

Short Note

# 4,4',4''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(1-methylpyridin-1-ium) Iodide

Lorenza Romagnoli, Andrea D'Annibale and Alessandro Latini \* 

Dipartimento di Chimica, Sapienza Università di Roma, Piazzale Aldo Moro 5, 00185 Roma, Italy; lorenza.romagnoli@uniroma1.it (L.R.); andrea.dannibale@uniroma1.it (A.D.)

\* Correspondence: alessandro.latini@uniroma1.it

**Abstract:** Despite having been known for a long time, quaternary 4,4'-bipyridinium salts, or viologens, are still a highly inspiring class of compounds, thanks to their peculiar redox and charge transfer properties. However, more complex structures containing multiple pyridinium rings, also interspaced by conjugated moieties, allow an even wider synthetic variability and tunability of their characteristics. The compound described herein is a star-shaped, fully conjugated molecule with three methylated pyridinium rings connected by a triple bond spacer to a central benzene core, which was synthesized from readily available building blocks, representing a quite simple model of multi-pyridyl extended viologen; its UV-visible absorption and fluorescence spectra have also been investigated.

**Keywords:** viologen; fluorescent probe; Sonogashira reaction

## 1. Introduction

The term viologens has since long been used to define diquaternized-4,4'-bipyridinium salts [1,2]. The first compound of this class to draw attention was methyl viologen dichloride, also called “paraquat”, which has been commercialized since 1962 and is extensively used as an herbicide [3,4], although its acute toxicity in humans and animals poses increasingly serious concerns [5,6] (for this reason, its use has been forbidden in the EU).

Besides herbicidal activity, many other interesting applications have been discovered for methyl viologen and related compounds [7–9]. Indeed, the most distinctive feature of viologens is represented by their redox behavior, since they can be reduced through a one-electron process to the corresponding radical cation first and then to the neutral form. The reduction is reversible, and the three redox states are all stable; moreover, they are characterized by different colors, that is, for methyl viologen, colorless for the dication, dark blue-violet for the radical cation, and yellow-brown for the neutral species. This property, called electrochromism, together with the tendency of viologens to act as electron acceptors and form charge transfer complexes, is of great usefulness and has therefore attracted considerable interest, in view of their utilization in various energy-related fields [10–12]. Among the ever-growing number of applications of viologens, it is possible to cite electrochromic [13] and memory devices [14], molecular machines [15], transistors and diodes [16], gas storage and separation processes [17], photocatalysis [18], hydrogen production [19], and energy conversion and accumulation in solar cells [20] and batteries [21].

Most importantly, the above-mentioned characteristics of viologens can be easily tuned by adjusting their structure and composition, for example, by varying the nature of the negative counterion or the substituents on the nitrogen atoms. As regards the groups attached to the pyridinium nitrogen, in particular, a multitude of moieties has been explored, and a number of synthetic routes have been developed [22], ranging from the simple *N*-alkylation, through the reaction with alkyl or benzyl halides, to the Zincke reaction [23], allowing the insertion of aromatic rings directly linked to the pyridinium ones, and the



**Citation:** Romagnoli, L.; D'Annibale, A.; Latini, A. 4,4',4''-(Benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(1-methylpyridin-1-ium) Iodide.

*Molbank* **2023**, *2023*, M1742.

