SUPPLEMENTAL MATERIAL

1 - Folios and areas of analysis

Figure S1.1. Folio 4, areas of analysis for microXRF (○), FORS (●), micro-samples for Raman and FTIR (●) and Raman in-situ (●).

Figure S1.2. Folio 10, areas of analysis for microXRF (○) and FORS (●).

Figure S1.3. Folio 16, areas of analysis for micro-samples for Raman and FTIR (●).

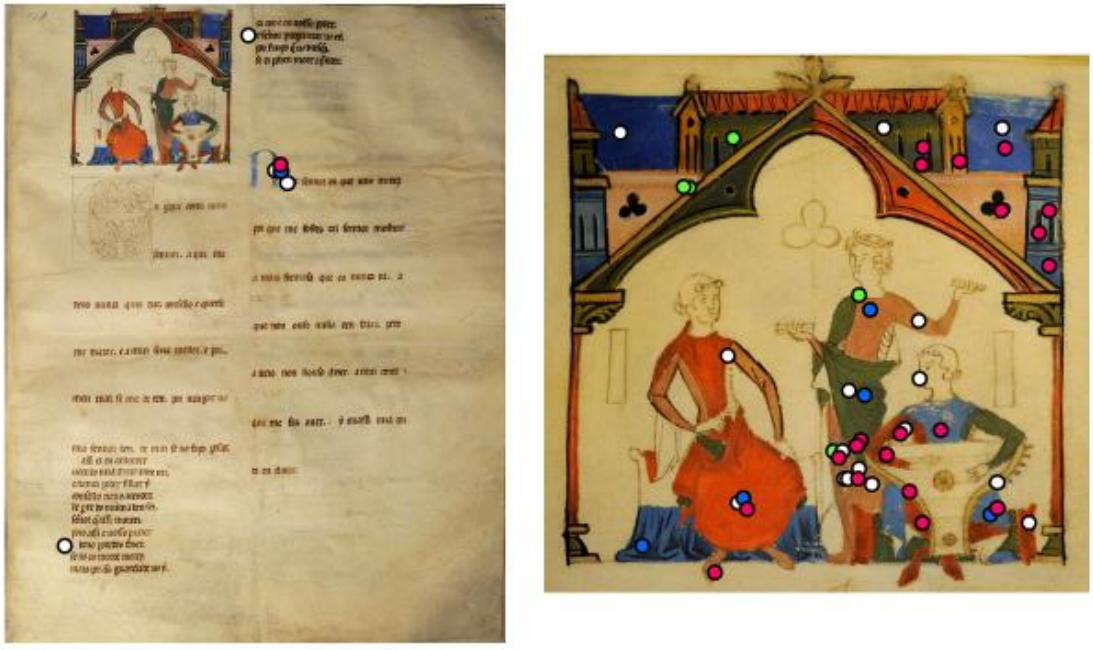

Figure S1.4. Folio 17, areas of analysis for microXRF (○), FORS (●), micro-samples for Raman and FTIR (●) and Raman in-situ (●).

Figure S1.5. Folio 21, areas of analysis for microXRF (○), FORS (●) and micro-samples for Raman and FTIR (●).

Figure S1.6. Folio 33, areas of analysis for microXRF (○) and FORS (●).

