

Electronic Supplementary Information (ESI)

Environmentally friendly salt-free and low-alkaline coloration of lyocell fiber in an ethanol-water mixture with excellent exhaustion

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CONCENTS

S1 Coloring procedure	3
S2 Characterization	4-5
S3 The molecular simulation method	6-7
Figure S1-S12	8-19
Table S1-S5	20-24
Equation S1-S14	25-26
Supplementary References	27

S1 Coloring procedure

The lyocell fiber swelling progress in the NaOH solution and dyeing procedure for the reactive dye in the EHS. Firstly, 5.0 g of lyocell fiber was swollen in the NaOH aqueous solution at a liquor ratio of 1:20, where the NaOH concentration, swelling temperature, and swelling time were varied 1 - 10 g·L⁻¹, 40 - 90°C, and 10 - 90 min, respectively. After the swelling process, the alkali swollen lyocell with 140% ± 10% pick-up (PR, was calculated by Equation S1 (Supporting Information)) was dyed in the ethanol-water mixture at a liquor ratio of 1:20, where the EtOH content, dye dosage, dyeing temperature, and dyeing time were varied from 10 - 90% in volume, 1% - 6% o.w.f, 30 - 90°C, and 10 - 90 min, respectively. The suitable conditions for the experiment were swelled at 60°C for 30 min, the constant temperature at 60°C for 60 min during the dyeing process, and a dye dosage of 2.0% o.w.f. In the process of conventional dyeing, Na₂SO₄ was chosen to reduce the electrostatic repulsion of anions between reactive dyes and fibers,¹ and the amount of Na₂SO₄ depends on the concentration of dyes in the dye solution.² The conventional staining procedure was conducted as follows. Lyocell fiber (5.0 g) was started to color in the dyeing solution at a liquor ratio of 1:20 at 60°C at 2% o.w.f dye dosage for 10 min. Following, 40 g·L⁻¹ Na₂SO₄ was added to the dye bath, which had a dyeing temperature of 60°C and was run for 30 min, then fixation with 15 g·L⁻¹ Na₂CO₃ in 60°C for 60 min. The procedures for reactive dyeing of lyocell fibers in the water systems are shown in Figure S5a (Supporting Information). As shown in Figure S5b (Supporting Information), at the end of each staining process, the samples were removed from the staining jar, dried at 80°C. The as-prepared samples were soaked in a solution containing 2 g·L⁻¹ soap powder and 2 g·L⁻¹ Na₂CO₃ and left at 100°C for 20 min at a liquid ratio of 30:1. Immediately thereafter, the samples were rinsed in warm water and dried at 80°C. Another set of samples that did not washed by the soaping procedure was used for the coloring power test.

S2 Characterization

Color characteristics. Absorption spectrum test and Exhaustion rate (E) calculation. The dyeing liquids before and after dyeing were taken out separately and placed in a 10 mm × 10 mm high precision cell and the absorption values were tested with a UV-3600 Plus UV Spectrophotometer (Shimadzu, Japan). The calculation formula of the exhaustion rate of the fiber dyeing was Equation S2 (Supporting Information). Color strength and Total fixation. The color strength (K/S values) of dyed fiber was assessed by using a CS-820 Spectrophotometer (Hangzhou CHNSpec Technology Co. Ltd, China) from 20 random points at D65 light source with 10° standard observer in the visible spectra 400 - 700 nm in SCI test modal and was calculated according to the Kubelka-Munk Equation as shown in Equation S3 (Supporting Information). The total fixation was determined by Equation S4 (Supporting Information). Colorfastness. Soap fastness to washing and fastness to rubbing after dyeing was tested by SW-12A Soap Fastness Tester (Dahua Electronic Instruments Co., Ltd., China) and Y571N Friction Fastness Tester (Nantong Hongda Experiment Instruments Co., Ltd., China) according to ISO 105-C10: 2006 and ISO 105-19: 2020, respectively. The grey sample card was then compared with the sample of the fastness test and rated on a color fastness scale from 1 to 5, the higher the value, the better the color fastness.

