Supporting Information

Emissive Ir(III) complexes bearing thienylamido ligands on a 1,10-phenanthroline scaffold

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Table S1. Computed first 20 vertical singlet electronic transition energies of **1 ,2 and 3.** The monoelectronic excitation contributions are calculated by TD-DFT at the D95(d);D95(2d) /SDD09/ M06/CAN level.

Complex **1**	Complex **2**	Complex **3**
HOMO is MO 130 and LUMO is MO131	HOMO is MO 162 and LUMO is MO 163	HOMO is MO 183 and LUMO is MO 184
>>>> Singlet states <<<<	>>>> Singlet states <<<<	>>>> Singlet states <<<<
eV nm cm^{-1} f	eV nm cm^{-1} f	eV nm cm^{-1} f
2.7509; 450.70; 22187.7; 0.0001	2.7341; 453.47; 22052.2; 0.0003	2.7380; 452.83; 22083.3; 0.0005
3.0175; 410.88; 24338.0; 0.0001	2.9246; 423.94; 23588.2; 0.0002	2.9207; 424.50; 23557.1; 0.0003
3.1843; 389.36; 25683.2; 0.0003	3.1675; 391.43; 25547.4; 0.0003	3.1741; 390.61; 25601.0; 0.0003
3.3456; 370.59; 26984.0; 0.0815	3.3145; 374.07; 26733.0; 0.0764	3.2627; 380.01; 26315.1; 0.7316
3.5194; 352.29; 28385.7; 0.0667	3.4364; 360.79; 27717.0; 0.1069	3.3277; 372.58; 26839.9; 0.0699
3.5772; 346.59; 28852.5; 0.0006	3.4914; 355.11; 28160.3; 0.0341	3.4401; 360.41; 27746.2; 0.0429
3.5792; 346.40; 28868.4; 0.0273	3.5519; 349.07; 28647.5; 0.0005	3.4722; 357.08; 28004.9; 0.0643
3.7474; 330.85; 30225.2; 0.0758	3.6711; 337.73; 29609.5; 0.0011	3.4947; 354.78; 28186.5; 0.0272
3.7762; 328.33; 30457.2; 0.0008	3.7497; 330.65; 30243.5; 0.0736	3.5564; 348.62; 28684.5; 0.0004
3.8494; 322.09; 31047.2; 0.0073	3.8246; 324.18; 30847.1; 0.0484	3.6651; 338.28; 29561.3; 0.0167
3.8939; 318.41; 31406.0; 0.0000	3.8541; 321.69; 31085.8; 0.0040	3.6683; 337.99; 29586.7; 0.2319
4.0333; 307.40; 32530.9; 0.0014	3.8676; 320.57; 31194.4; 0.0031	3.6844; 336.51; 29716.8; 0.0130
4.0797; 303.91; 32904.5; 0.0037	3.9051; 317.49; 31497.1; 0.2054	3.7485; 330.76; 30233.4; 0.0728
4.1396; 299.51; 33387.9; 0.0005	3.9835; 311.24; 32129.5; 0.0035	3.8540; 321.70; 31084.9; 0.0064
4.1587; 298.13; 33542.4; 0.0020	4.0170; 308.65; 32399.2; 0.0007	3.8733; 320.10; 31240.2; 0.0001
4.1942; 295.61; 33828.4; 0.0037	4.1050; 302.03; 33109.3; 0.0001	3.9002; 317.89; 31457.4; 0.0027
4.2586; 291.14; 34347.7; 0.0553	4.1757; 296.92; 33679.1; 0.0012	3.9798; 311.53; 32099.6; 0.0034
4.3251; 286.66; 34884.5; 0.0005	4.2268; 293.33; 34091.3; 0.0011	3.9891; 310.81; 32174.0; 0.0446
4.3352; 285.99; 34966.3; 0.0001	4.2598; 291.05; 34358.4; 0.0595	4.1082; 301.79; 33135.6; 0.0002
4.3729; 283.53; 35269.6; 0.0177	4.2838; 289.42; 34551.9; 0.1005	4.1261; 300.49; 33279.0; 0.0013
1 3 Excited State: Singlet-A	1 3 Excited State: Singlet-A	1 4 Excited State: Singlet-A
2.7509 eV 450.70 nm 22188.cm^{-1}	2.7341 eV 453.47 nm 22052.cm^{-1}	2.7380 eV 452.83 nm 22083.cm^{-1}
f=0.0001	f=0.0003	f=0.0005
130→131 0.69983 97.95 % 0→ 0	162→163 0.66751 89.11 % 0→ 0	183→184 0.56378 63.57 % 0→ 0
	162→164 0.20901 8.74 % 0→ 1	183→185 0.41250 34.03 % 0→ 1
2 6 Excited State: Singlet-A	2 5 Excited State: Singlet-A	2 6 Excited State: Singlet-A
3.0175 eV 410.88 nm 24338.cm^{-1}	2.9246 eV 423.94 nm 23588.cm^{-1}	2.9207 eV 424.50 nm 23557.cm^{-1}
f=0.0001	f=0.0002	f=0.0003
130→132 0.70240 98.67 % 0→ 1	162→163 -0.20755 8.62 % 0→ 0	183→184 -0.39533 31.26 % 0→ 0
	162→164 0.66751 89.11 % 0→ 1	183→185 0.55540 61.69 % 0→ 1
3 10 Excited State: Singlet-A		183→186 -0.17101 5.85 % 0→ 2
3.1843 eV 389.36 nm 25683.cm^{-1}	3 11 Excited State: Singlet-A	
f=0.0003	3.1675 eV 391.43 nm 25547.cm^{-1}	3 11 Excited State: Singlet-A
129→131 0.70164 98.46 % -1→ 0	f=0.0003	3.1741 eV 390.61 nm 25601.cm^{-1}
	161→163 0.66517 88.49 % -1→ 0	f=0.0003
4 11 Excited State: Singlet-A	161→164 0.21957 9.64 % -1→ 1	181→184 0.55542 61.70 % -2→ 0
3.3456 eV 370.59 nm 26984.cm^{-1}		181→185 0.42294 35.78 % -2→ 1
f=0.0815	4 12 Excited State: Singlet-A	
127→131 0.65896 86.85 % -3→ 0	3.3145 eV 374.07 nm 26733.cm^{-1}	4 12 Excited State: Singlet-A
129→132 0.22595 10.21 % -1→ 1	f=0.0764	3.2627 eV 380.01 nm 26315.cm^{-1}
	159→163 0.59282 70.29 % -3→ 0	f=0.7316
5 14 Excited State: Singlet-A	159→164 0.16791 5.64 % -3→ 1	179→184 -0.26667 14.22 % -4→ 0
3.5194 eV 352.29 nm 28386.cm^{-1}	161→164 -0.30992 19.21 % -1→ 1	179→185 -0.13645 3.72 % -4→ 1
f=0.0667		182→184 0.55496 61.60 % -1→ 0
127→131 -0.22230 9.88 % -3→ 0	5 15 Excited State: Singlet-A	182→185 -0.21397 9.16 % -1→ 1
129→132 0.66167 87.56 % -1→ 1	3.4364 eV 360.79 nm 27717.cm^{-1}	182→186 -0.18504 6.85 % -1→ 2
	f=0.1069	
6 17 Excited State: Singlet-A	159→163 0.33364 22.26 % -3→ 0	5 13 Excited State: Singlet-A
3.5772 eV 346.59 nm 28853.cm^{-1}	161→163 -0.19150 7.33 % -1→ 0	3.3277 eV 372.58 nm 26840.cm^{-1}
f=0.0006	161→164 0.58065 67.43 % -1→ 1	f=0.0699
128→131 0.70079 98.22 % -2→ 0		179→184 0.37679 28.39 % -4→ 0

7 18 Excited State: Singlet-A
3.5792 eV 346.40 nm 28868.cm^{-1}
f=0.0273
123→131 0.11497 2.64 % -7→ 0
127→132 0.69101 95.50 % -3→ 1

8 24 Excited State: Singlet-A
3.7474 eV 330.85 nm 30225.cm^{-1}
f=0.0758
130→133 0.67694 91.65 % 0→ 2

9 26 Excited State: Singlet-A
3.7762 eV 328.33 nm 30457.cm^{-1}
f=0.0008
126→131 -0.10258 2.10 % -4→ 0
128→132 0.68996 95.21 % -2→ 1

10 28 Excited State: Singlet-A
3.8494 eV 322.09 nm 31047.cm^{-1}
f=0.0073
130→134 0.68223 93.09 % 0→ 3

11 30 Excited State: Singlet-A
3.8939 eV 318.41 nm 31406.cm^{-1}
f=0.0000
126→131 0.69149 95.63 % -4→ 0

12 32 Excited State: Singlet-A
4.0333 eV 307.40 nm 32531.cm^{-1}
f=0.0014
123→132 -0.26143 13.67 % -7→ 1
124→131 0.63652 81.03 % -6→ 0

13 33 Excited State: Singlet-A
4.0797 eV 303.91 nm 32904.cm^{-1}
f=0.0037
125→131 0.38046 28.95 % -5→ 0
126→132 0.59124 69.91 % -4→ 1

14 34 Excited State: Singlet-A
4.1396 eV 299.51 nm 33388.cm^{-1}
f=0.0005
125→131 0.58783 69.11 % -5→ 0
126→132 -0.37914 28.75 % -4→ 1

15 35 Excited State: Singlet-A
4.1587 eV 298.13 nm 33542.cm^{-1}
f=0.0020
125→132 -0.11050 2.44 % -5→ 1
130→135 0.68205 93.04 % 0→ 4

16 36 Excited State: Singlet-A
4.1942 eV 295.61 nm 33828.cm^{-1}
f=0.0037
123→131 0.39821 31.71 % -7→ 0
124→132 0.57255 65.56 % -6→ 1

17 37 Excited State: Singlet-A
4.2586 eV 291.14 nm 34348.cm^{-1}
f=0.0553
127→134 0.12341 3.05 % -3→ 3
129→133 0.66352 88.05 % -1→ 2

6 17 Excited State: Singlet-A
3.4914 eV 355.11 nm 28160.cm^{-1}
f=0.0341
159→163 -0.14654 4.29 % -3→ 0
159→164 0.66781 89.19 % -3→ 1

7 19 Excited State: Singlet-A
3.5519 eV 349.07 nm 28648.cm^{-1}
f=0.0005
160→163 0.68179 92.97 % -2→ 0
160→164 0.16833 5.67 % -2→ 1

8 23 Excited State: Singlet-A
3.6711 eV 337.73 nm 29609.cm^{-1}
f=0.0011
160→163 -0.16467 5.42 % -2→ 0
160→164 0.67783 91.89 % -2→ 1

9 28 Excited State: Singlet-A
3.7497 eV 330.65 nm 30243.cm^{-1}
f=0.0736
162→166 0.67923 92.27 % 0→ 3

10 29 Excited State: Singlet-A
3.8246 eV 324.18 nm 30847.cm^{-1}
f=0.0484
153→164 -0.15101 4.56 % -9→ 1
155→163 -0.28846 16.64 % -7→ 0
157→163 0.60266 72.64 % -5→ 0

11 30 Excited State: Singlet-A
3.8541 eV 321.69 nm 31086.cm^{-1}
f=0.0040
162→167 0.67834 92.03 % 0→ 4

12 32 Excited State: Singlet-A
3.8676 eV 320.57 nm 31194.cm^{-1}
f=0.0031
158→163 0.66642 88.82 % -4→ 0
158→164 0.15972 5.10 % -4→ 1

13 33 Excited State: Singlet-A
3.9051 eV 317.49 nm 31497.cm^{-1}
f=0.2054
153→163 0.21469 9.22 % -9→ 0
155→164 -0.23309 10.87 % -7→ 1
156→164 -0.11538 2.66 % -6→ 1
157→164 0.58464 68.36 % -5→ 1

14 34 Excited State: Singlet-A
3.9835 eV 311.24 nm 32130.cm^{-1}
f=0.0035
156→163 0.13897 3.86 % -6→ 0
158→163 -0.14268 4.07 % -4→ 0
158→164 0.65344 85.40 % -4→ 1
162→165 -0.13397 3.59 % 0→ 2

15 35 Excited State: Singlet-A
4.0170 eV 308.65 nm 32399.cm^{-1}
f=0.0007
158→163 -0.10005 2.00 % -4→ 0
158→164 0.12570 3.16 % -4→ 1
179→185 0.31234 19.51 % -4→ 1
181→184 0.20121 8.10 % -2→ 0
181→185 -0.26110 13.63 % -2→ 1
182→184 0.16279 5.30 % -1→ 0
182→185 -0.30248 18.30 % -1→ 1

6 17 Excited State: Singlet-A
3.4401 eV 360.41 nm 27746.cm^{-1}
f=0.0429
179→184 0.28332 16.05 % -4→ 0
179→185 0.14548 4.23 % -4→ 1
181→184 -0.34093 23.25 % -2→ 0
181→185 0.47278 44.70 % -2→ 1
181→186 -0.14705 4.32 % -2→ 2
182→185 -0.16082 5.17 % -1→ 1

7 18 Excited State: Singlet-A
3.4722 eV 357.08 nm 28005.cm^{-1}
f=0.0643
179→184 0.19585 7.67 % -4→ 0
179→185 0.14180 4.02 % -4→ 1
182→184 0.36275 26.32 % -1→ 0
182→185 0.53215 56.64 % -1→ 1
182→186 0.10186 2.08 % -1→ 2

8 20 Excited State: Singlet-A
3.4947 eV 354.78 nm 28186.cm^{-1}
f=0.0272
179→184 -0.37078 27.50 % -4→ 0
179→185 0.55541 61.70 % -4→ 1
179→186 -0.16568 5.49 % -4→ 2

9 23 Excited State: Singlet-A
3.5564 eV 348.62 nm 28685.cm^{-1}
f=0.0004
180→184 0.59497 70.80 % -3→ 0
180→185 0.36742 27.00 % -3→ 1

10 28 Excited State: Singlet-A
3.6651 eV 338.28 nm 29561.cm^{-1}
f=0.0167
180→184 -0.33979 23.09 % -3→ 0
180→185 0.57118 65.25 % -3→ 1
180→186 -0.13523 3.66 % -3→ 2
182→186 0.15629 4.89 % -1→ 2

11 30 Excited State: Singlet-A
3.6683 eV 337.99 nm 29587.cm^{-1}
f=0.2319
180→185 -0.12931 3.34 % -3→ 1
182→184 0.12785 3.27 % -1→ 0
182→185 -0.18315 6.71 % -1→ 1
182→186 0.61737 76.23 % -1→ 2
183→186 0.18168 6.60 % 0→ 2

12 31 Excited State: Singlet-A
3.6844 eV 336.51 nm 29717.cm^{-1}
f=0.0130
182→186 -0.16590 5.50 % -1→ 2
183→184 -0.13274 3.52 % 0→ 0
183→185 0.11100 2.46 % 0→ 1
183→186 0.64832 84.06 % 0→ 2

129→137 -0.10798 2.33 % -1→ 6

18 38 Excited State: Singlet-A
4.3251 eV 286.66 nm 34885.cm^{-1}
f=0.0005
125→132 0.69167 95.68 % -5→ 1
130→135 0.11569 2.68 % 0→ 4

19 39 Excited State: Singlet-A
4.3352 eV 285.99 nm 34966.cm^{-1}
f=0.0001
127→133 0.44980 40.46 % -3→ 2
129→134 0.52276 54.66 % -1→ 3

20 40 Excited State: Singlet-A
4.3729 eV 283.53 nm 35270.cm^{-1}
f=0.0177
127→133 0.47515 45.15 % -3→ 2
128→133 0.18635 6.95 % -2→ 2
129→134 -0.40069 32.11 % -1→ 3
130→134 -0.11308 2.56 % 0→ 3
130→138 0.13773 3.79 % 0→ 7

