Two noncentrosymmetric complexes: [W(CO)$_4$(bipy)] and [W(CO)$_4$(phen)](bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline) obtained through solvothermal synthesis and their optical properties

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Abstract

Solvothermal treatments of W(CO)$_6$ with 2,2′-bipyridine and 1,10-phenanthroline give [W(CO)$_4$(bipy)] (**1**) and [W(CO)$_4$(phen)] (**2**), respectively, which both crystallize in noncentrosymmetric space groups, suggesting that they meet the requirement of second harmonic generation (SHG) investigations. The preliminary experiment indicates that they are SHG active, and approximately estimated to be that of urea.
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1. Introduction

Noncentrosymmetric space group symmetry is a requirement for a number of technologically relevant properties, including piezoelectricity, pyroelectricity, ferroelectricity, and second harmonic generation (SHG) [1]. SHG describes the ability of a material to double the frequency of incident light, a feature that is important to many advanced optoelectronics applications [2].The rational construction of structurally ordered noncentrosymmetric solid presents a formidable challenge to synthetic chemists. Recently, attempts to generate acentric metal-organic coordination polymers and organic solids by employing crystal engineering strategies have met with some success [3]. Especially, Ward et al. described a crystal engineering design strategy that produced a series of solid-state molecular host frameworks with prescribed lattice metrics and polar crystallographic symmetries. This represents a significant advance in crystal engineering [4]. We have accordingly become interested in generating coordination compound that possess useful physical properties, particularly, SHG responses, and we focused on the use of chiral building blocks to encourage crystallization in an appropriate space group [5]. The synthesis of such materials from achiral organic ligands has been a particularly noteworthy challenge. Although it is not always possible to exert synthetic control, a fascinating variety of acentric and novel metal-organic coordination compounds have been obtained from hydrothermal and solvothermal reactions [6]. These reactions are often quite complicated, and the products cannot normally be obtained by direct mixing of solutions of metal ions and ligands.

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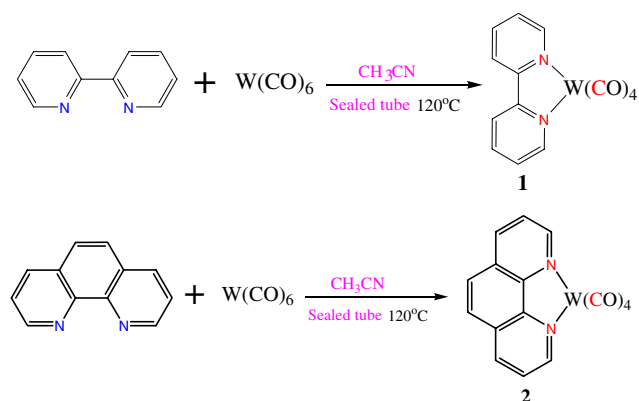
Scheme 1.

The reactions of $W(CO)_6$ and 1,10-phenanthroline (or 2,2′-bipyridine derivative) have appeared in many examples. While the corresponding compounds adopt centrosymmetric space groups, or include solvent reagent [8] (which is considered to impact the packing fashion of the compound, resulting in the formation of the noncentrosymmetry) in the crystal structure. To the best of our knowledge, this type compounds crystallizing in acentic space group have not been reported. Recently, we researched the reactions aforementioned under solvothermal condition. To our surprise, the products are monomers those do not include any solvent reagent molecule in the structure, but they all adopt noncentrosymmetric space group. The preliminary experiment indicates that they are SHG active.

We describe here the synthesis, X-ray single-crystal structure, preliminary SHG response and solid-state luminescent properties of $[W(CO)_4(bipy)]$ (bipy = 2,2′-bipyridine) (**1**) and $[W(CO)_4(phen)]$ (phen = 1,10-phenanthroline) (**2**). **1** was obtained by the reaction of $W(CO)_6$ and 2,2′-bipyridine in the presence of acetonitrile under solvothermal conditions at 120 °C. **2** was obtained under similar conditions by the reaction of $W(CO)_6$ and 1,10-phenanthroline (Scheme 1).

2. Experimental

2.1. Preparation of [W(CO)₄(bipy)] (bipy = 2,2′-bipyridine) (1) and [W(CO)₄(phen)] (phen = 1,10-phenanthroline) (2)

A heavy-walled Pyrex tube containing a mixture of $W(CO)_6$ (0.1 mmol, 0.0352 g) and 2,2′-bipyridine (0.1 mmol, 0.0156 g) (or 1,10-phenanthroline (0.1 mmol, 0.0198 g)), H_2O (0.2 mmol) and MeCN (1 mL) was frozen in liquid N_2, sealed under vacuum and placed inside

