Efficient Energy Transfer in Ethynyl Bridged Corrole-BODIPY Dyads

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1. Experiment details

1.1 Materials and equipment

All reagents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. Triethylamine (Et_3N) was distilled from CaH_2 under argon. Toluene was distilled from sodium under argon. Pyrrole and tetra-*n*-butylammonium hexafluorophosphate (TBAPF6) was purchased from Alfa Asar. Triphenylarsane($Asph_3$) and $Pd_2(dba)_3$ were purchases from Acros. The NMR spectra were measured on a Bruker 500 or 400 MHz spectrometer. UV-visible absorption spectra were measured on a Shimadzu UV-2550 double beam spectrophotometer. Fluorescence emission and excitation spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer with a 150 W-xenon arc lamp used as the light source at a working voltage of 400V. Fluorescence quantum yield values were determined on a Varian Eclipse spectrofluorometer. The absorbance values of the solution were between 0.04 and 0.05 at the excitation wavelength. Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). The excitation source was a diode laser (LDH-P-C-485 with a 10 MHz repetition rate, and a 88 ps pulse width). HR-MS data were measured on an Aglient 6540Q-TOF with $CHCl_3$ used as the solvent.

1.2 Synthesis details

5: Under typical Pd-mediated coupling conditions, **4** (37 mg,0.05 mmol), **1** (22.5 mg,0.05 mmol), $Asph_3$ (20.0 mg, 66 μmol) and $Pd_2(dba)_3$ (8.0 mg, 8.8 μmol) were placed in a 100 mL single-neck round-bottom flask containing 44 mL of toluene and Et_3N (3:1). The flask was stirred at 38 °C under argon. $Asph_3$ (15.0 mg, 40 μmol) and $Pd_2(dba)_3$ (5 mg,5.5 μmol) were added after 6 h, then the mixture was stirred for another 6 h. The solvent was removed under reduced pressure and the mixture was purified by column chromatography (silica gel; CH_2Cl_2/Petroleum ether, 50%) to yield the product (45 mg, 74%). ^1H NMR ($CDCl_3$, 400 MHZ): δ 9.13 (s,2 H), 8.74 (s, 2 H), 8.58 (s, 4 H), 8.22 (d, J = 6.4 Hz, 2 H), 7.99 (d, J = 7.6 Hz, 2 H), 7.83 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H),6.06 (s, 2 H), 2.59 (s, 6 H), 1.51 (s, 6 H). HPMS-ESI: m/z: cald for $[C_{58}H_{34}BF_{12}N_6]^+$:1053.2746, found: 1053.2747.

6: Under typical Pd-mediated coupling, **4** (37 mg,0.05 mmol), **2** (26.9 mg, 0.05 mmol), $Asph_3$ (20.0 mg, 66 μmol) and $Pd_2(dba)_3$ (8.0 mg, 8.8 μmol) were placed in a 100 mL single-neck round - bottom flask containing 44 mL of toluene and Et_3N (3:1). The flask was stirred at 38 °C under argon. $Asph_3$ (15.0 mg, 40 μmol) and $Pd_2(dba)_3$ (5 mg, 5.5 μmol) were added after 6 h, then the mixture was stirred for another 6 h. The solvent was removed under reduced pressure and the mixture was purified by column chromatography (silica gel; CH_2Cl_2/Petroleum ether, 50%) to yield the product (54.4 mg, 85%). ^1H NMR ($CDCl_3$, 400 MHZ): δ 9.12 (s, 2 H), 8.75 (s, 4 H), 8.57 (s, 2 H), 8.20 (s, 2 H), 7.98 (d, J = 6.4 Hz, 2 H), 7.78 (d, J = 16.0 Hz, 1 H), 7.66 (s, 3 H), 7.51 (m, 3 H), 7.34 (m, 2 H), 7.27(s, 1 H), 7.23(s, 1 H), 6.65 (s, 1 H), 6.05 (s, 1 H), 2.64(s, 3 H) 1.46 (s, 3 H), 1.42 (s, 3 H). HPMS-ESI: m/z: cald for $[C_{65}H_{38}BF_{12}N_6]^+$: 1141.3059, found: 1141.3066.

7: Under typical Pd-mediated coupling, **4** (73 mg, 0.1 mmol), **3** (26.9 mg, 0.05 mmol), $Asph_3$ (20.0 mg, 66 μmol) and $Pd_2(dba)_3$ (8.0 mg, 8.8 μmol) were placed in a 100 mL single-neck round-bottom flask containing 44 mL of toluene and Et_3N (3:1). The flask was stirred at 38 °C under argon. $Asph_3$ (15.0 mg, 40 μmol) and $Pd_2(dba)_3$ (5 mg,5.5 μmol) were added after 6 h, then the mixture was stirred for another 6 h. The solvent was removed under reduced pressure and the mixture was purified by column chromatography (silica gel; CH_2Cl_2/Petroleum ether, 50%) to yield the product (76.8 mg, 77%). ^1H NMR ($CDCl_3$, 400 MHZ): δ 9.10 (s, 4 H), 8.74 (s, 8 H), 8.55 (s, 4 H), 8.20 (s, 3 H), 7.99 (S, 4 H), 7.88 (d, J = 14.8 Hz, 2 H), 7.73 (s, 8 H), 7.54 (s, 4 H), 7.38 (d, J =14.4 Hz 4 H), 6.73 (s, 2 H), 1.50 (s, 6 H). HPMS-ESI: m/z: cald for $[C_{111}H_{56}BF_{22}N_{10}]^+$: 1957.4431, found: 1956.4439.

