

## **Supporting Information**

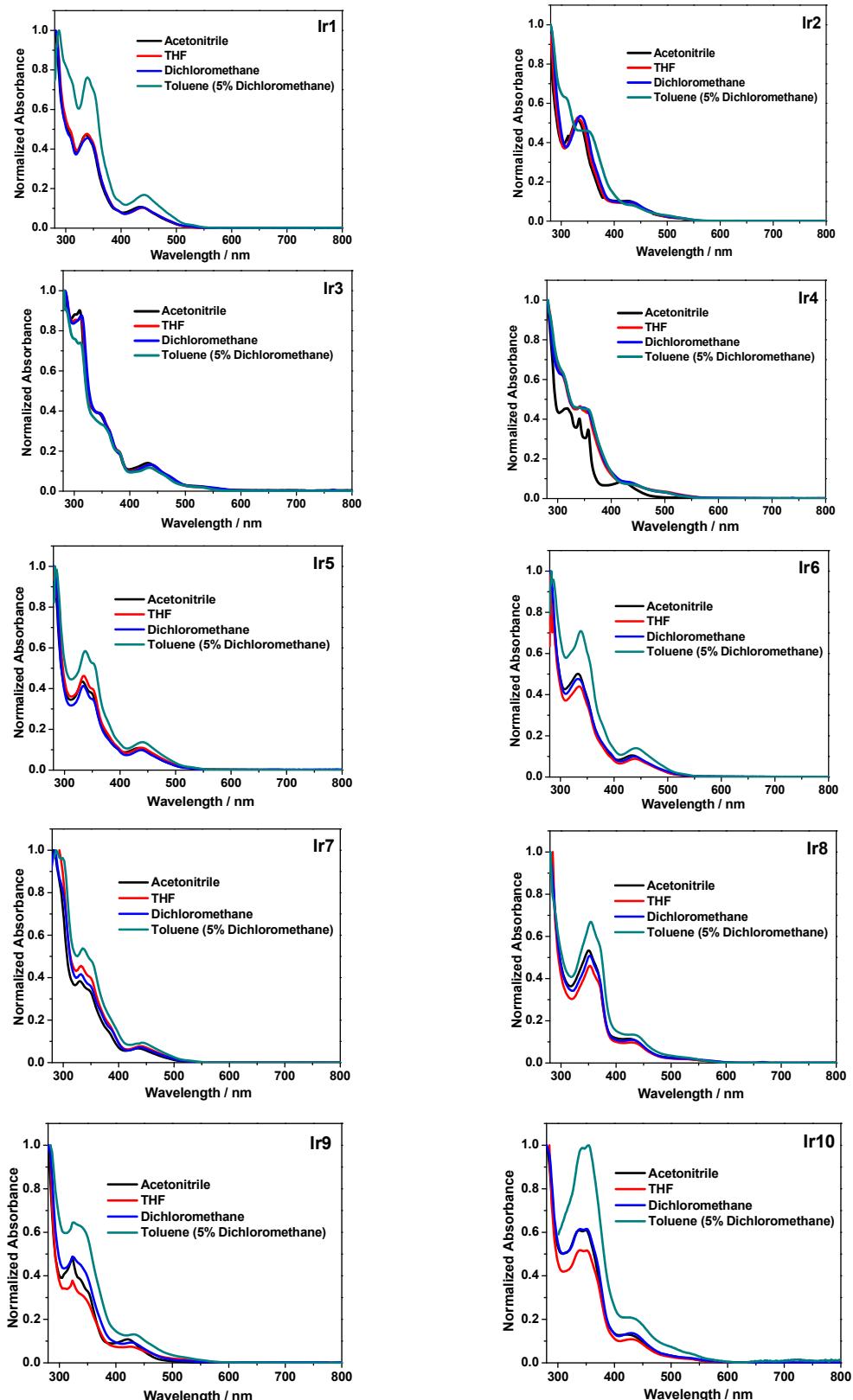
# **Impact of Benzannulation Site at the Diimine (N<sup>+</sup>N) Ligand on the Excited-State Properties and Reverse Saturable Absorption of Biscyclometalated Iridium(III) Complexes**

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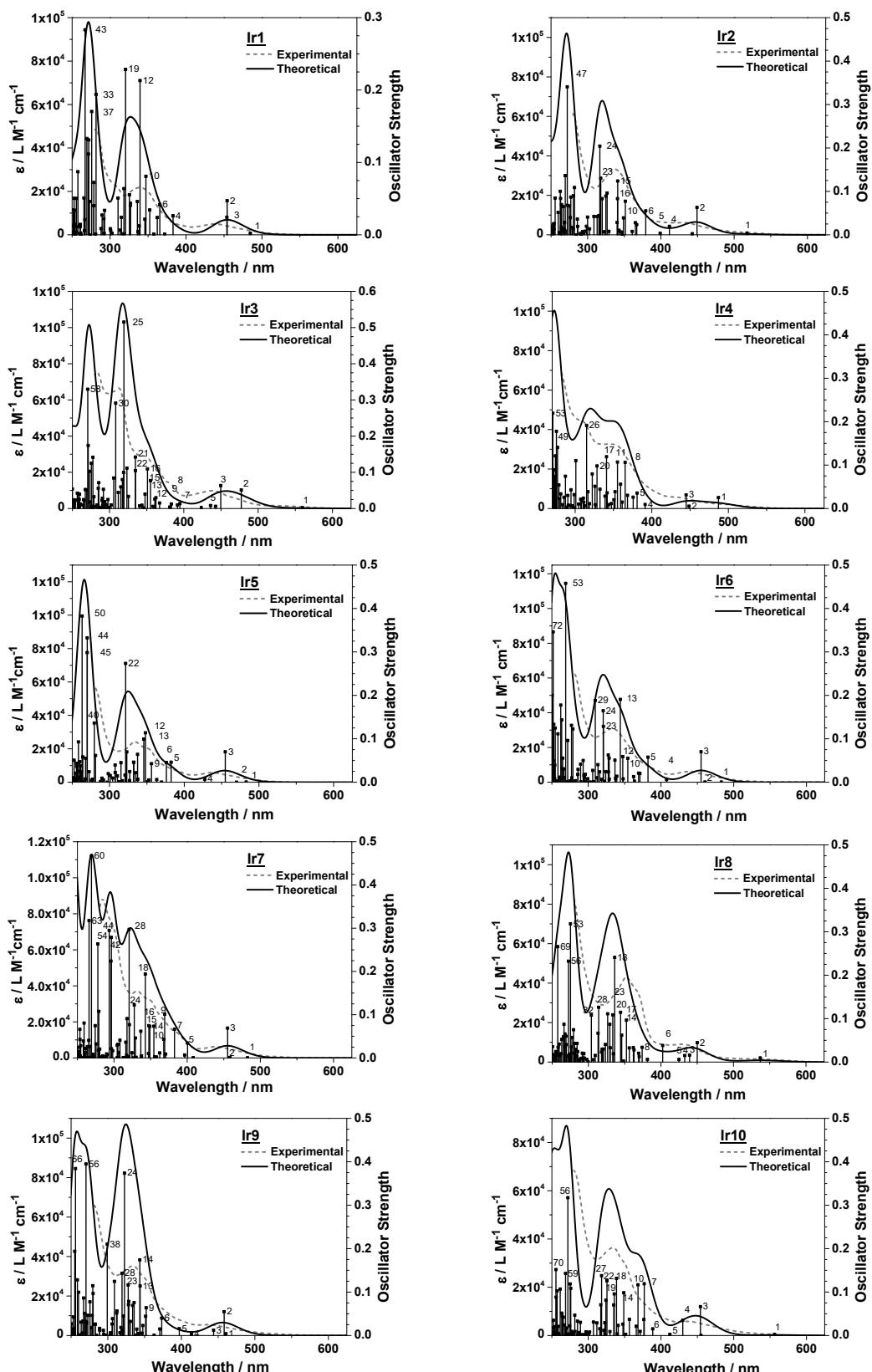
<sup>a</sup>Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58108–6050, United States

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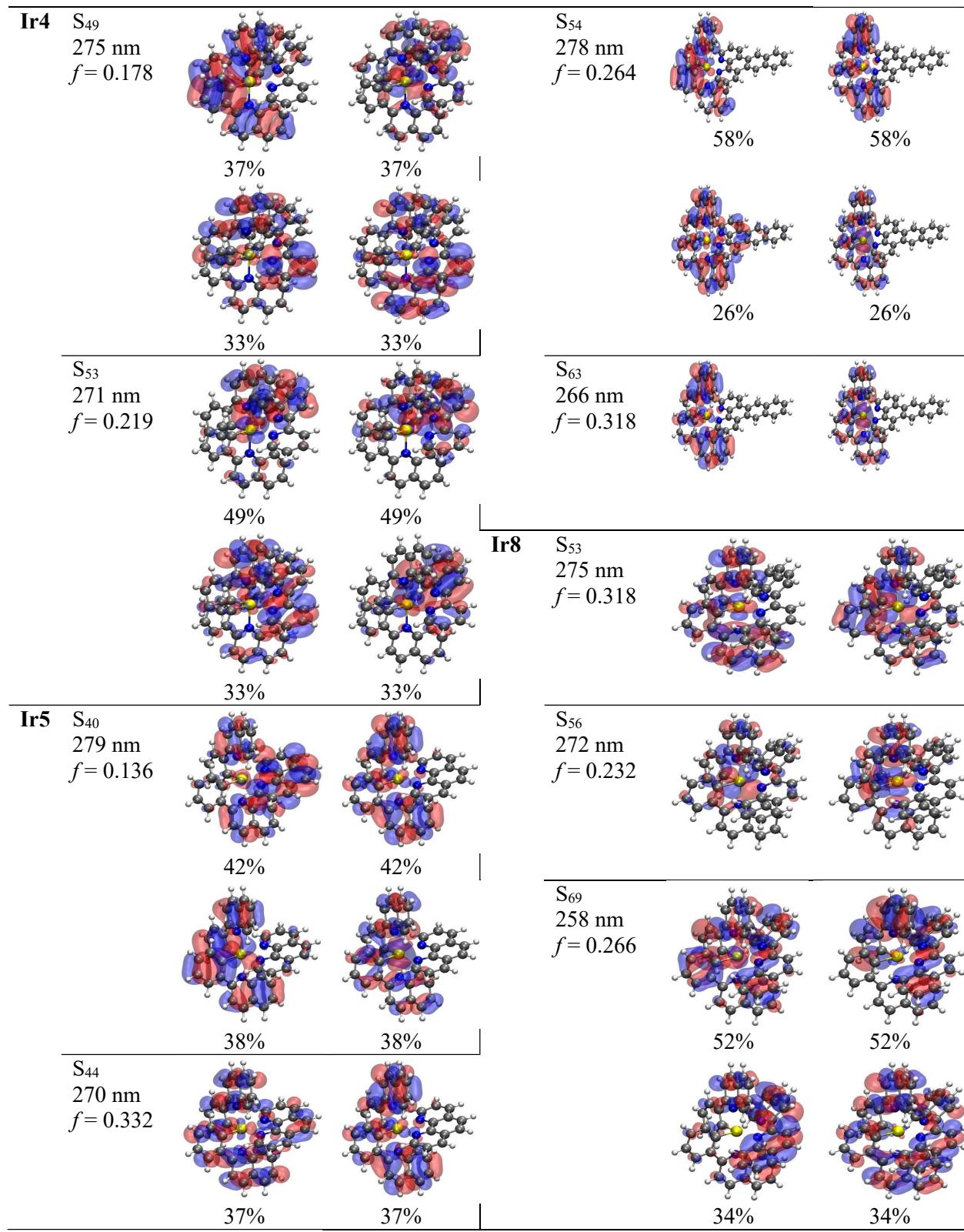
**Figure S1.** Normalized experimental absorption spectra of **Ir1–Ir10** in different solvents.

