

# Spontaneous Polarization of Cryo-Deposited Films for Five Normal Saturated Monohydroxy Alcohols, $C_nH_{2n+1}OH$ , $n = 1-5$

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## Supporting information

### A. Temperature ramps and desorption

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.

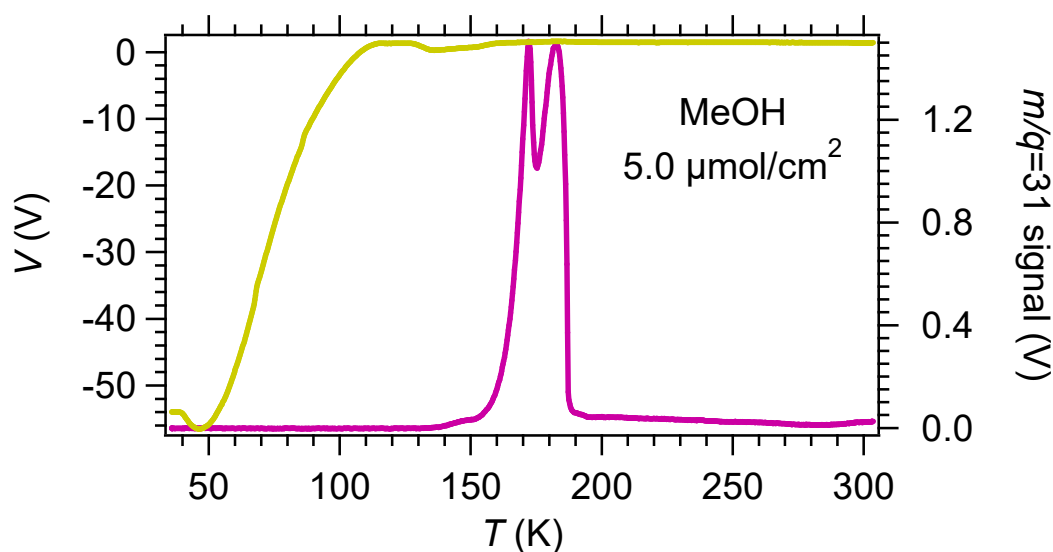


Figure S1. Voltage profile for **methanol** film deposited at 36 K during a temperature ramp of  $0.25 \text{ K s}^{-1}$  with the film evaporating above 150 K.

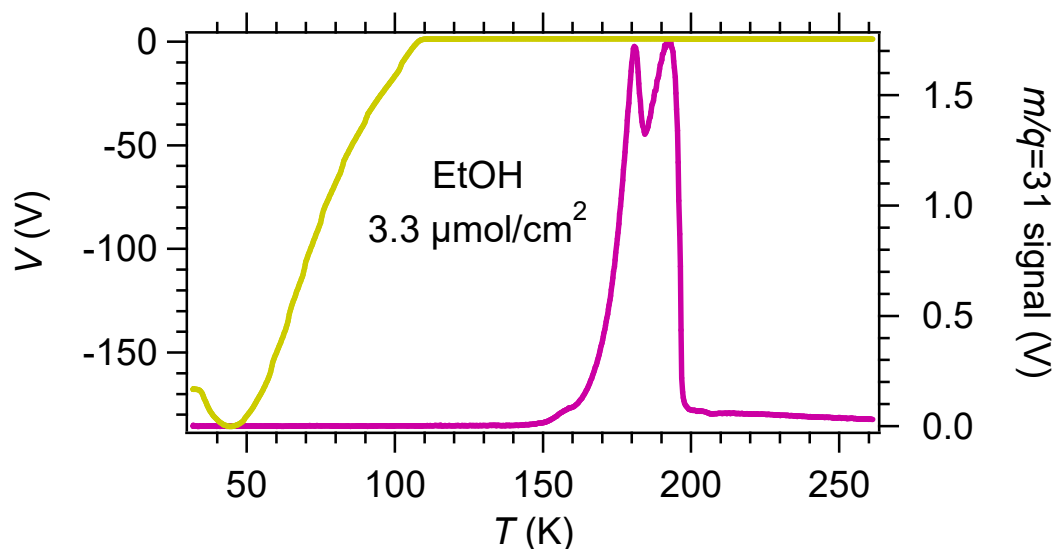


Figure S2. Voltage profile for **ethanol** film deposited at 32.2 K and ramped up at  $0.25 \text{ K s}^{-1}$  past 150 K where the film is seen through the mass spectrometer to evaporate.

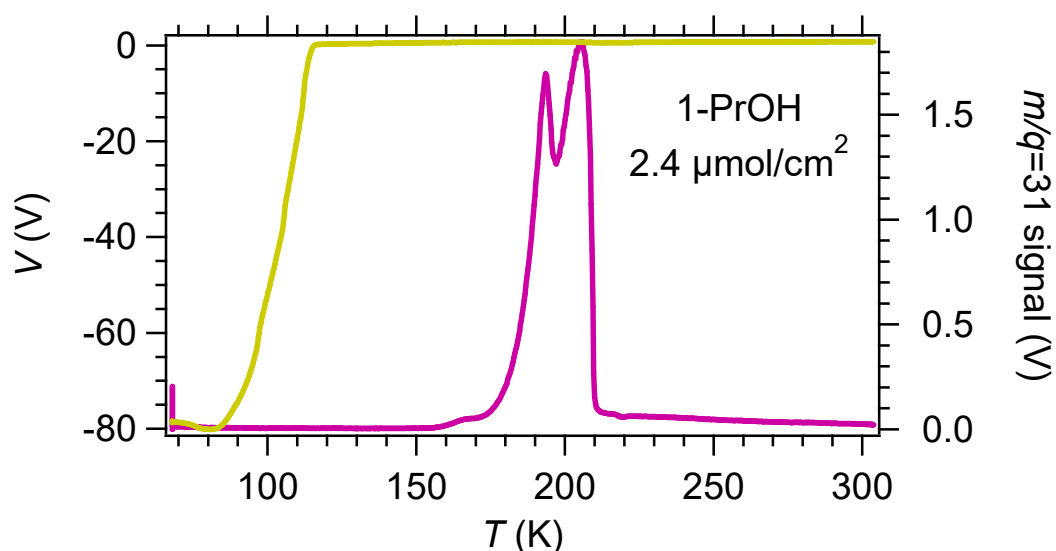


Figure S3. Voltage build-up on a **1-propanol** film deposited at 68.1 K and subsequently ramped up to 300 K.

