

Supporting Information

Synthesis and Photophysical Properties of Amino-Substituted

Benzodithiophene-Based Fluorophores

Shuguang Wen, Jie Liu, Meng Qiu, Yonghai Li, Dangqiang Zhu, Chuantao Gu, Liangliang Han, Renqiang Yang*

Table of Contents

General Experimental Details	S2
Synthesis	S3
X-ray Crystal Structure Analysis	S7
Photophysical Properties	S8
Theoretical Calculations	S9

General experimental details

All reactions and manipulations were carried out under Ar with the use of standard inert atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel 200-300 mesh. Benzo(1,2-b:4,5-b')dithiophene-4,8-dione (**1**) was synthesized according to the literature¹. Unless stated otherwise, the reagents were purchased from commercial sources, and used without further purification. ¹H NMR and ¹³C NMR spectra were performed in a Bruker AVANCE-III 600 MHz spectrometer using solutions in CDCl₃ and chemical shifts were recorded in ppm units with tetramethylsilane (TMS) as the internal standard. Elemental analyses were carried out using a vario EL cube elemental analyzer.

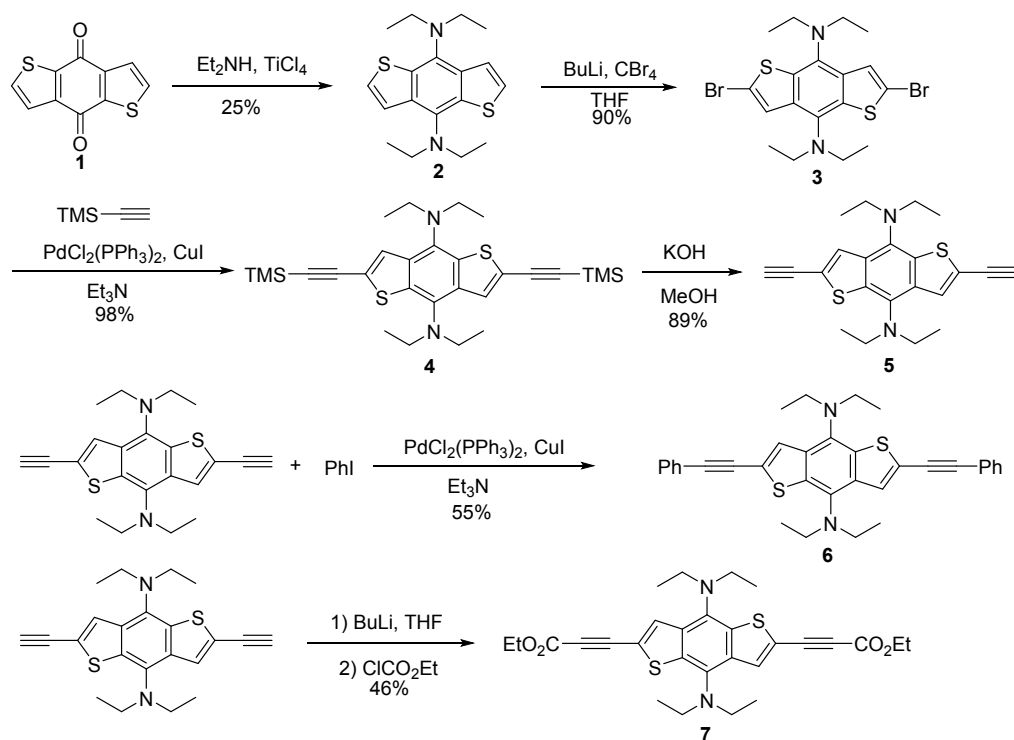
Crystal structural analysis: Crystals of **6** were grown by slow evaporation from the ethylacetate/dichloromethane solution. All single crystals data were collected on Rigaku Saturn diffractometer with CCD area detector. All calculations were performed using the SHELXL97² and crystal structure crystallographic software packages.

Potophysical properties: UV-vis spectra were recorded on a Lambda25 spectrophotometer. Fluorescence spectra and absolute quantum yields (Φ) were collected on a Horiba Jobin Yvon Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. Fluorescence quantum yields in different solvents were determined by using Quinine sulfate ($\Phi = 0.54$ in 0.1 M H₂SO₄) as a reference standard using the comparative method. PL images were recorded in grayscale with an Olympus FluoView FV1000 coupled to a BX-81 inverted microscope using Argon-ion (488 nanometer line), violet diode (405 nanometer), and green helium-neon (543 nanometer) lasers.

