Sign flipping of spontaneous polarization in vapour-deposited films of small polar organic molecules

G. M. Tourlakis, S. A. T. Adamopoulos, I. K. Gavra, A. A. Milpanis, L. F. Tsagri, A. S. G. Pachygianni, S. S. Chatzikokolis, and A. A. Tsekouras[a)]

Electronic Supplementary Information

Part A. Temperature ramps and film removal

Figures of single sample ramps showing fluctuations of the film voltage as well as sublimation, evaporation and desorption of the films as monitored via the mass spectrometer or the main chamber pressure.

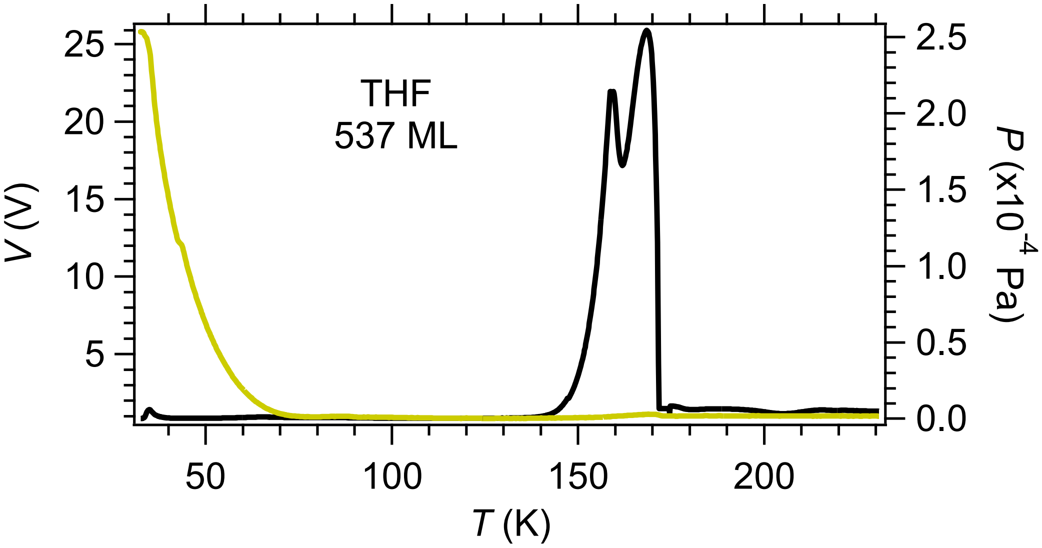


Figure SA1. Deposition of **tetrahydrofuran** generates a positive film voltage at 32.3 K and subsequent heating leads first to film voltage elimination and followed by film sublimation, as monitored via the chamber pressure, at much higher temperature. The pressure signal displays a split peak due to the close proximity of the Kelvin probe tip to the sample.

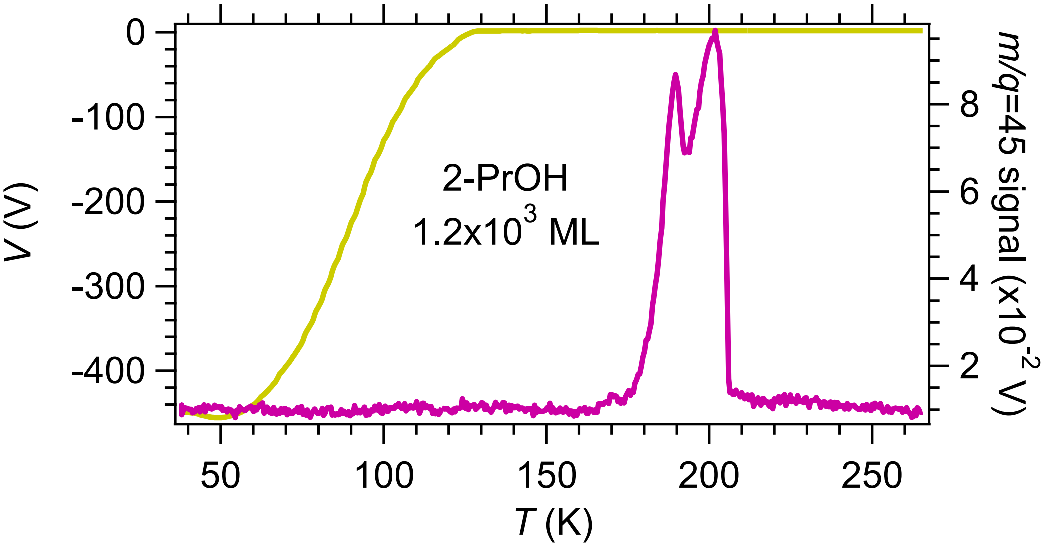


Figure SA2. Deposition of **2-propanol** generates a negative film voltage at 38.1 K and subsequent heating leads first to an increase in voltage, then gradual elimination and eventual film sublimation, as monitored by the mass spectrometer, above 180 K.

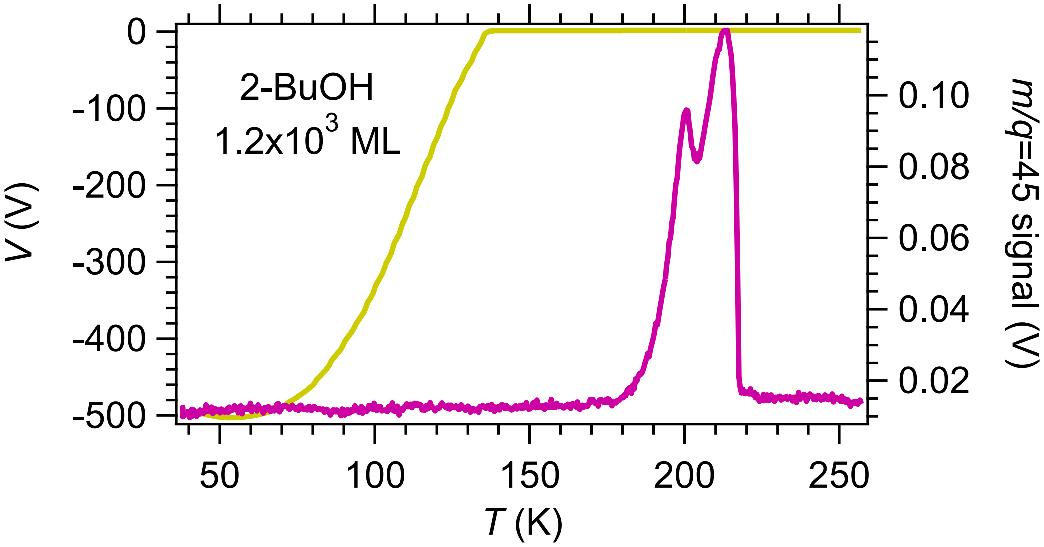


Figure SA3. Deposition of **2-butanol** generates a negative film voltage at 38 K and subsequent heating leads first to an increase in voltage, then gradual elimination and eventual film sublimation, as monitored by the mass spectrometer, above 190 K.

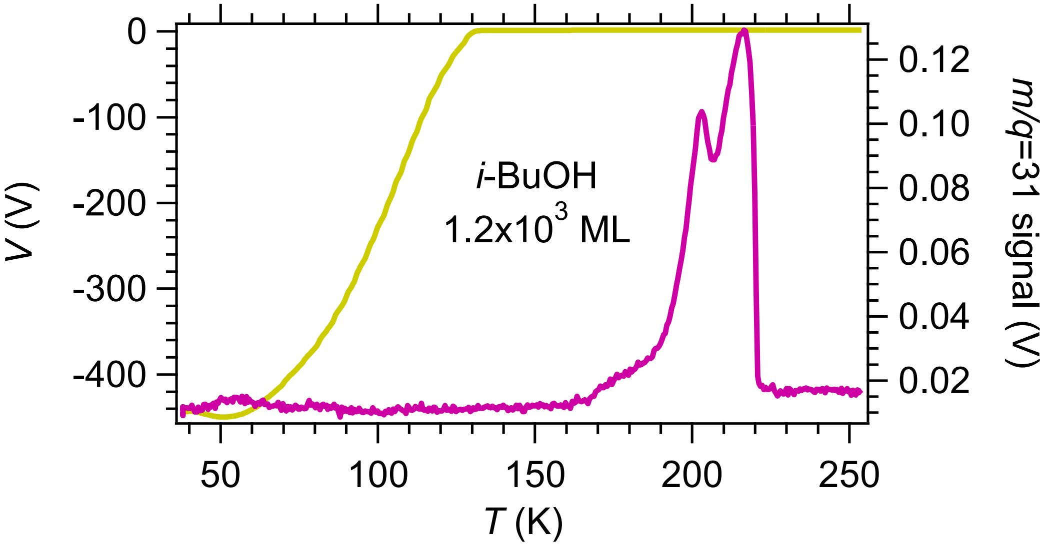


Figure SA4. Deposition of ***iso*-butanol** (2-methyl propan-1-ol) generates a negative film voltage at 38.1 K and subsequent heating leads first to an increase in voltage, then gradual elimination and eventual film sublimation, as monitored by the mass spectrometer, above 190 K.

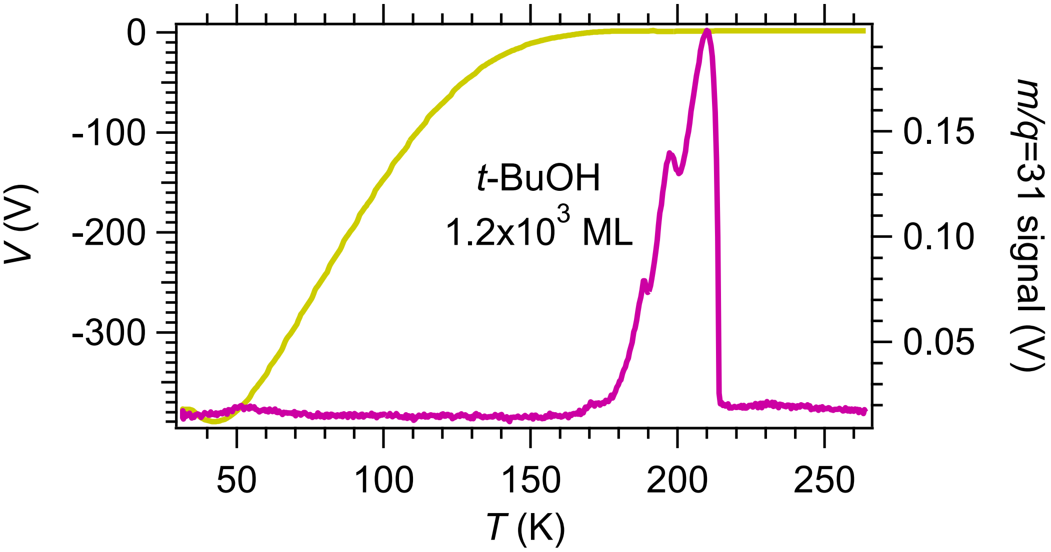


Figure SA5. Deposition of ***tert*-butanol** (2-methyl propan-2-ol) generates a negative film voltage at 31.9 K and subsequent heating leads first to an increase in voltage, then gradual elimination and eventual film sublimation, as monitored by the mass spectrometer, above 190 K.

