Highlight

Painting crystals

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Crystal dyeing is a form of water painting as well as a method of engineering 'oriented gases' of functional chromophores. Here, we provide a brief overview of the subject of dyeing crystals from the first crystal dyer in the middle of the nineteenth century through our work of the past decade. This highlight is illustrated by hand and the crystals are rendered with water colour, the preferred method of colour scientific illustration at the time when the subject of dyeing crystals first took shape. In so doing, we choose a self-referential representation that is most faithful to the objects themselves, and which underscores the roots of the subject.

Art is the compulsion of man towards crystallization.[1]

Edvard Munch

Dyeing as crystal engineering's progenitor

Crystal engineering is a comparatively new subject. As far as we are aware, the first monograph to carry this title was published in 1989,[2] the first print journal in 1998,[3] and the first electronic journal – this one – in 1999.[4] Of course, taken literally, crystal engineering embodies the invention of bronze and steel whereby alloy composition was optimized in order to achieve desired physical properties. However, colloquially, we restrict the term 'crystal engineering' to the organization of *molecules* in solids manifesting translational symmetry. Given this definition, who then was the first crystal engineer? Like many similarly ill-defined questions, this one probably has many answers. One candidate is surely Henri de Sénarmont (Fig. 1), a mid-nineteenth century Parisian mineralogist, who set out to organize organic chromophores within crystals in order to mimic a curious property of some minerals, pleochroism, the anisotropic absorption of light; tourmaline is a classic example. Sénarmont wondered whether he could produce pleochroism in otherwise transparent crystals by including in them some coloured molecule during growth. He loaded aqueous solutions of $Sr(NO_3)_2$ with a dye called hematein from the extract of the logwood tree.[5] In this way, he prepared pleochroic crystals of $Sr(NO_3)_2 \cdot 4H_2O$.[6] Thus was born the science of dyeing crystals, a small, frail branch of crystal engineering that we have been trying to restore to good health. Here follows a brief overview of the science of dyeing crystals. A comprehensive survey/history was published recently.[7]

Bart Kahr

Bart Kahr was born in New York City in 1961. He was introduced to chemical research by I. David Reingold and studied art with John Hunisak at Middlebury College. His graduate studies of the stereochemistry of unusual molecules with Kurt Mislow at Princeton University were followed in 1988 by postdoctoral research in crystal chemistry at the Yale University laboratory of J. Michael McBride. After two years he joined the faculty of Purdue University. He moved to Seattle in 1997 where he is currently professor of chemistry at the University of Washington. His research group is studying the growth, structure, and physical properties of crystalline materials, with generous support from the U.S. National Science Foundation.

Leonel Vasquez

Leonel Vasquez was born in Guatemala City, Guatemala, in 1967. He moved to Seattle in 1991 where he has taught himself the art of water painting. His still life compositions are shown regularly in the Pike Place Market. He currently works at the University of Washington where his dexterity is used in the preparation of cut and polished crystal sections for spectroscopic investigations.

The dyeing of crystals is a form of water painting. Whether we are painting crystals or paper, dyes dissolved in water are used to colour a ground producing organized structures during the process of drying. In order to underscore the close connection between crystal dyeing and water painting we have elected to illustrate this highlight by hand with crystals rendered in water-based pigments. We have another purpose for this

Fig. 1 Henri de Sénarmont (1808–1862).

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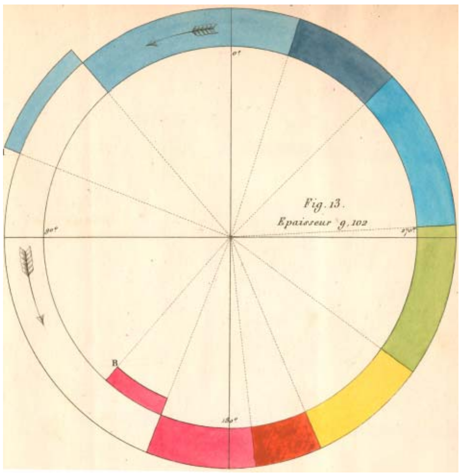

Fig. 2 Optical rotary dispersion in quartz as represented by Jean Baptiste Biot (1774–1862).[8]

anachronistic behaviour: to emphasise that even though this highlight will appear only in an on-line journal, the subject we illustrate was born during a time when drawing from nature was an essential skill, now lost, of all scientists. In special cases each copy of a journal or monograph was coloured by hand. The fidelity of coloured figures from the mid-nineteenth century is seen in Fig. 2, a spectrum from Biot's treatise on optical rotary dispersion in quartz, a copy of which is in the author's possession.[8] Paintings of dyed crystals have never appeared in the literature. Ironically, the hand-painted crystals in this highlight will appear only in a cyber journal that we are not meant to hold.

