Electronic Supplementary Information

A room-temperature phosphorescent polymer film containing a molecular web based on one-dimensional chiral stacking of a simple luminophore

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Methods

Fluorescence spectra and fluorescence lifetimes were investigated using a JASCO FP-6500 spectrofluorometer and a Hamamatsu Photonics Quantaurus-Tau fluorescence lifetime spectrometer, respectively. The florescence spectra on the crystalline solid of *G*-free **BT** was investigated using florescence measurement system on Hamamatsu Photonics Quantaurus-Tau fluorescence lifetime spectrometer. UV-visible absorption and circular dichroism (CD) spectra were obtained on a JASCO V-560 spectrophotometer and a JASCO J-725 spectrodichrometer, respectively. Confocal microscopy was performed by excitation at 488 nm on a Leica TCS 8SP confocal microscope. Transmission electron microscopy (TEM) was performed on a JEOL JEM-1400 plus microscope.

The *G*-**BT** solution was typically prepared as in the following example for the 0.15 mM solution: 4.81 mg of *G*-**BT** was mixed with 50 mL of methylcyclohexane. The mixture was externally sonicated for 10 min using a Kaijo Sono Cleaner 100D, and then heated for 5 min at 363 K to completely dissolve the solid. A similar procedure was applied to prepare *G*-free **BT** solution and *G*-**BT** solutions in chloroform, cyclohexane.

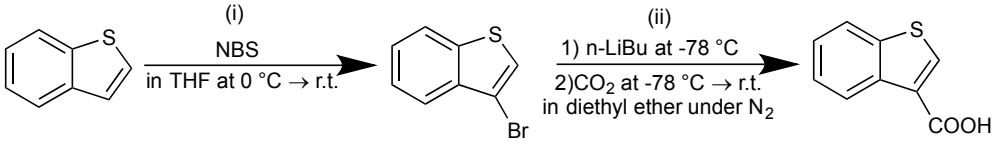
The obtained solution was placed in a quartz cell and heated until the solution became clear, maintained at this temperature for 10 min, and then cooled to 273 K in an ice bath for 15 min. To promote the stacking of the molecules, the solution was then kept at room temperature for 1 h. All samples were prepared and measured under an air atmosphere.

A transparent polymer film containing *G*-**BT** was obtained as the following: 1.0 g of a poly(ethylene-co-vinyl acetate)(vinyl acetate 40 %) was dissolved in 10 ml of distilled methylcyclohexane. 6.41 mg of *G*-**BT** was dissolved in the polymer solution, and the mixed solution was heated until the solution became clear. After heating, the solution was cooled in an ice bath at 273 K for 10 minutes. Then, the solution was put in the atmosphere until the temperature of the solution became room temperature. The solution was drop-casted on a quartz slide grass of 10 mm x 25 mm, and then dried at room temperature.

Experimental Procedures

Melting point was measured by a Yanaco MP-500P. NMR spectra, mass spectrum and IR absorption spectra were investigated by a JEOL JNM-EX400, a BRUKER autoflex III and a JASCO FT/IR-4100 spectrometer, respectively.

1. Synthesis of benzo[*b*]thiophene-3-carboxylic acid (*G*-free **BT**)



3-Bromobenzo[*b*]thiophene *G*-free **BT**

Benzo[*b*]thiophene-3-carboxylic acid was synthesized according to the previously reported procedures with slightly modification as following.

(i) Synthesis of 3-bromobenzo[*b*]thiophene [S1]

At 273 K, *N*-bromosuccinimide (9.88 g, 55.5 mmol) and benzo[*b*]thiophene (4.35 mL, 37 mmol) were mixed in a dried THF solution (150 mL), and the mixture was stirred for 0.5 h. After mixing, the solution was put in the atmosphere, and stirred for 36 h. The solution was evaporated, and the residue was dissolved by n-hexane. The resultant product was purified by a column chromatography (silica gel; hexanes as the eluent). The product was given a bright yellow oil. (7.96 g, 88%): IR (cm^{-1}): 3105, 3060. ^1H NMR (400 MHz, $CDCl_3$): 7.80-7.90 (2H, m), 7.30-7.50 (3H, m).

