

Stereoelectronic Control of Photophysics: Red and Yellow Axial and Equatorial Anomers of a Rhenium-Quinoline Complex

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General Considerations

Synthesis

All starting materials, reagents and solvents were purchased from commercial suppliers and used as supplied unless otherwise stated. $\text{Re}(\text{CO})_5\text{Br}^1$ and N,N' -bis(2-quinolinylmethyl)-1,2-ethylenediamine² were prepared according to literature methods.

Measurements

^1H -NMR and ^{13}C -NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker Avance III 400 and referenced to residual solvent peaks. Chemical shifts are reported in ppm, and coupling constants in Hz. IR spectra were recorded on an Agilent Technologies Cary 630 FTIR Spectrometer as solids and are reported in wavenumbers (cm^{-1}). UV-vis spectra were recorded on an Agilent Technologies Cary 60. Steady state emission and excitation spectra were recorded on an Agilent Technologies Cary Eclipse. Time-resolved spectra were recorded on a PicoQuant FluoTime 300 exciting with an LDH-P-C-375 and decays were analysed with the program FluoFit. Melting points are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre in Swansea on a Thermo Scientific LTQ Orbitrap XL. Elemental analyses were measured by Mr Stephen Boyer at London Metropolitan University.

Synthesis of compound 1

Quinoline 2-carboxaldehyde (3.14 g, 20 mmol) was added, in portions, to a stirred solution of 2,2-dimethyl-1,3-propane diamine (1.24 mL, 10 mmol) in ethanol (60 mL). The resulting orange/brown solution was heated at reflux for 3 h. After allowing the solution to cool to room temperature, sodium borohydride (1 x 1 g pellet, 26.5 mmol), was added with stirring, followed by more ethanol (40 mL). The reaction mixture was heated at reflux for a further 2 h before allowing to cool to room temperature. Water (50 mL) was added slowly to the reaction mixture, which was then extracted with dichloromethane (3 x 20 mL). The combined organic extracts were washed with brine (20 mL), dried (MgSO_4) and the solvents removed to leave a brown residue. Recrystallization from the minimum volume of hot dichloromethane gave the title compound as a colourless crystalline solid (2.34 g, 61%). ^1H NMR (400 MHz, CDCl_3) δ ppm: 8.17 (1H, d, $^3J_{\text{HH}} = 8.4$ Hz, ArH^4), 8.15 (1H, m, ArH^8), 8.09 (1H, d, $^3J_{\text{HH}} = 8.4$ Hz, ArH^4), 7.96 (1H, m, ArH^8), 7.84 (1H, d, $^3J_{\text{HH}} = 8.4$ Hz, ArH^3), 7.77 (2H, m, ArH^5), 7.75 (1H, d, $^3J_{\text{HH}} = 8.4$ Hz, ArH^3), 7.71 (1H, ddd, $^3J_{\text{HH}} = 8.6$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, ArH^7), 7.65 (1H, ddd, $^3J_{\text{HH}} = 8.6$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, ArH^7), 7.52 (1H, ddd, $^3J_{\text{HH}} = 8.6$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, ArH^6), 7.48 (1H, ddd, $^3J_{\text{HH}} = 8.6$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, ArH^6), 4.49 (1H, s, CH), 3.80 (1H, d, $^2J_{\text{HH}} = 14.6$ Hz, CH_2), 3.44 (1H, d, $^2J_{\text{HH}} = 14.6$ Hz, CH_2), 2.81 (1H, dd, $^2J_{\text{HH}} = 13.2$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, CH_2), 2.71 (1H, d, $^2J_{\text{HH}} = 13.2$ Hz, CH_2), 2.65 (1H, dd, $^2J_{\text{HH}} = 11.6$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, CH_2), 2.26 (1H, d, $^2J_{\text{HH}} = 11.6$ Hz, CH_2), 1.99 (1H, br s, NH), 1.31 (3H,

s, CH₃), 0.82 (3H, s, CH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm: 161.0 (ArC), 160.3 (ArC), 147.9 (ArC), 147.4 (ArC), 137.1 (ArCH), 136.2 (ArCH), 129.5 (2 x ArCH), 129.2 (ArCH), 128.8 (ArCH), 128.0 (ArC), 127.45 (ArCH), 127.43 (ArCH), 127.3 (ArC), 126.5 (ArCH), 125.9 (ArCH), 120.5 (ArCH), 119.4 (ArCH), 82.7 (CH), 64.5 (CH₂), 60.4 (CH₂), 57.2 (CH₂), 30.9 (C(CH₃)₂), 26.2 (CH₃), 23.7 (CH₃); MS, *m/z* (ES): 383 [M]⁺; IR, ν cm⁻¹: 3293 (w N–H stretch), 3057 (w), 2959(w), 2805 (w), 1600, 1500, 1485, 1472, 1424, 1135, 1084; UV-Vis (CHCl₃, λ_{max} nm (ε, M⁻¹ cm⁻¹)): 273 (12560), 290 (sh, 9560), 296 (sh, 7950), 303 (7680), 310 (sh, 5860), 317 (7950); Anal. Calcd for C₂₅H₂₆N₄: C, 78.50; H, 6.85; N, 14.65 %. Found: C, 78.34, H, 6.98, N, 14.53 %.