Surface morphology and structure characteristics. The surface morphology of the fibers was used to observe an RH-2000 digital microscope (DM, HIROX Co. Ltd, Japan). The surface micromorphology of the lyocell fibers was further analyzed using scanning electron microscopy (SEM, JSM-7800, Japan), and energy dispersive spectroscopy (EDS) was operated for the elemental analysis of the lyocell fiber color dye elements. The crystal structure determined of the raw lyocell fiber and dyed lyocell fiber were performed on X-ray diffractometers (XRD, Empyrean) operating at 40 mV and 40 mA with Cu-K α radiation, and the scan range from 5° to 90° (2 θ) for 10 min using absolute scan patterns. The crystallinity index (Crl) of samples was calculated by the equation of Segal et al.³ Aiming to explicate characteristics of diverse functional groups containing C, O, S, and N, etc. on the surface of raw lyocell fiber and dyed lyocell fiber, an X-ray photoelectron spectroscopy (XPS) device (Shimadzu/Krayos Axl Ultra Dld, Japan) containing the Al Ka X-ray source was employed in this study. To identify the specific distribution of various functional groups, the C1s (carbon 1 s), O1s (oxygen 1 s), S2p (sulfur 2 p), N1s (nitrogen 1 s), and their high-resolution XPS spectra acquired from XPS curves were further analyzed via using Casaxps software.

Single fiber tensile breaking strength. The raw lyocell fiber and dyed lyocell fiber samples were characterized for their tensile-breaking strength. The single-fiber tensile-breaking strength was determined on an Electronic Single Fiber Strength Tester (ESFST, YG004, China) from 5 random fibers at 10 mm·min⁻¹ tensile speed, and the single-fiber average tensile breaking strength ($\bar{F}$) was reported by Equation S5 (Supporting Information).

Thermal performance characteristics. To characterize the differences in the thermal

properties of the lyocell fiber after dyeing than raw lyocell fiber, the samples were used to measure thermal data by differential scanning calorimeter (DSC, DSC 204F1, Netzsch Inc., Germany). The DSC measurements experiments were adopted under a nitrogen atmosphere and with a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ for the temperature range from 30 - 400°C. The software is Proteus Analysis, which is used to analyze the data that the measured DSC data. To characterize the relationship between mass and temperature, all samples were tested using HIACHI (STA300, Hitachi High-Tech Science Corporation, Japan). During the tests, all samples were exposed to a nitrogen protective gas and a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ for temperatures ranging from 40 - 800°C. The HIACHI test data were analyzed using the software Job Gallery to obtain thermogravimetry (TG) and differential thermogravimetry (DTG) data.

S3 The molecular simulation method

The Dmol3, Amorphous Cell, and Forcite modules, incorporated in Material Studio Software 2019, were used for molecular simulation calculations. For the geometry optimization and properties analysis of Dmol3 modules, which provides details about the calculation. The BLYP (Becke-Lee-Yang-Parr) basis set is used with the generalized gradient approximation (GGA) of density functional theory (DFT), and the smearing used in electronic orbital occupancy. The electrostatic potential (ESP), higher occupied molecular orbital (HOMO), and lower unoccupied molecular orbital (LUMO), et al, were calculated and analyzed by Dmol³. The molecular dynamics (MD) simulations, forcefield types, and charge setting were performed by applying the Dreiding force field in the Forcite Module.⁴ The molecular geometry minimizations in the Forcite Module were performed by the steepest descent and quasi-Newton methods of the algorithm. The convergence criteria employed were set to 0.001 kcal·mol⁻¹ for energy and 0.5 (kcal·mol⁻¹·Å⁻¹) for force. The probability distribution of the possible system states was determined by the NVT ensemble in MD. Temperature control was made by the Nose algorithm.⁵ The standard Verlet algorithm was used to integrate Newton's law of motion, setting a time step of 1 fs. The simulation was conducted at a temperature of 333 K, consisting of two distinct phases. In the equilibrium phase, an NPT (constant temperature and pressure) simulation was performed for 50 ps to allow the system to reach thermal and mechanical equilibrium. Following this, the production phase was carried out using an NVT (constant temperature and volume) simulation for 150 ps, during which data was collected for subsequent analysis. The simulation box was created to construct the different systems by using an Amorphous Cell Module.

The HSAB (hard-soft-acid-base) principle in a global sense is used to calculate the electrochemical potential μ , the Energy gap ΔE , and the electrophilic index ω of the molecule. All these properties are characteristic of isolated-state molecular systems. These properties are calculated from the energies of the molecular orbitals EHOMO and ELUMO using the following Equation S6-S8 (Supporting Information).

The Fukui function $f(r)$ is defined as the determination of the electronic density $\rho(r)$ concerning the μ correlation, employing the Maxwell relation as shown in Equation S9 (Supporting Information).⁶ There are discontinuities in the molecule, so for $f(r)$ separate left and right derivatives are used to define positive $f^+(r)$ and negative Fukui function $f^-(r)$.⁷ The $f^+(r)$ Equation S10 (Supporting Information) is expressed as the molecule is subjected to nucleophilic substitution at this site and is susceptible to attack by electrophilic reagents, and conversely $f^-(r)$ Equation S11 (Supporting Information) is susceptible to electrophilic substitution at the site and is susceptible to nucleophilic reagent attack.

