

Electronics Supplementary Information (ESI)

Nitroaromatics as n-type organic semiconductors for field effect transistors

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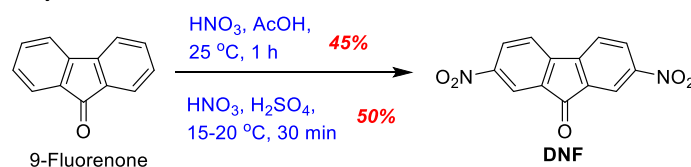
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Contents

| | |
|----------------------------------------------------|----|
| 1. Synthesis of nitrofluorenones | 1 |
| 2. OFET fabrication and characterization | 6 |
| 3. Cyclic voltammetry measurements | 8 |
| 4. Thermogravimetric analysis (TGA) | 9 |
| 5. UV-Vis absorption spectra measurements..... | 9 |
| 6. DFT calculations..... | 9 |
| 7. Single crystal X-ray diffraction analysis | 13 |
| 8. References | 16 |

1. Synthesis of nitrofluorenones

2,7-Dinitrofluorenone (DNF).

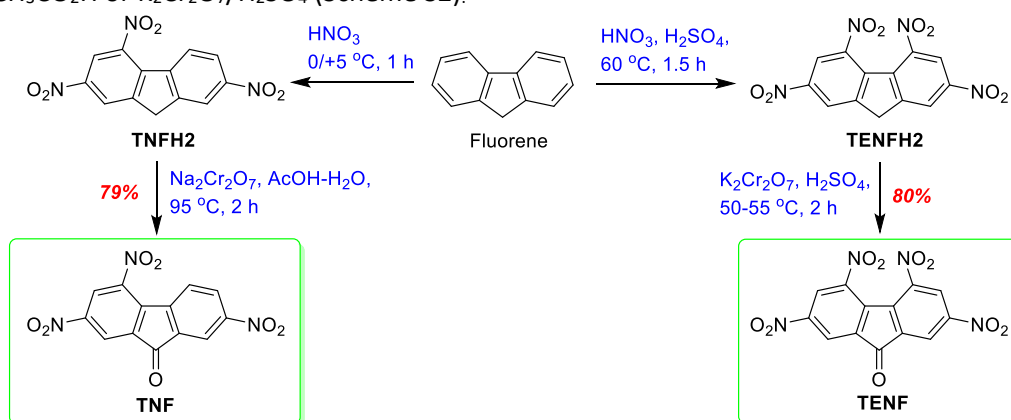


Scheme S1. Synthesis of **DNF**.

(Method A). 9-Fluorenone (2.00 g, 11.1 mmol) was added to the stirred mixture of fuming nitric acid (20 mL; $d = 1.51\text{ g/mL}$) and acetic acid (10 mL). Full dissolution was observed. The mixture was stirred at +25 °C for 1 hour and left to crystallize. DNF is crystallized from the reaction mixture as long yellow needles. It was filtered off, washed with small portions of cold acetic acid, then with water until pH7 and dried to afford pure **DNF**, 1.35 g (45%), m.p. 294–296 °C. Additional crystallization from acetic acid gave analytically pure sample with m.p. 296–297 °C.

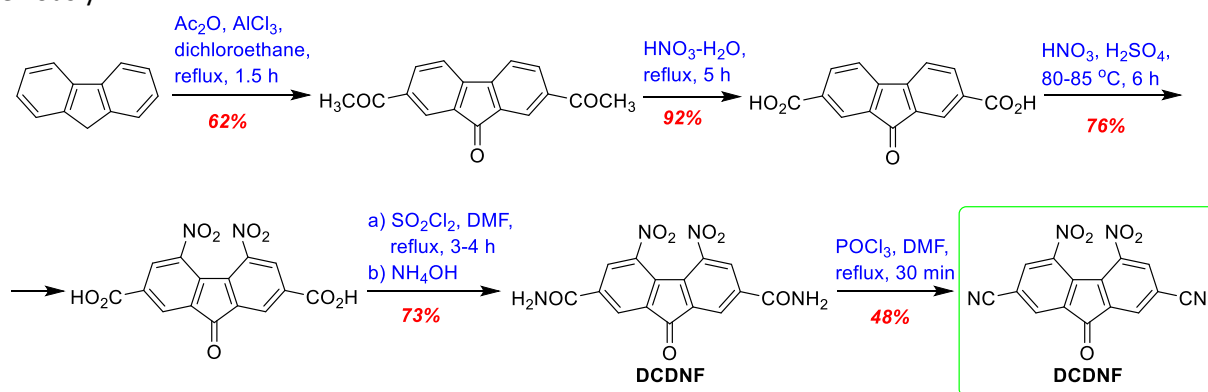
(Method B). 9-Fluorenone (3.00 g, 16.6 mmol) was dissolved in concentrated sulfuric acid (30 mL; $d = 1.84$ g/mL) at room temperature to form dark red solution. The solution was cooling to +5–10 °C and with stirring, fuming nitric acid (2.0 mL; $d = 1.51$ g/mL) was slowly added dropwise, keeping the temperature below +(15–20) °C. The mixture was stirred at +(15–20) °C for 30 min, the formed precipitate was filtered off, washed with water until pH7 and dried to afford crude product (2.71 g, 60%) as yellow solid, m.p. 290–295 °C. Crude product was recrystallized from acetic acid (400 mL) to afford pure **DNF** (2.25 g, 50%) as long yellow needles, m.p. 296–297 °C.
(Lit. m.p.: 293–295 °C,^{1,2} 296 °C,³ 289–290 °C.⁴)

2,4,7-Trinitrofluorenone (TNF) and **2,4,5,7-tetranitrofluorenone (TENF)** were obtained by nitration of fluorene by fuming nitric acid or its mixture with concentrated sulfuric acid to form 2,4,7-trinitrofluorene (**TNFH2**)^{5,6} or 2,4,5,7-tetranitrofluorene (**TENFH2**)^{5,7,8}, respectively, following their oxidation by $\text{Na}_2\text{Cr}_2\text{O}_7/\text{CH}_3\text{CO}_2\text{H}$ or $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (Scheme S2).⁹



