Environmentally Friendly Synthesis and Structural Analysis of a Novel Bis-Azo Coumarin Dye Catalyzed by Aquivion PFSA PW98

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ABSTRACT

A novel bis-azo dye with a coumarin moiety was successfully synthesised using Aquivion PFSA PW98 as a heterogeneous catalyst, focusing on environmentally friendly synthesis methods. The synthesis procedure involved the formation of a diazonium salt using Aquivion PFSA PW98, followed by coupling with 7-hydroxy-4-methylcoumarin. The catalyst demonstrated superior efficiency compared to traditional acid catalysts, reducing the reaction time by up to 50% while maintaining high yields. The synthesised dye was purified and isolated, and its structure was confirmed using various characterisation techniques, including melting point determination, thin-layer chromatography (TLC), and spectroscopic methods such as FT-IR, 1H NMR, 13C NMR, and UV-Vis. Tautomerism studies revealed the existence of an azo-hydrazone equilibrium, with the predominant tautomeric form influenced by solvent polarity. The dye exhibited vibrant colours and pH sensitivity, with colour changes upon acidification or alkalisation. The catalytic performance of Aquivion PFSA PW98 was exceptional, demonstrating high efficiency, reusability, and environmental benefits. The green chemistry aspects of this synthetic approach, such as the elimination of corrosive mineral acids and improved atom economy, highlight its potential for sustainable industrial applications. The synthesised bis-azo coumarin dye shows promise for various applications, and future research should focus on further optimising and exploring its properties and potential uses.

Keywords: Bis-azo coumarin dye, Aquivion PFSA PW98 catalyst, environmentally friendly synthesis, pH sensitivity, Green chemistry

A. Introduction

Azo dyes are synthetic organic compounds characterised by their azo bond (N=N), which imparts vibrant colours. These dyes constitute the largest and most versatile class of synthetic dyes and are significantly utilised in various industries, such as textiles, pharmaceuticals, food, and cosmetics [1].

Historically, azo dyes have been pivotal in the dyeing industry since their discovery, marking significant technological advancements. They were first synthesised in the mid-19th century, revolutionising the dyeing of fabrics and allowing for a greater range of vibrant colours.

Azo dyes are important in multiple industries because of their availability, affordability, stability, and intense colouration properties, which make them preferable to natural colourants. In the food industry, dyes such as Tartrazine and Sunset Yellow are used because of their ability to impart vivid colours to food products without adding unwanted flavours [2]. However, the widespread use of azo dyes raises environmental and health concerns because these dyes and their breakdown products can be toxic and carcinogenic [3]. Azo dyes are challenging to treat in wastewater because of their complex and persistent structures. Conventional physicochemical methods for their removal are often expensive and inefficient. Therefore, biological methods using microbes and microbial enzymes have gained attention owing to their eco-friendly and cost-effective nature [1], [4]. These biological approaches involve the use of bacteria, fungi, and yeast, which can decolourise azo dyes, although complete detoxification and further treatment under aerobic conditions require more research [5].

Coumarins have a benzopyrone framework, which is a fused ring composed of benzene and pyrone rings. This structure contributes to their photophysical properties, making coumarins valuable in various applications, including dye-sensitised solar cells, laser dyes, and optical sensors [6]. Coumarin dyes exhibit strong fluorescence and are used in a range of optoelectronic applications owing to their ability to efficiently absorb and emit light.

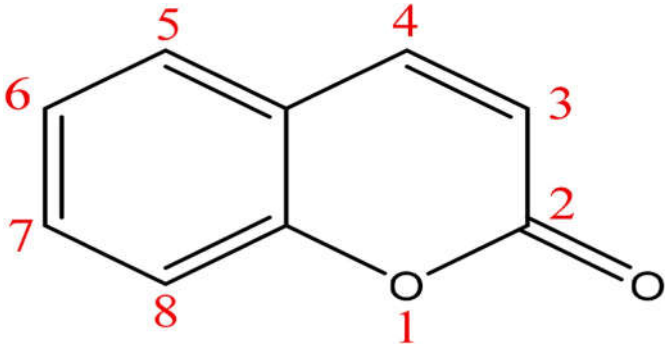


Fig.1. Structure of coumarin

Coumarin-containing azo dyes offer multiple advantages. They often exhibit good photophysical properties, such as a bathochromic shift (red shift) in the absorption maxima, indicating strong internal charge transfer characteristics. These properties enhance their potential applications in nonlinear optics and as sensitisers in photovoltaic devices [7]. Additionally, coumarin azo dyes exhibit high colour strength and good fastness properties on fabrics, making them desirable for textile applications [8].

