Electronic Supporting Information

Reaction of Antiaromatic Porphyrinoid with Active Methylene Compounds

Demin Ren,* Xinliang Fu,* Xiaofang Li,* Sebastian Koniarz, and Piotr J. Chmielewski*  

*a Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education,  
 Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical  
 Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 411201, China  
 b Department of Chemistry, University of Wroclaw, 14 F. Joliot-Curie Street, 50 383 Wroclaw,  
 Poland  
 E-mail: lixiaofang@iccas.ac.cn, pjc@wchuwr.pl
Table of contents

Crystallographic data                          S3
Figs. S1-S6 NMR spectra of 3a.                S4-S9
Fig. S7 HRMS spectrum of 3a.                  S10
Figs. S8-S9 NMR spectra of 3b.                S11
Fig. S10 HRMS spectrum of 3b.                 S12
Figs. S11-S12 NMR spectra of 3c.              S13
Fig. S13 HRMS spectrum of 3c.                 S14
Figs. S14-S15 NMR spectra of 3d.              S15-S16
Fig. S16 HRMS spectrum of 3d.                 S17
Figs. S17-S18 NMR spectra of 3e.              S18
Fig. S19 HRMS spectrum of 3e.                 S19
Figs. S20-S21 NMR spectra of 3f.              S20
Fig. S22 HRMS spectrum of 3f.                 S21
Figs. S23-S24 NMR spectra of 3g.              S22
Fig. S25 HRMS spectrum of 3g.                 S23
Figs. S26-S27 NMR spectra of 3h.              S24
Fig. S28 HRMS spectrum of 3h.                 S25
Figs. S29-S30 NMR spectra of 3i.              S26
Fig. S31 HRMS spectrum of 3i.                 S27
Fig. S32 Cyclic and differential pulse voltammetry for 3a S28
Fig. S33 Cyclic and differential pulse voltammetry for 3e S29
Fig. S34 Cyclic and differential pulse voltammetry for 3g S30
Fig. S35 Cyclic and differential pulse voltammetry for 3i S31
Fig. S36 Optical spectra of 3c in DCM, methanol, and in methanol containing NaOH S32
Fig. S36 Optical spectra of 3a in DCM and in methanol. S32

References                                    S33
Crystallographic data

Crystal data for 3c was collected at room temperature on Bruker APEX-II CCD using Mo Kα radiation (λ = 0.71073 Å). Data reduction and analysis were carried out with the SAINT program.¹ The structure was solved by using the SHELXT program² and refined by the full-matrix least-squares method on all F² data using the SHELXL program.³ The data was corrected for absorption effects (multi-scans method) using SADABS program.⁴ All hydrogen atoms, including those located in the difference density map, were placed in calculated positions and refined as the riding model. The SQUEEZE/PLATON procedure⁵ was applied for disordered lattice solvent molecules. See Table S1 for detailed data.

Table S1 Crystal data for 3c

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C₄₄H₄₀N₄NiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mᵣ</td>
<td>715.51</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2₁/c</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>296</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>19.861 (8), 13.383 (5), 18.290 (7)</td>
</tr>
<tr>
<td>β (°)</td>
<td>117.36 (1)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>4318 (3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>0.49</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.28 × 0.24 × 0.12</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Bruker APEX-II CCD</td>
</tr>
<tr>
<td>T_min, T_max</td>
<td>0.591, 0.745</td>
</tr>
<tr>
<td>No. of measured, independent and observed [I &gt; 2σ(I)] reflections</td>
<td>28670, 7501, 4559</td>
</tr>
<tr>
<td>Rint</td>
<td>0.041</td>
</tr>
<tr>
<td>(sin θ/λ)max (Å⁻¹)</td>
<td>0.595</td>
</tr>
</tbody>
</table>

Refinement

R[F² > 2σ(F²)], wR(F²), S | 0.054, 0.163, 1.05 |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of reflections</td>
<td>7501</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>469</td>
</tr>
<tr>
<td>H-atom treatment</td>
<td>H-atom parameters constrained</td>
</tr>
<tr>
<td>Δρmax, Δρmin (e Å⁻³)</td>
<td>0.45, −0.25</td>
</tr>
</tbody>
</table>
Fig. S1 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of 3a.
Fig. S2 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of 3a.
Fig. S3 $^1$H,$^1$H COSY spectrum (CDCl$_3$ 500 MHz, 298 K) of 3a.
Fig. S4 $^1$H,$^{13}$C HSQC spectrum (CDCl$_3$ 500/125 MHz, 298 K) of 3a.
Fig. S5 $^1$H,$^{13}$C HMBC spectrum (CDCl$_3$ 500/125 MHz, 298 K) of 3a.
Fig. S6 $^1$H, $^1$H NOESY spectrum (CDCl$_3$, 500MHz, 298 K) of 3a.
Chemical Formula: $C_{41}H_{34}N_5NiO_2^-$
Exact Mass: 686.2071

Fig. S7 HRMS ESI(−) spectrum of 3a.
Fig. S8 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of 3b.

