

Photophysics of Flavin Derivatives Absorbing in the Blue-Green Region: Thioflavins as Potential Cofactors of Photoswitches

Supporting Information

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Table S1: Vertical DFT/MRCI singlet and triplet excitation energies ΔE [eV] of aza-substituted and extended lumiflavin derivatives in vacuum in comparison with native lumiflavin. Oscillator strengths $f(r)$ of singlet absorptions are given in parentheses.

State	$\Delta E (f(r))$					
	LF	6A-LF	9A-LF	6,9DA-LF	DXLF	
1 ¹ A'	0.00	0.00	0.00	0.00	0.00	
2 ¹ A'	2.94 (0.322)	2.97 (0.405)	2.96 (0.405)	2.94 (0.457)	2.84 (0.412)	
1 ¹ A''	3.21 (0.002)	3.04 (0.002)	3.13 (0.002)	2.96 (0.000)	3.32 (0.002)	
2 ¹ A''	3.35 (0.001)	3.32 (0.000)	3.33 (0.000)	3.23 (0.000)	3.36 (0.001)	
3 ¹ A'	3.84 (0.208)	4.06 (0.049)	4.04 (0.046)	3.95 (0.044)	3.93 (0.123)	
:						
1 ³ A'	2.24	2.72	2.22	2.16	2.10	
1 ³ A''	2.90	2.72	2.84	2.67	2.94	
2 ³ A'	3.04	3.21	3.20	3.44	3.21	
2 ³ A''	3.22	3.32	3.40	3.12	3.18	

Table S2: Vertical DFT/MRCI singlet and triplet excitation energies ΔE [eV] of thio-substituted lumiflavin derivatives in vacuum in comparison with native lumiflavin. Oscillator strengths $f(r)$ of singlet absorptions are given in parentheses.

State	$\Delta E (f(r))$					
	LF	2T-LF	4T-LF	2,4T-LF	2TL-3DH-LF	
1 ¹ A'	0.00	0.00	0.00	0.00	0.00	0.00
2 ¹ A'	2.94 (0.322)	2.35 (0.506)	2.62 (0.377)	2.20 (0.384)	2.68 (0.280)	
1 ¹ A''	3.21 (0.002)	1.80 (0.000)	1.72 (0.000)	1.57 (0.000)	2.39 (0.001)	
2 ¹ A''	3.35 (0.001)	3.22 (0.000)	3.16 (0.000)	1.83 (0.000)	2.97 (0.002)	
3 ¹ A'	3.84 (0.208)	3.26 (0.089)	3.07 (0.061)	2.52 (0.252)	3.32 (0.257)	
⋮						
1 ³ A'	2.24	1.68	1.84	1.62	2.09	
1 ³ A''	2.90	1.74	1.61	1.49	2.27	
2 ³ A'	3.04	2.71	2.44	1.81	2.92	
2 ³ A''	3.22	2.92	2.83	1.77	2.75	

Table S3: Selected bond lengths [pm] of the DFT- (S_0), UDFT- (T_1) or TDDFT- (all other states) optimized structures of isolated **2T-LF**. Changes due to interaction with four water molecules are given in parentheses.

