Electronic supplementary information

Cascade energy transfer boosted near-infrared circularly polarized luminescence of nanofibers from exclusively achiral system

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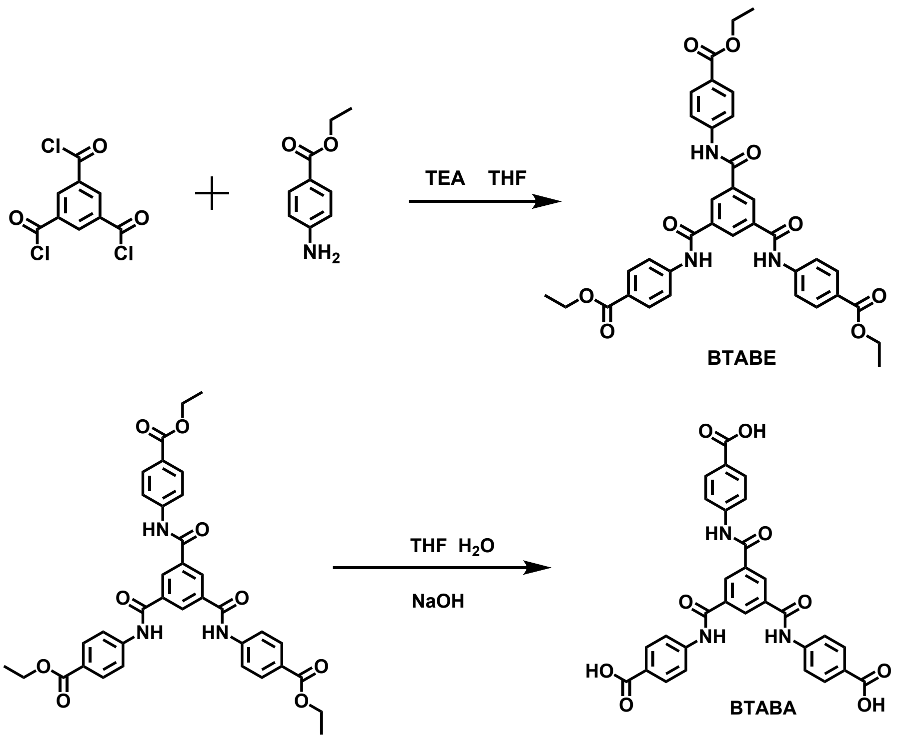
Characterization

The ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker Advance III 400 HD spectrometer. Mass spectral data were obtained by using a BIFLEIII matrix-assisted laser desorption/ionization time of fight mass spectrometry (MALDI-TOF-MS) instrument. UV-vis spectra, fluorescence spectra and CD spectra were obtained using a Hitachi U-3900, EDINBURGH FS5 and JASCO 1500 spectrometers, respectively. FDCD spectra were recorded on CD spectrometer J-1700 (JASCO) with standard FDCD attachment (PTC-517 & PML-534). CPL measurements were performed with JASCO CPL-200 spectrometer. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 FE-SEM with an accelerating voltage of 10 kV. Before SEM measurement, the samples on silicon wafers were coated with a thin layer of Pt to increase the contrast. Fourier transform-infrared (FT-IR) spectra were recorded on a Spotlight 200i with KBr background. Samples were vacuum-dried and made into plates with KBr for FT-IR spectral measurements. X-ray diffraction (XRD) analysis was performed on a PANalytical Empyrean X-ray diffractometer (Japan) with Cu Kα radiation (λ=1.5406Å), which was operated at a voltage of 40 kV and a current of 200 mA. The solid powder used in FT-IR, XRD and SEM was obtained by centrifuging and drying the assembled samples. Polarizing optical microscopy (POM) was recorded on the Olympus X83 using high-pressure mercury lamp as excitation source for fluorescent images.

