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Supporting information

Swellable SERS-active Polymer Films for the Forensic Examination of Blue Gel Inks and their Constituent Dyes

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Contents:

Figure S7: The chemical structures of standard dyes: (a) Victoria Pure Blue BO; (b) Victoria Blue R; (c) Victoria Blue B.

Figure S8: The SERS spectra of (a) Victoria Pure Blue BO, (b) Victoria Blue R and (c) Victoria Blue B using 633 nm excitation

Figure S9: The SERS spectra of (a) Victoria Pure Blue BO, (b) Victoria Blue R and (c) Victoria Blue B using 785 nm excitation

Table S2. List of pens studied and country of origin.

Figure S10: The SERS spectra of Group 1 samples and Brilliant Blue G using 633 nm excitation. The highlighted region shows their differences.

Figure S11: The SERS spectra Group 2 using 633 nm excitation. The coloured regions highlight the bands which are different in each group.

Figure S12 The 633 nm SERS spectrum of the Group 3 sample.

Figure S13: The SERS spectra of Pilot Acoball, Zebra Surai and Pilot Super Grip and their corresponding dye standards using 785 nm excitation

Figure S14: The SERS spectra of the Group 1* samples and Brilliant Blue G using 785 nm excitation. The pink region highlights the differences between the subgroups.

Figure S15: The TLC plate and the 785 nm SERS spectrum of the Staedeler Silver Ball sample

Table S1. Standard blue dyes studied and their absorbance wavelength (taken from Sigma-Aldrich product information)

Dye	Absorbance Maximum
Brilliant Blue G	610 nm (in ethanol)
Erioglaucine	627 - 631 nm (in water)
Ethyl Violet	593 - 599 nm (in water)
Crystal Violet	588 nm
Methyl Violet B base	580 nm
Victoria Pure Blue BO	619nm
Victoria Blue R	615nm
Victoria Blue B	592nm
Patent Blue V	638nm (in water)
Patent Blue VF	635 - 641 nm (in water)

SERS of dye standards

Brilliant Blue G and Erioglaucine

The molecular structures of Brilliant Blue G and Erioglaucine are shown in Figure S1. With either 633 or 785 nm excitation, their SERS spectra were different from each other, as shown in Figure S2 and 3.

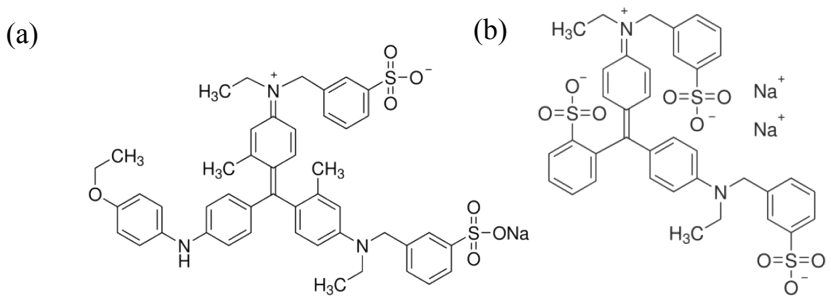

Figure S1: The molecular structure of standard dye: (a) Brilliant Blue G; (b) Erioglaucine.

