ELECTRONIC SUPPLEMENTARY INFORMATION

Solid-state organization of n-type carbazole-based semiconductors for organic thin-film transistors

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Crystallographic Data Collection and Refinement

Crystal structure of 2. A red prism-like specimen of $C_{19}H_{12}N_4$, approximate dimensions 0.071 mm x 0.169 mm x 0.398 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a Multilayer monochromator and a Cu microfocus (λ = 1.54178 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 25035 reflections to a maximum θ angle of 74.68° (0.80 Å resolution), of which 2930 were independent (average redundancy 8.544, completeness = 98.2%, R_{int} = 3.56%, R_{sig} = 1.84%) and 2623 (89.52%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.0914(2) Å, b = 12.8955(4) Å, c = 16.1234(6) Å, β = 99.0270(10)°, volume = 1456.18(8) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6903 and 0.7538. The structure was solved using the Bruker SHELXTL Software Package, and refined using SHELXL,[1] using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{19}H_{12}N_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 227 variables converged at R1 = 6.26%, for the observed data and wR2 = 14.20% for all data. The goodness-of-fit was 1.127. The largest peak in the final difference electron density synthesis was 0.440 e^-/Å^3 and the largest hole was -0.348 e^-/Å^3 with an RMS deviation of 0.050 e^-/Å^3. On the basis of the final model, the calculated density was 1.352 g/cm^3 and F(000), 616 e^-. Further details concerning the resolution and refinement of the crystal structure are presented in Table S1.

Crystal structure of 3. A red prism-like specimen of $C_{21}H_{16}N_4$, approximate dimensions 0.049 mm x 0.128 mm x 0.256 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 22892 reflections to a maximum θ angle of 27.51° (0.77 Å resolution), of which 3749 were independent (average redundancy 6.106, completeness = 99.6%, R_{int} = 14.97%, R_{sig} = 9.48%) and 2127 (56.74%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.7842(7) Å, b = 24.486(2) Å, c = 8.1096(8) Å, β = 110.652(3)°, volume = 1632.2(3) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6796 and 0.7456. The structure was solved using the Bruker SHELXTL Software Package, and refined using SHELXL,[1] using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{21}H_{16}N_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 227 variables converged at R1 = 5.65%, for the observed data and wR2 = 14.92% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 0.268 e^-/Å^3 and the largest hole was -0.292 e^-/Å^3 with an RMS deviation of 0.066 e^-/Å^3. On the basis of the final model, the calculated density was 1.320 g/cm^3 and F(000), 680 e^-. Further details concerning the resolution and refinement of the crystal structure are presented in Table S2.

[1] G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.

Crystal structure of 4. A red prism-like specimen of $C_{25}H_{24}N_4$, approximate dimensions 0.042 mm x 0.082 mm x 0.141 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 25848 reflections to a maximum θ angle of 27.72° (0.76 Å resolution), of which 5019 were independent (average redundancy 5.150, completeness = 98.0%, R_{int} = 9.69%, R_{sig} = 5.71%) and 1658 (33.03%) were greater than 2σ(F^2). The final cell constants of a = 7.917(3) Å, b = 8.777(4) Å, c = 16.892(7) Å, α = 92.79(2)°, β = 102.20(2)°, γ = 107.30(2)°, volume = 1087.5(8) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6046 and 0.7456. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{25}H_{24}N_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 263 variables converged at R1 = 8.27%, for the observed data and wR2 = 29.55% for all data. The goodness-of-fit was 0.991. The largest peak in the final difference electron density synthesis was 0.441 $e^-/Å^3$ and the largest hole was -0.337 $e^-/Å^3$ with an RMS deviation of 0.047 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.162 g/cm^3 and F(000), 404 e^-. Further details concerning the resolution and refinement of the crystal structure are presented in Table S3.

