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Electronic Supplementary Information

A two-dimensional molecule with large conjugation degree: synthesis, two-photon absorption and charge transport ability

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1. NMR spectra

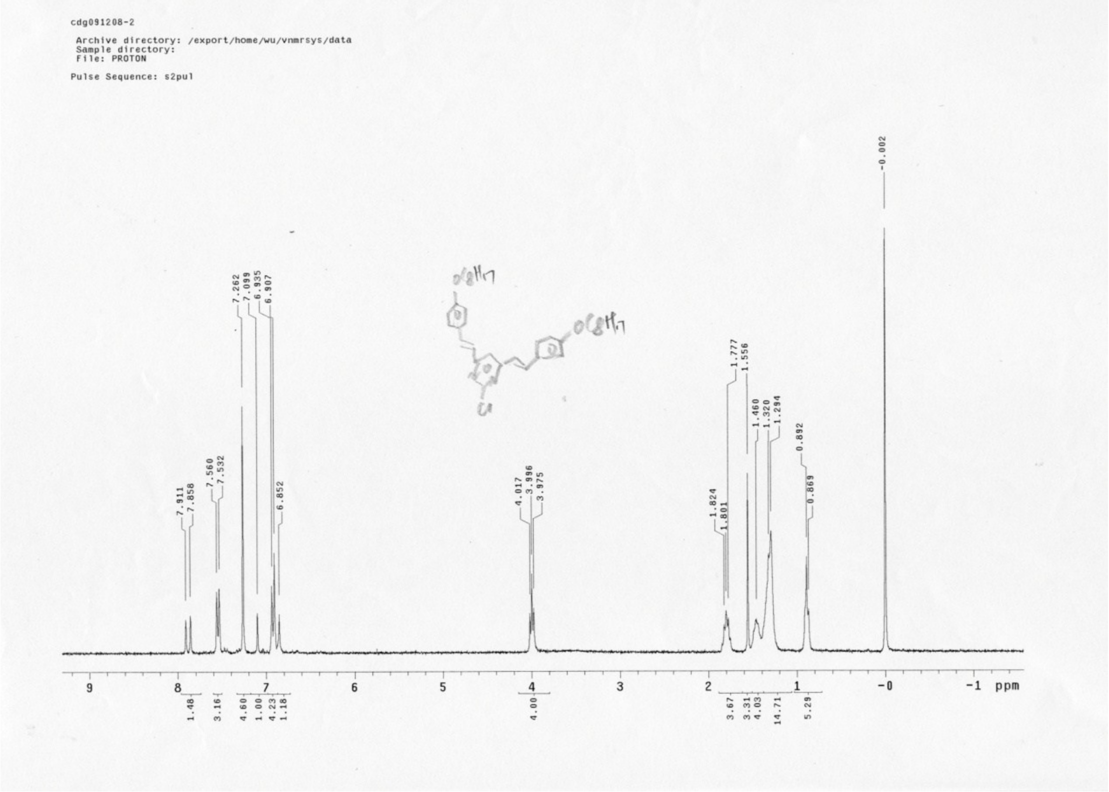

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Fig.S1 ^{1}H NMR of **Compound 4**

