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

Yi-Jen Chen, Szu-Shuo Chen, Shang-Shih Lo, Teng-Hui Huang, Chen-Chang Wu, Gene-Hsiang Lee, Shie-Ming Peng and Chen-Yu Yeh*;

aDepartment of Chemistry, National Chung Hsing University, 250 Kuo Kuang Road, Taichung 402, Taiwan
bDepartment of Chemistry, National Taiwan University, Taipei 106, Taiwan
cyyeh@dragon.nchu.edu.tw

Synthesis

Ni21: To a solution of compound Ni4 (28 mg, 0.03 mmol) in Et2NH (5 mL) under N2 was added trans-Pt(P(t-Bu)3)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) δH 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) λmax/nm (log ε): 449 (5.54), 552 (4.44), 595 (4.68); MS(ESI) m/z 2338, calculated for C140H172N8P2PtNi2 2338.
Zn$_2$I: Employing a procedure similar to that for Ni$_2$I to yield 64% of the product. $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ 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, 36H), 1.50 (s, 36H), 1.36-1.28 (m, 18H); UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$/nm (log $\varepsilon$): 444 (5.76), 574 (4.27), 616 (4.62); MS(FAB) $m/z$ 2351 (M+H$^+$) calculated for C$_{140}$H$_{170}$N$_8$P$_2$PtZn$_2$ 2350.

Zn$_2$: To a solution of compound Zn$_4$ (31 mg, 0.032 mmol) in a mixture of THF (4 mL) and NEt$_3$ (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 CH$_2$Cl$_2$:Hexanes = 1:5 as the eluent. The solvent was removed under reduced pressure to give the product (20 mg, 66%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ 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 (CH$_2$Cl$_2$) $\lambda_{max}$/nm (log $\varepsilon$): 450 (5.54), 481 (5.47), 565 (4.49), 678 (4.98); MS(ESI) $m/z$ 1922 calculated for C$_{128}$H$_{142}$N$_8$Zn$_2$ 1922.

Ni$_2$: A solution of Zn$_2$I (50 mg, 0.025 mmol) in CH$_2$Cl$_2$ (100 mL) was washed with aqueous HCl (10%, 100 mL) solution and then with aqueous NaHCO$_3$ solution. The organic layer was dried with Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. The solid was dissolved in DMF (20 mL). After addition of Ni(OAc)$_2$·4H$_2$O (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 CH$_2$Cl$_2$:Hexanes = 1:5 afforded the product (43 mg, 90%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta_H$ 9.71 (d, $J = 4.8$ Hz, 4H), 8.91 (d, $J = 4.8$ Hz, 4H), 8.72 (s, 8H), 8.05 (s, 4H), 7.83 (d, $J = 1.6$ Hz, 8H), 7.69 (t, $J = 1.6$ Hz, 2H), 1.48 (s, 72H), 1.45 (s, 36H); UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$/nm (log $\varepsilon$): 448 (5.22), 472 (5.22), 549 (4.38), 634 (4.67); MS(ESI) $m/z$ 1908 calculated for C$_{128}$H$_{142}$N$_8$Ni$_2$ 1908.

Ni$_5$: To a solution of compound Zn$_4$ (20 mg, 0.025 mmol) in Et$_2$NH (5 mL) under N$_2$ was added trans-Pt(P(Et)$_3$)$_2$Cl$_2$ (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 CH$_2$Cl$_2$:Hexanes = 1:6 as the eluent. The solvent was removed under reduced pressure to give the product in 65% yield. $^1$H NMR (CDCl$_3$, 400 MHz) : $\delta_H$ 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$_2$Cl$_2$): 
\( \lambda_{\text{max}}/\text{nm} \) (log $\varepsilon$): 442 (5.52), 552 (4.28), 588 (4.39); MS (FAB): \( m/z \) 1483 (M+H$^+$), calcd for C$_{81}$H$_{110}$N$_4$NiP$_2$PtSi 1482.

**Zn5:** Employing a procedure similar to that for Ni5 to yield 60% of the product. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$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$_2$Cl$_2$): $\lambda_{\text{max}}/\text{nm} \) (log $\varepsilon$): 446 (5.60), 576 (4.10), 618 (4.52); MS (FAB): \( m/z \) 1489 (M+H$^+$), calcd for C$_{81}$H$_{110}$N$_4$P$_2$PtSiZn 1488.
Figure S1. Absorption spectra of (a) Ni$_2$1 (solid), Ni3 (dash), and Ni5 (dot), and (b) Zn$_2$1 (solid), Zn3 (dash), Zn5 (dot) in CH$_2$Cl$_2$. 
Fig. S2 The cyclic voltammograms (solid) and differential pulse voltammograms (dot) of Ni$_2$1, Ni$_2$2, Zn$_2$1, and Zn$_2$2 in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$. 
The absorption spectra of (a) $\text{Zn}_2^1$ (solid), $\text{Zn}_2^1^+$ (dash), and $\text{Zn}_2^2^+$ (dot), and (b) $\text{Zn}_2^2$ (solid), $\text{Zn}_2^2^+$ (dash), and $\text{Zn}_2^2^2^+$ (dot) in $\text{CH}_2\text{Cl}_2$. The mono- and dicitations 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 $\text{Zn}_2^1$, the solution could contain three species $\text{Zn}_2^1$, $\text{Zn}_2^1^+$, and $\text{Zn}_2^2^+$ 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).

**Fig. S3** The absorption spectra of (a) $\text{Zn}_2^1$ (solid), $\text{Zn}_2^1^+$ (dash), and $\text{Zn}_2^2^+$ (dot), and (b) $\text{Zn}_2^2$ (solid), $\text{Zn}_2^2^+$ (dash), and $\text{Zn}_2^2^2^+$ (dot) in $\text{CH}_2\text{Cl}_2$. 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 $\text{Zn}_2^1$, the solution could contain three species $\text{Zn}_2^1$, $\text{Zn}_2^1^+$, and $\text{Zn}_2^2^+$ 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).