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Synthesis and nonlinear optical absorption properties of two new conjugated ferrocene-bridge-pyridinium compounds

Fan Yang,[a] Xiu-Ling Xu,[a] Yong-Hua Gong,[a] Wen-Wei Qiu,[a] Zhen-Rong Sun,[b] Jin-Wei Zhou,[a] Pierre Audebert[c] and Jie Tang[a,*]

[a] *Institute of Medicinal Chemistry, Department of Chemistry, East China Normal University, Shanghai 200062, China*
[b] *Key Laboratory of Optical and Magnetic Resonance Spectroscopy, East China Normal University, Shanghai 200062, China*
[c] *P.P.S.M., UMR 8531, Ecole Normale Supérieure de Cachan, Cachan 94235, France*

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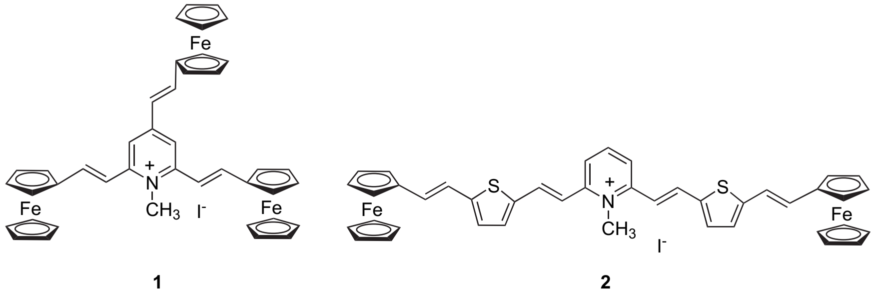
Abstract—Two electron donor–π-acceptor (D–π-A) chromospheres, with ferrocene as the electron donor and pyridinium as the electron acceptor, were synthesized. The nonlinear optical absorption (NOA) properties in the solution state were investigated by the Z-scan technique. Both compounds exhibited reverse saturable absorption (RSA) and optical limiting effect under nanosecond pulse irradiation.

1. Introduction

Nonlinear optical absorption (NOA) has shown its potential applications in optical information storage, laser radiation protection, and laser mode-locked. Thus searching for NOA materials has gradually become an interesting field.

Organometallic compounds are promising candidates for nonlinear optical materials.[1,2] Since the second-order nonlinear optical (NLO) properties of ferrocene derivatives was first reported by Green et al. in 1987,[3] the studies of organometallic compounds with ferrocenyl group have aroused more attention,[4–11] in which the more interesting compound was the substituted pyridinium with ferrocenylethenyl group. As demonstrated by Marder et al., the powder second harmonic generation (SHG) efficiencies of crystallized organic salts of (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridinium)ethylene showed strong dependence on the counterions.[12] By modifying the ferrocenyl group and changing the *N*-alkyl chain length, Davies investigated the variation of NLO properties of 4-substituted pyridinium.[13] Although the NLO properties of 4-substituted pyridinium system, with ferrocenylethenyl group as the electron donor, have been studied thoroughly, the investigation of NLO properties, especially NOA properties of the poly-substituted pyridinium has rarely been reported. In this paper, two new poly-substituted conjugated ferrocene-bridge-pyridinium compounds were synthesized (Scheme 1), and the NOA property and optical limiting effect were studied by Z-scan technique.



Scheme 1.

Keywords: Ferrocene; Pyridinium; Electron donor–acceptor; Reverse saturable absorption; Optical limiting effect.

* Corresponding author. Fax: +86 21 62232100; e-mail: jtang@chem.ecnu.edu.cn

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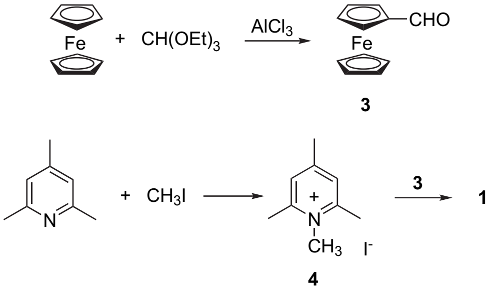
2. Results and discussion

2.1. Synthesis

2.1.1. *N*-Methyl-2,4,6-tri[(*E*)-ferrocenylethenyl]pyridinium iodide (1). According to the reported method of condensation of *N*,2-dimethyl pyridinium iodide with aldehyde,[14] we tried to synthesize compound (**1**) by the condensation of excess of ferrocenecarboxaldehyde with *N*-methyl-2,4,6-trimethyl pyridinium iodide in methanol. It was found that the produced product (**1**) concreted in the reaction system for the insolubility in methanol, which caused the stirring difficulty, so the reaction could not be carried out completely. However, altering the solvent with CH_3OH/$CHCl_3$ (3:1, v:v), the reaction could proceed successfully. Recrystallized twice with the component solvent, *N*-methyl-2,4,6-tri[(*E*)-ferrocenylethenyl]pyridinium iodide (**1**) was obtained with high purity.

