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Synthesis, spectroscopy and morphology of new ferrocene schiff base containing thiophene ring in the conjugation chain

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ABSTRACT

Novel Schiff bases derivative containing ferrocenylphenyl and thiophene was synthesized by facile method. The compound prepared was characterized by spectroscopic methods (IR, UV–visible, ^{1}H NMR) and elemental analysis. It was found that the compound can self-assemble nanoparticles by precipitation from $CHCl_3$ solution drop-cast on Si wafer. The self-assembly process can be controlled, and another different rod-like nanostructure was obtained by utilizing a mixed solvent system ($CHCl_3$ and EtOAc: 1:1, V/V).

KEYWORDS

Ferrocene;
Schiff base;
Morphology;
Synthesis.

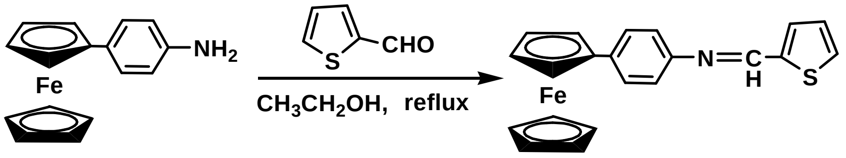
INTRODUCTION

One of the areas of organic chemistry that has undergone major developments in recent years is of ferrocene schiff base compounds. Ferrocene-based schiff bases have been employed in various fields, such as semiconductors[1,2], biosensors[3-5], asymmetric catalysis[6,7], biological activity including antifungal[8], antiviral[9] and anticancer activities[10]. In addition, experimental and theoretical studies on organic chromophores indicated that the presence of hetero-aromatics in the conjugation chain is highly beneficial to the observation of large non-linear optical properties[11,12]. Hereby we have initiated a program dealing with the synthesis of Schiff bases derivative containing ferrocenylphenyl and thiophene. In this manuscript, we report the preparation and characterization (IR, ^{1}H NMR, UV–visible and elemental analyses) of ferrocene Schiff bases **(2)** and first report its morphology, the tunable nanostructures of **(2)** from solution showed its potential applications in various integrated optoelectronic devices via solution process (Scheme 1)[13]. Application of this compound is under way.

RESULTS AND DISCUSSION

The elemental analyses of the product is in good agreement with the calculated values. The I.R spectra of the product show all the characteristic peaks. A broad absorption band at 1616cm^{-1} is assigned to $\nu_{C=N}$. The bands around 3100cm^{-1} can be attributed to aromatic ν_{C-H}. A sharp band around 1147 and 1003 cm^{-1} due to ferrocene is observed in the spectra of the compound. A thiophene ν_{C-H} stretching vibration is also seen around 709cm^{-1}.

All the characteristic signals are observed in the ^{1}H NMR spectra of the synthesized Schiff bases. The hydrogen atoms of the unsubstituted cyclopentadienyl ring moiety appear as a sharp singlet, in the 4.046ppm for five hydrogens and the substituted one at 4.323-



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Scheme 1 : The synthesis of compound 2

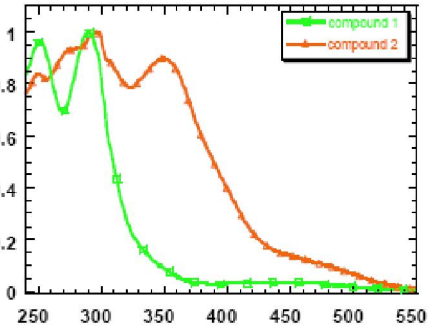

Figure 1 : The absorption spectra of compound 2 in $CHCl_3$ solution (10^{-4}M) at room temperature

