Supporting Information

Crystal engineering focusing on intermolecular CH-π interactions in 1,4-distyrylbenzene backbone for organic crystal laser media

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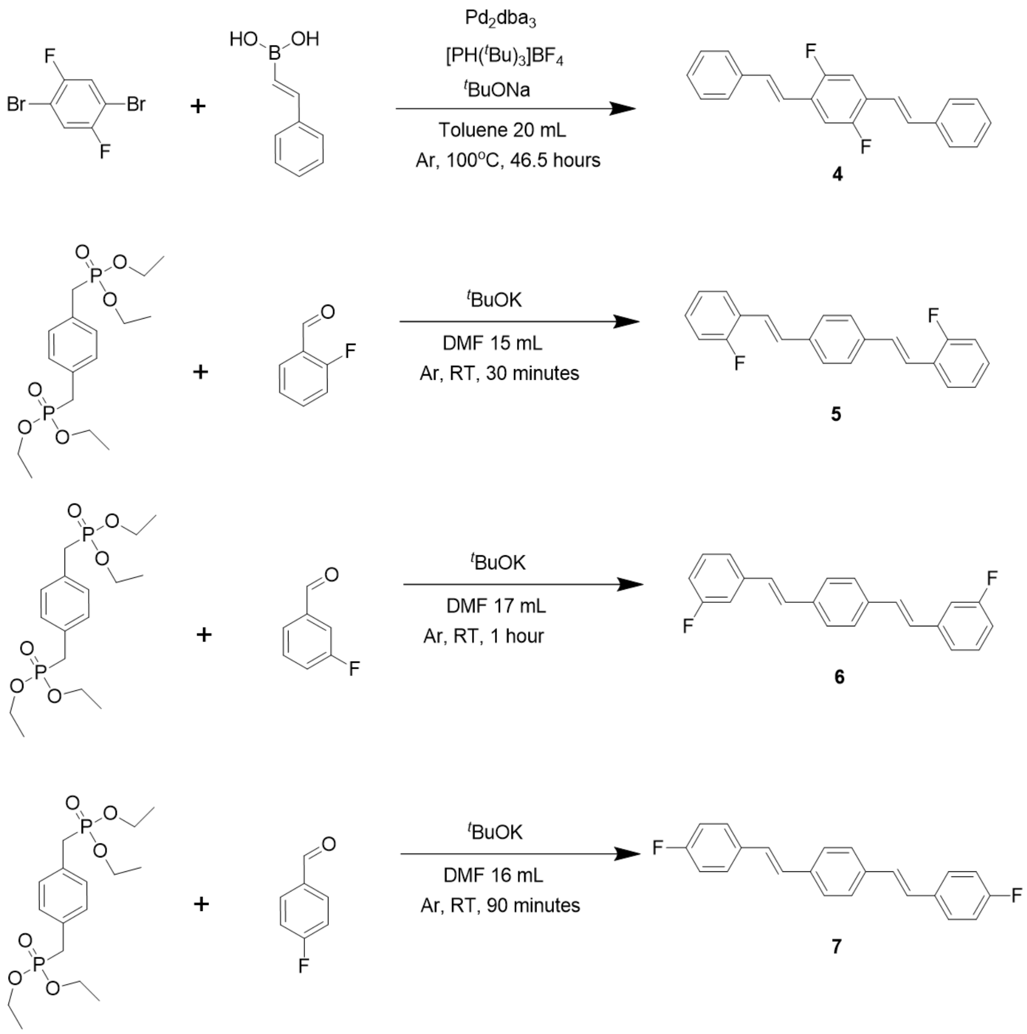
Synthesis

Synthesis scheme is summarized as follows.



Scheme S1. Synthesis of **4**, **5**, **6**, and **7**, respectively.

*Synthesis of 1,4-difluoro-2,5-bis(2-phenylethenyl)benzene (**4**):*

1,4-Dibromo-2,5-difluorobenzene (273 mg, 1.0 mmol), (*E*)-styrylboronic Acid (326 mg, 2.2 mmol), Tris(dibenzylideneacetone)dipalladium(0) (18 mg, 0.02 mmol), tri-tert-butylphosphonium Tetrafluoroborate (23 mg, 0.08 mmol), sodium *tert*-Butoxide (211 mg, 2.2 mmol), and stir chip were put in a 50 mL two-neck flask. The atmosphere of the flask was replaced with argon, then 20 mL of toluene was injected. The reaction was performed by heating at 100 ^{o}C under stirring for 46.5 hours. After that, extraction was performed for the reaction solution using distilled 40 mL of water and 100 mL of chloroform. After gathering the organic phase, the solvent was evaporated all. Next, the solution was concentrated and purified by short-column chromatography using SiO_2 and chloroform. After evaporating the solvent, the remained solid was dissolved in chloroform in a 200 mL one-neck flask making saturated solution. Then, 100 mL of methanol was quietly mounted on the solution, and successively placed in refrigerator (10 ^{o}C) to perform crystal growth. The crystal growth was performed for 17 hours. After that, white solids precipitated on the bottom of the flask and obtained the solid by filtration and following washing with methanol. The solid obtained on the filter paper was dried over 8 hours, yielding a thin yellow crystalline solid (230 mg, 0.72 mmol, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53 (d, *J* = 7.4 Hz, 4H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.30 (t, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 16 Hz, 2H), 7.16 (d, *J* = 16 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.0 (d, *J* = 242 Hz), 137.3, 132.2, 129.2, 128.8, 127.3, 125.9 (m), 120.2, 113.5 (m). Figure S1-S2.

