SUPPORTING INFORMATION

Self Assembled Multinuclear Complexes for Cobalt(II/III) Mediated Sensitized Solar Cells

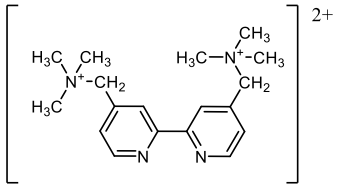
Edoardo Marchini *[1], Stefano Caramori *[1], Rita Boaretto [1], Vito Cristino [1], Roberto Argazzi [2], Alessandro Niorettini [1] and Carlo Alberto Bignozzi [1]

[1] Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy. E-mail: bar@unife.it, crsvti@unife.it, nrtlsn@unife.it, g4s@unife.it
[2] CNR-ISOF c/o Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121, Ferrara, Italy. E-mail: agr@unife.it
* Correspondence: E.M. mrcdrd@unife.it; S.C. cte@unife.it; Tel.: +39 0532455146

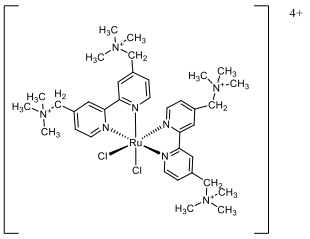
Table of contents:

Structure of the synthesized species

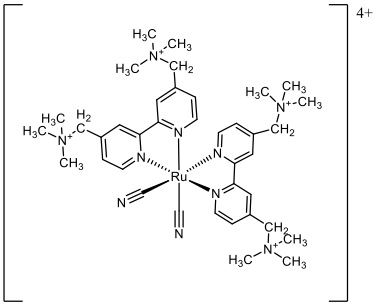
(a)



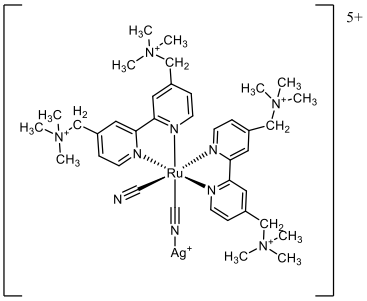
(b)



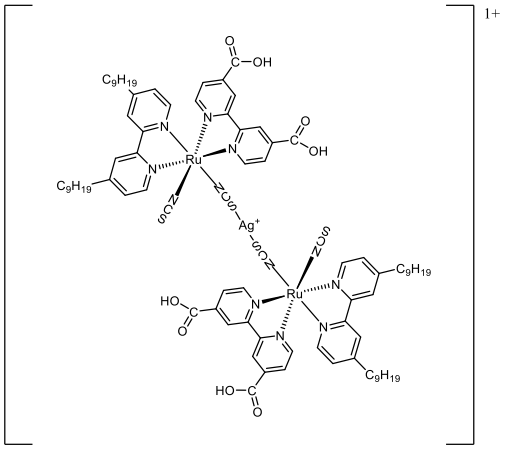
(c)



(d)



(e)



(f)

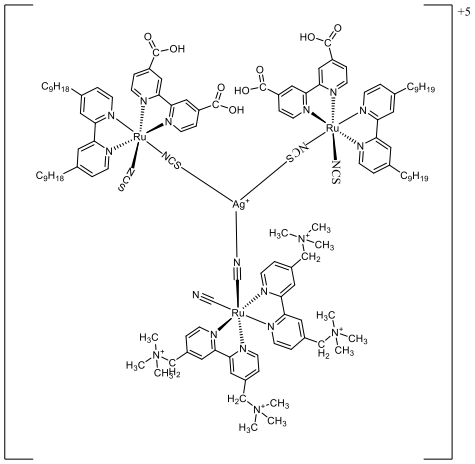


Figure S1: Structure of the chemical species reported in this work: (a) TMAM (4,4' -bis(trimethylaminomethyl)2,2'bipyridine), (b) $[Ru(TMAM)_2Cl_2](PF_6)_4$, (c) **1** (Ru(TMAM)), (d) **2** (Ru(TMAM))-Ag^+), (e) **3** (2Z907-Ag^+) and (f) **4** (2Z907-Ag^+-(Ru(TMAM)))

