Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Triisopropylsilylethynyl-Substituted Indenofluorenes: Carbonyl versus Dicyanovinylene Functionalization in One-Dimensional Molecular Crystals and Solution-Processed N-Channel OFETs

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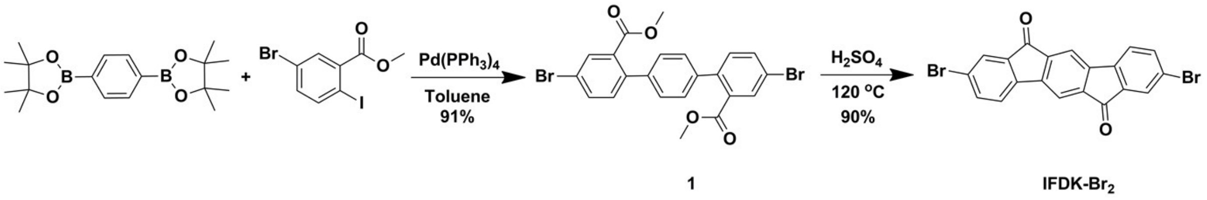


Scheme S1. Synthetic route to **IFDK-Br$_2$.**

Synthesis of dimethyl 4,4''-dibromo-[1,1':4',1''-terphenyl]-2,2''-dicarboxylate (1). Tetrakis(triphenylphosphine)palladium (0.529 g, 0.458 mmol) and sodium carbonate solution (1M) were added into a solution of 1,4-benzenediboronic acid bis(pinacol) ester (2.518 g, 7.63 mmol), methyl 5-bromo-2-iodobenzoate (5.697 g, 16.71 mmol), and aliquat 336 (0.911 mL, 1.98 mmol) in 55 mL of anhydrous toluene under nitrogen. The resulting mixture was stirred at 135 ℃ for 2 days. After completing reaction, it was allowed to cool down to room temperature. The reaction mixture was poured into water to yield a white precipitate. Then, it was extracted with hexane, dried with Na_2SO_4, filtered and concentrated to get the crude product. The crude was then purified through column chromatography on silica gel using dichloromethane as mobile phase to afford the final product as a white crystalline solid. (3.50 g, 91% yield).^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 3.71 (s, 6H), 7.32 (m, 6H), 7.67 (dd, 2H, J = 8.0 Hz and J = 2.0 Hz), 8.00 (d, 2H, 2.0 Hz).

Synthesis of 2,8-dibromoindeno[1,2-b]fluorene-6,12-dione (IFDK-Br$_2$). The solution of dimethyl 4,4''-dibromo-[1,1':4',1''-terphenyl]-2,2''-dicarboxylate **(1)** (0.550 g, 1.09 mmol) in 76-78% H_2SO_4 (50 mL) was kept stirring overnight at 120 °C. The reaction was then cooled down to room temperature and quenched with ice to yield a dark red precipitate. The precipitate was collected by vacuum filtration, and washed with water, saturated solution of sodium hydrogen carbonate, and methanol, respectively, to obtain the crude product. The crude was then purified through thermal gradient sublimation under high vacuum to afford pure product as a cherry red crystalline solid (0.427 g, 90% yield). During the sublimation single-crystals of this compound was also obtained. m.p.> 390 °C. Anal.calcd. for $C_{20}H_8O_2Br_2$: C, 54.58; H, 1.83 Found: C, 54.70; H, 1.96.

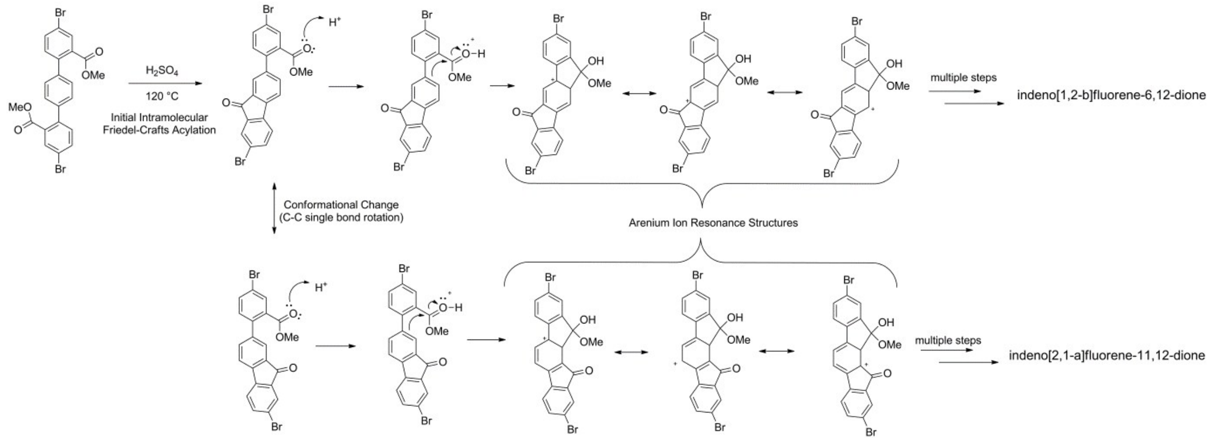
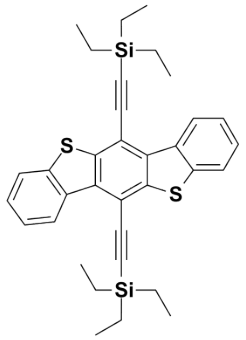


Figure S1. Proposed mechanisms for the second intramolecular Friedel-Crafts acylation reaction in the formation of indeno[2,1-*a*]fluorene-11,12-dione and indeno[1,2-*b*]fluorene-6,12-dione isomers showing plausible arenium resonance structures.



