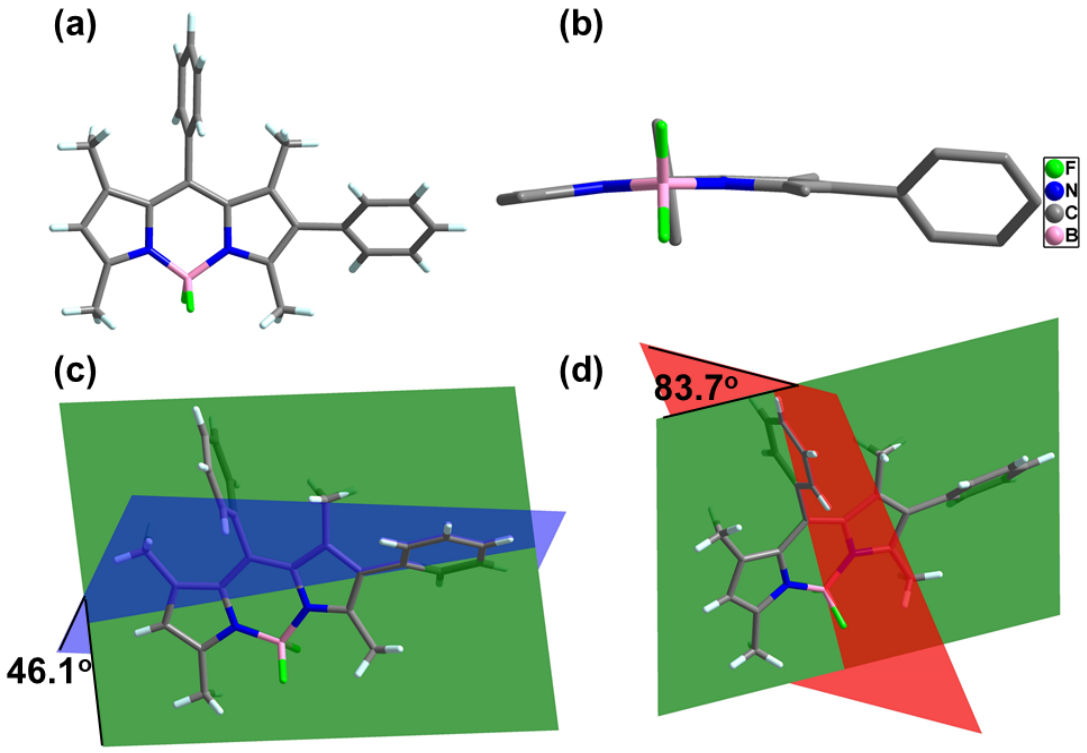
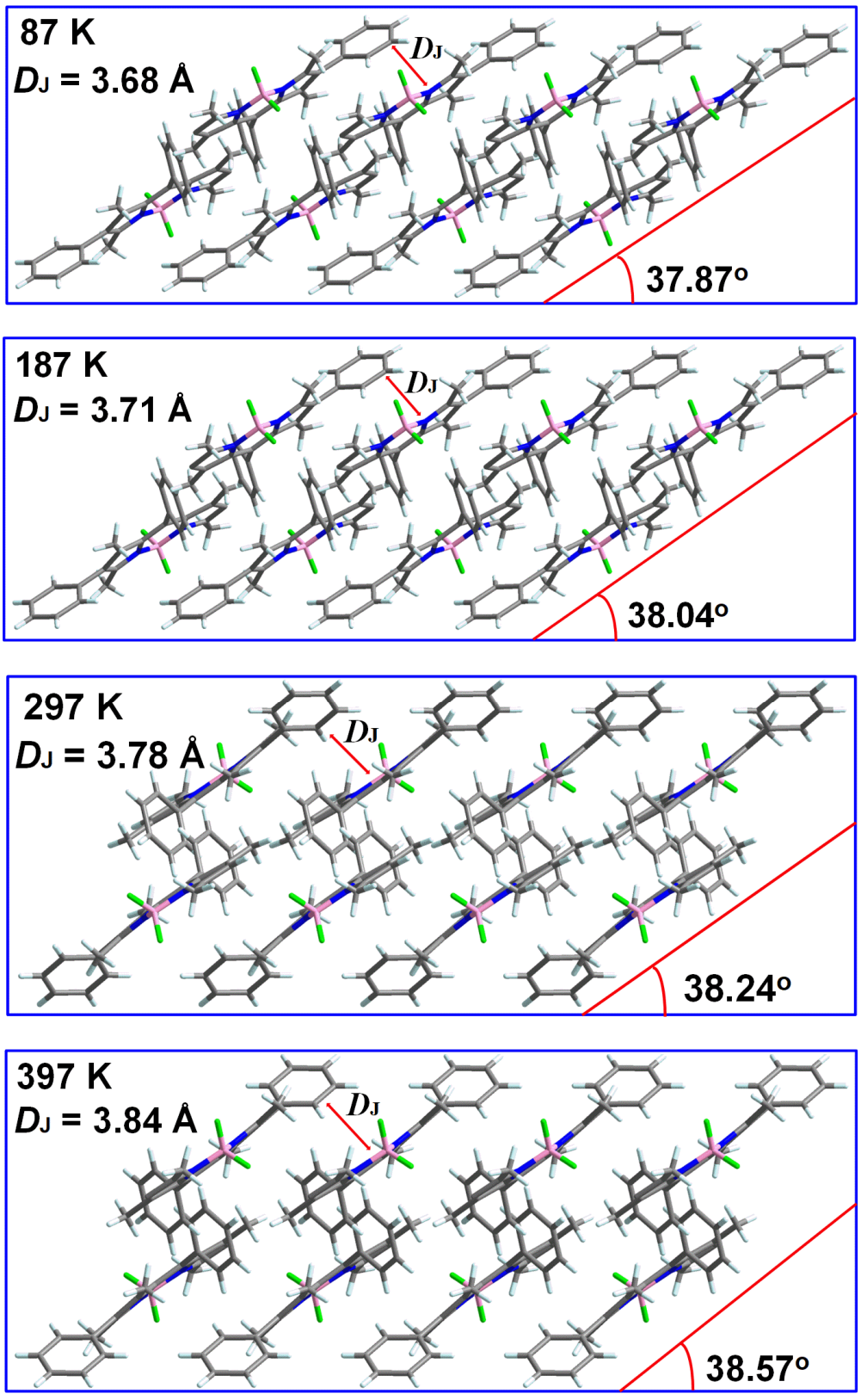
Domino-Like Multi-Emissions across Red and Near Infra-Red from Solid-State 2-/2,6-Aryl Substituted BODIPY Dyes

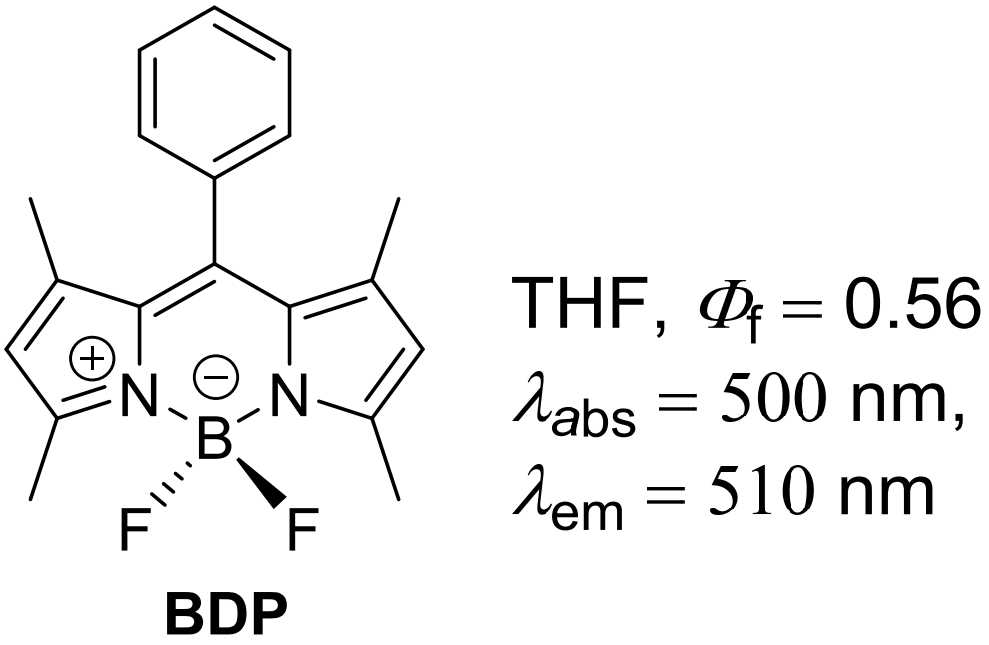
Tian, *et al*.



