Supplementary Material (ESI) for Chemical Communications

Supplementary Information for:

Organogel based on β-diketone-boron difluoride without alkyl chain and H-bonding unit directed by optimally balanced π-π interaction

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1. General methods:

^{1}H NMR spectra were recorded on a Mercury plus 500 MHz using $CDCl_3$ as solvent in all cases. Mass spectra were performed on AXIMA CFR MALDI/TOF matrix assisted laser desorption ionization/Time-of-flight) MS (COMPACT). C, H, and N elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. UV-vis spectra were determined on a Shimadzu UV-1601PC Spectrophotometer. The fresh gel was sandwiched in two glass slides for absorption measurement. Fluorescence (PL) spectra were carried out on a Shimadzu RF-5301 Luminescence Spectrometer. Fluorescence microscopy images were taken on Fluorescence Microscope (Olympus Reflected Fluorescence System BX51, Olympus, Japan) excited at 510-550 nm. FT-IR spectra were measured using a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr pellet. X-Ray diffraction (XRD) patterns were carried out on a Japan Rigaku D/max-γA instrument. XRD was equipped with graphite monochromatized Cu-Kα radiation (λ = 1.5418Å), employing a scanning rate of 0.02 s^{-1} in the 2θ range from 0.7 to 10. The sample for XRD or Fluorescence Microscope measurement was prepared by casting the organogel on glass wafer and dried at room temperature. Scanning electron microscopy (SEM) observations were carried out on a Japan Hitachi model X-650 San electron microscope. The samples for SEM were prepared by casting the organogel on silicon wafers and dried at room temperature, and then coated by gold. Transmission electron microscopy (TEM) was taken with a Hitachi H-8100 apparatus by wiping the samples onto a 200-mesh carbon coated copper grid followed by naturally evaporating the

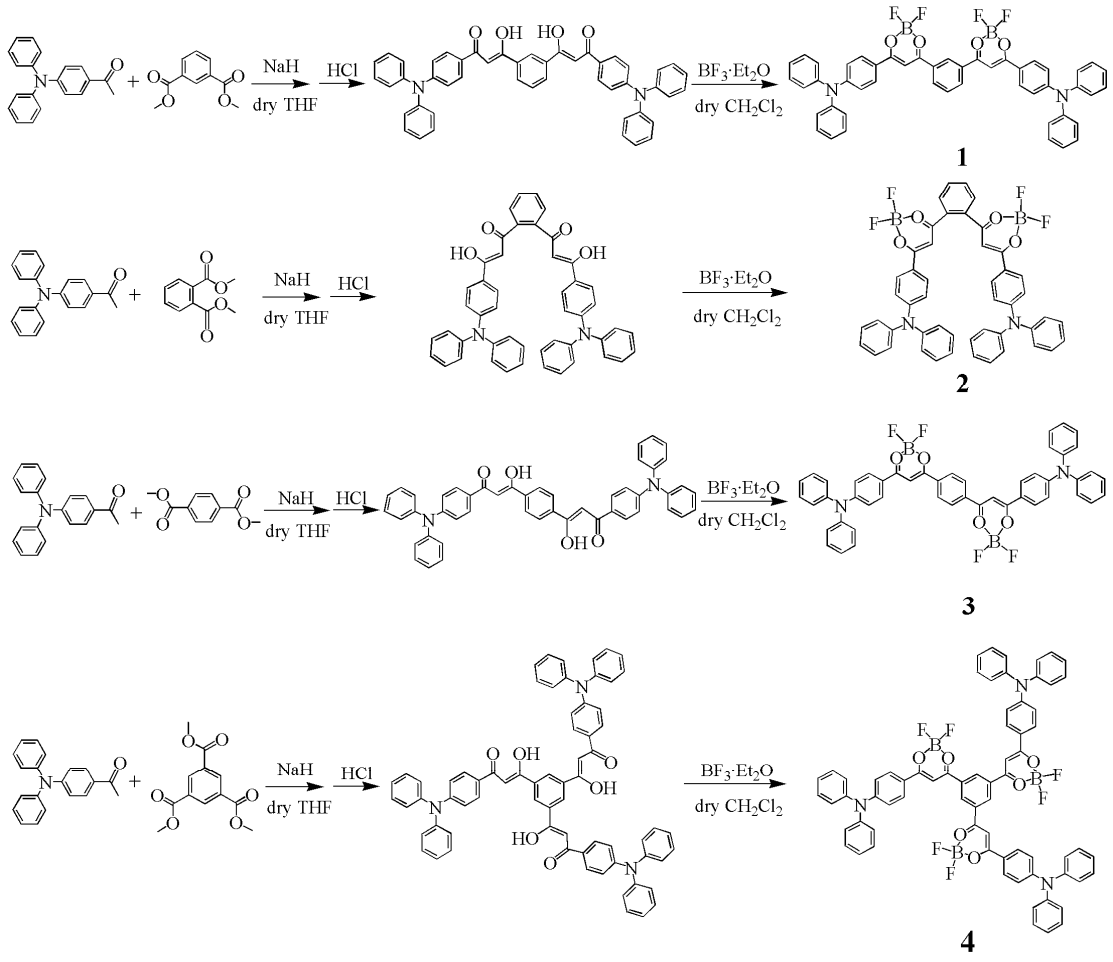
solvent.

The single crystal of **1** was obtained through a slow solvent-exchange process, which was realized via vapor diffusion within a closed chamber. Briefly, a test tube containing 0.6 mL $CHCl_3$ solution of **1** (6 mM) was placed in a 500 mL jar, which contained about 30 mL methanol, followed by sealing the jar for slow vapor diffusion between the two solvents. Because of the slow crystallization process controlled by the slow vapor diffusion, the crystal can be finally obtained after about five days. Suitable single crystal of **1** (0.2 × 0.15 × 0.15 mm) was selected for single-crystal X-ray diffraction analysis. The data collection and the structural analysis of **1** was performed on a Rigaku RAXIS-RAPID equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). The data processing was accomplished with the PROCESS-AUTO processing program. The data was collected at the temperature of 20 ± 2 °C. Structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL-97. The C, N, O, F, B and Cl atoms were easily located from the Fourier-difference maps. All non-hydrogen atoms were refined anisotropically. Experimental details for the structural determination are presented in the cif file.

The gel in the mixed solvent was obtained by the typical heating-cooling process. Taking the gel in $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM) as an example. 1.4 mg **1** was added in a sealed test tube containing 200 μL $CHCl_3$, then 300 μL cyclohexane was added. A clear solution of **1** was obtained by heating. After the hot solution was cooled to room temperature and aged for several minutes, the gel was formed.

