Challenging Synthesis of a Highly Strained π-Extended Viologen-Based Cyclophane

M. Mustafa Cetin^{1*}

Department of Chemistry, İstinye University, Sarıyer, İstanbul 34396, TÜRKİYE Received: 03/03/2025, Revised: 23/03/2025, Accepted: 24/03/2025, Published: 28/03/2025

Abstract

The challenging synthesis of a highly strained π -extended viologen-based cyclophane is achieved through a simple four-step process using readily available chemicals. The product was characterized by ¹H and ¹³C NMR spectroscopy, HRMS (ESI), and single-crystal X-ray analysis for its solid-state structure. This study thoroughly investigated the synthesis, characterization, and purification of the cyclophane, yielding promising results. These tetracationic cyclophanes have broad applications in molecular recognition, photocatalysis, electrochromic devices, molecular electronics, and more.

Keywords: Cyclophane, viologen, challenging synthesis, supramolecular chemistry, strained and π -extended

Yüksek Gerilimli π-Uzamış Viologen-Bazlı Siklofanın Zorlu Sentezi

Öz

Yüksek gerilimli π -uzamış viologen-bazlı siklofanın zorlu sentezi, basit ve kolayca erişilebilen kimyasallar kullanılarak dört adımlı süreçle gerçekleştirilmiştir. Elde edilen nihai ürün, ¹H ve ¹³C NMR spektroskopisi, HRMS (ESI) ile karakterize edilmiş ve katı hal yapısı tek kristal X-ışını analizi ile belirlenmiştir. Bu çalışma, siklofanın sentezini, karakterizasyonunu ve saflaştırılmasını ayrıntılı bir şekilde incelemiş ve umut verici sonuçlar elde etmiştir. Bu tetrakatiyonik siklofanlar, moleküler tanıma, fotokataliz, elektrokromik cihazlar, moleküler elektronikler ve daha birçok alanda geniş uygulama alanlarına sahiptir.

Anahtar Kelimeler: Siklofan, viologen, zorlu sentez, supramoleküler kimya, gergin ve π -uzamış

1. Introduction

Cyclophanes, cyclic compounds with aromatic units linked by bridging groups, have been extensively studied due to their unique structural features and diverse applications in supramolecular chemistry [1]. Their distinctive architectures impart remarkable electronic and steric properties, making them valuable in various applications, including molecular recognition, catalysis, and material science.

Within the cyclophane family, the viologen-based cyclophanes have emerged as prominent subjects of study due to their unique structural features and versatile applications in supramolecular chemistry. These compounds, characterized by their π -extended structures, exhibit distinctive photophysical and electrochemical properties, making them ideal candidates for host-guest (H–G) interactions, electron transfer processes, and sensor development.

A pivotal study by Berville *et al.* [2] demonstrated the redox-controlled H–G interactions in *bis*-viologen cyclophanes, highlighting their potential in selective guest encapsulation and release mechanisms. Further advancements by Dale *et al.* revealed cooperative reactivity in extended-viologen-based cyclophanes, emphasizing their enhanced reactivity compared to acyclic counterparts [3]. This reactivity is attributed to their unique cyclic structures. The development of selenoviologen-based tetracationic cyclophanes, as reported by Li *et al.* [4], introduced directional electron flow properties, paving the way for applications in molecular electronics and photonics. Additionally, Hassan and his coworkers' overview on zwitterionic viologen-based cyclophanes [5] emphasized their unique electrochemical functionalities, which are crucial for designing advanced materials with specific electronic properties.

Recent innovations [6] have also led to the development of three-dimensional (3D) printable viologen-based ionogels, combining the electrochromic properties of viologens with the structural integrity provided by 3D printing technologies. This advancement holds promise for creating flexible, transparent, and self-healing materials suitable for display and sensor applications. Collectively, these studies highlight the dynamic nature of viologen-based cyclophanes, illustrating their adaptability and potential in various applications, from molecular recognition to advanced material design.

