Electronic Supporting Information

The Unusual Aggregation-Induced Emission of Coplanar Organoboron Isomers and Their Lipid Droplets-Specific Applications

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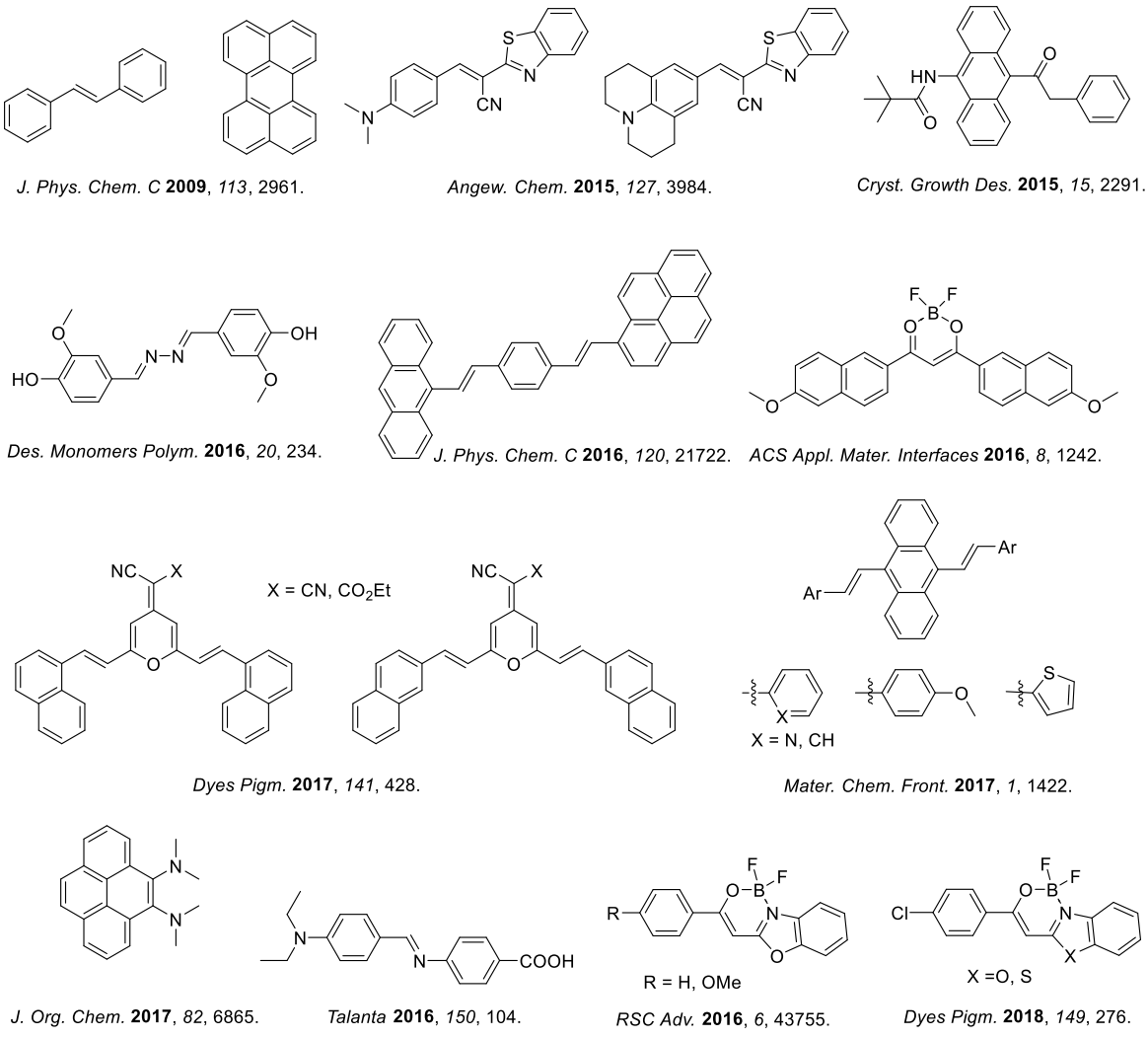
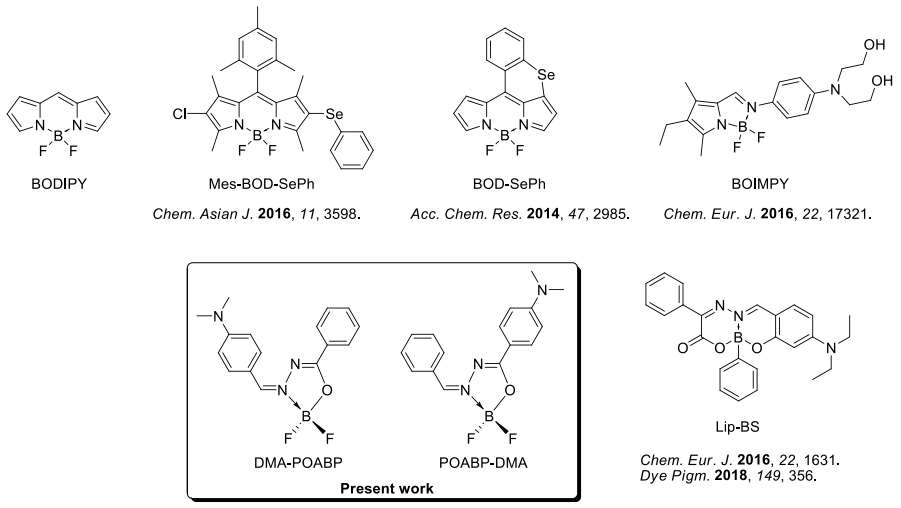


Scheme S1. Structures of near-coplanar AIEgens.



Scheme S2. Lipid droplets targeting probes based on organoboron materials.

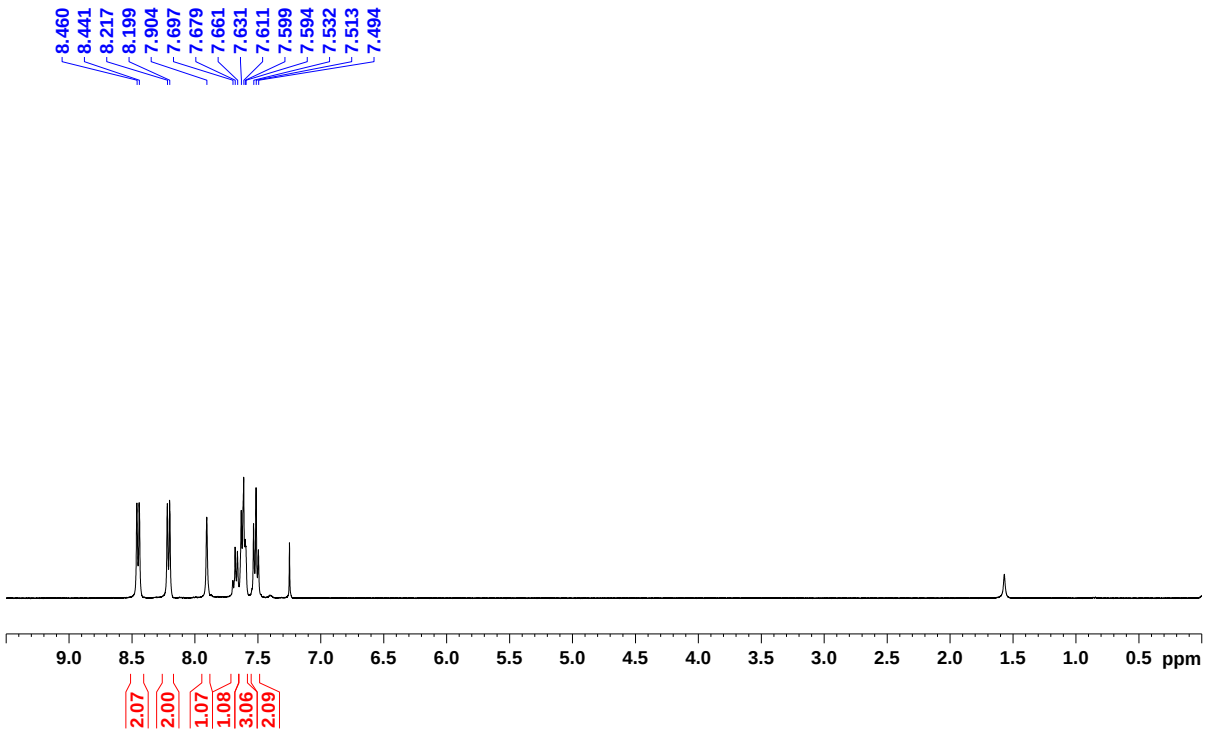


Figure S1. ^{1}H NMR spectrum of POABP in $CDCl_3$.

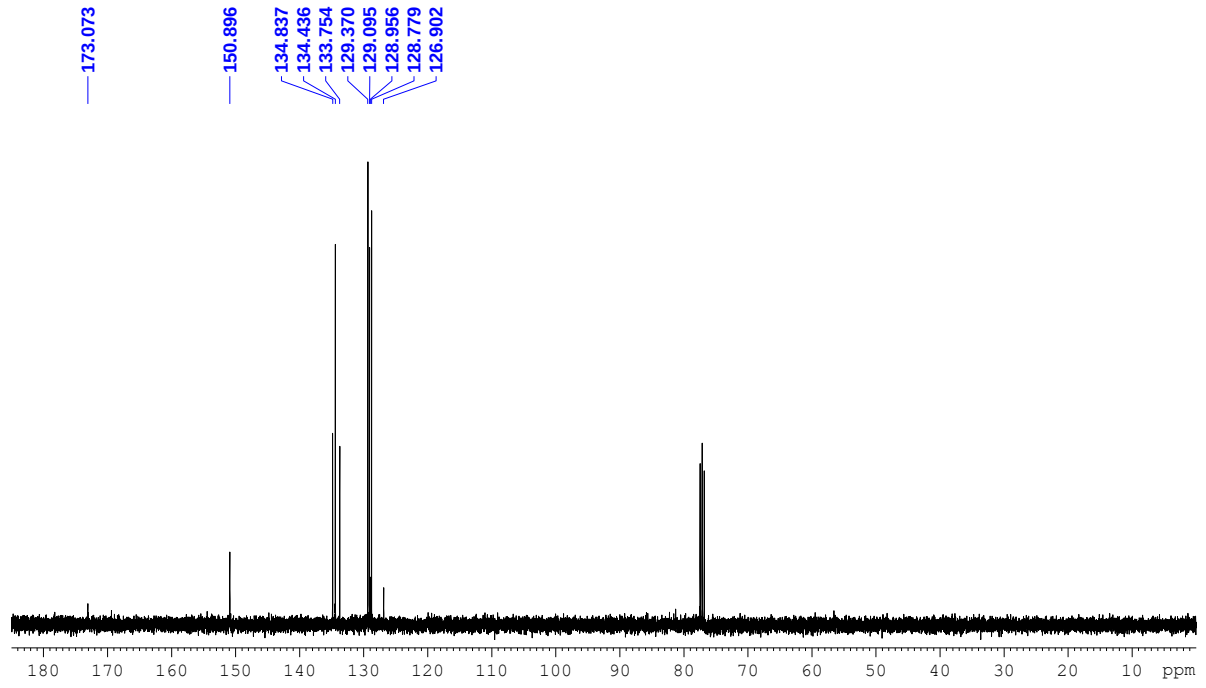


Figure S2. ^{13}C NMR spectrum of POABP in $CDCl_3$.

