



Research paper

Two-photon absorption properties of an acetylene derivative confined in the interlayer space of a smectite

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ABSTRACT

A composite consisting of synthetic saponite and 4,4'-[4,1-phenylenedi-2,1-ethylenediyl]bis[1-methylpyridinium] diiodide (Ac) was fabricated. The two-photon absorption (TPA) characteristics of Ac confined in the interlayer space of synthetic saponite were compared to those in water. The maximum TPA cross-section ($\sigma^{(2)}_{\text{peak}}$) of Ac in the interlayer space of the synthetic saponite was 2.1 times larger than that in water. This enhancement is explained in terms of the enhanced anisotropy of Ac by confinement within the two-dimensional interlayer space of saponite and by a reduction in the detuning energy.

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1. Introduction

Organic compounds exhibit specific functionalities in clay mineral–organic hybrid materials. Hybrid materials consisting of fluorescent organic dye and layered double hydroxide or hectorite have been proposed as efficient solid-state fluorescent materials (Iyi et al., 2002; Yan et al., 2011). The assembly of sepiolite with biopolymers was reported to act as new carrier for influenza vaccines (Ruiz-Hitzky et al., 2009). The removal of pollutants using an organically modified interlayer space has also been reported (Seki and Ogawa, 2010). In addition, efficient electron and energy transfer was obtained by controlling the molecular alignment of a cationic dye with the anionic surface of a clay (Bujdák et al., 2010).

Organic compounds in hybrids with clay minerals also exhibit salient nonlinear optical (NLO) properties. A clay–chiral ruthenium complex hybrid exhibited optical second-harmonic generation (SHG) ability, which is the most applicable NLO property (Suzuki et al., 2009). Another important NLO property is two-photon absorption (TPA), in which a material absorbs two photons simultaneously. The TPA rate increases quadratically with increasing excitation intensity. Therefore, light absorption can be induced specifically at a focal point using a tightly focused laser beam. This characteristic enables TPA to be utilized for three-dimensional optical data storage (Kawata and Kawata, 2000), two-photon fluorescence microscopy (Kawakami et al., 2013), three-

dimensional microfabrication (Daicho et al., 2013; Juodkazis et al., 2009), two-photon photodynamic therapy (Batat et al., 2011), and optical limiting (Zhao et al., 2013). However, the TPA cross-section (denoted by $\sigma^{(2)}$, i.e., the TPA efficiency per molecule) of most materials is too small for practical applications. Therefore, materials that exhibit a large $\sigma^{(2)}$ are strongly desired.

$\sigma^{(2)}$ of organic molecules are increased by the confinement of organic molecules into the interlayer spaces of a clay mineral (Kamada et al., 2007; Suzuki et al., 2011). In particular, $\sigma^{(2)}$ of a porphyrin derivative, tetrakis(1-methylpyridinium-4-yl)porphyrin *p*-toluene sulfonate (TMPyP), and a diacetylene derivative, 1,4-bis(2,5-dimethoxy-4-{2-[4-(*N*-methyl)pyridinium] ethenyl}phenyl)butadiyne triflate (MPPBT) were found to increase significantly. The π -electron system of TMPyP is considerably distorted in the solution state; however, confinement of TMPyP in the interlayer space of a clay mineral imposed planarity to the π -electron system (Suzuki et al., 2011). The rotational barrier of the diacetylene moiety in MPPBT was reported to be 0.67 kJ/mol (Kamada et al., 2007), which is considerably smaller than the thermal activation energy at room temperature ($T = 297$ K); $N_A kT = 2.5$ kJ/mol. Therefore, the rotational motion of MPPBT should be considerably active in the solution state. In contrast, such molecular motion of MPPBT was found to be considerably suppressed by confinement. In addition, the planarity of the MPPBT π -electron system was improved within the interlayer space of a clay mineral. These factors that enhance extension of the π -electron system, i.e., delocalization of the π -electrons, result in significant enhancement of $\sigma^{(2)}$ for TMPyP and MPPBT in a clay mineral. Therefore, the confinement of such compounds in the

