

Supporting Information to the article (part 1)

Synthesis, Solution and Solid State Properties of Homological Dialkylated Naphthalene Diimides. A Systematic Review of Molecules for Next-Generation Organic Electronics

Dorota Chlebosz^{1,2}, Waldemar Goldeman³, Krzysztof Janus^{1,2}, Michał Szuster¹, Adam
Kiersnowski^{1,2,*}

¹ Department of Physical and Quantum Chemistry, Wrocław University of Science and
Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

² The Leibniz Institute of Polymer Research, Hohe Strasse 6, D-01069 Dresden, Germany

³ Department of Medicinal and Organic Chemistry, Wrocław University of Science and
Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

*correspondence: Adam Kiersnowski, adam.kiersnowski@pwr.edu.pl

Table of contents

SI-1.	Summary of NMR data for the synthesized NDIs.....	page S3
SI-2.	UV-Vis study: spectra and solubility.....	page S5
SI-3.	FTIR spectra of NDIs.....	page S7
SI-4.	Crystal structure of NDIs.....	page S9
SI-5.	Thermal properties of NDIs: TGA and DSC study.....	page S11
SI-6.	Exemplary OFET characteristics of NDIC7.....	page S14
SI-7.	Supporting references.....	page S15

SI-1. Summary of NMR data for the synthesized NDIs

Table S1. ¹³C NMR data of the studied NDIs. Chemical shifts of the subsequent methylene carbon atoms in alkyl chains are given in columns under corresponding groups in the header. The carbon atoms are counted from the methyl group to the α-methylene group protons (NCH₂CH₂).

	Two 4° aromatic carbons ¹⁾	ArCH	C=O	NCH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₃
NDIC3	126.61 and 126.67	130.92	162.83	-	-	-	-	-	-	-	-	42.42	21.38	11.49
NDIC4	126.64 and 126.69	130.92	162.84	-	-	-	-	-	-	-	40.76	30.17	20.35	13.81
NDIC5	126.51*	130.82	162.67	-	-	-	-	-	-	40.91	29.16	27.71	22.38	13.96
NDIC6	126.60 and 126.64	130.87	162.78	-	-	-	-	-	40.98	31.49	28.02	26.74	22.54	14.04
NDIC7	126.60 and 126.57	130.87	162.74	-	-	-	-	40.98	31.73	28.98	28.08	27.04	22.59	14.07
NDIC8	126.62 and 126.65	130.89	162.79	-	-	-	41.00	31.80	29.29	29.19	28.09	27.10	22.64	14.09
NDIC9	126.61 and 126.65	130.90	162.79	-	-	41.00	31.85	29.49	29.33	29.26	28.09	27.09	22.66	14.11
NDIC10	126.56 and 126.58	130.86	162.72	-	40.98	31.88	29.55	29.53	29.33	29.30	28.07	27.09	22.68	14.11
NDIC11	126.65 and 126.69	130.92	162.83	41.01	31.92	29.60*	29.53	29.33*	28.10	27.10	22.70	14.12		

*Overlapped signals of two carbons; ¹⁾ two signals of two groups of quaternary carbon atoms: C9 and C10, and C1, C4, C5 and C8

Table S2. ¹H NMR data of the studied NDIs. Chemical shifts of the subsequent methylene protons in alkyl chains are given in columns under corresponding groups in the header. The protons are counted from the methyl group to the α-methylene group protons (NCH₂CH₂). Multiplets in the spectra are marked as: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet (complex pattern), br = broad.

	Naphthyl-H	NCH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₂	CH ₃
NDIC3	8.75 (s)	-	-	-	-	-	-	-	-	4.17 (m)*	1.78 (sext, 7.5Hz)	1.03 (t, 7.4Hz)
NDIC4	8.78 (s)	-	-	-	-	-	-	-	4.23 (m)*	1.76 (m)	1.48 (sext, 7.5Hz)	1.02 (t, 7.4Hz)
NDIC5	8.76 (s)	-	-	-	-	-	-	4.21 (m)*	1.77 (m)	1.38-1.48 (m)		0.94 (t, 7.1Hz)
NDIC6	8.78 (s)	-	-	-	-	-	4.21 (m)*	1.77 (m)	1.46 (m)	1.33-1.41 (m)		0.92 (t, 7.0Hz)
NDIC7	8.76 (s)	-	-	-		4.21 (m)*	1.76 (m)	1.45 (m)	1.39 (m)	1.27-1.36 (m)		0.90 (t, 7.0Hz)
NDIC8	8.77 (s)	-	-	-	4.21 (m)*	1.76 (m)	1.45 (m)	1.39 (m)		1.25-1.35 (m)		0.90 (t, 7.1Hz)
NDIC9	8.75 (s)	-	-	4.19 (m)*	1.74 (m)	1.43 (m)	1.36 (m)			1.22-1.35 (m)		0.87 (t, 7.1Hz)
NDIC10	8.75 (s)	-	4.19 (m)*	1.74 (m)	1.43 (m)	1.36 (quint, 7.2Hz)				1.20-1.33 (m)		0.87 (t, 7.2Hz)
NDIC11	8.75 (s)	4.19 (m)*	1.74 (m)	1.43 (m)	1.36 (quint, 7.4Hz)				1.20-1.32 (m)			0.87 (t, 7.1Hz)

