HYBRID FILMS CONSISTING OF A CLAY AND A DIACETYLENIC, TWO-PHOTON ABSORPTIVE DYE

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Abstract—Hybrid films consisting of Sumecton SA smectite (SSA) and a diacetylenic two-photon absorptive dye; 1,4-bis(2,5-dimethoxy-4-{2-[4-(N-methyl)pyridinium]ethenyl}phenyl) butadiyne triflate (MPPBT) were fabricated. The MPPBT-clay composites were prepared by the cation exchange method in a dimethylsulfoxide (DMSO)-water mixed solvent. A low-light-scattering film, suitable for use in optical devices, was obtained by filtration of the dispersion of the MPPBT-clay composites. Estimation of the two-photon absorption cross-section ($\sigma^{(2)}$) by means of the open-aperture Z-scan technique was performed using the present film. The $\sigma^{(2)}$ value of MPPBT in the film fabricated at the MPPBT loading levels *vs.* 20% cation exchange capacity was 1030 GM (1 GM = 1×10^{50} cm^4 s photon^{-1} molecule^{-1}) at an excitation wavelength of 800 nm. The value was 1.3 times greater than the maximum value of the $\sigma^{(2)}$ of MPPBT dissolved in DMSO without clay.

Key Words—Diacetylenic Dye, Film, Synthetic Saponite, Two-photon Absorption.

INTRODUCTION

Two-photon absorption (TPA) has attracted considerable attention because of its promising applications for optical limiting (Spangler, 1999; Lee *et al.*, 2003; Lei *et al.*, 2001), three-dimensional (3D) micro-fabrication (Sun *et al.*, 1999; Cumpston *et al.*, 1999; Kawata *et al.*, 2001), 3D fluorescence imaging (Caylor *et al.*, 1999), ultrasensitive detection in analytical chemistry (Zugel *et al.*, 2000), photodynamic cancer therapy (Bhawalker *et al.*, 1997), *etc*. For such applications, intense laser pulses with a peak intensity of MW cm^{-2} to GW cm^{-2} are needed because of the small total photon absorption (TPA) cross-sections ($\sigma^{(2)}$) of some materials. Improvement of the $\sigma^{(2)}$ value would make these applications possible with less intense laser pulses and open the way for new possibilities such as 3D optical data storage, 3D biological imaging, *etc*. A number of attempts have been made to develop new TPA materials with large $\sigma^{(2)}$ values (Reinhart *et al.*, 1998; Screen *et al.*, 2002; Akiba *et al.*, 2005; Ogawa *et al.*, 2005).

Hybridization of organic dyes with a clay offers some promise as a means of obtaining efficient TPA materials. Kamada *et al.* (2007) reported that the $\sigma^{(2)}$ value of 1,4-bis(2,5-dimethoxy-4-{2-[4-(N-methyl)pyridinium] ethenyl}phenyl)butadiyne triflate (MPPBT) (Figure 1) is enhanced in a cast film consisting of composites of MPPBT and Sumecton SA smectite (SSA). However, the light-scattering of the cast film of the MPPBT-SSA composites prevented sufficient characterization of the

optical properties of MPPBT in the film. The reasons the $\sigma^{(2)}$ of MPPBT was enhanced in the composite are still not clear, so a low-light-scattering film consisting of MPPBT-SSA composites is needed. In this study, attempts were made to fabricate such a film.

Several films fabricated by filtering a water dispersion of a clay and organic dye composite through a membrane filter were studied as inorganic-organic hybrids with various functionalities (Kuang *et al.*, 2003; Bujdák and Iyi, 2002, 2006). Among those films, one fabricated by Takagi *et al.* (2002, 2006) is known to possess low-light-scattering properties. In this study, MPPBT-SSA hybrid films were fabricated, based on the Takagi *et al.* (2002) protocol, with a range of cation exchange capacity (CEC) loadings, whereas in the previous study only 20% CEC loading was used. Z-scan measurements (Sheik-Bahae *et al.*, 1990) of the films were then performed in order to evaluate the $\sigma^{(2)}$ values of MPPBT in the films.