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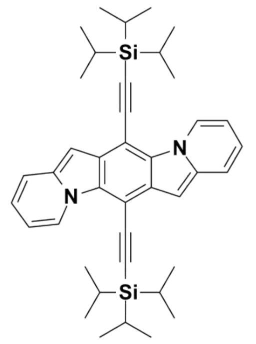

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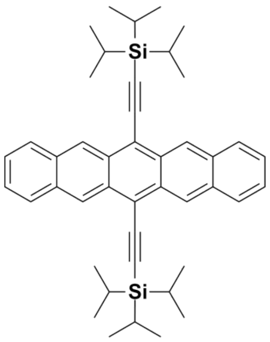

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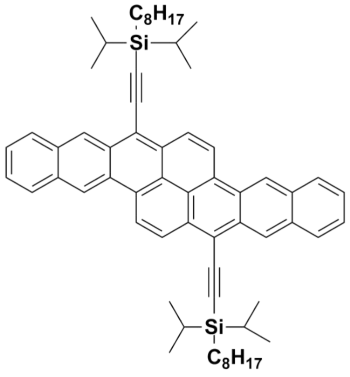

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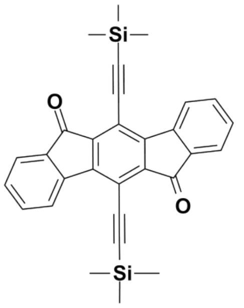

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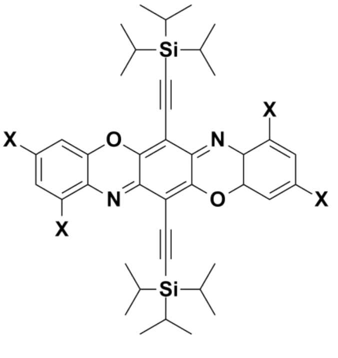


6, X=H
7, X=CN

Figure S2. Chemical structures of representative molecular semiconductors **1**[1], **2**[1], **3**[1–4], **4**[5], **5**[6], **6**[7], and **7**[8] substituted with (trialkylsilyl)ethynyl units on their short molecular axes.

