





Ground vs. excited state interaction in ruthenium-thienyl dyads

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Fig. S1. ¹H NMR spectra of **1b** (upper) and **2b** (lower) in CD₃CN (400 MHz).



Fig. S2. Changes in UV vis spectra of **1a** and **2a** between pH 0.5 and 10. (Inset differences spectra compared with completely the protonated complexes).



Fig. S3. Absorption and emission spectra for **1a/H1a** (left) and **2a/H2a** (right) in acetonitrile solution 298 K.



Fig. S4. Temperature dependent emission of 2a in EtOH:MeOH (4:1).



Fig. S5. Resonance Raman spectra of (i) **1a** (ii) **1b** (iii) **H1a** (iv) **H1b** in H₂O at $\lambda_{exc.}$ 457 nm.



Fig. S6. Resonance Raman spectra of (i) **1a** (ii) **H1a** in H₂O at $\lambda_{exc.}$ 488 nm.

MO		eV	Symmetry	Ru	bpy1	bpy2	pz	tr	th
154	L+10	-2.77	A	0	92	7	0	0	0
153	L+9	-2.78	А	1	1	1	0	33	63
152	L+8	-3.01	А	1	7	91	0	1	1
151	L+7	-3.86	А	1	5	2	80	11	1
150	L+6	-4.08	А	2	90	4	3	0	0
149	L+5	-4.23	А	3	75	21	1	0	0
148	L+4	-4.27	А	2	9	89	0	0	0
147	L+3	-4.53	А	3	14	70	11	3	0
146	L+2	-4.68	А	3	4	11	72	9	0
145	L+1	-5.13	А	5	91	3	1	0	0
144	LUMO	-5.35	А	4	4	91	1	0	0
143	HOMO	-7.45	А	7	1	0	5	29	58
142	H-1	-8.41	А	2	0	0	0	1	96
141	H-2	-8.46	А	72	6	5	1	5	11
140	H-3	-8.56	А	70	11	4	2	7	6
139	H-4	-8.66	А	73	4	12	6	4	2
138	H-5	-9.21	А	5	0	1	26	52	16
137	H-6	-9.24	А	1	1	0	0	97	2
136	H-7	-9.58	А	2	1	1	89	8	0
135	H-8	-10	А	0	94	1	0	4	1
134	H-9	-10.18	А	4	5	4	7	74	6
133	H-10	-10.21	А	1	1	95	1	2	0
МО		eV	Symmetry	Ru	bpy1	bpy2	pz	tr	th
MO 154	L+10	eV -5.19	Symmetry A	Ru 63	bpy1 17	bpy2 12	pz 8	tr 0	th 0
MO 154 153	L+10 L+9	eV -5.19 -5.29	Symmetry A A	Ru 63 4	bpy1 17 12	bpy2 12 82	pz 8 1	tr 0 1	th 0 0
MO 154 153 152	L+10 L+9 L+8	eV -5.19 -5.29 -6.4	Symmetry A A A	Ru 63 4 2	bpy1 17 12 91	bpy2 12 82 6	pz 8 1 0	tr 0 1 1	th 0 0 1
MO 154 153 152 151	L+10 L+9 L+8 L+7	eV -5.19 -5.29 -6.4 -6.52	Symmetry A A A A	Ru 63 4 2 2	bpy1 17 12 91 18	bpy2 12 82 6 33	pz 8 1 0 3	tr 0 1 1 20	th 0 0 1 25
MO 154 153 152 151 150	L+10 L+9 L+8 L+7 L+6	eV -5.19 -5.29 -6.4 -6.52 -6.57	Symmetry A A A A A	Ru 63 4 2 2 1	bpy1 17 12 91 18 19	bpy2 12 82 6 33 31	pz 8 1 0 3 6	tr 0 1 20 20	th 0 1 25 23
MO 154 153 152 151 150 149	L+10 L+9 L+8 L+7 L+6 L+5	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63	Symmetry A A A A A A	Ru 63 4 2 2 1 2	bpy1 17 12 91 18 19 42	bpy2 12 82 6 33 31 56	pz 8 1 0 3 6 0	tr 0 1 20 20 0	th 0 1 25 23 0
MO 154 153 152 151 150 149 148	L+10 L+9 L+8 L+7 L+6 L+5 L+4	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78	Symmetry A A A A A A A A	Ru 63 4 2 2 1 2 1	bpy1 17 12 91 18 19 42 24	bpy2 12 82 6 33 31 56 66	pz 8 1 0 3 6 0 7	tr 0 1 20 20 0 1	th 0 1 25 23 0 0
MO 154 152 152 151 150 149 148 147	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19	Symmetry A A A A A A A A A	Ru 63 4 2 2 1 2 1 2 1	bpy1 17 12 91 18 19 42 24 3	bpy2 12 82 6 33 31 56 66 6	pz 8 1 0 3 6 0 7 75	tr 0 1 20 20 0 1 11	th 0 1 25 23 0 0 5