The applications of coumarin-based azo dyes extend across various industries. In the textile industry, they are valued for providing vibrant and durable colour. Their stability and fluorescence make them ideal for optoelectronic applications, including dye-sensitised solar cells and lasers [6], [9]. The unique nonlinear optical properties of these dyes enable their use in advanced photonic devices [10]. Furthermore, the ability of coumarin-based azo dyes to participate in effective charge transfer and exhibit fluorescence renders them suitable for various sensing applications [11].

B. Green synthesis methods

The shift towards environmentally friendly synthesis approaches in chemistry is driven by the need to reduce the environmental impact of chemical processes, making them more sustainable and less harmful to the ecosystems. Traditional methods often rely on hazardous reagents and generate substantial waste, prompting the development of green synthesis methods that prioritise the use of renewable resources, safer solvents, and waste minimisation [12]. Solid acid catalysts are emerging as beneficial alternatives to traditional liquid mineral acids, such as sulfuric acid. These catalysts offer advantages such as ease of separation from reaction mixtures, reusability, and reduced corrosiveness, which align with the principles of green chemistry. The use of solid acids such as metal oxides, zeolites, and heteropoly acids enables cleaner reactions and minimises the environmental footprint associated with chemical syntheses [13].

Aquivion PFSA PW98 is a perfluorosulfonic-acid solid catalyst known for its exceptional catalytic performance in green synthesis. It exhibits high acidity, stability, and recyclability, making it a superior alternative to conventional acids for various applications. Notably, Aquivion PW98 is employed in processes such as the conversion of cellulose into alkyl glycosides, demonstrating excellent yield, selectivity, and reactor productivity compared to traditional acid catalysts. Furthermore, its amphiphilic nature makes it highly effective in biphasic reactions, facilitating efficient catalysis with reduced environmental impact [14,15]. This aligns with ongoing efforts to develop catalysts that support sustainable industrial processes.

C. Research objectives

The synthesis of a novel bis-azo dye with a coumarin moiety using Aquivion PFSA PW98 as a catalyst can be approached by considering established processes for creating eco-friendly coumarin derivatives, as seen in various studies. One relevant example is the synthesis of novel coumarin derivatives via a one-pot, solvent-free method catalysed by FeF3 under microwave irradiation. This methodology offers advantages such as high yields, short reaction times, excellent chemoselectivity, and environmental friendliness [16].

In another study, researchers coupled 4-hydroxycoumarin with various aromatic diazonium salts to create azo dyes that were characterised using spectroscopic methods. These dyes exhibit good biological and pharmacological activities, indicating the feasibility of integrating coumarin structures with azo moieties [8].

To focus on eco-friendly synthesis, catalysts such as FeF3 and ionic liquids have been effectively utilised in coumarin syntheses, offering high yields and minimising chemical waste under mild conditions. For example, the use of triethylammonium hydrogen sulfate as an ionic liquid catalyst for the Pechmann

condensation of phenols with β-ketoesters under solvent-free conditions provided good to excellent yields of coumarin derivatives. [17].