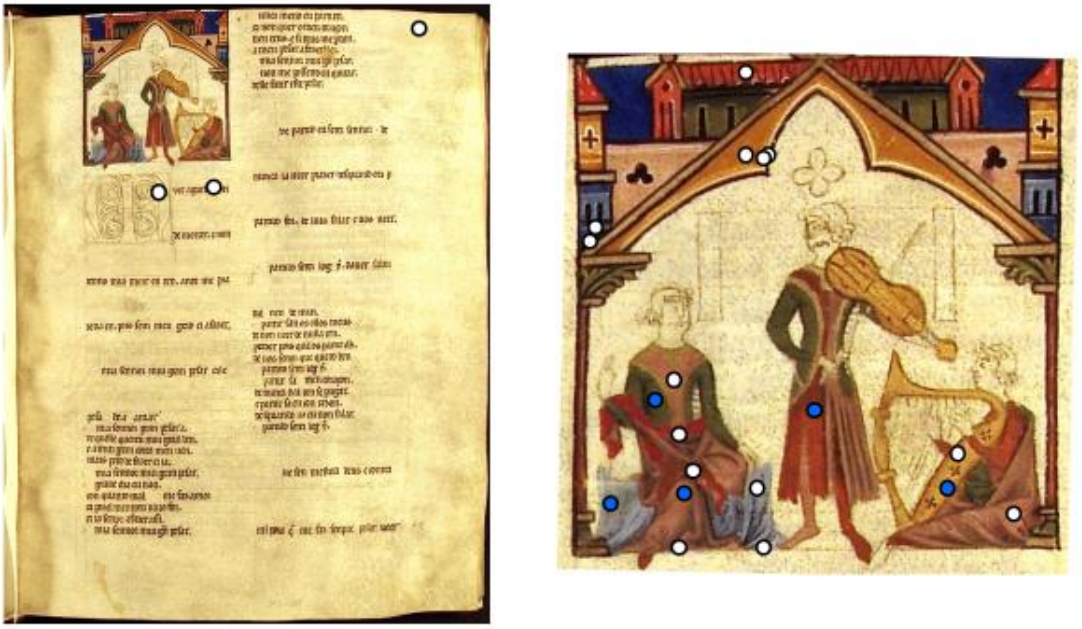

Figure S1.7. Folio 37, areas of analysis for microXRF (○) and FORS (●).

Figure S1.8. Folio 40v, areas of analysis for microXRF (○), FORS (●) and micro-samples for Raman and microFTIR (●).

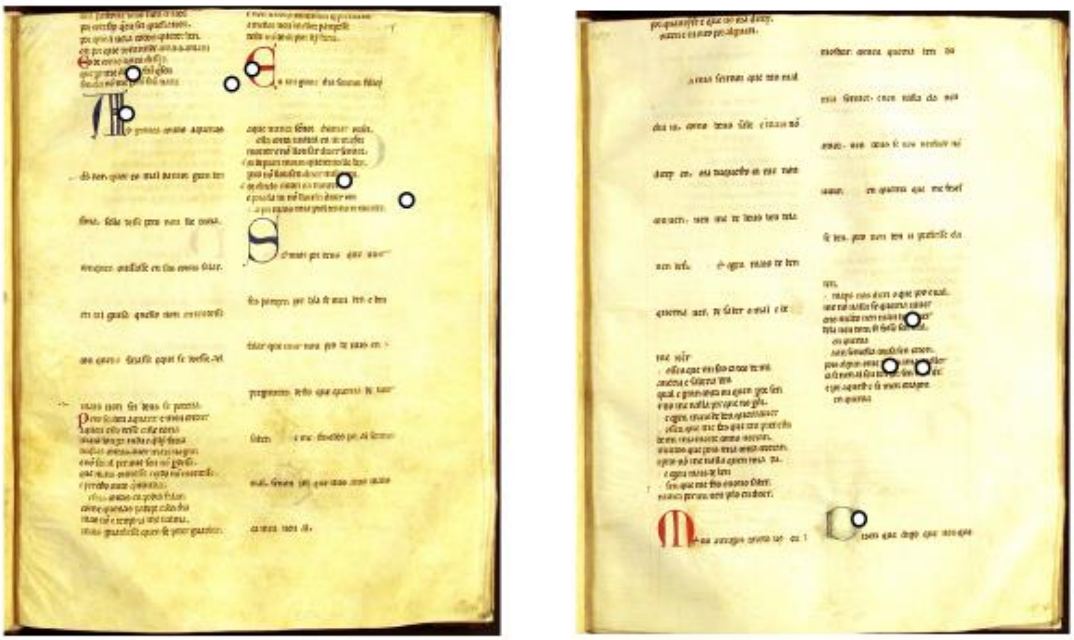

Figure S1.9. Folios 43 (left) and 45 (right), areas of analysis for microXRF (○).