^{1}H-NMR spectrum of the TMAM ligand

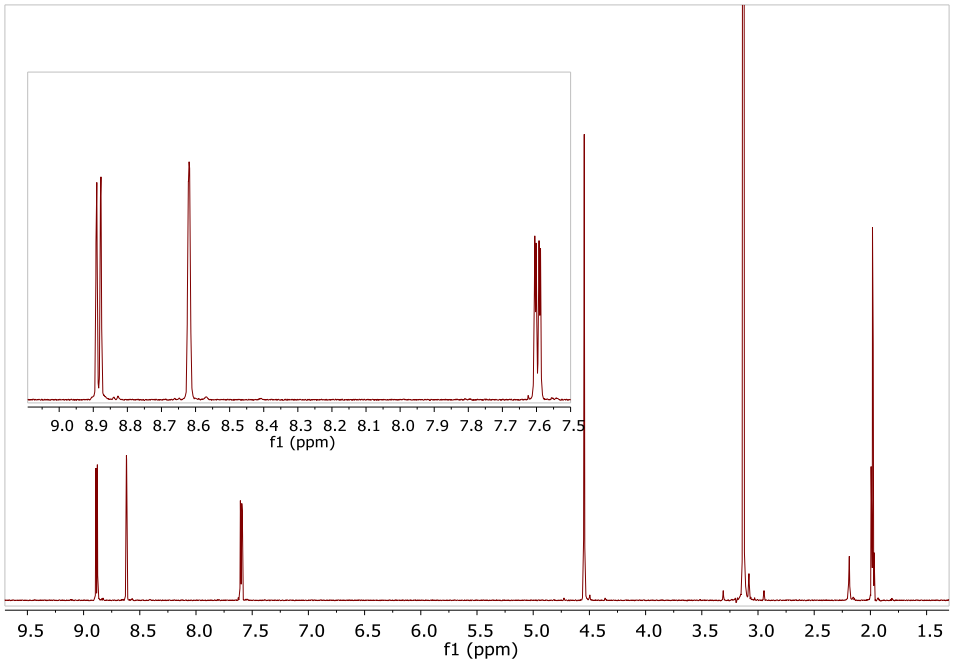


Figure S2: ^{1}H NMR (400 MHz, Acetonitrile-d_3, δ ppm) of TMAM: 8.88 (dd, *J* = 5.0, 0.8 Hz, 2H), 8.62 (dd, *J* = 1.9, 0.8 Hz, 2H), 7.60 (dd, *J* = 5.0, 1.8 Hz, 2H), 4.55 (s, 4H), 3.13 (s, 18H)

^{1}H and ^{13}C NMR spectra of the complex 1 (Ru(TMAM))

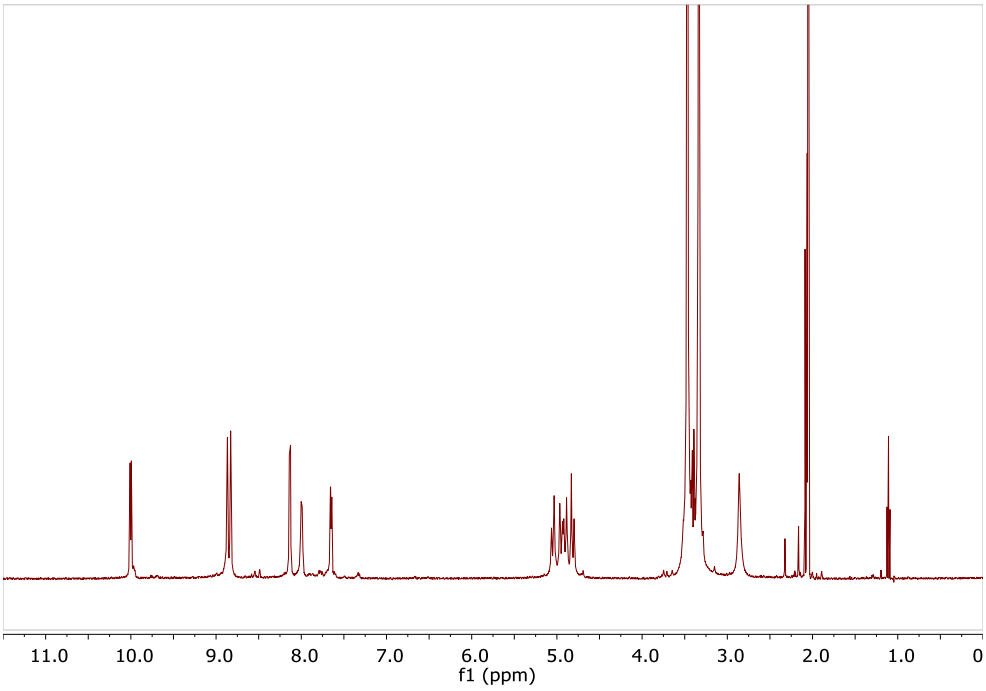


Figure S3: ^{1}H NMR (400 MHz, Acetone-d_6, δ ppm) of the complex **1** (Ru(TMAM)): 10.00 (d, J = 5.8 Hz, 2H), 8.87 (s, 2H), 8.83 (s, 2H) 8.13 (d, J = 5.7 Hz, 2H), 7.99 (d, J = 6.0 Hz, 2H), 7.65 (dd, J = 5.7, 1.7 Hz, 2H),5.06 – 4.86 (m, 8H), 3.49 (s, 18H), 3.39 (s, 18H)

