Smith *et al. Herit Sci (2019) 7:62*
https://doi.org/10.1186/s40494-019-0305-7

Heritage Science

RESEARCH ARTICLE

Open Access

Analytical characterization of 5,5′-dibromoindigo and its first discovery in a museum textile

Gregory Dale Smith[1*], Victor J. Chen[1], Amanda Holden[1], Melinda H. Keefe[2] and Shannon G. Lieb[3]

Abstract

The exploitation of natural sources and later synthetic molecules to generate blue to purple coloration in textiles has a long history in the dyer's craft. Natural indigoids such as indigo, woad, and Tyrian or shellfish purple served this purpose for millennia, but in the late 1800s synthetic analogs, in particular indigotin, quickly replaced natural sources. Halogenated versions of the dye were also created, and some like 5,5′-dibromoindigo were brought to market. Interestingly, these have not been significantly discussed in the literature, nor have they been found in forensic or technical art history investigations of textiles until now. This paper reports the first identification in a museum context of this unusual synthetic brominated analog of indigo, discovered on three twentieth century Japanese *yukata*. Analytical data collected on reference materials using liquid chromatography-mass spectrometry, UV–visible spectroscopy, Raman microspectroscopy, Fourier transform infrared spectroscopy, and X-ray fluorescence spectroscopy are provided to assist with future identifications of this relatively unknown colorant. Density functional theory applied to 5,5′-dibromoindigo was used to confirm the experimental Raman spectrum.

Keywords: 5,5′-Dibromoindigo, Vat Blue 35, Textile dye, Japanese *yukata*, Raman spectroscopy, Liquid chromatography–mass spectrometry, Density functional theory (DFT)

Introduction

The colors blue and purple have historically been prized in textile dyeing and have led to millennia of human exploration for new sources of these colored dyestuffs. Natural indigotin (Fig. 1a) extracted from the indigo and woad plants initially served this purpose for blue textile colors [1], and the painstaking extraction of Tyrian or shellfish purple, a 6,6′-dibromoindigo dye (6,6′-DBI, Fig. 1b) among other coloring compounds, from the hypobranchial glands of a variety of sea snails made purple a royal color for cloth in antiquity [2]. Natural indigo has traditionally been obtained from oxidation of precursor compounds isolated from the fermentation of macerated leaves of plants like *Indigofera tinctoria*, *Isatis tinctoria*, and *Polygonum tinctoria* [1, 3], which are widely distributed around the globe. Creating a colorant from indigo involves chemically reducing the insoluble indigotin to a water soluble *leuco*-form that can penetrate into the interstitial space within the fiber of a textile. Reoxidation of the *leuco*-indigotin by air or chemical means returns the compound to its insoluble form, trapping the colorant within the fiber. Thus, indigo is considered a 'vat dye' rather than a 'mordant dye,' and it can color natural fibers without the addition of inorganic salts [1].

Indigo's persistent popularity as a dye is due to its physical properties, which are unusual among dyestuffs. Indigoids in the solid state are relatively photochemically inert and remain insoluble in aqueous and many organic solvents, making indigo dyed textiles both lightfast and wash resistant [1]. Depending on the number of repetitions through the dye bath, indigo can produce various shades of blue, ranging from sky blue to deep ocean blue and even black [1]. Additionally, indigo has traditionally been combined with a yellow or red dye to obtain green and purple colors, respectively [1]. Outside of being a

---

*Correspondence: gdsmith@discovernewfields.org
[1] Conservation Science Department, Indianapolis Museum of Art at Newfields, 4000 Michigan Rd, Indianapolis, IN 46208, USA
Full list of author information is available at the end of the article

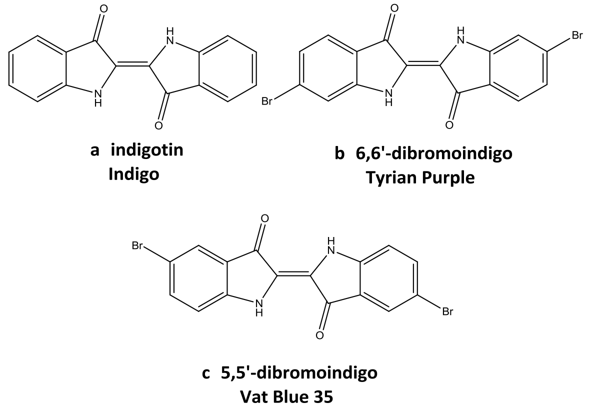

Fig. 1 Structures of **a** indigotin from indigo and woad, **b** 6,6′-DBI from sea snails, and **c** synthetic 5,5′-dibromoindigo

textile dye, indigo is used to color leather, paint, and ink, to make cosmetics, and to treat illnesses as a folk medicine [1]. As a pigment suitable for nearly all media, its use can be found in Asian, Western, South American, and African artworks throughout time.

Synthetic Indigoids

In the late 1800s, chemical synthesis of new dyes provided inexpensive and readily available color alternatives, which competed with and quickly replaced their natural counterparts. William Henry Perkin's creation of the coal tar dye mauveine in 1856 brought purple into everyday households and helped to launch the field of synthetic organic chemistry [4]. Studies on the chemical structure of natural indigo in Germany eventually led to its successful synthesis by Adolf von Bayer in the early 1880s [5]. Soon the indigo derived from plants was replaced by synthetic indigotin manufactured by major dye industries in Europe, notably Badische Anilin- und Soda-Fabrik (BASF) and Farbwerke Hoechst AG [6]. The European synthetic dye industry thrived.

By the 1910s the Germans were supplying at least 80% of the dyes sold on the world market [7]. At the start of WWI, the Dow Chemical Company, which was based in Midland Michigan, saw that there would soon be a shortage of the dyes used by the textile makers in the USA and embarked on an effort to establish a manufacturing process using their own chemical building blocks for making synthetic indigo. After several years of intensive laboratory investigation, their chemists evolved a complete synthesis of the dye based on the Heumann process. The operation of the indigo plant on a commercial scale was an acknowledged success in December, 1916, thus initiating the first production of synthetic indigo in the USA [7]. The determination of the chemical composition of indigo, with its resultant commercial production, placed in the hands of the chemist a new basic material.

