

Supplementary Material

Comparative Assessment of the Dyeing Process for Pristine and Modified Cotton Fabrics Towards the Reduction of the Environmental Fingerprint

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S1 Synthetic procedure of the polymer modifiers

Polymer 1, P(VBC₅₀-co-VBCTEAM₅₀):

A solution of polyvinyl benzyl chloride (1.5 g) at a concentration of 10% (w/v) in dimethylformamide solvent (15 mL) was introduced into a round bottom flask, where it was outgassed, while stirring, with argon–vacuum cycles. An amount (0.5eq) of triethylamine (TEAM) was added. The reaction mixture was left under argon and stirred at ambient temperature for 72 hours. The reaction mixture was precipitated in multiple volumes of acetone, where it was left under stirring for 12 hours at room temperature. This was followed by vacuum filtration, washing on the filter with acetone and then drying to obtain the polymer.

Polymer 2, P(MMA₆₀-co-VBC₃₀ co-TEAM₁₀):

First step (synthesis of P(MMA₆₀-co-VBC₄₀)): An amount of methyl methacrylate (MMA) and 4-vinylbenzyl chloride at a molar ratio 60:40 and total concentration of 30% (w/v) in tetrahydrofuran (THF) was added to a round-bottomed flask and was outgassed under stirring, with argon–vacuum cycles. The solution of AIBN initiator (0.01eq) in degassed THF solvent was added dropwise and the reaction mixture was left under argon and stirred at 70 °C for 48 hours. The reaction mixture was precipitated in multiple volumes of diethyl ether where it was left under stirring for 12 hours at room temperature. This was followed by vacuum filtration, washing the filter with diethyl ether and then drying to obtain the copolymer.

Second step (synthesis of P(MMA₆₀-co-VBC₃₀-co-TEAM₁₀)): A solution of the P(MMA₆₀-co-VBC₄₀) copolymer solution at a concentration of 25% (w/v) in tetrahydrofuran (THF) solvent was placed in a round-bottomed flask, where it was outgassed, under stirring, with argon–vacuum cycles. After the dissolution of the solid,

an amount of triethylamine (TEAM) was added (0.35 eq in terms of the total mols of the copolymer). The reaction mixture was left under argon and stirred at 70 °C for 48 hours. The reaction mixture was precipitated in multiple volumes of diethyl ether, where it was left under stirring for 12 hours at room temperature. This was followed by filtration under vacuum, washing the filter with diethyl ether and then drying to obtain the polymer.

S2 Cationic modification of cotton fabrics

Cotton samples were immersed in a 0.1% aqueous solution of the desirable polymeric modifier. The weight ratio of the fabric to the aqueous solution of the polymer, $W_{\text{text}}:V(\text{aq})_{\text{pol}}$ (w / v) was 1:20 w / v. The solution was adjusted to alkaline pH using an aqueous 0.25 M NaOH solution. The temperature of the modification bath was raised to the selected 60 °C. The modification bath was held at this temperature for 2h. Afterwards, the modified textiles were rinsed in water thoroughly at room temperature and dried at 80 °C for 12h.

S3 Dyeing procedure of modified fabrics

Dyeing Process 1 (for tricolored reactive dyes mixture):

The dyeing procedure was performed in the absence of salt (NaCl) and under mild alkaline conditions.

The main steps include:

- Loading the dyeing machine with soft water, sequeon agent (blend of phosphonates and acrylates) and the fabric, at 20 °C.
- Heating at 45 °C for 5 min.
- Gradual addition of dyes for 20 min.

- Retention for 20 min.
- Gradual addition of carbonate soda.
- Temperature increases at 60 °C with a rate 0.6 °C/min.
- Gradual addition of carbonate soda.
- Retention at 60 °C for 60 min.
- Sampling

Dyeing Process 2 (for acid dye):

The dyeing process in this case was performed under an acidic environment (buffer solution 0.7 g/L glacial acetic acid 99% and 1.2 g/L anhydrous sodium acetate) at 95 °C for 60 min in the absence of carbonate soda at 60 °C.

