Is π-Stacking Prone to Accelerate the Singlet-Singlet Energy Transfers?

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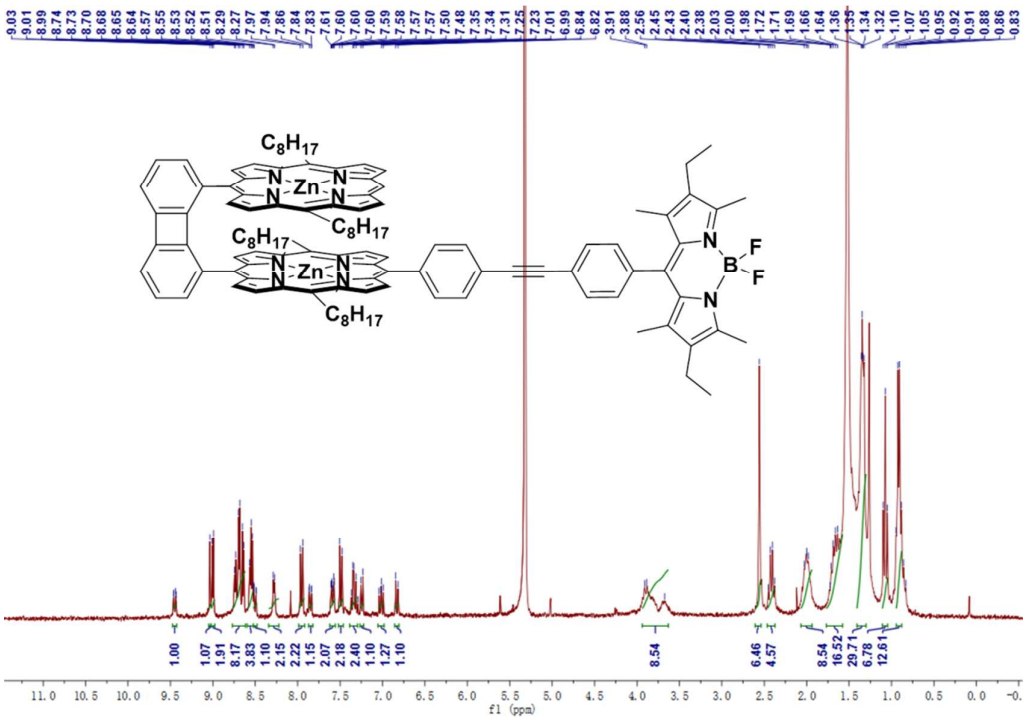


Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2.

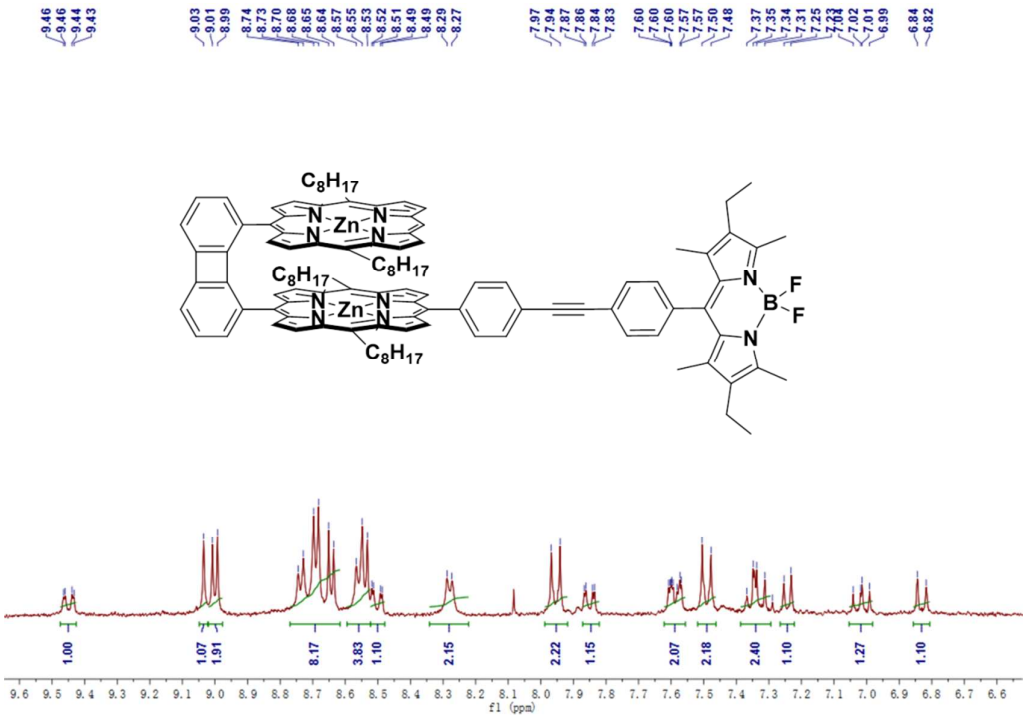


Figure S2. ^{1}H NMR spectrum of **1** in CD_2Cl_2.

