Supplementary Information

Probing Disorder in 2CzPN using Core and Valence States

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I. PEAK FIT ANALYSIS

Peak fit analysis of the experimental spectra was conducted using the Thermo Scientific Avantage software package. A Shirley type background and Voigt line shapes were used for all peak fits. The main chemical state peaks in each of the C and N 1s core level spectra were constrained to the same Voigt line shape, including full width at half maximum (FWHM) and Lorentzian contribution. The shake-up features at high binding energy were fitted for completeness and their line shapes were allowed to vary independently of the main photoionisation peaks. For the quantification of chemical state ratios the areas of the individual chemical state features were used and when needed the in-built atomic sensitivity factors of the Avantage software package were used.

II. ATOMIC STRUCTURE

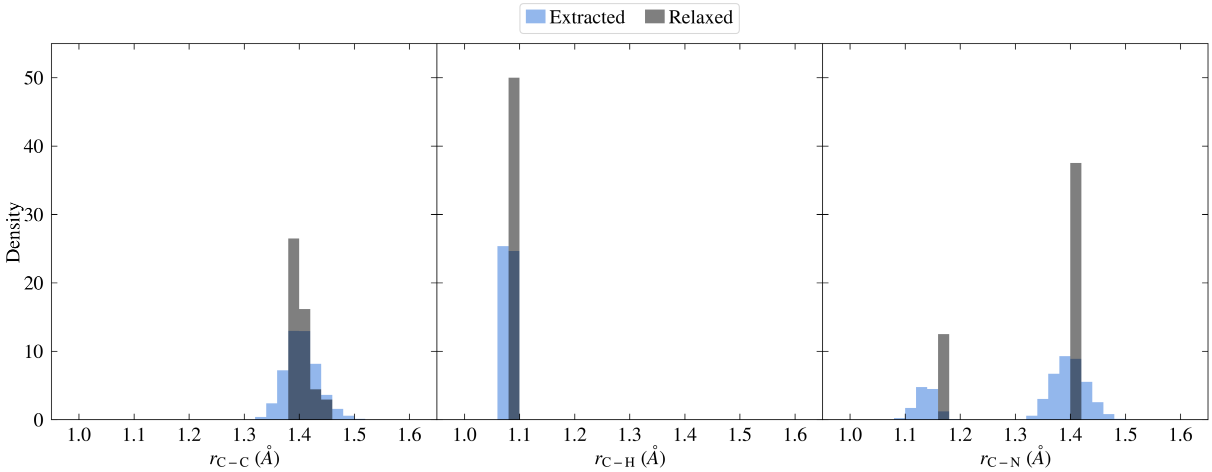

Figure S1: Distribution of bond lengths in the unmodified extracted molecules, compared to the relaxed molecule.

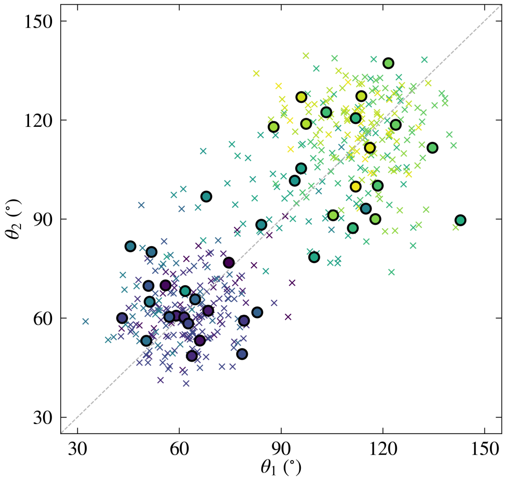

Figure S2: Depiction of the torsion angles for each molecule, when grouped by similar molecules (‘x’), where the colours correspond to the particular cluster, as depicted in the main paper. Also shown are the select representative molecules from each cluster (‘o’).