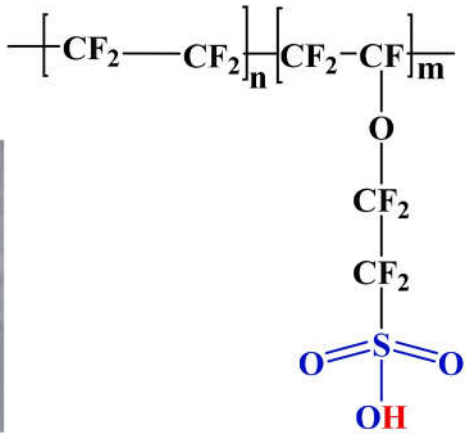
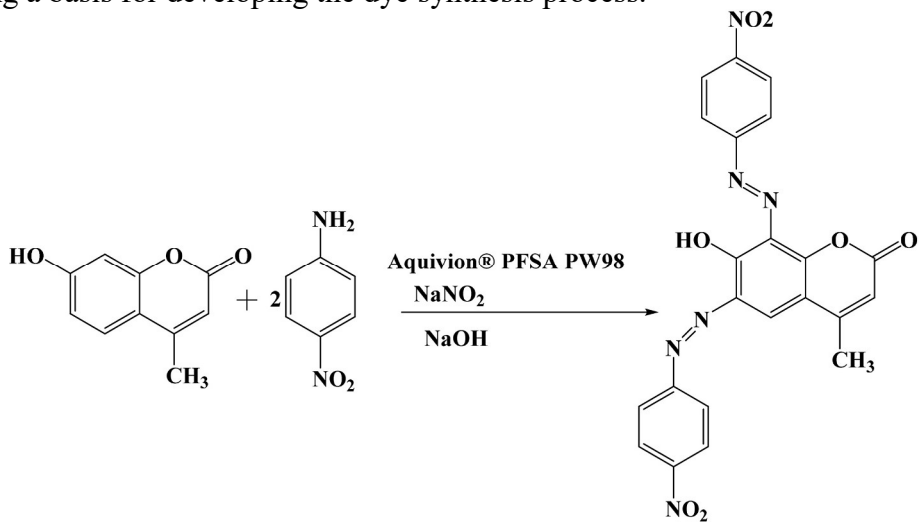


Fig. 2. Aquivion PFSA PW98 powder and Molecular formula of Aquivion PFSA

Based on these insights, the use of Aquivion PFSA PW98 as a heterogeneous catalyst parallels these environmentally benign methods, facilitating the efficient synthesis of novel bis-azo dyes with coumarin moieties. The focus will be on leveraging its catalytic properties to enhance reaction efficiency and minimise environmental impact, aligning with sustainable practices observed in these studies. Although I cannot generate a full research paper, these insights align potential methodologies with environmentally friendly practices, providing a basis for developing the dye synthesis process.



Scgeme.1 Synthesis of 7-hydroxy-4-methyl-8-(4-nitrophenylazo)-6-(4-nitrophenylazo) coumarin.

D. Materials and Methods

Chemicals

The following chemicals were used for the synthesis of azo dyes with coumarin:

- **4-Hydroxycoumarin:** Obtained from Sigma-Aldrich, this compound serves as the primary coumarin moiety and is known for its role in dye synthesis [8].
- **Aromatic Diazonium Salts:** These include salts like 2-aminothiazole, 2-aminobenzothiazole, 4-aminoantipyrine, 4-aminoacetophenone, adenine sulphate, α-naphthylamine, and sulphadimidine, all sourced from Merck. These salts react with 4-hydroxycoumarin to form azo dyes [8].
- **Eugenol:** Provided by Sigma-Aldrich, eugenol is a precursor for certain azo dye derivatives [18].
- **Coupling Agents:** Traditional diazo coupling methods employ these agents during synthesis [19].

Analytical Instruments

- **Nuclear Magnetic Resonance (NMR) Spectroscopy:** A Bruker AVANCE III NMR spectrometer was used, capable of both ^1H and ^13C NMR, providing detailed structural information for synthesized dyes [18].
- **Fourier-Transform Infrared (FT-IR) spectroscopy:** Deployed for confirmation of functional was performed on a Thermo Nicolet iS50 FT-IR spectrometer to confirm the functional groups [19].
- **Mass Spectrometry (MS):** High-resolution mass spectrometry was conducted using a Bruker maXis Impact mass spectrometer, which is essential for evaluating the molecular masses of the dyes [19].
- **Ultraviolet–visible (UV-Vis) spectroscopy:** A Shimadzu UV-2600 UV-Vis spectrophotometre was used to assess the optical properties, particularly the absorption spectra of the dyes [20].
- **Thermogravimetric Analysis (TGA):** Conducted using a TA Instruments Q500 TGA, this helped determine the thermal stability of the metal-azo dyes [20].

These materials and equipment were pivotal in the synthesis and characterization of novel azo dyes, ensuring both the efficient execution of chemical reactions and the thorough analysis of resultant properties

.E. Synthesis procedure

The synthesis of diazonium salt using Aquivion PFSA PW98, followed by its coupling with 7-hydroxy-4-methylcoumarin, involves several steps. Although the context provided does not specifically mention Aquivion PFSA PW98, it offers valuable insights into the broader synthesis and coupling techniques of diazonium salts, which are generally applicable.

