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Supplementary Materials: Ag-Nanostars for the Sensitive SERS Detection of Dyes in Artistic Cross-Sections—*Madonna della Misericordia* of the National Gallery of Parma: A Case Study

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1. Extinction Spectrum of AgNSs

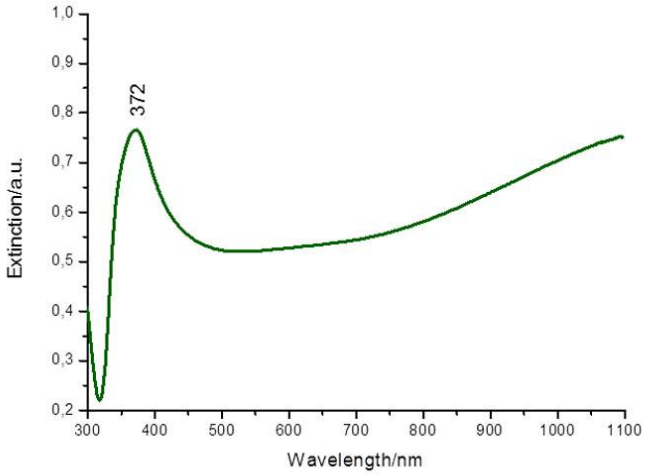


Figure SM1. UV-Vis extinction spectrum of the AgNSs colloid at pH 8.1.

2. *Madonna Della Misericordia*: Visual and Non-Invasive Analyses

As required by the analytical sequence [S1], the first examination of a painting is the visual one. This analysis revealed many conservation issues (losses of color, woodworm holes, etc.) and evidence of the past restoration interventions (Japanese paper on cracks, re-paintings, etc.) carried out in 1896 [S2] and in 1951 [S3] (Figure SM2).

Figure SM2. Picture showing some of the conservation issues of the *Madonna della Misericordia*: cracks, losses of color, lifting of the paint layer, woodworm holes.

Thereafter, IR reflectography was carried out by using a Hamamatsu vidicon tube camera, revealing the presence of well-defined underdrawings. Figure SM3 shows the detail of one of the two kneeling ladies: her image was accurately drawn before painting and particular attention was given to the pearls of the necklace, her eyes and the voile which covers her hair.

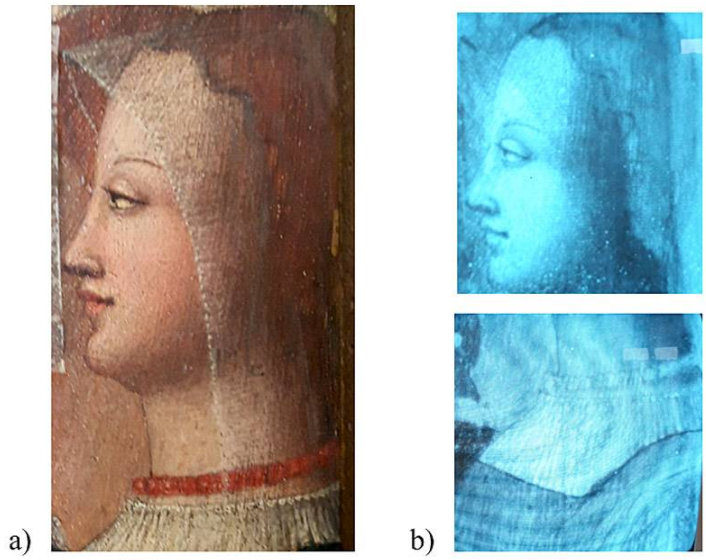


Figure SM3. (**a**) Detail of one kneeling lady and (**b**) its IR reflectography image which underlines the presence of precise underdrawings (pearls of the necklace, eyes, voile).

The observation under UV light by a commercial Wood lamp revealed the accurate location of many re-paintings which appear darker than the original paint and of a thick layer of restoration varnish characterized by the typical yellowish fluorescence [S1] (Figure SM4).

