

Supporting Information

Insight Into the Alkyl Chain Length and Substituent Bulkiness on the Mobility Anisotropy of Benzothieno[3,2-b][1]benzothiophenes

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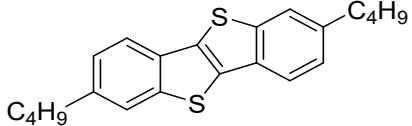
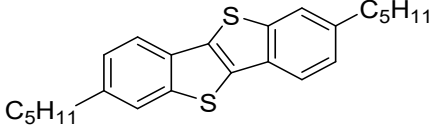
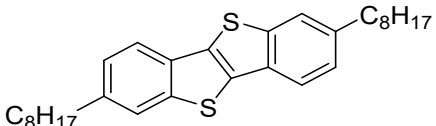
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Table S1. The calculated mobility anisotropic ratio and other related parameters of the unsubstituted and other alkylated BTBTs.

#	Name	Chemical Structure	i	r_i (Å)	θ_i (°)	V_i (meV)	λ (eV)	μ_{\max}/μ_{\min}	Theoretical μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
1	BTBT		P ₁	5.862	0	59.3	0.156	113.36	0.016-1.831
			T ₁	4.932	53.54	18.6			
			T ₂	4.932	126.46	18.6			
			P ₂	5.862	180	59.3			
			T ₃	4.932	233.54	18.6			
			T ₄	4.932	306.46	18.6			
2	di-C2-BTBT		P ₁	7.827	0	49.5	0.182	19920.18	0.000-1.911
			T ₁	5.719	46.82	4.8			
			T ₂	5.719	133.18	4.8			
			P ₂	7.827	180	49.5			
			T ₃	5.719	226.82	4.8			
			T ₄	5.719	313.18	4.8			
3	di-C3-BTBT		P ₁	4.683	0	3.5	0.182	44.39	0.002-0.087
			T ₁	7.453	95.64	12.2			
			T ₂	9.183	126.13	6.0			
			P ₂	4.683	180	3.5			
			T ₃	7.453	275.64	12.2			
			T ₄	9.183	306.13	6.0			

#	Name	Chemical Structure	i	r_i (Å)	θ_i (°)	V_i (meV)	λ (eV)	μ_{\max}/μ_{\min}	Theoretical μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
4	di-C4-BTBT		P ₁	4.642	0	1.9	0.184	17.94	0.002-0.027
			T ₁	7.652	95.75	5.1			
			T ₂	9.339	125.39	5.8			
			P ₂	4.642	180	1.9			
			T ₃	7.652	275.75	5.1			
			T ₄	9.339	305.39	5.8			
5	di-C5-BTBT		P ₁	4.760	0	9.3	0.186	13.38	0.008-0.103
			T ₁	8.681	102.31	12.9			
			T ₂	10.753	127.93	2.2			
			P ₂	4.760	180	9.3			
			T ₃	8.681	282.31	12.9			
			T ₄	10.753	307.93	2.2			
6	di-C8-BTBT		P ₁	5.927	0	42.4	0.180	155.25	0.005-0.724
			T ₁	4.930	53.05	12.4			
			T ₂	4.930	126.95	12.4			
			P ₂	5.927	180	42.4			
			T ₃	4.930	233.05	12.4			
			T ₄	4.930	306.95	12.4			

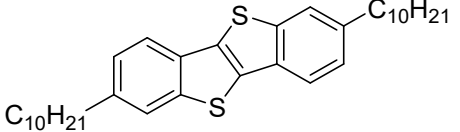
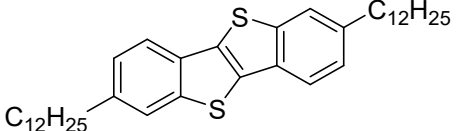
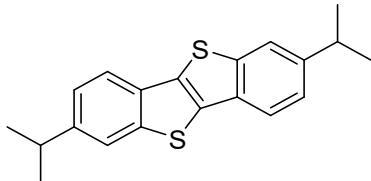
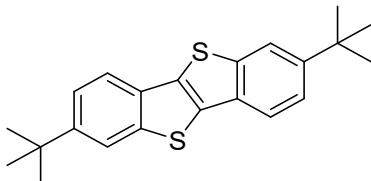
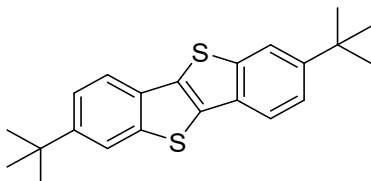
#	Name	Chemical Structure	i	r_i (Å)	θ_i (°)	V_i (meV)	λ (eV)	μ_{\max}/μ_{\min}	Theoretical μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
7	di-C10-BTBT		P ₁	5.923	0	49.4	0.172	10.88	0.074-0.804
			T ₁	4.912	52.92	28.5			
			T ₂	4.912	127.08	28.5			
			P ₂	5.923	180	49.4			
			T ₃	4.912	232.92	28.5			
			T ₄	4.912	307.08	28.5			
8	di-C12-BTBT		P ₁	5.864	0	58.0	0.158	3.92	0.283-1.109
			T ₁	4.855	52.85	44.4			
			T ₂	4.855	127.15	44.4			
			P ₂	5.864	180	58.0			
			T ₃	4.855	232.85	44.4			
			T ₄	4.855	307.15	44.4			