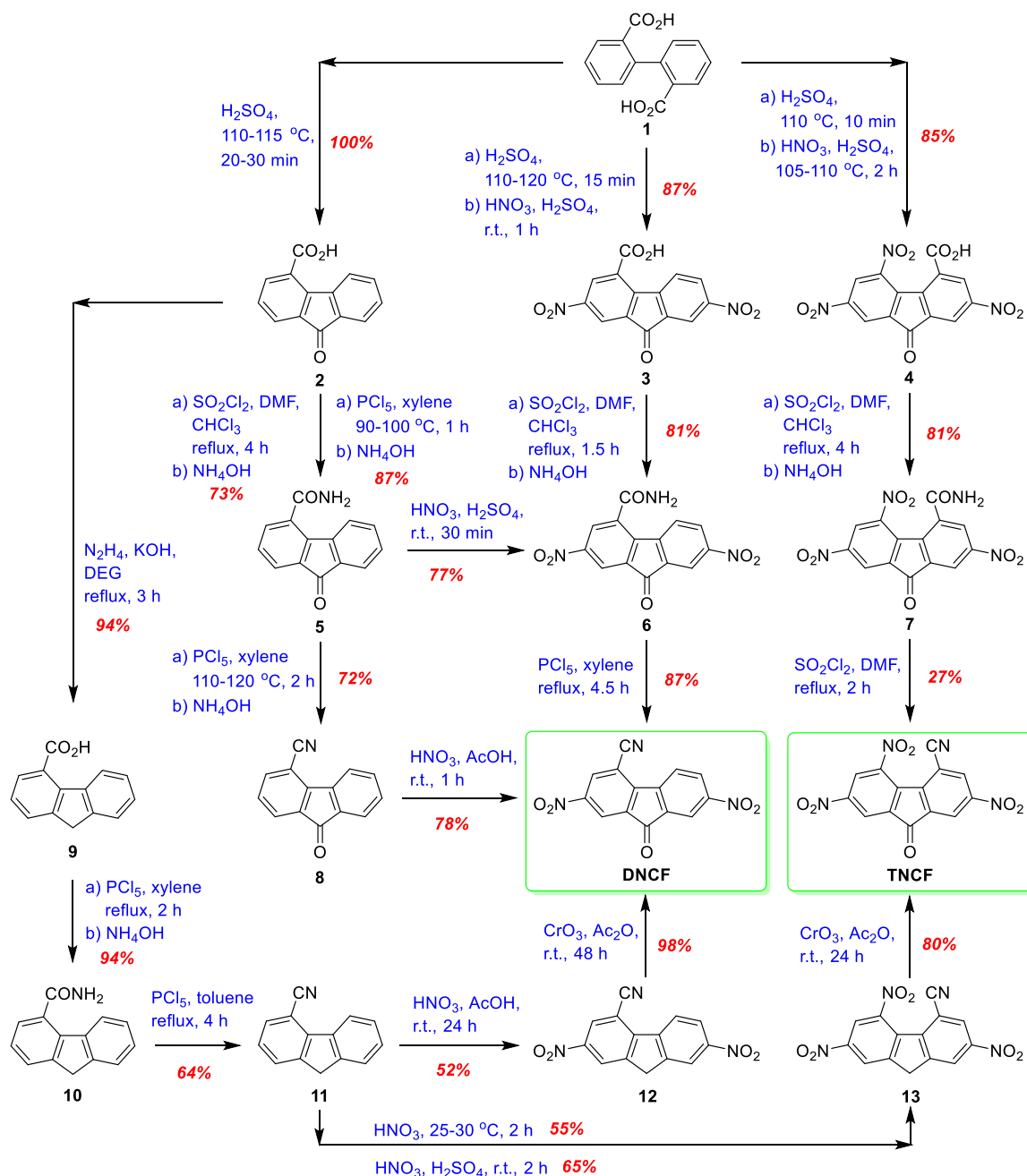
Scheme S2. Synthesis of **TNF** and **TENF**.^{5–9}

2,7-Dicyano-4,5-dinitrofluorenone (DCDNF) was obtained according to Scheme S3 as we described previously.¹⁰



Scheme S3. Synthesis of **DCDNF**.¹⁰

DNCF, **TNCF** and intermediates **5–13** were obtained according to Scheme S4 using methods described in our previous work,^{11,12,13,14} with slightly modified/amended procedures. Compounds **2–4** were obtained from diphenic acid (**1**) as described previously.¹⁵



Scheme S4. Synthesis of DNCF and TNCF.

Fluorenone-4-carboxamide (5).^{9,11}

(Method A). To the mixture of fluorenone-4-carboxylic acid (**2**)⁹ (8.00 g, 35.7 mmol), SOCl₂ (20 mL, 275 mmol) and chloroform (30 mL), *N,N*-dimethylformamide (DMF) (0.2 mL) was added. The mixture was stirred under reflux for 4 h and evaporated to dryness. The residual chloroanhydride was dissolved in dry dioxane (50 mL) and an excess of gaseous NH₃ was bubbled through the stirred solution. The mixture was stirred for 1 hour at room temperature and poured into water (250 mL). The precipitate was filtered off, washed with water until pH7 and dried to afford compound **5** (6.34 g, 80%) as yellow powder, m.p. 229–231 °C. Recrystallization from ethyl acetate (1.0 L) gave amide **5** (5.82 g, 73%) as yellow crystals, m.p. 230–231 °C. (Lit. m.p. 223–224 °C,¹⁶ 230–230.5 °C,¹¹ 230–231 °C⁹).

(Method B). Fluorenone-4-carboxylic acid (**2**)⁹ (14.0 g, 62.4 mmol) and PCl₅ (13.0 g, 62.4 mmol) in dry xylene (120 mL) were stirred with heating on oil bath at 90–100 °C for 1 hour. The mixture was concentrated by distilling off ~60 mL of xylene and formed POCl₃, cooled down to room temperature and with vigorous stirring, concentrated ammonia (25% NH₄OH; 35 mL) was added. The precipitate was filtered off, suspended in water, heated to 40 °C, filtered off again, washed with water until pH7 and dried to afford amide **5** (12.2 g, 87%) as light yellow solid, m.p. 230–231 °C.

2,7-Dinitrofluorenone-4-carboxamide (6).¹²

A mixture of 2,7-dinitrofluorenone-4-carboxylic acid (**3**)¹⁵ (18.0 g, 57.3 mmol), chloroform (40 mL), SOCl₂ (9.3 mL, 128 mmol) and DMF (4 drops) was stirred under reflux for 1.5 hours. Acid **3** was dissolved in ca. 10 min and the chloroanhydride started to crystallize in ca. 30 min. The mixture was cooled down to room temperature and the suspension was poured into concentrated aqueous ammonia (25% NH₄OH; 110 mL). The precipitate was filtered off, washed with 5% ammonia (3 × 50 mL), then with water until pH7 and dried to afford crude amide **6** (17.5 g, 97%), m.p. 291–293 °C. Crude product was recrystallized from DMF (~70 mL) to yield pure amide **6** (14.6 g, 81%) as yellow solid, m.p. 308–310 °C. (Lit.^{11,12} m.p. 309–310 °C).

2,7-Dinitrofluorenone-4-carboxamide (6).¹¹

4-Carbamoylfluorenone (**5**) (5.00 g, 22.4 mmol) was dissolved in concentrated sulfuric acid (125 mL) at 0 °C and fuming nitric acid (8.0 mL; *d* = 1.51 g/mL) was added dropwise with stirring, keeping the temperature at 0 °C. The mixture allowed to warm to room temperature, stirred for 30 min and poured onto ice (800 mL). The precipitate was filtered off, washed with water until pH7 and dried to afford amide **6** (6.60 g, 94%) as yellow solid. After recrystallization from DMF (~30 mL), amide **6** (5.40 g, 77%) was obtained as yellow crystals, m.p. 309–310 °C.

2,5,7-Trinitrofluorenone-4-carboxamide (7).¹²

A mixture of 2,5,7-trinitrofluorenone-4-carboxylic acid (**4**)¹⁵ (35.9 g, 100 mmol), SOCl₂ (10 mL, 180 mol), chloroform (100 mL) and DMF (0.5 mL) was stirred under reflux for 4 hours. The mixture was cooled down to room temperature and poured into concentrated aqueous ammonia (25% NH₄OH; 50 mL) to form brown suspension. Chloroform was removed under vacuum, the precipitate was filtered off, washed with 5% K₂CO₃ (5 × 100 mL) then with water until pH7 and dried to afford crude amide **7** (34.8 g, 97%). Crude product was dissolved in hot dioxane (~500 mL), filtered from insoluble grey solid, concentrated to the volume of ~200 mL and left to crystallize. The precipitate was filtered off, washed with cold dioxane and dried to yield amide **7** (28.9 g, 81%) as light orange solid, m.p. 294–296 °C. Additional recrystallization from dioxane gave amide **7** with m.p. 298–300 °C. (Lit.¹² m.p. 300.5–301.5 °C).

4-Cyanofluorenone (8).^{9,11,12}

4-Carbamoylfluorenone (**5**) (30.0 g, 134 mmol) was suspended in xylene (200 mL), PCl₅ (33.0 g, 158 mmol) was added and the mixture was stirred with heating at 110–120 °C for 2 hours. The solvent (and formed POCl₃) were removed by vacuum distillation, water (400 mL) was added to the residue and the mixture was neutralized by adding Na₂CO₃. The precipitate was filtered off, transferred into a beaker with hot water (400 mL), stirred for 15 min, filtered off again, washed with water until pH7 and dried to afford compound **8** (26.1 g, 95%) as yellow solid. It was recrystallized from dioxane to yield compound **8** (19.9 g, 72%) as light-yellow crystals, m.p. 241–242 °C. (Lit. m.p. 238–240 °C,¹⁷ 241–242 °C^{9,11,12}).

