Supplementary Information

Synthesis of 1,1'-diaryl-4,4'-bibenzo[*c*]thiophene derivatives with aryl substituents on the thiophene rings by Stille or Suzuki coupling reaction

Taiki Higashino,[a] Yasuto Hara,[a] Keiichi Imato,[a] Seiji Akiyama,[b] Mio Ishida[b] and Yousuke Ooyama*[a]

[a]*Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan. E-mail: yooyama@hiroshima-u.ac.jp; Fax: (+81) 82-424-5494*
[b]*Science & Innovation Center, Mitsubishi Chemical Corporation, 1000 Kamoshida-cho, Aoba-ku, Yokohama-shi, Kanagawa 227-8502, Japan*

General

Melting points were measured with an AS ONE ATM-02. IR spectra were recorded on a SHIMADZU IRTracer-100 by ATR method. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian-400 or -500 FT NMR spectrometer. High-resolution mass spectral data by APCI was acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. Recycling gel permeation chromatography (GPC) was performed using a RI-detector (SHIMADZU RID-20A), an UV-detector (SHIMADZU SPD-20A), and a pomp (SHIMADZU LC-20A) with two columns (Shodex GPC FP-2002). Photoabsorption spectra of solutions were observed with a Shimadzu UV-3600 plus spectrophotometer. Photoabsorption spectra of solids were recorded by a Shimadzu UV-3600 plus spectrophotometer with a calibrated integrating sphere system. Fluorescence spectra of solutions and solids were measured with a HORIBA FluoroMax-4 spectrofluorometer. The fluorescence quantum yields in solution and in solid state were determined using a HORIBA FluoroMax-4 spectrofluorometer with a calibrated integrating sphere system. Fluorescence decay measurements were performed on a HORIBA DeltaFlex modular fluorescence lifetime system, using a Nano LED pulsed diode excitation source (370 nm). Cyclic voltammetry (CV) curves were recorded in acetonitrile/Bu_4NClO_4 (0.1 M) or DMF/Bu_4NClO_4 (0.1 M) solution with a three-electrode system consisting of Ag/Ag^+ ($AgNO_3$ in acetonitrile/Bu_4NClO_4 or DMF/Bu_4NClO_4) as the reference electrode, a Pt plate as the working electrode and a Pt wire as the counter electrode using an Electrochemical Measurement System HZ-7000 (HOKUTO DENKO). Powder X-ray diffraction measurements were performed on a Rigaku MiniFlex600-C/CM diffractometer with Cu Kα radiator. Differential scanning calorimetry was carried out using a Shimadzu DSC-60.

Synthesis

1,1'-dibromo-4,4'-bibenzo[*c*]thiophene (1,1′-Br-4,4′-BBT). To a THF solution (1.2 mL) of **H4-4,4'-BBT-SO** (0.05 g, 0.17 mmol) under a nitrogen atmosphere at –78 °C was added tetramethylethylenediamine (0.15 mL, 0.99 mmol). After stirring for 10 min, a 1.6 M hexane solution of *n*BuLi (0.62 mL, 0.99 mmol) was added dropwise. After stirring for 10 min at room temperature, the reaction mixture was cooled to –78 °C, and then, a THF solution (4.0 mL) of tetrabromomethane (0.06 g, 0.83 mmol) was added dropwise. After stirring for 2 h at room temperature, the reaction mixture was quenched with water, and then, the solution was extracted with dichloromethane. The dichloromethane extract was dried over anhydrous $MgSO_4$, filtrated and concentrated. Recycling GPC (chloroform as eluent) for the residue was performed to give **1,1′-Br-4,4′-BBT** (0.016 g, yield 23 %) as a dark-yellow solid; decomposed at around 60 °C; FT-IR (ATR): $\tilde{\nu}$ = 3107, 3057, 1593, 1344, 1301, 1188 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6): δ = 7.26 (d, J = 6.5 Hz, 2H), 7.34–7.38 (m, 2H), 7.57 (dt, 2H), 7.74 (s, 2H) ppm; It was difficult to obtain the ^{13}C NMR spectrum due to the thermal instability of **1,1′-Br-4,4′-BBT** in any deuterated solvents; HRMS (APCI): *m*/*z* (%):[M+H$^+$] calcd. for $C_{16}H_9Br_2S_2$, 422.85069; found 422.85135.