Table S2. The calculated mobility anisotropic ratio and other related parameters of the bulky end-capped BTBTs

#	Name	-R=	i	r_i (Å)	θ_i (°)	V_i (meV)	λ (eV)	μ_{\max}/μ_{\min}	Theoretical μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
9	diiPr-BTBT		P ₁	6.242	0	63.8	0.189	6.52	0.189-1.231
			T ₁	6.651	62.01	35.0			
			T ₂	6.651	117.99	35.0			
			P ₂	6.242	180	63.8			
			T ₃	6.651	242.01	35.0			
			T ₄	6.651	297.99	35.0			
10	ditBu-BTBT		P ₁	6.044	0	60.4	0.209	1.40	0.450-0.630
			T ₁	6.081	60.20	53.4			
			T ₂	6.081	119.80	53.4			
			P ₂	6.044	180	60.4			
			T ₃	6.081	240.20	53.4			
			T ₄	6.081	299.80	53.4			
11	ditBu-BTBT-LT		P ₁	6.155	0	54.0	0.208	1.61	0.333-0.537
			T ₁	6.150	59.97	45.9			
			T ₂	6.150	120.03	45.9			
			P ₂	6.155	180	54.0			
			T ₃	6.150	239.97	45.9			
			T ₄	6.150	300.03	45.9			

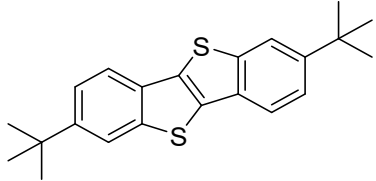
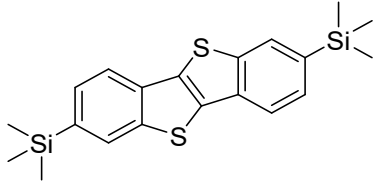
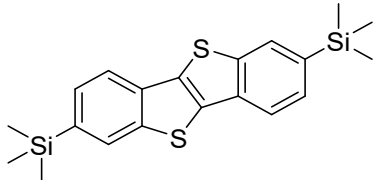
#	Name	-R=	i	r_i (Å)	θ_i (°)	V_i (meV)	λ (eV)	μ_{\max}/μ_{\min}	Theoretical μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
12	ditBu-BTBT- HT		P ₁	6.326	0	53.0	0.164	3.87	0.275-1.065
			T ₁	6.094	58.73	35.9			
			T ₂	6.094	121.27	35.9			
			P ₂	6.326	180	53.0			
			T ₃	6.094	238.73	35.9			
			T ₄	6.094	301.27	35.9			
13	diTMS- BTBT α form		P ₁	10.1	0	2.2	0.212	2.59	0.126-0.328
			T ₁	6.382	36.24	31.5			
			T ₂	6.225	142.70	38.4			
			P ₂	10.1	180	2.2			
			T ₃	6.382	216.24	31.5			
			T ₄	6.225	322.70	38.4			
14	diTMS- BTBT β form		P ₁	6.346	0	48.2	0.215	2.64	0.173-0.456
			T ₁	6.505	60.81	34.7			
			T ₂	6.505	119.19	34.7			
			P ₂	6.346	180	48.2			
			T ₃	6.505	240.81	34.7			
			T ₄	6.505	299.19	34.7			

Table S3. The dominant intermolecular interactions of the alkyl and bulky end-capped BTBTs.

Compounds	S···S interactions	S···C interactions	C···H interactions
BTBT	3.2	16.5	35.6
di-C2-BTBT	0.1	11.6	25.9
di-C3-BTBT	1	3.0	10.0
di-C4-BTBT	0.5	2.8	8.6
di-C5-BTBT	0	2.6	8.1
di-C8-BTBT	2.1	6.6	14.6
di-C10-BTBT	1.8	5.8	13.0
di-C12-BTBT	1.6	5.1	11.6
diiPr-BTBT	3.3	7.1	24.3
ditBu-BTBT	1.1	5.9	22.9
ditBu-BTBT-LT	1.1	5.5	22.8
ditBu-BTBT-HT	0.7	5.3	21.9
diTMS-BTBT α form	0	3.6	22.2
diTMS-BTBT β form	1.1	4.6	23.7

