 (d, \( J = 1.8 \text{ Hz, 4H, di-tert-butylphenyl-ortho}), 8.07 (d, \( J = 1.8 \text{ Hz, 2H, di-tert-butylphenyl-ortho}), 8.04 (m, 2H, thiophene), 7.81 (m, 2H, di-tert-butylphenyl-para), 7.78 \) (m, 1H, di-tert-butylphenyl-para), 7.69 (m, 2H, thiophene), 7.48 (m, 2H, thiophene), 1.56 (s, 36H, tert-butyl), 1.52 (s, 18H, tert-butyl) ppm; UV/Vis(CH₂Cl₂): \( \lambda_{\text{max}} (\varepsilon [\text{M}^{-1} \text{cm}^{-1}]) = 434 (297000), 556 (27000) \text{ nm}; \) HR-MS (ESI-TOF-MS): \( m/z = 1100.4803 \text{ calcd for (C}_{70}\text{H}_{76}\text{N}_4\text{S}_2\text{Zn}^+ = 1100.4797 ([M]^+); \) Fluorescence (CH₂Cl₂, \( \lambda_{\text{ex}} = 434 \text{ nm}): \( \lambda_{\text{max}} = 660 \text{ nm}, \Phi_\text{F} = 0.032. \)

5Zn: \(^1\text{H} \text{NMR (CDCl}_3\)): \( \delta 10.89 (s, 2\text{H}, \text{meso}), 9.52 (d, J = 4.6 \text{ Hz, 2H, pyrrole-}\beta), 9.40 (s, 2\text{H}, pyrrole-\beta), 9.18 (d, J = 4.6 \text{ Hz, 2H, pyrrole-}\beta), 9.10 (d, J = 4.6 \text{ Hz, 2H, pyrrole-}\beta), 9.06(d, J = 4.6 \text{ Hz, 4H, pyrrole-}\beta), 9.04 \) (d, \( J = 4.6 \text{ Hz, 2H, pyrrole-}\beta), 8.46 (s, 2H, thiophene), 8.23 (d, \( J = 1.8 \text{ Hz, 4H, di-tert-butylphenyl-ortho}), 8.14 \) (d, \( J = 1.8 \text{ Hz, 4H, di-tert-butylphenyl-ortho}), 8.11 (d, \( J = 1.8 \text{ Hz, 4H, di-tert-butylphenyl-ortho}), 7.86 (m, 2H,
di-tert-butylphenyl-para), 7.82 (m, 2H, di-tert-butylphenyl-para), 7.80 (m, 2H, di-tert-butylphenyl-para), 1.60 (s, 36H, tert-butyl), 1.56 (s, 36H tert-butyl), 1.52 (s, 36H, tert-butyl) ppm; UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} (\varepsilon [M^{-1} \text{cm}^{-1}]) = 421 \) (337000), 553 (45000), 593 (25000) nm, HR-MS (ESI-TOF-MS): \( m/z = 1956.9850 \), calcd for (C₁₂₈H₁₄₄N₈S₂Zn₂)⁺ = 1956.9815 (\([M]⁺\)); Fluorescence (CH₂Cl₂, \( \lambda_{\text{ex}} = 421 \) nm): \( \lambda_{\text{max}} = 611 \) nm. \( \Phi_F = 0.099. \)