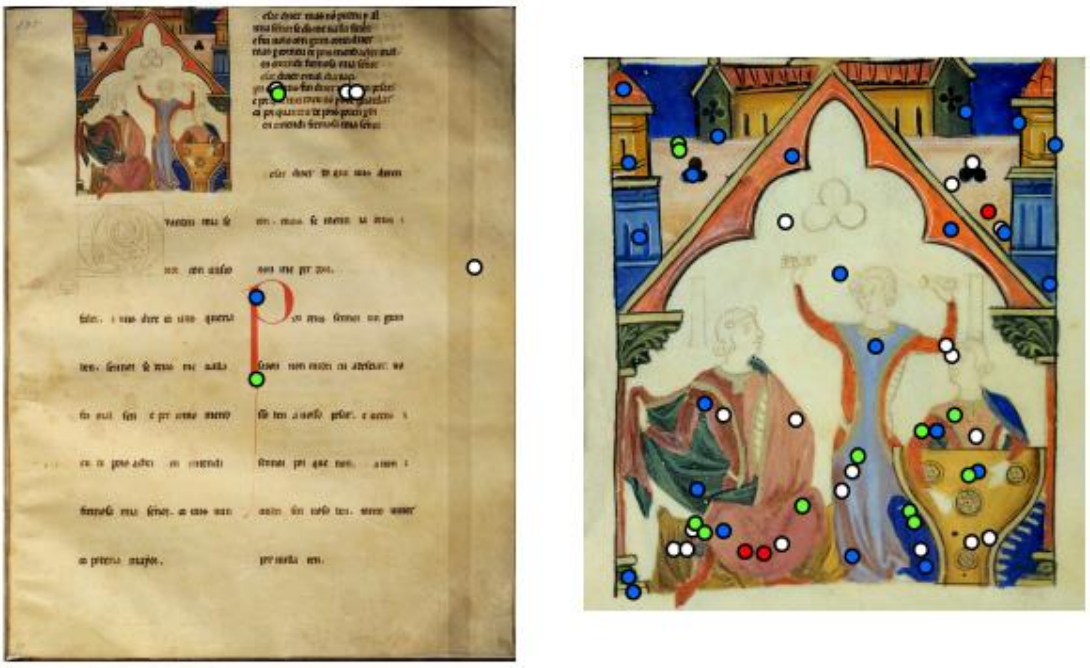

Figure S1.10. Folio 59, areas of analysis for microXRF (○), FORS (●), micro-samples for Raman and FTIR (●) and microspectrofluorimetry (●).

Figure S1.11. Folios 68v (left) and 70 (right), areas of analysis for microXRF (○).

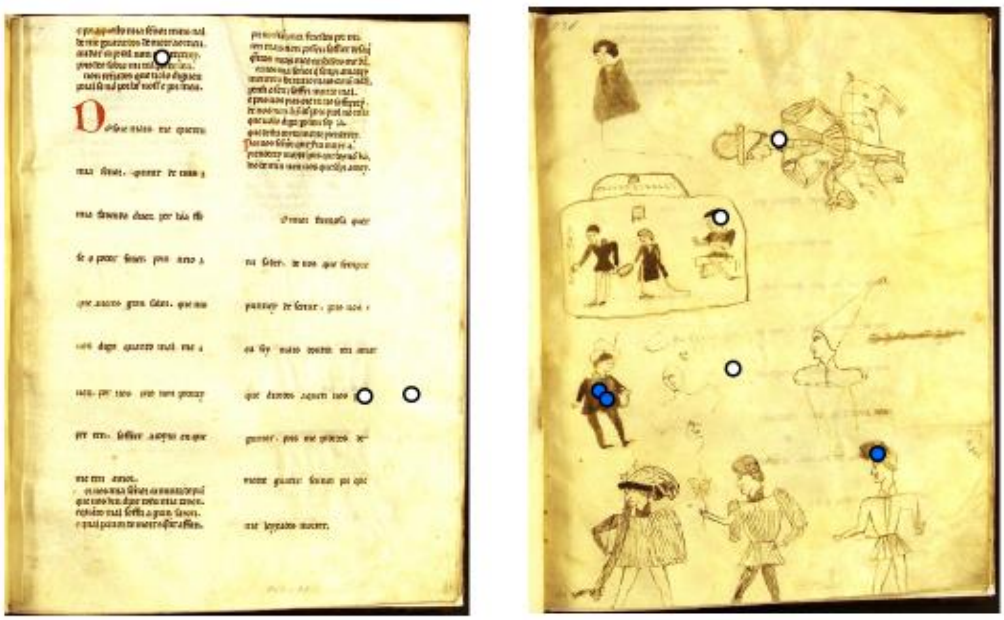

Figure S1.12. Folios 75 (left) and 77 (right), areas of analysis for microXRF (○) and FORS (●).