1,1'-Bis(4-(*tert*-butyl)phenyl)-4,4'-bibenzo[*c*]thiophene (1,1′-Ph*t*Bu-4,4′-BBT). (Method A: previous work)[1] A solution of **1,1′-Sn-4,4′-BBT** (0.20 g, 0.34 mmol), 1-bromo-4-*tert*-butylbenzene (0.12 g, 1.02 mmol), and $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol) in toluene (2.0 mL) was stirred for 21 h at 110 ºC under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in

dichloromethane and washed with water. The dichloromethane extract was dried over anhydrous $MgSO_4$, filtrated and concentrated. Recycling GPC (toluene as eluent) for the residue was performed to give **1,1′-Ph*t*Bu-4,4′-BBT** (0.08 g, yield 44 %) as a yellow solid. (Method B) A solution of **1,1′-Br-4,4′-BBT** (0.030 g, 0.071 mmol), 4-*tert*-butylphenylboronic acid (0.038 g, 0.212 mmol), $Pd(PPh_3)_4$ (0.008 g, 0.007 mmol), and Na_2CO_3 aq. (1.0 mL, 0.707 mmol) in a mixture of toluene (1.0 mL) and ethanol (1.5 mL) was stirred for 21 h at room temperature under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was dried over anhydrous $MgSO_4$, filtrated and concentrated. Recycling GPC (chloroform as eluent) for the residue was performed to give **1,1′-Ph*t*Bu-4,4′-BBT** (0.012 g, yield 32 %) as a yellow solid; m.p. 202–205 °C; FT-IR (ATR): $\tilde{\nu}$ = 3103, 2953, 2900, 2664, 1862, 1512, 1359 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6): δ = 1.41 (s, 18H, Ph-C($C\underline{H}_3$)$_3$), 7.26–7.30 (m, 4H, C<u>H</u> at 5,5',6,6'-posions on Ph-Ph), 7.62–7.66 (m, 6H, C<u>H</u> at 3,3'-posions on Th and C<u>H</u> at 3,5'-posions on *t*BuPh), 7.69–7.71 (m, 4H, C<u>H</u> at 2,6'-posions on *t*BuPh), 7.90–7.95 (m, 2H, C<u>H</u> at 7,7'-posions on Ph-Ph) ppm; ^{13}C NMR (125 MHz, acetone-d_6): δ = 31.61, 35.27, 117.06, 121.28, 124.76, 125.14, 127.05, 129.68, 132.50, 134.90, 135.32, 136.09, 139.97, 151.57 ppm; HRMS (APCI): *m*/*z* (%): [M+H^+] calcd. for $C_{36}H_{35}S_2$, 531.21747; found 531.21893.

1,1'-Bis(4-cyanophenyl)-4,4'-bibenzo[*c*]thiophene (1,1′-PhCN-4,4′-BBT). (Method A) A solution of **1,1′-Sn-4,4′-BBT** (0.087 g, 0.147 mmol), 4-bromobenzonitrile (0.080 g, 0.441 mmol), and $Pd(PPh_3)_4$ (0.008 g, 0.007 mmol) in toluene (9.0 mL) was stirred for 26 h at 110 ºC under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was dried over anhydrous $MgSO_4$, filtrated and concentrated. The residue was chromatographed on silica gel (dichloromethane : hexane = 1 : 1 as eluent) to give **1,1′-PhCN-4,4′-BBT** (0.034 g, yield 49 %) as a yellow solid. (Method B) A solution of **1,1′-Br-4,4′-BBT** (0.031 g, 0.073 mmol), 4-cyanophenylboronic acid (0.032 g, 0.219 mmol), $Pd(PPh_3)_4$ (0.008 g, 0.007 mmol), and Na_2CO_3 aq. (1.0 mL, 0.730 mmol) in a mixture of toluene (1.0 mL) and ethanol (1.5 mL) was stirred for 25 h at room temperature under a nitrogen atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract was dried over anhydrous $MgSO_4$, filtrated and concentrated. The residue was chromatographed on silica gel (dichloromethane : hexane = 1 : 1 as eluent) to give **1,1′-PhCN-4,4′-BBT** (0.006 g, yield 18 %) as a yellow solid; decomposed at around 245 °C; FT-IR (ATR): $\tilde{\nu}$ = 2222, 1601, 1510, 1176 cm^{-1}; ^1H NMR (400 MHz, dichloromethane-d_2): δ =7.26–7.30 (dd, *J* = 1.2 and 6.6 Hz, 2H, C<u>H</u> at 5,5'-posions on Ph-Ph), 7.31–7.35 (m, 2H, C<u>H</u> at 6,6'-posions on Ph-Ph), 7.67 (s, 2H, C<u>H</u> at 3,3'-posions on Th), 7.81 (d, *J* = 8.7 Hz, 4H, C<u>H</u> at 3,5'-posions on CNPh), 7.85 (d, *J* = 8.6 Hz, 4H, C<u>H</u> at 2,6'-posions on CNPh), 7.91–7.94 (dt, 2H, C<u>H</u> at 7,7'-posions on Ph-Ph) ppm; It was difficult to obtain the ^{13}C NMR spectrum due to the low solubility of **1,1′-PhCN-4,4′-BBT** in any deuterated solvents; HRMS (APCI): *m*/*z* (%): [M+H^+] calcd. for $C_{30}H_{17}N_2S_2$, 469.08277; found 469.08282.

