

## Supporting Information

### **Organometallic Ir(III) complexes: post-synthetic modification, photophysical properties and binuclear complex construction**

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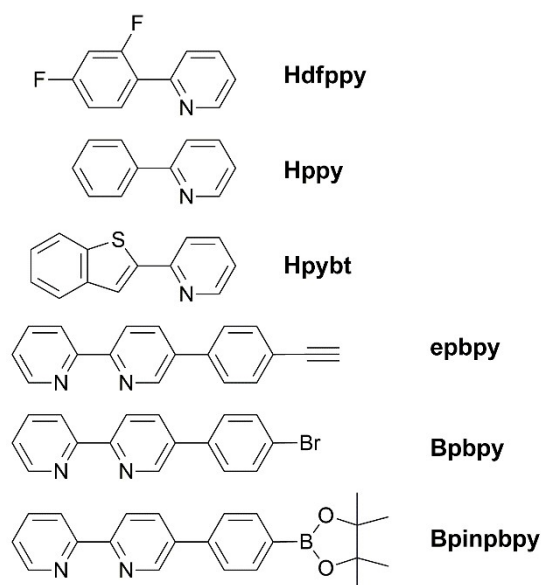
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## Content

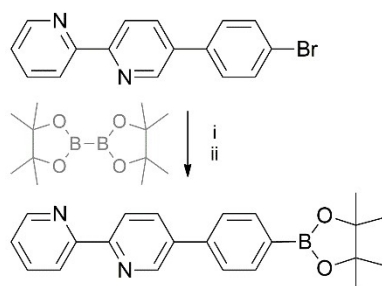
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**Scheme S1.** Abbreviations of C<sup>N</sup> and N<sup>N</sup> ligands.



**Scheme S2.** Synthesis of the boronic ether **Bpinpbpy**. *i* = KOAc, DMSO; *ii* = Pd(PPh<sub>3</sub>)<sub>4</sub>, 80°C, overnight.

### Synthesis of 5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2'-bipyridine, **Bpinpbpy**

5-(4-bromophenyl)-2,2'-bipyridine (**Bpbpy**) was synthesized according to the published procedure.<sup>1</sup> Bis(pinacolato)diboron was purchased from Aldrich/Merck and used without further purification. **Bpbpy** (500 mg, 1.61 mmol, 1 equiv.), bis(pinacolato)diboron (816 mg, 3.22 mmol, 2 equiv.) and KOAc (473 mg, 4.82 mmol, 3 equiv.) were mixed and dissolved in 30 ml of degassed DMSO. Then Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol. %, 93.1 mg, 0.08 mmol) was added, and the reaction mixture was stirring overnight at 80 °C. After cooling to room temperature the reaction mixture was diluted with water, and the product was extracted by EtOAc three times. EtOAc layer was washed twice with water and brine and dried over anhydrous MgSO<sub>4</sub>. The filtrate was evaporated, and the crude was washed with Et<sub>2</sub>O. The boronic ether **Bpinpbpy** was dried under reduced pressure resulting in a pale yellow crystalline precipitate. Yield: 486 mg (84 %). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO, 298 K): δ 9.01 (d, *J* = 1.9 Hz, 1H, pyridine ring), 8.75 – 8.66 (m, 1H, pyridine ring), 8.58 (d, *J* =

8.3 Hz, 1H, pyridine ring), 8.53 (d,  $J = 8.0$  Hz, 1H, pyridine ring), 8.23 (dd,  $J = 8.3, 2.4$  Hz, 1H, pyridine ring), 7.98 – 7.87 (m, 1H, pyridine ring), 7.86 – 7.78 (m, 2H, phenyl ring), 7.82 (d,  $J = 8.3$  Hz, 2H, phenyl ring), 7.43 (ddd,  $J = 7.5, 4.8, 1.0$  Hz, 1H), 1.37 (s, 12H, CH<sub>3</sub>). HRMS (ESI/QTOF)  $m/z$ :  $[M+H]^+$  calculated for  $[C_{22}H_{24}BN_2O_2]^+$  359.1932, found 359.1939. Elem. anal. calculated for C<sub>22</sub>H<sub>23</sub>BN<sub>2</sub>O<sub>2</sub>: C 73.76; H 6.47; N 7.82. Found: C 73.54; H 6.45; N 7.86.

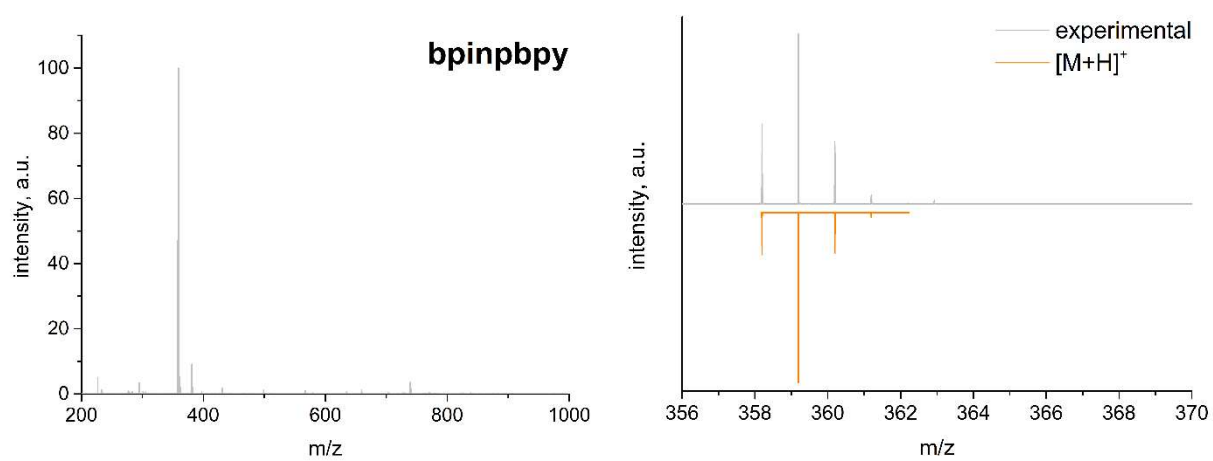
**Table S1.** Crystal data and structure refinement for **8**

Identification code	12309_vk281_sq
Empirical formula	C <sub>92</sub> H <sub>68</sub> F <sub>6</sub> Ir <sub>2</sub> N <sub>16</sub> P
Formula weight	1926.99
Temperature/K	99.99(13)
Crystal system	monoclinic
Space group	I2/a
$a/\text{\AA}$	42.9654(2)
$b/\text{\AA}$	33.9313(2)
$c/\text{\AA}$	15.77980(10)
$\alpha/^\circ$	90
$\beta/^\circ$	96.7680(10)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	22844.6(2)
$Z$	8
$\rho_{calc}$ g/cm <sup>3</sup>	1.121
$\mu/\text{mm}^{-1}$	4.999
F(000)	7640.0
Crystal size/mm <sup>3</sup>	0.2 × 0.16 × 0.1
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )
$2\theta$ range for data collection/ $^\circ$	4.142 to 140
Index ranges	$-51 \leq h \leq 52, -41 \leq k \leq 38, -19 \leq l \leq 19$
Reflections collected	119978
Independent reflections	21648 [ $R_{int} = 0.0495, R_{sigma} = 0.0292$ ]
Data/restraints/parameters	21648/3/1097
Goodness-of-fit on $F^2$	1.046
Final $R$ indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0344, wR_2 = 0.0947$
Final $R$ indexes [all data]	$R_1 = 0.0359, wR_2 = 0.0964$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	1.70/−1.60
CCDC Deposition Number	2224674

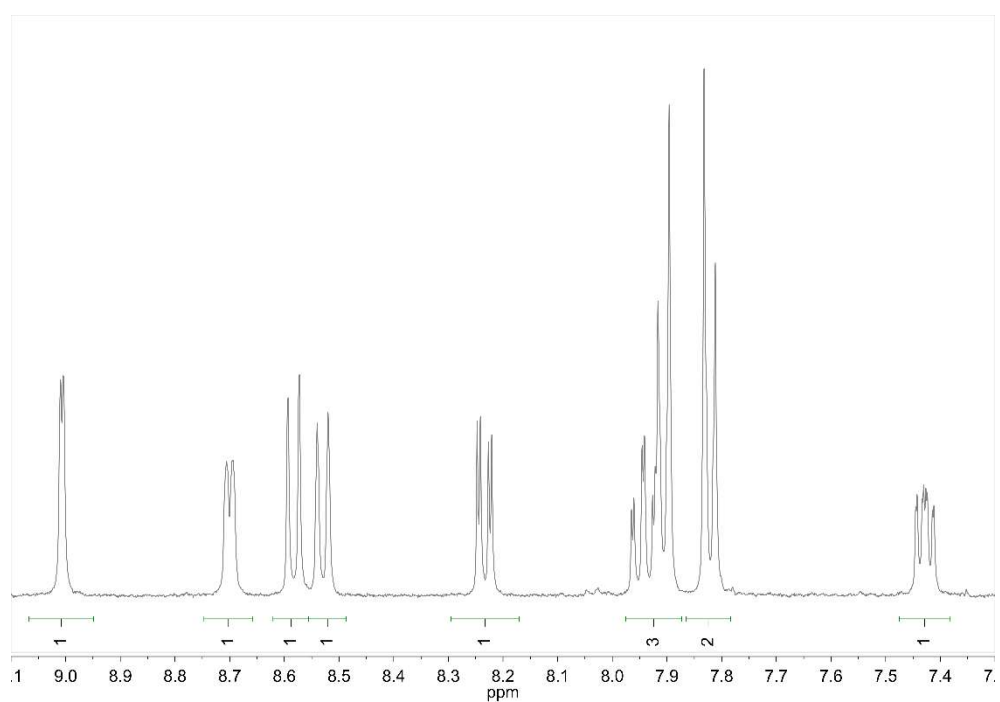
**Table S2.** Selected structural parameters for **8**

<b>Bond length, Å</b>	
Ir1–N44	2.058(3)
Ir1–C43	2.027(3)
Ir1–N3	2.134(2)
Ir1–N32	2.044(3)
Ir1–N2	2.136(2)
Ir1–C55	2.007(3)
<b>Angle, °</b>	
N2–Ir1–N44	91.5(1)
C55–Ir1–N44	81.0(1)
C43–Ir1–N44	95.0(1)
N3–Ir1–N44	97.4(1)
N2–Ir1–N32	93.2(1)
C55–Ir1–N32	94.8(1)
C43–Ir1–N32	80.4(1)
N3–Ir1–N32	87.6(1)
N44–Ir1–N32	173.8(1)
N2–Ir1–C43	173.3(1)
N3–Ir1–C55	169.4(1)

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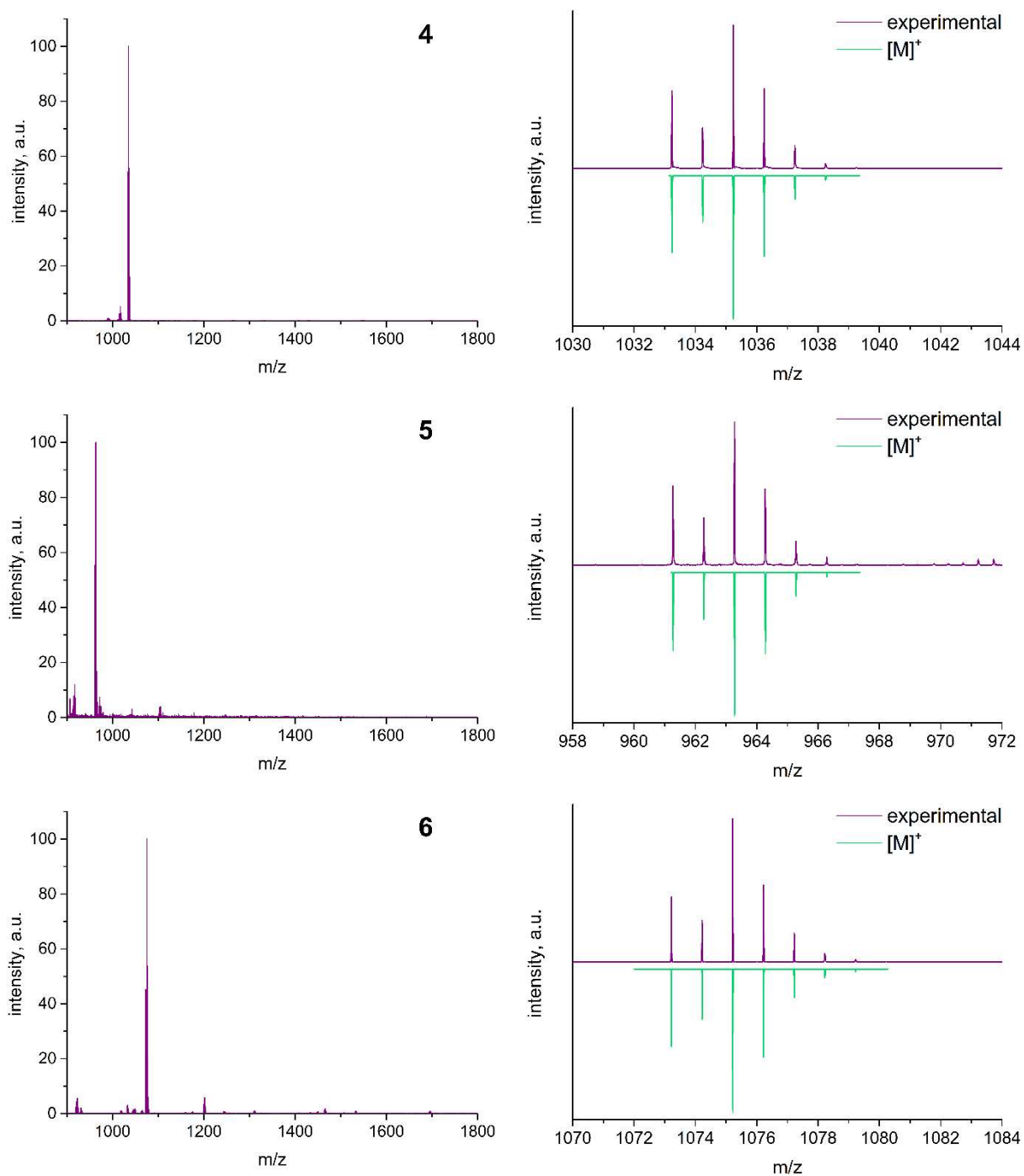