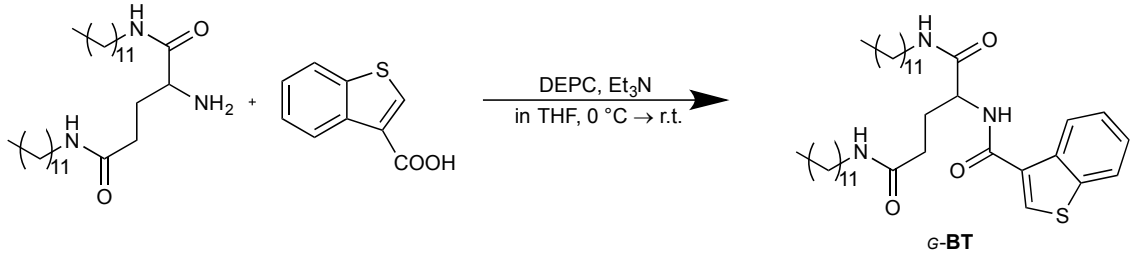
(ii) Synthesis of benzo[*b*]thiophene-3-carboxylic acid [S2]

3-Bromobenzo[*b*]thiophene (1.00 g, 4.78 mmol) was dissolved in a dried diethyl ether (20 mL) under N_2 atmosphere at 195 K. 1.6 M n-Buthyllithium hexane solution of 3.58 mL was added to the solution, and the mixed solution was stirred for 10 min at 195 K. The solution was put in atmosphere after a carbon dioxide (solid, excess) was added in the solution, and the mixture was stirred for 10 h. After stirring, an 1 M aqueous HCl (50 mL) was added in the solution, and the obtained mixture was extracted by a diethyl ether. Then, the organic phase was extracted by an 1 M aqueous NaOH. The water phase was separated, and was added a concentrated HCl solution under cooling by an ice bath until the pH became 1. The water phase was extracted by a diethyl ether. The solution was dried by a saturated solution of sodium chloride and a Na_2SO_4. The solution was evaporated, and the residue was recrystallized by toluene. A white crystal was obtained. (0.80 g, 4.49 mmol, 93%): m.p. 176.5-178 ˚C. IR (cm^{-1}) 3109, 2939, 2768, 2588, 1673. ^1H NMR (400 MHz, DMSO): δ 8.64 (1H, s), 8.51-8.49 (1H, d), 8.09-8.07 (1H, d), 7.52-7.43 (2H, m). Elemental analysis: Calc. (%) for $C_9H_6O_2S$: C, 60.66; H, 3.39; N, 0.00; found (%): C, 60.61; H, 3.39; N, 0.15.

2. Synthesis of *N',N''*-didodecyl L-glutamine (*G*)

N',N''-Didodecyl L-glutamine (*G*) was synthesized according to the previously reported procedures [S3, S4, S5]. m.p. 117-118 ˚C. IR (cm^{-1}): 3326, 2920, 2850, 1634, 1533, 1537. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.86-0.90 (m, 6H), 1.26 (m, 36H), 1.49 (m, 4H), 1.91-1.96 (q, 2H), 2.30-2.34 (m, 2H), 3.20-3.26 (m, 4H), 3.40-3.43 (t, 1H). Elemental analysis: Calc. (%) for $C_{29}H_{59}N_3O_2$: C, 72.3; H, 12.3; N, 8.7; found (%): C, 72.2; H, 12.3; N, 8.7.