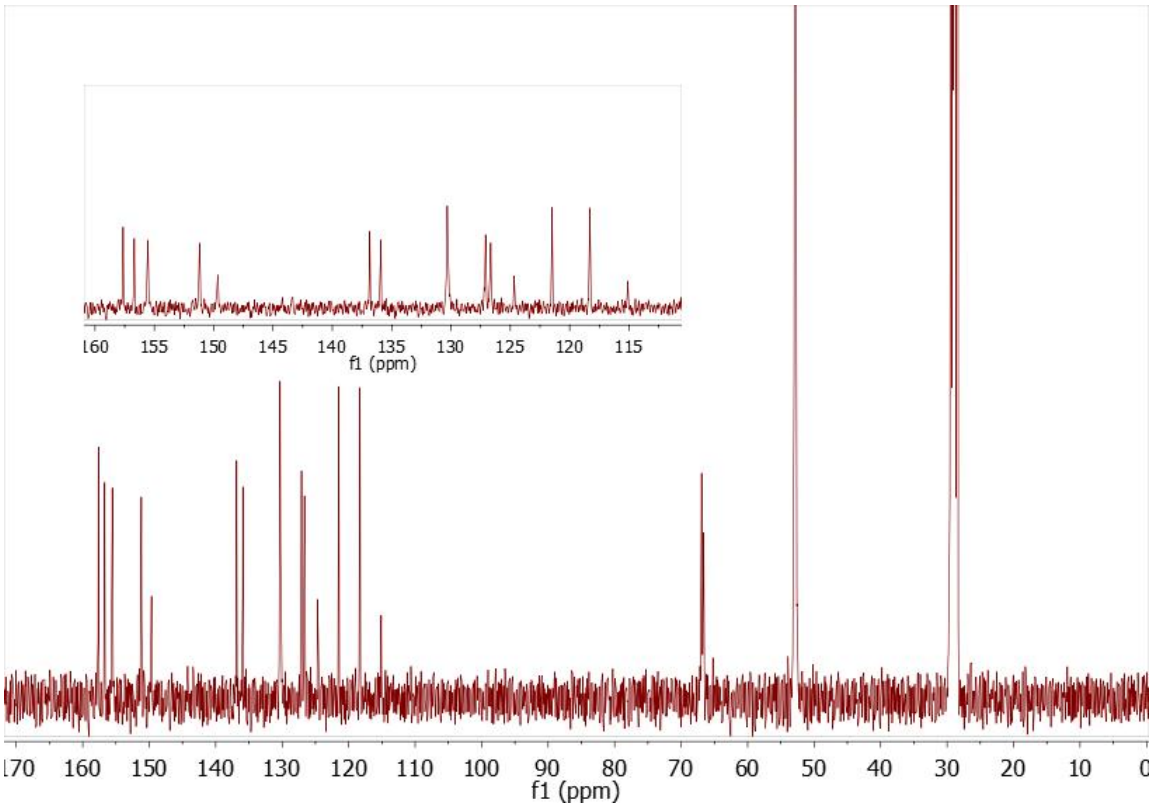


Figure S4: ^{13}C NMR (400 MHz, Acetone-d_6, δ ppm) of the Complex **1** (Ru(TMAM)): 157.63, 157.69, 155.55, 151.18, 149.65, 136.85, 135.92, 130.30, 127.09, 126.66, 66.92, 66.61, 52.91, 52.80

ESI-MS spectrum of the complex 1 (Ru(TMAM))

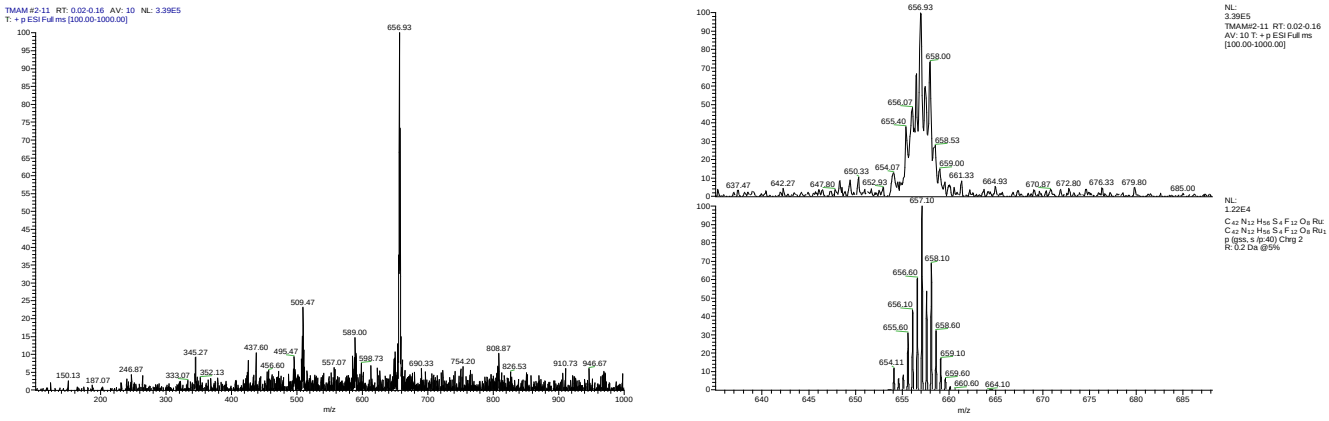


Figure S5: (a) ESI-MS spectrum of the complex **1** (Ru(TMAM)), m/z 656.93 $[M\text{-}2TFSI]^{2+}$, (b) Theoretical and experimental Ru distribution

^{1}H and ^{13}C NMR spectra of the complex 2 ((Ru(TMAM))-Ag^{+})

