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*Supplementary Material*

# Red Dyes in Transition: Investigating Natural and Synthetic Colourants in Javanese Batik Textiles by HPLC-DAD-MS/MS and SERS

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## Images of TPM batik textiles

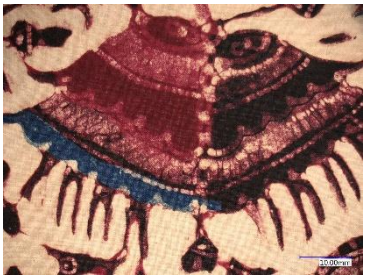
*Oeij Soen King, Pekalongan*

| Batik No. | Representative Image | Batik No. | Representative Image |
|---|---|---|---|
| TPM323 |  | TPM331 |  |
| TPM324 |  | TPM333 |  |
| TPM325 |  | TPM334 |  |

| | | | |
|---|---|---|---|
| TPM326 |  | TPM335 |  |
| TPM327 |  | TPM336 |  |
| TPM328 |  | TPM337 |  |
| TPM329 |  | TPM338 |  |
| TPM330 |  | | |

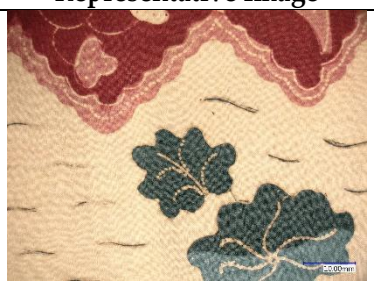
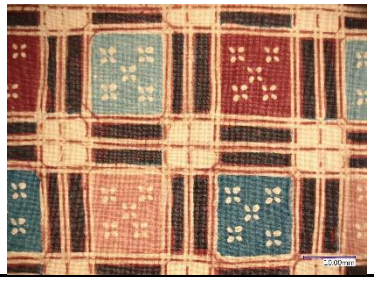
## Images of LKL batik textiles

*Ong Hong Hie, Lasem*

| Batik No. | Representative Image | Batik No. | Representative Image |
|---|---|---|---|
| LKL582 |  | LKL587 |  |
| LKL583 |  | LKL652 |  |
| LKL584 |  | LKL653 |  |
| LKL585 |  | LKL654 |  |
| LKL586 |  | LKL655 |  |

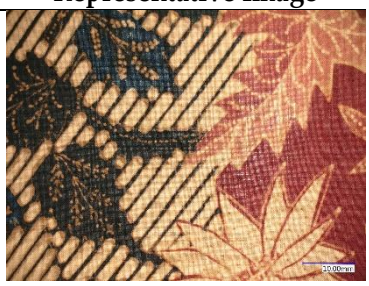
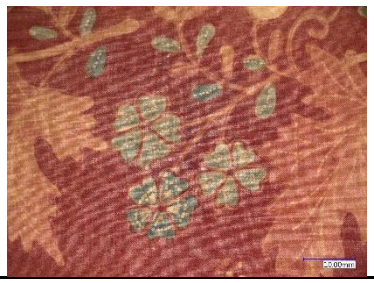
## Images of LKL batik textiles

*Eliza van Zuylen, Pekalongan*

| Batik No. | Representative Image | Batik No. | Representative Image |
|---|---|---|---|
| LKL175 |  | LKL825 |  |
| LKL176 |  | LKL992 |  |
| LKL928 |  | | |

## Images of LKL batik textiles

*J Jans, Pekalongan*

| Batik No. | Representative Image | Batik No. | Representative Image |
|---|---|---|---|
| LKL206 |  | LKL338 |  |
| LKL208 |  | LKL931 |  |
| LKL337 |  | | |

## Images of BM batik textiles

*Unknown workshop, Java, Cirebon, Madura (BM11 and BM26 from Mevr Fisfer, Pekalongan). All images are ©The Trustees of the British Museum.*

| Batik No. | Representative Image | Batik No. | Representative Image |
|---|---|---|---|
| BM2 |  | BM72 |  |
| BM11 |  | BM73 |  |
| BM14 |  | BM84 |  |
| BM26 |  | BM87 |  |
| BM27 |  | BM88 |  |

| | | | |
|---|---|---|---|
| BM51 |  | BM89 |  |
| BM55 |  | BM91 |  |
| BM62 |  | BM95 |  |
| BM66 |  | BM99 |  |
| BM70 |  | BMES |  |

