Molecular Mimicry and Assemblies of Asymmetric Organic Semiconductors

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Abstract

Molecular assembly is a crucial factor for charge transports in organic semiconductors (OSCs), and molecularly flexible alkyl chain substitution is a key design feature for achieving desired molecular assemblies. However, the high degree of freedom of alkyl chains leads to molecular fluctuations that are detrimental to OSC performances. Stabilization of alkyl chains via intermolecular interactions in packing structures exists in biological and materials systems, and such a strategy can be harnessed in OSCs to suppress molecular fluctuations. Here, we present a robust synthetic strategy for a series of asymmetric n-type benzo[de]isoquinolino[1,8-gh]quinolinetetracarboxylic diimide (BQQDI) OSCs with various alkyl chain lengths, and certain alkyl chains exhibit an unusual molecular mimicry with energetically favorable gauche conformer that shows isomorphic structures and small molecular fluctuations. Asymmetric n-type OSC with the optimum chain length exhibits satisfactory solubility, excellent electron mobility, and large-area single-crystalline thin films are fabricated for practical organic electronics.

Introduction

Molecularly flexible alkyl chains are of vital importance for controlling molecular assemblies of functional materials and biomolecules from liquid crystals to lipid bilayers. In the area of printable and flexible small-molecule organic semiconductors (OSCs), which self-aggregate via intermolecular interactions, effective molecular assemblies by rational alkyl chain engineering can lead to strong intermolecular orbital overlaps, high charge-carrier mobilities ($\mu$), and band-like charge transports. Another critical role of long alkyl chains is to control solubility and crystallinity of OSCs for solution-processability with common organic solvents and achieve large-area printable electronics. However, one common phenomenon with alkyl chains in functional materials and biological systems is the anti-gauche isomerization at different temperatures due to the relatively small energy difference between these rotamers, and such a thermal disordering causes severe molecular fluctuations in molecular systems. Although these properties may be harnessed for materials applications such as stimuli sensors, molecular fluctuations have been shown to be a detrimental factor for charge-transport properties as they disrupt intermolecular orbital overlaps. Currently, our knowledge on suppressing molecular fluctuations of OSCs from a molecular design point of view has been limited, but in biological systems, certain membrane proteins show stabilization of amino acid sidechains via intermolecular hydrogen bonding interactions, and similar stabilization effect of alkyl chain conformations can also be observed in host-guest materials.
systems\textsuperscript{18–20}. On the basis of these findings, inspirations can be drawn from nature for molecular design of OSCs, where motions of alkyl chains are stabilized by appropriate intermolecular interactions to achieve suppression of molecular fluctuations and such a feature is especially crucial for the molecular design of future high-performance OSCs.

**Fig. 1** General molecular features. 

- **a** Molecular structure and features of BQQDI.
- **b** Molecular assembly and fluctuations of PhC\textsubscript{2}–BQQDI.
- **c** Molecular design of asymmetric PhC\textsubscript{2}–BQQDI–C\textsubscript{n} (C\textsubscript{n}: linear alkyl chains, n-C\textsubscript{n}H\textsubscript{2n+1}).

Herein, we present an effective stabilization of alkyl chains with suppressed molecular fluctuations on electron-transporting n-type OSCs, which are an urgently demanded component for all-organic logic circuits\textsuperscript{21–25} along with high-performance p-type counterparts\textsuperscript{26–32}. Recently, our group developed a benzo[\textit{de}]isoquinino[1,8-\textit{gh}]quinolinetetracarboxylic diimide (BQQDI) \(\pi\)-electron core (\(\pi\)-core) for high-performance n-type OSCs (Fig. 1a)\textsuperscript{33–35}. Though the BQQDI molecular structure bares similarity with the vastly studied perylene diimide (PDI) \(\pi\)-core\textsuperscript{36–38}, the incorporated electronegative nitrogen atoms in BQQDI leads to a deep-lying lowest unoccupied molecular orbital (LUMO) level (Fig. 1a), which offers air-stability in n-type OSC operations without further chemical modifications. Symmetric phenethyl-substituted–BQQDI (PhC\textsubscript{2}–BQQDI) shows four-fold intermolecular hydrogen-bonding interactions and phenyl-to-phenyl interactions in the interlayers of the crystal structure (Fig. 1b). Molecular dynamic (MD) simulations suggest both
intra and interlayer interactions of PhC2–BQQDI suppress molecular fluctuations in the solid-state and ensure consistent molecular orbital overlaps for undisrupted charge transport (Fig. 1b). As a result, PhC2–BQQDI exhibits an outstanding and reliable $\mu_e$ of $3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, the high-performance PhC2–BQQDI exhibits issues of low solubility and difficulties with large-area thin-film fabrications due to the lack of alkyl chains. To further explore the molecular design for high-performance solution-processed OSCs with suppressed molecular fluctuations, we envisage an asymmetric PhC2–BQQDI–C$_n$ ($n = 5, 6, \text{ and } 7$) approach (Fig. 1c), where the favorable phenethyl sidechain is preserved on one side, and the substitution of flexible alkyl chains on the other side of BQQDI may lead to fine-tuning of molecular assemblies. The lack of flexible alkyl chains in PhC2–BQQDI results in low solubility and high temperature is required for solution-processed device fabrication, but the introduction of alkyl chains in current asymmetric PhC2–BQQDI–C$_n$ derivatives show orders of magnitude higher solubility that improves the solution processability of high-performance n-type OSCs. We discover that PhC2–BQQDI–C$_n$ alkyl chains mimic the overall shape of the surrounding phenyl groups by adopting the gauche conformation that is stabilized by multiple CH···π interactions that demonstrate the molecular mimicry assembly, and its alkyl chains surprisingly exhibit a similar degree of molecular fluctuations as the high-performance PhC2–BQQDI with rigid phenyl groups. In particular, the PhC2–BQQDI–C$_5$ derivative exhibits high n-type OSC performances in solution-processed OFETs, and inch-scale single-crystalline thin films are obtained for the fabrication of large-area electronics using the continuous edge-casting method$^{39,40}$ due to its high solution processability.