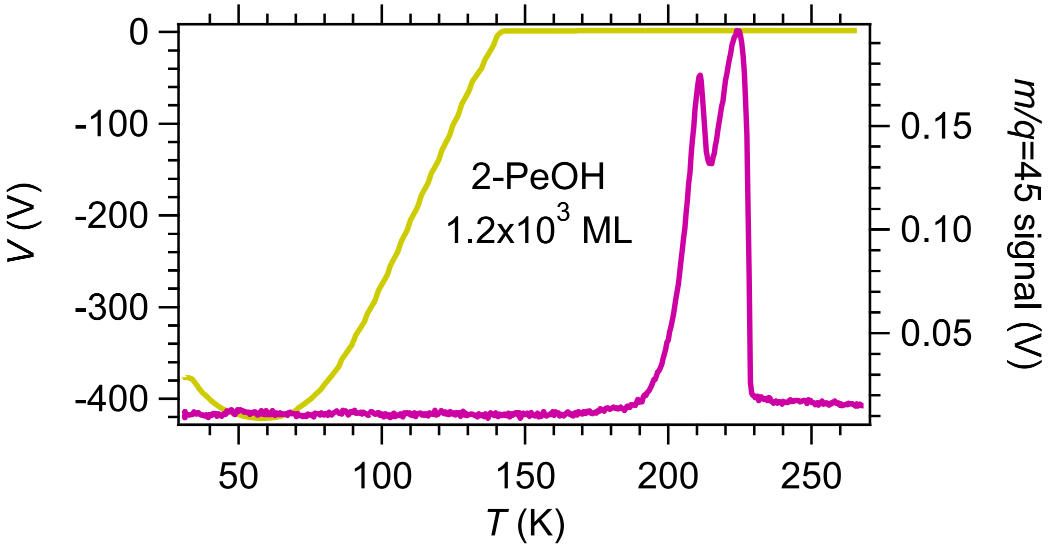


Figure SA6. Deposition of **2-pentanol** generates a negative film voltage at 31.2 K and subsequent heating leads first to an increase in voltage, then gradual elimination and eventual film sublimation, as monitored by the mass spectrometer, above 200 K.

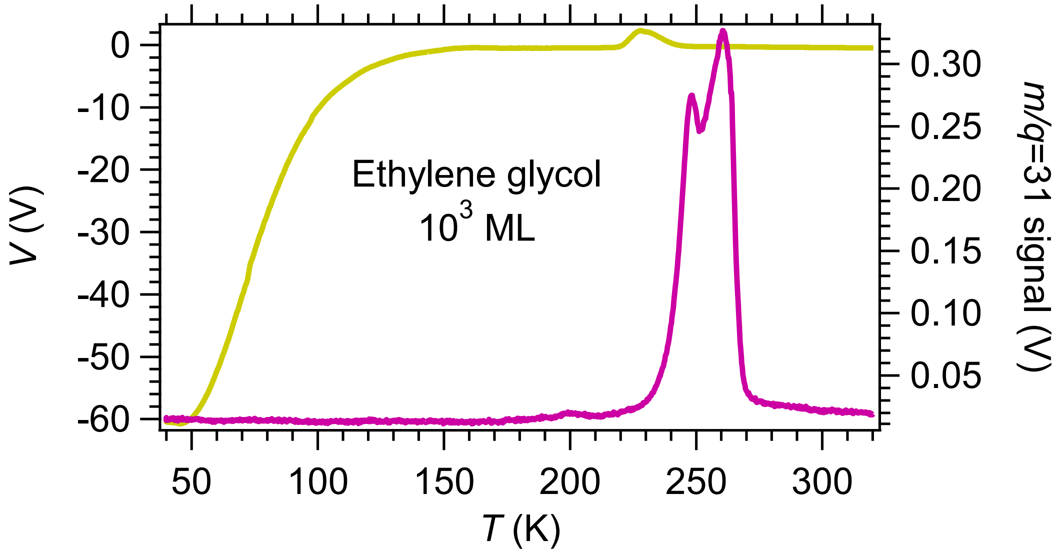


Figure SA7. Film voltage upon deposition of **ethylene glycol** at 40 K and subsequent heating at 0.25 K s^{-1} beyond voltage (green line) elimination and film desorption (purple line) above 240 K.

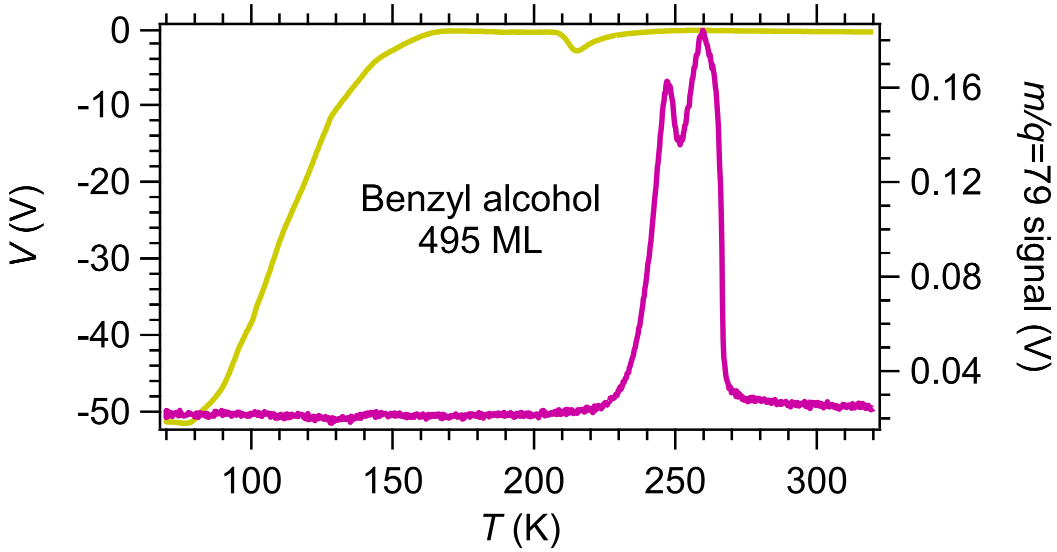


Figure SA8. Film voltage upon deposition of **benzyl alcohol** at 70 K and subsequent heating at 0.25 K s^{-1} beyond voltage elimination and film desorption above 180 K.

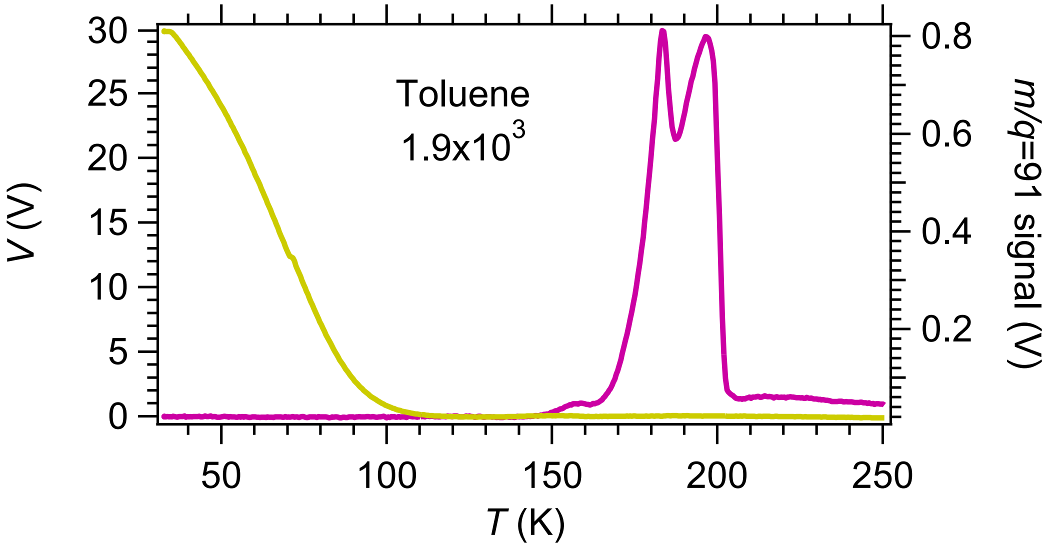


Figure SA9. Voltage for **toluene** film deposited at 32.6 K and ramped at 0.25 K s^{-1}. Film desorption monitored via the mass spectrometer signal at m/q = 91 a.m.u. indicates film vaporization above 170 K.

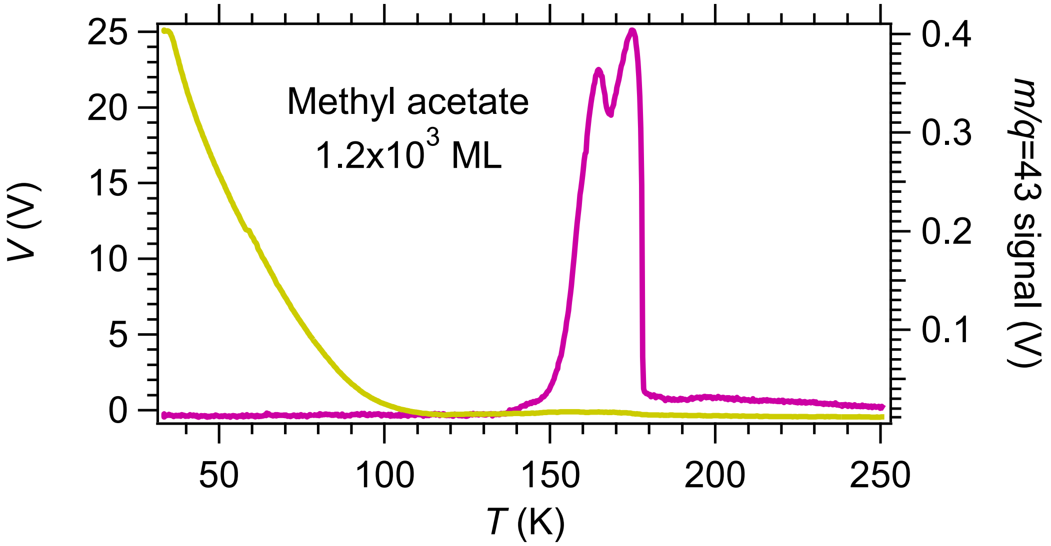


Figure SA10. Deposition of **methyl acetate** at 33.2 K followed by a temperature ramp at 0.25 K s^{-1} monitored through the film voltage and the mass spectrometer showing the evaporation of the film above 150 K.

