Electronic supplementary information (ESI) for:

A core-extended naphthalene diimide as p-channel semiconductor

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1. General methods

The starting compound *N*,*N*′-bis-(2′,6′-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide was prepared according to the literature.[1] All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.[2] Column chromatography was performed on silica gel (Merck Silica 60, particle size 0.040-0.063 mm). A preparative recycling GPC LC-9105, Japan Analytical Industry Co., Ltd. (JAI) with JAIGEL 2H+2.5H columns was used. Solvents for spectroscopic studies were of spectroscopic grade and used as received. ^{1}H and ^{13}C spectra were recorded in CD_2Cl_2 on a Bruker DMX 600 spectrometer. Residual undeuterated solvent was used as internal standard (5.32 ppm for ^{1}H, 53.80 ppm for ^{13}C). High-resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH). UV-vis measurements were performed in CH_2Cl_2 (10^{-5} M) in a conventional quartz cell (light pass 10 mm) on a Perkin-Elmer Lambda 950 spectrometer. Fluorescence quantum yields were determined under dilute conditions in CH_2Cl_2 ($<10^{-6}$ M) versus *N,N'*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide ($\Phi_f = 0.96$ in $CHCl_3$).[3] For cyclic voltammetry, a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature,[4] and recrystallized from ethanol/water. The measurements were carried out in dichloromethane at a concentration of about 10^{-4} M with ferrocene (Fc) as an internal standard for the calibration of the potential. Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively.

2. Experimental procedures, analytical and spectroscopic data

N,N′-Bis(2,6-diisopropylphenyl)-5*H*,12*H*-carbazolo[2,3-b]carbazol[6,7:13,14]-bis(tetracarboxylic acid diimide) 1

N,N′-Di-(2′,6′-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid diimide **2** (60.0 mg, 80.6 µmol), 2-bromoaniline (38.8 mg, 0.226 mmol), $Pd(OAc)_2$ (5.4 mg, 0.024 mmol) and K_2CO_3 (22.3 mg, 0.161 mmol) were placed under argon and dry DMF (5 mL) was added. The mixture was refluxed in an oil-bath (175 °C) for 2 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (dichloromethane / pentane 1:1) and recycling-GPC affording **1** as a black solid (7.2 mg, 12%).

^{1}H NMR (600 MHz, CD_2Cl_2): 11.52 (s, 2H), 9.71 (d, $^3J = 7.3$ Hz, 2H), 7.74 – 7.71 (m, 2H), 7.70 – 7.67 (m, 2H), 7.62 (t, $^3J = 7.9$ Hz, 2H), 7.47 (d, $^3J = 7.9$ Hz, 2H), 7.40 – 7.36 (m, 2H), 2.92 (sept, $^3J = 6.9$ Hz, 4H), 1.20 (2x d, $^3J = 6.9$ Hz, 24H).

^{13}C NMR (151 MHz, CD_2Cl_2):166.0, 164.9, 146.6, 144.7, 142.8, 131.6, 131.4, 131.0, 130.5, 130.1, 124.7, 122.2, 121.6, 121.1, 120.0, 111.7, 105.07, 29.66, 24.14, 24.11.

HRMS (ESI, acetonitrile/$CHCl_3$ 1:1, pos.-mode): calcd for $C_{50}H_{45}N_4O_4$ 765.3435. Found 765.3433 $[M+H]^+$.

Elemental Anal. Calcd. for $C_{50}H_{44}N_4O_4$: C, 78.51; H, 5.80; N, 7.32; O, 8.37. Found: C, 78.75; H, 5.84; N, 7.39.

CV (CH_2Cl_2, 0.1 M TBAHFP, vs. Fc/Fc$^+$): $E_{1/2}^{red}$ (X^-/X^{2-}) = -1.49 V, $E_{1/2}^{red}$ (X/X^-) = -1.07 V, E_p^{ox} (X/X^+) = 1.11 V.

UV-vis (CH_2Cl_2): λ_{max} (ε) = 622 nm (ε = 24200), 491 nm (ε = 38600 L mol^{-1} cm^{-1}). Fluorescence ($CH_2Cl_{2,}$ λ_{ex} = 446 nm): λ_{max} = 641 nm; Φ_{Fl} = 5%.

