Supporting Information

Synthesis, Photo-, and Electrochemistry of Ruthenium Tris(bipyridine) Complexes Comprising a *N*-heterocyclic Carbene Ligand

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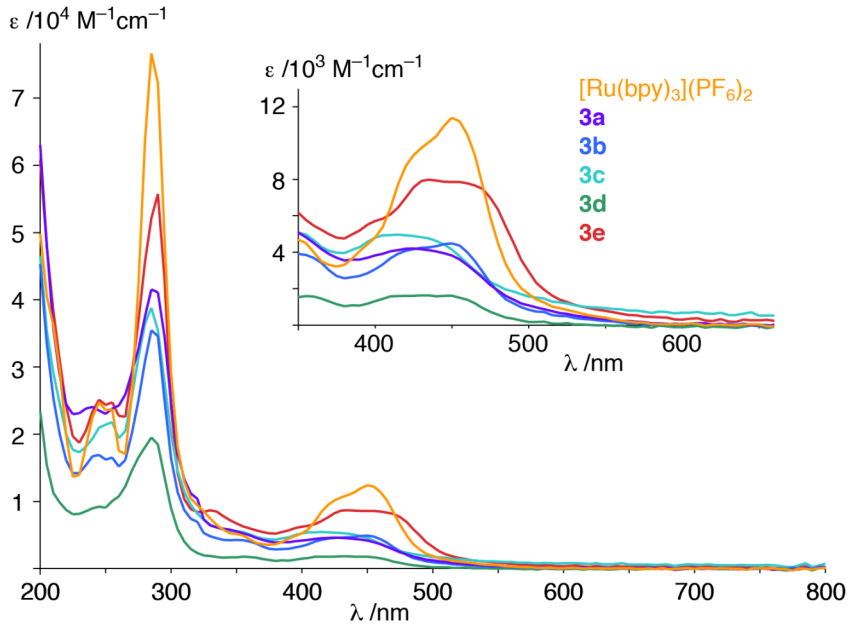

Figure S1 UV-vis spectra of complexes **3a–e** and $[Ru(bpy)_3](PF_6)_2$ recorded in MeCN solution, inset shows an expansion of the MLCT region.

Table S1. Maximum emission wavelengths of complexes **3a–e** upon irradiation at 355 nm.

complex	λ_{max}
3a	620 nm
3b	617 nm
3c	618 nm
3d	610 nm
3e	648 nm

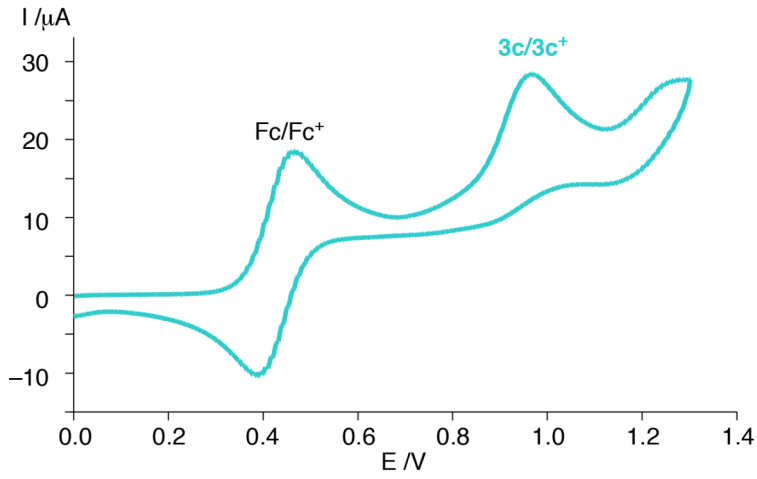

Figure S2 Cyclic voltammogram of complex **3c** in MeCN with internal standard ferrocene/ ferrocenium ($E_{1/2}$ = 0.46 V vs. SCE).

