Supplementary Information

Strong metal-metal coupling in mixed-valent intermediates [Cl(L)Ru(μ-tppz)Ru(L)Cl]$^{+}$, L = β-diketonato ligands, tppz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine

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Table S1 Selected parameters of symmetric tppz-bridged diruthenium complexes

Complexes	K_c	ν_{IVCT}/nm(ε/ $M^{-1}cm^{-1}$)	$\Delta\nu_{1/2}$ /cm^{-1} (expt)	class	V_{ab}/cm^{-1}	Ref..
$[(NH_3)_3Ru^{II}(tppz)Ru^{II}(NH_3)_3]^{4+}$ tppz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine	3.0×10^8	NA (Not available)	NA	-	-	7a
$[(L)Ru^{II}(tppz)Ru^{II}(L)]^{4+}$						
L = 2,2′:6′,2″-terpyridine	1.8×10^5	1527(7560) (CD_3CN)	970	II-III /III	3274(based on class III)	7b/ 7c
L = 4′-vinyl-2,2′:6′,2″-terpyridine	1.3×10^6	-	-	-		
L = tppz	1.4×10^9	-	-	-		
$[Cl(L)Ru^{II}(tppz)Ru^{II}(L)Cl]^{2+}$						7d/ 7e
L = 2,2′-bipyridine	8.2×10^4	1647(-) (CD_3CN)	-	-	-	
L = 4,4′-dimethy-2,2′-bipyridine	8.2×10^4	NA	NA	-	-	
$[Cl(L)Ru^{II}(tppz)Ru^{II}(L)Cl]^{2+}$ L = 2-phenylazopyridine	4.0×10^3	1890 (3800)	1650	II-III	-	7f

L = 2-[(4-methylphenyl)azo]-pyridine L = 2-[(4-chlorophenyl)azo]-pyridine L = 2-[(3-methylphenyl)azo]-pyridine	2.1×10^{4} 2.2×10^{3} 6.4×10^{3}	1890 (4600) 1890 (3000) NA	1650 1650 -	II-III II-III -	- - -	
$[Cl(L)Ru^{II}(tppz)Ru^{II}(L)Cl]^{2+}$ L = 2,2′-dipyridylamine	2.7×10^{6}	1700 (2250)	1390	III	2941	7g
$[Cl(L)Ru^{II}(tppz)Ru^{II}(L)Cl]^{2+}$ L = 2-(2-pyridyl)benzoxazole L = 2-(2-pyridyl)benzthiazole L = 1-methyl-2-(2-pyridyl)-1*H*-benzimidazole L = 2-(2-pyridyl)benzimidazolate	 3.8×10^{4} 5.6×10^{4} 2.6×10^{4} 2.6×10^{4}	 1635 (1400) 1465 (440) 1555 (423) -	 1790 2030 1530 -	 II-III II-III II-III -	 - - - -	7h
$[Cl(L)Ru^{II}(tppz)Ru^{II}(L)Cl]^{2+}$ L = 2,2′-dipyridylketone	2.5×10^{4}	1800 (1500)	700	II-III	-	7i
$[Cl(L)Ru^{II}(tppz)Ru^{II}(L)Cl]^{2+}$ L = 2,2′-bis(1-methylimidazolyl) ketone	1.2×10^{5}	1637 (1200)	1560	II-III	-	7j

$[(L^{-})Ru^{II}(tppz)Ru^{II}(L^{-})]^{2+}$ L = 1,3-di(2-pyridyl)benzene L = methyl 3,5-di(2-pyridyl)benzoate	 5.4×10^{4} 3.8×10^{5}	 1661(5500) 1686(7500) (CD_3CN)	 1033 1062	 - -	 - -	7k
$[(L)ClRu^{II}(tppz)Ru^{II}(L)Cl]$ L = 2-picolinate L = 2-quinolinecarboxylate L = 8-quinolinecarboxylate	 4.0×10^{6} 8.9×10^{6} 1.9×10^{7}	 1670 (2600) 1575 (1200) 1875 (2600)	 1620 1115 1370	 III III III	 2994 3174 2666	7l
$[Cl(Q^{\bullet-})Ru^{II}(tppz)Ru^{II}(Q^{\bullet-})Cl]$ $Q^{\bullet-}$ = o-benzosemiquinone $Q^{\bullet-}$ = 3,5- ditert-butyl-o-benzosemiquinone	 7.6×10^{2} 3.6×10^{3}	 NA NA	 NA NA	 - -	 - -	7m
$[Cl_3Ru^{II}(tppz)Ru^{III}Cl_3]^{-}$	1.0×10^{12}	1798 (3500) (CD_3CN)	1150	III	2780	7n
$[Cl(Q^{\bullet-})Ru^{III}(tppz)Ru^{III}(Q^{\bullet-})Cl]^{2+}$ $Q^{\bullet-}$ = 4,6-di-*tert*-butyl-*N*-phenyl-*o*-benzosemiquinonato	1.3×10^{6}	1853 (4150)	1350	III	2698	7o

$[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$ (**Creutz-Taube ion**)	4.1×10^{6}	1570 (5000) (D_2O)	1480	II-III /III	3185 (based on class III)	1b/7e
$[(L)ClRu^{II}(tppz)Ru^{II}(L)Cl]$						Present work
L = acetylacetonate	10^{10}	1680(2900)	1588	III	2976	
L = 3,5-heptanedionate	1.5×10^{10}	1688(3300)	1605	III	2962	
L = 2,2,6,6-tetramethyl-3,5-heptanedionate	1.1×10^{12}	1750(3000)	1994	III	2857	
L = 3-methyl-2,4-pentanedionate	10^{10}	1660(2300)	2135	III	3012	
L = 3-ethyl-2,4-pentanedionate	1.5×10^{10}	1674 (2239)	1843	III	2986	

Table S2 Crystallographic data and refinement parameters for $[(CH_3CN)_{0.8}(Cl)_{0.2}(L)Ru^{II}(\mu\text{-tppz})Ru^{II}(L)(CH_3CN)_{0.8}(Cl)_{0.2}](Cl)_2.4H_2O$ (**4′**)

	4′
Empirical formula	$C_{39.25}H_{47}Cl_{2.50}N_{7.50}O_8Ru_2$
Formula weight	1042.61
Crystal size (mm)	0.42 x 0.32 x 0.12
Crystal system	Monoclinic
Space group	*C 2/c*
a / Å	11.781(5)
b / Å	13.680(5)
c / Å	27.374(11)
α (°)	90
β (°)	95.375(15)
γ (°)	90
V / Å^3	4392(3)
Z	4
ρ_{calcd} / g cm^{-3}	1.577

μ / mm^{-1}	0.898
T / K	170(2)
hkl range	−13 to 14, −16 to 16, −32 to 29
F(000)	2118
θ range (^{o})	1.49 to 25.00
Reflns collected	17147
Unique reflns (R_{int})	3875 [0.0893]
Data/restraints/parameters	3875 / 25 / 298
R1, wR2 ($I>2\sigma(I)$)	0.0618, 0.1597
R1, wR2 (all data)	0.1107, 0.1874
GOF	1.029
Largest diff. peak/hole / e Å^{-3}	0.858/ −1.368

Table S3 Selected bond lengths (Å) and bond angles (°) for **4**/

Bond distances		Bond angels	
Ru-N2	1.918(6)	N2-Ru-O2	90.4(2)
Ru-N1	2.067(6)	N2-Ru-N1	80.0(2)
Ru-N3	2.057(6)	O2-Ru-N1	89.7(2)
Ru-O2	2.029(6)	N2-Ru-N3	81.0(2)
Ru-O1	2.060(5)	O2-Ru-N3	90.7(2)
Ru-N4	1.952(14)	O2-Ru-O1	88.8(2)
Ru-Cl3	2.45(2)	N1-Ru-O1	101.2(2)
		N3-Ru-O1	97.8(2)
		N2-Ru-N4	89.1(6)
		N1-Ru-N4	91.1(7)
		N3-Ru-N4	88.3(7)
		O1-Ru-N4	91.6(6)
		N1-Ru-N3	161.0(2)
		N2-Ru-O1	178.6(2)
		O2-Ru-N4	179.0(6)

N2-Ru-Cl3	94.3(8)
O2-Ru-Cl3	174.3(8)
N3-Ru-Cl3	93.2(8)
O1-Ru-Cl3	86.5(8)
N1-Ru-Cl3	87.9(9)

Table S4 Selected bond angles (°) for **1**-**3** and **5**

Bond angels	**1**		**2**	**3**		**5**
	X-ray	DFT		X-ray	DFT	
N2-Ru1-N1	80.44(11)	80.18	81.12(8)	80.75(15)	80.27	80.83(18)
N2-Ru1-O1	86.47(10)	85.54	90.54(8)	86.83(15)	88.60	95.34(19)
N1-Ru1-O1	91.30(10)	93.82	83.44(8)	84.94(14)	87.70	87.22(19)
N2-Ru1-N3	80.39(11)	80.16	80.49(8)	80.11(16)	80.01	79.66(19)
O1-Ru1-N3	96.03(10)	94.09	88.76(8)	95.51(14)	92.28	90.51(19)
N1-Ru1-O2	101.07(10)	100.3	97.83(8)	98.70(13)	100.5	98.76(18)
O1-Ru1-O2	91.17(9)	88.68	89.96(7)	89.12(14)	88.11	88.93(17)
N3-Ru1-O2	98.45(10)	100.1	100.64(8)	100.51(14)	96.32	101.00(18)
N2-Ru1-Cl1	96.81(8)	97.04	90.08(7)	96.67(13)	94.27	88.11(16)
N1-Ru1-Cl1	85.20(8)	86.55	96.80(7)	93.83(11)	90.89	92.53(16)
N3-Ru1-Cl1	88.60(8)	86.45	91.20(7)	86.89(12)	89.18	90.92(16)
O2-Ru1-Cl1	85.65(7)	88.73	89.43(6)	87.38(11)	89.01	87.61(14)
N1-Ru1-N3	158.99(11)	158.1	159.93(8)	160.79(14)	160.1	160.06(19)
N2-Ru1-O2	177.23(10)	174.2	178.78(8)	175.94(17)	176.6	175.7(2)

O1-Ru1-Cl1	174.73(7)	177.4	179.37(5)	176.07(10)	177.1	176.45(11)
N5-Ru2-N6				80.59(15)	80.16	80.49(19)
N5-Ru2-N4				79.57(15)	80.07	81.0(2)
N5-Ru2-O4				177.76(16)	177.1	91.33(19)
N6-Ru2-O4				101.33(13)	100.7	89.63(19)
N4-Ru2-O4				98.43(13)	99.15	89.92(19)
N6-Ru2-O3				87.13(15)	90.61	99.0(2)
N4-Ru2-O3				89.00(16)	90.39	99.6(2)
O4-Ru2-O3				90.87(14)	89.01	88.57(18)
N5-Ru2-Cl2				94.39(13)	93.72	89.80(16)
N6-Ru2-Cl2				92.64(12)	88.86	89.37(15)
N4-Ru2-Cl2				92.07(13)	90.14	91.45(15)
O3-Ru2-Cl2				177.46(10)	177.1	90.28(15)
N6-Ru2-N4				159.90(14)	160.1	161.43(19)
N5-Ru2-O3				88.07(15)	89.19	179.5(2)
O4-Ru2-Cl2				86.69(11)	89.07	178.34(12)

