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

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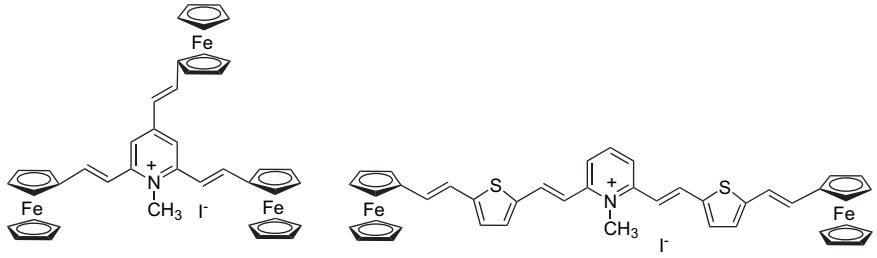
Abstract—Two electron donor–π-acceptor (D–π-A) chromospheres, with ferrocene as the electron donor and pyridinium as the electron acceptor, were synthesized. The nonlinear optical absorption (NOA) properties in the solution state were investigated by the Z-scan technique. Both compounds exhibited reverse 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.
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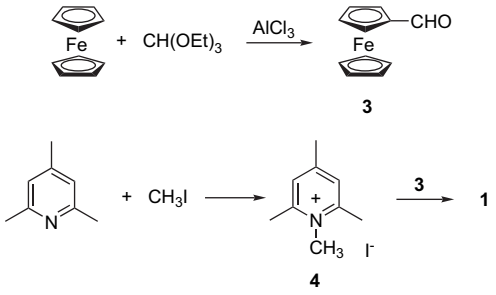
2. Results and discussion

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]

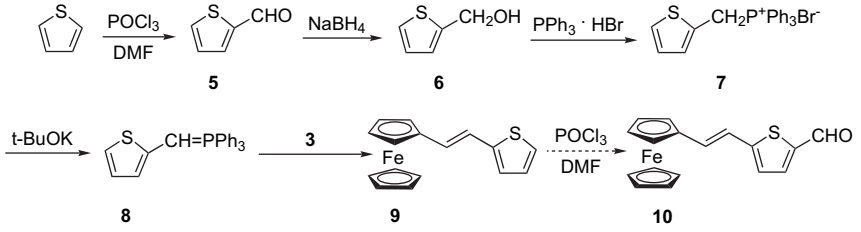


Scheme 2.

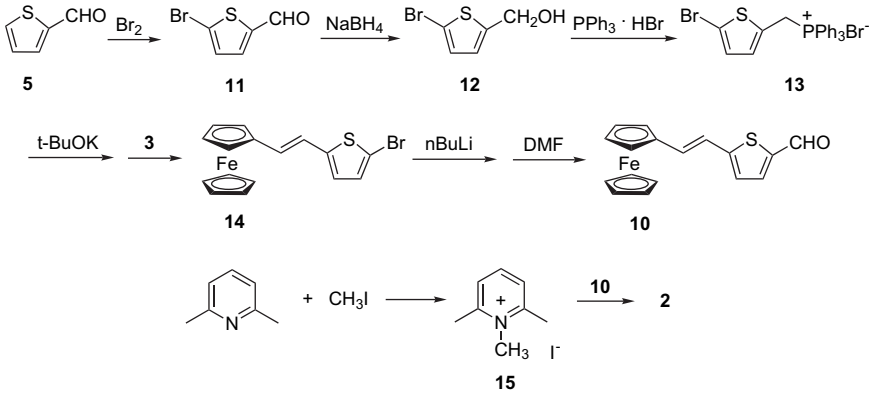
2.1.2. *N*-Methyl-2,6-di[(5-(*E*)-ferrocenylethenyl)thiophene-2-yl-(*E*)-ethenyl]pyridinium iodide (2). The synthesis of compound **2** may be realized, similar to compound **1**, by condensation of *trans*-5-(*E*)-(2-ferrocenylethenyl)thiophene-2-carbaldehyde (**10**) with *N*-methyl-2,6-dimethyl pyridinium 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.