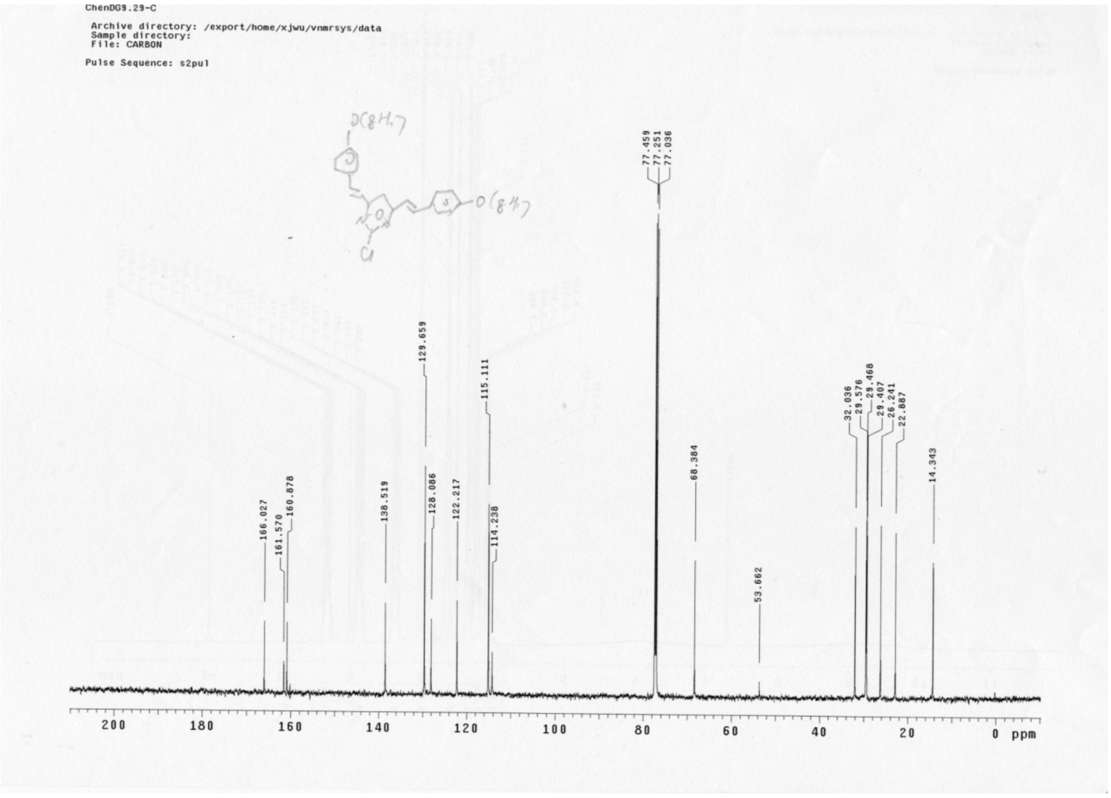

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Fig.S2 ^{13}C NMR of **Compound 4**

