Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

^{1}IL and ^{3}MLCT Excited States Modulated by H^{+}: Structure and Photophysical Properties of [(2-bromo-5-(1H-pyrazol-1-yl)pyrazine)$Re(CO)_3Br$]

by the authors:

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Table S1. Crystal data and structure refinement details for **I**.

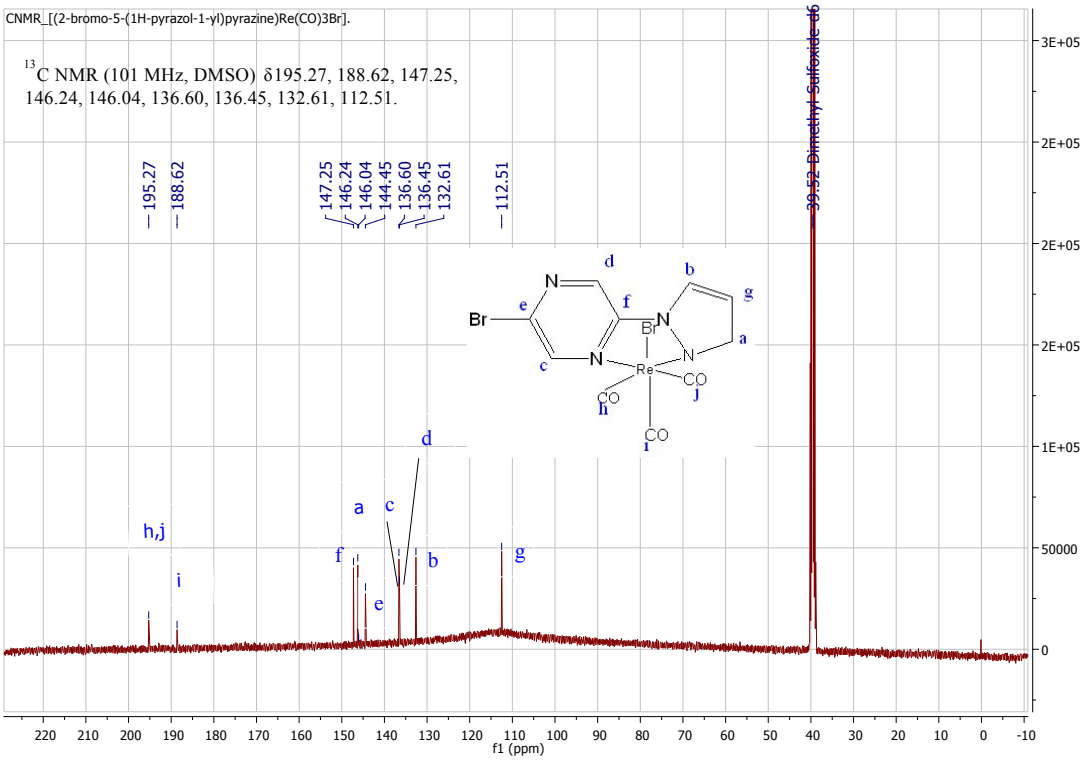
	298 K	**100 K**
FW/uma	575.20	575.20
Crystal System	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
a (Å)	6.769(4)	6.6120(19)
b (Å)	8.079(4)	7.947(2)
c (Å)	13.343(7)	13.079(4)
α (°)	106.008(7)	105.928(3)
β (°)	102.690(6)	102.163(3)
γ (°)	91.343(7)	92.124(3)
V (Å ^{3})	681.6(6)	642.7(3)
Z(Z')	2(2)	2(2)
δ (g cm^{-3})	2.803	2.972
μ **(mm^{-1})**	14.79	14.79
F(000)	524	524
θ **range**	1.6–26.0	1.6–26.0
hkl range	$-8 \le h \le 8$	$-8 \le h \le 8$
	$-9 \le l \le 9$	$-9 \le l \le 9$
	$-16 \le k \le 16$	$-16 \le k \le 16$
N_{tot}, N_{uniq} (R_{int}), N_{obs}	5316, 2664 (0.066), 2181	5034, 2520 (0.032), 2393
Ref. Parameters	181	182
GOF	1.06	1.06
R1, wR2 (obs)	0.052, 0.123	0.022, 0.050
Max. and min $\Delta\rho$ e Å^{-3}	3.55, −1.96	1.83, −0.82

Table S2. Selected bond distances (Å) for **I** as determined by X-rays diffraction compared to those computed from optimized models (DFT, Gas Phase).