## Supplementary Figures

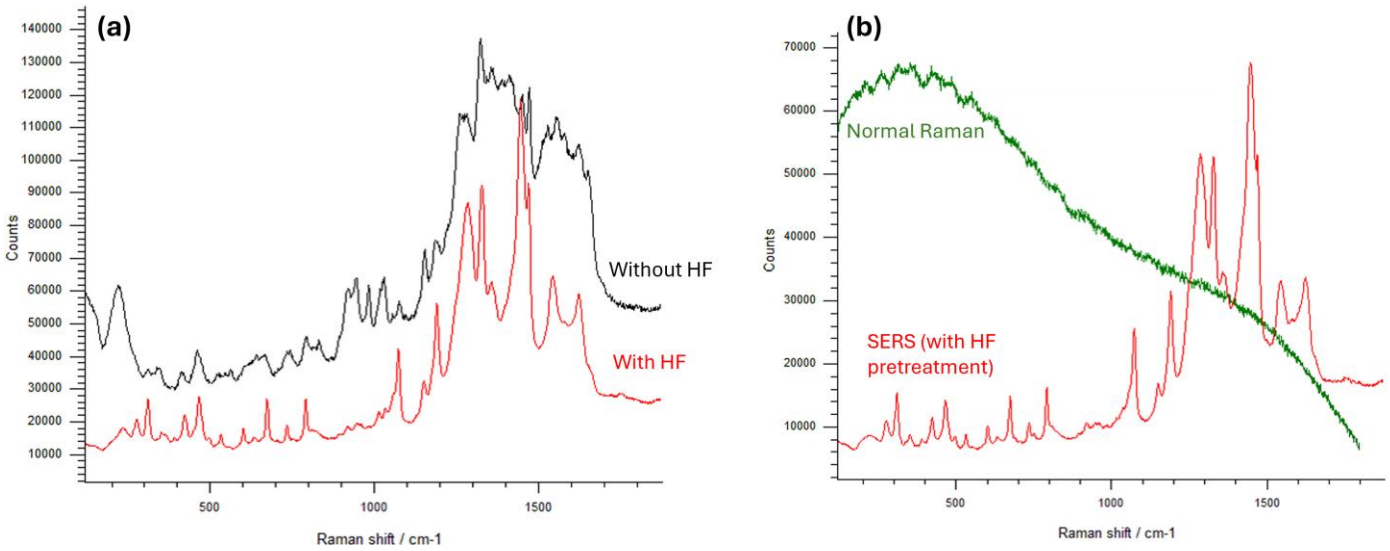



**Figure S1.** Different spectra qualities obtained with SERS and Normal Raman (NR) ($\lambda_{exc}$= 532 nm) on red dyed cotton obtained from a batik textile: **(a)** SERS (with and without HF pre-treatment) for the same sample LKL583; **(b)** NR and SERS with HF pretreatment for the same sample TPM337.