Table S5 Compositions and energies of some selected molecular orbitals of **1**

MO	Energy/ eV	Compositions (%)			
		Ru	L	tppz	Cl
LUMO+5	-1.05	06	01	93	0
LUMO+4	-1.10	03	0	97	0
LUMO+3	-1.12	03	0	97	0
LUMO+2	-1.79	07	01	92	0
LUMO+1	-2.33	26	02	71	01
LUMO	-2.61	06	01	93	0
HOMO	-4.48	66	06	12	16
HOMO-1	-4.70	58	18	14	10
HOMO-2	-4.83	53	18	15	14
HOMO-3	-5.14	68	10	08	14
HOMO-4	-5.16	36	04	25	35
HOMO-5	-5.20	67	14	08	11
HOMO-6	-6.20	16	74	10	0
HOMO-7	-6.24	22	71	03	04
HOMO-8	-6.32	19	02	14	65
HOMO-9	-6.34	13	05	05	77
HOMO-10	-6.37	21	04	13	62

Table S6 Selected molecular orbitals along with their energies and compositions of **3**

MO	Energy/ eV	Compositions (%)			
		Ru	L	tppz	Cl
LUMO+5	-1.06	03	01	96	0
LUMO+4	-1.15	05	02	93	0
LUMO+3	-1.17	03	02	95	0
LUMO+2	-1.84	07	06	87	0
LUMO+1	-2.33	24	04	70	02
LUMO	-2.83	08	03	89	0
HOMO	-4.51	65	06	12	17
HOMO-1	-4.71	56	17	10	17
HOMO-2	-4.82	50	20	13	17
HOMO-3	-5.10	59	13	11	17
HOMO-4	-5.17	47	10	19	24
HOMO-5	-5.20	60	15	12	13
HOMO-6	-6.18	22	69	08	01
HOMO-7	-6.20	23	68	02	07
HOMO-8	-6.29	13	05	13	69
HOMO-9	-6.35	16	03	18	63
HOMO-10	-6.44	24	05	13	58

Table S7 Selected molecular orbitals along with their energies and compositions of $\mathbf{1}^{+}$ (*S*=1/2)

α-spin					
MO	Energy/ eV	Composition (%)			
		Ru	L	tppz	Cl
LUMO+5	-3.76	01	0	96	03
LUMO+4	-3.77	05	01	95	0
LUMO+3	-3.78	03	0	97	0
LUMO+2	-4.50	05	01	94	0
LUMO+1	-5.32	13	02	85	0
LUMO	-5.34	03	01	96	0
SOMO	-7.88	43	40	08	09
HOMO-1	-7.94	38	44	07	11
HOMO-2	-8.25	51	09	09	31
HOMO-3	-8.40	50	16	07	27
HOMO-4	-8.42	48	21	06	25
HOMO-5	-8.59	33	07	10	50
HOMO-6	-9.09	30	41	29	0
HOMO-7	-9.20	48	43	09	0
HOMO-8	-9.40	15	08	71	06
HOMO-9	-9.59	25	03	25	47
HOMO-10	-9.61	28	03	18	51

β-spin					
LUMO+5	-3.81	03	0	97	0
LUMO+4	-3.83	04	0	96	0
LUMO+3	-4.47	11	01	87	01
LUMO+2	-4.93	45	04	47	04
LUMO+1	-5.35	04	01	95	0
LUMO	-5.96	67	06	16	11
HOMO	-7.70	27	07	47	19
HOMO-1	-7.71	46	32	12	10
HOMO-2	-7.79	44	31	12	13
HOMO-3	-8.22	58	16	07	19
HOMO-4	-8.25	55	21	07	17
HOMO-5	-9.00	30	56	14	0
HOMO-6	-9.06	39	54	06	01
HOMO-7	-9.32	09	10	03	78
HOMO-8	-9.42	10	03	69	18
HOMO-9	-9.46	10	33	04	53
HOMO-10	-9.52	21	02	25	52

Table S8 Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{+}$ (*S*=1/2)

α-spin					
MO	Energy/ eV	Composition (%)			
		Ru	L	tppz	Cl
LUMO+5	-3.69	02	01	97	0
LUMO+4	-3.71	04	04	92	0
LUMO+3	-3.73	03	03	94	0
LUMO+2	-4.46	04	06	90	0
LUMO+1	-5.15	13	03	83	01
LUMO	-5.47	05	03	91	01
SOMO	-7.71	45	25	07	23
HOMO-1	-7.86	43	29	08	20
HOMO-2	-8.02	50	11	10	29
HOMO-3	-8.10	47	29	10	14
HOMO-4	-8.29	42	27	10	21
HOMO-5	-8.36	37	08	09	46
HOMO-6	-8.97	22	31	41	06
HOMO-7	-9.03	38	49	06	07
HOMO-8	-9.12	22	19	39	20
HOMO-9	-9.31	14	30	09	47
HOMO-10	-9.33	06	59	06	29

β-spin					
LUMO+5	-3.73	02	02	96	0
LUMO+4	-3.74	03	03	94	0
LUMO+3	-4.41	14	06	78	02
LUMO+2	-4.75	42	06	49	03
LUMO+1	-5.47	07	03	90	0
LUMO	-5.87	62	07	21	10
HOMO	-7.41	32	08	41	19
HOMO-1	-7.53	51	20	08	21
HOMO-2	-7.74	48	17	14	21
HOMO-3	-7.96	50	25	15	10
HOMO-4	-8.12	53	24	09	14
HOMO-5	-8.85	29	55	10	06
HOMO-6	-8.92	31	59	07	03
HOMO-7	-8.97	12	07	10	71
HOMO-8	-9.13	10	04	48	38
HOMO-9	-9.23	12	27	06	55
HOMO-10	-9.30	06	63	05	26

Table S9 Selected molecular orbitals along with their energies and compositions of $\mathbf{1}^{2+}$ (*S*=1)

α-spin					
MO	Energy/ eV	Composition (%)			
		Ru	L	tppz	Cl
LUMO+5	-6.43	07	01	91	01
LUMO+4	-6.55	03	0	97	0
LUMO+3	-6.58	09	01	89	01
LUMO+2	-7.28	07	01	92	0
LUMO+1	-8.28	02	01	97	0
LUMO	-8.35	12	02	86	0
SOMO1	-10.56	34	54	06	06
SOMO2	-11.20	47	16	06	31
HOMO-2	-11.21	49	11	06	34
HOMO-3	-11.34	20	71	05	04
HOMO-4	-11.46	34	10	10	46
HOMO-5	-11.79	43	06	06	45
HOMO-6	-11.85	44	31	24	01
HOMO-7	-12.13	11	07	81	01
HOMO-8	-12.28	03	75	03	19
HOMO-9	-12.44	24	04	24	48
HOMO-10	-12.57	48	29	09	14

β-spin					
LUMO+5	-6.56	04	0	96	0
LUMO+4	-7.21	11	01	87	01
LUMO+3	-7.90	41	04	50	05
LUMO+2	-8.22	08	02	90	0
LUMO+1	-8.94	45	05	38	12
LUMO	-9.12	54	18	18	10
HOMO	-10.36	38	46	09	07
HOMO-1	-10.86	42	07	22	29
HOMO-2	-10.98	53	19	06	22
HOMO-3	-11.27	33	46	05	16
HOMO-4	-11.65	43	45	12	0
HOMO-5	-11.93	34	39	18	09
HOMO-6	-12.09	07	40	02	51
HOMO-7	-12.16	08	05	86	01
HOMO-8	-12.25	08	49	05	38
HOMO-9	-12.33	21	03	21	55
HOMO-10	-12.38	30	05	12	53

Table S10 Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{2+}$ (*S*=1)

α-spin					
MO	Energy/ eV	Composition (%)			
		Ru	L	tppz	Cl
LUMO+5	-6.31	06	02	91	01
LUMO+4	-6.33	02	01	97	0
LUMO+3	-6.41	05	01	93	01
LUMO+2	-7.13	03	06	91	0
LUMO+1	-8.03	12	03	84	01
LUMO	-8.31	04	02	94	0
SOMO1	-10.68	53	12	06	29
SOMO2	-10.77	24	62	03	11
HOMO-2	-10.90	21	68	03	08
HOMO-3	-10.96	34	18	11	37
HOMO-4	-11.25	47	12	07	34
HOMO-5	-11.27	46	08	07	39
HOMO-6	-11.82	13	17	68	02
HOMO-7	-11.91	35	34	12	19
HOMO-8	-11.91	03	80	04	13
HOMO-9	-11.93	07	66	15	12
HOMO-10	-12.07	40	30	06	24

β-spin					
LUMO+5	-6.34	03	02	95	0
LUMO+4	-7.10	05	06	89	0
LUMO+3	-7.75	32	08	58	02
LUMO+2	-8.22	13	03	83	01
LUMO+1	-8.49	57	17	15	11
LUMO	-8.82	37	17	36	10
HOMO	-10.35	57	13	07	23
HOMO-1	-10.69	39	16	15	30
HOMO-2	-10.82	35	41	07	17
HOMO-3	-10.82	33	44	06	17
HOMO-4	-11.45	52	40	08	0
HOMO-5	-11.49	42	44	08	06
HOMO-6	-11.80	10	13	48	29
HOMO-7	-11.86	03	81	04	12
HOMO-8	-11.89	03	76	06	15
HOMO-9	-11.97	16	08	22	54
HOMO-10	-12.01	15	07	32	46

Table S11 Selected molecular orbitals along with their energies and compositions of **1**$^{-}$ (*S*=1/2)

α-spin					
MO	Energy/ eV	Composition (%)			
		Ru	L	tppz	Cl
LUMO+5	1.79	07	10	83	0
LUMO+4	1.69	03	86	11	0
LUMO+3	1.69	03	90	07	0
LUMO+2	1.65	04	0	96	0
LUMO+1	0.93	08	01	91	0
LUMO	0.58	22	01	75	02
SOMO	-0.77	08	01	91	0
HOMO-1	-1.68	68	05	14	13
HOMO-2	-1.96	64	13	13	10
HOMO-3	-2.09	58	12	16	14
HOMO-4	-2.30	46	04	25	25
HOMO-5	-2.30	75	09	08	08
HOMO-6	-2.34	75	11	09	05
HOMO-7	-3.49	04	07	59	30
HOMO-8	-3.64	17	13	06	64
HOMO-9	-3.65	11	05	05	79
HOMO-10	-3.66	13	47	08	32

β-spin					
LUMO+5	1.75	04	0	96	0
LUMO+4	1.69	03	91	06	0
LUMO+3	1.69	04	93	03	0
LUMO+2	1.11	06	01	93	0
LUMO+1	0.65	19	01	79	01
LUMO	0.39	05	01	94	0
HOMO	-1.71	70	05	11	14
HOMO-1	-1.86	63	12	16	09
HOMO-2	-2.00	60	12	16	12
HOMO-3	-2.29	49	04	21	26
HOMO-4	-2.30	75	09	08	08
HOMO-5	-2.34	75	10	08	07
HOMO-6	-3.24	01	05	82	12
HOMO-7	-3.63	16	07	08	69
HOMO-8	-3.64	14	26	08	52
HOMO-9	-3.65	11	04	05	80
HOMO-10	-3.70	14	76	06	04

