Supporting Information

Engineering Highly Efficient Porphyrin Sensitizers through Metal, Ligand and Bridge Modification: A DFT Study

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Table S1. Dihedral angles of the engineered dyes.

Dye	Φ_1	Φ_2	Φ_3
SMD	0.00	0.04	-0.01
M1	0.00	0.03	-0.02
M2	0.02	-0.03	0.05
M3	0.05	0.39	-0.07
M4	0.02	-0.03	0.08
M5	0.07	0.48	0.28
M6	0.05	-0.04	0.15
M7	0.07	0.38	0.16
M8	0.09	-0.66	0.10
M9	0.08	-0.54	0.19
M10	0.03	0.21	0.23
A1	0.01	0.05	-0.02
A2	0.00	0.01	0.02
A3	0.00	0.02	-0.01
A4	0.02	0.01	0.03
A5	0.02	-0.11	-0.02
A6	0.01	-0.03	0.04
B1	0.01	0.10	0.02
B2	0.00	0.04	-0.01
B3	0.02	-0.52	0.03
B4	0.01	0.63	-0.02

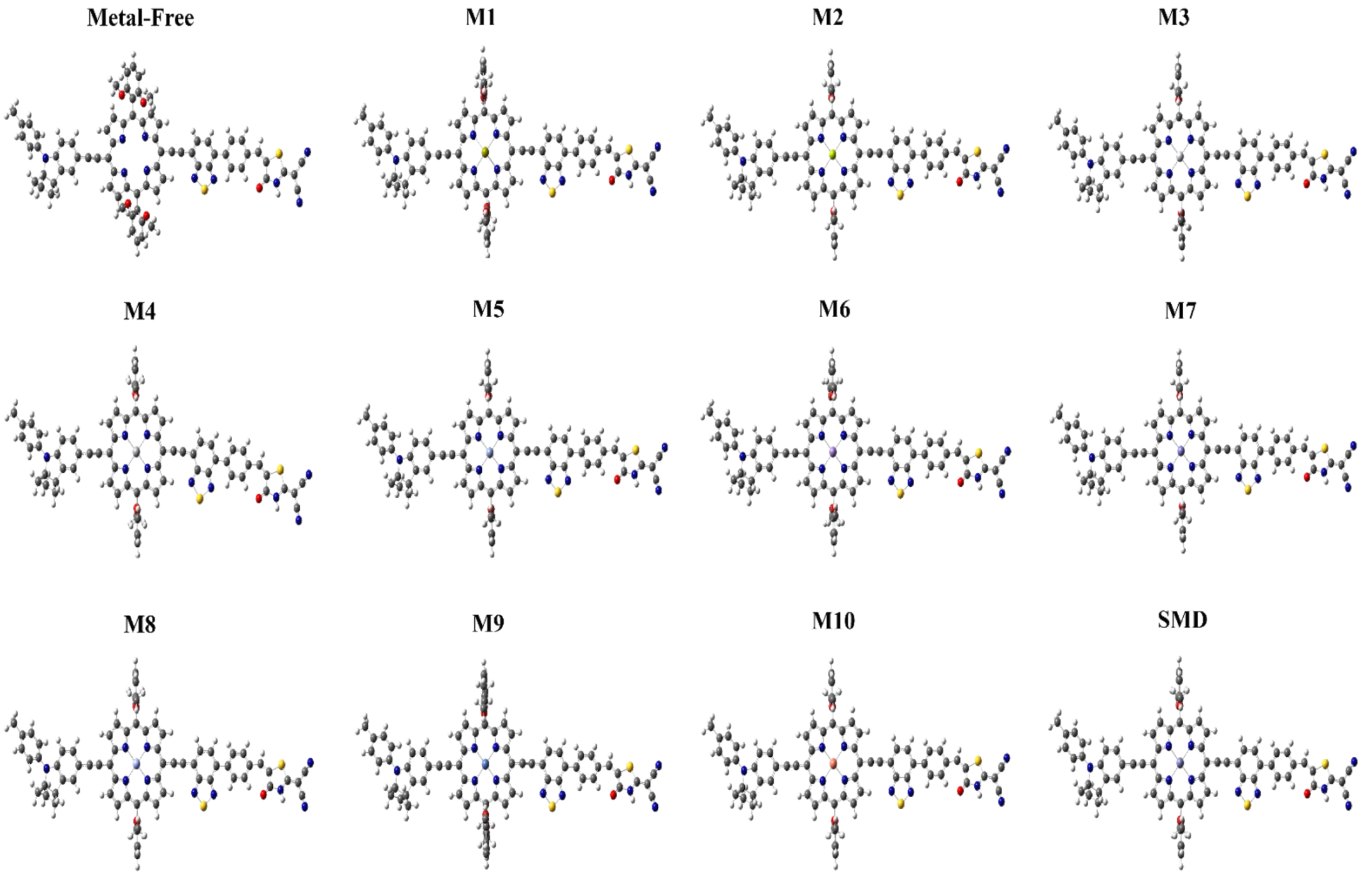

Figure S1. The optimized geometries of the metal-free, M1 to M10, and SMD dyes.

