



Singular thermochromic effects in dyeings with indigo, 6-bromoindigo, and 6,6'-dibromoindigo

Olga Lavinda^{a,1}, Irina Mironova^a, Sasan Karimi^b, Federica Pozzi^{c,d}, Jacopo Samson^e, Hiroko Ajiki^e, Lou Massa^{e,f}, Keith Ramig^{a,*}

^a Department of Natural Sciences, Box A0506, Baruch College of the City University of New York, 1 Bernard Baruch Way, New York, NY 10010, USA

^b Department of Chemistry, Queensborough Community College of the City University of New York, 222-05 56th Avenue, Bayside, NY 11364, USA

^c Department of Scientific Research, The Metropolitan Museum of Art, 1000 5th Avenue, New York, NY 10028, USA

^d Department of Chemistry, City College of the City University of New York, 160 Convent Avenue, New York, NY 10031, USA

^e Department of Chemistry, Hunter College and the Graduate School, City University of New York, 695 Park Avenue, New York, NY 10065, USA

^f Department of Physics, Hunter College and the Graduate School, City University of New York, 695 Park Avenue, New York, NY 10065, USA

ARTICLE INFO

Article history:

Received 8 June 2012

Received in revised form

16 July 2012

Accepted 17 July 2012

Available online 7 August 2012

Keywords:

Indigo

6-Bromoindigo

6,6'-Dibromoindigo

Thermochromic

Nanotube

Dyeing

ABSTRACT

Fundamental dyeing properties of three dyes of historical importance – indigo, 6-bromoindigo, and 6,6'-dibromoindigo – on 13 fabrics are examined. The hues of the dyed fabrics vary from blue-green to blue for indigo, blue to violet for 6-bromoindigo, and violet–blue to purple for 6,6'-dibromoindigo, as determined by reflectance measurements. Many of the dyed fabrics change color markedly with application of gentle heat. For indigo and 6-bromoindigo, the color changes are predominantly towards absorption of longer wavelengths (giving a bluer fabric color), while for 6,6'-dibromoindigo, the color changes are towards absorption of shorter wavelengths (giving a redder fabric color). The greatest thermochromic effects are seen for dyed wool: with 6-bromoindigo, the color changes from violet to blue, while with 6,6'-dibromoindigo, the color changes from violet to red–purple upon brief boiling in water. Transmission electron microscopy analysis of 6-bromoindigo-dyed carbon nanotubes, used as surrogates for dyed fabric fibers, suggests that the basis of the thermochromic effect is a change in the size distribution of dye aggregates.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Indigoid dyes have long and fascinating histories. Dyeing with natural indigo, obtained from such plants as *Indigofera tinctoria*, dates to 4000 years ago [1,2]. Its application to fibers continued well into the nineteenth century. The first preparation of synthetic indigo was devised by von Baeyer [3]; this was the beginning of the end for industrial production of the natural dye. Scientists have long been interested to know why the small molecule indigo is blue [4,5]. A blue-colored molecule – blue because of a very small gap between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO) – usually has an extended conjugated system of π electrons longer than that of indigo. The work of Klessinger and Luettke clearly illustrated that

the chromogen in indigo is the cross-conjugated H-chromophore which results in an unusually small HOMO-LUMO gap [6–8]. This gap may also be narrowed by factors which stabilize the LUMO, such as solvation or intermolecular hydrogen bonding [9]. This would result in absorption of longer wavelengths of light (giving a bathochromic or red shift), hence making the molecule appear more blue. Von Eller has explained the blue color of indigo based on the single-crystal X-ray structure analysis. She noted that indigo in the solid state forms aggregates *via* intermolecular hydrogen bonding, causing a red shift in light absorption compared to that of a single molecule [10]. In fact, indigo in the gas phase has a much shorter absorption λ_{\max} in the visible region, making it appear red [11].

The brominated indigoids 6-bromoindigo (monobromoindigo, or MBI) and 6,6'-dibromoindigo (DBI) have also been used as dyes for millennia. A mixture of these two plus smaller amounts of indigo and indirubins constitutes the dye known as royal or Tyrian purple (Fig. 1) [12–16]. The highest quality of the dye was found in Tyre on the Levantine coast in ancient times; hence, the name Tyrian purple. The earliest known occurrence of this mixture,

* Corresponding author. Tel.: +1 646 660 6243; fax: +1 646 660 6201.

E-mail address: keith.ramig@baruch.cuny.edu (K. Ramig).

¹ Current address: Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003, USA.

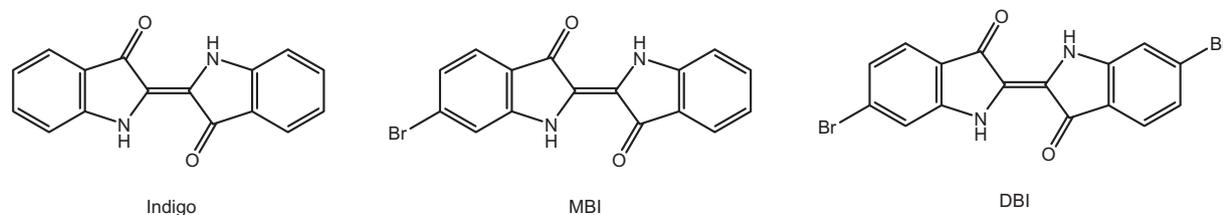


Fig. 1. The three indigoids under study, main components of Tyrian purple.

which was used as a pigment rather than a dye, was on the island of Thera about 3700 years ago [17]. The ancient Romans dyed their clothes with it, and it was so precious that only royalty or the priesthood had the means to obtain it. The production of the dye over 2000 years ago became an important part of the Phoenician economy [18]. Both Pliny [19] and Reinhold [20] wrote extensively about the significance and the preparatory method of Tyrian purple, which can be obtained from the Mediterranean shellfish *Murex brandaris*, *Murex trunculus*, and *Purpura haemastoma* [21]. The characteristic colorant of Tyrian purple, DBI, was identified by Friedländer [22]. Subsequently many syntheses of it have appeared, which have been reviewed by Cooksey [13], who, along with Clark also developed a synthesis of MBI [23]. A more recent treatment of existing DBI syntheses has been presented by Wolk and Frimer [24]. It is interesting to note that although the molecular skeletons of all three dyes are identical, indigo is obtained from plants while Tyrian purple is derived only from shellfish.

