Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Growth of Molecular Crystal Aggregates for Efficient Optical Waveguides

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Scheme 1. Synthetic route of benzothiadiazole derivatives

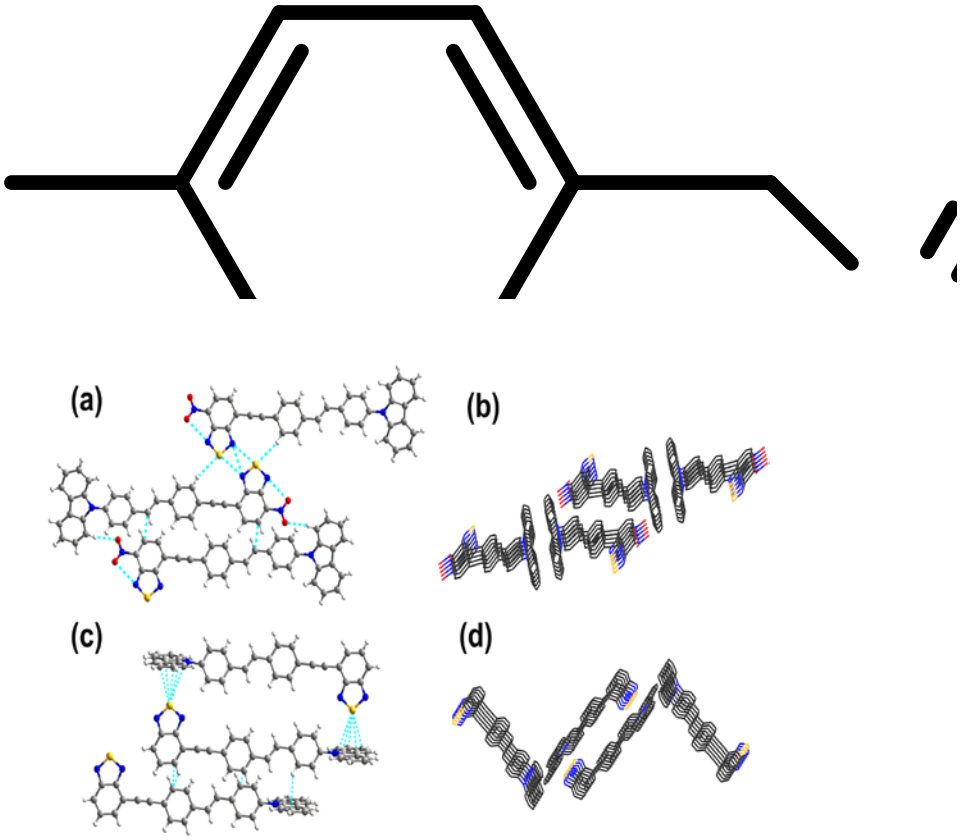

Fig. S1 Intermolecular stack contacts in adjacent **BTN-6** (a), **BTN-7** (c).View down the crystallographic *b*-axis of stacked molecules of **BTN-6** (b) and *a*-axis of stacked molecules of **BTN-7** (d).

