Supporting Information

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S1. General Instruments

\(^1\)H- and \(^{13}\)C-nuclear magnetic resonance (NMR) spectroscopies were obtained on a Bruker Avance III HD NanoBay 400 FT-NMR spectrometers using tetramethylsilane (\(^1\)H-NMR) and solvent residual peaks (\(^{13}\)C-NMR) as internal standards. Melting points (Mp) were determined on a Yanaco micro melting point apparatus MP-500D. Elemental analyses (EA) were performed on an Elementar vario EL cube in the CHN mode. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Shimadzu UV-1650 spectrophotometer in CHCl\(_3\) (10\(^{-5}\) M). Cyclic voltammetry (CV) measurements were carried out on a BAS 2323 bipotentiostat using a platinum disk working electrode, a platinum wire counter electrode, and a Ag/Ag\(^+\) reference electrode in a standard three-electrode cell. The voltammograms were collected in 0.1 M \(o\)-DCB /PhCN mixed solution of tetrabutylammonium hexafluorophosphate (Bu\(_4\)NPF\(_6\)), and the voltage-current characteristic was obtained at the scan rate of 100 mV/s. Redox potentials were calibrated using the ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple to be 4.8 eV below the vacuum. Theoretical calculations were performed on Gaussian 09W (Revision C.01) package of programs. The ground state structure was optimized with DFT calculation at the B3LYP/6-31G(d,p) level of theory. The theoretical absorption bands were estimated by TD-DFT calculation at the B3LYP/6-31G(d,p) level of theory. OFET measurements were performed in a vacuum or under ambient conditions. Electron mobilities (\(\mu_\text{e}\)) were determined from the equation \(I_{DS} = W/(2L)C_i\mu_\text{e}(V_{GS} - V_{th})\), where \(I_{DS}\), \(W\), \(L\), \(C_i\), \(V_{GS}\), and \(V_{th}\) are the source–drain current, channel width (38 mm), channel length (5 \(\mu\)m), capacitance of the SiO\(_2\) dielectric layers (10 nF·cm\(^{-2}\)), gate voltage, and threshold gate voltage, respectively. Grazing-incidence X-ray diffraction (GI-XRD) measurements were taken by an X-ray diffractometer FR-E equipped with a two-dimensional detector R-axis IV (Rigaku) involving an imaging plate (Fujifilm). Beam of 0.3-mm collimated Cu Ka radiation (\(l = 1.5418\) Å) was used as an X-ray, and the camera length was set at 250 mm. Film samples were placed onto a pulse motor stage and covered with a handmade chamber to control a relative humidity around the samples. An incident angle of the beam to the substrate surface was adjusted at ca. 0.18–0.22° by using a Z pulse motor stage ALV-300-HM and an oblique pulse motor stage ATS-C310-EM (Chuo Precision Industrial). X-ray exposed times were set at 30 min for each film prepared onto a HMDS-treated substrate. Atomic force microscopy (AFM) imaging was performed in a tapping mode under ambient conditions with an Oxford Instruments MFP-3D.
S2. NICS(0) values and conformation of target compounds

**Figure S1.** NICS(0) value of dithiarubicene and representation of aromaticity.

**Figure S2.** NICS(0) values (purple number) for four compounds calculated at the HF/6-311+G**/*B3LYP/6-31G** level of theory.

**Figure S3.** Dihedral angles between Core and substituents estimated by using DFT calculation (B3LYP/6-31G**). **BisDCNE**: top, **BisTCNE**: middle, and **TCNQE**: bottom.
S3. TD-DFT calculations

Table S1. Comparison of absorption bands between the observed value and theoretical value estimated by TD-DFT calculation (B3LYP/6-31G**).\(^1\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ(_{\text{obsd}}) [nm]</th>
<th>λ(_{\text{cacld}}) [nm]</th>
<th>Oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>615</td>
<td>648</td>
<td>0.12</td>
</tr>
<tr>
<td>BisDCNE</td>
<td>646</td>
<td>689</td>
<td>0.54</td>
</tr>
<tr>
<td>BisTCNE</td>
<td>653</td>
<td>683</td>
<td>0.73</td>
</tr>
<tr>
<td>TCNQE</td>
<td>738</td>
<td>712</td>
<td>0.79</td>
</tr>
</tbody>
</table>
S4. OFET characteristics

**Figure S4.** (A) Transfer and (B) output plots of BisDCNE-based OFET device fabricated on HMDS-treated SiO$_2$ insulation surface after the thermal annealing at 100 °C.
S5. 2D GIXRD images

Figure S5. 2D GIXRD images of thin films fabricated on HMDS-treated SiO$_2$ insulation surface after the thermal annealing.
S6. AFM images

**Figure S6.** AFM images of the device surfaces between the electrodes after the thermal annealing. The inset values indicate the root mean square roughness ($R_{\text{RMS}}$) calculated each image.
S7. NMR spectra

Core
Diformyl-Core (1)
BisDCNE

[Chemical structure image]

[1H NMR spectrum]

[13C NMR spectrum]
Diiodo-Core (2)
BisTCNE

\[
\begin{align*}
\text{C}_{10}H_{21} & \quad \text{CN} \\
\text{C}_{8}H_{17} & \quad \text{C} \quad \text{S} \\
\text{C}_{10}H_{21} & \quad \text{CN} \\
\text{C}_{8}H_{17} & \quad \text{CN} \\
\end{align*}
\]
Dibromo-Core (3)
TCNQE
S8. Reference