Supporting Information

Structural and Electronic Origin of Bis-Lactam Based High Performance Organic Thin Film Transistors

Jin Hong Kim,^{†,‡} Min-Woo Choi,^{†,‡} Won Sik Yoon,[†] Sangyoon Oh,[†] Seung Hwa Hong,[†] and Soo Young Park^{*,†}

[†]Center for Supramolecular Optoelectronic Materials, Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Korea.

Keywords: bis-lactam, organic field effect transistor, 2D, NTD, DPP

*Corresponding author: parksy@snu.ac.kr



Figure S1. DSC scans of (a) C8-NTDT and (b) C8-DPPT recorded at heating and cooling rates of 5 $^{\circ}$ C min⁻¹



Figure S2. (a) Molecular structure of isoDPPTMe. (b) 2D fingerprint plot for isoDPPTMe and (c) the corresponding Hirshfeld surface.

Discussion

We carried out the Hirshfeld surface and corresponding 2D fingerprint plot calculation based on the reported isoDPPTMe crystal information.^[SR1] The strong C-H····O=C intermolecular interactions that were not present in linear alkylated DPPT derivatives are also found in isoDPPTMe. Since the methyl units of isoDPPTMe participate in the C-H··· π intermolecular interactions, we could expect the C-H···O=C intermolecular interactions along the lateral direction of face-to-face stacking direction in linear alkyl substitued isoDPPT derivatives.



Figure S3. 2D fingerprint plots with the C-H $\cdots\pi$ intermolecular interactions highlighted in color for (a) C8-NTDT and for (c) C8-DPPT. Corresponding Hirshfeld surfaces with neighboring molecules for (b) C8-NTDT and for (d) C8-DPPT.



Figure S4. 2D-GIXD patterns of (a) C8-NTDT and (b) C8-DPPT thin films. The reflection columns are illustrated as red dotted line.



Figure S5. AFM and OM images of the thin films: for C8-NTDT at (a,f) RT, (b,g) 50 °C, (c,h) 70 °C, (d,i) 90 °C, and (e,j) 110 °C, respectively; for C8-DPPT at (k,p) RT, (l,q) 50 °C, (m,r) 70 °C, (n,s) 90 °C, and (o,t) 110 °C, respectively. Scale bar for AFM and OM images are 2 μ m and 20 μ m, respectively.



Figure S6. Substrate temperature dependent out of plane XRD of (a) C8-NTDT and (b) C8-DPPT. Powder XRD simulations from single crystal structure are shown as black line.



Figure S7. AFM images and corresponding thickness profiles along the dashed line: for C8-NTDT with nominally (a,f) 1 nm, (b,g) 3 nm, (c,h) 5 nm, (d,i) 7 nm, and (e,j) 9 nm thick films, respectively; for C8-DPPT with nominally (k,p) 1 nm, (l,q) 3 nm, (m,r) 5 nm, (n,s) 7 nm, and (o,t) 9 nm thick films, respectively.



Figure S8. (a) The highest occupied molecular orbitals (HOMO) of C8-NTDT. (b) Plot of the bond length change between neutral (d_n) and cationic (d_c) structure of C8-NTDT. (c) HOMO of C8-DPPT. (d) Plot of the bond length change between neutral and cationic structure of C8-DPPT. Note that creating a hole results increase of bonding character and decrease of antibonding character in bonds.



Figure S9. (a) Molecular structure of C8-BTBT. (b) Calculated angular dependent hole mobility. The reorganization energy for hole charge carrier is calculated to 248.9 meV in B3LYP/6-311 (d,p) DFT level. The transfer integral values for the t1 and t2(3) pairs are calculated to 42.9 meV and 12.9 meV in PW91/TZP DFT level, respectively.



Figure S10. Huang-Rhys factors related to hole transfer for (a) C8-NTDT and (b) C8-DPPT.



Figure S11. Transfer curves of typical device (a) stored in air and (b) stored in glove box.

The average mobility of the samples stored in the air was reduced from $0.58 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ to $0.16 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in one day, while the sample stored in the glove box showed almost same mobility over 1 year (Pristine : $0.89 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, after 380 days : $0.77 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$).



Figure S12. (a) Optical microscopy (OM), (b) AFM morphology, and (c) AFM phase images of spin-coated C8-NTDT film after annealing at 140 °C. Scale bar for OM and AFM images are 10 μ m and 2 μ m, respectively.



Figure S13. OFET characteristics of spin-coated C8-NTDT annealed at 140 °C. (a) A typical transfer curve, (b) output curves, and (c) the mobility distribution of 10 devices.