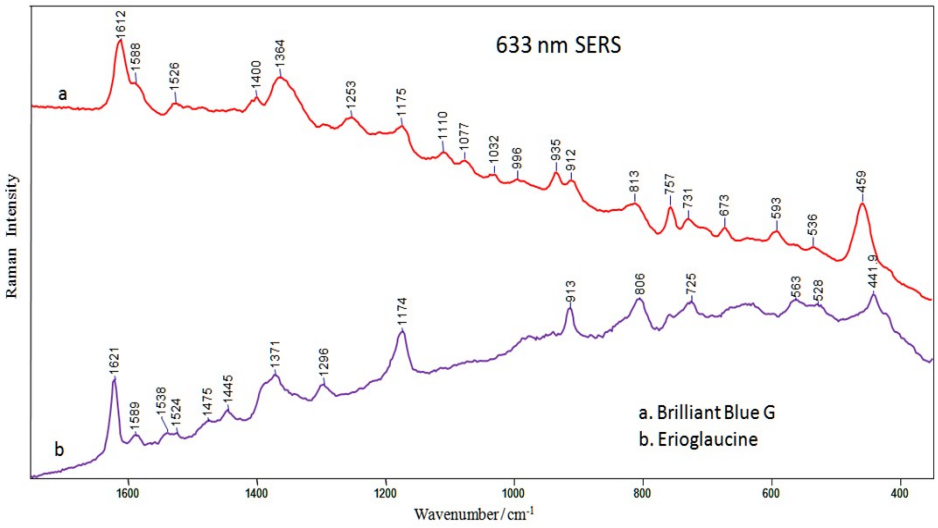

Figure S2: The SERS spectra of (a) Brilliant Blue G and (b) Erioglaucine using 633 nm excitation.

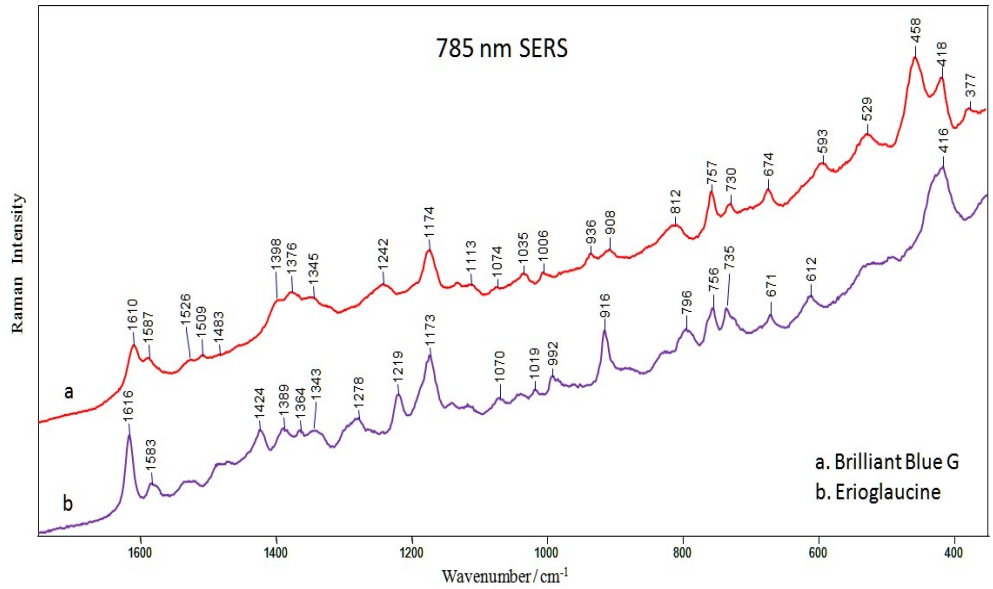

Figure S3: The SERS spectra of (a) Brilliant Blue G and (b) Erioglaucine using 785 nm excitation

Ethyl Violet, Crystal Violet and Methyl Violet B base

The molecular structures of Ethyl Violet Crystal Violet and Methyl Violet B are shown in Figure S4. With 633 nm excitation, Ethyl Violet is slightly different from Crystal Violet and Methyl Violet B base, as it shows five extra distinctive bands at 1423, 1187, 1161, 1075 and 458 cm^{-1}. Those bands are not present in Crystal Violet and Methyl Violet B base. The SERS spectra of Crystal Violet and Methyl Violet B base are extremely similar. The only discernible difference is in the profile of the band around 1374 cm^{-1} as shown in Figure S5 and S6.

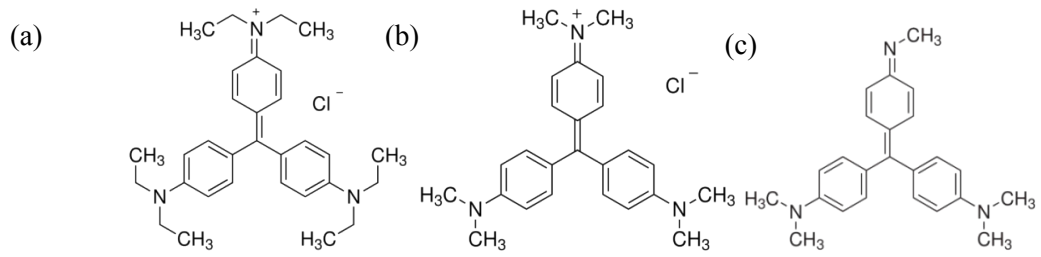

Figure S4: The chemical structure of standard dyes: (a) Ethyl Violet; (b) Crystal Violet; (c) Methyl Violet B base.

