Electronic Supporting Information

Low Bandgap Coplanar Conjugated Molecules Featuring Dynamic Intramolecular Lewis Acid-Base Coordination

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Supporting Information

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1. ^{1}H, ^{11}B, ^{13}C NMR Spectra

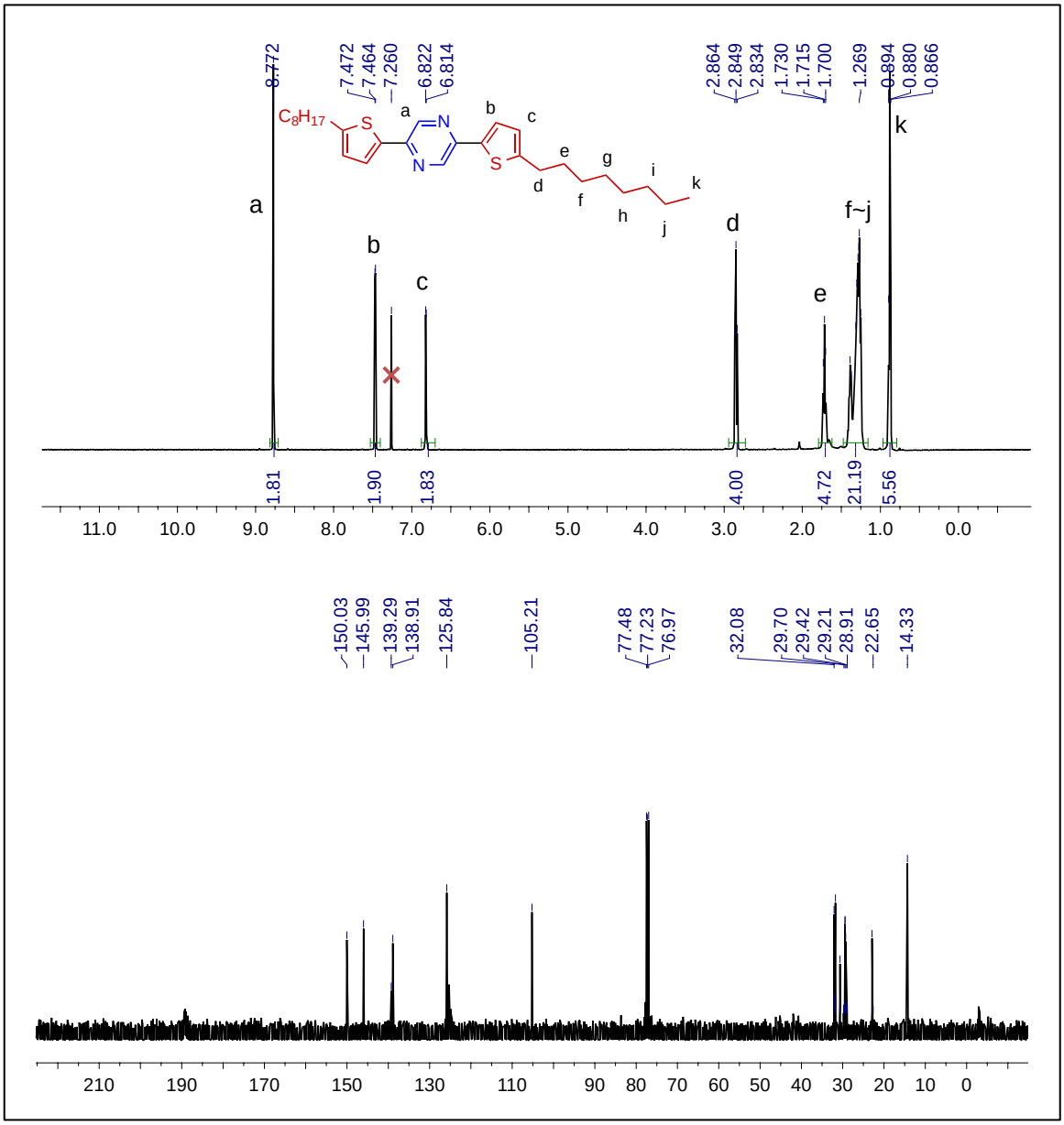


Figure S1. ^{1}H (500 MHz), ^{13}C NMR (125 MHz) spectra of **Compound 1** in $CDCl_3$ at room temperature.