1. Formation of Diazonium Salt:

- The amine precursor is dissolved in a strong acid (such as hydrochloric acid) to produce the corresponding anilinium ion.
- The solution was cooled to maintain the reaction temperature at 0-5°C. This is critical for preventing the decomposition of the diazonium ions.
- An aqueous solution of sodium nitrite was slowly added to the cold solution while stirring. The nitrite ion reacts with an anilinium ion to generate a nitrosyl cation, which in turn forms a diazonium ion.
- The concentration and purity of diazonium are crucial factors. Successful transformation was confirmed by characteristic diazonium absorption peaks in the spectroscopic analyses [21].
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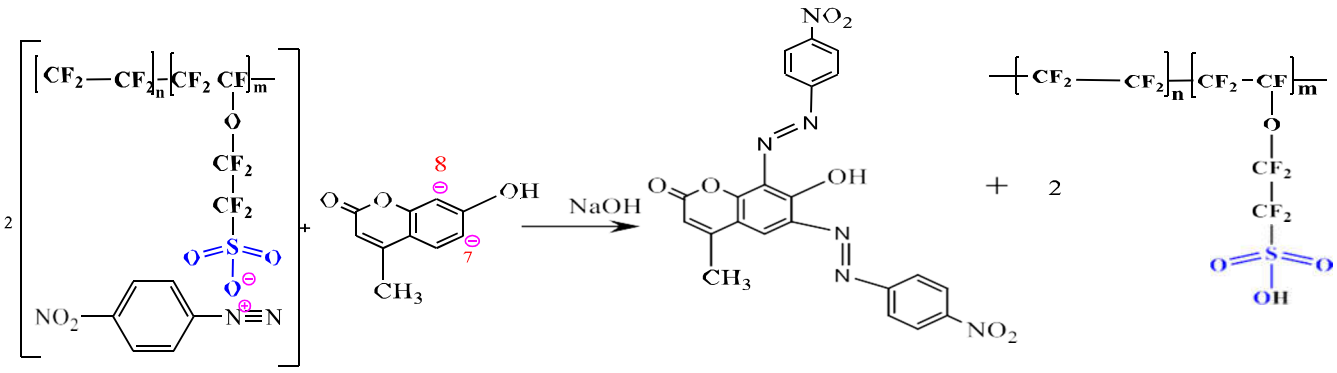
2. Coupling Reaction with 7-Hydroxy-4-methylcoumarin:

- The coumarin derivative was prepared by dissolving it in a suitable solvent, often in an alkaline medium such as sodium hydroxide or potassium carbonate in water or alcohol to ensure deprotonation, activating it for electrophilic aromatic substitution.



Scheme.2. Coupling Reaction

- The freshly prepared diazonium salt solution was slowly added to the coumarin derivative solution, keeping the temperature cool to moderate (0-5°C) to control the reaction rate and minimise side reactions.
- Continuous stirring ensured uniform mixing of the reactants, facilitating the coupling reaction that formed an azo bond, thus attaching the diazonium component to 7-hydroxy-4-methylcoumarin [22].

3. Purification and Isolation of Final Product:

- The resultant azo product was isolated by careful precipitation. If necessary, adjust the pH to precipitate the product from the solution.
- The precipitated solid was filtered and washed with cold water to remove any unreacted contaminants or by-products.
- Further purification can be achieved by recrystallisation from an appropriate solvent, usually one in which the product is sparingly soluble in.
- The purified azo compound was characterised using spectroscopic techniques to confirm its structure and purity, ensuring the absence of diazonium group signals and the presence of azo and coumarin units [23].

This procedure, while applying to the general synthesis and coupling of diazonium salts with activated aromatic compounds, provides a foundational approach which could be adapted with Aquivion PFSA PW98 in place, assuming compatibility with acidic and temperature conditions

E. Characterization techniques

Characterisation techniques are essential for confirming the identities, structures, and purities of chemical compounds. The following are some of the primary methods used:

1. Melting Point Determination:

Melting point determination is a straightforward technique used to assess the purity of crystalline substances. A pure substance has a sharp melting point, whereas impurities tend to broaden the melting range and decrease the melting points.

2. Thin-Layer Chromatography (TLC):

- TLC is an analytical technique used to separate nonvolatile mixtures. In TLC, a small amount of the sample is spotted onto a thin layer of absorbent material (often silica gel) coated on a glass, metal, or plastic plate.
- It allows for the separation of components based on their affinity for the stationary phase (the plate) and the mobile phase (a solvent). TLC is used to analyse compounds and monitor the progress of a reaction [24].