EXPERIMENTAL

Clay minerals

The MPPBT-SSA composites were prepared by mixing a water dispersion of SSA with a dimethylsulfoxide (DMSO) solution of MPPBT. The MPPBT-SSA hybrid films were prepared by filtration of the dispersion of the MPPBT-SSA composites. The light-scattering of the film obtained was sufficiently low even when the MPPBT loading levels *vs.* CEC were varied widely. The composites were fabricated using SSA (from Kunimine Industries Co., Ltd, Japan, and supplied by Prof. S. Takagi of Tokyo Metropolitan University), the particle size of which, when exfoliated to a single layer, is
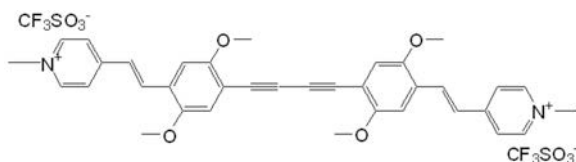
Figure 1. Chemical structure of 1,4-bis(2,5-dimethoxy-4-{2-[4-(*N*-methyl)-pyridinium]ethenyl}phenyl)butadiyne triflate (MPPBT).

considerably smaller than the wavelength of light (5 nm). The stoichiometric formula for the SSA is $[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]^{0.77-} \cdot (Na_{0.49}Mg_{0.14})^{0.77+}$, the surface area = 750 m^{2}g^{-1}, and the CEC, estimated by Takagi, was 0.997 meq g^{-1}. The average diameter of the SSA in the exfoliated state in the present study, confirmed by atomic force microscopy, is ~30 nm.

Fabrication of the hybrid films

The hybrid films were fabricated by filtration of the dispersion of the MPPBT-SSA composites using a membrane filter. Particles of clay-organic molecule composites in a dispersion are known to aggregate to some extent (Bujdák *et al.*, 2001). As the MPPBT-SSA composites were collected by a membrane filter, the size of the aggregates must be larger than the pore size of the membrane filter. However, for the purposes of light-scattering, the particle size should be as small as possible. Therefore, in order to obtain the aggregates, for which the average particle size is slightly larger than the pore size of the membrane filter, the polarity of the solvent was optimized by employing a mixed solvent consisting of water and DMSO.

The dispersion of SSA (in the exfoliated state) was prepared by mixing 3 mg of SSA with 60 mL of ultrapure water followed by ultrasonication (typically for 30 min) until the dispersion became transparent. The MPPBT was dissolved in DMSO. The MPPBT-SSA composites were prepared by injecting DMSO solution of MPPBT into vigorously stirred water dispersions of SSA. Attempts were made to fabricate composite films by varying the amounts of DMSO solution of MPPBT. As a result, a low-light-scattering film was obtained when 0.6 mL of DMSO solution of MPPBT was added to 60 mL of SSA dispersion. Therefore, the films used for spectroscopic studies were fabricated by using the MPPBT-SSA composites prepared in DMSO (1% v/v)-water mixed solvent. Composites with various % CEC values were fabricated using DMSO solutions of MPPBT with corresponding concentrations. The % CEC values were calculated under the assumption that an MPPBT dication occupied two anionic sites at the SSA layer surface. In the case of a 20% CEC, the concentration of the DMSO solution of MPPBT was 5×10^{-4} mol L^{-1}.

The MPPBT-SSA dispersion of the composites was filtrated using a mixed cellulose ester membrane filter

(0.1 μm pore size, 25 mm diameter). In order to avoid excess aggregation, the dispersion of the composites was filtrated soon after mixing the water dispersion of SSA and DMSO solution of MPPBT (typically within 2 min). The residue was orange, while the filtrate was colorless. The residue was transferred onto a clean glass substrate with an optically flat surface. The transfer was made immediately after filtration (within ~5 s), *i.e.* before the residue had dried completely. Otherwise, a low light-scattering film could not be obtained.

Optical measurements

Absorption spectra in the UV-vis region were measured using an Hitachi Model U-3300 spectrometer. Absorbance was recorded at an interval of 0.5 nm. The resolution of the spectrometer was set at 2.0 nm.

The open-aperture Z-scan technique (Kamada *et al.*, 2003) was employed for the $\sigma^{(2)}$ measurements. A femtosecond pulsed beam from a regenerative amplifier (Spectra-Physics, Spitfire) was used as the light source. The typical pulse duration was 180−200 fs with a repetition rate of 1 kHz. The incident beam was focused by a plano-convex lens (f = 150 mm) and the sample was scanned along the propagation axis of the incident beam. The average incident power was varied from 0.05 to 0.2 mW, corresponding to on-axis peak powers (I_0) of 0.25 to 1.11 MW cm^{-2}. The proportionality relations between the TPA absorbance, q_0, and the incident power, and hence I_0, was confirmed at each measurement.