Materials

All the starting materials and solvents were obtained from commercial suppliers and used as received. Milli-Q water (18.2 MΩ·cm) was used in all cases. 1,3,5-Benzenetricarbonyl trichloride, were purchased from Acros. Ethyl 4-aminobenzoate was purchased from J&K Chemical Ltd. Nile red was purchased from Saen Chemical Technology Co., Ltd. Cyanine 7 was purchased from Aladdin.

Synthetic Procedures



Synthesis of BTABE

At 0°C, a solution of 1,3,5-benzenetricarbonyl trichloride (1.06 g, 4.0 mmol) in dry THF was slowly treated with an excess of ethyl 4-aminobenzoate (2.64 g, 16.0 mmol) and triethylamine (4.4 mL, 32.0 mmol), and stirred overnight at ambient temperature. The reaction mixture was subsequently filtered and concentrated under reduced pressure. The resulting residue was dissolved in 100 mL of methanol, and the precipitate obtained was successively washed with water and methanol. The white powder obtained after drying yielded 73% of the product.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 10.80 (s, 3H), 8.74 (s, 3H), 7.92 – 7.62 (m, 12H), 4.54 – 3.98 (m, 6H), 1.27 (t, 9H). MALDI-TOF-MS m/z calcd for $C_{36}H_{33}N_3O_9$: 651.67; $[M+Na]^+$ found: 674.085.

Synthesis of BTABA

Slow addition of a 2 mL aqueous solution containing 4 M of sodium hydroxide to a suspension of 40 mL BTABE (1.31 g, 2 mmol) in a THF/H_2O (1/1, v/v) mixture ensued, which was stirred overnight at 60 °C. The resulting yellow solution was treated with 60 mL of water and subjected to 1 M dilute hydrochloric acid until the pH reached 1, resulting in the precipitation of a solid. The solid was subsequently filtered and washed with water and methanol, resulting in a final product yield of 60%.

^{1}H NMR (400 MHz, DMSO-d6) δ (ppm) 12.83 (s, 3H), 10.95 (s, 3H), 8.78 (s, 3H), 7.99 (m, 12H). MALDI-TOF-MS m/z calcd for $C_{30}H_{21}N_3O_9$: 567.51; $[M+Na]^+$ found: 690.003.

Theoretical Calculations

All calculations were performed using Gaussian 09. The calculations employed density functional theory (DFT) with the B3LYP/6-311G basis set. The ground-state (S0) geometries of BTABA and BTABA/NR were optimized using the DFT method. Starting with the planar geometries of BTABA and BTABA/NR, the first excited state (S1) was geometrically optimized using TD-DFT method with the PBE0/6-31G(d) basis set based on the optimized S0 geometry, and the transition properties of the low excited states were studied. The theoretical CD spectra were generated using SpecDis 1.71.[1]

Experimental Method

Preparation of BTABA Chiral Assemblies. In a 4 mL scale vial, BTABA monomer was dissolved in 0.6 mL of DMF solution, followed by mixing with 0.4 mL of deionized water. The resulting BTABA turbid solution was heated to transform into a transparent solution. Then, the solution was cooled down to 98° C and stabilized for 2 minutes on a vortex mixer with a temperature control attachment. Subsequently, the solution was subjected to vortex oscillation (with default parameters set as 2000 rpm and a duration of 10 minutes in clockwise direction) during synchronous cooling. The sample was then left at room temperature for 12 hours to fully mature and form randomly chiral supramolecular assemblies with either positive or negative CD signals. The chiral assemblies with special CD signals can serve as chiral seeds to control the chiral sign in the subsequent seed vortex treatment.

Seeded Vortex Treatment. In a 4 mL scale vial, BTABA monomer was dissolved in 0.6 mL of DMF and then mixed with 0.4 mL of deionized water. The resulting BTABA turbid solution was heated until it became transparent. The solution was then cooled to 98°C and stabilized on a vortex mixer with a temperature control attachment for 2 minutes. After adding seeds at a molar ratio of 1%, the solution was subjected to vortex oscillation during synchronous cooling (default parameters were set to 2000 rpm for 10 minutes in clockwise direction). The sample was then left at room temperature for 12 hours to fully mature and form chiral supramolecular assemblies with the same CD signal as the chiral seed.