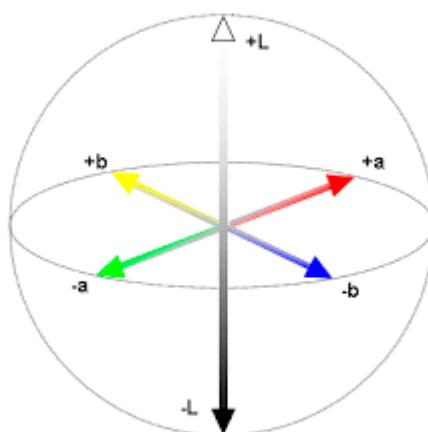


Figure S1. CIELAB colorimetry system.

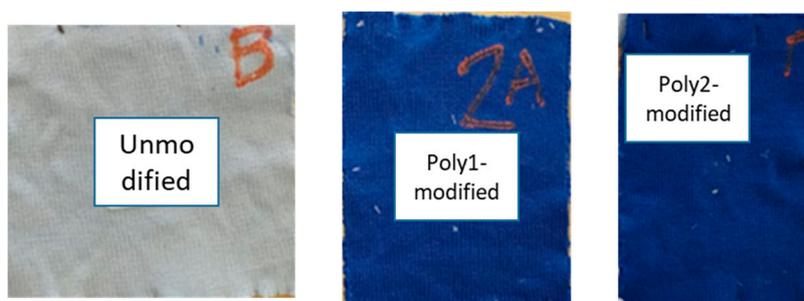


Figure S2. The three fabrics (unmodified, modified with Polymer 1 and modified with Polymer 2) colored by Acid Blue 281.

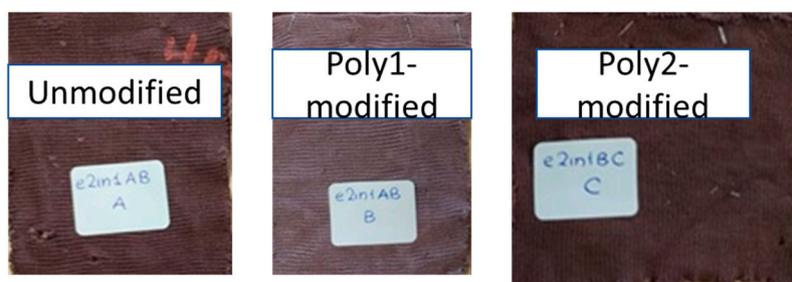


Figure S3. The three fabrics (unmodified, modified with Polymer 1 and modified with Polymer 2) colored by the mixture of the three reactive dyes Novacron Yellow S-3R (NY) Novacron Ruby S-3B (NR) and Novacron Dark Blue S-GL (NDB).

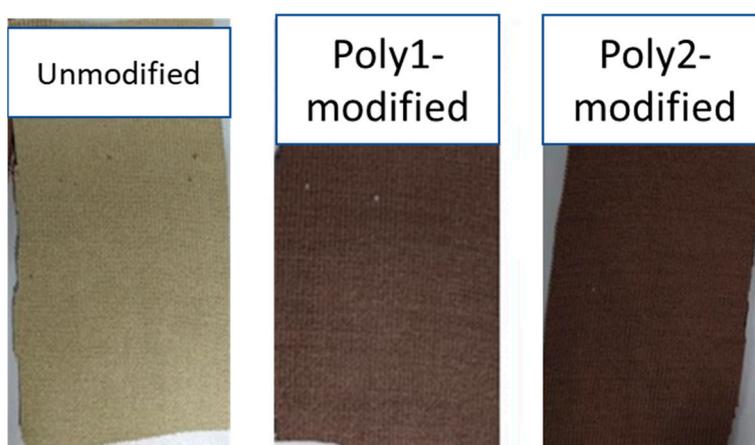


Figure S4. The three industrially prepared fabrics (unmodified, modified with Polymer 1 and modified with Polymer 2) colored by the mixture of the three reactive dyes Novacron Yellow S-3R (NY) Novacron Ruby S-3B (NR) and Novacron Dark Blue S-GL (NDB).

