Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary data for:

Water-soluble alkylated bis{4'-(4-pyridyl)-2,2':6',2''-terpyridine}ruthenium(II) complexes for use as photosensitizers in water oxidation: a complementary experimental and TD-DFT investigation

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Ru basis set used in Gaussian 09:

Ru 0

S 3 1.00

2.5650000 -1.0431056

1.5080000 1.3314786

0.5129000 0.5613065

S 4 1.00

2.5650000 0.8770128

1.5080000 -1.2634660

0.5129000 -0.8384987

0.1362000 1.0637773

S 1 1.00

0.0417000 1.0000000

P 3 1.00

4.8590000 -0.0945755

1.2190000 0.7434798

0.4413000 0.3668144

P 2 1.00

0.5725000 -0.0880864

0.0830000 1.0283970

P 1 1.00

0.0250000 1.0000000

D 3 1.00

4.1950000 0.0485729

1.3770000 0.5105223

0.4828000 0.5730028

D 1 1.00

0.1501000 1.0000000

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Ru Effective Core Potential (ECP):

RU 0

RU-ECP 3 28

f potential

5

0 554.3796303 -0.0515270

1 155.1066871 -20.1816536

2 48.4976263 -105.9966915

2 14.7701594 -42.2166788

2 5.2077363 -3.7675024

s-f potential

5

0 66.7118060 2.9578344

1 77.3503632 25.3748707

2 18.3571445 536.1262372

2 11.8404727 -651.2057221

2 8.1179479 381.3816943

p-f potential

5

0 54.9937915 4.9651557

1	13.9399212	23.8861501
2	15.2118246	464.4631344
2	10.5460691	-714.4451788
2	7.5539486	377.5503594

d-f potential

4

0	60.3444595	3.0352988
1	45.2100305	23.2901723
2	19.1190074	146.0926620
2	4.2712090	28.9129770

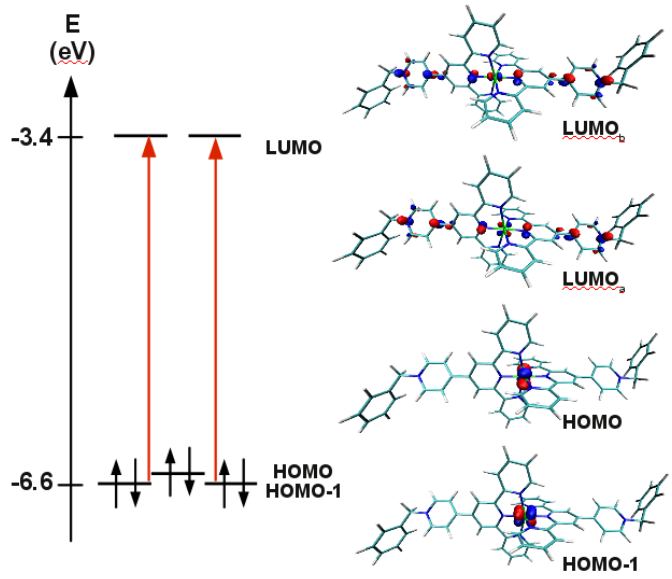

Fig. S1 Diagram showing the relative energies of the highest occupied and lowest unoccupied MOs of $[Ru(\mathbf{1})_2]^{4+}$, and transitions responsible for the MLCT absorption in the electronic spectrum. Isodensity surfaces are displayed on the right. The two HOMO–1 orbitals (shown together as the sum of two MOs) are close in energy but are non-degenerate, and similarly for the two orbitals labelled LUMO.