Synthesis of Rhenium Compounds **2** and **3**

Re(CO)₅Br (0.128 g, 0.316 mmol) was heated to 100 °C in toluene (10 mL) with stirring. When the solids had dissolved, **1** (0.121 g, 0.316 mmol) was added as a solid in one portion. The reaction mixture was left to stir at 100 °C for 20 min, during which time a yellow precipitate formed. Hot filtration of the reaction mixture afforded **2** (0.045 g, 19 %) as a yellow powder. Upon cooling, red crystals formed in the filtrate. These were recovered by filtration to give **3** (0.151 g, 65%) as a red crystalline solid.

Compound **2**: ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.87 (1H, d, ³J_{HH} = 8.8 Hz, ArH⁸), 8.38 (1H, d, ³J_{HH} = 8.4 Hz, ArH⁴), 8.19 (1H, d, ³J_{HH} = 8.4 Hz, ArH⁴), 8.17 (1H, d, ³J_{HH} = 7.6 Hz, ArH⁵), 8.10 (1H, d, ³J_{HH} = 8.4 Hz, ArH³), 7.94 (2H, m, ArH^{7,8}), 7.82 (1H, d, ³J_{HH} = 8.0 Hz, ArH⁵), 7.72 (2H, m, ArH^{5,6}), 7.55 (1H, m, ArH⁷), 7.49 (1H, d, ³J_{HH} = 8.4 Hz, ArH³), 7.01 (1H, m, CH), 5.10 (1H, br d, ³J_{HH} = 13.0 Hz, NH), 4.74 (1H, d, ²J_{HH} = 15.2 Hz, CH₂), 4.68 (1H, d, ²J_{HH} = 15.2 Hz, CH₂), 3.27 (1H, d, ²J_{HH} = 13.7 Hz, CH₂), 2.91 (1H, d, ²J_{HH} = 14.4 Hz, CH₂), 2.87 (1H, d, ²J_{HH} = 14.4 Hz, CH₂), 2.67 (1H, dd, ²J_{HH} = 13.7 Hz, ³J_{HH} = 13.0 Hz, CH₂), 1.27 (3H, s, CH₃), 0.69 (3H, s, CH₃); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ ppm: 195.2 (C≡O), 195.1 (C≡O), 191.4 (C≡O), 161.5 (ArC), 158.6 (ArC), 148.0 (ArC), 147.6 (ArC), 140.5 (ArCH), 137.2 (ArCH), 132.3 (ArCH), 130.4 (ArCH), 130.0 (ArCH), 129.2 (ArCH), 128.7 (ArCH), 128.7 (ArC), 128.15 (ArCH), 127.6 (ArCH), 127.4 (ArC), 126.7 (ArCH), 121.7 (ArCH), 120.5 (ArCH), 79.3 (CH), 63.9 (CH₂), 62.8 (CH₂), 56.9 (CH₂), 31.4(C(CH₃)₂), 26.1 (CH₃), 23.6 (CH₃); MS, *m/z* (ES): 747 (45%) [M + NH₄]⁺, 733 (65%) [M]⁺, 689 (90%) [M – CO]⁺, 653 (100 %) [M – Br]⁺; IR, ν cm⁻¹: 3175 (m, N–H stretch), 2951 (w), 2925 (w), 2851 (w), 2024 (s, C≡O), 1927 (s, C≡O), 1882 (s, C≡O), 1603, 1510, 1465, 1432, 1372, 1149, 1097; UV-Vis (CHCl₃, λ_{max} nm (ε, M⁻¹ cm⁻¹)): 265 (sh, 13,010), 305 (9700), 320 (9060), 349 (sh, 3400), 449 (sh, 190), 500 (100); Anal. Calcd for C₂₈H₂₉BrN₄O₃Re: C, 45.71; H, 3.97; N, 7.62 %. Found: C, 45.64, H, 3.92, N, 7.56 %.

Compound **3**: ¹H NMR (400 MHz, CDCl₃) δ ppm: 9.01 (1H, d, ³J_{HH} = 8.8 Hz, ArH⁸), 8.24 (1H, d, ³J_{HH} = 8.4 Hz, ArH⁴), 8.23 (1H, d, ³J_{HH} = 8.4 Hz, ArH⁴), 8.05 (1H, d, ³J_{HH} = 8.0 Hz, ArH⁸), 7.94 (1H, ddd, ³J_{HH} = 7.8 Hz, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 1.6 Hz, ArH⁷), 7.88 (1H, m, ArH⁵), 7.83 (1H, dd, ³J_{HH} = 8.0