Crystal structure of 5. A red prism-like specimen of $C_{29}H_{32}N_4$, approximate dimensions 0.048 mm x 0.120 mm x 0.260 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 27439 reflections to a maximum θ angle of 26.75° (0.79 Å resolution), of which 5387 were independent (average redundancy 5.094, completeness = 98.0%, R_{int} = 6.24%, R_{sig} = 4.22%) and 2328 (43.22%) were greater than 2σ(F^2). The final cell constants of a = 7.7023(13) Å, b = 8.9110(15) Å, c = 20.022(4) Å, α = 77.669(9)°, β = 84.775(8)°, γ = 73.953(7)°, volume = 1289.4(4) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6140 and 0.7454. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{29}H_{32}N_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 299 variables converged at R1 = 6.44%, for the observed data and wR2 = 18.12% for all data. The goodness-of-fit was 1.020. The largest peak in the final difference electron density synthesis was 0.202 $e^-/Å^3$ and the largest hole was -0.144 $e^-/Å^3$ with an RMS deviation of 0.029 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.124 g/cm^3 and F(000), 468 e^-. Further details concerning the resolution and refinement of the crystal structure are presented in Table S4.

Table S1 Crystal data and structure refinement for 9-ethyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole (**2**).

Identification code	9-ethyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole	
Empirical formula	C19 H12 N4	
Formula weight	296.33	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.0914(2) Å	α= 90°.
	b = 12.8955(4) Å	β= 99.0270(10)°.
	c = 16.1234(6) Å	γ = 90°.
Volume	1456.18(8) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.661 mm^{-1}	
F(000)	616	
Crystal size	0.398 x 0.169 x 0.071 mm^3	
Theta range for data collection	4.412 to 74.680°.	
Index ranges	-8<=h<=7, -16<=k<=16, -20<=l<=20	
Reflections collected	25035	
Independent reflections	2930 [R(int) = 0.0356]	
Completeness to theta = 67.679°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6903	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2930 / 5 / 227	
Goodness-of-fit on F^2	1.127	
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1362	
R indices (all data)	R1 = 0.0696, wR2 = 0.1420	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.440 and -0.348 $e.Å^{-3}$	

Table S2 Crystal data and structure refinement for 9-butyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole (**3**).

Identification code	9-butyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole	
Empirical formula	C21 H16 N4	
Formula weight	324.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.7842(7) Å	α= 90°.
	b = 24.486(2) Å	β= 110.652(3)°.
	c = 8.1096(8) Å	γ = 90°.
Volume	1632.2(3) $Å^3$	
Z	4	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	680	
Crystal size	0.256 x 0.128 x 0.049 mm^3	
Theta range for data collection	2.478 to 27.506°.	
Index ranges	-10<=h<=11, -31<=k<=31, -10<=l<=10	
Reflections collected	22892	
Independent reflections	3749 [R(int) = 0.1497]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6796	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3749 / 0 / 227	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1194	
R indices (all data)	R1 = 0.1300, wR2 = 0.1492	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.268 and -0.292 $e.Å^{-3}$	

Table S3 Crystal data and structure refinement for 9-octyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole (**4**).

Identification code	9-octyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole	
Empirical formula	C25 H24 N4	
Formula weight	380.48	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.917(3) Å	α= 92.79(2)°.
	b = 8.777(4) Å	β= 102.20(2)°.
	c = 16.892(7) Å	γ = 107.30(2)°.
Volume	1087.5(8) $Å^3$	
Z	2	
Density (calculated)	1.162 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	404	
Crystal size	0.141 x 0.082 x 0.042 mm^3	
Theta range for data collection	2.448 to 27.715°.	
Index ranges	-10<=h<=10, -11<=k<=11, -22<=l<=22	
Reflections collected	25848	
Independent reflections	5019 [R(int) = 0.0969]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6046	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5019 / 5 / 263	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0827, wR2 = 0.2271	
R indices (all data)	R1 = 0.2608, wR2 = 0.2955	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.441 and -0.337 $e.Å^{-3}$	

Table S4 Crystal data and structure refinement for 9-dodecyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole (**5**).

