Electronic Suplementary Information

Molecular order of air-stable p-type Organic Thin-Film Transistors by tuning the extension of the π-conjugated core: the cases of Indolo[3,2-*b*]carbazole and Triindole semiconductors

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Fig. S1 Absorption spectra of compounds **2**-**4** in dichloromethane at 10 μM and at 298 K.

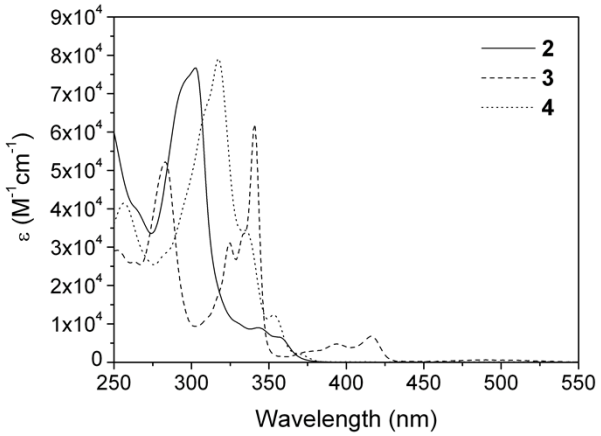


Fig. S2 Cyclic voltammograms of compounds a) **2** and b) **3** in dichloromethane solutions with Ag/AgCl as the reference electrode.

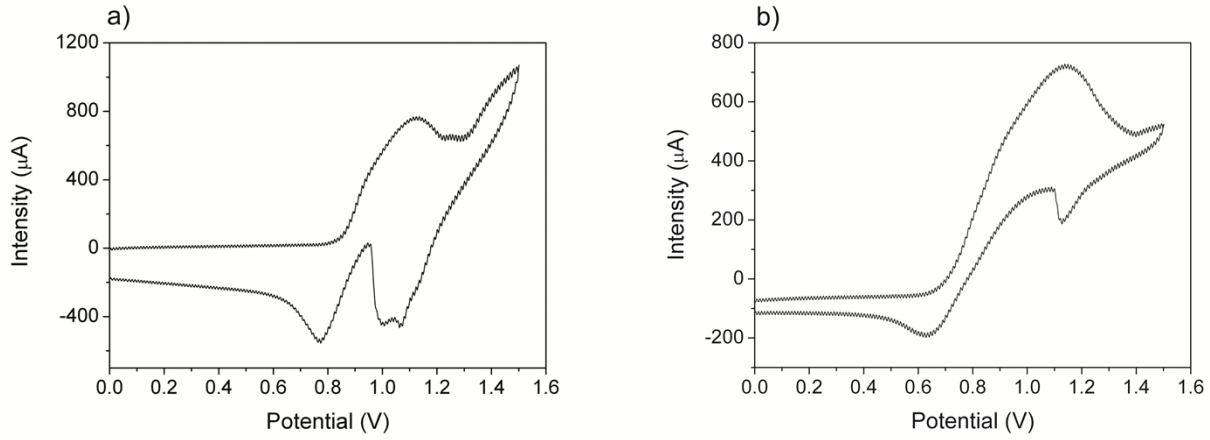


Fig. S3 OTFTs characteristics of device fabricated with **3** as the semiconductor layer and with PS treated substrate. a) Output characteristics at different gate voltages (V_G). b) Transfer (V_D = -20 V) and saturation characteristics. c) Mobility and threshold voltage of one representative device fabricated with **3** as the semiconductor layer and with PS treated substrate as a function of storage time in the air. d) Transfer characteristics for the 4th day and the 147th day of the experiment at V_D = -20 V. Inset figure shows the evolution with time of the I_{on}/I_{off} ratio of the selected device.