III. VALENCE STATES

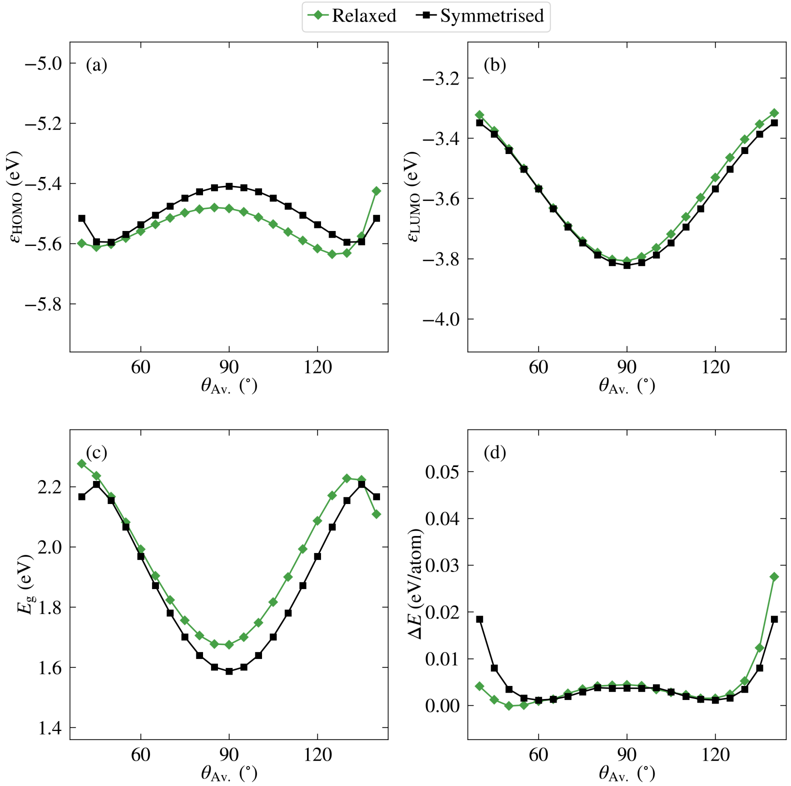

Figure S3: Comparison between various quantities calculated for rotated molecules generated by rotating the relaxed molecule without imposing any constraints (‘Relaxed’), and by rotating a molecule which has been relaxed with imposed symmetry ‘Symmetrised’.

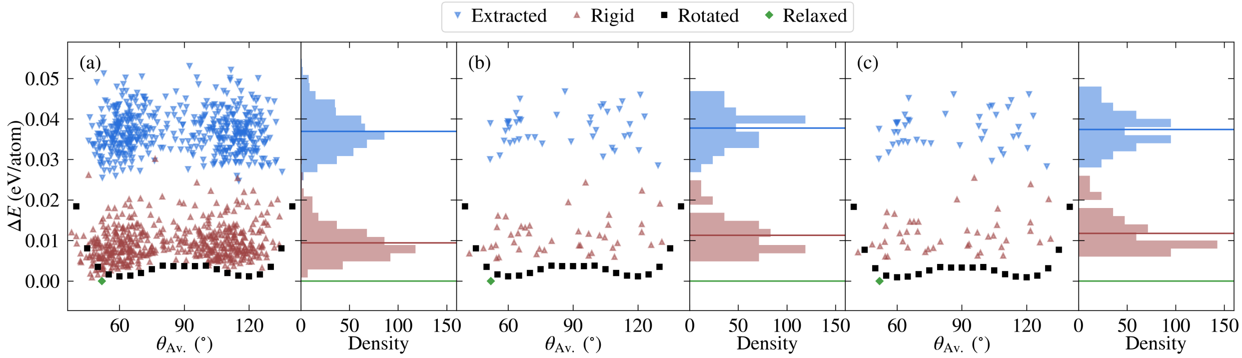

Figure S4: Variation in total energy relative to the relaxed structure, ΔE, with the average torsion angle, $\theta_{\mathrm{Av.}}$, as well as the probability density for (a) PBE calculations of all the molecules considered, and for (b) PBE and (c) PBE0 for select representative molecules. Horizontal lines denote average values, except in the case of the rotated molecules, where they correspond to the relaxed molecule. The data include the unmodified extracted, the rigidified molecules, and the explicitly rotated molecules.

