Supporting Information

Synthesis and Properties of Covalently Linked Phenyl Bridged 3-Pyrrolyl BODIPY-BODIPY Dyads

Abani Sarkar, Kanhu Charan Behera, Ankit Tumsare and Mangalampalli Ravikanth*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India, E-mail: ravikanth@chem.iitb.ac.in

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MATERIALS AND METHODS

Materials:

The chemicals, including $BF_3.OEt_2$, 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ), terepthaldehyde, 4-formyl phenyl boronic acid, trifluoroacetic acid (TFA), NBS, MnO_2, $NaBH_4$ etc. were procured from reputable suppliers such as Merck and TCI. Unless otherwise indicated, all additional chemicals utilized in the synthesis were of reagent grade quality. Column chromatography was conducted using silica gel (100-200 mesh) and basic alumina, ensuring the purity and separation of compounds during the purification process.

Methods:

- All the ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker 400 and 500 MHz instruments. The frequencies for the ^{13}C nucleus are 100.06 and 125.77 MHz for 400 and 500 MHz instruments, respectively. Similarly, the frequencies for the ^{11}B and ^{19}F nucleus are 193 and 376 MHz for 400 MHz instruments.
- Absorption and steady state fluorescence spectra were obtained with PerkinElmer Lambda-35.
- Cyclic voltammetry (CV) studies were carried out with the BAS electrochemical system utilizing the three-electrode configuration consisting of glassy carbon (working electrode), platinum wire (auxiliary electrode), and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using tetrabutylammonium perchlorate as a supporting electrolyte.
- Mass spectra were recorded with a Q-TOF micro mass spectrometer.
- Fluorescence quantum yields were determined[S1] in each case by comparing the corrected spectrum with that of Rhodamine 6G (Φ =0.95) in EtOH by taking the area under total emission using the procedure reported earlier.[S2]
- The exponential decay curve of compound **7-13** and dyad **1-2** were fitted appropriately with a mono/biexponential equation.The average life time (τ_{av}) was calculated following the equations depicted in literature.[S3]

- Single green block-shaped crystals of 2 were used as supplied. A suitable crystal with dimensions 0.40 × 0.20 × 0.20 mm^3 was selected and mounted on a Bruker APEX-II CCD diffractometer. The crystal was kept at a steady T = 150.15 K during data collection. The structure was solved with the olex 2. Solve 1.5 (Bourhis et al., 2015) solution program using dual space methods and by using Olex 2 1.5-dev (Dolomanov et al., 2009) as the graphical interface. The model was refined with olex2.refine 1.5-dev (Bourhis et al., 2015) using full matrix least squares minimisation on $\boldsymbol{F}^2$.[S4-S5]
- Crystal Data. $C_{35}H_{25}B_2F_4N_5$, Mr = 613.264, triclinic, P-1 (No. 2), a = 10.2752(9) Å, b = 11.7931(14) Å, c = 12.4578(13) Å, α = 80.037(9)°, β = 76.494(8)°, γ = 89.590(9)°, V = 1444.8(3) Å3, T = 150.15 K, Z = 2, Z' = 1, μ(Mo K_α) = 0.102, 51867 reflections measured, 5080 unique (Rint = 0.1062) which were used in all calculations. The final wR2 was 0.1338 (all data) and R1 was 0.0500 (I≥2 σ(I)).

- Quantum chemical calculations (gas phase / vacuum) for ground state energy minimized structures for dyad **1** and **2** were done employing density functional theory (DFT) in a Gaussian 09W program package.[S6] The ground state structural elucidation involved in optimization using DFT based Beck-3 Lee Young Parr (B3LYP) functional where 6-311G basis sets were used. To obtain the oscillator strengths, identical basis and functional hybrid set were used whereas the vertical excitation energies were obtained by the help of TD-DFT techniques.[S7] Under the Polarisable Continuum Model (PCM) in the toluene media all the computations were done using the Self-Consistent Reaction Field (SCRF). The electronic absorption spectra as well as the oscillator strengths were thoroughly examined using TD-DFT with PCM model on the basis of the optimized structures in the S0 state.

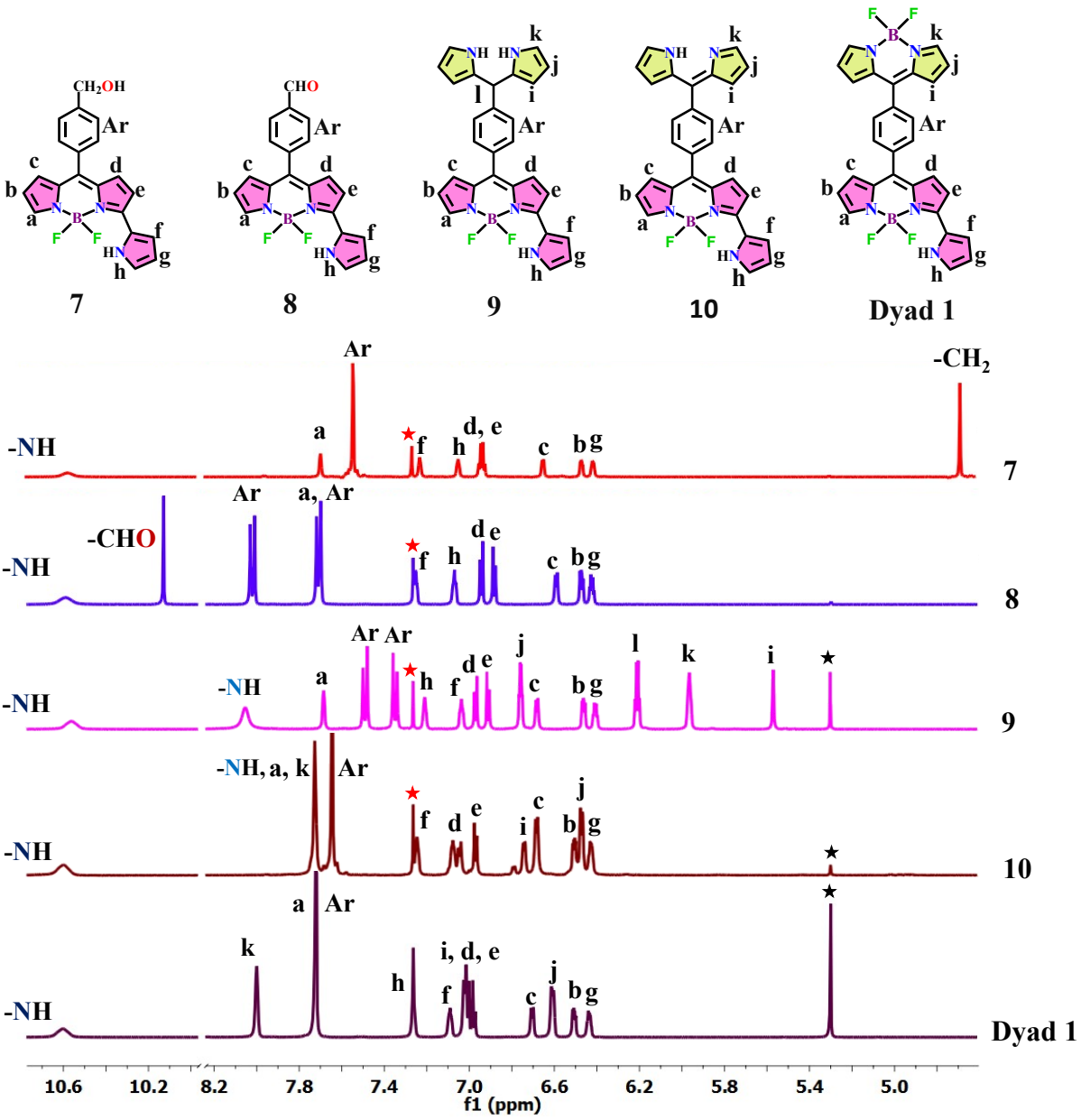


Fig. S1. Partial ^{1}H NMR spectra of **7-10** and dyad **1** in $CDCl_3$ at 25 °C.

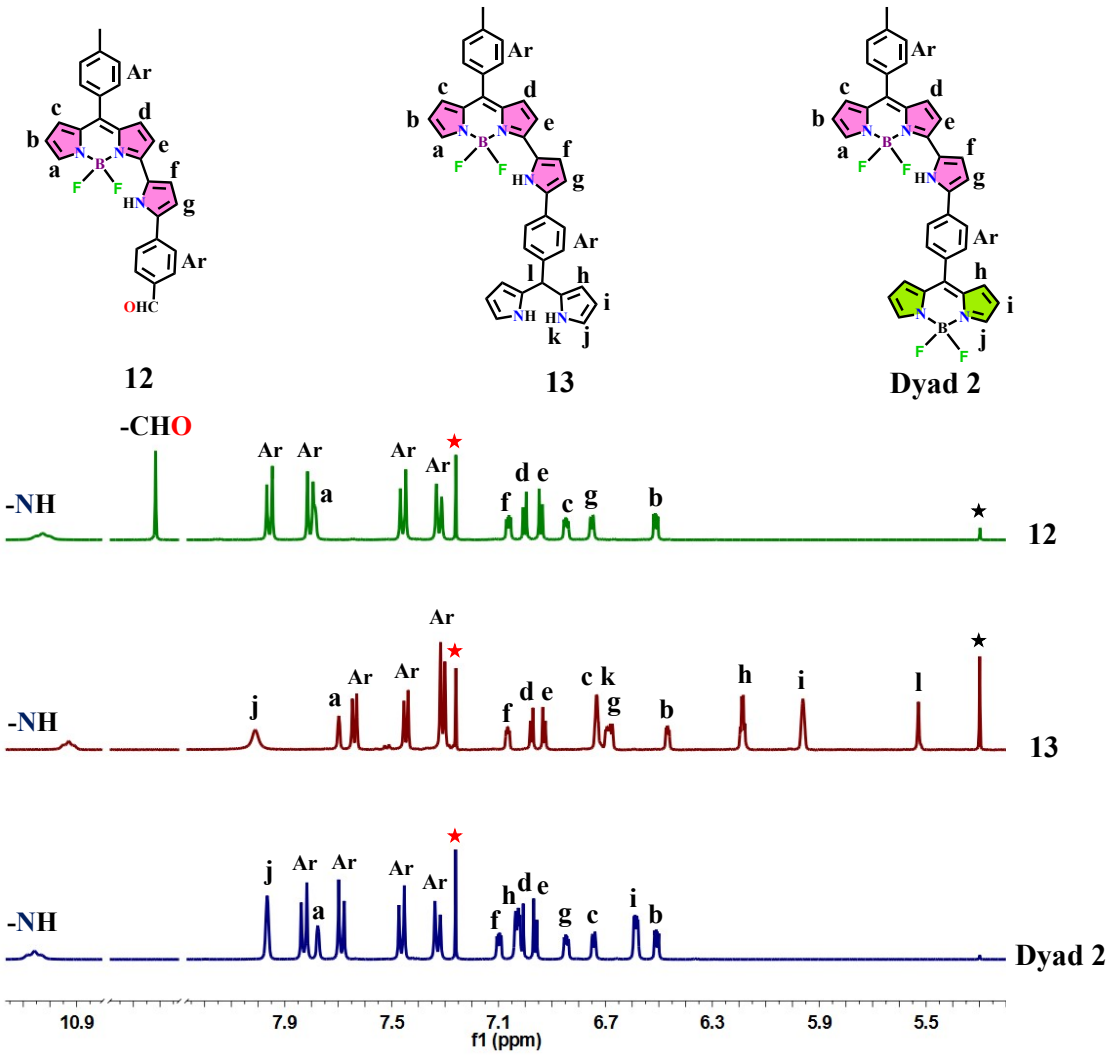


Fig. S2 Partial ^{1}H NMR spectra of **12, 13** and dyad **2** in $CDCl_3$ at 25 °C.

Table S1. Crystallographic Data and Processing Parameters of dyad **2**.

Compound	**2**
CCDC	2330174
Formula	$C_{35}H_{25}B_2F_4N_5$
Dcalc./ g cm^{-3}	1.410
μ/mm-1	0.102
Formula Weight	613.264
Colour	green
Shape	block-shaped
Size/mm3	0.40×0.20×0.20
T/K	150.15
Crystal System	triclinic
Space Group	*P-1*
a/Å	10.2752(9)
b/Å	11.7931(14)
c/Å	12.4578(13)
α/°	80.037(9)
β/°	76.494(8)
γ/°	89.590(9)
V/Å3	1444.8(3)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K□
Θmin/°	2.64
Θmax/°	25.00
Measured Refl's.	51867
Indep't Refl's	5080
Refl's I≥2 σ(I)	3881
Rint	0.1062
Parameters	417
Restraints	0
Largest Peak	0.4801
Deepest Hole	-0.2503
GooF	1.0601
wR2 (all data)	0.1338
wR2	0.1192
R1 (all data)	0.0689
R1	0.0500

Table S2. Bond length for dyad **2.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.397(3)	C8	C5	1.481(3)
F2	B1	1.396(3)	C24	C23	1.400(3)
F3	B2	1.392(3)	C24	C25	1.393(3)
F4	B2	1.372(3)	C9	C10	1.401(3)
N2	C13	1.407(3)	C13	C14	1.414(3)
N2	C16	1.357(3)	C20	C19	1.385(3)
N2	B1	1.557(3)	C23	C22	1.379(3)
N3	C20	1.365(3)	C26	C25	1.384(3)
N3	C17	1.375(3)	C28	C29	1.407(3)
N1	C9	1.390(3)	C6	C5	1.391(3)
N1	C12	1.357(3)	C6	C7	1.380(3)
N1	B1	1.524(3)	C16	C15	1.422(3)
N5	C32	1.395(3)	C16	C17	1.434(3)
N5	C35	1.342(3)	C2	C7	1.390(4)
N5	B2	1.540(3)	C2	C3	1.388(4)
N4	C28	1.398(3)	C2	C1	1.512(3)
N4	C31	1.337(3)	C15	C14	1.362(3)
N4	B2	1.552(3)	C4	C5	1.396(3)
C21	C20	1.460(3)	C4	C3	1.390(3)
C21	C26	1.394(3)	C17	C18	1.388(3)
C21	C22	1.403(3)	C33	C34	1.372(3)
C27	C32	1.393(3)	C10	C11	1.392(3)
C27	C24	1.478(3)	C29	C30	1.370(3)
C27	C28	1.400(3)	C12	C11	1.389(3)
C32	C33	1.410(3)	C19	C18	1.393(3)
C8	C9	1.418(3)	C35	C34	1.394(4)
C8	C13	1.383(3)	C31	C30	1.397(4)

Table S3. Hydrogen Bonds for **2.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3	H3	F1	0.8800	2.123(2)	2.872(2)	142.50(6)

Table S4. Bond Angles for **2.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	N2	C13	107.59(18)	C7	C6	C5	121.0(2)
B1	N2	C13	123.73(18)	C26	C25	C24	121.1(2)
B1	N2	C16	127.91(18)	C15	C16	N2	109.21(19)
C17	N3	C20	110.17(19)	C17	C16	N2	126.5(2)
C12	N1	C9	108.15(19)	C17	C16	C15	124.0(2)

