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A series of polyaromatic hydrocarbons conjugated viologens: synthesis, supramolecular structures in solid state, and electrochemical and photophysical properties

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ABSTRACT

Viologens have extensive applications in supramolecular chemistry and materials science. An efficient approach to tune the electrochemical and photophysical properties as well as supramolecular interactions of a viologen unit is to extend its conjugation extent. In this article, a series of conjugated viologens have been designed and synthesized by incorporating polyaromatic hydrocarbons into 4,4′-bipyridyl unit. X-ray crystallographic analyses revealed that they assembled into various supramolecular structures in solid state. Cyclic voltammetry, and UV–vis and fluorescence spectroscopy studies indicated that they displayed distinctive electrochemical and photophysical properties, which were different from non-conjugated viologens. Furthermore, a correlation between reduction potentials and the dihedral angles between bipyridyl unit and polyaromatic moieties was also revealed.

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1. Introduction

Viologens, 1,1′-disubstituted 4,4′-bipyridylium salts, have been widely utilized in supramolecular chemistry and materials science over the last few decades because of their electron-deficient feature and excellent electrochemical properties. Currently a myriad of viologen-based systems including host-guest complexes,[1] interlocked supermolecules,[2] sensors,[3] molecular machines,[4] supramolecular polymers,[5] solar cell prototype,[6] and organic electrochromic materials,[7] have been well established. In addition, novel structures consisting of multiple viologen units such as viologen oligomers,[8] dendrimers,[9] and even polymers[10] have also been reported recently. However, as far as electrochemical and optical properties are concerned, these compounds still exhibit similar feature as the simplest viologen, namely paraquat or 1,1′-dimethyl-4,4′-bipyridinium (DMBP) because the viologen units in these molecules are isolated by unconjugated substituents, usually alkyl or oligoglycol chains. In this context, tuning the electrochemical and optical properties of viologen is highly desired, especially for electronic materials. Incorporation of conjugated segments into viologen unit should be an efficient approach to change the electrochemical and optical properties of viologens. Moreover, extended conjugation of viologen unit could delocalize its positive charger from bipyridyl unit into the conjugated substituents and therefore might result in distinctive supramolecular interactions. However, examples for viologens with extended conjugation are very few.[11] The obtention of this type of viologens and detailed investigation on their properties should be beneficial not only to supramolecular chemistry but also to materials science. In this article, we report a series of extendedly conjugated viologens, which were constructed by incorporating polyaromatic moieties to 1′- nitrogen of 1-methyl-4,4′-bipyridin-1-ium (Scheme 1). The crystal structures of most of them and their precursors have been resolved, which revealed that they adopted different supramolecular structures in the solid state. Furthermore, they were found to exhibit different electrochemical and optical properties from unconjugated viologens. A structure-reduction potential relationship was also revealed.

2. Results and discussion

As an effective approach to synthesize 1,1′-diarylsubstituted-4,4′-bipyridylium compounds, Zincke reaction was used to prepare the target viologens.[12] The synthesis of **T1** and **T2** was provided in Scheme 2 as a representative. Refluxing Zincke salt **1** with 2-aminonaphthalene generated compound **T1**, which was further methylated by iodomethane to give compound **T2** in almost

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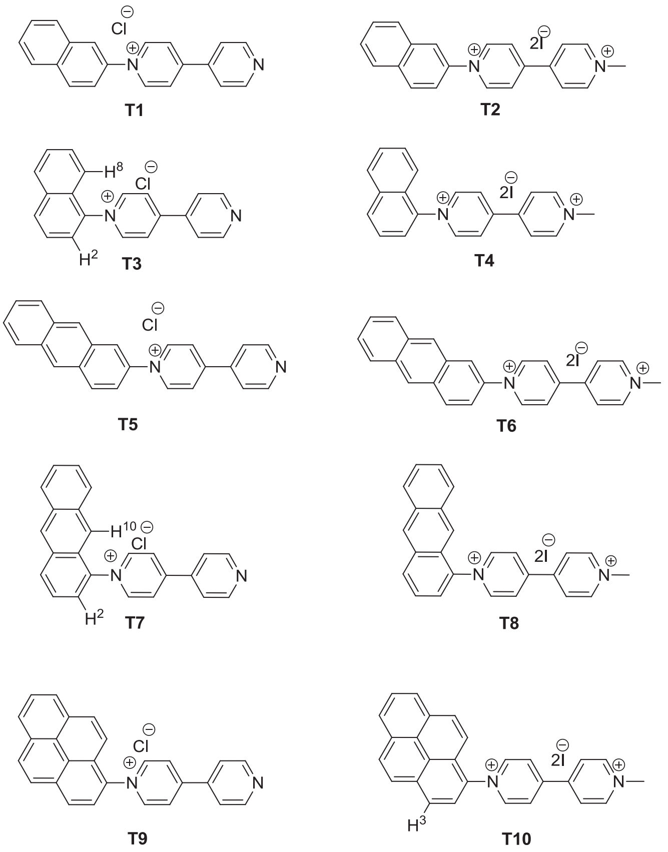
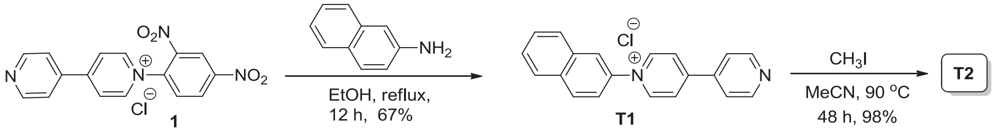


