Electronic Supporting Information

Controlling energy transfer in ytterbium complexes: oxygen dependent lanthanide luminescence and singlet oxygen formation

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General Procedures

Synthesis and characterisations

Commercially available solvents and chemicals were used without further purification unless otherwise stated. Cyclen was purchased from Chematech, lanthanide salts were purchased from Strem Chemicals while solvents were purchased from Sigma Aldrich. NMR spectra were recorded on a Bruker AVIII 400 or AVIII 500 spectrometer as specified. All chemical shift (δ) values are given in parts per million. Low-resolution mass spectra were recorded on a Waters Micromass LCT Premier XE spectrometer or on a Waters MALDI Micro MX system. Accurate masses were determined to four decimal places using Bruker μ TOF and Micromass GCT spectrometers at the Chemistry Research Laboratory of the University of Oxford. Yb.3 and Yb.4 were prepared as previously reported and characterised by ¹H-NMR and mass-spectrometry.^[1]

Details of photophysical studies

UV-visible spectroscopy was performed using a PG instruments T60 UV/VIS spectrophotometer. In the case of lifetimes luminescence measurements and emission spectra of Yb(III) complexes and singlet oxygen, the sample was excited using a pulsed nitrogen laser (PTI-3301-337nm). Light emitted at right angles to the excitation beam was focused onto the slits of the monochromator (PTI120), which was used to select the appropriate wavelength (980 and 1270 nm). The growth and decay of the luminescence at selected wavelengths was detected using a germanium photodiode (Edinburgh Instruments, EI-P) and recorded using a digital oscilloscope (Tektronix TDS220) before being transferred to the computer for analysis. Luminescence lifetimes were obtained by iterative deconvolution of the detector response (obtained by using a scatter) with exponential components for growth and decay of the metal centred luminescence For the measurement of growth and decay spectra with nanosecond resolution a Hamamatsu R5509-42 NIR PMT InGaAs detector cooled to -80° C was used instead of the germanium photodiode. Given the faster detector response, deconvolution of the detector response from the signal was not needed in this case. Solutions were degassed by 5 successive freeze pump thaw cycles. A Mettler-Toledo dissolved Oxygen probe was used to record dissolved oxygen concentration.

General procedure for the preparation of Ugi products

The lanthanide complex and Benzaldehyde were dissolved in minimum EtOH, and stirred with 100 mg of Na_2SO_4 for 6 hours. BnNC and 1-Pyrene-carboxylic acid were added and the reaction mixture was left to stir at room temperature for 72 hours. The solution was filtered, and the solvents removed under reduced pressure. The resultant solid was washed with Et₂O (5x20 ml) before being redissolved in minimum MeOH and precipitated with Et₂O. The solvents were removed under reduced pressure, and the resultant solid was purified by dialysis in H₂O to give the product upon removal of solvent under reduced pressure.

Yb.1



This complex was formed by following the procedure described for the Ugi reaction, using 100 mg of **Yb.3** (0.162 mmol), 0.018 ml of Benzaldehyde (0.1782 mmol), 0.022 ml of BnNC (0.1782 mmol) and 44 mg of 1-Pyrene-carboxylic acid (0.1782 mmol). (37 mg, 21%). ¹H NMR (400 MHz, D₂O) δ 122.15, 116.75, 116.08, 32.14, 26.22, 23.20, 19.59, 16.94, 16.37, 14.76, 14.26, -1.42, -2.00, -19.97, -23.96, -26.41, -27.95, -30.42, -37.25, -40.08, -43.37, -54.33, -56.38, -72.02, -74.51, -76.31. Only peaks outside the 0-10 ppm range are reported. MALDI MS: m/z 1092.14 (M+Na⁺).

Yb.2



This complex was prepared by an analogous procedure to the previous Ugi reactions, using 0.015 ml of Propylamine (0.1804 mmol), 40.5 mg of Pyrenecarboxaldehyde (0.176 mmmol), 100 mg of **Yb.4** (0.160 mmol) and 0.021 ml of BnNC (0.176 mmol). (134 mg, 82.9%). ¹H NMR (400 MHz, D₂O) δ 126.96, 122.36, 115.66, 114.90, 31.70, 26.51, 23.11, 20.15, 16.62, 15.55, 14.58, 14.02, 9.75, 7.39, 7.29, -18.50, -23.79, -26.10, -29.77, -39.31, -43.61, -53.76, -57.40, -71.42, -73.04, -73.56, -74.72. Only peaks outside the 0-5 ppm range are reported. MALDI MS (MeOH): m/z 1021.02 (M+H⁺).

NMR spectra

The spectra below all show dramatic pseudocontact shifts as a consequence of the presence of the paramagnetic ytterbium ion. In these broken symmetry systems the chemical shifts are approximated by the geometrical coordinates of the protons involved according to the equation:²

$$\sigma_{\rm PCS} = \frac{1}{12\pi} \left[\Delta \chi_{\rm ax} \frac{2z^2 - x^2 - y^2}{r^5} + \frac{3}{2} \Delta \chi_{\rm rh} \frac{x^2 - y^2}{r^5} \right]$$

In the absence of crystal structures and detailed information about the local crystal field and magnetic anisotropy, it is sufficient to assign these spectra by precedent. In all cases it is clear that the square antiprismatic geometry dominates at the lanthanide centre.^[2]







Figure S 3. ¹H-NMR spectrum of Yb.1 recorded in CD₃OD, T = 295K.



Figure S 4. ¹H-NMR spectrum of Yb.2 recorded in CD_3OD , T = 295K.

Photophysics



Figure S 5. UV-Vis spectrum of Yb.1 recorded in methanol, T = 295K.



Figure S 6. UV-Vis spectrum of Yb.2 recorded in methanol, T = 295K.



Figure S 7. Emission spectrum of Yb.2 in aerated and degassed solutions in methanol, T = 295 K, λ_{ex} = 337 nm, delay time = 1 us.



Figure S 8. Emission decay of a degassed solution of Yb.2 at 980 nm in methanol. T = 295 K, λ_{ex} = 337 nm. The lifetime decay was fitted by deconvolution with the detector response to give a lifetime for ${}^{2}F_{5/2}$ - ${}^{2}F_{7/2}$ of 4.2 µs.



Figure S 9. Singlet oxygen emission detected at 1270 nm of an air equilibrated solution of Yb.2 in methanol. T = 295 K, λ_{ex} = 337 nm. The lifetime decay was fitted by deconvolution with the detector response to give a lifetime for ${}^{1}O_{2}$ of 9.9 µs.



Figure S 10. Singlet oxygen emission detected at 1270 nm of an air equilibrated solution of Yb.1 in methanol. T = 295 K, λ_{ex} = 337 nm. The lifetime decay was fitted by deconvolution with the detector response to give a lifetime for ${}^{1}O_{2}$ of 9.7 µs.



Figure S 11. Emission decay of Yb.1 in an aerated and degassed solution of methanol upon excitation at 337 nm. T = 295 K.



Figure S 12. Emission decay of Yb.1 in an aerated and degassed solution of methanol upon excitation at 337 nm. T = 295 K.

References

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