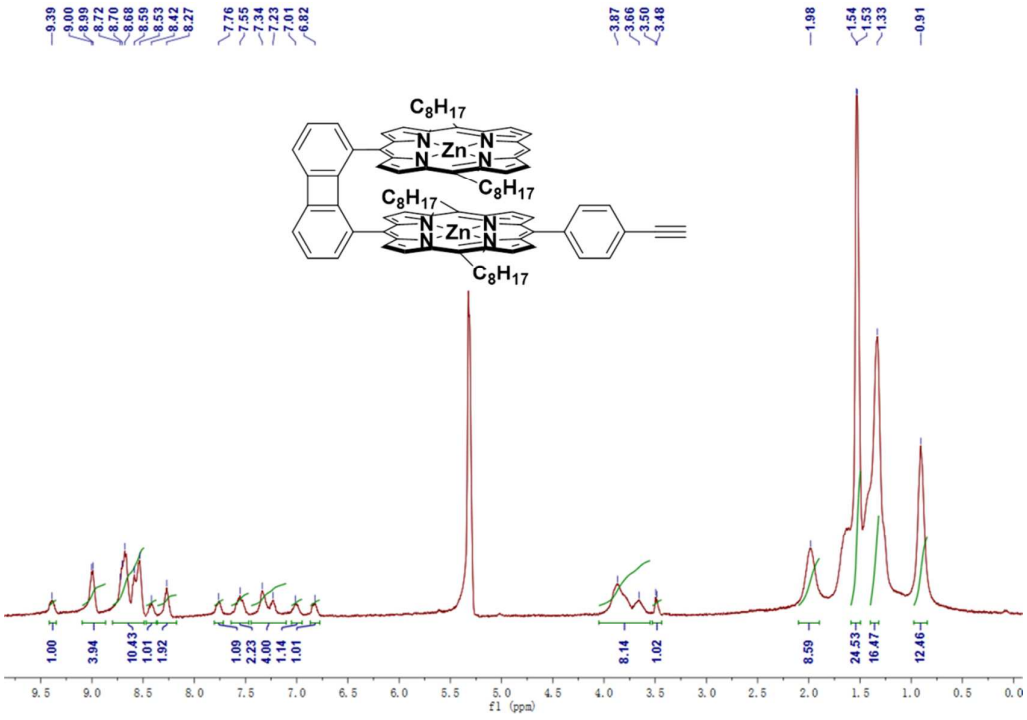


Figure S3. ^{1}H NMR spectrum of **2** in CD_2Cl_2.

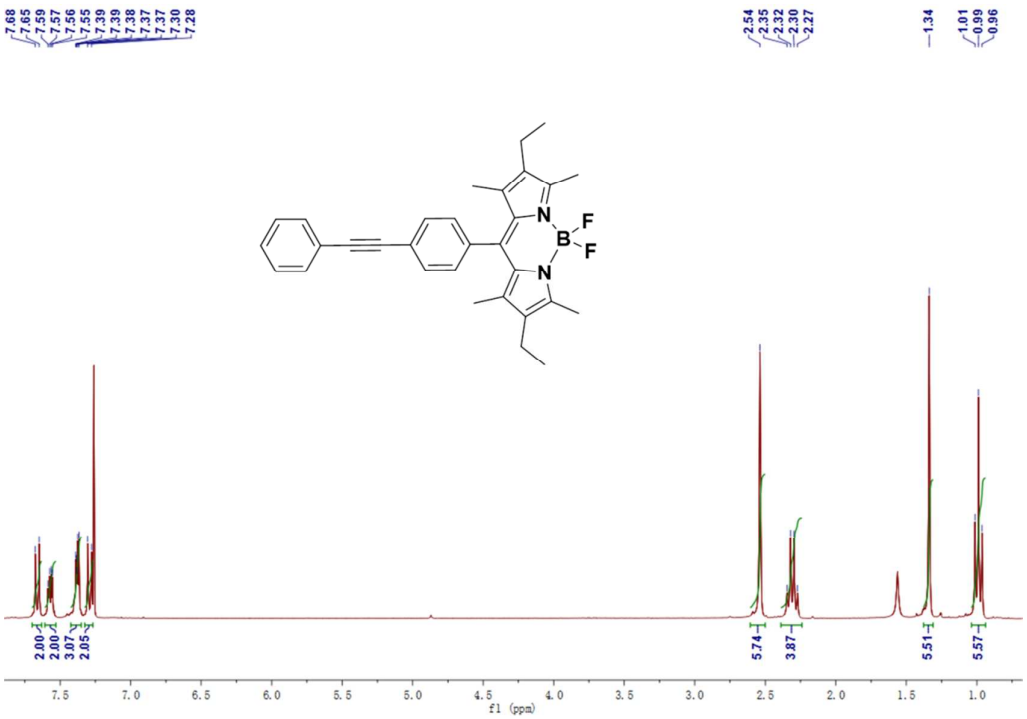


Figure S4. ^{1}H NMR spectrum of **3** in $CDCl_3$.

