

Preparation and nonlinear optical properties of ultrathin composite films containing both a polyoxometalate anion and a binuclear phthalocyanine

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An ultrathin composite film containing both polyoxometalate anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (PMo_{12}) and a planar binuclear phthalocyanine, bi-CoPc, has been prepared by the electrostatic layer-by-layer self-assembly method. UV-vis measurements revealed regular film growth with each four-layer $\{\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}/\text{PAH}\}$ adsorption. The film structure was characterized by small-angle X-ray reflectivity measurements, X-ray photoelectron spectra, and AFM images. The nanothick film shows a third-order nonlinear optical response of $\chi^{(3)} = 4.21 \times 10^{-12}$ esu. Experimental investigations also indicate that the combination of polyoxometalate anions $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ with the phthalocyanine bi-CoPc in multilayer films can enhance the third-order NLO susceptibility and modify the third-order NLO absorption of bi-CoPc.

In recent years, polyoxometalates (POMs) have attracted increasing attention in many fields of science, including catalysis, medicine, and materials,^{1–3} because polyoxometalates are extremely versatile inorganic building blocks for the construction of functionally active solid materials.^{4,5} Many potential applications in electrocatalytic, molecular electronic, and electro-optical devices require ultrathin composite films containing polyoxometalates. The layer-by-layer (LBL) electrostatic self-assembly technique provides a viable approach for the formation of various ordered film structures at the nanoscopic level; this offers a large range of potential advantages in device applications.^{6,7} Ichinose *et al.* prepared thin films containing isopolymolybdate $(\text{NH}_4)_4[\text{Mo}_8\text{O}_{26}]$ by means of alternating adsorption of ammonium octamolybdate and poly(allylamine hydrochloride) (PAH).⁸ Kurth's group recently reported the preparation of two ultrathin multilayer polyoxometalate-polyelectrolyte films, incorporating the polyoxometalate cluster $(\text{NH}_4)_{21}[\text{H}_3\text{Mo}_{57}\text{V}_6(\text{NO})_6\text{O}_{183}(\text{H}_2\text{O})_{18}]$ as well as the Keplerate cluster $(\text{NH}_4)_{42}[\text{Mo}_{132}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$, by the LBL method.^{9,10} Their research shows that the LBL method is also applicable for fabricating multilayer films of anionic POMs and polycationic PAH. However, the implementation of POMs as active components in functional devices remains a challenge in fundamental and applied research.¹¹

One of the fundamental properties of POM clusters is the capability for accepting charge from organic electron donors. Donors such as phthalocyanines (Pc) and their derivatives, with their extended two-dimensional π -electron delocalization, are also known for their nonlinear optical (NLO) properties,¹² which makes this class of compounds a promising candidate for optical switching and optical limiting devices.¹³ Much effort has been dedicated to synthesizing novel phthalocyanines in order to improve their functional characteristics.

From theoretical considerations we anticipate that charge-transfer interactions in suitable donor-acceptor complexes may enhance the NLO activity.¹⁴ Therefore, we want to explore methodologies that allow us to implement POMs as acceptors and phthalocyanines as donors in thin films in a systematic manner in order to tailor the NLO properties. In this paper, we report the fabrication of an ultrathin composite film containing both polyoxometalate anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and a planar binuclear phthalocyanine bi-CoPc (see Chart 1) by the layer-by-layer self-assembly method, and the nonlinear optical properties of the ultrathin film are also presented. To the best of our knowledge, this work is the first example in which polyoxometalate and phthalocyanines are combined as active components in a composite film with enhanced NLO properties.

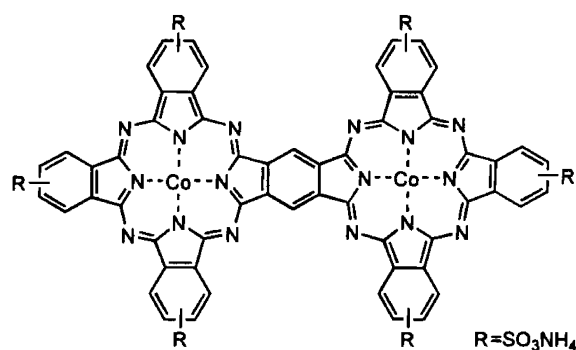


Chart 1 Chemical structure of bi-CoPc molecule.