The diffusion coefficient (D) of a substance serves as an indicator of its diffusion capacity and represents a fundamental physical property of that substance. The

diffusion of the dye coefficient is obtained by calculating the square of the average distance of all of the particles from their initial point at a certain point in time,⁸ which is known as the mean square displacement (MSD). Here, the D of dye in different systems was calculated by the Einstein method. After the MSD is obtained, the Einstein formula is used to calculate the dyes. The MSD fitted under smooth method: Savitzky-Golay, the D of the dye can be obtained. The MSD and D are the following by Equation S12-S13 (Supporting Information).⁹ The physical meaning of radial distribution function (RDF) is the probability that another atom can be found at a distance r in the system. The RDF $g(r)$ was determined by Equation S14.^{9, 10}

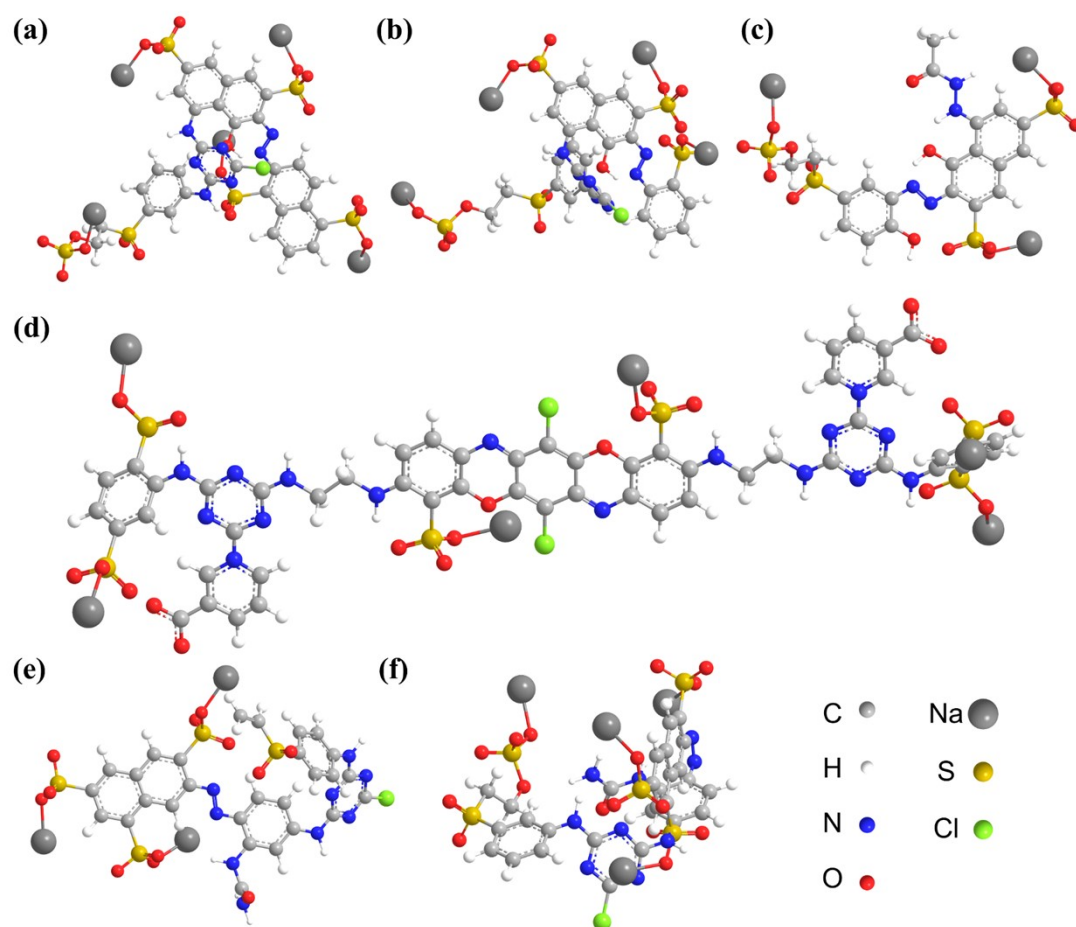


Figure S1 Chemical molecular structures of (a) C.I. Reactive Red 195, (b) C.I. Reactive Red 194, (c) C.I. Reactive Bule 187, (d) C.I. Reactive Bule 20, (e) C.I. Reactive Yellow 176, (f) C.I. Reactive Yellow 145.