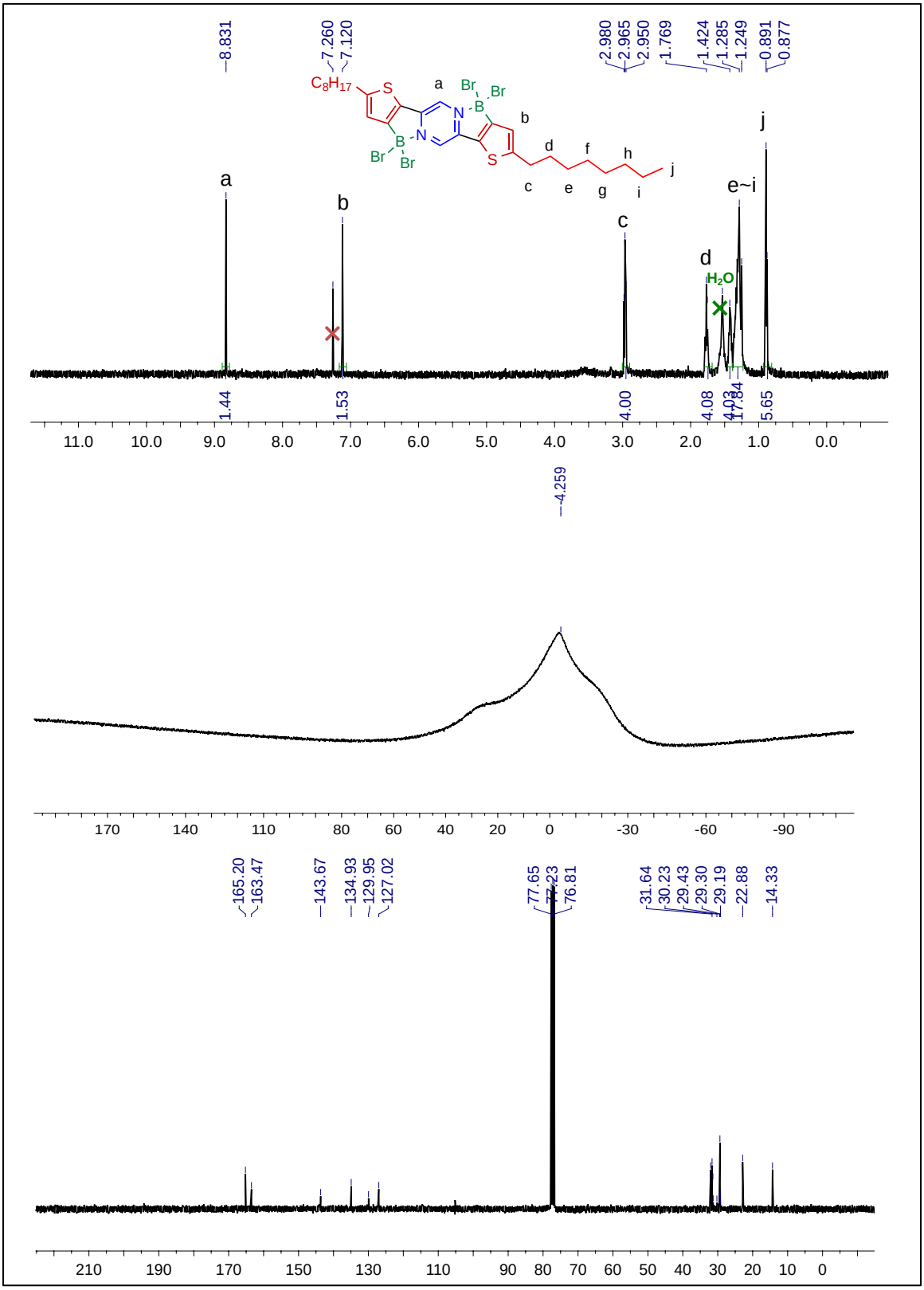


Figure S2. ^{1}H (500 MHz), ^{11}B (128 MHz), ^{13}C NMR (75 MHz) spectra of **Compound 2** in $CDCl_3$ at room temperature.