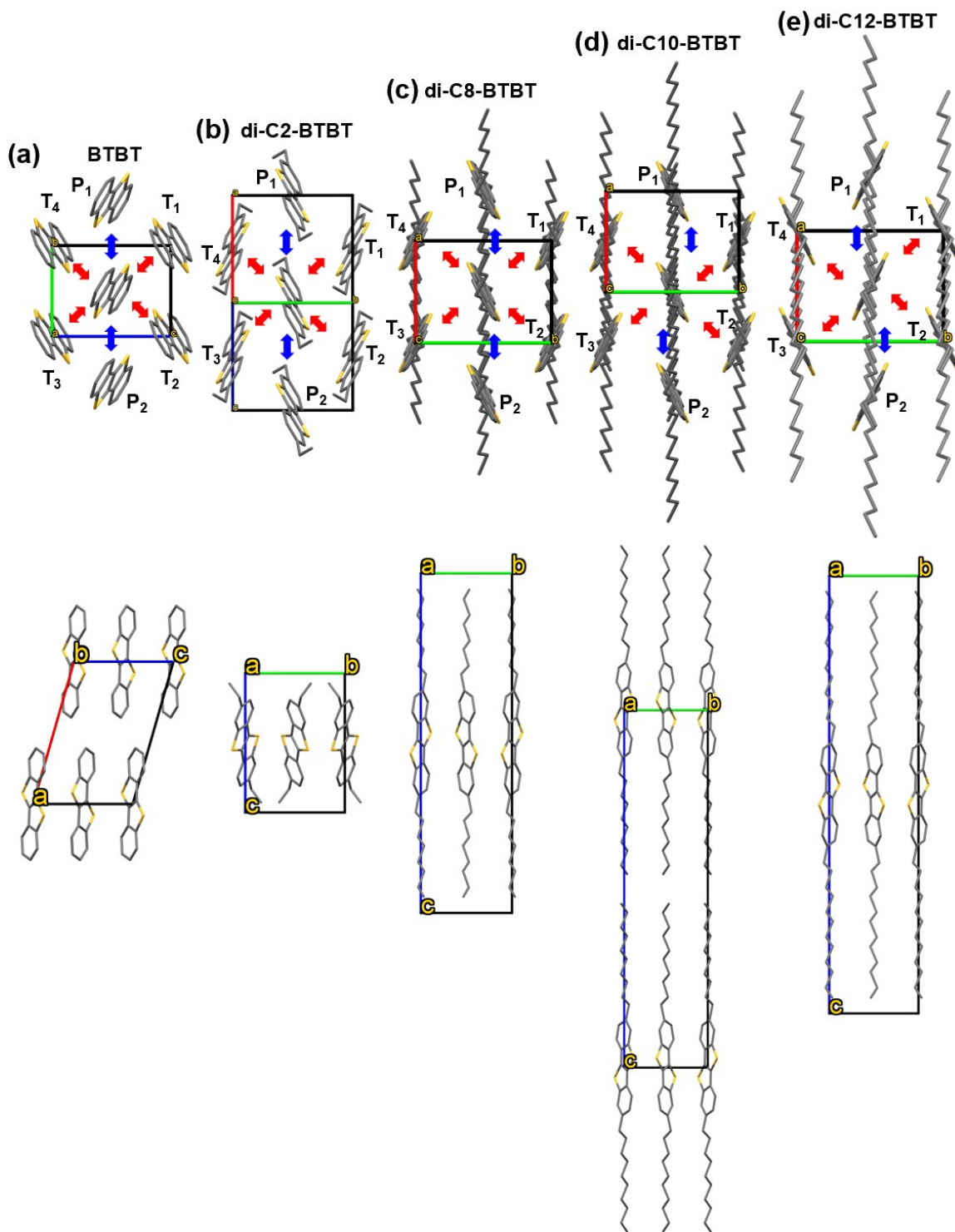
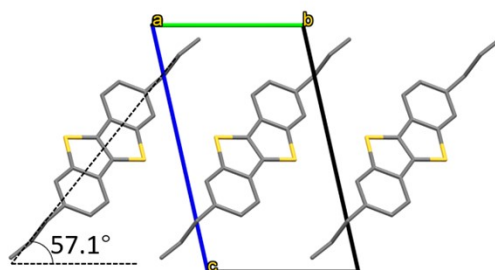
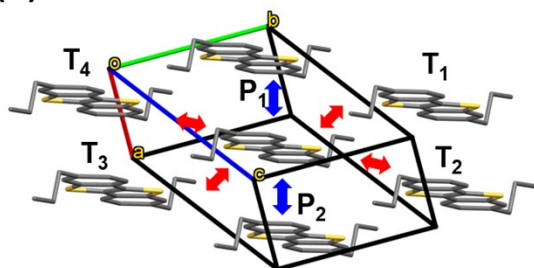
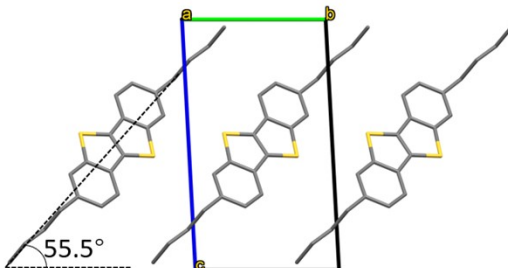
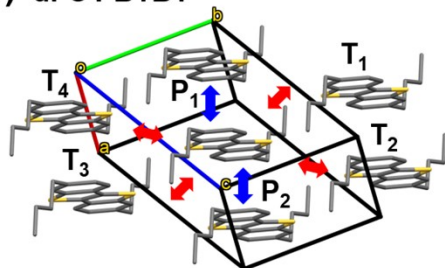


Figure S1. The LHB packing structures of (a) BTBT, (b) di-C2-BTBT, (c) di-C8-BTBT, (d) di-C10-BTBT, and (e) di-C12-BTBT.

