Supplementary information

Photophysical characteristic of imaging agents.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max,abs}}$(nm) (assignment)</th>
<th>$\lambda_{\text{max,em}}$(assignment) (nm)</th>
</tr>
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<tbody>
<tr>
<td>2</td>
<td>318 (IL) 365 (MLCT)</td>
<td>556 (MLCT)</td>
</tr>
<tr>
<td>8</td>
<td>318 (IL) 360 (MLCT)</td>
<td>554 (MLCT)</td>
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<td>9</td>
<td>316 (IL) 355 (MLCT)</td>
<td>554 (MLCT)</td>
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<td>10</td>
<td>319 (IL) 358 (MLCT)</td>
<td>552 (MLCT)</td>
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<td>14</td>
<td>313 (IL) 389 (MLCT)</td>
<td>553 (MLCT)</td>
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<td>15</td>
<td>313 (IL) 376 (MLCT)</td>
<td>539 (MLCT)</td>
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<td>285 (IL) 375 (MLCT)</td>
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<td>282 (IL) 378 (MLCT)</td>
<td>563 (MLCT)</td>
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<td>336 (IL) 393 (MLCT)</td>
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<td>29</td>
<td>314 (IL) 358 (MLCT)</td>
<td>551 (MLCT)</td>
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</tbody>
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X ray crystallography.
Crystal data for 15:
C$_{26}$H$_{34}$F$_{3}$N$_{4}$O$_{7}$ReS, $M = 779.75$, $0.20 \times 0.20 \times 0.20$ mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.1380(3)$, $b = 12.1560(3)$, $c = 19.4130(5)$ Å, $\beta = 105.8630(10)$°, $V = 2755.30(12)$ Å$^3$, $Z = 4$, $D_c = 1.880$ g/cm$^3$, $F_{000} = 1528$, MoK$\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 293(2)$K, $2\theta_{\text{max}} = 61.0$°, 11446 reflections collected, 7278 unique ($R_{\text{int}} = 0.0300$). Final $GooF = 1.071$, $R1 = 0.0373$, $wR2 = 0.0698$, $R$ indices based on 6007 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 379 parameters, 0 restraints. $L_p$ and absorption corrections applied, $\mu = 4.559$ mm$^{-1}$.

Molecular structure of 15 with atom labelling

Selected bond lengths and angles for 15

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Bond angle (°)</th>
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</thead>
<tbody>
<tr>
<td>Re1-C23</td>
<td>1.915(4)</td>
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<tr>
<td>Re1-C24</td>
<td>1.930(4)</td>
<td></td>
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</tbody>
</table>
Re1-C25 1.928(4)
Re1-N1 2.161(3)
Re1-N2 2.172(3)
Re1-N3 2.220(3)
N1-Re1-N2 74.83(12)
N1-Re1-N3 83.21(12)
N2-Re1-N3 84.21(12)
C23-Re1-N2 96.04(14)
C23-Re1-C24 89.79(16)
C25-Re1-N3 92.55(14)

NMR spectra of complexes 14, 15.

$^1$H NMR complex 14

$^{13}$C NMR complex 14
$^1\text{H NMR complex 15}$

$^{13}\text{C NMR complex 14}$
Quantitative cell measurements
To determine toxicity of rhenium complexes anionic (27) and cationic (9) complexes were incubated with MCF-7 cells as in general experimental (30 min at 4°C, final concentration 100 µg. ml⁻¹) and cell viability / membrane integrity investigated using trypan blue and propidium iodide respectively. After incubation, cells were stained with trypan blue (Sigma, final concentration 0.2%) for 5 min and with propidium iodide (Sigma, final concentration 2 µg. ml⁻¹) for 15 min, both at room temperature. Percentage cell viability was calculated using a haemocytometer (Improved Neubauer) according to the following equation:

\[
\text{% viability} = \frac{\text{number of live cells}}{\text{total number of cells}} \times 100
\]

Bright field microscopy was used to visualise trypan blue-stained cells, whilst fluorescence microscopy was used to visualise propidium iodide-stained cells.

Cell viability results
Table 1. MCF-7 cell viability after 30 min incubation with and without rhenium complexes at 4°C.

<table>
<thead>
<tr>
<th>complex</th>
<th>Trypan blue</th>
<th>Propidium iodide</th>
<th>% viability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Live (cells/ml)</td>
<td>Dead (cells/ml)</td>
<td>Total (cells/ml)</td>
</tr>
<tr>
<td>9</td>
<td>6 x 10⁴</td>
<td>2.2 x 10³</td>
<td>2.6 x 10⁵</td>
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<tr>
<td>23</td>
<td>7.6 x 10⁵</td>
<td>0</td>
<td>7.6 x 10⁷</td>
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<tr>
<td>control</td>
<td>6.4 x 10⁵</td>
<td>4 x 10³</td>
<td>6.8 x 10⁵</td>
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