Supplementary Materials: Photophysical and Electrocatalytic Properties of Rhenium(I) Triazole-Based Complexes

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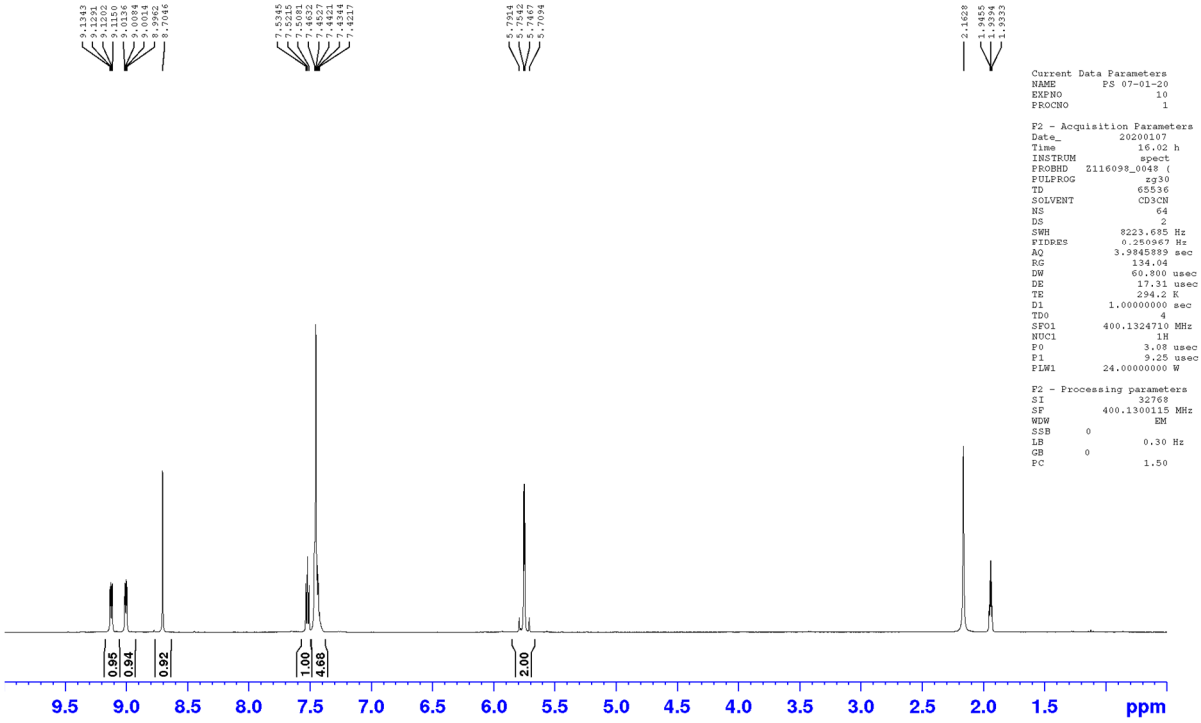

Figure S1. ^{1}H NMR (400 MHz, d_3-MeCN) spectrum of complex **2**.