	I (DRX 298 K)	**I (DRX 100 K)**	**I (DFT)**	**IH$^+$ (DFT)**
Re1—C14	1.895(15)	1.908(4)	1.929	1.940
Re1—C13	1.918(14)	1.912(5)	1.932	1.986
Re1—C15	1.959(12)	1.926(5)	1.922	1.955
Re1—N1	2.169(9)	2.140(4)	2.217	2.180
Re1—N3	2.199(10)	2.167(3)	2.193	2.099
Re1—Br1	2.6144(16)	2.5988(9)	2.657	2.618

Table S3. Summary of main energy, wavelength and oscillator strength computed for observed transitions in the absorption spectra of **I**, together with the orbitals implied.

N	**E / eV**	**λ / nm**	***f***	**Major Contributions**
				I
2	2.16	574	0.023	HOMO-1 → LUMO (97 %)
8	3.30	376	0.078	HOMO-4 → LUMO (80 %)
				HOMO-3 → LUMO+1 (12 %)
9	3.43	361	0.049	HOMO-4 → LUMO (12 %)
				HOMO-3 → LUMO+1 (85 %)
10	3.52	352	0.011	HOMO-4 → LUMO+1 (96 %)
12	3.98	312	0.013	HOMO-5 → LUMO+1 (11 %)
				HOMO → LUMO+2 (68 %)
				HOMO → LUMO+5 (10 %)
15	4.14	300	0.012	HOMO-1 → LUMO+4 (20 %)
				HOMO → LUMO+4 (52 %)
18	4.25	292	0.010	HOMO → LUMO+2 (14 %)
				HOMO → LUMO+3 (17 %)
				HOMO → LUMO+5 (56 %)
20	4.48	276	0.023	HOMO-1 → LUMO+3 (40 %)
				HOMO-1 → LUMO+5 (38 %)
21	4.56	272	0.033	HOMO-6 → LUMO (81 %)
22	4.58	271	0.011	HOMO-1 → LUMO+3 (46 %)
				HOMO-1 → LUMO+5 (34 %)
26	4.93	251	0.194	HOMO-6 → LUMO+1 (71 %)
28	5.04	246	0.014	HOMO-3 → LUMO+2 (32 %)
				HOMO → LUMO+7 (32 %)
30	5.09	244	0.016	HOMO-3 → LUMO+2 (16 %)
				HOMO → LUMO+6 (24 %)
				HOMO → LUMO+7 (17 %)