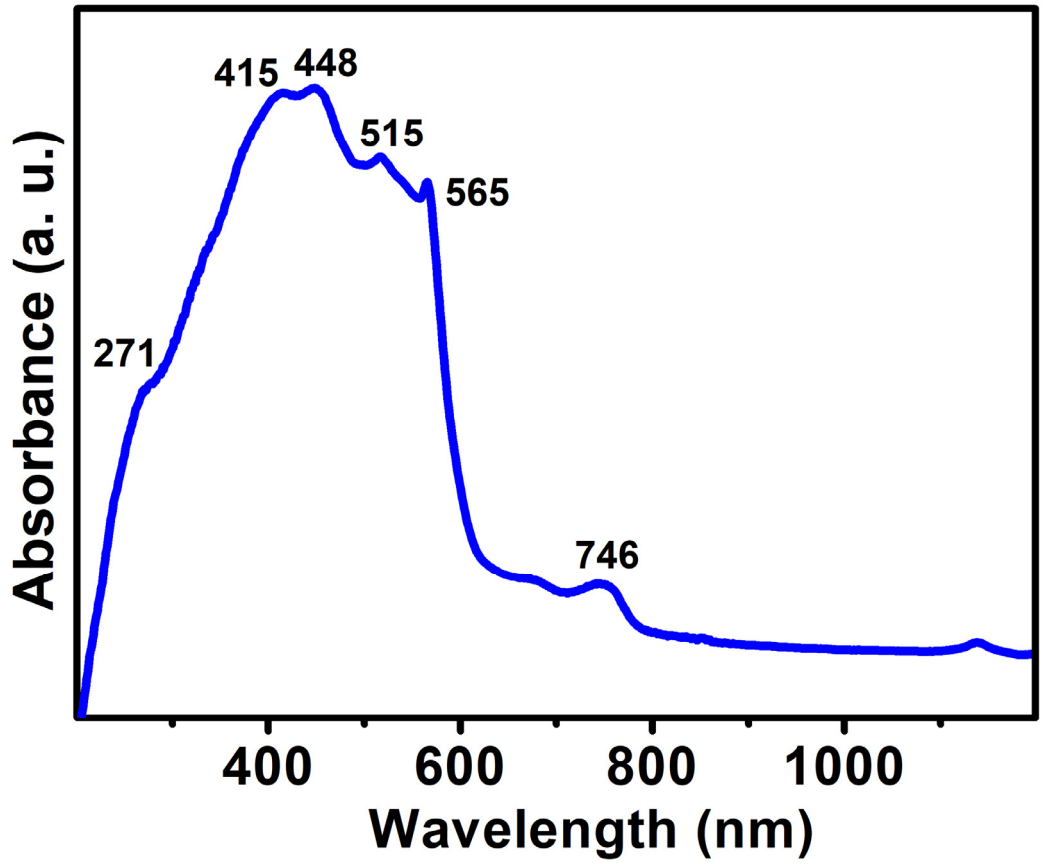
Supplementary Figure 1. (a) Top and (b) side view of single crystal X-ray diffraction structure of **BDP1**. The dihedral angles between (c) 2- and (d) 8-phenyl substituent and indacene plane.



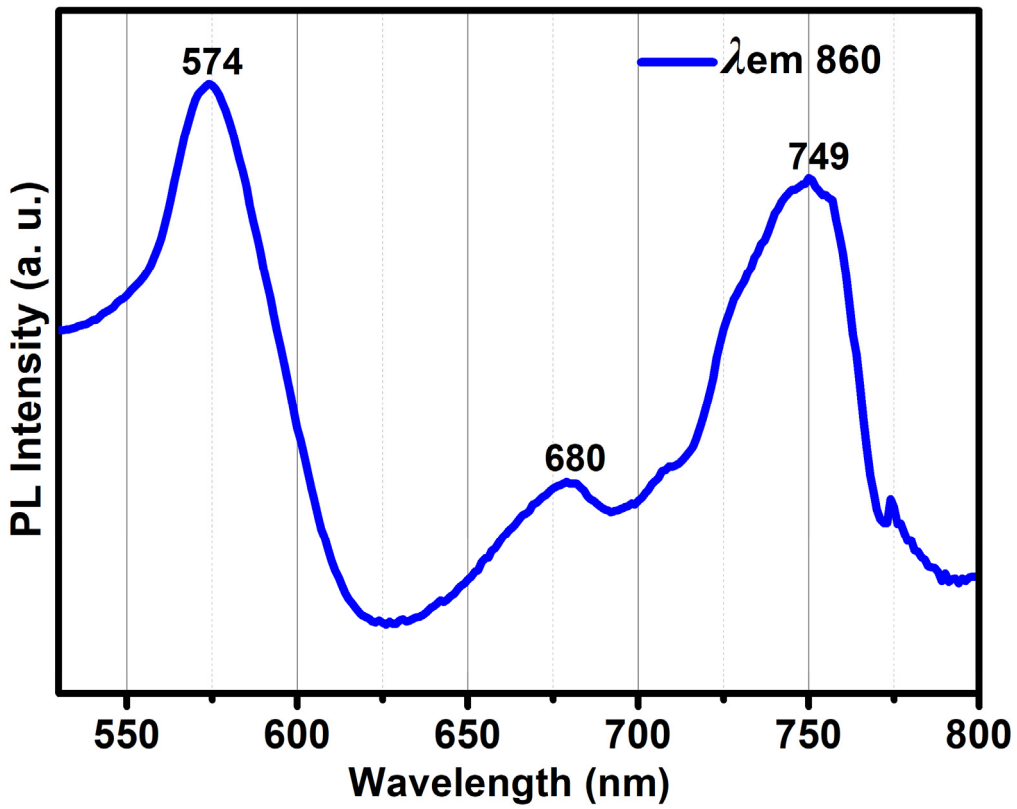
Supplementary Figure 2. Variations of the molecular packing mode at different temperatures viewed along the *c*-axis in the single crystal of **BDP1**.



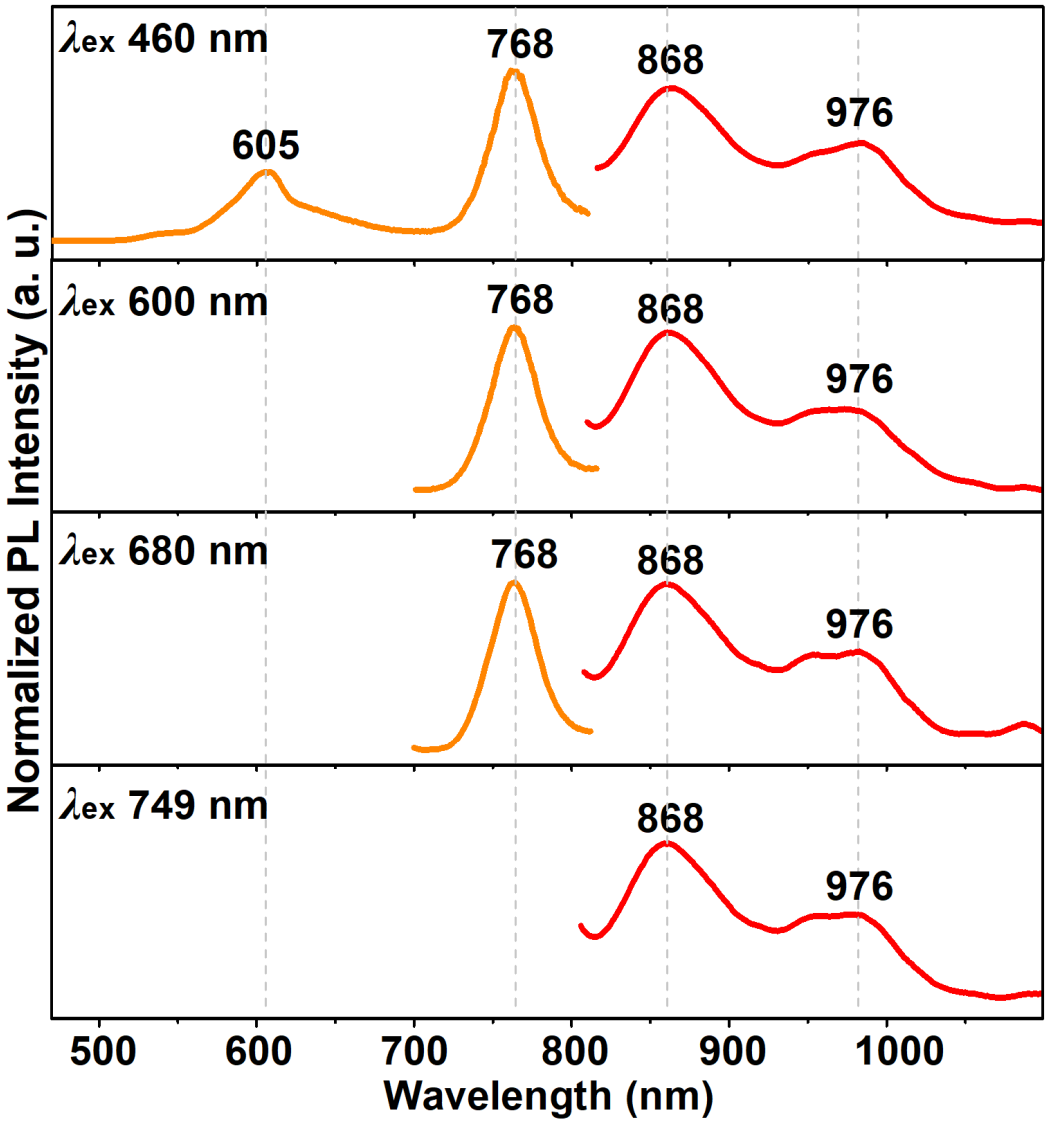
Supplementary Figure 3. Molecular structure and photophysical properties of **BDP**.