2.2. Nonlinear optical absorption properties

Nonlinear optical absorption (NOA) measurements of these two compounds were carried out at nanosecond scale by open aperture Z-scan technique. Figure 1 exhibits the normalized Z-scan transmittance of 2×10^{-4} mol/L solutions of compounds **1** and **2** in DMF. The nanosecond laser source was a Q-switch locked Nd:YAG (1064 nm) with a second harmonic generation of 532 nm, pulse width of 12 ns, repeat frequency of 10 Hz, average pulse energy of 0.114 mJ and peak irradiance of 0.670 GW/cm^2.

As the sample was moved away from the focus point, the transmittances of both compounds were nearly a flat line, which displayed the linear absorption under weak light irradiation. As the samples were moved close to the focus point, the transmittances decreased as the laser irradiance increased. At the focus point (Z=0) where the laser irradiance reached maximum, the normalized transmittance decreased to minus. These results indicated that both compounds **1** and **2** were of obvious reverse saturation absorption (RSA).

For conjugated D–π-A systems, the distortion of molecular cloud under strong laser irradiation was the reason for nonlinear phenomena. For conjugated π systems of organic compounds, the conjugation behavior of the molecular bone can be easily characterized by UV–vis spectroscopy. For this purpose, the UV–vis absorption spectra of compounds **1** and **2** were measured (Fig. 2). Absorption parameters obtained are listed in Table 1.

Table 1. UV–vis absorption parameters of compounds **1** and **2**

	Samples	
	1	**2**
λ_{max}	370	225
A (λ_{max})	2.835	1.992
A (λ=532 nm)	1.087	1.414

It was obvious that the λ_{max} of both compounds appeared in the UV region, and the λ_{max} of compounds **1** and **2** were at 370 nm and 225 nm, respectively. Except for the strong peak in the UV region, both of them had a peak in the 520–540 nm regions with moderate strength, which might be resulted from the characteristic internal charge transfer (ICT) transition from the donor of ferrocene unit to the poly-substituted pyridinium unit. Thus, with 532 nm laser irradiation, both compounds **1** and **2** exhibited significant reverse saturation absorption properties.

2.3. Optical limiting effect

The nonlinear optical limiting effect, or simply the optical limiting effect, refers to the fact that the transmittance of

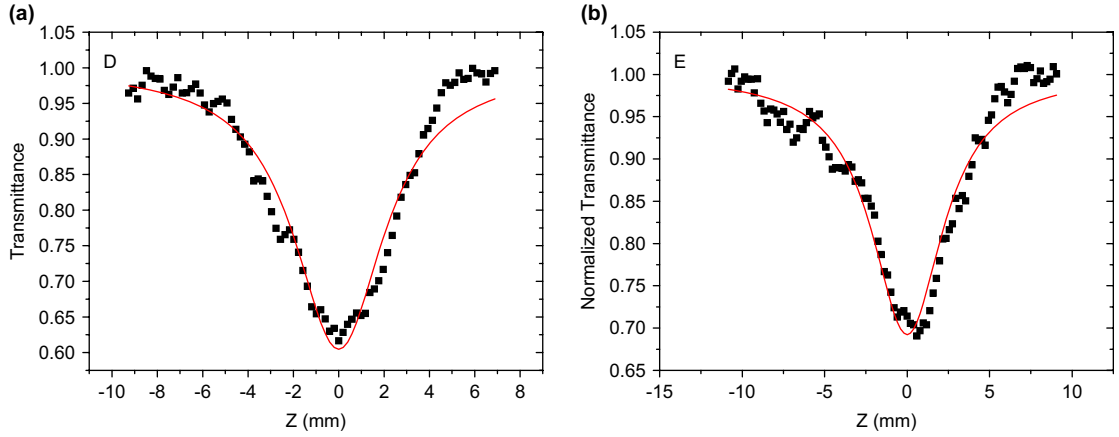


Figure 1. The reverse saturation absorption of compounds **1**(a) and **2**(b).