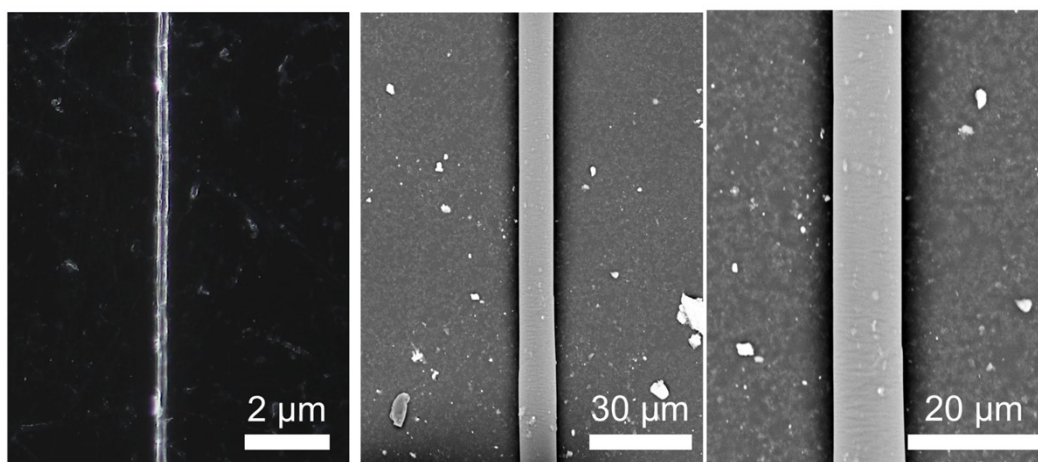


Figure S2 Digital micrograph, SEM images of swelling lyocell.

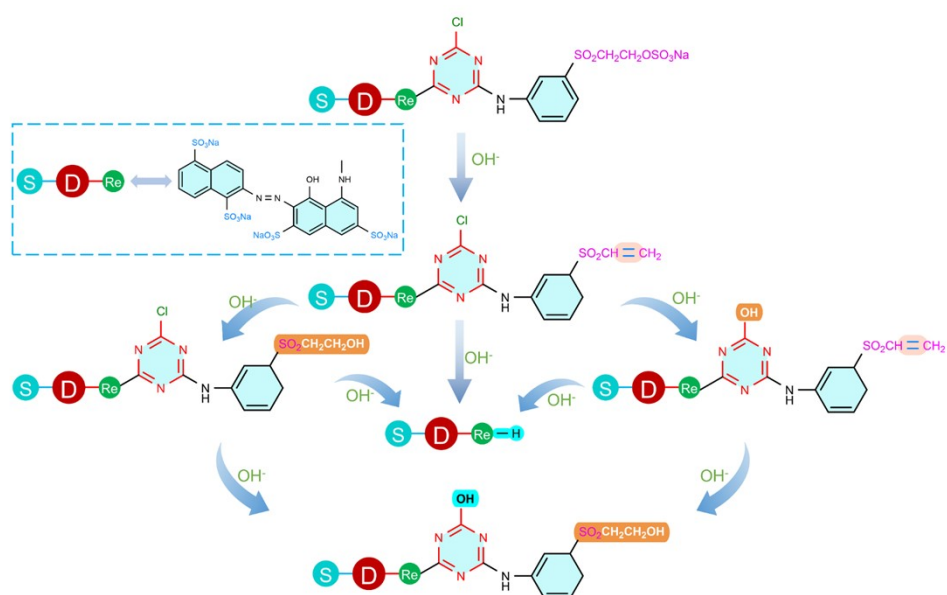


Figure S3 The Hydrolysis process of the dyes RR195 with a Monochlorotriazine and vinyl-sulfonesulfate reactive group in the alkaline solution.

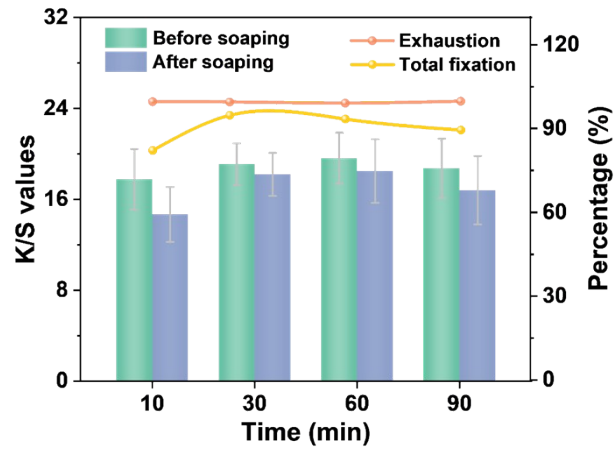


Figure S4 Exhaustion, total fixation rates, and K/S values of lyocell fibers before and after soaping at different swelling times.