Early synthetic strategies [1] focused on constructing [n]paracyclophanes, where n denotes the number of carbon atoms in the bridge. These methods often involved direct coupling reactions, such as the Bamford-Stevens reaction, leading to the formation of the cyclophane skeleton. Advancements in synthetic methodologies have introduced more efficient and selective routes. For instance, a light-promoted intramolecular Fries-type rearrangement has been developed [7], enabling the preparation of diverse cyclophane structures under mild conditions without the need for catalysts or additives. Recent reviews [5] have highlighted the evolution of cyclophane synthesis, emphasizing the development of new strategies and the exploration of their functional properties. These studies have expanded the scope of cyclophane applications, particularly in the development of novel materials with unique electronic and optical characteristics. In the case of viologen-based cyclophanes, Berville *et al.* [2] have synthesized flexible *bis*-viologen cyclophanes, demonstrating redox-controlled H–G interactions. In 2016, Dale *et al.* [3] developed an extended-viologen-based cyclophane with

strained triple bonds between pyridinium rings, exhibiting cooperative reactivity. Currently, Beldjoudi has provided an overview of zwitterionic viologen-based cyclophanes [5], highlighting their unique electrochemical functionalities. In addition, Li *et al.* have introduced [4] selenoviologen-based tetracationic cyclophanes with rigid electron-deficient cavities, synthesized via S_N2 reactions, and highlighted their favorable redox properties. All these studies underscore the versatility of viologen-based cyclophanes in supramolecular chemistry, paving the way for innovative applications in various technological domains.

Tetracationic cyclophanes are versatile molecular structures with a broad spectrum of applications across various fields. Key areas of their employment include: (i) Molecular **Recognition and Sensing:** These cyclophanes can selectively recognize and bind specific molecules, such as amino acids and adenosine derivatives, through electrostatic and π - π For example, tetraphenylethene-based tetracationic cyclophanes have interactions. demonstrated selective recognition capabilities in aqueous environments [8]; (ii) Photocatalysis and Energy Conversion: In the realm of photocatalysis, tetracationic cyclophanes have been utilized to enhance visible-light-driven hydrogen production. Selenoviologen-based tetracationic cyclophanes, for instance, exhibit strong absorption in the visible range and facilitate efficient hydrogen evolution under visible light irradiation [8]; (iii) *Electrochromic* Devices: These compounds are employed in electrochromic devices due to their reversible redox properties, enabling them to switch between different colors upon electrical stimulation. The green box, a selenoviologen-based tetracationic cyclophane, has been highlighted for its electrochromic behavior and potential applications in such devices [8]; (iv) Host-Guest Chemistry and Molecular Encapsulation: Tetracationic cyclophanes can encapsulate guest molecules, forming stable host-guest complexes. This property is valuable in various applications, including molecular separation and sensing. A dynamic tetracationic macrocycle has been shown to exhibit photoswitchable molecular encapsulation, allowing controlled binding and release of guest molecules upon exposure to light and heat [8,9]; (v) Environmental Remediation: These cyclophanes are capable of sequestering polyaromatic hydrocarbons (PAHs) through complexation, offering potential solutions for environmental pollution. They form electron donor-acceptor complexes with various PAHs, enabling their detection, separation, and removal from liquid or gaseous samples [8,9]; (vi) Bioimaging: Tetracationic cyclophanes with near-infrared (NIR) photoluminescence are suitable for bioimaging applications due to the deep tissue penetration and low photodamage of NIR light. A divinylanthracene-containing tetracationic cyclophane has been developed as a probe for live-cell imaging, demonstrating effective uptake and fluorescence in breast cancer cell lines [8,10]. These diverse applications emphasize the significant potential of tetracationic cyclophanes in advancing technologies related to sensing, energy conversion, environmental remediation, and biomedical imaging.

Building upon the importance of cyclophanes and their synthetic protocols highlighted in the literature, this work aims to push the boundaries of cyclophane synthesis. We report the successful synthesis of a strained π -extended viologen-based cyclophane through a novel and straightforward four-step process. This approach utilizes simple and readily accessible chemicals, offering a more efficient route to such complex compounds. The synthesis, characterization, and purification of the π -extended viologen-based cyclophane have been thoroughly investigated, yielding promising results that open up new avenues for future research and application in molecular electronics and beyond. In a world increasingly driven by advanced materials and innovative molecular design, the development of this new synthetic pathway for viologen-based cyclophanes not only fills a crucial gap in the field but also lays the groundwork for future breakthroughs in material science, sensing technologies, and molecular recognition. With these advances, we are on the cusp of creating highly functional, versatile compounds capable of transforming industries ranging from electronics to environmental sensing, and beyond.