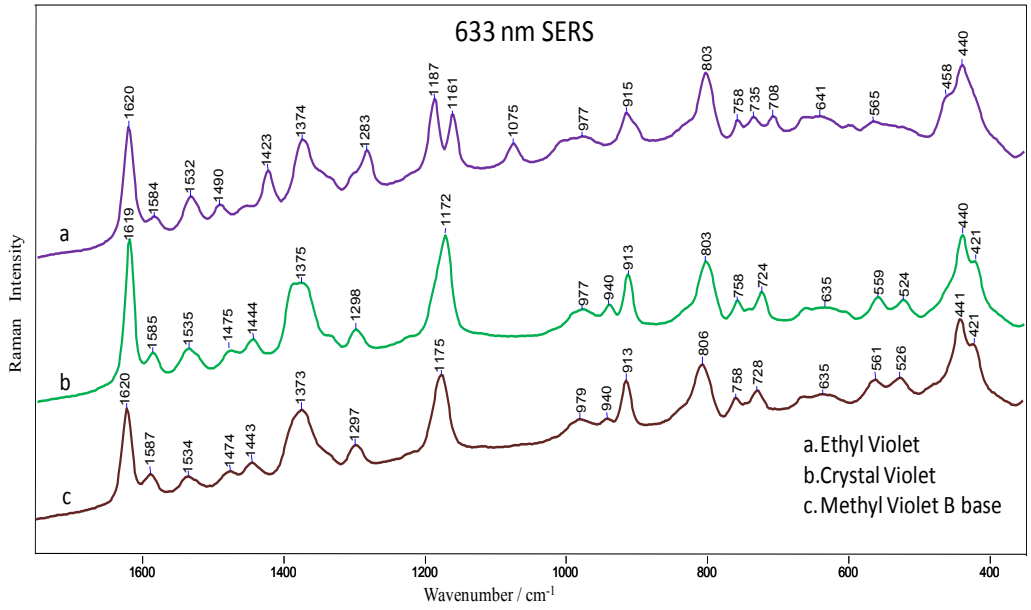

Figure S5: The SERS spectra of (a) Ethyl Violet, (b) Crystal Violet and (c) Methyl Violet B using 633 nm excitation.