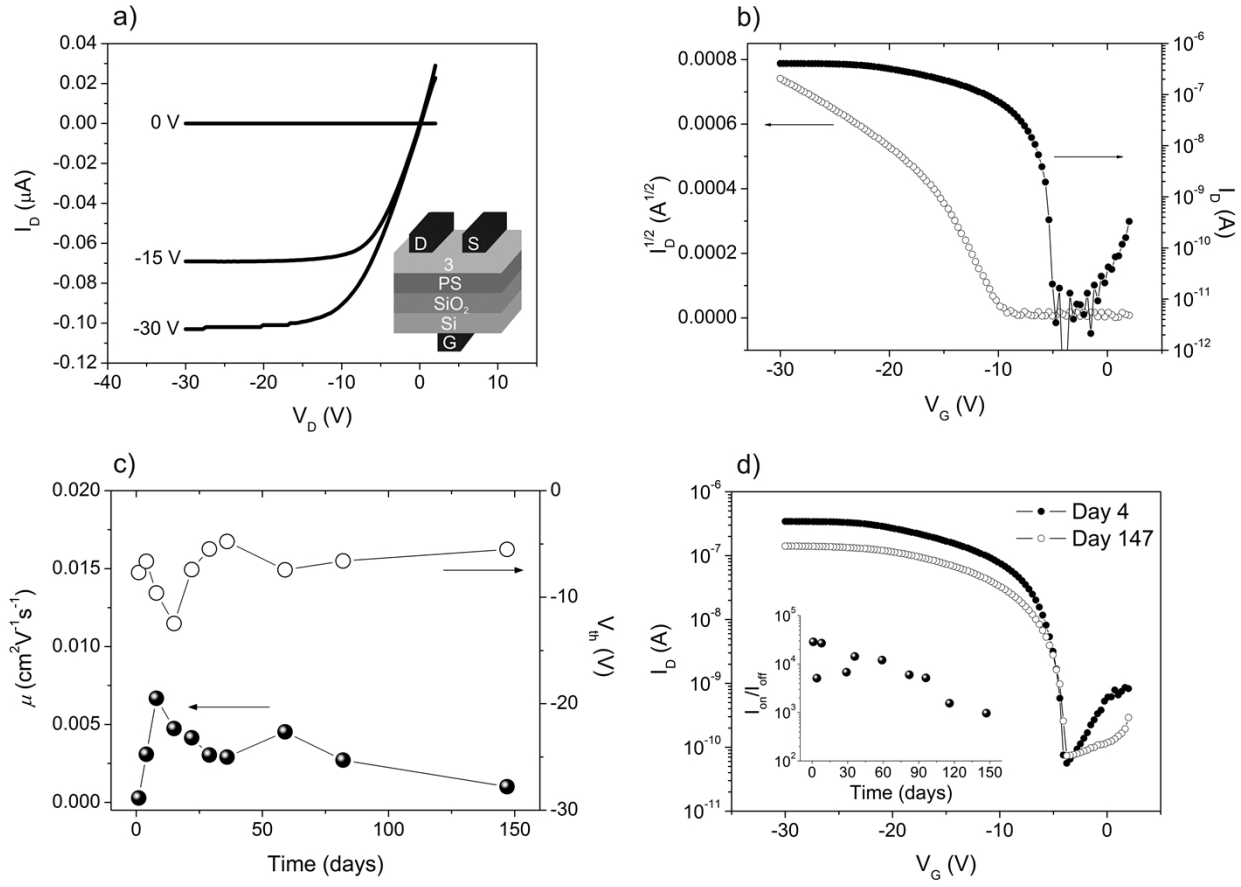


Table S1. Crystal data and structure refinement for 5,11-dimethyl-indolo[3,2-b]carbazole **3**.