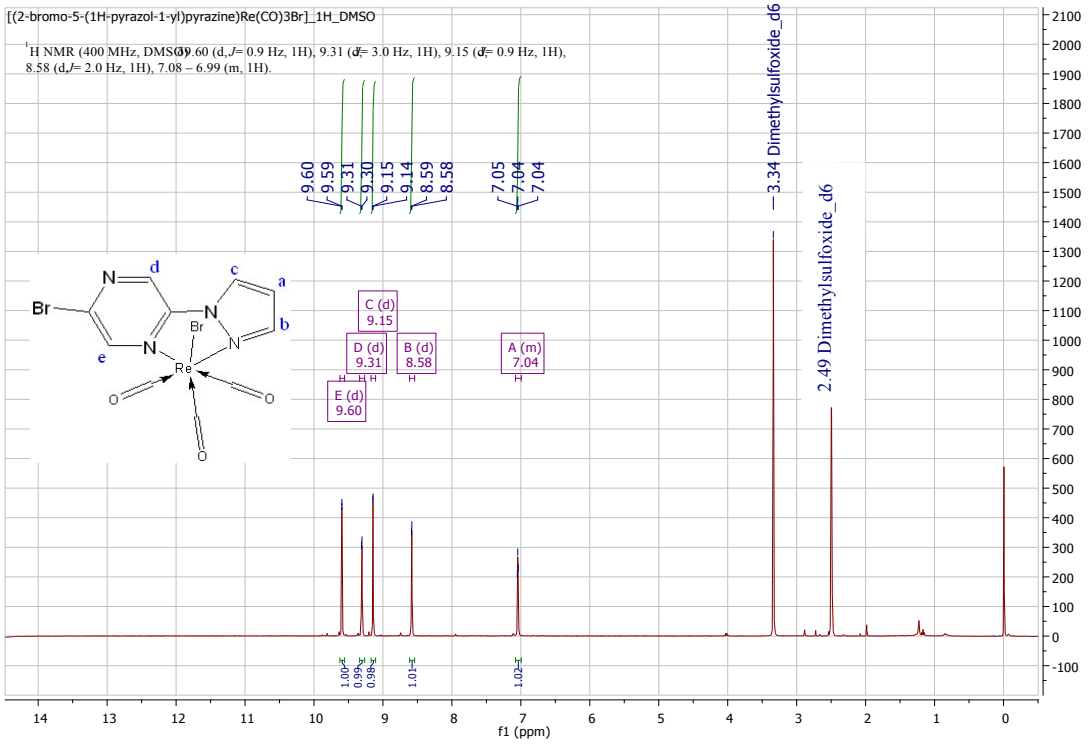


Figure S1. ^{13}CNMR and ^{1}HNMR spectra determined for **[(L$_l$)Re(CO)$_3$Br]**.

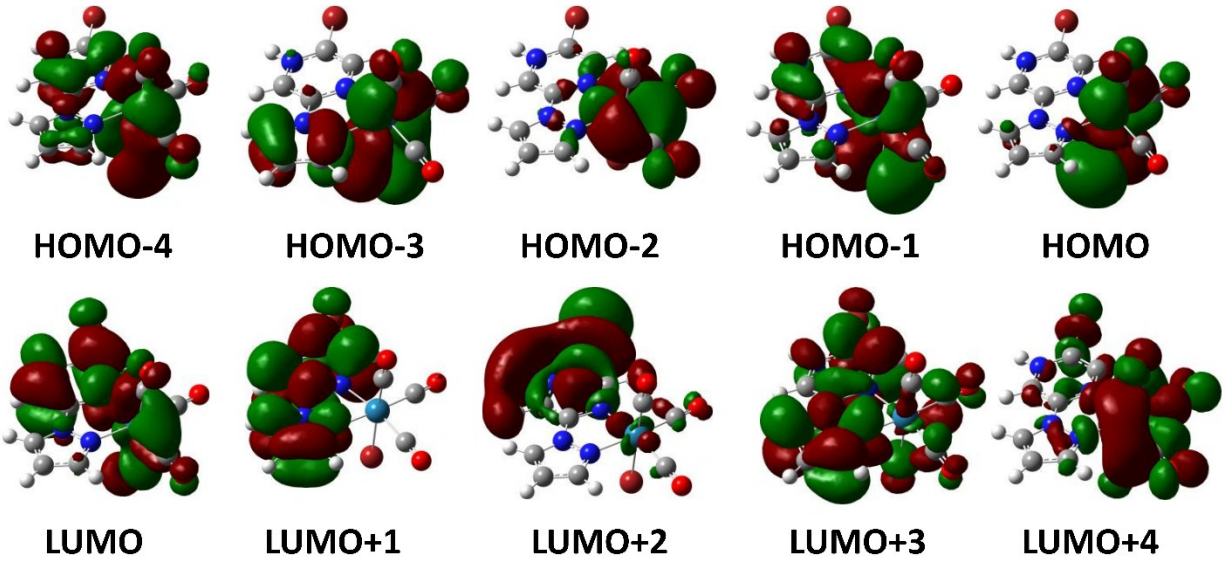


Figure S2. Frontier and near frontier Kohn-Sham orbitals computed for **IH**$^{+}$.

