Quantum Chemical Study Aimed at Modeling Efficient Aza-BODIPY NIR Dyes: Molecular and Electronic Structure, Absorption, and Emission Spectra

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Figure S1. Conformations of **A1–A7** dyes according to the GFN2-XTB/CREST meta-dynamical calculations. Next to the molecules are Gibbs free energy values relative to the lowest conformer.
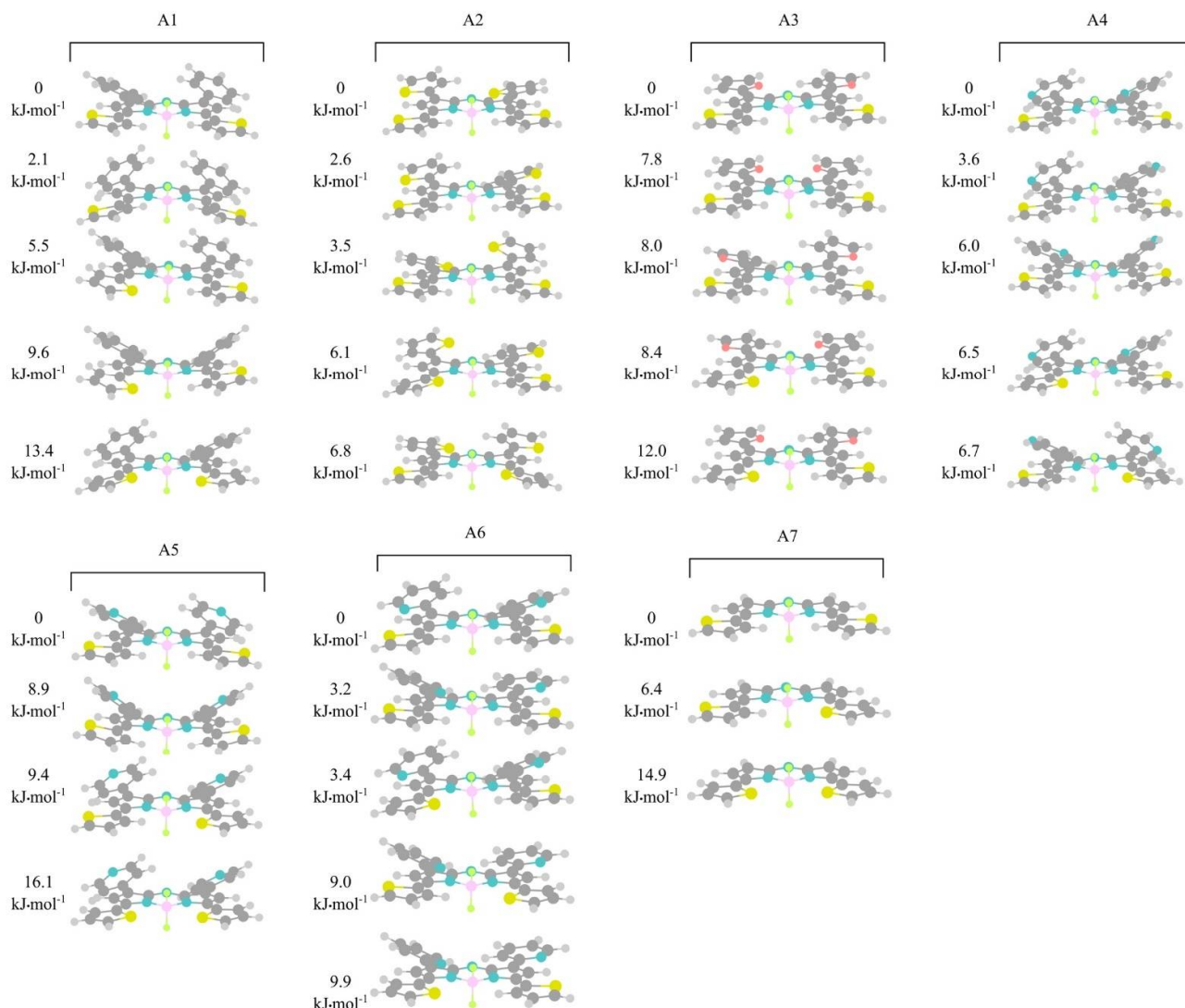
Figure S2. Conformations of **B1–B7** dyes according to the GFN2-XTB/CREST meta-dynamical calculations. Next to the molecules are Gibbs free energy values relative to the lowest conformer.
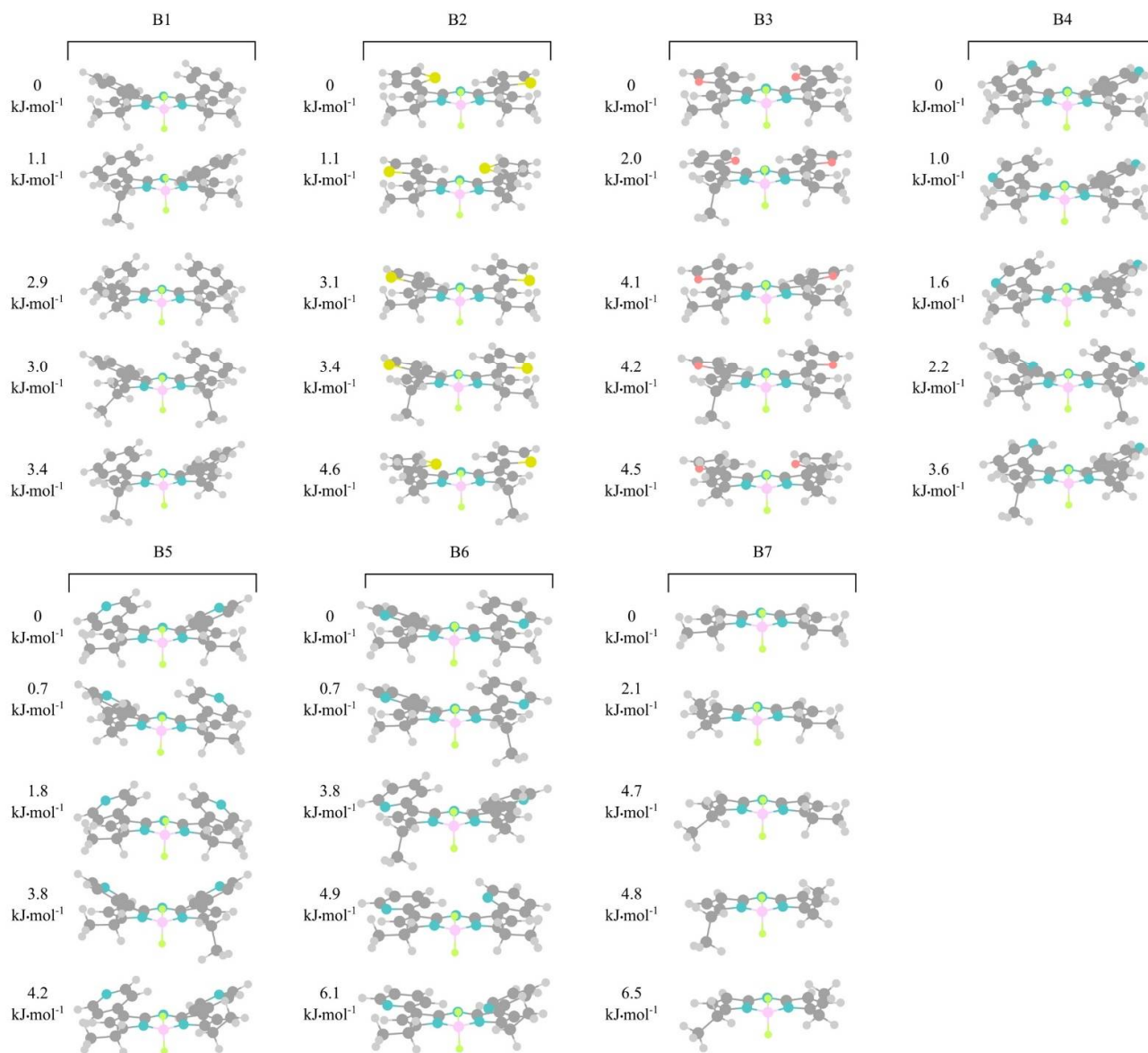
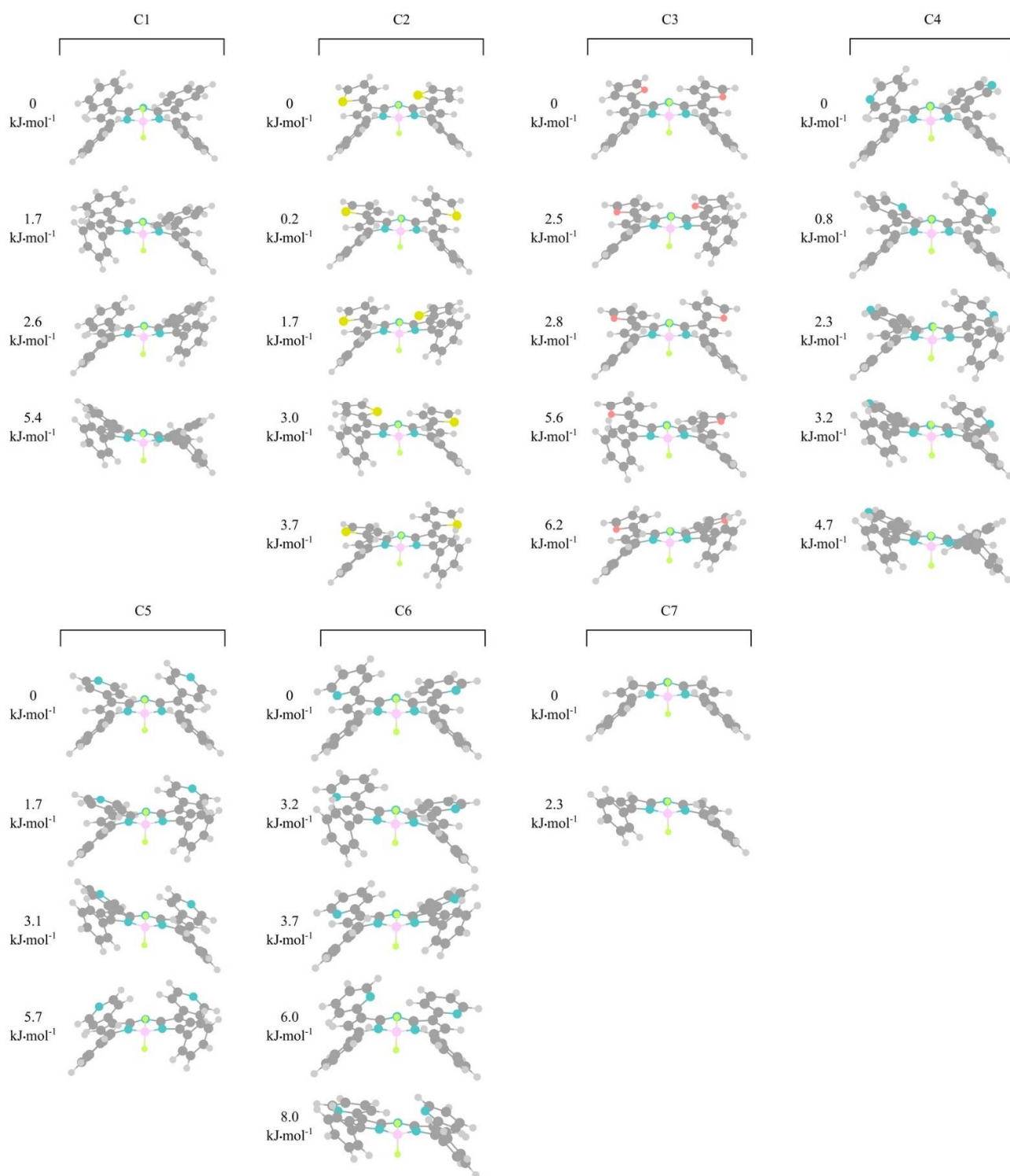**Figure S3.** Conformations of **C1–C7** dyes according to the GFN2-XTB/CREST meta-dynamical calculations. Next to the molecules are Gibbs free energy values relative to the lowest conformer.