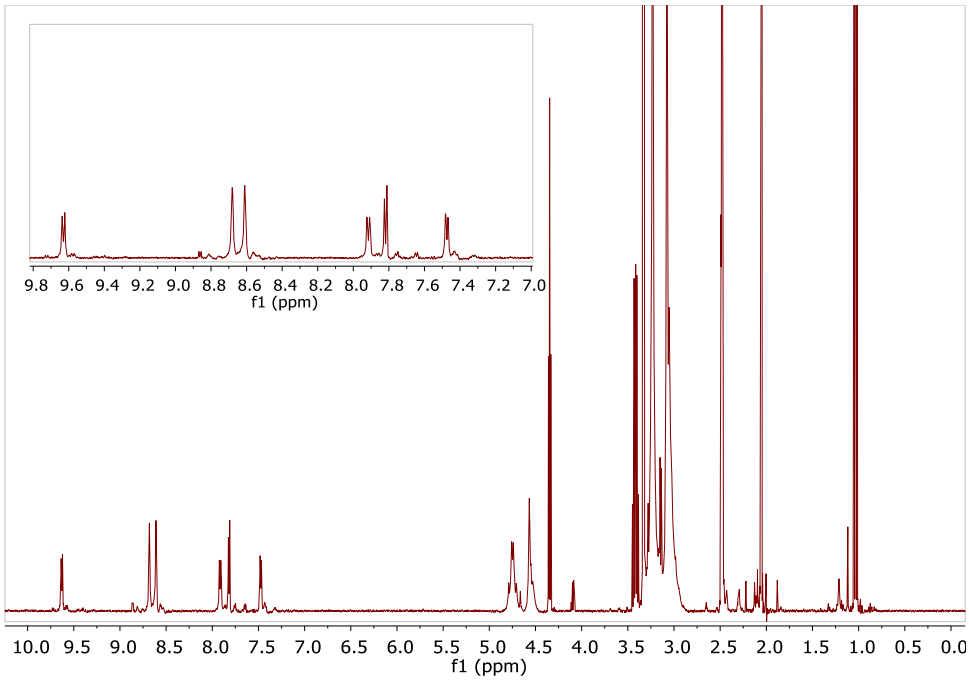


Figure S6:^{1}H NMR (400 MHz, DMSO-d_6, δ ppm) of the complex **2** (Ru(TMAM)-Ag^{+}): 9.63 (1H), 8.68 (1H), 8.61 (1H), 7.92 (1H), 7.82 (1H), 7.47 (1H), 4.74 (2H), 4.55 (2H), 3.23 (9H), 3.08 (9H)

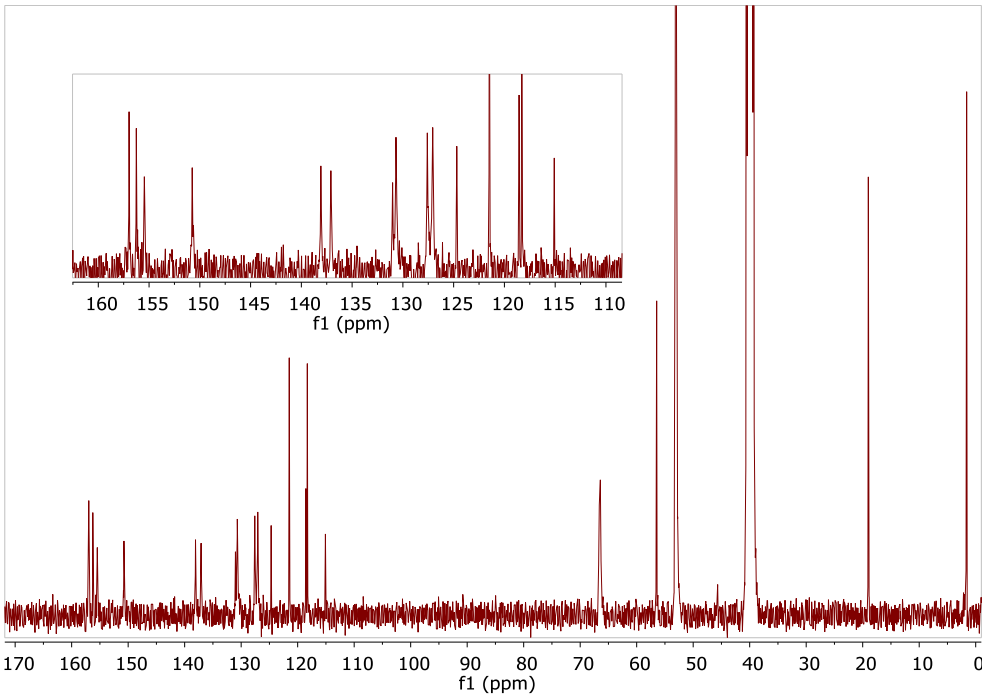


Figure S7: ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm) of the complex **2** (Ru(TMAM)-Ag^{+}): 156.97, 156.26, 155.47, 150.75, 138.08, 137.09, 131.01, 130.68, 127.59, 127.06, 118.55, 66.62, 66.43, 56.46, 53.14