Derivatization of organic colorants can lead to dyes with new shades of color, improved fiber binding, and better lightfastness. As the demand for indigo grew, derivatives were synthesized [5], and some were marketed [8–11]. A full range of halogenated indigoids were discovered in 1907 by Engi of the Swiss Society of Chemical Industry in Basle (CIBA) [12]. Looking for ways to make use of its principle product, bromine, along with its newly developed synthetic indigotin, Dow began producing in partnership with CIBA, brominated derivatives of indigo, offering the 5,5′-dibromoindigo analog (5,5′-DBI, Fig. 1c) as Midland Blue R by 1919 [7]. Bromination or chlorination was found to yield products which dyed cloth further to the red or green shades and enhanced considerably the fastness. Dow Midland Vat Blue brands MB, R, and 5B were soon also placed on the market. In due time, the faster bromine derivative Ciba Blue 2B (5,5′,7,7′-tetrabromoindigo) was manufactured by Dow through license from the patentee, CIBA. This last addition to the projects of the Dow Chemical Company completed the series of blue dyes of the indigo group [11].

Steen notes that Dow's brominated indigos, while a modest share of their synthetic indigoid line, became the "most profitable end" of their dye production by 1920 [9]. However, among those brominated derivatives of indigotin that were patented worldwide [13], it would appear that none of these made a significant and lasting commercial impact or challenged the supremacy of synthetic indigo as suggested by the scant scientific, trade, or industrial literature pertaining to them. In a telling example, a forensic study used absorption microspectrophotometry to search for indigo and its derivatives in samples from 160 blue denim garments of various brands and manufacturers from Asia, Europe, and America [14]. The researchers found only indigotin, suggesting that rarely have the halogenated indigos been used as dyestuffs for denim in modern times. Similarly, Raman analysis of historic and modern "jeans" in a French fashion museum collection found primarily indigotin, although three garments gave Raman spectra that could not be identified [15]. One of these, shown in their paper as Fig. 6a, could possibly be 5,5′-DBI based on the results of this research. Although fashion interest in these brominated indigos appears not to have been strong in the West, indigo and its halogenated analogs have recently been explored as possible additives to organic semiconductors [16], arguing for a more complete characterization of these dyes.

Japanese *Yukata*

In preparation for a recent museum exhibition on the chemistry of color, scientists at the Indianapolis Museum of Art (IMA) at Newfields investigated four blue Japanese *yukata* as possible examples of artworks colored with indigo. *Yukata* are traditional Japanese summer garments that generally resemble silk kimonos, but are less formal and are often woven from cotton. Those with a deep blue coloration are usually thought to be dyed with indigo. The designs of two of the IMA's *yukata* are created out of only blue and white using a method of resist dyeing known as *shibori* [1]. To achieve a pattern, the textile is tightly gathered and methodically stitched or bound creating a physical resist that protects the fabric from dye penetration. The bound textile is then immersed into a dye bath, presumably indigo. Upon completion of the dye cycle the protective binding materials are removed and the undyed white patterned fabric is revealed. To specify the presence of natural or synthetic indigo, chemical studies were performed on blue threads from these garments. Surprisingly, the results from two of the four robes indicated that the dye was not indigo, but rather an unusual blue halogenated derivative little discussed in the scientific literature and unknown in technical art history. The two relevant *yukata* are shown in Fig. 2. This report discusses the first identification in a museum context of 5,5′-DBI, known in the Colour Index as C.I. 73060 and Vat Blue 35, which was marketed in the US in the early to mid-1900s by Dow Chemical Company as Midland Blue R.

Experimental

Samples

Synthetic indigotin (C.I. 7300, Vat Blue 1) of 95% purity was obtained from Sigma Aldrich (#229296). An historic sample of 5,5′-DBI (C.I. 73060, Vat Blue 35) manufactured by BASF and labeled "Indigo rein BASF/RB" was obtained from the historic industrial dye collection at Technische Universität Dresden. Two historic dyed cotton fibers were obtained from industrial dye swatch trade publications: "Calcosol Blue R" from American Cyanamid and "Sulfanthrene Navy Blue MR" from Dupont, both of which appear as tradenames for Vat Blue 35 in the Colour Index #73060 [13]. A modern commercial sample was also obtained from the Sigma Aldrich Rare Chemical Library with no guarantee of purity or accuracy of contents (#PH002016). Natural 6,6′-dibromoindigo (C.I. 25800, Natural Violet 1) extracted from the *Purpura lapillus* snail was purchased from Kremer Pigmente as Tyrian Purple (#36010).

Sample extraction

Single blue fibers of approximately 1 cm length were cut from the raw edge inside the hems of the *yukata* so as to cause no visible damage to the textile. The dyes were recovered by heating single threads weighing 310 µg (IMA 2015.103) and 210 µg (IMA 2015.112) in 100 µL of spectrophotometric grade dimethyl sulfoxide (DMSO, Acros Organics) at 80 °C for 60 min. After cooling, the almost colorless fiber was discarded, and the blue DMSO extract was filtered through a 0.45 µm PTFE membrane. Reference material powders were similarly dissolved, heated, and filtered. A 5 µL aliquot of the filtered sample solution was analyzed by liquid chromatography. For vibrational spectroscopy analysis, a few µLs of the DMSO extract solution were