2. Synthetic Methods and Characterizations:

THF were freshly distilled from sodium and benzophenone. CH_2Cl_2 was distilled from CaH_2. Other chemicals were used as received. The synthetic routes for compounds **1-4** were shown in Scheme S1. 1-(4-(Diphenylamino)phenyl)ethanone was prepared according to the previously reported methods.[1]



Scheme S1. The synthetic routes for compounds **1-4**.

***m*-Bis((4,4'-(p-(diphenylamino)phenyl))-2,2'-difluoro-1,3,2-dioxaborine)-benzene (1)**: Dimethyl isophthalate (0.40 g, 2 mmol) and 1-(4-(diphenylamino)phenyl)-ethanone (1.43 g, 5 mmol) were dissolved in dry THF (50 mL) under an atmosphere

of nitrogen. Then, NaH (0.4 g, 10 mmol) was added. The mixture was stirred at 60 °C for 24 h, followed by poured into ice water (300 mL). HCl (6 M, 10 mL) was added to neutralize excess NaH. The mixture was extracted with CH_2Cl_2 for three times, and the organic phase was combined and dried over magnesium sulfate. After removal of solvent, the residue was used directly in the next step without purification. Then, the solution of *m*-bis((4,4'-(p-(diphenylamino)phenyl))-propan-1,3-dione)-benzene in dry dichloromethane (50 mL) was heated to reflux under an atmosphere of nitrogen, excess BF_3•Et_2O (0.5 mL) was added. The mixture was refluxed for 12 h. After the solvent was removed, the residue was purified by column chromatography using petroleum ether/CH_2Cl_2 (v/v = 1/1) as eluent, followed by recrystallization twice from the mixed solvents of CH_2Cl_2 and light petroleum to afford **1** (1.12 g, 70 %) as dark red solid. M.p. > 200 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ = 8.67 (1 H, s), 8.29 (2 H, d), 8.03 (4 H, d), 7.67 (1 H, s), 7.40 (8 H, t), 7.23 (8H, d), 7.11 (2 H, s), 7.26 (4 H, t), 6.97 (4 H, d) (See Fig. S13). IR (KBr, cm^{-1}): 3038, 1557, 1465, 1322, 1255, 1196, 1052. MS, m/z (%): cal: 800.2, found: 781.4 (100) $[M-F]^+$ (See Fig. S14), Elemental Analysis: cal. (%) for $C_{48}H_{34}B_2F_4N_2O_4$: C, 72.03; H, 4.28; B, 2.70; F, 9.49; N, 3.50; O, 8.00. Found: C, 71.94; H, 4.22; N, 3.45.

***o*-bis((4,4'-(p-(diphenylamino)phenyl))-2,2'-difluoro-1,3,2-dioxaborine)-benzene (2):** By following the synthetic procedure for compound **1** except using dimethyl phthalate as reagent, 1.05 g of **3** (66 %) as red solid was obtained. M.p. > 200 ° C. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ = 7.86-7.89 (6 H, m), 7.65-7.67 (2 H, m), 7.36 (8 H, t), 7.24 (4 H, t), 7.17 (8 H, d), 6.87 (2H, d), 6.58 (4 H, s) (See Fig. S15). IR (KBr,

cm^{-1}): 3051, 1547, 1476, 1332, 1265, 1182, 1034. MS, m/z (%): cal: 800.2, found: 781.4 (100) $[M-F]^+$ (See Fig. S16), Elemental Analysis: cal. (%) for $C_{48}H_{34}B_2F_4N_2O_4$: C, 72.03; H, 4.28; B, 2.70; F, 9.49; N, 3.50; O, 8.00. Found: C, 71.93; H, 4.35; N, 3.42.

***p*-bis((4,4'-(p-(diphenylamino)phenyl))-2,2'-difluoro-1,3,2-dioxaborine)-benzene (3):** By following the synthetic procedure for compound **1** except using dimethyl terephthalate as reagent, 0.85 g of **2** (53 %) as dark brown solid was obtained. M.p. > 200 °C. ^1H NMR ($CDCl_3$, 500 MHz, ppm), δ = 8.16 (4 H, s), 7.99 (4 H, d), 7.39-7.42 (8 H, m), 7.26 (4 H, t), 7.23 (8 H, d), 7.05 (2H, s), 6.96 (4 H, d) (See Fig. S17). IR (KBr, cm^{-1}): 3035, 1541, 1499, 1346, 1199, 1041. MS, m/z (%): cal: 800.2, found: 800.4 (5) $[M]^+$, 781.5 (100) $[M-F]^+$ (See Fig. S18), Elemental Analysis: cal. (%) for $C_{48}H_{34}B_2F_4N_2O_4$: C, 72.03; H, 4.28; B, 2.70; F, 9.49; N, 3.50; O, 8.00. Found: C, 71.90; H, 4.24; N, 3.43.

1,3,5-*tri*((4,4'-(p-(diphenylamino)phenyl))-2,2'-difluoro-1,3,2-dioxaborine)-benzene (4): By following the synthetic procedure for compound **1** except using trimethyl benzene-1,3,5-tricarboxylate (0.50 g, 2 mmol) as reagent, 1.05 g of **4** (45 %) as black solid was obtained. M.p. > 200 °C. ^1H NMR ($CDCl_3$, 500 MHz, ppm), δ = 8.89 (3 H, s), 8.09 (6 H, d), 7.42 (12 H, t), 7.21-7.29 (21 H, m), 7.00 (6 H, d) (See Fig. S19). IR (KBr, cm^{-1}): 2912, 2846, 1736, 1507, 1345, 1188, 1039. MS, m/z (%): cal: 1161.4, found: 1142.8 (100) $[M-F]^+$ (See Fig. S20), Elemental Analysis: cal. (%) for $C_{69}H_{48}B_3F_6N_3O_6$: C, 71.35; H, 4.17; B, 2.79; F, 9.81; N, 3.62; O, 8.26, Found: C, 71.29; H, 4.08; N, 3.56.

Table S1. Gelation properties of **1-4** in selected organic solvents.

Solvent	**1** (CGC [a])	**2**	**3**	**4**
Benzene	S	S	P	P
Toluene	S	S	P	P
Chlorobenzene	S	S	S	S
Ethyl acetate	S	S	S	S
1,2-Dichloroethane	S	S	S	S
Acetone	S	S	M	M
DMF	S	S	S	S
DMSO	S	S	S	S
Cyclohexane	M	M	I	I
Hexane	I	M	I	I
Ethanol	M	S	M	M
1,2-Dichloroethane/Cyclohexane (v/v = 1/3)	OG (1.9)	S	P	P
Chloroform/Cyclohexane (v/v = 2/3)	OG (2.3)	S	P	P
THF/Cyclohexane (v/v = 3/5)	OG (2.5)	S	P	P
Dichloromethane/Cyclohexane (v/v = 1/2)	PG	S	P	P
1,4-Dioxane/Cyclohexane (v/v = 1/2)	OG (2.7)	S	P	P
Anisole/Cyclohexane or n-Hexane (v/v = 1/1)	OG (2.6)	S	P	P
Toluene/Cyclohexane or n-Hexane (v/v = 2/1)	OG (2.4)	S	M	P
Xylene/Cyclohexane or n-Hexane (v/v = 5/2)	OG (2.5)	S	M	P
Mesitylene/Cyclohexane or n-Hexane (v/v = 5/2)	OG (2.6)	S	M	P
Chlorobenzene/Cyclohexane or n-Hexane (v/v = 2/3)	OG (2.5)	S	P	P
o-Dichlorobenzene/Cyclohexane or n-Hexane (v/v = 1/2)	OG (2.4)	S	P	P

S: Soluble; M: Microsolubility; I: Insoluble; OG: Opaque Gel; PG: Partly Gel; P: Precipitate.