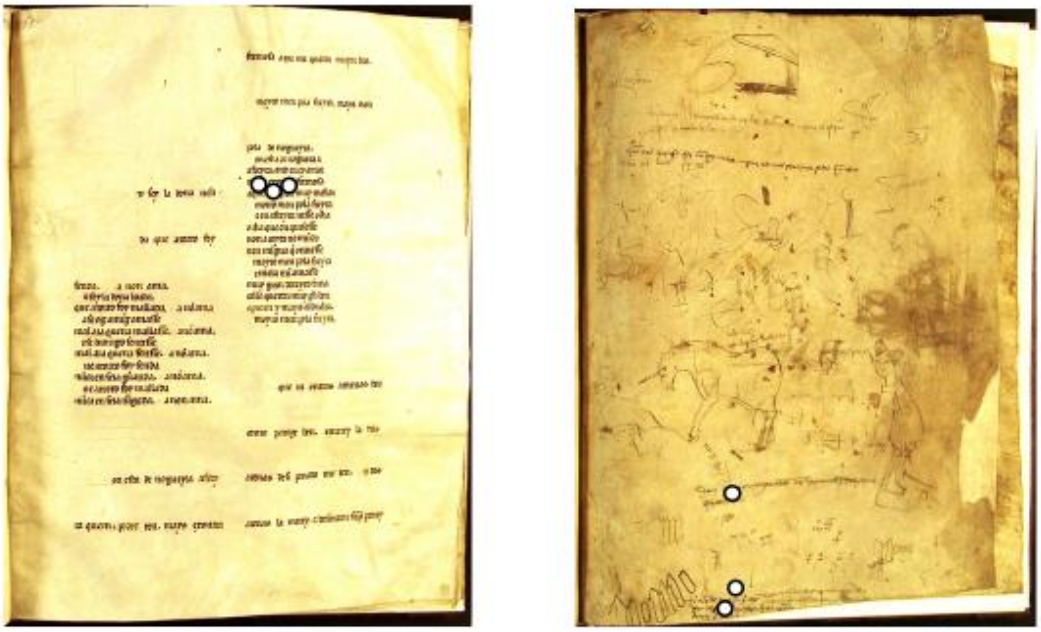

Figure S1.13. Folios 79 (left) and 87 (right), areas of analysis for microXRF (○).

2 - Equipment acquisition conditions

X-ray fluorescence spectra were obtained with an ArtTAX spectrometer of Intax GmbH, with a molybdenum (Mo) anode, Xflash detector refrigerated by the Peltier effect (Sidrift), with a mobile arm. The spatial resolution is 70 mm. The experimental parameters used were: 40 kV of voltage, 300 μA of intensity and 120 seconds of acquisition time (under Helium).

Reflectance spectra were obtained with a reflectance spectrophotometer Ocean Optics in the UV-Vis region through optical fibres at 90º, with 8 ms integration time and 15 scans. Measurements were conducted using a transparent mask and a plastic o-ring.

Raman microscopy was carried out using a Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne laser of 17mW power operating at 632.8nm (red laser), and a 532nm diode laser of 50 mW power operating at 75% (green laser). Spectra were recorded as an extended scan. The laser beam was focused either with a 50× or a 100× Olympus objective lens. The laser power at the surface of the samples was between 4.3 and 0.17 mW.

Infrared analyses were performed using a Nicolet Nexus spectrophotometer coupled to a Continuμm microscope (15x objective) with a MCT-A detector cooled by liquid nitrogen. Spectra were collected in transmission mode, using a Thermo diamond anvil compression cell, in 50 μm areas, 4 cm^{-1} and 128 scans.