Identification code	9-dodecyl-3-(1,2,2)-tricyanovinyl-9*H*-carbazole	
Empirical formula	C29 H32 N4	
Formula weight	436.58	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.7023(13) Å	α= 77.669(9)°.
	b = 8.9110(15) Å	β= 84.775(8)°.
	c = 20.022(4) Å	γ = 73.953(7)°.
Volume	1289.5(4) $Å^3$	
Z	2	
Density (calculated)	1.124 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	468	
Crystal size	0.260 x 0.120 x 0.048 mm^3	
Theta range for data collection	2.426 to 26.748°.	
Index ranges	-9<=h<=9, -11<=k<=11, -25<=l<=25	
Reflections collected	27439	
Independent reflections	5387 [R(int) = 0.0624]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6140	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5387 / 0 / 299	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0644, wR2 = 0.1438	
R indices (all data)	R1 = 0.1773, wR2 = 0.1812	
Absorption correction	multi-scan	
Max. and min. transmission	0.7454 and 0.6140	
Largest diff. peak and hole	0.202 and -0.144 $e.Å^{-3}$	

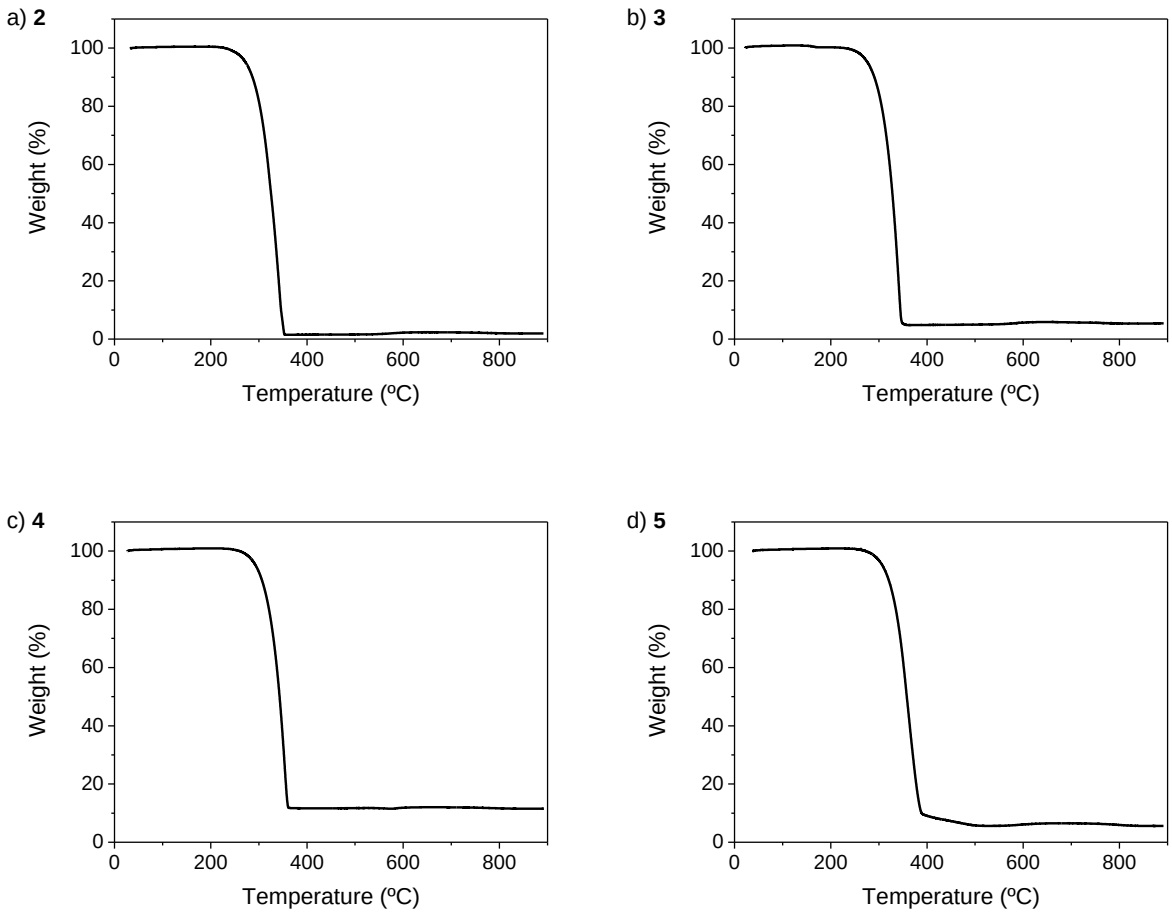

Figure S1. TGA curves of compounds **2**–**5** recorded at a scan rate of 20 °C min^{-1} under a nitrogen atmosphere.

