Electronic Supplementary Information

for

Phenyl- versus cyclohexyl-terminated substituents: Comparative study on aggregated structures and electron-transport properties in n-type organic semiconductors

Shohei Kumagai, [a,b]* Takeru Koguma, [b] Yutaro Arai, [c] Go Watanabe, [d,e] Hiroyuki Ishii, [f] Jun Takeya,[b,c] Toshihiro Okamoto [a,b,c]*

[a] *Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8502, Japan. E-mail: kumagai.s.am@m.titech.ac.jp; tokamoto@cap.mac.titech.ac.jp*

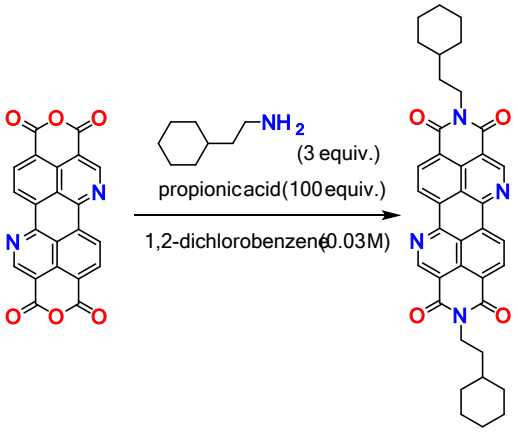
[b] *Material Innovation Research Center (MIRC) and Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan*

[c] *Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[d] *Department of Data Science, School of Frontier Engineering, Kitasato University, 1-15-1 Kitazato, Minami-ku, Sagamihara, Kanagawa 252-0373, Japan*

[e] *Kanagawa Institute of Industrial Science and Technology (KISTEC), 705-1 Shimoimaizumi, Ebina, Kanagawa 243-0435, Japan*

[f] *Department of Applied Physics, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan*



Scheme S1. Synthetic scheme for $ChxC_2$−BQQDI.

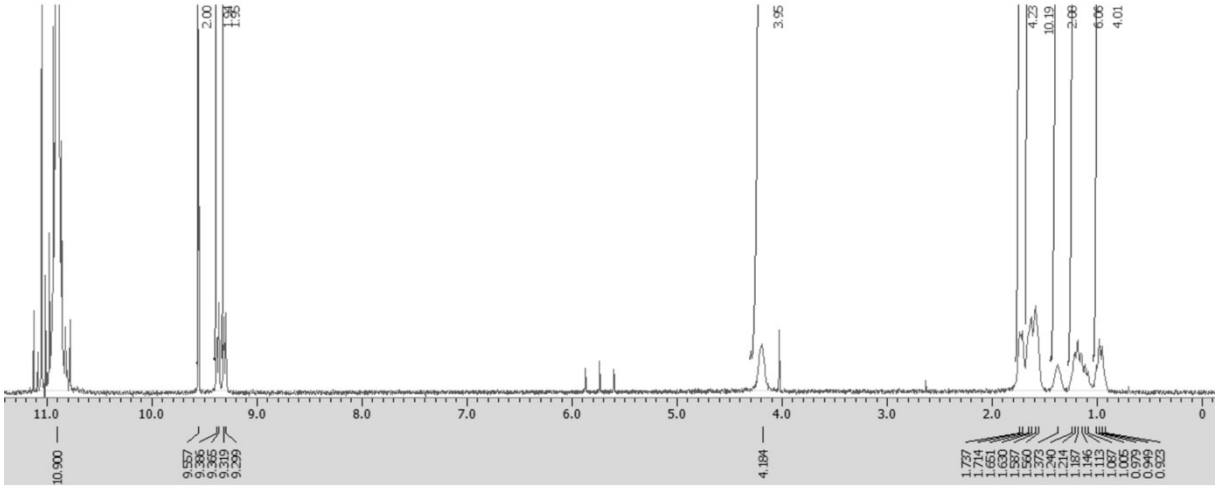


Figure S1. ^1H NMR spectrum of $ChxC_2$−BQQDI (400 MHz, D_2SO_4, 25 °C)