Figure S4. Conformations of **D1–D7** dyes according to the GFN2-XTB/CREST meta-dynamical calculations. Next to the molecules are Gibbs free energy values relative to the lowest conformer.
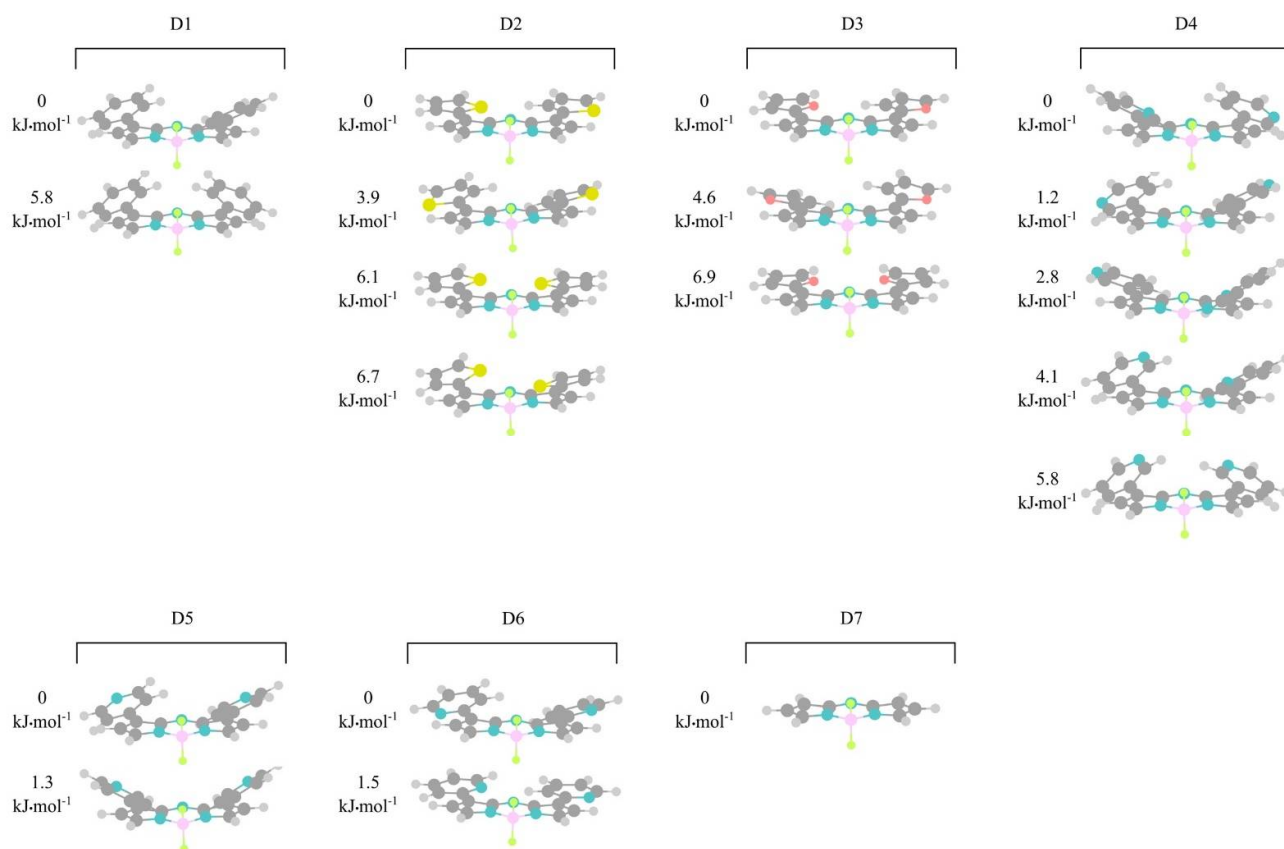
Table S1. Molecular parameters[a] of **A1-7** optimized at CAM-B3LYP/6-31+G(d,p) level.

	A1	A2	A3	A4	A5	A6	A7
Symmetry	C_2	C_1	C_2	C_2	C_2	C_2	C_2
$\|\chi(N_{4a}-B-N_{4b}-N_8)\|$	0.0	0.1	0.0	0.0	0.0	0.0	0.0
$\|\chi(C_2-C_1-C_{8a}-C_m)\|$	175.2	175.5	175.6	175.7	175.8	175.4	178.2
$\|\chi(C_3-N_{4a}-B-N_{4b})\|$	175.4	175.7	176.3	175.7	175.7	175.7	176.6
$\|\chi_1\|=\|\chi_2\|$ [b]	30.5	16.2 [b]	9.4	30.5	29.4	18.0	-
$\|\chi_3\|=\|\chi_4\|$	17.2	17.6	17.0	16.4	15.8	15.5	14.1
$r(C_1-X_{1\text{-Sub}})$	1.467	1.447	1.437	1.464	1.467	1.470	1.081
$r(C_3-C_{1\text{-Sub}})$	1.447	1.447	1.448	1.446	1.446	1.446	1.446
$r(C_{8a}-N_{4a})$	1.395	1.394	1.393	1.393	1.393	1.394	1.396
$r(C_3-N_{4a})$	1.357	1.359	1.361	1.357	1.357	1.358	1.356
$r(N_{4a}-B)$	1.550	1.550	1.550	1.552	1.552	1.550	1.552
$r(C_1-C_{8a})$	1.431	1.434	1.430	1.430	1.430	1.431	1.418
$r(N_8-C_{8a})$	1.316	1.315	1.316	1.316	1.316	1.316	1.318
$r(C_1-C_2)$	1.381	1.383	1.383	1.379	1.378	1.378	1.370
$r(C_2-C_3)$	1.416	1.413	1.413	1.418	1.419	1.417	1.427
$\varphi(C_{8a}-N_{4a}-B)$	122.2	122.4	122.2	122.2	122.2	122.3	122.1
$\varphi_e(N_{4a}-C_3-C_2)$	109.2	109.3	109.4	109.1	109.1	109.1	109.0
$\varphi(N_{4a}-B-N_{4b})$	107.0	106.9	106.9	107.0	107.0	107.0	107.0
$\varphi(C_1-C_2-C_3)$	108.6	108.5	108.1	108.4	108.4	108.5	107.8
$WI(C_1-C_{1\text{-Sub}})$	1.06	1.11	1.11	1.06	1.06	1.06	-
$WI(C_3-C_{1\text{-Sub}})$	1.13	1.12	1.12	1.13	1.13	1.13	1.13

[a] r - bond lengths in Å, φ – bond angles in degrees, χ - dihedral angle in degrees, WI - Wiberg bond indexes; [b] for **A2** – the average value of the deviation from the substituent's location in the plane, $\|\chi_1\|=17.0$ °, $\|\chi_2\|=164.7$ °. Natural charges and Wiberg bond indexes are given in Tables S7 and S11.

Table S2. Molecular parameters[a] of **B1-7** optimized at CAM-B3LYP/6-31+G(d,p) level.

	B1	B2	B3	B4	B5	B6	B7
Symmetry	C_2	C_1	C_2	C_2	C_2	C_2	C_{2v}
$\lvert\chi(N_{4a}\text{-}B\text{-}N_{4b}\text{-}N_8)\rvert$	0.0	0.1	0.0	0.0	0.0	0.0	0.0
$\lvert\chi(C_2\text{-}C_1\text{-}C_{8a}\text{-}C_m)\rvert$	177.0	178.6	177.9	177.5	177.6	177.2	180.0
$\lvert\chi(C_3\text{-}N_{4a}\text{-}B\text{-}N_{4b})\rvert$	178.9	179.8	179.7	179.1	179.2	179.1	180.0
$\lvert\chi_1\rvert=\lvert\chi_2\rvert$ [b]	29.3	13.4 [b]	7.6	29.5	28.4	17.3	-
$\lvert\chi_3\rvert=\lvert\chi_4\rvert$	0.0	0.2 [c]	0.6	0.3	0.2	0.8	0.0
$r(C_1\text{-}X_{1\text{-Sub}})$	1.466	1.447	1.436	1.464	1.467	1.470	1.081
$r(C_3\text{-}C_{1\text{-Sub}})$	1.494	1.494	1.494	1.494	1.494	1.494	1.494
$r(C_{8a}\text{-}N_{4a})$	1.396	1.393	1.395	1.395	1.394	1.395	1.398
$r(C_3\text{-}N_{4a})$	1.346	1.350	1.350	1.346	1.345	1.346	1.344
$r(N_{4a}\text{-}B)$	1.545	1.542	1.544	1.547	1.548	1.546	1.548
$r(C_1\text{-}C_{8a})$	1.432	1.431	1.431	1.431	1.431	1.433	1.419
$r(N_8\text{-}C_{8a})$	1.317	1.318	1.318	1.317	1.317	1.318	1.319
$r(C_1\text{-}C_2)$	1.388	1.394	1.391	1.387	1.385	1.385	1.377
$r(C_2\text{-}C_3)$	1.410	1.405	1.406	1.412	1.413	1.411	1.421
$\varphi(C_{8a}\text{-}N_{4a}\text{-}B)$	123.5	123.5	123.5	123.5	123.5	123.5	123.5
$\varphi_e(N_{4a}\text{-}C_3\text{-}C_2)$	123.5	123.5	123.5	123.5	123.5	123.5	123.5
$\varphi(N_{4a}\text{-}B\text{-}N_{4b})$	105.6	105.5	105.5	105.5	105.5	105.6	105.5
$\varphi(C_1\text{-}C_2\text{-}C_3)$	108.3	108.1	107.8	108.1	108.1	108.2	107.5
$WI(C_1\text{-}C_{1\text{-Sub}})$	1.07	1.11	1.11	1.06	1.06	1.06	-
$WI(C_3\text{-}C_{1\text{-Sub}})$	1.03	1.03	1.03	1.03	1.03	1.03	1.03

[a] r - bond lengths in Å, φ – bond angles in degrees, χ - dihedral angle in degrees, WI - Wiberg bond indexes; [b] for **B2** – the average value of the deviation from the substituent's location in the plane, $\lvert\chi_1\rvert=14.5°$, $\lvert\chi_2\rvert=167.7°$; [c] average value for nonequivalent parameters $\lvert\chi_3\rvert$, $\lvert\chi_4\rvert$. Natural charges and Wiberg bond indexes are given in Tables S8 and S12.

Table S3. Molecular parameters[a] of **C1-7** optimized at CAM-B3LYP/6-31+G(d,p) level.

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_s
$|\chi(N_{4a}\text{-}B\text{-}N_{4b}\text{-}N_8)|$	9.5	9.5	9.5	9.5	9.4	9.5	9.3
$|\chi(C_2\text{-}C_1\text{-}C_{8a}\text{-}C_m)|$	174.2	173.5	173.9	173.7	174.1	173.7	174.3
$|\chi(C_3\text{-}N_{4a}\text{-}B\text{-}N_{4b})|$	169.2	168.6	168.9	168.8	169.2	168.8	169.4
$|\chi_1|=|\chi_2|$ [b]	29.9	25.4 [b]	8.7	30.0	28.7	17.6	-
$|\chi_3|\approx|\chi_4|$ [c]	36.6 [c]	37.1 [c]	37.0 [c]	36.3 [c]	36.1 [c]	36.0 [c]	35.6
$r(C_1\text{-}X_{1\text{-Sub}})$	1.466	1.446	1.437	1.464	1.466	1.469	1.081
$r(C_3\text{-}C_{1\text{-Sub}})$	1.469	1.469	1.469	1.468	1.468	1.468	1.468
$r(C_{8a}\text{-}N_{4a})$	1.396	1.396	1.395	1.395	1.394	1.395	1.398
$r(C_3\text{-}N_{4a})$	1.352	1.354	1.356	1.352	1.352	1.353	1.351
$r(N_{4a}\text{-}B)$	1.553	1.553	1.552	1.555	1.556	1.553	1.556
$r(C_1\text{-}C_{8a})$	1.432	1.434	1.431	1.431	1.430	1.431	1.418
$r(N_8\text{-}C_{8a})$	1.316	1.315	1.316	1.316	1.316	1.317	1.318
$r(C_1\text{-}C_2)$	1.383	1.386	1.385	1.382	1.380	1.380	1.372
$r(C_2\text{-}C_3)$	1.414	1.411	1.411	1.416	1.417	1.415	1.424
$\varphi(C_{8a}\text{-}N_{4a}\text{-}B)$	121.7	121.8	121.6	121.7	121.7	121.7	121.7
$\varphi_e(N_{4a}\text{-}C_3\text{-}C_2)$	109.4	109.5	109.6	109.4	109.3	109.3	109.3
$\varphi(N_{4a}\text{-}B\text{-}N_{4b})$	106.6	106.5	106.5	106.5	106.5	106.6	106.6
$\varphi(C_1\text{-}C_2\text{-}C_3)$	108.5	108.4	108.1	108.4	108.4	108.4	107.8
$WI(C_1\text{-}C_{1\text{-Sub}})$	1.06	1.11	1.11	1.06	1.06	1.06	-
$WI(C_3\text{-}C_{1\text{-Sub}})$	1.06	1.06	1.06	1.07	1.07	1.07	1.07

[a] r - bond lengths in Å, φ – bond angles in degrees, χ - dihedral angle in degrees, WI - Wiberg bond indexes; [b] for **C2** – the average value of the deviation from the substituent's location in the plane, $|\chi_1|=18.9\,°$, $|\chi_2|=149.2\,°$; [c] average values for nonequivalent parameters $|\chi_3|$, $|\chi_4|$, for **C7** – $|\chi_3|\approx|\chi_4|$. Natural charges and Wiberg bond indexes are given in Tables S9 and S13.

Table S4. Molecular parameters[a] of **D1-7** optimized at CAM-B3LYP/6-31+G(d,p) level.