Table S12 Selected molecular orbitals along with their energies and compositions of $\mathbf{3}^{-}$ (*S*=1/2)

α-spin					
MO	Energy/ eV	Composition (%)			
		Ru	L	tppz	Cl
LUMO+5	1.67	08	50	42	0
LUMO+4	1.61	02	75	23	0
LUMO+3	1.57	03	43	53	01
LUMO+2	1.55	02	11	86	01
LUMO+1	0.82	09	07	84	0
LUMO	0.52	22	05	72	01
SOMO	-1.00	09	03	88	0
HOMO-1	-1.76	67	05	14	14
HOMO-2	-2.04	62	12	10	16
HOMO-3	-2.16	56	13	15	16
HOMO-4	-2.32	64	09	13	14
HOMO-5	-2.39	60	09	17	14
HOMO-6	-2.42	67	10	13	10
HOMO-7	-3.54	03	09	65	23
HOMO-8	-3.68	11	11	08	70
HOMO-9	-3.72	15	49	02	34
HOMO-10	-3.73	15	52	01	32

β-spin					
LUMO+5	1.66	02	14	84	0
LUMO+4	1.61	03	78	19	0
LUMO+3	1.60	03	66	31	0
LUMO+2	1.00	06	06	87	01
LUMO+1	0.60	18	04	76	02
LUMO	0.16	07	03	90	0
HOMO	-1.78	69	05	12	14
HOMO-1	-1.94	63	11	13	13
HOMO-2	-2.07	59	13	13	15
HOMO-3	-2.32	64	08	12	16
HOMO-4	-2.38	61	09	16	14
HOMO-5	-2.41	69	11	12	08
HOMO-6	-3.27	01	06	82	11
HOMO-7	-3.68	11	09	06	74
HOMO-8	-3.71	15	46	02	37
HOMO-9	-3.73	16	50	02	32
HOMO-10	-3.79	18	32	12	38

Table S13 Electronic transitions at the TD-DFT/B3LYP/6-31G(d) level for $\mathbf{3}^n$ (n= 0, +, 2+, –)

$E_{excitation}$ / eV	$\lambda_{excitation}$ / nm (expt.)	Oscillator Strength (expt.: ε/dm^3 mol^{-1}cm^{-1})	Transition	Character
3				
0.9025	1370 (1390)	0.0096 (1400)	(89%)HOMO→LUMO	Ru(dπ)→tppz(π*)
1.1942	1040 (1060)	0.0099 (1900)	(82%)HOMO-1→LUMO	Ru(dπ)→tppz(π*)
1.7556	706	0.0477	(28%)HOMO-4→LUMO+1 (26%)HOMO-3→LUMO+1	Ru(dπ)/Cl(pπ)→tppz(π*)
1.7910	690 (688)	0.0287 (19500)	(33%)HOMO-5→LUMO+1 (30%)HOMO-3→LUMO+1	Ru(dπ)/Cl(pπ)→tppz(π*)
1.8860	660	0.1369	(35%)HOMO-5→LUMO+1 (32%)HOMO-4→LUMO+1	Ru(dπ)/Cl(pπ)→tppz(π*)
2.4190	510 (505)	0.0594 (7800)	(87%)HOMO-2→LUMO+2	Ru(dπ)/Cl(pπ)→tppz(π*)
2.8784	430	0.0734	(59%)HOMO-1→LUMO+3	Ru(dπ)/Cl(pπ)→tppz(π*)
2.9509	420 (403)	0.0443	(79%)HOMO-1→LUMO+5	Ru(dπ)/Cl(pπ)→tppz(π*)

3^{+}				
0.6419	1930 (1750)	0.0094 (3000)	(57%)HOMO-2(β)→LUMO(β) (57%)HOMO-1(β)→LUMO(β)	Ru(dπ)→Ru(dπ)
0.9263	1340	0.0560	(49%)HOMO(β)→LUMO(β) (23%)HOMO-3(β)→LUMO(β)	Ru(dπ)/tppz(π)→Ru(dπ) Ru(dπ)/L→Ru(dπ)
1.8817	660 (639)	0.0289 (21000)	(63%)HOMO-2(α)→LUMO(α)	Ru(dπ)/Cl(pπ) → tppz(π*)
1.9873	620	0.0349	(51%)HOMO-7(β)→LUMO(β) (22%)HOMO-3(β)→LUMO+2(β)	Cl(pπ) →Ru(dπ) Ru(dπ)/L→Ru(dπ)
2.0179	610	0.0609	(49%)HOMO-2(α)→LUMO+1(α) (21%)HOMO-5(β)→LUMO(β)	Ru(dπ)/Cl(pπ) → tppz(π*) Ru(dπ)/L→Ru(dπ)
2.4862	500 (473)	0.0267	(37%)HOMO-6(β)→LUMO+1(β) (25%)HOMO-5(β)→LUMO+1(β)	Ru(dπ)/L→ tppz(π*)
2.6527	470	0.0353	(65%)SOMO(α)→LUMO+2(α)	Ru(dπ)/L→ tppz(π*)
3^{2+}				
1.5516	800	0.0299	(62%)HOMO-2(β)→LUMO(β)	Ru(dπ)/L→tppz(π*)/ Ru(dπ)
1.7997	690 (655)	0.0764 (9100)	(39%)HOMO-5(β)→LUMO(β) (27%)HOMO-3(β)→LUMO+1(β)	Ru(dπ)/L→tppz(π*)/ Ru(dπ) Ru(dπ)/L→Ru(dπ)
1.8530	670	0.0246	(66%)HOMO-3(β)→LUMO+1(β)	Ru(dπ)/L→Ru(dπ)

2.1005	590 (605)	0.0203	(56%)HOMO-7(β)→LUMO(β)	L→tppz(π^*)/Ru(dπ)
2.1235	580	0.0231	(42%)HOMO-8(β)→LUMO(β) (27%)HOMO-7(β)→LUMO(β)	L→tppz(π^*)/Ru(dπ)
2.3597	520 (518)	0.0109 (7200)	(71%)HOMO-7(β)→LUMO+1(β)	L→Ru(dπ)
2.5433	490	0.0216	(61%)HOMO-8(β)→LUMO+1(β)	L→ tppz(π^*)/Ru(dπ)
3^-				
1.0313	1200 (1177)	0.0031 (3400)	(54%)SOMO(α)→LUMO(α) (41%)HOMO(β)→LUMO+1(β)	tppz(π)→tppz(π^*) Ru(dπ)→tppz(π^*)
1.0437	1190	0.0102	(51%)SOMO(α)→LUMO+1(α) (40%)HOMO(β)→LUMO(β)	tppz(π)→tppz(π^*) Ru(dπ)→tppz(π^*)
1.1939	1040 (1048)	0.0248 (5200)	(53%)HOMO(β)→LUMO(β) (27%)SOMO(α)→LUMO+1(α)	Ru(dπ)→tppz(π^*) tppz(π)→tppz(π^*)
1.3084	950	0.0138	(92%)HOMO-1(β)→LUMO(β)	Ru(dπ)→tppz(π^*)
1.8096	680	0.0321	(43%)HOMO(β)→LUMO+1(β) (27%)HOMO-4(β)→LUMO+1(β)	Ru(dπ)→tppz(π^*)
1.8465	670 (665)	0.0461 (11500)	(47%)SOMO(α)→LUMO+2(α) (23%)HOMO-3(β)→LUMO+1(β)	tppz(π)→tppz(π^*) Ru(dπ)→tppz(π^*)
1.8981	650	0.0375	(43%)HOMO-3(β)→LUMO+1(β) (24%)HOMO-4(β)→LUMO+1(β)	Ru(dπ)→tppz(π^*)

2.0470	600	0.0245	(43%)HOMO-4(β)→LUMO+2(β) (24%)HOMO-5(β)→LUMO+2(β)	Ru(dπ)→tppz(π^*)
2.1314	580 (594)	0.0318 (12300)	(71%)HOMO-3(α)→LUMO+1(α)	Ru(dπ)→tppz(π^*)

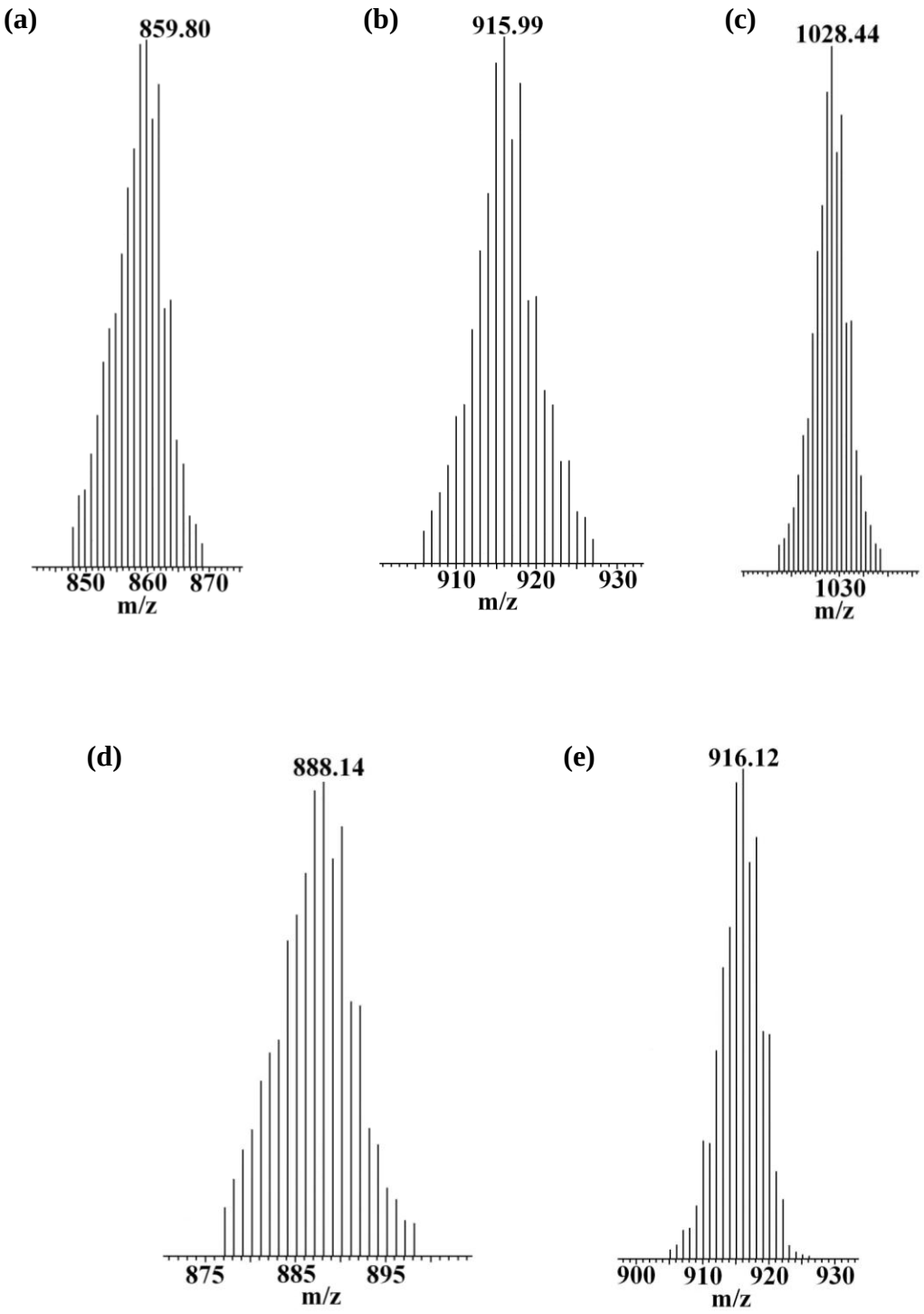


Fig. S1 Mass spectra of (a) **1**, (b) **2**, (c) **3**, (d) **4** and (c) **5** in CH_3CN.