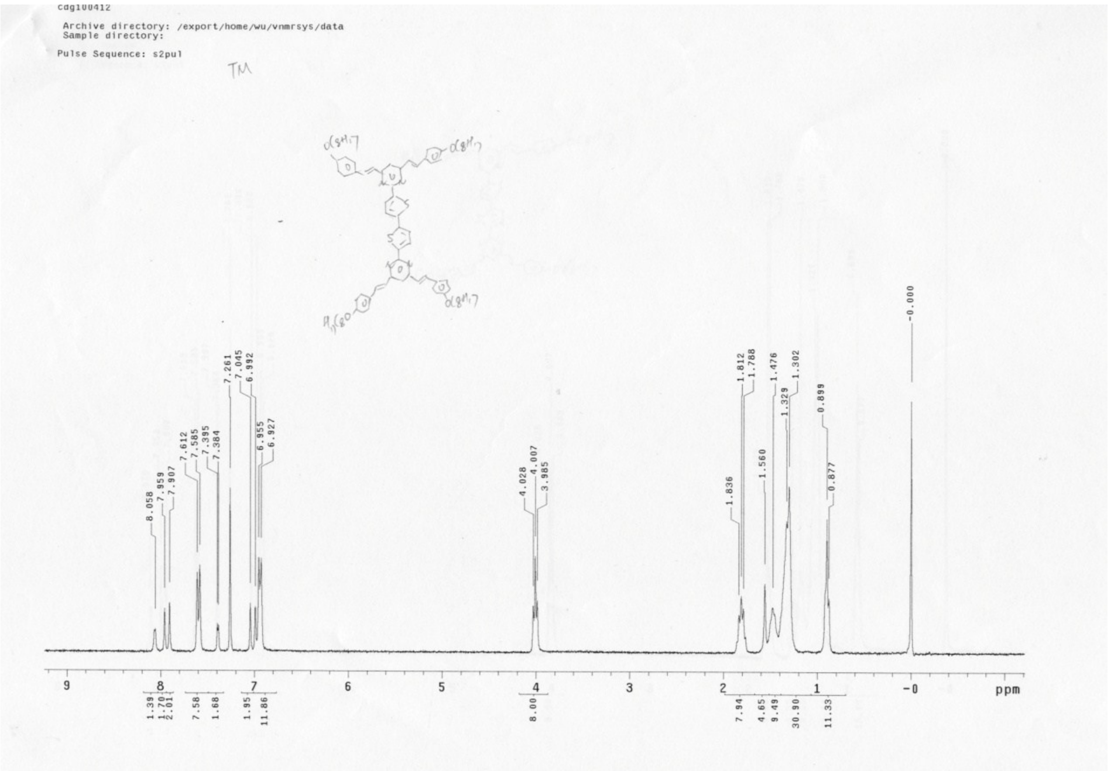

Fig.S3 ^{1}H NMR of **OSPB**

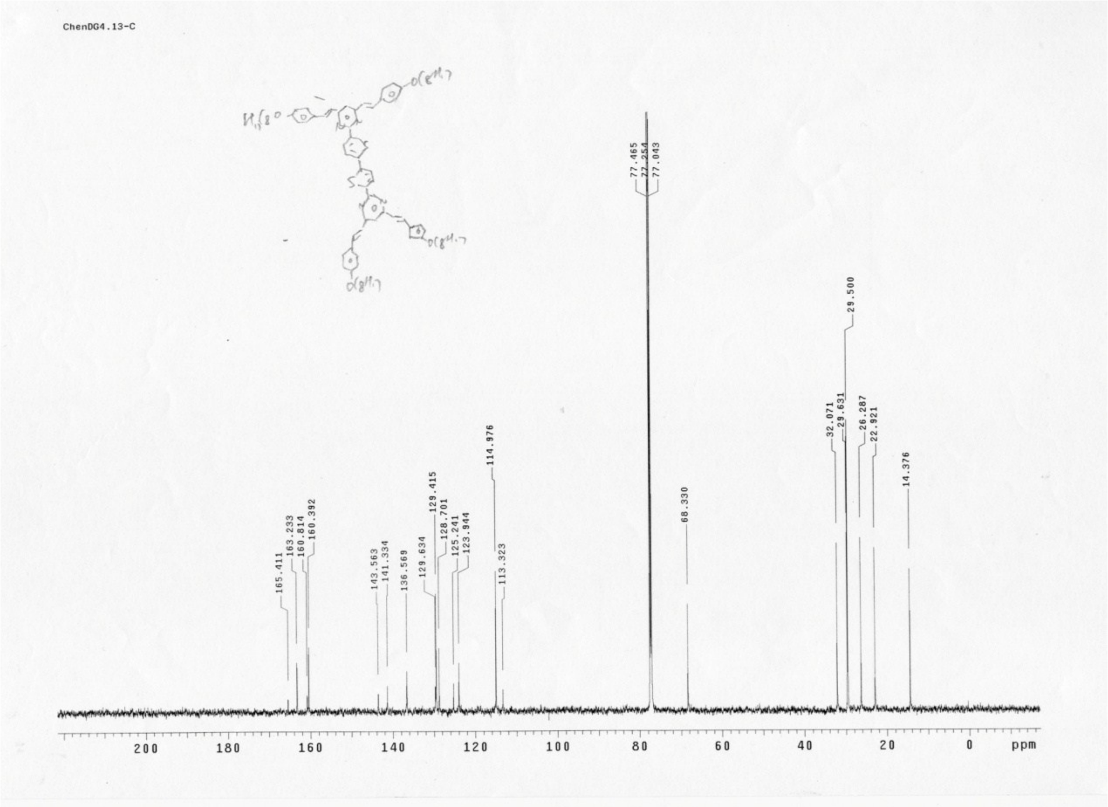

Fig.S4 ^{13}C NMR of **OSPB**

2. Synthesis of intermediates

*4,6-dimethy-2-hydroxypyrimidine hydrochloride (**1**)*[1]: Urea (3.0 g, 0.05 mol) was dissolved in 50 mL of ethanol, and the solution was heated to reflux. Then pentane-2,4-dione (5.0 g, 0.05 mol) was added to the solution at once followed by the addition of hydrochloric acid (37 %, 7 mL) drop by drop. After reaction for 24 h under reflux, the mixture was cooled to room temperature and filtered. The residue was washed by cold ethanol and diethyl ether in turns for 2 times. And the product was dried over vacuum. Compound **1** was obtained as a white solid (6.1 g, 74%).