162→165 0.58628 68.74 % 0→ 2
162→168 0.33800 22.85 % 0→ 5

16 36 Excited State: Singlet-A
4.1050 eV 302.03 nm 33109.cm^{-1}
f=0.0001
156→163 0.65630 86.15 % -6→ 0
156→164 0.15847 5.02 % -6→ 1
157→163 0.11929 2.85 % -5→ 0
158→164 -0.13784 3.80 % -4→ 1

17 37 Excited State: Singlet-A
4.1757 eV 296.92 nm 33679.cm^{-1}
f=0.0012
156→164 0.28355 16.08 % -6→ 1
162→165 -0.33292 22.17 % 0→ 2
162→168 0.53217 56.64 % 0→ 5

18 38 Excited State: Singlet-A
4.2268 eV 293.33 nm 34091.cm^{-1}
f=0.0011
156→163 -0.14679 4.31 % -6→ 0
156→164 0.60157 72.38 % -6→ 1
157→164 0.11782 2.78 % -5→ 1
162→165 0.10834 2.35 % 0→ 2
162→168 -0.28709 16.48 % 0→ 5

19 39 Excited State: Singlet-A
4.2598 eV 291.05 nm 34358.cm^{-1}
f=0.0595
159→167 0.11574 2.68 % -3→ 4
161→166 0.66133 87.47 % -1→ 3

20 40 Excited State: Singlet-A
4.2838 eV 289.42 nm 34552.cm^{-1}
f=0.1005
153→163 0.11847 2.81 % -9→ 0
153→164 0.17306 5.99 % -9→ 1
155→163 0.43697 38.19 % -7→ 0
155→164 -0.39438 31.11 % -7→ 1
157→163 0.24503 12.01 % -5→ 0
157→164 -0.11555 2.67 % -5→ 1

13 33 Excited State: Singlet-A
3.7485 eV 330.76 nm 30233.cm^{-1}
f=0.0728
183→187 0.67791 91.91 % 0→ 3

14 34 Excited State: Singlet-A
3.8540 eV 321.70 nm 31085.cm^{-1}
f=0.0064
183→188 0.67910 92.24 % 0→ 4

15 35 Excited State: Singlet-A
3.8733 eV 320.10 nm 31240.cm^{-1}
f=0.0001
178→184 0.58738 69.00 % -5→ 0
178→185 0.36396 26.49 % -5→ 1

16 36 Excited State: Singlet-A
3.9002 eV 317.89 nm 31457.cm^{-1}
f=0.0027
173→185 -0.15832 5.01 % -10→ 1
176→184 0.58857 69.28 % -7→ 0
176→185 0.27642 15.28 % -7→ 1

17 37 Excited State: Singlet-A
3.9798 eV 311.53 nm 32100.cm^{-1}
f=0.0034
177→184 0.10269 2.11 % -6→ 0
178→184 -0.34891 24.35 % -5→ 0
178→185 0.57918 67.09 % -5→ 1
178→186 -0.13383 3.58 % -5→ 2

18 38 Excited State: Singlet-A
3.9891 eV 310.81 nm 32174.cm^{-1}
f=0.0446
173→184 0.22766 10.37 % -10→ 0
176→184 -0.27911 15.58 % -7→ 0
176→185 0.56050 62.83 % -7→ 1

19 39 Excited State: Singlet-A
4.1082 eV 301.79 nm 33136.cm^{-1}
f=0.0002
177→184 0.59224 70.15 % -6→ 0
177→185 0.32399 20.99 % -6→ 1
183→189 -0.10921 2.39 % 0→ 5

20 40 Excited State: Singlet-A
4.1261 eV 300.49 nm 33279.cm^{-1}
f=0.0013
177→185 0.21249 9.03 % -6→ 1
183→189 0.65350 85.41 % 0→ 5

Figure S1. Experimental absorption spectra of **1, 2** and **3** with superimposed vertical transition energies computed by TD-DFT at the D95(d);D95(2d)/SDD09/M06/ACN level.

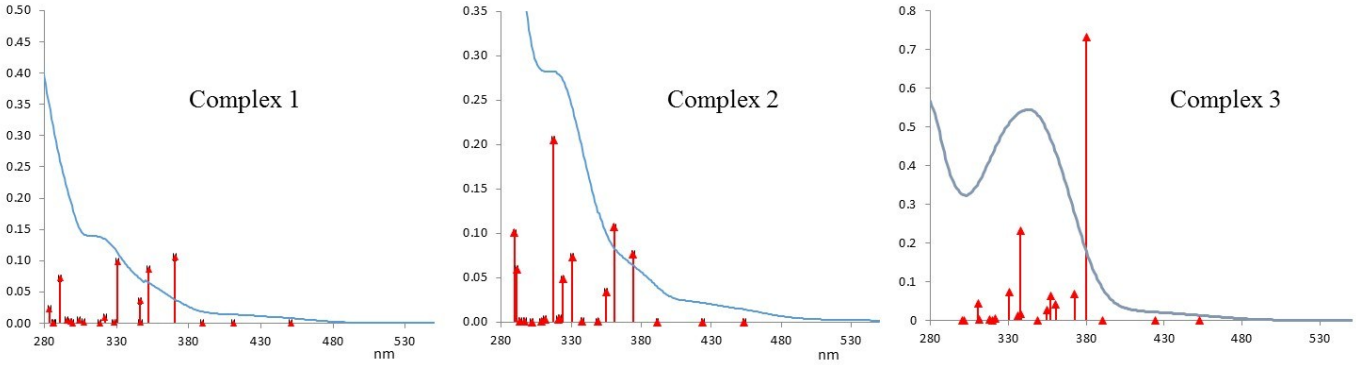
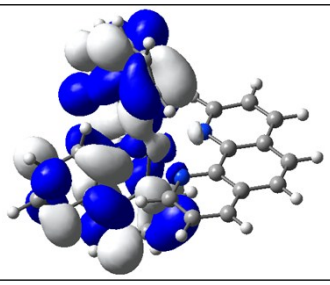
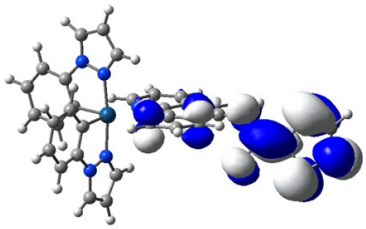
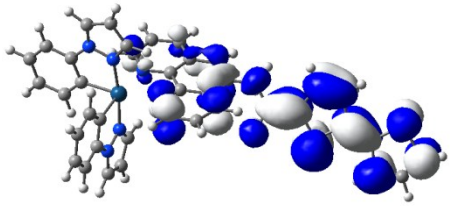
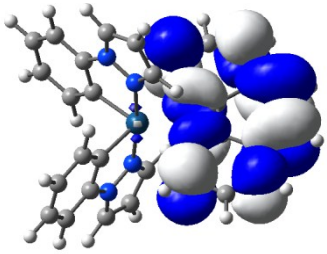
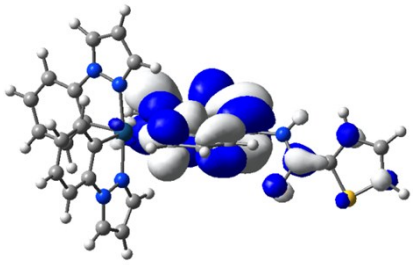
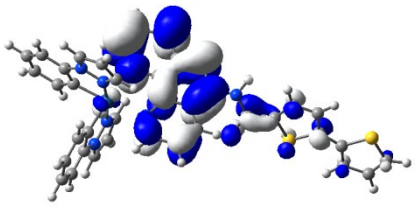
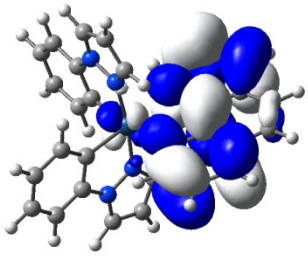
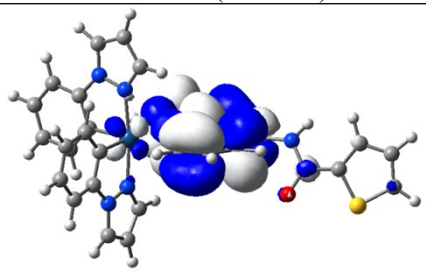
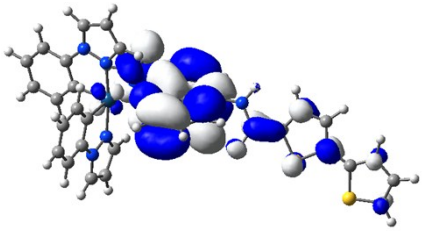
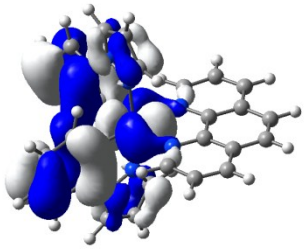
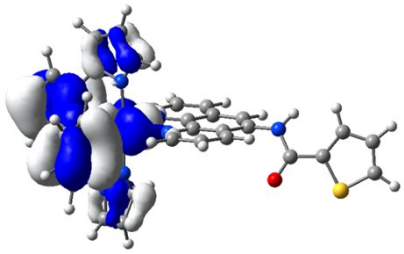
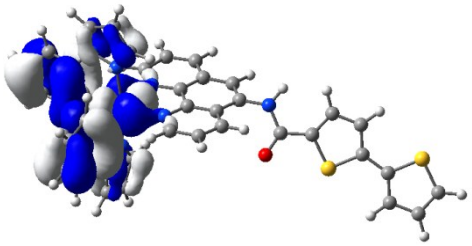
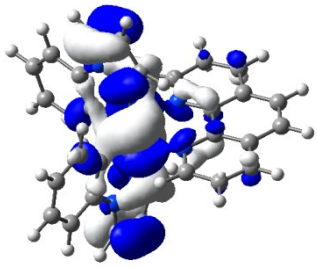
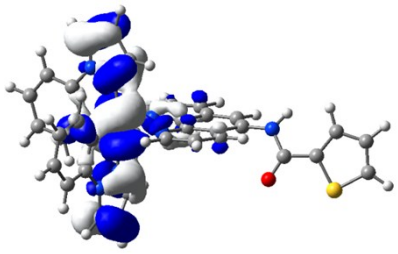
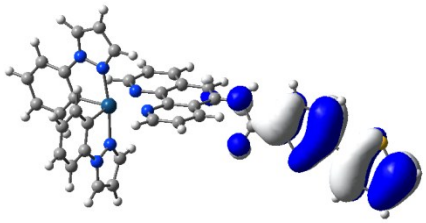


Figure S2. Most relevant MO's involved in the first 4 singlet vertical electronic transitions of **1**, **2** and **3** by TD-DFT at D95(d);D95(2d) /SDD09/ M06/ACN level of theory. The isovalue corresponds to $(0.02\ e/a.u^3)^{1/2}$**.**

1	2	3
		
LUMO+2 (-0.08047)	LUMO+2 (-0.05644)	LUMO+2 (-0.07102)
		
LUMO+1 (-0.08047)	LUMO+1 (-0.08511)	LUMO+1 (-0.08573)
		
LUMO (-0.08610)	LUMO (-0.08728)	LUMO (-0.08759)
		
HOMO (-0.22136)	HOMO (-0.21159)	HOMO (-0.22154)
		
HOMO-1 (-0.24259)	HOMO-1 (-0.24282)	HOMO-1 (-0.23067)

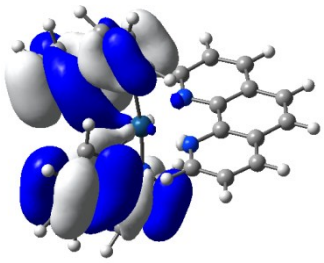
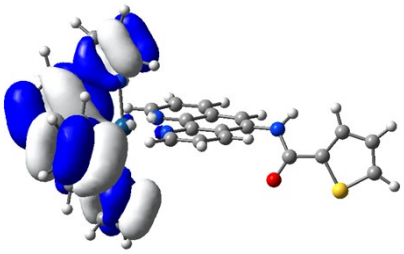
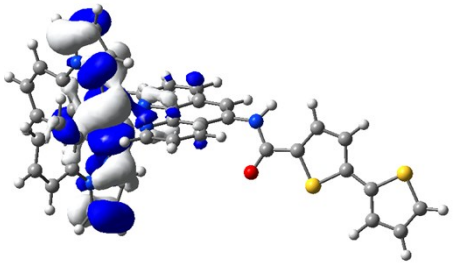
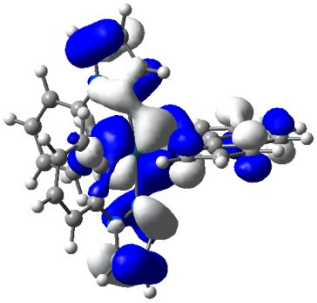
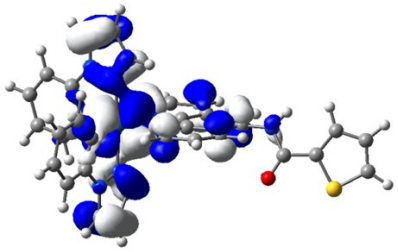
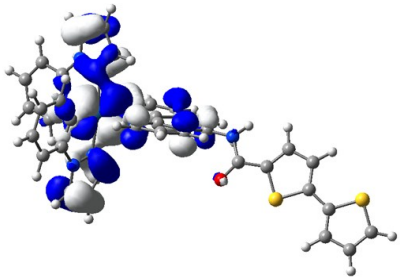
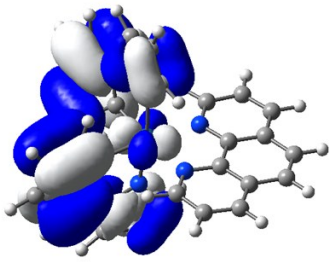
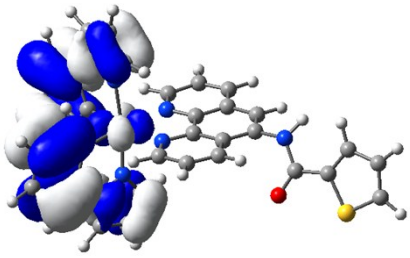
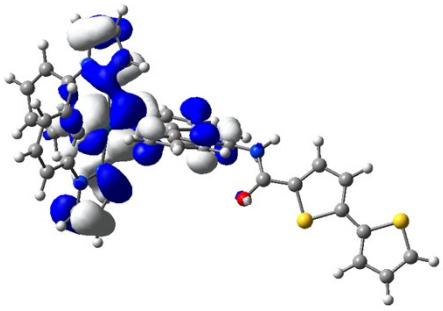
		
HOMO-2 (-0.24387)	HOMO-2 (-0.24387)	HOMO-2 (-0.24285)
		
HOMO-3 (-0.24475)	HOMO-3 (-0.24493)	HOMO-3 (-0.24386)
		
HOMO-4 (-0.25486)	HOMO-4 (-0.25489)	HOMO-4 (-0.24515)

Table S2. Computed first 5 vertical triplet electronic transition energies of **1, 2** and **3** at the S_0 geometry. The monoelectronic excitation contributions by TD-DFT are obtained at D95(d);D95(2d)/SDD09/M06/ACN level.