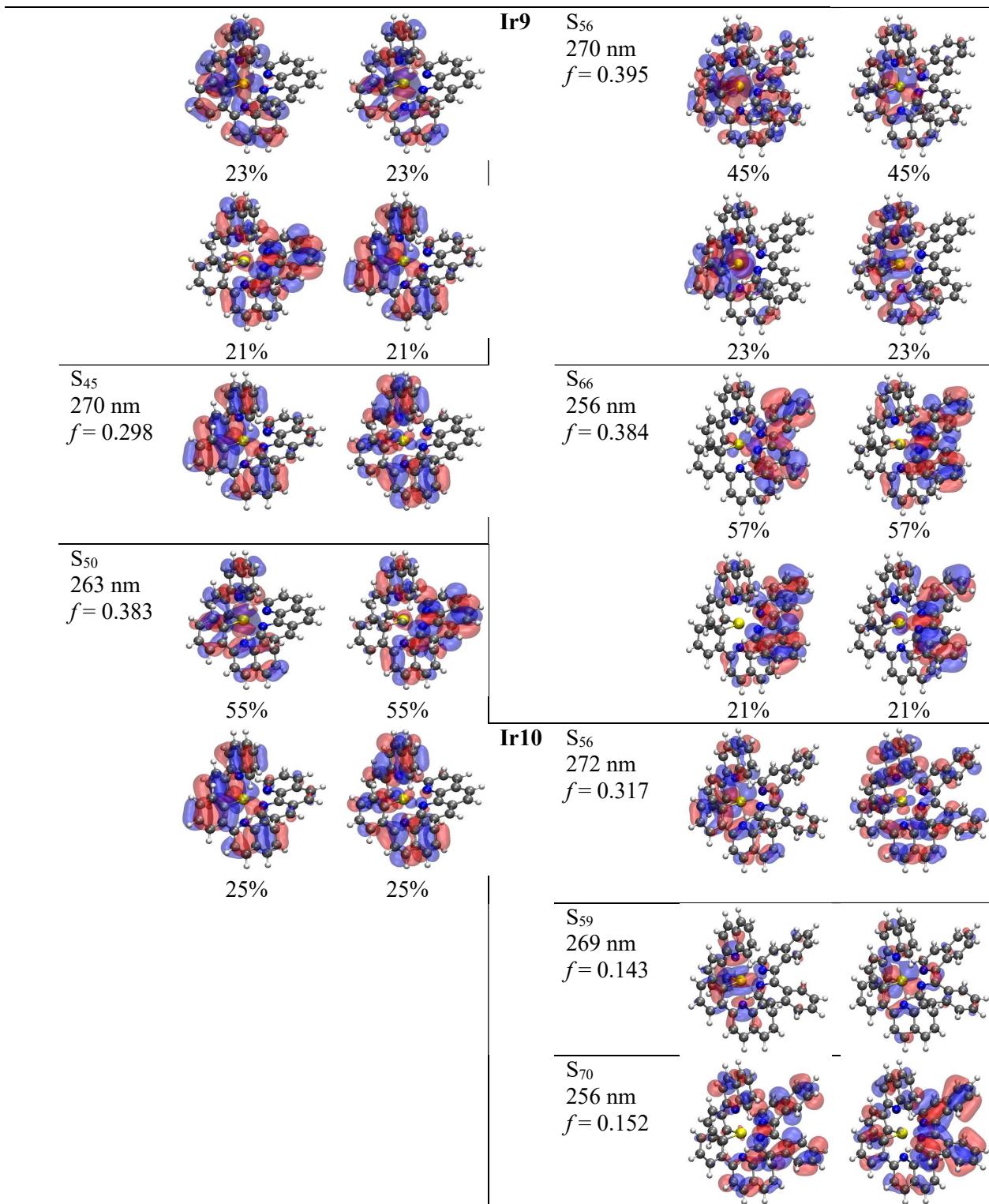


**Figure S2.** Comparison of the experimental and theoretical absorption spectra for **Ir1–Ir10** in  $CH_2Cl_2$ , the vertical sticks are the oscillator strength used to generate the theoretical spectra.

**Table S1.** NTOs for the high energy optical transitions (<300 nm) of **Ir1-Ir10** in CH<sub>2</sub>Cl<sub>2</sub>. The isovalue was set to 0.02.

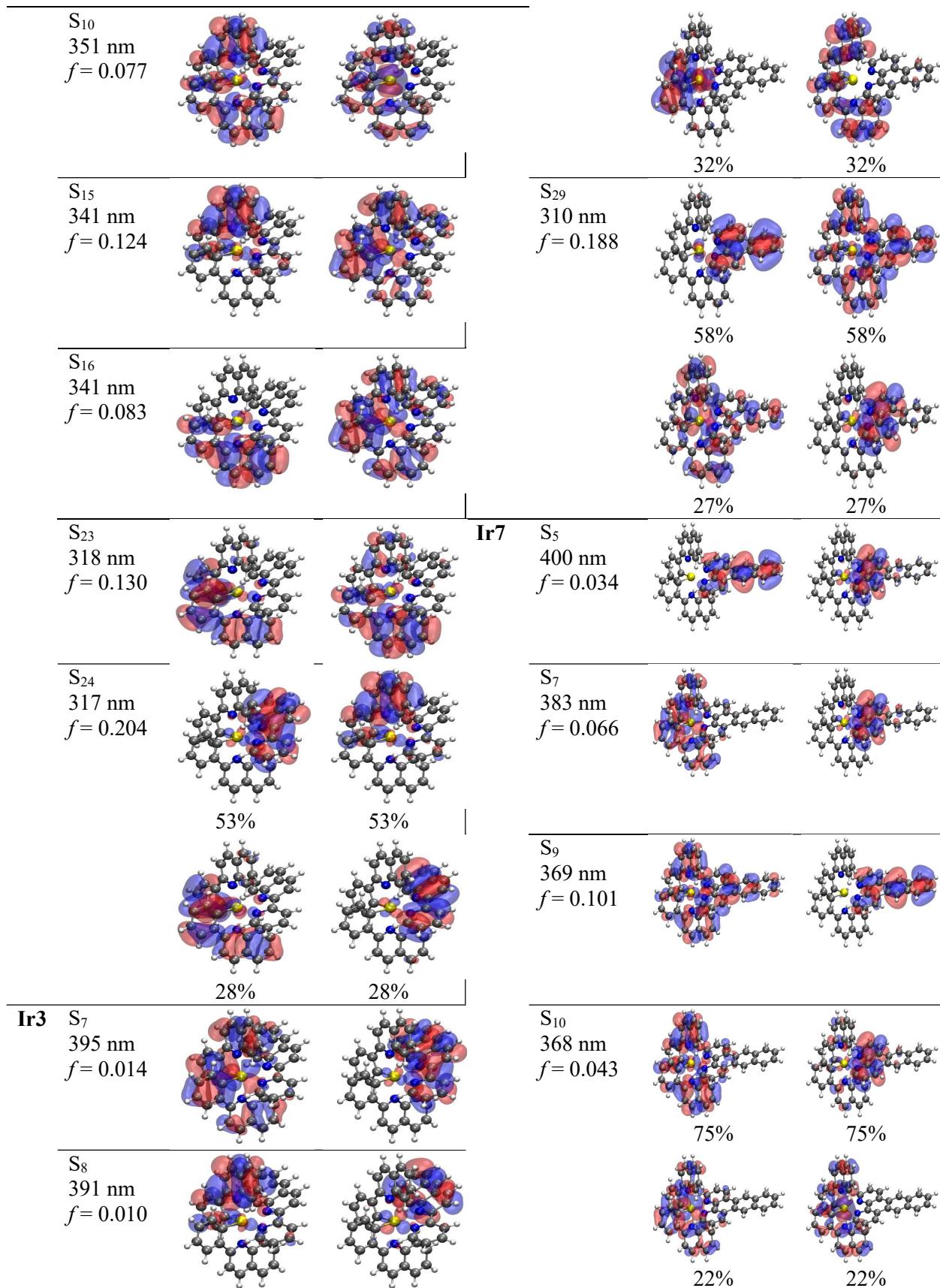
	State	Hole	Electron		State	Hole	Electron	
<b>Ir1</b>	S <sub>33</sub> 282 nm <i>f</i> = 0.194				<b>Ir6</b>	S <sub>53</sub> 269 nm <i>f</i> = 0.458		
<b>Ir1</b>	S <sub>37</sub> 276 nm <i>f</i> = 0.170				<b>Ir6</b>	S <sub>72</sub> 252 nm <i>f</i> = 0.346		
<b>Ir2</b>	S <sub>58</sub> 271 nm <i>f</i> = 0.330				<b>Ir7</b>	S <sub>42</sub> 296 nm <i>f</i> = 0.279		
<b>Ir3</b>	S <sub>47</sub> 272 nm <i>f</i> = 0.341							