3. Synthesis of *N',N''*-didodecyl-*N*-(3-benzo[3,4-*b*]thienocarboxy)-L-glutamine (*G*-**BT**)



G-**BT**

N',N''-Didodecyl L-glutamine (0.56 g, 1.16 mmol), triethylamine (0.112 mL, 0.80 mmol) and benzo[*b*]thiophene-3-carboxylic acid (0.22 g, 1.23 mmol) were mixed and stirred in dried THF (60 ml) under cooling by an ice bath. After stirring, diethyl cyanophosphonate (0.28 mL, 1.54 mmol) was added to the solution under cooling by an ice bath, and the mixed solution was stirred for one night. The solution was evaporated, and the residue was dissolved in chloroform (100 mL). The chloroform solution was washed three times by 0.5 M aqueous NaOH (20 mL) and 0.5 M aqueous HCl (20 mL). In addition, the solution was washed by a saturated solution of sodium chloride (60 mL) for anhydration. The organic phase was dried by an anhydrous sodium sulfate. The filtrated solution was evaporated, and the residue was dissolved by a small amount of chloroform. Gel-like substance was obtained by reprecipitation with an n-hexane. The gel-like substance was filtrated and dried under a vacuum. Then, a white crystal was obtained. (0.63 mg, 76 %). m.p. 158.0-159.5 ˚C. IR (cm^{-1}): 3283, 3095, 2919, 2850, 1652, 1631, 1557, 1536, 1468, 1372, 1278, 1246. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.86-0.89 (t, 6H), 1.26-1.29 (m, 36H), 1.46-1.52 (m, 4H), 2.18-2.23 (m, 2H), 2.35-2.65 (m, 2H), 3.24-3.29 (tt, 4H), 4.54-4.59 (q, 1H), 5.87-6.02 (t, 1H), 6.88-7.01 (t, 1H), 7.38-7.42 (t, 1H), 7.44-7.48 (t, 1H), 7.86-7.88 (d, 1H), 8.04-8.06 (d, 1H), 7.70-7.73 (d, 2H), 7.99-8.02 (t, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 173.32, 171.19, 164.19, 140.22, 136.97, 130.82, 130.58, 125.18, 125.06, 124.61, 122.47, 53.26, 39.94, 39.72, 33.17, 31.93, 29.66, 29.61, 29.56, 29.37, 29.30, 28.66, 26.96, 26.93, 22.71, 14.12. MALDI-TOF calcd. for $C_{38}H_{63}O_3N_3S$ $[M+H]^+$: 642.467, found: 642.158.