Experimental

Materials

The synthesis and purification of bi-CoPc was carried out according to the literature method.¹⁵ The product was identified by elemental analysis and its IR spectrum. Heteropoly acid of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ (PMo_{12}) was purchased from Beijing Chem. Corp. of China and used without further purification. Poly(allylamine hydrochloride) (PAH; MW 70,000; Aldrich), sodium poly(styrenesulfonate) (PSS; MW 70,000; Aldrich), and poly(ethylenimine) (PEI; MW 50,000; Aldrich) were used as purchased without further purification. Quartz and silicon wafers were cleaned in a 80 °C piranha solution (H_2SO_4 – H_2O_2 70 : 30 v/v) for 1 h and in a 80 °C H_2O – H_2O_2 – NH_3 (5 : 1 : 1 v/v/v) bath for 30 min and rinsed in water. This procedure results in a hydrophilic substrate surface. Quartz wafers were used for UV-vis and photoluminescence spectroscopy, silicon wafers for XRR and XPS measurements, and mica for AFM imaging. The water used in all experiments had a resistivity higher than 17.5 M Ω cm.

Film preparation

The fabrication of the multilayer film was carried out according to the following steps. The cleaned substrates (quartz, silicon, or mica), were immersed in a 10^{-2} M PEI solution for 20 min, rinsed with water, and dried under a nitrogen stream. The PEI-coated substrates were then exposed to a 10^{-2} M PSS solution for 20 min, followed by alternating 20 min immersions in PAH 10^{-2} M containing 1 M NaCl; pH 2.5–3), PMo_{12} (10^{-3} M, pH 2–3), bi-CoPc (10^{-4} M, pH 1–2), and PSS solutions, respectively. Water rinses and nitrogen drying steps were performed after each adsorption step.

Instrumentation

UV-vis spectra were measured on a Beckman DU8B spectrophotometer. XPS spectra were recorded on an Escalab MKII photoelectronspectrometer with ALK2 (1486.6 eV) as the excitation source. X-Ray reflectance experiments were performed with a Philips X'Pert instrument using copper K_α radiation ($\lambda = 1.5405$ Å). AFM images were taken using a Nanoscope IIIa instrument (Digital Instruments) operating in the tapping mode with silicon nitride tips. The laser output was produced with a Q-switched Nd:YAG laser system at a wavelength of 532 nm with a pulse width of 8 ns. The input and the output energies of the laser pulses were measured with an energy meter (Laser Precision Rjp-735).

Results and discussion

UV-vis spectra

UV-vis spectroscopy is used to monitor the layer-by-layer adsorption process. Since $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ can be easily dissolved in water to produce the stable anionic cluster $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (PMo_{12}), it is possible to adsorb $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ into the polyelectrolyte multilayers by the driving force of electrostatic attractions. Fig. 1 shows the UV-vis spectra of the $(\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}/\text{PAH})_n$ ($n = 1$ –6) multilayers deposited on a precursor (PEI/PSS/PAH) film on quartz substrates. The absorption band at 225 nm in the UV-vis spectrum of the precursor (PEI/PSS/PAH) film ($n = 0$) arises from the aromatic groups present in the PSS polyanion. The polycation PAH does not absorb above 200 nm, and its presence in the film does not contribute to the UV-vis spectra. As found in another reported example,¹⁶ the characteristic absorption band (at 309 nm) of PMo_{12} did not emerge, due to both the low content of POMs in the nanocomposite film and the low