*Synthesis of 1,4-bis[2-(2-fluorophenyl)ethenyl]benzene (**5**):*

Tetraethyl *p*-Xylylenediphosphonate (568 mg, 1.5 mmol), potassium *tert*-butoxide (505 mg, 4.5 mmol) and stir chip were placed in a 50 mL two-neck flask. The atmosphere of the flask was replaced with argon. Then, 2-fluorobenzaldehyde (1595 mg, 12.9 mmol) was injected with 15 mL of *N*,*N*-dimethylformamide (DMF). The reaction was performed by stirring at room temperature for 30 minutes. After that, reprecipitation was performed by injecting the reaction mixture to mixed solvent composed of 80 mL distilled water and 80 mL methanol. Next, the precipitated solid was filtered under vacuum, washing with small amount of methanol. After gathering the solid on filter paper, the solid was dried in vacuo over 8 hours, yielding a thin yellow crystalline solid (456 mg, 1.43 mmol, 95 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 7.80 (dd, *J* = 7.8 Hz, 7.8 Hz, 2H), 7.65 (s, 4H), 7.35 (d, *J* = 16 Hz, 2H), 7.34 (d, *J* = 16 Hz, 2H),7.36–7.30 (m, 2H), 7.24 (dd, *J* = 7.8 Hz, 7.8 Hz, 2H), 7.23 (dd, *J* = 7.8 Hz, 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.6 (d, *J* = 249 Hz), 137.0, 130.5 (d, *J* = 4.7 Hz), 129.0 (d, *J* = 8.1 Hz), 127.2, 125.3 (d, *J* = 12 Hz), 124.4, 124.3, 121.0 (d, *J* = 3.7 Hz), 116.0 (d, *J* = 22 Hz). Figure S3-S4.

*Synthesis of 1,4-bis[2-(3-fluorophenyl)ethenyl]benzene (**6**):*

Tetraethyl *p*-Xylylenediphosphonate (570 mg, 1.5 mmol), potassium *tert*-butoxide (505 mg, 4.5 mmol) and stir chip were placed in a 100 mL two-neck flask. The atmosphere of the flask was replaced with argon. Then, 3-fluorobenzaldehyde (968 mg, 7.8 mmol) was injected with 17 mL of *N*,*N*-dimethylformamide (DMF). The reaction was performed by stirring at room temperature for 1 hour. After that, reprecipitation was performed by injecting the reaction mixture to mixed solvent composed of 50 mL distilled water and 50 mL methanol. Next, the precipitated solid was filtered under vacuum, washing with small amount of methanol. After gathering the solid on filter paper, the solid was dried in vacuo over 5 hours, yielding a thin yellow crystalline solid (271 mg, 0.85 mmol, 56 %). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 7.63 (s, 4H), 7.48 (d, *J* = 11 Hz, 2H), 7.45-7.38 (m, 4H), 7.34 (d, *J* = 16 Hz, 2H), 7.31 (d, *J* = 16 Hz, 2H), 7.12–7.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.3 (d, *J* = 244 Hz), 139.8 (d, *J* = 7.7 Hz), 136.7, 130.3 (d, *J* = 8.1 Hz), 129.6, 127.7 (d, *J* = 2.8 Hz), 127.2, 122.6 (d, *J* = 2.7 Hz), 114.6 (d, *J* = 21 Hz), 112.9 (d, *J* = 22 Hz). Figure S5-S6.

*Synthesis of 1,4-bis[2-(4-fluorophenyl)ethenyl]benzene (**7**):*

Tetraethyl *p*-Xylylenediphosphonate (565 mg, 1.5 mmol), potassium *tert*-butoxide (505 mg, 4.5 mmol) and stir chip were placed in a 100 mL two-neck flask. The atmosphere of the flask was replaced with argon. Then, 4-fluorobenzaldehyde (826 mg, 6.7 mmol) was injected with 16 mL of *N*,*N*-dimethylformamide (DMF). The reaction was performed by stirring at room temperature for 90 minutes. After that, reprecipitation was performed by injecting the reaction mixture to mixed solvent composed of 50 mL distilled water and 50 mL methanol. Next, the precipitated solid was filtered under vacuum, washing with small amount of methanol. After gathering the solid on filter paper, the solid was dried in vacuo over 5 hours, yielding a thin yellow crystalline solid (303 mg, 0.95 mmol, 60 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 (s, 4H), 7.48 (dd, *J* = 8.6 Hz, 5.4 Hz, 4H), 7.07 (d, *J* = 16 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 4H), 7.01 (d, *J* = 16 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 162.5 (d, *J* = 246 Hz), 145.7, 136.7, 133.7, 128.1 (d, *J* = 7.9 Hz), 127.6, 126.9, 115.8 (d, *J* = 22 Hz). Figure S7-S8.

