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# Synthesis, crystal structure and properties of two novel ferrocenophane compounds

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#### ABSTRACT

The title compounds were synthesized *via* click reaction. They were characterized by IR, <sup>1</sup>H-NMR, elemental analysis, UV, fluorescence in solution were also applied to characterise their photophysical characterization and single-crystal X-ray diffraction analysis. 1,1'-Ferrocene-dicarboxyl-{[(3-methylphenyl)-imino]di-2,1-ethanediyl} 1 ( $C_{23}H_{23}FeNO_4$ ) crystallizes in the monoclinic system, with *a* = 7.4261(13), *b* = 29.911(5), *c* = 9.8426(13) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 118.251(10)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 1925.8(5) Å<sup>3</sup>, 1,1'-Ferrocene-dicarboxyl-{[(2-methylphenyl)-imino]di-2,1-ethanediyl} 2 ( $C_{23}H_{23}FeNO_4$ ) crystallizes in the monoclinic system, with *a* = 15.4000 (15) , *b* = 7.9007 (8), *c* = 16.0776 (15) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 94.266$  (2)°,  $\gamma = 90^{\circ}$ , V = 1950.8 (3)Å<sup>3</sup>, Both 1 and 2 form 3D net structures, which are further linked to form 3D supramolecular net structures via intermolecular C-H···C, C-H··· $\pi$  and C-H···C stacking interactions, respectively. Fluorescent and UV-vis absorption spectra were also investigated.

**KEYWORDS** 

Crystal structure; ferrocenophane; UV-vis and fluorescent

### Introduction

Synthesis and applications of ferrocene derivatives as ligands have been reported extensively. Many specific ligands containing O, S or/and N atoms [1–3] in their structures in order to have high transition metal coordination ability, were previously reported for chemical sensor, homogeneous catalysts, and conformationally switchable materials [4–9], Now we report two new ferrocenophane compounds which have well-defined structures.

#### Experimental

The title compounds 1 and 2 were obtained by esterification (purity: 99%). according to the following method. 1,10-Ferrocene-di(carbonyl chloride) (1.0 g, 3 mmol) were added dropwise over 8 h to a stirring mixture of The dihydric alcohols (3 mmol), 800 mL of dry DCM, and 0.5 mL (6 mmol) of pyridine at room temperature. The mixture was stirred for one day at room temperature and then refluxed for another 4 h (monitored by thin-layer chromatography, TLC). About 700 mL of the solvent was evaporated, and the residual solution was washed with 50 mL of water three times and dried over anhydrous MgSO4. After filtered, the solvent

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was removed to leaving a crude product. Column chromatography on silica gel (petroleum ether: ethyl acetate: dichloromethane = 8:2:1) afforded ester ferrocenophane (Scheme 1).

Single crystals of (I) and (II) suitable for X-ray diffraction studies were grown directly by slow evaporation of 10 ml of the maturated neat  $CH_2Cl_2/EtOAc$  (1/4 v/v) solution of either 1 or 2 on a microscope slide.



Scheme 1. Synthetic route for the title compounds [10, 11].

#### **Compound 1**

Red solid (45%).m.p. 165–166°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>)  $\delta$ : 7.17(m, 1H, aromatic), 6.63 m(m, 3H, aromatic), 4.70(m, 4H, Fc-H), 4.50(t, 4H, (-O-CH<sub>2</sub>-)), 4.47(m, 4H, Fc-H), 3.74(t, 4H, (-N-CH<sub>2</sub>-)), 2.34(s, 3H, (-CH<sub>3</sub>-)).IR (KBr)  $\upsilon$ : 3427, 3098, 2927, 1719, 1597, 1497, 1467, 1383, 1283, 1153, 1036, 921, 834, 766, 686, 597, 544, 506, 486, 435 cm<sup>-1</sup>. Anal. Calcd of C<sub>23</sub>H<sub>23</sub>FeNO<sub>4</sub>: calcd. C 63.76, H 5.35; found C 61.89, H 5.25. MALDI-TOP MS *m*/*z* = 434[M+H]<sup>+</sup>.