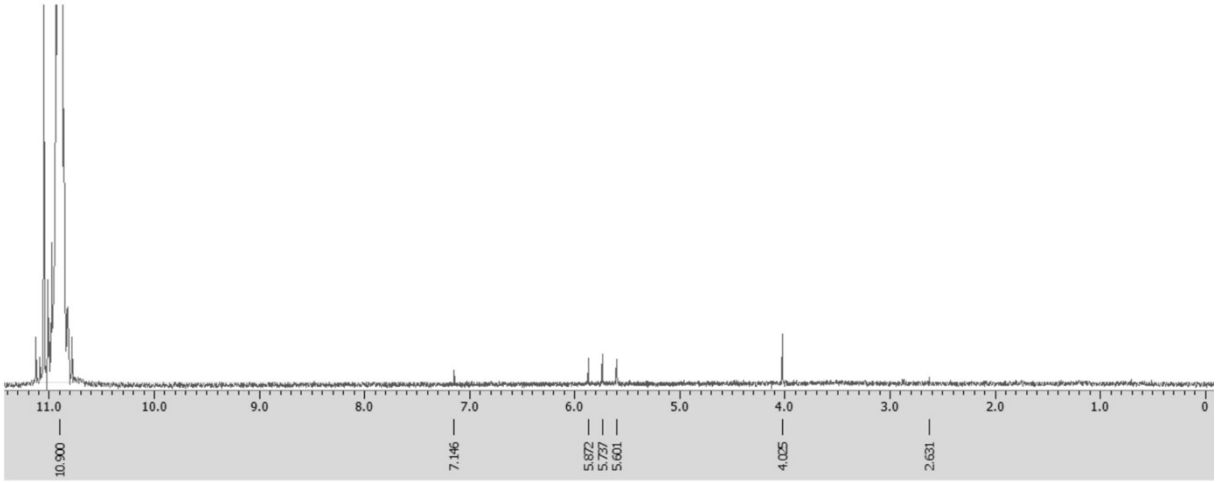


Figure S2. ^1H NMR spectrum of D_2SO_4 (400 MHz, 25 °C)

Table S1. X-ray crystallographic data.

Compound	$ChxC_2$−BQQDI [a]	PhC_2−BQQDI [S1]
Radiation type	Cu*K*α	Cu*K*α
Wavelength / Å	1.54187	1.54187
Formula	$C_{38}H_{36}N_4O_4$	$C_{38}H_{24}N_4O_4$
Formula mass	612.71	600.61
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
CCDC No.	2232687	1938483
Crystal size / mm^3	0.460×0.054×0.005	0.700×0.047×0.005
a / Å	4.9724(2)	7.7048(2)
b / Å	7.7301(3)	5.02249(15)
c / Å	38.8902(15)	35.8104(11)
β / °	90.514(6)	92.467(7)
V / $Å^3$	1494.77(10)	1384.48(7)
Z	2	2
T / K	295	296
μ / mm^{-1}	0.716	0.771
ρ_{calcd} / g cm^{-3}	1.361	1.441
F(000)	648	624
GOF on F^2	1.044	1.105
R_1, wR_2 [$I>2\sigma(I)$]	0.0847, 0.1123	0.443, 0.549
R_1, wR_2 [all data]	0.2171, 0.2428	0.1229,0.1297
Reflns. measured	2718	2522
θ range for data collection / °	4.548– 67.687	4.945−67.687
R_{int}	0.1016	0.0289

$R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$

[a] $w = 1 / [s^2(F_o^2) + (0.1530P)^2 + 0.2104P]$, where $P = (F_o^2 + 2F_c^2) / 3$