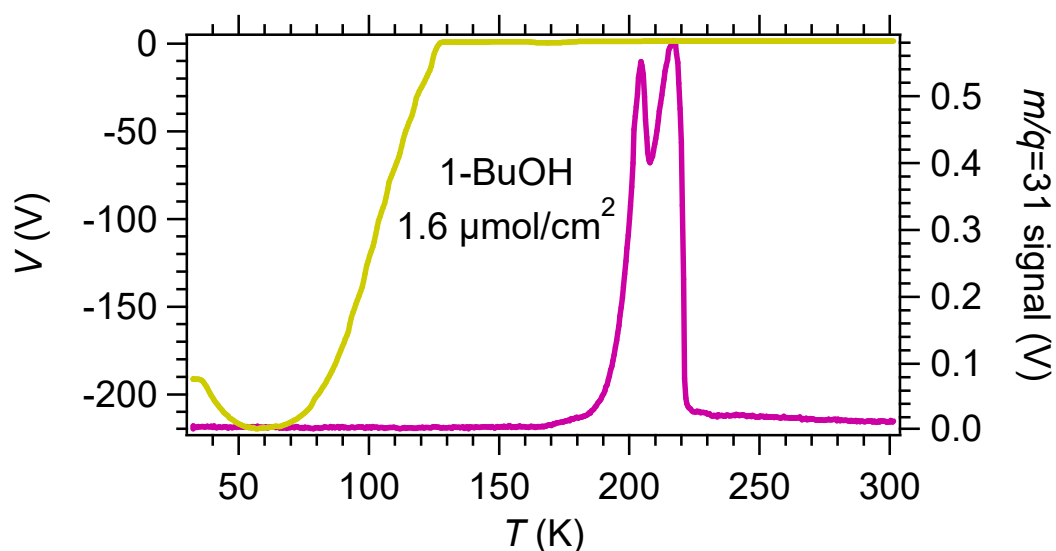


Figure S4. Voltage profile for a **1-butanol** film deposited at 32.6 K and ramped up at 0.25 K s<sup>-1</sup> and mass spectrometer signal for the main fragment of the deposited molecule.

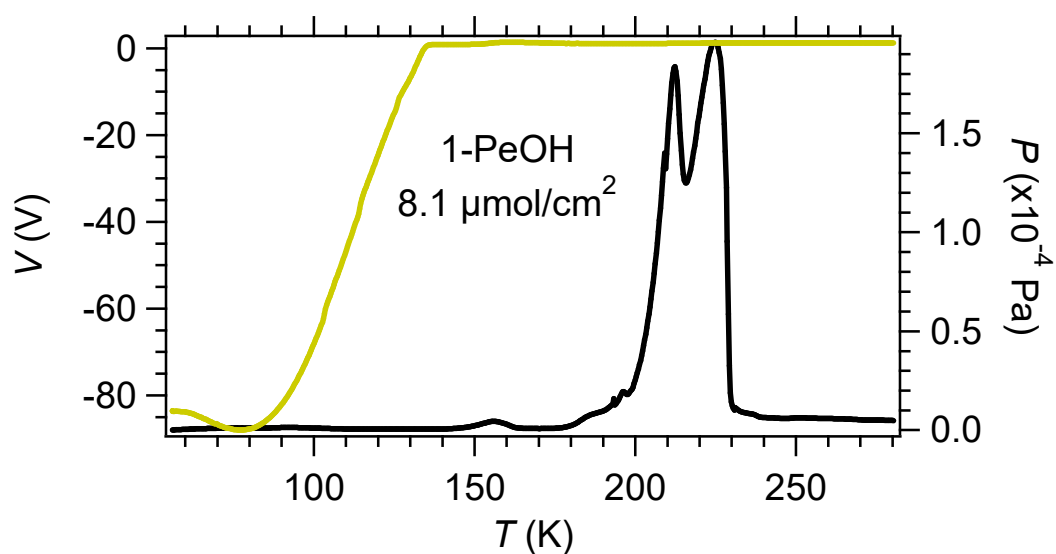


Figure S5. Variation of voltage as a function of temperature for a **1-pentanol** film deposited at 56 K and ramped up at  $0.25 \text{ K s}^{-1}$  along with the chamber pressure indicating the evaporation of the film above 200 K.

## B. Initial and extreme voltages

Figures of scaled voltages measured at the beginning of each ramp showing fluctuations with deposition temperature. The same figures also display the extremum exhibited during the subsequent temperature ramp. The temperature for the extremum is shown in a separate figure for each compound. Finally, the change in film voltage between the beginning and the extremum is depicted in a separate set of figures.

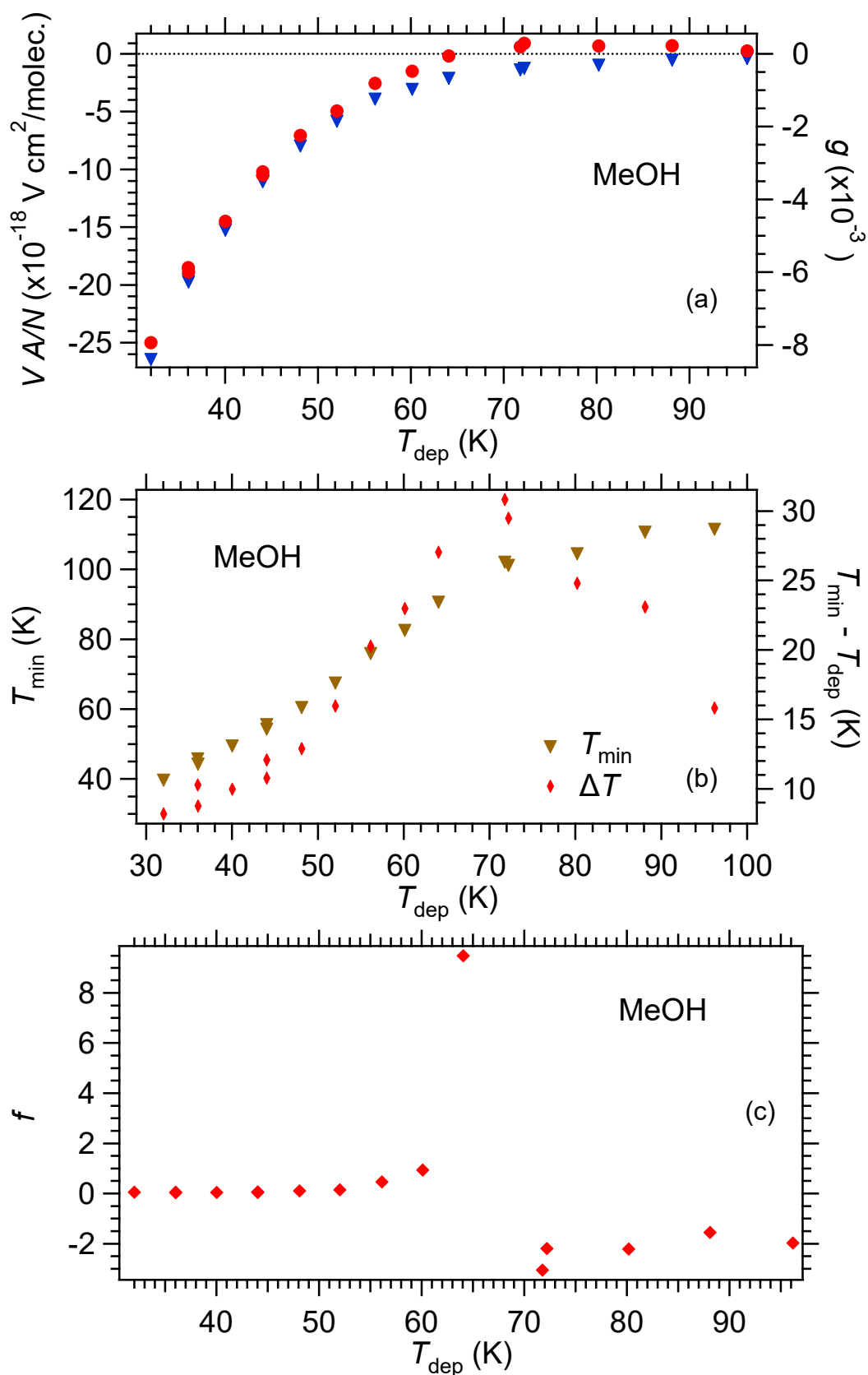


Figure S6. (a) Initial (red circles) and minimum (blue triangles) scaled voltage and calculated degree of polarization for **methanol** films as a function of deposition temperature. (b) Temperature at which film voltage reaches minimum (brown triangles) and difference between that and deposition temperature (red diamonds) as a

function of deposition temperature. (c) Fractional increase of film voltage,  $f = \frac{V_{\min} - V_{\text{start}}}{V_{\text{start}}}$ , during temperature ramp as a function of deposition temperature.