Fluorescence excitation and emission spectra were recorded with a Jobin Yvon/Horiba SPEX Fluorog 3-2.2 spectrofluorometer hyphenated to an Olympus BX51 M confocal microscope, with spatial resolution controlled with a multiple-pinhole turret. Dichroic filters of 500 and 600 nm were used at 45° to collect spectra on a 30 μm spot (pinhole 8) with the following slits set: emission slits = 3 / 3 / 3 mm, and excitation slits = 5 / 3 / 0.8 mm. Emission spectra were acquired exciting at 490 nm and excitation spectra were recorded collecting the signal at 610 nm. The optimization of the signal was performed for all pinhole apertures through mirror alignment in the optic pathway of the microscope, following the manufacturer's instructions. Spectra were collected after focusing on the sample (eye view) followed by signal intensity optimization (detector reading). Emission and excitation spectra were acquired, *in situ*, on the same spot whenever possible.

3 - Molecular data for the characterization of the Ajuda Songbook

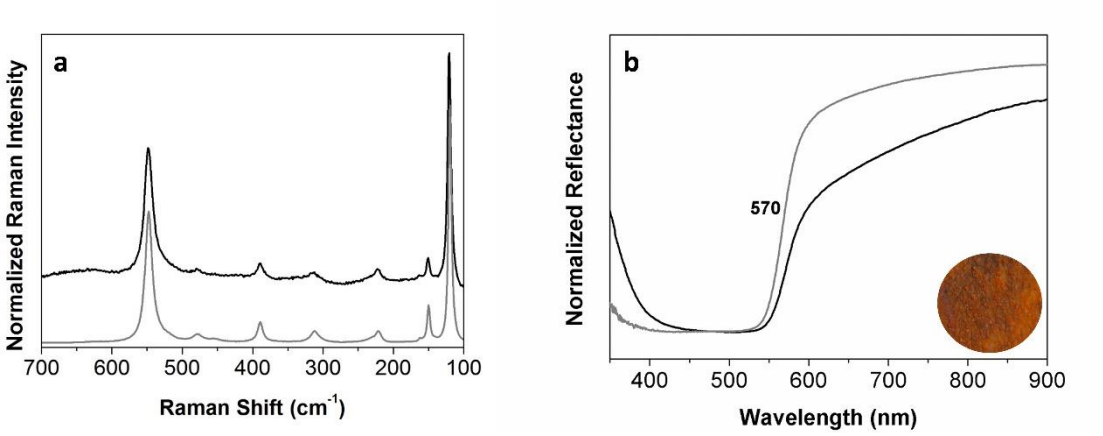

Figure S3.1. The orange colour in the characters' vestments, as well as some architecture details, was identified as being red lead. Here shown are the spectra for red lead reference (grey line) and for the noble's vestments, fol. 17 (black line): ***a)*** Raman; ***b)*** FORS.