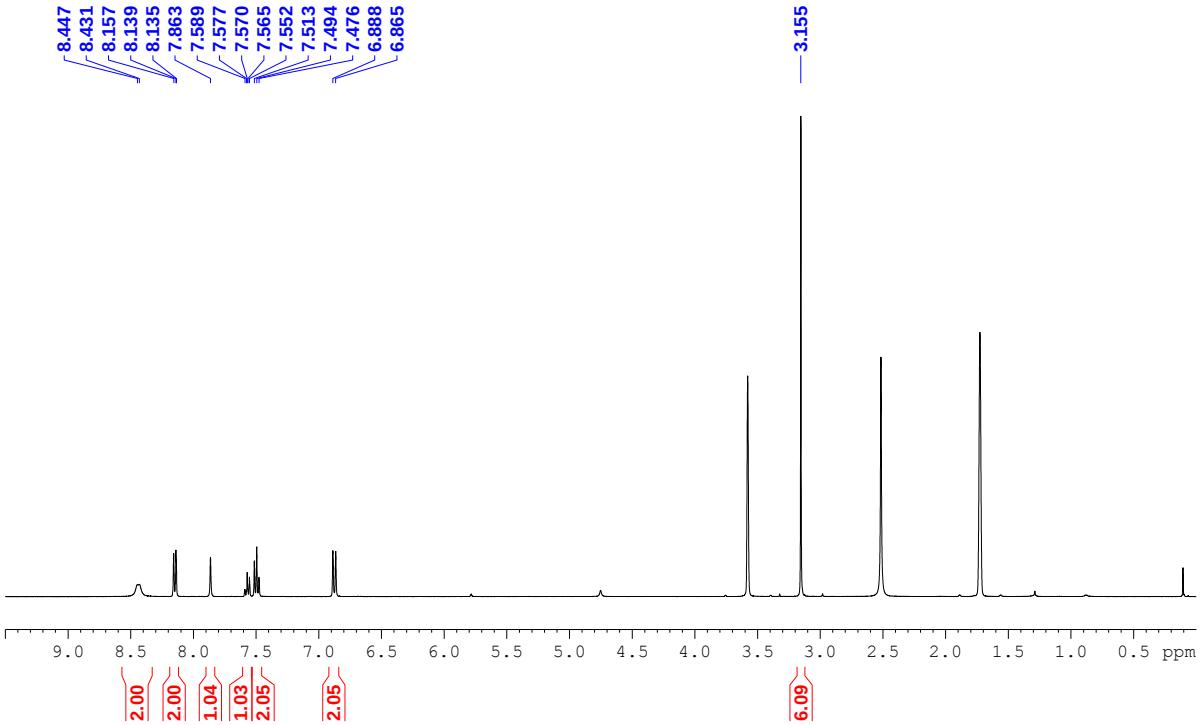


Figure S3. ^{1}H NMR spectrum of DMA-POABP in THF-d_8.

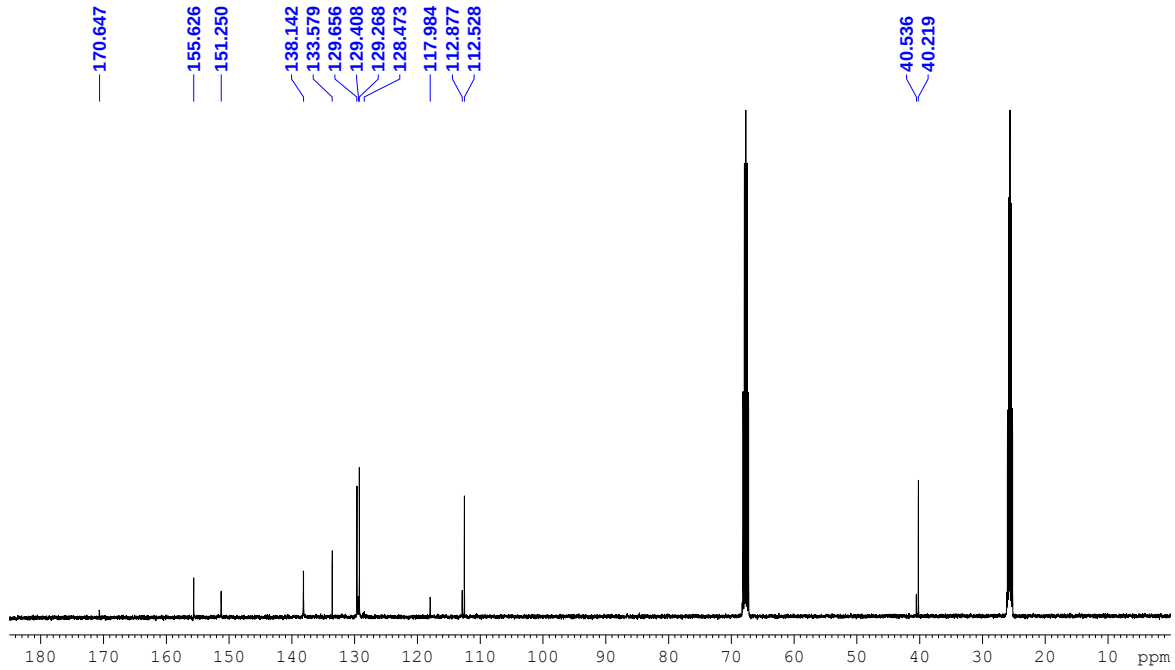


Figure S4. ^{13}C NMR spectrum of DMA-POABP in THF-d_8.

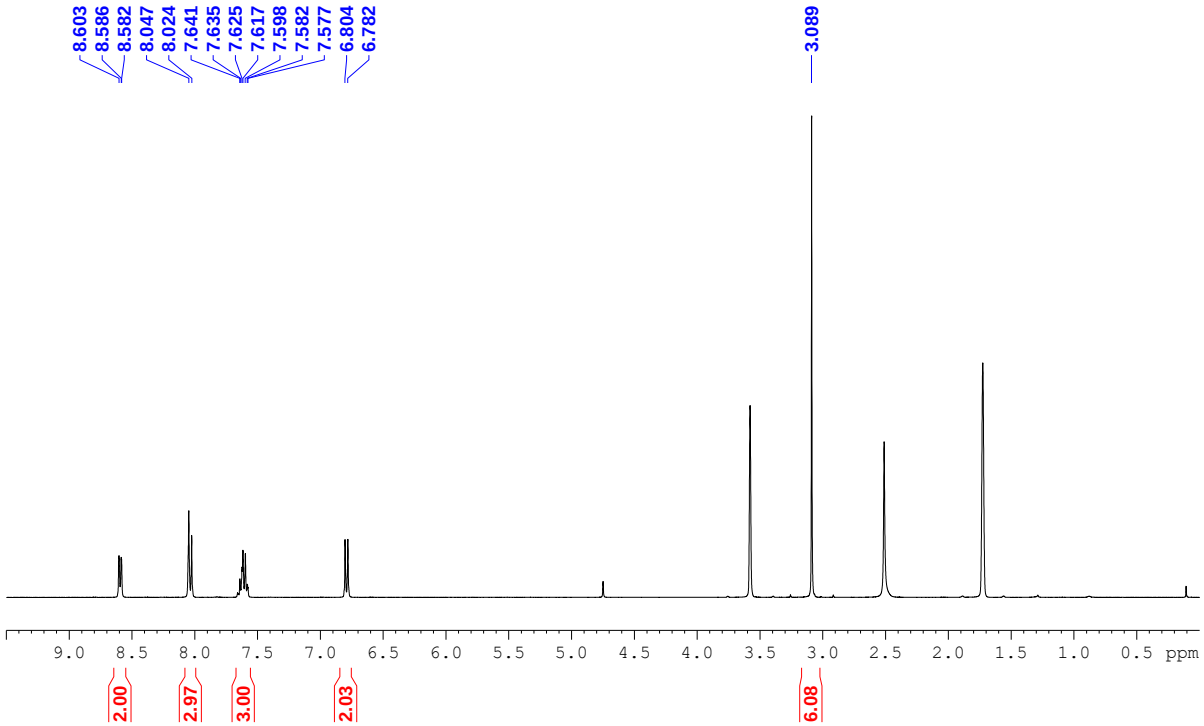


Figure S5. ^{1}H NMR spectrum of POABP-DMA in THF-d_8.

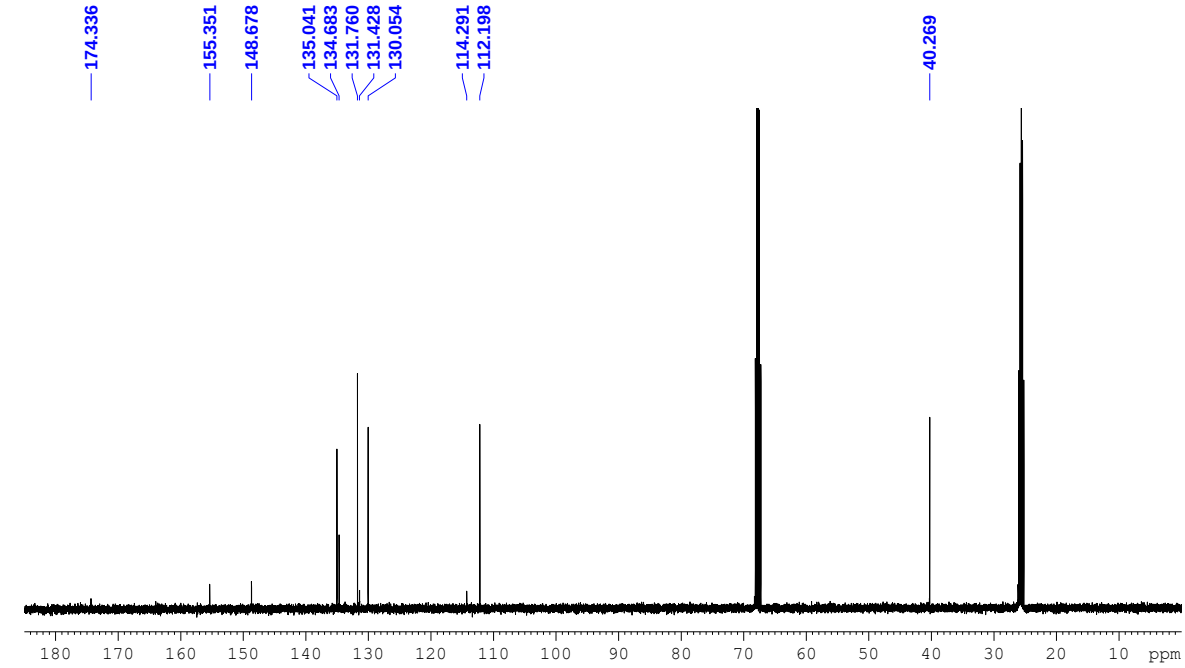


Figure S6. ^{13}C NMR spectrum of POABP-DMA in THF-d_8.

