Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Activation and deformation of immobilized lipase on self-assembled monolayers with tailored wettability

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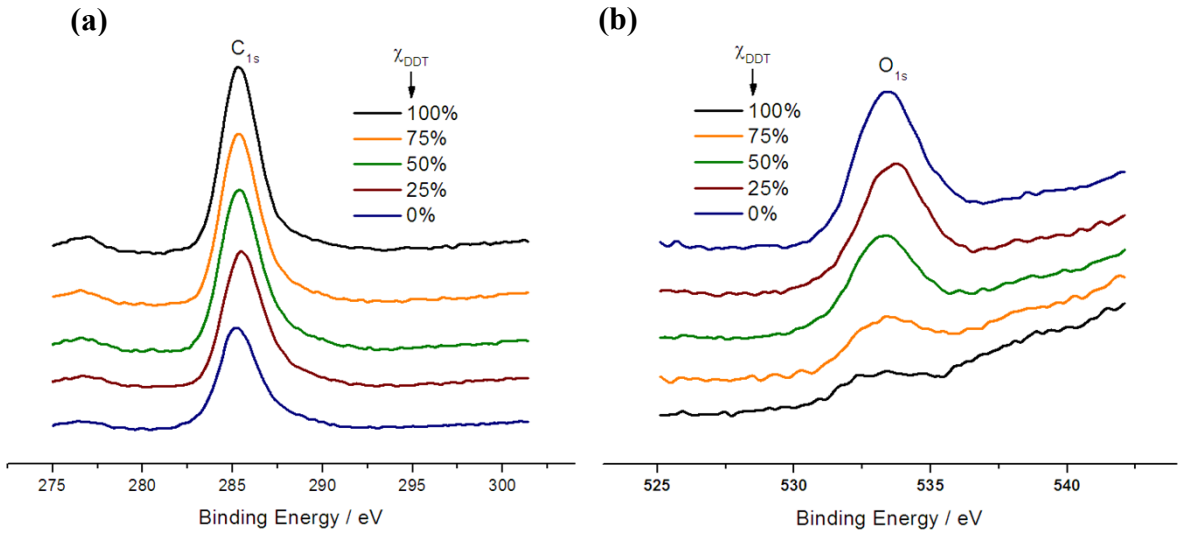


Figure S1. XPS C_{1s} (a) and O_{1s} (b) spectra of the mixed monolayers on the gold surfaces as a function of χ_{DDT} in the THF solution.

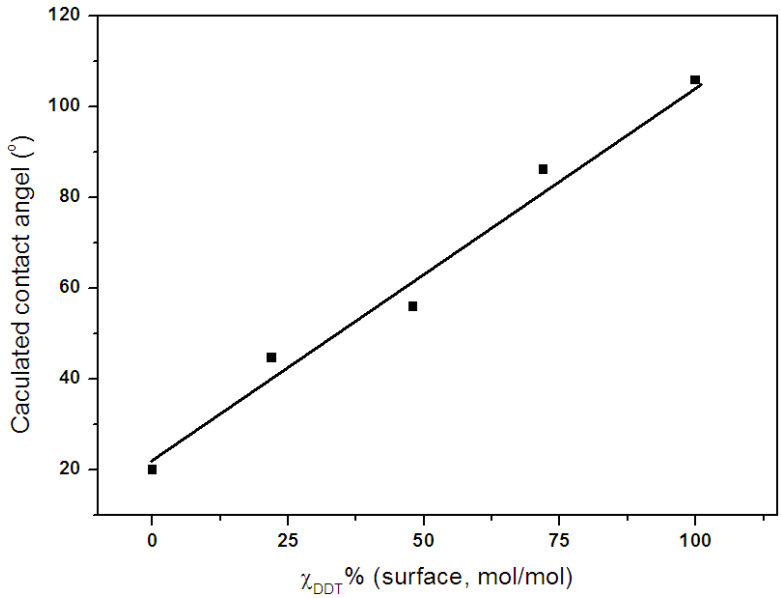


Figure S2. Calculated water contact angle results of different SAMs samples as a function of χ_{DDT} on the surface.