In the solid state, finely ground indigo and MBI are indistinguishable to the eye. When spread thinly, they are both dark blue, but when a thick layer is observed, they are both dark violet. On the other hand, finely ground DBI is dark purple. In solution, the colors of all three are difficult to distinguish amongst each other by eye; for example, the absorption λ_{\max} values in methanol are 598, 607, and 615 nm for DBI, MBI, and indigo, respectively [15]. The colors of natural fibers dyed with the three indigoids have been investigated by Clark and Cooksey [23] and Ziderman [25]. They noted that DBI gives more reddish dyed shades than MBI, which itself gives much redder dyeings than indigo. Clark and Cooksey found that the colors of MBI-dyed wool and DBI-dyed silk become more blue upon

dilution, while Ziderman has revealed that MBI-dyed wool when heated turns to a blue color very similar to the color of indigo-dyed wool. Synthetic fibers have also been dyed with either pure DBI [26] or the pigment from the *Ocenebra inornata* sea snail, which is mainly DBI [27].

Dyeing with these dyes is complicated by their limited water solubility. The indigoid must be first reduced to its water-soluble “leuco” or colorless form (Fig. 2). The dyeing process is completed by dipping the fabric into an aqueous solution of the leuco form until permeated, and then exposing the fabric to oxygen in the air (development), causing oxidation back to the colored form. The leuco form is highly sensitive to oxygen and, in the case of MBI and DBI, is subject to debromination by UV light [28–31].

We report here an improved dyeing procedure which gives consistent colors, taking into account the limited solubility and air-sensitivity of the leuco forms. This procedure is used for a comparison of the dyed colors of the three indigoids on 13 fabrics, both natural and synthetic. As far as we are aware, there is only one other comparative study [32] of the dyed colors of these three indigoids, when applied to both natural and synthetic fabrics. That study employed multi-fabric strips prepared by three of us (KR, OL, and SK) using an earlier method [23] of dyeing which we subsequently found to give variable colors. This will be commented upon in Section 3.1.

We also wish to report a systematic study of thermochromic effects and color changes upon dilution seen with fabrics dyed with all three of the indigoids under study here. And finally, we disclose that dyed carbon nanotubes can be used as a substitute for fabric fibers in analysis of the thermochromic effect by transmission electron microscopy (TEM).

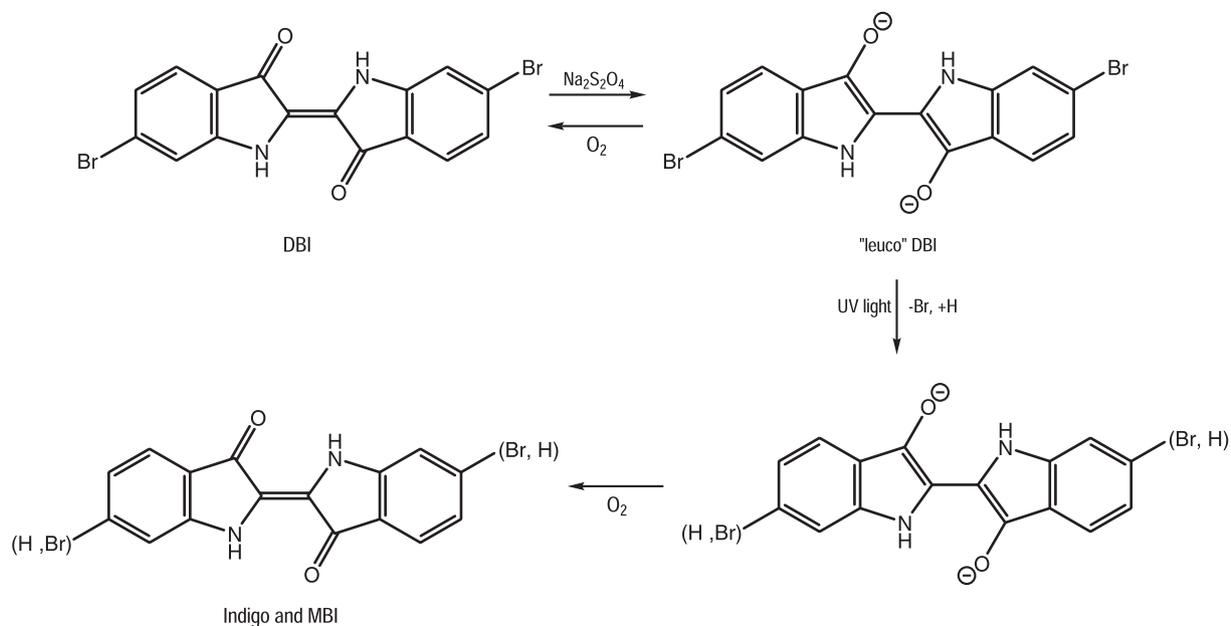


Fig. 2. Reversible reduction of DBI to its leuco form, and photolytic debromination of the leuco form to ultimately give indigo and MBI.

2. Materials and methods

2.1. Chemicals and materials

The 13 fabrics used in the dyeing were obtained as multi-fabric strips (style # 43) from Testfabrics, Inc. There were three natural fibers: wool, cotton, and silk; three cotton-based synthetics: filament acetate (diacetate), filament triacetate, and viscose (Rayon); three polyacrylics: SEF (modacrylic), Creslan 61, and Orlon 75; two polyesters: Dacron 54 and Dacron 64; Nylon 66; and polypropylene. Single-walled carbon nanotubes (40–60 wt % carbon basis, $D \times L$ 2–10 nm \times 1–5 μ m, bundle dimensions), tetrahydrofuran ($\geq 99.9\%$, inhibitor-free), sodium hydrosulfite (sodium dithionite; technical grade, 85%), and indigo (95%) were obtained from Sigma–Aldrich. MBI was prepared by the procedure of Clark and Cooksey [23]. DBI was synthesized by the procedure of Tanoue et al. [33]. The purities of MBI and DBI, as judged by HPLC peak areas, are 93% and 98%, respectively [32].