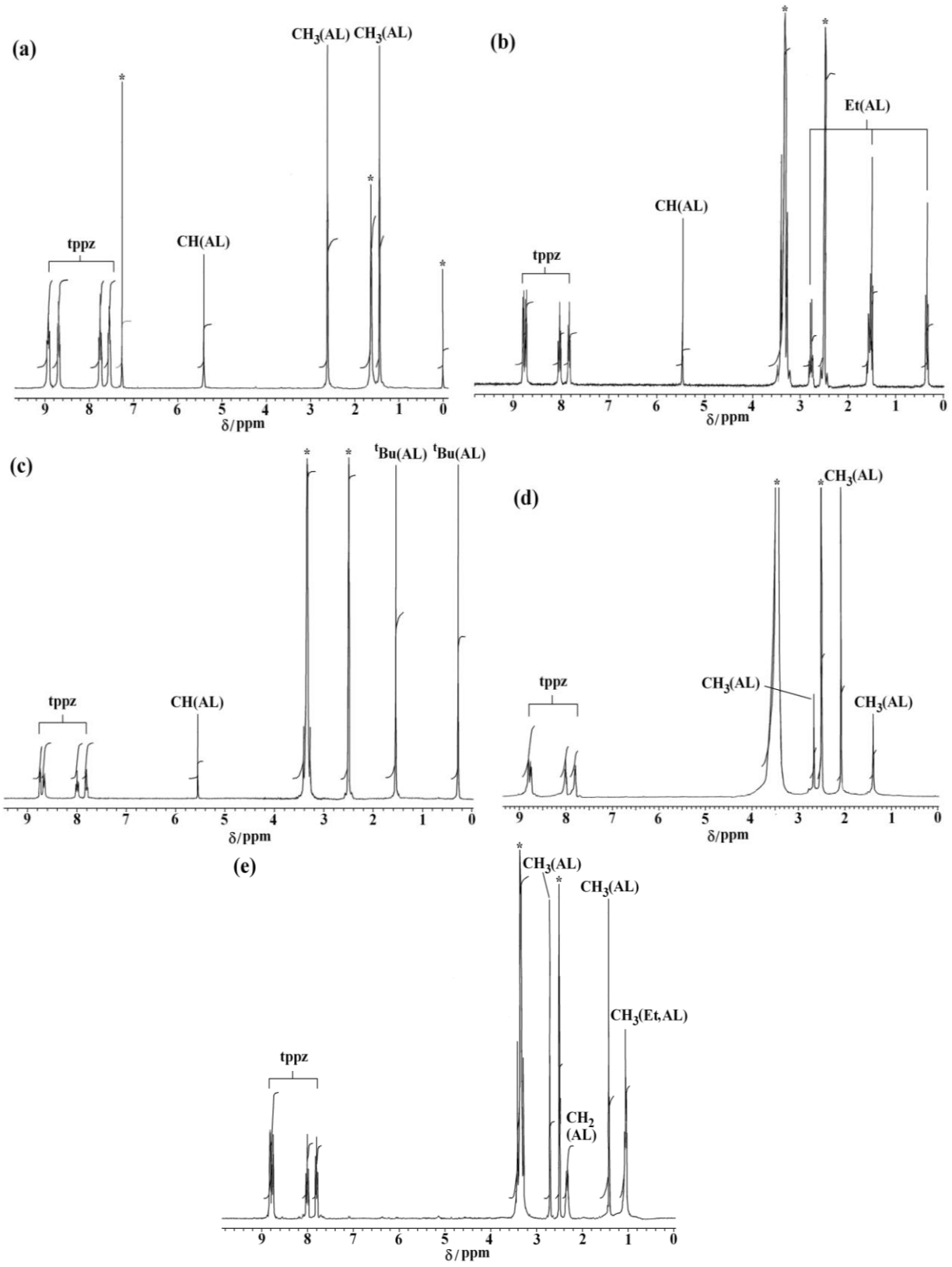

(a)
CH3(AL) CH3(AL)
tppz
CH(AL)
δ/ppm
(b)
Et(AL)
CH(AL)
tppz
δ/ppm
(c)
tBu(AL) tBu(AL)
tppz
CH(AL)
δ/ppm
(d)
CH3(AL)
tppz
CH3(AL)
CH3(AL)
δ/ppm
(e)
CH3(AL)
CH3(AL)
CH3(Et,AL)
tppz
CH2 (AL)
δ/ppm

Fig. S2 ^{1}H NMR spectra of (a) **1** in $CDCl_3$, (b) **2**, (c) **3**, (d) **4** and (e) **5** in $(CD_3)_2SO$ (* indicates solvent peak).

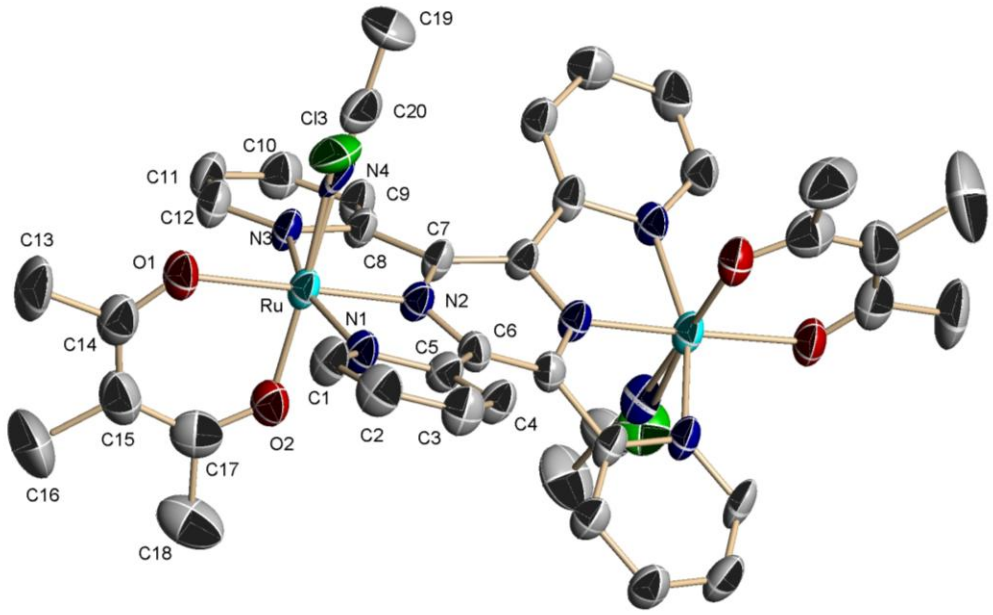
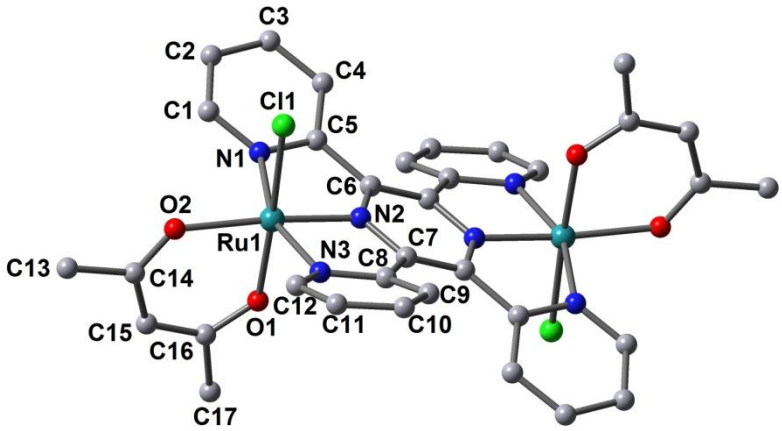


Fig. S3 ORTEP diagram of the dicationic form of **4′**. Counter anions, solvent of crystallisation and hydrogen atoms are omitted for clarity.

(a)



(b)

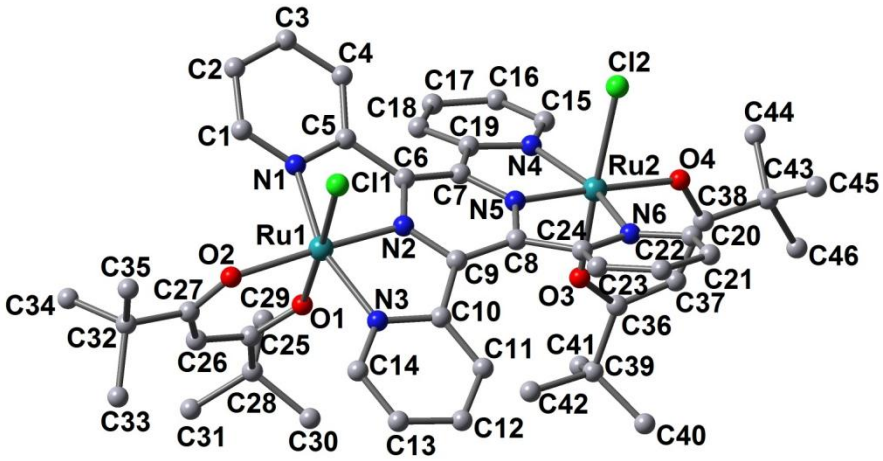


Fig. S4 DFT optimised structures of (a) **1** and (b) **3**.