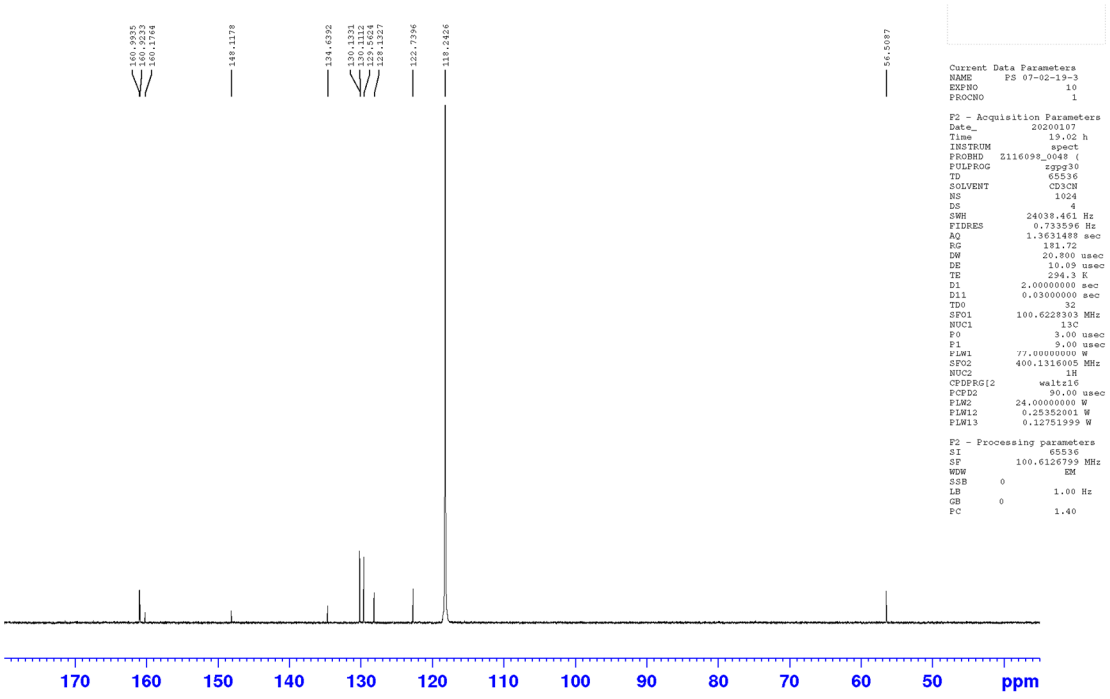

Figure S2. ^{13}C NMR (101 MHz, d_3-MeCN) spectrum of complex **2**.

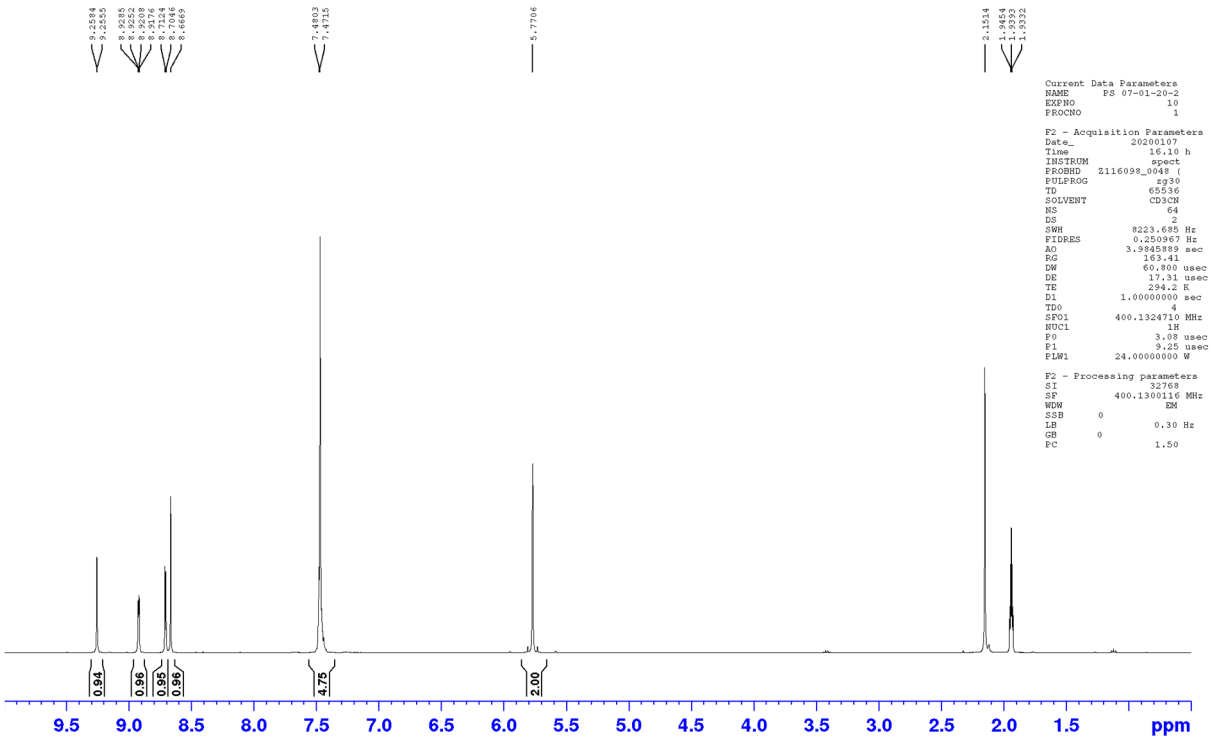

Figure S3. ^{1}H NMR (400 MHz, d_3-MeCN) spectrum of complex **3**.