Identification code	5,11-dimethyl-indolo[3,2-b]carbazole
Empirical formula	$C_{20}H_{16}N_2$
Crystal color, habit	Translucent light colourless prism- like specimen
Preparation	Grown from dichloromethane
Formula weight	284.35
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic,C2/c
Unit cell dimensions	a = 16.8377(13)Å α = 90° b = 5.6889(4)Å β = 106.671(2)° c = 15.3882(11)Å γ = 90°
Volume	1412.05(18) $Å^3$
Z, Calculated density	4, 1.338 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	600
Crystal size	0.345 x 0.312 x 0.295 mm
Theta range for data collection	2.76 to 25.07°
Limiting indices	-20<=h<=19, -6<=k<=6, -18<=l<=18
Reflections collected / unique	8984 / 1259 [R(int) = 0.0362]
Completeness to theta = 25.07	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6667
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1259 / 0 / 102
Goodness-of-fit on F^2	1.063
Final R indices [I>2σ(I)]	R1 = 0.0397, wR2 = 0.1031
R indices (all data)	R1 = 0.0412, wR2 = 0.1048
Extinction coefficient	0.031(3)
Largest diff. peak and hole	0.273 and -0.257 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 5,11-dimethyl-indolo[3,2-b]carbazole. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	2681(1)	-1349(2)	1119(1)	19(1)
C(1)	862(1)	-2818(3)	1908(1)	24(1)
C(2)	1656(1)	-3100(2)	1831(1)	22(1)
C(3)	1933(1)	-1447(2)	1317(1)	19(1)
C(4)	2676(1)	569(2)	560(1)	17(1)
C(5)	3283(1)	1284(2)	167(1)	18(1)
C(6)	1902(1)	1753(2)	400(1)	18(1)
C(7)	1430(1)	459(2)	891(1)	18(1)
C(8)	637(1)	705(2)	989(1)	21(1)
C(9)	355(1)	-943(3)	1494(1)	23(1)
C(10)	3362(1)	-2977(2)	1454(1)	23(1)

Table S3. Bond lengths (Å) and angles (°) for 5,11-dimethyl-indolo[3,2-b]carbazole.

N(1)-C(3)	1.3778(17)
N(1)-C(4)	1.3888(17)
N(1)-C(10)	1.4486(17)
C(1)-C(2)	1.385(2)
C(1)-C(9)	1.400(2)
C(1)-H(1)	0.9500
C(2)-C(3)	1.3931(19)
C(2)-H(2)	0.9500
C(3)-C(7)	1.4152(18)
C(4)-C(5)	1.3886(18)
C(4)-C(6)	1.4251(18)
C(5)-C(6)#1	1.3966(18)
C(5)-H(5)	0.9500
C(6)-C(5)#1	1.3966(18)
C(6)-C(7)	1.4444(19)
C(7)-C(8)	1.3946(18)
C(8)-C(9)	1.385(2)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-H(10)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(3)-N(1)-C(4)	108.97(10)
C(3)-N(1)-C(10)	125.16(11)
C(4)-N(1)-C(10)	125.87(11)
C(2)-C(1)-C(9)	121.76(13)
C(2)-C(1)-H(1)	119.1
C(9)-C(1)-H(1)	119.1
C(1)-C(2)-C(3)	117.39(13)
C(1)-C(2)-H(2)	121.3
C(3)-C(2)-H(2)	121.3
N(1)-C(3)-C(2)	128.95(12)
N(1)-C(3)-C(7)	109.31(12)
C(2)-C(3)-C(7)	121.73(13)
C(5)-C(4)-N(1)	128.74(12)
C(5)-C(4)-C(6)	122.54(12)
N(1)-C(4)-C(6)	108.69(11)
C(4)-C(5)-C(6)#1	116.53(12)
C(4)-C(5)-H(5)	121.7
C(6)#1-C(5)-H(5)	121.7
C(5)#1-C(6)-C(4)	120.93(12)
C(5)#1-C(6)-C(7)	132.66(12)
C(4)-C(6)-C(7)	106.37(11)
C(8)-C(7)-C(3)	119.46(12)
C(8)-C(7)-C(6)	133.85(12)
C(3)-C(7)-C(6)	106.66(12)
C(9)-C(8)-C(7)	119.05(13)
C(9)-C(8)-H(8)	120.5
C(7)-C(8)-H(8)	120.5
C(8)-C(9)-C(1)	120.60(13)
C(8)-C(9)-H(9)	119.7
C(1)-C(9)-H(9)	119.7
N(1)-C(10)-H(10)	109.5

N(1)-C(10)-H(10A)	109.5
H(10)-C(10)-H(10A)	109.5
N(1)-C(10)-H(10B)	109.5
H(10)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1/2,-z