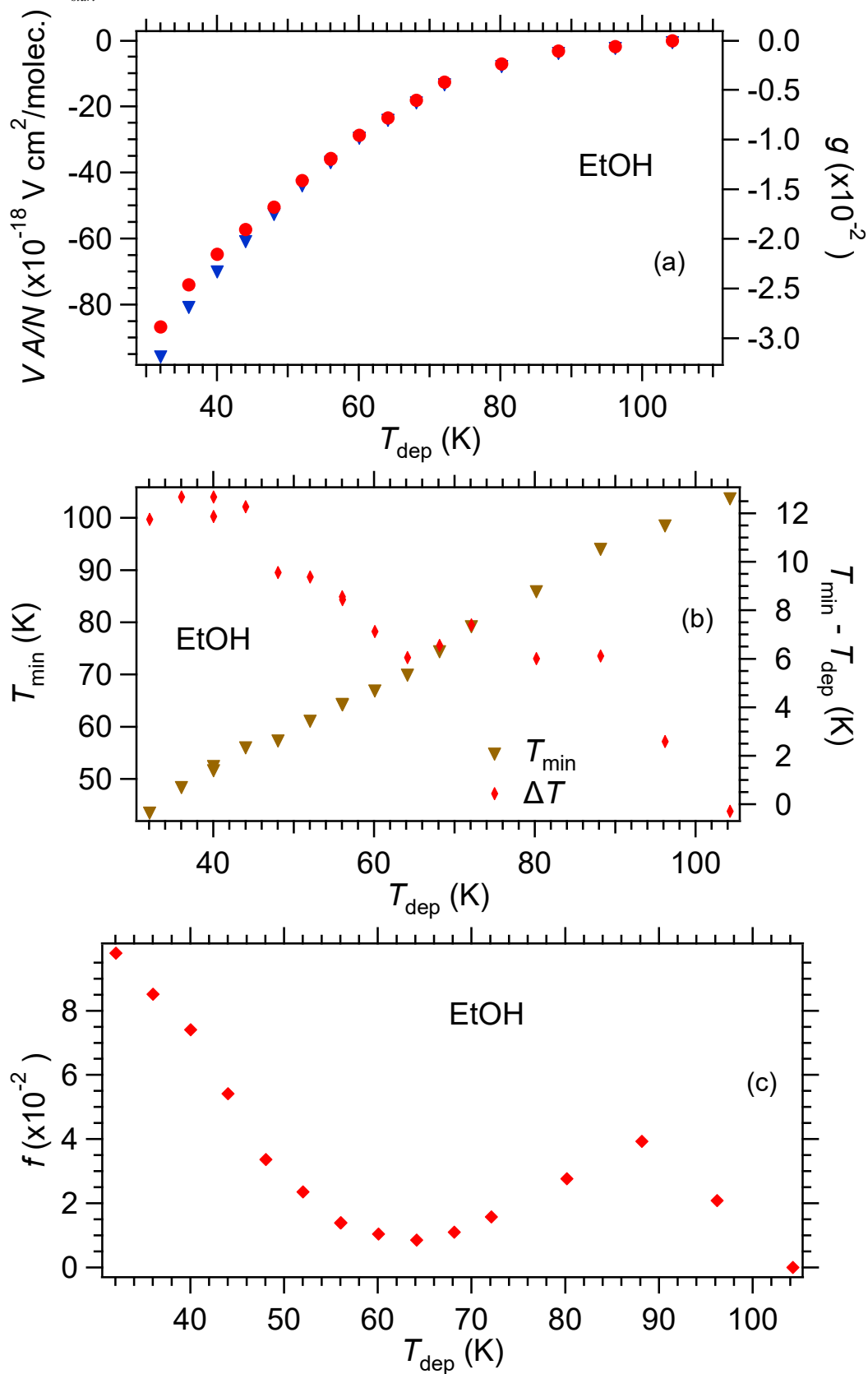


Figure S7. Same as Fig. S6 for **ethanol**.

