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Synthesis, crystal structure and nonlinear optical properties of two novel linear cluster polymers $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ and $[WOS_3Cu_3(CN)(py)_4]_n$

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Cluster polymers $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ **1** and $[WOS_3Cu_3(CN)(py)_4]_n$ **2** were synthesized by the reaction of $(NH_4)_2MO_2S_2$ (M = Mo, W) and CuCN with py. Their structures have been characterized by X-ray diffraction. Both of them show neutral nest-shaped structural units, and every structural unit forms two Cu1–N1–C1–Cu3 bridges with two other structural units leading to infinite one-dimensional polymers. In every unit cell of $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ there are four $[MoOS_3Cu_3(CN)(py)_3]$ structural units and two benzene molecules, and the four structural units are from four independent linear polymer molecules which are parallel. In every unit cell of polymer **2**, there are four $[WOS_3Cu_3(CN)(py)_4]$ structural units too, but they are only from two parallel linear polymer molecules. Polymer **1** shows good nonlinear optical (NLO) absorptive and NLO refractive properties, whereas strong NLO properties of polymer **2** are not observed.

Introduction

Cluster chemistry is one of the most important and active areas in inorganic chemistry, advanced materials, physical chemistry and biological chemistry.[1–4] Our research interest has been recently focused on Mo(W)–S cluster polymers. The reported polymers of this type are dinuclear infinite chain clusters $[AgMS_4(\gamma\text{-MepyH})]_n$, $[AgMoS_4(\alpha\text{-MepyH})]_n$ (Mepy = methylpyridine), $\{[AgWS_4][H_3NC(CH_2OH)_3]\}_n$-$[DMF]_{2n}$ and $\{[Bu_4N][MS_4Tl]\}_n$ (M = Mo, W);[5–8] tetranuclear 'open' one-dimensional polymers $[\{(CuNCS)_3WS_4\}_n]^{2-}$ and $[\{(CuNCS)_3WOS_3\}_n]^{2-}$;[9,10] pentanuclear 'open' polymers $[\{(CuBr)_4MoS_4\}_n]^{2-}$, $[\{(CuSCN)_4MS_4\}_n]^{2-}$ (M = Mo, W) and $[\{Cu_4(SCN)_5WS_4\}_n]^{2-}$;[10–12] heptanuclear two-dimensional network polymers $[MS_4Cu_6X_4(py)_4]_n$ (M = Mo, W; X = Br, I);[13–15] polymers $\{[W_4Ag_5S_{16}][M(DMF)_8]\}_n$ (M = Nd, La), $\{[W_4Ag_4S_{16}][Ca(DMSO)_6]\}_n$ and $\{[W_3Ag_3S_{12}][Nd(DMSO)_8]\}_n$.[16–18] Previous studies of the nonlinear optical (NLO) properties of Mo(W)–S cluster compounds have covered a number of structural types,[19–35] but the known cluster polymers showing good NLO properties are very rare. Mo(W)–Tl–S cluster polymers $\{[Bu_4N][MS_4Tl]\}_n$ exhibit strong NLO absorption and self-focusing effects and the two-dimensional network polymer $[MoS_4Cu_6I_4(py)_4]_n$ has the biggest third-order nonlinear absorptive index of all inorganic clusters and a very large optical limiting (OL) capability. (The OL threshold is 0.6 J cm^{-2} which is about three times better than that of C_{60}.[15]) In fact, cluster polymers possess the combined strength of both clusters and polymers, and exhibit special properties.

We now report another novel type of cluster polymer, neutral nest-shaped one-dimensional linear polymers $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ **1** and $[WOS_3Cu_3(CN)(py)_4]_n$ **2**, and a study of their NLO properties. The two polymers were characterized by X-ray crystallographic measurements. Polymer $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ shows good NLO absorption and NLO refraction, but we did not observe large NLO properties for the polymer $[WOS_3Cu_3(CN)(py)_4]_n$.

Experimental

The compounds $(NH_4)_2MoO_2S_2$ and $(NH_4)_2WO_2S_2$ were prepared according to the literature.[36] Other chemicals were of A.R. grade (pyridine was of C.P. grade containing a small amount of benzene) and used without further purification.

