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Supplementary Information

Highly stable and isomorphic donor–acceptor stacking in a family of *n*-type organic semiconductors of BTBT-TCNQ derivatives

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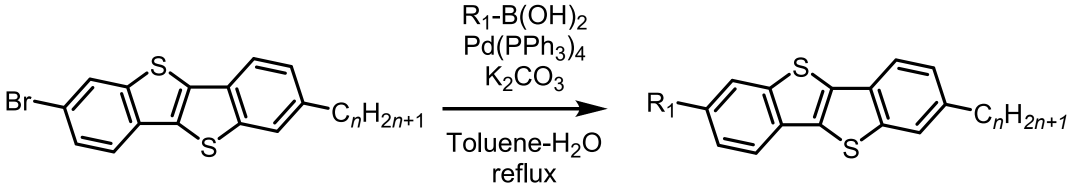
Synthesis

All chemicals and solvents are of reagent grade unless otherwise indicated. Commercially available materials were used as received. 7,7,8,8-tetracyanoquinodimethane (TCNQ, purified by sublimation), 2-fluoro-7,7,8,8-tetracyanoquinodimethane (F_1TCNQ), 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane (F_2TCNQ), tetrafluorotetracyanoquinodimethane (F_4TCNQ, purified by sublimation), dithieno[3,2-*b*:2'3'-*d*]thiophene (DTT), and benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS400 spectrometer at 400MHz. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (δ 0.00). The data of multiplicity are shown as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass analyses (MS) were performed on a Shimadzu GC-MS QP2010SE in an electron impact ionization procedure. Elemental analyses were collected on a J-Science Lab JM10.

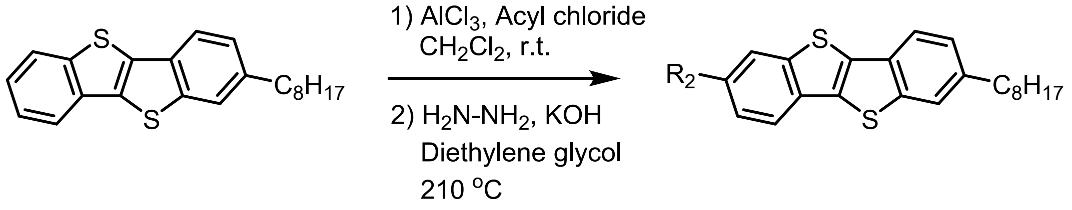
Synthesis of donor compounds

PhC12 [S1], *mono*C12 [S1], PEC12 [S2], and BTBT [S3] were synthesized by the reported procedure. MeC8, *o*TolC10, *m*TolC10, and *p*TolC10 were synthesized by using palladium-catalyzed Suzuki coupling reaction between Br-BTBT-C_n and corresponding boronic acid as shown in **Scheme S1**. EtC8, *n*BuC8, and *iso*BuC8 were synthesized by Friedel-Crafts acylation and subsequent Wolff-Kishner reduction as shown in **Scheme S2** with *mono*-C_8-BTBT. The intermediate acyl compounds after recrystallization, which contained a small amount of the starting material (*mono*-C_8-BTBT), were used without further purification. *tert*BuC8 was synthesized by acid-catalyzed tertiary-butylation as shown in **Scheme S3**. Corresponding Br-BTBT-C_n and *mono*-C_8-BTBT as starting compounds in the reaction scheme were synthesized by the reported procedure[S1)].



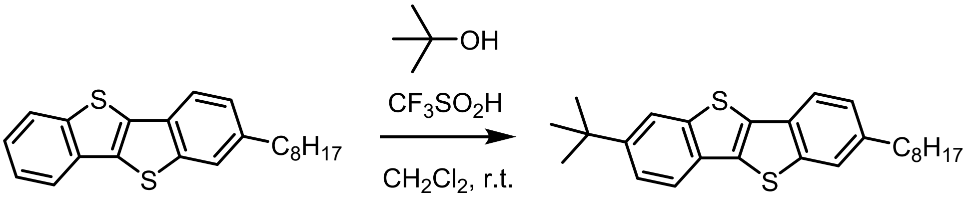
R_1 = methyl (n = 8)
ortho-Tolyl (n = 10), *meta*-Tolyl (n = 10), *para*-Tolyl (n = 10)

Scheme S1 Synthetic scheme of methyl and tolyl substituted BTBT derivatives.



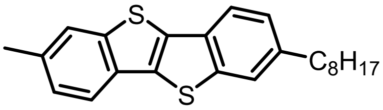
R_2 = ethyl, *n*-butyl, *iso*-butyl

Scheme S2 Synthetic scheme of ethyl, *n*-butyl, and *iso*-butyl substituted BTBT derivatives.



Scheme S3 Synthetic scheme of *tert*-butyl substituted BTBT derivatives.

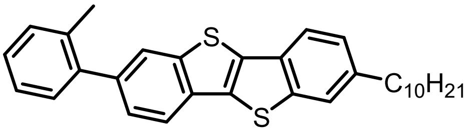
2-octyl-7-methyl[1]benzothieno[3,2-*b*][1]benzothiophene (MeC8)



A mixture of Br-BTBT-C_8 (863 mg, 2 mmol), methylboronic acid (180 mg, 3 mmol), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol), and potassium carbonate (829 mg, 6 mmol) in toluene (32 mL) and H_2O (8 mL) was stirred for 14 h at refluxing condition under N_2 atmosphere. After cooling down to room temperature, the reaction mixture was concentrated under reduce pressure to remove toluene. The resulting mixture was poured into 5 wt% aqueous HCl solution and extracted with chloroform. The organic layer was separated and concentrated under reduce pressure. The resulting crude product was purified by recycling gel permeation chromatography and passed through a silica gel pad with chloroform as eluent and to afford MeC8 (697 mg, 1.9 mmol, yield 95 %) as a white powder.

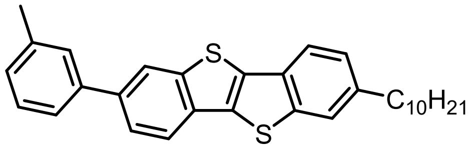
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, J = 8.0 Hz, 1H, ArH), 7.74 (d, J = 8.0 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.70 (s, 1H, ArH), 7.26 (m, 2H, ArH), 2.75 (t, J = 8.0 Hz, 2H, $ArCH_2$), 2.51 (s, 3H, $ArCH_3$), 1.69 (tt, J = 8.0, 7.2 Hz, 2H, CH_2), 1.34-1.27 (br, 10H, CH_2), 0.88 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.43, 142.38, 140.08, 134.86, 132.51, 132.47, 131.17, 131.00, 126.39, 125.84, 123.90, 123.32, 121.04, 121.02, 36.13, 31.89, 31.72, 29.49, 29.32, 29.26, 22.67, 21.64, 14.11. GC/MS (EI) *m*/*z* 366. Anal. Calcd for $C_{23}H_{26}S_2$: C, 75.36; H, 7.15 %. Found: C, 75.40; H, 7.38 %.