Ref. 1: K. Obayashi, S. Miho, M. Yasui, K. Imato, S. Akiyama, M. Ishida, and Y. Ooyama, *New J. Chem.*, 2021, **45**, 17085–17094.

X-ray crystallographic analysis: The reflection data of **1,1′-Ph*t*Bu-4,4′-BBT** were collected at 100 K on a Rigaku XtaLAB Synergy-R/DW diffractometer using monochromated Mo-Kα (λ = 0.71073 Å). The structure was solved by the SHELXT 2014/5 method and refined based on full-matrix least squares on F^2 using SHELXL-2018/3. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed geometrically and not refined. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC 2248179).

Crystal of 1,1′-Ph*t*Bu-4,4′-BBT: A suitable crystal of **1,1′-Ph*t*Bu-4,4′-BBT** was recrystallized from acetone as yellow plate crystal, air stable. Crystallographic data: $C_{36}H_{34}S_2$, M = 530.75, monoclinic, a = 10.3004(2), b = 11.6368(3), c = 47.0635(14) Å, β = 92.625(3)°, V = 5635.3(3) Å^3, D_{calcd} = 1.251 g cm^{-3}, space group $P2_1/n$ (no.14), Z = 8, 14483 reflections measured, 10317 unique (R_{int} = 0.0726), which were used in all calculations. The final R_1(reflections) = 0.0664 (7324) [$I > 2\sigma(I)$], wR_2(reflections) = 0.1642 (10317). GOF = 1.049.

Table S1 Crystal data and structure refinement parameters for **1,1′-Ph*t*Bu-4,4′-BBT** (CCDC 2248179).

Compound	**1,1′-Ph*t*Bu-4,4′-BBT**
Molecular formula	$C_{36}H_{34}S_2$
Formula weight	530.75
Number of reflection used for unit cell determination (2θ range/°)	51532 (3.606-50.7)
Temperature/K	100
Crystal System	monoclinic
Space group	$P2_1/n$
a/Å	10.3004(2)
b/Å	11.6368(3)
c/Å	47.0635(14)
α/°	
β/°	92.625(3)
γ/°	
V/Å^3	5635.3(3)
Z	8
D_c/g cm^{-3}	1.251
F(000)	2256
Radiation	Mo-Kα (λ = 0.71073 Å)
Crystal size/mm^3	0.145×0.113×0.024
Range of induces h; k; l	-12, 12; -14, 14; -56, 56
Reflections collected (unique)	10317
Reflection observed with $I_0>2\sigma I_0$	7324
Number of parameters	697
Final R indexes [$I_0>2\sigma I_0$]	R_1 = 0.0664, wR_2 =0.1488
Final R indexes [all data]	R_1 = 0.0994, wR_2 =0.1642
Goodness-of-fit on F^2	1.049
Max. Shift/Error in final cycle	0.00
Max. peak in final diff. map/e Å^{-3}	0.58
Min. peak in final diff. map/e Å^{-3}	-0.48