^{1}H and ^{13}C NMR spectra of the complex 3 (2Z907-Ag^{+})

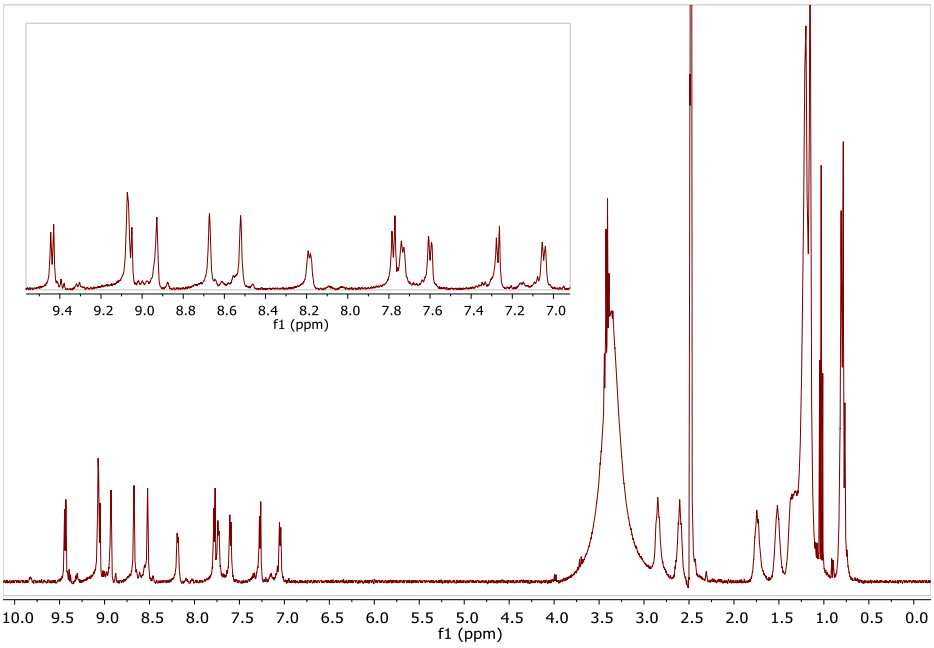


Figure S8:^{1}H NMR (400 MHz, DMSO-d_6, δ ppm) of the complex **3** (2Z907-Ag^{+}): 9.44 (1H), 9.06 (2H), 8.93 (1H), 8.67 (1H), 8.52 (1H), 8.19 (1H), 7.79 – 7.73 (2H), 7.60 (1H), 7.27 (1H), 7.06(1H), 2.85 (2H), 2.61 (2H), 1.75 (2H), 1.52 (2H), 1.32 – 1.15 (24H) 0.78 (6H)

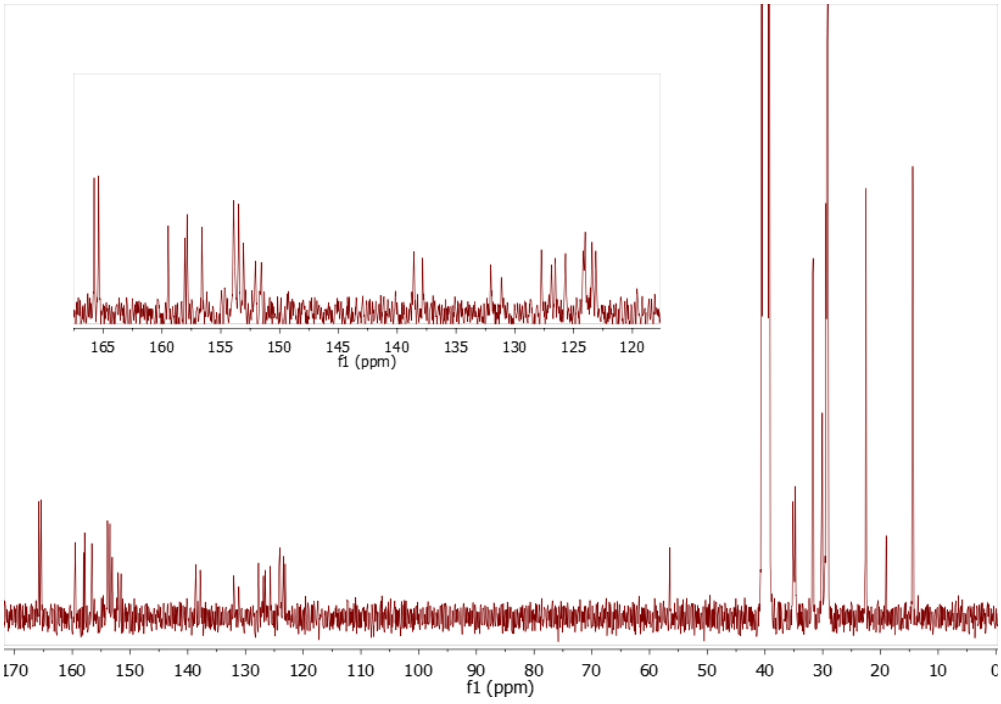


FIGURE S9: ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm) of the complex **3** (2Z907-Ag^{+}): 165.77, 165.39, 159.47, 158.06,157.87, 156.62, 153.90, 153.48,153.08, 152.06, 151.56,138.59, 137.84, 132.04, 131.15, 127.75, 126.56, 125.70, 124.18,124.02, 123.43,123.11, 35.14, 34.73, 31.76, 31.66, 30.28, 30.09, 29.42, 29.32, 29.28, 29.18, 29.14, 29.06, 22.57, 22.51, 14.43, 14.39