B1	N1	C9	126.37(18)	C3	C2	C7	118.2(2)
B1	N1	C12	125.43(19)	C1	C2	C7	121.4(2)
C35	N5	C32	107.0(2)	C1	C2	C3	120.4(2)
B2	N5	C32	125.43(19)	C14	C15	C16	107.3(2)
B2	N5	C35	126.9(2)	C3	C4	C5	120.4(2)
C31	N4	C28	107.6(2)	C6	C5	C8	121.2(2)
B2	N4	C28	124.53(19)	C4	C5	C8	120.6(2)
B2	N4	C31	127.7(2)	C4	C5	C6	118.2(2)
C26	C21	C20	122.9(2)	C16	C17	N3	127.5(2)
C22	C21	C20	119.1(2)	C18	C17	N3	106.82(19)
C22	C21	C26	118.0(2)	C18	C17	C16	125.4(2)
C24	C27	C32	119.6(2)	C34	C33	C32	107.8(2)
C28	C27	C32	120.1(2)	C11	C10	C9	107.6(2)
C28	C27	C24	120.3(2)	C15	C14	C13	108.3(2)
C27	C32	N5	120.8(2)	C30	C29	C28	107.7(2)
C33	C32	N5	107.69(19)	C2	C7	C6	121.0(2)
C33	C32	C27	131.5(2)	C11	C12	N1	109.5(2)
C13	C8	C9	119.9(2)	C4	C3	C2	121.1(2)
C5	C8	C9	119.4(2)	C18	C19	C20	108.0(2)
C5	C8	C13	120.5(2)	C34	C35	N5	110.9(2)
C23	C24	C27	120.26(19)	C12	C11	C10	107.1(2)
C25	C24	C27	121.4(2)	C19	C18	C17	107.9(2)
C25	C24	C23	118.3(2)	C35	C34	C33	106.6(2)
C8	C9	N1	120.3(2)	C30	C31	N4	110.1(2)
C10	C9	N1	107.61(19)	C31	C30	C29	107.1(2)
C10	C9	C8	132.0(2)	F2	B1	F1	107.49(19)
C8	C13	N2	122.1(2)	N2	B1	F1	110.6(2)
C14	C13	N2	107.50(19)	N2	B1	F2	110.02(19)
C14	C13	C8	130.1(2)	N1	B1	F1	111.27(19)
C21	C20	N3	123.8(2)	N1	B1	F2	110.0(2)
C19	C20	N3	107.14(19)	N1	B1	N2	107.46(18)
C19	C20	C21	129.0(2)	F4	B2	F3	110.0(2)
C22	C23	C24	120.6(2)	N5	B2	F3	109.7(2)
C25	C26	C21	120.8(2)	N5	B2	F4	111.5(2)
C27	C28	N4	120.8(2)	N4	B2	F3	108.7(2)
C29	C28	N4	107.4(2)	N4	B2	F4	111.1(2)
C29	C28	C27	131.3(2)	N4	B2	N5	105.67(18)
C23	C22	C21	121.2(2)				

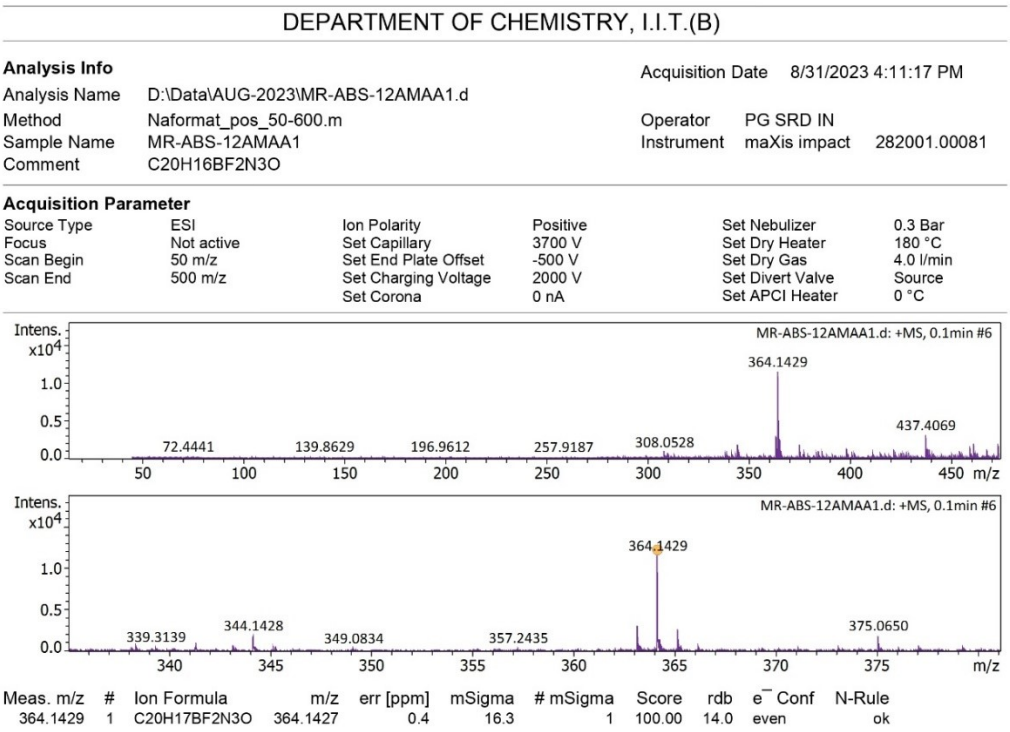


Fig. S3 High resolution mass spectrum of **7**.

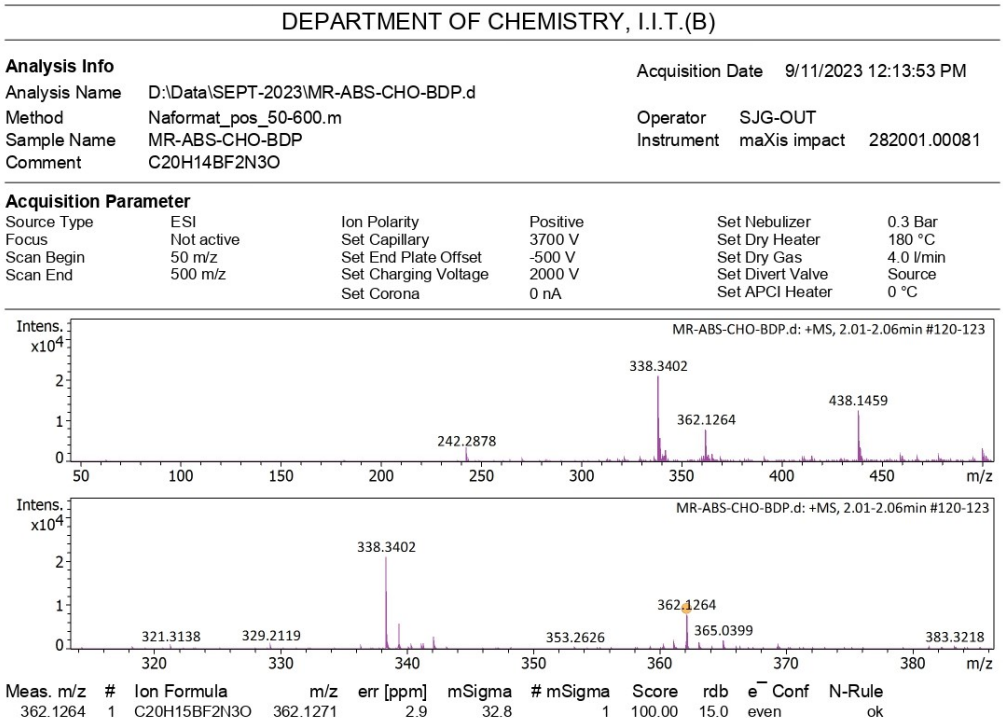


Fig. S4 High resolution mass spectrum of **8**.

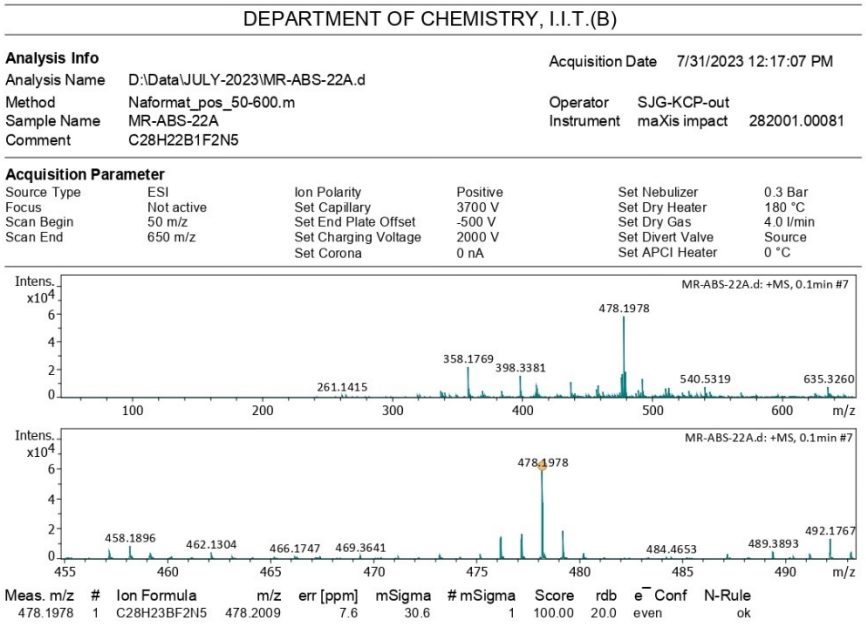


Fig. S5 High resolution mass spectrum of **9**.

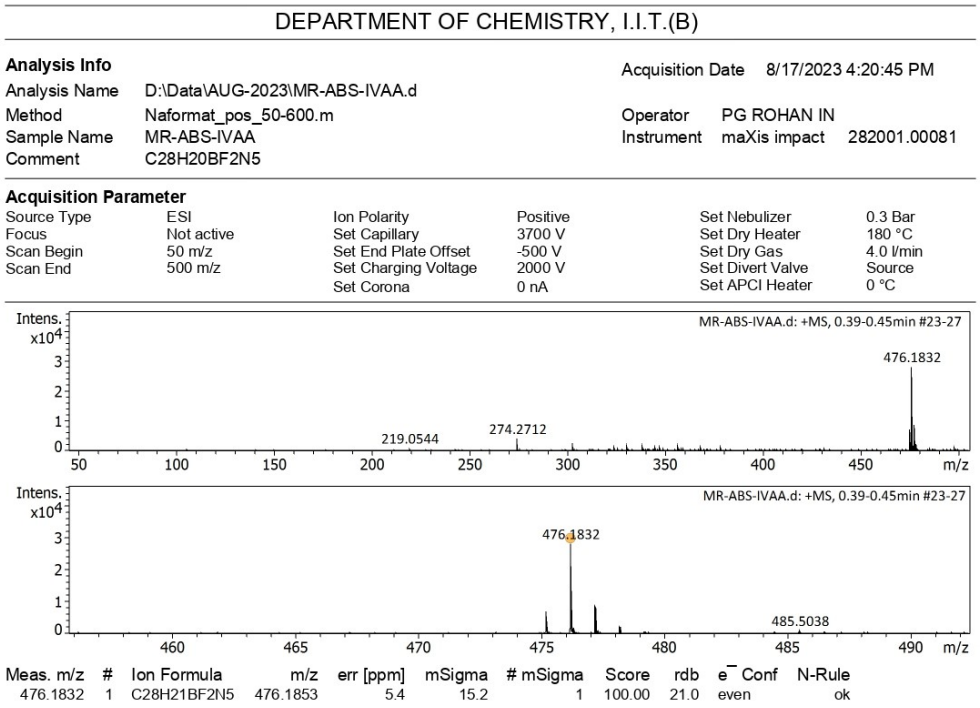


Fig. S6 High resolution mass spectrum of **10**.

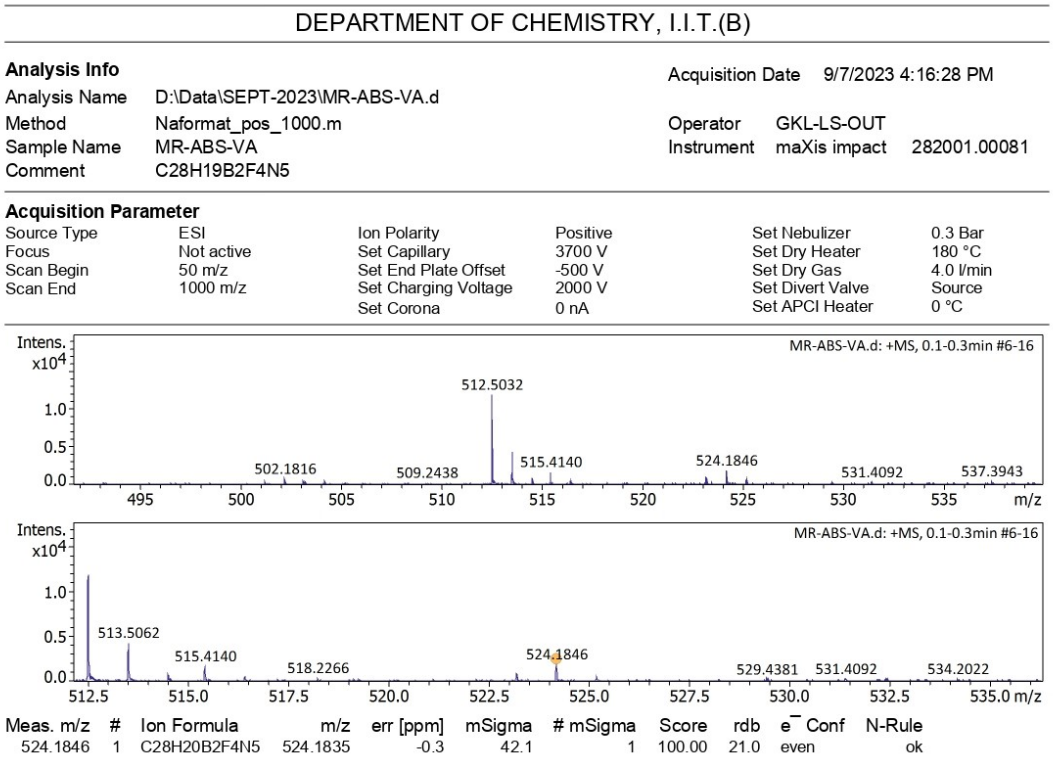


Fig. S7 High resolution mass spectrum of **dyad 1**.

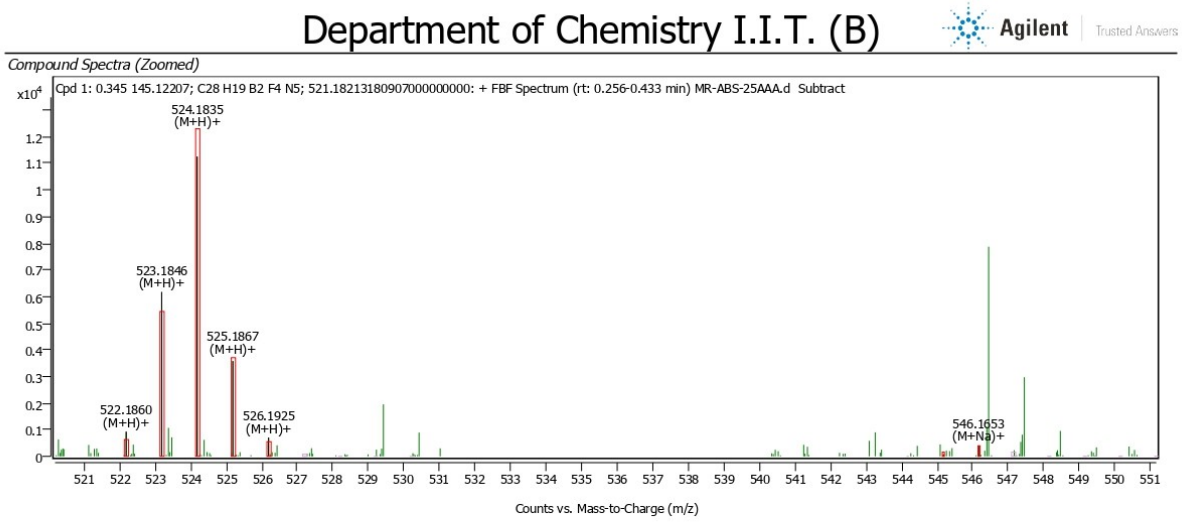


Fig. S8 High resolution mass spectrum of dyad **2**.