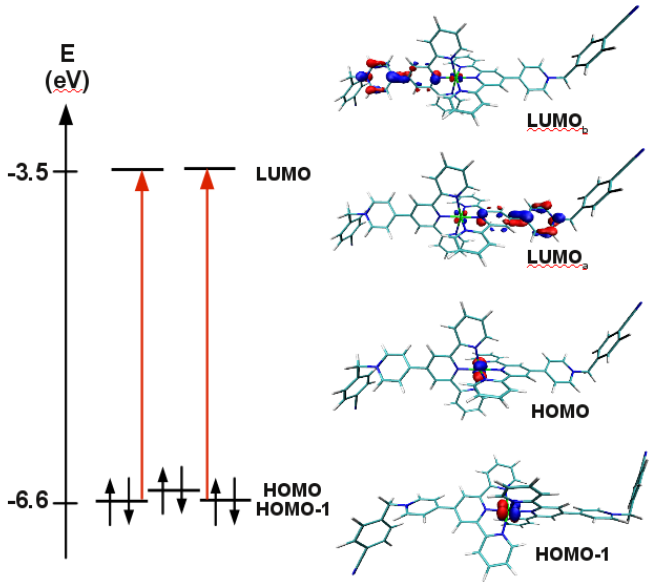

Fig. S2 Diagram showing the relative energies of the highest occupied and lowest unoccupied MOs of $[Ru(\mathbf{2})_2]^{4+}$, and transitions responsible for the MLCT absorption in the electronic spectrum. Isodensity surfaces are displayed on the right . The two HOMO–1 orbitals (shown together as the sum of two MOs) are close in energy but are non-degenerate, and similarly for the two orbitals labelled LUMO.

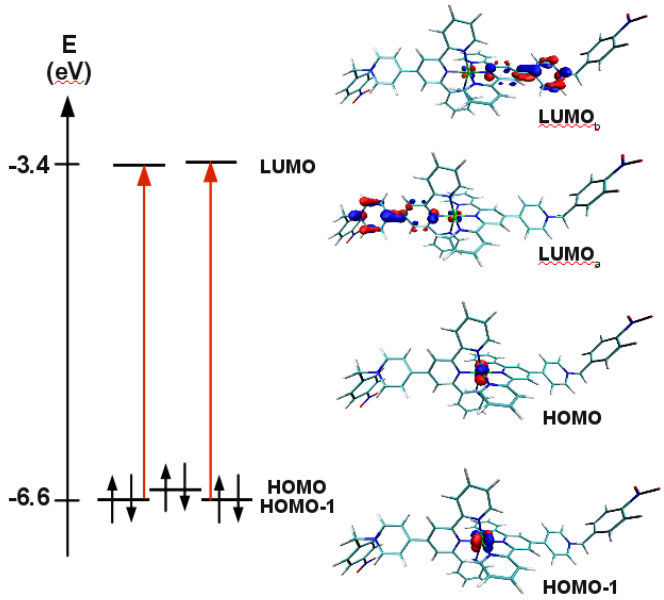

Fig. S3 Diagram showing the relative energies of the highest occupied and lowest unoccupied MOs of $[Ru(\mathbf{3})_2]^{4+}$, and transitions responsible for the MLCT absorption in the electronic spectrum. Isodensity surfaces are displayed on the right. The two HOMO–1 orbitals (shown together as the sum of two MOs) are close in energy but are non-degenerate, and similarly for the two orbitals labelled LUMO.