	D1	D2	D3	D4	D5	D6	D7
Symmetry	C_2	C_1	C_2	C_2	C_2	C_2	C_{2v}
$|\chi(N_{4a}\text{-}B\text{-}N_{4b}\text{-}N_8)|$	0.0	0.4	0.0	0.0	0.0	0.0	0.0
$|\chi(C_2\text{-}C_1\text{-}C_{8a}\text{-}C_m)|$	176.8	178.2	178.0	177.3	177.4	177.0	180.0
$|\chi(C_3\text{-}N_{4a}\text{-}B\text{-}N_{4b})|$	178.7	179.4	179.6	178.9	178.9	178.9	180.0
$|\chi_1|=|\chi_2|$ [b]	28.8	12.5[b]	6.7	29.3	28.7	17.2	-
$r(C_1\text{-}X_{1\text{-}Sub})$	1.465	1.444	1.435	1.463	1.466	1.469	1.081
$r(C_3\text{-}H_{1\text{-}Sub})$	1.082	1.082	1.082	1.082	1.082	1.082	1.082
$r(C_{8a}\text{-}N_{4a})$	1.396	1.395	1.394	1.395	1.395	1.395	1.398
$r(C_3\text{-}N_{4a})$	1.337	1.338	1.340	1.336	1.335	1.336	1.334
$r(N_{4a}\text{-}B)$	1.546	1.546	1.545	1.548	1.550	1.547	1.550
$r(C_1\text{-}C_{8a})$	1.435	1.438	1.434	1.434	1.434	1.435	1.421
$r(N_8\text{-}C_{8a})$	1.318	1.317	1.318	1.317	1.317	1.318	1.319
$r(C_1\text{-}C_2)$	1.391	1.395	1.394	1.389	1.387	1.387	1.379
$r(C_2\text{-}C_3)$	1.403	1.399	1.399	1.405	1.406	1.404	1.414
$\varphi(C_{8a}\text{-}N_{4a}\text{-}B)$	124.2	124.3	124.2	124.2	124.2	124.2	124.1
$\varphi_e(N_{4a}\text{-}C_3\text{-}C_2)$	110.7	110.9	110.9	110.7	110.7	110.7	110.6
$\varphi(N_{4a}\text{-}B\text{-}N_{4b})$	104.7	104.7	104.6	104.6	104.6	104.7	104.6
$\varphi(C_1\text{-}C_2\text{-}C_3)$	107.6	107.5	107.1	107.4	107.4	107.4	106.8
$WI(C_1\text{-}C_{1\text{-}Sub})$	1.07	1.12	1.12	1.07	1.06	1.06	-
$WI(C_3\text{-}H_{1\text{-}Sub})$	0.90	0.90	0.90	0.90	0.90	0.90	0.90

[a] r - bond lengths in Å, φ – bond angles in degrees, χ - dihedral angle in degrees, WI - Wiberg bond indexes; [b] for **D2** – the average value of the deviation from the substituent's location in the plane, $|\chi_1|=13.1°$, $|\chi_2|=168.2°$. Natural charges and Wiberg bond indexes are given in Tables S10 and S14.

Table S5. Rotation angles χ_1 (°) for aza-BODIPY derivatives according to PBE/6-31G(d) calculations.

Substituent	phenyl	2-thiophenyl	2-furanyl	3-pyridinyl	4-pyridinyl	2-pyridinyl
once substituted at position 1	17.5	0.0	0.0	19.5	16.7	0.0
doble substituted at positions 1, 7	22.0	13.8	7.8	24.3	22.3	11.5

Table S6. Relative energies (kJ mol^{-1}) of conformers II[a] in relation to conformer I for **A1-6.**

	A1	A2	A3	A4	A5	A6
CAM-B3LYP [b]	8.52	5.93	5.25	9.06	5.69	7.80
PBE [b]	9.49	0.92	-0.79	7.06	7.38	0.74

[a] See Figure 3; [b] see Computational details.

Table S7. Natural charges at atoms calculated[a] in the framework of natural population analysis for **A1-7**.

Symmetry	A1 C_2	A2 C_1	A3 C_2	A4 C_2	A5 C_2	A6 C_2	A7 C_2
N_{4a}	-0.63	-0.62	-0.62	-0.63	-0.63	-0.63	-0.62
C_{8a}	0.34	0.36	0.35	0.34	0.34	0.35	0.31
C_1	-0.02	-0.04	-0.05	-0.02	-0.04	-0.04	-0.20
C_2	-0.26	-0.29	-0.29	-0.28	-0.24	-0.26	-0.31
C_3	0.26	0.26	0.26	0.26	0.26	0.26	0.26
N_{4b}	-0.63	-0.62	-0.62	-0.63	-0.62	-0.63	-0.62
C_{8b}	0.34	0.34	0.35	0.34	0.35	0.35	0.31
C_7	-0.01	-0.03	-0.05	-0.03	-0.03	-0.05	-0.20
C_6	-0.29	-0.30	-0.29	-0.25	-0.27	-0.23	-0.31
C_5	0.26	0.26	0.26	0.26	0.27	0.25	0.26
B	1.35	1.31	1.31	1.35	1.35	1.35	1.31
N_m	-0.39	-0.40	-0.40	-0.40	-0.39	-0.40	-0.38
F	-0.56	-0.57	-0.57	-0.56	-0.56	-0.56	-0.56
F	-0.56	-0.57	-0.57	-0.56	-0.56	-0.56	-0.56

[a] CAM-B3LYP/6-31+G(d,p)

Table S8. Natural charges at atoms calculated[a] in the framework of natural population analysis for **B1-7**.

Symmetry	B1 C_2	B2 C_1	B3 C_2	B4 C_2	B5 C_2	B6 C_2	B7 C_{2v}
N_{4a}	-0.64	-0.64	-0.63	-0.63	-0.63	-0.63	-0.63
C_{8a}	0.32	0.33	0.34	0.33	0.33	0.33	0.30
C_1	0.00	-0.03	-0.05	-0.01	-0.02	-0.03	-0.20
C_2	-0.31	-0.31	-0.31	-0.31	-0.30	-0.29	-0.33
C_3	0.33	0.32	0.32	0.33	0.33	0.33	0.33
N_{4b}	-0.64	-0.64	-0.63	-0.63	-0.63	-0.63	-0.63
C_{8b}	0.32	0.33	0.34	0.32	0.33	0.33	0.30
C_7	0.00	-0.03	-0.05	0.00	-0.01	-0.02	-0.20
C_6	-0.32	-0.30	-0.31	-0.31	-0.30	-0.29	-0.33
C_5	0.33	0.32	0.32	0.33	0.33	0.33	0.33
B	1.35	1.35	1.31	1.35	1.35	1.36	1.31
N_m	-0.38	-0.38	-0.38	-0.38	-0.37	-0.38	-0.35
F	-0.56	-0.56	-0.57	-0.56	-0.56	-0.56	-0.57
F	-0.56	-0.56	-0.57	-0.56	-0.56	-0.56	-0.57

[a] CAM-B3LYP/6-31+G(d,p)

Table S9. Natural charges at atoms calculated[a] in the framework of natural population analysis for **C1-7**.

Symmetry	C1 C_1	C2 C_1	C3 C_1	C4 C_1	C5 C_1	C6 C_1	C7 C_s
N_{4a}	-0.62	-0.61	-0.62	-0.62	-0.61	-0.62	-0.61
C_{8a}	0.33	0.34	0.35	0.34	0.34	0.34	0.31
C_1	0.00	-0.05	-0.06	-0.04	-0.02	-0.04	-0.20
C_2	-0.30	-0.30	-0.30	-0.28	-0.28	-0.28	-0.31
C_3	0.29	0.30	0.29	0.29	0.30	0.29	0.30
N_{4b}	-0.62	-0.62	-0.62	-0.62	-0.61	-0.62	-0.61
C_{8b}	0.33	0.33	0.35	0.34	0.34	0.34	0.31
C_7	0.00	-0.05	-0.05	-0.03	-0.02	-0.03	-0.20
C_6	-0.30	-0.30	-0.30	-0.28	-0.29	-0.28	-0.31
C_5	0.30	0.29	0.29	0.30	0.30	0.30	0.30
B	1.35	1.32	1.32	1.35	1.35	1.35	1.31
N_m	-0.37	-0.38	-0.38	-0.39	-0.38	-0.39	-0.36
F	-0.55	-0.57	-0.57	-0.55	-0.55	-0.55	-0.56
F	-0.56	-0.56	-0.56	-0.54	-0.55	-0.54	-0.56

[a] CAM-B3LYP/6-31+G(d,p)

Table S10. Natural charges at atoms calculated[a] in the framework of natural population analysis for **D1-7**.

	D1	D2	D3	D4	D5	D6	D7
Symmetry	C_2	C_1	C_2	C_2	C_2	C_2	C_{2v}
N_{4a}	-0.63	-0.62	-0.62	-0.62	-0.62	-0.62	-0.61
C_{8a}	0.32	0.33	0.34	0.32	0.33	0.33	0.29
C_1	0.00	-0.02	-0.05	-0.01	-0.01	-0.05	-0.20
C_2	-0.32	-0.32	-0.31	-0.31	-0.30	-0.23	-0.34
C_3	0.10	0.10	0.09	0.10	0.10	0.08	0.11
N_{4b}	-0.62	-0.63	-0.62	-0.62	-0.62	-0.62	-0.61
C_{8b}	0.32	0.32	0.34	0.33	0.33	0.33	0.29
C_7	0.00	-0.02	-0.05	-0.01	-0.02	-0.05	-0.20
C_6	-0.32	-0.33	-0.31	-0.31	-0.30	-0.24	-0.34
C_5	0.10	0.10	0.09	0.10	0.10	0.08	0.11
B	1.35	1.31	1.31	1.35	1.35	1.35	1.31
N_m	-0.35	-0.34	-0.37	-0.36	-0.35	-0.36	-0.33
F	-0.56	-0.57	-0.57	-0.56	-0.56	-0.56	-0.56
F	-0.56	-0.57	-0.57	-0.56	-0.56	-0.56	-0.56

[a] CAM-B3LYP/6-31+G(d,p)

Table S11. Wiberg bond indexes calculated[a] for **A1-7**.

	A1	A2	A3	A4	A5	A6	A7
Symmetry	C_2	C_1	C_2	C_2	C_2	C_2	C_2
$C_{8a}-N_{4a}$	1.08	1.08	1.08	1.08	1.08	1.08	1.07
C_3-N_{4a}	1.25	1.24	1.24	1.25	1.26	1.25	1.27
$N_{4a}-B$	0.62	0.63	0.63	0.62	0.62	0.62	0.63
C_1-C_{8a}	1.18	1.16	1.17	1.18	1.18	1.18	1.22
N_m-C_{4a}	1.39	1.40	1.39	1.39	1.39	1.39	1.39
C_1-C_2	1.47	1.44	1.43	1.48	1.48	1.48	1.55
C_2-C_3	1.29	1.30	1.31	1.29	1.28	1.29	1.27
B-F	0.65	0.67	0.68	0.65	0.65	0.65	0.68

[a] CAM-B3LYP/6-31+G(d,p)

Table S12. Wiberg bond indexes calculated[a] for **B1-7**.

	B1	B2	B3	B4	B5	B6	B7
Symmetry	C_2	C_1	C_2	C_2	C_2	C_2	C_{2v}
$C_{8a}-N_{4a}$	1.06	1.07	1.07	1.07	1.07	1.07	1.05
C_3-N_{4a}	1.29	1.27	1.28	1.30	1.30	1.29	1.32
$N_{4a}-B$	0.62	0.62	0.63	0.62	0.62	0.61	0.63
C_1-C_{8a}	1.18	1.18	1.17	1.18	1.18	1.18	1.22
N_m-C_{4a}	1.40	1.39	1.40	1.40	1.40	1.40	1.40
C_1-C_2	1.45	1.40	1.41	1.45	1.46	1.46	1.53
C_2-C_3	1.33	1.36	1.35	1.32	1.31	1.32	1.30
B-F	0.66	0.65	0.68	0.66	0.66	0.65	0.68

[a] CAM-B3LYP/6-31+G(d,p)

Table S13. Wiberg bond indexes calculated[a] for **C1-7**.

	C1	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_s
C_{8a}-N_{4a}	1.07	1.07	1.08	1.08	1.08	1.08	1.06
C_3-N_{4a}	1.28	1.27	1.27	1.28	1.29	1.28	1.30
N_{4a}-B	0.62	0.62	0.62	0.62	0.61	0.62	0.63
C_1-C_{8a}	1.18	1.16	1.17	1.18	1.18	1.18	1.22
N_m-C_{4a}	1.40	1.40	1.40	1.39	1.40	1.39	1.40
C_1-C_2	1.46	1.44	1.43	1.47	1.48	1.47	1.55
C_2-C_3	1.31	1.32	1.33	1.30	1.30	1.30	1.28
B-F	0.66	0.65	0.65	0.64	0.64	0.64	0.66

[a] CAM-B3LYP/6-31+G(d,p)

Table S14. Wiberg bond indexes calculated[a] for **D1-7**.

