Heritage Science

RESEARCH ARTICLE

The synthesis characterization of historical novel azo pigments: implications for conservation science

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Abstract

A series of synthetic organic pigments (SOP's) with azo-containing linkages have been synthesized and characterized by Fourier transform infrared (FTIR) and Raman spectroscopies and laser desorption ionization mass spectrometry (LDI-MS). These pigments include representatives of the chemical classes arylide (Hansa) yellow, diarylide yellow and oranges, and Naphthol AS. Certain of these (PR7, PR10, PR11, PR18, PR19, PO14, PO15, PO16, PY49, PY98, PY106, PY113, PY124, PY203) are historical pigments, that is they were manufactured but subsequently were removed from production. Of these, some have been brought back into limited production. In addition to the above-mentioned pigments, 18 products of azo-linkage reactions formed between *N,N'*-bis(acetoacetyl)-*o*-toluidine and substituted anilines have been synthesized and characterized by the methods listed above as well as by visible reflectance spectroscopy. While not commercially available azo pigments, these colorants will serve as model systems to study substituent effects on pigment color.

Keywords: Raman microscopy, Synthetic organic pigments, Laser desorption ionization mass spectrometry, Arylide yellow, Naphthol AS-G, Diarylide

Introduction

Materials or substances pre-exist every created object, whether cultural, as a work of art, or chemical, as in a pigment or dyestuff. It is in the act of synthesis (from the Greek meaning "put together") that some *one* creates some *thing*. Composed of many physical components as well as human creativity, whether novel and valuable, or mundane and ordinary, the synthesis initiates part of the history of an object—a point that begins a timeline at that of the time of creation. The art historian puts art in a cultural context of (a) influences before and (b) influences after the creation. The conservator deals with and hopes to mitigate the interactions of time and all the travails that leave their mark on an object. The scientist can help inform both by analysis of the components of the object as they are now—with all the shadow of their history—a combination of history of the materials available

and used at the time of creation, and what has happened since.

Synthetic organic pigments (SOP's) have changed the look of life since they were first manufactured over 150 years ago. Their history began with the synthesis of mauveine by Perkin, but soon industrial and academic scientists were creating hundreds of new pigments and dyes—different in color, solubility and stability to light and heat—for artist, industrial and architectural paints, textiles, plastics and printing inks. After synthesis, each new commercial SOP begins its journey into history by a start date of manufacture. This can be useful in the art historical context of artworks. Because time and aging can be observed in the chemical components of art, knowledge of the SOP's can help inform conservation and display decisions as they can differ dramatically in their solvent and lightfastness.

Many early synthetic organic pigments are azo (–N=N–) containing. These linkages are found in pigment classes including β-naphthols, arylide (Hansa) yellows, Naphthol AS, diarylide yellow and oranges,

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BONA pigments, benzimidazolones, and disazo condensation pigments. More recently, polycyclic pigments such as quinacridones, phthalocyanines, perinones, perylenes and diketopyrrolopyrrole have been introduced [1].

Certain SOP's have come into and out of manufacture. These we call 'historical pigments' as they had a finite commercial life. You might think that this might make a "line segment" out of their timeline. It is certainly true that observation of a historical pigment can give art historical context to a work of art. However, just because a historical pigment is no longer manufactured does not remove these pigments from works of art, so their timeline continues. Nevertheless, it does make their identification a challenge.

This particular challenge became apparent to us in our attempts to examine the pigments used by Mark Rothko. Rothko was found to have used a variety of red colorants during his career, including the Naphthol AS pigment PR11. An unknown pigment in a painting by Rothko was ultimately identified as PO2, though we initially did not have a sample of this pigment, as it is no longer commercially produced [2]. This led us to investigate other pigments that might no longer be in commercial production, but that have been used in works of art. The reasons for removal often are not documented but can be due to newer pigments being introduced with more desirable properties or cost. Though some of these pigments have been reintroduced by limited numbers of manufacturers, they might be difficult to obtain as reference samples.

We, in this work, have re-synthesized fourteen historical pigments and analyzed them by infrared (IR) and Raman spectroscopy as well as laser desorption ionization (LDI) mass spectrometry. The small sample size required, sharp peaks and low energy cutoff of Raman spectroscopy make it an extremely useful technique to identify these pigments [3, 4]. LDI-MS, which can be performed in both positive and negative ion modes, provides pigment-specific information including the molecular weight and fragmentations [5, 6]. These pigments include members of the arylide (Hansa) yellows, diarylide yellow and oranges, and the Naphthol AS classes. The pigments were synthesized by a classic diazotization reaction, reacting an in situ generated diazonium salt with an appropriately functionalized coupling component.

In addition, we have synthesized eighteen novel pigments with a variety of substitutions on a common synthetic and structural backbone. These pigments are based on the coupling of Naphthol AS-G with substituted anilines and are not Colour Index pigments [7]. We present their analysis as well as the beginning of an investigation of how the substituents change their physical properties.

Methods/experimental

These pigments are made from a diazotization reaction from an in situ generated diazonium salt with a coupling component. The reaction sequence begins with the reaction of an amine with sodium nitrite ($NaNO_2$) under acidic conditions to form the diazonium salt. This salt is then reacted with a coupling component that has been deprotonated with sodium hydroxide (NaOH). The polar non-hydrogen-bonding solvent acetonitrile was used to solubilize the reactants, but the pigment produced is insoluble in this solvent.

Chemicals listed without sources are reagent grade and were not further purified. A typical synthetic pathway is described for a representative member of each class: Naphthol AS (PR11), arylide (Hansa) yellow (PY49) and diarylide yellow (PY124).

PR11

Preparation of coupling component: 0.227 g (1.604 mmol) 5-Cl-2-methylaniline was combined with 2.5 mL acetonitrile in a 10 mL Erlenmeyer flask. 0.0850 g (0.802 mmol) Na_2CO_3 was then added to the solution while stirring in an ice bath. Once the solution was sufficiently cooled, 0.1107 g (1.604 mmol) $NaNO_2$ dissolved in 1–2 mL acetonitrile was added to the flask. 2 mL of water were added to the flask to partially dissolve any remaining solids, while stirring in an ice bath.

Preparation of amide for coupling

In a second 10 mL Erlenmeyer flask, 0.500 g (1.604 mmol) 5′-Cl-3-OH-2′-Me-2-napthanilide was dissolved in 1.2 mL of 3 M NaOH. If any solid amide remained, minimal amounts of acetonitrile were added to dissolve it.

Preparation of diazonium salt

In a 25 mL Erlenmeyer flask, 0.44 mL reagent grade (37%) hydrochloric acid was combined with 2 mL of ice-cold acetonitrile. The coupling component from the first step was then poured in 4–5 portions into the 25 mL flask containing cold HCl/acetonitrile solution. Any remaining solids were rinsed in with water. The flask was left stirring in an ice bath for 5 min.