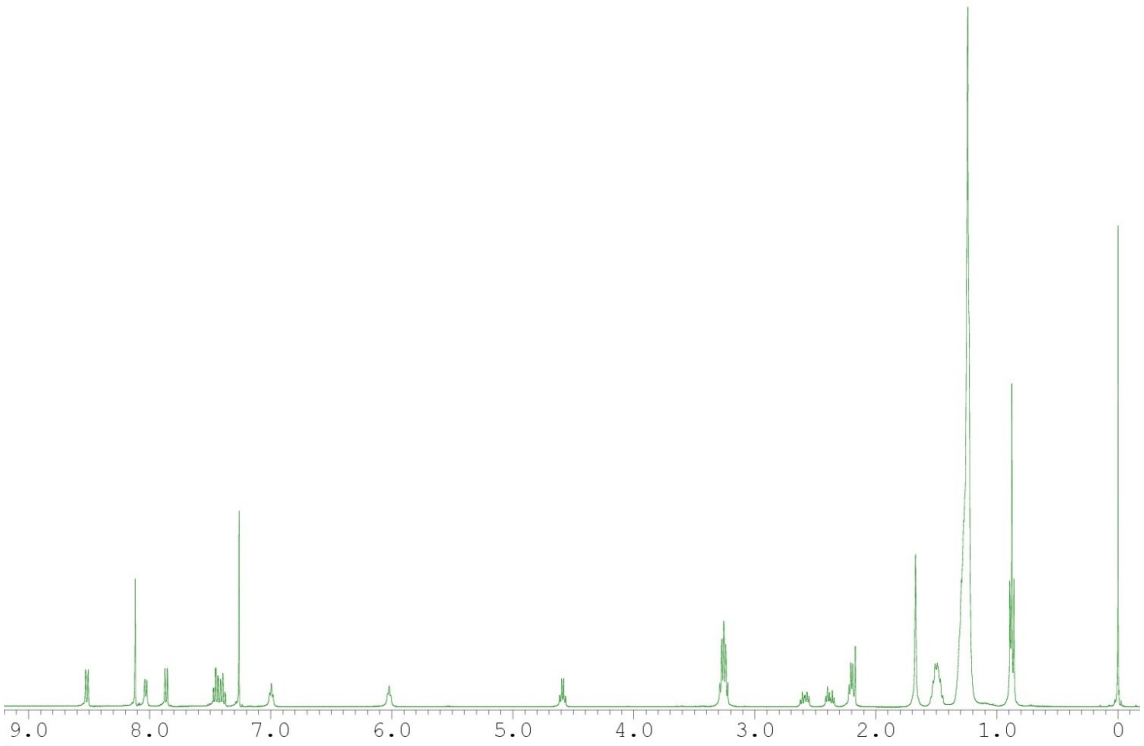


Figure EP 1 ^{1}H NMR (400 MHz, $CDCl_3$) of *G*-**BT**

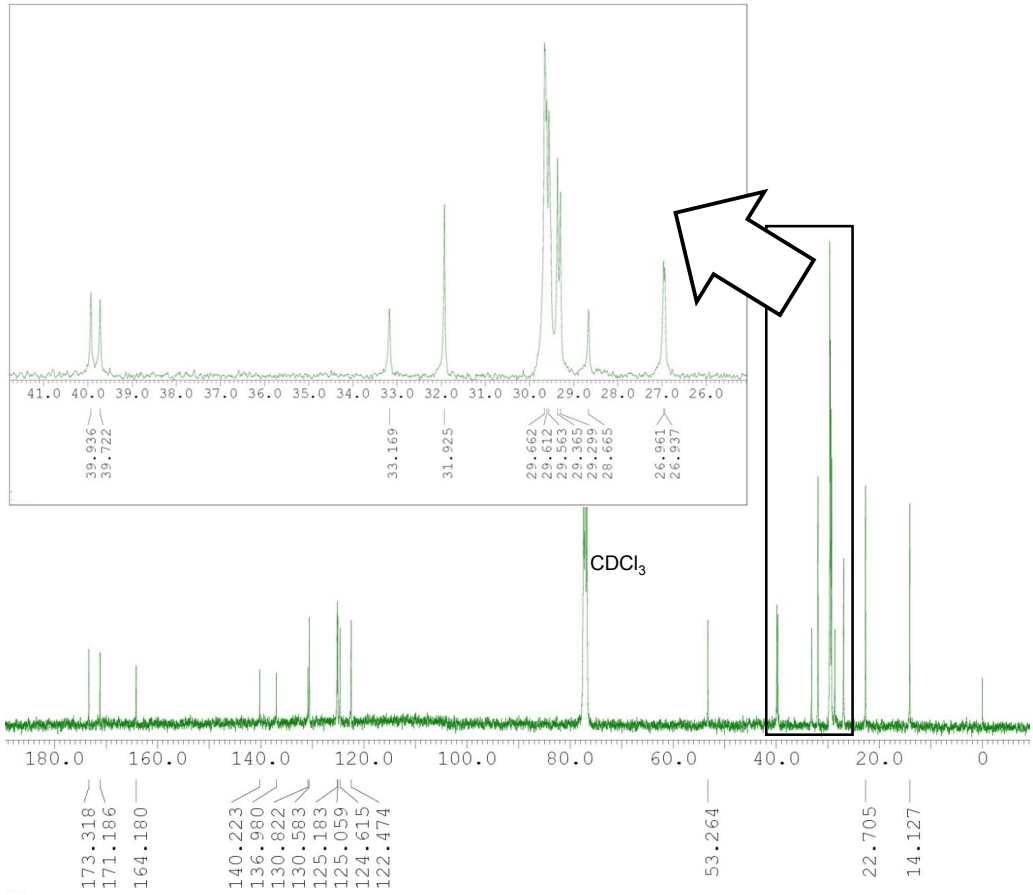


Figure EP 2 ^{13}C NMR (400 MHz, $CDCl_3$) of *G*-**BT**

4. Observation of confocal microscopy of the *G*-**BT** solution

Confocal microscopy was performed by excitation at 488 nm on a Leica TCS 8SP confocal microscope with high sensitivity photo detector, a Leica HyD. The used lens was HC PL APO CS2 100x/1.40 OIL. In this confocal microscope system, the spatial resolution was calculated as ca. 210 nm.