^{1}H and ^{13}C NMR spectra of the complex 4 (2Z907-Ag^{+}-(Ru(TMAM)))

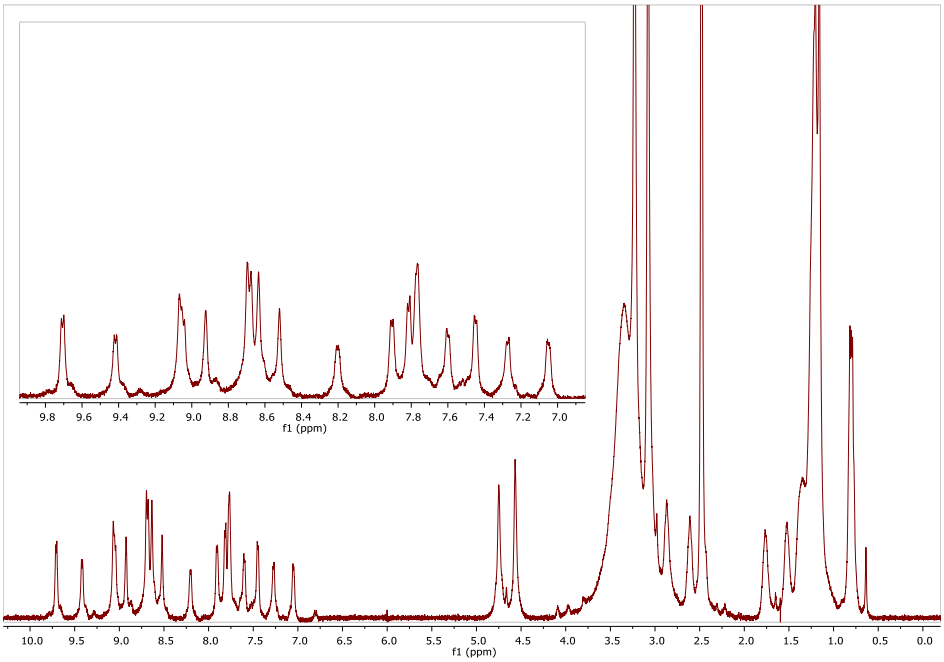


Figure S10: ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm) of the complex **4** (2Z907-Ag^{+}-Ru(TMAM)): 9.71 (1H), 9.42 (1H), 9.05 (2H), 8.93 (1H), 8.72 -8.63 (3H), 8.52 (1H), 8.21 (1H), 7.91 (1H), 7.82 (1H), 7.77 (2H), 7.60 (1H), 7.45 (1H), 7.28(1H),7.05 (1H), 4.75 (2H), 4.57 (2H), 3.21 (3H),2.98 (3H), 2.87 (2H), 2.61 (2H), 1.76 (2H), 1.52 (2H), 1.28 – 1.14 (24H), 0.8 (6H)

