

## Synthesis, Structure, Photoluminescence and Theoretical Study of (MQ)(CdBr<sub>4</sub>) with MQ<sup>2+</sup> Generated *In Situ* (MQ<sup>2+</sup> = *N*-Me-4,4'-bipyridinium)

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A new compound (MQ)(CdBr<sub>4</sub>) (**1**; MQ<sup>2+</sup> = *N*-Me-4,4'-bipyridinium), in which the MQ<sup>2+</sup> was generated in situ, has been synthesized *via* hydrothermal reaction. The title compound features an isolated structure, based on discrete MQ<sup>2+</sup> moieties and tetrahedral cadmium atoms terminally coordinated by four bromine atoms. The MQ<sup>2+</sup> moieties and tetrabromo-cadmium dianions are linked *via* hydrogen bonds. Photoluminescent investigation reveals that the title compound displays a strong blue-light emission, which is attributed to a ligand-to-ligand charge-transfer (LLCT; from the HOMO of the bromine atoms to the LUMO+1 of the MQ<sup>2+</sup> moieties) mechanism probed by molecular orbital (MO) calculations.

**Keywords:** Cadmium, Crystal structure, LLCT, MO, Photoluminescence

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### INTRODUCTION

Recently, enormous metal compounds have been synthesized, among which many are transition metal compounds that play a very important role in many areas of chemistry and biology [1]. Transition metal compounds containing group 12 (IIB) elements are particularly attractive for many reasons, such as, the variety of coordination numbers and geometries provided by the d<sup>10</sup> configuration of the IIB metal ions, the well-known toxicity of cadmium and mercury, photoelectric properties, fluorescent properties, and the essential role in biological systems of zinc, *etc.*

Fluorescent materials, particularly blue fluorescent materials have been of intense interest because blue fluorescence is one of the key color components required for full-color EL displays and blue fluorescent materials are still rare. Nowadays, some IIB metal compounds possessing fluorescent properties have been reported [2]. Our recent

efforts in synthesizing novel IIB-based compounds have focused largely on the systems with photoluminescence. Herein, we report the solvothermal synthesis, structure, photoluminescence and theoretical study of (MQ)(CdBr<sub>4</sub>) (**1**) with MQ<sup>2+</sup> generated in situ (MQ<sup>2+</sup> = *N*-Me-4,4'-bipyridinium). The electronic transition in the photoluminescent process of **1** has been studied by means of time-dependent density functional theory (TDDFT) calculation.

### EXPERIMENTAL

#### Instrumentation

All reactants of A.R. grade were obtained commercially and used without further purification. The solid-state fluorescent study was conducted at room temperature on a JY Fluorolog-322 fluorescence spectroscopy instrument. Time-dependent density functional theory (TDDFT) calculations were performed, employing the Gaussian98 suite of programs, at the B3LYP level. The intensity data set was collected on Rigaku Mercury CCD X-ray diffractometer with

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graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using a  $\omega$  scan technique. Crystal Clear software was used for data reduction and empirical absorption correction [3]. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software [4]. The difference Fourier maps based on these atomic positions yield the other non-hydrogen atoms. The hydrogen atom positions were generated symmetrically, allowed to ride

on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structures were refined using a full-matrix least-squares refinement on  $F^2$ . All atoms except for hydrogen atoms were refined anisotropically. A summary of crystallographic data and structure analysis is listed in Table 1, and selected bond distances and bond angles are given in Table 2.