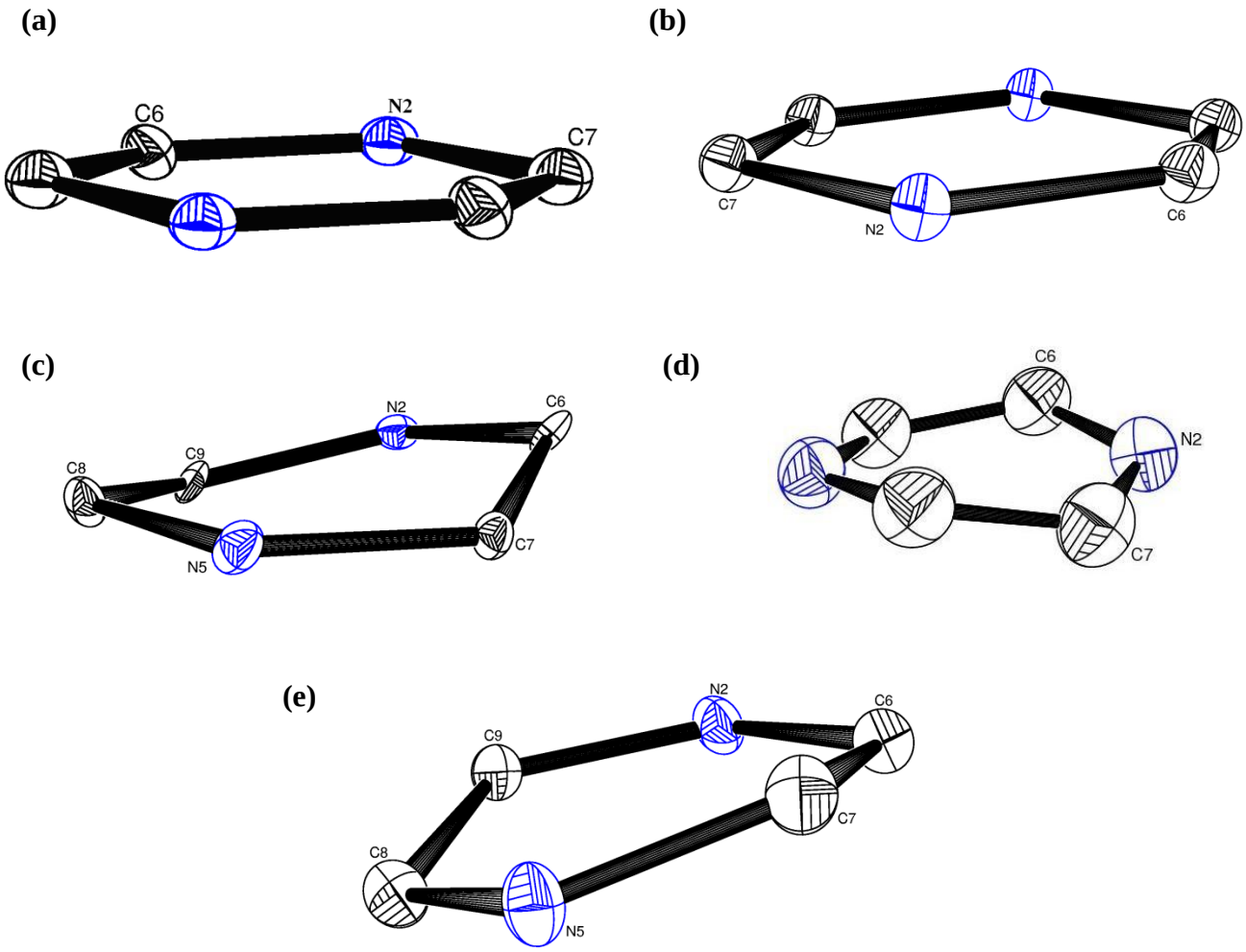


Fig. S5 Non-planarity of the pyrazine ring of tppz in the crystal structures of (a) **1**, (b) **2**, (c) **3**, (d) **4**′ and (e) **5**.

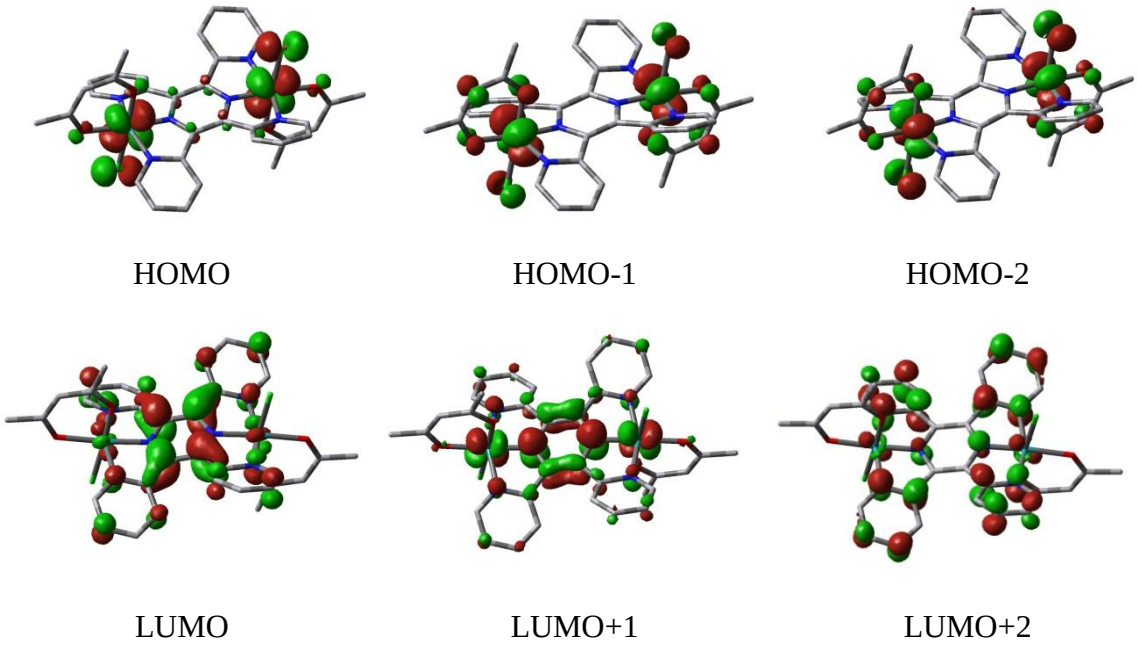


Fig. S6 Selected molecular orbitals of **1**.

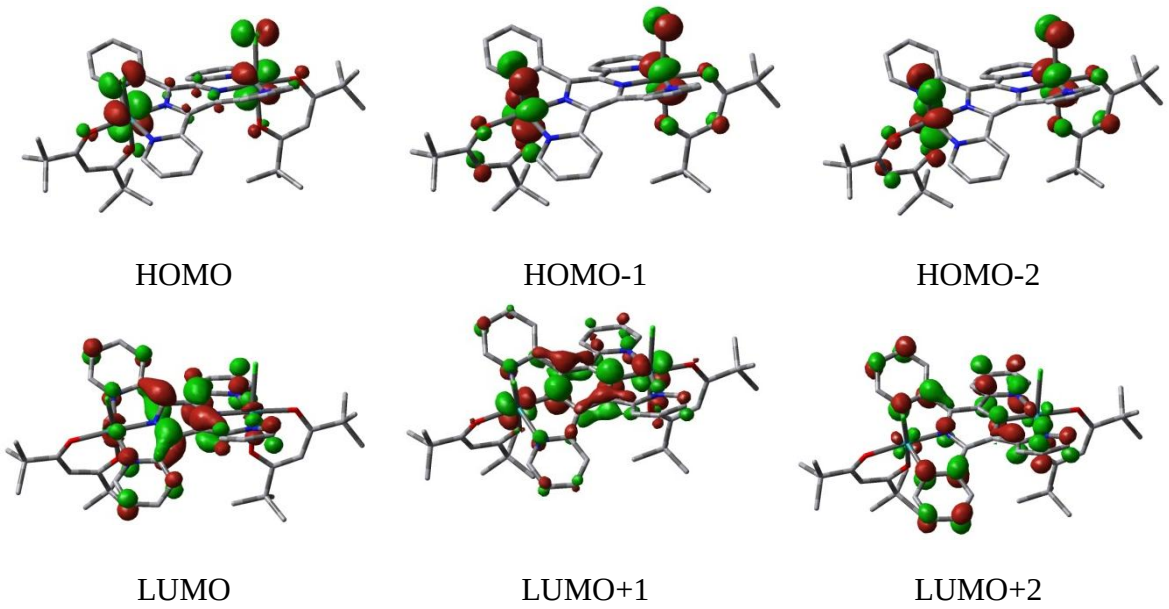


Fig. S7 Selected molecular orbitals of **3**.

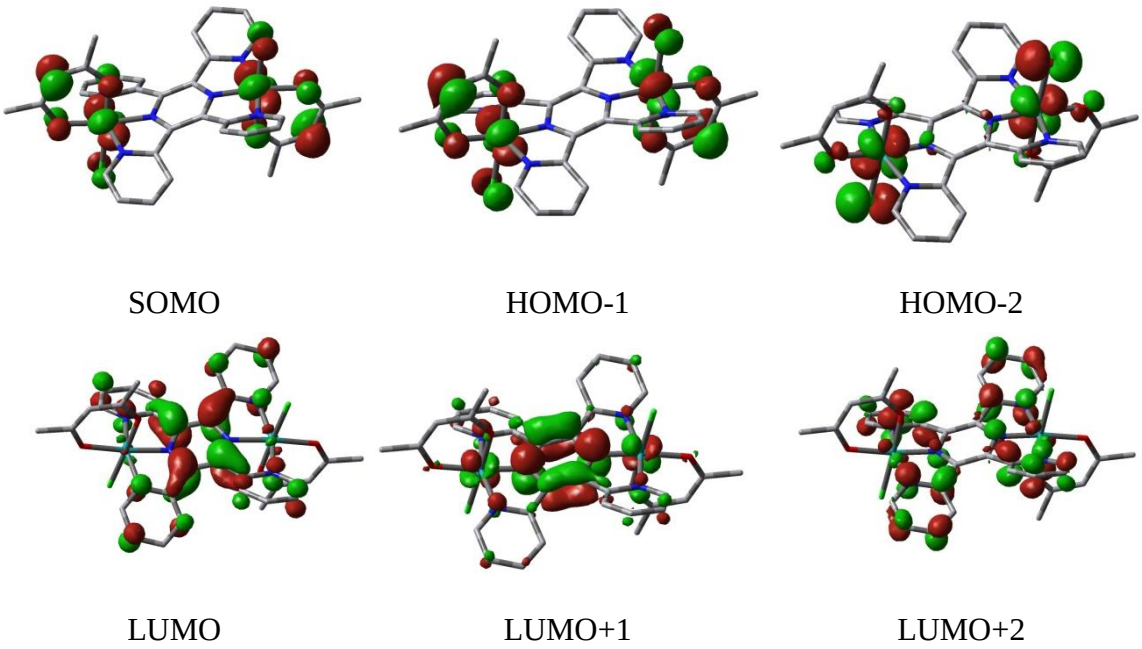


Fig. S8 Selected molecular orbitals of $\mathbf{1}^{+}$ (α-spin).