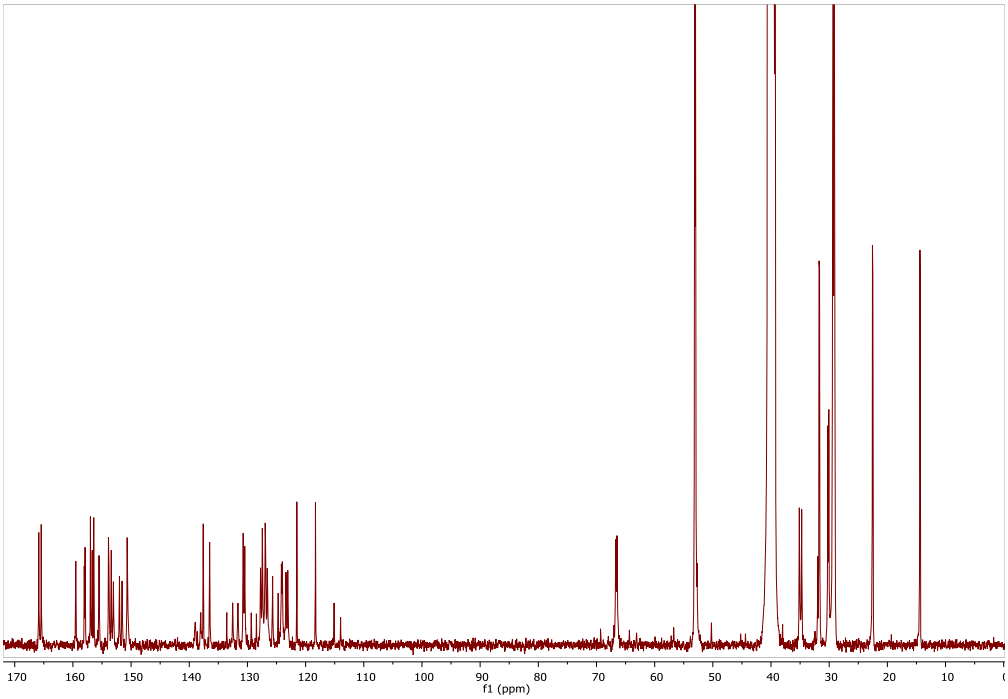


FIGURE S11: ^{13}C NMR (400 MHz, DMSO-d_6, δ ppm) of the complex **4** (2Z907-Ag^{+}-Ru(TMAM)): 165.87, 165.45, 159.51, 158.05, 157.91, 156.99, 156.48, 156.42, 155.51, 153.89, 153.41, 153.04, 152.00, 151.55, 150.66, 138.99, 138.03, 137.60, 136.50, 133.55, 132.53, 130.73, 130.46, 129.35 128.46, 127.75, 127.43, 126.95, 126.58, 125.67, 124.72, 124.16, 124.00, 123.37, 123.06, 66.68, 66.47, 53.12, 52.99, 35.13, 34.73, 31.75, 31.65, 30.22, 30.07, 29.42, 29.32, 29.26, 29.17, 29.12, 29.04, 22.56, 22.50, 14.41, 14.36

Spectroscopic features of the complexes

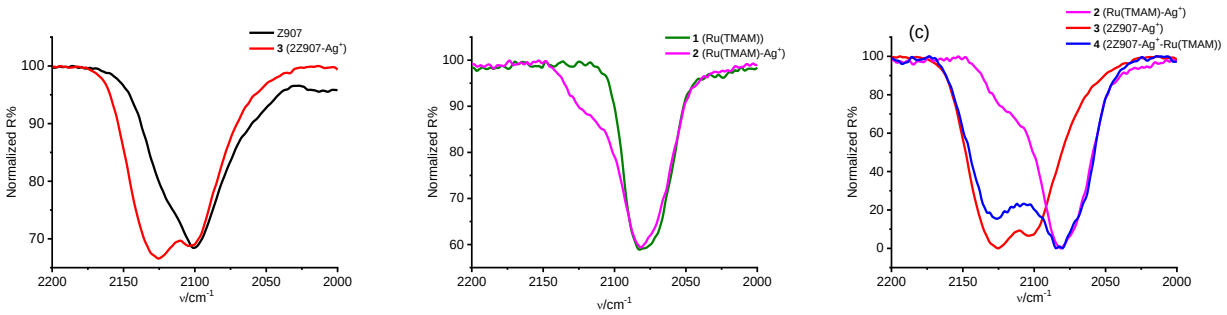


Figure S12: IR normal modes of NCS and CN groups in (a) **Z907** and of **3** (2Z907-Ag^+), (b) **1** (Ru(TMAM) and **2** (Ru(TMAM)-Ag^+) and (c) **2** (Ru(TMAM)-Ag^+), **3** (2Z907-Ag^+) and **4** (2Z907-Ag^+-Ru(TMAM))

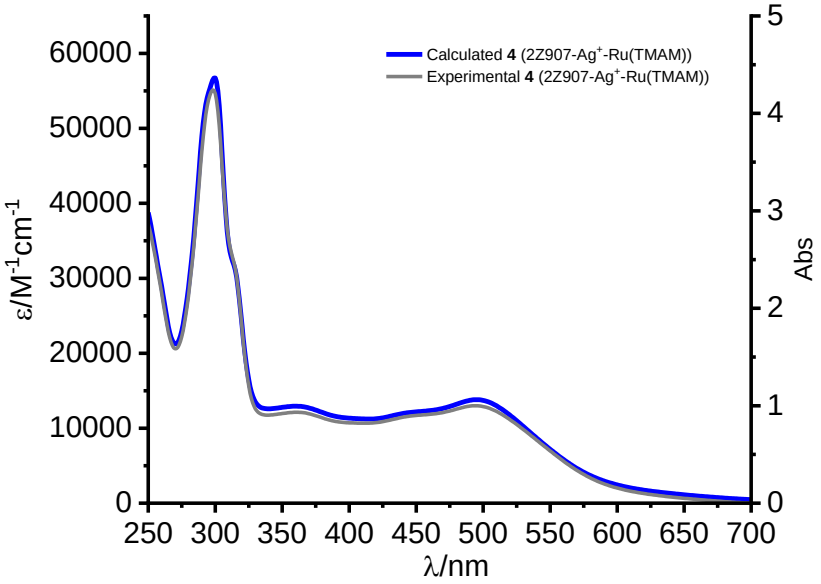


Figure S13: Comparison between calculated and experimental absorption spectra of the complex **4** (2Z907-Ag^+-Ru(TMAM))