2 .Supplementary data

2.1

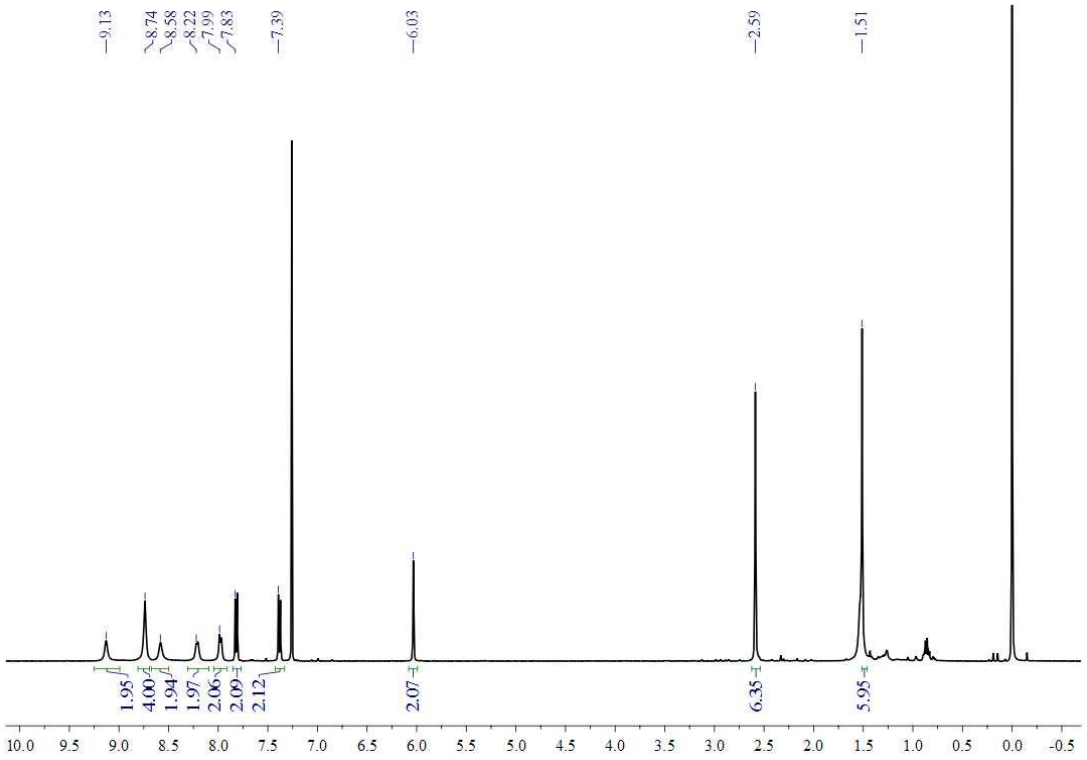

Figure S1. ^{1}H NMR spectrum of conjugate **5** in $CDCl_3$ at 298K.

2.2

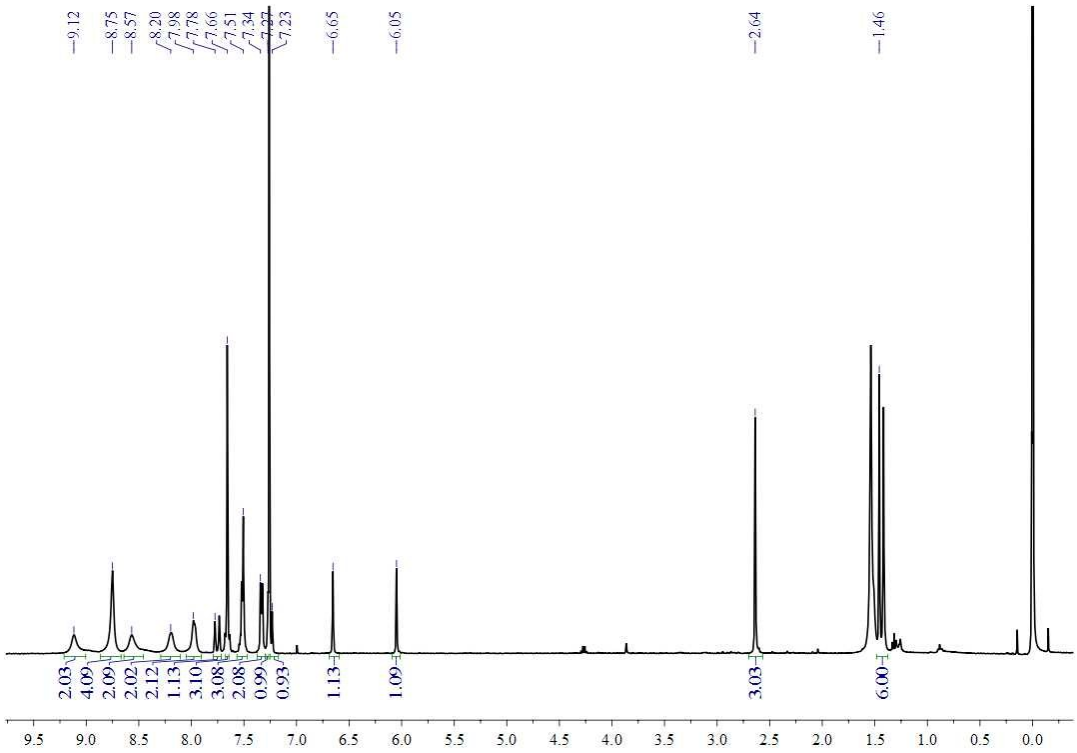

Figure S2. ^{1}H NMR spectrum of conjugate **6** in $CDCl_3$ at 298K.