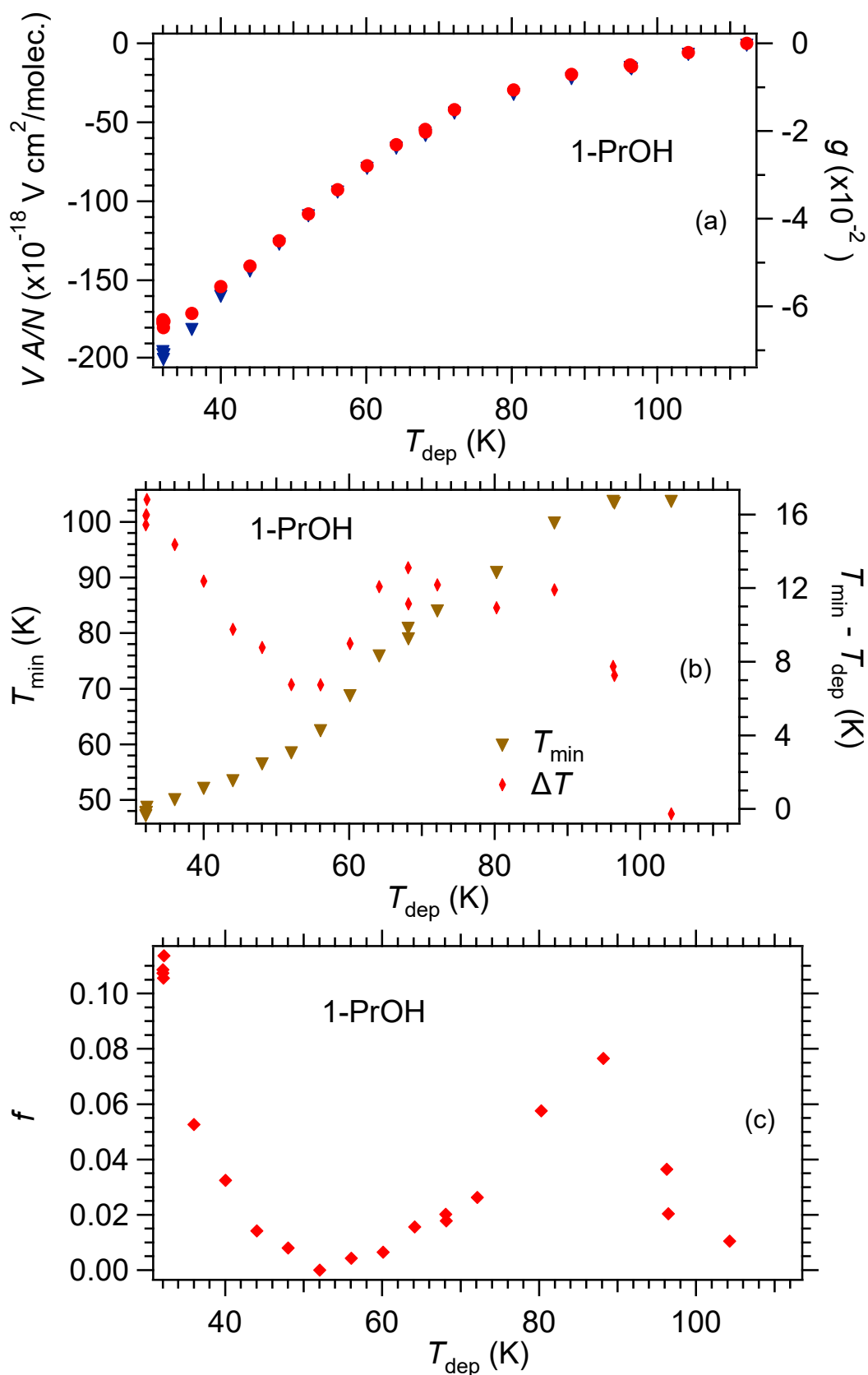


Figure S8. Same as Fig. S6 for **1-propanol**.

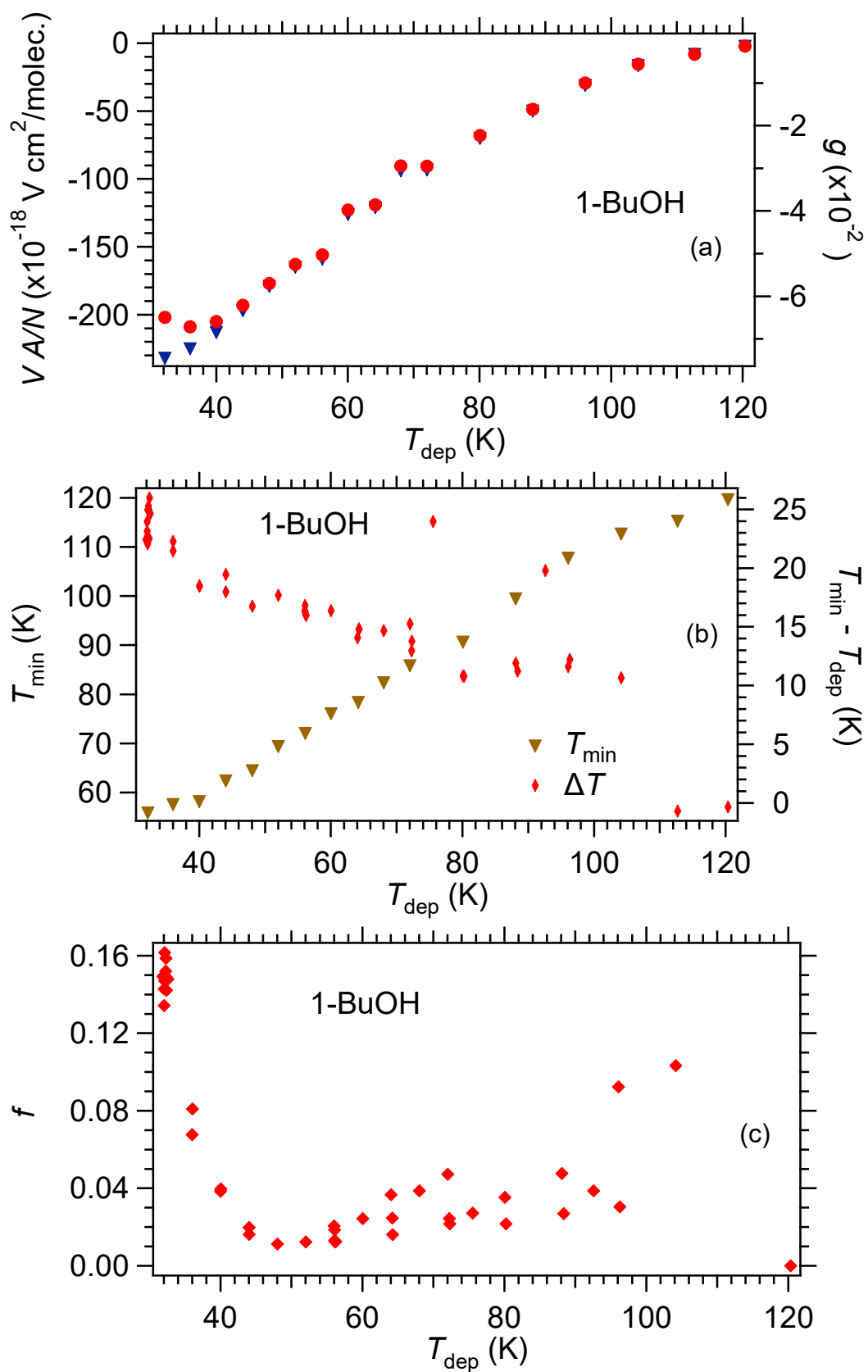


Figure S9. Same as Fig. S6 for **1-butanol**.