of an oven at 120 °C. The red-brown block crystals were obtained after heating of 2d, with a yield of 0.015 g (33.2%) for $W(CO)_4(bipy)$ (**1**) and 0.016 g (33.6%) for $W(CO)_4(phen)$ (**2**). Anal. Calc. for $C_{14}H_8N_2O_4W$: C, 37.19; H, 1.79; N, 6.20. Found: C, 37.70; H, 1.68; N, 6.12%. IR (KBr, cm^{-1}): 3115(w), 3070(w), 2002.23(s), 1969(s), 1909(s), 1810(s, b), 1598(m), 1468(m), 1440(m), 1315(w), 1277(w), 963.8(w), 762(s), 731(w), 626(m), 575(m). Anal. Calc. for $C_{16}H_8N_2O_4W$: C, 40.36; H, 1.69; N, 5.88. Found: C, 40.24; H, 1.79; N, 5.92%. IR (KBr, cm^{-1}): 3078(m), 1996(s), 1838(s,b), 1511(w), 1448(w), 1426(m), 1411(m), 1209(m), 948(w), 8447(s), 771(m), 722(m), 624(m), 578(m), 562(m), 507(w).

2.2. X-ray crystallogrphy of [W(CO)₄(bipy)] (bipy = 2,2′-bipyridine) (1) and [W(CO)₄(phen)] (phen = 1,10-phenanthroline) (2)

Data were collected at room temperature using exp-oxy-coated crystals mounted on glass fiber. All measurements wereee made on a CCD Smart diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied in each case. Relevant crystallographic data are presented in Table 1. The structure was solved with Direct methods using the program SHELXTL. All the non-hydrogen atoms were located from thetrial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions

Table 1
Crystal and data collection parameters for compounds **1** and **2**

Compound	1	2
Formula	$C_{14}H_8N_2O_4W$	$C_{16}H_8N_2O_4W$
Formula weight	452.07	476.09
Crystal system	Monoclinic	Monoclinic
Space group	*Pn*	*C2*
Unit cell dimensions		
a (Å)	8.9266(11)	15.512(3)
b (Å)	6.4121(5)	12.033(2)
c (Å)	12.6382(13)	8.2327(16)
β (°)	107.376(8)	107.32(2)
Volume (Å^3)	690.38(12)	1467.0(5)
Z	2	4
D_{calc} (g/cm^3)	2.175	2.156
Crystal size (mm)	$0.15 \times 0.05 \times 0.05$	$0.35 \times 0.15 \times 0.03$
Temperature (K)	295 (2)	295 (2)
$2\theta_{max}$ (°)	55	55
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
Number of reflection meads (total, unique)	1594, 1594	1772, 1772
Number of observed reflections ($I > 2\sigma$)	1461	1393
$F_{(0\,0\,0)}$	424	896
μ(Mo Kα) (cm^{-1})	83.82	78.96
R	0.0242	0.0513
R_w	0.0592	0.1262

Table 2
Selected bond lengths (Å) and angles (°) for **1**

W–C(4)	1.933(11)	W–C(3)	1.938(10)
W–C(2)	2.000(11)	W–C(1)	2.032(11)
W–N(2)	2.261(8)	W–N(1)	2.272(8)
C(4)–W–C(3)	93.3(5)	C(4)–W–C(2)	86.8(5)
C(3)–W–C(2)	86.3(5)	C(4)–W–C(1)	88.9(5)
C(3)–W–C(1)	86.6(4)	C(2)–W–C(1)	171.4(5)
C(4)–W–N(2)	168.4(4)	C(3)–W–N(2)	98.2(4)
C(2)–W–N(2)	93.5(4)	C(1)–W–N(2)	92.2(4)
C(3)–W–N(1)	169.5(4)	C(2)–W–N(1)	95.8(4)
C(1)–W–N(1)	92.1(4)	N(2)–W–N(1)	71.4(3)
C(5)–N(1)–C(9)	118.0(9)	C(5)–N(1)–W	123.6(8)
C(9)–N(1)–W	118.3(6)	C(14)–N(2)–C(10)	117.8(9)
C(14)–N(2)–W	123.0(7)	C(10)–N(2)–W	119.1(6)
O(1)–C(1)–W	171.2(10)	O(2)–C(2)–W	171.4(10)
O(3)–C(3)–W	176.2(10)	O(4)–C(4)–W	178.7(10)