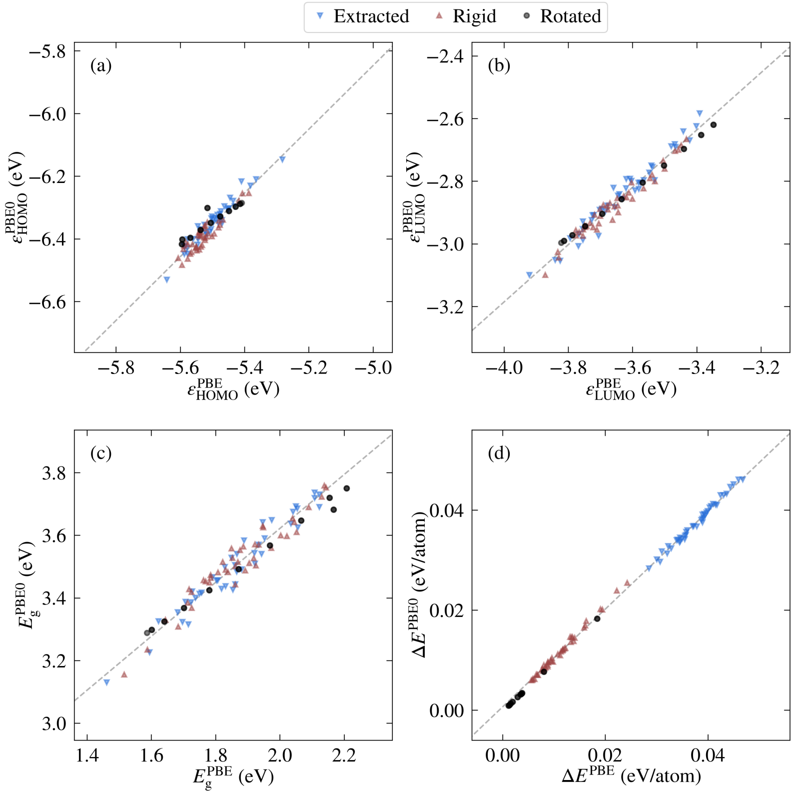

Figure S5: Comparison between PBE and PBE0-calculated values for (a) the highest occupied molecular orbital energy, $\varepsilon_{\mathrm{HOMO}}$, (b) the lowest unoccupied molecular orbital energy, $\varepsilon_{\mathrm{LUMO}}$, (c) the band gap, E_{g}, and (d) total energies relative to the relaxed molecule, ΔE. The data include the unmodified extracted, the rigidified molecules, and the explicitly rotated molecules.

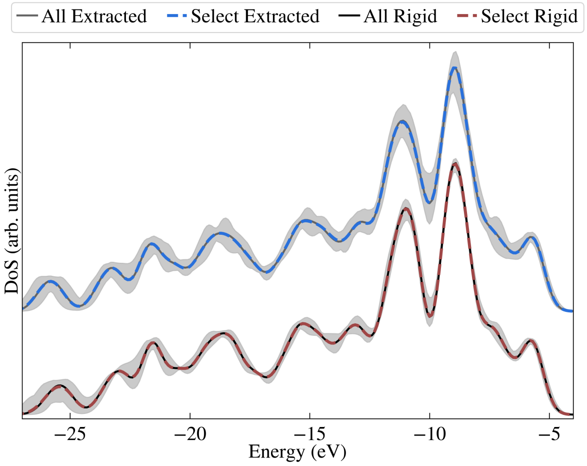

Figure S6: Total density of states calculated as an average over all the unmodified extracted (rigidified) molecules, as well as an average over select representative unmodified extracted (rigidified) molecules. The light grey area indicates the variation in calculated densities of states across all unmodified extracted (rigidified) molecules. Calculations employed PBE.