Preparation of PS films: In a tube glass, each solid sample (2 mg) was dissolved in 5 mL THF solution of polystyrene (40 mg). The resulting solution was dropped onto a quartz plate (10 mm × 10 mm) and spin-coated at 1000 rpm for 20 sec. The deposited film was dried under reduced pressure at room temperature for 1.5 h.

Computational methods: The ground-state geometry of the compounds has been optimized at the density functional theory (DFT) at the B3LYP/6-31G(d) level of theory using the Gaussian 09 package³. The time-dependent density functional theory (TD-DFT) calculations were conducted at the B3LYP/6-31G(d) level of theory.

Synthesis



Scheme S1. Synthetic approaches for compound 4-7.

Compound 2⁴. To the solution of benzo(1,2-b:4,5-b')dithiophene-4,8-dione (3.3 g, 15 mmol) and TiCl₄ (5.71 g, 3.3 mL, 30 mmol) in toluene (100 mL), Et₂NH (21 mL) was added dropwise at 0 °C. The reaction was stirred overnight at room temperature and quenched by water. Then the mixture was extracted with EtOAc, concentrated, and purified by column chromatography on silica gel to give the product **2** as white solid (1.23 g, 25%). M. P. 151-153 °C. ¹H NMR (600 MHz, CDCl₃, δ): 7.52 (d, *J* = 5.6 Hz, 2 H), 7.34 (d, *J* = 5.6 Hz, 2 H), 3.36 (q, *J* = 7.1 Hz, 8 H), 1.01 (t, *J* = 7.1 Hz, 12 H). ¹³C NMR (150 MHz, CDCl₃, δ): 140.0, 136.5, 135.8, 126.0, 121.9, 48.6, 14.4. IR (film): ν_{max} 3446, 2970, 2927, 2855, 1739, 1374, 811, 733. HRMS (APCI) calcd for C₁₈H₂₅N₂S₂ [M+H]⁺: 333.1454, found: 333.1457. Anal. Calcd. For C₁₈H₂₄N₂S₂: C,

65.02; H, 7.27; N, 8.42; S, 19.29. Found: C, 65.27; H, 7.15; N, 8.32; S, 19.26.

Compound 3. Under the protection of argon, *n*-BuLi (6.52 mL, 10.4 mmol, 1.6 M in hexanes) was added dropwise to compound **2** (1.38 g, 4.2 mmol) in THF (30 mL) at -78 °C. After stirring for 30 min the solution was warmed to room temperature and stirred for 1h. Then a solution of CBr₄ (4.15 g, 12.5 mmol) in THF (10 mL) was added dropwise at -78 °C. The reaction was allowed to warm to room temperature overnight. The reaction mixture was quenched with water, extracted with EtOAc, dried with Na₂SO₄ and concentrated in vacuum. Crude compound was purified by column chromatography on silica gel to give compound **3** as yellow solid (1.85 g, 90%). M. P. 189-190 °C. ¹H NMR (600 MHz, CDCl₃, δ): 7.47 (s, 2 H), 3.27 (q, *J* = 7.1 Hz, 8 H), 1.0 (t, *J* = 7.1 Hz, 12 H). ¹³C NMR (150 MHz, CDCl₃, δ): 141.9, 134.9, 134.8, 124.5, 115.9, 48.7, 14.3. IR (film): ν_{\max} 2967, 2927, 2833, 1742, 1375, 1247, 1087, 743. HRMS (APCI) calcd for C₁₈H₂₃Br₂N₂S₂ [M+H]⁺: 490.9644, found: 490.9643. Anal. Calcd. for C₁₈H₂₂Br₂N₂S₂: C, 44.09; H, 4.52; N, 5.71; S, 13.08. Found: C, 44.32; H, 4.67; N, 5.62; S, 12.93.

Compound 4⁵. Ethynyltrimethylsilane (694 mg, 7.07 mmol) was added to the mixture of **3** (1.596 g, 3.256 mmol), PdCl₂(PPh₃)₂ (104 mg, 0.148 mmol), CuI (8.4 mg, 0.045 mmol) in 15 mL of dry Et₃N under Argon. The mixture was refluxed 16 h and then cooled down. The mixture was quenched by H₂O and then extracted with ethyl acetate. The organic extract was dried over anhydrous Na₂SO₄, filtered and evaporated under reduced pressure. The crude compound was purified by flash column chromatography over silica gel to afford the compound **4** as a yellow solid (1.68 g, 98%). M. P. 257-258 °C. ¹H NMR (600 MHz, CDCl₃, δ): 7.63 (s, 2 H), 3.30 (q, *J* = 7.1 Hz, 8 H), 0.99 (t, *J* = 7.1 Hz, 12 H), 0.27 (s, 18 H). ¹³C NMR (150 MHz, CDCl₃, δ): 140.7, 136.3, 135.9, 127.6, 122.8, 101.1, 98.5, 48.6, 14.3, -0.2. IR (film): ν_{\max} 2956, 2926, 2854, 2145, 1464, 850, 690. HRMS (APCI) calcd for C₂₈H₄₁N₂S₂Si₂ [M+H]⁺: 525.2245, found: 525.2238. Anal. Calcd. for C₂₈H₄₀N₂S₂Si₂: C, 64.07; H, 7.68; N, 5.34; S, 12.22. Found: C, 64.35; H, 7.53; N, 5.42; S, 12.33.