**Results**

**Synthesis.** Although nature synthesizes asymmetric biomolecules with marvelous efficiencies$^{41}$, it is a challenge for synthetic chemists to prepare asymmetric compounds due to poor selectivity and low yields$^{42}$. In the case of n-type OSCs, several studies on the synthesis of asymmetric PDI have been reported$^{43–45}$. The commonly employed strategy involves sequential imidizations that results in the desired monoimidized product, along with unreacted and difunctionalized species, which are attributed to the high reactivity of primary R–NH$_2$. Owing to the relatively low solubility of PDI, purification of the desired asymmetric compound can be difficult, which leads to poor yields and low purity. Thus, we speculate that similar synthetic strategies for asymmetric PDI may not be applicable to the less-soluble BQQDI, and a more rational and selective method is developed to prepare asymmetric BQQDI. We lower the reactivity of the phenethylamine by functionalizing it with the $p$-methoxybenzyl (PMB)
group (Fig. 2), which is a heat-stable protecting group that can endure imidization reactions at elevated temperatures and eventually be removed by acid.

**Fig. 2 Synthesis of PhC$_2$–BQQDI–C$_n$.** Preparation of PMB-protected phenethylamine, and synthesis of PhC$_2$–BQQDI–C$_n$ ($n= 5, 6,$ and $7$).

Here, we began our synthesis from the previously reported trichlorophenyl formate-containing compound 1 (Fig. 2) as the versatile electron-deficient formate can be readily displaced by alkylamines and purified by column chromatography. The PMB-protected amine was then reacted with compound 1 in refluxed $o$-dichlorobenzene ($o$-DCB) for 40 min to give intermediate 2 in 45% yield. Although the first reaction generated the desired and difunctionalized products, as well as unreacted compound 1 indicated by high-performance liquid chromatography (HPLC), compound 2 was readily isolated by column chromatography. From the key precursor 2, we carried out a highly selective one-pot synthesis to furnish a series of PhC$_2$–BQQDI–C$_n$ ($n= 5, 6,$ and $7$) from intermediate 2 (Fig. 2), as PMB removal and ring-closing steps can be simultaneously facilitated by TfOH, and the one-pot synthesis resulted in excellent yields of 90-92%. One drawback for the high-performance PhC$_2$–BQQDI is the low solubility in common organic solvents due to the lack of flexible alkyl chains, and high temperature ($>150$ $^\circ$C) is required for large-area device fabrications. Current asymmetric PhC$_2$–BQQDI–C$_n$ show more than one order of magnitude higher solubility in $o$-DCB than PhC$_2$–BQQDI (Supplementary Table 1), which indicates high solution-processability.

**Fundamental properties.** The thermal stability of PhC$_2$–BQQDI–C$_n$ compounds was evaluated by thermalgravimetric-differential thermal analysis (TG-DTA), and the crystal phase stability/transition was measured by differential scanning calorimetry (DSC). All PhC$_2$–
BQQDI–Cₙ derivatives showed excellent thermal stability with 5% weight loss temperatures (T₉₅) and decomposition temperatures above 370 °C and 380 °C, respectively (Supplementary Fig. 8). DSC measurements indicated no apparent phase transitions of PhC₂–BQQDI–Cₙ up to 250°C (Supplementary Fig. 9). All PhC₂–BQQDI–Cₙ derivatives exhibited completely reversible reduction waves in cyclic voltammetry (CV) measurements (Supplementary Fig. 10). The length of alkyl chains did not impose noticeable effects in electrochemical properties, as all derivatives showed first half-width reduction waves at –0.68 V that corresponded to the lowest unoccupied molecular orbital (LUMO) \( E_{\text{LUMO}} = -4.12 \text{ eV} \), and the second reduction waves at –1.0 V appeared to be reversible and electrochemically stable. The electrochemical properties of PhC₂–BQQDI–Cₙ indicate a deep-lying LUMO level that is suitable for air-stable n-channel OFET operations.