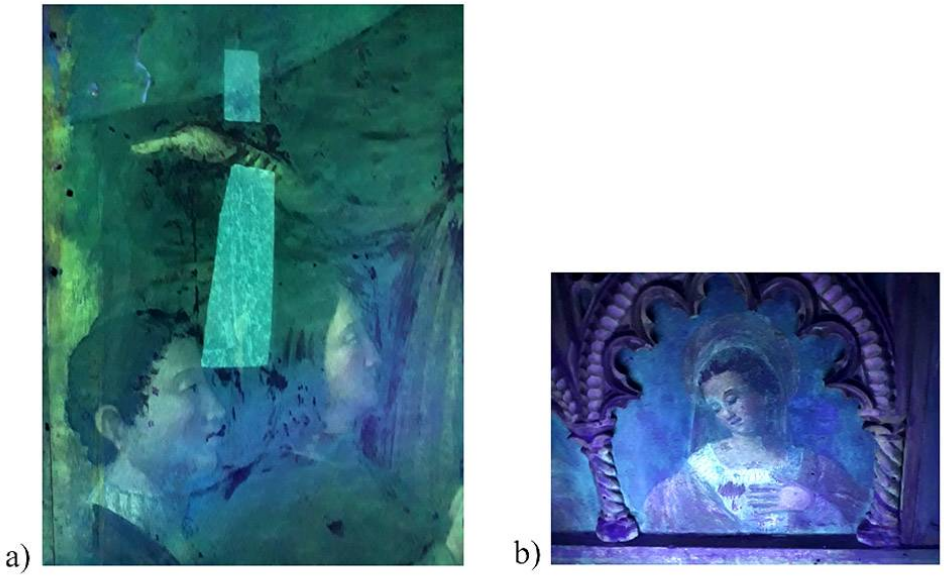


Figure 4. Detail of (**a**) the two gentlemen and (**b**) Santa Caterina in the *predella*: several dark areas indicate the position of re-paintings and the yellowish fluorescence is due to the presence of restoration varnish.

After these assays, some areas of interest of the painting were examined by optical microscopy in reflected light. The repainted details were easily recognized by examining the different kinds of *craquelure*: the original paint shows an homogeneous network of shell-like cracks (Figure SM5-a) while the retouched details, plastered and repainted, present a scratched surface to mimic the aged pictorial layer [S1] (Figure SM5-b).