TCSPC decay on ZrO_2

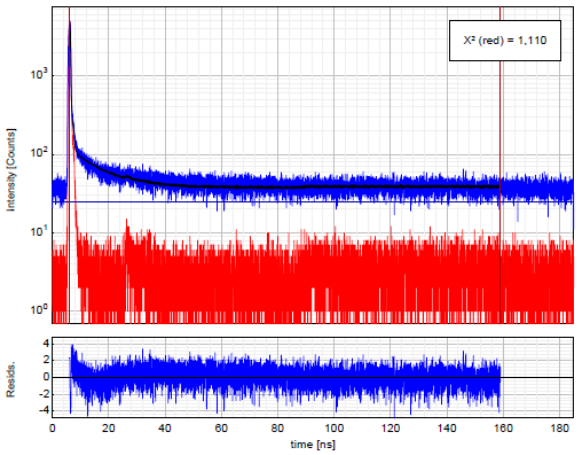


Figure S14: Bi-exponential decay of the luminescence of **4** (2Z907-Ag^+-Ru(TMAM)) loaded on ZrO_2 recorded at 640 nm (blue line)

Cyclic voltammetry of the complexes loaded on TiO_2

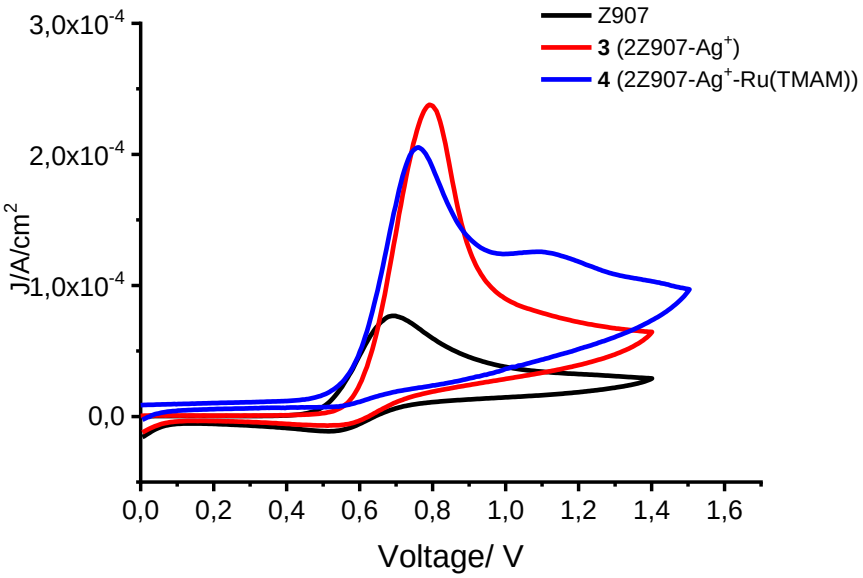


Figure S15: CVs of **Z907** (black line), **3** (2Z907-Ag^+) (red line) and of **4** (2Z907-Ag^+-Ru(TMAM)) (blue line) loaded on TiO_2 thin films

Charge separated state decay of 3 (2Z907-Ag$^+$)

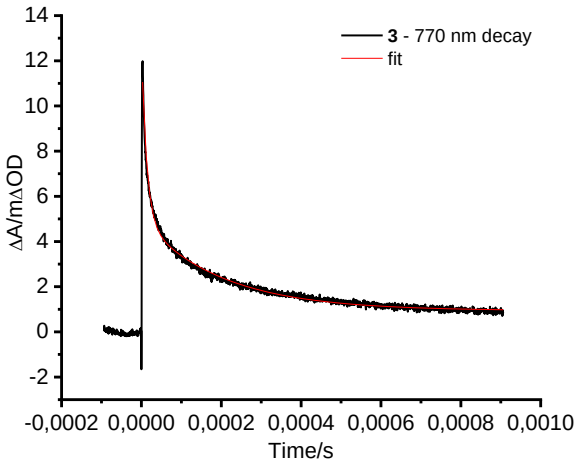


Figure S16: Bi-exponential decay of the transient absorption of the charge separated state of **3** (2Z907-Ag$^+$) on TiO_2 at 770 nm

Integrated current density

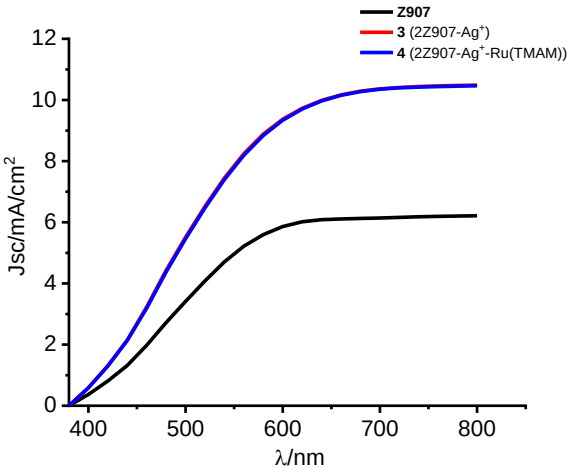


Figure S17: Integrated current density for **Z907** (black line), **3** (2Z907-Ag$^+$) (red line) and **4** (2Z907-Ag$^+$-Ru(TMAM)) (blue line) extracted via integration of the photoaction spectrum.