	S_0	S_1	S_2	T_1	T_2^a
N1-C2	135.9 (-0.5)	130.8 (+0.8)	132.9 (-0.2)	131.9 (+0.5)	130.3
C2-N3	139.4 (± 0.0)	135.3 (-0.2)	136.0 (± 0.0)	136.4 (-0.3)	135.4
N3-C4	138.4 (-1.7)	142.7 (-2.6)	143.3 (-1.9)	141.1 (-1.8)	142.3
C4-C4a	149.6 (-0.7)	146.1 (-1.1)	144.6 (-1.0)	147.2 (-1.0)	146.6
C4a-N5	129.5 (+0.2)	134.8 (± 0.0)	136.4 (+0.2)	134.7 (± 0.0)	134.1
N5-C5a	136.6 (-0.3)	134.1 (± 0.0)	131.5 (+0.2)	135.6 (+0.4)	134.9
C5a-C6	140.5 (+0.2)	141.7 (-0.1)	143.2 (± 0.0)	140.7 (-0.1)	141.2
C6-C7	138.0 (-0.1)	137.8 (-0.1)	136.5 (+0.1)	138.4 (± 0.0)	138.2
C7-C8	142.1 (+0.1)	142.0 (+0.1)	144.1 (± 0.0)	142.0 (+0.2)	141.6
C8-C9	138.9 (-0.1)	139.3 (-0.2)	138.2 (-0.1)	139.1 (-0.2)	139.5
C9-C9a	140.1 (± 0.0)	139.5 (± 0.0)	140.3 (-0.1)	139.8 (+0.1)	139.4
C9a-N10	138.5 (± 0.0)	139.8 (+0.1)	138.3 (± 0.0)	139.0 (+0.1)	140.0
N10-C10a	138.1 (+0.4)	136.8 (-0.1)	135.6 (-0.3)	139.4 (-0.3)	137.2
C10a-N1	130.8 (+0.1)	135.3 (+0.3)	135.0 (-0.2)	135.1 (-0.6)	135.4
C5a-C9a	141.6 (+0.3)	142.9 (-0.2)	144.7 (+0.1)	143.3 (± 0.0)	142.6
C4a-C10a	145.3 (-0.7)	141.4 (± 0.0)	143.0 (-0.6)	140.4 (+0.1)	141.2
C2-S	167.0 (+0.7)	175.6 (+0.1)	175.0 (+0.5)	173.9 (+0.1)	176.1
C4-O	121.1 (+1.6)	121.1 (+1.6)	121.3 (+1.6)	121.2 (+1.8)	121.1

a : For the **2T-LF** · **4 H₂O** cluster the $^3(n_S \rightarrow \pi_S^*)$ could not be optimized at the TDDFT level employing the B3-LYP functional.

Table S4: Isolated **2T-LF**: DFT/MRCI singlet and triplet excitation energies ΔE [eV] at ground- and excited-state minimum geometries. Adiabatic excitation energies are underlined. The squared coefficients c^2 of the dominant excitations in the DFT/MRCI expansion, oscillator strengths $f(r)$ and dipole moments μ [Debye] refer to the ground-state geometry.

State	ΔE			Electronic structure	$f(r)$	μ		
	S_0	$1^1A''$	$2^1A'$				$1^3A'$	$1^3A''$
$1^1A'$	0.00	0.39	0.46	0.32	0.39	(0.94) <i>ground state</i>	—	9.72
$1^1A''$	1.80	<u>1.44</u>	1.61	1.49	1.43	(0.76) $ns \rightarrow \pi_L^*$	0.0000	6.46
$2^1A'$	2.35	1.91	<u>1.95</u>	1.96	1.93	(0.80) $\pi_H \rightarrow \pi_L^*$	0.5056	7.61
$2^1A''$	3.22	3.17	3.20	3.25	3.18	(0.44) $n_N \rightarrow \pi_L^*$		
$3^1A'$	3.26	3.30	3.31	3.21	3.32	(0.22) $ns \rightarrow \pi_{L+1}^*$	0.0017	6.41
\vdots						(0.73) $\pi_{H-2} \rightarrow \pi_L^*$	0.0890	7.44
$1^3A'$	1.68	1.38	1.49	<u>1.39</u>	1.38	(0.85) $\pi_H \rightarrow \pi_L^*$		6.77
$1^3A''$	1.74	1.41	1.58	1.46	<u>1.40</u>	(0.76) $ns \rightarrow \pi_L^*$		6.39
$2^3A'$	2.71	2.85	2.83	2.79	2.87	(0.49) $\pi_{H-2} \rightarrow \pi_L^*$		
						(0.19) $\pi_H \rightarrow \pi_{L+1}^*$		
						(0.16) $\pi_{H-3} \rightarrow \pi_L^*$		7.29
$2^3A''$	2.92	3.14	3.16	3.12	3.15	(0.63) $n_N \rightarrow \pi_L^*$		
						(0.11) $n_{N'} \rightarrow \pi_L^*$		9.28