MO 154 153 152 151 150 149 148 147 146	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51	Symmetry A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 4	bpy1 17 12 91 18 19 42 24 3 92	bpy2 12 82 6 33 31 56 66 6 2	pz 8 1 0 3 6 0 7 75 75 1	tr 0 1 20 20 0 1 11 0	th 0 1 25 23 0 0 5 0
MO 154 153 152 151 150 149 148 147 146 145	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65	Symmetry A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 4 5	bpy1 17 12 91 18 19 42 24 3 92 2	bpy2 12 82 6 33 31 56 66 6 2 90	pz 8 1 0 3 6 0 7 75 1 2	tr 0 1 20 20 0 1 11 0 1	th 0 1 25 23 0 5 0 0
MO 154 153 152 151 150 149 148 147 146 145 144	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97	Symmetry A A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 4 5 5	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 2	bpy2 12 82 6 33 31 56 66 6 6 2 90 4	pz 8 1 0 3 6 0 7 75 1 2 64	tr 0 1 20 20 0 1 11 0 1 22	th 0 1 25 23 0 0 5 0 0 3
MO 154 153 152 151 150 149 148 147 146 145 144 143	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO HOMO	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01	Symmetry A A A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 1 4 5 5 39	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3	bpy2 12 82 6 33 31 56 66 6 2 90 4 2	pz 8 1 0 3 6 0 7 75 1 2 64 5	tr 0 1 20 20 0 1 11 0 1 22 17	th 0 1 25 23 0 0 5 0 5 0 3 34
MO 154 153 152 151 150 149 148 147 146 145 144 143 142	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO HOMO H-1	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27	Symmetry A A A A A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 2 1 4 5 5 39 70	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3 9	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8	pz 8 1 0 3 6 0 7 75 1 2 64 5 3	tr 0 1 20 20 0 1 11 0 1 22 17 3	th 0 1 25 23 0 0 5 0 5 0 0 3 4 7
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO HOMO H-1 H-2	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4	Symmetry A A A A A A A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 2 1 4 5 5 39 70 75	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3 92 4	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11	pz 8 1 0 3 6 0 7 75 1 2 64 5 3 7	tr 0 1 20 20 0 1 11 0 1 22 17 3 1	th 0 1 25 23 0 0 5 0 5 0 0 3 4 7 1
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141 140	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO HOMO H-1 H-2 H-3	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4 -11.45	Symmetry A A A A A A A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 2 1 4 5 5 39 70 75 50	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3 92 2 3 9 4 7	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11 2	pz 8 1 0 3 6 0 7 75 1 2 64 5 3 7 0	tr 0 1 20 20 0 1 11 0 1 22 17 3 1 9	th 0 1 25 23 0 0 5 0 0 5 0 0 3 4 7 1 31
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141 140 139	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO H-1 H-2 H-3 H-4	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4 -11.45 -11.87	Symmetry	Ru 63 4 2 2 1 2 1 2 1 4 5 5 39 70 75 50 0	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3 92 2 3 92 4 7 0	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11 2 0	pz 8 1 0 3 6 0 7 5 1 2 64 5 3 7 0 0 0	tr 0 1 20 20 0 1 11 0 1 22 17 3 1 9 1	th 0 1 25 23 0 0 5 0 0 5 0 0 3 4 7 1 31 99