Fluorene-4-carboxylic acid (9).¹³

Fluorenone-4-carboxylic acid (**2**) (68.0 g, 0.30 mol), KOH (51 g, 0.9 mol) and 85% hydrazine hydrate (68 mL, 1.8 mol) in diethylene glycol (500 mL) was heated under reflux for 3 hours. The mixture was cooled down to room temperature and poured into water (3.0 L). Small portion of activated carbon was added, the mixture was stirred for 30 min, filtered from the solid and the filtrate was acidified with concentrated HCl to ~pH3. The precipitate was filtered off, washed with water until ~pH7 and dried to afford acid **9** (60.3 g, 94%), m.p. 179–180 °C (from acetic acid).

Fluorene-4-carboxamide (10).¹⁴

To the stirred suspension of fluorene-4-carboxylic acid (**9**) (30.0 g, 143 mol) in dry *m*-xylene (250 mL), PCl₅ (32.0 g, 154 mol) was added by portions. The mixture was heated under reflux for 2 hours and concentrated by distilling off *m*-xylene and formed POCl₃ (~230 mL of distillate). The residue was partly cooled down (avoiding crystallization) and poured into vigorously stirred aqueous ammonia (25% NH₄OH, 150 mL) cooled to 0 °C. The mixture was vigorously stirred for 30 min, the precipitate was filtered off and dried under air flow on the filter. The precipitate was suspended in warm water, filtered off, washed with water and dried to yield amide **5** (28.2 g, 94%) as yellow solid. M.p. 223–223.5 °C. (Lit.¹⁴ m.p. 223–224.5 °C). It was used in the next step without further purification.

4-Cyanofluorene (**11**).¹⁴

Fluorene-4-carboxamide **10** (28.2 g, 135 mmol) and PCl_5 (30.0 g, 144 mmol) in dry toluene (250 mL) were heated (oil bath, 120–130 °C) with stirring for 4 hours, cooled down and diluted with water (100 mL). Toluene layer was separated, washed with water until pH7 and the solvent was evaporated. The residue was purified by vacuum distillation to afford compound **11** (21.0 g, 81%). It was recrystallized from 2-propanol (~100 mL) to yield pure 4-cyanofluorene (**11**) (16.5 g, 64%), m.p. 78.5–79.5 °C. (Lit.¹⁴ m.p. 78–79 °C).

2,7-Dinitro-4-cyanofluorene (**12**).¹⁴

Mixture of fuming nitric acid (20 mL; $d = 1.51$ g/mL) and acetic acid (40 mL) was cooled down to –10 °C and, with stirring, 4-cyanofluorene (**11**) (5.00 g, 26.1 mmol) was added to this mixture by portions. The mixture was stirred at 0 °C for 2 hours, additional portion of fuming nitric acid (30 mL; $d = 1.51$ g/mL) and the mixture was stirred at room temperature for 24 hours. It was diluted with acetic acid (100 mL) and left for 4 hours. The precipitate was filtered off, washed with acetic acid (2 × 10 mL), then with water until pH7 and dried to afford compound **12** (5.80 g, 79%) as yellowish solid. Crude product was recrystallized from dioxane to yield compound **12** (3.80 g, 52%) as yellowish solid, m.p. 256–258 °C (from dioxane). (Lit.¹⁴ m.p. 257–258 °C).

2,5,7-Trinitro-4-cyanofluorene (**13**).^{13,14}

(Metod A) 25 mL round-bottom flask was charged with fuming nitric acid (12.5 mL, $d = 1.51$ g/mL) and cooled down to –10 °C. With stirring, 4-cyanofluorene (**11**) (0.96 g, 5.0 mmol) was added by portions, keeping the temperature below –5 °C. The mixture was stirred at 0 °C for 30 min, then for 2 h at 25–30 °C and poured onto ice-water (100 mL). The precipitate was filtered off, washed with water until pH7 and dried to afford crude compound **13** (1.51 g, 92%) as light-grey solid. For purification, crude product was recrystallized from nitromethane (25 mL) to yield compound **13** (0.90 g, 55%) as beige crystals, m.p. 241–242 °C (dec.). (Lit. m.p. 239–240 °C (dec.),¹³ 240–241 °C (dec.),¹⁴ 243–244 °C (dec.)¹⁴).

(Method B) Mixture of fuming nitric acid (70 mL, $d = 1.51$ g/mL) and concentrated sulfuric acid (5 mL, $d = 1.84$ g/mL) was cooled down to –10 °C and, with stirring, 4-cyanofluorene (**11**) (5.73 g, 30 mmol) was added by portions, keeping the temperature below –5 °C. The mixture was stirred at –5 to 0 °C for 30 min, then for 2 h at room temperature, and orange solution was poured onto ice-water (1 L). The precipitate was filtered off, washed with water until pH7 and dried to afford crude compound **13** (9.45 g, 97%) as yellowish solid. For purification, crude product was stirred under reflux with methanol (90 mL), filtered off and recrystallized from nitromethane (110 mL) to yield compound **13** (6.40 g, 65 %) as beige crystals, m.p. 239–240 °C (dec.).

2,7-Dinitro-4-cyanofluorenone (DNCF).¹²

2,7-Dinitrofluorenone-4-carboxamide (**6**) (2.87 g, 9.2 mmol) and PCl_5 (3.00 g, 14.4 mmol) in dry *m*-xylene (80 mL) were stirred under reflux for 4.5 hours. The solvent and formed POCl_3 were distilled off to dryness (in the end of the process under the vacuum). The residue was diluted with water, the precipitate was filtered off, washed with water until pH7 and dried to afford crude product (2.94 g, >100%), m.p. 263–267 °C. Crude product was recrystallized from dioxane (15 mL) to yield pure DNCF (2.35 g, 87%) as yellow crystals, m.p. 267–268 °C. Alternatively, crude product can be purified by dissolution in hot dioxane (50 mL/g) and dilution with hot water (50 mL/g), to form yellow needles of DNCF. (Lit. m.p. 265–266 °C,^{11,12} 267–267.5 °C¹⁴).

2,7-Dinitro-4-cyanofluorenone (DNCF).^{11,12}

4-Cyanofluorenone (**8**) (2.05 g, 10.0 mmol) was slowly added to concentrated sulfuric acid (30 mL) cooled to +5 °C and stirred until full dissolution. Fuming nitric acid (2.0 mL, $d = 1.51$ g/mL) was added dropwise to this solution, keeping the temperature at +5–10 °C. The mixture was stirred at room temperature for 1 h and poured onto ice (300 mL). The precipitate was filtered off, washed with water until pH7 and dried to afford crude DNCF (2.90 g, 98%), m.p. 262–267 °C. Crude product was recrystallized from dioxane (15 mL) to yield pure DNCF (2.30 g, 78%) as light-yellow crystals, m.p. 267–269 °C.

2,7-Dinitro-4-cyanofluorenone (DNCF).¹⁴

2,7-Dinitro-4-cyanofluorene (**12**) (0.56 g, 2.00 mmol) was suspended in acetic anhydride (10 mL) (not full dissolution) and CrO_3 (0.48 g, 4.80 mmol) was added by portions. The mixture was stirred at room temperature for 2 days and poured into water (50 mL). After stirring for 2 h, the precipitate was filtered off,

washed with water until pH7 and dried to afford **DNCF** (0.58g, 98%) as yellow solid. After recrystallization from dioxane, m.p. 267–267.5 °C.

