

Thienyl peripherally substituted rubrene analogue with constant emissions and good film forming ability

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Experimental Section

Materials and Instrumentations

All chemicals were purchased from Alfa Aesar and used without further purification. Water was purified by using a Millipore filtration system. ^1H NMR and ^{13}C NMR spectra were recorded on BrukerAvance 400 MHz spectrometer or BrukerAvance 300 MHz spectrometer. High resolution mass spectra (HRMS) were determined on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (APEX IV). Absorption spectra were recorded on a JASCO V-570 UV/Vis spectrophotometer. Steady-state fluorescence spectra were recorded on Hitachi (F-4500) spectrophotometers at 25 °C. All photographs were taken with a Canon digital camera. Density functional theory (DFT) calculations were performed at the B3LYP/6-31G* level of theory by using the Gaussian 09 program package.

Synthesis of Compound 3 and Compound 4

Compound 3: n-BuLi (1.6 M in THF, 10.4 mL, 1.1 equiv.) was added to a solution of 2-ethynylthiophene (15 mmol, 1.0 equiv.) in dry THF at -78 °C under the atmosphere of argon. After the resulting solution was stirred for 40 min at -78 °C, a solution of di(thiophen-2-yl)methanone (15 mmol, 1 equiv.) in dry THF was added slowly. After 15 min, the resulting solution was slowly warmed up to room temperature and stirred for another 10 h. Finally, the resulting mixture was quenched by saturated aqueous NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3 \times 30 mL). The combined organic layers were washed with brine (20 mL), dried with MgSO_4 , concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: n-hexane: CH_2Cl_2 = 1:2) to give dark brown solids of the title compound (**3**). yield: 75%. ^1H NMR (400 MHz, CD_2Cl_2) δ (ppm): δ 7.35 (dd, J = 4.1, 2.3 Hz, 2H), 7.15 (d, J = 3.8 Hz, 1H), 6.99 (dd, J = 4.8, 3.0 Hz, 5H), 6.86 (d, J = 3.8 Hz, 1H), 3.41 (s, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ (ppm): δ 153.2, 150.6, 133.0, 126.8, 126.6, 126.3, 126.0, 122.2, 81.8, 76.7 and 76.2. HRMS calcd for $\text{C}_{15}\text{H}_{10}\text{OS}_3^+$, 301.9888; found: 301.9862.

Compound 4: Propargyl alcohol of compound **3** (3.02 g, 10 mmol, 1equiv) was dissolved in dry toluene (30 mL) with moderate heating, then the solution was cooled and stirred at 0 °C under a nitrogen atmosphere. Triethylamine (NEt_3) (2.0 mL, 14 mmol, 1.4 equiv) and enzenesulfonyl

chloride (PhSO₂Cl) (1.5 mL, 11.7 mmol, 1.17 equiv) were added dropwise to the solution successively to keep the temperature of the reaction below 10 °C. After the addition, the solution was stirred at 0 °C for 15 min, then warmed up to room temperature for 15 min and then heated to 110 °C for 24 h. Finally, the reaction was cooled, diluted with ethyl acetate (100 mL) and washed with 2.0 M HCl. The organic layers were collected, dried over MgSO₄, concentrated under reduced pressure, and purified by flash column chromatography on silica gel (eluent: n-hexane) to give yellow solid of the title compound **4**. yield: 25%. ¹H NMR (400 MHz, CD₂Cl₂) δ (ppm): 7.36 (d, *J* = 5.8 Hz, 2H), 7.29 (dd, *J* = 5.2, 1.2 Hz, 2H), 7.25 (dd, *J* = 5.2, 1.2 Hz, 2H), 6.99 (d, *J* = 5.8 Hz, 2H), 6.86 (dd, *J* = 5.1, 3.5 Hz, 2H), 6.83 (dd, *J* = 5.2, 3.5 Hz, 2H), 6.80 (dd, *J* = 3.5, 1.2 Hz, 2H), 6.74 (dd, *J* = 3.5, 1.2 Hz, 2H) ¹³C NMR (100 MHz, CD₂Cl₂) δ (ppm): 143.3, 142.7, 141.8, 140.5, 130.2, 129.9, 129.2, 128.7, 127.0, 126.8, 126.7, 126.1, 126.0, 125.6 and 124.2. HRMS calcd for C₃₀H₁₆S₆⁺, 567.9571; found: 567.9490; Elemental analysis calculated for C₃₀H₁₆S₆ (%): C, 63.40; H, 2.84. found: C, 63.38; H, 2.86.