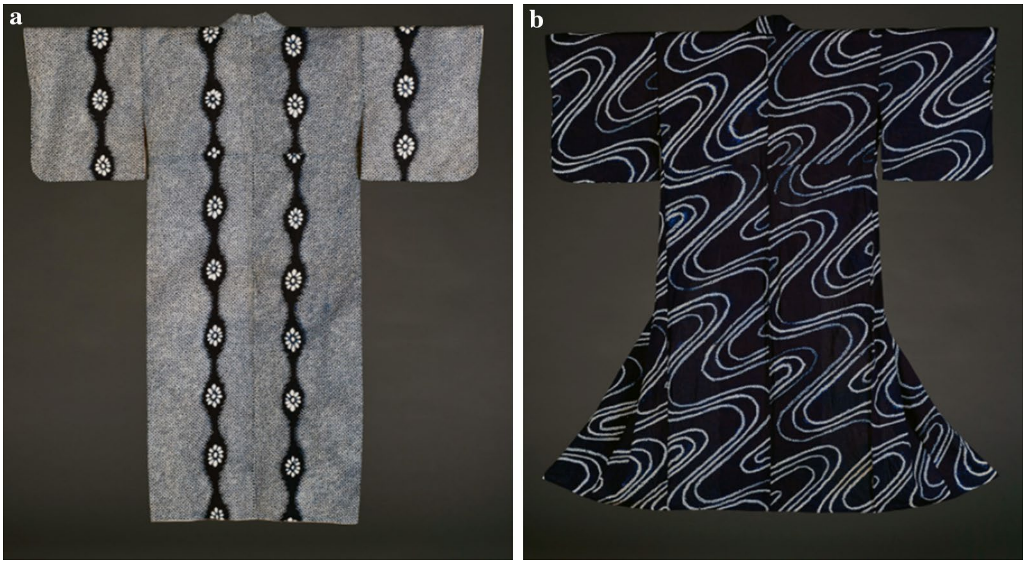

Fig. 2 Two cotton *yukata* dyed using the *shibori* method. **a** IMA 2015.103, 61 × 49¼ in., 1940–1950 and **b** IMA 2015.112, 60 × 50¾ in., 1950s. Gift of Jeffery Krauss. Photo courtesy of Newfields

pipetted onto a small PTFE sheet and allowed to dry in air, creating microcrystals of the dye.

Liquid chromatography-diode array detector-electrospray ionization-mass spectrometry (LC-DAD-ESI-MS)

Dye extracts were analyzed on a Thermo Accela LC coupled in series to a photodiode array detector and a Thermo LTQ ion trap MS with an ESI source. Dye separation was performed on a Restek Ultra C18 reverse-phase column (150 mm × 4.5 mm, 5 μm particles) held isothermally at 30 °C and eluted at 0.5 mL/min with a gradient of acetonitrile (ACN) in aqueous 0.1% formic acid. Formic acid and ACN were Fisher Optima grade for LCMS while 18.2 MΩ water was acquired from a Millipore Milli-Q Direct 8 purification system. Nitrogen sheath and auxiliary gases for the MS were delivered from a gas generator (Peak Scientific) at 99.5% purity, and helium for collision-induced dissociation (CID) was > 99.99% purity (Indiana Oxygen).

A 5–25 μL volume of sample was injected using a partially or fully filled 25 μL sample loop. The column was equilibrated at 3% ACN, and beginning 6 min after sample injection, a linear gradient of ACN was applied, increasing to 93% in 60 min. Considering the limited sample from artworks, the slow gradient elution was designed for detecting and identifying all possible extractable compounds from the sample in a single run. The effluent from the column was monitored by DAD in the range of 200 to 800 nm at 20 Hz and 1.2 nm resolution. Chromatograms are based on the sum of the DAD absorbances over the wavelength range 300 to 700 nm. For routine analysis, the LTQ mass spectrometer was programmed to scan in alternating positive and negative polarity at 910 μs/u in "zoom scan" mode. In each polarity, a full scan mass spectrum (FSMS) was made in the m/z range 50–2000 followed by two tandem mass spectral scans (MS2) that monitored the daughter ions derived from CID of the highest and second highest abundant ions detected in the FSMS. For structural confirmation, an additional injection was made involving an MS2 event targeting specific ions of interest, such as $m/z = 263$ for indigotin and $m/z = 419$, 421, and 423 for the isotopic clusters of dibromoindigos in positive ionization. A solvent blank was run immediately before each sample to confirm there was no carryover. The ion transfer capillary in the ion source was set at a temperature of 350 °C; sheath nitrogen gas flow was set at 80, and auxiliary nitrogen gas flow at 10. CID was set to target singularly charged ions using an isolation width of 2.00, collision energy setting of 45, activation Q of 0.25, and activation time of 30 ms.

Raman microspectroscopy

Raman spectra were acquired using a Bruker Senterra microspectrometer on a Z-axis gantry. The spectrometer utilizes 3 selectable excitation lasers (532, 633, and 785 nm), an Andor Peltier-cooled CCD detector, and a 50 μm confocal pinhole. Laser power at the sample was generally below 1 mW to avoid thermal degradation or band broadening. The spectra are the result of 3 s integrations with 10–50 coadditions. A 50X ultra-long working distance objective was used to focus on dye agglomerates located on fiber samples or on pigment particles for neat samples of the dyes. The analysis spot size was on the order of 1 μm, and the spectral resolution was in the range of 3–5 cm^{-1} for reference spectra and 9–15 cm^{-1} for analyses performed on samples from the textile. OPUS software allowed for automated cosmic spike removal, peak shape correction, and spectral calibration. For neat dye samples, superior data was obtained using the 532 nm laser; however native fluorescence of the textile samples restricted the analyses to 785 nm excitation for dyed fibers.

Density functional theory (DFT) calculations

Theoretical Raman spectra were calculated using DFT by the Gaussian09 computer program for indigotin, 6,6′-DBI, and 5,5′-DBI. The spectra were computed using the density functional method B3LYP and a reasonably large basis set of 6–31G**.

Fourier Transform Infrared (FTIR) microspectroscopy

FTIR microspectroscopy was performed on a Continuum microscope with an MCT A detector coupled to a Nicolet 6700 spectrometer purged with dry, CO_2-free air. The spectra are the sum of 32 coadditions at 4 cm^{-1} spectral resolution. Microsamples were crushed on a diamond compression cell and held on a single diamond window during the analysis.