**Molecular assemblies and charge transport.** We examined the plate-like single crystals of PhC₂–BQQDI–Cₙ grown by means of slow cooling in solutions (Supplementary Table 2), and all derivatives crystallized in the monoclinic system. Within each crystallographic layer, PhC₂–BQQDI–Cₙ derivatives form the 2D brickwork packing motif with vertical \( \pi-\pi \) stacking and lateral hydrogen-bonding interactions (Fig. 3a). To our surprise, the asymmetric molecules did not form the expected phenyl-to-phenyl interlayer interactions shown in PhC₂–BQQDI, instead, PhC₂–BQQDI–Cₙ derivatives demonstrate the *layer-by-layer* molecular assembly where the alkyl chains interact with phenyl groups in the adjacent layer (Fig. 3a). An intriguing finding of PhC₂–BQQDI–Cₙ derivatives is their molecular mimicry assemblies by the alkyl chain conformations. Instead of the expected linear *anti* conformation, PhC₂–BQQDI–C₅ shows a *gauche* conformation at the C2–C3 bond with a torsion angle of –71.4°, and PhC₂–BQQDI–C₆ exhibits *gauche* conformations at C2–C3, and C4–C5 bonds with torsion angles of 69.3° and –4.8°, respectively. By further extending the alkyl chain to \( n = 7 \), such a molecular mimicry is still retained, with torsion angles of –64.1° and 101.1° (Fig. 3a). Though, the long C₇ alkyl chain with the *gauche* conformation likely causes severe thermal disordering compared to other two derivatives. We then performed a torsion angle energy scan at C2–C3 of PhC₂–BQQDI–C₅ (Fig. 3b), and the potential energy profile of the single molecule showed a textbook-like profile, where the most energetically favorable rotamer is the *anti* form, though the *gauche* conformation is merely 0.86 kcal mol⁻¹ higher than that of the *anti* conformation. However, in the crystal structure of PhC₂–BQQDI–C₅, each alkyl chain is surrounded by four phenyl groups, and when this “aromatic pocket” is taken into consideration in the DFT calculation, the *gauche* rotamer becomes the most stable form and the *anti* rotamer is now 25
kcal mol$^{-1}$ higher in energy than the *gauche* due to steric hinderance (Fig. 3c). The stabilization of the molecular mimicry is arguably attributed to the multiple CH⋯π interactions within the aromatic pocket, and the large energy barrier between the *anti* and *gauche* rotamers would make conformational isomerization unlikely at room temperature, and usual alkyl chain molecular fluctuations may be suppressed. The powders of PhC$_2$–BQQDI–C$_5$ are further subjected to temperature-variant powder X-ray diffractions (PXRD) at SPring-8 RIKEN Materials Science Beamline (BL44B2)$^{49,50}$, where the PXRD pattern is the same as its single-crystal structure, and consistent diffraction patterns are observed up to 200 °C, indicating that the intriguing molecular assembly is persistent (Supplementary Fig. 11). The current findings of the molecular mimicry of PhC$_2$–BQQDI–C$_n$ is unique among OSCs including the asymmetric benzothieno-[3,2-b][1]benzothiophene (Ph–BTBT–C$_n$) derivatives reported by Hasegawa and Hanna groups$^{51,52}$, where alkyl substituents are found to adopt the expected linear *anti* conformations.
Fig. 3 Molecular assemblies and alkyl chain conformations. a Packing structures and interlayer interactions of PhC2–BQQDI–Cₙ. b–c Torsion angle energy scans (C2–C3, starting from −71.4°) of PhC2–BQQDI–C₅ monomer and pentamer (structures from the single crystal) at the B3LYP/6-31G+(d) level of theory.

Besides the intriguing interlayer assemblies, we investigated the charge-transport capabilities of PhC2–BQQDI–Cₙ. Multi-fold hydrogen-bonding interactions with force constants in the range of −6.72 to −7.45 kJ mol⁻¹ were suggested by our calculations between the BQQDI π-cores in PhC2–BQQDI–Cₙ crystals, and four other vertical π-π interactions are present in the 2D brickwork packing motif. To quantify the degree of LUMO overlap within the brickwork motif of PhC2–BQQDI–Cₙ, the t values (t₁,₂, t₂,₅, t₃,₆) were calculated at the PBEPBE/6-31G(d) level of theory (Fig. 4a). The vertical π-π interactions of PhC2–BQQDI–Cₙ
exhibit large $t_{1,4}$ and $t_{2,5}$ values with $t_{2,5}$ values being larger than those of $t_{1,4}$, which suggests slightly anisotropic charge-transport properties. The hydrogen-bonding interactions in the transverse direction also result in effective LUMO overlaps with positive $t_{3,6}$ values ranging from $+17.3$ to $+18.1$ meV. With the tight-binding approximation, effective mass for electron carriers ($m^*$) of PhC$_2$–BQQDI–C$_n$ are estimated from the bottom edge of their LUMO band dispersions, and by plotting the inversed $m^*$ with respect to the crystal axes, the anisotropic charge transport of PhC$_2$–BQQDI–C$_n$ derivatives is clearly visualized by the peanut-like shapes (Fig. 4b–c). Nevertheless, the minimum $m^*$ of PhC$_2$–BQQDI–C$_n$ are estimated to be 1.4–1.5, which are promising for achieving high $\mu_e$ in OFETs.

|          | $t_{1,4}$ | $t_{3,6}$ | $t_{2,5}$ |
|----------|-----------|-----------|-----------|
| PhC$_2$–BQQDI–C$_4$ | $+53.2$ meV | $+81.1$ meV | $+18.1$ meV |
| PhC$_2$–BQQDI–C$_6$ | $+55.4$ meV | $+83.8$ meV | $+17.3$ meV |
| PhC$_2$–BQQDI–C$_7$ | $+54.7$ meV | $+85.6$ meV | $+17.9$ meV |

Fig. 4 Charge-transport capability of PhC$_2$–BQQDI–C$_n$. a Transfer integral ($t$) in the 2D brickwork packing motif calculated at the PBEPBE/6-31G(d) level of theory. b–c Effective mass and angle-dependent inversed effective mass (relative to crystallography axes) by the tight-binding approximation, respectively.

Molecular fluctuations. The detrimental effect of molecular fluctuations or dynamic disorder of OSCs on charge transport has been studied in recent years$^{11–15}$, here, we intend to explore the interlayer interactions and molecular fluctuations of PhC$_2$–BQQDI–C$_n$ using MD simulations, with constant number of molecules (N), temperature (T) and pressure (P) (isothermal-isobaric, NTP ensemble). In the previous study, we have demonstrated small molecular fluctuations of PhC$_2$–BQQDI (Fig. 1b) attributed by strong intralayer $\pi$-core and
interlayer phenyl-to-phenyl interactions. Surprisingly, despite having the molecularly flexible alkyl group, the interlayer chains of asymmetric PhC$_2$–BQQDI–C$_5$ also show similarly small degree of molecular fluctuations (small B-factors) as PhC$_2$–BQQDI (Fig. 5a), which is possibly due to the stabilization effect on the molecular mimicry by the “aromatic pocket” (Fig. 3d), and the $\pi$-core of PhC$_2$–BQQDI–C$_5$ also shows small degree of fluctuations. Based on this result, we argue that the alkyl chain PhC$_2$–BQQDI–C$_5$ does not behave as an ordinary flexible alkyl chain, but it rather mimics a structurally rigid phenyl group, which leads to suppressed molecular fluctuations. Similarly, PhC$_2$–BQQDI–C$_6$ also exhibits small amplitude of molecular fluctuations in the $\pi$-cores, but the alkyl chains show noticeably large B-factors and destabilization of the molecular mimicry conformation (Fig. 5b). The thermally disordered PhC$_2$–BQQDI–C$_7$ expectedly demonstrates large degree of molecular fluctuations in the alkyl chains and the molecular mimicry in the single-crystal structure is no longer retained during the MD simulations (Fig. 5c). In addition, the $\pi$-cores of PhC$_2$–BQQDI–C$_7$ show larger amplitudes of molecular fluctuations which could potentially affect the charge-transport capability.