2,5,7-Trinitro-4-cyanofluorenone (TNCF).¹²

2,5,7-Trinitrofluorenone-4-carboxamide (**7**) (10.0 g, 27.9 mmol), SOCl₂ (30 mL, 0.41 mol) and DMF (2 mL) were stirred under reflux for 2 hours and left to crystallize the product. The precipitate was filtered off, washed with water until pH7 and dried to afford crude product (3.80 g, 40%) as yellow powder, m.p. 212–215 °C. Crude product was recrystallized from dioxane to yield **TCNF** (2.55 g, 27%), m.p. 222–225 °C. Additional crystallization from dioxane gave pure **TNCF** with m.p. 229–230 °C. (Lit. m.p. 228.5–229.5 °C,¹² 230–231 °C^{13,14}).

2,5,7-Trinitro-4-cyanofluorenone (TNCF).¹³

(Method A). 2,5,7-Trinitro-4-cyanofluorene (**13**) (5.30 g, 16.2 mmol) was stirred in acetic anhydride (65 mL) (not full dissolution) and CrO₃ (4.0 g, 40 mmol) was added by portions. Slight exotherm in the reaction and full dissolution of the solid was observed and after stirring for 2 h at room temperature some product started to precipitate. The mixture was stirred at room temperature for 24 h, the precipitate was filtered off, washed with acetic acid (3 × 5 mL), diluted HCl, then with water until pH 7 and dried to afford **TNCF** (4.40 g, 80%) as light yellow solid, m.p. 230–231 °C.

(Method B). To fuming nitric acid (25 mL; *d* = 1.51 g/mL) cooled to –10 °C, 4-cyanofluorene (**11**) (1.91 g, 10 mmol) was added by portions, keeping the temperature of the mixture at –5–0 °C. The mixture was stirred at +20–25 °C for 1.5 h and poured into ice-water (200 mL). The precipitate was filtered off, washed with water until pH7 and dried to afford crude 2,5,7-trinitro-4-cyanofluorene (**13**) (3.15 g, 96.7%), m.p. 220–230 °C. Crude compound **13** was suspended in acetic anhydride (35 mL) and to this stirred suspension CrO₃ (4.15 g, 41.5 mmol) was added by portion keeping the temperature below +40 °C. The mixture was stirred for 16 h, the precipitate was filtered off, washed with acetic acid (4 × 5 mL), then with water until pH7 and dried to afford **TNCF** (2.25 g, 66%) as light yellow solid, m.p. 228–230 °C. After recrystallization from acetic anhydride (20 mL), m.p. 231–232 °C.

2. OFET fabrication and characterization

Pre-patterned (purchased from Fraunhofer IPMS) bottom contact bottom gate Si/SiO₂ were used to characterize thin films of nitrofluorenones (NFs). The substrates have 230 ± 10 nm SiO₂ as a dielectric and gold electrode of 30 nm thickness as source/drain with 10 nm thick ITO as adhesion layer. The devices have channel lengths of 2.5 μm and channel width of 10 mm. All the substrates were thoroughly rinsed with acetone, isopropanol and blow dried with nitrogen before exposing them to an air plasma for 10 minutes. The substrates were treated with 2,3,4,5,6-pentafluorothiophenol (PFTBT) (10mM solution in ethanol) for 20 minutes to modify the gold electrodes for improved charge injection. The substrates were thoroughly rinsed with ethanol after the PFTBT self-assembly process. The thin films of all NFs (except DNF) were spin coated from 5 mg/mL chlorobenzene solutions at 1000 rpm. Electrical measurements were performed in vacuum using a semiconductor parameter analyzer Keithley 4200 SCS. Field-effect mobilities were calculated using the standard thin-film model in saturation regime of the device using equation (S1), where *L*, *W* and *C_i* are the channel length, channel width and geometric capacitance of the dielectric, respectively.

$$\mu_{sat} = \frac{2L}{WC_i} \frac{\partial^2 I_{DS}^{sat}}{\partial V_{GS}^2} \quad (S1)$$

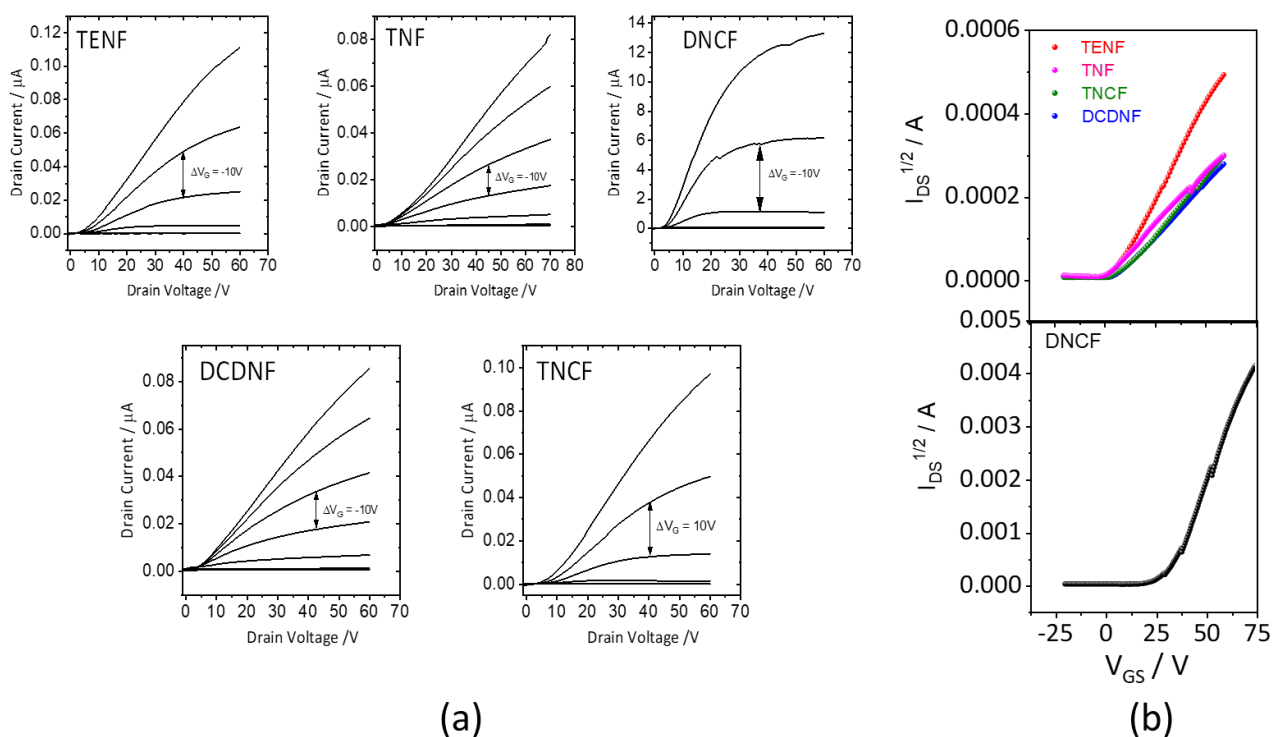


Fig. S1 (a) and (b) Output and transfer ($I_{DS}^{1/2}$ vs V_{GS}) characteristics of NFs.