**Table 1.** Summary of Crystallographic Data and Structure Analysis for **1**

Formula	$\text{C}_{11}\text{H}_{13}\text{Br}_4\text{CdN}_2$
FW	605.27
colour	yellow
Crystal size ( $\text{mm}^3$ )	0.35 0.20 0.20
Crystal system	monoclinic
Space group	$P2_1/c$
$a$ ( $\text{\AA}$ )	8.153(4)
$b$ ( $\text{\AA}$ )	23.060(3)
$c$ ( $\text{\AA}$ )	9.519(5)
$\beta$ ( $^\circ$ )	107.031(6)
$V$ ( $\text{\AA}^3$ )	1711.3(12)
$Z$	4
$2\theta_{\text{max}}$ ( $^\circ$ )	50.7
Reflections collected	13153
Independent, observed reflections ( $R_{\text{int}}$ )	3037, 1367 (0.1477)
$d_{\text{calcd.}}$ ( $\text{g cm}^{-3}$ )	2.349
$\mu$ ( $\text{mm}^{-1}$ )	10.601
$T$ (K)	293(2)
$F(000)$	1124
$R1, wR2$	0.0760, 0.1821
$S$	0.890
Largest and Mean $\Delta/\sigma$	0.001, 0
$\Delta\rho$ (max/min) ( $\text{e/\AA}^3$ )	1.915, -0.670

**Table 2.** Selected Bond Lengths ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ )

Cd(1)-Br(1)	2.6409(5)	Br(1)-Cd(1)-Br(3)	109.98(3)
Cd(1)-Br(2)	2.6465(13)	Br(1)-Cd(1)-Br(4)	108.197(19)
Cd(1)-Br(3)	2.6657(6)	Br(2)-Cd(1)-Br(3)	116.701(14)
Cd(1)-Br(4)	2.6554(10)	Br(2)-Cd(1)-Br(4)	109.79(4)
Br(1)-Cd(1)-Br(2)	107.553(13)	Br(3)-Cd(1)-Br(4)	104.35(3)

## Synthesis

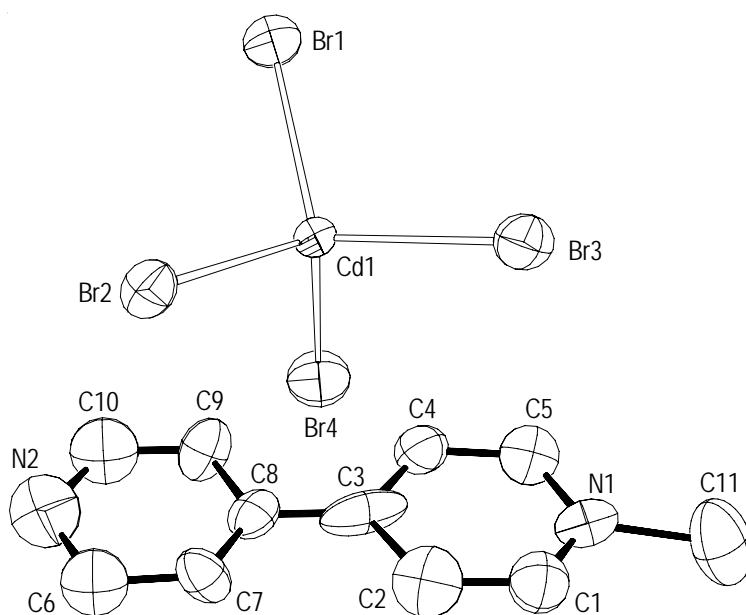
**(MQ)(CdBr<sub>4</sub>) (1).** CdBr<sub>2</sub>·4H<sub>2</sub>O (0.3 mmol, 103.2 mg), 4,4'-bipy (0.2 mmol, 31.2 mg), HBr acid (5 ml), methanol (2 ml) and distilled water (5 ml) were loaded into a Teflon-lined stainless steel autoclave (25 ml) and kept at 373 K for 3 days. After being slowly cooled to room temperature at a rate of 8 K h<sup>-1</sup>, yellow crystals suitable for X-ray analysis were obtained. Yield: 71% (based on cadmium).