RESULTS AND DISCUSSION

One-photon absorption spectra

Dispersion of MPPBT-SSA composites. Considerable solvatochromism is often seen for efficient TPA compounds (*e.g.* see Woo *et al.*, 2005). Therefore, UV-visible spectra were recorded for the DMSO solution of MPPBT, for the dispersion of MPPBT-SSA composites (20% CEC) in DMSO (1% v/v)-water mixed solvent; and for MPPBT without SSA in DMSO (1% v/v)-water mixed solvent. The results are shown in Figure 2. As summarized in Table 1, the absorption peaks (λ_{max}) of the solution of MPPBT taken in the DMSO (1% v/v)-water mixed solvent and in pure DMSO were found at 455 nm and 466 nm, respectively, indicating that the one-photon absorption property of MPPBT is sensitive to chemical species surrounding the molecule. The λ_{max} value observed for the dispersion of MPPBT-SSA composites was 486 nm at 20% CEC. These values show good agreement with those reported by Kamada *et al.* (2007). Typically, the spectrum of a cationic dye shows a red shift when it hybridizes with a clay (Bujdák and Iyi, 2002; Kawamata and Hasegawa, 2006; Kawamata *et al.*, 2006). The red shift found in Figure 2 suggests that the MPPBT-SSA composites are formed in the present dispersion.
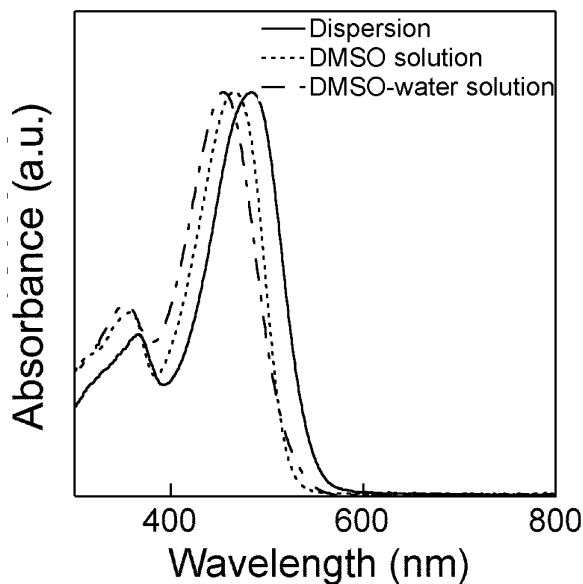
Figure 2. Absorption spectra (normalized at the peak) of MPPBT in: a DMSO (1% v/v)-water mixed solvent (dot-and-dashed); a dispersion of MPPBT-SSA composites in DMSO (1% v/v)-water mixed solvent (solid); and DMSO (dashed).

Although the λ_{max} value of the dispersion of the 40% CEC (486 nm) was the same as that of the 20% CEC, those of the 60% and 80% CEC were blue shifted (480, 473 nm). A similar blue shift accompanying the decrease of the intermolecular distance between molecules adsorbed onto a clay was reported for a hemicyanine dye (Kawamata and Hasegawa, 2006). Some dyes, such as hemicyanines, tend to form an aggregate. In hybrid materials, some dyes are reported to be aggregated (Carpenter *et al.*, 1992). As for such materials, the λ_{max} values are reported to shift depending on the ratio of aggregated and non-aggregated dyes. In the case of the hemicyanine dye-clay composite, the reason for the blue shift is thought to be due to the increase in the

population of a molecular assembly such as H-aggregate. In the present study, the formation of the H-aggregate-like assembly of MPPBT at a greater % CEC value is considered to be similar to the case of the hemicyanine dye.

MPPBT-SSA films. The UV-visible spectra of the MPPBT-SSA hybrid films are shown in Figure 3. The λ_{max} values are also summarized in Table 1. The λ_{max} was found to be blue shifted as the % CEC value increased. In case of greater % CEC values, larger amounts of MPPBT molecules should be adsorbed onto the surface of the SSA particles. Therefore, it is possible that the amount of adsorbed molecules overlapping with molecules adsorbed on the neighboring composites should be increased in films fabricated at higher % CEC values. As discussed above, an increase in the population of a molecular assembly such as H-aggregate leads to a blue shift. Therefore, the most likely reason for the blue shift observed for the present films, as the % CEC value was increased, is the increase in the population of a molecular assembly such as H-aggregate.

