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Molecular structures of n-type semiconducting material 2,5-difluoro-1,4-phenylene-3,3′-bis{2-[(4-trifluoromethyl)phenyl]acrylonitrile} and its photo dimerization product

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ABSTRACT

The absolute molecular structure of air stable n-type semiconducting material 2,5-difluoro-1,4-phenylene-3,3′-bis{2-[(4-trifluoromethyl)phenyl]acrylonitrile} was determined by using twin crystal treatment X-ray diffraction analysis. The compound was readily dimerized in solution via irradiating of UV or Sun light. The exact molecular structure of the dimer also determined by X-ray analysis.

1. Introduction

π-Conjugated systems have broad range of applications in organic electronics as semiconducting materials [1–7]. They have been used as semiconducting materials in organic photovoltaic cells, sensors, organic light-emitting diodes and organic field-effect transistors (OFETs) due to the offering of low-cost, large-area, and flexible electronic devices [8–11]. n-type semiconductor materials are important components for the fabrication of organic complementary circuits [12,13]. However, these materials are less explored due to the low mobilities, instability in air and difficulties in synthesis. The n-type organic semiconductor with high performance transport characteristics is strongly desired in organic electronics. One of the fundamental principles in designing n-type air stable semiconducting material is to incorporating electron withdrawing groups. Due to the incorporation of electron withdrawing groups, electron affinity of materials increases and LUMO energy gap will decrease [14–16]. Jones and co-workers have explored the n-type air stable perylenediimide derivatives by incorporating cyano (CN) and fluorine (F) substituent [17,18]. Recently, we have reported n-type transport characteristics of *p*-phenylenevinylene derivative of 2,5-difluoro-1,4-phenylene-3,3′-bis{2-[(4-trifluoromethyl)phenyl] acrylonitrile} having two cyano (CN) and two trifluoromethyl (CF_3) substituents [19]. We also reported the synthesis of title compound and fabricated OFET using this compound, exhibited good n-channel OTFT properties with high electron mobility [20]. Herein, we have determined the absolute molecular structures of the title compound and its photo-dimerization product using twin crystal treatment X-ray diffraction analysis with the hope that this study will provide better understanding of structure-property relationships of these compounds and may be helpful to material chemists in designing new materials with a view to achieve desired performance in devices and circuits.

We also discussed the photochemical properties by molecular orbital (MO) calculation.

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Table 1
Selected intermolecular short contacts (Å) of the monomer **3**.

Short contacts (between the side columns)		Short contacts (between molecules in the column)	
N1–H7′	2.725	C3–C3*	3.313
N1–H11′	2.442	F4–F6*	2.896
H17–N2′	2.748	F6–F4*	2.896
H21–N2′	2.669	F7–C18**	3.168
F2–H6′	2.609	C18–F7**	3.168
H3–F1′	2.616		
N2–H17″	2.748		
N2–H21″	2.669		
H7–N1″	2.725		
H11–N1″	2.442		
H6–F2″	2.609		
F1–H3″	2.616		

2. Experimental

2.1. Experimental procedure for the synthesis of 2,5-difluoro-1,4-phenylene-3,3′-bis{2-[(4-trifluoromethyl)phenyl]acrylonitrile} **3**

In a first Schlenk vessel 2,5-difluoro-1,4-benzenedicarbaldehyde **1** (680 mg, 0.40 mmol) and (4-trifluoromethyl)phenylacetonitrile **2** (1.48 g, 0.80 mmol) were taken in absolute ethanol (50 mL). In a second Schlenk vessel, sodium ethoxide (0.400 g, 5.76 mmol) and freshly distilled dry pyridine (4.96 mmol, 0.40 mL) were taken in absolute ethanol (50 mL). Under protection from air, the two solutions were mixed and heated to reflux for 3 h. Then, pyridine and volatiles were removed under reduced pressure. Under protection from air, the residue was repeatedly extracted with small portions (15 mL) of dichloromethane. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and then, filtered through a syringe filter. The extract was evaporated under reduced pressure to leave the residue affording 2,5-difluoro-1,4-phenylene-3,3′-bis{2-[(4-trifluoromethyl)phenyl]acrylonitrile} **3** in 90% yield.