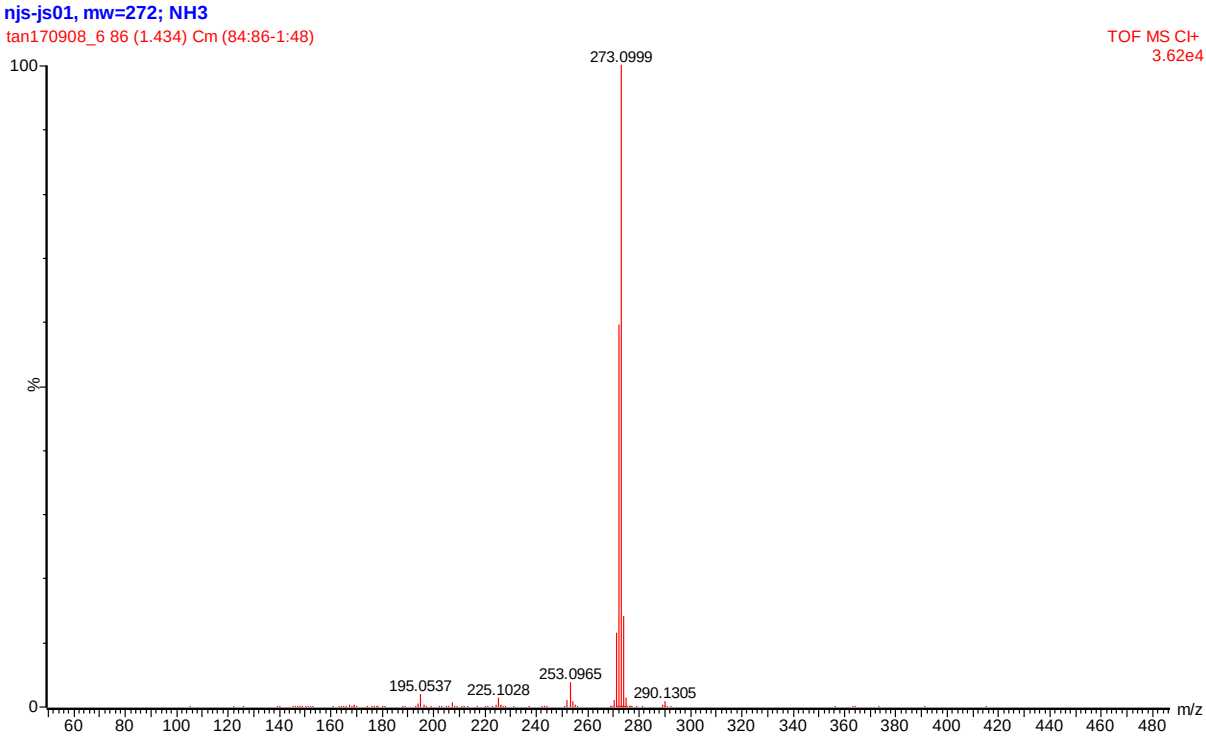


Figure S7. High-resolution mass spectrum of POABP.

Figure S8. High-resolution mass spectrum of DMA-POABP.

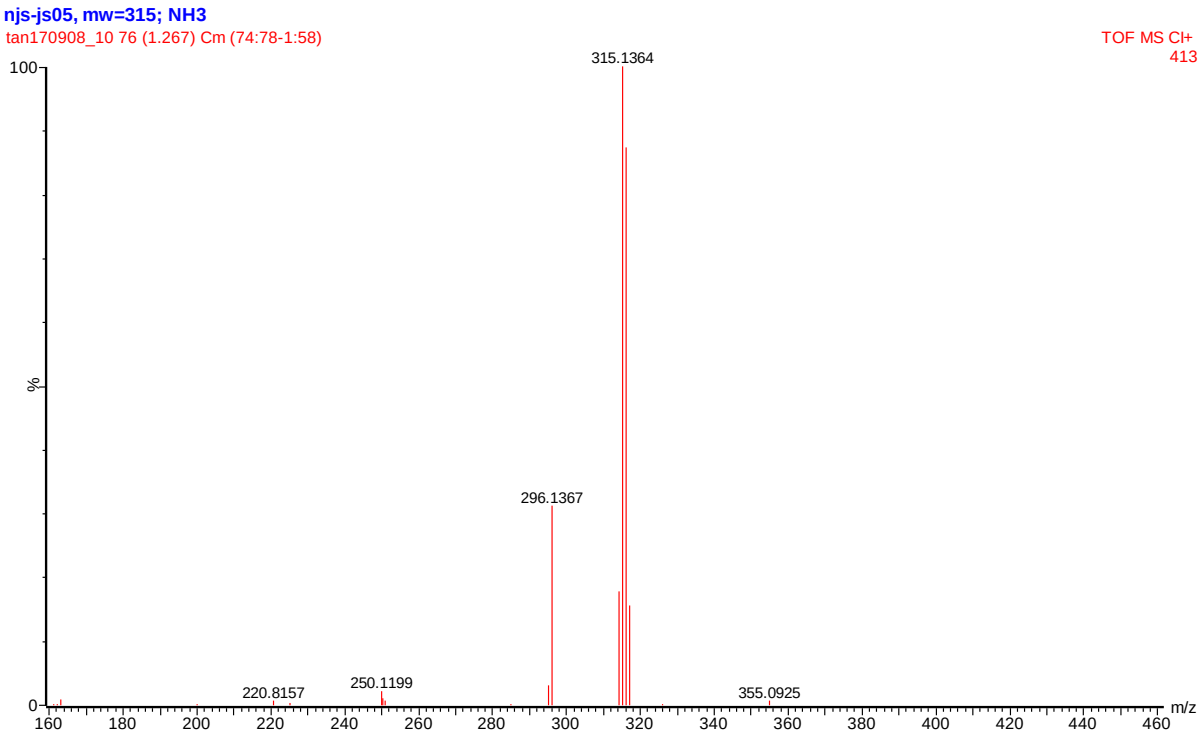


Figure S9. High-resolution mass spectrum of POABP-DMA.

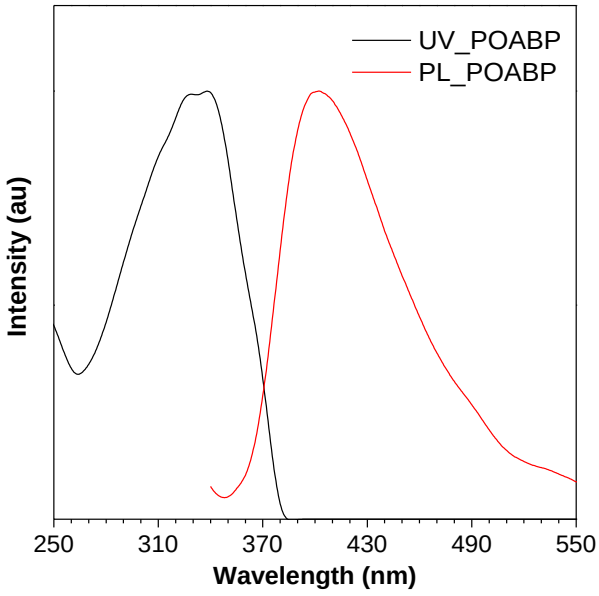


Figure S10. Normalized UV-vis and PL spectra of POABP in THF (10 μM).

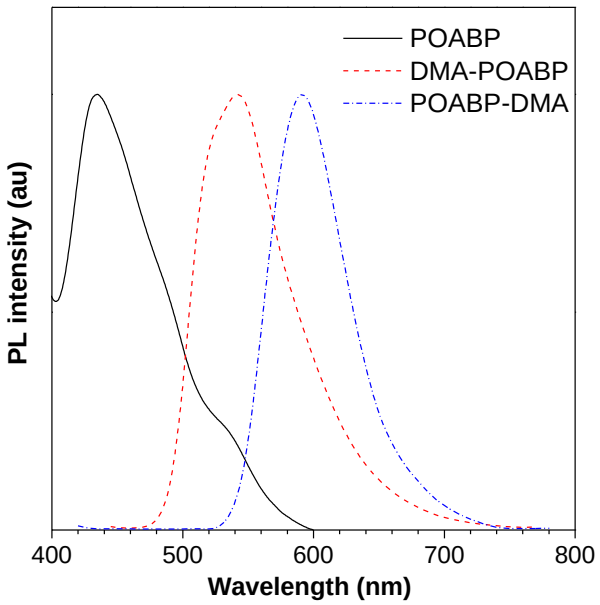


Figure S11. Normalized PL spectra of POABP, DMA-POABP and POABP-DMA in the solid state.

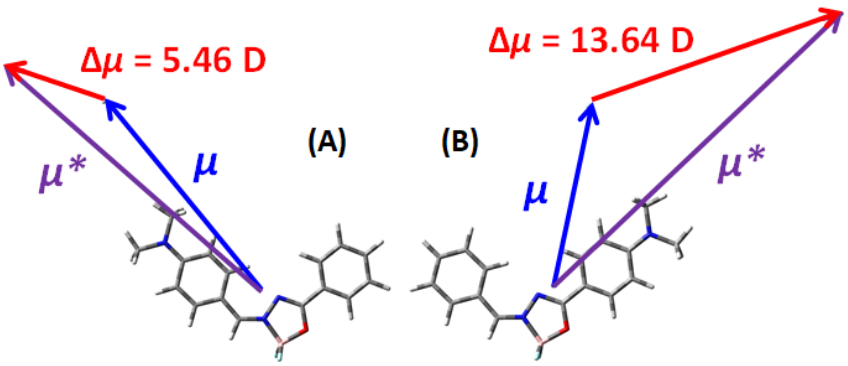


Figure S12. Molecular dipole moments of S_0 and S_1 states of (A) DMA-POABP and (B) POABP-DMA calculated with TD-DFT based on the solvation of THF. μ and μ* denoted the dipole moment of geometries in the ground and excited states, respectively, and $\Delta\mu$ denoted the difference of the dipole moments between the ground and excited states.