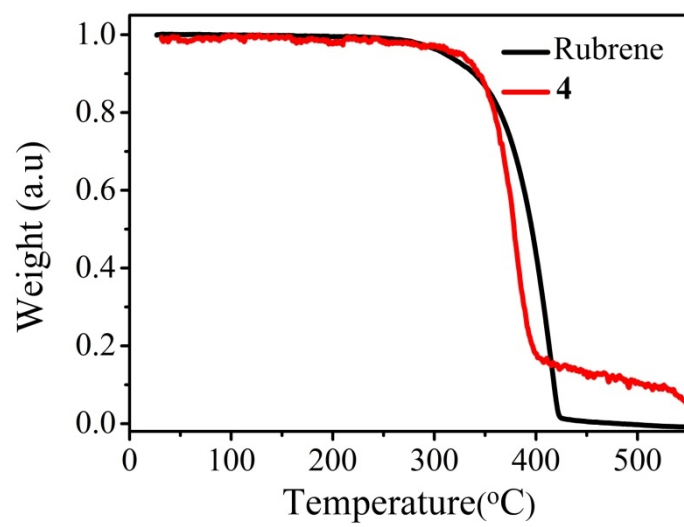


Fig. S1. TGA curve of compound **4** and rubrene, with a heating rate of 10 °C/min under nitrogen.

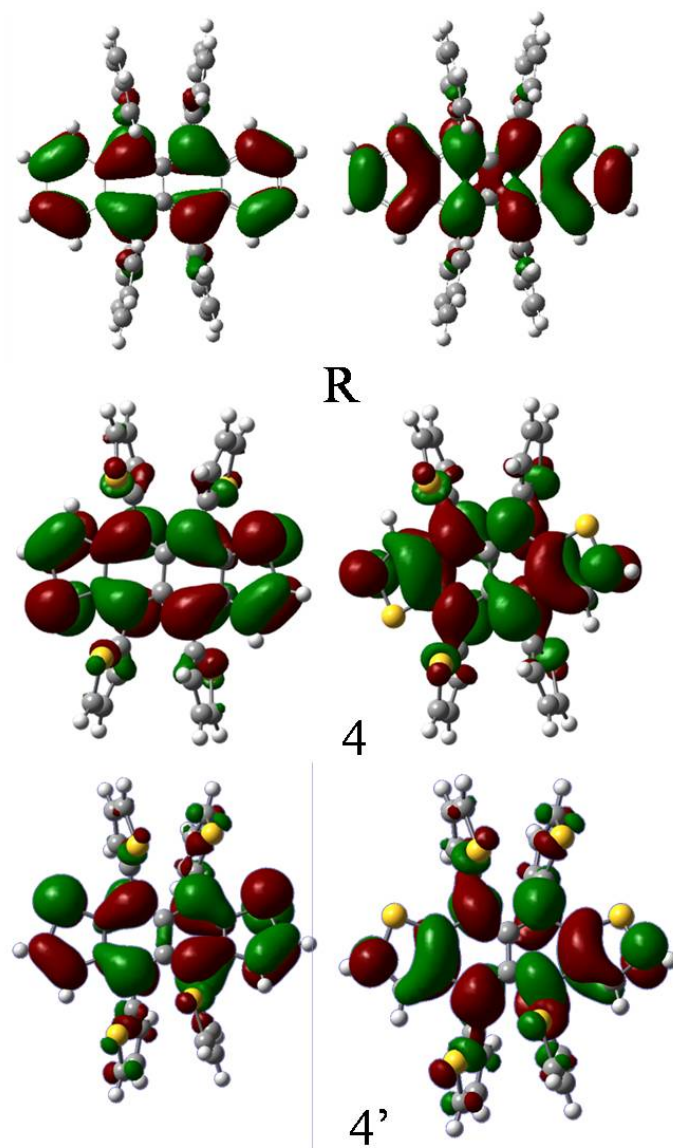


Fig. S2. HOMO (left) and LUMO (right) orbitals of rubrene (R), compounds 4 and isomer 4' calculated by DFT theory.