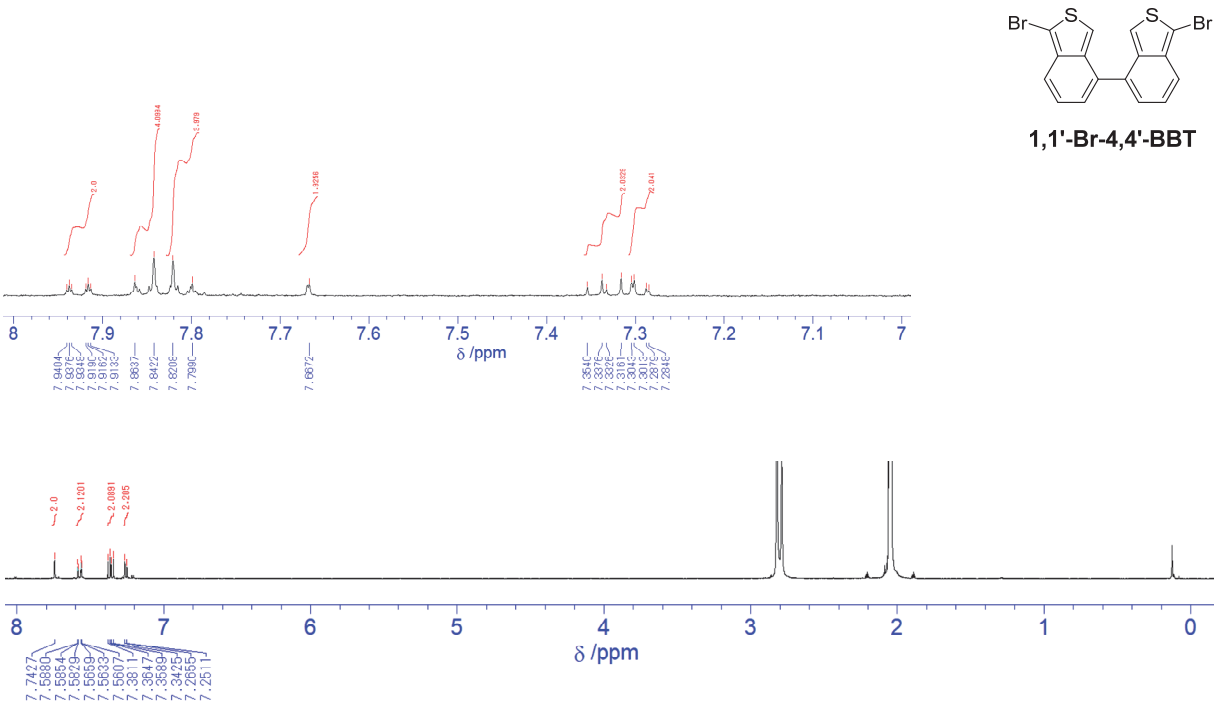

Fig. S1 ^{1}H NMR (500 MHz) spectrum of **1,1′-Br-4,4′-BBT** in acetone-d_6.