Crystal growth for Xray measurements

Xray measurements were performed for crystal **4** using as yielded crystals. Crystal growth of **5** was performed by vapor diffusion process. 15 mg of the powder was dissolved in 3 mL of chloroform. To yield crystals, the solution was exposed to methanol vapor for 2 days. Crystal growth of **6** was performed by sublimation of powder of **6** (30 mg) heating at 350 ^{0}C for 20 minutes under N_2 gas flowing condition (0.1 L/min.). Crystal growth of **7** was performed by sublimation of powder of **7** (30 mg) heating at 320 ^{0}C for 60 minutes under N_2 gas flowing condition (0.1 L/min.).

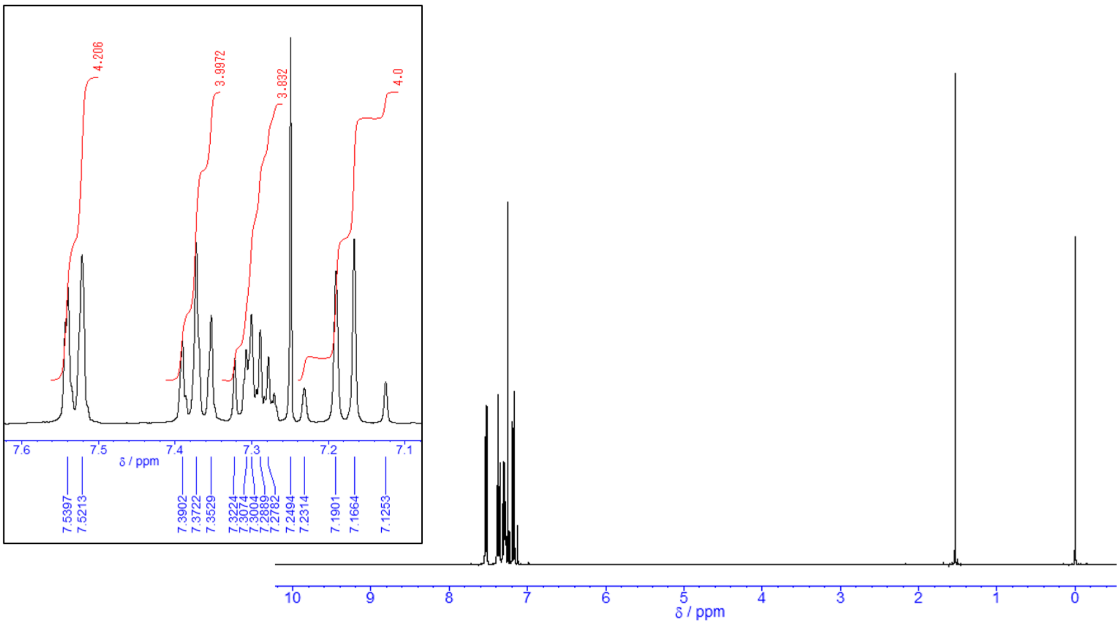


Fig. S1. ^{1}H NMR spectrum of **4**.

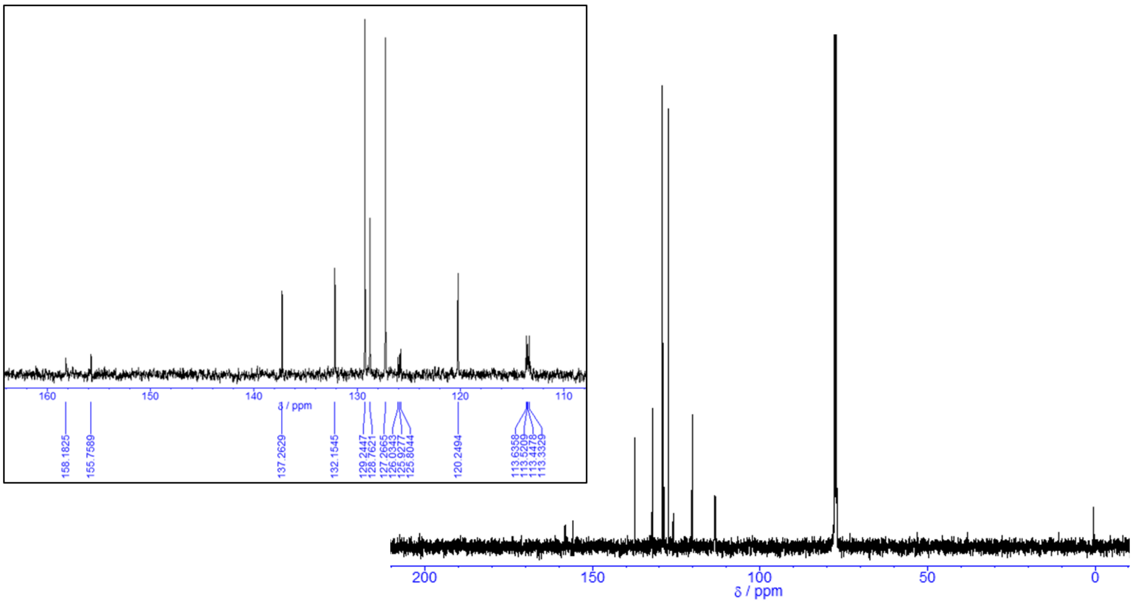


Fig. S2. ^{13}C NMR spectrum of **4**.