2.3

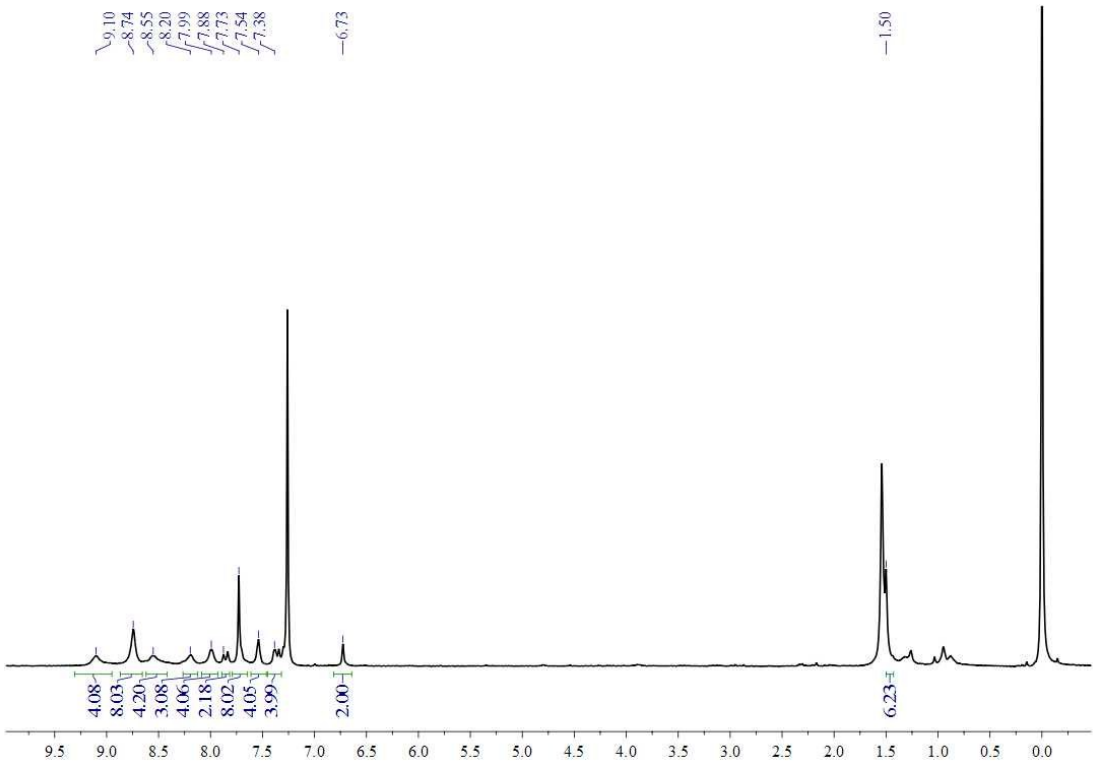

Figure S3. ^{1}H NMR spectrum of conjugate **7** in $CDCl_3$ at 298K.

2.4

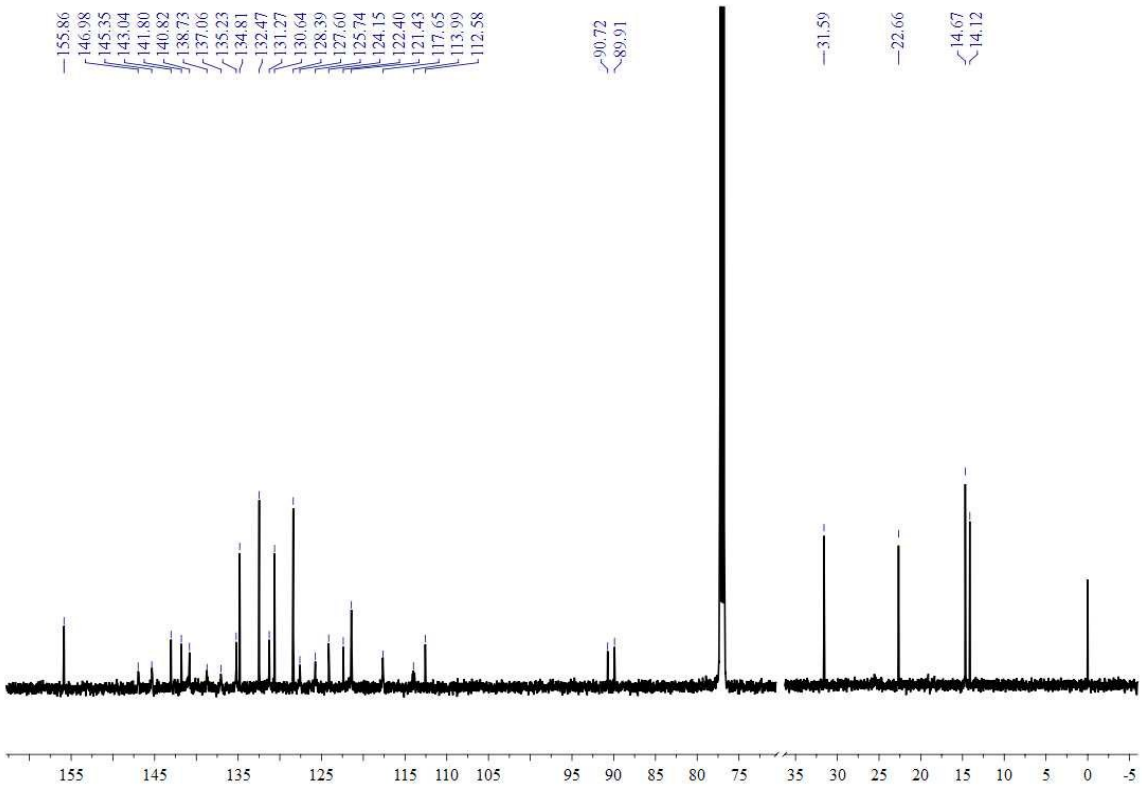

Figure S4. ^{13}C NMR spectrum of conjugate **5** in $CDCl_3$ at 298 K.

