# Synthesis, Crystal Structure and Luminescence Properties of the Inorganic-Organic Hybrid Compound $[FTMA]_2[CdI_4]$ (FTMA = Ferrocenylmethyltrimethylammonium Cation)

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The title compound $[FTMA]_2[CdI_4]$ has been synthesized from [FTMA]I (ferrocenylmethyltrimethylammonium iodide) and $3\,CdSO_4 \cdot 8H_2O$ and was characterized by elemental analysis, IR spectra and single-crystal X-ray diffraction. The Cd(II) atom has a slightly distorted tetrahedral coordination sphere. In the solid state there are C-H$\cdots\pi$ interactions between adjacent ferrocenyl cations to generate a chain structure. The luminescence properties of the title compound were investigated in the solid state at room temperature.

*Key words:* Inorganic-Organic Hybrid, Crystal Structure, Luminescence Properties

## Introduction

Inorganic-organic hybrid materials have attracted considerable attention because of their special functional properties such as redox and photophysical activity, magnetism and catalysis [1 – 4]. The synthesis of hybrid materials using coordination anions as counterions is a useful strategy allowing us to probe systematically the effect of modifications to the anion backbone through which we are attempting to control the precise topography of the crystal structure [5 – 7]. In our previous studies we have assembled inorganic-organic hybrid crystals by the reactions of thiocyanato-cadmium anions with counterions such as 1-(4′-$NO_2$-benzyl)-quinolinium, $[O_2NBzQL]^+$, and 1-(4′-R-benzyl)pyridinium, $[RBzPy]^+$ (R = Cl and Br) [8, 9].

To ferrocene and its derivatives much attention is paid because of their fascinating sandwich structure and unusual properties [10 – 12], which continue to attract great interest, in particular because of their potential and developed applications in the fields of photochemistry, electrochemistry, catalysis, and medicine [13 – 16]. Our current interest is the construction of inorganic-organic hybrid materials by the use of ferrocenyl derivatives as counterions instead of the above cations, and this change is anticipated to affect the crystal structure and to obtain compounds with interesting physical properties. As a part of our continuing investigations on inorganic-organic hybrid compounds and their photoluminescence properties [8, 9, 17 – 21], herein we report the synthesis and crystal structure of a new hybrid compound $[FTMA]_2[CdI_4]$, **1**, (ferrocenylmethyltrimethylammonium tetraiodocadmate) displaying fluorescent emission at r. t.

## Experimental Section

### General

*Materials:* All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. [FTMA]I (ferrocenylmethyltrimethylammonium iodide) was prepared according to literature methods [15].

*Instrumentation:* Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded from KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000 – 400 $cm^{-1}$ region. The UV/Vis spectra were measured in aqueous solution with a Hitachi U-4100 spectrophotometer, and the luminescence spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer.

### Synthesis

10 mL of an aqueous solution of $3\,CdSO_4 \cdot 8H_2O$ (0.020 g, 0.026 mmol) was slowly added to 10 mL of an ethanol solution of [FTMA]I (0.030 g, 0.077 mmol). After stirring for 20 min, the resultant brown solution was filtered and left for slow evaporation at r. t. to obtain dark-red block-shaped crystals suitable for X-ray structure determination. – Elemental analysis for $C_{28}H_{40}Fe_2N_2CdI_4$ (1136.4): calcd. C 29.60, H 3.55, N 2.47; found C 29.52, H 3.61, N 2.49.

### X-Ray crystallographic study

A suitable crystal of size $0.37 \times 0.29 \times 0.22$ $mm^3$ was chosen for the crystallographic study and mounted on a

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Table 1. Summary of crystal data and refinement results for compound **1**.

| | |
|---|---|
| Formula | $C_{28}H_{40}Fe_2CdI_4$ |
| $M_r$ | 1136.32 |
| Crystal size, mm$^3$ | $0.37 \times 0.29 \times 0.22$ |
| Crystal system | monoclinic |
| Space group | $C2/c$ |
| $a$, Å | 26.647(3) |
| $b$, Å | 10.464(1) |
| $c$, Å | 15.528(2) |
| $\beta$, deg | 123.338(1) |
| $V$, Å$^3$ | 3617.4(7) |
| $Z$ | 4 |
| $D_{\text{calcd}}$, g cm$^{-3}$ | 2.09 |
| $\mu(\text{Mo}K_\alpha)$, cm$^{-1}$ | 4.8 |
| $F(000)$, e | 2136 |
| $\theta$ range data collection, deg | 2.15 – 25.49 |
| *hkl* range | $-26 \le h \le 32$, $-8 \le k \le 12$, $-17 \le l \le 18$ |
| Refl. measured / unique / $R_{\text{int}}$ | 8860 / 3365 / 0.023 |
| Param. refined | 169 |
| $R1(F)$ / $wR2(F^2)$ [$I \ge 2\sigma(I)$] | 0.0338 / 0.0815 |
| $R1(F)$ / $wR2(F^2)$ (all refl.) | 0.0412 / 0.0846 |
| Gof ($F^2$) | 1.060 |
| $\Delta\rho_{\text{fin}}$ (max / min), e Å$^{-3}$ | 1.32 / −1.27 |