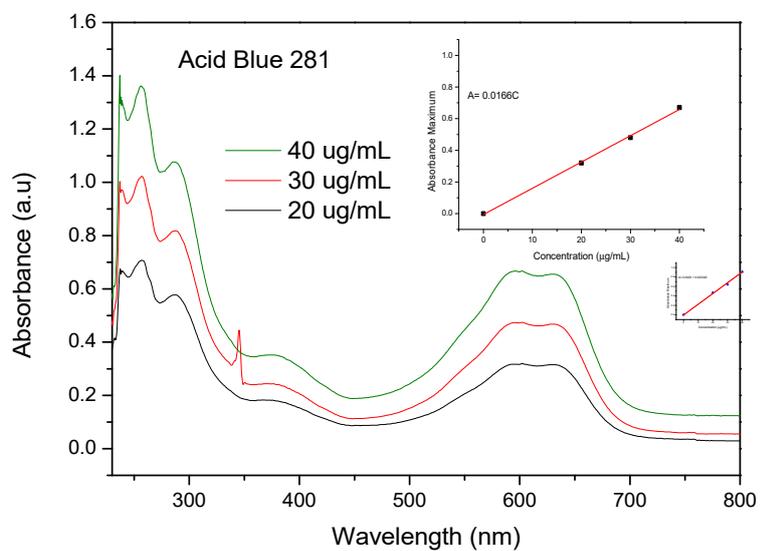
S4 Washing procedure of modified fabrics (for modified cotton only)

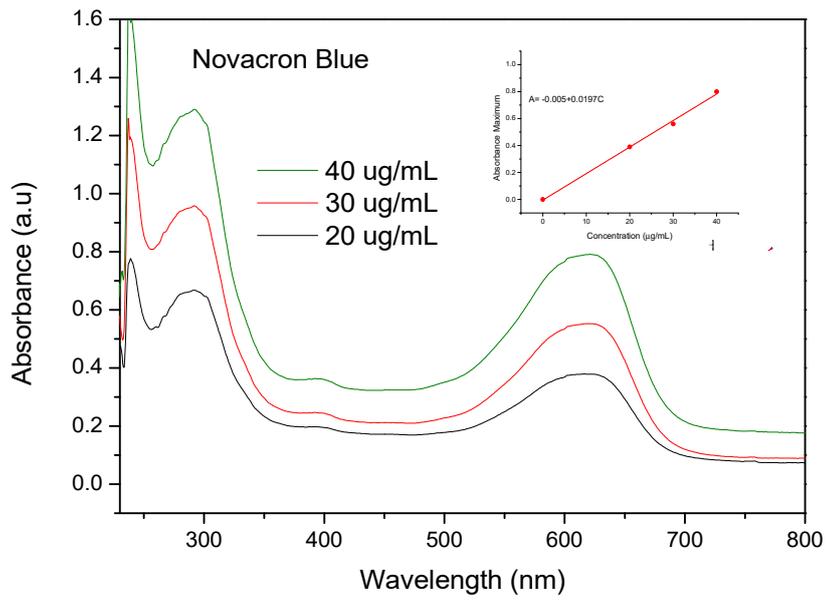
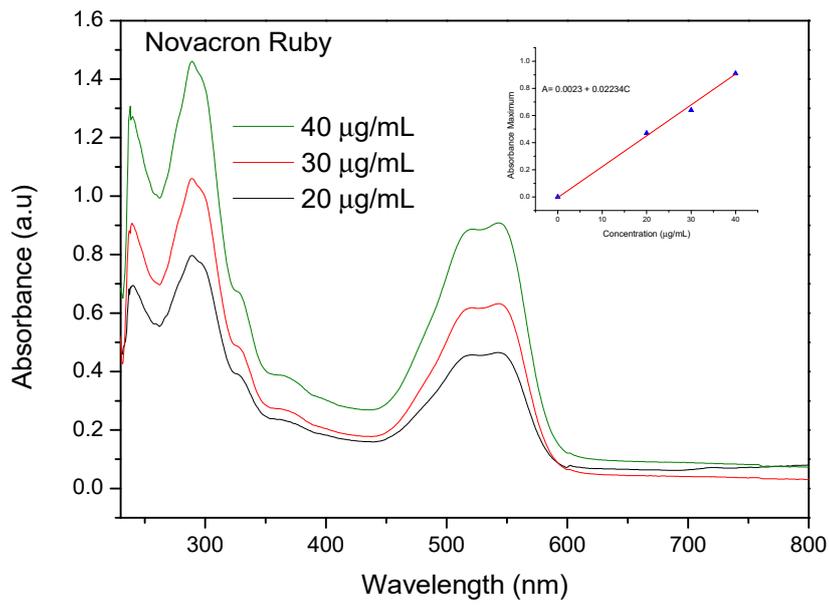
- Rinsing 10 min
- Neutralizing 10 min with 1g/L HCOOH 85%
- Hot washing 95 °C -10 min
- Hot washing 80 °C -10 min
- Rinsing 10 min
- Squeezing and drying.