Compound 5. To solution of **4** (619 mg, 1.18 mmol) in CH₂Cl₂ (25 mL) was added solution of KOH (371 mg) in MeOH (6 mL). The mixture was stirred at room

temperature overnight. After workup with EtOAc/H₂O, the organic phase was concentrated and purified by column chromatography on silica gel to give compound **5** as yellow solid (400 mg, 89%). M. P. decomposed. ¹H NMR (600 MHz, CDCl₃, δ): 7.69 (s, 2 H), 3.45 (s, 2 H), 3.31 (q, *J* = 7.1 Hz, 8 H), 1.00 (t, *J* = 7.1 Hz, 12 H). ¹³C NMR (150 MHz, CDCl₃, δ): 140.7, 136.4, 135.8, 128.2, 121.9, 83.0, 77.9, 48.6, 14.3. IR (film): ν_{\max} 3274, 2956, 2920, 2851, 1464, 1088, 1021, 801. HRMS (APCI) calcd for C₂₂H₂₅N₂S₂ [M+H]⁺: 381.1454, found: 381.1457. Anal. Calcd. for C₂₂H₂₄N₂S₂: C, 69.43; H, 6.36; N, 7.36; S, 16.85. Found: C, 69.32; H, 6.46; N, 7.25; S, 16.97.

Compound 6⁵. To the mixture of **5** (102 mg, 0.269 mmol), PdCl₂(PPh₃)₂ (8.4 mg, 0.012 mmol), CuI (1.0 mg, 0.005 mmol) and PhI (110 mg, 0.538 mmol) was added Et₃N (3 mL) under Ar. The reaction was stirred at reflux for 16h and quenched by water. The mixture was extracted by EtOAc, dried and concentrated in vacuum. The crude product was purified by column chromatography over silica gel to afford the compound **6** as yellow solid (79 mg, 55%). M. P. 240-243 °C. ¹H NMR (600 MHz, CDCl₃, δ): 7.70 (s, 2 H), 7.57-7.55 (m, 4 H), 7.37-7.25 (m, 6 H), 3.35 (q, *J* = 7.1 Hz, 8 H), 1.04 (t, *J* = 7.1 Hz, 12 H). ¹³C NMR (150 MHz, CDCl₃, δ): 140.9, 136.3, 136.1, 131.6, 128.7, 128.5, 127.0, 123.1, 122.7, 95.1, 83.8, 48.7, 14.4. IR (film): ν_{\max} 3360, 2955, 2924, 2853, 1734, 1460, 1377, 750, 686. HRMS (APCI) calcd for C₃₄H₃₃N₂S₂ [M+H]⁺: 533.2080, found: 533.2081. Anal. Calcd. for C₃₄H₃₂N₂S₂: C, 76.65; H, 6.05; N, 5.26; S, 12.04. Found: C, 76.47; H, 6.16; N, 5.36; S, 12.01.

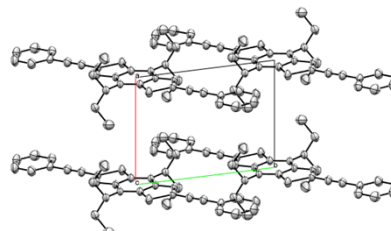
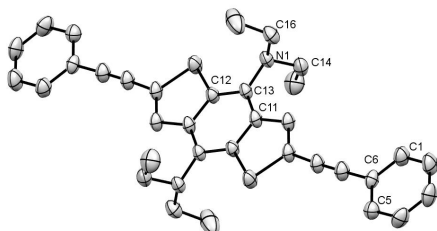
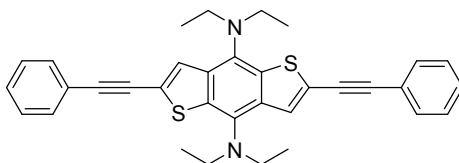
Compound 7⁶. To a solution of **5** (233 mg, 0.61 mmol) in THF (5 mL) at -78 °C was added a solution of *n*-BuLi in hexane (0.77 mL, 1.6 M) dropwise via syringe. The reaction mixture was stirred at -30 °C 30 minutes and warmed up to 0 °C and stirred for 30 minutes. Then the resulting turbid mixture was cooled down to -78 °C and a solution of ethyl chloroformate (133 mg, 1.22 mmol) in 1 mL of THF was added dropwise. The reaction mixture was stirred at -78 °C for 1h and warmed to room temperature during a period of 1 hour. The reaction was quenched by water and extracted with EtOAc. The organic phase was washed with brine, dried over Na₂SO₄ and concentrated. The product was purified by column chromatography on silica gel to give compound **7** as orange solid (146 mg, 46%). M. P. decomposed. ¹H NMR (600