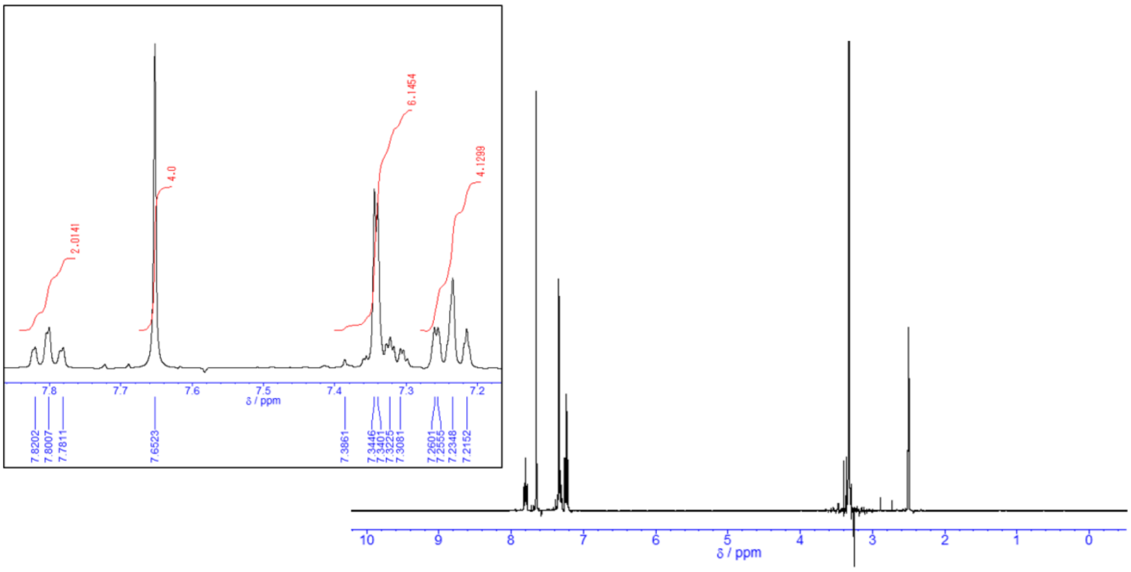


Fig. S3. ^{1}H NMR spectrum of **5**.

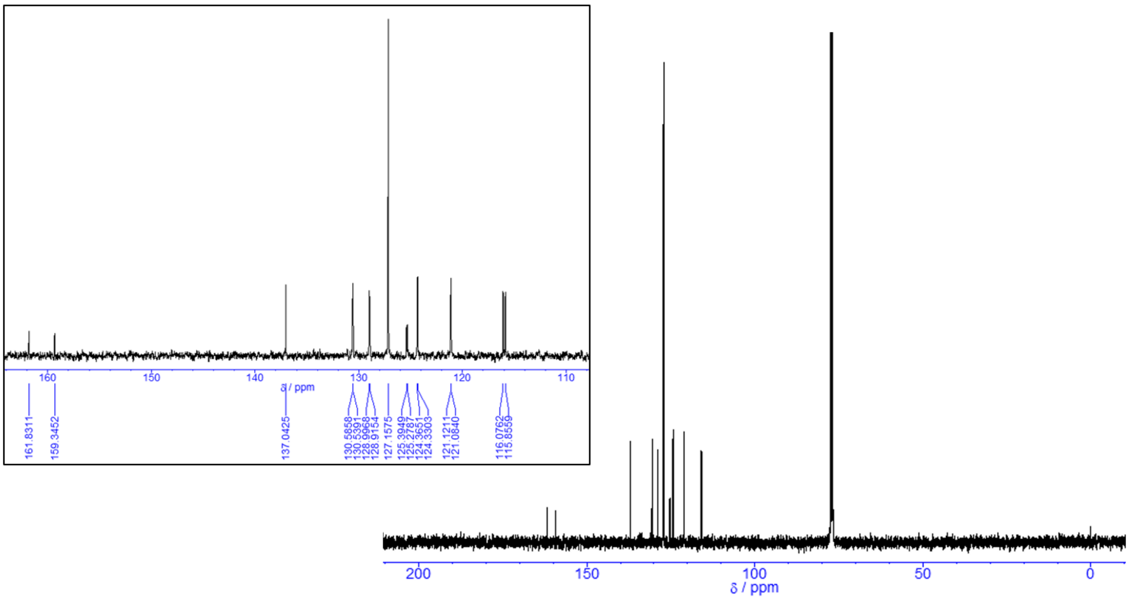


Fig. S4. ^{13}C NMR spectrum of **5**.