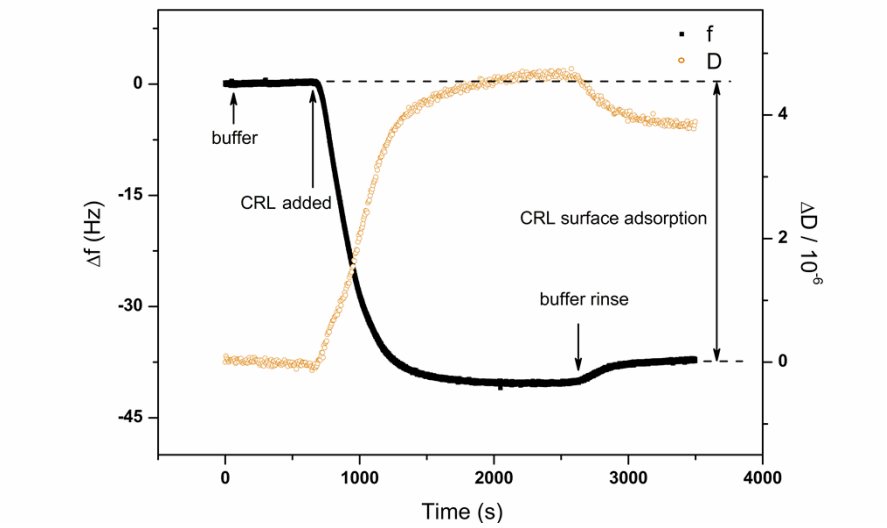


Figure S3. Typical CRL adsorption isomers in the QCM-D measurements.

Δf depended on the CRL concentration, from which we calculated the rate constant of enzyme binding (k_{on}) and dissociation (k_{off}) on SAMs with varied wettabilities by equation (S1)–(S3):

$$CRL + SAM \underset{k_{off}}{\overset{k_{on}}{\longleftrightarrow}} CRL/SAM \tag{S1}$$

$$[CRL/SAM]_t = [CRL/SAM]_\infty \{1 - \exp(-t/\tau)\} \tag{S2}$$

$$\tau^{-1} = k_{on}[CRL] + k_{off} \tag{S3}$$

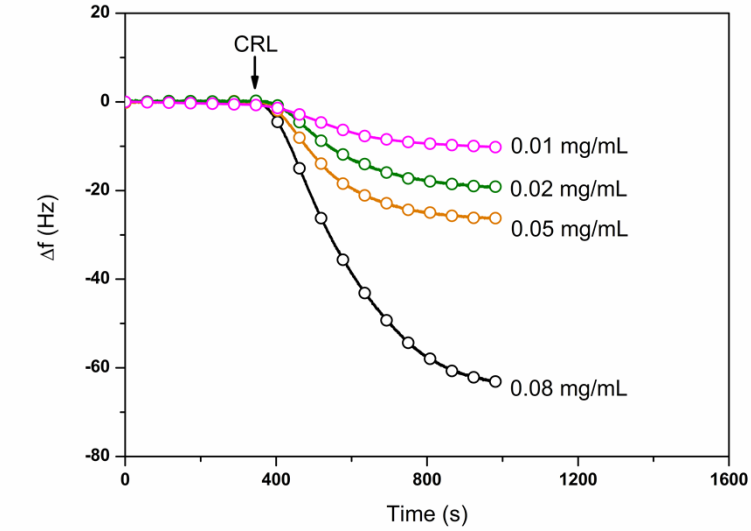


Figure S4. Influence of enzyme concentration on the adsorption of CRL onto SAMs.