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for 5,11-dimethyl-indolo[3,2-b]carbazole. The anisotropic displacement factor exponent takes the form:

$-2\,\pi^2\,[\,h^2\,a^{*2}\,U_{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U_{12}\,]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	19(1)	18(1)	20(1)	2(1)	5(1)	4(1)
C(1)	27(1)	24(1)	23(1)	1(1)	10(1)	-2(1)
C(2)	26(1)	20(1)	20(1)	1(1)	6(1)	2(1)
C(3)	21(1)	19(1)	16(1)	-3(1)	5(1)	1(1)
C(4)	19(1)	17(1)	15(1)	-2(1)	3(1)	2(1)
C(5)	18(1)	19(1)	18(1)	-2(1)	3(1)	3(1)
C(6)	17(1)	19(1)	16(1)	-3(1)	4(1)	1(1)
C(7)	21(1)	18(1)	15(1)	-3(1)	3(1)	0(1)
C(8)	21(1)	22(1)	18(1)	-2(1)	4(1)	2(1)
C(9)	21(1)	27(1)	22(1)	-2(1)	8(1)	0(1)
C(10)	23(1)	21(1)	24(1)	2(1)	5(1)	5(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 5,11-dimethyl-indolo[3,2-b]carbazole.

	x	y	z	U(eq)
H(1)	655	-3928	2251	29
H(2)	1998	-4370	2117	26
H(5)	3797	480	279	22
H(8)	294	1985	714	25
H(9)	-187	-800	1560	28
H(10)	3148	-4589	1396	34
H(10A)	3641	-2638	2093	34
H(10B)	3757	-2805	1099	34

Fig. S4 Unit cell representation of compound **3** seen from two different perspectives (a,b).

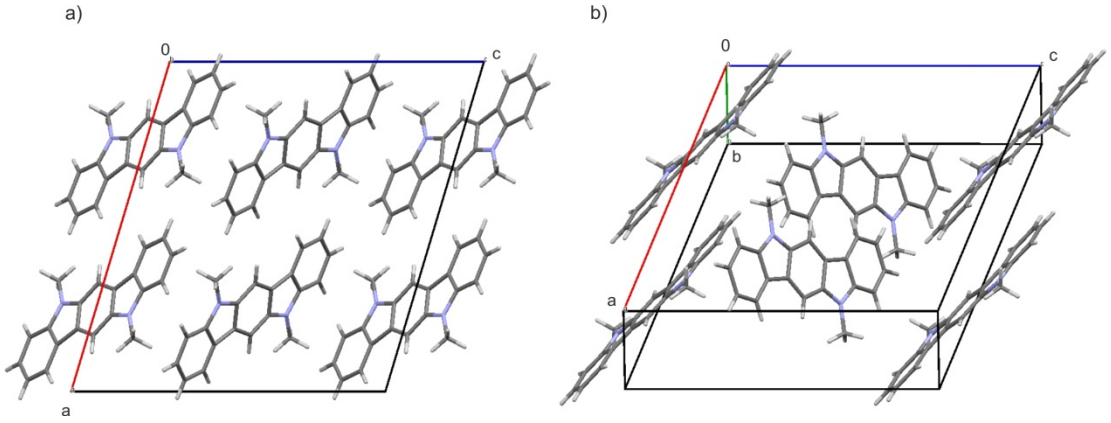


Fig. S5 Powder XRD pattern of a) compound **3** and b) compound **4**.

