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Electron-Accepting π-Conjugated Molecules with Fluorine-Containing Dicyanovinylidene as Terminal Groups: Synthesis, Properties, and Semiconducting Characteristics

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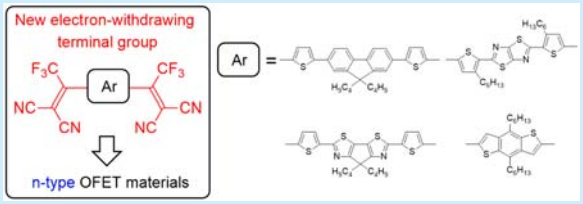
Supporting Information

ABSTRACT: A series of electron-accepting π-conjugated molecules having fluorine-containing dicyanovinylidene as terminal groups has been synthesized for the application to electron-transporting semiconductors. This terminal group can be easily incorporated into π-conjugated frameworks. Electrochemical measurements indicated that these compounds showed low-lying lowest unoccupied molecular orbital energy levels, which could be fine-tuned by the combination of central unit. The thin films fabricated by solution process showed typical electron-transporting characteristics in field-effect transistors.



Development of new π-conjugated compounds has been extensively investigated in recent years toward the application to organic semiconducting materials in organic field-effect transistors (OFETs) and organic photovoltaics (OPVs).[1] The advantage of such materials includes the fine-tunability of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels by the structural modification of π-conjugated backbones and/or the incorporation of substituents.[2,3] Compared with p-type semiconducting OFET materials, the development of n-type materials has still lagged behind due to the difficulty of molecular design for lowering the LUMO energy level with concomitant acquirement of electron-transporting characteristics in the film state.[4] Although the introduction of electron-withdrawing group into π-conjugated systems has become a rational approach to fulfill this requirement, effective functional groups are still limited to those such as fluorine,[5] fluoroalkyl,[3] carbonyl,[6a] fluoroacyl,[6] imide,[7,8] and cyano groups.[9] Thus, one of the main focuses of research interest is the design of new electron-accepting modules to broaden the repertories of n-type semiconducting materials.

In view of the fact that dicyanovinylidene and fluoroalkyl groups have a powerful electron-withdrawing nature, we previously designed an electron-accepting terminal thiophene unit (**T-Cp(CN)$_2$CF$_2$**) with an annelated cyclopentene ring containing two dicyanomethylenes and two fluorines (denoted as **Cp(CN)$_2$CF$_2$**) (Figure 1).[10] The LUMO energy levels of **T-Cp(CN)$_2$CF$_2$**-incorporated π-conjugated molecules were significantly decreased to −4.1 to −4.2 eV, which contributed to the appearance of their functions as n-type OFET and OPV materials.[10,11]

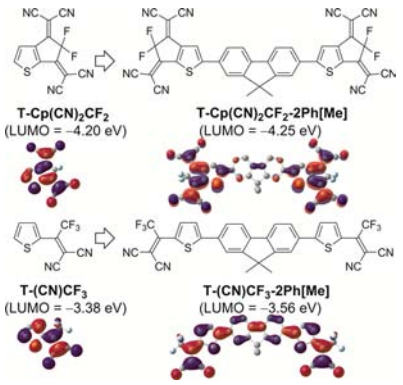


Figure 1. Chemical structures of electron-accepting molecules and calculated LUMOs and energies.

However, the strong electron-withdrawing characteristics of **Cp(CN)$_2$CF$_2$** caused the orbital-energy mismatch with the central units. For instance, the theoretical calculations, performed by density functional theory (DFT) at the B3LYP/6-31 G(d,p) level, indicated that the LUMO of **T-Cp(CN)$_2$CF$_2$-2Ph[Me]** is localized on the **T-Cp(CN)$_2$CF$_2$** units (Figure 1). Since the degree of intermolecular overlap between orbitals participating in