Coupling

After 5 min, the liquid amide solution was added directly to the cold diazonium salt. If the amide solution crystallized before addition it was redissolved in minimal amounts of acetonitrile before adding to the diazonium salt. After the product precipitated, it was collected through vacuum filtration on a Buchner funnel and oven dried.

Using the same method with the appropriate starting materials PR7, PR10, 17, 18 and 19 were synthesized.

PY49

The same method with similar amounts of solvent, acid and base were used with 4-chloro-2-methylaniline (0.2652 g, 1.873 mmol), Na_2CO_3 (0.0975 g, 0.920 mmol), $NaNO_2$ (0.1276 g, 1.849 mmol), and 2,5-dimethoxy-4-chloroacetanilide (0.4996 g, 1.839 mmol) to yield the yellow solid, PY49 (1.1077 g, 86%).

Using the same method with the appropriate starting materials PY98 and PY203 were synthesized.

PY124

3,3′-Dichlorobenzidine (100 mg, 0.3951 mmol) was placed in a 25 mL beaker and dissolved in acetonitrile (3 mL) followed by addition of Na_2CO_3 (75 mg, 0.708 mmol) and $NaNO_2$ (60 mg, 0.87 mmol). In a separate 25 mL beaker 2′4′-dimethoxyacetoacetanilide (300 mg, 1.26 mmol) was dissolved in 3 M NaOH (0.5 mL) and acetonitrile (3 mL). A third 25 mL beaker contained water (3 mL) which was cooled on ice and then conc. HCl (0.5 mL, 5.75 mmol) was added. The HCl was then added to the 3,3′-dichlorobenzidine beaker in 10 portions with strong mixing, forming the diazonium salt. This mixture was then added to the 2′4′-dimethoxyace-toacetanilide beaker in 1 mL portions and the resulting mixture was stirred for 10 min. This product was vacuum filtered and washed thoroughly with acetonitrile and water then oven dried.

Using the same method with the appropriate starting materials PY106, PY113, PO14, PO15 and PO16 were synthesized.

LDI MS

LDI was performed on a Shimadzu Axima MALDI-MS (Matrix Assisted LDI) system. The samples were affixed to the plate with a polybutylmethacrylate (PBMA)/acetonitrile solution. The solvent evaporated and the PBMA prevented the fine powder pigment from flying into and fouling the instrument. The samples were desorbed by a pulsed N_2 laser and detected in both positive and negative modes. The data was calibrated using values in a range from 400 to 1200 amu from the known pigments PB15 (514.54), PB60 (442.42), PG7 (1065.65), PR144 (828.92), PY1 (340.34) and PY138 (693.96), each affixed with PBMA.

Raman spectroscopy

Raman spectra were collected using one of two Renishaw Invia Raman microscopes with a 785 nm laser (1200 L/mm grating). Aluminum foil backing for pigment samples typically increased signal-to-noise. Some samples as were run with gold nanoparticle surface enhancement. The resolution for the two spectrometers was approximately 3 cm^{-1}.

Infrared spectroscopy

FT-IR was performed on a Nicolet iS50 FT-IR in attenuated total reflectance mode from 600 to 4000 cm^{-1}. The spectra were run at 4 cm^{-1} resolution.
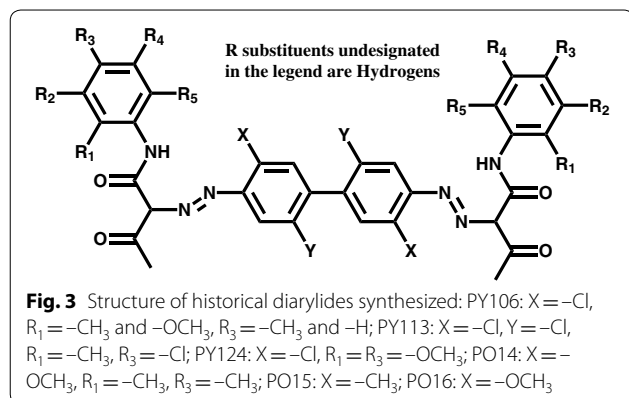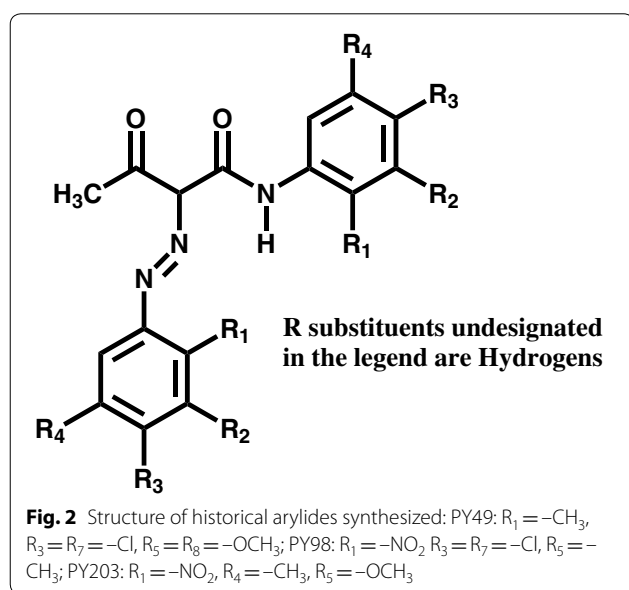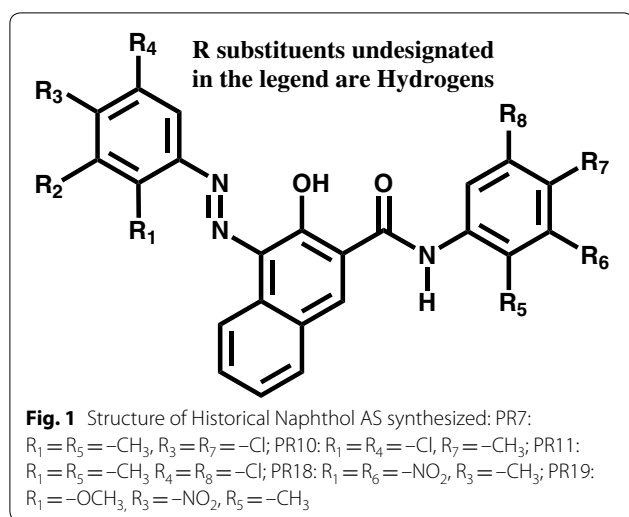
Visible spectroscopy

Visible spectroscopy was performed on solid samples, typically about 10–20 mg, on a JASCO V-670 Spectrophotometer. A solid, white sample provided by the manufacturer was used as a standard and the solid pigment sample was added to the sample cell and scanned from 400 to 800 nm. The data was normalized by assuming the maximum and minimum reflectance were 100% and 0%, respectively. The inflection point was determined graphically based on least squared fits of the trends at lower and higher wavelengths from the rise in reflectance. The bis-(4-methoxy)-substituted Naphthol AS-G had two distinct rises at lower and higher wavelength than the region between 540 and 560 nm. The region between 540 and 560 nm was used for analysis of both of these rises.

