Electronic Supplementary Material (ESI) for Nanoscale Advances.

Accurate Electromechanical Characterization of Soft Molecular Monolayers using Piezo Force Microscopy

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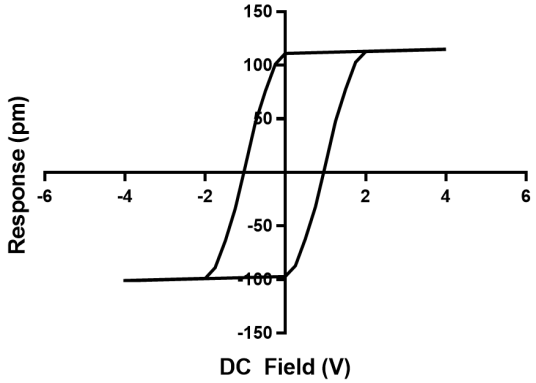

Figure 1: Suggested V_{DC} sweep technique on non-fixed polar piezoelectric materials where the remnant polarization switches under the coercive field.

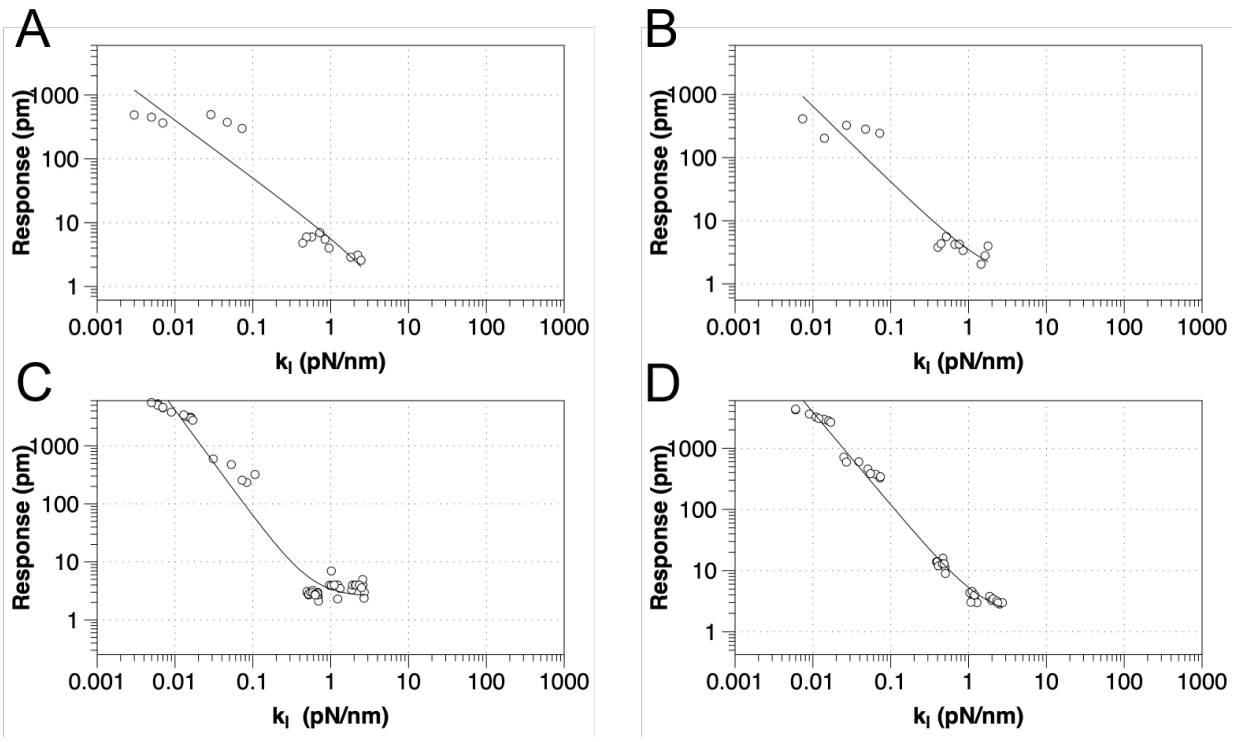

Figure 2: Relationship between tip response and k_l for various SAMs using AFM levers with spring constants from 0.02-2.8 N/m, for (a) **DDT**, (b) **MUA**, (c) peptide **A** and (d) peptoid **B** respectively. The best-fit line is to $y = a + bx^c$.

