

Supplementary Materials for: Trap Polarity and the p/n Asymmetry in Oxidised DNTT: A Frontier-Shift Rule

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S1 Trap-concentration analysis: capacitance–voltage of the DNTT MIS structure

The trap concentration returned by the DLTS system is not measured directly; it is obtained by scaling the transient amplitude,

$$N_T = 2 N_S \frac{\Delta C}{C_R}, \quad (\text{S1})$$

by the shallow (doping) concentration N_S , which the system extracts from the capacitance–voltage (C–V) characteristic. For the present devices this route returns a physically impossible value, for the reasons set out below. Because the extraction rests entirely on N_S , the activation energy—obtained from the emission time constant τ_e (Arrhenius analysis), not from the amplitude—is unaffected by any of the following.

A categorical model error. The measured device is a metal–insulator–semiconductor (MIS) capacitor (highly doped Si gate / 100 nm thermal SiO₂ / DNTT, top Ag contacts), but the system applied a Schottky (Mott–Schottky) C–V model, which is the root cause. The recorded capacitance (Figure S1) returns $N_S = N_{SP} = 3.09 \times 10^{25} \text{ cm}^{-3}$, a diffusion voltage $U_D = -103.9 \text{ V}$, a barrier $\varphi_B = 103.1 \text{ eV}$ and a fit correlation of only 0.943. These values are unphysical: N_S exceeds the molecular density of DNTT ($\approx 2.7 \times 10^{21} \text{ cm}^{-3}$) by about four orders of magnitude—one cannot have more dopants than molecules—while φ_B merely mirrors $|U_D|$ and the correlation of 0.943 confirms that the $1/C^2$ characteristic is not linear.

Why the extraction diverges. In a MIS structure the accumulation side is pinned to the oxide capacitance C_{ox} , so that $1/C^2$ versus bias is nearly flat (indeed slightly decreasing) over the branch on which the regression lies, whereas the Mott–Schottky analysis requires a linear *increase*. The extracted slope tends to zero (or becomes negative); since $N_S \propto 1/\text{slope}$, a gigantic N_S results and the intercept extrapolates to the spurious $U_D \approx -104 \text{ V}$.

A secondary area error. The nominal area $F = 8 \times 10^{-3} \text{ cm}^2$ (0.8 mm²) underestimates the true device area. From the accumulation capacitance ($C \rightarrow C_{\text{ox}} \approx 700 \text{ pF}$), the effective area is

$$A_{\text{eff}} = \frac{C_{\text{ox}} d_{\text{ox}}}{\varepsilon_0 \varepsilon_r} = \frac{700 \text{ pF} \times 100 \text{ nm}}{\varepsilon_0 \times 3.9} \approx 2.0 \times 10^{-2} \text{ cm}^2, \quad (\text{S2})$$

about 2.5 times the nominal value. As $N_S \propto 1/F^2$, this inflates N_S by a further factor of $(2.0/0.8)^2 \approx 6.3$. It should be stressed, however, that correcting the area alone does not resolve the discrepancy: even then N_S would remain of the order of $5 \times 10^{24} \text{ cm}^{-3}$, still far above the molecular density. The dominant error is the model, not the area.

Full depletion of the thin film. At the few-volt bias used, the C–V is saturated, indicating that the ≈ 50 nm, nearly intrinsic film is fully depleted. The capacitance is then geometric ($C = \epsilon A/d$, bias-independent), so the depletion width is pinned to the film thickness and cannot be modulated. The bulk assumption on which Equation (S1) rests—a bias-modulated depletion width in a semi-infinite semiconductor—therefore fails, and the extraction of N_S (and hence of N_T) is invalid.

Consequence. In a fully depleted film a *volume* trap concentration is not a well-defined quantity; only an areal trap density N_{ss} (cm^{-2}) is meaningful, subject to the hard cap $N < 2.7 \times 10^{21} \text{ cm}^{-3}$. The concentration of the order of 10^{23} cm^{-3} returned by the standard analysis should therefore be regarded as an artefact of applying a bulk Schottky model to a thin-film MIS structure, and not taken at face value. A physically meaningful extraction would require subtracting the series oxide capacitance ($1/C = 1/C_{ox} + 1/C_{HL}$) and restricting the Mott–Schottky fit to a genuinely linear depletion branch, using A_{eff} rather than the nominal area.