**Figure S1.** ESI<sup>+</sup> MS spectra of **Bpinbpy** with simulated isotope pattern of key signal.

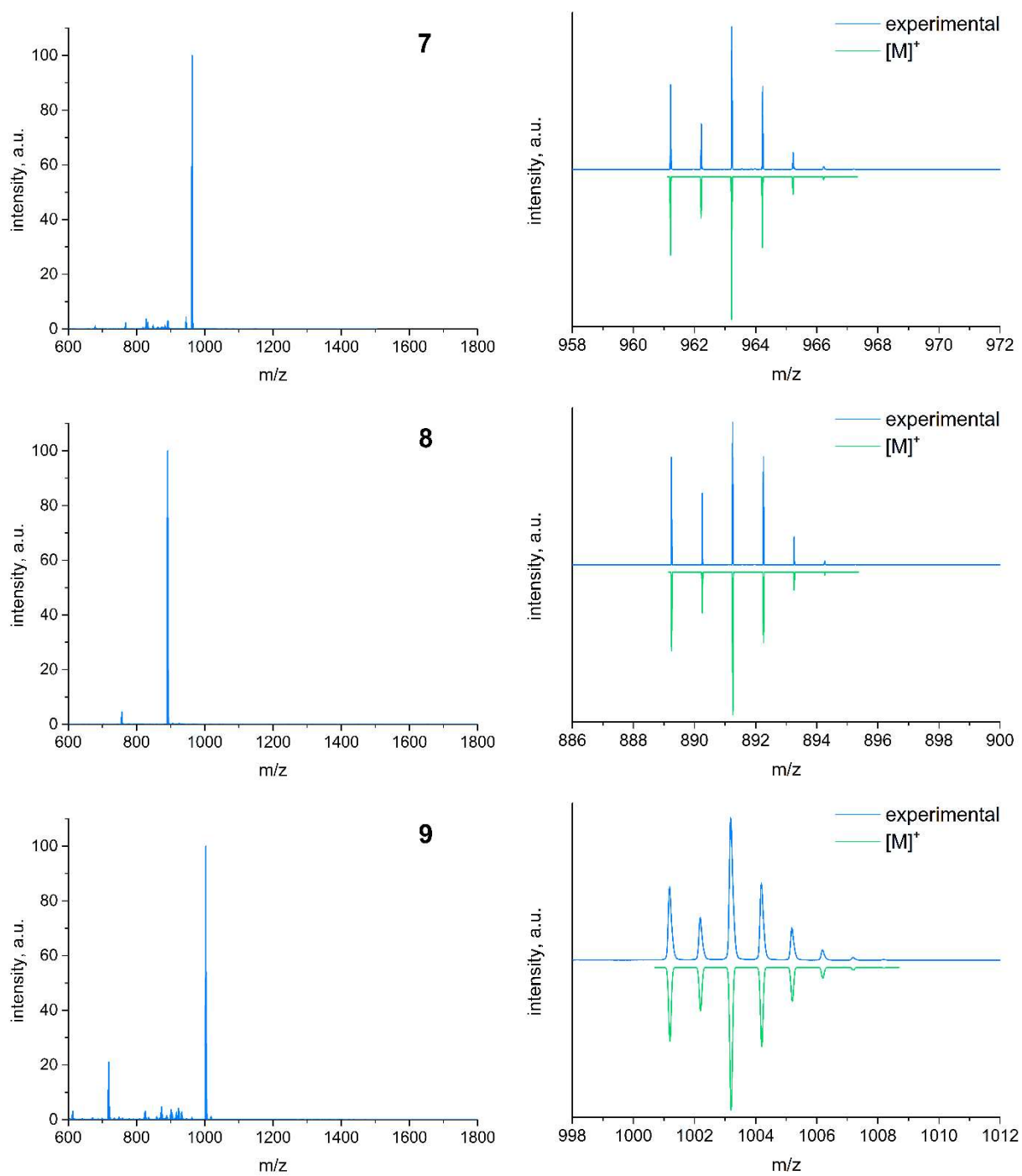


**Figure S2.** <sup>1</sup>H NMR spectra of **Bpinbpy**, aromatic range, acetone-d<sub>6</sub>, r.t.

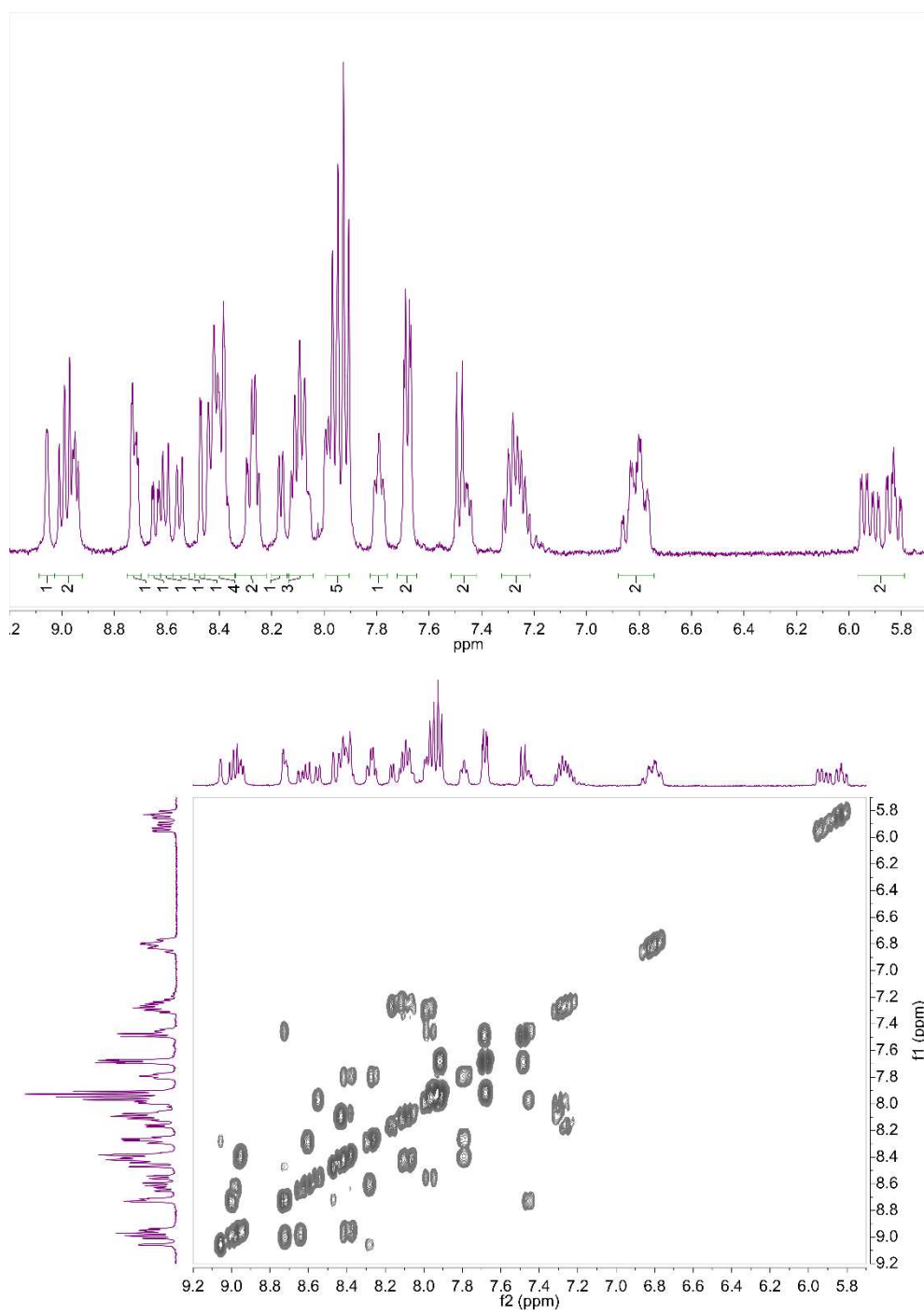




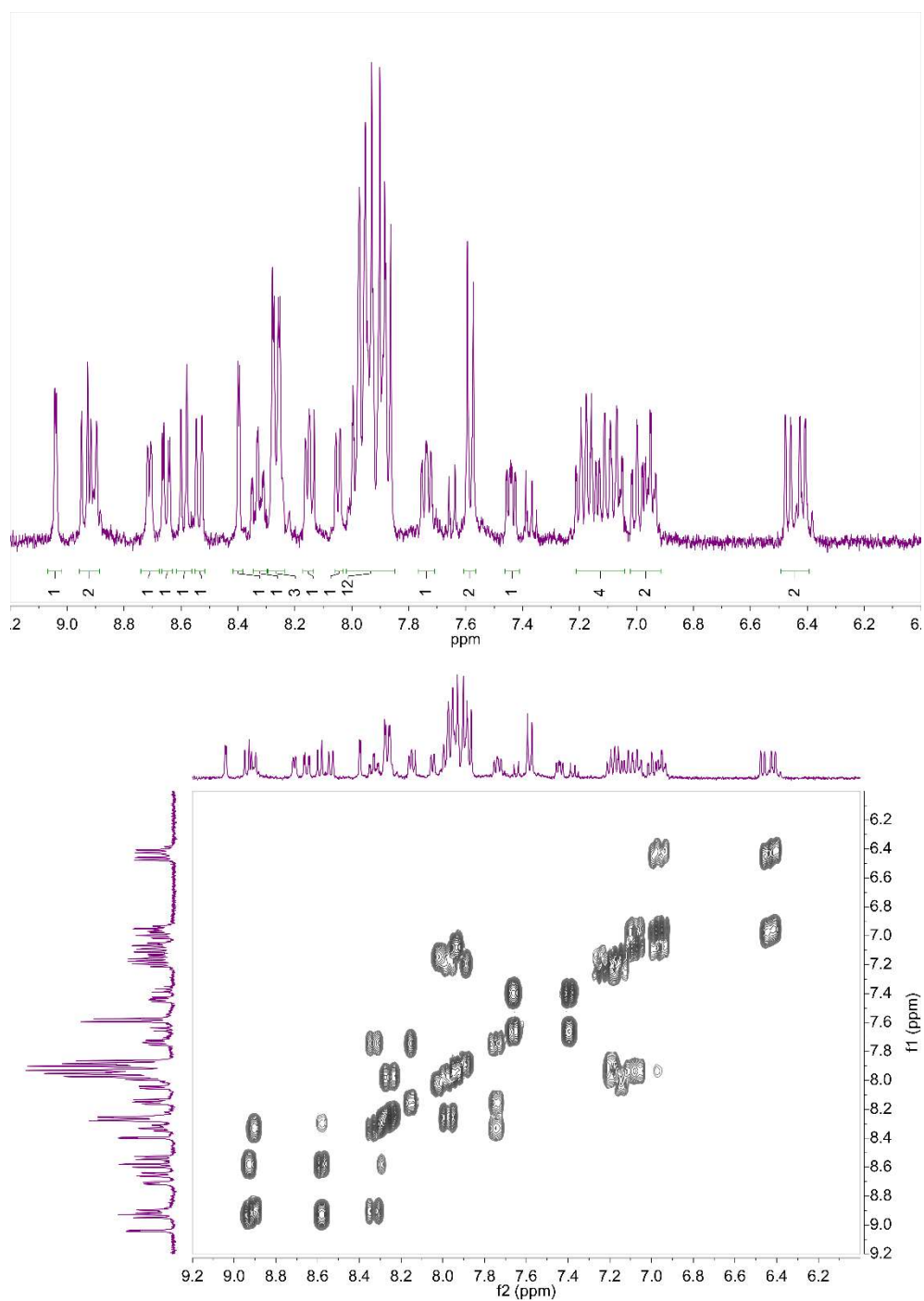
**Figure S3.** ESI<sup>+</sup> MS spectra of complexes 4–6 with simulated isotope pattern of key signal.



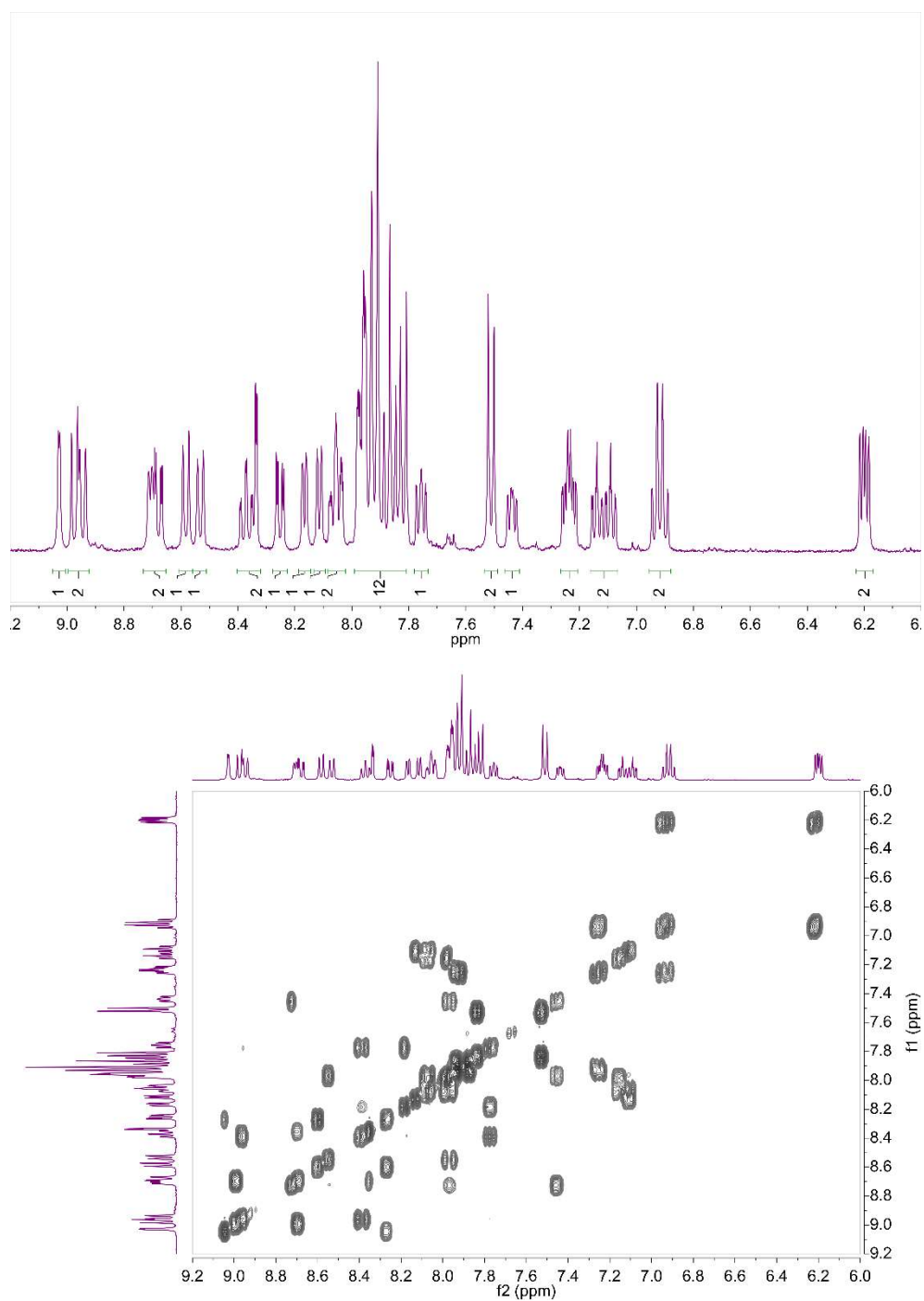
**Figure S4.** ESI<sup>+</sup> MS spectra of complexes 7–9 with simulated isotope pattern of key signal.



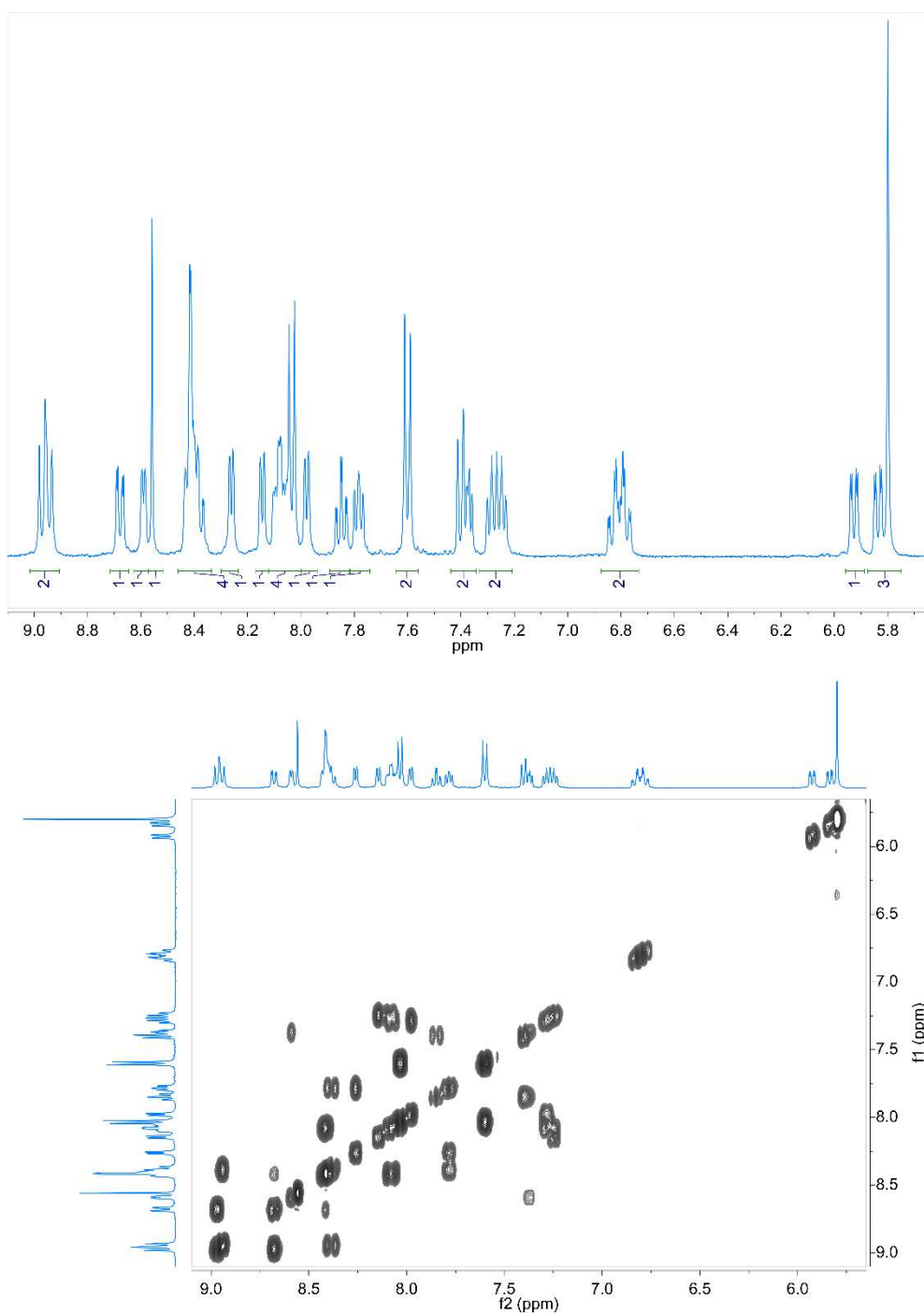
**Figure S5.** <sup>1</sup>H and <sup>1</sup>H<sup>1</sup>H COSY NMR spectra of **4**, aromatic range, acetone-d<sub>6</sub>, r.t.



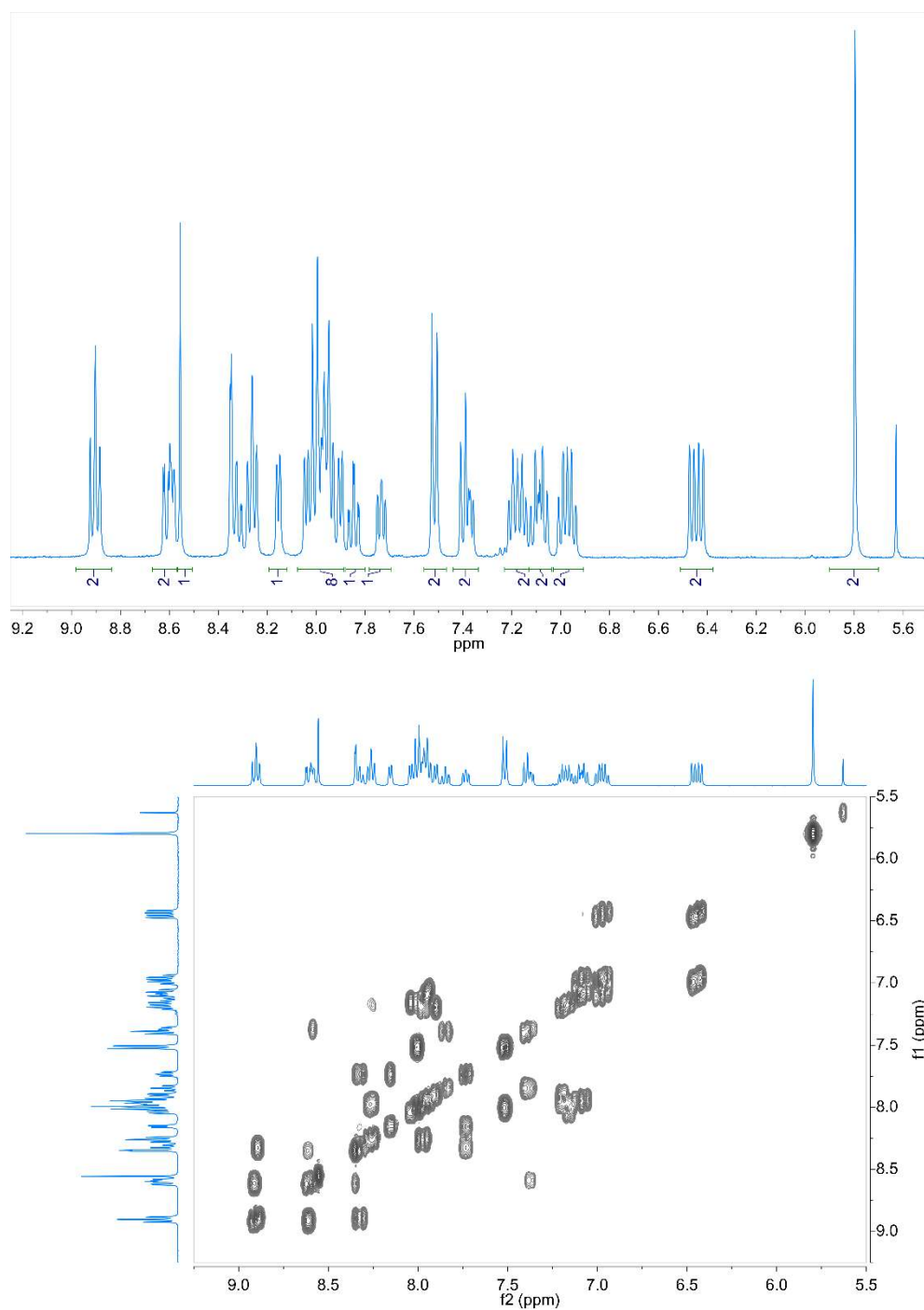
**Figure S6.**  $^1\text{H}$  and  $^1\text{H}^1\text{H}$  COSY NMR spectra of **5**, aromatic range, acetone- $d_6$ , r.t.



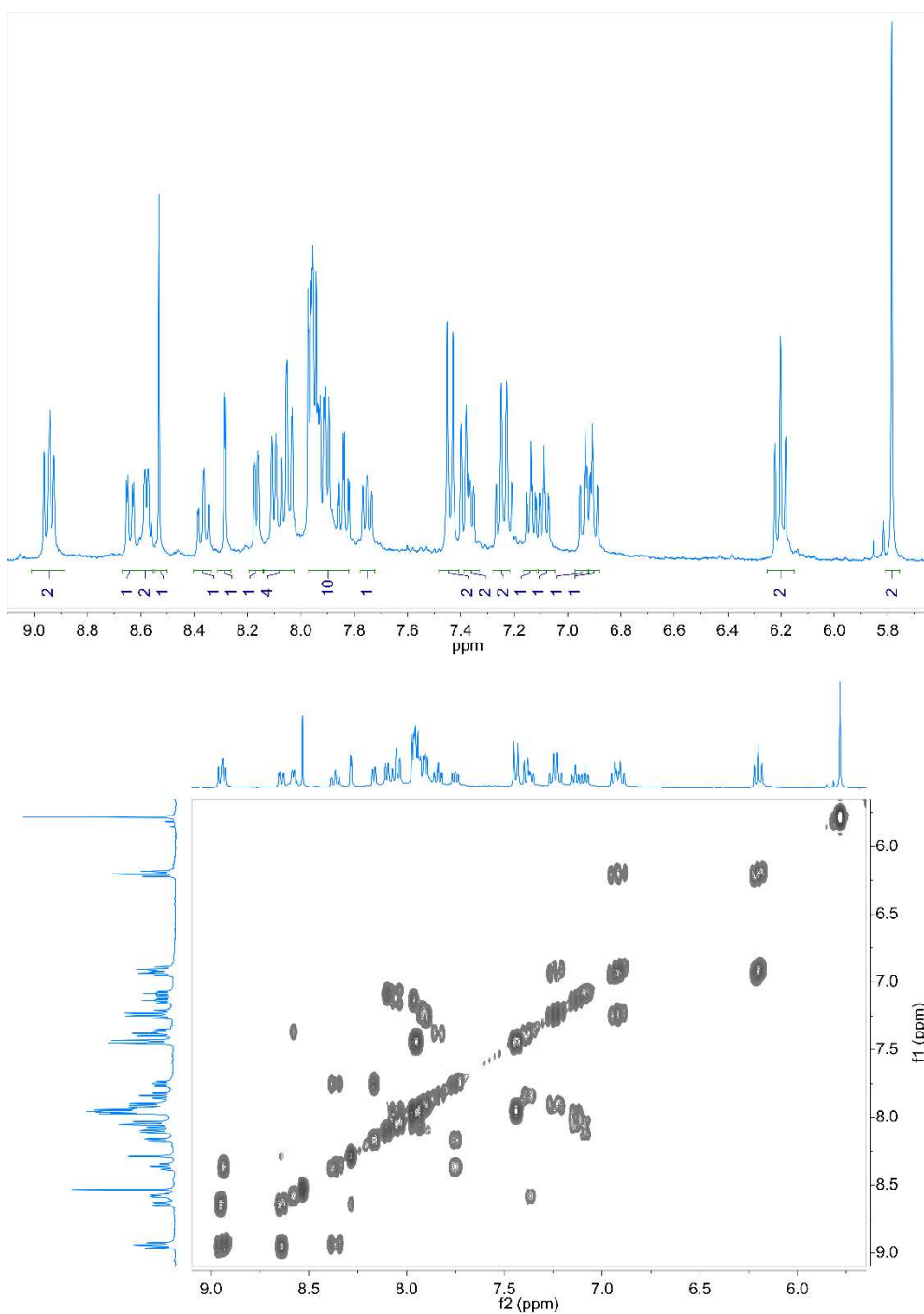
**Figure S7.**  $^1\text{H}$  and  $^1\text{H}$  $^1\text{H}$  COSY NMR spectra of **6**, aromatic range, acetone- $d_6$ , r.t.



**Figure S8.**  $^1\text{H}$  and  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectra of **7**, aromatic range, acetone- $\text{d}_6$ , r.t.