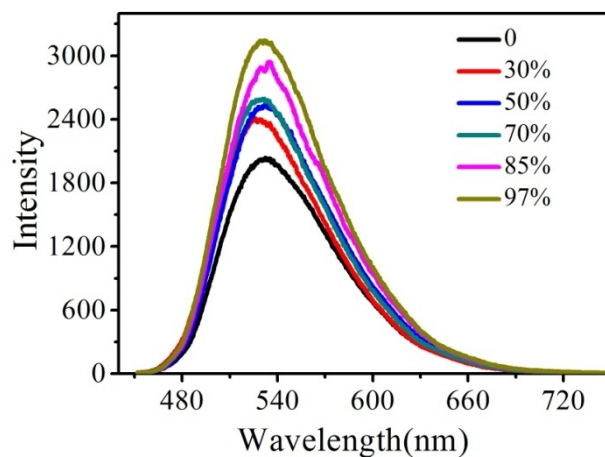


Fig. S3. The dependence of the PL intensity on the composition of hexane (solvent: CH_2Cl_2). The concentration was kept at $40 \mu\text{M}$, excitation wavelength: 442 nm .

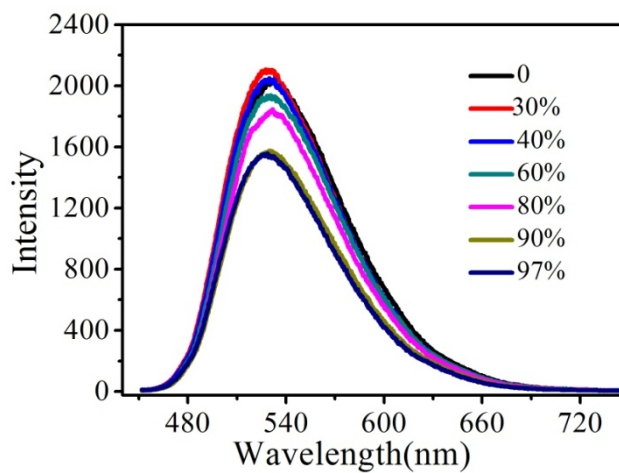


Fig. S4. The dependence of the PL intensity on the composition of methanol (solvent: CH_2Cl_2). The concentration was kept at $40 \mu\text{M}$, excitation wavelength: 442 nm .