<https://doi.org/10.3390/M1742>

Received: 26 October 2023

Revised: 3 November 2023

Accepted: 6 November 2023

Published: 8 November 2023



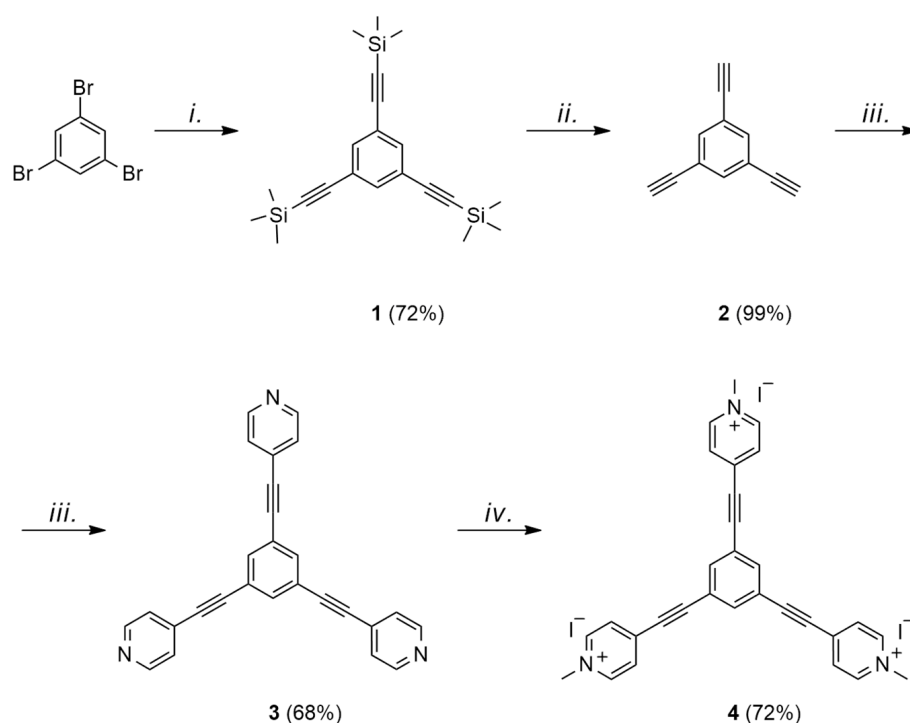
**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

reductive coupling of 4-cyanopyridinium quaternary salts [24], just to cite a few. However, the quaternarized pyridinium rings do not necessarily need to be directly connected with each other, to retain the peculiarities of viologens, provided that conjugation between them is ensured by an appropriate spacer. Therefore, a variety of extended viologens have also been prepared, such as those containing just an unsaturated bond as the central unit or being characterized by aromatic or heteroaromatic rings as the conjugated spacer. More complex structures were also described, such as branched multi-pyridinium salts with large central polycyclic architectures [25–27].

Herein, the practical and straightforward synthesis, starting from inexpensive building blocks, of a conjugated star-shaped tripyridinium salt is described, and its structural characterization is detailed. Moreover, the absorption and emission spectra of the compound in H<sub>2</sub>O solution have been carried out. We believe this salt, with its easy synthesis and advantageous branched structure, can constitute a convenient archetype to explore the behavior of more complex quaternary pyridinium-based functional materials.

## 2. Results and Discussion

The title compound **4** features a symmetrical structure, the core of which is constituted by a benzene moiety, 1,3,5-trisubstituted with tethers, in which the three methyl pyridinium moieties are connected to the aromatic core by triple bonds. The devised strategy for its preparation (Scheme 1), in four steps, envisaged two subsequent palladium-copper-catalyzed Sonogashira Csp<sup>2</sup>–Csp cross-couplings, due to the effectiveness of this reaction in connecting aromatic building blocks to acetylenic units [28].



**Scheme 1.** Synthesis of compound **4**; *i.* Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3 mol%), CuI (3 mol%), TMSA, Et<sub>3</sub>N, 65 °C, 24 h; *ii.* KOH, THF/MeOH, 20 °C, 16 h; *iii.* 4-bromopyridine-HCl (3 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (20 mol%), CuI (5 mol%), Et<sub>3</sub>N, 70 °C, 48 h; *iv.* MeI, CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, 48 h.

The first step of the synthesis was then represented by the Sonogashira reaction of 1,3,5-tribromobenzene with trimethylsilylacetylene in triethylamine in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI, which afforded, after chromatographic purification, the desired product **1**, a pale yellow solid, with a 72% yield. The subsequent introduction of the pyridyl rings required the preliminary removal of the trimethylsilyl protecting group on the alkyne moieties. Compound **1** was therefore stirred overnight at room temperature with KOH in

a THF/CH<sub>3</sub>OH solution, followed by quenching with HCl solution and extraction with CH<sub>2</sub>Cl<sub>2</sub>, after which column chromatography yielded almost quantitatively compound **2**, that is, 1,3,5-triethynylbenzene, as a white solid.

