Heteropleptic ruthenium bis-terpyridine complexes bearing a 4-(dimethylamino)phenyl donor and free coordination sites for hydrogen photo-evolution

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Supporting Information

Synthesis

Preparation of 2-acetyl-4-*tert*-butylpyridine (work-up modified from previous report[1]):

In a 250 mL round-bottomed flask, 4-*tert*-butylpyridine (5 g), $AgNO_3$ (0.5 g) and pyruvic acid (9 g) were combined, followed by dichloromethane (50 mL) and water (10 mL). This mixture is cooled to 0 °C using an ice-water bath. Separately, $(NH_4)_2S_2O_8$ (12.5 g) was dissolved in water (40 mL) and concentrated H_2SO_4 (3 mL). This aqueous solution is then added dropwise over a period of about 15 minutes in the cooled round-bottomed flask, under stirring. Once the addition is complete, the biphasic mixture is slowly warmed-up to room temperature then refluxed for 4 hours. Once cooled down, the reaction mixture is poured onto ice (100 mL). Carefully, NaOH (10 M) is added until the pH is basic (9-10). The mixture is then filtered to remove the grey Ag_2O that formed upon addition of base. The two phases are then separated. The aqueous phase is washed with dichloromethane (50 mL). The two dichloromethane fractions are then combined and dried on Na_2SO_4. The Na_2SO_4 is washed with diethyl ether (50 mL) and the filtrate is added to the dichloromethane solution. The solvents are then removed under reduced pressure, until only about 20-30 mL of solution is left. It is then diluted with diethyl ether (75 mL), and this organic phase is washed three times with an aqueous citric acid solution (0.75M, 25 mL) [to remove the remaining 4-*tert*-butylpyridine which can be recycled using the workup described below]. The organic phase is then washed three times with hydrochloric acid (1 M, 25 mL). [The organic phase only contains the bis-acetyl by-product at this point.] The acidic aqueous phase is poured onto ice (50 ml) and neutralize with caution with NaOH (10 M) till pH 9-10. It is then extracted twice with diethyl ether (50 ml). The ether solution is filtered over a 1 cm bed of silica gel, the silica being washed with diethyl ether (30 mL). The diethyl ether is then removed under reduced pressure without heat, affording 2-acetyl-4-*tert*-butylpyridine as a light orange oil whose ^{1}H NMR spectra matched the literature. The yield varies between 25-30 % of 2-acetyl-4-*tert*-butylpyridine.

The reaction and purification can be followed by TLC on SiO_2 with 7/3 Hexane/Diethyl ether.

1. B. Laramée-Milette, T. Auvray, S. Nguyen, S. Tremblay, C. Lachance-Brais, M. Donguy, V. Taylor, D. Deschênes and G. S. Hanan, *Synthesis*, 2015, **47**, 3849-3858.