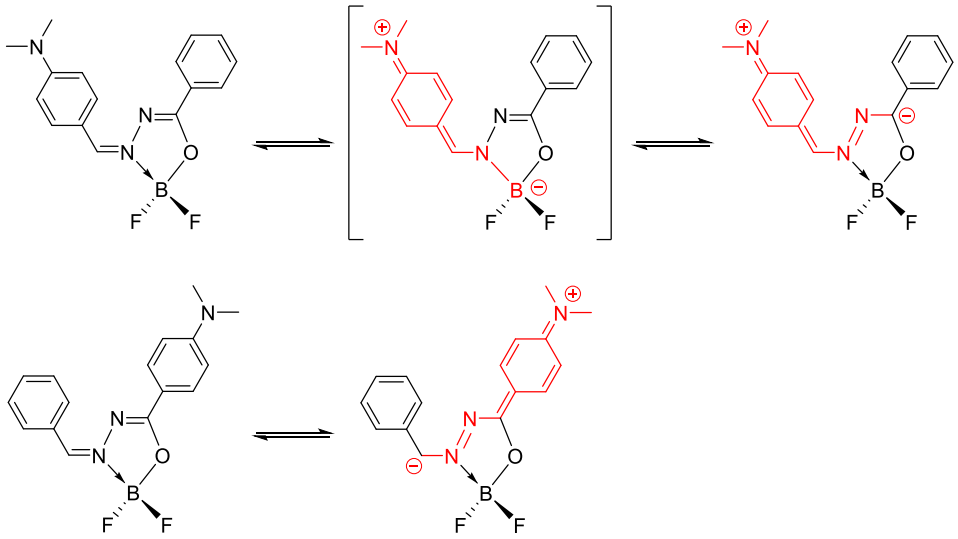


Figure S13. The speculation of conjugation mode of DMA-POABP and POABP-DMA.

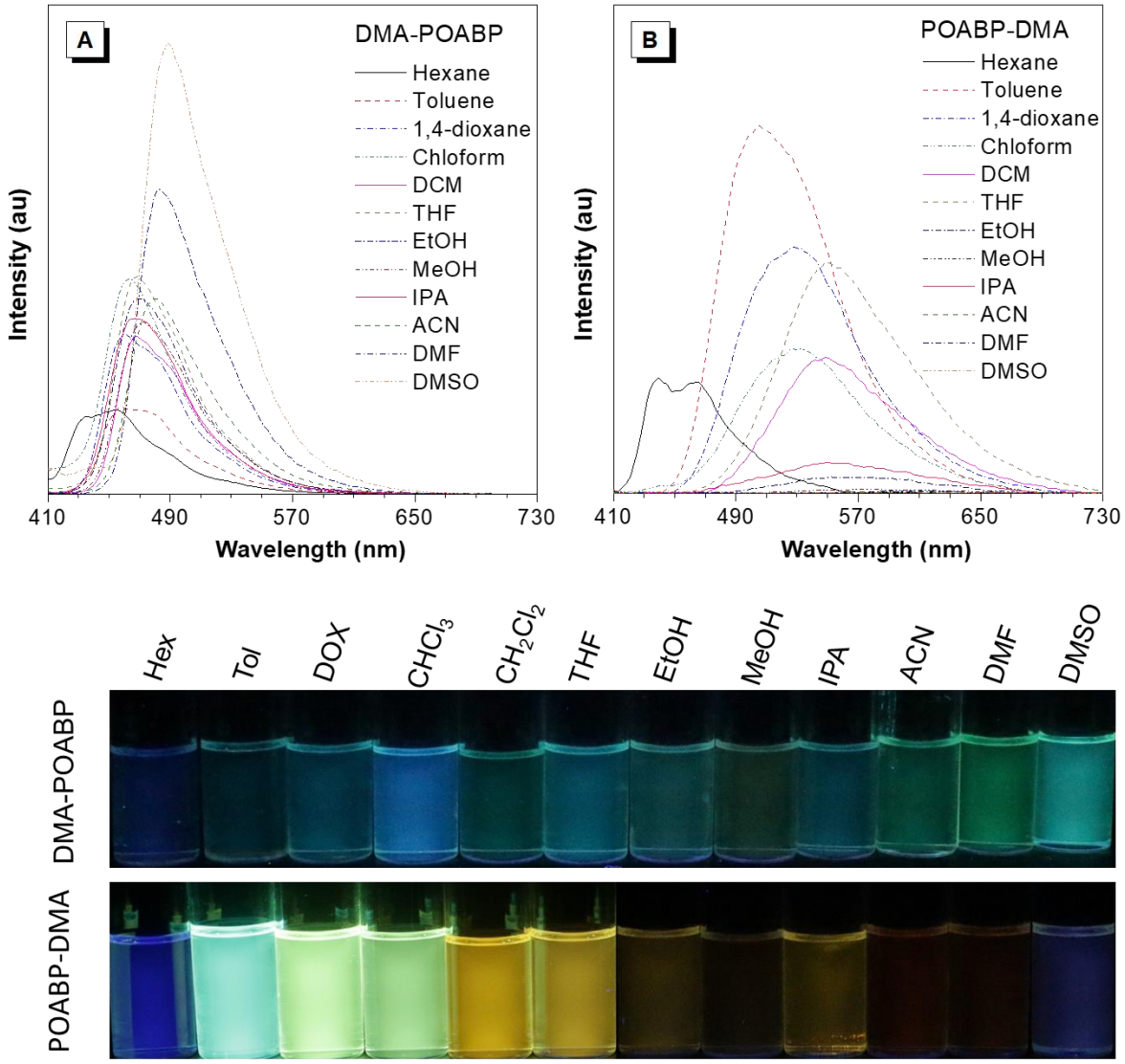


Figure S14. (A and B) PL spectra of (A) DMA-POABP and (B) POABP-DMA in the different solvents and (bottom) the fluorescent photos of their solutions taken under 365 nm UV irradiation from a hand-held UV lamp.

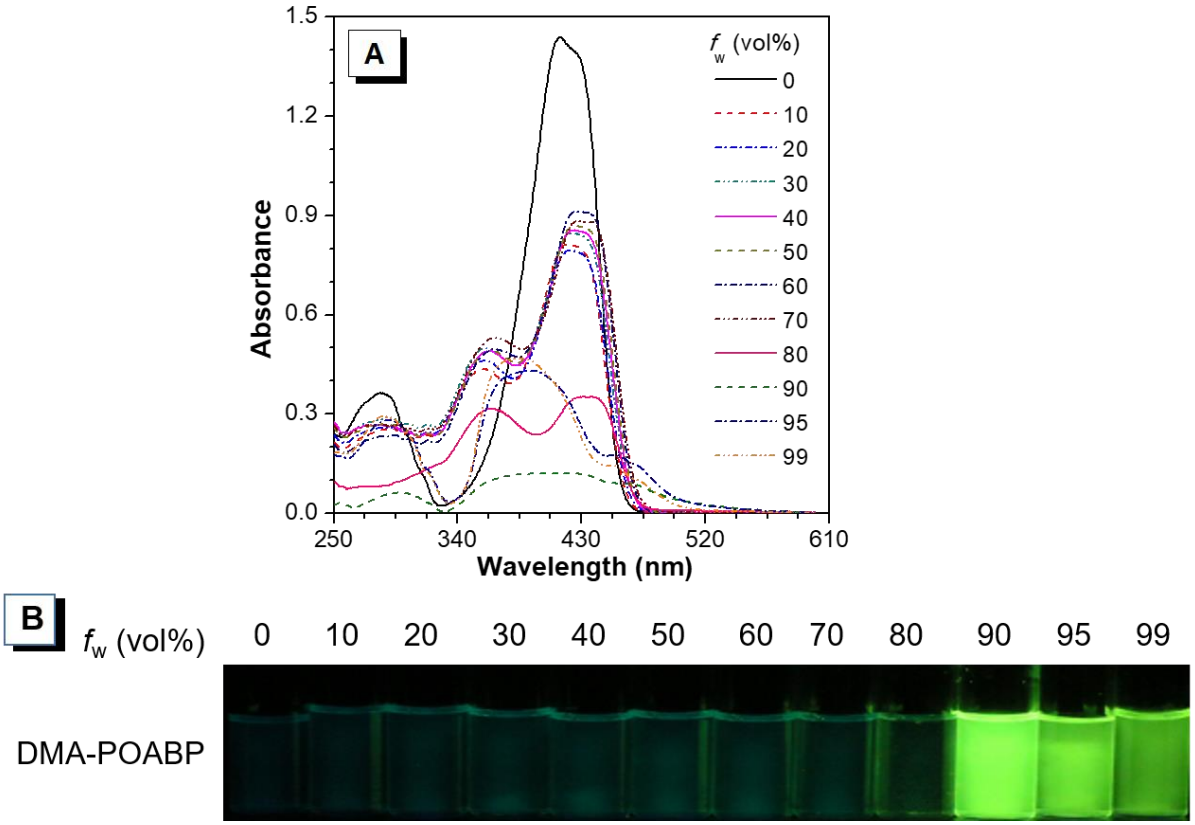


Figure S15. (A) UV-vis spectra and (B) the color changing under UV irradiation of 365 nm wavelength in THF and THF/water mixtures with the different water fractions (f_w) of DMA-POABP.