#### **Compound 2**

Yellow solid (38%).m.p. 150–151°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>)  $\delta$ : 7.26(m, 3H, aromatic), 7.09 m (m, 1H, aromatic), 4.81(m, 4H, Fc-H), 4.51(m, 4H, Fc-H), 4.30(t, 4H, (-O-CH<sub>2</sub>-)), 3.41(t, 4H, (-N-CH<sub>2</sub>-)), 2.50(s, 3H, (-CH<sub>3</sub>-)). IR (KBr)  $\upsilon$ : 3430, 3100, 2922, 1723, 1626, 1578, 1461, 1374, 1279, 1147, 1027, 917, 825, 763, 730, 604, 535, 472 cm<sup>-1</sup>. Anal. Calcd of C<sub>23</sub>H<sub>23</sub>FeNO<sub>4</sub>: calcd. C 63.76, H 5.35; found C 61.89, H 5.25. MALDI-TOP MS  $m/z = 434[M+H]^+$ .

#### **Results and discussion**

Compounds 1 and 2 crystallize in different space groups, P2<sub>1</sub>/c and P2<sub>1</sub>/n. The molecular structures of 1 and 2 with atomic numbering scheme are presented in Fig. 1. Traditional hydrogen bonding interactions (such as O-H…O) are not observed in compound 1 and 2 for the hydroxyl H atom, and the absence of such bonding could be attributed to steric and electronic effects. The ultima supramolecule formed due to the synergic effects of these weak interactions. Interestingly, the aggregate is neither traditional J- nor H-aggregates. In ferrocene, the cyclopentadiene(Cp) rings are parallel to each others, but in 1 and 2 the (Cp) rings are almost parallel with the average deviations from the least-squares planes of 5.02 and 2.35Å, respectively. The Cp and Phenyl rings are almost vertical in 1, but are almost coplanar in 2. In both compounds, the C–C bond distances in the Cp rings range between 1.407 and 1.431Å. The C=O bond lengths in molecules 1 are 1.199Å(3) for O(1)-C(6) and 1.206Å(2) for O(3)-C(11), in molecules 2 are 1.199Å(5) for O(4)-C(11) and 1.203Å(4) for O(1)-C(6). Additionaly, the bond lengths are 1.467Å(3) for C(5)-C(6) and 1.477Å(3) for C(11)-C(12) in molecules 2 respectively, which are shorter than a normal C-C single bond lengths (1.53Å) and longer



Figure 1. Asymmetric unit of the compound 1 and 2 with labelling and thermal ellipsoids at the 50% probability level.

than a normal double bond lengths (1.32Å). These structural features in complexes 1 and 2 indicate that there is partial delocalization of electrons from the ferrocene to C=O groups. A view of the crystal packing of 1 in the unit cell is shown in Fig. 2. The crystal packing of the compound is stabilized by several non-bonded interactions. In an individual supramoecule, the chains of 1 are connected to each other in an inversion dimmer *via* C-H···O interactions  $(C(9)-H(9B)\cdots O(4) = 2.477 \text{ Å and } C(8)-H(8A)\cdots O(1) = 2.480 \text{ Å})$  (Fig. 2a). These inversion dimers are further connected by C-H···C contacts (Fig. 2b). In the crystal packing of 2, the molecules related by inversion are linked to each other via C-H···O interactions  $(C(1)-H(1)\cdots O(1) = 2.694 \text{ Å and } C(8)-H(8B)\cdots O(3) = 2.573 \text{ Å})$  arranged into chains (Fig. 3a).

The bond angles around the central tetrahedra N, which are range from  $110.89^{\circ}(15)$  to  $113.64^{\circ}(15)$  for 1 and those are from  $116.5^{\circ}(3)$  to  $121.8^{\circ}(4)$  for 2. it is close to the value for a regular tetrahedron. The C atoms in the Ph-rings deviate significantly from coplanarity, the torsion angles of C-C-C-C are vary in the range  $[-0.9^{\circ}(4)-1.0^{\circ}(3)$  for 1 and  $-1.2^{\circ}(7)-1.1^{\circ}(7)$  for 2]. also the torsion angles of C-C-C-C in two Cp rings are vary in the range  $[-0.5^{\circ}(2)-0.4^{\circ}(2)$  for 1 and  $-0.9^{\circ}(5)-0.9^{\circ}(5)$  for 2], What's more, the methyl on the Phenylrings are in a *trans* disposition to Cp in 1 and 2, These data show that both the size and the tilt angle of Cp lessen after cyclization. In the molecule, the corresponding bonds also are different on the two bridges, such as C-O, C-C and C-N bonds, we choose the right angles to analyze the complex 1both the two Cp rings and the two bridges are almost overlapping, but this phenomenon cannot occur to the complex 2. those difference maybe caused by the different steric and stack interactions.