^{1}H NMR spectra

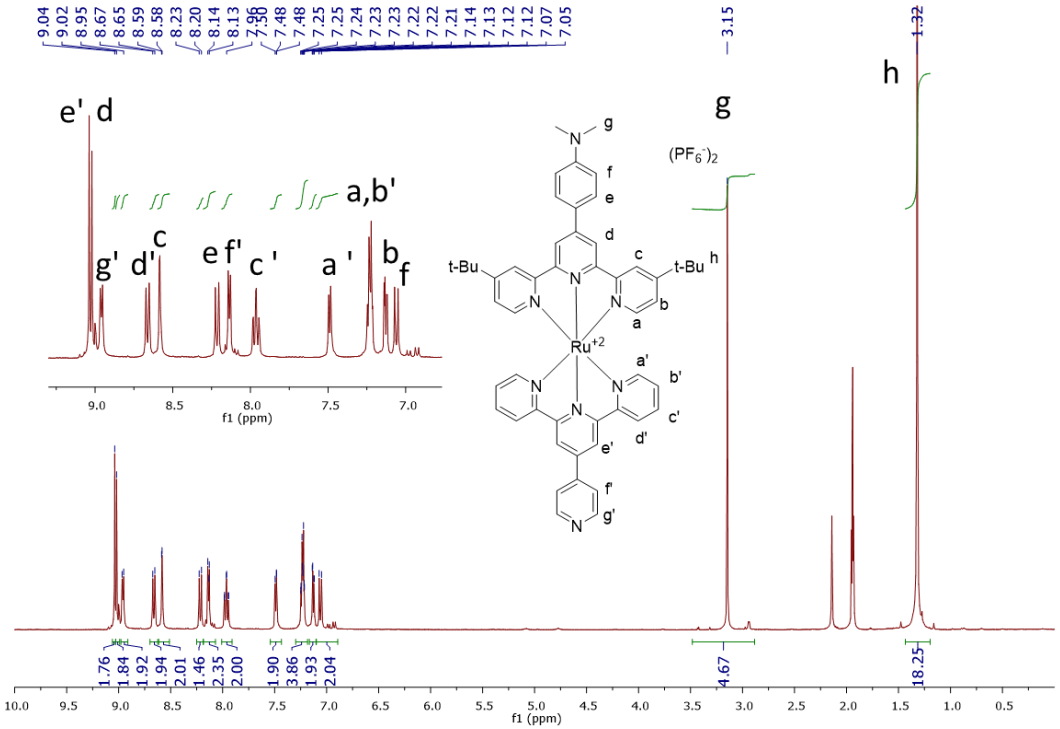


Figure S1 ^{1}H NMR spectra of complex **C1** in CD_3CN

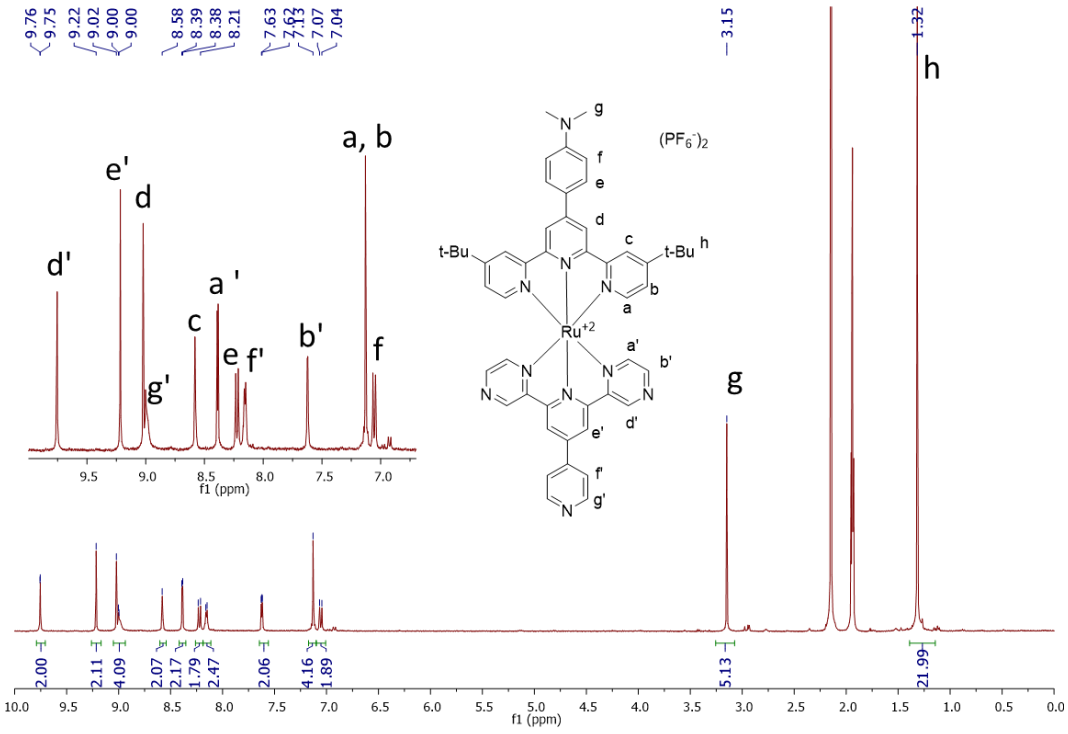


Figure S2 ^{1}H NMR spectra of complex **C2** in CD_3CN

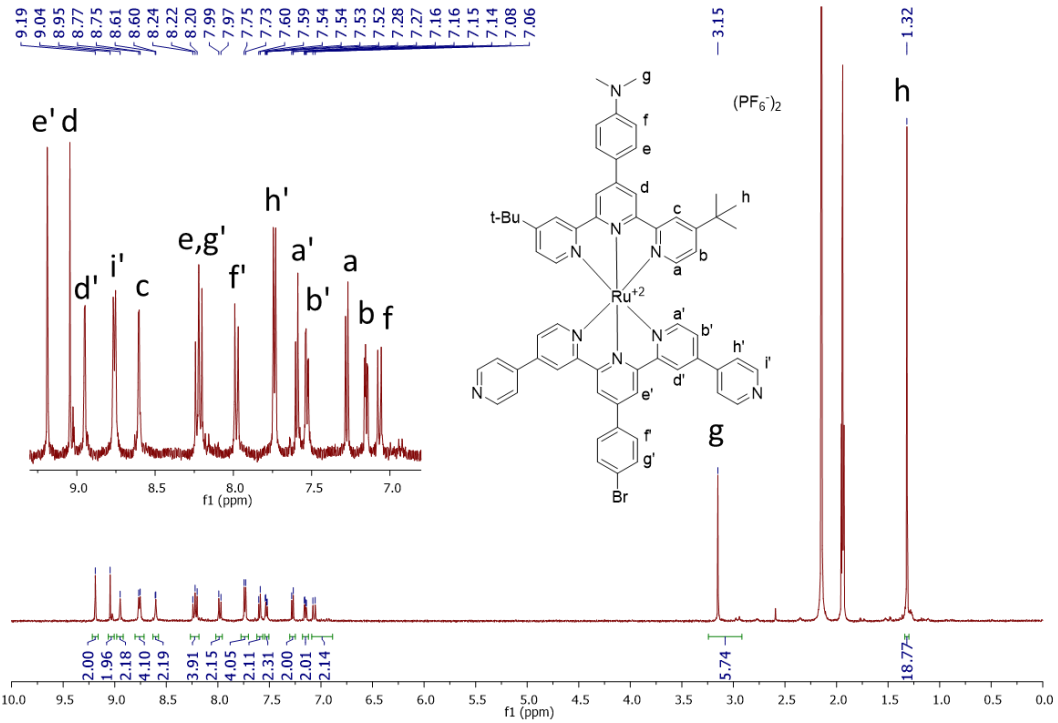


Figure S3 ^{1}H NMR spectra of complex **C3** in CD_3CN

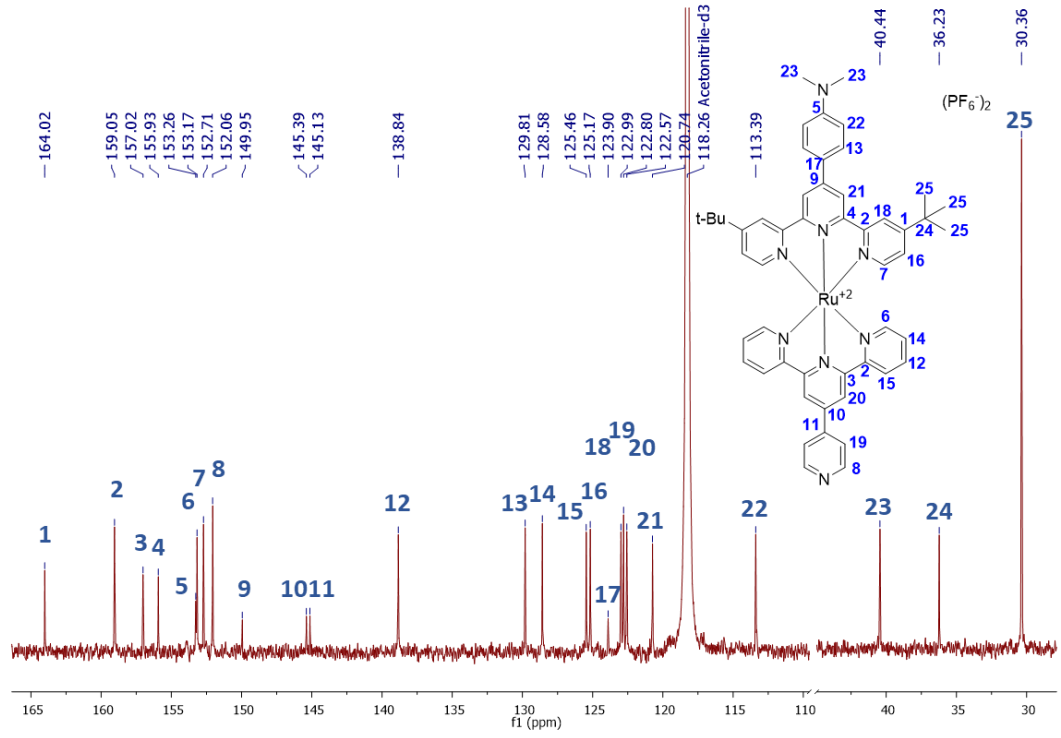


Figure S4 ^{13}C NMR spectra of complex **C1** in CD_3CN

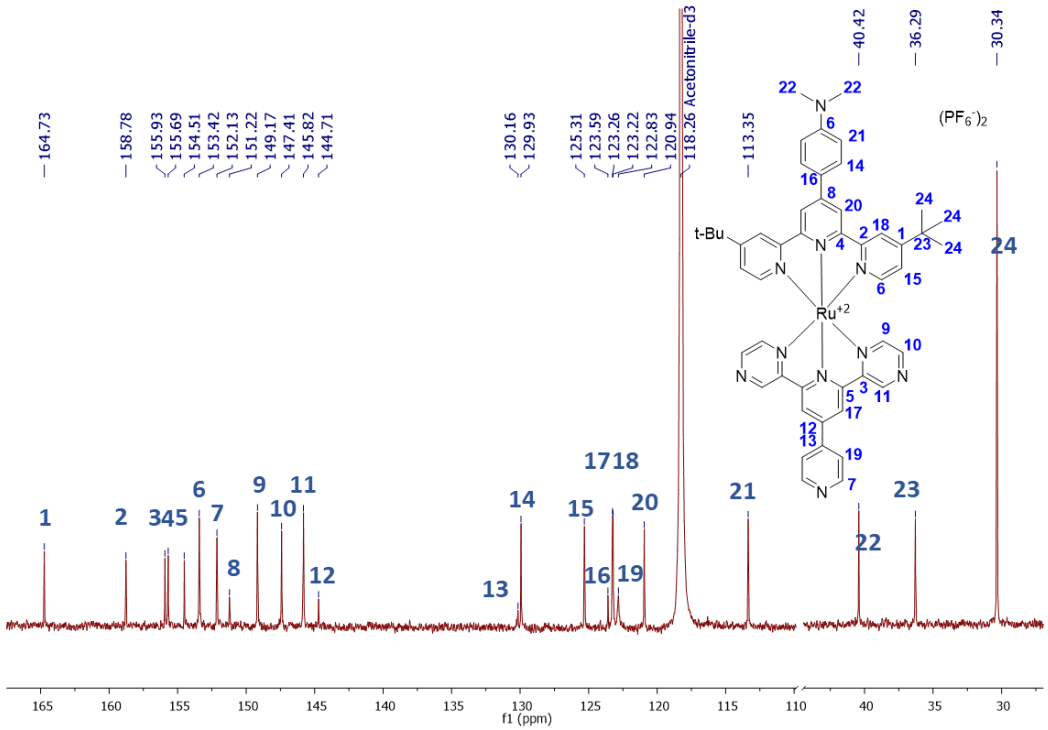


Figure S5 ^{13}C NMR spectra of complex **C2** in CD_3CN

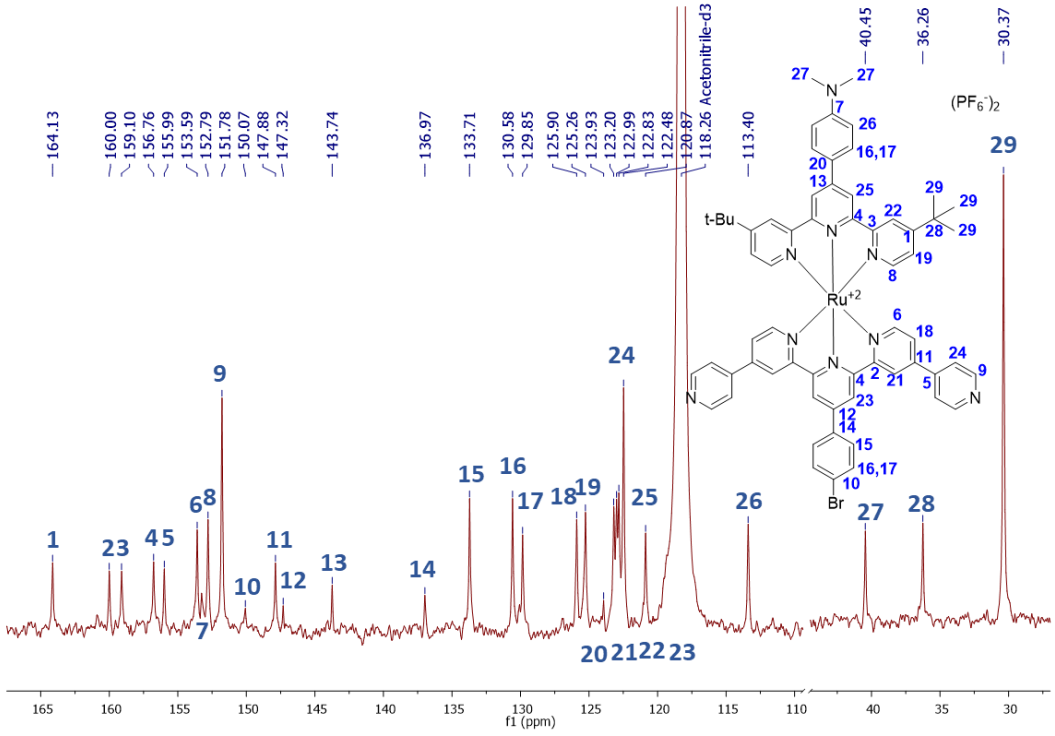


Figure S6 ^{13}C NMR spectra of complex **C3** in CD_3CN

ESI-MS (MeCN)

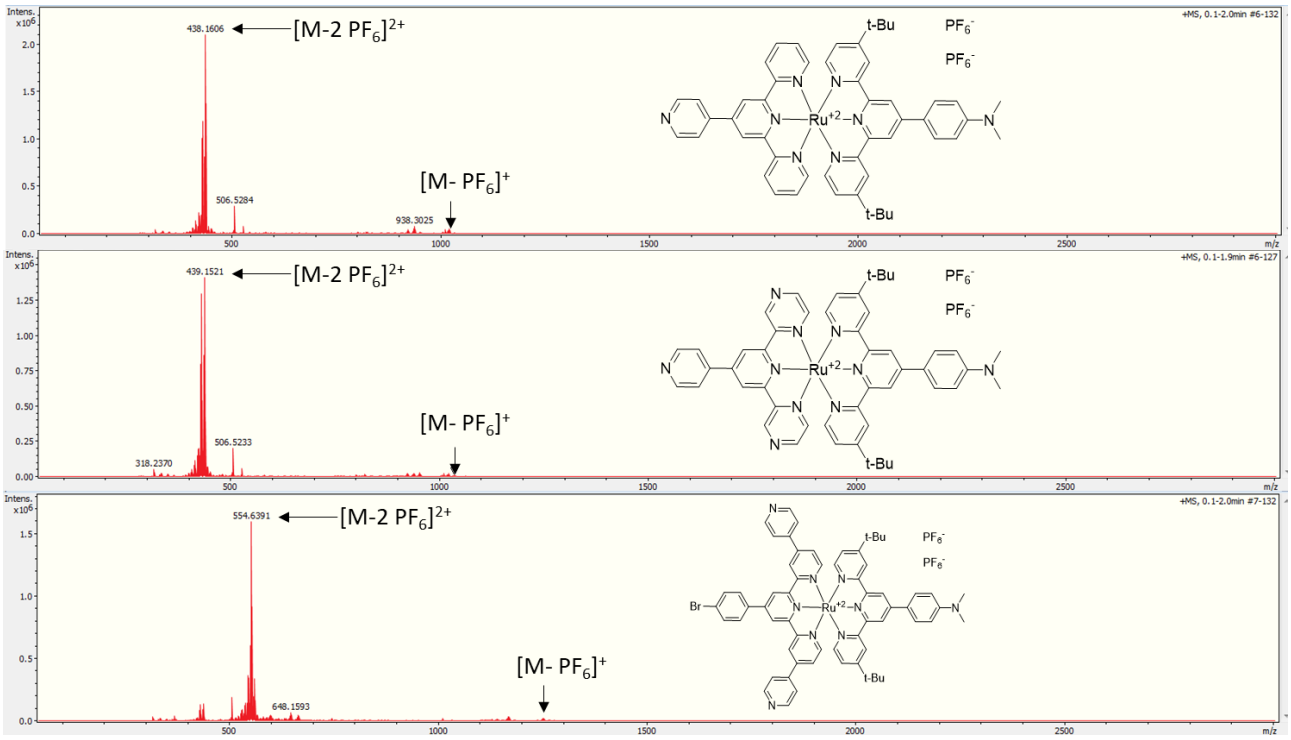


Figure S7 Complete chromatograms obtained by ESI-MS (CH_3CN, positive mode) for complexes **C1-C3**.

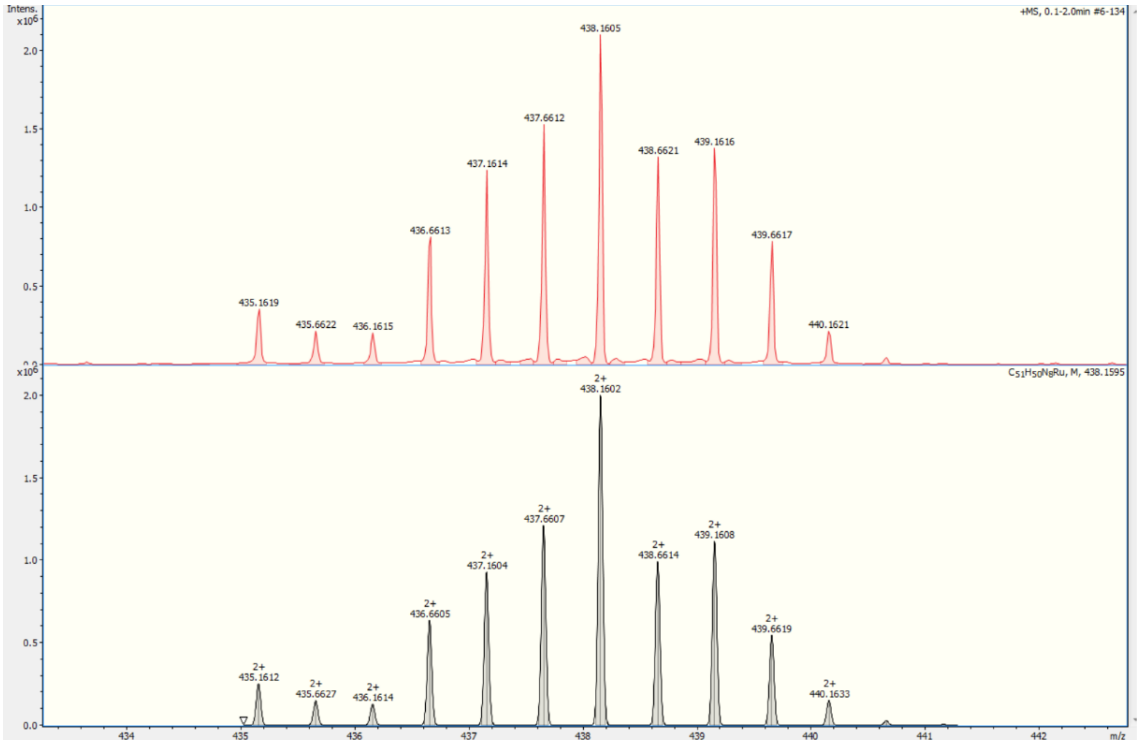


Figure S8 Experimental (top) and calculated (bottom) isotopic pattern for complex **C1**$^{2+}$

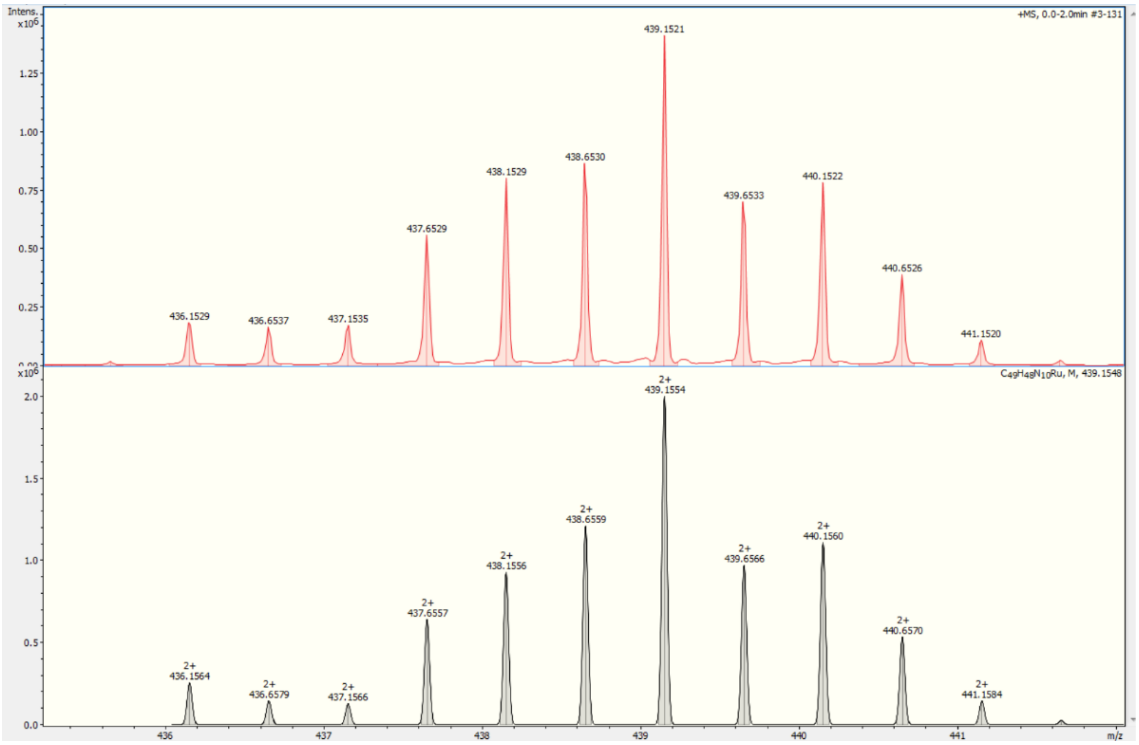


Figure S9 Experimental (top) and calculated (bottom) isotopic pattern for complex **C2**$^{2+}$

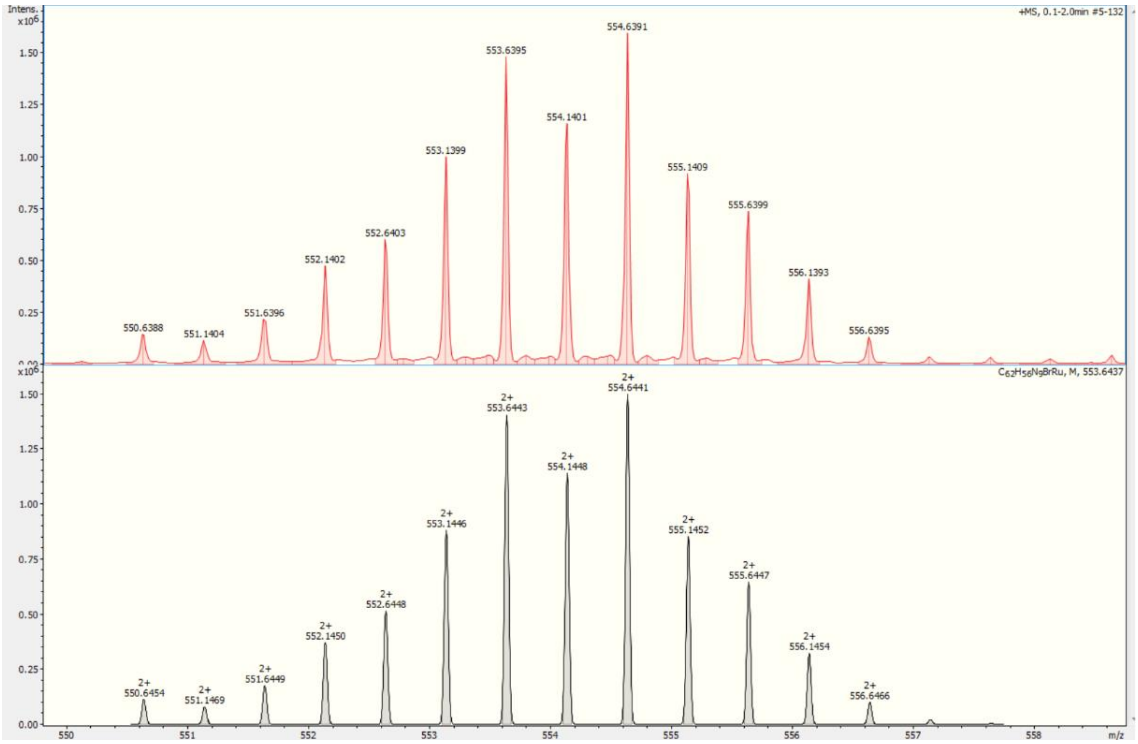


Figure S10 Experimental (top) and calculated (bottom) isotopic pattern for complex **C3**$^{2+}$

Electrochemical studies

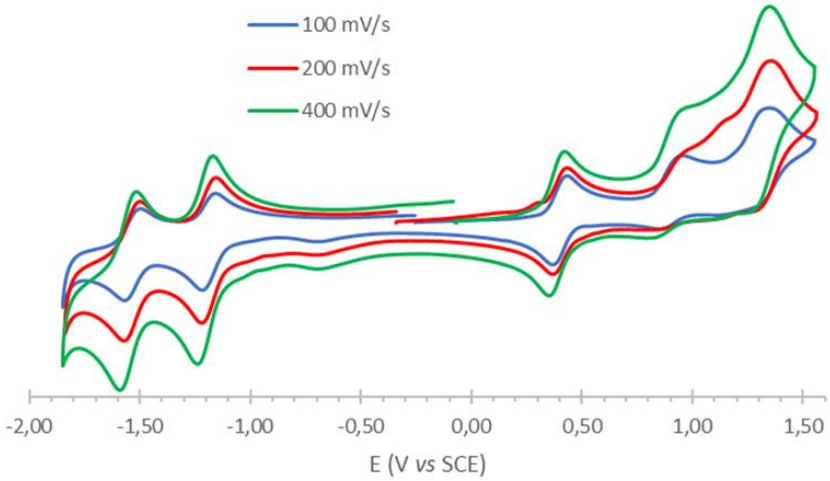


Figure S11 Cyclic voltammogram for **C1** in CH_3CN/TBAP 0.1 M with ferrocene at various scan rates.