*second-order AA'XX' spin system (for comments see the main text of manuscript)

SI-2. UV-Vis study: spectra and solubility

Table S3. Wavelength (λ) and molar absorptivity (ϵ) of the main bands of NDIs (spectra shown in Figure S1). Spectra acquired for 0.1 mmol/L solutions in chloroform.

	λ_1 [nm]	$\epsilon_1 \cdot 10^{-3}$ [M ⁻¹ cm ⁻¹]	λ_2 [nm]	$\epsilon_2 \cdot 10^{-3}$ [M ⁻¹ cm ⁻¹]	λ_3 [nm]	$\epsilon_3 \cdot 10^{-3}$ [M ⁻¹ cm ⁻¹]
NDIC3	342	12.6	360	20.4	380	24.8
NDIC4	342	11.5	360	19.2	380	24.1
NDIC5	343	12.7	360	21.9	380	27.7
NDIC6	342	12.7	360	22.0	380	27.8
NDIC7	342	12.9	360	22.2	380	28.1
NDIC8	343	13.7	360	23.8	381	30.3
NDIC9	342	16.0	360	21.6	381	27.3
NDIC10	342	13.1	360	22.7	381	28.8
NDIC11	343	13.0	360	22.3	380	28.3

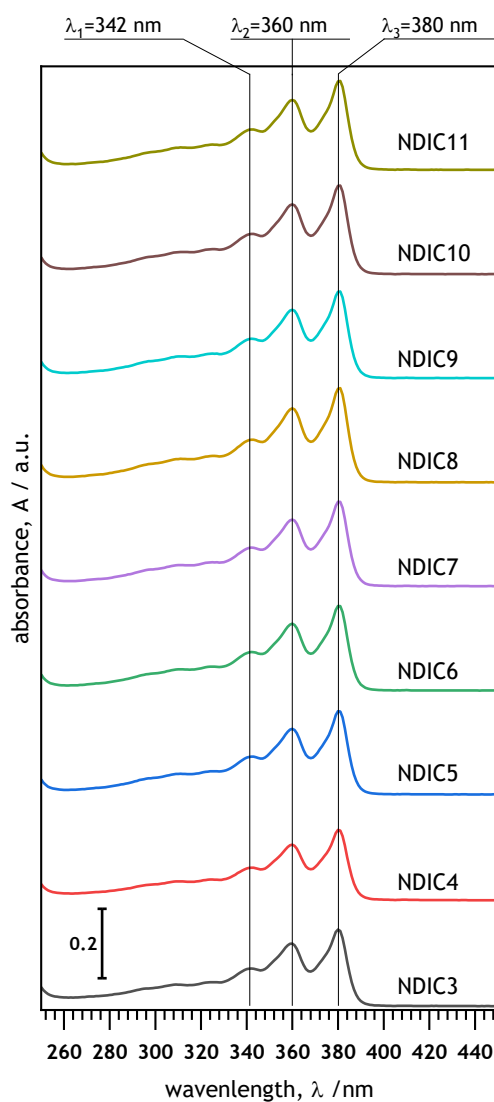


Figure S1. UV-VIS spectra of the NDIs in the study (CHCl₃, 0.1 mM).

Table S4. Solubility of NDIs in n-heptane

	solubility	
	mg/mL	mmol/L
NDIC3	0.048±0.003	0.137±0.008
NDIC4	0.056 ± 0.009	0.148±0.024
NDIC5	0.172 ± 0.005	0.423±0.012
NDIC6	0.321 ± 0.007	0.739±0.016
NDIC7	0.268 ± 0.018	0.579±0.039
NDIC8	0.327 ± 0.010	0.666±0.020
NDIC9	0.440 ± 0.053	0.848±0.102
NDIC10	0.472 ± 0.057	0.863±0.104
NDIC11	0.619 ± 0.047	1.08±0.082

Table S5. Solubility of NDIs in toluene

	solubility	
	mg/mL	mmol/L
NDIC3	6.3 ± 0.4	18.0±1. 1
NDIC4	3.9 ± 0.3	10.3±0.8
NDIC5	15.4 ± 0.4	37.9±1.0
NDIC6	24.0 ± 0.5	55.2±1.2
NDIC7	20.9 ± 0.8	45.2±1.2
NDIC8	20.5 ± 0.8	41.8±1.6
NDIC9	5.1 ± 0.5	9.8±1.0
NDIC10	10.2 ± 0.4	18.7±0.7
NDIC11	2.0 ± 0.4	3.5±0.7

