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# Core-Fluorinated Naphthalene Diimides: Synthesis, Characterization, and Application in n-Type Organic Field-Effect Transistors

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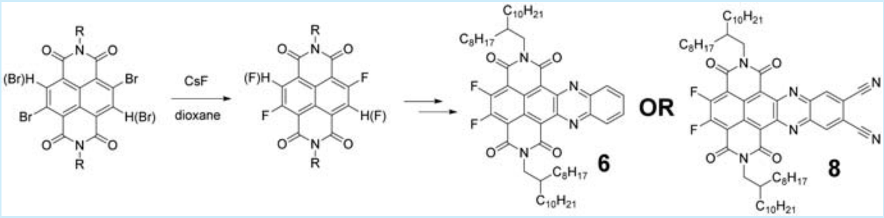
S Supporting Information

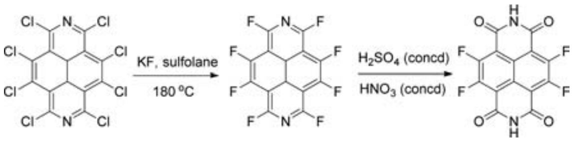


**ABSTRACT:** A series of difluoro- and tetrafluoro-substituted naphthalene diimides (NDIs) were synthesized by halogen exchange reactions of corresponding bromo-NDIs with CsF in dioxane. Two strong electron acceptor molecules **6** and **8** with low-lying LUMO energy levels of −4.27 and −4.54 eV were obtained, starting from tetrafluoro-NDI. Organic field-effect transistors (OFETs) based on these fluorinated NDIs were fabricated by vapor deposition, exhibiting n-channel field-effect character under ambient conditions with the highest mobility of 0.1 $cm^2\ V^{-1}\ s^{-1}$.

Organic semiconductors are used for high throughput, low-cost electronic circuitry on flexible substrates.[1] High-performance n-type semiconductors are still rare compared to their p-type counterparts.[2] Besides fullerenes, naphthalene diimides (NDIs) with compact and electron deficient cores have demonstrated potential as n-type semiconductors in organic field-effect transistors (OFETs) and solar cells.[3] Although the unsubstituted NDIs display an electron mobility as high as 6.2 $cm^2\ V^{-1}\ s^{-1}$, the OFET devices degrade significantly in air.[4] To obtain air-stable semiconducting NDIs, electron-withdrawing cyano, perfluoroalkyl, and chloro groups have been introduced to the conjugated cores of NDIs toward lower-lying LUMO energy levels and better air stability.[5]

Many chloro and bromo substituted NDIs turned out to be extraordinary n-type semiconductors.[6,7] For example, dichloro-NDIs and tetrachloro-NDIs have been proven to be air-stable n-type semiconductors with a high charge carrier mobility of 8.6 $cm^2\ V^{-1}\ s^{-1}$ based on single crystal OFETs.[8] In this regard, fluorinated NDIs with similar electron affinity are expected to be air-stable and good substrates for further nucleophilic substitutions.[9] However, to date, only a 1988 patent described the synthesis of tetrafluoro-NDIs, in that case starting from a perchlorinated diazapyrene (Scheme 1),[10] and neither further functionalization nor tetrafluoro-NDI derivatives were reported after that. Another recent paper reported the synthesis of difluoro-NDI derivatives with the fluoronation method of perylene diimides.[9,11] Herein, we synthesized a series of tetrafluoro- and difluoro-NDIs with a concise procedure (Scheme 2). OFETs based on these fluorinated NDIs were fabricated by vapor deposition. Strong electron acceptor molecules **6** and **8** were obtained starting from tetrafluoro-NDIs, and their LUMO energy levels are 0.64 and 0.91 eV lower than that of unsubstituted NDIs, respectively.

**Scheme 1. Sole Reported Synthesis of Tetrafluoro-NDI**



As shown in Scheme 2, fluorinated NDIs **2a−d**[11] and **4a−b** were obtained as colorless solids by halogen exchange reactions, starting from dibromo-NDIs and tetrabromo-NDIs, respectively. Our initial attempts with starting material **3a** using common halogen displacement conditions such as potassium fluoride (KF) in dry DMSO or sulfolane produced no target compounds, but instead only some dark spots were observed on TLC plates. When dry dioxane and CsF were employed as nonnucleophilic solvent and the fluoride source, respectively, high yields were obtained upon reflux (~101 °C) or microwave heating. A much higher temperature (>200 °C) is essential when KF is used instead of CsF. Tetrafluoro-NDIs **4** are readily attacked by nucleophiles because of their electron-deficient cores. For example, they react with water in refluxing dioxane and are even somewhat unstable to silica gel chromatography. In contrast, difluoro-NDIs **2** with less electron-withdrawing F