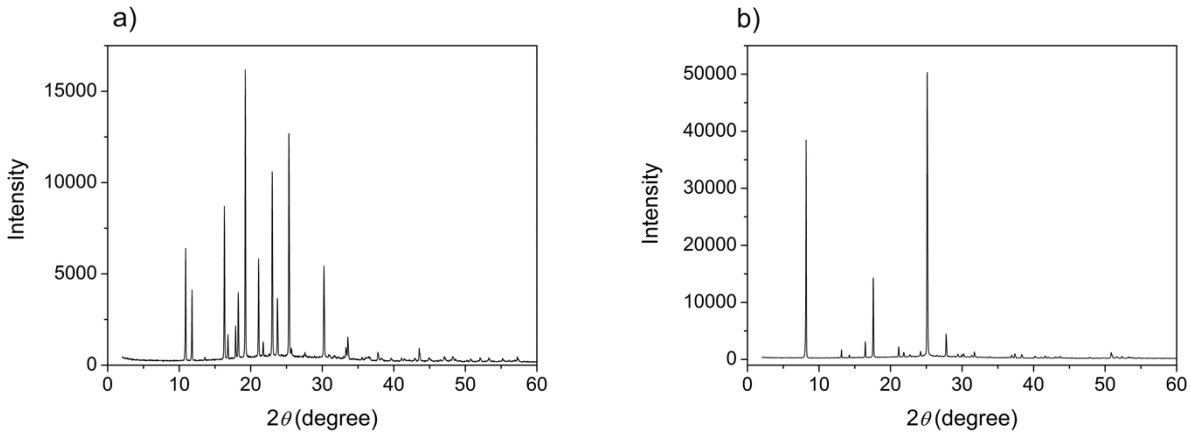
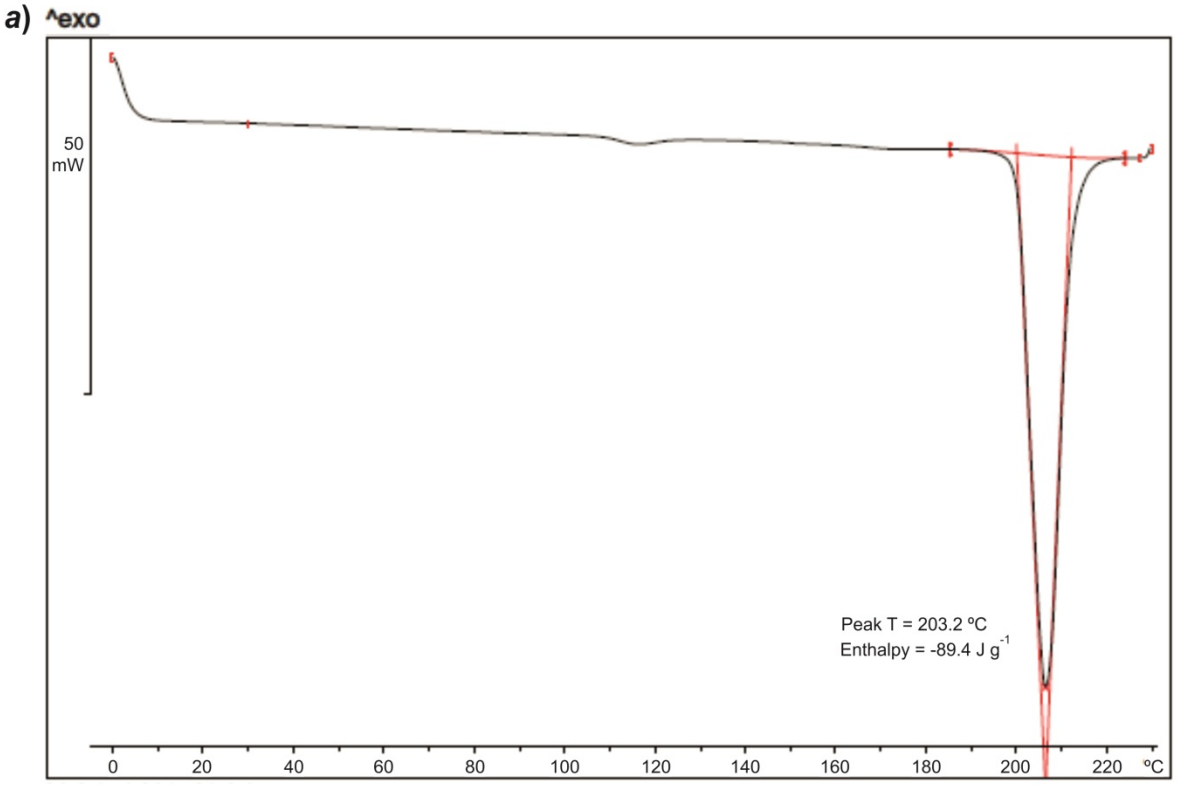


Fig. S6 Heating (***a***) and cooling (***b***) DSC thermogram of compound **2** at a scan rate of 30 and 10 °C min^{-1} respectively.