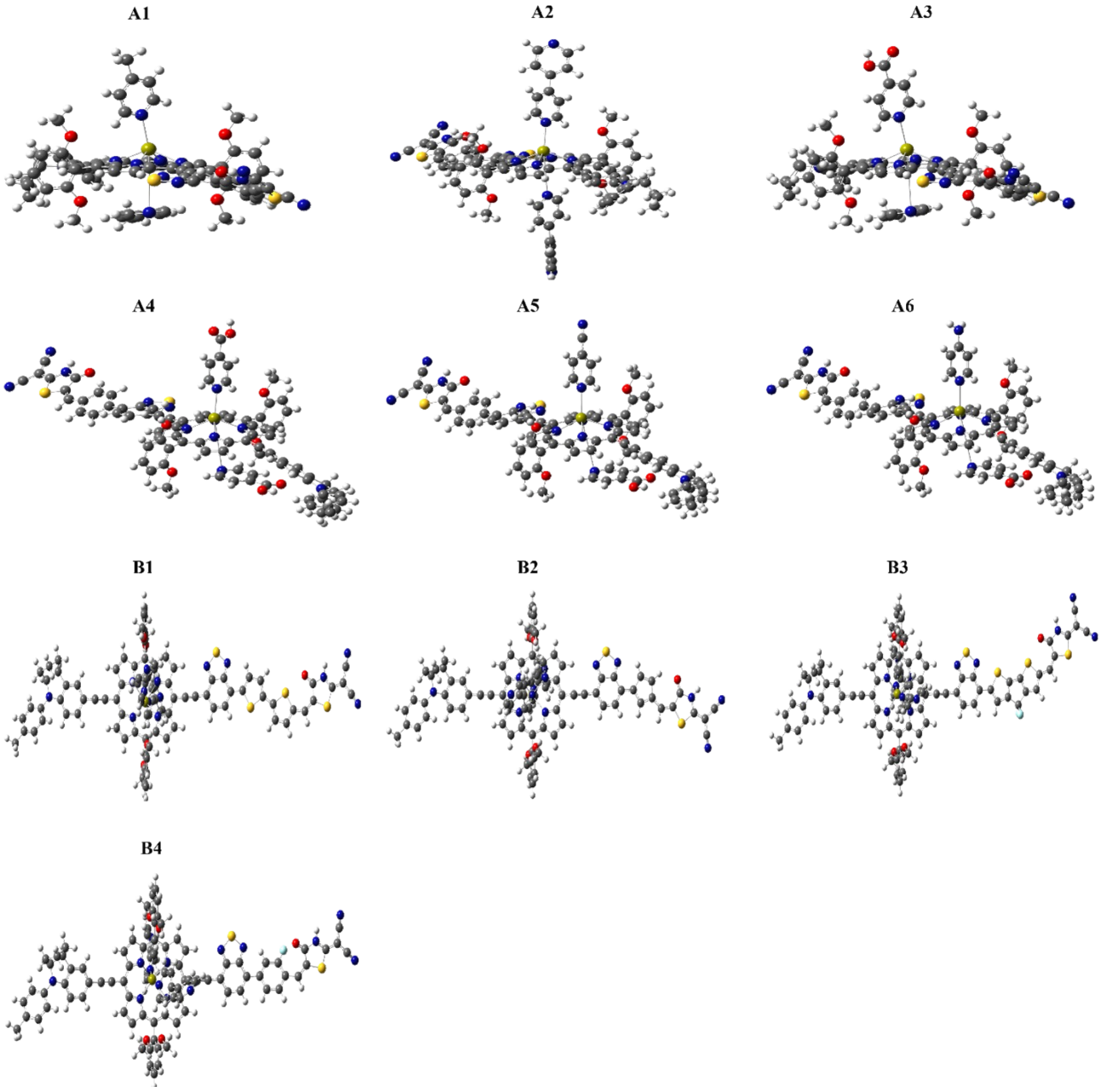

Figure S2. The optimized geometries of the A1 to A6 and B1 to B4 dyes.

