Electronic Supplementary Information

Spotting aged dyes on paper with SERS

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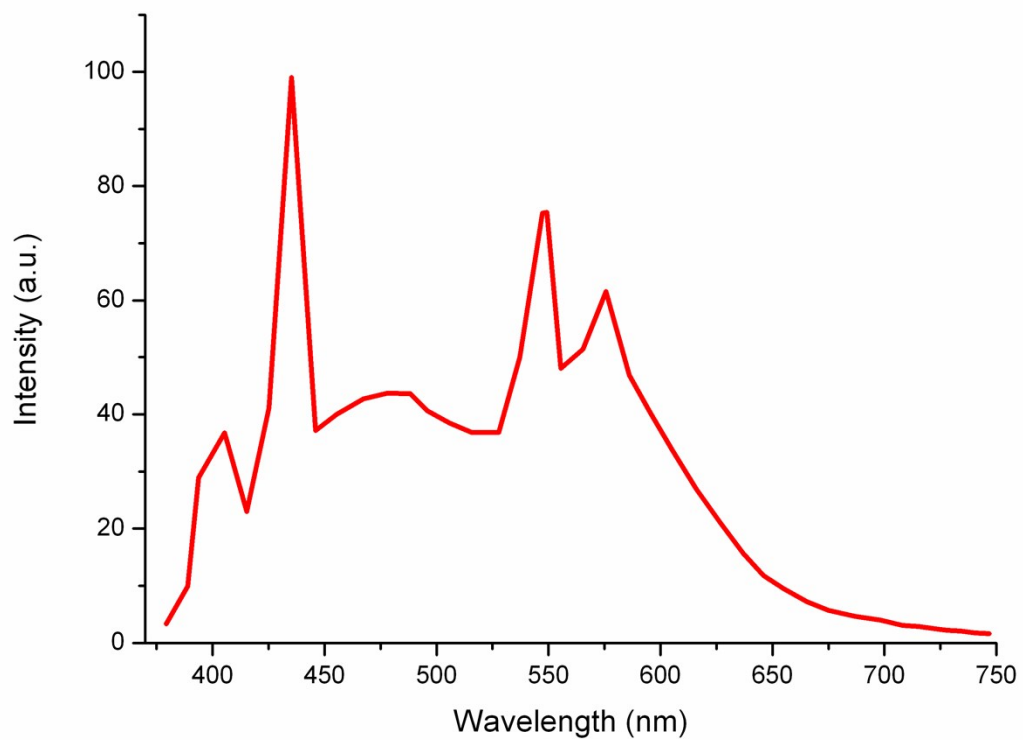
Fiorentino (Florence), Italy

