Large Third-Order Nonlinear Optical Susceptibilities of Multiply-Bonded $M_2(pyphos)_4$ and $M_2Pd_2Cl_2(pyphos)_4$ (M = Cr, Mo; Pyphos = 6-Diphenylphosphino-2-pyridonate) by Picosecond Degenerate Four-Wave Mixing Method

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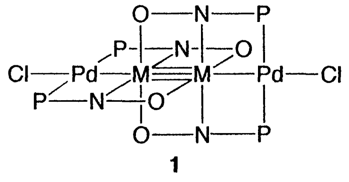
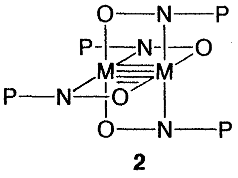
Multiply-bonded tetranuclear complexes $M_2Pd_2Cl_2(pyphos)_4$ (**1**) and dinuclear complexes $M_2(pyphos)_4$ (**2**) (**a**, M = Mo; **b**, M = Cr; pyphos = 6-diphenylphosphino-2-pyridonate) are found to exhibit large hyperpolarizability γ of nonlinear optical property by using the picosecond degenerate four-wave mixing (DFWM) method; the γ values of **1a** (1.5×10^{-30} esu), **1b** (5.2×10^{-31} esu), and **2a** (6.9×10^{-31} esu) are greater than those (ca. 10^{-35}—10^{-33} esu) of transition metal poly(yne) polymers.

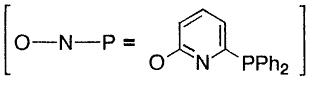
New materials exhibiting large third-order nonlinear optical (NLO) properties have attracted much attention for their device applications in optical communication and optical data processing.[1] Organic compounds with one-dimensional pπ electron delocalization system, *i.e.*, poly(diacetylene)s and poly(thiophene)s,[2-5] have been investigated. Recently, organometallic compounds such as metal poly-yne and alkynylmetal complexes that involve dπ-pπ delocalized systems have also been studied.[6-10] One-dimensional transition metal complexes (dπ system) without metal-to-metal bond have been found to show large third-order optical nonlinearity.[11-14] Thus, it is expected that one-dimensional metal complexes bearing metal—metal multiple bonds show still larger nonlinear optical properties because of strong interaction among dπ orbitals of each metal. Since we already synthesized linear tetrametal conjugated M—Mo—Mo—M moieties (M = Pd, Pt),[15,16] the investigation of NLO property of these complexes may provide a new material system. In this communication, we report third-order nonlinear optical susceptibilities of solutions of such multiply-bonded complexes, $M_2Pd_2Cl_2(pyphos)_4$ (**1**) and $M_2(pyphos)_4$ (**2**) (**a**, M = Mo; **b**, M = Cr; pyphos = 6-diphenylphosphino-2-pyridonate).[15,16]



1
a: M = Mo
b: M = Cr



2
a: M = Mo
b: M = Cr



The third-order nonlinear hyperpolarizabilities, γ, of **1** and **2** were measured in dichloromethane solution by using the picosecond degenerate four-wave mixing (DFWM) method.[17,18] Concentration dependent plots shown in Figure 1, where $\chi^{(3)}$ is the value observed for the dichloromethane solution of complexes **1** and **2** in various concentrations and $\chi^{(3)}(CH_2Cl_2)$ is the observed value of dichloromethane, gave values of hyperpolarizabilities; **1a** (1.5×10^{-30} esu), **2a** (6.9×10^{-31} esu), **1b** (5.2×10^{-31} esu), and **2b** ($\leq 10^{-33}$ esu). The γ value of the tetranuclear Mo_2Pd_2 complex **1a** is twice larger than that of the dinuclear Mo_2 complex **2a**, indicating that the longer dπ-dπ conjugated system has higher value, although the origin of this large effect needs further study.[19] This is consistent with the theoretically predicted tendency for one-dimensional π-conjugated organic systems that show large optical nonlinearity.[20] The molybdenum complex **1a** is superior to the corresponding chromium complex **1b**. The observed hyperpolarizabilities of **1a**, **2a**, and **1b** are larger than those (ca. 10^{-35}—10^{-33} esu) found for the transition metal poly(yne) polymers.[6,21]

The $\chi^{(3)}$ value of a crystal of **1a** can be estimated[18] using the density of crystal (1.645 gcm^{-3} calculated on the basis of X-ray crystallographic study)[15,16] and $n = 1.5$ (estimated value) to be 3.2×10^{-9} esu. Similarly, a $\chi^{(3)}$ value of a crystal of **2a** is estimated to be 1.7×10^{-9} esu, while that of **1b** could not be