Bruker SMART APEX CCD diffractometer. The measurement was performed at room temperature using graphite-monochromatized Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Data were collected in $\omega$- and $\phi$-scan mode in the range of 2.12° < $\theta$ < 25.49°. The structure was solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares on $F^2$ using SHELXL-97 [22]. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were geometrically fixed and allowed to ride on the parent atoms to which they were attached. Space group, lattice parameters and data pertinent to data collection and structure refinement are listed in Table 1.

CCDC 793690 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

## Results and Discussion

### *IR and UV spectra*

Compared with the values 3042, 2936 and 1471 cm$^{-1}$ assigned to the Ar-H, N-$CH_3$ and $CH_2$ groups of [FTMA]I, compound **1** exhibits these bands at 3075, 2983 and 1472 cm$^{-1}$, respectively. Bands of **1** at 1407, 1103, 981, 826, and 481 cm$^{-1}$ are assigned to the stretching vibrations of ferrocene. These results agree well with those of related compounds [15]. The UV spectra of compound **1** and of [FTMA]I in aqueous solution display strong absorption peaks at 244 and 225 nm, respectively. The 19 nm red-shift suggests coordination of the iodine atom to Cd in **1**. These observations have been confirmed by X-ray single-crystal structure analysis.

### *X-Ray crystal structure*

The structure analysis revealed that compound **1** crystallizes in the monoclinic space group $C2/c$. An ORTEP diagram with the atomic numbering scheme is

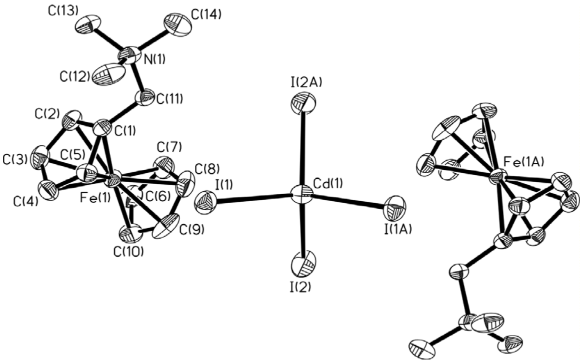

Fig. 1. ORTEP drawing of compound **1** with crystallographic atom numbering scheme. The atoms are drawn as 30 % displacement ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity (symmetry code: A: $-x$, $y$, $-z + 1/2$).

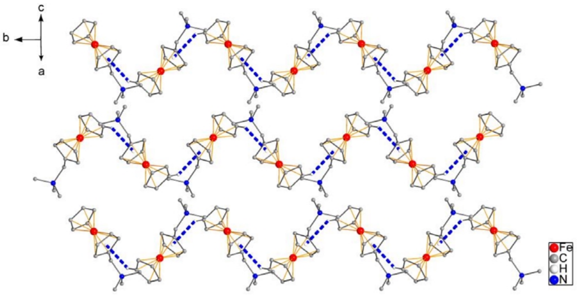

Fig. 2 (color online). Illustration of the zigzag chains of the cations in compound **1** ($[CdI_4]^{2-}$ anions have been omitted) with C-H$\cdots\pi$ interactions indicated as dashed lines.

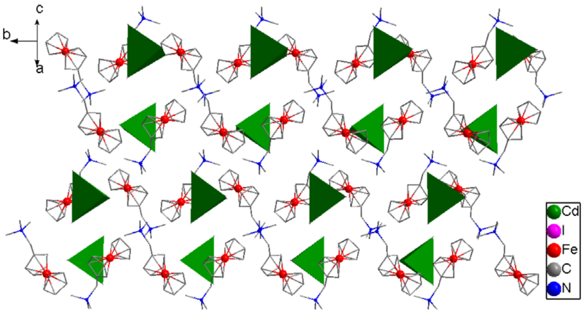

Fig. 3 (color online). Packing diagram of compound **1**.