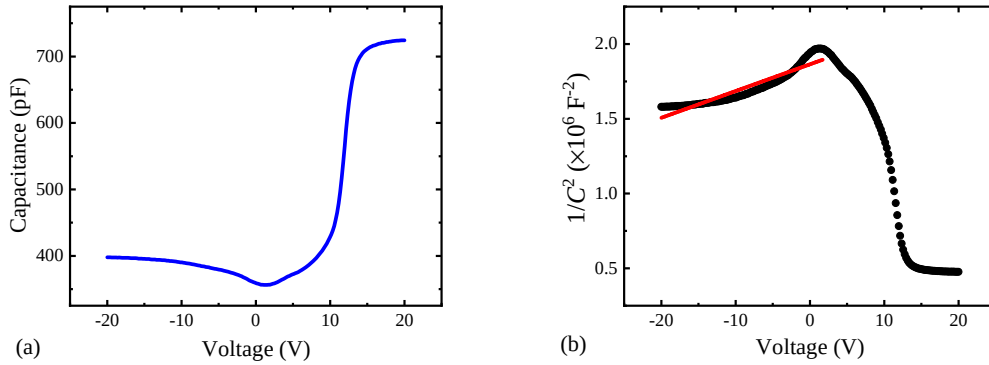


Figure S1: (a) Capacitance–voltage and (b) $1/C^2$ characteristics of the DNTT MIS structure. The accumulation plateau pins the capacitance to C_{ox} , so the $1/C^2$ branch fitted by the system (red line) is nearly flat; the resulting Mott–Schottky extraction yields the unphysical N_S , U_D and φ_B quoted in the text.

S2 Complete defect map

Figure S2 shows representative chemical structures for the closed-shell defect classes; the complete numerical map follows in Table S1.

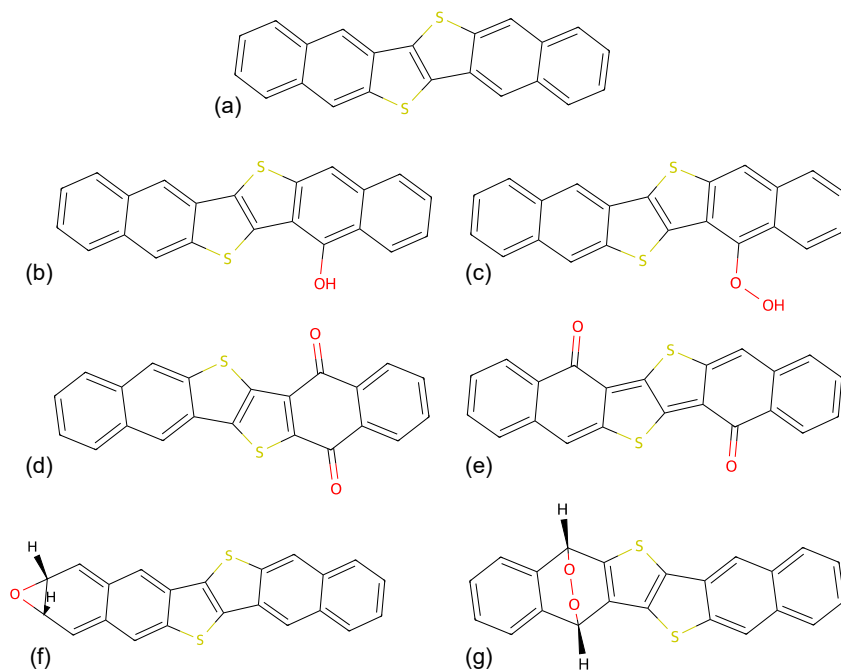


Figure S2: Representative chemical structures of the defect classes discussed in the main text: (a) pristine DNTT; (b) the peri hydroxyl (12-OH); (c) the peri hydroperoxide (12-OOH); (d) the 7,12-*para*-quinone; (e) the 5,12-diketone; (f) the 9,10-epoxide; and (g) the 7,12-endoperoxide. The identifiers match those used in Table 1 and Figure 5 of the main text and the data of Table S1.