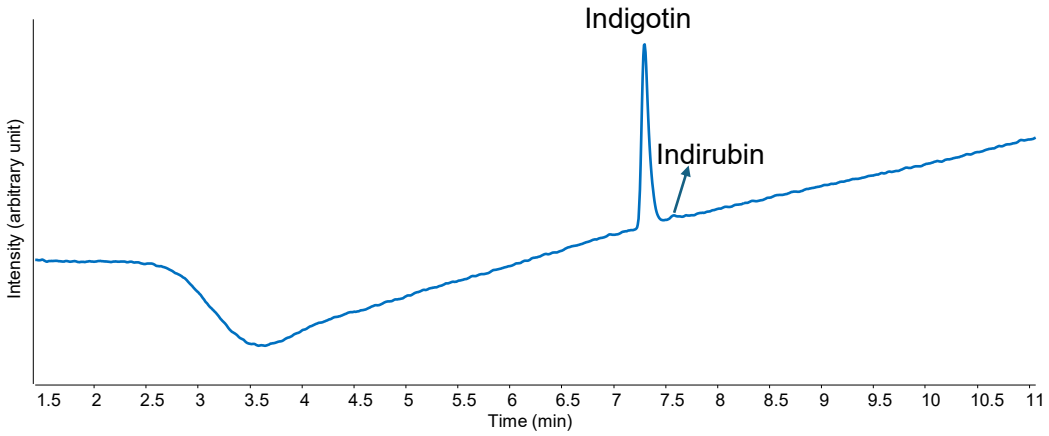
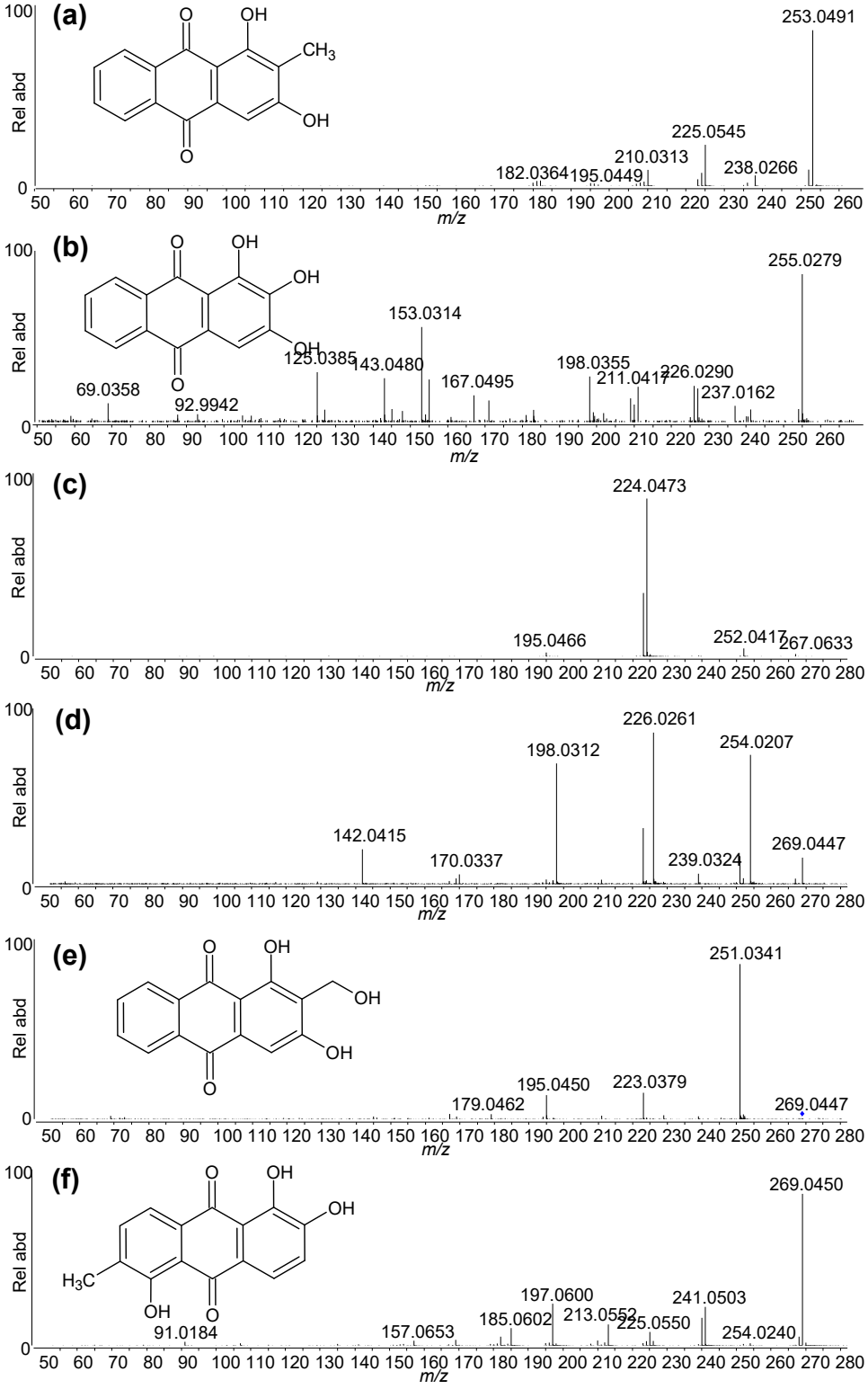



**Figure S2.** DAD chromatogram extracted at 600 nm of the blue sample from TPM327. ©The Trustees of the British Museum.


(a)
O
OH
CH3
OH
O
253.0491
225.0545
210.0313
238.0266
182.0364
195.0449
(b)
OH
OH
OH
O
255.0279
153.0314
125.0385
143.0480
167.0495
198.0355
211.0417
226.0290
237.0162
69.0358
92.9942
(c)
224.0473
195.0466
252.0417
267.0633
(d)
226.0261
198.0312
254.0207
142.0415
170.0337
239.0324
269.0447
(e)
OH
OH
OH
O
251.0341
195.0450
223.0379
179.0462
269.0447
(f)
OH
OH
H3C
OH
O
269.0450
197.0600
241.0503
213.0552
185.0602
225.0550
254.0240
91.0184
157.0653
Rel abd
m/z