2.2. Instrumentation

TEM data were collected at 200 kV on a Jeol 2100 instrument equipped with EDAX at the eucentric height to ensure reproducibility of measurements.

Visible reflectance spectra were obtained in dual-beam mode using a Varian Cary 50 Bio UV–Vis spectrophotometer equipped with a Barreliano remote diffuse reflection probe by Harrick Scientific and a xenon flash lamp. The scan range was 200–800 nm with a maximum scan rate of 120 nm/s. Spectra of undyed fabrics were taken before each measurement and used as a calibration reference. The data were processed using Cary WinUV and Origin softwares.

2.3. Dyeing procedures

2.3.1. Dyeing of multi-fabric strips

The procedure reported by Clark and Cooksey [23] was modified. A 250-mL 3-neck round-bottom flask fitted with a water condenser is swept with nitrogen gas, and kept under a positive pressure of nitrogen during the dyeing. Distilled water (100 mL) and THF (15 mL) are introduced, followed by NaOH (0.50 g, 13 mmol). The solution is brought to reflux (75–80 °C) with magnetic stirring, and Na₂S₂O₄ (0.50 g, 85% purity, 2.4 mmol) is added, followed immediately by the indigoid (0.050 mmol), which had been finely ground in an agate mortar. At this point, for MBI and DBI, the lights are turned off and the flask is wrapped in aluminum foil. A yellow to yellow-green homogeneous solution is obtained after 15 min at reflux. After addition of NH₄Cl (2.0 g, 37 mmol), the fabric (1.4 g), which had been soaked in dilute soap solution, is introduced. The stirring rate is reduced, and the solution is heated at reflux for 15 min. The fabric is removed from the flask and exposed to air, while still protected from light. After at least 30 min of air exposure, the fabric is rinsed in aqueous 1% HOAc solution and allowed to dry. Second and third passes are made in the same manner with additional fabric strips. After the third pass, the dye vat is completely exhausted, as evidenced by lack of formation of insoluble dye particles when the vat is left open to air overnight.

Some of the MBI-dyed fabrics take several days at ambient conditions to reach their final color; right after the development, some are more red or more blue than samples which had been aged for a few days. We find that the colors from high-temperature dyeing are the same shades as those we obtain from dyeing at 50 °C, although fabrics after dyeing are subject to thermochromic effects at 60 °C (see section 3.2).

2.3.2. Dyeing of silk alone

A dye vat at double the above scale is used to dye 3-g pieces of silk fabric. Three passes for each of the three indigoids (0.10 mmol each) are made. The fabric permeation is performed at reflux, and the vat is cooled to <55 °C before the fabric is removed and exposed to air.

2.3.3. Dyeing of nanotubes

A 1-dram vial is purged with nitrogen gas, and carbon nanotubes (30 mg) are introduced. The vial is placed in a water bath at 50 ± 2 °C, and 2 mL of a solution containing the leuco form of MBI, prepared as above, is added. After 15 min of stirring under N₂, the black suspension is suction filtered, washing with 3 portions of distilled water. After 30 min of suction, the black powder is washed with 1 mL 1% HOAc solution. The filtrates are all clear and colorless. After 30 min of air-drying, 28 mg of black powder is isolated. At 40 \times magnification, the powder shows a metallic luster, while undyed carbon nanotubes are flat black.

2.4. TEM analysis

A suspension of MBI-dyed carbon nanotubes (1 mg) in acetonitrile (1 mL) is diluted by a factor of 37 and is sonicated for 30 s. A 8- μ L drop of the diluted suspension is placed on a 300-mesh carbon-coated copper grid (TED Pella Inc., Redding, California, USA) and allowed to dry for 1 min. The excess liquid is removed using filter paper. Energy Dispersive X-Ray Spectroscopy analysis (performed by EDAX) confirms the presence of bromine atoms, most likely within the darker areas of the image. These areas represent MBI molecular aggregates (see Fig. 1 from the Supporting Materials). A control sample prepared in the same way in the absence of MBI did not show these darker areas in the image. Since a carbon-coated grid was used and carbon nanotubes are present in the mixture, the Netcounts method (sample area minus control area) [34] is not used. As a result, the X-ray scattered lines from the copper grid show up in the background of the spectrum.

3. Results and discussion

3.1. Dyeing with indigo, MBI, and DBI, and analysis of dyed fabrics

First we present our results of dyeing of various fabrics with the three indigoids. Using the procedure of Clark and Cooksey at 50 °C [23] inconsistent results are obtained. We trace this to premature oxidation of the leuco form back to the water-insoluble indigoid. If the leuco formation and fabric permeation steps are not performed under an atmosphere of nitrogen gas, then particles of the oxidized dye tend to form, creating a thin film on top of the solution. These particles will not be adsorbed into the fabric but may adhere to the surface of it, giving false colors. In dyeings with DBI, we find that upon addition of ammonium chloride to the solution of leuco form, an off-white precipitate forms when the vat is kept at 50 °C, but is absent when the vat is kept at its boiling point (75–80 °C). We believe that the precipitate is the leuco form, which is only fully soluble at the higher temperature. Possibly for this reason, we have found DBI dyeings performed at 50 °C to be plagued by faint and variable colors. Also, after three passes of dyeing with both MBI and DBI at this temperature, particles of dye form in the vat upon exposure to air, giving evidence that the vat is not exhausted. This is not the case for three-pass dyeings done at the higher temperature (see Section 2.3). Also, the colors are much more rich and intense at the higher temperature; this has been found for some dyeings with indigo [35]. Additionally, Cooksey and Sinclair [26] have modified the original procedure [23] by using a higher temperature in dyeing with DBI.



Fig. 3. Multi-fabric strips dyed with indigoids, top to bottom: indigo, MBI, DBI. Fabrics, l to r: filament acetate (diacetate), SEF (modacrylic), filament triacetate, bleached cotton, Creslan 61, Dacron 54, Dacron 64, Nylon 66, Orlon 75, spun silk, polypropylene, viscose (Rayon), worsted wool.