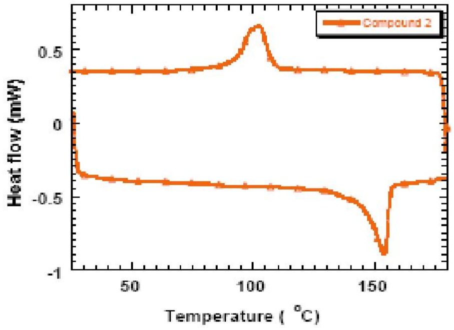

Figure 2 : Temperature for phase transformation of compound 2

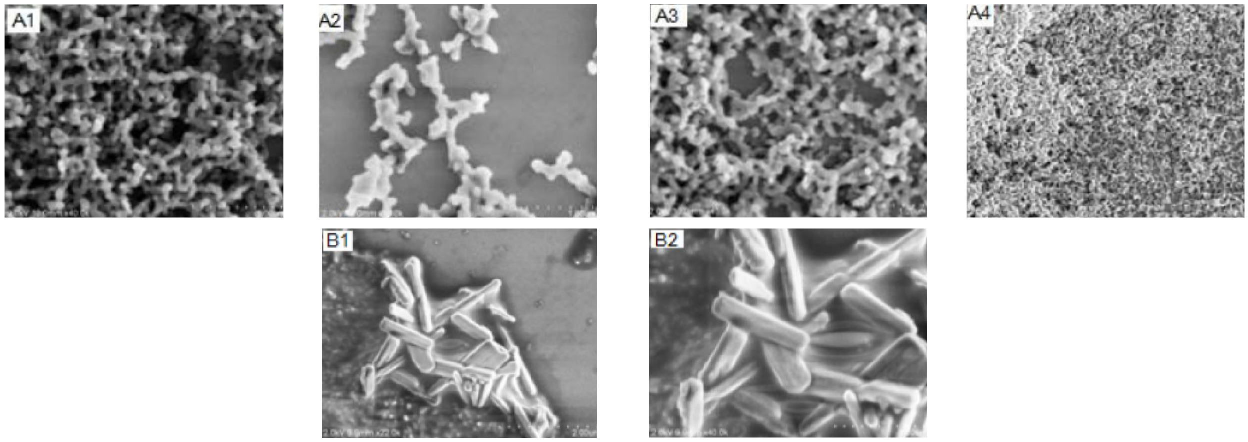

Figure 3 : Morphology of self-assembled compound 2: (A) SEM images of a sample prepared by precipitate from $CHCl_3$ solution drop-cast on Si wafer. (Scale bars: A1-A3:1µm; A4: 5µm.). (B) SEM images of a sample prepared by precipitate from $CHCl_3$:EtOAc(1:1)solution drop-cast on Si wafer; Scale bars: (Scale bars: B1:2µm; B2: 1µm.). Figure 3A illustrates the SEM image of compound 2 directly precipitated from $CHCl_3$ solution. Compound 2 showed molecular assembly nanoparticles. The self-assembly process can be controlled, and another different nanostructure was obtained by utilizing a mixed solvent system ($CHCl_3$ and EtOAc: 1:1, V/V) as shown in Figure 3B. Nanorods were obtained through dissolving compound 2 in a mixture of $CHCl_3$ and EtOAc(1:1, V/V) and evaporating the solvents slowly. The tunable nano or microstructures of 2 from different solutions showed its potential applications in various integrated optoelectronic devices via solution process

4.335ppm for two hydrogens and at 4.652-4.664ppm for the other two hydrogens.

The hydrogen atom of the imine function shows a sharp singlet at 8.647ppm. Signals at 7.163-7.264ppm belonged to thiophene protons and 7.747-7.505ppm belonged to phenyl protons.

UV–visible studies were carried out in trichloromethane (Figure 1). The absorption spectra of compound **(2)** in dilute $CHCl_3$ solution (10^{-4} M) exhibited two major bands with absorption λ_{max} at about 298, 350nm. compared with the thiophene-2-carbadehyde **(1)**, the peak at 251nm red-shifted about 47 nm to 298nm, while the absorption band at 290nm also red-shifted 60 nm to 350nm. Such absorption results indicated the conjugated chain growth of compound **(2)**. The differential scanning calorimetry (DSC) investigation results indicate that no liquid-crystalline behavior was observed for compound **(2)**, whereas the melting point of compound **(2)** is 154°C, freezing point of compound 2 is 105°C(Figure 2).

EXPERIMENTAL

General procedure

Commercially available chemicals were used without further purification unless stated otherwise. Melting point (uncorrected) was measured with a XT_4 melting point apparatus. ^1H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) spectrometer in $CDCl_3$ with TMS as the reference. IR spectra were obtained using KBr pellets on a Nicolet 179SX FT-IR spectrometer. Elemental analysis of the compound was performed on a Elementar Vario EL (Germany) instrument. UV-vis spectra were recorded on Perkin Elmer Lambda 35 UV-vis spectra.