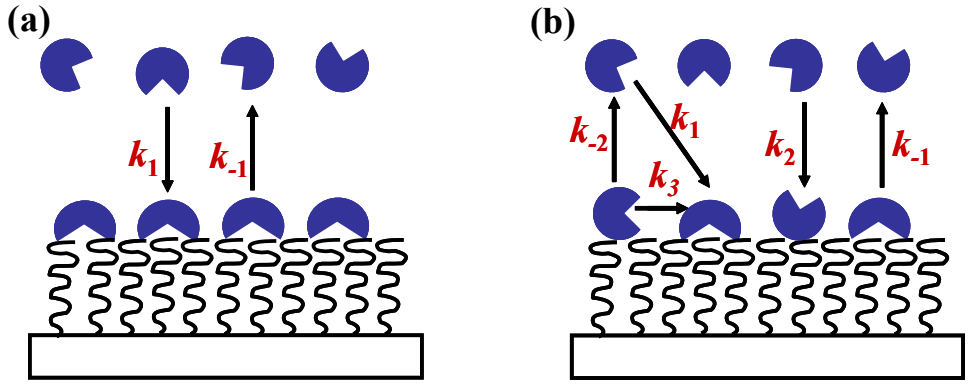


Figure S5. Schematic representation of possible interactions between lipase in solution with the support surface. (a): pseudo-first order model; (b): biphasic model.

In the monophasic pseudo-first order model, protein in the solution (P) reversibly interacts with the surface (S) to form a surface-bound complex and the binding sites are assumed to possess homogenous affinities. The corresponding mechanism and kinetic rate equation are described as:

$$\mathrm{P} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \mathrm{PS} \tag{S4}$$

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1 \cdot (q_1 - q_t) - k_{-1} \cdot q_t \tag{S5}$$

Where q_1 is the amount of protein adsorbed at equilibrium, ng·cm^{-2}; k_1 and k_{-1} are the forward and backward rate constants, respectively, min^{-1}.

In the biphasic model, the protein contacts a surface, resulting in two configurations: a stable and tight surface-bound complex (PS_1), and a loose one (PS_2). This model also considers the reversibility of PS_2 to PS_1 with the possible reorientation of protein molecules. The mechanism and kinetic rate equations are described as:

$$P + S \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} PS_1 \quad \text{(S6)}$$

$$P + S \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} PS_2 \quad \text{(S7)}$$

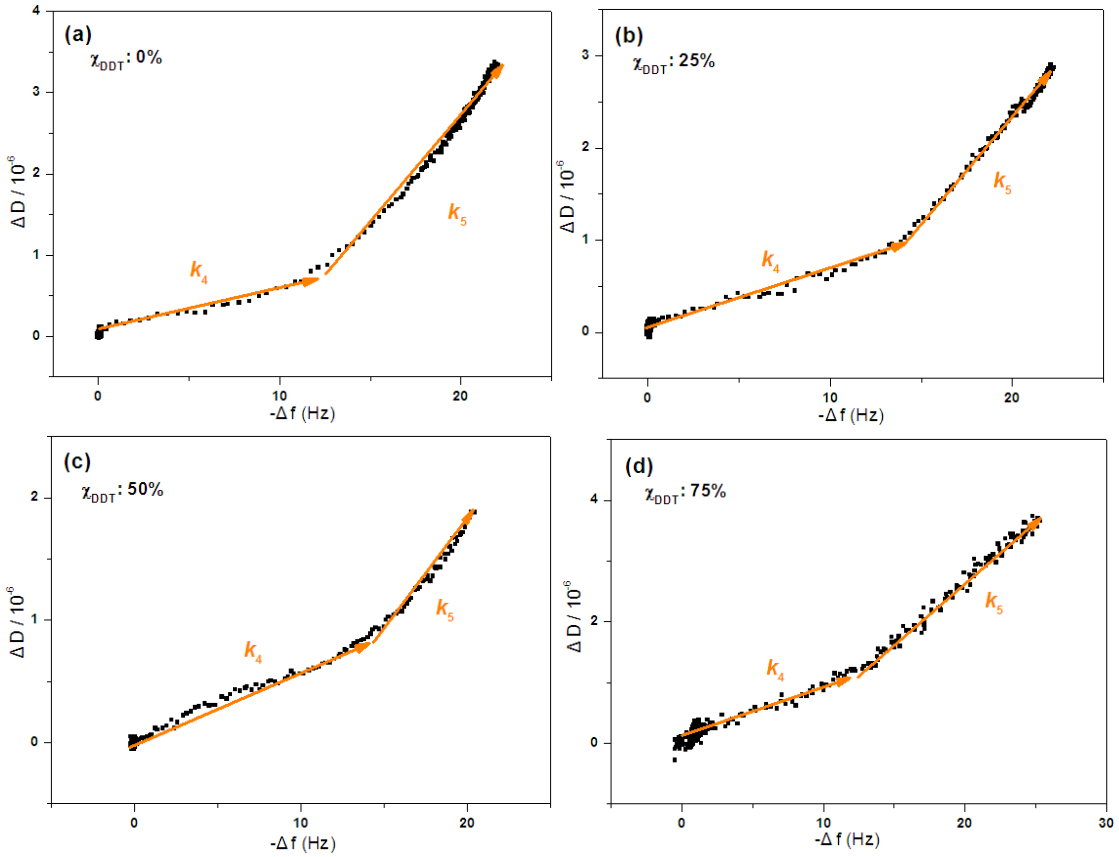
$$PS_2 \xrightarrow{k_3} PS_1 \quad \text{(S8)}$$