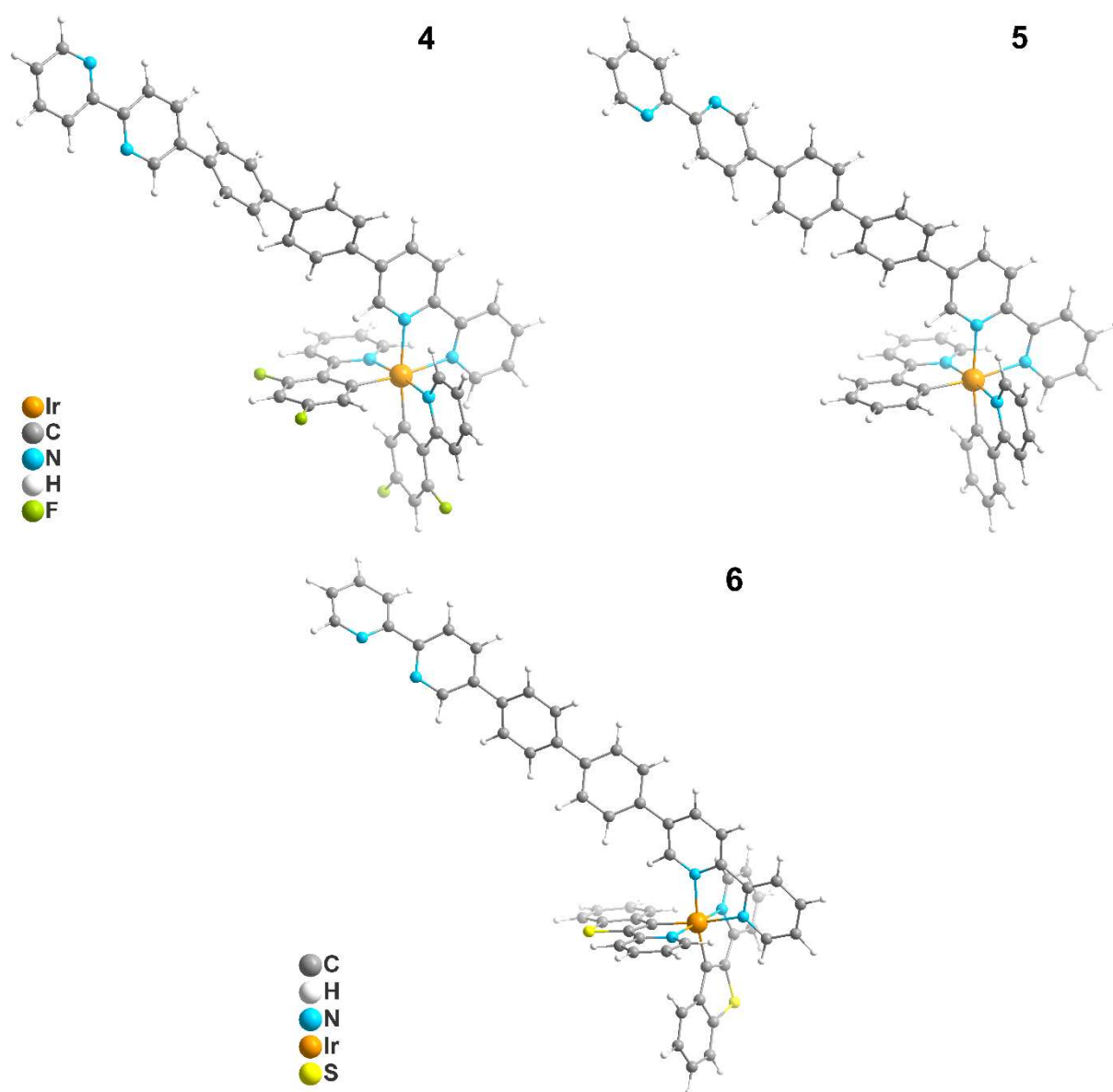


**Figure S9.**  $^1\text{H}$  and  $^1\text{H}^1\text{H}$  COSY NMR spectra of **8**, aromatic range, acetone- $\text{d}_6$ , r.t.

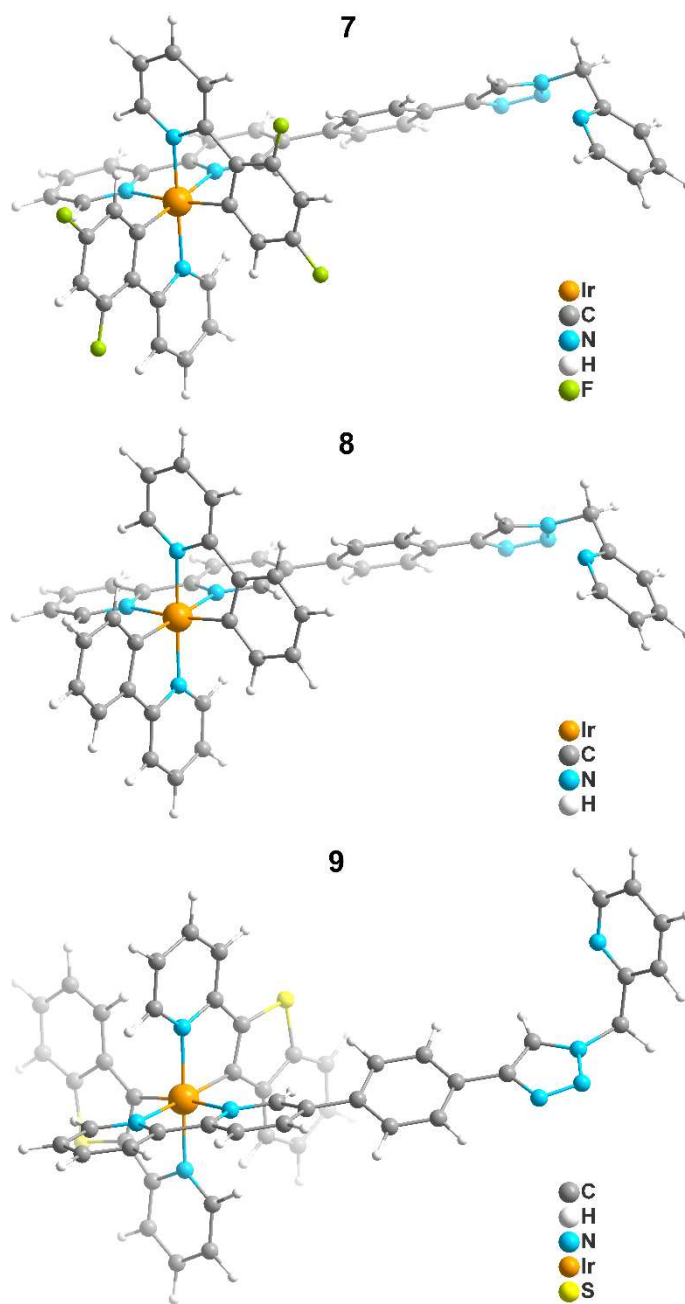


**Figure S10.**  $^1\text{H}$  and  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectra of **9**, aromatic range, acetone- $d_6$ , r.t.

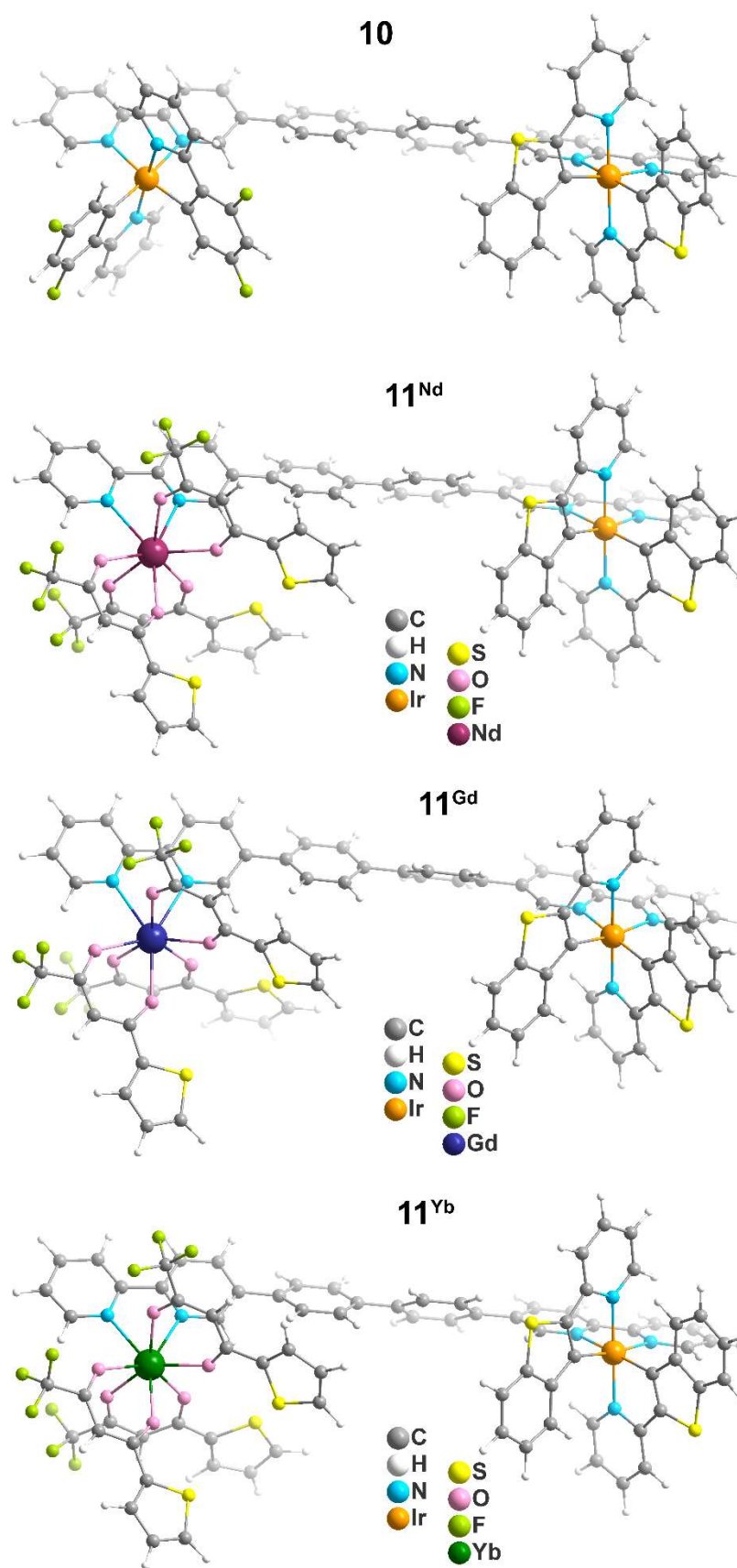




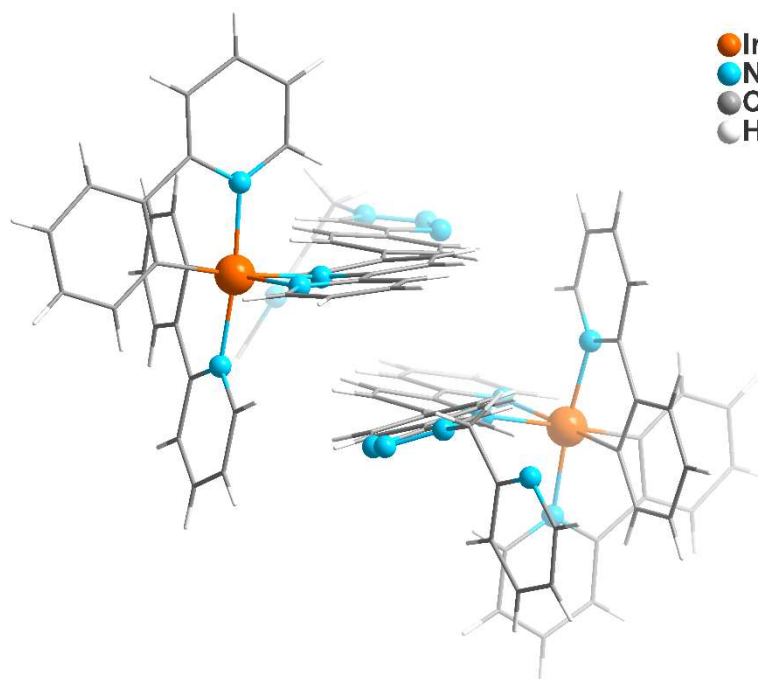
**Figure S11.** DFT-optimized structures of the complexes 4–6.



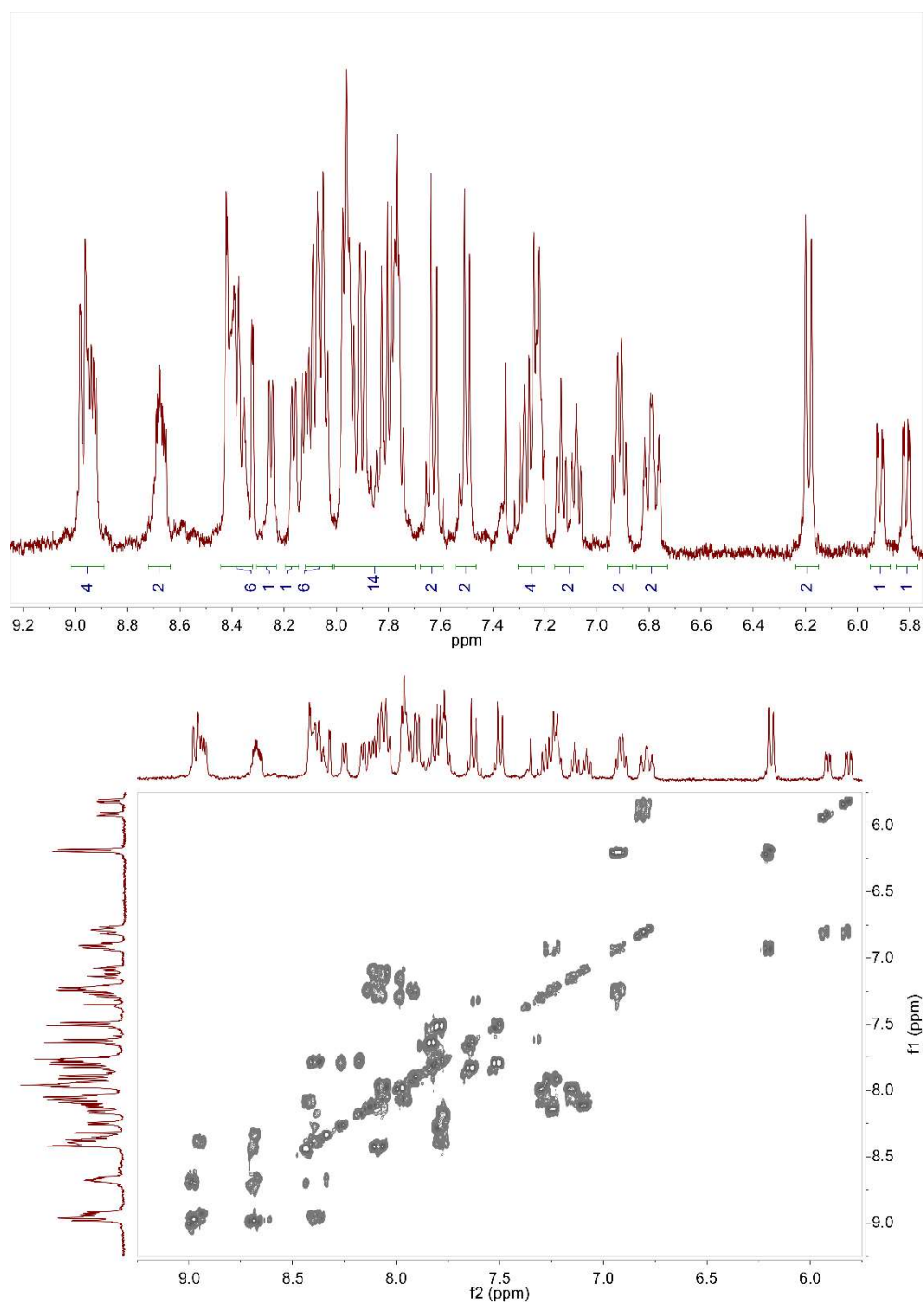
**Figure S12.** DFT-optimized structures of the complexes 7–9.



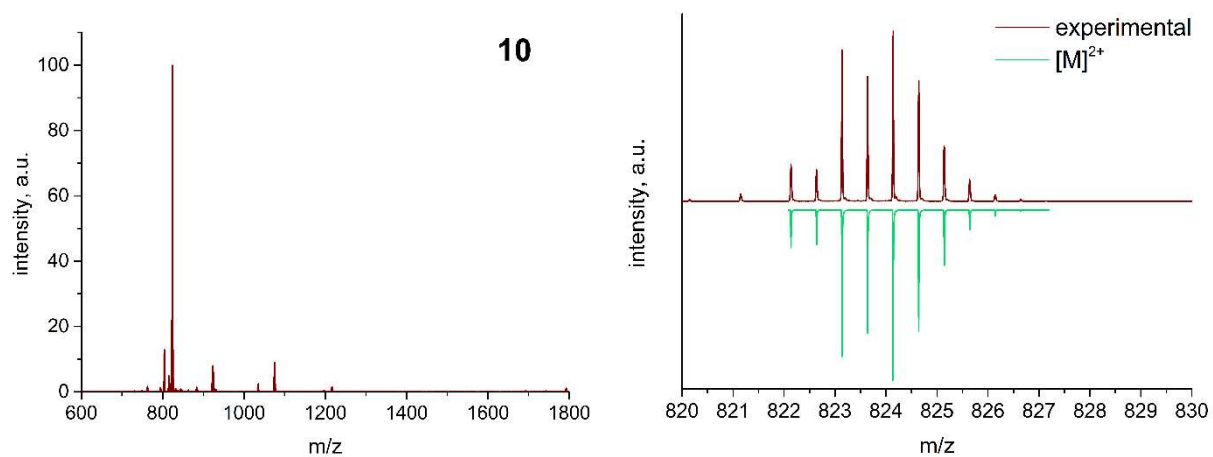
**Figure S13.** DFT-optimized structures of binuclear complexes **10** and **11<sup>Ln</sup>** (Ln = Nd, Gd, Yb).



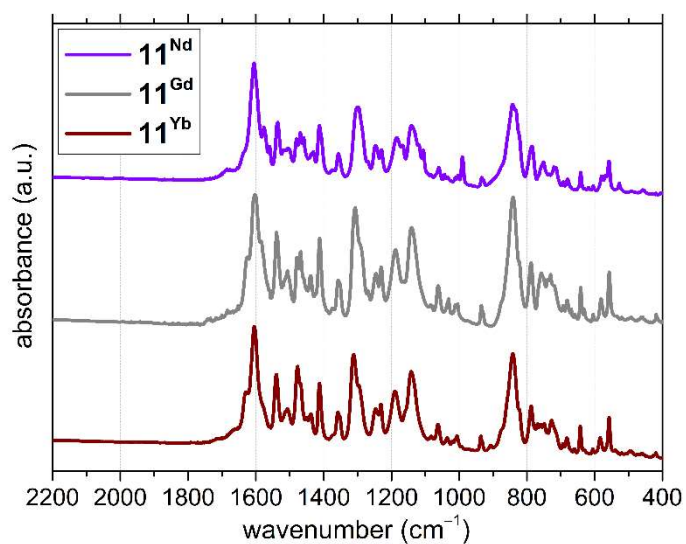
**Figure S14.** Visualization of molecular arrangement in **8** crystal. Anions  $[\text{PF}_6]^-$  are not shown. Colour legend: carbon – grey, nitrogen – sky blue, iridium – orange, hydrogen – white.



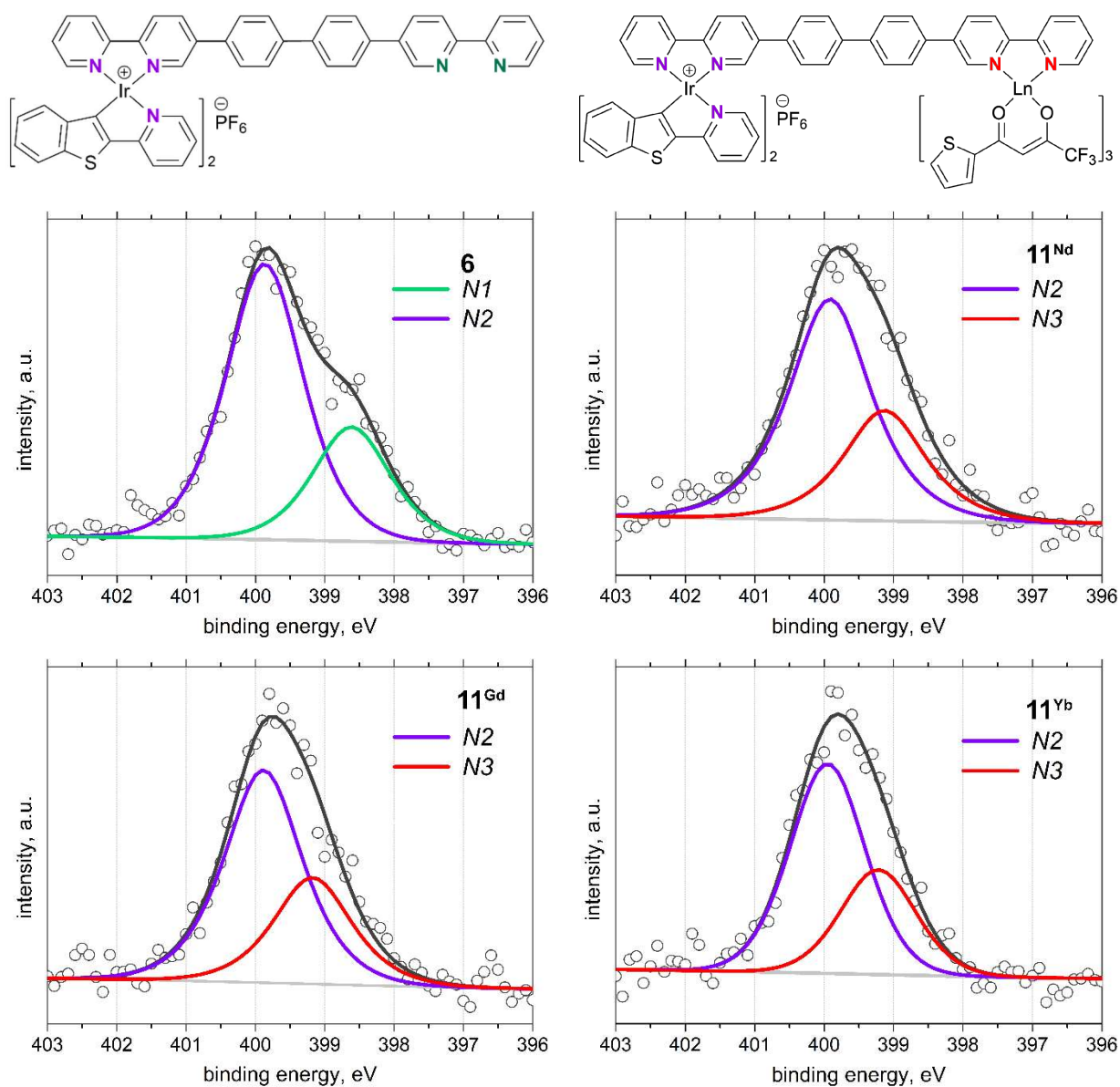
**Figure S15.**  $^1\text{H}$  and  $^1\text{H}$  $^1\text{H}$  COSY NMR spectra of **10**, aromatic range, acetone- $d_6$ , r.t.