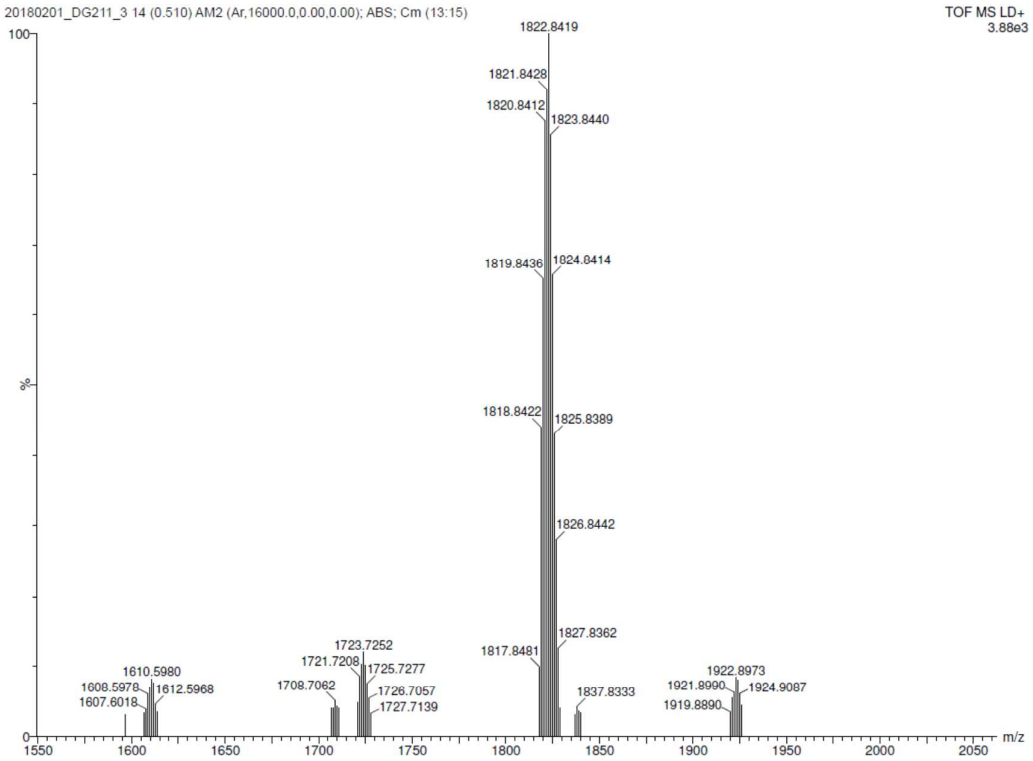


Figure S5. High-resolution MALDI-TOF mass spectrum of **1**.

