Supporting Information for

Synthesis and characterisation of luminescent rhenium tricarbonyl complexes with axially coordinated 1,2,3-triazole ligands

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**Figure S1** Comparative UV-vis absorption spectra for complexes

**Comparison of X-ray crystal structure of 2a and 2b.**

**Figure S2** ORTEP plot of the single-crystal X-ray structure of 2a

**Figure S3** ORTEP plot of the single-crystal X-ray structure of 2b

**Table S1** Selected bond lengths and angles for single-crystal X-ray structures

**Figure S1** $^1$H NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (1a)

**Figure S2** $^{13}$C NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (1a)

**Figure S3** $^1$H NMR spectrum of 4-phenyl-1-propyl-1,2,3-triazole (1b)

**Figure S4** $^{13}$C NMR spectrum of 4-phenyl-1-propyl-1,2,3-triazole (1b)

**Figure S5** $^1$H NMR spectrum of 1-benzyl-4-phenyl-1,2,3-triazole (1c)

**Figure S6** $^{13}$C NMR spectrum of 1-benzyl-4-phenyl-1,2,3-triazole (1c)

**Figure S7** $^1$H NMR spectrum of 1-propyl-4-tolyl-1,2,3-triazole (1d)

**Figure S8** $^{13}$C NMR spectrum of 1-propyl-4-tolyl-1,2,3-triazole (1d)

**Figure S9** $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1a)]PF$_6$ (2b)

**Figure S10** $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1a)]PF$_6$ (2b)

**Figure S11** $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1b)]PF$_6$ (2b)

**Figure S12** $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1b)]PF$_6$ (2b)

**Figure S13** $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1c)]PF$_6$ (2b)

**Figure S14** $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1c)]PF$_6$ (2b)

**Figure S15** $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1d)]PF$_6$ (2b)

**Figure S16** $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1d)]PF$_6$ (2b)
Fig. S1 Comparative UV-vis absorption spectra for complexes, a) [Re(bpy)(CO)3(1a)]PF6, b) [Re(bpy)(CO)3(1b)]PF6, c) [Re(bpy)(CO)3(1c)]PF6, d) [Re(bpy)(CO)3(1d)]PF6.

Comparison of X-ray crystal structure of 2a and 2b.

Fig. S2 ORTEP plot of the single-crystal X-ray structure of [Re(bpy)(CO)3(1a)]PF6 (hydrogen atoms and PF6− counterion omitted for clarity, ellipsoids at 50% probability).
**Fig. S3** ORTEP plot of the single-crystal X-ray structure of [Re(bpy)(CO)$_3$(1b)]PF$_6$ (hydrogen atoms and PF$_6^-$ counterion omitted for clarity, ellipsoids at 50 % probability).

**Table 2** Selected bond lengths (Å) and angles (°) for single-crystal X-ray structures of [Re(bpy)(CO)$_3$(1b)]PF$_6$ (2a) and [Re(bpy)(CO)$_3$(1b)]PF$_6$ (2b).

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<th>Bond</th>
<th>[Re(bpy)(CO)$_3$(1a)]PF$_6$</th>
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<tr>
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<td>Re-N2</td>
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<td>2.170(4)</td>
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<td>C24-Re-C27</td>
<td>86.9(2)</td>
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[Re(bpy)(CO)$_3$(1a)]PF$_6$ crystallised in the space group C2/c whereas [Re(bpy)(CO)$_3$(1b)]PF$_6$ crystallises in the space group Pbca. As can be seen from Figures S1 and S2, both complexes adopt a distorted octahedral geometry with a facial arrangement of the carbonyl ligands. The triazole ligands are coordinated to the metal through the N3 position of the ring which would be expected to be the more basic of the two potential N-donor atoms. The Re-N bonds to bpy are approximately 2.17 Å. The Re-N bond lengths to the axial triazole ligands in 2a and 2b are 2.2186(14) and 2.198(4) Å. C-O bond lengths are unremarkable for both complexes varying from 1.145 to 1.155 Å. The Re-C and C-O bond lengths trans to the triazole ligands are indistinguishable to those trans to bpy within experimental error.

Despite the seemingly simple difference between the two complexes in terms of the methyl versus propyl substituents of the triazole ring, these ligands are oriented quite differently in the solid state for the two complexes. For the propyltriazole complex 2b the Re-N4 bond length is 2.198(4) Å and the triazole ligand is oriented such that the phenyl group lies above the carbonyl ligands. For the methyltriazole 2a complex the Re-N3 bond length is longer at 2.2186(14) Å and the triazole ligand is oriented such that it brings the phenyl ring over one of the pyridyl rings of the bpy ligand. The planes of the phenyl and pyridyl rings are almost parallel and are separated by a distance of approximately 3.3 Å indicative of a π-stacking interaction. The formation of this π-stacking interaction in 2a leads to significant twisting of the bpy ligand and a tilting of the triazole ligand. The plane of the triazole ring is tilted by 13° with respect to the N3-Re bond which compares to a much smaller tilt of 7.1° for the propyl-substituted ligand. As a result of the π-stacking interaction with the phenyl ring of the ligand 1a the participating pyridyl ring is twisted such that it is inclined by 3.4° with respect to the N1-Re bond and is twisted by 14.9° with respect to the plane defined by the Re atom and the carbonyl carbon atoms trans to bpy. This twisting results in an angle of 8.8° between the planes of the two pyridyl rings and a more severe deviation from coplanarity of the second pyridyl ring with respect to the square plane about the Re centre. Here the ring has an inclination of the 15° with respect to the N2-Re bond and a twist of 22.5° relative to the same plane defined by the Re atom and carbonyl ligands. In comparison, the propyl triazole complex experiences
much less distortion. The twist between rings in the bpy ligand is only 6.1 °, the rings have inclinations with respect to their Re-N bonds of only 1.7 and 4.1 ° and are twisted relative to the plane of the Re atom and the trans carbonyl carbon atoms by 2.7 and 3.5 °.
Figure S4 $^1$H NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (1a) (CDCl$_3$).

Figure S5 $^{13}$C NMR spectrum of 1-methyl-4-phenyl-1,2,3-triazole (1a) (CDCl$_3$).
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Figure S7 $^{13}$C NMR spectrum of 4-phenyl-1-propyl-1,2,3-triazole (1b) (CDCl$_3$).
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Figure S9 $^{13}$C NMR spectrum of 1-benzyl-4-phenyl-1,2,3-triazole (1c) (CDCl$_3$).
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Figure S11 $^{13}$C NMR spectrum of 1-propyl-4-p-toly1,2,3-triazole (1d) (CDCl$_3$).
Figure S12 $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1a)]PF$_6$ (2a) (CD$_3$CN).

Figure S13 $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1a)]PF$_6$ (2a) (CD$_3$CN).
Figure S14 $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1b)]PF$_6$ (2b) (CD$_3$CN).

Figure S15 $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1b)]PF$_6$ (2b) (CD$_3$CN).
Figure S16 $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1c)]PF$_6$ (2c) (CD$_3$CN).

Figure S17 $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1c)]PF$_6$ (2c) (CD$_3$CN).
**Figure S18** $^1$H NMR spectrum of [Re(bpy)(CO)$_3$(1d)]PF$_6$ (2d) (CD$_3$CN).

**Figure S19** $^{13}$C NMR spectrum of [Re(bpy)(CO)$_3$(1d)]PF$_6$ (2d) (CD$_3$CN).