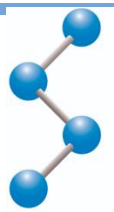

THE SCRIPPS RESEARCH INSTITUTE®

The Chemistry of Colorants

Dyes & Pigments

28 June 2018

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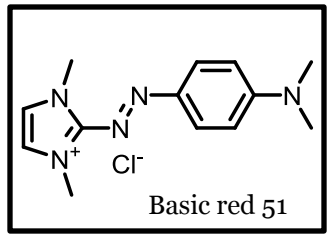
Dyes & Pigments

28 June 2018

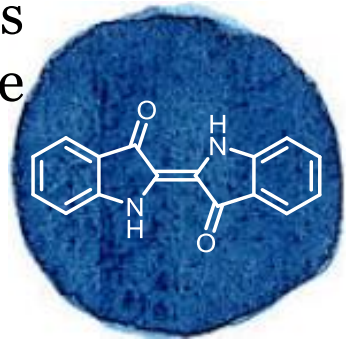
1. (Brief) History of colorants
2. Classifications
3. Physical chemistry
4. Types of dyes and pigments
5. Eight modern research examples
6. Why you might care/current industry

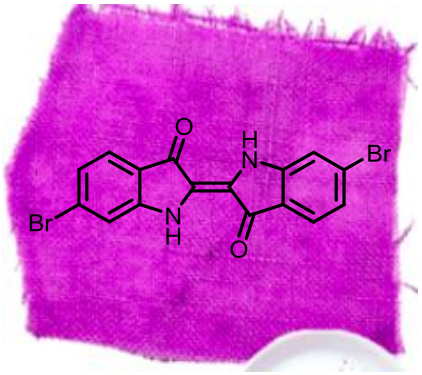
History of dyes and pigments



Basic red 51

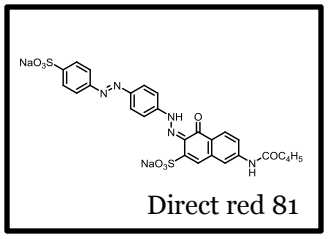
- Dyes have been derived from plants, animals, and minerals
  - Indigoid dye represents the arguably oldest natural dye
    - From plant *Indigofera tinctoria*
    - Used in India for ~4000 years
  - Woad was another source of blue in Europe
    - From *Isatis tinctoria*
    - Used in Bronze Age Europe (2500-800 BC)
  - Tyrian purple produced the royal color
    - From shell fish Purpura and Murex
    - Made in Tyre and Sidon since 800 BC
    - Produced an awful smell
    - Only source of purple for thousands of years





Samanta AS, Agarwal P (2009) Application of natural dyes on textiles. Indian J Fibre Text 34:384–399
Schaefer B (2014) Colourants. In: Schaefer B (ed) Natural products in the chemical ındustry. Springer-Verlag, Berlin, Germany, pp 13–44
Melo MJ (2009) Natural colorants in textile dyeing. In: Mussak RAM, Bechtold T (eds) Handbook of natural colorants. Wiley, Chichester, UK, pp 3–20

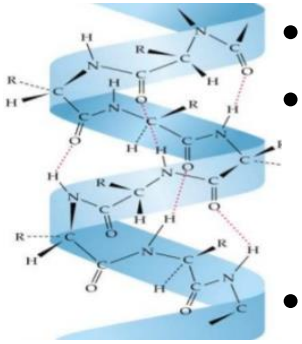
History of dyes and pigments

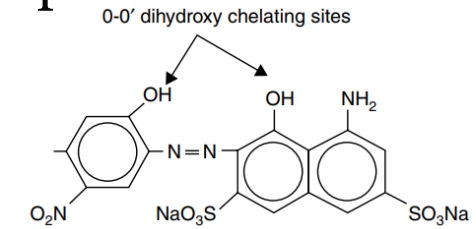


Direct red 81

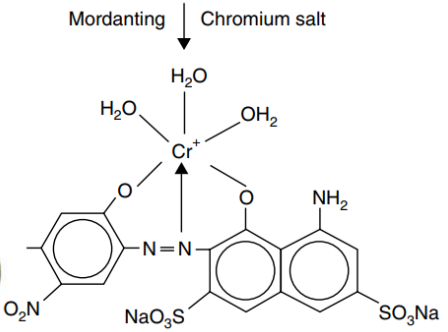
- Many natural dyes have a low chemical affinity to textiles
  - It was a multistep process to prepare fibers:

1. A mordant (metal salt) is used to impregnate the fibers
   - Metal ion complexes with functional groups
   - Often Al, Fe, Sn, Cr, Cu
   - Commonly used were potash alum $[KAl(SO_4)_2 \cdot 12H_2O]$ and iron sulfate $[FeSO_4 \cdot 7H_2O]$ and $(SnCl_2)$
   - Treatment of fabric occurred often in metal vats or with iron nails present
2. The dye was introduced to coordinate with the metal-impregnated fabric



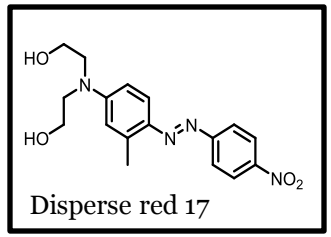


CI Mordant Green 17, C.I. 17225 (Colour Index, 1987)



Pozzi F (2011) Development of innovative analytical procedures for the identification of organic colorants of interest in art and archaeology. Ph.D. Thesis, University of Milan, Milano, Italy
J.N. Chakraborty, in Handbook of Textile and Industrial Dyeing, 2011

Moving away from natural sources



Disperse red 17

- First two synthetic pigments developed:

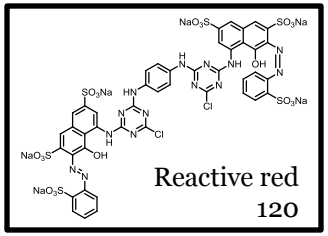
1. White lead, basic lead carbonate [$2PbCO_3 \cdot Pb(OH)_2$]
   - Described first by Theophrastus of Eresos (~300 BC)
   - Created by combining lead and acetic acid in the presence of CO_2

2. Blue Frit, Egyption Blue [$CaCuSi_4O_{10}$]
   - First evidenced in Egypt (~3000 BC)
   - Created by heating together quartz sand, copper, calcium carbonate, and alkali from ash up to 800-1,000 ^oC

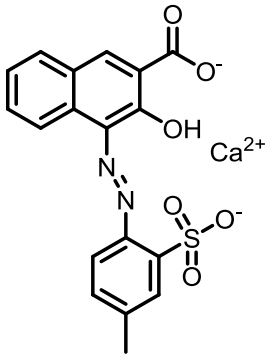
$$Cu_2CO_3(OH)_2 + 8\ SiO_2 + 2\ CaCO_3 \rightarrow 2\ CaCuSi_4O_{10} + 3\ CO_2 + H_2O$$

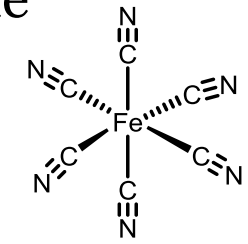
Emeish S (2013) Energy savings in cement industries. Stand Sci Res Essays 1(8):177–186

Moving into Modernity



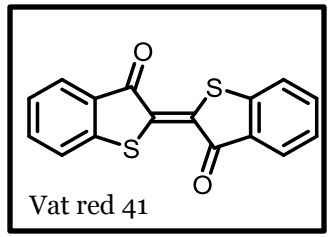
- Prussian Blue
  - First truly modern synthetic pigment arising as a result of a deliberately conducted chemical reactions
  - Produced by Diesbach in Berlin in 1704 trying to produce a lake pigment (metal coordinated natural pigment)
  - Created originally by mixing potash, iron sulfate, and *blood*
  - Cyanide in Greek means “dark blue”



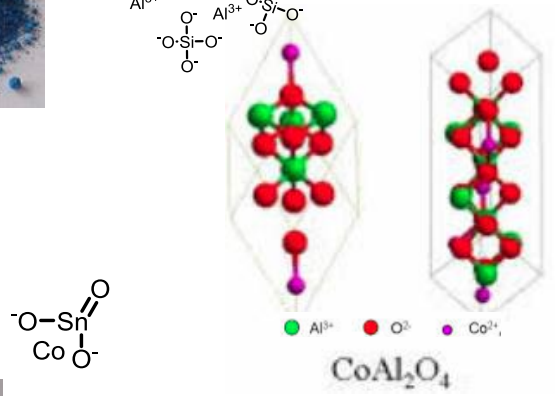


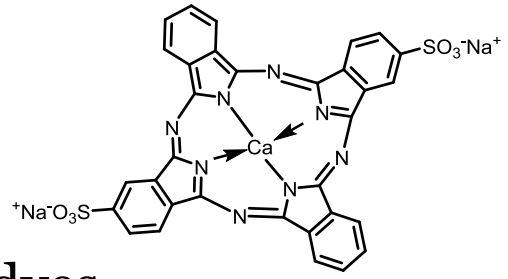
Kirby J, Saunders D (2004) Fading and colour change of Prussian Blue: methods of manufacture and the influence of extenders’. Natl Gallery Tech Bull 25:73–99

Moving into Modernity



- By the early 19th century, synthetic blue colorants existed:
  - French ultramarine
    - Synthesized-1826
    - $Al_6Na_8O_{24}S_3Si_6$
  - Cobalt blue
    - Synthesized-1802 (Thenard)
    - $CoAl_2O_4$
  - Cerulean blue
    - Discovered 1789 (Hopfner)
    - CoO_3Sn
  - Phthalo blue (CuPc)
    - Discovered 1927

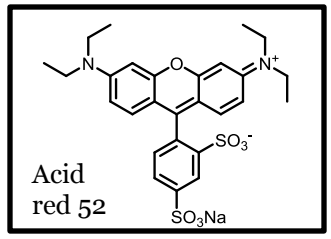




- Soon in the 20th century, reddish-purples, blues, violets, greens, and red dyes started replacing more expensive natural dyes

Vettese Forster S, Christie RM (2013) The significance of the introduction of synthetic dyes in the mid-19th century on the democratization of western fashion. J Int Colour Assoc 11:1–17

Dyes and Pigments

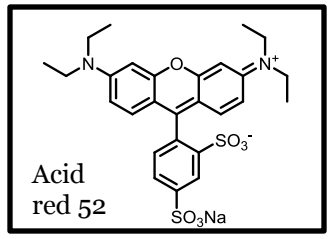


Dyes

Pigments

Broadbent AD (2001) Basic principles of textile coloration. Society of Dyers and Colourists, West Yorkshire, England

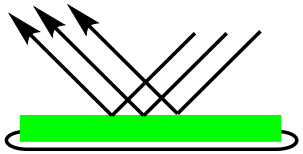
Dyes and Pigments



Dyes

Dyes are required to solvate during the application process; they often also have some affinity for the material being colored.