2-decyl-7-(2-methylphenyl)[1]benzothieno[3,2-*b*][1]benzothiophene (*o*TolC10)



The title compound was synthesized by a similar procedure as that for MeC8 using Br-BTBT-C_{10} and 2-methylphenylboronic acid under air atmosphere, in which the final purification was carried out by the additional recrystallization from a mixed solution of chloroform and ethanol to afford *o*TolC10 (yield 38 %) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, J = 8.0 Hz, 1H, ArH), 7.84 (s, 1H, ArH), 7.79 (d, J = 8.0 Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.42 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 7.33-7.26 (m, 5H, ArH), 2.77 (t, J = 8.0 Hz, 2H, $ArCH_2$), 2.34 (s, 3H, $ArCH_3$), 1.71 (tt, J = 8.0, 7.2 Hz, 2H, CH_2), 1.35-1.27 (br, 14H, CH_2), 0.88 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.69, 142.21, 141.49, 140.46, 138.82, 135.61, 133.56, 132.51, 132.02, 131.14, 130.49, 130.06, 127.54, 126.52, 126.00, 125.92, 124.40, 123.44, 121.29, 120.91, 36.21, 31.96, 31.77, 29.68, 29.65, 29.59, 29.39, 22.74, 20.64, 14.18. GC/MS (EI) *m*/*z* 470. Anal. Calcd for $C_{31}H_{34}S_2$: C, 79.10; H, 7.28 %. Found: C, 78.55; H, 7.45 %.

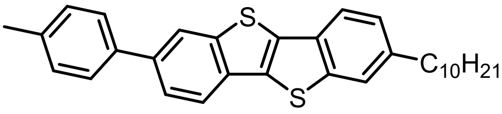


2-decyl-7-(3-methylphenyl)[1]benzothieno[3,2-*b*][1]benzothiophene (*m*TolC10)

The title compound was synthesized by a similar reaction condition as that for MeC8 using Br-BTBT-C_{10} and 3-methylphenylboronic acid. After cooling down to room temperature, the reaction mixture was concentrated under reduce pressure to remove toluene. The resulting mixture was poured into 5 wt% aqueous HCl solution and extracted with chloroform. The organic layer was separated and concentrated under reduce pressure. The resulting crude product was washed with chloroform and the insoluble residuals were removed by the filtration. The filtered solution was again concentrated under reduce pressure. The resulting crude product was recrystallized from a mixed solution of chloroform and ethanol to afford *m*TolC10 (yield 71 %) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11 (s, 1H, ArH), 7.91 (d, *J* = 8.0 Hz, 1H, ArH), 7.79 (d, *J* = 8.0 Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH), 7.51 (s, 1H, ArH), 7.49 (d, *J* = 8.0 Hz, 1H, ArH), 7.37 (dd, *J* = 8.0, 8.0 Hz, 1H, ArH), 7.29 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH), 7.20 (d, *J* = 8.0 Hz, 1H, ArH), 2.77 (t, *J* = 8.0 Hz, 2H, $ArCH_2$), 2.46 (s, 3H, $ArCH_3$), 1.70 (tt, *J* = 8.0, 7.2 Hz, 2H, CH_2), 1.35-1.27 (br, 14H, CH_2), 0.88 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.87, 142.66, 140.78, 140.44, 138.54, 138.23, 133.65, 132.39, 132.30, 131.08, 128.82, 128.18, 128.11, 125.96, 124.47, 124.44, 123.38, 122.31, 121.52, 121.24, 36.16, 31.91, 31.71, 29.63, 29.61, 29.54, 29.34, 22.69, 21.59, 14.13. GC/MS (EI) *m*/*z* 470. Anal. Calcd for $C_{31}H_{34}S_2$: C, 79.10; H, 7.28 %. Found: C, 78.70; H, 7.58 %.

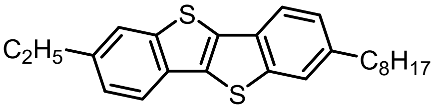
2-decyl-7-(4-methylphenyl)[1]benzothieno[3,2-*b*][1]benzothiophene (*p*TolC10)



The title compound was synthesized by a similar reaction condition as that for *m*TolC10 using 4-methylphenylboronic acid as a coupling partner, in which final recrystallization was carried out using chloroform to afford *p*TolC10 (yield 85 %) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10 (s, 1H, ArH), 7.91 (d, *J* = 8.0 Hz, 1H, ArH), 7.79 (d, *J* = 8.0 Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H, ArH), 7.59 (d, *J* = 8.0 Hz, 2H, ArH), 7.29 (m, *3*H, ArH), 2.77 (t, *J* = 8.0 Hz, 2H, $ArCH_2$), 2.42 (s, 3H, $ArCH_3$), 1.70 (tt, *J* = 8.0, 7.2 Hz, 2H, CH_2), 1.36-1.27 (br, 14H, CH_2), 0.88 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.86, 142.64, 140.40, 138.09, 137.91, 137.26, 133.53, 132.40, 132.15, 131.09, 129.65, 127.14, 125.95, 124.30, 123.38, 122.06, 121.54, 121.22, 36.20, 31.95, 31.75, 29.66, 29.64, 29.57, 29.38, 22.73, 21.18, 14.16. GC/MS (EI) *m*/*z* 470. Anal. Calcd for $C_{31}H_{34}S_2$: C, 79.10; H, 7.28 %. Found: C, 79.03; H, 7.30 %.

2-ethyl-7-octyl[1]benzothieno[3,2-*b*][1]benzothiophene (EtC8)

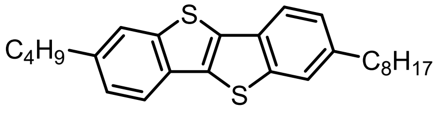


To a solution of *mono*-C_8-BTBT (1.06 g, 3 mmol) and acetyl chloride (306 mg, 3.9 mmol) in dichloromethane (100 mL) at 0 °C was added aluminium (III) chloride (533 mg, 4 mmol). After being stirred for 6 h at room temperature, the reaction mixture was poured into 5 wt% aqueous HCl solution and extracted with chloroform. The organic layer was separated and concentrated under reduce pressure. The resulting crude product was recrystallized from a mixed solution of chloroform and ethanol to afford an acylated compound containing a small amount of the starting material (*mono*-C_8-BTBT), which used without further purification.