(a) di-C3-BTBT



(b) di-C4-BTBT



(c) di-C5-BTBT

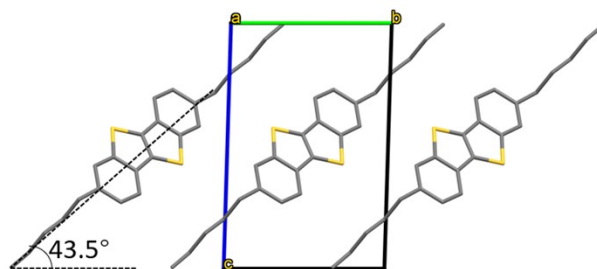
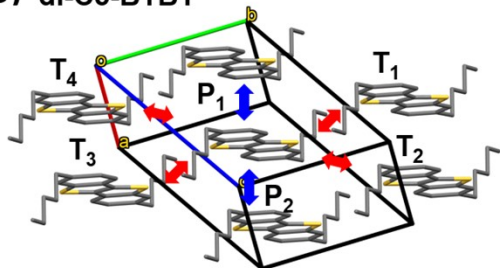


Figure S2. The lamellar packing structures of (a) di-C3-BTBT, (b) di-C4-BTBT, and (c) di-C5-BTBT.

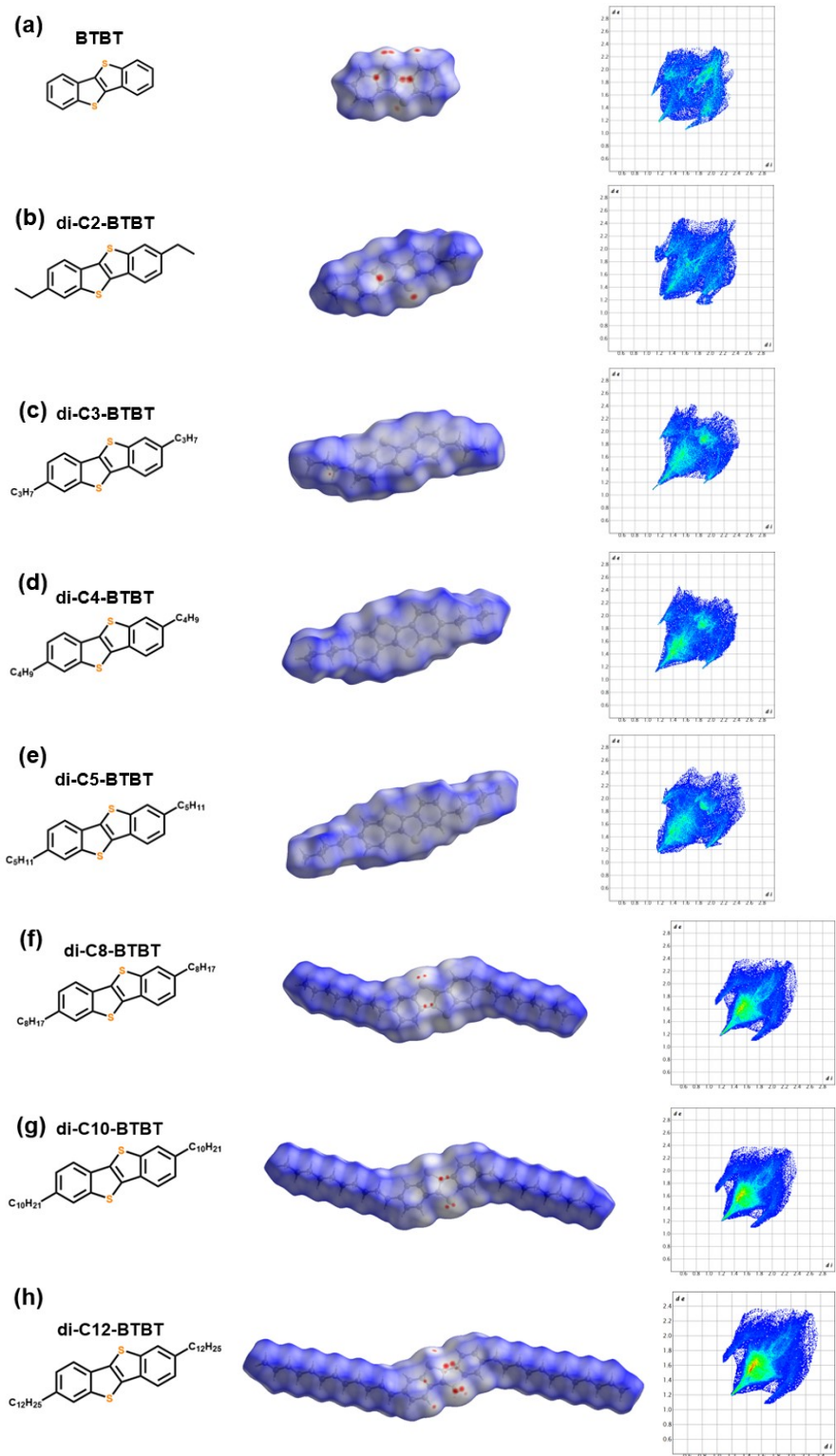


Figure S3. The Hirshfeld surfaces and fingerprint plots of (a) BTBT, (b) di-C2-BTBT, (c) di-C3-BTBT, (d) di-C4-BTBT, (e) di-C5-BTBT, (f) di-C8-BTBT, (g) di-C10-BTBT, and (h) di-C12-BTBT.