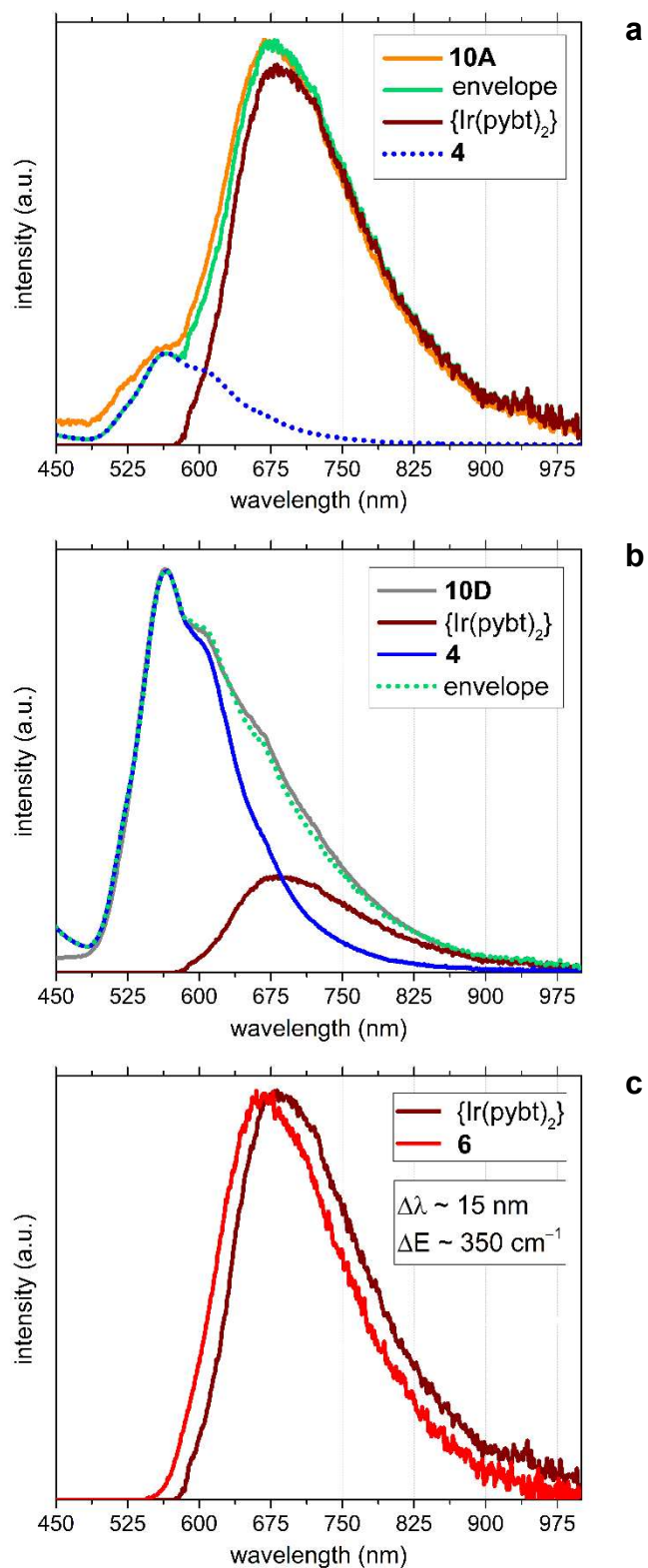
**Figure S16.** ESI<sup>+</sup> MS spectra of **10** with simulated isotope pattern of key signal corresponding to binuclear composition.



**Figure S17.** FTIR spectra of **11**<sup>Ln</sup>, KBr pellet, r.t.

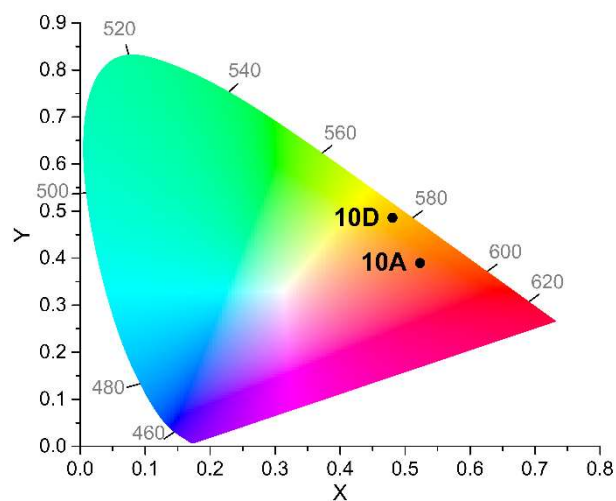


**Figure S18.** High-resolution N 1s XPS spectra of **6** and **11<sup>Ln</sup>**.



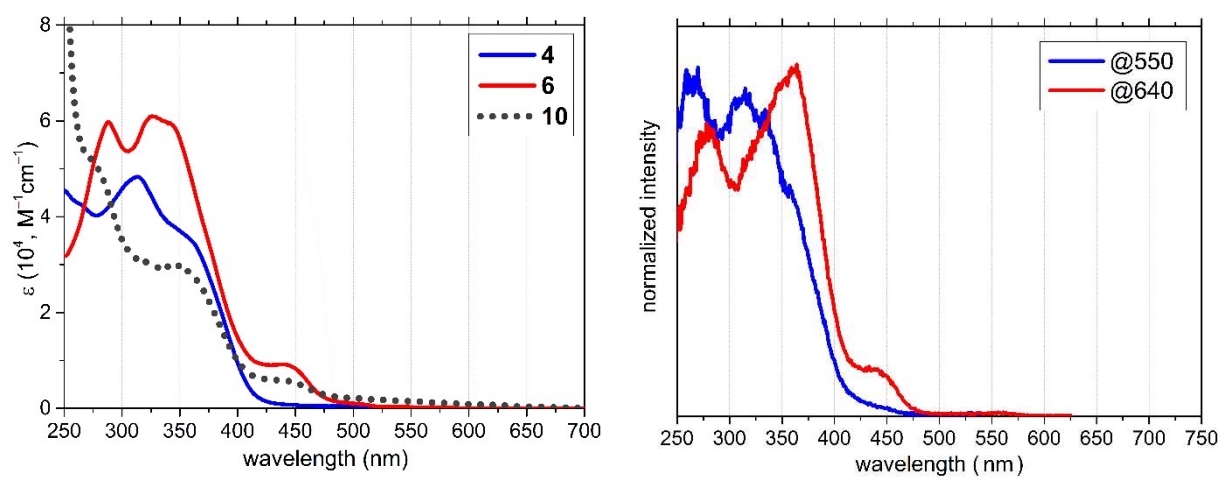
**Figure S19.** Deconvolution of the emission spectrum of **10** into two independent bands; (a) aerated DCE solution, (b) deaerated DCE solution, (c) difference between native emission band of **6** and emission band used for deconvolution {Ir(pybt)<sub>2</sub>}.



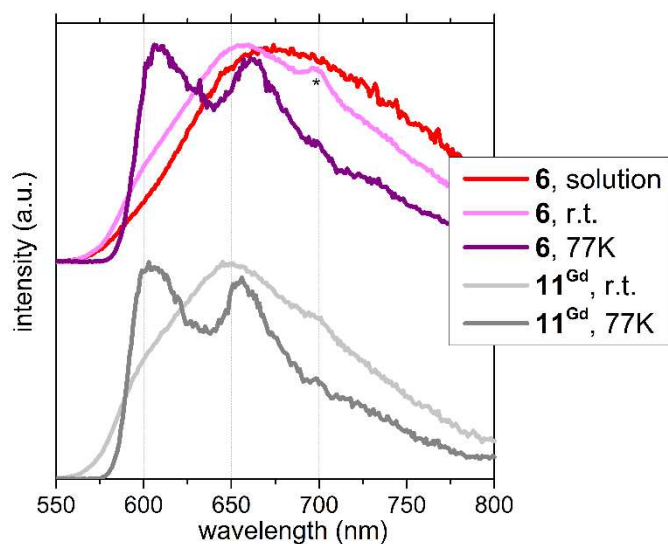


	x	y
<b>10D</b>	0.48	0.49
<b>10A</b>	0.52	0.39

**Figure S20.** CIE 1931 coordinates for **10** (A = aerated, D = de-aerated) in solution, DCE, r.t.



**Figure S21.** UV-vis spectra of **4**, **6** and **10** (left) and normalized excitation spectra of **10** (right), DCE solution, r.t.



**Figure S22.** Comparison of solid-state emission of **6** and **11<sup>Gd</sup>** at variable temperature with emission of **6** in DCE solution.

**Table S3.** Optical and photophysical properties of **11<sup>Ln</sup>** (Ln = Nd, Gd, Yb) complexes

	$\lambda_{abs}$ , nm ( $\epsilon$ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{em}$ ,* nm [media]	$\tau_{obs}$ , $\mu\text{s}$ [ $\lambda_{em}$ , nm] <sup>#</sup>
<b>11<sup>Nd</sup></b>	289(81), 305(76) <sup>sh</sup> , 325(85), 337(83) <sup>sh</sup> , 345(84), 422(10) <sup>sh</sup> , 440(9)	689 [DCE]	–
<b>11<sup>Gd</sup></b>	289(77), 305(71) <sup>sh</sup> , 325(81), 337(78) <sup>sh</sup> , 345(79), 422(10) <sup>sh</sup> , 440(9)	r.t. 645 [solid] 77K 603** [solid]	–
<b>11<sup>Yb</sup></b>	289(71), 305(66) <sup>sh</sup> , 325(74), 337(72) <sup>sh</sup> , 345(73), 422(10) <sup>sh</sup> , 440(9)	689; 975 [DCE]	0.3 [689]; 9.8 [975]

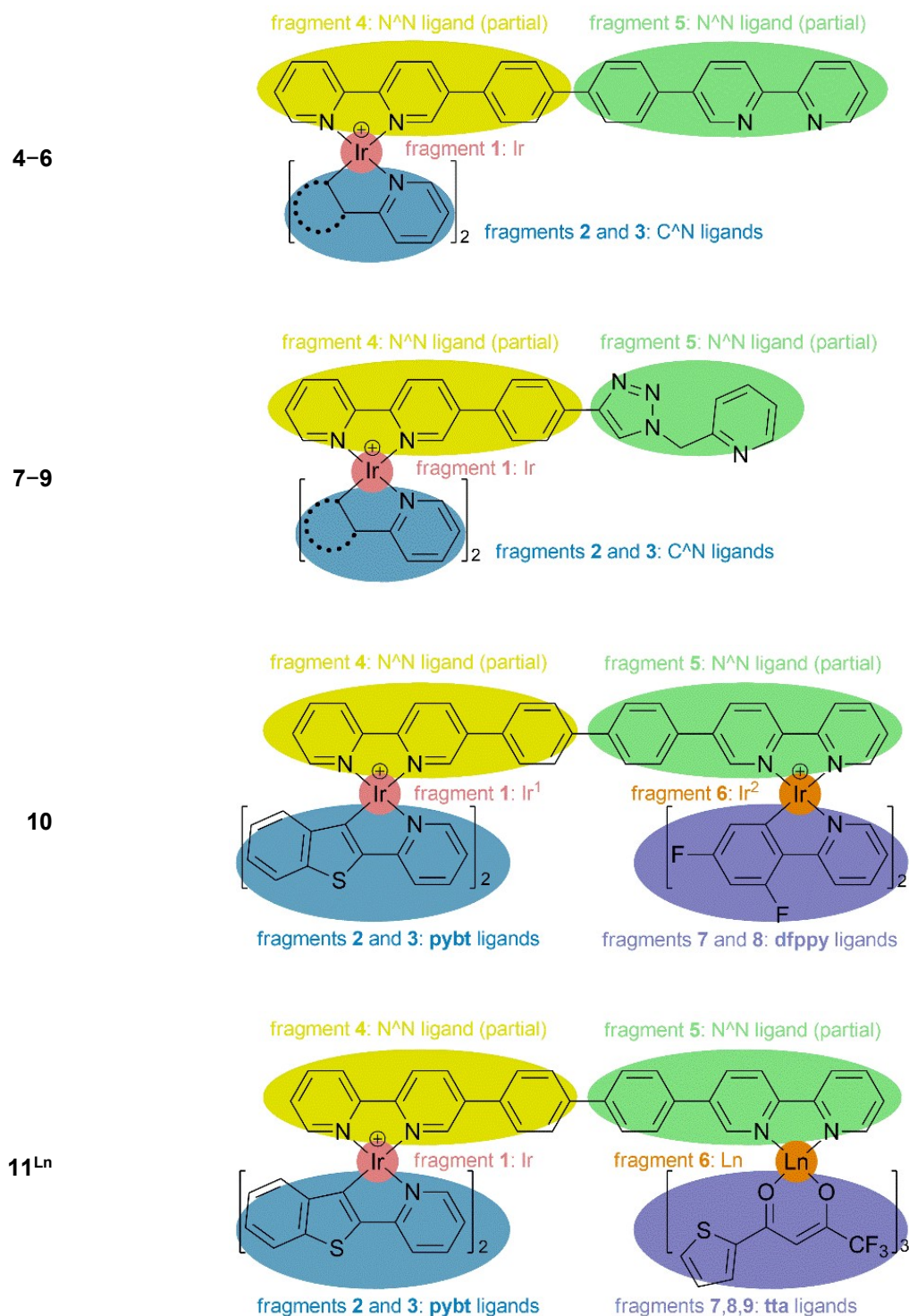
\*  $\lambda_{excit}$  351 nm

\*\* vibronic spacing is *ca.* 1250  $\text{cm}^{-1}$

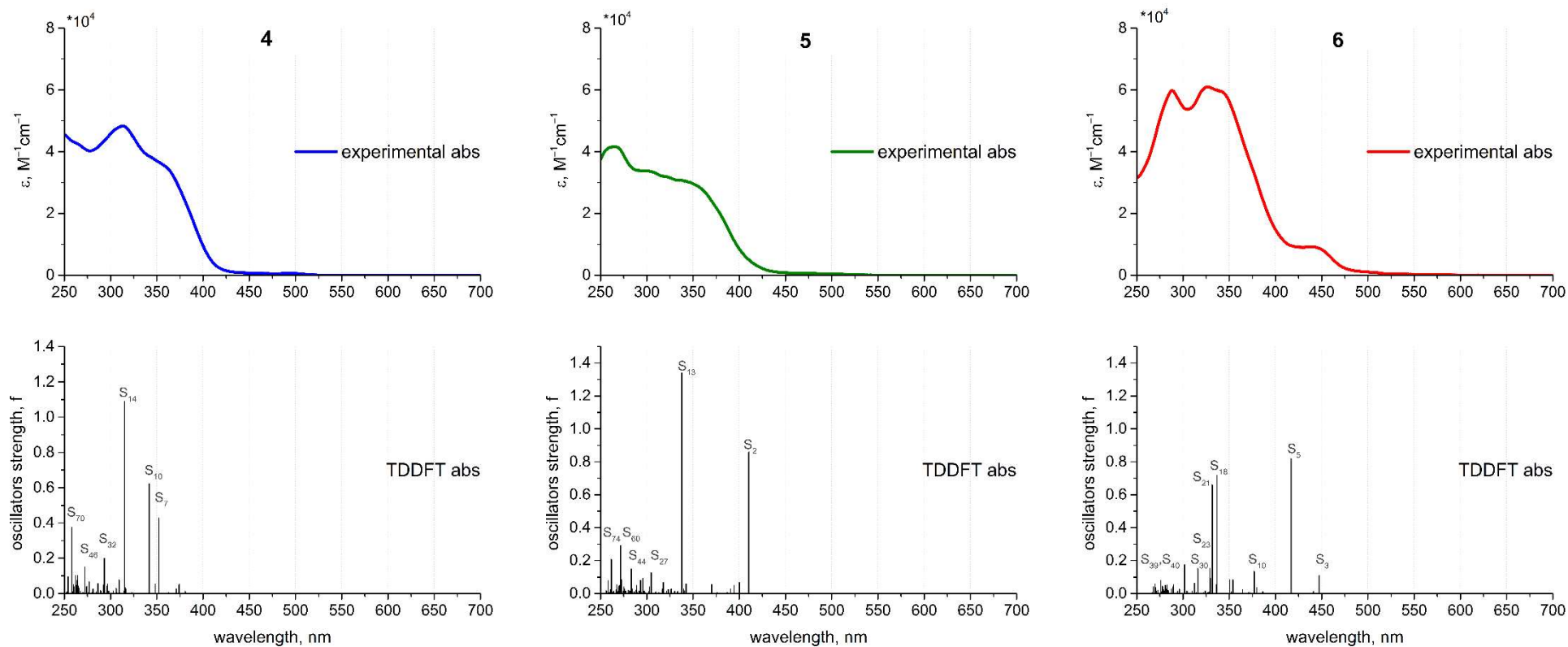
# deaerated DCE solution

**Table S4.** The energy of f→f transitions of Nd(III) from the  $^4\text{I}_{9/2}$  ground state between  $^4\text{F}_{3/2}$ .(emissive level) and  $^2\text{G}_{7/2}$  level.<sup>2</sup>

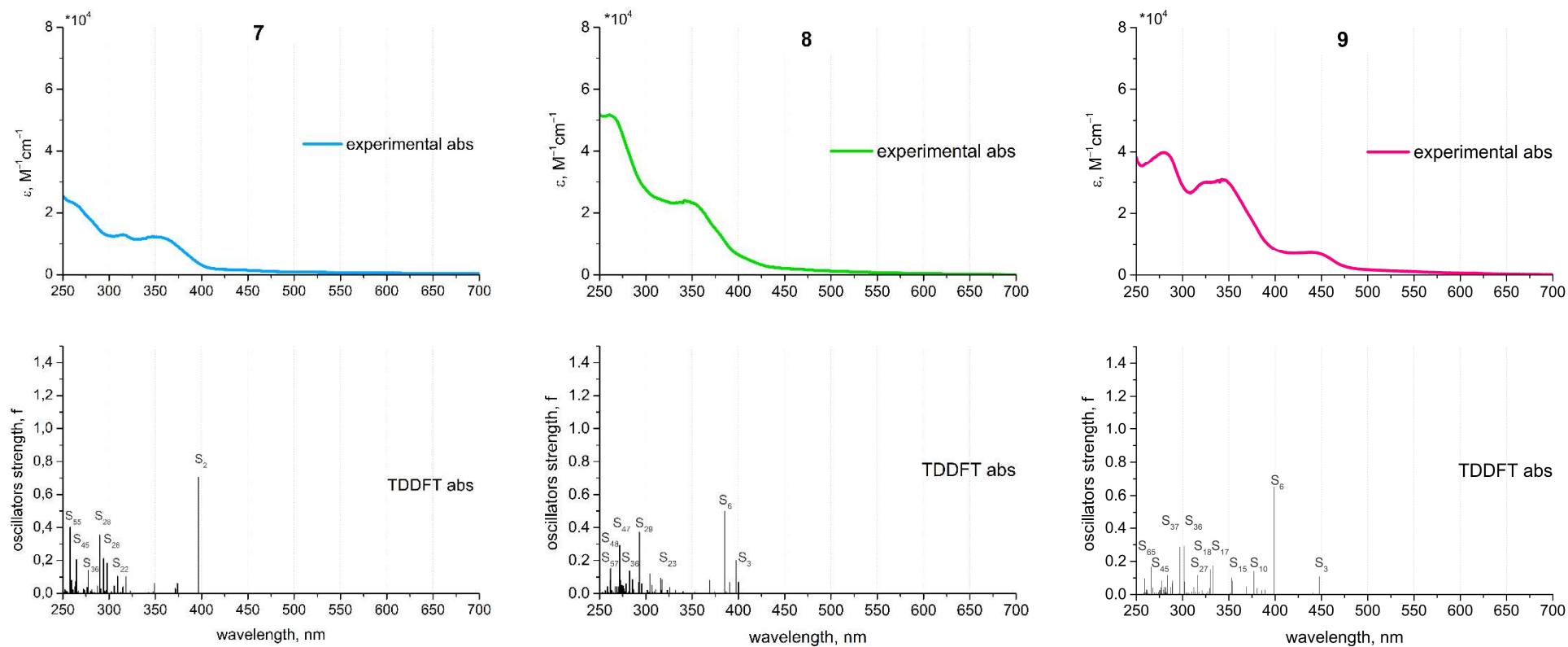
Level	E, $\text{cm}^{-1}$
<b><math>^2\text{G}_{7/2}</math></b>	<b>17460</b>
$^4\text{G}_{5/2}$	17300
$^2\text{H}_{11/2}$	15870
$^4\text{F}_{9/2}$	14700
$^4\text{F}_{7/2}$ , $^4\text{S}_{3/2}$	13500
$^2\text{H}_{9/2}$	12590
$^4\text{F}_{5/2}$	12480
<b><math>^4\text{F}_{3/2}</math></b>	<b>11460</b>



