Compound	**1a**	**2a**	**1b**	**2b**	**3a**	**3b**	**4a**
Empirical Formula	$C_{26}H_{19}F_6N_6OPRu$	$C_{26}H_{19}F_6N_6PRuS$	$C_{21}H_{18}F_6N_9O_{1.50}PRu$	$C_{21}H_{18}F_6N_9PRuS$	$C_{55}H_{39}FeN_{11}O_4PRu$	$C_{50}H_{38}FeN_{14}O_9PRu$	$C_{55}H_{39}CrN_{11}O_2PRu$
fw	677.51	693.57	666.48	674.54	1105.86	1166.83	1070.01
T / K	293(2)	293(2)	293(2)	298(2)	298(2)	298(2)	293(2)
λ / Å	0.71073	0.71069	0,71073	0.71069	0.71069	0.71073	0.71073
Cell	triclinic	triclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space Group	P-1	P-1	C 1 2/c 1	P-1	P-1	P-1	P-1
a / Å	8.8528 (8)	8.850 (5)	16.1761 (7)	8.6230 (2)	12.9718 (18)	11.1358 (2)	12.977 (5)
b / Å	10.2803 (8)	10.115 (5)	20.1670 (6)	10.4796 (2)	13.3882 (12)	13.3970 (2)	13.373 (5)
c / Å	16.3142 (16)	16.037 (5)	17.1565 (6)	14.7558 (4)	17.290 (2)	19.2367 (3)	17.402 (5)
α / °	78.212 (7)	77.086 (5)	90	87.312 (2)	102.217 (9)	88.057 (1)	101.762 (5)
β / °	77.158 (8)	78.323 (5)	111.174 (4)	81.518 (2)	96.540 (11)	76.142 (1)	96.183 (5)
γ / °	67.662 (8)	70.776 (5)	90	73.325 (2)	113.410 (11)	81.981 (1)	114.356 (5)
V / $Å^3$	1327.1 (2)	1308.3 (11)	5219.0 (3)	1263.36 (5)	2626.7 (5)	2759.07 (8)	2630.4 (16)
Z	2	2	8	2	2	2	2
$dens._{calc}$	1.695	1.761	1.696	1.773	1.398	1.405	1.351
μ (abs. coef.) / mm^{-1}	0.73	0.81	0.74	0.84	0.65	0.63	0.57
final index (R1)	0,0713	0,1238	0,0489	0,0372	0,0678	0,0350	0,0783
I>2σ(I) (wR2)	0,1942	0.3379	0,1393	0,0981	0,1671	0,1064	0,2022
all data (R1)	0,0815	0,1835	0,0643	0,0455	0,1100	0,0436	0,1570
all data (wR2)	0,2065	0.3574	0,1491	0,1019	0,1998	0,1106	0,2384

Table S1. Crystallographic data for compounds **1a-b**, **2a-b**, **3a-b** and **4a**.

2a	**2b**	**4a**
Distances / Å		
Ru-NCS 2,053(10) **RuN-CS** 1.127(18) **RuNC-S** 1.646(17)	**Ru-NCS** 2,034(3) **RuN-CS** 1.161(5) **RuNC-S** 1.622(4)	**Ru-NC_{bridge}** 2,037(2) **RuN-C_{bridge}** 1,144(3) **NC_{bridge}-Cr** 2.076(3) **Ru-Cr** 5,218
Ru-N_{tpy} 2.068 (11) 2.056 (12) 1.970 (10)	**Ru-N_{tpm}** 2.051(3) 2.084(3) 2.081(3)	**Ru-N_{tpy}** 2,078(2) 2,060(2) 1,966(2)

Ru-N_{bpy} 2.085 (11) 2.042 (11)	**Ru-N_{bpy}** 2.048(3) 2.056(3)	**Ru-N_{bpy}** 2,076(2) 2,049(2)
Angles / º		
Ru-N-CS 174.41 (12)	**Ru-N-CS** 168.6(3)	**Ru-N-C_{bridge}** 170,1(2)
N-C-S 179.49 (15)	**N-C-S** 178,8 (4)	**N-C_{bridge}-Cr** 173,8(3)
N_{tpy}-Ru-N_{tpy} 80.46 (4) 78.87 (4)	**N_{tpm}-Ru-N_{tpm}** 87.22(10) 86.24(10) 82.16(10)	**N_{tpy}-Ru-N_{tpy}** 79,33(9) 79,23(10)
N_{bpy}-Ru-N_{bpy} 78.52 (4)	**N_{bpy}-Ru-N_{bpy}** 78.78(11)	**N_{bpy}-Ru-N_{bpy}** 78,52(8)
		torsion 0.78

Table S2. Selected bond distances and angles for the compounds **2a**, **2b, 4a.**