Preparation of BTABA/Dyes Co-assemblies. In a 4 mL vial, 3mg of BTABA and different amounts of dyes were first dissolved in 0.6 mL of dimethylformamide (DMF) by sonication, and then 0.4 mL of Milli-Q water was injected. A compact supramolecular assembly formed instantly in the mixed solvent. The chiral assemblies were prepared by using the seeded vortex treatment.

Supplementary Figures

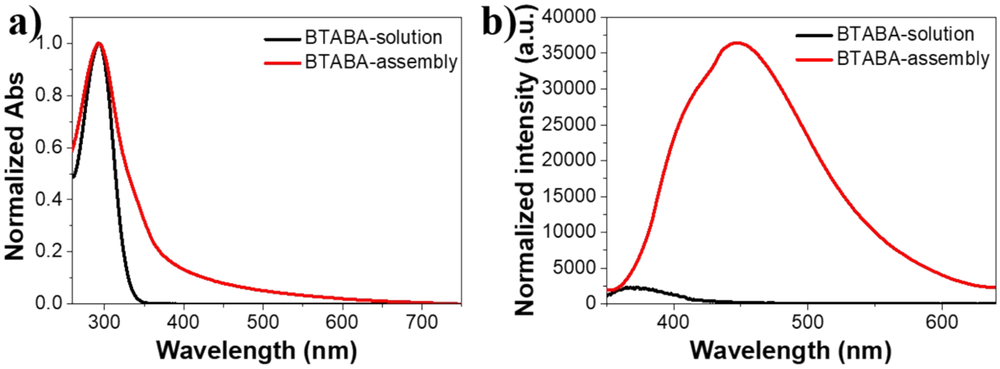


Figure S1 a) UV-Vis and b) FL spectra of BTABA assembly and its DMF solution. λ_{ex} = 330 nm. [BTABA] = 5.29 mM.

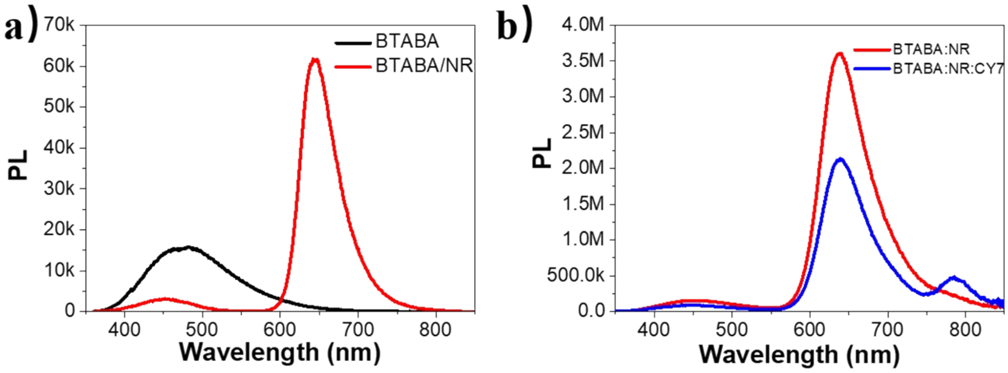


Figure S2 a) Fluorescence spectra of BTABA and BTABA/NR assembly. b) Fluorescence spectra of BTABA/NR and BTABA/NR/CY7 assembly. λ_{ex} = 330 nm. BTABA/NR = 60/1. BTABA/NR/CY7 = 60/1/1. [BTABA] = 5.29 mM.