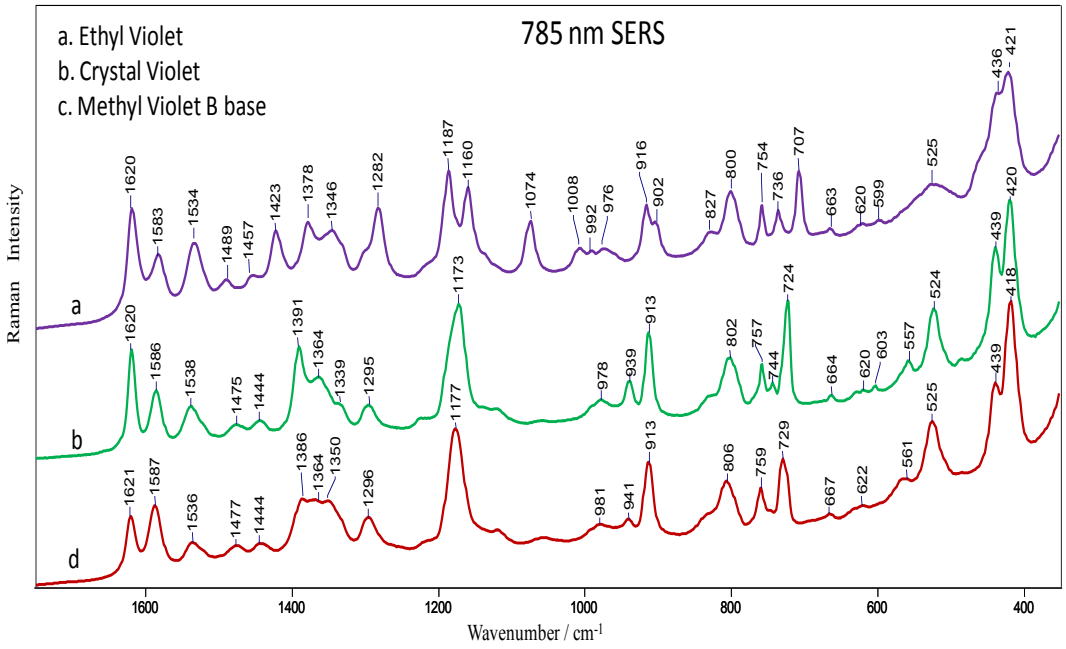

Figure S6: The SERS spectra of (a) Ethyl Violet, (b) Crystal Violet and (c) Methyl Violet B base using 785 nm excitation.

Victoria Pure Blue BO, Victoria Blue R and Victoria Blue B

The molecular structures Victoria Pure Blue BO, Victoria Blue R and Victoria Blue B are shown in Figure S7. All of these could be distinguished from each other using 633 nm SERS (Figure S8).

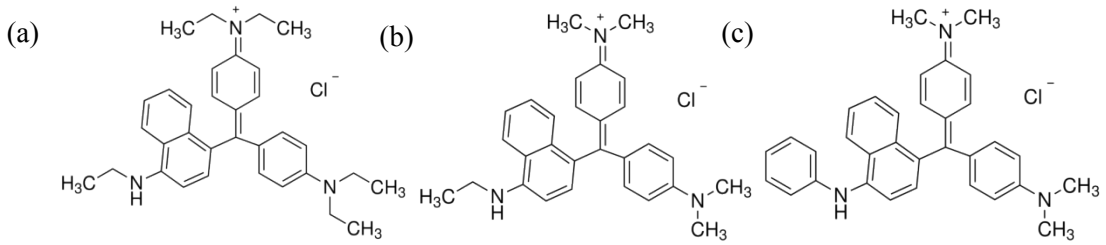

Figure S7: The chemical structures of standard dyes: (a) Victoria Pure Blue BO; (b) Victoria Blue R; (c) Victoria Blue B.

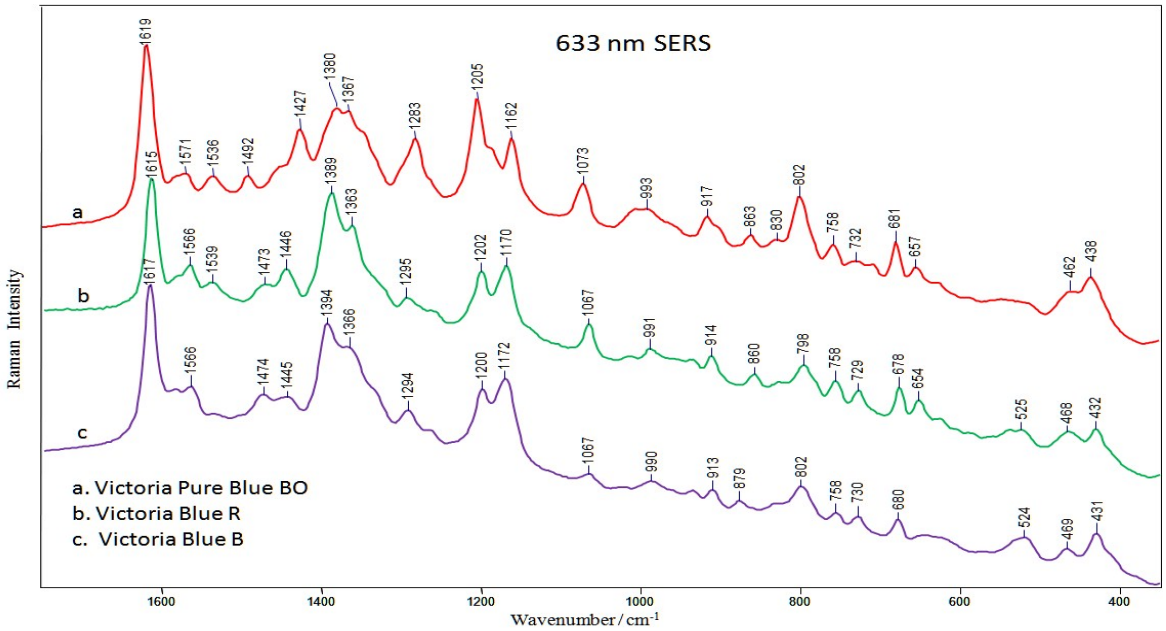

Figure S8: The SERS spectra of (a) Victoria Pure Blue BO, (b) Victoria Blue R and (c) Victoria Blue B using 633 nm excitation.