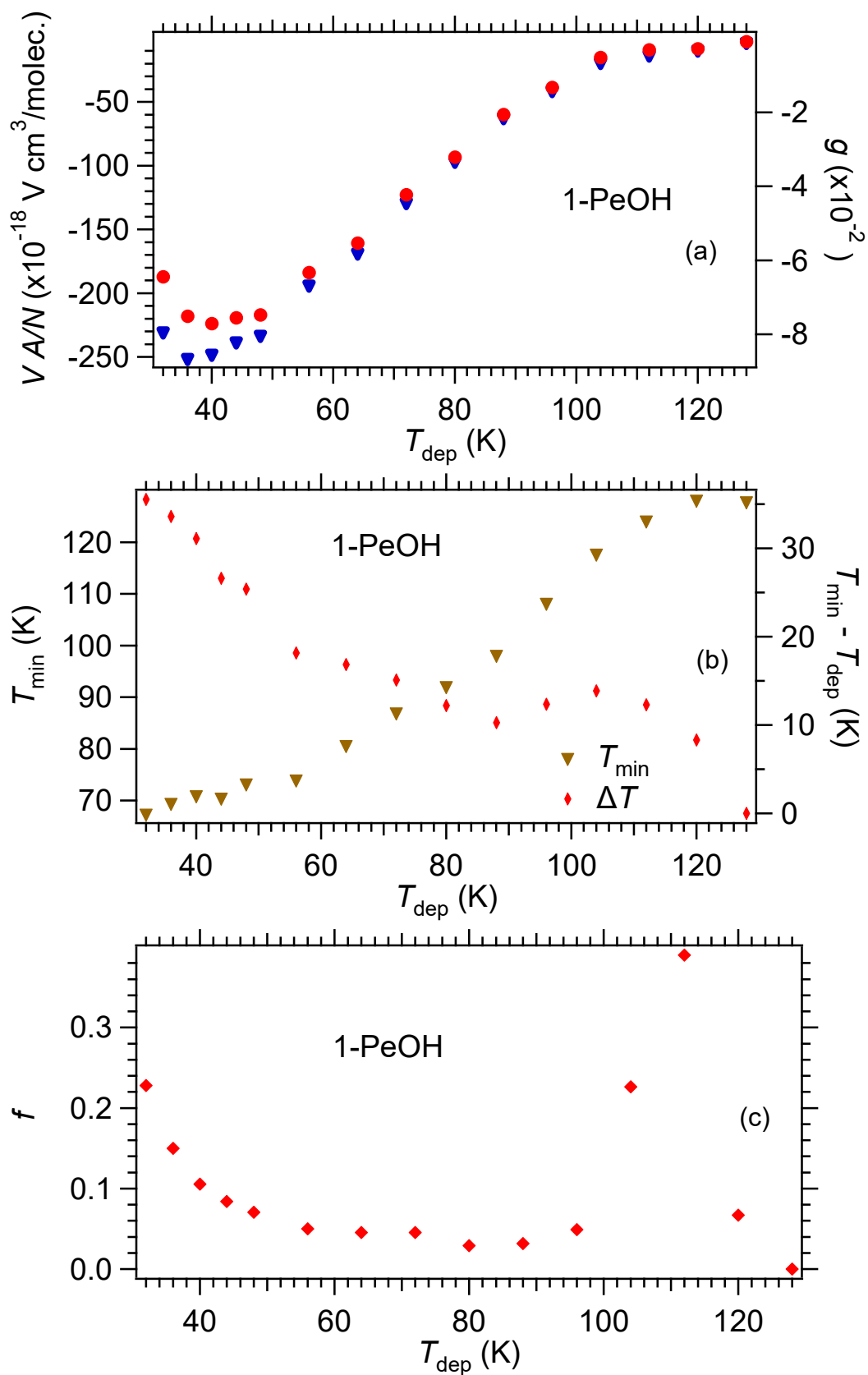


Figure S10. Same as Fig. S6 for **1-pentanol**.



### C. Data fits

A reviewer suggested scaling the deposition temperatures shown in Fig. 7(a) by the glass transition temperature of each alcohol. The result is shown in Fig. S11. There is no noticeable difference from Fig. 7(a) because all  $T_g$ s are very similar.

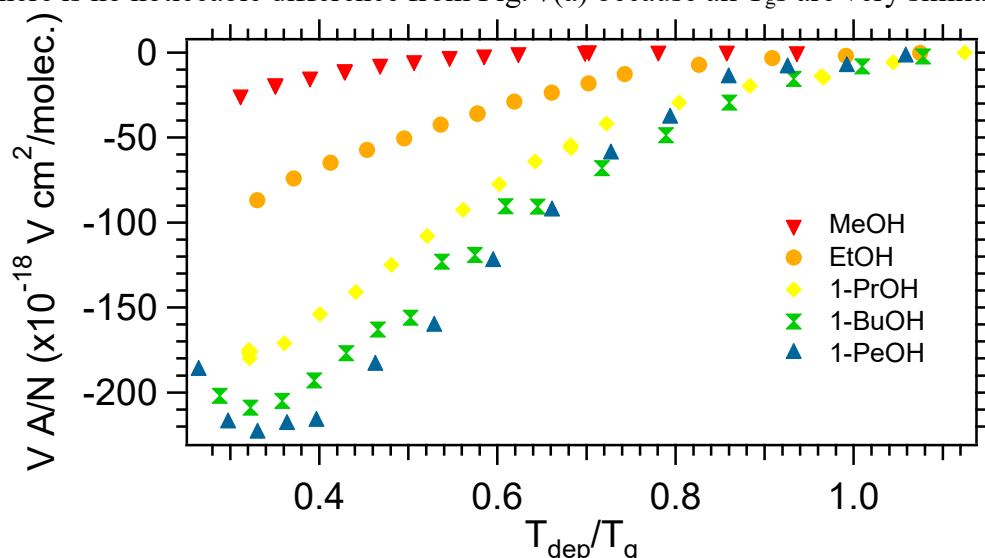


Figure S11. Initial scaled voltage for  $n$ -alcohol films as a function of deposition temperature scaled by the corresponding glass transition temperature.

Another fitting approach was suggested by a reviewer, namely scaling the temperature rather than shifting it. The results are shown in Fig. S12 and Table S1.

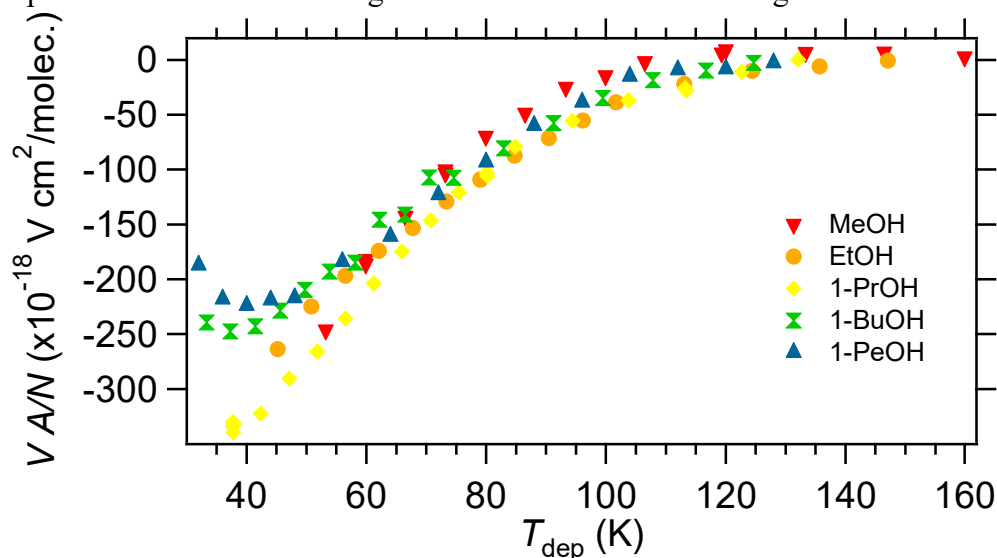


Figure S12. Adjusted initial scaled voltage for  $n$ -alcohol films as a function of scaled deposition temperature. This is the least-squares fit result.

**Table S1.**

| Compound   | Fitting parameters           |                                  |
|------------|------------------------------|----------------------------------|
|            | Voltage Scale ( $1 \sigma$ ) | Temperature Scale ( $1 \sigma$ ) |
| methanol   | 0.10 (0.12)                  | 1.7 (0.6)                        |
| ethanol    | 0.33 (0.07)                  | 1.4 (0.1)                        |
| 1-propanol | 0.53 (0.04)                  | 1.18 (0.05)                      |
| 1-butanol  | 0.84 (0.06)                  | 1.04 (0.03)                      |
| 1-pentanol | 1 (0)                        | 0 (0)                            |

Figure S13(a) shows the lowest (not initial as in Fig. 7) scaled film voltage measured for each compound during the temperature ramps at the corresponding deposition temperature. Again, we attempted a fit to make these curves overlap by using the 1-pentanol curve as a template. The result is seen in Fig. S13(b). The fitting parameters ( $1\ \sigma$  uncertainties) are given in the two middle columns of Table S2. Although the second fit is slightly worse (c.f. parameter uncertainties) than the one for the initial voltages (Table S2, 2<sup>nd</sup> and 3<sup>rd</sup> column, transferred from Table 2, 2<sup>nd</sup> and 3<sup>rd</sup> column), the parameter values are similar; of course, the maximum scaled voltage (Table S2, 6<sup>th</sup> column) is larger for the lowest voltages; the locations of the minima (Table S2, 7<sup>th</sup> column) are predicted at somewhat lower temperatures than those for the initial voltages (Table 2, 5<sup>th</sup> column).