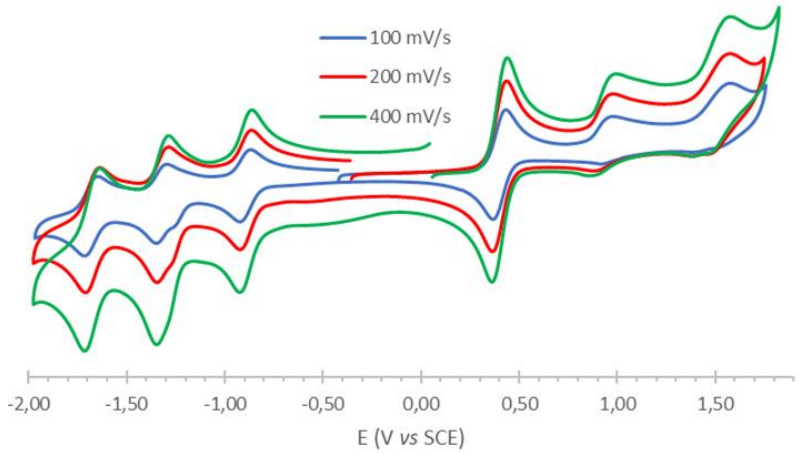


Figure S12 Cyclic voltammogram for **C2** in CH_3CN/TBAP 0.1 M with ferrocene at various scan rates.

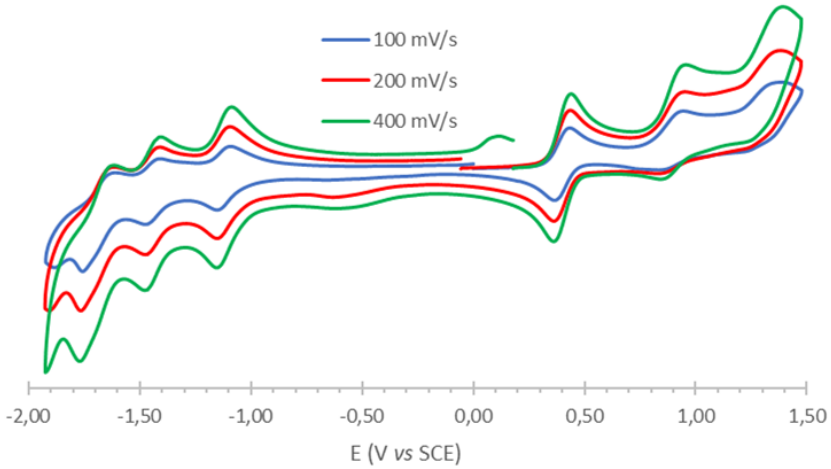


Figure S13 Cyclic voltammogram for **C3** in CH_3CN/TBAP 0.1 M with ferrocene at various scan rates.

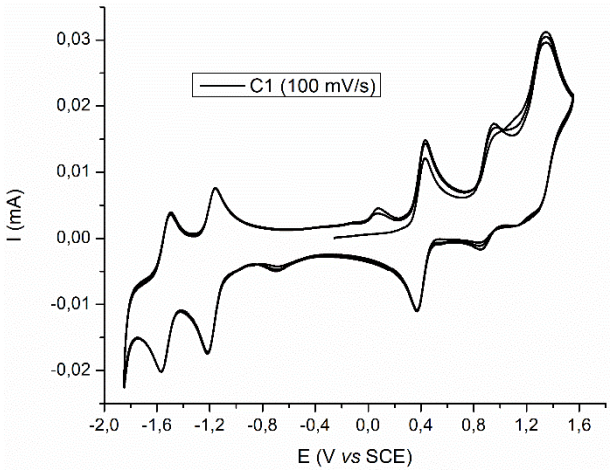


Figure S14 Cyclic voltammogram for **C1** in CH_3CN /TBAP 0.1 M at 100mV/s with ferrocene as internal standard.

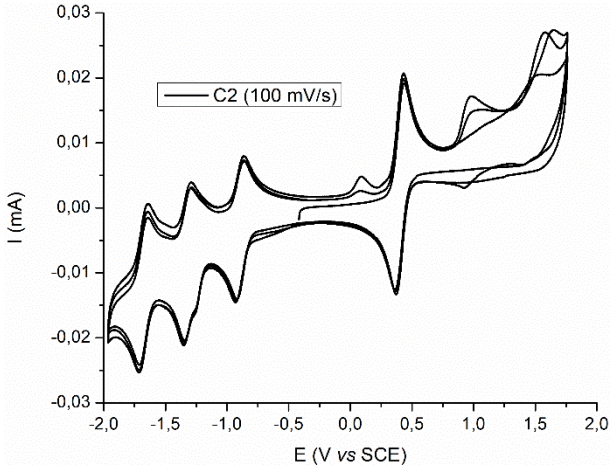


Figure S15 Cyclic voltammogram for **C2** in CH_3CN /TBAP 0.1 M at 100mV/s with ferrocene as internal standard.

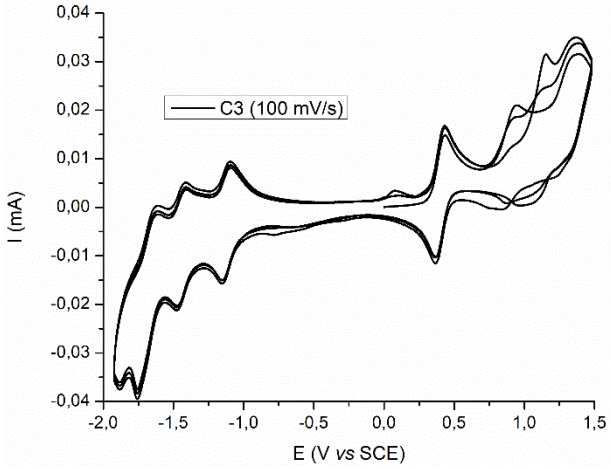


Figure S16 Cyclic voltammogram for **C3** in CH_3CN /TBAP 0.1 M at 100mV/s with ferrocene as internal standard.

Theoretical study

Table S1 Kohn-Sham representation of the first three unoccupied orbitals of **C1**$^{2+}$, **C2**$^{2+}$ and **C3**$^{2+}$.

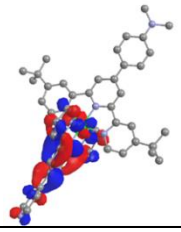
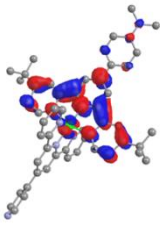
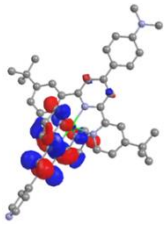
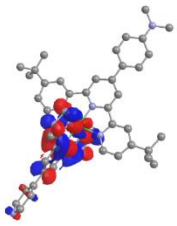
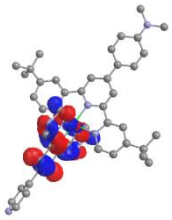
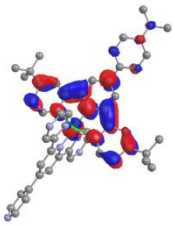
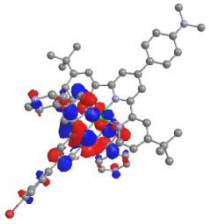
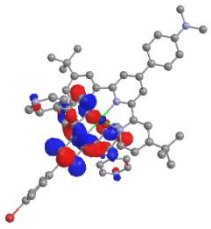
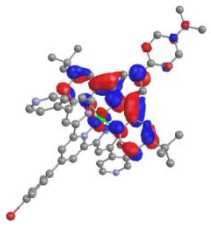
Complex	LUMO	LUMO+1	LUMO+2
C1			
C2			
C3			

Table S2 Kohn-Sham representation of the first three occupied orbitals of **C1**$^{2+}$, **C2**$^{2+}$ and **C3**$^{2+}$.

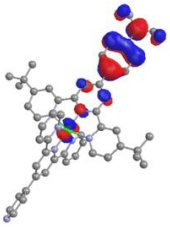
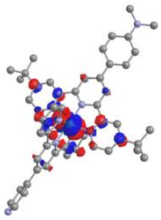
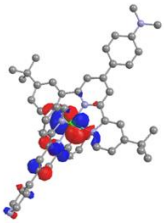
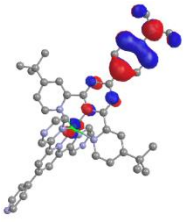
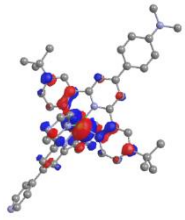
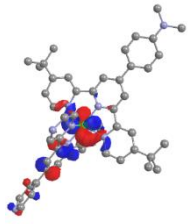
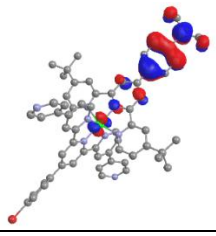
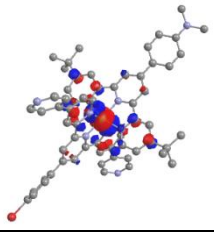
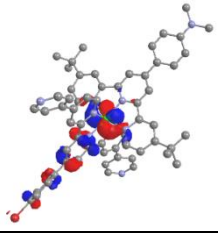
Complex	HOMO	HOMO-1	HOMO-2
C1			
C2			
C3			

Table S3 Contributions of each unit to selected frontiers orbitals of **C1**$^{2+}$

MO	eV	DMAPh	tbu_2tpy	Ru	4-py	tpy
L+2	-2.6	0	9	1	0	90
L+1	-2.61	7	85	7	0	1
LUMO	-2.84	0	2	9	11	79
HOMO	-5.69	82	9	8	0	1
H-1	-6.39	0	18	67	0	15
H-2	-6.51	0	9	67	4	20

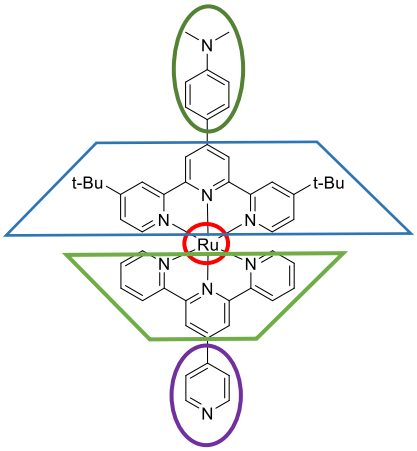


Table S4 Contributions of each unit to selected frontiers orbitals of **C2**$^{2+}$

MO	eV	DMAPh	tbu_2tpy	Ru	4-py	pzpypz
L+2	-2.73	7	86	6	0	1
L+1	-2.95	0	2	3	0	95
LUMO	-3.26	0	2	9	4	85
HOMO	-5.75	85	9	5	0	1
H-1	-6.75	0	21	64	0	15
H-2	-6.79	0	9	65	4	22

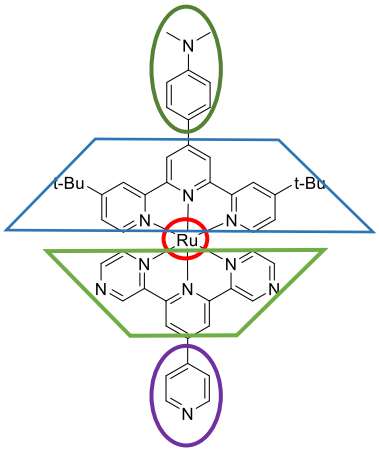
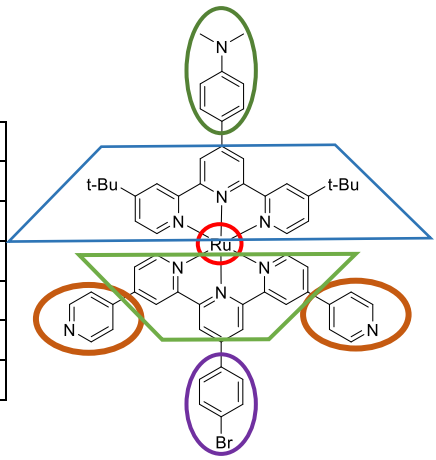


Table S5 Contributions of each unit to selected frontiers orbitals of **C3**$^{2+}$

MO	eV	DMAP	tbu_2tpy	Ru	4'(4BrPh)	tpy	4 and 4'' py
L+2	-2.62	7	85	6	0	1	0
L+1	-2.7	0	5	2	0	85	8
LUMO	-2.95	0	1	8	4	76	11
HOMO	-5.7	82	9	8	0	1	0
H-1	-6.39	0	17	65	0	15	3
H-2	-6.48	0	8	63	9	19	1



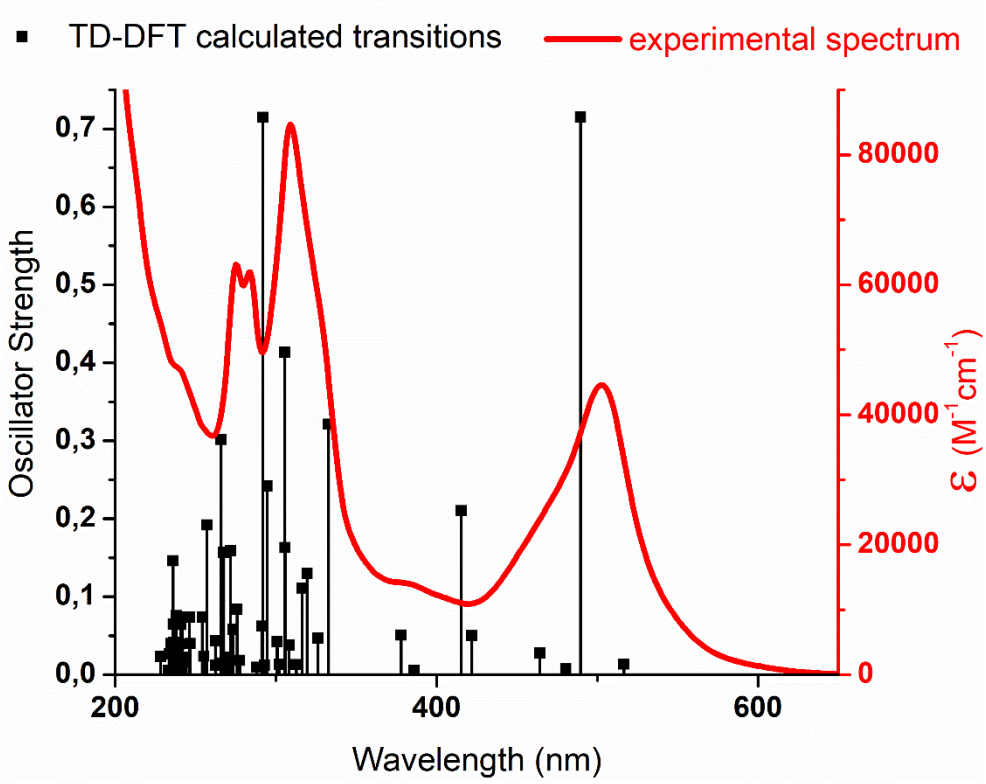


Figure S17 Overlap of the experimental absorption spectra and calculated transitions for **C1**$^{2+}$