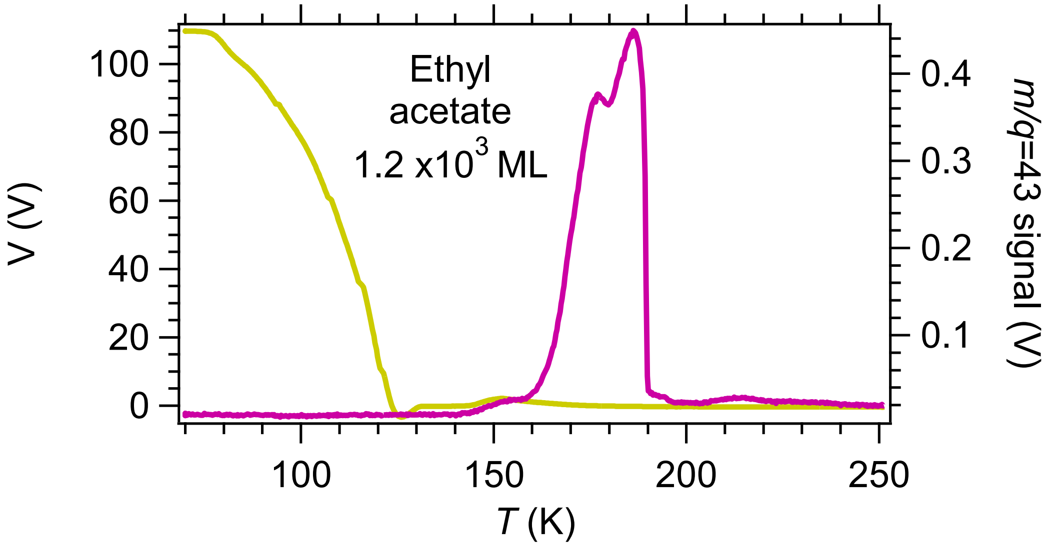


Figure SA11. Film voltage evolution for an **ethyl acetate** film deposited at 70 K and ramped up to 250 K at 0.25 K s^{-1}. As seen from the mass spectrometer signal the film is removed at temperatures above 150 K.

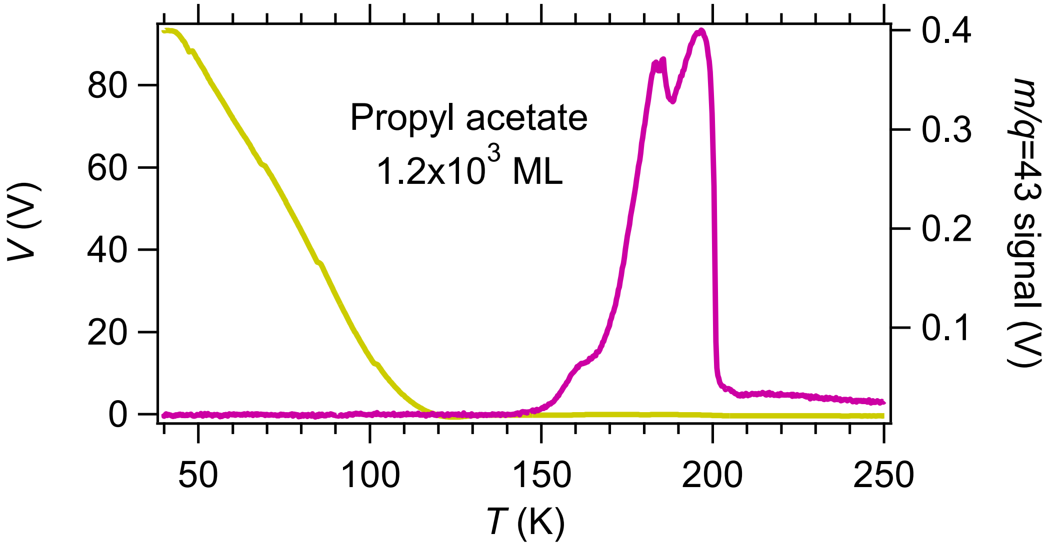


Figure SA12. Evolution of voltage of a **propyl acetate** film deposited at 40 K and ramped up to 250 K at 0.25 K s^{-1}. The mass spectrometer signal indicates that removal of the film started at 150 K.

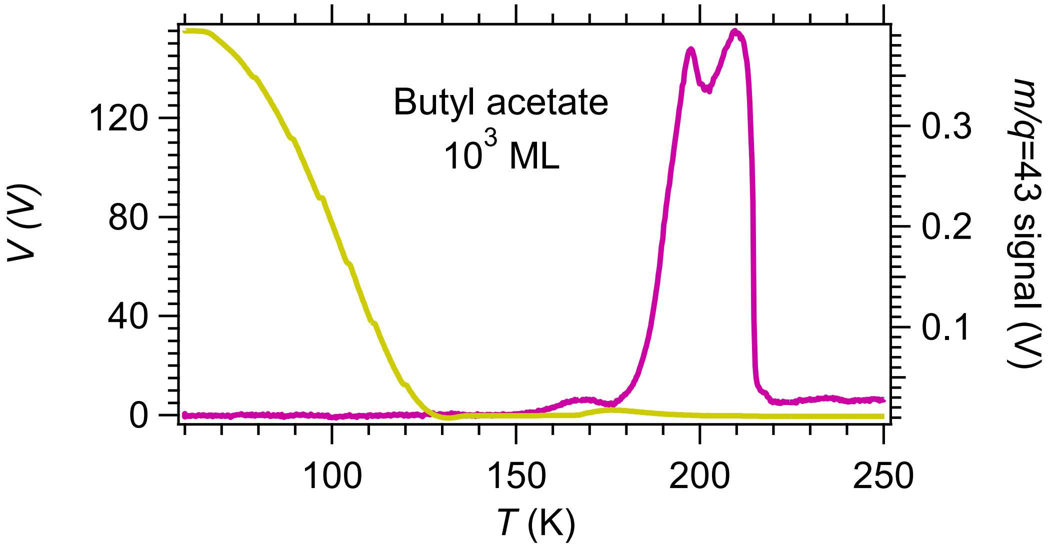


Figure SA13. Voltage variation of a **butyl acetate** film deposited at 60 K and ramped up to 250 K at a rate of 0.25 K s^{-1}. Based on the mass spectrometer signal the bulk of film is seen to transfer to the gas phase above 170 K.

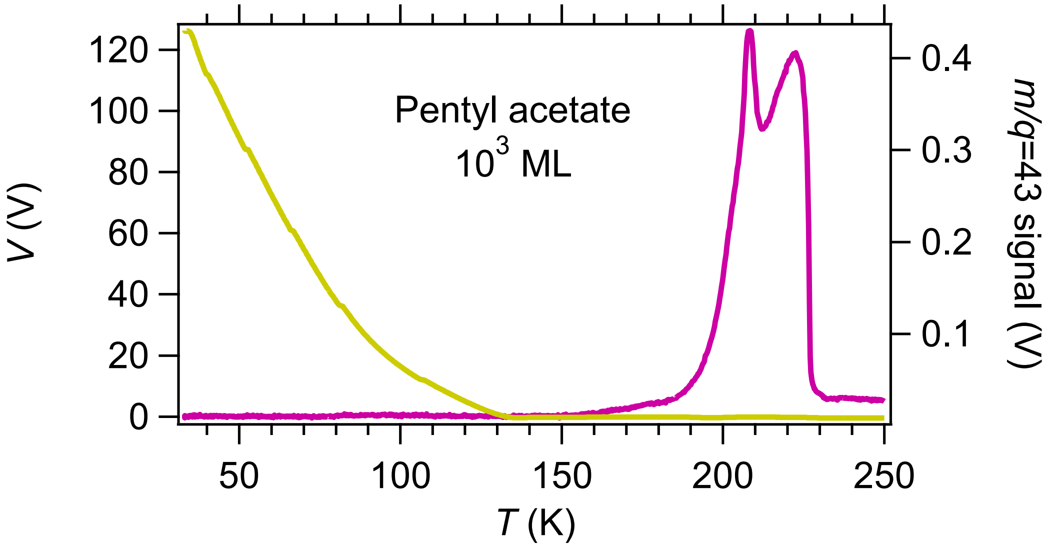


Figure SA14. Voltage variation for a **pentyl acetate** film deposited at 33 K and subsequently ramped up to 250 K at 0.25 K s^{-1}. Removal of the film is observed above 180 K.

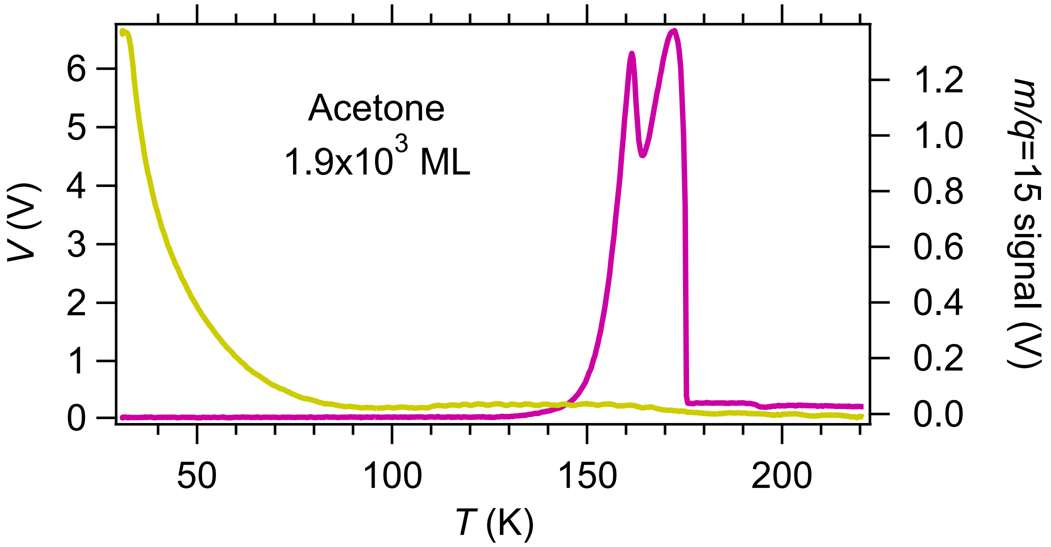


Figure SA15. After deposition of 1.9×10^3 ML of **acetone** at 30.8 K, the platinum temperature was ramped at 0.25 K s^{-1}. The initial positive film voltage, measured with a Kelvin probe as contact potential difference (cpd), is eliminated gradually and irreversibly. At around 150 K the film molecules leave the substrate as determined with a quadrupole mass spectrometer. The mass spectrometer signal displays a split peak due to the close proximity of the Kelvin probe tip to the sample.

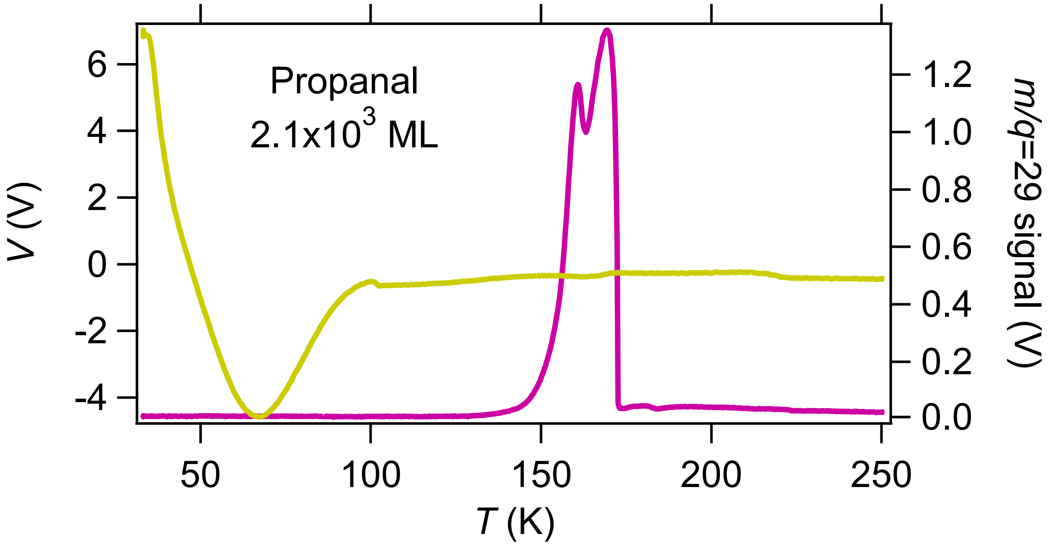


Figure SA16. Deposition of **propanal** at 33.2 K and subsequent ramping of the sample temperature at 0.25 K s^{-1}.