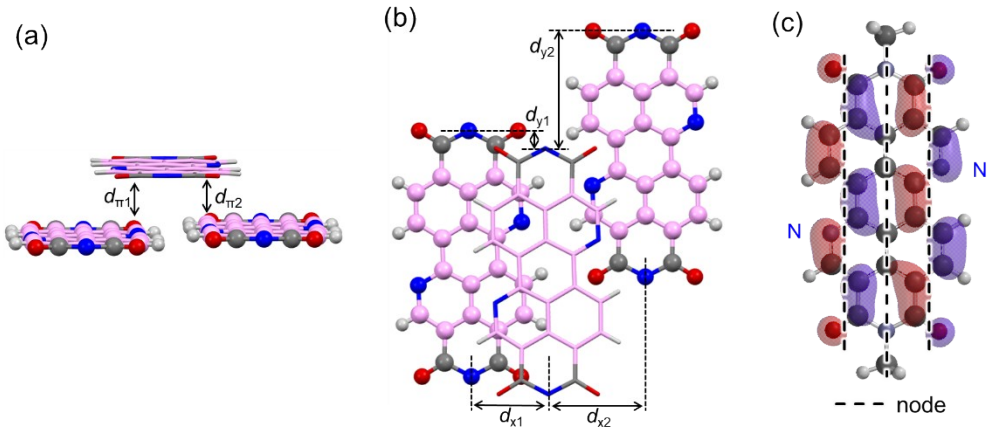


Figure S3 (a, b) Definition of d_x, d_y and d_π. C atoms in the BQQ moiety are colored by pink. (c) LUMO of methyl-substituted BQQDI calculated at the B3LYP/6-31+G(d) level of DFT.

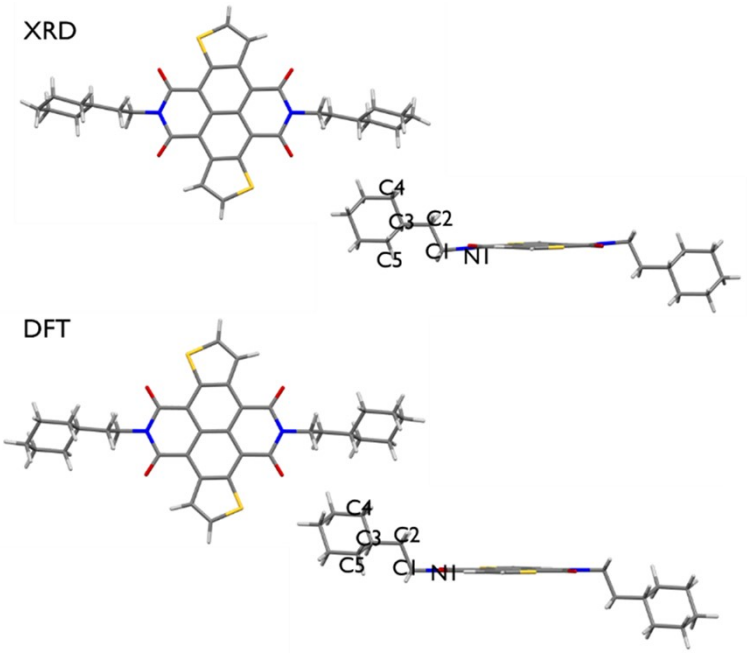


Figure S4 Single molecular geometries of *N*,*N*′-bis(2-cyclohexylethyl)naphtho[2,3-*b*:6,7-*b*′]dithiophene-4,5,9,10-tetracarboxylic acid diimide.[S2]

Table S2. Summary of bond and torsion angles of *N*,*N*′-bis(2-cyclohexylethyl)naphtho[2,3-*b*:6,7-*b*′]dithiophene-4,5,9,10-tetracarboxylic acid diimide.

	XRD	DFT
Bond angle ∠(N1-C1-C2) (°)	111.1	112.1
Bond angle ∠(C1-C2-C3) (°)	116.1	113.7
Torsion angle ∠(N1-C1-C2-C3) (°)	11.4	4.7
Torsion angle ∠(C1-C2-C3-C4) (°)	1.6	10.0
Torsion angle ∠(C1-C2-C3-C5) (°)	44.1	66.1