Once the terminal triyne **2** had been obtained, it was subjected to another palladium-copper-catalyzed coupling, using Pd(PPh<sub>3</sub>)<sub>4</sub> and CuI as catalysts, with three equivalents of 4-bromopyridine. However, the latter is commercially available as hydrochloride and therefore requires its preliminary conversion into the free amine (which is rather unstable and tends to polymerize with an exothermic reaction) by washing it with 2 N NaOH solution and extracting the aqueous phase with CH<sub>2</sub>Cl<sub>2</sub>. This was mandatory due to unsuccessful preliminary attempts to carry out the reaction by using 4-bromopyridine hydrochloride. The crude product from the aqueous workup of the reaction was then purified by column chromatography to give compound **3** as a pale-yellow solid in 68% yield. Finally, the target salt **4** was obtained by reacting the tripyridyl compound **3** with an excess of iodomethane in CH<sub>2</sub>Cl<sub>2</sub> at 40 °C for 2 days to ensure the complete methylation of the three nitrogen atoms, since a <sup>1</sup>H-NMR analysis of the product obtained after 24 h reaction times revealed the presence of mono- and disubstituted species, together with the desired trication. The product, a pale yellow solid insoluble in CH<sub>2</sub>Cl<sub>2</sub>, after precipitation from the reaction mixture and subsequent filtration, was obtained with a 72% yield. Its identity and purity, assessed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, allowed it to be used without further purification.

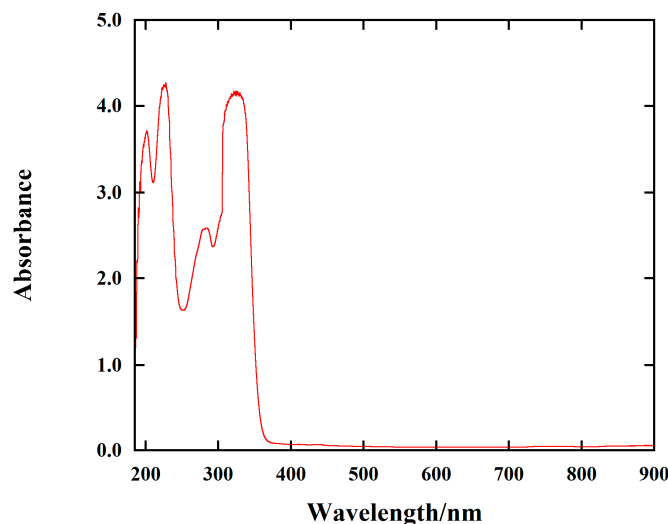
Given the rather simple structure of the organic trication, signal assignments of monodimensional NMR spectra have been easily accomplished. The highly symmetrical structure of this species results in the low number of signals in the spectra. Its <sup>1</sup>H-NMR spectrum (Figure S1), performed in CD<sub>3</sub>OD, displays a sharp singlet at δ 4.42 ppm, ascribed to the nine protons of the methyl groups connected to the positively charged nitrogen atoms, while another singlet is found at δ 8.26 ppm and can be attributed to the three equivalent protons on the central phenyl ring. This signal almost overlaps with one of those produced by the protons on the pyridinium rings, precisely the one attributable to protons in position 3, that is the multiplet at δ 8.24, while the protons adjacent to nitrogen atoms (position 2) produce the multiplet at δ 8.95 ppm. It should be noted that the protons on the pyridinium rings give rise to a second-order AA'XX' spin system due to their chemical but not magnetical equivalence.