The λ_{max} of a film fabricated at 20% CEC was 496 nm. The value was smaller than that observed for the previous cast film (507 nm). As described below, the light-scattering of the present films was considerably less than that of the cast films. This means that the size and population of the gaps in the present films are considerably smaller than those in the cast films, and thus the composites must be stacked densely in the present film. Therefore, MPPBT molecules in the present films must be overlapped to a considerable extent compared to the cast films. The reason for the

Table 1. Optical properties of MPPBT in various solvents and in films.

Sample	λ_{max}[1] (nm)	TPA cross-section[2] (GM)
DMSO solution	466	770
DMSO (1% v/v)-water mixed solvent	455	
Dispersion (20% CEC)	486	
Dispersion (40% CEC)	486	
Dispersion (60% CEC)	480	
Dispersion (80% CEC)	473	
Film (20% CEC)	496	1030
Film (40% CEC)	486	900
Film (60% CEC)	478	
Film (80% CEC)	476	500

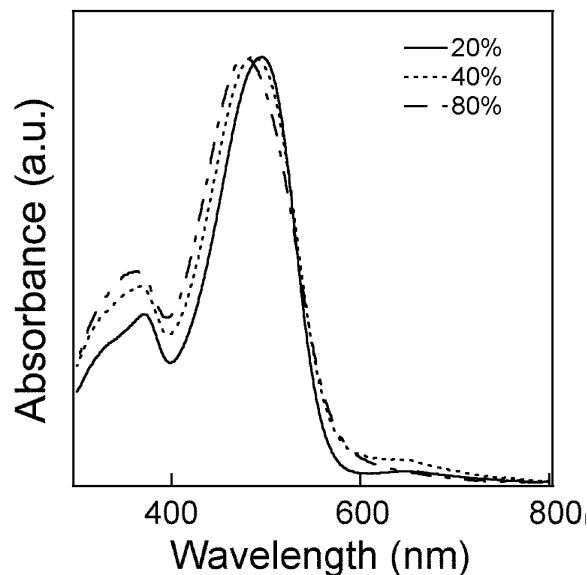[1] wavelengths of absorption peak, [2]: values at 800 nm

Figure 3. Absorption spectra (normalized at the peak) of the MPPBT-SSA hybrid films fabricated at 20% (solid), 40% (dotted), and 80% (dot-and-dashed) CEC.
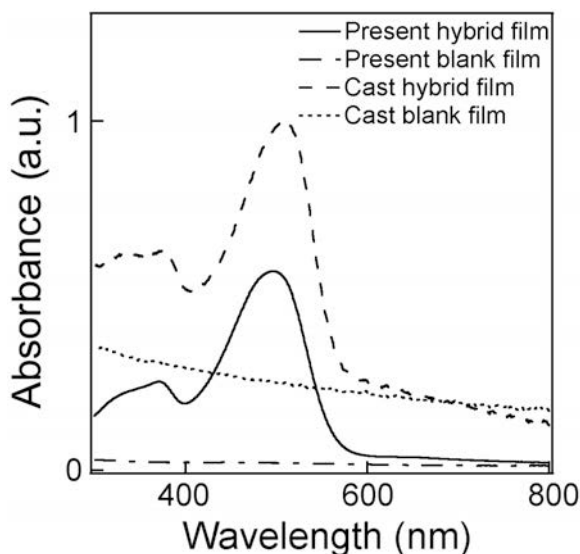
Figure 4. Absorption spectra of the MPPBT-SSA hybrid film (solid), of the blank clay film fabricated in the present technique (dot-and-dashed), of the cast film of MPPBT-SSA composites (dashed), and of the cast blank film (dotted). The % CEC values of the films were identical (20%).

smaller λ_{max} values for the present films compared to the cast films is thought to be due to the greater population of a molecular assembly such as H-aggregation in the present films.

