

**Supporting Information Accompanying:**

**Spin-State Control of Thermal and Photochemical Bergman  
Cyclization**

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**Experimental Section**

Synthesis and Characterization of **1-4**

**X-ray structure analyses**

**Figure 1S.** ORTEP Plot of **1**.

**Figure 2S.** ORTEP Plot of **2**.

**Figure 3S.** ORTEP Plot of **4**.

**Spectrographic data**

**Figure 4S.** Transient absorption spectra for **3** in benzonitrile.

**Figure 5S.** Visible absorption spectra for (2,3-diethynyl-5,10,15,20-tetraphenylporphyrinato) zinc(II) in dichloromethane.

## Experimental Methods

**Nanosecond Transient Absorption Spectroscopy.** Nanosecond transient absorption measurements were made using a Proteus spectrometer (Ultrafast Systems LLC) equipped with a 150 W Xe-arc lamp (Newport), a Chromex monochromator (Bruker Optics), appropriate diffraction gratings for visible and NIR dispersion, and Si or InGaAs photodiode detectors (DET 10A and DET 10C, Thorlabs) optically coupled to the exit slit of the monochromator. Excitation of the samples was achieved using a computer-controlled Nd:YAG laser/OPO system (Opotek, Vibrant LD 355 II) operating at 10 Hz. Single wavelength kinetic data were processed separately in Origin 8.5 with the goodness-of-fit established through visual inspection of the residuals.

The triplet lifetimes of the dialkynyl porphyrins were determined using transient absorption flash photolysis with specific instrumentation described above. All samples were prepared either in a 1 cm quartz cell purchased from Starna Cells or in a specially designed 1 cm optical cell with a 3.5 mL nominal volume bearing a side arm round-bottom flask and were subjected to a minimum of three freeze-pump-thaw degas cycles prior to all measurements.

**Synthetic Materials and General Procedures.** All chemicals and solvents used were of the highest purity available from Aldrich and Strem. Air-sensitive reactions were carried out under nitrogen using Schlenk techniques and air-sensitive compounds were handled in an inert atmosphere dry box. Compounds were purified using flash chromatography with activated neutral aluminum oxide or silica gel. NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra were recorded on a VXR 400, i400, or Gem 300 NMR spectrometer using the residual proton resonance of the solvent as an internal reference. Infrared spectra (KBr) were measured with a Nicolet 510P FT IR

spectrophotometer. MALDI-TOF data were obtained using a Bruker Biflex III Maldi-TOF mass spectrometer. ESI and EI-HRMS spectra were recorded on PE-Sciex API III Triple Quadrupole and Thermo Finnigan MAT 95 XP high mass resolution spectrometer, respectively. Elemental analyses were obtained from Robertson Microlit Laboratories, Inc. Electronic absorption spectra were acquired on a Perkin-Elmer Lambda 19 UV/vis/near-IR spectrometer. All differential scanning calorimetry (DSC) traces were measured on a TA Instruments Q10 DSC at a heating rate of 10 °C min<sup>-1</sup>.

**(2,3-Dibromo-5,10,15,20-tetraphenylporphyrinato)platinum(II) 1:** Pt(acac)<sub>2</sub> (229 mg, 0.584 mmol) was placed in a pressure tube under N<sub>2</sub>, and dry benzonitrile (20 mL) was added by cannula. The solution was heated to 190 °C for 30 min, then allowed to cool for 10 min. This was then added to another pressure tube containing 2,3-dibromo-5,10,15,20-tetraphenylporphyrin and further reacted at 190 °C for 6.5 h. The solvent was removed by vacuum transfer, and the crude compound purified by activated neutral aluminum oxide column chromatography. Yield: 88%. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε × 10<sup>-4</sup>) = 406 (24.41), 515 (2.10), 548 (0.91); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.78-7.68 (m, 12H, ArH), 8.02 (d, J = 6.8 Hz, 4H, ArH), 8.74 (s, 2H, β-pyrrole H), 8.13 (d, J = 6.0 Hz, 4H, ArH), 8.63 (d, J = 4.8 Hz, β-pyrrole H), 8.67 (d, J = 4.8 Hz, 2H, β-pyrrole H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ-142.13, 141.42, 140.78, 134.10, 133.82, 132.38, 131.09, 130.61, 128.32, 128.00, 126.98, 126.91, 123.32, 122.82, 121.79; IR (cm<sup>-1</sup>): 700, 753, 795, 1019, 1052, 1073, 1318, 1347, 1356, 1442, 1599, 2346, 3448; MALDI-TOF MS m/z = 966 [M<sup>+</sup>], ESI-TOF HRMS [MH<sup>+</sup>] calculated: 967.0237; found: 967.0215.