Concerning the <sup>13</sup>C-NMR spectrum (Figure S2), which was carried out in DMSO-d<sub>6</sub>, the signal produced by the methyl carbons can be easily identified as the one at δ 48.5 ppm, while those relative to the *sp* carbons of the triple bonds give peaks at δ 87.5 and 98.6 ppm. As regards the signals produced by the aromatic moieties, the one at δ 146.4 ppm can be clearly ascribed to carbons in position 2 on the pyridinium rings, while those in position 3 give a peak at δ 129.7 ppm, and, lastly, the quaternary pyridyl carbons adjacent to the triple bonds produce the weak signal at δ 136.1 ppm; peaks attributable to carbons of the central phenyl ring are constituted by the one at δ 137.8, relative to the C-H, and that at δ 122.5 ppm, ascribed to the quaternary carbons linked to the acetylenes.

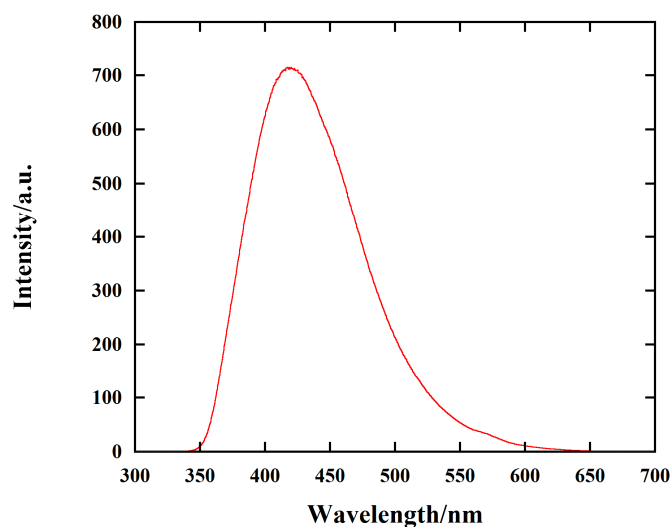
While compound **4** is insoluble in non-polar solvents, it was found instead to be fairly soluble in organic polar solvents such as methanol, as well as in H<sub>2</sub>O; the UV-visible absorption spectrum (Figure 1) was then measured in H<sub>2</sub>O (5.0 × 10<sup>-5</sup> M). This spectrum shows several intense bands in the region between 185 nm and 360 nm, thus all falling completely in the UV range. Among these, the one at the lowest wavelengths presents a first maximum for λ<sub>max</sub> = 202 nm, characterized by ε<sub>max</sub> = 74,260 M<sup>-1</sup>cm<sup>-1</sup>, followed by another at λ<sub>max</sub> = 228 nm, with ε<sub>max</sub> = 85,320 M<sup>-1</sup>cm<sup>-1</sup>, which constitutes the most intense band of the spectrum. At higher wavelengths, there is a weaker band, with λ<sub>max</sub> = 284 nm and ε<sub>max</sub> = 51,600 M<sup>-1</sup>cm<sup>-1</sup>, and then a large, composite band, centered around λ<sub>max</sub> = 324 nm, characterized by ε<sub>max</sub> = 83,400 M<sup>-1</sup>cm<sup>-1</sup>.

As regards the fluorescence spectrum of compound **4**, it was also performed in H<sub>2</sub>O solution, with the same concentration used in the measurement of its absorption. Different wavelengths of excitation were tested in the region where the absorption bands are

present. In every case, the spectrum shows a large, asymmetric emission band, presenting a maximum at  $\lambda = 420$  nm, followed by a shoulder peak around  $\lambda = 450$  nm, suggesting the presence of different transitions. However, the highest fluorescence intensity has been obtained for the spectrum carried out using  $\lambda_{\text{exc}} = 284$  nm (Figure 2).



**Figure 1.** UV-visible absorption spectrum ( $5.0 \times 10^{-5}$  M in  $\text{H}_2\text{O}$ ) of compound 4.



**Figure 2.** Fluorescence spectrum ( $5.0 \times 10^{-5}$  M in  $\text{H}_2\text{O}$ ,  $\lambda_{\text{exc}} = 284$  nm) of compound 4.