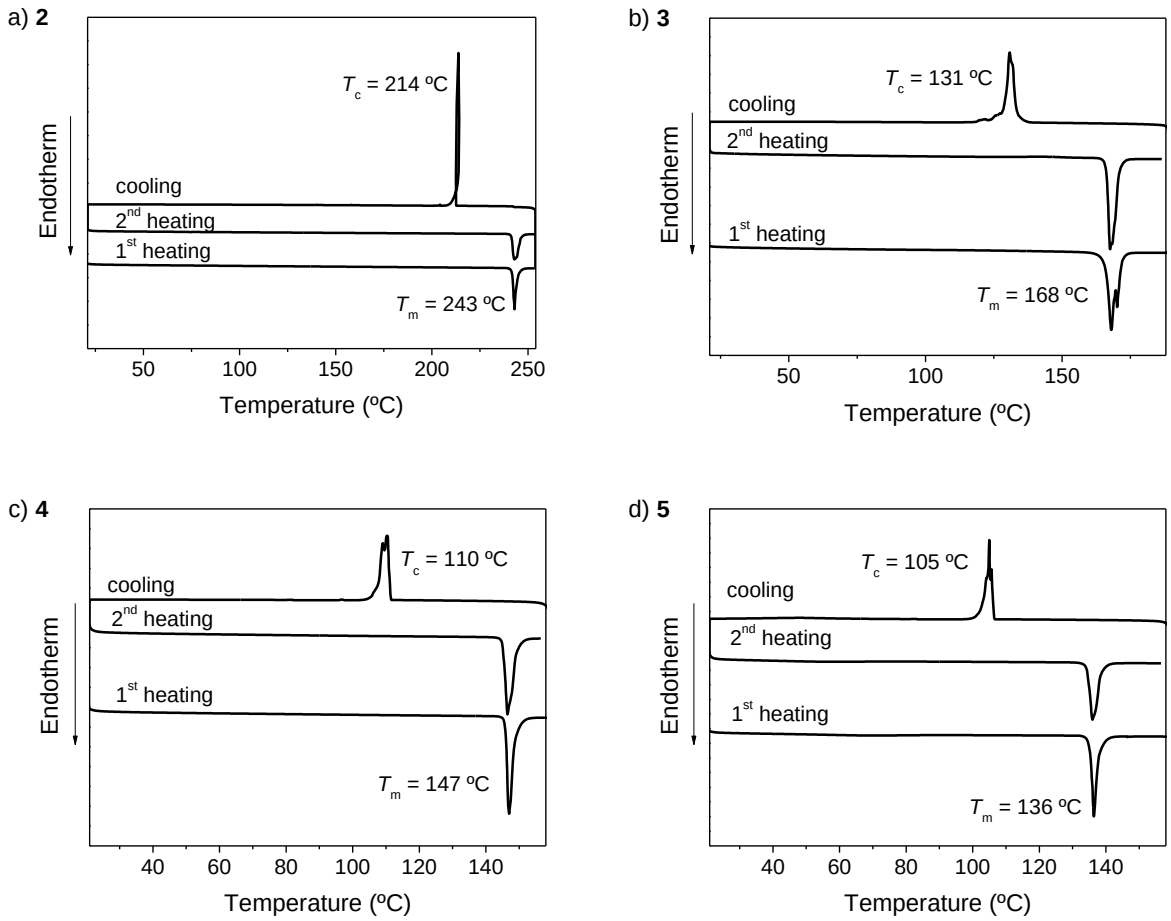

Figure S2. DSC curves of compounds **2**–**5** recorded at a scan rate of 10 °C min^{-1} under a nitrogen atmosphere.