Fig. S5 ^1H NMR and ^{13}C NMR of compound 3

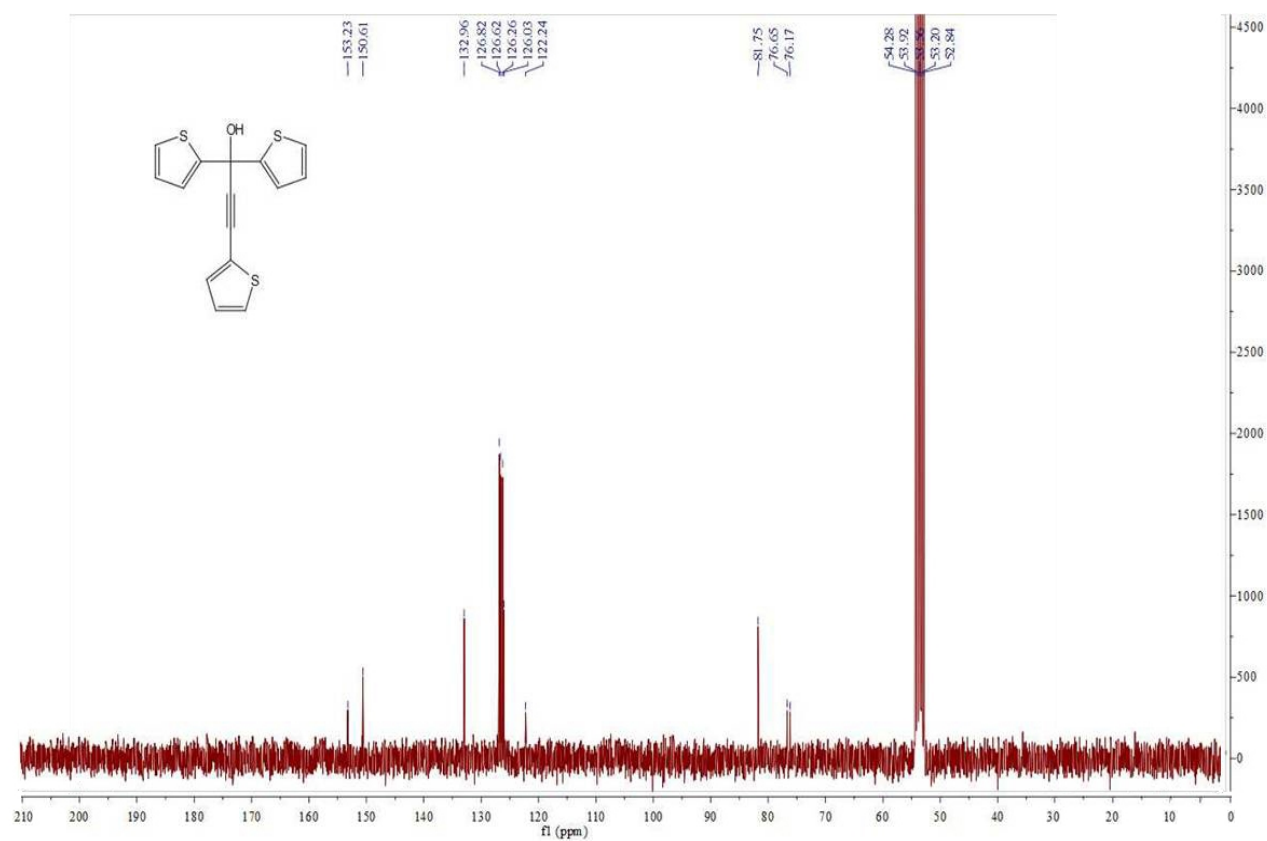
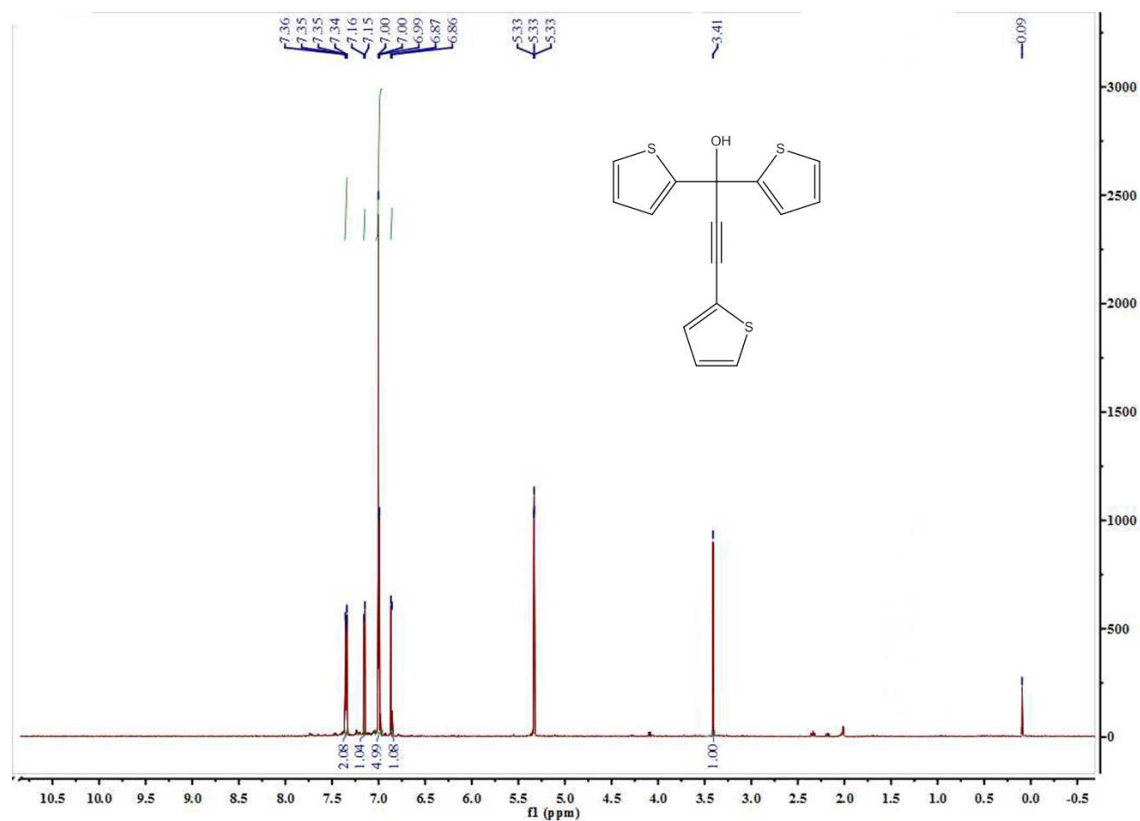


Fig. S6 ^1H NMR and ^{13}C NMR of compound 4