3. ^{1}H NMR, ^{13}C NMR spectra and ESI-HRMS

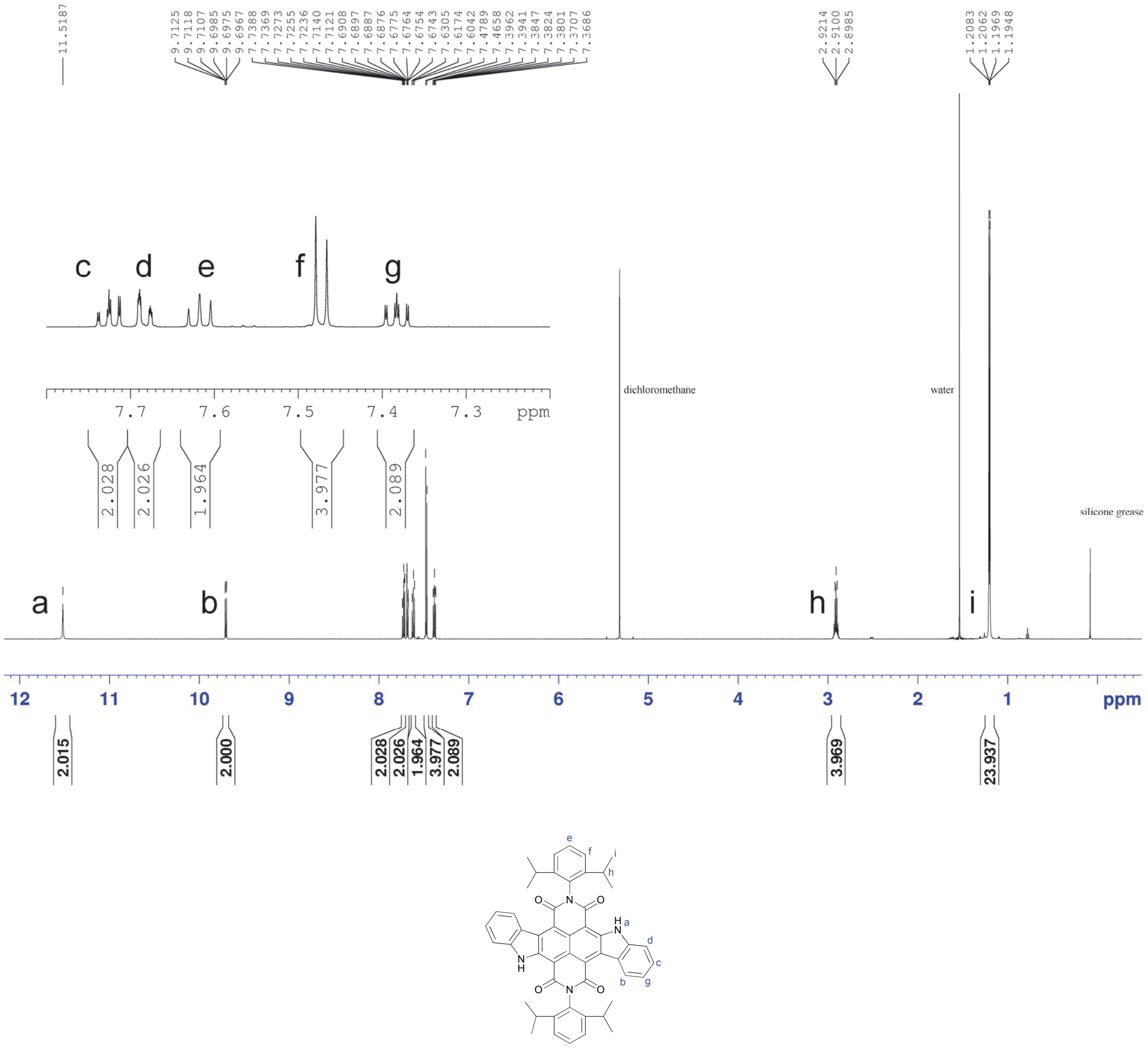

Fig. S1 ^{1}H NMR spectrum (600 MHz) of NDI **1** in CD_2Cl_2 and structural correlation of the signals.