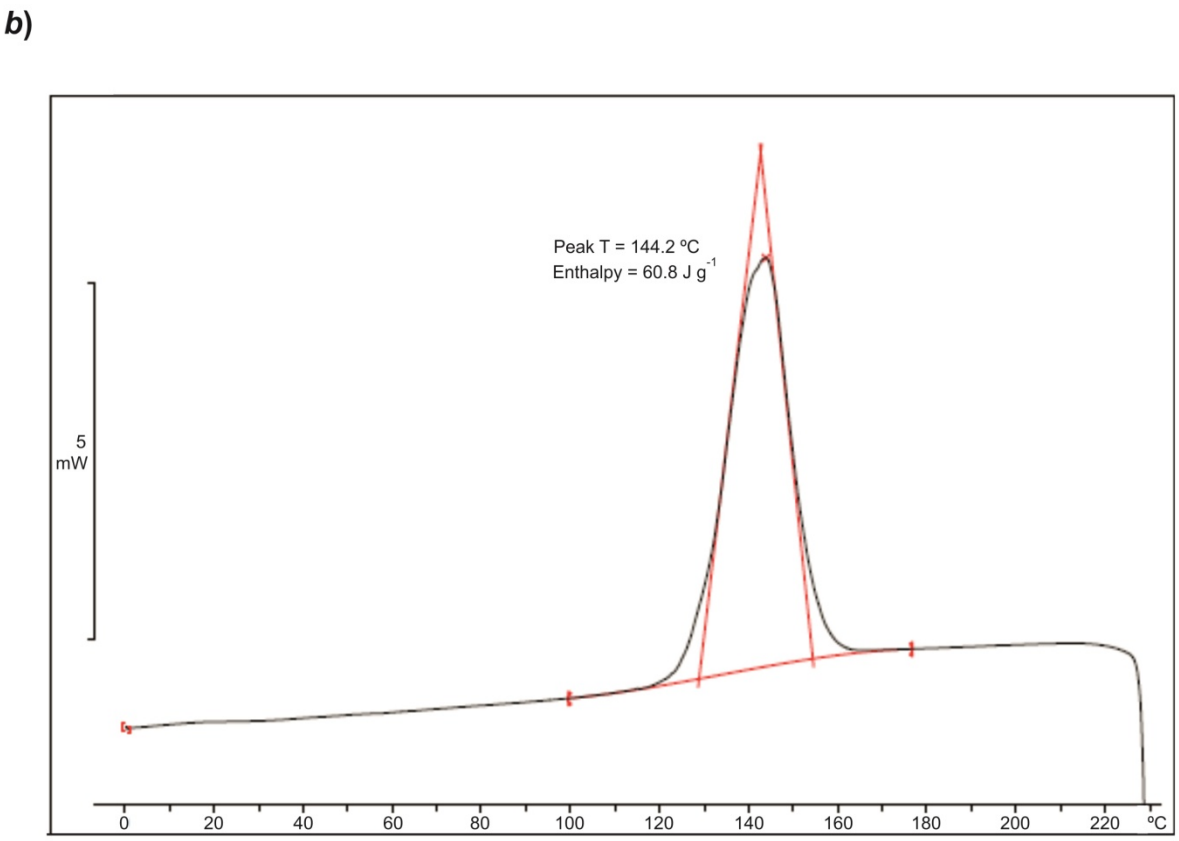


Fig. S7 Global (***a***) and first heating (***b***) DSC thermogram of compound **3** at a scan rate of 30°C min^{-1}.