IR spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets. Electronic spectra were taken on a Hitachi U-3410 spectrophotometer. Carbon, hydrogen and nitrogen analyses were performed on a PE 240C Elemental Analyzer.

Synthesis of $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ 1

A well-ground mixture of $(NH_4)_2MoO_2S_2$ (0.12 g, 0.5 mmol) and CuCN (0.09 g, 1 mmol) was dissolved in py (10 ml). After stirring for 2 h and filtering a clear deep red solution was obtained. Dropwise addition of isopropanol (7 ml) to the top of the solution resulted in the formation of deep red crystals (0.1 g, yield 60%) after standing for two weeks. The crystals show characteristic infrared absorption peaks at 912 cm^{-1}, $\nu(Mo\text{–}O_t)$; 441 and 412 cm^{-1}, $\nu(Mo\text{–}S_{br})$; and 2151 cm^{-1}, $\nu(CN)$. Calc. for $C_{19}H_{18}N_4Cu_3MoOS_3$: C, 32.52; H, 2.59; N, 8.00. Found: C, 31.68; H, 2.55; N, 8.45%.

Synthesis of $[WOS_3Cu_3(CN)(py)_4]_n$ 2

In a pure nitrogen atmosphere, the orange-yellow cluster **2** was prepared in a similar manner to that used for compound **1**. Crystals of X-ray quality were obtained after the solution was allowed to stand for two months. Yield 20%, 0.04 g. Characteristic infrared absorption peaks are: 925 cm^{-1}, $\nu(W\text{–}O_t)$; 428

cm^{-1}, ν(W–S$_{br}$); 2115 cm^{-1} ν(CN). Calc. for $C_{21}H_{20}N_5Cu_3S_3OW$: C, 30.40; H, 2.41; N, 8.44. Found: C, 29.95; H, 2.36; N, 8.57%.

Crystal structure analysis

A crystal (deep-red prismatic for polymer **1** or orange prismatic for polymer **2**) was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of 18 ± 1 °C and corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ($I > 2.00\sigma(I)$) and variable parameters. All calculations were performed using the SHELX-97 software package.[37] Table 1 shows crystal data and structure refinement for the two polymers. Selected bond lengths and bond angles are listed in Table 2.

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See http://www.rsc.org/suppdata/dt/1999/2953/ for crystallographic files in .cif format.

Table 1 Crystal data and structure refinement for $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ **1** and $[WOS_3Cu_3(CN)(py)_4]_n$ **2**

	1	2
Empirical formula	$C_{19}H_{18}Cu_3MoN_4OS_3$	$C_{21}H_{20}Cu_3N_5OS_3W$
Formula weight	701.14	829.09
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	11.952(2)	13.023(3)
b/Å	11.247(2)	12.199(2)
c/Å	18.779(4)	17.579(4)
β/°	101.89(3)	95.09(3)
V/Å^3	2470.1(9)	2781.7(10)
T/°C	18 ± 1	18 ± 1
Z	4	4
μ(Mo-Kα)/cm^{-1}	33.16	66.32
Reflections collected	4512	3708
Final $R1$, Rw indices ($I > 2\sigma(I)$)	0.0451, 0.1183	0.0865, 0.2257

Nonlinear optical measurements

A CH_3CN solution of polymer (**1** or **2**) was placed in a 1 mm quartz cuvette for NLO measurements. Their NLO properties were measured with a 7 ns pulsed laser at 532 nm as described in the literature.[33,38]

Results and discussion

Synthesis of cluster polymers 1 and 2

For the synthesis of polymers **1** and **2**, $(NH_4)_2MO_2S_2$ (M = Mo, W), CuCN and py (C.P. grade) were used as starting materials. Benzene units exist in polymer **1**, and these have been identified by X-ray measurement. If we used purified py as starting material red powder was produced, and crystals suitable for X-ray determination could not be obtained. It is interesting that there are no benzene units in polymer **2**.