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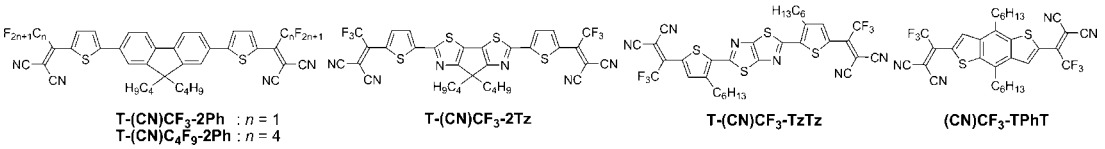
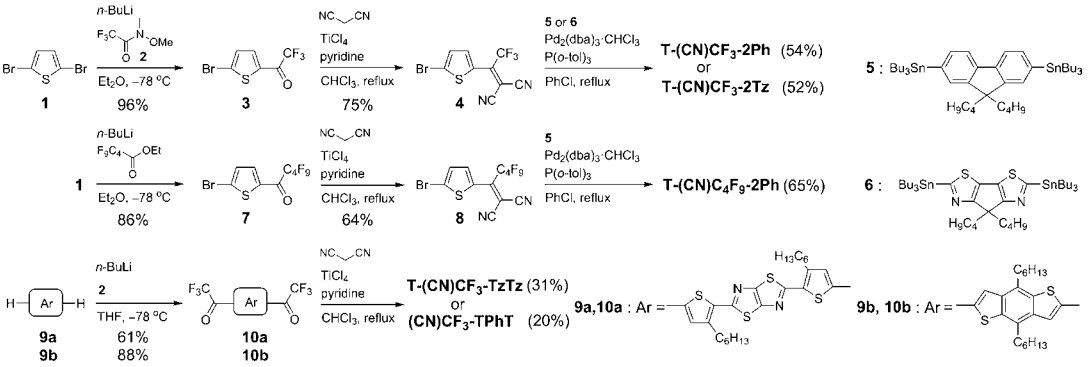


Figure 2. Chemical structures of compounds synthesized in this study.

Scheme 1. Synthetic Routes of T-(CN)CF_3-2Ph, T-(CN)C_4F_9-2Ph, T-(CN)CF_3-2Tz, T-(CN)CF_3-TzTz, and (CN)CF_3-TPhT



carrier-transport correlates with the degree of carrier mobilities,[12] the localized LUMO is disadvantageous to electron mobility. The calculations also indicated that the central unit has a negligible influence on the LUMO energy level of the π-conjugated molecules (Figure 1), resulting in similar LUMO energy levels irrespective of the central units. We expected that the modification of electron-withdrawing characteristics of **Cp-(CN)$_2$CF$_2$** may circumvent these situations and thus designed a new electron-accepting terminal thiophene unit (**T-(CN)-C$_n$F$_{2n+1}$**) with a fluorine-containing dicyanovinylidene group (**(CN)C$_n$F$_{2n+1}$**). As shown in Figure 1, the calculated LUMO of **T-(CN)CF$_3$-2Ph[Me]** is delocalized in the whole π-conjugated backbones, indicating that the LUMO energy level can be precisely tuned by central units. Although π-conjugated molecules containing the **(CN)C$_n$F$_{2n+1}$** structure were known to show several functions,[13−15] the application to semiconducting materials has not been reported. In this contribution, we report the synthesis, properties, and electron-transporting semiconducting performance of **(CN)C$_n$F$_{2n+1}$**-incorporated π-conjugated compounds in combination with electronically varied central units (**T-(CN)CF$_3$-2Ph**, **T-(CN)C$_4$F$_9$-2Ph**, **T-(CN)CF$_3$-2Tz**, **T-(CN)CF$_3$-TzTz**, and **(CN)CF$_3$-TPhT**) (Figure 2).

Since the previously reported synthetic routes for the **(CN)C$_n$F$_{2n+1}$** derivatives have faced on the narrow generality,[13−15] we established an easily accessible route (Scheme 1). 2,5-Dibromothiophene (**1**) was monolithiated with *n*-BuLi and then treated with *N*-methoxy-*N*-methyltrifluoroacetamide (**2**) to afford trifluoroacetyl compound **3** in 96% yield. The Knövenagel condensation reaction of **3** with an excess amount of malononitrile in the presence of $TiCl_4$ and pyridine gave **4** in 75% yield. Note that the other typical reaction conditions such as hexamethyldisilazane/AcOH, piperidine/AcOH, and β-alanine/ethanol gave inferior yields of **4**. Finally, **T-(CN)CF$_3$-2Ph** was synthesized by the Stille cross-coupling reaction between **4** and **5** with $Pd_2(dba)_3$·$CHCl_3$ as the catalyst. Compound **T-(CN)CF$_3$-2Tz** was synthesized in the same manner by the reaction between **4** and **6**. The use of 2,2,3,3,4,4,5,5,5-nonafluoropentanoic acid ethyl ester instead of **2** allowed formation of the corresponding perfluoroacyl-substituted monomer **7**, leading to **T-(CN)C$_4$F$_9$-2Ph**. Furthermore, this perfluoroacylation−dicyanomethylation method was successfully applied to the synthesis of **T-(CN)CF$_3$-TzTz** and **(CN)CF$_3$-TPhT**. This introduction of plural **(CN)CF$_3$** groups indicates the versatility of this method in installing **(CN)C$_n$F$_{2n+1}$** groups at both terminal positions of π-conjugated backbones. The alkyl groups in the central moiety ensured the solubility of the molecules. The chemical structures were characterized by NMR, MS, and elemental analysis.