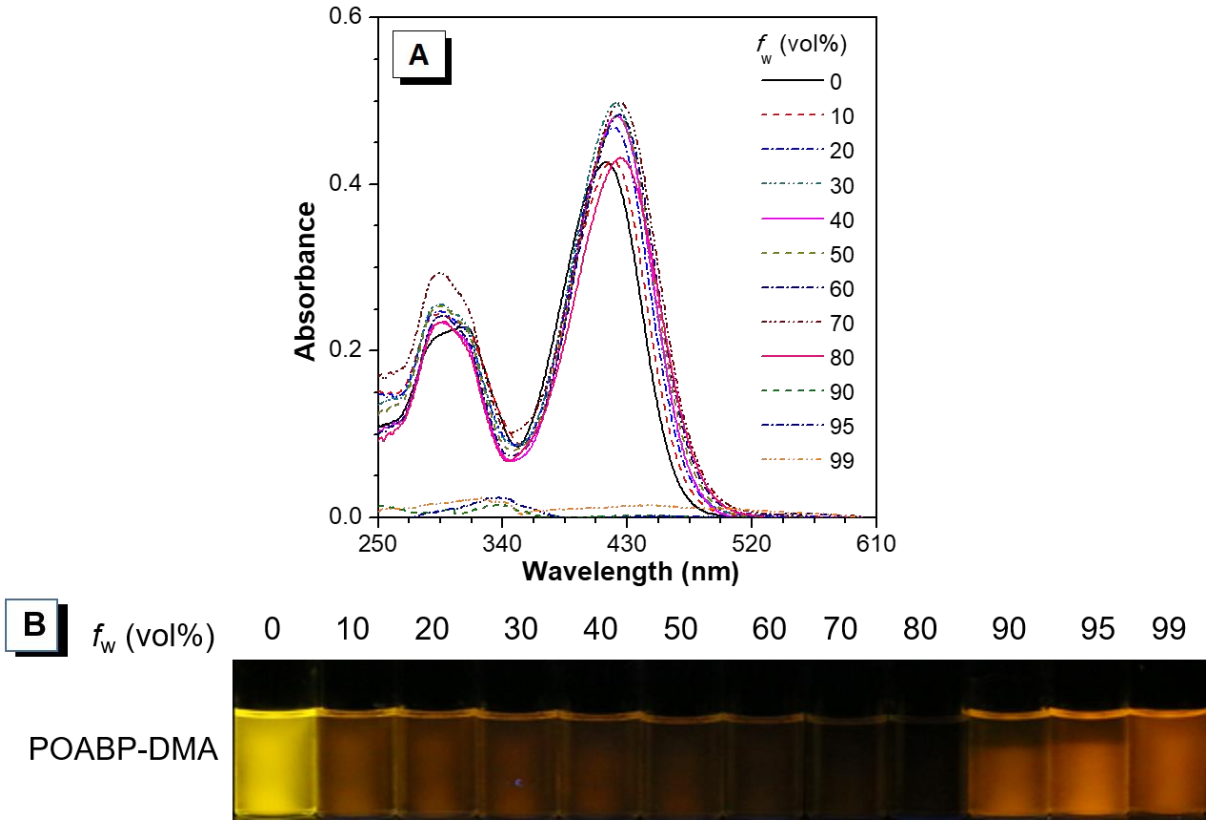


Figure S16. (A) UV-vis spectra and (B) the color changing under UV irradiation of 365 nm wavelength in THF and THF/water mixtures with the different water fractions (f_w) of POABP-DMA.

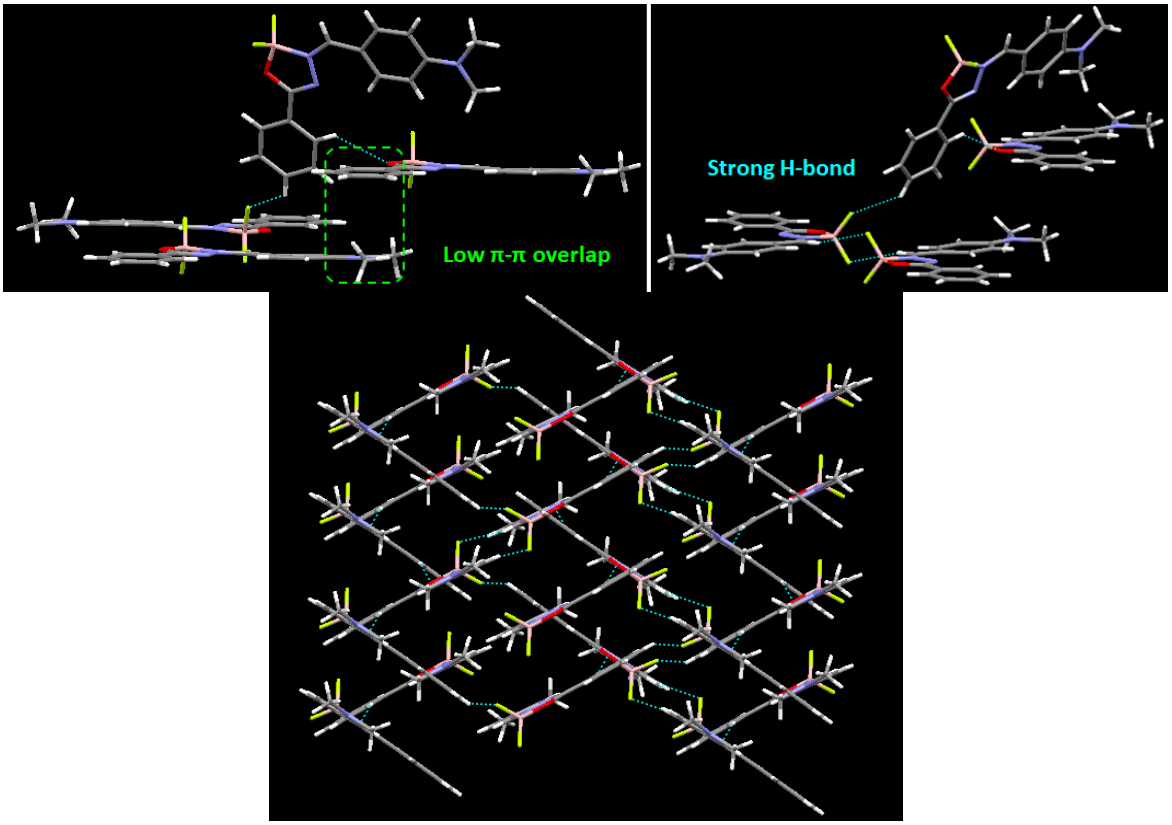


Figure S17. The packing structure of single crystals of DMA-POABP.

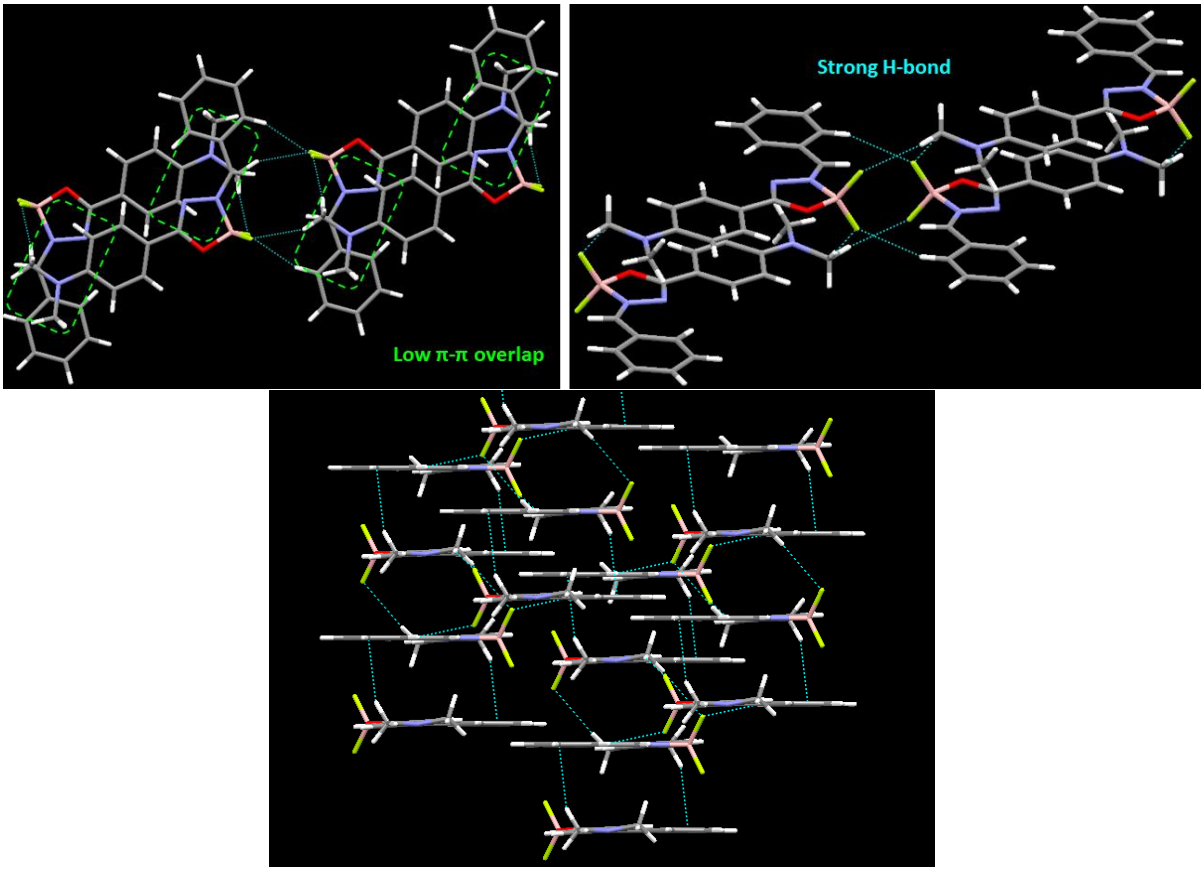
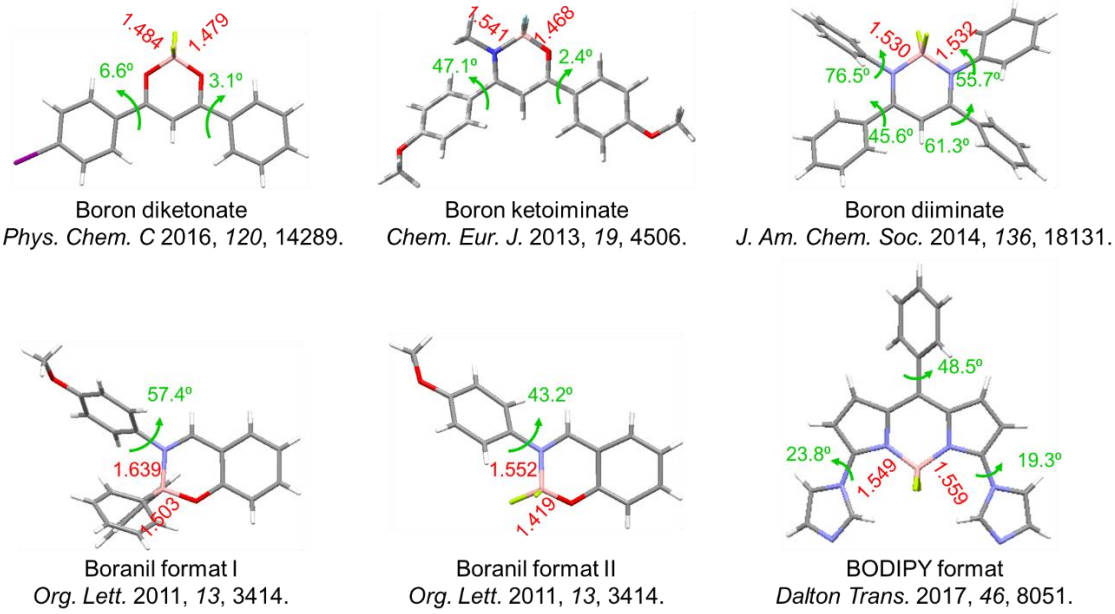


Figure S18. The packing structure of single crystals of POABP-DMA.



Boron diketonate
J. *Phys. Chem. C* 2016, *120*, 14289.