**Fig. 5 Molecular fluctuations by MD simulations.** a–c Color-coded B-factor ($\AA^2$ s$^{-1}$) distribution of PhC$_2$–BQQDI–C$_n$ ($n=5, 6, and 7$) obtained from the trajectories during the last 10 ns of a 100 ns MD simulations in the NTP ensemble and variant transfer integrals ($t_1$ and $t_3$) at 100 ns of the MD simulations. d–f Variant $t$ value distributions and standard deviations ($\sigma$) revealing the magnitude of the dynamic fluctuations.
We calculated the variant $t$ values to understand the effect of molecular fluctuations on charge transport in the $\pi-\pi$ stacking directions of PhC$_2$–BQQDI–C$_n$ based on the MD simulations. PhC$_2$–BQQDI–C$_5$ exhibits the smallest standard deviations ($\sigma$) of 23.0 meV and 13.2 meV in the $t_1$ and $t_3$ directions, respectively (Fig. 5d), which suggests that the charge-transport capability of PhC$_2$–BQQDI–C$_5$ does not appear to be affected by molecular fluctuations. The $\sigma$ values of PhC$_2$–BQQDI–C$_5$ are in fact lower than the high-performance PhC$_2$–BQQDI (13.9 meV and 24.2 meV)$^{33}$ in their respective directions, which further demonstrates the effectiveness of molecular mimicry in suppressing molecular fluctuations. On the other hand, PhC$_2$–BQQDI–C$_n$ ($n = 6$ and 7) result in large $\sigma$ of $t$ values compared to PhC$_2$–BQQDI–C$_5$ due to their molecular fluctuations (Fig. 5e–f), which suggests potentially compromised charge-transport capabilities. In addition, it has been reported that the ratio of $\sigma$ and averaged $t$ values ($\sigma/t_{Avg.}$) quantifies the effect of molecular fluctuations on charge transport$^{55}$, and PhC$_2$–BQQDI–C$_5$ shows the smallest $\sigma/t_{Avg.}$ in both $t_1$ and $t_3$ directions (0.30 and 0.40) (Fig. 5d) among current derivatives, indicating its promising OSC performances.

**Device performances.** To evaluate n-type OSC performances of PhC$_2$–BQQDI–C$_n$ ($n = 5, 6,$ and 7) under ambient conditions, we fabricated bottom-gate/top-contact single-crystalline thin-film OFETs via the edge-casting method$^{53}$. We have confirmed that the single-crystalline thin films of all three PhC$_2$–BQQDI–C$_n$ are consistent with their bulk single crystal structures to correlate their estimated charge-transport capabilities and device performances (Supplementary Fig. 12–14). PhC$_2$–BQQDI–C$_5$ with the molecular mimicry demonstrates excellent single-crystalline thin films (Fig. 6a) and the best OFET behavior demonstrating textbook-like transfer and output characteristics with a high $\mu_e$ of 1.4 cm$^2$ V$^{-1}$ s$^{-1}$ and a reliability factor ($r$)$^{54}$ of 0.86, which leads to an effective $\mu_e$ of 1.0 cm$^2$ V$^{-1}$ s$^{-1}$ (Fig. 6b–c). The highest $\mu_e$ of 1.4 cm$^2$ V$^{-1}$ s$^{-1}$ can be obtained for PhC$_2$–BQQDI–C$_5$, and it shows an averaged $\mu_e$ of 1.2 cm$^2$ V$^{-1}$ s$^{-1}$ over seven devices using the same fabrication method (Supplementary Fig. 15), which further demonstrates the reliability of its OFET performance. PhC$_2$–BQQDI–C$_6$ with the similar charge-transport capability and exhibits a similar $\mu_e$ of 1.2 cm$^2$ V$^{-1}$ s$^{-1}$, though it displays a non-ideal transfer curve with a low $r$ of 0.28 and an effective $\mu_e$ of 0.33 cm$^2$ V$^{-1}$ s$^{-1}$ (Supplementary Fig. 16a). Similarly, PhC$_2$–BQQDI–C$_7$ demonstrates nonlinearity in its transfer characteristic, its highest $\mu_e$ of 1.0 cm$^2$ V$^{-1}$ s$^{-1}$ is accompanied by a low $r$ of 0.36 and an effective $\mu_e$ of 0.36 cm$^2$ V$^{-1}$ s$^{-1}$ (Supplementary Fig. 16b). The device performances of PhC$_2$–BQQDI–C$_n$ herein presents a curious case since all three derivatives demonstrate extremely similar $t$ and $m^*$ values but completely different effective $\mu_e$. However, based on our
MD calculations, we observe that PhC₂–BQQDI–C₅ exhibits the smallest molecular fluctuations and variations in $t$ values, due to the stability of its molecular mimicry conformation. While the other two PhC₂–BQQDI–Cₙ derivatives ($n = 6$ and 7) clearly display large molecular fluctuations and affected charge-transport capabilities compared to PhC₂–BQQDI–C₅, which possibly affected their thin-film crystallinity and result in lower effective $\mu_e$ (Supplementary Fig 17).

