International Conference
NEW PERSPECTIVES in SCIENCE EDUCATION

New Perspectives on Old Dyes: The Electro-organic Synthesis of Aniline Black

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Abstract

Aniline black (polyaniline) is one of the oldest, if not the oldest, synthetic dyes, produced since 1834 through the oxidation and polymerization of aniline [1]. Aniline black was initially used for dyeing cotton and for lacquering, but is still of interest today as it may be used in the construction of batteries and as a medium for energy storage [2].
This makes aniline black a polymer that is both historically and chemically interesting, but one that has rarely been used in school lessons due to safety concerns:
The handling of aniline itself is not the primary concern, as it can be used in schools under controlled conditions, such as in a fume hood and with appropriate protective equipment. However, the oxidizing agents such as potassium chromate or potassium dichromate, which are needed to oxidize the aniline, are much more dangerous. These oxidizing agents are highly toxic, mutagenic and carcinogenic and therefore strictly prohibited in schools.
To make chemical and industrial processes safer, to reduce the need of dangerous chemicals, and to thereby achieve a more sustainable chemistry, electrochemical alternatives have been increasingly developed in recent decades [3]. This means that dangerous oxidizing or reducing agents can often be fully replaced by electrical current.
In this contribution, we present simple school experiments to produce aniline black from aniline electrochemically. The oxidation process shows good results even at room temperature and using simple carbon electrodes, enabling an interesting and unexpected link between organic chemistry and electrochemistry. The experiments can also be used to discuss organic catalysis: nitrate is added as a catalyst, is oxidized at the electrode to a nitrate radical, and subsequently reacts with aniline, causing the oxidation and polymerization. Nitrate thus acts as a catalyst in an electrochemical reaction (a so-called mediator) – a phenomenon that is usually only known from non-electrochemical experiments.
We also present the electrochemical generation of polymethylpyrrole from n-methylpyrrole as an even safer alternative. Unlike aniline, methylpyrrole can be used in schools without any safety precautions and it reacts in the same way as aniline to form a black polymer. The use of nitrate as a catalyzing mediator can also be easily demonstrated in this experiment.
These new, safe experiments open up opportunities for students to investigate historic synthetic dyes while also engaging with modern, sustainable synthesis methods.

Keywords: *Aniline black, synthetic dyes, electrochemical oxidation, mediators, sustainable electrochemistry*

1. Introduction

Colors and visual impressions are among the first phenomena consciously perceived in childhood. From an early age, learners encounter a wide range of color experiences in everyday contexts, e.g. when drawing and painting, through clothing, or when observing the natural environment. These experiences evoke curiosity, emotions, and aesthetic interest. Because colors are so immediate and tangible, they are a particularly suitable topic for science education.
From an educational perspective, dyes offer an easy entry point to central chemical concepts, including material properties and substance classes, structure-property relationships, and reaction mechanisms underlying dye synthesis [4]. At the same time, they enable hands-on, inquiry-based, and experimental learning environments that foster motivation and support sustainable understanding. Synthesizing dyes can also connect historical and cultural developments with modern chemistry.
While certain dyes (such as indigo, colored coordination complexes, and acid-base indicators) are already well-established in schools, the systematic exploration of the color black often remains marginal. Yet, black offers a particularly rich opportunity to explore fundamental concepts in physics and chemistry.

In physical terms, black is not a spectral color of visible light. Rather, a material is perceived as black when it absorbs most of the light that strikes it. Whereas colored substances absorb certain wavelengths and reflect others, black materials absorb broadly across the visible spectrum, reflecting very little light back to the observer.
Black materials play an important role in technological applications, e. g. to minimize reflections in optical instruments or to create solar absorbers for photothermal processes [5]. Beyond science and technology, black is ubiquitous in everyday objects, fashion, and art, where it can signal elegance, simplicity, or mourning, depending on context. These intersections of physical, chemical, technological, and cultural meanings offer versatile possibilities for science teaching.
Colors can also be linked to sustainability and Green Chemistry, especially to the criteria of waste prevention, less hazardous chemical synthesis, or energy efficiency [6]. The production of many synthetic dyes requires a lot of energy and raw materials, can generate hazardous by-products, and often involves the use of toxic chemicals during manufacturing. In response, researchers are increasingly exploring alternative synthetic routes that rely on renewable feedstocks or employ novel reaction pathways [7]. These approaches can be directly used in schools to exemplify the transition towards a more sustainable chemistry.
Unfortunately, color and dyes receive only limited attention in many science curricula [4]. Where included, colors are often only described as a simple material property. This makes it all the more important to design simple experiments that connect color to broader scientific concepts, such as organic reaction mechanisms, electrochemistry, or Green Chemistry. The experiments presented in this article aim to contribute to this goal by focusing on the color black as a unifying theme.