All experiments involving polymer **1** were carried out in air, and it was easy to produce single crystals from the reaction solution in about two weeks. If $(NH_4)_2WO_2S_2$ and CuCN react with py in air, the pyridine solution changes from orange to green in one week, and a green powder is produced. When the reaction of $(NH_4)_2WO_2S_2$ with CuCN in py solution was carried out under a nitrogen atmosphere both a green powder and orange crystals were obtained after two months. The orange crystals were suitable for X-ray determination.

In the reaction of $(NH_4)_2MO_2S_2$ and CuX (X = Br, I, CN, SCN) with py, we found that only nest-shaped structural clusters were obtained, the other types of clusters were not observed. It appears that a nest-shaped structure is the most stable skeleton (Scheme 1).

Crystal structures of cluster polymers 1 and 2

The structural unit of $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ is depicted in Fig. 1. The structural unit consists of $[MoOS_3Cu_3(CN)(py)_3]$ showing a nest-shaped skeleton, in which three S atoms, three Cu atoms and one Mo atom occupy seven corners. Compared to the free $MoOS_3^{2-}$ ion, the $MoOS_3$ fragment deviates slightly from C_3 symmetry, with three O–Mo–S bond angles of 111.05(10), 111.45(10) and 111.53(10)°. The Mo–O bond length of 1.705(3) Å is typical for a double bond. The three Mo–S bond distances, 2.2640(10), 2.2679(11) and 2.2779(12) Å, are in the range typical for a single bond.

The three Cu atoms exhibit two different coordination

Table 2 Selected bond lengths (Å) and bond angles (°)

$\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$							
Mo(1)–O(1)	1.705(3)	Mo(1)–S(2)	2.2640(10)	Mo(1)–S(1)	2.2679(11)	Cu(3)–S(3)	2.2397(12)
Mo(1)–S(3)	2.2779(12)	Mo(1)–Cu(2)	2.6829(10)	Mo(1)–Cu(3)	2.6591(8)	Cu(3)–S(1)	2.2332(12)
Mo(1)–Cu(1)	2.7046(7)	Cu(1)–S(1)	2.3062(12)	Cu(1)–S(2)	2.2904(12)	Cu(2)–N(3)	2.130(3)
Cu(1)–N(1)	1.961(4)	Cu(2)–S(2)	2.2738(12)	Cu(2)–S(3)	2.2837(12)	Cu(3)–C(1A)	1.898(4)
O(1)–Mo(1)–S(2)	111.45(10)	O(1)–Mo(1)–S(1)	111.05(10)	S(2)–Mo(1)–Cu(2)	53.92(3)	Cu(2)–Mo(1)–Cu(3)	89.37(2)
O(1)–Mo(1)–S(3)	111.53(10)	S(2)–Mo(1)–S(1)	108.43(4)	S(1)–Cu(1)–Mo(1)	53.10(3)	Cu(2)–Mo(1)–Cu(1)	89.15(2)
S(2)–Mo(1)–S(3)	107.71(4)	S(1)–Mo(1)–S(3)	106.47(5)	Cu(1)–Mo(1)–S(1)	54.41(3)	Cu(1)–Mo(1)–S(3)	119.97(3)
O(1)–Mo(1)–Cu(2)	123.68(10)	S(1)–Mo(1)–Cu(2)	125.26(4)	Mo(1)–Cu(3)–S(1)	54.39(3)	Cu(3)–C(1A)–N(1A)	178.4(4)
Cu(1)–N(1)–C(1)	176.0(4)						
$[WOS_3Cu_3(CN)(py)_4]_n$							
W(1)–O(1)	1.693(8)	W(1)–S(1)	2.262(3)	W(1)–S(2)	2.250(3)	Cu(3)–S(2)	2.353(4)
W(1)–S(3)	2.251(3)	W(1)–Cu(2)	2.7211(16)	W(1)–Cu(3)	2.7403(18)	Cu(2)–N(3)	2.240(11)
W(1)–Cu(1)	2.6963(18)	Cu(1)–S(1)	2.294(4)	Cu(1)–S(3)	2.324(4)	Cu(3)–N(5)	1.988(13)
Cu(2)–S(1)	2.307(4)	S(2)–Cu(2)	2.315(4)	S(3)–Cu(3)	2.293(4)	Cu(3)–N(4)	2.137(10)
Cu(2)–C(21A)	1.872(11)						
O(1)–W(1)–S(2)	109.5(3)	O(1)–W(1)–S(1)	110.0(3)	W(1)–Cu(3)–S(3)	52.21(9)	S(2)–Cu(3)–S(3)	103.78(13)
O(1)–W(1)–S(3)	111.1(3)	S(2)–W(1)–S(1)	108.22(12)	Cu(1)–S(3)–Cu(3)	114.24(15)	W(1)–S(2)–Cu(2)	73.16(11)
S(2)–W(1)–S(3)	108.63(13)	S(1)–W(1)–S(3)	109.41(12)	Cu(3)–N(5)–C(21)	175.8(11)	Cu(2A)–C(21)–N(5)	169.3(11)
Cu(1)–W(1)–Cu(3)	90.98(5)	Cu(1)–W(1)–Cu(2)	92.55(5)	W(1)–S(3)–Cu(3)	74.18(11)	N(4)–Cu(3)–N(5)	110.5(4)