Boron ketoiminate
Chem. Eur. J. 2013, *19*, 4506.

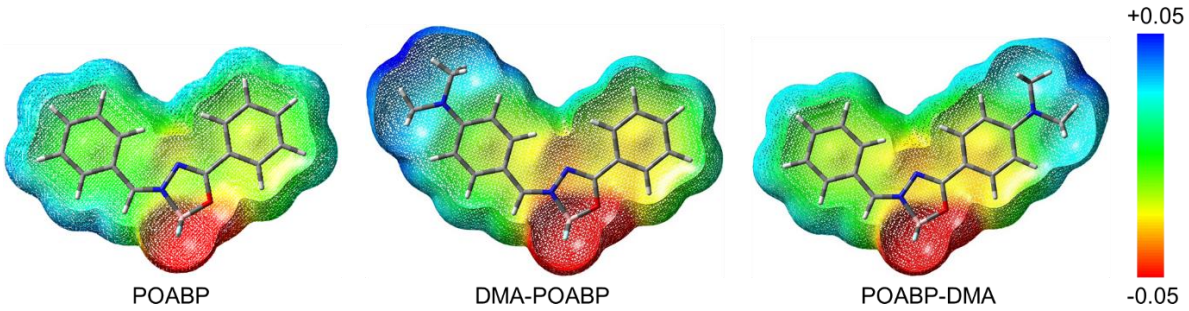
Boron diiminate
J. Am. Chem. Soc. 2014, *136*, 18131.

Boranil format I
Org. Lett. 2011, *13*, 3414.

Boranil format II
Org. Lett. 2011, *13*, 3414.

BODIPY format
Dalton Trans. 2017, *46*, 8051.

Figure S19. Single crystals of organoboron compounds reported previously and their bond lengths and dihedral angles.



POABP DMA-POABP POABP-DMA

Figure S20. The molecular electrostatic potential of POABP, DMA-POABP and POABP-DMA in S_0 state.

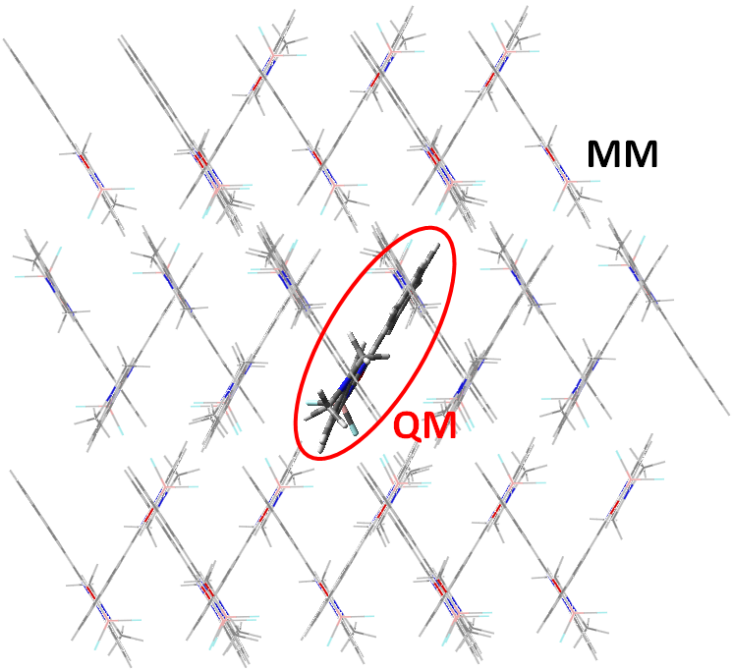


Figure S21. Setup of our QM/MM model for a cluster of DMA-POABP molecules cut from the crystal structure with the central one as QM region and the surrounding 37 molecules as MM region.

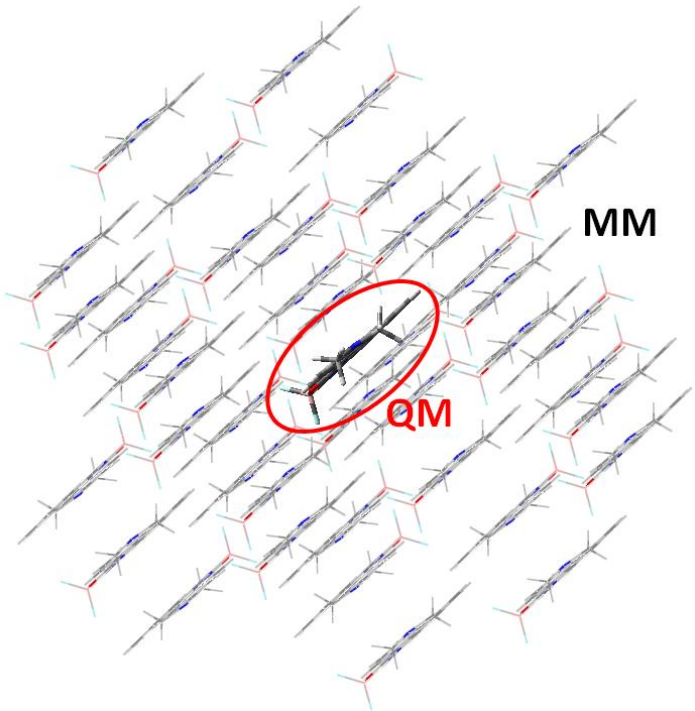


Figure S22. Setup of our QM/MM model for a cluster of POABP-DMA molecules cut from the crystal structure with the central one as QM region and the surrounding 41 molecules as MM region.

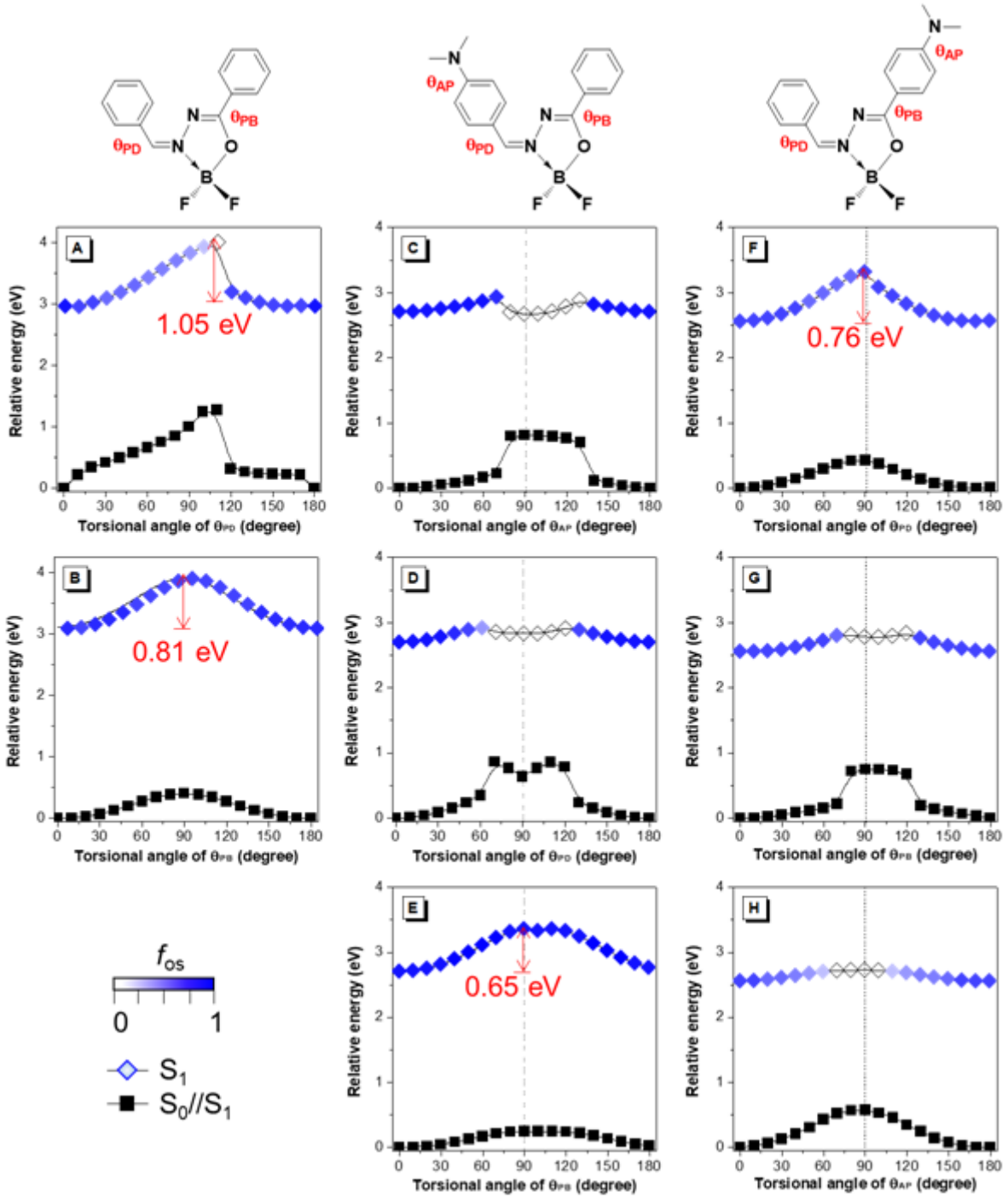


Figure S23. The potential energy surfaces of S_1 state at different dihedral angles of (A and B) POABP, (C, D and E) DMA-POABP and (F, G and H) POABP-DMA, calculated with TD-DFT as the level of PBE0/6-31G* based on solvation of THF.