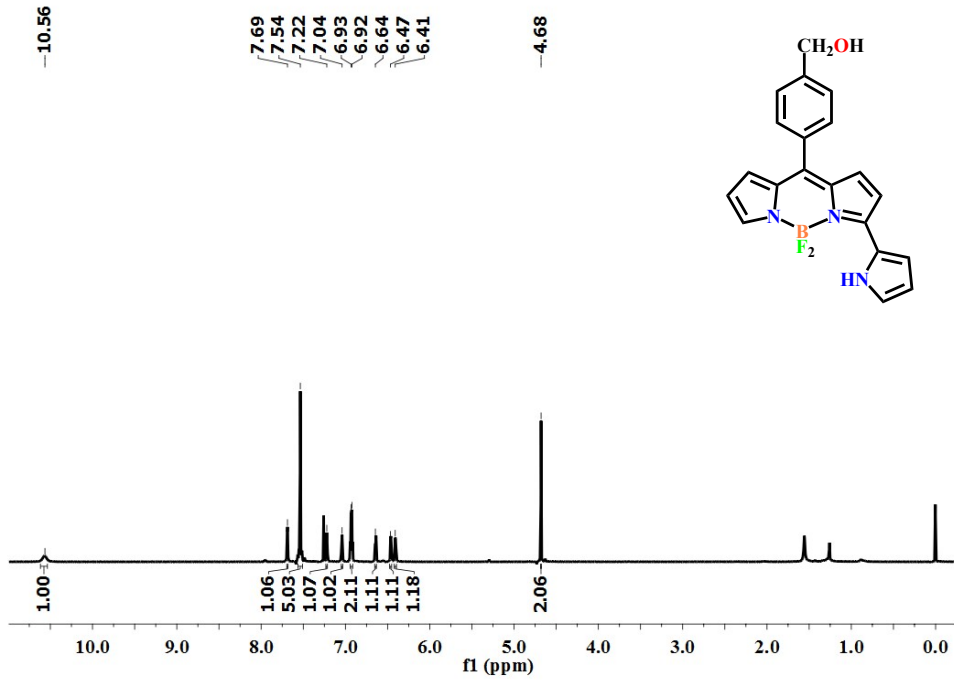


Fig. S9 ^{1}H NMR spectrum of compound **7** in $CDCl_3$ at room temperature.

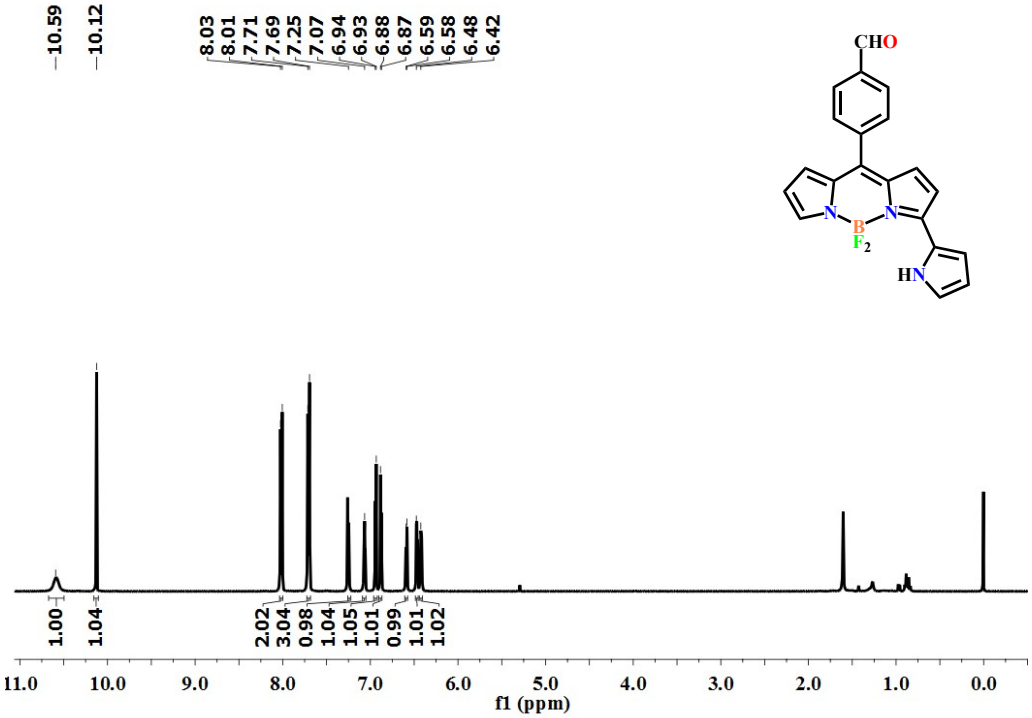


Fig. S10 ^{1}H NMR spectrum of compound **8** in $CDCl_3$ at room temperature.

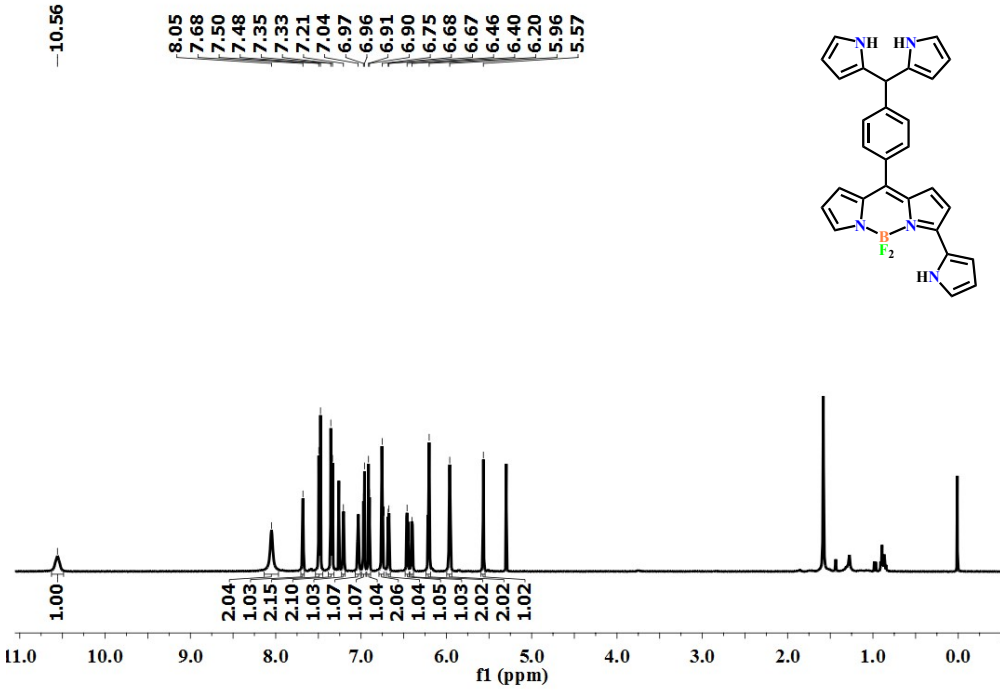


Fig. S11 ^{1}H NMR spectrum of compound **9** in $CDCl_3$ at room temperature.

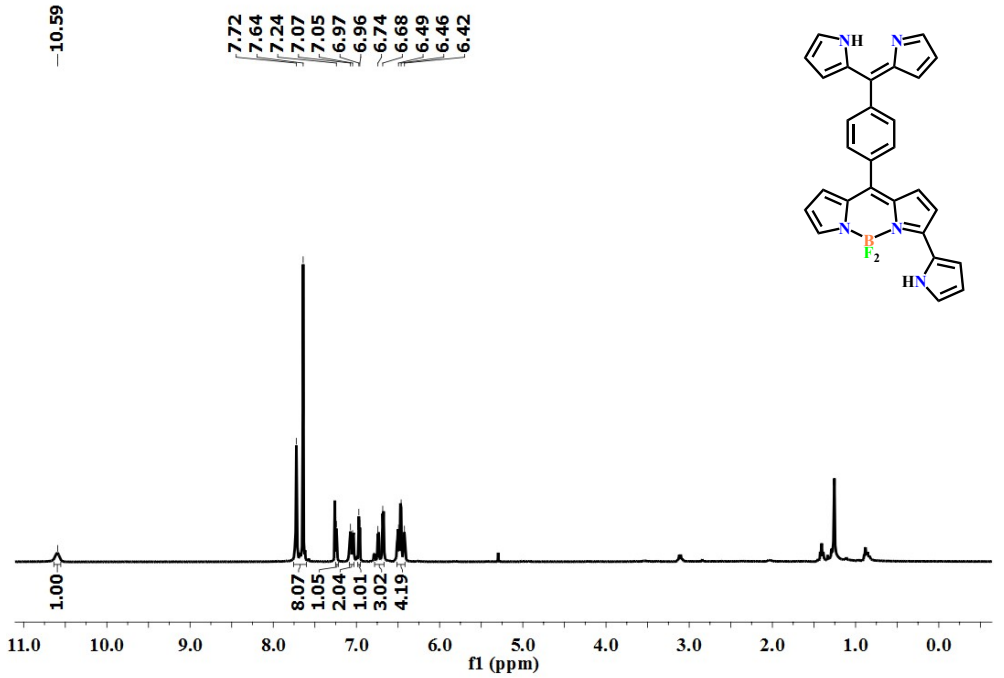


Fig. S12 ^{1}H NMR spectrum of compound **10** in $CDCl_3$ at room temperature.

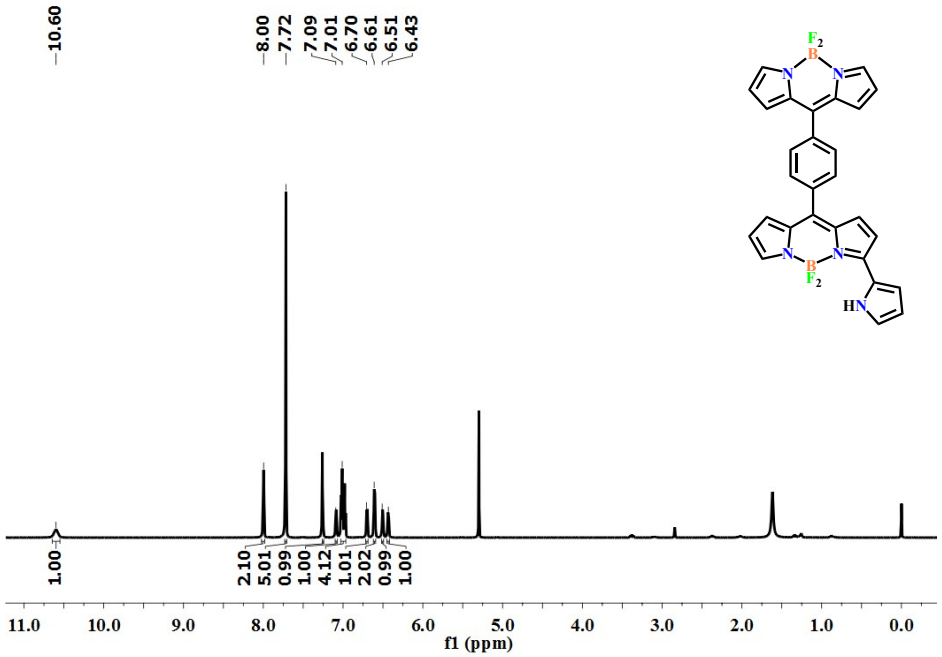


Fig. S13 ^{1}H NMR spectrum of compound dyad **1** in $CDCl_3$ at room temperature.

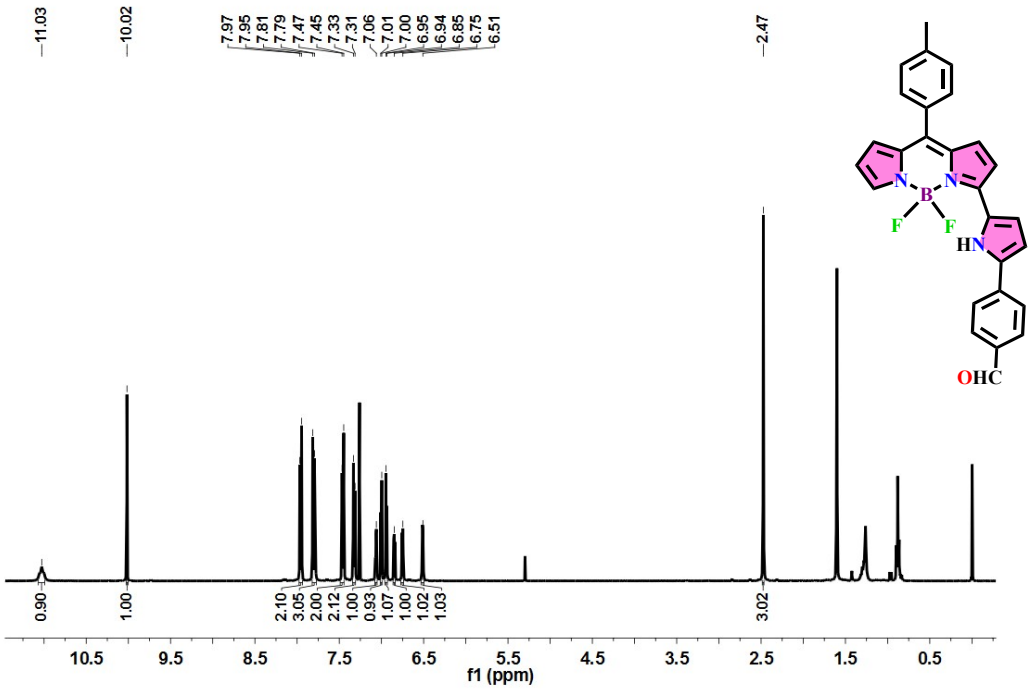


Fig. S14 ^{1}H NMR spectrum of compound **12** in $CDCl_3$ at room temperature.

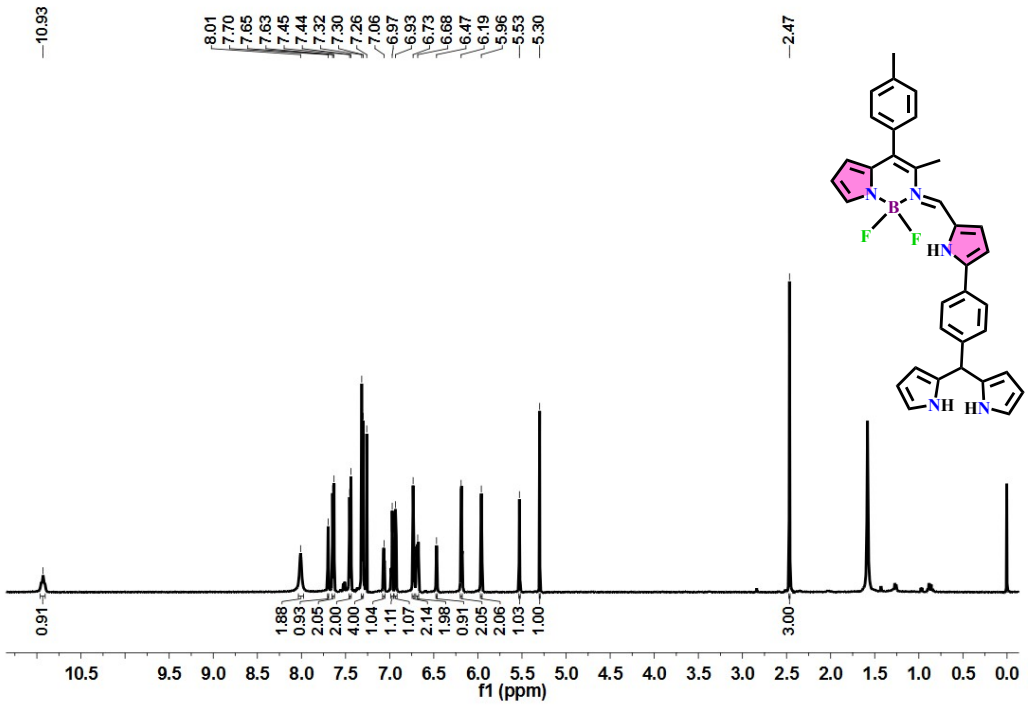


Fig. S15 ^{1}H NMR spectrum of compound **13** in $CDCl_3$ at room temperature.