2. Historical Background

Throughout human history, a wide range of techniques and colorants from diverse sources have been used to dye textiles and other materials. Plant-based dyes, in particular, have been employed for millennia across many cultures. Prominent examples include indigo, henna and turmeric. In addition, readily available materials such as onion skins, walnut husks, marigold, and charcoal have served as important dyes and pigments, providing a wide spectrum of yellows, reds, blues, and browns. [8] However, they often show limited resistance to light and washing and therefore tend to fade over time. Achieving a deep, saturated black with plant-based dyes alone proved particularly challenging and typically required mixing several colorants.
To obtain more intense black tones, dyers frequently turned to animal sources. These included bone black (produced from charred animal bones) and the ink of squids. [8] Iron gall ink, formed by the complexation of iron(II) salts with gallotannins, became especially important in Europe from the early Middle Ages onward. It produced a deep, durable black color, but has the well-known drawback of being chemically aggressive, often leading to the long-term degradation of paper. Producing a deep black color was therefore long considered a difficult and specialized craft.
This changed in the early 19th century with the discovery of aniline and the development of the first aniline-based synthetic dyes. In 1834, Friedlieb Ferdinand Runge isolated aniline from coal tar and observed that it reacted with dichromate and hydrochloric acid to form an intense green to black material [9]. Although this finding did not immediately lead to industrial applications, it is regarded as the first synthesis of polyaniline, later known as aniline black. [1] [9]
Over the following decades, numerous aniline derivatives were discovered. William Henry Perkin played a particularly prominent role in this development. In 1856, he discovered the oxidation of aniline that yielded mauveine (aniline purple), widely considered the first commercially successful synthetic dye. [8]
In the 1860s, improved synthetic procedures also enabled the reliable production of aniline black on textile fibers, leading to a series of patents and rapid industrial adoption. In the late 19th and early 20th centuries, aniline black was widely used to dye cotton fabrics, including mourning attire, and it also found application in hair dyes. From the 1930s onward, however, aniline dyes gradually lost prominence due to concerns about toxic aniline residues in finished products and to the emergence of new classes of synthetic dyes. [1]

3. Properties of Aniline Black

Aniline black is not a pure substance but rather a mixture of various aniline-based polymers (Polyaniline, PA) [9]. A defining feature of polymers is their construction from identical or structurally similar repeating units, known as monomers. In the case of PA, the monomer is aniline, an aromatic amine consisting of a phenyl group bonded to an amino group (cf. figure 1).

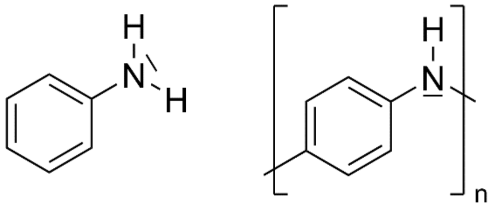

Fig. 1 Structures of Aniline (left) and Polyaniline (right).

Since the discovery of aniline black, numerous synthetic routes for producing this dye have been developed. However, the precise chain-growth mechanisms and structures of the resulting polymer mixture are still not fully resolved. It has been demonstrated that the structures formed also depend on the synthesis method and reaction conditions [9]. The research on aniline black therefore also reflects the ambiguity and evolving nature of science.

PA is typically encountered in the form of the deep green emeraldine salt. This form is half-oxidized and can be reduced to leucoemeraldine or oxidized to pernigraniline (Fig. 2). These three oxidation states may exist either as protonated salts or as their corresponding base forms, which significantly influence their properties, including color and electrical conductivity [9] [10]. The distinct redox states of PA give rise to a broad spectrum of applications, and accordingly PA has been investigated as a material in energy storage systems, sensors, optical and electrochromic devices, coatings and solar cells [9]. This broad range of uses has established PA as one of the most extensively studied conducting polymers in recent decades [9].