N-Methyl-2,4,6-trimethyl pyridinium iodide was prepared by reaction of 2,4,6-trimethylpyridine with methyl iodide, and ferrocenecarboxaldehyde was prepared according to the literature (Scheme 2).[15]

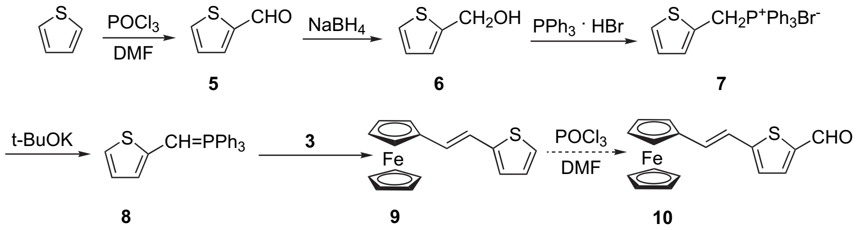


Scheme 2.

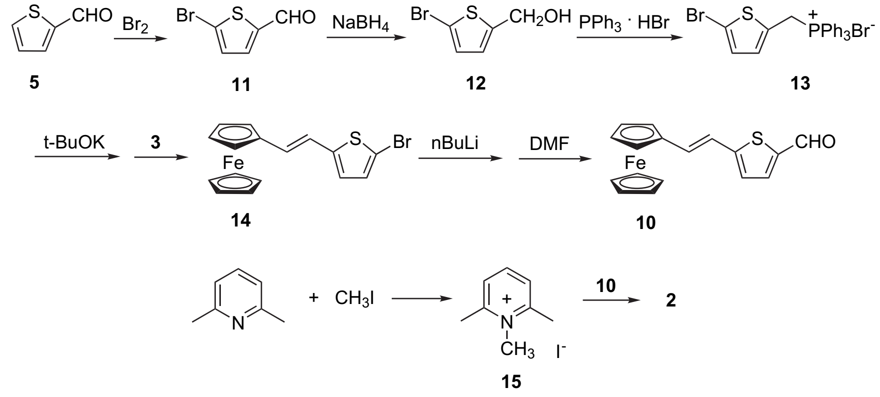
2.1.2. *N*-Methyl-2,6-di[(5-(*E*)-ferrocenylethenyl)thiophene-2-yl-(*E*)-ethenyl]pyridinium iodide (2). The synthesis of compound **2** may be realized, similar to compound **1**, by condensation of *trans*-5-(*E*)-(2-ferrocenylethenyl)thiophene-2-carbaldehyde (**10**) with *N*-methyl-2,6-dimethyl pyridinium iodide (**15**). With regard to the synthesis of compound **10**, Thomas reported a method, which is shown in Scheme 3.[16,17]

However, when preparing compound **10** from (*E*)-2-ferrocenylethenylthiophene (**9**) by Vilsmeier reaction, the products were complicated although compound **9** was converted completely, and only little desired product was obtained. Maybe the cyclopentyldiene rings of the ferrocene group could also be hydroformylated, which resulted in the complication of product. Hence, we designed a new route as follows (Scheme 4).

Thiophene-2-carbaldehyde (**5**), prepared by formylation of thiophene, was brominated to give 5-bromothiophene-2-carbaldehyde (**11**), then compound **11** was reduced, and the product (5-bromothiophen-2-yl)methanol (**12**) was transformed to the corresponding Wittig reagent. Finally, the Wittig reagent reacted with ferrocenecarboxaldehyde to give a mixture of *cis*- and *trans*-5-bromo-2-(2-ferrocenylethenyl)thiophene (**14**). The cis-isomer could be conveniently transformed to the trans-isomer by adding a small amount of iodine, and the *trans*-5-bromo-2-(2-ferrocenylethenyl)thiophene could be easily formylated. After purification, *trans*-5-(*E*)-(2-ferrocenylethenyl)thiophene-2-carbaldehyde (**10**) was obtained with 60% yield and high purity. Catalyzed by base, condensation of compound **10** with *N*-methyl-2,6-dimethyl pyridinium iodide (**15**) was carried out to give the final product *N*-methyl-2,6-di[(5-(*E*)-ferrocenylethenyl)thiophene-2-yl-(*E*)-ethenyl]pyridinium iodide (**2**) in 79% yield.



Scheme 3.



Scheme 4.