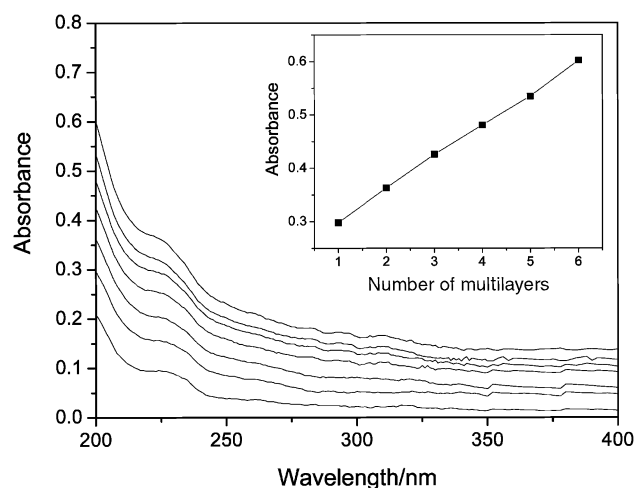


Fig. 1 UV-vis spectra of $(\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}/\text{PAH})_n$ multilayer films with $n = 0$ –6 on PEI/PSS/PAH-modified quartz substrates (both sides). These curves, from bottom to top, correspond to $n = 0, 1, 2, 3, 4, 5$ and 6, respectively. The inset displays the absorbance growth at 200 nm as a function of the number of $(\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}/\text{PAH})$ multilayers for the same films.

intensity of this absorption band. However, an abrupt increase of the absorbance at 210 nm in the UV-vis spectra after each POM deposition indicates that POM anions have been deposited on the film.

As shown in the inset of Fig. 1, the plot of absorbance at 200 nm versus the number of $\{\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}/\text{PAH}\}$ layers results in a nearly straight line, which confirms linear growth of the multilayer. It can also be seen from the inset of Fig. 1 that the absorbance value corresponding to the deposition of PMo_{12} onto the precursor PEI/PSS/PAH film is larger than those obtained for subsequent PMo_{12} depositions, such that the linear plot does not pass through the origin. This reflects the greater amount of PMo_{12} adsorbed by the precursor PEI/PSS/PAH film (compared to that in subsequent layers) and may result from the aggregated PMo_{12} nanoparticles penetrating into the polyelectrolyte layers.

As mentioned above, the stable anionic clusters $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (PMo_{12}) presumably adsorb to the positively charged polyelectrolyte interface by electrostatic attractions. By electrophoresis we have found that the binuclear phthalocyanine bi-CoPc, which readily dissolves in HCl solution, yields a cationic form. Therefore, bi-CoPc can bind to the anionic $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ layer through self-assembly mediated by electrostatic interactions. After the deposition of these three sub-layers of $\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}$, a subsequent adsorption of PAH was carried out to produce an interface with a positive charge, so that further deposition of PMo_{12} can occur on the sub-layer of PAH. UV-vis measurements reveal that the deposition of PAH on the $\{\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}\}$ layer results in partial loss of material. Due to the small size and few charges of the POM cluster, it is feasible that PAH extracts some material from the interface. In contrast, subsequent deposition of PMo_{12} on the PAH interface results in an excess deposition of clusters as indicated by UV-vis measurements. Presumably, the small cluster can diffuse through the multilayer to some extent. Despite the partial loss of material during PAH deposition, the steady increase in absorbance shows that a sufficient amount of the components are deposited in the multilayer films by the layer-by-layer method.

IR spectrum

In the IR spectrum of the multilayer film $\{(\text{PEI}/\text{PSS}/\text{PAH})/(\text{PMo}_{12}/\text{bi-CoPc}/\text{PSS}/\text{PAH})_6\}$ (see Fig. 2), there are four bands at 1063, 965, 880 and 805 cm^{-1} assigned to $\nu_{\text{as}}(\text{Mo}=\text{O})$,

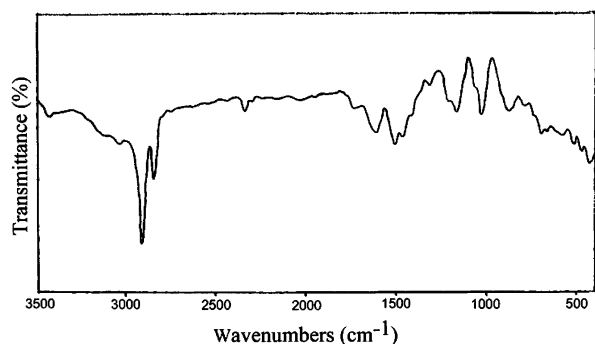


Fig. 2 IR spectrum of a {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)₆} multilayer film.