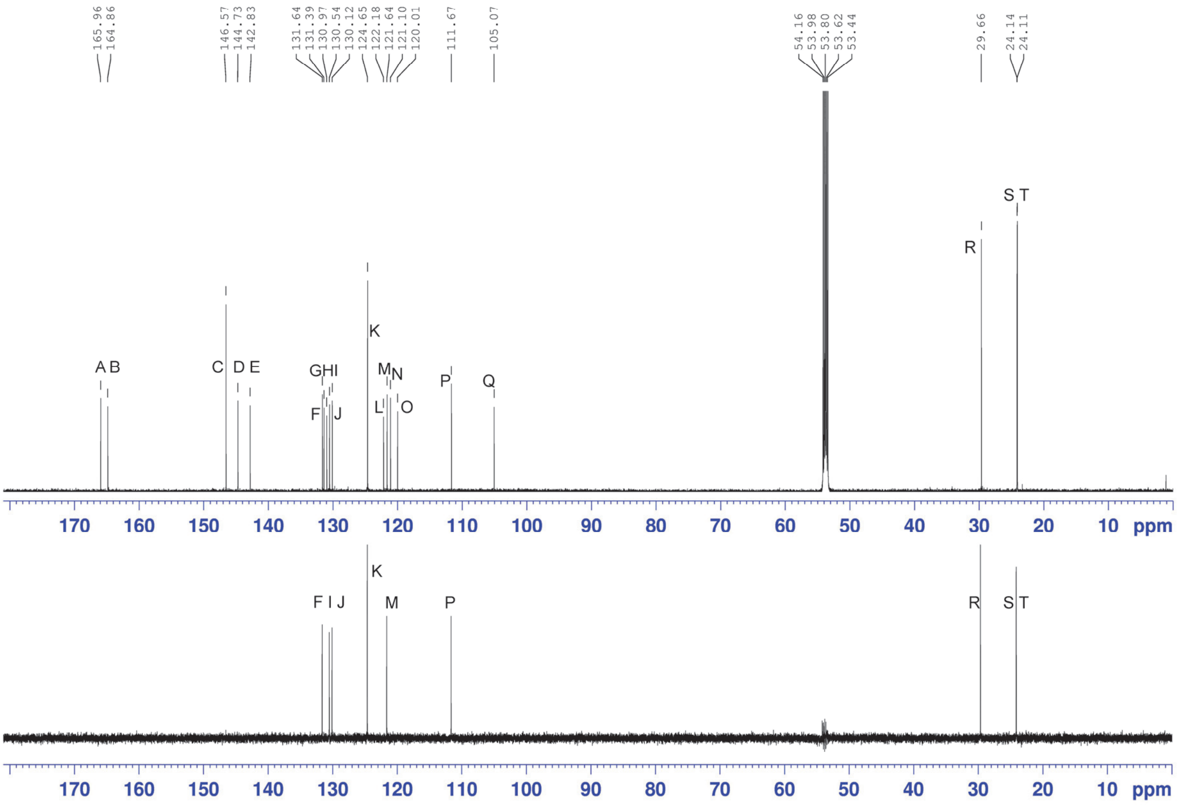

Fig. S2 ^{13}C NMR and DEPT-135 (151 MHz) spectra of NDI **1** in CD_2Cl_2.