A mixture of the acylated compound (789 mg), potassium hydroxide (561 mg, 10 mmol), and hydrazine monohydrated (2.0 g, 40 mmol) in diethylene glycol was stirred for 1h at 120 °C and then further stirred for 5h at 210 °C. After cooling down to room temperature, the reaction mixture was poured into 5 wt% aqueous HCl solution and extracted with chloroform. The combined extract was washed with 5 wt% aqueous HCl solution to remove diethylene glycol. The organic layer was separated and concentrated under reduce pressure. The resulting crude product was purified by recycling gel permeation chromatography and reprecipitated using ethanol to afford EtC8 (571 mg, 1.5 mmol, yield 70 % (2 steps)) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 8.0 Hz, 1H, ArH), 7.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.71 (s, 1H, ArH), 7.28 (m, 2H, ArH), 2.81 (q, *J* = 8.0 Hz, 2H, $ArCH_2$), 2.76 (t, *J* = 8.0 Hz, 2H, $ArCH_2$), 1.69 (tt, *J* = 8.0, 7.2 Hz, 2H, CH_2), 1.37-1.28 (br, 10H, CH_2), 1.33 (t, *J* = 8.0 Hz, 3H, CH_3), 0.88 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.49, 142.40, 141.36, 140.09, 132.58, 132.52, 131.22, 131.19, 125.84, 125.38, 123.33, 122.75, 121.16, 121.07, 36.14, 31.89, 31.73, 29.50, 29.33, 29.27, 29.07, 22.68, 15.84, 14.11. GC/MS (EI) *m*/*z* 380. Anal. Calcd for $C_{24}H_{28}S_2$: C, 75.74; H, 7.42 %. Found: C, 75.86; H, 7.73 %.

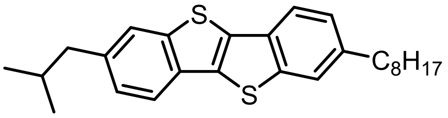
2-*n*-butyl-7-octyl[1]benzothieno[3,2-*b*][1]benzothiophene (*n*BuC8)



The title compound was synthesized by a similar procedure as that for EtC8 using butyryl chloride to afford *n*BuC8 (yield 59 % (2 steps)) as a white powder.

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.71 (s, 1H, ArH), 7.71 (s, 1H, ArH), 7.28 (m, 2H, ArH), 2.76 (t, *J* = 8.0 Hz, 2H, ArCH$_2$), 2.75 (t, *J* = 8.0 Hz, 2H, ArCH$_2$), 1.72-1.65 (m, 4H, CH$_2$), 1.43-1.27 (m, 12H, CH$_2$), 0.96 (t, *J* = 7.2 Hz, 3H, CH3), 0.88 (t, *J* = 7.2 Hz, 3H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 142.41, 140.07, 140.02, 132.54, 125.84, 123.33, 121.07, 36.14, 35.81, 33.86, 31.89, 31.73, 29.50, 29.34, 29.27, 22.68, 22.37, 14.11, 13.98. GC/MS (EI) *m*/*z* 408. Anal. Calcd for $C_{26}H_{32}S_2$: C, 76.42; H, 7.89 %. Found: C, 76.33; H, 8.00 %.

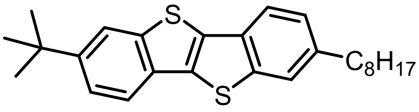
2-isobutyl-7-octyl[1]benzothieno[3,2-*b*][1]benzothiophene (*iso*BuC8)



The title compound was synthesized by a similar procedure as that for EtC8 using butyryl chloride to afford *iso*BuC8 (yield 66 % (2 steps)) as a white powder.

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.67 (s, 1H, ArH), 7.25 (m, 2H, ArH), 2.75 (t, *J* = 8.0 Hz, 2H, ArCH$_2$), 2.61 (d, *J* = 8.0 Hz, 2H, ArCH), 1.96 (qt, *J* = 8.0, 7.2 Hz, 1H, CH), 1.70 (tt, *J* = 8.0, 7.2 Hz, 2H, CH$_2$), 1.34-1.25 (br, 10H, CH$_2$), 0.95 (d, *J* = 7.2 Hz, 6H, CH$_3$), 0.88 (t, *J* = 7.2 Hz, 3H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 142.42, 142.29, 140.08, 138.82, 132.58, 132.53, 131.25, 131.19, 126.44, 125.84, 124.05, 123.33, 121.07, 120.92. GC/MS (EI) *m*/*z* 408. Anal. Calcd for $C_{26}H_{32}S_2$: C, 76.42; H, 7.89 %. Found: C, 76.25; H, 8.08 %.

2-*tert*-butyl-7-octyl[1]benzothieno[3,2-*b*][1]benzothiophene (*tert*BuC8)



To a solution of *mono*-C$_8$-BTBT (704 mg, 2 mmol) and *tert*-butyl alcohol (163 mg, 2.2 mmol) in dichloromethane (150 mL) at 0 ^{o}C was added a solution of trifluoromethanesulfonic acid (3.0 g, 20 mmol) in dichloromethane (20 mL). After being stirred for 6 h at room temperature, the reaction mixture was poured into water. The resulting organic layer was separated and concentrated under reduce pressure. The crude product was washed with refluxing ethanol (15 mL), and then the precipitated tar-like residual was separated by the decantation. The organic layer was concentrated under reduce pressure. The resulting crude product was purified by recycling gel permeation chromatography to afford *tert*BuC8 (490 mg, 1.2 mmol, yield 60 %) as a white powder.

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.90 (s, 1H, ArH), 7.78 (d, *J* = 8.0 Hz, 1H, ArH), 7.77 (d, *J* =

8.0 Hz, 1H, ArH), 7.71 (s, 1H, ArH), 7.50 (d, *J* = 8.0 Hz, 1H, ArH), 7.28 (d, *J* = 8.0 Hz, 2H, ArH), 2.75 (t, *J* = 8.0 Hz, 2H, $ArCH_2$), 1.70 (tt, *J* = 8.0, 7.2 Hz, 2H, CH_2), 1.42 (s, 9H, CH_3), 1.42-1.28 (br, 10H, CH_2), 0.88 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.31, 142.45, 142.39, 140.10, 132.83, 132.40, 131.20, 130.93, 125.82, 123.34, 123.01, 121.12, 120.89, 120.25, 36.14, 35.10, 31.89, 31.74, 31.54, 29.50, 29.34, 29.27, 22.67, 14.11. GC/MS (EI) *m*/*z* 408. Anal. Calcd for $C_{26}H_{32}S_2$: C, 76.42; H, 7.89 %. Found: C, 76.26; H, 8.21 %.