$\nu_{\text{as}}(\text{P-O})$, and $\nu_{\text{as}}(\text{Mo-O-Mo})$ 2 peaks, respectively, which characteristically reflects the Keggin structure of the [PMo₁₂O₄₀]³⁻ anion. The features at 1650, 1520 and 1465 cm⁻¹ are associated with the antisymmetric and symmetric stretching vibrations of the C=C and C=N bonds. The characteristic vibration of $\nu(\text{S=O})$ gives two bands at 1319 and 1180 cm⁻¹. These infrared spectrum results indicate that both the inorganic heteropoly anion [PMo₁₂O₄₀]³⁻ and organic phthalocyanine bi-CoPc molecule have been incorporated into the multilayer film.

X-Ray photoelectron spectrum (XPS)

To identify the elemental composition of the multilayer films, we measured the X-ray photoelectron spectrum (XPS) of the {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)} film. The ratio of elements is determined to be C : N : S : O : Mo : P : Co = 484 : 59.0 : 22.6 : 92.0 : 12.9 : 1.2 : 1.05. Thus, the expected molar ratio of 1 : 12 for P to Mo is also approximately established. The XPS data suggest that we indeed incorporate PMo₁₂ anion and bi-CoPc into the multilayer films, in agreement with the UV-vis results. Moreover, the appearance of double N_{1s} peaks at 401.5 and 398.7 eV in the XPS measurement shows two kinds of nitrogen atoms (see Fig. 3). One kind of nitrogen atom comes from polyelectrolytes PEI and PAH, corresponding to an N_{1s} peak at 401.5 eV. The other kind is attributed to the nitrogen atom of the N-Co coordination bond in bi-CoPc. Because of the possible occurrence of a N←Co feedback π -bond in bi-CoPc, which often exists in some complexes with nitrogen ligand,¹⁷ the electron binding energy of N_{1s} decreases to 398.7 eV.

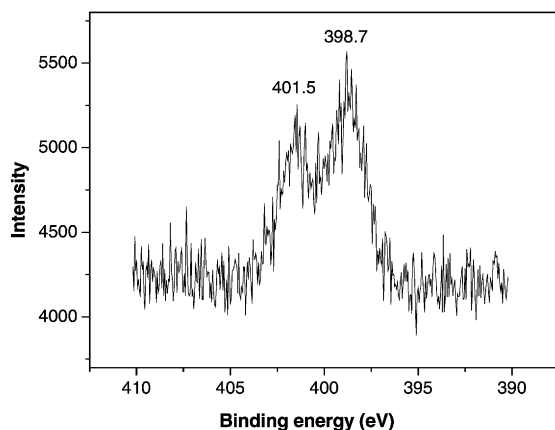


Fig. 3 Nitrogen atom peaks in the X-ray photoelectron spectrum for the {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)} film.