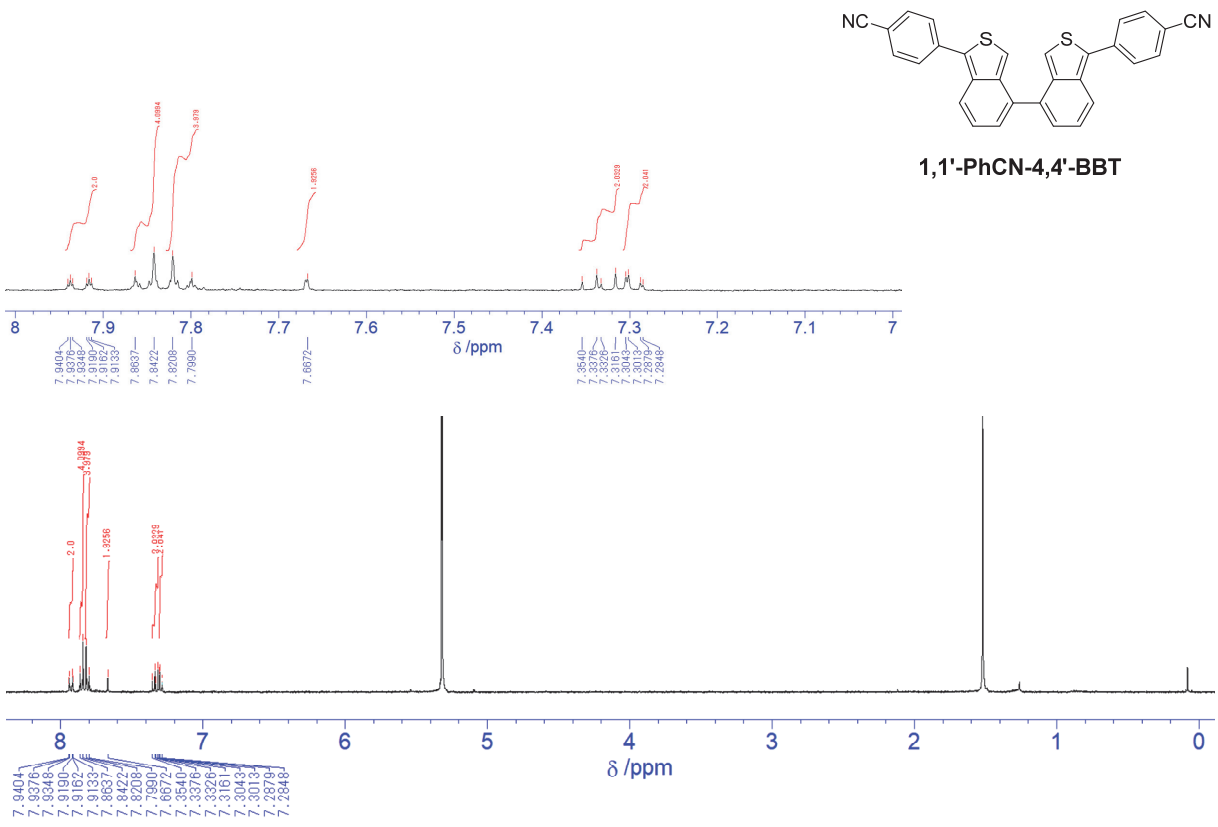

Fig. S2 ^{1}H NMR (400 MHz) spectrum of **1,1′-PhCN-4,4′-BBT** in dichloromethane-d_2.

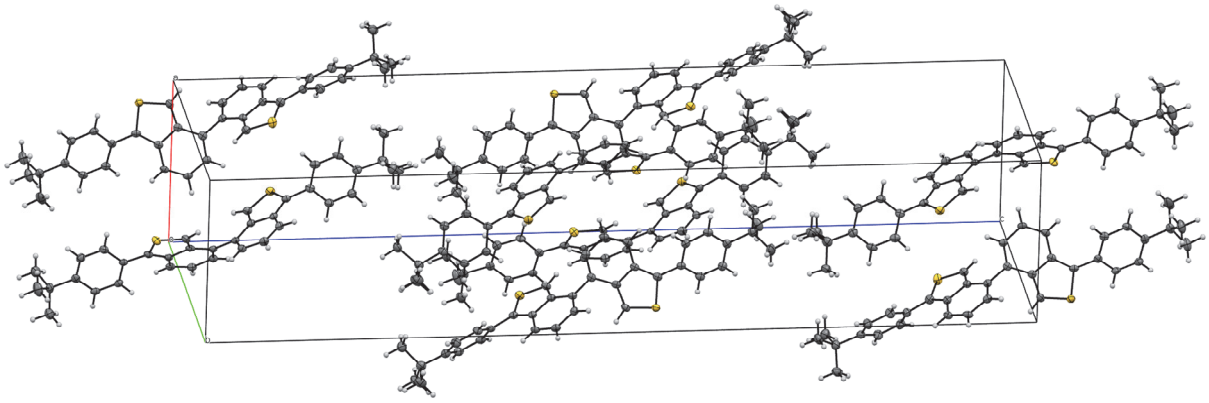

Fig. S3 Crystal structure of **BBT-Ph*t*Bu**: molecular packing structure.

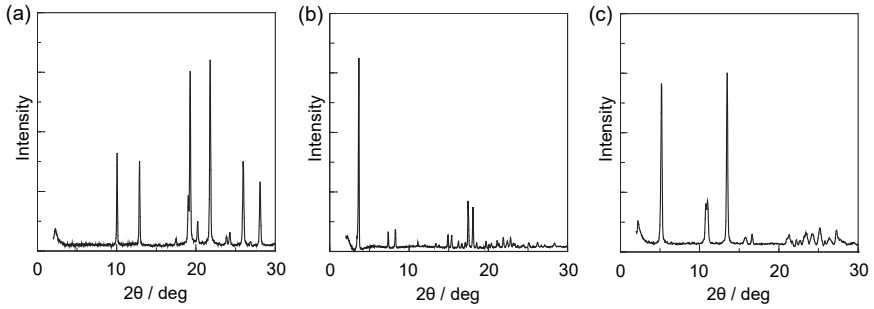

Fig. S4 XRD patterns of (a) **BBT-H**, (b) **BBT-Ph*t*Bu**, and (c) **BBT-PhCN**.