CCSD(T) calculations of interaction potential of thiophene-tetracyanoethylene complex

The interaction potential calculated for the thiophene-tetracyanoethylene complex by the dispersion corrected DFT calculations (B3LYP/6-311G** level calculations with Grimme's D3 correction) was compared with the CCSD(T) level potential to confirm the accuracy of the dispersion corrected DFT calculations for the evaluation of the intermolecular interactions of donor-acceptor complex, since the CCSD(T) level intermolecular interaction energies at the basis set limit are close to the gas phase experimental values in general.

The MP2/cc-pVTZ level optimized geometries of isolated molecules were used for calculations of the intermolecular interaction energy potentials. The interaction energy potentials were calculated without further geometry optimizations. The BSSE was corrected by the counterpoise method in the calculations of the complex. The MP2 interaction energy at the basis set limit [$E_{\mathrm{MP2(limit)}}$] for the complex was estimated by Helgaker et al.'s method [S4] from the calculated MP2 interaction energies (E_{MP2}) using the cc-pVTZ and cc-pVQZ basis sets. The CCSD(T) interaction energy at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] was calculated as the sum of the $E_{\mathrm{MP2(limit)}}$ and the estimated CCSD(T) correction term [ΔCCSD(T) = $E_{\mathrm{CCSD(T)}}$ - E_{MP2}] at the basis set limit [ΔCCSD(T)(limit)], which was estimated from the difference between the calculated CCSD(T) and MP2 level interaction energies using the aug-cc-pVDZ basis set. [S5]

The MP2 level interaction energy at the basis set limit [$E_{\mathrm{MP2(limit)}}$] for the complex was obtained by Helgaker et al.'s method from the MP2 interaction energies (E_{MP2}) obtained using the cc-pVTZ and cc-pVQZ basis sets. In Helgaker et al.'s method the calculated MP2 level interaction energies (E_{MP2}) were fitted to a form a + b X^{-3} (where X is 3 for cc-pVTZ and 4 for cc-pVQZ). The $E_{\mathrm{MP2(limit)}}$ was then calculated by an extrapolation. Helgaker et al.'s method was originally proposed for calculating the electron correlation contribution at the basis set limit. But we used this method to calculate the $E_{\mathrm{MP2(limit)}}$, since the basis set dependence of HF level interaction energy (E_{HF}) is small.

The CCSD(T) level interaction energy at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] for the complex was obtained according to equation (1)

$$E_{\mathrm{CCSD(T)(limit)}} = E_{\mathrm{MP2(limit)}} + \Delta\mathrm{CCSD(T)(limit)}, \qquad (1)$$

where ΔCCSD(T)(limit) denotes the CCSD(T) correction term [ΔCCSD(T)] at the basis set limit. The ΔCCSD(T) [= $E_{\mathrm{CCSD(T)}}$ - E_{MP2}] is the difference between the CCSD(T) level interaction energy

[$E_{\mathrm{CCSD(T)}}$] and the MP2 level interaction energy (E_{MP2}). The ΔCCSD(T)(limit) was obtained by equation (2)

$$\Delta\mathrm{CCSD(T)(limit)} = \Delta\mathrm{CCSD(T)(M)} + \Delta\ \mathrm{(M)}\Delta\mathrm{CCSD(T)}, \qquad (2)$$

where ΔCCSD(T)(M) denotes ΔCCSD(T) obtained using a Medium size basis set. The aug-cc-pVDZ basis set was used for the Medium size basis set in this work. The ΔCCSD(T) has a weak basis set dependence. Δ(M)ΔCCSD(T) is a correction term for slight underestimation of the ΔCCSD(T) by the Medium size basis set. The Δ(M)ΔCCSD(T) corresponds to a difference between the ΔCCSD(T)(limit) and ΔCCSD(T)(M).

We can calculate the Δ(M)ΔCCSD(T), if we know the value of $F_{\mathrm{corr(M)}}$, which is defined by equation (3)

$$F_{\mathrm{corr(M)}} = \Delta\mathrm{CCSD(T)(M)}/\Delta\mathrm{CCSD(T)(limit)} \quad (3).$$

From equations (2) and (3) we can obtaine equation (4)

$$\Delta\mathrm{(M)}\Delta\mathrm{CCSD(T)} = \Delta\mathrm{CCSD(T)(M)}\ \mathrm{x}\ (1 - F_{\mathrm{corr(M)}})/F_{\mathrm{corr(M)}} \quad (4).$$

We calculated the $F_{\mathrm{corr(M)}}$ value by equation (5) in this work

$$F_{\mathrm{corr(M)}} = E_{\mathrm{corr(MP2)(M)}}/E_{\mathrm{corr(MP2)(limit)}} \quad (5),$$

where the $E_{\mathrm{corr(MP2)(M)}}$ denotes the MP2 level electron correlation effect on the calculated interaction energy ($E_{\mathrm{corr(MP2)}} = E_{\mathrm{MP2}} - E_{\mathrm{HF}}$) using the medium size basis set. The $E_{\mathrm{corr(MP2)(limit)}}$ denotes the MP2 level electron correlation effect at the basis set limit (= $E_{\mathrm{MP2(limit)}} - E_{\mathrm{HF(limit)}}$). We can obtain sufficiently accurate $F_{\mathrm{corr(M)}}$ value by equation (5), if the basis set dependence of the CCSD(T) level electron correlation effect is close to that of $E_{\mathrm{corr(MP2)}}$. The E_{HF} calculated using the cc-pVQZ basis set was used as the $E_{\mathrm{HF(limit)}}$, since the basis set dependence of the E_{HF} is very small.