2. Materials and Methods

General Methods, Materials and Instrumentation

All chemicals and reagents were purchased from commercial suppliers (Sigma, Aldrich, Alfa Aesar or Fisher) and used without further purification. The dry solvents (*e.g.*, MeCN) used in the synthetic protocols were directly obtained from the Solvent Purification System built by Pure Process Technology (PPT), or were either freshly distilled over CaH₂ under nitrogen or dried over molecular sieves (*e.g.*, CH₂Cl₂). Compounds 1 and 2 (Scheme 1) were prepared according to previous literature procedure [11] with slight modifications. All reactions were carried out in dried glassware under an argon and/or a nitrogen atmosphere.

To remove solvents and other volatile impurities under reduced pressure, a Büchi Rotavapor R-114 and an Edwards oil pump were used.

Thin layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). Column chromatography was carried out on silica gel 60F (Merck 9385, 0.040–0.063 mm). High-resolution mass spectra were measured on an Agilent 6210 Time of Flight (TOF) LC–MS, using an ESI source, coupled with Agilent 1100 HPLC stack, using direct infusion (0.6 mL/min). Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 500 and Agilent DD MR–400 spectrometers, with working frequencies of 500 and 400 MHz, respectively. Chemical shifts were reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CD₃CN: δ 1.94 ppm for ¹H NMR, and 1.32 and 118.26 ppm for ¹³C NMR). For the single crystal X-ray crystallography, single crystal X-ray diffraction studies were measured on a Bruker APEX-II4 diffractometer using Mo-K α radiation ($\lambda = 0.71079$ Å) or Cu-K α radiation ($\lambda = 1.5407$ Å) equipped with an Oxford cryostream variable temperature device.

Synthesis and Characterization



Scheme 1. The straightforward four-step protocol to achieve the desired π -extended viologenbased cyclophane, 4•4PF₆ (*in blue*).

The detailed synthetic procedures and structural characterization data for the intermediates and desired compounds are presented. According to the synthetic procedures, a 200 mL ethanol solution containing potassium hydroxide (0.480 g, 8.00 mmol) was prepared and placed in an ice bath. To this solution, 4-pyridylaldehyde (4.28 g, 40.0 mmol) was added, while stirring magnetically. Over a period of 2 hours, phenylacetaldehyde (10.6 g, 88.0 mmol) in 10 mL ethanol was slowly added dropwise. After stirring the reaction mixture at room temperature for 24 hours, hydroxylamine hydrochloride (11.1 g, 160. mmol) was introduced into the mixture. The resulting mixture was then refluxed for 2 hours. Once the reaction was complete, the mixture was evaporated to dryness. The residue was then suspended in 300 mL of water, and the pH was adjusted to alkaline using a 10% aqueous solution of sodium hydroxide. The white solid formed was collected by filtration, washed sequentially with water and ethanol, and dried under vacuum. The yield of 3,5-diphenyl-4,4'-bipyridine (1) was 11.1 g (90.0%), and the melting point range, ¹H and ¹³C NMR, and mass analyses matched with the literature [11].

Upon synthesis of compound 1 in high yield, 2,7-diazadibenzo[e,l]pyrene (2) was synthesized utilizing the following protocol: A 4.00 g (14.0 mmol) sample of compound 1 was dissolved in 80 mL of 5% hydrochloric acid. The solution was then diluted to a final volume of 1 L and exposed to 300 nm UV light at room temperature for 24 hours, with stirring in air. After irradiation, 28% aqueous ammonia was added to adjust the pH to 8, and the resulting precipitate was collected by filtration. The filtrate was concentrated under vacuum to obtain a second crop.

The combined solids were recrystallized from acetic acid, yielding the pure product as a yellow powder. The yield of compound **2** (π -extended viologen) was 3.83 g (97.0%), and the melting point (> 300), ¹H and ¹³C NMR, and mass analyses matched with the literature [11].