	D1	**D2**	**D3**	**D4**	**D5**	**D6**	**D7**
Symmetry	C_2	C_1	C_2	C_2	C_2	C_2	C_{2v}
C_{8a}-N_{4a}	1.07	1.07	1.08	1.07	1.07	1.07	1.06
C_3-N_{4a}	1.32	1.31	1.30	1.33	1.34	1.33	1.35
N_{4a}-B	0.61	0.63	0.63	0.61	0.61	0.61	0.62
C_1-C_{8a}	1.18	1.17	1.17	1.18	1.18	1.18	1.22
N_m-C_{4a}	1.40	1.41	1.40	1.40	1.40	1.40	1.40
C_1-C_2	1.44	1.42	1.40	1.45	1.46	1.45	1.54
C_2-C_3	1.36	1.38	1.39	1.35	1.35	1.35	1.33
B-F	0.67	0.69	0.69	0.67	0.67	0.67	0.69

[a] CAM-B3LYP/6-31+G(d,p)

Table S15. Contributions of aza-BODIPY core and substituent groups R_1-R_4 to frontier MOs of **A1-7**, **B1-B7**, **C1-C7**, **D1-7**.

| Molecule	HOMO contributors, %					LUMO contributors, %				
	Core	R_1	R_2	R_3	R_4	Core	R_1	R_2	R_3	R_4
A1	61.5	3.2	3.2	16.1	16.1	72.8	4.1	4.1	9.5	9.5
A2	57.9	6.8	7.1	13.9	14.2	68.8	6.9	7.0	8.9	8.4
A3	56.8	8.2	8.2	13.4	13.4	69.1	6.7	6.7	8.8	8.8
A4	61.4	2.3	2.3	17.0	17.0	72.7	4.1	4.1	9.6	9.6
A5	61.3	1.6	1.6	17.7	17.7	72.5	4.2	4.2	9.5	9.5
A6	61.3	2.3	2.3	17.1	17.1	71.9	4.8	4.8	9.3	9.3
A7	64.5	0.0	0.0	17.7	17.7	78.1	0.1	0.1	10.9	10.9
B1	81.5	7.2	7.2	2.1	2.1	85.8	5.6	5.6	1.5	1.5
B2	66.8	15.4	15.4	1.6	1.6	79.0	9.2	9.2	1.3	1.3
B3	63.5	16.8	16.8	1.5	1.5	80.3	8.5	8.5	1.4	1.4
B4	84.9	5.3	5.3	2.3	2.3	85.8	5.6	5.6	1.5	1.5
B5	84.9	5.3	5.3	2.3	2.3	85.8	5.6	5.6	1.5	1.5
B6	84.9	5.3	5.3	2.3	2.3	84.1	6.5	6.5	1.4	1.4
B7	95.1	0.0	0.0	2.4	2.4	96.3	0.1	0.1	1.8	1.8
C1	70.9	4.4	4.8	9.8	10.1	78.4	4.7	4.9	6.0	6.0
C2	63.0	11.5	10.2	7.5	7.9	73.5	8.1	7.5	5.3	5.6
C3	60.7	12.9	12.0	7.0	7.3	74.7	7.2	7.4	5.3	5.4
C4	71.5	3.1	3.4	10.7	11.2	75.7	4.7	4.9	5.8	6.0
C5	72.4	2.0	2.2	11.5	11.9	78.3	4.9	5.1	5.9	5.8
C6	71.8	3.3	3.1	10.6	11.1	77.6	5.6	5.4	5.6	5.8
C7	76.9	0.0	0.0	11.5	11.5	84.2	0.1	0.1	7.4	7.4
D1	77.4	11.2	11.2	0.0	0.0	88.6	5.6	5.6	0.1	0.1
D2	59.6	20.2	20.2	0.0	0.0	82.5	8.7	8.7	0.1	0.1
D3	55.5	22.2	22.2	0.0	0.0	82.8	8.5	8.5	0.1	0.1
D4	84.0	7.9	7.9	0.1	0.1	88.6	5.5	5.5	0.1	0.1
D5	90.9	4.5	4.5	0.1	0.1	88.8	5.6	5.6	0.1	0.1
D6	84.1	7.9	7.9	0.1	0.1	87.6	6.1	6.1	0.1	0.1
D7	99.8	0.0	0.0	0.1	0.1	99.7	0.1	0.1	0.1	0.1
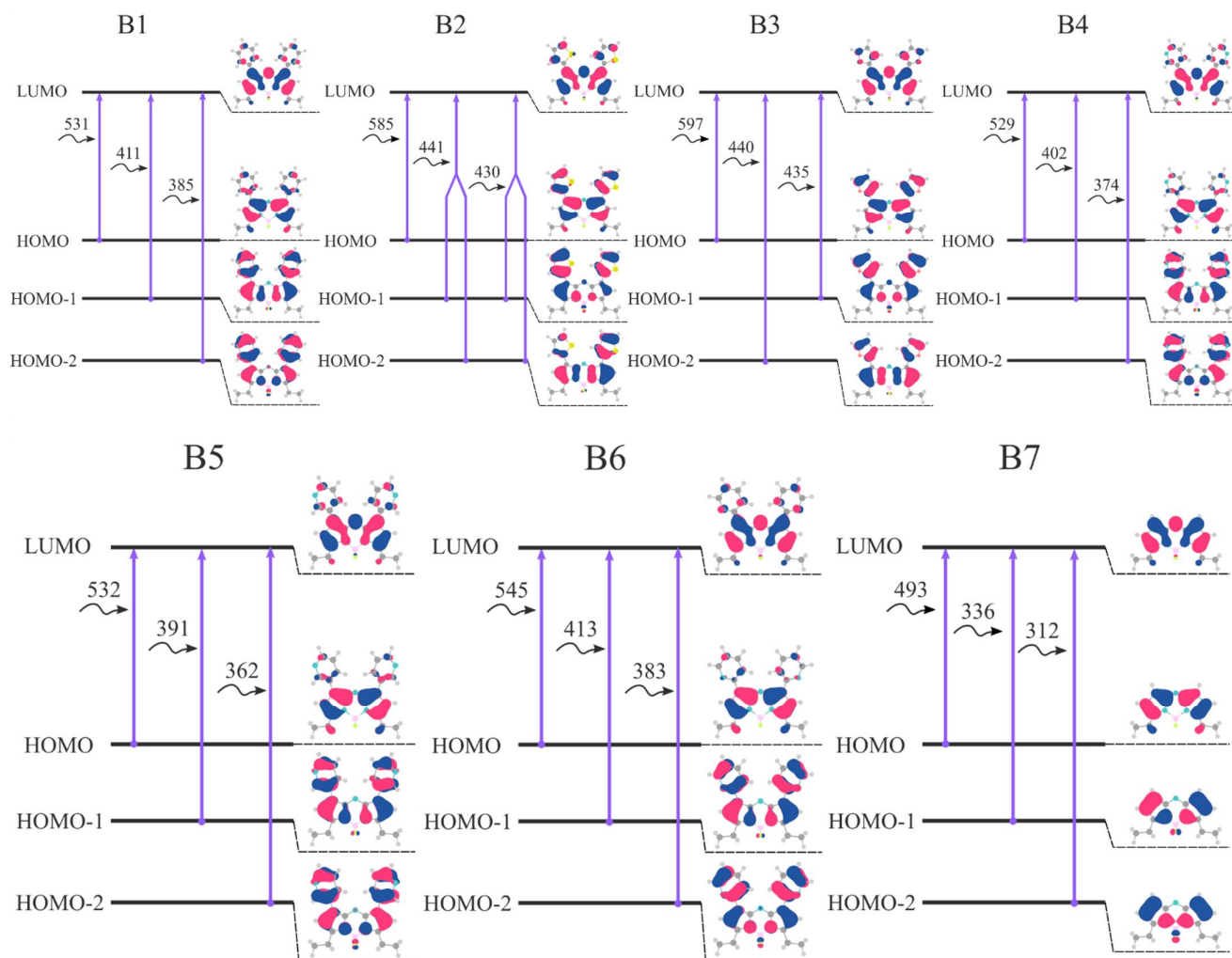
Figure S5. Visual representation of the first three transitions for molecules **B1-7** calculated at CAM-B3LYP/6-31+G(d,p) level. Isosurface cutoff is 0.03.
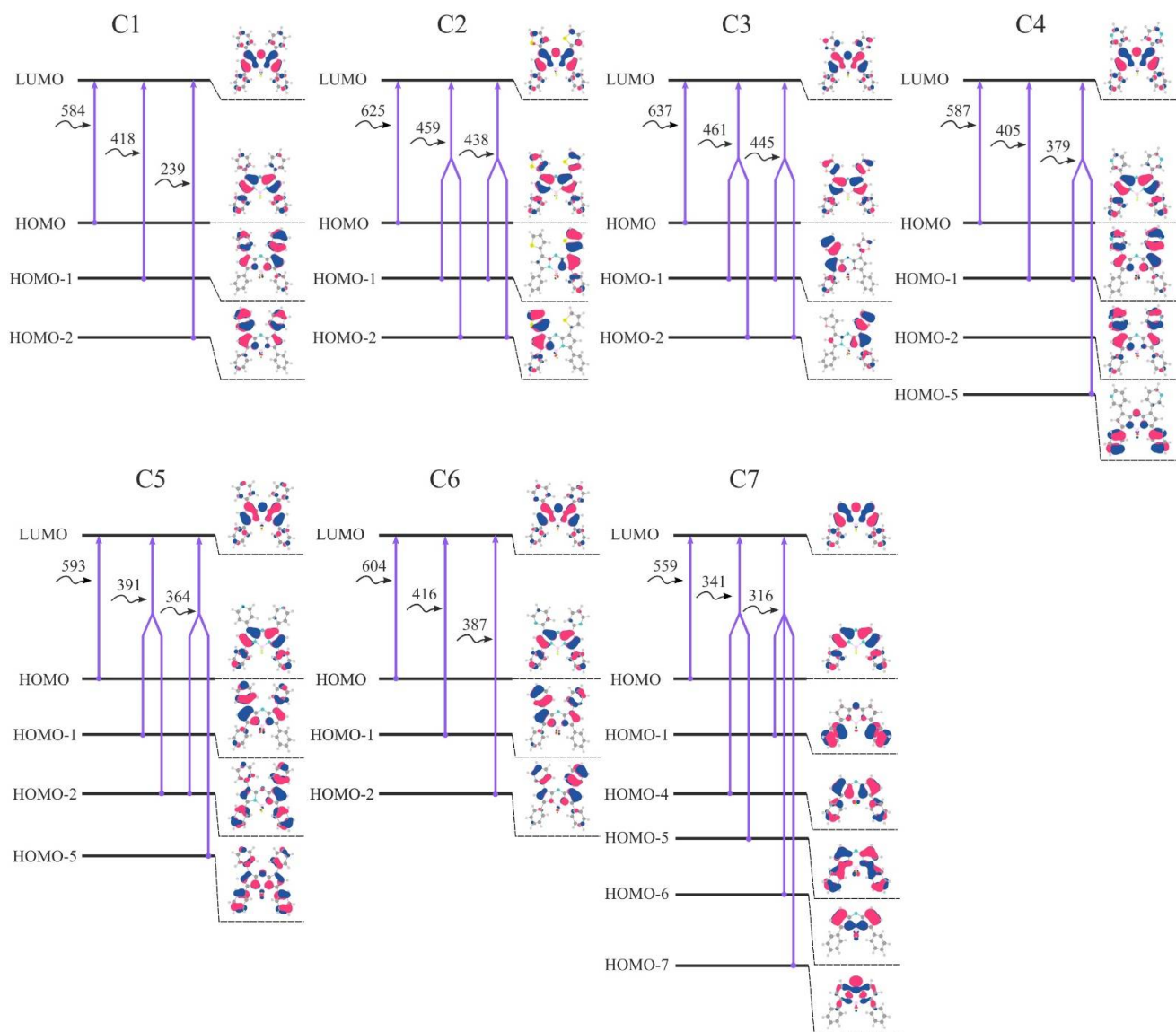
Figure S6. Visual representation of the first three transitions for molecules **C1-7** calculated at CAM-B3LYP/6-31+G(d,p) level. Isosurface cutoff is 0.03.
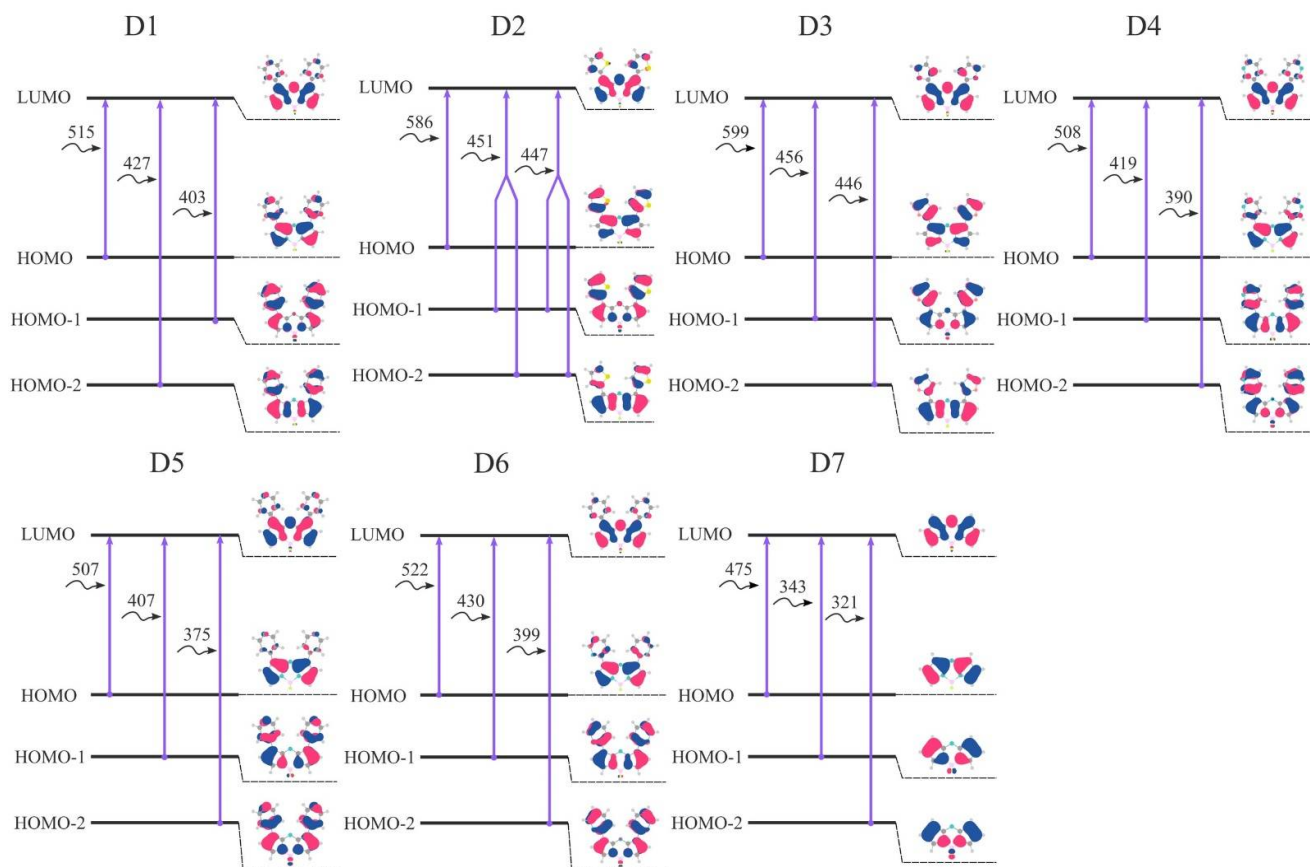
Figure S7. Visual representation of the first three transitions for molecules **D1-7** calculated at CAM-B3LYP/6-31+G(d,p) level. Isosurface cutoff is 0.03.