Table 1: Summary of tip-dependent (k_l) response across four organic self-assembled monolayers, indicating best-fit parameters of tip response to $a + bx^c$.

Material	Constant (a)	Coefficient (b)	Power (c)	R^2
DDT	-0.786	6.35	-0.901	0.886
MUA	0.973	2.52	-1.21	0.903
Peptide A	2.51	0.899	-1.83	0.965
Peptoid B	1.73	3.57	-1.52	0.988

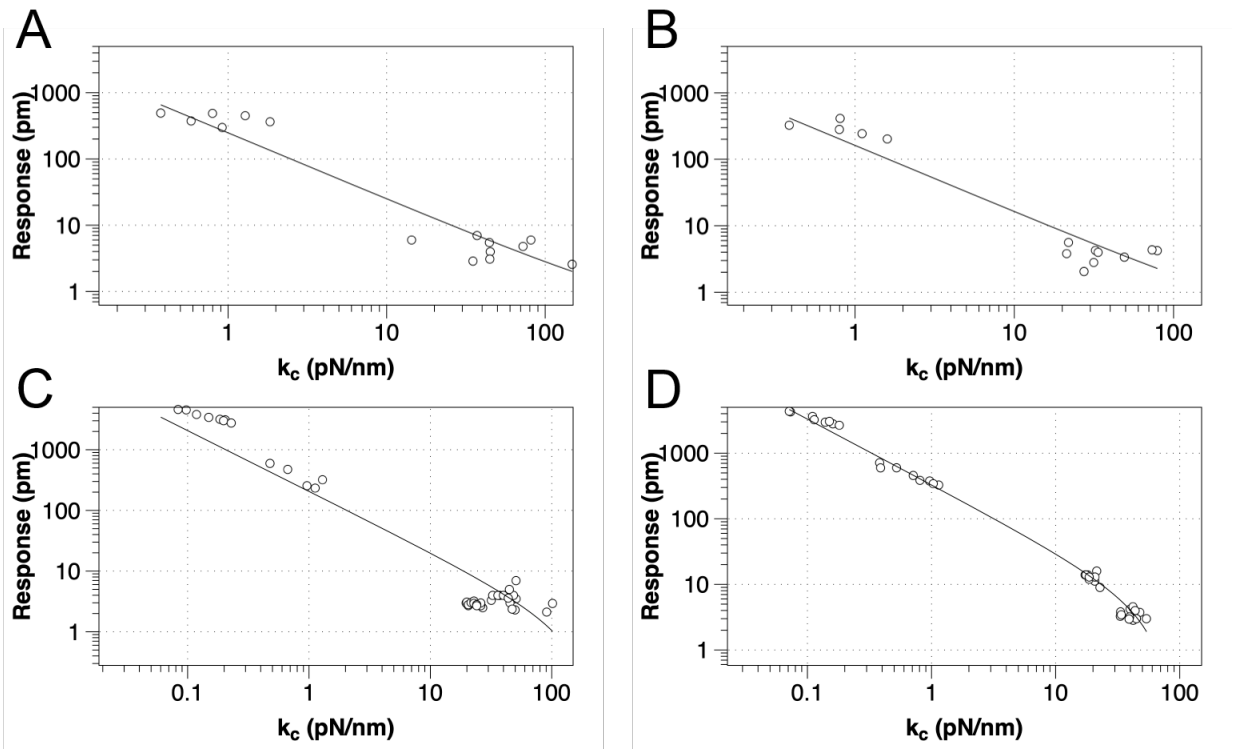

Figure 3: Relationship between tip response and k_c for various SAMs using AFM levers with spring constants from 0.02-2.8 N/m, for (a) **DDT**, (b) **MUA**, (c) peptide **A** and (d) peptoid **B** respectively. The best-fit line is to $y = a + bx^{-1}$.

Table 2: Summary of tip-dependent (k_c) response across four organic self-assembled monolayers, indicating best-fit parameters of tip response to $a + bx^{-1}$.

