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New evidence for the intentional use of calomel as a white pigment

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Abstract
In this work, we report the results of the in situ application of micro-Raman spectroscopy to the analysis of two historic painted objects: a 15th-century illuminated manuscript and a late 16th-century portrait miniature. Both objects were unexpectedly found to contain calomel (Hg_2Cl_2), intentionally used as a white pigment. Calomel was a widespread and popular medicine until it fell out of use at the end of the 19th century due to its toxicity, and a material called 'mercury white' is referred to in 16th-century technical literature on painting. However, although calomel has been recognised in the past as a degradation product of cinnabar in both wall and easel paintings, its deliberate use as a pigment on cultural heritage objects has only been documented recently in white areas painted on 17th-century South American objects. The present study describes the first ever verified use of calomel as a white pigment on European works of art, both of which predate its documented use in South America.

KEYWORDS
calomel, illuminated manuscripts, mercury white, micro-Raman spectroscopy, portrait miniatures

1 | INTRODUCTION

The Fitzwilliam Museum in Cambridge (United Kingdom) hosts a large collection of mediaeval and Renaissance illuminated manuscripts, covering the period from the 9th to the 16th century, most of which preserve their original decoration. Since 2012, many of them have been undergoing a comprehensive programme of cross-disciplinary study, including in-depth scientific investigation, as part of an extensive research project. Among these, a 15th-century volume nicknamed the 'Fitzwilliam Missal' (MS 34; see Figure 1) shows bright white decorative motifs, which have given rise to matching dark outlines on the facing pages. The museum also owns almost 400 portrait miniatures, dating from the mid-16th to the 19th century. Seven of them are attributed to Isaac Oliver (ca. 1565–1617), one of the most renowned 'limners' (miniature painters) working in London in the late 16th and early 17th century. These have also recently undergone technical and scientific study, together with examples of Oliver's oeuvre from other collections. Among the Fitzwilliam's miniatures by Oliver is the portrait of a fashionably attired but unknown lady (FM 3868; see Figure 2), considered to be a typical example of his work. The recent analyses, however, have revealed that a large part of the white collar and lace ruff in her costume have been heavily overpainted at some point in the 18th or 19th century, covering or perhaps substituting the original pigments.

FIGURE 1 The so-called 'Fitzwilliam Missal' (Cambridge, Fitzwilliam Museum, MS 34, fols. 137v-138r; York, England, ca. 1470), with magnified details of a coloured decoration (right) and the corresponding dark offset (left) from the outer borders of the pages

FIGURE 2 Portrait of an unknown lady by Isaac Oliver (Cambridge, Fitzwilliam museum, FM 3868; England, ca. 1595–1600): comparison between visible-light photograph (left) and ultraviolet image (right)

This paper discusses the application of a portable Raman system to examine noninvasively the nature of the white pigment identified in both objects, unexpectedly found to be calomel, a mercury (I) chloride mineral with formula Hg_2Cl_2. Although well known in different fields, including medicine and electrochemistry, very little documentation exists about its use as a pigment. The only historic reference that might imply the use of calomel as a white pigment for painting is a treatise on the art of limning published by Nicholas Hilliard around 1600.[1] Until very recently, the presence of calomel had only been detected in frescos and paintings as a degradation product of cinnabar.[2–6] Its deliberate use as a white pigment has now been documented on a few cultural heritage objects originating from South America and dating to the 17th century.[7,8] To the best of the authors' knowledge, however, the present study constitutes the first report of calomel, reliably identified as part of the original palette of two late Renaissance and early modern English works of art.

2 | MATERIALS AND METHODS

2.1 | A 15th-century illuminated manuscript

The so-called ‘Fitzwilliam Missal’ (MS 34) was most probably made in York around 1470 for Sir Richard Fitzwilliam and his wife, Elizabeth Clarell.[9] It remained in the possession of the Fitzwilliam family until another Richard, 7th Viscount Fitzwilliam, bequeathed it to the University of Cambridge together with the rest of his library and art collection upon his death in 1816. The manuscript is illuminated in typical 15th-century English style, with imposing figures that are, however, stiff and not executed with particular success. The borders are richly decorated with gilded frames and coloured floral and foliate motifs, some of which display dark offsets with the same shape on the opposite page (Figure 1), suggesting that a degradation process might have affected some pigments. On the basis of the presence or absence of a correspondence between the dark offsets and their specular coloured images on the opposite page, it is possible to conclude that the manuscript was disbound and the pages reordered at least twice in the past. Technical analysis of the manuscript is still ongoing; only selected results are reported here.