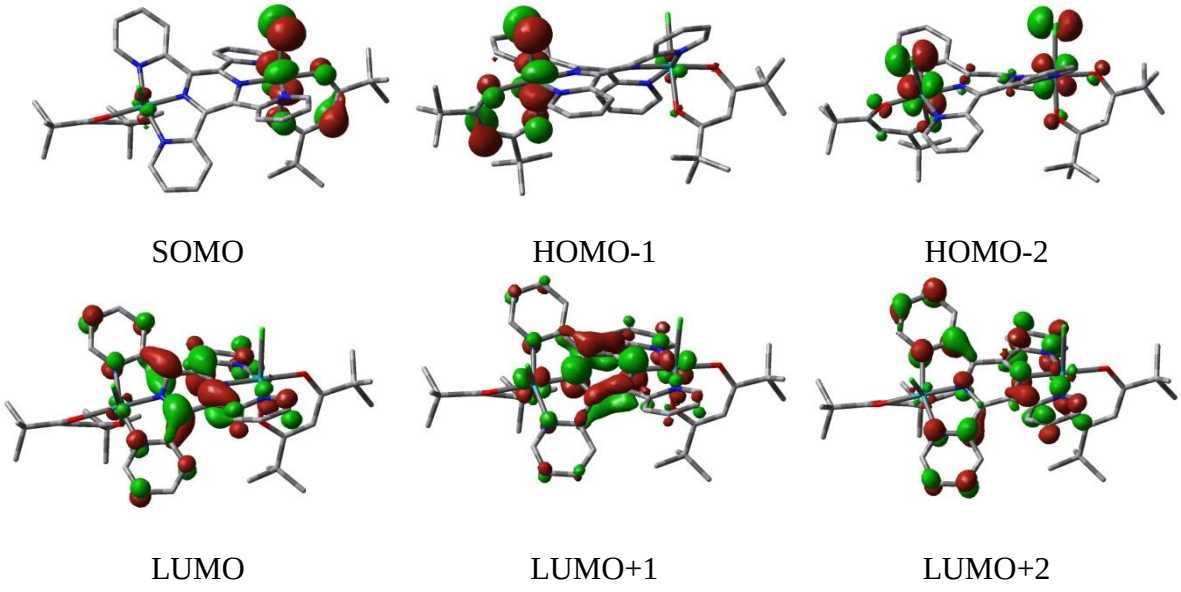


Fig. S9 Selected molecular orbitals of $\mathbf{3}^{+}$ (α-spin).

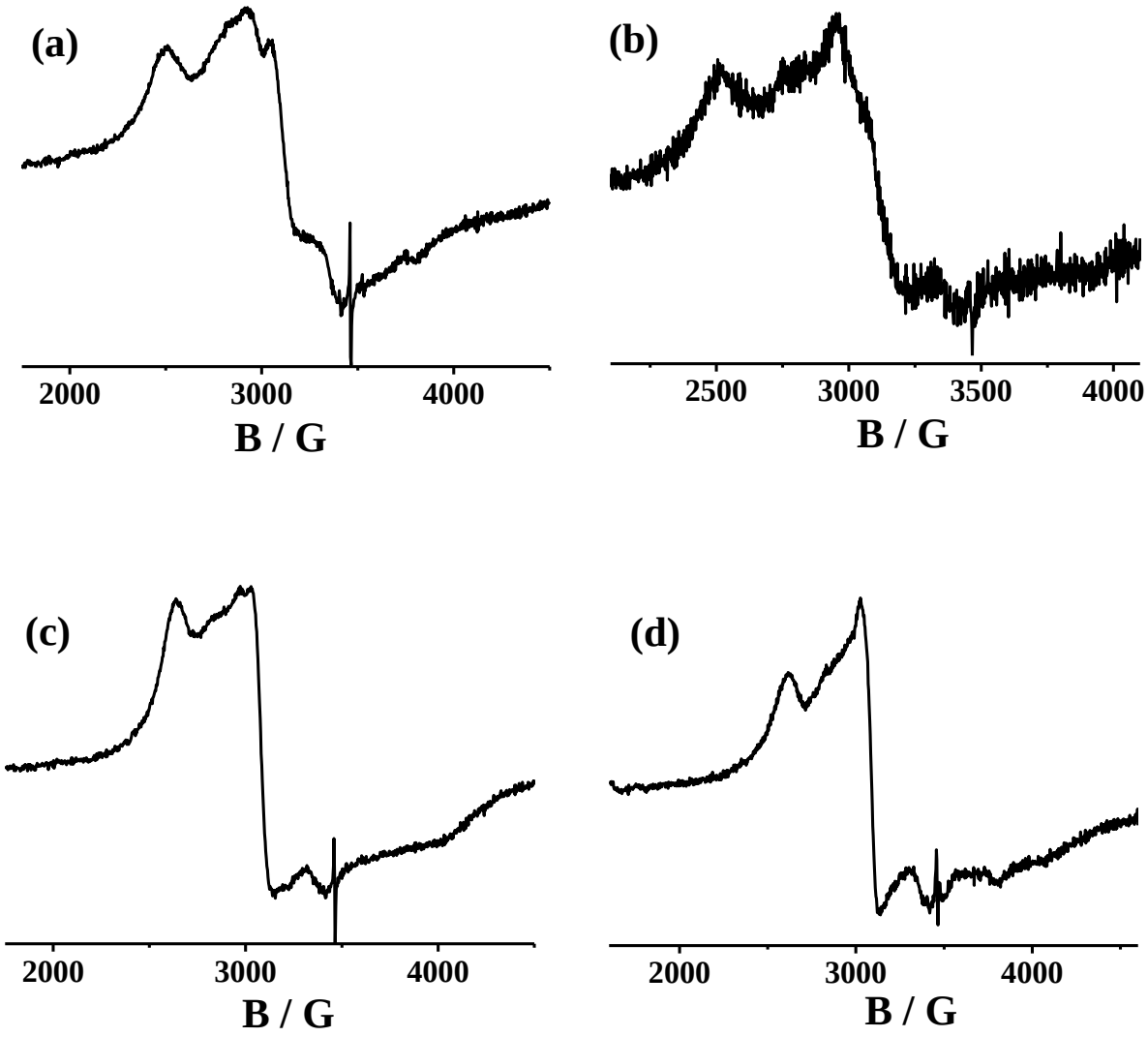


Fig. S10 EPR spectra of (a) $\mathbf{1}^{+}$, (b) $\mathbf{2}^{+}$, (c) $\mathbf{4}^{+}$ and (d) $\mathbf{5}^{+}$ in CH_3CN, 0.1 mol dm^{-3} Bu_4NPF_6 at 110 K.

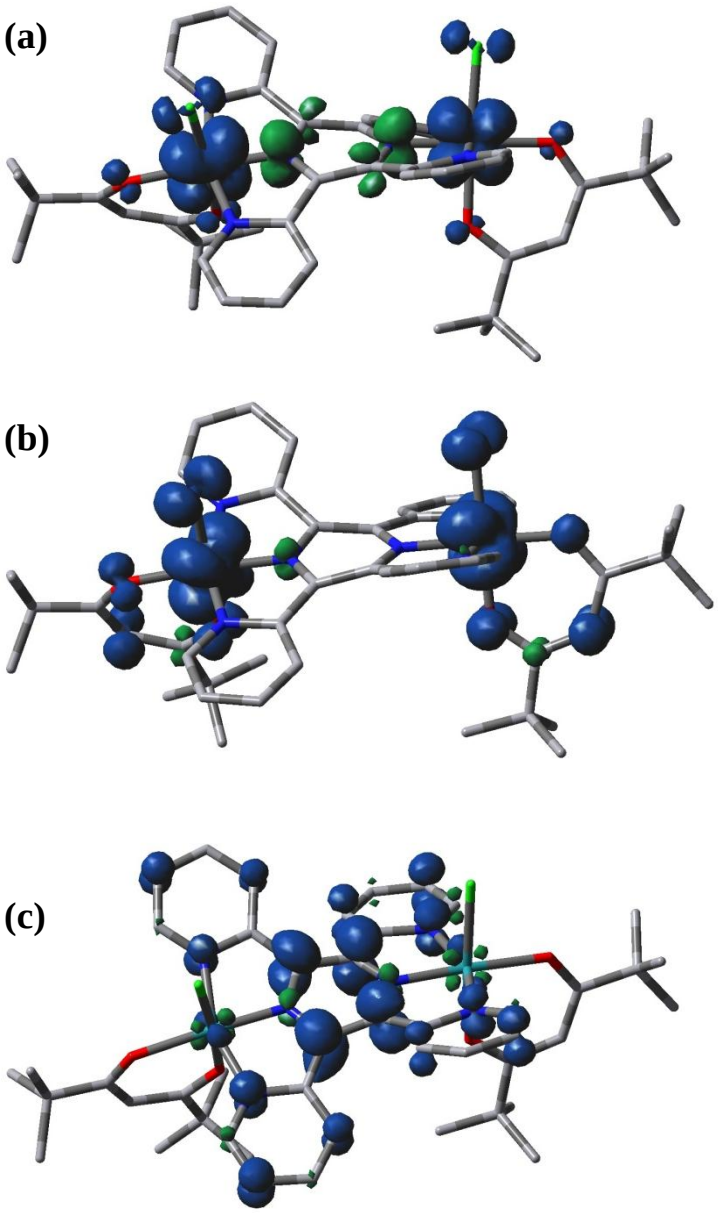


Fig. S11 Spin density plots of (a) $\mathbf{3}^{+}$, (b) $\mathbf{3}^{2+}$ and (b) $\mathbf{3}^{-}$.

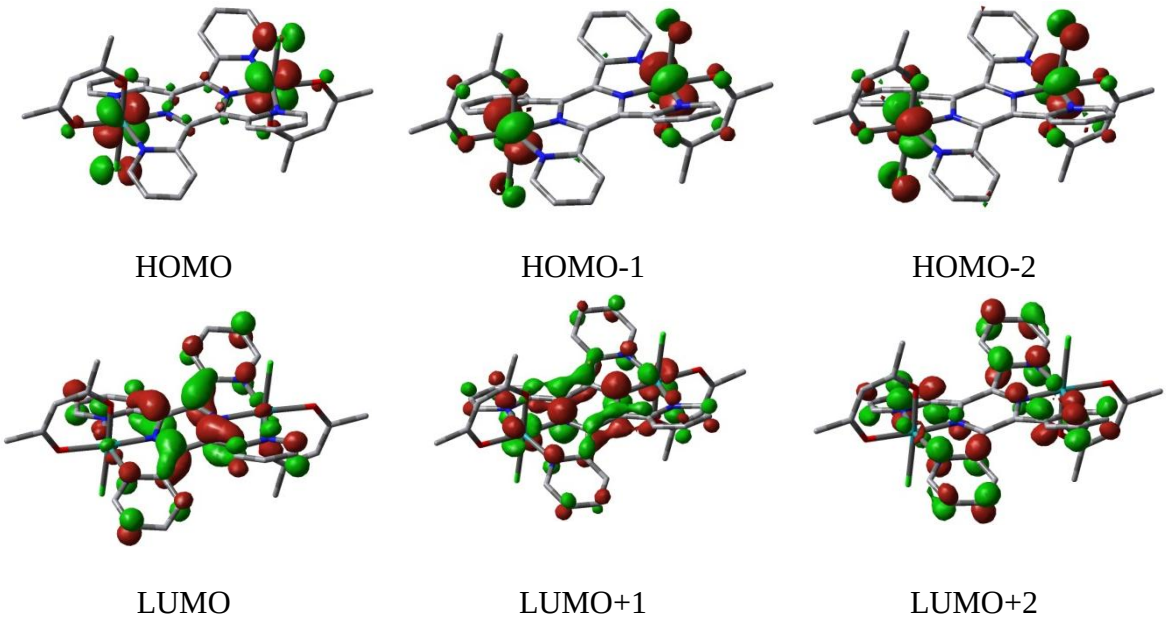


Fig. S12 Selected molecular orbitals of $\mathbf{1}^{-}$ (β-spin).