Table S6. Solubility of NDIs in 1,2-dichlorobenzene

	solubility	
	mg/mL	mmol/L
NDIC3	26.8 ± 0.4	76.5±1. 1
NDIC4	9.8 ± 0.2	25.9±0.5
NDIC5	31.9 ± 0.6	78.6±1.5
NDIC6	42.8 ± 0.6	98.5±1.4
NDIC7	39.0 ± 1.2	84.3±2.6
NDIC8	34.9 ± 0.6	71.2±1.2
NDIC9	9.4 ± 0.2	18.1±0.4
NDIC10	18.1 ± 0.8	33.1±1.5
NDIC11	3.5 ± 0.2	6.1±0.4

SI-3. FTIR spectra of NDIs

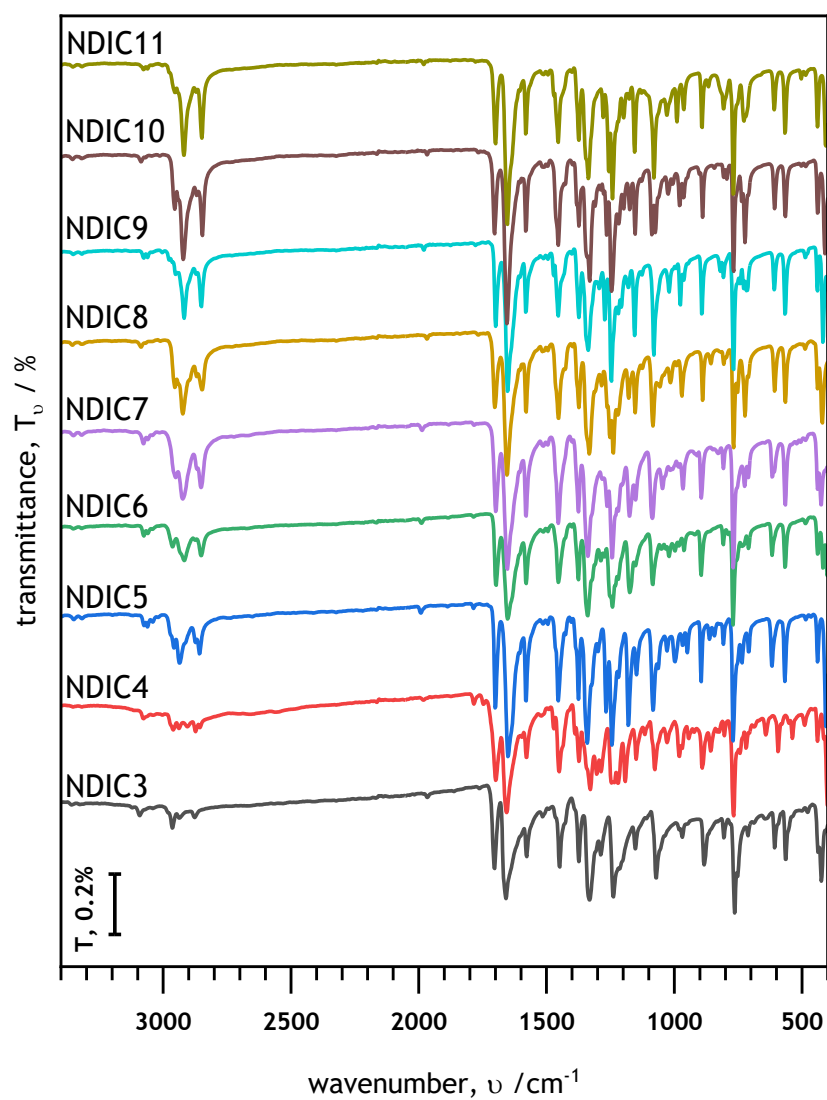


Figure S2. Series of FTIR spectra of all investigated NDIs. For the sake of clarity the spectra are shifted along the transmittance scale. The transmittance scale bar in the lower left corner. Abbreviations are explained in the main part of the paper.

Table S7. Positions and intensities of the main FTIR absorption bands of the NDIs