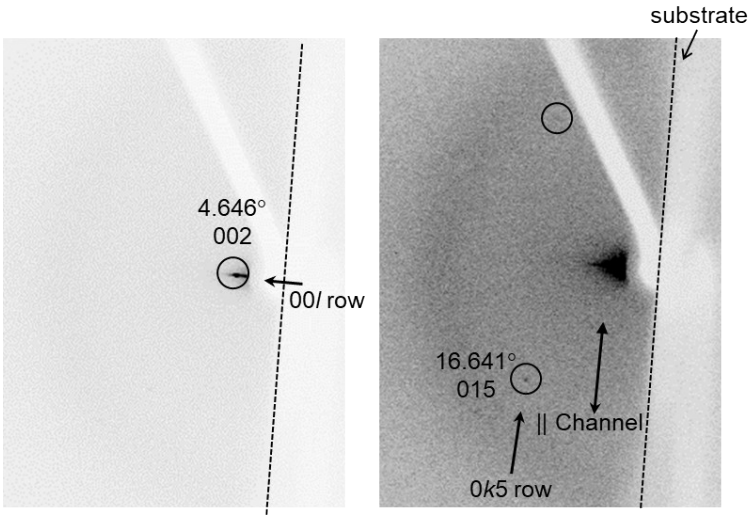


Figure S5 X-ray diffraction images of the single-crystal $ChxC_2$–BQQDI OTFT. X-ray was irradiated nearly parallel to the substrate. Two images are the same data shown by different contrasts.

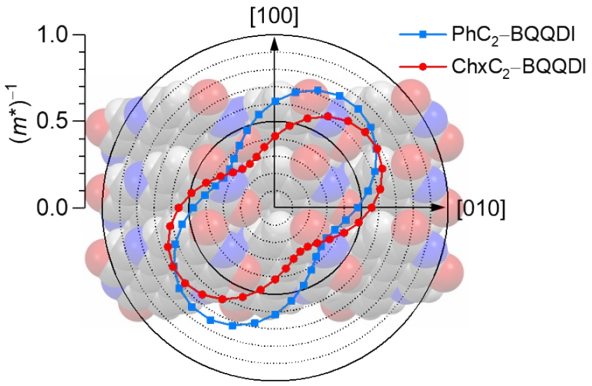


Figure S6 Azimuthal plot of the inverse of effective mass of electrons $(m^*)^{-1}$ in the *ab* plane. Image behind the plot shows the corresponding packing structure of $ChxC_2$–BQQDI (2-cyclohexylethyl substituents are omitted for clarity).

Table S3. Initial parameters for MD simulations.

Compound	$ChxC_2$–BQQDI	PhC_2–BQQDI
Num. of molecules	600	600
Temperature (K)	295	296
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (nm)	4.9724	7.7048
b (nm)	7.7301	5.0225
c (nm)	11.6671	10.7431
α (°)	90	90
β (°)	90.51	92.47
γ (°)	90	90

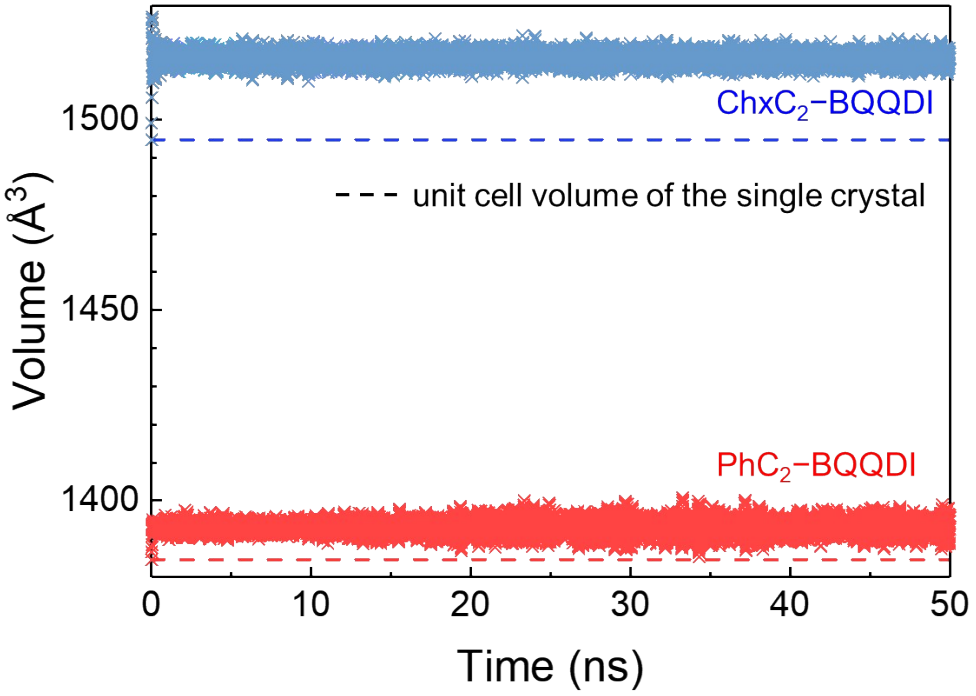


Figure S7 Time trace of the unit cell volume during the NTP run. The volume is corrected from the 10 × 10 × 3 supercell volume for MD simulations to a reduced cell volume corresponding to the dimensions of single crystal data. The average volume for the last 20 ns of 50 ns MD runs is 1393.0±2.0 and 1516.1±1.6 Å^3 for PhC_2–BQQDI and $ChxC_2$–BQQDI, respectively.