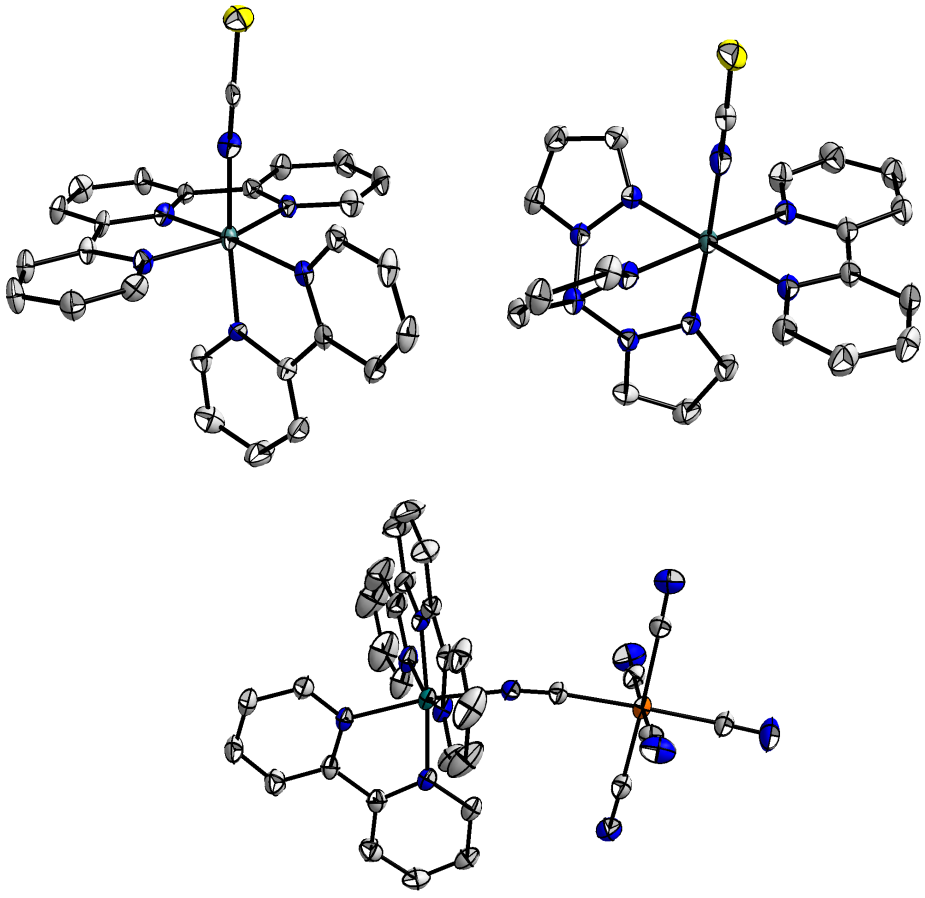

Figure S1. Crystal structures of the complexes **2a** (top, left), **2b** (top, right) and **4a** (bottom). Ellipsoids drawn with 30% displacement probability. Hydrogen atoms, counter ions and solvent molecules were omitted for clarity.

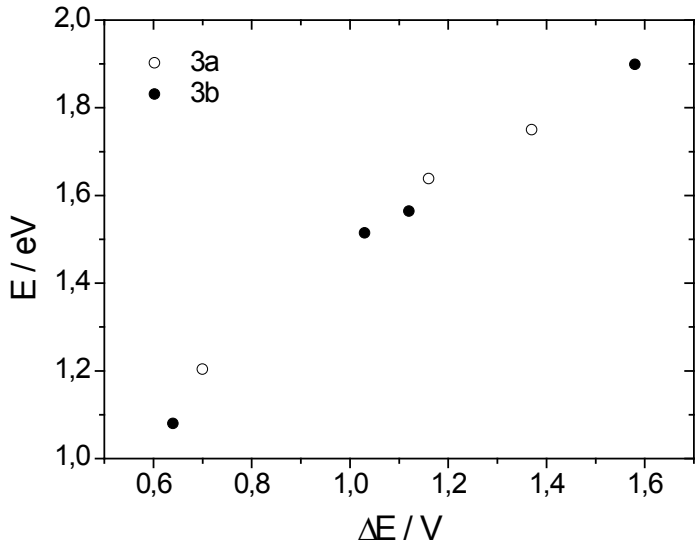

Figure S2. Correlation between the energy of the MM'CT band and the difference in the redox potentials of iron and ruthenum centers for compounds **3a** and **3b** in water, MeOH, EtOH and ACN.

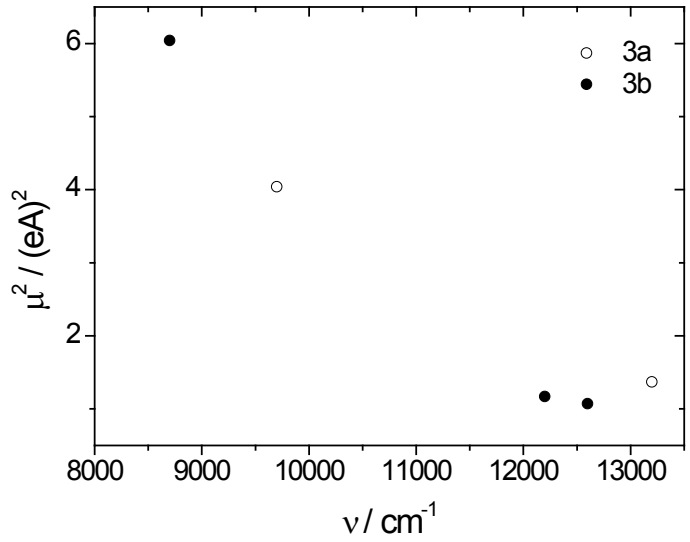

Figure S3. Correlation between the transition moment and the energy of the MM'CT transition for compounds **3a** and **3b** in water, MeOH and EtOH.