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Stacking of hydrazone-bridged linear tetrathiafulvalene radical cations

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ABSTRACT

Four compounds **M1**, **M2**, **M3**, **M4**, and one polymer **P1** containing tetrathiafulvalene (TTF) units have been synthesized by the condensation of TTF-derived aldehyde and acylhydrazine precursors. UV–vis absorption and electron paramagnetic resonance spectroscopy as well as scanning electron microscopy reveal that the TTF$^{\bullet+}$ stacking of the polymer is considerably enhanced compared to that of the shorter compounds in polar solvents.

1. Introduction

In the past few decades, tetrathiafulvalene (TTF) and its derivatives have been of extensive interest in supramolecular and materials chemistry due to their specific reversible redox properties.[1–7] In 1979, Torrance et al. reported the dimerization of TTF radical cation.[8] This stacking has been demonstrated to be driven mainly by the inherent multicenter covalent π–π bonding of TTF radical cation species.[9] Because of low stability of the dimer, this prototypical radical cation dimer was studied only in the solid state. In the past decade, great effort has been devoted to develop efficient methods to enhance the stability of the radical cation dimer.[10–15] Recently, we reported that incorporating TTF units into preorganized scaffolds remarkably enhances the intermolecular dimerization of the TTF$^{\bullet+}$ units, leading to the formation of new macrocyclic and two- and three-dimensional supramolecular polymeric architectures.[11,12] Further investigation of TTF$^{\bullet+}$ stacking in different molecular or macromolecular backbones would help to achieve a comprehensive understanding of this unique non-covalent interaction, which should be useful for future applications in supramolecular self-assembly and materials design.[10]

Hydrazone building blocks, formed from the reaction of aldehydes and hydrazine, have been widely utilized for developing pharmacologically and biologically active molecules, adaptive materials, as well as optoelectronic devices.[16] Upon acylated with salicylic acid derivatives, linear rigid scaffolds were constructed. Because of the efficiency of dynamic covalent C=N bonds formation, it is easy to synthesize a linear structure by this scaffold. To investigate the stacking property of TTF$^{\bullet+}$ in linear scaffolds, we prepared compounds **M1**–**M4** and polymer **P1** by the condensation of TTF-derived aldehyde and acylhydrazine precursors. UV–vis absorption and electron paramagnetic resonance spectroscopy as well as scanning electron microscopy reveal that the stacking of the TTF$^{\bullet+}$ units in the polymer is considerably enhanced compared to that incorporated in the shorter compounds in polar solvents.

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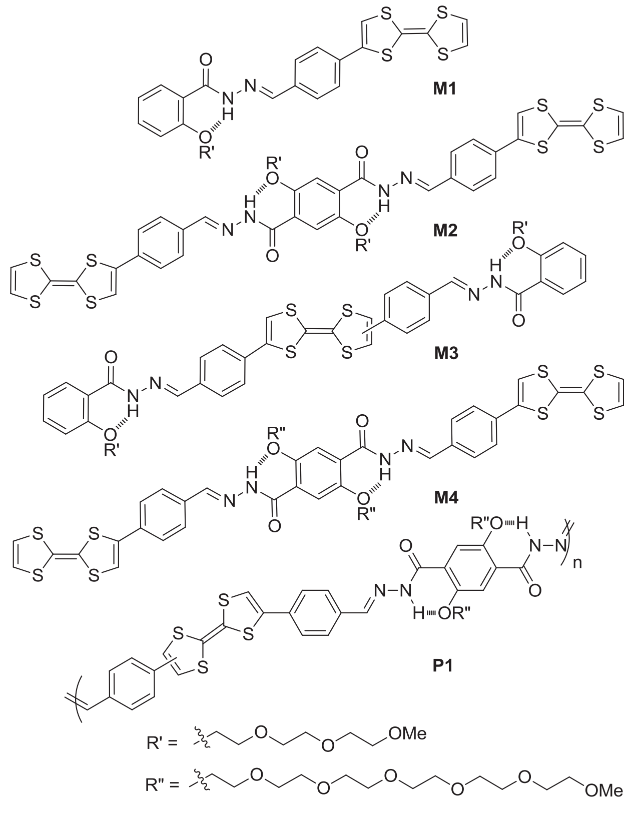
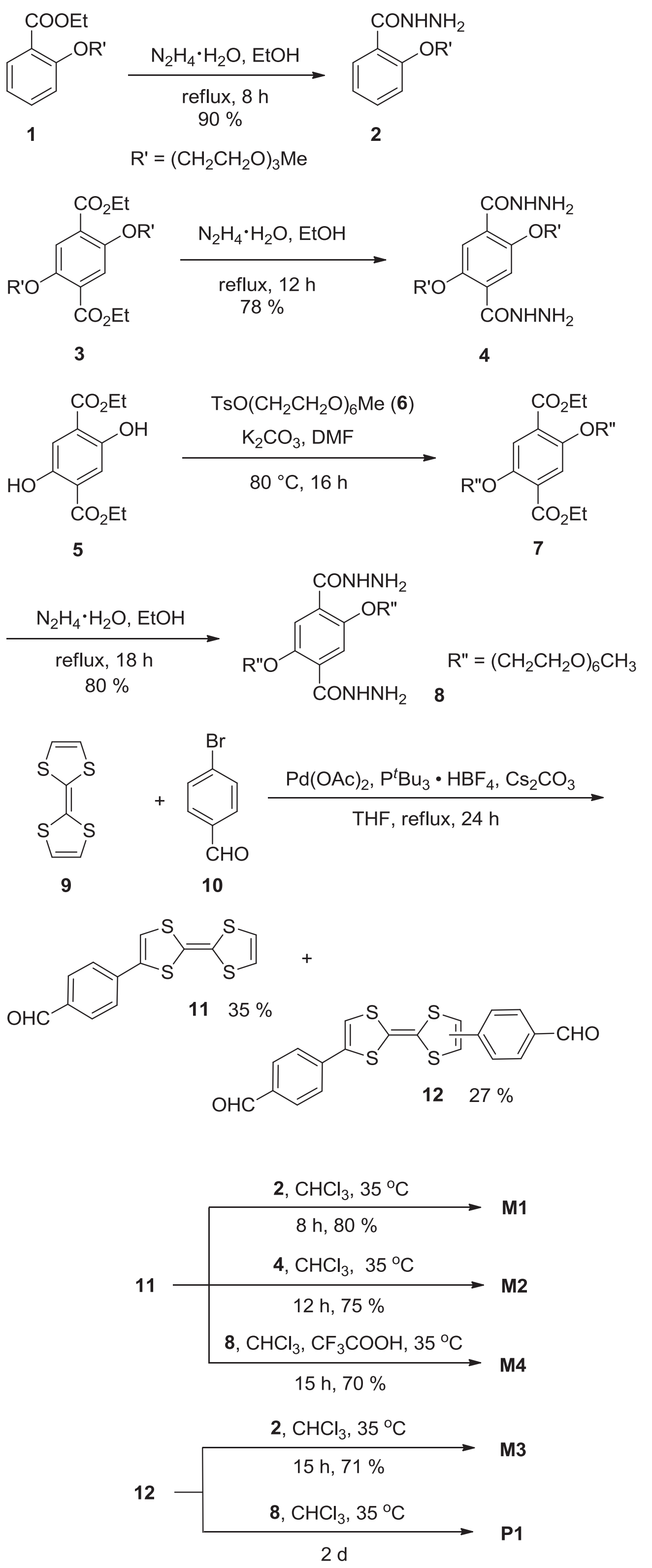