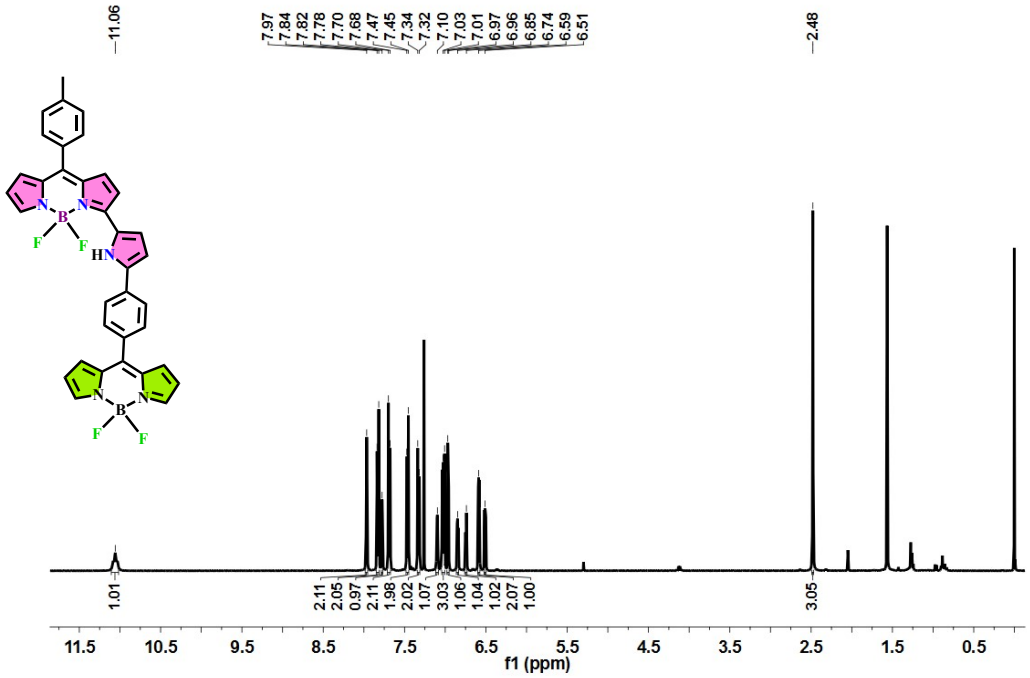


Fig. S16 ^{1}H NMR spectrum of dyad **2** in $CDCl_3$ at room temperature.

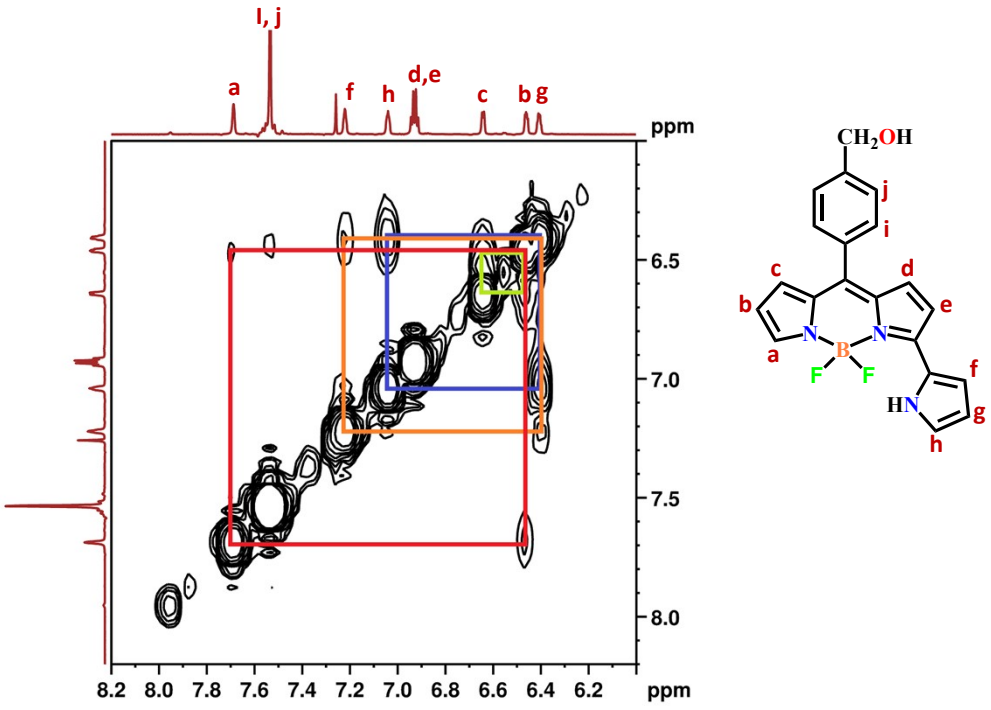


Fig. S17 ^{1}H-^{1}H NOESY spectrum of the **7** in $CDCl_3$ at room temperature.

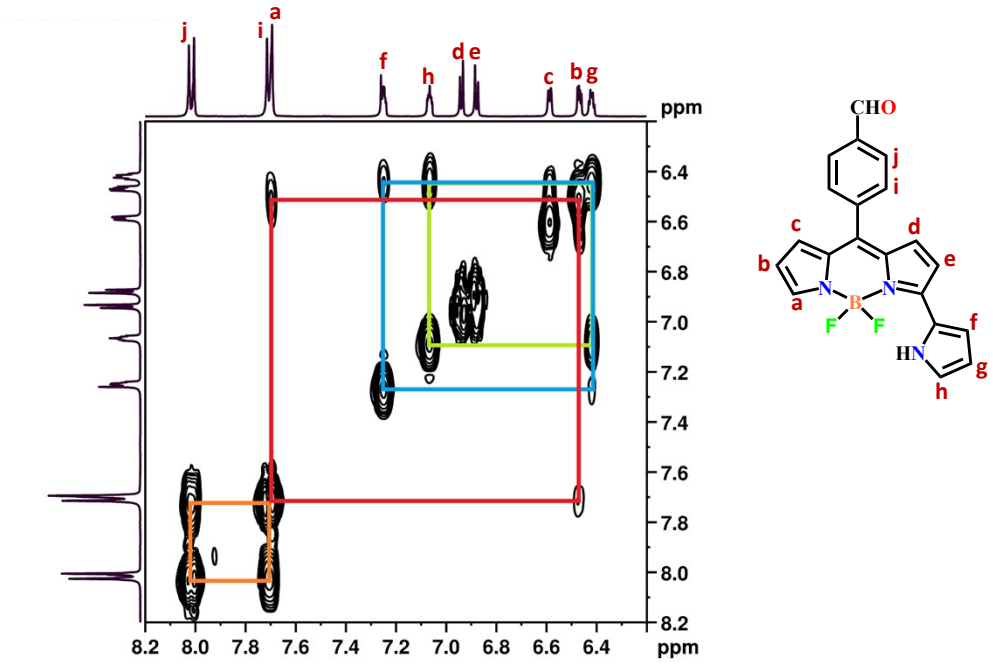


Fig. S18 ^{1}H-^{1}H NOESY spectrum of the **8** in $CDCl_3$ at room temperature.

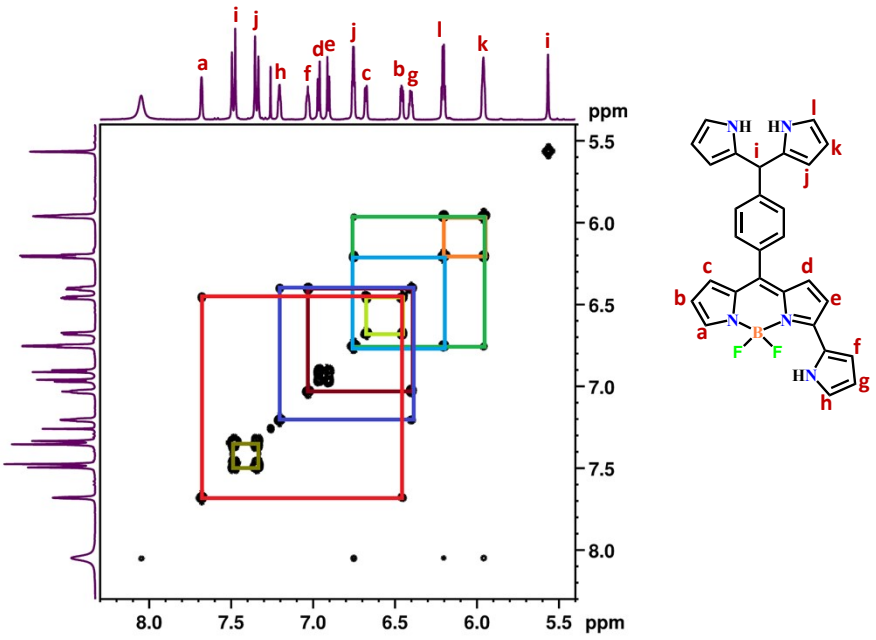


Fig. S19 ^{1}H-^{1}H NOESY spectrum of the **9** in $CDCl_3$ at room temperature.

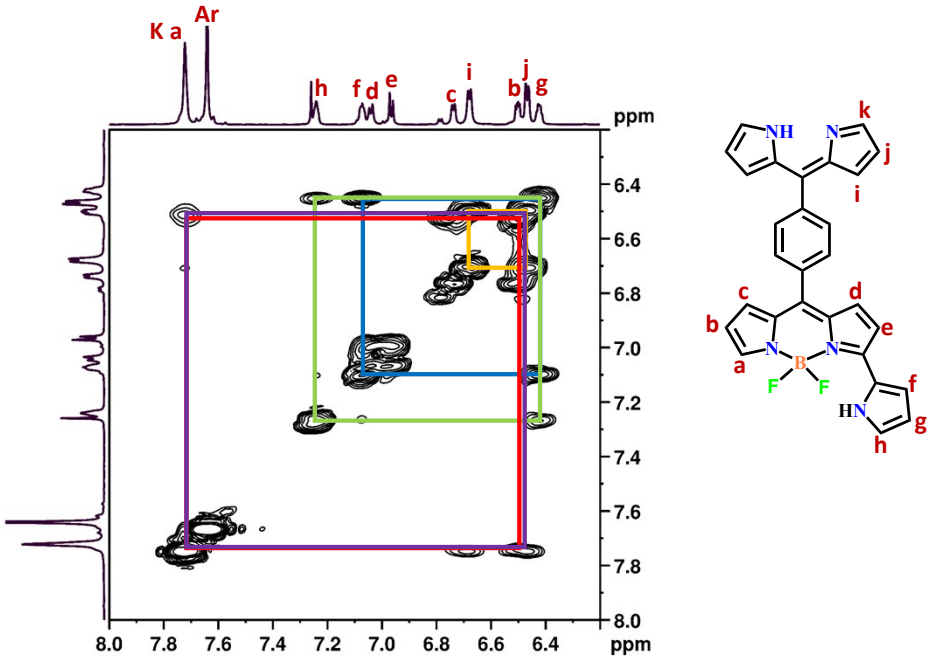


Fig. S20 ^{1}H-^{1}H NOESY spectrum of the **10** in $CDCl_3$ at room temperature.

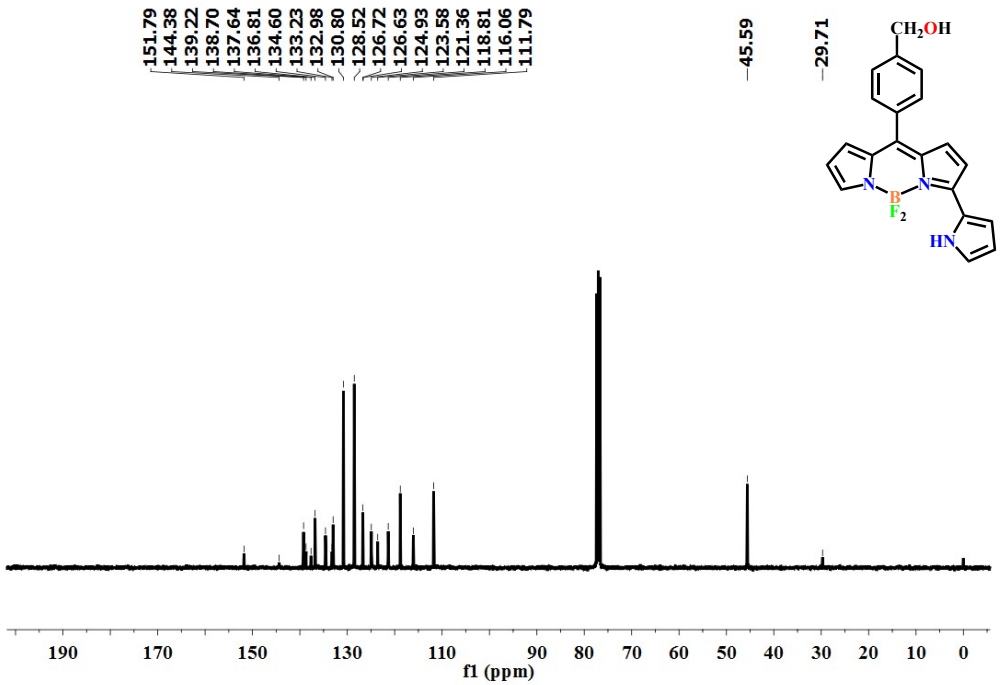


Fig. S21 ^{13}C NMR spectrum of the compound **7** recorded in $CDCl_3$.

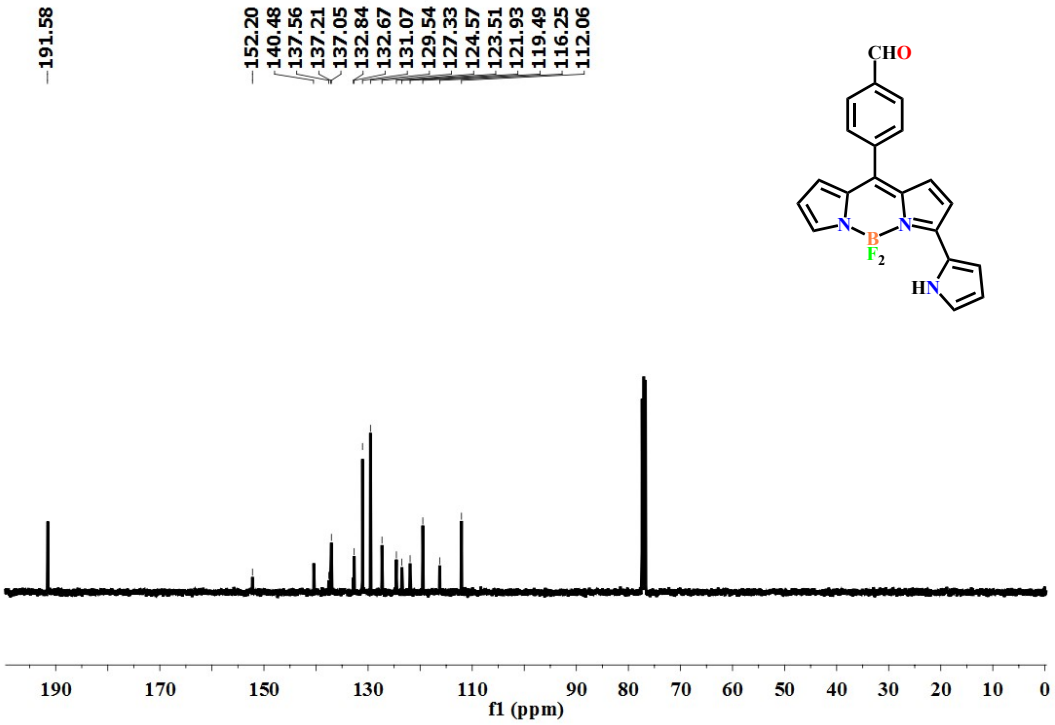


Fig. S22 ^{13}C NMR spectrum of the compound **8** recorded in $CDCl_3$.