[a] CGC: critical gelation concentration (mM).

Table S2. The maximum emission wavelength and fluorescence quantum yields of compound **1** in different solvents and in gel state.

1	λ^{em}_{max} (nm)	Φ_F [a] (%)
In cyclohexane	530	81.2
In toluene	585	47.6
In diethylether	604	7.3
In 1,4-dioxane	617	5.3
In ethylacetate	633	3.0
In chloroform	642	2.7
Gel [b]	646	10.0

[a] The fluorescence quantum yields were determined against fluorescein in 0.1 M NaOH (Φ_F = 0.90) as the standard.[2]

[b] Gel **1** obtained from $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM).

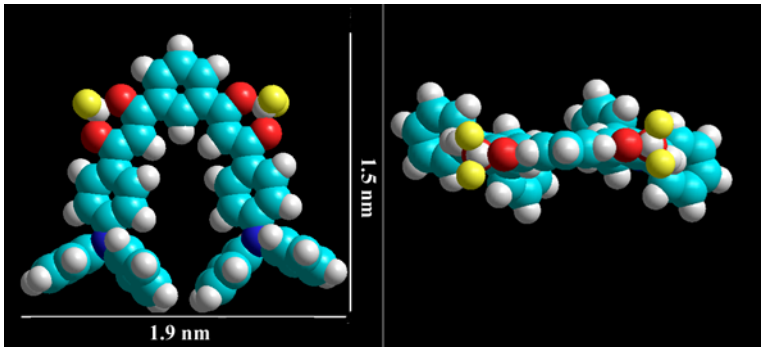


Figure S1. The optimized structure of **1** through the AM1 quantum mechanical calculations.

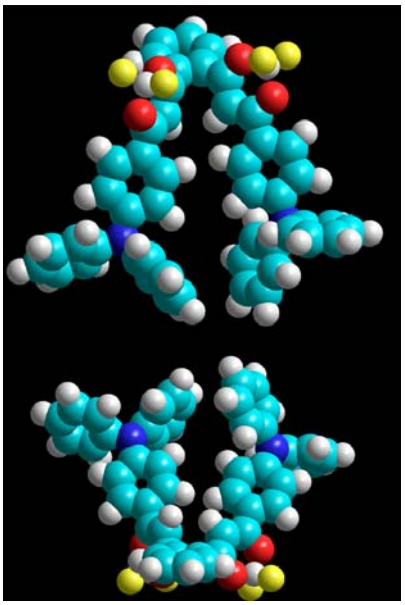


Figure S2. The optimized structure of **2** through the AM1 quantum mechanical calculations.

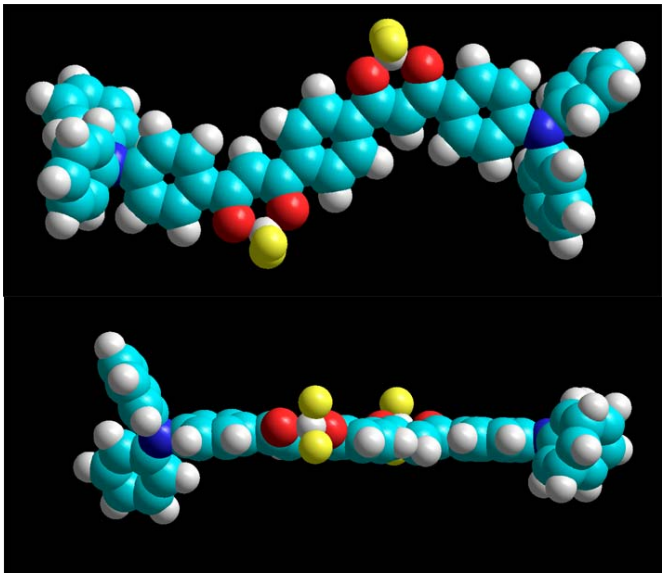


Figure S3. The optimized structure of **3** through the AM1 quantum mechanical calculations.

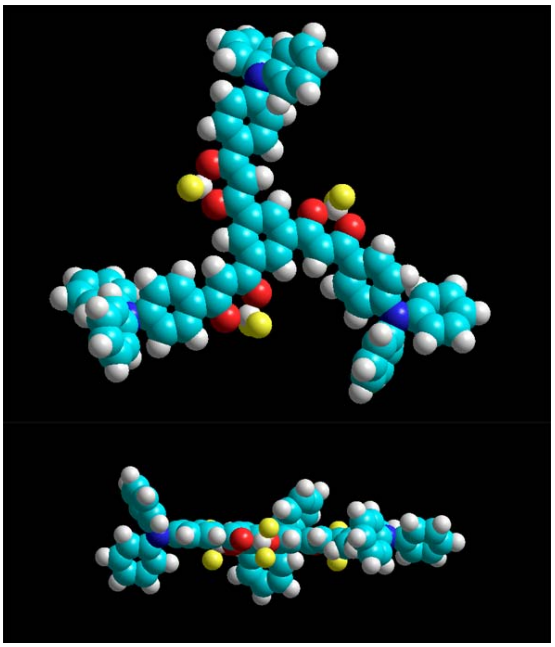


Figure S4. The optimized structure of **4** through the AM1 quantum mechanical calculations.