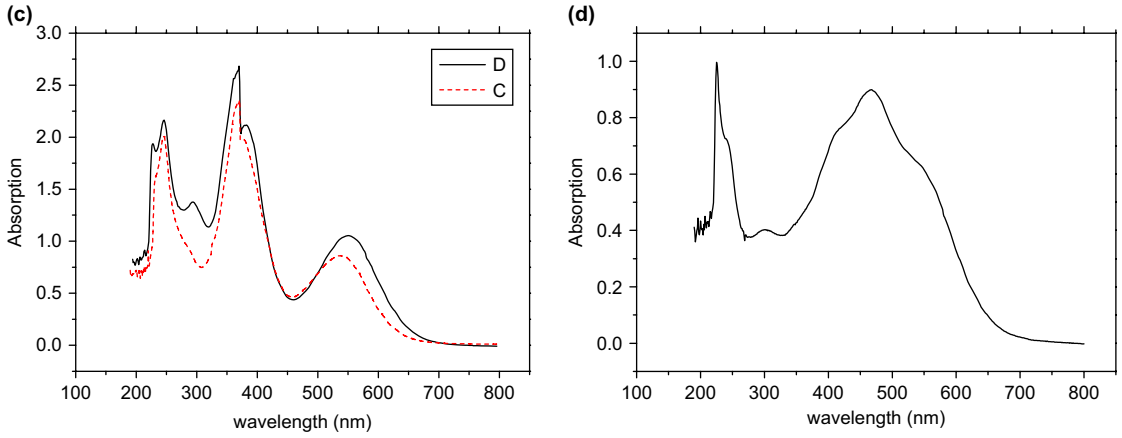


Figure 2. UV–vis absorption spectra of compounds **1**(c) and **2**(d).

a material decreases with increase of the input light fluence or intensity, which has attracted considerable attention because of its potential application in the fields of laser protection and optical communication. Using the Nd:YAG laser with pulse width of 12 ns as the light source, the optical limiting properties of both compounds were measured under three different concentrations. The input–output energy plots are shown in Figure 3.

When the input laser energy was weak, the output energy increased linearly as the input energy increased. The absorption coefficient was independent on the laser irradiance (I_0). As the input laser irradiance (I_0) increased continuously, the increase in output energy deviated from the linear relationship, which was less than that predicted from the slop of the linear region. This meant that the absorption coefficients of the samples increased as the input laser irradiance (I_0) increased.

Transmittance of the sample was obtained by dividing the output energy by input energy. The variation of transmittance (T) against light irradiance (I) provides a measurement of optical limiting property of the sample. Figure 4 exhibits the plots of transmittance of compounds **1** and **2** against light irradiance at different concentrations.

At low light irradiance, the T–I plot was flat, that indicated a linear optical behavior. The transmittance had no dependence on the irradiance of the laser. As light irradiance increased continuously, transmittance started to decrease. In other words, both compounds showed optical limiting effect. For compound **2**, the optical limiting threshold value (E_L), defined as the light irradiance at which transmittance turns down in the T–I plot, was about 3.7 mJ. For compound **1**, the E_L value was less than 1 mJ. Except for the difference in the E_L values, the strengths of optical limiting effects for the two compounds were different too. At light irradiance of 7 mJ, the transmittance decrease for compound **1** was about 40% as compared with that of the linear region. For compound **2**, the decrease was only 14.6%. The optical limiting effect for compound **1** was far more significant than that of compound **2**. This behavior was consistent with the strength of their reverse saturation absorption behavior. For the two compounds at same concentration, the transmittance for compound **1** was larger than that of compound **2** in the linear region. When light irradiance increased, the trend of the change of T–I plot for a given compound was about the same. Based on the results obtained above, we concluded that compound **1** was a better optical limiting material for the two compounds synthesized.

Comparing the molecular structures of compound **1** with **2**, both of them are of the same electron acceptor, the difference is that compound **1** has got three ferrocenyl groups as the electron donor. The increase of the electron-donating group is favored to the delocalization of π-electron, and the electron

