National Textile Center
FY 2003 (Year 12) Project Proposal

Project No. C03-PH01

Competency: Chemistry

Universal Set of Dyes for Digital Inkjet Textile Printing

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Objective:
The primary focus of this project is to develop a universal set of dyes for inkjet digital printers that enables printing on *chemically diverse textile materials*. An important outgrowth of this project is the creation of an integrated laboratory within the Center for Excellence of Digital Inkjet Printing for Textiles at Philadelphia University. This center is devoted to fundamental research aimed at improving the performance and environmental compatibility of the chemicals used in inkjet printing for the US textile industry.

Progress Statement:
This project commenced during May of 2003 and progress has been made in the following areas:

- The basic combinatorial building blocks required for the construction of a class of dyes that contain both an anthraquinone and an azo chromophore have been identified, and a practical synthetic methodology has been developed. The chemistry associated with this methodology has been demonstrated in the synthesis of five new dyes, see Table 1, containing the skeleton shown below. These dyes have been thoroughly characterized and their textile technical properties, *e.g.*, lightfastness, washfastness, and substantivity have been assessed using conventional procedures. Of particular interest is the case with R=$B(OH)_2$, since this group has the potential to bind to textile substrates that contain hydroxyl groups.

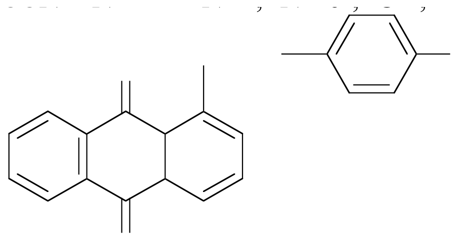

Table 1:

R	Coupling component	Yield %	Melting Point ºC	_max/nm (methanol)	Log __
$-NH_2$	Aniline	65	228-229	475	3.45
$-NMe_2$	N,N-dimethyl aniline	80	239-240	430	3.84
-OH	Phenol	78	242-243	410	3.18
-OMe	Anisole	53	237-238	472	3.18
$-B(OH)_2$	Phenyl boronic acid	70	230-231	470	3.43

- One important aspect of this project is to determine the extent to which boronic acid-based dyes facilitate binding to textile substrates containing hydroxyl groups, *e.g.* cellulose. To understand this binding process, extensive calculations have been performed to elucidate the thermodynamics and kinetics of the underlying chemical reactions. In particular, several model dehydration reactions have been studied to determine the energetic requirements for the formation of the boron-oxygen-carbon linkage that is fundamental to the overall mechanism. Based on the results of these calculations, we now have a better understanding of how to utilize boronic-acid based dyes in a textile environment; it seems clear that an internal Lewis base will be required to enhance the functionality of the acid. Results from this investigation have been accepted for publication (J. Mol. Struct., 2003).

- Calculations have also been performed on the structure of 4-[4-dimethylamino-phenylazo]benzene boronic acid. These calculations have provided considerable insight into the structural and electronic changes that are involved when a boronic acid group is grafted onto an azo dye. The results of this investigation have been accepted for publication (Struct. Chem., 2004).

Final Year's Goals:
The efficiency of a boronic acid group that can function as a sensor on different chromophores and act as a binding site for specific textile materials is currently being evaluated. During the next year the chemistry that we have developed over the past 6 months will be automated on our fully integrated synthesizer-purification system. A variety of boronic acids are now commercially available for use as building blocks, and many of these acids already contain an additional functional group that can serve as an auxochrome. This will enable us to create a much larger combinatorial library of new boronate dyes for testing on textile materials. Emphasis will be placed on improving substantivity, vividness, as well as, photo- and thermal-stability. Moreover, we are committed to designing dyes that are nonmutagenic, and we are currently developing quantitative structure-activity relationships (QSARs) that correlate the observed mutagenic behavior of azo dyes with a variety of molecular descriptors calculated using quantum-chemical semiempirical methodology; this research will be expanded to include anthraquinone dyes over the next few years.

Our synthetic and computational efforts in the second and third years of this project will expand to incorporate two binding sites on the dyes being developed. Our current design thoughts include incorporating both a boronic acid group and a guanidinium moiety appropriately separated on the dye. The cationic nature of the guanidinium unit will enhance the solubility of the dyes and establish an electrostatic interaction with ionic substrates. The power of including such a guanidinium group for the binding of anionic guest molecules in competitive media has been recently described [1]. Depending on spacing, the guanidinium group may act as the Lewis base for the boronic acid converting the trigonal form of this acid to the more reactive tetrahedral form; this will enable the binding process to occur at neutral pH, an important practical consideration.