### 3. Materials and Methods

All the reagents were purchased from Merck, Fluorochem, and TCI and used as received unless otherwise stated. Dry solvents were distilled according to standard procedures: tetrahydrofuran was distilled over Na/benzophenone, triethylamine was distilled over KOH, and dichloromethane was distilled over  $\text{P}_2\text{O}_5$ . Reactions and chromatographic separations were monitored by thin layer chromatography (TLC) on 0.25 mm silica gel plates (Merck Kieselgel 60 F254) and revealed under a UV lamp ( $\lambda = 254$  nm). Column chromatography was carried out on silica gel Merck-Kieselgel 60 (0.063–0.20 mm, 70–230 mesh) as a stationary phase.

$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using 5 mm tubes and chloroform-*d* ( $\text{CDCl}_3$ ), methanol-*d*<sub>4</sub> ( $\text{CD}_3\text{OD}$ ), and dimethyl sulfoxide-*d*<sub>6</sub> ( $\text{DMSO-}d_6$ ) as solvents. Spectral data of compounds 1–3 are in agreement with those reported in the literature [29,30].

The UV–Vis spectrum was acquired with a Shimadzu (Japan) UV2600 UV–vis spectrophotometer, while fluorescence spectra were measured on a Cary Eclipse (Varian) spectrofluorometer using SUPRASIL quartz cells (10 × 10 mm).

**Synthesis of 1,3,5-tris(trimethylsilyl)ethynylbenzene (1):** In a flame-dried Schlenk tube, under an argon atmosphere, 300 mg (0.953 mmol) of 1,3,5-tribromobenzene is dissolved in 20 mL of anhydrous degassed Et<sub>3</sub>N, then 20 mg (0.028 mmol) of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and 6 mg (0.032 mmol) of CuI are added; the suspension is stirred for 20 min at room temperature, then 1 mL (7.2 mmol) of trimethylsilylacetylene is added, and the mixture is heated to 65 °C and stirred for 24 h. After that, the reaction mixture is cooled, filtered to remove the solids, and concentrated under vacuum. The crude product is purified by column chromatography in hexane to yield 252 mg (0.687 mmol) of pure **1** (72%) as a pale-yellow solid. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.49 (s, 3H), 0.24 (s, 27H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ 135.2, 122.9, 82.7, 81.7, −0.3.

**Synthesis of 1,3,5-triethynylbenzene (2):** In a flame-dried round-bottom flask under an argon atmosphere, 252 mg (0.687 mmol) of **1** is dissolved in 2.5 mL of anhydrous THF, and a solution of 344 mg (6.14 mmol) of anhydrous KOH in 2.5 mL of CH<sub>3</sub>OH is added. The reaction mixture is stirred at room temperature overnight, then concentrated under vacuum, and 8.3 mL of 1 N HCl is added. The solution is extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL), the collected organic phases are dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum, and then the crude product is purified by column chromatography in hexane to afford 103 mg (0.687 mmol) of pure **2** (99%) as a white volatile solid. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.57 (s, 3H), 3.11 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ 135.6, 123.0, 81.6, 78.7.

**Synthesis of 1,3,5-tris(pyridin-4-ylethynyl)benzene (3):** In a flame-dried Schlenk tube, under an argon atmosphere, 60 mg (0.40 mmol) of **2** is dissolved in 20 mL of anhydrous degassed Et<sub>3</sub>N, together with 389 mg of 4-bromopyridine-HCl (washed with a 2 N aqueous NaOH solution and extracted three times with CH<sub>2</sub>Cl<sub>2</sub>, followed by concentration of the solution in vacuo at room temperature, immediately before use, due to 4-bromopyridine instability), 92 mg (0.08 mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub>, and 4 mg (0.02 mmol) of CuI, and the reaction mixture is refluxed for 48 h. The solvent is then evaporated under vacuum, and the solid residue is dissolved in ethyl acetate, washed with a saturated NH<sub>4</sub>Cl solution, and then with H<sub>2</sub>O, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum. The crude product is purified by column chromatography (3:7→3:17 hexane/ethyl acetate) to afford 103 mg (0.27 mmol) of pure **3** as a pale-yellow solid (68%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.55 (m, 6H), 7.64 (s, 3H), 7.28 (m, 6H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ 150.2, 135.4, 130.8, 125.7, 123.6, 91.6, 88.4.