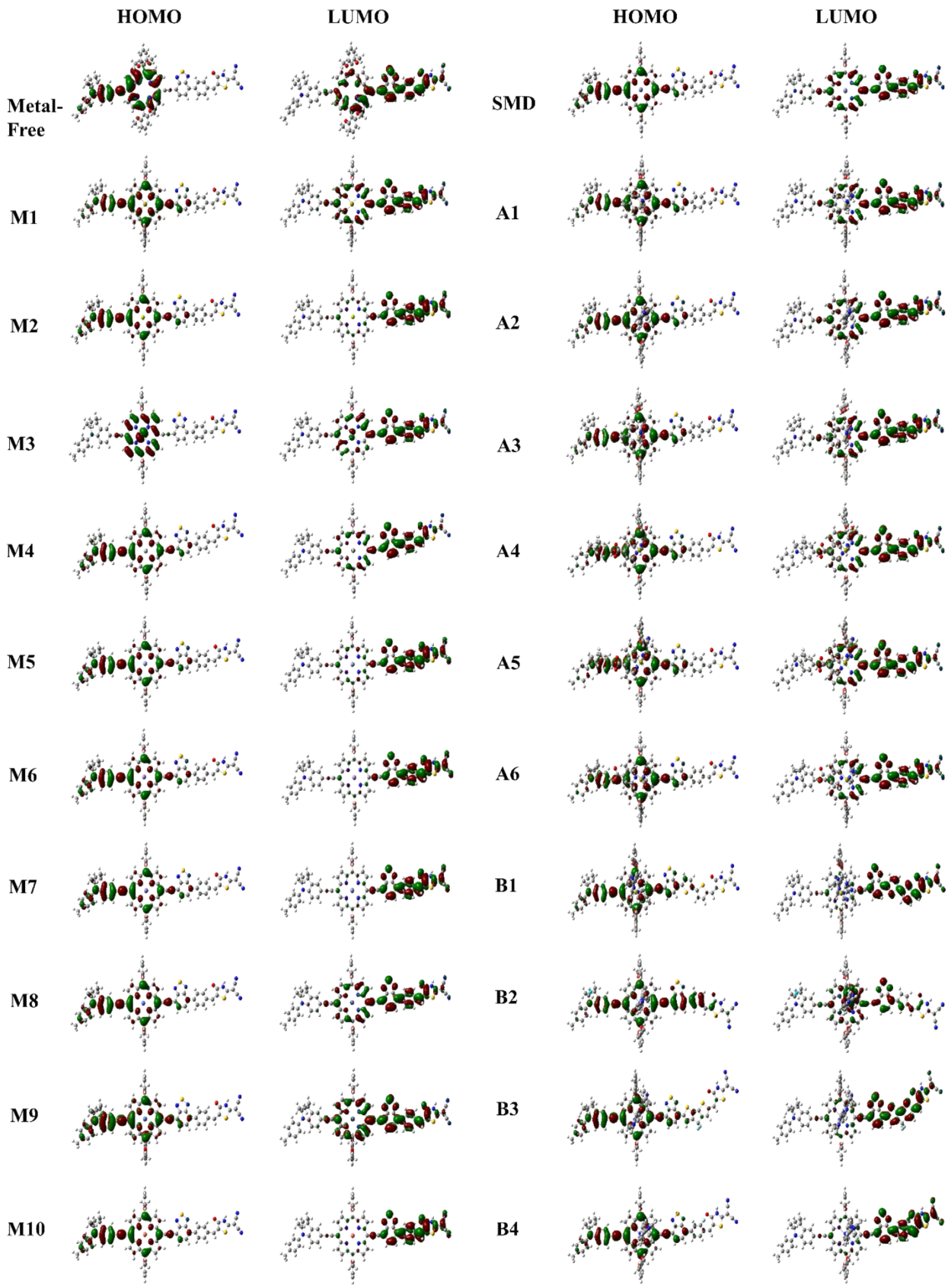

Figure S3. The FMOs of the engineered dyes.