MHz, CDCl₃, δ): 7.92 (s, 2 H), 4.33 (q, *J* = 7.1 Hz, 4 H), 3.32 (q, *J* = 7.1 Hz, 8 H), 1.38 (t, *J* = 7.1 Hz, 6H), 1.03 (t, *J* = 7.1 Hz, 12 H). ¹³C NMR (150 MHz, CDCl₃, δ): 153.7, 141.7, 137.4, 136.3, 132.0, 120.0, 86.0, 80.4, 62.3, 48.6, 14.3, 14.1. IR (film): ν_{\max} 3420, 2955, 2923, 2852, 2209, 1660, 1460, 1337, 743. HRMS (APCI) calcd for C₂₈H₃₃N₂O₄S₂ [M+H]⁺: 525.1877, found: 525.1878. Anal. Calcd. for C₂₈H₃₂N₂O₄S₂: C, 64.09; H, 6.15; N, 5.34; S, 12.22. Found: C, 64.32; H, 6.18; N, 5.43; S, 12.37.

References

- 1 J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li., Y. Yang *Macromolecules*, 2008, **41**, 6012.
- 2 SHELX-97, Program for the Refinement of Crystal Structure, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), 1997.
- 3 Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 4 M. Tamano, Y. Nagai, J. Koketsu, *Nippon Kagaku Kaishi*, 1988, 1977.
- 5 K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467.
- 6 R. K. Dieter, K. Lu, *J. Org. Chem.*, 2002, **67**, 847.

Data of X-ray crystallographic analysis of compound 6



Empirical formula	C ₃₄ H ₃₂ N ₂ S ₂
Formula weight	532.74 g/mol
Temperature	296 (2)
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1 (2)
Unit cell dimensions	a=7.615(6) Å α=83.045(12)° b=9.543(7) Å β=77.140(11)° c=10.259(8) Å γ=81.412(12)°
Volume	715.68(90) Å ³
Z	1
Calc. density	1.236 g/cm ³
Absorption coefficient	0.212 mm ⁻¹
F(000)	282
Crystal size	0.19 x 0.15 x 0.12 mm ³
Theta range for data collection	2.84 to 24.56
Limiting indices	-7 ≤ h ≤ 9, -8 ≤ k ≤ 11, -11 ≤ l ≤ 12
Reflections collected / unique	2493/1936 [R _{int} = 0.0169]
Completeness to theta = 25.50°	97.8%
Max. and min. transmission	0.9609 to 0.9751
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2493 / 0 / 174
Goodness-of-fit on F ²	1.084
Final R indices [I > 2σ(I)]	R1 = 0.0445, wR2 = 0.1192
R indices (all data)	R2 = 0.0606, wR2 = 0.1279
Largest diff. peak and hole	0.246 and -0.282 e Å ⁻³

Photophysical Properties

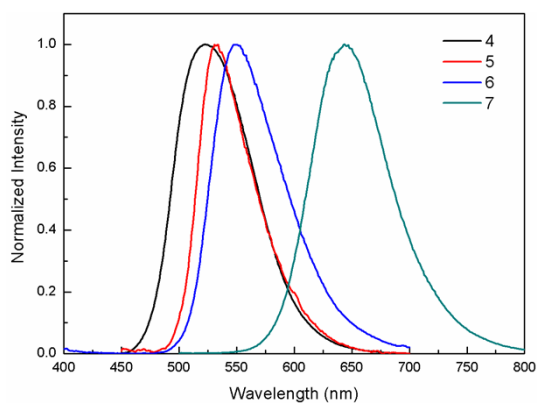


Figure S1. PL spectra of 4-7 in pure solid states.