The profiles of absorption spectra of the present film and of the cast film are compared in Figure 4 together with those of the blank clay films prepared in the same way as the MPPBT-SSA hybrid films. For a blank clay film, fabricated by the casting technique, a broad spectrum with a monotonic increase as the wavelength shortens was observed. This is due to light-scattering of the film. A similar degree of light-scattering to that of a cast film of MPPBT-SSA composites can also be seen in the spectrum. For a blank clay film fabricated in the present study, the intensity of the broad spectrum was reduced considerably. The absorbance at the λ_{max} value of the present MPPBT-SSA hybrid film (498 nm) compared to the blank film, fabricated under the same conditions, was almost the same as that of the cast film (at 507 nm). This indicates that the amount of MPPBT molecules existing in the present films was almost the same as that of the cast film. Therefore, the MPPBT-SSA composite existing in a unit volume should be almost the same, because the % CEC values were identical in both cases. Nevertheless, a tail of absorbance found in the present film at the wavelength region from 600 nm to 800 nm is apparently reduced compared with that of the cast film. This indicates that the light-scattering from the present film is reduced considerably.

Plots of absorbance of the λ_{max} *vs.* the amount of filtrated dispersion (Figure 5, inset) revealed that both the λ_{max} value at 495 nm and the absorbance over the whole measured range increased steadily as the amount

of filtrated dispersion increased. This linear relationship indicates that the thickness of the film, *i.e.* the optical density of the film, can be controlled while retaining the low-light scattering property. Films of organic materials obtained by spin coating are used widely as optical materials because of their low-light-scattering nature. However, fabrication of a thick film by spin coating is difficult. This limits the applicability of spin-coat films for devices which require low-light-scattering materials with high optical densities. The film fabricated in the present work offers promise in this respect.

Two-photon absorption properties

The $\sigma^{(2)}$ value of MPPBT in the present film was measured by the open-aperture Z-scan technique. This technique, using a femtosecond pulsed laser, is an established means by which to estimate $\sigma^{(2)}$ reliably. However, the measurement requires a low-light-scattering sample. The Z-scan trace observed from the previous cast film was considerably distorted due to light-scattering. Therefore, normalization was required to analyze the Z-scan trace. On the other hand the trace obtained for the present film without any normalization had a regular shape (Figure 6), as expected for a low-light-scattering sample. Therefore, a film fabricated by the present technique offers promise as a TPA material. The linear relationship between two-photon absorbance, q_0, and the incident power, I_0, (Figure 7) also proves that the observed nonlinear absorption is due to TPA (Kamada *et al.*, 2003). If higher-order absorption such as simultaneous three-photon absorption or excited-state absorption induced by TPA is involved in the observation, the plot should deviate upward from the linear line at the high incident power. On the other hand, if the plot deviates downward at higher power, the saturable absorption is included in the observation.

The $\sigma^{(2)}$ value was estimated from the slope of the q_0-I_0 plot. The $\sigma^{(2)}$ value of MPPBT in the present film with 20% CEC was estimated to be 1030 GM at 800 nm. The maximum $\sigma^{(2)}$ value of MPPBT in DMSO was 770 GM at 800 nm. Considering the difference of the λ_{max} between a DMSO solution of MPPBT and the present hybrid film, the wavelength where the maximum $\sigma^{(2)}$ value is observed is quite likely to be different between the DMSO solution of MPPBT and the present hybrid film. Therefore, the $\sigma^{(2)}$ at 800 nm observed for MPPBT in the present film should not be the maximum value. Nevertheless, the $\sigma^{(2)}$ value of MPPBT in the present film observed at 800 nm was still 1.3 times greater than the maximum $\sigma^{(2)}$ of MPPBT in DMSO. Therefore, the conclusion is that the low-light-scattering film fabricated in the present study retains the enhanced TPA characteristics as can be observed in the previous cast film. From the viewpoint of practical applications, 800 nm is one of the most attractive wavelengths of TPA excitation because of the availability of a laser light source favorable to TPA excitation. Therefore, the enhanced $\sigma^{(2)}$ value of
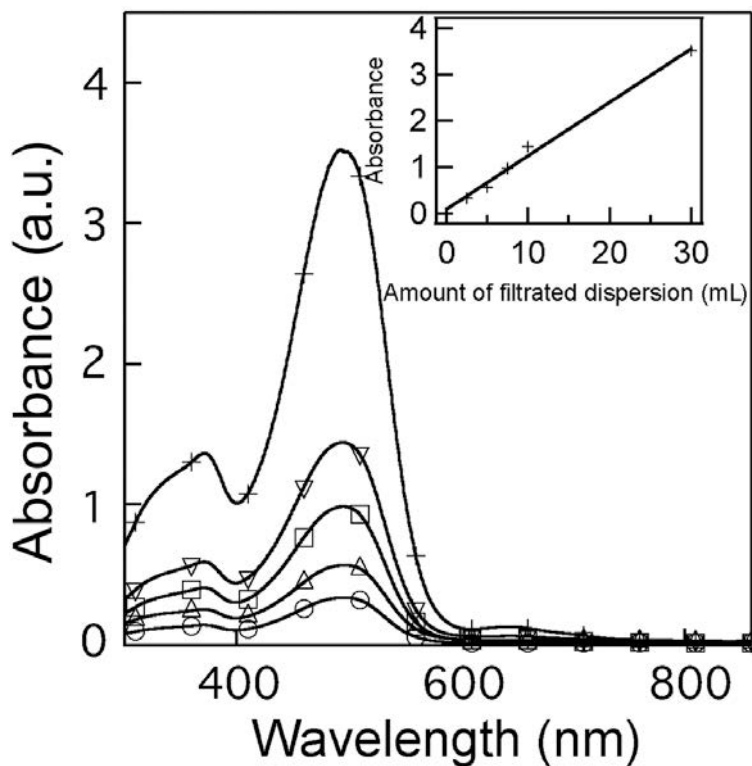
Figure 5. Absorption spectra of MPPBT-SSA hybrid films (20% CEC) fabricated by filtrating different amounts of dispersion (2.5 mL (○), 5 mL (△), 7.5 mL (□), 10 mL (▽), 30 mL (+)). Absorbance at the λ_{max} (498 nm) *vs.* the amount of the filtrated dispersion are plotted in inset.