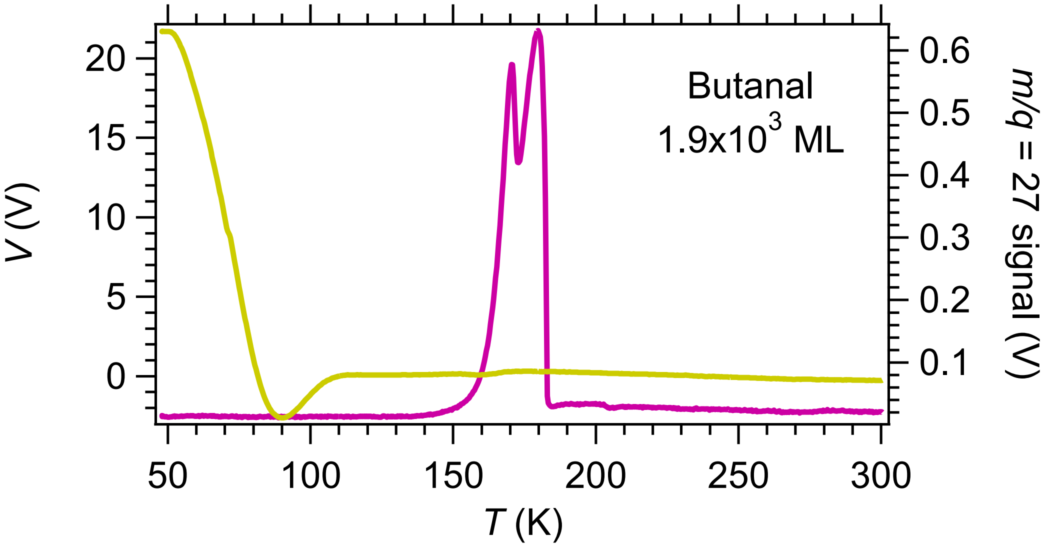


Figure SA17. Deposition of **butanal** at 48 K and followed by a temperature ramp leading to a switch in film voltage sign and gradual elimination of the voltage, before film desorption at temperatures above 150 K.

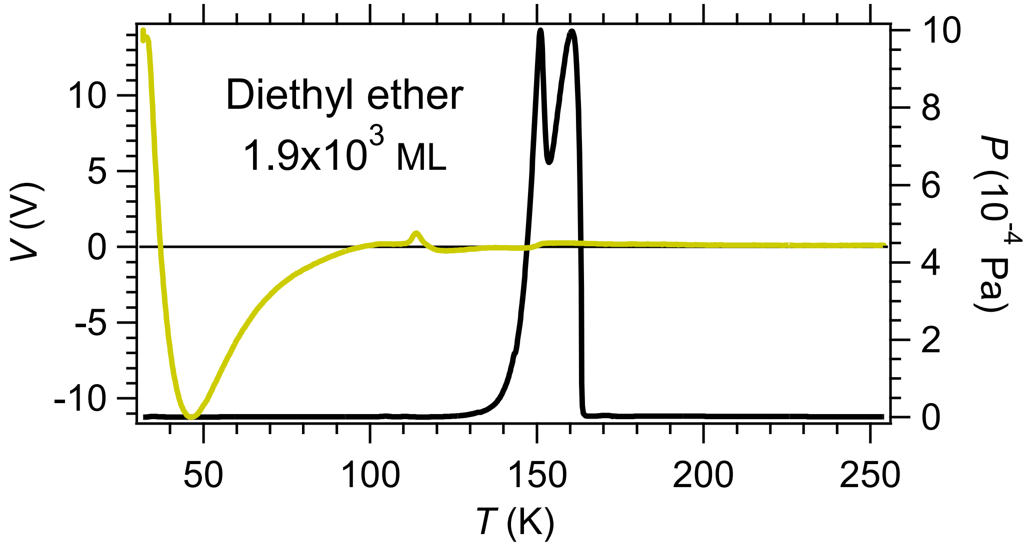
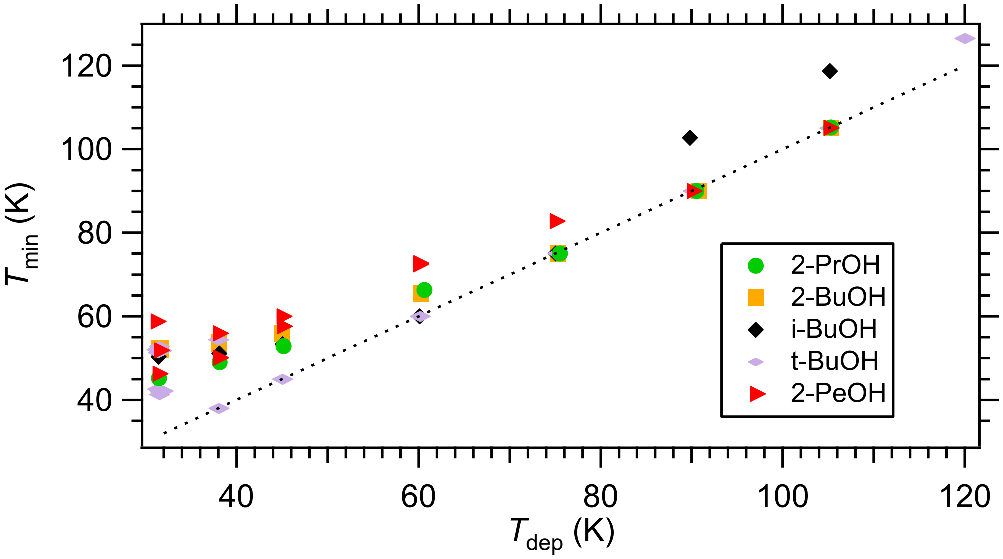


Figure SA18. Deposition of **diethyl ether** at 32.5 K with a subsequent 0.25 K s^{-1} temperature ramp shows an abrupt switch in sign of the film voltage followed by elimination of the voltage at temperatures well below film sublimation.

Part B. Initial and extreme voltages

Figures of scaled voltages measured at the beginning of each ramp showing fluctuations with deposition temperature. For samples that exhibited an extremum during the subsequent temperature ramp, these figures display this information as well.



SB1. Temperature of minimum film voltage appearance during temperature ramps as a function of deposition temperature for aliphatic monohydroxy alcohols. The straight dotted line is drawn as a guide for the eye to indicate the case of the minimum temperature coinciding with the deposition temperature.

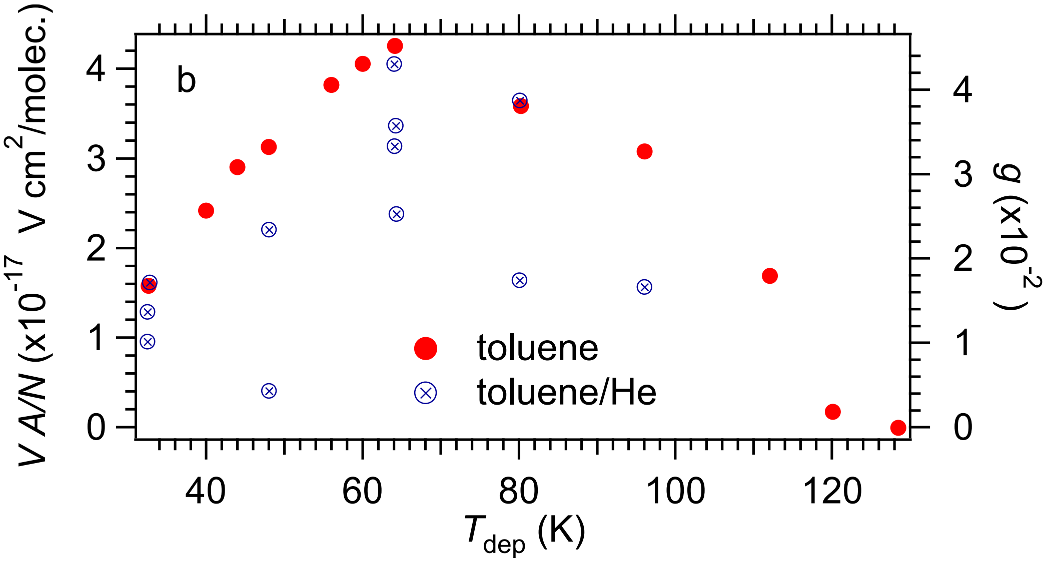


Figure SB2. Initial scaled voltage and calculated degree of polarization for toluene films as a function of deposition temperature. Also shown are measurements taken with toluene diluted with non-condensing helium gas.

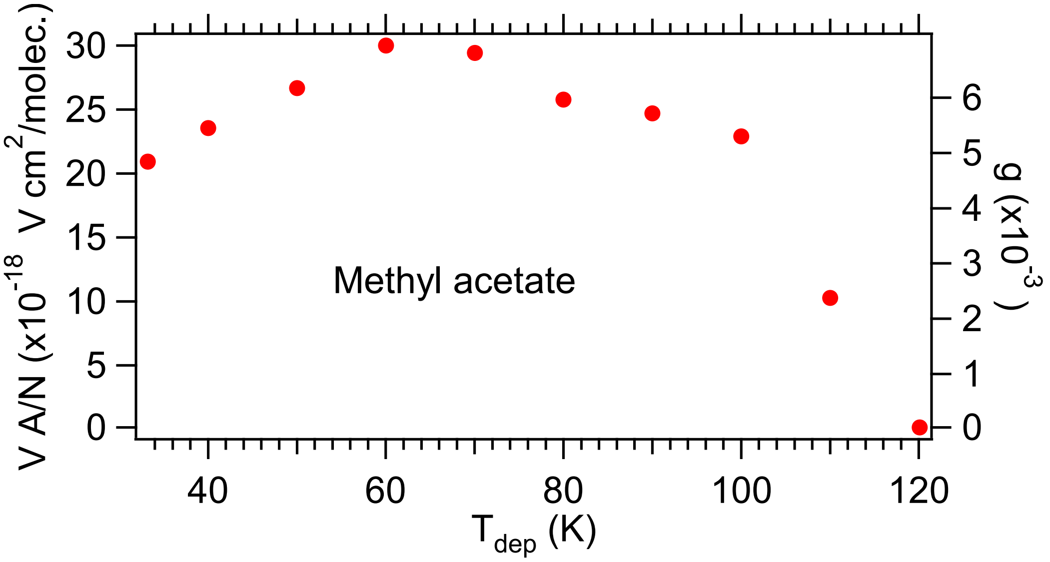


Figure SB3. Initial scaled film voltage and calculated degree of polarization for **methyl acetate** films.