	aromatic				alkyl		symmetric and asymmetric imide C=O stretching	C-N stretching
	C-H stretching	C=C stretching	C-H in-plane bending	C-H out-of-plane bending	C-H stretching	C-H bending		
NDIC3	3043 3061 3076(vw)	1581(m)	1080(s) 1242(s)	770(s)	2850 2920 2953(w)	1373(m) 1454(m)	1653(vs) 1699(s)	1337(s)
NDIC4	3040 3064 3076(vw)	1578(m)	1076(s) 1246(s)	768(s)	2858 2873 2939 2960(w)	1373(m) 1450(m)	1654(vs) 1699(s)	1329(s)
NDIC5	3041 3063 3074(vw)	1580(m)	1084(s) 1180(s) 1244(s)	770(s)	2858 2874 2935 2958(w)	1375(m) 1454(m)	1650(vs) 1701(s)	1340(s)
NDIC6	3041 3061 3076(vw)	1580(m)	1084(s) 1175(s) 1242(s)	770(s)	2852 2916 2964(w)	1375(m) 1454(m)	1652(vs) 1697(s)	1338(s)
NDIC7	3041 3061 3078(vw)	1580(m)	1086(s) 1175(s) 1244(s)	770(s)	2852 2868 2924 2951(m)	1375(m) 1454(m)	1653(vs) 1699(s)	1338(s)
NDIC8	3043 3070 3088(vw)	1580(m)	1084(s) 1154(m) 1238(s)	768(s)	2848 2868 2924 2955(m)	1374(m) 1452(m)	1655(vs) 1703(s)	1333(s)
NDIC9	3041 3061 3076(vw)	1581(m)	1080(s) 1155(m) 1246(s)	768(s)	2850 2918 2951(m)	1373(m) 1454(m)	1652(vs) 1699(s)	1337(s)
NDIC10	3045 3068 3087(vw)	1581(m)	1074(s) 1088(s) 1153(m) 1246(s)	768(s)	2847(m) 2922(s) 2955(m)	1373(m) 1454(m)	1655(vs) 1703(s)	1331(s)
NDIC11	3043 3061 3076(vw)	1581(m)	1080(s) 1155(m) 1242(s)	768(s)	2848(m) 2918(s) 2953(w)	1375(m) 1454(m)	1653(vs) 1699(s)	1335(s)

Peaks intensity abbreviation: vs, very strong; s, strong; m, medium; w, weak; vw, very weak

SI-4. Crystal structure of NDIs

SI-4.1 Selected crystal data and structure refinement for NDIC7, NDIC9 and NDIC11:

Crystal Data for **NDIC7**: *CCDC number 2242898* $C_{28}H_{34}N_2O_4$ ($M = 462.57$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 7.8730(2)$ Å, $b = 4.84356(13)$ Å, $c = 33.0246(9)$ Å, $\beta = 95.025(3)^\circ$, $V = 1254.50(6)$ Å³, $Z = 2$, $T = 293(2)$ K, $\mu(\text{MoK}\alpha) = 0.082$ mm⁻¹, $D_{\text{calc}} = 1.225$ g/cm³, 12647 reflections measured ($5.234^\circ \leq 2\theta \leq 55.124^\circ$), 2655 unique ($R_{\text{int}} = 0.0226$, $R_{\text{sigma}} = 0.0179$) which were used in all calculations. The final R_1 was 0.0463 ($I > 2\sigma(I)$) and wR_2 was 0.1182 (all data).

Crystal Data for **NDIC9**: *CCDC number 2242899* $C_{32}H_{42}N_2O_4$ ($M = 518.67$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 7.8486(5)$ Å, $b = 4.8383(5)$ Å, $c = 37.741(2)$ Å, $\beta = 95.026(6)^\circ$, $V = 1427.66(19)$ Å³, $Z = 2$, $T = 293(2)$ K, $\mu(\text{AgK}\alpha) = 0.050$ mm⁻¹, $D_{\text{calc}} = 1.207$ g/cm³, 4992 reflections measured ($6.7^\circ \leq 2\theta \leq 44.368^\circ$), 3040 unique ($R_{\text{int}} = 0.0148$, $R_{\text{sigma}} = 0.0275$) which were used in all calculations. The final R_1 was 0.0439 ($I > 2\sigma(I)$) and wR_2 was 0.1189 (all data).

Crystal Data for **NDIC11**: *CCDC number 2242897* $C_{36}H_{50}N_2O_4$ ($M = 574.78$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 7.8478(6)$ Å, $b = 4.8691(3)$ Å, $c = 42.509(3)$ Å, $\beta = 92.142(6)^\circ$, $V = 1623.19(19)$ Å³, $Z = 2$, $T = 290(2)$ K, $\mu(\text{MoK}\alpha) = 0.076$ mm⁻¹, $D_{\text{calc}} = 1.176$ g/cm³, 5554 reflections measured ($3.836^\circ \leq 2\theta \leq 55.312^\circ$), 3274 unique ($R_{\text{int}} = 0.0179$, $R_{\text{sigma}} = 0.0358$) which were used in all calculations. The final R_1 was 0.0492 ($I > 2\sigma(I)$) and wR_2 was 0.1192 (all data).

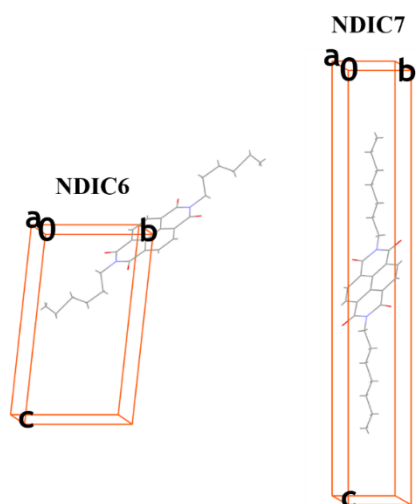


Figure S3. Unit cells of NDIC6 and NDIC7.