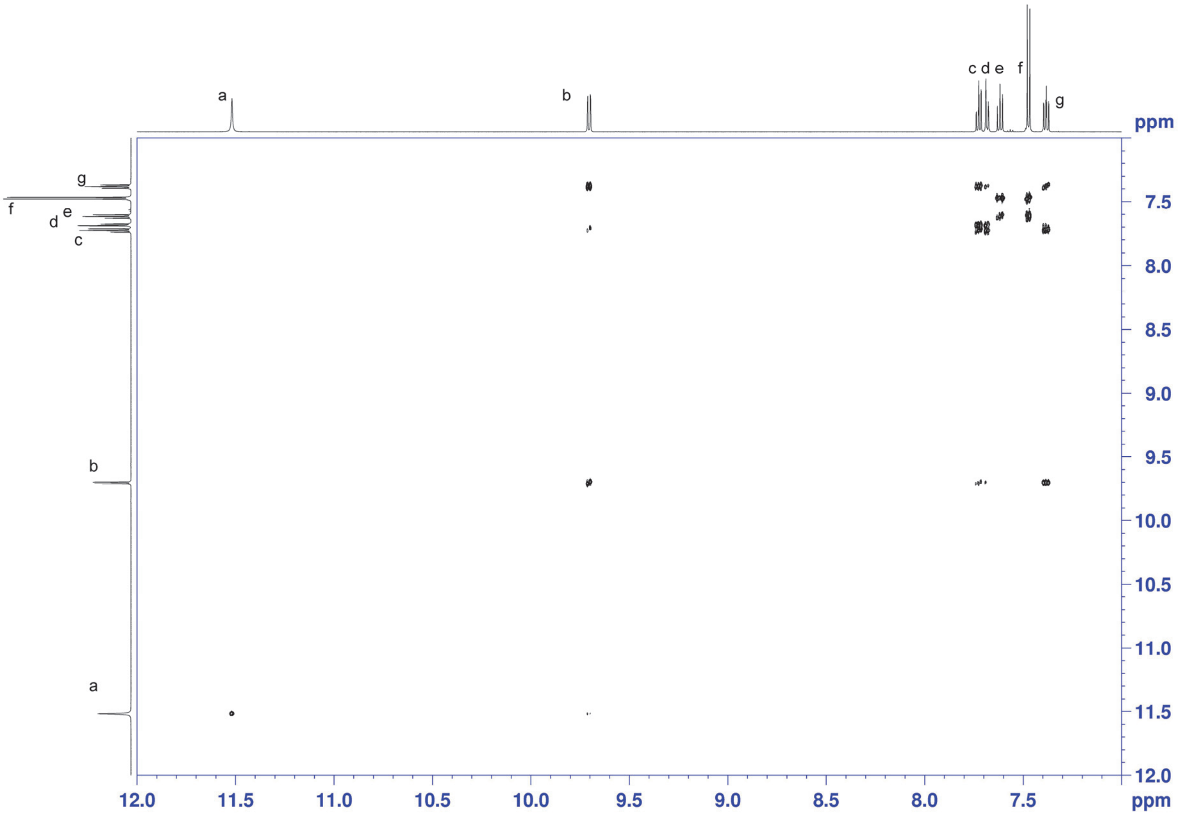

Fig. S3 COSY 45 spectrum of NDI **1** in CD_2Cl_2.