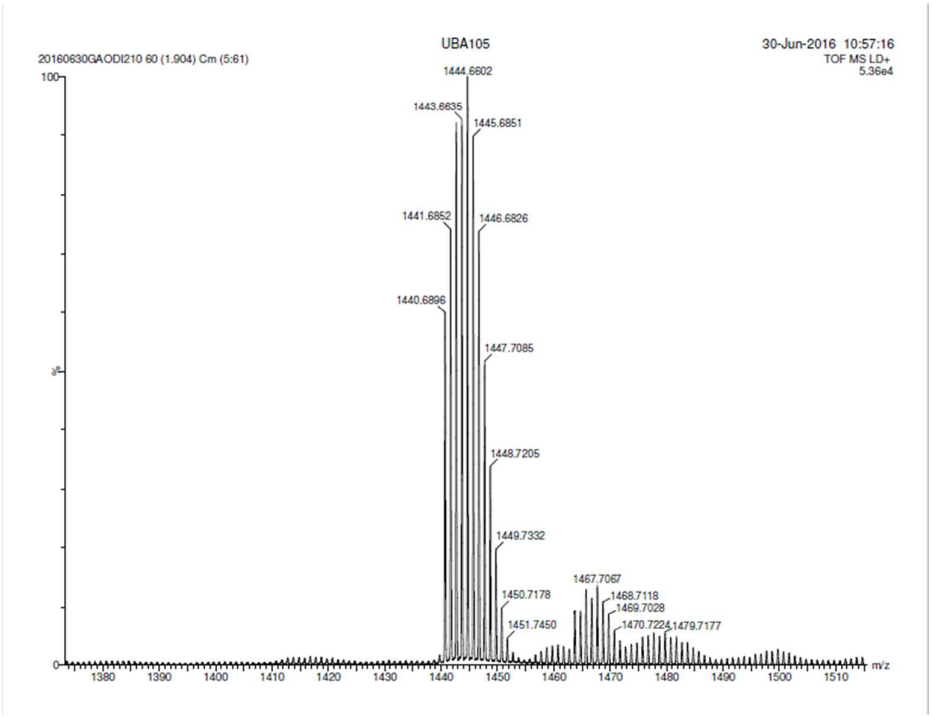


Figure S6. MALDI-TOF mass spectrum of **2**.

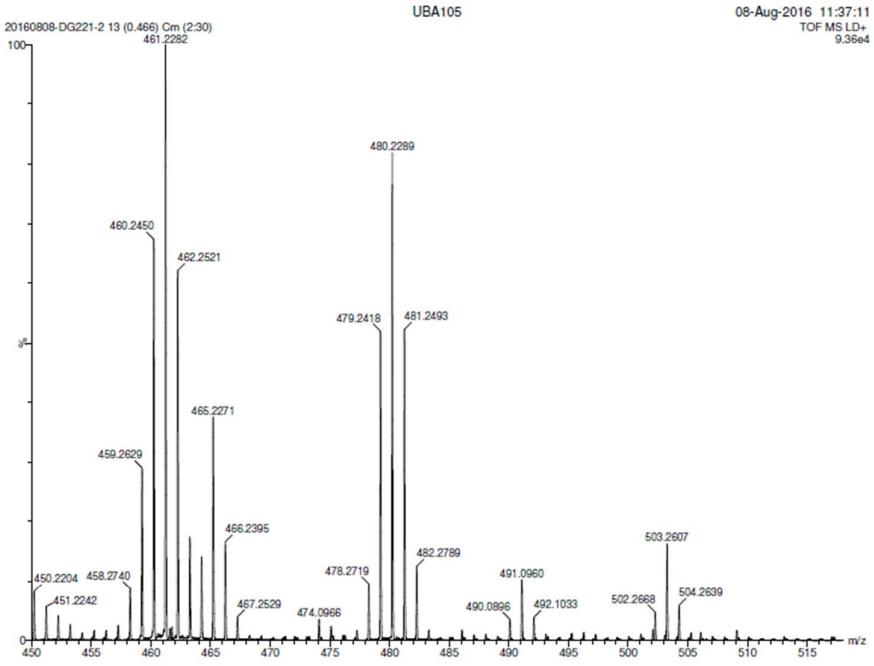


Figure S7. MALDI-TOF mass spectrum of **3**.

Table S1. Calculated position, oscillator strength (f) and major contributions of the first 100 singlet-singlet electronic transitions for **1**.