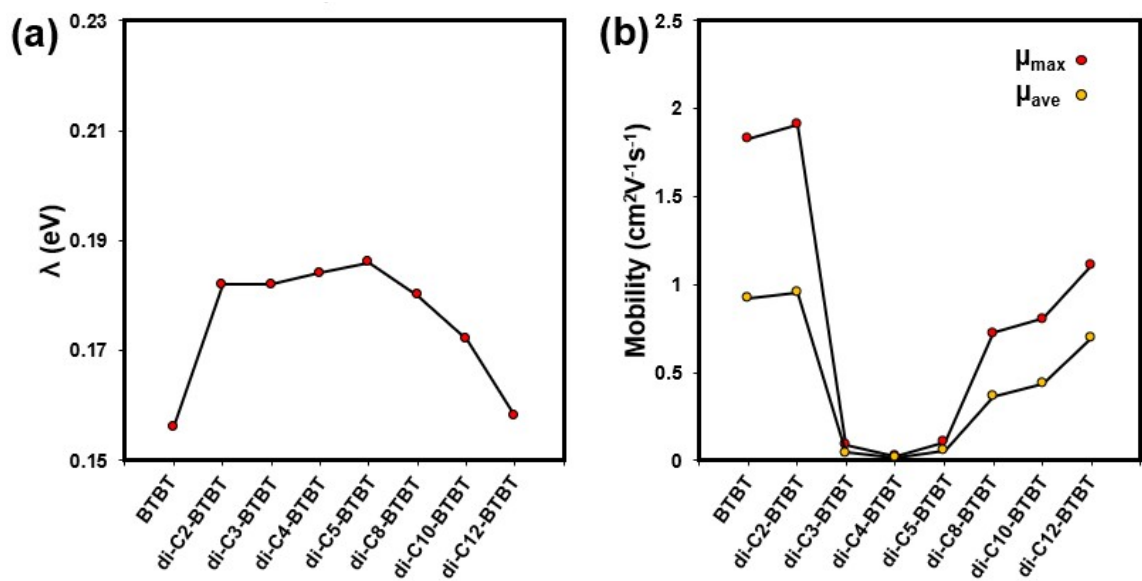


Figure S4. The calculated (a) reorganization energies and (b) maximum and average mobilities of the unsubstituted BTBT and other alkylated BTBTs.

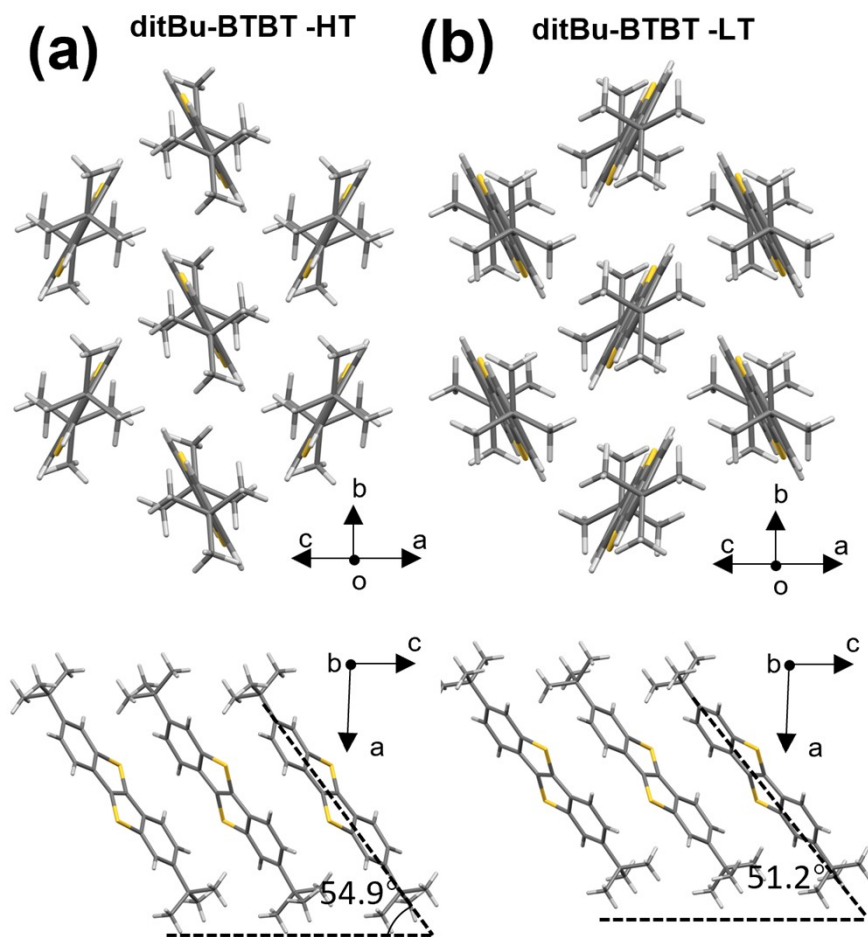


Figure S5. The molecular packing structures of (a) ditBu-BTBT-HT and (b) ditBu-BTBT-LT.