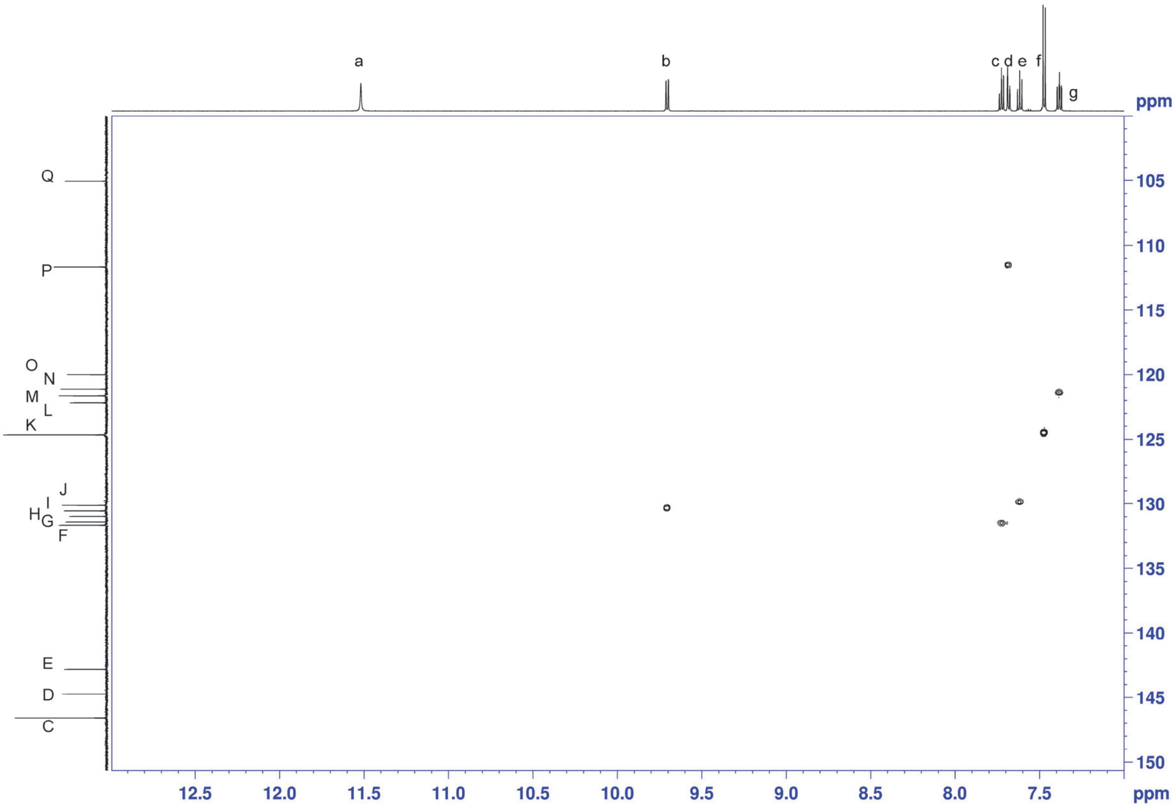

Fig. S4 HSQC spectrum of NDI **1** in CD_2Cl_2.

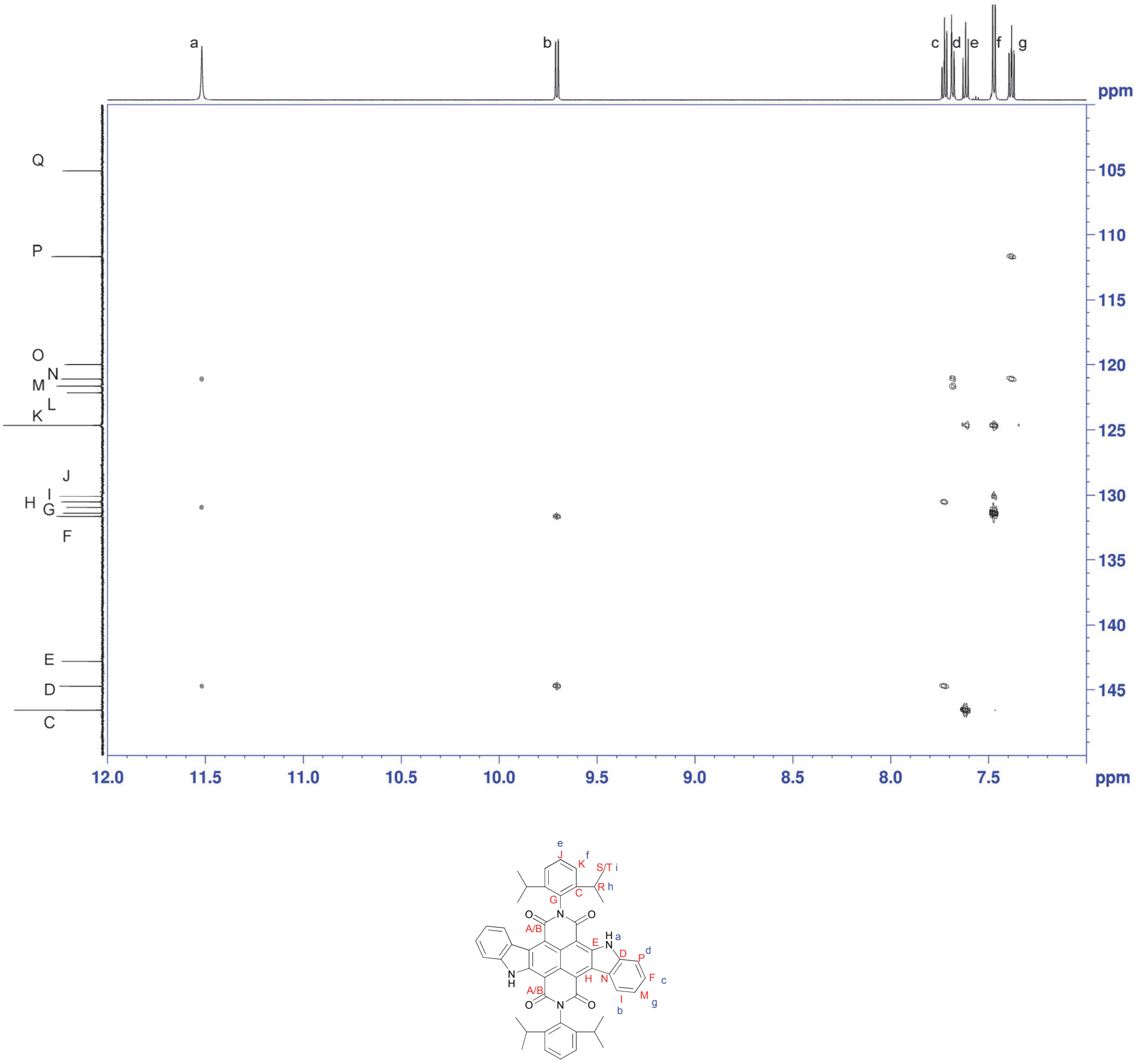

Fig. S5 HMBC spectrum of NDI **1** in CD_2Cl_2 and structural correlation of the signals.