Energies and composition of the first 5 triplet states for complex **1-3** @S0 geometry		
Complex **1**	Complex **2**	Complex **3**
HOMO is MO 130 and LUMO is MO131 >>>> Triplet states <<<<	HOMO is MO 162 and LUMO is MO 163 >>>> Triplet states <<<<	HOMO is MO 183 and LUMO is MO 184 >>>> Triplet states <<<<

eV nm cm^{-1} f	eV nm cm^{-1} f	eV nm cm^{-1} f
2.6664; 464.99; 21505.8; 0.0000 2.7336; 453.56; 22047.8; 0.0000 2.9649; 418.17; 23913.7; 0.0000 3.0098; 411.93; 24276.0; 0.0000 3.1232; 396.98; 25190.2; 0.0000	2.5787; 480.80; 20798.7; 0.0000 2.7149; 456.67; 21897.7; 0.0000 2.9171; 425.03; 23527.8; 0.0000 2.9474; 420.65; 23772.7; 0.0000 3.0487; 406.68; 24589.4; 0.0000	2.1834; 567.85; 17610.3; 0.0000 2.5746; 481.56; 20765.8; 0.0000 2.7188; 456.02; 21928.9; 0.0000 2.9126; 425.68; 23491.8; 0.0000 2.9449; 421.02; 23751.8; 0.0000
1 1 Excited State: Triplet-A 2.6664 eV 464.99 nm 21506.cm^{-1} 123 →131 0.24140 11.65 % -7 → 0 123 → 135 0.11019 2.43 % -7 → 4 124 → 132 0.44094 38.89 % -6 → 1 127 → 132 0.32334 20.91 % -3 → 1 129 → 131 -0.27344 14.95 % -1 → 0 130 → 131 0.12652 3.20 % 0 → 0 2 2 Excited State: Triplet-A 2.7336 eV 453.56 nm 22048.cm^{-1} 130 → 131 0.68731 94.48 % 0 → 0 3 4 Excited State: Triplet-A 2.9649 eV 418.17 nm 23914.cm^{-1} 124 → 131 0.22982 10.56 % -6 → 0 127 → 131 0.61655 76.03 % -3 → 0 129 → 132 -0.14646 4.29 % -1 → 1 4 5 Excited State: Triplet-A 3.0098 eV 411.93 nm 24276.cm^{-1} 130 → 132 0.69420 96.38 % 0 → 1 5 7 Excited State: Triplet-A 3.1232 eV 396.98 nm 25190.cm^{-1} 125 → 134 -0.10162 2.07 % -5 → 3 125 → 138 0.14278 4.08 % -5 → 7 126 → 133 -0.24092 11.61 % -4 → 2 128 → 134 0.33908 23.00 % -2 → 3 130 → 133 0.44472 39.56 % 0 → 2 130 → 137 -0.17707 6.27 % 0 → 6	1 1 Excited State: Triplet-A 2.5787 eV 480.80 nm 20799.cm^{-1} 153 → 163 0.17062 5.82 % -9 → 0 153 → 164 0.11934 2.85 % -9 → 1 155 → 163 0.11600 2.69 % -7 → 0 155 → 164 -0.25901 13.42 % -7 → 1 157 → 163 -0.16188 5.24 % -5 → 0 157 → 164 0.31219 19.49 % -5 → 1 159 → 163 -0.12783 3.27 % -3 → 0 159 → 164 0.32696 21.38 % -3 → 1 161 → 163 0.19967 7.97 % -1 → 0 2 2 Excited State: Triplet-A 2.7149 eV 456.67 nm 21898.cm^{-1} 162 → 163 0.66428 88.25 % 0 → 0 162 → 164 0.21030 8.85 % 0 → 1 3 4 Excited State: Triplet-A 2.9171 eV 425.03 nm 23528.cm^{-1} 159 → 163 -0.10440 2.18 % -3 → 0 162 → 163 -0.20852 8.70 % 0 → 0 162 → 164 0.65168 84.94 % 0 → 1 4 6 Excited State: Triplet-A 2.9474 eV 420.65 nm 23773.cm^{-1} 155 → 163 -0.12477 3.11 % -7 → 0 157 → 163 0.12072 2.91 % -5 → 0 159 → 163 0.56075 62.89 % -3 → 0 159 → 164 0.22654 10.26 % -3 → 1 161 → 164 0.13784 3.80 % -1 → 1 162 → 164 0.12977 3.37 % 0 → 1 5 7 Excited State: Triplet-A 3.0487 eV 406.68 nm 24589.cm^{-1} 154 → 165 0.18972 7.20 % -8 → 2 155 → 165 0.30337 18.41 % -7 → 2 157 → 163 0.11310 2.56 % -5 → 0 157 → 164 -0.20597 8.48 % -5 → 1 157 → 165 0.40187 32.30 % -5 → 2 161 → 163 0.26825 14.39 % -1 → 0	1 1 Excited State: Triplet-A 2.1834 eV 567.85 nm 17610.cm^{-1} 182 → 184 -0.28085 15.78 % -1 → 0 182 → 185 0.23486 11.03 % -1 → 1 182 → 186 0.56771 64.46 % -1 → 2 182 → 190 -0.11722 2.75 % -1 → 6 2 2 Excited State: Triplet-A 2.5746 eV 481.56 nm 20766.cm^{-1} 173 → 184 0.11893 2.83 % -10 → 0 173 → 185 0.16192 5.24 % -10 → 1 176 → 184 -0.30506 18.61 % -7 → 0 176 → 185 0.31202 19.47 % -7 → 1 176 → 186 -0.13713 3.76 % -7 → 2 179 → 184 -0.19654 7.73 % -4 → 0 179 → 185 0.23779 11.31 % -4 → 1 179 → 186 -0.10549 2.23 % -4 → 2 181 → 184 0.15093 4.56 % -2 → 0 181 → 185 0.14437 4.17 % -2 → 1 182 → 186 0.10855 2.36 % -1 → 2 3 3 Excited State: Triplet-A 2.7188 eV 456.02 nm 21929.cm^{-1} 183 → 184 0.55969 62.65 % 0 → 0 183 → 185 0.41200 33.95 % 0 → 1 4 5 Excited State: Triplet-A 2.9126 eV 425.68 nm 23492.cm^{-1} 179 → 184 -0.10824 2.34 % -4 → 0 183 → 184 -0.38873 30.22 % 0 → 0 183 → 185 0.53180 56.56 % 0 → 1 183 → 186 -0.16794 5.64 % 0 → 2 5 7 Excited State: Triplet-A 2.9449 eV 421.02 nm 23752.cm^{-1} 176 → 184 0.14330 4.11 % -7 → 0 176 → 185 0.16579 5.50 % -7 → 1 179 → 184 0.43202 37.33 % -4 → 0 179 → 185 0.37040 27.44 % -4 → 1 181 → 184 -0.10370 2.15 % -2 → 0 181 → 185 0.10318 2.13 % -2 → 1 182 → 184 -0.11627 2.70 % -1 → 0 182 → 185 -0.12871 3.31 % -1 → 1 183 → 185 0.14329 4.11 % 0 → 1

Emission Spectra Fitting

Emission spectra have been analyzed according to the procedure first reported by Yersin *et al.*[1] and then modified by J.P.Claude[2] where the spectra are fit by application of the one-mode Frank-Condon analysis according to the following equation:

$$I(\tilde{\nu}) = \sum_{\upsilon_M = 0}^{5} \left\{ \left(\frac{E_0 - \nu_M \hbar\omega_M}{E_0} \right)^3 \left(\frac{S_M^{\nu_M}}{\nu_M^{!}} \right) x\, exp\left[-4\, ln(2) \left(\frac{\tilde{\nu} - E_0 + \nu_M \hbar\omega_M}{\Delta\tilde{\nu}_{0,1/2}} \right)^2 \right] \right\}$$

Where E_0 is the energy gap between the lowest energy triplet excited state and the ground state, S_M is the electron-vibrational coupling constant or Huang-Rhys factor, $\hbar\omega_M$ is the quantum spacing for the medium frequency acceptor mode, and $\Delta\tilde{\nu}_{0,1/2}$, is the width at half-maximum of the 0-0 vibronic component which includes average values for the C=C and C=N stretching modes of the aromatic ligands. The parameters E_0, S_M, $\hbar\omega_M$ and $\Delta\tilde{\nu}_{0,1/2}$ were optimized using the first 5 vibrational quanta in the ω_M average mode.[3] The values of E_0 for **1-3** in solution are very similar whereas the values of E_0 for **1** and **2** in PMMA are slightly different. The observed shift to higher energy in PMMA can be explained by the Marcus theory[4] where the total solvent reorganization energy λ_0, contains two factors $\lambda_{0,0}$ and $\lambda_{0,i}$. $\lambda_{0,0}$ arises from large amplitude reorientations which are frozen in rigid media and $\lambda_{0,i}$ to single molecule rotations and phonon-like modes. In rigid medium (r) the emission energy $E_{0,r}$ is obtained by adding $\lambda_{0,0}$ to the emission energy in non-rigid medium (nr) according to the relation

$$E_{0,r} = E_{0,nr} + \lambda_{0,0}$$

In this case, the values of $E_{0,r}$ in PMMA are shifted to higher energy by 48 and 43 nm for **1** and **2** respectively, suggesting that the $\lambda_{0,0}$ contribution is similar for the two complexes.

Figure S3. Experimental and fitted emission spectra of **1-3** in acetonitrile and PMMA.

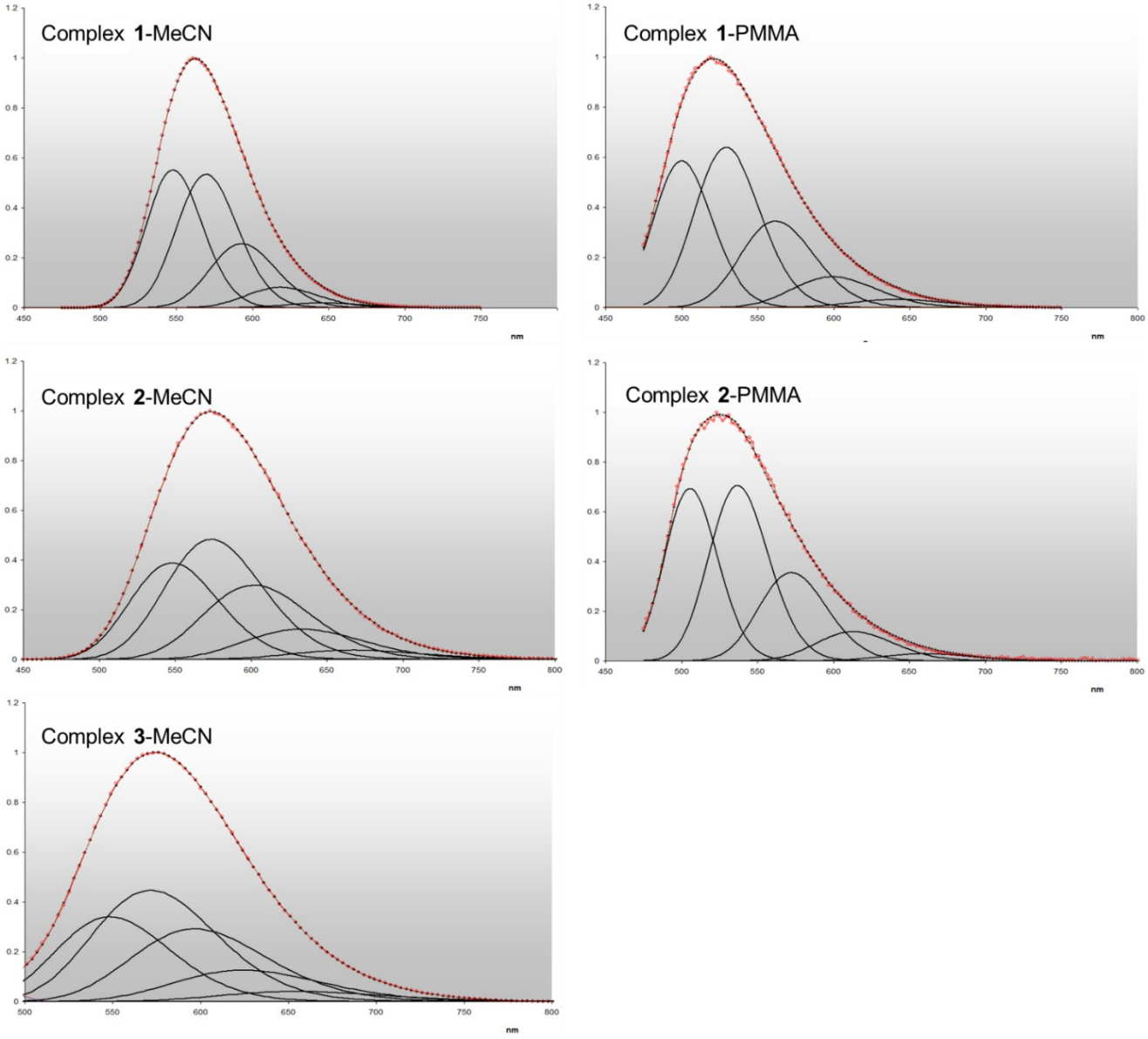


Figure S4. Variable temperature emission spectra of (a) **1** (b) **2** and (c) **3**

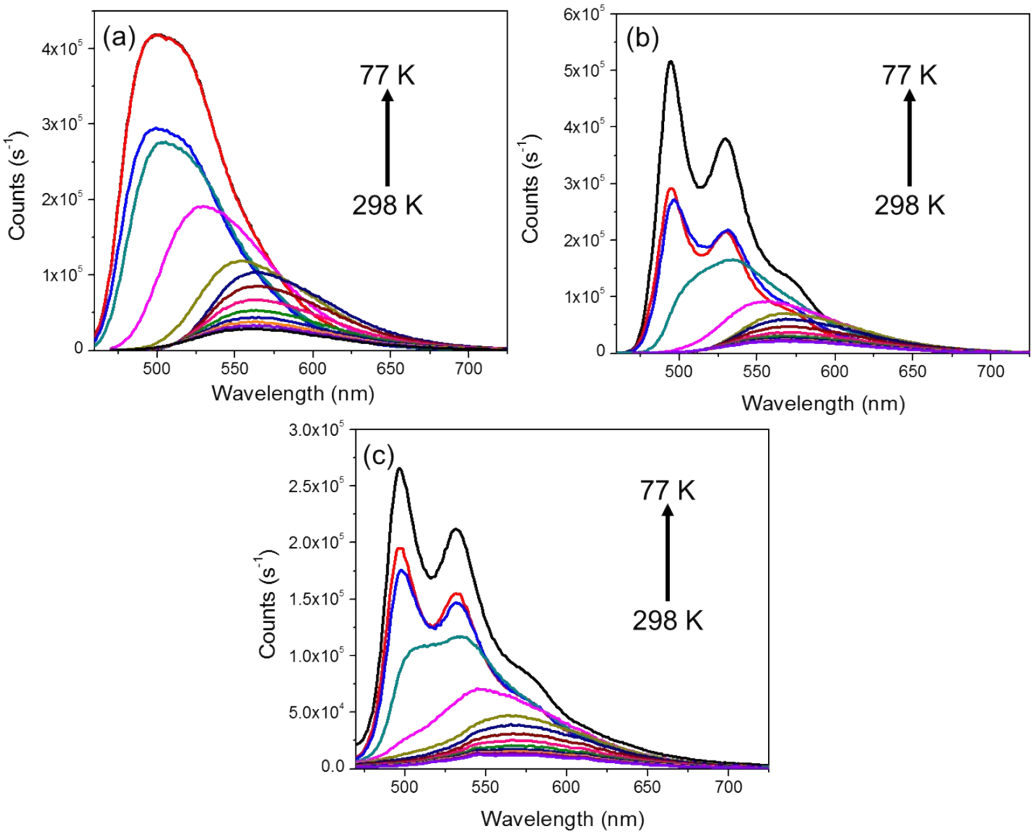


Table S3. Fitting parameters for emission spectra of **1-3** in acetonitrile and PMMA.