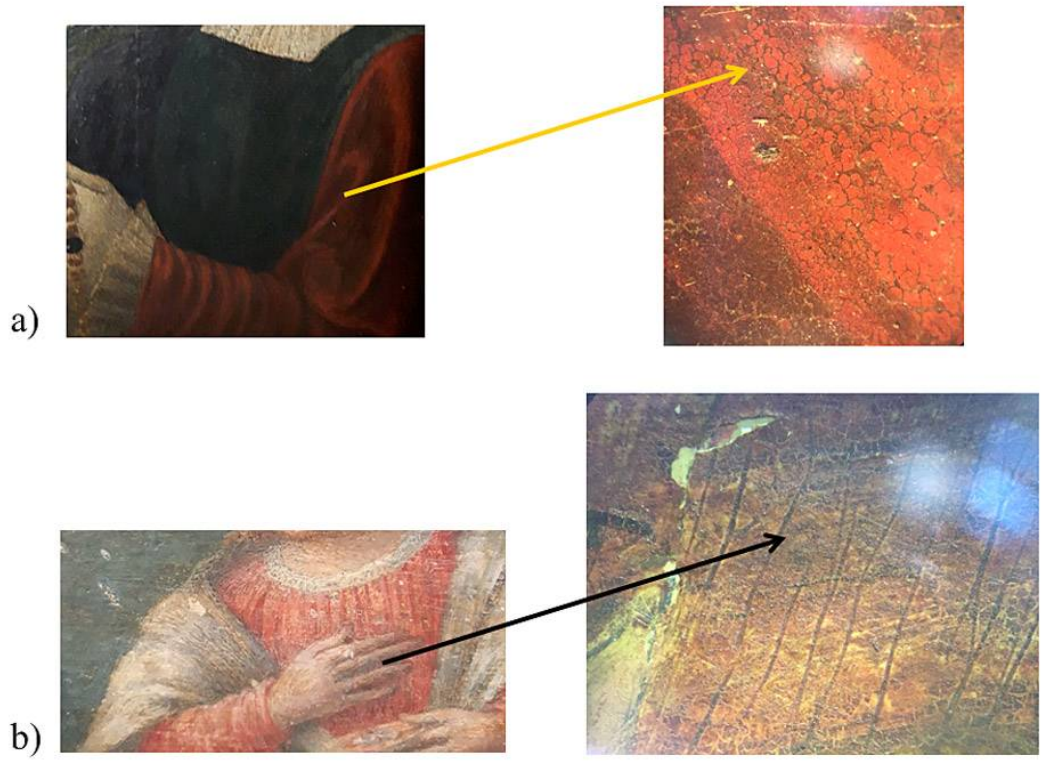


Figure SM5. *Craquelure* of a) the original pictorial layer characterized by shell-like cracks and of b) a plastered detail where the ageing of the paint layer was simulated by scratches.

3. Raman Spectral Data for Copper Alpha-Phthalocyanine PB 15:2

Table S1. Comparison of the experimental and reference spectral bands (s: strong; m: medium; w: weak) of copper alpha-phthalocyanine PB 15:2 [S4], [S5].

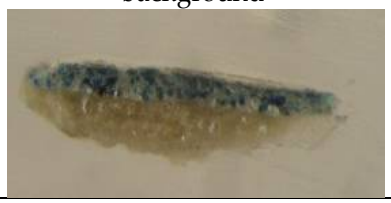
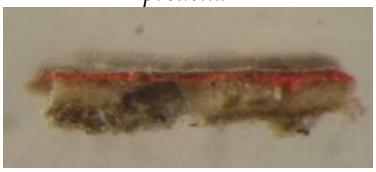
Experimental SERS bands (cm^{-1}); present work	Literature reference bands (cm^{-1}) [S4, S5]	Attribution
1566 (m)		
1514 (s)	1518 (s)	Out-of-phase stretching of the CNC bridges
1438 (w)	1446 (m)	Out-of-phase benzene rings deformations
1400 (w)		
1379 (m)		Out-of-phase indole rings expansion and benzene rings deformations
1343 (s)	1334 (s)	In-phase Cu-N stretches/ indole and benzene ring deformations
1303 (m)	1303 (w)	
	1181 (w)	
1142 (w)	1140 (m)	Out-of-phase expansions of both the indole and benzene rings.
1104 (s)	1105 (w)	In-phase stretches of the Cu-N bonds/indole rings deformations/benzene rings expansions
1002 (m)	1005 (w)	In-phase expansions of the benzene rings
720 (m)	745 (s)	Out-of-phase deformations of the indole groups

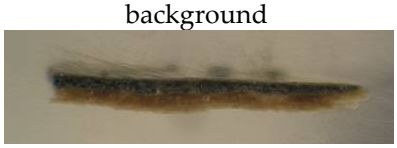
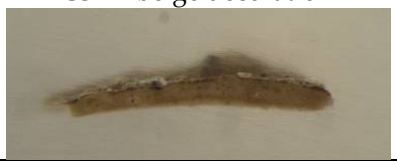
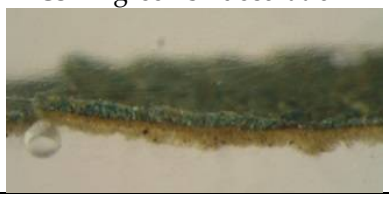
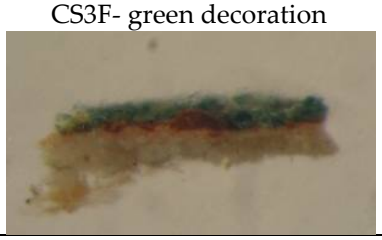
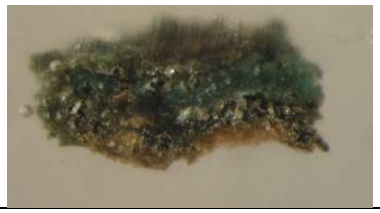
679 (m)	679 (m)	Symmetric stretches of the four CNC bridges/ deformations in the indole and benzene rings
649 (m)		
585 (w)	592 (w)	
479 (w)	483 (m)	
	255 (w)	Ring breathing

