Mononuclear and dinuclear Re(I) complexes incorporating 1-(2-pyridylazo)-2-naphthol: synthesis, structure, spectral, DFT and TDDFT study†

Pallab Mondal, Amar Hens, Sucharita Basak, and Kajal Krishna Rajak*
**Fig. S1** Isodensity plot of frontier orbitals of \([\text{Re}_2(\text{PAN})_2(\text{CO})_6]\), 2.
**Fig. S2** Isodensity plot of frontier orbitals of [Re(PAN)(CO)(P–P)], 3.
**Table S1** Frontier Molecular Orbital Composition (%) in the Ground State for [Re$_2$(PAN)$_2$(CO)$_6$], 2.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (eV)</th>
<th>Contribution (%)</th>
<th>Main bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re</td>
<td>CO</td>
<td>PAN</td>
</tr>
<tr>
<td>L+8</td>
<td>-0.851</td>
<td>10.4</td>
<td>36.0</td>
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<tr>
<td>L+7</td>
<td>-0.906</td>
<td>15.1</td>
<td>44.7</td>
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<tr>
<td>L+6</td>
<td>-0.976</td>
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<td>45.0</td>
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<td>8.0</td>
<td>23.4</td>
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<td>L+4</td>
<td>-1.202</td>
<td>9.1</td>
<td>20.4</td>
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<td>L+3</td>
<td>-1.721</td>
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<td>7.0</td>
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<td>-1.772</td>
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<td>3.4</td>
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<td>H-5</td>
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<td>48.1</td>
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<td>-6.663</td>
<td>36.9</td>
<td>15.0</td>
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<td>H-7</td>
<td>-6.724</td>
<td>37.2</td>
<td>14.0</td>
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<td>H-8</td>
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<td>31.2</td>
<td>12.7</td>
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Table S2 Frontier Molecular Orbital Composition (%) in the Ground State for [Re(PAN)(CO)(P–P)].

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<th>Orbital</th>
<th>Energy (eV)</th>
<th>Contribution (%)</th>
<th>Main bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>L+8</td>
<td>-0.590</td>
<td>1.6 0.3 6.0 92.1</td>
<td>( \pi^*(P–P) )</td>
</tr>
<tr>
<td>L+7</td>
<td>-0.633</td>
<td>1.1 0.8 3.5 94.6</td>
<td>( \pi^*(P–P) )</td>
</tr>
<tr>
<td>L+6</td>
<td>-0.798</td>
<td>4.0 0.2 30.3 65.5</td>
<td>( \pi^<em>(PAN)^+ + \pi^</em>(P–P) )</td>
</tr>
<tr>
<td>L+5</td>
<td>-0.832</td>
<td>3.3 0.4 44.0 52.2</td>
<td>( \pi^<em>(PAN)^+ + \pi^</em>(P–P) )</td>
</tr>
<tr>
<td>L+4</td>
<td>-0.876</td>
<td>1.1 0.1 6.0 92.8</td>
<td>( \pi^*(P–P) )</td>
</tr>
<tr>
<td>L+3</td>
<td>-0.946</td>
<td>0.7 0 2.3 97.0</td>
<td>( \pi^*(P–P) )</td>
</tr>
<tr>
<td>L+2</td>
<td>-1.102</td>
<td>5.5 0.6 24.8 69.1</td>
<td>( \pi^<em>(PAN)^+ + \pi^</em>(P–P) )</td>
</tr>
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<td>( \pi^*(P–P) )</td>
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<tr>
<td>L</td>
<td>-2.042</td>
<td>28.5 1.4 57.5 12.6</td>
<td>( p(Re)^+ + \pi^<em>(PAN)^+ + \pi^</em>(P–P) )</td>
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<tr>
<td>H</td>
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<td>( d(Re)^+ + \pi(PAN) )</td>
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<tr>
<td>H-1</td>
<td>-5.264</td>
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<td>( \pi(PAN) )</td>
</tr>
<tr>
<td>H-2</td>
<td>-5.399</td>
<td>39.2 11.8 41.8 7.1</td>
<td>( d(Re)^+ + \pi(CO)^+ + \pi(PAN) )</td>
</tr>
<tr>
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<td>( d(Re)^+ + \pi(CO) )</td>
</tr>
<tr>
<td>H-4</td>
<td>-6.191</td>
<td>5.0 0.5 92.1 2.3</td>
<td>( \pi(PAN) )</td>
</tr>
<tr>
<td>H-5</td>
<td>-6.769</td>
<td>15.3 2.7 80.0 2.0</td>
<td>( d(Re)^+ + \pi(PAN) )</td>
</tr>
<tr>
<td>H-6</td>
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<td>( \pi(PAN)^+ + \pi(P–P) )</td>
</tr>
<tr>
<td>H-7</td>
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<td>( \pi(PAN)^+ + \pi(P–P) )</td>
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<tr>
<td>H-8</td>
<td>-7.143</td>
<td>0.8 0.4 7.0 91.8</td>
<td>( \pi(P–P) )</td>
</tr>
<tr>
<td>L+8</td>
<td>-0.590</td>
<td>1.6 0.3 6.0 92.1</td>
<td>( \pi^*(P–P) )</td>
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</table>
**Fig. S3** Linear correlation between the experimental and calculated $^{13}$C NMR chemical shifts of $[\text{Re}_2(\text{PAN})_2(\text{CO})_6]$, 2.