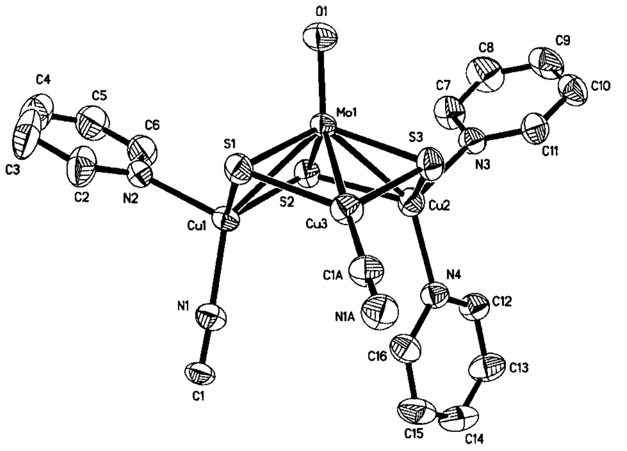


Fig. 1 ORTEP[40] diagram (30% probability ellipsoids) showing the structural unit of $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$.

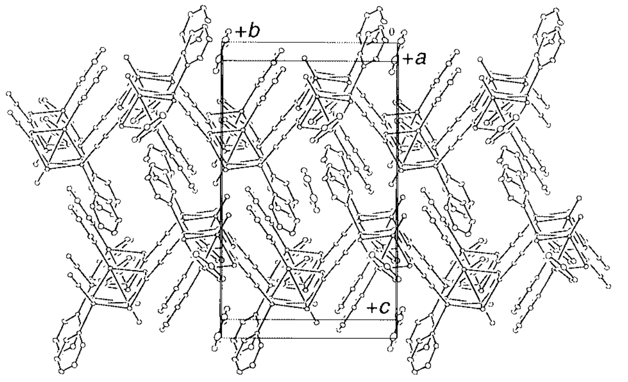
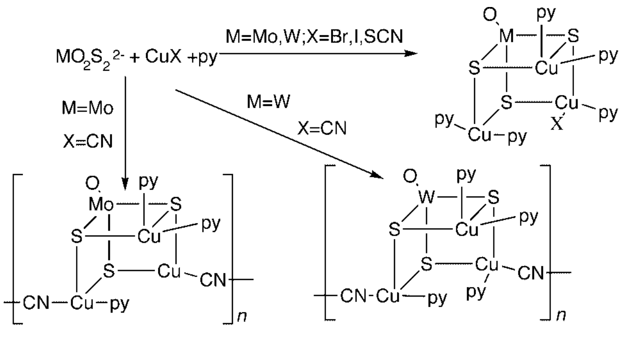


Fig. 2 View of the one-dimensional polymeric structure of $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$.



