Supporting Information for:

Laser initiation of Fe(II) complexes of 4-nitropyrazolyl substituted tetrazine ligands

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Contribution from M division¹; W division²; and Chemistry division³; Los Alamos National Laboratory, P. O. Box 1663, Los Alamos, NM 87544 (USA).
Figure S1. $^1$HNMR (top) and $^{13}$CNMR (bottom) spectra of H$_2$NHNTzTrz (4).
Figure S2. $^1$HNMR (top) and $^{13}$CNMR (bottom) spectra of $\text{H}_2\text{NTzTrz}$ (5)
Figure S3. $^1$HNMR (top) and $^{13}$CNMR (bottom) spectra of $^\text{NO}_2\text{Pyr}_2\text{Tz}$ (6).
Figure S4. $^1$HNMR (top) and $^{13}$CNMR (bottom) spectra of H$_2$NTz$^{\text{NO}_2}$Pyr (7)
Figure S5. $^1$HNMR (top) and $^{13}$CNMR (bottom) spectra of H$_2$NHNTz$^{\text{NO2}}$Pyr (8).
Figure S6. $^1$HNMR (top) and $^{13}$CNMR (bottom) spectra of H$_2$NTriTz$^{\text{NO}_2}$Pyr (9).
**Table S1.** Crystallographic information for [(H$_2$NTz$^{\text{NO2}}$Pyr)$_2$Fe(MeCN)$_2$][ClO$_4$]$_2$ (10).

<table>
<thead>
<tr>
<th></th>
<th>10</th>
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</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{14}$H$</em>{14}$ClFeN$<em>{18}$O$</em>{12}$</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
<td>0.08 x 0.12 x 0.20</td>
</tr>
<tr>
<td><strong>Formula weight, g mol$^{-1}$</strong></td>
<td>753.18</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2$_1$/c</td>
</tr>
<tr>
<td><strong>a, Å</strong></td>
<td>8.017(3)</td>
</tr>
<tr>
<td><strong>b, Å</strong></td>
<td>12.597(4)</td>
</tr>
<tr>
<td><strong>c, Å</strong></td>
<td>13.612(4)</td>
</tr>
<tr>
<td><strong>α, deg</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>β, deg</strong></td>
<td>100.28(2)</td>
</tr>
<tr>
<td><strong>γ, deg</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>V, Å$^3$</strong></td>
<td>1352.6(8)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>T, K</strong></td>
<td>170</td>
</tr>
<tr>
<td><strong>ρ, calcd, g cm$^{-3}$</strong></td>
<td>1.849</td>
</tr>
<tr>
<td><strong>Refl. collected/2θ$_{\text{max}}$</strong></td>
<td>2110/50.71</td>
</tr>
<tr>
<td><strong>Unique refl./ I&gt;2σ(I)</strong></td>
<td>2110/860</td>
</tr>
<tr>
<td><strong>Parameters/restraints</strong></td>
<td>215/0</td>
</tr>
<tr>
<td><strong>λ, Å/μ(Kα), cm$^{-1}$</strong></td>
<td>0.71073</td>
</tr>
<tr>
<td><strong>R$_1$/GOF</strong></td>
<td>0.1053/0.989</td>
</tr>
<tr>
<td><strong>wR$_2$(I&gt;2σ(I))</strong></td>
<td>0.2530</td>
</tr>
<tr>
<td><strong>Residual density, e Å$^{-3}$</strong></td>
<td>1.284/-1.204</td>
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</tbody>
</table>

**Table S2.** Selected bond lengths and angles in [(H$_2$NTz$^{\text{NO2}}$Pyr)$_2$Fe(MeCN)$_2$][ClO$_4$]$_2$ (10).

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Fe-N$_{\text{Tz}}$</td>
<td>1.951(2)</td>
</tr>
<tr>
<td>Fe-N$_{\text{Pyr}}$</td>
<td>1.971(2)</td>
</tr>
<tr>
<td>Fe-N$_{\text{MeCN}}$</td>
<td>1.939(2)</td>
</tr>
<tr>
<td>N$<em>{\text{Pyr}}$-Fe-N$</em>{\text{Tz}}$</td>
<td>81.4(4)</td>
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<tr>
<td>N$<em>{\text{Pyr}}$-Fe-N$</em>{\text{MeCN}}$</td>
<td>91.8(4)</td>
</tr>
<tr>
<td>N$<em>{\text{Tz}}$-Fe-N$</em>{\text{Pyr}}$</td>
<td>98.6(4)</td>
</tr>
<tr>
<td>N$<em>{\text{Tz}}$-Fe-N$</em>{\text{Pyr}}'$</td>
<td>180.0</td>
</tr>
<tr>
<td>N$<em>{\text{Tz}}$-Fe-N$</em>{\text{MeCN}}$</td>
<td>92.9(4)</td>
</tr>
<tr>
<td>N$<em>{\text{Tz}}$-Fe-N$</em>{\text{Tz}}'$</td>
<td>180.0</td>
</tr>
</tbody>
</table>
Figure S7. DSC plot of 10 at a heating rate of 10 °C min⁻¹ (Exo up).

Figure S8. DSC plot of 10 at a heating rate of 10 °C min⁻¹ (Exo up).