$$\frac{dq_{t1}}{dt} = k_1 \cdot (q_1 - q_{t1} - q_{t2}) - k_{-1} \cdot q_{t1} + k_3 \cdot q_{t2} \quad \text{(S9)}$$

$$\frac{dq_{t2}}{dt} = k_2 \cdot (q_1 - q_{t1} - q_{t2}) - k_{-2} \cdot q_{t2} - k_3 \cdot q_{t2} \quad \text{(S10)}$$

$$q_t = q_{t1} + q_{t2} \quad \text{(S11)}$$

Where q_{t1} and q_{t2} are the amounts of tightly adsorbed and loosely adsorbed protein at time t, respectively, ng·cm^{-2}; k_1 and k_{-1} are the forward and backward rate constants for tightly bound protein, respectively, min^{-1}; k_2 and k_{-2} are the forward and backward rate constants for loosely bound protein, respectively, min^{-1}.



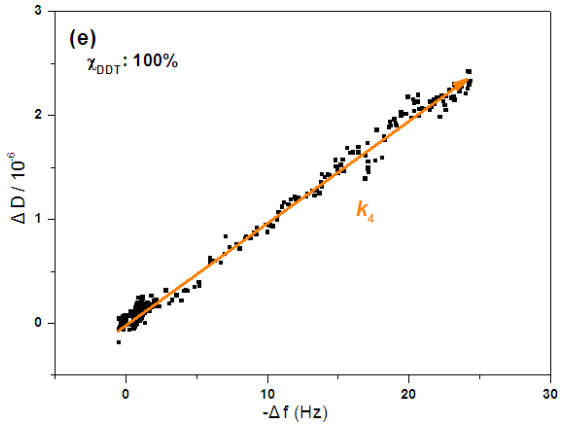
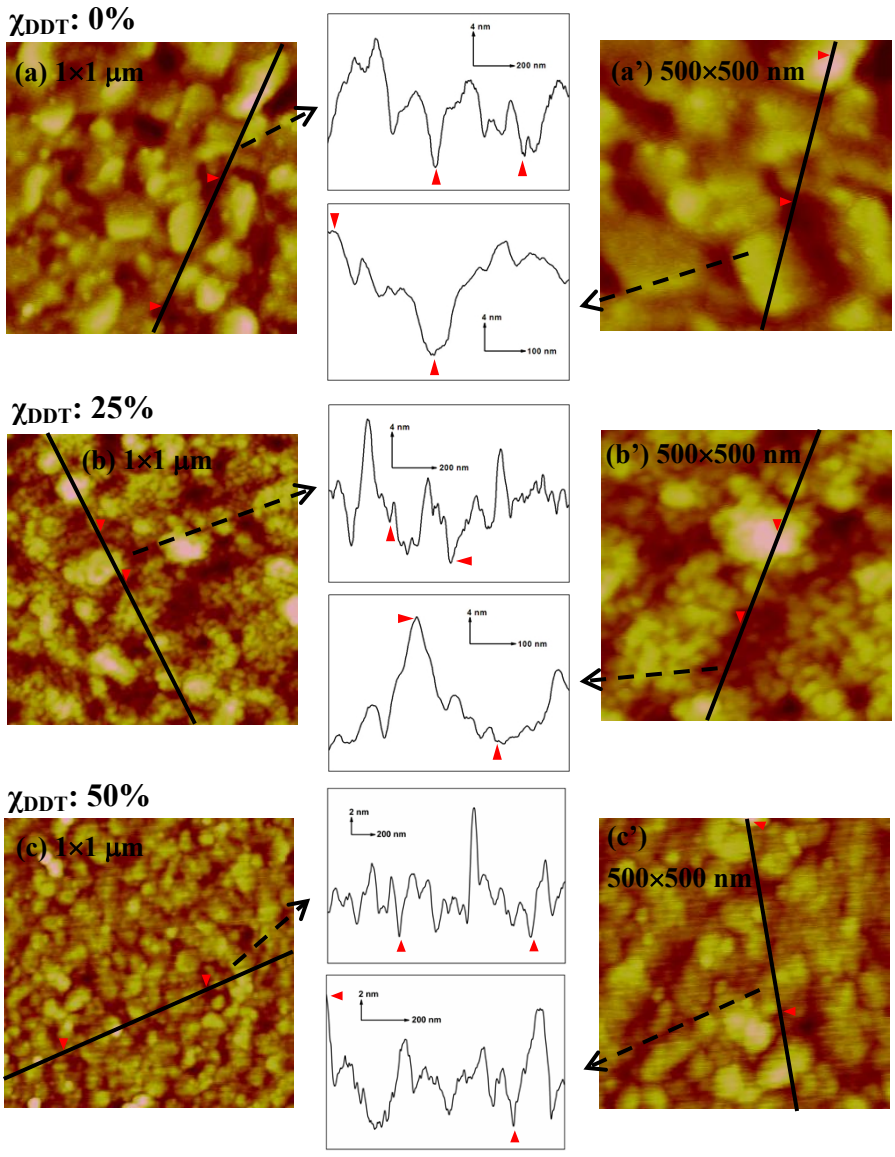