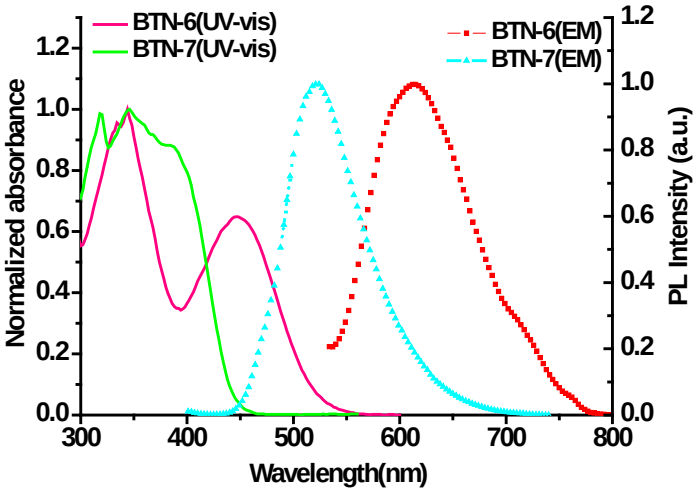

Fig. S2 Uv-vis and fluorescence (film) spectra of **BTN-6** and **BTN-7.**

Table S1. Photophysical Properties of **BTNs**

Compound	λ^{abs}_{max}[nm]	λ^{em}_{max}[nm]	Φ_f[a]	Stoke's shift [nm]	λ^{em}_{max}[nm] [b]
BTN-6	334,344,448				626
BTN-7	318,346,384	552	0.46	168	522

[a] Fluorescent quantum yield relative to Fluorescein in ethanol (0.97).

[b] in the film.

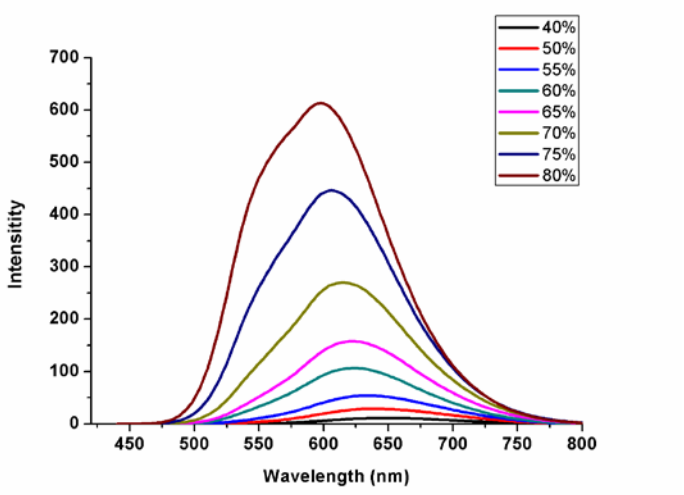

Fig. S3 Fluorescence spectra of **BTN-6** suspended in different fractions of hexane with excitation wavelength of 436 nm

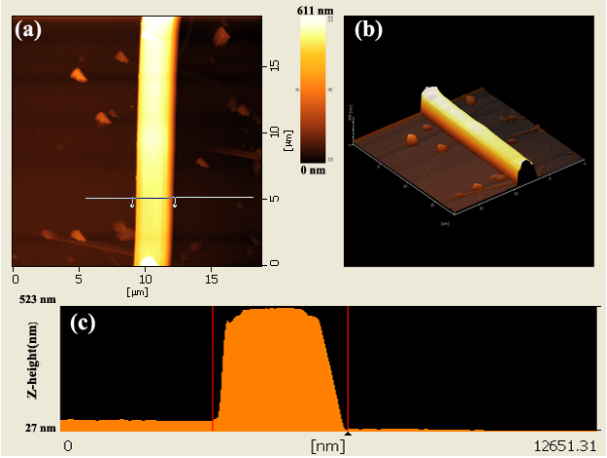

Fig.S4 2D (a) and 3D (b) AFM images over a single microtube; (c) A line-scan profile (marked in a) clearly reveals the flat top of the microtube.

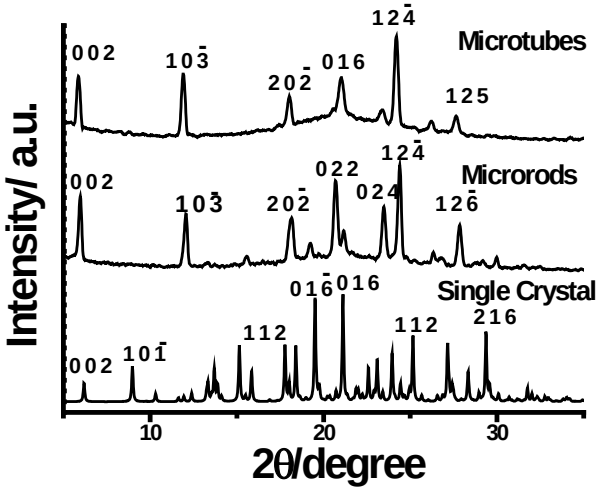

Fig. S5 Powder XRD patterns of **BTN-6**, the single-crystal (bottom), as-prepared microrods (middle) and microtubes (top).