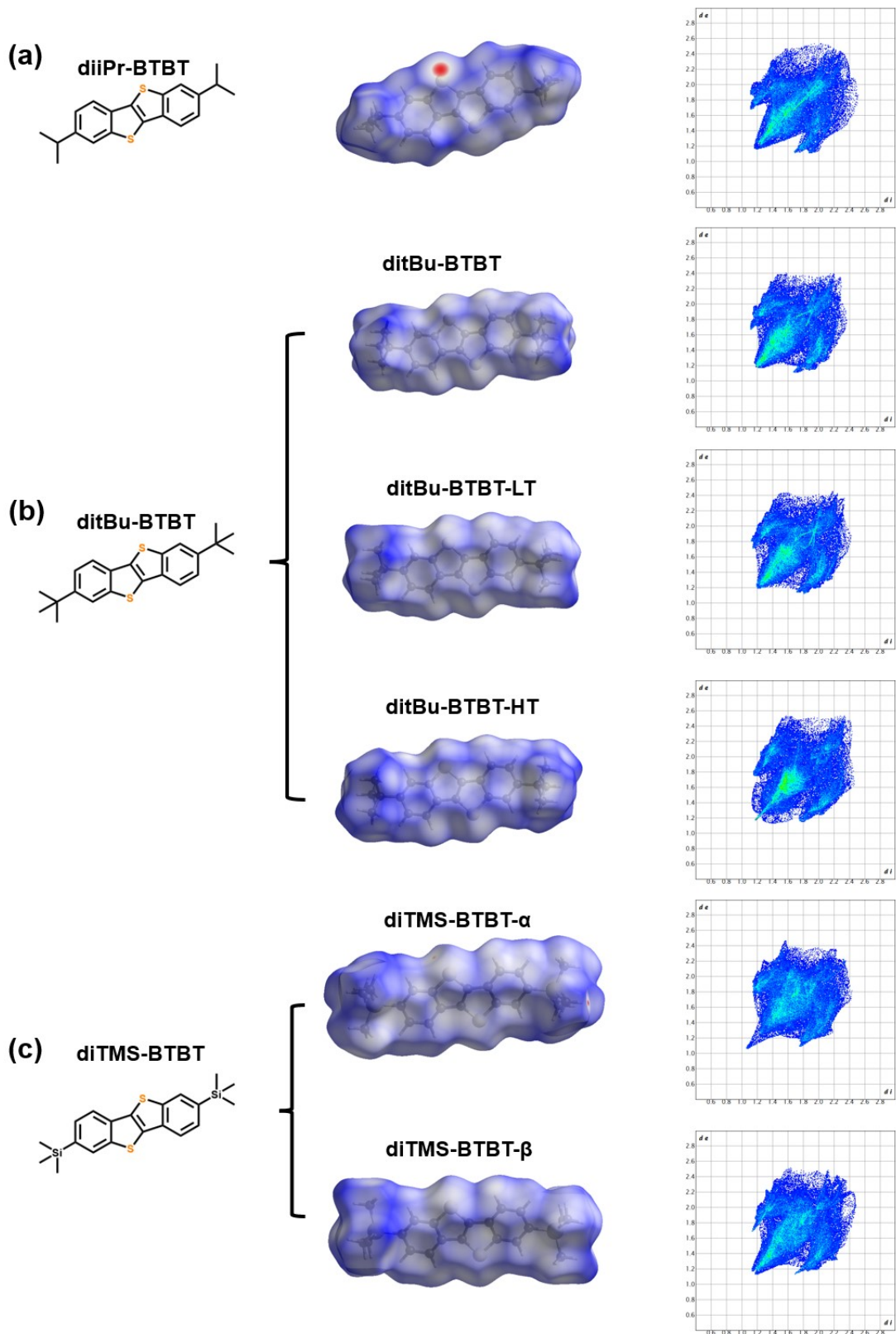


Figure S6. The Hirshfeld surfaces and fingerprint plots of (a) diiPr-BTBT, (b) ditBu-BTBTs (including LT and HT forms), and (c) diTMS-BTBTs (α and β forms).