2.5

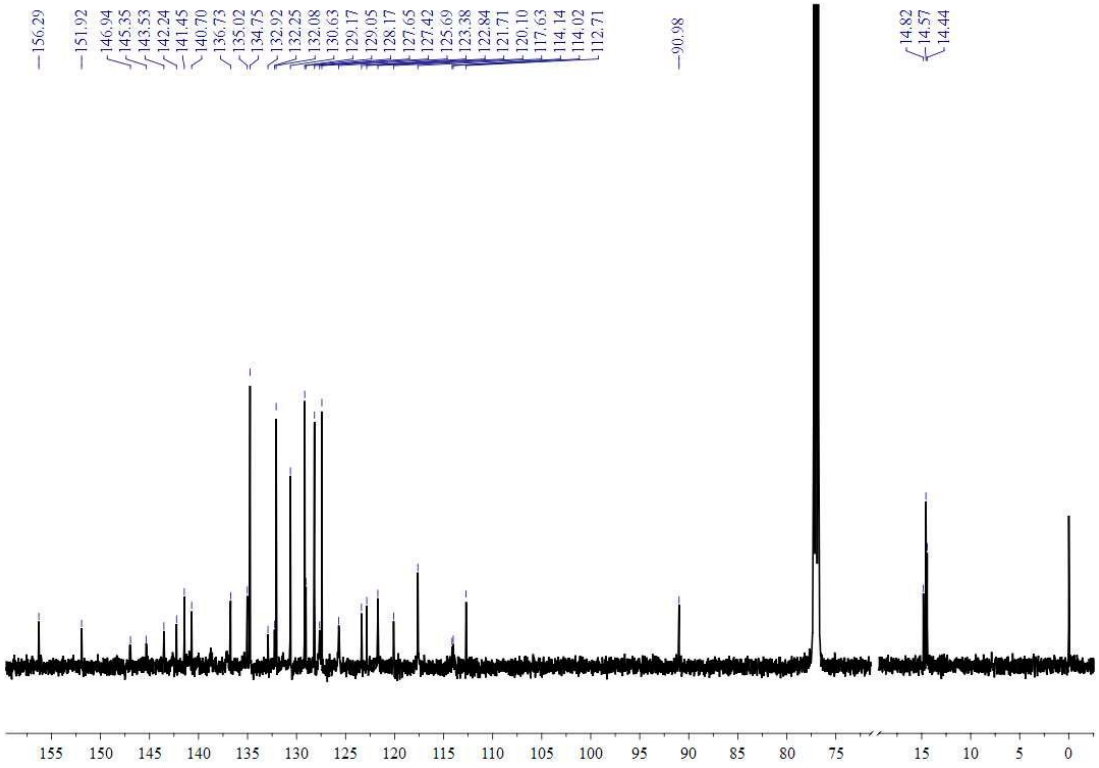

Figure S5. ^{13}C NMR spectrum of conjugate **6** in $CDCl_3$ at 298 K.

2.6

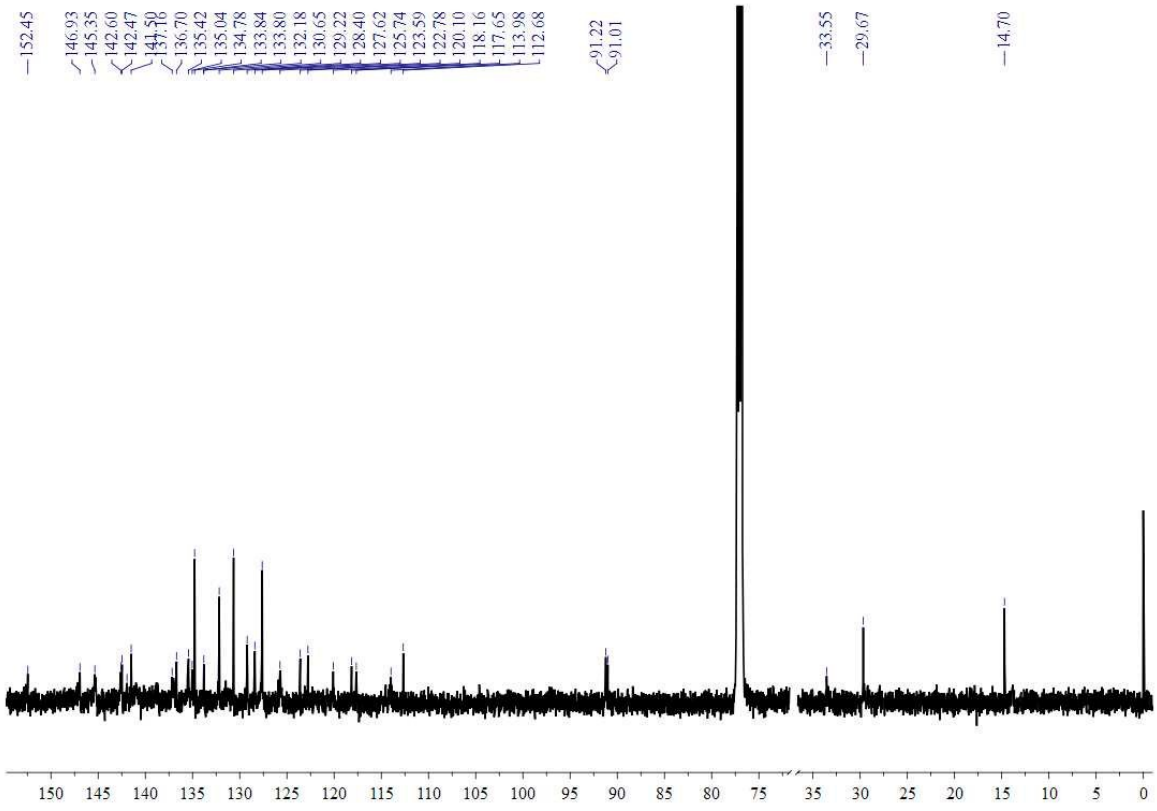

Figure S6. ^{13}C NMR spectrum of conjugate **7** in $CDCl_3$ at 298 K.