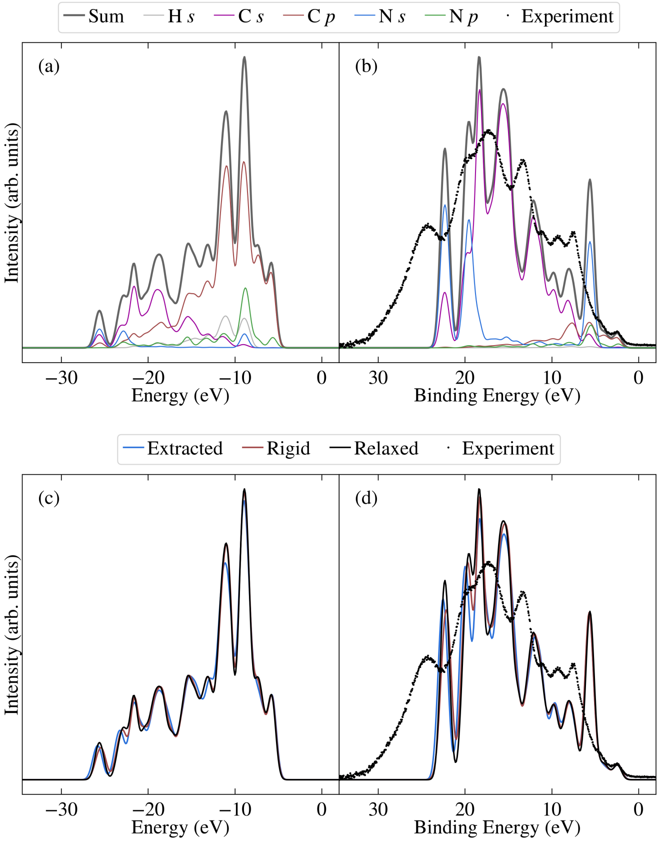

Figure S7: PBE-calculated occupied projected density of states for the relaxed molecule, both (a) unweighted and (b) cross-section weighted. Also shown are the sum over contributions for the relaxed molecule, the average over select unmodified extracted molecules, and the average over rigidified molecules, for both (c) unweighted and (d) cross-section weighted. The weighted spectra have been aligned to experiment.