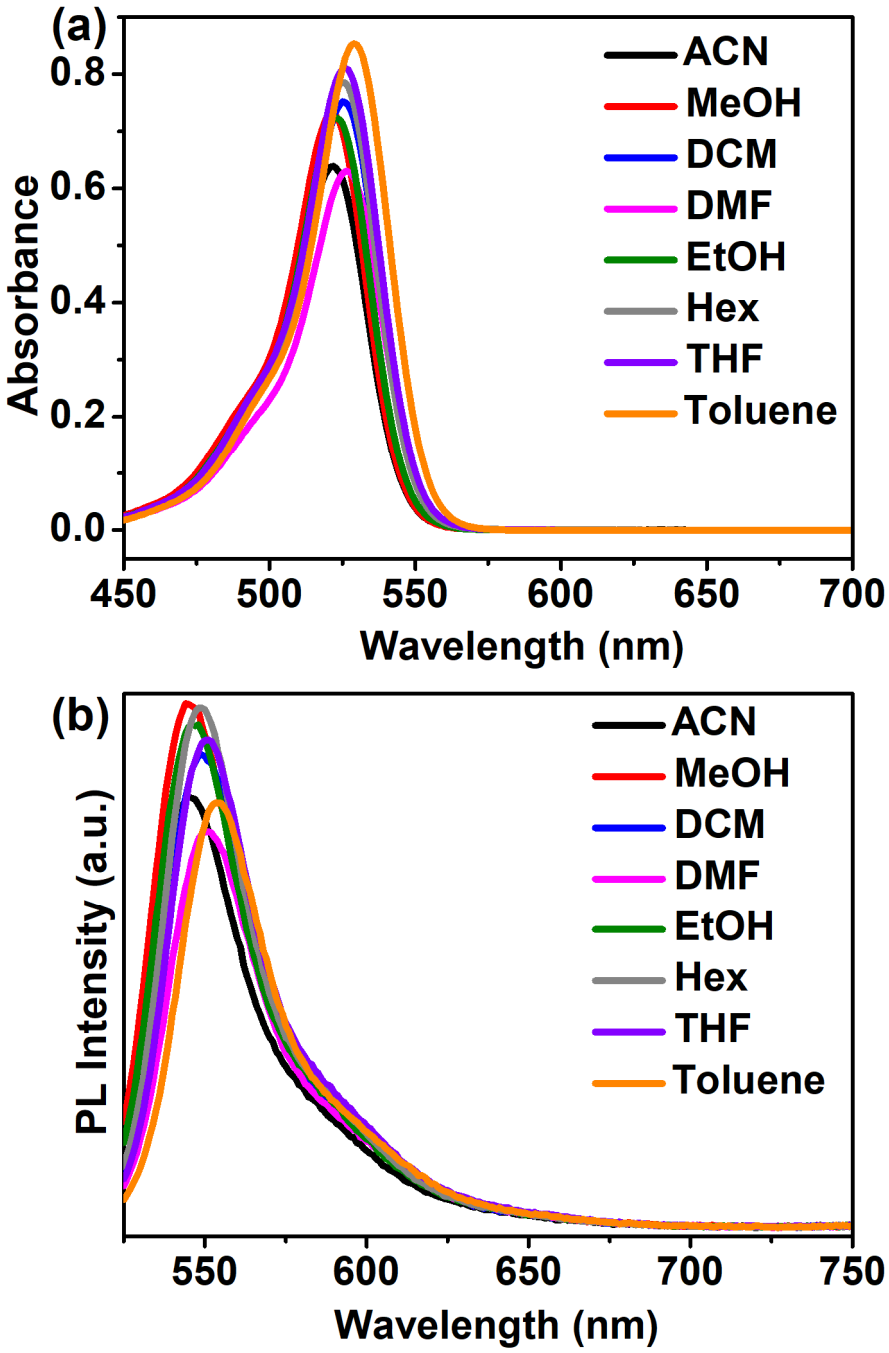
Supplementary Figure 4. UV-vis absorption spectrum of microcrystalline powder state **BDP1**.



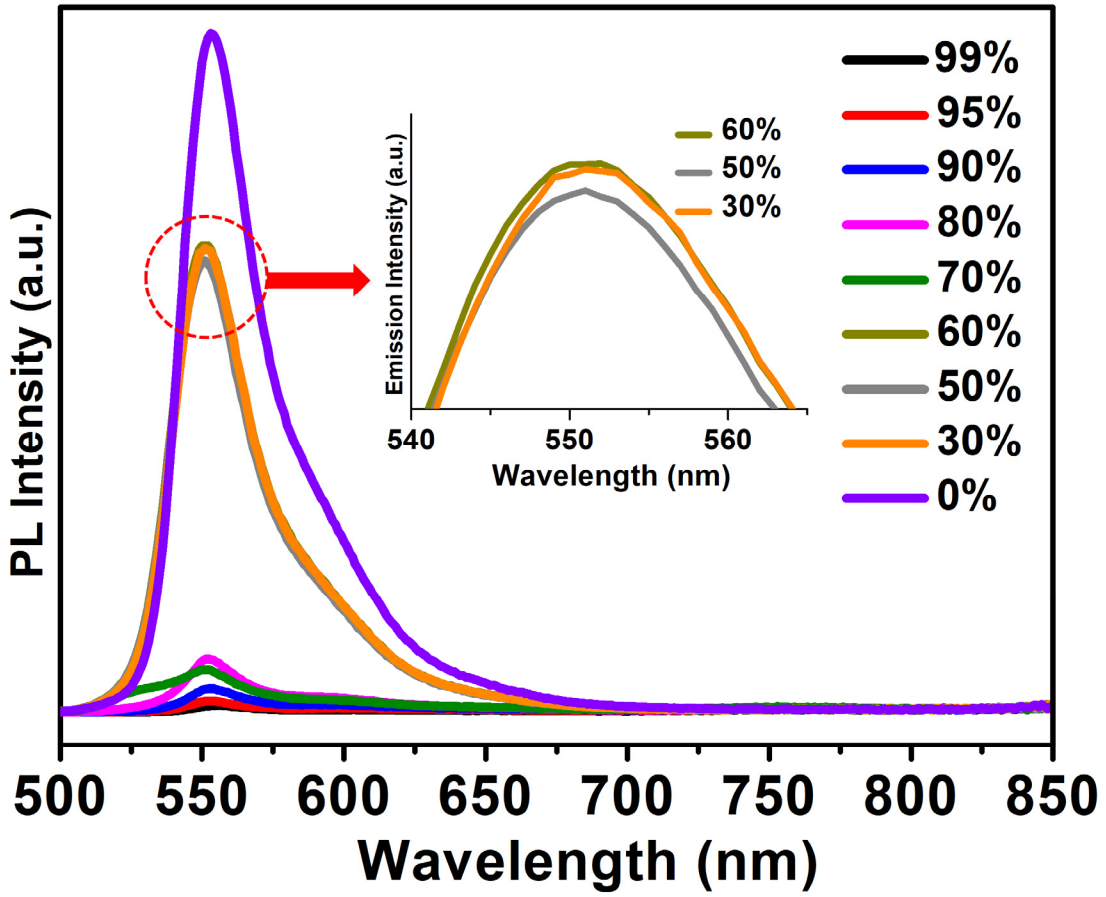
Supplementary Figure 5. Excitation spectrum of microcrystalline powder state **BDP1** when the emission was fixed at 860 nm.



