Second-order non-linear optical response of a novel type of charge-transfer complex, $[4\text{-DMSP}]_4[NH_2Me_2]_2HSiFeMo_{11}O_{40}\cdot3H_2O$

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A novel charge-transfer complex, $[4\text{-DMSP}]_4[NH_2Me_2]_2HSiFeMo_{11}O_{40}\cdot3H_2O$ 1 {4-[DMSP]I = 4[*p*-(dimethylamino)styryl]pyridine methiodide} prepared and crystallized in a non-centrosymmetric (space group *P*1) structure, exhibits second harmonic generation (SHG) of 1064 nm radiation with an efficiency 1.2 times that of KH_2PO_4 under the same conditions.

Non-linear optical (NLO) materials have attracted great interest in recent years, for their wide range of applications in laser technology, telecommunications, data storage and optical switches.$^{1-6}$ Most investigations, so far, have concentrated on inorganic crystals, organometallic compounds, organic molecules and polymers with delocalized π-electron systems.$^{7-15}$ It is known that there are three main factors influencing the magnitude of second harmonic generation, namely, (*a*) the presence of electron donor and acceptor groups in the molecule, (*b*) the nature and relative position of the groups and their ability to promote charge-transfer transitions between them and (*c*) extension of the conjugated path through which electrons are transferred under the influence of electric fields.

According to the concepts of 'molecular self-organization' and 'molecular engineering', we have designed and synthesized a new type of charge-transfer compound. We chose a hemicyanine dye as the organic cation, which contains electron donor and acceptor groups and possesses large SHG efficiency.^{16,17} Since SHG is only observed in acentric materials, a simple way to meet this condition is to use molecules that can crystallize in accentric space groups. We selected Keggin structure heteropolyanions $XM_{12}O_{40}$ (X = P, Si; M = Mo, W) as electron acceptors, as XO_4 in the polyanions has T_d symmetry and readily accepts electrons.^{18} By using this method, a non-centrosymmetric molecular material is obtained when [4-DMSP]I and $[NBu_4]_4KH_2SiFeMo_{11}O_{40}$ are reacted. The procedure of design of such NLO molecular materials can be expressed by eqn. (1).

$$[\text{donor–}\pi\text{–acceptor}]^{+}{}_{n}[\text{polyanion}]^{n②} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftharpoons}} [\text{donor–}\pi\text{–acceptor}]^{1+\delta}{}_{n}[\text{polyanion}]^{②\,n(1+\delta)} \qquad (1)$$

In this work, we synthesized the charge-transfer salt $[4\text{-DMSP}]_4[NH_2Me_2]_2HSiFeMo_{11}\cdot3H_2O$ **1**, and determined its SHG and crystal structure.

The determination of the second harmonic intensity of powdered samples (Kurtz powder test) was made relative to that of powdered KH_2PO_4. A pulse Q-switched Nd : YAG laser with a pulse (width 60 ps, repetition 1 Hz) of energy 1 mJ at a wavelength of 1064 nm was used to generate an SHG signal from the sample. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter which transmits only 532 nm radiation. Boxcar gate sampling was used to provide data points averaged over ten pulses and the mean of ten of these points provided the quoted values of relative harmonic intensity for second harmonic generation.

The electronic spectra of **1** [4-DMSP]I and $[NBu_4]_4KH_2SiFeMo_{11}O_{40}$ (*ca.* 1 ③ $10^{②3}$ M) are shown in Fig. 1. Neither the cation 4-DMSP$^+$ nor $[NBu_4]_4KH_2SiFeMo_{11}O_{40}$ show any absorption in the range 600–1100 nm. However, **1** shows a broad absorption in this range, and a weak absorption at *ca.* 1000 nm, which suggests the presence of a strong charge-transfer interaction between the polyanion and the organic cation and explains the source of second harmonic generation.

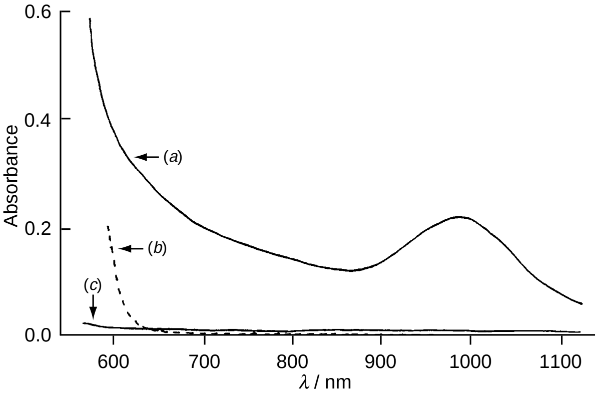

Fig. 1 Comparison of the electronic spectra of [4-DMSP]I, $[NBu_4]_4KH_2SiFeMo_{11}O_{40}$ and **1** in dmf; (*a*) **1**, (*b*) [4-DMSP]I, (*c*) $[NBu_4]_4KH_2SiFeMo_{11}O_{40}$. All spectra were obtained for 1 ③ $10^{②3}$ M solutions at 15 °C.