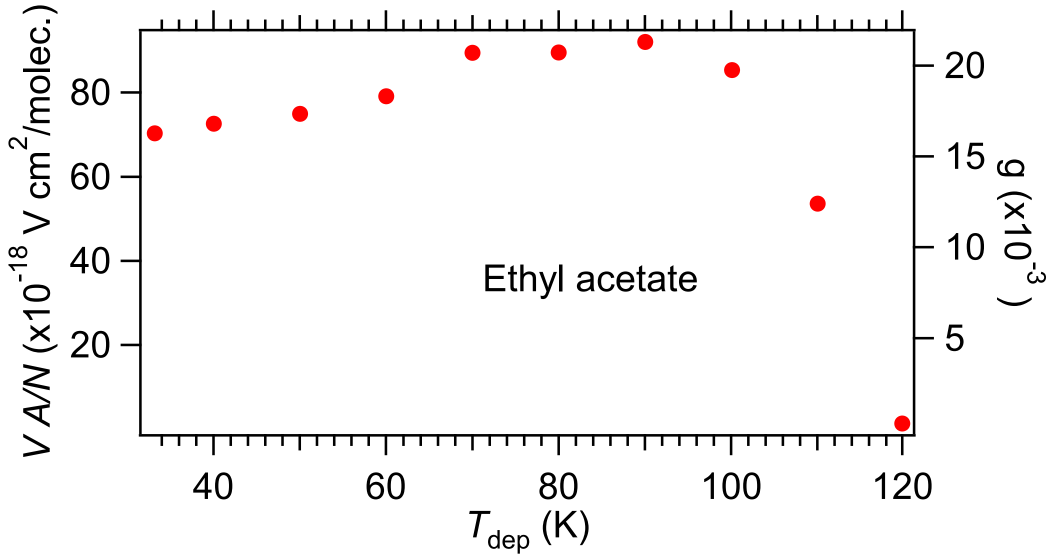


Figure SB4. Initial scaled voltages for **ethyl acetate** films as a function of deposition temperature.

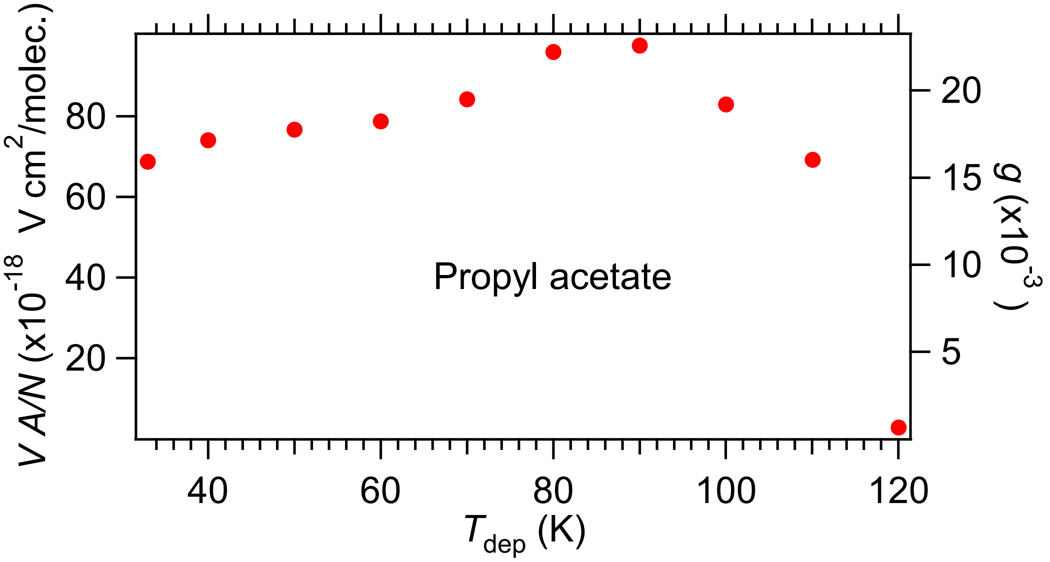


Figure SB5. Initial scaled voltage for **propyl acetate** films as a function of deposition temperature.

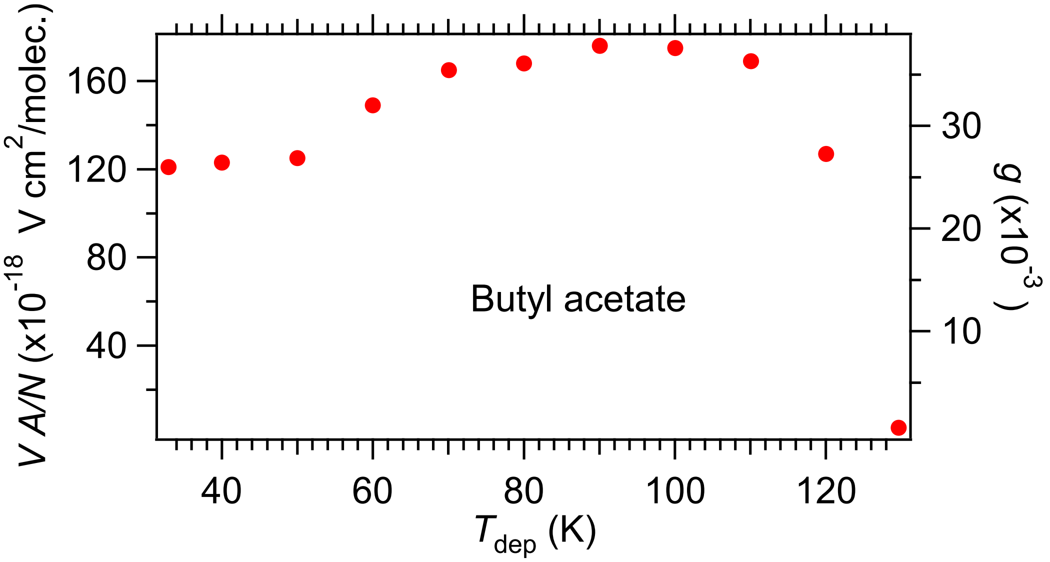


Figure SB6. Initial scaled voltage for **butyl acetate** films as a function of deposition temperature.

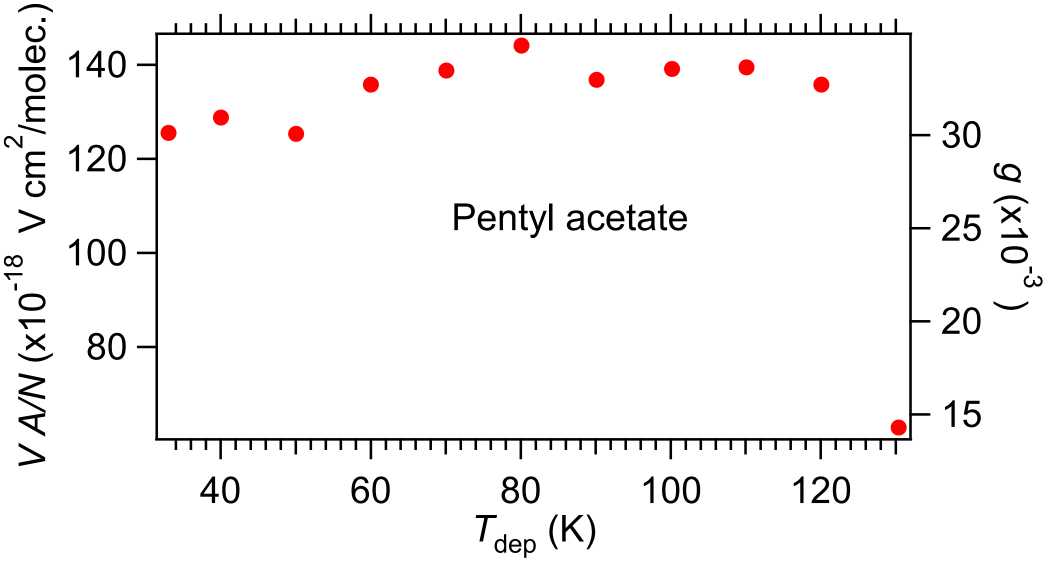


Figure SB7. Initial scaled voltage for **pentyl acetate** films as a function of deposition temperature.

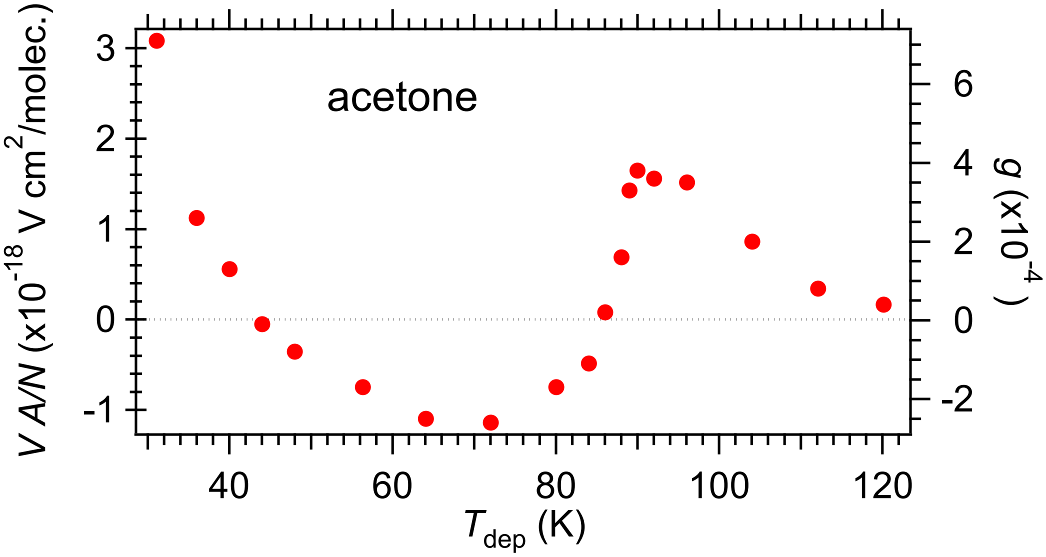


Figure SB8. The first point of each curve in Fig. 4a is represented here and interpreted as degree of polarization, *g*, according to Eq. 1. Each point is based on several measurements, involving varying numbers of deposited molecules.