Scheme 1

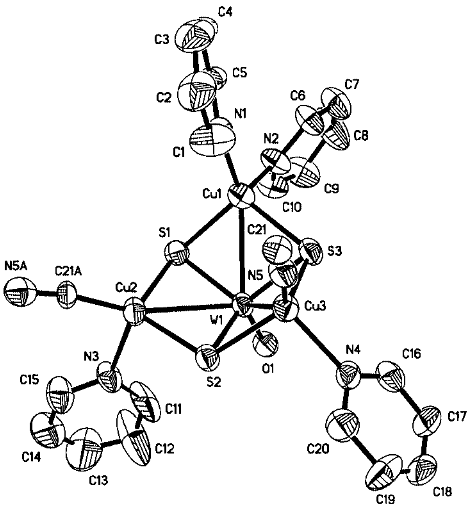


Fig. 3 ORTEP diagram (30% probability ellipsoids) showing the structural unit of $[WOS_3Cu_3(CN)(py)_4]_n$.

modes. Both Cu1 and Cu2 adopt a distorted tetrahedral geometry, Cu1 is coordinated by two S atoms, one py and one NC group, while Cu2 bonds to two py units and two S atoms. In addition, weak interactions exist between the three Cu atoms and the Mo atom. Owing to different coordination environments, the Mo–Cu1 distance of 2.7046(7) Å is longer than that of the Mo–Cu2 [2.6829(10) Å], and the Cu1–S bond lengths [2.2904(12) and 2.3062(12) Å] are longer than those of the Cu2–S bond lengths [2.2738(12) and 2.2837(12) Å]. Atom Cu3 is in an approximately triangular planar environment (one CN unit and two S atoms). The Mo–Cu3 distance [2.6591(8) Å] is shorter than that of Mo–Cu1 and Mo–Cu2, and the Cu3–S bond lengths of 2.2332(12) and 2.2397(12) Å are shorter than the corresponding Cu1 and Cu2 ones.

Every $[MoOS_3Cu_3(CN)(py)_3]$ unit forms Cu1–N1–C1–Cu3A and Cu3–C1A–N1A–Cu1A bridges with two identical units, leading to an infinite one-dimensional polymer. The Cu3–C1A bond length and Cu3–C1A–N1A bond angle are 1.898(4) Å and 178.4(4)° respectively, and the Cu1–N1 bond length and Cu1–N1–C1 bond angle are 1.961(4) Å and 176.0(4)° respectively. In every unit cell, there are four $[MoOS_3Cu_3(CN)(py)_3]$ units and two benzene molecules. The four $[MoOS_3Cu_3(CN)(py)_3]$ units are from four independent linear polymers, $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$, which are parallel (Fig. 2).

Fig. 3 gives the structural unit of polymer $[WOS_3Cu_3(CN)(py)_4]_n$. The unit exhibits a nest-shaped skeleton too, but the tetrahedral coordination geometry is adopted by all three of the Cu atoms. Atoms Cu1 and Cu2 have the same coordination environment as Cu1 and Cu2 in polymer **1**. Atom Cu3 is coordinated by two S atoms, one py group and one NC unit, differing from the Cu3 atom of polymer **1**. From the W–Cu distances of 2.6963(18), 2.7211(16) and 2.7403(18) Å it appears that the three Cu atoms are weakly bound to W through three μ_3-S atoms. Owing to the similar coordination environment of Cu1, Cu2 and Cu3, the structure of the WOS_3^{2-} ion is close to a perfect tetrahedral geometry. The S(O)–W–S bond angles are in the range 108.22(12)–111.1(3)°. The polymer, which is formed by Cu2–C21A–N5A–Cu3A and Cu3–N5–C21–Cu2A bridges, is the same as polymer **1**. The Cu2–C21A and Cu3–N5 bond distances are 1.872(11) Å and 1.988(13) Å respectively, and the Cu2–C21A–N5A and Cu3–N5–C21 bond angles are 169.3(11)° and 175.8(11)° respectively. In every unit cell there are four $[WOS_3Cu_3(CN)(py)_4]$ units, but the four units are from two parallel linear polymers (Fig. 4), in contrast to polymer **1**. It is interesting to note that in a similar cluster, $[MoOS_3Cu_3(SCN)(py)_5]$, a polymer is not formed by CuSCNCu bridges.[39]