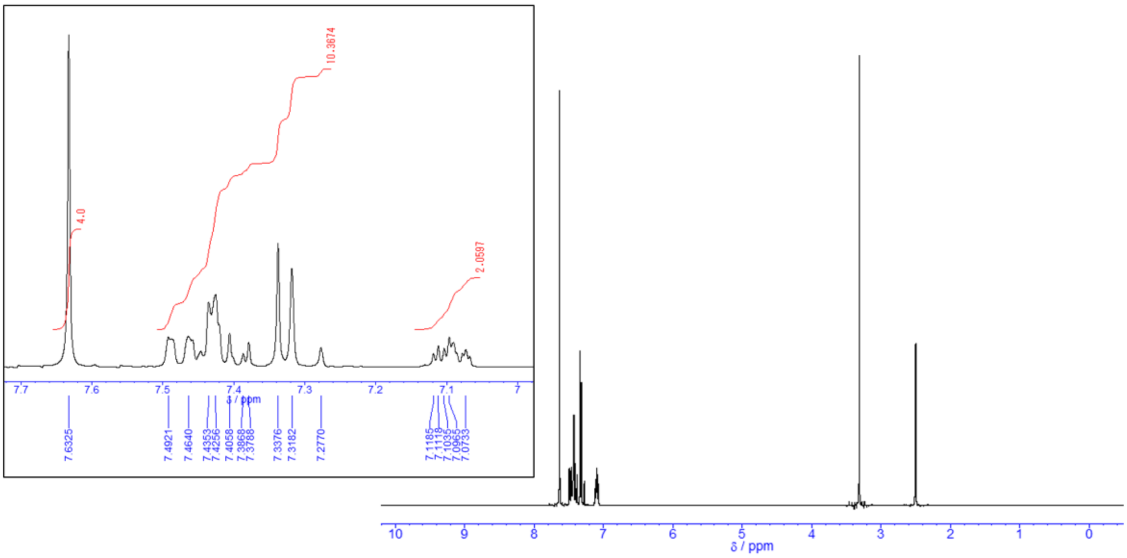


Fig. S5. ^{1}H NMR spectrum of **6**.

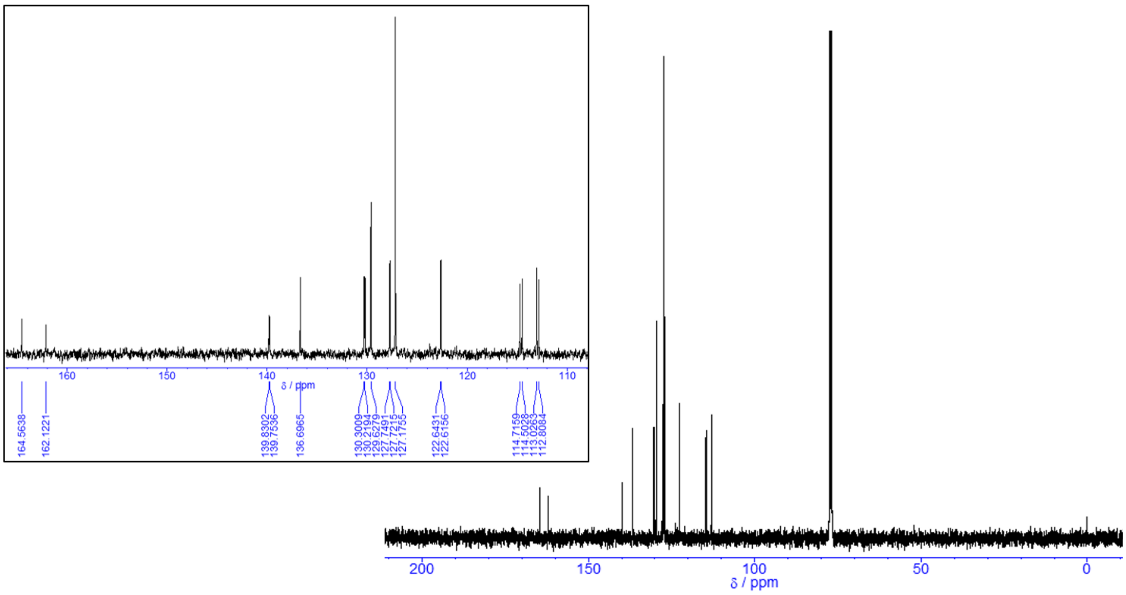


Fig. S6. ^{13}C NMR spectrum of **6**.

