

Electronic Supplementary Information for “Porphyrin Dimers Bridged by a Platinum-diacetylide Unit”

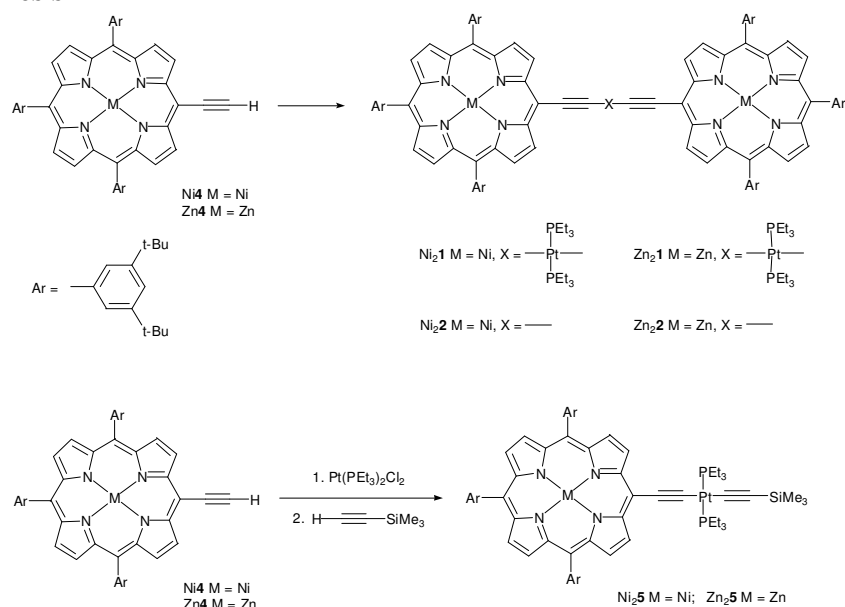
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Synthesis



Ni₂1: To a solution of compound **Ni4** (28 mg, 0.03 mmol) in Et₂NH (5 mL) under N₂ was added *trans*-Pt(PEt₃)₂Cl₂ (7.5 mg, 0.015 mmol). The mixture was heated at 60 °C for 6 hr. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using CH₂Cl₂:Hexanes = 1:7 as the eluent. The solvent was removed under reduced pressure to give a purple solid (23 mg, 68%). ¹H NMR (400 MHz, CDCl₃) δ_H 9.64 (d, *J* = 4.4 Hz, 4H), 8.76 (d, *J* = 4.4 Hz, 4H), 8.68 (s, 8H), 7.86 (d, *J* = 1.6 Hz, 8H), 7.83 (d, *J* = 1.6 Hz, 4H), 7.70 (t, *J* = 1.6 Hz, 4H), 7.67 (t, *J* = 1.6 Hz, 2H), 2.41-2.38 (m, 12H), 1.48 (s, 72H), 1.45 (s, 36H), 1.46-1.38 (m, 18H); UV/Vis (CH₂Cl₂) λ_{max}/nm (log ε): 449 (5.54), 552 (4.44), 595 (4.68); MS(ESI) *m/z* 2338, calculated for C₁₄₀H₁₇₂N₈P₂PtNi₂ 2338.

Zn₂1: Employing a procedure similar to that for Ni₂1 to yield 64% of the product. ¹H NMR (400 MHz, CDCl₃) δ_H 9.77 (d, *J* = 4.4 Hz, 4H), 8.95 (d, *J* = 4.4 Hz, 4H), 8.87 (s, 8H), 8.06 (d, *J* = 1.6 Hz, 8H), 8.03 (d, *J* = 1.6 Hz, 4H), 7.78 (t, *J* = 1.6 Hz, 4H), 7.75 (t, *J* = 1.6 Hz, 2H), 2.41-2.36 (m, 12H), 1.53 (s, 72H), 1.50 (s, 36H), 1.36-1.28 (m, 18H); UV/Vis (CH₂Cl₂) λ_{max}/nm (log ε): 444 (5.76), 574 (4.27), 616 (4.62); MS(FAB) *m/z* 2351 (M+H⁺) calculated for C₁₄₀H₁₇₀N₈P₂PtZn₂ 2350.