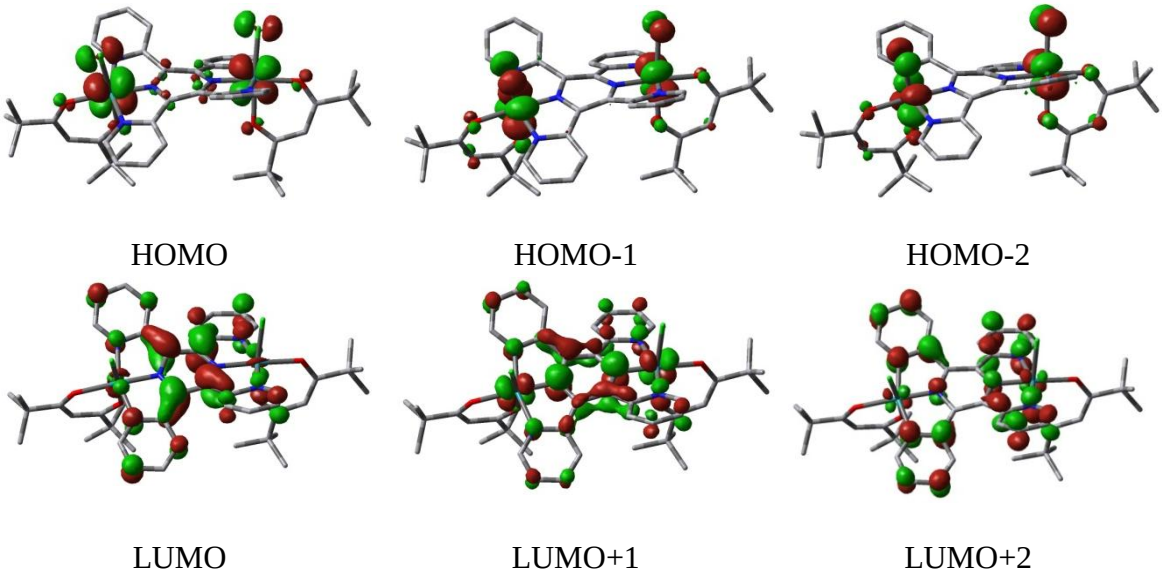


Fig. S13 Selected molecular orbitals of $\mathbf{3}^{-}$ (β-spin).

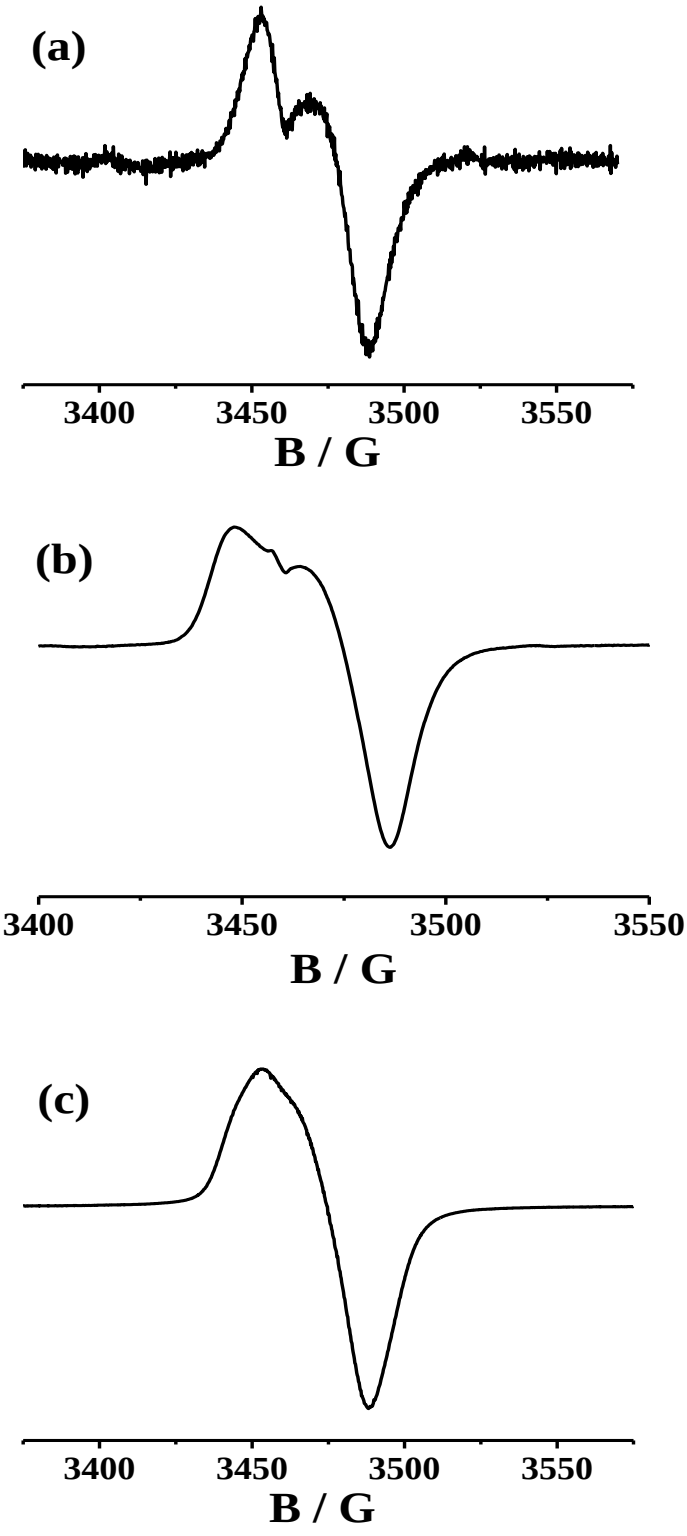


Fig. S14 EPR spectra of (a) $\mathbf{1}^{-}$, (b) $\mathbf{2}^{-}$ and (c) $\mathbf{5}^{-}$ in CH_3CN, 0.1 mol dm^{-3} Bu_4NPF_6 at 110 K.

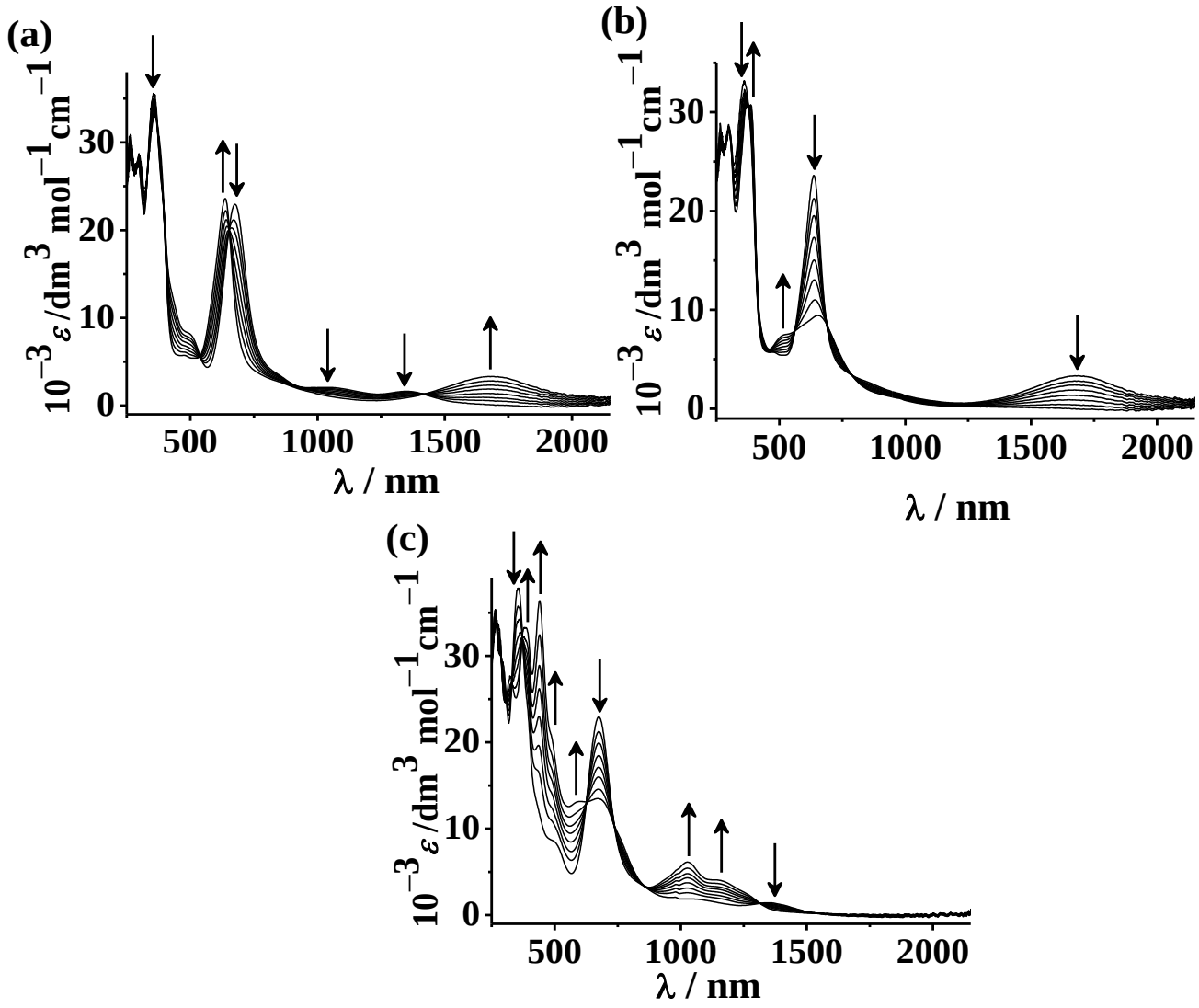


Fig. S15 UV-VIS-NIR spectroelectrochemistry for the conversions of (a) $\mathbf{2} \rightarrow \mathbf{2}^{+}$, (b) $\mathbf{2}^{+} \rightarrow \mathbf{2}^{2+}$ and (c) $\mathbf{2} \rightarrow \mathbf{2}^{-}$ in CH_3CN, 0.1 mol dm^{-3} Bu_4NPF_6.