Material	Constant (a)	Coefficient (b)	R^2
DDT	0.342	247	0.932
MUA	0.239	162	0.927
Peptide A	-1.02	207	0.944
Peptoid B	-4.24	331	0.992

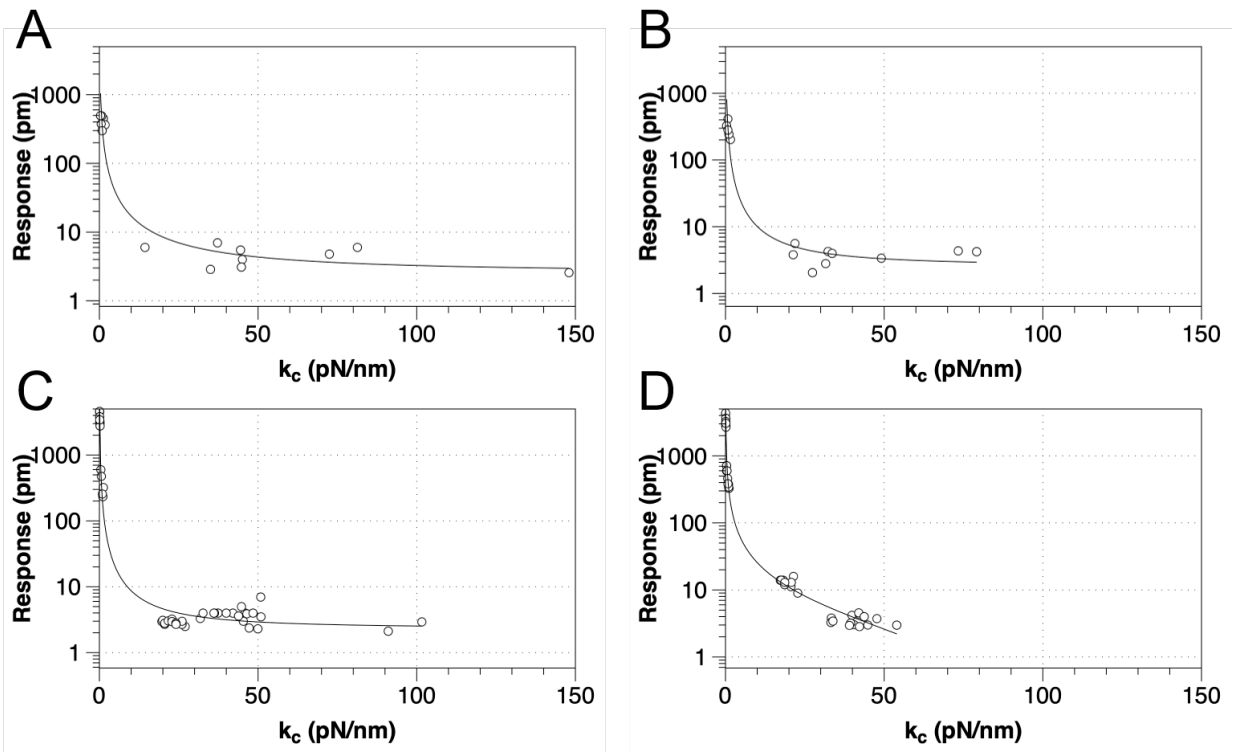

Figure 4: Relationship between tip response and k_c for various SAMs using AFM levers with spring constants from 0.02-2.8 N/m, for (a) **DDT**, (b) **MUA**, (c) peptide **A** and (d) peptoid **B** respectively. The best-fit line is to $y = a + bx^c$. A replotting of Figure 2 from the main text but in log linear scaling to emphasize the asymptotic nature of the fits.

Table 3: AMFM results for the measurement of k_c with corresponding k_l based on implemented lever.

Material	Lever k_l (N/m)	k_l (μN/m)	k^* (μN/m)	k^* Error (μN/m)
QCM	2.8	$1.66x10^6$	1684	165
	0.09	$4.41x10^4$	132.9	54.1
DDT	2.8	$1.69x10^6$	1937	162
	0.09	$3.69x10^4$	131.3	35.0
MUA	2.8	$1.66x10e^6$	1272	197
	0.09	$3.51x10^4$	103.5	35.8
Peptide A	2.8	$1.68x10^6$	1174	158
	0.09	$3.59x10^4$	26.77	8.13
Peptoid B	2.8	$1.73x10^6$	1244	140
	0.09	$3.41x10^4$	65.10	26.4

Table 4: Coefficient values and calculated d_{33} from tip response as a function of V_{AC} on peptoid B using 0.09 N/m k_l levers at varying V_{DC}.