The SERS spectra of these dyes were also collected using 785 nm excitation (Figure S9).

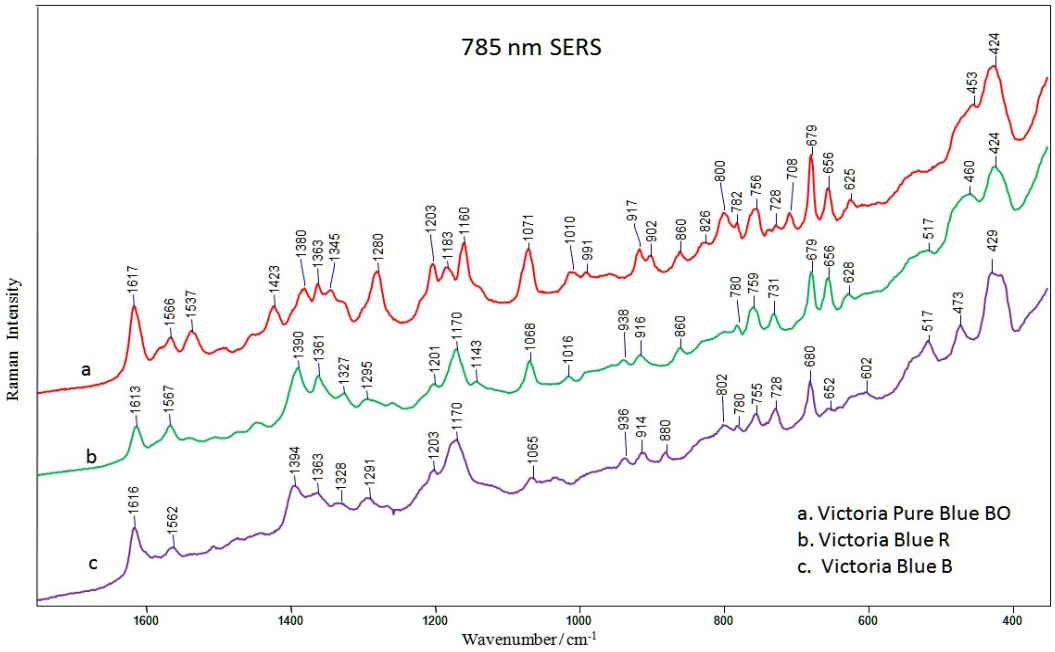

Figure S9: The SERS spectra of (a) Victoria Pure Blue BO, (b) Victoria Blue R and (c) Victoria Blue B using 785 nm excitation.

SERS of pen inks at 633and 785 nm excitation

Table S2. List of the various pens which were tested at 633 and 785 nm and the country where they were purchased.

- Pilot Acroball (TWN)
- Zebra Surai (TWN)
- Pilot G-1 (U.K)
- Pilot G-2 (U.K)
- Pilot G-2 (TWN)
- Pilot G2 (SIN)
- Zebra Z-Grip (U.K)
- Pilot V7 (U.K)
- Pilot Super Grip (TWN)
- Pentel Energel (U.K)
- Pentel Energel (TWN)
- Pentel Ball (U.K)
- Staedler Silver Bell (U.K)

Group 1

Group 1 pens were composed of mainly Brilliant Blue G as shown in Figure S10.