UV−vis absorption spectra of the synthesized target compounds are shown in Figure 3 and Figures S1 and S2 in the Supporting Information, and their absorption maxima (λ_{max}) and molar extinction coefficients (ε) are summarized in Table 1. The absorption spectra of **T-(CN)CF$_3$-2Ph**, **T-(CN)C$_4$F$_9$-2Ph**, **T-(CN)CF$_3$-2Tz**, and **T-(CN)CF$_3$-TzTz** in $CHCl_3$ solutions exhibited an intense band originated from the HOMO−LUMO transition in the range of 400−700 nm. On the other hand,

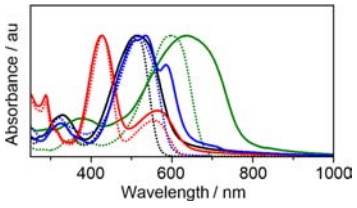


Figure 3. UV−vis absorption spectra of **T-(CN)CF$_3$-2Ph** (black), **T-(CN)CF$_3$-2Tz** (green), **T-(CN)CF$_3$-TzTz** (blue), and **(CN)CF$_3$-TPhT** (red) in $CHCl_3$ (dashed line) and thin films (solid line).

Table 1. Properties of Compounds

compd	λ_{max}[a] (nm) ($\varepsilon \times 10^4$ (M cm^{-1}))	ΔE_g^{opt}[b] (eV)	$E_{1/2}^{red}$[c] (V)	E_{LUMO}^{CV} (eV)
T-(CN)CF$_3$-2Ph	513 (6.9)	2.19	−1.07	−3.72
T-(CN)C$_4$F$_9$-2Ph	520 (6.7)	nd[d]	−1.05	−3.75
T-(CN)CF$_3$-2Tz	599 (6.6)	1.60	−0.89	−3.91
T-(CN)CF$_3$-TzTz	518 (5.7)	2.07	−0.89	−3.91
(CN)CF$_3$-TPhT	429 (4.2), 555	2.00	−0.84	−3.97

[a]In $CHCl_3$. [b]Determined by the onset of the UV−vis absorption spectrum in the film. [c]In CH_2Cl_2 containing 0.1 M $TBAPF_6$. V vs Fc/Fc^+. [d]No data.

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(CN)CF$_3$-TPhT showed two bands at 429 and 555 nm. These bands represent mainly HOMO-1−LUMO and HOMO−LUMO transitions, respectively, as confirmed by time-dependent (TD)-DFT calculations at the B3LYP/6-31 G(d,p) level (see the Supporting Information). The appearance of the HOMO-1−LUMO absorption is due to the next HOMO that lies close to the HOMO and matches with the LUMO for symmetrically allowed optical transition. Compared to the solution spectra, a well-structured shoulder was observed for **T-(CN)CF$_3$-TzTz** in the thin-film state, whereas the absorption spectra of **T-(CN)CF$_3$-2Tz** in the films were red-shifted with an apparent broadening, compared to that in the solution. These phenomena are attributed to the intermolecular electronic interactions of $\pi-\pi$ stacked backbones. In contrast, uniform **T-(CN)C$_4$F$_9$-2Ph**-films were not formed due to the oil-repellent nature of the perfluorobutyl group. The thin film data are summarized in Table S1 in the Supporting Information.