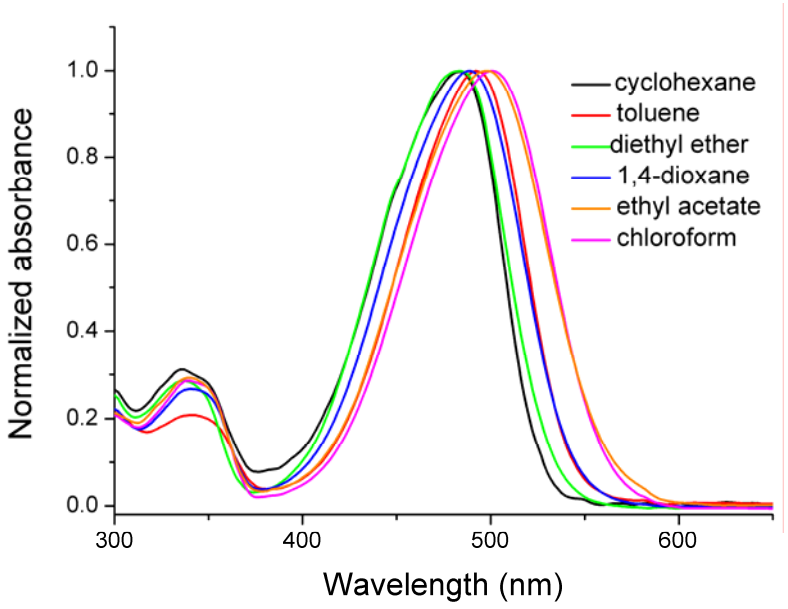


Figure S5. Absorption spectra of **1** in organic solvents with different polarities.

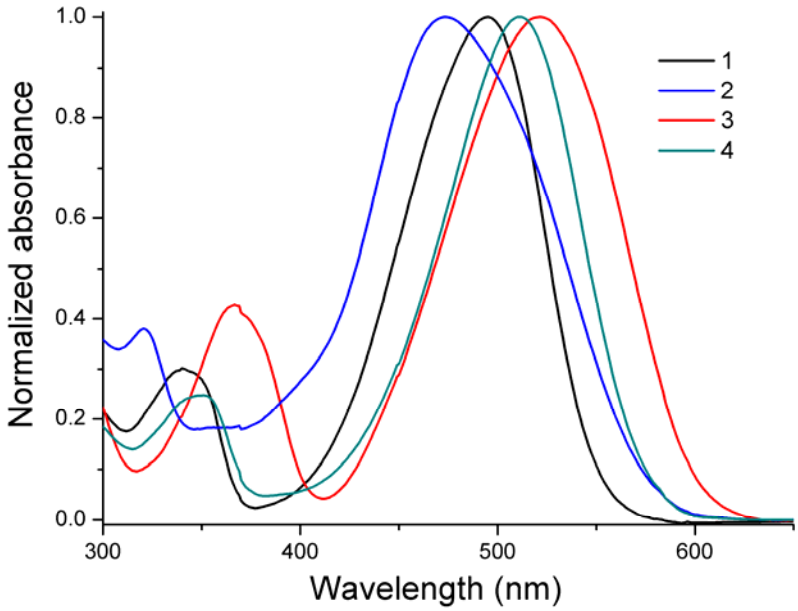


Figure S6. The normalized absorption spectra of **1-4** in $CHCl_3$/cyclohexane (v/v = 2/3).

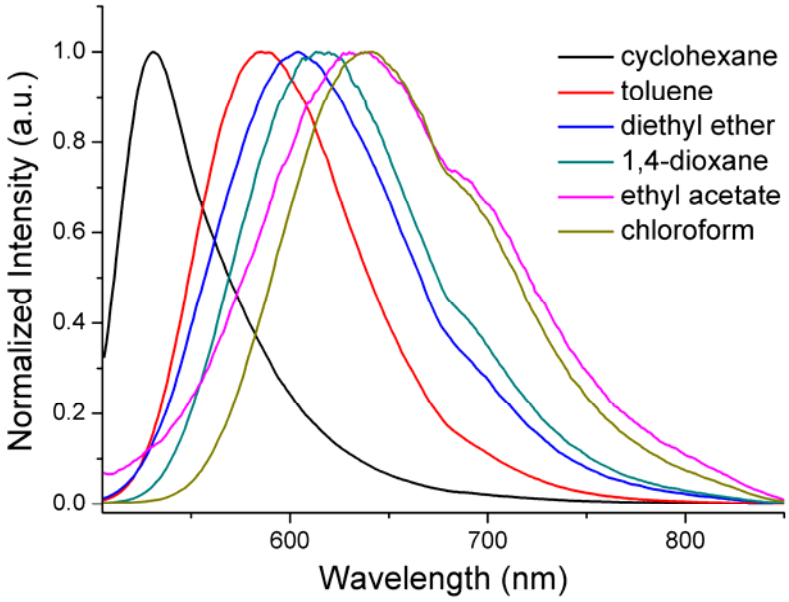


Figure S7. Normalized emission spectra of **1** in the solvents with different polarity (λ_{ex} = 490 nm).

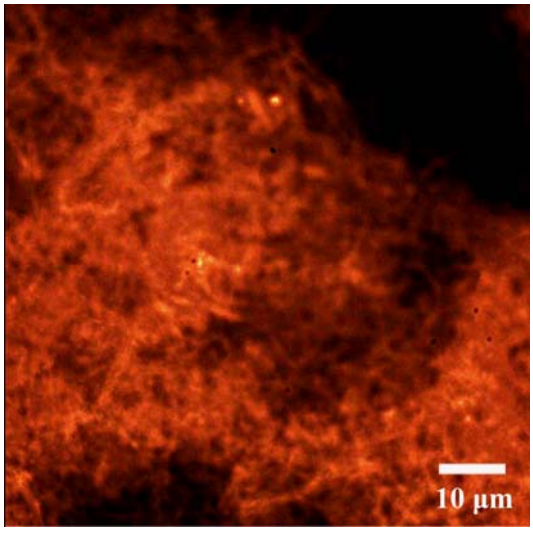


Figure S8. Fluorescence microscopy (FM) images for gel **1** obtained from $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM).

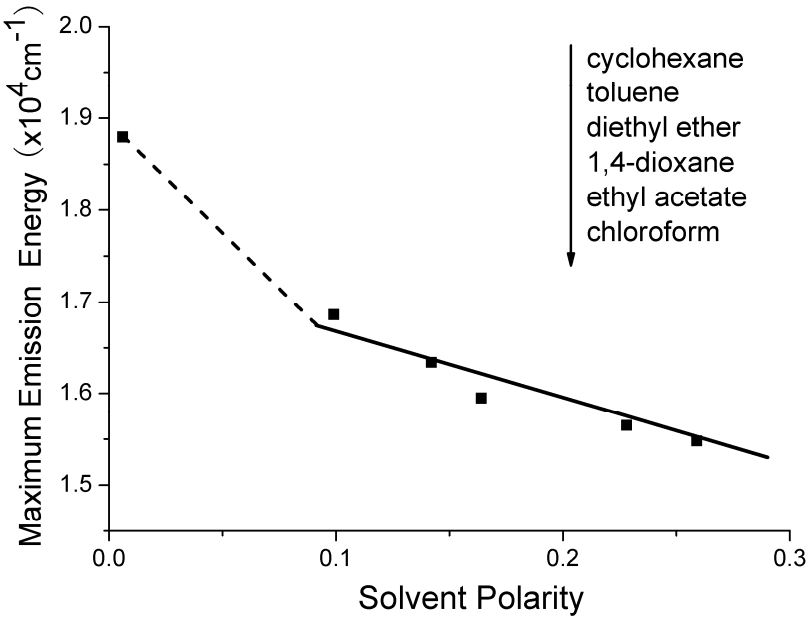


Figure S9. Lippert-Mataga plot: fluorescence emission maximum energy of **1** as a function of solvent polarity.