Fig. 6 OFET performances of PhC₂–BQQDI–C₅. a–c Polarized microscopic image of single-crystalline thin-film OFET, transfer (black and gray dashed lines represent the fit to $|I_0|^{1/2}$ and the slope of an electrically ideal OFET$^{54}$, respectively) and output characteristics evaluated under ambient conditions. d–e Fan-shaped OFETs on the inch-scale single-crystalline thin film with channels in every 30° relative to the printing direction ($L = \sim 40 \mu m$, $W = \sim 90 \mu m$), and the resulting azimuthal $\mu_e$.

In light of the excellent OFET performance of PhC₂–BQQDI–C₅, we successfully fabricated its centimeter-scale single-crystalline thin films using our recently reported continuous edge-casting solution-processed method$^{39,40}$ (Supplementary Fig. 18), the excellent processability is attributed to its high crystallinity and suitable solubility, which also shows potentials for applicable electronics. We examined the device performance as well as anisotropic $\mu_e$ of the large-area single-crystalline thin film of PhC₂–BQQDI–C₅ (Fig. 6d). For the preliminary devices of PhC₂–BQQDI–C₅, we constructed the OFET channel along its crystal growth direction ($b$-axis). However, both our effective mass and anisotropic $\mu_e$ of the large-area single-crystalline device suggest that the $b$-axis/printing direction is not the best charge-transport
direction. From the plotted azimuthal \( \mu_e \) (Fig. 6e), it is apparent that the \( a \)-axis direction gives the best charge transport, and the experimental result herein is approximately consistent with our angular-dependent inversed effective mass calculations. We anticipate that with optimized device engineering condition, PhC\(_2\)–BQQDI–C\(_5\) has the potential to show further improved \( \mu_e \) with the appropriate OFET channel direction.

Discussion

In summary, we have developed an effective and efficient synthetic strategy for asymmetric PhC\(_2\)–BQQDI–C\(_n\) (\( n = 5\), 6, and 7) compounds. The intriguing molecular mimicry of alkyl chains in the single-crystal structure of PhC\(_2\)–BQQDI–C\(_5\) with the gauche conformations have shown to be energetically favorable and persistent at elevated temperatures attributed to the CH···\( \pi \) stabilization from the neighboring phenyl groups. Although varying the alkyl chain length did not appear to impose a pronounce effect on the intralayer charge transport of PhC\(_2\)–BQQDI–C\(_n\), we noticed a dramatic difference in molecular fluctuations from these derivatives that may have distinct consequences in their charge-transport capabilities. The alkyl chains of PhC\(_2\)–BQQDI–C\(_5\) are stabilized by the “aromatic pocket” and mimic the behavior of rigid phenyl groups that results in small degree of molecular fluctuations. From the results of variant \( t \) calculations, PhC\(_2\)–BQQDI–C\(_5\) show the smallest \( \sigma \) of \( t \) values, which demonstrates the effectiveness of such a molecular mimicry in suppressing molecular fluctuations. PhC\(_2\)–BQQDI–C\(_5\) shows the best OFET characteristics among current asymmetric PhC\(_2\)–BQQDI–C\(_n\) OSCs with the highest \( \mu_e \) of 1.4 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and an excellent averaged \( \mu_e \) of 1.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) is obtained over seven devices. In addition, we demonstrate that PhC\(_2\)–BQQDI–C\(_5\) possesses suitable solubility and high crystalline thin-film quality for large-area device fabrication that is promising for the development of future printable organic electronics.

Methods

Materials and General Characterization Methods. Reagents and anhydrous solvents were purchased from Tokyo Chemical Industry Co., Ltd and Kanto Chemicals, respectively, and \( o \)-dichlorobenzene was purified by the solvent purification system prior to use. All reactions were carried out under an atmosphere of argon. Analytical thin-layer chromatography (TLC) was performed on glass plates with silica gel containing fluorescent indicator (Merck TLC Silica gel 60 F254, 1 mm). Column chromatography was performed on Kanto silica gel 60. All HPLC spectra were recorded on a column by Phenomenex (Kinetex 5u C18 100A, New column 150×4.6 mm) with the mixture of solvent of THF: H\(_2\)O = 6.2: 3.8, and the flow rate was 1.0
mL min\(^{-1}\). \(^{13}\)C NMR of compound 3 was recorded on an AVANCE 700 III, and all other NMR spectra were recorded on JEOL ECS400 spectrometer. Chemical shifts were reported in parts per million (ppm, d scale) from residual protons in the deuterated solvent for \(^1\)H NMR (5.93 ppm for 1,1,2,2-tetrachloroethane-\(d_2\) (TCE-\(d_2\)) and \(^{13}\)C NMR (73.78 ppm for 1,1,2,2-tetrachloroethane-\(d_2\) (TCE-\(d_2\)) and 77.16 ppm for chloroform-\(d\) (CDCl\(_3\))). The data were presented in the following format: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quint = quintet, m = multiplet, br = broad, brm = broad multiplet), coupling constant in Hertz (Hz), signal area integration in natural numbers.