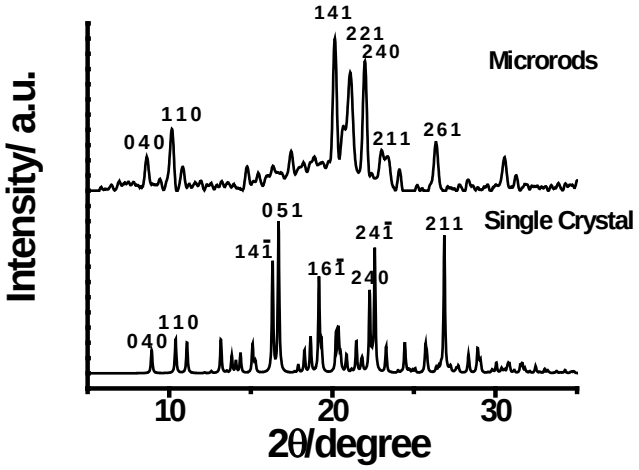

Fig. S6 Powder XRD patterns of **BTN-7**, the single-crystal (bottom),and as-prepared microrods (top) .

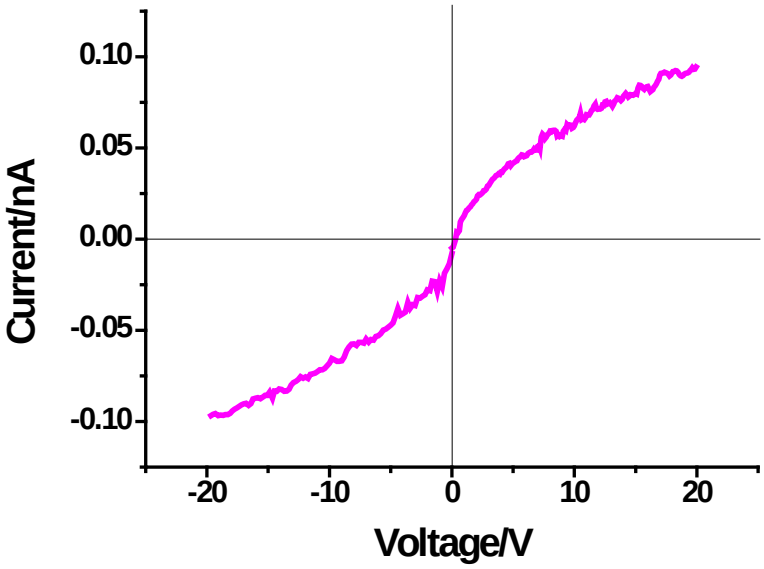

Fig. S7 Typical I-V curve for a single **BTN-6** microrod.

Experimental Section

Characterization. UV-Vis spectra were measured on a Hitachi U-3010 spectrometer. The fluorescence spectra were measured on a Hitachi F-4500 spectrometer. SEM images were taken from Hitachi S-4800 microscopes at an accelerating voltage of 10 kV or 15 kV. TEM images were taken from a JEOL JEM-1011 microscope at an accelerating voltage of 100 kV. AFM measurements were carried out with Multimode Nanoscope controller IIIa (Veeco Inc.) operated in tapping mode. Fluorescence