As complementary results of the confocal microscopy, the luminescence spectra in the *G*-**BT** (0.15 mM) of methylcyclohexane solution were determined under excitation at UV and blue light (405 and 470 nm) by photon counting method with the fluorescence lifetime spectrometer (Quantaurus-Tau, Hamamatsu Photonics), as shown in Figure S2. The luminescent spectra excited at 405 and 470 nm showed similar spectrum of species B in Fig. 2 for the *G*-**BT** solution.

Supplementary Figures

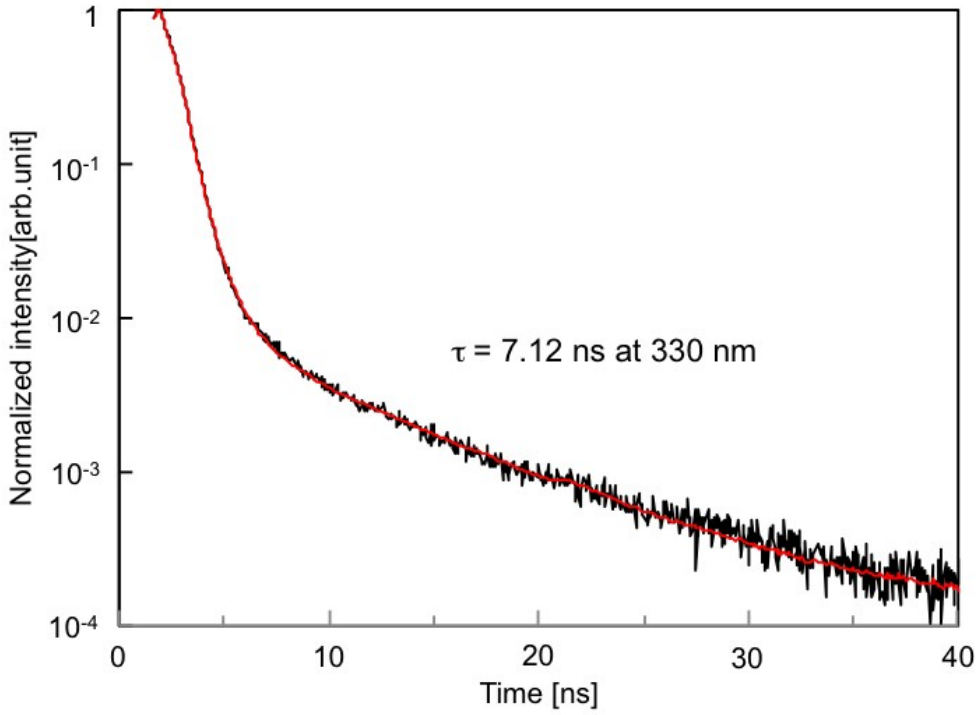


Figure S1. Fluorescence lifetime of the species A at 330 nm in *G*-**BT**. The luminescence decay was measured by irradiation at 280 nm. The black and red lines are the measured decay and the fitting curve, respectively.