S3 Additivity of bis-hydroxyl shifts

For the bis-hydroxyls the HOMO shift is, to a good approximation, the sum of the shifts of the two constituent mono-hydroxyls,

$$\Delta E_{\text{HOMO}}(\text{A}, \text{B}) \approx \Delta E_{\text{HOMO}}(\text{A}) + \Delta E_{\text{HOMO}}(\text{B}). \quad (\text{S3})$$

Table S2 compares this additive prediction with the computed value for the five non-catechol bis-hydroxyls (positions related by the molecular inversion symmetry, e.g. 4 and 11, are treated as equivalent); the agreement is within a few percent throughout. This near-additivity reflects the essentially independent, local nature of each hydroxyl perturbation and underlies the linear reactivity–depth relation of the main text. The single exception, the *ortho*-catechol, is discussed in Section S4.

S4 The *ortho*-catechol sub-additive outlier

The 8,9-(OH)₂ defect, in which the two hydroxyls occupy adjacent (*ortho*) positions, departs strongly from additivity: its computed shift of +0.037 eV lies far below the additive prediction of +0.121 eV, a reduction of about 69%. The origin is an intramolecular O–H···O hydrogen bond between the neighbouring hydroxyls, which ties up one oxygen lone pair and thereby suppresses its π -donation into the ring. The pair therefore acts as a much weaker donor than two independent hydroxyls, and the *ortho*-catechol emerges as the shallowest of the bis-hydroxyl hole traps.

Table S1: Complete map of the 39 computed oxygen- and hydroxyl-related defect identities of DNTT (GFN2-xTB). HOMO, LUMO and their shifts ΔHOMO , ΔLUMO relative to pristine DNTT, and the gap, are in eV; the dipole moment (dip) is in D. Open-shell radicals (conf = open) are singly occupied: for these the ΔHOMO column reports ΔSOMO , which is not directly comparable with the closed-shell values, and the LUMO and gap are not tabulated.

Defect	conf	HOMO	LUMO	ΔHOMO	ΔLUMO	gap	dip
Pristine DNTT	closed	-9.7598	-7.7751	0.000	0.000	1.985	0.00
<i>Class A — Hydroxyls</i>							
10-OH	closed	-9.7077	-7.7547	+0.052	+0.020	1.953	1.73
9-OH	closed	-9.7222	-7.7276	+0.038	+0.048	1.995	1.23
8-OH	closed	-9.6770	-7.7046	+0.083	+0.071	1.972	1.50
11-OH	closed	-9.6655	-7.6824	+0.094	+0.093	1.983	—
7-OH	closed	-9.6214	-7.6943	+0.138	+0.081	1.927	1.52
12-OH	closed	-9.5789	-7.6345	+0.181	+0.141	1.944	—
8,9-(OH) ₂ (catechol)	closed	-9.7225	-7.7943	+0.037	-0.019	1.928	2.27
9,12-(OH) ₂	closed	-9.5497	-7.5851	+0.210	+0.190	1.965	1.89
7,11-(OH) ₂	closed	-9.5304	-7.6031	+0.229	+0.172	1.927	3.05
4,12-(OH) ₂ (cross)	closed	-9.4907	-7.5463	+0.269	+0.229	1.944	0.45
11,12-(OH) ₂	closed	-9.4806	-7.5245	+0.279	+0.251	1.956	3.85
7,12-(OH) ₂	closed	-9.4388	-7.5840	+0.321	+0.191	1.855	3.40
5,12-(OH) ₂	closed	-9.4033	-7.5026	+0.357	+0.272	1.901	0.00
<i>Class B — Alkoxy/carbonyl radicals (open-shell, SOMO)</i>							
12=O [•]	open	-9.5052	—	+0.255	—	—	3.87
7=O [•]	open	-9.5550	—	+0.205	—	—	4.40
11=O [•]	open	-9.6460	—	+0.114	—	—	5.76
8=O [•]	open	-9.6898	—	+0.070	—	—	5.91
9=O [•]	open	-9.7644	—	-0.005	—	—	9.00
10=O [•]	open	-9.8168	—	-0.057	—	—	8.27
<i>Class C — Peroxyl radicals (open-shell)</i>							
12-O-O [•]	open	-9.7077	-7.9261	+0.052	-0.151	1.782	4.91
7-O-O [•]	open	-9.7417	-8.1111	+0.018	-0.336	1.630	6.56
11-O-O [•]	open	-9.7473	-8.0805	+0.013	-0.305	1.667	6.20
8-O-O [•]	open	-9.8978	-8.2023	-0.138	-0.427	1.695	8.11
9-O-O [•]	open	-9.8966	-8.2522	-0.137	-0.477	1.644	10.17
10-O-O [•]	open	-9.9511	-8.2369	-0.191	-0.462	1.714	8.82
<i>Class D — Hydroperoxides</i>							
12-O-OH	closed	-9.6722	-7.7583	+0.088	+0.017	1.914	1.01
7-O-OH	closed	-9.7806	-7.8339	-0.021	-0.059	1.947	1.12
11-O-OH	closed	-9.7311	-7.7738	+0.029	+0.001	1.957	0.95
8-O-OH	closed	-9.8321	-7.8546	-0.072	-0.079	1.977	2.35
9-O-OH	closed	-9.8491	-7.9211	-0.089	-0.146	1.928	3.35
10-O-OH	closed	-9.9043	-7.9440	-0.144	-0.169	1.960	3.45
<i>Class E — Quinones and diketone</i>							
5,12-diketone (<i>trans</i>)	closed	-10.1980	-9.3300	-0.438	-1.555	0.867	0.00
7,12-quinone (<i>para</i>)	closed	-10.2660	-9.0640	-0.506	-1.289	1.202	1.67
8,11-quinone (<i>para</i>)	closed	-10.2870	-9.2300	-0.527	-1.455	1.057	4.49
8,9-quinone (<i>ortho</i>)	closed	-10.3600	-9.1990	-0.600	-1.424	1.161	9.09
<i>Class F — Cyclic (endoperoxides, epoxides)</i>							
7,12-endoperoxide	closed	-10.0790	-7.7432	-0.319	+0.032	2.336	3.68
8,11-endoperoxide	closed	-10.0135	-7.8065	-0.254	-0.031	2.207	3.72
11a,12-epoxide	closed	-9.8727	-8.0493	-0.113	-0.274	1.823	2.23
9,10-epoxide	closed	-9.6903	-8.2030	+0.069	-0.428	1.487	2.24