SI-4.2. Exemplary calculation of the interplanar spacings (d_{hkl}):

The interplanar spacings (d_{hkl}) were calculated from the Miller indices (hkl) and the values of the reticular parameters (unit cell axes). Equations to calculate the interplanar spacings (d_{hkl}) in a monoclinic (Equation ES1) and triclinic (Equation ES2) crystal system are shown below. The Miller indices corresponding to crystallographic planes parallel to the NDI cores are given in Table S4. Distance between these planes are considered π - π stacking distance (see main article).

$$\text{Monoclinic: } \frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos\beta}{ac} \right) \quad \text{ES1}$$

$$\text{Triclinic: } \frac{1}{d_{hkl}^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl) \quad \text{ES2}$$

where:

V – volume of unit cell

$$S_{11} = b^2 c^2 \sin^2 \alpha$$

$$S_{22} = a^2 c^2 \sin^2 \beta$$

$$S_{33} = a^2 b^2 \sin^2 \gamma$$

$$S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma)$$

$$S_{23} = a^2 bc (\cos \beta \cos \gamma - \cos \alpha)$$

$$S_{13} = ab^2 c (\cos \gamma \cos \alpha - \cos \beta)$$

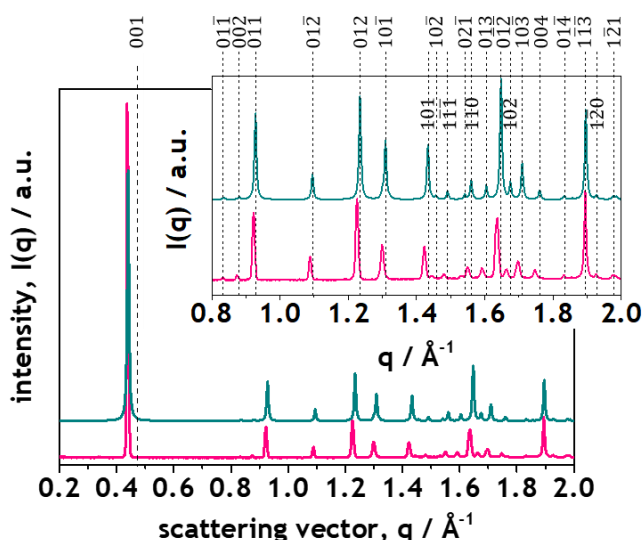


Figure S4. Exemplary one-dimensional $I(q)$ profiles of NDIC6: simulated in Mercury software (blue curve) and experimental (pink curve). Vertical dash lines mark positions of NDIC6 peaks; the numbers denote Miller indices of the peaks.

Table S8. π - π stacking planes

	π - π stacking plane
NDIC3	-
NDIC4	(1 $\bar{1}\bar{2}$)
NDIC5	(11 $\bar{5}$)
NDIC6	(1 $\bar{1}\bar{3}$)
NDIC7	(116)
NDIC8	(1 $\bar{1}$ 0)
NDIC9	(1 $\bar{1}$ 8)
NDIC10	(110)
NDIC11	(11 $\bar{9}$)