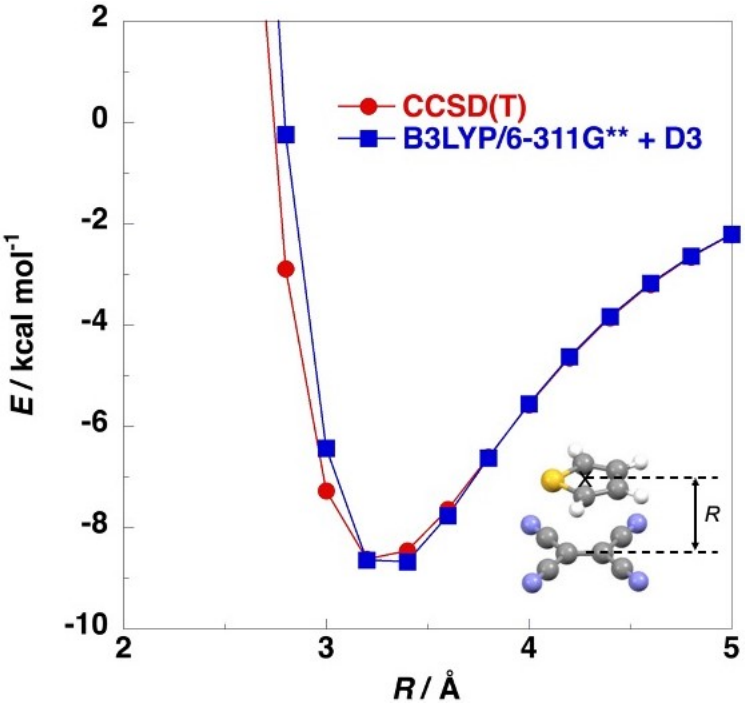


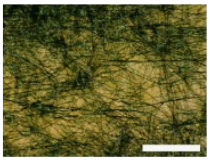
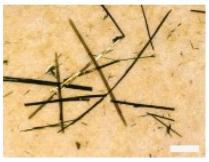
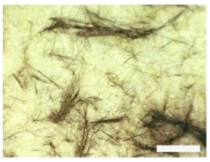
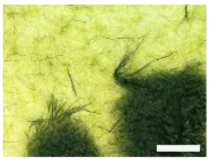
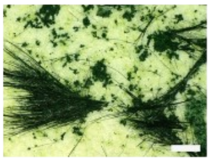
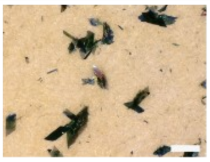
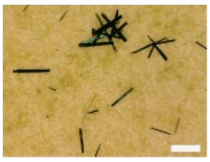
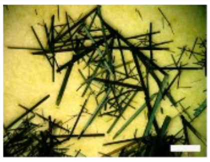
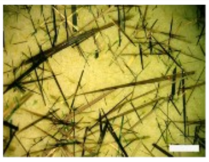
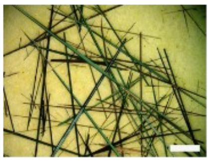
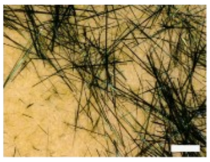
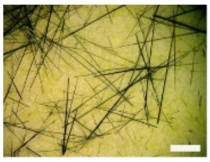
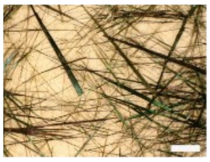
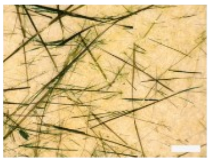
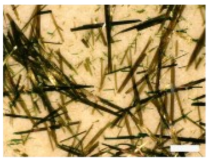
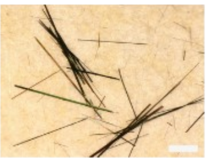
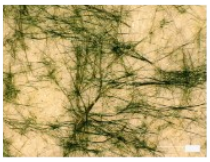
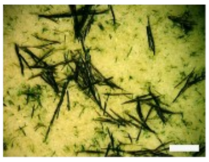
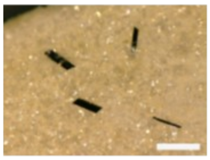
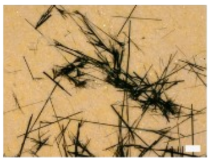
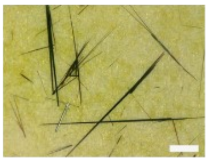
Fig. S1 The interaction energy potential calculated for the thiophne-tetracyanoethylene complex at the B3LYP/6-311G** level with Grimme's D3 dispersion correction and the estimated CCSD(T) interaction energy potential at the basis set limit. The thiophne-tetracyanoethylene complex has C_s symmetry. The midpoint of C_2 and C_5 of thiophene is on the symmetry axis of tetracyanoethylene. The π planes of thiophene and tetracyanoethylene are parallel.

Combination of molecular compounds

	F0	F1	F2	F4
*mono*C12	○	△	△	○
MeC8	△	△	△	△
EtC8	○	△	○	○
*n*BuC8	○	△	○	○
*tert*BuC8	△	△	△	△
*iso*BuC8	△	△	△	△
PhC12	×	△	×	○
PEC12	×	△	×	○
*o*TolC10	○	△	○	○
*m*TolC10	○	×	○	○
*p*TolC10	×	×	×	×
DTT	○	○	○	×
BDT	○	×	○	○

○ :analyzed △ :crystalized × :not crystalized

Table S1 List of the synthesized compounds.

	F0	F1	F2	F4
*mono*C12				
MeC8				
EtC8				
*n*BuC8				
*tert*BuC8				
*iso*BuC8				
*m*TolC10				
*o*TolC10				

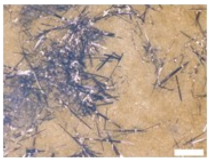
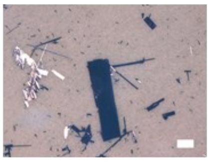
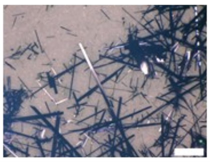
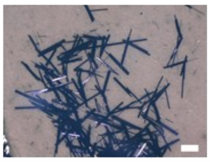
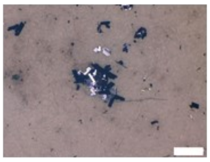
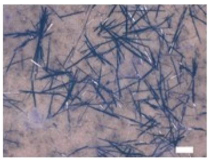
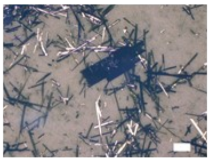
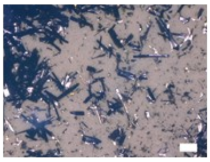
	F0	F1	F2	F4
PhC12				
PEC12				
DTT				
BDT				

Fig. S2 Photographs of the compound crystals. All scale bars are 500 μm.