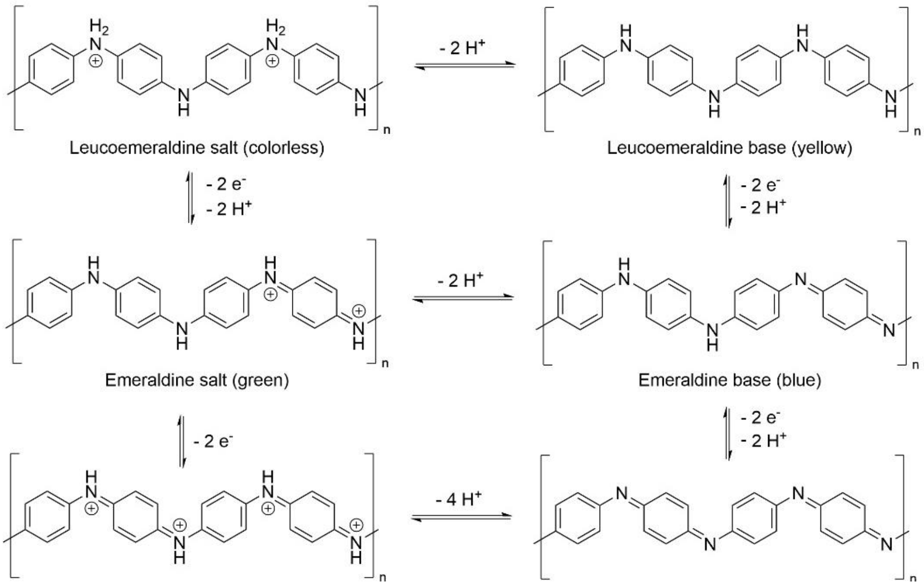

Fig. 2 Common structures and oxidation states of PA.

4. Preparation of Aniline Black

A variety of synthetic routes are available for the preparation of aniline black. Classical reactions typically employ dichromates or potassium chlorate as oxidizing agents for aniline salts, usually with metal salts serving as catalysts [9].

A simple procedure – yet not permitted in schools – for the synthesis of PA, for example, involves boiling a mixture of 0.4 mL of aniline, 0.5 g of potassium dichromate, and 0.1 g of copper sulfate in 50 mL of water acidified with hydrochloric acid for approximately five minutes. If a cotton cloth is placed in the solution during the reaction, its color will turn deep black (Fig. 3).

Fig. 3 Classically prepared PA and a cotton cloth dyed with PA.

The formation of aniline black from aniline follows a radical and oxidative polymerization mechanism (Fig. 4) [9] [11]. As with radical polymerization, the first step is to form a radical through the oxidation of aniline. Two radicals then react to form a dimer. The dimers are oxidized again into radicals by the oxidizing agent, allowing the chain to continue to grow. Therefore, once the oxidizing agent is depleted, polymerization stops. This mechanistic pathway is of particular educational relevance, as electron transfer reactions, radical formation, and polymerization are core topics in chemistry education, particularly at the upper secondary school level.

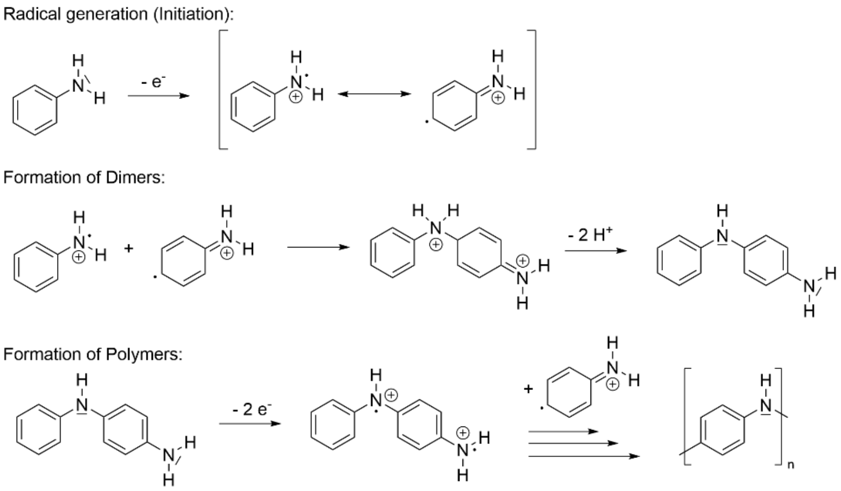

Fig. 4 Generally accepted mechanism of the oxidation of Aniline to PA.