V_{DC} (V)	R^2	Intercept (pm)	d_{eff} (pm/V)
3.0	0.998	7.19	241
2.0	0.995	13.9	148
1.0	0.956	22.8	50.6
-1.0	0.991	-32.6	137
-2.0	0.996	-35.7	229
-3.0	0.999	-38.0	325

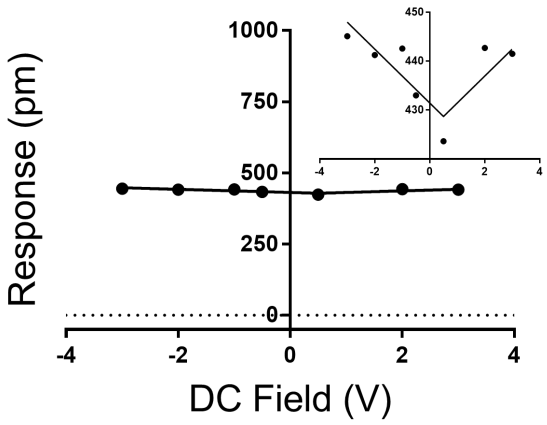

Figure 3: PFM tip response from V_{DC} sweep technique on PZT at 3.0 V_{AC} with R2 levers (2.8 N/m). The resulting slope of the fit was 5.51 pm/V_{DC} with an R^2 value of 0.704. With a calculated d_{eff} of 143 pm/V_{AC}.

