



Review

Conjugated radical cation dimerization-driven generation of supramolecular architectures



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ABSTRACT

This paper summarizes the recent advance in utilizing conjugated radical cation dimerization (CRCD) for constructing new unimolecular, such as foldamers, and supramolecular ordered structures, such as three-dimensional supramolecular polymers and two-dimensional supramolecular organic framework. Particularly, the stacking or dimerization of tetrathiafulvalene and 4,4'-dipyridium subunits has been highlighted, and the approaches for enhancing the stability of their radical cation dimers have been discussed.

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1. Introduction

Stacking is a common phenomenon for conjugated molecules or segments. The driving force is usually electrostatic attraction between electron-rich aromatic donor(s) and electron-deficient aromatic acceptor(s) or solvophobicity, as observed in water for the base pairs of DNA and the aromatic units of proteins. One unconventional stacking pattern involves the homodimerization of conjugated radical cations, which has been demonstrated to be driven by the inherent multicenter covalent π - π bonding of the radical species or the electrostatic attraction of paired anions in the solid state [1]. In 1964, Kosower and co-workers reported the dimerization of viologen (V^{2+}) (1) radical cation [2], and in 1979, Bozio and co-workers described the dimerization of tetrathiafulvalene (TTF) (2) radical cation [3] (Fig. 1). However, the stability of both prototypical radical cation dimers was low and thus they had been observed only in the solid state or in concentrated solutions at low temperatures. In the past decade, several strategies have been developed to enhance this self-binding motif of the $V^{\bullet+}$ and $TTF^{\bullet+}$ radical cations, which include using a rigid macrocycle or capsule to encapsulate the dimer [4], holding two radical cation units in place with a preorganized framework [5], and stabilizing the dimer

utilizing mechanical bonding in interlocked systems [6]. In addition to the enhanced stability in both organic and aqueous media, the dimerization of the $V^{\bullet+}$ and $TTF^{\bullet+}$ radical cations can be conveniently monitored by recording the absorption of the dimers in the visible light area. As a result, this unique non-covalent interaction has been developed as a new useful driving force for the construction of supramolecular architectures. This short review summarizes the recent advance in this field.

2. Intramolecular dimerization: foldamers

Solvophobicity driven aromatic stacking usually occurs in polar or less polar solvents, but is weak in the so-called “good” solvents, such as chloroform. CRCD can take place in nearly all solvents of low and high polarity and thus provides a new approach to designing supramolecular systems. Becher and co-workers reported that $TTF^{\bullet+}$ units incorporated in a macrocycle could undergo strong intramolecular stacking in acetonitrile [7]. Hasegawa and co-workers also found that the two $TTF^{\bullet+}$ units in naphthalene-based $3^{2(\bullet+)}$ (Fig. 2) was forced to arrange in a face-to-face style and formed a stable intramolecular dimer in a 1:1 mixture of dichloromethane and acetonitrile, which was supported by the appearance of a typical absorption around 732 nm in the absorption spectrum [8]. We recently found that intramolecular hydrogen bonding-induced preorganization of $4^{2(\bullet+)}$ (Fig. 2) could drive the two appended $TTF^{\bullet+}$ units to stack intramolecularly into $(TTF^{\bullet+})_2$ in less polar solvents like dichloromethane [9–11].

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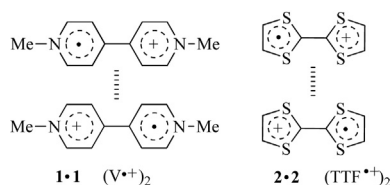


Fig. 1. The structure of dimer of viologen (1) and TTF (2) radical cation.

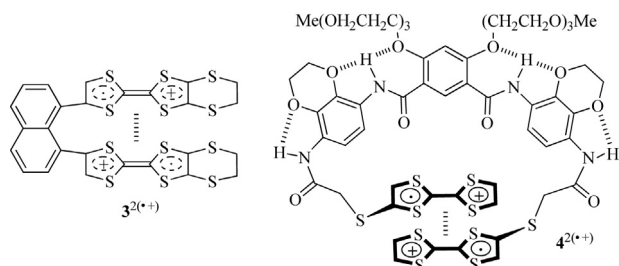


Fig. 2. The structure of radical cations $3^{2(+)}$ and $4^{2(+)}$, highlighting the intramolecular stacking of the TTF^{•+} units.

Successive stacking of the TTF^{•+} subunits can take place for linear molecules that contain multiple TTF subunits. For example, Misaki and co-workers showed that the two inner TTF^{•+} subunits of compound $5^{4(+)}$ (Fig. 3) could stack from both sides in benzonitrile [12]. Amabilino and coworkers demonstrated that, upon one-electron oxidation of the TTF subunits, the resulting TTF^{•+} subunits of polymer **P6** (Fig. 3) also underwent intramolecular stacking in benzonitrile [13].