Table 2. Selected bond lengths (Å) and angles (deg) for compound **1**.[a]

| | | | |
|---|---|---|---|
| Cd(1)–I(1) | 2.7945(5) | Cd(1)–I(2) | 2.7621(5) |
| Fe(1)–C(1) | 2.019(4) | Fe(1)–C(2) | 2.038(5) |
| Fe(1)–C(3) | 2.058(5) | Fe(1)–C(4) | 2.044(6) |
| Fe(1)–C(5) | 2.031(5) | Fe(1)–C(6) | 2.042(6) |
| Fe(1)–C(7) | 2.039(6) | Fe(1)–C(8) | 2.026(6) |
| Fe(1)–C(9) | 2.022(6) | Fe(1)–C(10) | 2.037(6) |
| I(1)–Cd(1)–I(2) | 109.364(16) | I(1)–Cd(1)–I(1A) | 110.48(2) |
| I(1A)–Cd(1)–I(2) | 106.841(14) | I(2)–Cd(1)–I(2A) | 113.97(3) |

[a] Symmetry code: A: $-x$, $y$, $-z+1/2$.

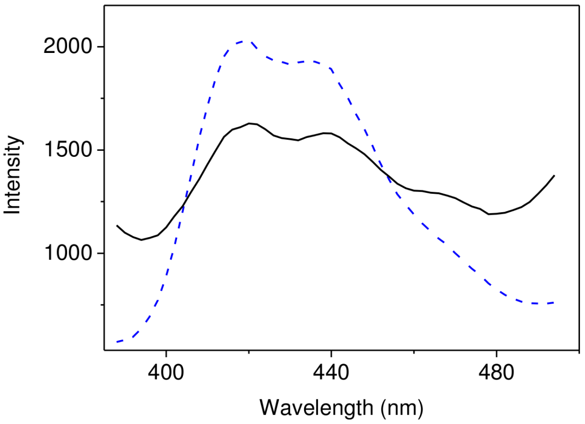

Fig. 4 (color online). Emission spectrum of compound **1** (solid) and [FTMA]I (dashed) upon excitation at 270 nm in the solid state at room temperature.

depicted in Fig. 1. A chain of the cations connected through C-H$\cdots\pi$ interactions is illustrated in Fig. 2, the packing diagram of cations and complex anions in Fig. 3. Selected bond lengths and angles are listed in Table 2.

The asymmetric unit consists of one $[FTMA]^+$ cation and one half $[CdI_4]^{2-}$ anion. The cadmium atom is surrounded by four iodine atoms to attain a slightly distorted tetrahedral coordination geometry. The average Cd–I bond length is 2.778 Å, and the average bond angle at the Cd center is 109.5°. Analysis of the molecular packing of **1** suggests that adjacent $[FTMA]^+$ building blocks generate a 1D zigzag chain through strong C-H$\cdots\pi$ interactions, in which each cation acts as a 2-connected node. The C-H$\cdots\pi$ interaction is characterized by a H(6AA)$\cdots$M [midpoint of the Cp ring C(1)-C(5)] distance of 2.86 Å and a C(6A)$\cdots$M distance of 3.73 Å, with the C-H$\cdots$M angle at 148°. The adjacent chain adopts a transoid configuration to give rectangular voids in which the $[CdI_4]^{2-}$ anions are inserted.

### *Luminescence properties*

A strategy of the incorporation of a ferrocenyl derivative into a luminescent system is anticipated to lead to functional hybrid materials with new physical properties, in which ferrocene is acting as the redox center of a photochemically active compound [10]. Our previous work focused mainly on the investigation of a series of inorganic-organic hybrid compounds containing pyridinium derivatives as the counterions of Cd-containing anions and their photoluminescence properties [8, 9]. Instead of pyridinium cations, herein the ferrocenyl cation $[FTMA]^+$ has been selected to prepare a new hybrid compound. To enrich the database on fluorescence of this type, the solid-state luminescence properties of compound **1** and [FTMA]I were investigated at r. t. As shown in Fig. 4, upon excitation at 270 nm, compound **1** shows emission bands at 420 and 440 nm, while the emission bands of [FTMA]I are at 419 nm and 438 nm. The weakened fluorescence suggests an interaction between the ferrocenyl cations and the $[CdI_4]^{2-}$ anions. These emissions can be attributed to charge-transfer transitions between the anions and the cations as also observed in pyridinium iodide derivatives [23, 24].

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