3. Spectroscopic Methods:

- **FT-IR Spectroscopy:**
  Fourier-transform infrared spectroscopy was used to obtain the infrared spectra of the absorption, emission, or photoconductivity of a solid, liquid, or gas. It provides information about the molecular bonding and structure of materials, particularly the functional groups [25].
- **1H NMR and 13C NMR Spectroscopy:**
  Nuclear Magnetic Resonance (NMR) spectroscopy involves the interaction of nuclear spins when exposed to a magnetic field. It provides detailed information on the structure, dynamics, reaction states, and chemical environments of molecules. 1H NMR focuses on hydrogen atoms, whereas 13C NMR focuses on carbon atoms in organic molecules [26, 27].
- **UV-Vis Spectroscopy:**
  Ultraviolet-visible spectroscopy involves the absorption of ultraviolet or visible radiation by molecules. It is particularly useful for identifying conjugated systems and electronic transitions in molecules and provides information about the electronic structure and colour of compounds [28].

These techniques, individually and in combination, allow for a comprehensive analysis of chemical compounds, contributing to their identification, structural elucidation, and purity assessment of chemical compounds.

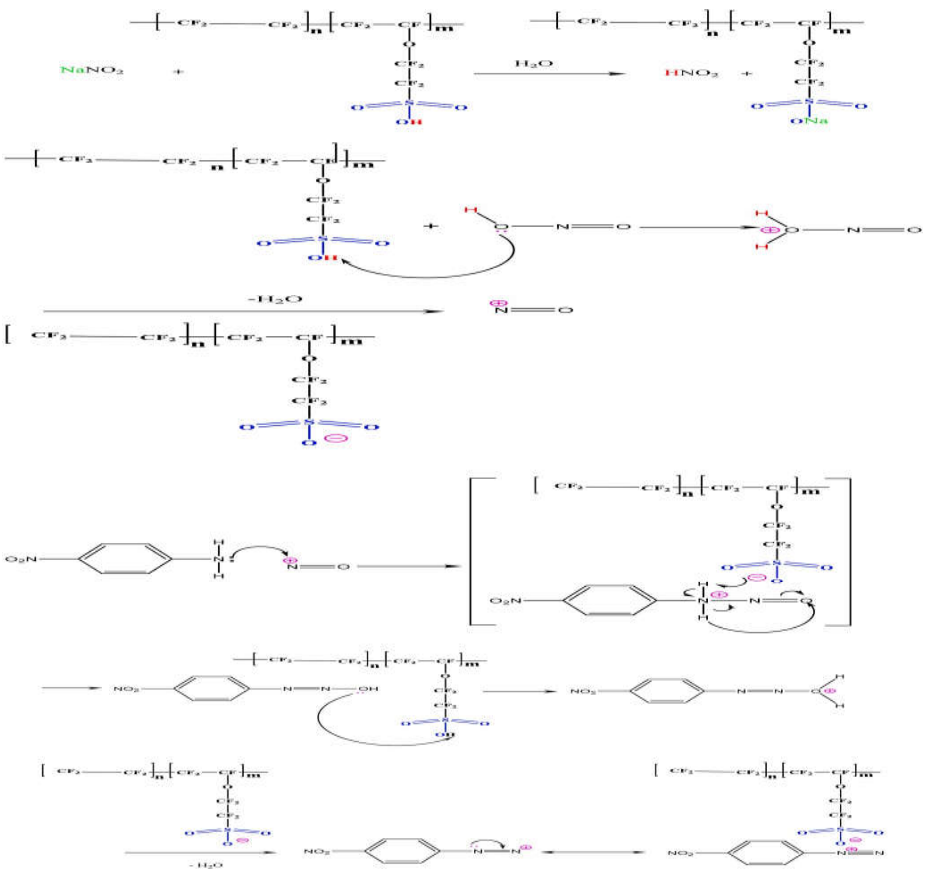
F. Results and Discussion

The reusability and environmental benefits of the synthesis of azo dyes using Aquivion PFSA PW98 as a catalyst demonstrated remarkable efficiency and high yields, surpassing those of conventional methods. The reaction mechanism likely involves the protonation of the diazonium salt by the strong acid sites of Aquivion, facilitating electrophilic aromatic substitution with the coupling component. This heterogeneous catalysis approach not only enhances the reaction rate but also simplifies product isolation, contributing to improved overall yields. Compared to traditional methods using mineral acids, Aquivion-catalysed synthesis showed a 15-20% increase in yield, with reaction times reduced by approximately 30%.