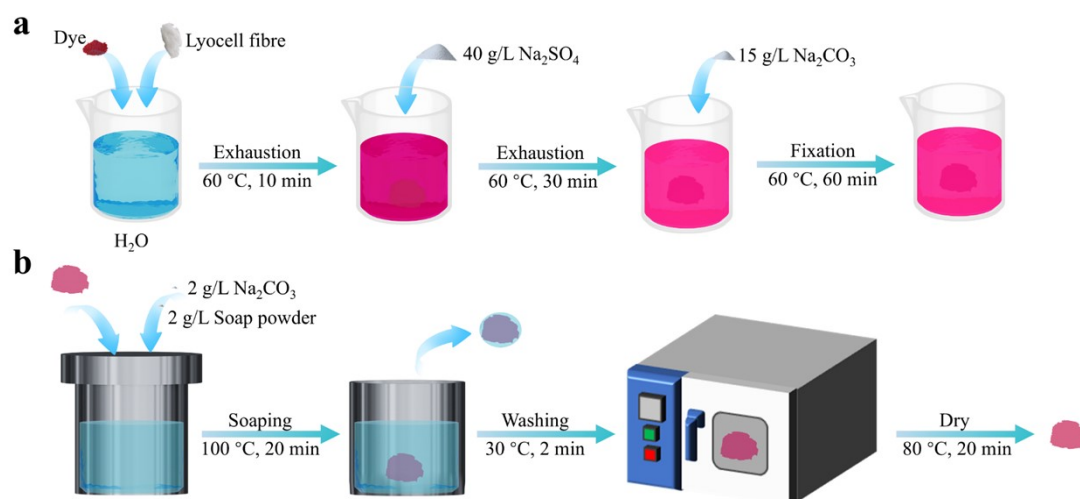


Figure S5 (a) The sequential processes involved in the reactive dyeing of lyocell fibers utilizing a purely aqueous system; (b) The soaping, washing, and drying processes of dyed lyocell fiber.

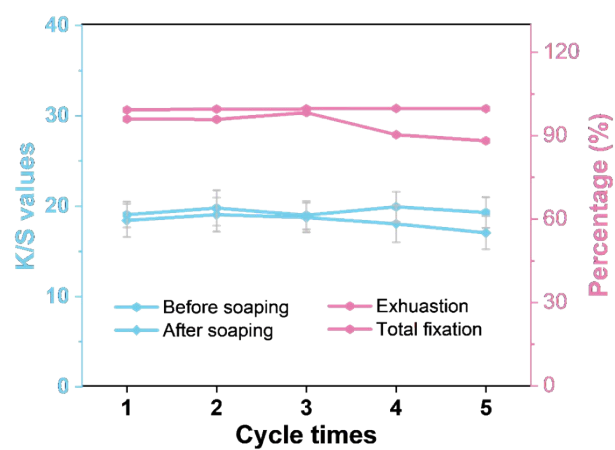


Figure S6 Exhaustion, total fixation rates, and K/S values of lyocell fibers at swelling liquid used to cycle.



Figure S7 The dyes distributed with time conventional H₂O system (CHS) and EtOH-H₂O solvent system (EHS).

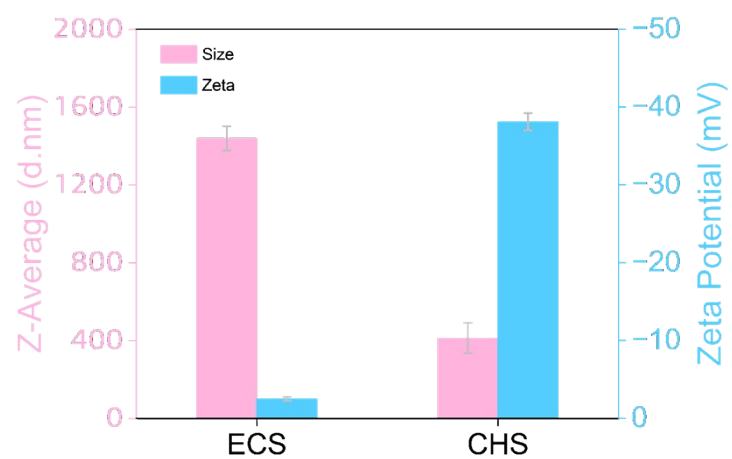


Figure S8 Size and Zeta of dye RR195 in ECS and CHS, respectively.