Zn₂2: To a solution of compound Zn4 (31 mg, 0.032 mmol) in a mixture of THF (4 mL) and NEt₃ (0.4 mL) under air was added CuI (0.6 mg, 0.003 mmol). The mixture was stirred at room temperature for 1 hr. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using CH₂Cl₂:Hexanes = 1:5 as the eluent. The solvent was removed under reduced pressure to give the product (20 mg, 66%). ¹H NMR (400 MHz, CDCl₃) δ_H 10.04 (d, *J* = 4.4 Hz, 4H), 9.13 (d, *J* = 4.4 Hz, 4H), 8.93 (s, 8H), 8.12 (s, 8H), 8.05 (s, 4H), 7.82 (t, *J* = 0.8 Hz, 4H), 7.78 (t, *J* = 0.8 Hz, 2H), 1.54 (s, 72H), 1.52 (s, 36H); UV/Vis (CH₂Cl₂) λ_{max}/nm (log ε): 450 (5.54), 481 (5.47), 565 (4.49), 678 (4.98); MS(ESI) *m/z* 1922 calculated for C₁₂₈H₁₄₂N₈Zn₂ 1922.

Ni₂2: A solution of Zn₂2 (50 mg, 0.025 mmol) in CH₂Cl₂ (100 mL) was washed with aqueous HCl (10%, 100 mL) solution and then with aqueous NaHCO₃ solution. The organic layer was dried with Na₂SO₄ and the solvent was evaporated under reduced pressure. The solid was dissolved in DMF (20 mL). After addition of Ni(OAc)₂ · 4H₂O (125 mg, 0.50 mmol), the mixture was refluxed for 2 hr. The solution was concentrated, and the crude product was precipitated by addition of water and was then filtered. Chromatography on silica gel eluting with CH₂Cl₂:Hexanes = 1:5 afforded the product (43 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ_H 9.71 (d, *J* = 4.8 Hz, 4H), 8.91 (d, *J* = 4.8 Hz, 4H), 8.72 (s, 8H), 7.87 (d, *J* = 1.6 Hz, 8H), 7.83 (d, *J* = 1.6 Hz, 4H), 7.73 (t, *J* = 1.6 Hz, 4H), 7.69 (t, *J* = 1.6 Hz, 2H), 1.48 (s, 72H), 1.45 (s, 36H); UV/Vis (CH₂Cl₂) λ_{max}/nm (log ε): 448 (5.22), 472 (5.22), 549 (4.38), 634 (4.67); MS(ESI) *m/z* 1908 calculated for C₁₂₈H₁₄₂N₈Ni₂ 1908.

Ni₂5: To a solution of compound Zn4 (20 mg, 0.02 mmol) in Et₂NH (5 mL) under N₂ was added *trans*-Pt(PEt₃)₂Cl₂ (20 mg, 0.039 mmol). The mixture was heated at 60 °C for 30 min, after which trimethylsilylacetylene (50 μL, 0.35 mmol) was added. The mixture was heated at 60 °C for further 30 min. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using CH₂Cl₂:Hexanes = 1:6 as the eluent. The solvent was removed under reduced pressure to give the product in 65% yield. ¹H NMR (CDCl₃, 400 MHz) : δ_H 9.50 (d, *J*

= 4.8 Hz, 2H), 8.70 (d, $J = 4.8$ Hz, 2H), 8.65 (s, 4H), 7.82 (d, $J = 1.6$ Hz, 4H), 7.81 (d, $J = 1.6$ Hz, 2H), 7.69 (d, $J = 1.6$ Hz, 2H), 7.66 (d, $J = 1.6$ Hz, 1H), 2.26 – 2.18 (m, 12H), 1.46 (s, 36H), 1.44 (s, 18H), 1.31–1.24 (m, 18H), 0.13 (s, 9H); UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$): 442 (5.52), 552 (4.28), 588 (4.39); MS (FAB) : m/z 1483 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{81}\text{H}_{110}\text{N}_4\text{NiP}_2\text{PtSi}$ 1482.

Zn5: Employing a procedure similar to that for Ni5 to yield 60% of the product. ^1H NMR (CDCl_3 , 400 MHz) : δ_{H} 9.80 (d, $J = 4.4$ Hz, 2H), 8.93 (d, $J = 4.4$ Hz, 2H), 8.86 (s, 4H), 8.28 (d, $J = 1.6$ Hz, 4H), 8.04 (d, $J = 1.6$ Hz, 2H), 7.78 (d, $J = 1.6$ Hz, 2H), 7.75 (d, $J = 1.6$ Hz, 1H), 2.42 – 2.22 (m, 12H), 1.54 (s, 36H), 1.50 (s, 18H), 1.42–1.28 (m, 18H), 0.17 (s, 9H); UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$): 446 (5.60), 576 (4.10), 618 (4.52) ; MS (FAB) : m/z 1489 ($\text{M}+\text{H}^+$), calcd for $\text{C}_{81}\text{H}_{110}\text{N}_4\text{P}_2\text{PtSiZn}$ 1488.