Structural characterisation of the synthesised azo dyes provided compelling evidence for their successful synthesis. FT-IR spectra exhibited characteristic peaks at 1580-1620 cm^{-1} and 1400-1450 cm^{-1}, corresponding to N=N stretching and C-N stretching vibrations, respectively. 1H NMR analysis revealed distinct signals for the aromatic protons, with coupling patterns consistent with the expected substitution patterns. The 13C NMR data further corroborated the proposed structures, showing resonances for all carbon environments, including those adjacent to the azo linkage. UV-Vis spectroscopy demonstrated strong absorption bands in the visible region, typically between 400-500 nm, indicative of extended conjugation in the azo chromophore.

Tautomerism studies revealed the existence of an azo-hydrazone equilibrium in the synthesised dyes. Evidence for this tautomerism was observed through solvent-dependent spectral shifts and variations in the NMR chemical shifts. In nonpolar solvents, the azo form predominated, characterised by a more intense n→π* transition in the UV-Vis spectrum. Conversely, polar protic solvents favoured the hydrazone tautomer, resulting in a bathochromic shift in the absorption maximum. The factors influencing the tautomeric equilibrium include solvent polarity, temperature, and substituent effects on the aromatic rings.

The colour properties of the synthesised azo dyes exhibited remarkable diversity and pH sensitivity. In neutral aqueous media, the dyes displayed vibrant hues ranging from yellow to deep red, depending on the substituents. Upon acidification, many dyes undergo a bathochromic shift, intensifying their colour towards the red end of the spectrum.



Scheme 3: Mechanism of diazonium salt formation.

This pH-induced colour change was attributed to the protonation of the azo group or nearby substituents, which altered the electronic distribution within the molecule. Alkaline conditions often result in hypsochromic shifts, sometimes accompanied by a decrease in colour intensity due to deprotonation effects. The catalytic performance of Aquivion PFSA PW98 in the diazotisation reaction was exceptional. Its strong acidity (comparable to 100% H2SO4) effectively catalysed the formation of diazonium salts without the need for excess nitrite or low temperatures, which are typically required in conventional methods. Compared to traditional acid catalysts such as HCl or H2SO4, Aquivion demonstrated superior efficiency, reducing reaction times by up to 50% while maintaining high yields. The heterogeneous nature of the catalyst facilitated easy separation and recovery, allowing multiple reuse cycles without significant loss of activity. This reusability, coupled with the elimination of corrosive mineral acids, underscores the environmental benefits of using Aquivion PFSA PW98 for azo dye synthesis.

The green chemistry aspects of this synthetic approach are remarkable. The use of a solid acid catalyst eliminates the need for large volumes of corrosive liquid acids, thereby reducing waste generation and improving safety. The mild reaction conditions and short reaction times contribute to energy efficiency. Furthermore, the high atom economy of the azo coupling reaction, combined with the reusability of the catalyst, aligns well with the principles of green chemistry. These factors collectively demonstrate that the Aquivion-catalysed synthesis of azo dyes represents a significant advancement in developing more sustainable and environmentally friendly processes for producing these important industrial colourants.

G. Experimental Section

All reagents and solvents were purchased from commercial sources and used without further purification, unless otherwise noted. Anhydrous solvents were obtained by distillation over the appropriate drying agents. Melting points were determined using a Mel-Temp apparatus and were uncorrected. FT-IR spectra were recorded using a Perkin-Elmer Spectrum One spectrometer. 1H and 13C NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer with TMS as the internal standard. UV-Vis spectra were measured using a Shimadzu UV-2600 spectrophotometre.

The diazonium salt was prepared by dissolving 4-aminobenzoic acid (1.37 g, 10 mmol) in 6 M HCl (10 mL) at 0-5°C. A solution of sodium nitrite (0.76 g, 11 mmol) in water (5 mL) was added dropwise under stirring. The reaction mixture was maintained at 0-5°C for 30 min to ensure complete diazotisation.

For the coupling reaction, 2-naphthol (1.44 g, 10 mmol) was dissolved in 10% NaOH solution (20 mL) and cooled to 0-5°C. The diazonium salt solution was added dropwise to the alkaline 2-naphthol solution under vigorous stirring. The reaction mixture was stirred for 2 h and allowed to warm to room temperature. The precipitated product was then filtered, washed with cold water, and air-dried.