## RESULTS AND DISCUSSION

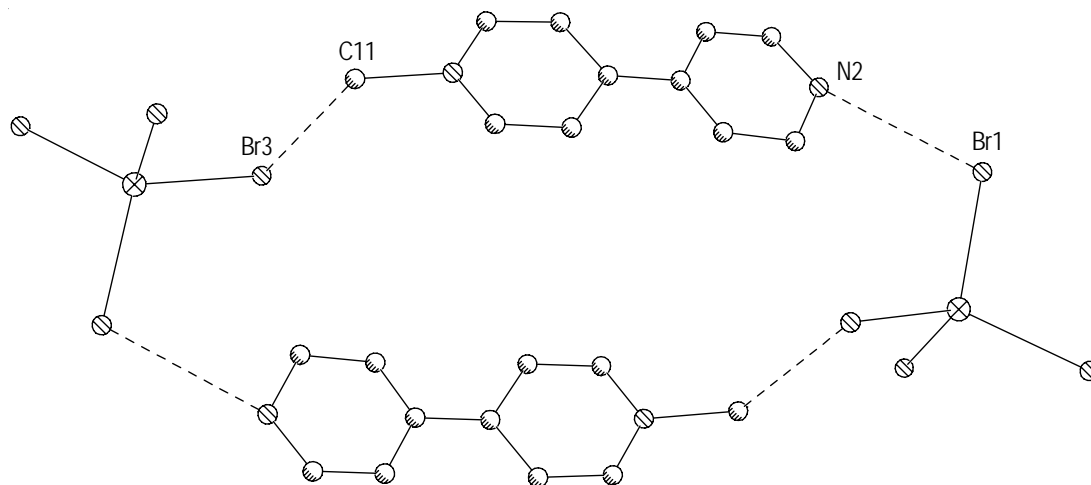
Hydro(solvo) thermal synthesis has recently been proven to be a useful technique in the preparation of solid-state materials and this method is well-known for its effectiveness in *in situ* reactions. When superheated, water behaves very differently from what is observed under ambient conditions. The significantly lowered viscosity, for example, increases the solubility as well as the diffusion rate of the reagents, therefore possibly leading to *in situ* reactions. A variety of novel compounds synthesized *in situ* have been documented [5]. However, viologen-containing *in situ* reactions are relatively rare [6].

An ORTEP drawing of **1** is shown in Fig. 1. The structure of **1** consists of MQ<sup>2+</sup> cations and CdBr<sub>4</sub><sup>2-</sup> anions. All the crystallographically independent atoms are in general

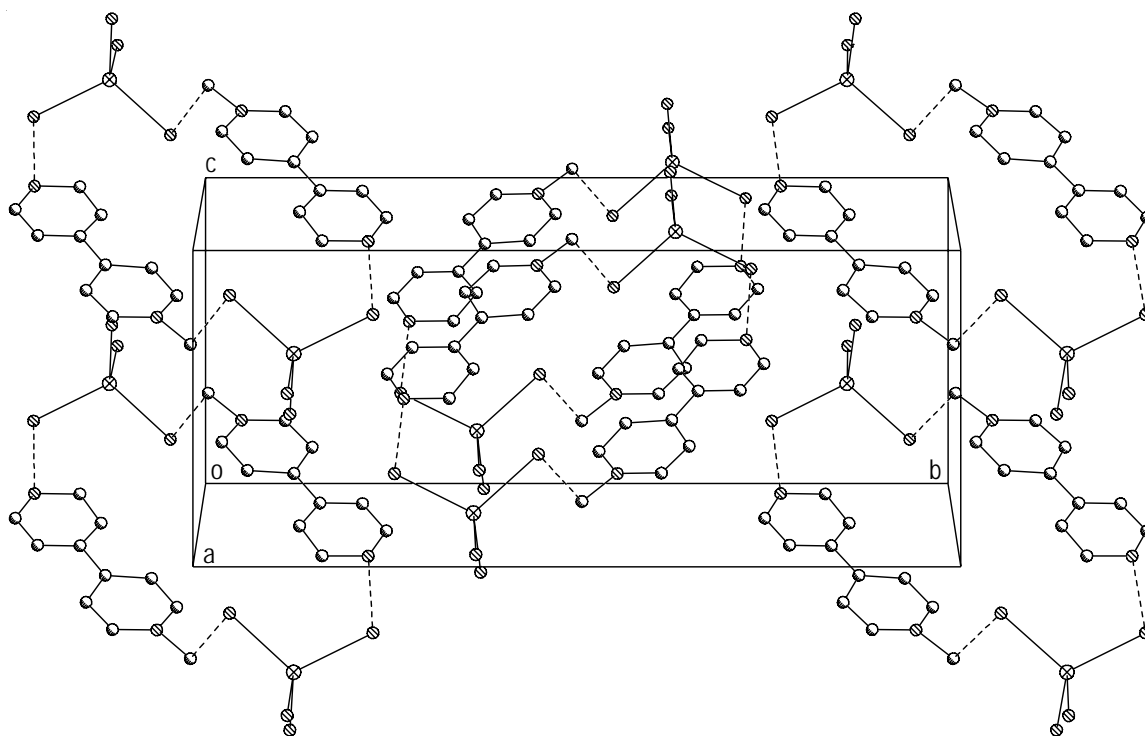
positions. The Cd1 atom has a slightly distorted tetrahedral geometry, coordinating with four terminal bromine atoms with the bond lengths of Cd1-Br1, Cd1-Br2, Cd1-Br3 and Cd1-Br4 being 2.6409(5), 2.6465(13), 2.6657(6) and 2.6554(10) Å which are comparable with those in the reference [7], and the bond angles of Br-Cd-Br ranging from 104.35(3) to 116.701(14)°, respectively, which are close to those in a regular tetrahedron. For the requirement of charge balance, the nitrogen atoms must be protonated, as the cases found in other compounds [8]. The MQ<sup>2+</sup> moieties and tetrabromo-cadmium dianions are linked *via* the hydrogen bonds C11...Br3(-1-x, 1-y, -z) and N2...Br1(x, y, 1+z) with the bond lengths being of 3.184(4) and 3.410(5) Å, respectively. Every two MQ<sup>2+</sup> cations and two tetrabromo-cadmium dianions interconnect to each other *via* such hydrogen bonds in head-to-tail mode to give a four-membered ring-like structure, as shown in Fig. 2. These four-membered ring-like moieties pack in -ABAB- mode along the *b* axis (Fig. 3). The two pyridyl rings of the MQ<sup>2+</sup> ligand are twisted with a small dihedral angle of *ca.*, 2.27°, which is comparable with those previously documented [9]. There is no π...π stacking interactions between the MQ<sup>2+</sup> ligand in the title compound. Therefore, the hydrogen bonds and the electrostatic interactions between the MQ<sup>2+</sup> cations and tetrabromo-cadmium dianions contribute to the stabilization of the crystal packing of **1** (Fig. 3).