Portable X-ray fluorescence spectroscopy (pXRF)

A Bruker Tracer III–V handheld XRF spectrometer with rhodium tube, silicon-pin detector, and polymer window (~ 3 × 5 mm oval spot) was used in the analysis. Experimental parameters included 40 keV tube voltage, 6.5 μA current, and 60 s live time acquisitions. A vacuum attachment allowed for light element detection. Elemental survey spectra were collected in the region from 0 to 40 keV with no source filter.

Results and discussion

LC-DAD-ESI-MS

Analysis of the fiber extracts was performed for the original sample set of 4 *yukata* with the expectation that all would be dyed using natural or synthetic indigo. One of the textiles was found to contain indigo, and one contained a synthetic dye (not shown) that did not have the spectroscopic properties of an indigoid. The robes shown in Fig. 2, however, presented indistinguishable chromatographic and spectral properties, as seen in Fig. 3 (rows 1 & 2), suggesting that they contain the same dye. Comparison with the chromatogram for synthetic indigotin (row 3) reveals that the *yukata* dye is not indigo. The *yukata* dye elutes later in the chromatogram than indigotin, and its visible absorption band at 618 nm shows a bathochromic shift from that of indigotin at 609 nm.

Tellingly, the *yukata* dye's positive ion mass spectrum contains a triplet at m/z 419, 421, and 423 characterized by a ratio of approximately 1:2:1 with the central member being 158 amu greater than m/z 263, the $[M+H]^+$ ion for indigotin. This mass increase is consistent with a dibrominated substitution for two hydrogens in indigo, with members of the triplet peaks assignable to the three dibromo isotopic variants $^{79}Br^{79}Br$, $^{79}Br^{81}Br$, and $^{81}Br^{81}Br$ as reported in the literature for 6,6′-DBI from the ancient dye Tyrian purple [17].

Comparison of the data from the two *yukata* (Fig. 3, rows 1 & 2) with that of a reference sample of Tyrian purple (row 4), shows excellent correlation in both retention time and mass spectrum. However, the *yukata* are a deep blue color and not purple, which is reflected in the solution absorption spectra of their dye extract as seen in the DAD data in the middle column of Fig. 3. Tyrian purple's primary absorption band detected in the acetonitrile/water eluent lies at 596 nm compared to the *yukata* dye's peak at 618 nm in the same solvent solution. Although 6,6′-DBI has been shown to produce various shades of color based on the fabric substrate used for dyeing, all have a reddish to purple cast that is unlike the appearance of the *yukata* [18]. Two other possible explanations for the anomalous color can be discounted based on the LC–MS experiment. First, only a single major chromatographic peak exists for the blue *yukata* dyes, ruling out the possibility of a dye mixture such as indigo and Tyrian purple. Second, although monobromoindigotins

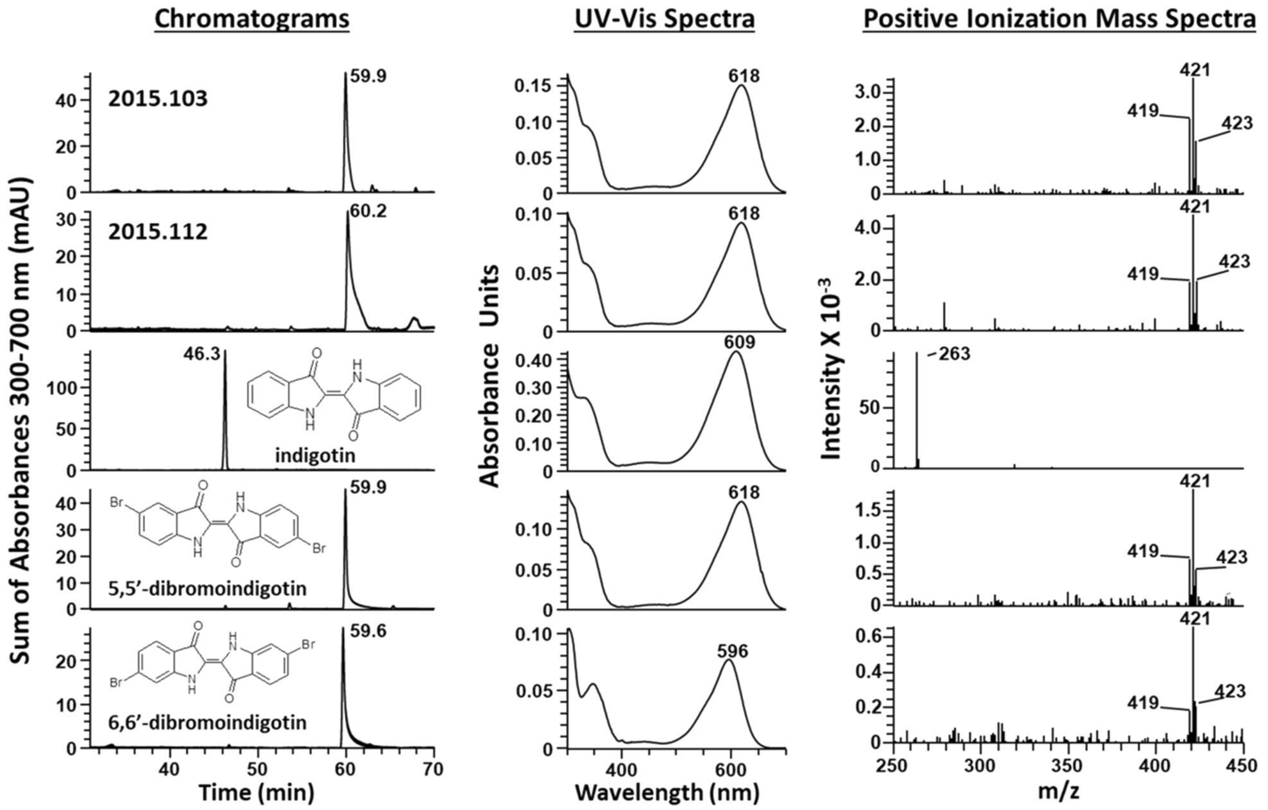

Fig. 3 Comparison of LC-DAD-ESI-MS analyses of extracts of the blue dyed *yukata* shown in Fig. 2 with indigoid reference materials. The data include chromatograms in column 1, UV–vis DAD spectra of the primary chromatographic peak in column 2, and FSMS spectra in column 3. Spectra presented were subjected to a baseline correction routine that included a two-range subtraction using the regions immediately before and after the occurrence of the chromatographic peak

like 6′-monobromoindigo can produce deep blue shades on dying certain fabrics, its color on cotton is best described as lavender in shade [18]. Moreover, the FSMS spectra of the *yukata* dyes clearly indicate a dibrominated species in each instance.