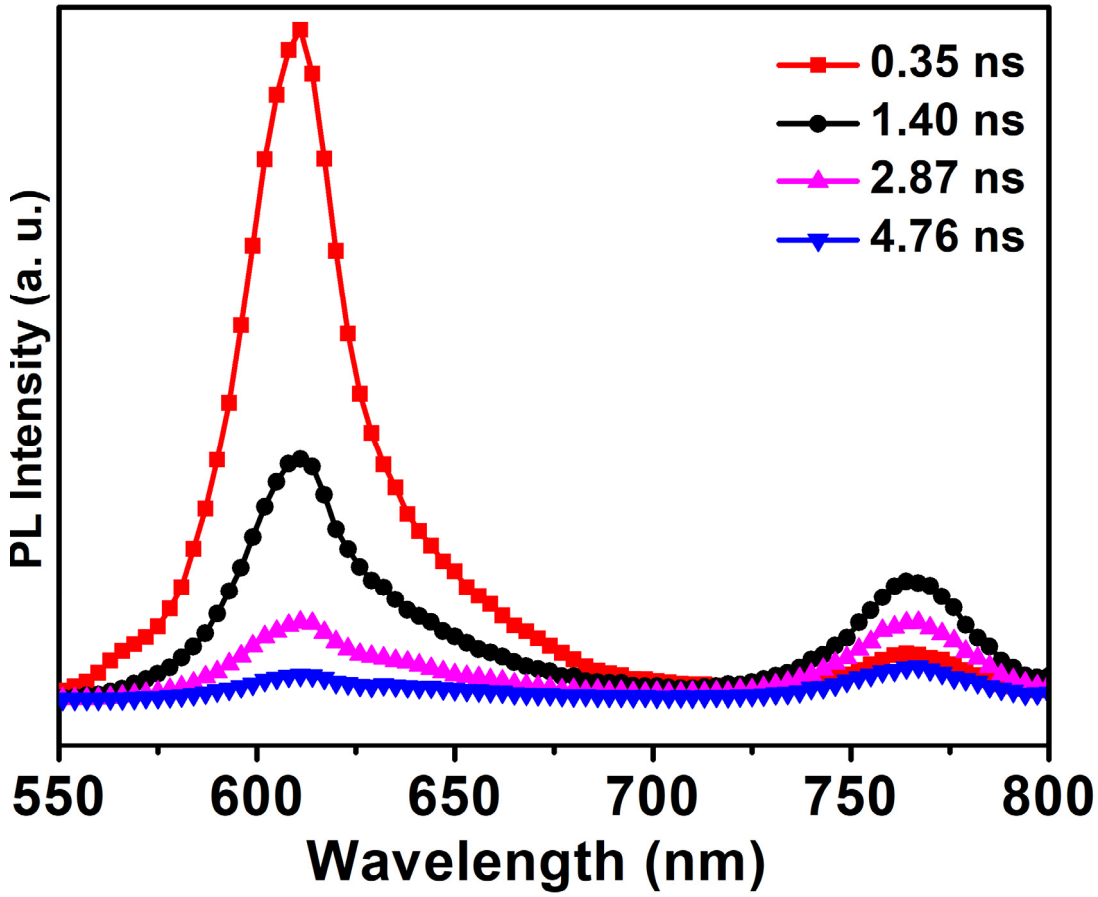
Supplementary Figure 6. Fluorescence spectra of microcrystalline powder state **BDP1** excited with light at different wavelengths (460, 600, 680, and 749 nm).



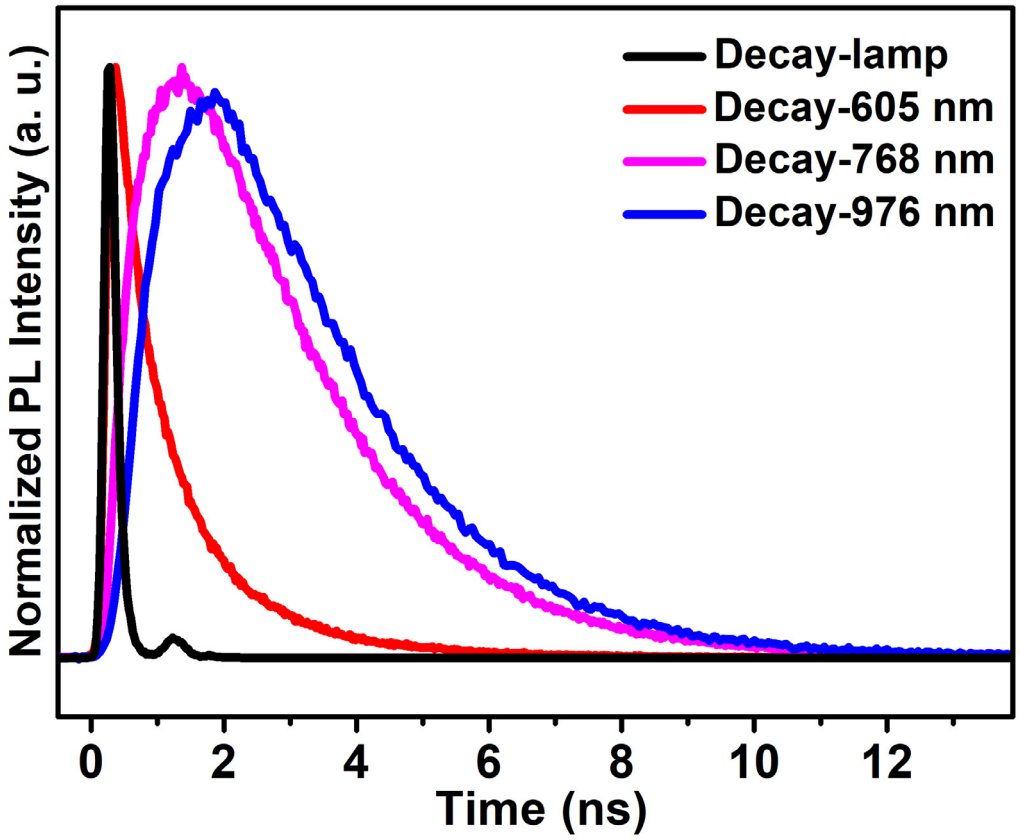
Supplementary Figure 7. Absorption and emission spectra (slit width: 1 nm, 0.5 nm) of **BDP1** (1×10^{-5} mol L^{-1}) in different solvents (ACN: Acetonitrile; MeOH: Methanol; DCM: Dichloromethane; DMF: Dimethylforamide; EtOH: Ethanol; Hex: Hexane; THF: Tetrahydrofuran).



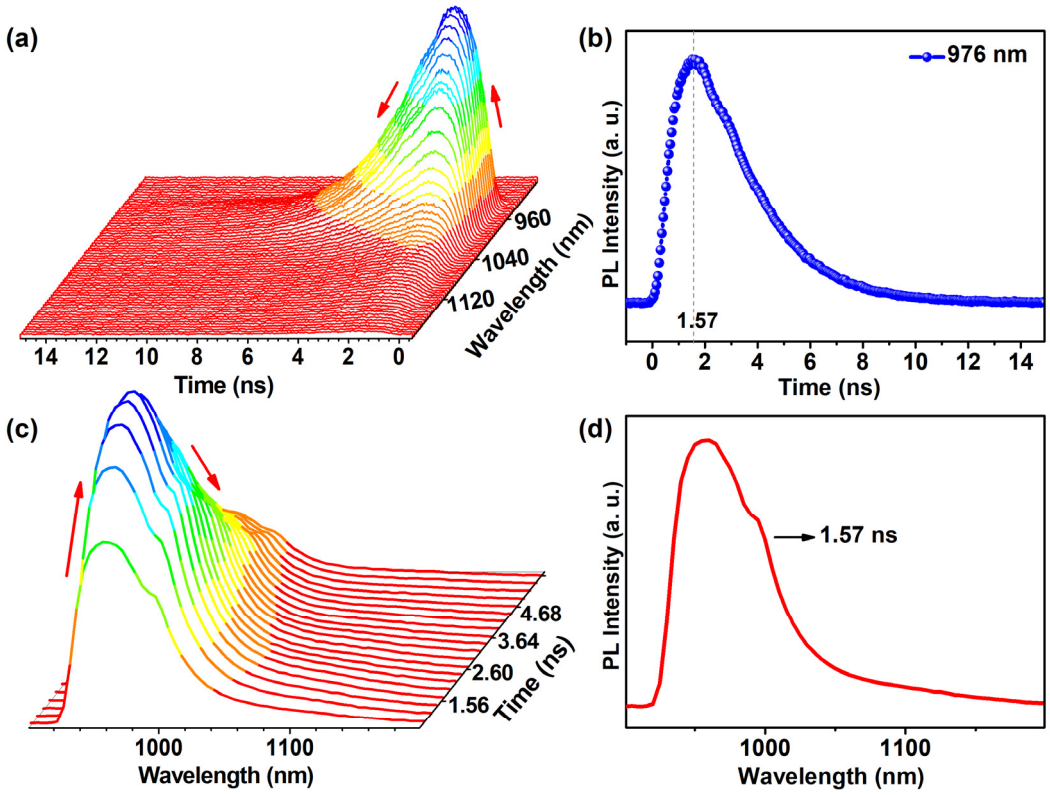
Supplementary Figure 8. Fluorescence spectra of **BDP1** (1×10^{-5} mol L^{-1}) in THF solution mixed with varied volumetric fractions of water (f_w) (λ_{ex} = 480 nm, slit width: 1 nm, 1 nm).