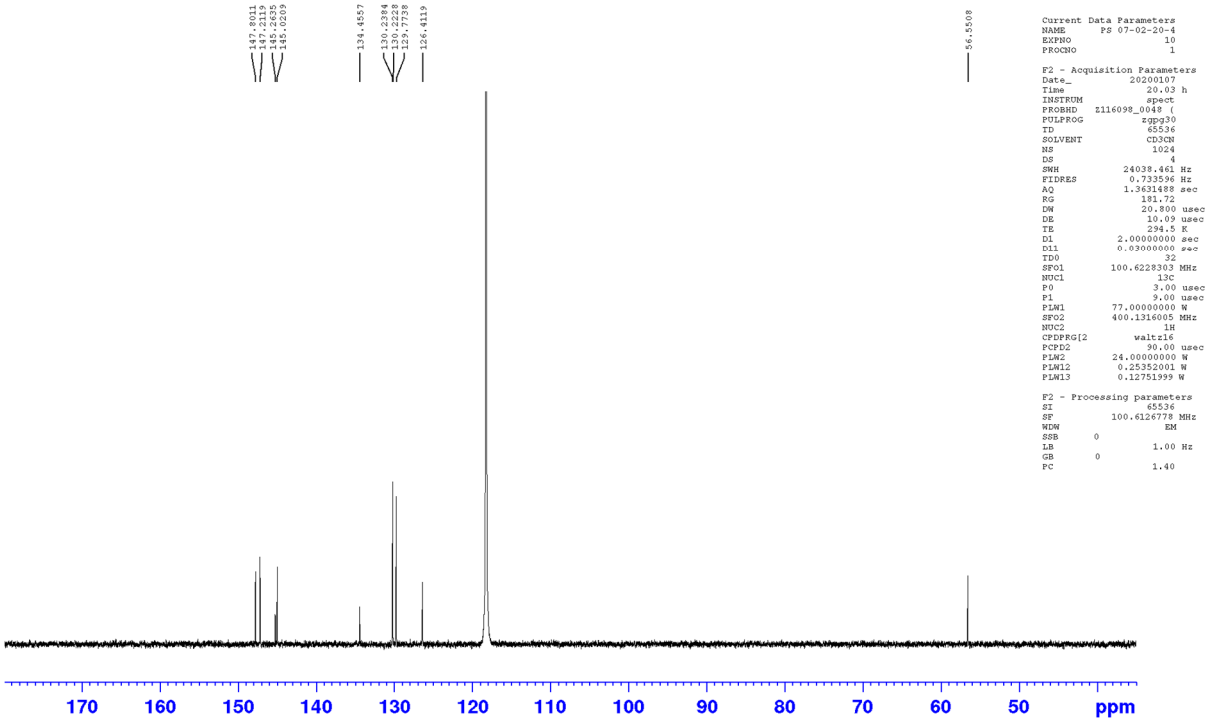

Figure S4. ^{13}C NMR (101 MHz, d_3-MeCN) spectrum of complex **3**.

Time-Dependent DFT Analysis

Time-dependent DFT (TDDFT) calculations were carried out on the optimised ground state geometries of each complex in order to determine vertical excitation energies and the nature of the lowest energy singlet excited states. The excitations to the S_1 state of all complexes are primarily HOMO → LUMO in character, however, they are of negligible oscillator strength and will therefore contribute little to the observed absorption spectra. The energies associated with transitions S_1 follow

the trend of the HOMO-LUMO gap reported in Table 3. The lowest energy major transitions observed for all complexes, arising between 240 and 270 nm, involve mainly the orbitals HOMO-3 to LUMO and are primarily ^{1}LC $\pi \rightarrow \pi^*$ in character. Complex **3** also presents a transition at 339 nm assigned as having predominantly ^{1}MLCT character.

Table S1. Main excitation energies and oscillator strengths for complex **1** (orbital 79 = HOMO and orbital 80 = LUMO).

Transition	Energy/eV	Energy/nm	Oscillator Strengths/f	Character/%
S_1	3.849	322.060	0.003	79 → 80 72% 79 → 81 4%
S_7	4.757	260.61	0.150	76 → 80 57% 78 → 84 13% 77 → 83 5%
S_8	4.827	256.82	0.118	76 → 80 23% 77 → 83 17% 78 → 84 16% 78 → 82 14% 78 → 80 5%
S_{23}	5.793	214.02	0.122	75 → 80 63% 76 → 81 18%

Table S2. Main excitation energies and oscillator strengths for complex **2** (orbital 79 = HOMO and orbital 80 = LUMO).