**Figure S23.** Fragment decomposition of complexes used for excited state population analysis.

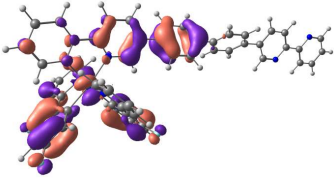
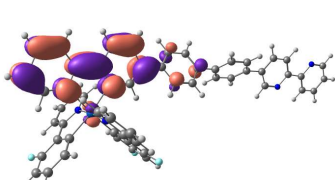
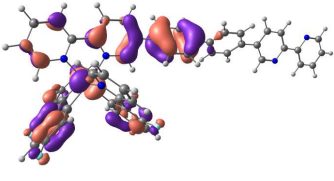
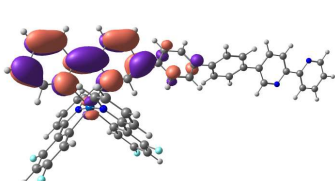
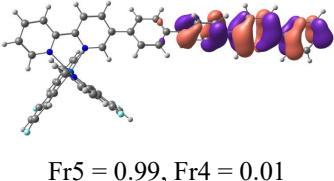
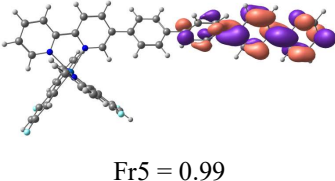
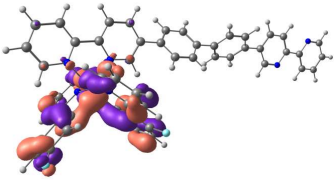
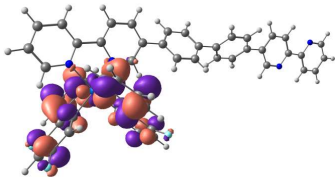
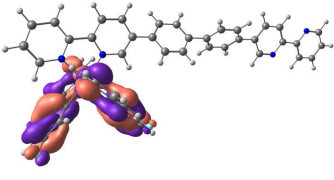
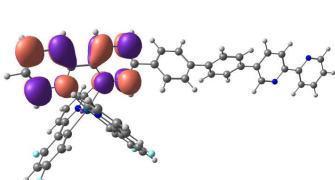
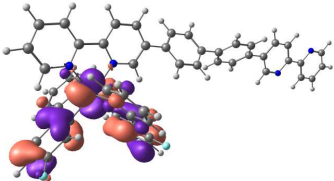
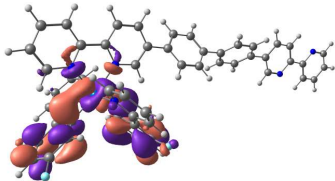


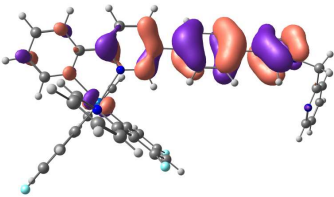
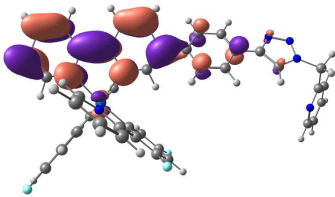
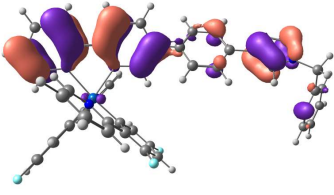
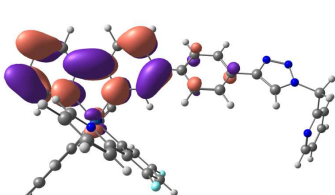
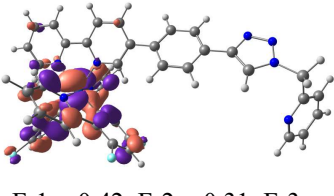
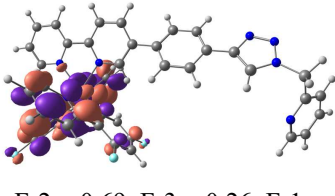
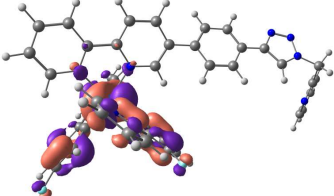
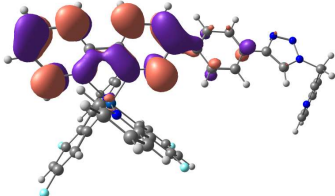
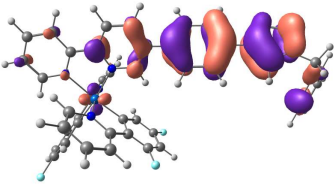
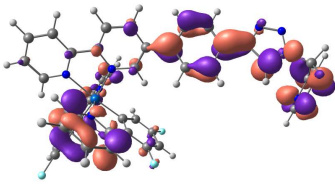
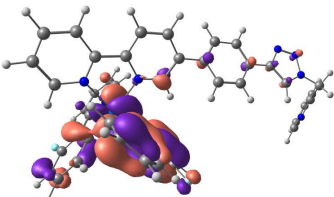
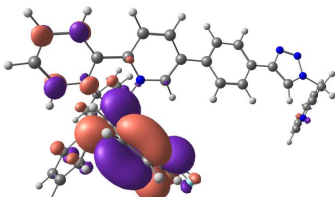
**Figure S24.** TDDFT spectra of 4–6. Singlets with  $f > 0.1$  are indicated. Experimental spectra are given for comparison.

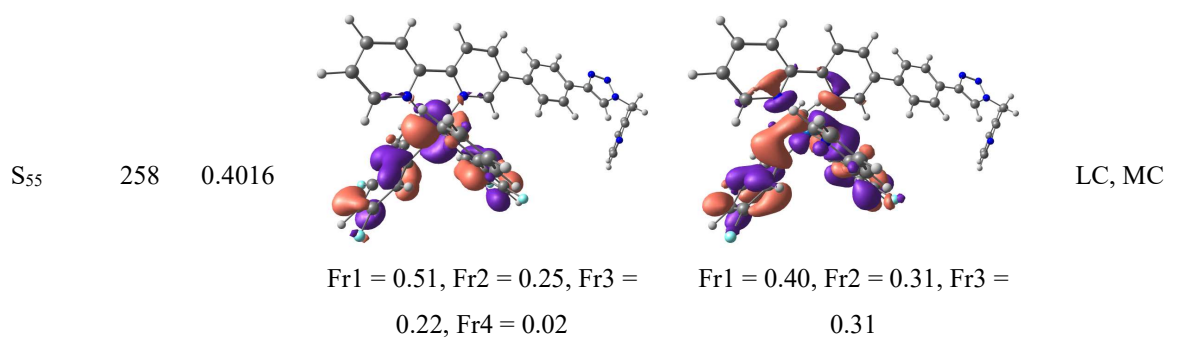


**Figure S25.** TDDFT spectra of 7–9. Singlets with  $f > 0.1$  are indicated. Experimental spectra are given for comparison.

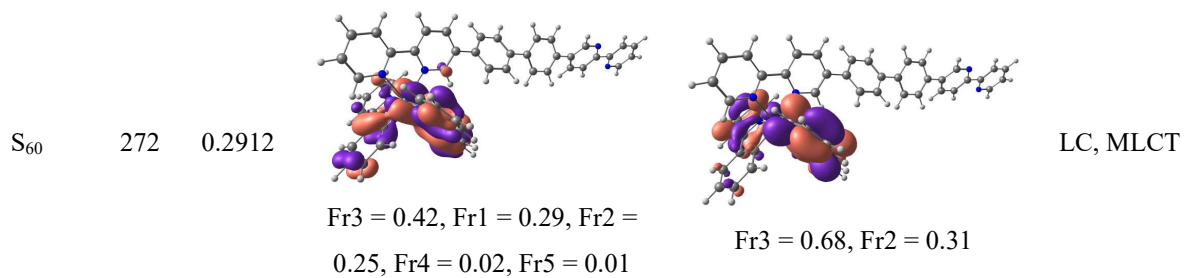
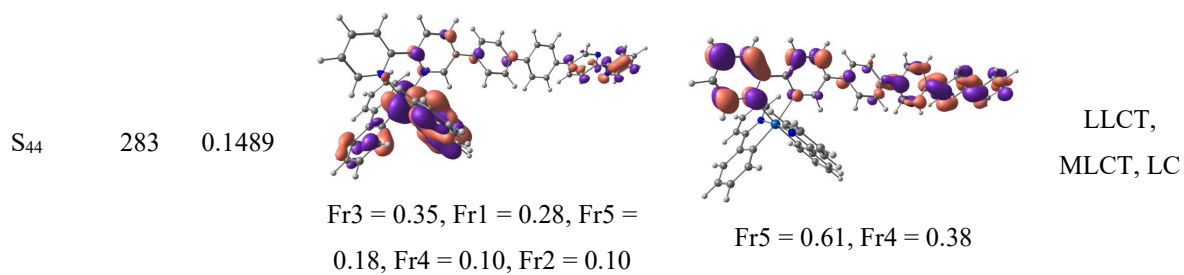
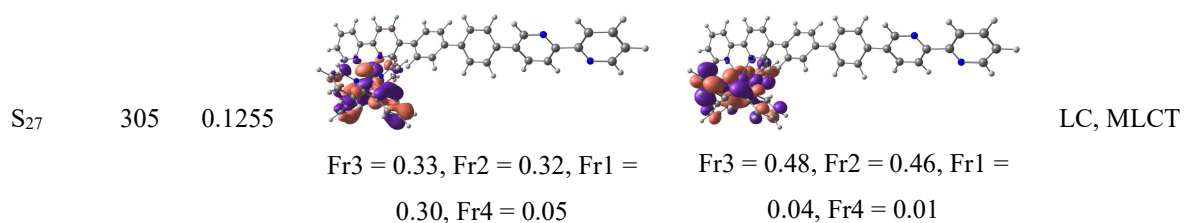
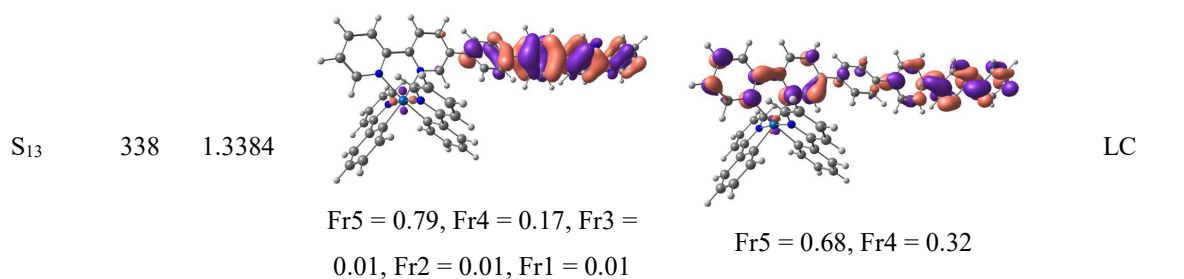
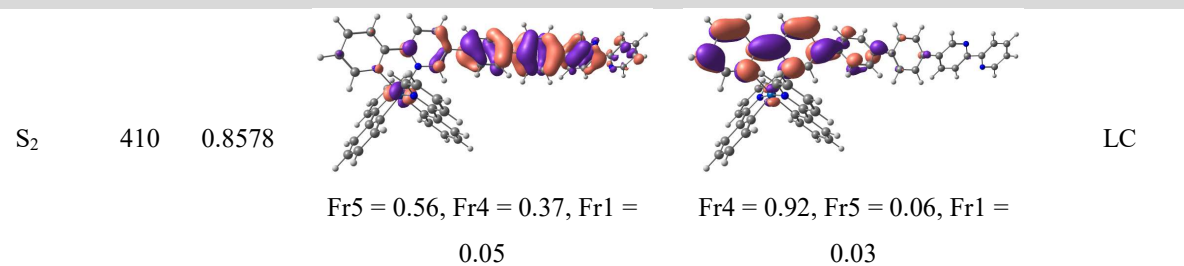
**Table S5.** Natural Transition Orbital analysis of **singlets** with oscillator strength  $f > 0.1$  in 4–9.

Excited state	$\lambda$ , nm	$f$	NTO and its population over fragments <sup>#</sup>	NTO* and its population over fragments <sup>#</sup>	Transition character
<b>4</b>					
S <sub>7</sub>	352	0.4268	 Fr4 = 0.41, Fr2 = 0.36, Fr3 = 0.14, Fr1 = 0.08, Fr5 = 0.01	 Fr4 = 0.98, Fr1 = 0.01	LC, LLCT
S <sub>10</sub>	342	0.6221	 Fr4 = 0.52, Fr2 = 0.22, Fr1 = 0.14, Fr3 = 0.10, Fr5 = 0.01	 Fr4 = 0.98, Fr1 = 0.03	LC, LLCT, MLCT
S <sub>14</sub>	315	1.0882	 Fr5 = 0.99, Fr4 = 0.01	 Fr5 = 0.99	LC
S <sub>32</sub>	293	0.1980	 Fr3 = 0.35, Fr1 = 0.33, Fr2 = 0.27, Fr4 = 0.05	 Fr2 = 0.52, Fr3 = 0.43, Fr1 = 0.05	LC, MLCT
S <sub>46</sub>	272	0.1494	 Fr2 = 0.47, Fr3 = 0.41, Fr1 = 0.10, Fr4 = 0.02	 Fr4 = 1.00, Fr1 = 0.02	LLCT, MLCT
S <sub>70</sub>	258	0.3741	 Fr1 = 0.51, Fr2 = 0.24, Fr3 = 0.23, Fr4 = 0.02	 Fr1 = 0.38, Fr3 = 0.32, Fr2 = 0.28, Fr4 = 0.02	LC, MC

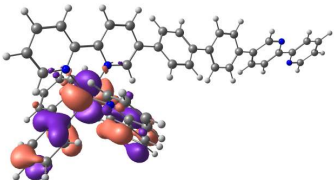
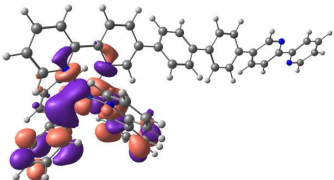
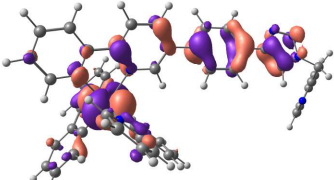
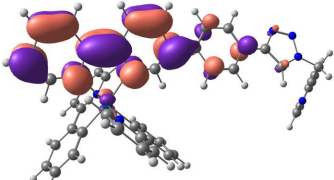
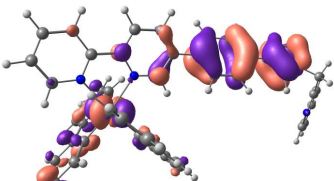
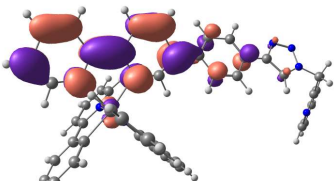
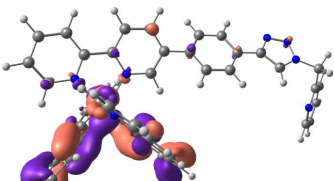
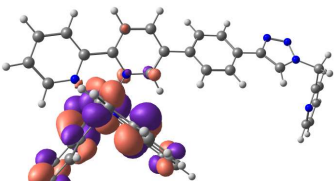
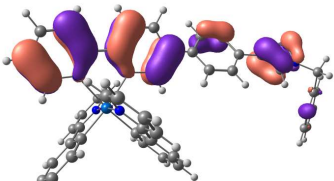
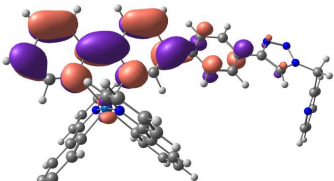
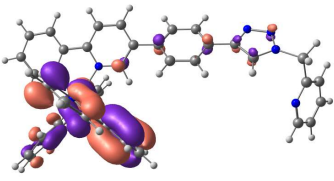
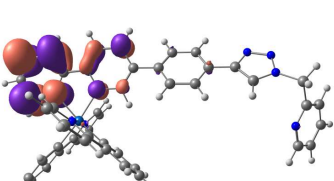
S <sub>2</sub>	397	0.7039			LC
			Fr4 = 0.65, Fr5 = 0.31, Fr1 = 0.04	Fr4 = 0.96, Fr1 = 0.03, Fr5 = 0.02	
S <sub>22</sub>	298	0.1820			LC
			Fr4 = 0.74, Fr5 = 0.23, Fr1 = 0.02	Fr4 = 0.98, Fr1 = 0.03	
S <sub>26</sub>	294	0.2114			MLCT, LC
			Fr1 = 0.42, Fr2 = 0.31, Fr3 = 0.20, Fr4 = 0.06	Fr2 = 0.69, Fr3 = 0.26, Fr1 = 0.05	
S <sub>28</sub>	290	0.3540			MLCT, LC
			Fr1 = 0.53, Fr3 = 0.23, Fr2 = 0.20, Fr4 = 0.04	Fr4 = 0.96, Fr3 = 0.03, Fr2 = 0.02, Fr5 = 0.01	
S <sub>36</sub>	277	0.1403			LC, LLCT
			Fr4 = 0.52, Fr5 = 0.42, Fr1 = 0.02, Fr2 = 0.02, Fr3 = 0.02	Fr5 = 0.44, Fr4 = 0.28, Fr3 = 0.19, Fr2 = 0.10	
S <sub>45</sub>	265	0.2060			LC
			Fr3 = 0.45, Fr1 = 0.29, Fr2 = 0.17, Fr4 = 0.06, Fr5 = 0.03	Fr3 = 0.73, Fr2 = 0.12, Fr4 = 0.10, Fr5 = 0.03, Fr1 = 0.02	

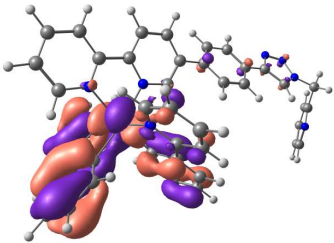
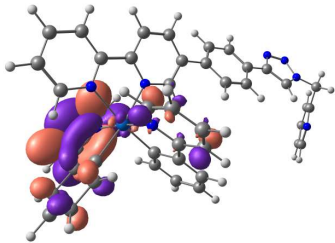
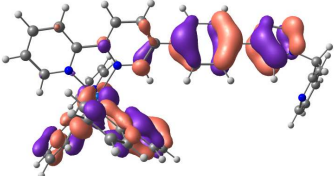
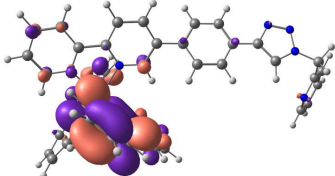
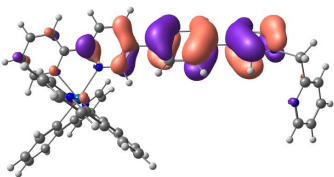
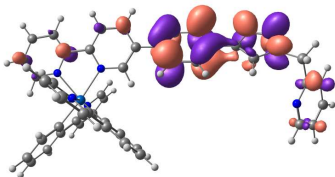


## 5

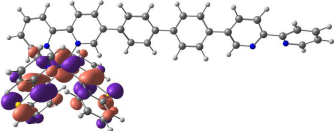
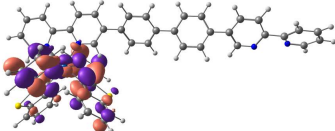
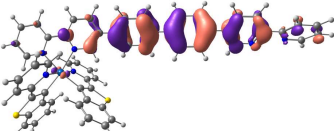
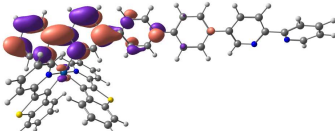
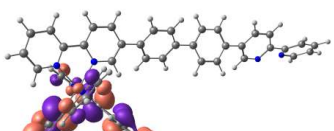
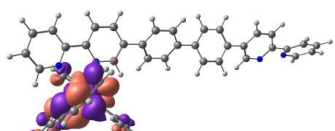


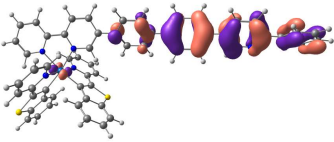
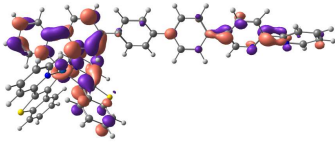
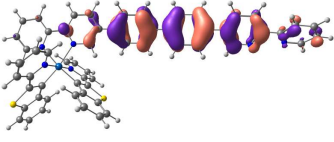
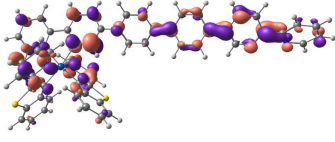
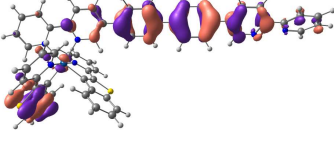
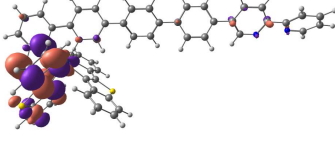
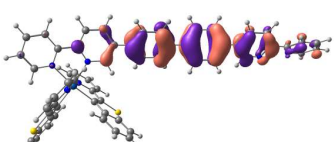
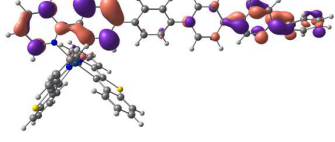
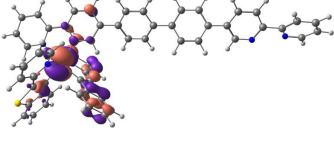
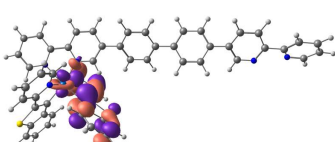
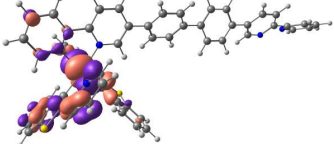
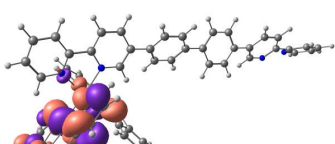
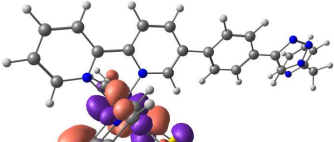
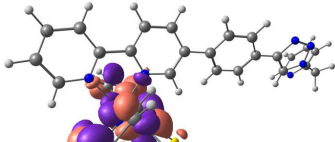