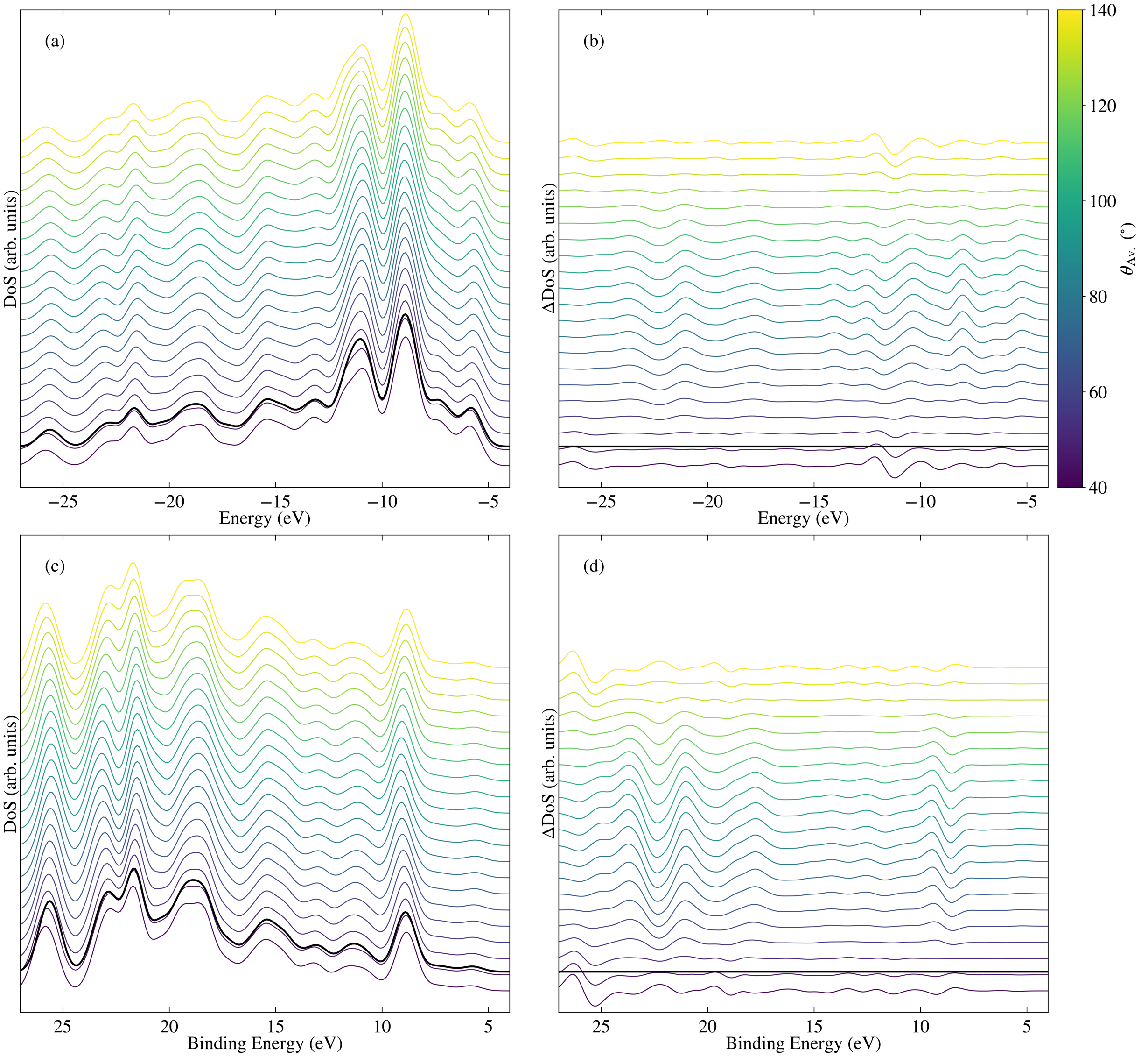

Figure S8: Variation in the PBE-calculated total density of states with average torsion angle, for the explicitly rotated molecules, where the relaxed molecule is highlighted with thick black lines. Plots are shown for both (a) the unweighted and (c) the weighted density of states. Also shown is the difference in density of states with respect to the relaxed molecule for (c) the unweighted and (d) the weighted density of states.

IV. CORE STATES

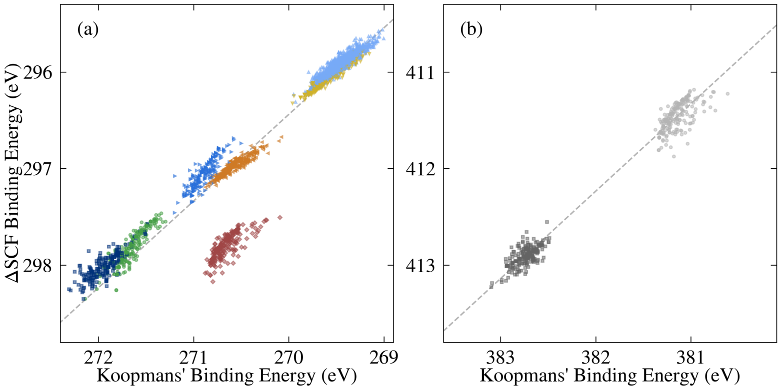

Figure S9: Comparison between binding energies calculated using Koopmans' and ΔSCF for (a) C 1*s* and (b) N 1*s*, where the colours refer to the different atomic sites (see main paper).

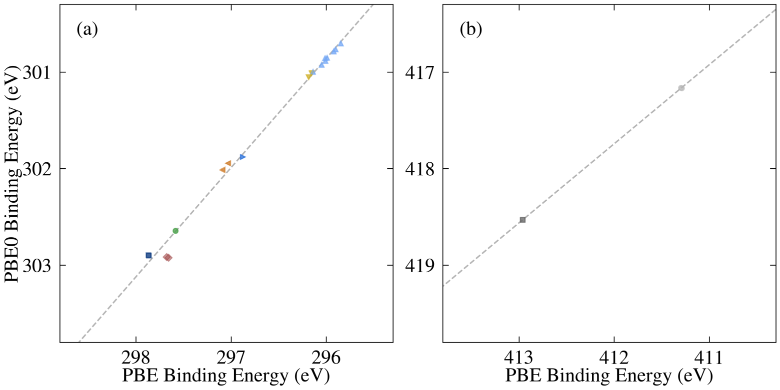

Figure S10: Comparison between PBE and PBE0 ΔSCF-calculated core binding energies of the relaxed molecule for (a) C 1*s* and (b) N 1*s*, where the colours refer to the different atomic sites (see main paper).