No.	Wavelength (nm)	Osc. Strength	Major Contribs (%)
1	553.0	0.0467	HOMO→L+1 (65)
2	549.4	0.0057	H-2→L+1 (10), H-1→L+1 (28), HOMO→L+2 (44)
3	543.0	0.0018	H-2→L+3 (10), H-1→L+1 (10), H-1→L+2 (32), HOMO→L+3 (18)
4	539.0	0.0009	H-3→L+1 (12), H-2→L+2 (10), H-1→L+1 (12), H-1→L+2 (10), H-1→L+3 (20), HOMO→L+4 (11)
5	535.2	0.0009	H-1→L+1 (38), HOMO→L+2 (29), HOMO→L+3 (14)
6	528.1	0.0038	H-1→L+2 (14), H-1→L+3 (26), HOMO→L+3 (31)
7	523.9	0.0043	H-1→L+4 (11), HOMO→L+4 (57)
8	520.2	0.0065	H-1→L+3 (17), H-1→L+4 (43)
9	516.5	0.0001	HOMO→LUMO (100)
10	506.8	0	H-1→LUMO (100)
11	494.4	0.0055	H-3→L+1 (36), H-2→L+1 (41)
12	487.1	0.0054	H-3→L+2 (21), H-3→L+3 (30), H-2→L+2 (31)
13	484.1	0.0016	H-3→L+2 (23), H-3→L+3 (13), H-2→L+2 (11), H-2→L+3 (11), H-2→L+4 (29)
14	480.9	0.0098	H-3→L+4 (38), H-2→L+3 (26), H-2→L+4 (13)
15	474.1	0	H-2→LUMO (99)
16	465.4	0	H-3→LUMO (99)
17	431.5	0.1868	H-5→L+1 (24), H-4→LUMO (44)
18	431.2	0.3139	H-5→L+1 (30), H-4→LUMO (33)
19	429.4	0.0591	H-4→LUMO (10), H-4→L+1 (85)
20	426.0	0.0674	H-5→L+1 (25), H-5→L+2 (45)
21	422.0	0.1628	H-5→L+2 (27), H-5→L+3 (24), HOMO→L+5 (19)
22	421.0	0	H-4→L+2 (99)
23	416.3	0.1142	H-5→L+3 (60), HOMO→L+5 (22)
24	415.5	0	H-4→L+3 (99)
25	410.1	0.0001	H-4→L+4 (99)
26	408.8	0.0277	H-5→L+4 (75)
27	405.7	0.0352	H-5→L+4 (15), HOMO→L+5 (19), HOMO→L+6 (21)
28	404.6	0.0181	H-5→L+2 (10), H-1→L+6 (11), HOMO→L+5 (18)
29	404.1	0.0004	H-5→LUMO (95)
30	400.0	0.0014	H-1→L+5 (88)
31	398.5	0.0052	H-6→LUMO (91)
32	398.0	0.0288	H-1→L+6 (49), HOMO→L+6 (24)
33	392.7	0.0543	H-2→L+5 (10), H-1→L+6 (25), HOMO→L+6 (34)
34	383.3	0.0001	H-4→L+5 (94)
35	383.0	0.0465	H-3→L+5 (14), H-2→L+5 (58)
36	377.0	0.6727	H-6→L+1 (11), H-3→L+5 (32), H-2→L+5 (15)
37	374.8	0.4934	H-6→L+1 (17), H-3→L+5 (36), H-2→L+5 (11)
38	374.1	0.174	H-7→LUMO (83), H-4→LUMO (13)
39	371.6	0.1713	H-2→L+6 (66)
40	367.0	0.0142	H-9→L+1 (23), H-6→L+1 (32), H-3→L+6 (26)
41	365.2	0.0758	H-9→L+1 (37), H-3→L+6 (36)

42	364.5	0.7481	H-6→L+2 (11)
43	362.7	0.0246	H-10→L+2 (33), H-10→L+3 (13), H-9→L+2 (11), H-8→L+2 (14)
44	361.2	0.0056	H-9→L+2 (21), H-9→L+3 (13), H-9→L+4 (14), H-6→L+2 (23)
45	359.5	0.0033	H-10→L+1 (10), H-10→L+3 (16), H-10→L+4 (20), H-5→L+6 (15)
46	359.0	0.0051	H-6→L+2 (13), H-5→L+6 (50)
47	357.5	0.6539	H-12→LUMO (13), H-6→L+1 (21), H-3→L+6 (13)
48	356.8	0.0159	H-12→LUMO (86)
49	355.1	0.4956	H-6→L+2 (40)
50	352.4	0.1716	H-6→L+3 (73)
51	348.4	0.006	H-6→L+4 (79)
52	346.8	0.0419	HOMO→L+7 (81)
53	344.4	0.0157	H-1→L+7 (63)
54	343.9	0.0491	H-13→L+1 (24), H-1→L+7 (23)
55	342.1	0.0249	H-13→L+2 (18), H-8→L+1 (25)
56	340.4	0.0284	H-11→L+2 (17), H-8→L+1 (12)
57	337.9	0.0246	H-11→L+1 (22), H-8→L+2 (19)
58	335.9	0.0606	H-14→L+1 (31), H-11→L+1 (25)
59	332.7	0.0525	H-14→L+2 (11), H-11→L+2 (36)
60	332.2	0.0035	H-15→L+2 (14), H-11→L+3 (18), H-8→L+2 (18)
61	331.3	0.0024	H-10→L+1 (37), H-9→L+1 (12), H-8→L+1 (20)
62	330.1	0.0269	H-13→L+1 (16), H-8→L+3 (10)
63	329.9	0.0281	H-13→L+2 (13), H-11→L+1 (11)
64	328.9	0.0051	H-5→L+5 (92)
65	328.3	0.0228	H-9→L+3 (10), H-2→L+7 (33)
66	328.1	0.0215	H-9→L+2 (25), H-9→L+3 (29), H-2→L+7 (19)
67	327.8	0	H-4→L+6 (100)
68	327.8	0.0439	H-11→L+4 (11), H-2→L+7 (32)
69	327.2	0.0473	H-11→L+4 (13), H-8→L+3 (18)
70	326.7	0.0011	H-10→L+2 (17), H-10→L+3 (18), H-10→L+4 (21), H-8→L+4 (13)
71	325.6	0.0033	H-9→L+3 (10), H-9→L+4 (37)
72	325.1	0.0064	H-14→L+1 (12), H-10→L+4 (12), H-9→L+4 (12)
73	324.0	0.0002	H-3→L+7 (95)
74	323.6	0.0004	H-15→L+2 (16), H-14→L+1 (13), H-13→L+2 (15)
75	322.6	0.01	H-14→L+2 (17), H-11→L+3 (11), H-11→L+4 (11), HOMO→L+8 (14)
76	321.8	0.0392	H-11→L+4 (12), HOMO→L+8 (60)
77	321.4	0.0006	H-16→L+1 (52), H-13→L+2 (14)
78	320.9	0.0034	H-15→L+1 (19), H-15→L+2 (12), H-15→L+3 (15), H-11→L+3 (11), HOMO→L+8 (13)
79	320.1	0.0134	H-14→L+3 (12), H-13→L+3 (46)
80	319.9	0.0002	H-7→L+1 (96)
81	319.3	0.0006	H-1→L+8 (75)
82	319.2	0.0001	H-8→LUMO (87)
83	318.7	0	H-9→LUMO (87)
84	318.4	0.0136	H-16→L+2 (12), H-16→L+3 (14), H-13→L+4 (30)
85	317.8	0	H-10→LUMO (94)