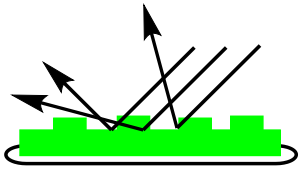
Selectively absorb light due to specific chemical nature of dye



Pigments

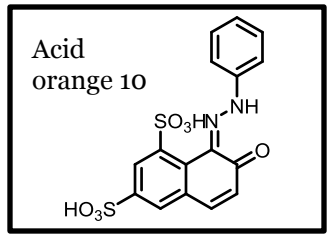
Pigments are specific colorants composed of particles insoluble in the application medium; they are colored, colorless, or fluorescent and can be organic or inorganic, finely divided solids

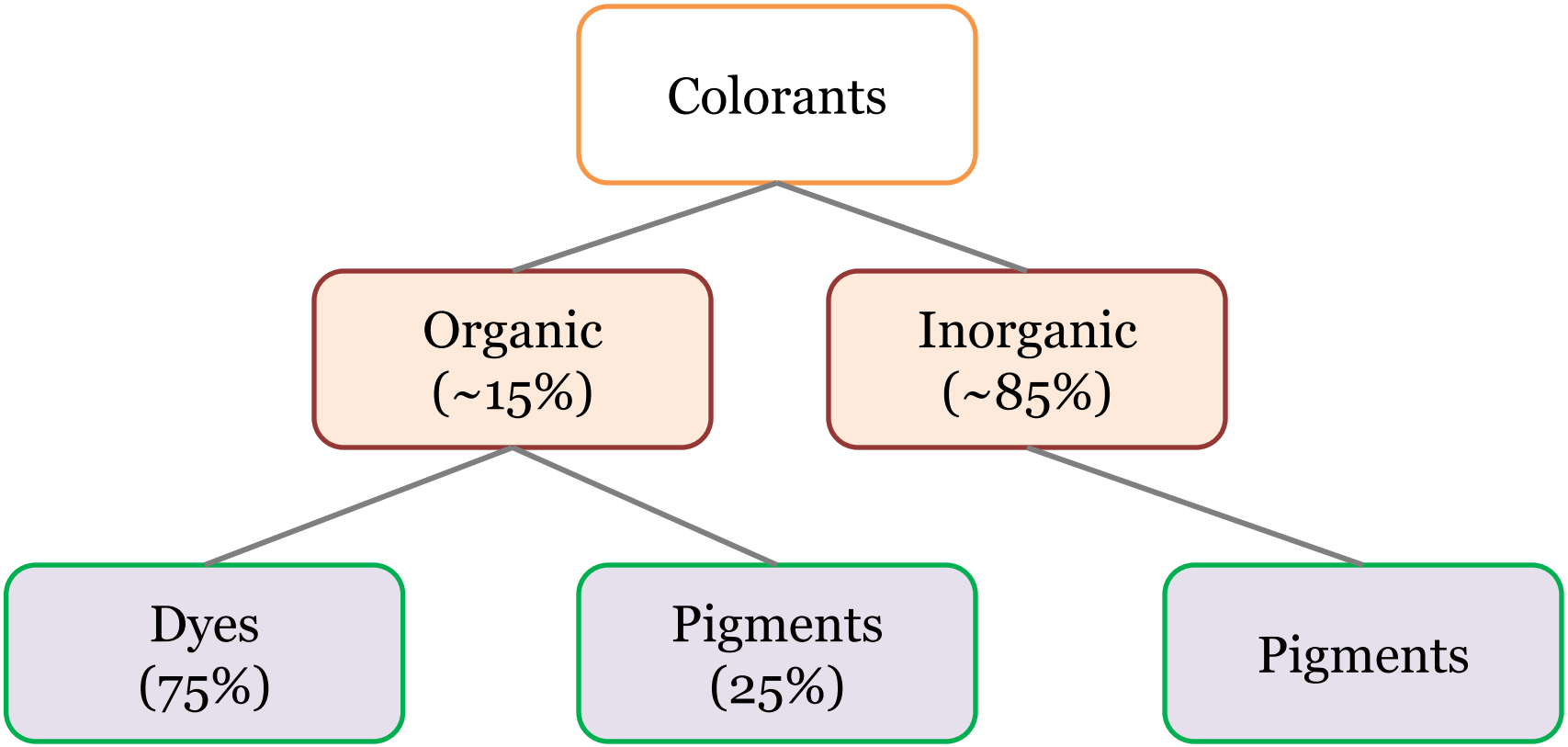
Selectively absorb and/or scatter light due to pigment & material



Broadbent AD (2001) Basic principles of textile coloration. Society of Dyers and Colourists, West Yorkshire, England

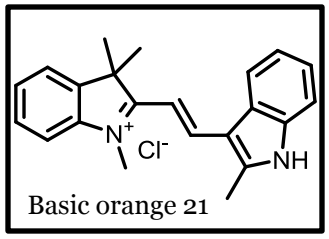
Dyes and Pigments





Chakraborty JN (2010) Colouring materials. In: Chakraborty JN (ed) Fundamentals and practices in colouration of textiles New Delhi. Woodhead Publishing, India

The Chemical Physics of Colorants



Basic orange 21

- Industrial value of dyes depends on *wavelength* and *intensity* of the absorption band as a function of dye concentration

Lambert—Beer law

$$A = \log_{10} \frac{I_o}{I} = \varepsilon l c$$

Absorbance

Intensity of incoming light

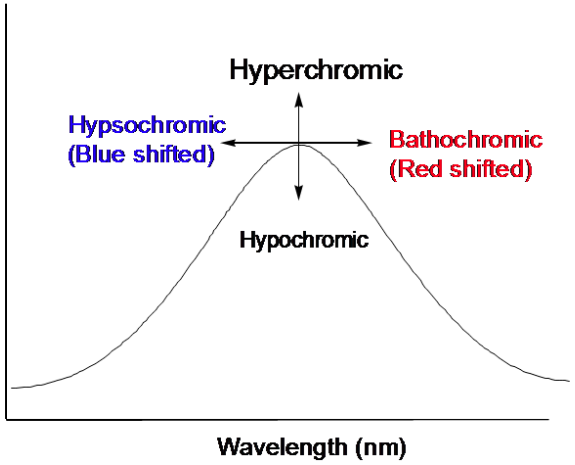
Intensity of transmitted light

Path length

Concentration

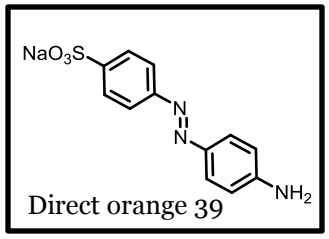
Molar extinction coefficient

Technically important dyes display extinction coefficients in excess of 10^4-10^5 M^{-1} cm^{-1}

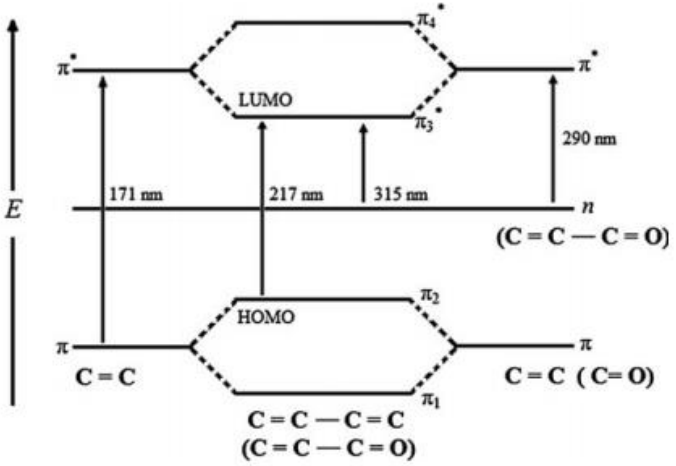


Zollinger H. (2001) Color Chemistry; Synthesis, Properties, and Applications of Organic Dyes and Pigments

The Chemical Physics of Colorants

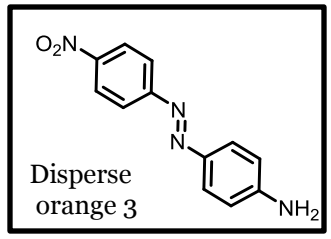


- Chromophores absorb light within the UV or visible range
  - *Examples:* C=C, C≡C, C=O, C≡N, N=N, NO_2
- Different transitions can occur with chromophores
  - $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$
- Auxochromes are covalently saturated groups that change the wavelength or intensity of the absorption maximum
  - *Examples:* NH_2, OH, SH, halogens
  - Tend to increase wavelngth and intensity through conjugation resonance
- Conjugated chromophores tend to increase wavelength and intensity
  - Create an additional set of HOMO/LUMO pairs and increase conjugation area
  - Energy difference between HOMO & LUMO is lowered leading to a bathochromic shift



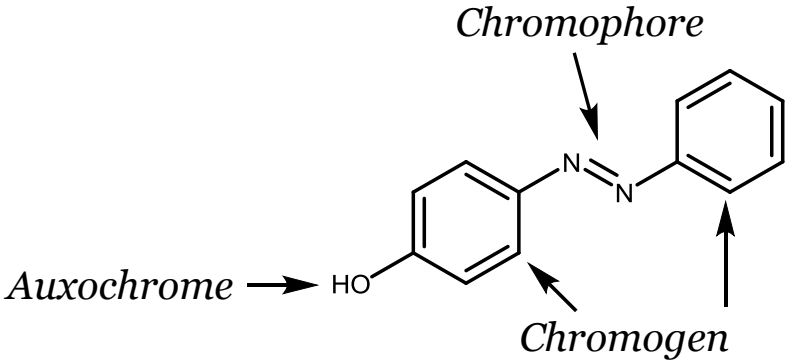
Yadav LDS (2005) Organic spectroscopy. Springer, Dordrecht

The Chemical Physics of Colorants



- Chromogens are chemical compounds that are colored or could be made colored by the attachment of a suitable substituent (increases the conjugated system size)

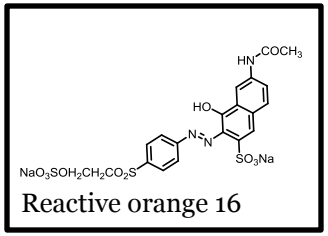
- Solvent yellow 7 (4-Hydroxyazobenzene) as an example:



- Colorants possess several important traits
  - Absorbs light in the visible spectrum (400-700 nm)
  - Have at least one chromophore
  - Have a conjugated system
  - Exhibit resonance of electroms

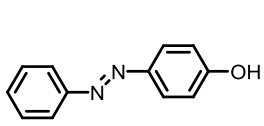
Hossain I (2014). Investigation into cotton knit dyeing with reactive dyes to achieve right first time (RFT) shade. Master Thesis. Daffodil International University, Bangladesh

The Chemical Physics of Colorants

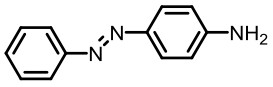


Reactive orange 16

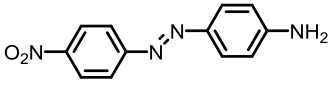
- General rules for adjusting color:
  - Adding electron-donating groups gives a bathochromic effect
  - Electron-donating and electron-accepting groups in conjugation provide an intense bathochromic effect
  - Increasing the number of electron-attracting groups conjugated with electron-donor groups has a bathochromic effect
  - The electron donating group are enhanced by adding alkyl groups to the N-atom



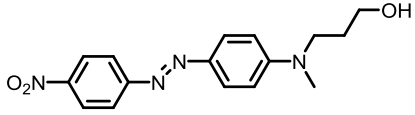
347nm



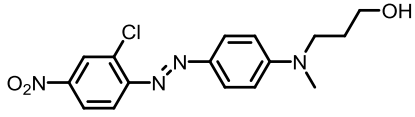
386nm



443nm



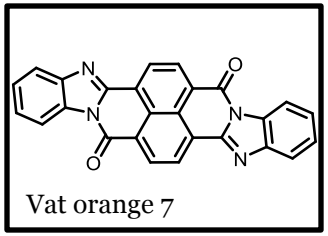
502nm



517nm

Asiri AM (2001) Organometallic dyes: Part 1. Synthesis of orange to cyan dyes based on donor-conjugated-acceptor-chromogenes using ferrocene as the donor group. Appl Organomet Chem 15:907–915