2.2 | A portrait miniature by Isaac Oliver

Isaac Oliver's portrait of a fashionably attired unknown lady (FM 3868) depicts a young, stylishly attired woman, with a black hat and a profusion of white lace and pearls. She has long been considered a ‘typical’ example of this artist's work.

It is interesting to note, however, that the ultraviolet (UV) image (Figure 2) shows that numerous areas have been retouched. These include portions of her hat and black blouse, which display a greenish fluorescence under UV illumination, indicative of the presence of modern pigments, such as zinc white (as confirmed by additional X-ray fluorescence [XRF] analysis). Extensive repainting can also be identified throughout the white passages of the costume.

In the case of the white collar and lace, the white overpainting appears to be covering dull grey (original) paint, whose muted colour must have been the reason for the extensive intervention.

2.3 | Mercury chloride compounds

Calomel is a mercury (I) chloride mineral with formula Hg_2Cl_2, mainly used nowadays as a component of reference electrodes in electrochemistry. A mercury chloride compound, often assimilated with calomel but traditionally called ‘(corrosive) sublimate’ was in common use as a medicine to treat a wide range of ailments until the end of the 19th century when it fell out of use because of its toxicity.[10] In relation to early modern England specifically, there is a reference to the use of a mercury-based compound in the work of Richard Haydocke, an English physician who in 1598 translated and published Paolo Lomazzo's treatise on painting, carving and building. Haydocke expanded the original manuscript with a section on female cosmetics, where he wrote ‘Diverse women use sublimate diversely prepared for increase of their beauty. Some bray it with quicksilver in a marble morter … and this they call argentatum … The composition whereof is of salte, quicksilver and vitriol, distilled together in a glassen vessel’.[11] Haydocke's sublimate, composed of ‘salte,’ ‘quicksilver’ (mercury) and ‘vitriol’ (sulfuric acid) and distilled in a glass vessel, was probably mercury (II) chloride, which is a corrosive white powder and is soluble in water. For this reason, it is not suitable to be used as a pigment. However, through a reduction of mercury, the corrosive and highly toxic mercury (II) chloride can be turned into mercury (I) chloride—calomel—which is insoluble in water and therefore much less toxic.

The Raman spectra of the two compounds are clearly different (Figure 3); in particular, the main peak of mercury (I) chloride is due to the fully symmetric vibration at 165 cm^{-1}, whereas the main peak of mercury (II) chloride is at 312 cm^{-1}.

2.4 | Analytical methods

Both of the analysed objects were subjected to extensive technical investigation aimed at identifying the painting materials and techniques used by their respective artists. The analytical protocol included a range of

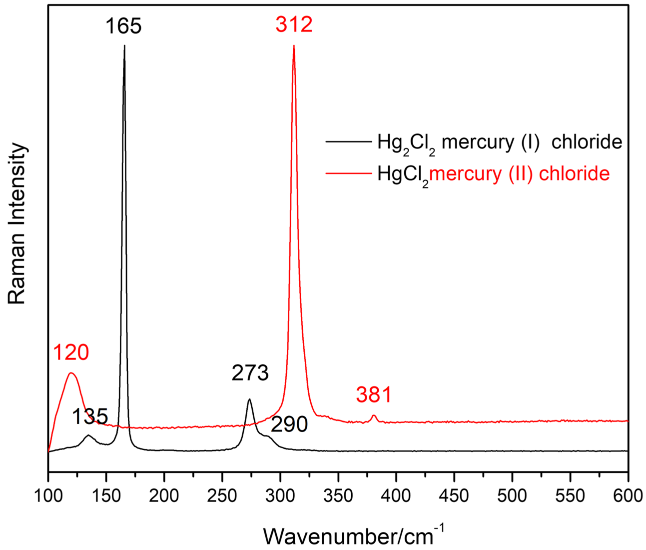

FIGURE 3 Reference Raman spectra of mercury (I) chloride (black line) and mercury (II) chloride (red line) collected in house using commercially available compounds (Carlo Erba Reagents); Raman spectra obtained with excitation laser at 633 nm

complementary, noninvasive analyses, such as UV and near-infrared imaging, reflectance spectroscopy (fiber optics reflectance spectroscopy [FORS]) in the UV, visible and near-infrared (UV–vis–NIR) range and digital microscopy. Specific details about the instrumentation and the experimental conditions used can be found elsewhere.[12,13]

The protocol also included Raman spectroscopy and XRF spectroscopy, the latter used both in single-point and in mapping mode. These two methods were the ones specifically used for the identification of calomel and are therefore further discussed here.