Transition	Energy/eV	Energy/nm	Oscillator strengths/f	Character/%
S_1	3.761	329.62	0.003	79 → 80 83% 79 → 82 6%
S_{13}	5.077	244.21	0.237	76 → 80 67% 77 → 81 10%
S_{19}	5.413	229.05	0.140	76 → 81 43% 78 → 82 14% 79 → 89 5%
S_{26}	5.810	213.39	0.167	74 → 80 68% 76 → 81 7% 73 → 80 5%

Table S3. Main excitation energies and oscillator strengths for complex **3** (orbital 79 = HOMO and orbital 80 = LUMO).

Transition	Energy/eV	Energy/nm	Oscillator Strengths/f	Character/%
S_1	3.475	356.75	0.002	79 → 80 92%
S_2	3.656	339.08	0.103	78 → 80 92%
S_8	7.499	275.57	0.241	76 → 80 86% 78 → 81 5%
S_{23}	5.612	220.92	0.235	74 → 80 19% 76 → 81 47% 77 → 89 6%

Atomic Coordinates for Calculated Ground State of Complex 1

#
28
Geometry

C	1.71115	−2.02149	−0.17689
C	1.17629	−0.36913	1.94515
C	2.64547	0.54136	−0.18423
O	3.66949	1.05467	−0.31839
O	2.16725	−3.06921	−0.30914
O	1.33485	−0.42237	3.09142
C	−1.67891	1.48791	0.10714
C	0.18201	2.86806	0.14383
C	−2.53426	2.58847	0.07869
C	−0.60835	4.00884	0.11438
H	1.26132	2.93819	0.16231
C	−1.99269	3.86663	0.08128
H	−3.60645	2.44058	0.04933
H	−0.13948	4.98424	0.11288
H	−2.63883	4.73588	0.05507
N	−0.33055	1.62766	0.14445
N	−1.21469	−0.89381	0.15126
C	−2.14406	0.10812	0.10756
Cl	0.37246	−0.06971	−2.41787
Re	0.90277	−0.27111	0.03822
N	−1.7932	−2.0583	0.15031
N	−3.111	−1.82646	0.10569
C	−3.38071	−0.49895	0.07693
H	−4.38417	−0.11227	0.03196
C	−4.04032	−2.95004	0.05774
H	−4.78007	−2.85383	0.85282
H	−4.53497	−2.9849	−0.91377
H	−3.45755	−3.85649	0.20394

Atomic coordinates for calculated ground state of complex 2

#
27
Geometry

C	1.73527	−2.00181	−0.20103
C	1.17568	−0.39048	1.94575
C	2.64651	0.57147	−0.15994
O	3.66524	1.09859	−0.27895
O	2.20288	−3.04158	−0.34936
O	1.32939	−0.46103	3.09122
C	−1.68027	1.47536	0.1182
C	0.12861	2.88825	0.14838
C	−0.73207	3.97501	0.11566
H	1.20401	3.01015	0.16491
H	−0.35065	4.98708	0.10657
N	−0.3338	1.62946	0.15627
N	−1.20869	−0.9049	0.13778
C	−2.13614	0.09615	0.11132
Cl	0.39287	−0.01379	−2.41339
Re	0.91154	−0.26152	0.0381
N	−1.79297	−2.06562	0.13032
N	−3.11374	−1.82401	0.09931

C	−3.37712	−0.4972	0.08446
H	−4.3705	−0.08497	0.05285
C	−4.04772	−2.94316	0.0292
H	−4.87514	−2.77072	0.7169
H	−4.42303	−3.05447	−0.98903
H	−3.50566	−3.84018	0.31955
H	−2.83084	4.50413	0.06788
C	−2.09703	3.70467	0.0916
N	−2.57466	2.45938	0.0943

Atomic Coordinates for Calculated Ground State of Complex 3

#
27
Geometry

C	1.66792	−2.05381	−0.18564
C	1.1696	−0.39764	1.94872
C	2.65428	0.49918	−0.17885
O	3.68603	0.99531	−0.31135
O	2.10037	−3.10913	−0.32518
O	1.32857	−0.46105	3.09335
C	−1.63583	1.51772	0.10567
C	0.22291	2.86877	0.142
C	−2.43934	2.6601	0.07956
C	−0.60293	3.98693	0.11297
H	1.30044	2.96177	0.15899
H	−3.52091	2.57113	0.05165
H	−0.1755	4.98338	0.111
N	−0.28563	1.62882	0.14405
N	−1.23508	−0.86636	0.14852
C	−2.14215	0.15659	0.10481
Cl	0.37905	−0.07024	−2.41476
Re	0.89629	−0.28349	0.03969
N	−1.84104	−2.01641	0.14509
N	−3.15331	−1.7536	0.09798
C	−3.39301	−0.42073	0.07134
H	−4.38697	−0.01016	0.02499
C	−4.10999	−2.85539	0.06179
H	−4.78733	−2.78895	0.9137
H	−4.67425	−2.82662	−0.87083
H	−3.53845	−3.77891	0.11607
N	−1.93512	3.88938	0.08438