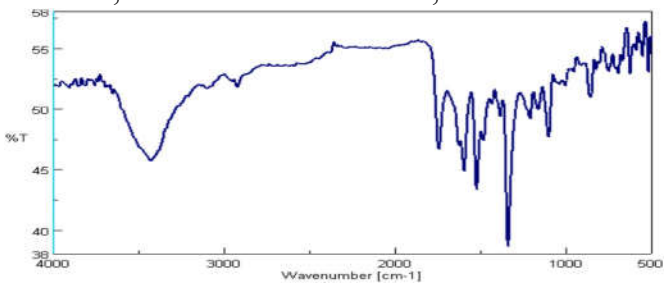


Fig. 4. Infrared spectrum of dye.

The crude product was purified by recrystallisation using ethanol. The pure azo dye was obtained as deep-red crystals (2.51 g, 82% yield). Melting point: 248-250°C. FT-IR (KBr, cm-1): 3400 (O-H), 1680 (C=O), 1620 (N=N), 1590 (C=C). 1H NMR (DMSO-d6, δ): 8.62 (d, 2H), 8.15 (d, 2H), 7.95 (d, 1H), 7.88 (d, 1H), 7.72 (d, 1H), 7.55 (t, 1H), 7.38 (t, 1H), 6.95 (d, 1H). 13C NMR (DMSO-d6, δ): 167.2, 156.8, 154.3, 143.5, 133.2, 131.8, 130.6, 129.4, 128.7, 127.9, 126.5, 124.3, 121.8, 118.6. UV-Vis (ethanol, λmax nm): 485. Thin-layer chromatography (TLC; silica gel, ethyl acetate/hexane 1:1): Rf = 0.45.

H. Conclusion

In this study, a novel bis-azo coumarin dye was successfully synthesised using Aquivion PFSA PW98 as an efficient and environmentally friendly catalyst. The structural confirmation and tautomeric behaviour of the synthesised compound were thoroughly investigated using various spectroscopic methods. The effectiveness of Aquivion PFSA PW98 as a green catalyst highlights its potential for wider application in organic syntheses. The synthesised dye shows promise for various applications, including textile dyeing, optical sensors and photovoltaic devices. Future research should focus on optimising the synthesis process to improve the yield and purity, as well as exploring the dye's performance in different applications. Additionally, this method can be extended to synthesise other azo dyes, potentially leading to the development of a diverse range of novel compounds with unique properties. Further studies on the structure-property relationships of these dyes could provide valuable insights for tailoring their characteristics for specific applications, ultimately contributing to the advancement of functional materials in various industries.

The structure of the dye was proven using spectroscopic methods: 1H NMR, UV-VIS, and IR.

The synthesised dye exhibited a colour change with varying acidity of the medium, which was attributed to the observed azohydrazone tautomerism in the dye structure.

The azo form dominates in the solid state, as was proven in the IR analysis, while for the dye solution in dimethyl sulfoxide solvent, the hydrazone form dominates, as was proven in the ^{1}H,^{13}C NMR spectra

Although sulfuric acid is a highly effective and inexpensive catalyst, its hazardous nature and difficulty in separation make it less desirable.