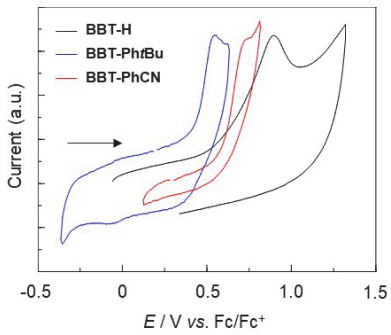

Fig. S5 Cyclic voltammograms of **BBT-H** and **BBT-Ph*t*Bu** in acetonitrile containing 0.1 M Bu_4NClO_4 and **BBT-PhCN** in DMF containing 0.1 M Bu_4NClO_4 at a scan rate of 100 mV s^{-1}. The arrow denotes the direction of the potential scan

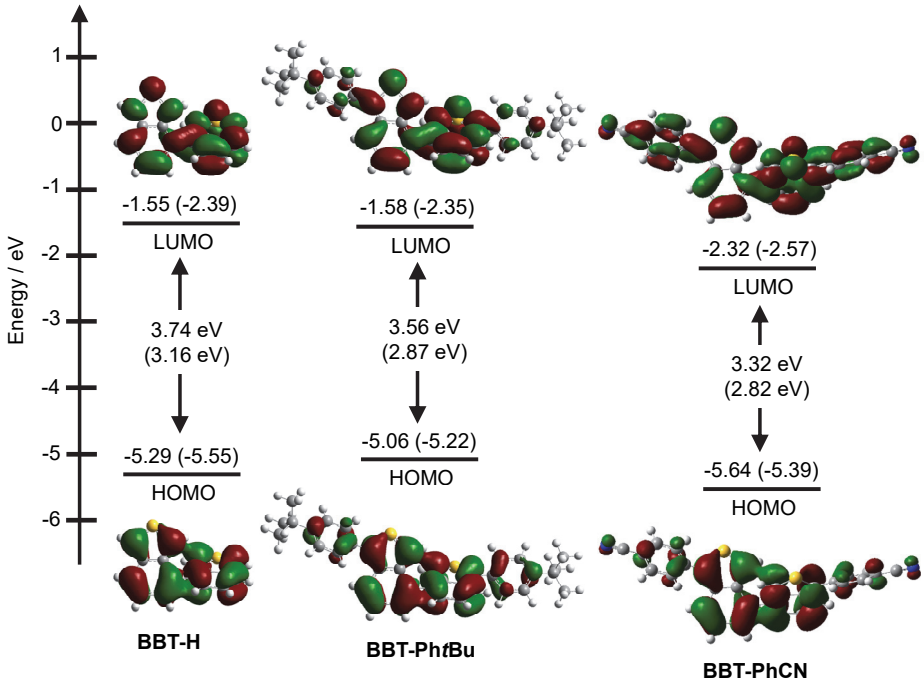

Fig. S6 Energy level diagram, HOMO and LUMO of **BBT-H**, **BBT-Ph*t*Bu** and **BBT-PhCN** derived from DFT calculations at the B3LYP/6-31G(d,p) level. Numbers in parentheses are the experimental values.

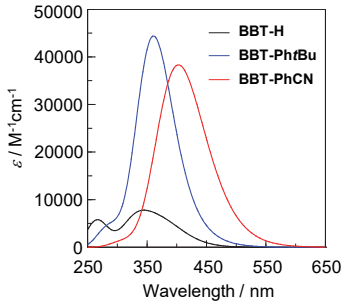

Fig. S7 Photoabsorption spectra of **BBT-H**, **BBT-Ph*t*Bu** and **BBT-PhCN** derived from TD-DFT calculations.