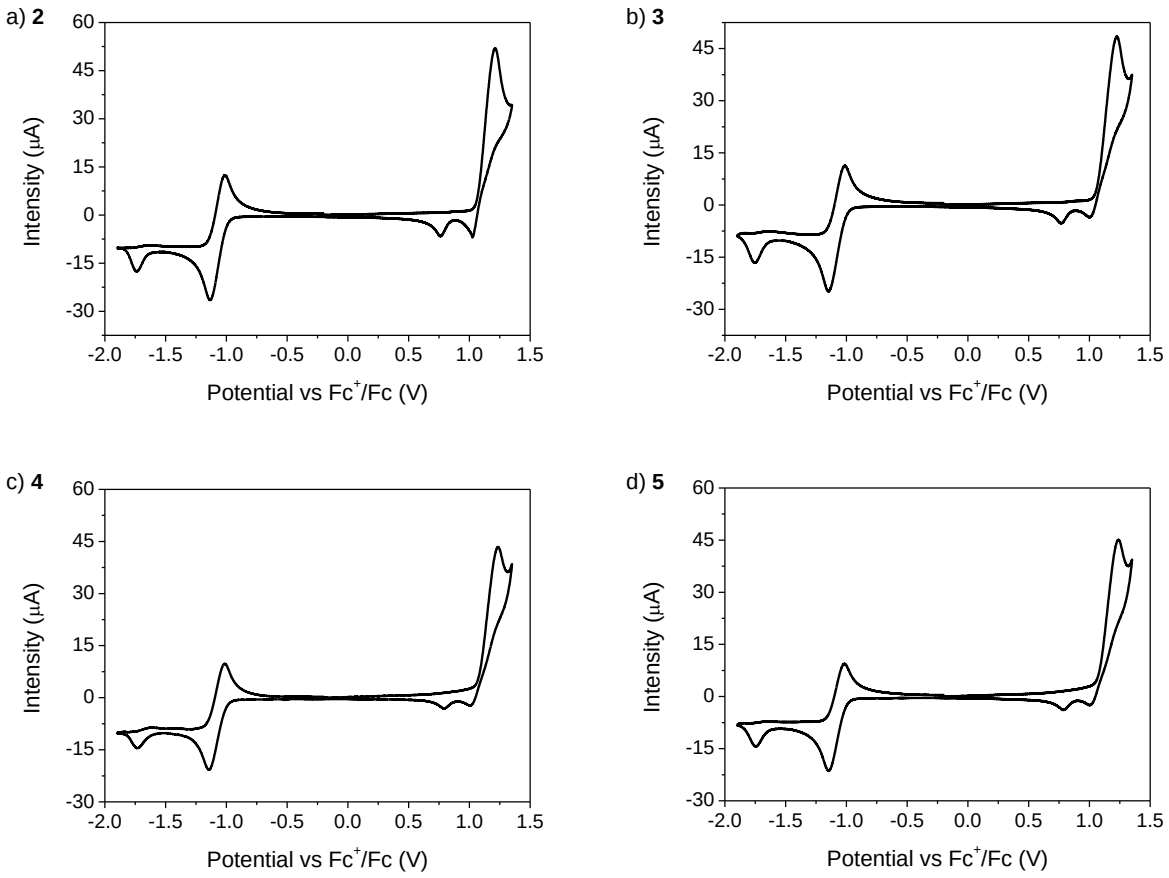

Figure S3. Cyclic votammograms of compounds **2**–**5** recorded at 100 mV s^{-1} in argon-purged dichloromethane solutions (1 mM).