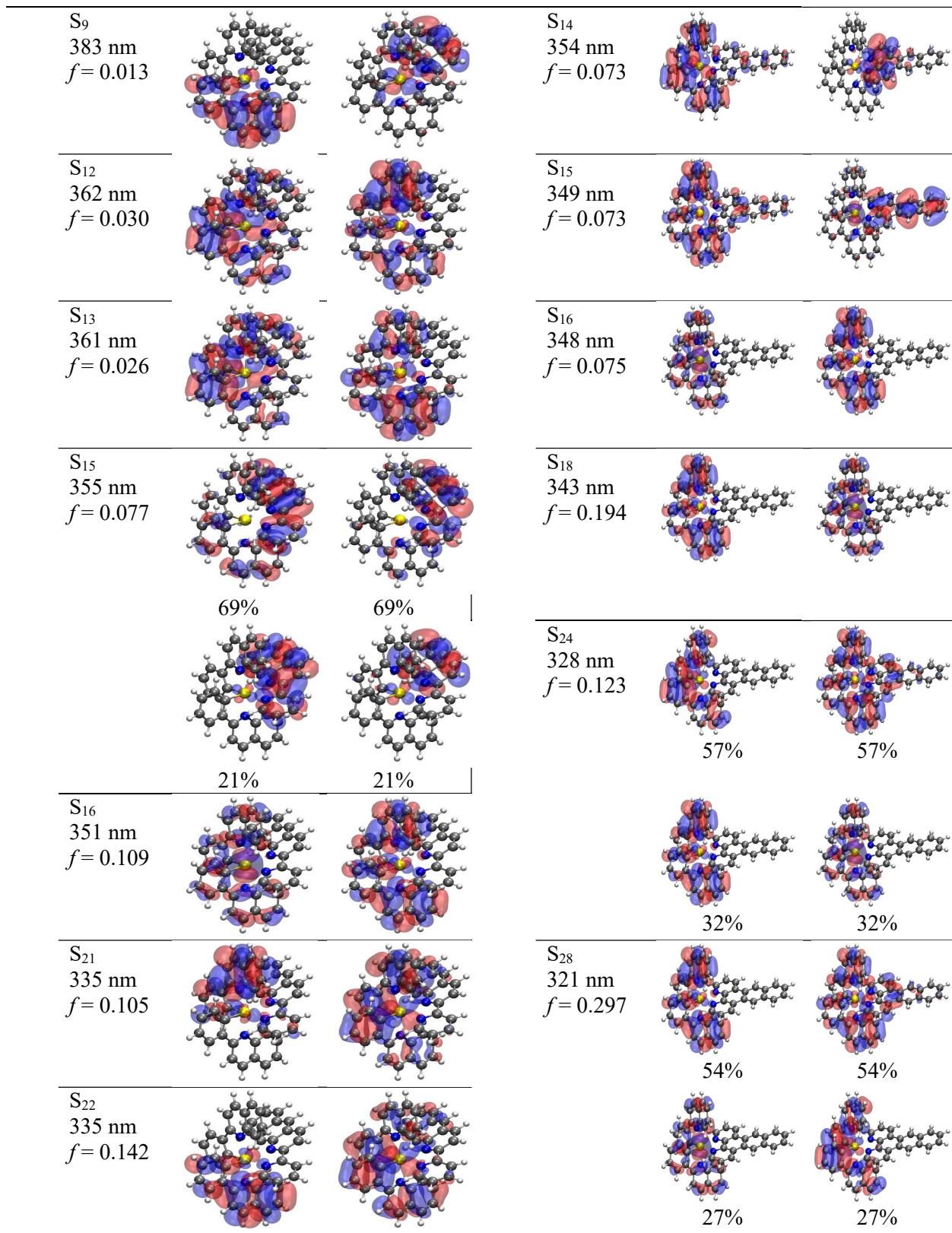


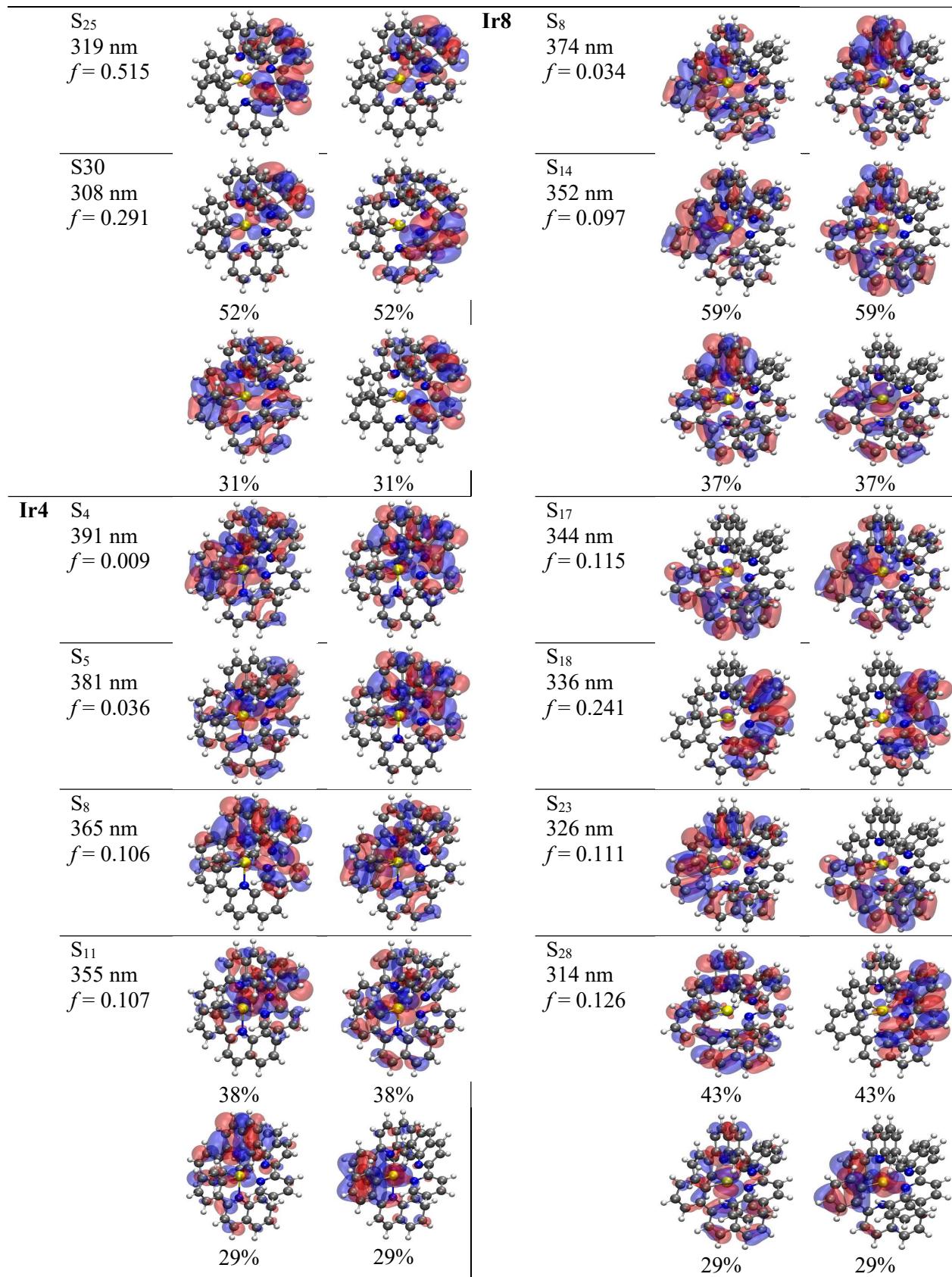


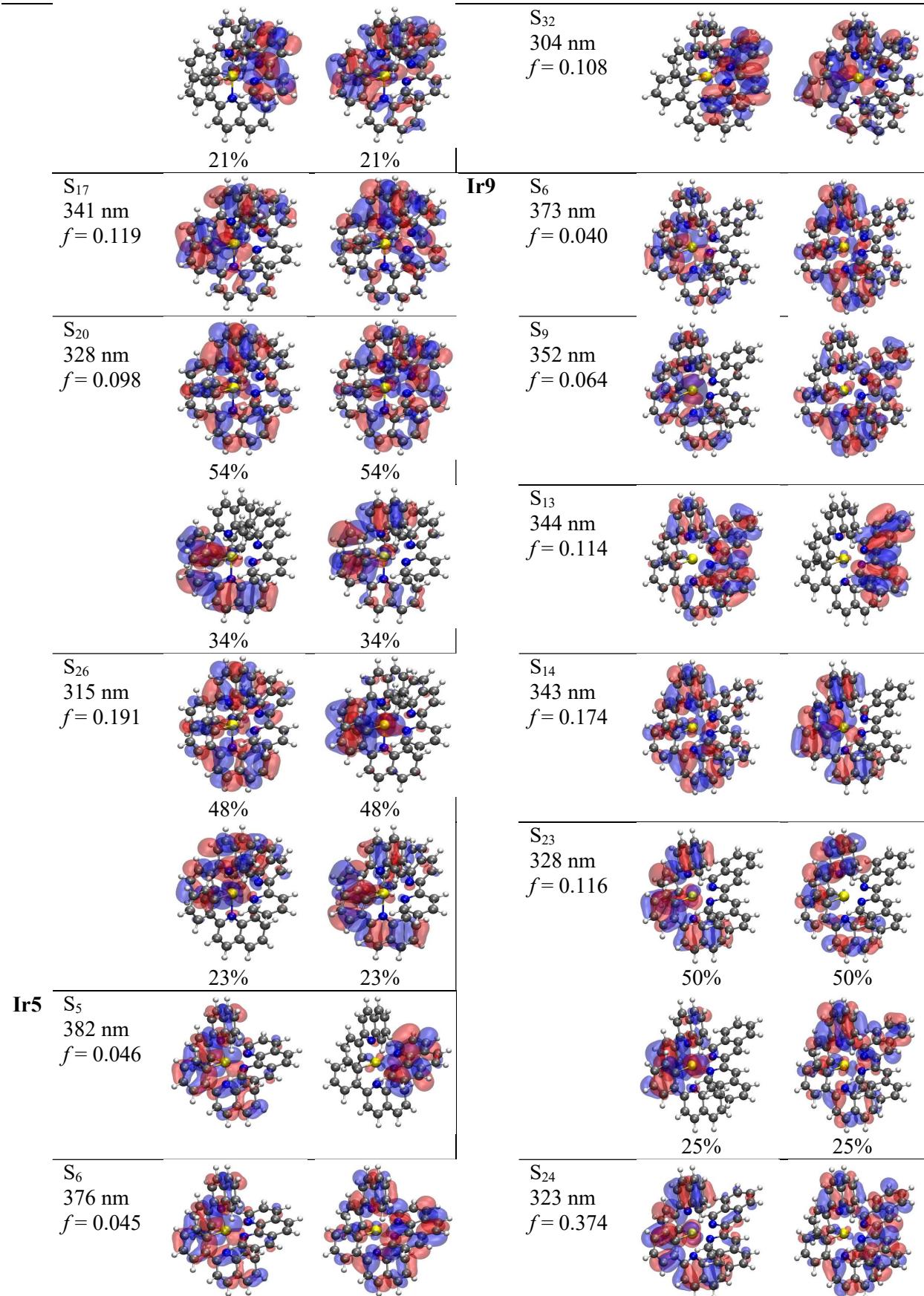
**Table S2.** NTOs for the optical transitions at 300 – 400 nm for **Ir1-Ir10** in CH<sub>2</sub>Cl<sub>2</sub>. The isovalue was set to 0.02.