Table S16. Calculated (CAM-B3LYP/6-31+G(d,p)) composition of five lowest excited states and corresponding oscillator strengths.

Compound	Transition and state symmetry	Main determinant contributions (CI expansion coefficient squared), %	Energy, eV	Energy, cm^{-1}	Wavelength, nm	Oscillator Strength
A1	1 (B)	HOMO -> LUMO, 98.4	1.92	15486	647	0.918
	2 (B)	HOMO-1 -> LUMO, 91.4	3.00	24197	413	0.013
	3 (A)	HOMO-2 -> LUMO, 87.5 HOMO-3 -> LUMO, 7.2	3.17	25568	391	0.536
	4 (A)	HOMO-2 -> LUMO, 8.3 HOMO-3 -> LUMO, 85.9	3.71	29923	334	0.388
	5 (B)	HOMO-5 -> LUMO, 43.5 HOMO-11 -> LUMO, 50.7	3.84	30972	323	0.150
A2	1 (A)	HOMO -> LUMO, 98.4	1.83	14760	679	0.886
	2 (A)	HOMO-1 -> LUMO, 83.9 HOMO-2 -> LUMO, 10.0	2.69	21697	460	0.005
	3 (A)	HOMO-1 -> LUMO, 10.1 HOMO-2 -> LUMO, 83.7	2.83	22826	438	0.570
	4 (A)	HOMO-3 -> LUMO, 90.7	3.67	29601	338	0.376
	5 (A)	HOMO-4 -> LUMO, 48.8 HOMO-5 -> LUMO, 35.5 HOMO-11 -> LUMO, 11.5	3.81	30730	326	0.051
A3	1 (B)	HOMO -> LUMO, 98.6	1.79	14437	693	0.879
	2 (B)	HOMO-1 -> LUMO, 94.3	2.66	21455	466	0.006
	3 (A)	HOMO-2 -> LUMO, 94.6	2.78	22422	446	0.582
	4 (A)	HOMO-3 -> LUMO, 91.6	3.67	29601	338	0.373
	5 (B)	HOMO-4 -> LUMO, 28.1 HOMO-6 -> LUMO, 46.1 HOMO-11 -> LUMO, 14.7	4.01	32343	309	0.002
A4	1 (B)	HOMO -> LUMO, 98.4	1.89	15244	657	0.913
	2 (B)	HOMO-2 -> LUMO, 90.1	3.10	25003	400	0.024
	3 (A)	HOMO-1 -> LUMO, 74.8 HOMO-3 -> LUMO, 18.9	3.28	26455	378	0.551
	4 (A)	HOMO-1 -> LUMO, 21.0 HOMO-3 -> LUMO,73.1	3.66	29520	339	0.341
	5 (B)	HOMO-6 -> LUMO, 30.6 HOMO-11 -> LUMO, 45.3 HOMO-13 -> LUMO, 11.9	3.92	31617	317	0.006
A5	1 (B)	HOMO -> LUMO, 98.4	1.86	15002	666	0.896
	2 (B)	HOMO-2 -> LUMO, 88.9	3.22	25971	385	0.029
	3 (A)	HOMO-1 -> LUMO, 49.0 HOMO-3 -> LUMO, 28.9 HOMO-5 -> LUMO, 15.2	3.42	27584	363	0.569
	4 (A)	HOMO-1 -> LUMO, 46.7 HOMO-3 -> LUMO, 38.7 HOMO-5 -> LUMO, 7.9	3.61	29117	343	0.294
	5 (B)	HOMO-7 -> LUMO, 28.2 HOMO-8 -> LUMO, 11.5 HOMO-11 -> LUMO, 50.5	3.83	30891	324	0.003
A6	1 (B)	HOMO -> LUMO, 98.5	1.83	14760	676	0.892
	2 (B)	HOMO-2 -> LUMO, 91.4	3.02	24358	411	0.020
	3 (A)	HOMO-1 -> LUMO, 77.5 HOMO-3 -> LUMO, 17.1	3.21	25891	387	0.539
	4 (A)	HOMO-1 -> LUMO, 18.5 HOMO-3 -> LUMO, 76.2	3.61	29117	343	0.377
	5 (B)	HOMO-4 -> LUMO, 8.4 HOMO-10 -> LUMO, 7.9 HOMO-11 -> LUMO, 55.3 HOMO-12 -> LUMO, 18.4	3.92	31617	317	0.009
A7	1 (B)	HOMO -> LUMO, 98.5	1.98	15970	627	0.875

	2 (B)	HOMO-2 -> LUMO, 7.2 HOMO-4 -> LUMO, 80.2 HOMO-5 -> LUMO, 9.8	3.63	29278	341	0.043
	3 (A)	HOMO-1 -> LUMO, 88.0 HOMO-6 -> LUMO, 5.8	3.72	30004	333	0.325
	4 (A)	HOMO-1 -> LUMO, 8.6 HOMO-3 -> LUMO, 35.1 HOMO-6 -> LUMO, 53.8	3.95	31859	314	0.114
	5 (B)	HOMO-2 -> LUMO, 14.1 HOMO-7 -> LUMO, 80.2	4.06	32746	306	0.019
B1	1 (B)	HOMO -> LUMO, 99.0	2.33	18793	531	0.824
	2 (B)	HOMO-1 -> LUMO, 93.5	3.02	24358	411	0.002
	3 (A)	HOMO-2 -> LUMO, 94.4	3.22	25971	385	0.322
	4 (B)	HOMO-4 -> LUMO, 28.2 HOMO-7 -> LUMO, 66.9	3.84	30972	323	0.005
	5 (A)	HOMO-3 -> LUMO, 95.3	4.09	32988	303	0.000
B2	1 (A)	HOMO -> LUMO, 98.8	2.12	17099	585	0.731
	2 (A)	HOMO-1 -> LUMO, 10.7 HOMO-2 -> LUMO, 84.1	2.81	22664	441	0.044
	3 (A)	HOMO-1 -> LUMO, 85.3 HOMO-2 -> LUMO, 10.6	2.88	23229	430	0.357
	4 (A)	HOMO-3 -> LUMO, 45.9 HOMO-4 -> LUMO, 21.5 HOMO-7 -> LUMO, 28.6	3.85	31053	322	0.030
	5 (A)	HOMO-3 -> LUMO, 51.4 HOMO-4 -> LUMO, 22.8 HOMO-7 -> LUMO, 22.2	3.97	32020	312	0.001
B3	1 (B)	HOMO -> LUMO, 99.2	2.08	16776	597	0.723
	2 (B)	HOMO-2 -> LUMO, 94.9	2.81	22664	440	0.049
	3 (A)	HOMO-1 -> LUMO, 96.4	2.85	22987	435	0.377
	4 (B)	HOMO-5 -> LUMO, 5.2 HOMO-7 -> LUMO, 90.4	4.01	32343	309	0.002
	5 (B)	HOMO-3 -> LUMO, 58.1 HOMO-5 -> LUMO, 34.5	4.70	37908	264	0.001
B4	1 (B)	HOMO -> LUMO, 98.9	2.34	18873	529	0.818
	2 (B)	HOMO-1 -> LUMO, 93.7	3.08	24842	402	0.012
	3 (A)	HOMO-2 -> LUMO, 93.7	3.32	26778	374	0.293
	4 (B)	HOMO-3 -> LUMO, 28.3 HOMO-7 -> LUMO, 34.7 HOMO-9 -> LUMO, 29.9	3.87	31214	320	0.001
	5 (A)	HOMO-3 -> LUMO+1, 5.1 HOMO-4 -> LUMO, 85.2	4.44	35811	279	0.000
B5	1 (B)	HOMO -> LUMO, 98.8	2.33	18793	532	0.790
	2 (B)	HOMO-1 -> LUMO, 95.6	3.17	25568	391	0.027
	3 (A)	HOMO-2 -> LUMO, 95.8	3.43	27665	362	0.261
	4 (B)	HOMO-4 -> LUMO, 27.0 HOMO-5 -> LUMO, 12.7 HOMO-7 -> LUMO, 60.5	3.79	30569	327	0.005
	5 (A)	HOMO-3 -> LUMO, 94.7	4.14	33392	299	0.000
B6	1 (B)	HOMO -> LUMO, 99.0	2.27	18309	545	0.794
	2 (B)	HOMO-1 -> LUMO, 94.3	3.00	24197	413	0.009
	3 (A)	HOMO-2 -> LUMO, 94.4	3.24	26132	383	0.308
	4 (B)	HOMO-5 -> LUMO, 8.3 HOMO-7 -> LUMO, 21.1 HOMO-8 -> LUMO, 64.8	3.86	31133	321	0.002
	5 (A)	HOMO-3 -> LUMO+2, 2.4 HOMO-3 -> LUMO, 87.3 HOMO-4 -> LUMO+1, 8.1	4.13	33311	301	0.002
B7	1 (B2)	HOMO -> LUMO, 97.8	2.51	20245	493	0.696
	2 (B2)	HOMO-1 -> LUMO, 97.1	3.69	29763	336	0.105
	3 (A1)	HOMO-2 -> LUMO, 98.3	3.97	32021	312	0.055

|						
	4 (B1)	HOMO-3 -> LUMO, 97.4	4.01	32344	309	0.002
	5 (A2)	HOMO -> LUMO+3, 9.5 HOMO -> LUMO+1, 80.9	5.58	45007	222	0.000
C1	1 (A)	HOMO -> LUMO, 98.3	2.12	17099	584	0.902
	2 (A)	HOMO-1 -> LUMO, 89.4	2.97	23955	418	0.011
	3 (A)	HOMO-2 -> LUMO, 90.4	3.16	25487	392	0.446
	4 (A)	HOMO-4 -> LUMO, 38.0 HOMO-11 -> LUMO, 51.3	3.78	30488	328	0.033
	5 (A)	HOMO-3 -> LUMO, 95.2	4.00	32262	310	0.004
C2	1 (A)	HOMO -> LUMO, 98.4	1.98	15970	625	0.842
	2 (A)	HOMO-1 -> LUMO, 75.7 HOMO-2 -> LUMO, 18.1	2.70	21777	459	0.036
	3 (A)	HOMO-1 -> LUMO, 18.8 HOMO-2 -> LUMO, 76.5	2.83	22826	438	0.476
	4 (A)	HOMO-3 -> LUMO, 51.4 HOMO-6 -> LUMO, 19.0 HOMO-7 -> LUMO, 13.7 HOMO-11 -> LUMO, 6.1	3.82	30811	325	0.040
	5 (A)	HOMO-3 -> LUMO, 37.3 HOMO-6 -> LUMO, 16.1 HOMO-7 -> LUMO, 6.7 HOMO-11 -> LUMO, 29.4	3.85	31053	322	0.099
C3	1 (A)	HOMO -> LUMO, 98.7	1.95	15728	637	0.832
	2 (A)	HOMO-1 -> LUMO, 35.5 HOMO-2 -> LUMO, 58.4	2.69	21697	461	0.029
	3 (A)	HOMO-1 -> LUMO, 59.8 HOMO-2 -> LUMO, 36.0	2.79	22503	445	0.505
	4 (A)	HOMO-4 -> LUMO, 20.4 HOMO-5 -> LUMO, 33.9 HOMO-10 -> LUMO, 7.1 HOMO-11 -> LUMO, 26.8	3.90	31456	318	0.190
	5 (A)	HOMO-3 -> LUMO, 71.5 HOMO-4 -> LUMO, 17.8	4.08	32908	304	0.006
C4	1 (A)	HOMO -> LUMO, 98.2	2.11	17018	587	0.895
	2 (A)	HOMO-1 -> LUMO, 89.6	3.06	24681	405	0.022
	3 (A)	HOMO-2 -> LUMO, 86.8 HOMO-5 -> LUMO, 5.0	3.27	26375	379	0.420
	4 (A)	HOMO-4 -> LUMO, 9.4 HOMO-5 -> LUMO, 20.2 HOMO-6 -> LUMO, 15.4 HOMO-11 -> LUMO, 26.7 HOMO-13 -> LUMO, 14.6	3.81	30730	325	0.083
	5 (A)	HOMO-4 -> LUMO, 9.0 HOMO-5 -> LUMO, 43.9 HOMO-6 -> LUMO, 12.2 HOMO-11 -> LUMO, 10.7	4.03	32504	308	0.321
C5	1 (A)	HOMO -> LUMO, 98.2	2.09	16857	593	0.871
	2 (A)	HOMO-1 -> LUMO, 87.6 HOMO-2 -> LUMO, 5.1	3.17	25568	391	0.034
	3 (A)	HOMO-2 -> LUMO, 57.7 HOMO-5 -> LUMO, 33.3	3.41	27504	364	0.380
	4 (A)	HOMO-2 -> LUMO, 8.9 HOMO-5 -> LUMO, 17.8 HOMO-7 -> LUMO, 12.5 HOMO-8 -> LUMO, 5.7 HOMO-11 -> LUMO, 41.2	3.73	30085	332	0.068
	5 (A)	HOMO-2 -> LUMO, 22.2 HOMO-4 -> LUMO, 9.1 HOMO-5 -> LUMO, 27.4 HOMO-7 -> LUMO, 17.0 HOMO-11 -> LUMO, 12.6	3.96	31940	313	0.329
C6	1 (A)	HOMO -> LUMO, 98.3	2.05	16535	604	0.871