Figure S6. ΔD — $-\Delta f$ plots for the CRL adsorption with different χ_{DDT} on the surface.

The solid lines with arrows are provided to guide the eye.



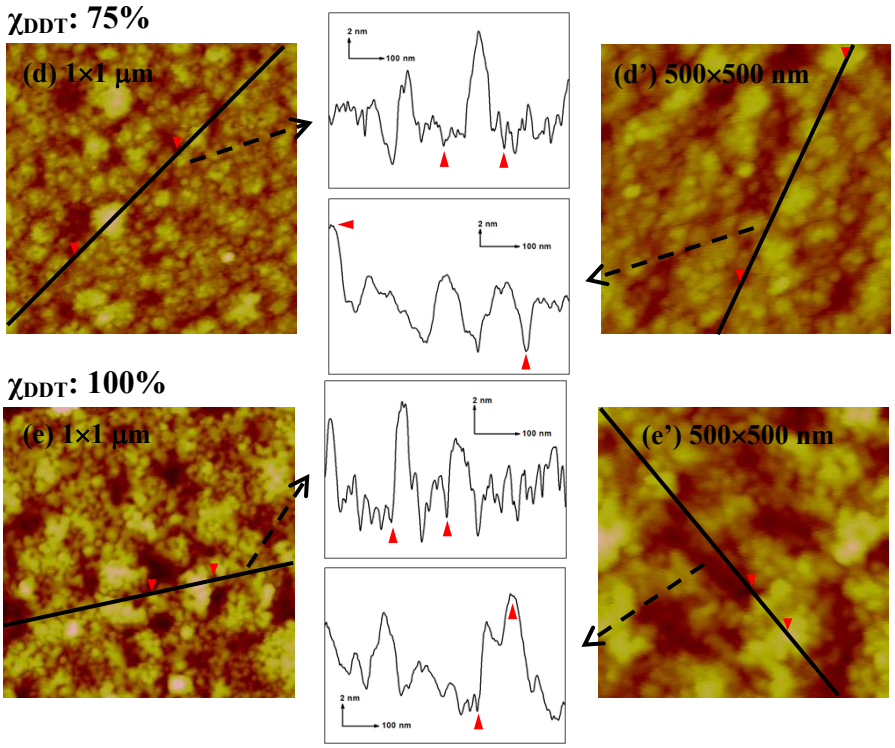


Figure S7. Tapping-mode AFM images and cross-sectional surface profiles of QCM-D chips modified with different χ_{DDT} after CRL adsorption. The red triangles correspond to those in the cross-sectional profiles.