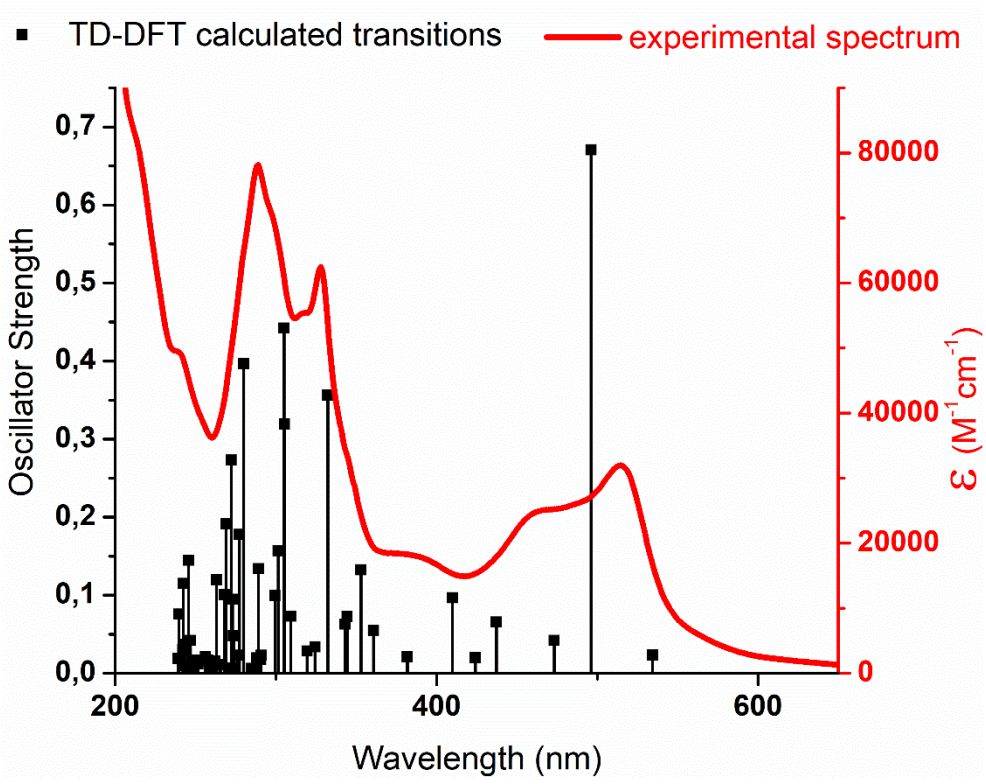


Figure S18 Overlap of the experimental absorption spectra and calculated transitions for **C2**$^{2+}$

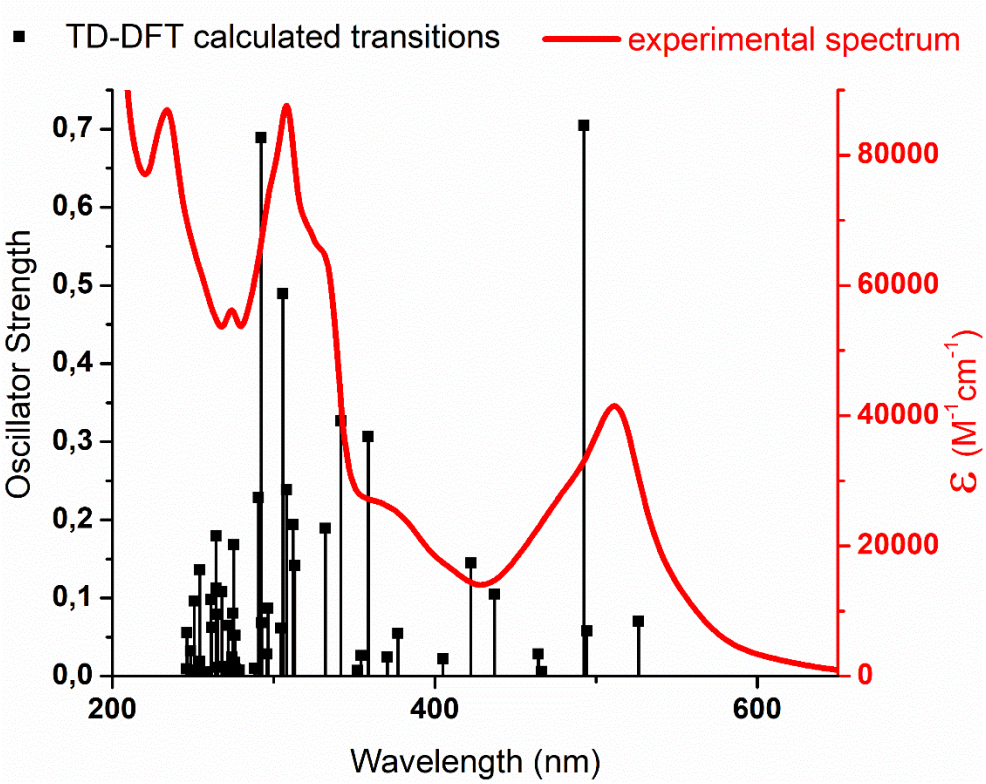


Figure S19 Overlap of the experimental absorption spectra and calculated transitions for **C3**$^{2+}$

Table S6 Calculated transitions and contributions of each unit for **C1**$^{2+}$.

$S_0 \rightarrow S_x$	Wavelength (nm)	Osc. Strength	Major contribs	DMAP	tbu2tpy	Ru	4-py	tpy
1	551.60	0.0	H-3->LUMO (25%), HOMO->LUMO (73%)	64-->0 (-64)	11-->2 (-9)	22-->9 (-13)	0-->11 (11)	3-->78 (75)
2	516.58	0.0135	H-1->LUMO (97%)	0-->0 (0)	18-->2 (-16)	67-->9 (-58)	0-->11 (11)	15-->78 (63)
3	489.53	0.7149	H-2->LUMO (10%), HOMO->L+1 (84%)	69-->6 (-63)	9-->77 (68)	17-->7 (-10)	0-->1 (1)	3-->9 (6)
4	480.32	0.0071	HOMO->L+2 (69%), HOMO->L+3 (22%)	76-->0 (-76)	10-->28 (18)	13-->1 (-12)	0-->0 (0)	2-->70 (68)
5	468.48	0.0013	H-1->L+1 (35%), HOMO->L+3 (50%)	48-->3 (-45)	13-->80 (67)	33-->4 (-29)	0-->0 (0)	7-->14 (7)
6	464.22	0.0279	H-1->L+1 (61%), HOMO->L+2 (12%), HOMO->L+3 (22%)	29-->4 (-25)	15-->75 (60)	46-->5 (-41)	0-->0 (0)	10-->16 (6)
7	450.10	0.0044	H-2->LUMO (51%), H-1->L+2 (32%)	5-->1 (-4)	13-->17 (4)	64-->5 (-59)	2-->6 (4)	17-->71 (54)
8	449.36	0.0	H-2->L+1 (90%)	4-->6 (2)	9-->78 (69)	64-->7 (-57)	3-->1 (-2)	19-->8 (-11)
9	433.28	0.0	H-3->LUMO (68%), HOMO->LUMO (23%)	28-->1 (-27)	15-->8 (-7)	49-->9 (-40)	0-->10 (10)	7-->73 (66)
10	421.89	0.0499	H-2->L+2 (92%)	0-->0 (0)	9-->13 (4)	66-->1 (-65)	4-->1 (-3)	21-->85 (64)
11	415.30	0.21	H-2->LUMO (14%), H-1->L+2 (60%), H-1->L+3 (24%)	1-->0 (-1)	16-->28 (12)	66-->2 (-64)	1-->2 (1)	16-->67 (51)
12	404.20	0.0009	H-3->L+1 (51%), H-1->L+3 (29%)	14-->4 (-10)	16-->78 (62)	59-->5 (-54)	0-->1 (1)	10-->12 (2)
13	396.17	0.0004	H-2->L+3 (92%)	0-->1 (1)	9-->84 (75)	67-->3 (-64)	4-->0 (-4)	20-->13 (-7)
14	386.11	0.0051	H-3->L+2 (86%), HOMO->L+2 (11%)	22-->0 (-22)	16-->10 (-6)	55-->1 (-54)	0-->0 (0)	7-->89 (82)
15	377.95	0.0508	H-3->L+3 (91%)	17-->1 (-16)	17-->88 (71)	58-->3 (-55)	0-->0 (0)	7-->8 (1)
16	363.50	0.0013	H-3->L+1 (37%), H-2->LUMO (10%), H-1->L+3 (36%)	6-->3 (-3)	17-->72 (55)	63-->5 (-58)	1-->2 (1)	13-->18 (5)
17	358.07	0.0	HOMO->L+4 (87%)	76-->0 (-76)	10-->0 (-10)	13-->0 (-13)	0-->32 (32)	2-->67 (65)
$S_0 \rightarrow T_x$								
1	630.55	0.0	H-2->LUMO (57%), HOMO->L+1 (28%)	26-->3 (-23)	10-->34 (24)	46-->7 (-39)	4-->7 (3)	14-->48 (34)
2	616.53	0.0	H-2->LUMO (36%), HOMO->L+1 (45%)	42-->5 (-37)	11-->52 (41)	34-->7 (-27)	2-->4 (2)	10-->32 (22)
3	572.41	0.0	H-3->LUMO (34%), HOMO->LUMO (64%)	57-->0 (-57)	12-->2 (-10)	27-->9 (-18)	0-->11 (11)	3-->78 (75)
4	568.81	0.0	H-1->LUMO (94%)	0-->0 (0)	18-->2 (-16)	65-->8 (-57)	0-->11 (11)	16-->78 (62)
5	517.38	0.0	H-1->L+1 (43%), HOMO->L+3 (43%)	42-->4 (-38)	15-->82 (67)	36-->4 (-32)	0-->0 (0)	8-->10 (2)
6	508.09	0.0	H-1->L+1 (49%), HOMO->L+2 (13%), HOMO->L+3 (32%)	38-->4 (-34)	15-->76 (61)	38-->4 (-34)	0-->0 (0)	8-->16 (8)
7	494.89	0.0	H-1->L+2 (48%), H-1->L+3 (24%)	2-->0 (-2)	18-->32 (14)	54-->2 (-52)	5-->2 (-3)	21-->64 (43)
8	476.22	0.0	H-3->L+2 (12%), HOMO->L+2 (66%), HOMO->L+3 (15%)	69-->0 (-69)	11-->25 (14)	18-->1 (-17)	0-->0 (0)	2-->73 (71)
9	471.515	0.0	H-4->L+3 (11%), H-3->L+1 (15%), H-1->L+2 (13%), H-1->L+3 (35%)	17-->3 (-14)	28-->74 (46)	44-->3 (-41)	1-->0 (-1)	11-->19 (8)
10	465.13	0.0	H-2->L+1 (95%)	2-->7 (5)	9-->83 (74)	66-->7 (-59)	4-->0 (-4)	20-->4 (-16)

Table S7 Calculated transitions and contributions of each unit for **$C2^{2+}$**.

$S_0 \rightarrow S_x$	λ(nm)	Osc. Strength	Major contribs	DMAP	tbu2tpy	Ru	4-py	pzpypz
1	635.36	0.0	H-3->LUMO (16%), HOMO->LUMO (83%)	73-->0 (-73)	11-->2 (-9)	15-->9 (-6)	0-->4 (4)	2-->84 (82)
2	534.44	0.0235	H-1->LUMO (97%)	0-->0 (0)	21-->2 (-19)	64-->9 (-55)	0-->4 (4)	15-->84 (69)
3	529.96	0.0001	HOMO->L+1 (92%)	79-->0 (-79)	10-->2 (-8)	10-->3 (-7)	0-->0 (0)	1-->95 (94)
4	496.14	0.6709	H-2->LUMO (26%), HOMO->L+2 (69%)	60-->5 (-55)	9-->63 (54)	23-->6 (-17)	1-->1 (0)	7-->24 (17)
5	484.37	0.0	H-3->LUMO (81%), HOMO->LUMO (16%)	23-->0 (-23)	17-->2 (-15)	53-->9 (-44)	0-->4 (4)	8-->84 (76)
6	473.31	0.0034	HOMO->L+3 (97%)	83-->1 (-82)	10-->95 (85)	7-->2 (-5)	0-->0 (0)	1-->2 (1)
7	473.22	0.0419	H-2->LUMO (48%), H-1->L+1 (22%), HOMO->L+2 (25%)	21-->2 (-19)	12-->25 (13)	50-->7 (-43)	2-->2 (0)	14-->65 (51)
8	437.24	0.0656	H-2->L+1 (94%)	0-->0 (0)	9-->3 (-6)	64-->3 (-61)	4-->1 (-3)	22-->93 (71)
9	424.04	0.0198	H-1->L+2 (86%)	4-->6 (2)	20-->76 (56)	62-->5 (-57)	0-->0 (0)	14-->13 (-1)
10	417.41	0.0	H-2->L+2 (97%)	0-->7 (7)	9-->85 (76)	65-->6 (-59)	5-->0 (-5)	21-->2 (-19)
11	413.93	0.0018	H-3->L+1 (62%), H-1->L+2 (12%), HOMO->L+5 (12%)	23-->1 (-22)	16-->15 (-1)	52-->4 (-48)	0-->0 (0)	9-->81 (72)
12	410.94	0.0004	HOMO->L+4 (93%)	81-->0 (-81)	10-->0 (-10)	8-->0 (-8)	0-->18 (18)	1-->81 (80)
13	409.85	0.0968	H-2->LUMO (15%), H-1->L+1 (69%)	4-->1 (-3)	18-->13 (-5)	62-->4 (-58)	1-->1 (0)	15-->81 (66)
14	398.74	0.0001	H-3->L+1 (16%), HOMO->L+5 (80%)	71-->0 (-71)	11-->4 (-7)	16-->2 (-14)	0-->0 (0)	2-->93 (91)
15	381.70	0.0206	H-3->L+2 (58%), H-1->L+3 (36%)	7-->5 (-2)	19-->88 (69)	62-->4 (-58)	0-->0 (0)	11-->4 (-7)
16	371.33	0.0004	H-2->L+3 (95%)	0-->1 (1)	9-->93 (84)	65-->3 (-62)	5-->0 (-5)	22-->4 (-18)
17	360.73	0.0548	H-3->L+3 (92%)	13-->1 (-12)	18-->93 (75)	60-->2 (-58)	0-->0 (0)	9-->4 (-5)
18	352.87	0.1326	H-3->L+2 (20%), H-2->L+4 (17%), H-1->L+3 (46%), H-1->L+5 (11%)	3-->2 (-1)	19-->65 (46)	63-->3 (-60)	1-->3 (2)	15-->27 (12)
$S_0 \rightarrow T_x$								
1	665.94	0.0	H-2->LUMO (93%)	1-->0 (-1)	9-->3 (-6)	62-->9 (-53)	5-->5 (0)	23-->83 (60)
2	657.22	0.0	H-3->LUMO (25%), HOMO->LUMO (74%)	65-->0 (-65)	11-->2 (-9)	20-->9 (-11)	0-->4 (4)	3-->84 (81)
3	614.85	0.0	HOMO->L+2 (80%)	76-->8 (-68)	11-->85 (74)	11-->5 (-6)	0-->0 (0)	2-->2 (0)
4	604.86	0.0	H-1->LUMO (94%)	0-->0 (0)	21-->2 (-19)	62-->9 (-53)	0-->5 (5)	16-->84 (68)
5	537.01	0.0	HOMO->L+1 (86%)	77-->0 (-77)	10-->5 (-5)	11-->3 (-8)	0-->0 (0)	2-->91 (89)
6	518.61	0.0	H-1->L+1 (69%)	1-->0 (-1)	19-->7 (-12)	52-->3 (-49)	3-->2 (-1)	25-->88 (63)
7	511.59	0.0	HOMO->L+3 (88%)	79-->1 (-78)	10-->92 (82)	9-->2 (-7)	0-->0 (0)	2-->5 (3)
8	499.78	0.0	H-3->LUMO (71%), HOMO->LUMO (26%)	30-->0 (-30)	16-->2 (-14)	47-->9 (-38)	0-->4 (4)	8-->84 (76)
9	475.07	0.0	H-2->L+1 (92%)	0-->0 (0)	9-->5 (-4)	63-->3 (-60)	5-->0 (-5)	23-->92 (69)
10	465.79	0.0	H-1->L+2 (87%)	3-->7 (4)	25-->86 (61)	57-->5 (-52)	0-->0 (0)	14-->2 (-12)

Table S8 Calculated transitions and contributions of each unit for **C3**$^{2+}$.