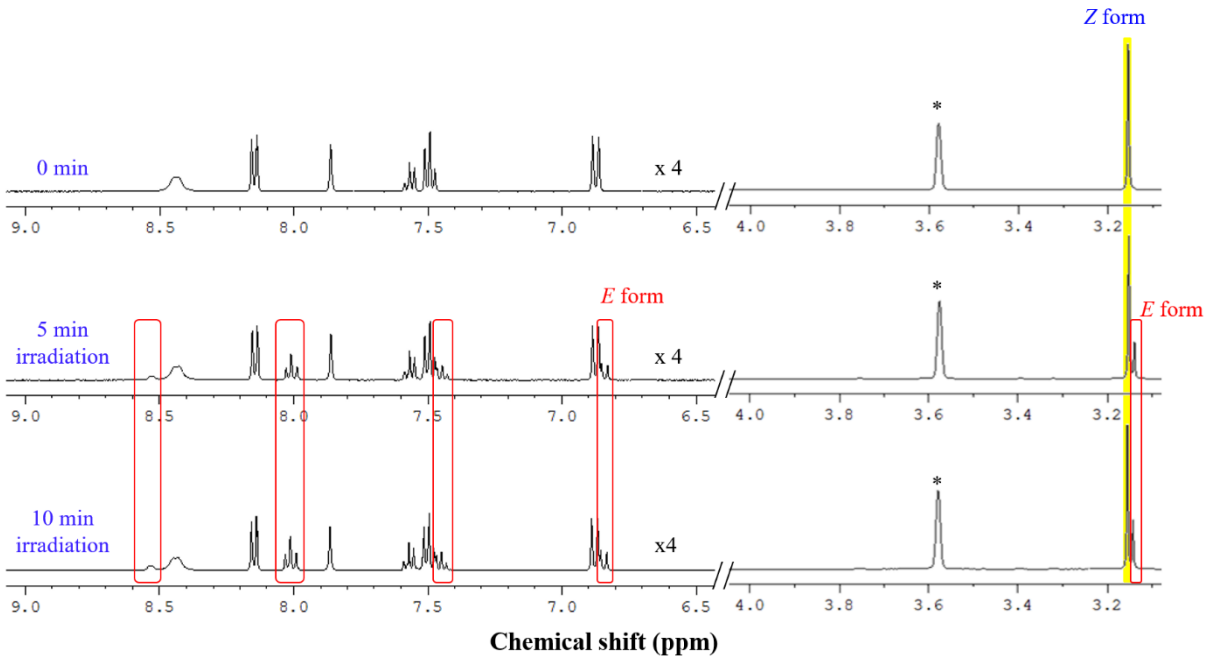


Figure S24. Monitoring the *E*/*Z* isomerization of DMA-POABP by ^{1}H NMR spectroscopy by irradiating its pure *Z* form in THF-d_8 (40 mM) with a blue LED lamp for 5 and 10 min. Solvent peak was marked with asterisk.

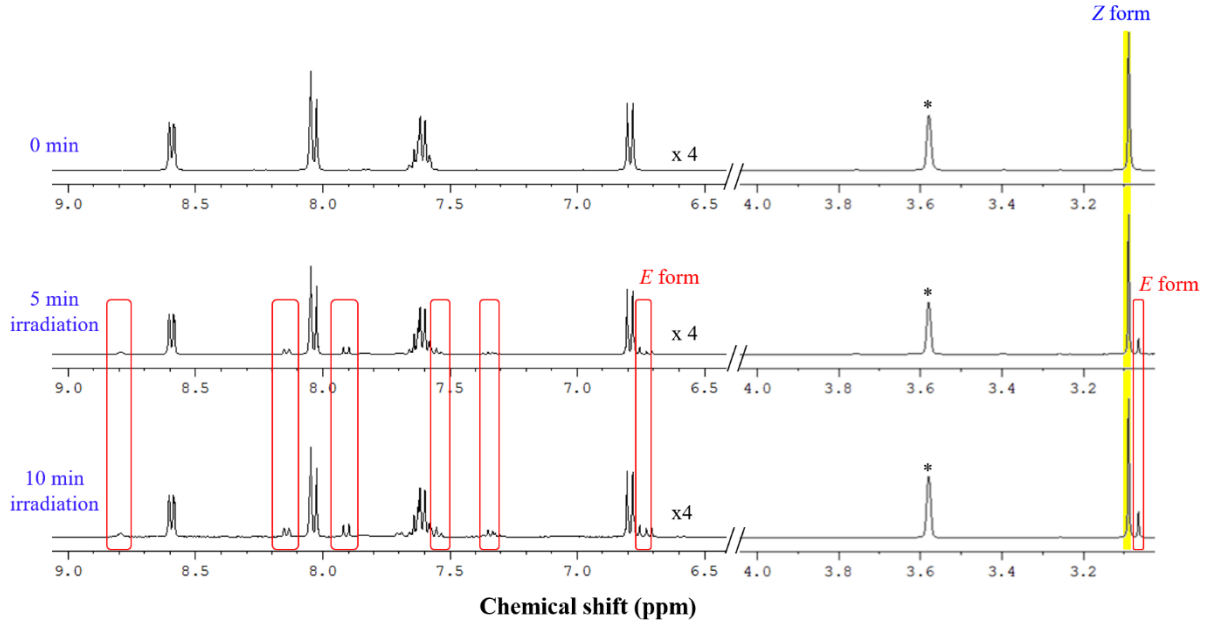


Figure S25. Monitoring the *E*/*Z* isomerization of POABP-DMA by ^{1}H NMR spectroscopy by irradiating its pure *Z* form in THF-d_8 (40 mM) with a blue LED lamp for 5 and 10 min. Solvent peak was marked with asterisk.

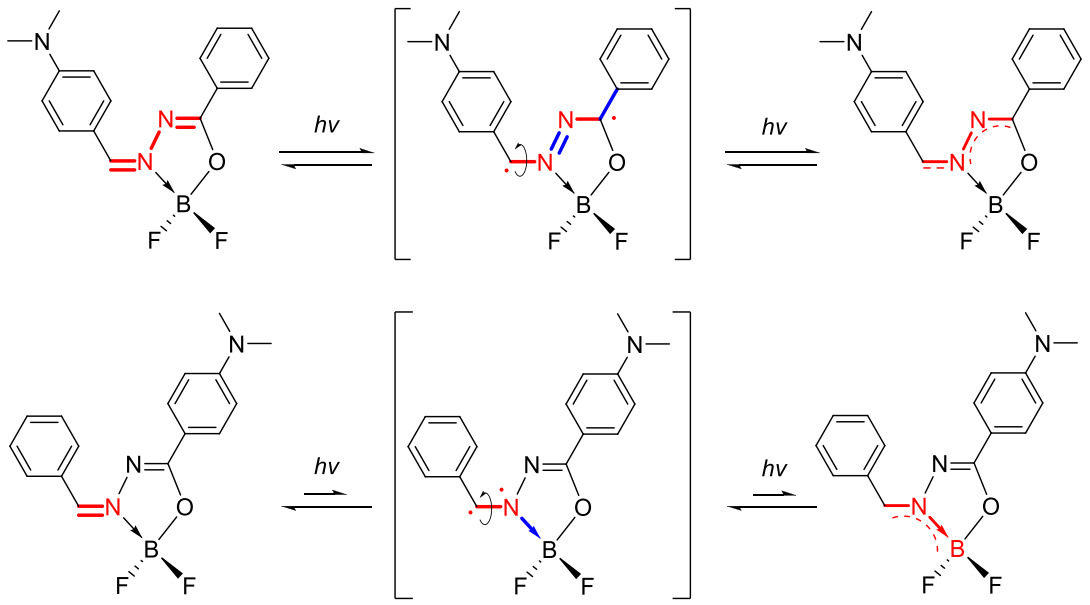


Figure S26. The proposal rotation of the double bond in the excited state of DMA-POABP and POABP-DMA according to the variations of bond lengths in S_0 and S_1 states (Table S8).

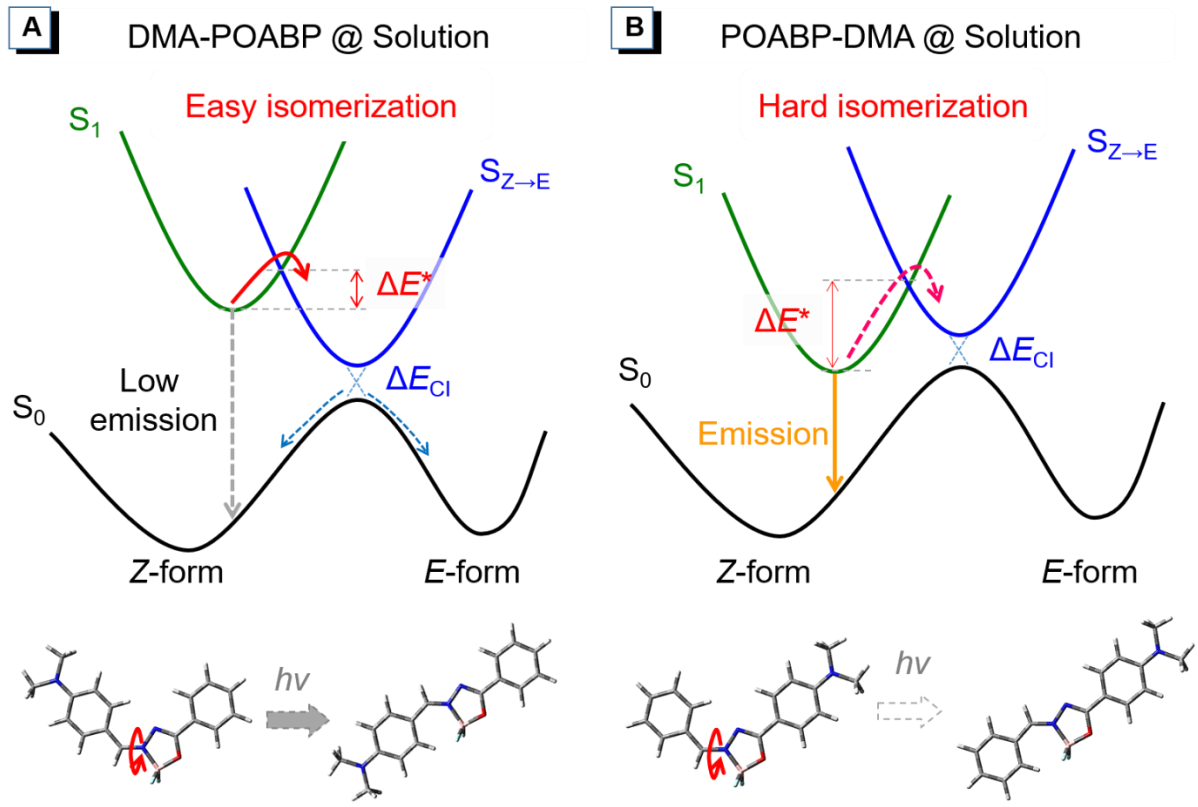


Figure S27. A proposed model for the excited-state of *E*/*Z* isomerization of (A) DMA-POABP and (B) POABP-DMA. ΔE^* denoted the energy barrier from *Z* to *E*-form, and ΔE_{CI} denoted the energy gap of the de-excitation pathway through the conical intersection between the S_0 and $S_{Z\rightarrow E}$ states.

Table S1. Calculation data of DMA-POABP and POABP-DMA in S_0 state.[a)]

Luminogen	Excited states	Configurations	E (eV)	λ (nm)	f_{os}
POABP	S_{01}	H → L (99%)	3.65	339.87	0.97
	S_{02}	H–2 → L (93%), H → L+2 (4%)	4.31	287.34	0.03
DMA-POABP	S_{01}	H → L (99%)	3.18	390.39	1.12
	S_{02}	H–1 → L (70%), H → L+1 (28%)	4.30	288.42	0.15
POABP-DMA	S_{01}	H → L (99%)	2.95	420.64	0.89
	S_{02}	H–1 → L (87%), H → L+1 (12%)	4.03	307.54	0.42

[a)] Calculated with TD-DFT at the level of PBE0/6-31G* based on solvation of THF, in which the vertical excitation as linear response solvation was used. S_{01} and S_{02} denoted the first and second vertical transition from the S_0 state to the S_1 and S_2, respectively, and f_{os} denoted oscillator strength between the ground and excited states.