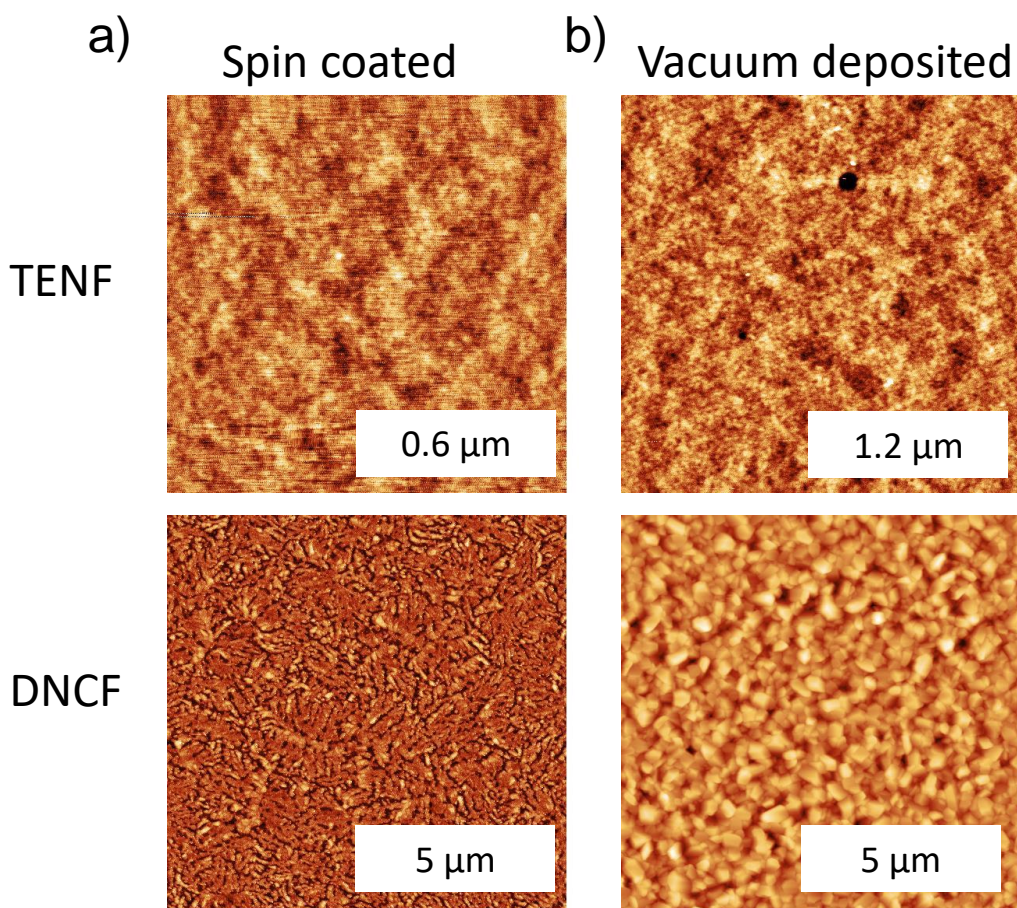


Fig. S2 Atomic force microscopy images: (a) spin coated and (b) vacuum deposited thin films of **TENF** and **DNCF**.

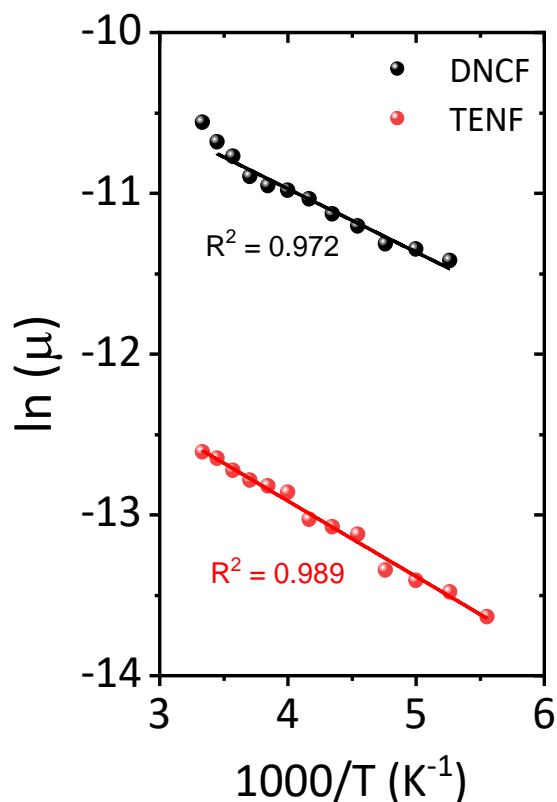


Fig. S3 Charge carrier mobility as a function of temperature for **DNCF** and **TENF** thin films. The slopes of these plots have been used to estimate activation energies (E_A).

3. Cyclic voltammetry measurements

Electrochemical experiments were carried out using CHI760C electrochemical workstation. Cyclic voltammetry (CV) measurements were performed in a three-electrode cell equipped with a platinum disk ($d = 1.6$ mm) as the working electrode, platinum wire as a counter electrode, and a non-aqueous Ag/Ag⁺ reference electrode (0.01 M AgNO₃ and 0.1 M Bu₄NPF₆ in acetonitrile). Cyclic voltammograms were recorded at room temperature in dry acetonitrile, deoxygenated by argon flow, with 0.1 M Bu₄NPF₆ as supporting electrolyte and ohmic drop compensation. The potentials were corrected with the Ferrocene/Ferrocenium redox couple (Fc/Fc⁺) as an internal standard. LUMO energies (LUMO^{CV}) were estimated from the half-wave reduction potentials using the widely used relationship (equation S2).

$$\text{LUMO}^{\text{CV}} [\text{eV}] = -4.8 - eE_{1\text{red}}^{1/2} \quad (\text{S2})$$

where $E_{1\text{red}}^{1/2}$ is the reduction potential versus Fc/Fc⁺ redox couple and -4.8 eV is the potential of Fc versus Fermi level.

4. Thermogravimetric analysis (TGA)

TGA experiments were performed using 2500 Discovery (TA instruments) under N₂ atmosphere.

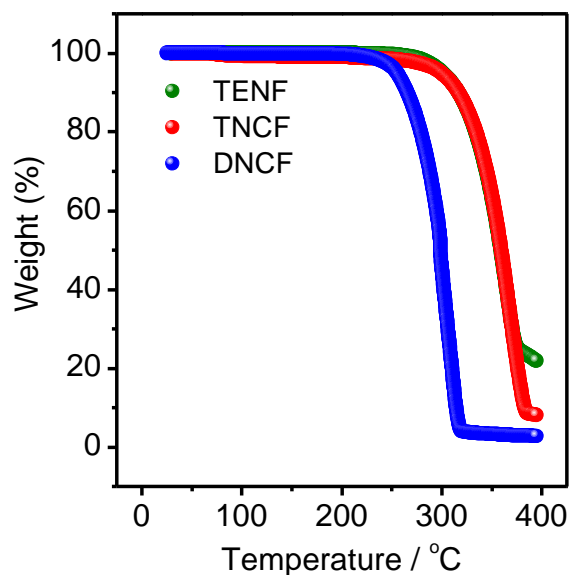


Fig. S4 TGA traces of nitrofluorenes under N₂ atmosphere.

5. UV-Vis absorption spectra measurements

UV-Vis absorption spectra of NFs were recorded on a JASCO V-670 spectrophotometer. Solutions of NFs were prepared in DCM and the spectra were recorded in 10 mm path length quartz cells. Solid state absorption spectra were recorded for thin films, spin-coated on quartz substrates from 5 mg/mL chlorobenzene solutions at 1000 rpm.

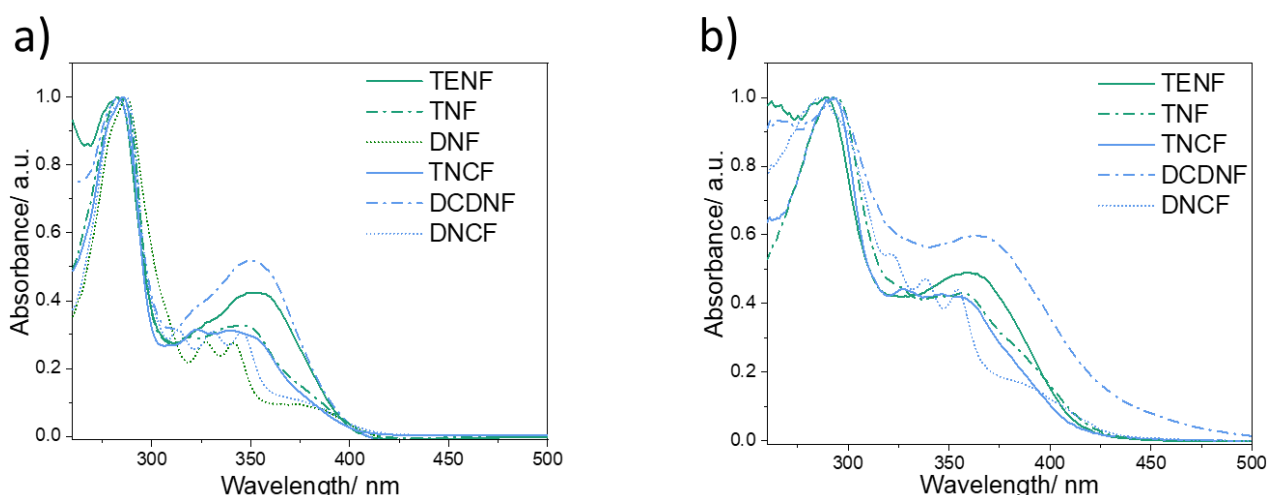


Fig. S5 UV-Vis absorption spectra of NFs: a) in DCM solutions, b) in thin films, spin-coated on quartz slides. The spectra have been normalized to the short wavelength maxima.