4. Summary of the Results Obtained from the Analysis of Each Cross-Section

In order to make the description of the obtained results clearer, a brief summary of the detected materials in each cross section is presented in Table S2.

Table S2. Summary of the material identified in the cross sections sampled from the *Madonna della Misericordia*.

Sample	Analytical technique(s)	Composition
CS1- upper left part of the bluish background 	Optical microscopy, SEM-EDS, Raman spectroscopy and SERS	Preparation: gypsum 1st paint layer: azurite and lead white 2nd paint layer: titanium white
CS2- bluish background in the *predella* 	Optical microscopy, SEM-EDS, Raman spectroscopy and SERS	Preparation: gypsum Paint layer: titanium white, copper alpha-phtalocyanine, ultramarine blue
CS3- Virgin Mary's blue mantle 	Optical microscopy, SEM-EDS, Raman spectroscopy	Preparation: gypsum Paint layer: azurite, iron oxides and lead white
CS4- Santa Lucia's red tunic in the *predella* 	Optical microscopy, SEM-EDS, Raman spectroscopy	Preparation: gypsum Paint layer: vermilion
CS5- client's red sleeve 	Optical microscopy, SEM-EDS, Raman spectroscopy	Preparation: gypsum Paint layer: vermilion
CS6- client's white bonnet	Optical microscopy, SEM-EDS, Raman	Preparation: gypsum Paint layer: lead white

	spectroscopy	
CS7- left lower part of the bluish background 	Optical microscopy, SEM-EDS, Raman spectroscopy and SERS	1st preparation: gypsum 1st paint layer: azurite and lead white 2nd preparation: gypsum 2nd paint layer: titanium white, copper alpha -phtalocyanine, ultramarine blue
CS1F- beige decoration 	Optical microscopy, SEM-EDS, Raman spectroscopy	Preparation: gypsum Paint layer: lead white
CS2F- greenish decoration 	Optical microscopy, SEM-EDS, Raman spectroscopy and SERS	Preparation: gypsum Paint layer: titanium white and copper alpha -phtalocyanine
CS3F- green decoration 	Optical microscopy, SEM-EDS, Raman spectroscopy and SERS	Preparation: gypsum 1st red paint layer: red lead 2nd green paint layer: copper alpha -phtalocyanine
CS4F- bluish decoration 	Optical microscopy, SEM-EDS, Raman spectroscopy	Paint layer: supposed Scheele's green
CS6F- bluish decoration 	Optical microscopy, SEM-EDS, Raman spectroscopy	Paint layer: supposed Scheele's green

References

[S1] Pinna D., Galeotti M., Mazzeo R., *Scientific examination for the investigation of paintings. A handbook for restorers* **2011**, Centro Di Firenze, Italy.

[S2] Ricci C., *La R. Galleria di Parma* **1896**, L. Battei, Parma.

[S3] Fornari-Schianchi L., Galleria Nazionale di Parma, Catalogo delle opere dall'antico al Cinquecento 1997, F.M. Ricci, Milano.

[S4] Scherrer N.C., Zumbuehl S., Delavy F., Fritsch A., Kuehnen R., Synthetic

organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection. Spectrochim. Acta A 2009, 73, 505-524. [DOI: 10.1016/j.saa.2008.11.029]

[S5] Tackley D.R., Dent G., Smith W.E., IR and Raman assignments for zinc phthalocyanine from DFT calculations. Phys. Chem. Chem. Phys., 2000, 3949-3955. [DOI: 10.1039/b0050911]