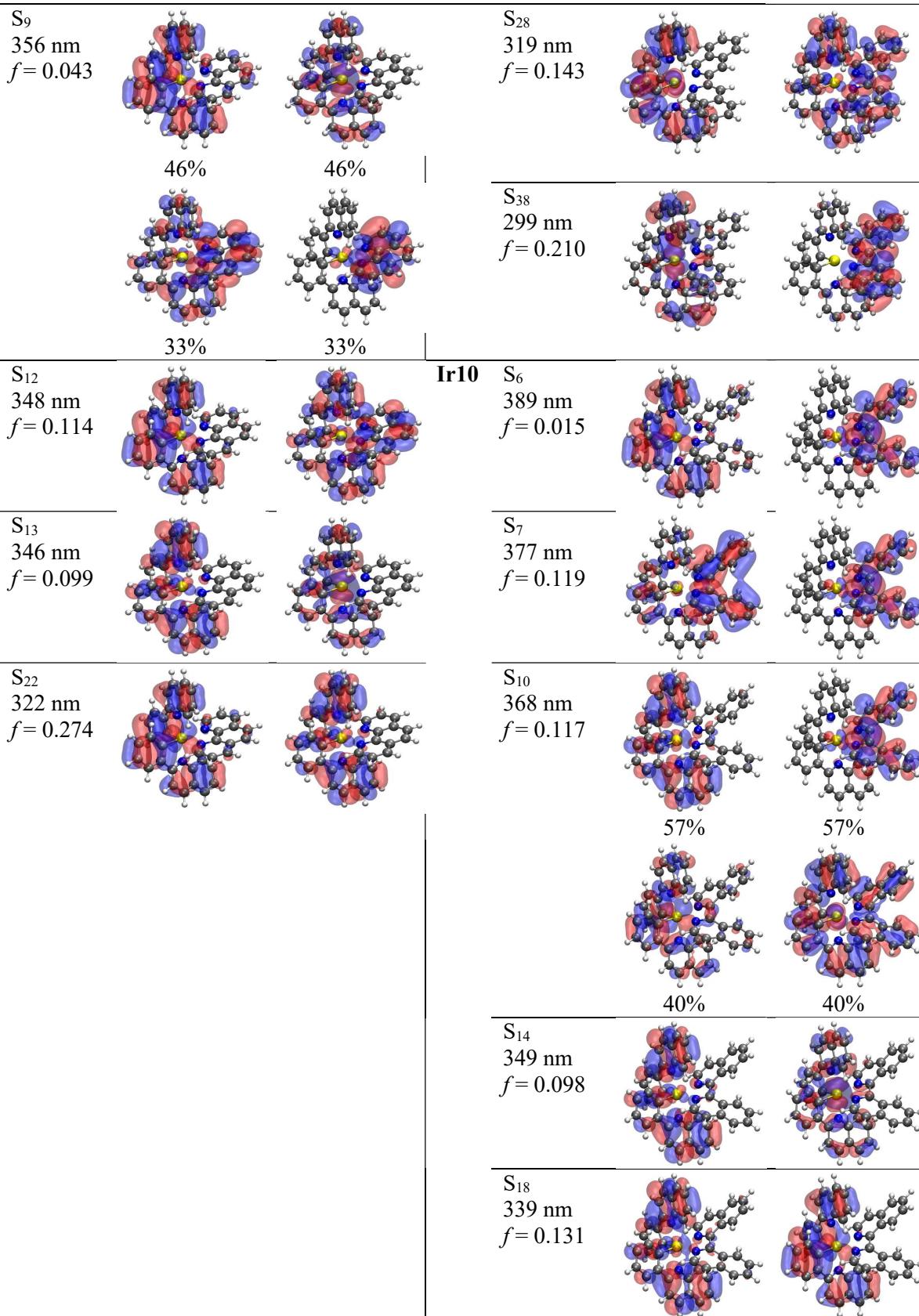
	State	Hole	Electron		State	Hole	Electron
<b>Ir1</b>	S <sub>4</sub> 383 nm $f = 0.026$				<b>Ir6</b> S <sub>5</sub> 382 nm $f = 0.058$		
	S <sub>6</sub> 365 nm $f = 0.042$				S <sub>10</sub> 354 nm $f = 0.055$		
	S <sub>10</sub> 347 nm $f = 0.081$				S <sub>12</sub> 347 nm $f = 0.059$		
	S <sub>12</sub> 339 nm $f = 0.213$				S <sub>13</sub> 344 nm $f = 0.191$		
	S <sub>19</sub> 320 nm $f = 0.229$				S <sub>23</sub> 321 nm $f = 0.129$		
		54%	54%			56%	56%
		39%	39%			27%	27%
<b>Ir2</b>	S <sub>6</sub> 379 nm $f = 0.055$				S <sub>24</sub> 321 nm $f = 0.164$		
						54%	54%

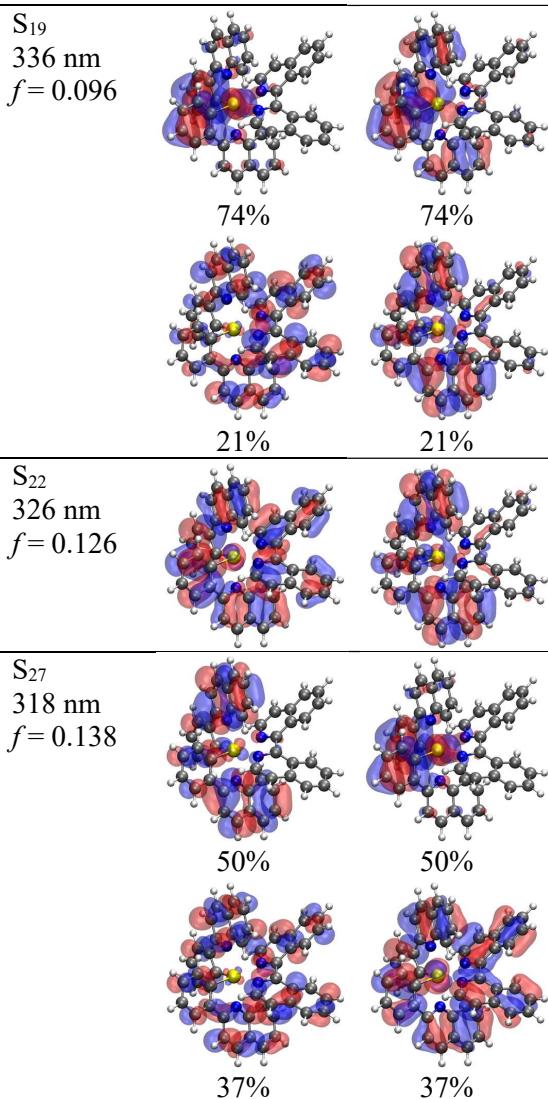




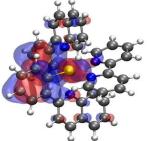
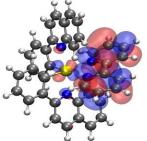
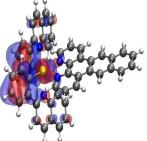
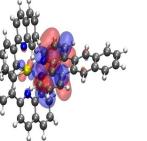
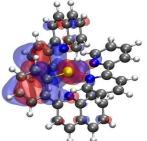
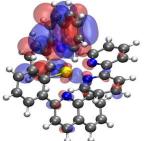
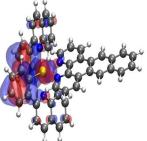
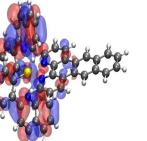
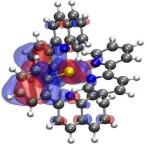
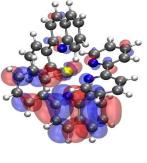
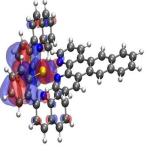
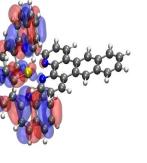
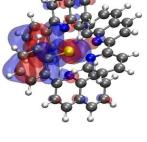
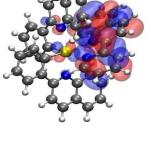
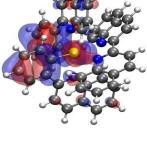
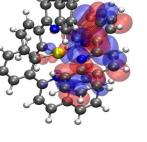
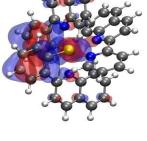
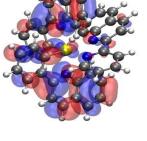
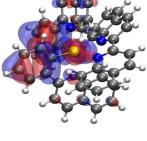
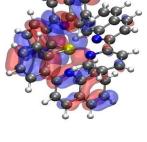
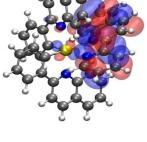
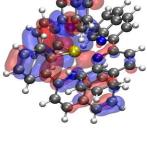
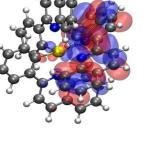
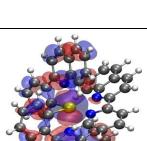
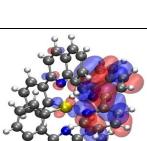
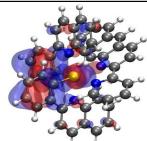
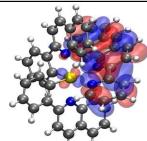
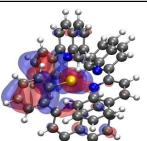
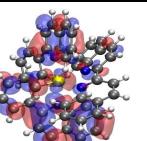