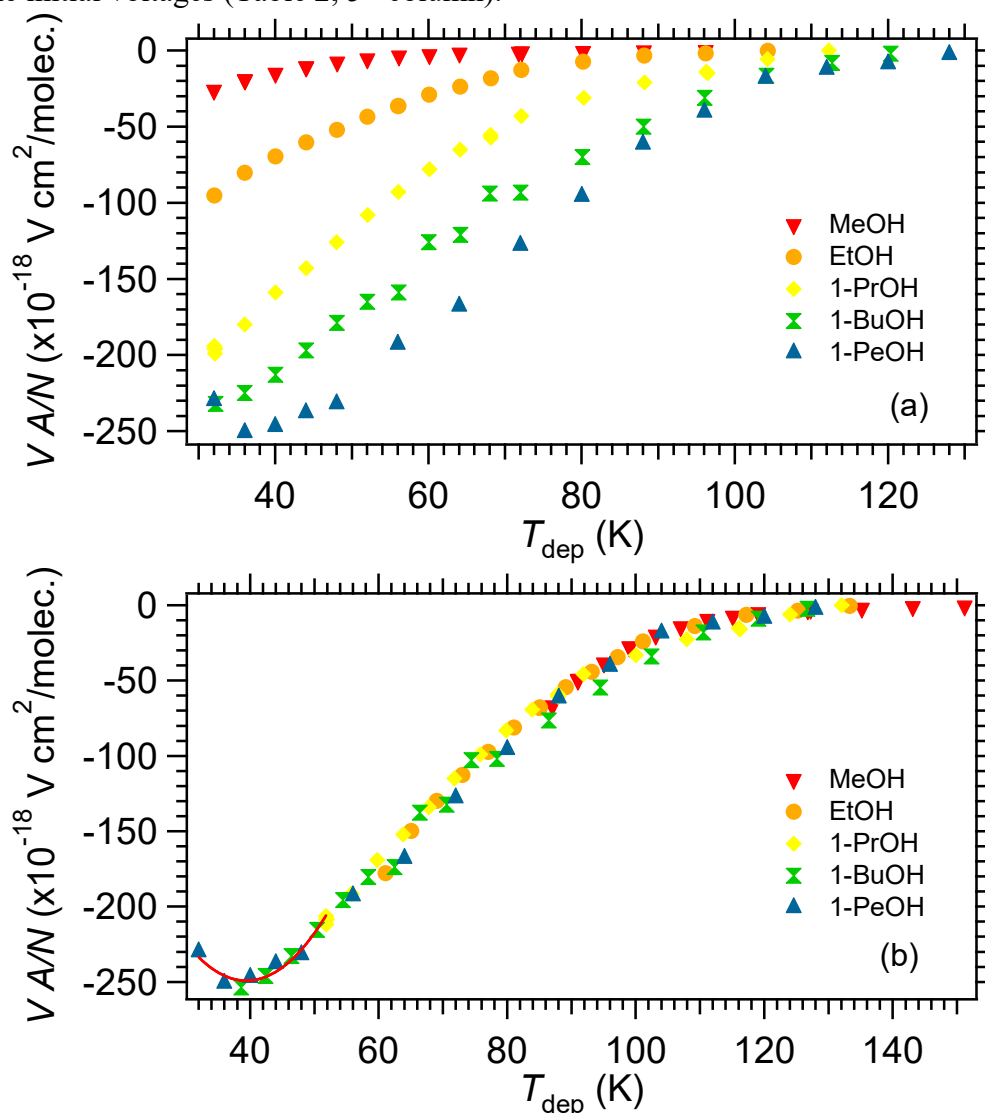


Figure S13. (a) Minimum scaled voltage for *n*-alcohol films as a function of deposition temperature. (b) Same data scaled vertically and shifted horizontally for optimum overlap based on a least squares fit. The resulting fitting parameters (see Table 2) are statistically indistinguishable from the corresponding fit of the initial voltages. The solid line is a parabola fit for the determination of the location of the extremum.

| Table S2. Fitting parameters for: |                      |             |                      |             | Derived values for:  |                       |                        |
|-----------------------------------|----------------------|-------------|----------------------|-------------|--|-----------------------|------------------------|
|                                   | Initial film voltage |             | Minimum film voltage |             | Peak scaled voltage  | Peak temperature      | Degree of polarization |
| Compound                          | Scale                | Shift (K)   | Scale                | Shift (K)   | $V A/N_{\max}$<br>( $10^{-18}$ V<br>cm <sup>2</sup> /molec.) | $T_{\text{peak}}$ (K) | $g_{\max}$             |
| methanol                          | 0.37 (0.11)          | -55 (4.4)   | 0.39 (0.14)          | -56 (5)     | -98  | -16                   | -0.031                 |
| ethanol                           | 0.49 (0.03)          | -29.0 (1.7) | 0.54 (0.04)          | -31.0 (1.8) | -133   | 8                     | -0.042                 |
| 1-propanol                        | 0.88 (0.02)          | -19.8 (0.9) | 0.94 (0.03)          | -21.6 (1.0) | -234   | 18                    | -0.080                 |
| 1-butanol                         | 0.92 (0.01)          | -6.4 (0.6)  | 0.915 (0.014)        | -7.1 (0.7)  | -227   | 32                    | -0.080                 |
| 1-pentanol                        | 1 (0)                | 0 (0)       | 1 (0)                | 0 (0)       | -249 (2)   | 39.4 (0.5)            | -0.080                 |

Figure S14(a) shows the lowest scaled film voltage measured for each compound during the temperature ramps at the temperature of the appearance of the minimum. It differs from Fig. 8 only in that the data are shown as a function of the temperature for the appearance of the minimum during the ramp. We attempted a fit to make these curves overlap by using the 1-butanol curve as a template. The result is seen in Fig. S14(b). The fitting parameters (1  $\sigma$  uncertainties) are given in the two middle columns of Table S3. A second attempt on the same data using the 1-pentanol curve for shape reference is seen in Fig. S14(c) and in the last two columns of Table S3. Neither fit is realistic: the first one does not shift the methanol data far enough to the right or the pentanol data to lower temperatures with respect to the butanol curve; the second fit should have made all the curves move to the right of the turning point of the pentanol data seen at the low temperature side, yet the noise in the data runs over this fine detail of the pentanol curve.