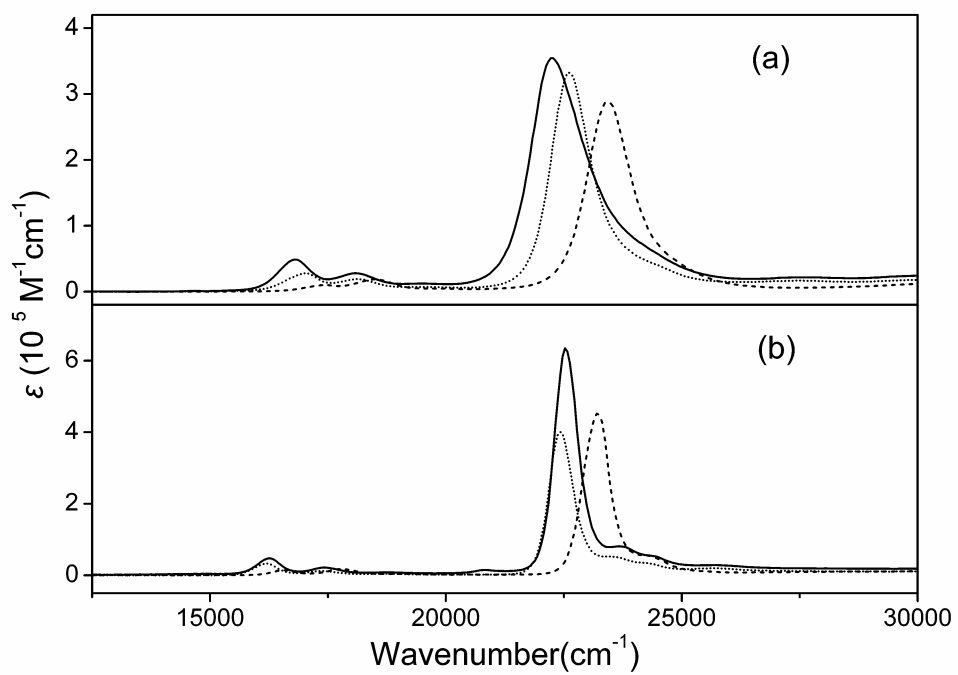


Figure S1. Absorption spectra of (a) Ni₂1 (solid), Ni3 (dash), and Ni5 (dot), and (b) Zn₂1 (solid), Zn3 (dash), Zn5 (dot) in CH₂Cl₂.