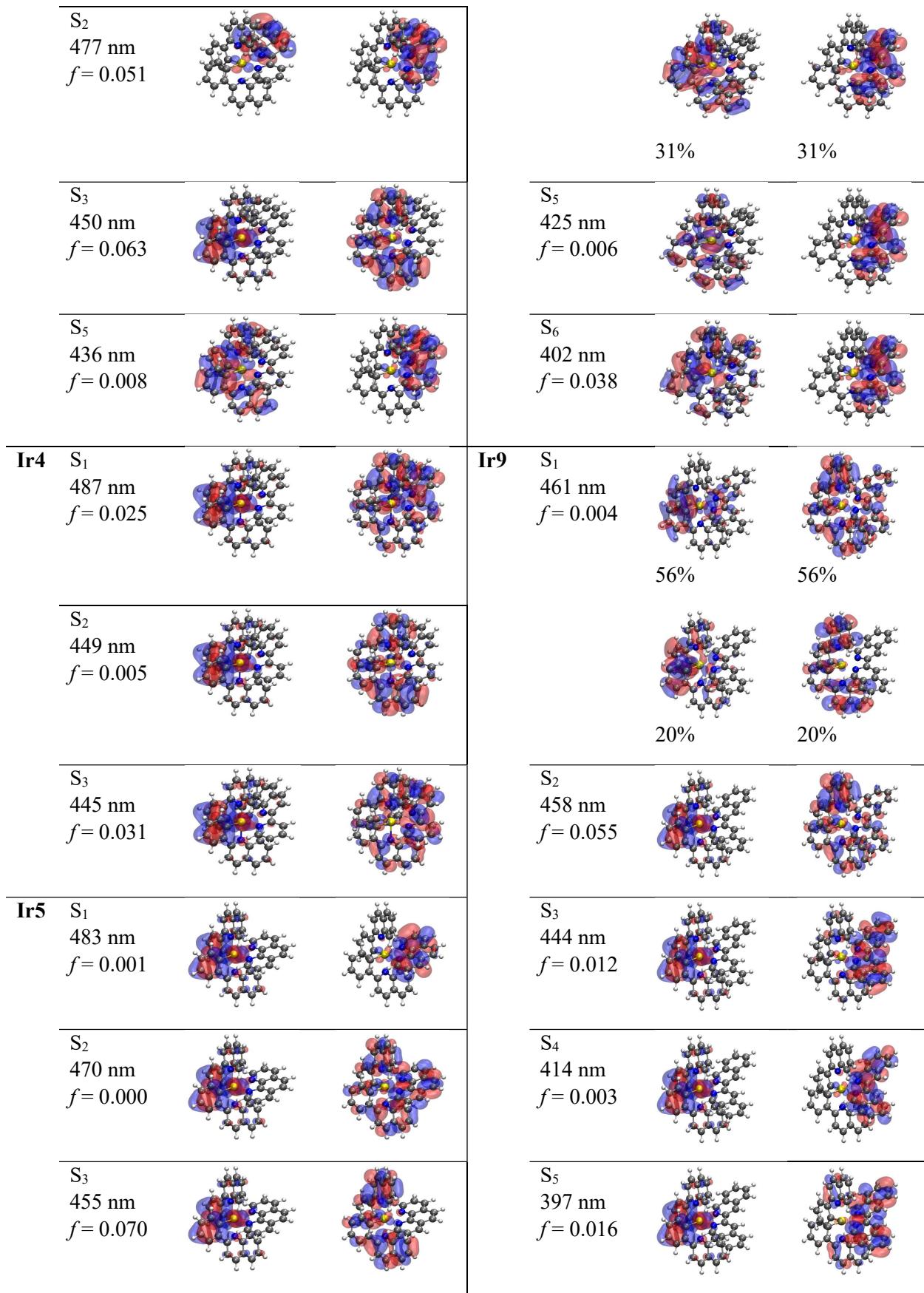


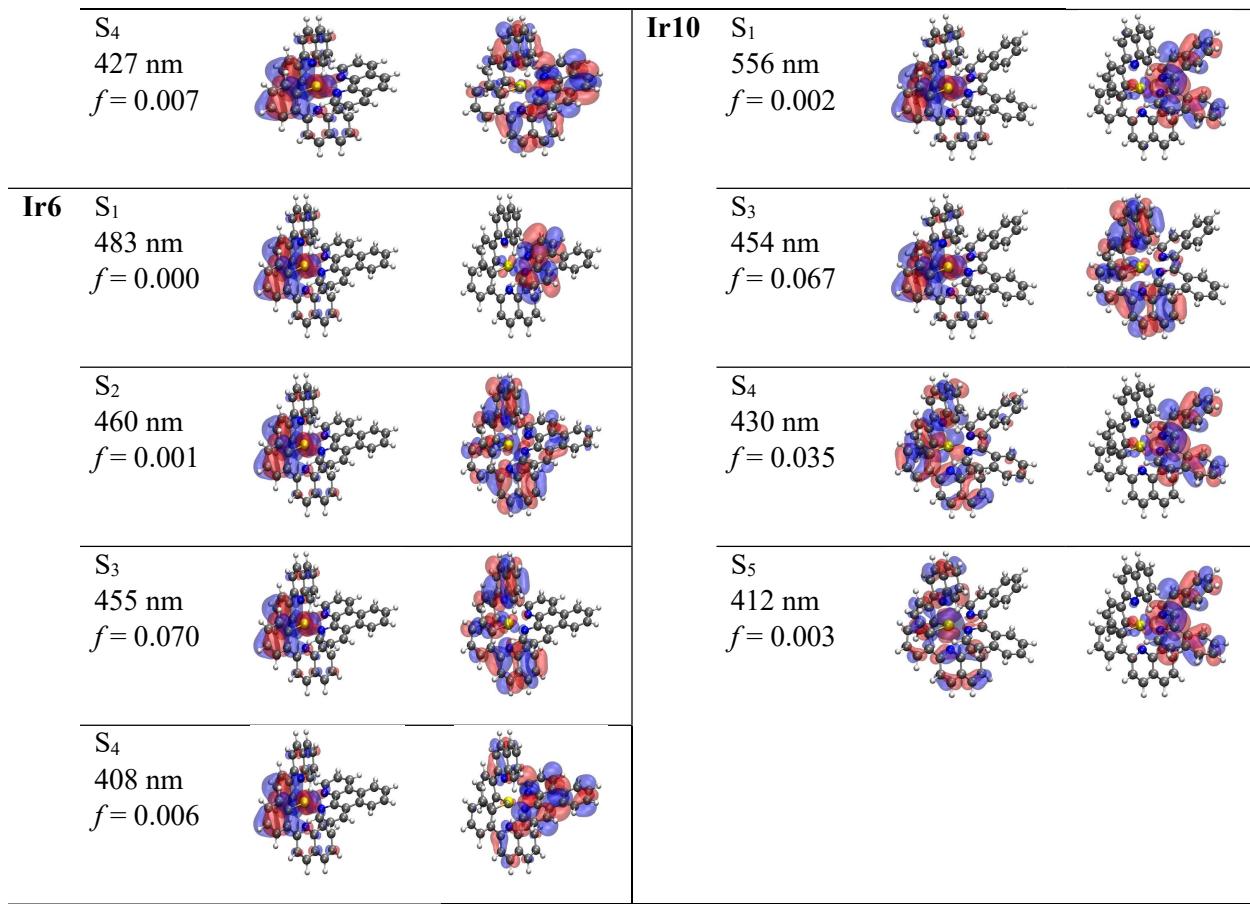




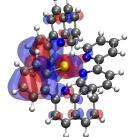
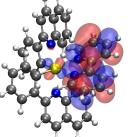
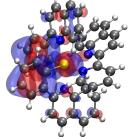
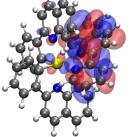
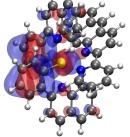
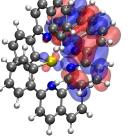
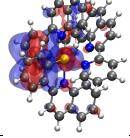
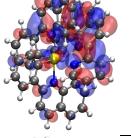
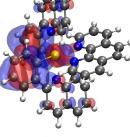
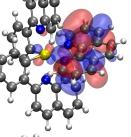
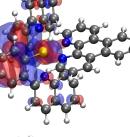
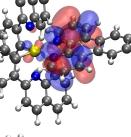
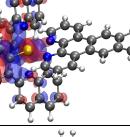
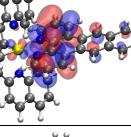
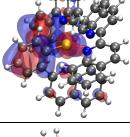
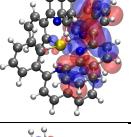
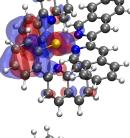
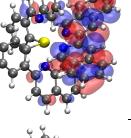
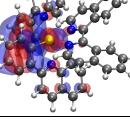
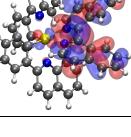
**Table S3.** NTOs for the optical transitions at 400 – 500 nm for **Ir1–Ir10** in CH<sub>2</sub>Cl<sub>2</sub>. The isovalue was set to 0.02.

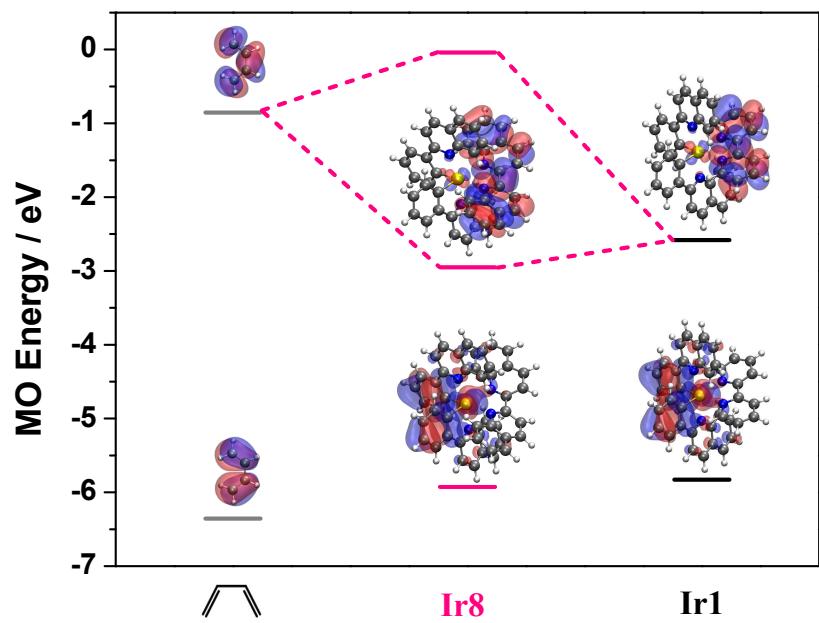
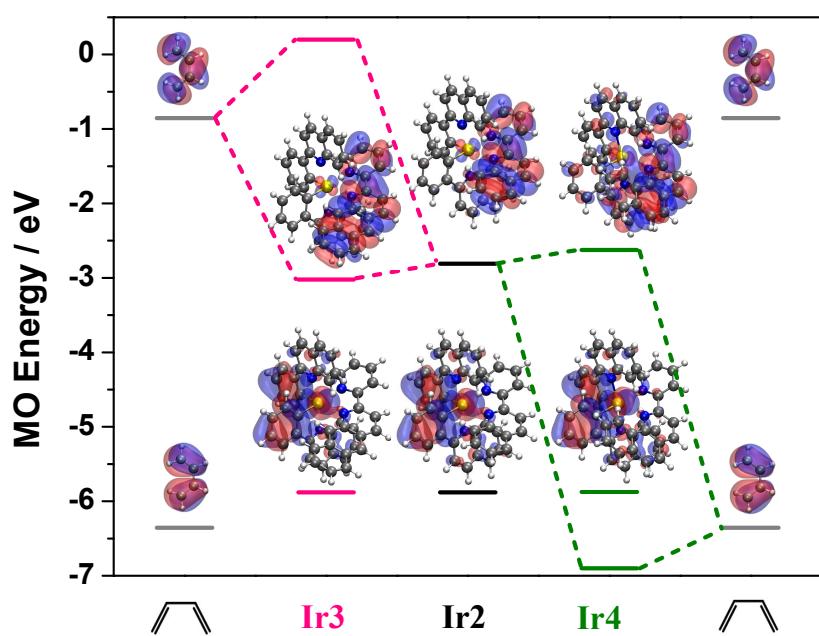
	State	Hole	Electron		State	Hole	Electron	
<b>Ir1</b>	S <sub>1</sub> 485 nm <i>f</i> = 0.002				<b>Ir7</b>	S <sub>1</sub> 482 nm <i>f</i> = 0.000		
	S <sub>2</sub> 454 nm <i>f</i> = 0.047					S <sub>2</sub> 458 nm <i>f</i> = 0.001		
	S <sub>3</sub> 454 nm <i>f</i> = 0.024					S <sub>3</sub> 455 nm <i>f</i> = 0.069		
<b>Ir2</b>	S <sub>1</sub> 517 nm <i>f</i> = 0.004				<b>Ir8</b>	S <sub>1</sub> 537 nm <i>f</i> = 0.010		
	S <sub>2</sub> 449 nm <i>f</i> = 0.063					S <sub>2</sub> 450 nm <i>f</i> = 0.045		
	S <sub>4</sub> 412 nm <i>f</i> = 0.019					S <sub>3</sub> 439 nm <i>f</i> = 0.016		
	S <sub>5</sub> 399 nm <i>f</i> = 0.003					69%	69%	
<b>Ir3</b>	S <sub>1</sub> 560 nm <i>f</i> = 0.002				<b>Ir8</b>	S <sub>4</sub> 433 nm <i>f</i> = 0.015		
						29%	29%	68% 68%