Hz, $^4J_{\text{HH}} = 1.2$ Hz, ArH⁵), 7.75 (1H, m, ArH⁷), 7.74 (1H, d, $^3J_{\text{HH}} = 8.4$ Hz, ArH³), 7.69 (1H, m, ArH⁶), 7.61 (1H, d, $^3J_{\text{HH}} = 8.4$ Hz, ArH³), 7.59 (1H, m, ArH⁶), 5.55 (1H, d, $^3J_{\text{HH}} = 10.1$ Hz, CH), 4.49 (1H, m, NH), 4.42 (1H, d, $^2J_{\text{HH}} = 15.2$ Hz, CH₂), 3.94 (1H, d, $^2J_{\text{HH}} = 15.2$ Hz, CH₂), 3.75 (1H, dm, $^2J_{\text{HH}} = 13.2$ Hz, CH₂), 3.40 (1H, dd, $^2J_{\text{HH}} = 13.2$ Hz, $^3J_{\text{HH}} = 13.0$ Hz, CH₂), 3.29 (1H, d, $^2J_{\text{HH}} = 14.4$ Hz, CH₂), 3.13 (1H, dd, $^2J_{\text{HH}} = 14.4$ Hz, $^4J_{\text{HH}} = 2.0$ Hz, CH₂), 1.47 (3H, s, CH₃), 0.96 (3H, s, CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) δ ppm: 195.6 (C=O), 195.2 (C=O), 190.4 (C=O), 159.9 (ArC), 158.0 (ArC), 147.9 (ArC), 147.6 (ArC), 140.4 (ArCH), 137.1 (ArCH), 132.2 (ArCH), 130.9 (ArCH), 129.9 (ArCH), 129.1 (ArCH), 128.8 (ArC), 128.6 (ArCH), 128.18 (ArCH), 127.6 (ArCH), 127.3 (ArC), 126.6 (ArCH), 119.7 (ArCH), 119.5 (ArCH), 87.1 (CH), 66.2 (CH₂), 59.8 (CH₂), 53.6 (CH₂), 31.3 (C(CH₃)₂), 27.5 (CH₃), 27.0 (CH₃); MS, m/z (ES): 747 (15%) [M + NH₄]⁺, 733 (100%) [M]⁺, 689 (15%) [M – CO]⁺, 653 (30%) [M – Br]⁺, 383 (50%) [M – Br – 3(CO)]⁺; IR, ν cm⁻¹: 3197 (m, N–H stretch), 2959 (w), 2928 (w), 2910 (w), 2020 (s, C≡O), 1909 (s, C≡O), 1871 (s, C≡O), 1599, 1510, 1462, 1432, 1376, 1302, 1227, 1153, 1115; UV-Vis (CHCl₃, λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 305 (7434), 320 (5155), 335 (3520), 449 (sh, 262), 494 (149), 635 (69); Anal. Calcd for C₂₈H₂₉BrN₄O₃Re.C₇H₈: C, 50.78; H, 4.51; N, 6.77 %. Found: C, 50.66, H, 4.47, N, 6.67 %.

Synthesis of Compound 4

Re(CO)₅Br (0.122 g, 0.30 mmol) was heated to 100 °C in toluene (8 mL) with stirring. When the solids had dissolved, *N,N'*-bis(2-quinolinylmethyl)-1,2-ethylenediamine (0.103 g, 0.30 mmol) was added in toluene (2 mL), *via* a pipette. The reaction mixture was left to stir at 100 °C for 30 min, during which time the reaction mixture turned beige and a pale yellow precipitate formed. Hot filtration of the reaction mixture afforded **4** (0.084 g, 39 %) as an off white powder. The filtrate was also identified as **4**. Crystals suitable for single crystal X-ray diffraction were grown by slow evaporation from a chloroform solution. ^1H NMR (400 MHz, CDCl₃) δ ppm: 8.22 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, ArH), 8.14 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, ArH), 7.84 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, ArH), 7.77 (2H, m, ArH), 7.59 (2H, m, ArH), 7.35 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, ArH), 5.26 (2H, m, NH), 4.81 (2H, m, CH₂), 4.77 (2H, m, CH₂), 3.62 (2H, m, CH₂), 2.89 (2H, m, CH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl₃) δ ppm: 194.3 (C=O), 193.8 (C=O), 192.5 (C=O), 154.7 (ArC), 147.6 (ArC), 137.5 (ArC), 130.2 (ArC), 129.0 (ArC), 128.2 (ArC), 127.6 (ArC), 127.0 (ArC), 119.8 (ArC), 62.3 (CH₂), 51.7 (CH₂); HRMS, m/z (ES): Calcd for C₂₅H₂₃BrN₄O₃Re, 693.0489 [M + H]⁺; Found, 693.0483.