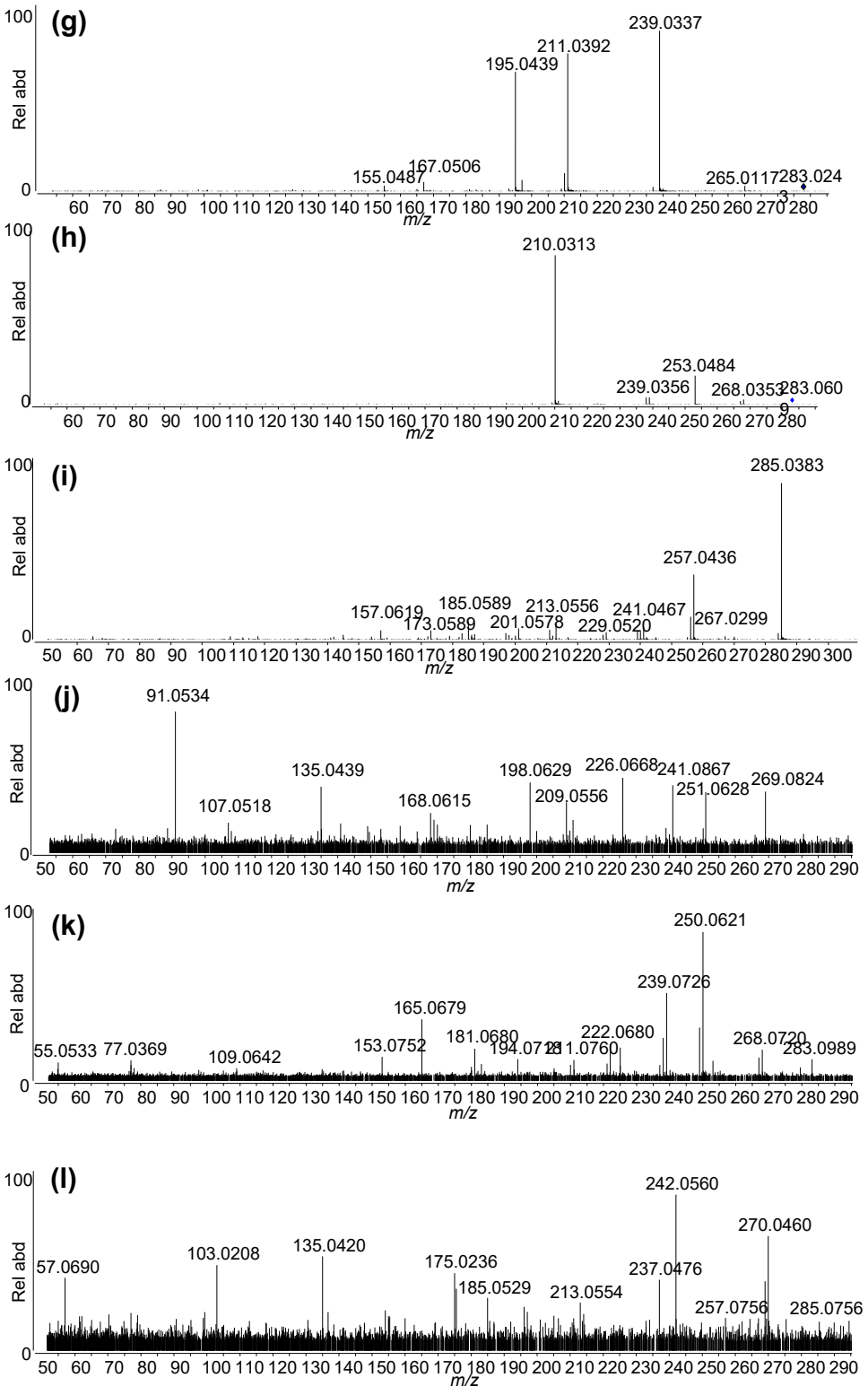



**Figure S3.** Tandem mass spectra in negative ionisation mode (**a-i**, collision energy = 30 eV) and positive ionisation mode (**j-l**, collision energy = 35 eV) of the main components detected in the *M. citrifolia* reference samples: (**a)** rubiadin; (**b)** anthragallol, (**c)** *m/z* 267.0656 – $C_{16}H_{12}O_4$; (**d)** *m/z* 269.0443 – $C_{15}H_{10}O_5$; (**e)** lucidin; (**f**) morindone; (**g**) *m/z* 283.0243 – $C_{15}H_8O_6$; (**h**) *m/z* 283.0609 - $C_{16}H_{12}O_5$; (**i**). *m/z* 285.0401 - $C_{15}H_{10}O_6$; (**j**) *m/z* 269.0803 – $C_{16}H_{12}O_4$; (**k**) *m/z* 283. 0967 - $C_{17}H_{14}O_4$; and (**l**) *m/z* 285.0756 - $C_{16}H_{12}O_5$. ©The Trustees of the British Museum.