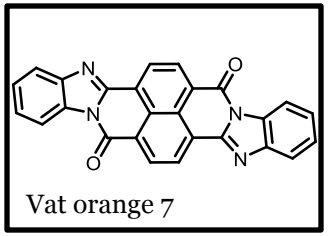
Common Classes of Colorants



Vat orange 7

- Dyes:
  - Acid Dyes
  - Anthraquinone Dyes
  - Azo Dyes
  - Basic Dyes
  - Direct Dyes
  - Disperse Dyes
  - Indigoid Dyes
  - Nitro and Nitroso Dyes
  - Phthalocyanine Dyes
  - Reactive Dyes
  - Sulfur Dyes
  - Vat Dyes
- Pigments:
  - Inorganic Pigments
  - Organic Pigments

Common Classes of Colorants



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- Pigments:
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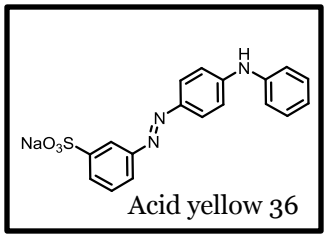
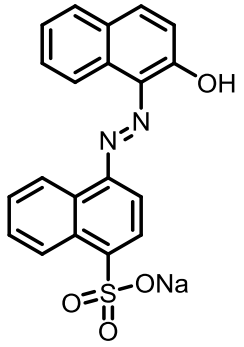
Acid Dyes

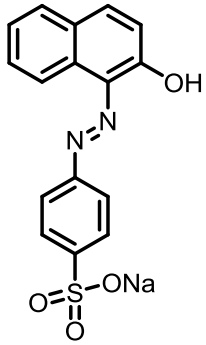


Acid yellow 36

- Generally comprised of organic sulfonic acids
- Commercially available as sodium salts; excellent water solubility
- Contains azo, anthraquinone, triphenylmethane, nitro, and nitroso chromophoric groups
- Used to dye many types of fiber:
  - Cotton
  - Polyester
  - Rayon
  - Wool
  - Silk



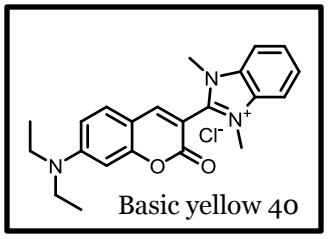
Acid red 88



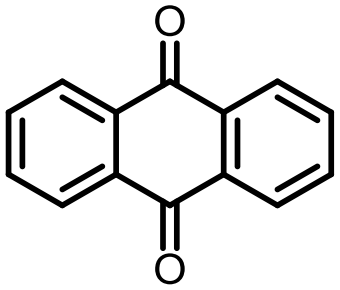
Acid orange 7

Ayad MM, El-Nasr AA (2012) Anionic dye (acid green 25) adsorption from water by using polyaniline nanotubes salt/silica composite. J Nanostructure Chem 3(3):2–9

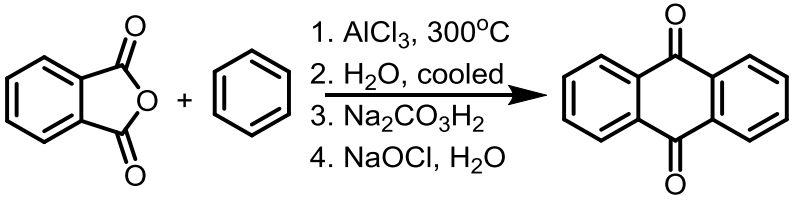
Anthraquinone Dyes

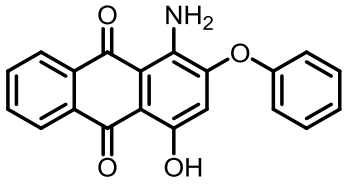


- Based around an anthraquinone central structure

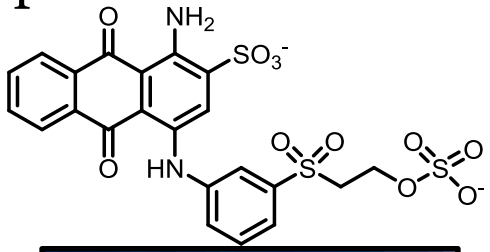


- Some of the oldest types of dyes (found >4000 years ago)
- Good brightness and fastness
- Most synthetic substitution occurs at the α-position with sulfonation or nitration
- For β-substituted dyes, synthesis usually starts from phthalic anhydride or benzene derivatives





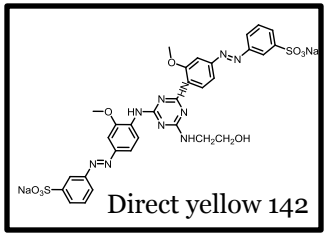
Disperse red 60



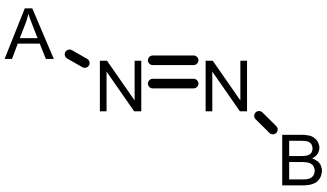
Reactive blue 19

Gregory P (1990) Classification of dyes by chemical structure. In: Waring DR, Hallas G (eds) The chemistry and application of dyes. Plenum Press, New York, USA
Jianhong J. et al. (2007) Process for preparation of anthraquinone derivatives

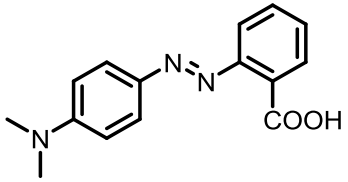
Azo Dyes



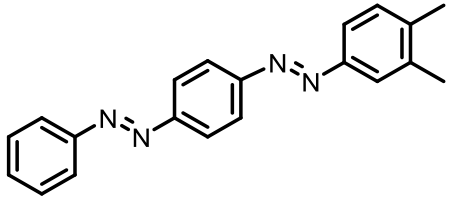
- Most common and most widely used; >60% of the dyes



- Often contain two aromatic groups in A & B, but must have at least one
- Exist in the trans form
- "A" often contains electron-accepting substituents while "B" contains electron-donating substituents



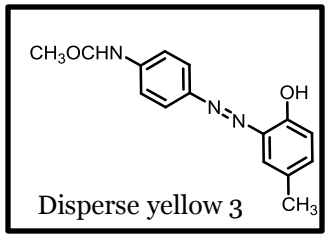
Acid red 2



Disperse yellow 7

Shah M (2014) Effective treatment systems for azo dye degradation: a joint venture between physico-chemical & microbiological process. Int J Environ Bioremediat Biodegradation 2 (5):231–242
Gregory P (1990) Classification of dyes by chemical structure. In: Waring DR, Hallas G (eds) The chemistry and application of dyes. Plenum Press, New York, USA

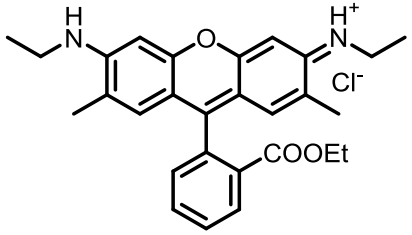
Basic Dyes



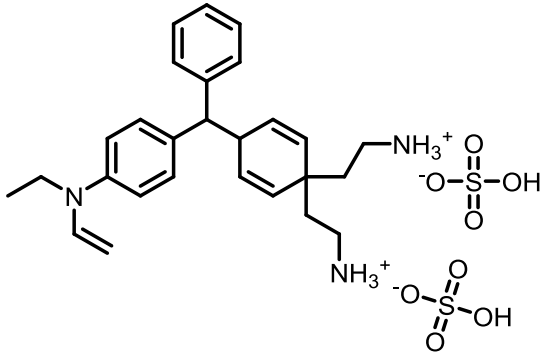
Disperse yellow 3

- Also called cationic dyes due to the presence of a positive charge, often caused by an ammonium cation
- Being water soluble, they were originally used for paper, silk and wool
- Generally low color fastness
  - Forms covalent bonds with acrylic fibers negating this issue

Basic red 1

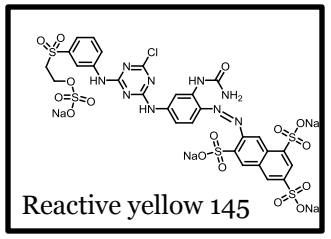


Basic green 1



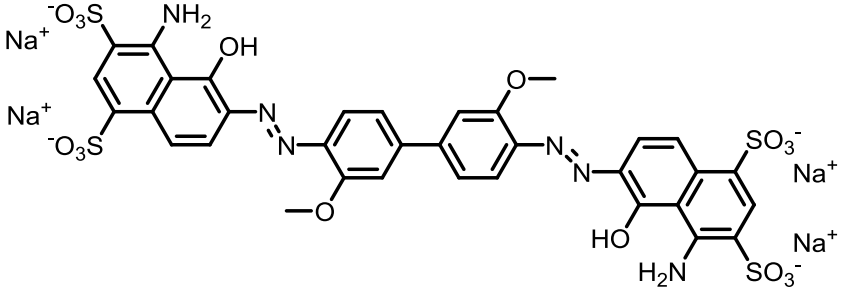
Hunger K (2003) Industrial dyes: chemistry, properties, applications. Wiley-VCH, Weinheim

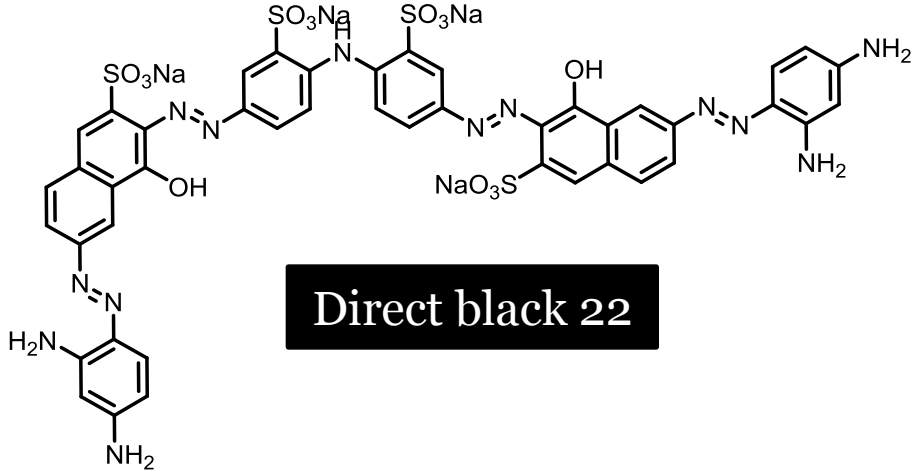
Direct Dyes


Reactive yellow 145

- Water-soluble and easily applied to cellulose
  - Anionic; forms bonds with cellulosic fibers
  - No mordant required
  - Applied from aqueous mixture containing an electrolyte
- Generally have high molecular masses
  - Promotes dye aggregation
  - Promotes substantively to the fiber
- Also called substantive dye

Direct blue 1

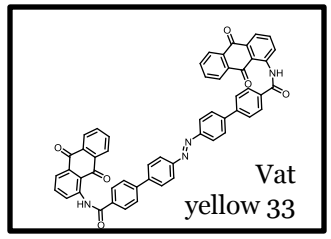




Direct black 22

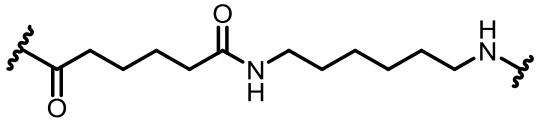
Hunger K (2003) Industrial dyes: chemistry, properties, applications. Wiley-VCH, Weinheim
Considine DM (1995) Van Nostrand's scientific encyclopedia. Springer, New York, USA
Broadbent AD (2001) Basic principles of textile coloration. Society of Dyers and Colourists, England