**(2,3,-Bis[trimethylsilylethynyl]-5,10,15,20-tetraphenylporphyrinato)platinum(II) 2:** To (Ph<sub>3</sub>P)<sub>4</sub>Pd, a solution of **23** (25 mg, 0.026 mmol) in dry THF (15 mL) was added at room temperature. Then, trimethyl(trimethylstannylethynyl)silane (20 mg, 0.078 mmol) in dry THF

(10 mL) was added to the reaction mixture and refluxed at 70-80 °C for 6 hours. The solvent was removed under reduced pressure and the resulting solid was purified by activated neutral aluminum oxide column chromatography. Yield: 58%; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ ) = 418 (23.48), 524 (2.27), 564 (2.34); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.70 (s, 2H,  $\beta$ -pyrrole H), 8.62 (d, J = 5.4 Hz, 2H,  $\beta$ -pyrrole H), 8.51 (d, J = 5.4 Hz, 2H,  $\beta$ -pyrrole H), 8.12-8.10 (m, 4H, ArH), 8.05 (d, J = 7.5 Hz, ArH), 7.77-7.63 (m, 12H, ArH), 0.22 (s, 18H, SiCH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  1.07, 98.91, 110.00, 122.56, 126.91, 127.06, 128.10, 128.74, 130.68, 131.10, 131.28, 132.22, 133.97, 134.35, 141.10, 141.20, 141.50, 141.65, 142.55; IR (cm<sup>-1</sup>): 700, 755, 795, 837, 856, 867, 1019, 1080, 1149, 1246, 1349, 1367, 1442, 1599, 2136, 3453; MALDI-TOF MS m/z = 1000 [M<sup>+</sup>]; ESI-TOF HRMS [MH<sup>+</sup>] calculated: 1001.2845; found: 1001.2792.

**(2,3-Diethynyl-5,10,15,20-tetraphenylporphyrinato)platinum(II) 3:** To a solution of **24** (150 mg, 0.150 mmol) in THF (50 mL), 1 M solution of *tetra*-butylammoniumfluoride in THF (0.5 mL) was added. The reaction mixture was stirred at room temperature for 1.5 h. After completion of the reaction, the solvent was evaporated and resulting residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> solution was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude compound was purified by activated neutral aluminum oxide column chromatography. Yield: 40%; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ ) = 414 (22.58), 521 (1.92), 560 (1.73); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.56 (s, 2H), 7.63 (t, 3H), 7.79-7.72 (m, 8H), 8.02 (d, J = 7.2 Hz), 8.13 (d, J = 6.0 Hz, 4H), 8.68 (s, 4H), 8.73 (s, 2H); MALDI-TOF MS m/z = 856 [MH<sup>+</sup>]. ESI-TOF HRMS [M<sup>+</sup>] calculated: 855.1966; found: 855.2024.

**(10,15-Diphenyl-piceno[20,1,2,3,4,5-fghij]porphyrinato)platinum(II) 4:** A solution of **25** (5 mg, 0.006 mmol) in toluene (15 mL), was heated in a pressure tube at 95 °C for 2 hours. The solvent was evaporated under reduced pressure and the resulting solid was purified by

activated neutral aluminum oxide column chromatography. Yield: 60%; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  ( $\epsilon \times 10^{-4}$ ) = 440 (11.60), 603 (3.28), 611 (3.76); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.81 (m, 6H), 8.04 (t, 2H), 8.13 (t, 2H), 8.21-8.20 (m, 4H), 8.60 (s, 2H), 8.95 (d, J = 4.8 Hz, 2H), 9.31 (d, J = 7.6 Hz, 2H), 9.40 (s, 2H), 9.82 (d, J = 8.0 Hz, 2H), 9.90 (d, J = 4.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  114.00, 125.09, 125.23, 126.94, 127.62, 128.16, 128.16, 128.51, 128.54, 128.92, 128.94, 128.97, 129.70, 134.42, 135.73, 139.23, 140.75; MALDI-TOF MS m/z = 853 [M<sup>+</sup>], 854 [MH<sup>+</sup>].