X-Ray reflectivity measurements

Small-angle X-ray reflectance (XRR) was also used to investigate the film structure. Fig. 4 shows the X-ray reflectance curves for the multilayer films {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)_n} ($n=3$ and 6). A broad oscillation observed after $2\theta=0.3^\circ$ in each XRR curve of the multilayer films is considered to be a Kiessig fringe, which results from X-ray interferences from the substrate-film and film-air interfaces, suggesting that the film surface is moderately smooth. Although we have attempted to fit the data with a box model simulation,¹⁸ satisfactory results were not achieved. Thus, the total film thickness may be estimated from the spacing of the Kiessig fringes.¹⁹ Firstly, the distance between the two ends of the Kiessig fringe can be obtained from Fig. 4(a) or (b), using the reflectance angle θ as the unit of measure. Then the ΔQ_z value is derived from the equation $Q_z (\text{\AA}^{-1}) = 4\pi \sin\theta/\lambda$,¹⁹ where λ (1.5405 \AA) is the wavelength of the copper K α radiation used in the X-ray reflectance experiment. We found ΔQ_z ca. 0.018 \AA^{-1} for the $n=6$ film and ca. 0.041 \AA^{-1} for the $n=3$ film, corresponding to a total film thickness ($d_{\text{total}} = [2\pi/\Delta Q_z]$) of ca. 350 and 153 \AA , respectively. From a difference of the film thickness between $n=6$ and $n=3$, the thickness of a (PMo₁₂/bi-CoPc/PSS/PAH) layer can be estimated to be ca. 65 \AA . This value is reasonable if we consider that polyelectrolytes, such as PSS and PAH, have a typical film thickness of ca. 2 nm. In fact, the absence of Bragg peaks in the XRR curves indicates the absence of a lattice-like layer structure and points to entanglement between the layers. In addition, the result of X-ray reflectivity measurements for the multilayer films on silicon wafers was similar to that on quartz substrates, suggesting that the multilayer films have the same growth model on both silicon wafers and quartz substrates.

Atomic force microscopy (AFM)

The AFM images of both a (PEI/PSS/PAH) precursor film and a {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)} multilayer film were taken to provide detailed information about the surface morphology and the homogeneity of the deposited films. The outer PAH surface layer of the precursor film is uniform and smooth, with a mean roughness of 0.5 nm. After adsorption of a (PMo₁₂/bi-CoPc/PSS/PAH) multilayer, the mean interface roughness increased to 1.92 nm. In addition, a vertical grain structure of the multilayer surface is observed from the three-dimensional AFM image of this sample (see Fig. 5), showing an almost uniform distribution of aggregated

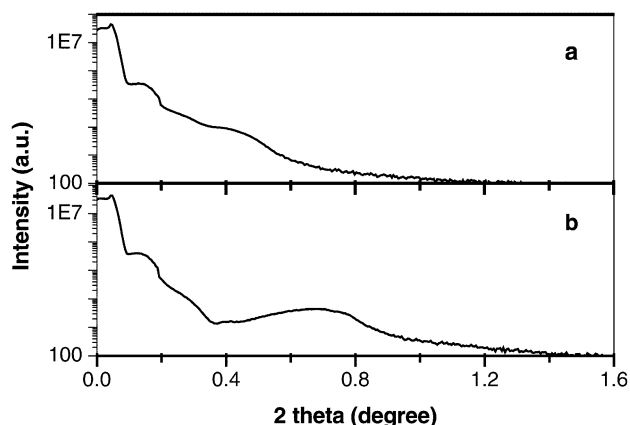


Fig. 4 X-ray reflectance curves for the {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)_n} ($n=3, 6$) multilayer films on silicon: (a) $n=6$; (b) $n=3$.