$S_0 \rightarrow S_x$	λ (nm)	Osc. Strength	Major contributions	DMAP	tpyd	Ru	4'(4BrPh)	tpy	4 and 4'' py
1	569.73	0.0	H-3->LUMO (21%), HOMO->LUMO (77%)	67-->0 (-67)	11-->2 (-9)	20-->8 (-12)	0-->4 (4)	2-->75 (73)	0-->11 (11)
2	526.49	0.0703	H-1->LUMO (96%)	0-->0 (0)	17-->2 (-15)	65-->8 (-57)	0-->4 (4)	15-->75 (60)	3-->11 (8)
3	494.26	0.058	H-3->L+1 (10%), HOMO->L+1 (82%)	73-->0 (-73)	10-->10 (0)	14-->2 (-12)	0-->0 (0)	2-->79 (77)	0-->7 (7)
4	492.51	0.7051	H-2->LUMO (17%), HOMO->L+2 (72%)	64-->5 (-59)	9-->66 (57)	21-->6 (-15)	2-->1 (-1)	5-->19 (14)	0-->2 (2)
5	471.84	0.0039	HOMO->L+3 (91%)	76-->1 (-75)	10-->91 (81)	12-->3 (-9)	0-->0 (0)	2-->5 (3)	0-->1 (1)
6	466.04	0.0059	H-2->LUMO (48%), H-1->L+1 (32%), HOMO->L+2 (12%)	10-->1 (-9)	12-->18 (6)	56-->5 (-51)	5-->2 (-3)	15-->65 (50)	1-->8 (7)
7	464.27	0.0285	H-1->L+2 (94%)	3-->7 (4)	17-->83 (66)	63-->6 (-57)	0-->0 (0)	14-->3 (-11)	3-->0 (-3)
8	453.44	0.0001	H-3->LUMO (26%), H-2->L+2 (60%), HOMO->LUMO (11%)	12-->4 (-8)	11-->53 (42)	56-->7 (-49)	7-->2 (-5)	14-->30 (16)	0-->4 (4)
9	444.07	0.0001	H-3->LUMO (49%), H-2->L+2 (36%), HOMO->LUMO (12%)	17-->3 (-14)	13-->32 (19)	55-->7 (-48)	4-->3 (-1)	11-->48 (37)	0-->7 (7)
10	436.95	0.105	H-2->L+1 (93%)	0-->0 (0)	8-->7 (-1)	62-->2 (-60)	9-->1 (-8)	19-->82 (63)	1-->8 (7)
11	422.21	0.1452	H-2->LUMO (17%), H-1->L+1 (60%), H-1->L+3 (15%)	3-->0 (-3)	15-->21 (6)	62-->3 (-59)	2-->1 (-1)	15-->66 (51)	2-->7 (5)
12	404.91	0.0223	H-3->L+2 (44%), H-1->L+3 (44%)	12-->4 (-8)	17-->85 (68)	59-->5 (-54)	0-->0 (0)	11-->5 (-6)	1-->1 (0)
13	399.05	0.0	HOMO->L+5 (86%)	74-->0 (-74)	10-->4 (-6)	14-->1 (-13)	0-->0 (0)	2-->65 (63)	0-->30 (30)
14	398.00	0.0013	H-2->L+3 (93%)	0-->1 (1)	8-->89 (81)	62-->3 (-59)	10-->0 (-10)	19-->6 (-13)	1-->1 (0)
15	397.64	0.0	HOMO->L+4 (91%)	77-->0 (-77)	10-->1 (-9)	12-->1 (-11)	0-->11 (11)	1-->62 (61)	0-->25 (25)
16	396.44	0.0008	H-3->L+1 (80%), HOMO->L+1 (10%)	25-->0 (-25)	16-->6 (-10)	52-->2 (-50)	0-->0 (0)	7-->82 (75)	0-->9 (9)
17	377.07	0.0548	H-3->L+3 (92%)	16-->1 (-15)	17-->91 (74)	59-->3 (-56)	0-->0 (0)	7-->5 (-2)	0-->1 (1)
18	370.54	0.0242	H-3->L+2 (35%), H-1->L+3 (25%), H-1->L+5 (26%)	5-->3 (-2)	17-->57 (40)	63-->4 (-59)	1-->1 (0)	13-->25 (12)	2-->10 (8)
19	358.61	0.3067	H-1->L+4 (91%)	0-->0 (0)	17-->1 (-16)	64-->1 (-63)	0-->11 (11)	16-->62 (46)	3-->25 (22)
20	354.08	0.0262	H-2->L+4 (52%), H-1->L+5 (39%)	0-->0 (0)	12-->5 (-7)	63-->1 (-62)	5-->6 (1)	18-->61 (43)	2-->26 (24)
21	351.93	0.0072	H-2->L+5 (93%)	0-->0 (0)	8-->3 (-5)	62-->1 (-61)	9-->1 (-8)	19-->64 (45)	1-->31 (30)
$S_0 \rightarrow T_x$									
1	632.70	0.0	H-2->LUMO (66%), HOMO->L+2 (18%)	16-->2 (-14)	9-->22 (13)	50-->7 (-43)	8-->4 (-4)	16-->56 (40)	1-->9 (8)
2	617.24	0.0	H-3->L+2 (11%), H-2->LUMO (21%), HOMO->L+2 (56%)	53-->6 (-47)	11-->63 (52)	26-->6 (-20)	2-->2 (0)	7-->20 (13)	1-->3 (2)
3	589.98	0.0	H-1->LUMO (87%)	4-->0 (-4)	17-->2 (-15)	60-->7 (-53)	0-->4 (4)	15-->75 (60)	4-->12 (8)
4	588.89	0.0	H-3->LUMO (28%), HOMO->LUMO (64%)	57-->0 (-57)	12-->2 (-10)	27-->8 (-19)	0-->4 (4)	4-->75 (71)	0-->11 (11)
5	520.75	0.0	H-1->L+1 (64%), H-1->L+3 (11%)	1-->0 (-1)	16-->16 (0)	53-->2 (-51)	1-->1 (0)	21-->71 (50)	8-->10 (2)
6	516.56	0.0	H-1->L+2 (29%), HOMO->L+3 (57%)	54-->3 (-51)	13-->84 (71)	27-->4 (-23)	0-->0 (0)	6-->8 (2)	1-->1 (0)
7	509.09	0.0	H-1->L+2 (52%), HOMO->L+1 (26%), HOMO->L+3 (13%)	34-->4 (-30)	15-->62 (47)	40-->4 (-36)	0-->0 (0)	9-->27 (18)	2-->3 (1)
8	493.84	0.0	H-3->L+1 (11%), H-1->L+2 (11%), HOMO->L+1 (52%), HOMO->L+3 (21%)	62-->1 (-61)	12-->36 (24)	22-->3 (-19)	0-->0 (0)	4-->55 (51)	0-->5 (5)
9	470.99	0.0	H-5->L+3 (12%), H-3->L+2 (13%), H-1->L+3 (43%)	17-->3 (-14)	29-->83 (54)	42-->4 (-38)	0-->0 (0)	10-->9 (-1)	2-->1 (-1)
10	468.15	0.0	H-2->L+1 (81%)	1-->1 (0)	8-->16 (8)	61-->3 (-58)	9-->0 (-9)	20-->73 (53)	1-->7 (6)

Table S9 Atomic coordinates of **C1**$^{2+}$ after optimization

Center Number	Atomic number	Coordinates (Angstroms)			Center Number	Atomic number	Coordinates (Angstroms)		
		X	Y	Z			X	Y	Z
1	6	3.934175	0.000089	0.000057	56	7	-1.237261	0.008663	2.039348
2	7	1.143358	0.000023	0.000216	57	6	-2.066182	0.020984	4.712428
3	6	3.200113	-1.211804	0.004842	58	6	0.327652	0.014761	3.041171
4	6	3.200015	1.211923	0.004874	59	6	-2.581745	0.008613	2.349418
5	6	1.805961	1.188470	0.000176	60	6	-3.011533	0.014451	3.680530
6	6	1.806058	-1.188462	0.000137	61	6	0.702850	0.021189	4.386793
7	1	3.722064	-2.159821	0.037364	62	1	0.715067	0.014361	2.749363
8	1	3.721899	2.159981	0.037260	63	1	-4.069689	0.013812	3.912344
9	6	0.895459	2.348799	0.006929	64	1	0.061228	0.025995	5.154839
10	6	0.956081	4.390234	0.018781	65	1	-2.387815	0.025726	5.747681
11	7	0.445061	2.038622	0.008008	66	6	-7.086148	0.000042	0.000702
12	6	1.329723	3.678182	0.011113	67	7	-9.922954	0.000150	0.001075
13	6	0.410622	4.740138	0.017622	68	6	-7.818490	0.648932	1.014196
14	6	-1.342002	3.052836	0.013638	69	6	-7.818708	0.649071	-1.012599
15	1	2.392717	3.880184	0.009058	70	6	-9.217719	0.624130	0.972451
16	1	-2.388725	2.775241	0.014012	71	6	-9.217510	0.623883	0.974416
17	1	-1.731173	5.148055	0.023389	72	1	-7.322115	-1.189970	1.812516
18	6	0.895646	-2.348861	0.006467	73	1	-7.322503	1.190073	-1.811050
19	6	0.955745	-4.390432	0.017908	74	1	-9.797516	1.123923	-1.741854
20	6	1.330009	-3.678213	0.010376	75	1	-9.797143	-1.123632	1.743972
21	7	0.444895	-2.038782	0.007618	76	7	9.657062	0.000325	0.000708
22	6	-1.341764	-3.053061	0.013047	77	6	10.392322	-1.147654	0.526745
23	6	0.410984	-4.740236	0.016668	78	1	10.155438	-2.068434	0.023252
24	1	2.393019	-3.880136	0.008249	79	1	11.463534	0.964974	0.430051
25	1	-2.388505	-2.775535	0.013502	80	1	10.172906	-1.317225	-1.589727
26	1	-1.730782	-5.148311	0.022362	81	6	10.392078	1.148471	0.528127
27	6	5.404792	0.000151	0.000223	82	1	10.172099	1.318394	1.590931
28	6	8.280993	0.000266	0.000540	83	1	10.155518	2.069087	0.022298
29	6	6.145440	1.092583	0.507902	84	1	11.463336	0.965710	0.432094
30	6	6.145640	-1.092217	0.507309	85	6	0.835589	-6.209636	0.022052
31	6	7.537274	-1.100217	0.515655	86	6	0.835122	6.209566	0.023336
32	6	7.537073	1.100700	0.516539	87	6	0.265932	6.891137	-1.291218
33	1	5.630869	1.947376	0.938278	88	1	0.827999	6.841010	-1.326876
34	1	5.631228	-1.947044	0.937806	89	1	0.661112	6.422060	-2.200107
35	1	8.050181	-1.958523	0.933651	90	6	2.364537	6.375134	0.021290
36	1	8.049822	1.959068	0.934604	91	1	2.822521	5.934294	0.872624
37	44	0.849396	0.000096	0.000114	92	1	2.610374	7.442815	0.025643
38	7	-1.237808	0.008881	-2.039471	93	1	2.825770	5.926282	0.909529
39	6	-2.067392	0.021225	-4.712338	94	1	0.553734	7.948984	-1.298087
40	6	-2.582368	0.008811	-2.349203	95	6	0.261253	6.902576	1.236203
41	6	0.328445	0.015019	-3.041515	96	1	0.653270	6.441916	2.150748
42	6	0.703978	0.021458	-4.387044	97	1	0.832788	6.852516	1.268413
43	6	-3.012489	0.014660	-3.680208	98	1	0.548805	7.960514	1.234441
44	1	0.714342	0.014645	-2.749951	99	6	0.266487	-6.891519	1.289806
45	1	0.059908	0.026293	-5.155280	100	1	0.661671	-6.422616	2.198783
46	1	-4.070703	0.014006	-3.911758	101	1	0.554354	-7.949350	1.296434
47	1	-2.389282	0.025972	-5.747512	102	1	0.827446	-6.841466	1.325514
48	7	-2.830762	0.000108	0.000138	103	6	0.261729	-6.902418	-1.237617
49	6	-5.604615	0.000014	0.000507	104	1	0.832317	-6.852439	-1.269776
50	6	-3.490482	0.001357	1.191545	105	1	0.549365	-7.960333	-1.236094
51	6	-3.490802	0.001525	-1.191093	106	1	0.653676	-6.441528	-2.152076
52	6	-4.886968	0.001920	-1.213396	107	6	2.365015	-6.375096	0.019920
53	6	-4.886644	0.001846	1.214218	108	1	2.826246	-5.926405	0.908242
54	1	-5.416357	0.026783	-2.158086	109	1	2.822938	-5.934027	0.873912
55	1	-5.415782	0.026750	2.159047	110	1	2.610929	-7.442760	0.024030

Table S10 Atomic coordinates of **C2**$^{2+}$ after optimization.