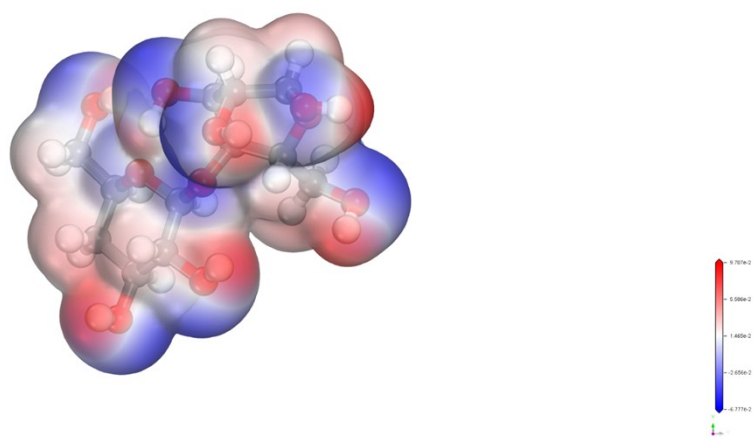


Figure S9 ESP of lyocell fiber.

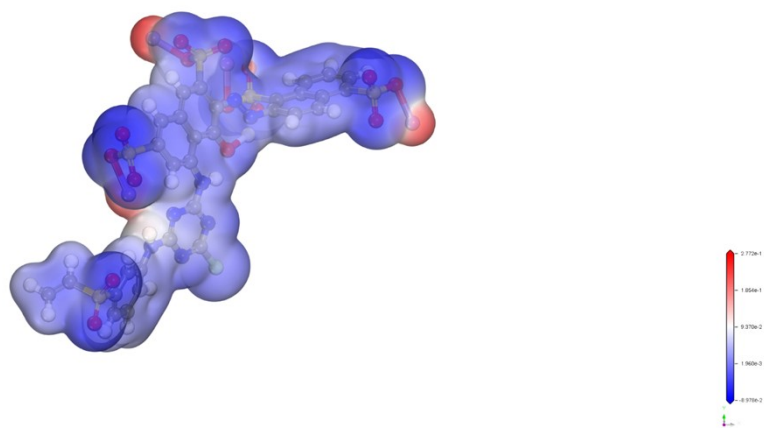


Figure S10 ESP of RR195-vinylsulfone dye.

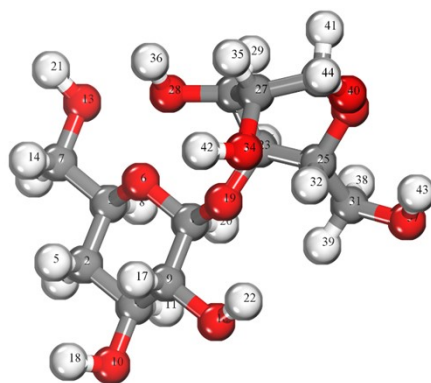


Figure S11 Active sites lyocell monomolecular structure.

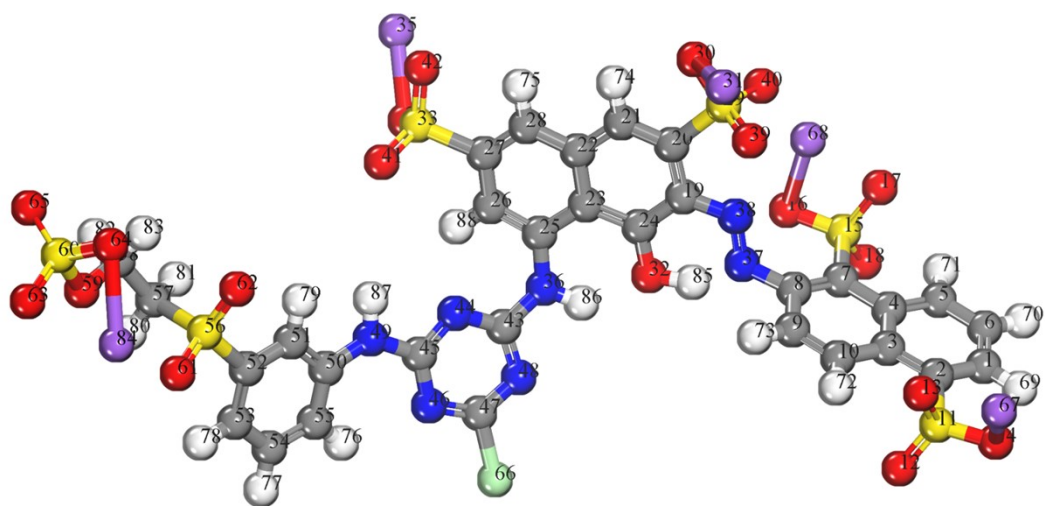


Figure S12 Active sites of RR195 molecule.