Bending angles of alkyl chain in BTBT molecules

Torsion angle	core-C1 C2-C3	C1-C2 C3-C4	C2-C3 C4-C5	C3-C4 C5-C6	C4-C5 C6-C7	C5-C6 C7-C8
(*di*C4)(F0)	31.93	177.08				
(*di*C4)(F2)	14.72	179.34				
(*di*C4)(F4)	9.36	177.13				
(*di*C8)(F0)	75.32	178.21	169.13	179.04	179.87	178.04
(*di*C8)(F2)	75.92	179.59	169.46	179.27	179.35	178.74
(*di*C8)(F4)	77.49	178.06	170.24	179.35	178.90	178.19
(*di*C12)(F0)	76.41	179.83	171.09	179.17	178.95	179.53
(*di*C12)(F2)	76.04	179.88	171.64	178.76	178.69	178.77
(*di*C12)(F4)	77.86	179.67	170.49	179.02	178.78	179.70
(*mono*C12)(F0)	76.19	179.86	171.20	179.00	178.62	178.99
(*mono*C12)(F4)	77.84	178.53	171.32	178.70	179.66	178.89
(PhC12)(F4)	78.09	179.28	170.90	178.64	179.34	178.33
(PEC12)(F4)	83.93	175.10	173.66	179.82	179.88	178.77
(*m*TolC10)(F0)	171.86	176.51	176.16	175.50	177.23	177.70
(*m*TolC10)(F2)	76.39	178.59	169.89	179.66	177.49	178.21
(*m*TolC10)(F4)	77.70	178.41	170.33	179.31	177.07	178.24
(*o*TolC10)(F0)	78.11	178.75	170.90	179.31	177.43	178.33
(*o*TolC10)(F2)	77.27	179.82	170.59	178.92	177.48	178.10
(*o*TolC10)(F4)	78.91	179.29	170.69	178.93	177.48	178.09
(EtC8)(F0) (BTBT-pair)	175.51 (168.20)	178.02 (170.15)	179.50 (179.60)	178.53 (174.07)	179.36 (176.50)	177.85 (117.05)
(EtC8)(F2)	81.06	178.98	166.47	177.86	180.00	177.63
(EtC8)(F4)	83.23	177.67	168.02	179.54	179.73	180.00
(*n*BuC8)(F0)	73.59	176.30	162.65	178.58	178.16	175.91
(*n*BuC8)(F2)	73.05	177.93	164.66	179.23	178.30	178.23
(*n*BuC8)(F4)	74.24	176.43	168.11	177.60	171.73	176.71

□ 0～160°　▨ 160～175°　■ 175～180°

Torsion angle	core-C1 C2-C3	C1-C2 C3-C4	C2-C3 C4-C5	C3-C4 C5-C6	C4-C5 C6-C7	C5-C6 C7-C8
*di*C4	177.85	179.86				
*di*C8	174.74	177.04	177.31	179.56	178.94	179.39
*di*C12	174.62	178.13	177.19	179.79	179.38	178.38
*mono*C9	176.52	175.93	178.16	179.84	179.15	178.91
PhC10	172.52	177.02	178.05	178.75	179.23	179.83
PEC12	173.08	179.38	176.37	178.65	177.93	179.97
*m*TolC10	175.47	176.27	177.47	179.25	179.46	179.03

☐ 0～160° ▨ 160～175° 🟧 175～180°

Table S2 Torsion angles at each carbon-carbon bond on alkyl chain in the DA compound crystals and in the single-component crystals. The abbreviations of carbon atoms are drawn in Fig. S2(a).

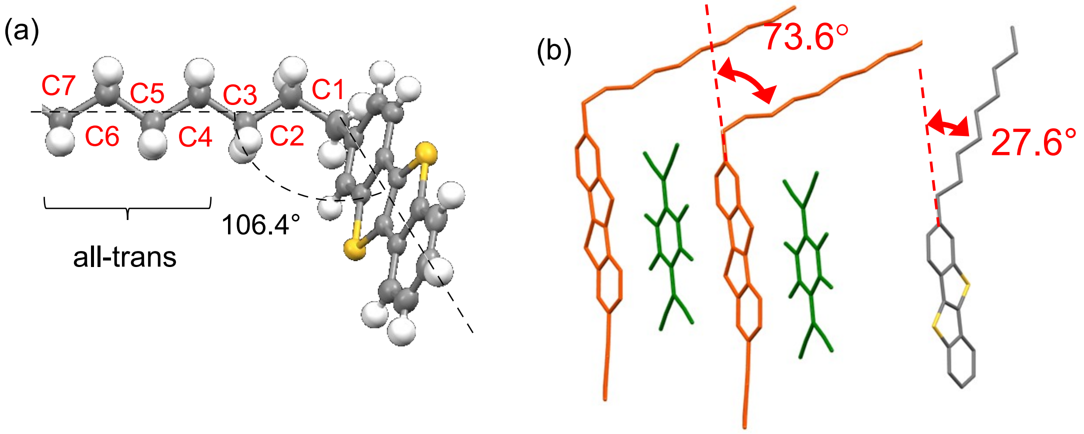


Fig. S3 (a) Molecular structure expanded around the root of alkyl chain of donor unit. (b) Bending angles of alkyl chain in BTBT derivatives in the DA compound crystals and in the single-component crystals.