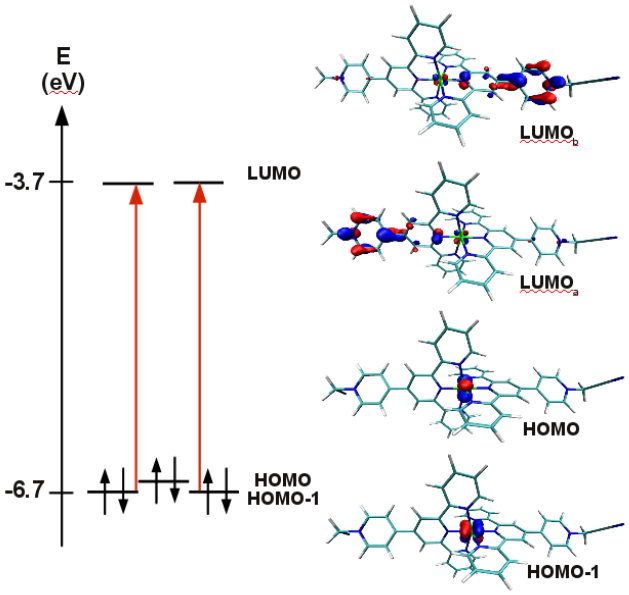

Fig. S4 Diagram showing the relative energies of the highest occupied and lowest unoccupied MOs of $[Ru(\mathbf{5})_2]^{4+}$, and transitions responsible for the MLCT absorption in the electronic spectrum. Isodensity surfaces are displayed on the right. The two HOMO–1 orbitals (shown together as the sum of two MOs) are close in energy but are non-degenerate, and similarly for the two orbitals labelled LUMO.

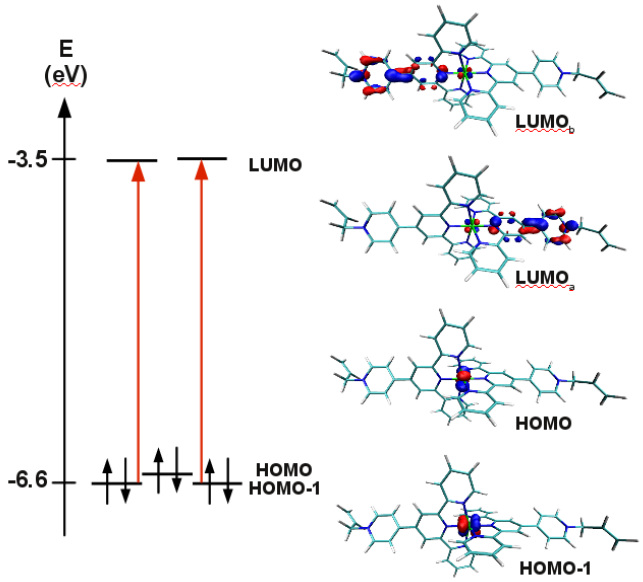

Fig. S5 Diagram showing the relative energies of the highest occupied and lowest unoccupied MOs of $[Ru(\mathbf{6})_2]^{4+}$, and transitions responsible for the MLCT absorption in the electronic spectrum. Isodensity surfaces are displayed on the right. The two HOMO–1 orbitals (shown together as the sum of two MOs) are close in energy but are non-degenerate, and similarly for the two orbitals labelled LUMO.

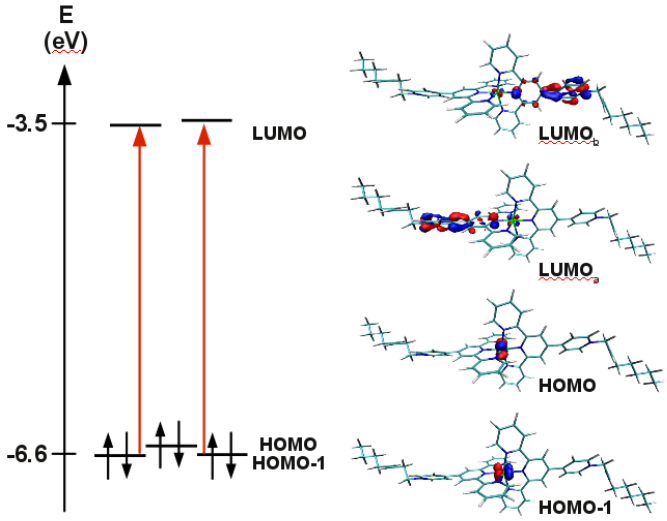

Fig. S6 Diagram showing the relative energies of the highest occupied and lowest unoccupied MOs of $[Ru(\mathbf{7})_2]^{4+}$, and transitions responsible for the MLCT absorption in the electronic spectrum. Isodensity surfaces are displayed on the right. The two HOMO–1 orbitals (shown together as the sum of two MOs) are close in energy but are non-degenerate, and similarly for the two orbitals labelled LUMO.