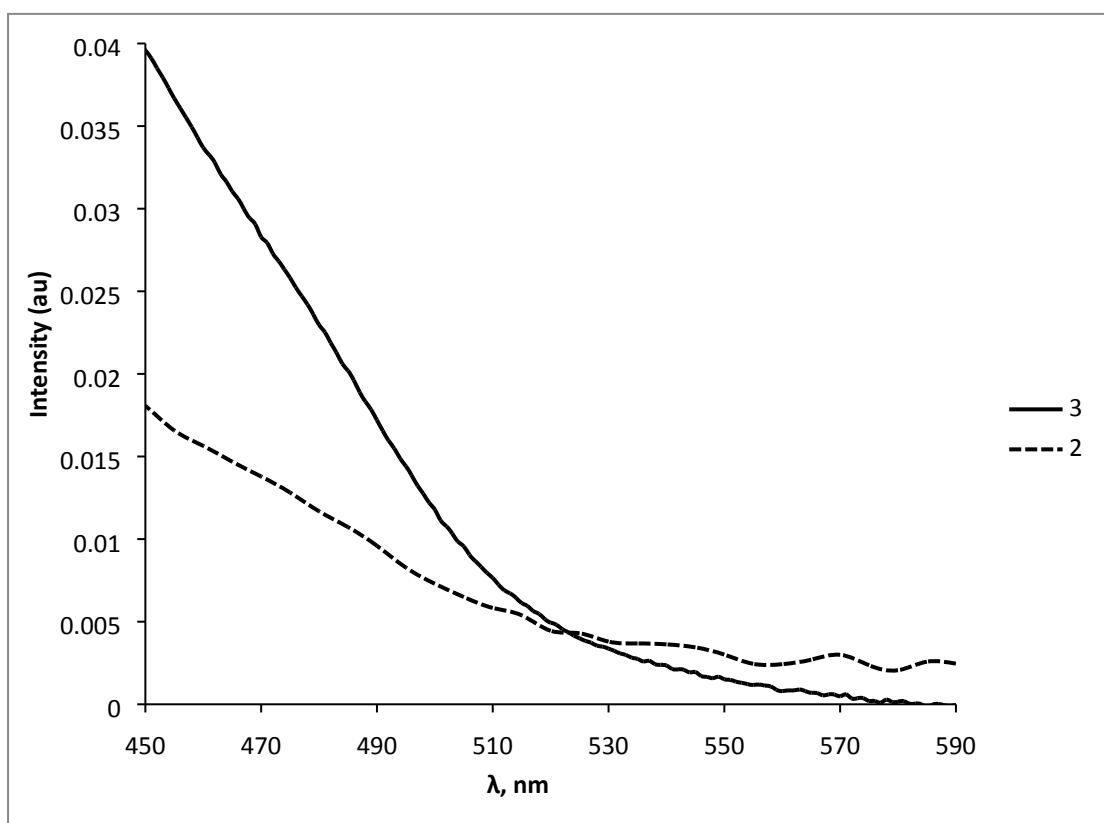
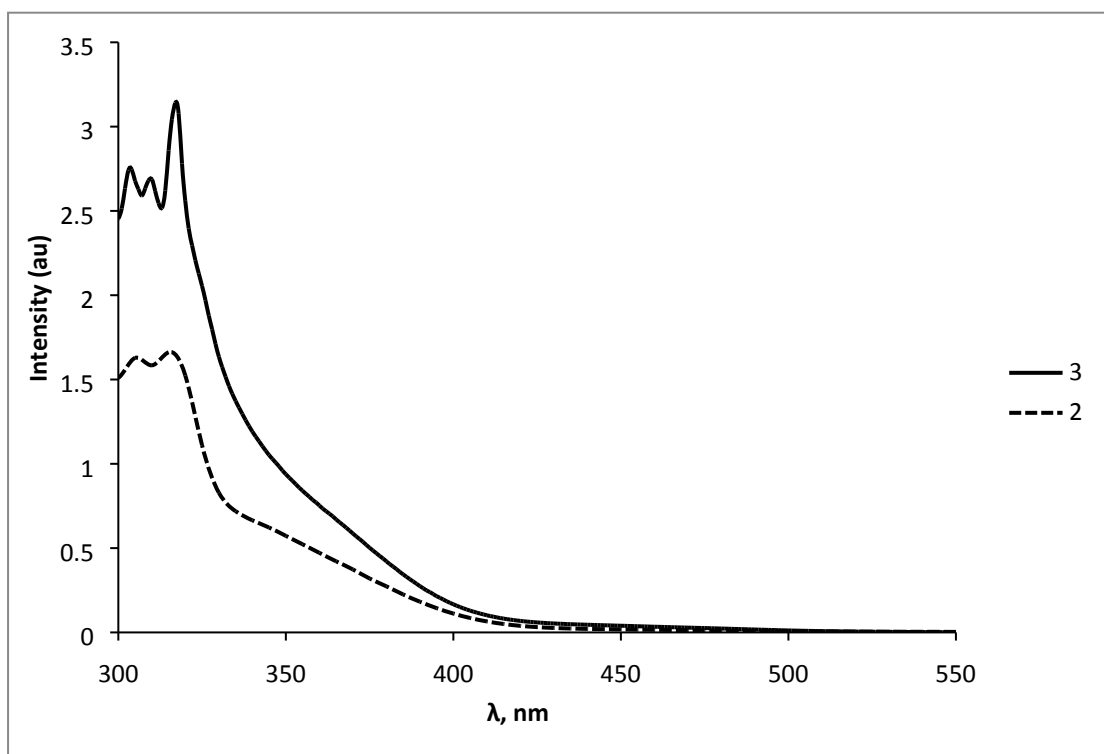