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO HOMO H-1 H-2 H-3 H-4 H-5	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4 -11.45 -11.87 -12.36	Symmetry	Ru 63 4 2 2 1 2 1 2 1 4 5 39 70 75 50 0 1	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3 92 2 2 3 9 4 7 0 96	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11 2 0 2	pz 8 1 0 3 6 0 7 75 1 2 64 5 3 7 0 0 0 0	tr 0 1 20 20 0 1 11 0 1 22 17 3 1 9 1 0	th 0 1 25 23 0 0 5 0 0 5 0 0 3 34 7 1 31 99 0
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO HOMO H-1 H-2 H-3 H-4 H-5 H-6	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4 -11.45 -11.87 -12.36 -12.5	Symmetry	Ru 63 4 2 2 1 2 1 2 1 2 1 4 5 5 39 70 75 50 0 1 1	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3 92 2 3 92 2 3 92 2 2 3 92 2 2 3 92 2 2 2	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11 2 0 2 92	pz 8 1 0 3 6 0 7 75 1 2 64 5 3 7 0 0 0 5 5	tr 0 1 20 20 0 1 11 0 1 22 17 3 1 9 1 0 0	th 0 1 25 23 0 0 5 0 0 5 0 0 3 34 7 1 31 99 0 0 0
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO HOMO H-1 H-2 H-3 H-4 H-5 H-6 H-7	eV -5.19 -5.29 -6.4 -6.52 -6.57 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4 -11.45 -11.87 -12.36 -12.5 -12.56	Symmetry A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 2 1 2 1 2 1 5 5 70 75 50 0 1 1 1	bpy1 17 12 91 18 19 42 24 3 92 2 2 2 3 9 4 7 0 96 2 1	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11 2 0 2 92 5	pz 8 1 0 3 6 0 7 75 1 2 64 5 3 7 0 0 0 5 91	tr 0 1 20 20 0 1 11 0 1 22 17 3 1 9 1 0 0 2	th 0 1 25 23 0 0 5 0 0 5 0 0 34 7 1 31 99 0 0 0 0 0 0 0 0 0 0 0 0 0
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO H-1 H-2 H-3 H-4 H-5 H-6 H-7 H-8	eV -5.19 -5.29 -6.4 -6.52 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4 -11.45 -11.87 -12.36 -12.5 -12.56 -13.07	Symmetry A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 2 1 2 1 2 1 5 5 70 75 50 0 1 1 1 1 1	bpy1 17 12 91 18 19 42 24 3 92 2 2 3 9 4 7 0 96 2 1 2	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11 2 0 2 92 5 0	pz 8 1 0 3 6 0 7 75 1 2 64 5 3 7 0 0 0 5 91 46	tr 0 1 20 20 0 1 11 0 1 22 17 3 1 9 1 0 0 2 33	th 0 1 25 23 0 0 5 0 0 5 0 0 34 7 1 31 99 0 0 0 18
MO 154 153 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134	L+10 L+9 L+8 L+7 L+6 L+5 L+4 L+3 L+2 L+1 LUMO H-1 H-2 H-3 H-4 H-5 H-6 H-7 H-8 H-9	eV -5.19 -5.29 -6.4 -6.52 -6.63 -6.78 -7.19 -7.51 -7.65 -7.97 -11.01 -11.27 -11.4 -11.45 -11.87 -12.36 -12.56 -13.07 -13.55	Symmetry A A A A A A A A A A A A A	Ru 63 4 2 2 1 2 1 2 1 2 1 2 1 2 1 2 5 5 70 75 50 0 1 1 1 1 2	bpy1 17 12 91 18 19 42 24 3 92 2 2 3 9 4 7 0 96 2 1 2 2 2	bpy2 12 82 6 33 31 56 66 6 2 90 4 2 8 11 2 0 2 92 5 0 4	pz 8 1 0 3 6 0 7 75 1 2 64 5 3 7 0 0 5 91 46 2	tr 0 1 20 20 0 1 11 0 1 22 17 3 1 9 1 0 0 2 33 88	th 0 1 25 23 0 0 5 0 0 5 0 0 34 7 1 31 99 0 0 0 18 2

Fig. S7. Molecular orbital data for **2a** (top) and **H2a** (bottom).