2.7

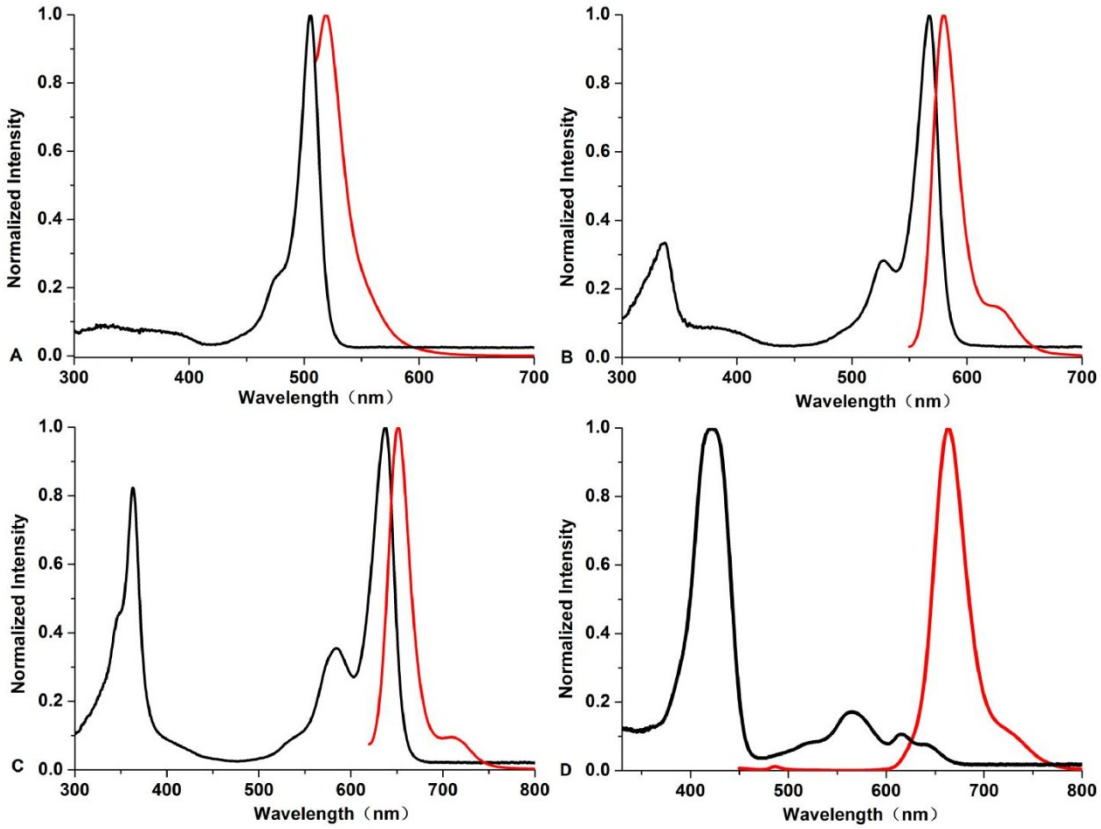

Figure S7. Absorption (black) and emission (red) spectra of **1-4** in toluene (1×10^{-5} M) at room temperature. (A) BODIPY **1** (λ_{ex}= 480 nm). (B) BODIPY **2** (λ_{ex}= 540 nm). (C) BODIPY **3** (λ_{ex}= 620 nm). (D) corrole **4** (λ_{ex}= 422 nm).