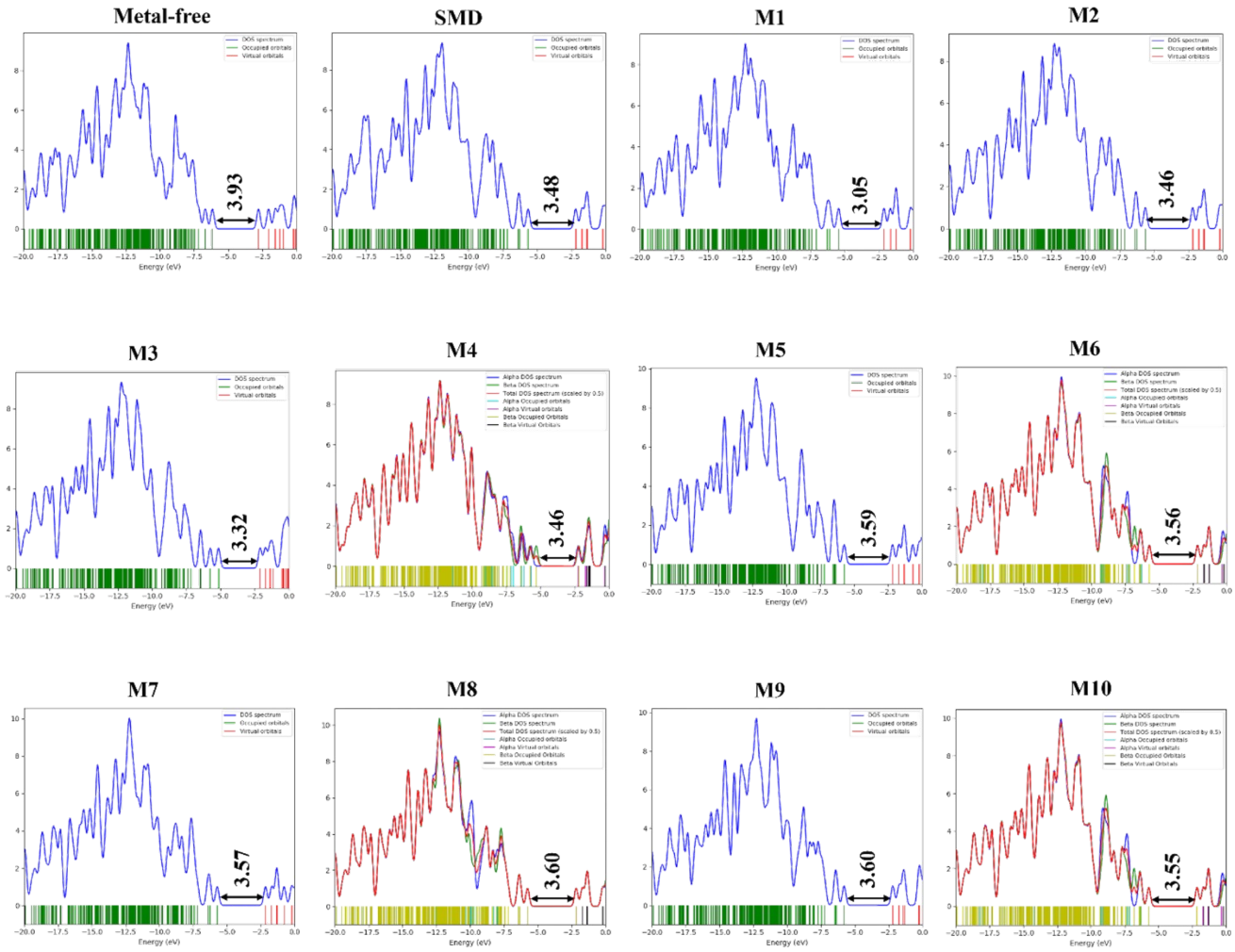

Figure S4. The DOS plots of the metal-free, SMD, and M1 to M10 dyes.