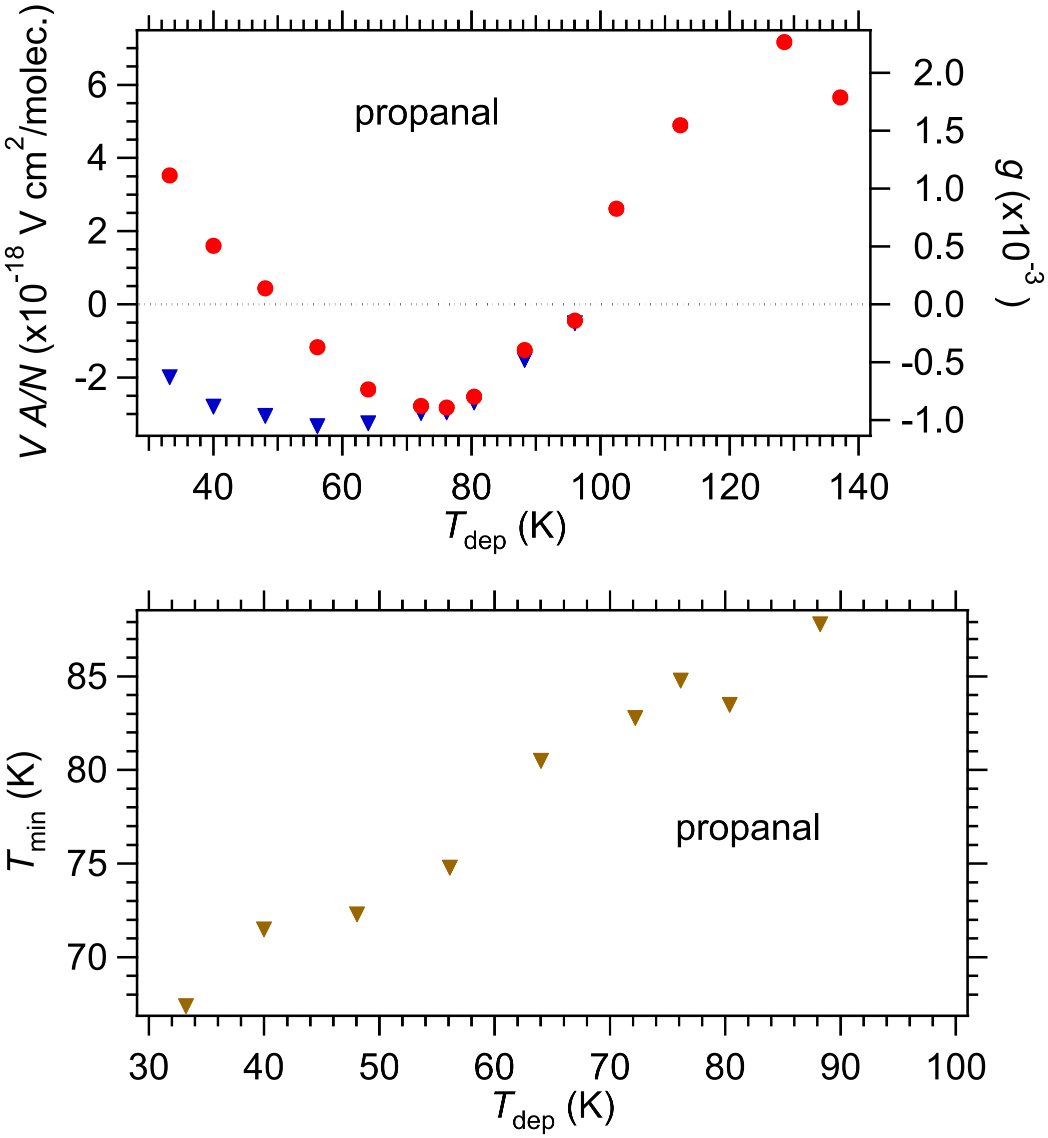


Figure SB9. Top: Initial (circle) and minimum (triangle) scaled voltage for **propanal** films deposited at the temperatures shown and calculated degree of polarization. Bottom: Temperature at which propanal film voltage reaches minimum as a function of deposition temperature.

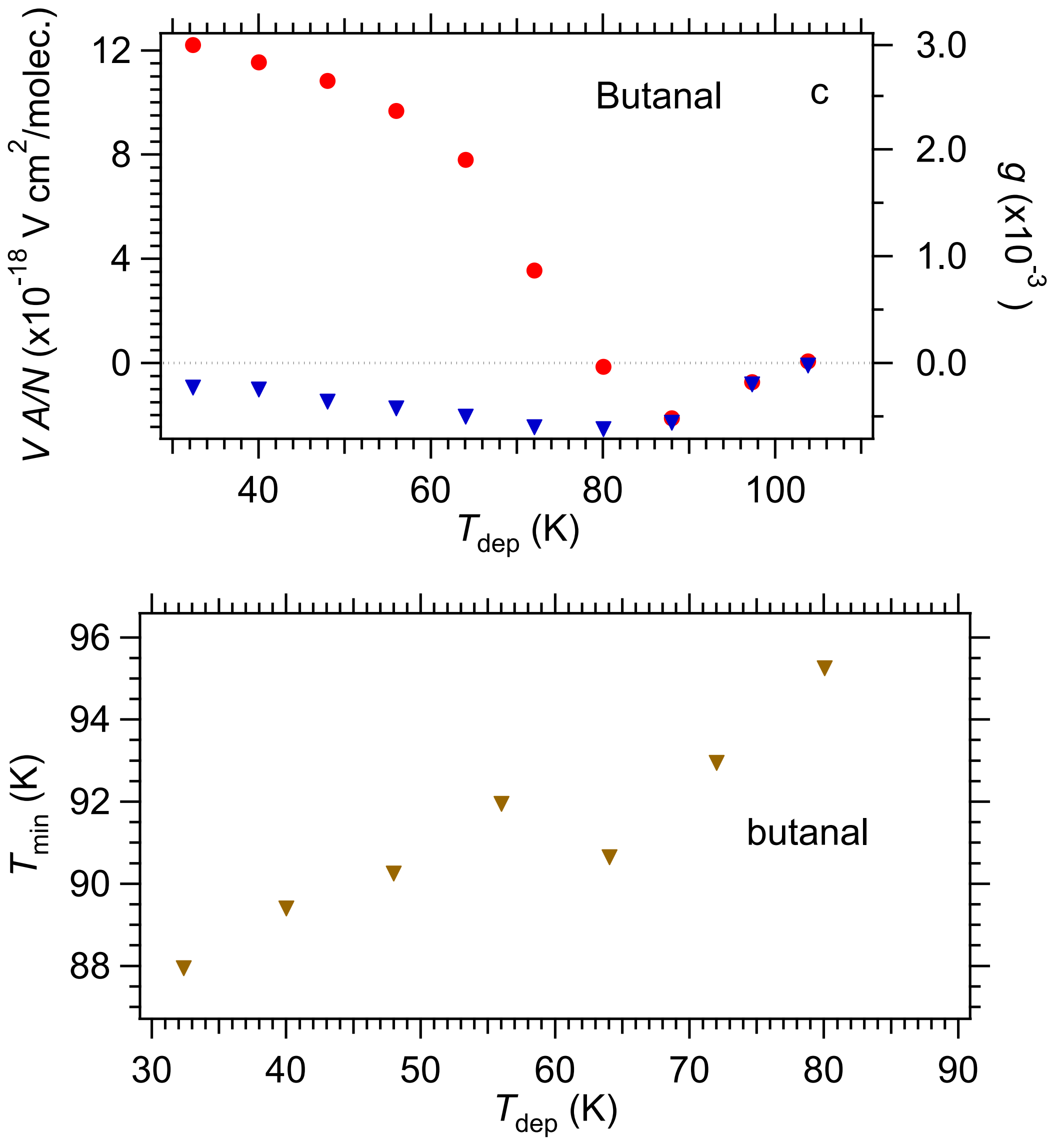


Figure SB10. Top: Initial (red circles) and minimum (blue triangles) scaled voltage and calculated degree of polarization for **butanal** films. Bottom: Temperature of minimum voltage during ramp w.r.t. deposition temperature for butanal films.

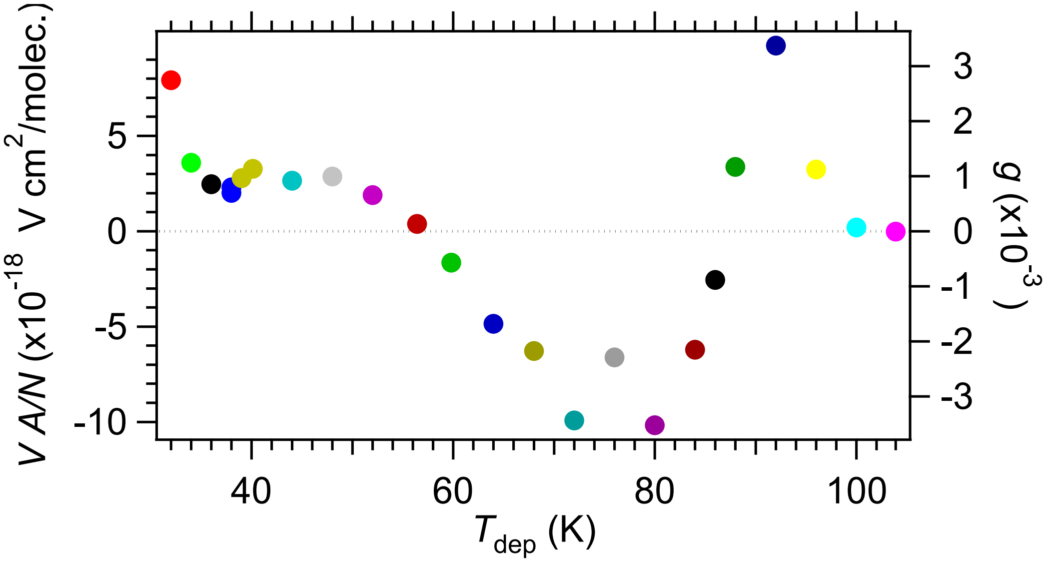


Figure SB11. Initial scaled film voltage and corresponding degree of polarization for **diethyl ether**.

Part C. Half-way temperatures and voltage slopes

Figure SC1 shows characteristic temperatures in the ramps for benzyl alcohol. During the temperature ramp the film voltage changes monotonically and the change may be gradual over the whole ramp or slow at the beginning and much faster towards the end of the ramp. This information is summarized in Fig. SC1 by identifying the temperature at which the absolute value of the film voltage drops to half its initial value. Similar features are displayed for acetate films in Fig. SC2 where we show the rate of voltage drop at these characteristic temperatures and try a fit to match these patterns by shifting and scaling (see main text for explanation).

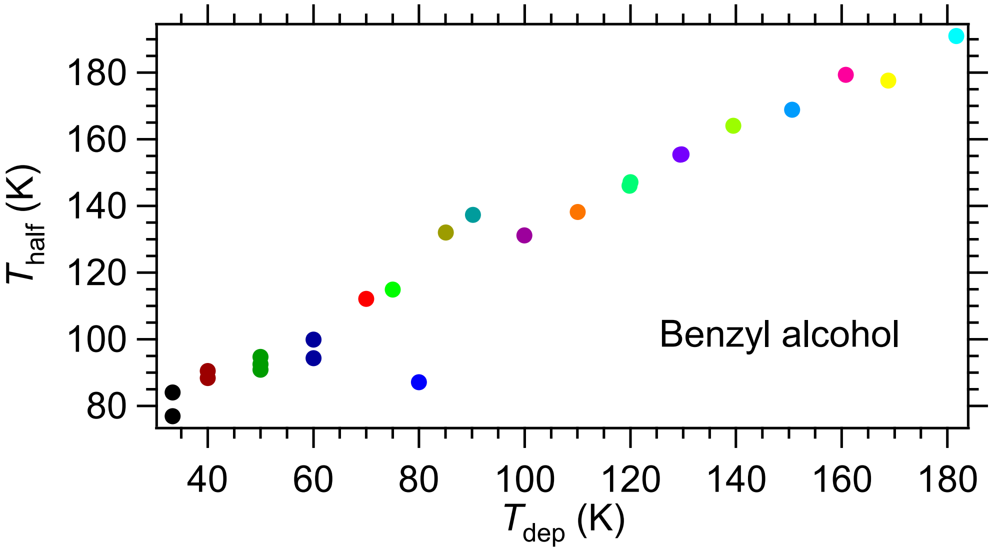


Figure SC1. Temperature during ramp where benzyl alcohol film voltage has been reduced to half its initial value. The point at 80 K stands out because the corresponding initial film voltage was 0.