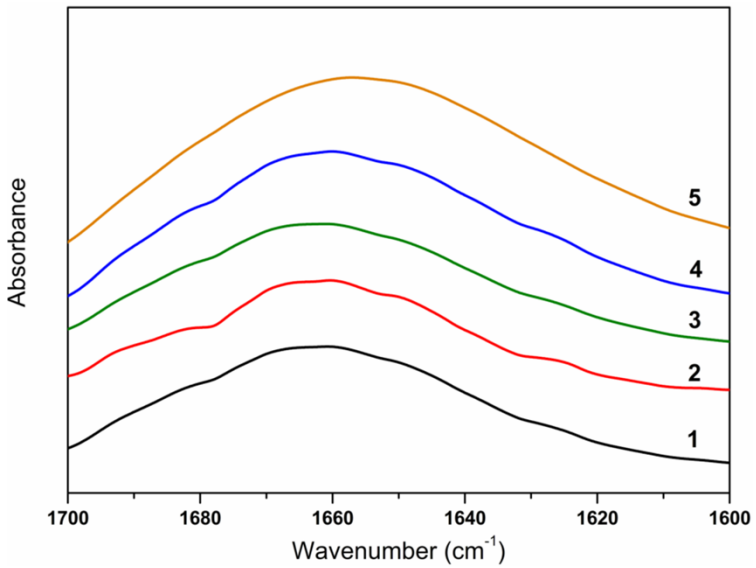


Figure S8. Superimposed ATR/FTIR spectra (absorbance scale arbitrary) of CRL immobilized on surfaces with varied χ_{DDT} (1~5: χ_{DDT} from 0% to 100%).

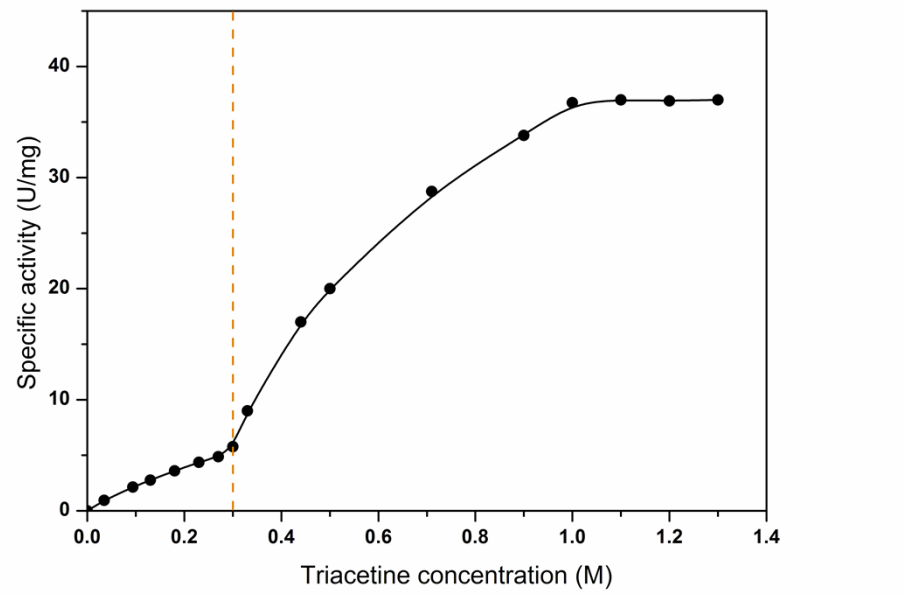


Figure S9. Dependence of free CRL activity on TA concentration.