Figure S5. Ahiba Polymat washing machine.

S5 Evaluation of the after-wash water through UV/Vis and SERS





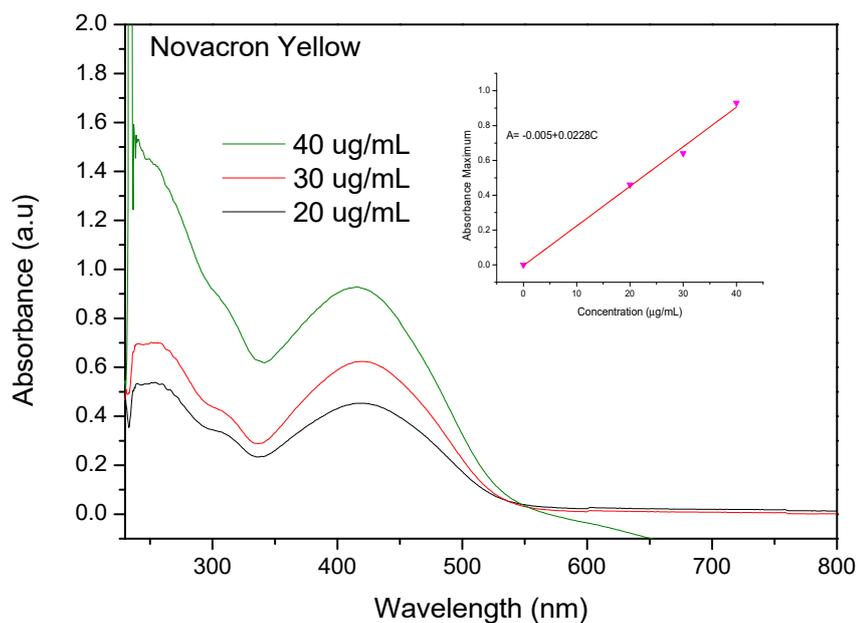
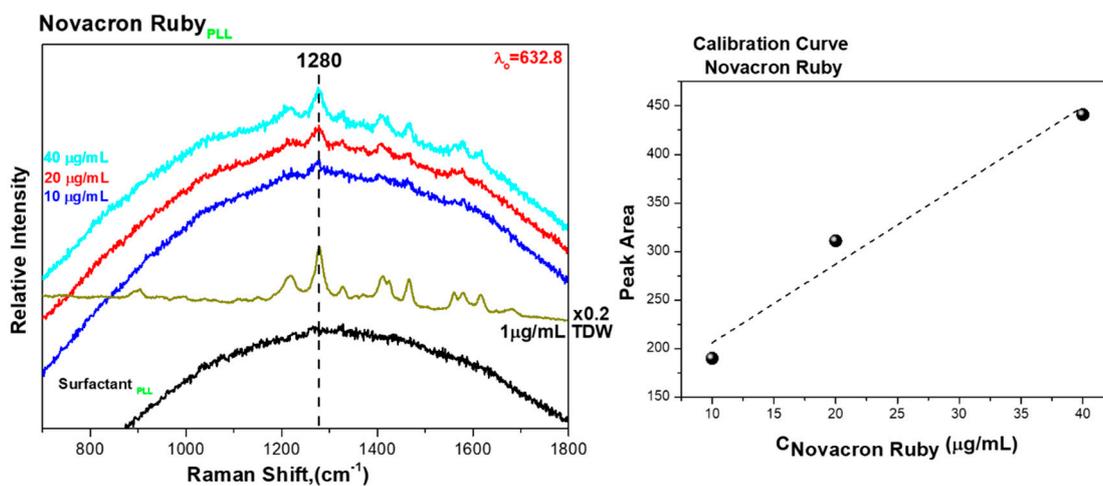


Figure S6. Calibration curves of soap solutions at various concentrations of the different dyes through UV/Vis spectroscopy.