SI-5. Thermal properties of NDIs: TGA and DSC study

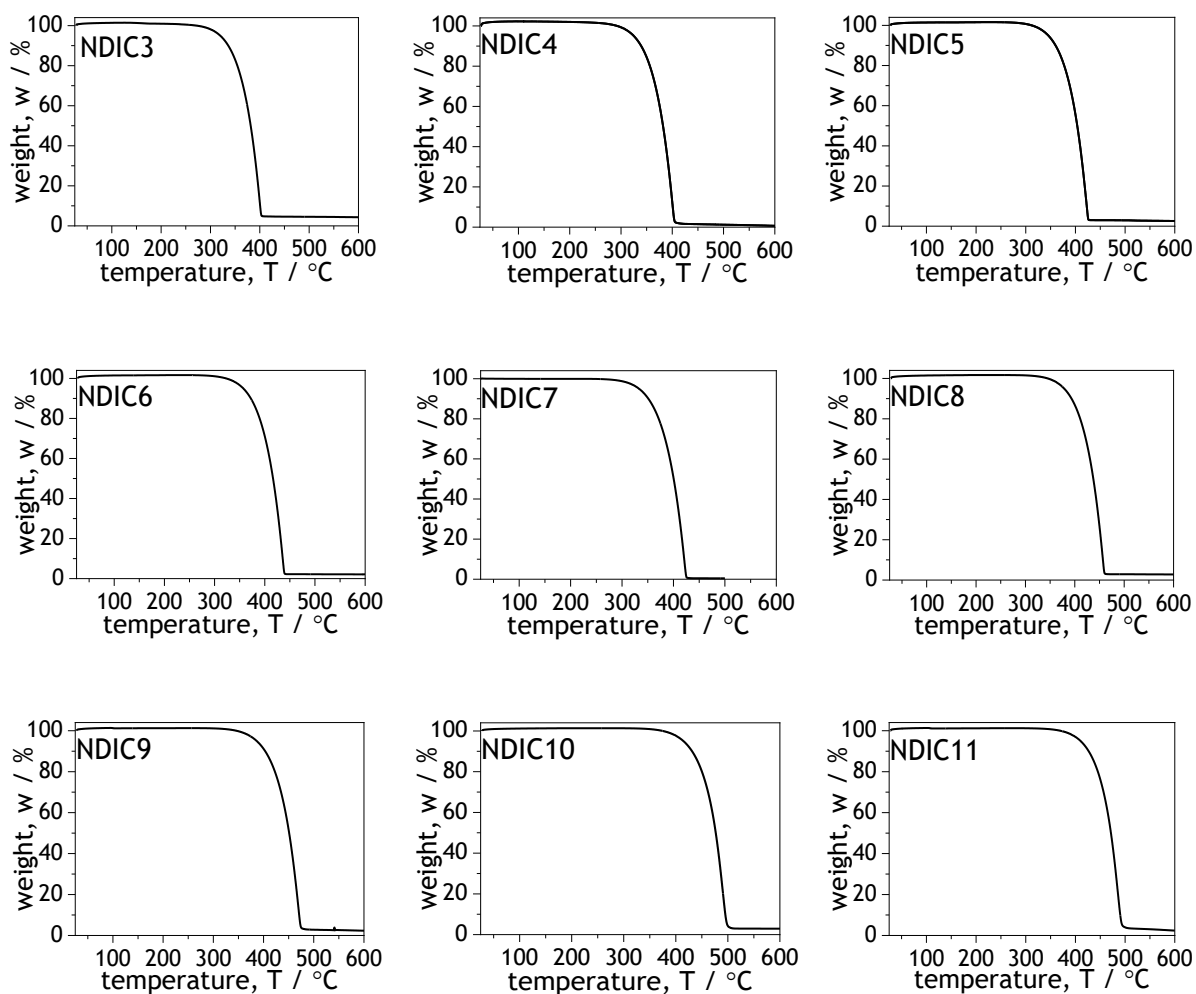


Figure S5. TGA curves of NDIs.

Table S9. Thermal decomposition temperatures of NDIs: temperatures of 3, 5 and 10 % weight loss

	weight loss		
	3 %	5 %	10 %
NDIC3	310	320	336
NDIC4	316	325	339
NDIC5	338	346	360
NDIC6	349	358	373
NDIC7	320	333	351
NDIC8	370	379	393
NDIC9	376	387	404
NDIC10	406	416	432
NDIC11	401	411	427