Results and discussion

The Colour Index was used as a starting point to determine which synthetic organic pigments were no longer manufactured or are of extremely limited manufacture. Pigments belonging to the azo-containing classes of arylide yellow, Naphthol AS and diarylide yellows and oranges were selected. The synthesis of azo-containing pigments has two synthetic advantages that have been utilized over the years. First, the smaller coupling reactants are often soluble in water. However, we found that for the small scale benchtop reactions necessary to make authentic samples for micro-analysis to compare with samples from works of art, acetonitrile helped keep starting materials in solution until the ultimate coupling reaction could occur. We found for the compounds we synthesized, the amount of acetonitrile did not change the nature of the solution so much that the product dissolved, thereby maintaining one of the defining characteristics of a pigment: its insolubility. Second, not surprisingly, that by coupling through the π-bond of the azo-linkage, the conjugation increased from the colorless to light yellow of the starting materials to the deep color of the pigment product. This, again, made it simple to recognize the reaction and ease the isolation of the product.

The following pigments were synthesized using the diazotization process described above: PR7, PR10, PR11,

Fig. 1 Structure of Historical Naphthol AS synthesized: PR7: $R_1 = R_5 = -CH_3$, $R_3 = R_7 = -Cl$; PR10: $R_1 = R_4 = -Cl$, $R_7 = -CH_3$; PR11: $R_1 = R_5 = -CH_3$ $R_4 = R_8 = -Cl$; PR18: $R_1 = R_6 = -NO_2$, $R_3 = -CH_3$; PR19: $R_1 = -OCH_3$, $R_3 = -NO_2$, $R_5 = -CH_3$

Fig. 2 Structure of historical arylides synthesized: PY49: $R_1 = -CH_3$, $R_3 = R_7 = -Cl$, $R_5 = R_8 = -OCH_3$; PY98: $R_1 = -NO_2$ $R_3 = R_7 = -Cl$, $R_5 = -CH_3$; PY203: $R_1 = -NO_2$, $R_4 = -CH_3$, $R_5 = -OCH_3$

Fig. 3 Structure of historical diarylides synthesized: PY106: $X = -Cl$, $R_1 = -CH_3$ and $-OCH_3$, $R_3 = -CH_3$ and $-H$; PY113: $X = -Cl$, $Y = -Cl$, $R_1 = -CH_3$, $R_3 = -Cl$; PY124: $X = -Cl$, $R_1 = R_3 = -OCH_3$; PO14: $X = -OCH_3$, $R_1 = -CH_3$, $R_3 = -CH_3$; PO15: $X = -CH_3$; PO16: $X = -OCH_3$

PR18, PR19, PO14, PO15, PO16, PY49, PY98, PY106, PY113, PY124 and PY203 [8].

Figure 1 shows the structures of the Naphthol AS pigments synthesized, while Figs. 2 and 3 show the structures of arylide (Hansa) yellow pigments and the diarylide pigments synthesized. Hydrogens fill any undesignated R-groups on the aromatic rings.

The pigments were examined by FTIR, Raman spectroscopy and LDI-MS. FTIR is very useful in the identification of pure pigments but is less useful in identifying these pigments in paints or works of art due to the presence of fillers, which include strongly infrared absorbing materials such as barium sulfate, calcium carbonate and calcium sulfate. Raman spectroscopy is often better suited in the examination of the pigments and is particularly useful for azo containing pigments as the −N=N− bond is polarizable but has no dipole change. In addition, peaks due to the fillers do not interfere with the peaks due to the colorant.

The FTIR spectra in Fig. 4 are the Naphthol AS pigments PR7 and PR11 which are positional isomers, and the spectra are consistent with that of other Naphthol AS pigments. Peaks unassociated with the positional differences are largely unchanged, such as, from highest energy: (a) the secondary amide absorptions at 1675 and 1547 cm^{-1}, (b) the naphthalene C=C absorbs at 1607 cm^{-1}, (c) a weak absorbance at 1400 cm^{-1} due to a trans aromatic azo, and d) the peak at 1360 cm^{-1} due to the naphthalenic ring vibration of naphthol. Peaks associated with differences (PR7 vs. PR11) in the isomers change, such as the C–Cl stretches at 1092 vs. 1075 cm^{-1}. The subtly of infrared spectroscopy is highlighted with the two compounds, which are both 1,2,3-trisubstituted benzenes: PR7: −N, −CH$_3$, −Cl; PR11: −CH$_3$, −N, −Cl. PR7 has peaks due to this substitution pattern at 866, 809 and 748 cm^{-1} while PR11 has peaks in the same region at 864 (more intense), 796 and a doublet at 760 and 745 cm^{-1}.

Figure 5 shows the Raman spectrum of the typical arylide yellow, PY203. Arylide yellows such as PY49, PY98 and PY203 have amide bands around 1250–1260 cm^{-1}, with a weaker amide band between 1660 and 1670 cm^{-1}. This class often has an absorbance at 1140 cm^{-1} due to the C-N stretching vibration, though it can be absent in some of these pigments. There is an absorbance just below 1400 cm^{-1} due to a trans aromatic azo. The OCH$_3$ stretch is found at 1330 cm^{-1} and the Ar–Cl peaks are found at 1090 and 670 cm^{-1}.