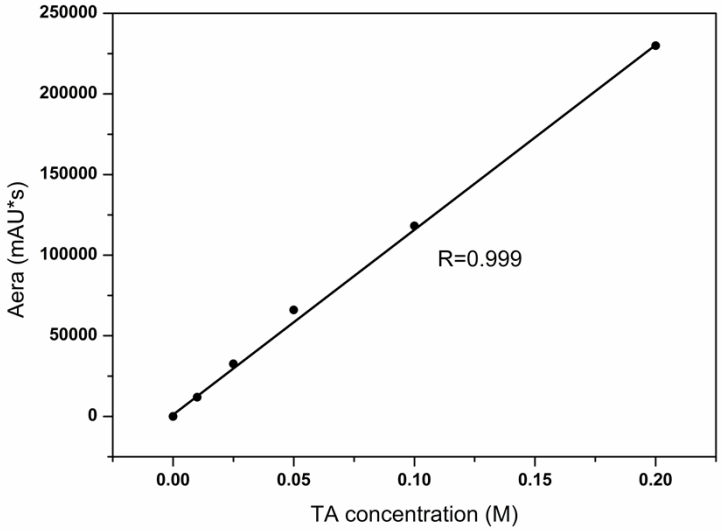
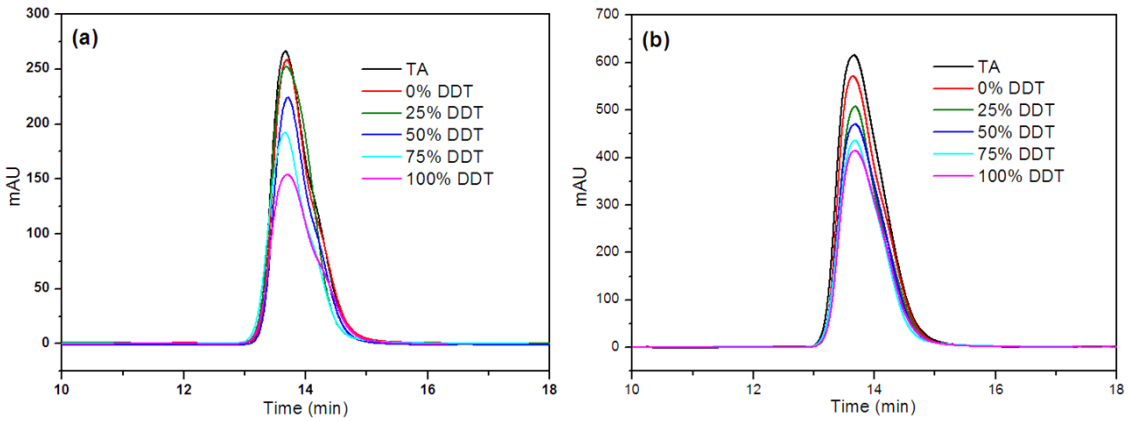


Figure S10. Calibration curve from standard TA solutions.