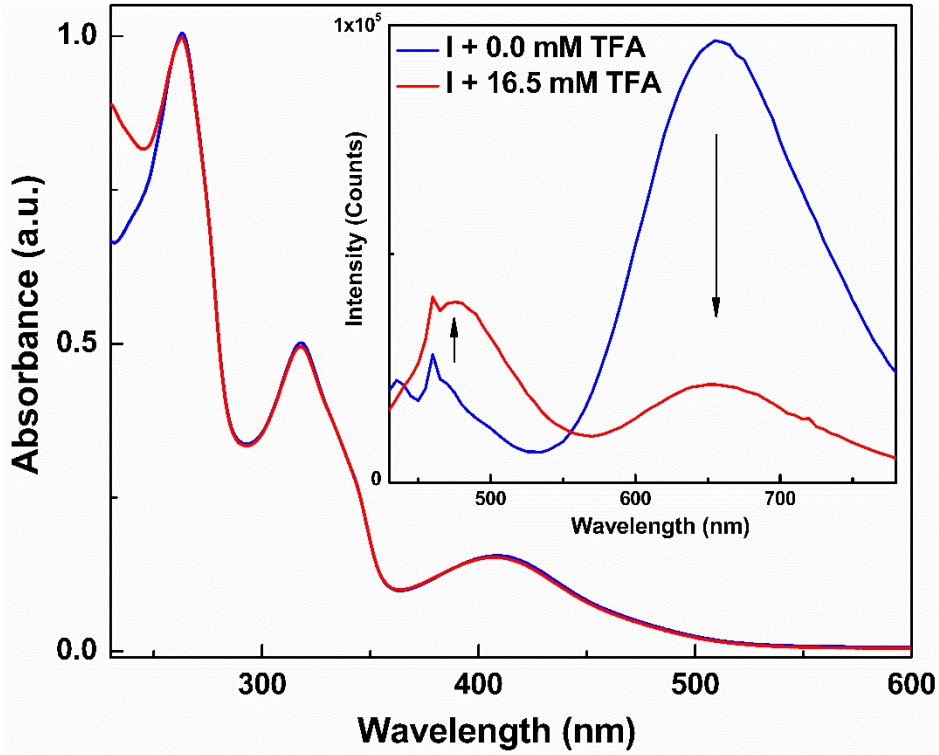


Figure S3. Absorption spectrum of **[(L$_I$)Re(CO)$_3$Br]** in DCM solution in absence of TFA (blue line) and in presence of 16.5 mM TFA (red line). Inset: Emission spectrum of **[(L$_I$)Re(CO)$_3$Br]** in DCM solution in absence and presence of TFA (λ_{exc} = 405 nm).

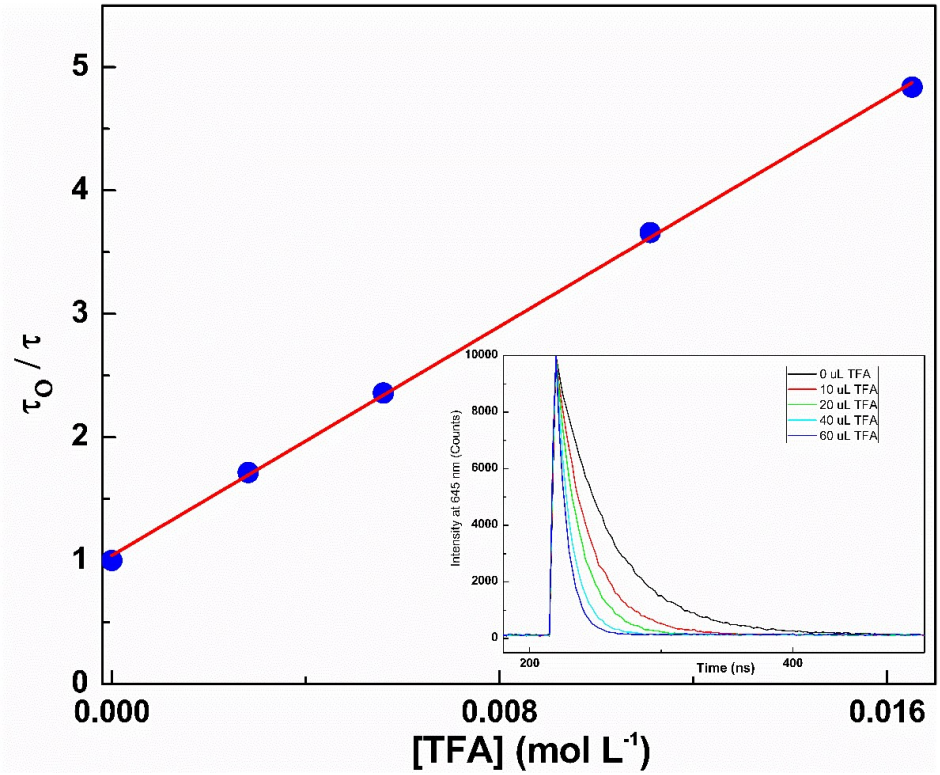


Figure S4. Stern-Volmer plot for the dynamic quenching of the MLCT excited state of **[(L_l)Re(CO)$_3$Br]** upon addition of trifluoroacetic acid in DCM solution. (λ_{exc} = 405 nm, λ_{em} = 645 nm).