Table S2. Photophysical parameters of DMA-POABP and POABP-DMA in various solvents.

Solvent	DMA-POABP				POABP-DMA			
	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	$\tilde{\nu}$ (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	$\tilde{\nu}$ (cm^{-1})
Acetonitrile	422	482	60	2950	417	602	185	7370
Dibutylether	420	459	39	2023	407	496	89	4409
DMSO	433	493	60	2811	425	618	193	7348
Ethyl acetate	418	469	51	2601	407	554	147	6519
Ethanol	411	473	62	3189	414	564	150	6424
Hexane	415	457	42	2215	416	484	68	3377
Isopropanol	411	471	60	3099	411	552	141	6215
Triethylamine	419	463	44	2268	414	495	81	3953

Table S3. Molecular dipole moments of organoboron compounds in S_0 and S_1 states.

Luminogen	State	X (Debye)	Y (Debye)	Z (Debye)	Total (Debye)
POABP	S_0	2.7057	-6.3690	0.0001	6.9199
	S_1	1.3520	-7.2337	0.0001	7.3590
DMA-POABP	S_0	-10.2878	-7.6370	-0.0002	12.8126
	S_1	-15.7137	-8.2403	-0.0091	17.7433
POABP-DMA	S_0	-4.3747	-8.2008	0.0004	9.2947
	S_1	-17.9997	-8.9299	-0.0145	20.0931

[a)] Calculated with TD-DFT as the level of PBE0/6-31G* based on solvation of THF, in which the vertical excitation as linear response solvation was used.

Table S4. Crystal data and structure refinement for DMA-POABP and POABP-DMA.

Empirical formula	DMA-POABP	POABP-DMA
Formula weight	315.13	315.13
Temperature/K	297.0	220.01(10)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a /Å	9.4912(16)	7.4604(4)
b /Å	17.4789(16)	9.2599(4)
c /Å	10.2389(12)	11.5405(6)
α /°	90	86.303(4)
β /°	110.403(15)	81.372(4)
γ /°	90	72.383(4)
Volume /$Å^3$	1592.0(4)	751.10(7)
Z	4	2
ρ_{calc} /gcm^{-3}	1.315	1.393
μ /mm^{-1}	0.099	0.881
F(000)	656.0	328.0
Crystal size /mm^3	0.60 × 0.48 × 0.30	0.45 × 0.4 × 0.4

Table S5. Dihedral angles and bond lengths of single crystals of DMA-POABP and POABP-DMA.

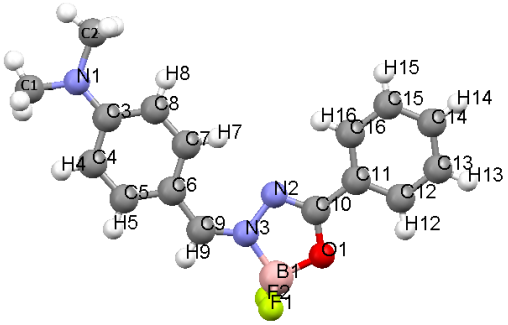
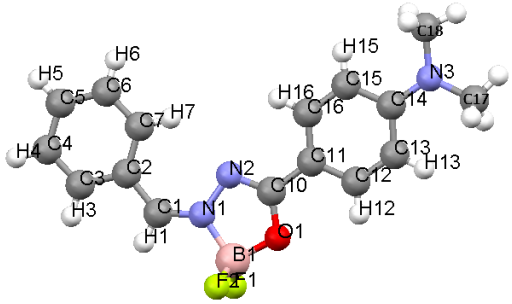
DMA-POABP		POABP-DMA	
			
θ_{AP}: C2-N1-C3-C4 (°)	2.09	θ_{AP}: C18-N3-C14-C15 (°)	6.75
θ_{PD}: C5-C6-C9-H9 (°)	0.81	θ_{PD}: C7-C2-C1-N1 (°)	0.43
θ_{ZE}: H9-C9-N3-B1 (°)	2.27	θ_{ZE}: H1-C1-N1-B1 (°)	0.46
θ_{PB}: N2-C10-C11-C16 (°)	1.23	θ_{PB}: C12-C11-C10-O1 (°)	2.88
H7…N2 (Å)	2.332	H7-N2 (Å)	2.359
N3→B1 (Å)	1.566	N1→B1 (Å)	1.587
N3−N2 (Å)	1.398	N1−N2 (Å)	1.389
N2=C10 (Å)	1.292	N2=C10 (Å)	1.310
C10−O1 (Å)	1.325	C10−O1 (Å)	1.331
O1−B1 (Å)	1.473	O1−B1 (Å)	1.461
B1−F1 (Å)	1.362	B1−F1 (Å)	1.362

Table S6. Calculated data of organoboron compounds in S_1 state.[a)]

Luminogen	Excited state	Configurations	E (eV)	λ (nm)	f_{os}
POABP	S_{10}	H → L (~100%)	2.96	418.37	1.14
DMA-POABP	S_{10}	H → L (99%)	2.71	458.36	1.29
POABP-DMA	S_{10}	H → L (99%)	2.56	485.06	0.90

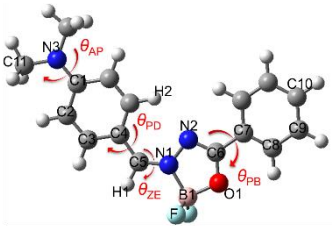
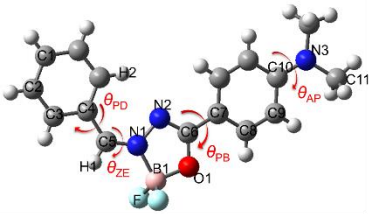
[a)] Calculated with TD-DFT at the level of PBE0/6-31G* based on solvation of THF, in which the vertical excitation as **linear response solvation** was used. S_{10} denoted the first vertical radiation from the S_1 state to the S_0 state, and f_{os} denoted oscillator strength between the ground and excited states.

Table S7. Calculated data of DMA-POABP and POABP-DMA in S_1 state.[a)]

Luminogen	Excited state	Configurations	E (eV)	λ (nm)	f_{os}
DMA-POABP	S_{10}	H → L (99%)	3.08	402.69	0.80
POABP-DMA	S_{10}	H → L (~100%)	2.32	535.42	0.56

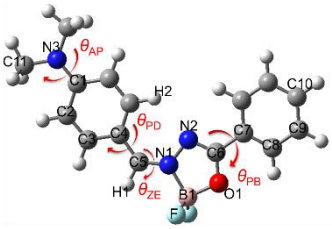
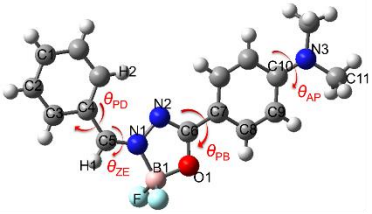
[a)] Calculated with TD-DFT at the level of PBE0/6-31G* based on solvation of THF, in which vertical excitation as **state-specific solvation** was used. S_{10} denoted the first vertical radiation from the S_1 state to the S_0 state, and f_{os} denoted oscillator strength between the ground and excited states.

Table S8. Dihedral angles and bond lengths of DMA-POABP and POABP-DMA in S_0 and S_1 states. [a)]

Luminogen	DMA-POABP		POABP-DMA	
				
State	S_0	S_1	S_0	S_1
θ_{AP}: C11-N3-C1-C2 (°)	0.004	-0.376	0.038	0.004
θ_{PD}: C3-C4-C5-H1 (°)	-0.005	-0.108	0.030	-0.207
θ_{PB}: C8-C7-C6-O1 (°)	-0.014	0.021	-0.119	-0.009
θ_{ZE}: H1-C5-N1-B1 (°)	0.002	-0.010	-0.001	-0.212
C4−C5 (Å)	1.427	1.418 (↓0.009)	1.447	1.410 (↓0.036)
C5=N1 (Å)	1.302	1.344 (↑0.042)	1.295	1.345 (↑0.050)
N1−N2 (Å)	1.375	1.323 (↓0.052)	1.364	1.371 (↑0.007)
N2=C6 (Å)	1.309	1.353 (↑0.044)	1.321	1.305 (↓0.016)
C6−O1 (Å)	1.317	1.321 (↑0.004)	1.318	1.323 (↑0.005)
O1−B1 (Å)	1.487	1.480 (↓0.007)	1.481	1.494 (↑0.013)
N1→B1 (Å)	1.587	1.586 (↓0.001)	1.598	1.561 (↓0.037)
C6−C7 (Å)	1.462	1.423 (↓0.039)	1.444	1.460 (↑0.016)
H2···N2 (Å)	2.292	2.262 (↓0.030)	2.271	2.314 (↑0.043)

[a)] Calculated with TD-DFT at the level of PBE0/6-31G* based on solvation of THF.

Table S9. Dihedral angles and bond lengths of DMA-POABP and POABP-DMA in S_0 and S_1 states.[a)]

	DMA-POABP		POABP-DMA	
Luminogen				
State	S_0	S_1	S_0	S_1
θ_{AP}: C11-N3-C1-C2 (°)	-2.03	-10.80	6.06	1.16
θ_{PD}: C3-C4-C5-H1 (°)	1.48	3.81	1.05	1.03
θ_{PB}: C8-C7-C6-O1 (°)	-2.01	-1.10	-2.27	-3.64
θ_{ZE}: H1-C5-N1-B1 (°)	2.16	1.76	1.22	1.84
C4−C5 (Å)	1.427	1.449 (↑0.022)	1.445	1.408 (↓0.037)
C5=N1 (Å)	1.304	1.317 (↑0.013)	1.294	1.337 (↑0.043)
N1−N2 (Å)	1.374	1.331 (↓0.043)	1.365	1.407 (↑0.042)
N2=C6 (Å)	1.307	1.357 (↑0.050)	1.320	1.280 (↓0.040)
C6−O1 (Å)	1.316	1.322 (↑0.006)	1.320	1.319 (↓0.001)
O1−B1 (Å)	1.492	1.474 (↓0.018)	1.475	1.507 (↑0.032)
N1→B1 (Å)	1.589	1.602 (↑0.013)	1.596	1.550 (↓0.046)
C6−C7 (Å)	1.461	1.418 (↓0.043)	1.444	1.496 (↑0.052)
H2…N2 (Å)	2.264	2.212 (↓0.052)	2.280	2.334 (↑0.054)

[a)] Calculated with TD-DFT at the level of PBE0/6-31G*, in which high-level QM/MM method in ONIOM methodology in solid was used.