A search of the literature for blue indigoid dyes uncovered the previously mentioned 5,5′-dibromoindigo, Vat Blue 35 (C.I. 73060), that was marketed at one point as a textile dye [4–14, 19]. This dye has not appeared previously in cultural heritage studies and was unknown at the time by the authors. In this dihalogenated species, the symmetrical bromine substitutions occur in the 5,5′ positions leading to a bathochromic shift in the absorption spectrum when compared to purple 6,6′-DBI, resulting in a deep blue dye like that seen in the *yukata* [10, 11]. According to Dow product literature from the late 1920s [11], "Bromine can combine chemically with indigoes of different bromine content. They surpass indigo in brilliancy, fastness, and affinity for the fibre." The shade varies from a reddish-blue to a greenish-blue with increasing degree of bromination. These dyes were marketed for their excellent fastness to acid, alkali, soap, light, and resistance to chlorine bleach. Midland Vat Blue R, Midland Vat Blue MB, Midland VAT Blue 5B, Midland Vat Blue 6B, CIBA Blue 2B, and CIBA 2BD are listed as the various bromine derivatives of indigo that were produced. The lower brominated products show close relationship to indigo, both as regards to their tinctorial behavior and their fastness. Company trade advertisements from the time, Fig. 4, show that they intensely marketed Midland Blue R to industrial dyers as an improvement over synthetic indigo, stating that it was "faster, brighter, stronger, better than indigo" [8]. The exact dates of production for Midland Blue R could not be discovered, although company records indicate that it was still in production in 1938 along with the tetrabrominated Ciba Blue 2B [18]. Furthermore, a photograph found in the Dow archives held by the Chemical Heritage Foundation indicates production beyond that date. The photo shows two large shipping drums stenciled with "Midland Vat Blue R" on a loading dock. The image is hand labelled in pen with "15051," the meaning of which is uncertain, and dated 1947. Dow Chemical Company is said to have ended its indigoid dye manufacturing in the early 1950s [8]. The German chemical giant BASF also produced 5,5′-DBI under the name Indigo RR, RB, and RBN [10, 19], and Bayer; Cassella Co.; Sandoz Ltd.; and Meister, Lucius, & Brüning Ltd. all also took out patents on the manufacture of 5,5′-DBI, possibly in order to market commercial products [13]. In light of this long production history and intense marketing, it is surprising that examples of 5,5′-DBI have not been found previously in museum textiles. Samples of the colorant were acquired to compare to the dye extract from the two *yukata*.

MIDLAND

BLUE R

FASTER
BRIGHTER
STRONGER
BETTER
THAN INDIGO

A Distinctly New Product of the American Dyestuff Industry

For Sale by:
ANILINE DYES AND CHEMICALS, INC.
CEDAR AND WASHINGTON STS.,
NEW YORK CITY.

Manufactured by:
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN.

Fig. 4 A 1919 trade advertisement for Dow Chemical's Midland Blue R vat dye [8]

A commercially acquired sample of 5,5′-DBI from Sigma Aldrich's Rare Chemical Library yielded a single major chromatographic peak as seen in row 5 of Fig. 3. Taken together, the LC-DAD-ESI-MS data from this reference sample suggest that the *yukata* dye is nearly pure 5,5′-DBI with only minor contributions from unreacted starting materials and synthetic byproducts. However, identical chromatographic analysis of a historic example of Vat Blue 35 labelled "Indigo rein BASF/RB" showed the presence of indigotin, 5-bromoindigo, and 5,5′-DBI in significant relative quantities (not shown) as mentioned by Thorpe and Ingold [10] and previously reported by those examining the use of bromoindigoids in organic semiconductors [16]. By contrast, the dyes "Calcosol Blue R" from American Cyanamid and "Sulfanthrene Navy Blue MR" from Dupont were extracted from fibers collected from period sample swatch books distributed by the manufacturers, and these samples showed a single peak for 5,5′-DBI (not shown), similar to that observed in the *yukata*. Based on these data, BASF could possibly be excluded as the manufacturer of the dye used on the *yukata* if the example studied here was typical of that German company's production, but a specific manufacturer for the dyestuff on the Japanese garments cannot be determined based on this data alone. The dye may even represent an as yet unknown Asian producer, but this can only be speculation at this point.

Raman microspectroscopy

To confirm the identification and provide currently unavailable reference spectral data for 5,5′-DBI, Raman microspectroscopy was applied to the dried DMSO extract of the *yukata* dyes as well as reference powder samples of indigo; 6,6′-DBI; and 5,5′-DBI. Band positions and assignments have been previously published for indigotin and Tyrian purple [20], but a similar assignment is not yet available for the 5,5′-DBI analog. The Raman spectra collected using 532 nm excitation for these samples are given in Fig. 5, however the spectra at 633 and 785 nm were similar, albeit weaker. Only the data from one *yukata* is provided, although both garments yielded identical results. It is clear from the comparison in Fig. 5 that Raman spectroscopy adequately distinguishes the three indigoid dyes and verifies that the dye used in the *yukata* is consistent with 5,5′-DBI. It is also obvious that the positional isomers of DBI are easily identified by their unique Raman spectra, especially in the relative intensity and wavenumber differences in the ν(CBr) band, which appears weakly at 315 cm^{-1} in 5,5′-DBI and strongly at 308 cm^{-1} in 6,6′-DBI [20]. Importantly, in situ analysis of the dyed *yukata* fibers was also successful using 785 nm excitation. However, the spectrum (not shown) revealed small band shifts and intensity variations compared to that of the dried extract. This has been reported for indigo as well where it was attributed to changes in the planarity of the molecule upon interaction with the fiber [15].