**Synthesis of 4,4',4''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(1-methylpyridin-1-ium) iodide (4):** In a flame-dried Schlenk tube, 87 mg (0.23 mmol) of **3** is dissolved in 10 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub>, and 12 mL (32.1 mmol) of CH<sub>3</sub>I is added under an argon atmosphere. The mixture is stirred at 40 °C for 48 h, then cooled to room temperature and filtered under vacuum. The solid is washed with several portions of CH<sub>2</sub>Cl<sub>2</sub> and dried for 1 h under suction to yield 133 mg (0.165 mmol) of pure **4** as a yellow solid (72%). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 400 MHz) δ 8.95 (m, 6H), 8.26 (s, 3H), 8.24 (m, 6H), 4.42 (s, 9H); <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ 146.4, 137.8, 136.1, 129.7, 122.5, 98.6, 87.5, 48.5.

#### 4. Conclusions

A tridentate star-shaped extended viologen derivative, featuring a central benzene core, has been synthesized through a four-step synthesis with a total yield of 35%, and its UV–visible absorption and fluorescence have been measured in H<sub>2</sub>O solution. The new tripyridinium salt displays several very intense absorption bands in the UV region, the highest of which has λ<sub>max</sub> = 228 nm, and a broad emission band arising from different transitions, with a maximum at λ = 420 nm. The effectiveness of light absorption and fluorescence of this compound, together with its easy synthesis, make this compound a suitable candidate for the investigation of conjugated multi-pyridyl salts optoelectronic properties.

**Supplementary Materials:**  $^1\text{H}$  (Figure S1) and  $^{13}\text{C}$  NMR (Figure S2) spectra of the title compound can be downloaded.

**Author Contributions:** Investigation, L.R.; conceptualization, A.D. and A.L.; methodology, A.D. and L.R.; supervision, A.L. and A.D.; writing—original draft preparation, L.R.; writing—review and editing, A.L. and A.D.; funding acquisition, A.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors wish to thank Sapienza Università di Roma for financial support (project no. RP12218139999A63).