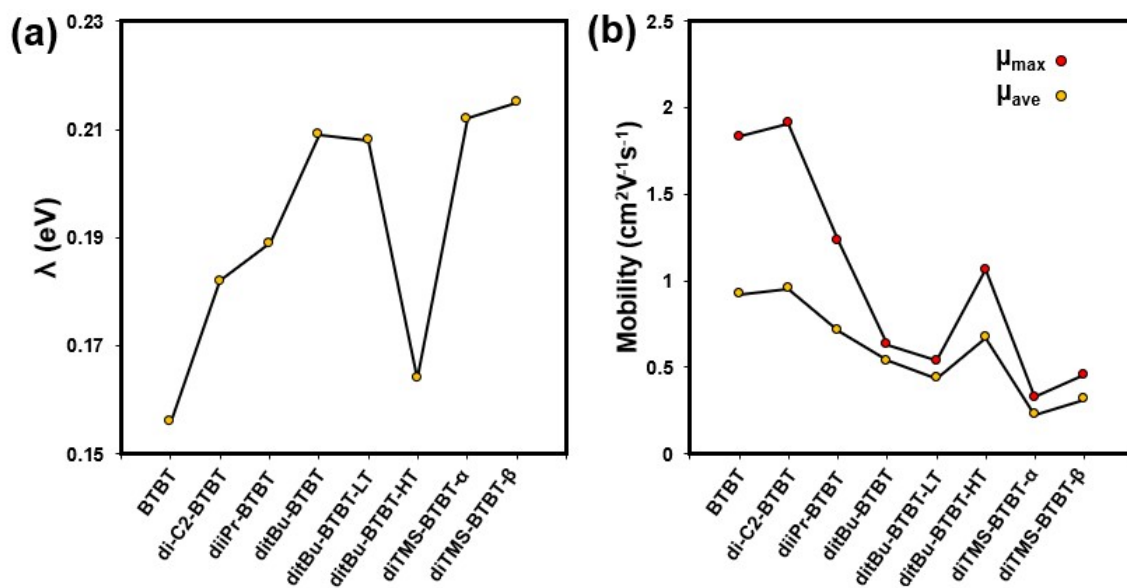


Figure S7. The calculated (a) reorganization energies and (b) maximum and average mobilities of the bulky end-capped BTBTs.

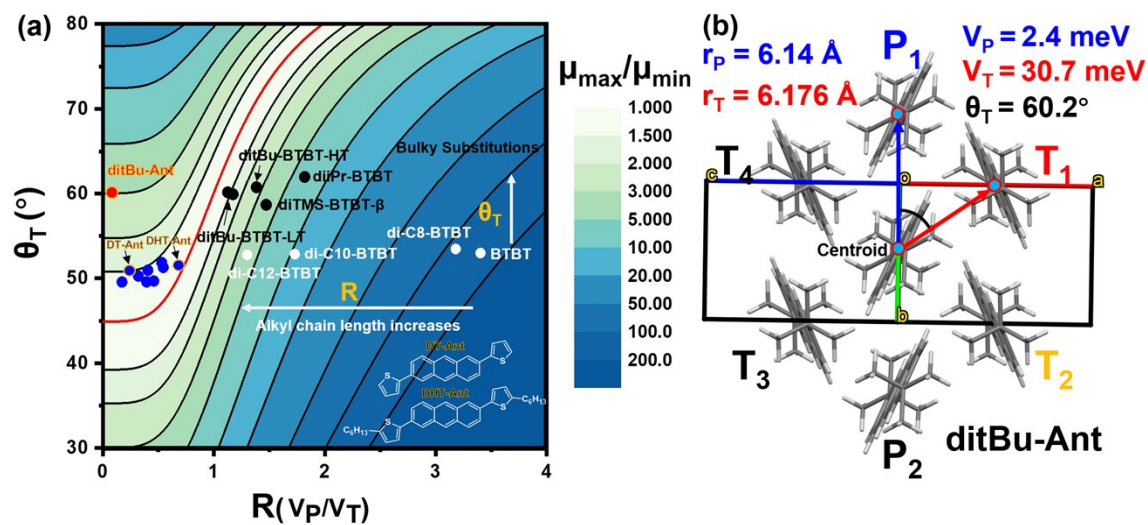


Figure S8. (a) the contour map including the alkyl and bulky end-capped BTBTs and 2,6-Ants; (b) The molecular packing structure and intermolecular transfer integrals of ditBu-Ant.

Theoretical Methodology

In Wen's model, the charge-transfer along a specific transistor channel could be calculated by considering the relative hopping probability of various dimers to the channel, as shown in Figure 1. The transfer mobility $\mu(\varphi)$ can be defined as below:

$$\mu(\varphi) = \sum_i \mu_i \cos^2 \gamma_i \cos^2 (\theta_i - \varphi) \quad (1)$$

where φ is the angle between the transistor channel and the reference axis (P_1 direction in Figure 1), i represents a specific hopping path with individual mobility μ_i , θ_i is the angles of the projected hopping path of dimers relative to the reference axis, and γ_i is the angle between the charge hopping path and the plane of interest.

To further understand the mobility anisotropy in relation to the molecular packing architecture parameters and the electronic coupling, we develop a theoretical model based on the Wen's model, which is specific for predicting the mobility anisotropic ratio (μ_{max}/μ_{min}). In this model, we must simplify the equ. (1) to a lower order, as below:

$$\mu(\varphi) = \sum_i \frac{1}{2} \mu_i \cos^2 \gamma_i [1 + \cos (2\theta_i - 2\varphi)] \quad (2)$$

This equation can be further simplified as:

$$\mu(\varphi) = A \cos 2\varphi + B \sin 2\varphi + C \quad (3)$$

Herein, the factors A , B and C are:

$$A = \frac{1}{2} \sum_i \mu_i \cos^2 \gamma_i \cos 2\theta_i \quad (4)$$

$$B = \frac{1}{2} \sum_i \mu_i \cos^2 \gamma_i \sin 2\theta_i \quad (5)$$

$$C = \frac{1}{2} \sum_i \mu_i \cos^2 \gamma_i \quad (6)$$

Thereby, the analytic functions to determine the maximum and minimum mobilities for any type of OSCs can be derived as:

$$\mu_{max} = C + \sqrt{A^2 + B^2} \quad (7)$$

$$\mu_{min} = C - \sqrt{A^2 + B^2} \quad (8)$$

Based on the above model, the mobility anisotropy ratio (μ_{max}/μ_{min}) can be directly calculated from the molecular packing architecture parameters and the electronic property parameters for any types of OSCs. Meanwhile, the factor A and B are require to approach zero as close as possible if the OSCs would like to achieve low-anisotropy in mobility. Moreover, the mobility anisotropic ratio is strongly depending on the balance of the transfer integral (V) of the nearest neighbour contacts. Unbalanced transfer integrals can

cause an extremely large mobility along a direction with strong electronic coupling, significantly raise the value of factor A or B , and then lead to large anisotropic ratio.