Table S2 Geometrical coordinates of the optimized **4,4′-BBT** by DFT at the B3LYP/6-31G(d,p) level.[2]

Cartesian coordinates:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	3.014613	0.092656	0.246587
2	C	0	3.469568	1.192933	1.038642
3	C	0	2.586725	2.181467	1.372708
4	C	0	1.21901	2.12832	0.956653
5	C	0	0.713504	1.089175	0.210163
6	C	0	1.622641	0.033794	-0.17567
7	S	0	2.781034	-2.035549	-1.172737
8	C	0	-1.622642	0.033794	0.17567
9	C	0	-0.713504	1.089175	-0.210163
10	C	0	-1.21901	2.128319	-0.956655
11	C	0	-2.586726	2.181466	-1.372709
12	C	0	-3.469569	1.192933	-1.038641
13	C	0	-3.014613	0.092656	-0.246585
14	S	0	-2.781033	-2.035551	1.172734
15	H	0	4.506637	1.23322	1.358132
16	H	0	2.916292	3.02579	1.971013
17	H	0	0.549238	2.927872	1.258602
18	H	0	-0.549238	2.927871	-1.258604
19	H	0	-2.916292	3.025789	-1.971014
20	H	0	-4.506638	1.23322	-1.35813
21	C	0	3.751548	-0.981598	-0.225472
22	H	0	4.800145	-1.191301	-0.070182
23	C	0	1.369808	-1.078593	-0.963293
24	H	0	0.437756	-1.375725	-1.419233
25	C	0	-1.369809	-1.078591	0.963295
26	H	0	-0.437757	-1.375723	1.419236
27	C	0	-3.751549	-0.981596	0.225475
28	H	0	-4.800146	-1.191299	0.070187

Table S3 Geometrical coordinates of the optimized **1,1′-Ph*t*Bu-4,4′-BBT** by DFT at the B3LYP/6-31G(d,p) level.[2]

Cartesian coordinates:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	1.620738	1.023449	-0.238209
2	C	0	3.025876	1.083365	0.133791
3	C	0	3.480829	2.153026	0.966515
4	C	0	2.599335	3.125970	1.351629
5	C	0	1.227636	3.087165	0.953848
6	C	0	0.714470	2.062505	0.193584
7	C	0	1.336319	-0.081327	-1.024700
8	C	0	3.769099	0.014305	-0.378440
9	H	0	4.513994	2.178448	1.294241
10	H	0	2.936109	3.941171	1.985304
11	H	0	0.560206	3.875452	1.288908
12	C	0	-0.723119	2.057954	-0.192642
13	C	0	-1.620980	1.009232	0.233300
14	C	0	-1.244761	3.083294	-0.946208
15	C	0	-3.026897	1.060861	-0.136954
16	C	0	-1.327522	-0.098276	1.012655
17	C	0	-2.617111	3.114170	-1.342468
18	H	0	-0.583701	3.878787	-1.276837
19	C	0	-3.490857	2.132239	-0.962509
20	C	0	-3.761439	-0.016958	0.369271
21	H	0	-2.960676	3.930748	-1.970701
22	H	0	-4.524518	2.151998	-1.289170
23	S	0	2.735530	-1.032475	-1.302779
24	S	0	-2.719378	-1.061424	1.286306
25	C	0	-5.191529	-0.323611	0.241465
26	C	0	-5.642122	-1.634856	0.021131
27	C	0	-6.168773	0.683249	0.357653
28	C	0	-7.001455	-1.925985	-0.083290
29	H	0	-4.916929	-2.436052	-0.089229
30	C	0	-7.521328	0.384853	0.239351
31	H	0	-5.862729	1.701833	0.572165
32	C	0	-7.977949	-0.925731	0.015913
33	H	0	-7.291094	-2.955810	-0.257229
34	H	0	-8.237111	1.195472	0.340234