\( 8\text{Zn} \): \(^{1}H\) NMR (CDCl₃): \( \delta \) 12.73 (s, 2H, meso), 12.71 (s, 2H, meso), 9.28 (s, 4H, pyrrole-β), 9.26 (s, 4H, pyrrole-β), 9.02 (d, \( J = 4.6 \) Hz, 4H, pyrrole-β), 8.99 (d, \( J = 4.6 \) Hz, 4H, pyrrole-β), 8.28 (d, \( J = 1.8 \) Hz, 4H, di-tert-butylphenyl-ortho), 8.19 (d, \( J = 1.8 \) Hz, 8H, di-tert-butylphenyl-ortho), 8.09 (d, \( J = 1.8 \) Hz, 4H, di-tert-butylphenyl-ortho), 8.07 (s, 8H, thiophene), 7.94 (m, 2H, di-tert-butylphenyl-para), 7.87 (m, 4H, di-tert-butylphenyl-para), 7.80 (m, 2H, di-tert-butylphenyl-para), 1.68 (s, 36H, tert-butyl), 1.60 (s, 72H, tert-butyl), 1.53 (s, 36H, tert-butyl) ppm; UV/Vis (CH₂Cl₂): \( \lambda_{\text{max}} (\varepsilon [M^{-1} \text{cm}^{-1}]) = 433 \) (391000), 496 (179000), 565 (73000) nm; HR-MS (ESI-TOF-MS): \( m/z = 2948.2549 \), calcd for (C₁₈₈H₁₉₇N₁₂S₂Zn₃)⁺ = 2948.2544 (\([M + H]⁺\)). Fluorescence (CHCl₃, \( \lambda_{\text{ex}} = 433 \) nm): \( \lambda_{\text{max}} = 707 \) nm. \( \Phi_F = 0.005. \)
Figure S1. $^1$H NMR spectrum of 2H in CDCl$_3$. 
Figure S2. $^1$H NMR spectrum of 2Zn in CDCl$_3$. 
Figure S3. $^1\text{H}$ NMR spectrum of 2Ni in CDCl$_3$. 
Figure S4. $^1$H NMR spectrum of 3H in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of 3Zn in CDCl$_3$. 
Figure S6. $^1$H NMR spectrum of 3Ni in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum of 4Zn in CDCl$_3$. 
Figure S8. $^1$H NMR spectrum of 5Zn in CDCl$_3$. 
Figure S9. $^1$H NMR spectrum of linear 8Zn.
Figure S10. UV/vis absorption spectra of (a) 2Zn (black line), 3Zn (red line), 4Zn (green line), 5Zn (blue line) and 8Zn (shallow blue line) and (b) 2Ni (black line), 3Ni (red line), 3H (green line), and 2H (blue line) in CH$_2$Cl$_2$.

Figure S11. Fluorescence emission spectra of (a) 2Zn (black line), 3Zn (red line), 4Zn (green line), 5Zn (blue line), and 8Zn (shallow blue line) and (b) 2H (black line) and 3H (red line) in CH$_2$Cl$_2$. 
Two-photon Absorption Cross-Section ($\sigma^{(2)}$)

Figure S12. Two photon absorption cross section measurement.

<table>
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<th>Zn</th>
<th>$\tau_f$ (ns)</th>
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<tr>
<td>2Zn</td>
<td>1.75</td>
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<tr>
<td>3Zn</td>
<td>1.38</td>
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<tr>
<td>4Zn</td>
<td>2.44</td>
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<tr>
<td>5Zn</td>
<td>1.83</td>
</tr>
<tr>
<td>8Zn</td>
<td>1.25</td>
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Figure S13. Singlet-state lifetime obtained by time correlated single photon counting technique.
Table S1. Summary of Photophysical Data

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<th>Sample</th>
<th>$\Phi_f$</th>
<th>$\tau_f$(ns)</th>
<th>Wave. (nm)</th>
<th>Con. (mM)</th>
<th>$\sigma^{(2)}$ (GM)</th>
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</thead>
<tbody>
<tr>
<td>2Zn</td>
<td>0.008</td>
<td>1.75</td>
<td>800</td>
<td>0.15</td>
<td>7000 ± 300</td>
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<tr>
<td>3Zn</td>
<td>0.056</td>
<td>1.38</td>
<td>800</td>
<td>0.15</td>
<td>8600 ± 300</td>
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<tr>
<td>4Zn</td>
<td>0.032</td>
<td>2.44</td>
<td>800</td>
<td>0.96</td>
<td>970 ± 50</td>
</tr>
<tr>
<td>5Zn</td>
<td>0.099</td>
<td>1.83</td>
<td>800</td>
<td>0.39</td>
<td>3300 ± 300</td>
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<tr>
<td>8Zn</td>
<td>0.005</td>
<td>1.25</td>
<td>800</td>
<td>0.10</td>
<td>17300 ± 500</td>
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