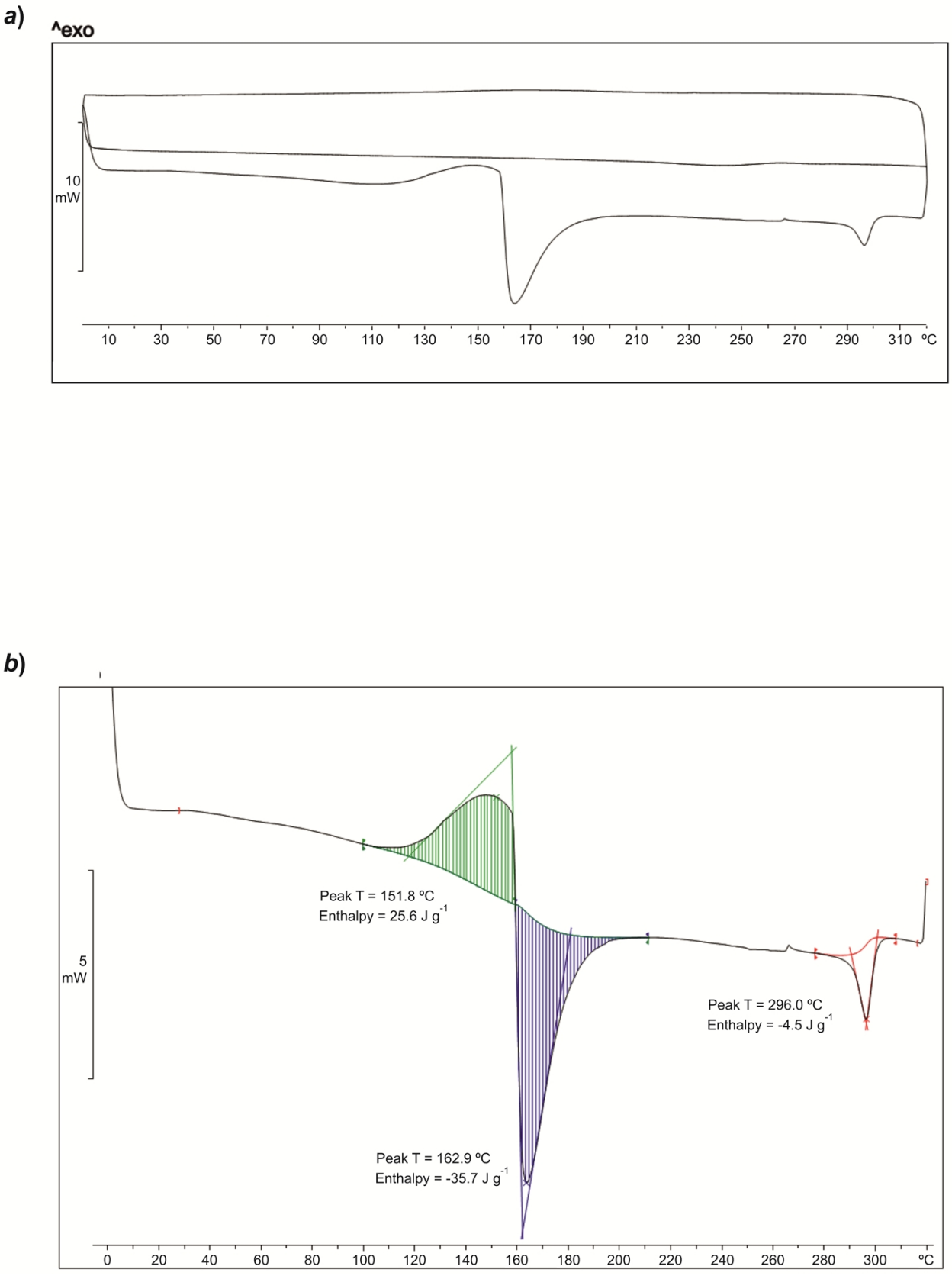


Fig. S8 Cooling (***a***) and second heating (***b***) DSC thermogram of compound **3** at a scan rate of 13°C min^{-1}.