The Raman spectrum of the diarylide orange pigment PO15 is shown in Fig. 6. The strong aromatic ring vibration is found at 1608 cm^{-1} due to the biphenyl and this is the predominant peak in the Raman spectra of diarylide pigments. Due to the structure of the molecule, this band
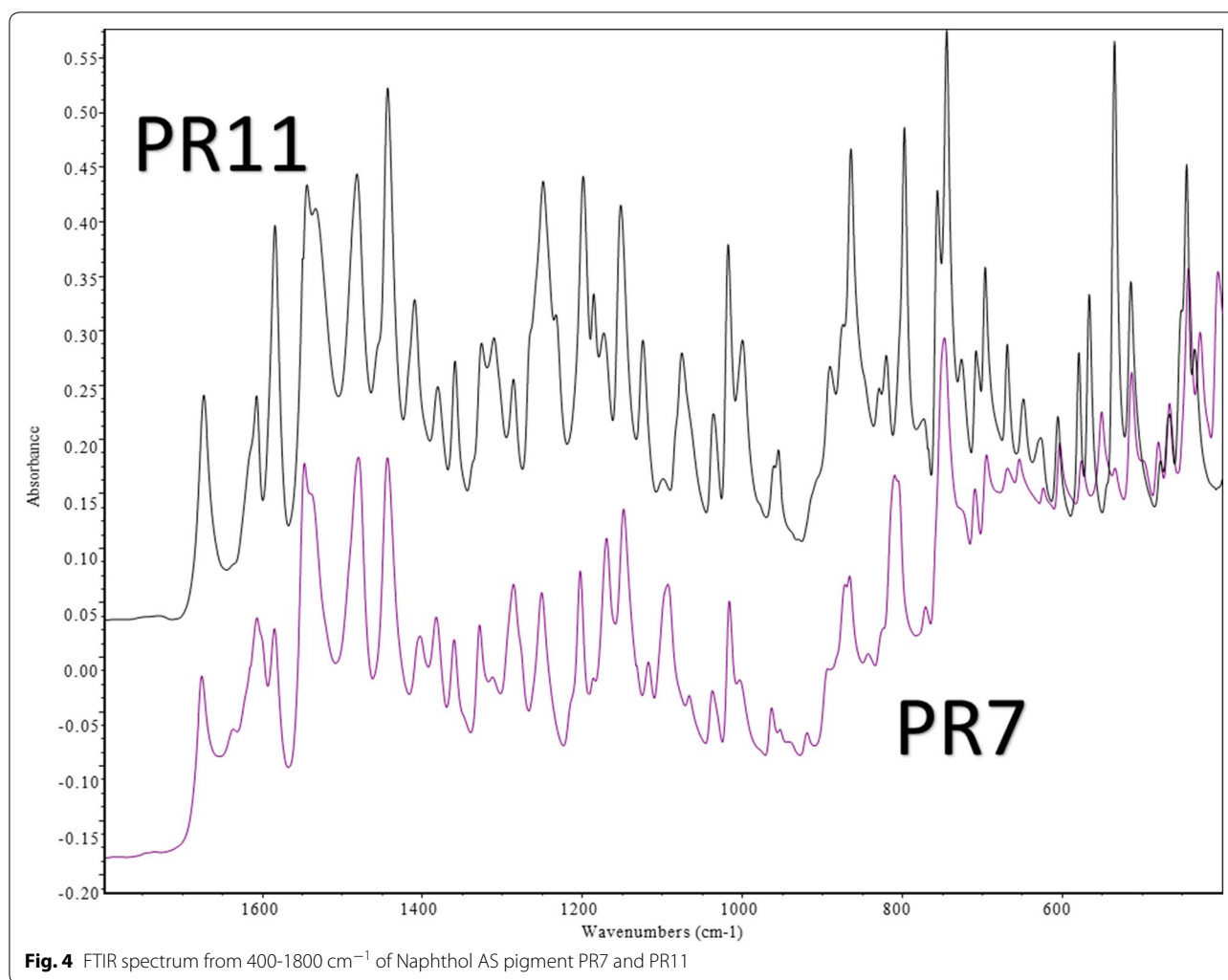
Fig. 4 FTIR spectrum from 400-1800 cm^{-1} of Naphthol AS pigment PR7 and PR11

is infrared inactive due to symmetry considerations [9]. The peak at 1389 cm^{-1} is due to the symmetric –N=N– stretch, the peak at 1309 cm^{-1} is also due to the symmetric stretching vibration of the azo group. The peak at 1269 cm^{-1} is due to the C–H bending vibration, and the peak at 1117 cm^{-1} is due to the C–N stretch.

LDI MS provides complementary information to the vibrational spectroscopy. In general, negative ion mode produced the molecular ion M$^-$ or (M–H)$^-$ with little fragmentation, while positive ion mode provided more fragmentation information [10].

The LDI-MS spectrum of PY124 (negative ion mode) is shown in Fig. 7. Three clusters of masses, each due to the presence of the chlorine substituents, are obvious. The molecule is dichlorinated, and chlorine atoms have two isotopes (natural abundance Cl-35, 75.53% and Cl-37, 24.47%). An LDI ion is produced from the molecule with specific isotopes and gives rise to a cluster of the molecular ion or fragments, rather than a single peak

representing the weighted average. Additionally, due to the high molecular weight of the pigment, the contributions from less abundant isotopes, such as C-13 and N-15 are significant. The clusters shown as insets above the main pattern are found at 749 amu, 497 amu and 256 amu and correspond to the molecular ion along with two fragmentations. Overlaid on top of the clusters are line-patterns derived from ChemDraw™ of the percent relative abundances for each m/z for these molecular ion and fragments. They correlate nicely with the observed isotope pattern of the LDI-MS. The other clusters in the overall spectrum represent fragmentation between the two nitrogen on one of the diazo linkages. Since azo pigments exist in a hydrazone (–NH–N=) tautomer, this can be envisaged by cleavage of a N–N single bond and is a common fragmentation pattern for azo pigments.