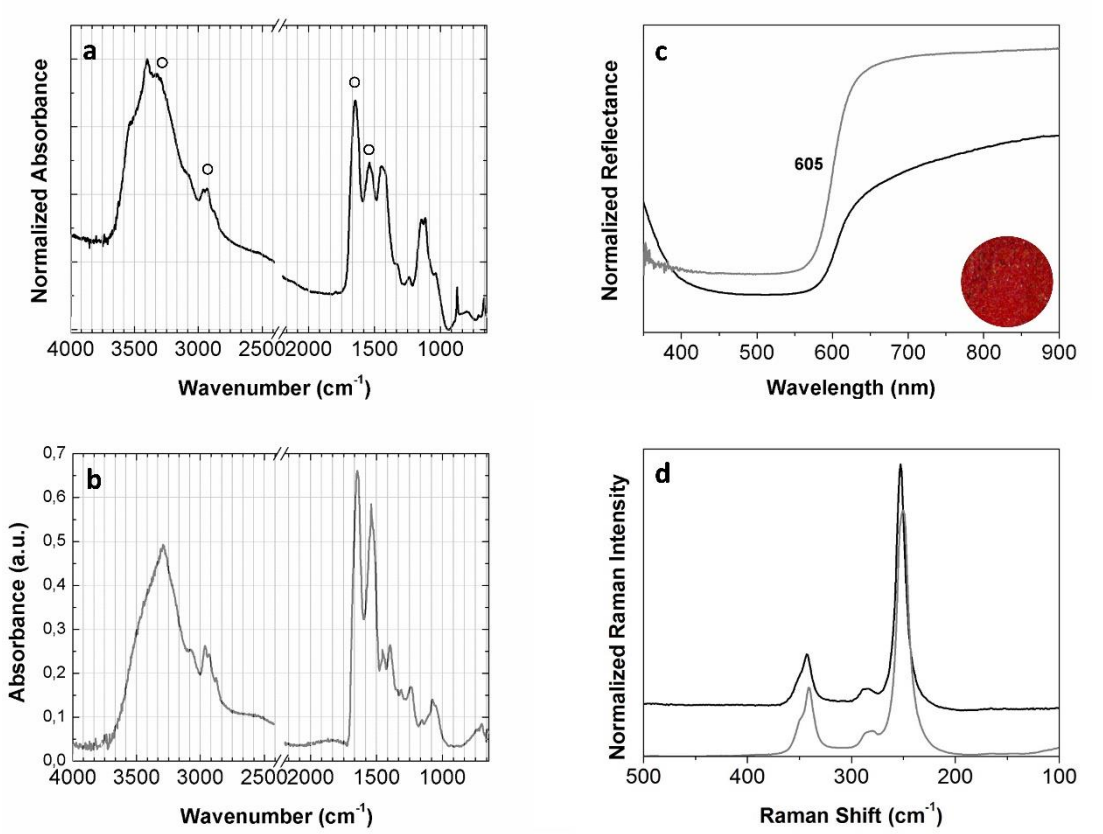

Figure S3.2. Vermilion was used in the architectural elements and vestments, as proved by its molecular spectra. Here shown are the spectra for vermilion reference (grey line) and for the noble's vestments, fol. 40v (black line): ***a)*** Infrared; with characteristic peaks of the binder (○); ***c)*** FORS; ***d)*** Raman; ***b)*** Infrared spectrum for protein binder.