86	317.4	0.0013	H-16→L+2 (17), H-16→L+3 (10), H-14→L+3 (12), H-13→L+4 (23)
87	316.9	0.0365	H-15→L+1 (31), H-15→L+3 (20)
88	316.6	0.0229	H-13→L+4 (23), HOMO→L+9 (54)
89	316.1	0	H-13→LUMO (19), H-11→LUMO (73)
90	315.3	0.0064	H-16→L+2 (11), H-16→L+3 (17), H-14→L+2 (10), H-14→L+3 (18), H-14→L+4 (11), HOMO→L+9 (15)
91	315.2	0.0001	H-7→L+2 (98)
92	315.0	0	H-13→LUMO (69), H-11→LUMO (23)
93	314.6	0.0051	H-14→L+4 (20), H-1→L+9 (47)
94	313.9	0.0042	H-14→L+4 (42), H-1→L+9 (34)
95	313.2	0.0027	H-15→L+2 (15), H-15→L+3 (20), H-15→L+4 (42)
96	312.4	0.0058	H-16→L+4 (62)
97	312.1	0	H-7→L+3 (99)
98	311.9	0.0003	H-15→LUMO (13), H-14→LUMO (78)
99	311.8	0.0505	H-17→L+3 (13), H-17→L+6 (10), H-16→L+4 (16), H-5→L+7 (36)
100	309.5	0.8813	H-17→L+1 (16), H-6→L+5 (62)