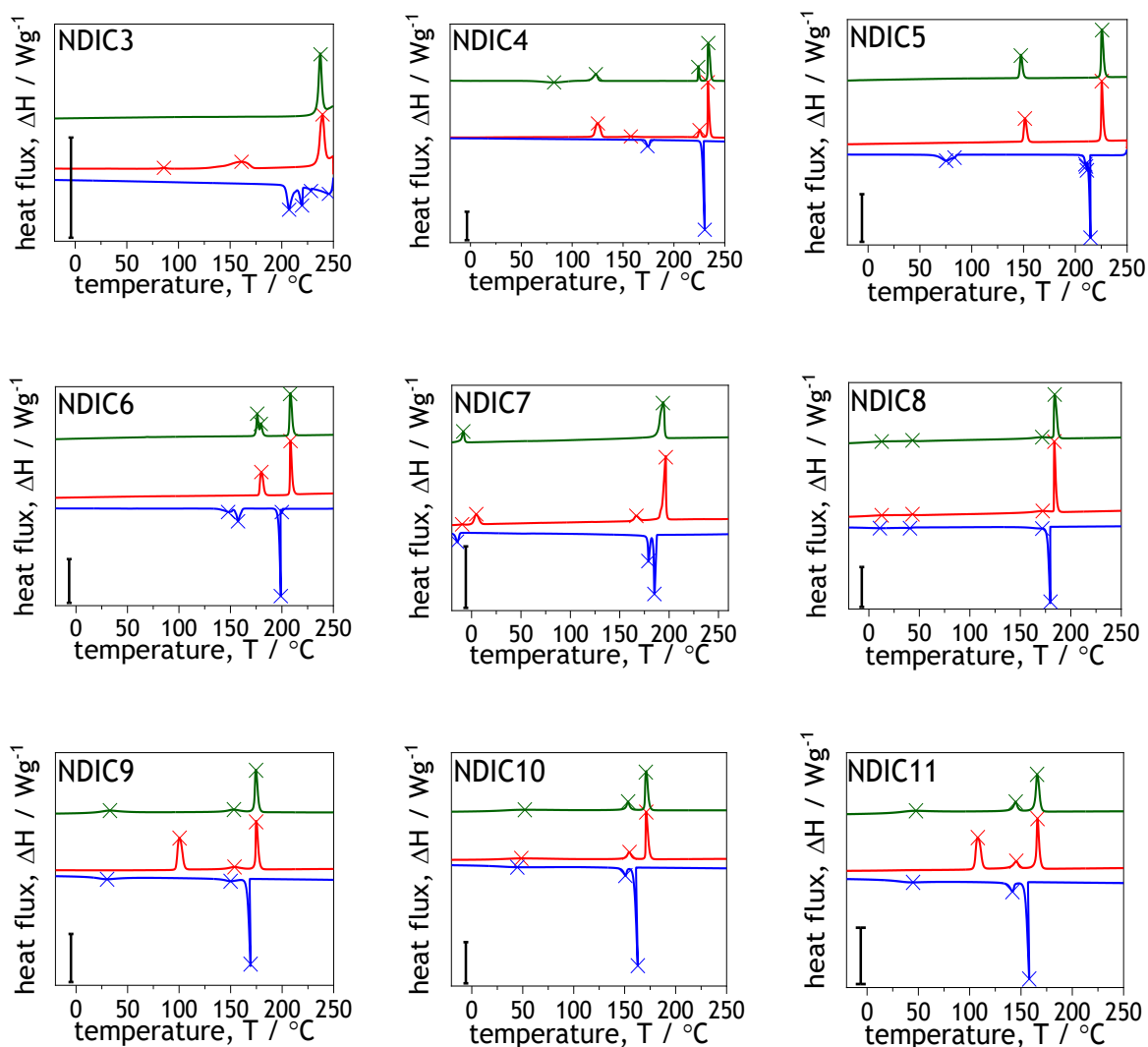


Figure S6. DSC plots for the 1st heating (red line) and 1st cooling (blue line) cycles, and 2nd heating (green line) cycle of NDIs. The heat flux scale bar in the lower left corner corresponds to 3.0 W/g. For the sake of clarity the curve of the 2nd heating cycle is vertically shifted.

Table S10. DSC data for the first heating and cooling cycles for the studied NDIs, together with literature data

	1-st heating cycle				1-st cooling cycle			
	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)
NDIC3		85.9; 0.7	160.7; 27.9	239.3; 42.6	207.1; -19.5	219.6; -8.2	228.3; -0.7	245.3; -4.2
NDIC4	125.0; 50.0	157.1; 3.6	225.7; 13.0	233.5; 61.9			175.0; -14.2	230.3; -63.6
Lit. data:								
[SI1]	131.8; 18.2		227.2; 3.8	234.1; 21.7			169.7; -5.2	227.5; -22.2
[SI2]							160; -3	226; -23
NDIC5			151.5; 30.4	225.5; 60.0		83.1 and 75.6; -28.5 (bimodal)	211.2, 210.3 and 209.6; -4.4 (trimodal)	214.7; -33.6
NDIC6		180.2; 35.3		208.2; 50.5	148.6; -8.0	157.3; -18.8	198.9; -46.1	200.3; -1.1
Lit. data:								
[SI1]		178.5; 16.5		207.9; 22.2	49.1; -5.1	148.1; -13.0		200; -21.1
[SI3]		187; 29.5		208; 41.2				
[SI4]						150; -61.9		204; -92.2
NDIC7	-9.3; 0.6	4.7; 16.6	166.6; 7.4	196.5; 59.1	-14.3; -10.9		179.1; -15.0	185.1; -34.6
NDIC8	12.7; 5.3	43.2; 0.8	172.2; 4.8	183.7; 61.2	10.9; -5.2	40.6; -1.0	171.4*	179.8; -77.3*
Lit. data:								
[SI1]				190.0; 31.0				185.9; -30.7
[SI2]								181; -32
[SI5]								180; -40.3
[SI6]							171.1; -	185.1; -
NDIC9		100.3; 64.0	153.6; 8.6	174.9; 54.4		30.1; -20.6	150.0; -7.0	169.3; -54.8
NDIC10	48.7; 21.6	154.3; 16.8		171.0; 57.9	53.4; -20.4	150.8; -11.4		162.4; -57.8
Lit. data:								
[SI1]		163.1; 7.3		180.8; 34.6		160.3; -7.2		178.2; -30.2
NDIC11		107.9; 58.0	145.4; 12.9	166.1; 53.7	44.8; -20.5		141.7; -13.9	158.0; -55.1
Lit. data:								
[SI4]							144; -19.1	162; -72.7
[SI6]						104.5; -	148.2; -	169.8; -

*Due to overlapping of the peaks at 171.4 and 179.8 °C ΔH=-77.3 J/g was measured for both peaks together