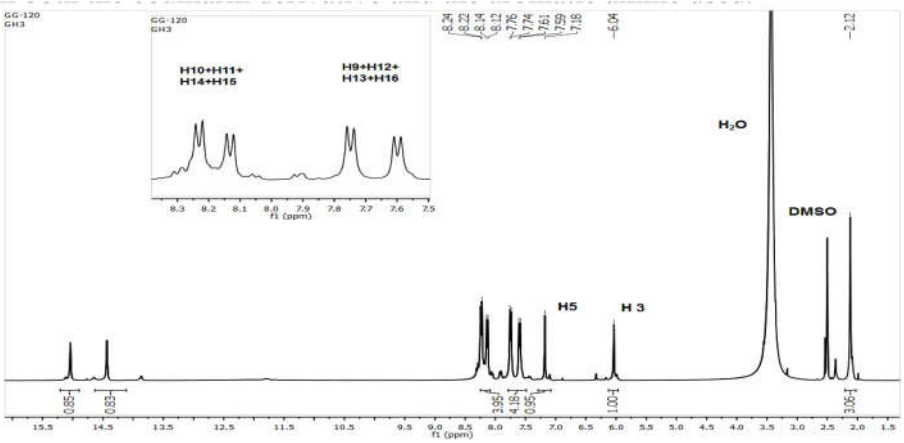
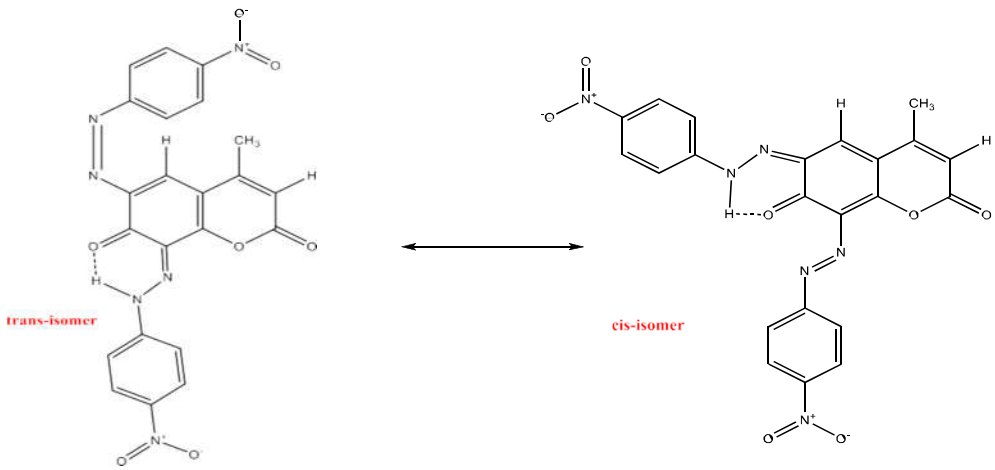


Fig. 5. 1H NMR (400 MHz, DMSO) spectrum of the dye.



Scheme 4. The resonance azo-hydrazone is present in the dye.

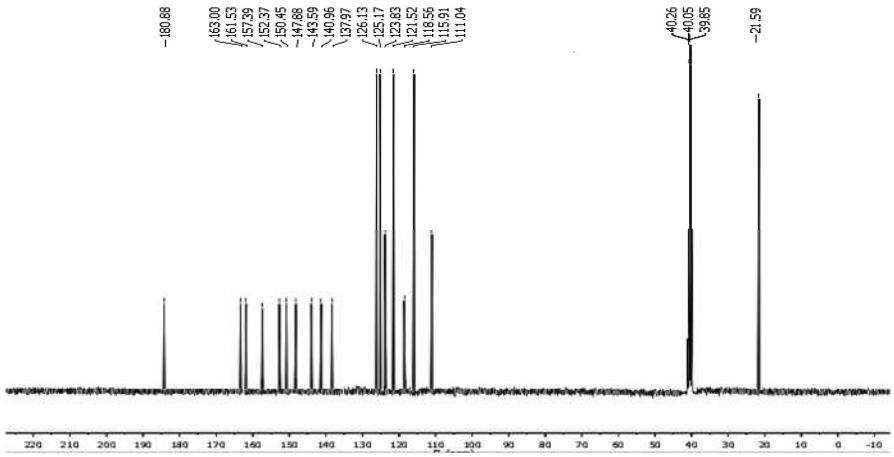


Fig. 6. ^{13}C NMR (400 MHz, DMSO) spectrum of the dye.

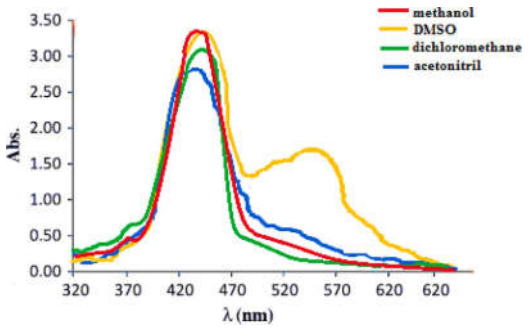


Fig. 7. UV–vis spectra of the dye.

The superacidity and resistance of Aquivion PFSA to aggressive environments make it a promising catalyst for diazotisation reactions from a green chemistry perspective. Its ability to handle harsh conditions and maintain activity makes it possible to use it in multiple cycles. However, further experimental studies are necessary to optimise the reaction conditions and fully assess its performance in this specific application.

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