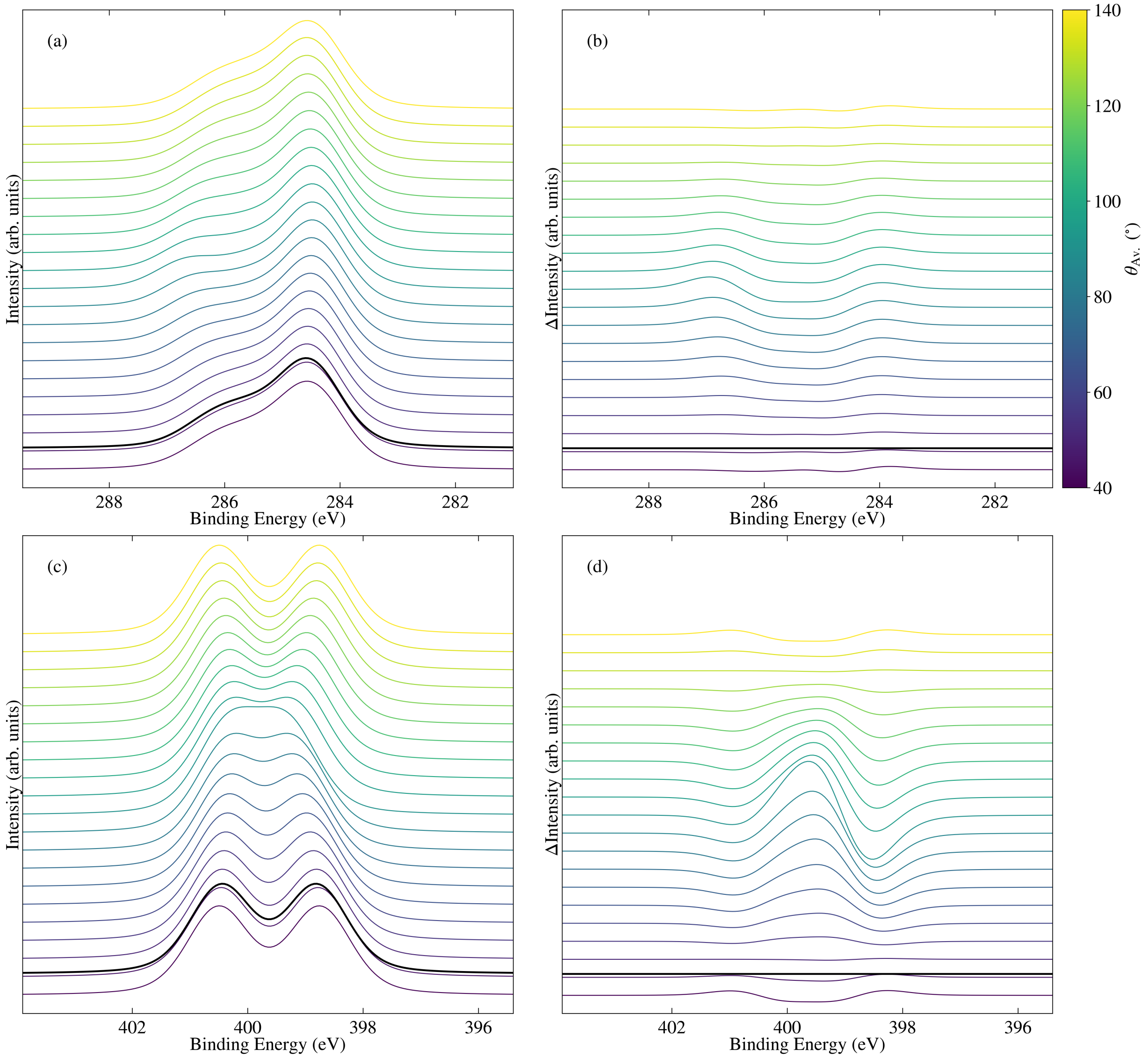

Figure S11: Variation in the calculated core spectra with average torsion angle, for the explicitly rotated molecules for (a) C 1s and (c) N 1s, where the relaxed molecule is highlighted with thick black lines. Also shown is the difference in density of states with respect to the relaxed molecule for (b) C 1s and (d) N 1s. The spectra have been shifted following the alignment described in the main paper.