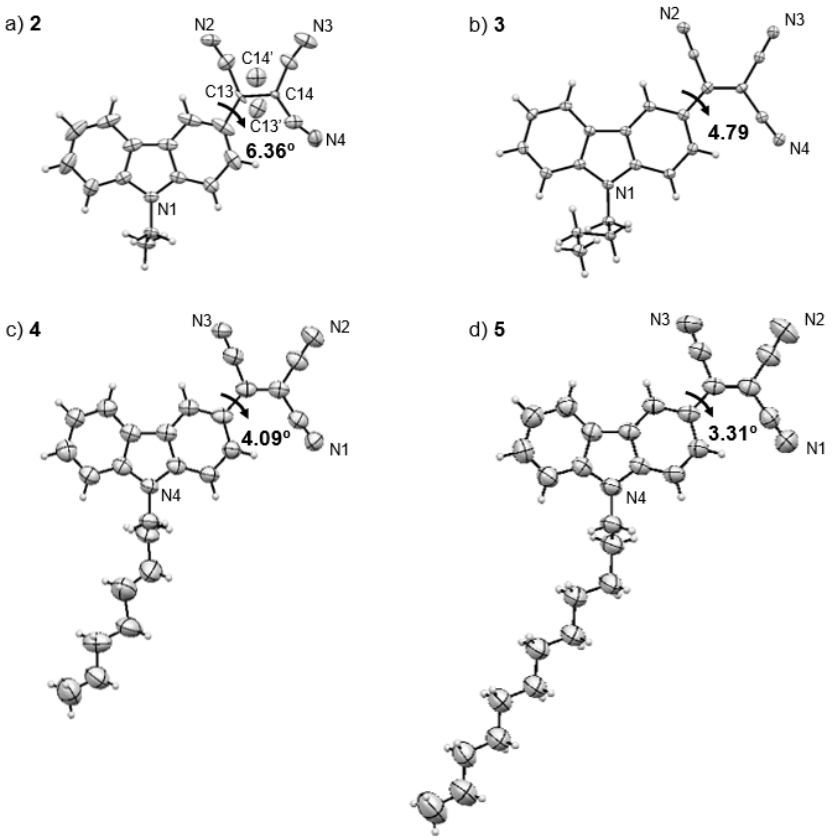

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Figure S4. X-ray crystal structures of molecules **2**–**5**, showing the 50% probability displacement.

Regarding the crystal structure of *N*-ethyl derivative **2**, the tricyanovinyl group is presented in two different conformations, showing a free rotational barrier under the crystallization conditions.

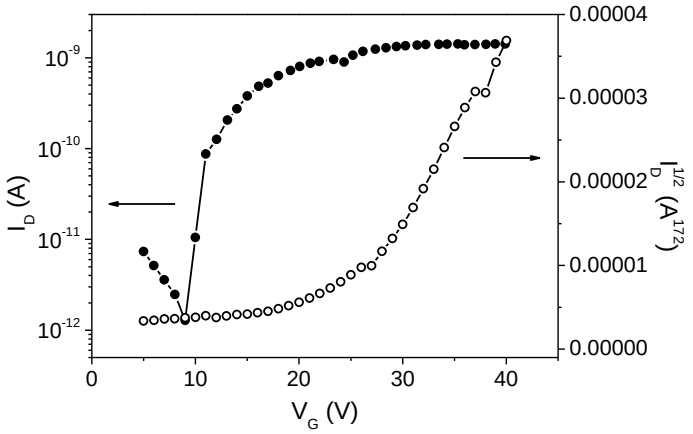


Figure S5. Transfer (V_D = 40 V) and saturation characteristics of an OTFT device fabricated with **1** as the semiconductor layer on OTS-treated c-Si/SiO_2 substrate.

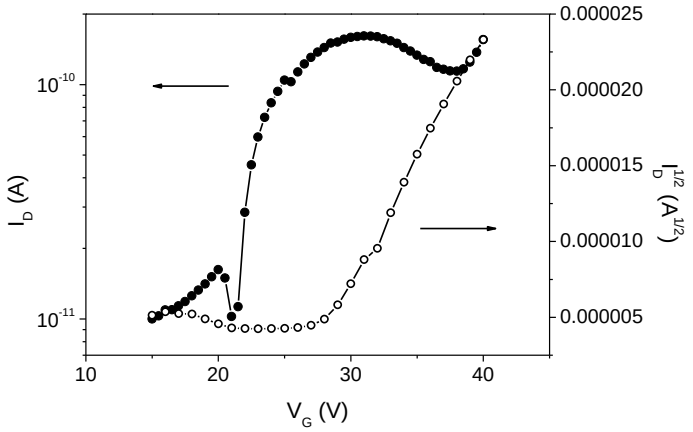


Figure S6. Transfer (V_D = 10 V) and saturation characteristics of an OTFT device fabricated with **2** as the semiconductor layer and with PS-treated c-Si/SiO_2 substrate.