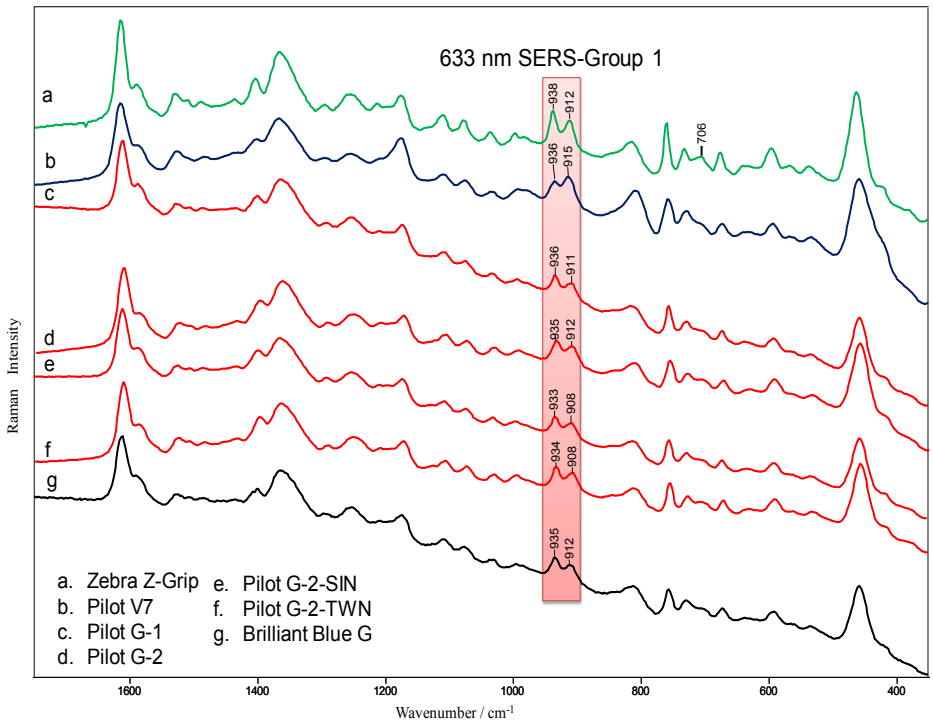

Figure S10: The SERS spectra of Group 1 samples and Brilliant Blue G using 633 nm excitation. The highlighted region shows their differences.

Group 2

The spectra of these pens resembled that of Crystal Violet or Methyl Violet B base as shown in Figure S11.