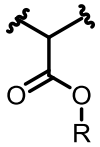
Disperse Dyes

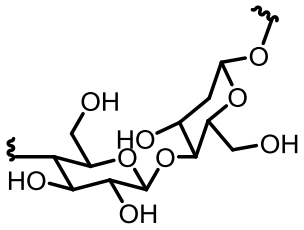


- Often contain azo, anthraquinone, and nitro groups

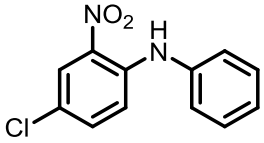
- Water-insoluble dyes with affinity for hydrophobic fibers
  - Nylon
  - Cellulose
  - Acrylic



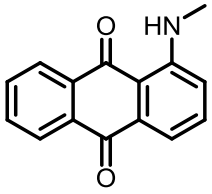




Disperse yellow 26

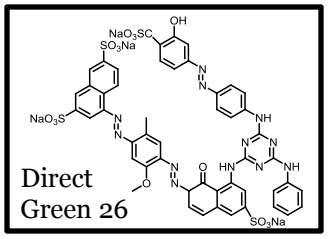


Disperse red 9

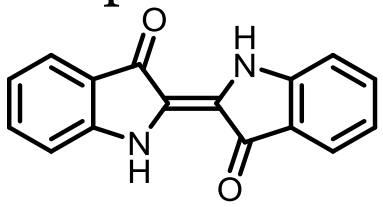


Burkinshaw SM (2016) Physico-chemical aspects of textile coloration. John Wiley & Sons, Hoboken, New Jersey

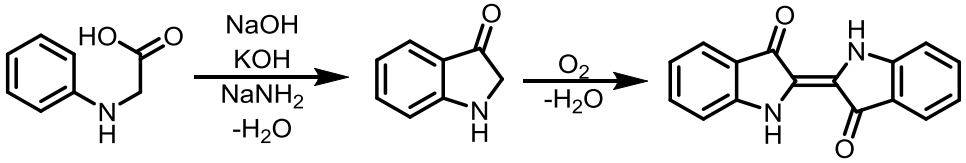
Indigoid Dyes



- All based on the organic compound—indigo



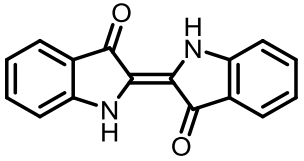
- Obtained from natural sources for ~5000 years until the 19th century
- One of the first natural molecules synthesized
- Pflegers's method is used to create most of the high quality indigo



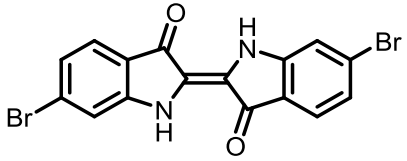
pH

Below 11.4 | Above 13.0

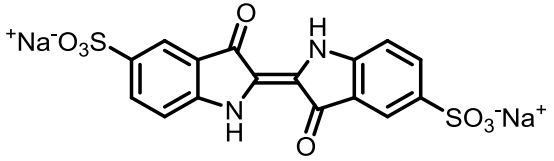
Indigo



Tyrian Purple



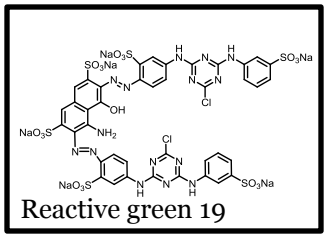
Indigo carmine



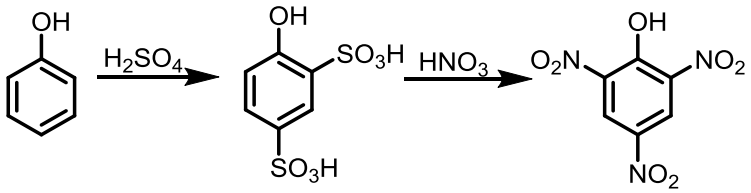
Głowacki ED, Voss G, Leonat L, Irimia-Vladu M, Bauer S, Sarıçiftçi NS (2012) Indigo and tyrian purple—from ancient natural dyes to modern organic semiconductors. Isr J Chem 52:1–12

Ünlü M (2008) Indigo dyeing wastewater treatment by the membrane based filtration process, Master Thesis, Middle East Technical University, Ankara, Turkey

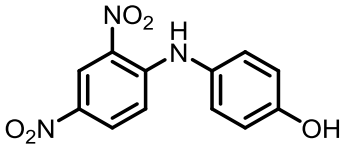
Nitro and Nitroso Dyes


Reactive green 19

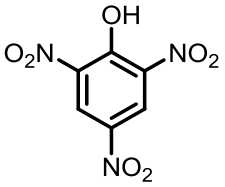
- Minor commercial importance
- Of interest for their small molecular structure
- Used in acid form to dye natural fibers such as silk or wool



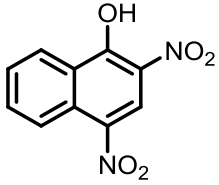
Disperse yellow 1



Picric Acid

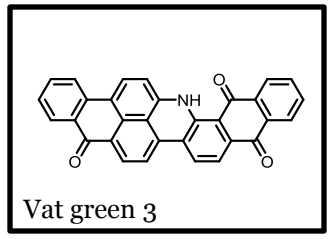


Acid yellow 24



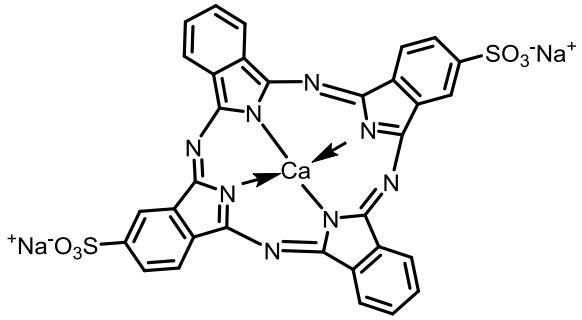
Gregory P (1990) Classification of dyes by chemical structure. In: Waring DR, Hallas G (eds) The chemistry and application of dyes. Plenum Press, New York, USA

Phthalocyanine Dyes



- A class of macrocyclic compounds possessing a highly conjugated electron system with intense near-IR absorption

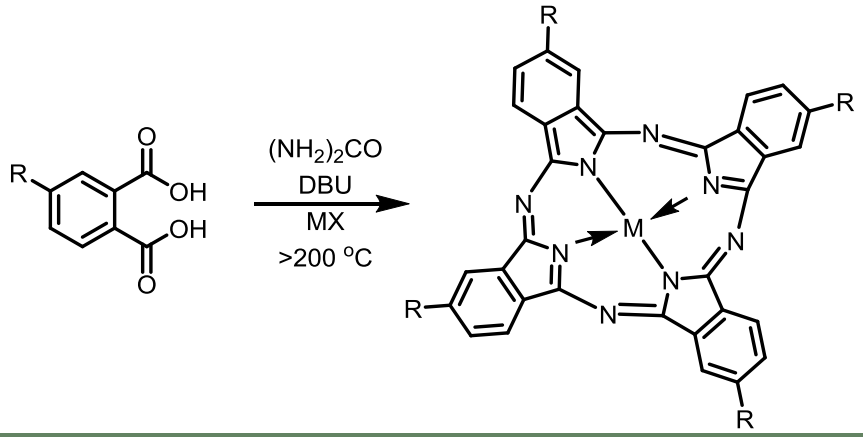
- They have a number of unique properties:
  - Increased stability
  - Diverse coordination properties
  - Architectural flexibility

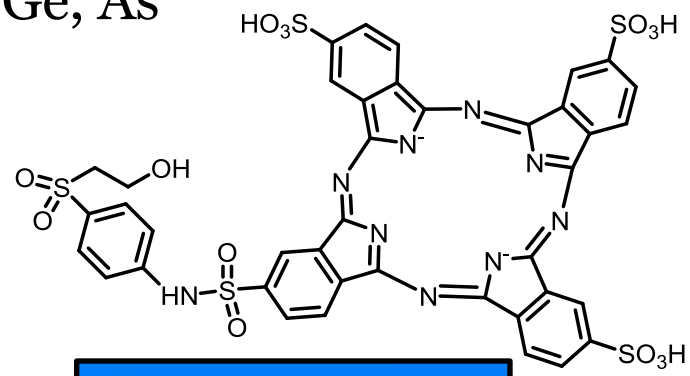


Direct Blue 86

- Often intense color in 650-750 nm range

- Coordinates with metals such as Cu, Fe, Si, Ge, As

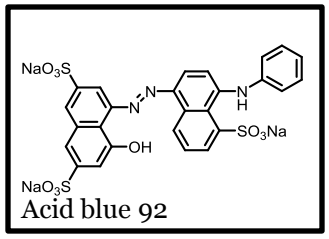




Reactive Blue 21

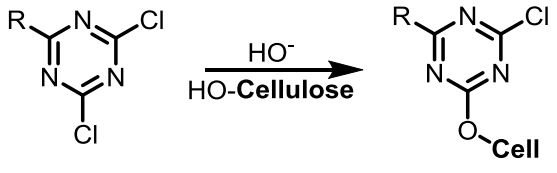
Durmuş M, Nyokong T (2008) Photophysicochemical and fluorescence quenching studies of benzyloxyphenoxy-substituted zinc phthalocyanines. Spectrochim Acta A 69(4):1170–1177; Wöhrle D, Schnurpfeil G, Makarov SG, Kazarin A, Suvorova ON (2012) Practical applications of phthalocyanines–from dyes and pigments to materials for optical, electronic and photo-electronic devices. Macroheterocycles 5(3):191–202; Hunger K (2003) Industrial dyes: chemistry, properties, applications. Wiley-VCH, Weinheim; Sahin S, Altun S, Altındal A, Odabas Z (2015) Synthesis of novel azo-bridged phthalocyanines and their toluene vapour sensing properties. Sens Actuat B-Chem 206:601–608

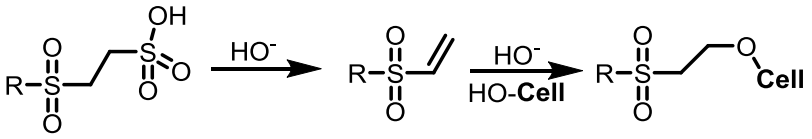
Reactive Dyes



- Differ from other dyes because their molecules react to form covalent bonds with functional groups on the fibers

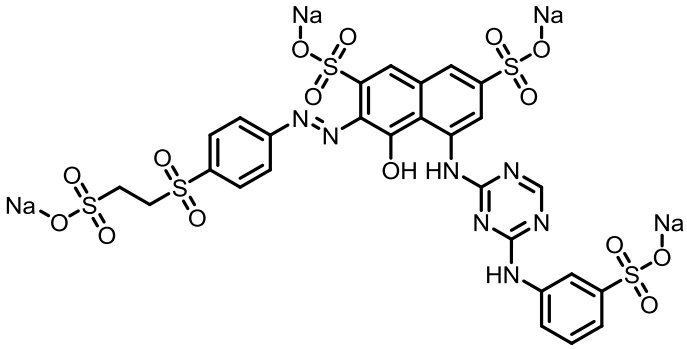
- Have exceptional qualities:
  - High wet-fastness
  - Brilliant
  - Large range of hues





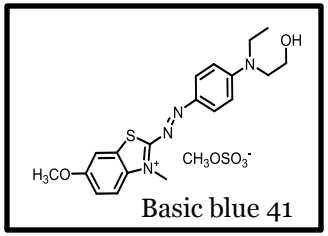
- Usually contain –NH–, –CO–, or –SO_2– as linking group