the present MPPBT-SSA composite excited at 800 nm is valuable. However, in order to obtain a much more attractive TPA material, the reason why the $\sigma^{(2)}$ value of MPPBT was enhanced by the hybridization with SSA needs to be understood more clearly. For this, measure-ments of $\sigma^{(2)}$ over a wide wavelength region is required, though the spectrum measurement of $\sigma^{(2)}$ is not easy, due mainly to the lack of availability of a suitable light source.

The $\sigma^{(2)}$ value of MPPBT in films at greater % CEC values are summarized in Table 1. The $\sigma^{(2)}$ value
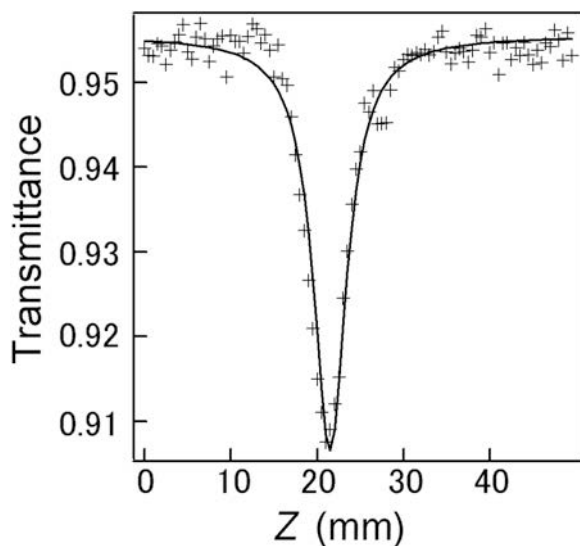

Figure 6. The open-aperture Z-scan trace observed for a film fabricated by filtrating 30 mL of the dispersion of MPPBT-SSA composites (20% CEC).
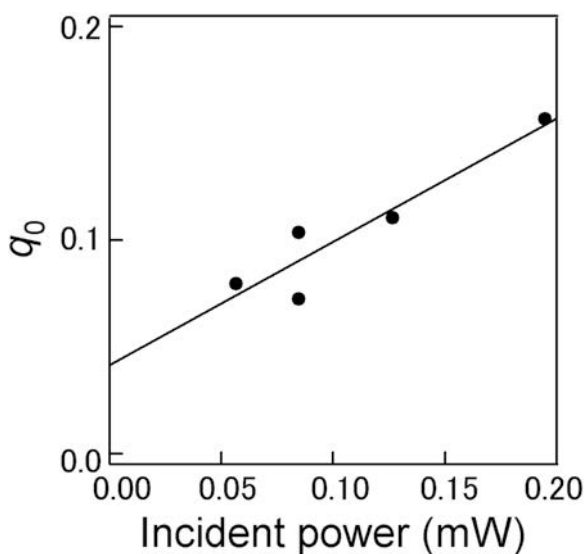

Figure 7. An example of the plot of the parameter q_0 *vs.* the incident power.