### X-ray structure analysis

**Data collection, structure solution, and refinement.** Data collections were carried out at IUMSC using a Bruker platform diffractometer equipped with a SMART6000 CCD detector and Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å, graphite monochromator) or at the APS, ChemMatCARS, using synchrotron radiation ( $\lambda = 0.49595$ , diamond 111 monochromator, two mirrors to exclude higher harmonics). The intensity data were corrected for absorption (SADABS).<sup>1</sup> Final cell constants were calculated from the xyz centroids of strong reflections in the actual data after integration (SAINT).<sup>2</sup> Space groups were determined based on intensity statistics and systematic absences. Structures were solved with direct methods using SIR-92<sup>3</sup> or SHELXL-97<sup>4</sup> and refined with full-matrix least squares / difference Fourier cycles using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters unless noted otherwise. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative or individual isotropic displacement parameters.

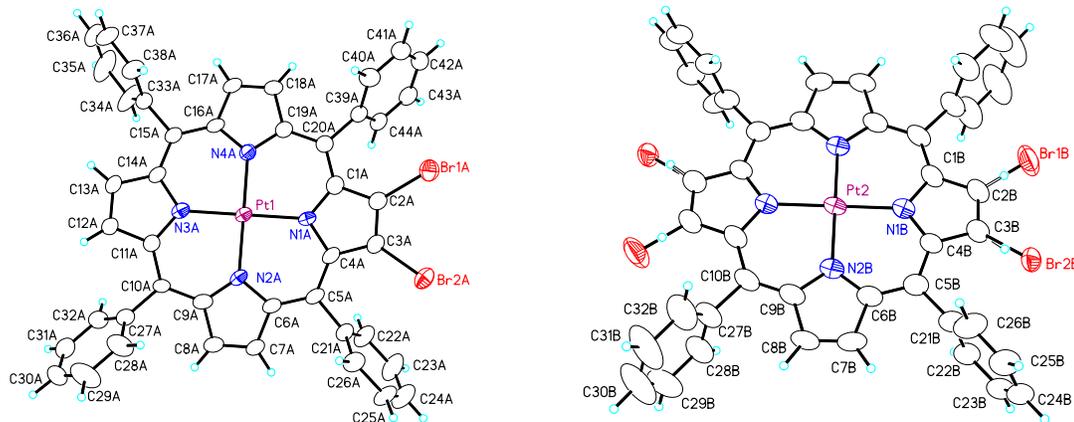
<sup>1</sup> SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.

<sup>2</sup> An empirical correction for absorption anisotropy, R. Blessing, Acta Cryst. A51, 33 – 38 (1995).

<sup>3</sup> SIR-92, A. Altomare; G. Cascarno; C. Giacovazzo; A. Gualardi; J. Appl. Cryst. 26, 343-350 (1993).