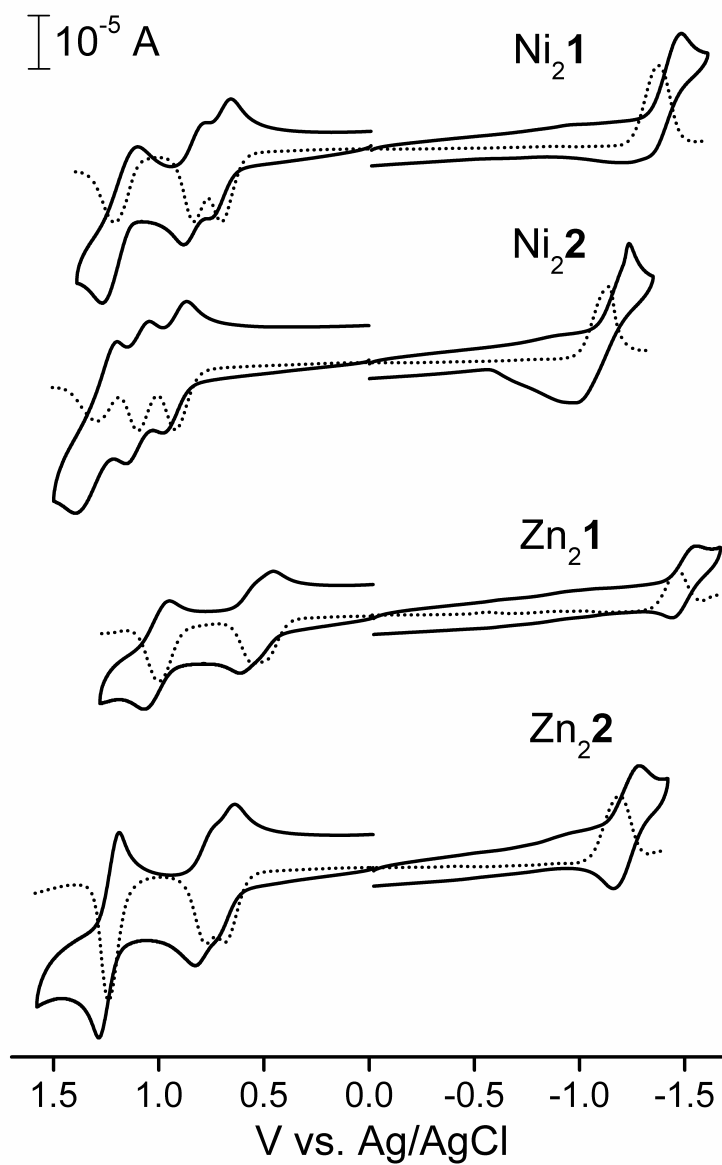


Fig. S2 The cyclic voltammograms (solid) and differential pulse voltammograms (dot) of Ni₂1, Ni₂2, Zn₂1, and Zn₂2 in CH₂Cl₂ containing 0.1 M TBAPF₆.

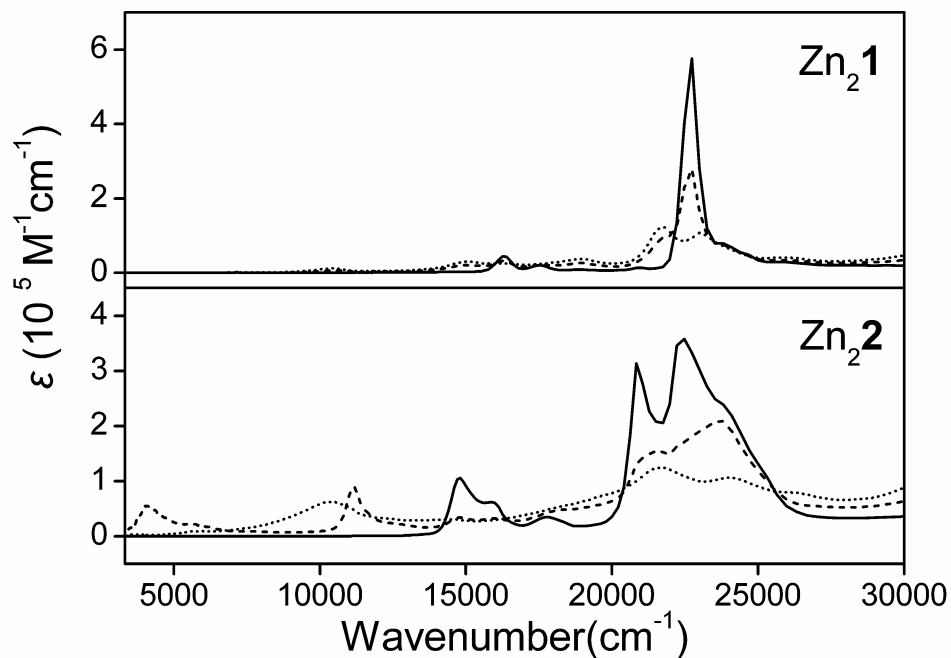


Fig. S3 The absorption spectra of (a) $\text{Zn}_2\mathbf{1}$ (solid), $\text{Zn}_2\mathbf{1}^+$ (dash), and $\text{Zn}_2\mathbf{1}^{2+}$ (dot), and (b) $\text{Zn}_2\mathbf{2}$ (solid), $\text{Zn}_2\mathbf{2}^+$ (dash), and $\text{Zn}_2\mathbf{2}^{2+}$ (dot) in CH_2Cl_2 . The mono- and dications were generated *in situ* by reacting the neutral molecules with 1 and 2 eq $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$, respectively. In the case of $\text{Zn}_2\mathbf{1}$, the solution could contain three species $\text{Zn}_2\mathbf{1}$, $\text{Zn}_2\mathbf{1}^+$, and $\text{Zn}_2\mathbf{1}^{2+}$ in the presence of 1 eq $[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{SbCl}_6]$ since the potential separation for the first and second oxidations is small ($\Delta E = 60$ mV).