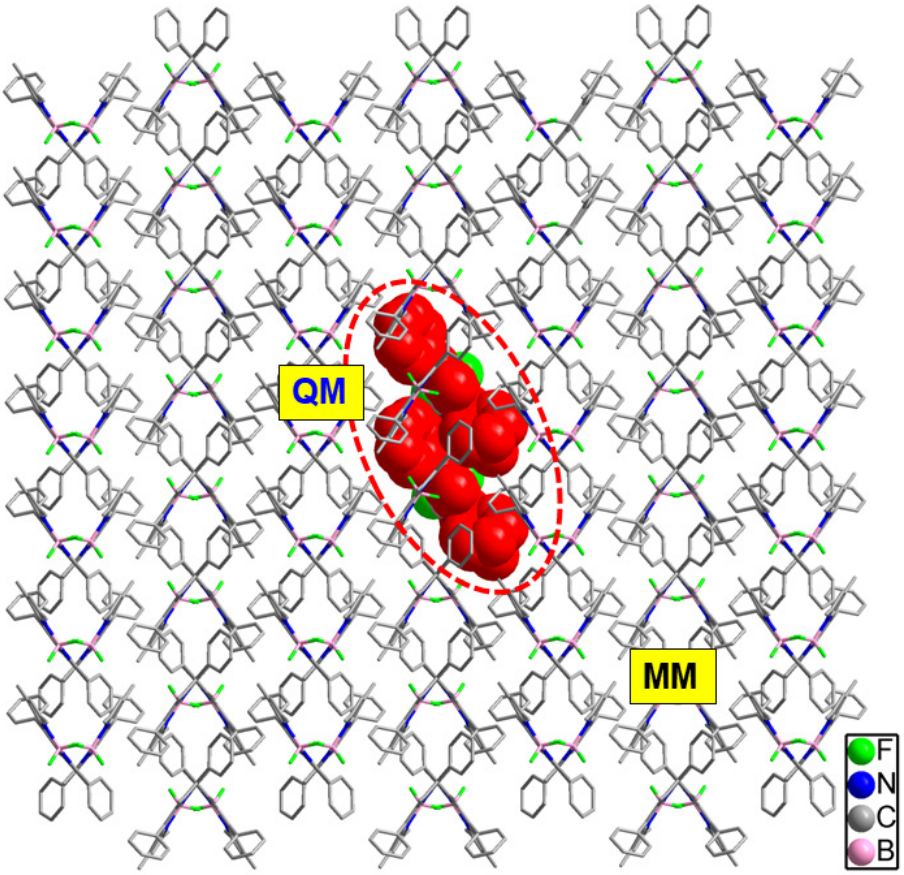
Supplementary Figure 9. Time-resolved fluorescence spectra of microcrystalline powder state **BDP1** at 0.35, 1.40, 2.87, and 4.76 ns.



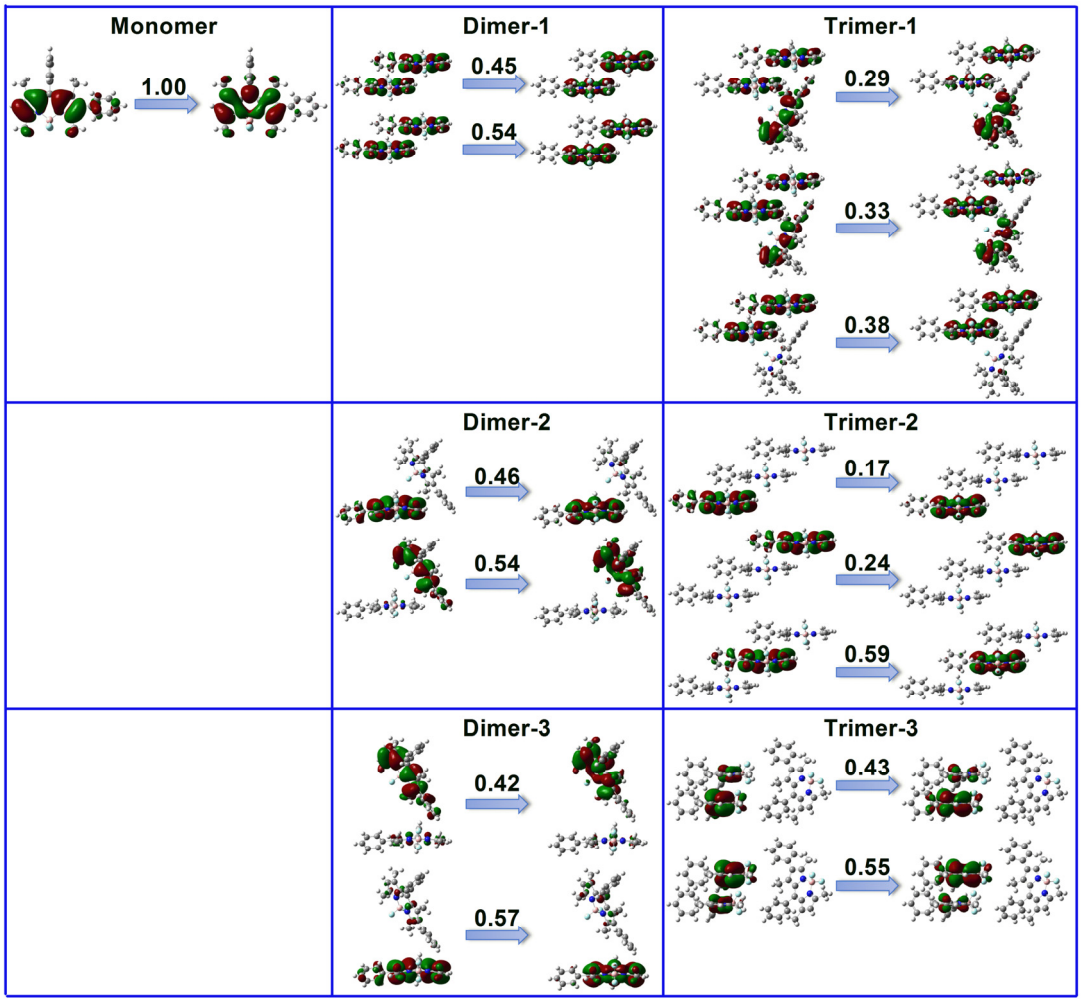
Supplementary Figure 10. Fluorescence decay curves of **BDP1** at 605, 768, and 976 nm. All samples measured were in the microcrystalline powder state.