6. DFT calculations

Geometry optimization of NFs were performed by DFT calculations at B3LYP/6-31G(d) level of theory in a gas phase using Gaussian 16 software package.¹⁸ The restricted Hartree-Fock formalism was employed for calculations of the neutral molecules. No constraints were used, and all structures were free to optimize.

HOMO and LUMO energies were calculated for the optimized geometries. The orbital surfaces were obtained using GaussView 6.0.

The reorganization energy λ is defined as the energy difference between the anion and neutral nitrofluorenes at the two different geometries.

$$\lambda = (E_{anion}^{neutral\ geom.} - E_{neutral}) + (E_{neutral}^{anion\ geom.} - E_{anion}) \quad (S3)$$

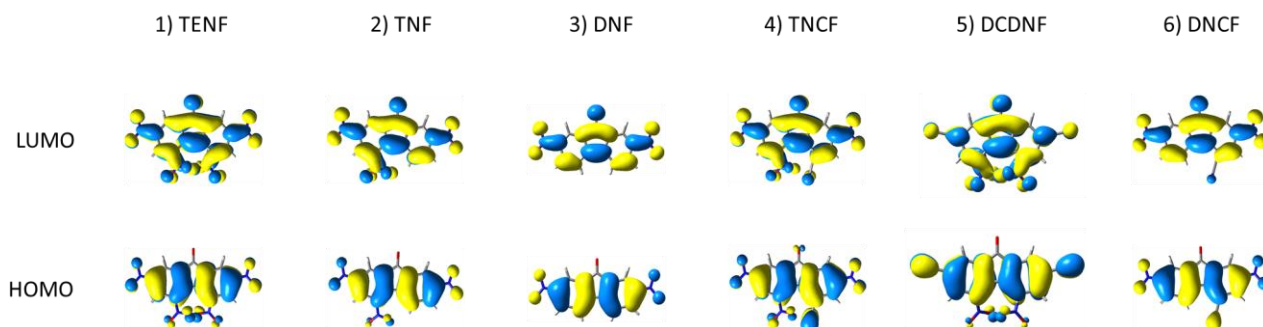


Fig. S6 The HOMO/LUMO orbital coefficients of studied nitrofluorenes from B3LYP/6-31G(d) calculations.

Atom coordinates, total energies and HOMO/LUMO energy levels for B3LYP/6-31G(d) optimized geometries of nitrofluorenes

TENF

$E_{total} = -1393.399139$ Hartree

$E_{HOMO} = -0.30673$ Hartree; $E_{LUMO} = -0.16192$ Hartree

| | | | |
|---|-------------|-------------|-------------|
| C | -3.45647200 | -0.70563900 | -0.05224800 |
| C | -3.08287800 | 0.62228100 | 0.12092600 |
| C | -1.72821200 | 0.94816600 | 0.20173600 |
| C | -0.74511500 | -0.03149400 | 0.03019300 |
| C | -1.18421300 | -1.37118500 | -0.06514900 |
| C | -2.51874100 | -1.73605600 | -0.10916400 |
| C | 0.74511600 | -0.03149300 | -0.03037100 |
| C | 1.18421800 | -1.37119500 | 0.06487600 |
| C | 0.00000700 | -2.28346900 | -0.00018100 |
| C | 1.72822100 | 0.94817300 | -0.20176900 |
| C | 3.08288300 | 0.62230100 | -0.12089000 |
| C | 3.45647200 | -0.70563400 | 0.05229000 |
| C | 2.51874800 | -1.73605300 | 0.10903700 |
| O | 0.00000300 | -3.49584000 | -0.00023900 |
| N | -4.89432100 | -1.03322400 | -0.12803000 |
| O | -5.18877000 | -2.21701900 | -0.26850700 |
| O | -5.69028800 | -0.10219400 | -0.04735300 |
| N | -1.41710900 | 2.32467300 | 0.62795300 |
| O | -2.19318500 | 3.21110000 | 0.30077200 |
| O | 0.42686200 | 2.46004400 | -1.34569200 |
| N | 4.89430400 | -1.03322700 | 0.12828500 |
| O | 5.69030100 | -0.10223000 | 0.04776700 |
| O | 5.18870200 | -2.21704500 | 0.26882700 |
| N | 1.41711400 | 2.32466600 | -0.62800000 |
| O | -0.42698600 | 2.46004000 | 1.34583400 |
| O | 2.19334800 | 3.21106000 | -0.30105800 |
| H | -3.83404300 | 1.39561900 | 0.21903100 |
| H | -2.82409800 | -2.77352800 | -0.17929000 |
| H | 3.83401400 | 1.39568600 | -0.21885100 |
| H | 2.82412200 | -2.77352400 | 0.17912900 |

TNF $E_{\text{total}} = -1188.9201895$ Hartree $E_{\text{HOMO}} = -0.29243$ Hartree; $E_{\text{LUMO}} = -0.14775$ Hartree

| | | | |
|---|-------------|-------------|-------------|
| C | 3.65688100 | -0.07444800 | -0.04243800 |
| C | 3.17506800 | 1.23271100 | -0.07549200 |
| C | 1.79847400 | 1.47992300 | -0.03404100 |
| C | 0.92128500 | 0.39635300 | 0.03471700 |
| C | 1.44793500 | -0.91678700 | 0.05285200 |
| C | 2.80618000 | -1.17872600 | 0.02048400 |
| C | -0.57027400 | 0.29487100 | 0.05715000 |
| C | -0.91352900 | -1.07903900 | 0.05997800 |
| C | 0.33581600 | -1.90692200 | 0.08118500 |
| C | -1.63623100 | 1.20402400 | 0.02020200 |
| C | -2.96219800 | 0.76230500 | -0.03467600 |
| C | -3.23180100 | -0.59842700 | -0.01602300 |
| C | -2.21217800 | -1.55038000 | 0.03552300 |
| O | 0.40675900 | -3.11868000 | 0.10817500 |
| N | 5.11485300 | -0.29811600 | -0.08028900 |
| O | 5.50636600 | -1.46261900 | -0.04972900 |
| O | 5.84020400 | 0.69234600 | -0.14027200 |
| O | -0.48731300 | 3.10389200 | 0.67573000 |
| N | -4.63747900 | -1.04334000 | -0.05408400 |
| O | -5.50557700 | -0.17513900 | -0.09020400 |
| O | -4.83922800 | -2.25489100 | -0.04677900 |
| N | -1.45936900 | 2.66692400 | 0.06145400 |
| O | -2.31299300 | 3.35294400 | -0.49052500 |
| H | 3.88300100 | 2.05085400 | -0.12895800 |
| H | 3.19472400 | -2.19012600 | 0.03693500 |
| H | -3.77172700 | 1.47852100 | -0.08521600 |
| H | -2.43038400 | -2.61202400 | 0.04692800 |
| H | 1.44004300 | 2.49892400 | -0.04694700 |