Pale-green solid, M.p: 259–261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.76 (d, phenyl, 4 H, $J = 8.2$ Hz), 7.83 (s, 2 H, ethenyl–H), 7.85 (d, 4 H, phenyl, $J = 8.2$ Hz), 8.21 (t, 2H, phenyl, J = 8.4 Hz). EI-MS (MH^+): 503. Elemental analysis calculated for $C_{26}H_{12}F_8N_2$: C, 61.91%; H, 2.40%; N, 5.55%. Found: C, 61.80%; H, 2.55%; N, 5.64%.

2.2. Experimental procedure for the synthesis of the dimer **4**

2,5-Difluoro-1,4-phenylene-3,3′-bis{2-[(4-trifluoromethyl) phenyl]acrylonitrile} **3** (150 mg, 0.30 mmol) in ethanol (100 mL) in a first Schlenk vessel. Under protection from air, the solution was irradiated with UV light using 350 nm high-pressure UV lamp (Ushio Denki UN-402) for 90 min. Then, most volatile materials were removed on a vacuum line. Under protection from air, the residue was repeatedly extracted with small portions (2 mL) of warm, dry ethanol. The resulting residue was dried under reduced pressure, affording 2,5-difluoro-1,4-phenylene-3,3′-bis{[2-(4-trifluoromethyl)phenyl]acrylonitrile} photo dimer **4** in quantitative yield.

Colorless solid, M.p.: 251–253 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 5.68 (s, 2 H, cyclobutane–H), 7.36 (s, 2 H, phenyl), 7.70 (s, 2 H, ethenyl–H), 7.55 (d, 8 H, phenyl, $J = 8.2$ Hz), 7.72 (s, 2 H, phenyl), 7.83 (d, 8 H, phenyl, $J = 8.2$ Hz). EI-MS (M^+): 1007. Elemental

Table 2
Crystallographic and structural refinement data for monomer **3** and the dimer **4**.

Parameters measured	**3**	**4**
Empirical formula	$C_{26}H_{12}F_8N_2$	$C_{52}H_{24}F_{12}N_4\ C_6H_6$
Formula weight (g mol^{-1})	504.38	1164.97
Crystal shape, color	Prism, green	Prism, colorless
Temperature	90 K	90 K
Radiation type	Mo Kα	Mo Kα
Wavelength (Å)	0.7107	0.7107
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Unit cell dimensions	a = 6.960(6) Å b = 8.837(7) Å c = 17.761(15) Å α = 77.693(7)° β = 78.831(7)° γ = 84.346(7)°	a = 8.4365(10) Å b = 12.9867(15) Å c = 13.4147(15) Å α = 67.6410(10)° β = 78.7930(10)° γ = 85.7630(10)°
Volume	1045.2(15) Å^3	1333.3(3) Å^3
Z	2	1
Calculated density (Mg m^{-3})	1.603	1.451
Absorption coefficient (Mg m^{-3})	0.145	0.125
F(000)	508	592
Crystal size (mm)	0.45 × 0.25 × 0.15	0.50 × 0.45 × 0.20
Theta range for data collection	1.19–25.03°	1.67–25.03°
Limiting indices	−8 < h < 8, −10 < k < 10 0 < l < 21	−10 < h < 10, −15 < k < 15 −15 < l < 15
Reflections collected/unique	11,363/3652 [Rint = 0.253]	12,977/4690 [*R*int = 0.200]
Completeness to theta (%)	98.0	99.7
Max. and min. transmission	0.978 and 0.798	0.975 and 0.876
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3652/0/326	4690/0/379
Goodness-of-fit on F^2	1.408	1.037
Final *R* indices	*R*1 = 0.0603	*R*1 = 0.0432
[I > 2 sigma (I)]	*w*R2 = 0.1603	*w*R2 = 0.1144
R indices (all data)	*R*1 = 0.0817 *w*R2 = 0.1767	*R*1 = 0.0505 *w*R2 = 0.1259
Largest diff. peak and hole	0.430 and −0.382	0.628 and −0.498