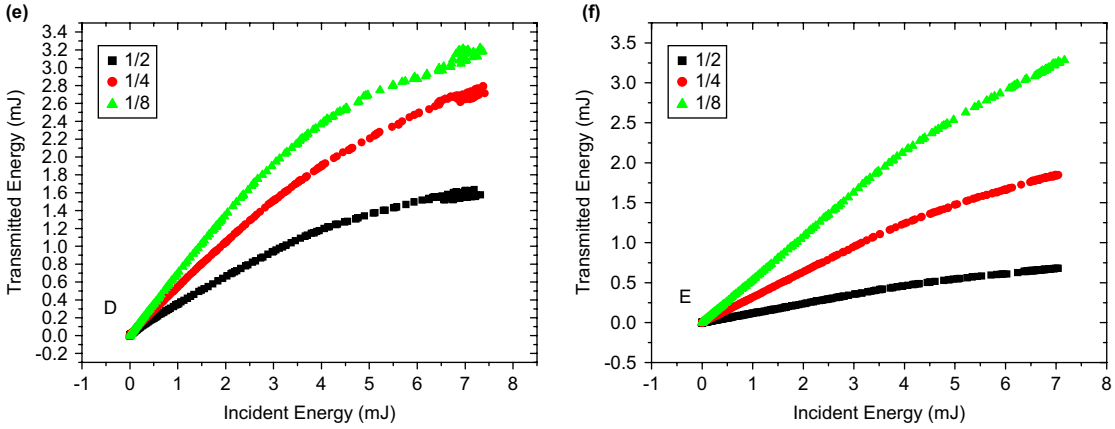


Figure 3. Optical limiting effect of compounds **1**(e) and **2**(f).

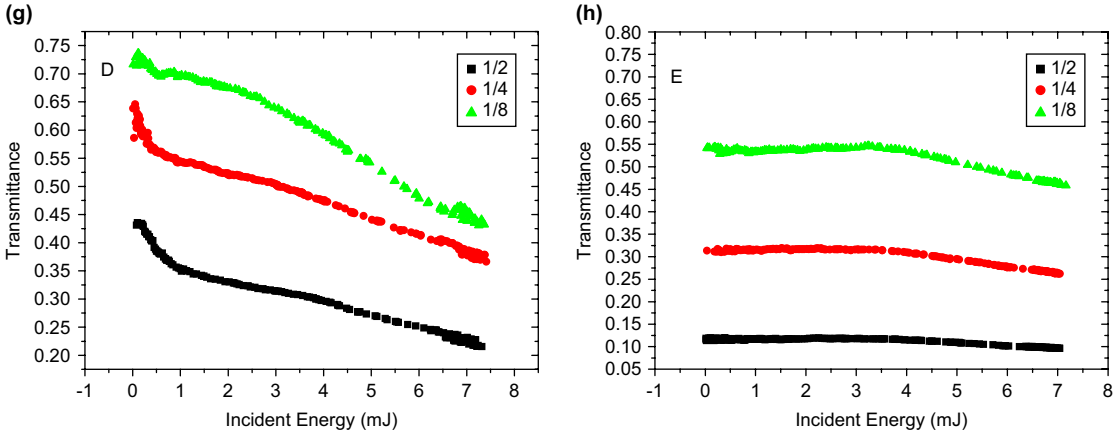


Figure 4. Transmittance–input energy curves for compounds **1**(g) and **2**(h).

cloud is looser, which is susceptible to distortion when excited by laser light. So the nonlinear optical absorption effect of compound **1** is more remarkable. As for compound **2**, although a thiophenethenyl group was inserted in the bridge as the chromophore, both of the reverse saturation absorption and optical limiting effects are worse than that of compound **1**. Clearly, increase in the number of the electron-donating group may be more effective for promotion of the nonlinear optical absorption properties of the pyridinium salts.

3. Conclusion

1. We designed two new poly-substituted conjugated ferrocene-bridge-pyridinium compounds, *N*-methyl-2,4,6-tri[(*E*)-ferrocenylethenyl]pyridinium iodide (**1**) and *N*-methyl-2,6-di[(5-(*E*)-ferrocenylethenyl)thiophene-2-yl-(*E*)-ethenyl]pyridinium iodide (**2**). Compound **1** could be synthesized conveniently by the reaction of ferrocenecarboxaldehyde with *N*-methyl-2,4,6-trimethyl pyridinium iodide. To synthesize compound **2**, a new route for a key intermediate, *trans*-5-(*E*)-(2-ferrocenylethenyl)thiophene-2-carbaldehyde (**10**), was designed and successfully actualized. Then compound **10** reacted with *N*-methyl-2,6-dimethyl pyridinium iodide to give the target compound.
2. The nonlinear optical absorption of the two compounds was investigated by the Z-scan technique. Both compounds exhibited reverse saturable absorption (RSA) and optical limiting effect under nanosecond pulse irradiation, and compound **1** showed more obvious optical limiting effect.