We also advocate performing the dyeing under subdued lighting, based on a hint from the literature. While it has long been known that the leuco forms of brominated indigoids can be debrominated by UV light [28–31], there appears to be some evidence that room lighting will cause an unspecified amount of debromination of the leuco form of DBI [12]. However, Cooksey and Sinclair [26] note that tungsten room lighting does not cause debromination of DBI during a dyeing experiment. To probe this matter further, we have exposed a solution of the leuco form of MBI to fluorescent room lighting overnight under an atmosphere of nitrogen gas before fabric permeation and development. Subsequent dyeing gives fabric colors that are indistinguishable from the same fabrics dyed with indigo, indicating debromination. However, during the much shorter time of a dyeing experiment, we find that the colors and reflectance spectra of dyeings done in the dark vs. those unprotected from room lighting are indistinguishable from each other, so the amount of debromination must be insignificant. In Section 3.1.2 we will present a three-pass MBI silk dyeing done under subdued lighting. We find that this dyeing is indistinguishable, both by eye and reflectance spectra, from the same dyeing done under normal room lighting. Just to be safe though, we normally protect the MBI and DBI leuco solutions from room light.

3.1.1. Analysis of dyed multi-fabric strips

The improved procedure described above is used to dye 13 fabrics, which are parts of a multi-fabric strip (Fig. 3). All of the fabrics show a consistent reddening of their colors, on proceeding from indigo to MBI to DBI. This corresponds to a blue shift in the absorption spectrum, or an increase in the HOMO–LUMO gap of the adsorbed molecules. The indigo-dyed fabrics from the first pass vary from blue-green to blue, MBI-dyed fabrics vary from blue to violet, and DBI-dyed fabrics vary from violet-blue to purple. Several of the MBI-dyed fabrics appear black, due to high affinity of the dye molecule or its leuco form for the fabrics.

The colors of the dyed fabrics seen by the eye were put on a more exact basis by recording reflectance spectra. Figs. 4 and 5 show the results of three-pass dyeings. Indigo-dyed fabrics showed either only one minimum in the region of interest (500–650 nm), or a shoulder in the curve at shorter wavelengths. The positions of the minima do not vary appreciably with concentration, thus the corresponding fabric colors from the three passes do not change in hue. This is typified by the indigo-dyed wool from Fig. 5a. On the other hand, the spectra of the fabrics dyed with the two brominated indigoids all feature two minima, or sometimes a minimum accompanied by a shoulder at shorter or longer wavelength. Representative of this behavior are the spectra of wool dyed with MBI (Fig. 5b; reflectance data for the other fabrics will appear at a later date). While the minimum of the MBI first pass is at 530 nm (perceived violet color), there is a prominent shoulder centered around 620 nm (perceived blue color). Thus, the expected violet shade inferred from the minimum would be shifted somewhat towards a blue-violet color. The second-pass curve shows these same features, and therefore the wool is expected to appear very similar in color to the wool from the first pass. The third-pass curve shows two actual minima, with the less prominent one at 530 nm, and the more prominent one at 620 nm. So the wool from the third pass appears more blue than the others. The DBI-dyed wool of Fig. 5c shows these same general features. Clark and Cooksey [23] saw this trend towards longer absorbed wavelengths for increasingly diluted dyeings with MBI and DBI, and ascribed this to diminution of



Fig. 4. Three-pass dyeings with (a) MBI (t to b: 1st, 2nd, 3rd pass); (b) DBI (t to b: 1st, 2nd, 3rd pass). See Fig. 3 for fabric identity.

dye-aggregate size. Their reflectance curves of diluted MBI-dyed wool and DBI-dyed silk show that the shoulder at longer wavelength becomes more pronounced at lower concentration, and becomes the actual minimum after the fourth pass.

Another example from the literature is illustrative: Koren [21] has attempted to reproduce an ancient Tyrian purple wool dyeing, using *Murex trunculus* from the eastern Mediterranean area as the source of dye. The colorant obtained from these mollusks, both ancient and modern, in this region is composed primarily of DBI, with minor amounts of MBI and indigo [16]. In Koren's study, the reflectance curves of the dyed wool showed a minimum at short wavelength,

and a shoulder at longer wavelength, similar to Fig. 5b and c. The second-pass wool showed a lessening in the prominence of the minimum at shorter wavelength, making the wool appear blue. Koren originally attributed the minimum and shoulder to DBI and indigo, respectively; however in his later study [15], HPLC analysis did not confirm that DBI was the major component. The dyed wool from the first pass contained primarily MBI and indigo. Since MBI- and DBI-dyed wool have nearly identical reflectance spectra, the peak misassignment is understandable. What remains a mystery is why the eastern Mediterranean sea snails which produce a dye rich in DBI should give a dyeing containing very little of this component.