Fig. S1: UV-vis Spectra of 2 and 3

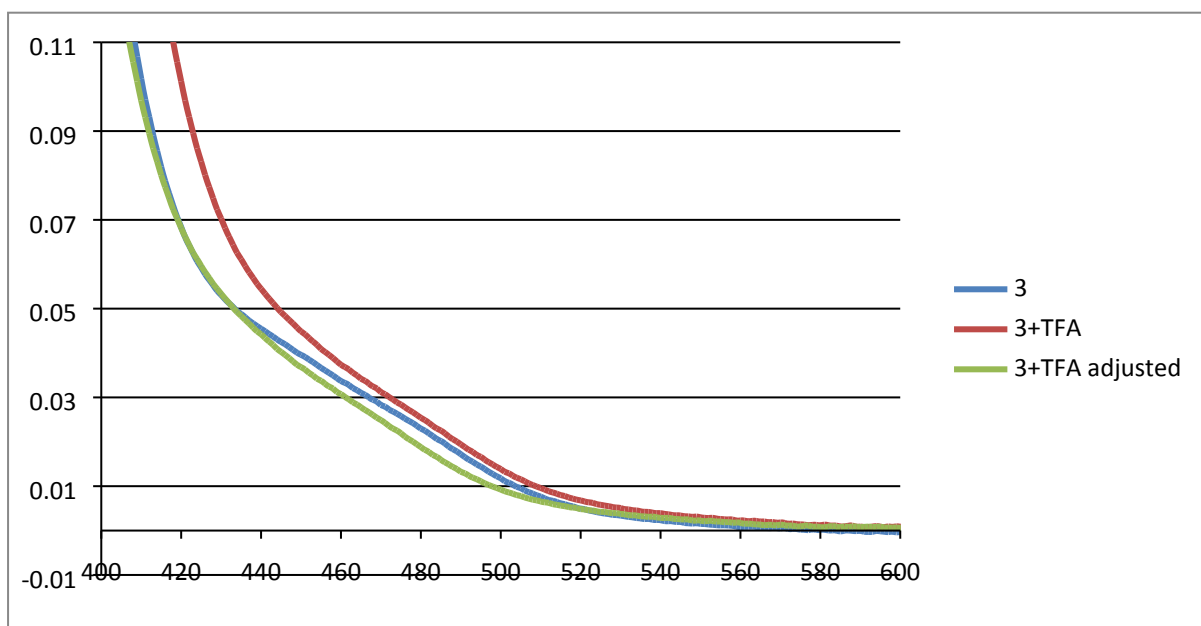


Fig. S2: UV-Vis absorbance spectrum of 3 with addition of TFA (showing red shift) and adjusted to overlap neutral spectrum showing loss of intensity of 450-500nm band.