2.4.1 | Raman spectroscopy

A portable i-Raman Plus spectrometer (B&W TEK Inc., Newark, USA) provided with a 785-nm excitation laser line and a high quantum efficiency charge-coupled device (CCD) array detector with deeper cooling and high dynamic range was used to analyse the illuminated manuscript. The spectral range of the spectrometer is 65–3,350 cm^{-1} with a resolution of 3.9 cm^{-1}. The spectrometer and laser are connected to a probe head with optical fibre cables. The Raman microprobe was attached to a video microscope with an integrated camera and an LED illuminator to allow precision spot sampling. The video microscope with the Raman microprobe was mounted on a tripod with an *X-Y* microstage. A 40× long-distance objective lens was used providing a laser spot size of about 50 mm in diameter. The laser power was kept at about 0.3 mW during the measurements to prevent pigment photodecomposition. Each spectrum was collected for 10 s, with a single accumulation. The spectra were not processed further. The experimental spectra were compared with online resources and databases[14,15] as well as to reference spectra collected in house on commercially available mercury (I) chloride and mercury (II) chloride (Carlo Erba Reagents).

The miniature was analysed using a portable Raman spectrometer assembled by Professor Andrew Beeby (Durham University) and kindly loaned to the Fitzwilliam Museum for 1 month.

The system has been described elsewhere[16]; briefly, it is composed by a HeNe laser (632.8 nm, spectral resolution 4 cm^{-1}), which is focused into a fibre-optic cable for delivery to the sampling accessory (Horiba 'SuperHead'). This is equipped with an ultralong working distance ×40 microscope lens, providing a working distance of approximately 10 mm from the surface under analysis. The laser power at the sample was kept below 0.3 mW during measurements, with the laser spot at the sample estimated to be approximately 30 μm in diameter. The Raman sampling head was mounted on a vertical translation stage, itself mounted on a sliding rail fitted to a gantry that holds the head vertically over the object. A portable microscope was attached to the instrument to facilitate positioning and focusing of the measuring head over the area under analysis.

2.4.2 | XRF spectroscopy

XRF analyses were performed using a Bruker Artax micro X-ray spectrometer with a rhodium anode. The X-ray tube was operated at 50 kV and 600 μA. The measurements lasted 200 s each and were performed with no filters. The measurement spot size is about 0.65 mm in diameter. Images of each of the analysed areas, captured with the instrument's in-built camera, were also saved. Before undertaking XRF analysis of the illuminated manuscript's pages, transmitted light images of each folio were acquired to avoid interference from text and decoration present on the reverse side. The operating conditions used to collect the XRF map were 50-kV anode voltage, 600-μA filament current, 50-s measurement time, 0.5-mm step size and no filters. In order to cover the selected surface of the manuscript (11 × 7.5 mm^2), 368 measurements were acquired over 5 h and 45 min.

3 | RESULTS AND DISCUSSION

Overall, the palette employed to paint the Fitzwilliam Missal is fairly standard for a 15th-century English manuscript[16] and includes lead white, red lead, lead-tin yellow type I, massicot, azurite and copper-based greens.

Among the foliate and floral motifs enriching the page borders, one can note that some portions of the decoration give rise on the opposite page to dark offsets with the same shape (Figure 4a). Under close scrutiny, it is revealed that the dark spots match the pale-coloured and thick impasto-like highlights outlining the decoration (Figure 4b). Initially presuming the presence of degraded lead-based pigments, easily prone to darkening, such as lead white, a spot was selected within this pale-coloured area and first examined by XRF.