According to the definition of energy transfer efficiency $\Phi_{ET} = 1 - I_{DA}/I_D$, where I_{DA} and I_D are the fluorescence intensities of the donor in the presence and absence of the acceptor. The Φ_{ET} of different combinations are calculated as follows:

Table1 energy transfer efficiency

Combination	Spectral analysis method
BTABA/NR	80.5%
BTABA/NR/CY7	41.3%

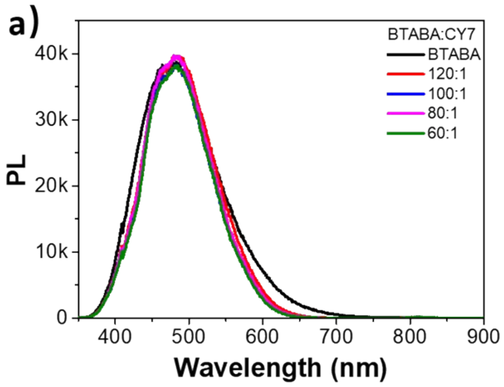


Figure S3 Fluorescence spectra of BTABA/CY7 assembly in the presence of different amount of CY7. λ_{ex} = 330 nm. [BTABA] = 5.29 mM.

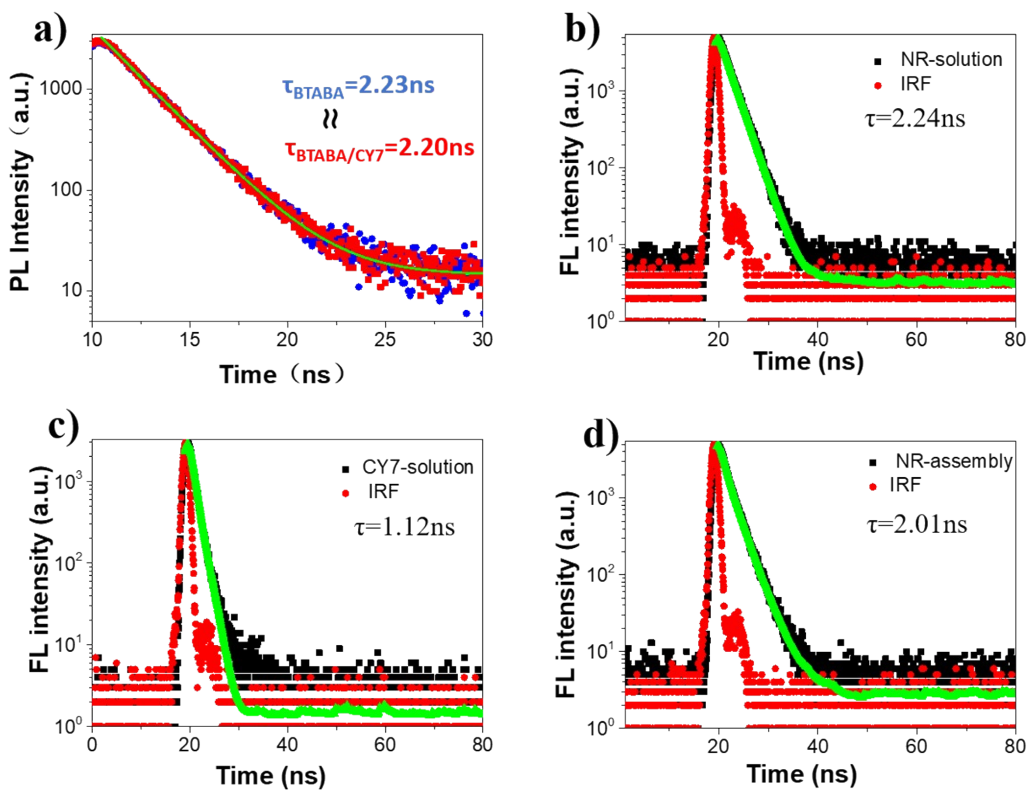


Figure S4 a) Fluorescence decay of BTABA (blue curve) and BTABA/CY7 (red curve) detected at 450 nm. b) Fluorescence decay of NR DMF solution detected at 640 nm. c) Fluorescence decay of CY7 DMF solution detected at 775 nm. d) Fluorescence decay of BTABA/NR assembly detected at 640 nm. λ_{ex} = 320 nm. [BTABA] = 5.29 mM. [NR] = 0.088 mM. [CY7] = 0.088 mM.