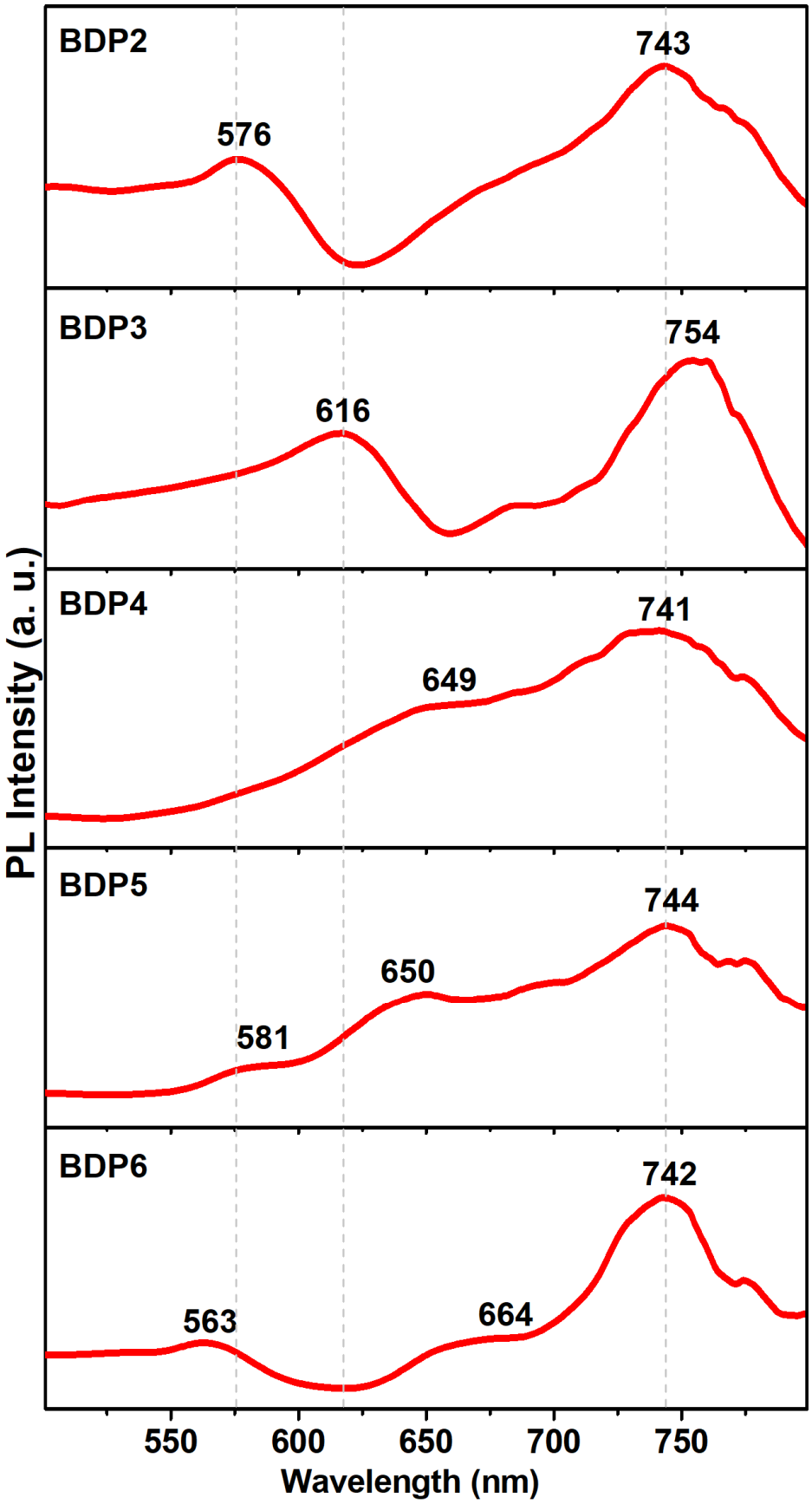
Supplementary Figure 11. (a) Fluorescence decay curves of **BDP1**. The emission wavelength (λ_{em}) varied from 900 to 1200 nm. (b) Fluorescence decay curve of **BDP1** at emission wavelength of 976 nm. (c) Time-resolved emission spectra of **BDP1**. (d) Time-resolved fluorescence spectra of **BDP1** at 1.57 ns. All samples measured were in the microcrystalline powder state.



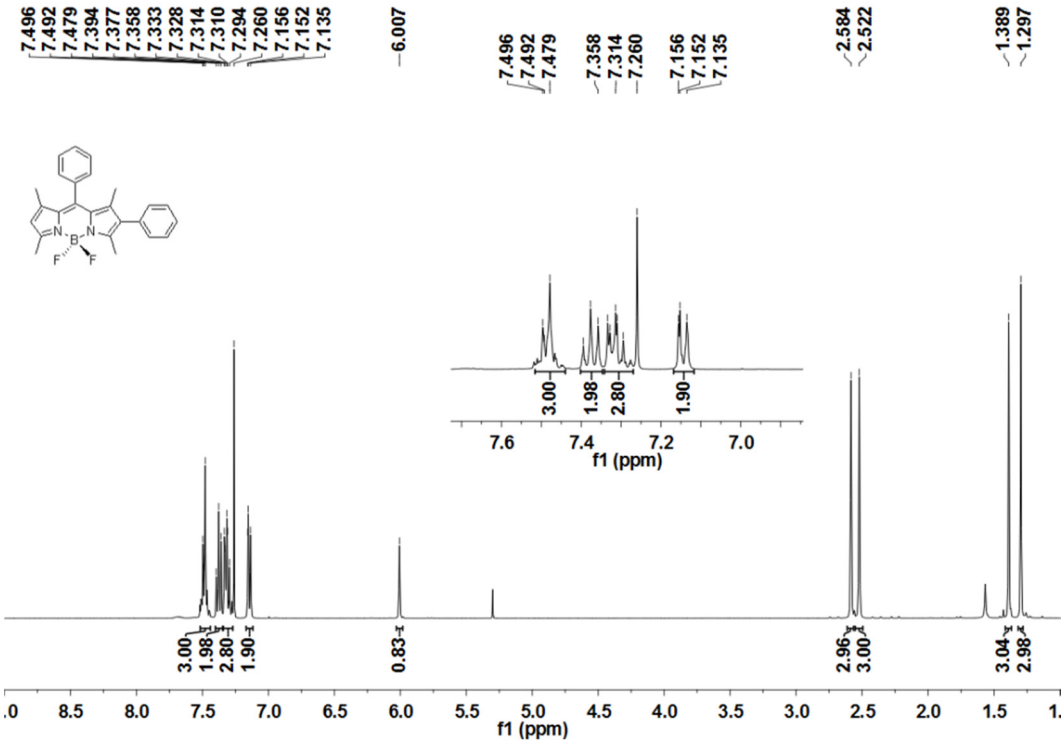
Supplementary Figure 12. Set up of QM/MM model for **BPD1** taking QM dimer as an example.



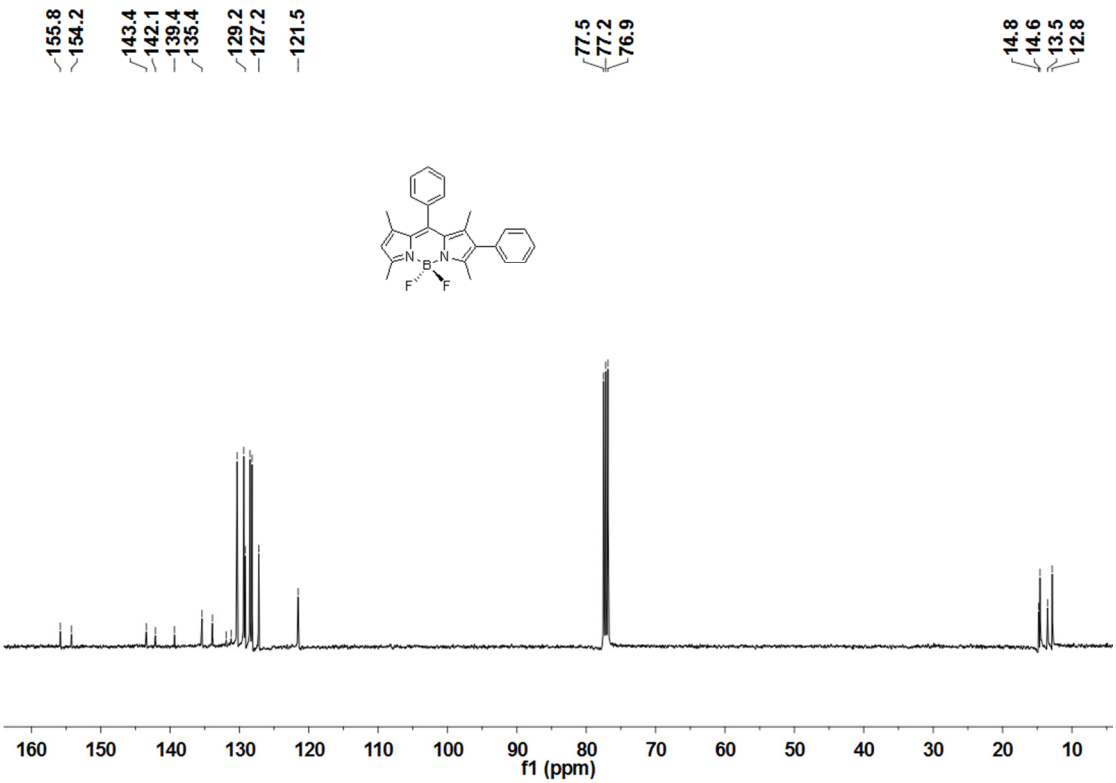
Supplementary Figure 13. Calculated NTOs of **BDP1** monomer, dimer-1, and trimer-1 for the lowest singlet states (S_1).