Nonlinear optical (NLO) properties

The only cluster polymers showing strong NLO properties are $\{[Bu_4N][MS_4Tl]\}_n$ (M = Mo, W) and $[MoS_4Cu_6I_4(py)_4]_n$. Both of them have strong NLO absorption and refraction; $[MoS_4Cu_6I_4(py)_4]_n$ also exhibits a large optical limiting capability. We have found that polymer $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ possesses good NLO absorptive and refractive effects too. However, good NLO properties of polymer $[WOS_3Cu_3(CN)(py)_4]_n$ were not observed.

The UV-vis spectrum of polymer **1** is depicted in Fig. 5. polymer **1** displays two absorption peaks with the first maximum located at 395 nm. The polymer has relatively low linear absorption in the visible and near-IR regions. It shows linear and nonlinear optical properties similar to the nest-shaped Mo clusters $[Bu_4N]_2[MoOS_3Cu_3BrCl_2]$, $[Bu_4N]_2[MoOS_3(CuSCN)_3]$, $[MoOS_3Cu_3I(py)_5]$ and the twin nest-shaped $[Et_4N]_4[Mo_2O_2S_6Cu_6I_6]$. Absorption peaks were observed at about 400 and 290 nm in these known clusters. Both strong NLO absorption and self-defocusing effects were observed with these clusters too.

Fig. 6(a) shows typical Z-scan measurements of polymer **1**

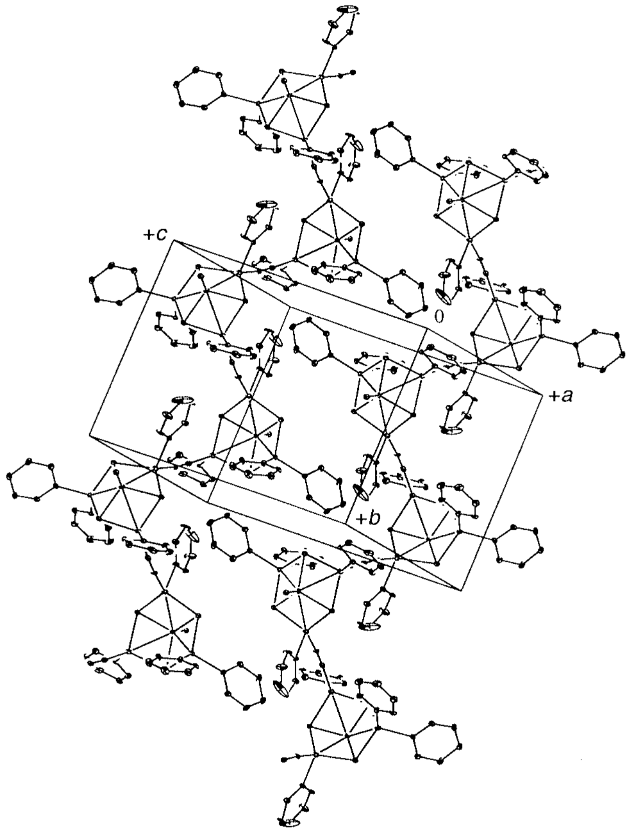


Fig. 4 View of the one-dimensional polymeric structure of $[WOS_3Cu_3(CN)(py)_4]_n$.

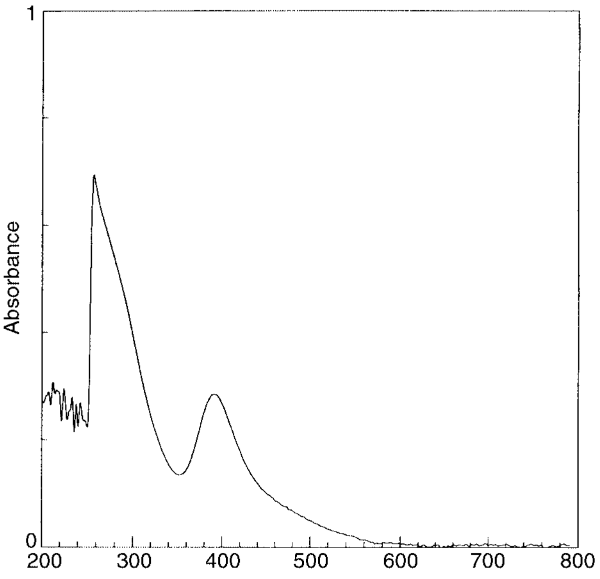


Fig. 5 UV-vis spectrum of $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$.