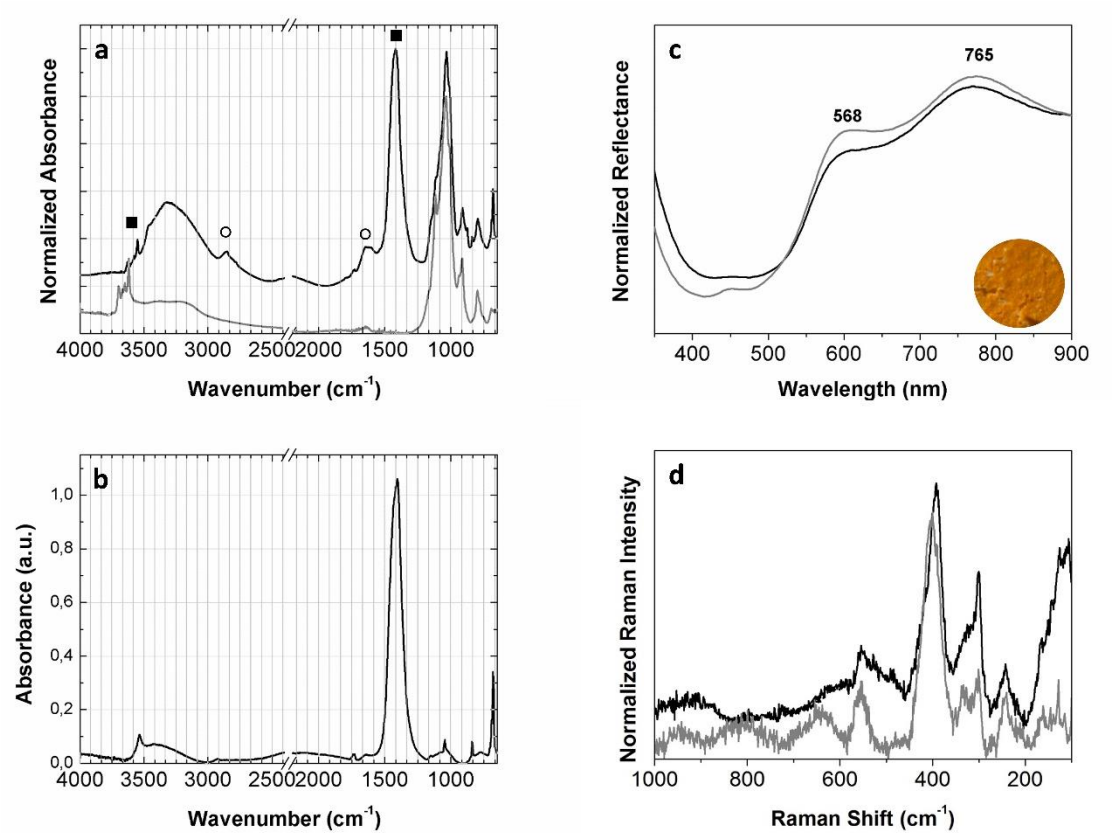

Figure S3.3. Yellow ochre was used in the architecture, as well as in the musical instruments. Spectra for yellow ochre reference (grey line) and for the building, fol. 4 (black line): ***a)*** Infrared, with the characteristic peaks of lead white and protein binder (lead white, ■, and protein,○); ***c)*** FORS; ***c)*** Raman; ***b)*** Infrared reference spectrum of lead white.

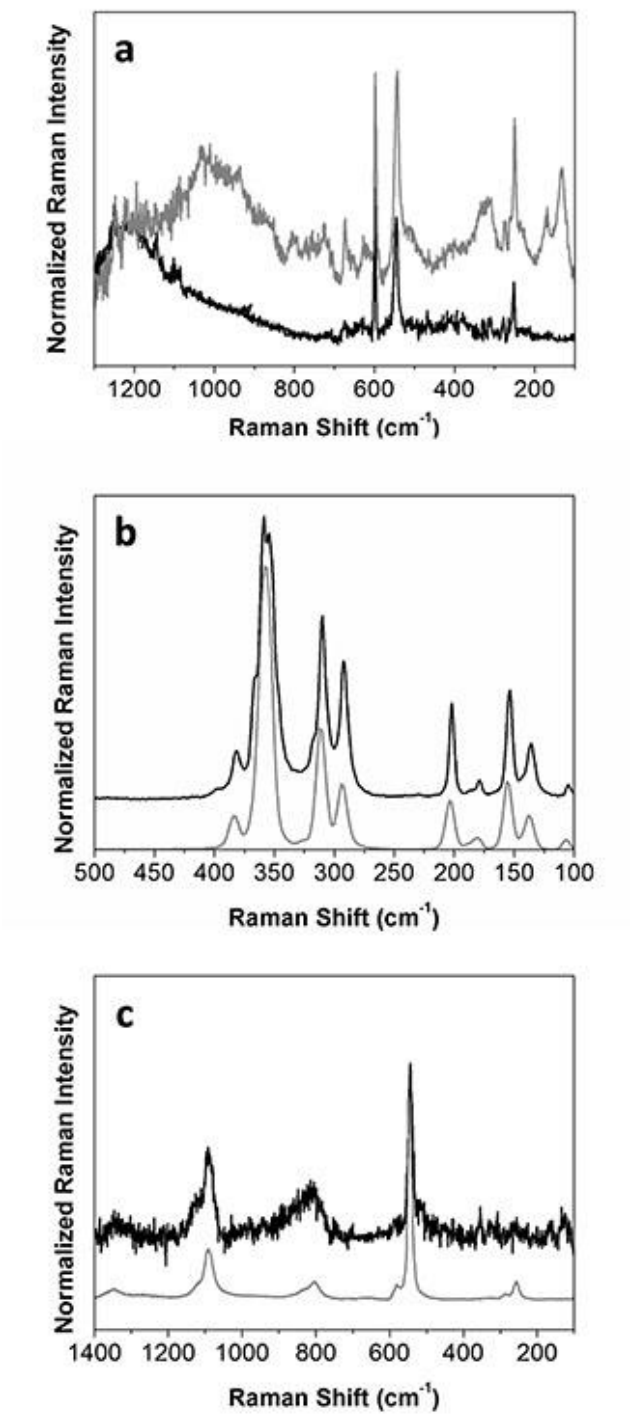

Figure S3.4. The green colour was applied has a combination of a yellow and a blue colorant. Here shown are the Raman spectra for the reference (grey line) and for the architecture and vestment details, fols. 4 and 17 (black line): ***a)*** spectra of the dancer's vestments in fol. 17 and reference of indigo; ***b)*** spectra of the column chapiter in fol. 4 and reference of orpiment; ***c)*** spectra of the building in fol. 17 and reference for lapis lazuli.