Research in the second and third years of this project will also focus on ink formulations using the most promising dyes developed from our synthetic and computational efforts. Low viscous dyes, rather than pigments, have been the traditional ink colorant of choice for inkjet printers because of fluidity and anti-clogging requirements. Preparation of inks with the proper rheology, homogeneity and fixations properties is extremely critical. A fine balance must be maintained between developing inks that optimize drop formation and those that create sharp, dense and permanent images. Performance of our ink formulations with respect to jettability, jet sustainability, flow rate, decap, colorfastness, etc. will be evaluated on Epson DX-3 piezo electric inkjet printing systems, which is widely used in current digital textile printing and is available in Philadelphia University's Center for Excellence of Digital Inkjet Printing for Textiles. Image quality will be quantified using line (blurriness and raggedness) and area (grain, mottle, and density) analyses using the IAS Image Analysis System based on ISO 13660 criteria; these facilities are also available in the Center.

Approach:
A multi-disciplinary approach using combinatorial chemistry and chemoinformatics is being employed to develop dyes that exhibit chemoselective affinity for a variety of chemically different textile substrates. This is a formidable task because some substrates are hydrophobic (*e.g.* polyester, nylon) while others are polar or ionic (*e.g.* cotton, silk). Ordinarily, coloring such chemically diverse materials requires significantly different types of dyes and/or pretreatments. The core idea in this project is to incorporate chemical-sensor subgroups onto various chromophores that will serve as affinity ligands that can distinguish between different substrate functional groups. This approach has proved to be extremely beneficial in medicinal chemistry [2], but has not been explored in the context of textile chemistry. In addition to introducing chemical sensor technology to the printing industry, other approaches, including immobilization, derivatization, and paper-to-fabric transfer reactions with a variety of groups present as a linker system will also be pursued. The pretreatment process, *if* it is still required, will be designed to complement the chemistry of the newly developed inks.

- Combinatorial chemistry [3] – sometimes abbreviated to combichem – is primarily a synthesis technique, entailing a grid-based sampling of physical and chemical variables. In less than a decade, combichem has become an integral component of many leading national and international research and development laboratories. In fact, dynamic combinatorial library strategies have recently lead to the discovery and synthesis of new catalysts, drugs, and chemical sensors [4]. The purpose of combinatorial chemistry is two-fold. First, to assemble as quickly as possible a collection of compounds for screening, with the objective of finding a 'lead' compound with the desired properties. This usually involves synthesizing small quantities of a large number of related compounds. Secondly, once such a lead compound has been identified, combinatorial chemistry can help focus analogue synthesis to improve the potency, efficacy, and/or selectivity of the compound – as a potential drug, a catalyst or, for this particular project, as a dye with superior technical properties that can be used on multiple textile substates with digital inkjet printing systems.

- Chemoinformatics and molecular modeling have matured over the past decade into valuable research tools for designing novel chemicals, as well as, correlating molecular structure with a wide variety of physical, chemical, and toxicological properties. In conjunction with molecular modeling, a comprehensive structure-property database will be established to incorporate performance results of the "library" generated from our combinatorial syntheses. This database will be augmented with information from the vast experimental literature on classical anthraquinone and azo dyes. Quantitative structure-activity and structure-property relationships (QSAR/QPARs) will be developed from the database to guide the additional synthetic work required to optimize the technical performance of the colorants and simultaneously, to reduce their genotoxicity; both multilinear regression (CODESSA™) and artificial neural network methodology will be employed for this purpose [5,6]. Since the auxochromes generated in this project will alter various physical properties of the molecule, time-dependent density functional theory will be used to predict changes in the UV-vis spectrum and enable us to develop a wider gamut of colorants.

In summary, a multifaceted laboratory will be created during this project to perform fundamental research designed to improve the technical performance and safety of chemicals used for digital printing. This laboratory will integrate existing resources at Philadelphia University to facilitate:

- the design and synthesis of new, non toxic dyes that function on chemically diverse textile materials;
- the development of ink formulations and/or pretreatment procedures that complement these new dyes;
- the performance evaluation of new inks with respect to jettability, jet sustainability, flow rate, decap, colorfastness, *etc.* on commercially-available (piezo electric) inkjet printing systems;
- the use of chemoinformatics and molecular modeling to develop QSAR/QPARs that correlate molecular function with molecular structure and properties.

Outreach to Industry:

This project will be conducted in conjunction with the Center for Excellence of Digital Inkjet Printing for Textiles at Philadelphia University. The following industrial partners of the Center have agreed to participate in this research project: Ciba Specialty Chemicals Corporation USA, Mutoh America, Inc., MacDermid Colorspan, DuPont, Wasatch Computer Technology, Mimaki USA, and Rohm and Haas. These collaborations will enable experimental testing of promising new dyes and ink formulations under industrial conditions.

New Resources Required:

2X600MHZ R14000A/2MB processor ($16,495).
Software (CODESSA (qsar/qpar), $2,000; Glide (screening) + QSITE (qm/mm) $4,275).
Synthetic Reagents ($3,250).
Epson 3000 printer ($1,200).

References:

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