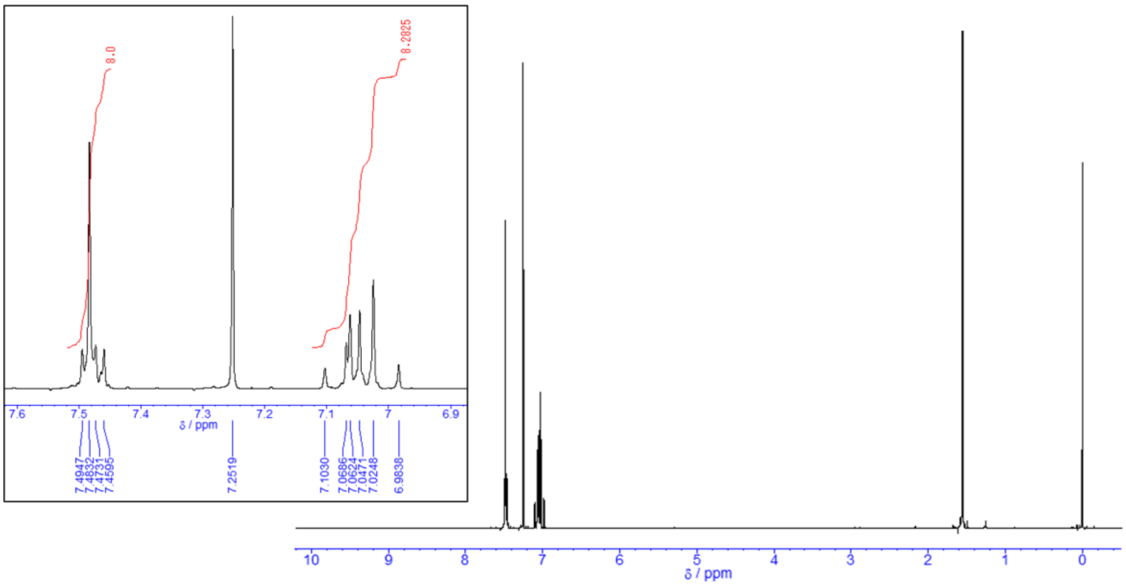


Fig. S7. ^{1}H NMR spectrum of **7**.

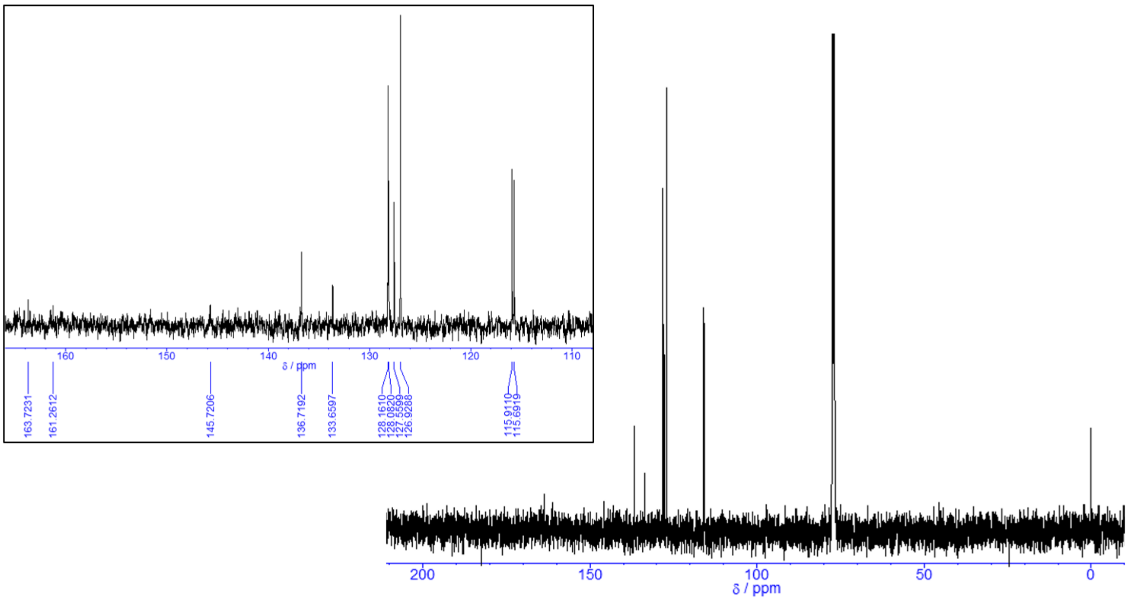


Fig. S8. ^{13}C NMR spectrum of **7**.