**Data Availability Statement:** Data are contained within the article and Supplementary Materials.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Michaelis, L.; Hill, E.S. The viologen indicators. *J. Gen. Physiol.* **1933**, *16*, 859–873. [[CrossRef](#)]
2. Moss, G.P.; Smith, P.A.S.; Tavernier, D. Glossary of class names of organic compounds and reactivity intermediates based on structure (IUPAC Recommendations 1995). *Pure Appl. Chem.* **1995**, *67*, 1307–1375. [[CrossRef](#)]
3. Ross, J.H.; Krieger, R.I. Synthesis and properties of paraquat (methyl viologen) and other herbicidal alkyl homologues. *J. Agric. Food Chem.* **1980**, *28*, 1026–1031. [[CrossRef](#)]
4. Sartori, F.; Vidrio, E. Environmental fate and ecotoxicology of paraquat: A California perspective. *Toxicol. Environ. Chem.* **2018**, *100*, 479–517. [[CrossRef](#)]
5. Tsai, W.-T. A review on environmental exposure and health risks of herbicide paraquat. *Toxicol. Environ. Chem.* **2013**, *95*, 197–206. [[CrossRef](#)]
6. Stuart, A.M.; Merfield, C.N.; Horgan, F.G.; Willis, S.; Watts, M.A.; Ramírez-Muñoz, F.; Sánchez, U.J.; Utyasheva, L.; Eddleston, M.; Davis, M.L.; et al. Agriculture without paraquat is feasible without loss of productivity—Lessons learned from phasing out a highly hazardous herbicide. *Environ. Sci. Pollut. Res.* **2023**, *30*, 16984–17008. [[CrossRef](#)]
7. Striepe, L.; Baumgartner, T. Viologens and Their Application as Functional Materials. *Chem. Eur. J.* **2017**, *23*, 16924–16940. [[CrossRef](#)]
8. Škorjanc, T.; Shetty, D.; Olson, M.A.; Trabolsi, A. Design Strategies and Redox-Dependent Applications of Insoluble Viologen-Based Covalent Organic Polymers. *ACS Appl. Mater. Interfaces* **2019**, *11*, 6705–6716. [[CrossRef](#)]
9. Li, X.; Yang, J.; Yang, Y.-W. Recent advances of stimuli-responsive viologen-based nanocomposites. *Mater. Chem. Front.* **2023**, *7*, 1463–1481. [[CrossRef](#)]
10. Kanagaraj, M.; Velayutham, D.; Suryanarayanan, V.; Kathiresan, M.; Ho, K.-C. Viologen-based electrochromic materials and devices. *J. Mater. Chem. C* **2019**, *7*, 4622–4637.
11. Shah, K.W.; Wang, S.-X.; Soo, D.X.Y.; Xu, J. Viologen-Based Electrochromic Materials: From Small Molecules, Polymers and Composites to Their Applications. *Polymers* **2019**, *11*, 1839. [[CrossRef](#)] [[PubMed](#)]
12. Feng, F.; Guo, S.; Ma, D.; Wang, J. An overview of electrochromic devices with electrolytes containing viologens. *Sol. Energy Mater. Sol. Cells* **2023**, *254*, 112270. [[CrossRef](#)]
13. Shi, Y.; Wang, G.; Chen, Q.; Zheng, J.; Xu, C. Electrochromism and electrochromic devices of new extended viologen derivatives with various substituent benzene. *Sol. Energy Mater. Sol. Cells* **2020**, *208*, 110413. [[CrossRef](#)]
14. Dashitsyrenova, D.D.; Adonin, S.A.; Gorokh, I.D.; Kraevaya, O.A.; Pavlova, A.V.; Abramov, P.A.; Frolova, L.A.; Sokolov, M.N.; Fedin, V.P.; Troshin, P.A. Memory devices based on novel alkyl viologen halobismuthate(III) complexes. *Chem. Commun.* **2020**, *56*, 9162–9165. [[CrossRef](#)]
15. Zhang, L.; Qiu, Y.; Liu, W.G.; Chen, H.; Shen, D.; Song, B.; Cai, K.; Wu, H.; Jiao, Y.; Feng, Y.; et al. An electric molecular motor. *Nature* **2023**, *613*, 280–286. [[CrossRef](#)]
16. Kandpal, S.; Ghosh, T.; Rani, C.; Tanwar, M.; Sharma, M.; Rani, S.; Pathak, D.K.; Bathia, R.; Sameera, I.; Jayabalan, J.; et al. Bifunctional Application of Viologen-MoS<sub>2</sub>-CNT/Polythiophene Device as Electrochromic Diode and Half-Wave Rectifier. *ACS Mater. Au* **2022**, *2*, 293–300. [[CrossRef](#)] [[PubMed](#)]
17. Wang, S.; Wu, Y.; Li, X.; Zhang, W.; Ma, H. Trace SO<sub>2</sub> Gas Capture in Stable 3D Viologen Ionic Porous Organic Framework Microsphere. *ACS Appl. Mater. Interfaces* **2023**, *15*, 30312–30319. [[CrossRef](#)] [[PubMed](#)]
18. Sun, X.; Zhang, J.; Tan, A.; Fu, Z. A Highly Efficient Near-Infrared-Activated Photocatalyst Based on an Electron-Deficient Copper-Viologen-Polyoxometalate Framework with a Copper {Cu<sub>3</sub>} Cluster Decorated Phosphotungstate as a Building Block. *Cryst. Growth Des.* **2019**, *19*, 6845–6849. [[CrossRef](#)]
19. Sui, Q.; Li, R.; Zhang, Y.; Huang, M.; Wang, T.; Yang, M.; Cao, M.; Hong, X.; Li, B. High-efficient C<sub>3</sub>N<sub>4</sub>-viologen charge transfer systems for promoting photocatalytic H<sub>2</sub> evolution through band engineering. *Int. J. Hydrogen Energy* **2023**, *48*, 16330–16340. [[CrossRef](#)]
20. Ling, Z.; Nugraha, M.I.; Hadmojo, W.T.; Lin, Y.; Jeong, S.Y.; Yengel, E.; Faber, H.; Tang, H.; Laquai, F.; Emwas, A.-H.; et al. Over 19% Efficiency in Ternary Organic Solar Cells Enabled by n-Type Dopants. *ACS Energy Lett.* **2023**, *8*, 4104–4112. [[CrossRef](#)]