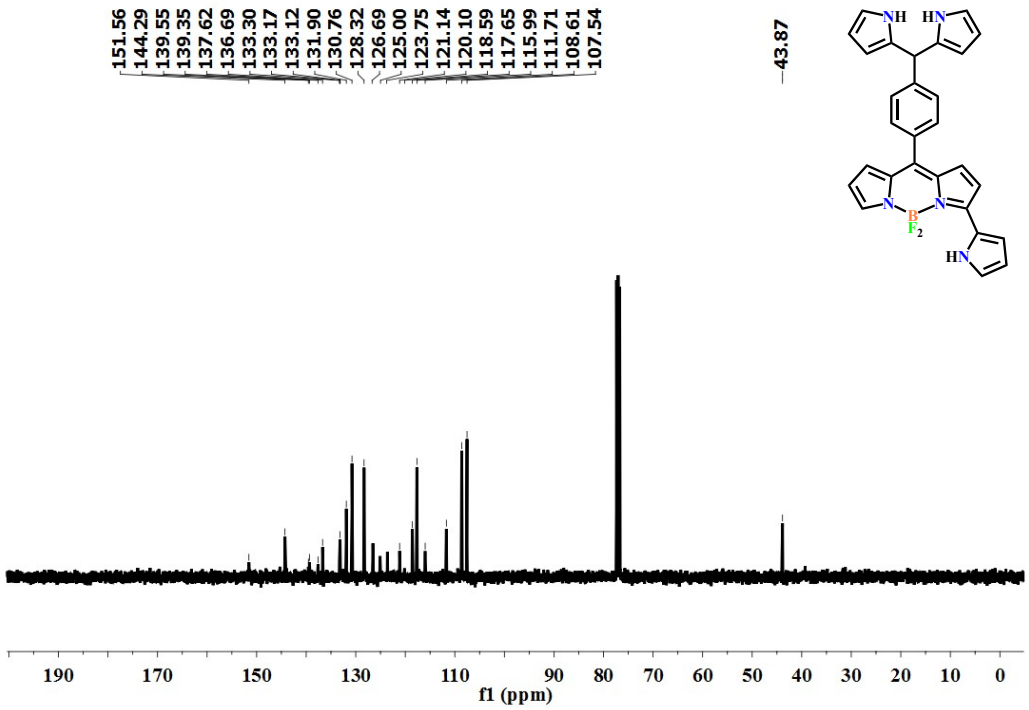


Fig. S23 ^{13}C NMR spectrum of the compound **9** recorded in $CDCl_3$.

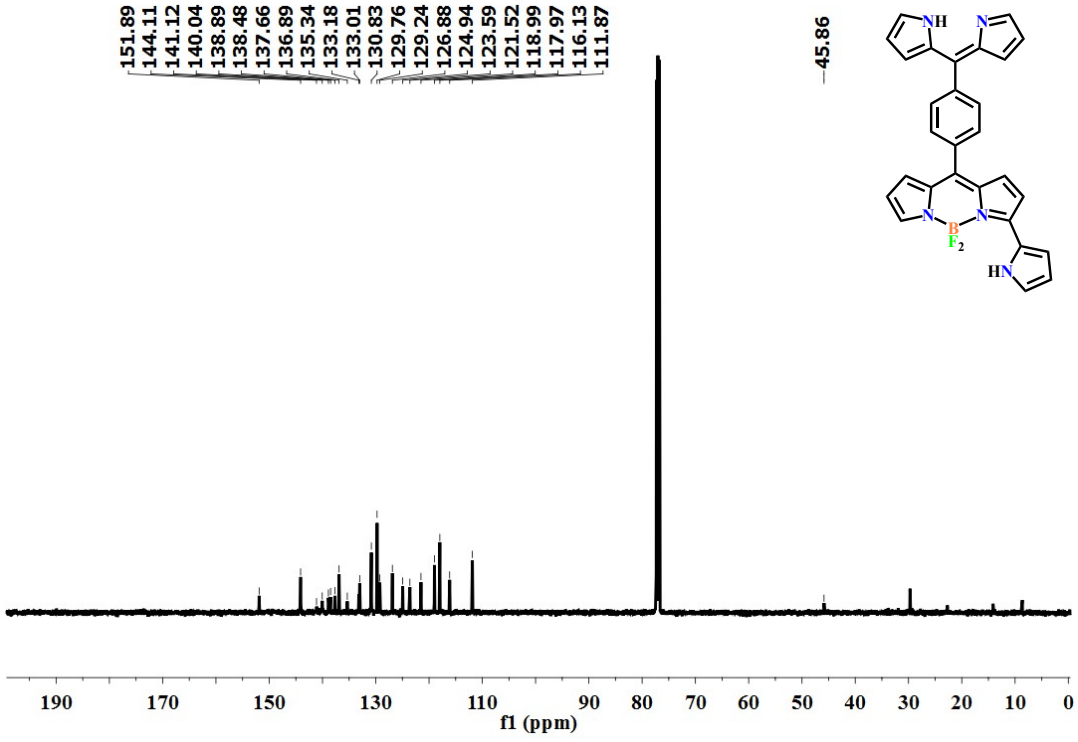


Fig. S24 ^{13}C NMR spectrum of the compound **10** recorded in $CDCl_3$.

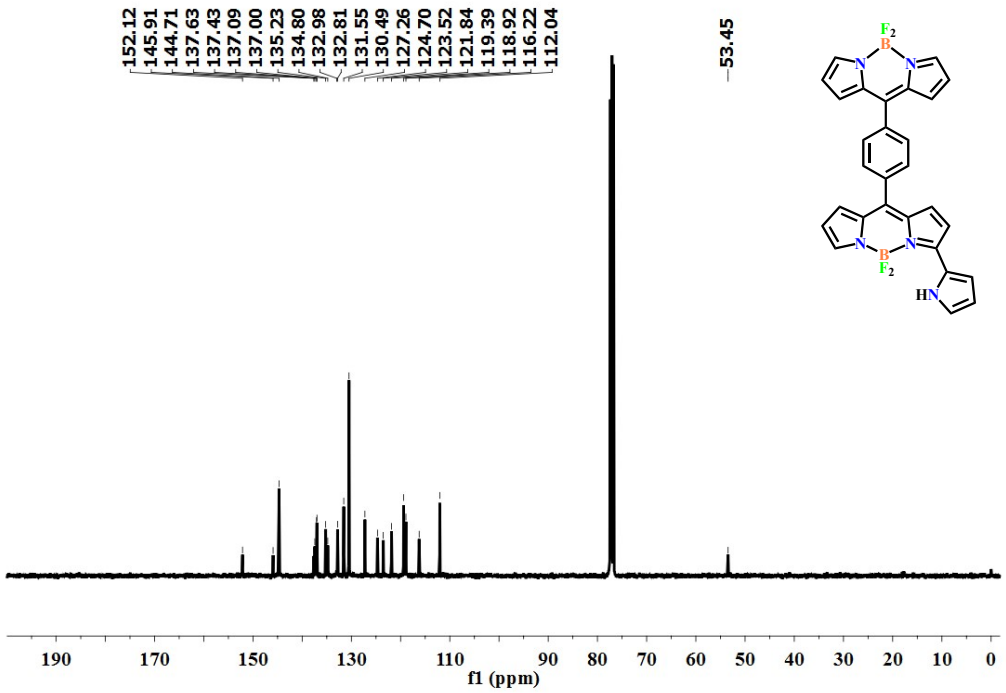


Fig. S25 ^{13}C NMR spectrum of the compound dyad **1** recorded in $CDCl_3$.

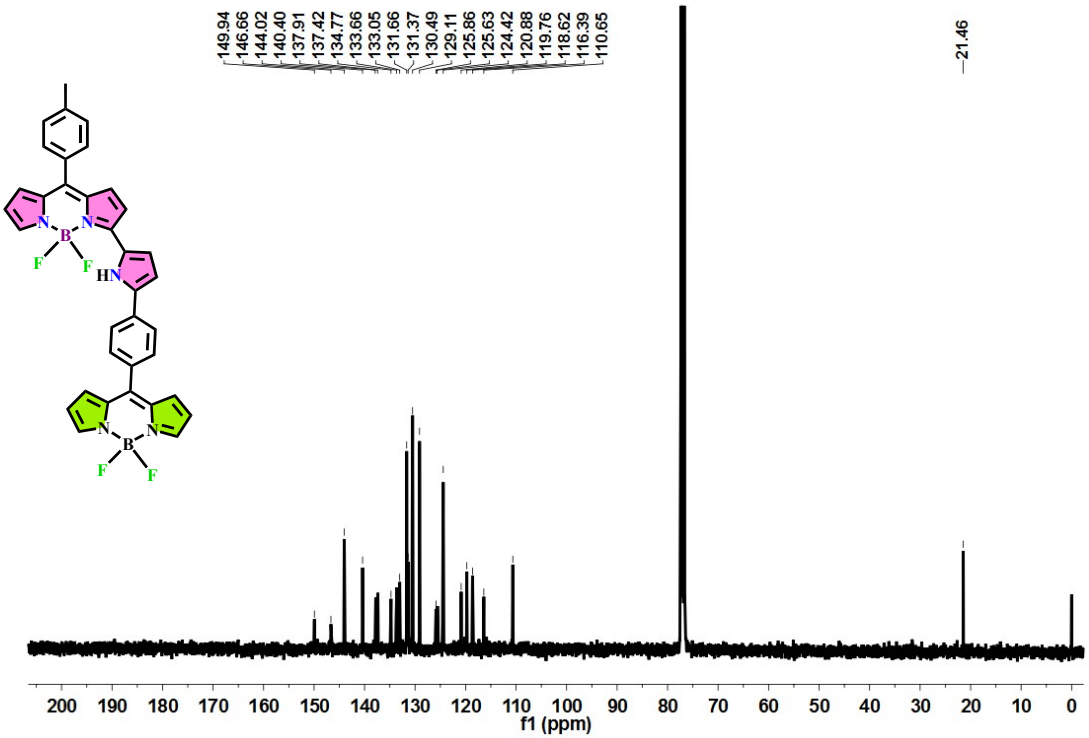


Fig. S26 ^{13}C NMR spectrum of the compound dyad **2** recorded in $CDCl_3$.

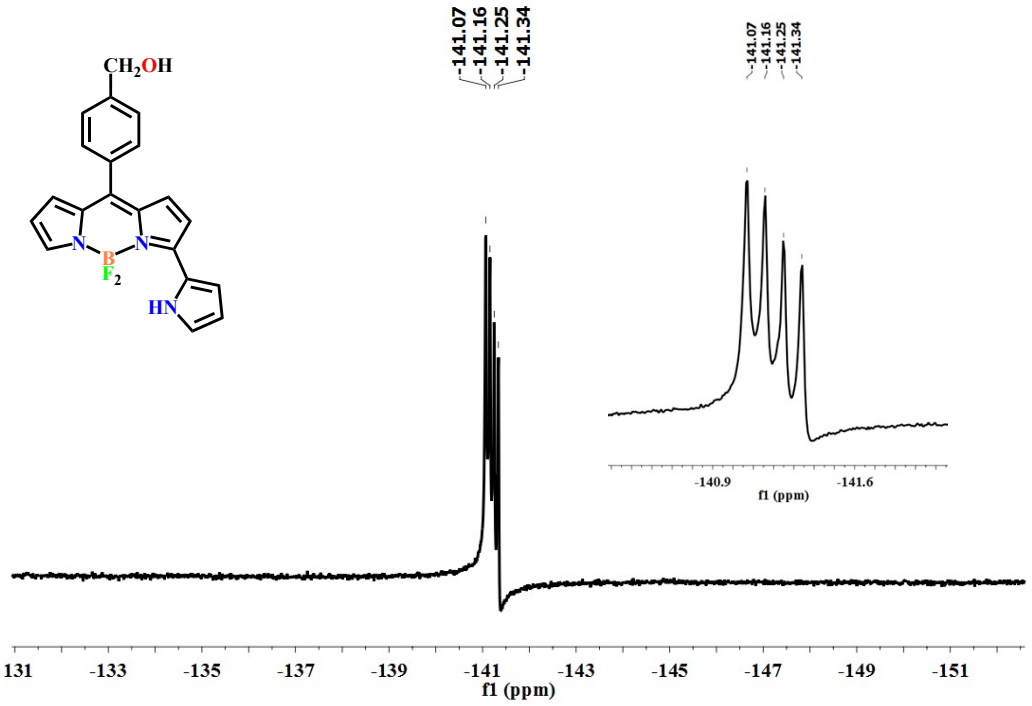


Fig. S27 ^{19}F NMR spectrum of **7** in $CDCl_3$ at room temperature.

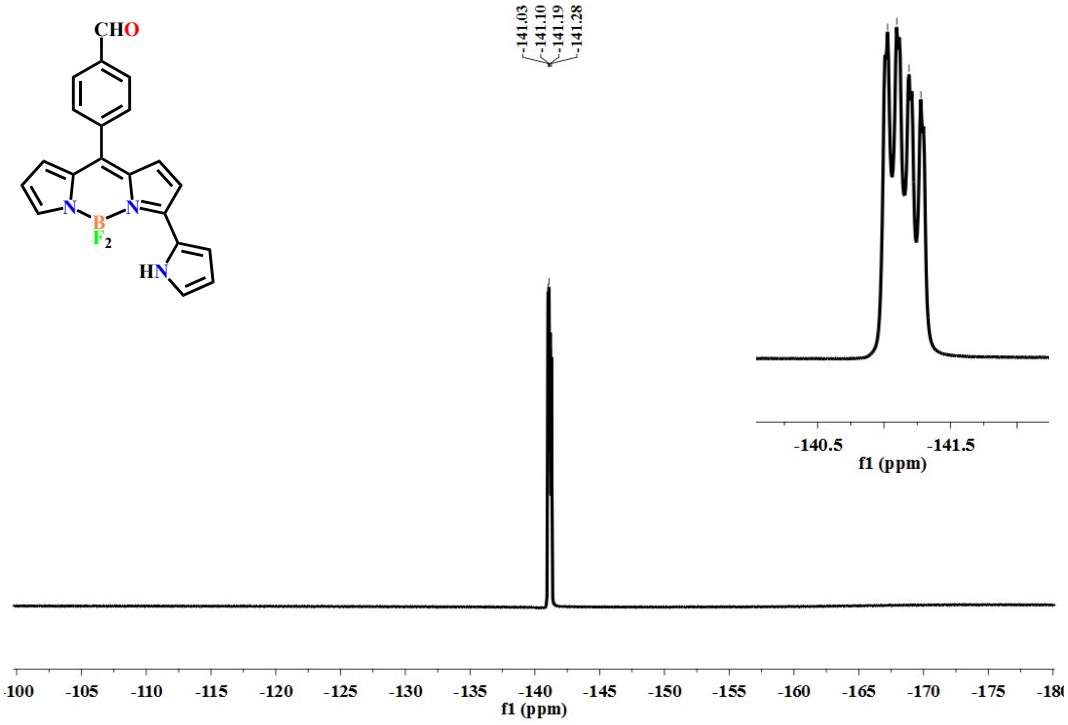


Fig. S28 ^{19}F NMR spectrum of **8** in $CDCl_3$ at room temperature.

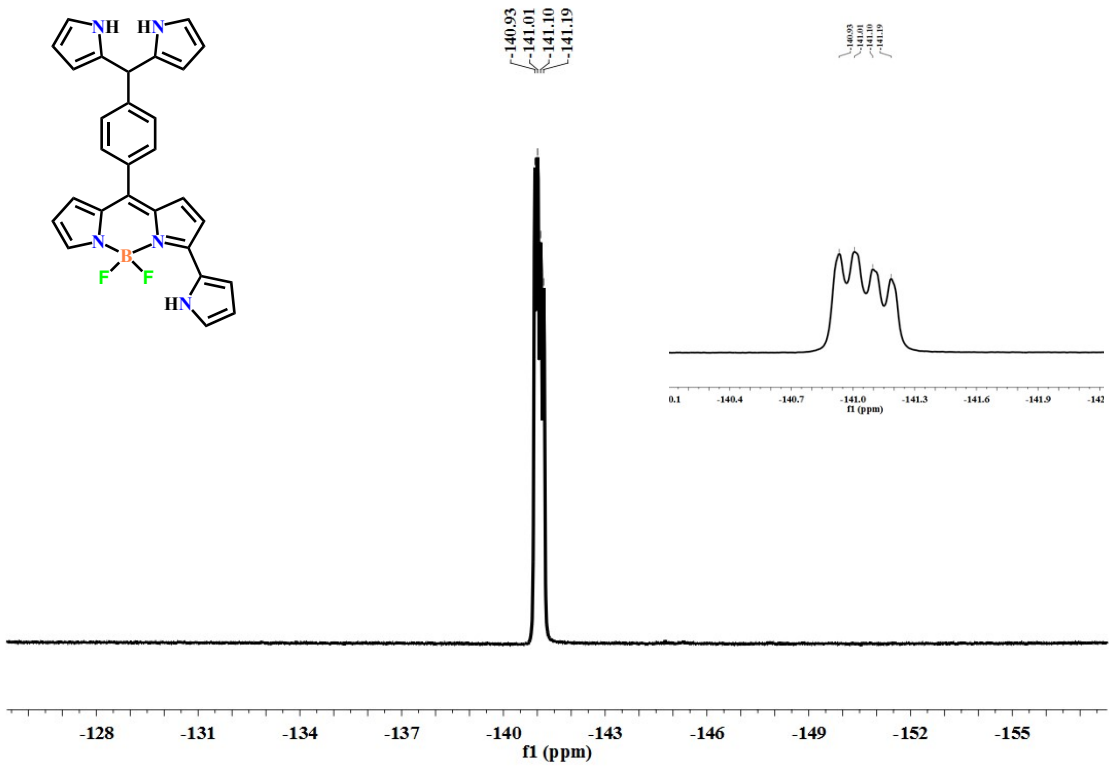


Fig. S29 ^{19}F NMR spectrum of **9** in $CDCl_3$ at room temperature.