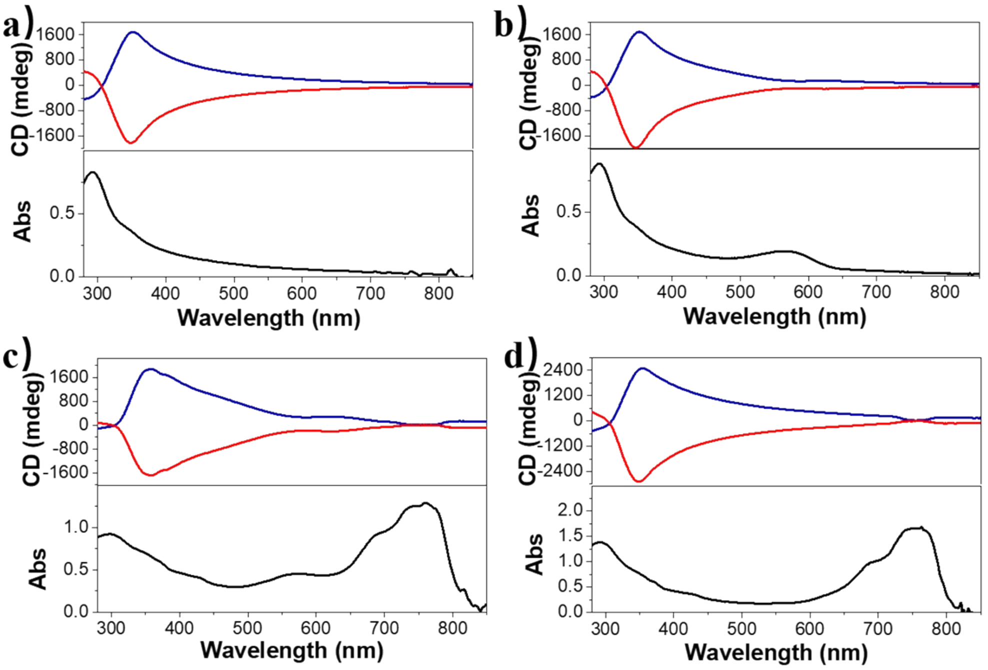


Figure S5 CD spectra of a）BTABA assembly, b) BTABA/NR = 60/1 assembly, c) BTABA/NR/CY7 = 60/1/1 assembly and d) BTABA/CY7 = 60/1 assembly. [BTABA] =5.29 mM. [NR] = 0.088 mM. [CY7] = 0.088 mM.

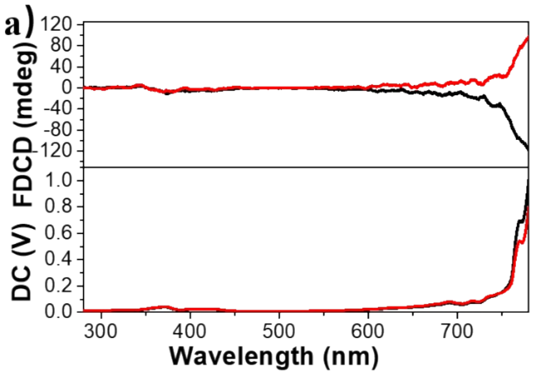


Figure S6 FDCD spectra of BTABA/CY7 assembly. Detected emission wavelength was set at 755 nm. BTABA/CY7 = 60/1. [BTABA] = 5.29 mM.