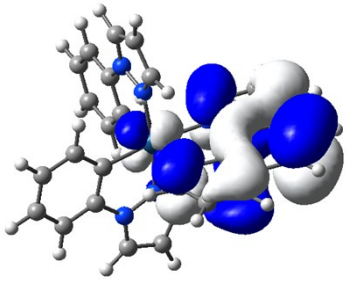
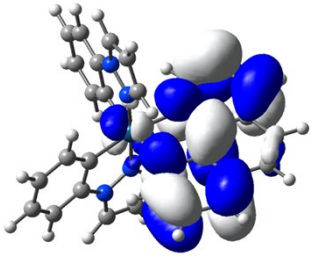
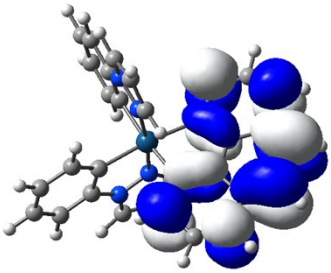
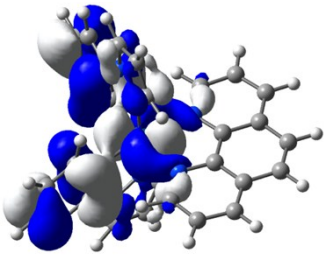
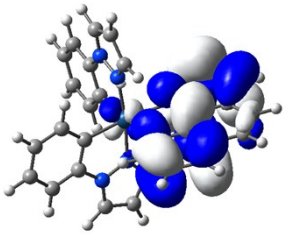
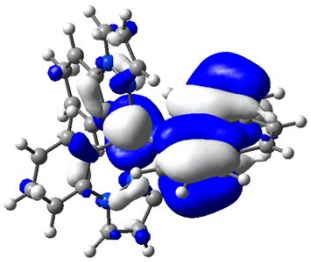
	Acetonitrile						
	E_{00} (cm^{-1})	**E_{00}** (nm)	**S_m**	**$\hbar*\omega_n/2\pi$** (cm^{-1})	**fwhm** (cm^{-1})	**λ_{max}** (nm)	[$E(T_1@T_1)$-$E(S_0@S_0)$][a]
1	18251	548	1.0864	693	1440	564	531
2	18249	548	1.4279	815	2279	573	538
3	18236	548	1.4866	739	2530	576	535
	PMMA						
1	20008	500	1.2958	1105	1802	518	531
2	19788	505	1.2234	1156	1593	523	538
3							535

[a]includes the Zero Point Energy contributions for S_0 and T_1

Table S4. Energies @T_1 geometry using as reference E(S_0@T_1) and composition in terms of monoelectronic excitations of the first four triplet states computed by TD-DFT at the D95(d);D95(2d)/SDD09/M06/ACN level of theory.

Complex **1**	Complex **2**	Complex **3**
1 1 Excited State: Triplet-A	1 1 Excited State: Triplet-A	1 1 Excited State: Triplet-A
2.1962 eV 564.53 nm 17714.cm^{-1}	2.1606 eV 573.83 nm 17427.cm^{-1}	2.1610 eV 573.75 nm 17429.cm^{-1}
130➐131 0.70139 98.39 % 0➐ 0	162➐163 0.70060 98.17 % 0➐ 0	183➐184 0.70021 98.06 % 0➐ 0
2 3 Excited State: Triplet-A	2 3 Excited State: Triplet-A	2 3 Excited State: Triplet-A
2.5009 eV 495.75 nm 20171.cm^{-1}	2.4552 eV 504.98 nm 19803.cm^{-1}	2.1880 eV 566.66 nm 17647.cm^{-1}
114➐131 -0.10197 2.08 % -16➐ 0	153➐163 0.29707 17.65 % -9➐ 0	182➐185 0.30480 18.58 % -1➐ 1
123➐131 -0.33487 22.43 % -7➐ 0	154➐164 -0.10351 2.14 % -8➐ 1	182➐186 0.60006 72.01 % -1➐ 2
124➐132 -0.31979 20.45 % -6➐ 1	155➐164 -0.24070 11.59 % -7➐ 1	182➐190 -0.11825 2.80 % -1➐ 6
127➐131 0.42710 36.48 % -3➐ 0	157➐164 -0.19073 7.28 % -5➐ 1	
129➐132 -0.23785 11.31 % -1➐ 1	159➐163 0.38987 30.40 % -3➐ 0	3 4 Excited State: Triplet-A
	161➐163 -0.11032 2.43 % -1➐ 0	2.4542 eV 505.19 nm 19795.cm^{-1}
3 4 Excited State: Triplet-A	161➐164 0.24364 11.87 % -1➐ 1	173➐184 0.29222 17.08 % -10➐ 0
2.6418 eV 469.33 nm 21307.cm^{-1}		176➐184 0.11957 2.86 % -7➐ 0
124➐131 0.19222 7.39 % -6➐ 0	3 4 Excited State: Triplet-A	176➐185 -0.29942 17.93 % -7➐ 1
128➐131 -0.14344 4.12 % -2➐ 0	2.6253 eV 472.27 nm 21174.cm^{-1}	179➐184 0.38669 29.91 % -4➐ 0
129➐131 0.64076 82.11 % -1➐ 0	155➐163 -0.11618 2.70 % -7➐ 0	181➐184 -0.11712 2.74 % -2➐ 0
	160➐163 -0.20469 8.38 % -2➐ 0	181➐185 0.22690 10.30 % -2➐ 1
4 5 Excited State: Triplet-A	161➐163 0.61894 76.62 % -1➐ 0	
2.8115 eV 440.99 nm 22676.cm^{-1}		4 5 Excited State: Triplet-A
130➐132 0.69871 97.64 % 0➐ 1	4 5 Excited State: Triplet-A	2.6215 eV 472.96 nm 21143.cm^{-1}
	2.7106 eV 457.40 nm 21863.cm^{-1}	176➐184 -0.14420 4.16 % -7➐ 0
	162➐164 0.69683 97.11 % 0➐ 1	180➐184 -0.14601 4.26 % -3➐ 0
		181➐184 0.61742 76.24 % -2➐ 0
		182➐184 0.12092 2.92 % -1➐ 0

Figure S5. NTO's and their respective weights for complex **1** related to the S_0-T_1 and S_0-T_2 transitions @S_0 and @T_1 equilibrium geometries. Singly occupied NTO's are identified as hole and electron. Hole and electron indicate the composition of the NTO's from where the electron has been respectively ejected and housed. Isovalue corresponds to $(0.02\ e/a.u^3)^{1/2}$.

T_1@S_0	T_1@T_1
 NTO 2 electron 0.61455	 NTO 1 electron 0.99881
 NTO 2 hole 0.61455	 NTO 1 hole 0.99881
 NTO 1 electron 0.32776	
 NTO 1 hole 0.32776	

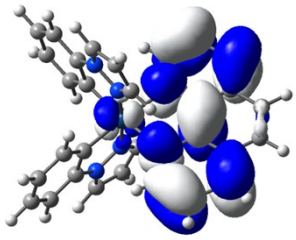
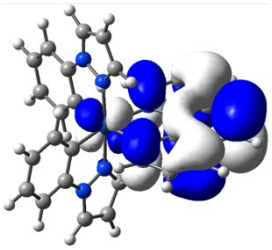
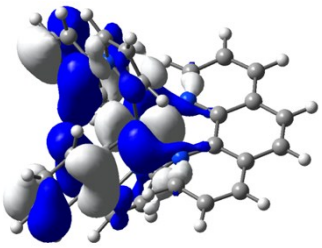
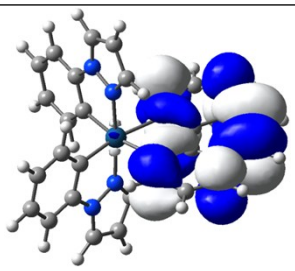
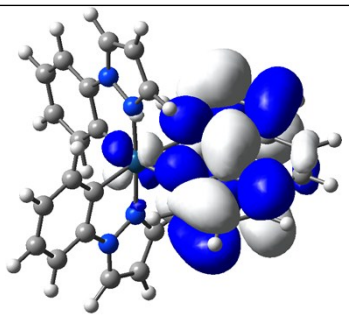
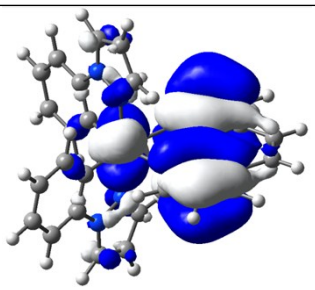
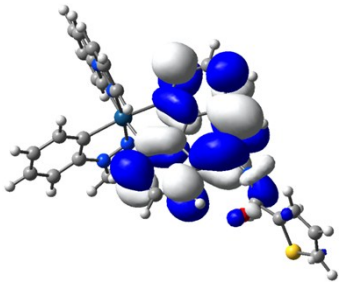
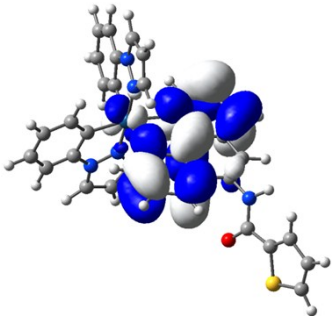
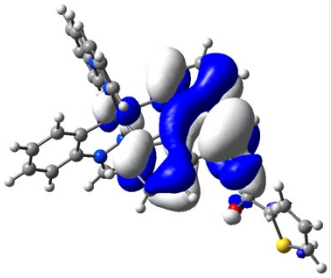
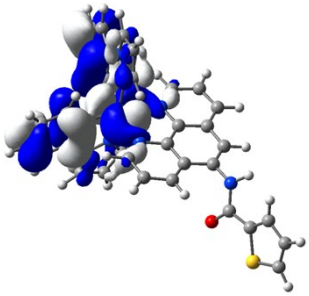
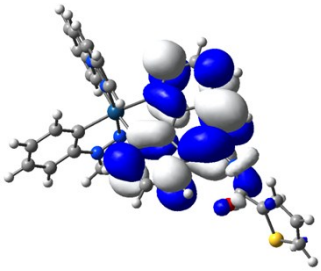
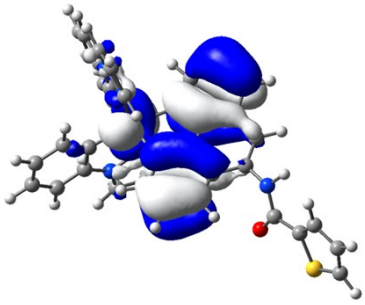
T_2@S_0	T_2@T_1
 NTO 1 electron 0.97042	 NTO 1 electron 0.33448
 NTO 1 hole 0.97042	 NTO 1 hole 0.33448
	 NTO 2 electron 0.62603
	 NTO 2 hole 0.62603

Figure S6. NTO's and their respective weights for complex **2** related to the S_0-T_1 and S_0-T_2 transitions @S_0 and @T_1 equilibrium geometries. Singly occupied NTO's are identified as hole and electron. Hole and electron indicate the composition of the NTO's from where the electron has been respectively ejected and housed. Isovalue corresponds to $(0.02\ e/a.u^3)^{1/2}$.

T_1@S_0	T_1@T_1
 NTO 1 electron; 0.73931	 NTO 1 electron; 0.99847
 NTO 1 hole; 0.73931	 NTO 1 hole; 0.99847
 NTO 2 electron; 0.21036	
 NTO 2 hole; 0.21036	
T_2@S_0	T_2@T_1

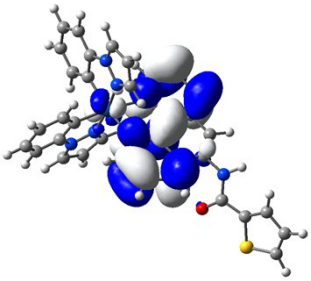
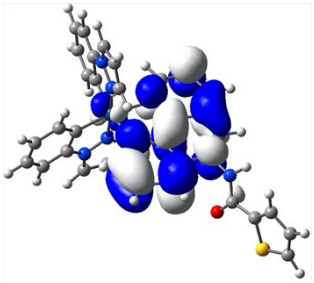
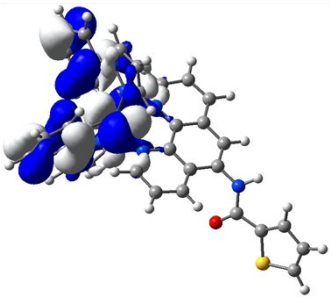
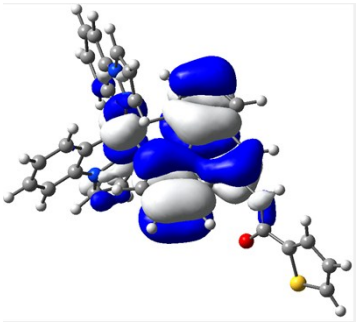
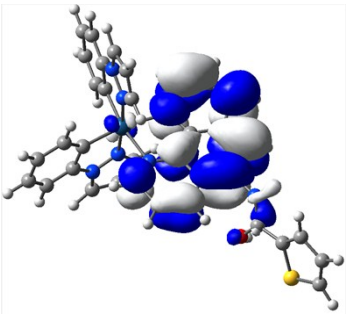
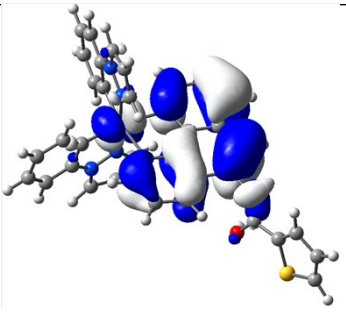
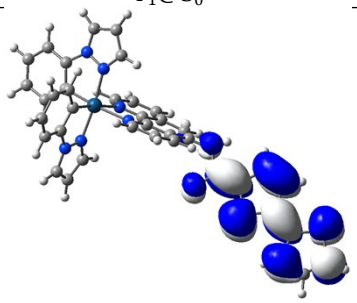
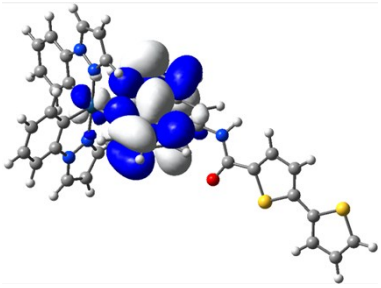
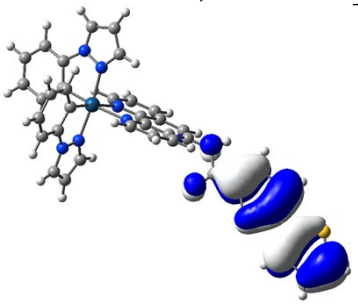
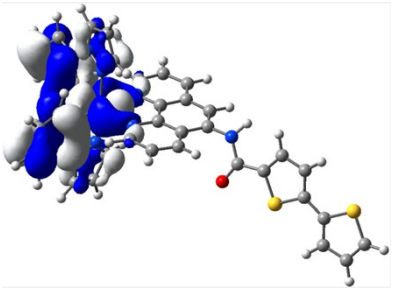
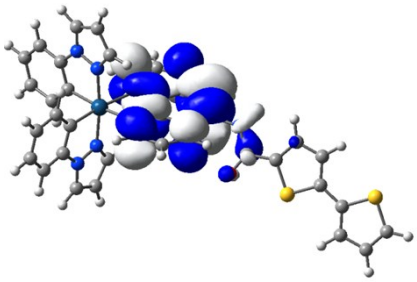
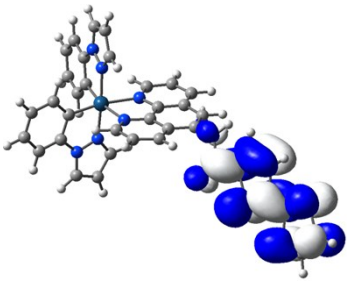
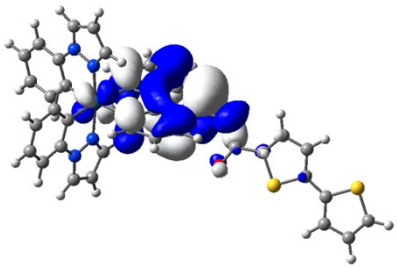
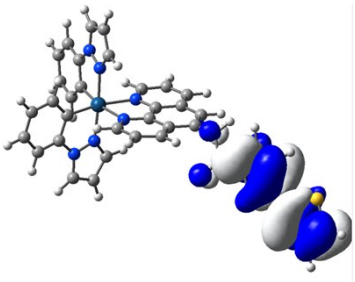
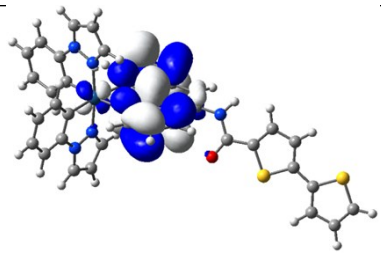
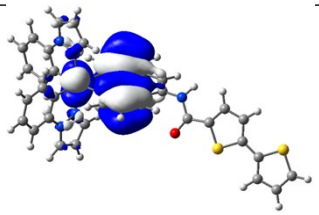
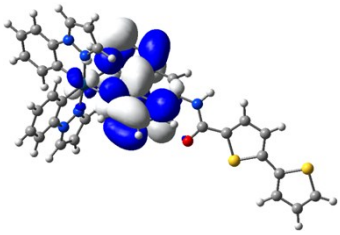
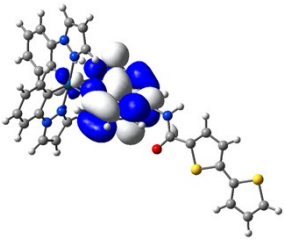
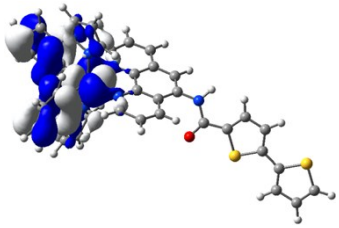
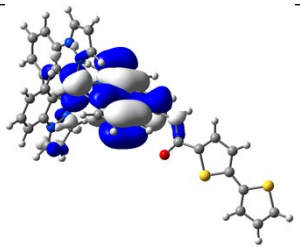
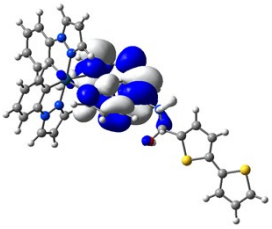
 NTO 1 electron; 0.99328	 NTO 1 electron; 0.60346
 NTO 1 hole; 0.99328	 NTO 1 hole; 0.60346
	 NTO 2 electron; 0.35786
	 NTO 2 hole; 0.35786