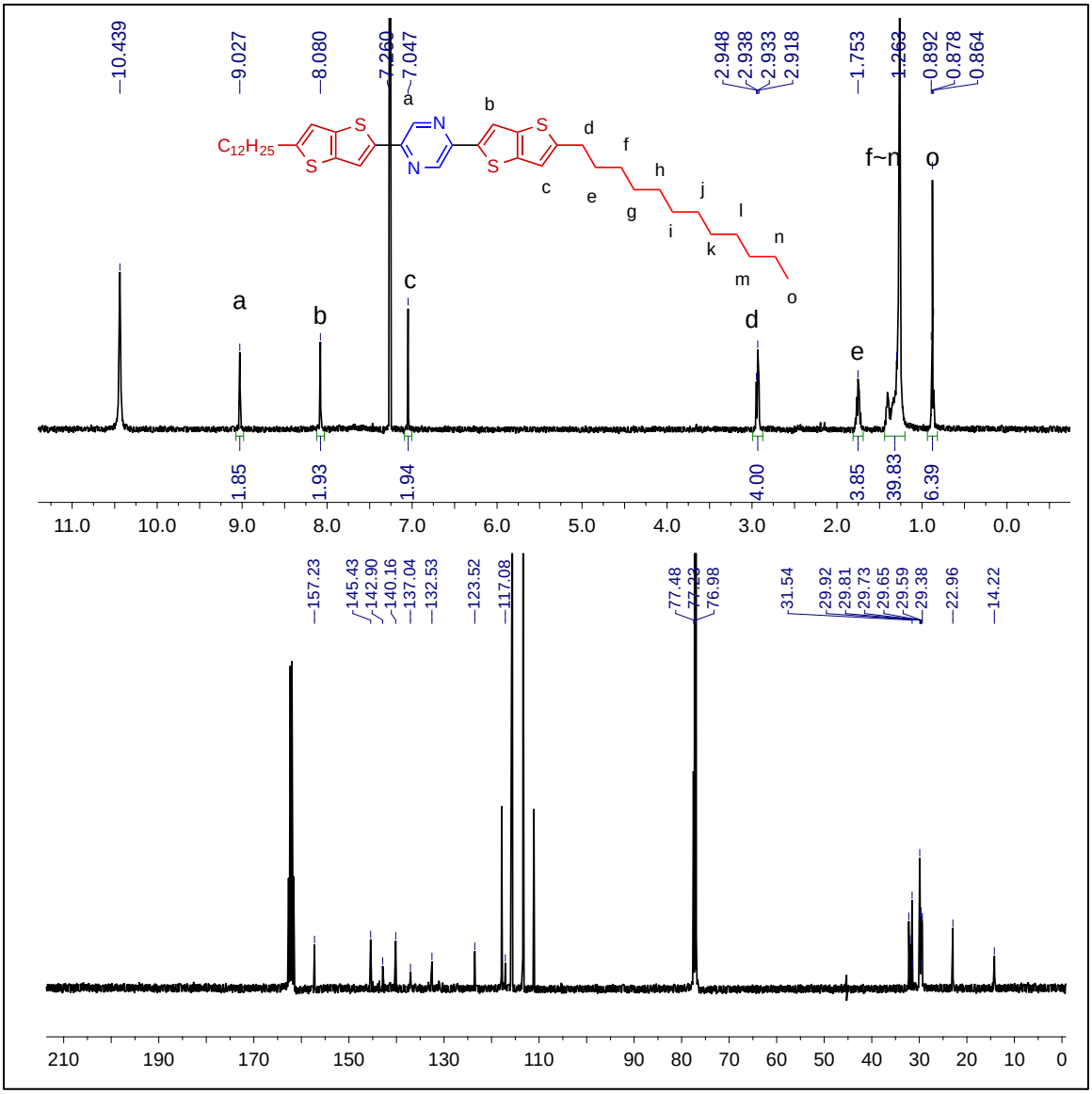
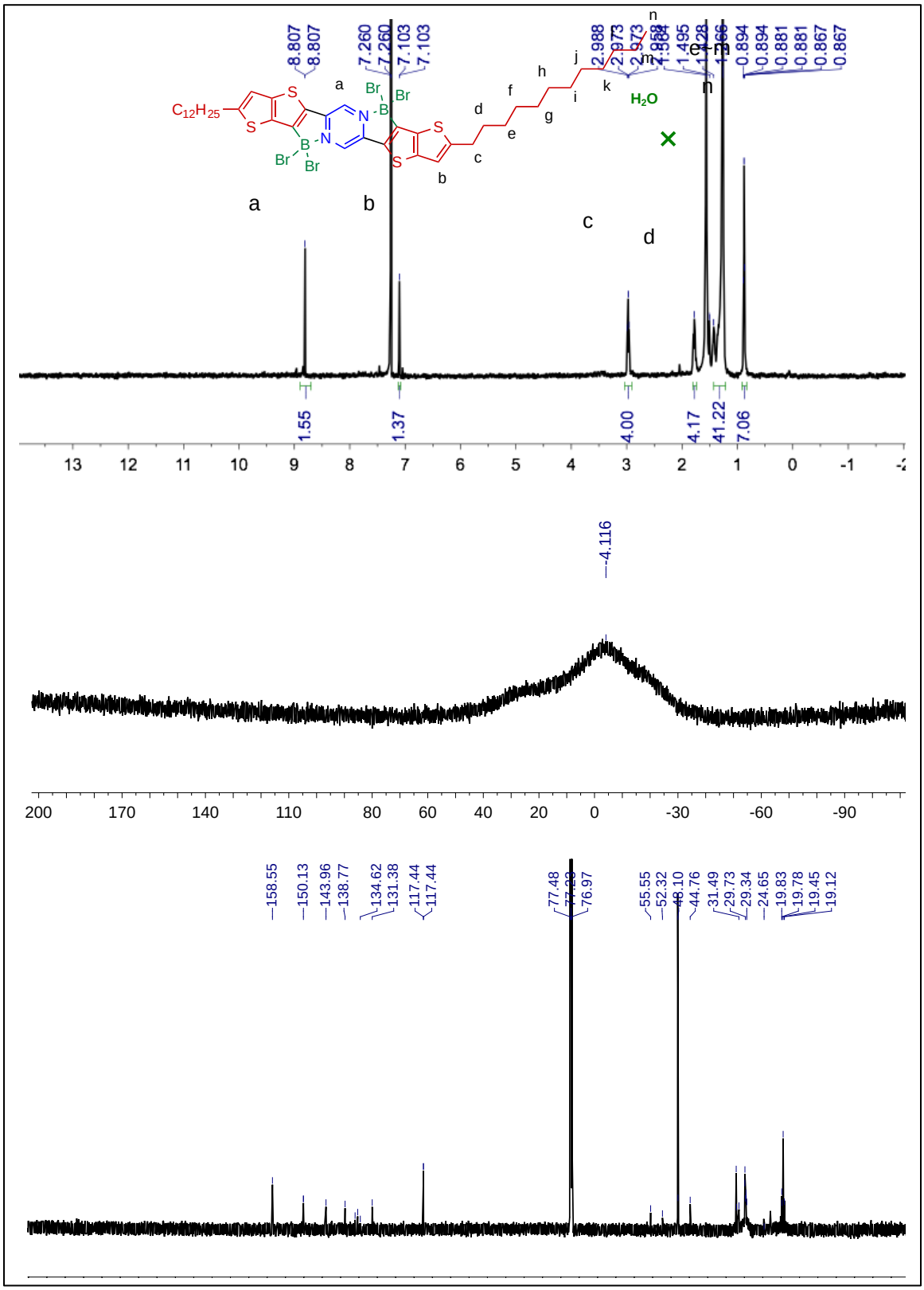


Figure S3. ^{1}H (500 MHz), ^{13}C NMR (125 MHz) spectra of **Compound 3** in $CDCl_3$ & TFA at room temperature.

Figure S4. ^{1}H (500 MHz), ^{11}B (128 MHz), ^{13}C NMR (125 MHz) spectra of **Compound 4**



in $CDCl_3$ at room temperature.