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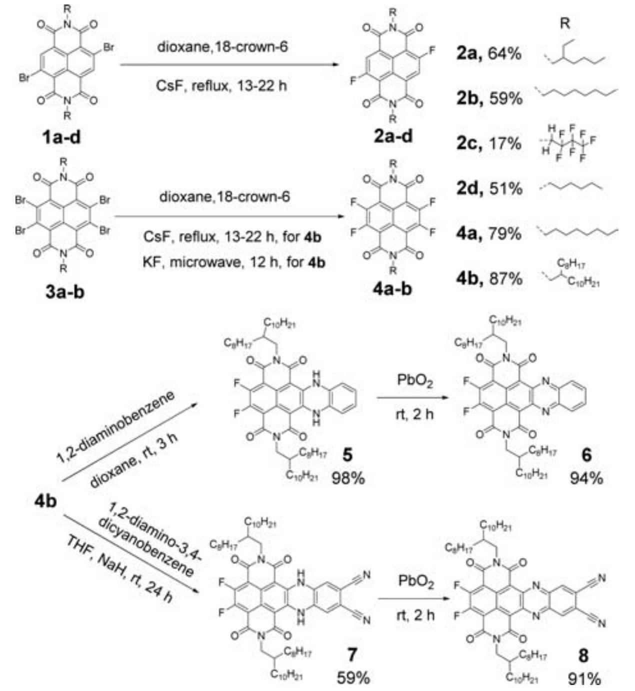
Scheme 2. Synthesis of Compounds 2a−d, 4a−b, 6, and 8



atoms are chemically more stable than tetrafluoro-NDIs and can be purified through silica gel columns conveniently. Therefore, several difluoro-NDIs **2** with different side chains were synthesized and purified for further applications in electronic devices.

Taking advantage of the high reactivity of tetrafluorinated NDIs, nucleophilic substitutions of **4b** with 1,2-diaminobenzene and 1,2-diamino-4,5-dicyanobenzene afforded **5** and **7**, respectively. Subsequently, strong acceptors **6** and **8** were obtained by oxidation of **5** or **7** in $PbO_2$ at room temperature in yields higher than 90%.

The above new compounds **2a**, **2b**, **2c**, **4a**, **4b**, **6**, and **8** were characterized unambiguously by $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, and HRMS. The poor solubility of **2c** prevented collection of $^{13}$C NMR data while single crystals suitable for X-ray analysis could be grown. Single crystals of **2b** and **4a** were obtained by slow diffusion of methanol into $CH_2Cl_2$ solutions. All three crystals belong to the monoclinic $P2_1/c$ space group, and exhibit herringbone arrangements (Figures 1 and S1−S2).[5e] Compound **4a** with four fluorine atoms at the NDI core has a nearly planar conjugated core (torsion angles ≤1.6°), while **2c** bears a slightly twisted core with a torsional angle up to 3.0°. The smaller size of fluorine atoms (atomic radius: F, 0.5 Å vs Cl, 1.0 Å) decreases the repulsion between F and neighboring O; thus, the twisting within NDI cores is much less than that of tetrachloro-NDIs and dichloro-NDIs (with a torsional angle up to 7.2° and 5.1° respectively).[5e,12] Considering that bisheptafluorobutyl-substituted 2,6-dichloro-NDI exhibits the best FET performance in the series of halogenated NDIs, it is important to compare the packing behavior of **2c** and **4a** with that of dichloro-NDI. As shown in Figure 1, despite their smaller F-substituents, **2c** and **4a** stack with larger $\pi-\pi$ interaction distances of 3.372 and 3.299 Å, smaller slipping angles of 48° and 46°, and lower packing densities of 2.021 and 1.397 g cm$^{-3}$, respectively, compared with those of bisheptafluorobutyl-substituted 2,6-dichloro-NDI (packing distance, slipping angle, and packing density are 3.274 Å, 62°, and 2.046 g cm$^{-3}$, respectively).[8a]