However, the oxidizing agents used in the classical synthesis are highly toxic, hazardous to the environment, and often carcinogenic, making them unsuitable for schools. Due to these hazards, alternative reaction pathways are also being pursued in industrial contexts.

A particularly promising approach is the electrochemical synthesis of aniline black, which entirely avoids the use of chemical oxidants and instead relies solely on electrical energy, ideally generated from fully sustainable sources.

In the electrochemical alternative, radical formation does not occur through an oxidizing agent, but directly at the anode through an electron transfer process (Fig. 5) [9]. The following polymerization mechanism remains analogous to the classical polymerization shown in Fig. 4.

Electrochemical polymerization can also easily be carried out in school experiments using commercially available graphite foil electrodes. Electrolysis may be performed either directly in aniline or with added nitrate serving as a catalyst for the reaction. In this case, nitrate is oxidized at the electrode to form a nitrate radical, which then reacts with aniline [3] [12]. Nitrate is therefore a charge carrier between the electrode surface and the reactant, which is why it is also referred to as a mediator [3].

The role of nitrate illustrates the function of a catalyst particularly well in this reaction: it participates in the reaction and accelerates it, it is transformed during the reaction, but is ultimately converted back to nitrate again.

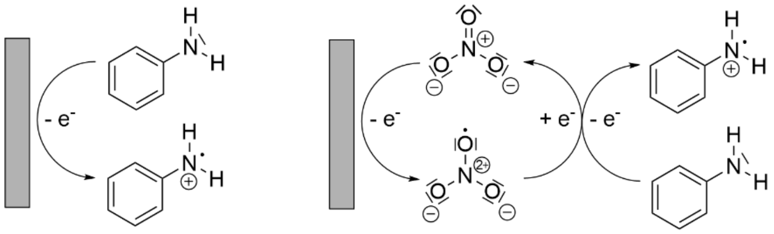

Fig. 5 Radical generation directly on the electrode surface (left) or via nitrate as a mediator (right).

If the aim is to demonstrate electrochemical radical formation and subsequent polymerization in schools while avoiding the use of aniline, a straightforward substitution is easily possible:
Pyrrole is structurally quite similar to aniline and can likewise undergo polymerization to form polypyrrole, a conductive black polymer. Although pyrrole is less hazardous than aniline, it remains toxic. Consequently, methylpyrrole may be employed as an even safer alternative. In this case, electrochemical polymerization produces polymethylpyrrole, observable as a characteristic color change to a dark bluish black in the vessel. [13]
Given the technological relevance of polypyrrole as a conductive polymer in electrical engineering [13], this alternative experiment is also a great opportunity to integrate fundamental chemical concepts into a technology- and sustainability-oriented teaching context.

5. Experiments

5.1 Experiment 1: Electrochemical Synthesis of Aniline Black

Chemicals: Acetonitrile (GHS03, GHS07), aniline (GHS05, GHS06, GHS07, GHS09), silver nitrate (GHS03, GHS05, GHS09) or ammonium nitrate (GHS03, GHS07)
Materials: Power source, 2 cables, alligator clips, 2 graphite foil electrodes, U-tube, spatula, glass rod, pipettes

The experiment must be carried out in a fume hood and with protective gloves!
Each graphite foil electrode is attached to a cable using an alligator clip and connected to a power supply. The electrodes are then positioned such that one electrode extends into each arm of the U-tube.
0.5 mL of aniline are then added to 40 mL of acetonitrile. Then add about 1 g of silver nitrate or ammonium nitrate to the solution and stir carefully. Pour this solution into the U-tube and immerse the electrodes in it. Caution: Do not immerse the alligator clip in the solution!
Turn on the power supply and electrolyze at approximately 7 V for a few minutes.
During electrolysis, a deep brown to black color spreads out from the anode (Figure 6). This can be attributed to the polymerization of aniline to PA.