The electrochemical properties were investigated by cyclic voltammetry measurements in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. Oxidation waves were not detected within the available potential range of CH_2Cl_2. Reflecting the electron-accepting nature of **(CN)C$_n$F$_{2n+1}$** group, all of the compounds showed one reversible reduction wave (Figure 4). The observed

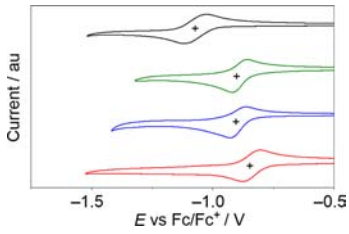

Figure 4. Cyclic voltammograms of **T-(CN)CF$_3$-2Ph** (black), **T-(CN)CF$_3$-2Tz** (green), **T-(CN)CF$_3$-TzTz** (blue), and **(CN)CF$_3$-TPhT** (red) in CH_2Cl_2 containing 0.1 M $TBAPF_6$.

good reversibility indicates the stable formation of anionic species. The half-wave reduction potentials ($E^{red}_{1/2}$) are calibrated against ferrocene/ferrocenium (Fc/Fc^+), and these values are listed in Table 1. The length difference of perfluoroalkyl chains has little influence on the electrochemical as well as photoabsorption properties (**T-(CN)CF$_3$-2Ph** vs **T-(CN)C$_4$F$_9$-2Ph**) (Figure S3). On the premise that the energy level of Fc/Fc^+ is −4.8 eV below the vacuum level,[16] the LUMO energy levels ($E_{LUMO}{}^{CV}$s) of these compounds are estimated (Table 1), which, as we expected, vary between −3.72 and −3.97 eV according to the π-conjugated central unit. These LUMO energy levels are consistent with those by the DFT calculation (Figure S4).

Based on the ionization potentials of thin films measured by photoelectron spectroscopy in air (PESA) (Figure S5) and the optical HOMO−LUMO energy gaps ($\Delta E_g{}^{opt}$) of the thin films, we also estimated the LUMO energy levels ($E_{LUMO}{}^{opt}$) in the film states (Table S1). Except for **T-(CN)CF$_3$-2Tz** that showed prominent red-shift in the film state, the $E_{LUMO}{}^{opt}$s are qualitatively in good agreement with the $E_{LUMO}{}^{CV}$s.

Single crystals of **T-(CN)CF$_3$-2Ph**, **T-(CN)C$_4$F$_9$-2Ph**, and **(CN)CF$_3$-TPhT** suitable for X-ray crystallographic analysis were obtained by the method described in the Supporting Information. As shown in Figure 5a and Figure S6a, **T-(CN)CF$_3$-2Ph** and **T-(CN)C$_4$F$_9$-2Ph** adopt almost planar structures with dihedral angles of less than 10° between the fluorene and thiophene rings. In addition, the C−C═C(CN)$_2$ planes in the **(CN)C$_n$F$_{2n+1}$**

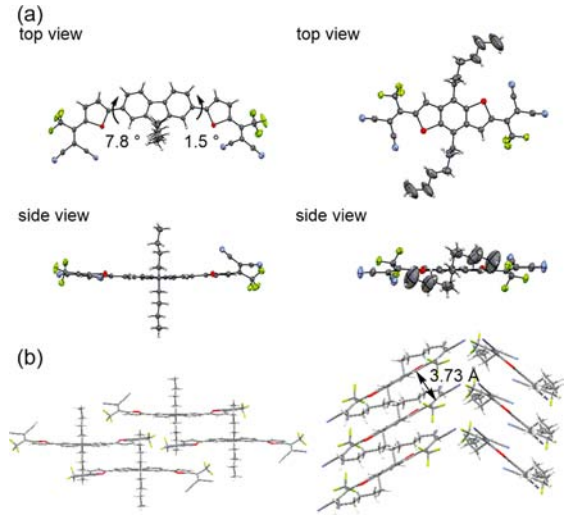

Figure 5. (a) Molecular structures and (b) packing diagrams of **T-(CN)CF$_3$-2Ph** (left) and **(CN)CF$_3$-TPhT** (right).

groups lie almost on the π-conjugated planes. In the crystal packing, **T-(CN)CF$_3$-2Ph** and **T-(CN)C$_4$F$_9$-2Ph** are arranged in a slipped π-stacked motif to prevent the steric congestion of two butyl groups on 9-position of fluorene, which contrasts with a herringbone motif adopted by **(CN)CF$_3$-TPhT** with two in-plane-oriented hexyl groups (Figure 5b and Figure S6b). The observed intermolecular $\pi-\pi$ distances for these molecules are between 3.47 and 3.75 Å.