Figure S1. Emission spectrum of the Neon Light Colour 765 BASIC Daylight Beghelli lamps used in the work.
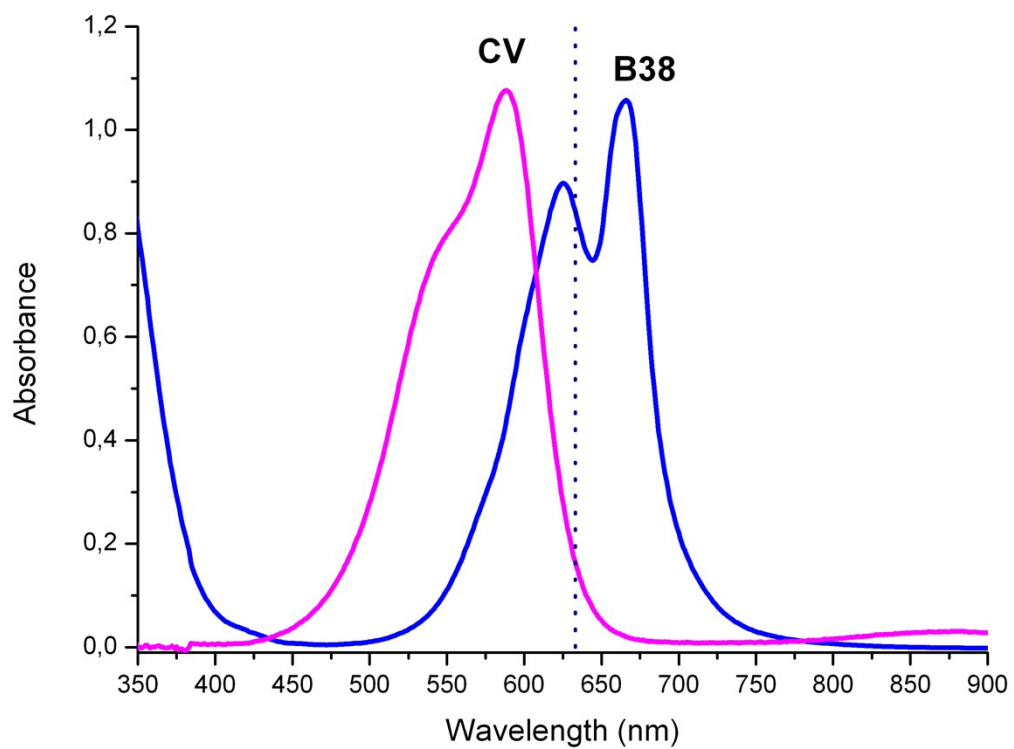
Figure S2. Visible spectra of Crystal Violet (CV) and Blue 38 (B38) in water solution. The black dotted line mark the position of the Raman laser wavelenght (633 nm) used in the work.
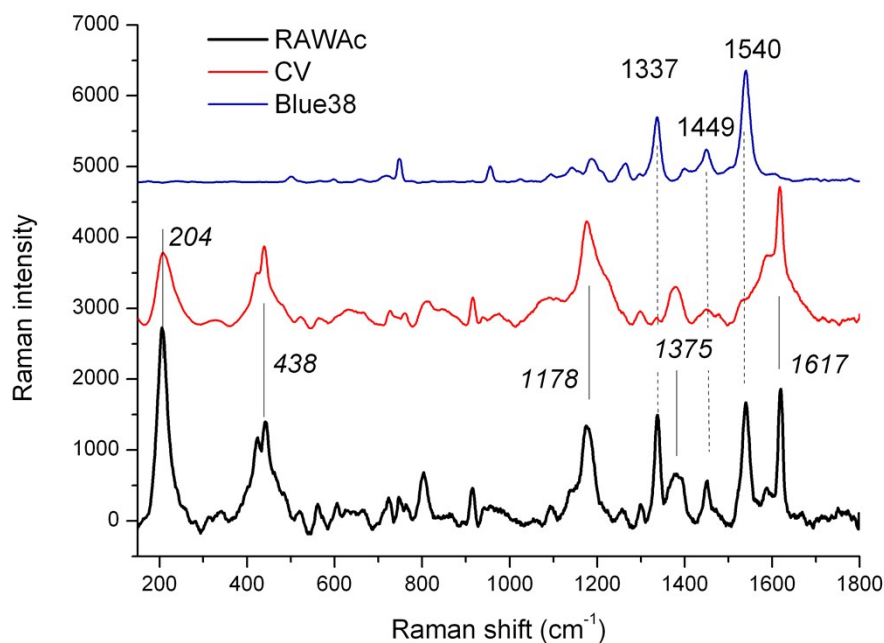
Figure S3. Raman spectrum of the inked area in RAWAc compared to the Raman spectra of reference dyes CV and B38 (the intensity scale of the reference compounds is shifted for clarity). The Raman spectrum of RAWSt, not shown, is very similar to RAWAc.

The most intense peaks at 1617, 1375, 1178, 438 and 204 cm-1 belong to CV, whereas those at 1540, 1449, 1335 cm-1 belong to B38.30,31 The solid lines mark the main bands belonging to CV, while the dotted lines mark the main bands belonging to B38. A complete assignment of the peaks is reported in Table S1. The Raman spectra of the RAWAc and RAWSt samples do not show significant differences, indicating that the substrate does not modify the structure and chemistry of the dyes.

Table S1. Assignments of the main bands observed in the experimental Raman spectra of: inked

samples (first column), Crystal Violet (CV, second column) and Solvent Blue 38 (B38, fourth

column). In the third column we listed the most closely involved benzene mode and the other main atomic motions associated with each vibration, according to Cañamares et al. [1]. Wilson's notation is also reported to identify benzene modes. In the fifth column the main atomic motions involved in the vibration of Blue 38 are listed on the basis of the work of Li, Peng et al [2].

Observed frequencies - Ink on paper	Observed frequencies - Crystal Violet	Assigned main vibrational modes of Crystal Violet (from literature) [a]	Observed frequencies - Solvent Blue 38	Assigned main vibrational modes due to internal vibrations of the phthalocyanine macrocycle of Solvent Blue 38 (from literature) [b]
206 vs	207 s	Benzene breath/$\tau(CH_3)$		
423 s	423 s	$\tau(CCCC)$ 16a/$\delta(CNC)$/$\delta(CC_{center}C)$		
442 s	439 s	$\tau(CCCC)$ 16a/$\delta(CNC)$		
605 w	608 w	$\delta(CCC)$/$\delta(CNC)$/$\nu_s(CC_{center}C)$		
747 w			748 m	$\nu_s(CuN)$/$\delta_s(CNC)$
763 w	761 w	$\nu^*(CCC)$ 6a/$\nu_s(CC_{center}C)$/$\nu(CN)$		
803 m	810 m	$\pi(CC')$/10a		
915 m	915 m, sh	$\pi(CN)$/17a		
			954 m	$\delta_s(NCuN)$/$\eta_{as}(N,N)$ on C_2/ρ_r(pyrrolic rings)
1137 m, sh	1140 vw, sh	$\delta(CC_{center}C)$/$\nu(CN)$	1142 m	$\delta(CH)$
1175 s	1177 vs	$\nu^*(CC')$ 9a/$\nu_s(CC_{center}C)$/$\nu_{as}(CC_{center}C)$/ $\delta(CCC)_{breathing}$/$\rho_r(CH_3)$	1186 m	$\rho_r(CH)$/$\delta(CH)$/$\delta_s(NCuN)$/$\rho_r(NCuN)$
1257 w	1259 w, sh		1264 m	$\rho_r(CC)$/$\rho_r(CH)$