21. Liu, Y.; Li, Y.; Zuo, P.; Chen, Q.; Tang, G.; Sun, P.; Yang, Z.; Xu, T. Screening Viologen Derivatives for Neutral Aqueous Organic Redox Flow Batteries. *ChemSusChem* **2020**, *13*, 2245–2249. [[CrossRef](#)] [[PubMed](#)]
22. Ding, J.; Zheng, C.; Wang, L.; Lu, C.; Zhang, B.; Chen, Y.; Li, M.; Zhai, G.; Zhuang, X. Viologen-inspired functional materials: Synthetic strategies and applications. *J. Mater. Chem. A* **2019**, *7*, 23337–23360. [[CrossRef](#)]
23. Das, G.; Skorjanc, T.; Sharma, S.K.; Gándara, F.; Lusi, M.; Rao, D.S.S.; Vimala, S.; Prasad, S.K.; Raya, J.; Han, D.S.; et al. Viologen-Based Conjugated Covalent Organic Networks via Zincke Reaction. *J. Am. Chem. Soc.* **2017**, *139*, 9558–9565. [[CrossRef](#)] [[PubMed](#)]
24. Wang, N.; Kähkönen, A.; Damlin, P.; Ääritalo, T.; Kankare, J.; Kvarnström, C. Electrochemical synthesis and characterization of branched viologen derivatives. *Electrochim. Acta* **2015**, *154*, 361–369. [[CrossRef](#)]
25. Hoffmann, M.; Kärnbratt, J.; Chang, M.H.; Herz, L.M.; Albinsson, B.; Anderson, H.L. Enhanced  $\pi$  conjugation around a porphyrin[6] nanoring. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 4993–4996. [[CrossRef](#)] [[PubMed](#)]
26. Natali, M.; Luisa, A.; Iengo, E.; Scandola, F. Efficient photocatalytic hydrogen generation from water by a cationic cobalt(II) porphyrin. *Chem. Commun.* **2014**, *50*, 1842–1844. [[CrossRef](#)]
27. Gao, P.; Pan, Y.; Han, H.; Gu, Z.; Chen, H.; Wu, Z.; Liu, H.; Peng, S.; Zhang, X.-P.; Zhang, R.; et al. Molecular engineering of  $\pi$ -extended viologens consisting of thiophene-based bridges for electrochromic devices. *J. Mol. Struct.* **2023**, *1288*, 135769. [[CrossRef](#)]
28. Kanwal, I.; Mujahid, A.; Rasool, N.; Rizwan, K.; Malik, A.; Ahmad, G.; Shah, S.A.A.; Rashid, U.; Nasir, N.M. Palladium and Copper Catalyzed Sonogashira cross Coupling an Excellent Methodology for C-C Bond Formation over 17 Years: A Review. *Catalysts* **2020**, *10*, 443. [[CrossRef](#)]
29. Yuan, K.; Zhuang, X.; Fu, H.; Brunklaus, G.; Forster, M.; Chen, Y.; Feng, X.; Scherf, U. Two-Dimensional Core-Shelled Porous Hybrids as Highly Efficient Catalysts for Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* **2016**, *55*, 6858–6863. [[CrossRef](#)]
30. Anderson, H.L.; Walter, C.J.; Vidal-Ferran, A.; Hay, R.A.; Lowden, P.A.; Sanders, J.K.M. Octatetrayne-linked porphyrins: ‘stretched’ cyclic dimers and trimers with very spacious cavities. *J. Chem. Soc. Perkin Trans.* **1995**, *1*, 2275–2279. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.