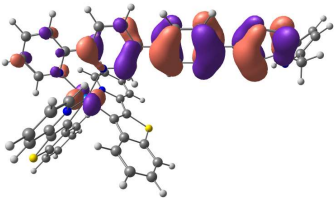
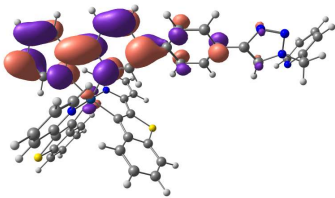
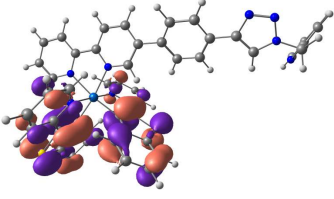
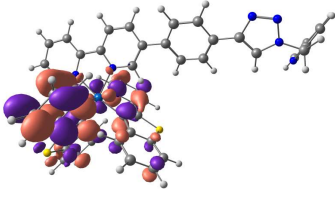
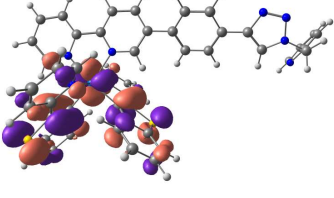
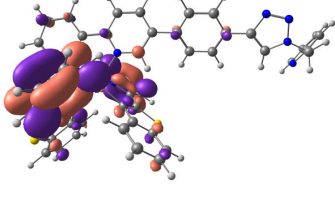
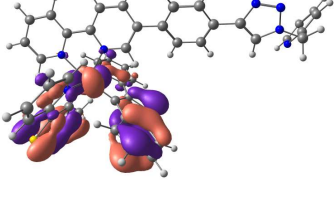
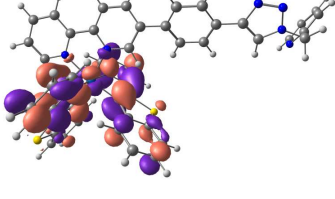
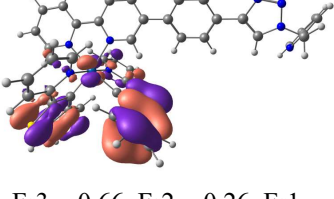
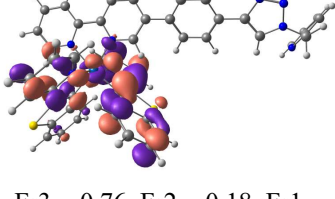
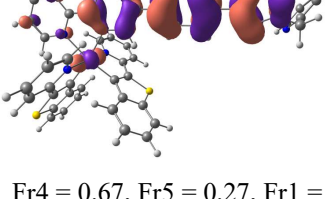
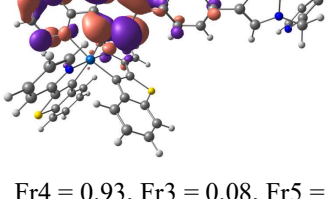
S <sub>74</sub>	262	0.2069			LC, MC
			Fr1 = 0.50, Fr2 = 0.24, Fr3 = 0.24, Fr4 = 0.02	Fr1 = 0.36, Fr3 = 0.31, Fr2 = 0.31, Fr4 = 0.02	
<b>8</b>					
S <sub>3</sub>	398	0.1985			LC, MLCT
			Fr1 = 0.51, Fr4 = 0.24, Fr3 = 0.09, Fr2 = 0.09, Fr5 = 0.08	Fr4 = 0.96, Fr1 = 0.03, Fr5 = 0.01	
S <sub>6</sub>	385	0.4987			LC, LLCT, MLCT
			Fr4 = 0.44, Fr5 = 0.22, Fr2 = 0.14, Fr1 = 0.14, Fr3 = 0.06	Fr4 = 0.96, Fr1 = 0.03, Fr5 = 0.02	
S <sub>23</sub>	304	0.1162			LC, MLCT
			Fr3 = 0.34, Fr2 = 0.32, Fr1 = 0.26, Fr4 = 0.07, Fr5 = 0.01	Fr2 = 0.48, Fr3 = 0.43, Fr1 = 0.04, Fr4 = 0.04	
S <sub>29</sub>	293	0.3710			LC
			Fr4 = 0.79, Fr5 = 0.20, Fr1 = 0.02	Fr4 = 0.97, Fr1 = 0.03, Fr5 = 0.01	
S <sub>36</sub>	282	0.1367			LLCT, MLCT
			Fr1 = 0.39, Fr3 = 0.28, Fr2 = 0.17, Fr4 = 0.11, Fr5 = 0.05	Fr4 = 0.99, Fr1 = 0.02	

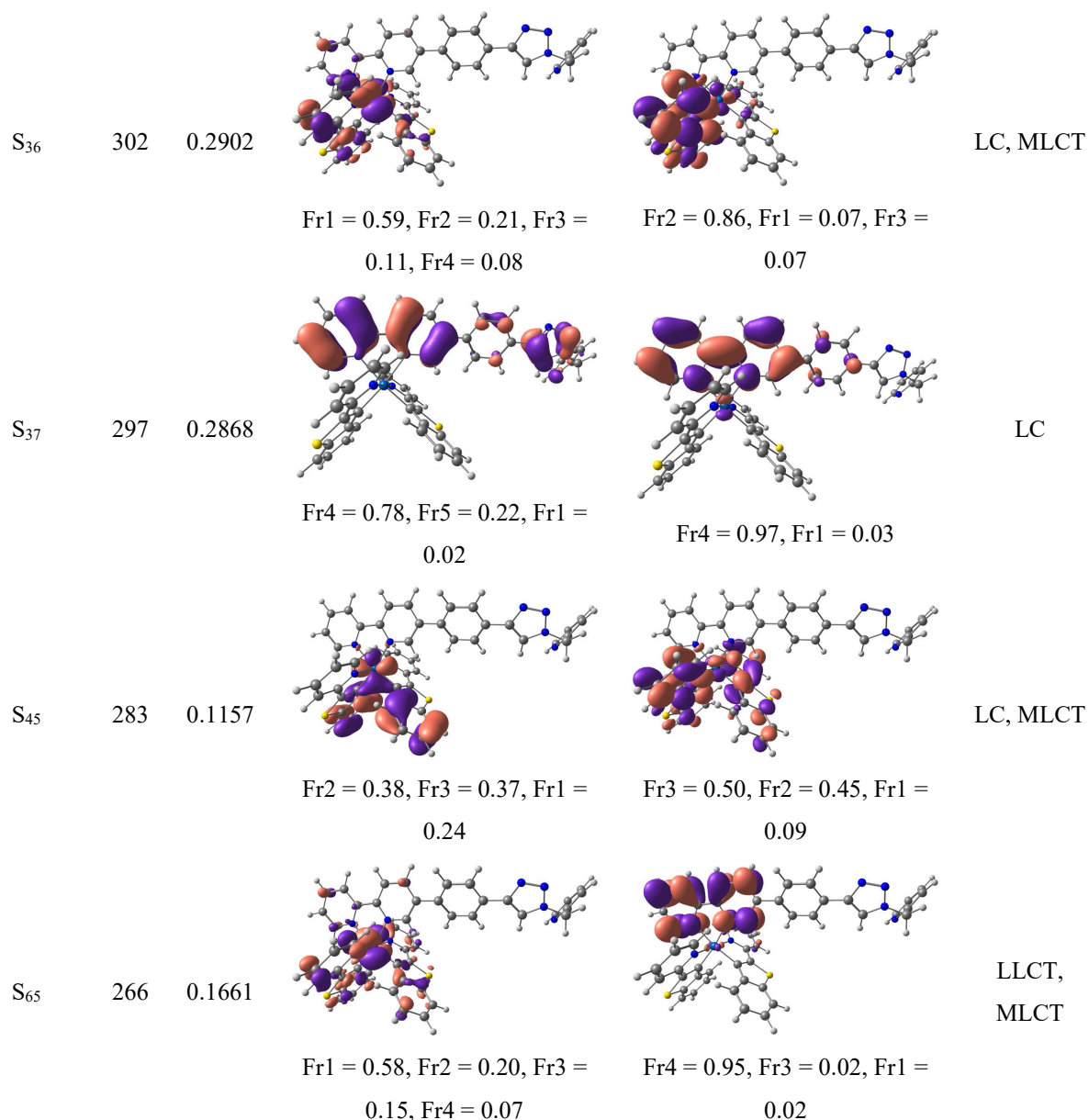
S <sub>47</sub>	272	0.2926			LC, MLCT
			Fr2 = 0.41, Fr3 = 0.26, Fr1 = 0.26, Fr4 = 0.06, Fr5 = 0.02	Fr2 = 0.84, Fr3 = 0.12, Fr4 = 0.04	
S <sub>48</sub>	271	0.1170			LC, MLCT
			Fr4 = 0.34, Fr3 = 0.24, Fr5 = 0.17, Fr1 = 0.14, Fr2 = 0.11	Fr3 = 0.68, Fr2 = 0.19, Fr4 = 0.10, Fr5 = 0.03	
S <sub>57</sub>	262	0.1510			LC
			Fr4 = 0.63, Fr5 = 0.34, Fr1 = 0.01, Fr2 = 0.01	Fr4 = 0.70, Fr5 = 0.27, Fr3 = 0.02, Fr2 = 0.01	

## 6

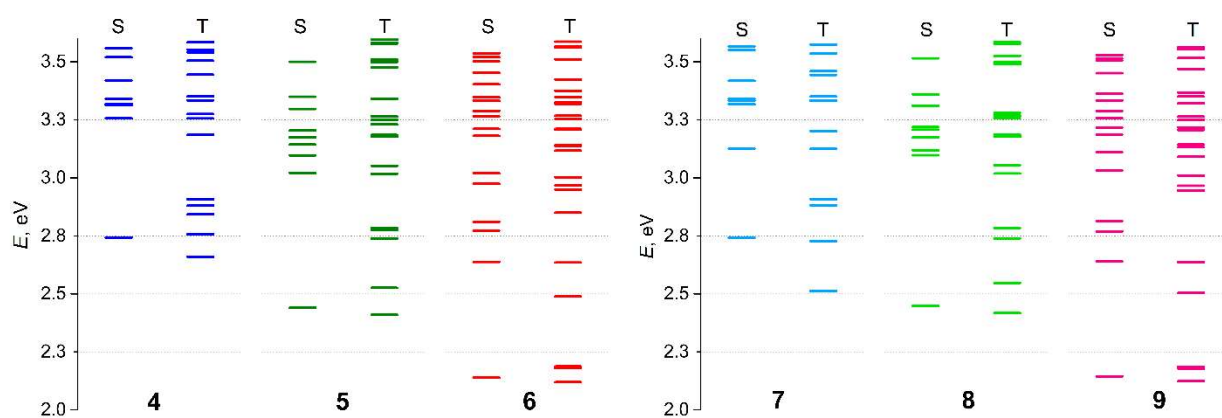
S <sub>3</sub>	447	0.1084			LC, MLCT
			Fr2 = 0.36, Fr3 = 0.33, Fr1 = 0.29, Fr4 = 0.01	Fr3 = 0.58, Fr2 = 0.34, Fr1 = 0.09	
S <sub>5</sub>	417	0.8185			LC
			Fr5 = 0.59, Fr4 = 0.40, Fr1 = 0.01	Fr4 = 0.93, Fr5 = 0.05, Fr1 = 0.03	
S <sub>10</sub>	377	0.1340			LC
			Fr2 = 0.49, Fr3 = 0.47, Fr1 = 0.03	Fr2 = 0.65, Fr3 = 0.29, Fr1 = 0.05	

S <sub>18</sub>	337	0.7174			LC, LLCT
			Fr5 = 0.83, Fr4 = 0.13, Fr1 = 0.02, Fr3 = 0.02	Fr4 = 0.40, Fr3 = 0.37, Fr5 = 0.20, Fr1 = 0.04	
S <sub>21</sub>	332	0.6597			LC, LLCT
			Fr5 = 0.61, Fr4 = 0.35, Fr2 = 0.02, Fr3 = 0.01	Fr4 = 0.33, Fr5 = 0.32, Fr3 = 0.19, Fr2 = 0.15, Fr1 = 0.01	
S <sub>23</sub>	329	0.1506			LC, LLCT
			Fr5 = 0.45, Fr4 = 0.29, Fr2 = 0.24, Fr1 = 0.02	Fr2 = 0.83, Fr5 = 0.07, Fr1 = 0.05, Fr4 = 0.05	
S <sub>30</sub>	316	0.1508			LC
			Fr5 = 0.61, Fr4 = 0.38	Fr4 = 0.62, Fr5 = 0.34, Fr3 = 0.04, Fr2 = 0.02	
S <sub>39</sub>	302	0.1655			LC, MLCT
			Fr1 = 0.59, Fr3 = 0.23, Fr2 = 0.10, Fr4 = 0.07	Fr3 = 0.93, Fr1 = 0.08	
S <sub>40</sub>	302	0.1739			LC, MLCT
			Fr1 = 0.60, Fr2 = 0.22, Fr3 = 0.11, Fr4 = 0.07	Fr2 = 0.93, Fr1 = 0.08	
9					
S <sub>3</sub>	448	0.1075			LC, MLCT
			Fr2 = 0.37, Fr3 = 0.33, Fr1 = 0.29, Fr4 = 0.01	Fr3 = 0.61, Fr2 = 0.33, Fr1 = 0.09	

S <sub>6</sub>	399	0.6523			LC
			Fr4 = 0.62, Fr5 = 0.28, Fr1 = 0.07, Fr3 = 0.02, Fr2 = 0.02	Fr4 = 0.96, Fr1 = 0.03, Fr5 = 0.02	
S <sub>10</sub>	377	0.1407			LC
			Fr2 = 0.49, Fr3 = 0.48, Fr1 = 0.03	Fr2 = 0.66, Fr3 = 0.29, Fr1 = 0.05	
S <sub>15</sub>	353	0.1013			LC, MLCT
			Fr2 = 0.39, Fr3 = 0.35, Fr1 = 0.25, Fr4 = 0.01	Fr2 = 0.56, Fr3 = 0.40, Fr4 = 0.04, Fr5 = 0.01	
S <sub>17</sub>	333	0.1731			LC, MLCT
			Fr3 = 0.44, Fr2 = 0.33, Fr1 = 0.21, Fr4 = 0.03	Fr3 = 0.60, Fr2 = 0.35, Fr1 = 0.08	
S <sub>18</sub>	330	0.1510			LC
			Fr3 = 0.66, Fr2 = 0.26, Fr1 = 0.05, Fr4 = 0.02	Fr3 = 0.76, Fr2 = 0.18, Fr1 = 0.07	
S <sub>27</sub>	316	0.1159			LC
			Fr4 = 0.67, Fr5 = 0.27, Fr1 = 0.05, Fr3 = 0.02	Fr4 = 0.93, Fr3 = 0.08, Fr5 = 0.01	

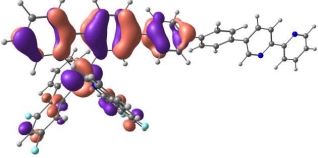
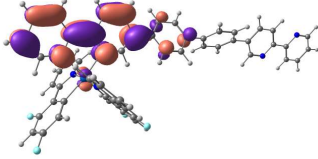
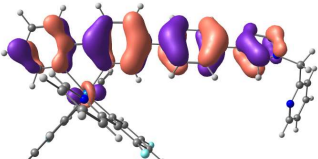
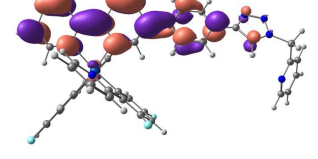
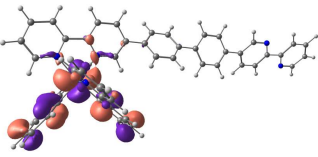
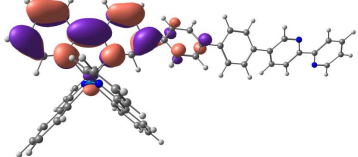
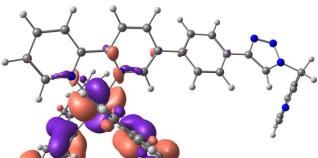
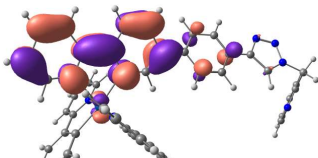
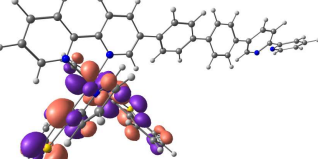
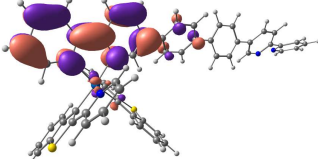
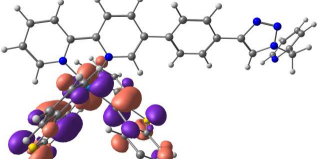
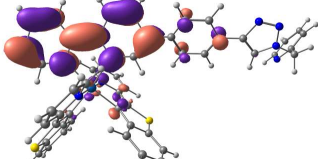


# for fragmentation scheme see Figure S23

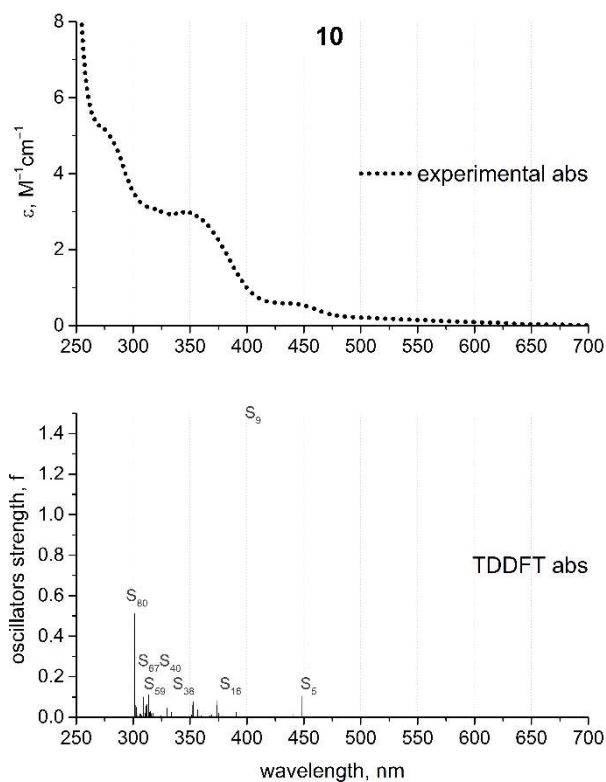


**Figure S26.** Excited state diagrams for 4–9 obtained from TDDFT calculations.

**Table S6.** Natural Transition Orbital analysis of **first triplets** in 4–9.

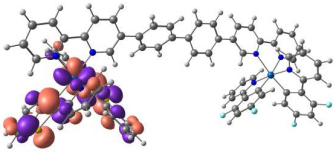
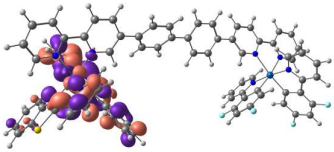
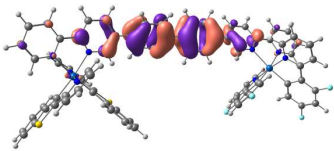
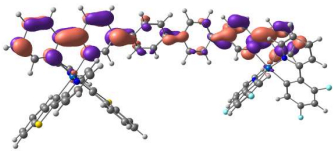
Complex	$\Delta E(S_0-T_1)$ , eV	NTO and its population over fragments <sup>#</sup>	NTO* and its population over fragments <sup>#</sup>	Transition character
4	2.6594	 Fr4 = 0.60, Fr1 = 0.21, Fr3 = 0.11, Fr2 = 0.08	 Fr4 = 0.98, Fr1 = 0.03	LC, MLCT
7	2.5122	 Fr4 = 0.81, Fr5 = 0.14, Fr1 = 0.04, Fr3 = 0.01	 Fr4 = 0.95, Fr5 = 0.04, Fr1 = 0.02	LC
5	2.4094	 Fr1 = 0.43, Fr3 = 0.25, Fr2 = 0.24, Fr4 = 0.07	 Fr4 = 0.96, Fr1 = 0.04, Fr5 = 0.02	LLCT, MLCT
8	2.4168	 Fr1 = 0.43, Fr3 = 0.25, Fr2 = 0.24, Fr4 = 0.08	 Fr4 = 0.97, Fr1 = 0.04, Fr5 = 0.01	LLCT, MLCT
6	2.1991	 Fr3 = 0.38, Fr2 = 0.34, Fr1 = 0.27, Fr4 = 0.01	 Fr4 = 0.88, Fr3 = 0.04, Fr2 = 0.03, Fr1 = 0.03, Fr5 = 0.01	LLCT, MLCT
9	2.1240	 Fr3 = 0.39, Fr2 = 0.34, Fr1 = 0.26, Fr4 = 0.01	 Fr4 = 0.85, Fr3 = 0.06, Fr2 = 0.04, Fr1 = 0.03, Fr5 = 0.01	LLCT, MLCT

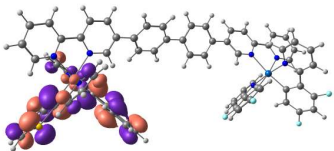
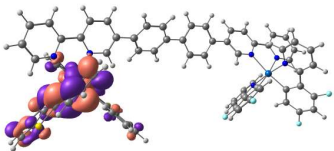
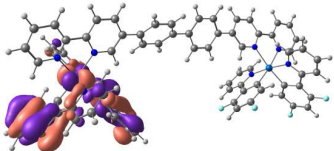
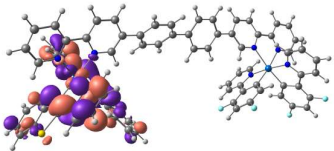
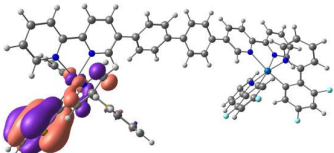
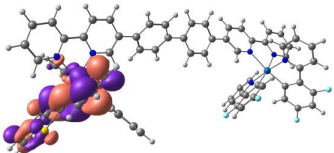
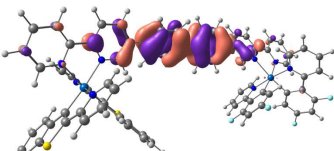
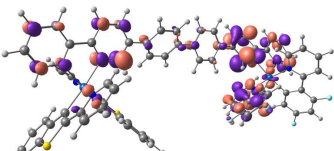
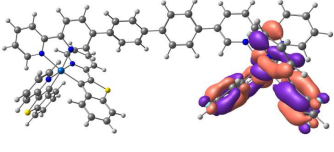
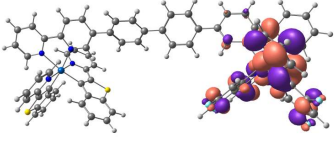
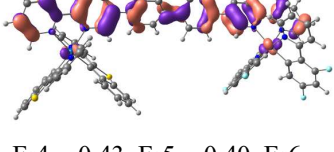
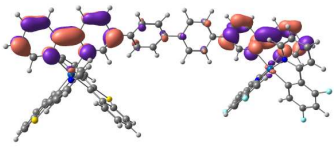
<sup>#</sup> for fragmentation scheme see Figure S23



**Figure S27.** TDDFT spectra of **10**. Singlets with  $f > 0.1$  are indicated. Experimental spectra are given for comparison.