The electron mobility (μ_e) of the developed compounds was evaluated by using OFETs. We fabricated bottom-gate bottom-contact configuration devices, and the active layers were prepared by spin-coating of 1.0 wt % $CHCl_3$ solution onto octadecyltrichlorosilane (ODTS)- or hexamethyldisilazane (HMDS)-modified Si/SiO_2 substrates. However, as mentioned above, uniform **T-(CN)C$_4$F$_9$-2Ph** films were not formed, resulting in no OFET response. On the other hand, the films of other **(CN)CF$_3$**-incorporated compounds showed typical n-type behavior under vacuum conditions. Although the device performance was influenced by thermal annealing as summarized in Table S2, these compounds showed moderate μ_e's the order of 10^{-3} cm^2 V^{-1} s^{-1}. These values are comparable to those of the **T-Cp(CN)$_2$F$_2$**-incorporated compounds.[10] The transfer characteristics are shown in Figure S7, and the representative device parameters of threshold voltage (V_{th}), current on/off ratio (I_{on}/I_{off}), and μ_e are summarized in Table 2.

In order to investigate the crystallinity and morphology of these thin films, X-ray diffraction (XRD) and atomic force microscopy (AFM) measurements were performed. As shown in Figure S8, the XRD patterns of **T-(CN)CF$_3$-2Ph**, **T-(CN)CF$_3$-TzTz**, and

Table 2. Field-Effect Characteristics

compd	cond	V_{th} (V)	I_{on}/I_{off}	μ_e (cm^2 V^{-1} s^{-1})
T-(CN)CF$_3$-2Ph[a]	vacuum	0.3	10^3	6.2×10^{-3}
T-(CN)CF$_3$-2Tz[b]	vacuum	31	10^2	1.6×10^{-3}
T-(CN)CF$_3$-2Tz[b]	air	16	10^4	2.0×10^{-4}
T-(CN)CF$_3$-TzTz[b]	vacuum	9	10^5	2.0×10^{-4}
T-(CN)CF$_3$-TzTz[b]	air	18	10^5	1.7×10^{-4}
(CN)CF$_3$-TPhT[b]	vacuum	5	10^3	1.2×10^{-3}
(CN)CF$_3$-TPhT[b]	air	10	10^4	7.1×10^{-4}

[a]ODTS treatment. [b]HMDS treatment.

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(CN)CF$_3$-TPhT thin films showed diffraction peaks, indicating certain crystallinity of the thin films. The corresponding AFM images showed several-micrometer-size crystalline domains (Figure S9). In contrast, XRD analysis of the **T-(CN)CF$_3$-2Tz** film showed no reflection peaks, and domainless AFM images of this film remained almost unaltered even after the annealing, indicating its amorphous nature regardless of the thermal treatment. However, the presence of intermolecular $\pi-\pi$ interactions that implied by the UV−vis measurements of **T-(CN)CF$_3$-2Tz** in the film state (Figure 3) might form nondirectional charge-transport pathways.[17] These results imply that the **(CN)CF$_3$** group contributes to bringing the electron-transporting characteristics in both crystalline and amorphous films.

The acquirement of operational stability under air-exposed conditions for n-type OFET materials is recognized as a critical issue.[18] When these devices were driven in air, **T-(CN)CF$_3$-2Tz**, **T-(CN)CF$_3$-TzTz**, and **(CN)CF$_3$-TPhT** retained n-type characteristics, though **T(CN)CF$_3$-2Ph** lost the FET response. It is reasonable to consider that the stability under air-exposed conditions was acquired by both the relatively low-lying LUMO energy levels (−3.91 to −3.97 eV) and the partial contribution of the kinetic barrier, which arises from a tight packing of the fluoroalkyl groups and prevents the penetration of air oxidants (O_2 and H_2O).

In summary, we have presented a useful approach of fine-tuning the LUMO energy level using a newly designed **(CN)C$_n$F$_{2n+1}$** group to develop a series of electron-accepting π-conjugated molecules. These molecules exhibited n-type OFET characteristics, irrespective of molecular alignment in the film states. These findings are helpful for the development of organic semiconducting materials toward not only n-type OFET materials but also n-type OPV materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02070.

Synthetic details, characterization data, calculations, PESA, X-ray analysis, OFET, XRD, as well as AFM images (PDF)
X-ray data for **(CN)CF$_3$-TPhT** (CIF)
X-ray data for **T-(CNC$_4$F$_9$-2Ph** (CIF)
X-ray data for **T-(CN)CF$_3$-2Ph** (CIF)

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Notes

The authors declare no competing financial interest.

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