Supplementary Material (ESI) for Chemical Communications

A. Labeling of L1-L4 with $^{99m}Tc(CO)_3^+$.

B. Absorption and Fluorescence Studies.

C. X-ray Structure of L2.

Supplementary Material (ESI) for Chemical Communications

A. Labeling of L1-L4 with $^{99m}Tc(CO)_3^+$. Labeling was accomplished in two steps using the readily prepared IsoLink™ kits (Mallinckrodt) to generate the $[^{99m}Tc(CO)_3(H_2O)_3]^+$ precursor (100μl), which was introduced to a methanol solution (0.5 mL) of the appropriate ligand (0.25 mg). The sealed vial was heated at 90° C for 20 minutes. After cooling, the reaction was checked for purity via HPLC using a Vydac C18 column (4.6mm x 25cm x 5μm) and methanol as eluant. The purity, analyzed using C18 HPLC, was >95% radiochemical purity. The labeling yields were all > 85%, and achievable at levels as low as 1 μg / ml.

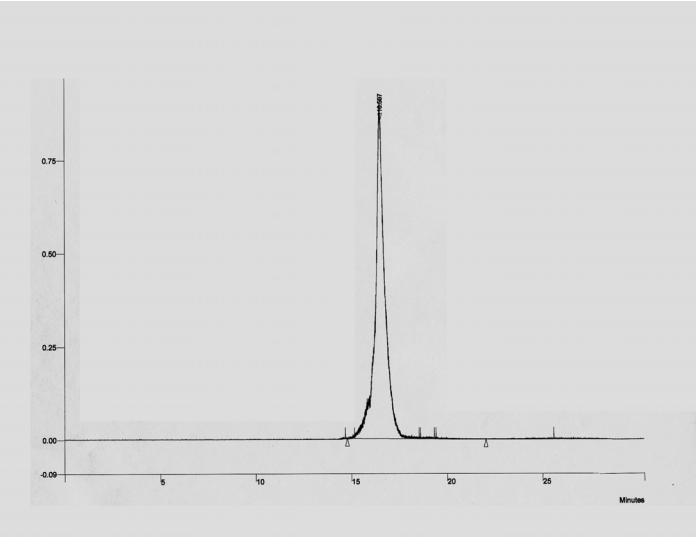

Figure S1. Radiochromatogram of the crude reaction product, $[^{99m}Tc(CO)_3\mathbf{L3}]^+$.

B. Absorption and Fluorescence Studies

Absorbance Spectra and Extinction Coefficient

All absorbance measurements were taken using a Varian model CARY -50 Bio UV-Visible spectrophotometer. **Figure 3** shows the absorption spectrum of $[Re(CO)_3\mathbf{L4}]Br$ in ethylene glycol. Absorption maxima are seen near 321 and 414 nm. The extinction coefficients at 321 and 414 nm are 17729 and 1215 mol^{-1} cm^{-1} respectively.

Supplementary Material (ESI) for Chemical Communications

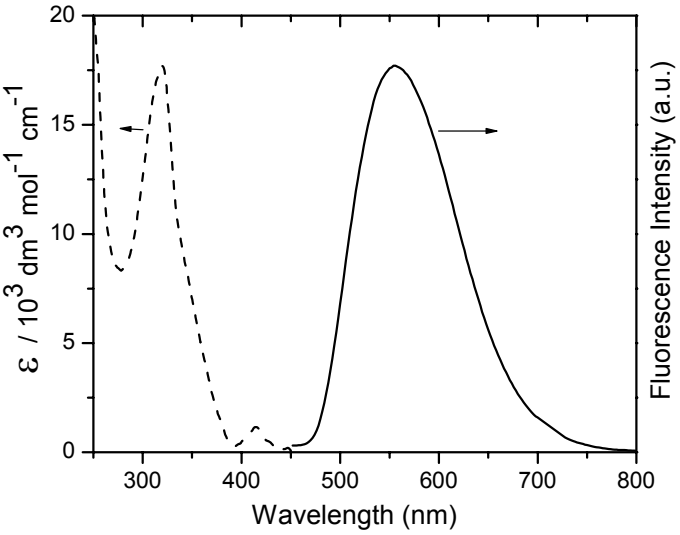

Figure S2: Absorbance spectra of [Re(CO)$_3$**L4**]Br in ethylene glycol at room temperature.

Fluorescence Spectroscopy

Steady state fluorescence measurements were recorded with a PTI fluorimeter. Emission was monitored from 400 to 800 nm with an excitation wavelength of 321 nm in 1 nm increments with an integration time of 0.5 sec. Samples of [Re(CO)$_3$**L4**]Br were prepared in ethylene glycol (1×10^{-5} M).