2.8

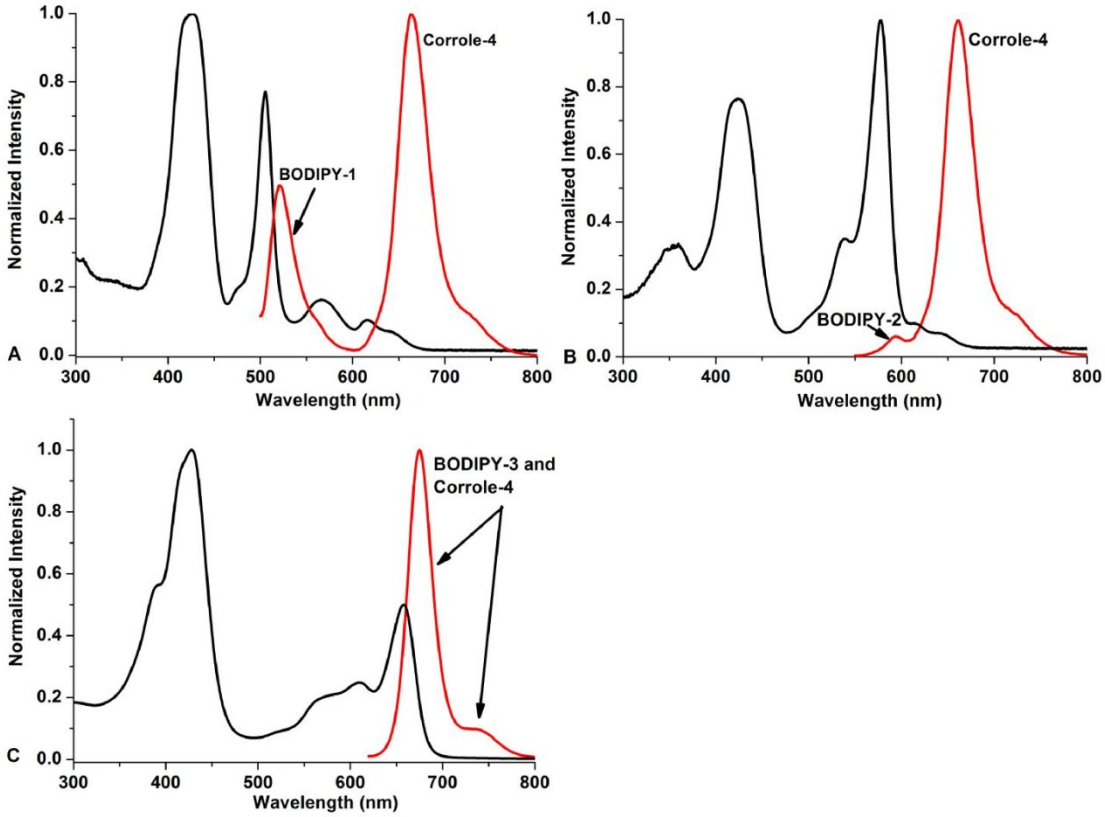

Figure S8. Absorption (black) and emission (red) spectra of **5-7** in toluene (1×10^{-5} M) at room temperature. (A) **5** (λ_{ex}= 480 nm). (B) **6** (λ_{ex}= 540 nm). (C) **7** (λ_{ex}= 422 nm).

2.9

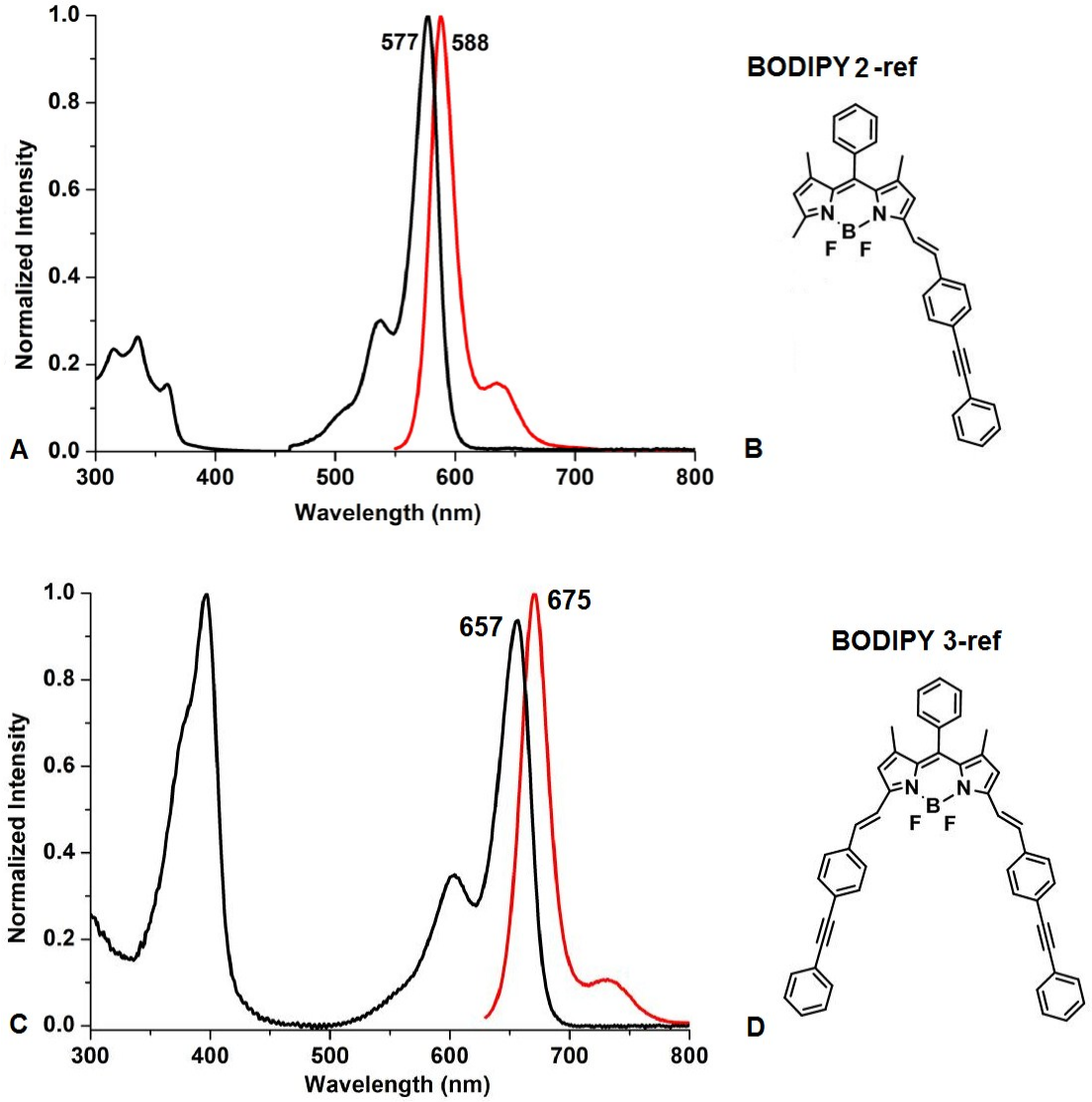

Figure S9. (A) Absorption (black) and emission (red) spectra of BODIPY **2-ref** in toluene (1 μM) at 298 K (λ_{ex} = 577 nm). (B) Structure of BODIPY **2-ref**. (C) Absorption (black) and emission (red) spectra of BODIPY **3-ref** in toluene (1 μM) at 298 K (λ_{ex} = 620 nm). (D) Structure of BODIPY **3-ref**.