What is a dyed crystal?

While any marriage of a dye and a crystal could literally be called a 'dyed crystal' we restrict the term to solution-grown crystals that have oriented and overgrown organic chromophores. The role of support and mordant is played by the bulk crystal. The dyeing is controlled by the specificity of non-covalent interactions between the coloured molecules and the growing crystal interfaces. In this way, surfaces that are not related by symmetry reveal the differences in the dynamic interactions at growing crystal interfaces in the colours of their respective growth sectors. This type of chemical segregation is called inter-growth sectoral chemical zoning. Illustrated in Fig. 3 are crystals of phthalic acid grown in the presence of the dyes methyl red and Nile red which show distinct photophysical properties in adjacent growth sectors. Methyl red has a complex acid–base equilibrium in solution. Protonated, deprotonated, neutral and zwitterionic forms have been spectroscopically differentiated in solution.[9] Phthalic acid crystals selectively incorporate the yellow, neutral form in the {010} sectors while {021} includes the azo N-protonated species. Nile red is a highly solvatochromic dye[10] that similarly shows different colours in phthalic acid depending upon the face through which it has adsorbed. Surprisingly, Nile red has the same polarisation in either growth sector; therefore, the orientation (presuming the molecular transition moments are not much altered) is the same even though the molecule is found in more than one environment. This subtle difference underscores the remarkable chemical selectivity of crystal faces.

How do you dye a crystal?

Many crystals can be dyed by children. In some cases, this can be accomplished by letting saturated solutions of harmless salts containing food colourings evaporate in the open air. Here follows a fool-proof recipe for preparing 50 mm^3 sized crystals of KH_2PO_4 dyed by amaranth (C.I. No. 16185) in the {101} growth sectors.[11] (1) Dissolve 17 g of KH_2PO_4 (potassium phosphate mono-basic) in a 250 mL beaker charged with 50 mL of water (distilled, de-ionised water is preferred but most tap water is sufficient for growing crystals of good quality). (2) Warm the beaker while stirring to ensure dissolution. The hot solution may be filtered but this is not critical. (3) Add 4 mL of a 1 mg mL^{-1} solution of amaranth to the KH_2PO_4 solution and stir for approximately 2 min with glass rod or spoon. A magnetic stir-bar works well in the laboratory. (4) Carefully transfer the solution to a 100 mL crystallising dish placed upon a vibration-free surface. (5) KH_2PO_4 crystals containing red 'bow-ties' (10^{-4} mol% of dye) will precipitate within 4–6 h.

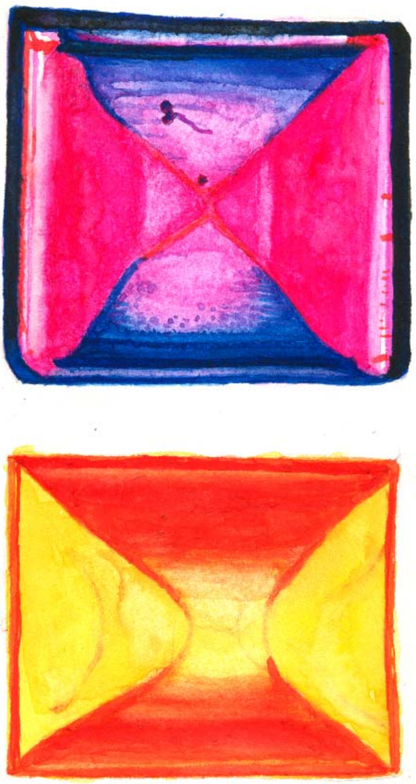

Fig. 3 Water painting of crystals of phthalic acid grown in the presence of the acid–base indicator methyl red (bottom) and the solvatochromic dye Nile red (top). Crystals are *ca.* 0.5 mm in width. Phthalic acid incorporates protonated and neutral methyl red molecules in the {101} and {021} growth sectors, respectively. The nature of the difference in the Nile red environments in the corresponding growth sectors is not known, but presumably arises from slight differences in the first coordination sphere. See photographs by S. Lovell in ref. 7.