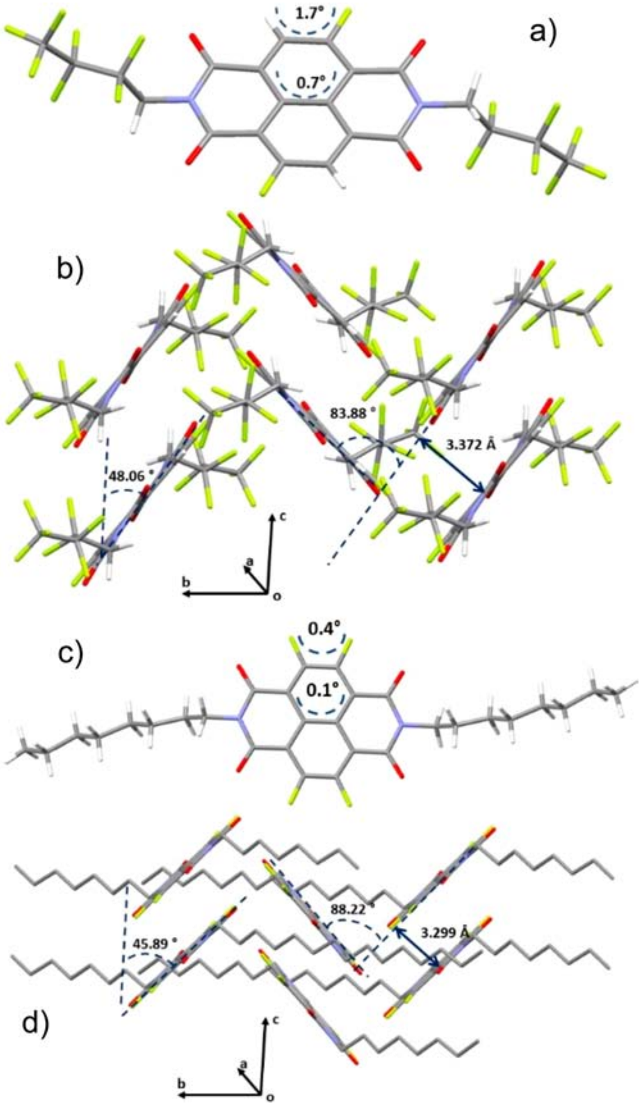


Figure 1. (a) Single crystal structure of **2c**. (b) Herringbone packing mode of **2c** molecules in the single crystal. (c) Single crystal structure of **4a**. (d) Herringbone packing mode of **4a** molecules in the single crystal.

Cyclic voltammetry was measured for these fluorinated naphthalene diimides with *N,N′*-bis(2-ethylhexyl)naphthalene diimide (**RNDI**) as a reference. The reduction potentials and estimated LUMO and HOMO energies are summarized in Table 1. As shown in Figures S3−S4, all compounds exhibit two reversible reduction waves but no oxidation waves within the accessible scanning potential range in $CH_2Cl_2$. For all fluorinated NDI molecules, both the first and the second reduction waves are at lower potentials (by 0.16−0.91 eV) than those of **RNDI**. They are stronger acceptors than core-unsubstituted NDIs. Notably, the LUMOs of **6** and **8** are as low as −4.27 and −4.54 eV pointing toward ultrastrong acceptors.

The UV−vis absorption spectra of difluoro-NDI **2b**, tetrafluoro-NDI **4a**, **RNDI**, **6**, and **8** in $CH_2Cl_2$ are displayed in Figure 2. Core-fluorinated NDIs (**2b** and **4a**) have no absorption in the visible range. Optical energy gaps of **2b** and **4a** are 3.10 and 3.18 eV, close to that of unsubstituted **RNDI**

**Table 1. Half-Wave Reduction Potentials (in V vs Fc/Fc$^+$), Optical Band Gaps, and LUMO and HOMO energies of 2a–d, 4a–b, 6, 8, and RNDI**

|  | $E$ (M/M$^{-1}$)[a] | $E$ (M$^{-1}$/M$^{-2}$)[a] | LUMO (eV)[b] | HOMO (eV)[c] |
|---|---|---|---|---|
| **2a** | −1.01 | −1.50 | −3.79 | −6.87 |
| **2b** | −1.00 | −1.46 | −3.80 | −6.89 |
| **2c** | −0.83 | −1.32 | −3.97 | −7.05 |
| **2d** | −1.07 | −1.58 | −3.73 | −6.81 |
| **4a** | −0.95 | −1.42 | −3.85 | −7.03 |
| **4b** | −0.98 | −1.48 | −3.82 | −7.00 |
| **6** | −0.53 | −0.96 | −4.27 | −6.26 |
| **8** | −0.26 | −0.80 | −4.54 | −6.61 |
| RNDI[d] | −1.17 | −1.63 | −3.63 | −6.78 |

[a] Measured in $Bu_4NPF_6$ solution in $CH_2Cl_2$ with a scan rate of 100 mV/s. [b] Ferrocene serves as internal standard. The energy of Fc/Fc$^+$ is assumed at −4.8 eV relative to vacuum.[13] [c] Calculated with the formula HOMO = LUMO − optical energy gap. [d] *N,N′*-Bis(2-ethylhexyl) naphthalene diimide.