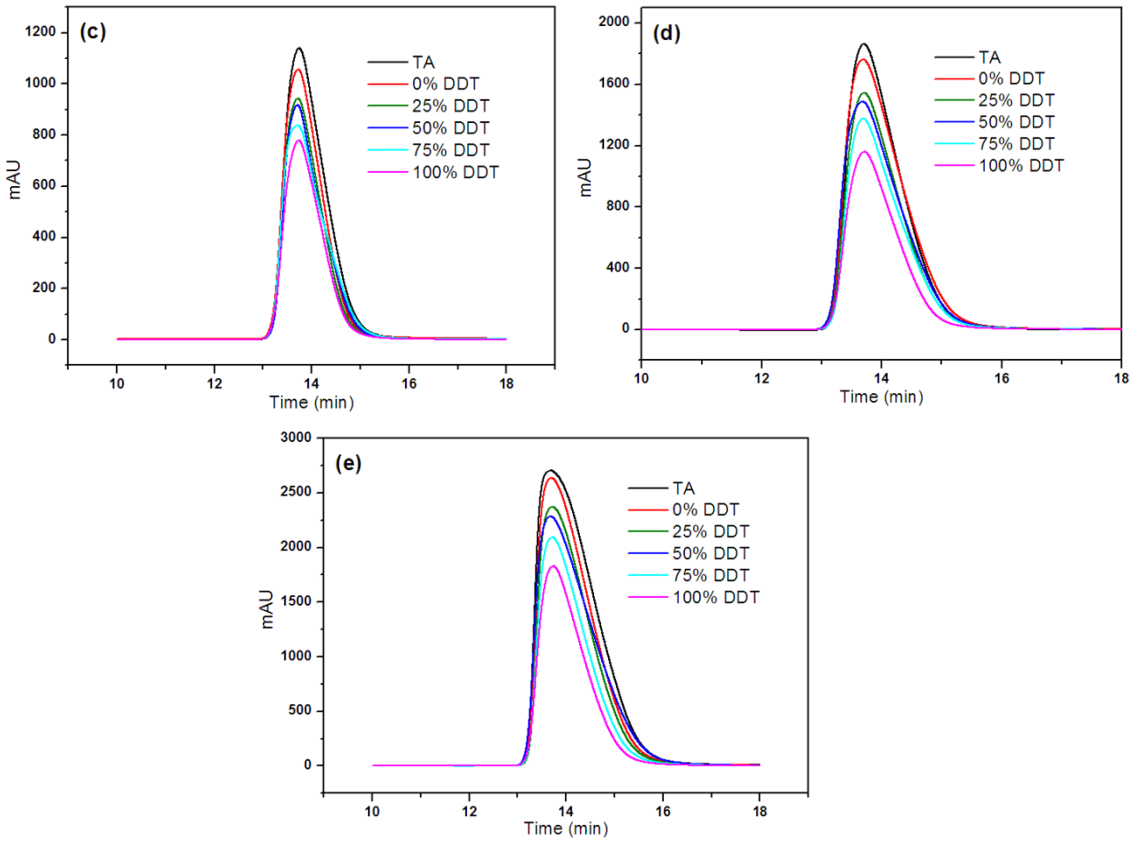


Figure S11. Liquid chromatograms of TA before and after hydrolysis reaction, catalyzed by CRL immobilized on surface with varied χ_{DDT}. TA concentration: (a) 0.01 M; (b) 0.025 M; (c) 0.05 M; (d) 0.1 M; (e) 0.2 M.

$$V = \frac{V_{max}[S]}{K_m + [S]} \tag{S12}$$

Where V is the initial hydrolysis reaction rate, U/mg protein; K_m is the Michaelis constant, M; V_{max} is the maximum reaction rate, U/mg protein; [S] is the substrate concentration, M.

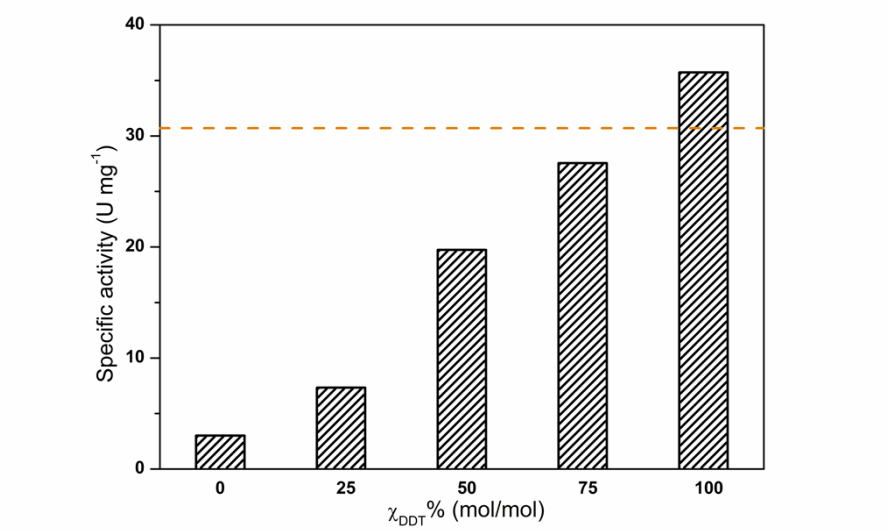


Figure S12. Specific activity of CRL immobilized on SAMs with different wettabilities. The orange dash lines refer to values for free CRL (TA solution concentration: 0.2 M).