Establishing Template-induced Polymorphic Domains for API Crystallisation: The case of Carbamazepine

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X-ray Photoelectron Spectroscopy (XPS): XPS spectra were obtained on all functionalised glass cover slips using a ThermoFisher Scientific Instruments & Theta Probe X-ray Photoelectron Spectrometer (ThermoFisher Scientific Instruments & Theta Probe, East Grinstead, U.K.). After removal of the non-linear (Shirley) background, high resolution core level spectra were used for the quantification of the elemental composition on the surface. Gaussian – Lorentzian product function was used for peak fitting. The high resolution data was fitted using the *Avantage* software (ThermoFisher Scientific Instruments & Theta Probe, East Grinstead, U. K.). The software incorporates sensitivity factors and corrects for the electron energy analyser transmission function. Relevant spectra from the XPS analysis are provided in figure S1.

Ellipsometry: Ellipsometry was used to determine the thickness of the silane layer coating that was formed via silanisation. Ellipsometry was conducted on the [100] facet of a Si wafer which was subjected to silanisation following the same method that was used for glass templates. Ellipsometric data was fitted using combined Cauchy layer model with a refractive index of 1.45 for the silane and SiO_2 layers on Si wafer surface and the thickness of silane layer was calculated by subtracting the SiO_2 layer thickness from the total Cauchy layer thickness. The thickness for the silane layer was found to be 1.37 ± 0.03 nm, which corresponds to 2–3 layers of silane molecules.

Contact angle analysis: A Krüss Drop Shape Analyser DSA 10 (Krüss GmbH, Hamburg, Germany) was used for the dynamic sessile drop contact angle measurement. Advancing contact angle of three probe liquids (water, formamide, and diiodomethane) were measured at ambient conditions. The shape of the droplet was fitted using the tangent method to obtain the contact angle using the Drop Shape Analysis software (DSA version 1.0) (Krüss GmbH, Hamburg, Germany). A minimum of 5 droplets on 3 different samples of the same surface chemistry were measured. The contact angle of the three probe liquids on the template surfaces are provided in Table S1.

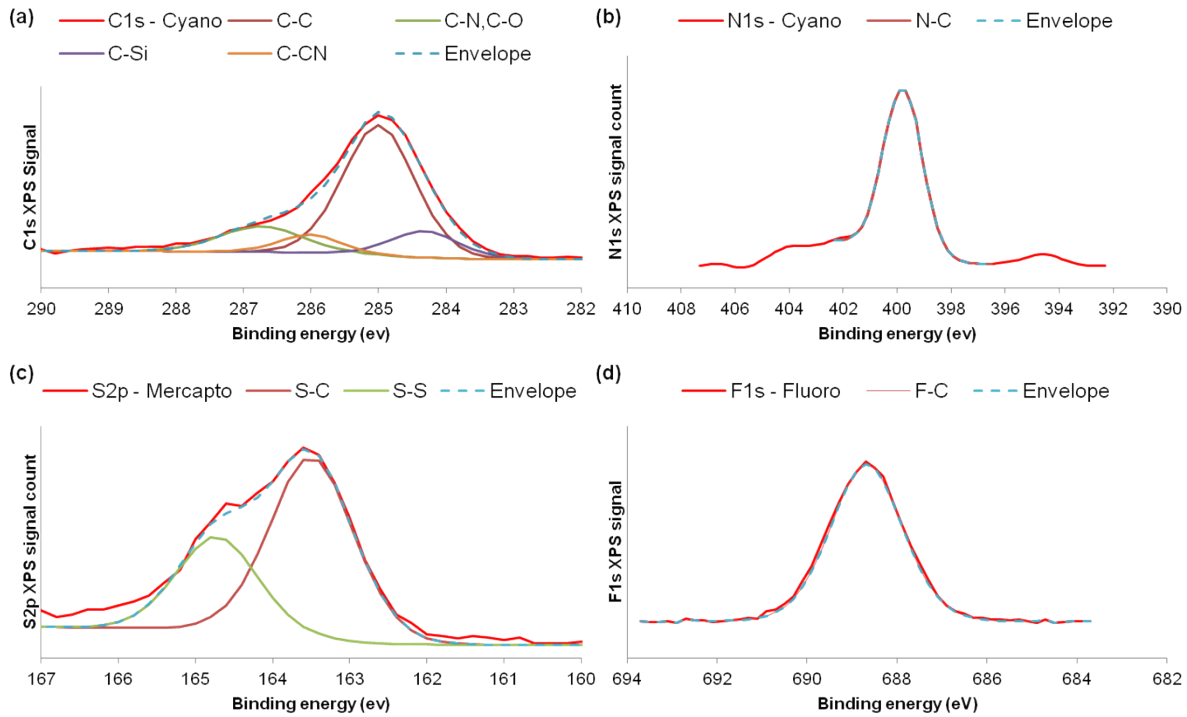

Figure S1: XPS spectra of selected surfaces. (a) & (b) C1s and N1s spectra for cyano template, (c) S2p spectra for mercapto template and (d) F1-s spectra fluoro template.

Surface energy of the template surface was calculated using the Acid–Base method proposed by van Oss, Chaudhury and Good (vOCG). The calculated values of surface energy are provided in Table S2. From the surface energy calculations, it can be observed that the cyano surface has similar dispersive surface energy component to that of mercapto surface, but differ significantly in the polar component. The polar surface free energy component of cyano surface arises from the basic surface component. Between mercapto and fluoro surfaces, the dispersive components of surface energy are significantly different; however, the values of polar components of surface energy are relatively similar.

Table S1: Contact angle (°) of probe liquids on template surfaces.

	Cyano	**Mercapto**	**Fluoro**
Water	55.2 ± 1.7	74.9 ± 2.7	96.4 ± 3.2
Diiodomethane	35.3 ± 3.4	36.4 ± 2.2	74.3 ± 2.4
Formamide	38.8 ± 2.1	58.1 ± 1.3	83.0 ± 1.8

Table S2: Surface energy of template surface computed from contact angle measurements.

Functional head group	**vOCG approach**			
	γ^{LW} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-} (mJ/m^2)	γ^{Tot} (mJ/m^2)
Cyano (-CN)	41.9	0.7	9.3	47.0
Mercapto (-SH)	41.4	0.0	3.7	41.4
Fluoro (-CF_3)	20.5	0.4	1.0	21.8
vOCG approach: superscripts LW, +, -,Tot stands for Lifshitz–van der Waals, acid, base,total surface energy of the solid.				