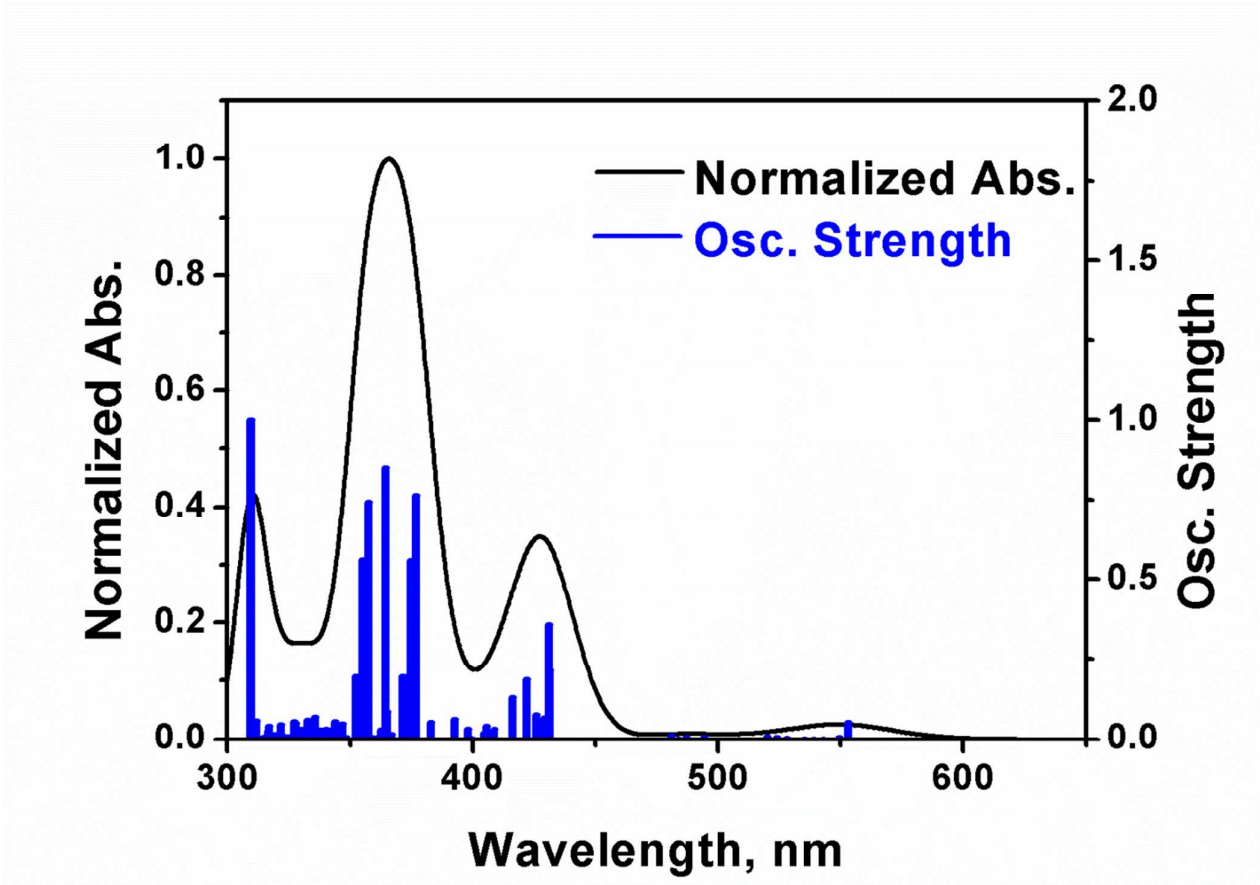


Figure S8. Bar graph reporting the calculated oscillator strength and calculated position of the 100st electronic transitions calculated by TDDFT for **1** (bar graph; f = computed oscillator strength). The black line is generated by assigning a thickness of 1000 cm^{-1} to each bar.

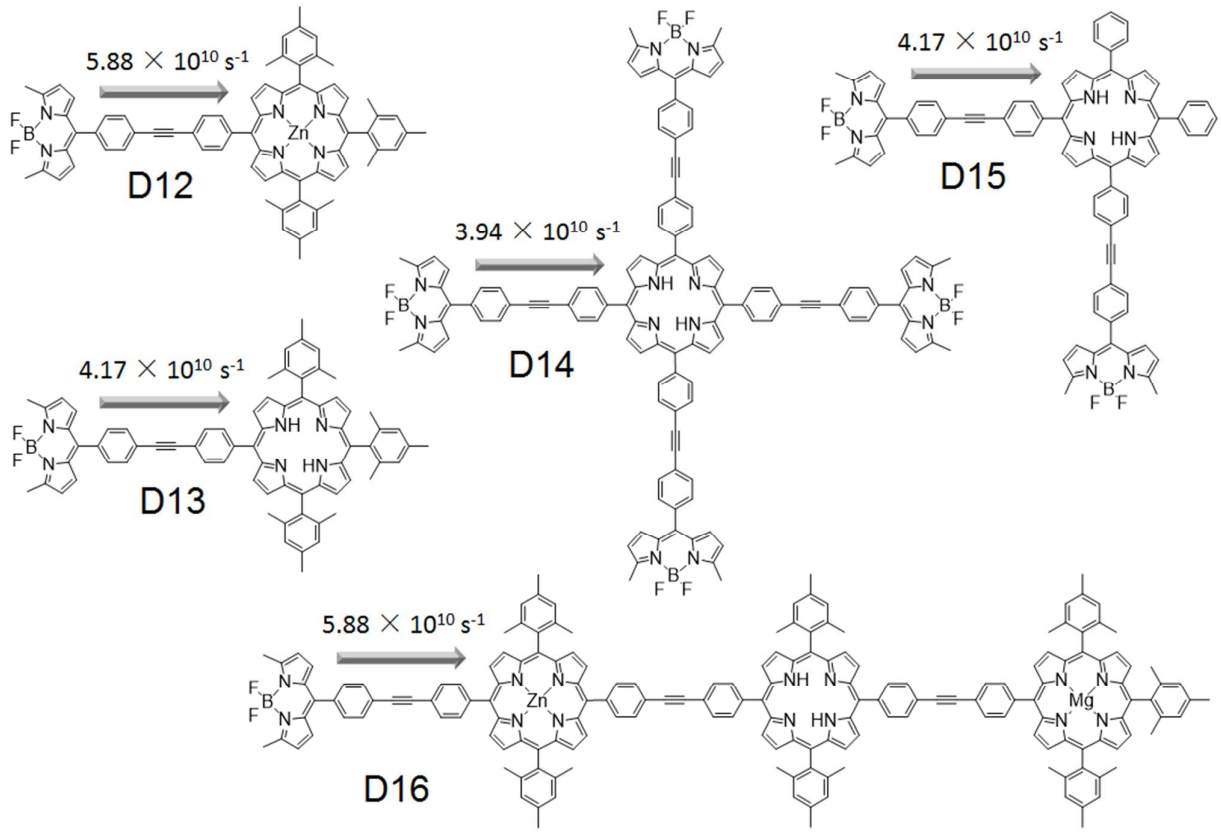
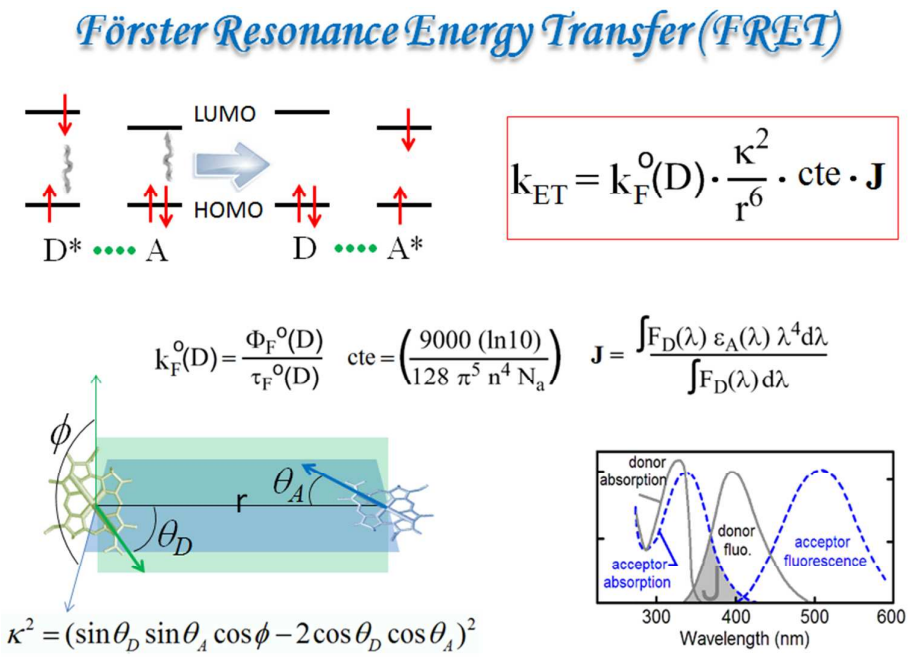