Center Number	Atomic number	Coordinates (Angstroms)			Center Number	Atomic number	Coordinates (Angstroms)		
		X	Y	Z			X	Y	Z
1	6	3.937218	0.000006	0.000015	55	7	-1.234519	0.007055	2.027363
2	7	1.147051	0.000005	0.000103	56	7	-2.093625	0.015939	4.698760
3	6	3.202251	-1.212005	0.004609	57	6	0.344937	0.012170	3.045456
4	6	3.202241	1.212012	0.004521	58	6	-2.579578	0.006560	2.337355
5	6	1.808835	1.188035	0.000453	59	6	-2.979315	0.010585	3.680975
6	6	1.808845	-1.188039	0.000277	60	6	0.780484	0.016851	4.375136
7	1	3.723199	-2.160344	0.037060	61	1	0.707093	0.012340	2.795181
8	1	3.723178	2.160356	0.037016	62	1	-4.028602	0.009328	3.950360
9	6	0.898927	2.349276	0.005577	63	1	0.064885	0.021126	5.188236
10	6	0.951668	4.391814	0.015412	64	6	-7.089534	0.000013	0.000313
11	7	0.441511	2.041189	0.006533	65	7	-9.924603	0.000021	0.000475
12	6	1.333872	3.677716	0.008900	66	6	-7.820884	0.653100	1.010886
13	6	0.415069	4.740408	0.014370	67	6	-7.820764	0.653130	-1.011596
14	6	-1.338704	3.054879	0.011156	68	6	-9.219829	0.628081	0.971497
15	1	2.396829	3.879295	0.006924	69	6	-9.219944	0.628042	0.970627
16	1	-2.385726	2.778959	0.011429	70	1	-7.324903	-1.197640	1.807054
17	1	-1.726375	5.149845	0.019223	71	1	-7.324688	1.197668	-1.807706
18	6	0.898945	-2.349287	0.005798	72	1	-9.799629	1.130929	-1.738791
19	6	0.951639	-4.391834	0.015782	73	1	-9.799834	-1.130887	1.737855
20	6	1.333897	-3.677724	0.009228	74	7	9.657609	0.000052	0.000344
21	7	0.441496	-2.041207	0.006713	75	6	10.393246	-1.157434	0.506891
22	6	-1.338683	-3.054901	0.011407	76	1	10.152018	-2.068712	0.056596
23	6	0.415100	-4.740421	0.014781	77	1	11.464268	0.975197	0.407987
24	1	2.396855	-3.879296	0.007288	78	1	10.178115	-1.342874	-1.568012
25	1	-2.385706	-2.778986	0.011632	79	6	10.393310	1.157485	0.506229
26	1	-1.726341	-5.149869	0.019649	80	1	10.178321	1.342825	1.567398
27	6	5.406411	0.000012	0.000057	81	1	10.152008	2.068817	0.057139
28	6	8.282456	0.000037	0.000235	82	1	11.464319	0.975263	0.407157
29	6	6.147489	1.099986	0.491776	83	6	0.840924	-6.209114	0.019567
30	6	6.147448	-1.099954	0.491974	84	6	0.840883	6.209105	0.019034
31	6	7.538497	-1.108003	0.500612	85	6	0.271431	6.891589	-1.286418
32	6	7.538540	1.108059	0.500243	86	1	0.822541	6.842825	-1.321612
33	1	5.633849	1.960984	0.910479	87	1	0.665823	6.422936	-2.195814
34	1	5.633770	-1.960962	0.910608	88	6	2.370389	6.373361	0.017280
35	1	8.051349	-1.971898	0.906838	89	1	2.828414	5.931817	0.876245
36	1	8.051424	1.971961	0.906412	90	1	2.616733	7.440858	0.020836
37	44	0.851075	0.000011	0.000053	91	1	2.831166	5.925244	0.906108
38	7	-1.234271	0.007081	-2.027299	92	1	0.560405	7.949042	-1.292386
39	7	-2.093076	0.015963	-4.698797	93	6	0.267476	6.901011	1.241435
40	6	-2.579297	0.006576	-2.337446	94	1	0.659184	6.439284	2.155520
41	6	0.344576	0.012207	-3.045294	95	1	0.826590	6.852311	1.273692
42	6	0.779972	0.016887	-4.375023	96	1	0.556252	7.958536	1.240329
43	6	-2.978880	0.010602	-3.681112	97	6	0.271546	-6.891484	1.287045
44	1	0.707427	0.012389	-2.794907	98	1	0.665965	-6.422728	2.196376
45	1	0.064279	0.021169	-5.188040	99	1	0.560550	-7.948928	1.293107
46	1	-4.028136	0.009340	-3.950615	100	1	0.822427	-6.842750	1.322285
47	7	-2.832960	0.000009	0.000060	101	6	0.267451	-6.901141	-1.240807
48	6	-5.608161	0.000008	0.000227	102	1	0.826615	-6.852425	-1.273019
49	6	-3.494747	0.000562	1.190259	103	1	0.556211	-7.958670	-1.239607
50	6	-3.494603	0.000570	-1.190460	104	1	0.659125	-6.439512	-2.154957
51	6	-4.890518	0.001538	-1.214381	105	6	2.370430	-6.373360	0.017746
52	6	-4.890664	0.001548	1.214013	106	1	2.831259	-5.925059	0.906454
53	1	-5.420059	0.026102	-2.159132	107	1	2.828396	-5.931995	0.875898
54	1	-5.420316	0.026122	2.158701	108	1	2.616782	-7.440855	0.021500

Table S11 Atomic coordinates of **C3**$^{2+}$ after optimization.

Center Number	Atomic number	Coordinates (Angstroms)			Center Number	Atomic number	Coordinates (Angstroms)		
		X	Y	Z			X	Y	Z
1	6	-5.061183	0.000331	0.022569	66	6	6.681791	-1.015713	0.696659
2	7	-2.270583	0.001359	0.007409	67	6	8.081518	-1.022328	0.709268
3	6	-4.320438	0.012562	-1.230392	68	6	8.089453	1.016606	0.628873
4	6	-4.333653	0.014097	1.193242	69	1	6.171279	1.793362	-1.177081
5	6	-2.939537	0.019065	1.177314	70	1	6.156908	-1.796464	1.238411
6	6	-2.926597	0.016505	-1.199359	71	1	8.615460	-1.805250	1.236481
7	1	-4.837204	0.005407	-2.181619	72	1	8.629637	1.798885	-1.150655
8	1	-4.860616	0.004361	2.138837	73	7	-10.783768	0.003814	0.054976
9	6	-2.035339	0.030477	2.342671	74	6	-11.512010	0.550795	-1.198321
10	6	0.195192	0.051902	4.394432	75	1	-11.271981	0.014460	-2.126315
11	7	0.693042	0.024387	2.040293	76	1	-12.584352	0.454271	-1.022355
12	6	-2.477043	0.048098	3.669438	77	1	-11.288961	-1.615655	-1.350296
13	6	-1.563859	0.059195	4.736511	78	6	-11.525825	0.541991	1.080016
14	6	0.198237	0.035167	3.059323	79	1	-11.305679	1.607036	1.234886
15	1	-3.541156	0.053773	3.865427	80	1	-11.296061	0.005621	2.010597
16	1	1.246445	0.030326	2.787430	81	1	-12.595945	0.444433	0.891541
17	1	0.575629	0.059606	5.156564	82	6	-1.929174	0.072923	-6.214972
18	6	-2.009868	0.027495	-2.354874	83	6	-1.996683	0.078405	6.203382
19	6	0.147533	0.048971	-4.386535	84	6	-1.434610	-1.179755	6.908505
20	6	-2.437097	0.043882	-3.686388	85	1	0.340540	-1.219095	6.864731
21	7	0.670982	0.022241	-2.037951	86	1	-1.829829	-2.095098	6.452198
22	6	0.231369	0.033160	-3.047230	87	6	-3.526992	0.087129	6.360203
23	6	-1.512380	0.054932	-4.743467	88	1	-3.980064	0.974826	5.902038
24	1	-3.498980	0.048521	-3.894038	89	1	-3.778827	0.101100	7.426397
25	1	1.276612	0.029187	-2.764117	90	1	-3.988117	0.807227	5.923578
26	1	0.631480	0.056903	-5.140278	91	1	-1.727997	-1.168624	7.964779
27	6	-6.531676	0.000733	0.030758	92	6	-1.423433	1.347531	6.879200
28	6	-9.407797	0.002878	0.047115	93	1	-1.809901	2.255506	6.401185
29	6	-7.278957	0.522558	1.049759	94	1	0.329013	1.375869	6.835660
30	6	-7.265879	0.525209	-1.119650	95	1	-1.717653	1.363892	7.935165
31	6	-8.657398	0.534946	-1.135461	96	6	-1.357128	1.184336	-6.913647
32	6	-8.670588	0.530214	1.049717	97	1	-1.755660	2.100314	-6.461513
33	1	-6.769672	0.966043	1.900996	98	1	-1.638973	1.173917	-7.973065
34	1	-6.746282	0.968007	-1.964993	99	1	0.263527	1.221739	-6.857946
35	1	-9.165052	0.966121	-1.990365	100	6	-1.350889	-1.342998	-6.884717
36	1	-9.188592	0.960579	1.898793	101	1	0.257073	-1.373479	-6.828961
37	44	0.277826	0.000895	0.003325	102	1	-1.633366	-1.358534	-7.943898
38	7	0.110783	-2.034203	0.027448	103	1	-1.744407	-2.250337	-6.411265
39	6	0.952330	-4.727487	0.052008	104	6	-3.457688	0.078769	-6.388514
40	6	1.454246	-2.347327	0.030881	105	1	-3.921912	0.816210	-5.956473
41	6	0.791138	-3.042694	0.039987	106	1	-3.917388	0.965854	-5.935815
42	6	0.413183	-4.383674	0.052923	107	1	-3.697861	0.091750	-7.457404
43	6	1.884444	-3.674811	0.042726	108	6	8.772024	0.003317	0.043581
44	1	-1.836040	-2.759793	0.033030	109	35	10.723055	0.004608	0.053188
45	1	-1.186022	-5.143176	0.040709	110	6	1.396647	6.141971	0.060811
46	1	2.946098	-3.888912	0.066254	111	7	2.234484	8.850819	0.096384
47	7	1.705491	0.000207	0.011588	112	6	2.597276	6.528369	0.688192
48	6	4.483766	0.000823	0.022331	113	6	0.627893	7.153749	0.546837
49	6	2.366644	1.190118	0.001157	114	6	1.080258	8.477794	0.506221
50	6	2.365644	-1.190212	0.027305	115	6	2.971623	7.877239	0.682171
51	6	3.761344	-1.213229	0.029897	116	1	3.227137	5.807510	-1.198085
52	6	3.762350	1.212103	0.007501	117	1	0.296259	6.925567	1.066276
53	1	4.289848	-2.158503	0.013850	118	1	0.503940	9.269312	0.974430
54	1	4.291422	2.157017	0.026202	119	1	3.890233	8.193949	-1.165612
55	7	0.112418	2.035683	0.015729	120	6	1.391914	-6.141432	0.059660
56	6	0.956059	4.728403	0.042278	121	7	2.228114	-8.850848	0.073894
57	6	0.788708	3.044911	0.024931	122	6	0.625168	-7.140469	0.690450
58	6	1.456110	2.347831	0.016892	123	6	2.589661	-6.540757	0.565097
59	6	1.887319	3.674975	0.030199	124	6	2.963292	-7.889491	0.534136
60	6	0.409729	4.385593	0.037318	125	6	1.076691	-8.465335	0.674010
61	1	-1.833818	2.762718	0.029088	126	1	0.296630	-6.901443	1.209226
62	1	2.949168	3.888445	0.010493	127	1	3.217539	-5.830280	-1.091781
63	1	-1.182053	5.145167	0.065997	128	1	3.879620	-8.216270	-1.015200
64	6	5.964468	0.001522	0.029571	129	1	0.502009	-9.247136	1.160221
65	6	6.689665	1.011816	0.630246					

Table S12 Contributions of each unit to selected frontiers orbitals of **C1**$^{+}$

MO	eV	DMAPh	tbu$_2$tpy	Ru	4-py	tpy
α L+2	-2.05	0	13	4	1	82
α L+1	-2.24	1	84	1	0	14
α LUMO	-2.33	6	83	9	0	2
α SOMO	-3.61	0	1	8	15	76
α H-1	-5,50	65	11	22	0	3
α H-2	-6.51	0	16	67	0	17
β L+2	-2.01	0	2	8	17	73
β L+1	-2.22	1	93	1	0	5
β LUMO	-2.32	6	82	10	0	2
β HOMO	-5.48	62	11	25	0	3
β H-1	-5.69	0	7	62	6	25
β H-2	-5.81	0	16	67	0	17

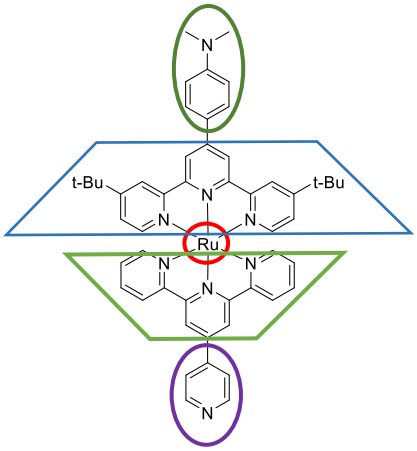


Table S13 Contributions of each unit to selected frontiers orbitals of **C2**$^{+}$

MO	eV	DMAPh	tbu$_2$tpy	Ru	4-py	pzpypz
α L+2	-2.26	1	91	4	0	5
α L+1	-2.42	6	84	8	0	1
α LUMO	-2.60	0	7	4	0	88
α SOMO	-3.96	0	2	8	4	85
α H-1	-5.58	75	9	14	0	2
α H-2	-6.11	0	16	64	0	20
β L+2	-2.32	0	69	0	0	31
β L+1	-2.38	0	2	9	9	80
β LUMO	-2.42	6	84	8	0	2
β HOMO	-5.57	73	10	16	0	2
β H-1	-6.01	0	7	65	4	24
β H-2	-6.11	0	16	65	0	19

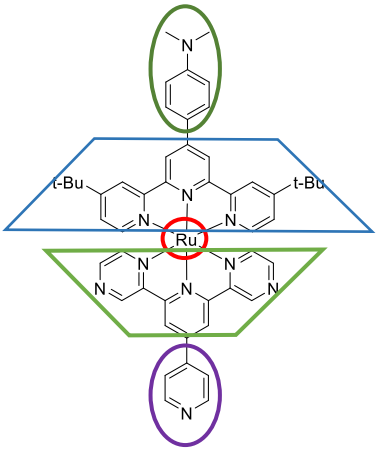


Table S14 Contributions of each unit to selected frontiers orbitals of **C3**$^{+}$

MO	eV	DMAPh	tbu$_2$tpy	Ru	4'(4BrPh)	tpy	4 and 4'' py
α L+2	-2.21	1	89	4	0	5	2
α L+1	-2.35	6	83	9	0	2	0
α LUMO	-2.47	0	9	3	0	69	18
α SOMO	-3.65	0	1	7	4	78	10
α H-1	-5.52	68	10	19	0	2	0
α H-2	-5.86	0	15	65	0	18	3
β L+2	-2.05	0	9	5	1	70	14
β L+1	-2.24	1	83	2	0	11	3
β LUMO	-2.35	4	55	8	1	24	8
β HOMO	-5.51	66	10	21	0	3	0
β H-1	-5.82	0	14	63	1	19	3
β H-2	-6.16	29	17	48	0	6	0

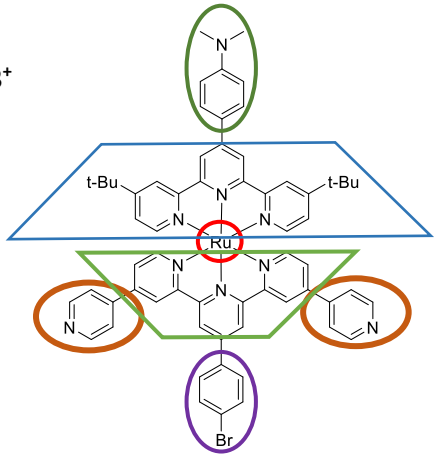


Table S15 Atomic coordinates of **C1**$^{+}$ after optimization.