	2 (A)	HOMO-1 -> LUMO, 89.9	2.98	24036	416	0.023
	3 (A)	HOMO-2 -> LUMO, 87.7	3.21	25891	387	0.422
	4 (A)	HOMO-4 -> LUMO, 12.9 HOMO-5 -> LUMO, 24.4 HOMO-11 -> LUMO, 8.2 HOMO-12 -> LUMO, 30.3 HOMO-13 -> LUMO, 11.1	3.79	30569	327	0.130
	5 (A)	HOMO-4 -> LUMO, 8.0 HOMO-5 -> LUMO, 42.5 HOMO-12 -> LUMO, 22.2	3.99	32182	311	0.274
C7	1 (A'')	HOMO -> LUMO, 98.0	2.22	17906	559	0.829
	2 (A'')	HOMO-4 -> LUMO, 81.4 HOMO-5 -> LUMO, 15.9	3.64	29359	341	0.077
	3 (A')	HOMO-1 -> LUMO, 38.7 HOMO-6 -> LUMO, 13.2 HOMO-7 -> LUMO, 42.7	3.93	31698	316	0.067
	4 (A')	HOMO-6 -> LUMO, 80.3 HOMO-7 -> LUMO, 16.2	3.95	31859	314	0.065
	5 (A'')	HOMO-2 -> LUMO, 93.8	4.12	33230	301	0.015
D1	1 (B)	HOMO -> LUMO, 99.1	2.41	19438	515	0.768
	2 (B)	HOMO-2 -> LUMO, 93.7	2.90	23390	427	0.003
	3 (A)	HOMO-1 -> LUMO, 94.7	3.08	24842	403	0.290
	4 (B)	HOMO-4 -> LUMO, 36.4 HOMO-7 -> LUMO, 58.4	3.72	30004	333	0.007
	5 (A)	HOMO-3 -> LUMO, 96.4	3.90	31456	318	0.000
D2	1 (A)	HOMO -> LUMO, 98.5	2.12	17099	586	0.628
	2 (A)	HOMO-1 -> LUMO, 89.2 HOMO-2 -> LUMO, 7.0	2.75	22180	451	0.300
	3 (A)	HOMO-1 -> LUMO, 7.1 HOMO-2 -> LUMO, 87.5	2.78	22422	447	0.113
	4 (A)	HOMO-3 -> LUMO, 64.3 HOMO-4 -> LUMO, 19.4 HOMO-7 -> LUMO, 13.3	3.71	29923	334	0.036
	5 (A)	HOMO-3 -> LUMO, 31.8 HOMO-4 -> LUMO, 54.5 HOMO-7 -> LUMO, 10.6	3.83	30891	324	0.010
D3	1 (B)	HOMO -> LUMO, 98.9	2.07	16696	599	0.624
	2 (A)	HOMO-1 -> LUMO, 96.6	2.72	21938	456	0.334
	3 (B)	HOMO-2 -> LUMO, 94.9	2.78	22422	446	0.102
	4 (B)	HOMO-7 -> LUMO, 94.5	3.92	31617	316	0.002
	5 (B)	HOMO-3 -> LUMO, 71.7 HOMO-5 -> LUMO, 22.5	4.65	37505	267	0.001

	1 (B)	HOMO -> LUMO, 98.5	1.98	15970	627	0.875
A7	2 (B)	HOMO-2 -> LUMO, 7.2 HOMO-4 -> LUMO, 80.2 HOMO-5 -> LUMO, 9.8	3.63	29278	341	0.043
	3 (A)	HOMO-1 -> LUMO, 88.0 HOMO-6 -> LUMO, 5.8	3.72	30004	333	0.325
	4 (A)	HOMO-1 -> LUMO, 8.6 HOMO-3 -> LUMO, 35.1 HOMO-6 -> LUMO, 53.8	3.95	31859	314	0.114
	5 (B)	HOMO-2 -> LUMO, 14.1 HOMO-7 -> LUMO, 80.2	4.06	32746	306	0.019
B1	1 (B)	HOMO -> LUMO, 98.9	2.36	19035	525	0.820
	2 (B)	HOMO-1 -> LUMO, 93.5	3.06	24681	405	0.005
	3 (A)	HOMO-2 -> LUMO, 94.5	3.26	26294	381	0.330
	4 (B)	HOMO-4 -> LUMO, 27.0 HOMO-7 -> LUMO, 67.8	3.86	31133	321	0.006
	5 (A)	HOMO-3 -> LUMO, 95.0	4.12	33230	301	0.000
B2	1 (A)	HOMO -> LUMO, 98.8	2.15	17341	576	0.736
	2 (A)	HOMO-1 -> LUMO, 11.1 HOMO-2 -> LUMO, 83.7	2.83	22826	438	0.035
	3 (A)	HOMO-1 -> LUMO, 85.0 HOMO-2 -> LUMO, 11.1	2.91	23471	426	0.366
	4 (A)	HOMO-3 -> LUMO, 43.5 HOMO-4 -> LUMO, 20.0 HOMO-7 -> LUMO, 31.8	3.87	31214	320	0.027
	5 (A)	HOMO-3 -> LUMO, 53.5 HOMO-4 -> LUMO, 21.5 HOMO-7 -> LUMO, 21.0	4.00	32262	310	0.001
B3	1 (B)	HOMO -> LUMO, 99.1	2.12	17099	586	0.045
	2 (B)	HOMO-2 -> LUMO, 95.1	2.83	22826	438	0.382
	3 (A)	HOMO-1 -> LUMO, 96.5	2.88	23229	431	0.003
	4 (B)	HOMO-5 -> LUMO, 9.1 HOMO-6 -> LUMO, 94.6	4.03	32504	308	0.002
	5 (B)	HOMO-3 -> LUMO, 56.3 HOMO-2 -> LUMO, 35.3	4.75	38312	261	0.202
B4	1 (B)	HOMO -> LUMO, 98.8	2.37	19116	524	0.813
	2 (B)	HOMO-1 -> LUMO, 93.7	3.13	25245	396	0.018
	3 (A)	HOMO-2 -> LUMO, 93.7	3.36	27020	369	0.303
	4 (B)	HOMO-3 -> LUMO, 27.6 HOMO-7 -> LUMO, 41.8 HOMO-8 -> LUMO, 23.0	3.90	31456	318	0.000
	5 (A)	HOMO-3 -> LUMO+3, 2.6 HOMO-3 -> LUMO+1, 5.4 HOMO-4 -> LUMO, 84.6	4.48	36134	277	0.000
B5	1 (B)	HOMO -> LUMO, 98.8	2.35	18954	527	0.785
	2 (B)	HOMO-1 -> LUMO, 95.6	3.23	26052	384	0.034
	3 (A)	HOMO-2 -> LUMO, 95.8	3.48	28068	357	0.272
	4 (B)	HOMO-4 -> LUMO, 20.5 HOMO-5 -> LUMO, 12.3 HOMO-7 -> LUMO, 61.1	3.82	30811	325	0.005
	5 (A)	HOMO-3 -> LUMO, 94.4	4.19	33795	296	0.000
B6	1 (B)	HOMO -> LUMO, 98.9	2.30	18551	539	0.789
	2 (B)	HOMO-1 -> LUMO, 94.3	3.05	24600	407	0.014
	3 (A)	HOMO-2 -> LUMO, 94.6	3.28	26455	378	0.319
	4 (B)	HOMO-5 -> LUMO, 8.3 HOMO-7 -> LUMO, 37.9 HOMO-8 -> LUMO, 47.8	3.89	31375	319	0.002
	5 (A)	HOMO-3 -> LUMO, 86.6 HOMO-4 -> LUMO+1, 8.5	4.16	33553	298	0.002

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B7	1 (A'')	HOMO -> LUMO, 98.0	2.53	20406	491	0.695
	2 (A'')	HOMO-1 -> LUMO, 97.4	3.76	30327	330	0.108
	3 (A')	HOMO-2 -> LUMO, 63.4 HOMO-3 -> LUMO, 34.4	4.03	32504	307	0.039
	4 (A')	HOMO-2 -> LUMO, 34.6 HOMO-3 -> LUMO, 62.6	4.03	32504	307	0.025
	5 (A'')	HOMO -> LUMO+3, 13.9 HOMO -> LUMO+1, 76.6	5.59	45087	222	0.000
C1	1 (A)	HOMO -> LUMO, 98.3	2.12	17099	584	0.902
	2 (A)	HOMO-1 -> LUMO, 89.4	2.97	23955	418	0.011
	3 (A)	HOMO-2 -> LUMO, 90.4	3.16	25487	392	0.446
	4 (A)	HOMO-4 -> LUMO, 38.0 HOMO-11 -> LUMO, 51.3	3.78	30488	328	0.033
	5 (A)	HOMO-3 -> LUMO, 95.2	4.00	32262	310	0.004
C2	1 (A)	HOMO -> LUMO, 98.4	1.98	15970	625	0.842
	2 (A)	HOMO-1 -> LUMO, 75.7 HOMO-2 -> LUMO, 18.1	2.70	21777	459	0.036
	3 (A)	HOMO-1 -> LUMO, 18.8 HOMO-2 -> LUMO, 76.5	2.83	22826	438	0.476
	4 (A)	HOMO-3 -> LUMO, 51.4 HOMO-6 -> LUMO, 19.0 HOMO-7 -> LUMO, 13.7 HOMO-11 -> LUMO, 6.1	3.82	30811	325	0.040
	5 (A)	HOMO-3 -> LUMO, 37.3 HOMO-6 -> LUMO, 16.1 HOMO-7 -> LUMO, 6.7 HOMO-11 -> LUMO, 29.4	3.85	31053	322	0.099
C3	1 (A)	HOMO -> LUMO, 98.7	1.95	15728	637	0.832
	2 (A)	HOMO-1 -> LUMO, 35.5 HOMO-2 -> LUMO, 58.4	2.69	21697	461	0.029
	3 (A)	HOMO-1 -> LUMO, 59.8 HOMO-2 -> LUMO, 36.0	2.79	22503	445	0.505
	4 (A)	HOMO-4 -> LUMO, 20.4 HOMO-5 -> LUMO, 33.9 HOMO-10 -> LUMO, 7.1 HOMO-11 -> LUMO, 26.8	3.90	31456	318	0.190
	5 (A)	HOMO-3 -> LUMO, 71.5 HOMO-4 -> LUMO, 17.8	4.08	32908	304	0.006
C4	1 (A)	HOMO -> LUMO, 98.2	2.11	17018	587	0.895
	2 (A)	HOMO-1 -> LUMO, 89.6	3.06	24681	405	0.022
	3 (A)	HOMO-2 -> LUMO, 86.8 HOMO-5 -> LUMO, 5.0	3.27	26375	379	0.420
	4 (A)	HOMO-4 -> LUMO, 9.4 HOMO-5 -> LUMO, 20.2 HOMO-6 -> LUMO, 15.4 HOMO-11 -> LUMO, 26.7 HOMO-13 -> LUMO, 14.6	3.81	30730	325	0.083
	5 (A)	HOMO-4 -> LUMO, 9.0 HOMO-5 -> LUMO, 43.9 HOMO-6 -> LUMO, 12.2 HOMO-11 -> LUMO, 10.7	4.03	32504	308	0.321

	1 (A)	HOMO -> LUMO, 98.2	2.09	16857	593	0.871
	2 (A)	HOMO-1 -> LUMO, 87.6 HOMO-2 -> LUMO, 5.1	3.17	25568	391	0.034
	3 (A)	HOMO-2 -> LUMO, 57.7 HOMO-5 -> LUMO, 33.3	3.41	27504	364	0.380
C5	4 (A)	HOMO-2 -> LUMO, 8.9 HOMO-5 -> LUMO, 17.8 HOMO-7 -> LUMO, 12.5 HOMO-8 -> LUMO, 5.7 HOMO-11 -> LUMO, 41.2	3.73	30085	332	0.068
	5 (A)	HOMO-2 -> LUMO, 22.2 HOMO-4 -> LUMO, 9.1 HOMO-5 -> LUMO, 27.4 HOMO-7 -> LUMO, 17.0 HOMO-11 -> LUMO, 12.6	3.96	31940	313	0.329
	1 (A)	HOMO -> LUMO, 98.3	2.05	16535	604	0.871
	2 (A)	HOMO-1 -> LUMO, 89.9	2.98	24036	416	0.023
	3 (A)	HOMO-2 -> LUMO, 87.7	3.21	25891	387	0.422
C6	4 (A)	HOMO-4 -> LUMO, 12.9 HOMO-5 -> LUMO, 24.4 HOMO-11 -> LUMO, 8.2 HOMO-12 -> LUMO, 30.3 HOMO-13 -> LUMO, 11.1	3.79	30569	327	0.130
	5 (A)	HOMO-4 -> LUMO, 8.0 HOMO-5 -> LUMO, 42.5 HOMO-12 -> LUMO, 22.2	3.99	32182	311	0.274
	1 (A'')	HOMO -> LUMO, 98.0	2.22	17906	559	0.829
	2 (A'')	HOMO-4 -> LUMO, 81.4 HOMO-5 -> LUMO, 15.9	3.64	29359	341	0.077
C7	3 (A')	HOMO-1 -> LUMO, 38.7 HOMO-6 -> LUMO, 13.2 HOMO-7 -> LUMO, 42.7	3.93	31698	316	0.067
	4 (A')	HOMO-6 -> LUMO, 80.3 HOMO-7 -> LUMO, 16.2	3.95	31859	314	0.065
	5 (A'')	HOMO-2 -> LUMO, 93.8	4.12	33230	301	0.015
	1 (B)	HOMO -> LUMO, 99.1	2.41	19438	515	0.768
	2 (B)	HOMO-2 -> LUMO, 93.7	2.90	23390	427	0.003
D1	3 (A)	HOMO-1 -> LUMO, 94.7	3.08	24842	403	0.290
	4 (B)	HOMO-4 -> LUMO, 36.4 HOMO-7 -> LUMO, 58.4	3.72	30004	333	0.007
	5 (A)	HOMO-3 -> LUMO, 96.4	3.90	31456	318	0.000
	1 (A)	HOMO -> LUMO, 98.5	2.12	17099	586	0.628
	2 (A)	HOMO-1 -> LUMO, 89.2 HOMO-2 -> LUMO, 7.0	2.75	22180	451	0.300
D2	3 (A)	HOMO-1 -> LUMO, 7.1 HOMO-2 -> LUMO, 87.5	2.78	22422	447	0.113
	4 (A)	HOMO-3 -> LUMO, 64.3 HOMO-4 -> LUMO, 19.4 HOMO-7 -> LUMO, 13.3	3.71	29923	334	0.036
	5 (A)	HOMO-3 -> LUMO, 31.8 HOMO-4 -> LUMO, 54.5 HOMO-7 -> LUMO, 10.6	3.83	30891	324	0.010
	1 (B)	HOMO -> LUMO, 98.9	2.07	16696	599	0.624
	2 (A)	HOMO-1 -> LUMO, 96.6	2.72	21938	456	0.334
D3	3 (B)	HOMO-2 -> LUMO, 94.9	2.78	22422	446	0.102
	4 (B)	HOMO-7 -> LUMO, 94.5	3.92	31617	316	0.002
	5 (B)	HOMO-3 -> LUMO, 71.7 HOMO-5 -> LUMO, 22.5	4.65	37505	267	0.001