Table S1 Reactive dyes used in the experiment

Sample of dyes	Abbreviation	Molecular formula	Molecular weight	Chromophoric group	Reactive group
C. I. Reactive Red 195	RR195	$C_{31}H_{19}N_7O_{19}Na_5S_6Cl$	1136.290	Azo	Monochlorotriazine and vinyl-sulfone
C. I. Reactive Red 194	RR194	$C_{27}H_{18}N_7O_{16}Na_4S_5Cl$	984.187	Azo	Monochlorotriazine and vinyl-sulfone
C. I. Reactive Bule 20	RB20	$C_{20}H_{19}N_4O_{15}Na_3S_4$	752.594	Azo	Vinyl-sulfone
C. I. Reactive Bule 187	RB187	$C_{52}H_{32}N_{16}O_{24}Na_6S_6Cl_2$	1666.120	Triphenoxazines	Dinicotinic acid
C. I. Reactive Yellow 176	RY176	$C_{28}H_{19}N_9O_{12}Na_3S_4Cl$	906.174	Azo	Monochlorotriazine and vinyl-sulfone
C. I. Reactive Yellow 145	RY145	$C_{28}H_{20}N_9O_{16}Na_4S_5Cl$	1026.230	Azo	Monochlorotriazine and vinyl-sulfone

Table 2 The dyed lyocell fiber friction fastness

Dry friction fastness	Wet friction fastness
5 grade	4-5 grade

Table S3 Total energy contributions of the dye RR195/lyocell fiber systems.

Systems	Total energy (kcal/mol)	Valence energy (diag. terms)				Non-bond energy		
		Bond	Angle	Torsion	Inversion	Hydrogen bond	van der Waals	Electrostatic
CHS	-143257.28	1747.15	3932.37	750.53	62.42	-5233.511	10092.59	-160079.72
EHS	-6815.26	1750.754	4146.557	750.046	56.577	-789.972	316.471	-18234.214

Table S4 Fukui indices (Mulliken analyses) of dye RR195 and lyocell fiber.

	Mulliken atomic charge	f^-	f^+
lyocell fiber	O(10): -0.646; O(13): -0.667; H(18): 0.378; O(16): -0.635; O(19): -0.517; H(21): 0.420; H(22): 0.387; O(28): -0.663; C(33): 0.356; O(34): -0.656; H(36): 0.428; O(37): -0.643; O(40): -0.652; H(42): 0.421; H(43): 0.372; H(44): 0.400.	O(10): 0.064; O(13): 0.124; O (16): 0.045; O(19): 0.016; O(28): 0.080; O(30): 0.029; O(34): 0.076; O(37): 0.060; O(40): 0.010.	H(18): 0.084; H(22): 0.174; H(43): 0.191; H(44): 0.111.
RR195	C(3): 0.054; S(11): 0.617; O(13): -0.589; O(17): -0.551; C(22): 0.096; C(24): 0.313; N(36): -0.550; N(37): -0.353; O(42): -0.583; Cl(66): -0.096; Na(68): 0.837; Na(84): 0.867	O(16): 0.040; O(17): 0.050; O(18): 0.053; H(69): 0.037; H(70): 0.042.	C(24): 0.050; N(37): 0.074; N(38): 0.089; Cl(66): 0.033.

Table S5 E_{HOMO} , E_{LUMO} , chemical potential (μ), global hardness (η) and the electrophilicity index (ω) for lyocell monomolecular and lyocell monomolecular.

	$E_{\text{HOMO}}(\text{eV})$	$E_{\text{LUMO}}(\text{eV})$	$\mu(\text{eV})$	$\omega(\text{eV})$
lyocell fiber	-5.901	0.338	-5.562	2.479
RR195 dye	-5.022	-3.381	-8.403	21.503

Equation

Pick-up value (PR) was calculated by Equation S1.

$$PR = \left(\frac{W_P - W_I}{W_I} \right) \times 100\% \quad (\text{Equation S1})$$

where the PR denote pick-up value, the W_P and W_I denote the weight of the initial and the pick-up lyocell weight after swelling, respectively.