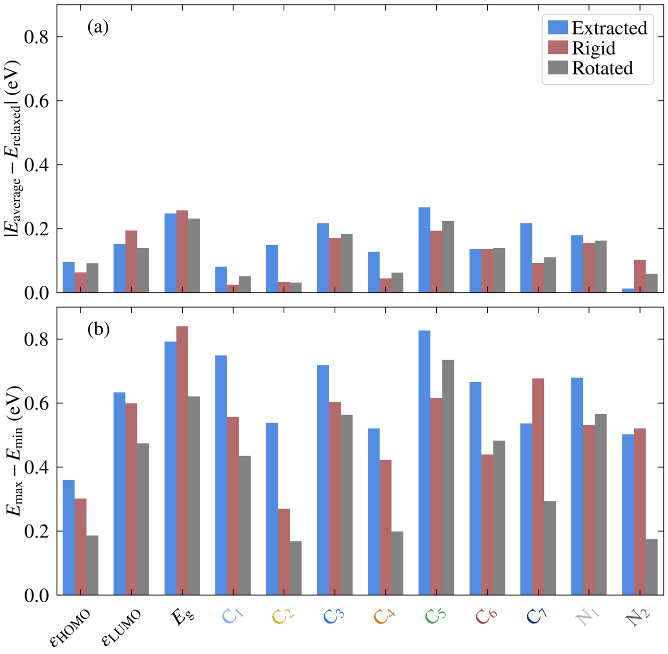

Figure S12: Variation in frontier orbital energies and core binding energies for the unmodified extracted, the rigidified and the explicitly rotated molecules. Shown is (a) the difference between the average values and the corresponding value for the relaxed molecule and (b) the difference between the maximum and minimum values for each set of molecules.

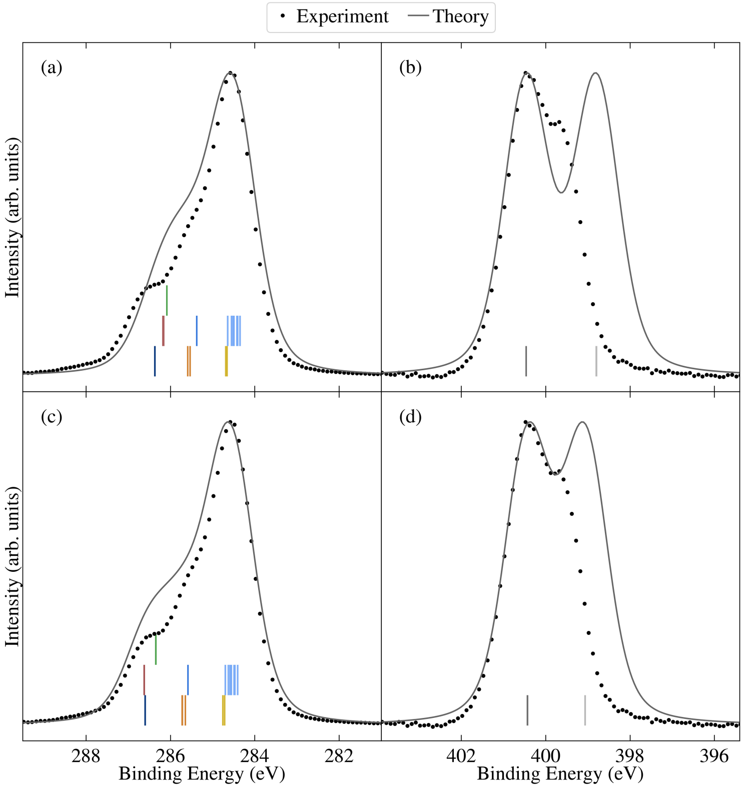

Figure S13: Core spectra for the relaxed molecule calculated using PBE for (a) C 1*s* and (b) N 1*s*, as well as with PBE0 for (c) C 1*s* and (d) N 1*s* where the colours refer to the different atomic sites (see main paper).

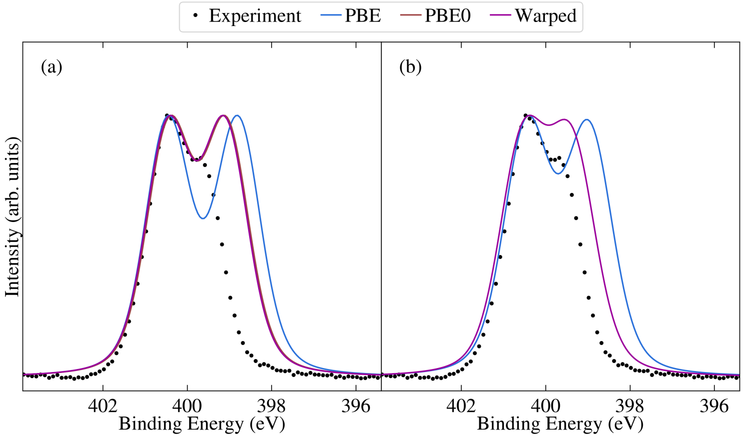

Figure S14: Core N 1*s* spectra calculated using PBE, PBE0, and applying a simple spectral warping for (a) the relaxed molecule, and (b) the average over unmodified extracted molecules.