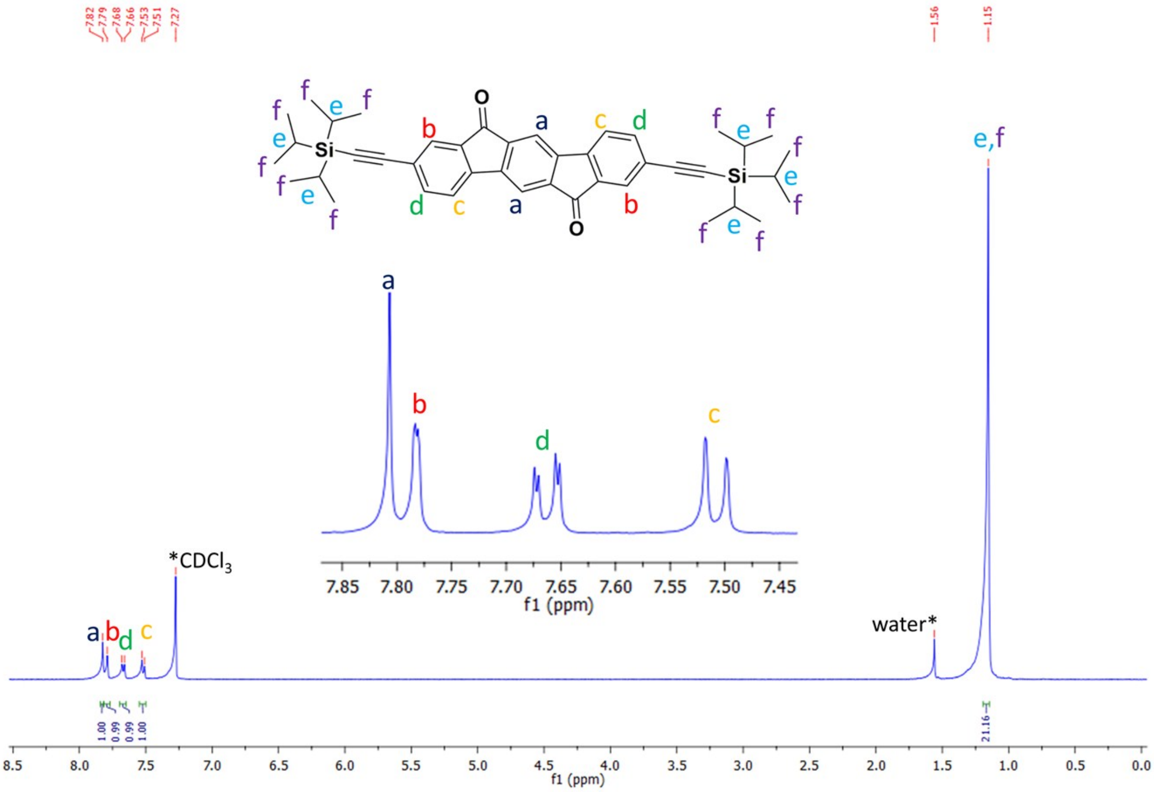


Figure S3. ^{1}H NMR spectra of **TIPS-IFDK** measured in $CDCl_3$ (inset shows the