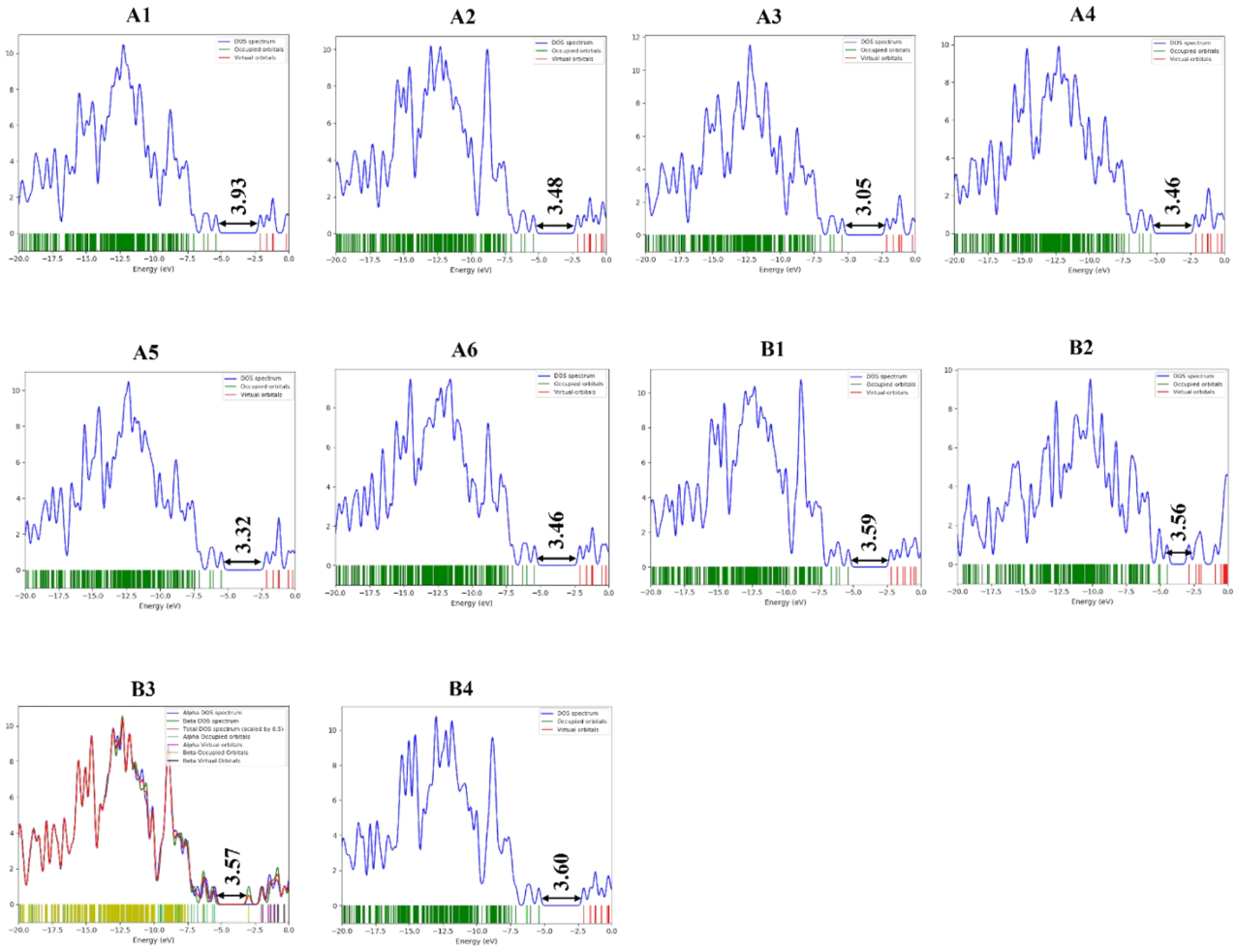

Figure S5. The DOS plots of the A1 to A6 and B1 to B4 dyes.