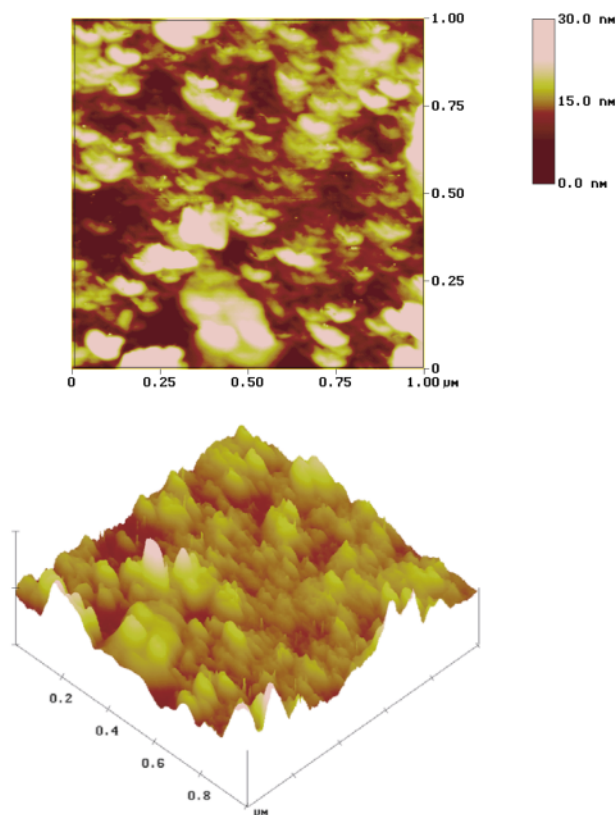


Fig. 5 Tapping mode AFM images of a {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)} film and corresponding three-dimensional image.

nanoclusters. This should be explained not only as a result of polyelectrolyte deposition but also as an indirect reflection of PMo₁₂ aggregation. In addition, the AFM image of a film with more deposition cycles, for example, of the {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)₃} multilayer film, showed a slightly decreased surface roughness.

Nonlinear optical (NLO) measurements

The third-order nonlinear optical (NLO) properties were investigated using the Z-scan technique.²⁰ The open-aperture and the closed-aperture Z-scan curves of the film sample are shown in Fig. 6(a) and (b), respectively. The open-aperture Z-scan curve of the film appears as a single peak at the focus position [Fig. 6(a)], suggesting that this film possesses a

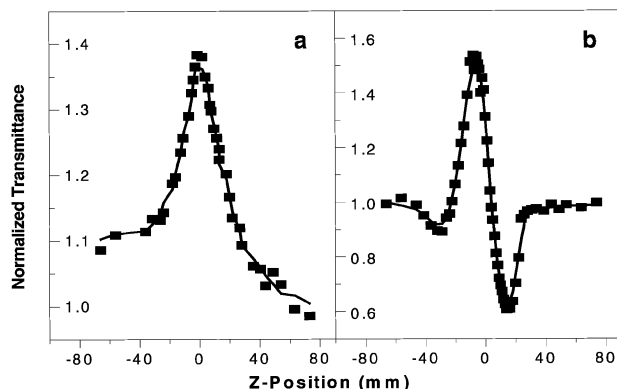


Fig. 6 Z-scan curves of a {(PEI/PSS/PAH)(PMo₁₂/bi-CoPc/PSS/PAH)} multilayer film: (a) the open-aperture configuration showing saturable NLO absorption; (b) the closed-aperture configuration showing the self-defocusing effect.

nonlinear saturable absorption. The peak-valley pattern of the normalized transmittance curve obtained under the closed-aperture configuration shows the characteristic self-defocusing behavior of the propagating wave in the film, a property with wide application in the protection of optical sensors, like night-vision devices.²¹ The closed-aperture curve in Fig. 6(b) exhibits a sharp peak at -7.2 mm before the focus and two valleys; the right one is at 15.2 mm behind and the left one at -30.1 mm before the focus. Thus, the sign of the nonlinear refractive index n_2 can be determined to be negative. According to Sheik-Bahae *et al.*'s theoretical equations,²⁰ the nonlinear refractive index n_2 was calculated to be $8.56 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$. Because the nonlinear absorption effect has been deducted from Z-scan data, the third-order NLO susceptibility $\chi^{(3)}$ of the multilayer films can be calculated from the n_2 value by using the following equation:²²

$$\chi^{(3)} = \chi_R^{(3)} = cn_0 n_2 / 16\pi^2 = 4.21 \times 10^{-12} \text{ esu}$$

where c is the velocity of light and n_0 is the linear refractive index for the sample film, equal to 1.608 as determined by a refractometer.