**Fig. S4** Linear correlation between the experimental and calculated $^{13}$C NMR chemical shifts of $[\text{Re}(\text{PAN})(\text{CO})(\text{P–P})]$, 3.
<table>
<thead>
<tr>
<th>Excitation</th>
<th>Composition</th>
<th>E (eV)</th>
<th>Oscillator strength (f)</th>
<th>$\lambda_{\text{tho}}$ (nm)</th>
<th>Assign</th>
<th>$\lambda_{\text{exp}}$ (nm)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>H-1 $\rightarrow$ L (100%)</td>
<td>2.4892</td>
<td>0.1749</td>
<td>498.09</td>
<td>MLCT/LLCT/ILCT</td>
<td>511</td>
</tr>
<tr>
<td>2</td>
<td>H $\rightarrow$ L+1 (100%)</td>
<td>2.5405</td>
<td>0.0676</td>
<td>488.04</td>
<td>MLCT/LLCT/ILCT</td>
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<tr>
<td>3</td>
<td>H-3 $\rightarrow$ L+1 (23%)</td>
<td>2.9337</td>
<td>0.5455</td>
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<td>MLCT/LLCT/ILCT</td>
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<tr>
<td>4</td>
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<td>3.1253</td>
<td>0.0190</td>
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<td>0.0791</td>
<td>394.17</td>
<td>MLCT/LLCT/ILCT</td>
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<tr>
<td>6</td>
<td>H-11 $\rightarrow$ L (16%)</td>
<td>3.3822</td>
<td>0.0567</td>
<td>366.57</td>
<td>MLCT/ILCT</td>
<td>300</td>
</tr>
<tr>
<td>7</td>
<td>H-10 $\rightarrow$ L+1 (12%)</td>
<td>3.6494</td>
<td>0.0399</td>
<td>339.74</td>
<td>MLCT/LLCT/ILCT</td>
<td>300</td>
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<tr>
<td>8</td>
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<td>0.0144</td>
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<td>11</td>
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<td>ILCT/MLCT</td>
<td>300</td>
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<tr>
<td>Excitation</td>
<td>Composition</td>
<td>E (eV)</td>
<td>Oscillator strength (f)</td>
<td>$\lambda_{\text{theo}}$ (nm)</td>
<td>Assign</td>
<td>$\lambda_{\text{exp}}$ (nm)</td>
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<tr>
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<td>H-2 $\rightarrow$ L (26%)</td>
<td></td>
<td></td>
<td></td>
<td>MLCT/ILCT</td>
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<tr>
<td></td>
<td>H-1 $\rightarrow$ L (26%)</td>
<td></td>
<td></td>
<td></td>
<td>LMCT/ILCT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H $\rightarrow$ L (35%)</td>
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<td></td>
<td>MLCT/ILCT</td>
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</tr>
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<td>2</td>
<td>H-2 $\rightarrow$ L (38%)</td>
<td>2.8598</td>
<td>0.2298</td>
<td>433.54</td>
<td>MLCT/ILCT</td>
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</tr>
<tr>
<td></td>
<td>H-1 $\rightarrow$ L (46%)</td>
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<td>LMCT/ILCT</td>
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</tr>
<tr>
<td></td>
<td>H $\rightarrow$ L+1 (16%)</td>
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<td>LMCT/ILCT</td>
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<td>3</td>
<td>H $\rightarrow$ L+1 (58%)</td>
<td>3.4318</td>
<td>0.0872</td>
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<td>MLCT/ILCT</td>
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<td>H $\rightarrow$ L+3 (27%)</td>
<td></td>
<td></td>
<td></td>
<td>MLCT/ILCT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H $\rightarrow$ L+5 (14%)</td>
<td></td>
<td></td>
<td></td>
<td>MLCT/ILCT</td>
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</tr>
<tr>
<td>4</td>
<td>H-4 $\rightarrow$ L (12%)</td>
<td>3.5803</td>
<td>0.1163</td>
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<td>LMCT/ILCT</td>
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<td></td>
<td>H $\rightarrow$ L+1 (21%)</td>
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<td></td>
<td>MLCT/ILCT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H $\rightarrow$ L+2 (15%)</td>
<td></td>
<td></td>
<td></td>
<td>MLCT/ILCT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H $\rightarrow$ L+3 (40%)</td>
<td></td>
<td></td>
<td></td>
<td>MLCT/ILCT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H $\rightarrow$ L+5 (11%)</td>
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<td></td>
<td></td>
<td>MLCT/ILCT</td>
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</tr>
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<td>5</td>
<td>H-4 $\rightarrow$ L (22%)</td>
<td>3.6087</td>
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<td></td>
<td>MLCT/ILCT</td>
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</tr>
<tr>
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<td>H $\rightarrow$ L+3 (12%)</td>
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<td>MLCT/ILCT</td>
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<td>3.6586</td>
<td>0.0765</td>
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<td>LMCT/ILCT</td>
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<td>H $\rightarrow$ L+1 (12%)</td>
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<td></td>
<td>H $\rightarrow$ L+2 (15%)</td>
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<td>H $\rightarrow$ L+4 (12%)</td>
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<td>MLCT/ILCT</td>
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<td>H $\rightarrow$ L+5 (9%)</td>
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<td>H $\rightarrow$ L+4 (46%)</td>
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<td>MLCT/ILCT</td>
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<td>H $\rightarrow$ L+5 (42%)</td>
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<td>MLCT/ILCT</td>
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</table>