2.10

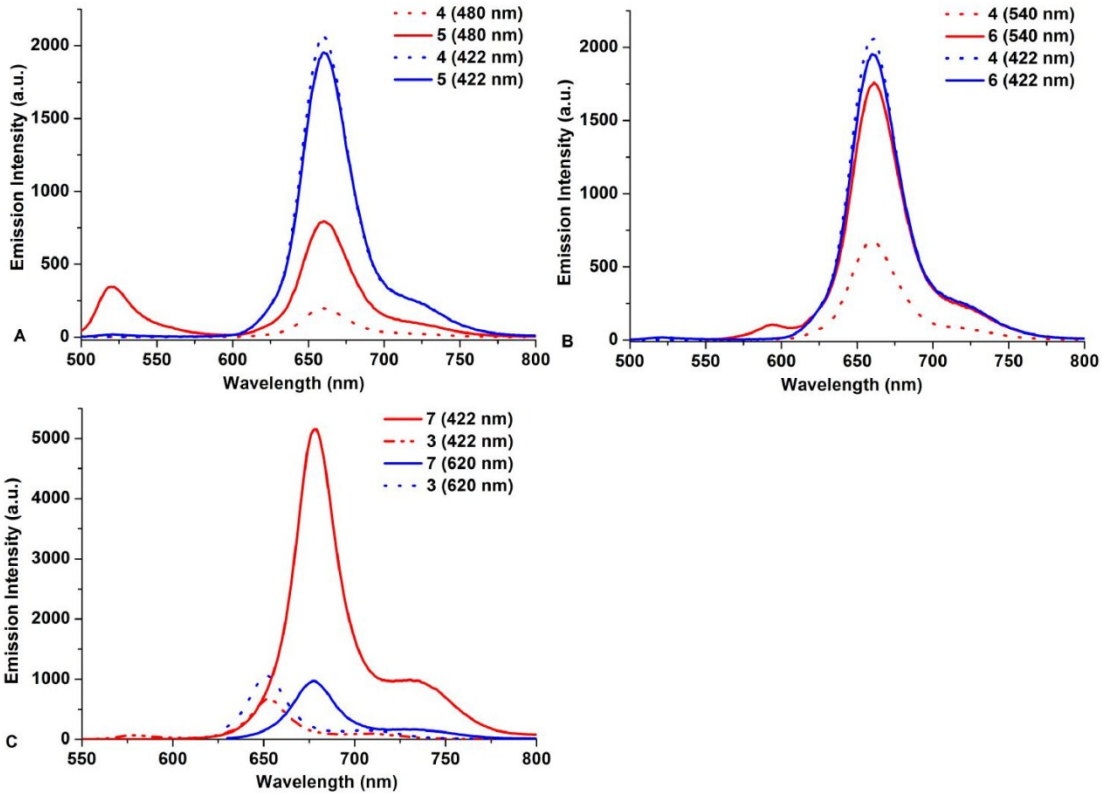

Figure S10. (A) Emission spectra of **5** (solid line) and **4** (dashed line) in toluene (1×10^{-5} M) at room temperature. Red and blue lines are used for fluorescence spectra measured at λ_{ex}= 480 and 422 nm. (B) Emission spectra of **6** (solid line) and 4 (dashed line) in toluene (1×10^{-5} M) at room temperature. Red and blue lines are used for fluorescence spectra measured at λ_{ex}= 422 and 620 nm. (C) Emission spectra of **7** (solid line) and **3** (dashed line) in toluene (1×10^{-5} M) at room temperature. Red and blue lines are used for fluorescence spectra measured at λ_{ex}= 422 and 620 nm.

2.11

Table S1. TD-DFT calculations for the B3LYP geometries of **1-7**carried out with the CAM-B3LYP functional and 6-31G(d) basis sets