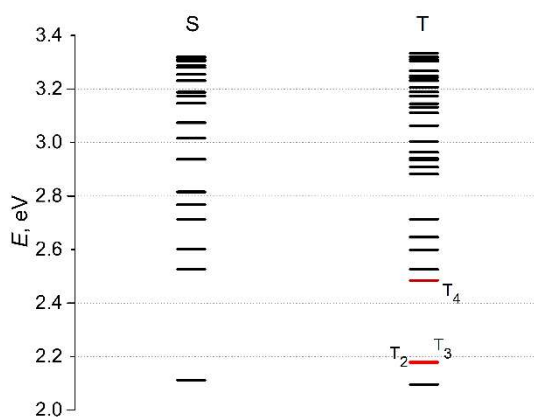
**Table S7.** Natural Transition Orbital analysis of **singlets** with oscillator strength  $f > 0.1$  in complex **10**.

Excited state	$\lambda$ , nm	$f$	NTO and its population over fragments <sup>#</sup>	NTO* and its population over fragments <sup>#</sup>	Transition character
$S_5$	448	0.1015	 Fr2 = 0.39, Fr3 = 0.31, Fr1 = 0.29, Fr4 = 0.01	 Fr3 = 0.69, Fr2 = 0.24, Fr1 = 0.09	LC, MLCT
$S_9$	403	1.4490	 Fr4 = 0.49, Fr5 = 0.46, Fr1 = 0.03, Fr6 = 0.01	 Fr4 = 0.53, Fr5 = 0.45, Fr1 = 0.01, Fr6 = 0.01	LC

S <sub>16</sub>	377	0.1217			LC
			Fr2 = 0.48, Fr3 = 0.48, Fr1 = 0.03, Fr4 = 0.01	Fr2 = 0.74, Fr3 = 0.20, Fr1 = 0.05	
S <sub>38</sub>	333	0.1685			LC, MLCT
			Fr2 = 0.52, Fr3 = 0.27, Fr1 = 0.20	Fr2 = 0.49, Fr3 = 0.45, Fr1 = 0.08	
S <sub>40</sub>	330	0.1339			LC
			Fr2 = 0.52, Fr3 = 0.40, Fr1 = 0.08	Fr3 = 0.56, Fr2 = 0.40, Fr1 = 0.04	
S <sub>59</sub>	314	0.1115			LC, LLCT
			Fr5 = 0.51, Fr4 = 0.39, Fr8 = 0.05, Fr6 = 0.03	Fr5 = 0.49, Fr7 = 0.28, Fr4 = 0.17, Fr2 = 0.04, Fr6 = 0.02	
S <sub>67</sub>	309	0.1002			LC, MLCT
			Fr8 = 0.35, Fr6 = 0.31, Fr7 = 0.30, Fr5 = 0.04	Fr8 = 0.59, Fr7 = 0.33, Fr6 = 0.06	
S <sub>80</sub>	301	0.5113			LC
			Fr4 = 0.43, Fr5 = 0.40, Fr6 = 0.07, Fr8 = 0.04, Fr1 = 0.03, Fr2 = 0.01	Fr4 = 0.58, Fr5 = 0.40, Fr1 = 0.02, Fr6 = 0.01	

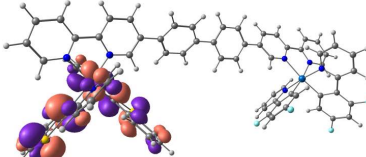
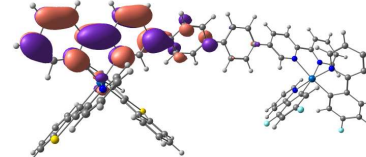
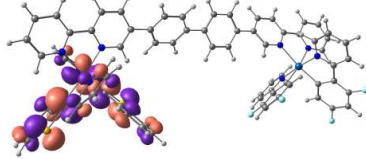
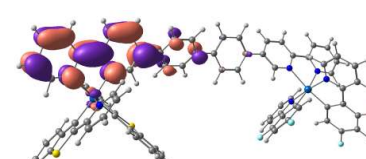
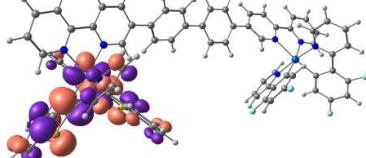
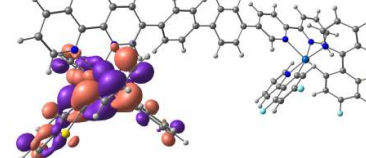
# for fragmentation scheme see Figure S23

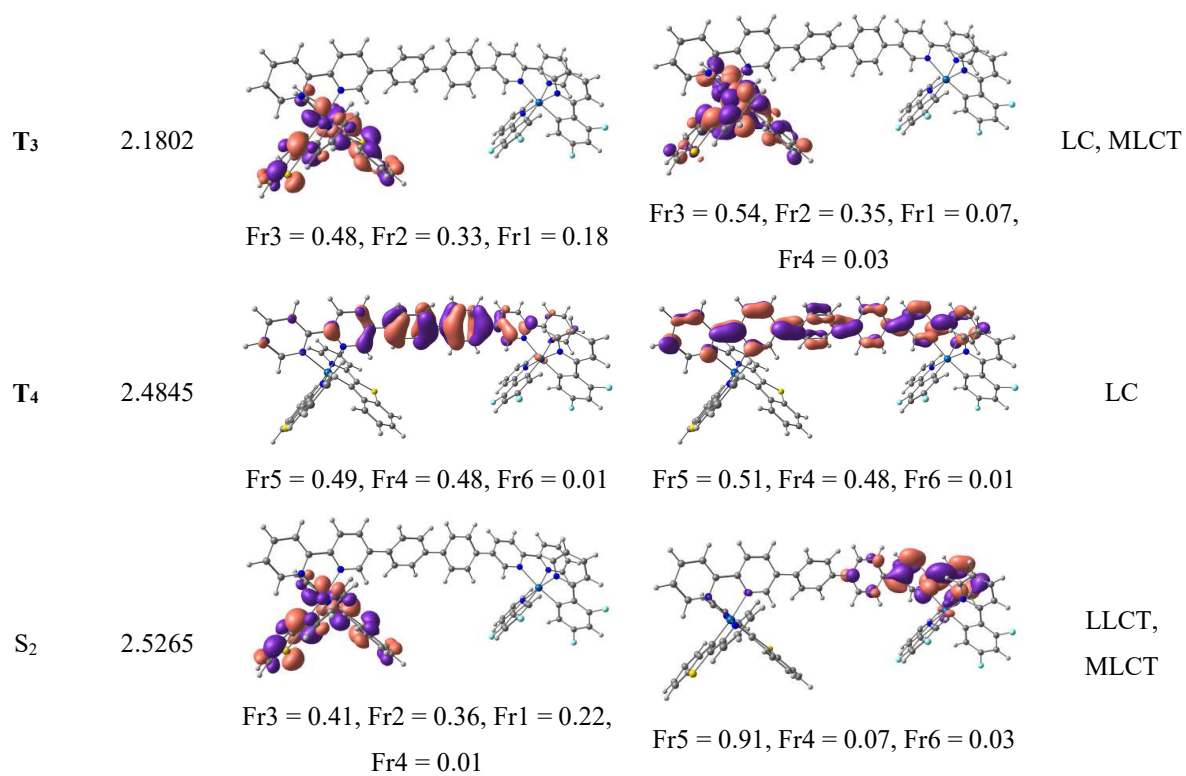




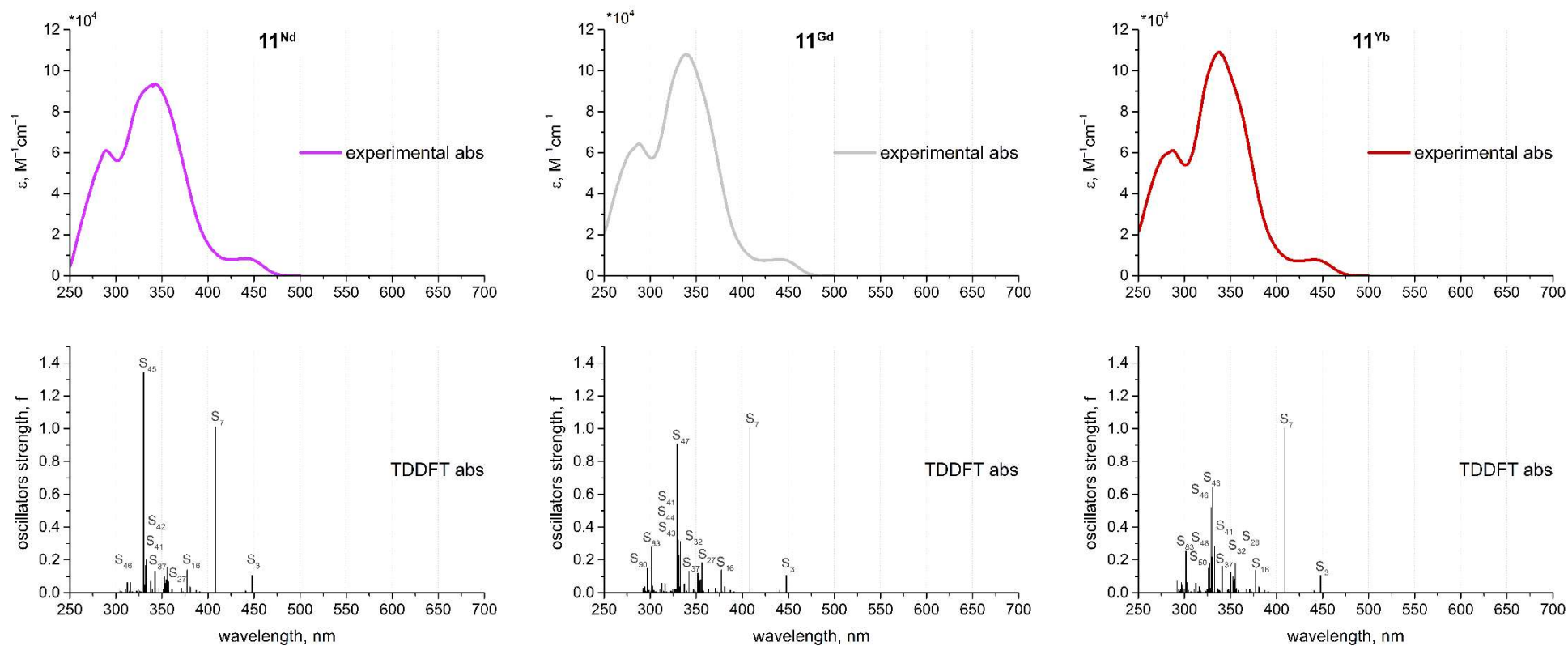
**Figure S28.** Excited state diagrams for **10** obtained from TDDFT calculations. Degenerated  $T_2$  and  $T_3$  states located on pybt ligands and  $T_4$  state located on  $N^{\wedge}N$  ligand are indicated.

**Table S8.** Natural Transition Orbital analysis of **low-energy excited states** in complex **10**.

Excited state	$\Delta E$ , eV	NTO and its population over fragments <sup>#</sup>	NTO* and its population over fragments <sup>#</sup>	Transition character
$T_1$	2.0960	 Fr3 = 0.36, Fr2 = 0.36, Fr1 = 0.27, Fr4 = 0.01	 Fr4 = 0.90, Fr5 = 0.04, Fr1 = 0.03, Fr2 = 0.02, Fr3 = 0.02	LLCT, MLCT
$S_1$	2.1120	 Fr2 = 0.37, Fr3 = 0.35, Fr1 = 0.27, Fr4 = 0.01	 Fr4 = 0.94, Fr5 = 0.04, Fr1 = 0.03	LLCT, MLCT
$T_2$	2.1778	 Fr2 = 0.53, Fr3 = 0.29, Fr1 = 0.17	 Fr2 = 0.61, Fr3 = 0.35, Fr1 = 0.05	LC, MLCT

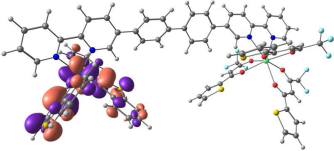
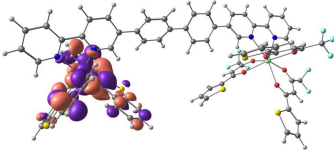
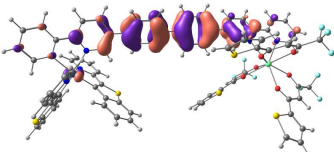
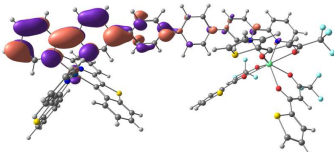
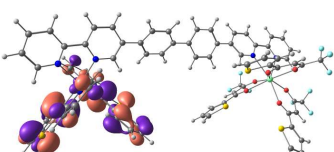
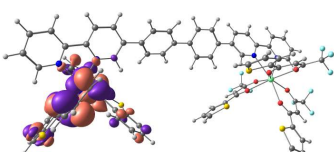
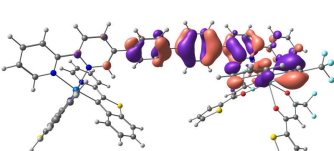
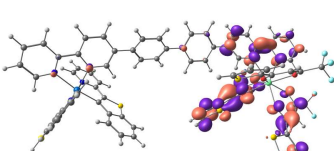
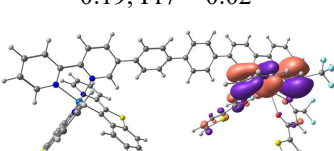
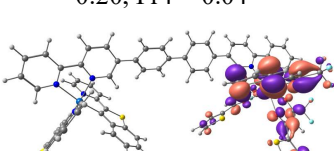
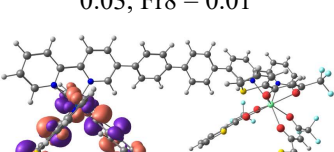
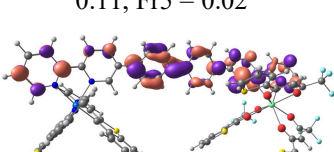


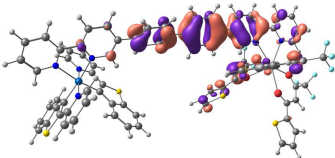
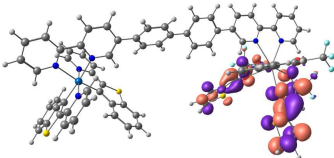
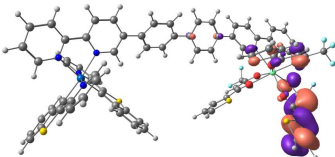
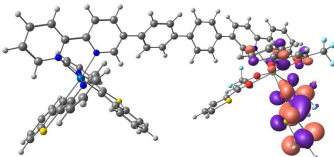
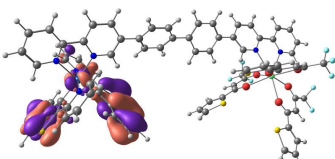
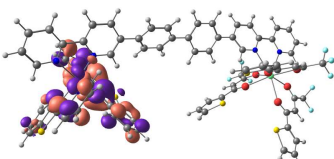
# for fragmentation scheme see Figure S23



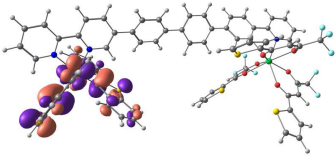
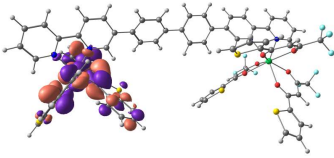
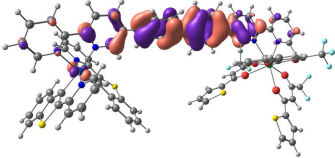
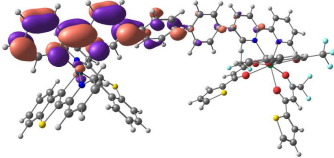
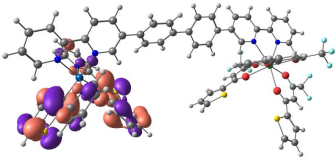
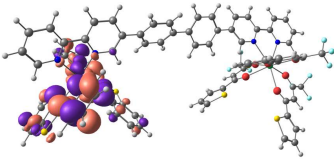
**Figure S29.** TDDFT spectra of  $11\text{Ln}$  (Ln = Nd, Gd, Yb). Singlets with  $f > 0.1$  are indicated. Experimental spectra are given for comparison.

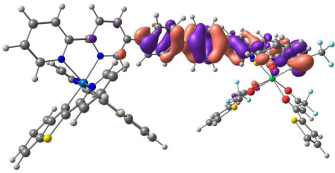
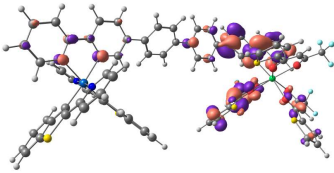
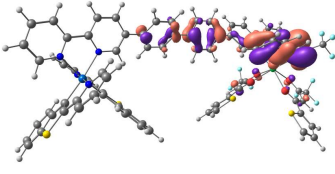
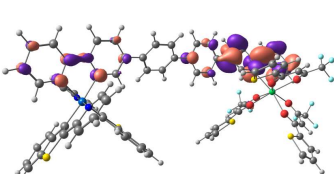
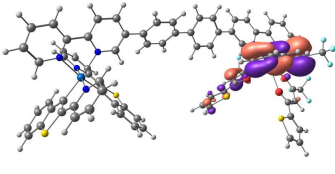
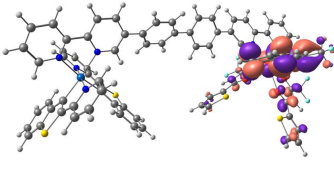
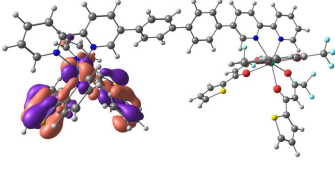
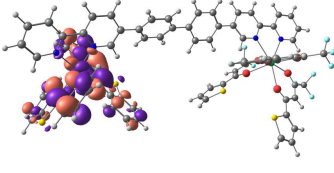
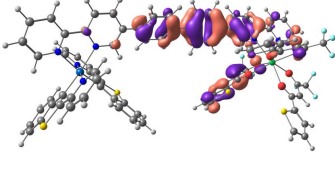
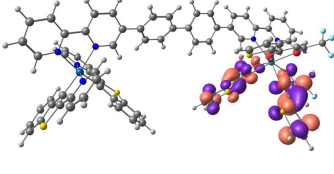
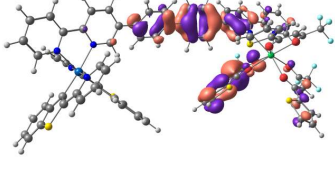
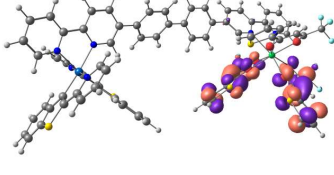
**Table S9.** Natural Transition Orbital analysis of **singlets** with oscillator strength  $f > 0.1$  in  $11^{Ln}$  (Ln = Nd, Gd, Yb).