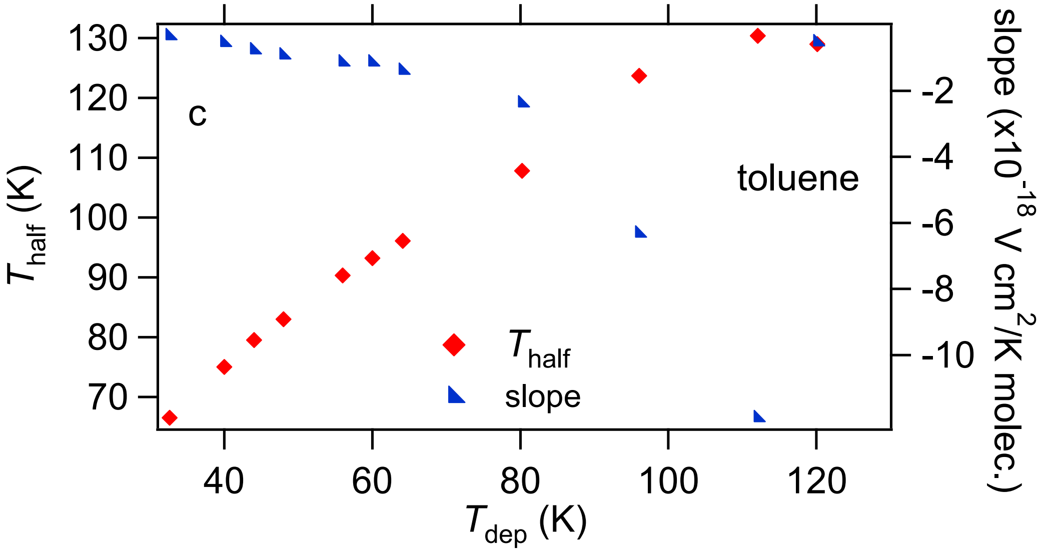


Figure SC2. Temperatures during ramp where toluene film voltages reach half their initial value and voltage slope at these temperatures.

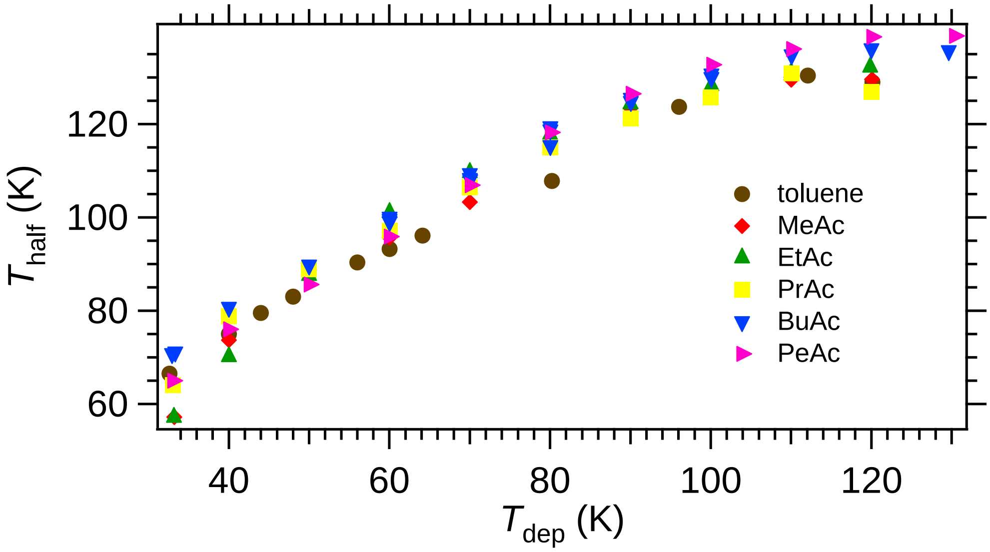
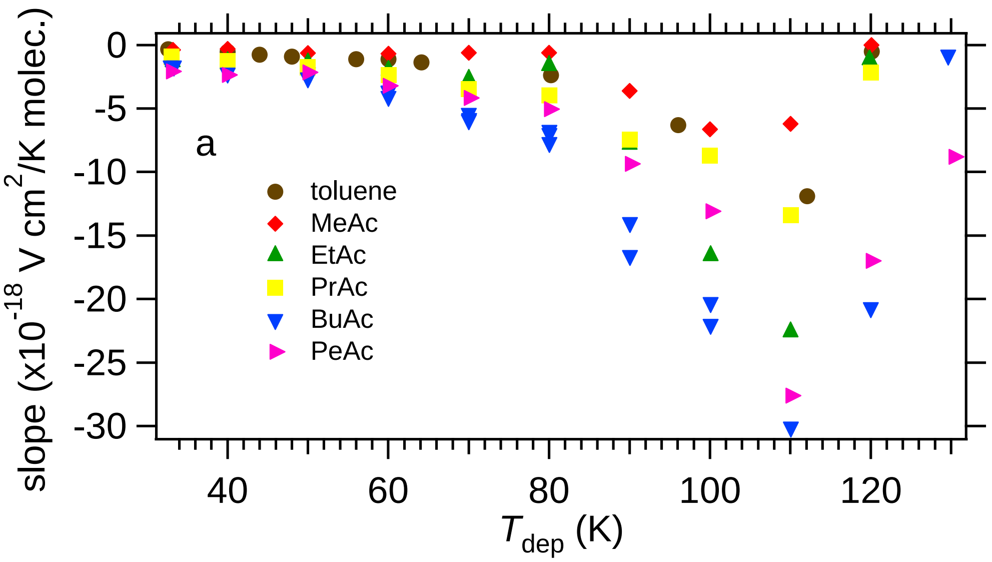
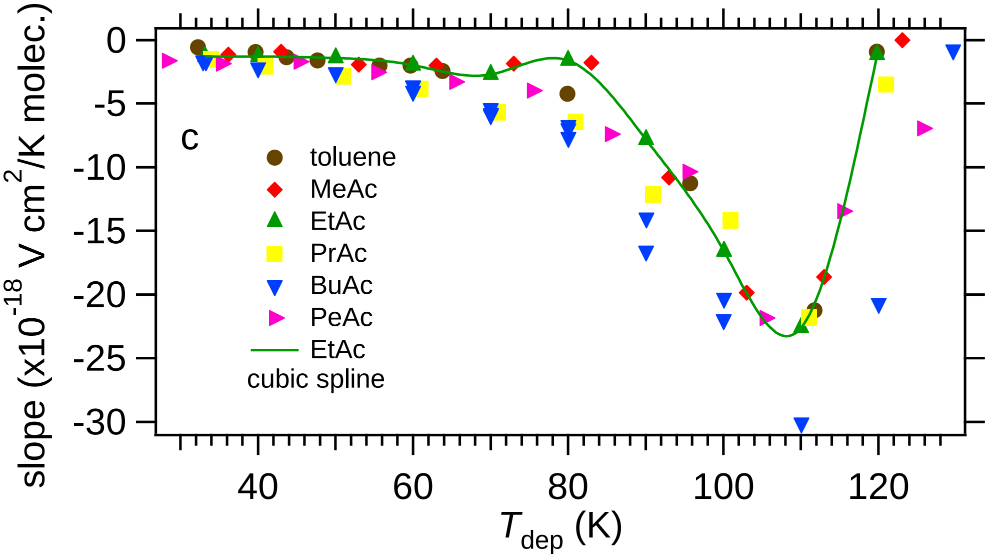


Figure SC3. Temperature at which the film voltage drops to half its initial value during temperature ramps as a function of deposition temperature for alkyl acetates and toluene films.


a
toluene
MeAc
EtAc
PrAc
BuAc
PeAc
0
-5
-10
-15
-20
-25
-30
slope (x10^{-18} V cm^2/K molec.)
40
60
80
100
120
T_{dep} (K)


c
toluene
MeAc
EtAc
PrAc
BuAc
PeAc
EtAc
cubic spline
0
-5
-10
-15
-20
-25
-30
slope (x10^{-18} V cm^2/K molec.)
40
60
80
100
120
T_{dep} (K)

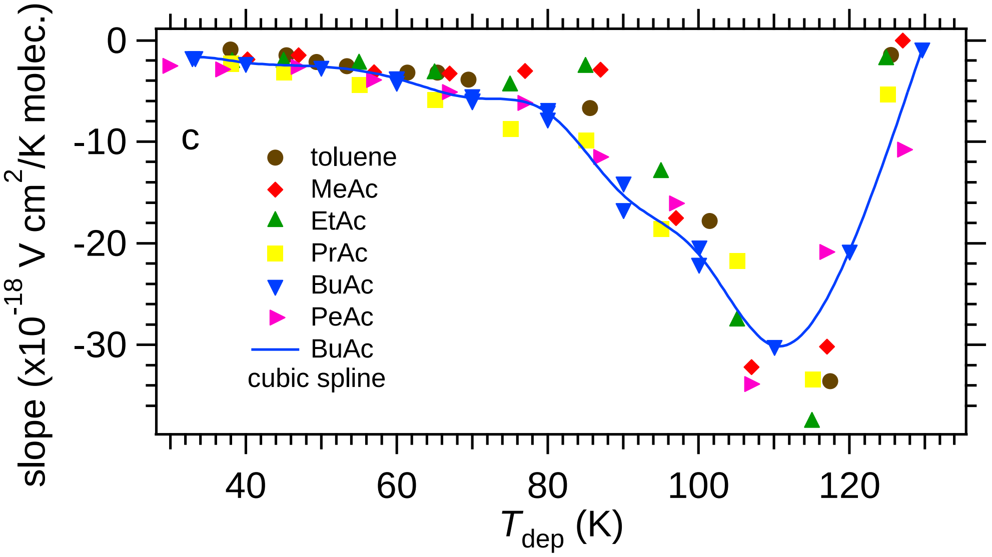

c
toluene
MeAc
EtAc
PrAc
BuAc
PeAc
BuAc
cubic spline
0
-10
-20
-30
slope (x10^{-18} V cm^2/K molec.)
40
60
80
100
120
T_{dep} (K)

Figure SC4. Voltage slope at half its value during temperature ramp as a function of deposition temperature for alkyl acetates and toluene films. Lower panels. Data shown in panel a shifted and scaled separately for each compound to match the profile of b. ethyl acetate data, c. butyl acetate; fitting parameters used and associated uncertainties are shown in Table 3.