Obtaining the π -extended viologen (2) in the previous step led the synthesis of 3-2PF₆ possible. 2,7-Bis(bromomethyl)naphthalene (500 mg, 1.59 mmol) was added to dry MeCN (200 mL) in a 250 mL round-bottomed two-neck flask and the resulting mixture was refluxed under nitrogen atmosphere while stirring until all the solid material dissolved. While the reaction mixture was stirring at reflux, a solution of compound 2 (72.1 mg, 0.237 mmol) in MeCN (200 mL) was added slowly over 10 hours via a syringe pump (20 mL/h). After 2 hours, however, a yellow precipitate began to appear, indicative of 3.2Br formation. The reaction mixture was refluxed under N₂ overnight, followed by addition of NH₄PF₆ (~400-600 mg) in MeCN (40 mL). The reaction mixture was stirred at reflux for an additional 2 hours, and cooled to RT. The solvent was removed under reduced pressure using a rotary evaporator and the crude product was obtained. The crude solid was dissolved in deionized water (500 mL) and the pale yellow precipitate of 3.2PF₆ was collected by filtration, and washed with additional deionized water (2x 200 mL) and CH₂Cl₂ (2x 100 mL) in order to remove both the unreacted starting materials and excess of NH₄PF₆; (123 mg, 54.0%); ¹H NMR (500 MHz, CD₃CN, 298 K) δ 10.2 (s, 4H), 8.20 (d, J = 3.8 Hz, 4H), 7.47 (d, J = 3.8 Hz, 4H), 7.23 (d, J = 4.2 Hz, 8H), 7.19 (d, J = 4.1 Hz, 8H), 5.97 (s, 4H), 4.56 (s, 4H); ¹³C NMR (125 MHz, CD₃CN, 298 K) δ 146.2, 135.1, 134.7, 129.2, 128.9, 128.5, 127.2, 125.7, 124.2, 62.8, 33.5; HRMS (ESI) m/z calcd for $C_{38}H_{28}Br_2F_6N_2P^+$ [*M-PF*₆]⁺ 817.0251, found 817.0266.

In the very final protocol, the sample of **3**•2PF₆ (500 mg, 0.520 mmol) was dissolved in dry MeCN (100 mL) in a 250 mL round-bottomed two-neck flask and the resulting mixture was refluxed under nitrogen atmosphere while stirring until all the solid material dissolved. To this solution, a commercially available pyrene (105 mg, 0.520 mmol) was added as templating agent. Upon templating, a solution of compound **2** (158 mg, 0.520 mmol) in dry MeCN (100 mL) was added slowly over 2 hours via a syringe pump (4 mL/h). The reaction mixture was refluxed 17 hours upon addition under N₂ atmosphere. Upon completion, the reaction mixture was cooled to RT. The solvent was removed under reduced pressure using a rotary evaporator and very small amount of the crude product (~2-3 mg) was obtained. Without any further purification, the product **4**•4PF₆ was confirmed by the NMR spectroscopy and the sample was left for the crystallization via slow vapor diffusion of ¹Pr₂O into dry MeCN; (2.00 mg, 0.276%); ¹H NMR (500 MHz, CD₃CN, 298 K) δ 10.1 (s, 8H), 8.70 (d, J = 3.4 Hz, 8H), 8.30 (d, J = 3.2 Hz, 8H), 7.60 (s, 8H), 6.41 (s, 8H); ¹³C NMR (125 MHz, CD₃CN, 298 K) δ 146.2, 136.0, 134.9, 129.8, 129.0, 128.7, 127.6, 125.9, 63.7; HRMS (ESI) m/z calcd for C₆₀H₄₀F₁₂N₄P₂²⁺ [*M*-(*2PF*₆)]²⁺ 553.1263, found 553.1217.

Synthesizing such complex and highly strained π -extended viologen-based cyclophane was very challenging due to the larger size of the π -extended polycyclic aromatic hydrocarbons (PAHs), which introduce significant strain on the cyclophane ring, making the synthesis more difficult. The synthesis of the molecule with such a low yield has also been justified. The isolated yield of the desired product, 4•4PF₆, with styrene-templated protocol has been increased to 2% in the second trial. Despite these inherent challenges, our synthetic approach successfully enabled the creation of this structurally intricate and visually striking cyclophane, using a commercially available pyrene unit as the template.