decreased as the % CEC value increased. As discussed above, the population of a molecular assembly such as H-aggregate is thought to be increased in films fabricated at higher % CEC values. A nonlinear optical susceptibility of an organic dye which tends to form an aggregate is known to correlate with the residual amount of the non-aggregated dye as a function of a total dye concentration in a hybrid material (Carpenter *et al.*, 1992). Therefore, a decrease in the residual amount of the non-aggregated MPPBT fabricated at greater % CEC values is thought to be the reason why the $\sigma^{(2)}$ value of MPPBT in films fabricated at greater % CEC values was less. Consequently, the formation of a hybrid composite with a non-aggregated MPPBT molecular assembly is thought to be an important factor in obtaining a composite with a large $\sigma^{(2)}$.

CONCLUSIONS

In this study, a low-light-scattering hybrid film consisting of SSA and MPPBT was fabricated, making an efficient TPA dye. Light-scattering by the hybrid film is reduced considerably by optimizing the film-fabrication conditions. Because control of the optical density is now possible while maintaining the low-light-scattering property, the film-fabrication protocol established is now suitable for fabricating optical materials. The $\sigma^{(2)}$ value estimated for MPPBT in the present film fabricated at 20% CEC, 1030 GM (1 GM = 1×10^{50} cm^4 s photon^{-1} molecule^{-1}) at 800 nm, was 1.3 times greater than that of MPPBT estimated in a DMSO solution without clay. The hybrid films fabricated in this study possess both an enhanced $\sigma^{(2)}$ value and a low-light-scattering nature. Hence, the TPA dyes-SSA hybrid films fabricated in the present study show promise as TPA materials.

REFERENCES

Akiba, M., Morinaga, N., Takizawa, H., Ogiyama, M., Ichijima, S., Tani, T., Harada, A., and Inagaki, Y. (2005) A novel chromophore with a large two-photon absorption cross-section: 2,7-bis[3-(4-N,N-dimethylaminophenyl)propenylidene]cyclohepta-3,5-dien-1-one. *Nonlinear Optics, Quantum Optics*, **34**, 179−182.

Bhawalkar, J.D., Kumar, N.D., Zhao, C.-F., and Prasad, P.N. (1997) Two-photon photodynamic therapy. *Journal of Clinical Laser Medicine and Surgery*, **15**, 201−204.

Bujdák, J. and Iyi, N. (2002) Visible spectroscopy of cationic dyes in dispersions with reduced-charge montmorillonites.

Clays and Clay Minerals, **50**, 446−454.

Bujdák, J. and Iyi, N. (2006) Molecular aggregation of rhodamine dyes in dispersions of layered silicates: influence of dye molecular structure and silicate properties. *Journal of Physical Chemistry B*, **110**, 2180−2186.

Bujdák, J., Janek, M., Madejová, J., and Komadel, P. (2001) Methylene blue interactions with reduced-charge smectites. *Clays and Clay Minerals*, **49**, 244−254.

Carpenter, M.A., Willand, C.S., Penner, T.L., Williams, D.J., and Mukamel, S. (1992) Aggregation in hemicyanine dye Langmuir-Blodgett films: ultraviolet-visible absorption and second harmonic generation studies. *Journal of Physical Chemistry*, **96**, 2801−2804.

Caylor, C.L., Dobrianov, I., Kimmer, C., Thorne, R.E., Zipfel, W., and Webb, W.W. (1999) Two-photon fluorescence imaging of impurity distributions in protein crystals. *Physical Review E*, **59**, 3831−3834.

Cumpston, B.H., Ananthavel, S.P., Barlow, S., Dyer, D.L., Ehrlich, J.E., Erskine, L.L., Heikal, A.A., Kuebler, S.M., Lee, I.-Y.S., McCord-Maughon, D., Qin, J., Röckel, H., Rumi, M., Wu, X.-L., Marder, S.R., and Perry, J.W. (1999) Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication. *Nature*, **398**, 51−54.

Kamada, K., Ohta, K., Iwase, Y., and Kondo, K. (2003) Two-photon absorption properties of symmetric substituted diacetylene: drastic enhancement of the cross section near the one-photon absorption peak. *Chemical Physics Letters*, **372**, 386−393.

Kamada, K., Tanamura, Y., Ueno, K., Ohta, K., and Misawa, H. (2007) Enhanced two-photon absorption of chromophores confined in two-dimensional nanospace. *Journal of Physical Chemistry C*, **111**, 11193−11198.