Figure S7. NTO's and their respective weights for complex **3** related to the S_0-T_1 and S_0-T_2 transitions @S_0 and @T_1 equilibrium geometries. Same weight singly occupied NTO's are related and identified as hole and electron. Hole and electron indicate the composition of the NTO's from where the electron has been respectively ejected and housed.

T_1@S_0	T_1@T_1
 NTO 1 electron; 0.97016	 NTO 1 electron; 0.99817
 NTO 1 hole; 0.97016	 NTO 1 hole; 0.99817
T_2@S_0	T_2@T_1
 NTO 1 electron 0.74282	 NTO 1 electron 0.96927
 NTO 1 hole 0.74282	 NTO 1 hole; 0.96927

 NTO 2 electron 0.20289	
 NTO 2 hole 0.20289	
$T_3@S_0$	$T_3@T_1$
 NTO 1 electron 0.99761	 NTO 1 electron 0.60717
 NTO 1 hole 0.99761	 NTO 1 hole; 0.60717
	 NTO 2 electron 0.35126

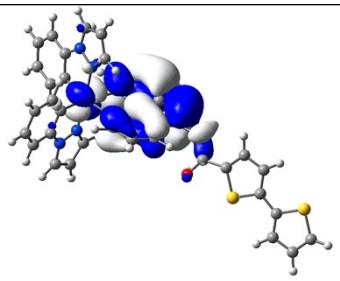
	 NTO 2 hole 0.35126

Figure S8. Energies of the 10 lowest triplet states computed at the T_1 relaxed geometries. Energies are in eV and computed by TD-DFT using the optimized geometry of the most stable triplet state computed by UDFT at the D95(d);D95(2d)/SDD09/ACN level of theory. Triplet energies at the T_1 relaxed geometry use as a reference the S_0 energy at the S_0 geometry. Dotted lines connect triplet energy levels identified by the same composition as indicated by the NTO analysis. In case of complex **3** the state at 2.48 eV involves the transition localized within the bi-thiophene substituent (see Figure S7).

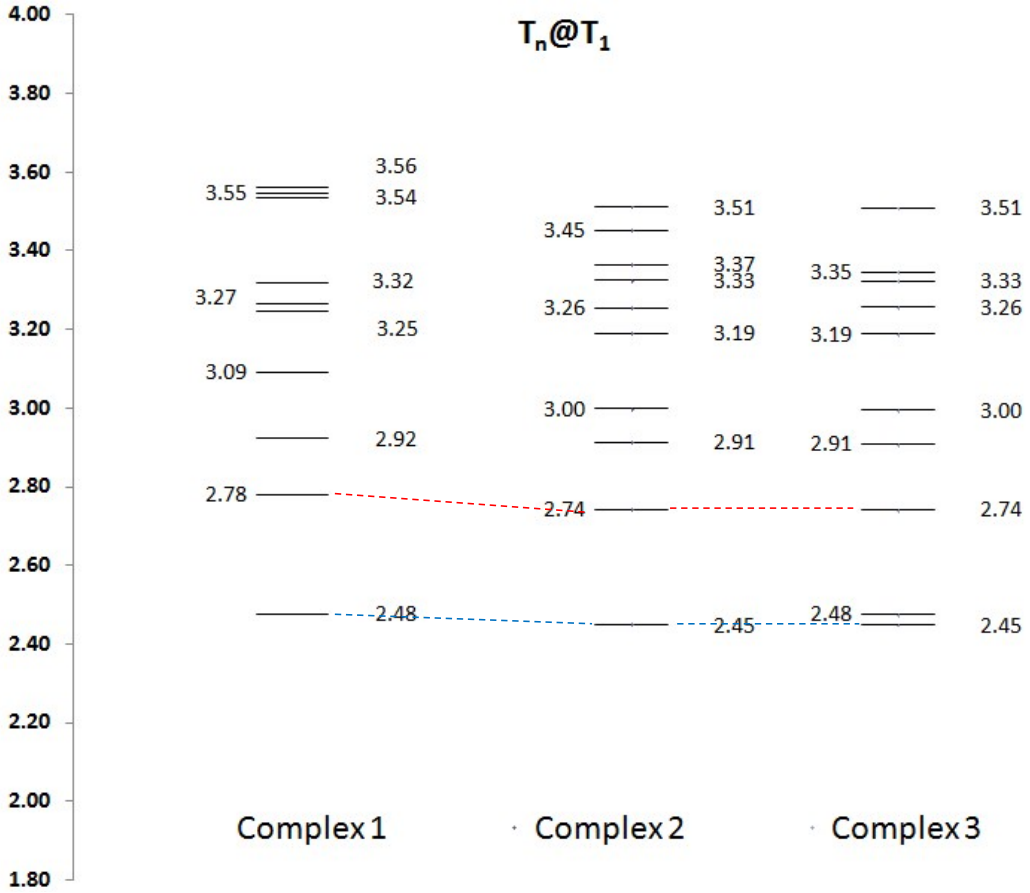
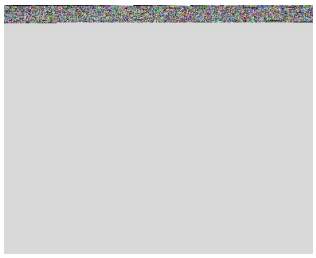
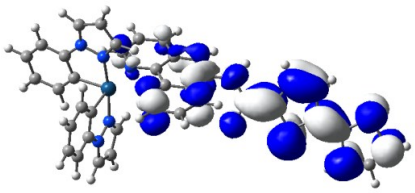
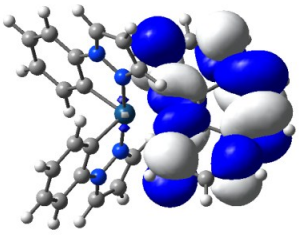
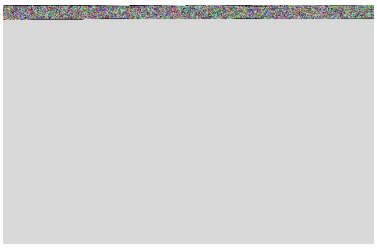
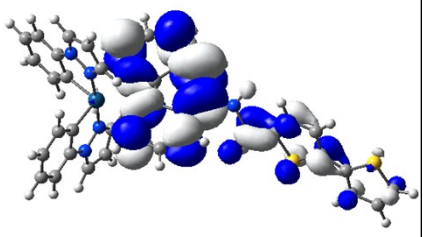
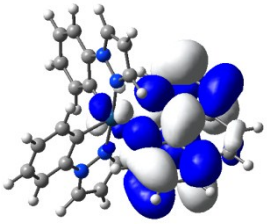
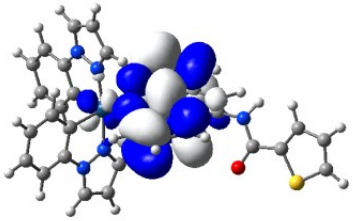
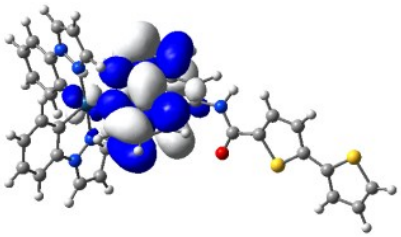
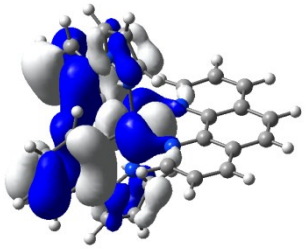
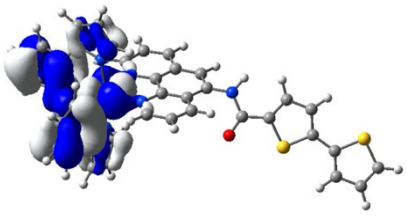


Figure S9. Most relevant MO's involved in the first 4 triplet excitations for geometry relaxed @T1 equilibrium geometry computed by TD-DFT at D95(d);D95(2d) /SDD09/ M06/ACN level of theory. Isovalue corresponds to $(0.02\ e/a.u^3)^{1/2}$.

1	2	3
		
LUMO+2 (-0.04448)	LUMO+2 (-0.05559)	LUMO+2 (-0.07118)
		
LUMO+1 (-0.09704)	LUMO+1 (-0.08490)	LUMO+1 (-0.08575)
		
LUMO (-0.09765)	LUMO (-0.09889)	LUMO(-0.09898)
		
HOMO (-0.21303)	HOMO (-0.21350)	HOMO (-0.21352)

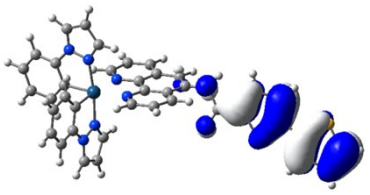
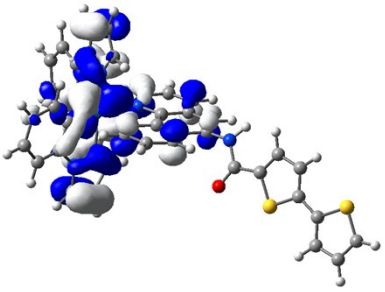
		
HOMO-1 (-0.24280)	HOMO-1 (-0.24331)	HOMO-1 (-0.2309)
		
HOMO-2 (-0.24419)	HOMO-2 (-0.24443)	HOMO-2 (-0.24340)
HOMO-3 (-0.24554)	HOMO-3 (-0.24600)	HOMO-3 (-0.24437)
HOMO-4 (-0.25556)	HOMO-4 (-0.25580)	HOMO-4 (-0.24600)

Table S5. Energy optimized Cartesian coordinates (Å) of the singlet and triplet state geometries for **1, 2** and **3** computed at the D95(d);D95(2d)/SDD09/M06/ACN level of theory.

Ir 2PhPyrazole phenanthroline Singlet in ACN				Ir 2PhPyrazole phenanthroline triplet in ACN			
Ir	0.351203439	0.040587879	0.052093669	Ir	0.3683833430	-0.0865104123	0.0612206717
N	1.350755285	-0.076876629	-1.721798208	N	1.3387804791	-0.1592613918	-1.7307321682
N	2.450366646	-0.871809244	-1.710112906	N	2.5159372158	-0.8364439291	-1.7072068027
N	-0.615482581	-0.085021626	1.843551829	N	-0.5824880018	-0.1584654965	1.8636305253
N	-1.465191757	-1.135891944	1.965437379	N	-1.5382561223	-1.1188186632	1.9587979169
C	1.212253516	0.382539864	-2.967376550	C	1.1675433619	0.2927256907	-2.9705663152
H	0.389173764	1.043545312	-3.217065443	H	0.2824578680	0.8668225927	-3.2239985021
C	2.239777291	-0.127296029	-3.780127443	C	2.2554490955	-0.1024931014	-3.7736767678
H	2.402487375	0.058531852	-4.833176569	H	2.4078276597	0.1075933033	-4.8235102448
C	3.006577842	-0.922641262	-2.941956894	C	3.0919217496	-0.8163853027	-2.9351017797
H	3.894999724	-1.509491791	-3.139629233	H	4.0415854008	-1.3009736893	-3.1250633514
C	2.773746503	-1.474935003	-0.465775692	C	2.8885542328	-1.3866000591	-0.4648815006
C	3.904641530	-2.274748403	-0.313875999	C	4.0701285233	-2.0980256723	-0.2946399618
H	4.580507537	-2.465159125	-1.146988119	H	4.7592766757	-2.2655615289	-1.1200166508
C	4.158838977	-2.830753175	0.941522649	C	4.3603647294	-2.5959103793	0.9779728819
H	5.035658774	-3.458717248	1.086234494	H	5.2822605750	-3.1519822808	1.1342451465
C	3.284713549	-2.575814556	2.004078593	C	3.4793123687	-2.3816032179	2.0514305210
H	3.482253713	-3.010981702	2.983022543	H	3.7220394129	-2.7778179748	3.0352801737
C	2.157249528	-1.766363930	1.818996580	C	2.3015793564	-1.6665769253	1.8581755167
H	1.491397060	-1.584925499	2.666031014	H	1.6266869316	-1.5055501341	2.6995091318
C	1.868106062	-1.185052949	0.575880726	C	1.9598093862	-1.1579127253	0.5885278015
C	-0.776949721	-1.604085288	-0.263925939	C	-0.8727625404	-1.6039876991	-0.2783300866
C	-0.878023789	-2.411013801	-1.406518292	C	-1.0433536275	-2.3596068425	-1.4562528073
H	-0.267750824	-2.181615855	-2.283268396	H	-0.4189295032	-2.1468801377	-2.3246415260
C	-1.747366232	-3.507673751	-1.453629715	C	-1.9862302926	-3.3804337018	-1.5236540381
H	-1.803866182	-4.113573021	-2.357187727	H	-2.0965510520	-3.9620784819	-2.4365507538
C	-2.543169316	-3.831795164	-0.349203479	C	-2.7998366041	-3.6655722135	-0.4140417528
H	-3.219661797	-4.683285037	-0.386835858	H	-3.5387519179	-4.4619042857	-0.4722567855
C	-2.469317187	-3.056529126	0.809800267	C	-2.6761473427	-2.9334502716	0.7693314615
H	-3.086628320	-3.299100225	1.674215313	H	-3.3122901731	-3.1584397908	1.6231124455
C	-1.593470357	-1.972855424	0.825372195	C	-1.7281775059	-1.9182938396	0.8143935380
C	-2.012052463	-1.157022865	3.202326955	C	-2.1229843546	-1.0774434077	3.1820231999
H	-2.717226621	-1.923900184	3.497944147	H	-2.9143779174	-1.7636951018	3.4568472261
C	-1.499366836	-0.076786278	3.904694926	C	-1.5213625633	-0.0563211988	3.8946882546
H	-1.725861196	0.206558813	4.923682299	H	-1.7442864955	0.2529187844	4.9067069513
C	-0.627650281	0.566245739	3.008632359	C	-0.5610039655	0.4940547447	3.0231806319
H	-0.013651877	1.449823575	3.146575013	H	0.1359130886	1.3115093166	3.1757221717
N	-1.099696674	1.516636927	-0.607879347	N	-1.0780319309	1.3791168830	-0.5946049558
C	-0.687180678	2.803230658	-0.441085034	C	-0.6557041121	2.6893361916	-0.4238517422
C	-2.297080304	1.291439530	-1.138137030	C	-2.2956334239	1.1667308862	-1.1326707396
C	0.611781844	3.020459922	0.129537803	C	0.6126116500	2.9009859506	0.1288154174
C	-1.482421640	3.907547461	-0.810037117	C	-1.4816115730	3.7904033830	-0.8042568551
C	-3.156290630	2.331188637	-1.535666031	C	-3.1459618183	2.1897960109	-1.5239864497
H	-2.587879459	0.247044228	-1.256204161	H	-2.5945991925	0.1248095202	-1.2568229190
C	1.079180276	4.336533065	0.323282546	C	1.1104387553	4.2236002626	0.3338686874
C	-0.982828171	5.236153736	-0.604920968	C	-0.9665952935	5.1195525205	-0.5940261384
C	-2.750131942	3.641534004	-1.371158792	C	-2.7322415808	3.5314248022	-1.3558408267
H	-4.123714415	2.085067552	-1.963858675	H	-4.1132032175	1.9403794168	-1.9511244028
C	2.550706626	2.103012982	1.002419880	C	2.5829850322	1.9824200269	1.0142808819
C	2.361089954	4.497665431	0.892016908	C	2.3742149941	4.3852964989	0.8925549410
C	0.249816911	5.442681589	-0.058099198	C	0.2663248883	5.3256320721	-0.0522636654
H	-1.611935241	6.075864097	-0.896371128	H	-1.5943078544	5.9630038030	-0.8824062037
H	-3.391728340	4.469974428	-1.667283612	H	-3.3755372457	4.3593990878	-1.6515253247
C	3.096315099	3.378458840	1.232394108	C	3.1247547813	3.2386111085	1.2407631660
H	3.105241643	1.200411527	1.261398648	H	3.1444669757	1.0850803700	1.2786942318
H	2.754770208	5.499609457	1.055637662	H	2.7698262049	5.3870995576	1.0559126301