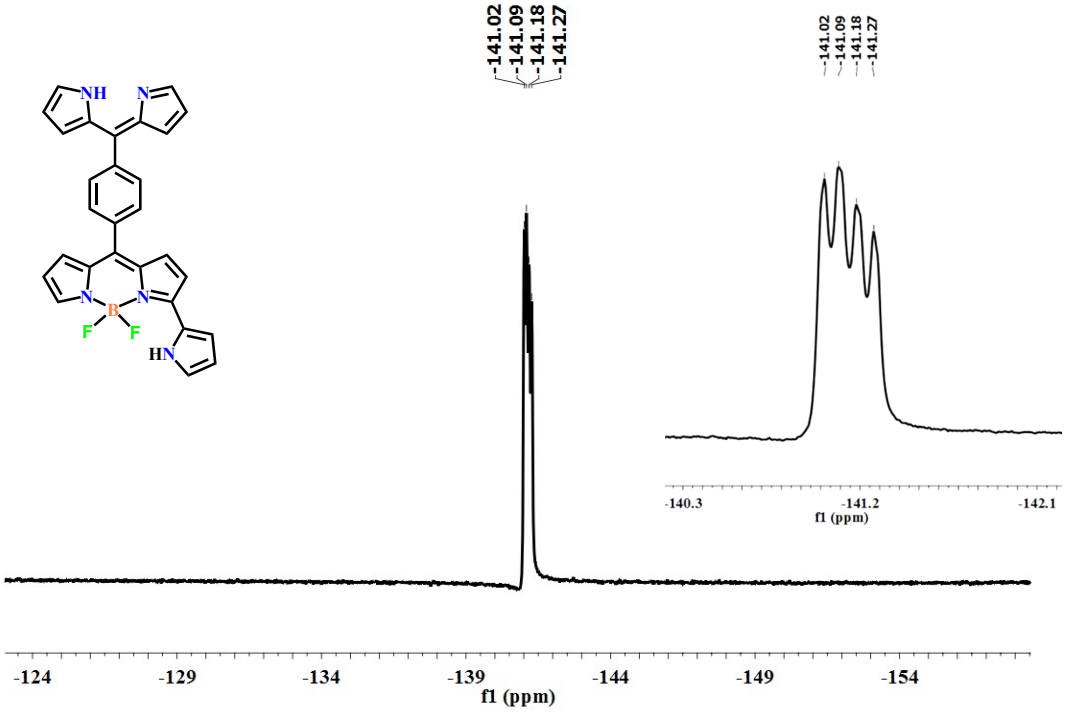


Fig. S30 ^{19}F NMR spectrum of **10** in $CDCl_3$ at room temperature.

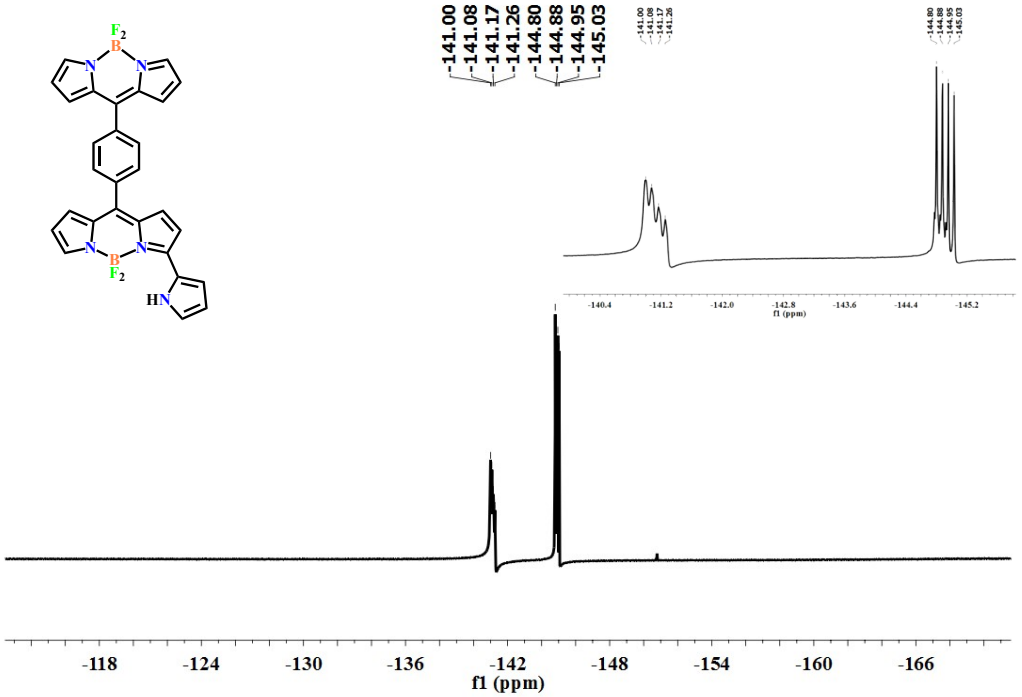


Fig. S31 ^{19}F NMR spectrum of dyad **1** in $CDCl_3$ at room temperature.

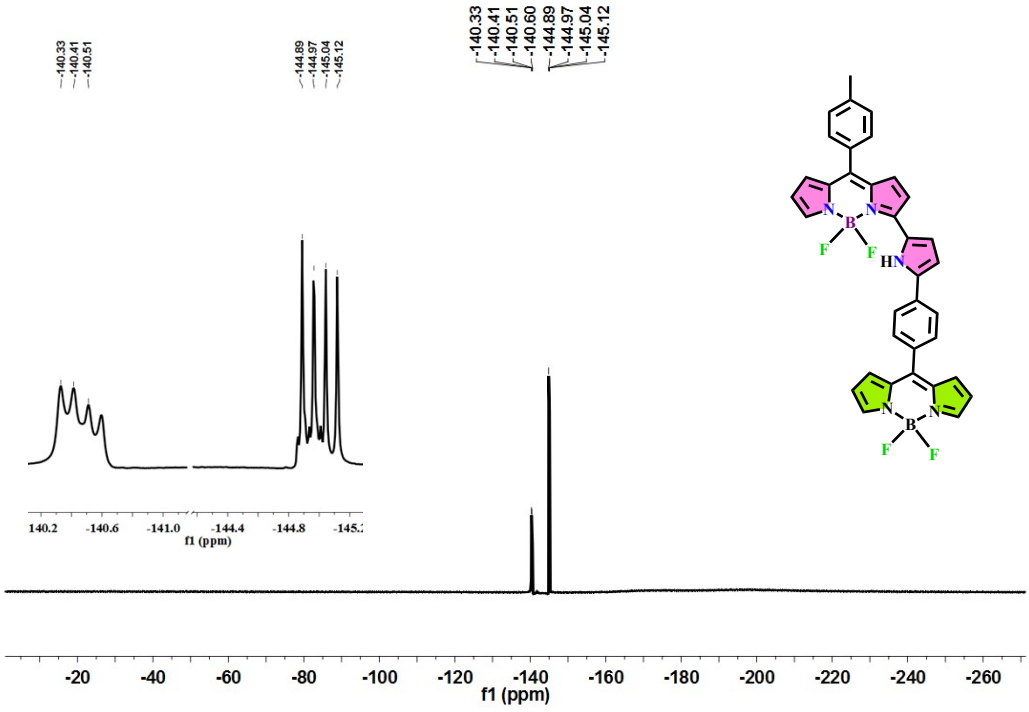


Fig. S32 ^{19}F NMR spectrum of dyad **2** in $CDCl_3$ at room temperature.

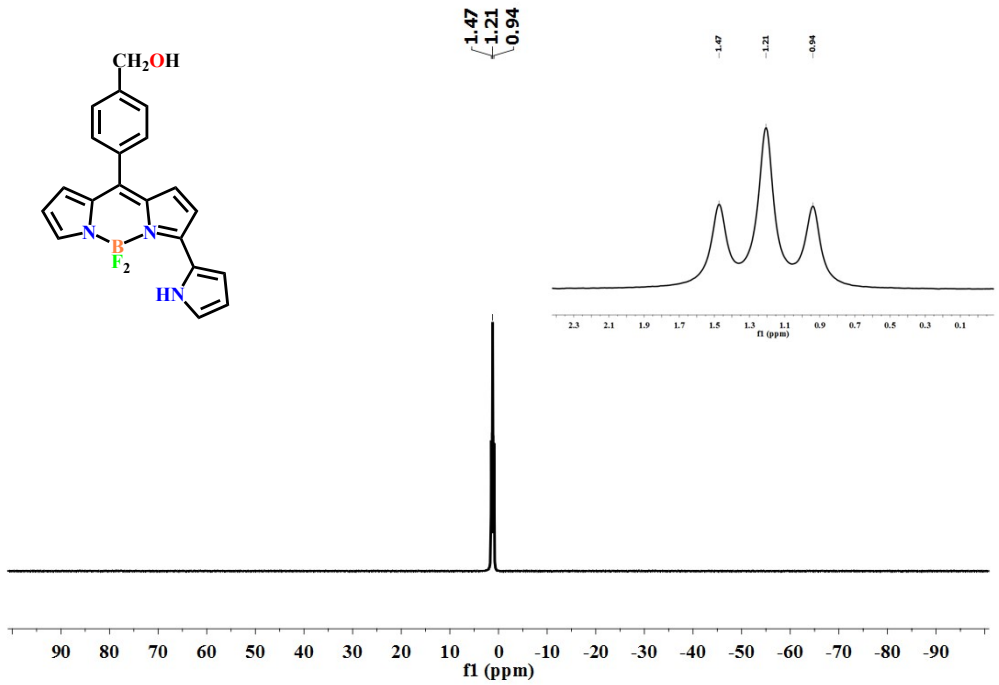


Fig. S33 ^{11}B NMR spectrum of **7** in $CDCl_3$ at room temperature.

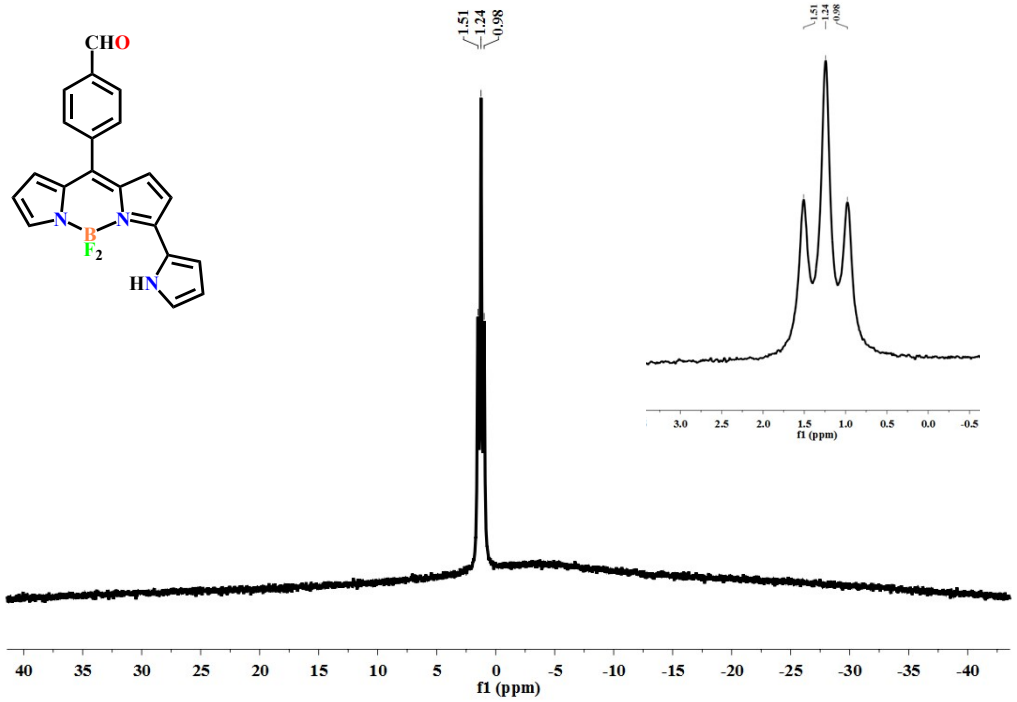


Fig. S34 ^{11}B NMR spectrum of **8** in $CDCl_3$ at room temperature.

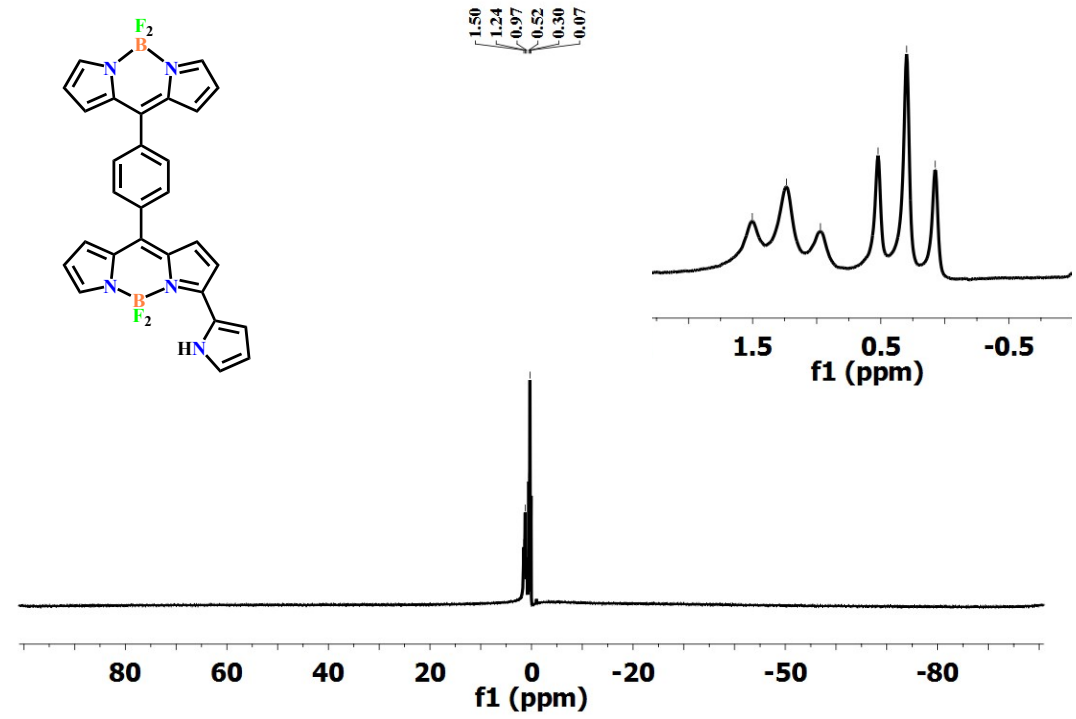


Fig. S35 ^{11}B NMR spectrum of dyad **1** in $CDCl_3$ at room temperature.