Reactive Red 198



Pereira L, Alves M (2012) Dyes-environmental impact and remediation. In: Malik A, Grohmann E (eds) Environmental protection strategies for sustainable development, strategies for sustainability. Springer, New York
Ferus-Comelo M (2002) Control of the adsorption of dyes on cotton. Ph. D. Thesis, University of Leeds, Leeds, UK

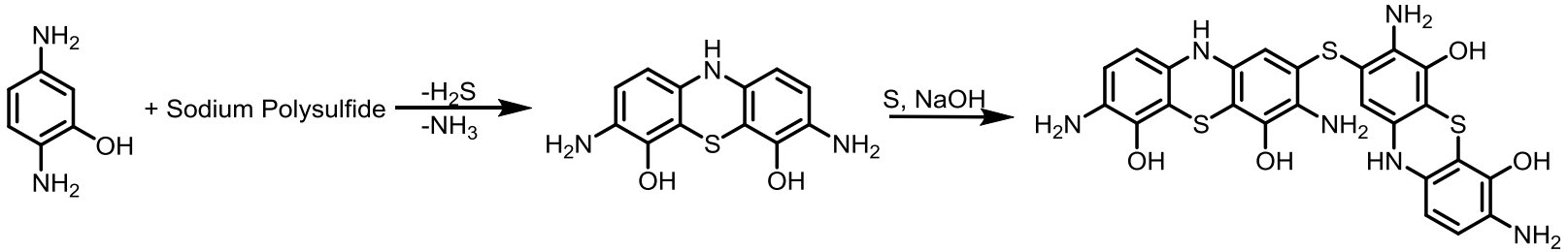
Sulfur Dyes



Basic blue 41

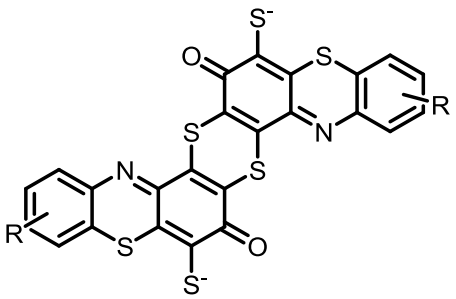
- Almost always used for dyeing cellulosic fibers

- Insoluble in water
  - Reduced to the water-soluble leuco (white/reduced) form
  - Applied using sodium sulfide solution
  - Dye formed via oxidation while impregnated in the fiber



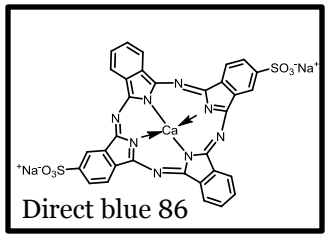
- Often they don't have well defined structures or compositions due to oligermerization & di/poly-sulfide links

Sulfur Black 1



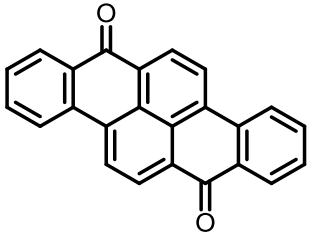
Springer RM (1997) Chemistry and Applications of Leuco Dyes
Hunger K (2003) Industrial dyes: chemistry, properties, applications. Wiley-VCH, Weinheim

Vat Dyes

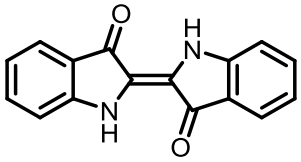


- Water-insoluble pigments
  - Called dyes because in alkaline solution, reduction occurs forming a water-soluble leuco form
- Held to cellulose via van der Waals forces and hydrogen bonding
- Oxidizes on drying to become water-insoluble again leading to high color fastness
- Lack of industry knowledge and basics for application techniques have led to a decrease of usage

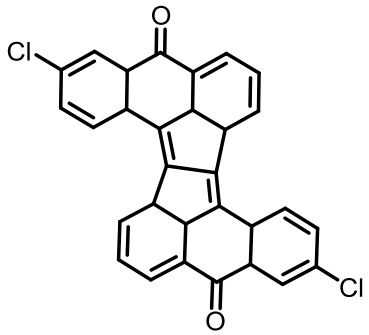
Vat yellow 4



Vat blue 1 / Indigo

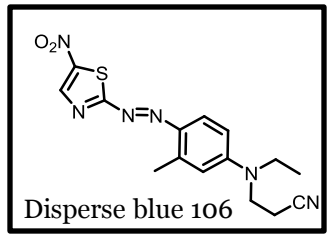


Vat brown 45



Considine DM (1995) Van Nostrand's scientific encyclopedia. Springer, New York, USA
Broadbent AD (2001) Basic principles of textile coloration. Society of Dyers and Colourists, England
Ferus-Comelo M (2002) Control of the adsorption of dyes on cotton. Ph. D. Thesis, University of Leeds, Leeds, UK

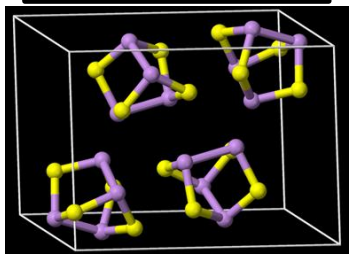
Inorganic Pigments



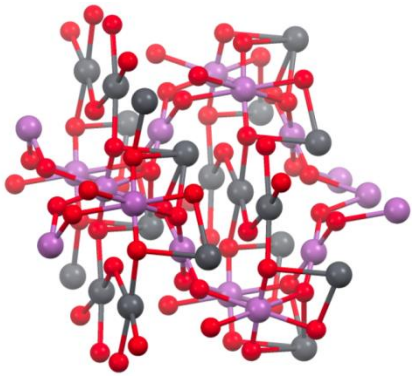
Disperse blue 106

- Broken into four categories:
  1. White
  2. Black
  3. Colored
  4. Miscellaneous
     - Metal effect
       - Flakes/lamella-shaped particles of soft, ductile metals
       - Avoid issues of organic molecules hindering cold welding
     - Nacreous
       - Pearlescence due to multiple partial reflections
       - Fish-scales (guanine)
     - Transparent
       - Used in protection as a lacquer
       - Blocks UV light with small particles
     - Luminescent
       - Solid fine particulates
       - Reemit absorbed energy as light
       - Rely on fluorescence or phosphorescence

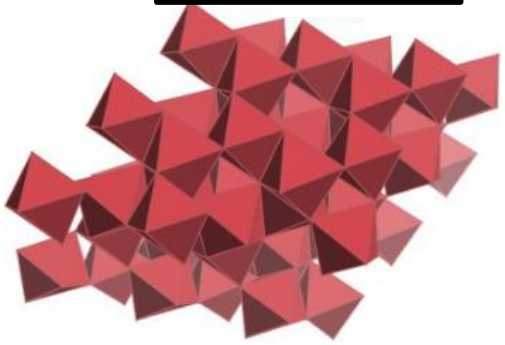
As_4S_4



$Pb_2Sb_2O_7$

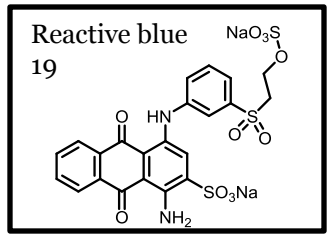


Ti_2O_3



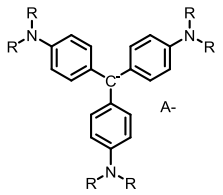
Buchel KH, Moretto H, Werner D (2015) Industrial Inorganic Chemistry
Völz HG et al. (2011) Pigments, inorganic. In: Ullmann's encyclopedia of industrial chemistry. Wiley-VCH, Weinheim

Organic Pigments

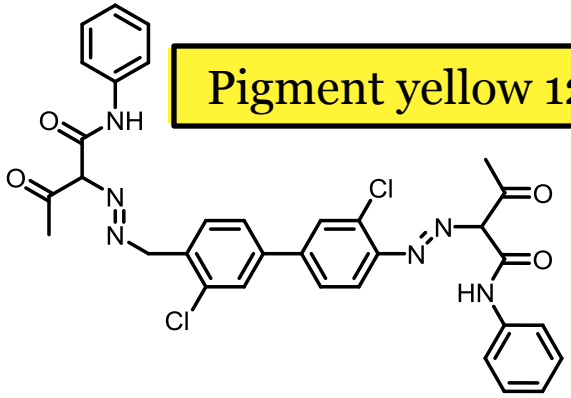


- Based on carbon chains and carbon rings
  - Can have metallic elements for stabilization
  - Must be insoluble at the time of application
  - Have a smaller average particle size than inorganic pigments

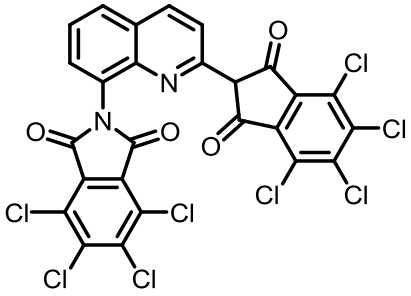
- Broken down into six main categories:
  1. Azo
  2. Triaryl carbonium
  3. Anthraquinone
  4. Dioxazine
  5. Polyclic
  6. Quinophthalone



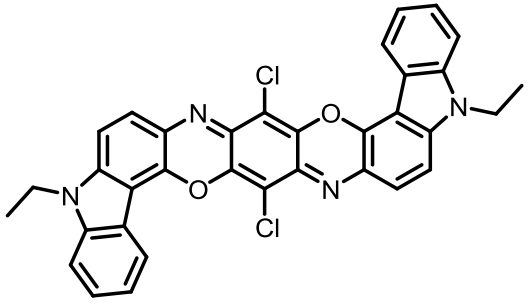
Pigment yellow 12



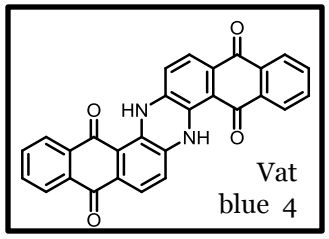
Pigment yellow 138



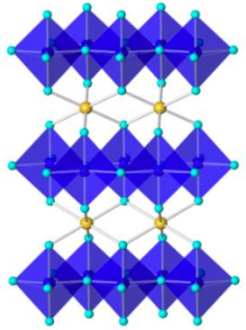
Pigment violet 23



YInMn Blue



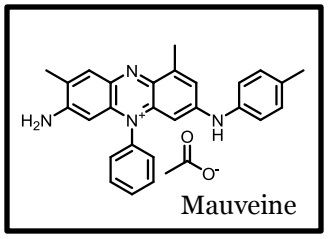
- Discovered accidentally by Andrew Smith and Prof. Mas Subramanian at Oregon State University in 2009
  - Looking for multiferroics
  - Instead formed, at 2,000 °F upon mixing of $YInO_3$ and $YMnO_3$, a bright blue compound
- Prof. Subramanian recognized the potential use as a pigment
  - Had worked for DuPont Co.
  - Filed patent disclosure covering the pigment