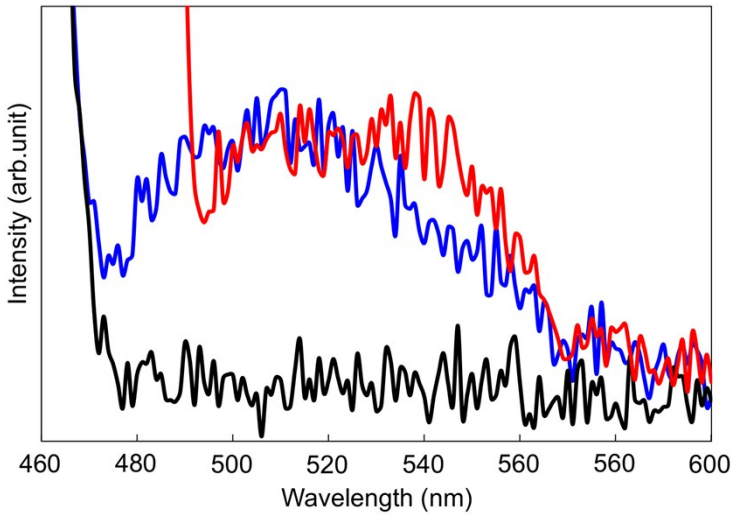


Figure S2. Luminescence spectra of *G*-BT in methylcyclohexane excited at 405 nm (blue line) and 470 nm (red line), and of only methylcyclohexane excited at 405 nm (black line).

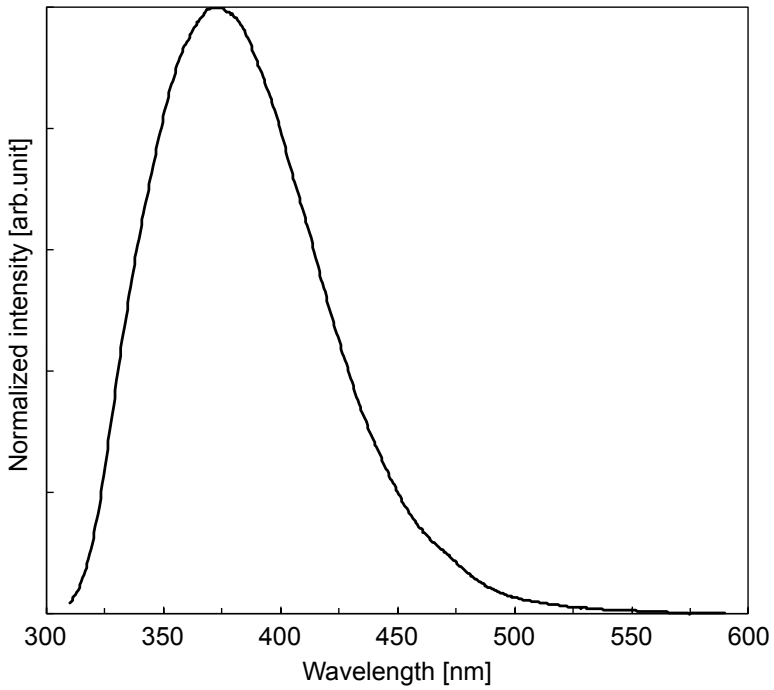


Figure S3. Fluorescence spectrum excited at 300 nm of *G*-**BT** with TFA (0.05 vol%) in methylcyclohexane at 298 K.