Kawamata, J. and Hasegawa, S. (2006) Clay-assisted disaggregation and stabilization in hemicyanine Langmuir-Blodgett films. *Journal of Nanoscience and Nanotechnology*, **6**, 1620−1624.

Kawamata, J., Seike, R., Higashi, T., Inada, Y., Sasaki, J., Ogata, Y., Tani, S., and Yamagishi, A. (2006) Clay templating Langmuir-Blodgett films of a nonamphiphilic ruthenium(II) complex. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **284−285**, 135−139.

Kawata, S., Sun, H.-B., Tanaka, T., and Takada, K. (2001) Finer features for functional microdevices. *Nature*, **412**, 697−698.

Kuang, W., Facey, G.A., Detellir, C., Casal, B., Serratosa, J.M., and Ruiz-Hitzky, E. (2003) Nanostructured hybrid materials formed by sequestration of pyridine molecules in the tunnels of sepiolite. *Chemistry of Materials*, **15**, 4956−4967.

Lee, K.-S., Yang, H., Lee, J.H., Kim, O., Woo, H.Y., Choi, H., Cha, M., and Blanchard-Desce, M. (2003) Optical power limiting properties of two-photon absorbing fluorene and dithieno-thiophene-based chromophores. *Proceedings of SPIE − The International Society for Optical Engineering*, **4991**, 175−182.

Lei, H., Wang, H.Z., Wei, Z.C., Tang, X.J., Wu, L.Z., Tung, C.H., and Zhou, G.Y. (2001) Photophysical properties and TPA optical limiting of two new organic compounds. *Chemical Physics Letters*, **333**, 387−390.

Ogawa, K., Ohashi, A., Kobuke, Y., Kamada, K., and Ohta, K. (2005) Two-photon absorption properties of self-assemblies of butadiyne-linked bis(imidazolylporphyrin). *Journal of Physical Chemistry B*, **109**, 22003−22012.

Reinhardt, B.A., Brott, L.L., Clarson, S.J., Dillard, A.G., Bhatt, J.C., Kannan, R., Yuan, L., He, G.S., and Prasad, P.N. (1998) Highly active two-photon dyes: design, synthesis, and characterization toward application. *Chemistry of*

Materials, **10**, 1863−1874.

Screen, T.E.O., Thorne, J.R.G., Denning, R.G., Bucknall, D.G., and Anderson, H.L. (2002) Amplified optical non-linearity in a self-assembled double-strand conjugated porphyrin polymer ladder. *Journal of the American Chemical Society*, **124**, 9712−9713.

Sheik-Bahae, M., Said, A.A., Wei, T.-H., Hagan, D.J., and Stryland, E.W.V. (1990) Sensitive measurement of optical nonlinearities using a single beam. *IEEE Journal of Quantum Electronics*, **26**, 760−769.

Spangler, C.W. (1999) Recent development in the design of organic materials for optical power limiting. *Journal of Materials Chemistry*, **9**, 2013−2020.

Sun, H.-B., Matsuo, S., and Misawa, H. (1999) Three-dimensional photonic crystal structures achieved with two-photon-absorption photopolymerization of resin. *Applied Physics Letters*, **74**, 786−788.

Takagi, S., Shimada, T., Eguchi, M., Yui, T., Yoshida, H., Tryk, D.A., and Inoue, H. (2002) High-density adsorption of cationic porphyrins on clay layer surfaces without aggregation: the size-matching effect. *Langmuir*, **18**, 2265−2272.

Takagi, S., Eguchi, M., Tryk, D.A., and Inoue, H. (2006) Porphyrin photochemistry in inorganic/organic hybrid materials: clays, layered semiconductors, nanotubes, and mesoporous materials. *Journal of Photochemistry and Photobiology C*, **7**, 104−126.

Woo, H.Y., Liu, B., Kohler, B., Korystov, D., Mikhailovsky, A., and Bazan, G.C. (2005) Solvent effects on the two-photon absorption of distyrylbenzene chromophores. *Journal of the American Chemical Society*, **127**, 14721−14729.

Zugel, S.A., Burke, B.J., Regnier, F.E., and Lytle, F.E. (2000) Electrophoretically mediated microanalysis of leucine aminopeptidase using two-photon excited fluorescence detection on a microchip. *Analytical Chemistry*, **72**, 5731−5735.