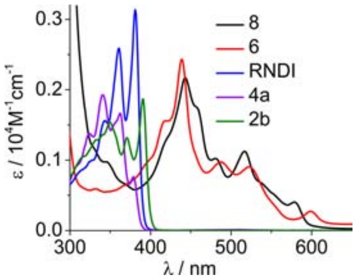


Figure 2. UV–vis absorption of **2b**, **4a**, **RNDI**, **6**, and **8** in $CH_2Cl_2$ ($10^{-5}$ mol/L).

(3.15 eV), which indicates that F substituents lower the LUMO and HOMO energies simultaneously.

We evaluated the charge carrier transport properties of the compounds **2a**, **2b**, **2c**, **4a**, **4b**, and **6** by fabricating field-effect transistors (FETs) in a "bottom-contact top-gate" geometry. To this end, degenerately doped silicon wafers that had been coated with 30 nm of $Al_2O_3$ grown via atomic layer deposition were functionalized with a tetradecylphosphonic acid self-assembled monolayer. Subsequently, the organic semiconductors were thermally evaporated onto these substrates. In order to tune the morphology of the semiconductors during the vacuum deposition, the substrates were held at five different temperatures between 30 and 120 °C during deposition of the small molecules. Silver source and drain contacts were subsequently patterned via thermal evaporation through a shadow mask to define the semiconducting channel (width, 500 $\mu$m; length, 50 $\mu$m). All electrical measurements were performed in ambient air in the darkness using a B1500 semiconductor parameter analyzer (Keysight). While compounds **4b** and **6** did not show charge transport, FETs based on compounds **2a** and **2b** yielded an n-type charge carrier mobility of around $10^{-3}$ cm$^2$/(V s). The best electrical data were obtained with compounds **4a** and **2c**, whose transfer curves are shown in Figure 3. Transistors based on **2c** had a maximum electron mobility $\mu$ of 0.1 cm$^2$/(V s), an on/off ratio of close to $10^4$, and a threshold voltage ($V_{th}$) of −9 V when deposited at a substrate temperature of 40 °C. FETs based on **4a** had a maximum electron mobility of 0.02 cm$^2$/(V s), with an on/off ratio of $10^2$ and a $V_{th}$ of −9.6 V when deposited at a substrate temperature of 100 °C. It is worthy to note that the FET results of both **4a** and **2c** are not as good as those of chlorinated NDIs. Especially, the transfer curve of **4a** shows an S-shape. The poor FET performance indicates the possible poor contact between the semiconductors and the electrodes. The major reason for this weak interaction could be due to the small slipping angle of the stack (48° for **2c**, 46° for **4a**, but 62° for bisheptafluorobutyl-substituted 2,6-dichloro-NDI) and the small dihedral angle (84° for **2c**, 88° for **4a**, but 139° for bisheptafluorobutyl-substituted 2,6-dichloro-NDI) of the edge-to-face herringbone arrangement in the crystal structure.

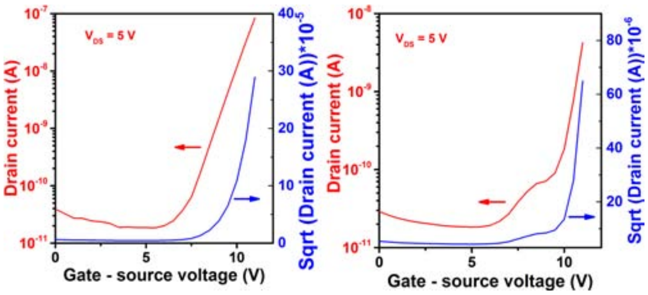


Figure 3. Transfer curve of compound **2c** (left) and **4a** (right) measured in ambient air in the dark.

In conclusion, difluoro- and tetrafluoro-NDIs have been synthesized with a facile procedure. These compounds feature high planarity, dense packing in the solid, and short interplanar distances and exhibit a maximum electron mobility $\mu$ of 0.1 cm$^2$/(V s). Ultrastrong acceptors **6** and **8** were obtained from tetrafluoro-NDIs. A number of nucleophilic replacement reactions may be further used to explore new compounds based on these electron-deficient fluorinated-NDIs. Similar to chlorine, the fluorine atoms could also impart sufficient electron-withdrawing character to the NDI cores to stabilize injected electrons against environmental traps, and it is possible to screen more high-performance air-stable n-type semiconductors from fluorinated NDIs.

## ■ ASSOCIATED CONTENT

### Supporting Information

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Full experimental details and characterization data (PDF)

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### Notes

The authors declare no competing financial interest.

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