2. Results and discussion

2.1. Synthesis and characterization

The synthetic routes for five samples **M1**, **M2**, **M3**, **M4**, and **P1** are shown in Scheme 1. Firstly, compounds **1**,[17] **3**,[18] **6**,[19] **11**, and **12**[20] were prepared according to reported methods. Acylhydrazines **2**, **4**, and **8** were obtained by hydrazinolysis of corresponding esters, respectively. Compared to compound **4**, longer oligoglycol chains were introduced into compound **8** for achieving better solubility in organic solvents of varying polarity. Then acylhydrazines reacted with mono- (**11**) or di-aldehyde (**12**) to achieve the desired TTF–acylhydrazone compounds **M1**, **M2**, **M3**, and **M4** as well as the polymer **P1** in acceptable yields. The structures of **M1–4** were characterized by IR, ^{1}H, ^{13}C NMR, and MS spectra. The average degree of polymerization (DP) of polymer **P1** was estimated by ^{1}H NMR. No terminal aldehyde proton signal was observed in ^{1}H NMR spectrum. Considering the resolution of the ^{1}H NMR, we assumed that at least 95% of the aldehyde group had been converted into the hydrazone group.[21] On the basis of this assumption, we could estimate that DP of polymer **P1** was at least 10.



Scheme 1. The synthesis of compounds **M1**, **M2**, **M3**, **M4**, and polymer **P1**.

2.2. UV–vis absorption spectroscopy

UV–vis spectra of **M1**, **M2**, **M3**, **M4**, and **P1** in chloroform were first recorded at different TTF oxidation states, which were realized by adding different equivalent of Fe(ClO$_4$)$_3$ with respect to the total TTF concentration.[11] The typical spectra are showed in Fig. 1. For all the compounds and polymer, adding 1.0 equiv of Fe(ClO$_4$)$_3$, relative to the total TTF unit, caused the TTF unit to be oxidized to radical cation TTF$^{\bullet+}$, which was evidenced by the formation of the absorption band around 550–750 nm.[11] The TTF$^{\bullet+}$ radical cations stacked to form radical cation dimer (TTF$^{\bullet+}$)$_2$, which was supported by the typical absorption centered at around 830 nm for **M1** and **M3** and at around 880 nm for **M2**, **M4**, and **P1**. When another 1.0 equiv of Fe(ClO$_4$)$_3$ was added, the TTF$^{\bullet+}$ radical cation was further oxidized to TTF^{2+}, which was evidenced by the formation of the typical absorption band around 450 nm and the disappearance of the absorptions of both TTF$^{\bullet+}$ and (TTF$^{\bullet+}$)$_2$.

UV–vis dilution experiments were then performed for all five samples in different solvents. By fitting the maximum absorption of dimer (TTF$^{\bullet+}$)$_2$ to a nonlinear self-binding equation,[11] the apparent