DNF $E_{\text{total}} = -984.4337281$ Hartree $E_{\text{HOMO}} = -0.27609$ Hartree; $E_{\text{LUMO}} = -0.13127$ Hartree

| | | | |
|---|-------------|-------------|-------------|
| C | 3.43603600 | -0.17064400 | -0.00003900 |
| C | 3.02171000 | -1.50368000 | -0.00002700 |
| C | 1.65710400 | -1.80910000 | -0.00008000 |
| C | 0.74013000 | -0.76132600 | -0.00016300 |
| C | 1.18876300 | 0.57637600 | -0.00020000 |
| C | 2.53444500 | 0.89815500 | -0.00011800 |
| C | -0.74013200 | -0.76132500 | -0.00012300 |
| C | -1.18876300 | 0.57637700 | -0.00006200 |
| C | 0.00000100 | 1.49321300 | -0.00031100 |
| C | -1.65710500 | -1.80909900 | -0.00008800 |
| C | -3.02171100 | -1.50367900 | 0.00002200 |
| C | -3.43603600 | -0.17064300 | 0.00009700 |
| C | -2.53444500 | 0.89815600 | 0.00006300 |
| O | 0.00000100 | 2.70741100 | -0.00000600 |
| N | 4.88101000 | 0.11839300 | 0.00003600 |
| O | 5.22121300 | 1.29973600 | 0.00011500 |
| O | 5.65416700 | -0.83859500 | 0.00006700 |
| N | -4.88101000 | 0.11839300 | 0.00019700 |
| O | -5.65416500 | -0.83859600 | 0.00025700 |
| O | -5.22121500 | 1.29973600 | 0.00015000 |
| H | 3.77313700 | -2.28376800 | 0.00003800 |
| H | 2.88301000 | 1.92419900 | -0.00014500 |
| H | -3.77313900 | -2.28376600 | 0.00006300 |
| H | -2.88300900 | 1.92420100 | 0.00009400 |
| H | 1.33601000 | -2.84629400 | -0.00005800 |
| H | -1.33601100 | -2.84629300 | -0.00009700 |

TNCF $E_{\text{total}} = -1281.1442745$ Hartree $E_{\text{HOMO}} = -0.30411$ Hartree; $E_{\text{LUMO}} = -0.15926$ Hartree

| | | | |
|---|-------------|-------------|-------------|
| C | 3.55536700 | -0.43910100 | -0.00133300 |
| C | 3.12886100 | 0.86646700 | -0.20532200 |
| C | 1.75264600 | 1.17179400 | -0.23424500 |
| C | 0.82763700 | 0.13562700 | -0.00497600 |
| C | 1.31364300 | -1.18640700 | 0.10413000 |
| C | 2.65986500 | -1.50216300 | 0.12106400 |
| C | -0.66138500 | 0.08143900 | 0.04436100 |
| C | -1.05256400 | -1.27632000 | -0.01778000 |
| C | 0.16463100 | -2.14266600 | 0.07566500 |
| C | -1.68413200 | 1.03059900 | 0.14807300 |
| C | -3.02490100 | 0.65388100 | 0.04076200 |
| C | -3.34675100 | -0.69182100 | -0.08629200 |
| C | -2.37118200 | -1.68954500 | -0.07986000 |
| O | 0.20593800 | -3.35410400 | 0.11281200 |
| N | 5.00633400 | -0.71357800 | 0.03263500 |
| O | 5.34856600 | -1.88236800 | 0.18925400 |
| O | 5.76601600 | 0.24250800 | -0.09555900 |
| O | -0.50394200 | 2.61923300 | 1.30890700 |
| N | -4.76946800 | -1.07396300 | -0.18588400 |
| O | -5.59940700 | -0.16958500 | -0.16773100 |
| O | -5.01838200 | -2.27259600 | -0.28171700 |
| N | -1.43617400 | 2.43245600 | 0.52978300 |
| O | -2.20397200 | 3.28507200 | 0.10312300 |
| H | 3.86335100 | 1.64681400 | -0.36221600 |
| H | 3.00642300 | -2.52510800 | 0.21068100 |
| H | -3.80486200 | 1.40335800 | 0.08624900 |
| H | -2.63821500 | -2.73910200 | -0.12146700 |
| C | 1.39023200 | 2.49806900 | -0.63678300 |
| N | 1.15687500 | 3.55646300 | -1.05806700 |

DCDNF $E_{\text{total}} \text{ energy} = -1168.8857161$ Hartree $E_{\text{HOMO}} = -0.29171$ Hartree; $E_{\text{LUMO}} = -0.15364$ Hartree

| | | | |
|---|-------------|-------------|-------------|
| C | 3.48620700 | -0.84401200 | 0.08531800 |
| C | 3.08575600 | 0.48820200 | -0.09156000 |
| C | 1.73272300 | 0.81713300 | -0.18479700 |
| C | 0.74474800 | -0.15802100 | -0.02361100 |
| C | 1.18386400 | -1.49719000 | 0.07369300 |
| C | 2.51597600 | -1.86216500 | 0.12930600 |
| C | -0.74473500 | -0.15802800 | 0.02372500 |
| C | -1.18383100 | -1.49720100 | -0.07364000 |
| C | 0.00001800 | -2.40920200 | 0.00006400 |
| C | -1.73272600 | 0.81712700 | 0.18484900 |
| C | -3.08575700 | 0.48817400 | 0.09153200 |
| C | -3.48618100 | -0.84404200 | -0.08537200 |
| C | -2.51593700 | -1.86218600 | -0.12931100 |
| N | 1.42957500 | 2.19503500 | -0.61191200 |
| O | 2.20678200 | 3.07931300 | -0.27884700 |
| O | -0.44571900 | 2.33643100 | 1.33669100 |
| O | 0.44545100 | 2.33637700 | -1.33638300 |
| H | 3.82041900 | 1.27881500 | -0.18583900 |
| H | 2.79699600 | -2.90791500 | 0.19964700 |
| H | -3.82043700 | 1.27877300 | 0.18577100 |
| H | -2.79694900 | -2.90793600 | -0.19967800 |
| O | -2.20664500 | 3.07935400 | 0.27854400 |
| O | 0.00002800 | -3.62217800 | 0.00004000 |
| C | 4.88041600 | -1.16473500 | 0.17311000 |
| C | -4.88038100 | -1.16479000 | -0.17322000 |
| N | -6.00963200 | -1.43154400 | -0.24612200 |
| N | 6.00967400 | -1.43147100 | 0.24597000 |
| N | -1.42964100 | 2.19505100 | 0.61195300 |

DNCF

E_{total} Energy= -1076.6699571 Hartree

E_{HOMO} = -0.28952 Hartree; E_{LUMO} = -0.14482 Hartree

| | | | |
|---|-------------|-------------|-------------|
| C | -3.35043500 | -0.25454600 | 0.00001800 |
| C | -2.99776100 | 1.08975400 | 0.00000400 |
| C | -1.63821600 | 1.45721500 | -0.00001800 |
| C | -0.66369900 | 0.44650500 | 0.00001200 |
| C | -1.07081600 | -0.90276100 | 0.00003200 |
| C | -2.40053100 | -1.28120000 | 0.00002800 |
| C | 0.81731100 | 0.49736000 | -0.00005000 |
| C | 1.30358600 | -0.82907700 | -0.00005200 |
| C | 0.14910300 | -1.78131800 | 0.00000600 |
| C | 1.70672100 | 1.57075400 | -0.00005200 |
| C | 3.07906600 | 1.29691700 | -0.00003100 |
| C | 3.52894900 | -0.02345600 | -0.00002700 |
| C | 2.65710200 | -1.11559100 | -0.00005000 |
| N | -4.78378900 | -0.60548200 | -0.00000100 |
| O | -5.06738500 | -1.80050600 | 0.00009300 |
| O | -5.59399600 | 0.31838900 | -0.00011400 |
| N | 4.98287200 | -0.27615100 | 0.00001800 |
| O | 5.72967800 | 0.70018700 | 0.00010400 |
| O | 5.35043300 | -1.44889200 | -0.00004800 |
| H | -3.77526400 | 1.84366800 | -0.00004200 |
| H | -2.70169500 | -2.32237100 | 0.00004200 |
| H | 3.80806200 | 2.09806600 | 0.00001000 |
| H | 3.03192000 | -2.13229900 | -0.00005100 |
| C | -1.28565700 | 2.84592800 | -0.00002500 |
| N | -0.98627900 | 3.96979700 | 0.00010200 |
| O | 0.17835500 | -2.99438400 | 0.00003100 |
| H | 1.36233700 | 2.59852200 | -0.00009000 |

7. Single crystal X-ray diffraction analysis

Single crystal X-ray structures of **DNCF** and **DCDNF** are given in the ESI – see CIF files.