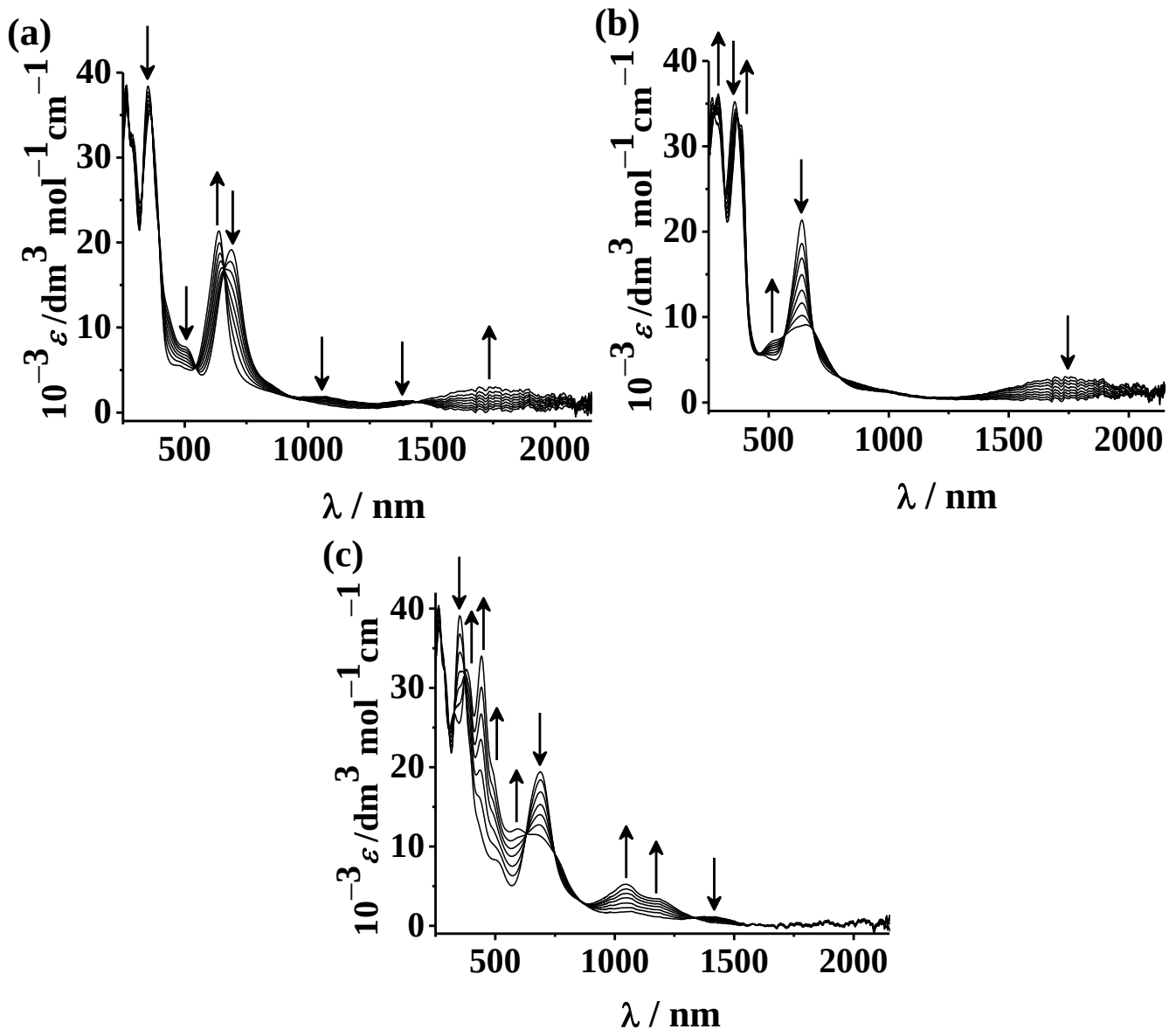


Fig. S16 UV-VIS-NIR spectroelectrochemistry for the conversions of (a) **3**→ **3**$^{+}$, (b) **3**$^{+}$→ **3**$^{2+}$ and (c) **3**→ **3**$^{-}$ in CH_3CN, 0.1 mol dm^{-3} Bu_4NPF_6.

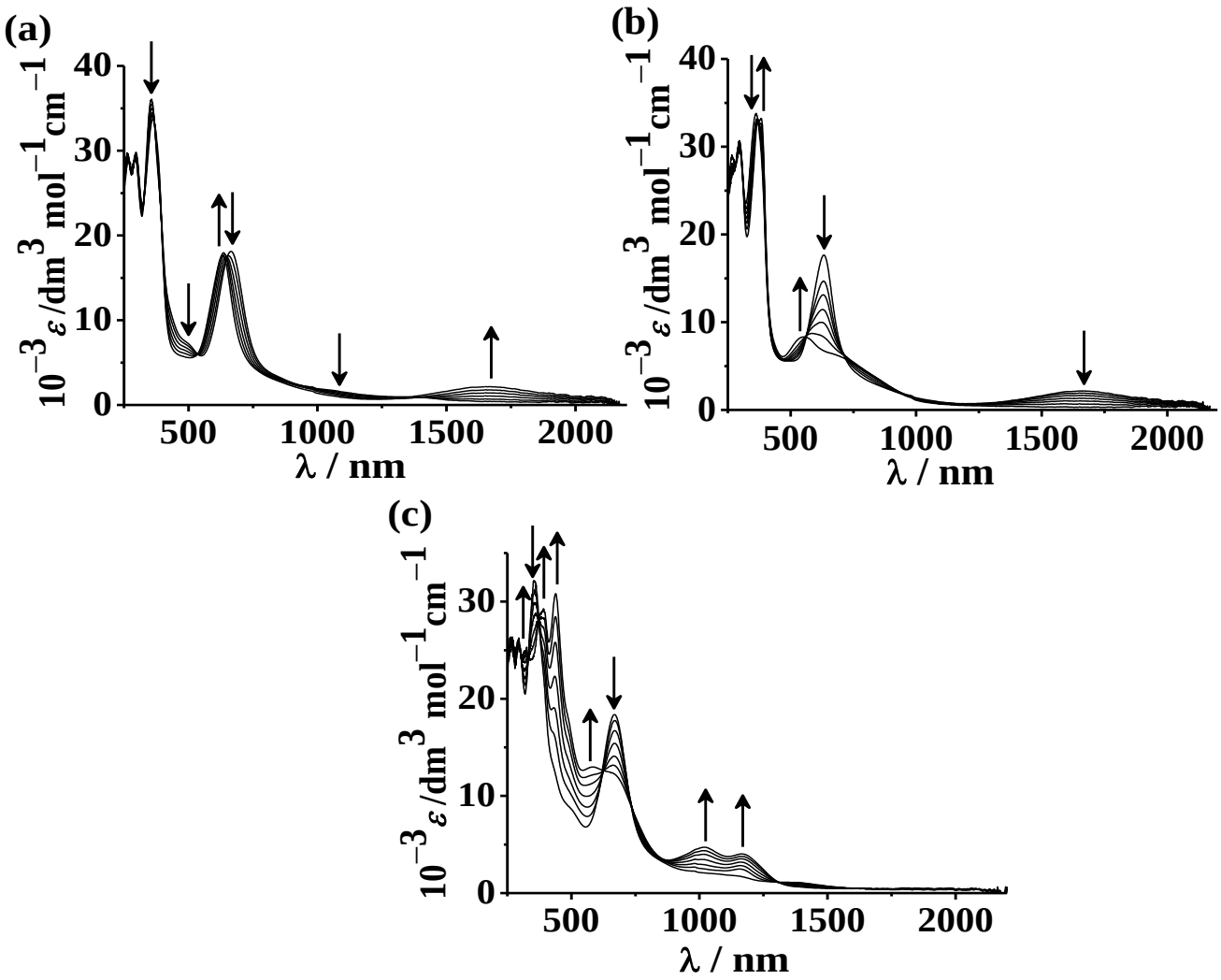


Fig. S17 UV-VIS-NIR spectroelectrochemistry for the conversions of (a) **4**→ **4**$^{+}$, (b) **4**$^{+}$→ **4**$^{2+}$ and (c) **4**→ **4**$^{-}$ in CH_3CN, 0.1 mol dm^{-3} Bu_4NPF_6.

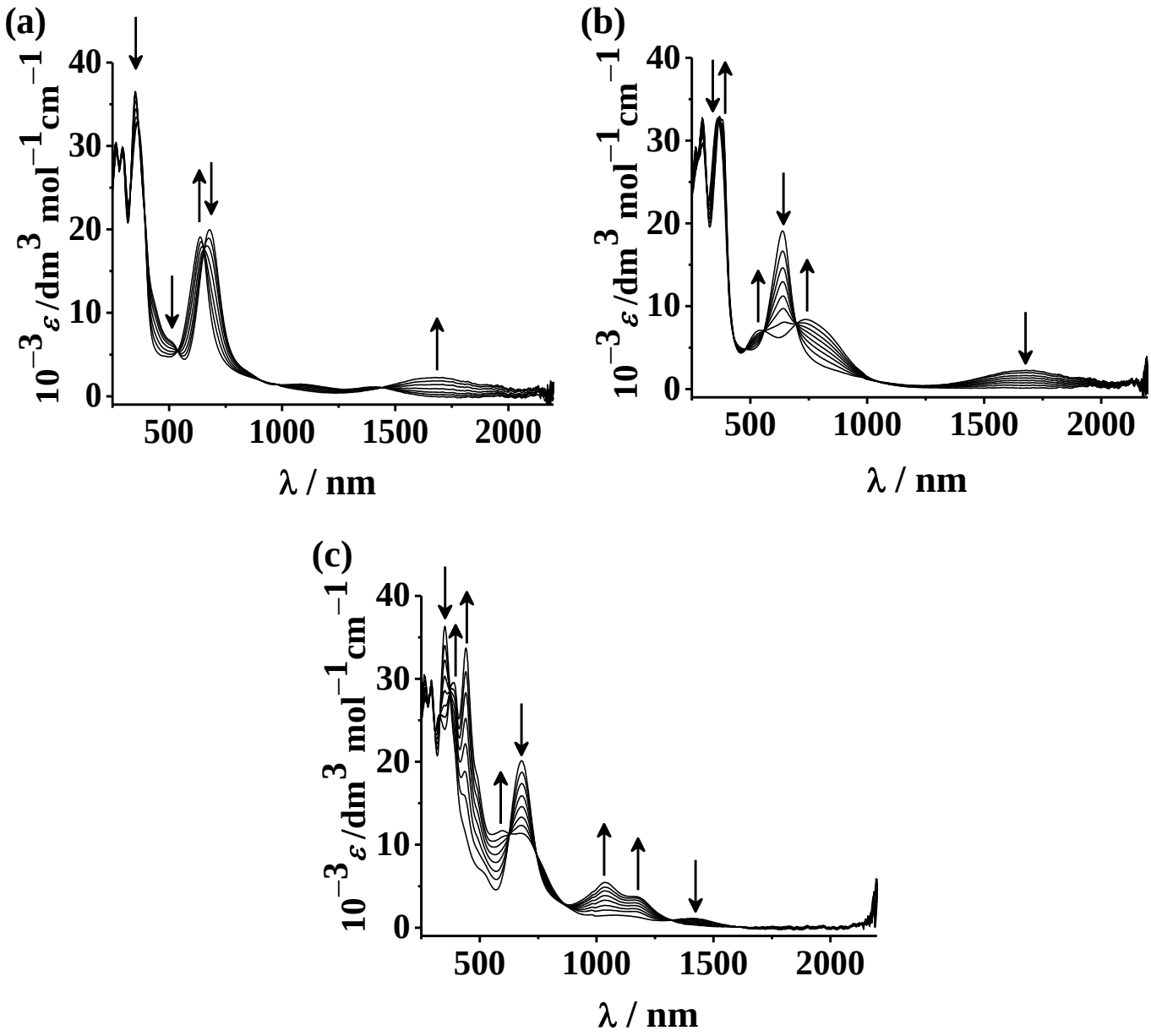


Fig. S18 UV-VIS-NIR spectroelectrochemistry for the conversions of (a) **5**→ **5**$^{+}$, (b) **5**$^{+}$→ **5**$^{2+}$ and (c) **5**→ **5**$^{-}$ and in CH_3CN, 0.1 mol dm^{-3} Bu_4NPF_6.