Atomic Coordinates for Calculated Triplet State of Complex 1

#
28
Geometry

C	1.45516	−2.21658	0.14834
C	1.03518	−0.18015	1.9893
C	2.6706	0.30703	−0.21358
O	3.74928	0.6753	−0.35425

O	1.78267	−3.30669	0.2433
O	1.17856	−0.12095	3.12409
C	−1.53509	1.63543	0.01852
C	0.52591	2.83131	0.02551
C	−2.2311	2.85141	−0.05051
C	−0.12413	4.02869	−0.02524
H	1.60716	2.79183	0.05182
C	−1.55771	4.05092	−0.07462
H	−3.31506	2.82892	−0.08151
H	0.45041	4.94544	−0.03491
H	−2.09494	4.9891	−0.12577
N	−0.11134	1.61451	0.03
N	−1.3009	−0.74914	0.10327
C	−2.13653	0.35078	0.06089
Cl	0.58957	−0.62695	−2.37571
Re	0.82744	−0.3035	0.01657
N	−1.98632	−1.8704	0.12947
N	−3.26519	−1.51651	0.10461
C	−3.43066	−0.16822	0.06249
H	−4.40202	0.29261	0.03659
C	−4.29532	−2.54714	0.10807
H	−4.95069	−2.41546	0.97012
H	−4.87788	−2.49398	−0.81279
H	−3.79299	−3.50962	0.16954

Atomic Coordinates for Calculated Triplet State of Complex 2

#
27
Geometry

C	1.55314	−2.15783	0.13225
C	1.01186	−0.16822	2.00023
C	2.66781	0.39863	−0.18909
O	3.7346	0.80341	−0.31893
O	1.93647	−3.2302	0.21388
O	1.12853	−0.12054	3.13806
C	−1.58323	1.59009	0.03042
C	0.40232	2.86784	0.00074
C	−0.34874	4.00435	−0.04776
H	1.48474	2.90846	0.00668
H	0.12164	4.97745	−0.07799
N	−0.15356	1.61803	0.03127
N	−1.27554	−0.78706	0.09293
C	−2.13994	0.28562	0.0604
Cl	0.6277	−0.57372	−2.37296
Re	0.8445	−0.27275	0.02
N	−1.93323	−1.92487	0.10928
N	−3.22327	−1.59898	0.08702
C	−3.42041	−0.25654	0.05629
H	−4.39391	0.19912	0.03132
C	−4.22839	−2.65475	0.07934
H	−4.8896	−2.54403	0.93965

H	−4.80857	−2.60812	−0.84319
H	−3.70348	−3.60538	0.13596
H	−2.42726	4.73067	−0.09306
C	−1.77838	3.8616	−0.05923
N	−2.35797	2.67935	−0.02113

Atomic Coordinates for Calculated Triplet State of Complex 3

#
27
Geometry

C	1.52549	−2.17856	0.14703
C	1.03509	−0.1538	1.99323
C	2.67244	0.36195	−0.21431
O	3.74209	0.75231	−0.35544
O	1.88942	−3.25686	0.24044
O	1.16648	−0.08911	3.12779
C	−1.55974	1.60585	0.02175
C	0.42128	2.8667	0.02572
C	−2.26442	2.80617	−0.04424
C	−0.32747	4.00496	−0.02894
H	1.50218	2.91197	0.04881
H	−3.35204	2.77282	−0.07276
H	0.16002	4.97228	−0.04445
N	−0.14657	1.61229	0.0418
N	−1.28678	−0.77294	0.10412
C	−2.14474	0.30367	0.06027
Cl	0.59309	−0.58232	−2.36927
Re	0.84223	−0.28677	0.0137
N	−1.94631	−1.90797	0.12783
N	−3.23359	−1.58173	0.10033
C	−3.42397	−0.23729	0.05843
H	−4.40303	0.20725	0.02991
C	−4.24347	−2.63369	0.10186
H	−4.90096	−2.51639	0.96407
H	−4.82602	−2.59037	−0.81923
H	−3.72146	−3.58568	0.16196
N	−1.70611	4.00876	−0.06626