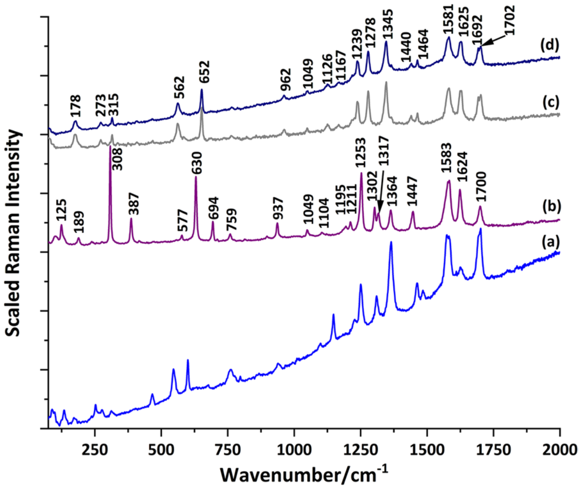

Fig. 5 Raman spectral comparisons of **a** synthetic indigotin, **b** 6,6′-DBI from natural Tyrian purple, **c** the extracted dye crystals from *yukata* IMA 2015.112, and **d** 5,5′-DBI from Sigma. Peak wavenumbers are provided for the two isomers of DBI

Density functional theory calculations

The experimental Raman spectrum of 5,5′-DBI reported here for the first time was verified by comparison to band energies calculated using DFT. Table 1 presents the comparison of the calculated peak positions with the

Table 1 Experimentally determined Raman bands in the range of 170 to 1700 cm^{-1} for 5,5′-DBI compared to the calculated B3LYP/6-31G bands from DFT. Group symmetries for each matching band pair are given assuming C_{2h} symmetry for the molecule**

Sym	DFT/cm^{-1}	Expt/cm^{-1}	Scaled/cm^{-1}	Sym	DFT/cm^{-1}	Expt/cm^{-1}	Scaled/cm^{-1}
B_g	173	178	171		935		
A_g	275	273	273	B_g	972	961	966
A_g	315	315	313		976		
	330			A_g	1074	1050	1067
	377			A_g	1151	1125	1144
A_g	417	409	414		1192		
B_g	466	467	463	A_g	1244	1237	1236
	501			A_g	1266	1278	1258
B_g	571	562	567	A_g	1320	1346	1312
	579				1394		
A_g	659	652	655	A_g	1412	1441	1404
	699			A_g	1479	1463	1470
	734				1503		
A_g	785	765	780	A_g	1627	1582	1617
	800			A_g	1655	1627	1645
	832			A_g	1695	1698	1685
	873						

Calculated values were scaled based on the linear regression fit of the experimental and calculated peak positions in Fig. 6

experimentally determined Raman peak positions for the Sigma Aldrich reference sample of 5,5′-DBI analyzed using the 532 nm excitation laser. For clarity, all vibrational modes from the DFT calculation are shown, but the Raman active modes are indicated by their A_g and B_g symmetries.

Figure 6 shows the linear regression fit of the two data sets that is used to generate the scaled series of peak positions listed in Table 1. The scaled calculated data represent the best fit between experiment and theory. Scaling resulted in a root mean square deviation (RMSD) of 18 cm^{-1} and an average absolute deviation of 1.3% between the experimental and scaled frequencies. The correlation between the experimentally determined Raman spectrum and the DFT calculation provides further evidence that the *yukata* dye is indeed 5,5′-DBI.

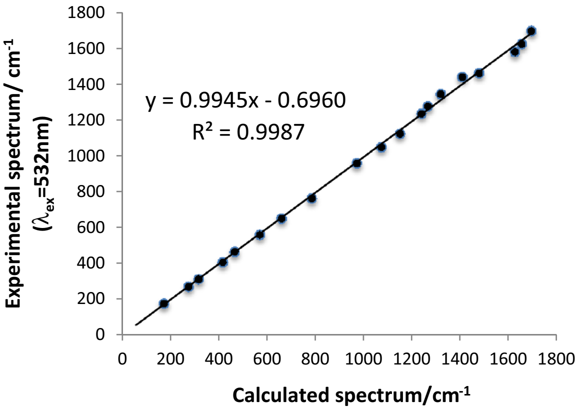

Fig. 6 Correlation plot of the experimental Raman peaks for 5,5′-DBI using 532 nm excitation with their associated DFT calculated peaks. The linear regression was used to create a set of "scaled" Raman peak positions that present the best match of experiment and theory

FTIR spectroscopy

Direct analysis of the dyed cotton fiber using FTIR attenuated total reflection (ATR) spectroscopy provided a spectrum dominated by cellulose with only a few very weak bands indicating the presence of the dye (not shown). Even when the undyed fiber was used for spectral subtraction, the resulting spectrum of the dye was noisy and yielded only the highest intensity IR bands. To confirm the identification and provide valuable reference data, FTIR microspectroscopy was performed on the dried crystallites obtained by extracting the *yukata* textile fibers with DMSO.

Figure 7 shows the spectrum of (a) the dried dye extract from one of the *yukata* compared to (b) the Sigma Aldrich reference sample of 5,5′-DBI. The strong overlap of the two spectra confirms the identification of the *yukata* dye as 5,5′-DBI. The two ν(CH) stretching bands in the extracted dye sample at 2922 and 2853 cm^{-1}, however, do not appear strongly in the reference sample. Similarly, the extract shows a broad, low intensity carbonyl feature at approximately 1710 cm^{-1} that is also absent in the reference spectrum of 5,5′-DBI. These vibrational bands do not appear to be intrinsic to the FTIR spectrum of 5,5′-DBI. These additional spectral features from the *yukata* dye are likely due to an unidentified organic material that was inadvertently leached from the fiber along with the blue dye by the DMSO extraction. It is possible that an organic residue from the *shibori* dying or possibly a fabric treatment applied post dyeing could exist on the finished fiber.