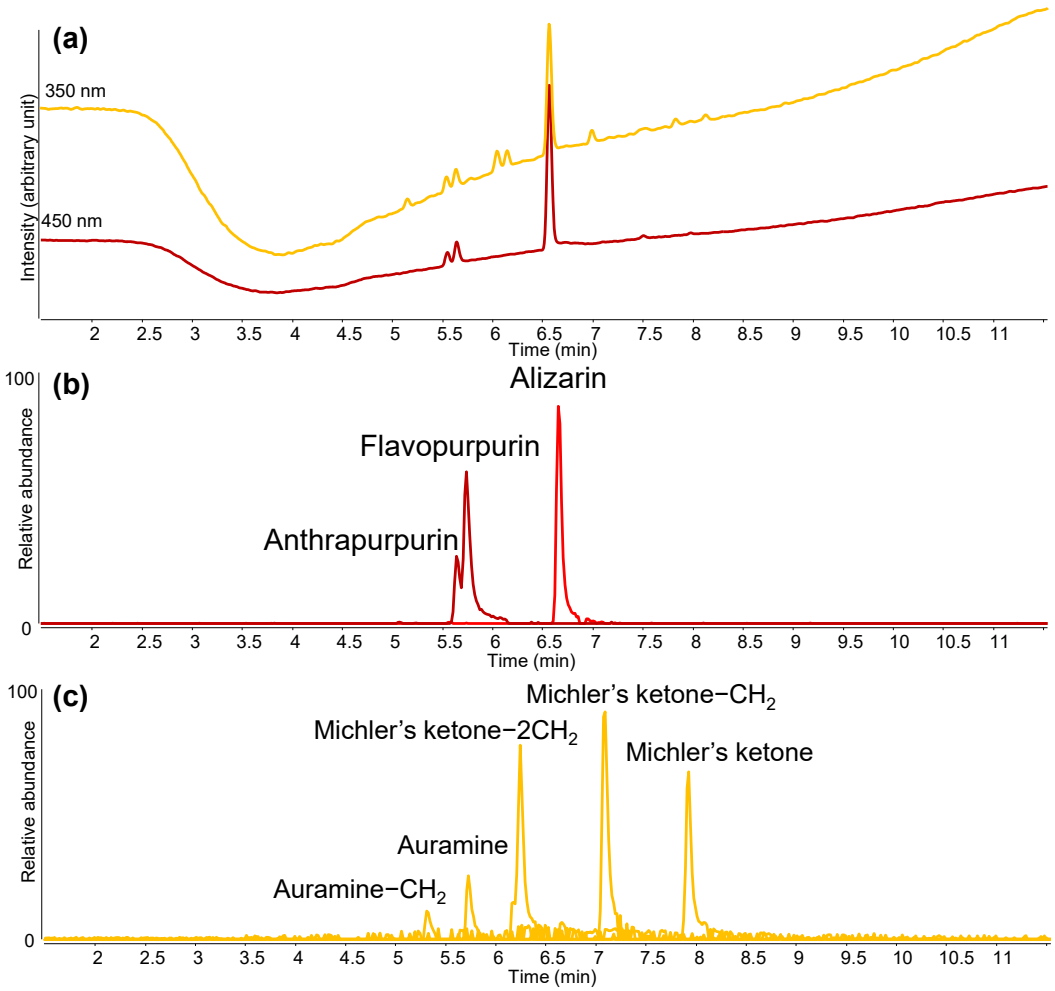



**Figure S4.** Results obtained from HPLC analysis of sample LKL653. **(a)** DAD chromatograms extracted at 350 and 450 nm; **(b)** extracted ion chromatograms in negative ionisation mode of $[M-H]^-$ = *m*/*z* 239.0343 (alizarin) and $[M-H]^-$= *m*/*z* 255.0308 (anthrapurpurin and flavopurpurin); **(c)** extracted ion chromatograms in positive ionisation mode of [M]+ = *m*/*z* 254.1652 (demethylated auramine), [M]+ = *m*/*z* 268.1808 (auramine), [M]+ = *m*/*z* 241.1335 (bisdemethylated Michler's ketone), [M]+ = *m*/*z* 255.1492 (demethylated Michler's ketone), [M]+ = *m*/*z* 269.1648 (Michler's ketone). ©The Trustees of the British Museum.