spectral region for aromatic protons).

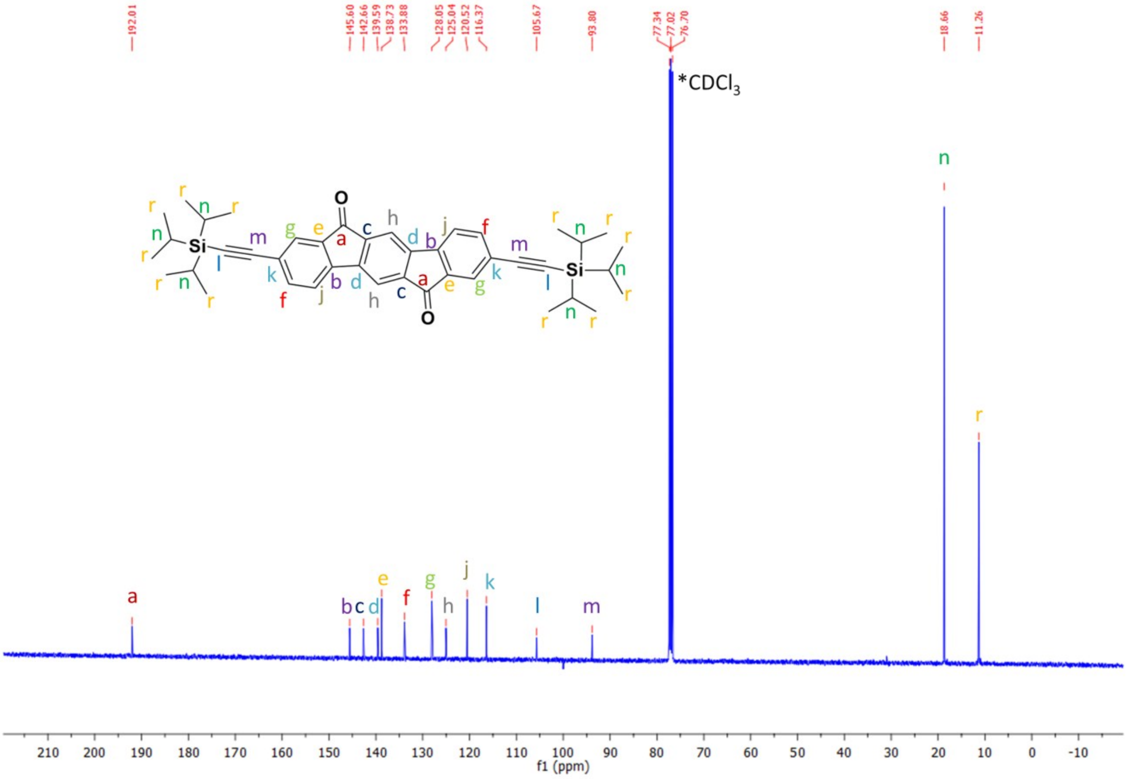
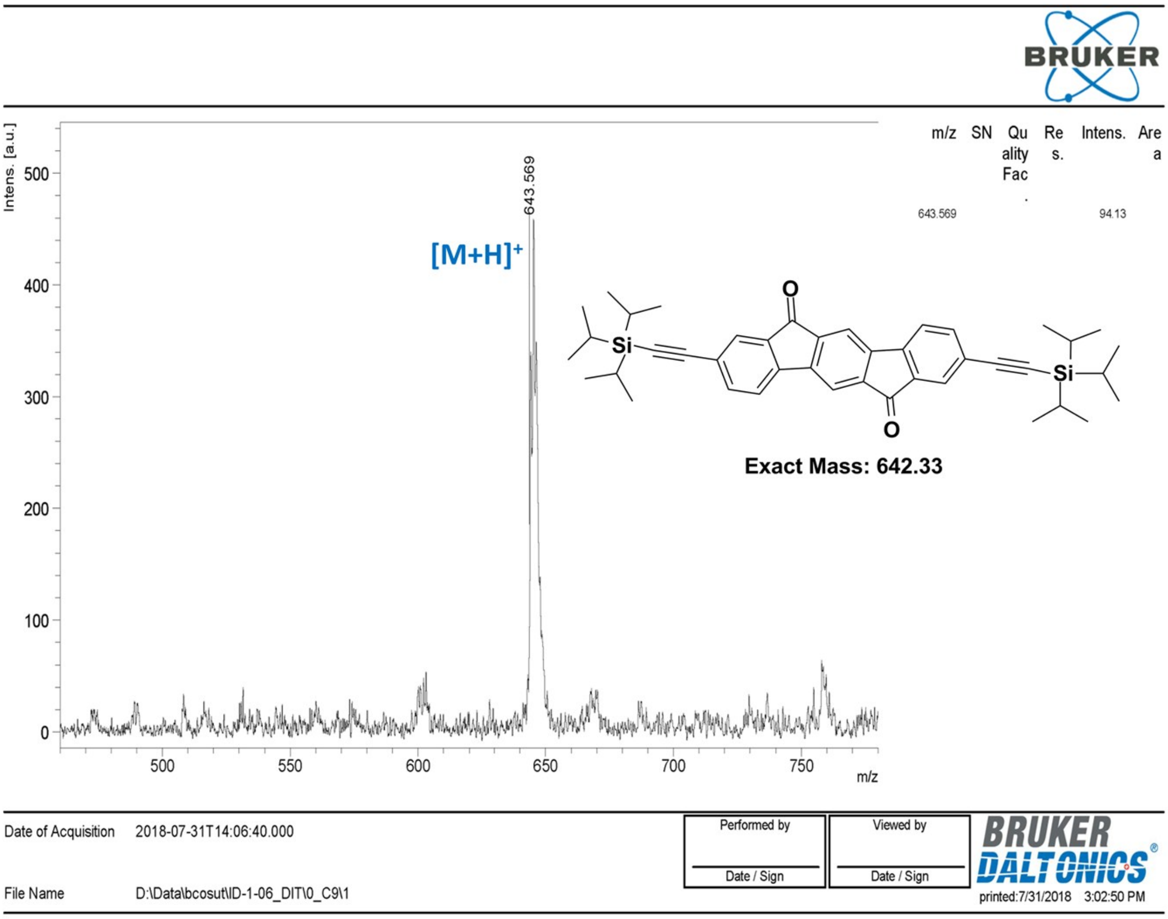