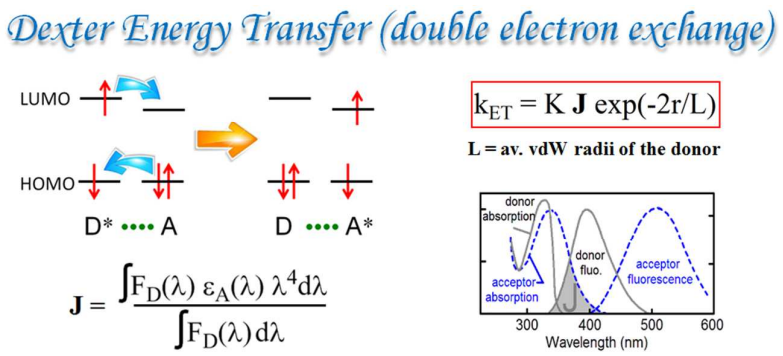
Figure S9. Comparison of $k_{ET}(S_1)$ for various literature dyads: **D12,**[S1] **D13,**[S1] **D14,**[S2] **D15**[S2] and **D16**[S3] at 298 K. Note that these dyads do not bare methyl groups at the β-position of **[bod]**.



where D* = donor in its S_1 excited state, A = acceptor, k_{ET} = rate for S_1 energy transfer, $k_F°$ = fluorescence rate constant of the donor in the absence of energy transfer, κ^2 = orientation factor for the relative orientation of the transition moments of the donor and the acceptor (see green and blue arrows

on the left hand side at the bottom); this value can range between 0 (for perpendicular cases) and 4 (for parallel or anti-parallel cases), r = center-to-center separation between the donor and the acceptor, J = normalized J-integral, F_D = the fluorescence intensity (in wavelength scale), εA = absorptivity of the acceptor, n = average refractive index of the medium, and Na = avogadro's number.

Figure S10. Description of the Förster's theory.[S4]



where D* = donor in its S_1 excited state, A = acceptor, k_{ET} = rate for S_1 energy transfer, K = a pre-exponential factor, r = center-to-center separation between the donor and the acceptor, L = average van der Waals radii of the donor, J = normalized J-integral, F_D = the fluorescence intensity (in wavelength scale), ε_A = absorptivity of the acceptor.

Figure S11. Description of the Dexter's theory.[S5]

References

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