H	0.628580306	6.451402718	0.099551769	H	0.6429566956	6.3370525891	0.1019225803
H	4.086001191	3.460255782	1.672466791	H	4.1151350198	3.3169092281	1.6803394133
N	1.346797550	1.925910438	0.468721129	N	1.3631056613	1.7869351643	0.4749205417

Ir_2PhPzol_Phenantro 5 NHCO-thiofene _NH cis C6 phenant _S cis O

Ir	-0.248838179	0.006419091	-0.008823888
N	-0.346636857	1.269239420	1.590431599
N	-1.289247295	2.241125205	1.497863399
N	-0.397355292	-1.257286521	-1.602903350
N	-1.323347167	-2.240476174	-1.471858710
C	0.239992193	1.404391463	2.781819448
H	1.032494055	0.726757115	3.080982187
C	-0.335242468	2.482647990	3.476580998
H	-0.078577294	2.844707428	4.462959021
C	-1.305759921	2.988570819	2.625076722
H	-1.992360532	3.817275420	2.747222696
C	-2.044765247	2.267870500	0.295771848
C	-3.013143920	3.242202039	0.063263193
H	-3.224982219	4.017538253	0.798639111
C	-3.712195032	3.206380284	-1.144948892
H	-4.473356238	3.956381383	-1.350528929
C	-3.428500830	2.206935741	-2.082370839
H	-3.974812879	2.178326911	-3.024395694
C	-2.448807872	1.242101071	-1.818688564
H	-2.248918745	0.472254311	-2.567788795
C	-1.721565189	1.244833882	-0.619581633
C	-1.685491342	-1.245818563	0.659470020
C	-2.367844262	-1.248506363	1.884526253
H	-2.148326227	-0.475823513	2.625231946
C	-3.327678248	-2.222450959	2.185417447
H	-3.838954786	-2.197754395	3.147022567
C	-3.636435125	-3.225812633	1.260233159
H	-4.382413715	-3.982571675	1.494685732
C	-2.982429920	-3.256636022	0.026937582
H	-3.214958185	-4.034340382	-0.699873874
C	-2.032356985	-2.273583891	-0.241915579
C	-1.374296849	-2.990815872	-2.595877810
H	-2.054315425	-3.828587373	-2.688209088
C	-0.444466290	-2.474674490	-3.485772056
H	-0.221755281	-2.835975946	-4.480659219
C	0.143743162	-1.387572471	-2.816174983
H	0.914621234	-0.699974792	-3.147461405
N	1.473119934	-1.117446970	0.697248226
C	2.671123903	-0.601905146	0.304928821
C	1.458667482	-2.205656651	1.458077040
C	2.645047360	0.605761211	-0.471389532
C	3.901302055	-1.192325226	0.660845126
C	2.636896303	-2.837708621	1.888963552
H	0.477813334	-2.583551422	1.748252867
C	3.857550214	1.197951456	-0.874889166
C	5.126422702	-0.586600152	0.196293139
C	3.859025514	-2.332555930	1.491720876
H	2.567854987	-3.712421348	2.528997225
C	1.389696968	2.263532321	-1.489478393
C	3.787148972	2.389231268	-1.629020700
C	5.094673138	0.569065117	-0.532753115
H	4.782334210	-2.800647309	1.823594189
C	2.549831861	2.920726387	-1.936320152
H	0.398457413	2.657607386	-1.715752212
H	4.704853798	2.872318458	-1.960314355
H	6.024752738	1.022325230	-0.874472243
H	2.451475633	3.834964752	-2.514479373

Triplet Ir_2PhPzol_Phenantro 5 NHCO-thiofene _NH cis C6 phenant _S cis O

Ir	-0.361933066	0.004334347	0.002634980
N	-0.416512641	1.239226385	1.623944353
N	-1.261932626	2.295261474	1.501856009
N	-0.453997213	-1.235081001	-1.613782114
N	-1.272166889	-2.307624927	-1.455524245
C	0.159408488	1.329854055	2.820194355
H	0.879445554	0.582267905	3.136270091
C	-0.325564025	2.467537192	3.494617577
H	-0.052811698	2.811585825	4.482904793
C	-1.225514471	3.055707909	2.624614035
H	-1.830143961	3.948233529	2.727064716
C	-1.962378045	2.388469128	0.282583967
C	-2.845845945	3.426926040	0.013001366
H	-3.039276557	4.214791162	0.738283485
C	-3.484286804	3.441874700	-1.229468905
H	-4.176343356	4.248278688	-1.462411078
C	-3.236820691	2.433738614	-2.176207005
H	-3.743946700	2.461490749	-3.138461512
C	-2.347143762	1.403961083	-1.885616203
H	-2.161703215	0.628521684	-2.629603002
C	-1.692139959	1.339327550	-0.639280787
C	-1.654006353	-1.340976147	0.690264751
C	-2.277260269	-1.402875488	1.953752233
H	-2.086327412	-0.616382939	2.684750342
C	-3.141151597	-2.443951802	2.277569771
H	-3.623053693	-2.470067280	3.252725795
C	-3.395312089	-3.466521206	1.347795855
H	-4.067175578	-4.281983813	1.606959966
C	-2.790835870	-3.453604850	0.088427244
H	-2.990722479	-4.251810363	-0.623758832
C	-1.932945904	-2.403231421	-0.215066671
C	-1.257093841	-3.076160558	-2.573466758
H	-1.845404493	-3.982084693	-2.648934066
C	-0.399741975	-2.476330304	-3.477495989
H	-0.152317359	-2.822568893	-4.471652506
C	0.083063327	-1.323234723	-2.828055708
H	0.776277015	-0.563829153	-3.174391252
N	1.351450167	-1.106600038	0.705441698
C	2.567757327	-0.582947689	0.292044336
C	1.359392828	-2.202649371	1.492853864
C	2.540756463	0.591751657	-0.467918232
C	3.802592712	-1.202545767	0.656125653
C	2.521388014	-2.830193642	1.905543838
H	0.385176189	-2.581000815	1.805474737
C	3.751844264	1.203564902	-0.912077598
C	5.020028417	-0.587418810	0.164263676
C	3.771350401	-2.324534658	1.476360158
H	2.454081989	-3.704581010	2.546536399
C	1.273403268	2.273829023	-1.498681527
C	3.679362885	2.372642603	-1.662272005
C	4.988434653	0.560226297	-0.572379441
H	4.697180618	-2.802770694	1.787940389
C	2.413693779	2.918881119	-1.962119566
H	0.285041491	2.678094424	-1.722656830
H	4.594452774	2.850364793	-2.010049817
H	5.921518090	1.003088287	-0.922889008
H	2.307587869	3.829493409	-2.544547173

N	1.432849821	1.140782750	-0.780083977
N	6.369374275	-1.162024963	0.551017006
C	6.758229533	-2.404225711	0.082807448
H	7.107067119	-0.508776527	0.798661984
O	6.009061192	-3.129317512	-0.565967709
C	8.131059179	-2.801814757	0.435374195
C	9.033060212	-2.249459907	1.323739220
S	8.778949121	-4.207586220	-0.331876408
C	10.255041837	-2.967932338	1.371358998
H	8.828215747	-1.377824829	1.942105835
C	10.253200963	-4.050746088	0.519450276
H	11.095998692	-2.704083397	2.006355474
H	11.050407112	-4.766960506	0.351620782

Ir_2PhPzol_Phenantro_NHCO_bis-thiof_Hc6_ScO_StS_EM60_D95d_M06_ACN

Ir	1.692604915	-0.001420751	0.027140690
N	2.187523500	-1.218076702	1.587584630
N	3.397222746	-1.824530525	1.482793256
N	1.432744745	1.297179188	-1.524527221
N	1.985820935	2.523367154	-1.345599402
C	1.669860048	-1.577065988	2.764250301
H	0.696994681	-1.206077206	3.068570926
C	2.562182415	-2.429745528	3.437303625
H	2.432079975	-2.887886745	4.408459520
C	3.650565476	-2.561681785	2.588167122
H	4.570916330	-3.121887742	2.697655575
C	4.127840952	-1.562625337	0.293513909
C	5.362816669	-2.158696380	0.045826343
H	5.813286080	-2.848706182	0.758623941
C	6.017866241	-1.852903132	-1.148935137
H	6.983514440	-2.305279454	-1.365723390
C	5.427978962	-0.968200705	-2.058497360
H	5.940068882	-0.728955974	-2.989732302
C	4.184861018	-0.387057086	-1.780701713
H	3.748106359	0.300902027	-2.508533720
C	3.492564897	-0.670137463	-0.594681569
C	2.636608769	1.626378467	0.760291542
C	3.271049099	1.808358374	1.997571538
H	3.310111698	0.980826074	2.709953983
C	3.857878491	3.030864600	2.346335174
H	4.341973171	3.140219345	3.316080414
C	3.828877470	4.112184537	1.458640840
H	4.285126949	5.062040851	1.730171576
C	3.209500148	3.971712475	0.215173076
H	3.180160736	4.808062599	-0.482417971
C	2.635187100	2.742494354	-0.101892403
C	1.799568838	3.288012937	-2.445431756
H	2.170137466	4.304203660	-2.499205258
C	1.097153431	2.528431930	-3.368781311
H	0.777691901	2.831745604	-4.356646055
C	0.889873771	1.286372426	-2.743919751
H	0.388789035	0.397112058	-3.111104377
N	-0.309883871	0.487087001	0.720321945
C	-1.275410863	-0.358395419	0.264095751
C	-0.658504442	1.497999815	1.507364581
C	-0.850344772	-1.472389458	-0.535611196
C	-2.639481426	-0.186599893	0.577300516
C	-1.988327835	1.720047192	1.901907680
H	0.146964444	2.149493841	1.847872885
C	-1.805179250	-2.400254775	-0.995375223
C	-3.601335160	-1.120482625	0.042754257
C	-2.980339157	0.879789372	1.436913828

N	1.305202961	1.143650939	-0.771960591
N	6.272926446	-1.160728948	0.513489129
C	6.693510919	-2.369062277	0.007526576
H	6.985109129	-0.522792299	0.855201512
O	5.991908810	-3.071977112	-0.717148373
C	8.054463358	-2.776463406	0.407716146
C	8.910307085	-2.267806171	1.364148180
S	8.749263174	-4.135037323	-0.402248141
C	10.136108489	-2.980315557	1.429856863
H	8.670566803	-1.430634511	2.016818753
C	10.183140930	-4.015851311	0.522904797
H	10.944894281	-2.745131641	2.116081322
H	10.992997723	-4.717621761	0.354497786

Triplet Ir_2PhPzol_Phenantro_NHCO_bis-thiof_Hc6_ScO_ScisS_EM60_D95d_M06_ACN_3plt

Ir	2.870391637	0.065996295	0.007553522
N	3.494520996	-1.203997714	1.476401588
N	4.749671985	-1.695202411	1.317020016
N	2.472746908	1.435877347	-1.450481208
N	2.922313525	2.690954873	-1.197390688
C	3.029171694	-1.685158173	2.631106597
H	2.033262931	-1.421393275	2.970685900
C	4.002204261	-2.501183382	3.234157816
H	3.927964967	-3.033538430	4.172802741
C	5.083455335	-2.480980576	2.366146932
H	6.049817047	-2.966083629	2.426670628
C	5.434949985	-1.292108267	0.140282754
C	6.712300205	-1.760905853	-0.160348658
H	7.232348587	-2.454415716	0.499742929
C	7.318508852	-1.321435625	-1.339089268
H	8.315734595	-1.672863764	-1.596331514
C	6.639448381	-0.433409861	-2.180697832
H	7.113262790	-0.089880678	-3.099490652
C	5.355852226	0.018015230	-1.850751790
H	4.849344745	0.711596796	-2.526182938
C	4.710333148	-0.401436792	-0.678738618
C	3.684331563	1.718166108	0.836314820
C	4.322032894	1.873436026	2.075592131
H	4.443606183	1.007735836	2.731063444
C	4.808429592	3.116671178	2.497879041
H	5.298003913	3.204058491	3.467109389
C	4.672054561	4.246900377	1.684173433
H	5.050213634	5.212910131	2.012760697
C	4.045405307	4.134756215	0.441448787
H	3.932407753	5.009236885	-0.198517822
C	3.572603756	2.883851747	0.050201225
C	2.651898565	3.506553524	-2.241819594
H	2.933566891	4.552218363	-2.232747234
C	2.000390912	2.750823467	-3.204791356
H	1.638521791	3.088986861	-4.166369180
C	1.911020437	1.457509573	-2.661113741
H	1.481050382	0.554056924	-3.080211180
N	0.847783255	0.330211899	0.759135524
C	-0.051416025	-0.562392575	0.258468973
C	0.432202766	1.247598499	1.624568053
C	0.453603204	-1.579018132	-0.620600181
C	-1.418862647	-0.531830906	0.603148290
C	-0.900915374	1.320209740	2.059753633
H	1.186202326	1.941659808	1.997404050
C	-0.426523678	-2.555541115	-1.127315726
C	-2.309268531	-1.506899756	0.017023485
C	-1.827665254	0.432442221	1.549729312