Charge distribution of donor and acceptor units

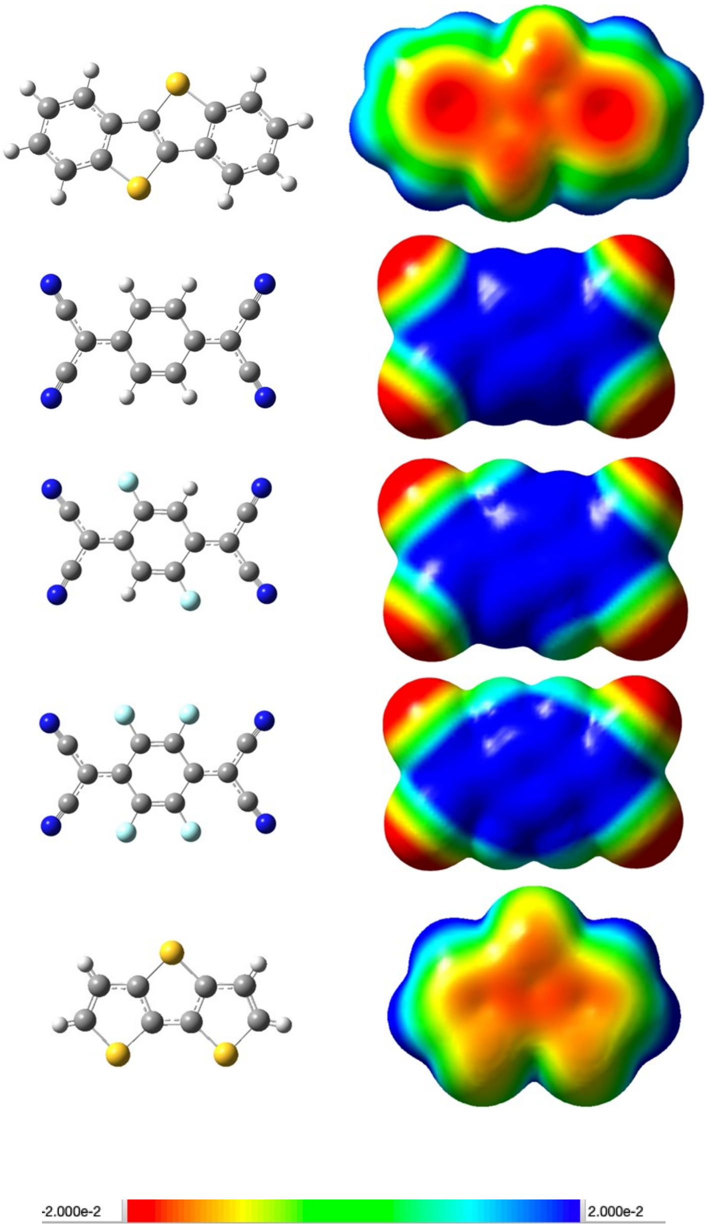


Fig. S4 Electrostatic potentials for single component molecules of the donor and acceptor units. The calculation was conducted by Gaussian 16 with B3LYP/6-311G** wave functions.

Electrochemical measurements

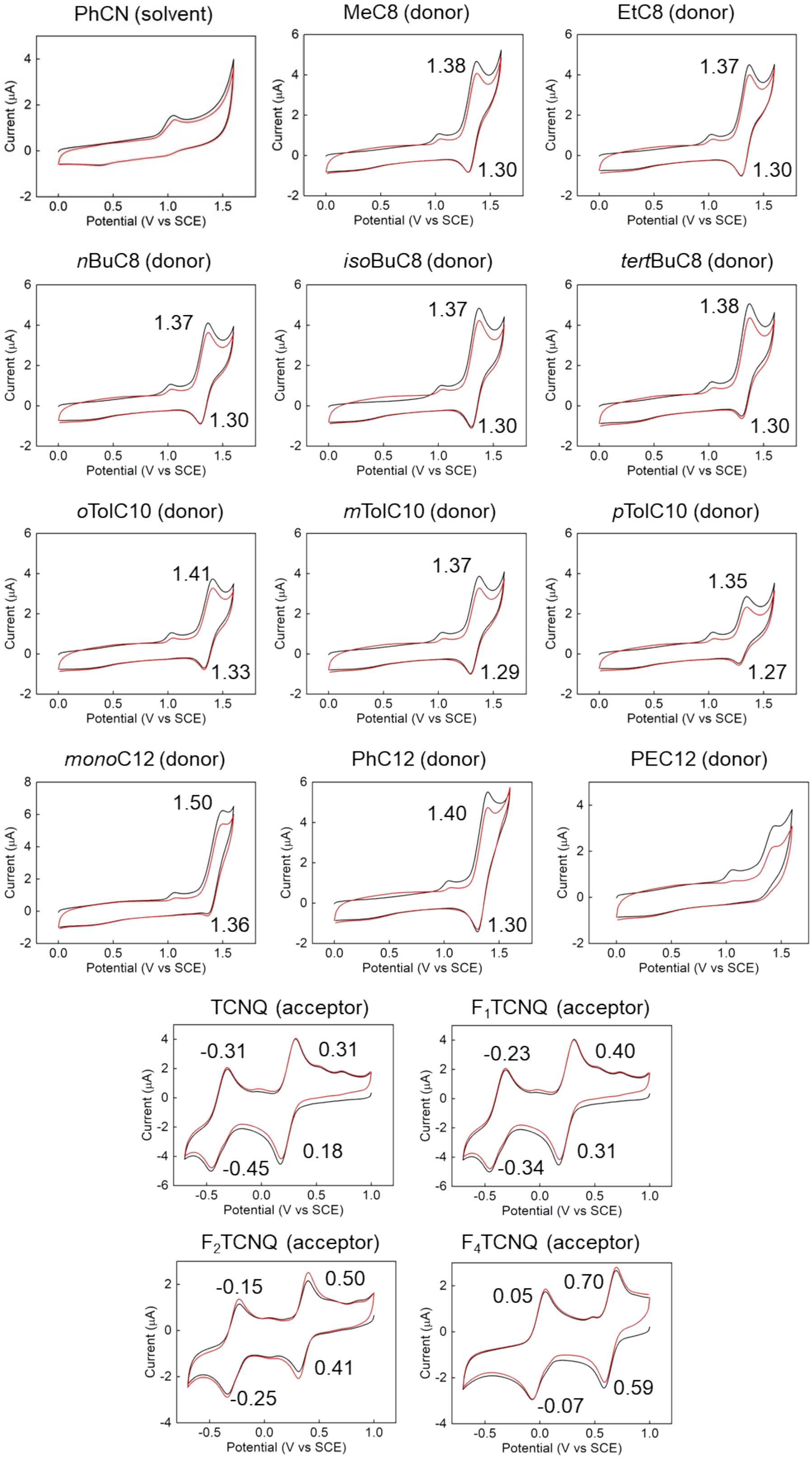

PhCN (solvent)
MeC8 (donor)
EtC8 (donor)
*n*BuC8 (donor)
*iso*BuC8 (donor)
*tert*BuC8 (donor)
*o*TolC10 (donor)
*m*TolC10 (donor)
*p*TolC10 (donor)
*mono*C12 (donor)
PhC12 (donor)
PEC12 (donor)
TCNQ (acceptor)
F_1TCNQ (acceptor)
F_2TCNQ (acceptor)
F_4TCNQ (acceptor)

Fig. S5 Cyclic voltammograms for the donor and acceptor units.