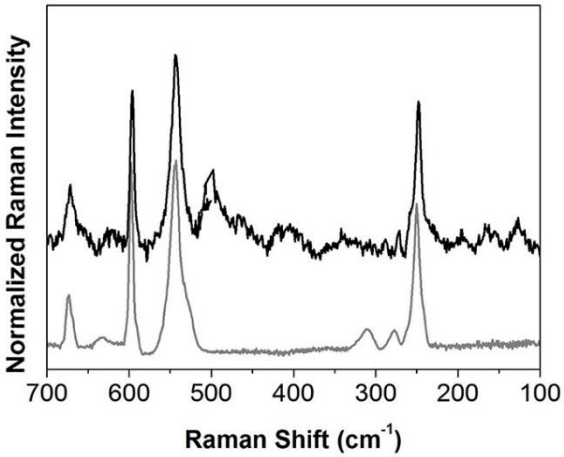

Figure S3.5. Indigo was identified in the vestments, as proved by its molecular spectra. Here shown is the Raman spectra for indigo reference (grey line) and for the blue shade of the musician's vestments, fol. 40v (black line).

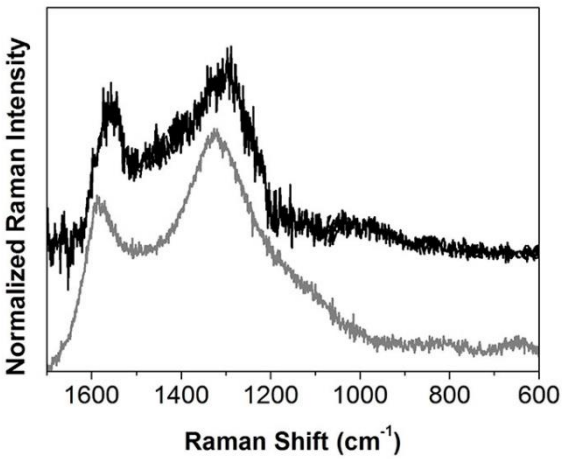

Figure S3.6. Carbon black was identified in the vestments as well as to shade other colours. Raman spectra for the pigment reference (grey line) and for the architecture detail, fol. 17 (black line).

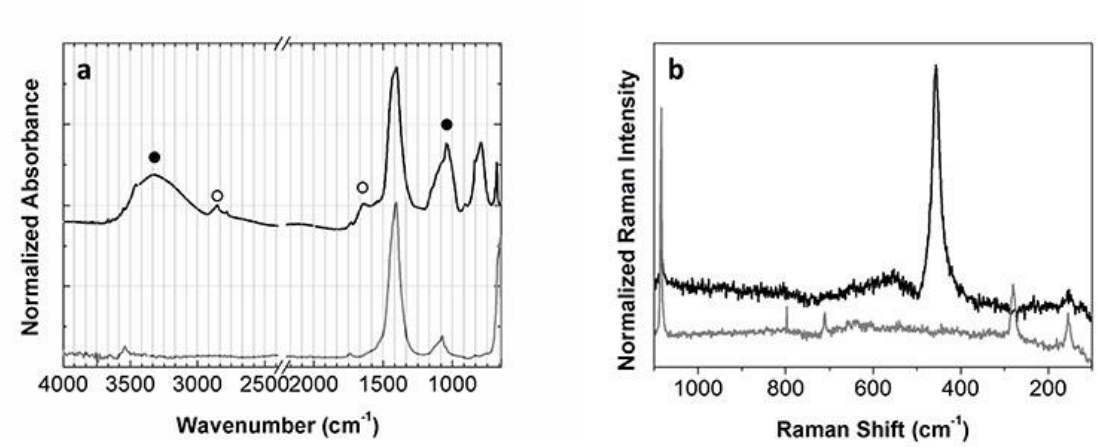

Figure S3.7. Lead white was used to highlight some details, as proved by its molecular spectra. Spectra for lead white reference (grey line) and for the architecture white detail, fol. 17 (black line): ***a)*** Infrared with lead white reference, with the characteristic peaks of the binder highlighted (protein, ○, and polysaccharide, ●); ***b)*** Raman spectra with chalk reference.