4. Experimental

4.1. General

NMR, UV and elemental analysis were carried out on Bruker AM-500 MHz, UnicamHelios α UV spectrophotometer and Elementar ZAROIO-EL elemental analyzer. Except specially stated, all reagents used were analysis grade and were treated before use. Ferrocenecarboxaldehyde was prepared according to the literature.[15]

4.2. Preparation of *N*-methyl-2,4,6-tri[(*E*)-ferrocenylethenyl]pyridinium iodide (1)

4.2.1. *N*-Methyl-2,4,6-trimethylpyridinium iodide. Methyl iodide (7.10 mL, 0.114 mol) was added dropwise to a solution of 2,4,6-trimethylpyridine (4.85 g, 0.04 mol) in dichloromethane at 0 °C. After stirring at room temperature overnight, the solvent was evaporated to give a white solid, which was recrystallized in methanol to give 8.95 g product as white crystal with yield of 84.7%. Mp 213–215 °C; ^{1}H NMR (D_2O, δ): 2.45 (s, 3H), 2.68 (s, 6H), 3.95 (s, 3H), 7.51 (s, 2H).

4.2.2. *N*-Methyl-2,4,6-tri[(*E*)-ferrocenylethenyl]pyridinium iodide (1). *N*-Methyl-2,4,6-trimethylpyridinium iodide (1.32 g, 5 mmol), ferrocenecarboxaldehyde (6.42 g, 30 mmol), methanol (20 mL), and chloroform (10 mL) were added into a round bottom flask, then piperidine (1.5 mL) was added. The mixture was refluxed for 6 h under the protection of N_2, and then cooled slowly. The solid was collected, and crystallized twice with methanol/chloroform, 3.68 g of violet plate crystal product was obtained, yield 86.4%. Anal. Calcd for $C_{42}H_{38}Fe_3IN$: C, 59.22; H, 4.37; N, 1.65. Found: C, 59.45; H, 4.76; N, 1.68; UV: λ_{max}=370 nm (CH_3CN); ^{1}H NMR (DMSO-d_6, δ): 4.16 (s, 3H, NC**H**$_3$), 4.18–4.21 (m, 15H, C_5**H**$_5$+2C_5**H**$_5$), 4.51–4.53 (m, 6H, C_5**H**$_2$+2C_5**H**$_2$), 4.78–4.81 (m, 6H, C_5**H**$_2$+2C_5**H**$_2$), 6.83 (d, 1H, J=15.9 Hz, CH=C**H**), 6.99 (d, 2H, J=15.0 Hz, 2CH=C**H**), 7.58 (d, 2H, J=15.0 Hz, 2CH=C**H**), 7.75 (s, 2H, C_5**H**$_2$N), 7.80 (d, 1H, J=15.9 Hz, CH=C**H**).

4.3. Preparation of *N*-methyl-2,6-di[(5-(*E*)-ferrocenylethenyl)thiophene-2-yl-(*E*)-ethenyl]pyridinium iodide (2)

4.3.1. Thiophene-2-carbaldehyde (5). To a three-necked round bottom flask were added 16 mL (0.19 mol) of thiophene, 16.3 mL (0.21 mol) of anhydrous DMF and 40 mL of anhydrous chloroform. The solution was cooled to ~0 °C, and 19.6 mL of $POCl_3$ (0.21 mol) was added dropwise with stirring. The solution was then warmed to room temperature followed by refluxing for 4 h, then cooled to room temperature and poured into ice water. The water layer was extracted with dichloromethane (3×50 mL), and the organic layers were combined, washed with water (2×50 mL) and saturated aqueous sodium bicarbonate (2×50 mL), and then dried over $MgSO_4$. After evaporation of the solvent, 25 g pure thiophene-2-carbaldehyde (**5**) was obtained by fractional distillation as a colorless liquid (70% yield; bp 108–112 °C/53 mmHg, lit.[17] 44–45 °C/1 mmHg).