**Fig. 1.** ORTEP drawing of **1** with 30% thermal ellipsoids (hydrogen atoms omitted for clarity).



**Fig. 2.** The hydrogen bonding ring-like structure with the hydrogen bonds (Å) C11...Br3(-1-x, 1-y, -z) 3.184(4) and N2...Br1(x, y, 1+z) 3.410(5).



**Fig. 3.** Packing diagram of **1** with the dashed lines representing the hydrogen bonds.

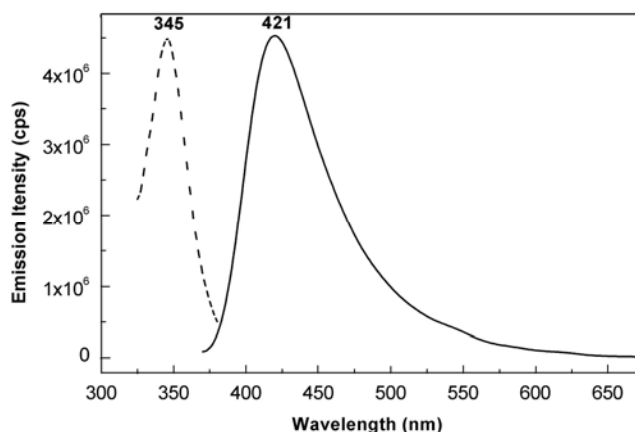
Unlike the syntheses of other viologen-based compounds, in which the viologen cation was derived from the starting reagent [10], the preparation of **1** resulted in *in situ* generation of the MQ<sup>2+</sup> dication. This provides a route for the synthesis of

viologenbased compounds, and makes the synthesis of viologen comparatively less toxic and more efficient. To our knowledge, this is the first example of the *in situ* generation of the MQ<sup>2+</sup> dication (MQ<sup>2+</sup> = N-Me-4,4'-bipyridinium), although

an unprecedented *in situ* generation of the  $MV^{2+}$  dication ( $MV^{2+} = N,N'$ -dimethyl-4,4'-bipyridinium) was reported before [6]. Obviously, the  $MQ^{2+}$  dication in **1** ( $MQ^{2+} = N$ -Me-4,4'-bipyridinium) is different from the  $MV^{2+}$  dication ( $MV^{2+} = N,N'$ -dimethyl-4,4'-bipyridinium) reported before.