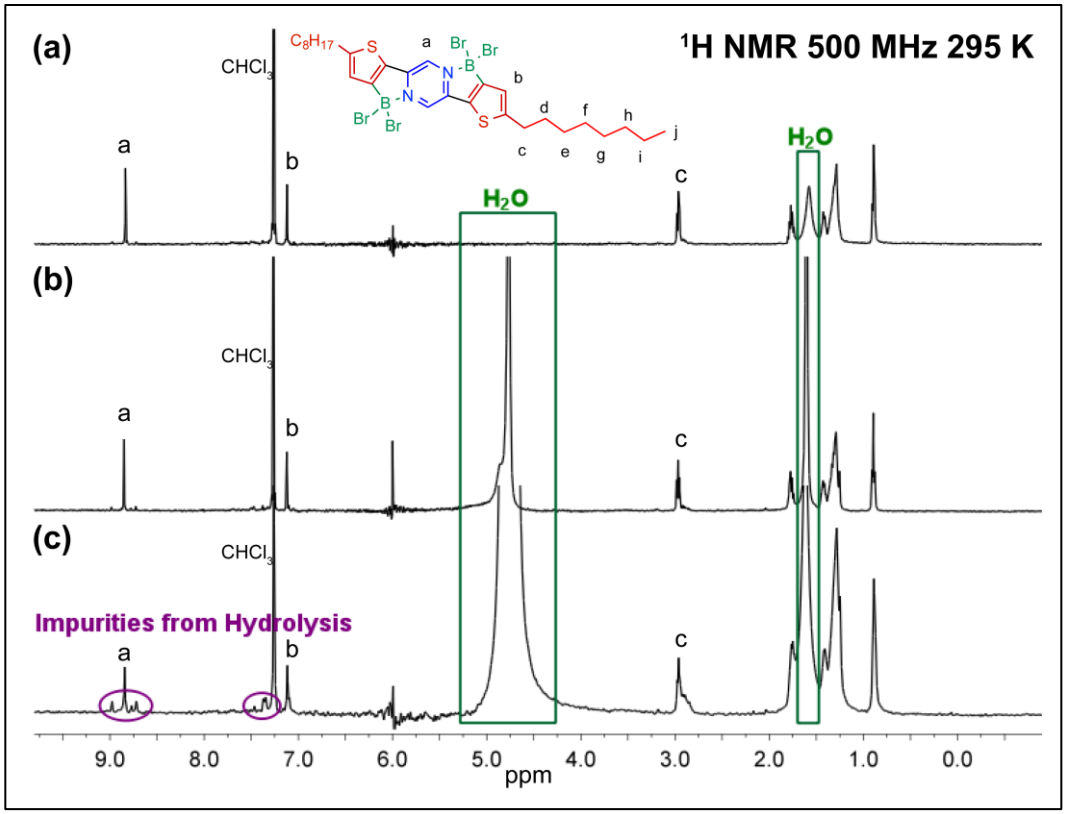


Figure S5. ^{1}H NMR spectra of (a) Freshly prepared $CDCl_3$ solution of **Compound 2**; (b) $CDCl_3$ solution of **Compound 2**, 10 min after adding water; (c) $CDCl_3$ solution of **Compound 2**, 2hrs after adding water.

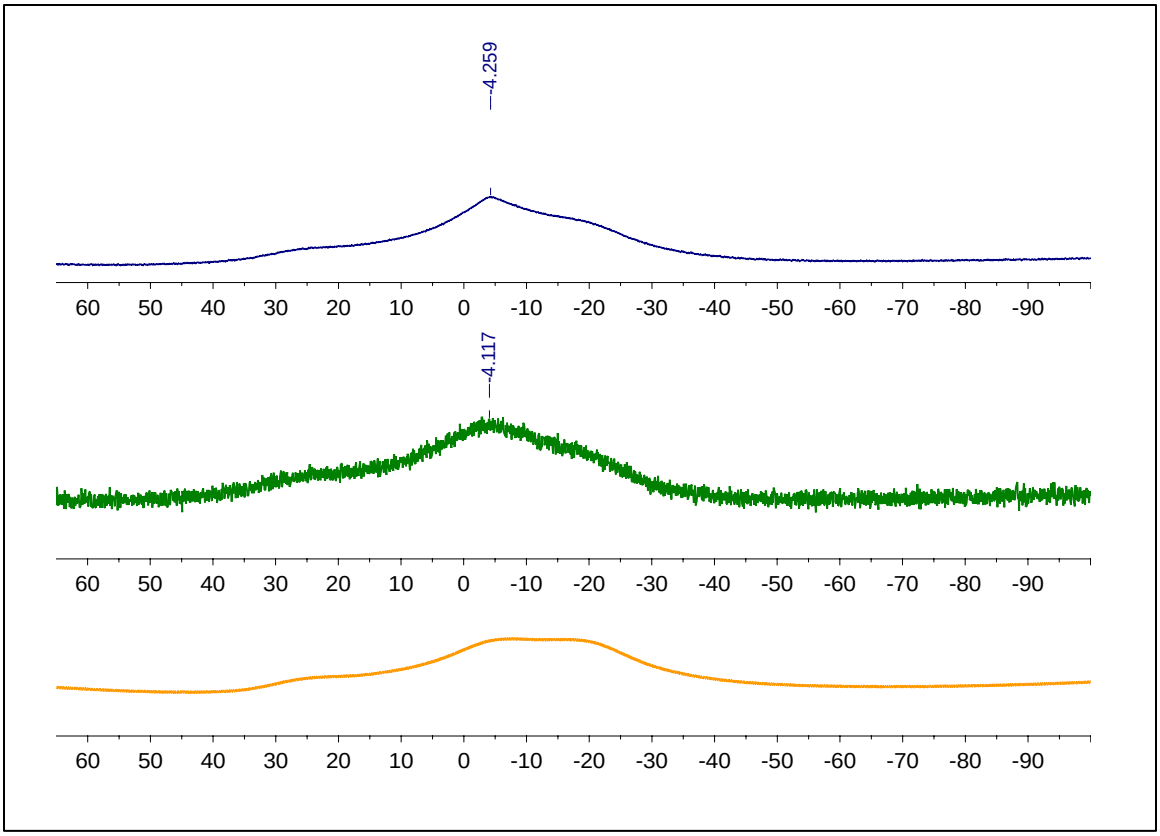


Figure S6. ^{11}B NMR spectra of **Compound 2** (blue) and **Compound 4** (green) in $CDCl_3$, and a background ^{11}B NMR of D_2O (orange). The broad signal between 25 pm and -20 ppm is a result of glassy NMR probe containing boron.