H	-2.214763632	2.548793765	2.566339658	H	-1.182139114	2.072853539	2.790524604
C	0.889698983	-2.628676536	-1.533466711	C	2.268550766	-2.510512815	-1.716454113
C	-1.343322392	-3.491500975	-1.762760591	C	0.114347135	-3.549120058	-1.973008273
C	-3.187796572	-2.191869697	-0.698846938	C	-1.814383579	-2.488939154	-0.799432441
H	-4.014069243	1.028953961	1.738091378	H	-2.861321385	0.467547533	1.882275629
C	0.007065048	-3.604257169	-2.030131591	C	1.463679643	-3.524714450	-2.265858019
H	1.960460235	-2.687267067	-1.731139170	H	3.336464106	-2.462158392	-1.931326495
H	-2.053981545	-4.227222210	-2.135706191	H	-0.536595158	-4.318517379	-2.385048159
H	-3.919219644	-2.899139021	-1.089229654	H	-2.487793190	-3.231036957	-1.228059448
H	0.403504538	-4.428254817	-2.616307897	H	1.918422064	-4.270456655	-2.911563463
N	0.476861568	-1.593418422	-0.809717084	N	1.780882739	-1.565543134	-0.919580968
N	-4.974864117	-0.955874007	0.337991567	N	-3.680595185	-1.491572670	0.341166307
C	-5.693657301	0.131636541	-0.128152080	C	-4.500133588	-0.404413719	0.034341451
H	-5.494090915	-1.811339186	0.512038231	H	-4.126843666	-2.404566064	0.344120285
O	-5.159803808	1.081829857	-0.695707799	O	-4.049253640	0.663108083	-0.394404171
C	-7.140383597	0.081811924	0.119963352	C	-5.916120436	-0.602257294	0.274867624
C	-7.912667159	-0.789943689	0.862375348	C	-6.620931919	-1.703913092	0.849713287
S	-8.103578549	1.325674692	-0.601670330	S	-6.983342203	0.694381975	-0.203189192
C	-9.284283452	-0.454665664	0.841183460	C	-7.973935283	-1.515878114	0.891275651
H	-7.517449019	-1.633514447	1.424628674	H	-6.129478010	-2.594479741	1.234800464
C	-9.551687286	0.674179587	0.082439314	C	-8.393775756	-0.239929450	0.346619860
H	-10.053435856	-1.017096671	1.367079466	H	-8.679879196	-2.237086130	1.294879907
C	-10.833877058	1.302038493	-0.163625683	C	-9.678430049	0.235379455	0.247899979
C	-11.108508347	2.429444227	-0.913563991	C	-10.895883541	-0.418969704	0.658226295
S	-12.291408837	0.648984345	0.516500229	S	-10.046359792	1.820567547	-0.438666630
C	-12.489637978	2.758916007	-0.935019424	C	-12.026042997	0.349664176	0.414718963
H	-10.340265970	3.001460879	-1.431811533	H	-10.906433919	-1.407821632	1.108637610
C	-13.249553308	1.879028497	-0.201317312	C	-11.742521281	1.585977706	-0.173652567
H	-12.906584087	3.608622767	-1.468438486	H	-13.039078252	0.035778508	0.651669738
H	-14.322188386	1.884429081	-0.041598750	H	-12.443457793	2.362022079	-0.461573168

Table S6. Vibrational frequencies (cm^{-1}) for **1, 2** and **3** in the S_0 and T_1 states computed at the D95(d);D95(2d)/SDD09/M06/ACN level of theory.

Ir_2PhPzol_Phenantro Singlet			Ir_2PhPzol_Phenantro Triplet		
26	31	42	24	33	34
42	47	49	36	43	47
81	93	103	78	91	99
154	157	164	137	156	164
172	173	190	165	167	188
196	202	226	192	197	213
230	232	259	224	234	254
278	291	296	267	270	289
306	314	320	296	301	314
334	410	416	328	400	402
428	431	442	408	416	432
456	458	490	433	454	457
510	510	520	506	507	510
526	535	542	511	519	520
549	558	611	524	550	601
612	622	642	604	605	623
653	656	665	655	656	657
665	699	700	658	671	701
724	728	733	702	715	730
735	743	747	732	740	743
747	757	757	744	754	754
779	805	842	757	757	787
842	844	861	823	860	860
864	865	876	865	867	877
884	884	914	888	896	898
914	918	942	899	899	909
942	963	964	910	944	944
964	967	984	952	956	957

985	985	999	962	979	984
1003	1029	1032	994	994	998
1042	1046	1049	1032	1033	1044
1068	1070	1079	1053	1066	1068
1079	1085	1107	1071	1074	1082
1114	1124	1127	1099	1117	1121
1142	1147	1151	1127	1142	1148
1152	1153	1153	1151	1156	1157
1217	1220	1225	1188	1200	1215
1238	1243	1261	1219	1219	1246
1262	1276	1320	1248	1255	1259
1322	1359	1359	1319	1326	1331
1360	1369	1384	1361	1363	1386
1384	1390	1427	1388	1407	1409
1457	1458	1458	1428	1440	1448
1459	1463	1464	1451	1461	1462
1471	1472	1503	1466	1466	1483
1520	1523	1538	1499	1515	1521
1556	1558	1570	1523	1557	1563
1625	1625	1646	1567	1599	1599
1648	1649	1653	1603	1617	1618
1668	1690	3140	1639	1662	3156
3140	3171	3171	3156	3161	3166
3171	3171	3176	3166	3174	3174
3176	3179	3188	3179	3188	3188
3188	3194	3195	3195	3195	3207
3195	3221	3221	3207	3210	3210
3244	3244	3263	3243	3243	3264
3263	3282	3282	3264	3284	3284
Ir_2PhPzol_Phenantro_NHCO_Hc6_ScO Singlet			Ir_2PhPzol_Phenantro_NHCO_Hc6_ScO Triplet		

11	22	25	14	22	25
34	37	38	33	36	37
41	43	48	40	44	49
69	89	90	66	89	93
100	115	133	102	119	134
153	164	166	137	157	165
173	175	188	168	173	185
192	197	206	188	196	209
224	230	246	212	223	247
256	271	293	251	264	270
295	302	305	290	295	299
313	321	332	308	315	327
343	410	415	332	398	407
424	429	440	408	415	432
455	456	461	434	441	452
465	478	498	455	461	471
516	520	533	507	509	517
536	541	543	519	521	530
565	567	606	547	567	602
610	611	642	602	603	621
646	652	655	629	655	656
664	665	665	656	658	660
680	698	700	673	685	701
722	724	733	702	717	729
737	741	746	730	740	741
747	748	755	745	753	753
757	758	802	756	757	758
811	826	838	760	783	814
842	842	849	849	857	857
860	862	865	858	865	867
873	884	884	867	876	895

913	913	914	897	898	899
918	924	939	908	910	915
940	962	963	926	943	948
964	966	983	951	957	958
985	995	1000	962	980	993
1028	1031	1039	994	997	1032
1043	1045	1047	1033	1040	1043
1067	1070	1074	1053	1062	1066
1076	1079	1082	1067	1069	1071
1084	1108	1118	1078	1081	1103
1119	1124	1139	1108	1118	1125
1149	1150	1151	1146	1148	1151
1152	1166	1202	1154	1155	1170
1214	1218	1232	1200	1209	1209
1236	1255	1258	1215	1236	1246
1270	1284	1307	1248	1257	1283
1318	1320	1355	1312	1316	1326
1358	1359	1369	1330	1360	1362
1380	1383	1383	1375	1380	1385
1391	1414	1455	1387	1419	1428
1457	1458	1462	1438	1442	1452
1463	1466	1470	1461	1462	1465
1471	1472	1485	1466	1471	1478
1516	1519	1522	1498	1502	1514
1543	1556	1558	1519	1530	1557
1574	1576	1624	1563	1568	1577
1625	1646	1649	1599	1599	1604
1650	1653	1668	1616	1621	1638
1692	1759	3138	1667	1754	3159
3140	3171	3171	3160	3165	3166
3174	3174	3176	3167	3176	3187

3176	3179	3190	3187	3193	3193
3195	3195	3197	3194	3195	3206
3210	3219	3220	3207	3213	3214
3223	3243	3244	3216	3241	3242
3246	3259	3261	3244	3261	3262
3282	3282	3596	3284	3286	3601

Ir_2PhPzol_Phenantro_NHCO_bis-thiof_Hc6_ScO_StS Singlet			Ir_2PhPzol_Phenantro_NHCO_bis-thiof_Hc6_ScO_StS Triplet		
7	11	13	8	12	17
20	28	32	26	29	30
35	37	42	33	38	42
46	54	70	45	55	71
81	87	92	84	90	93
101	114	144	100	116	134
153	163	166	145	153	163
169	174	178	165	176	180
190	194	199	187	194	197
218	225	229	213	223	227
256	270	278	252	265	269
290	295	304	279	289	295
306	310	314	299	305	313
331	337	344	328	333	335
359	409	415	359	398	408
428	440	446	416	425	433
455	456	461	434	443	454
464	493	498	456	466	492
516	520	520	507	509	517
534	537	542	520	521	521
543	566	567	533	548	568
600	603	610	600	601	602
611	630	643	603	620	630

650	652	655	633	655	656
664	665	676	656	657	671
696	697	698	681	694	696
700	723	733	701	702	729
736	740	742	731	739	740
746	747	748	743	748	751
751	755	757	752	753	755
799	803	811	756	759	783
826	827	837	804	815	827
841	842	849	848	854	857
860	862	870	858	863	865
883	883	893	875	891	896
894	906	913	896	898	898
914	914	919	898	906	909
939	940	960	910	926	944
963	964	967	950	952	955
982	985	995	957	963	980
1001	1029	1032	993	994	997
1038	1043	1045	1033	1034	1040
1046	1063	1066	1043	1053	1062
1069	1075	1076	1068	1069	1072
1077	1083	1085	1075	1076	1077
1106	1119	1122	1087	1106	1110
1125	1141	1149	1119	1125	1147
1150	1151	1153	1149	1151	1155
1165	1200	1209	1156	1172	1203
1214	1218	1228	1208	1211	1214
1237	1255	1257	1219	1237	1246
1267	1271	1278	1253	1256	1267
1306	1319	1320	1277	1313	1318
1336	1356	1358	1326	1330	1336

1360	1369	1383	1361	1362	1379
1384	1391	1399	1385	1387	1398
1414	1455	1457	1419	1428	1440
1458	1462	1463	1444	1452	1461
1466	1470	1471	1462	1465	1466
1479	1486	1504	1474	1486	1496
1515	1519	1522	1499	1508	1514
1543	1556	1559	1520	1531	1557
1562	1574	1607	1563	1563	1570
1624	1626	1646	1599	1599	1606
1649	1650	1653	1609	1616	1622
1668	1691	1752	1638	1667	1748
3137	3138	3170	3157	3160	3165
3170	3173	3174	3167	3168	3178
3175	3176	3179	3185	3187	3188
3185	3188	3191	3189	3194	3194
3195	3195	3202	3194	3205	3206
3210	3216	3223	3207	3213	3215
3224	3243	3244	3215	3241	3242
3248	3260	3262	3248	3263	3264
3280	3281	3595	3285	3286	3601

Table S7. Selected crystal structure data for $[Ir(ppz)_2(phen)][PF_6]$ **(1)**

	$[Ir(ppz)_2(phen)][PF_6] \cdot 3CH_2Cl_2$
formula	$C_{33}H_{28}IrN_6F_6PCl_6$
habit	yellow, prism
dimensions/ mm	0.02 x 0.11 x 0.20
temperature/ K	90
cryst syst	monoclinic
space group	$P\ 2_1/c$
a/ Å	14.953(5)
b/ Å	22.622(7)
c/ Å	18.916(6)
α/ °	90
β/ °	95.823(6)
γ/ °	90
V/ Å^3	6366(6)
Z	4
μ/ cm^{-1}	45.53
$R[F^2 > 2\sigma(F^2)]^a$	0.097
$R_w\,(F^2)^a$	0.149
goodness of fit	1.24

[a]Function minimized by $R = \Sigma \|\|F_o| - |F_c\|\| / \Sigma|F_o|$, $R_w = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

Table S8. Selected crystal structure data for $[Ir(ppz)_2(phen\text{-}T)][PF_6]$ **(2)**

	$[Ir(ppz)_2(phen\text{-}T)][PF_6] \cdot 0.5CH_2Cl_2 \cdot 0.2C_6H_{14}$
formula	$C_{36.75}H_{28.75}ON_7F_6PIrSCl$
habit	yellow, prism
dimensions/ mm	0.07 x 0.13 x 0.22
temperature/ K	100
cryst syst	monoclinic
space group	*C* 2/c
a/ Å	26.311(3)
b/ Å	16.555(2)
c/ Å	16.918(2)
α/ °	90
β/ °	96.839(7)
γ/ °	90
V/ Å^3	7316(2)
Z	8
μ/ cm^{-1}	38.97
$R[F^2 > 2\sigma(F^2)]^a$	0.081
$R_w(F^2)^a$	0.130
goodness of fit	1.09

[a]Function minimized by $R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$, $R_w = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

Table S9. Selected crystal structure data for the cation of **3** as a BF_4 salt $[Ir(ppz)_2(phen\text{-}bT)][BF_4]$ (**3-BF_4**)

	$[Ir(ppz)_2(phen\text{-}bT)][PF_6] \cdot 2CH_2Cl_2$
formula	$C_{41}H_{31}O_{0.25}N_7F_4BIrS_2Cl_2$
habit	yellow, irregular
dimensions/ mm	0.04 x 0.05 x 0.07
temperature/ K	90
cryst syst	monoclinic
space group	*C* 2/c
a/ Å	32.990(8)
b/ Å	16.515(4)
c/ Å	15.788(7)
α/ °	90
β/ °	99.572(5)
γ/ °	90
V/ $Å^3$	8482(3)
Z	8
μ/ cm^{-1}	35.37
$R[F^2 > 2\sigma(F^2)]^a$	0.098
$R_w(F^2)^a$	0.129
goodness of fit	1.05

[a]Function minimized by $R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$, $R_w = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

^{1}H and ^{13}C NMR Data

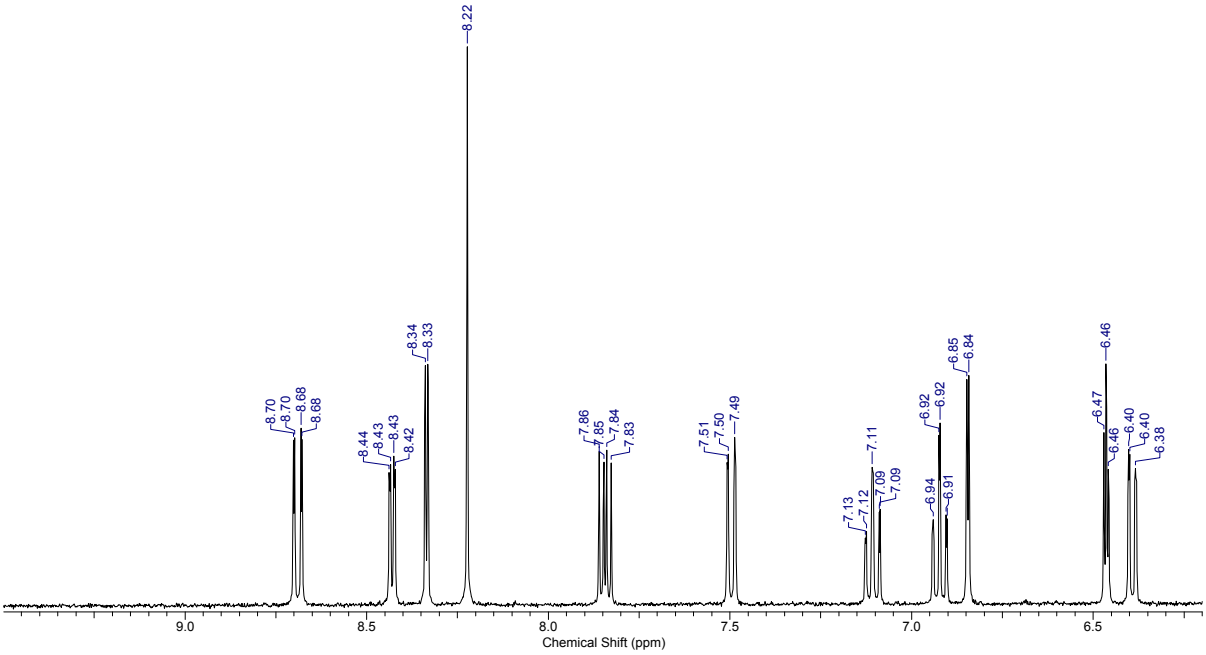


Figure S10. ^{1}H NMR spectrum of complex **1** in CD_3CN.