Figure S4. ^{13}C NMR spectra of **TIPS-IFDK** measured in $CDCl_3$.



m/z	SN	Quality Fac.	Res.	Intens.	Area
643.569				94.13	

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Figure S5. Positive ion and linear mode MALDI TOF-MS spectrum of **TIPS-IFDK**.

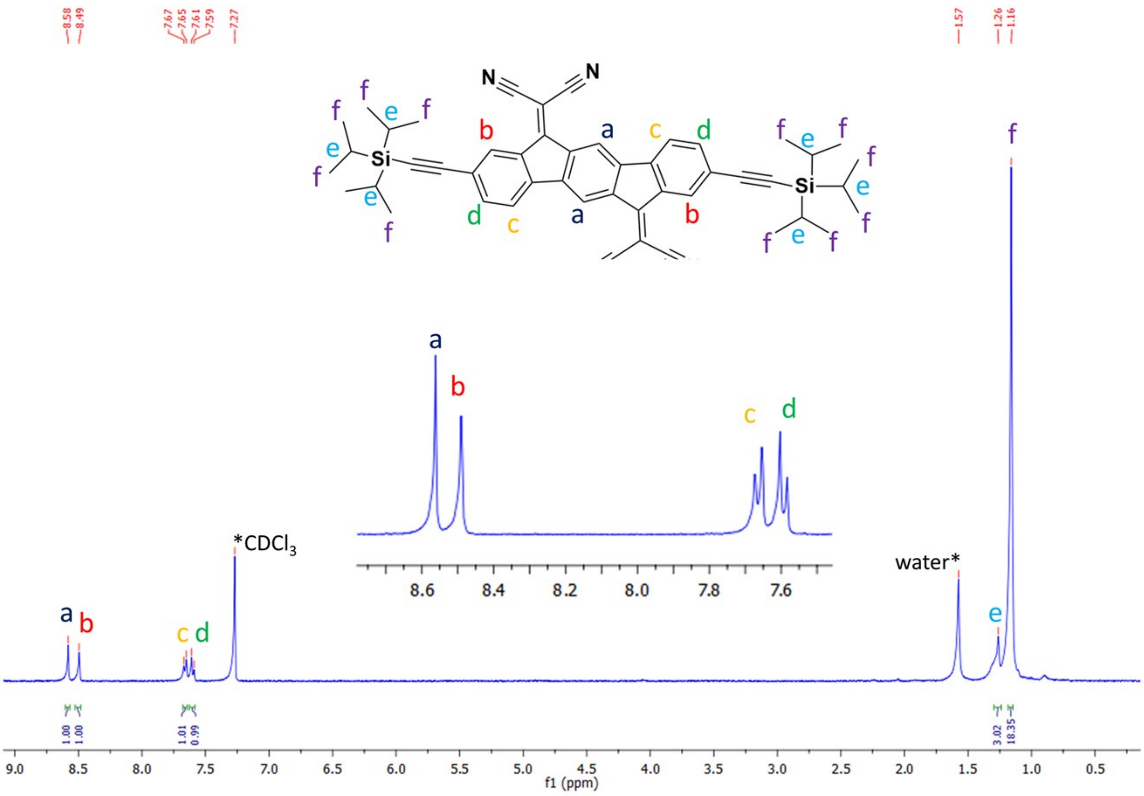


Figure S6. ^{1}H NMR spectra of **TIPS-IFDM** measured in $CDCl_3$ (inset shows the spectral region for aromatic protons).

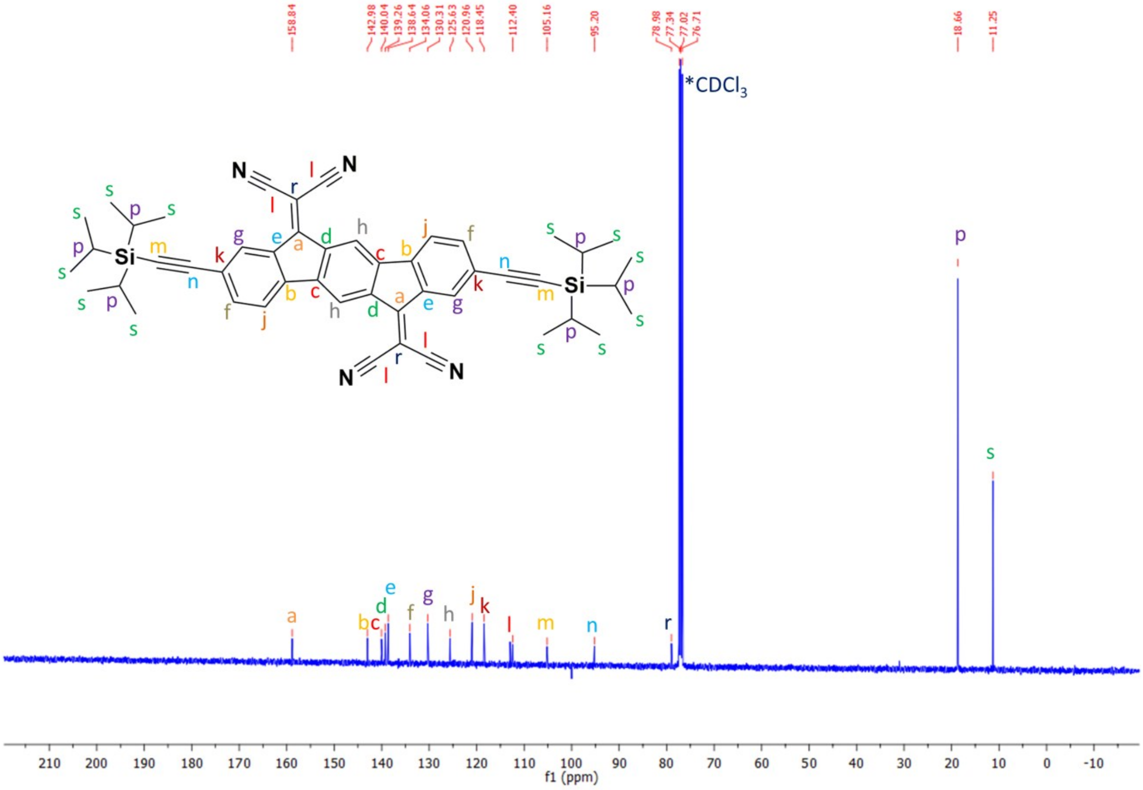
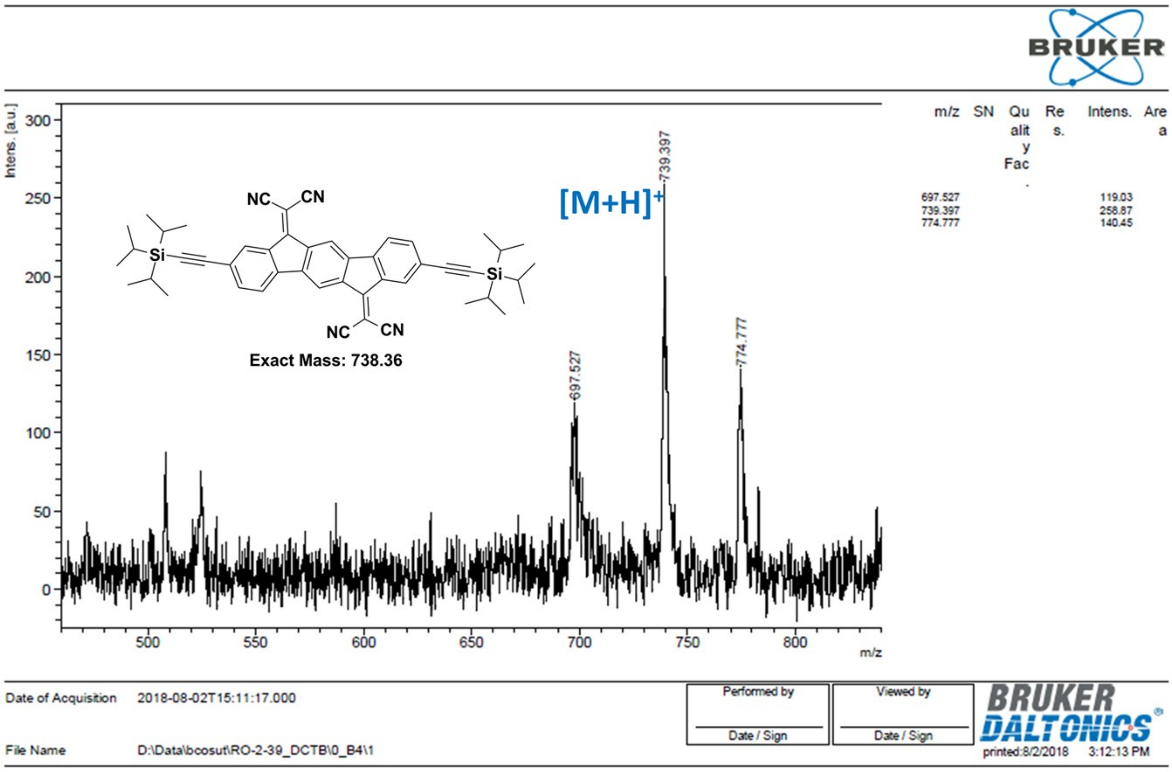