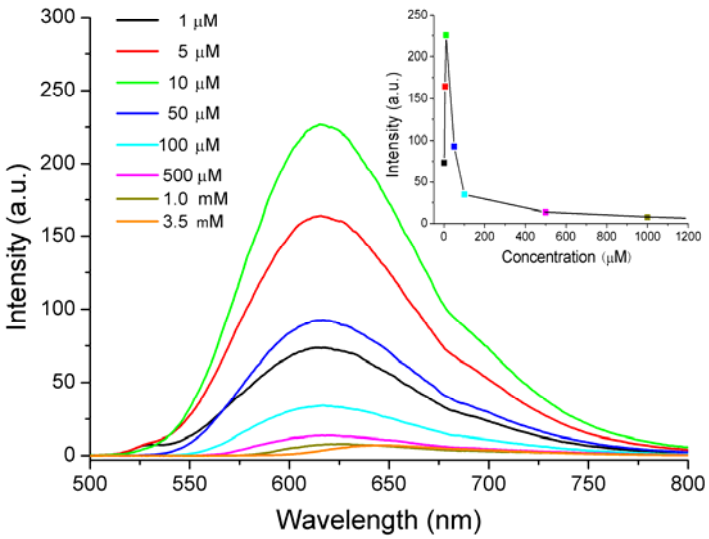


Figure S10. Concentration-dependent fluorescence spectra of **1** in $CHCl_3$/cyclohexane (v/v = 2/3). The inset was the changes of the fluorescence intensity at 616 nm varied with the concentrations.

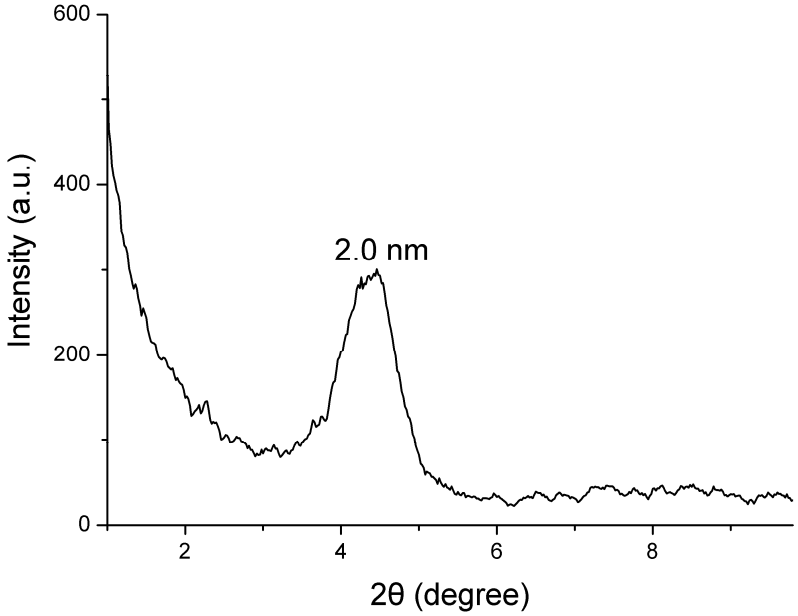


Figure S11. XRD pattern of the dried gel **1** obtained from $CHCl_3$/cyclohexane (v/v = 2/3, 3.5 mM).

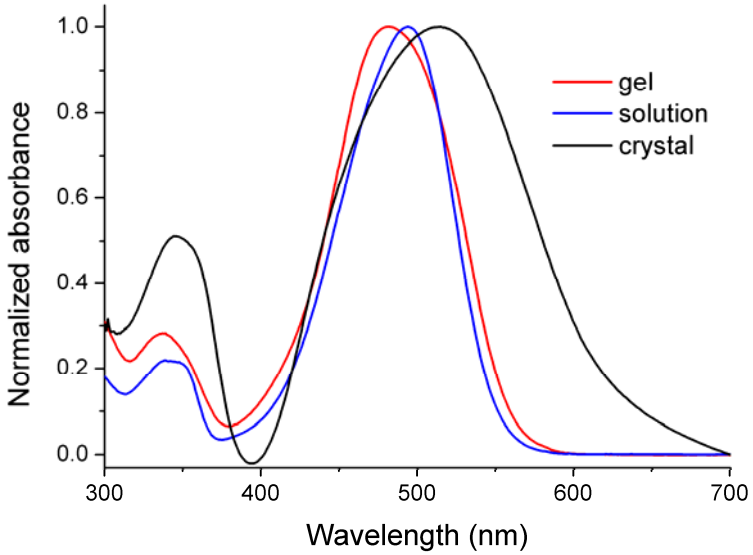


Figure S12. Normalized absorption spectra of **1** in dilute solution ($CHCl_3$/cyclohexane, v/v = 2/3, 1.0 μM), gel state ($CHCl_3$/cyclohexane, v/v = 2/3, 3.5 mM) and single crystal state.