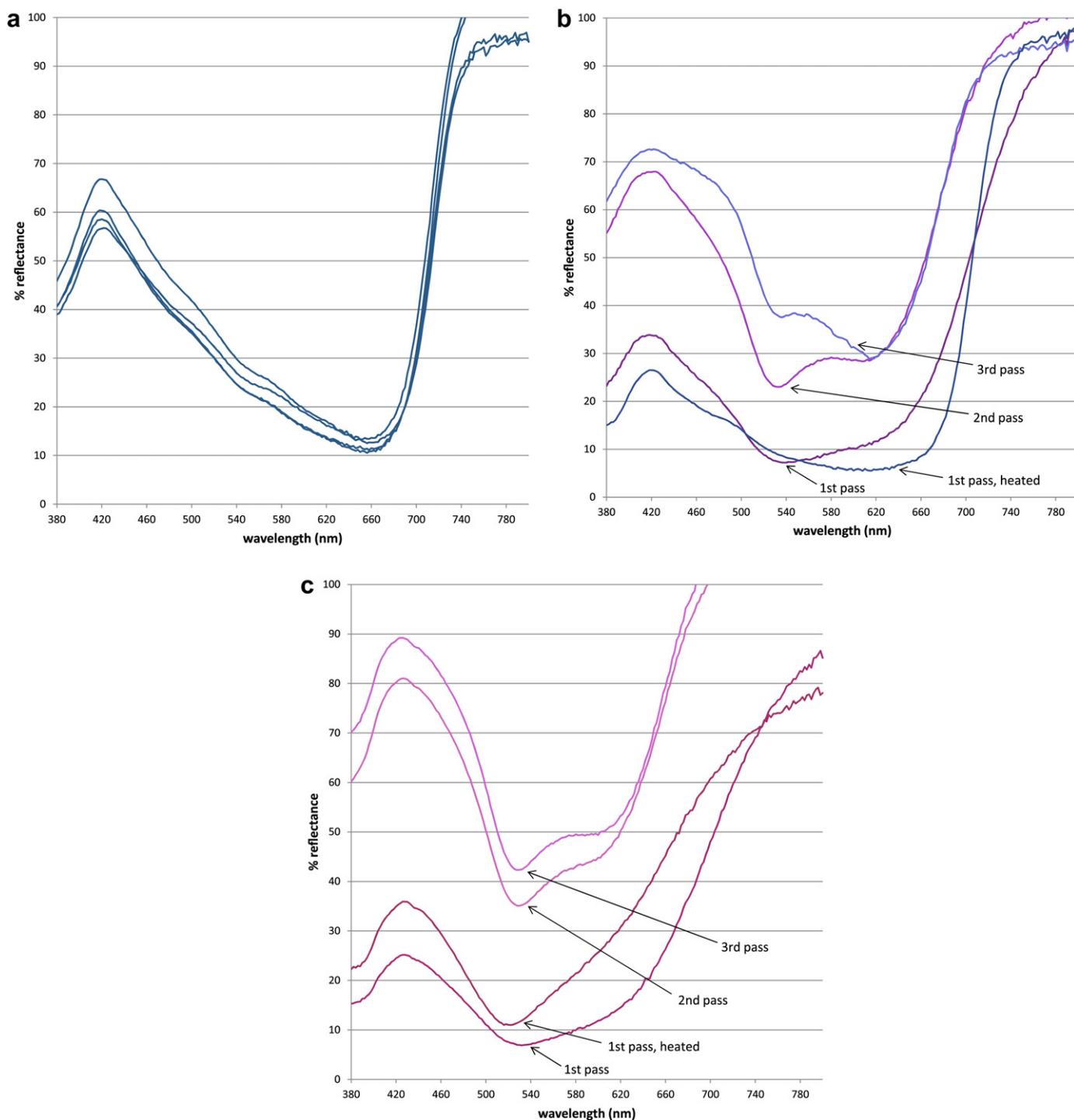


Fig. 5. Reflectance spectra of wool from multi-fabric strips dyed with (a) indigo, (b) MBI, and (c) DBI.

The color of the fabrics in the present case and in these previous examples depends on the relative intensities of two reflectance minima. We speculate that they represent two different types or colors of molecular aggregates. This is somewhat analogous to the behavior of MBI and certain other indigoids, which can form dimers in solution characterized by specific λ_{\max} values in the visible absorption spectra [23,36]. Drawing conclusions like these from our reflectance spectra alone can be a shaky proposition. However, Koren's recent colorimetric analysis of our dyed fabrics mentioned in the Introduction indicates that MBI- and DBI-dyed wool show only two color components, red and blue [32]. All the other dyed fabrics in that study show only two components as well.

In Section 3.2 we show that the relative intensities of two minima seen in the reflectance spectra of these dyed fabrics will also change after application of gentle heat, resulting in reddening or bluing of the fabric. It is possible that both the dilution- and heat-induced color changes are due to size redistribution of molecular aggregates.

3.1.2. An all-silk dyeing

An all-silk dyeing was performed and characterized by reflectance spectra. Three passes for each indigoid were made (Figs. 6 and 7). The curves for indigo show the expected blue to blue-green minima, the positions and shapes of which were not very sensitive to concentration. The curves for MBI show marked changes upon dilution, with minima shifting from 530 to 620 nm. The DBI curves show wonderful symmetry, and best illustrate the redistribution of colored aggregates upon dilution. The first-pass curve shows a minimum at 530 nm, and a longer-wavelength shoulder; the perceived color is purple–violet. The second-pass curve shows a narrower distribution of aggregates with more equal amounts of blue and red ones; the perceived color is violet–blue. In the third-pass curve, the shorter- and longer-wavelength minima are in approximately the same positions as they were in the first and second passes, and are equal in intensity; the perceived color is nearly blue.

3.2. Analysis of thermochromic properties of indigo, MBI, and DBI

The most interesting feature of the dyed fabrics is their color change upon heating. We have subjected each of the fabrics from

Figs. 3 and 6 to boiling water for 10 min (after this time, no further color change appears to occur), and find that many of them change color quite markedly (Figs. 5b, c, 6, 7b, c, 8). Color changes are evident even after a short time at 60 °C. For indigo- and MBI-dyed fabrics, the colors shifted predominantly towards blue upon heating. Surprisingly, fabrics dyed with DBI show the reverse trend, becoming more red upon heating. A full set of reflectance data will be published at a later date.

The heat-induced color changes do not depend strongly on the fabric's chemical composition. We also note that the color change is most likely physical rather than chemical in nature. For example, HPLC analysis of MBI extracted from heat-treated dyed wool does not show a chemical change [37]. We propose that heat induces the redistribution of molecular aggregates, similar to the way changes in dye concentration cause it, which is best shown in Fig. 7c. After heating the silk from all three passes, the shoulder at longer wavelength lessens appreciably, while the minimum shifts slightly towards red. The main determinant of the color change is most likely not the shift of the minimum, but is the disappearance of the "blue" aggregates, indicated by disappearance of the shoulder in the blue region of the spectrum. In Section 3.3, we will correlate these apparent aggregate redistributions to the actual size of the aggregates.