In preparation for investigation of substituent-effects on extended conjugated pigment systems in SOP's, we report on the synthesis a series of azo pigments based on
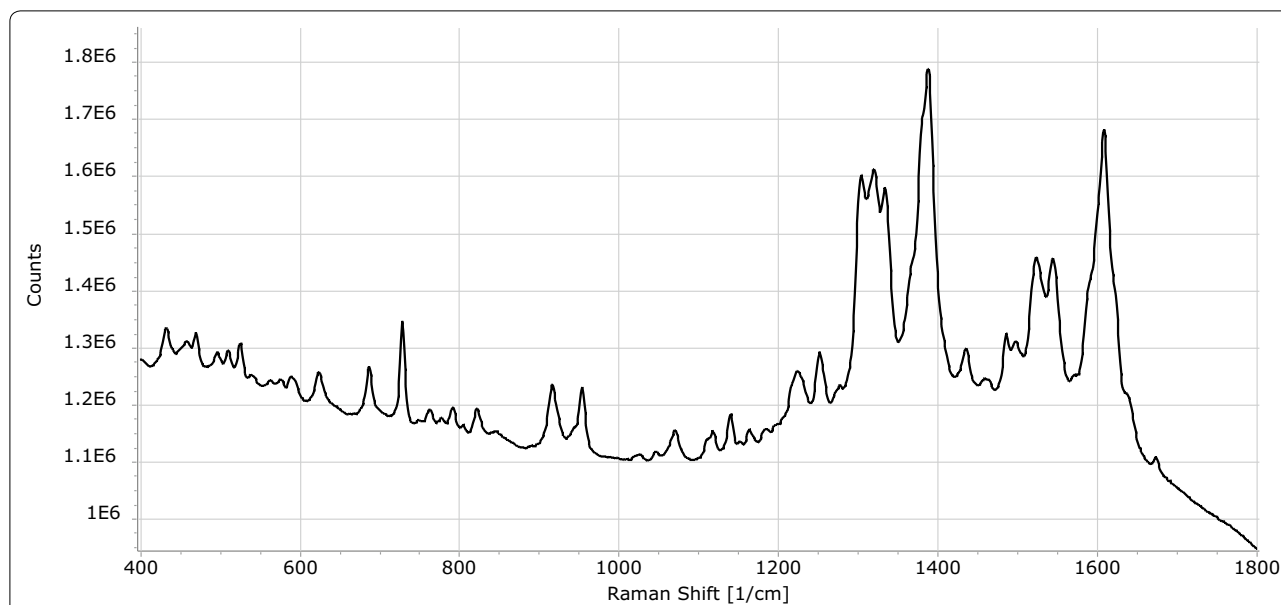
Fig. 5 Raman spectrum of arylide yellow PY203. Peak positions (cm^{-1}): 1673, 1608 (s), 1544 (m), 1523 (m), 1498, 1486, 1459, 1435, 1387 (vs), 1335 (m), 1319 (m), 1304 (m), 1251, 1223, 1183, 1163, 1140, 1117, 1070, 1045, 1026, 953 (m), 916 (m), 846, 822, 791, 762, 728 (m), 686, 623, 588, 574, 525, 509, 496, 469, 457, 431, 402
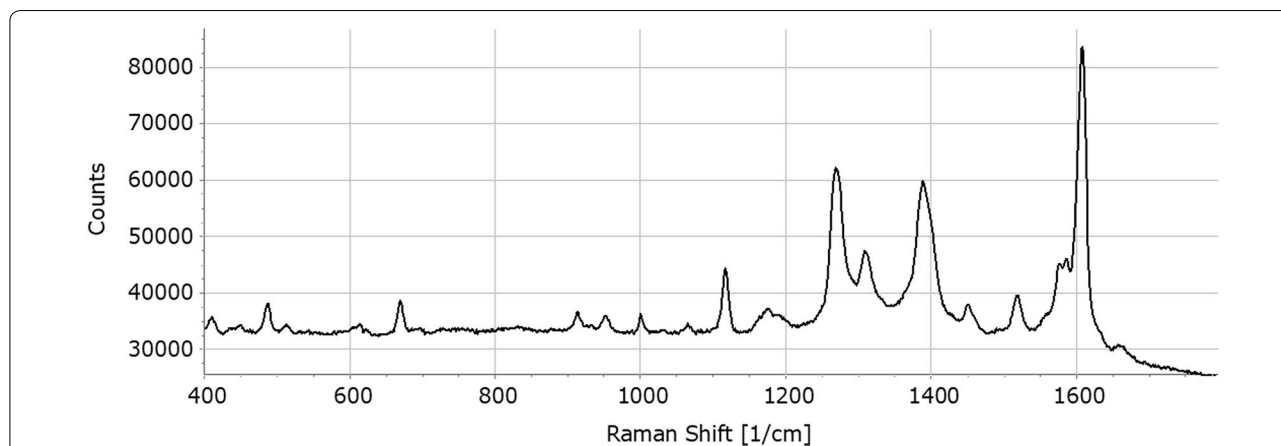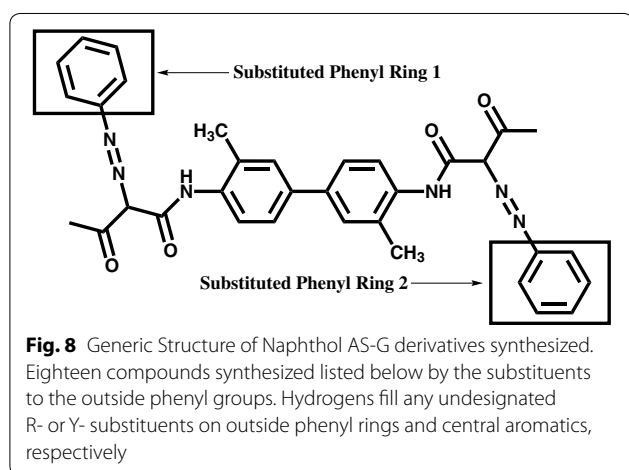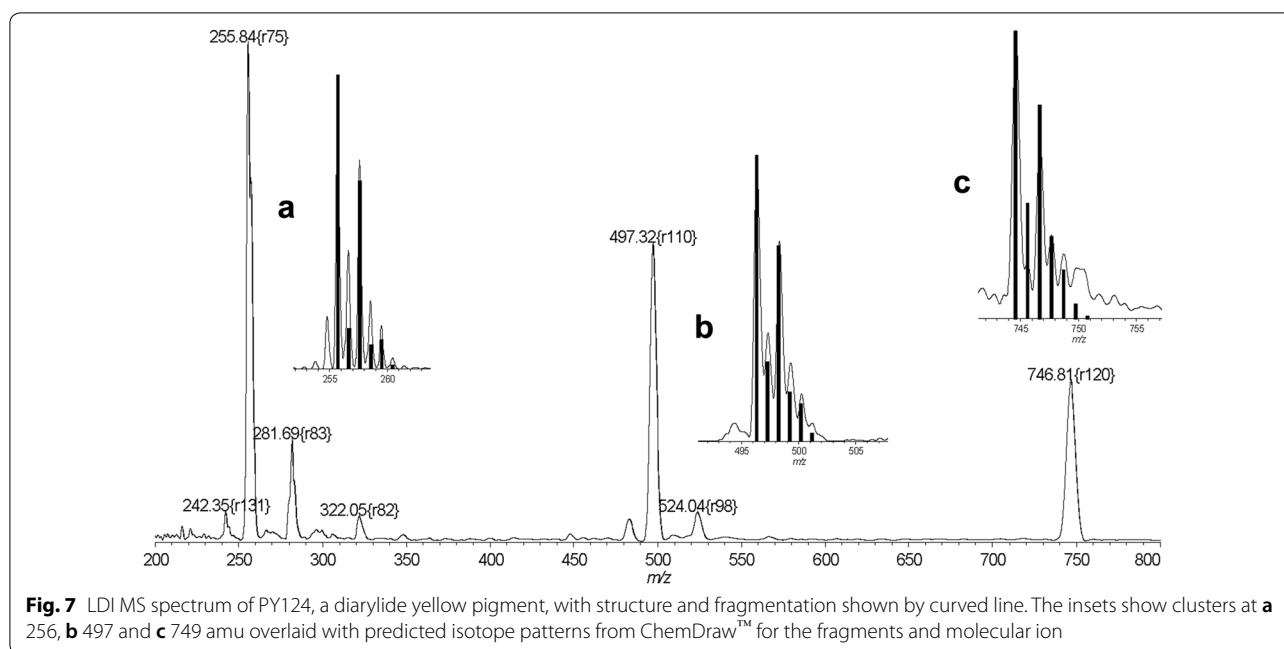

Fig. 6 Raman spectrum of the diarylide orange PO15. Peak positions (cm^{-1}): PO15: 1652, 1604 (vs), 1573, 1516, 1448, 1387, 1305 (m), 1270 (s), 1174, 1115 (m), 1064, 999, 951, 912, 694, 669, 613, 487, 436, 411

Naphthol AS-G (*N,N′*-bis(acetoacetyl)-*o*-toluidine) (see Fig. 8). Curiously, despite the name of this molecule, it does not possess a naphthol group, but rather a biphenyl structure similar to that found in diarylide pigments. It is a "Naphthol AS" in the sense that it is used like the amide substituted β-naphthol as coupling partners in the preparation of some azo dyes. Naphthol AS-G can easily react with diazonium salts prepared by substituted anilines at its two functional sites at the acidic carbons between pairs of acetoacetyl-carbonyls. We found by using two substituted anilines, 2-nitroaniline and 2-methyl-5-chloroaniline Naphthol AS-G can be reacted sequentially by

two different diazonium salts (shown as A and B in the reaction scheme in Fig. 9) in sequence to form exclusively the mixed product.