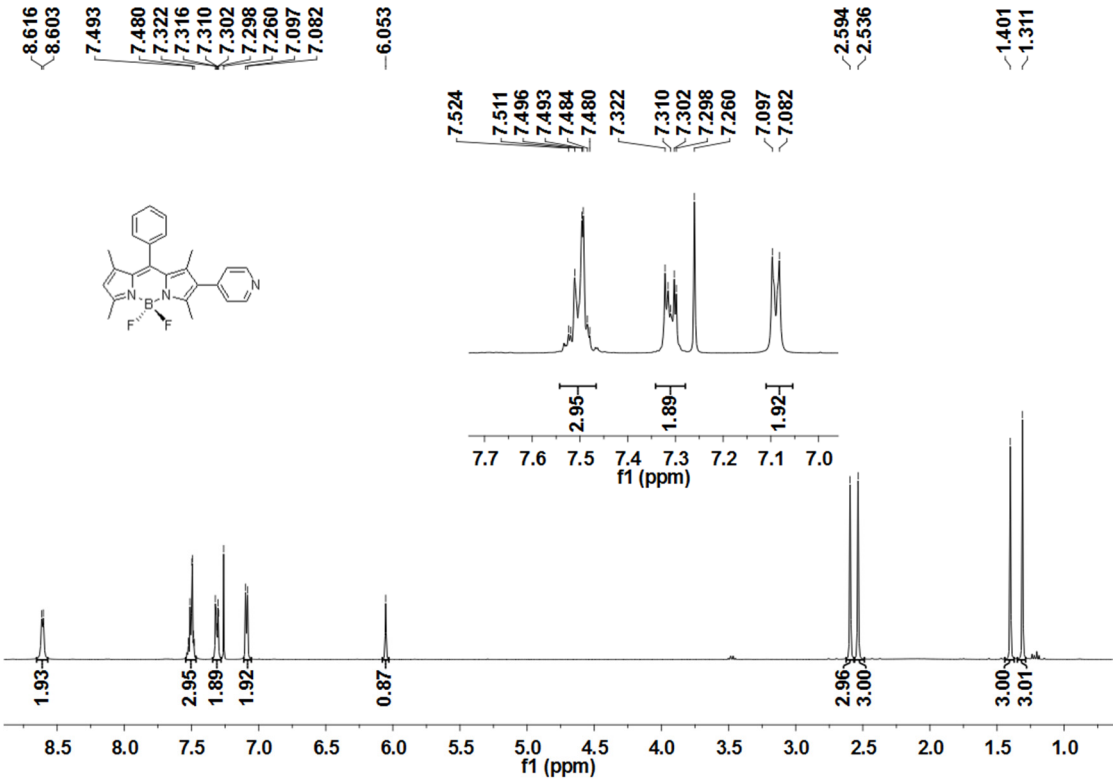
Supplementary Figure 14. Excitation spectra of **BDP2-6** in microcrystalline powder state when the emission was fixed at 900 nm.



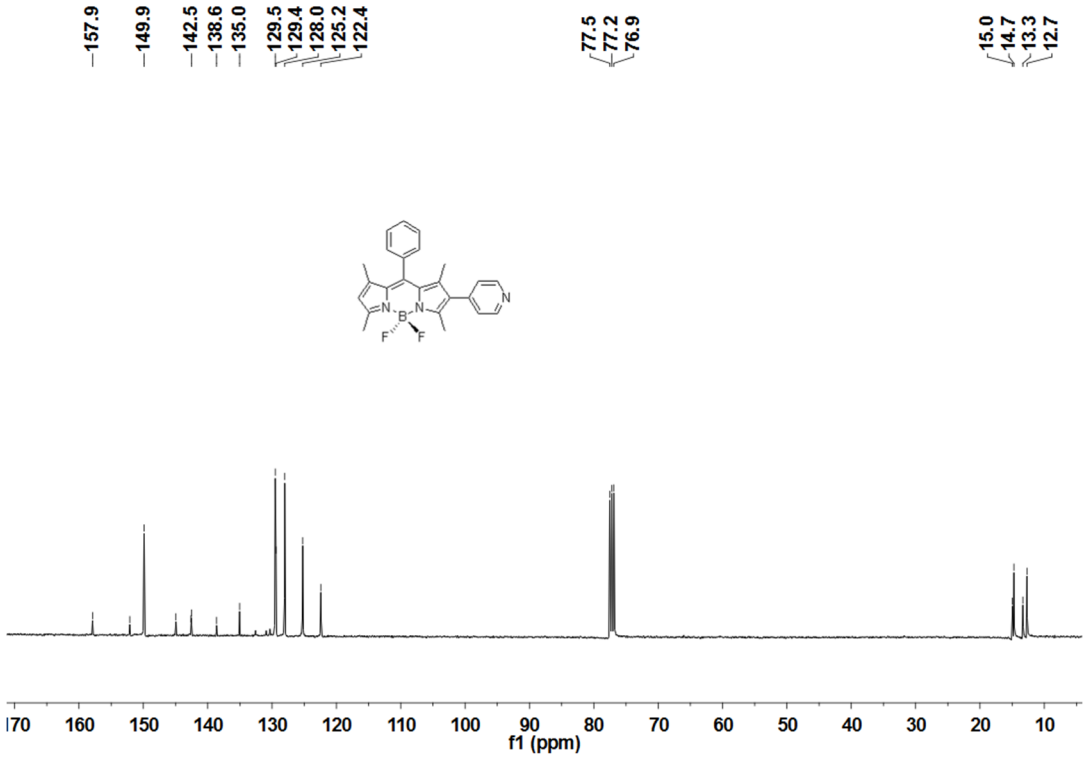
Supplementary Figure 15. ^{1}H NMR of **BDP1** in $CDCl_3$.



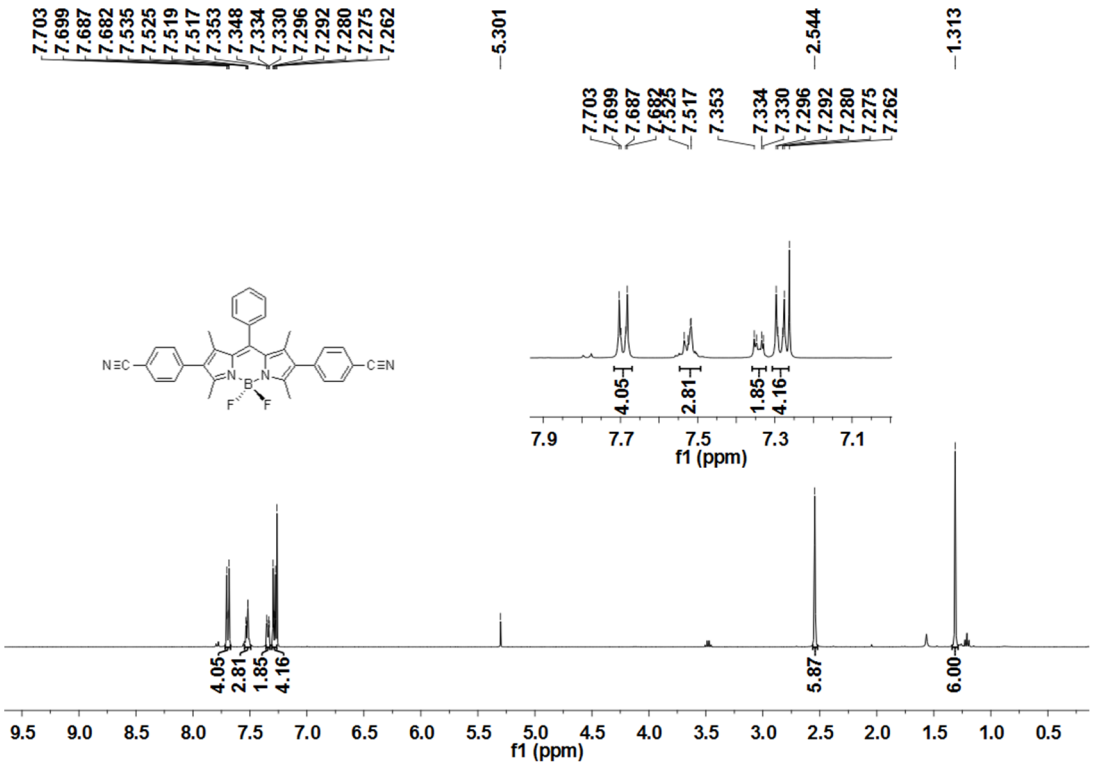
Supplementary Figure 16. ^{13}C NMR of **BDP1** in $CDCl_3$.