Ziderman [25] has reported that MBI after sublimation and vapor deposition changes from its original color to blue, and is of a different type of crystallinity. Also, he states that MBI itself when not adsorbed onto fabric also turns blue upon heating [38]. This would indicate that the thermochromism we note above is not related to the molecule's adsorption on the fabric, but is a property of the molecule itself. However, we have made some observations at variance with this. We find that after purification by slow recrystallization the product predominantly forms dark-violet elongated prismatic crystals, easily visible at 10× magnification and suitable for X-ray structure determination [39], which show a metallic sheen. These crystals undergo no color change upon heating to around 200 °C, at which point they start to sublime. It seems unlikely that the apparent new blue crystalline form obtained after sublimation at high temperature and vapor deposition has any relation to the low-temperature color change of MBI-dyed wool. To bolster this assertion, we will report elsewhere new X-ray crystal data obtained at high temperatures which will show that there is no change in the crystal structure up to 70 °C.



Fig. 6. Three-pass silk dyeing with indigo (left column), MBI, (middle column), and DBI (right column). Top to bottom: 1st, 2nd, 3rd passes; insets are heated.

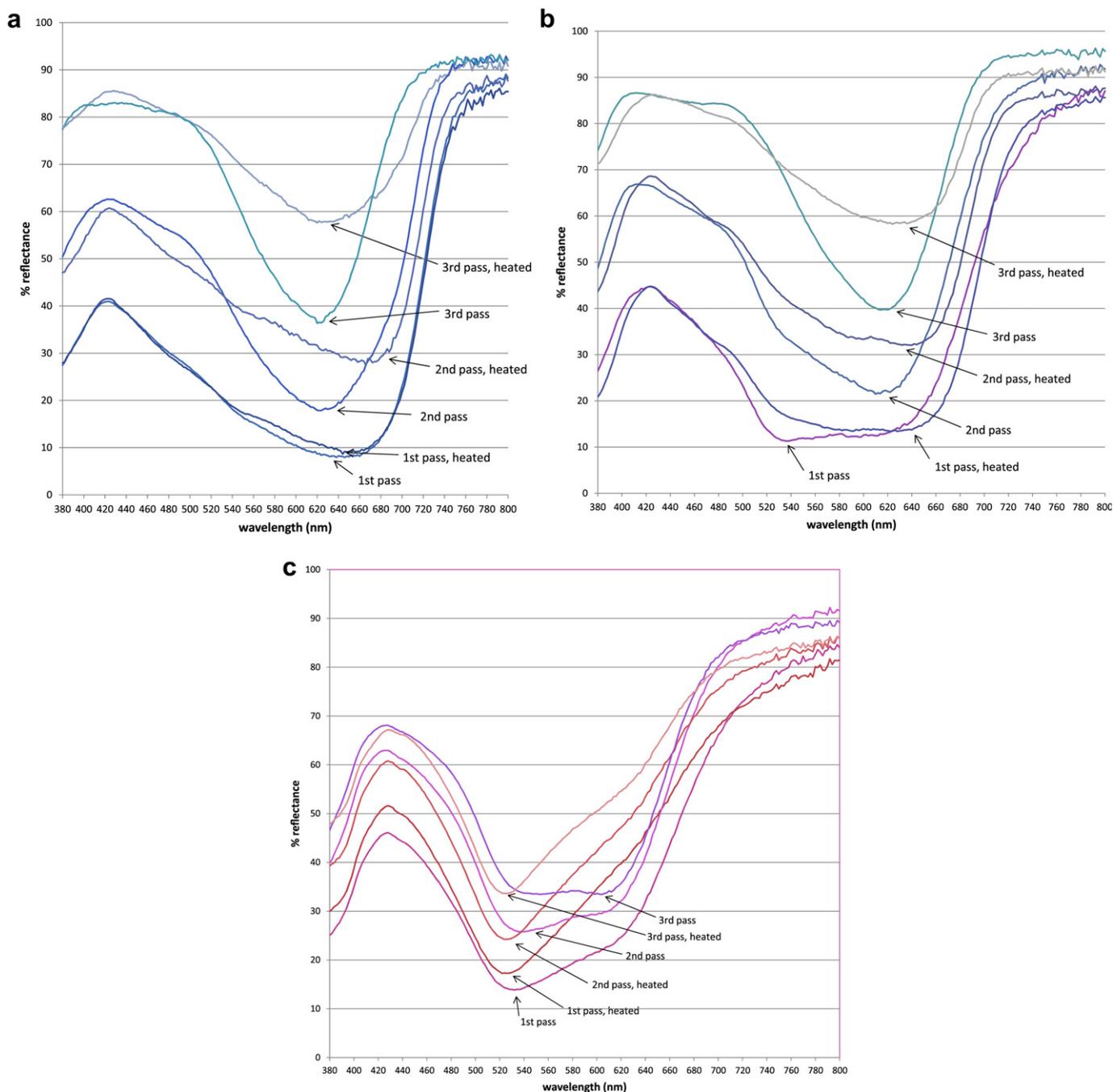


Fig. 7. Reflectance spectra of three passes of silk dyed with (a) Indigo, (b) MBI, and (c) DBI, with post-dyeing heat.

3.3. Analysis of TEM results

TEM analysis suggests that the color change upon heating of the fabric may be due to a change in the aggregation state of dye molecules adsorbed onto it; this corroborates the reflectance data. We find that carbon nanotubes can be used as surrogates for fibers in an MBI dyeing. This choice is necessary to overcome problems associated with the detection of nanometrically sized MBI molecular aggregates on macroscopic fibers when using electron microscopy imaging. Since the aggregation effects we posit seem not to depend heavily on the structure of the fabric, it is likely that these surrogate fibers will behave in a similar manner. When the nanotubes are dyed with MBI in the usual way, the resulting dyed-fabric model is



Fig. 8. Thermochromicity of multi-fabric strips dyed with DBI and MBI. Top to bottom: DBI heated, DBI unheated, MBI unheated, MBI heated. See Fig. 3 for fabric identities.