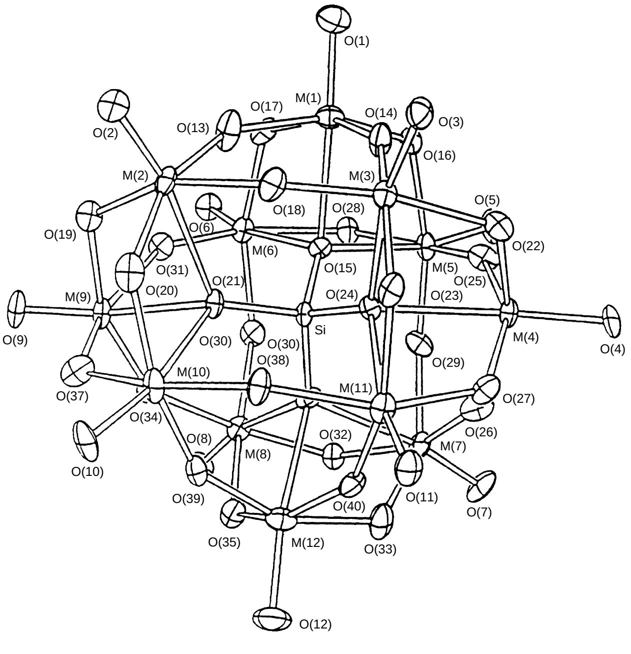

Fig. 2 ORTEP of the polyoxoanion $[SiFeMo_{11}O_{40}]^{7②}$, showing 30% thermal elipsoids; M represents Fe or Mo (SOF = 11/12 for Mo and 1/12 for Fe at each M atom). Average bond distances (Å) for the polyoxoanion: Si–O$_a$ (central) 1.612(3), M–O$_a$ 2.357(3), M–O$_t$ (terminal) 1.673(3), M–O$_b$ (bridging) 1.871(3).

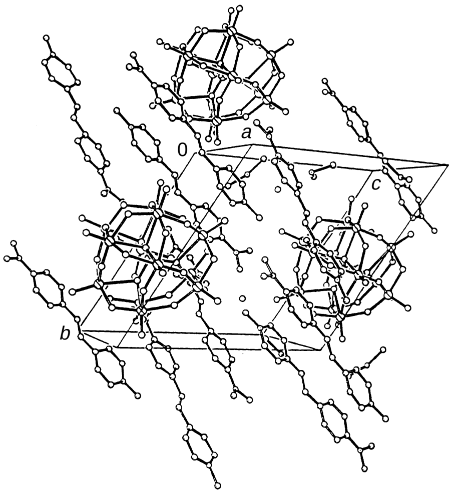

Fig. 3 Crystal packing of **1** viewed down the *a* axis

The X-ray crystal structure analysis indicates that **1** crystallizes in the space group *P*1, and the molecular structure is shown in Fig. 2, with the molecule packing diagram shown in Fig. 3. The shortest contacts between the polyanion and organic cation are C(16)···O(4) 3.056(3) Å and C(49)···O(5) 2.963(3) Å, respectively, indicating the presence of strong hydrogen bonding. This means that there is an interaction between the polyanion and the organic substrate, leading to partial charge transfer.

A significant new result from the work is that the design and synthesis of a new type of charge-transfer salt from the view point of molecular engineering has led to a material which possesses a larger SHG than KH_2PO_4 and is the most efficient than that we have ever reported.[19] However, the SHG is lower than that reported for some transition-metal complexes.[20] The above result shows that a new system showing non-linear optical properties is found and we expect enhanced properties if the polyoxometalates are mixed valence species.[21]

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Footnotes

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† Complex **1** was prepared by reacting 139.4 mg (0.5 mmol) of $[NBu_4]_4KH_2SiFeMo_{11}O_{40}$[22] dissolved in 20 ml of acetonitrile with 915.6 mg (2.5 mmol) of [4-DMSP]I. A suitable red prism crystal obtained from dmf was investigated by single-crystal X-ray diffraction.

‡ *Crystal data* for $C_{68}H_{97}FeMo_{11}N_{10}O_{43}Si$, triclinic, space group *P*1, $a = 13.647(3)$, $b = 14.877(2)$, $c = 15.279(2)$ Å, $\alpha = 105.53(1)$, $\beta = 108.71(2)$, $\gamma = 111.35(2)°$, $U = 2462.7(6)$ Å^3, $Z = 1$. A red prismatic crystal with dimensions of 0.32 ③ 0.28 ③ 0.22 mm was mounted on a glass fibre. The intensities were collected at 291 K on a Siemens P4 four-circle diffractometer with monochromated Mo-Kα ($\lambda = 0.710\,73$ Å) radiation using the θ–2θ scan mode with a variable scan speed 5.0–50.0° min② 1 in ω. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL (version 5.0). The two $NH_2Me_2^+$ ions are disordered [site occupancy factor (SOF) is 1/2 for N(10), C(68) and N(11), C(69), C(70), respectively]. In the polyanion structure, the positions of Fe and Mo atom can not be indentified; M represents Fe or Mo (SOF = 11/12 for Mo, and 1/12 for Fe at each M atom). All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in caculated positions (C–H 0.96 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic *U* of the atoms to which they are attached (1.5 times for the methyl groups) and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure-factor calculations. Structure solution and refinement based on 12 255 reflections and 1234 parameters gave $R_1 = 0.0667$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/465.

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