Synthesis of *N*-(Thienylidene)-4- ferrocenylaniline

To a solution of 4-ferrocenylaniline (277mg, 1.0 mmol) in absolute ethanol (20ml) stirred 15min and then added thiophene-2-carbadehyde (123mg, 1.1 mmol), The reaction mixture was refluxed for 4 h, After cooling the product was collected by filtration, washed with cold absolute ethanol, recrystallized from absolute ethanol and characterized by spectroscopic methods and elemental analyses. Yield: 306mg (82.5%). M.p.151~153°C.

IR (KBr, ν_{max}, cm^{-1}): The IR spectrum indicated the presence of the unsubstituted cyclopentadienyl ring (1104 and 1003cm^{-1}), 1022.0~1147.6cm^{-1} (single substituted cyclopentadienyl), 487cm^{-1} and 510cm^{-1} (ν_{Fe-C}), 709(Thiophene),1616cm^{-1}(N = CH); ^1H NMR (300 MHz, CDCl3, TMS, δppm): 8.647(s, 1H, CH = N), 7.747-7.505 (m, 4H, C_6H_4,), 7.163-7.264 (m, 3H, Thiophene), 4.652-4.664 (t, J = 1.8, 2H, C_5H_4), 4.323-4.335(t, J = 1.8, 2H, C_5H_4) , 4.046 (s, 5H, Fc-unsubstituted ring). Anal. Calcd. for $C_{22}H_{17}SFe$: C, 67.93; H, 4.62. Found: C, 67.89; H, 4.60%. UV–visible [λ_{max} ($CHCl_3$), nm]: 298, 350nm.

CONCLUSION

Novel Schiff bases derivative containing ferrocenylphenyl and thiophene was synthesized by facile method. The compound prepared was characterized by spectroscopic methods. It was found that the compound can self-assemble nanoparticles by precipitation from $CHCl_3$ solution drop-cast on Si wafer. The self-assembly process can be controlled, and another different rod-like nanostructure was obtained by utilizing a mixed solvent system.

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REFERENCES

[1] Masahiro Muraoka, L.Stephen Gillett, W.Thomas Bell; Angew.Chem.Int.Ed., **41(19)**, 3653-3656 **(2002)**.

[2] R.Andrew Pike, C.Lyndsey Ryder, R.Benjamin Horrocks, William Clegg, A.Bernard Connolly, Andrew Houlton; Chem.Eur.J., **11**, 344-353 **(2005)**.

[3] Dhrubajyoti Basak, Biswanath Mallik; Synthetic Metals, **156**, 176-184 **(2006)**.

[4] Casas-Solvas, M.Juan, Ortiz-Salmeron, Emilia, Garcia-Fuentes, Luis, Vargas-Berenguel, Antonio; Org.Biomol.Chem., **22,** 4230-4235 **(2008)**.

[5] Y.Huang, Suni II; J.Electrochem.Soc.**, 155,** 350-354 **(2008)**.

[6] Tiejian Zhu, Qingsheng Wu, Ping Chen, Yaping Ding; J.Organomet.Chem., **694**, 21-26 **(2009)**.

[7] Lisa Diab, Maryse Gouygou, Eric Manoury, Philippe Kalck, Martine Urrutigoïty; Tetrahedron Letters, **49**, 5186-5189 **(2008)**.

[8] Haibo Yu, Ling Shao, Jianxin Fang; J.Organomet. Chem., **692**, 991-996 **(2007)**.

[9] Marcella de Champdoré, Giovanni Di Fabio, Anna Messere, Daniela Montesarchio, Gennaro Piccialli, Roberta Loddo, Massimiliano La Colla, Paolo La Colla; Tetrahedron, **60**, 6555-6563 **(2004)**.

[10] Gregg Caldwell, G.Maria Meirim, W.Eberhard Neuse, E.J.Constance; Appl.Organomet.Chem., **12**, 793-799 **(1998)**.

[11] Joong Tark Han, Dae Ho Lee, Chang Yeol Ryu, Kilwon Cho; J.Am.Chem.Soc., **126**, 4796-4797 **(2004)**.

[12] Evangelia Xenogiannopoulou, Miroslav Medved, Kostas Iliopoulos, Stelios Couris, G.Manthos Papadopoulos, Davide Bonifazi, Chloè Sooambar; Chem.Phys.Chem., **8**, 1056-1064 **(2007)**.

[13] Markus Sailer, Frank Rominger, J.J.Thomas Müller; J.Organomet.Chem., **691**, 299-308 **(2006)**.