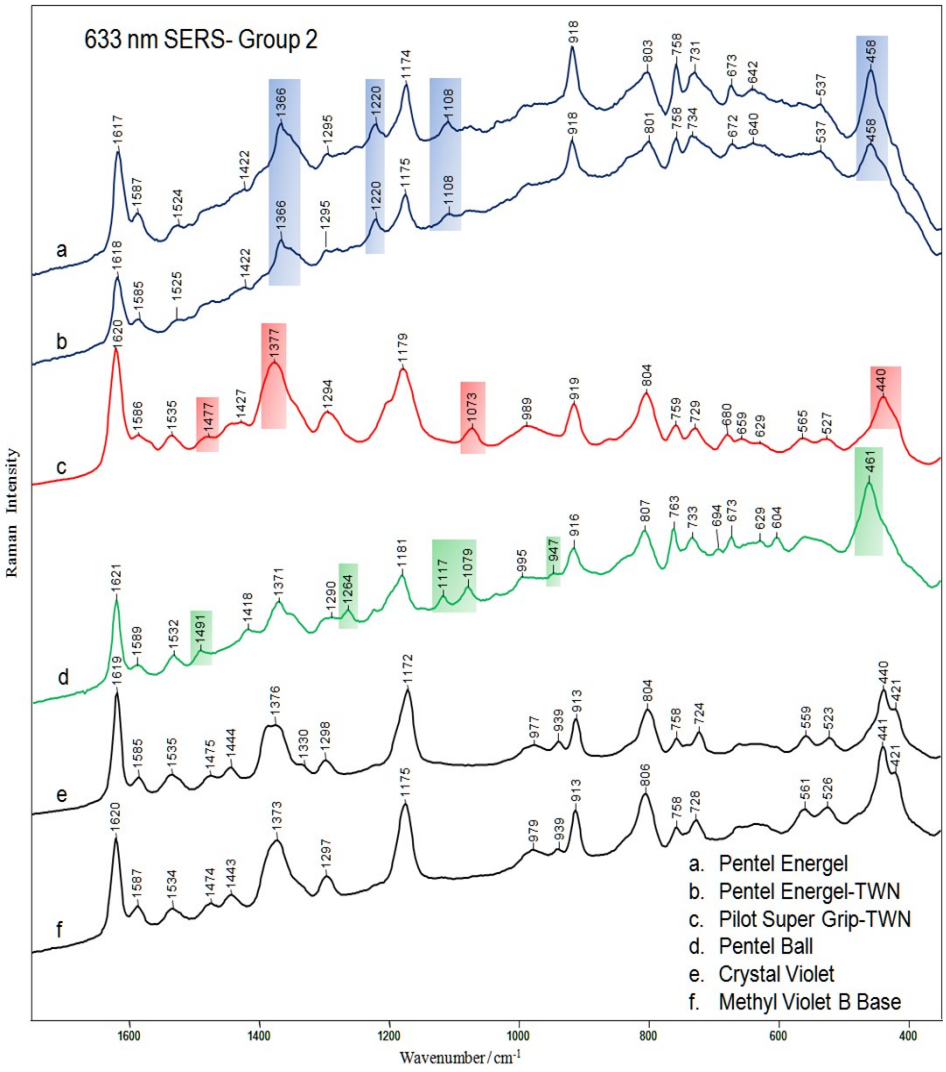

Figure S11: The SERS spectra Group 2 using 633 nm excitation. The coloured regions highlight the bands which are different in each group.

Group 3

Group 3 is comprised a single sample whose spectrum does not match to any of the ten standard blue dyes tested. Its SERS spectrum is shown in Figure S12.

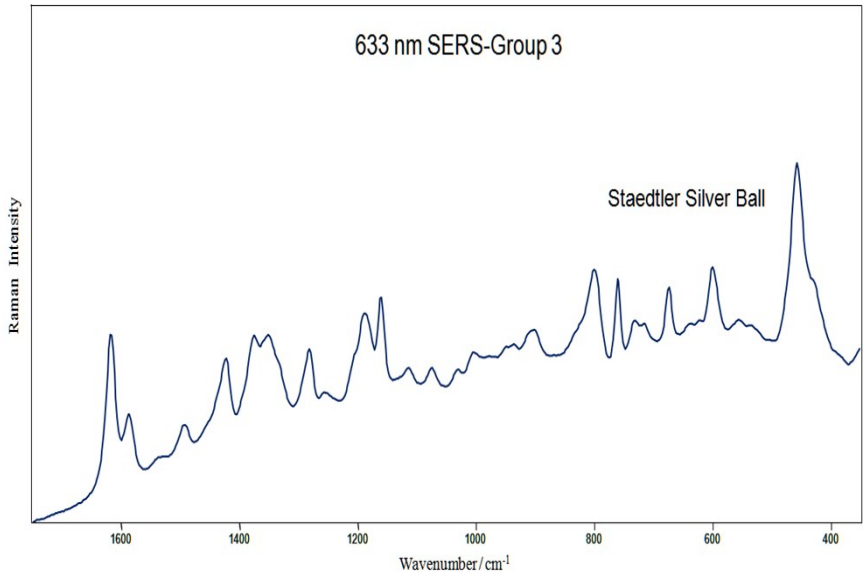

Figure S12 The 633 nm SERS spectrum of the Group 3 sample.

SERS of pen inks at 785 nm excitation

Pilot Acroball (TWN), Zebra Surari (TWN) and Pilot Super grip (TWN) could be directly matched to one type of standard are shown in Figure S13.