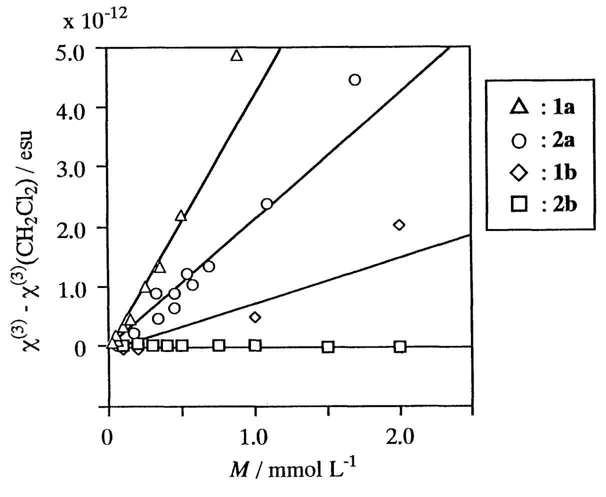


Figure 1. Plots of the light absorption corrected $[\chi^{(3)} - \chi^{(3)}(CH_2Cl_2)]$ values *vs.* concentration of the dichloromethane solution of **1** and **2** (*M*).

estimated due to the lack of X-ray analysis of **1b**. These results may be compared with the largest value of susceptibility of organic and inorganic compounds reported so far. The $\chi^{(3)}$ value of **1a** and **2a** are comparable to that found for poly(diacetylene) and poly(thiophene),[1] but are smaller only by 10—10^2 to those of the large $\chi^{(3)}$ values: *e.g.*, poly(α-[5,5'-bithiophenediyl]benzylidene-block-α-[5,5'-bithio-phenequinodimethanediyl]), 2.7 x 10^{-7} esu;[2] Zn(*meso*-substituted tetrabenzporphyrin), 1.2—2.8 x 10^{-8} esu.[22] Thus, the multiply-bonded complex **1a** has a notable $\chi^{(3)}$ value among organic and organometallic compounds.

In the calculation of $\chi^{(3)}$ of **1a** and **2a**, the crystal is assumed to be an isotropic material. The actual value of **1a** along the molecular axis in the crystal is expected to be much larger than the estimation mentioned above. Thus, the linearly conjugated multimetal systems with metal—metal multiple bonds are now found to have an excellent property for nonlinear optical materials.

Our results clearly indicated that metal—metal bonded dinuclear and tetranuclear complexes exhibit large third-order optical nonlinearity as the first example. This study also indicated the possibility for controlling the NLO properties of this type of low-dimensional metal cluster complexes by using a wide variety of transition metal species. An extension of our finding toward different kinds of metal—metal bonded dinuclear and polynuclear complexes is of our further interest.

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17 a) *Measurements of Third Order Nonlinear Optical Susceptibilities.* The third order nonlinear optical susceptibilities were measured by picosecond degenerate four-wave mixing method (DFWM) employing backward-wave geometry. The experimental setup of DFWM is the same as that in the literature. The 532 nm wavelength pulses of 40 ps were generated by a frequency doubled Q-switched Nd: YAG laser of Quantel YG571C. The average pulse power density was 70 MWcm^{-2}. A streak camera (Hamamatsu C1587) was used as a photodetector. The vertically polarized output was split into three beams, which were temporally and spatially overlapped in a 1 mm thick cell filled with a sample. The data were obtained using the first single pulse to exclude any possible hysterisis. b) T. Sakaguchi, Y. Shimizu, M. Miya, T. Fukumi, K. Ohta, and A. Nagata, *Chem. Lett.*, **1992**, 281.

18 The third-order hyperpolarizability, which indicates the nonlinear response of a single molecule, is related to $\chi^{(3)}$ in isotropic media by the following equation:

$$\gamma = \frac{\chi^{(3)}}{f^4 N}$$

where N is the number density of a solute molecule and f is the Lorentz local field factor given by $f = (n^2+2)/3$.

19 For complex **1a**, femtosecond optical Kerr effect (OKE) experiment was also carried out with 70 fs laser pulses centered at 790 nm. As the photon energy at the wavelength was smaller than the energy of the lowest transition band (peak 640 nm), non-resonant hyperpolarizability dominantly contributes to the hyperpolarizability observed at the wavelength. In spite of different wavelengths and pulse durations, the observed hyperpolarizability was found to be approximately in the same order (10^{-31} esu) of the hyperpolarizability measured with picosecond pulses at 532 nm. For isotropic solution, the hyperpolarizability measured by OKE experiment can be directly compared with that by DFWM method. This result suggests that the major part of the hyperpolarizability measured at 532 nm should originate from non-resonant nonlinearity.

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