When the molecule-based material absorbs the excitation light, some portion of the ground state molecules are pumped into an excited state. If the excited state refrangibility is greater than that of the ground state, the refractive index of the material increases, and if it is smaller the refractive index decreases. If the refrangibilities are equal, the material's refractive index remains unchanged. Therefore, the optical nonlinearity of the material arises from the relative properties of the excited and the ground states.²³ Upon coordination by metals, the macrocycle electronic properties of the phthalocyanine molecule can be fine tuned by varying the coordinated metal. Moreover, Neher *et al.* have observed that the linear and nonlinear optical properties of phthalocyanine thin films depend strongly on the relative distance between the macrocycles and therefore the electronic coupling between the macrocycles.²⁴ Since polyoxometalates are generally electron acceptors, their introduction into the phthalocyanine thin films is expected to modify the electronic properties of the macrocycles *via* the charge-transfer interaction between the Pc and POM.

To investigate the contribution of bi-CoPc in the films to the third-order NLO effect of the film, we measured the third-order NLO properties of simple bi-CoPc multilayer films {(PEI/PSS)(bi-CoPc/PSS)₆}. The open-aperture and the closed-aperture Z-scan curves of the {(PEI/PSS)(bi-CoPc/PSS)₆} film sample are shown in Fig. 7(a) and (b), respectively. Under the same experimental conditions as for the {PMo₁₂/bi-CoPc} films, an n_2 value of $2.48 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$ was obtained,

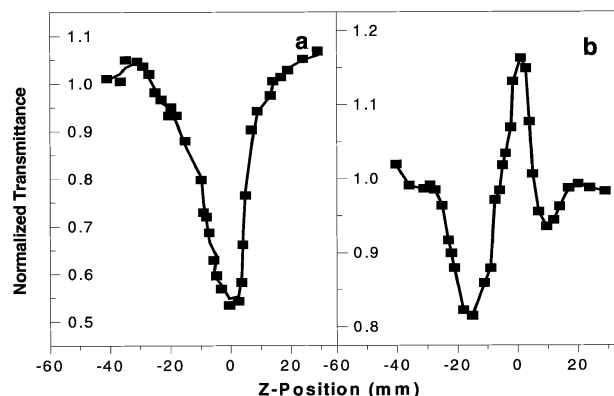


Fig. 7 Z-scan curves of a {(PEI/PSS/PAH)(PEI/PSS)(bi-CoPc/PSS)} multilayer film: (a) the open-aperture configuration showing reverse saturable NLO absorption; (b) the closed-aperture configuration showing the self-focusing effect.

thus the $\chi^{(3)}$ value for the bi-CoPc films can be calculated to be 9.24×10^{-13} esu. The open-aperture Z-scan curve of the bi-CoPc films exhibits a deep valley in the focus position, indicating the existence of reverse saturable absorption, which is in contrast to that of the {PMo₁₂/bi-CoPc} films. It is noteworthy that after introduction of POMs into the Pc thin films the optical nonlinear absorption property changes from reverse saturable absorption to saturable absorption. This result reveals that the combination of POMs with Pc influences the optical nonlinearity of Pc, although the driving force of the combination only depends on the electrostatic interaction. This modification of the optical nonlinear absorption properties is of significance for the development of optical limiting materials.

Obviously, the combination of polyoxometalate anion [PMo₁₂O₄₀]³⁻ with phthalocyanine bi-CoPc in multilayer films can enhance the third-order NLO susceptibility and modify the third-order NLO absorption properties of bi-CoPc. Due to their strong oxidative power, polyoxometalate anions generally act as electron acceptors. Several polyoxometalate-based inorganic-organic charge-transfer compounds, such as H₄SiW₁₂O₄₀·4hexamethylphosphoramide·2H₂O²⁵ and (C₉H₇NO)₄H₇PMo₁₂O₄₀·3H₂O,²⁶ exhibit good third-order NLO susceptibilities. The strong electrostatic interaction between POMs and bi-CoPc may induce an increased extent of π -electron delocalization on the bi-CoPc macrocycles, resulting in a $\chi^{(3)}$ enhancement in the multilayer film. Although the $\chi^{(3)}$ value is not large enough for device application, the fact that the combination of POM anions with phthalocyanines can modify the original optical nonlinearity informs us of a new way to explore the POMs-Pc type of third-order nonlinear optical materials.