4.3.2. 5-Bromothiophene-2-carbaldehyde (11).[18] To an ice-cooled solution of thiophene-2-carbaldehyde (16.2 g, 0.14 mol) and $NaHCO_3$ (12.6 g, 0.15 mol) in dry chloroform, bromine (7.4 mL, 0.14 mol) was added dropwise with stirring, and the mixture was left at room temperature for 2 h, then poured into water. After separation, the water layer was extracted with dichloromethane (3×20 mL), and the organic layers were combined, washed with saturated aqueous sodium bicarbonate and water, and then dried with $MgSO_4$. After a short column (silica, 1:20 ethyl acetate/petroleum ether) 21.4 g of **11** was obtained as a colorless liquid (80% yield). ^{1}H NMR ($CDCl_3$, δ): 9.78 (s, 1H), 7.52 (d, 1H, J=4.0 Hz), 7.19 (d, 1H, J=4.0 Hz).

4.3.3. (5-Bromothiophen-2-yl)methanol (12). To an ice-cooled solution of 15 g (0.079 mol) of 5-bromothiophene-2-carbaldehyde (**11**) in 50 mL of methanol, $NaBF_4$ (6 g, 0.16 mol, 2 equiv) was added portionwise, and the mixture was stirred at room temperature for about 4 h. After evaporation of the solvent, dichloromethane was added to dissolve the residue and the insoluble salts were filtered. After a short column chromatography (silica, 1:10 ethyl acetate/petroleum ether) 11 g of **12** was obtained as a colorless liquid (73% yield). ^{1}H NMR ($CDCl_3$, δ): 6.92 (d, 1H, J=3.7 Hz), 6.76 (d, 1H, J=3.7 Hz), 4.75 (s, 2H), 1.73 (s, br, 1H).

4.3.4. [(5-Bromothiophen-2-yl)methyl]triphenylphosphonium bromide (13).[19] (5-Bromothiophen-2-yl)methanol (5 g, 0.026 mol), triphenylphosphine hydrobromide (8.9 g, 0.026 mol) and 40 mL of anhydrous chloroform

were added into a flask equipped with a condenser. After refluxing for 1 h, the condenser was replaced by distillation equipment. The solvent was distillated off slowly until dryness for 1 h. The crude product was then dissolved in chloroform, and the pure phosphonium bromide **13** was recovered by precipitation with the addition of diethyl ether, washed twice with ether, and isolated by filtration (12.8 g, 96%).

4.3.5. *trans*-5-Bromo-2-(2-ferrocenylethenyl)thiophene (14).[20] [(5-Bromothiophen-2-yl)methyl]triphenylphosphonium bromide (5.18 g, 0.01 mol) was dissolved in 30 mL of dry THF under N_2 atmosphere and cooled to ~0 °C. Potassium *tert*-butoxide (1.39 g, 0.012 mol) was added slowly while stirring the solution vigorously. The generated deep red solution was stirred at 0 °C for another 30 min, and then brought to room temperature. Ferrocenecarboxaldehyde (2.14 g, 0.01 mol) was added portionwise and the mixture was heated to reflux for 4 h. The solution was poured into ice water and extracted with diethyl ether. The ether layer was washed with brine and dried with $MgSO_4$. A mixture of *cis*- and *trans*-5-bromo-2-(2-ferrocenylethenyl)thiophene was obtained by a short column chromatography (silica, 1:6 dichloromethane/petroleum ether) as a red solid (3.2 g, 86%).

Recrystallization of the mixture from hot hexane gave 1.3 g of pure *trans*-5-bromo-2-(2-ferrocenylethenyl)thiophene (**14**). The mixture recovered from filtrate (*cis*/*trans*=4:1) was treated with 0.01 equiv of I_2 in refluxing toluene under N_2 atmosphere for 1 h to give quantitative pure trans-product. ^{1}H NMR ($CDCl_3$, δ): 6.90 (d, 1H, J=4.0 Hz), 6.64 (q, 2H, J=16.0 and 3.0 Hz), 6.56 (d, 1H, J=16.0 Hz), 4.47 (s, 2H), 4.34 (s, 2H), 4.18 (s, 5H).