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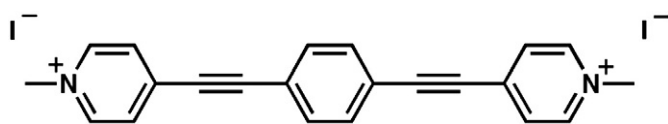


Fig. 1. Chemical structure of 4,4'-[4,1-phenylenedi-2,1-ethynediyl]bis[1-methylpyridinium] diiodide (Ac).

interlayer space of clay minerals is an effective strategy to extend their π -electron systems and thus enhances $\sigma^{(2)}$.

The rotational barriers of mono-acetylene compounds are larger than those of diacetylene compounds. For example, that of diphenylacetylene was reported to be 2.4 kJ/mol (Kamada et al., 2007). This value is comparable to the thermal activation energy at room temperature; therefore, the rotational motion of diphenylacetylene is expected to be suppressed, even in the solution state at room temperature. However, the rotational motion of diphenylacetylene in the solution state has yet to be fully understood.

Here, we propose a novel method to monitor the rotational motion of an acetylene bond in a diphenylacetylene derivative. The motion should be impossible when the molecule is confined in the interlayer space of a clay mineral. Therefore, if the motion is active in the solution state, $\sigma^{(2)}$ of the molecule in the solution state should be considerably smaller than that in the interlayer space of the clay mineral. Thus, a cationic diphenylacetylene analogue was synthesized, 4,4'-[4,1-phenylenedi-2,1-ethynediyl]bis[1-methylpyridinium] diiodide (Ac; Fig. 1), which is thought to efficiently interact with a clay mineral surface bearing a negative charge when oriented parallel to the surface. The $\sigma^{(2)}$ of Ac in the interlayer space of synthetic saponite was compared with that in water. As a result, the enhancement of $\sigma^{(2)}$ by confinement can be explained in terms of the enhanced anisotropy of Ac in the two-dimensional interlayer space of saponite and by a reduction of the detuning energy, which indicates that the rotational motion of Ac is negligible, even in water.

2. Experiments

2.1. Materials

2.1.1. Clay mineral

The synthetic saponite used in this study was purchased from the Clay Science Society of Japan (Smecton SA (SSA); synthesized by Kunimine Industries Co. Ltd., Japan). The stoichiometric formula of SSA and its cation exchange capacity (CEC) are reported to be $[(\text{Si}_{7.20}\text{Al}_{0.80}) (\text{Mg}_{5.97}\text{Al}_{0.03})\text{O}_{20}(\text{OH})_4]^{0.77-} (\text{Na}_{0.49}\text{Mg}_{0.14})^{0.77+}$ and 0.997 mEq/g, respectively (Takagi et al., 2002). The average SSA particle diameter in the in-plane direction was estimated to be ca. 30 nm from previous atomic force microscopy (AFM) measurements (Kawamata et al., 2010).

2.1.2. Syntheses of organic molecules

2.1.2.1. 1,4-Bis(4-pyridinylethynyl)benzene. 4-Bromopyridine (HCl salt) (339 mg, 1.74 mmol, 2.2 eq), diethynylbenzene (100 mg, 0.793 mmol, 1.0 eq), $\text{PdCl}_2(\text{PPh}_3)_2$ (60 mg, 0.08 mmol, 10 mol.%) and CuI (15 mg, 0.08 mmol, 10 mol.%) were suspended in a mixture of 10 mL of dry

acetonitrile and 1.5 mL of triethylamine under an argon atmosphere. The reaction mixture was stirred for 3 days at room temperature and the obtained compound was then extracted to an organic phase using a mixture of 10% aq. NaHCO_3 and toluene. The organic phase was washed with water, dried over MgSO_4 , evaporated and chromatographed (silica gel, hexane:ethyl acetate = 1:1 with 5% NEt_3) to obtain 1,4-bis(4-pyridinylethynyl)benzene as a pale yellow solid (67% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3 ppm): 8.63 (d, 4H, pyridyl), 7.56 (s, 4H, phenyl), and 7.39 (d, 4H, pyridyl). The NMR spectrum is shown in Fig. S1.