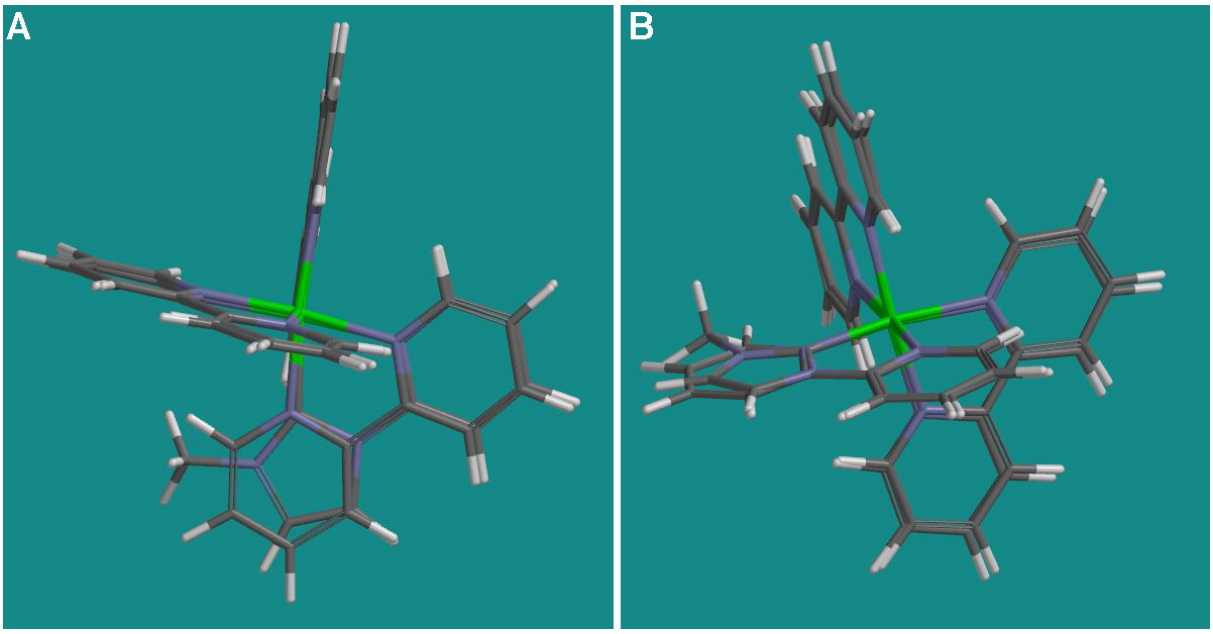

Figure S3 Superimposition of geometry-optimized structures (mm2) of $[Ru(bpy)_3]^{2+}$ and complex cation of **3a**, indicating the similar steric demand of the bpy and the carbene-pyridyl ligand with a methyl wingtip group. Panel A: view orthogonal to the carbene plane, with the carbene/pyridine superimposition at the bottom. Panel B: in-plane view with the carbene/pyridine superimposition on the left, clearly indicating a very similar steric impact of both ligands. The calculated bite angles of the pyridyl-carbene ligand (β = 77.7°) is only marginally different from the bite angle of the bpy ligand (β = 77.3°).

Table S2. Crystal data and structure refinement for complexes **2a** and **5**.

	2a	**5**
CCDC number	922584	922585
Empirical formula	$C_{19}H_{23}ClF_6N_3PRu$	$C_{25}H_{30}F_6N_6O_8RuS_4$
Formula weight	574.89	885.86
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1$ (#4)
Unit cell dimensions	a = 11.9352(4) Å	a = 9.3866(3) Å
	b = 10.9933(3) Å	b = 10.9572(3) Å
	c = 16.9445(4) Å	c = 16.3408(5) Å
	β = 96.926(2)°	β = 91.475(3)°
Volume	2206.99(10) $Å^3$	1680.11(9) $Å^3$
Z	4	2
Density (calculated)	1.730 Mg m^{-3}	1.751 Mg m^{-3}
Absorption coefficient	0.966 mm^{-1}	0.805 mm^{-1}
F(000)	1152	896
Crystal size	0.132 × 0.096 × 0.061 mm^3	0.149 × 0.096 × 0.087 mm^3
θ range	3.35–33.15°	3.35–29.81°
Index ranges	$-18 \le h \le 17$, $-16 \le k \le 16$, $-25 \le l \le 25$	$-12 \le h \le 12$, $-15 \le k \le 15$, $-22 \le l \le 21$
Reflections collected	113230	30148
Independent reflections	8059 [R(int) = 0.0591]	8421 [R(int) = 0.0291]
Completeness	99.9 % (θ = 31.00°)	99.3 % (θ = 28.00°)
Absorption correction	Analytical	Analytical
Max., min. transmission	0.954, 0.912	0.942, 0.911
Data	8059	8421
Restraints, parameters	0, 284	1, 457
Goodness–of–fit	1.062	1.063
Final R indices [I>2σ(I)]	R1 = 0.0386, wR2 = 0.1009	R1 = 0.0335, wR2 = 0.0814
R indices (all data)	R1 = 0.0493, wR2 = 0.1055	R1 = 0.0357, wR2 = 0.0829
Flack parameter	n.a.	–0.01(2)
Largest diff. peak, hole	3.692, –1.334 e $Å^{-3}$	1.922, –0.602 e $Å^{-3}$