*4-(octyloxy)benzaldehyde (**2**)*[2]: 4-hydroxybenzaldehyde (4.0 g, 32.8 mmol) and 1-bromooctane (7.6 g, 39.4 mmol) was dissolved in 100 mL of acetone, then anhydrous K_2CO_3 (9.0g, 66 mmol) and a catalytic amount of KI (10 mg) was added to the solution. The mixture was stirred and heated to reflux overnight. After removing the solvent acetone via rotary evaporation, water was added and the mixture was extracted with CH_2Cl_2. The organics were collected and dried over anhydrous Na_2SO_4. The solvent was concentrated and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether (v/v, 1:3) as eluent to give **2** as colorless oil (6.9 g, 90%). ^1H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 9.88 (s, 1H), 7.83 (d, 2H), 6.99 (d, 2H), 4.04 (t, 2H), 1.82 (m, 2H), 1.47-1.29 (m, 10H), 0.89 (t, 3H).

*2,2'-bithiophene (**5**)*[3]: 2-bromothiophene (4.89 g, 30 mmol), $Ni(PPh_3)_2Cl_2$ (1.96 g, 3 mmol), Zn powder (1.95 g, 30 mmol), PPh_3 (1.57 g, 6 mmol) and KI (0.2 g, 1.2 mmol) were mixed in a Schlenk tube which was then connected to a vacuum line and filled full with argon. 80 mL of THF was added to the tube by syringe, and the solution was heated to 66 ºC for 24 h. The mixture was filtered under reduced pressure, and the residue was washed with THF for several times. The filtrate was collected and the solvent was removed via rotary evaporation. The crude product was purified by column chromatography on silica gel with petroleum ether as eluent to give compound **5** as oil which change to light green solid (4.0 g, 80%) after refrigerated overnight at 2~8 ºC. ^1H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 7.22-7.18 (m, 4H), 7.03-7.00 (m, 2H).

*5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**6**)*[4]: 2,2'-bithiophene (1.0 g, 6.02 mmol) was put in a Schlenk tube which was then filled full with argon. 80 mL of THF was added to the tube by syringe. The solution was cooled to –78 ºC and n-BuLi (2.18 M in THF, 6.9 mL, 15 mmol) was added dropwise. The reaction was stirred at this temperature for 30 min, and then moved to room temperature for another 1 h. The reaction was cooled to –78 ºC again, and trimethyltin chloride (1 M in hexane, 15 mL) was added at once. After 30 min, the reaction was allowed to warm to room temperature and stirred overnight. Saturated NaCl solution was added, and the mixture was extracted with ethyl ether. The organic layer was washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under vacuum, and the crude product was recrystallized by ethanol to give white solid (2.1 g, 84%). ^1H NMR (*d*-DMSO, 300 MHz) δ [ppm]: 7.33 (d, 2H), 7.14-7.12(m, 2H), 0.35 (s, 18 H).

3. TPEF spectra of OSPB in THF and water

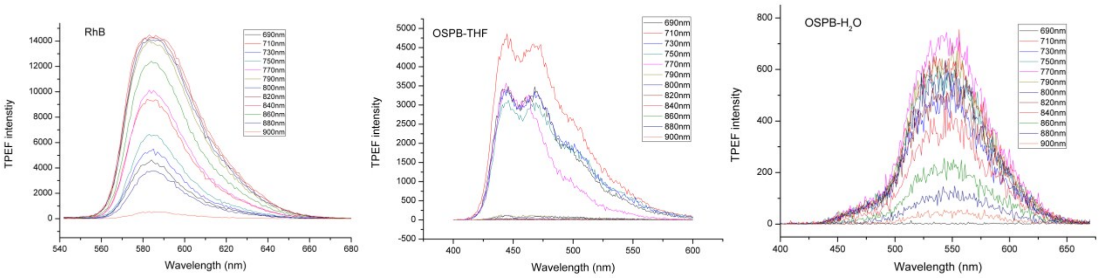

Fig.S5 TPEF spectra of **RhB** in EtOH and **OSPB** in THF and water

Reference

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