Figure S7. ^{13}C NMR spectra of **TIPS-IFDM** measured in $CDCl_3$.



m/z	SN	Quality Fac.	Res.	Intens.	Area
697.527				119.03	
739.397				258.87	
774.777				140.45	

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Figure S8. Positive ion and linear mode MALDI TOF-MS spectrum of **TIPS-IFDM**.

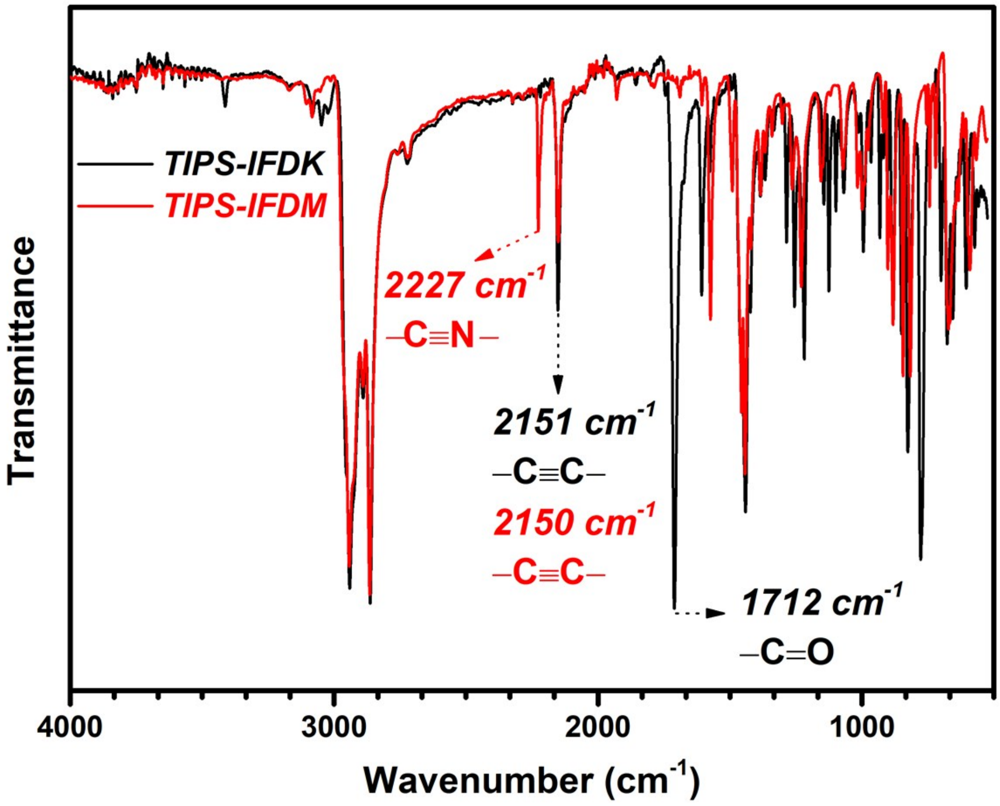


Figure S9. ATR FTIR Spectra of the semiconductors **TIPS-IFDK** and **TIPS-IFDM** showing key stretching vibrational peaks.