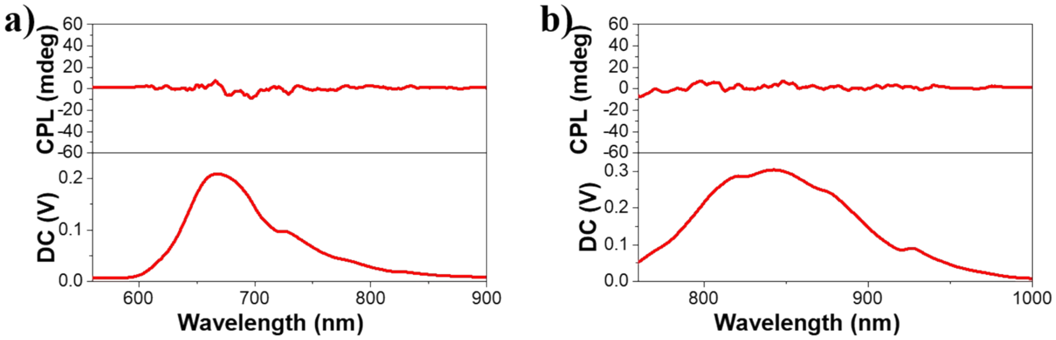


Figure S7 a) The CPL spectra of NR in DMF solution (λ_{ex} = 532 nm). b) The CPL spectra of CY7 in DMF solution (λ_{ex} = 730 nm). [NR] = 0.088 mM. [CY7] = 0.088 mM.

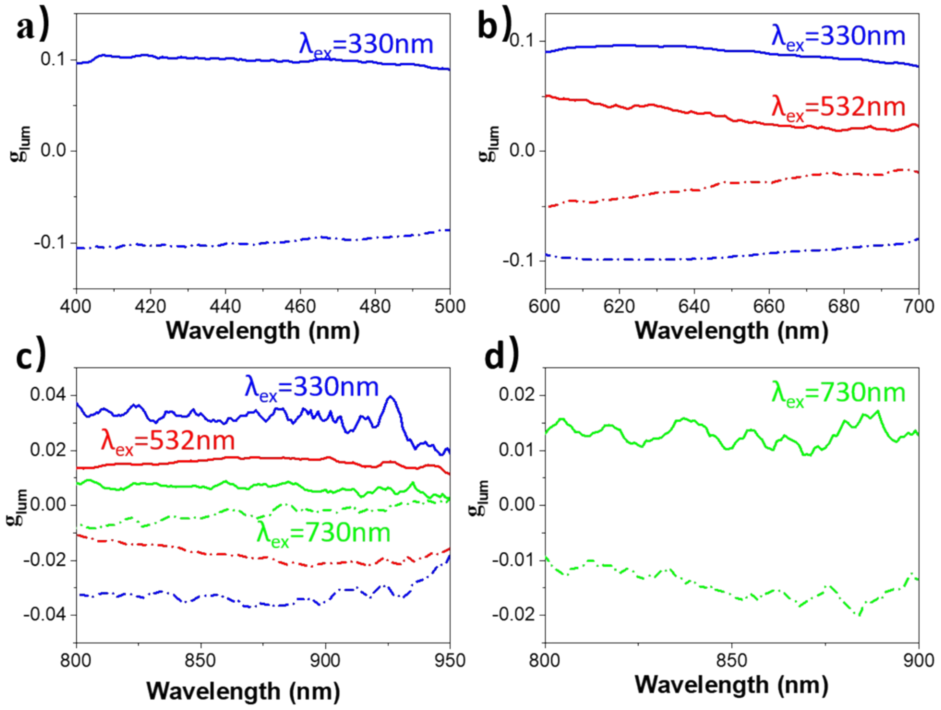


Figure S8 The g_{lum} of CPL for a) BTABA assembly excited with 330 nm irradiation, (b) BTABA/NR = 60/1 assembly, excited for BTABA (λ_{ex} = 330 nm) or for NR (λ_{ex} = 532 nm), (c) BTABA/NR/CY7 = 60/1/1 assembly, excited at 330 nm (for BTABA), 532 nm (for NR) and 730 nm (for CY7) respectively and (d) BTABA/CY7 = 60/1 assembly, excited for CY7 (λ_{ex} = 730 nm). [BTABA] = 5.29 mM.