35	C	0	5.201196	-0.282539	-0.250771
36	C	0	6.170612	0.728347	-0.353774
37	C	0	5.659903	-1.596599	-0.041115
38	C	0	7.529954	0.440675	-0.233028
39	H	0	5.859547	1.747053	-0.560373
40	C	0	7.017124	-1.875039	0.064558
41	H	0	4.939188	-2.403175	0.058676
42	C	0	7.991545	-0.865298	-0.021292
43	H	0	8.234102	1.259752	-0.323341
44	H	0	7.320017	-2.904717	0.230199
45	C	0	-9.485922	-1.207807	-0.103694
46	C	0	-10.194232	-0.784326	1.205258
47	C	0	-10.068685	-0.397330	-1.285873
48	C	0	-9.783967	-2.698677	-0.350176
49	H	0	-9.806257	-1.347436	2.060215
50	H	0	-10.056906	0.280065	1.417014
51	H	0	-11.271276	-0.973248	1.133891
52	H	0	-9.591034	-0.681927	-2.229011
53	H	0	-11.144773	-0.581379	-1.380499
54	H	0	-9.926232	0.678901	-1.151312
55	H	0	-10.865229	-2.850065	-0.429325
56	H	0	-9.332181	-3.056357	-1.281161
57	H	0	-9.422617	-3.327826	0.469783
58	C	0	9.483081	-1.218948	0.113186
59	C	0	9.735187	-1.865939	1.496049
60	C	0	9.877491	-2.219551	-0.999142
61	C	0	10.390958	0.019082	-0.010132
62	H	0	9.471771	-1.176559	2.304760
63	H	0	9.148300	-2.779060	1.631881
64	H	0	10.792881	-2.130630	1.605747
65	H	0	9.716301	-1.785638	-1.991275
66	H	0	10.936574	-2.487300	-0.912821
67	H	0	9.295294	-3.143808	-0.940900
68	H	0	11.438677	-0.280433	0.094187
69	H	0	10.283797	0.508253	-0.983784
70	H	0	10.180459	0.758259	0.769674
71	H	0	0.386327	-0.369831	-1.448330
72	H	0	-0.374954	-0.382235	1.433564

Table S4 Geometrical coordinates of the optimized **1,1′-PhCN-4,4′-BBT** by DFT at the B3LYP/6-31G(d,p) level.[2]

Cartesian coordinates:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	-0.249146	1.611493	0.866384
2	C	0	0.120699	3.016993	0.901592
3	C	0	0.865542	3.510639	2.017186
4	C	0	1.236605	2.647208	3.012357
5	C	0	0.903384	1.260144	2.958729
6	C	0	0.179881	0.721690	1.920006
7	C	0	-0.395896	3.738311	-0.183192
8	H	0	1.108075	4.564956	2.083962
9	H	0	1.795246	3.017025	3.866865
10	H	0	1.237068	0.607500	3.759591
11	C	0	-0.179881	-0.721690	1.920006
12	C	0	0.249146	-1.611493	0.866384
13	C	0	-0.903384	-1.260144	2.958729
14	C	0	-0.120699	-3.016993	0.901592
15	C	0	-1.236605	-2.647208	3.012357
16	H	0	-1.237068	-0.607500	3.759591
17	C	0	-0.865542	-3.510639	2.017186
18	C	0	0.395896	-3.738311	-0.183192
19	H	0	-1.795246	-3.017025	3.866865
20	H	0	-1.108075	-4.564956	2.083962
21	C	0	-0.236755	5.152114	-0.530686
22	C	0	-1.304628	5.890395	-1.080503
23	C	0	0.997236	5.809469	-0.347514
24	C	0	-1.153412	7.225749	-1.426795
25	H	0	-2.269605	5.412318	-1.215891
26	C	0	1.153170	7.148693	-0.679028
27	H	0	1.847973	5.252397	0.027988
28	C	0	0.077847	7.871746	-1.222424
29	H	0	-1.987123	7.780460	-1.843623
30	H	0	2.110349	7.638774	-0.536387
31	C	0	0.236755	-5.152114	-0.530686
32	C	0	1.304628	-5.890395	-1.080503
33	C	0	-0.997236	-5.809469	-0.347514
34	C	0	1.153412	-7.225749	-1.426795

35	H	0	2.269605	-5.412318	-1.215891
36	C	0	-1.153170	-7.148693	-0.679028
37	H	0	-1.847973	-5.252397	0.027988
38	C	0	-0.077847	-7.871746	-1.222424
39	H	0	1.987123	-7.780460	-1.843623
40	H	0	-2.110349	-7.638774	-0.536387
41	C	0	-0.236755	-9.252526	-1.568717
42	N	0	-0.366177	-10.374434	-1.849540
43	C	0	0.236755	9.252526	-1.568717
44	N	0	0.366177	10.374434	-1.849540
45	S	0	-1.338062	2.688549	-1.198553
46	S	0	1.338062	-2.688549	-1.198553
47	C	0	1.050890	-1.310846	-0.224295
48	C	0	-1.050890	1.310846	-0.224295
49	H	0	-1.470469	0.354420	-0.497486
50	H	0	1.470469	-0.354420	-0.497486

Ref. 2 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 16, Revision B.01* , Gaussian, Inc., Wallingford CT, 2016.