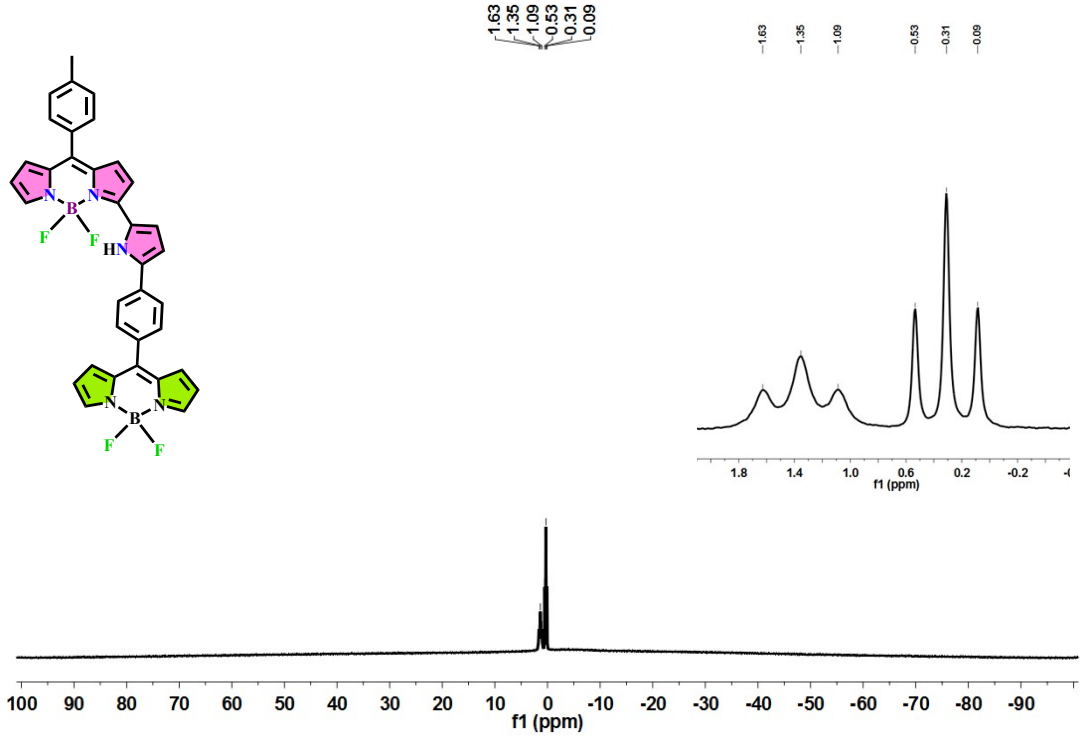
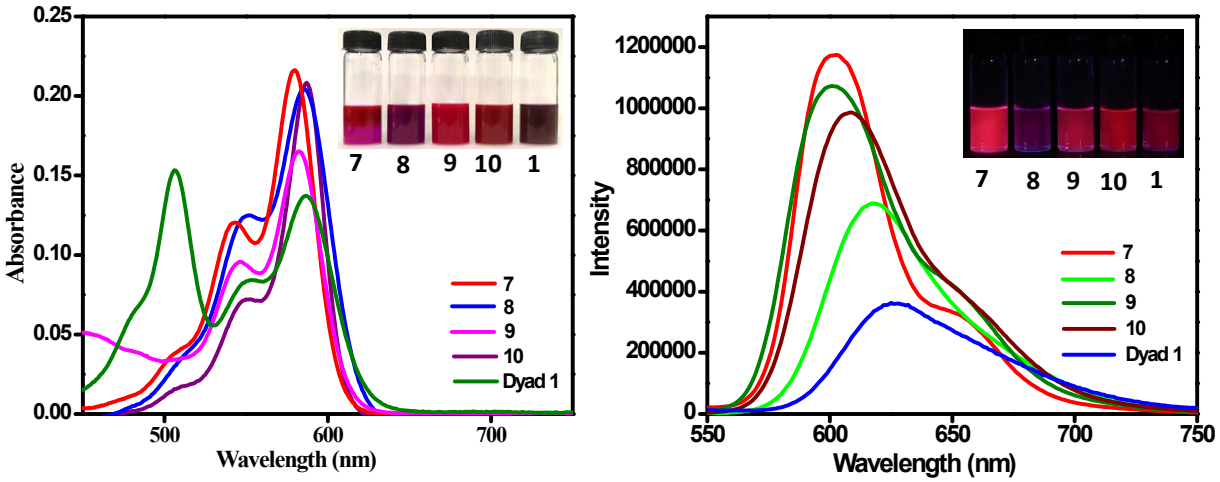
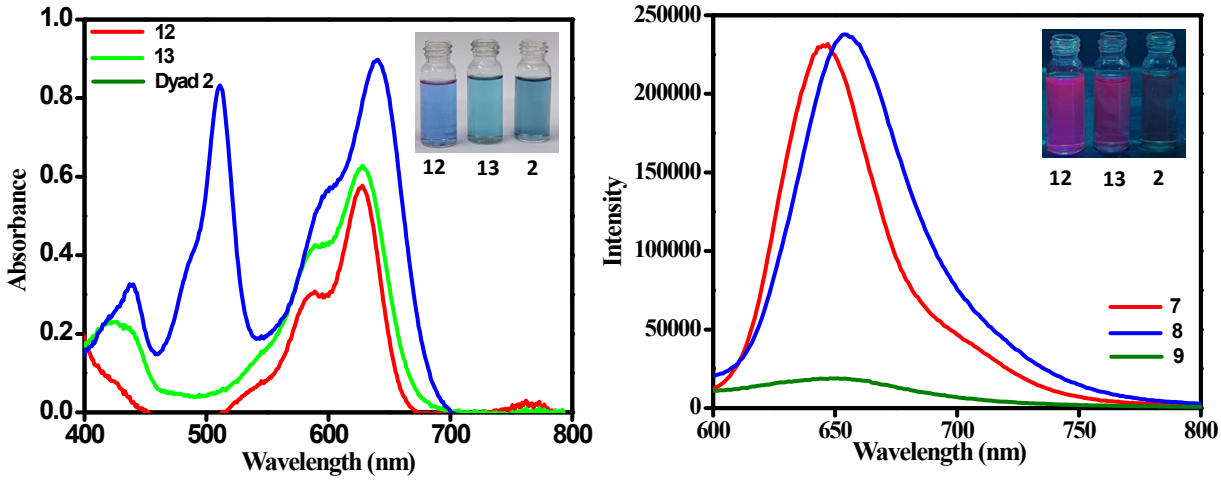


Fig. S36 ^{11}B NMR spectrum of dyad **2** in $CDCl_3$ at room temperature.



(a) (b)

Fig. S37 (a) Absorption and (b) emission spectra of **7-10** and dyad **1.** Conditions: **[7-10= [1]=** 10μM in Toluene.



(a) (b)

Fig. S38 (a) Absorption and (b) emission spectra of **12, 13** and dyad **2.** Conditions: **[12]= [13]= [2]=** 10μM in Toluene.

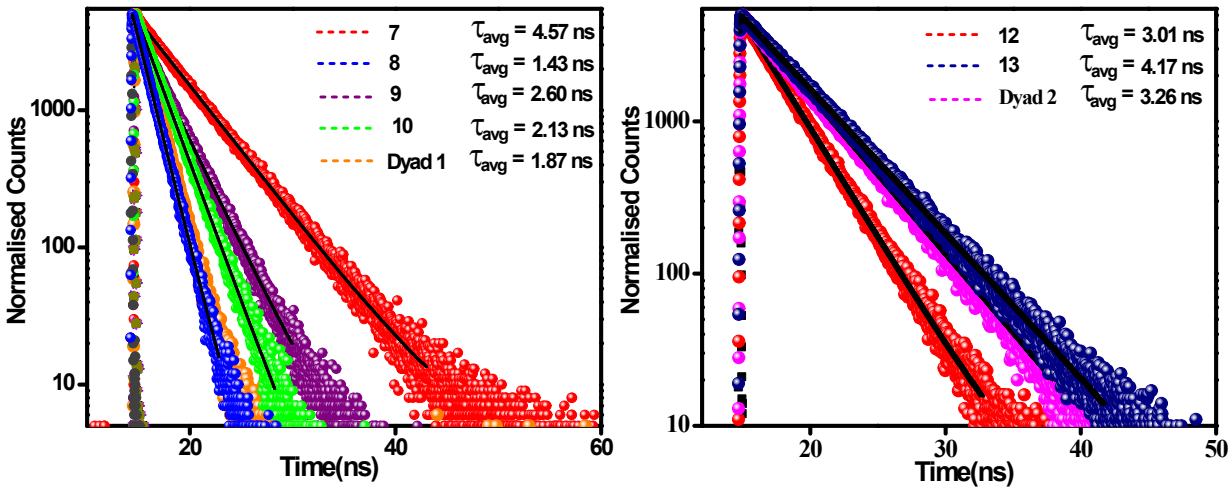


Fig. S39 (a) Excited-state lifetime decay profiles of **7-10** and dyad **1** (b) **12, 13** and dyad **2** recorded in toluene medium. λex.= 520 nm

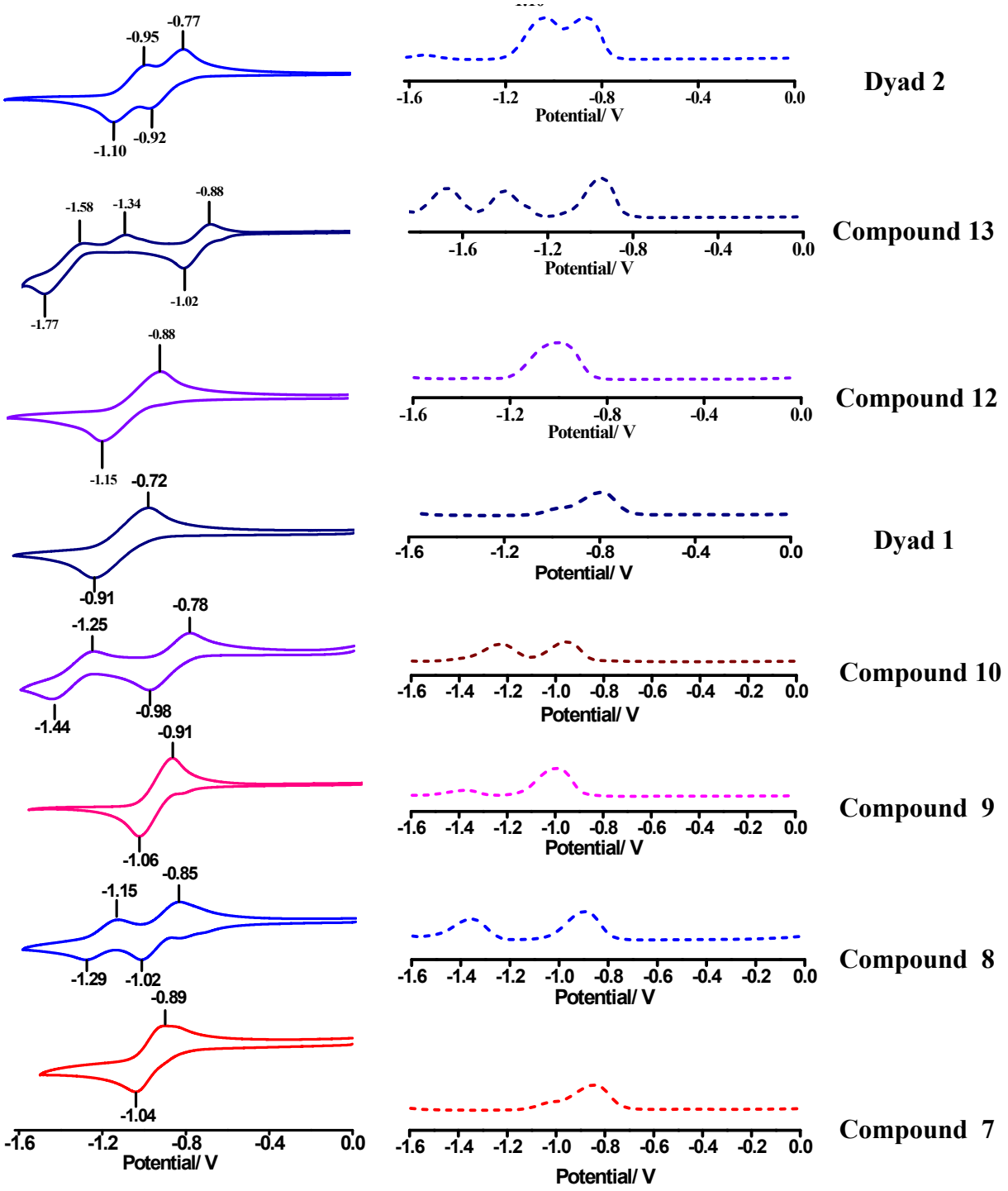


Fig. S40 Cyclic voltammograms of compounds **7-13** and dyad **1** and **2** recorded in CH_2Cl_2 containing 0.1 MTBAP as the supporting electrolyte and a saturated calomel electrode as the reference electrode at a scan rate of 50 mV s^{-1}.

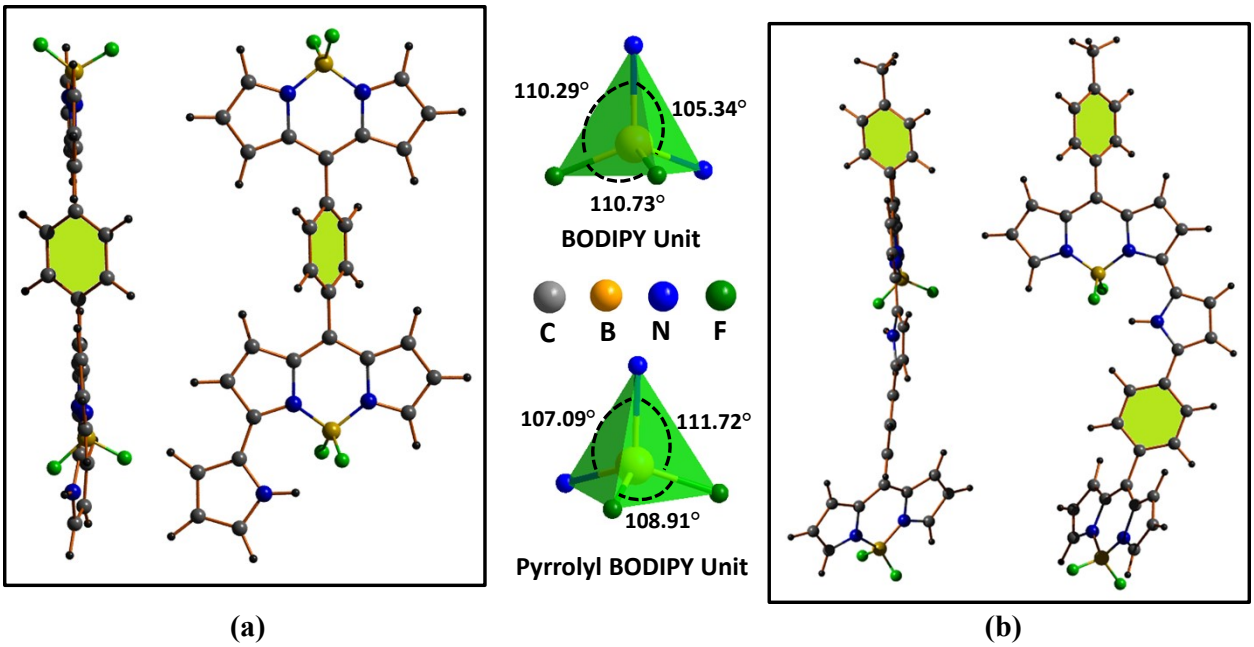


Fig. S41 DFT optimized structure of (a) dyad **1** and (b) dyad **2**.

Table S5. S_0 optimized geometry of the compound **1** at B3LYP/6-31g (d,p).