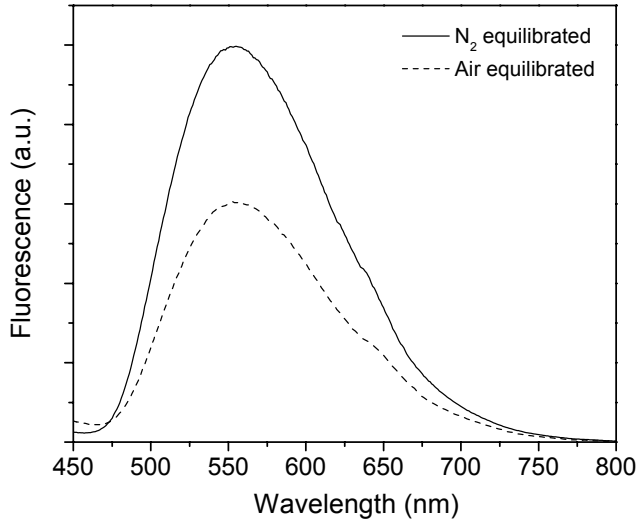

Figure S3: Emission spectra of [Re(CO)$_3$**L4**]Br in either air equilibrated or nitrogen equilibrated ethylene glycol.

Emission spectrum of the rhenium probe shows a maximum at 555 nm. As shown in **Figure 4** the equilibration of the samples with a nitrogen gas atmosphere drastically increases the quantum yield of the rhenium probe. Using a standard reference material, in this case ruthenium bipyridine, a quantitative value of quantum yield can be calculated by using the following equation where Q and Q_R are the quantum yields, I and I_R are the integrated emission intensities, OD and OD_R are the optical densities, and n and n_R are the refractive indexes of the solvents of the unknown and reference materials (subscript R indicating reference).

$$Q = Q_R \frac{I}{I_R}\frac{OD_R}{OD}\frac{n^2}{n_R^2}$$

Table 1 gives the values measured and resulting quantum yields for [Re(CO)$_3$**L4**]Br

Table 1: Quantum Yield Data

	Rhenium in Ethylene Glycol (Air Equil.)	Rhenium in Ethylene Glycol (N_2 Equil.)
Emission Intensity‡	1.99 x10^8	3.23 x10^8

Refractive index	1.43	1.43
Quantum Yield	0.0091	0.015

‡Emission was measured between 400 and 800 nm with an excitation of 321 nm in 1 nm increments with an integration time of 0.5 sec. Excitation bandpass was 1 nm and emission bandpass was 2 nm.

Time resolved fluorescence decays were recorded using a PTI fluorimeter. The 321 nm output of the flash lamp was the excitation wavelength for emission lifetime measurements. The emission of the $[Re(CO)_3$**L4**$]Br$ was monitored at 555 nm. The fluorescence intensity decay was fit to a single exponential function: $I = \alpha \exp(-t/\tau)$, where τ is the fluorescence lifetime and α is the preexponential factor. In ethylene glycol under nitrogen atmosphere the fluorescence lifetime of $[Re(CO)_3$**L4**$]Br$ was measured to be 16.7 μsec.

C. X-ray Structure of L2.

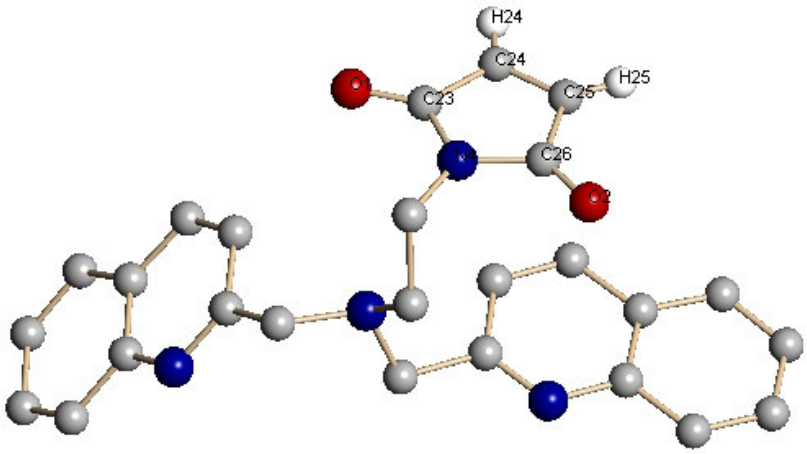

Figure S4. The structure of **L2**.