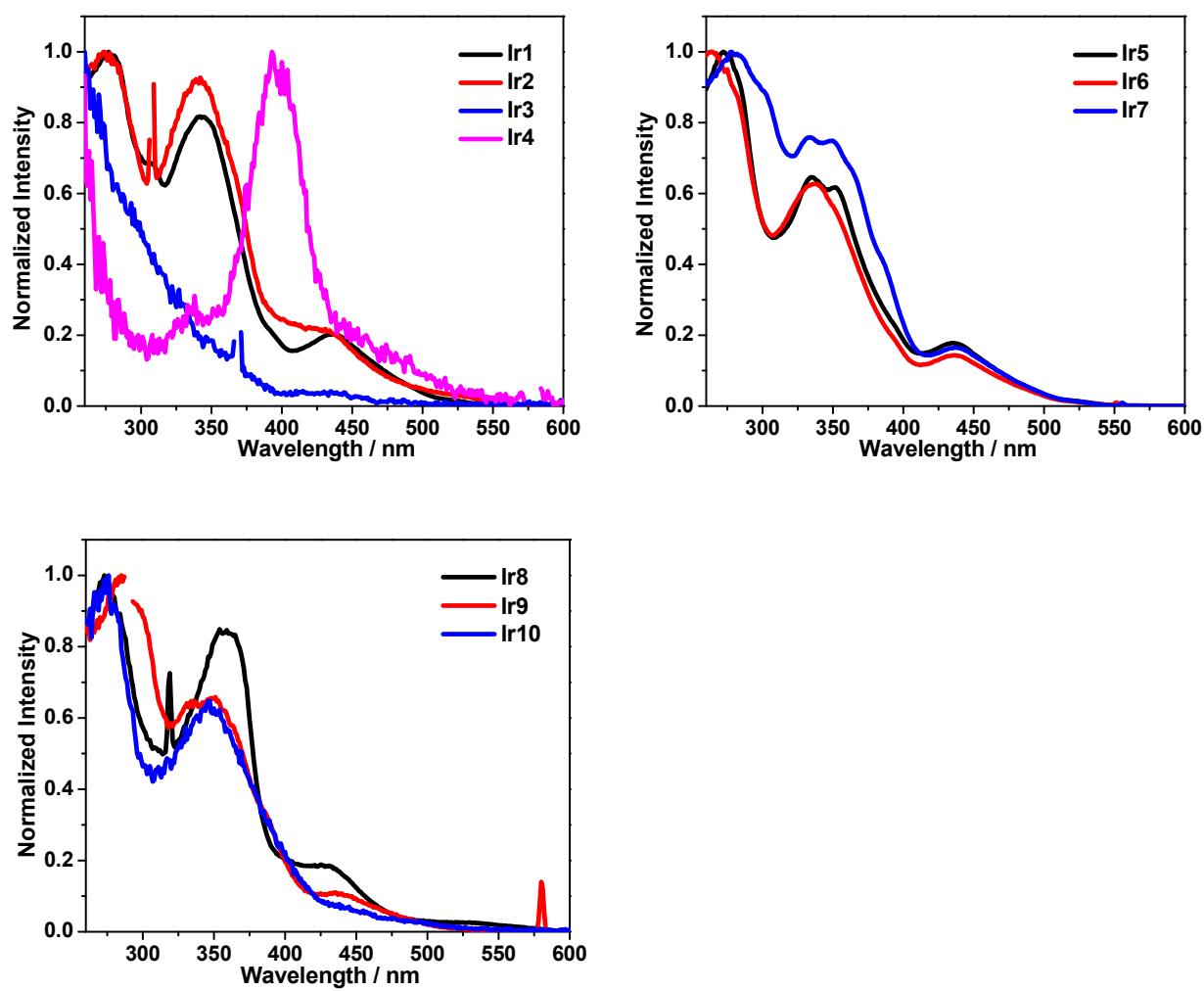


**Table S4.** HOMOs and LUMOs of Ir1–Ir10 in CH<sub>2</sub>Cl<sub>2</sub> and the contribution of HOMO→LUMO transition to the S<sub>1</sub> state.

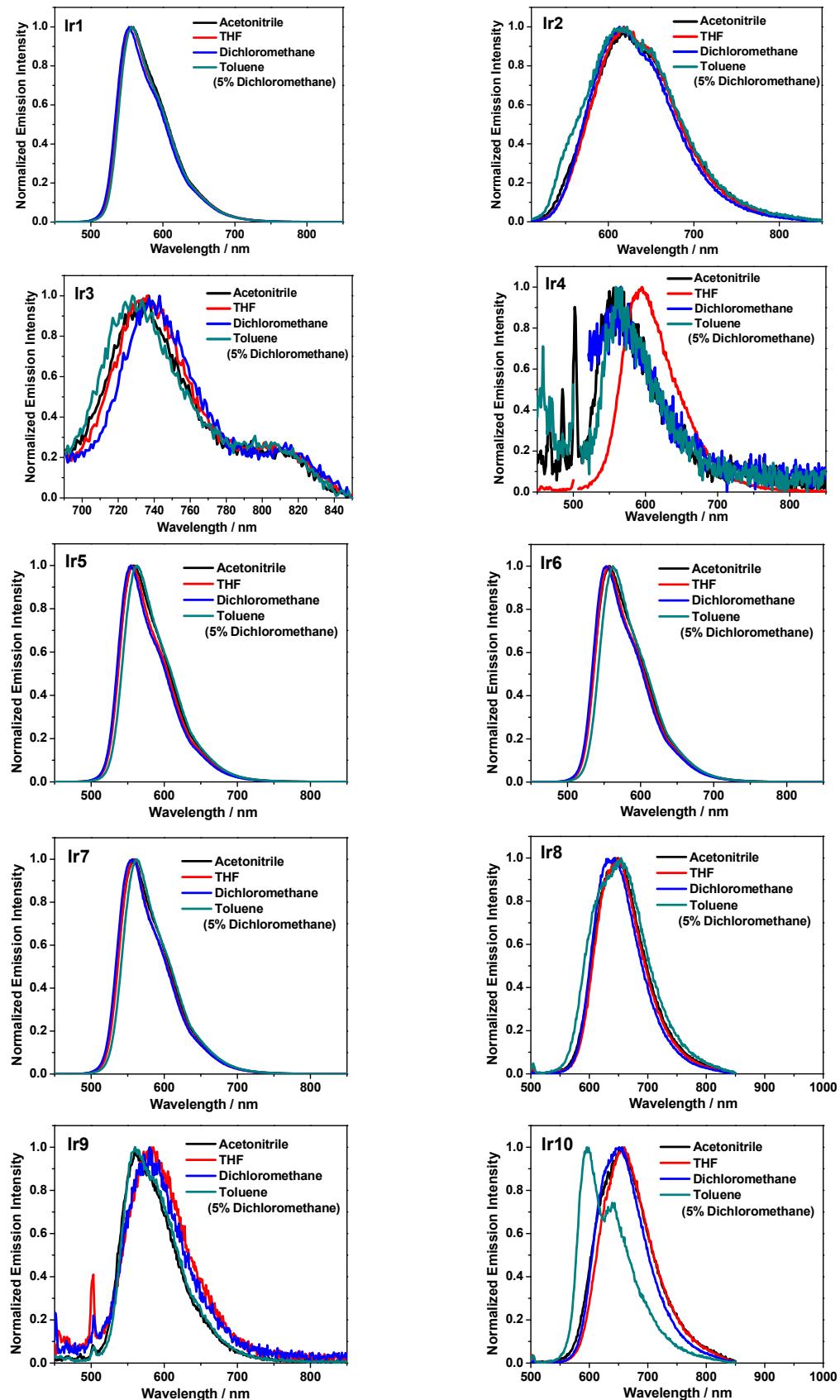
	HOMO	LUMO	Percentage Contribution of H/L Transition to S <sub>1</sub> State
<b>Ir1</b>			70%
<b>Ir2</b>			70%
<b>Ir3</b>			70%
<b>Ir4</b>			68%
<b>Ir5</b>			70%
<b>Ir6</b>			70%
<b>Ir7</b>			69%
<b>Ir8</b>			70%
<b>Ir9</b>			S <sub>1</sub> H/L 0%; H/L+1 69% S <sub>2</sub> H/L 43% S <sub>3</sub> H/L 56% S <sub>4</sub> H/L 70%
<b>Ir10</b>			70%



**Figure S3.** Molecular orbital mixing between **Ir2** and *cis*-1,3-butanediene to generate **Ir3** and **Ir4**, or between **Ir1** and *cis*-1,3-butanediene to generate **Ir8**.



**Figure S4.** Normalized excitation spectra of **Ir1 – Ir10** in dichloromethane at room temperature. The spectra were obtained by monitoring the emission at 554 nm for **Ir1**, 618 nm for **Ir2**, 739 nm for **Ir3**, 580 nm for **Ir4**, 557 nm for **Ir5**, 553 nm for **Ir6**, 557 nm for **Ir7**, 640 nm for **Ir8**, 582 nm for **Ir9**, and 650 nm for **Ir10** at a concentration of  $5 \times 10^{-6}$  mol·L<sup>-1</sup>.

