Supporting Information for:

Optical and relaxometric properties of monometallic (Eu$^{III}$, Tb$^{III}$, Gd$^{III}$) and heterobimetallic (Re$^{I}$/Gd$^{III}$) systems based on a functionalized bipyridine-containing acyclic ligand

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**Figure S3**: $^1$H NMR (300 MHz; CDCl$_3$) spectra of compounds 9 and 10.

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**Figure S6**: HPLC-UV chromatogram and ES$^+$/HRMS spectrum of Gd-BPMNTA complex (HPLC conditions are provided in the experimental part).

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**Figure S9**: Plot of emission intensity of the $^5$D$_0$→$^7$F$_2$ transition (617 nm) of Eu-BPMNTA complex (1 µM) vs. time in the presence of 1000 molar equivalents of EDTA in Tris buffer (pH 7.4).

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**Figure S15**: Temperature (278 – 318 K) dependence of the proton longitudinal relaxivity, $r_1$, of Gd-BPMNTA complex and dinuclear complex 13 in water at 20 MHz.

**Table S1**: Parameters obtained from the theoretical fitting of the O-17 data of dinuclear Re/Gd complex 13 in water at 11.75 T.

**Table S2**: Relaxivity values at 20 and 60 MHz (T = 310 K) and parameters obtained from the theoretical fitting of the proton NMRD data in water at 310 K of dinuclear Re/Gd complex 13.
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Figure S5: $^1$H NMR (400 MHz, D$_2$O) and ES$^+$/HRMS spectra of compound 12.
Figure S6: HPLC-UV chromatogram and ES'/HRMS spectrum of Gd-BPMNTA complex (HPLC conditions are provided in the experimental part).
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Figure S12: Absorption (left) and emission (right) spectra of compound 9 in CH$_3$CN.

Figure S13: Absorption (left) and emission (right) spectra of compound 10 in CH$_3$CN.
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Table S1: Parameters obtained from the theoretical fitting of the O-17 data of dinuclear Re/Gd complex 13 in water at 11.75 T.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
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<tbody>
<tr>
<td>$\tau_M^{310K}$ [ns]</td>
<td>9.0 ± 3.0</td>
</tr>
<tr>
<td>$\Delta H^\circ$ [kJ mol$^{-1}$]</td>
<td>55.5 ± 0.7</td>
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<tr>
<td>$\Delta S^\circ$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>87.9 ± 0.6</td>
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<tr>
<td>$A/\hbar$ [$10^6$ rad s$^{-1}$]</td>
<td>-3.9 ± 0.3</td>
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<tr>
<td>$B$ [$10^{20}$ s$^{-2}$]</td>
<td>4.71 ± 0.85</td>
</tr>
<tr>
<td>$\tau_v^{298K}$ [ps]</td>
<td>1.35 ± 0.3</td>
</tr>
<tr>
<td>$E_v$ [kJ mol$^{-1}$]</td>
<td>4.95 ± 3.5</td>
</tr>
</tbody>
</table>

Table S2: Relaxivity values at 20 and 60 MHz (T = 310 K) and parameters obtained from the theoretical fitting of the proton NMRD data in water at 310 K of dinuclear Re/Gd complex 13.

In the fitting procedure using the IS and OS model, some parameters were fixed: $q = 1$, $\tau_M = 9$ ns, $r_{GdH} = 0.31$ nm, $d = 0.36$ nm and $D = 2.93 \times 10^{-9}$ m$^2$ s$^{-1}$.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_M^{310K}$ [ns]</td>
<td>9</td>
</tr>
<tr>
<td>$\tau_R^{310K}$ [ps]</td>
<td>138 ± 3.3</td>
</tr>
<tr>
<td>$\tau_{SO}^{310K}$ [ps]</td>
<td>87.6 ± 1.4</td>
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<tr>
<td>$\tau_v^{310K}$ [ps]</td>
<td>25.6 ± 1.5</td>
</tr>
<tr>
<td>$r_1$ (mM$^{-1}$ s$^{-1}$) at 20 MHz</td>
<td>6.6</td>
</tr>
<tr>
<td>$r_1$ (mM$^{-1}$ s$^{-1}$) at 60 MHz</td>
<td>6.0</td>
</tr>
</tbody>
</table>

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