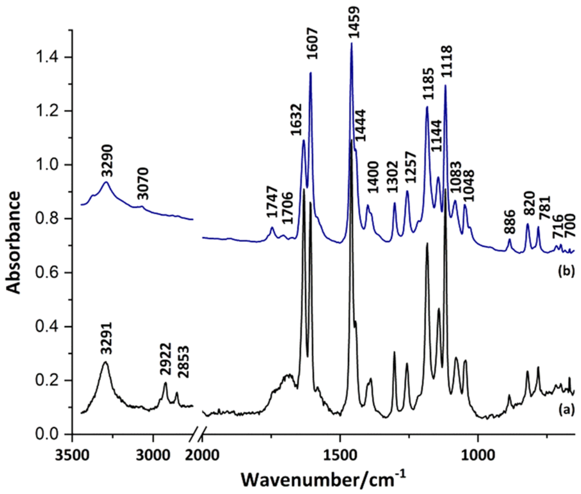

Fig. 7 FTIR spectral comparison of **a** the dried dye extract from *yukata* IMA 2015.112 and **b** 5,5′-DBI

Handheld pXRF analysis

Half of the original set of Japanese textiles examined for the possible presence of indigo were in fact colored with the relatively unknown dye 5,5′-DBI. The question remains how common this dye might be in traditional twentieth century Japanese fashion. To facilitate surveys of large museum textile collections, pXRF was explored as a rapid, sensitive, and non-invasive analytical technique capable of identifying blue brominated indigoids on museum textiles. Although shellfish purple could also generate an intense bromine signal, this would have to be investigated further to rule out the possibility of a dye mixture of blue 5,5′-DBI and a red colorant in purple dyed cloth. The potential for interferences from other brominated non-indigoid dyes or brominated fiber treatments was considered unlikely.

Figure 8a shows the spectrum acquired from a dark blue region of *yukata* IMA 2015.103. The strong Br

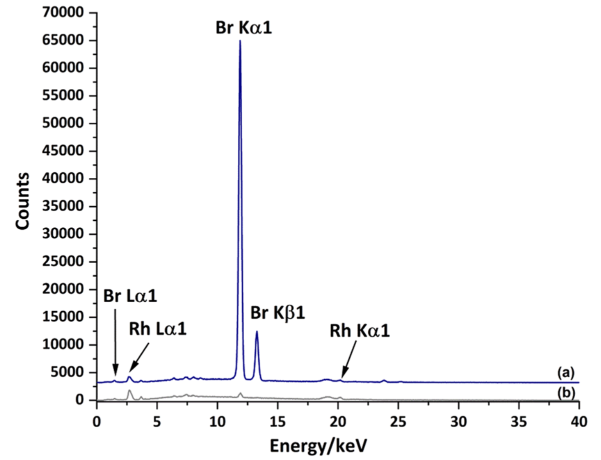

Fig. 8 XRF spectral comparison of **a** a blue dyed area and **b** an undyed area of IMA 2015.103 *yukata* showing the strong Br Kα_1 peak of the dye. The spectra have been offset for clarity

Fig. 9 A cotton *yukata* with 5,5′-DBI decoration. IMA 2016.46, 55½ × 47¼ in., 1880–1910, Gift of Dale Carolyn and Jonathan S. Gluckman. Photo courtesy of Newfields

Kα_1 peak at 11.92 keV was easily observed with a 60 s experiment even in lightly dyed areas of the textile. The intensity of the Br signal relative to the background and scattered radiation suggests even shorter experiments could be used for the non-invasive screening for blue brominated dyes. Only a very weak Br signature was detected in the mostly white areas of the same garment as seen in Fig. 8b.

A further exploration of 11 additional Japanese textiles from the twentieth century with deep blue coloration belonging to the IMA's collection was undertaken with pXRF. One additional cotton *yukata*, Fig. 9, showed intense bromine peaks in a pXRF analysis conducted on the blue squares patterning the surface. An extracted fiber sample from the object was subjected to LCMS analysis, which confirmed the presence of 5,5′-DBI. The white cotton fabric in this *yukata* is a plain weave, with a pattern of deep blue squares and thin blue S-curve lines achieved not by the *shibori* method in this instance, but through the use of a paste resist applied through stencils to protect the white fabric from dye penetration. The cloth was then immersed into a dye bath. Once the paste resist was removed the deep blue squares and curves are revealed. The object was originally dated by the donor to the late Meiji Period (1880–1910). However, the discovery of 5,5′-DBI sets a *terminus post quem*, or date after which, of at least 1907, which is the first reported synthesis of the dye by Engi [12]. This result highlights the use of dye analysis to refine the dating of museum textiles [21]. Of the fifteen twentieth century blue dyed Japanese textiles surveyed at the IMA, 20% of the objects were found to contain 5,5′-DBI, which included 100% of the cotton *yukata* examined. Similar surveys should be undertaken on larger collections of Asian fashion and textiles, and of indigo colored fabric from other parts of the world, to determine the extent and dates of use for this unusual colorant.

Conclusion

The unusual dibrominated indigoid 5,5′-DBI has been identified for the first time in a museum textile collection, having been serendipitously discovered on two Japanese *yukata* from the 1940s or 50s and on one thought originally to originate from the Late Meiji Period (1880–1910), leading to a reassessment of its age as post 1907. This dyestuff, which does not appear at this time to have had significant use in the West, was found on 20% of a small sampling of textiles from mid-twentieth century Japan, begging the question of whether Dow Chemical Company's Midland Blue R or one of its European rivals' product was used more commonly to color Eastern garments. The possibility of an Asian source for the dyes also cannot be discounted, although attempts to identify a historic producer in Japan or China proved fruitless. In light of this discovery, museum scientists, curators, and conservators cannot take for granted that these blue dyed traditional garments contain indigo, as previously thought. However, relatively quick and non-destructive analysis by pXRF can identify those textiles likely to contain 5,5′-DBI, with verification possible using vibrational spectroscopy in situ or on dried dye samples extracted from a small excised fiber.