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D4	1 (B)	HOMO -> LUMO, 98.9	2.44	19680	508	0.775
	2 (B)	HOMO-1 -> LUMO, 93.6	2.96	23874	419	0.003
	3 (A)	HOMO-2 -> LUMO, 93.9	3.18	25649	390	0.266
	4 (B)	HOMO-3 -> LUMO, 29.0 HOMO-7 -> LUMO, 16.1 HOMO-9 -> LUMO, 48.3	3.77	30407	329	0.002
	5 (A)	HOMO-4 -> LUMO, 87.8	4.28	34521	290	0.001
D5	1 (B)	HOMO -> LUMO, 98.6	2.45	19761	507	0.739
	2 (B)	HOMO-1 -> LUMO, 95.3	3.05	24600	407	0.027
	3 (A)	HOMO-2 -> LUMO, 96.0	3.30	26617	375	0.241
	4 (B)	HOMO-4 -> LUMO, 25.0 HOMO-5 -> LUMO, 11.8 HOMO-7 -> LUMO, 53.8 HOMO-8 -> LUMO, 5.5	3.69	29762	336	0.006
	5 (A)	HOMO-3 -> LUMO, 96.1	3.97	32020	312	0.000
D6	1 (B)	HOMO -> LUMO, 99.0	2.38	19196	522	0.751
	2 (B)	HOMO-1 -> LUMO, 94.3	2.88	23229	430	0.002
	3 (A)	HOMO-2 -> LUMO, 94.7	3.10	25003	399	0.279
	4 (B)	HOMO-5 -> LUMO, 6.3 HOMO-9 -> LUMO, 84.2	3.77	30407	329	0.002
	5 (A)	HOMO-3 -> LUMO+2, 2.0 HOMO-3 -> LUMO+1, 89.6 HOMO-4 -> LUMO, 6.6	3.99	32182	311	0.002
D7	1 (B2)	HOMO -> LUMO, 96.4	2.61	21051	475	0.592
	2 (B2)	HOMO-1 -> LUMO, 96.0	3.62	29198	343	0.146
	3 (A1)	HOMO-2 -> LUMO, 98.6	3.86	31133	321	0.062
	4 (B1)	HOMO-3 -> LUMO, 98.1	3.90	31456	318	0.003
	5 (A2)	HOMO-5 -> LUMO, 94.8	5.84	47103	212	0.000
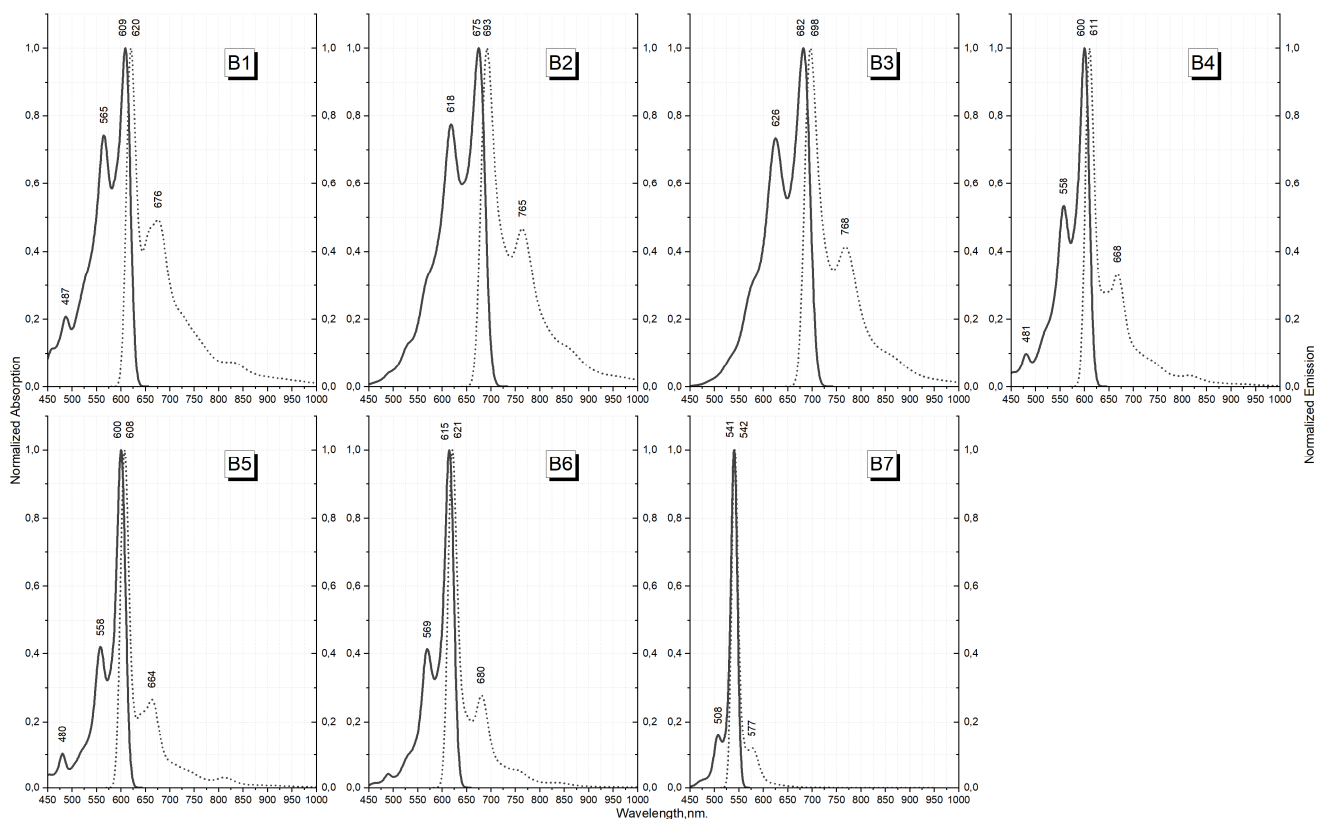
Figure S8. Calculated vibronic (FC, CAM-B3LYP/6-31G(d)) electronic absorption and emission spectra for **B1-B7** aza-BODIPY derivatives. Solid lines correspond to absorption and dotted lines correspomd to emission.
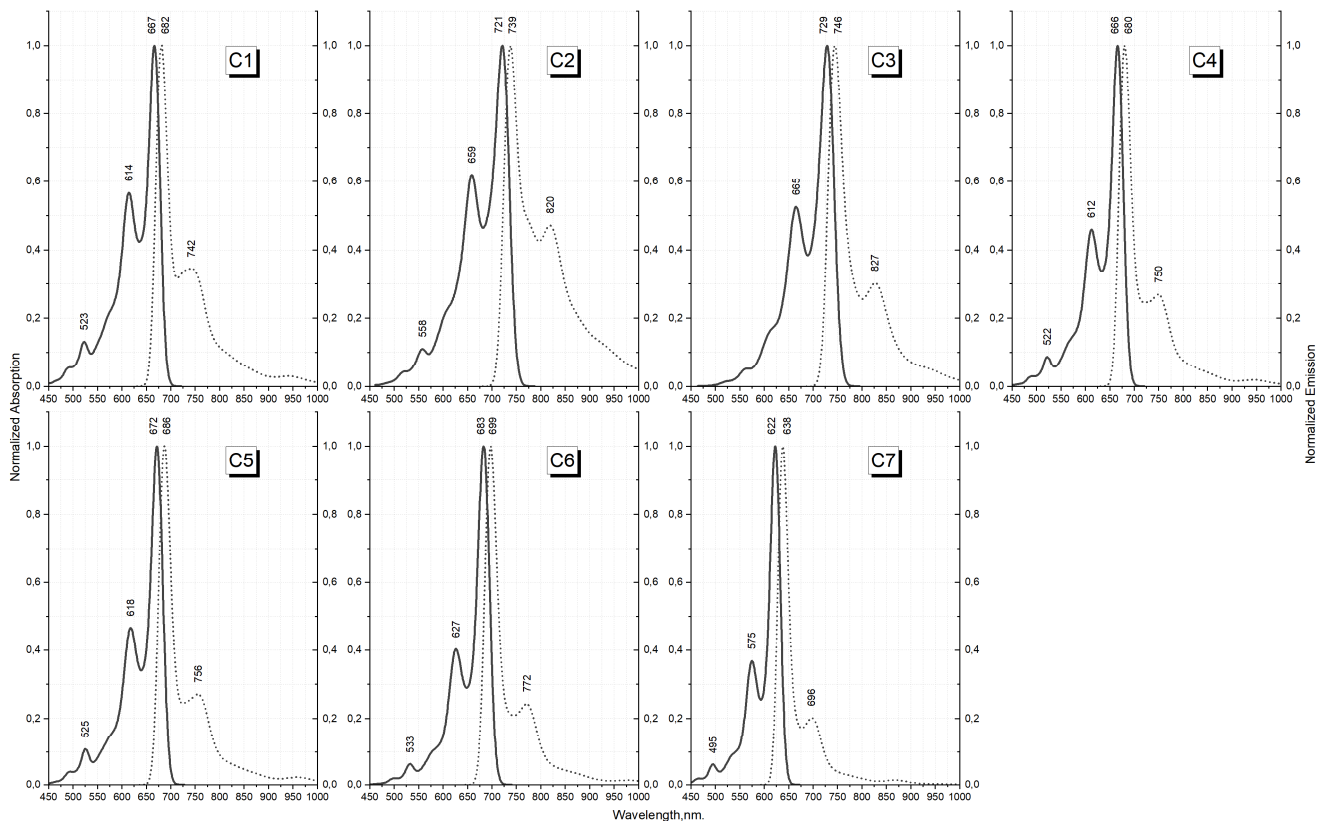
Figure S9. Calculated vibronic (FC, CAM-B3LYP/6-31G(d)) electronic absorption and emission spectra for **C1**-**C7** aza-BODIPY derivatives. Solid lines correspond to absorption and dotted lines correspomd to emission.
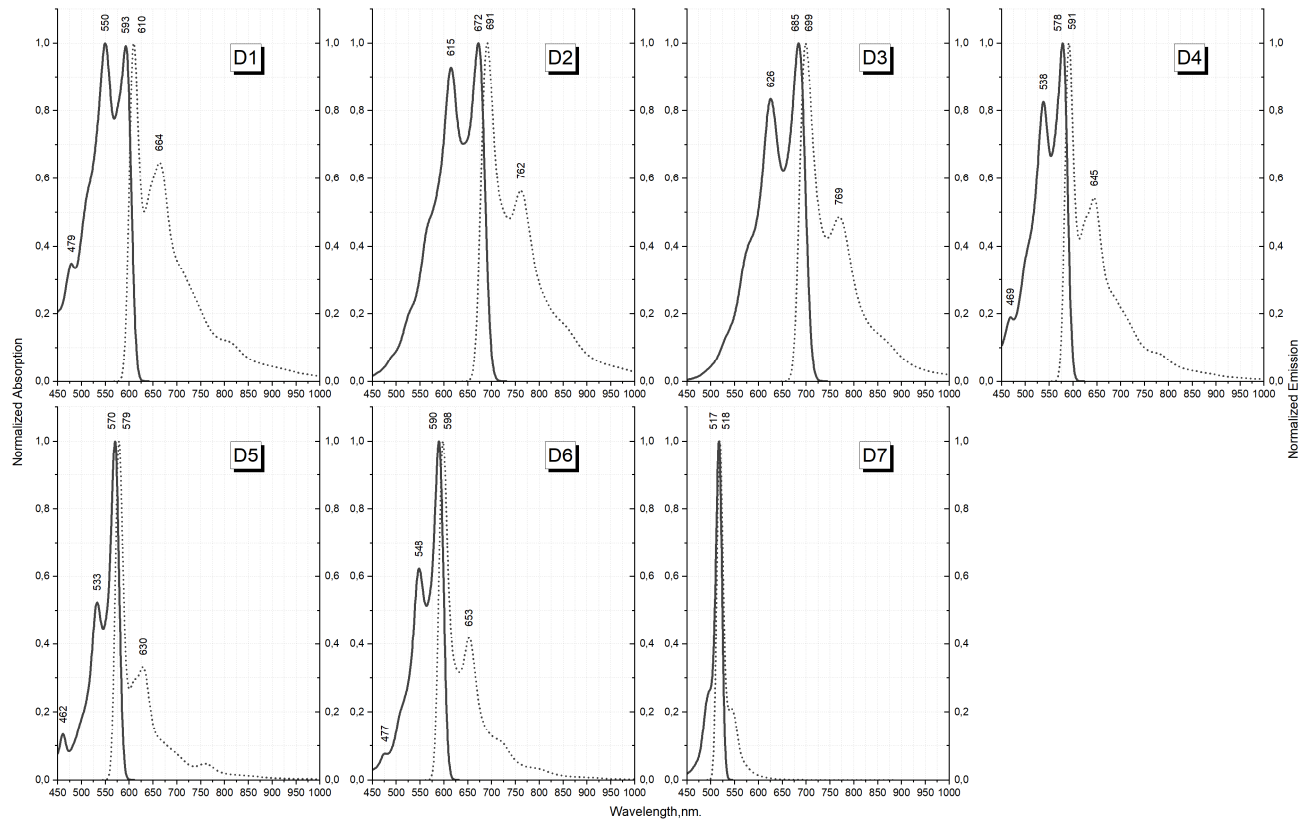