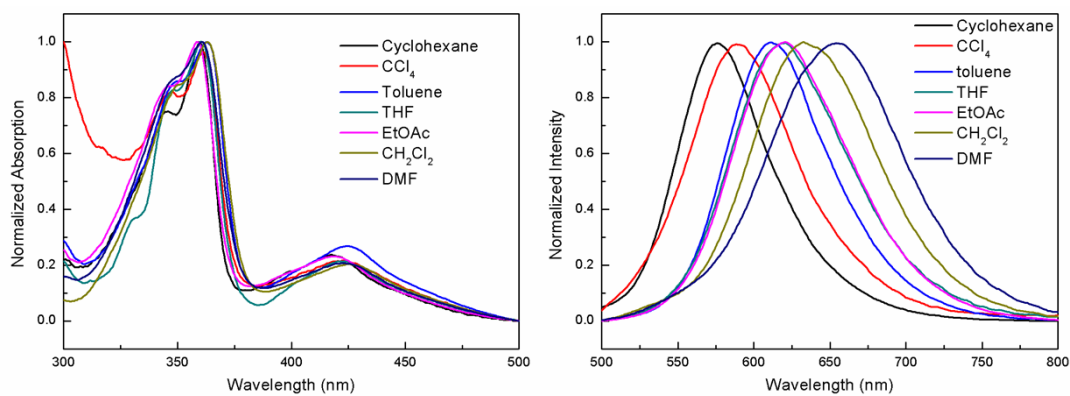


Figure S2. Normalized absorption and emission spectra of 7 in various solvents.

Theoretical Calculations

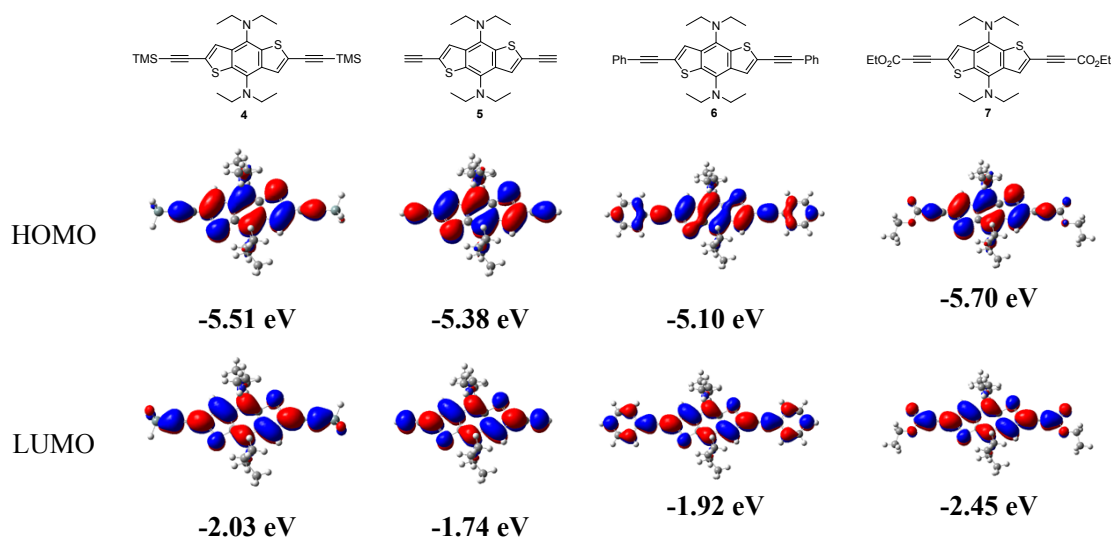


Figure S3. Pictorial representation of the Kohn-Sham HOMOs and LUMOs of fluorophores 4-7, calculated at the B3LYP/6-31G(d) level of theory.

Table S1. Absorption parameters obtained by TD-DFT computations for compounds 4-7.

Electronic transitions S_0-S_1	$\lambda_{\max}^{\text{abs}}$ (nm)	Exp (nm) ^a	f^b	Excitation energies (eV)	Main configurations
4	386	395	0.4955	3.2098	HOMO-LUMO
	339	347	0.7125	3.6558	HOMO-3-LUMO
5	368	389	0.2944	3.3684	HOMO-LUMO
	323	336	0.468	3.8332	HOMO-3-LUMO+1
6	421	407	1.6036	2.9415	HOMO-LUMO
	367	363	0.5176	3.3764	HOMO-1-LUMO
7	417	417	0.4197	2.9689	HOMO-LUMO
	356	359	0.983	3.4774	HOMO-3-LUMO

^a Measured in cyclohexane. ^b Oscillator strength.