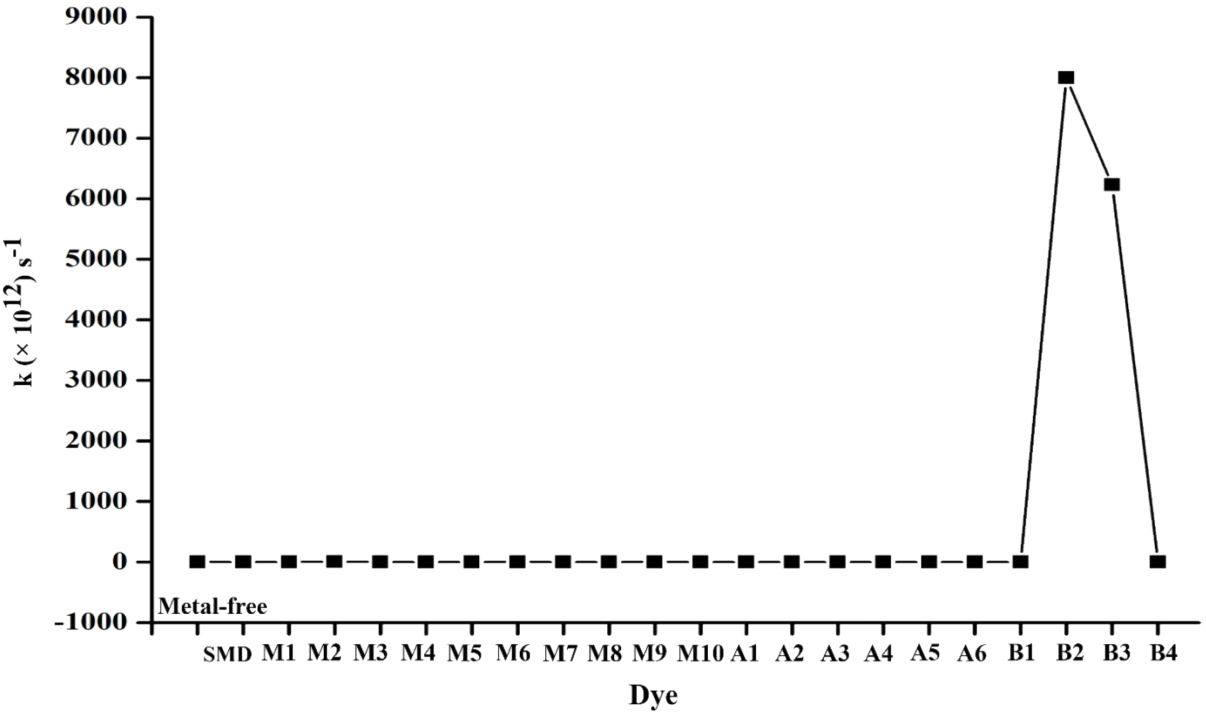

Figure S6. The IET rate of the dyes.

Table S2. The isotropic polarizability (α) of the engineered dyes.