It is worth to mention that the OSCs exhibit the LHB-ISs, which can satisfy a specific condition of $V_{T1} = V_{T2}$, $r_{T1} = r_{T2}$, and $\theta_{T1} = \pi - \theta_{T2}$ (Figure 1). Herein, V_{T1} and V_{T2} represent the transfer integrals between neighbor dimers along the directions of T_1 and T_2 with hopping distances of r_{T1} and r_{T2} , respectively. Under this specific condition, the equivalent hopping paths of T_1 and T_2 can be simplified as T , and the transfer integrals of V_{T1} and V_{T2} and the angles of θ_{T1} and θ_{T2} can also be simplified as V_T and θ_T . In addition, the charge hopping paths are in the plane of interest, indicating that the angle γ_i is equal to 0. Thereby, we only require to consider the charge mobilities of μ_P and μ_T at parallel and transverse directions, which could be derived from V_P , V_T , and θ_T as below:

$$\frac{\mu_P}{\mu_T} = (V_P/V_T)^4 (r_P/r_T)^2 = (R)^4 (2\cos \theta_T)^2 \quad (9)$$

where V_P and V_T are the transfer integrals at the parallel and transverse contacts with hopping distances of r_P and r_T , respectively. R is the ratio between V_P and V_T ($R \equiv V_P/V_T$).

Moreover, the LHB-IS directly causes that the factor B equal to 0. Hence, the factors A , B and C could be simplify as;

$$A = \mu_T [R^4 (2\cos \theta_T)^2 + 2\cos 2\theta_T] \quad (10)$$

$$B = 0 \quad (11)$$

$$C = \mu_T [R^4 (2\cos \theta_T)^2 + 2] \quad (12)$$

A function of $f(R, \theta_T)$ specific for insight evaluating the mobility anisotropic ratio in relation to the transfer integral and the angle θ_T could be derived from eq. (7) and (8) and shown as below:

$$\begin{aligned} \frac{\mu_{max}}{\mu_{min}} &= \frac{C + |A|}{C - |A|} = f(R, \theta_T) \\ &= \frac{R^4 (2\cos \theta_T)^2 + 2 + |R^4 (2\cos \theta_T)^2 + 2\cos 2\theta_T|}{R^4 (2\cos \theta_T)^2 + 2 - |R^4 (2\cos \theta_T)^2 + 2\cos 2\theta_T|} \end{aligned} \quad (13)$$

For calculation of the reorganization energy (λ), adiabatic potential energy surfaces method was applied, which could be described with the following equation,

$$\lambda = (E_0^* - E_0) + (E_+^* - E_+) \quad (14)$$

where E_0 and E_+ represent the energies of the neutral and cationic species in their lowest-energy geometries, respectively; E_0^* is the energy of neutral state with the geometry of the cationic species, and E_+^* is the energy of the cationic state with the geometry of the neutral species. All geometric optimizations and energy evaluations in the process were conducted with Amsterdam

Modeling Suite (AMS) using PW91 functional (GGA:PW91) and the basis set of triple-Z 2 plus polarization functions (TZ2P).

The transfer integral of each dimer (V_i) was calculated from the corresponding spatial overlap (S_{RP}), charge transfer integral (J_{RP}), site energies (H_{RR} , H_{RP}) of the dimer,

$$V_i = \frac{J_{RP} - S_{RP}(H_{RR} + H_{RP})/2}{1 - S_{RP}^2} \quad (15)$$

Assuming that the Kohn-Sham Hamiltonian of the dimer system (h_{ks}) is consists of two monomers. The φ_{HOMO}^{C1} and φ_{HOMO}^{C2} represent the highest occupied molecular orbitals (HOMO) of two monomers. The required essential parameters (S_{RP} , J_{RP} , H_{RR} , and H_{RP}) for the calculation of the transfer integral (V_i) of OSCs can be obtained by

$$J_{RP} = \langle \varphi_{HOMO}^{C1} | h_{ks} | \varphi_{HOMO}^{C2} \rangle$$

$$S_{RP} = \langle \varphi_{HOMO}^{C1} | \varphi_{HOMO}^{C2} \rangle$$

$$H_{RR} = \langle \varphi_{HOMO}^{C1} | h_{ks} | \varphi_{HOMO}^{C1} \rangle \quad (16)$$

$$H_{PP} = \langle \varphi_{HOMO}^{C2} | h_{ks} | \varphi_{HOMO}^{C2} \rangle$$

When the AMS calculation is completed, the corresponding results of the spatial overlap (S_{RP}), charge transfer integral (J_{RP}), site energies (H_{RR} , H_{RP}) and hole transfer integral can be directly obtained in the output file of AMS software.