**Synthetic procedure for N-(4-methoxybenzyl)-phenethylamine.** A flame-dried round-bottom flask was charged with anhydrous CH\(_2\)Cl\(_2\) (208 mL), MgSO\(_4\) (250 g, 2.08 mol, 10 equiv.), phenethylamine (25.3 g, 208 mmol, 1.0 equiv.) and \(p\)-anisaldehyde (28.4 g, 208 mmol, 1.0 equiv.). The mixture was stirred at room temperature for 2 h and filtered via vacuum filtration and the solvent was removed \textit{in vacuo}. \((E)-1-(4\text{-}\text{methoxyphenyl})\-N\-phenethylmethanimine was obtained as a yellow liquid (43.3 g) and used without any purification. Subsequently, the obtained imine (43.3 g, 181 mmol, 1.0 equiv.), NaBH\(_4\) (18.9 g, 500 mmol, 2.8 equiv.), anhydrous CH\(_2\)Cl\(_2\) (362 mL), MeOH (362.48 mL) were added to a round-bottom flask under argon. The mixture was stirred at 0 °C for 2 h and the reaction was quenched by water. The compound was extracted with CH\(_2\)Cl\(_2\) and 2M HCl (100 mL) was added to the organic layer and the precipitates were collected via filtration. The filtrates were dissolved in water (150 mL) and sodium carbonate was added until the white solids disappeared, and the compound was then extracted with CH\(_2\)Cl\(_2\) (50 mL × 3). After CH\(_2\)Cl\(_2\) was removed \textit{in vacuo}, the title compound was obtained as a light-yellow liquid without further purification (36.1 g, 72% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.31-7.19 (m, 7H), 6.87-6.83 (m, 2H), 3.77 (d, \(J\) = 17.6 Hz, 5H), 2.92-2.81 (m, 4H). The spectrum is in good agreement with the reported data\(^{56}\).

**Synthetic procedure for 3,9-dimethyl 4-(2,4,6-trichlorophenyl) 10-((4-methoxybenzyl)(phenethyl)carbamoyl)benzo[de]isoquinolino[1,8-\(gh\)]quinoline-3,4,9-tricarboxylate (2).** A flame-dried three-neck round bottom flask equipped with an Ar inlet and reflex condenser was charged with 3,9-dimethyl 10,4-bis(2,4,6-trichlorophenyl)benzo[de]isoquinolino[1,8-\(gh\)]quinoline-3,4,9,10-tetracarboxylate (1) (2.45 g, 3.00 mmol, 1.0 equiv.) and anhydrous \(o\)-DCB (90 mL). After the complete dissolution of 1 at 180 °C, a solution of PMB amine (2.89 g, 12.0 mmol, 4.0 equiv.) was added in one portion to the system. The reaction was carried out at 180 °C and monitored by HPLC. After the peak
area of 2 reached the maximum value (ca. 40 min), the mixture was cooled down to room
temperature and the solvent was removed in vacuo. The crude product was purified by silica
gel column chromatography using PhMe/EtOAc as eluents to afford compound 2 as an orange
solid. (780 mg, 45% yield). $^1$H NMR (400 MHz, TCE-d$_2$, 100 °C): δ 9.23-8.84 (m, 5H), 8.73-
7.65 (brm, 1H), 7.46(s, 2H), 7.43-6.82 (brm, 9H), 5.55-4.08 (brm, 2H), 4.08-3.93 (brm, 3H),
3.89 (s, 3H), 3.82 (s, 3H), 3.75-3.62 (brm, 2H), 3.08-2.87 (brm, 2H). HRMS (APCI+-TOF):
Calcd for C$_{46}$H$_{32}$Cl$_3$N$_3$O$_8$ [M+H] 860.1333. Found, 860.1325. Elemental Analysis. Calcd for
C$_{46}$H$_{32}$Cl$_3$N$_3$O$_8$: C 64.16; H 3.75; N 4.88. Found: C 64.02; H 3.87; N 4.90.

**General synthetic procedure for one-pot synthesis of PhC$_2$–BQQDI–C$_n$.** A flame-dried
Schlenk tube equipped with a stir bar was charged with compound 2 (400 mg, 1.0 equiv.),
alkylamine (1.5 equiv.), and anhydrous o-DCB (0.05 M). The mixture was heated at 150 °C
for one hour under argon and subsequently cooled to room temperature. To the dark red
solution was added TfOH (2.5 equiv.) and the mixture was then stirred at 150 °C for three hours
under argon. As the reaction completion was indicated by $^1$H NMR, the mixture was added
dropwise to a stirring MeOH solution and the dark precipitates were collected via vacuum
filtration. The products were recrystallized from o-DCB to afford the target compounds.

**Characterization of PhC$_2$–BQQDI–C$_5$.** 240 mg, 91% yield. $^1$H NMR (400 MHz, TCE-d$_2$,
100 °C): δ 9.65 (s, 2H), 9.28 (d, J = 7.6 Hz, 2H), 8.84 (d, J = 8.0 Hz, 2H), 7.34-7.19 (m, 5H),
4.45 (t, J = 7.6 Hz, 8.0 Hz, 2H), 4.20 (t, J = 7.2 Hz, 7.2 Hz, 2H), 3.08 (t, J = 8.0 Hz, 7.2 Hz,
2H), 1.81 (quint, J = 8.8 Hz, 6.0 Hz, 6.8 Hz, 6.0 Hz, 2H), 1.44-1.27 (m, 10H), 0.95 (t, J = 6.4
Hz, 3H). HRMS (APCI+-TOF): Calcd for C$_{35}$H$_{26}$N$_4$O$_4$ [M+H] 567.1954. Found 567.1958.
Elemental Analysis. Calcd for C$_{35}$H$_{26}$N$_4$O$_4$: C 74.19; H 4.63; N 9.89. Found 74.17; H 4.73; N
9.80.

**Characterization of PhC$_2$–BQQDI–C$_6$.** 243 mg, 90% yield. $^1$H NMR (400 MHz, TCE-d$_2$,
100 °C): δ 9.64 (s, 2H), 9.28 (d, J = 7.6 Hz, 2H), 8.84 (d, J = 8.0 Hz, 2H), 7.34-7.19 (m, 5H),
4.45 (t, J = 7.2 Hz, 8.4 Hz, 2H), 4.20 (t, J = 7.6 Hz, 7.2 Hz, 2H), 3.08 (t, J = 7.2 Hz, 84 Hz),
1.78 (quint, J = 8.0 Hz, 6.4 Hz, 7.2 Hz, 8.0 Hz, 2H), 1.47-1.27 (m, 6H), 0.92 (t, J = 6.4 Hz, 6.8
Hz, 3H). HRMS (APCI+-TOF): Calcd for C$_{36}$H$_{28}$N$_4$O$_4$ [M+H] 581.2111. Found 581.2124.
Elemental Analysis. Calcd for C$_{36}$H$_{28}$N$_4$O$_4$: C 74.47; H 4.86; N 9.65. Found C 74.32; H 4.96;
N 9.44.