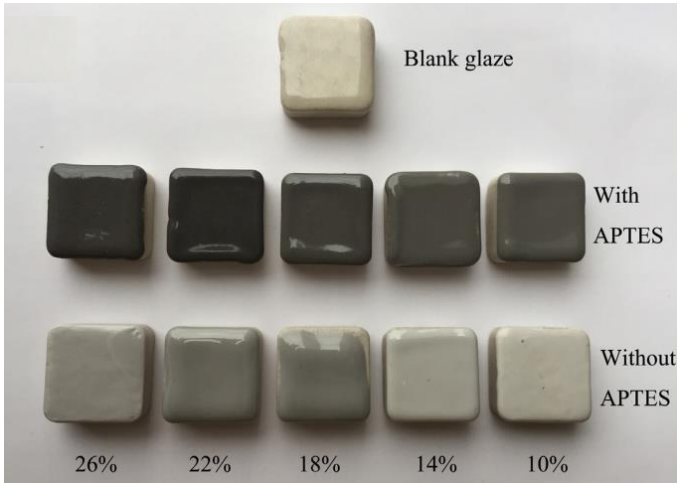
- Notable features
  - Extremely vibrant, near-perfect blue
  - Extremely stable; does not fade (as does ultramarine/ Prussian blue)
  - Non-toxic (as is cobalt blue)
  - Strong infrared radiation reflection (useful for energy-saving cool coatings)
- Crayola created the “Bluetiful” crayon, replacing Dandelion (2017)
- Being released as an acrylic paint by Matisse
- Can adjust color by changing ratios; $YIn_{0.8}Mn_{0.2}O_3$–optimal

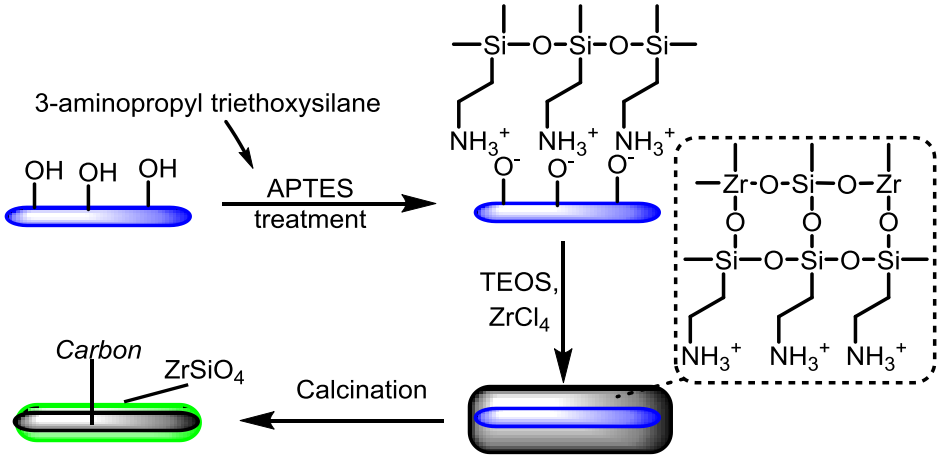
Smith, Andrew E.; Mizoguchi, Hiroshi; Delaney, Kris; Spaldin, Nicola A.; Sleight, Arthur W.; Subramanian, M. A. (2009-12-02). "Mn3+ in Trigonal Bipyramidal Coordination: A New Blue Chromophore". *Journal of the American Chemical Society*. **131** (47): 17084–17086. doi:10.1021/ja9080666
Smith, Andrew E.; Comstock, Matthew C.; Subramanian, M. A. (2016-10-01). "Spectral properties of the UV absorbing and near-IR reflecting blue pigment, YIn1-xMnxO3". *Dyes and Pigments*. **133**: 214–221. doi:10.1016/j.dyepig.2016.05.029

$C@ZrSiO_4$



- Published 2016 by Weihui Jiang at Jingdezhen Ceramic Inst.
- A zircon-based black pigment consisting of *in-situ* polycondensation
- After enameling on tiles at 1200 °C, $C@ZrSiO_4$ pigment appeared a promising candidant for high temp. ceramics
  - Smooth, clean, deep hue
  - High tinting ability
  - Absence of any surfactants

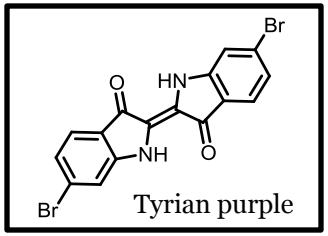




- 30m in air at 1200 °C
- No cracks or holes seen
- Inclusion of pigment has good thermal and chemical stability in the glaze at high temp.

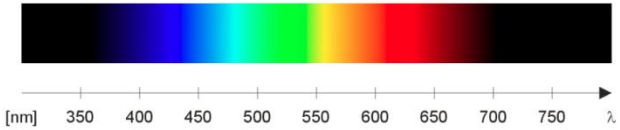
T. Chen, et al., Synthesis and application of C@ZrSiO4 inclusion ceramic pigment from cotton cellulose as a colorant, J Eur Ceram Soc (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2015.07.021

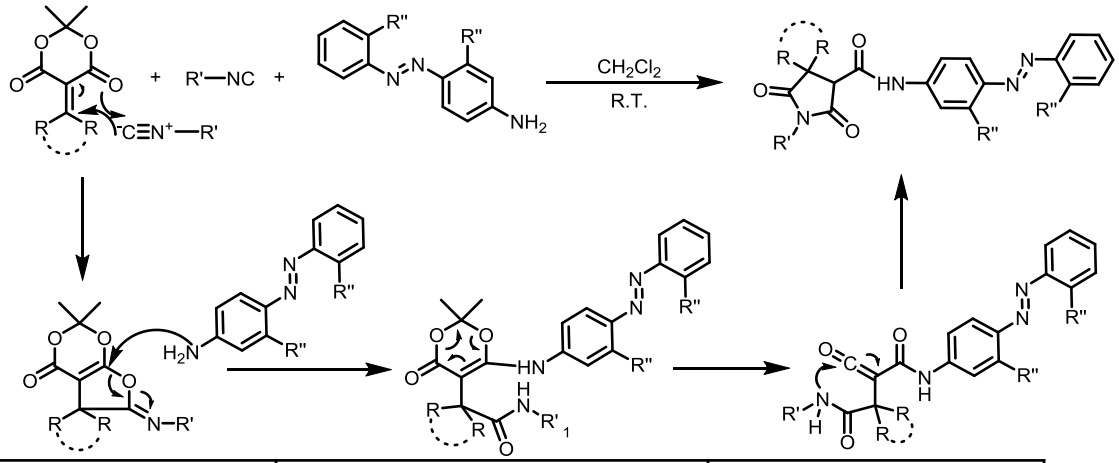
Synthetic Development of Succinimide Dyes



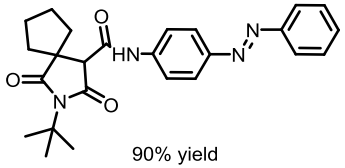
- Published 2014 by Yousef Valizadeh
- Developed a one-pot reaction of *Meldrum's acid*, alkyl isocyanide, and 4-(2-phenyldiazenyl)benzenamine

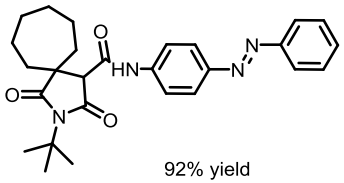
$$A = \log_{10}\frac{I_o}{I} = \varepsilon\, l\, c$$

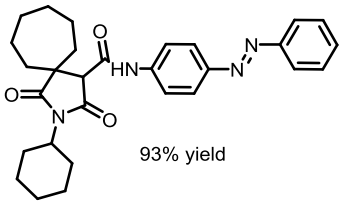


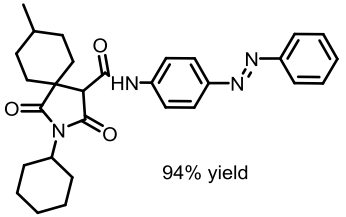


λ_{max}(nm)	348	346.7	344	344
A	1.66	0.4	1.35	1.32
ε	30,180	40,000	26,470	24,900


90% yield

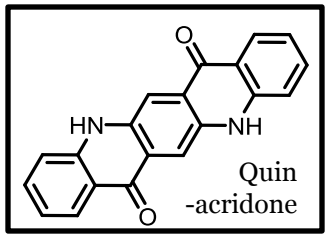

92% yield


93% yield


94% yield

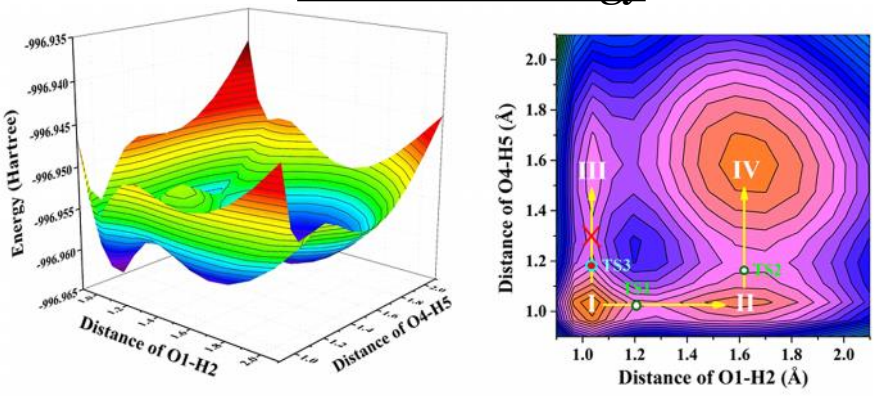
A. Habibi et al. / Dyes and Pigments 113 (2015) 481e486

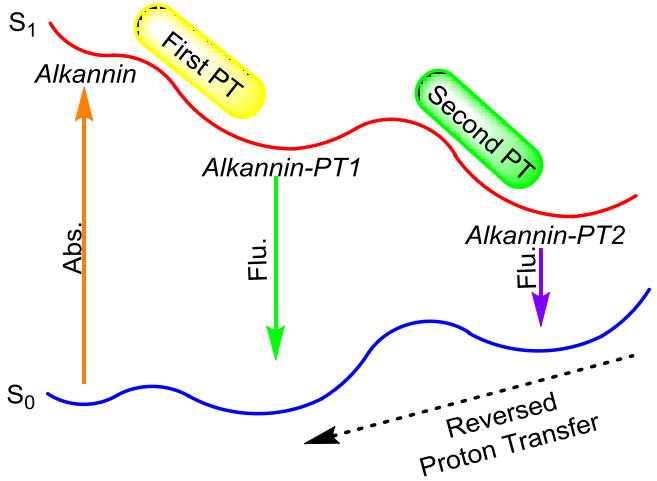
Theoretical/Computational Studies

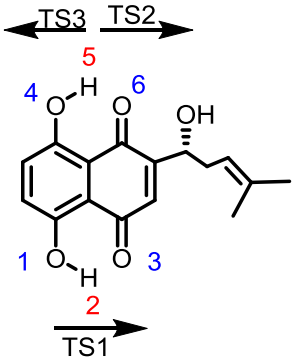


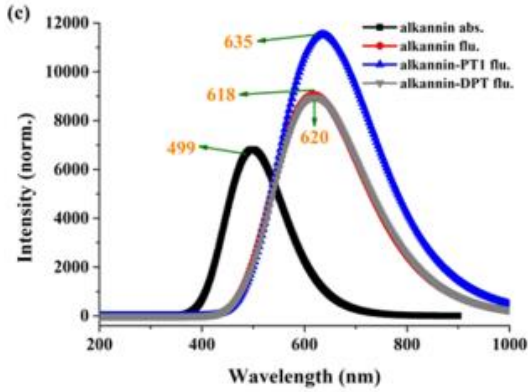
- Yujun Zheng's group at Shandong University study the most important component of modern deep red pigments—alkannin
- The group explores the mechanism of the double proton transfer