Dye	α_{xx} (10^3)	α_{yy} (10^3)	α_{zz} (10^2)	α (10^3)	Δα (10^3)
Metal-free	3.17	1.19	5.95	1.65	2.33
SMD	3.96	1.22	5.58	1.91	3.12
M1	6.35	1.25	5.61	2.72	5.48
M2	3.99	1.22	5.58	1.92	3.15
M3	4.31	1.22	5.73	2.03	3.46
M4	4.25	1.23	5.67	2.02	3.40
M5	3.94	1.22	5.64	1.91	3.10
M6	3.90	1.22	5.64	1.89	3.06
M7	3.82	1.21	5.60	1.86	2.99
M8	3.97	1.31	5.68	1.95	3.09
M9	3.71	1.18	6.39	1.84	2.84
M10	3.87	1.21	5.60	1.88	3.04
A1	4.49	1.32	7.01	2.17	3.52
A2	4.53	1.06	12.60	2.28	3.37
A3	4.42	1.33	7.18	2.16	3.44
A4	4.26	1.30	7.55	2.10	3.27
A5	4.23	1.31	7.43	2.09	3.24
A6	4.41	1.31	7.27	2.15	3.43
B1	5.59	1.05	13.65	2.67	4.39
B2	6.70	1.07	12.61	3.01	5.54
B3	5.92	1.08	13.93	2.80	4.69
B4	4.16	1.01	13.19	2.16	3.02

Table S3. The hyperpolarizability (β) of the engineered dyes.

Dye	β_{xxx} (10^5)	β_{xxy} (10^3)	β_{xyy} (10^3)	β_{yyy} (10^2)	β_{xxz} (10^4)	β_{yyz} (10^1)	β_{xzz} (10^3)	β_{yzz} (10^2)	β_{zzz} (10^1)	β_{tot} (10^5)	P (10^5)
Metal-free	2.76	-8.36	2.96	20.74	-1.92	162.61	7.83	-3.05	-120.80	2.88	2.89
SMD	8.32	2.99	-2.56	-1.26	-0.55	8.86	0.18	-0.67	1.07	8.29	8.30
M1	-11.64	0.22	2.73	1.70	-5.06	-16.34	3.18	-1.35	53.12	11.59	11.61
M2	8.47	2.46	-2.74	-0.70	-0.55	7.32	0.14	-0.49	0.52	8.44	8.45
M3	-8.63	-15.89	-0.23	-1.82	0.12	6.62	1.20	0.88	-55.58	8.62	8.64
M4	9.55	2.42	-3.29	-1.18	-1.65	11.53	0.78	-0.19	44.93	9.52	9.54
M5	8.14	3.50	-2.09	-1.74	-0.55	7.54	0.16	-0.62	0.66	8.13	8.14
M6	8.18	2.96	-2.31	-0.85	-0.55	8.88	0.20	-0.70	1.64	8.16	8.17
M7	8.01	2.80	-2.00	-0.89	-0.61	7.38	0.15	-0.62	0.99	7.99	8.01
M8	8.15	3.51	-2.08	-1.79	-0.55	7.63	0.16	-0.61	0.66	8.14	8.15
M9	7.50	1.91	-1.80	-1.15	-2.29	-5.30	7.25	1.40	29.14	7.55	7.56
M10	8.04	2.89	-2.22	-0.95	-0.58	8.24	0.18	-0.65	0.71	8.024	8.04
A1	10.35	6.24	-3.00	-1.08	-2.60	4.32	1.19	0.12	28.20	10.34	10.36
A2	-10.50	-27.08	-0.54	-1.31	-0.38	-4.08	2.61	1.08	2.40	10.49	10.51
A3	9.99	9.01	-2.90	-1.56	-2.50	10.06	1.24	-1.79	55.83	9.98	10.01
A4	9.12	12.71	-2.29	-1.99	-4.85	11.83	5.73	-0.71	9.52	9.17	9.19
A5	8.83	8.28	-2.55	-1.41	-4.51	10.64	5.19	-0.52	23.49	8.87	8.89
A6	9.91	6.43	-2.76	-1.38	-5.23	7.35	5.24	1.24	-40.50	9.95	9.97
B1	-13.90	-22.21	-0.75	-2.01	0.14	7.99	1.76	0.05	-4.48	13.89	13.91
B2	32.26	-41.09	9.23	-0.72	-1.49	-1.64	0.89	0.42	4.65	32.37	32.40
B3	-13.95	-15.01	0.84	0.06	-0.30	-20.10	-0.13	4.64	-86.77	13.94	13.96
B4	12.89	-1.21	-0.49	0.23	-0.30	-0.59	0.58	-1.34	25.60	12.89	12.91