Exhaustion rate (E) was calculated by Equation S2.

$$E\% = \left(1 - \frac{n_{dye-after} \times A_{dye-after}}{n_{dye-before} \times A_{dye-before}} \right) \times 100 \quad (\text{Equation S2})$$

where $A_{dye-before}$ and $A_{dye-after}$ denote the absorbance of the initial dye solution and the residual solution after dyeing, respectively, $n_{dye-before}$ and $n_{dye-after}$ denote dilution multiple of the initial dye solution and the residual solution after the dyeing, respectively.

Color strength (K/S) and Total fixation (T) was determined by Equation S3-S4.

$$K/S = \frac{(1 - R)^2}{2R} \quad (\text{Equation S3})$$

where R represents the observed reflectance value of dyed fiber at the maximum absorption wavelength.

$$T\% = E \times \frac{(K/S)_{soap-after}}{(K/S)_{soap-before}} \quad (\text{Equation S4})$$

where the subscripts soap-before and soap-after are the values measured before and after soaping, respectively.

The single-fiber average tensile breaking strength ($\bar{F}$) by Equation S5.

$$\bar{F} = \frac{\sum_{i=1}^{i=n} F_i}{n} \quad (\text{Equation S5})$$

where the n and F are Number of samples and tensile breaking strength, respectively.

The electrochemical potential μ , the Energy gap ΔE , and the electrophilic index ω of the molecule are calculated by the following Equation S6-S8.

$$\mu = E_{HUMO} + E_{LUMO} \quad (\text{Equation S6})$$

$$\Delta E = E_{LUMO} - E_{HUMO} \quad (\text{Equation S7})$$

$$\omega = \mu^2 / (2\Delta E) \quad (\text{Equation S8})$$

The Fukui function was calculated by Equation S9-S11.

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)} \quad (\text{Equation S9})$$

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)}^+ = \rho_{N+1}(r) - \rho_N(r) \quad (\text{Equation S10})$$

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{V(r)}^- = \rho_N(r) - \rho_{N-1}(r) \quad (\text{Equation S11})$$

where $f(r)$ is Fukui function, $\rho(r)$ is electronic density, $f^+(r)$ is positive $f(r)$, and $f^-(r)$ negative $f(r)$.

The MSD and D are the following by Equation S12-S13.

$$MSD = \frac{1}{N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_\alpha} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (\text{Equation S12})$$

$$D = \frac{1}{6} MSD \quad (\text{Equation S13})$$

Where D is the diffusion coefficient of the system, N is the total number of dye particles, t is the time, $r_i(t)$ and $r_i(0)$ are the positions of the particles at t and t0, respectively.

The RDF $g(r)$ was determined by Equation S14.

$$g(r) = \frac{V \langle n_i(r, r + \Delta r) \rangle}{4\pi r^2 \rho \Delta r N} \quad (\text{Equation S14})$$

Where V represents the volume, $n_i(r, r + \Delta r)$ indicates the number of atoms within the spherical shell ranging from distances r to $r + \Delta r$, and N stands for the total number of atoms.

Supplementary References

- 1 A. Wang, L. Xia, S. Zhou, H. Guo, Y. Wang and W. Xu, *Journal of Cleaner Production*, 2020, **267**, 122062.
- 2 L. Xia, A. Wang, C. Zhang, Y. Liu, H. Guo, C. Ding, Y. Wang and W. Xu, *Green Chemistry*, 2018, **20**, 4473-4483.
- 3 K. S. Salem, N. K. Kasera, M. A. Rahman, H. Jameel, Y. Habibi, S. J. Eichhorn, A. D. French, L. Pal and L. A. Lucia, *Chem Soc Rev*, 2023, **52**, 6417-6446.
- 4 K. Mazeau and M. Wyszomirski, *Cellulose*, 2012, **19**, 1495-1506.
- 5 S. Nosé, *The Journal of Chemical Physics*, 1984, **81**, 511-519.
- 6 T. Y. Kim, J. H. Kim, H. B. Kim, K. H. Park, J. W. Lee and S. Y. Cho, *International Journal of Electrochemical Science*, 2018, **13**, 3935-3947.
- 7 K. H. Toumi, M. Bergaoui, M. Khalfaoui, Y. Benguerba, A. Erto, G. L. Dotto, A. Amrane, S. Nacef and B. Ernst, *Journal of Molecular Liquids*, 2018, **271**, 40-50.
- 8 A. Meyer, W. Petry, M. Koza and M. P. Macht, *Applied Physics Letters*, 2003, **83**, 3894-3896.
- 9 Z. Cui, X. Zhou and Q. Meng, *Metals*, 2020, **10**, 1660.
- 10 A. D. Wade, L. P. Wang and D. J. Huggins, *J Chem Inf Model*, 2018, **58**, 1766-1778.