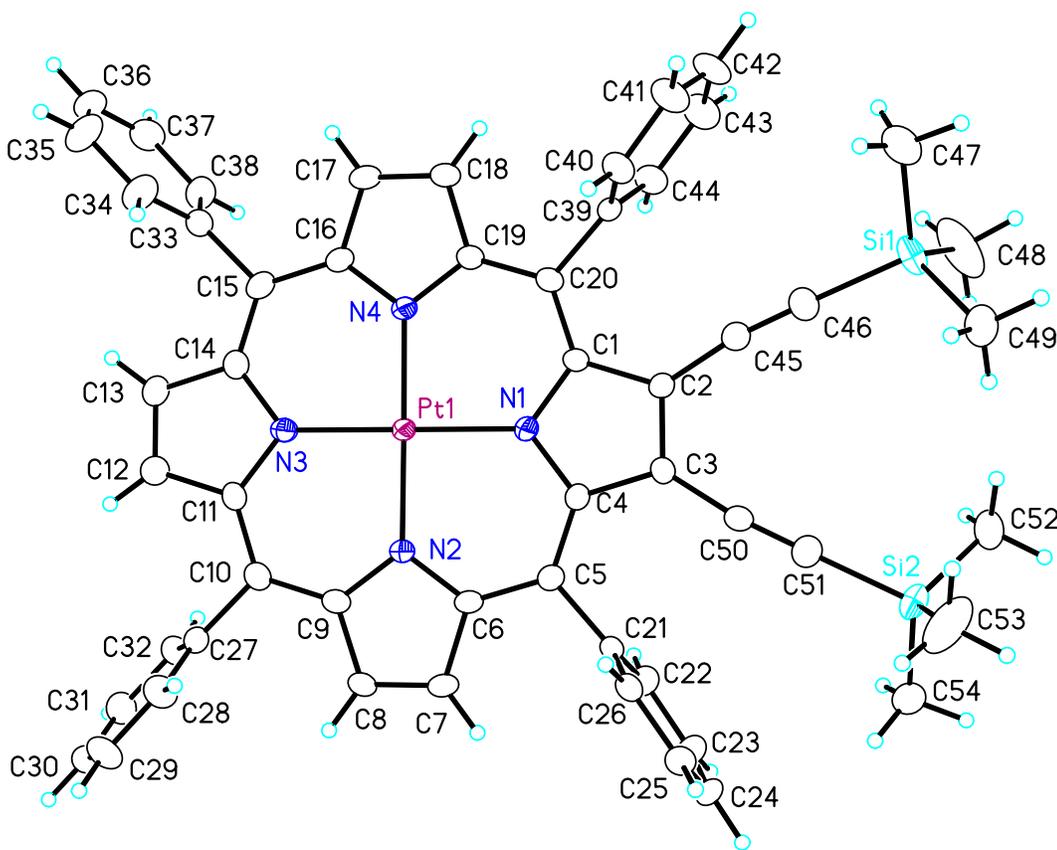
<sup>4</sup> SHELXTL-Plus, Bruker Analytical X-Ray Systems, Madison, WI, current version.

**Pt1.** Orange plate (approximate dimensions  $0.20 \times 0.20 \times 0.05 \text{ mm}^3$ ). The final full matrix least squares refinement converged to  $R1 = 0.0438$  and  $wR2 = 0.1057$  ( $F^2$ , all data). The remaining electron density is located near the bromine atoms; maximum peak and hole are of similar magnitude. The structure contains  $1\frac{1}{2}$  porphyrins and one solvent molecule in the asymmetric unit. Thus for the porphyrins with half of the molecule crystallographically unique and with an inversion center in the center of the molecule, the bromine and hydrogen positions are disordered statistically with one another. (CCDC 882454)  $C_{44.67}H_{27.33}Br_2Cl_{1.33}N_4Pt$ ,  $M = 1022.22$ , triclinic P-1,  $a = 13.8145(7) \text{ \AA}$ ,  $b = 13.8947(7) \text{ \AA}$ ,  $c = 16.8785(8) \text{ \AA}$ ,  $\alpha = 67.9340(10)^\circ$ ,  $\beta = 75.4790(10)^\circ$ ,  $\gamma = 66.1330(10)^\circ$ ,  $V = 2727.0(2) \text{ \AA}^3$ ,  $Z = 3$ ,  $T = 150(2) \text{ K}$ , MoK $\alpha$ , 43759 reflections, 11103 unique ( $R_{int} = 0.0450$ ).  $R1 = 0.0438$ ,  $wR2 = 0.0975$  (for 8618 observed reflections with  $I > 2\sigma(I)$  and 727 parameters, 49 restraints including same distance restraints and rigid bond restraints).