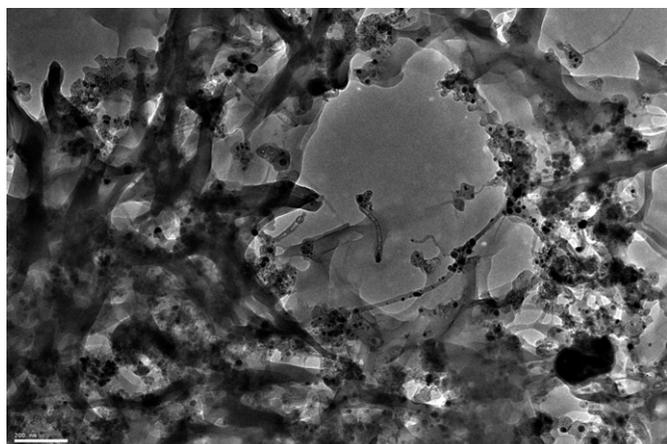


Fig. 9. TEM image of MBI dye aggregates on carbon nanotubes.

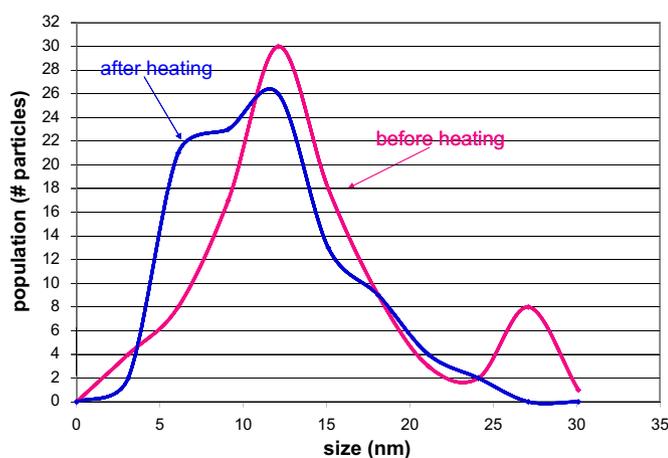


Fig. 10. Histogram of MBI-dyed nanotubes.

amenable to TEM. The TEM images show that MBI organizes itself in clusters (nanoparticles), representing molecular aggregates, on the surface of the carbon nanotubes (Fig. 9). No particles are observed detached from the carbon nanotube fibers. This confirms the templating/seeding role of the carbon nanotubes. Immediately after dyeing, there are large numbers of particles 12 nm in size, with a secondary maximum in the histogram at 27 nm (Fig. 10). When these dyed nanotubes are heated in boiling water for 10 min, redistribution in particle size is observed. The particles in the heated sample are on average smaller. Even though a dramatic change in morphology is not observed between the heated and unheated samples, size-related redistribution of the aggregates does occur. The relatively narrow distribution present in the unheated sample is most likely to be associated with two different topologies of molecular aggregates. The reflectance data on the dyed fabrics show that the MBI-dyed fabrics treated with heat display a red shift in the absorbance spectrum. This is in agreement with the known behavior of the UV absorbance of J-type molecular aggregates, which shift toward the red region of the spectrum when re-aggregation takes place [40]. Work is in progress to obtain further evidence of re-aggregation using dyed nanotubes, and to extend the method to the other indigoids and possibly to dyes of other types.

4. Conclusion

While indigo and its derivatives have been used as fabric dyes for millennia, the mechanisms for their color production have been

under investigation only recently. These studies require a consistent dyeing procedure, which we attempt to achieve by using a high temperature and excluding atmospheric oxygen and light. While it is well known that UV light debrominates the leuco forms of MBI and DBI, we show that ambient fluorescent lighting will do the same, given enough time. Application of indigo, MBI and DBI to 13 fabrics (3 natural and 10 synthetic) shows that there is little correlation between fabric and dye structures, and colors achieved. However, there is a consistent reddening trend of the fabrics upon substitution by bromine atoms in the adsorbed dye molecules. At lower dye concentration, many of the fabrics dyed with MBI and DBI become more blue. We interpret this as a redistribution of two types of molecular aggregates, indicated by two separate reflectance minima and shoulders on the curves. The dyed fabrics when heated in water produce surprising color changes: indigo- and MBI-dyed fabrics show color changes toward blue, while DBI-dyed fabrics give the opposite color change, toward red. We propose that these color changes are caused by aggregate redistributions similar to those seen upon dilution of the dye vat. Use of MBI-dyed carbon nanotubes as a fabric surrogate confirms that the nature of the color changes may be physical rather than chemical: TEM analysis shows that dye particles on the nanotubes undergo a change in their aggregation state upon heating, a phenomenon which could be operative in all the color changes reported here.

Role of the funding source

The Professional Staff Congress of the City University of New York, which funded this work, had no role in study design; in the collection, analysis, and interpretation of data; in the writing of the report; or in the decision to submit the manuscript for publication.

Acknowledgments

Professor Zvi Koren of Shenkar College of Engineering and Design, Israel, is thanked for introducing this project to us and for performing the HPLC analysis of MBI and DBI. Testfabrics Inc. of Pittston, Pennsylvania, USA, is thanked for supplying the fabric strips used. Mr. Allen Ko is thanked for experimental assistance. OL thanks Anatoliy Lavinda for inspiring discussions. The Professional Staff Congress of the City University of New York is acknowledged for financial support of this work. The TEM instrument was purchased by funds from the RCMI programs G12 RR003037 and 8 G12 MD007599 from the National Institutes of Health.

Appendix A. Supplementary material

Supplementary data related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.dyepig.2012.07.014>.

References

- [1] Waring DR, Hallas G. The chemistry and application of dyes. New York: Plenum Press; 1990. p. 2–9.
- [2] Wisniak J. Dyes from antiquity to synthesis. *Ind J Hist Chem* 2004;39:75–100.
- [3] Cooksey CJ, Dronsfield AT. Adolph von Baeyer and the indigo molecule. *Dyes Hist Archaeol* 2001;18:87–90.
- [4] Gordon PF, Gregory P. Organic chemistry in colour. Berlin, Heidelberg and New York: Springer-Verlag; 1983. p. 211–3.
- [5] Christie RM. Why is indigo blue? *Biotech Histochem* 2007;82:51–6.
- [6] Luettker W, Klessinger M. Theoretical and spectroscopic investigations with indigo dyes. I. Infrared and light absorption spectra of simple indigo dyes. *Chem Ber* 1964;97:2342–57.
- [7] Luettker W, Hermann H, Klessinger M. Theoretically and experimentally determined properties of the fundamental indigo chromophore. *Angew Chem Int Ed Engl* 1966;5:598–9.
- [8] Klessinger M. Theoretical and spectroscopic studies on indigo dyes. V. PPP calculations for the indigo chromophore. *Tetrahedron* 1966;19:3355–65.