Surprisingly, the XRF analysis (Figure 4c) revealed not only the presence of lead but also intense lines for mercury (Hg), in addition to chlorine and copper, the latter most likely due to the presence of azurite in the blue area below. The occurrence of high amounts of mercury is usually linked to red pigments, such as vermilion or its mineral equivalent cinnabar (both HgS), rather than to white ones. In illuminated manuscripts, vermilion is used extensively, both alone and mixed with other compounds to depict red, pink, orange and brown passages. It is also employed as red ink to write portions of text, to paint pen-work infills and to rule musical staves. In this instance, however, the pale-coloured area where mercury was detected does not show any red particles in its matrix. On the basis of stylistic comparisons with other contemporary manuscripts, it is clear that the pale area is meant to act as a white ‘filigree’ highlight over the blue and pink foliage found in the borders. Additionally, no evidence for text or other red decoration is present in underlying layers or on the reverse side of the page, thus excluding any interference of cinnabar with the measurement.

In order to clarify the nature of this pale pigment, the same area was then analysed with Raman spectroscopy (Figure 4d). Interestingly, the experimental spectrum revealed two lines whose polarisation corresponds to fully symmetric vibrations at 167 and 275 cm^{-1}, matching those of a reference spectrum of calomel.

The peaks are sharp and well defined, and the same spectrum was obtained from various measurements across the manuscript, confirming the deliberate choice of mercury chloride as a white pigment.

To investigate further the presence of calomel across the entire surface of the decorative motif, a selected area (see Figure 4b) was scanned with XRF. The elemental distribution maps of Hg and Cl shown in Figure 5a,b indicate that both signals mostly derive from the same areas. Their co-related presence confirms the employment of calomel in the pale outlines, with high-intensity signals in the centre of the image likely to correspond to a thicker layer of paint.

When considering the Hg-M, Pb-M and Cu-K maps (Figure 5c), the composition of surrounding areas also becomes clear, with azurite $[Cu_3(CO_3)_2(OH)_2]$ in blue areas and lead white $[2PbCO_3{\cdot}Pb(OH)_2]$ in white and light-blue ones. The RGB false colour map (Figure S1) also allows to see that calomel is used as a white pigment alone in limited areas, rather than mixed with other colours to modify their hues—lead white appears to have been employed for this purpose.

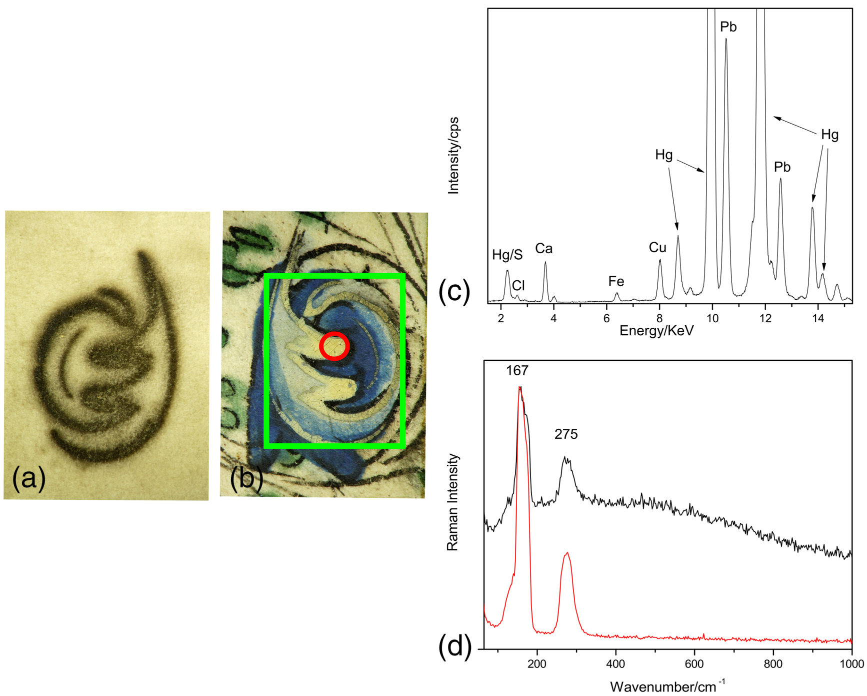

FIGURE 4 MS 34, fols. 137v-138r: (a) dark offset on fol. 137v; (b) decorative motif, with coloured dots indicating where the X-ray fluorescence (XRF) and Raman spectra were acquired (red circle) and where the XRF mapping in Figure 5 was performed (green square); (c) XRF spectrum of the pale area outlined in Figure 4b. Ca and Fe are due to the parchment support; Pb to lead white used in white and light blue areas nearby/below; Cu to azurite used in blue areas nearby/below; (d) Raman spectrum of the pale area outlined in Figure 4b (black line) and reference Raman spectrum of commercially available Hg_2Cl_2 (red line); Raman spectra obtained with excitation laser at 785 nm