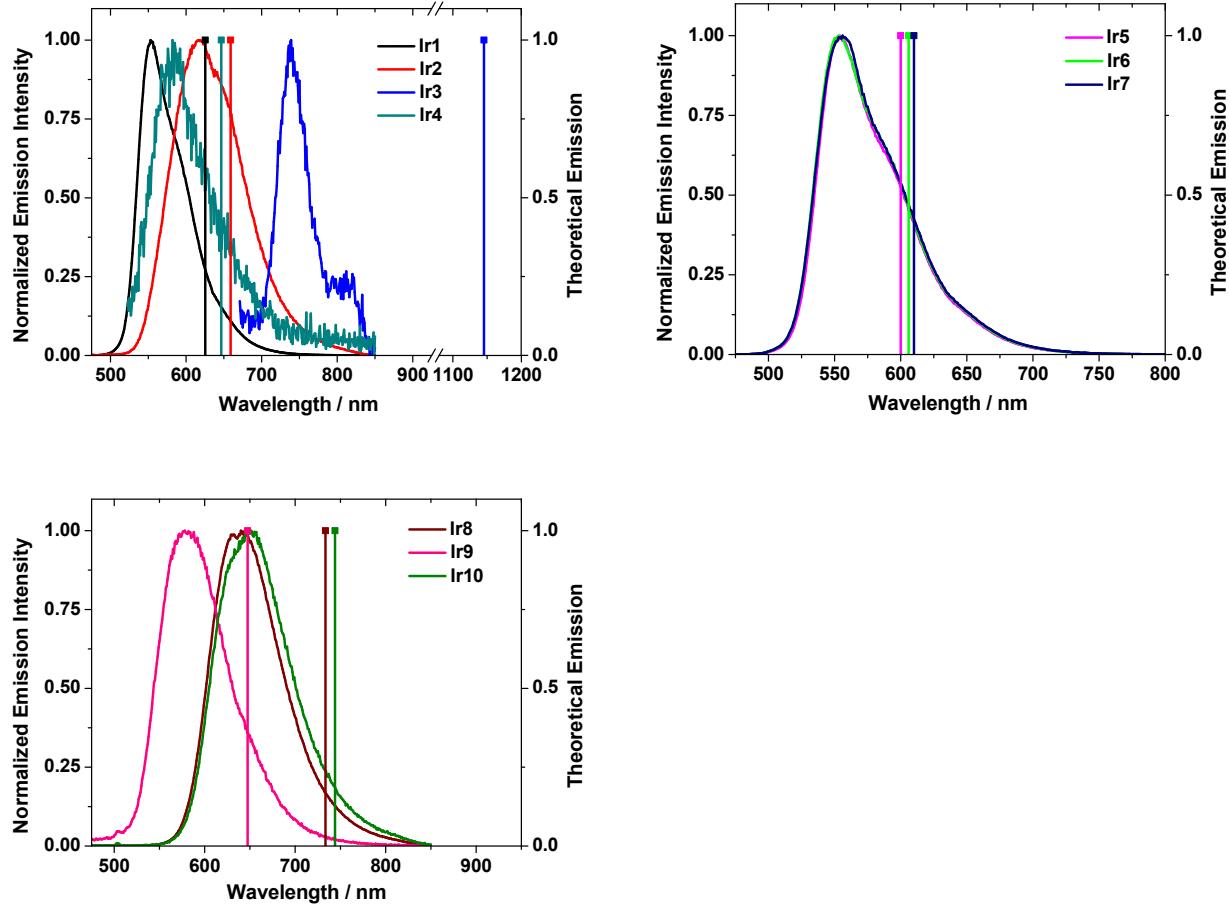


**Figure S5.** Normalized emission spectra of Ir1–Ir10 in different solvents ( $\lambda_{\text{ex}} = 436 \text{ nm}$ ).

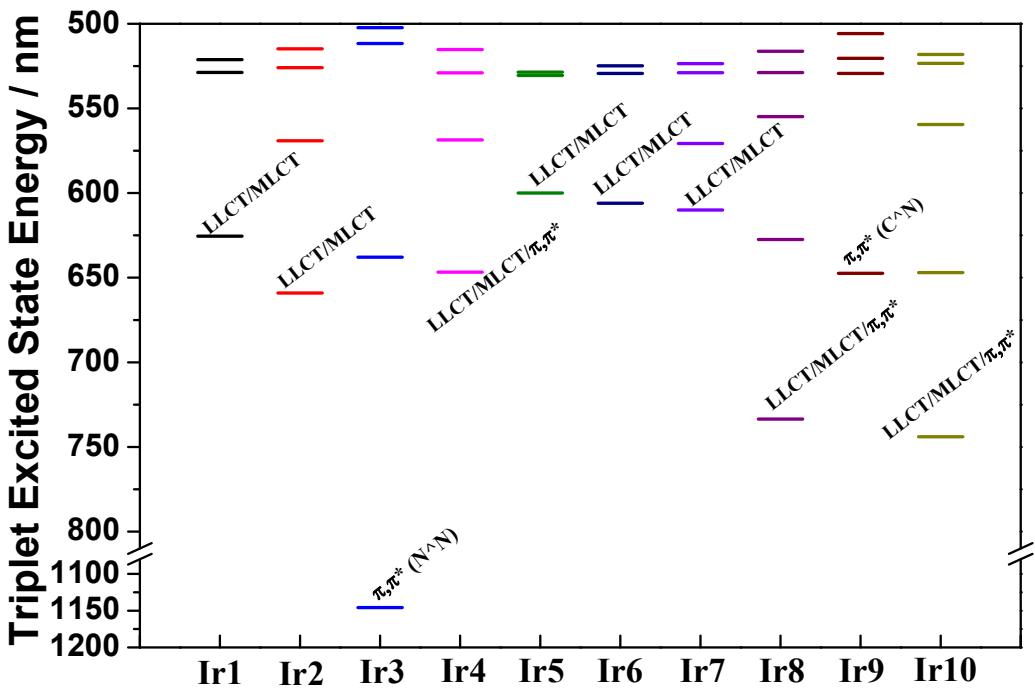
**Table S5.** Emission characteristics of complexes **Ir1–Ir10** in different solvents at room temperature.

	$\lambda_{\text{em}}/\text{nm}$ ( $\tau_{\text{em}}/\mu\text{s}$ ) <sup>a</sup> ; $\Phi_{\text{em}}^{\text{b}}$	Acetonitrile	THF	Toluene/5% $\text{CH}_2\text{Cl}_2$
<b>Ir1</b>	557 (2.48); 0.47	555 (2.22); 0.75	557 (2.15); 0.34	
<b>Ir2</b>	608 (0.30); 0.035	618 (0.36); 0.050	616 (0.18); 0.045	
<b>Ir3</b>	733 (3.38); 0.0044	735 (2.06); 0.0098	733 (-) <sup>c</sup> ; 0.0061	
<b>Ir4</b>	572 (-) <sup>c</sup> ; - <sup>c</sup>	587 (1.10); 0.0032	562 (-) <sup>c</sup> ; - <sup>c</sup>	
<b>Ir5</b>	558 (2.91); 0.59	556 (2.47); 0.62	560 (2.09); 0.56	
<b>Ir6</b>	557 (2.69); 0.56	556 (2.37); 0.65	562 (2.11); 0.61	
<b>Ir7</b>	559 (19.2); 0.22	558 (16.2); 0.17	562 (11.9); 0.24	
<b>Ir8</b>	649 (0.64); 0.037	644 (0.69); 0.042	653 (0.41); 0.032	
<b>Ir9</b>	560 (-) <sup>c</sup> ; 0.0026	596 (-) <sup>c</sup> ; 0.0013	560 (-) <sup>c</sup> ; 0.0038	
<b>Ir10</b>	653 (0.25); 0.035	656 (0.28); 0.076	596 (0.03); 0.025	

<sup>a</sup>The emission band maxima ( $\lambda_{\text{em}}$ ) and lifetimes ( $\tau_{\text{em}}$ ) for **Ir1–Ir10** at room temperature. <sup>b</sup>Absolute QY measurements were performed using a fiber coupled Ocean Optics integrating sphere.  $\lambda_{\text{ex}} = 450 \text{ nm}$ , detection wavelength range was  $350 – 1700 \text{ nm}$ . The integration range was  $380-820 \text{ nm}$  for **Ir1–Ir10** except for **Ir3**, for which the integration was done in the range of  $380-900 \text{ nm}$ . <sup>c</sup>Too weak to be measured.