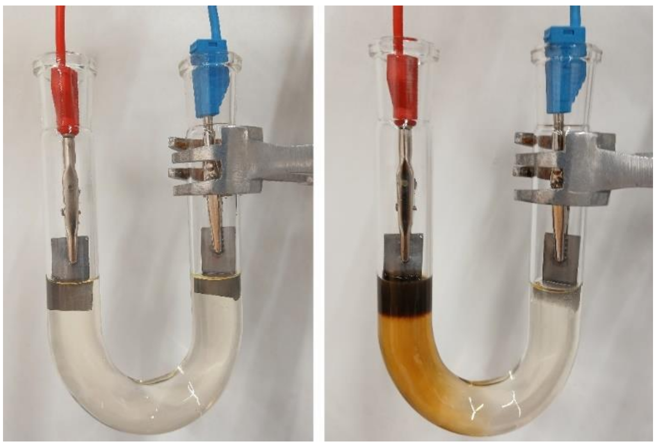

Fig. 6 Electrolysis of aniline after 0 minutes (left) and 5 minutes (right).

5.2 Experiment 2: Electrochemical Synthesis of Polymethylpyrrole

Chemicals: Acetonitrile (GHS03, GHS07), N-methylpyrrole (GHS02, GHS07), silver nitrate (GHS03, GHS05, GHS09) or ammonium nitrate (GHS03, GHS07)
Materials: Power source, 2 cables, alligator clips, 2 graphite foil electrodes, U-tube, spatula, glass rod, pipettes

The experiment is carried out analogously to experiment 1. However, the use of protective gloves or a fume hood is no longer required.
As in experiment 1, a dark color forms after a few minutes, starting from the anode. In contrast to the first experiment, however, this color is bluish black instead of brownish black (Figure 7). This coloration is attributable to the polymerization of methylpyrrole to polymethylpyrrole.

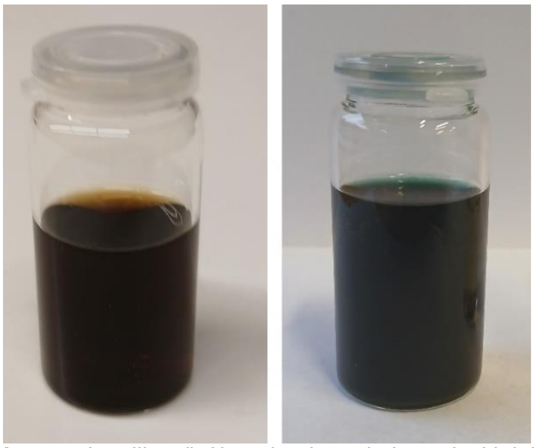

Fig. 7 Polyaniline (left) and polymethylpyrrole (right).

The graphite foils used in the experiments are then disposed of as solid chemical waste, while the solutions are discarded in the designated container for organic solvent waste.

6. Conclusion and Outlook

The experiments presented in this paper provide a safer and visually impressive approach to sustainably produced colored polymers that are both historically important and continue to be of considerable scientific interest. Building on these experiments, key topics such as reaction mechanisms, organic structures, radicals, and catalysis can be revisited, deepened and expanded in chemistry classes.
Moreover, these experiments offer an opportunity to establish a conceptual link to current research initiatives. In many electrochemical reactions, not only electrons but also protons are transferred (cf. Figure 2). These processes are therefore called proton-coupled electron transfer (PCET). In 2024, the dedicated Collaborative Research Center 1633 was established at the University Göttingen focusing exclusively on this topic, investigating strategies to optimize the energy efficiency of electro-organic syntheses. The use of nitrate as a mediator in organic synthesis is also a central subject of investigation within this research framework [3].
Linking contemporary research projects with historically important experiments not only enriches chemistry education but also highlights the dynamic nature of scientific progress and the continual emergence of new ideas, refinement, and creative innovation.

7. Acknowledgements

This project was kindly supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - 510228793 – SFB 1633.

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