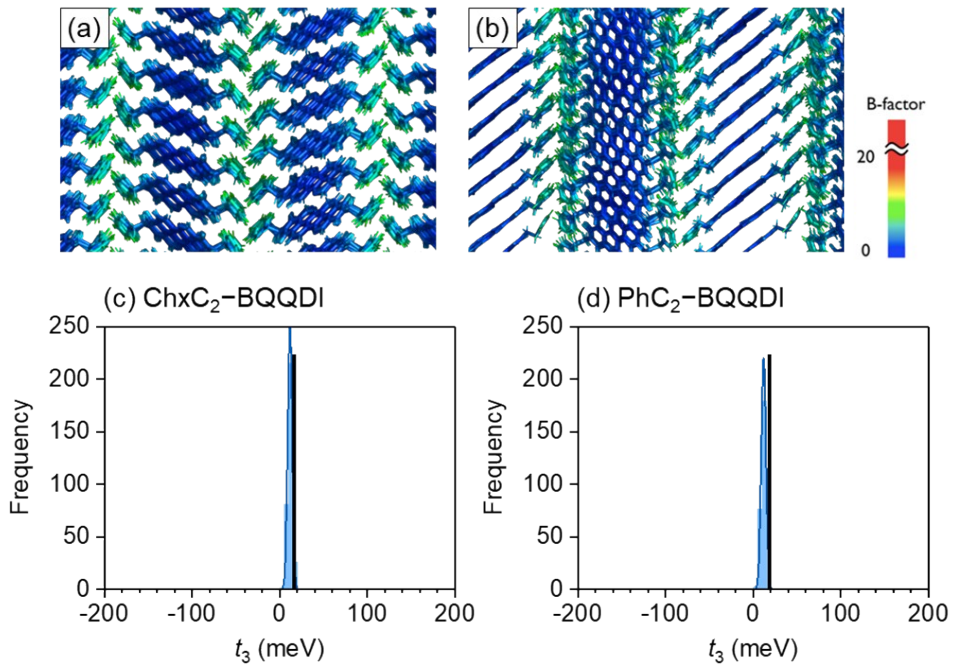


Figure S8 Additional results of MD simulation. (a, b) Color-coded *B*-factor distribution (unit: Å^2) obtained from the trajectory of the crystal structure of PhC_2−BQQDI during the last 10 ns of 100 ns MD runs at 296 K. (c, d) Histogram of t_3 for (c) $ChxC_2$−BQQDI and (d) PhC_2−BQQDI.

Table S4. Summary of transfer integrals based on crystal structure and MD simulation.

	t (meV) [a)]	t_{avg} (meV) [b)]	σ (meV) [b)]	σ/t_{avg}
ChxC_2−BQQDI				
t_1	+82.1	+71.6	27.2	0.38
t_2	+53.8	+37.8	15.3	0.41
t_3	+18.2	+11.6	2.6	0.22
PhC_2−BQQDI				
t_1	+90.7	+82.7	26.4	0.32
t_2	+58.5	+40.8	14.7	0.36
t_3	+18.9	+11.8	2.7	0.23

[a)] Calculated based on the crystallographic data. [b)] Calculated based on MD simulations.

References in the Supplementary Information

S1 T. Okamoto, S. Kumagai, E. Fukuzaki, H. Ishii, G. Watanabe, N. Niitsu, T. Annaka, M. Yamagishi, Y. Tani, H. Sugiura, T. Watanabe, S. Watanabe and J. Takeya, *Sci. Adv.*, 2020, **6**, eaaz0632.

S2 M. Nakano, D. Hashizume and K. Takimiya, *Molecules*, 2016, **21**, 981.