images of the microstructures were taken by using a laser-based fluorescence microscope (Olympus IX81) and an intensified charge-coupled device (CCD, Olympus DP71) detection system. To measure the microarea PL spectra of single microrod, the microrods dispersed on a glass cover-slip were excited with a UV laser (λ=351 nm, Beamlok, Spectra-physics). The excitation laser was filtered with a band-pass filter (330-380 nm), then focused to excite the microrod with an objective (50x, N.A.=0.80). The spot size was less than 2 μm. The collected PL emission was coupled to a grating spectrometer (Acton, SP-2358) with matched ProEm: 512B EMCCD camera (Princeton Instruments). The optical loss coefficient (α) was calculated by a single exponential fitting [$I_{tip}/I_{body}=Aexp^{-\alpha x}$, where x is the distance between the exciting site and the emitting tip, and A is the ratio of the light escaping from the excitation spot and that of light propagating along the fiber].

General procedure for the synthesis of **(E)-9-(4-(4-iodostyryl)phenyl)-9H-carbazole (1).**To a mixture of 4-(9H-carbazol-9-yl)benzaldehyde (516 mg, 2 mmol) and diethyl diethyl 4-iodobenzylphosphonate (708 mg, 2 mmol) in 20 mL of THF at 0 °C under nitrogen atmosphere, was added potassium tert-butoxide (267 mg, 2.4 mmol) slowly. After totally added, the resulted mixture was stirred at room temperature for 30 min, water (20 mL) was added. The solid formed was filtered and washed with ethanol to give crude **1** which was purified by recrystallization with EtOAc to afford pure **1** (753 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.18(m, 2 H, CH=CH), 7.25 (m, 4 H, Ar H), 7.43 (s, 4 H, Ar H), 7.56 (d, *J* = 6.8 Hz, 2 H, Ar H), 7.21 (d, *J* = 5.9 Hz, 4 H, Ar H), 8.14 (d, *J* = 6.8 Hz, 2 H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 139.8, 136.9, 136.3, 135.7, 135.2, 127.6, 127.5,127.4, 127.0, 126.3, 125.1, 122.6, 119.4, 119.1, 108.9, 92.2; HRMS (EI, *m/z*): [M^+] calcd for $C_{26}H_{18}IN$: 471.0484 ; found: 471.0491.

(E)-9-(4-(4-ethynylstyryl)phenyl)-9H-carbazole (2). $PdCl_2(PPh_3)_2$ (21 mg, 0.030 mmol), CuI (11 mg, 0.060 mmol), and trimethylsilylacetylene (0.14 mL, 2.0 mmol) were added to a solution of **1** (706 mg, 1.5 mmol) in $(i\text{-Pr})_2NH$ (10 mL) and THF (30 mL) and the mixture was stirred under Ar at 25 °C for 60 min. The solvent was evaporated in vacuo. The mixture was purified by SiO_2 chromatography with CH_2Cl_2 to obtain desired TMS-protected acetylenes. The above TMS-protected acetylene

dissolved in THF (20 mL) and MeOH (20 mL) was added K_2CO_3 (414 mg, 3 mmol) and the reaction mixture was stirred for 30 min under Ar. Then the solvent was evaporated in vacuo. The mixture was purified by SiO_2 chromatography with CH_2Cl_2/petroleum ether (PE) (1/1, v/v) to obtain desired compound **2** (421 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.17 (s, 1 H,CH), 7.20 (t, *J* = 9.8 Hz, 2 H,CH=CH), 7.32 (d, *J* = 6.8 Hz, 2 H, Ar H), 7.44 (m, 4 H, Ar H), 7.53 (s, 4 H, Ar H), 7.58 (d, *J* = 8.2 Hz, 2 H, Ar H), 7.73 (d, *J* = 8.2 Hz, 2 H, Ar H), 8.17 (d, *J* = 7.8 Hz, 2 H, Ar H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 139.9, 136.7, 136.3, 135.2, 131.7, 127.9, 127.8,127.1, 126.3, 125.6, 125.1, 122.6, 120.4, 119.5, 119.1, 108.9, 82.8, 77.2; HRMS (EI, *m/z*): [M^+] calcd for $C_{28}H_{19}N$: 369.1517; found: 369.1523.