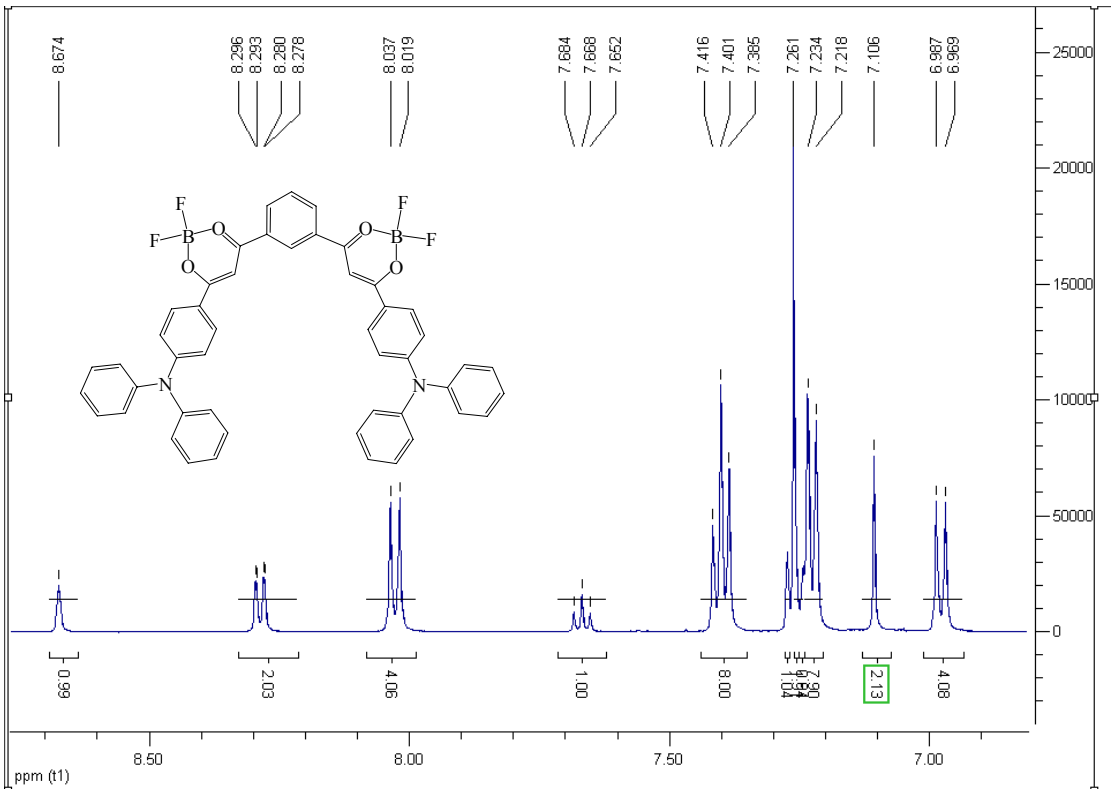


Figure S13. ^{1}H NMR (500 MHz) spectrum of compound **1**.

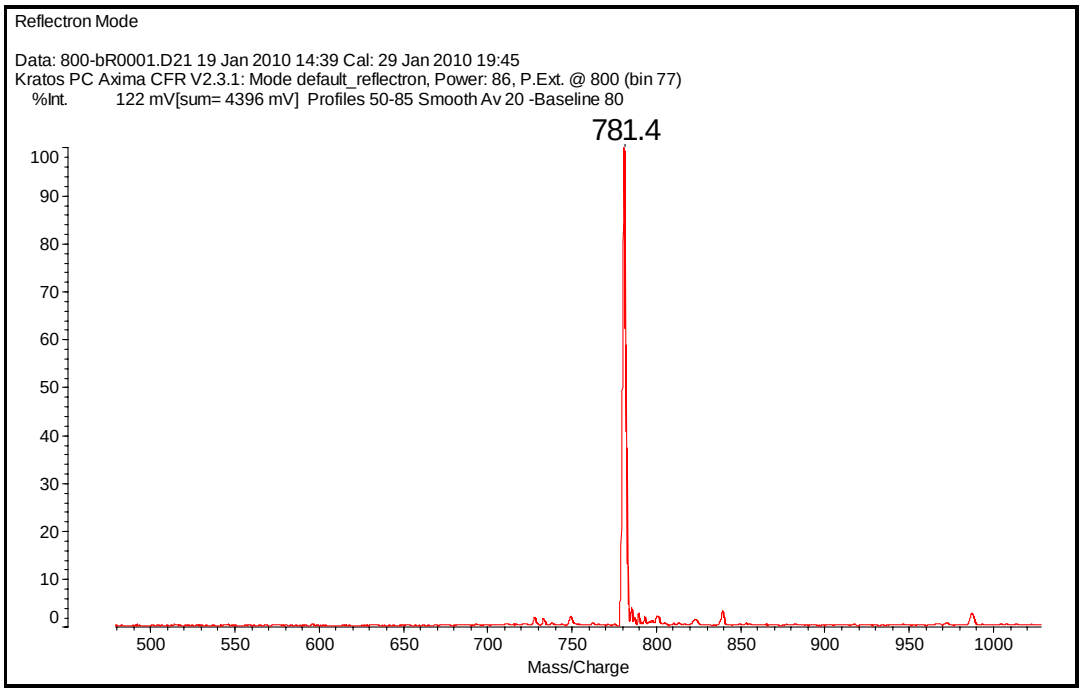


Figure S14. MALDI/TOF MS spectrum of compound **1**.

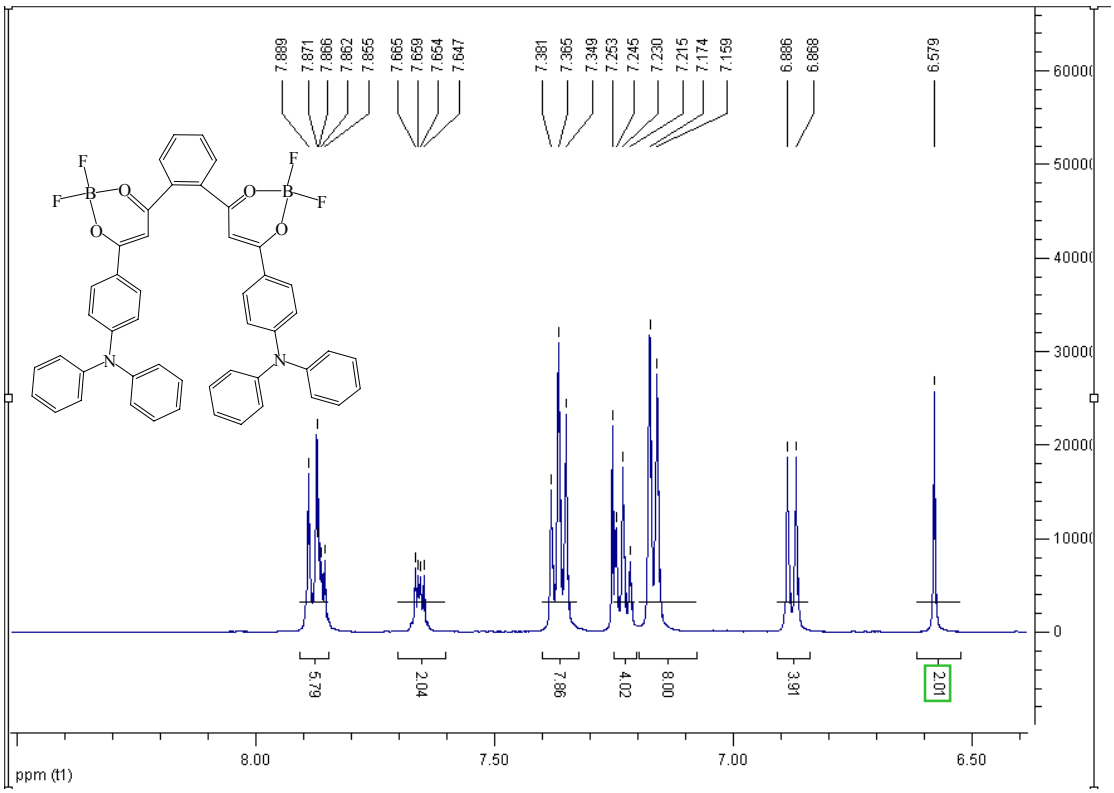


Figure S15. ^{1}H NMR (500 MHz) spectrum of compound **2**.