4.3.6. *trans*-5-(*E*)-(2-Ferrocenylethenyl)thiophene-2-carbaldehyde (10). To a cooled (−78 °C) solution of 1.64 g (4.4 mmol) of *trans*-5-bromo-2-(2-ferrocenylethenyl)thiophene (**14**) in THF was added dropwise 3.3 mL of *n*-butyllithium (1.6 M in hexane, 5.3 mmol, 1.2 equiv). The mixture was stirred for 15 min, allowing the temperature to rise to −50 °C, and then cooled again to −78 °C. After dropwise addition of anhydrous DMF (0.41 mL, 5.3 mmol, 1.2 equiv), the reaction temperature was allowed to rise to 0 °C for 2 h. The reaction mixture was then stirred for 4 h at 0 °C and 2 h at room temperature, then poured into ice water and extracted with dichloromethane, which was then washed with water (2×30 mL) and dried over $MgSO_4$. After a short column chromatography (silica, 1:6→1:2 dichloromethane/petroleum ether) 0.85 g of pure **10** was obtained as a violet solid (60%). ^{1}H NMR ($CDCl_3$, δ): 9.83 (s, 1H), 7.61 (d, 1H, J=4.0 Hz), 7.01 (d, 1H, J=4.0 Hz), 6.96 (d, 1H, J=16.0 Hz), 6.79 (d, 1H, J=16.0 Hz), 4.47 (d, 2H, J=2 Hz), 4.26 (t, 2H, J=2 Hz and J=1 Hz), 4.16 (s, 5H).

4.3.7. *N*-Methyl-2,6-dimethylpyridinium iodide (15). Methyl iodide (10 mL, 0.16 mol) was added dropwise to a solution of 10.7 g (0.1 mol) of 2,6-lutidine in dichloromethane at 0 °C. After stirring at room temperature overnight, the solvent was evaporated to give a white solid, which was recrystallized in methanol to give the product (16 g) as white needles (64%).

4.3.8. *N*-Methyl-2,6-di[(5-(*E*)-ferrocenylethenyl)thiophene-2-yl-(*E*)-ethenyl]pyridinium iodide (2). To a 50 mL flask equipped with a condenser, 31 mg (0.12 mmol) of *N*-methyl-2,6-dimethyl pyridinium iodide (**15**), 150 mg (0.37 mmol, 3 equiv) of *trans*-5-(*E*)-(2-ferrocenylethenyl)thiophene-2-carbaldehyde (**10**), 25 mL of anhydrous methanol and two drops of piperidine were added. After refluxing for 4 h under N_2 atmosphere, the solution was cooled to room temperature. The solvent was evaporated and the residue was passed through a column chromatography (silica, 1:15 methanol/dichloromethane) to give 84 mg of **2** as a dark violet solid (79%). Anal. Calcd for $C_{42}H_{36}Fe_2INS_2$: C, 58.83; H, 4.23; N, 1.63. Found: C, 58.54; H, 4.52; N, 1.56; UV: λ_{max}=225 nm (CH_3CN); ^{1}H NMR (DMSO-d_6, δ): 8.34 (t, 1H, J=8.1 Hz), 8.20 (d, 2H, J=8 Hz), 7.97 (d, 2H, J=15.5 Hz), 7.51 (d, 2H, J=3.7 Hz), 7.21 (d, 2H, J=15.5 Hz), 7.16 (d, 2H, J=3.7 Hz), 7.03 (d, 2H, J=15.8 Hz), 6.88 (d, 2H, J=15.8 Hz), 4.63 (s, 4H), 4.40 (s, 4H), 4.21 (s, 3H), 4.17 (s, 10H); ^{13}C NMR (DMSO-d_6, δ): 152.67, 147.32, 137.42, 135.04, 133.47, 130.32, 126.27, 122.68, 118.62, 116.29, 81.87, 69.63, 69.12, 67.16, 41.25; HRMS *m*/*z*: 730 $[C_{42}H_{36}Fe_2NS_2]^+$.

Acknowledgements

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