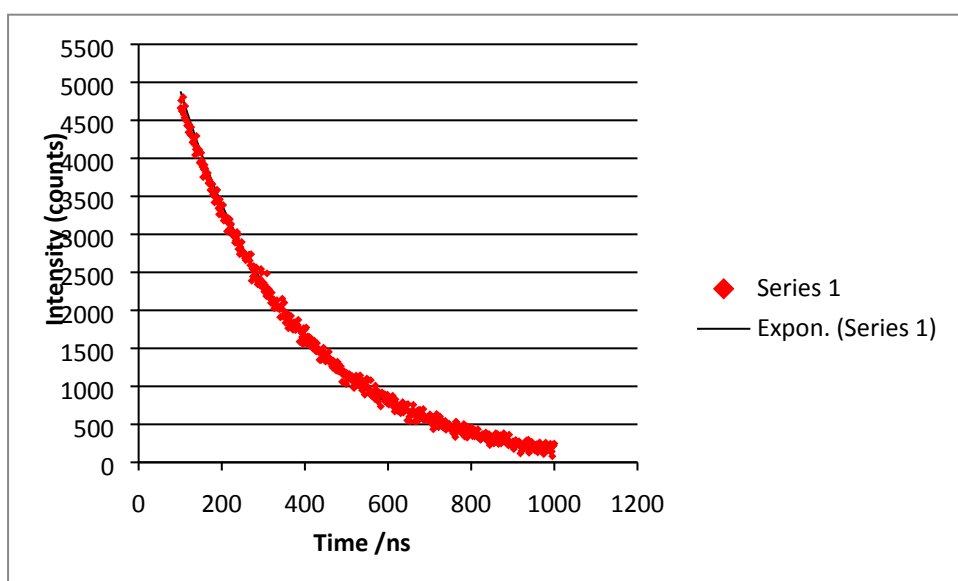


Fig. S3: Decay Plot for Lifetime Calculation for 2

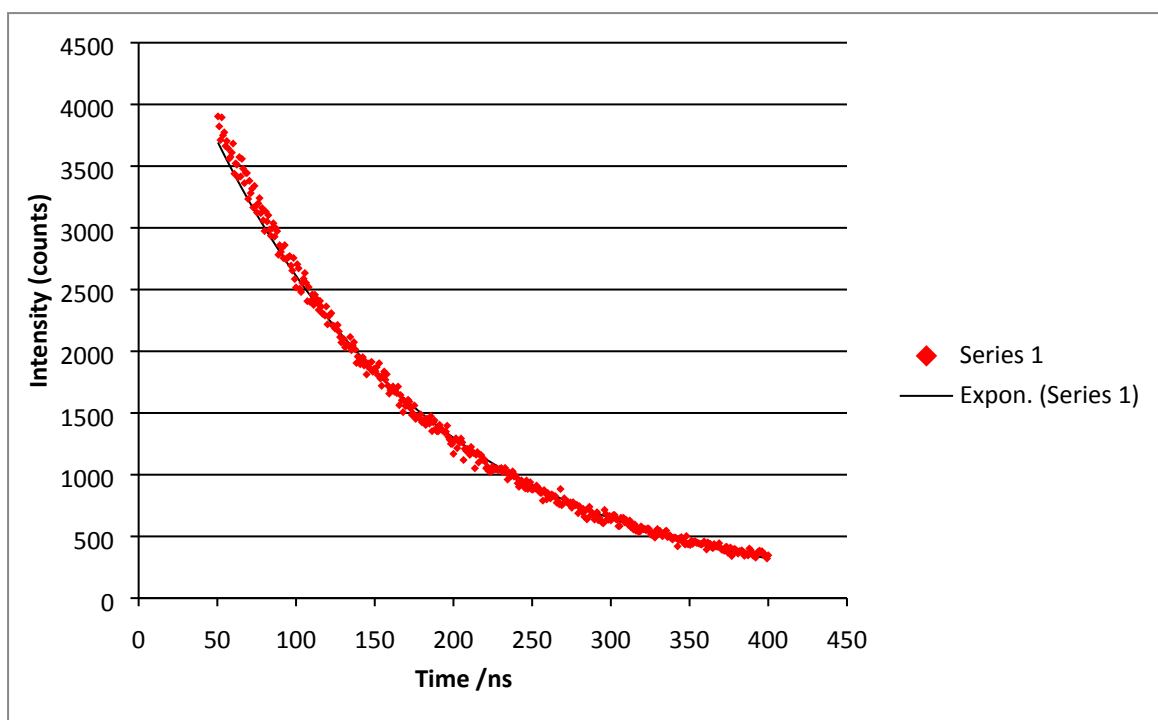


Fig. S4: Decay Plot for Lifetime Calculation for 3

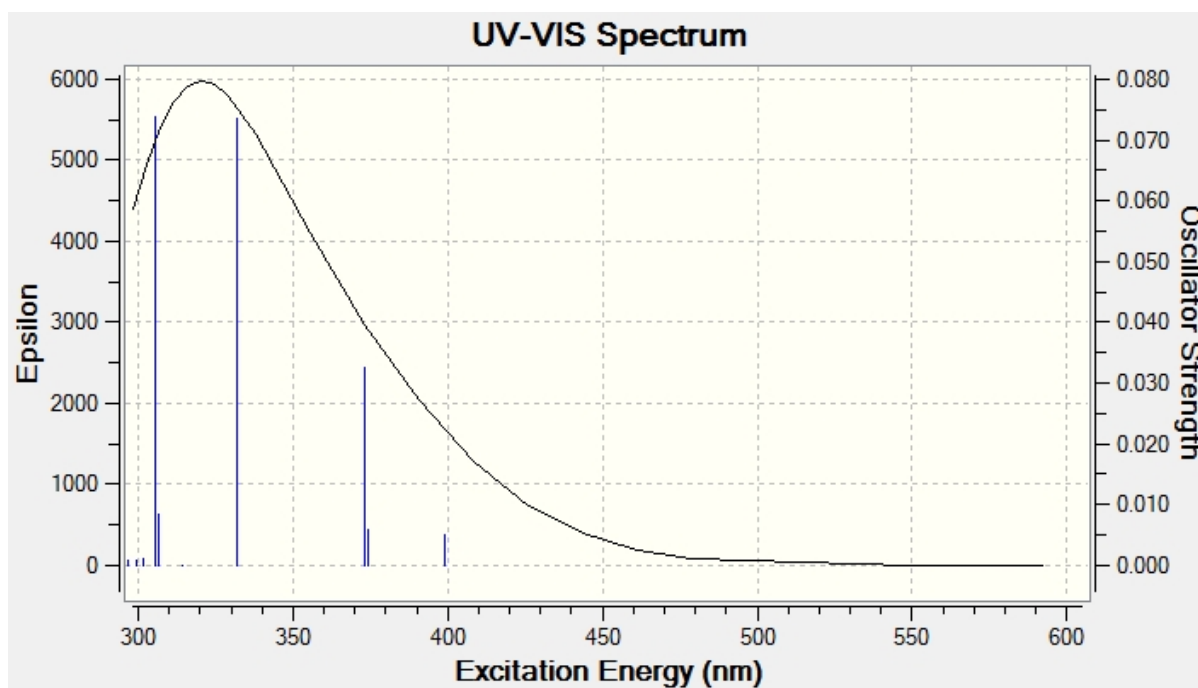


Fig S5: Simulated UV-Vis spectrum of 2.