**Characterization of PhC$_2$–BQQDI–C$_7$.** 254 mg, 92% yield. $^1$H NMR (400 MHz, TCE-d$_2$,
100 °C): δ 9.64 (s, 2H), 9.27 (d, J = 8.0 Hz, 2H), 8.84 (d, J = 7.6 Hz, 2H), 7.34-7.19 (m, 5H),
4.45 (t, J = 7.6 Hz, 8.4 Hz, 2H), 4.20 (t, J = 7.2 Hz, 7.6 Hz, 2H), 3.08 (t, J = 7.6 Hz, 8 Hz, 2H), 1.79 (quint, J = 7.6 Hz, 7.2 Hz, 7.2 Hz, 7.6 Hz, 2H), 1.43-1.32 (m, 9H), 0.90 (t, J = 6.8 Hz, 6.8 Hz, 3H). HRMS (APCI^+-TOF): Calcd for C_{37}H_{30}N_4O_4 [M+H] 595.2345. Found 595.2348.

Elemental Analysis. Calcd for C_{37}H_{30}N_4O_4: C 74.73; H 5.09; N 9.42. Found C 74.71; H 5.16; N 9.22.

**Theoretical calculations.** Theoretical calculations of transfer integral and effective mass were conducted using the GAMESS package. The Kohn–Sham eigenstates of all compounds in this work were calculated at the PBEPBE/6-31G(d) level of theory. Transfer integrals (t) between LUMOs of neighboring molecules in the crystal structures were estimated by the dimer method. To further understand the carrier transporting capabilities in the single-crystal state, their LUMO band structures E(k) were calculated by the tight-binding approximation using transfer integrals. Intermolecular interaction energy between two adjacent molecules were obtained at the M06-2X/6-31++G(d,p) level of DFT with counterpoise correction for the basis set superposition error. The calculations were performed using the Gaussian 09 program package.

**Electrochemical measurements.** Cyclic voltammetry was conducted on a BAS electrochemical analyzer ALS 622D using a three-electrode cell with a glassy carbon as the working electrode, a Pt wire as the counter electrode and 0.01 M Ag/AgNO₃ (in benzonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆)) as the reference electrode. The measurements were carried out under an argon atmosphere using a benzonitrile solution at 100 °C with a concentration of 0.25 mM, and 0.1 M TBAPF₆ as a supporting electrolyte with a scan rate of 0.1 V s⁻¹. The redox potentials were calibrated with ferrocene (Fc; E(Fc/Fc⁺) = 0 V) as an internal standard. Benzonitrile was passed through a pad of aluminum oxide 60 for purification prior to use.

**Thermal property measurements.** Thermogravimetric–differential thermal analysis was performed on a Rigaku Thermo Plus EVO II TG 8121 at a heating rate of 1 K min⁻¹ under a nitrogen flow of 100 mL min⁻¹. The differential scanning calorimetry measurements were performed with a Rigaku Thermo Plus EVO II DSC 8270 at a heating rate of 5 K min⁻¹ under a nitrogen flow of 50 mL min⁻¹.

**Solubility measurements.** To a weighed sample of around 1 mg was added 200 µL of o-DCB, repeatedly. The resulting suspension was shaken and heated at 100 °C until complete dissolution. The total amount of solvent in mL was converted into solubility in wt%.
**X-ray crystallography.** PhC$_2$–BQQDI–C$_n$ single crystals were obtained by means of slow-cooling over a period of 48 hours in a mixture of nitrobenzene and 1–methylnaphthalene, and PhC$_2$–BQQDI–C$_5$ crystals were grown in the mixture of nitrobenzene and 1-chloronaphthalene. Single-crystal X-ray diffraction data were collected on either a Rigaku R-AXIS RAPID II imaging plate diffractometer with CuKα radiation ($\lambda = 1.54187$ Å) or a Rigaku XtaLAB Synergy-Custom instrument with CuKα radiation ($\lambda = 1.54184$ Å) at room temperature. The structures were solved by direct methods [SHELXT (2015)] and refined by full-matrix least-squares procedures on F2 for all reflections [SHELXL (Ver. 2014/7) or SHELXL (Ver. 2018/3)]. While positions of all hydrogen atoms were calculated geometrically, and refined by applying riding model, all other atoms were refined anisotropically. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as a supplementary publication. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif. The temperature-variant PXRD studies of PhC$_2$–BQQDI–C$_5$ was carried out using the synchrotron X-ray powder diffraction with the wavelength of 0.8 Å at BL44B2 at SPring-8 RIKEN Materials Science Beamline (BL44B2)$^{49,50}$. Powders of PhC$_2$–BQQDI–C$_5$ were packed in glass capillaries and the diffraction patterns are recorded in the temperature ranged from 25 to 200 °C. The intensities of diffraction patterns at different temperatures were normalized for better comparison.

**Preparation of OFET substrates.** A highly n$^{++}$-doped silicon wafer was used as the substrate, which the surface was treated by a fluorinated insulating polymer, AL-X601 (40 nm). The highly n$^{++}$-doped silicon wafer with thermally grown SiO$_2$ layer (200 nm) was ultrasonicated in acetone and isopropanol, and then dried on a hotplate in air. Following UV−O$_3$ treatment, AL-X601 diluted with propylene glycol monomethyl ether acetate (PGMEA) was spin-coated onto the wafer and cured at 150 °C for 30 min in air.