2.1.2.2. 4,4'-[4,1-Phenylenedi-2,1-ethynediyl]bis[1-methylpyridinium] diiodide. Methyl iodide (0.156 mL, 2.5 mmol) was added to 1,4-bis(4-pyridinylethynyl)benzene (280 mg, 1 mmol) in dichloromethane (5 mL) at room temperature and the solution was stirred for 3 h. The residue was filtered off to obtain 4,4'-[4,1-phenylenedi-2,1-ethynediyl]bis[1-methylpyridinium] diiodide (Ac) as a yellow solid (60% yield). $^1\text{H NMR}$ (400 MHz, DMSO- d_6 , ppm): 8.98 (d, 4H, pyridyl), 8.26 (d, 4H, pyridyl), 7.71 (d, 4H, phenyl), and 4.32 (s, 6H, $-\text{CH}_3$). The NMR spectrum is shown in Fig. S2. The obtained crystal was water soluble and thus suitable for the fabrication of a hybrid with clay by ion-exchange reaction in an aqueous dispersion of clay.

2.1.3. Fabrication of hybrid films

Low-light-scattering hybrid films were fabricated according to the method reported in our previous paper (Kawamata et al., 2010). A schematic representation of the film fabrication procedure is shown in Fig. 2. Ac-SSA hybrid dispersions were prepared by ion-exchange reaction. The hybrid dispersion was prepared with an Ac loading level versus CEC of 1% (1% CEC); 100 mL of an aqueous dispersion of SSA (0.1 g/dm³) was mixed with 0.5 mL solution of Ac (10^{-4} mol/dm³) in dimethyl sulfoxide (DMSO). For hybrid dispersions with Ac loading level versus CEC of 10% (10% CEC), 100 mL of the aqueous SSA dispersion (0.01 g/dm³) was mixed with 0.5 mL of Ac (10^{-4} mol/dm³) in DMSO.

Hybrid films were prepared by filtering the aqueous dispersions of Ac-SSA under vacuum through a mixed cellulose ester membrane filter (Advantec, A010A025A; 100 nm pore size, 25 mm diameter). The films obtained on the membrane filter were then transferred to a glass substrate.

2.2. Measurements

2.2.1. UV-vis spectra

The absorption spectrum of an aqueous solution of Ac (10^{-5} mol/dm³) in a 10 mm quartz cuvette was measured with a UV-vis spectrometer (Jasco, U-670). The same spectrometer equipped with an attachment for films (Jasco, VTA-752) was used to obtain absorption spectra of the hybrid films.

2.2.2. Photoluminescence spectra and quantum efficiencies

Photoluminescence spectra and quantum efficiencies of Ac in water and in the hybrid films were measured with an absolute photoluminescence quantum yield measurement system (Hamamatsu Photonics, C9920-02G). The spectrum of the aqueous Ac solution was measured with an Ac concentration of 10^{-6} mol/dm³.

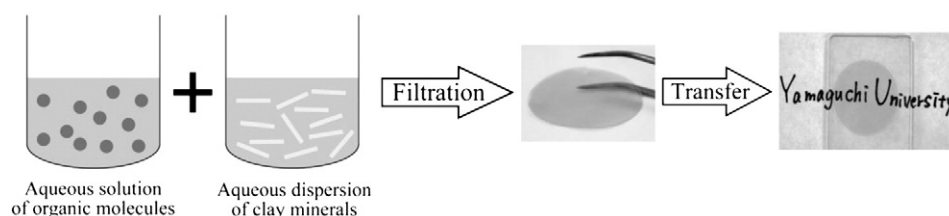


Fig. 2. Schematic representation of the fabrication procedure for a low light-scattering clay-organic compound hybrid film.

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