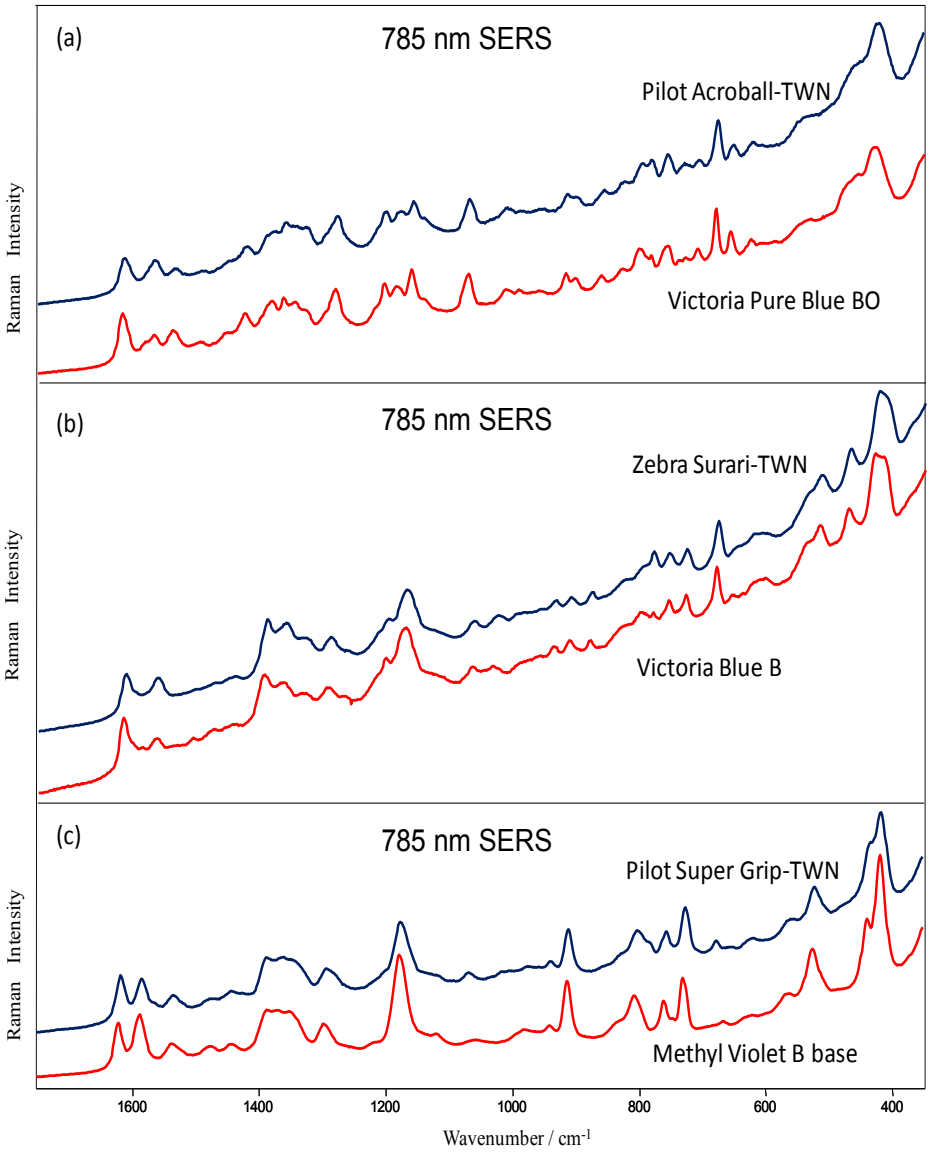

Figure S13: The SERS spectra of Pilot Acoball, Zebra Surai and Pilot Super Grip and their corresponding dye standards using 785 nm excitation.

*Group 2**

Group 2* consisted of one pen; Staedeler Silver Ball. Consistent with 633 nm excitation, the spectrum did not match any of the ten standard blue dyes tested in this work. After TLC separation of the ink, only a single blue line showed on the TLC plate, therefore, the main dye in this sample is single blue unknown dye. Figure S15 shows the TLC plate result and the SERS spectrum of sample.

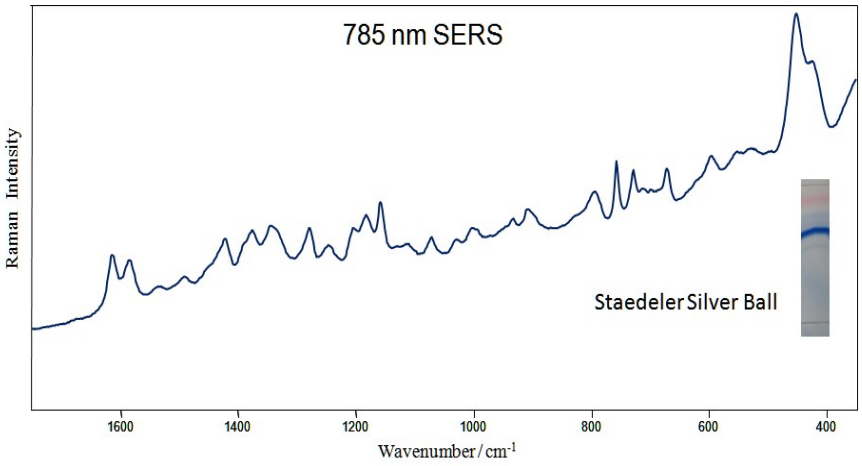

Figure S15: The TLC plate and the 785 nm SERS spectrum of the Staedeler Silver Ball sample.