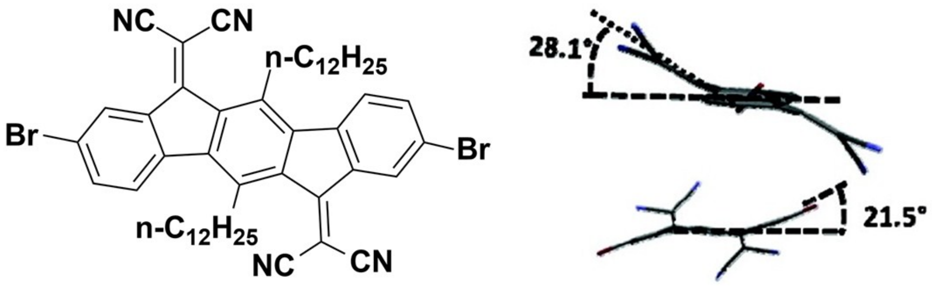
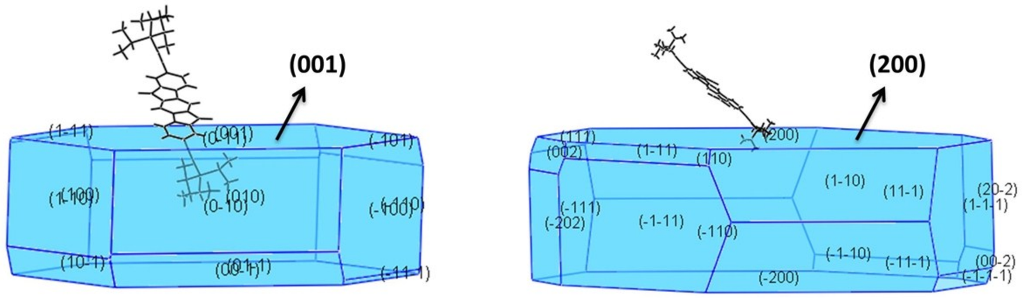


Figure S10. The chemical structure of 2,2'-(2,8-Dibromo-5,11-didodecylindeno[1,2-b]fluorene-6,12-diylidene)dimalononitrile, and its “wavy” molecular structure determined by single-crystal X-ray analysis in the corresponding reference.[9]



TIPS-IFDK **TIPS-IFDM**

Figure S11. The BFDH (Bravais, Friedel, Donnay and Harker) theoretical crystal morphologies for **TIPS-IFDK** and **TIPS-IFDM** showing the corresponding (001) and (200) crystal planes.

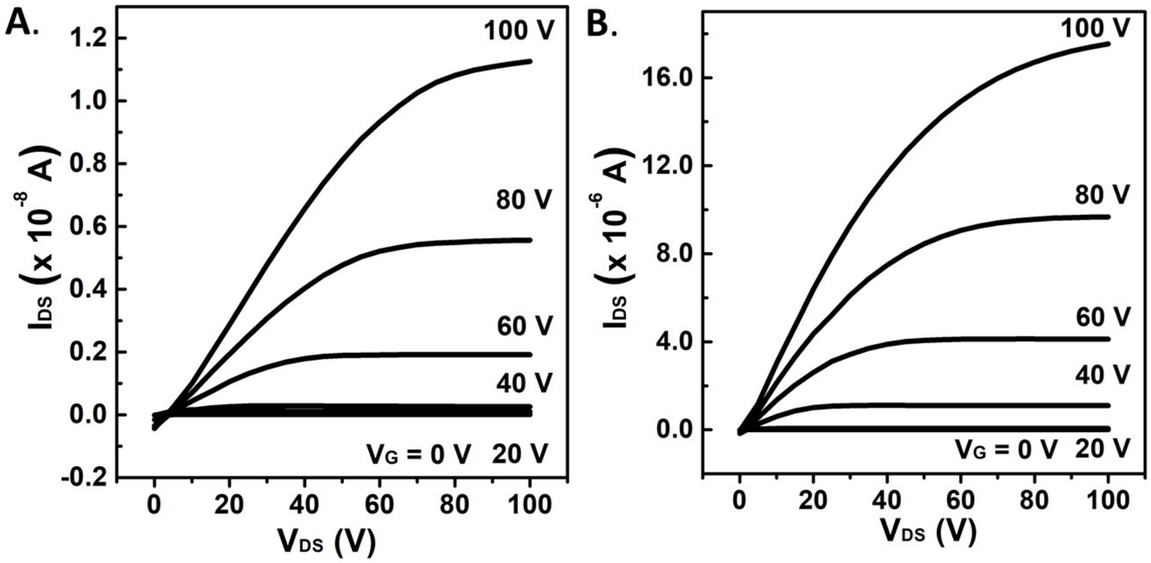


Figure S12. Representative output curves in the *n*-channel region for Au/semiconductor/PS(polystyrene)-brush/SiO$_2$(300 nm)/n^{++}-Si top-contact/bottom-gate (TC-BG) OFET devices fabricated with solution-sheared **TIPS-IFDK** (A) and **TIPS-IFDM** (B) semiconductor thin-films.