Acknowledgements

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References

- 1 M. Misono, *Catal. Rev. Sci. Eng.*, 1987, **29**, 269.
- 2 F. Bussereau, M. Picard, C. Malik, A. Teze and J. Blancou, *Ann. Inst. Pasteur/Virol.*, 1988, **32**, 33.
- 3 L. Ouahab, *Chem. Mater.*, 1997, **9**, 1909.
- 4 M. T. Pope and A. Müller, *Polyoxometalates: From Platonic Solid to Anti-Retroviral Activity*, Kluwer, Dordrecht, 1994.
- 5 C. L. Hill, *Chem. Rev.*, 1998, **98**, 1.
- 6 D. Piscecic, W. Knoll and M. Tarlov, *J. Supramol. Sci.*, 1995, **2**, 99.
- 7 A. C. Fou, O. Onisuka, M. Ferreira and M. F. Rubner, *J. Appl. Phys.*, 1996, **79**, 7501.
- 8 I. Ichinose, H. TagawaMizuki, Y. Lvov and T. Kunitake, *Langmuir*, 1998, **14**, 3462.
- 9 F. Caruso, D. G. Kurth, D. Volkmer, M. J. Koop and A. Müller, *Langmuir*, 1998, **14**, 187.
- 10 D. G. Kurth, D. Volkmer, M. Ruttorf, B. Richter and A. Müller, *Chem. Mater.*, 2000, **12**, 2829.
- 11 J. H. Fendler, *Chem. Mater.*, 1998, **10**, 2205.
- 12 (a) G. de la Torre, P. Vazquez, F. Agullo-Lopez and T. Torres, *J. Mater. Chem.*, 1998, **8**, 1671; (b) H. S. Nalwa, in *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Miyata, CRC Press, Boca Raton, FL, 1997; H. S. Nalwa and J. S. Shirk, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publishers (LSK) Ltd., Cambridge, 1996, vol. 4, p. 79.
- 13 G. de la Torre, T. Torres and F. Agullo-Lopez, *Adv. Mater.*, 1997, **9**, 265.
- 14 C. T. Chen and G. Z. Liu, *Annu. Rev. Mater. Sci.*, 1986, **16**, 203.
- 15 Y. Zhang, L. Li, S. Jiang, Y. Zhao, T. Li, X. Du and S. Yang, *Langmuir*, 1999, **15**, 2183.
- 16 C. Sun and J. Zhang, *Electrochim. Acta*, 1998, **43**, 943.
- 17 C. C. Su and J. W. Faller, *J. Organomet. Chem.*, 1975, **84**, 53.
- 18 A. Asmussen and H. Riegler, *J. Chem. Phys.*, 1996, **104**, 8159.
- 19 J. Schmitt, T. Grunewald, G. Decher, P. S. Pershan, K. Kjaer and M. Losche, *Macromolecules*, 1993, **26**, 7058.
- 20 M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.*, 1996, **26**, 760.
- 21 T. Norman, *Conference on Laser and Electro-Optics*, OSA Technical Digest Series, Optical Society of America, Washington, DC, 1993, vol. 11, p. 614.
- 22 L. Yang, *Opt. Lett.*, 1992, **17**, 323.
- 23 G. Fang, Y. Song and Y. Wang, *Opt. Commun.*, 2000, **183**, 523.
- 24 D. Neher, A. Kaltbeitzel, A. Wolf, C. Bubeck and G. Wegner, in *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, NATO ARW Series, ed. J. L. Bredas and R. R. Chance, Kluwer, Dordrecht, 1990, vol. E182, p. 387.
- 25 J. Niu, X. You, C. Duan, H. Fun and Z. Zhou, *Inorg. Chem.*, 1996, **35**, 4211.
- 26 Y. Zhou, E. Wang, J. Peng, J. Liu, R. Huang and W. You, *Polyhedron*, 1999, **18**, 1419.