in a 5.3×10^{-5} mol dm^{-3} CH_3CN solution. The filled circles are the experimental data measured under an open aperture. It clearly illustrates that the absorption increases as the incident light irradiance rises. The normalized transmittance drops to about 92% at the focus. The effective nonlinear absorptive index a_2 is estimated to 5×10^{-11} m W^{-1} in CH_3CN solution.

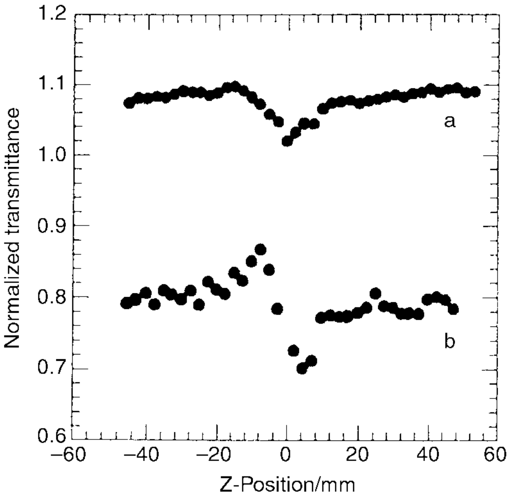


Fig. 6 Z-Scan data of $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ in a 5.3×10^{-5} mol dm^{-3} CH_3CN solution. (a) The data were collected under an open aperture configuration. (b) The data were obtained by dividing the normalized Z-scan measured under a closed aperture configuration by the normalized Z-scan data of (a).

The filled circles in Fig. 6(b) are assessed by dividing the normalized Z-scan data obtained under a closed aperture configuration by the normalized Z-scan data obtained under an open aperture configuration. The data show that the polymer $\{[MoOS_3Cu_3(CN)(py)_3]\cdot 0.5C_6H_6\}_n$ has a negative sign for refractive nonlinearity, which gives rise to self-defocusing behavior. The effective third-order NLO refractive index n_2 is given by:

$$n_2 = \frac{\lambda a_0}{0.812\pi I(1 - e^{-a_0 L})} \Delta T_{V-P}$$

where ΔT_{V-P} is the difference between normalized transmittance values at valley and peak positions, a_0 is the linear coefficient, L is the sample thickness, I is the peak irradiation intensity at focus and λ is the wavelength of the laser. The refractive index n_2 is calculated to be -8×10^{-18} m^2 W^{-1}. These data are comparable to those of inorganic clusters and other cluster polymers. For example, the n_2 values of $[MoOS_3Cu_2(PPh_3)_3]$, $[MoOS_3Cu_3I(py)_5]$, $[MoOS_3Cu_3(SCN)(py)_5]$, $[MoS_4Cu_6I_4(py)_4]_n$ and $\{[Bu_4N][MoS_4Tl]\}_n$ are 5×10^{-17}, -3.0×10^{-17}, -6.8×10^{-17}, -2.5×10^{-17} and 3.1×10^{-18} m^2 W^{-1}, respectively.[8,15,19,23,39] Polymer **2** only has very weak NLO properties, although it shows a similar structure to that of polymer **1**.

Recently research on NLO materials has been focused on conjugated polymers, metal clusters, *etc.* In fact, cluster polymers combine the strength of both conjugated polymers and cluster compounds, and show better NLO properties; $\{[Bu_4N][MS_4Tl]\}_n$ (M = Mo, W) and $[MoS_4Cu_6I_4(py)_4]_n$ are good examples. It is obvious that more data need to be accumulated by the synthesis and NLO determination of further cluster polymers.

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