Figure S10. Calculated vibronic (FC, CAM-B3LYP/6-31G(d)) electronic absorption and emission spectra for **D1-D7**. Solid lines correspond to absorption and dotted lines correspomd to emission.
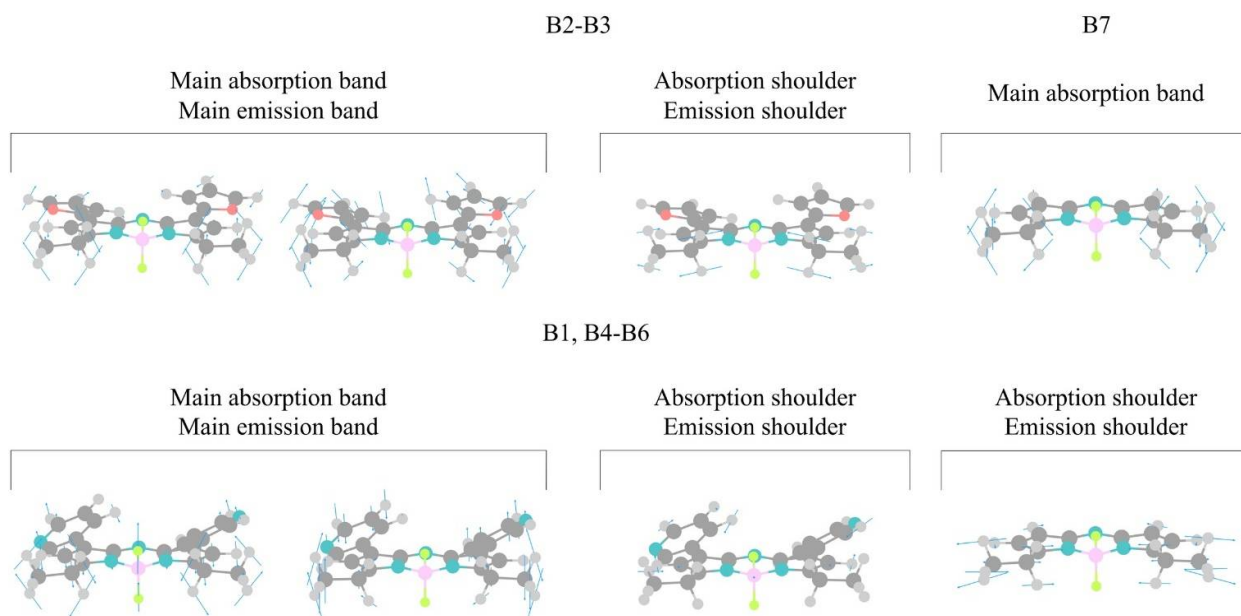
Table S17. Experimental [42] and theoretical (CAM-B3LYP/6-31G(d)) bands of absorption and emission spectra.

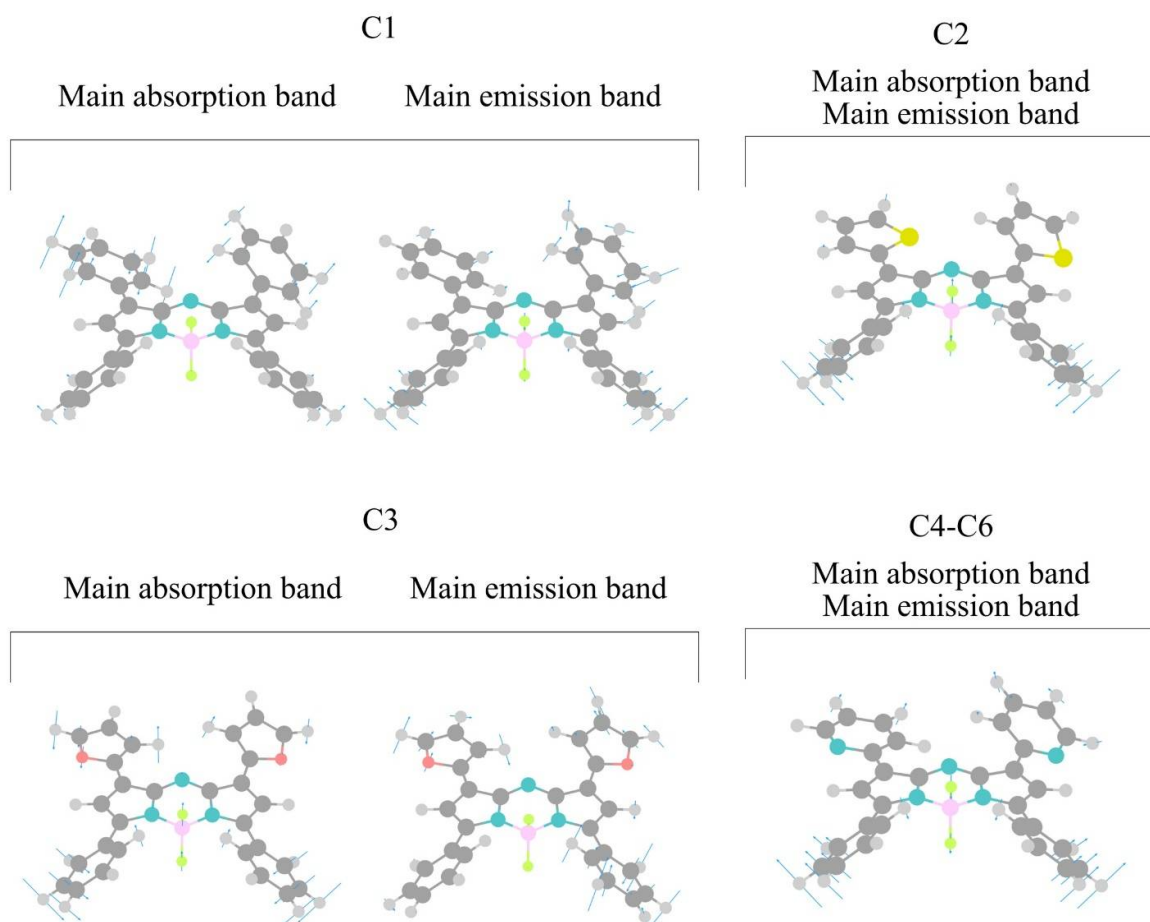|		A1	A2	C1
Abs main	Exp	710	733	643
	Theor	739	781	672
Abs shoulder	Exp	~645	~660	-
	Theor	671	706	618
Em main	Exp	732	757	673
	Theor	793	795	682
Em shoulder	Exp	-	-	-
	Theor	891	891	742

A1-A3
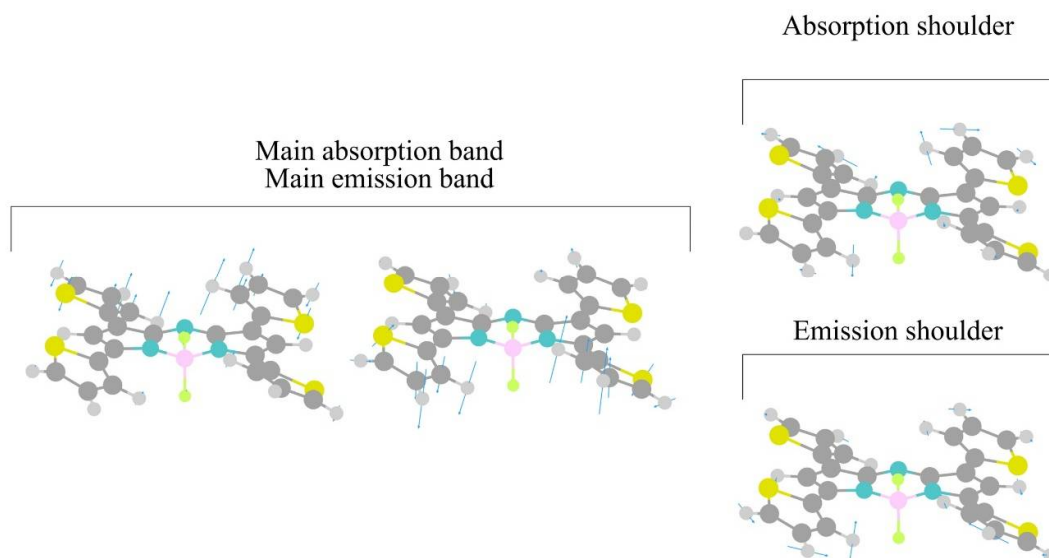
Figure S11. Scaled displacement vectors for some of the main molecular vibrations affecting the line shapes of absorption/emission for **A1**-**A3** (this is shown by the example of **A2**).

B2-B3

B7

Main absorption band
Main emission band

Absorption shoulder
Emission shoulder

Main absorption band

B1, B4-B6

Main absorption band
Main emission band

Absorption shoulder
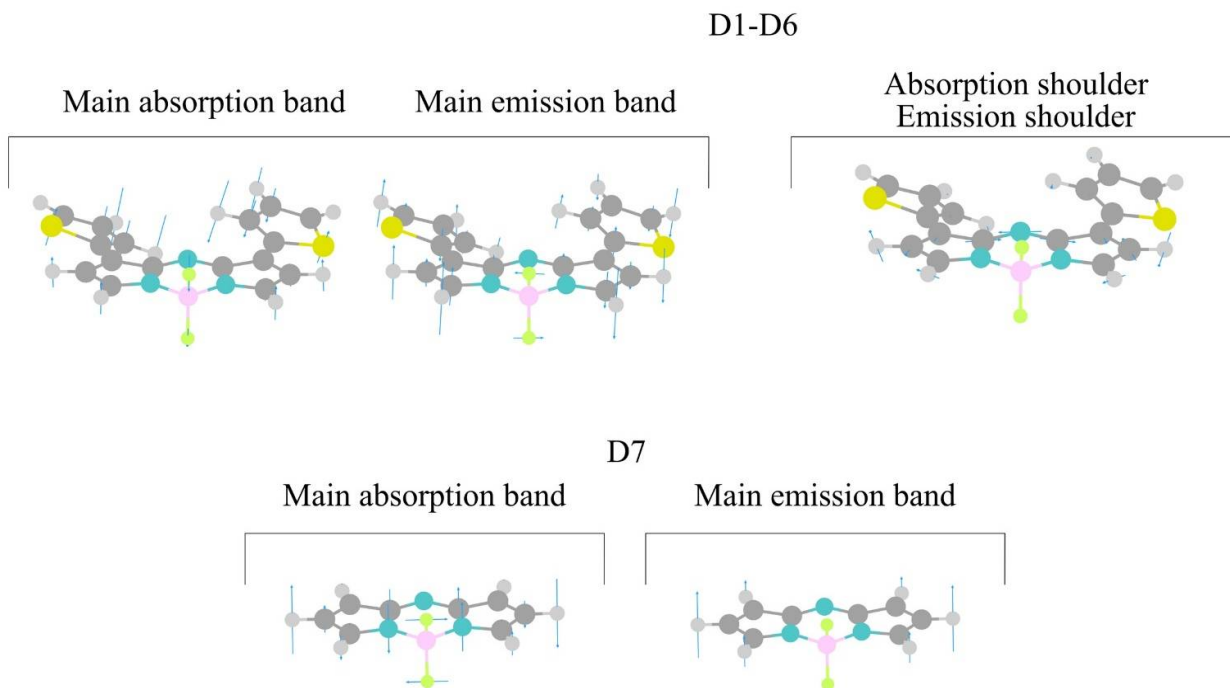Emission shoulder

Absorption shoulder
Emission shoulder

Figure S12. Scaled displacement vectors for some of the main molecular vibrations affecting the lineshapes of absorption/emission for **B1**-**B7** (for **B2**-**B3** – is shown by the example of **B3**, for **B1, B4-B6** – is shown by the example of **B4**).

C1

Main absorption band   Main emission band

C2

Main absorption band
Main emission band

C3

Main absorption band   Main emission band

C4-C6

Main absorption band
Main emission band

Figure S13. Scaled displacement vectors for some of the main molecular vibrations affecting the lineshapes of absorption/emission for **C1**-**C6** (for **C4**-**D6** – is shown by the example of **D6**).

D1-D6

Main absorption band   Main emission band

Absorption shoulder
Emission shoulder

D7

Main absorption band   Main emission band

Figure S14. Scaled displacement vectors for some of the main molecular vibrations affecting the lineshapes of absorption/emission for **D1**-**D7** (for **D1**-**D6** – is shown by the example of **D2**).