Center Number	Atomic number	Coordinates (Angstroms)			Center Number	Atomic number	Coordinates (Angstroms)		
		X	Y	Z			X	Y	Z
1	6	3.940614	0.000035	0.000066	56	7	-1.240576	0.013654	2.037235
2	7	1.149055	0.000010	0.000364	57	6	-2.064210	0.032410	4.719138
3	6	3.208431	-1.212196	0.009224	58	6	0.328806	0.021896	3.044193
4	6	3.208393	1.212241	0.009494	59	6	-2.595240	0.014185	2.349447
5	6	1.813166	1.190623	0.004628	60	6	-3.009268	0.023385	3.695447
6	6	1.813206	-1.190623	0.004066	61	6	0.692730	0.031533	4.387791
7	1	3.732910	-2.159288	0.044745	62	1	0.713192	0.020712	2.746248
8	1	3.732849	2.159351	0.044861	63	1	-4.067479	0.023405	3.930834
9	6	0.900151	2.348890	0.015115	64	1	0.074259	0.038053	5.153331
10	6	0.957500	4.387315	0.033324	65	1	-2.381050	0.039931	5.756541
11	7	0.441369	2.035888	0.014252	66	6	-7.092033	0.000010	0.000775
12	6	1.331047	3.681076	0.024696	67	7	-9.967600	0.000011	0.001248
13	6	0.409590	4.740127	0.034731	68	6	-7.852202	0.294641	1.164511
14	6	-1.340414	3.049019	0.022859	69	6	-7.852590	0.294652	-1.162717
15	1	2.393866	3.885492	0.024251	70	6	-9.247326	0.282087	-1.116505
16	1	-2.384593	2.760262	0.021300	71	6	-9.246961	0.282068	1.118752
17	1	-1.733252	5.144859	0.040214	72	1	-7.373084	0.554223	2.101755
18	6	0.900224	-2.348916	0.014498	73	1	-7.373762	0.554211	-2.100115
19	6	0.957372	-4.387393	0.032585	74	1	-9.822251	0.512799	-2.009106
20	6	1.331157	-3.681091	0.024034	75	1	-9.821581	0.512788	2.011549
21	7	0.441305	-2.035951	0.013634	76	7	9.669127	0.000237	0.000402
22	6	-1.340322	-3.049107	0.022157	77	6	10.403179	-1.135224	0.553380
23	6	0.409728	-4.740168	0.034029	78	1	10.168960	-2.068439	0.023007
24	1	2.393982	-3.885476	0.023580	79	1	11.474762	0.953997	0.456449
25	1	-2.384508	-2.760377	0.020568	80	1	10.180804	-1.282915	-1.619233
26	1	-1.733104	-5.144958	0.039415	81	6	10.403001	1.135402	0.555025
27	6	5.414147	0.000064	0.000095	82	1	10.180921	1.282123	1.621086
28	6	8.291076	0.000150	0.000361	83	1	10.168313	2.068980	0.025526
29	6	6.154567	1.080211	0.531552	84	1	11.474609	0.954622	0.457540
30	6	6.154729	-1.080067	0.531168	85	6	0.830204	-6.211470	0.046293
31	6	7.547577	-1.088377	0.538895	86	6	0.830027	6.211440	0.047025
32	6	7.547413	1.088589	0.539567	87	6	0.258800	6.887250	-1.316889
33	1	5.638566	1.925146	0.979777	88	1	0.835018	6.833121	-1.351789
34	1	5.638859	-1.925059	0.979436	89	1	0.654712	6.415289	-2.224078
35	1	8.060367	-1.938104	0.974556	90	6	2.359052	6.381480	0.047151
36	1	8.060073	1.938276	0.975460	91	1	2.818806	5.944943	0.848001
37	44	0.831603	0.000037	0.000257	92	1	2.602558	7.449824	0.056300
38	7	-1.241238	0.013722	-2.037599	93	1	2.820376	5.929332	0.933711
39	6	-2.065691	0.032465	-4.719261	94	1	0.543162	7.946164	-1.328785
40	6	-2.596015	0.014228	-2.349406	95	6	0.256415	6.909474	1.209649
41	6	0.329777	0.021981	-3.044839	96	1	0.650949	6.453841	2.125737
42	6	0.694106	0.031613	-4.388327	97	1	0.837438	6.855541	1.243653
43	6	-3.010442	0.023423	-3.695288	98	1	0.540360	7.968551	1.203234
44	1	0.712308	0.020812	-2.747194	99	6	0.258951	-6.887336	1.316116
45	1	0.072660	0.038148	-5.154091	100	1	0.654820	-6.415393	2.223333
46	1	-4.068725	0.023427	-3.930361	101	1	0.543342	-7.946243	1.327987
47	1	-2.382854	0.039983	-5.756566	102	1	0.834869	-6.833240	1.350983
48	7	-2.823841	0.000049	0.000061	103	6	0.256650	-6.909480	-1.210422
49	6	-5.627988	0.000013	0.000525	104	1	0.837202	-6.855568	-1.244458
50	6	-3.498986	0.002886	1.203993	105	1	0.540619	-7.968550	-1.204030
51	6	-3.499394	0.002925	-1.203683	106	1	0.651204	-6.453808	-2.126482
52	6	-4.887384	0.000269	-1.220478	107	6	2.359233	-6.381472	0.046468
53	6	-4.886966	0.000289	1.221268	108	1	2.820514	-5.929322	0.933049
54	1	-5.406344	0.021256	-2.171570	109	1	2.819008	-5.944913	0.848663
55	1	-5.405601	0.021322	2.172534	110	1	2.602765	-7.449810	0.055610

Table S16 Atomic coordinates of **C2**$^{+}$ after optimization.

Center Number	Atomic number	Coordinates (Angstroms)			Center Number	Atomic number	Coordinates (Angstroms)		
		X	Y	Z			X	Y	Z
1	6	3.937951	0.000003	0.000025	55	7	-1.227109	0.008062	2.018109
2	7	1.148354	0.000008	0.000060	56	7	-2.103519	0.019701	4.709496
3	6	3.205370	-1.212309	0.005598	57	6	0.343359	0.012615	3.055128
4	6	3.205366	1.212301	0.005594	58	6	-2.589128	0.008569	2.336056
5	6	1.810519	1.189883	0.000719	59	6	-2.977639	0.014174	3.690461
6	6	1.810524	-1.189897	0.000636	60	6	0.772736	0.018619	4.375513
7	1	3.729250	-2.159597	0.038376	61	1	0.710418	0.011509	2.806707
8	1	3.729246	2.159590	0.038330	62	1	-4.030149	0.014165	3.954067
9	6	0.898279	2.349894	0.007843	63	1	0.058723	0.022622	5.190236
10	6	0.955545	4.391629	0.020154	64	6	-7.089485	0.000015	0.000197
11	7	0.443105	2.040570	0.008166	65	7	-9.940974	0.000033	0.000306
12	6	1.331690	3.680562	0.013227	66	6	-7.832414	0.551616	1.067628
13	6	0.411745	4.741524	0.020140	67	6	-7.832489	0.551655	-1.067177
14	6	-1.340795	3.053839	0.013876	68	6	-9.230198	0.529052	-1.026082
15	1	2.394670	3.883438	0.011907	69	6	-9.230126	0.528995	1.026639
16	1	-2.385887	2.768978	0.013409	70	1	-7.341250	-1.019490	1.913864
17	1	-1.730093	5.150233	0.024854	71	1	-7.341384	1.019522	-1.913452
18	6	0.898288	-2.349911	0.007716	72	1	-9.808136	0.955556	-1.840352
19	6	0.955530	-4.391653	0.019909	73	1	-9.808007	0.955492	1.840954
20	6	1.331703	-3.680579	0.013030	74	7	9.664273	0.000011	0.000235
21	7	0.443097	-2.040591	0.008051	75	6	10.398703	-1.137744	0.548961
22	6	-1.340784	-3.053863	0.013702	76	1	10.164250	-2.068619	0.014802
23	6	0.411762	-4.741543	0.019884	77	1	11.470171	0.955995	0.452309
24	1	2.394684	-3.883451	0.011706	78	1	10.176575	-1.289361	-1.614226
25	1	-2.385876	-2.769005	0.013254	79	6	10.398655	1.137888	0.549241
26	1	-1.730076	-5.150259	0.024557	80	1	10.176398	1.289744	1.614443
27	6	5.410463	0.000002	0.000079	81	1	10.164288	2.068652	0.014846
28	6	8.286949	0.000009	0.000179	82	1	11.470132	0.956088	0.452784
29	6	6.150909	1.082972	0.526431	83	6	0.835352	-6.211726	0.027271
30	6	6.150952	-1.082961	0.526226	84	6	0.835331	6.211708	0.027617
31	6	7.543352	-1.091111	0.534378	85	6	0.265561	6.892161	-1.295732
32	6	7.543307	1.091132	0.534674	86	1	0.828346	6.840792	-1.330992
33	1	5.635421	1.930049	0.971020	87	1	0.660673	6.422235	-2.204273
34	1	5.635501	-1.930040	0.970854	88	6	2.364663	6.378572	0.026612
35	1	8.056137	-1.942545	0.966561	89	1	2.823323	5.938575	0.867389
36	1	8.056060	1.942575	0.966876	90	1	2.610010	7.446456	0.032217
37	44	0.836245	0.000011	0.000038	91	1	2.825561	5.928718	0.914538
38	7	-1.227268	0.008081	-2.018157	92	1	0.552401	7.950366	-1.304093
39	7	-2.103861	0.019710	-4.709480	93	6	0.262260	6.906371	1.231249
40	6	-2.589306	0.008581	-2.336008	94	1	0.655234	6.446903	2.146041
41	6	0.343588	0.012635	-3.055234	95	1	0.831716	6.855112	1.264395
42	6	0.773058	0.018634	-4.375591	96	1	0.548807	7.964687	1.228301
43	6	-2.977913	0.014182	-3.690384	97	6	0.265732	-6.892223	1.295430
44	1	0.710205	0.011535	-2.806881	98	1	0.660926	-6.422305	2.203941
45	1	0.059102	0.022637	-5.190364	99	1	0.552604	-7.950419	1.303739
46	1	-4.030441	0.014168	-3.953918	100	1	0.828173	-6.840888	1.330808
47	7	-2.830763	0.000010	0.000032	101	6	0.262137	-6.906350	-1.231551
48	6	-5.612581	0.000006	0.000140	102	1	0.831841	-6.855062	-1.264582
49	6	-3.496282	0.000343	1.203848	103	1	0.548659	-7.964672	-1.228654
50	6	-3.496377	0.000352	-1.203730	104	1	0.655027	-6.446872	-2.146374
51	6	-4.890659	0.001749	-1.219329	105	6	2.364684	-6.378585	0.026084
52	6	-4.890565	0.001742	1.219551	106	1	2.825695	-5.928623	0.913897
53	1	-5.421092	0.022582	-2.164434	107	1	2.823228	-5.938693	0.868027
54	1	-5.420928	0.022597	2.164696	108	1	2.610035	-7.446468	0.031780

Table S17 Atomic coordinates of **C3**$^{+}$ after optimization.

Center Number	Atomic number	Coordinates (Angstroms)			Center Number	Atomic number	Coordinates (Angstroms)		
		X	Y	Z			X	Y	Z
1	6	-5.064006	0.009230	0.019465	66	6	6.696134	-1.056806	0.604942
2	7	-2.272725	0.014324	0.010255	67	6	8.095861	-1.069423	0.599177
3	6	-4.335511	0.018746	-1.194669	68	6	8.094980	1.026923	0.643186
4	6	-4.327561	0.037443	1.228840	69	1	6.175104	1.831074	-1.137022
5	6	-2.932571	0.044040	1.202315	70	1	6.177332	-1.859094	1.120445
6	6	-2.940334	0.021053	-1.177300	71	1	8.632648	-1.877043	1.085304
7	1	-4.862609	0.014991	-2.140853	72	1	8.630715	1.831888	-1.134855
8	1	-4.848497	0.028776	2.178412	73	7	-10.791856	0.002983	0.040099
9	6	-2.016608	0.066885	2.358130	74	6	-11.529316	0.581548	-1.077700
10	6	0.154561	0.102972	4.391869	75	1	-11.297140	0.077154	-2.025654
11	7	0.676239	0.055599	2.042302	76	1	-12.600350	0.478842	0.896517
12	6	-2.444525	0.098260	3.690747	77	1	-11.307922	-1.651199	-1.196543
13	6	-1.520611	0.117456	4.747643	78	6	-11.522400	0.585671	1.163385
14	6	0.225044	0.072931	3.052891	79	1	-11.302716	1.655850	1.280645
15	1	-3.506791	0.108045	3.897574	80	1	-11.281950	0.081798	2.109553
16	1	1.268961	0.062064	2.763672	81	1	-12.594499	0.480378	0.990170
17	1	0.623114	0.115115	5.147309	82	6	-1.977609	0.163846	-6.199874
18	6	-2.031829	0.050526	-2.338827	83	6	-1.937708	0.152500	6.219455
19	6	0.182782	0.109930	-4.383825	84	6	-1.371896	-1.099260	6.932580
20	6	-2.468278	0.089321	-3.668494	85	1	0.278462	-1.142150	6.876719
21	7	0.689423	0.041351	-2.031509	86	1	-1.774329	-2.018250	6.489925
22	6	0.205382	0.071333	-3.047525	87	6	-3.466299	0.166468	6.392669
23	6	-1.551115	0.120181	-4.730975	88	1	-3.921961	1.050242	5.929448
24	1	-3.531880	0.096548	-3.868509	89	1	-3.707273	0.192070	7.461299
25	1	1.251115	0.064193	-2.764805	90	1	-3.933785	0.731099	5.969553
26	1	0.590096	0.132627	-5.143928	91	1	-1.653389	-1.076762	7.992074
27	6	-6.537236	0.007674	0.024547	92	6	-1.355348	1.426836	6.877146
28	6	-9.414031	0.004562	0.035047	93	1	-1.745020	2.330706	6.393774
29	6	-7.274475	0.567433	1.092611	94	1	0.261378	1.452517	6.820943
30	6	-7.281012	0.553613	-1.038165	95	1	-1.637851	1.455043	7.936226
31	6	-8.673735	0.563287	-1.041157	96	6	-1.411398	1.080777	-6.925093
32	6	-8.667162	0.574103	1.105794	97	1	-1.807624	2.004349	-6.486368
33	1	-6.756164	1.039120	1.923198	98	1	-1.699403	1.052088	-7.982689
34	1	-6.767829	-1.024194	-1.872547	99	1	0.317484	1.119776	-6.876102
35	1	-9.189046	-1.022748	-1.876684	100	6	-1.404401	-1.444920	-6.852474
36	1	-9.177356	1.032423	1.945086	101	1	0.310178	-1.474261	-6.803661
37	44	0.292294	0.012926	0.003854	102	1	-1.694292	-1.479539	-7.909361
38	7	0.090223	-2.015218	0.048044	103	1	-1.794013	-2.343923	-6.360072
39	6	0.945449	-4.730932	0.093914	104	6	-3.507305	0.173008	-6.363408
40	6	1.455989	-2.337182	0.055720	105	1	-3.968656	0.729296	-5.943641
41	6	0.807927	-3.039095	0.063377	106	1	-3.963449	-1.051759	-5.891198
42	6	0.441043	-4.373433	0.082753	107	1	-3.755098	0.205099	-7.430305
43	6	1.868985	-3.679704	0.081200	108	6	8.783733	0.023603	0.026889
44	1	-1.854140	-2.754252	0.065700	109	35	10.738312	0.029412	0.037967
45	1	-1.219534	-5.126247	0.117588	110	6	1.414378	6.151651	0.133106
46	1	2.932727	-3.890188	0.063970	111	7	2.255907	8.868723	0.194598
47	7	1.702937	0.008740	0.000317	112	6	0.613501	7.159870	0.710086
48	6	4.487099	0.009503	0.002384	113	6	2.650846	6.554326	0.414989
49	6	2.375695	1.200159	0.028735	114	6	3.025117	7.901138	0.362031
50	6	2.358624	-1.204151	0.030763	115	6	1.067131	8.483334	0.719088
51	6	3.759464	-1.216637	0.028739	116	1	0.340683	6.927057	-1.169661
52	6	3.766112	1.218253	0.030892	117	1	3.310794	5.843964	0.900887
53	1	4.286990	-2.163958	0.024600	118	1	3.971630	8.223800	0.784586
54	1	4.299720	2.161304	0.025292	119	1	0.462407	9.266713	-1.165428
55	7	0.119151	2.039787	0.044000	120	6	1.377233	-6.138787	0.105628
56	6	0.973954	4.741479	0.102845	121	7	2.201666	-8.874289	0.120306
57	6	0.778571	3.060710	0.073822	122	6	2.660111	-6.529988	0.556538
58	6	1.471465	2.353677	0.047271	123	6	0.523843	-7.178545	0.331904
59	6	1.898383	3.686129	0.074526	124	6	0.969503	-8.503702	0.308230
60	6	0.400787	4.395937	0.105062	125	6	3.022436	-7.879290	0.544212
61	1	-1.824773	2.779712	0.065408	126	1	3.369422	-5.803638	0.937905
62	1	2.962174	3.892592	0.098321	127	1	0.470162	-6.968680	0.710619
63	1	-1.173439	5.155939	0.105524	128	1	0.319782	-9.304495	0.648924
64	6	5.965978	0.014788	0.009315	129	1	4.004485	-8.184670	0.893008
65	6	6.694930	1.023900	0.630339					