Table 3
Selected bond lengths (Å) and angles (°) for **2**

W–C(3)	1.94(4)	W–C(1)	1.95(5)
W–C(2)	2.001(12)	W–C(4)	2.012(16)
W–N(2)	2.19(3)	W–N(1)	2.30(3)
C(3)–W–C(1)	93.8(11)	C(3)–W–C(2)	86.9(16)
C(1)–W–C(2)	83.9(17)	C(3)–W–C(4)	87(2)
C(1)–W–C(4)	84(2)	C(2)–W–C(4)	166.2(11)
C(3)–W–N(2)	95.8(14)	C(1)–W–N(2)	170.0(15)
C(2)–W–N(2)	93.8(12)	C(4)–W–N(2)	99.2(15)
C(3)–W–N(1)	169.2(14)	C(1)–W–N(1)	97.0(15)
C(2)–W–N(1)	95.4(13)	N(2)–W–N(1)	73.5(4)
C(4)–W–N(1)	92.5(16)	C(14)–N(1)–W	125(3)
C(14)–N(1)–C(15)	119(3)	C(15)–N(1)–W	115(2)
C(5)–N(2)–C(16)	119(3)	C(5)–N(2)–W	127(2)
C(16)–N(2)–W	114.0(18)	O(1)–C(1)–W	172(3)
O(2)–C(2)–W	172(4)	O(3)–C(3)–W	174(3)
O(4)–C(4)–W	162(5)		

were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. The selected bond distances and angles of **1** and **2** are listed in Tables 2 and 3, respectively.

2.3. The measurement of SHG responses

Approximate estimations of the second-order nonlinear optical intensity were obtained by comparison of the results obtained from a pellet (Kurtz powder test) of powdered sample (80–150 μm diameter) [7], with that obtained for urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter that transmits only 532 nm radiation. Thus, the SHG responses of **1** and **2** are approximately equal to that of urea, respectively.

3. Results and discussion

The IR spectrum of compound **1** shows the characteristic $v(CO)$ absorption bands at 2002(m), 1969(s), 1969(s), and 1810(s) cm^{-1}. The band at 1598(w) cm^{-1} may be assigned to $v(C–N)$. The $v(C–C)$ absorption bands appear at 1468(m) and 1440(m) cm^{-1}. The vibration stretch of C–H$_{ar}$ can be observed at 3115(w) and 3070(w) cm^{-1}. All these data are basically in agreement with the previous reported values [9]. Similar to that of compound **1**, the IR of compound **2** has analogous four diagnostic $v(CO)$ absorption bands at the range 1996–1838 cm^{-1}. The difference from that of compound **1** is that there exists overlap at ambient 1838 cm^{-1}, displaying triple peaks.

The crystal structure of **1** was confirmed by an X-ray single crystal structure determination. The local coordination geometry around the W center can be best described as a slightly distorted octahedron (Fig. 1). The W center coordinates to one 2-pyridyl N atoms and one carbonyl C atom with a W–N distance of 2.261(8) Å and a W–C distance of 1.933(11) Å in the axial positions and to one 2-pyridyl N atom of 2,2′-bipyridine ligand and three C atoms of three carbonyl ligands in a *cis* fashion with a W–N distance of 2.272(8) Å and W–C distances of 2.032(11), 1.938(10) and 2.000(11) Å, respectively. **1** crystallized in an acentric space group *Pn*.

Similar to compound **1**, in the structure of **2**, the W center also possesses a slightly octahedral geometry with its equatorial sites occupied by two 2-pyridyl N atoms and two carbonyl C atoms and its axial position occupied by two C atoms of two carbonyl ligands (Fig. 2). Meanwhile, the compound **2** adopted a chiral space group *C2*.
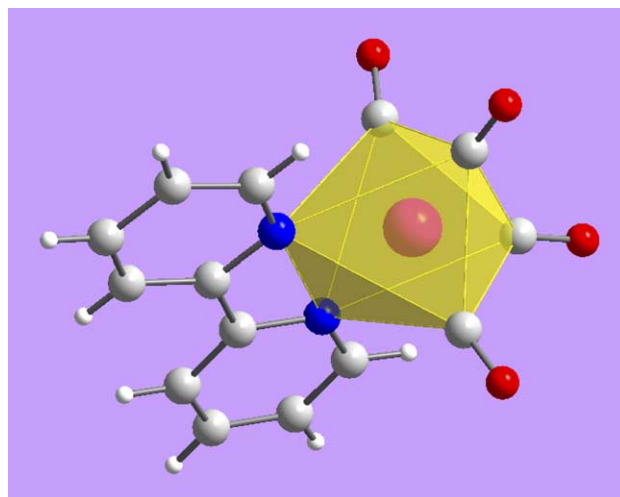