Crystal analysis of **DNCF** shows that the **DNCF** molecule is centered on an inversion center, making it disordered upon itself. Searching for bigger unit cells and different space groups was not successful. We resolved this disorder in two individual molecules (A and B). The end model proposed here is well-resolved with a good R1 factor, but due to the fact that we described a full molecule in an asymmetric unit space containing the volume for only half a molecule, the low data to parameter ratio trigger structure A (alert in “Checkcif”). Also, there is a disorder of the cyano group and one nitro group in the crystal. The ratio in this case is 0.37:0.13. Restraints (SIMU and SADI) were only used for the disordered nitro group, all the rest of the thermal ellipsoids and bond lengths behave very well despite being very close to each other in space.

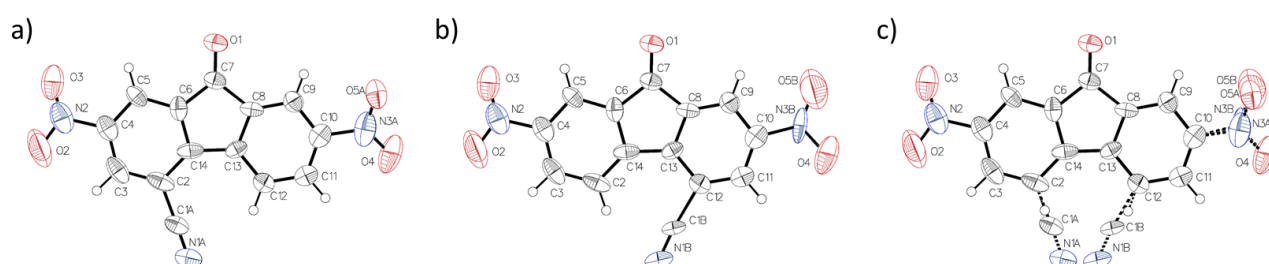


Fig. S7 Molecular structures of **DNCF** from single crystal X-ray diffraction data. Disorder of: a) molecule A and b) molecule B of **DNCF**. c) Both molecules are shown as overlaps, with the disordered centers shown with dashed lines.

Table 1. Crystal data and structure refinement for DNCF.

| | |
|---------------------------------------------|---------------------------------------------------------------|
| Empirical formula | C ₁₄ H ₅ N ₃ O ₅ |
| Formula weight | 295.21 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | P2 ₁ /c |
| a/Å | 5.0814(2) |
| b/Å | 6.9825(3) |
| c/Å | 17.0804(8) |
| α/° | 90 |
| β/° | 93.994(2) |
| γ/° | 90 |
| Volume/Å ³ | 604.56(5) |
| Z | 2 |
| ρ _{calc} /g/cm ³ | 1.622 |
| μ/mm ⁻¹ | 1.092 |
| F(000) | 300.0 |
| Crystal size/mm ³ | 0.113 × 0.105 × 0.055 |
| Radiation | CuKα (λ = 1.54178) |
| 2θ range for data collection/° | 10.384 to 140.168 |
| Index ranges | -6 ≤ h ≤ 6, -8 ≤ k ≤ 8, -20 ≤ l ≤ 20 |
| Reflections collected | 15821 |
| Independent reflections | 1152 [R _{int} = 0.0173, R _{sigma} = 0.0073] |
| Data/restraints/parameters | 1152/18/236 |
| Goodness-of-fit on F ² | 1.053 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0356, wR ₂ = 0.1015 |
| Final R indexes [all data] | R ₁ = 0.0374, wR ₂ = 0.1047 |
| Largest diff. peak/hole / e Å ⁻³ | 0.08/-0.17 |

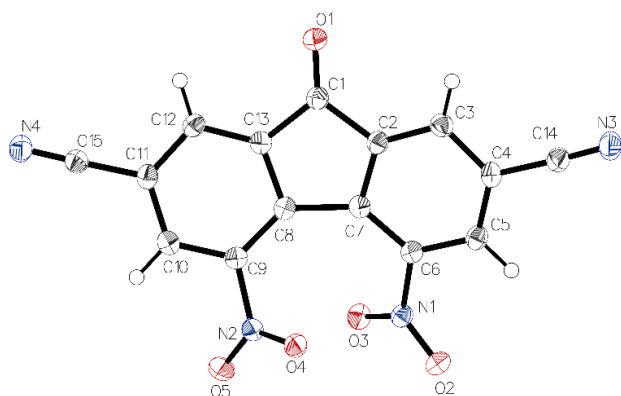


Fig. S8 Molecular structure of DCDNF from single crystal X-ray diffraction data.

The data for DCDNF were collected from a shock-cooled single crystal at 100 K on a Bruker Smart APEX three-circle diffractometer with a Microfocus Source using Quazar MX Mirror Optics as monochromator and a Bruker APEX2 CCD detector. The diffractometer was equipped with a Bruker Kryoflex low temperature device and used CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). All data were integrated with SAINT and a multi-scan absorption correction using SADABS-2016/2 was applied. The structure was solved by dual methods using SHELXT 2014/5 (Sheldrick, 2015a) and refined by full-matrix least-squares methods against F^2 by SHELXL 2018/3 (Sheldrick, 2015b). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

Table 2. Crystal data and structure refinement for DCDNF

| | |
|-------------------------------------------------|-------------------------------------------------------------------|
| Empirical formula | C ₁₅ H ₄ N ₄ O ₅ |
| Formula weight | 320.22 |
| Temperature [K] | 100 |
| Crystal system | 'monoclinic' |
| Space group (number) | $P2_1/c$ (14) |
| a [\AA] | 7.8806(3) |
| b [\AA] | 8.6623(3) |
| c [\AA] | 19.5240(7) |
| α [$^\circ$] | 90 |
| β [$^\circ$] | 95.543(1) |
| γ [$^\circ$] | 90 |
| Volume [\AA^3] | 1326.56(8) |
| Z | 4 |
| ρ_{calc} [g/cm^3] | 1.603 |
| μ [mm^{-1}] | 1.074 |
| F(000) | 648 |
| Crystal size [mm^3] | 0.22 \times 0.16 \times 0.11 |
| Crystal color | 'clear light colorless' |
| Crystal shape | block |
| Radiation | CuK α ($\lambda=1.54178 \text{ \AA}$) |
| 2 θ range [$^\circ$] | 11.18 to 140.20 (0.82 \AA) |
| Index ranges | -9 $\leq h \leq 9$ -9 $\leq k \leq 10$ -23 $\leq l \leq 23$ |
| Reflections collected | 25909 |
| Independent reflections | 2517 |
| | Rint = 0.0341 |
| | Rsigma = 0.0180 |
| Completeness to $\theta = 67.679^\circ$ | 99.8 % |
| Data / Restraints / Parameters | 2517/0/217 |
| Goodness-of-fit on F^2 | 1.041 |
| Final R indexes [$\geq 2\sigma(I)$] | R1 = 0.0331 |
| | wR2 = 0.0879 |
| Final R indexes [all data] | R1 = 0.0334 |
| | wR2 = 0.0881 |
| Largest peak/hole [$\text{e}\text{\AA}^{-3}$] | 0.25/-0.21 |

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