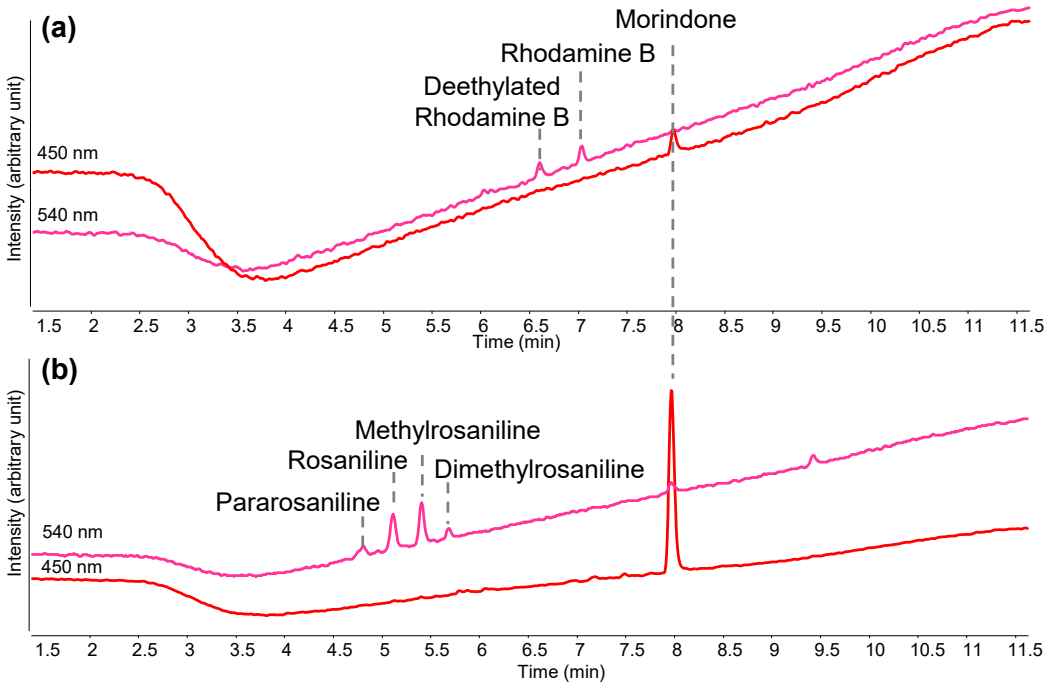



**Figure S5.** DAD chromatograms extracted at 450 and 540 nm of samples **(a)** BM11P (corresponding to Dye D in SERS analysis) and **(b)** BM2D (corresponding to Dye A and E in SERS analysis). The molecular components of rhodamine B (a) and fuchsin (b) are detected in addition to morindone. ©The Trustees of the British Museum.

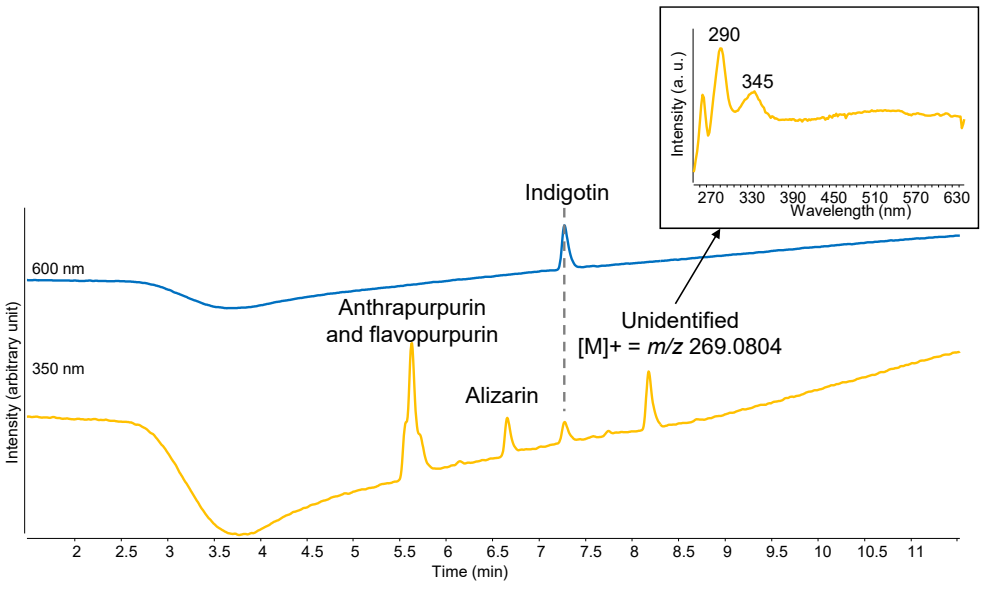



**Figure S6.** DAD chromatograms extracted at 350 and 600 nm of sample LKL655D, corresponding to Dye F in SERS analysis. The unidentified molecule is indicated and its UV-Vis absorption spectrum is reported (insert). ©The Trustees of the British Museum.