- [9] Amat A, Rosi F, Miliani C, Sgamelotti A, Fantacci S. Theoretical and experimental investigation on the spectroscopic properties of indigo dye. *J Mol Struct* 2011;993:43–51.
- [10] von Eller H. Structure de colorants indigoides. III. Structure cristalline de l'indigo. *Bull Chim Soc Fr* 1955;106:1433–8.
- [11] Sadler PW. Absorption spectra of indigoid dyes. *J Org Chem* 1956;21:316–8.
- [12] Koren ZC. HPLC analysis of natural scale insect, madder and indigoid dyes. *J Soc Dyers Colourists* 1994;110:273–7.
- [13] Cooksey CJ. Tyrian Purple: 6,6'-dibromoindigo and related compounds. *Molecules* 2001;6:736–69.
- [14] Ziderman II. Revival of biblical *tekhelet* dyeing with banded dye-murex (*Phyllonotus trunculus*): chemical anomalies. *Dyes Hist Archaeol* 2001;18: 87–90.
- [15] Koren ZC. HPLC-PDA analysis of brominated indirubinoid, indigoid, and isatinoid dyes. In: Meijer L, Guyard N, Skaltsounis L, Eisenbrand G, editors. *Indirubin, the red shade of indigo*. Roscoff: Life in Progress Editions; 2006. p. 45–53.
- [16] Koren ZC. Archaeo-chemical analysis of royal purple on a Darius I stone jar. *Microchim Acta* 2008;162:381–92.
- [17] Karapanagiotis I. Identification of indigoid natural dyestuffs used in art objects by HPLC coupled to APCI-MS. *Am Lab* 2006;38:36–40.
- [18] Ziderman II. Biblical dyes of animal origin. *Chem Br* 1986;22(5):419–21. 454.
- [19] Pliny the elder. *Historia naturalis*. Cambridge Mass: Rackham H. Harvard University Press; 1949; (a) Vol. III Book IX; pp. 247–59. (b) Vol. IV Book XV; p. 349. (c) Vol. V Book XX; p. 449. (d) Vol. VI Book XXII; pp. 295–9. (e) Vol. IX Book XXXV; pp. 283, 292–297, 371, 395–402.
- [20] Reinhold M. The history of purple as a status symbol in antiquity. *Collect Latomus* 1970;116:1–73.
- [21] Koren ZC. The first optimal all-murex all-natural purple dyeing in the Eastern Mediterranean in a millennium and a half. *Dyes Hist Archaeol* 2005;20:136–49.
- [22] Friedlaender P. Ueber den Farbstoff des antiken Purpurs aus murex brandaris. *Ber Dtsch Chem Ges* 1909;42:765–70.
- [23] Clark RJH, Cooksey CJ. Monobromoindigos: a new general synthesis, the characterization of all four isomers and an investigation into the purple colour of 6,6'-dibromoindigo. *New J Chem* 1999;23:323–8.
- [24] Wolk WJ, Frimer AA. Preparation of Tyrian purple (6,6'-dibromoindigo): past and present. *Molecules* 2010;15:5473–508.
- [25] Ziderman II, Wallert A, Hoffman R, Ozery Y. Bathochromic effect of heating 6-bromoindigotin to 60 °C. 23rd Dyes in history and archaeology meeting, Montpellier, 2004.
- [26] Cooksey CJ, Sinclair RS. Colour variations in Tyrian purple dyeing. *Dyes Hist Archaeol* 2005;20:127–35.
- [27] Terada T. Dyeing properties of shellfish purple obtained from *Ocenebra inornata*. *Kwassui Bull* 2011;54:35–42.
- [28] van Alphen J. Remarks on the action of light on indigo dyes in a reducing medium. *Rec Trav Chim Pays-Bas* 1944;63:95–6.
- [29] Voss G, Schramm W. Selectively C-deuterated indigotins. *Helv Chim Acta* 2000;83:2884–92.
- [30] Hoffman RC, Zilber RC, Hoffman RE. NMR spectroscopic study of the *Murex trunculus* dyeing process. *Magn Res Chem* 2010;48:892–5.
- [31] Driessen LA. Ueber eine charakteristische Reaktion des antiken Purpurs auf der Faser. *Melliand Textilberichte* 1944;25:66.
- [32] Koren ZC. Chromatographic and colorimetric characterizations of brominated indigoid dyeings. *Dyes Pigments* 2012. <http://dx.doi.org/10.1016/j.dyepig.2012.06.016>.
- [33] Tanoue Y, Terada A, Sakata K, Hashimoto M, Morishita SI, Hamada M, et al. A facile synthesis of Tyrian purple based on a biosynthetic pathway. *Fish Sci* 2001;67:726–9.
- [34] Samson J, Piscopo I, Yampolski A, Nahirney P, Parpas A, Aggarwal A, et al. Fabrication of size-tunable metallic nanoparticles using plasmid DNA as a biomolecular reactor. *Nanomaterials* 2011;1:64–78.
- [35] Son Y-A, Hong J-P, Kim T-K. An approach to the dyeing of polyester fiber using indigo and its extended wash fastness properties. *Dyes Pigments* 2004;61: 263–72.
- [36] Milani C, Romani A, Favaro G. A spectrophotometric and fluorimetric study of some anthraquinoid and indigoid colorants used in artistic paintings. *Spectrochim Acta A* 1998;54:581–8.
- [37] Koren ZC. Personal communication.
- [38] Ziderman II. The biblical dye *tekhelet* and its use in Jewish textiles. *Dyes Hist Archaeol* 2008;23:36–44.
- [39] Szalda DJ, Ramig K, Lavinda O, Koren ZC, Massa L. 6-Bromoindigo dye. *Acta Cryst* 2012;C68:o160–3.
- [40] Mishra A, Behera RK, Behera PK, Mishra BK, Behera GP. Cyanines during the 1990s: a review. *Chem Rev* 2000;100:1973–2011.