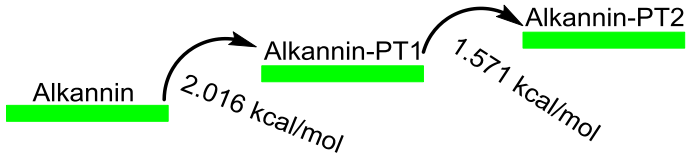
Model the energy











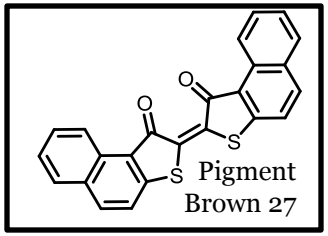
- Confirm importance TS1
- Suggest the stepwise excited state double proton transfer

Alkannin

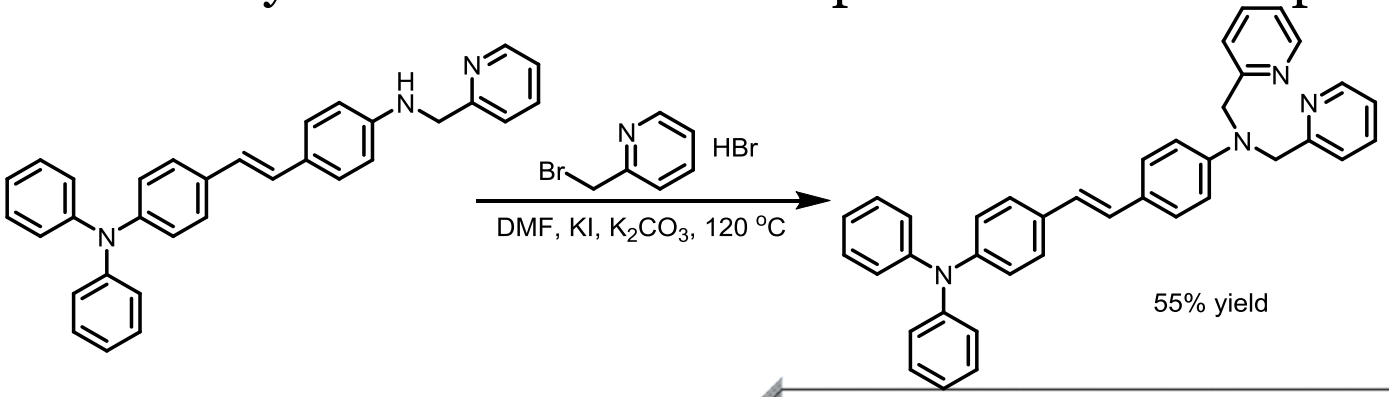
635nm

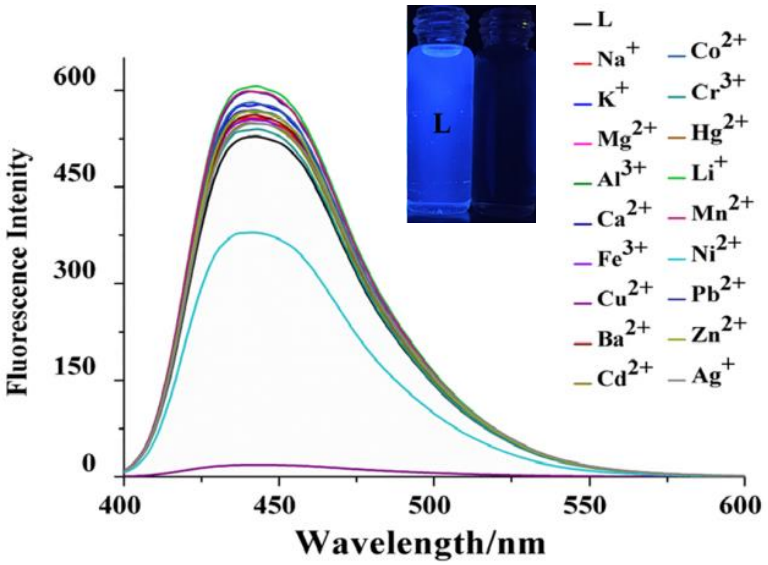
Zhao J, Dong H, Zheng Y J. Phys. Chem. A 2018, 122, 1200–1208

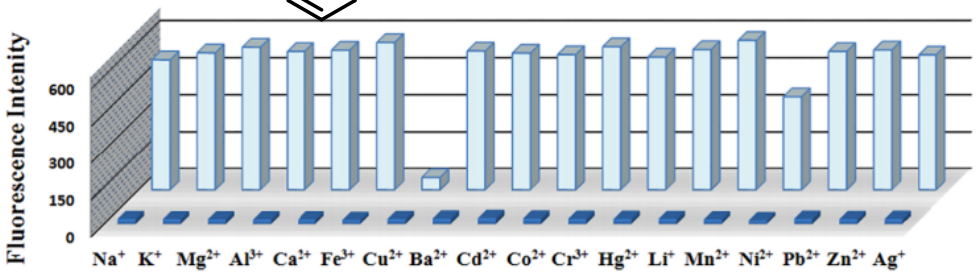
Development of a New Chelating Dye

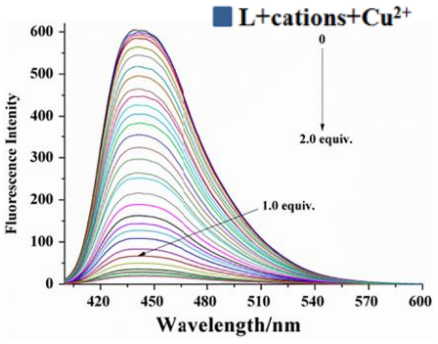


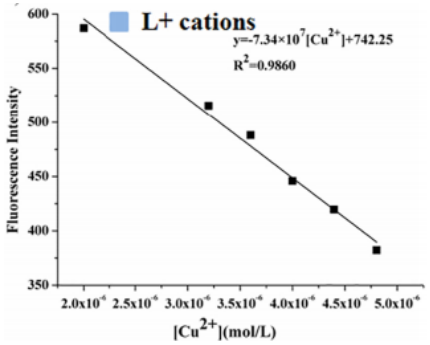
- Hongping Zhou in Anhui University in 2018 developed a copper sensitive dye for use in water samples and *in vivo* experiments





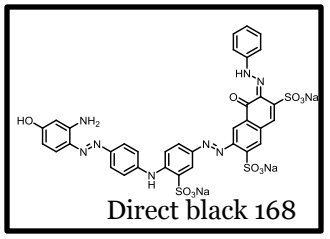




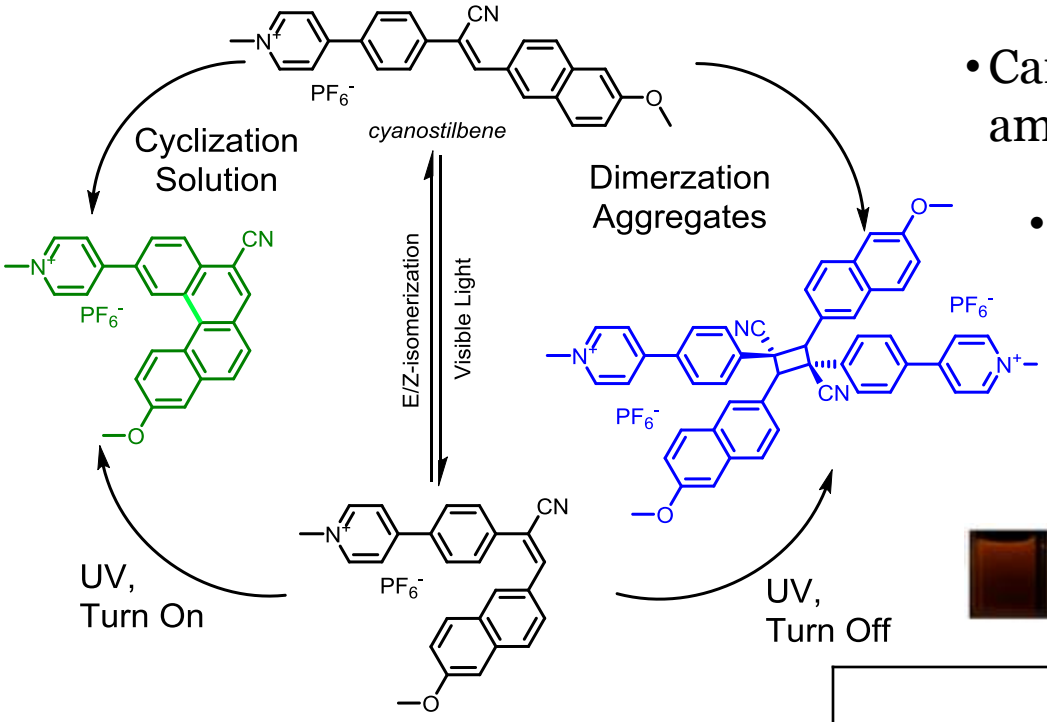


Huihui Zhang, Zeyue Wei, Ying Xia, Min Fang, Weiju Zhu, Xingyuan Yang, Fei Li, Yupeng Tian, Xuanjun Zhang, Hongping Zhou , Exploration research on synthesis and application of a new dye containing di-2-picolyamine. Saa(2017), https://doi.org/10.1016/j.saa.2018.02.023

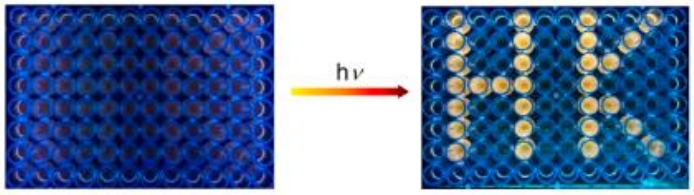
Photochromic Colorants



- Ben Zhong Tang at HKUST-Shenzhen Research Institute published in 2018 a multiphotochrome molecule



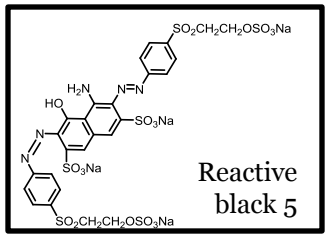
- Can "turn-on" or "turn-off" based on amount of water present in CH_3CN
- Could be doped into a polymer matrix to act as miroactuators and create a corresponding macroscopic behavior in the material



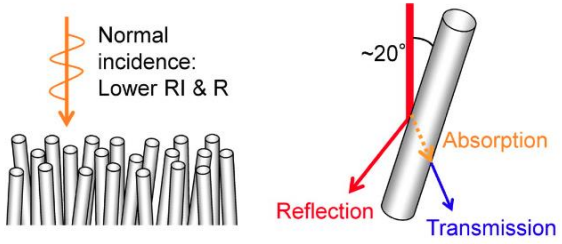
	Fraction of water (vol %)				
	0	50	70	80	99
Dimerized	<1%	<4%	<4%	90%	99%
Cyclized	99%	96%	96%	<10%	<1%

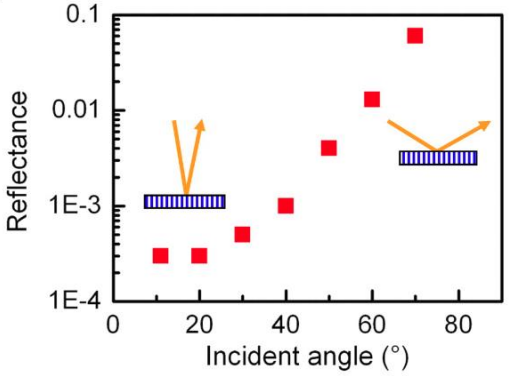
Peifa Wei, Jing-Xuan Zhang, Zheng Zhao, Yuncong Chen, Xuewen He, Ming Chen, Junyi Gong, Herman H.-Y. Sung, Ian D. Williams, Jacky W. Y. Lam, and Ben Zhong Tang *J. Am. Chem. Soc.* 2018, 140, 1966–1975