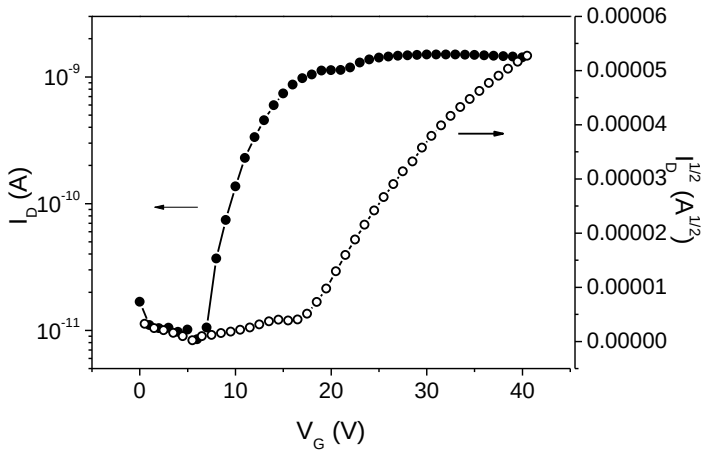


Figure S7. Transfer (V_D = 10 V) and saturation characteristics of an OTFT device fabricated with **3** as the semiconductor layer on PS-treated c-Si/SiO_2 substrate.

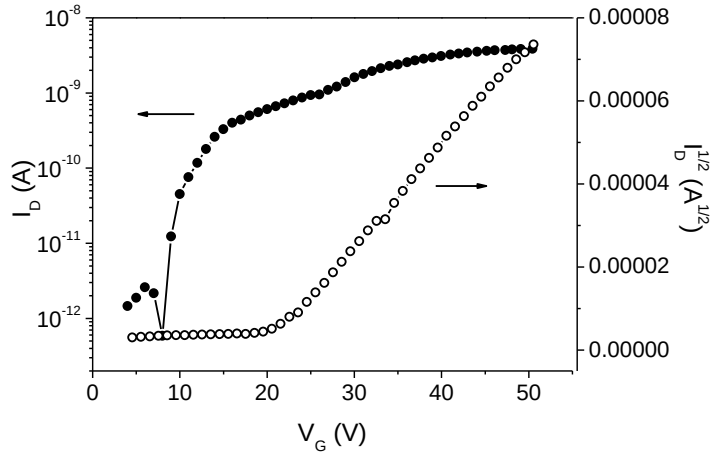


Figure S8. Transfer (V_D = 10 V) and saturation characteristics of an OTFT device fabricated with **4** as the semiconductor layer and with PS-treated c-Si/SiO_2 substrate.