(E)-4-((4-(4-(9H-carbazol-9-yl)styryl)phenyl)ethynyl)-7-nitrobenzo[c][1,2,5]thiadiazole (BTN-6). To a stirred solution of **2** (369 mg, 1.0 mmol) and 4-bromo-7-nitrobenzo[c][1,2,5]thiadiazole (258 mg, 1.0 mmol) in THF/ (*i*-Pr)$_2$NH (3/1, v/v) were added $PdCl_2(PPh_3)_2$ (28 mg) and CuI (15 mg) under an argon flow at room temperature. The reaction mixture was then stirred for 4 h at room temperature. The solvent was then evaporated under reduced pressure. The mixture was purified by SiO_2 chromatography with CH_2Cl_2 to obtain desired compound **BTN-6** (290 mg, 53% yield) as a yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.31 (m, 2 H,Ar H), 7.45 (m, 5 H,Ar H,CH), 7.57 (d, *J* = 16.3 Hz, CH), 7.67 (d, *J* = 8.6 Hz, 2 H, Ar H), 7.75 (d, *J* = 8.1 Hz, 2 H, Ar H), 7.82 (d, *J* = 8.1 Hz, 2 H, Ar H), 7.94 (d, *J* = 8.3 Hz, 1 H, Ar H), 8.14 (d, *J* = 7.7 Hz, 1 H, Ar H), 8.25 (d, *J* = 7.7 Hz, 2 H, Ar H) 8.71 (d, *J* = 8.3 Hz, 2 H, Ar H) ppm; HRMS (EI, *m/z*): [M^+] calcd for $C_{34}H_{20}N_4O_2S$:548.1307; found: 548.1315.

(E)-4-((4-(4-(9H-carbazol-9-yl)styryl)phenyl)ethynyl)benzo[c][1,2,5]thiadiazole (BTN-7). To a stirred solution of **2** (369 mg, 1.0 mmol) and 4-bromobenzo[c][1,2,5]thiadiazole (214 mg, 1.0 mmol) in THF/ (*i*-Pr)$_2$NH (3/1, v/v) were added $PdCl_2(PPh_3)_2$ (28 mg) and CuI (15 mg) under an argon flow at room temperature. The reaction mixture was then stirred for 8 h under reflux, and then cooled to room temperature. The solvent was then evaporated under reduced pressure. The mixture was purified by SiO_2 chromatography with CH_2Cl_2/petroleum ether (PE)

(1/1, v/v) to obtain desired compound **BTN-7** (226 mg, 45% yield) as a light yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 7.31 (m, 2 H, Ar H), 7.45 (m, 5 H, Ar H,CH), 7.54 (d, *J* = 16.7 Hz, 1 H, CH), 7.68 (t, *J* = 7.8 Hz, 4 H, Ar H), 7.78 (t, *J* = 8.0 Hz, 3 H, Ar H), 7.93 (d, *J* = 8.3 Hz, 2 H, Ar H), 7.98 (d, *J* = 6.9 Hz, 1 H, Ar H), 8.16 (d, *J* = 8.9 Hz, 1 H, Ar H), 8.25 (d, *J* = 7.7 Hz, 2 H, Ar H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 85.3, 95.0, 108.9, 116.3, 119.2, 119.4, 120.9, 121.0, 122.6, 125.1, 125.7, 126.3, 127.1, 127.8, 128.0, 128.4, 131.5, 131.7, 135.2, 163.3, 136.8, 139.8, 153.7, 153.8. ppm. HRMS(EI, *m/z*): [M^+] calcd for $C_{34}H_{21}N_3S$: 503.1456; found: 503.1463.

Reference:

K. Takazawa, *J. Phys. Chem. C* **2007**, *111*, 8671-8676.