Because of the ease of synthesis of mixed and bis-substituted Naphthol AS-G pigments, we were able to make 15 more different and new products with the Naphthol AS-G and only five additional substituted anilines, leading to the synthesis of 18 total products. The anilines used to create the diazo-salt reactants were: 3-aminobenzonitrile, *p*-anisidine, 2,5-dichloroaniline, 2,4-dinitroaniline and 4-(trifluoromethyl)aniline, and all combinations made, also, are listed in Table 1. With these compounds
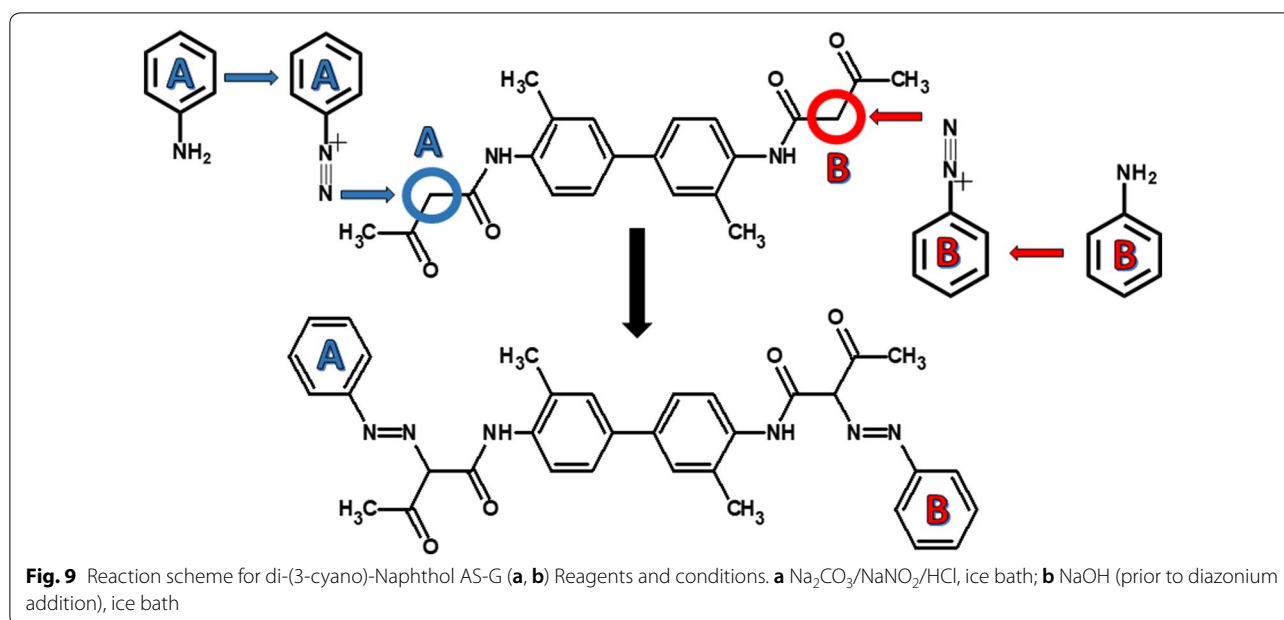
Fig. 7 LDI MS spectrum of PY124, a diarylide yellow pigment, with structure and fragmentation shown by curved line. The insets show clusters at **a** 256, **b** 497 and **c** 749 amu overlaid with predicted isotope patterns from ChemDraw™ for the fragments and molecular ion

Fig. 8 Generic Structure of Naphthol AS-G derivatives synthesized. Eighteen compounds synthesized listed below by the substituents to the outside phenyl groups. Hydrogens fill any undesignated R- or Y- substituents on outside phenyl rings and central aromatics, respectively

we were systematically able to investigate the effects of electron-donating and electron-withdrawing (σ and π) substituents on the spectral properties of pigments.

Each of these pigments synthesized was examined by FTIR, Raman, reflectance visible spectroscopy and LDI-MS spectrometry. The FTIR spectra of reaction products of Naphthol AS-G with five substituted anilines (2,5-dichloro, 2,4-di-nitro, 4-methoxy, 3-cyano, 4-trifluoromethyl) are presented in Additional file 1. The FTIR spectra have a number of peaks consistent with the Naphthol AS-G moiety, including 1717 cm^{-1} (carbonyl), 1652 and 1526 (amide), 1484–1490 (aromatic), and 818, 804 and 679 cm^{-1} (substituted aromatic). All of the cyano-containing pigments (that is those using 3-aminobenzonitrile as a starting material) have a strong absorption between

2229 and 2231 cm^{-1}. The methoxy-containing pigments have the expected C–O–C absorbance between 1243 and 1248 cm^{-1}, chloro-substituted pigments have a peak at 623 cm^{-1} and nitro-substituted pigments have an absorbance at 1350 cm^{-1}. The 4-trifluoromethyl-substituted colorants have two absorbances, one at 1064 and one at 1109 cm^{-1}. The Raman spectral features, also, are consistent with the structures. The spectra of the methoxy-substituted products were difficult to obtain because of excessive fluorescence, although, spectra collected in the presence of gold nanoparticles reduce the fluorescence and increased the Raman scattering.

LDI-MS proved very useful in the confirmation of structures of these additional pigments synthesized, particularly for the chloro- vs. fluoro-substituted pigments. Their known isotopic pattern helped in distinguishing pigments with one CF$_3$ substituent (formula mass ^{12}C(^{19}F)$_3$: 69 amu) compared to a di-chloro substituted (^{35}Cl^{35}Cl: 70 amu; ^{35}Cl^{37}Cl: 72 amu; ^{37}Cl^{37}Cl: 74 amu), as shown in Fig. 10. Often masses of parent ions in LDI-MS are different by 1–3 amu because the large molecules pick up or lose a hydrogen or two after ionization. Though one might suspect that this uncertainty would make the three pigment ion masses indistinguishable, because of the resolution of LDI-MS, the fragment ratios guide us to a clear interpretation.

The ease of synthesis of a series of pigments with a wide variety of aromatic substituents (alkyls, halides, nitro, alkoxy, cyano) in a variety of positions on the phenyl ring allows us to observe their effect on color via reflectance spectra, a fundamental question of pigment synthesis.