| Table S3.  |                      |            |                      |             |
|------------|----------------------|------------|----------------------|-------------|
|            | Minimum film voltage |            | Minimum film voltage |             |
| Compound   | Scale                | Shift (K)  | Scale                | Shift (K)   |
| methanol   | 0.15 (0.08)          | -32 (11)   | 0.11 (0.07)          | -33 (14)    |
| ethanol    | 0.62 (0.06)          | -29 (2)    | 0.45 (0.07)          | -31 (3)     |
| 1-propanol | 0.78 (0.02)          | -8.6 (0.7) | 0.79 (0.02)          | -22.4 (0.8) |
| 1-butanol  | 1 (0)                | 0 (0)      | 0.95 (0.016)         | -9.8 (0.4)  |
| 1-pentanol | 1.46 (0.03)          | 0.05 (0.6) | 1 (0)                | 0 (0)       |

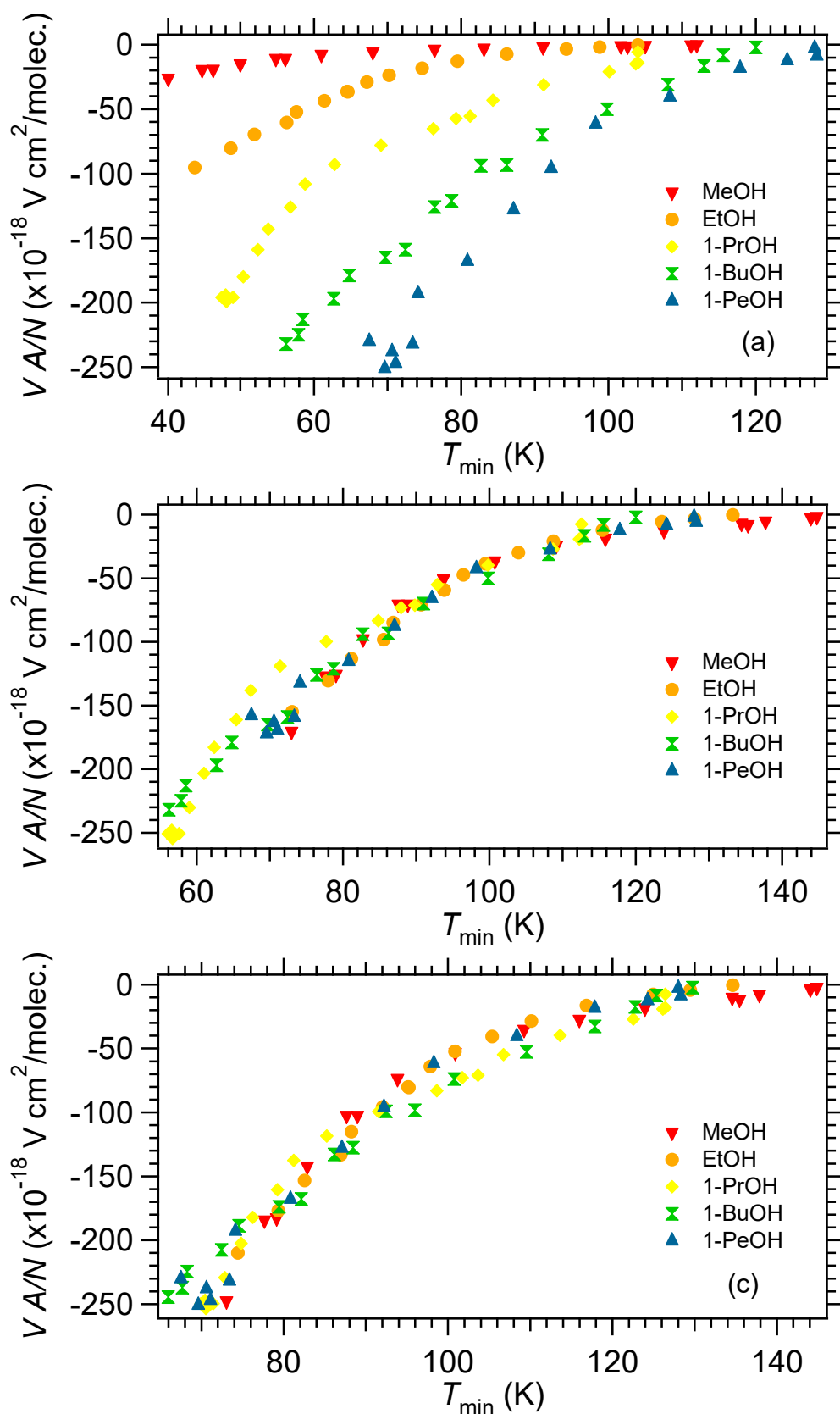


Figure S14. (a) Minimum scaled voltage for  $n$ -alcohol films as a function of temperature of minimum voltage. (b) Same data scaled vertically and shifted horizontally for optimum overlap based on a least squares fit using the 1-butanol curve as a template. (c) Same data scaled vertically and shifted horizontally for optimum overlap based on a least squares fit using the 1-pentanol curve as a template.

All alcohols studied share almost the same value for their dipole moment. Given that there appears to be a correlation between film voltage and molecular size, we considered the polarizability as a proxy for the molecular size. Figure S15 shows that polarizability varies almost linearly with chain length. So, we can simply use the number of carbon atoms to plot the peak value of the scaled voltage for each alcohol (Fig. 11). The correlation appears to be poor. There is no point trying the molecular mass as the abscissa, because the mass is a linear function of the number of carbon

atoms:  $\frac{M}{\text{g mol}^{-1}} = 14n + 18$ .

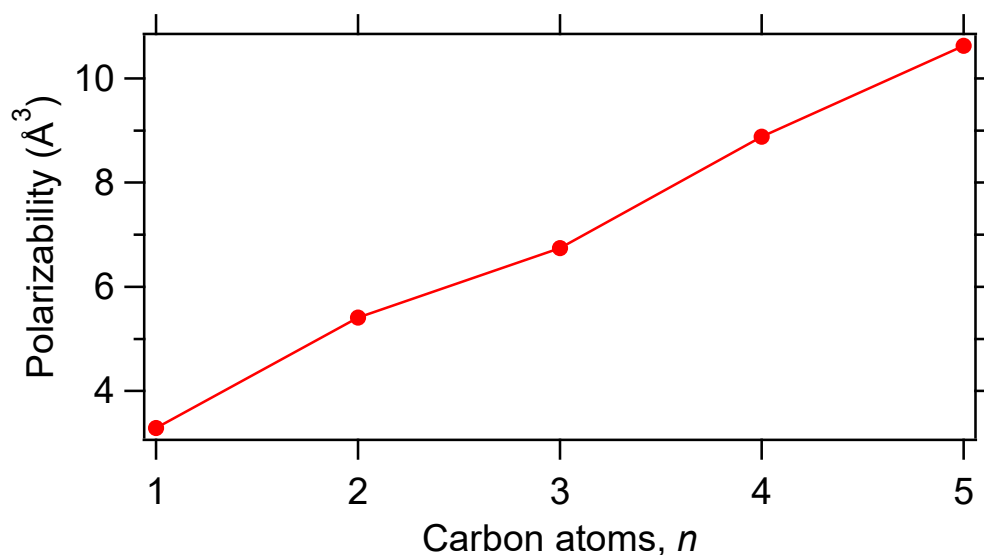


Figure S15. Experimental values of polarizability for methanol through 1-pentanol.