**Table S4** Main calculated optical transition for the complex [Re(PAN)(CO)(P-P)], 3 with composition in terms of molecular orbital contribution of the transition, Vertical excitation energies, oscillator strength in acetonitrile.
**Fig. S5** Experimental absorption spectra of 2 and 3 in acetonitrile media.
Fig. S6 The simulated absorption spectra of complex \([\text{Re}_2(\text{PAN})_2(\text{CO})_6]\), 2 at the TDDFT (B3LYP)/LANL2DZ level in acetonitrile media.
Fig. S7 The simulated absorption spectra of complex [Re(PAN)(CO)(P–P)], 3 at the TDDFT (B3LYP)/LANL2DZ level in acetonitrile media.
Table S5 Frontier Molecular Orbital Compositions (%) in the Excited State for [Re₂(PAN)₂(CO)₆], 2.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Energy (eV)</th>
<th>Contribution (%)</th>
<th>Main bond type</th>
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<td></td>
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<td>Re</td>
<td>CO</td>
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<td>196</td>
<td>-0.853</td>
<td>14.4</td>
<td>66.3</td>
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<td>195</td>
<td>-1.029</td>
<td>9.7</td>
<td>28.0</td>
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<td>-1.044</td>
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<td>38.4</td>
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<td>-1.075</td>
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<td>35.1</td>
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<td>-1.203</td>
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<td>191</td>
<td>-1.206</td>
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<td>190</td>
<td>-1.662</td>
<td>3.5</td>
<td>9.6</td>
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<tr>
<td>189</td>
<td>-1.700</td>
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<td>188</td>
<td>-4.229</td>
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<td>4.7</td>
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<td>187</td>
<td>-4.401</td>
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<td>2.8</td>
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Table S6 Calculated Triplet Excited State of Complex [Re₂(PAN)₂(CO)₆], 2 in Acetonitrile Based on the Lowest Lying Triplet State Geometry. Main Calculated Vertical Transitions with Compositions in Terms of Molecular Orbital Contribution of the Transition, Vertical Excitation Energies and Oscillator Strength

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<tr>
<th>Excitation</th>
<th>Composition</th>
<th>Energy (eV)</th>
<th>Oscillator Strength (f)</th>
<th>λ_cal (nm)</th>
<th>Character</th>
<th>λ_exp (nm)</th>
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</thead>
<tbody>
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<td>1</td>
<td>189→187 (15%)</td>
<td>2.0277</td>
<td>0.0422</td>
<td>611.44</td>
<td>3ILCT</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>191→187 (9%)</td>
<td></td>
<td></td>
<td></td>
<td>3LLCT/3ILCT</td>
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</tr>
<tr>
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<td>190→188 (75%)</td>
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<td></td>
<td></td>
<td>3ILCT</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>190→187 (57%)</td>
<td>2.1235</td>
<td>0.0321</td>
<td>583.88</td>
<td>3ILCT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>190→188 (22%)</td>
<td></td>
<td></td>
<td></td>
<td>3ILCT</td>
<td></td>
</tr>
<tr>
<td></td>
<td>196→188 (21%)</td>
<td></td>
<td></td>
<td></td>
<td>3MLCT/3LLCT/3ILCT</td>
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</tr>
<tr>
<td>3</td>
<td>189→187 (59%)</td>
<td>2.1846</td>
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</tr>
<tr>
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<td>191→187 (7%)</td>
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<td></td>
<td></td>
<td>3LLCT/3ILCT</td>
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</tr>
<tr>
<td></td>
<td>190→188 (10%)</td>
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<td>3ILCT</td>
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<tr>
<td></td>
<td>192→188 (14%)</td>
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<td>194→188 (9%)</td>
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<td>4</td>
<td>189→187 (11%)</td>
<td>2.3017</td>
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<td>195→187 (12%)</td>
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<td>192→188 (48%)</td>
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