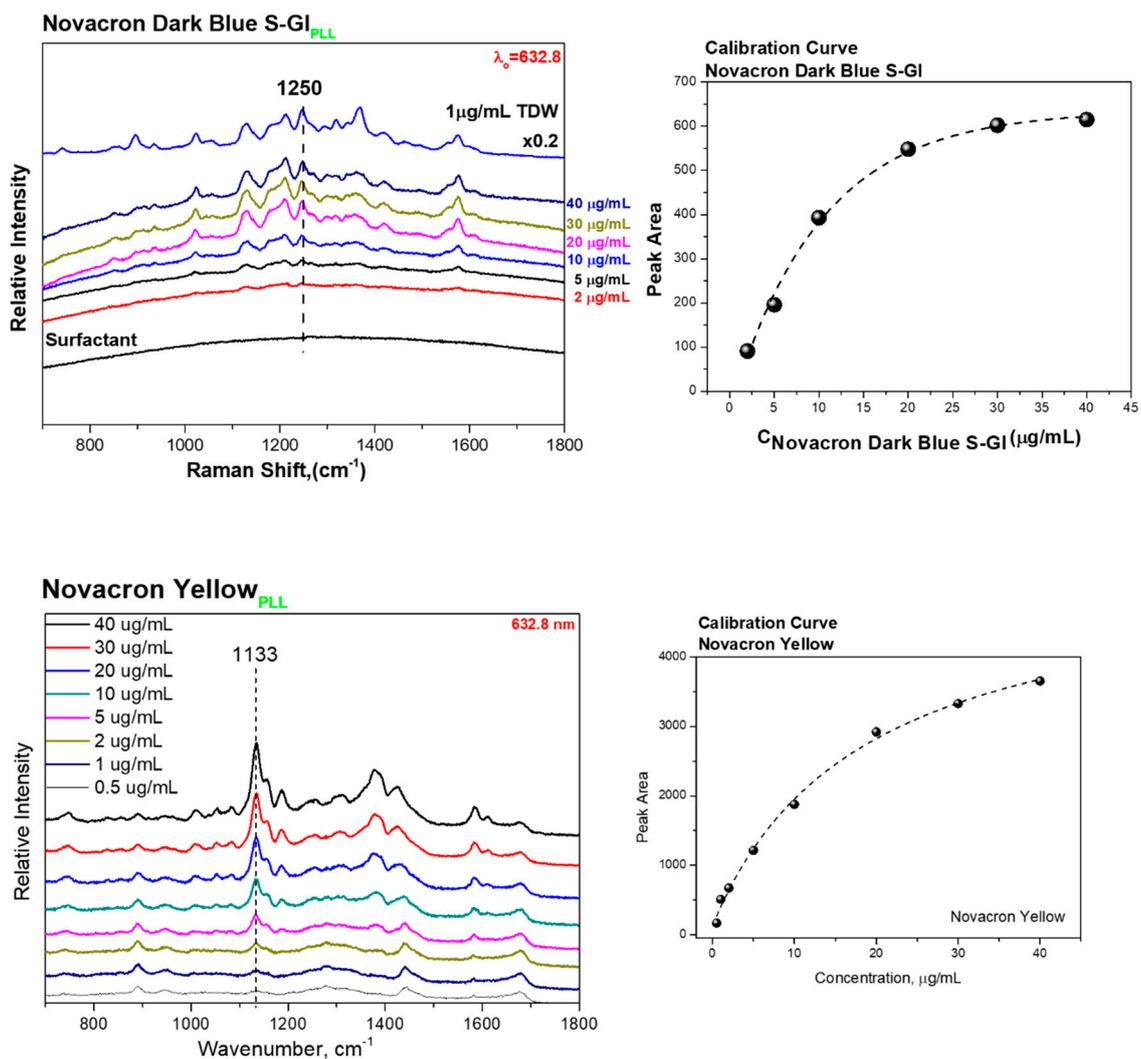


Figure S7. Calibration curves of soap solutions at various concentrations of the different dyes through SERS spectroscopy.