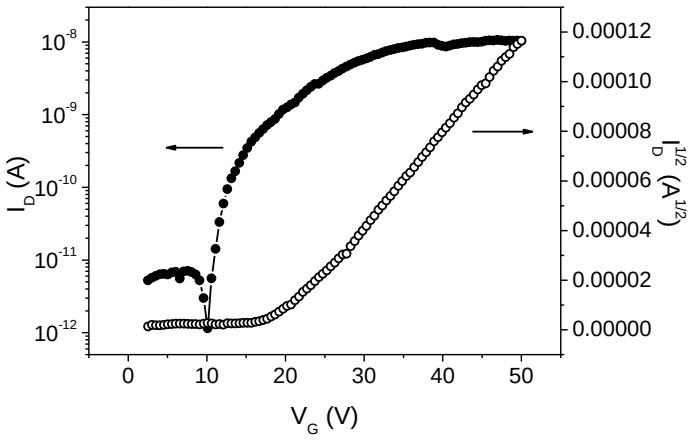
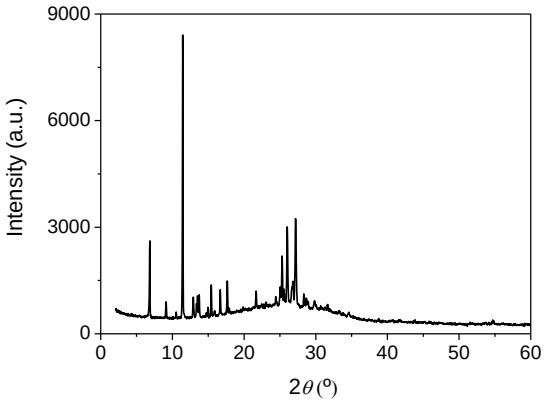
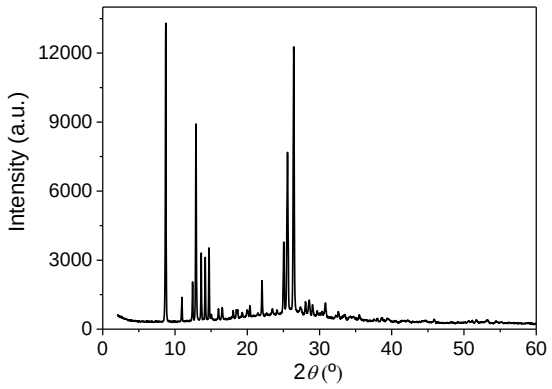


Figure S9. Transfer (V_D = 10 V) and saturation characteristics of an OTFT device fabricated with **5** as the semiconductor layer and with PS-treated c-Si/SiO_2 substrate.

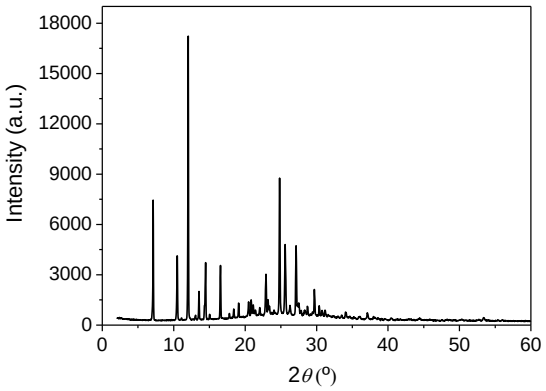
a) **1**



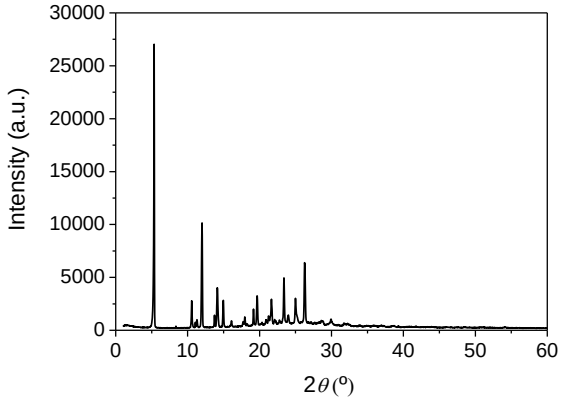
b) **2**



c) **3**



d) **4**



e) **5**

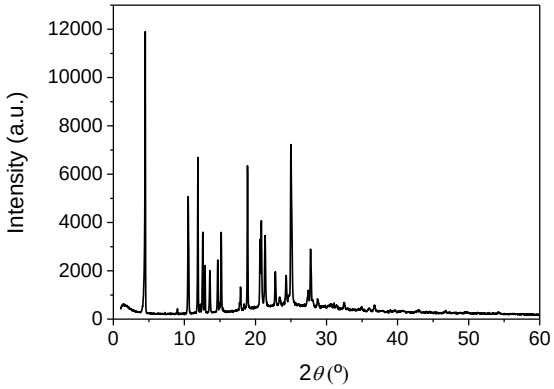


Figure S10. Powder XRD patterns of compounds **1**–**5**.