Table S2: Additivity of the bis-hydroxyl HOMO shifts (eV): the additive prediction from the two constituent mono-hydroxyls, the computed value, and the relative deviation.

Bis-hydroxyl	Constituents	Additive	Computed	Dev.
9,12-(OH) ₂	9-OH + 12-OH	+0.219	+0.210	−4.1%
7,11-(OH) ₂	7-OH + 11-OH	+0.232	+0.229	−1.3%
4,12-(OH) ₂	4-OH + 12-OH	+0.275	+0.269	−2.2%
11,12-(OH) ₂	11-OH + 12-OH	+0.275	+0.279	+1.5%
7,12-(OH) ₂	7-OH + 12-OH	+0.319	+0.321	+0.6%

S5 Thienothiophene-bridge delocalisation

The two naphthalene wings of DNTT are not electronically isolated: the frontier orbital delocalises across the central thienothiophene bridge. This is shown by comparing two bis-hydroxyls with the *same* additive prediction: 11,12-(OH)₂, with both hydroxyls on the same wing, and 4,12-(OH)₂, with one hydroxyl on each wing (positions 4 and 11 being related by the molecular inversion symmetry). Their computed shifts, +0.279 and +0.269 eV, differ by only about 10 meV, so that the cross-wing defect retains roughly 96% of the same-wing shift. In other words, the thienothiophene bridge transmits the HOMO delocalisation between the wings almost without loss, so that a hydroxyl on one wing is felt, electronically, on the other.

S6 α -Oxygen Mulliken charges

The progressive loss of π -donor strength across the three single-oxygen species at a given site, invoked in Section 3.3 of the main text, is quantified by the Mulliken charge on the oxygen bonded to the ring. Table S3 lists the α -oxygen charge $q(\alpha\text{O})$ for the peroxy and hydroperoxide families at the six ring positions. For the closed-shell hydroxyls the single oxygen carries $q(\text{O}) \approx -0.38$ (nearly position-independent; the computed mono-hydroxyls range from -0.381 to -0.390), placing them at the strong-donor end of the sequence hydroxyl (≈ -0.38) $\rightarrow$ hydroperoxide (≈ -0.17) $\rightarrow$ peroxy (≈ -0.04).

Table S3: α -oxygen Mulliken charge $q(\alpha\text{O})$ (in e) of the peroxy and hydroperoxide defects at the six ring positions of DNTT.

Position	Hydroperoxide $q(\alpha\text{O})$	Peroxy $q(\alpha\text{O})$
12 (peri)	−0.167	−0.041
7	−0.184	−0.036
11	−0.182	−0.035
8	−0.148	−0.036
9	−0.152	−0.036
10	−0.149	−0.034