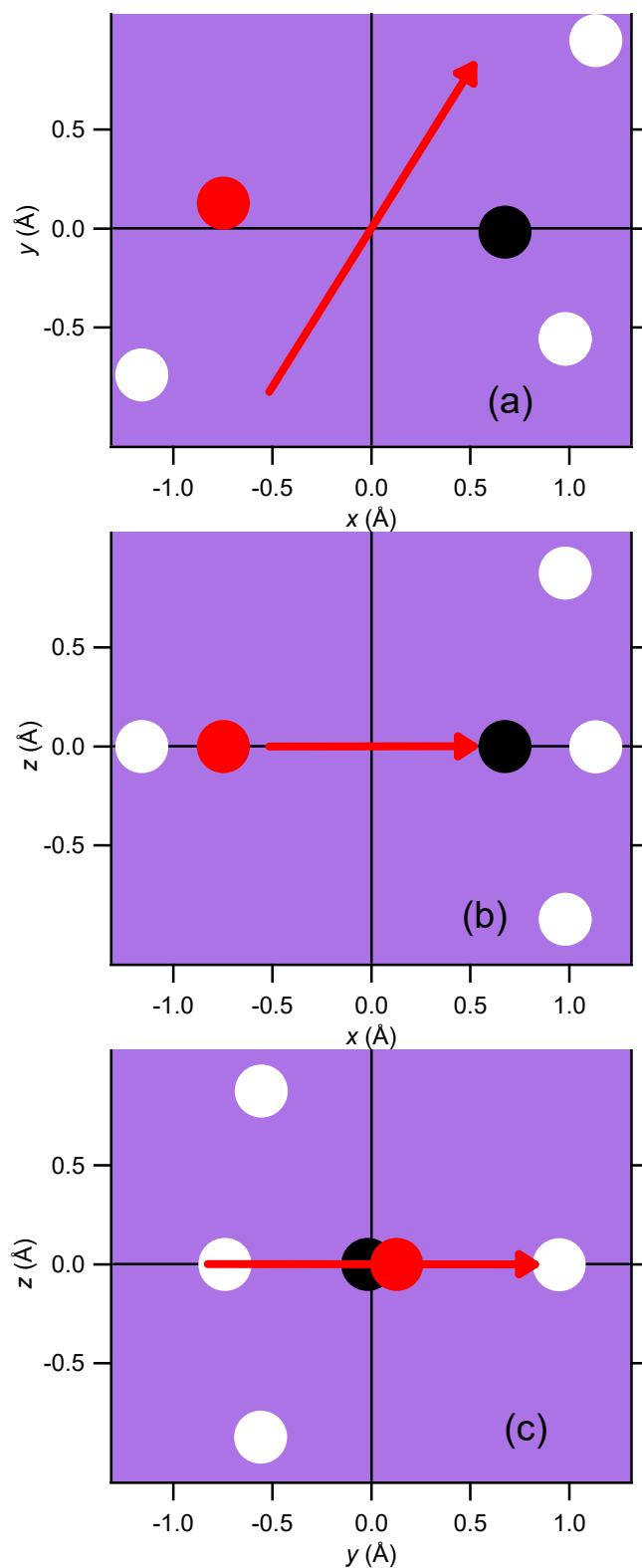


Figure S14. Projection of the dipole moment vector (red arrow) of methanol on (a) the  $xy$ -plane, (b) the  $xz$ -plane, and (c) the  $yz$ -plane. Calculations were done using Gaussian at the B3LYP level of theory using 6-311+g(d,p) basis sets. The  $x$ ,  $y$ ,  $z$  axes are almost coincident with the principal axes of rotation.

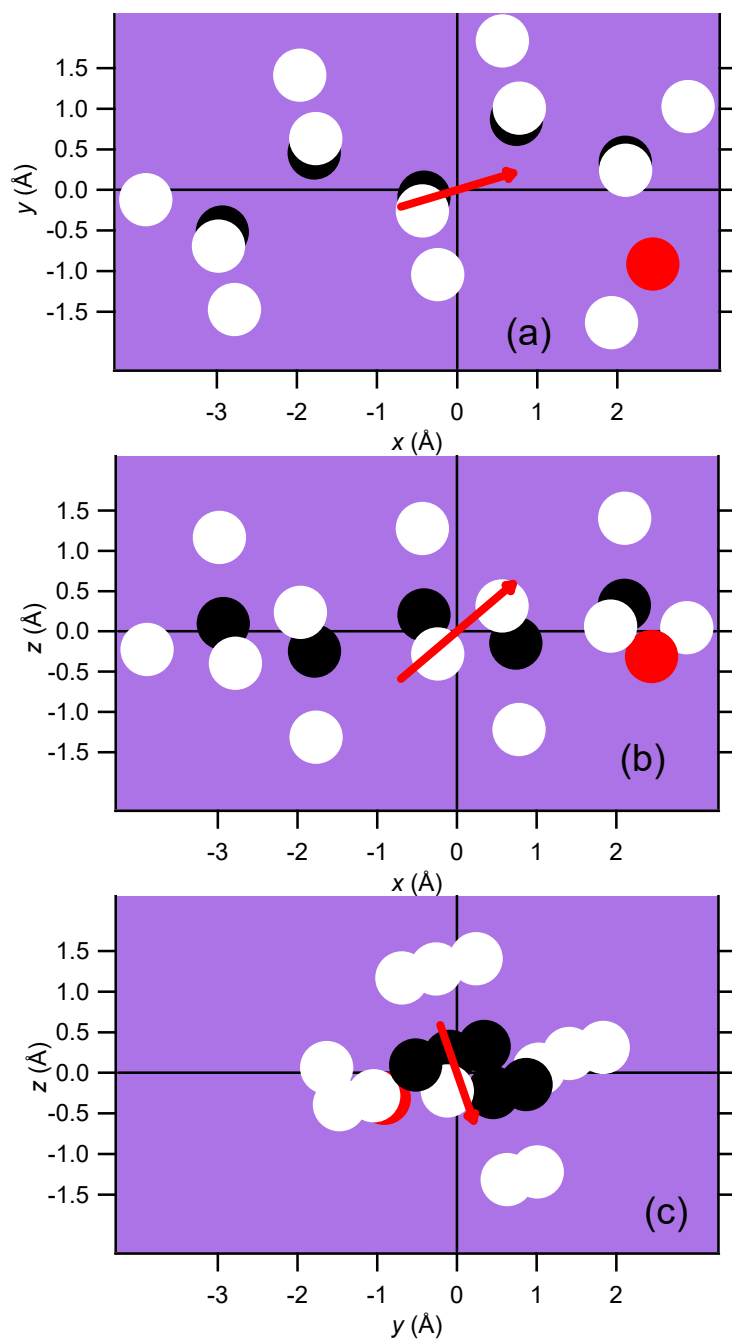


Figure S15. Projection of the dipole moment vector (red arrow) of 1-pentanol on (a) the  $xy$ -plane, (b) the  $xz$ -plane, and (c) the  $yz$ -plane. Calculations were done using Gaussian at the B3LYP level of theory using 6-311+g(d,p) basis sets. The  $x$ ,  $y$ ,  $z$  axes are almost coincident with the principal axes of rotation.