2. UV/vis Absorption Spectroscopy

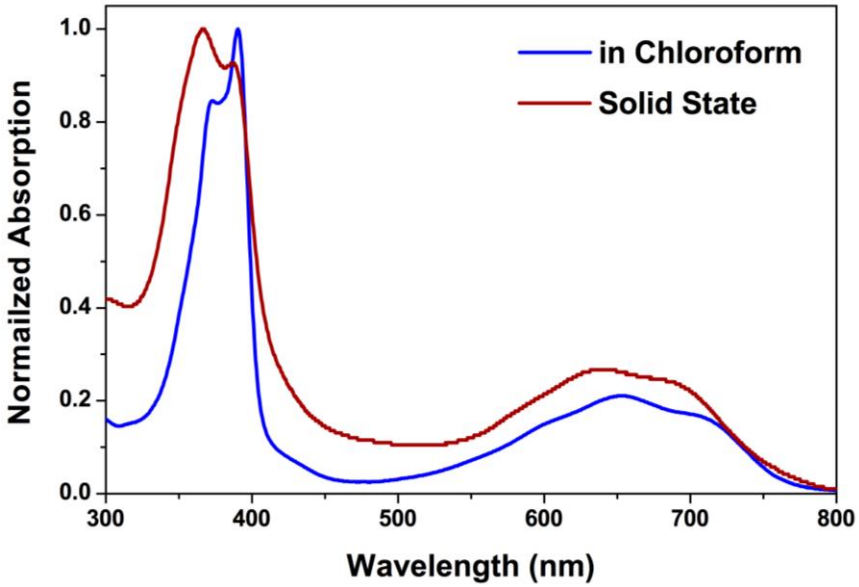


Figure S7. Normailzed UV-vis absorption spectra of **Compound 2** in chloroform (9.9×10^{-6} M) and in solid state.

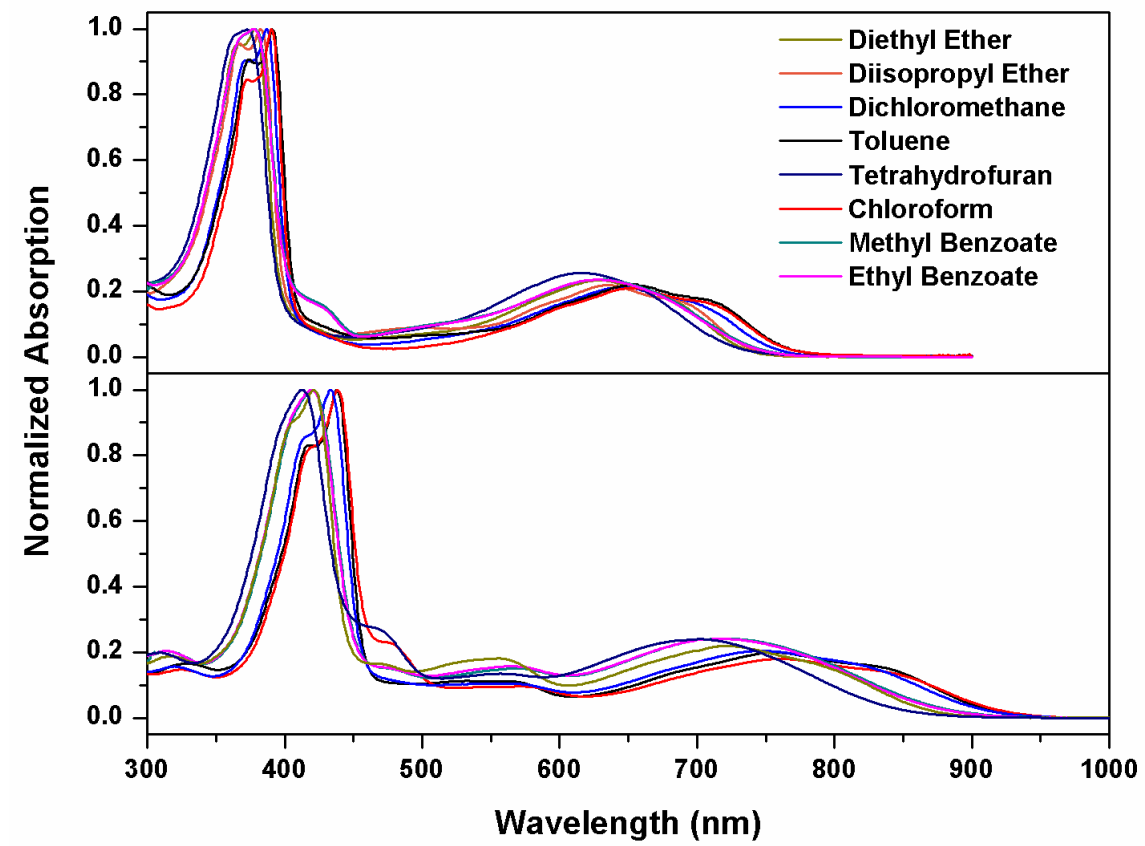


Figure S8. Normalized absorption spectra of **Compound 2** (top, concentration: 9.9×10^{-6} M) and **Compound 4** (bottom, concentration: 9.7×10^{-6} M) in a series of organic solvents at room temperature.

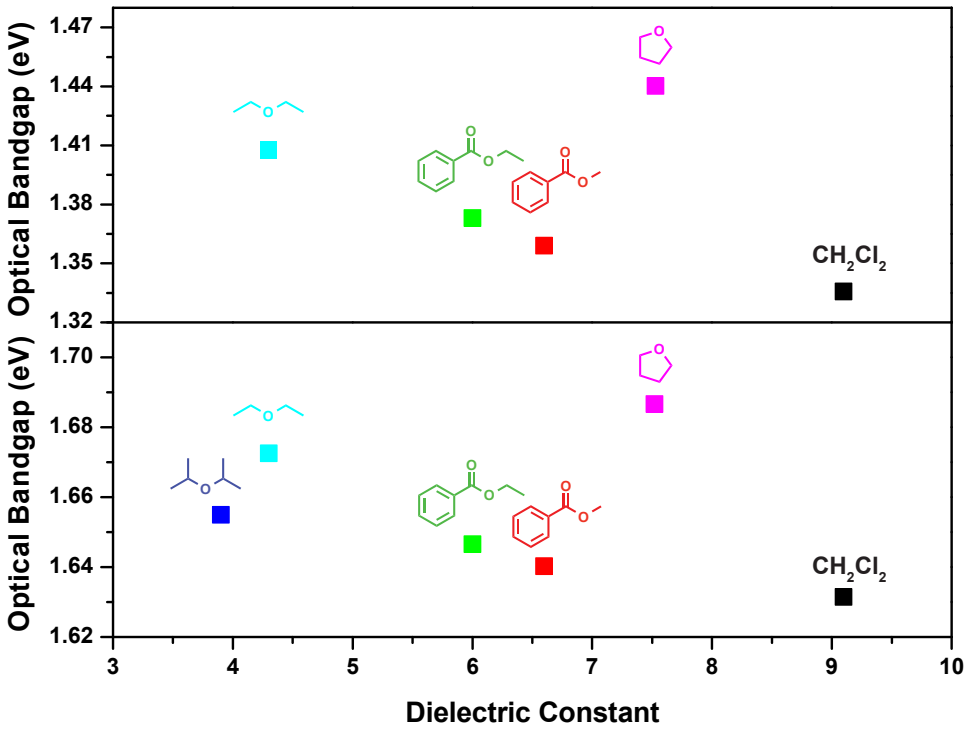


Figure S9. Plots of optical bandgaps of **2** (bottom) and **4** (top) against dielectric constants of organic solvents[1,2,3].