3. Results and Discussion

Building upon the well-established importance of cyclophanes and their synthetic strategies [12–14], this study primarily aims to advance the field forward by introducing a novel synthetic route for π -extended viologen-based cyclophanes for their photo- and electrochromic properties (photoluminescense) as well as the reversible redox properties. Such molecules are highly important for the science and technology applications such as molecular electronics, electrochromic materials, supramolecular assemblies, redox sensors, fuel cells, batteries, and more [8–10].

In this context, our research group successfully synthesized a highly strained π -extended viologen-based cyclophane through a straightforward and efficient four-step process. While the synthetic steps themselves were relatively simple, the final step—obtaining the desired compound 4•4PF₆—proved to be exceptionally challenging due to the high strain and complex structural nature of the π -extended viologen cyclophane, which also led to a low isolated yield of the desired compound. Despite initial expectations that combining the PF₆⁻ salt of dicationic 3•2PF₆ with compound 2 would be nearly impossible, this study provides compelling evidence for the successful synthesis of the highly strained and intricate compound 4•4PF₆. The resulting structure was thoroughly characterized using NMR spectroscopy (Figure 1), high-resolution mass spectrometry (HRMS, ESI), and the solid-state arrangement was confirmed through single-crystal X-ray diffraction analysis (Figures 2–6).



Figure 1. Annotated and simplified (a) ¹H NMR spectrum (500 MHz, CD₃CN, 298 K), and (b) ¹³C NMR spectrum (125 MHz, CD₃CN, 298 K) of 4•4PF₆.

The synthesis of compounds 1, 2, $3 \cdot 2PF_6$, and the cyclophane $4 \cdot 4PF_6$ is outlined in Scheme 1. The cyclophane was synthesized using a styrene unit as the templating agent. The reaction between $3 \cdot 2PF_6$ and compound 2, in the presence of the template, was carried out in a 1:1:1 ratio in dry acetonitrile (MeCN) and refluxed for 17 days. Following the reaction, the solvent was removed and the crude mixture was washed with deionized water (H₂O) and dichloromethane (CH₂Cl₂), yielding a clean crude solid. The formation of the desired $4 \cdot 4PF_6$ was confirmed through a combination of ¹H and ¹³C NMR spectroscopy (Figure 1) and HRMS (ESI).

According to the annotated ¹H and ¹³C NMR spectra of $4 \cdot 4PF_6$, five distinct proton and nine distinct carbon signals were observed, as anticipated. The singlet near the positively charged nitrogen atom (ammonium unit) confirms the significant deshielding effect on this proton, resulting in a downfield shift (10.1 ppm). The two protons, A and B, exhibited two separate doublets with coupling constants (*J*) of 3.4 Hz and 3.2 Hz, respectively. The singlet

observed at 6.41 ppm is attributed to the eight $-CH_2$ protons, which are highly deshielded, leading to the downfield shift of the signal due to the ammonium unit. Since the desired molecule is highly symmetrical, only nine distinct carbon signals were observed in the spectrum, corresponding to nine different carbons. The carbon C and D were highly deshielded and the signals for these carbons appeared as downfield shifts at 63.7 and 146.2 ppm, respectively. Both ¹H and ¹³C NMR spectra of 4•4PF₆ confirmed the formation of the desired product.

Single crystals of $3 \cdot 2PF_6$ (Figures 2 and 3) and $4 \cdot 4PF_6$ (Figures 4–6) were grown by vapor diffusion of iPr_2O into a MeCN solution for 3–4 days. Single crystal X-ray studies of both compounds were undertaken to reveal the relationship between the structures of the compounds and their packing in the crystalline state. The presence of a phenyl units with π -extended viologens has very significant influence on the overall packing of these molecules.



Figure 2. Crystallographic analysis of **3**•2PF₆ in (a) in an asymmetric unit, (b) view along with *a*-axis, (c) view along with *b*-axis, and (d) view along with *c*-axis.

Compound **3**•2PF₆ has triclinic / space group = *P*-1 along with colorless crystals (Z=1), a = 7.6010 Å, b = 8.2318 Å, c = 15.1772 Å, $\alpha = 91.324^{\circ}$, $\beta = 93.255^{\circ}$, $\gamma = 110.421^{\circ}$, V = 887.59 Å, and d = 1.800 g/cm³, and the molecule has very strong π - π interactions between both phenyl rings and the π -extended viologen units (**Figure 3**) that provides a very well organized packing in the solid state.