Such intramolecular stacking has also been observed for viologen derivatives. For example, Bucher and co-workers prepared viologen radical cation derivative $7^{2(+)}$ (Fig. 4) [14] and found that in DMF or DMSO, the two V^{•+} subunits underwent intramolecular stacking to produce a folded conformation. Bucher *et al.* also reported that ferrocene-derived biradical cation $8^{2(+)}$ (Fig. 4) formed the similar intramolecular stacking of the V^{•+} subunits [15]. Upon oxidation of the V^{•+} subunits to V²⁺, the two V²⁺ subunits were repelled electrostatically to lead to an extended

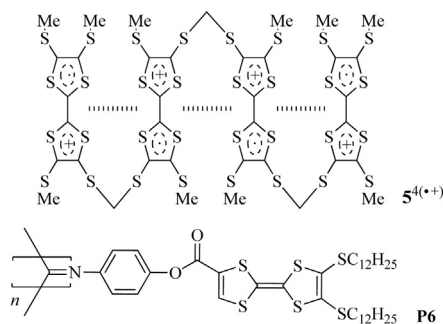


Fig. 3. The structure of radical cation $5^{4(+)}$ and **P6**.

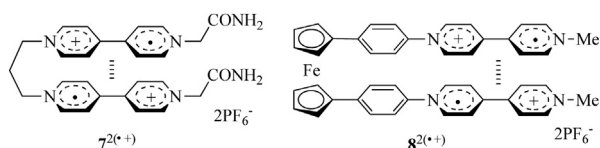


Fig. 4. The structure of radical cations $7^{2(+)}$ and $8^{2(+)}$, highlighting the intramolecular stacking of the V^{•+} units.

conformation. Thus, the compound gave rise to a redox-tuned reversible switching system. Winter and co-workers also reported that bisviologen radical cations connected with a tetramethylene linker formed intramolecular (V^{•+})₂ dimer at room temperature and, when the temperature was increased to 95 °C, the dimer decomposed to produce an extended conformation [16].

Wang and co-workers reported that V^{•+} subunits appended to the periphery of hyperbranched polyglycerols exhibited enhanced intramolecular dimerization [17], even though the flexibility of the dendrimeric framework restricted the establishment of an explicit stacking pattern. Trabolsi and co-workers prepared phosphazene derivative $9^{6(+)}$ (Fig. 5) by reducing the appended six viologen subunits to V^{•+} with sodium hydrosulfite [18]. It was demonstrated that the two V^{•+} subunits connected to the same P atom formed one pair of dimer in the intramolecular way. The three pairs of dimers were very stable and did not decompose in the presence of cucurbit[7]uril (CB[7]), which is a good host to encapsulate one V^{•+} subunit.

Such intramolecular radical cation stacking also occurs in long linear polymers. For example, Chen and co-workers prepared polymers **P10a** and **P10b** (Fig. 6) by forming hydrazine bonds from the corresponding di(acyl hydrazide) and dialdehyde precursors [19]. In acetonitrile, both polymers formed pleated foldamers due to intramolecular donor-acceptor interaction between the electron-rich TTF subunit and the electron-deficient V subunit (Folding A, Fig. 7). When the TTF subunits were oxidized to TTF^{•+}, the polymers did not form confined conformations (Unfolding A, Fig. 7). In contrast, when the V²⁺ subunits were reduced to V^{•+}, these V^{•+} subunits underwent intramolecular stacking to induce the backbones to form another kind of pleated conformations

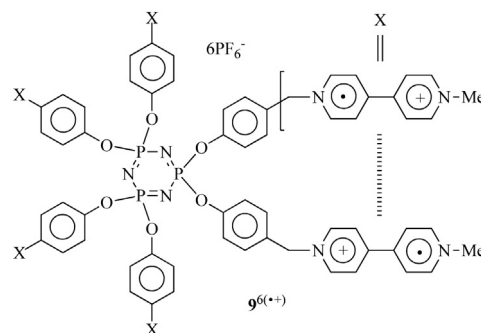


Fig. 5. The structure of radical cation $9^{6(+)}$, having three V^{•+} dimers.

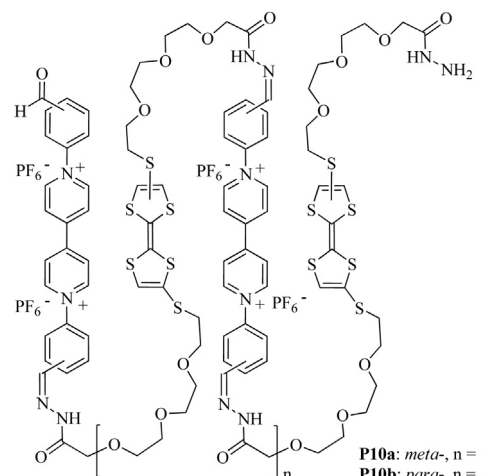


Fig. 6. The structure of polymers **P10a** and **P10b**.

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