Table S5: Environment effects on vertical DFT/MRCI excitation energies ΔE [eV] of 2T-LF. The squared coefficients c^2 of the dominant excitations in the DFT/MRCI expansion, oscillator strengths $f(r)$ and dipole moments μ [Debye] refer to the water model using micro hydration plus polarizable continuum with relative permittivity $\epsilon_r = 78$.

iso- State	$\cdot 4H_2O$		$\cdot 4H_2O$		$\cdot 4H_2O$		Electronic structure	$f(r)$	μ
	$\epsilon_r = 78$	$\epsilon_r = 78$	$\epsilon_r = 33$	$\epsilon_r = 33$	$\epsilon_r = 78$	$\epsilon_r = 78$			
$1^1A'$	0.00	0.00	0.00	0.00	0.00	0.00	(0.94) <i>ground state</i>	0.0000	10.91
$1^1A''$	1.80	1.94	2.30	2.53	2.55	2.55	(0.78) $n_S \rightarrow \pi_L^*$	0.0018	5.64
$2^1A'$	2.35	2.25	2.40	2.49	2.50	2.50	(0.82) $\pi_H \rightarrow \pi_L^*$	0.5265	8.73
$2^1A''$	3.22	3.44	3.31	3.48	3.49	3.49	(0.66) $n_N \rightarrow \pi_L^*$	0.0093	9.69
$3^1A'$	3.26	3.31	3.20	3.23	3.23	3.23	(0.80) $\pi_{H-2} \rightarrow \pi_L^*$	0.1724	15.78
$1^3A'$	1.68	1.98	1.62	1.90	1.91	1.91	(0.88) $\pi_H \rightarrow \pi_L^*$		8.91
$1^3A''$	1.74	2.50	1.88	2.47	2.49	2.49	(0.77) $n_S \rightarrow \pi_L^*$		5.48
$2^3A'$	2.71	2.70	2.73	2.72	2.64	2.64	(0.76) $\pi_{H-2} \rightarrow \pi_L^*$		16.58
$3^3A'$	2.92	2.99	2.83	2.86	2.95	2.95	(0.60) $\pi_{H-3} \rightarrow \pi_L^*$		
							(0.16) $\pi_H \rightarrow \pi_{L+1}^*$		6.56

Table S6: Selected bond lengths [pm] of the DFT- (S_0), UDFT- (T_1 and T_2) or TDFFT- (all other states) optimized structures of isolated **4T-LF**. Changes due to interaction with four water molecules are given in parentheses.

	S_0	S_1	S_2	T_1	T_2	T_3
N1-C2	137.5 (-0.3)	134.8	131.6	136.7	138.3	135.8
C2-N3	141.7 (-0.1)	146.3	155.4	143.7	140.4	139.2
N3-C4	136.3 (-1.6)	133.2	130.2	135.4	136.9	137.3
C4-C4a	148.2 (-0.1)	141.5	145.8	139.1	140.1	145.3
C4a-N5	129.6 (+0.3)	135.0	135.2	134.6	136.2	133.5
N5-C5a	136.2 (-0.3)	134.6	134.5	135.7	133.9	136.1
C5a-C6	140.7 (+0.2)	141.4	141.5	140.8	141.8	139.8
C6-C7	137.9 (-0.1)	137.9	137.8	138.4	137.5	139.7
C7-C8	142.1 (+0.1)	141.8	142.0	141.7	142.7	141.6
C8-C9	138.9 (-0.1)	139.4	139.4	139.4	139.2	139.0
C9-C9a	140.1 (± 0.0)	139.4	139.7	139.5	139.6	140.3
C9a-N10	138.4 (+0.1)	139.7	138.6	140.4	139.1	138.6
N10-C10a	138.2 (-0.6)	138.0	139.6	137.4	138.4	140.0
C10a-N1	130.2 (+0.4)	132.3	135.0	131.3	130.7	132.8
C5a-C9a	141.5 (+0.2)	143.1	143.4	142.7	143.7	143.0
C4a-C10a	146.5 (-0.7)	142.1	139.2	143.7	145.2	142.5
C2-O	121.1 (+0.5)	121.2	120.7	121.4	121.4	123.7
C4-S	165.9 (+2.0)	173.4	175.1	174.4	173.4	169.4