Fig. S9 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of 3b.
Chemical Formula: $\text{C}_{39}\text{H}_{29}\text{N}_{6}\text{Ni}^-$
Exact Mass: 639.1813

Fig. S10 HRMS ESI(−) spectrum of 3b.
Fig. S11 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of $3c$.

Fig. S12 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of $3c$. 
Chemical Formula: C_{44}H_{39}N_{4}NiO_{2}^-  
Exact Mass: 713.2432

Fig. S13 HRMS ESI(–) spectrum of 3c.
Fig. S14 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of 3d.
Fig. S15 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of 3d.
Chemical Formula: $C_{43}H_{40}N_4NiO_4$
Exact Mass: 734.2403

Fig. S16 HRMS ESI(+) spectrum of 3d.
Fig. S17 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of 3e.

Fig. S18 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of 3e.
Fig. S19 HRMS ESI(−) spectrum of 3e.
$^{1}$H NMR of 3f

Fig. S20 $^{1}$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of 3f.

Fig. S21 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of 3f.
Chemical Formula: $\text{C}_{45}\text{H}_{34}\text{N}_{5}\text{NiO}^-$
Exact Mass: 718.2122

Fig. S22 HRMS ESI(−) spectrum of 3f.
Fig. S23 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of $3g$.

Fig. S24 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of $3g$. 
Chemical Formula: $\text{C}_{42}\text{H}_{39}\text{N}_4\text{NiO}_3^+$
Exact Mass: 705.2370

Fig. S25 HRMS ESI(+) spectrum of 3g.
Fig. S26 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of 3h.

Fig. S27 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of 3h.
Chemical Formula: C_{42}H_{35}N_{4}NiO_{2}⁻

Exact Mass: 685.2119

Fig. S28 HRMS ESI(−) spectrum of 3h.
Fig. S29 $^1$H NMR spectrum (CDCl$_3$ 500 MHz, 298 K) of 3i.

$^{13}$C NMR of 3i

Fig. S30 $^{13}$C NMR spectrum (CDCl$_3$, 125 MHz, 298 K) of 3i.
Chemical Formula: $\text{C}_{41}\text{H}_{37}\text{N}_4\text{NiO}_2^+$

Exact Mass: 675.2265

![Chemical Structure](image)

Fig. S31 HRMS ESI(+) spectrum of 3i.
Fig. S32 Cyclic (top) and differential pulse (bottom) voltammetry for 3a recorded within various potential limits, with various starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, [Bu₄N]PF₆; working electrode, glassy carbon; reference electrode, AgCl/Ag; auxiliary electrode, platinum rod. The number associated with peaks are halfwave potentials (in volts) referenced with ferrocene/ferrocenium couple.
Fig. S33 Cyclic (top) and differential pulse (bottom) voltammetry for 3e recorded within various potential limits, with various starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, [Bu₄N]PF₆; working electrode, glassy carbon; reference electrode, AgCl/Ag; auxiliary electrode, platinum rod.
**Fig. S34** Cyclic (black trace) and differential pulse (red trace) voltammetry for 3g with starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, [Bu₄N]PF₆; working electrode, glassy carbon; reference electrode, AgCl/Ag; auxiliary electrode, platinum rod. The number associated with peaks are halfwave potentials (in volts) referenced with ferrocene/ferrocenium couple.
Fig. S35 Cyclic (top) and differential pulse (bottom) voltammetry for 3i recorded within various potential limits, with various starting potentials and directions of potential sweep marked with sticks and arrows, respectively. Conditions: solvent, DCM; supporting electrolyte, [Bu₄N]PF₆; working electrode, glassy carbon; reference electrode, AgCl/Ag; auxiliary electrode, platinum rod. The number associated with peaks are halfwave potentials (in volts) referenced with ferrocene/ferrocenium couple.
**Fig. S36** Optical spectra of 3c in DCM (black), methanol (red), and in methanol containing 1% of NaOH (blue).

**Fig. S37** Optical spectra of 3a in DCM (black) and in methanol (red).
References