3. Variable-Temperature NMR Result

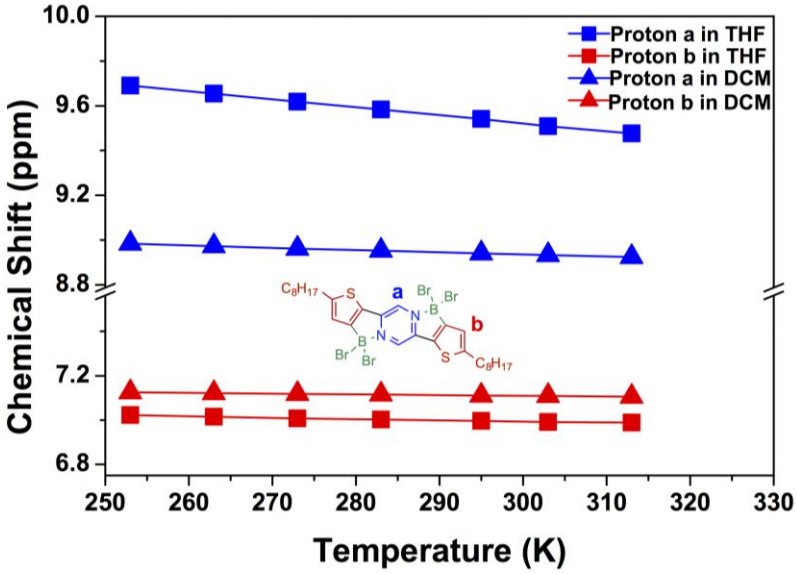


Figure S10. Chemical shift change of protons in the aromatic region of **Compound 2** in CD_2Cl_2 and d_8-THF against the temperature.

4. Cyclic Voltammetry

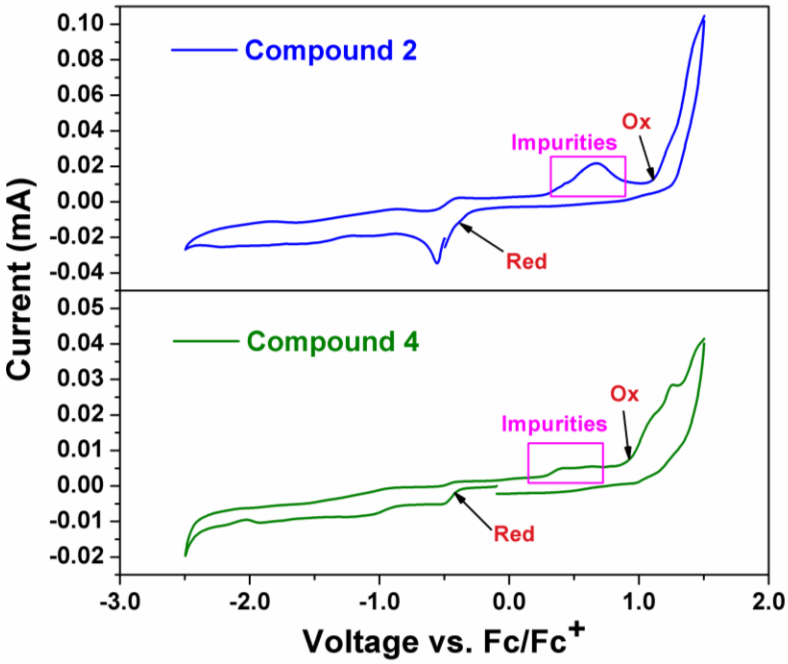


Figure S11. Cyclic voltammetry of **2** and **4**, 0.10 M *n*-Bu_4NPF_6 in CH_2Cl_2, Fc = ferrocene.

5. DFT Calculation

Atomic structures of **1**−**4** were optimized with Density Functional Theory (DFT) calculations using B3LYP/6-311g(d,p). Molecular orbitals shapes and energies were calculated at the optimized geometries. The alkyl chain were replaced with methyl groups for computational simplicity. Orbital pictures were generated with Gaussview 5.08. For computed UV/vis spectra of **2** and **4**, Time-Dependent Density Functional Theory [B3YLP/6-311g(d,p)] was applied to the optimized geometry. All quantum chemical calculations were performed with Gaussian09 package[4].

a) Atom Coordinates

Compound 1

Total Energy: -1446.79328748 a.u.

Atom Coordinates:

C	1.34846400	-0.14834500	-0.00057300
C	0.72301100	1.11197600	-0.00040500
C	-1.34845900	0.14840600	-0.00063000
C	-0.72298800	-1.11193800	-0.00102300
C	2.79612500	-0.32583100	-0.00044000
C	-2.79612900	0.32585600	-0.00049200
C	3.48224800	-1.51453200	-0.00192100
C	4.89228800	-1.35346200	-0.00146800
C	5.30105500	-0.04717500	0.00031300
S	3.92057700	1.02187200	0.00181200
C	-3.48228700	1.51453800	-0.00220600
C	-4.89232500	1.35343400	-0.00173900
C	-5.30106100	0.04713800	0.00036000
S	-3.92055300	-1.02187200	0.00197600
C	6.69735100	0.49395000	0.00121600
C	-6.69734400	-0.49402400	0.00136200
H	1.31202100	2.02525700	-0.00044800
H	-1.31201800	-2.02520800	-0.00143000
H	2.96725900	-2.46467900	-0.00331700
H	5.59118900	-2.18062400	-0.00250200
H	-2.96732200	2.46469600	-0.00374800
H	-5.59124600	2.18057900	-0.00297200
H	7.41150600	-0.33172400	-0.00031600
H	6.89569900	1.10818100	0.88483300
H	6.89562300	1.11138100	-0.88018300
H	-6.89591900	-1.11076200	-0.88045800

H	-7.41152500	0.33162800	0.00075000
H	-6.89535000	-1.10896100	0.88456000
N	0.59233600	-1.26236700	-0.00092200
N	-0.59233500	1.26241100	-0.00043600

Compound 2

Total Energy: -11792.10130680 a.u.