Photocatalytic studies

Hydrogen evolution was monitored using a Perkin Elmer Clarus-480 gas chromatograph (GC) with a thermal conductivity detector, argon as carrier and eluent gas, a 7 ft. HayeSep N 60/80 pre-column, a 9 ft. molecular sieve 13 x 45/60 column and a 2 ml injection loop. Three distinct solutions for the sacrificial electron donor and proton source, the photosensitizer and the catalyst were prepared and mixed together to obtain 5 ml of solutions in standard 20 ml headspace vials. Using DMF as a solvent, the resulting molar concentration of photocatalytic medium are: 1 M for triethanolamine (TEOA), 0.1 M for HBF4, 0.56 M for water (*pH*apparent= 8.9). The concentration of active species were: 0.1 mM for the photosensitizer, 1 mM of cobalt pre-catalyst $[Co(H_2O)_6](BF_4)_2$ and 6 mM of dimethylglyoxime. The vials were placed on top of a LED in an aluminum cast connected to a thermostatic bath set at 20 °C. They were sealed with a rubber septum pierced with two stainless steel tubes. The first tube carried an argon flow pre-bubbled in DMF. The flow was set between at 5 ml/min (adjusted with calibrated mass flow MCseries from Alicat) and referenced with a digital flowmeter (Perkin Elmer FlowMark). The second tube led the flow to the GC sample loop through a 2 ml overflow protection vial, then through an 8-port stream select valve (VICCI) and finally to GC sample loop. A microprocessor (Arduino Uno) coupled with a custom PC interface allowed for timed injections. For calibration testing, stock cylinders of known concentration of H_2 in argon replaced the argon flow (inserted at the pre-bubbler, to keep the same vapor matrix). The measured results, independent of flow rate (under same pressure) can be easily converted into a rate of hydrogen production following equation 1. The errors associated to the *TON* (TurnOver Number) and *TOF* (TurnOver Frequency) were estimated to be within 10 %. They are calculated using the equations below.

(Eq. 1) H_2 rate (µL/min) = [H_2 standard] (ppm) × Ar flow rate (mL/min)

(Eq. 2) H_2 rate (nmol/min) = H_2 rate (µL/min) / 24.45 × 1000

(Eq. 3) TOF ($mmol_{H2}.mol_{PS}.min^{-1}$) = H_2 rate (nmol/min) / n_{PS} (mol) / 10^6

The amount of hydrogen produced between two injections is calculated using the average rate over that period of time [t_i ; t_j], multiplied by the time between two injections (tj-ti).

(Eq. 4) $n_{H2\ total}$ (nmol) = $\sum_{t0}^{tf} n_{H2}[ti\ ;\ tj]$ = $\sum_{t0}^{tf}$((H_2 rate (ti) + H_2 rate (tj)) /2) × (tj-ti))

(Eq. 5) For a chosen length of experiment (t_f) TON(t_f) = $n_{H2(tf)}$ / n_{PS}

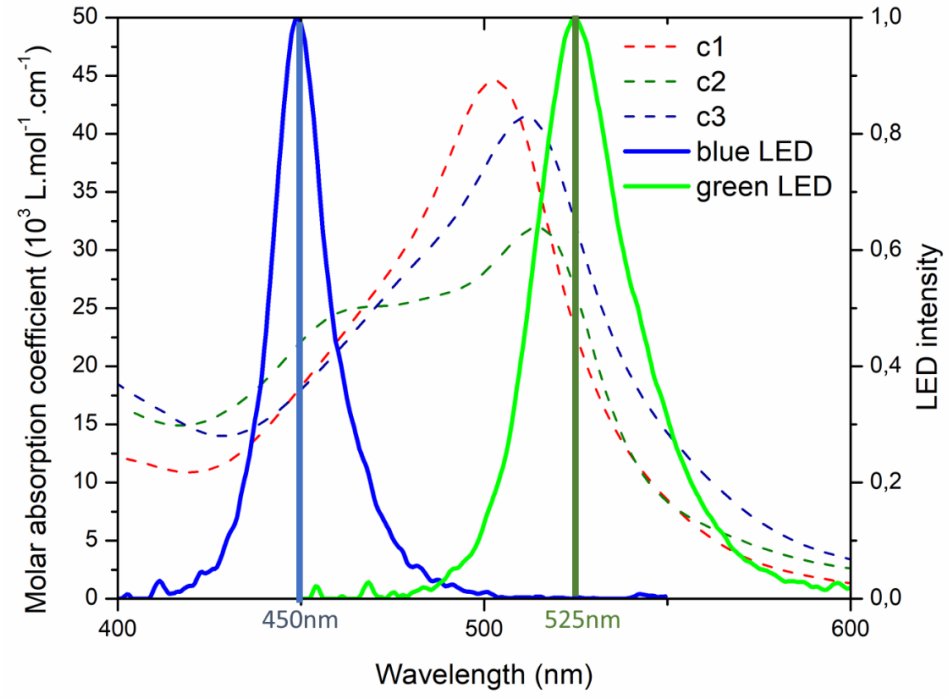


Figure S20 Overlap of the emission spectra of the LEDs used for photocatalytic experiments with the absorption spectra of the photosensitizers in this study.

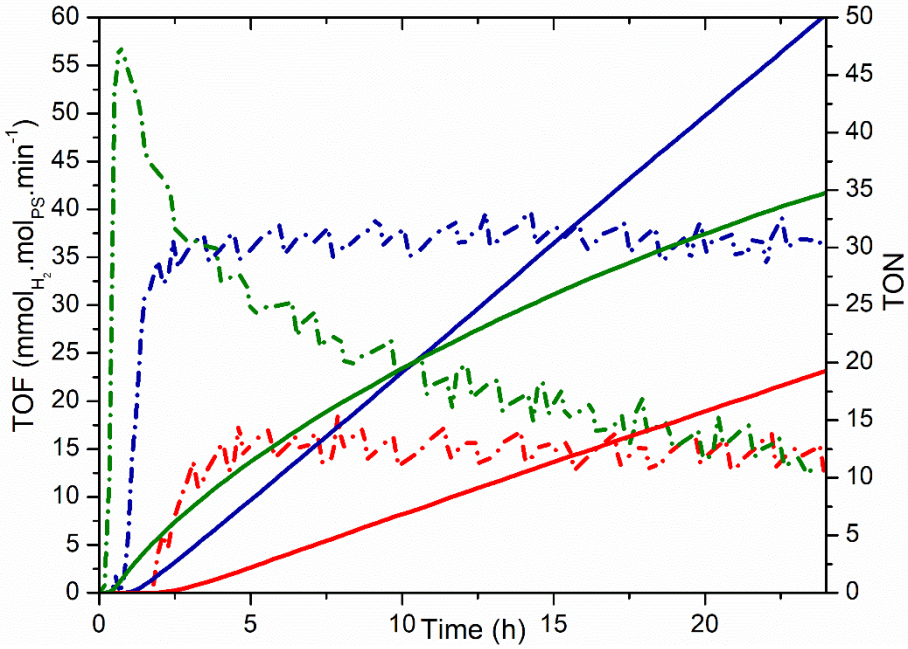


Figure S21 Photocatalytic hydrogen evolution performances obtained using fresh stock solutions of **C1**, **C2** or **C3** in DMF with 1M TEOA and 0.1M HBF4 under 450 nm irradiation (62 mW) with 1mM $[Co(H_2O)_6](BF_4)_2$ and 6mM $dmgH_2$ as precursors for the catalyst.

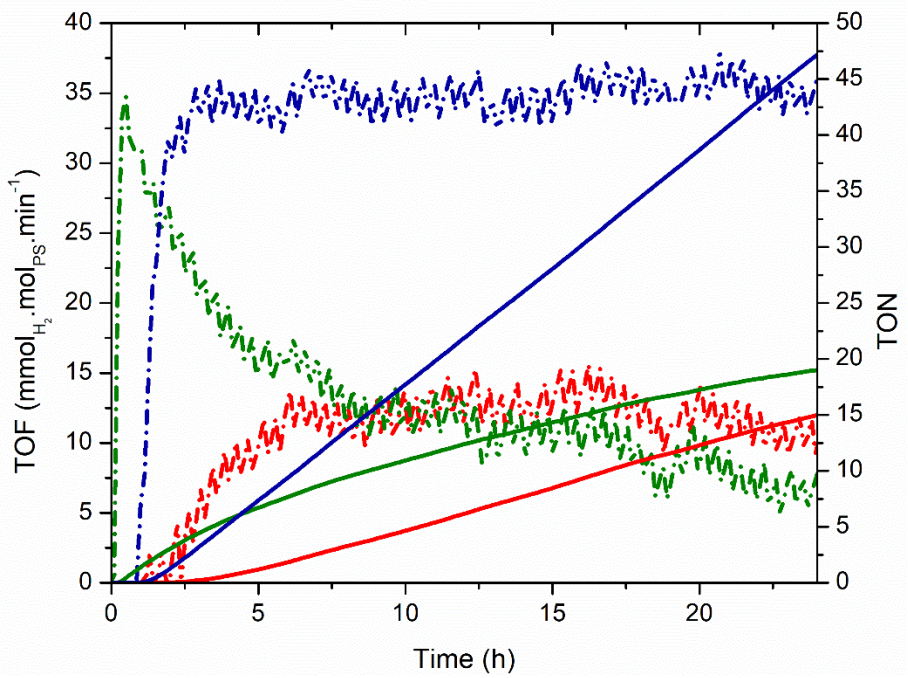


Figure S22 Photocatalytic hydrogen evolution performances obtained using fresh stock solutions of **C1**, **C2** or **C3** in DMF with 1M TEOA and 0.1M HBF4 under 525 nm irradiation (53mW) with 1mM $[Co(H_2O)_6](BF_4)_2$ and 6mM $dmgH_2$ as precursors for the catalyst.

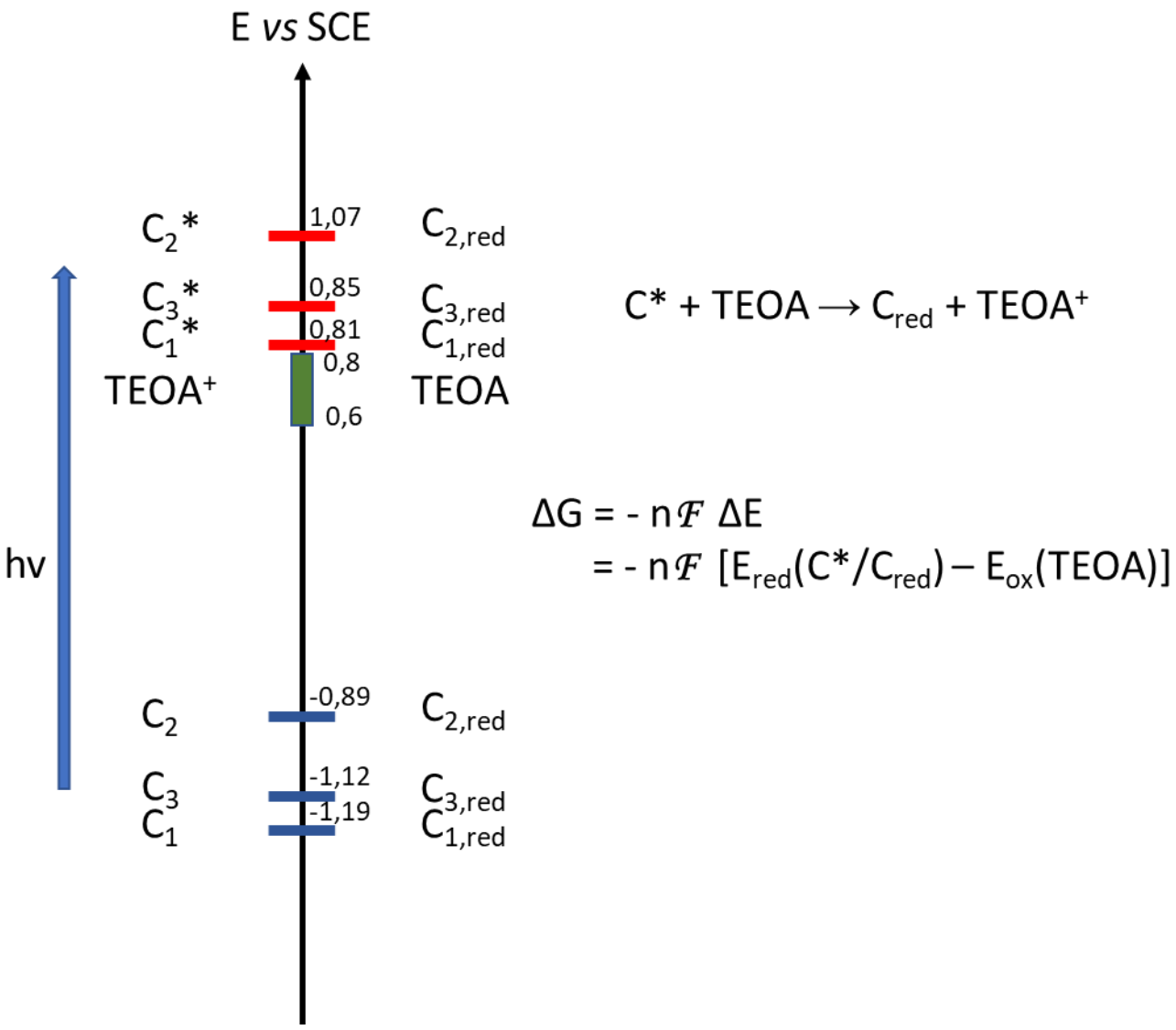


Figure S23 Scale of redox potentials highlighting the variation in driving force based on the relative position of the excited state reduction potential of the different PS (determined using the emission onset) compared to the oxidation range of triethanolamine.