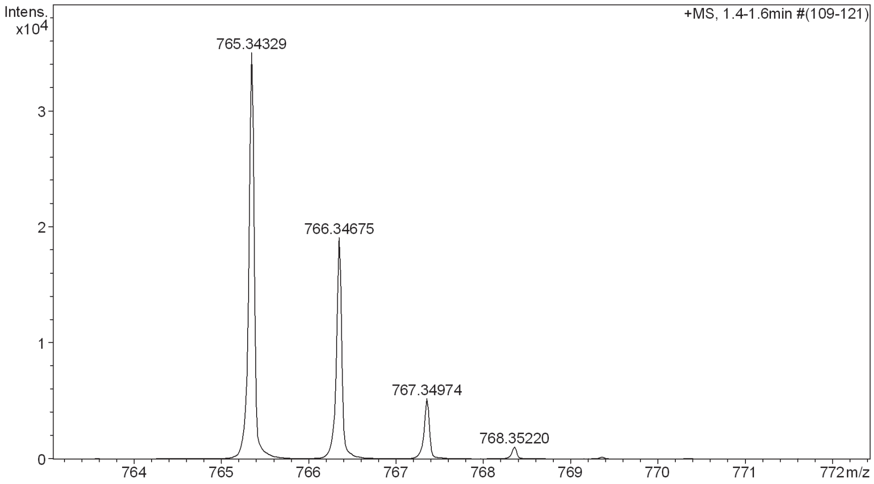

Fig. S6 High-resolution ESI-TOF mass spectrum of NDI **1** in acetonitrile/chloroform 1:1.

4. Cyclic voltammogram

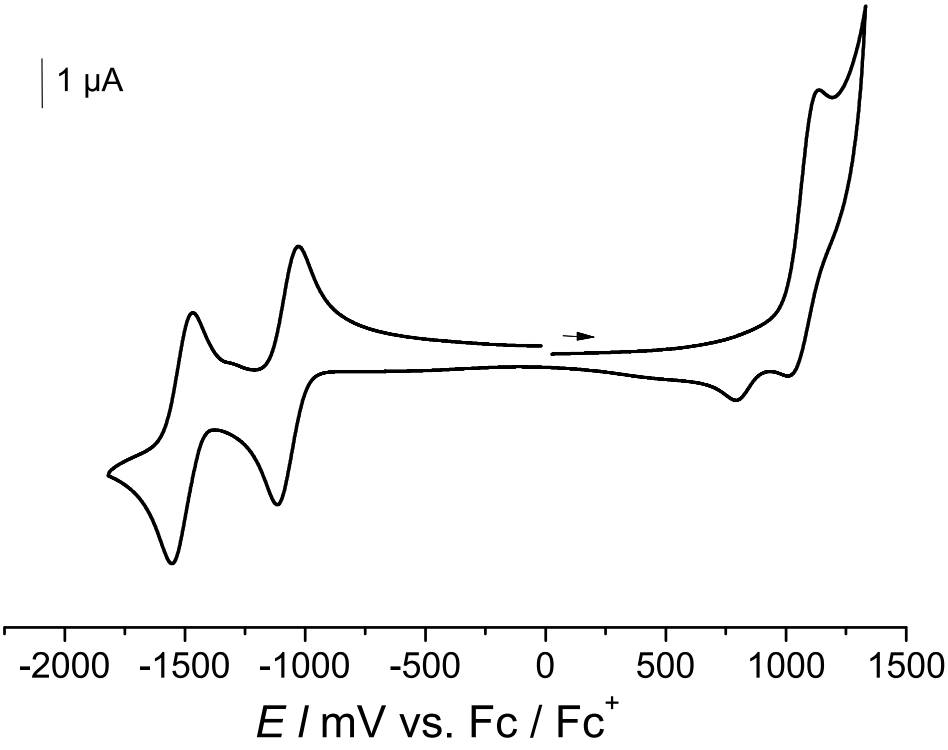

Fig. S7 Cyclic voltammogram of **1** in dichloromethane (10^{-4} M) using ferrocene as an internal standard at a of scan rate 100 mV s^{-1}; supporting electrolyte: tetrabutylammonium hexafluorophosphate (NBu_4PF_6, 0.1 M).