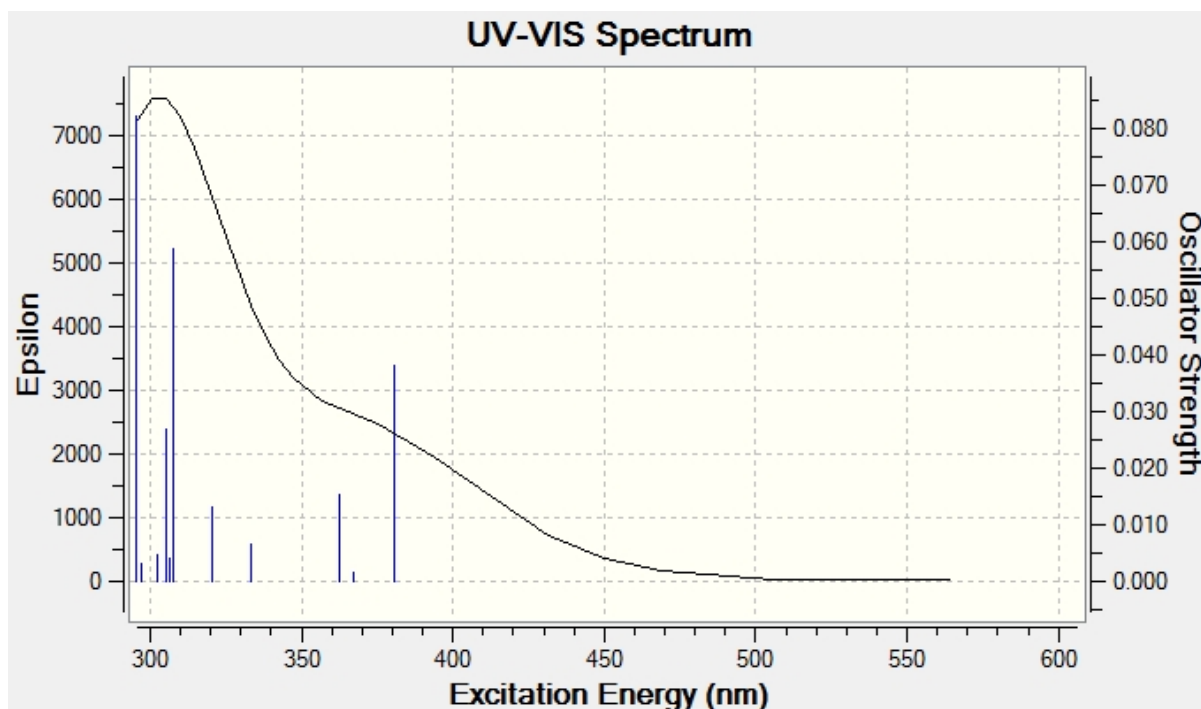


Fig. S6: Simulated UV-Vis spectrum of **3**

Computational Details

All calculations were performed using Gaussian09,³ using the B3LYP functional,⁴ with Stuttgart-Dresden basis set and associated ECP on Re⁵ and 6-31+G(d,p) on all remaining atoms.⁶ Structures of individual complexes of **2** and **3** were extracted from the crystalline environment and fully geometry optimised within a polarizable continuum model (PCM) simulation of toluene. Calculation of absorption bands using TD-DFT, as well as frontier orbitals, were performed at this optimum geometry, again in PCM toluene.

Crystallographic Data

Data were collected by the EPSRC UK National Crystallography Service at the University of Southampton. Refinement was carried out using the SHELX program⁷ in the WINGX package.⁸ ORTEP 3⁹ and POV-ray¹⁰ programs were used for image generation.