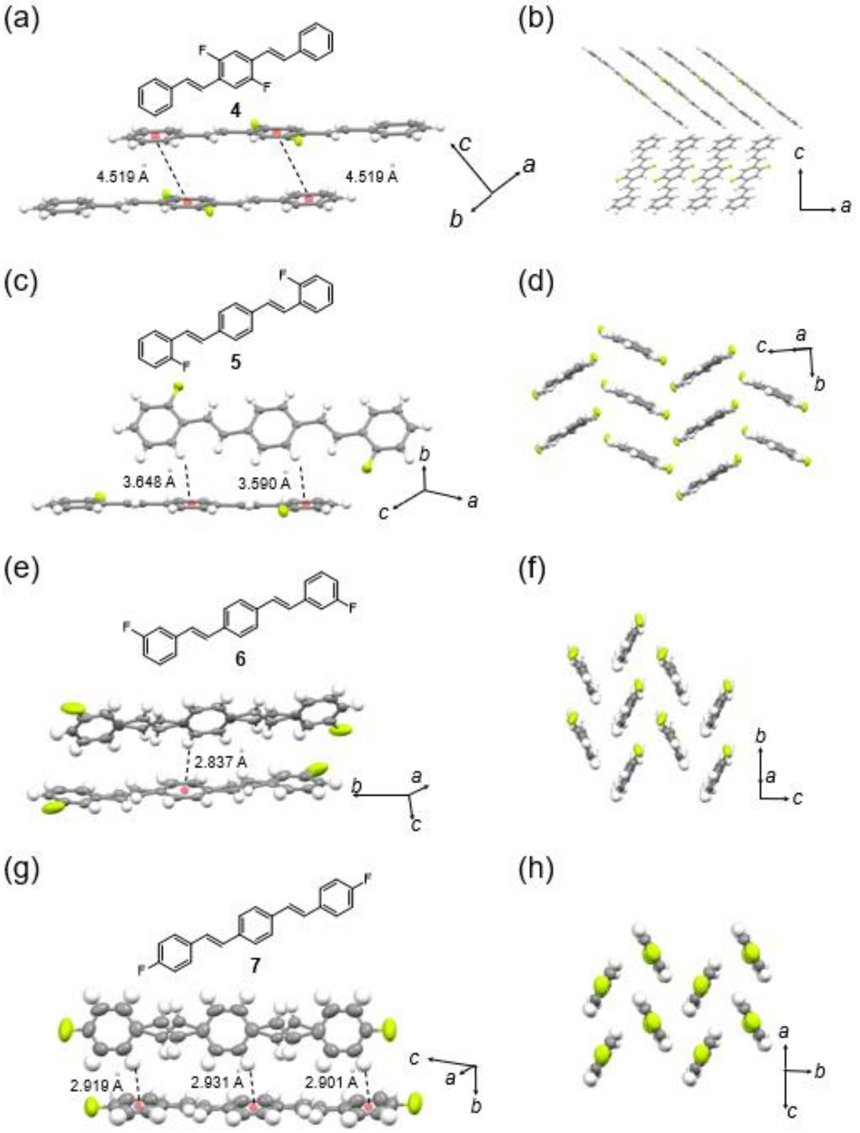


Fig. S9. (a) Crystal structure of **4** showing π-π stacking aggregation motif, containing the chemical structure of **4**. (b) Molecular orientation of **4** in a crystal showing π-stacked layer. (c) Crystal structure of **5** showing CH-π interaction, containing the chemical structure of **5**. (d) Molecular orientation of **5** showing herringbone packing motif. (e) Crystal structure of **6** showing CH-π interaction, containing the chemical structure of **6**. (f) Molecular orientation of **6** showing herringbone packing motif. (g) Crystal structure of **7** showing CH-π interaction, containing the chemical structure of **7**. (h) Molecular orientation of **7** showing herringbone packing motif.

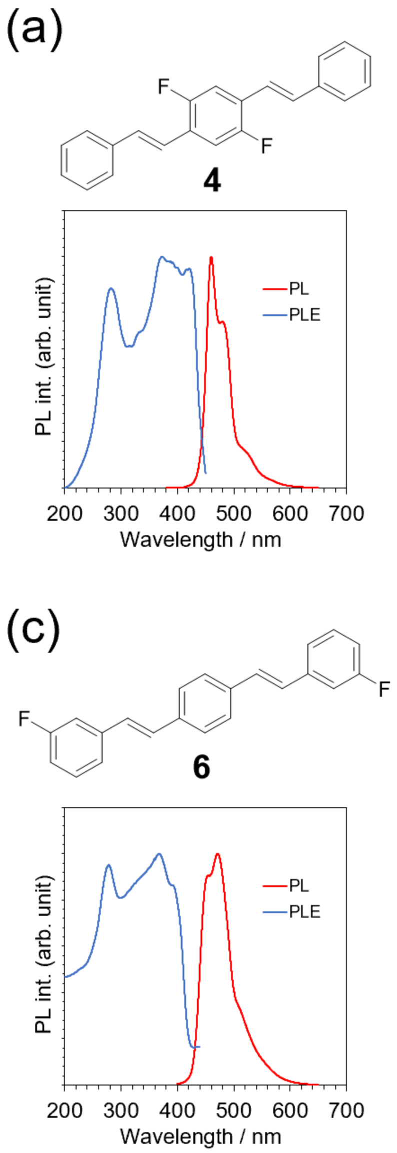


Fig. S10. (a-d) PL and PLE spectra measured for crystals of **1**, **2**, **3**, and **4**, respectively. Chemical structures are included as each inset.