Figure 3. Strong π-π interactions (3.6 Å) between, (a) phenyl rings of two 3•2PF₆ units, and
(b) the π-extended viologens of two 3•2PF₆ units. (c) The resulting packing of 3•2PF₆ in solid state.

On the other hand, the desired product **4**•4PF₆ (**Figure 4**) has orthorhombic / space group = P 4/n b m (125) along with red crystals (Z=4), a = 24.224 Å, b = 24.224 Å, c = 11.613 Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 6814.41 Å, and d = 1.569 g/cm³, and the molecule has very strong π - π interactions (**Figure 5**) that provides a very well organized packing (**Figure 6**), like baklava slice, in the solid state. In **Figure 5b**, it can be seen that the desired compound has a highly strained structure due to the bond angles of 110°, causing the structure to bend significantly. This also explains why the isolated yield of the desired compound is very low. Without the templated protocol, synthesis of **4**•4PF₆ was not achievable.



Figure 4. Crystallographic analysis of **4**•4PF₆ in (a) view along with *a*-axis, (b) view along with *b*-axis, and (c) view along with *c*-axis.



Figure 5. Strong π - π interactions (a) phenyl rings (3.6 Å) and the π -extended viologens (3.5 Å) of the two **4**•4PF₆ units. (b) The resulting highly-strained unit of **4**•4PF₆ in the solid state.



Figure 6. A very well organized packing of $4 \cdot 4PF_6$ due to strong $\pi \cdot \pi$ interactions among phenyl rings and the π -extended viologen units.

As previously discussed, the synthesis of such a complex and highly strained π -extended viologen-based cyclophane presents significant challenges due to the larger size of the π -extended polycyclic aromatic hydrocarbons (PAHs), which induce substantial strain on the cyclophane ring (**Figure 5b**), complicating the synthesis of such systems. Despite the inherent difficulties, our synthetic protocol successfully facilitated the creation of this structurally intricate and aesthetically remarkable cyclophane.

4. Conclusions

In conclusion, a novel π -extended viologen unit was designed and synthesized from readily available materials via a concise, three-step route. This synthetic approach is characterized by its simplicity and high efficiency. The successful synthesis of this aesthetically striking viologen unit facilitated the inherently challenging synthesis of the complex and highly strained π -extended viologen-based cyclophane. The desired viologen unit and the product was characterized by ¹H and ¹³C NMR spectroscopy, HRMS (ESI), and the solid-state structure was determined by single-crystal X-ray analysis. Utilizing easily accessible chemicals, this new method offers a streamlined and significantly improved approach to synthesizing such complex compounds compared to traditional methods. In this study, the synthesis, characterization, and purification of the π -extended viologen-based cyclophane were meticulously investigated, yielding promising results. These findings open avenues for further research in fields such as

molecular electronics and advanced material design. Not only does this new synthetic route address a gap in cyclophane chemistry, but it also establishes a foundation for future innovations in material science, sensor development, and molecular recognition. The successful synthesis of these compounds marks a critical step toward the development of highly functional and versatile materials with the potential to revolutionize industries ranging from electronics to environmental monitoring. These viologen units and the novel cyclophane molecule demonstrate excellent electrochemical properties and high thermal stability. Additionally, the π -extension introduces novel photophysical and electrochemical characteristics, positioning these compounds for potential applications in both traditional viologen-based fields and molecular electronics. To demonstrate the versatility of this new platform due by the extended viologen units, further photophysical and electrochemical property studies, including photoluminescence and altered redox potentials, and optimization of synthetic protocols are still being conducted in our laboratories.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

Author contributions

This manuscript and related documents regarding writing, reviewing, editing, data analysis, and other details have been prepared by M. Mustafa Cetin (M.M.C.).

Conflict of interest

There are no conflicts to declare. The author also declares no competing financial interest.