Acknowledgements
The authors are indebted to IMA curator of textiles Niloo Paydar for allowing access to the *yukata* and providing background on their acquisition and history. Images of the *yukata* were taken by Newfields photographer Eric Lubrick. We would like to recognize Dr. Chris Cooksey for his encyclopedic knowledge of indigoids and his helpful discussions regarding this unusual example. We are grateful for the historic BASF Vat Blue 35 sample provided by Prof. Horst Hartman of TU Dresden and for the Calcosol Blue R dyed fiber sample from Jennifer Poulin of the Canadian Conservation Institute. The assistance of senior archivist Andrew Mangravite of the Chemical Heritage Foundation was invaluable when researching the Dow archives for information regarding bromoindigoids. Ms. Maddie Zook is recognized for her assistance in the initial experiments with pXRF to detect bromoindigoids in the *yukata*.

Authors' contributions
GDS and AH jointly planned and coordinated the research project. AH sampled from the *yukata*. GDS and VJC conducted the analyses and interpreted the results. SGL undertook and interpreted the DFT calculations. MHK surveyed the Dow archives at the Chemical Heritage Foundation and the Midland Historical Society. All authors read and approved the final manuscript.

Funding
The IMA exhibition *CSI: Chemistry of Color*, which gave rise to this research, was supported in part by an award from the National Endowment for the Arts (15-4400-7116). The Carter Family Fund, the Frenzel Family Charitable Trust, and Sarah and John Lechleiter are recognized for their financial support of this research.

Availability of data and materials
The datasets analyzed during the current study are available from the corresponding author on reasonable request and may be released upon consultation with the relevant curatorial and administrative departments.

Competing interests
The authors declare that they have no competing interests.

Author details
[1] Conservation Science Department, Indianapolis Museum of Art at Newfields, 4000 Michigan Rd, Indianapolis, IN 46208, USA. [2] Dow, 1712 Building, Midland, MI 48674, USA. [3] Chemistry Department, Butler University, 4600 Sunset Blvd, Indianapolis, IN 46208, USA.

Received: 21 May 2019 Accepted: 9 August 2019

References

1. Balfour-Paul J. Indigo: Egyptian mummies to blue jeans. Buffalo: Firefly Books; 2011.
2. Cooksey C. Tyrian purple: 6,6′-dibromoindigo and related compounds. Molecules. 2001;6:736–69.
3. Cardon D. Natural dyes: sources, tradition, technology and science. London: Archetype; 2007.
4. Morris PTJ, Travis AS. A history of the international dyestuff industry. Am Dyest Rep. 1992;81:59–109.
5. Sumpter WC, Miller FM. Chapter 5: indigo, $\Delta^{2,2'}$-bispseudoindoxyl. Chemistry of heterocyclic compounds, vol. 8. London: Interscience; 1954. p. 171–95.
6. Schmidt H. Indigo—100 jahr industrielle synthese. Chem unserer Zeit. 1997;31:121–8.
7. Whitehead D. The Dow story. New York: McGraw-Hill; 1968.
8. Baptista RJ. Dow chemical company, Midland, Michigan, first U.S. producer of synthetic indigo; 2008. http://www.colorantshistory.org/DowIndigo.html. Accessed 13 Apr 2019.
9. Steen K. The American synthetic organic chemicals industry: war and politics, 1910–1930. Chapel Hill: UNC Press; 2014.
10. Thorpe JF, Ingold CK. Chapter 5: substitution products and homologues of indigo. Synthetic colouring matters: vat colours. London: Longmans, Green and Co.; 1923. p. 86–106.
11. Dow Indigo, Midland Vat Blues, Ciba Blues. Midland, MI: Dow Chemical Company; No publication date given.
12. Engi G. Die Cibafarbstoffe der Gesellschaft fur chemische Industrie in Basel. Chem Ztg. 1908;98:1178–9.
13. Colour Index, 3rd edn, vol 4. Bradford, Yorkshire: Society of Dyers and Colourists, American Association of Textile Chemists and Colorists; 1971.
14. Grieve MC, Biermann TW, Schaub W. The use of indigo derivatives to dye denim material. Sci Justice. 2006;46:15–24.
15. Coupry C, Sagon G, Gorguet-Ballesteros P. Raman spectroscopic investigation of blue contemporary textiles. J Raman Spectrosc. 1997;28:85–9.
16. Głowacki ED, Voss G, Demirak K, Havlicek M, Sünger N, Okur AC, Monkowius U, Gąsiorowski J, Leonat L, Sariciftci NS. A facile protection-deprotection route for obtaining indigo pigments as thin films and their applications in organic bulk heterojunctions. Chem Commun. 2013;49:6063–5.
17. McGovern PE, Lazar J, Michel RH. The analysis of indigoid dyes by mass spectrometry. Color Technol. 1990;106:22–5.
18. Lavinda O, Mironova I, Karimi S, Pozzi F, Samson J, Ajiki H, Massa L, Ramig K. Singular thermochromic effects in dyeings with indigo, 6-bromoindigo, and 6,6′-dibromoindigo. Dyes Pigments. 2013;96:581–9.
19. Lunge G, Keane C, Thorne P. Lunge and Keane's technical methods of chemical analysis. 2nd ed. London: Gurney and Jackson; 1924. p. 1040.
20. Karapanayiotis T, Jorge Villar SE, Bowen RD, Edwards HGM. Raman spectroscopic and structural studies of indigo and its four 6,6′-dihalogeno analogues. Analyst. 2004;129:613–8.
21. Chen VJ, Smith GD, Holden A, Paydar N, Kiefer K. Chemical analysis of dyes on an Uzbek ceremonial coat: objective evidence for artifact dating and the chemistry of early synthetic dyes. Dyes Pigments. 2016;131:320–32.

Publisher's Note