The intermolecular short contact C–H···O, C–H··· $\pi$  and C–H···C stacking interactions play significant roles in forming the 3-D structures. the whole molecular form a "foldered" scoop structure 1 and a dragonfly structure 2 (Fig. 4). This kind of conformation is crucial to its photochromic and photoinduced properties



(a)



**Figure 2.** Crystal structure description of 1. The carbonyl C=O oxygen of the ester group is involved in short contact with CH<sub>2</sub> via a C-H···O interaction that leads to the formation of a one-dimensional (1D) short contacted network (Fig. 2a). Such 2D networks are further self-assembled via C-H··· $\pi$  (Ph) interactions and form a 2D sheet and 3D short contacted sheets via C-H···C. (Fig. 2b).



**Figure 3.** Crystal structure description of 2: The carbonyl C=O oxygen of the ester group is involved in short contact with CH<sub>2</sub> via a C-H···O interaction that leads to the formation of a 1D network (Fig. 3a). Such 3D networks are further self-assembled via C-H··· $\pi$  interactions (Fig 3b). 3D short contacted network formed by the C-H···C short contact interaction (Fig 3c).

#### Photophysical properties of compounds

The absorption and fluorescence spectra of the two compounds in dichloromethane  $(CH_2Cl_2)$  solutions at room temperature are shown in Fig. 5 and Fig. 6. we can see that the absorption spectra exhibit two peak at about 228 nm and 257 nm, it is obvious the higher peak of the complex 1 generally red shifts compare with 2, and the different could be caused by the twisted intramolecular charge transfer (TICT) .Taking into account the excellent photoluminescent properties of  $d^6$  coordination polymers, the photoluminescent properties of complexes 1 and 2 were studied in dichloromethane ( $CH_2Cl_2$ ) at room temperature. As depicted in Fig. 5. and Fig. 6. while both 1 and 2 exhibit an intense broad emission at at 334 nm and 395 nm ( $\lambda ex = 257$  nm), which is quite similar. Therefore, the origin of emissions of complexes 1 and



Figure 4. Assembling of the molecules of 1 into a "foldered" scoop and 2 into a lot of " dragonfly " threedimensional structure (3D).



Figure 5. The UV-vis spectroscopic measurements studies of compounds 1 and 2 in  $CH_2Cl_2$  (1 × 10<sup>-4</sup> mol/L).



Figure 6. The fluorescence properties studies of compounds 1 and 2 in  $CH_2CI_2$  (10<sup>-6</sup>mol/L).



Figure 7. IR spectra of 1 and 2.

2 may be attributed to the internal charge transfer ( $\pi \rightarrow \pi^*$  transitions) and the absorption is attributed to  $\pi$ - $\pi^*$  transition of the whole  $\pi$ -conjugated system. The observation indicates that their potential applications as enzyme models and molecular recognition hosts.

The infrared spectra of the two complexes were recorded in the range of  $4000 \sim 400 \text{ cm}^{-1}$  with KBr pallets, as shown in Fig. 7. The C=O absorption peak of carboxyl groups at 1719 cm<sup>-1</sup> for 1 and 1723 cm<sup>-1</sup> for 2 which means the formation of carboxylates. At the same time, other different absorption peaks at 1626 cm<sup>-1</sup> are observed in 2, should be ascribed



Figure 8. <sup>1</sup>H NMR spectrum of 1 and 2 in CDCl<sub>3</sub>.

to the asymmetrical stretching vibration of -COO- groups. but it is not observed in 1, The changes of IR spectra indicate different intramolecular contact in the two complexes. In order to verify the structure change, we investigate the <sup>1</sup>H NMR spectral changes of 3-CH<sub>3</sub> and 2-CH<sub>3</sub> forms. The <sup>1</sup>H NMR analysis of compound 1 in CDCl<sub>3</sub> exhibited the signal changes of protons in Fig. 8. For instance, the phenyl proton of compound 1 appeared as a singlet at  $\delta$ : 7.17 and 6.63. However, the phenyl proton of compound 2 exhibited a singlet signals at  $\partial$ :7.26 and 7.09, respectively. The methyl resonance of compound 1 is observed at  $\partial$ : 2.34, and those of the compound 2 appeared at  $\partial$ : 2.50, which may be attributed to the steric effect on the methyl resonance in the different position.

#### Conclusion

In this study, two new ferrocenophane compounds were synthesized and mainly characterized by <sup>1</sup>H-NMR and X-ray diffraction. The molecular structures and packing diagrams of the title compounds showed that the molecules form dimers and various ring motifs as part of the chains stabilized by several non-bonded interactions. As expected, complexes 1 and 2 show different photophysical properties. The title compounds have a potential of new chemical sensors.

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