The emission spectrum of **1** in the solid state at room temperature is investigated. It can be observed that an intense emission with a maximum wavelength of 421 nm upon photo-excitation at 345 nm for **1**, as shown in Fig. 4. To understand the nature of the fluorescent emission of **1**, theoretical computation has been performed on **1**. The ground state geometry was adapted from the X-ray data. On the basis of this geometry, time-dependent DFT (TDDFT) calculation using the B3LYP functional was performed [11]. The result indicate that the lowest singlet excitation is dominated by the HOMO→LUMO+1 transition, in which the HOMO consists of p orbital of bromine atoms, while the LUMO+1 is distributed on the  $MQ^{2+}$  moieties (Fig. 5), suggesting that the emission band of **1** is attributed to the ligand-to-ligand charge transfer (LLCT).

In conclusion, a novel compound has been synthesized and characterized. Photoluminescent investigation reveals that it displays strong emission in blue region, in combination with the molecular orbital (MO) calculation, lead us to conclude that the emission originates from ligand-to-ligand charge transfer (LLCT) transition. It is the first example of the *in situ* generation of the  $MQ^{2+}$  dication ( $MQ^{2+} = N$ -Me-4,4'-bipyridinium). The *in situ* formation of  $MQ^{2+}$  in the title

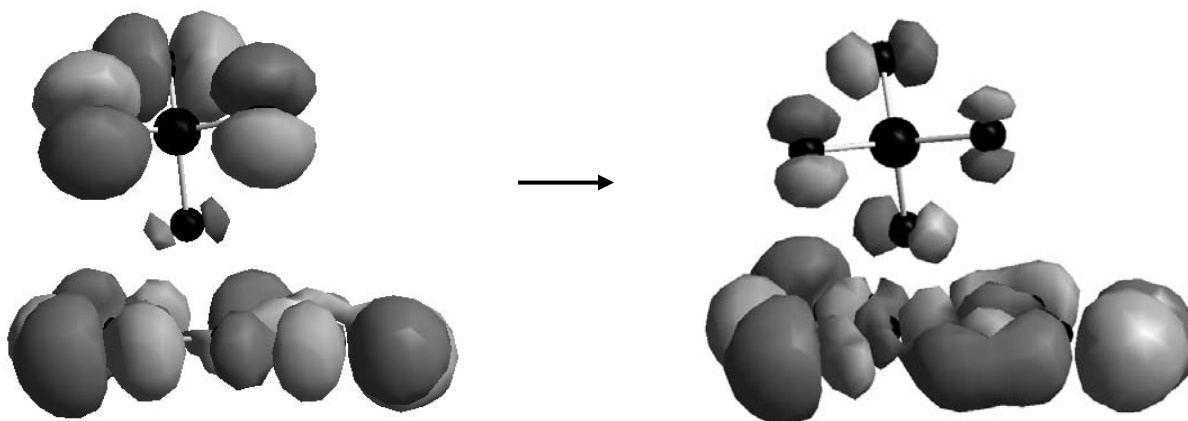


**Fig. 4.** Solid-state emission and excitation spectra of **1** at room temperature. Solid line: emission spectrum; dashed line: excitation spectrum.

compound may serve as a more efficient approach for the synthesis of viologenbased compounds. The scope for the syntheses of new viologenbased compounds with novel structures and properties appear to be very large, and further systematically experimental and theoretical investigations on this system are in progress.

## SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center



**Fig. 5.** The electron-density distribution of HOMO (left) and LUMO+1 (right) calculated for **1**. The isosurfaces correspond to electronic density differences of  $-0.01 e\text{\AA}^{-3}$  (white gray) and  $+0.01 e\text{\AA}^{-3}$  (dark gray).

No. 676752 for 1. Copies of this information can be had free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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