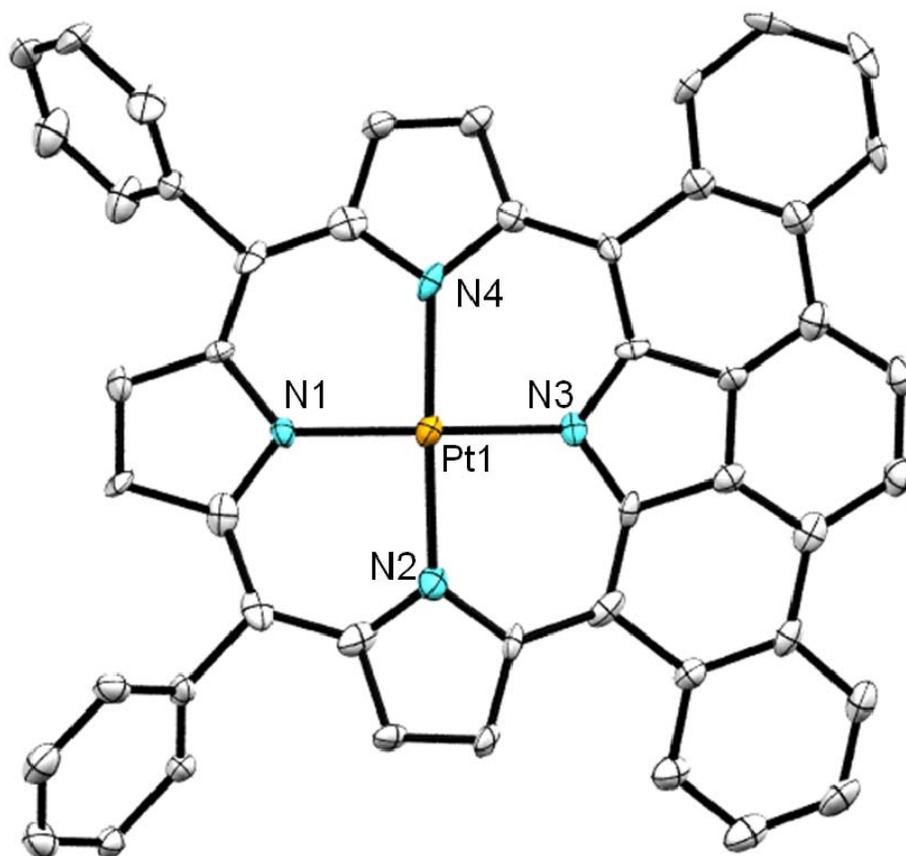
**Figure 1S.** ORTEP plots for both crystallographically independent molecules for **1** at 50% probability are shown side by side; only the unique portions of the molecules are labeled.

**Pt2.** A red crystal (approximate dimensions  $0.21 \times 0.18 \times 0.12 \text{ mm}^3$ ). The final full matrix least squares refinement converged to  $R1 = 0.0291$  and  $wR2 = 0.0607$  ( $F^2$ , all data). The remaining electron density is located near the metal ion and on bonds. **2** (CCDC 882455)  $\text{C}_{54}\text{H}_{44}\text{N}_4\text{PtSi}_2$ ,  $M = 1000.20$ , triclinic  $P-1$ ,  $a = 11.7158(10) \text{ \AA}$ ,  $b = 12.6374(11) \text{ \AA}$ ,  $c = 17.1090(14) \text{ \AA}$ ,  $\alpha = 73.831(2)^\circ$ ,  $\beta = 89.353(2)^\circ$ ,  $\gamma = 68.496(2)^\circ$ ,  $V = 2251.9(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $T = 150(2) \text{ K}$ ,  $\text{MoK}\alpha$ , 41504 reflections, 11116 unique ( $R_{\text{int}} = 0.0416$ ).  $R1 = 0.0291$ ,  $wR2 = 0.0577$  (for 9616 observed reflections with  $I > 2\sigma(I)$  and 556 parameters, 0 restraint).