5. Theoretical investigations

NDI **1** was calculated with the DFT method in combination with the B3-LYP[5] functional. The calculations were performed with the TURBOMOLE program (version 5.10).[6] The TZVP[7] basis for C, N, O, and S atoms was combined with the TZV[6] basis for the H atom. This basis is designated as TZV(P) and was found to be an excellent compromise between accuracy and computational effort for systems of similar size.[8] NDI **1** was fully geometry-optimized, emanating from a structure computed on semi-empirical AM1 level.

6. Fabrication and characterization of organic TFTs and AFM

Organic TFTs were fabricated based on two different architectures: one with a thick SiO_2/AlO_x/SAM gate dielectric, the other with a thin AlO_x/SAM gate dielectric. In both cases, heavily doped silicon was used as the substrate. For the TFTs with the thick SiO_2/AlO_x/SAM gate dielectric, the silicon substrate was thermally oxidized to obtain a 100 nm thick layer of SiO_2, which was then covered with an 8 nm thick layer of AlO_x grown by atomic layer deposition (ALD). The $Si/SiO_2/AlO_x$ substrate was then immersed in a 2-propanol solution of 12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-pentadecylfluoro-octadecylphosphonic acid (FC18-PA) or tetradecylphosphonic acid (HC14-PA) to allow a densely packed monolayer with a thickness of 2.1 nm (FC18-PA) or 1.7 nm (HC14-PA) to self-assemble on the AlO_x surface. In principle, phosphonic acid SAMs can also be obtained on SiO_2, but we have found that AlO_x is a more suitable surface for high-quality phosphonic acid SAMs. The total thickness of the SiO_2/AlO_x/SAM gate dielectric is about 110 nm.

For the TFTs with the thin AlO_x/SAM gate dielectric, a 20 nm thick aluminum gate electrode was first deposited onto the silicon substrate by thermal evaporation. The aluminum was then briefly exposed to an oxygen plasma to obtain 3.6 nm thick AlO_x, on the surface of which a self-assembled monolayer with a thickness of 2.1 nm (FC18-PA) or 1.7 nm (HC14-PA) was obtained from a 2-propanol solution. The total thickness of the AlO_x/SAM gate dielectric is 5.7 nm in the case of FC18-PA and 5.3 nm in case of HC14-PA.

A 30 nm thick layer of the organic semiconductor NDI **1** was then deposited onto the SAM by thermal sublimation in a vacuum evaporator at a substrate temperature of 100 °C. TFTs were completed by evaporating 30 nm thick gold source and drain contacts through a polyimide shadow mask, defining a channel length of 100 µm and a channel width of 200 µm. The current-voltage characteristics were measured using an Agilent 4156C Semiconductor Parameter Analyzer in ambient air.

The AFM images were processed with WSXM, a freeware scanning probe microscopy software.[9]

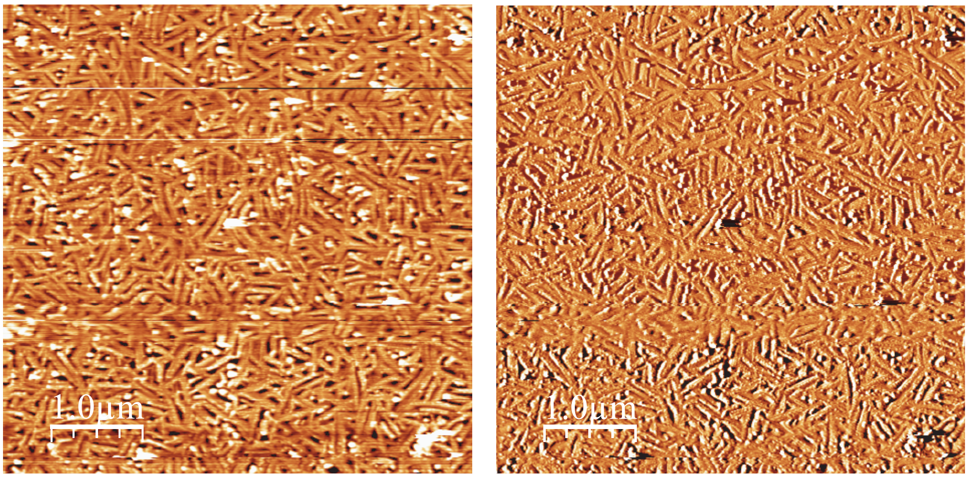

Fig. S8 AFM topography (left) and amplitude (right) images of vacuum deposited thin films of **1** onto SiO_2/AlO_x/SAM gate dielectric deposited at a substrate temperature of 100 °C.