Table S7: Isolated **4T-LF**: DFT/MRCI singlet and triplet excitation energies ΔE [eV] at ground- and excited-state minimum geometries. Adiabatic excitation energies are underlined. The squared coefficients c^2 of the dominant excitations in the DFT/MRCI expansion, oscillator strengths $f(r)$ and dipole moments μ [Debye] refer to the ground-state geometry.

State	S_0	ΔE				Electronic structure	$f(r)$	μ	
		$1^1A''$	$2^1A'$	$1^3A''$	$2^3A'$				
$1^1A'$	0.00	0.37	0.73	0.37	0.31	0.22	(0.94) <i>ground state</i>	—	9.46
$1^1A''$	1.72	<u>1.47</u>	1.85	1.43	1.50	1.66	(0.77) $n_S \rightarrow \pi_L^*$	0.0000	5.02
$2^1A'$	2.62	2.33	<u>2.44</u>	2.37	2.33	2.48	(0.81) $\pi_H \rightarrow \pi_L^*$	0.3767	9.00
$3^1A'$	3.07	3.12	3.49	3.12	2.92	2.87	(0.77) $\pi_{H-2} \rightarrow \pi_L^*$	0.0610	6.74
$2^1A''$	3.16	3.37	3.62	3.34	3.20	3.31	(0.63) $n_N \rightarrow \pi_L^*$	0.0019	8.87
							(0.12) $n_O \rightarrow \pi_{L+1}^*$		
:									
$1^3A''$	1.61	1.38	1.78	1.34	1.42	1.58	(0.78) $n_S \rightarrow \pi_L^*$		5.13
$1^3A'$	1.84	1.64	1.98	1.62	<u>1.55</u>	1.76	(0.77) $\pi_H \rightarrow \pi_L^*$		6.75
$2^3A'$	2.44	2.60	2.92	2.62	2.49	<u>2.33</u>	(0.67) $\pi_{H-2} \rightarrow \pi_L^*$		8.45
$2^3A''$	2.83	3.09	3.42	3.06	2.94	2.99	(0.58) $n_N \rightarrow \pi_L^*$		
							(0.12) $n_O \rightarrow \pi_{L+1}^*$		
							(0.11) $n_{N'} \rightarrow \pi_L^*$		9.48

Table S8: Environment effects on vertical DFT/MRCI excitation energies ΔE [eV] of **4T-LF**. The squared coefficients c^2 of the dominant excitations in the DFT/MRCI expansion, oscillator strengths $f(r)$ and dipole moments μ [Debye] refer to the water model using micro hydration plus polarizable continuum with relative permittivity $\epsilon_r = 78$.

iso- State	$\cdot 4H_2O$			$\cdot 4H_2O$			Electronic structure	$f(r)$	μ
	$\epsilon_r = 78$	$\epsilon_r = 4$	$\epsilon_r = 78$	$\epsilon_r = 78$	$\epsilon_r = 4$	$\epsilon_r = 78$			
$1^1A'$	0.00	0.00	0.00	0.00	0.00	0.00	(0.94) <i>ground state</i>	—	8.99
$1^1A''$	1.72	2.17	2.19	2.31	2.40	2.40	(0.75) $n_S \rightarrow \pi_L^*$	0.0000	6.28
$2^1A'$	2.62	2.60	2.56	2.57	2.57	2.57	(0.81) $\pi_H \rightarrow \pi_L^*$	0.3952	9.74
$3^1A'$	3.07	3.18	3.02	3.09	3.11	3.11	(0.75) $\pi_{H-2} \rightarrow \pi_L^*$	0.0528	11.25
$2^1A''$	3.16	3.31	3.27	3.36	3.40	3.40	(0.62) $n_N \rightarrow \pi_L^*$	0.0016	8.62
$1^3A''$	1.61	2.07	2.08	2.21	2.29	2.29	(0.75) $n_S \rightarrow \pi_L^*$		6.37
$1^3A'$	1.84	1.98	1.91	1.97	1.99	1.99	(0.84) $\pi_H \rightarrow \pi_L^*$		8.56
$2^3A'$	2.44	2.51	2.41	2.47	2.49	2.49	(0.68) $\pi_{H-2} \rightarrow \pi_L^*$		10.88
$2^3A''$	2.83	2.98	2.94	3.03	3.07	3.07	(0.56) $n_N \rightarrow \pi_L^*$		8.86