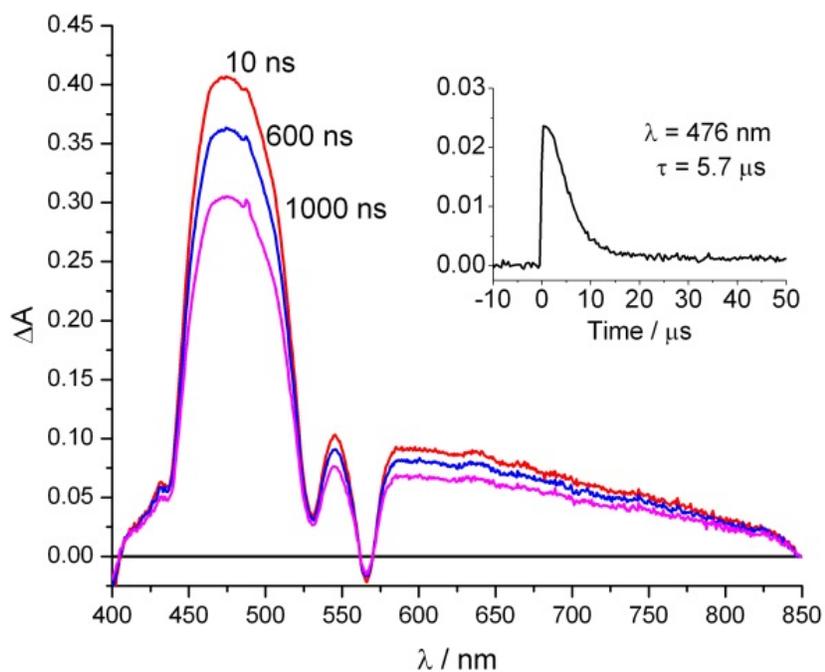


**Figure 2S.** ORTEP plot for **2** at 50% probability

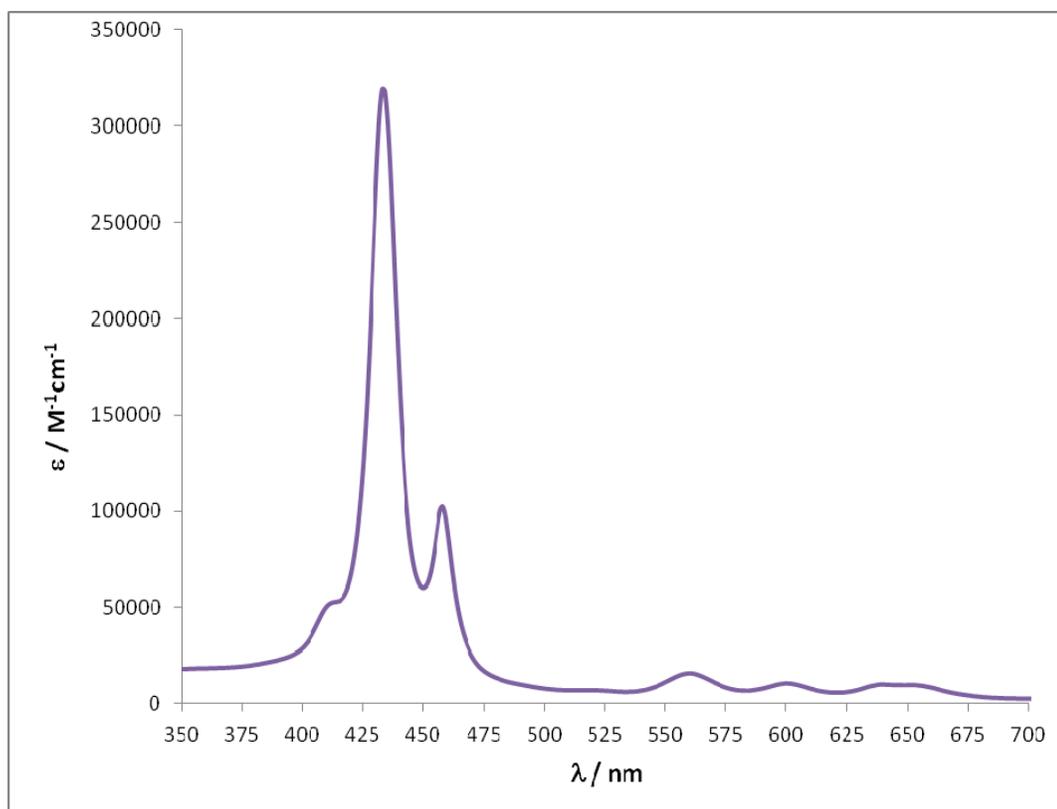
**Pt4.** Purple plate-like crystal (approximate dimensions  $0.07 \times 0.06 \times 0.05$  mm<sup>3</sup>). The remaining electron density is minuscule and located on bonds. (CCDC 882456) C<sub>48</sub>H<sub>26</sub>N<sub>4</sub>Pt, M = 853.82, orthorhombic Pna2<sub>1</sub>, a = 7.2411(10) Å, b = 21.366(3) Å, c = 20.202(2) Å, V = 3125.5(7) Å<sup>3</sup>, Z = 4, T = 150(2) K, MoKα, 18126 reflections, 6443 unique (Rint = 0.0744). R1 = 0.0388, wR2 = 0.0626 (for 4692 observed reflections with I > 2σ(I) and 455 parameters, 1 restraint).



**Figure 3S.** ORTEP plot for **4** at 50% probability.



**Figure 4S.** Transient absorption spectra for **3** in benzonitrile at 10, 600, and 1000 ns after the pulse. The decay of **4** at 476 nm is shown in the inset.



**Figure 5S.** UV/visible spectra for (2,3-diethynyl-5,10,15,20-tetraphenylporphyrinato) zinc(II) in dichloromethane.