Optical properties of the compounds with DTT and BDT as donor unit

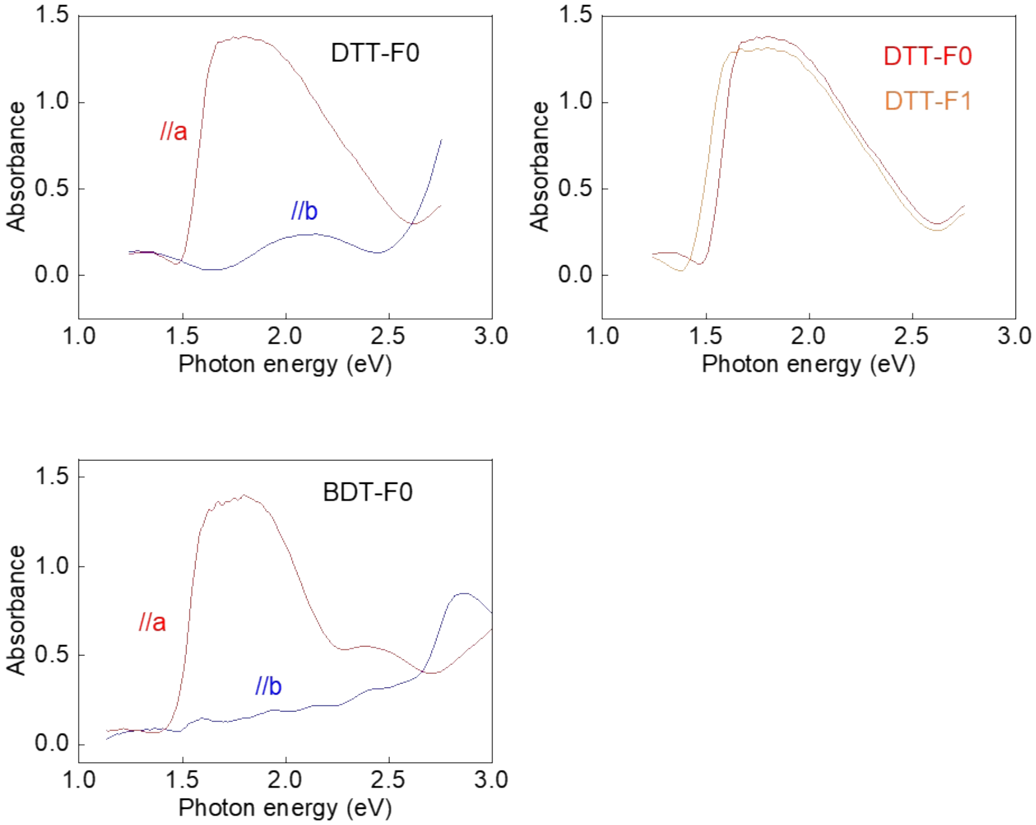


Fig. S6 Polarized optical absorption spectra for (DTT)(F_mTCNQ) and (BDT)(TCNQ) compounds. In parallel direction to *a* axis, the former has a single peak of CT transition, whereas the latter has two peaks as with (BTBT derivatives)(F_mTCNQ) compounds.

Transfer property for (*o*TolC10)(F4) thin-film

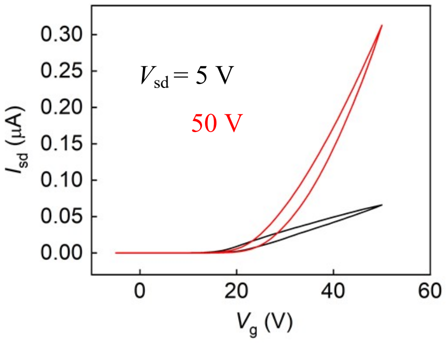


Fig. S7 Typical transfer property for (oTolC10)(F4) thin film fabricated by blade-coat.

Thermal property of compound

We conducted the thermogravimetry-differential thermal analysis (TG-DTA) measurements to examine the sublimation point of the (substituted BTBT)(F_mTCNQ) compounds. Figure S6 shows the results for (*n*BuC8)(F*m*) [*m*=1,2,4] and (*di*-C8-BTBT)(F2). All of them present the decrease of compound crystal weight at around 160°C. The measurements were conducted at 1.0 K/min from 20°C to 250°C. The down-peak in DTA means the exothermic phase shift.

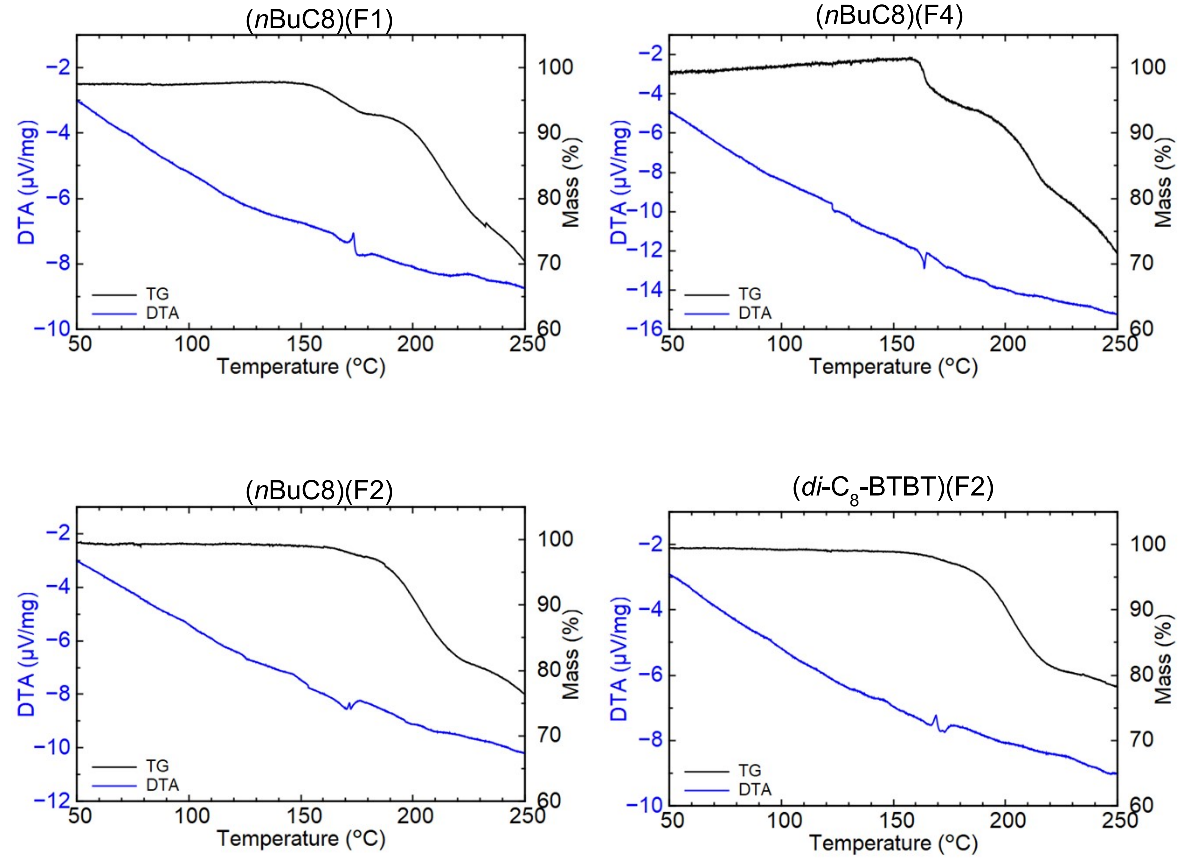


Fig. S8 TG-DTA for the compounds.

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