Table S9: Selected bond lengths [pm] of the DFT- (S_0), UDFT- (T_1 and T_2) or TDDFT- (all other states) optimized structures of isolated **2,4DT-LF**. Changes due to interaction with four water molecules are given in parentheses.

	S_0	S_1	S_2	S_3	T_1	T_2
N1-C2	135.6 (-0.5)	131.3	132.1	133.0	132.7	133.3
C2-N3	139.5 (± 0.0)	134.9	138.3	135.9	138.2	136.2
N3-C4	136.7 (-1.2)	141.0	135.6	141.7	137.9	138.9
C4-C4a	148.0 (± 0.0)	143.9	142.6	142.0	141.3	144.0
C4a-N5	129.7 (+0.4)	134.5	134.4	136.2	134.6	135.5
N5-C5a	136.2 (-0.1)	134.1	134.8	131.8	135.7	134.5
C5a-C6	140.6 (+0.3)	141.6	141.2	142.8	140.9	141.3
C6-C7	137.9 (-0.1)	137.8	138.1	136.6	138.3	137.8
C7-C8	142.1 (+0.2)	142.1	141.8	143.9	141.5	142.6
C8-C9	138.9 (-0.1)	139.2	139.4	138.3	139.5	139.1
C9-C9a	140.1 (± 0.0)	139.4	139.3	140.4	139.3	139.7
C9a-N10	138.5 (-0.2)	139.9	140.0	138.4	140.4	138.9
N10-C10a	138.0 (-0.5)	136.3	137.1	135.4	136.8	138.7
C10a-N1	130.8 (+0.1)	132.3	133.8	134.6	133.3	133.8
C5a-C9a	141.6 (+0.4)	142.6	142.8	144.2	142.2	143.7
C4a-C10a	145.8 (-0.7)	142.9	142.0	144.3	143.3	141.9
C2-S	167.0 (+0.2)	175.2	171.9	174.6	171.0	172.3
C4-S	165.9 (+1.0)	166.8	171.2	166.9	170.9	167.6

Table S10: Isolated **2,4DT-LF**: DFT/MRCI singlet and triplet excitation energies ΔE [eV] at ground- and excited-state minimum geometries. Adiabatic excitation energies are underlined. The squared coefficients c^2 of the dominant excitations in the DFT/MRCI expansion, oscillator strengths $f(r)$ and dipole moments μ [Debye] refer to the ground-state geometry.