Table S11. DSC data for the second heating cycle for the studied NDIs , together with literature data

	2-nd heating cycle			
	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)	T (°C); ΔH (J/g)
NDIC3				237.4; 39.8
NDIC4	82.0; -23.8	123.2; 23.2	224.1; 13.5	233.8; 63.6
Lit. data:				
[1]	123.0; 17.6	162.8; 1.1	225.2; 3.9	233.2; 18.8
NDIC5			147.7; 27.0	225.6; 52.1
NDIC6		176.2; 13.2	179.6; 5.6	208.3; 51.0
Lit. data:				
[1]	68.3; 4.5	173.5; 2.3	180.2; 7.1	208.0; 22.6
NDIC7	-8.3; 11.8			194.0; 56.4
NDIC8	12.6; 6.2	43.2; 0.8	171.7; 4.1	184.0; 61.0
Lit. data:				
[1]				192.7; 30.5
NDIC9	32.9; 21.7		152.9; 9.1	174.4; 53.2
NDIC10	52.1; 23.5		153.2; 16.6	171.0; 56.2
Lit. data:				
[1]		163.2; 8.3	178; -	182.8; 31.3
[7]			153; 5.6	171; 25.6
NDIC11	47.3; 22.1		144.7; 15.2	165.6; 52.5
Lit. data:				
[7]			146; 7.5	166; 26.4

SI-6. Exemplary OFET characteristics of NDIs

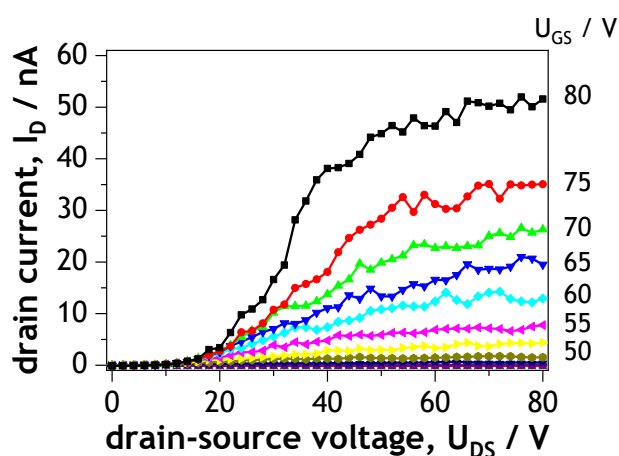


Figure S7. Exemplary output current-voltage characteristics for NDC7.

SI-7. Supporting references

- SI1. Milita, S.; Liscio, F.; Cowen, L.; Cavallini, M.; Drain, B. A.; Degousée, T.; Luong, S.; Fenwick, O.; Guagliardi, A.; Schroeder, B. C.; Masciocchi, N., Polymorphism in N,N'-dialkyl-naphthalene diimides. *Journal of Materials Chemistry C* **2020**, 8, (9), 3097-3112.
- SI2. Alvey, P. M.; Reczek, J. J.; Lynch, V.; Iverson, B. L., A Systematic Study of Thermochromic Aromatic Donor–Acceptor Materials. *The Journal of Organic Chemistry* **2010**, 75, (22), 7682-7690.
- SI3. Ofir, Y.; Zelichenok, A.; Yitzchaik, S., 1,4;5,8-naphthalene-tetracarboxylic diimide derivatives as model compounds for molecular layer epitaxy. *Journal of Materials Chemistry* **2006**, 16, (22), 2142-2149.
- SI4. Reczek, J. J.; Villazor, K. R.; Lynch, V.; Swager, T. M.; Iverson, B. L., Tunable Columnar Mesophases Utilizing C2 Symmetric Aromatic Donor–Acceptor Complexes. *Journal of the American Chemical Society* **2006**, 128, (24), 7995-8002.
- SI5. Leight, K. R.; Esarey, B. E.; Murray, A. E.; Reczek, J. J., Predictable Tuning of Absorption Properties in Modular Aromatic Donor–Acceptor Liquid Crystals. *Chemistry of Materials* **2012**, 24, (17), 3318-3328.
- SI6. Ichikawa, M.; Yokota, Y.; Jeon, H. G.; Banoukepa, G. D.; Hirata, N.; Oguma, N., Comparative study of soluble naphthalene diimide derivatives bearing long alkyl chains as n-type organic thin-film transistor materials. *Organic Electronics* **2013**, 14, (2), 516-522.
- SI7. Jung, B. J.; Lee, K.; Sun, J.; Andreou, A. G.; Katz, H. E., Air-Operable, High-Mobility Organic Transistors with Semifluorinated Side Chains and Unsubstituted Naphthalenetetracarboxylic Diimide Cores: High Mobility and Environmental and Bias Stress Stability from the Perfluorooctylpropyl Side Chain. *Advanced Functional Materials* **2010**, 20, (17), 2930-2944.