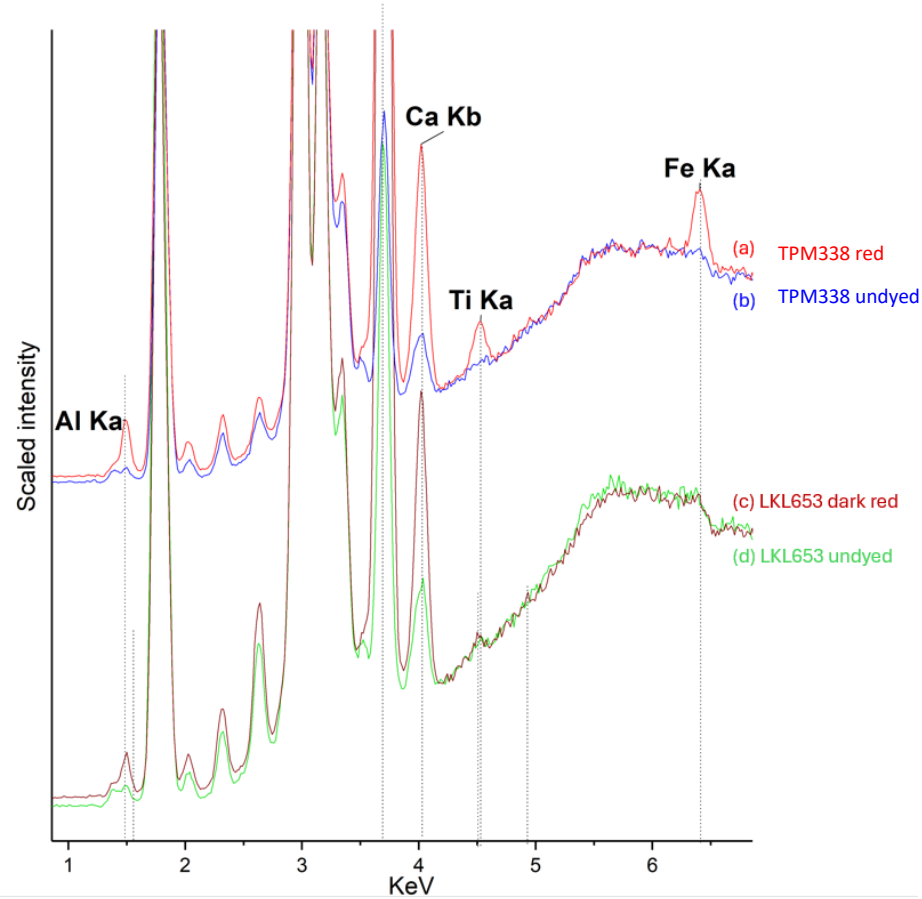



**Figure S7.** Example XRF spectrum of a red dyed and undyed area in a batik **(a)** red area on TPM338, **(b)** undyed area on TPM338, **(c)** red area on LKL653, **(d)** undyed area on LKL653. XRF of TPM and LKL reds all show minor amounts of calcium (Ca) and traces of aluminum (Al), not as evident in undyed areas. Traces of iron (Fe) and titanium (Ti) are also detected randomly.

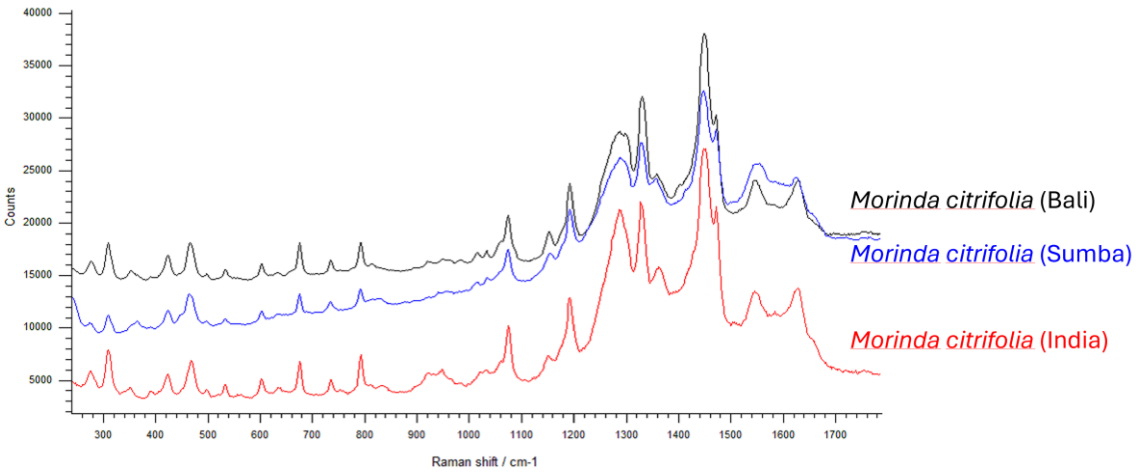



**Figure S8.** SERS spectra ($\lambda_{exc}$= 532 nm) of reference cotton samples dyed with *Morinda citrifolia* from India, Bali and Sumba. Samples are pretreated with HF.