Table S1. Lattice parameters from single crystal and in-plane lattice parameters from thin filmfor C8-NTDT and C8-DPPT.

		a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
C8-NTDT	Single crystal	16.00	5.67	17.52	90.00	111.92	90.00
	Thin film		5.56	17.70	90.68		
C8-DPPT	Single crystal	16.73	5.26	15.68	90.00	90.65	90
	Thin film		5.25	15.94	86.47		

	Bond	$d_n({\rm \AA})^{a}$	$d_c ({ m \AA})^{b}$	$\Delta \mathbf{d_n} \cdot \mathbf{d_c} (\mathbf{\mathring{A}})$
	C1-C2	1.3999	1.4348	0.0349
	C4-C5	1.4556	1.4284	0.0272
<	C5-C6	1.3837	1.4030	0.0193
5	C6-C8	1.4131	1.3961	0.0170
~ >	C2-C3	1.4127	1.3968	0.0159
S - C N1 C 01	C4-C5	1.4641	1.4790	0.0149
0 N C2 C3 C4 C5 S1 C6 C7	C3-C4	1.3751	1.3890	0.0139
	N1-C1	1.3908	1.3775	0.0133
>	C7-C8	1.3693	1.3823	0.0130
>	S1-C8	1.7254	1.7134	0.0120
	O1-C9	1.2302	1.2195	0.0107
	N1-C10	1.4758	1.4862	0.0104
	S1-C5	1.7581	1.7633	0.0052
	N1-C9	1.3983	1.4021	0.0038

Table S2. Bond lengths for neutral and cationic structure of C8-NTDT core unit and their absolute bond length changes. Average bond length change is 0.015 Å.

 ${}^{a}d_{n}$: bond length of neutral structure. ${}^{b}d_{c}$: bond length of cationic structure

	Bond	$d_n({\rm \AA})^{a}$	$d_c(\text{\AA})^b$	$\Delta \left \mathbf{d_n} \cdot \mathbf{d_c} \right (\mathbf{\mathring{A}})$
	C3-C4	1.39411	1.43885	0.04474
1	C2-C3	1.42061	1.38064	0.03997
λ	N1-C4	1.39263	1.36673	0.02590
ζ	C4-C5	1.44229	1.41964	0.02265
CS No	C1-C2	1.44403	1.45886	0.01483
	C5-C6	1.38619	1.40061	0.01442
C3 S1-C8	01-C1	1.22329	1.20975	0.01354
λ	C6-C7	1.41308	1.40024	0.01284
ζ	S1-C8	1.72511	1.71291	0.01220
/	N1-C9	1.46107	1.47246	0.01139
	C7-C8	1.36805	1.37729	0.00924
	N1-C1	1.43469	1.44252	0.00783
	S1-C5	1.76169	1.76458	0.00289

Table S3. Bond lengths for neutral and cationic structure of C8-DPPT core unit and their absolute bond length changes. Average bond length change is 0.018 Å.

 ${}^{a}d_{n}$: bond length of neutral structure. ${}^{b}d_{c}$: bond length of cationic structure

Compound	Dimer pair	V (meV)	λ (meV)	$\mu_{cal} ({\rm cm}^2{\rm V}^{-1}{\rm s}^{-1})$	
	t1	91.3	220	0.01 ~ 1.64	
C8-NTDT	t2(3)	17.7	238		
	t1	26.1	250	2.6×10 ⁻⁵ ~	
C8-DPP1	t2(3)	0.3	352	3.3×10 ⁻²	
со ртрт	t1	42.9	240	1.010-3 0.22	
C9-B1B1	t2(3)	12.9	249	$1.6 \times 10^{-2} \sim 0.55$	

Table S4. Theoretically calculated parameters for the C8-NTDT, C8-DPPT and C8-BTBT.

T_{sub} (°C) ^a	$\mu_{\rm avg} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})^{ {\rm b}}$	$\mu_{\rm max} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})^{\rm c}$	Ion/Ioff
RT	0.09 ± 0.03	0.14	10 ⁷
50	0.11 ± 0.03	0.18	10 ⁷
100	0.19 ± 0.09	0.43	107
120	0.37 ± 0.09	0.54	107
140	0.82 ± 0.13	1.10	10 ⁷

 Table S5. OFET characteristics of the C8-NTDT based on spin-coating process

^{a)} T_{ann} : annealing temperature, ^{b)}Average mobility, ^{c)}Maximum mobility

References

[SR1] Lu, S.; Drees, M.; Yao, Y.; Boudinet, D.; Yan, H.; Pan, H.; Wang, J.; Li, Y.; Usta, H.; Facchetti, A. 3,6-Dithiophen-2-yl-diketopyrrolo[3,2-b]pyrrole (isoDPPT) as an Acceptor Building Block for Organic Opto-Electronics. Macromolecules 2013, 46, 3895-3906.