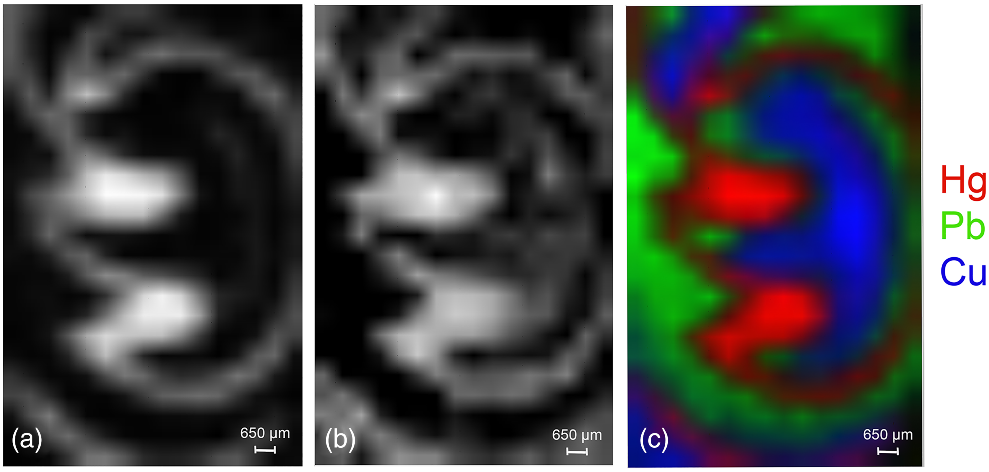

FIGURE 5 MS 34, fol. 138v: (a) X-ray fluorescence (XRF) map of Hg-M in the area outlined in green in Figure 4b; (b) XRF map of Cl-K in the area outlined in green in Figure 4b; (c) RGB composite of XRF maps with R: Hg-M; G: Pb-M; B: Cu-K

The portrait miniature by Isaac Oliver (FM 3868) displays many typical characteristics of the artist's work and a palette generally compatible with its creation in the late 16th century. The exception to this is the extensive repainting with barium white ($BaSO_4$) identified by XRF (Figure 6b) throughout the white ruff and the lace decorating the lady's costume. The XRF spectrum also reveals intense lines of copper due to the azurite used to paint the blue background, as well as small peaks for lead and clear peaks for both mercury and chlorine. Close observation of the analysed area reveals that the bright barium white layer appears to be covering dull grey paint passages, which one might assume to be the reason for this widespread 19th century intervention. High quality lead white would have been the obvious pigment to choose for white lace, and it is indeed what has generally been found when analysis on miniatures of the 16th and 17th centuries has been undertaken.[17,18]

On the basis of the XRF results, however, and on the successful identification of calomel in the Fitzwilliam Missal, a Raman spectrum was collected in one area of the lace (Figure 6c) and resulted in the identification of the same unusual pigment.