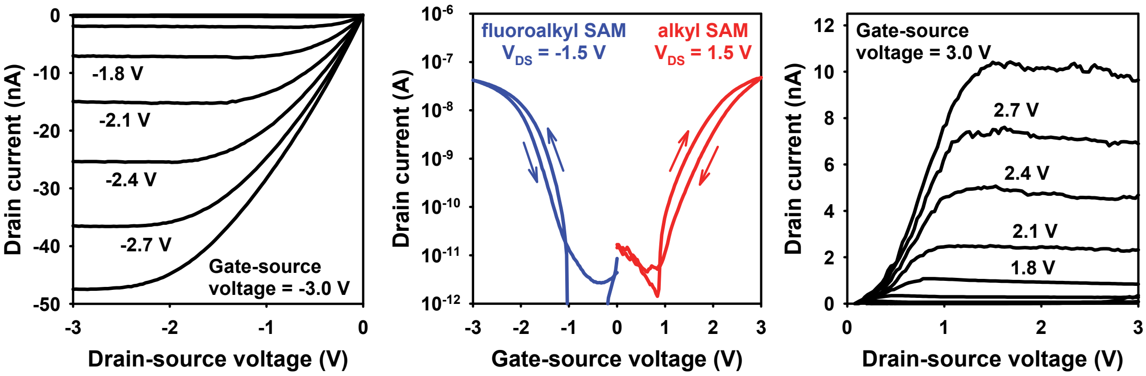

Fig. S9 Output and transfer characteristics of two TFTs based on the semiconductor NDI **1** with thin AlO_x/SAM gate dielectrics in which the SAM is composed either of a fluoroalkyl phosphonic acid (FC18-PA) or an alkyl phosphonic acid (HC14-PA).

Table S1 Field-effect mobilities measured for p-channel (holes) and n-channel operation (electrons) in TFTs based on NDI **1** using either thick SiO_2/AlO_x/SAM or thin AlO_x/SAM gate dielectrics.

gate dielectric	**hole mobility (cm^2/Vs)**	**electron mobility (cm^2/Vs)**
SiO_2 / AlO_x / FC18-PA SAM	0.56	$<10^{-5}$
SiO_2 / AlO_x / HC14-PA SAM	0.01	$\sim10^{-5}$
AlO_x / FC18-PA SAM	0.03	$<10^{-5}$
AlO_x / HC14-PA SAM	0.007	0.02

7. References

1 S. Chopin, F. Chaignon, E. Blart and F. Odobel, *J. Mater. Chem.*, 2007, **17**, 4139.

2 D. D. Perrin, W. L. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals* –Pergamon Press Ltd.: Oxford, 1980, 2nd edn.

3 R. Gvishi, R. Reisfeld and Z. Burshtein, *Chem. Phys. Lett.* 1993, **213**, 338.

4 A. J. Fry, in *Laboratory Techniques in Electroanalytical Chemistry*, ed. Peter Kissinger and William R. Heineman, Marcel Dekker Ltd., New York; 1996, 2nd edn.

5 A. D. Becke, *Phys. Rev. A,* 1988, **38**, 3098; C. Lee, W. Yang and R. G. Parr; *Phys. Rev. B,* 1988, **37**, 785; A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.

6 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Köhmel, *Chem. Phys. Lett.,* 1989, **162**, 165; R. Ahlrichs and M. von Arnim, *Methods and Techniques in Computational Chemistry: METECC-95*; Clementi, E.; Corongiu, G., Eds.; Club Européen MOTECC, 1995.

7 A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.,* 1994, **100**, 5829.

8 R. F. Fink, J. Seibt, V. Engel, M. Renz, M. Kaupp, S. Lochbrunner, H.-M. Zhao, J. Pfister, F. Würthner and B. Engels, *J. Am. Chem. Soc.,* 2008, **130**, 12858.

9 I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A. M. Baro, *Rev. Sci. Instrum.,* 2007, **78**, 013705-1.