Supplementary information

Photophysical characteristic of imaging agents.

| Complex | $\lambda \max_{abs}(nm)$ (assignment) | $\lambda \max_{em}(assignment) (nm)$ | | |
|---------|---------------------------------------|--------------------------------------|--|--|
| 2 | 318 (IL) 365 (¹ MLCT) | 556 (³ MLCT) | | |
| 8 | 318 (IL) 360 (¹ MLCT) | 554 (³ MLCT) | | |
| 9 | 316 (IL) 355 (¹ MLCT) | 554 (³ MLCT) | | |
| 10 | 319 (IL) 358 (¹ MLCT) | 552 (³ MLCT) | | |
| 14 | 313 (IL) 389 (¹ MLCT) | 553 (³ MLCT) | | |
| 15 | 313 (IL) 376 (¹ MLCT) | 539 (³ MLCT) | | |
| 22 | 285 (IL) 375(¹ MLCT) | 566 (³ MLCT) | | |
| 23 | 282 (IL) 378(¹ MLCT) | 563 (³ MLCT) | | |
| 28 | 336 (IL) 393 (¹ MLCT) | 558 (³ MLCT) | | |
| 29 | 314 (IL) 358 (¹ MLCT) | 551 (³ MLCT) | | |

X ray crystallography.

Crystal data for 15:

C₂₆H₂₄F₃N₄O₇ReS, *M* = 779.75, 0.20 × 0.20 × 0.20 mm³, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 12.1380(3), *b* = 12.1560(3), *c* = 19.4130(5) Å, β = 105.8630(10)°, *V* = 2755.30(12) Å³, *Z* = 4, *D*_c = 1.880 g/cm³, *F*₀₀₀ = 1528, MoKα radiation, λ = 0.71073 Å, *T* = 293(2)K, 2 θ_{max} = 61.0°, 11446 reflections collected, 7278 unique (R_{int} = 0.0300). Final *GooF* = 1.071, *RI* = 0.0373, *wR2* = 0.0698, *R* indices based on 6007 reflections with I >2sigma(I) (refinement on *F*²), 379 parameters, 0 restraints. Lp and absorption corrections applied, μ = 4.559 mm⁻¹.

Molecular structure of 15 with atom labelling



Selected bond lengths and angles for 15 Bond

Bond length (Á)

Bond angle (°)

| Re1-C23 | 1.915(4) |
|---------|----------|
| Re1-C24 | 1.930(4) |

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| 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.



2



¹H NMR complex **15**



¹³C 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 μ g. ml⁻¹) and cell viability / membrane integrity investigated using trypan blue and propidium iodide respectivley. After incubation, cells were stained with trypan blue (Sigma, final concentration 0.2%) for 5 min and with propidium iodide (Sigma, final concentration 2 μ g. ml⁻¹) for 15 min, both at room temperature. Percentage cell viability was calculated using a haemocytometer (Improved Neubauer) according to the following equation:

% viability = <u>number of live cells</u> x 100

total number of cells

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.

| | Trypan blue | | | Propidium iodide | | | | |
|---------|-------------------|-------------------|-------------------|------------------|-----------------------|-------------------|-----------------------|------------|
| complex | Live | Dead | Total | % | Impermeant | Permeant | Total | % |
| | (cells/ml) | (cells/ml) | (cells/ml) | viability | (cells/ml) | (cells/ml) | (cells/ml) | impermeant |
| 9 | $6 \ge 10^4$ | 2.2×10^5 | 2.6×10^5 | 23 | $1.8 \ge 10^5$ | 2.2×10^5 | $4 \ge 10^5$ | 45 |
| 23 | $7.6 \ge 10^5$ | 0 | $7.6 \ge 10^5$ | 100 | 8.6 x 10 ⁵ | $1 \ge 10^4$ | 8.7 x 10 ⁵ | 99 |
| control | 6.4×10^5 | 4×10^4 | 6.8×10^5 | 94 | 4.2×10^5 | 3×10^4 | 4.5×10^5 | 93 |