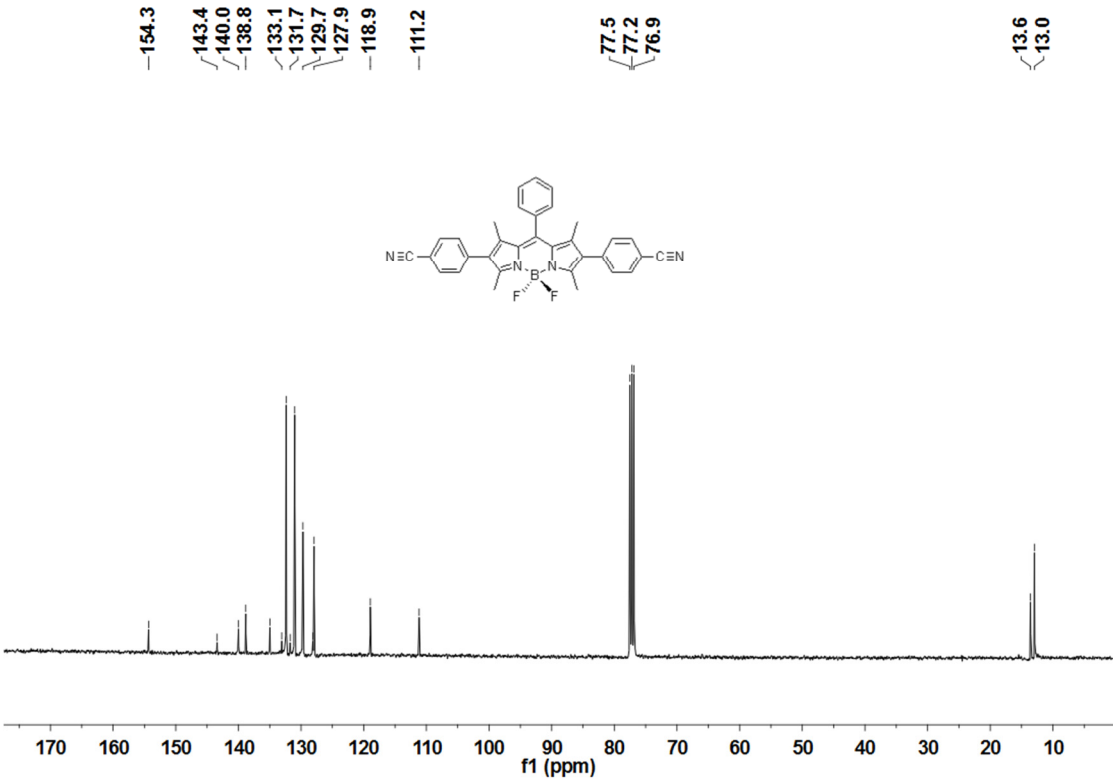
Supplementary Figure 17. ^{1}H NMR of **BDP4** in $CDCl_3$.



Supplementary Figure 18. ^{13}C NMR of **BDP4** in $CDCl_3$.



Supplementary Figure 19. ^{1}H NMR of **BDP6** in $CDCl_3$.



Supplementary Figure 20. ^{13}C NMR of **BDP6** in $CDCl_3$.

Supplementary Table 1 Packing parameters of single crystal **BDP1** at different temperatures

	θ_J (°)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
87 K	37.87	6.9797	15.278	18.956	90	94.895	90	2014.20
187 K	38.04	6.9985	15.496	18.927	90	94.112	90	2045.19
297 K	38.24	7.0285	15.740	19.565	90	106.019	90	2080.40
397 K	38.57	7.0667	15.950	19.556	90	105.993	90	2118.92

Supplementary Table 2 Fluorescence lifetimes of microcrystalline powder state **BDP1**

λ_{em} (nm)	605	768	976
τ_1 (ns)	0.83	0.73	0.99
a_1 (%)	55.61	-62.79	-91.86
τ_2 (ns)	2.89	1.37	12.9
a_2 (%)	5.96	5.53	3.65
τ_3 (ns)	1.88	1.93	1.84
a_3 (%)	38.43	157.27	188.22
Average Lifetime	0.92	1.31	1.46

Supplementary Table 3 Calculated vertical excitation energies and oscillator strength (*f*) of the lowest singlet states (S_1) for monomer, dimer, and trimer of **BDP1**

S_1	monomer	Dimer			Trimer		
		1	**2**	**3**	**1**	**2**	**3**
***E* (eV)**	2.960	2.951	2.947	2.962	2.912	2.916	2.946
f	0.647	1.263	0.345	0.346	0.654	1.786	1.026

Supplementary Table 4 Crystallographic data and structure refinement for **BDP1**

	BDP1-87 K	**BDP1-187 K**	**BDP1-297 K**	**BDP1-397 K**
CCDC number	**1540363**	**1837300**	**1540364**	**1837301**
Formula	$C_{25}H_{23}BF_2N_2$	$C_{25}H_{23}BF_2N_2$	$C_{25}H_{23}BF_2N_2$	$C_{25}H_{23}BF_2N_2$
M_w	400.26	400.26	400.26	400.26
Temperature (K)	87 K	187 K	297 K	397 K
Wavelength (Å)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
	(λ = 0.71073)	(λ = 0.71073)	(λ = 0.71073)	(λ = 0.71073)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Cell dimensions	a = 6.9797(4)Å	a = 6.9985(4) Å	a = 7.0285(16) Å	a = 7.0667(14) Å
	b = 15.278(8) Å	b = 15.4964(9) Å	b = 15.74(4) Å	b = 15.95(4) Å
	c = 18.956(11) Å	c =18.9276(13) Å	c = 19.565(4) Å	c = 19.556(4) Å
	α = 90°	α = 90°	α = 90°	α = 90°
	β = 94.895(2)°	β = 94.911(2) °	β = 106.019(9) °	β = 105.993(8) °
	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume (Å^3)	2014.0(2)	2045.2(2)	2080.4(8)	2118.9(8)
Z	4	4	4	4
Completeness (%)	99.6	98.9	99.7	97.9
μ (mm^{-1})	0.09	0.088	0.087	0.085
Dc (g/cm^3)	1.320	1.300	1.278	1.255
R(int)	0.0628	0.087	0.0889	0.1105
R(sigma)	0.0885	0.1364	0.1187	0.1733
Index ranges	$-8 \le h \le 9$	$-8 \le h \le 9$	$-9 \le h \le 9$	$-8 \le h \le 9$
	$-19 \le h \le 19$	$-20 \le h \le 19$	$-20 \le h \le 20$	$-17 \le h \le 20$
	$-16 \le h \le 24$	$-16 \le h \le 24$	$-17 \le h \le 26$	$-25 \le h \le 24$
GOF on F^2	1.008	1.008	1.018	0.945
R_1 [$I > 2\sigma(I)$]	0.0509	0.0701	0.0695	0.0759
wR_2 [$I > 2\sigma(I)$]	0.0915	0.1151	0.1128	0.1482

Supplementary Methods.

Detailed characterization of BDP1-6. NMR spectra were recorded on a Bruker AVANCE III HD400. Chemical shifts (δ) were reported in ppm relative to $Si(CH_3)_4$ (^1H, ^{13}C) and coupling constants (*J*) were given in Hz. Data for ^1H NMR are reported as follows: chemical shift (multiplicity, coupling constants where applicable, and number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet). Mass spectra were obtained on a LCQ (ESI-MS, ThermoFinnigan) mass spectrometer.

BDP1: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm = 7.49 (m, 3H), 7.38 (t, J = 7.3 Hz, 2H), 7.32 (m, 3H), 7.15 (m, 2H), 2.58 (s, 3H), 2.52 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*/ppm = 155.8, 154.2, 143.4, 142.1, 139.4, 129.2, 127.2, 121.5, 14.8, 14.6, 13.5, 12.8. ESI-MS: calcd, $[M]^+$ = 400.278, found, $[M]^+$ = 400.236.

BDP4: ^1H NMR (400 MHz, $CDCl_3$) δ/ppm = 8.61 (d, J = 5.1 Hz, 2H), 7.50 (m, 3H), 7.31 (m, 2H), 7.09 (d, J = 5.9 Hz, 2H), 6.05 (s, 1H), 2.59 (s, 3H), 2.54 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*/ppm = 157.9, 149.9, 142.5, 138.6, 135.0, 129.5, 129.4, 128.0, 125.2, 122.4, 15.0, 14.7, 13.3, 12.7. ESI-MS: calcd, $[M]^+$ = 401.266, found, $[M]^+$ = 401.269.

BDP6: ^1H NMR (400 MHz, $CDCl_3$) *δ*/ppm = 7.69 (m, 4H), 7.52 (dd, J = 4.8, 2.4 Hz, 2H), 7.34 (dd, J = 7.4, 2.0 Hz, 2H), 7.29 (m, 4H), 2.54 (s, 6H), 1.31 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) *δ*/ppm = 154.3, 143.4, 140.0, 138.8, 133.1, 131.7, 129.7, 127.9, 118.9, 111.2, 13.6, 13.0. ESI-MS: calcd, $[M]^+$ = 526.218, found, $[M]^+$ = 526.256.