## Supplementary Table

**Table S1.** Colorimetry (l, a, b) results of red shades on batik texitles, for plotting Figure 7.

| Sample No. | HPLC result | L* | a* | b* | Pseudo-colour |
|---|---|---|---|---|---|
| TPM323 | *Morinda* | 27.03 | 28.12 | 10.55 | |
| TPM324 | *Morinda* + synthetic | 28.69 | 31.82 | 12.93 | |
| TPM325 | *Morinda* + synthetic | 28.61 | 31.06 | 12.72 | |
| TPM326 | *Morinda* | 26.49 | 28.7 | 12.5 | |
| TPM327 | *Morinda* | 25.39 | 25.49 | 9.85 | |
| TPM327D | *Morinda* + indigo | 20.73 | 11.29 | 2.75 | |
| TPM328 | *Morinda* | 22.82 | 22.15 | 8.45 | |
| TPM329 | *Morinda* | 27.7 | 25.42 | 11.24 | |
| TPM330 | *Morinda* | 25.83 | 26.07 | 11.66 | |
| TPM331 | *Morinda* | 29.68 | 32.62 | 16.69 | |
| TPM333 | *Morinda* | 27.36 | 32.17 | 16.52 | |
| TPM334 | *Morinda* | 30.29 | 28.72 | 17.27 | |
| TPM335 | *Morinda* | 27.57 | 28.96 | 13.4 | |
| TPM336 | *Morinda* | 27.59 | 32.25 | 16.38 | |
| TPM337 | *Morinda* | 33.12 | 33.88 | 21.5 | |
| TPM337D | *Morinda* + indigo | 21.67 | 5.54 | 3.24 | |
| TPM338 | *Morinda* | 27.52 | 31.43 | 17.21 | |
| LKL582 | *Morinda* | 28.89 | 30.36 | 17.19 | |
| LKL583 | *Morinda* | 28.57 | 30.39 | 16.44 | |
| LKL584 | *Morinda* | 25.96 | 26.1 | 14.07 | |
| LKL585 | *Morinda* | 28.94 | 29.79 | 17.72 | |
| LKL586 | *Morinda* | 27.53 | 28.28 | 14.27 | |
| LKL587 | *Morinda* | 26.73 | 29.4 | 15.74 | |
| LKL652 | synthetic | 25.83 | 33.84 | 16.14 | |
| LKL653 | synthetic | 24.42 | 28.99 | 11.78 | |
| LKL653D | synthetic + indigo | 18.07 | 5.41 | 0.25 | |
| LKL654 | synthetic | 24.63 | 28.8 | 11.92 | |
| LKL655 | synthetic | 26.73 | 33.59 | 16.37 | |
| LKL655D | synthetic + indigo | 19.52 | 8.92 | 3.44 | |
| LKL175 | *Morinda* | 33.39 | 34.89 | 18.07 | |
| LKL176 | synthetic + indigo | 27.45 | 21.11 | 6.75 | |
| LKL928 | *Morinda* | 35.71 | 35.58 | 22.07 | |
| LKL825 | synthetic | 26.32 | 22.73 | 10.81 | |
| LKL992 | *Morinda* + synthetic | 32.28 | 35.8 | 19.9 | |
| LKL206 | *Morinda* | 31.82 | 26.79 | 15.86 | |
| LKL206D | *Morinda* + indigo | 25.29 | 13.17 | 7.39 | |
| LKL208 | *Morinda* + synthetic | 25.65 | 29.14 | 11.97 | |
| LKL208B | *Morinda* + synthetic | 38.05 | 43.79 | 19.65 | |
| LKL337 | *Morinda* | 32.12 | 28.51 | 17.87 | |
| LKL338 | *Morinda* | 31.16 | 30.88 | 18.04 | |
| LKL931 | *Morinda* | 26.64 | 26.32 | 12.66 | |

| Sample No. | HPLC result | L* | a* | b* | Pseudo-colour |
|---|---|---|---|---|---|
| BM2D | *Morinda* + synthetic | 17.98 | 15.9 | 6.46 | |
| BM11P | *Morinda* + synthetic | 52.99 | 18.45 | 14.63 | |
| BM11L | *Morinda* | 35.86 | 36.98 | 17.51 | |
| BM11D | *Morinda* | 24.39 | 27.06 | 10.52 | |
| BM14 | *Morinda* | 23.77 | 22.14 | 9.47 | |
| BM26L | *Morinda* | 38.24 | 31.96 | 14.96 | |
| BM26D | *Morinda* | 27.71 | 25.23 | 9.12 | |
| BM27 | *Morinda* + indigo | 29.69 | 31.2 | 16.1 | |
| BM51 | *Morinda* | 31.14 | 31.61 | 15.19 | |
| BM55P | *Morinda* | 44.45 | 26.12 | 18.32 | |
| BM55 | *Morinda* + synthetic+ indigo | 29 | 25.55 | 11.32 | |
| BM62L | synthetic | 40.77 | 38.46 | 20.87 | |
| BM66 | *Morinda* | 28.14 | 28.18 | 17.93 | |
| BM70D | *Morinda* + synthetic | 20.73 | 24.01 | 8.32 | |
| BM72 | *Morinda* | 26.49 | 29.64 | 14.11 | |
| BM73 | *Morinda* | 21.78 | 22.8 | 8.64 | |
| BM84R | *Morinda* + synthetic | 34.11 | 29.82 | 21.52 | |
| BM84 | *Morinda* + synthetic | 32.96 | 39.4 | 19 | |
| BM87 | *Morinda* | 24.96 | 24.98 | 11.31 | |
| BM88D | *Morinda* + indigo | 18.37 | 6.26 | 0.05 | |
| BM89 | *Morinda* | 29.45 | 34.46 | 19.78 | |
| BM91 | *Morinda* | 29.1 | 26.64 | 14.67 | |
| BM95 | *Morinda* | 27.36 | 24.16 | 11.92 | |
| BM99 | *Morinda* | 34.46 | 32.83 | 19.29 | |
| BM99P | *Morinda* | 50.32 | 27.75 | 23.53 | |
| BMES | *Morinda* | 25.91 | 24.79 | 9.58 | |