Acknowledgement

The author thanks to Prof Sir Fraser Stoddart for his endless support in the discussion of the obtained results, sage advice, insightful criticism and discussion, and patient encouragement during this work. The author greatly thanks to his wife Mine and sons Metehan Arda and Mert Kaan for willingly giving him time to complete this work.

References

- [1] Kotha, S., Shirbhate, M. E., & Waghule, G. T. (2015). Selected synthetic strategies to cyclophanes. Beilstein Journal of Organic Chemistry, 11, 1274-1331.
- [2] Berville, M., Karmazin, L., Wytko, J. A., & Weiss, J. (2015). Viologen cyclophanes: redox controlled host–guest interactions. Chemical Communications, 51, 15772-15775.
- [3] Dale, E. J., Ferris, D. P., Vermeulen, N. A., Henkelis, J. J., Popovs, I., Juríček, M., Barnes, J. C., Schneebeli, S. T., & Stoddart, J. F. (2016). Cooperative reactivity in an extended-viologen-based cyclophane. Journal of the American Chemical Society, 138(11), 3667-3670.
- [4] Li, N., Li, Y., Wang, Z., Cao, T., Liu, C., Wang, H. Li, G., & He, G. (2024). Directional Electron Flow in a Selenoviologen-Based Tetracationic Cyclophane for Enhanced

Visible-Light-Driven Hydrogen Evolution. Angewandte Chemie International Edition, 63(47), e202410525.

- [5] Hassan, Z., Lahann, J., Bräse, S. (2024). Cyclophanes as Emerging Materials From Synthesis To Functions. Advanced Functional Materials, 34(47), 2410027.
- [6] Han, Z., Yuan, H., Zhang, H., Zhang, Y., Lv, J., Zhang, X., Wang, Z., Li, N., Liang, C., Yan, N., Maximov, M., Huang, Y., & He, H. (2025). Three-Dimensional Printable Viologen-Based Ionogel for Visible Sensing and Display, Chinese Chemical Society Chemistry, 7, 854-866.
- [7] Szcześniak, P. & Furman, B. (2023). Diversity-oriented synthesis of medium-sized cyclophanes via the photo-fries rearrangement of N-aryl lactams, Reaction Chemistry and Engineering, 8, 1923-1929.
- [8] Li, Y., Li, N., Li, G., Yi, Q., Zhang, M., Zhang, L. Guo, Q.-H. & He, G. (2023). The Green Box: Selenoviologen-Based Tetracationic Cyclophane for Electrochromism, Host–Guest Interactions, and Visible-Light Photocatalysis. Journal of the American Chemical Society, 145(16), 9118-9128.
- [9] Stoddart, J. F., Barnes, J. C. & Juri, M. (2016). Tetracationic cyclophanes and their use in the sequestration of polyaromatic hydrocarbons by way of complexation. United States Patent, US9290495B2.
- [10] Sun, S.-K., Wang, H.-F. & Yan, X.-P. (2018). Engineering Persistent Luminescence Nanoparticles for Biological Applications: From Biosensing/Bioimaging to Theranostics. Accounts of Chemical Research, 51(5), 1131-1143.
- [11] Yang, Y., Liu, D., Song, M., Shi, D., Liu, B., Cheng, K., Lu, Y., Liu, H., Yang, M., Wang, W., Li, J., & Wei, J. (2017). Facile Synthesis of p-Extended Viologens: Electron-Deficient Polycyclic Aza-aromatics. Chemistry A European Journal, 23(31), 7409-7413.
- [12] Dale, E. J., Vermeulen, N. A., Juríček, M., Barnes, J. C., Young, R. M., Wasielewski, M., R. & Stoddart, J. F. (2016). Supramolecular Explorations: Exhibiting the Extent of Extended Cationic Cyclophanes, Accounts of Chemical Research, 49(2), 262-273.
- [13] Ghasemabadi, P. G., Tieguang, Y., & Bodwell, G. J. (2015). Cyclophanes containing large polycyclic aromatic hydrocarbons, Chemical Society Reviews, 44, 6494-6518.
- [14] Watson, M. D., Jäckel, F., Severin, N., Rabe, J. P., & Müllen K. (2004). A Hexa-perihexabenzocoronene Cyclophane: An Addition to the Toolbox for Molecular Electronics, Journal of the American Chemical Society, 126(5), 1402-1407.