Compound	1	2	3	4
Empirical formula	C ₂₅ H ₂₆ N ₄	C ₂₈ H ₂₆ BrN ₄ O ₄ Re	C ₂₈ H ₂₆ BrN ₄ O ₃ Re. (C ₇ H ₈)	C ₂₅ H ₂₂ BrN ₄ O ₃ Re
Formula weight	382.50	748.64	824.77	692.57
Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Wavelength	0.71075 Å	0.71073 Å	0.71075 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>a</i>
Unit cell dimensions	a = 16.3443(11) Å b = 5.9490(4) Å c = 21.3716(15) Å α = 90.000° β = 106.773(3)° γ = 90.000°	a = 10.2026(7) Å b = 11.8088(8) Å c = 13.1060(9) Å α = 63.263(4)° β = 86.265(5)° γ = 73.684(4)°	a = 8.9603(5) Å b = 11.1814(8) Å c = 17.0562(11) Å α = 71.987(3)° β = 79.252(4)° γ = 86.961(4)°	a = 13.2087(9) Å b = 7.5055(5) Å c = 24.8936(18) Å α = 90.000° β = 104.400(5)° γ = 90.000°
Volume	1989.6(2) Å ³	1349.94(17) Å ³	1596.55(18) Å ³	2390.3(19) Å ³
<i>Z</i>	4	2	2	4
Density (calculated)	1.277 Mg/m ³	1.842 Mg/m ³	1.716 Mg/m ³	1.925 Mg/m ³
Absorption coefficient	0.077 mm ⁻¹	6.022 mm ⁻¹	5.098 mm ⁻¹	6.790 mm ⁻¹
<i>F</i> (000)	816	728	812	1336
Crystal size	0.36 x 0.06 x 0.04 mm ³	0.08 x 0.07 x 0.03 mm ³	0.23 x 0.09 x 0.04 mm ³	0.07 x 0.04 x 0.01 mm ³
Theta range for data collection	3.57 to 27.48°	2.456 to 27.510°	3.00 to 27.48°	2.843 to 27.484°
Index ranges	-21 ≤ <i>h</i> ≤ 21 -6 ≤ <i>k</i> ≤ 7 -27 ≤ <i>l</i> ≤ 27	-13 ≤ <i>h</i> ≤ 13 -15 ≤ <i>k</i> ≤ 15 -15 ≤ <i>l</i> ≤ 16	-11 ≤ <i>h</i> ≤ 11 -14 ≤ <i>k</i> ≤ 14 -22 ≤ <i>l</i> ≤ 21	-17 ≤ <i>h</i> ≤ 17 -7 ≤ <i>k</i> ≤ 9 -30 ≤ <i>l</i> ≤ 32
Reflections collected	17443	17641	21710	15745
Independent reflections	4497 [<i>R</i> _{int} = 0.0379]	6179 [<i>R</i> _{int} = 0.0282]	7305 [<i>R</i> _{int} = 0.0372]	5378 [<i>R</i> _{int} = 0.0385]
Completeness to theta = 27.48°	98.4 %	99.7 %	99.8 %	98.4 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.774	1.000 and 0.774	1.000 and 0.763	1.000 and 0.694
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4497 / 0 / 268	6179 / 6 / 393	7305 / 0 / 404	5378 / 0 / 315
Goodness-of-fit on <i>F</i> ²	1.021	1.041	1.046	1.023
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0387 <i>wR</i> 2 = 0.0927	<i>R</i> 1 = 0.0227, <i>wR</i> 2 = 0.0587	<i>R</i> 1 = 0.0233 <i>wR</i> 2 = 0.0591	<i>R</i> 1 = 0.0281 <i>wR</i> 2 = 0.0545
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0596 <i>wR</i> 2 = 0.1019	<i>R</i> 1 = 0.0234 <i>wR</i> 2 = 0.0591	<i>R</i> 1 = 0.0243 <i>wR</i> 2 = 0.0597	<i>R</i> 1 = 0.0442 <i>wR</i> 2 = 0.0598
Largest diff. peak and hole	0.237 and -0.232 eÅ ⁻³	2.160 and -1.429 eÅ ⁻³	1.357 and -0.867 eÅ ⁻³	0.797 and -0.841 eÅ ⁻³

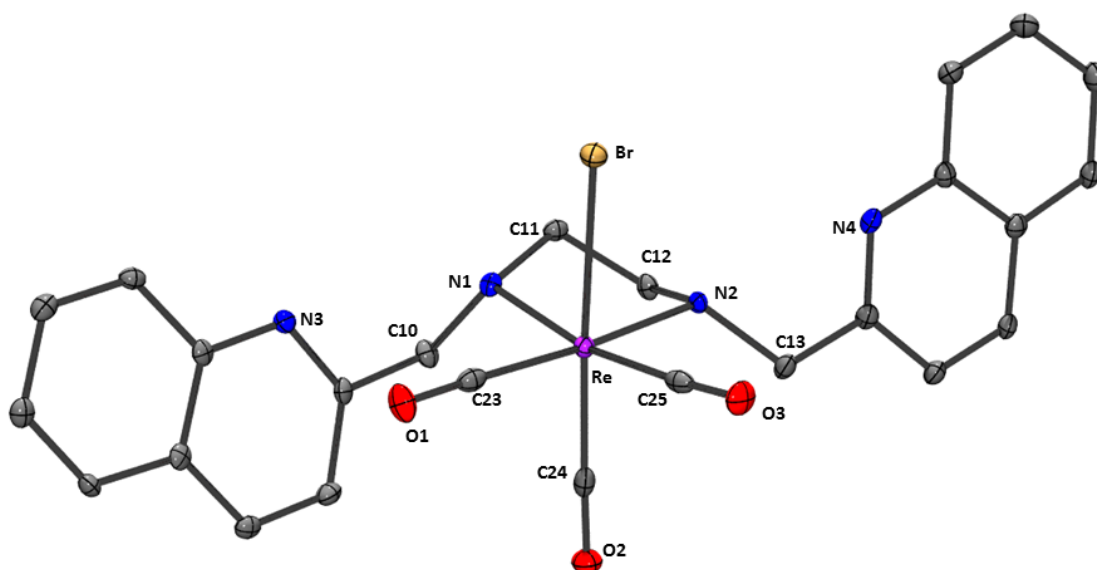


Fig. S7: Molecular Structure of Compound 4

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