Atom Coordinates:

C	-1.11144700	0.81148500	0.00001900
C	0.17365200	1.35841200	0.00003200
C	1.11144900	-0.81150300	-0.00012500
C	-0.17364000	-1.35842400	-0.00013300
C	-2.40935100	1.40952300	0.00005900
C	2.40937000	-1.40952200	-0.00022500
C	-3.43049400	0.47749000	0.00001400
C	-4.70041900	1.10128400	0.00003600
C	-4.63945200	2.47430700	0.00008800
S	-2.98042500	3.05007900	0.00011400
C	3.43050100	-0.47749100	-0.00020900
C	4.70043300	-1.10128900	-0.00010200
C	4.63948100	-2.47430300	-0.00000500
S	2.98042300	-3.05008900	-0.00004700
C	-5.77481200	3.44915100	0.00012800
C	5.77481900	-3.44916500	0.00009800
Br	-3.14517400	-2.04200300	-1.69306000
Br	-3.14505900	-2.04196500	1.69305400
Br	3.14500200	2.04218700	-1.69302800
Br	3.14521600	2.04179800	1.69308100
H	0.35917200	2.42404300	0.00005900
H	-0.35916800	-2.42405300	-0.00020800
H	-5.64157900	0.56703000	0.00001800
H	5.64158800	-0.56702300	-0.00010300
H	-6.72245000	2.90842100	0.00010400
H	-5.75320600	4.09477300	-0.88271600
H	-5.75320900	4.09469800	0.88302700
H	5.75325800	-4.09477400	-0.88275700
H	5.75313900	-4.09473100	0.88298200
H	6.72247300	-2.90846300	0.00014900
N	-1.23160800	-0.55727000	-0.00006400

N	1.23161300	0.55726200	-0.00003500
B	-2.80475800	-0.97881000	-0.00004500
B	2.80475400	0.97880300	-0.00008800

Compound 3

Total Energy: -2395.67447480 a.u.

Atom Coordinates:

C	-1.35367500	0.05059700	-0.00008300
C	-0.56744600	1.21604400	0.00066600
N	0.75650600	1.18452500	0.00064000
C	1.35902600	-0.01786400	-0.00012800
C	0.57070300	-1.18644200	-0.00101600
N	-0.75056800	-1.15632500	-0.00095200
C	-2.80978200	0.06469800	0.00001800
C	2.81157400	-0.03753200	-0.00013000
C	3.66953900	-1.11547000	0.00059300
C	5.02301200	-0.70792500	0.00020800
C	5.20293600	0.66941300	-0.00072700
S	3.67519300	1.50352200	-0.00116900
C	-3.63266200	-1.03723500	-0.00048800
C	-4.99917900	-0.67546200	-0.00038400
C	-5.23243900	0.69312900	0.00019200
S	-3.73185200	1.57560700	0.00058900
S	-6.51113200	-1.55004700	-0.00049300
C	-7.42645000	-0.04174600	0.00027700
C	-6.60804500	1.05337900	0.00060000
S	6.56487500	-1.53057800	0.00103400
C	7.42464500	0.01097900	0.00013000
C	6.56684100	1.07489600	-0.00074200
C	-8.92334700	-0.07016300	0.00046300
C	8.92154200	0.03628400	0.00049200
H	-1.02577600	2.20104300	0.00133500
H	1.02963300	-2.17036100	-0.00185200
H	3.34028300	-2.14498900	0.00153900
H	-3.23653700	-2.04192000	-0.00088500
H	-6.98382700	2.06774500	0.00109500
H	6.90671200	2.10198300	-0.00139100
H	-9.31239700	0.94977400	0.00149100
H	-9.31943100	-0.58068500	-0.88271900

H	-9.31918400	-0.58236200	0.88277900
H	9.27327800	1.06968000	-0.00066000
H	9.33554300	-0.45935200	0.88397000
H	9.33603800	-0.46149400	-0.88154300

Compound 4

Total Energy: -12740.98393760 a.u.

Atom Coordinates:

C	-1.20547100	0.66652000	0.00009800
C	0.00176600	1.37015100	0.00012300
C	1.20547100	-0.66652000	0.00009600
C	-0.00176600	-1.37015100	0.00012300
C	-2.56419800	1.09963400	0.00020300
C	2.56419800	-1.09963400	0.00019900
C	3.46017300	-0.04062100	0.00020700
C	4.77921200	-0.52916900	0.00000500
C	4.87650300	-1.92440400	-0.00009900
S	3.30258900	-2.68898600	-0.00003900
C	-3.46017300	0.04062100	0.00021300
C	-4.77921200	0.52916900	0.00001100
C	-4.87650300	1.92440400	-0.00009000
S	-3.30258900	2.68898600	-0.00003000
S	-6.36758100	-0.18913600	0.00036800
C	-7.12442600	1.39845400	0.00037600
C	-6.20551800	2.41566000	0.00013400
S	6.36758100	0.18913600	0.00033900
C	7.12442600	-1.39845300	0.00034300
C	6.20551800	-2.41566000	0.00011000
C	-8.61628200	1.51857900	0.00067600
C	8.61628200	-1.51857800	0.00073900
Br	-2.86928600	-2.41986900	1.69227200
Br	-2.86932100	-2.41901500	-1.69281800
Br	2.86932100	2.41902400	-1.69281300
Br	2.86928600	2.41986000	1.69227700
H	0.05069800	2.45080100	0.00016400
H	-0.05069800	-2.45080100	0.00016400
H	-6.48302400	3.46082700	0.00002900
H	6.48302400	-3.46082700	-0.00000700
H	-8.90594000	2.57078300	-0.00022100