The same substance in the hands of a skilful scientist can be manipulated in investigations of crystal growth mechanisms. Zaitseva *et al.* grew large (1 dm^3) dyed KH_2PO_4 crystals on rotating platforms contained in continuous filtered metastable solutions of high supersaturation at programmed temperatures.[12] When KH_2PO_4 was grown in this way with amaranth added during the later stages of growth, the dye served to image growth-active surface structures *via* the selective staining of vicinal hillock slopes. This is an example of *intra*-growth sectoral chemical zoning, whereby only a sub-volume of a single growth sector takes up the additive.

Shown in Fig. 4 is a dramatic example of intrasectoral zoning that results from the selective recognition of the distinct slopes of growth spirals. The blue luminescence is associated with *ortho*-aminobenzene sulfonate that recognised only one side of the growth spirals on the {021} faces of K_2SO_4.[13]

The ease with which crystals can orient and overgrow ungainly guest molecules or ions is counterintuitive. How do

Fig. 4 Water painting of a crystal of K_2SO_4 (width *ca.* 1 cm) grown in the presence of *ortho*-aminobenzene sulfonate. The blue luminescence of the benzene derivative from the (021) sector is excited with ultraviolet light. Additionally, a visible light was reflected from the rightmost face. The pattern of light results from the selective staining of macro-growth spirals. See photograph by R. W. Gurney in ref. 7.

the guests get in? What are the mechanisms by which they are overgrown? The burden is now upon us to study the kinetics of growth step propagation in the presence of dyes using contemporary scanning probe microscopies.[14] We must characterise the way in which dye binding alters growth step morphology while at the same time establishing the effects of adsorption and overgrowth on the photophysics of individual chromophores.[15]

What are dyed crystals good for?

Dyed crystals, coated with varnish, are well-suited as jewellery. Lapidaries have yet to take an interest. Dyed crystals can also be grown in high schools and in freshman chemistry laboratories to teach principles of crystal growth.[16] Even though dyed crystals have not been objects of systematic study for generations, they may appeal to modern scientists because of their rich stereochemistry, and because crystals containing oriented, mono-dispersed organic dyes promise spectroscopic and photonic applications. For example, dyed crystals have been fashioned into new kinds of laser gain media.[17] We showed how structural studies of some historical dye inclusions were used in the design of new crystals with prescribed physical properties.[18] Dyed crystals illustrate the complexity and specificity of non-covalent assembly during crystal growth and identify growth-active surface structures.[19] Dyed crystals have been used in the analysis of biopolymers[20] and eximers.[21]

More interesting than any particular use or application are those general insights about crystals that are acquired in the process of dyeing. Dyed crystals have undermined our long-held over-reliance on the principle of isomorphism and have served to generalise the synthesis of mixed crystals. Dyed crystals also underscore the false picture of crystals given by the legions of single crystal X-ray structures now assembled in the Cambridge Structural Database. As X-ray scattering is insensitive to minor crystal species we have come to believe that crystals are first and foremost mathematical objects rather than imperfect ensembles of molecules which are capable of orienting a wide range of substances bearing no size, shape, or constitutional similarity to the host species.

Crystallisation lies at the heart of crystal engineering.[22] By painting crystals with molecules that are selective in their associations and optically responsive to their environments, growing crystals can often 'flash forth'[23] their symmetry and crystallisation history in patterns of light and colour. In this way, crystal engineers can develop insights about the nature of chemical interactions that are occurring at interfaces during growth from solution.[24] However, this will require a great deal of work; the characterisation of dyed crystals has only just begun. We would be delighted to see other scientists and artists take to painting crystals whether in beakers or on paper.

Acknowledgements

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