State	ΔE				Electronic structure	$f(r)$	μ		
	S_0	$1^1A''$	$2^1A''$	$2^1A'$				$1^3A''$	$2^3A''$
$1^1A'$	0.00	0.35	0.25	0.42	0.26	0.25	(0.92) <i>ground state</i>	—	9.57
$1^1A''$	1.57	<u>1.38</u>	1.41	1.51	1.40	1.45	(0.51) $n_{S2} \rightarrow \pi_L^*$	0.0000	3.35
$2^1A''$	1.83	1.84	<u>1.63</u>	1.87	1.68	1.72	(0.27) $n_{S4} \rightarrow \pi_L^*$	0.0000	4.23
$2^1A'$	2.20	1.80	1.94	<u>1.83</u>	1.98	1.85	(0.48) $n_{S4} \rightarrow \pi_L^*$	0.3839	7.87
$3^1A'$	2.52	2.62	2.32	<u>2.60</u>	2.36	2.43	(0.27) $n_{S2} \rightarrow \pi_L^*$	0.2519	6.93
\vdots							(0.78) $\pi_H \rightarrow \pi_L^*$		
$1^3A''$	1.49	1.35	1.35	1.49	<u>1.33</u>	1.42	(0.77) $\pi_{H-2} \rightarrow \pi_L^*$		
$1^3A'$	1.62	1.35	1.46	1.45	1.51	<u>1.38</u>	(0.45) $n_{S2} \rightarrow \pi_L^*$		3.99
$2^3A''$	1.77	1.76	1.58	1.80	1.63	1.64	(0.34) $n_{S4} \rightarrow \pi_L^*$		7.93
$2^3A'$	1.81	1.93	1.64	1.91	1.63	1.79	(0.82) $\pi_H \rightarrow \pi_L^*$		4.94
							(0.42) $n_{S4} \rightarrow \pi_L^*$		5.26
							(0.33) $n_{S2} \rightarrow \pi_L^*$		
							(0.77) $\pi_{H-2} \rightarrow \pi_L^*$		

Table S11: Environment effects on vertical DFT/MRCI excitation energies ΔE [eV] of **2,4DT-LF**. The squared coefficients c^2 of the dominant excitations in the DFT/MRCI expansion, oscillator strengths $f(r)$ and dipole moments μ [Debye] refer to the water model using micro hydration plus polarizable continuum with relative permittivity $\epsilon_r = 78$.

State	iso-			·4H₂O			·4H₂O			Electronic structure	$f(r)$	μ
	labeled	$\epsilon_r = 78$	$\epsilon_r = 78$	$\epsilon_r = 4$	$\epsilon_r = 78$	$\epsilon_r = 78$	$\epsilon_r = 4$	$\epsilon_r = 78$				
1 ¹ A'	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	(0.93) <i>ground state</i>	—	10.10	
1 ¹ A''	1.57	2.02	1.89	2.12	2.12	2.22	2.12	2.22	(0.48) $n_{S4} \rightarrow \pi_L^*$	0.0001	5.68	
2 ¹ A''	1.83	2.45	2.12	2.29	2.29	2.45	2.29	2.45	(0.31) $n_{S2} \rightarrow \pi_L^*$	0.0045	5.61	
2 ¹ A'	2.20	2.38	2.14	2.25	2.25	2.32	2.25	2.32	(0.48) $n_{S2} \rightarrow \pi_L^*$	0.3952	9.74	
3 ¹ A'	2.52	2.76	2.52	2.63	2.63	2.73	2.63	2.73	(0.29) $n_{S4} \rightarrow \pi_L^*$	0.1742	3.98	
1 ³ A''	1.49	1.93	1.84	2.04	2.04	2.13	2.04	2.13	(0.82) $\pi_H \rightarrow \pi_L^*$	—	—	
									(0.77) $\pi_{H-2} \rightarrow \pi_L^*$	—	—	
									(0.51) $n_{S4} \rightarrow \pi_L^*$	—	—	
1 ³ A'	1.62	1.80	1.58	1.71	1.71	1.77	1.71	1.77	(0.25) $n_{S2} \rightarrow \pi_L^*$	6.20	6.20	
2 ³ A''	1.77	2.40	2.03	2.22	2.22	2.40	2.22	2.40	(0.85) $\pi_H \rightarrow \pi_L^*$	9.24	9.24	
									(0.53) $n_{S2} \rightarrow \pi_L^*$	—	—	
2 ³ A'	1.81	2.18	1.94	2.09	2.09	2.20	2.09	2.20	(0.22) $n_{S4} \rightarrow \pi_L^*$	6.12	6.12	
									(0.70) $\pi_{H-2} \rightarrow \pi_L^*$	5.25	5.25	