Table S1: Summary of calculated values for the frontier orbitals and core binding energies. Average, minimum and maximum values are given across the datasets; in the case where only one value exists (e.g. frontier orbitals for the relaxed molecule), minimum and maximum values are omitted. Values are across all data, i.e. for frontier orbitals with PBE this includes all 500 extracted/rigid molecules, while for PBE0 frontier orbitals and PBE core binding energies, values are across the 42 selected molecules only.

	Relaxed				Rotated				Rigid				Extracted			
	Av.	Min.	Max.	Range	Av.	Min.	Max.	Range	Av.	Min.	Max.	Range	Av.	Min.	Max.	Range
PBE																
$\varepsilon_{\mathrm{HOMO}}$	-5.60	-	-	-	-5.50	-5.60	-5.41	0.19	-5.53	-5.65	-5.35	0.30	-5.53	-5.64	-5.28	0.36
$\varepsilon_{\mathrm{LUMO}}$	-3.46	-	-	-	-3.60	-3.82	-3.35	0.47	-3.66	-3.96	-3.36	0.60	-3.66	-3.97	-3.34	0.63
E_{g}	2.13	-	-	-	1.90	1.59	2.21	0.62	1.87	1.39	2.23	0.84	1.87	1.45	2.24	0.79
C_1	296.0	295.8	296.1	0.3	295.9	295.7	296.2	0.4	296.0	295.7	296.2	0.6	295.9	295.6	296.3	0.7
C_2	296.2	296.2	296.2	0.0	296.1	296.1	296.3	0.2	296.1	296.0	296.3	0.3	296.0	295.8	296.3	0.5
C_3	296.9	296.9	296.9	0.0	297.1	296.8	297.4	0.6	297.0	296.7	297.3	0.6	297.1	296.7	297.5	0.7
C_4	297.1	297.0	297.1	0.1	297.0	296.9	297.1	0.2	297.0	296.8	297.2	0.4	296.9	296.7	297.2	0.5
C_5	297.6	297.6	297.6	0.0	297.8	297.5	298.3	0.7	297.8	297.5	298.1	0.6	297.9	297.5	298.3	0.8
C_6	297.7	297.7	297.7	0.0	297.8	297.6	298.1	0.5	297.8	297.6	298.0	0.4	297.8	297.5	298.2	0.7
C_7	297.9	297.9	297.9	0.0	298.0	297.9	298.2	0.3	298.0	297.6	298.2	0.7	298.1	297.8	298.4	0.5
N_1	411.3	411.3	411.3	0.0	411.5	411.2	411.8	0.6	411.4	411.2	411.7	0.5	411.5	411.2	411.9	0.7
N_2	413.0	413.0	413.0	0.0	412.9	412.8	413.0	0.2	412.9	412.6	413.1	0.5	412.9	412.7	413.2	0.5
PBE0																
$\varepsilon_{\mathrm{HOMO}}$	-6.43	-	-	-	-6.34	-6.42	-6.29	0.13	-6.39	-6.48	-6.25	0.23	-6.39	-6.53	-6.15	0.38
$\varepsilon_{\mathrm{LUMO}}$	-2.71	-	-	-	-2.83	-3.00	-2.62	0.38	-2.88	-3.10	-2.67	0.43	-2.88	-3.10	-2.58	0.52
E_{g}	3.72	-	-	-	3.52	3.29	3.75	0.46	3.51	3.16	3.76	0.60	3.51	3.13	3.74	0.61
C_1	300.8	300.7	301.0	0.3	-	-	-	-	-	-	-	-	-	-	-	-
C_2	301.0	301.0	301.1	0.0	-	-	-	-	-	-	-	-	-	-	-	-
C_3	301.9	301.9	301.9	0.0	-	-	-	-	-	-	-	-	-	-	-	-
C_4	302.0	301.9	302.0	0.1	-	-	-	-	-	-	-	-	-	-	-	-
C_5	302.6	302.6	302.6	0.0	-	-	-	-	-	-	-	-	-	-	-	-
C_6	302.9	302.9	302.9	0.0	-	-	-	-	-	-	-	-	-	-	-	-
C_7	302.9	302.9	302.9	0.0	-	-	-	-	-	-	-	-	-	-	-	-
N_1	417.2	417.2	417.2	0.0	-	-	-	-	-	-	-	-	-	-	-	-
N_2	418.5	418.5	418.5	0.0	-	-	-	-	-	-	-	-	-	-	-	-

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