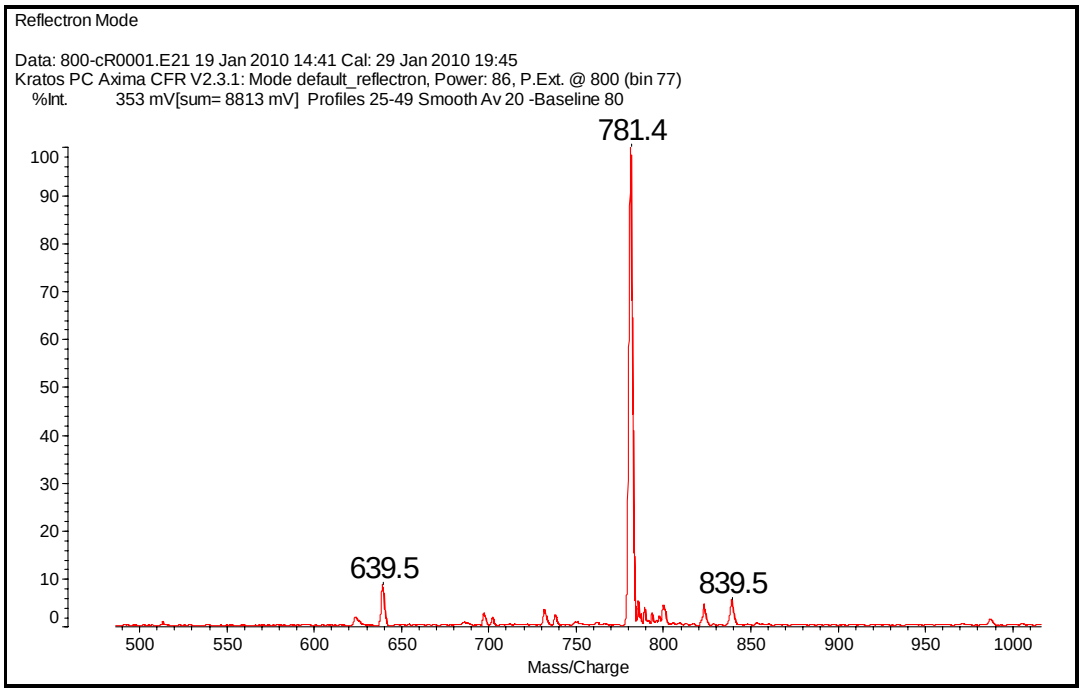


Figure S16. MALDI/TOF MS spectrum of compound **2**.

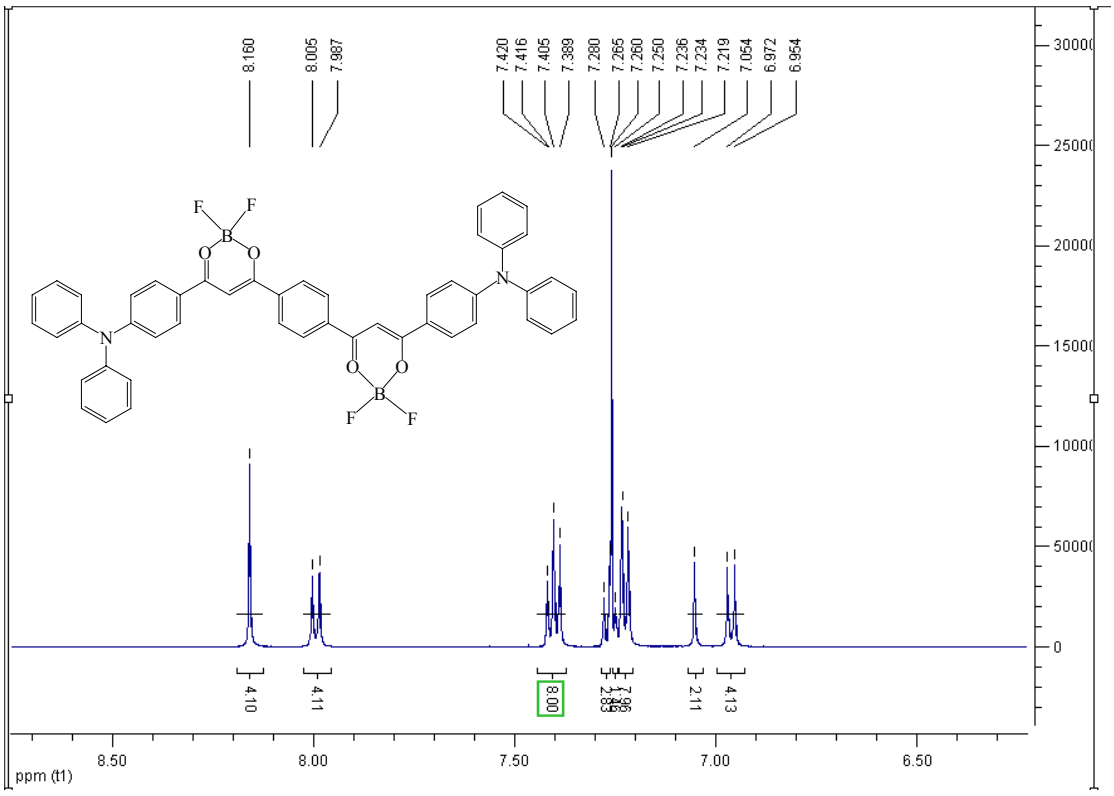


Figure S17. ^{1}H NMR (500 MHz) spectrum of compound **3**.