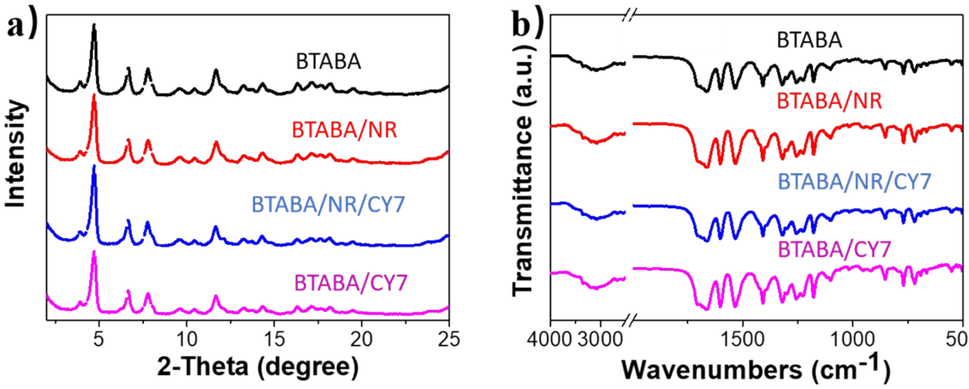


Figure S9 XRD and FT-IR spectra of BTABA, BTABA/NR = 60/1, BTABA/NR/CY7 = 60/1/1 and BTABA/CY7 = 60/1. [BTABA] = 5.29 mM.

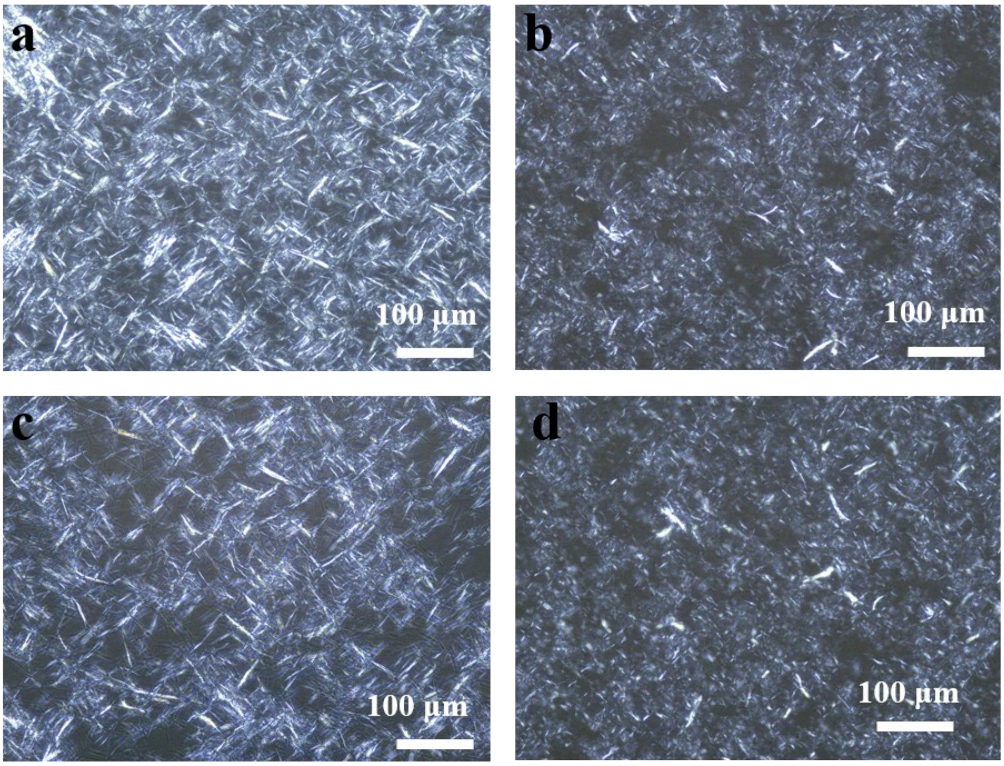


Figure S10 Polarizing optical microscopy (POM) images of BTABA, BTABA/NR = 60/1, BTABA/NR/CY7 = 60/1/1 and BTABA/CY7 = 60/1. [BTABA] = 5.29 mM.

References

(1) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.