Scheme 1. Chemical structures of the conjugated viologens and their precursors studied in this work.

quantitative yield. It should be noted that ion-exchange occurred during the process of methylation, which led to full iodide salt of **T2**, not mixed salt with one iodide and one chloride, as revealed by crystallographic analyses (vide infra) and elemental analyses. Compounds **T3**–**T10** were prepared following the same procedure but using corresponding amines, respectively.



Scheme 2. Synthesis of compounds **T1** and **T2**.

The single crystals of **T1**–**T5**, **T7**, **T8**, and **T10** suitable for X-ray crystallographic analysis were grown by slow evaporation of their solutions in ethanol (for **T7**) or methanol (for the others) at room temperature.[13] Comparison of their crystal structures revealed that they adopted different supramolecular structures in solid state, which are illustrated as follows and the crystallographic data are provided in Supplementary data.

As revealed by the crystal structure of **T1**, its two pyridine rings are almost coplanar (torsion angle 2.0°) and the dihedral angle between the pyridine ring and naphthalene moiety is 44.3° (Fig. S1 in Supplementary data). **T1** adopted a head-to-tail packing in solid state, in which the electron-deficient 4,4′-bipyridin-1-ium (BPI) units stacked with the relative electron-rich naphthalene moiety in an offset face-to-face manner. The distance between the plane of BPI and the plane of naphthalene moiety is 0.35 nm, which is a typical distance for aromatic stacking. Dictating by such stacking, a one-dimensional (1D) extended packing of **T1** along crystallographic a-axis generated (Fig. 1a). Interestingly, the methylated product of **T1**, that is, compound **T2**, adopted different packing style in solid state (Fig. 1b). **T2** did not adopt the head-to-tail stacking manner of **T1**. Instead, a zig-zag arrangement was observed. In this way, only one pyridylium ring of the 4,4′-bipyridin-1,1′-diium (BPD) unit was found to stack with naphthalene moiety with a mean distance of 0.34 nm. Different from that of **T1**, the two pyridylium rings of **T2** were not coplanar anymore. They had a torsion angle of 30.3°, which could be attributed to the electrostatic repulsion between them. Furthermore, the dihedral angle between the plane of naphthalene moiety and its neighboring pyridylium ring decreased to 43.0° (Fig. S2 in Supplementary data).

The difference between **T3** and **T1** is that in the former the naphthalene moiety is 1-substituted whereas in the latter it is 2-substituted. In the solid state of **T3** (Fig. 2a–b), while the two pyridine rings still kept almost coplanar as that of **T1** (torsion angle 9.4°), its naphthalene moiety was perpendicular to the plane of BPI (the dihedral angle being 89.4°, see Fig. S3 in Supplementary data), which was almost twice of that in **T1**. It is reasonable because under such conformation the steric hindrance between the α-H of pyridylium and H^2 and H^8 of naphthalene moiety can be minimized. This conformation made **T3** to adopt a totally different packing style from **T1**. In this system, no stacking between BPI unit and naphthalene moiety was observed. In contrast, the BPI units stacked each other in an offset face-to-face and head-to-tail manner (with an average distance of 0.37 nm). The naphthalene moieties also adopted an offset face-to-face stacking each other. Both the stackings led to a linearly extended packing (Fig. 2a). As for **T4**, an almost perpendicular arrangement of naphthalene moiety and BPD unit (dihedral angle being 83.6°) also existed (Fig. S4 in Supplementary data). Unexpectedly, in the assembling structure of **T4** in solid, although electrostatic repulsion might arise, weak aromatic stacking with a distance of 0.39 nm was observed between the methylated pyridylium units. Different from that of **T2**, only intermolecular $C{-}H\cdots\pi$ interaction was observed between α-H of its pyridylium ring and the naphthalene moiety, and no aromatic stacking existed between them (Fig. 2).

Compound **T5** adopted quite similar conformation and packing style as that of **T1** (Fig. 3 and Fig. S5 in Supplementary data). Head-to-tail stacking between BPI unit and anthracene moiety in an offset manner was observed. Its two pyridine rings were almost coplanar (torsion angle 3.1°) and the dihedral angle between it and naphthalene moiety was 40.2°. Attempt to grow single crystals of **T6** suitable for crystallographic analysis was unsuccessful. It was anticipated that its solid structure should be similar to that of **T2** due to their similar chemical structures.

Similar to that of **T3**, in the crystals of compound **T7** the steric hindrance between the α-H of pyridine ring and H^2 and H^{10} of anthracene moiety resulted in a dihedral angle of 70.1° between the plane of BPI and anthracene moiety (Fig. S6 in Supplementary data). The head-to-tail stacking between BPI units and the face-

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