Fig. 1. Molecular structure of W(CO)$_4$(bipy) (**1**). Color codes: W, purple; Cl, green; O, red; N, blue; C, light gray; H, white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
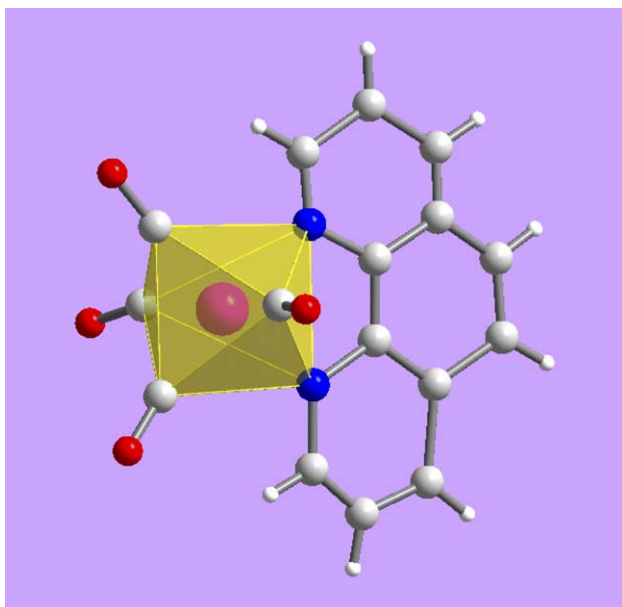
Fig. 2. Molecular structure of $W(CO)_4(phen)$ (**2**). Color codes: W, purple; Cl, green; O, red; N, blue; C, light gray; H, white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Luminescent spectrum of $W(CO)_4(phen)$ (**2**) in the solid at room temperature. (a) Emission spectrum; (b) excite spectrum.

In **1** and **2**, there are both intermolecular hydrogen bonds existing between the uncoordinated O atoms of the carbonyl ligands and the H atoms of aromatic rings belonging to another molecule.

Although the luminescent spectra of the title compounds **1** and **2** have been investigated in various solvents [9], their solid-state luminescent properties still have not been studied so far. The luminescent spectra of **1** and **2** in the solid state are shown in Figs. 3 and 4, respectively. When they are excited by $\lambda_{max} = 452$ and 441 nm blue light, they emit red light at $\lambda_{max} = 663$ and 686 nm with multiple emission, respectively. In contrast to the emission spectrum of $M(CO)_4L$ (M: Cr, Mo, W; 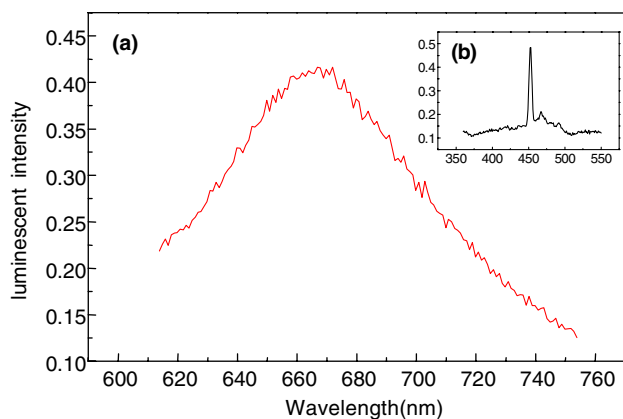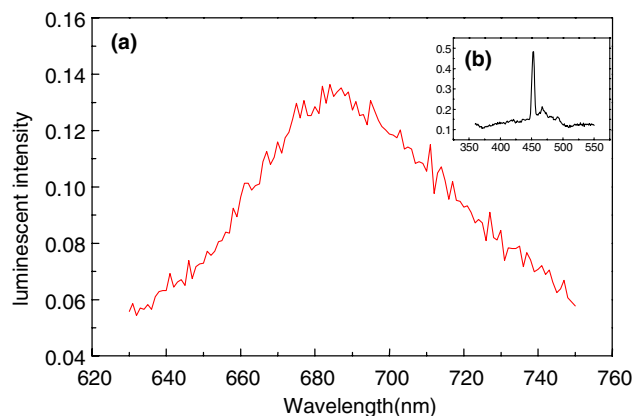L: 2,2′-bipyridine, 1,10-phenanthroline) complexes in various solvents, it is found that the maximum emissions of **1** and **2** locate in low energy region and occur bathochromic shift by 80 and 100 nm due to no solvent effect, respectively; moreover previous dual emission bands change into multiple bands with long tail. Both emission bands of **1** and **2** are assigned as MLCT transitions. The observance of multiple emission indicates that interconversion between the emitting states is relatively slow compared to the radiative deactivation routes of the molecule and implies that the characters of these excited states are somewhat different. It may be ascribe to the overlap of MLCT and intraligand (IL) transition [10].

Given that the products **1** and **2** crystallize in the acentric space groups (*Pn* and *C2*, respectively) those belong to the crystal class 2 and point groups (C_s and C_2) where their optical activity can occur as a specific physical effect [11]. Due to dipolar moment not be cancelled in their crystal packing [12], preliminary examinations of powdered sample indicate that both **1** and **2** are SHG active with an approximate response similar to that of urea.

Acknowledgements

Fig. 3. Luminescent spectrum of $W(CO)_4(bipy)$ (**1**) in the solid at room temperature. (a) Emission spectrum; (b) excite spectrum.

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