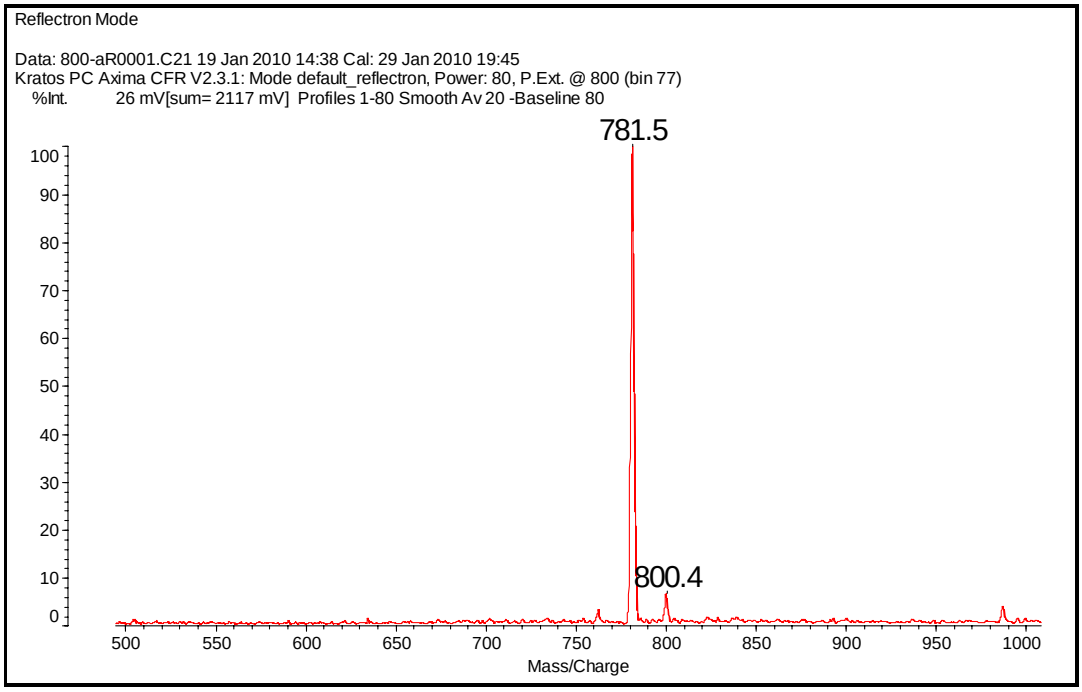


Figure S18. MALDI/TOF MS spectrum of compound **3**.

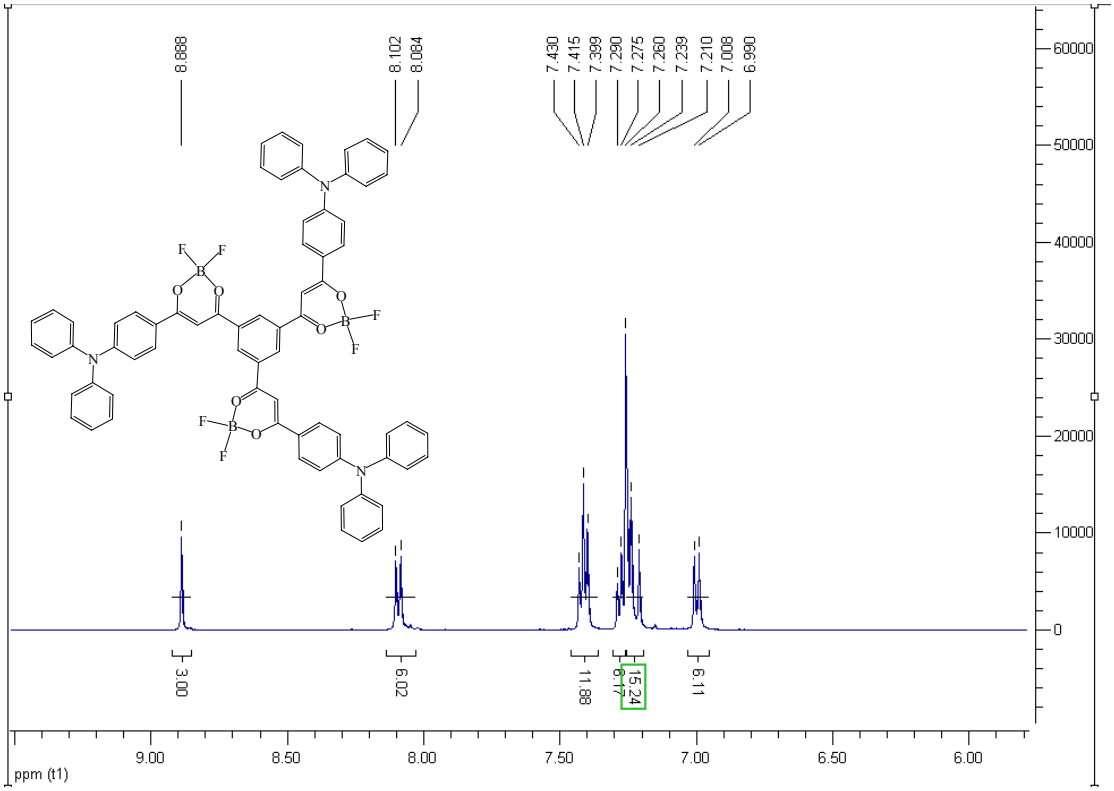


Figure S19. ^{1}H NMR (500 MHz) spectrum of compound **4**.

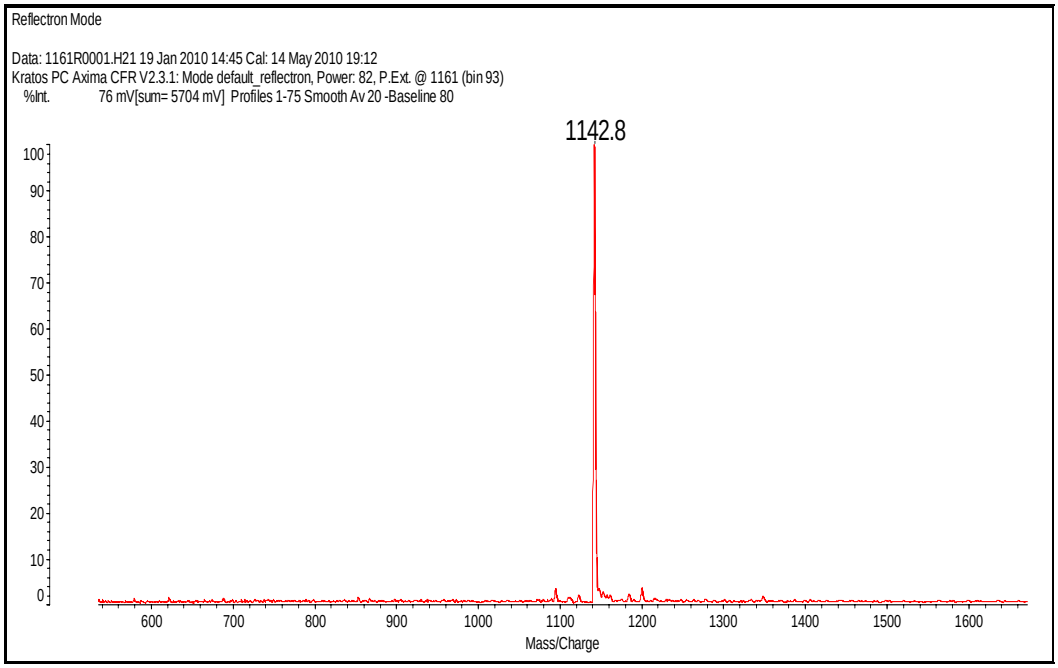


Figure S20. MALDI/TOF MS spectrum of compound **4**.

References:

1. C. J. Fox and A. L. Johnson, J. Org. Chem., 1964, 29, 3536-3538.

2. J. N. Demas and G. A. Crosby, J. Phys. Chem., 1971, 75, 993-1024.