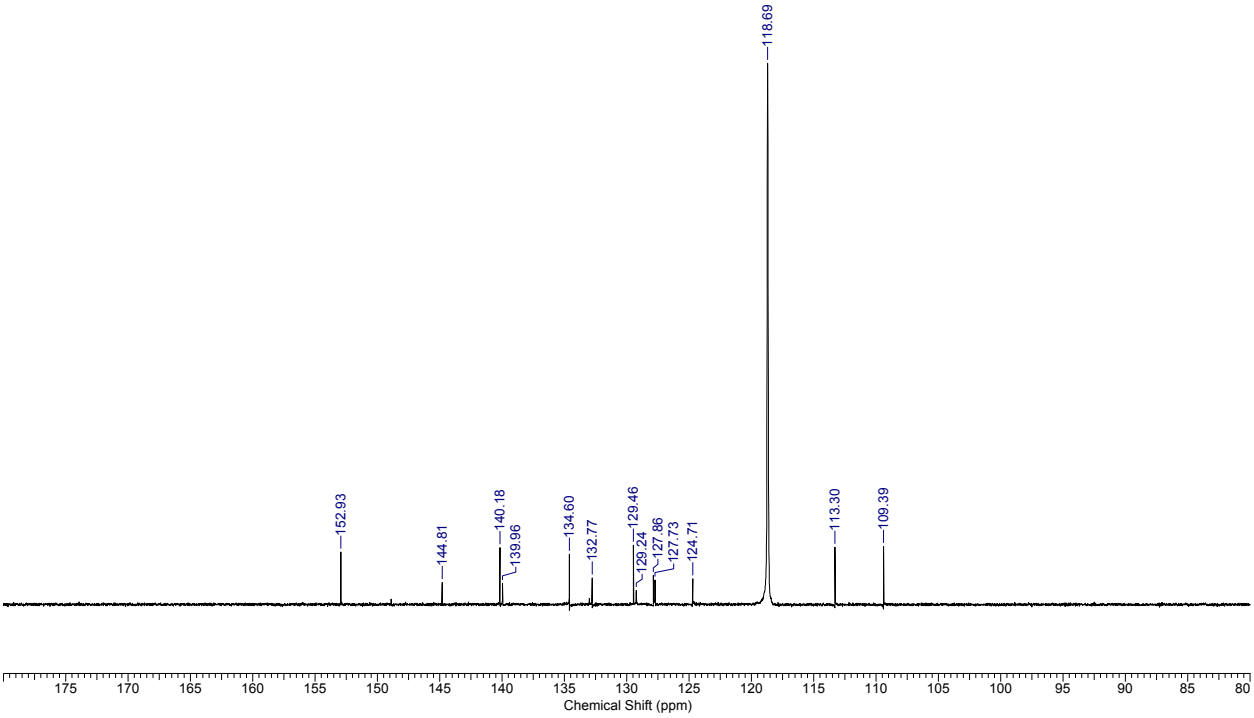


Figure S11. ^{13}C NMR spectrum of complex **1** in CD_3CN.

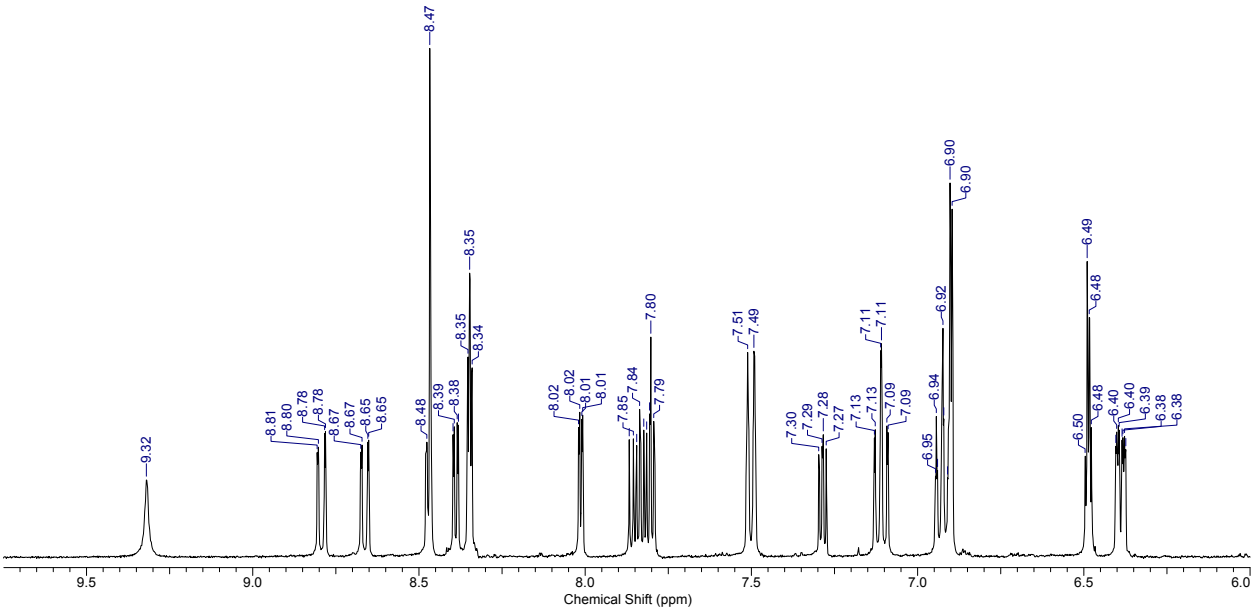


Figure S12. ^{1}H NMR spectrum of complex **2** in CD_3CN.

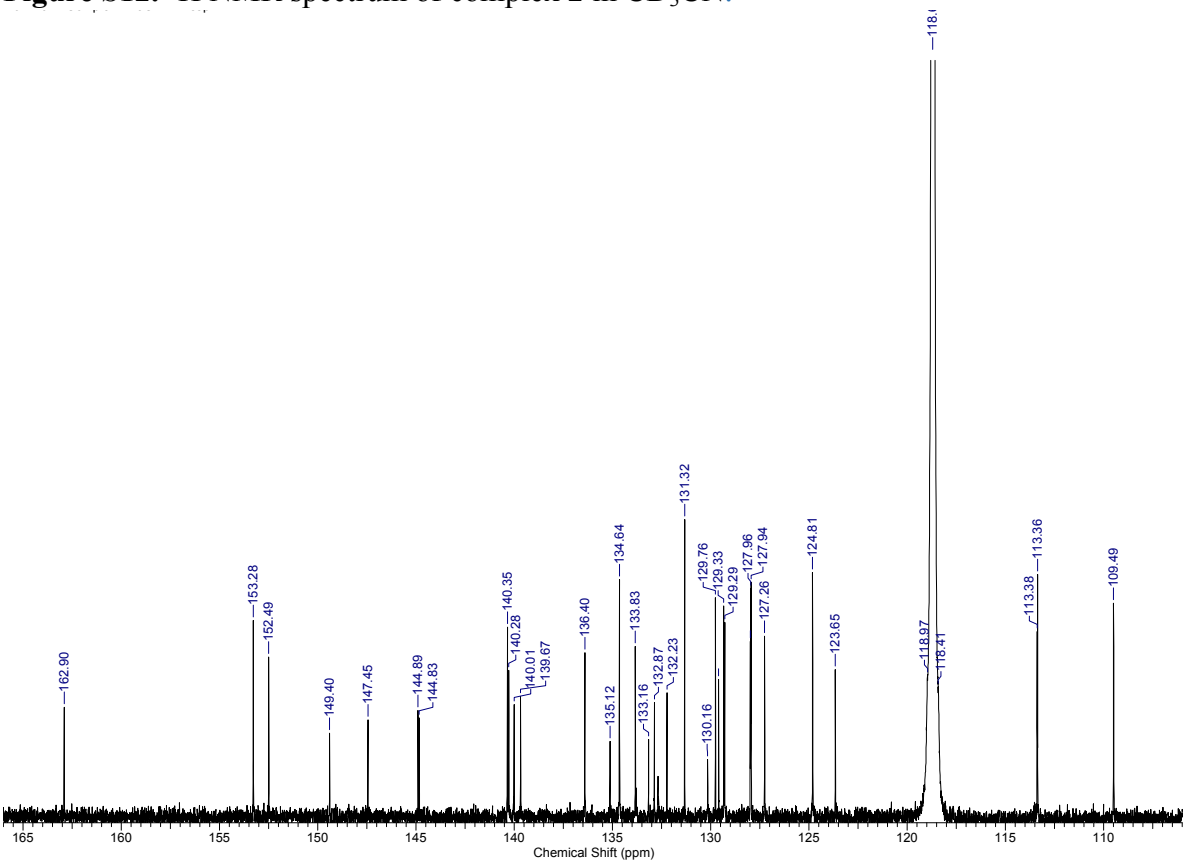


Figure S13. ^{13}C NMR spectrum of complex **2** in CD_3CN.

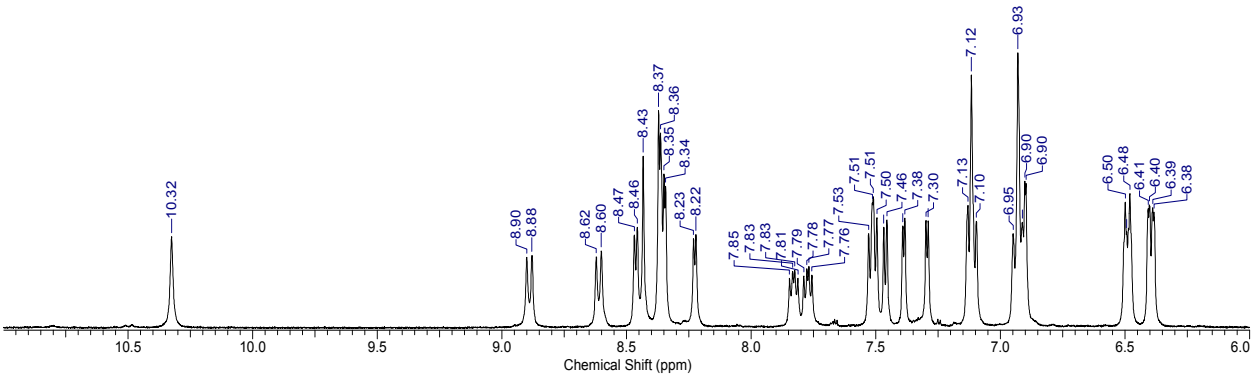


Figure S14. ^{1}H NMR spectrum of complex **3** in CD_3CN.

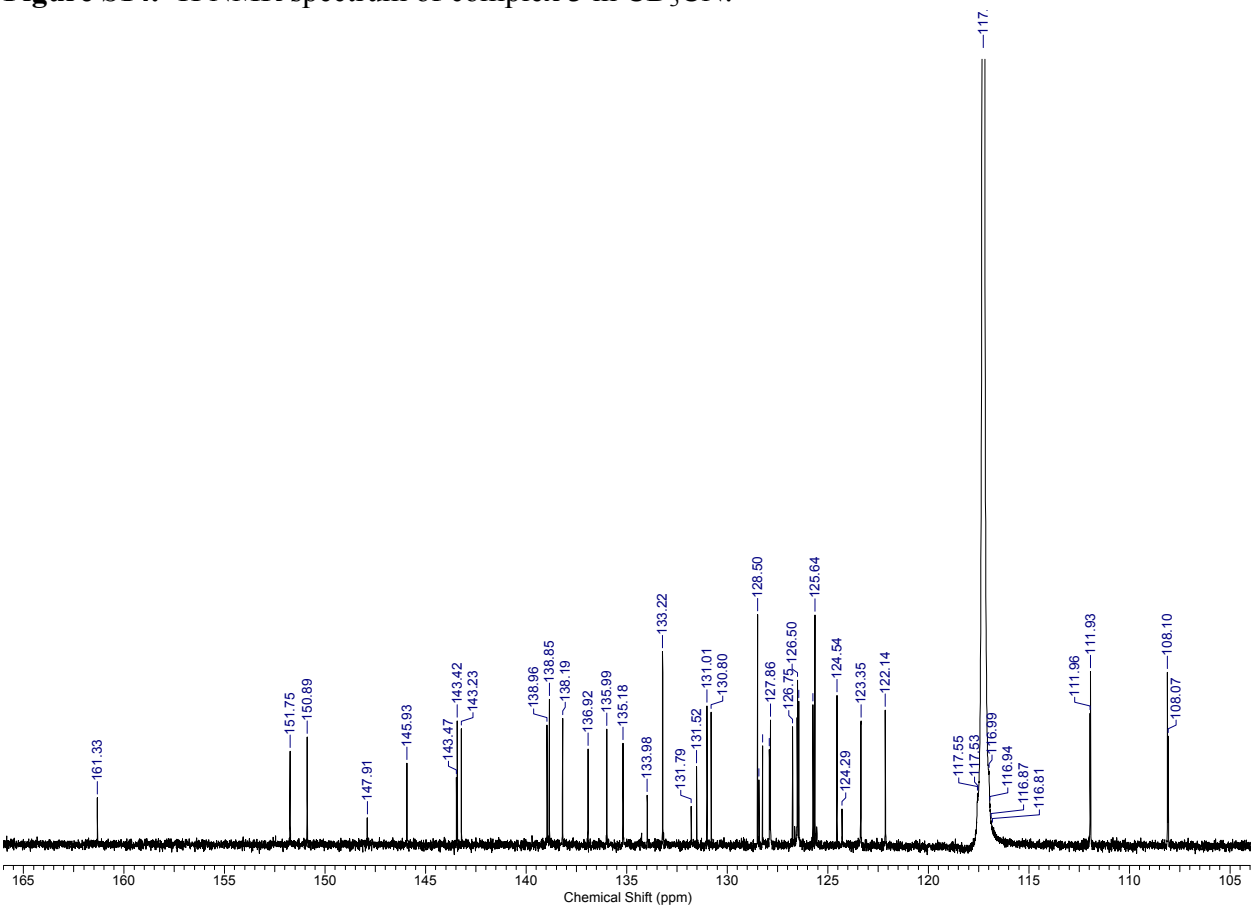


Figure S15. ^{13}C NMR spectrum of complex **3** in CD_3CN.

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