1299 w	1298 w	$\nu_{as}(CC_{center}C)/\delta(CCC)_{ring}/\delta(CH)$			
1337 s	1336 w	$\delta(\text{ø-}N)/\delta(CCC)_{ring}/\nu_{as}(CC_{center}C)/\delta(CH)$		1338 s	$\nu_s(CN)/\delta_s(CNC)/\nu_s(CC)$
1379 m	1379 m	$\nu(\text{ø-}N)/\nu_{as}(CC_{center}C)/\delta(CCC)_{ring}/\delta(CH)$			
1450 m	1449 w, br	$\nu(CC)_{ring}$ 19b$/\delta_{as}(CH_3)$		1450 m	$\nu_s(CN)/\rho_r(CNC)$
1471 vw	1478 vw	$\nu(CC)_{ring}$ 19a$/\delta_{as}(CH_3)$			
1539 s	1533, m, sh	$\nu(CC)_{ring}/\nu(C_{ring}N)/\delta(CH_3)$	8b	1539 vs	$\nu_s(CN)/\delta_s(CNC)$
1586 w	1588 m, sh	$\nu(CC)_{ring}$ 8a			
1618 s	1617 vs	$\nu(CC)_{ring}$ 8a			

Vs: very strong; s, strong; m, medium; w, weak; vw, very weak, sh, shoulder. *v*, stretching (*s*, symmetric; *as*, asymmetric); ν^*, stretching substituent-sensitive mode of benzene; δ, bending; γ, out-of-plane deformation; τ, torsion; ρ_r, rocking; π, wagging; η, heaving of the bond in the specified direction as reported in *b*.
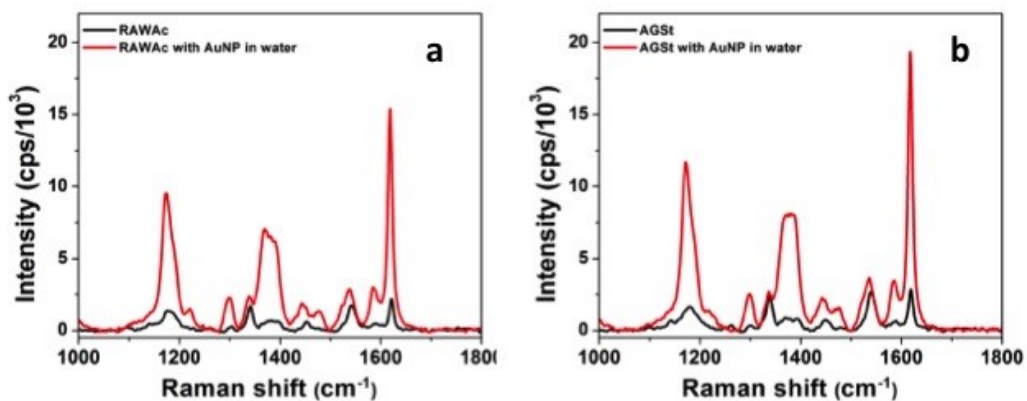
Figure S4. Comparison between the Raman (black line) and SERS (red line) spectra of RAWAc (a) and RAWSt (b) samples.

Short description of the colorimetric parameters discussed in the article

The CIELAB color space describes all the colors visible to the human eye using three coordinates: L* represent the lightness of the color and it changes from 0 (black) to 100 (diffuse white); a* is the green/magenta color component, with negatives values corresponding to green and positive values to magenta; b* is the blue/yellow color component, with negatives values corresponding to blue and positive values to yellow. Every existing color is therefore characterized by a set of three values, i.e. it is a point in the CIELAB space. The difference between two colors is expressed in terms of the ΔE* parameter. In the past, ΔE* was simply calculated as the Euclidean distance of two points in a three-dimensional space. During the years, several corrections have been introduced to the original formula to take into account the different response of the human eye to different colors. In the present study, the ΔE* parameter as a function of the ageing was calculated from the experimental colorimetric coordinates, obtained from reflectance spectra (standard illuminant D65 and a standard observer at 10°) according to the most recent definition, i.e., the CIEDE2000, which includes, among other corrections, compensations for lightness, chroma and hue. A complete description of the CIEDE2000 definition of ΔE* is reported elsewhere[3].

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