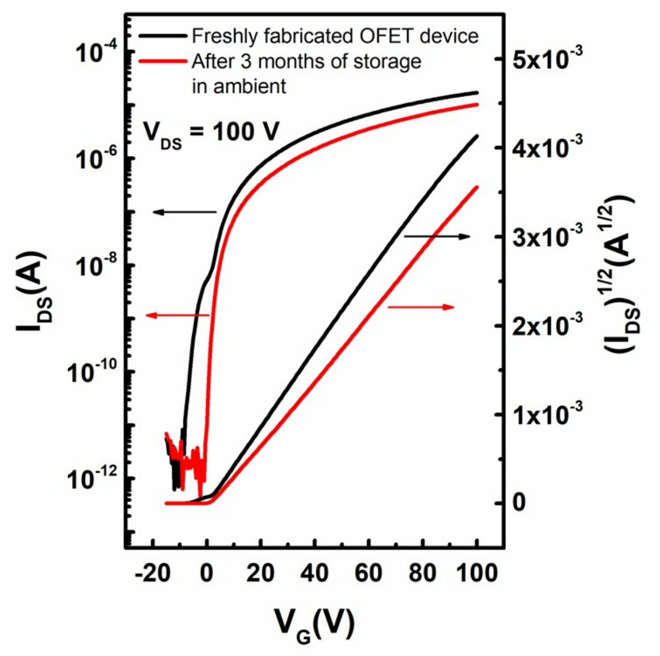


Figure S13. Transfer curves in the *n*-channel region for freshly fabricated Au/TIPS-IFDM/PS(polystyrene)-brush/SiO$_2$(300 nm)/n^{++}-Si top-contact/bottom-gate (TC-BG) OFET device (black line) and after 3 months storage in ambient without exclusion of humidity and light (red line).

X-ray data collection and structure refinement

Data were obtained with Bruker APEX II QUAZAR three-circle diffractometer. Indexing was performed using APEX2 [APEX2, version 2014.11-0, Bruker (2014), Bruker AXS Inc., Madison, WI]. Data integration and reduction were carried out with SAINT [SAINT, version 8.34A, Bruker (2013), Bruker AXS Inc., Madison, WI]. Absorption correction was performed by multi-scan method implemented in SADABS [SADABS, version2014/5, Bruker (2014), Bruker AXS Inc., Madison, WI.]. The structure was solved using SHELXT[10] and then refined by full-matrix least-squares refinements on F^2 using the SHELXL[11] in SHELXTL Software Package [Bruker, SHELXTL, version 6.14, Bruker AXS Inc., Madison, Wisconsin, USA, 2010]. All non-hydrogen atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. Aromatic and aliphatic C-bound H atoms were positioned geometrically and refined using a riding mode. Crystallographic data and refinement details of the data collection for compounds **TIPS-IFDK** and **TIPS-IFDM** are given in Table 1. Crystal structure validations and geometrical calculations were performed using Platon software[12,13] Mercury software[14] was used for visualization of the cif files. Additional crystallographic data with CCDC reference numbers 1854236 (**TIPS-IFDK),** 1854237 (**TIPS-IFDM)** have been deposited within the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/deposit.

Table 1. Crystal data and refinement parameters for compounds **TIPS-IFDK** and **TIPS-IFDM**.

	TIPS-IFDK	**TIPS-IFDM**
CCDC	1854236	1854237
Empirical Formula	$C_{42}H_{50}O_2Si_2$	$C_{48}H_{50}N_4Si_2$
Formula weight (g. mol^{-1})	643.00	739.10
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*C*2/*c*
a **(Å)**	7.6019(6)	39.755(5)
b **(Å)**	7.7795(7)	10.0294(12)
c **(Å)**	17.7908(15)	11.4351(14)
α(°)	94.036(5)	90
β(°)	92.577(5)	102.874(8)
γ(°)	114.867(4)	90
Crystal size (mm)	0.04 x 0.36 x 0.47	0.03 x 0.32 x 0.41
V **(Å^3)**	948.98(14)	4444.8(9)
Z	1	4
ρ_{calcd} (g. cm^{-3})	1.125	1.104
μ (mm^{-1})	0.126	0.115
***F*(000)**	346	1576
θ range for data collection (°)	2.96 -25.00	2.10 - 25.03
h/k/l	-9<=h<=9, -9<=k<=9, -21<=l<=21	-37<=h<=47, -11<=k<=11, -13<=l<=10
Reflections collected	13766	16272
Independent reflections	3303 [R(int) = 0.0573]	3918 [R(int) = 0.0967]
Data/restraints/parameters	3303 / 0 / 214	3918 / 19 / 250
Goodness-of-fit on F^2 (S)	1.078	1.016
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0860, wR_2 = 0.2596	R_1 = 0.1097, wR_2 = 0.3031
R **indices (all data)**	R_1 = 0.0982, wR_2 = 0.2746	R_1 = 0.2020, wR_2 = 0.3730
Largest diff. peak and hole (e.Å^{-3})	0.978 and -0.381	0.414 and -0.234

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