Table SC1 Parameters for fits shown in Figures 14c and SC2

	Slope data fit based on EtAc					Slope data fit based on BuAc				
Compound	scale	*σ*	Δ*T* (K)	*σ* (K)	T_x (K)	scale	*σ*	Δ*T* (K)	*σ* (K)	T_x (K)
toluene	1.8	(0.4)	0.3	(1.7)	108	3.0	(0.4)	-5	(2)	107
MeAc	3.0	(0.9)	-3	(4)	105	4.9	(1.0)	-7	(3)	105
EtAc	1	(0)	0	(0)	108	1.67	(0.11)	-5.1	(1.1)	107
PrAc	1.6	(0.3)	-1	(3)	107	2.5	(0.3)	-5.1	(1.7)	107
BuAc	0.72	(0.05)	-1.2	(1.0)	107	1	(0)	0	(0)	112
PeAc	0.79	(0.07)	4.7	(0.9)	113	1.23	(0.06)	3.3	(0.8)	115

Part D. Derivatives of voltage profiles during sample heating. Color coding is the same as in the corresponding figures of the original data.

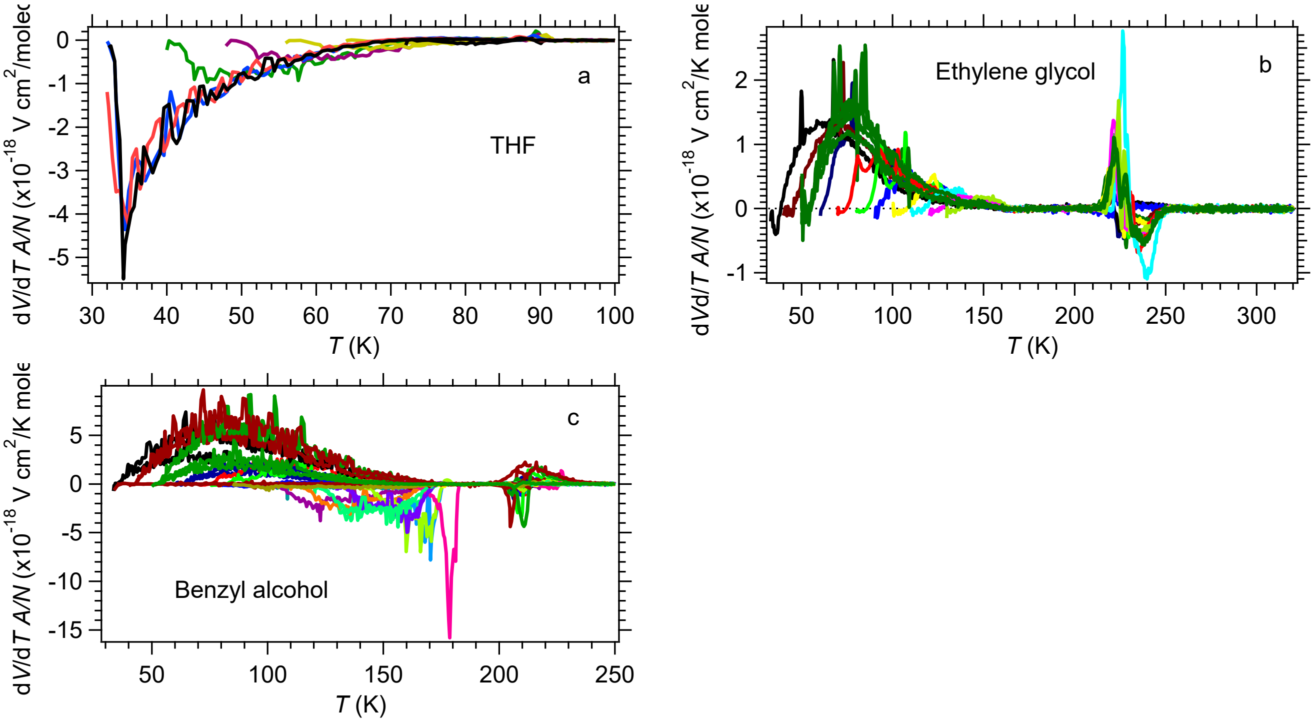


Figure SD1. Derivatives with respect to temperature of film voltages during heating for named compounds.

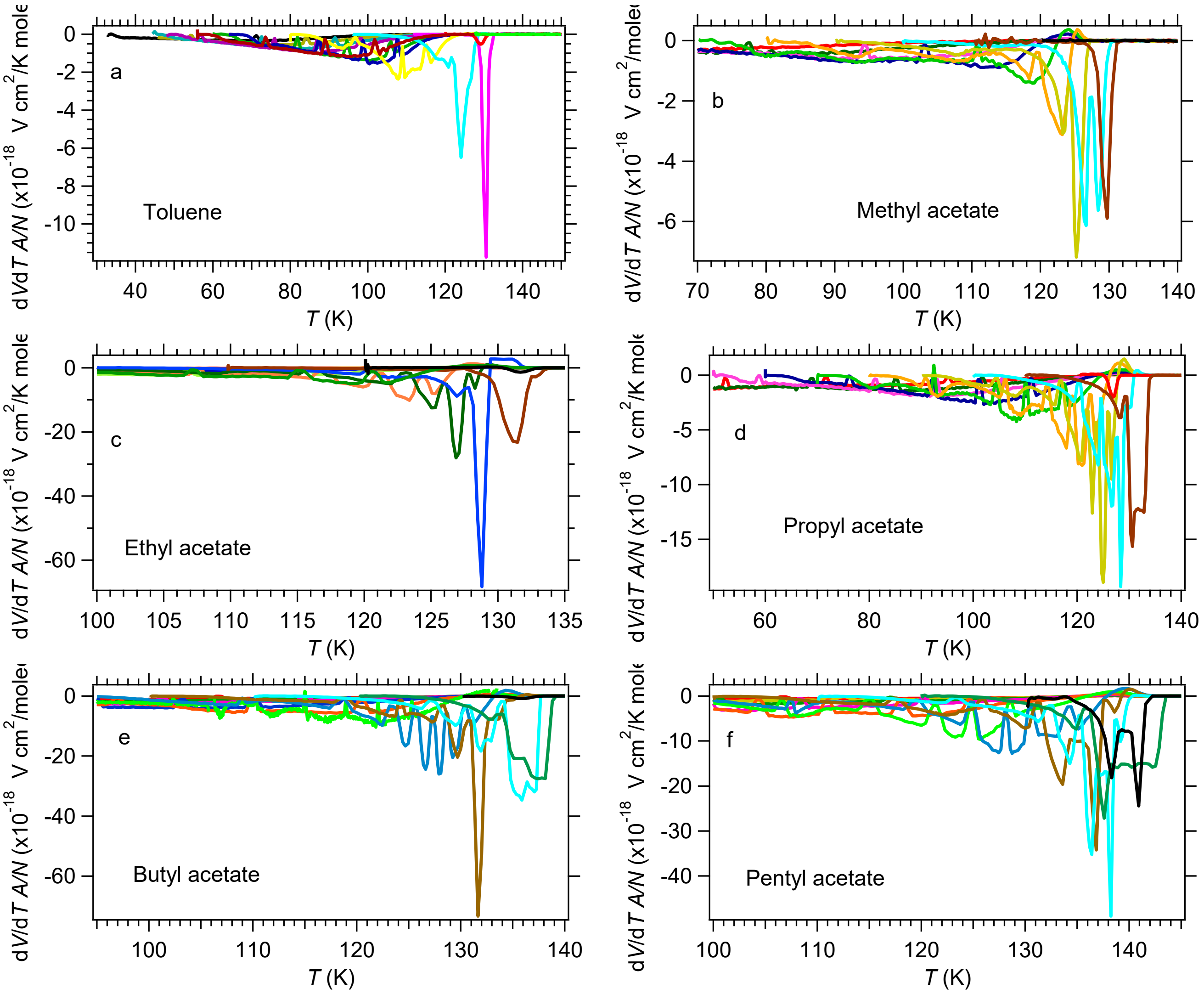


Figure SD2. Derivatives with respect to temperature of film voltages during heating for named compounds.

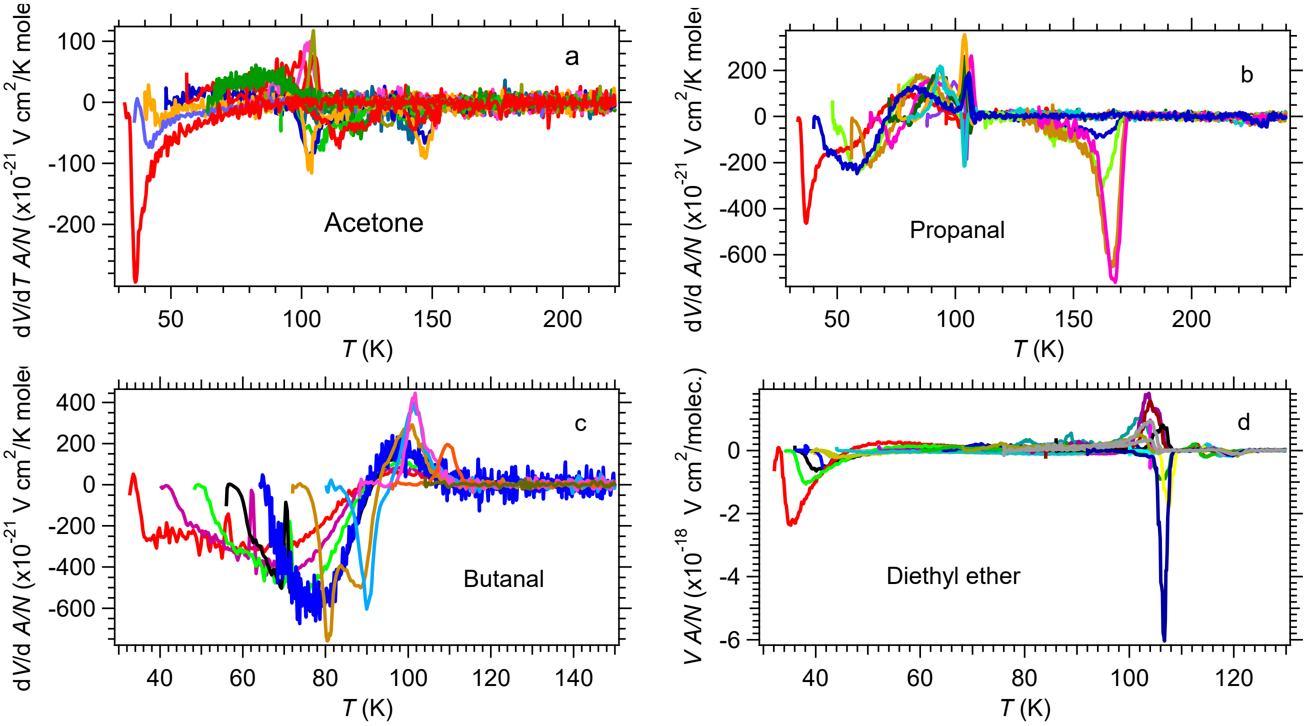


Figure SD3. Derivatives with respect to temperature of film voltages during heating for named compounds.