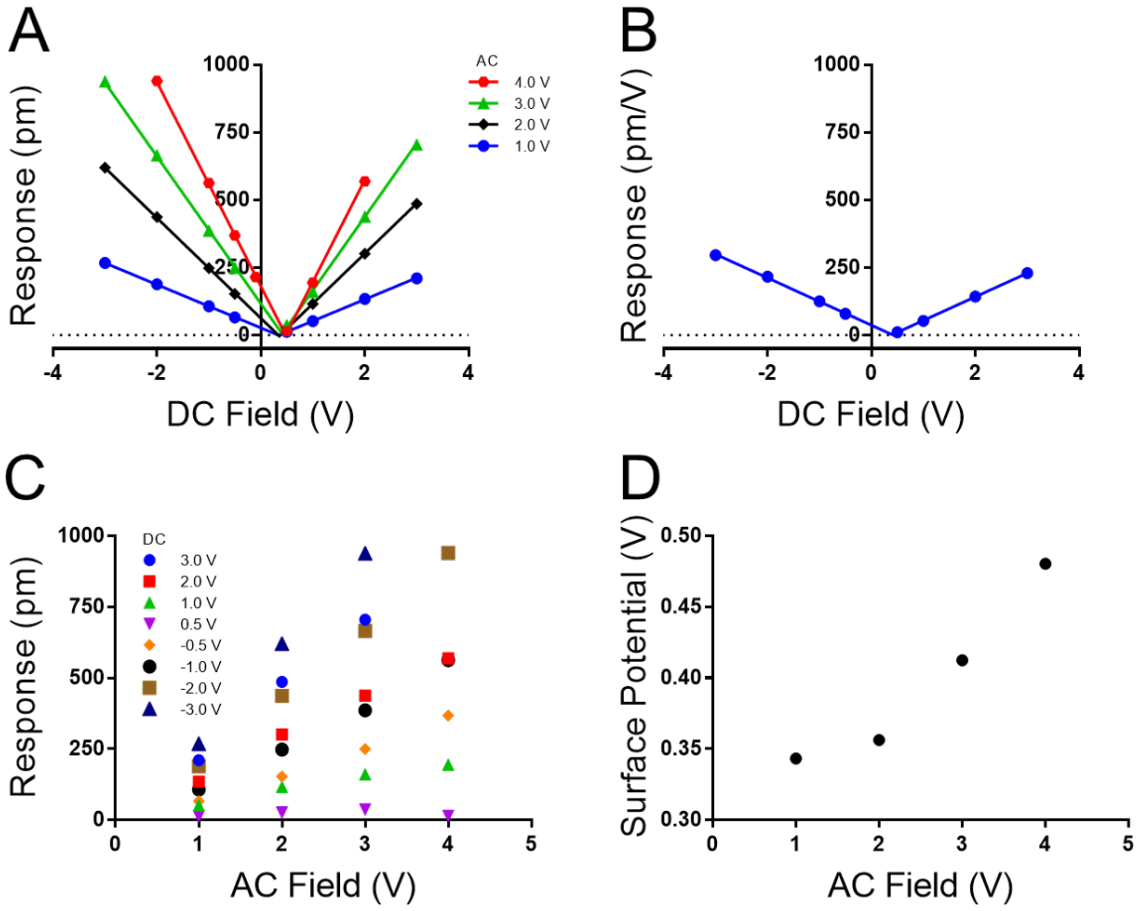

Figure 4: (a) PFM tip response from V_{DC} sweep technique on ZNO with TRS levers (0.09 N/m) at varying V_{AC}. (b) DC- dependent response. (c) PFM response from V_{AC} at indicated V_{DC}. (d) Measure V_{CPD} as a function of V_{AC}.

Table 5: Coefficient values and calculated d_{33} from tip response as a function of V_{DC} on ZNO using 0.09 N/m k_l levers at varying V_{AC}.

V_{AC} (V)	V_{CPD} (V)	Slope (A)	R^2	d_{eff} (pm/V)
4.0	0.480	278	0.999	0.040
3.0	0.412	185	0.999	1.61
2.0	0.356	86.0	0.996	-1.54
1.0	0.343	43.9	0.999	-0.291
NA	0.401	87.5	0.999	1.90

Table 6: Coefficient values and calculated d_{33} from tip response as a function of V_{AC} on ZNO using 0.09 N/m k_l levers at varying V_{DC}.

V_{DC} (V)	R^2	Intercept (pm)	d_{eff} (pm/V)
3.0	0.996	-27.5	247
2.0	0.997	0.675	144
1.0	0.980	12.2	47.3
0.5	0.996	0.740	12.3
-0.5	0.995	-41.9	100
-1.0	0.997	-50.3	151
-2.0	0.999	-62.7	248
-3.0	0.999	-62.8	336

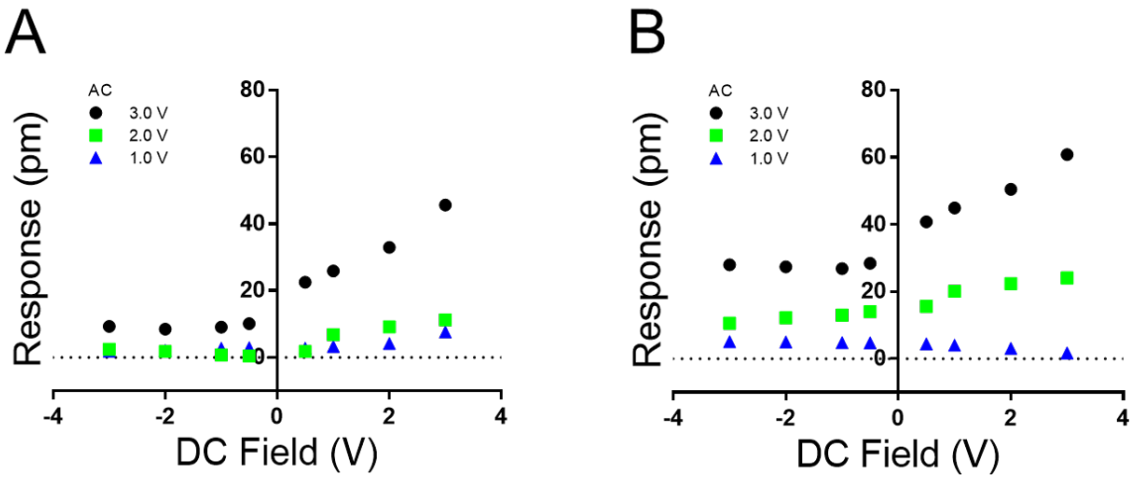

Figure 5: PFM tip response from V_{DC} sweep technique on PPLN at various V_{AC} using R2 levers (2.8 N/m). (a) and (b) represent measured response of PPLN with phase up (+180º) and phase down (-180º) respectively.

Table 7: SKPFM results for the measurement of V_{CPD} for various materials using 2.8 N/m levers.

Material	V_{CPD} (mV)	Error (mV)
DDT	172	5.95
MUA	-198	19.6
Peptide A	-139	16.2
Peptoid B	-362	23.6
QCM	1100	161
ZnO	-745	160