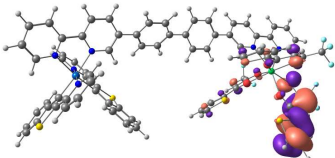
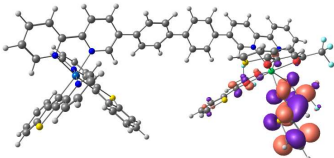
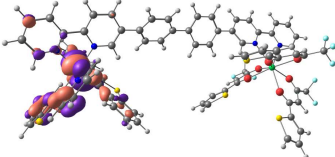
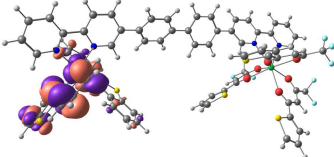
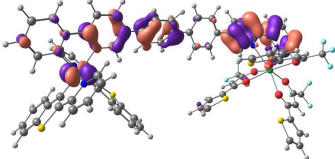
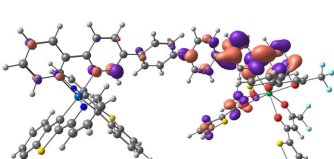
Excited state	$\lambda$ , nm	$f$	NTO and its population over fragments <sup>#</sup>	NTO* and its population over fragments <sup>#</sup>	Transition character
<b><math>11^{Nd}</math></b>					
S <sub>3</sub>	448	0.1045	 Fr2 = 0.37, Fr3 = 0.33, Fr1 = 0.29, Fr4 = 0.01	 Fr3 = 0.61, Fr2 = 0.32, Fr1 = 0.09	LC, MLCT
S <sub>7</sub>	408	1.0084	 Fr5 = 0.51, Fr4 = 0.46, Fr1 = 0.02	 Fr4 = 0.88, Fr5 = 0.10, Fr1 = 0.03	LC
S <sub>16</sub>	377	0.1377	 Fr2 = 0.48, Fr3 = 0.48, Fr1 = 0.03	 Fr2 = 0.64, Fr3 = 0.29, Fr1 = 0.05, Fr4 = 0.01	LC
S <sub>27</sub>	356	0.1554	 Fr5 = 0.46, Fr9 = 0.32, Fr4 = 0.19, Fr7 = 0.02	 Fr7 = 0.48, Fr5 = 0.26, Fr8 = 0.20, Fr4 = 0.04	LC, LLCT
S <sub>37</sub>	343	0.1318	 Fr9 = 0.82, Fr7 = 0.13, Fr6 = 0.03, Fr8 = 0.01	 Fr9 = 0.69, Fr8 = 0.19, Fr7 = 0.11, Fr5 = 0.02	LC
S <sub>41</sub>	333	0.1991	 Fr3 = 0.43, Fr2 = 0.34, Fr1 = 0.22, Fr4 = 0.01	 Fr5 = 0.57, Fr4 = 0.39, Fr6 = 0.01	LLCT, MLCT

S <sub>42</sub>	333	0.1655			LLCT, LC
			Fr5 = 0.52, Fr4 = 0.22, Fr7 = 0.15, Fr9 = 0.08, Fr8 = 0.03	Fr8 = 0.67, Fr7 = 0.26, Fr9 = 0.03, Fr5 = 0.01	
S <sub>45</sub>	330	1.3418			LC
			Fr8 = 0.78, Fr9 = 0.13, Fr5 = 0.05, Fr4 = 0.02	Fr8 = 0.83, Fr9 = 0.14, Fr5 = 0.02, Fr7 = 0.01	
S <sub>46</sub>	330	0.2098			LC
			Fr3 = 0.67, Fr2 = 0.27, Fr1 = 0.05	Fr3 = 0.66, Fr2 = 0.30, Fr1 = 0.04	

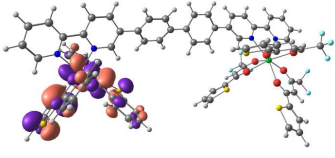
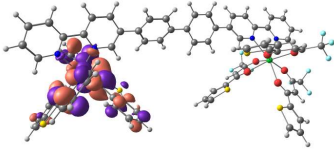
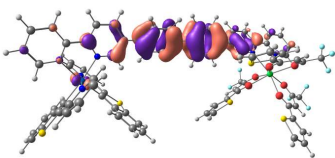
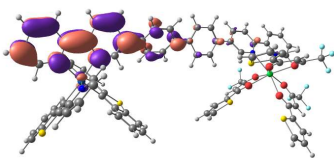
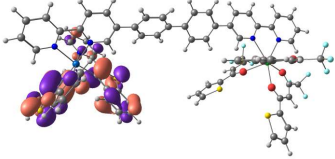
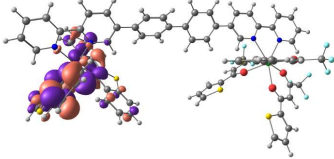
### 11<sup>Gd</sup>

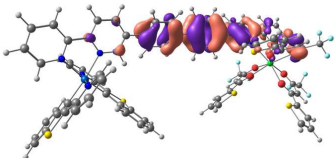
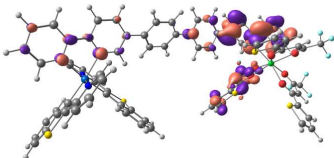
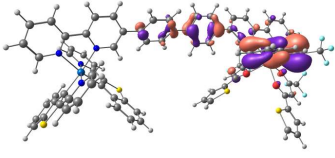
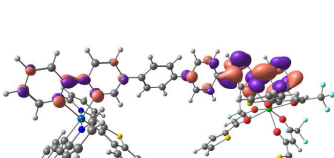
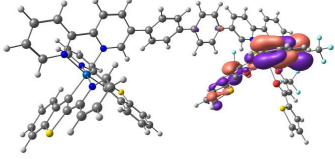
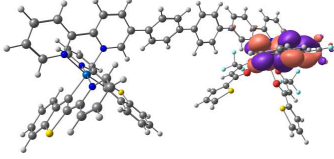
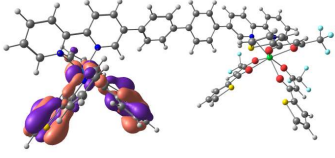
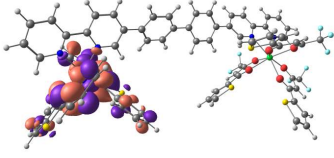
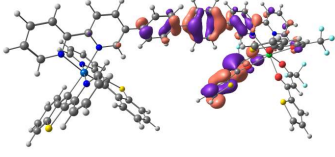
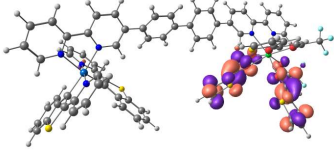
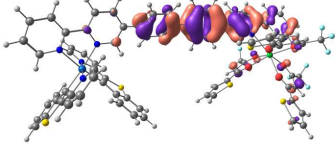
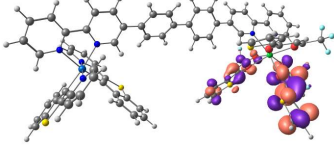
S <sub>3</sub>	448	0.1039			LC, MLCT
			Fr2 = 0.37, Fr3 = 0.32, Fr1 = 0.29, Fr4 = 0.01	Fr3 = 0.63, Fr2 = 0.30, Fr1 = 0.09	
S <sub>7</sub>	408	1.0026			LC
			Fr5 = 0.51, Fr4 = 0.46, Fr1 = 0.02	Fr4 = 0.89, Fr5 = 0.09, Fr1 = 0.03	
S <sub>16</sub>	377	0.1377			LC
			Fr2 = 0.48, Fr3 = 0.48, Fr1 = 0.03, Fr4 = 0.01	Fr2 = 0.66, Fr3 = 0.27, Fr1 = 0.05, Fr4 = 0.01	

S <sub>27</sub>	356	0.1838			LC, LLCT
			Fr5 = 0.50, Fr8 = 0.27, Fr4 = 0.20, Fr7 = 0.03	Fr5 = 0.54, Fr7 = 0.27, Fr4 = 0.10, Fr9 = 0.08, Fr6 = 0.02	
S <sub>32</sub>	352	0.1196			LLCT, LC
			Fr8 = 0.66, Fr5 = 0.17, Fr4 = 0.08, Fr7 = 0.05, Fr6 = 0.02, Fr9 = 0.02	Fr5 = 0.82, Fr4 = 0.14, Fr6 = 0.02	
S <sub>37</sub>	342	0.1302			LC
			Fr8 = 0.80, Fr7 = 0.14, Fr6 = 0.03, Fr5 = 0.02, Fr4 = 0.01	Fr8 = 0.79, Fr9 = 0.13, Fr7 = 0.06, Fr5 = 0.02	
S <sub>41</sub>	333	0.3107			LC, MLCT
			Fr2 = 0.43, Fr3 = 0.36, Fr1 = 0.19, Fr4 = 0.02, Fr5 = 0.01	Fr3 = 0.51, Fr2 = 0.43, Fr1 = 0.08	
S <sub>43</sub>	331	0.2249			LLCT, LC
			Fr5 = 0.46, Fr7 = 0.25, Fr4 = 0.19, Fr8 = 0.08, Fr9 = 0.02	Fr9 = 0.60, Fr7 = 0.34, Fr8 = 0.04, Fr5 = 0.01	
S <sub>44</sub>	330	0.3216			LC, LLCT
			Fr7 = 0.43, Fr5 = 0.33, Fr4 = 0.14, Fr9 = 0.08, Fr8 = 0.01	Fr9 = 0.54, Fr7 = 0.39, Fr5 = 0.04, Fr8 = 0.02, Fr4 = 0.01	

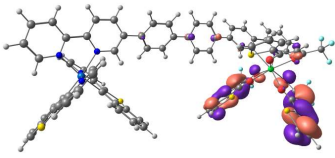
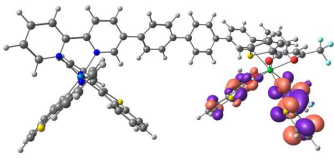
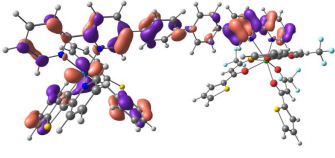
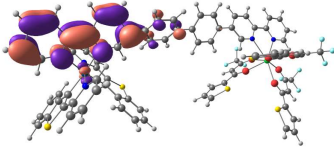
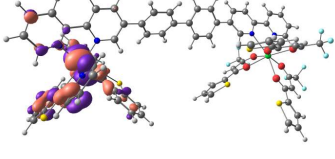
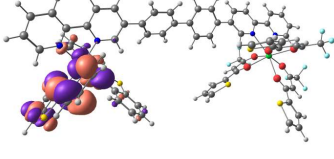
S <sub>47</sub>	329	0.9061			LC
			Fr9 = 0.82, Fr8 = 0.09, Fr7 = 0.06, Fr5 = 0.02	Fr9 = 0.86, Fr7 = 0.08, Fr8 = 0.05, Fr5 = 0.02	
S <sub>83</sub>	302	0.2795			LC, MLCT
			Fr1 = 0.58, Fr2 = 0.21, Fr3 = 0.13, Fr4 = 0.07	Fr2 = 0.79, Fr3 = 0.13, Fr1 = 0.06	
S <sub>90</sub>	297	0.1478			LC, LLCT, MLCT
			Fr5 = 0.48, Fr4 = 0.28, Fr1 = 0.12, Fr3 = 0.04, Fr8 = 0.04, Fr7 = 0.03, Fr2 = 0.01	Fr5 = 0.71, Fr7 = 0.13, Fr4 = 0.13, Fr6 = 0.03, Fr9 = 0.01	

11<sup>Yb</sup>

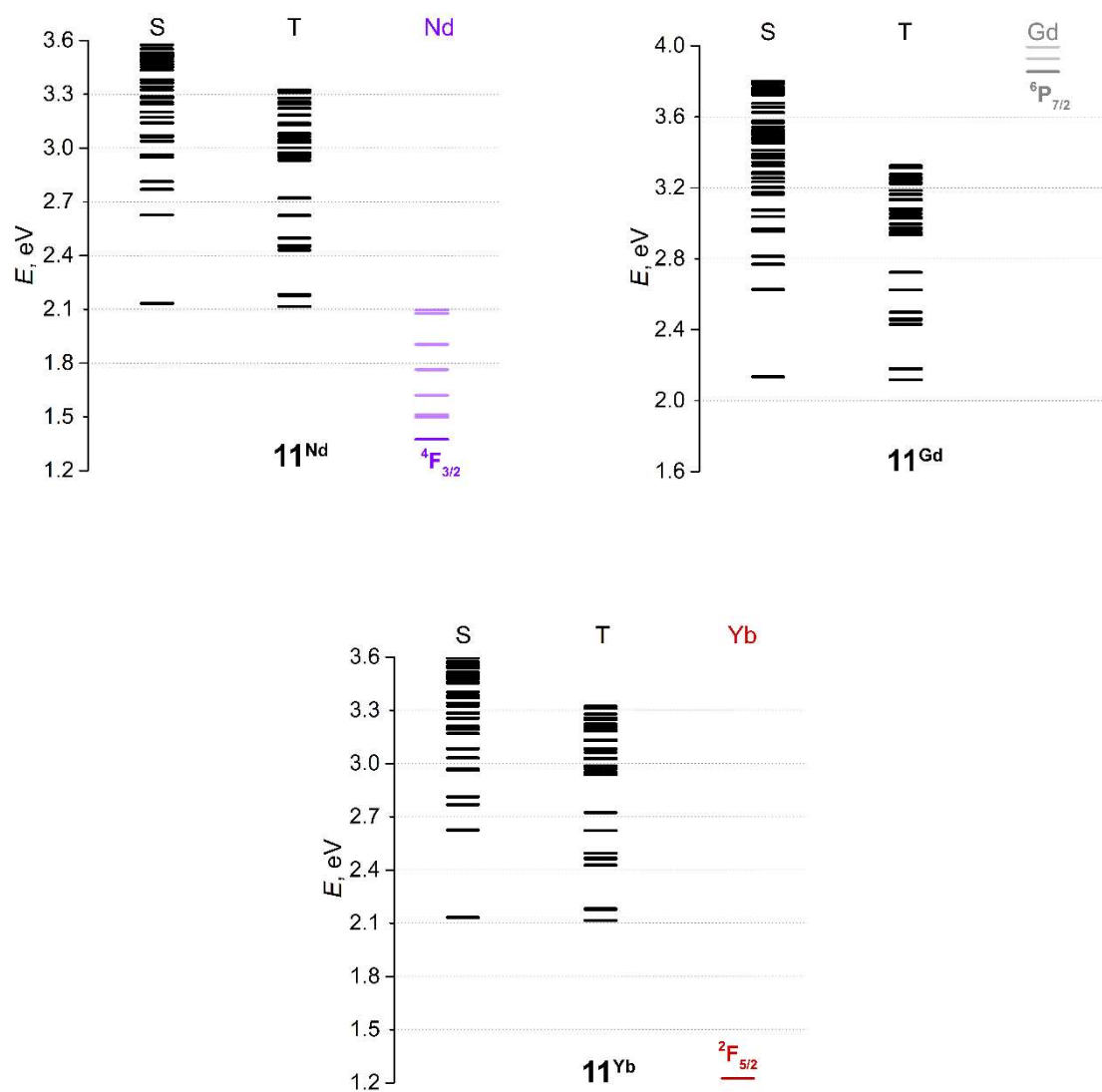
S <sub>3</sub>	448	0.1042			LC, MLCT
			Fr2 = 0.37, Fr3 = 0.32, Fr1 = 0.29, Fr4 = 0.01	Fr3 = 0.62, Fr2 = 0.31, Fr1 = 0.09	
S <sub>7</sub>	409	1.0003			LC
			Fr5 = 0.51, Fr4 = 0.45, Fr1 = 0.02	Fr4 = 0.89, Fr5 = 0.09, Fr1 = 0.03	
S <sub>16</sub>	377	0.1380			LC
			Fr2 = 0.48, Fr3 = 0.48, Fr1 = 0.03, Fr4 = 0.01	Fr2 = 0.66, Fr3 = 0.28, Fr1 = 0.05, Fr4 = 0.01	

S <sub>28</sub>	355	0.1766			LC, LLCT
			Fr5 = 0.62, Fr4 = 0.25, Fr7 = 0.12	Fr5 = 0.64, Fr8 = 0.21, Fr4 = 0.12, Fr9 = 0.02	
S <sub>32</sub>	350	0.1258			LLCT, LC
			Fr7 = 0.67, Fr5 = 0.17, Fr4 = 0.08, Fr8 = 0.06, Fr6 = 0.01, Fr9 = 0.01	Fr5 = 0.83, Fr4 = 0.14	
S <sub>37</sub>	341	0.1603			LC
			Fr7 = 0.70, Fr8 = 0.21, Fr5 = 0.05, Fr4 = 0.02, Fr6 = 0.02	Fr7 = 0.93, Fr5 = 0.04, Fr8 = 0.01	
S <sub>41</sub>	333	0.2828			LC, MLCT
			Fr2 = 0.41, Fr3 = 0.36, Fr1 = 0.19, Fr4 = 0.02, Fr5 = 0.01	Fr3 = 0.52, Fr2 = 0.43, Fr1 = 0.08	
S <sub>43</sub>	330	0.6382			LLCT, LC
			Fr8 = 0.53, Fr5 = 0.29, Fr4 = 0.11, Fr7 = 0.04	Fr8 = 0.54, Fr9 = 0.39, Fr3 = 0.03, Fr7 = 0.02, Fr5 = 0.01	
S <sub>46</sub>	329	0.5194			LLCT
			Fr5 = 0.63, Fr4 = 0.21, Fr9 = 0.07, Fr8 = 0.05, Fr7 = 0.03	Fr9 = 0.75, Fr8 = 0.19, Fr4 = 0.02, Fr7 = 0.02, Fr5 = 0.01	



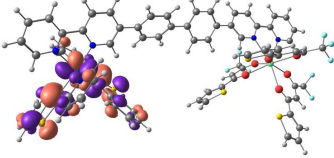
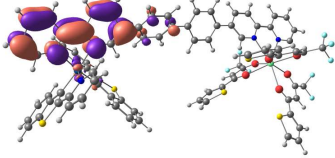
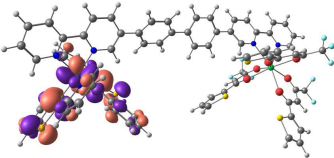
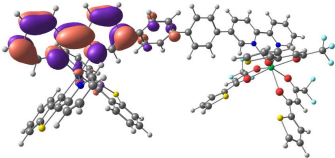
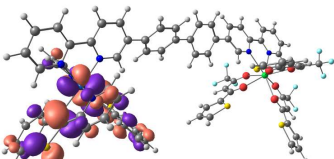
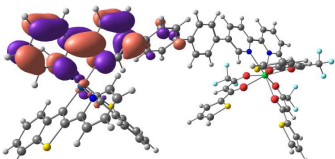
S <sub>48</sub>	327	0.1772	 Fr9 = 0.56, Fr8 = 0.28, Fr5 = 0.06, Fr7 = 0.05, Fr4 = 0.03, Fr6 = 0.02	 Fr9 = 0.73, Fr8 = 0.23, Fr7 = 0.02	LC
S <sub>50</sub>	326	0.1480	 Fr5 = 0.31, Fr4 = 0.29, Fr1 = 0.14, Fr3 = 0.13, Fr2 = 0.13	 Fr4 = 0.94, Fr5 = 0.03, Fr1 = 0.03	LC, LLCT, MLCT
S <sub>83</sub>	302	0.2505	 Fr1 = 0.59, Fr2 = 0.20, Fr3 = 0.13, Fr4 = 0.07	 Fr2 = 0.80, Fr3 = 0.12, Fr1 = 0.07, Fr4 = 0.01	LC, MLCT

# for fragmentation scheme see Figure S23



**Figure S30.** Excited state diagrams for  $11^{\text{Ln}}$  ( $\text{Ln} = \text{Nd, Gd, Yb}$ ) obtained from TDDFT calculations. Energy levels of lanthanides are shown in colour.

**Table S10.** Natural Transition Orbital analysis of **first triplets** in **11<sup>Ln</sup>** (Ln = Nd, Gd, Yb).

Complex	$\Delta E(S_0-T_1)$ , eV	NTO and its population over fragments <sup>#</sup>	NTO* and its population over fragments <sup>#</sup>	Transition character
<b>Ir(pybt)1<sup>Nd</sup></b>	2.1153	 Fr3 = 0.37, Fr2 = 0.35, Fr1 = 0.27, Fr4 = 0.01	 Fr4 = 0.89, Fr1 = 0.03, Fr3 = 0.03, Fr2 = 0.03, Fr5 = 0.02	LLCT, MLCT
<b>Ir(pybt)1<sup>Gd</sup></b>	2.1167	 Fr3 = 0.37, Fr2 = 0.34, Fr1 = 0.27, Fr4 = 0.01	 Fr4 = 0.89, Fr3 = 0.03, Fr1 = 0.03, Fr2 = 0.03, Fr5 = 0.02	LLCT, MLCT
<b>Ir(pybt)1<sup>Yb</sup></b>	2.1150	 Fr3 = 0.37, Fr2 = 0.34, Fr1 = 0.27, Fr4 = 0.01	 Fr4 = 0.90, Fr1 = 0.03, Fr3 = 0.03, Fr2 = 0.03, Fr5 = 0.02	LLCT, MLCT

<sup>#</sup> for fragmentation scheme see Figure S23

## References

- 1 V. N. Kozhevnikov, O. V. Shabunina, D. S. Kopchuk, M. M. Ustinova, B. König and D. N. Kozhevnikov, *Tetrahedron*, 2008, **64**, 8963–8973.
- 2 V. S. Sastri, J.-C. Bünzli, V. R. Rao, G. V. S. Rayudu and J. R. Perumareddi, in *Modern Aspects of Rare Earths and Their Complexes*, Elsevier, 2003, pp. 569–731.