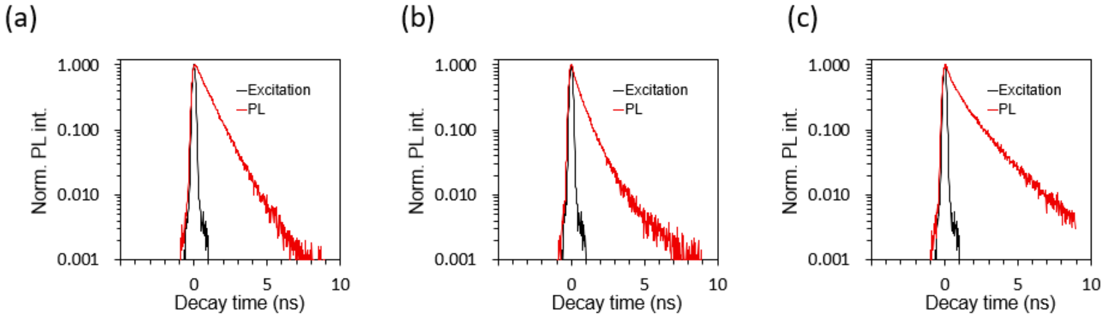


Fig. S11. (a) PL lifetime measured for crystals of (a) **1**, (b) **2**, and (c) **3**, respectively.

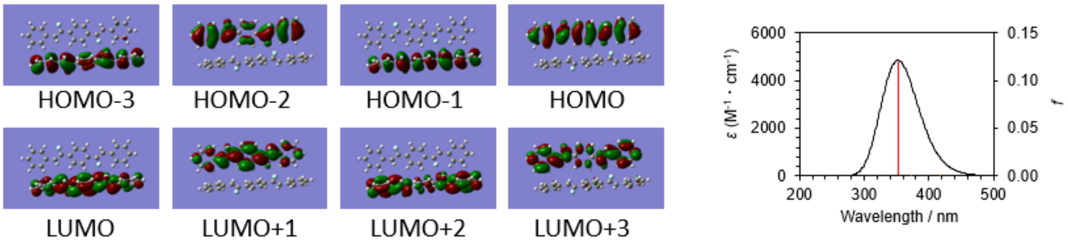


Fig. S12. Results of TDDFT calculation for crystal **1**.

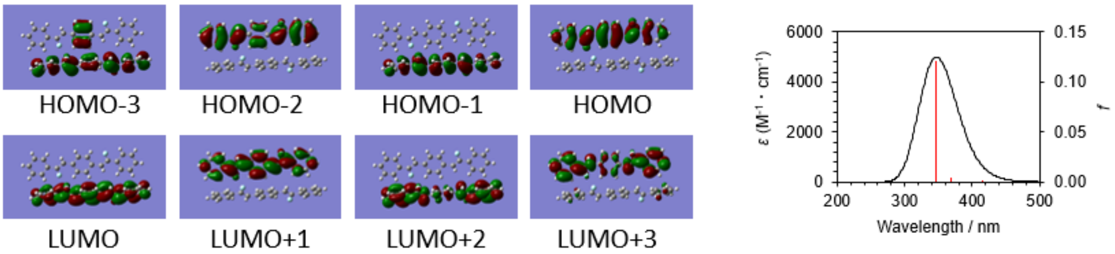


Fig. S13. Results of TDDFT calculation for crystal **2**.

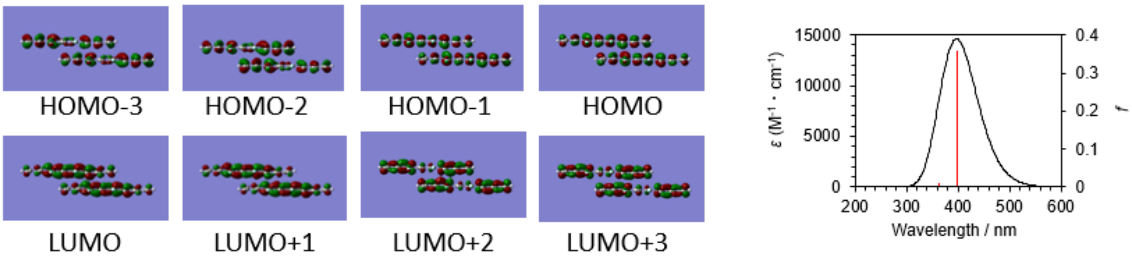
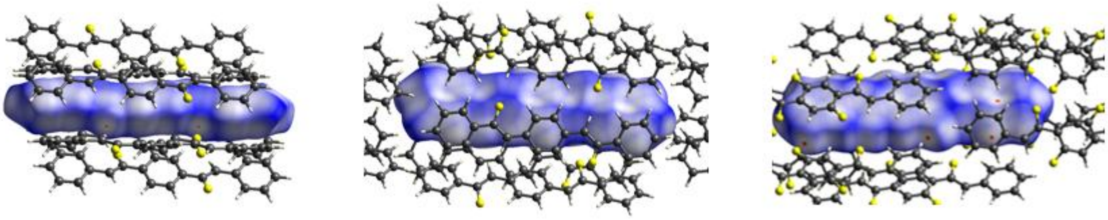


Fig. S14. Results of TDDFT calculation for crystal **3**.



1 2 3

Fig. S15. Results of Hirschfeld surface analysis for crystal **1**, **2**, and **3**, respectively.