**Fabrication of solution-processed single-crystalline thin films.** PhC$_2$–BQQDI–C$_n$ were investigated in the bottom-gate, top-contact OFET structure. Preparations of single-crystalline thin films were carried out by the solution-processed edge-casting method$^{53}$. Thin-film crystals of PhC$_2$–BQQDI–C$_n$ were grown from 0.02–0.03 wt% 1-methylnaphthalene solutions at 90–115 °C. After the completion of crystallization, thin films were thoroughly dried in a vacuum oven at 100 °C for 10 hours. Then, 40 nm-thick gold layers were vacuum deposited through a metal shadow mask, acting as source and drain electrodes. Objective channel regions were edged by the conventional Nd:YAG laser etching technique or manually by using cotton swabs.
Before measurements, thermal annealing at 100 °C for 10 hours were conducted to remove residual water and improve gold electrode–semiconductor contacts.

**Fabrication of large-area single-crystalline thin films.** The single-crystalline film of PhC$_2$–BQD–C$_5$ (0.02 wt% in 1-methylnaphthalene) was prepared on a glass substrate encapsulated by a 55 nm-thick AL-X601 insulating layer by means of the continuous edge-casting method. The stage temperature was maintained at 140 °C and the velocity of the moving stage was set to 24 µm s$^{-1}$.

**OFET measurements.** Electrical evaluations of the TFTs were conducted on a Keithley 4200-SCS semiconductor parameter analyzer in air. For AL-X601-containing gate dielectrics, the gate capacitance per unit area ($C_i$) was estimated using a Toyo FCE-3 ferroelectric test system on metal–insulator–metal structures. Electron mobility and threshold voltage were extracted from the transfer characteristics by using the conventional equation for the saturation regime:

$$\sqrt{|I_D|} = \frac{W \mu_e C_i}{2L} (V_G - V_{th}),$$

where $I_D$ is the drain current, $W$ the channel width, $\mu_e$ the electron mobility, $C_i$ the gate capacitance per unit area, $L$ the channel length, $V_G$ the gate voltage, and $V_{th}$ the threshold voltage.

**Molecular dynamic simulations.** Molecular dynamics (MD) simulations of single crystal structures in this study were carried out by using the MD program GROMACS 2016.3. Since the intra- and interatomic interactions should be treated explicitly for analyzing the atomistic dynamics, an all-atom model was employed in accordance with generalized Amber force field parameters$^{60}$. The partial atomic charges of the simulated molecules were calculated using the restrained electrostatic potential (RESP)$^{61}$ methodology, based on DFT calculations with the 6-31G(d) basis set using the GAUSSIAN 09 program$^{59}$.

For each system, the pre-equilibration run was initially performed at the given temperature for 5 ns after the steepest descent energy minimization. All systems were subjected to pre-equilibration runs in the NTV ensemble before their equilibration runs. During the pre-equilibration runs for the NTV ensemble, the Berendsen thermostat$^{62}$ was used to maintain the temperature of the system with relaxation time of 0.2 ps and the volume of the MD cell was kept constant. Subsequently, for the NTP ensemble the equilibration run was performed using the Nosé-Hoover thermostat$^{63-65}$ and Parrinello-Rahman barostat$^{66}$ with relaxation times of 1.0 and 5.0 ps, respectively. For all MD simulations in the NTP ensemble, the pressure of the
The system was kept at 1.0 bar. The smooth particle-mesh Ewald (PME)\(^6\) method was employed to treat the long-rang electrostatic interactions and the real space cutoff and the grid spacing are 1.2 and 0.30 nm, respectively. The time step was set to 1 fs.

To compare temperature dependence of thermal atomic fluctuations between different molecules, we calculated the B-factors related to the thermal stability as expressed below:

\[
B = \frac{8}{3} \pi^2 \Delta_i^2
\]

where \(\Delta_i\) is the root mean square fluctuations (RMSF) of atom \(i\). The RMSF values can be estimated by using following equation:

\[
\Delta_i = \sqrt{\frac{1}{T} \sum_{j=1}^{T} |\mathbf{r}_i(t_j) - \bar{\mathbf{r}}_i|^2}
\]

where \(T\) is the time step, \(\mathbf{r}_i(t_j)\) is the position coordinate of atom \(i\), and \(\bar{\mathbf{r}}_i\) is the average of \(\mathbf{r}_i(t_j)\). The RMSF values were analyzed from MD trajectories during the last 10 ns in the equilibrium.

**Data availability**

The data reported in this study are available from the corresponding author (Toshihiro Okamoto; tokamoto@k.u-tokyo.ac.jp) upon reasonable requests. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre (CCDC) as a supplementary publication under accession nos. CCDC-1989643 (PhC\(_2\)–BQQDI–C\(_5\), 298 K), CCDC-1989644 (PhC\(_2\)–BQQDI–C\(_6\), 298 K), CCDC-1989645 (PhC\(_2\)–BQQDI–C\(_7\), 293 K). These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif.

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**Author contributions**

T.O. conceived and designed the work, while C.P.Y., S.K., M.T., T.K., H.S., Y.T., T.I., and T.W. synthesized the compounds. S.K., C.P.Y., T.K., H.S., and A.Y. performed the single-crystal analyses. T.K. and D.H. performed the temperature-variant PXRD measurements. C.P.Y., S.K., and M.T. evaluated the electrochemical and physicochemical properties, conducted device experiments, and analyzed the data. H.I. and C.P.Y. calculated the transfer integrals and effective masses. G.W. performed the molecular dynamics simulations. C.P.Y. performed the DFT studies. C.P.Y., S.K., and T.O. wrote the manuscript. J.T. and T.O. supervised the work. All authors discussed the results and reviewed the manuscript.

**Competing interests**

The authors declare no competing interests.