Fig. 9 Reaction scheme for di-(3-cyano)-Naphthol AS-G (**a**, **b**) Reagents and conditions. **a** $Na_2CO_3/NaNO_2/HCl$, ice bath; **b** NaOH (prior to diazonium addition), ice bath

Table 1 Substituents to the diazo salts reacted with Naphthol AS-G

Substituent 2	Substituent 1						
	2-NO$_2$–	2-CH$_3$, 5-Cl-	2,5-di-Cl	2,4-di-NO$_2$	4-OCH$_3$	3-CN	4-CF$_3$
2-NO$_2$–	X						
2-CH$_3$, 5-Cl-	X	X					
2,5-di-Cl			X				
2,4-di-NO$_2$			X	X			
4-OCH$_3$			X	X	X		
3-CN			X	X	X	X	
4-CF$_3$			X	X	X	X	X

Over the years a number of empirical attempts have been made to rationalize and quantify the substituent effect, most well-known are the Woodward Fieser rules [11–13]. However, these do not include –N=N– (azo) linkages, and all deal with determining the peak in the ultraviolet–visible spectroscopy, not an edge (vide supra). SOP's are large conjugated systems, and even a series of SOP's with the same central structure can be expected to have many and varied frontier orbitals that will change energies depending upon the nature and position of the electron-donating, electron-withdrawing and/or lone-pair containing substituents.

Visible Reflectance Spectroscopy was performed on the solid mixed- and bis-substituted Naphthol AS-G pigments products. Most compounds have one dominant edge where the blue end of the visible fully absorbs and the red end fully transmits giving the characteristic yellow through orange color of the pigments which is reminiscent of a band edge of a semiconductor. Clearly, these SOP's do not have a large enough density of states in the π-orbital derived HOMO's and LUMO's to be considered semiconductors, but the electronic transitions between these orbital sets are found in the visible spectral region. The wavelength at the inflection point is plotted versus the Hammett σ-parameter (which increases with increasing electron-withdrawing), and this plot is show in Fig. 11. The average of Hammett σ-parameters is plotted with mixed substituents. The wavelength at the inflection point of those ten compounds that do not contain the methoxy-substituted compound generally goes down as the electron withdrawing ability of the substituent increases (least squares fit of this data in blue). That would mean that the difference in energy between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) increases with increasing electron withdrawing substituents.
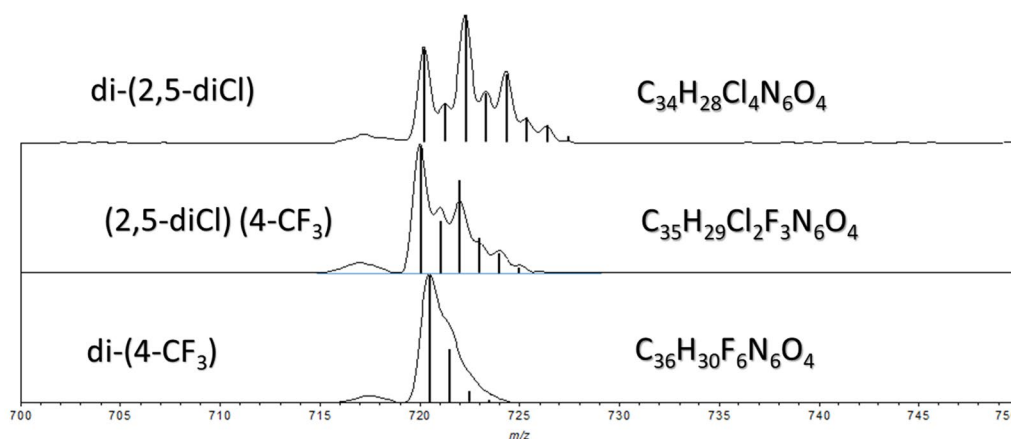
Fig. 10 LDI-MS of the parent peaks of di-(2,5-dichloro)-Naphthol AS-G, di-(2,5-dichloro)- (4-trifluoromethyl)-Naphthol AS-G and di-(4-trifluoromethyl)-Naphthol AS-G di-Cl. Molecular formulas used for determination of intensity overlays are given to the right of each spectrum

The trend of energies for the wavelength at the inflection point versus Hammett parameter is not so straightforward with methoxy-substituted compounds. Figure 12 shows an overlay of the visible reflectance vs. wavelength spectra of all five compounds that include a methoxy-substituent. As with the ten spectra mentioned above, the three spectra of the mixed-substituted compounds with the 4-methoxy and the three most electron withdrawing (2,4-dinitro-, 4-trifluoromethyl- and 3-cyano-) substituents look fairly conventional. They absorb in the blue and reflect in the red, though shifted to much lower wavelength (higher energy). Assuming an influence of the 4-methoxy, the band
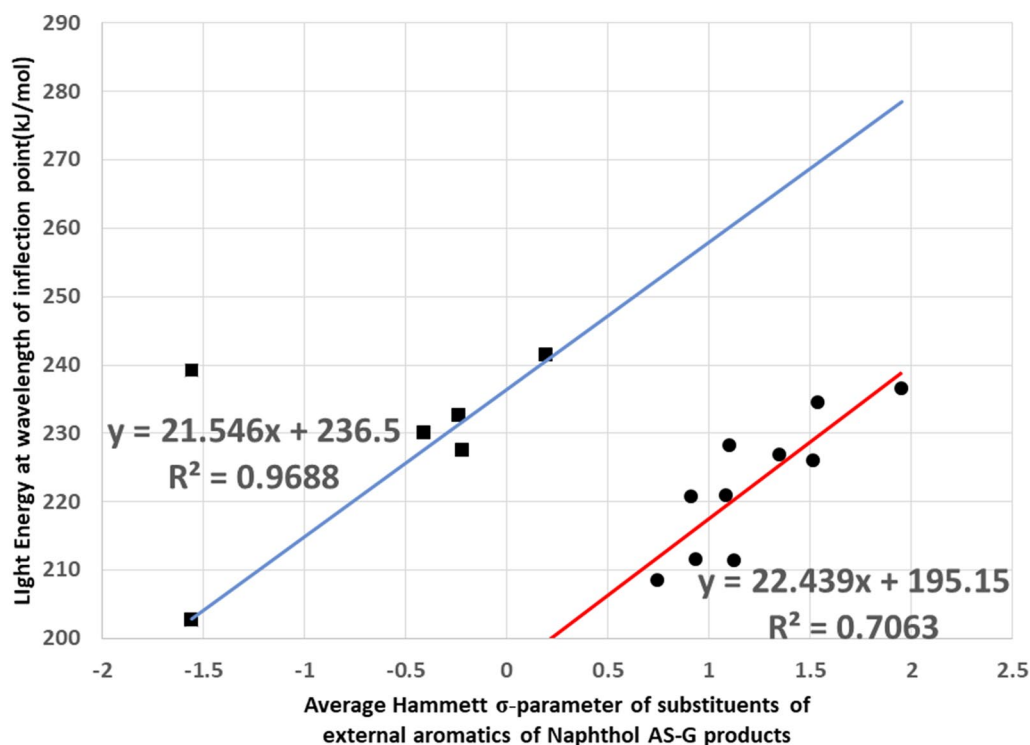

Fig. 11 Plot of the energy of light at inflection point of the spectrum versus Hammett parameter. The compounds are di-substituted Naphthol AS-G diazo-reaction products. The Hammett parameters are averages of the parameters for the substituents of the external aromatic rings. The least squares best fit lines are A-methoxy substituted, and B-substituents without methoxy substituents

edge is shifted about 40 kJ/mol energy higher than those without methoxy-substitution (red line in Fig. 11). However, the spectra of the two compounds with π-donors substituents on external rings are anomalous. First, the rise is not a single "band edge", but there seems to be at least two features in each. The bis-methoxy-substituted compound has two distinct edges (inflection points at 500 and 590 nm). The 2,4-dichloro-/methoxy- substituted product has inflection at 520 nm and its reflectance rise seems to start about 710 nm and does not seem to be complete by the highest wavelength measured.