Atom	X	Y	Z	Atom	X	Y	Z
F	-1.675478000000	-0.699536000000	0.615749000000	F	-2.237299000000	-0.891100000000	-1.588356000000
N	-3.705951000000	-1.857193000000	0.076340000000	N	-3.568609000000	0.618866000000	-0.233080000000
N	-0.671443000000	1.582273000000	-0.356971000000	H	-0.730577000000	0.662453000000	0.072769000000
C	-4.961230000000	0.650383000000	-0.082355000000	C	-5.083905000000	-1.759490000000	0.226966000000
C	-5.722875000000	-0.503355000000	0.137157000000	C	-9.225789000000	-0.838960000000	1.547190000000
H	-9.700799000000	-1.235242000000	2.441019000000	C	-7.843416000000	-0.932894000000	1.412411000000
H	-7.253043000000	-1.388903000000	2.200510000000	C	-5.382892000000	2.007762000000	-0.156337000000
H	-6.400272000000	2.348177000000	-0.035559000000	C	-3.362714000000	-3.156836000000	0.198654000000
H	-2.330520000000	-3.463634000000	0.105678000000	C	-10.014398000000	-0.236953000000	0.557061000000

C	-3.139831000000	1.902484000000	-0.414556000000
H	-4.523496000000	-5.006993000000	0.566398000000
C	-7.982493000000	0.199170000000	-0.711334000000
C	-5.592950000000	-3.062250000000	0.438384000000
C	-9.366096000000	0.279669000000	-0.571992000000
C	0.465654000000	2.293894000000	-0.620052000000
H	-4.213879000000	3.853067000000	-0.454450000000
C	-11.516357000000	-0.172677000000	0.691851000000
H	-1.965777000000	4.415288000000	-1.366015000000
H	0.720228000000	4.354033000000	-1.394186000000
C	2.938597000000	2.547348000000	-0.483479000000
C	4.398462000000	0.634949000000	-0.130485000000
C	1.985750000000	0.343056000000	-0.248588000000
H	2.825882000000	3.616452000000	-0.630418000000
H	3.377858000000	-1.253791000000	0.072636000000
C	6.637748000000	0.614426000000	0.983020000000
C	7.620001000000	1.719060000000	2.694751000000
N	7.927227000000	0.111135000000	1.140251000000
H	7.827110000000	2.378853000000	3.524977000000
C	5.754781000000	0.068443000000	0.030980000000
C	6.363508000000	-2.719056000000	-2.241943000000
C	6.162995000000	-1.025336000000	-0.756469000000
H	8.461008000000	-3.163436000000	-1.547622000000
C	-4.505256000000	-3.935292000000	0.429875000000
C	-7.196204000000	-0.410297000000	0.279927000000
H	-7.505505000000	0.590422000000	-1.604101000000
H	-6.634424000000	-3.312976000000	0.573406000000
H	-9.952945000000	0.748443000000	-1.357676000000
C	-4.264885000000	2.777280000000	-0.373344000000
C	-1.787710000000	2.343270000000	-0.603490000000
C	-1.336204000000	3.595463000000	-1.052192000000
C	0.063117000000	3.561889000000	-1.066337000000
B	-2.747500000000	-0.712458000000	-0.316664000000
C	4.210740000000	2.016108000000	-0.323502000000
C	3.259342000000	-0.189038000000	-0.096746000000
C	1.796111000000	1.724889000000	-0.449098000000
H	5.075910000000	2.668867000000	-0.370357000000
H	1.132874000000	-0.328041000000	-0.222131000000
C	6.441264000000	1.620865000000	1.966704000000
C	8.507634000000	0.767113000000	2.156158000000
H	5.528103000000	2.176583000000	2.119434000000
H	9.516998000000	0.524838000000	2.458812000000
C	7.545240000000	-2.591735000000	-1.485989000000
C	5.496611000000	-1.730470000000	-1.795160000000
N	7.429504000000	-1.587059000000	-0.604828000000
H	6.185834000000	-3.445722000000	-3.021579000000

H	4.504778000000	-1.514576000000	-2.163299000000	H	-11.985525000000	-1.086948000000	0.307574000000
H	-11.820278000000	-0.068139000000	1.737592000000	H	-11.933627000000	0.667820000000	0.130083000000
B	8.583326000000	-1.040862000000	0.305171000000	F	9.601410000000	-0.538282000000	-0.485265000000
F	9.040895000000	-2.033720000000	1.150777000000				

Table S6. S_0 optimized geometry of the compound **2** at B3LYP/6-31g (d,p).

Atom	**X**	**Y**	**Z**	**Atom**	**X**	**Y**	**Z**
F	-5.682701000000	1.367825000000	-0.974477000000	F	-5.473882000000	1.225608000000	1.294296000000
N	-3.679064000000	2.244091000000	0.018173000000	N	-4.068232000000	-0.219068000000	-0.046124000000
C	-3.890545000000	3.577397000000	-0.052182000000	H	-4.896358000000	3.973507000000	-0.039730000000
C	-2.665330000000	4.250026000000	-0.144204000000	H	-2.534857000000	5.320761000000	-0.216191000000
C	-1.665874000000	3.272626000000	-0.135909000000	H	-0.598780000000	3.419921000000	-0.214503000000
C	-2.309786000000	2.021148000000	-0.027771000000	C	-1.800380000000	0.701580000000	-0.021068000000
C	-2.676826000000	-0.382757000000	-0.013099000000	C	-2.398958000000	-1.776985000000	0.087809000000
H	-1.410378000000	-2.207310000000	0.144723000000	C	-3.602620000000	-2.437748000000	0.103143000000
H	-3.771930000000	-3.503529000000	0.152302000000	C	-4.636012000000	-1.454666000000	0.019868000000
C	0.253271000000	-0.415445000000	-0.927166000000	H	-0.370084000000	-0.930502000000	-1.649489000000
C	-0.339693000000	0.481877000000	-0.022194000000	C	0.485620000000	1.177284000000	0.878668000000
H	0.036209000000	1.857693000000	1.593038000000	B	-4.776013000000	1.165311000000	0.094534000000
F	7.574433000000	-0.685738000000	1.296596000000	F	7.822019000000	-0.666199000000	-0.975948000000
N	5.815403000000	-1.659612000000	-0.043296000000	N	6.163038000000	0.797654000000	0.000812000000
C	6.024961000000	-2.985853000000	-0.031700000000	C	4.796300000000	-3.674077000000	-0.002541000000
H	4.673019000000	-4.747783000000	0.011890000000	C	3.797688000000	-2.707157000000	0.013381000000
H	2.729994000000	-2.863262000000	0.055433000000	C	4.439010000000	-1.441585000000	-0.023794000000
C	3.913321000000	-0.137694000000	-0.019003000000	C	4.780538000000	0.968699000000	-0.023691000000
C	4.514799000000	2.358976000000	-0.129820000000	H	3.531725000000	2.800567000000	-0.198651000000

C	5.742363000000	3.010523000000	-0.154570000000	H	5.921935000000	4.073507000000	-0.232529000000
C	6.732287000000	2.011210000000	-0.076767000000	H	7.809152000000	2.111612000000	-0.082352000000
C	1.861488000000	0.976814000000	0.878908000000	H	2.486158000000	1.497933000000	1.595608000000
C	2.452734000000	0.073213000000	-0.021499000000	C	1.628811000000	-0.619837000000	-0.925213000000
H	2.078219000000	-1.293482000000	-1.645912000000	B	6.921283000000	-0.563942000000	0.075300000000
C	-6.031112000000	-1.765114000000	0.010508000000	C	-6.626803000000	-3.004075000000	0.289995000000
C	-8.017966000000	-2.850305000000	0.153610000000	H	-6.093787000000	-3.898363000000	0.580446000000
C	-8.247130000000	-1.527677000000	-0.215129000000	H	-8.775942000000	-3.605698000000	0.305729000000
H	-9.169266000000	-1.007897000000	-0.430928000000	N	-7.052493000000	-0.887169000000	-0.290650000000
H	-6.897409000000	0.069366000000	-0.593215000000	H	7.031731000000	-3.381006000000	-0.032882000000

Table S7. Major transitions were calculated using TD-DFT studies of **1**.

Wavelength (nm)	**Osc. Strength**	**Major contribs**
630.70	0.1703	HOMO->LUMO (94%)
503.14	0.6744	HOMO->L+1 (93%)
457.48	0.1645	H-1->LUMO (89%), H-1->L+1 (10%)
407.03	0.2609	H-1->L+1 (83%)
397.76	0.4155	H-2->LUMO (92%)
371.36	0.0338	H-3->LUMO (73%)
363.37	0.1384	H-5->LUMO (83%)
357.03	0.0368	H-4->LUMO (71%), H-3->LUMO (12%)
350.37	0.1423	H-6->LUMO (12%), H-2->L+1 (73%)

346.48	0.0276	H-7->LUMO (71%), H-6->LUMO (18%)
338.21	0.1377	H-7->LUMO (20%), H-6->LUMO (55%)
329.73	0.0109	H-9->LUMO (12%), H-8->LUMO (55%), H-3->L+1 (17%)
328.91	0.0217	H-8->LUMO (15%), H-3->L+1 (60%)
323.26	0.0065	H-9->LUMO (82%)
318.37	0.0046	H-4->L+1 (76%)
313.32	0.0096	H-5->L+1 (91%)
308.96	0.0085	HOMO->L+2 (96%)
308.84	0.0245	H-6->L+1 (57%), HOMO->L+3 (30%)
302.65	0.0075	H-6->L+1 (28%), HOMO->L+3 (65%)
297.58	0.0069	H-7->L+1 (91%)
296.64	0.0104	H-9->L+1 (27%), H-8->L+1 (62%)
293.63	0.0062	H-9->L+1 (69%), H-8->L+1 (24%)
267.85	0.0064	H-1->L+2 (100%)
264.87	0.0296	H-1->L+3 (99%)
258.44	0.2221	H-10->LUMO (38%), HOMO->L+4 (53%)
256.23	0.2948	H-10->LUMO (58%), HOMO->L+4 (36%)
240.41	0.0028	H-11->LUMO (35%), H-10->L+1 (60%)
239.27	0.0893	H-11->LUMO (46%), H-10->L+1 (33%)
237.00	0.0002	H-12->LUMO (81%), H-12->L+1 (15%)
236.01	0.0082	H-9->L+3 (11%), H-2->L+2 (79%)
229.53	0.0042	H-2->L+3 (85%)
224.51	0.0001	H-13->LUMO (59%), H-13->L+1 (27%)
223.35	0.002	H-14->LUMO (10%), H-11->L+1 (63%), HOMO->L+6 (10%)

223.13	0.003	H-4->L+2 (11%), H-3->L+2 (58%), H-2->L+2 (10%)
222.51	0.0	H-1->L+4 (98%)
220.08	0.0098	H-14->LUMO (13%), H-3->L+2 (10%), H-3->L+3 (62%)
219.70	0.0183	H-14->LUMO (59%)
218.58	0.0067	H-9->L+3 (12%), H-6->L+2 (33%), H-3->L+2 (19%), H-3->L+3 (16%)
217.68	0.0005	HOMO->L+5 (100%)
217.43	0.0058	H-5->L+2 (99%)
215.35	0.0821	H-2->L+4 (14%), HOMO->L+6 (62%)
215.22	0.0011	H-5->L+3 (92%)
211.44	0.0005	H-4->L+3 (73%)
210.93	0.0022	H-6->L+2 (12%), H-4->L+2 (72%)
209.97	0.0004	H-7->L+2 (94%)
209.62	0.0017	H-17->LUMO (79%), H-17->L+1 (10%)
209.41	0.0451	H-6->L+3 (18%), H-2->L+4 (52%)
207.88	0.0094	H-7->L+3 (79%), H-6->L+3 (13%)
207.10	0.0173	H-15->LUMO (67%), H-15->L+1 (22%)
206.03	0.0031	H-18->LUMO (13%), H-7->L+3 (14%), H-6->L+3 (35%)

Table S8. Major transitions were calculated using TD-DFT studies of **2**.

Wavelength (nm)	**Osc. Strength**	**Major contribs**
631.25	0.7257	HOMO->LUMO (94%)
532.66	0.4538	HOMO->L+1 (94%)
448.81	0.0976	H-1->LUMO (91%)
410.44	0.3223	H-1->L+1 (87%)
402.74	0.3472	H-2->LUMO (92%)
376.94	0.0259	H-3->LUMO (23%), H-2->L+1 (70%)
369.60	0.0189	H-3->LUMO (54%), H-3->L+1 (15%), H-2->L+1 (17%)
355.60	0.1132	H-4->LUMO (72%), H-4->L+1 (19%)
352.61	0.063	H-5->LUMO (66%), H-5->L+1 (17%)
341.03	0.0279	H-7->LUMO (28%), H-7->L+1 (12%), H-6->LUMO (46%), H-6->L+1 (10%)
337.50	0.0132	H-8->LUMO (74%), H-8->L+1 (20%)
336.75	0.0063	H-7->LUMO (47%), H-6->LUMO (35%)
332.32	0.1679	H-3->LUMO (19%), H-3->L+1 (67%)
328.18	0.0076	H-9->LUMO (65%), H-6->L+1 (12%)
322.24	0.0417	H-10->LUMO (50%), H-10->L+1 (11%), HOMO->L+2 (21%)
316.92	0.3774	H-10->LUMO (19%), H-5->LUMO (10%), H-5->L+1 (18%), HOMO->L+2 (28%)
316.22	0.0144	H-4->LUMO (19%), H-4->L+1 (72%)
313.10	0.1897	H-5->L+1 (56%), HOMO->L+2 (22%)
310.48	0.0237	H-9->LUMO (12%), H-7->L+1 (22%), H-6->L+1 (52%)
300.26	0.0018	H-9->L+1 (22%), H-7->L+1 (31%), H-6->L+1 (19%)

300.08	0.0025	H-9->L+1 (17%), H-8->LUMO (13%), H-8->L+1 (43%), H-7->L+1 (10%)
299.58	0.0011	H-9->L+1 (27%), H-8->L+1 (34%)
294.03	0.0076	H-11->LUMO (58%), HOMO->L+3 (27%)
292.42	0.0104	H-11->LUMO (31%), HOMO->L+3 (50%)
288.74	0.0028	H-10->LUMO (19%), H-10->L+1 (69%)
283.90	0.0568	HOMO->L+4 (78%), HOMO->L+5 (19%)
282.57	0.0325	H-1->L+2 (97%)
282.27	0.0068	HOMO->L+4 (20%), HOMO->L+5 (74%)
277.87	0.015	H-11->L+1 (86%)
257.33	0.0068	H-1->L+3 (99%)
254.95	0.1751	H-2->L+2 (51%), HOMO->L+6 (38%)
251.09	0.0069	H-12->LUMO (46%), HOMO->L+6 (36%)
243.23	0.1065	H-12->LUMO (37%), H-2->L+2 (33%), HOMO->L+6 (12%)
238.61	0.0202	H-13->LUMO (39%), H-12->L+1 (40%)
234.55	0.002	H-13->LUMO (30%), H-12->L+1 (38%), H-2->L+3 (16%)
234.23	0.001	H-13->LUMO (14%), H-12->L+1 (13%), H-9->L+2 (13%), H-2->L+3 (38%)
232.59	0.0026	H-3->L+4 (19%), H-2->L+4 (21%), H-2->L+5 (17%)
230.72	0.0001	H-1->L+4 (85%), H-1->L+5 (14%)
230.68	0.0004	H-14->LUMO (63%), H-14->L+1 (33%)
230.08	0.0002	H-1->L+4 (15%), H-1->L+5 (84%)
228.74	0.0165	H-3->L+2 (87%)
226.51	0.0016	H-4->L+2 (92%)
225.90	0.0265	H-13->L+1 (80%)

224.64	0.0452	H-2->L+4 (40%), H-2->L+5 (36%)
223.31	0.0101	H-7->L+2 (15%), H-6->L+2 (17%), H-5->L+2 (48%)
222.59	0.0078	H-6->L+2 (31%), H-5->L+2 (41%)
219.56	0.006	HOMO->L+7 (99%)
219.30	0.0103	H-3->L+4 (17%), H-2->L+4 (23%), H-2->L+5 (30%)
218.94	0.0031	H-16->LUMO (20%), H-15->LUMO (43%), H-15->L+1 (18%)
218.22	0.0065	H-8->L+2 (96%)

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