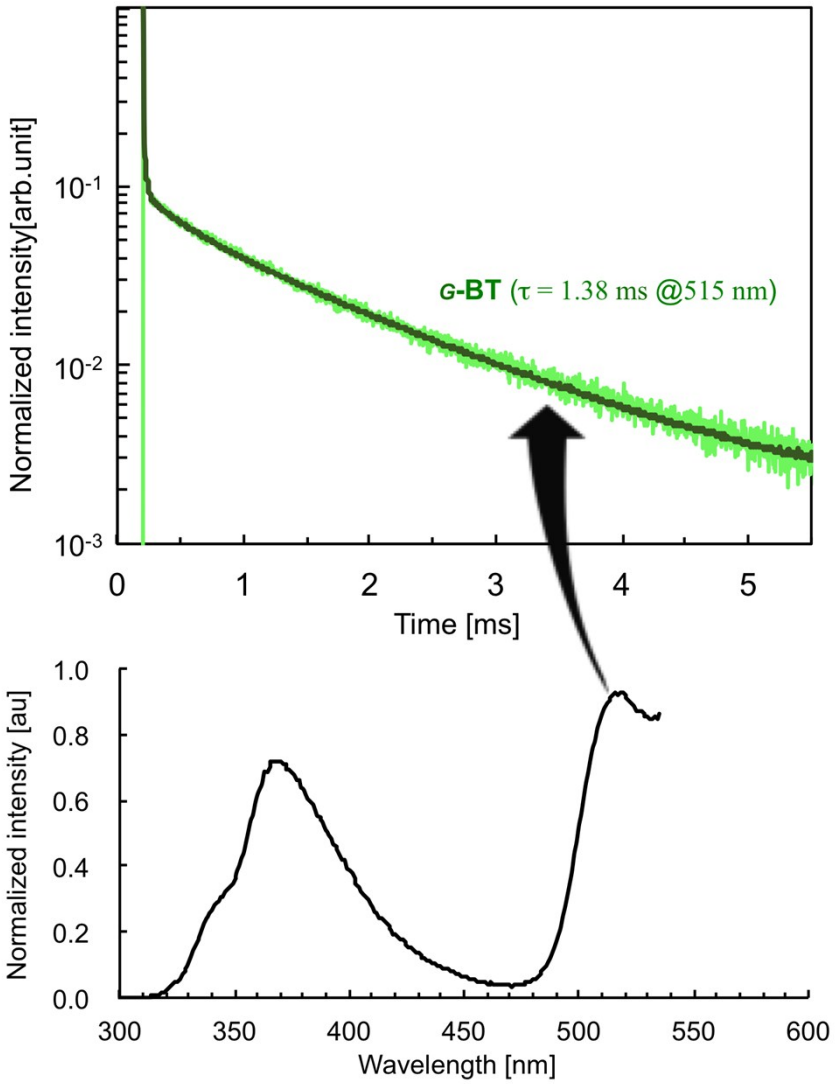


Figure S4. Luminescence decay curves and fluorescence spectra of the crystalline *G*-free **BT** at 298 K. The fluorescence spectra and the luminescence decay curves were obtained by irradiation at 280 nm. The solid dark green line shows the fitting curve. The spectrum data of longer wavelength than 535 nm was removed because of containing strong second-order diffracted light.

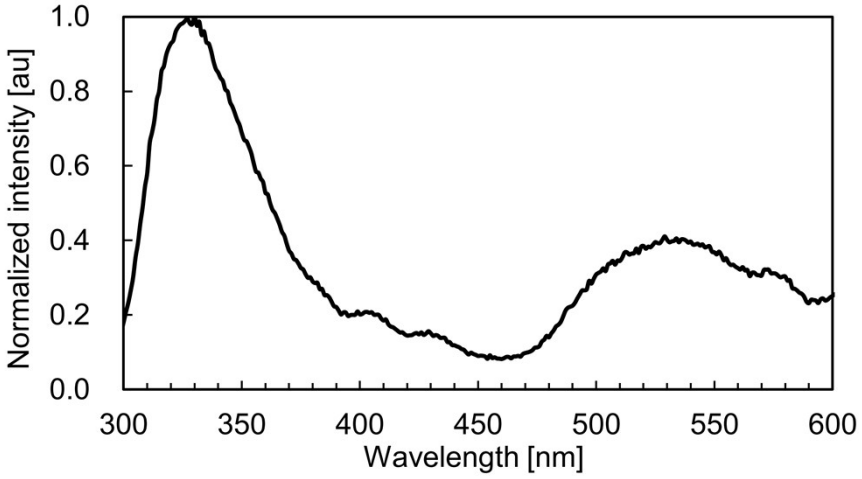


Figure S5. Florescence spectrum of a transparent poly(ethylene-co-vinyl acetate) (EVA) film containing 0.64 wt% *G*-**BT**. The fluorescence spectrum was obtained by irradiation at 280 nm.

References

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