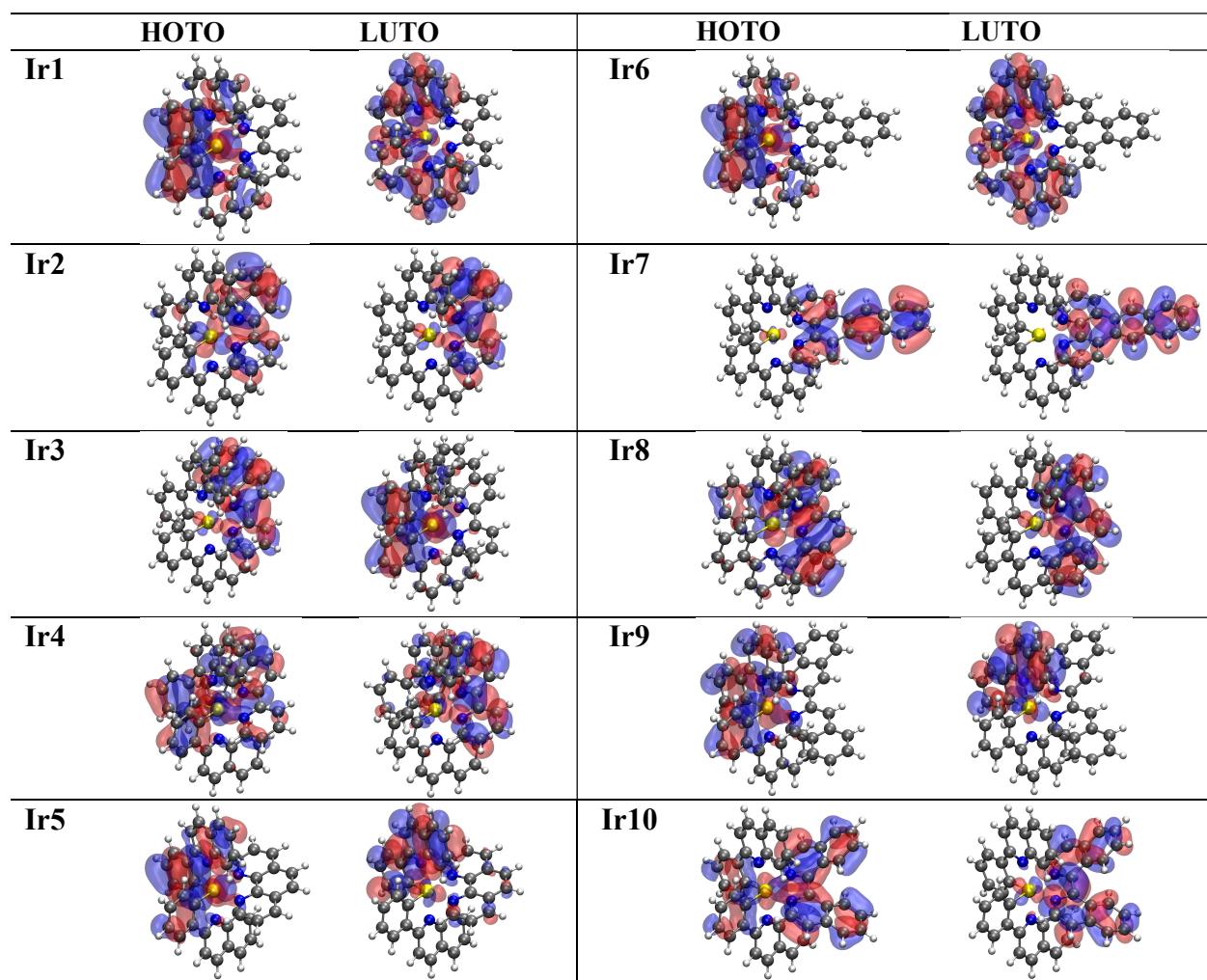


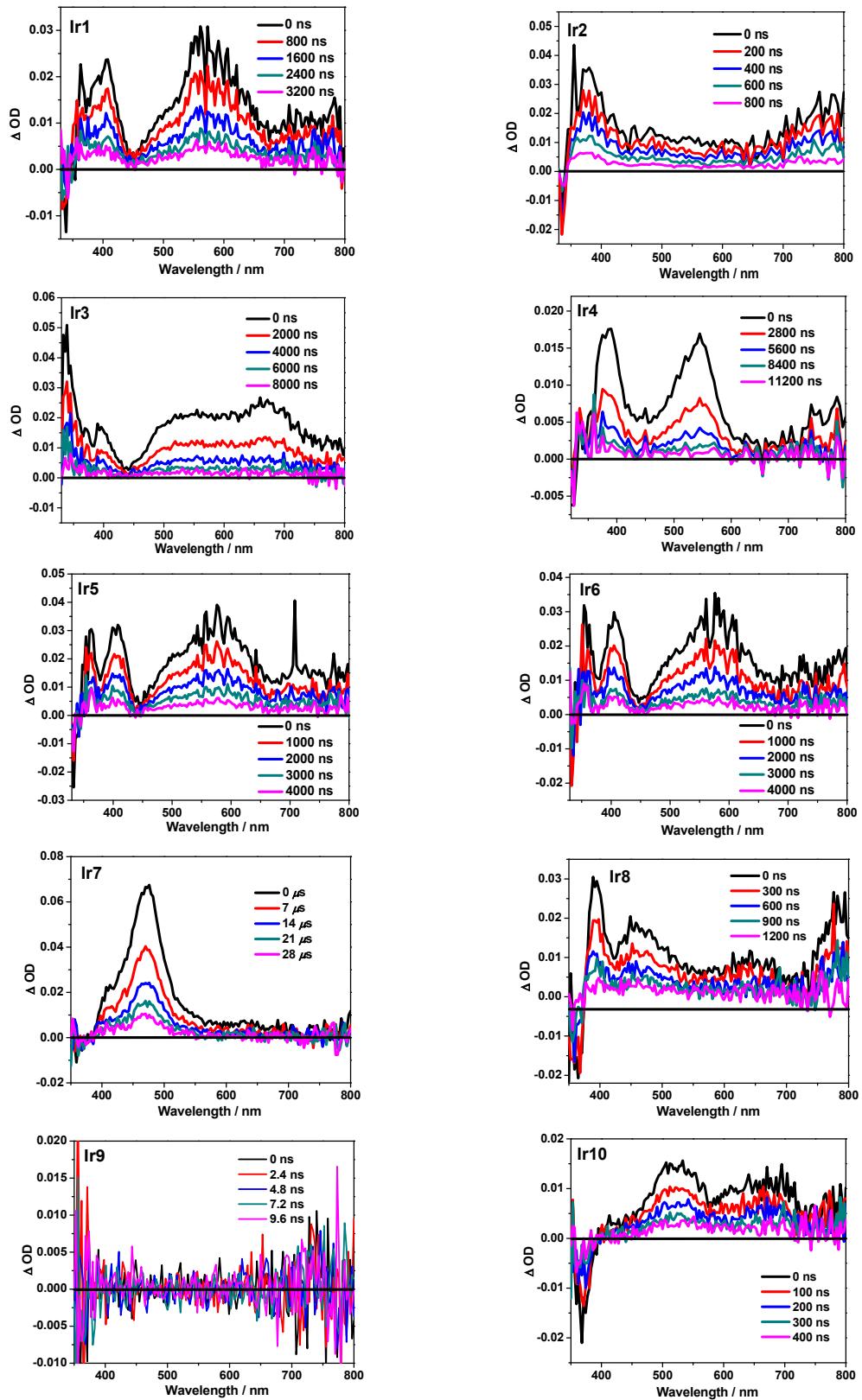
**Figure S6.** Comparing experimental emission spectra to TDDFT  $\Delta$ SCF energy for **Ir1–Ir10** in dichloromethane.



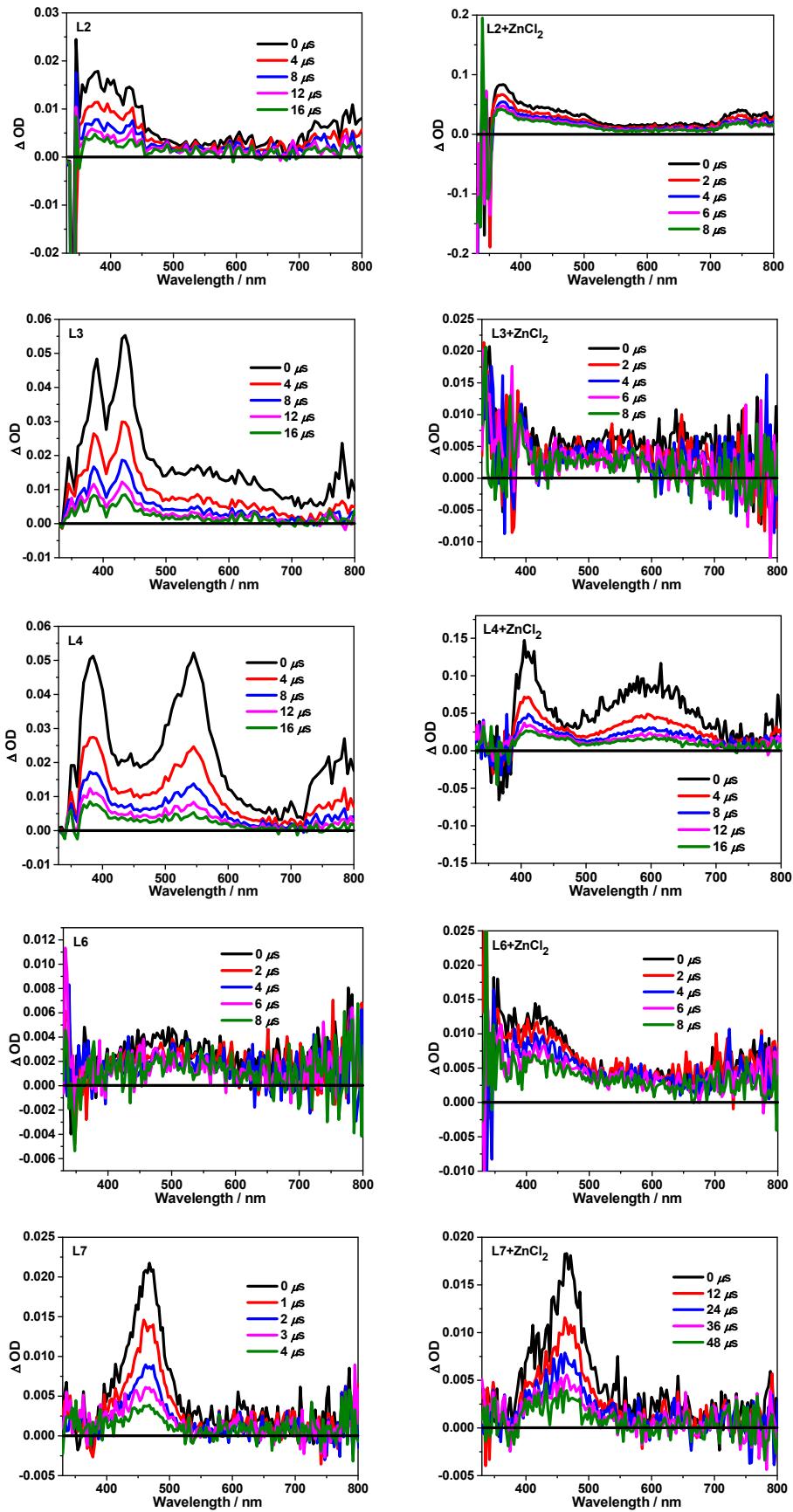
**Figure S7.** Triplet excited state energy diagram for **Ir1-Ir10** in  $\text{CH}_2\text{Cl}_2$ .

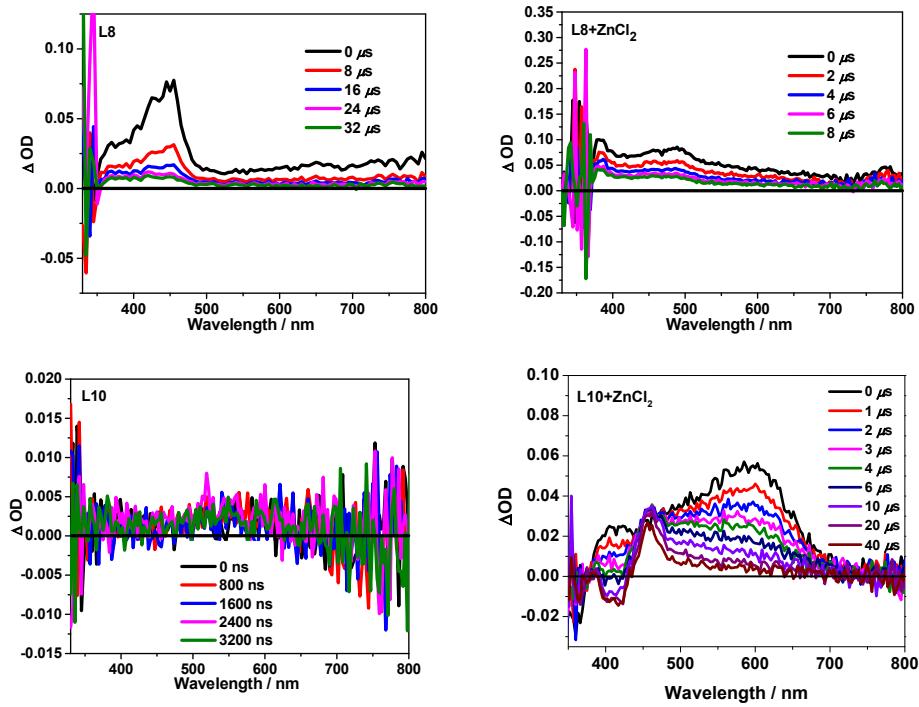
**Table S6.** NTOs for the second triplet excited states ( $T_2$ ) of **Ir1-Ir10** in  $\text{CH}_2\text{Cl}_2$ .



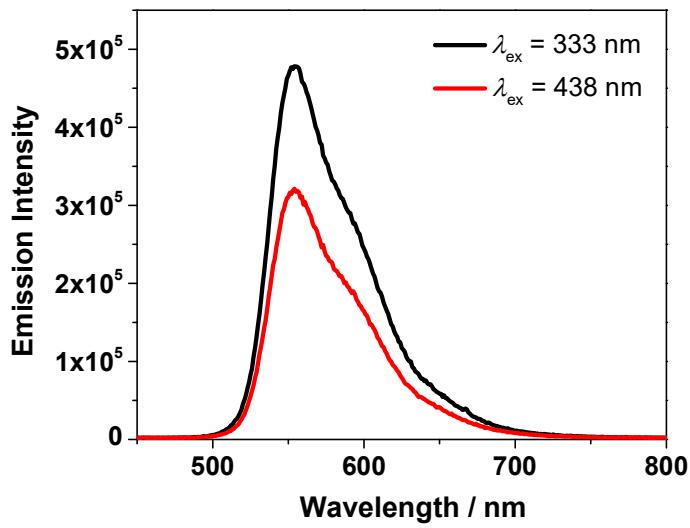


**Figure S8.** Nanosecond time-resolved transient differential absorption spectra of **Ir1–Ir10** at zero-time decay in acetonitrile.  $\lambda_{\text{ex}} = 355 \text{ nm}$ ,  $A_{355} = 0.4$  in a 1-cm cuvette.





**Figure S9.** Nanosecond time-resolved transient absorption (TA) spectra of the diimine ligands used in complexes **Ir2-Ir4**, **Ir6-Ir8** and **Ir10** and their corresponding  $\text{ZnCl}_2$  complexes in  $\text{CH}_3\text{CN}$ . The diimine ligands used in **Ir1**, **Ir5** and **Ir9** and their corresponding  $\text{ZnCl}_2$  complexes did not show any TA signals.  $\lambda_{\text{ex}} = 355 \text{ nm}$ , and  $A_{355} = 0.4$  in a 1-cm cuvette.



**Figure S10.** Comparison of the emission spectrum of **Ir5** in degassed  $\text{CH}_2\text{Cl}_2$  solution using different excitation wavelengths. The concentration of the solution was  $1 \times 10^{-5} \text{ mol/L}$ .

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