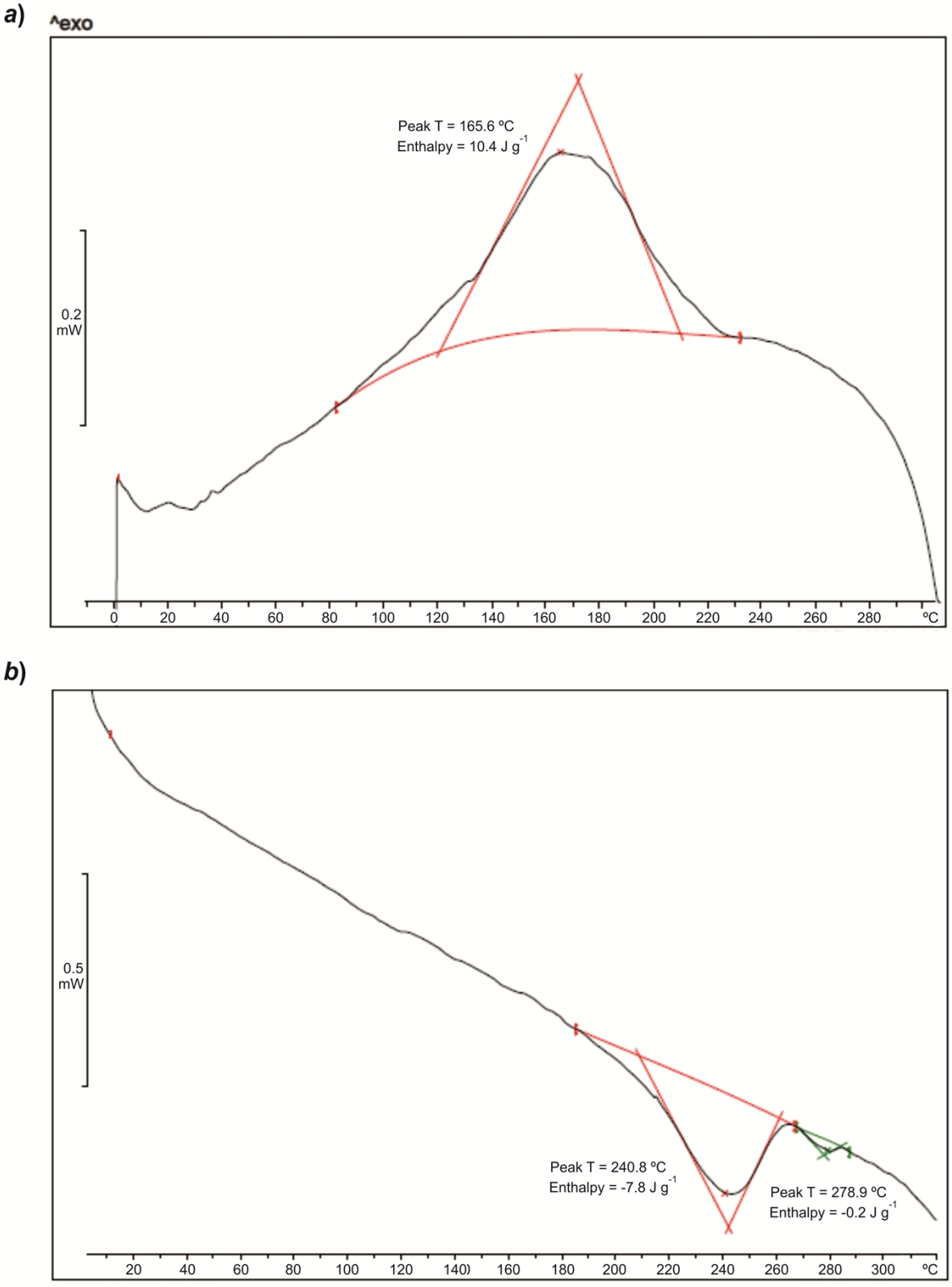


Fig. S9 Heating (***a***) and cooling (***b***) DSC thermogram of compound **4** at a scan rate of 30 and 12°C min^{-1} respectively.