Changes in the absorbance in the visible light region typically have to do with electronic transitions between frontier orbitals, often between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Similar behavior in the reflectance may be indicative of a similar source of the HOMO and LUMO along with shifts caused by the effect of the substituent's electron withdrawing or donating behavior on them. One might speculate that this might be happening with the compounds that do not have a methoxy substituent. However, we are not able to speculate whether the rise in energy with increasing electron withdrawing in the substituent is due to a lowering of energy of the HOMO, raising of energy of the LUMO or both.

Changes associated with methoxy substitution are too complicated to allow for any speculation without a molecular orbital treatment [14]. It is fair to say that it has to do with additional complications to the π-system because of increasing π-donation (di-chloro < methoxy), but further insight must wait for additional work which we hope to pursue in the future.

Conclusions

Since their introduction, the visual impact and ease of production of SOP's have made them popular additions to the palette of artists, even supplanting many mineral and plant-based colorants. However, due to the hundreds of synthetic organic pigments that can have been used, identification of them in works of art can prove challenging. They are structurally similar, and because of their high tinting strength, fillers and extenders are used along with a much smaller amount of the actual pigment. A further complication is the fact that a number of these pigments have been removed from commercial production so that standards may not be available for characterization. These historical pigments, precisely because of their limited commercial history, can inform the art history of a piece.
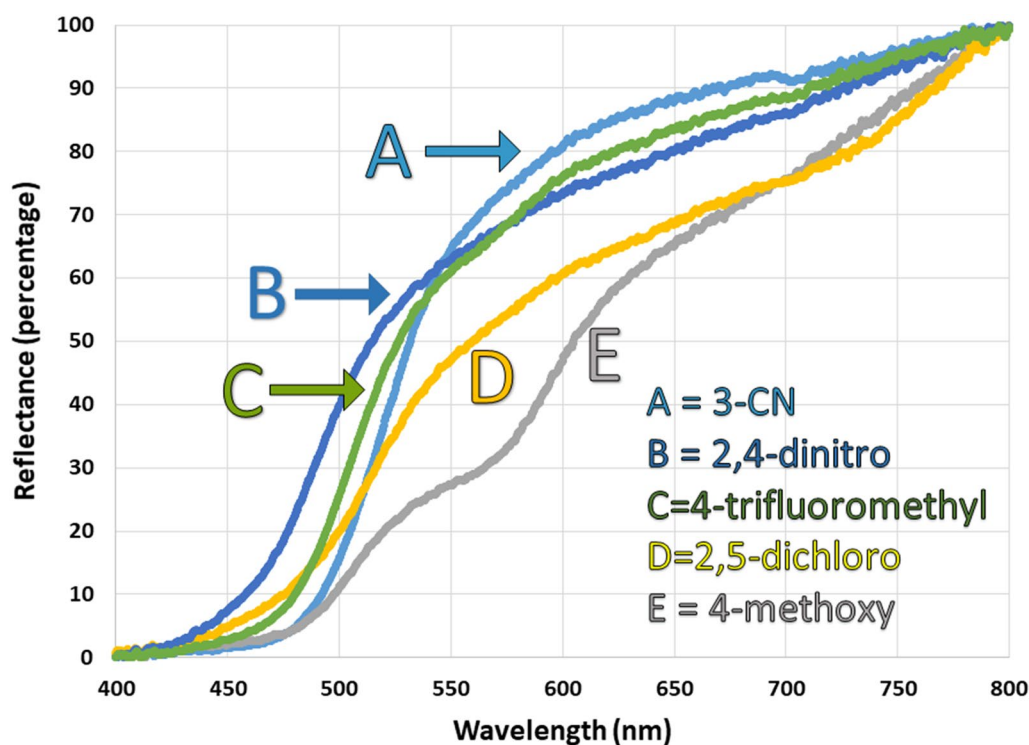

Fig. 12 Plot of visible reflectance for di-substituted Naphthol AS-G diazo-reaction products. Substitution: A 4-methoxy-/3-CN-; B 4-methoxy-/2,4-dinitro-; C 4-methoxy-/4-trifluoromethyl-; D 4-methoxy-/2,4-dichloro-; E bis-(4-methoxy-)

In this project, a number of synthetic organic pigments were synthesized based on their lack of suppliers in the colour index. All the pigment syntheses were carried out by classic diazotization reactions. The colour indexed compounds are represented by the arylide (Hansa) yellow, Naphthol AS and diarylide yellow and oranges classes. Additionally, the diazotization reaction was used to create 18 colorants based on Naphthol AS-G. Reaction of diazonium salts generated from various anilines with this coupling component produced homo and hetero bisazo compounds. While not cataloged Colour Index pigments, nor intended to be as such, these pigments serve as model compounds to explore the effects of various substituents on the visible spectra of pigments. Initial results were presented, which in the case of the methoxy substituted colorants, led to more questions than answers.

The vibrational spectroscopy techniques of Raman and FTIR are particularly complementary with pigments and dyes. They probe, respectively, (a) the highly polarizable and conjugated π-system and (b) the dipoles of the oxygen, nitrogen and halide containing bonds with carbon and hydrogen. LDI-MS is very useful in proving that a coupling has occurred and, somewhat that the isolated product is reasonably pure. The two classes, vibrational spectroscopy and mass spectrometry, probe different aspects of the pigment—vibrational the complicated bonding system and mass spectrometry the mass of the molecule and its fragments—thus, they are excellent complementary editors to an assertion, and thereby can be used in concert to unambiguously identify historical and novel pigments. Now, with authentic samples characterized by modern micro-analytical techniques, compounds and spectra are available for comparisons to those historical pigments that might be present in works of art.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s40494-019-0343-1.

> **Additional file 1.** The FTIR spectra of reaction products of Naphthol AS-G with five substituted anilines (2,5-di-chloro, 2,4-di-nitro, 4-methoxy, 3-cyano, 4-trifluoromethyl).

Abbreviations
Ar: aryl; amu: atomic mass unit; FTIR: Fourier transform infrared spectroscopy; HOMO: highest occupied molecular orbital; LDI-MS: laser desorption ionization mass spectrometry; LUMO: lowest unoccupied molecular orbital; m/z: mass to charge; SOP: synthetic organic pigment.

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