Vertically Aligned Nanotube Arrays

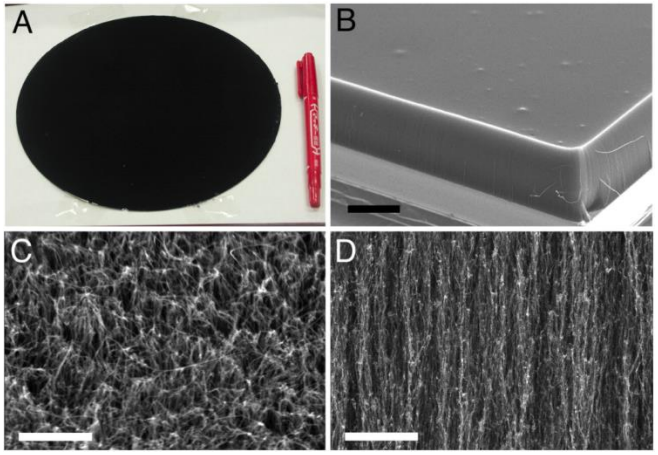


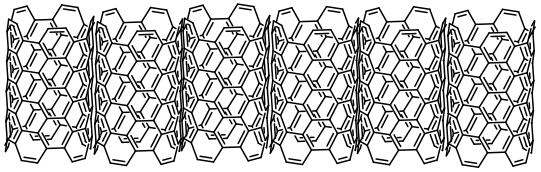
- Original development by Lehman in the UK for use in thermal detection applications in the infrared
- Spectrally flat over most visible wavelengths
  - Absorbs 99.965% of visible light
  - Vertical nanotubes are grown using chemical vapor deposition
  - Light doesn't reflect out, but gets trapped in the tubes until absorption





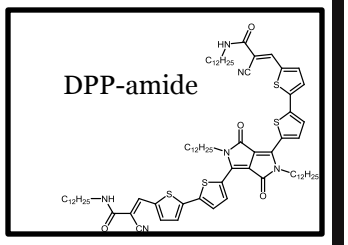
Anish Kapoor Art



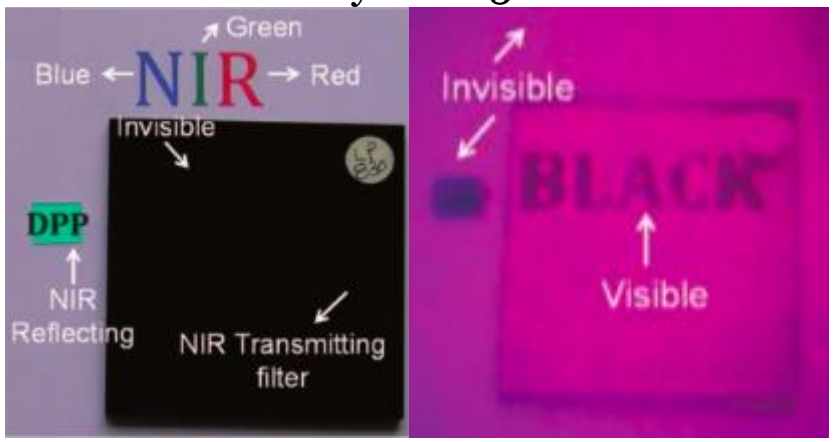


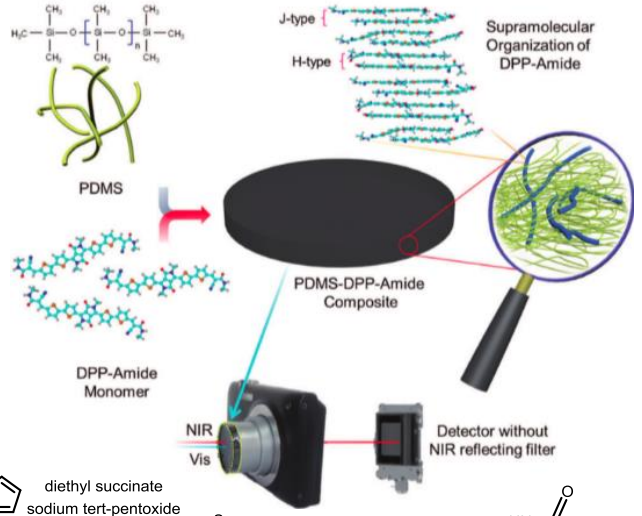
Theocharous, E.; Deshpande, R.; Dillon, A. C.; Lehman, J. "Evaluation of a pyroelectric detector with a carbon multiwalled nanotube black coating in the infrared". Applied Optics. 45 (6): 1093. doi:10.1364/AO.45.001093
"Vantablack, the world's darkest material, is unveiled by UK". South China Morning Post - World. 15 July 2014.
Kohei Mizuno, Juntaro Ishii, Hideo Kishida, Yuhei Hayamizu, Satoshi Yasuda, Don N. Futaba, Motoo Yumura, and Kenji Hata PNAS April 14, 2009. 106 (15) 6044-6047; https://doi.org/10.1073/pnas.0900155106

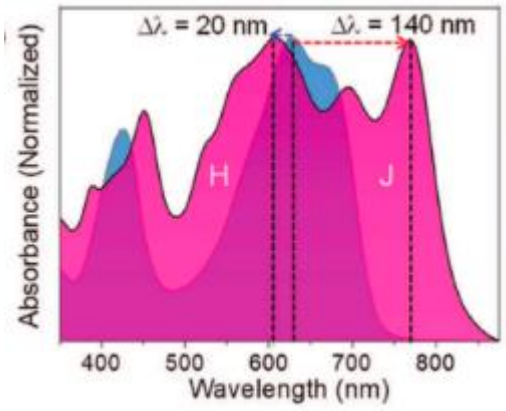
Near-Infrared-Transmitting Optical Filter

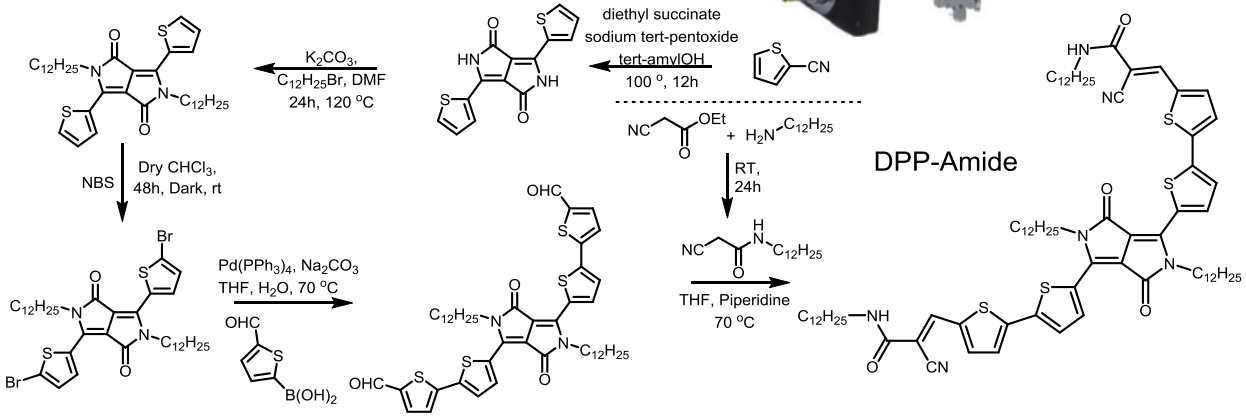


- Developed by Ayyappanpillai in 2017
- Visibly opaque but NIR-transparent materials are important for security systems and night-vision technology
  - DPP-Amide blocks 300-800 nm light by H-bonding and π-stacking
  - Transmits beyond 850



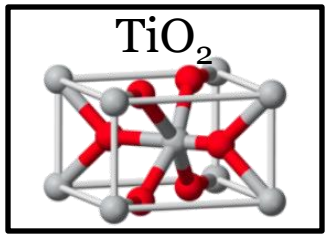






S. Ghosh, Dr. S. Cherumukkil, Dr. C. H. Suresh, Prof. A. Ajayaghosh *Adv. Mater*. 2017, 29, 1703783

Industrial Opportunities



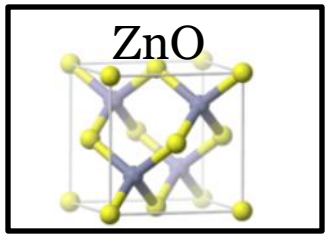
- Typical Education Requirement
  - Ph.D. required for most research positions
  - Postdoctoral work required for most academic positions
    - Synthetic chemistry
    - Analytical chemistry
    - Organic chemistry
    - Polymer chemistry
    - Material chemistry
- Laboratories
  - Academic
  - Industrial
  - Government

- Salaries (2015)
  - Lab managers: $76,000 median
  - Pigment chemists: $65,400 median
  - Ink chemists: $60,200 median
  - (note: B.S. chemists earn $50 to $80K)

- Future Employment Trend
  - Steady growth in paints & varnishes
    - Accounts for 43% of pigment and 27% of plastic colorant demand
  - Niche markets expected to grow
    - Photochromic colorants
    - Medical dyes
    - Infrared dyes for security
    - Hair dyes
  - High-tech applications up-and-coming
    - Inkjet microfabrication
    - 3D printing

Houlton, S. Who's Who: Colourful Chemistry. Chem. World [Online], 2009.
Dyes, Pigments and Inks [Online] American Chemical Society, 2018
Market Study: Pigments [Online]; 3rd Edition; Ceresana Market Intelligence Consulting: Constance, Germany, November 2013.
US Currency Education Program
Steven Van Belleghem

Industrial Opportunities



- Typical work
  - Develop applications for existing dyes and pigments
  - Examine health, environmental, and safety concerns of colorants
  - Design, create, and characterize novel products and formulations
  - Analyze historical artifacts and artwork for pigments and dyes used
  - Work in crime scene analytics determining dyes and pigments in evidence
  - Teach courses and train students

Professional Organizations

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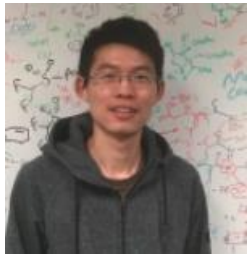
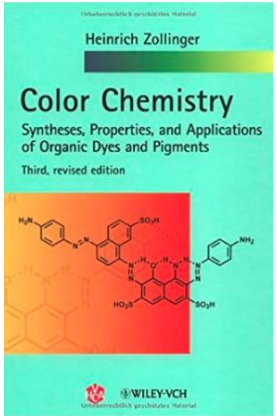
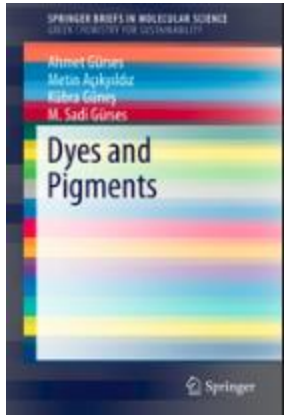


Great resources

A. Gürses, M. Açıkyıldız, K. Güneş, M. S. Gürses, *Dyes and Pigments, Springer International Publishing,* ***2016.***



H. Zollinger, *Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments, VCH,* ***1991.***



L. R. Milgrom, *The Colours of Life, Oxford University Press,* ***1997.***