H	-9.05717800	1.04655100	0.88368400
H	-9.05769100	1.04489400	-0.88117700
H	9.05705900	-1.04716100	0.88413600
H	9.05780900	-1.04428300	-0.88072300
H	8.90594100	-2.57078200	-0.00084500
B	2.65343500	1.32507000	0.00005600
B	-2.65343500	-1.32507000	0.00005800
N	-1.15190500	-0.70936400	0.00007800
N	1.15190500	0.70936500	0.00007600

b) Energy Levels and Transtion Energies

Dihedral Angle (°)	0	10	20	30	40	50
LUMO (eV)	-4.064	-4.063	-4.058	-4.048	-2.663	-2.656
HOMO (eV)	-6.417	-6.417	-6.418	-6.421	-6.368	-6.523
Bandgap (eV)	2.353	2.354	2.360	2.373	3.705	3.867
HOMO->LUMO Transition (eV)	1.8368	1.8371	1.8350	1.8352	3.0986	3.2175

Table S1. Calculated energy levels and HOMO → LUMO transition energies of **Compound 2** at different dihedral angles. (B3LYP/6-311g(d,p))

Dihedral Angle (°)	0	10	20	30	40	50
LUMO (eV)	-4.019	-4.017	-4.011	-4.001	-2.622	-2.674
HOMO (eV)	-5.999	-6.001	-6.007	-6.019	-5.952	-6.085
Bandgap (eV)	1.980	1.984	1.996	2.018	3.330	3.411
HOMO->LUMO Transition (eV)	1.5348	1.5364	1.5384	1.5434	2.7902	2.8252

Table S2. Calculated energy levels and HOMO → LUMO transition energies of **Compound 4** at different dihedral angles. (B3LYP/6-311g(d,p))

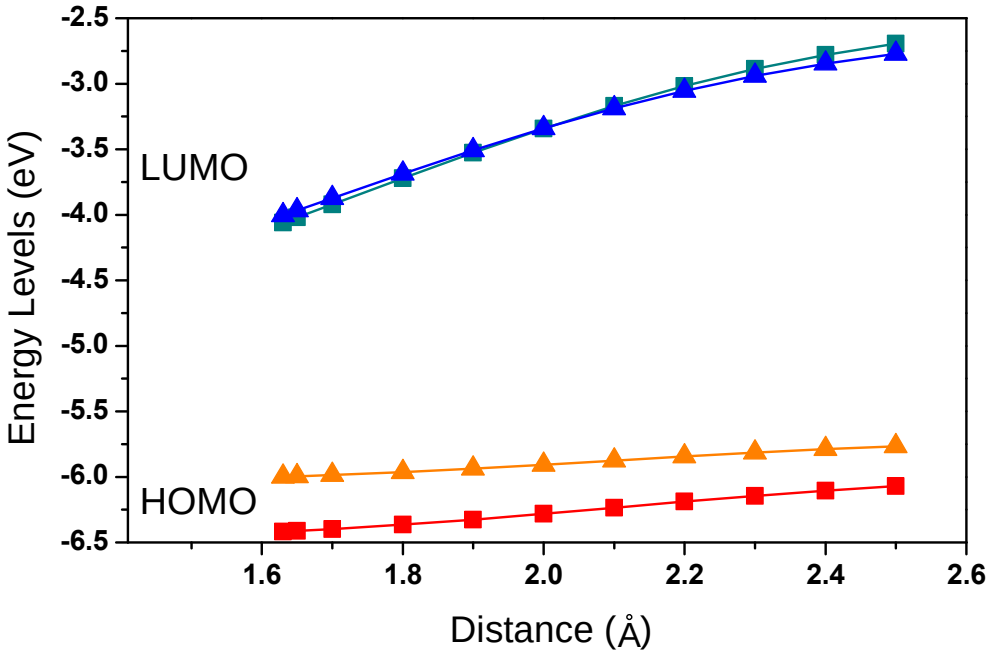


Figure S12. Correlation between B—N bond length and calculated energy levels of **Compound 2 (□) and Compound 4 (△)** . (B3LYP/6-311g(d,p))

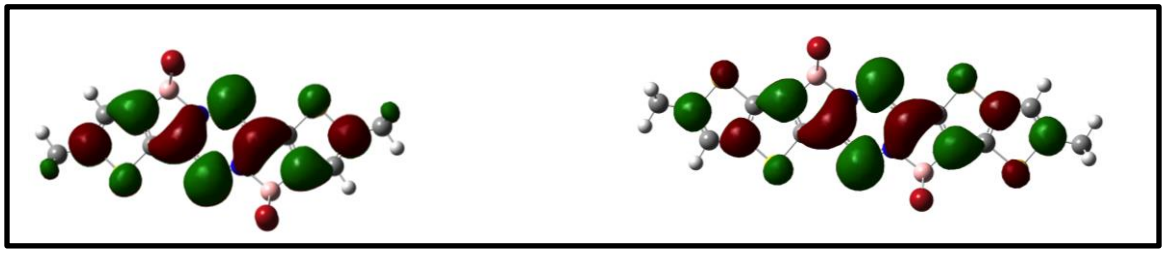


Figure S13. Calculated LUMO+1 orbitals of **Compound 2** (left) and **Compound 4** (right). (B3LYP/6-311g(d,p))

6. Reference

1. https://www.organicdivision.org/orig/organic_solvents.html
2. http://solvdb.ncms.org/solvdb.htm
3. https://www.kabusa.com/Dilectric-Constants.pdf
4. Gaussian 09 (Gaussian, Inc., Wallingford, CT, USA, 2009).