Band[a]	# [b]	E[c][eV]	$\lambda_{(calc)}$[d][nm]	f[e]	$\lambda_{(obs)}$[f][nm]	Wavefunction =[g]
					1	
BDY	S	3.01	412	0.55	505	**96 % BDY-H →BDY-L**; …
					2	
BDY	S	2.64	470	1.05	567	**96 % BDY-H →BDY-L**; …
					3	
BDY	S	2.32	536	1.08	637	**96 % BDY-H →BDY-L**; …
					4a	
Q	S_1	2.13	582	0.13	--	**58 % s→-a**; **18%a→-s**;
Q	S_2	2.33	533	0.06	--	**46 % a→-a**; **30%s→-s**; ...
B	S_3	3.26	380	1.20	--	**54 % s→-s**; **36% a→-a**; ...
B	S_4	3.27	368	1.17		**61 % a→-s**; **18 % s→-a**; ...
					4b	
Q	S_1	2.24	553	0.13	621	**37 % a→-a**; **34 % s→-a**; **19 % s→-s**; …
Q	S_2	2.32	536	0.19	575	**45 % s→-a**; **29 % a→-a**; …
B	S_3	3.40	365	1.13	422	**65 % s→-s**; **32 % a→-a**; …
B	S_4	3.50	354	1.12		**67 % a→-s**; **18 % s→-a**; …
					5a	
Q	S_1	2.13	583	0.13	--	**57% s→-a**; **18% a→-s**; …
Q	S_2	2.32	534	0.06	--	**45% a→-a**; **30 % s→-s**; **17% s→-a**; …
BDY	S_3	3.01	412	0.52	--	**96% BDY-H→BDY-L**; …
B	S_4	3.22	385	1.76	--	**54% s→-s**; **37% a→-a**; …
B	S_5	3.36	369	1.19		**62% a→-s**; **19% s→-a**; …
					5b	
Q	S_1	2.24	553	0.13	615	**37% a→-a**; **34% s→-s**; **19% s→-a**; …
Q	S_2	2.31	536	0.18	576	**45% s→-a**; **29% a→-a**; **13% s→-a**; …
BDY	S_3	3.01	412	0.51	505	**96% BDY-H→BDY-L**; …
B	S4	3.36	369	1.67	426	**64% s→-a**; **31% a→-s**; …
B	S5	3.49	355	1.12		**67% a→-a**; **18% s→-s**; …
					6a	
Q	S_1	2.12	584	0.14	--	45% s→BDY-L; **17% a→-s**; ….
Q	S_2	2.32	535	0.07	--	44% a→BDY-L; **23% s→-s**; …
BDY	S_3	2.54	487	1.75	--	**58% BDY-H→BDY-L**; 31% s→BDY-L
B	S_4	3.2	387	1.64	--	**41% s→-s**; 32% a→BDY-L; …
B	S_5	3.36	369	1.12	--	**59% a→-s**; 18% s→BDY-L
					6b	
Q	S_1	2.24	554	0.15	616	**36% a→-a**; **24% s→-a**; …
Q	S_2	2.31	536	0.18	578	**33% s→-a**; **30% a→-a**; …
BDY	S_3	2.55	487	1.63	577	**72% BDY-H→BDY-L**; 20% s→BDY-L
B	S_4	3.34	371	1.56	423	**30% s→-s**; **23% a→-a**; 20% BDY-H→-s; …
B	S_6	3.52	353	0.99		**56% a→-s**; **27% s→-a**; …
					7a	
Q	S_1	2.10	589	0.06	--	**27% s′→-a**; **17% s→-a′**; ….
Q	S_2	2.12	584	0.08	--	**21% s→-a′**; **18% s→-a**; …
BDY	S_3	2.18	570	1.07	--	**53% BDY-H→BDY-L**; 18% s→BDY; …
Q	S_4	2.31	537	0.26	--	**20% a′→-a**; **19% a′→-a′**; **10% s′→-s**; …
Q	S_5	2.32	534	0.1	--	**23% a→-a**; **16% a→-a′**; **11% s′→-s′**; …
B	S_6	3.14	395	4.73		**14% s→-s′**; 14% H-5→BDY-L; 13% s′→BDY-L; 11% BDY-H→-s
B	S_7	3.17	391	0.29		**21% s′→-s**; **11% a→-a**; 11% BDY-H→-s′,
					--	**10% s→-s′**; **10% a→-a′**; …
B	S_8	3.32	374	1.77		**21% a′→-s**; **20% a′→-s′**; **11% a→-s′**; ….
B	S_9	3.34	371	0.26		20% BDY→-a; 14% H-5→BDY-L, 12% s′→BDY-L, **11% a→-s**; ….
					7b	

Q	S_1	2.11	587	0.07	--	**38% s→-a**; **17% a→-s**; 10% BDY-H→-a; …
BDY	S_2	3.17	570	065	--	**45% BDY-H→BDY-L**; 13% s′→BDY-L, 10% BDY-H→-a′; …
Q	S_3	2.21	562	0.34	--	**27% a′→-a′**; **24% s′→-a′**; **13% s′→-s′**; …
Q	S_4	2.29	542	0.45	--	**29% a′→-a′**; **26% s′→-a′**; **10% s′→-s′**; …
Q	S_5	2.32	535	0.09		**40% a→-a**; **18% s→-s**; …
B	S_6	3.15	394	3.65		**23% a→-a**; **20% s→-s**; 13% BDY-H→-s; 11% H-5→BDY-L; …
B	S_7	3.21	386	1.35	428	**21% s′→-s′**; **18% a′→-a′**; …
B	S_8	3.26	381	0.02		46% BDY-H→-a′; **39% s→-a′**; ….
B	S_9	3.33	373	1.40		**52% a→-s**; 14% BDY-H→-a; ….
					7c	
BDY	S_1	2.18	570	0.62	658	**56% BDY-H→BDY-L**; …
Q	S_2	2.20	563	0.53		25% **s′′→-a′**; **24% a′→-a′**;
					617	16% BDY-H→BDY-L; …
Q	S_3	2.24	554	0.17		**32% a→-a**; **30% s→-a**; …
Q	S_4	2.28	543	0.32	578	**29% a′→-a′**; **28% s′→-a′**; …
Q	S_5	2.31	536	0.13		38% **s→-a**, **28% a→-a**; …
B	S_6	3.19	388	4.04		17% H-5→BDY-L; **16% a′→-a′**; …
B	S_7	3.28	378	0.74	428	**18% s→-s**; 16% BDY-H→-a; …
B	S_8	3.32	373	0.15		58% BDY-H→-a; 20% BDY-H→-a′; …
B	S_9	3.34	371	0.11		46% BDY-H→-a′; 14% BDY-H→-a; …

a − Band assignment described in the text. b − The number of the state assigned in terms of ascending energy within the TD-DFT calculation. c-e − Calculated band energies (eV), wavelengths (nm) and oscillator strengths in parentheses (*f*). f − Observed wavelengths (nm) in toluene in Figs 1 and 5 of the main text. The wavelengths of the intense Faraday $\mathbf{B_0}$ terms in the Q band region of the MCD spectra of **4-7** are used to assign the observed Q band wavelengths, while the band maxima in the absorption spectra are used for the wavelengths of the corrole B band and the main BODIPY spectral band. g − The wavefunctions based on the eigenvectors predicted by TD-DFT. One-electron transitions between the four frontier π-MOs of the the corrole rings that are associated with Michl's perimeter model,[1]or between the HOMO (BDY-H) and LUMO (BDY-L) of the BODIPY core are highlighted in bold. H and L denote the HOMO and LUMO of the entire dyad, and an apostrophe is used to distinguish between frontier π-MOs localized on the two corrole rings of **7**.

Reference

1. (a) J. Michl, *J. Am. Chem. Soc.* 1978, 100, 6801; (b) J. Michl, *J. Am. Chem. Soc.* 1978, 100, 6812; (c) J. Michl, *Pure Appl. Chem.* 1980, 52, 1549; (d) J. Michl, *Tetrahedron* 1984, 40, 3845.