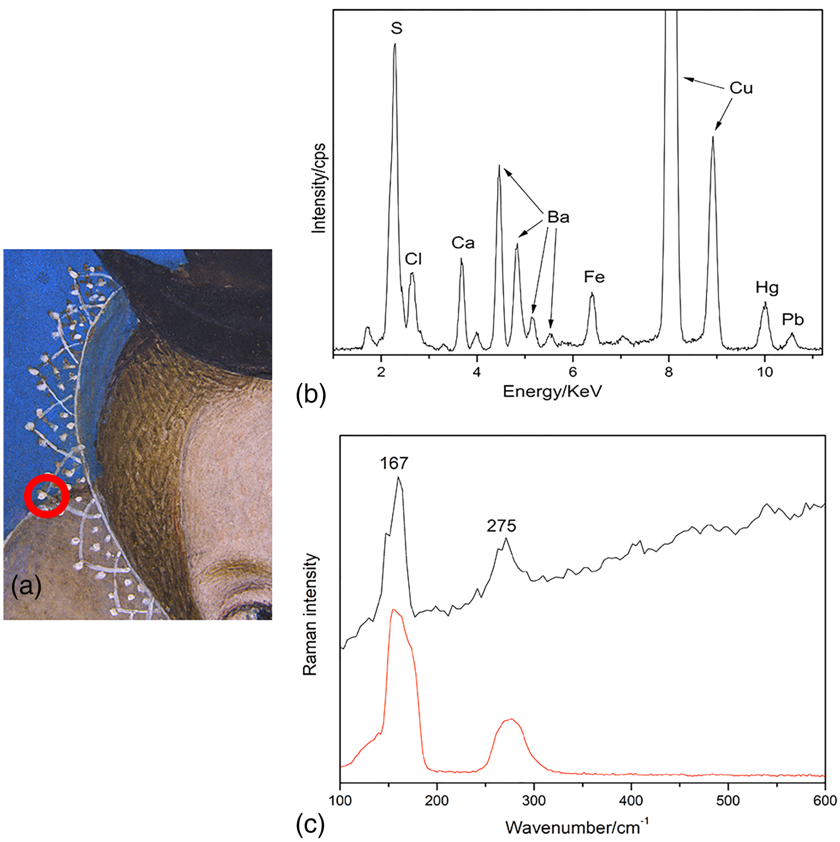

FIGURE 6 FM 3868: (a) visible detail with coloured dots indicating the white area where the X-ray fluorescence and Raman spectra were acquired (red circle); (b) X-ray fluorescence spectrum from white area. Ca and Fe are due to the parchment support; Ba and S to barium white used for retouching; Cu to azurite used in blue areas nearby/below; Pb to lead white used in white areas nearby/below; (c) Raman spectrum from white area (black line) with reference Raman spectrum of commercially available Hg_2Cl_2 (red line); Raman spectra obtained with excitation laser at 785 (reference spectrum) and 632.8 nm (Raman spectrum from white area)

Similarly to what is the case for the manuscript, it would not be historically appropriate to suggest that the lace had originally been painted in a red colour and that the calomel identified here is indeed the result of the degradation of vermilion. Further support to the hypothesis that the lace had originally been intended as white is the fact that retouches were made in the 19th century with a white, rather than a red, pigment.

Interestingly, a mercury-based white pigment, called 'quicksilver white' is mentioned by Nicholas Hilliard, the most famous miniature painter for the Tudor and Stuart courts, who presumably trained Oliver.

In his treatise on the 'art of limning,'[1] Hilliard defines quicksilver white as a compound that 'the women painters use'; but he also adds 'it draweth a very fine line,' suggesting that he may himself have experimented with it as a pigment. It is also worth noting that the name calomel derives from the Greek words Kalos ('beautiful') and Melos ('black'), so it must have been known that it blackened upon exposure to ammonia and light as well as being photosensitive. In the case of the Isaac Oliver miniature, the most likely explanation for the detected composition and colour of the original lace is that calomel was indeed employed by the artist, and although it was most probably white initially, exposure to light or possibly alkali turned it grey, thus making necessary the extensive repainting.

4 | CONCLUSIONS

The noninvasive analysis of two objects belonging to the Fitzwilliam Museum collection revealed some unexpected discoveries. The results presented here demonstrate that thanks to the use of Raman microscopy, it was possible to identify the presence of calomel in a 15th-century English illuminated manuscript and in a late 16th-century English portrait miniature.

The presence of sharp and well-defined peaks in the Raman spectra as well as stylistic considerations on the most 'appropriate' colour to appear in these areas confirm the deliberate choice of calomel as a white pigment to depict fine, intricate details in both objects. This remarkable finding attests the first ever verified presence of calomel within the painting palette of Western European works of art, predating its documented use in South America.

With ever-increasing possibilities to undertake noninvasive analyses of museum objects, it is quite possible that in the near future, calomel will no longer be considered an unusual pigment but rather will take its place as an integral part of the palette used by artists in England and beyond during the late Renaissance and the early modern period.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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