

ENHANCED SECOND-ORDER OPTICAL NONLINEARITY OF DYE MOLECULES ADSORBED ONTO LAPONITE PARTICLES

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INTRODUCTION

Nonlinear-optical investigations of new materials are important for 2 complementary reasons. First, the requirements for materials to be used in device applications that utilize nonlinear interactions are very demanding. New approaches to materials research can yield materials with favorable properties compared to traditional nonlinear materials, as shown recently in several supramolecular systems (Cox et al. 1990; Stucky and MacDougall 1990; Clays et al. 1993; Kelderman et al. 1993; Kauranen et al. 1995; Lehn 1995). This is particularly true for 2nd-order nonlinear optics that require noncentrosymmetric materials (Prasad and Williams 1991). On the other hand, nonlinear-optical processes can provide new techniques to study the properties of new materials. The nonlinear techniques have the potential of being more sensitive than the existing techniques or providing information that is not accessible at all using the existing techniques (Shen 1984). Here again, 2nd-order processes are particularly important because they provide an extremely sensitive tool to study symmetry properties of materials.

In this Note, we present the 1st results on nonlinear optical properties of clay-dye composites. In particular, we investigate 2nd-order nonlinear properties of methylene blue (MB) adsorbed onto laponite. We show that the efficiency of 2nd-harmonic generation from adsorbed molecules, as measured by hyper-Rayleigh scattering (HRS), can be enhanced by a factor exceeding 100 compared to free molecules. The enhancement is associated with the surface interaction between the dye molecules and the clay particles, which effectively increases the noncentrosymmetry of the molecules. Our results suggest that laponite-MB composites have favorable nonlinear optical properties compared to free MB molecules and that nonlinear techniques provide a new ultrasensitive tool to study clay-dye interactions.

EXPERIMENTAL

We studied MB adsorbed onto laponite particles. Laponite is the synthetic analog of hectorite. It has a small particle size (20–30 nm) and does not require fractionation before use. Another advantage is that laponite forms stable aqueous suspensions that are non-absorbing and nonscattering in the visible spectral region. This was verified by linear-light-scattering measurements, where no difference between the laponite suspensions and neat water was observed.

MB-exchanged samples were prepared by dialysis of 0.5% laponite suspensions against MB solutions of different concentration. After end-over-end rotation for 24 h, adsorption was complete. The suspensions were collected and used as such. The MB loading was varied between 0.09% and 10% of the cation exchange capacity (CEC), the latter being 500 mmol kg⁻¹. MB is a cationic dye and its structure is shown in Figure 1. At the low loadings of the present investigation, MB is ion-exchanged on the clay (Cenens and Schoonheydt 1988) and does not influence the stability of the dispersions. The linear absorption spectra of the laponite-MB suspensions are compared with the spectrum of a 10⁻⁶ M aqueous solution of MB in Figure 2. For the solution, the absorption maximum is at 664 nm with a shoulder around 610 nm. This is typical for monomeric MB. On the laponite surface, 3 bands are observed with maxima at 672, 654 and 615 nm. The relative intensity of the 2 first bands changes with loading: the 672-nm band is the most intense one at the lowest loading of 0.36% of the CEC (1.8 mmol kg⁻¹), whereas at higher loadings the 654-nm band is dominant. This indicates that, in agreement with earlier observations (Cenens and Schoonheydt 1988), there are 2 types of monomers on the surface or 2 types of adsorption sites.

We measured the 1st hyperpolarizability of individual MB molecules and that of molecules adsorbed onto laponite by HRS (Terhune et al. 1965; Clays and Per-

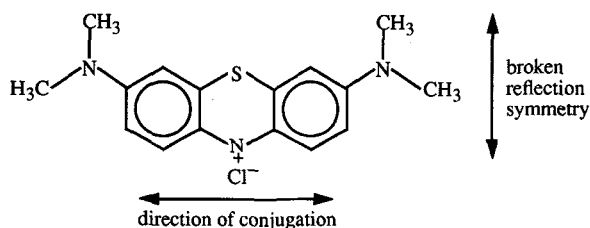


Figure 1. Chemical structure of methylene blue. The centrosymmetry is broken in the direction orthogonal to the direction of conjugation.

soons 1991) in aqueous solutions and suspensions, respectively. For each loading of MB on laponite, a series of 5 concentrations was prepared to verify the linear dependence of the HRS signal on concentration. In filling the measurement cells, the samples were filtered by a 0.45- μm Millipore filter to avoid laser-induced breakdown due to impurities. The beam of an Nd:YAG laser (1064 nm, ~ 10 ns, 10 Hz) was applied to give rise to incoherent 2nd-harmonic scattering at 532 nm. The standard HRS measurements were complemented by depolarization measurements (Terhune et al. 1965; Heesink et al. 1993), which are sensitive to molecular structure. The HRS signal from unloaded laponite was negligible compared to samples containing MB.

RESULTS AND DISCUSSION

The measured hyperpolarizability of individual MB molecules in aqueous solution was 198×10^{-30} esu. Monomeric MB molecules are expected to have high translational and rotational mobility on the clay particles and can therefore be treated as individual scatterers (S'heeren et al. 1993). For low loading (Figure 3), the hyperpolarizability per MB molecule is 2234×10^{-30} esu, representing a factor of ~ 11 increase compared to the value of individual molecules in aqueous solution. This factor corresponds to more than a 100-fold increase in the efficiency of the nonlinear response. However, the hyperpolarizability decreases rapidly for increasing loading, which suggests that the effective scatterers become more centrosymmetric for increasing loading. The measured depolarization ratio of the individual MB molecules was 9.8. The depolarization ratio of the MB/laponite system (Figure 3) is very different and increases monotonously from 1.0 to 4.7 for increasing loading. This difference indicates a significant change in the symmetry of the effective scatterers in the clay environment. The symmetry is also dependent on loading.

At the lowest loading, on the average 1 MB molecule is present per individual clay particle (assuming complete dispersion). The observed 11-fold increase in the hyperpolarizability and the ~ 10 -nm shift in the linear absorption spectrum (664 nm \rightarrow 672 nm) dem-

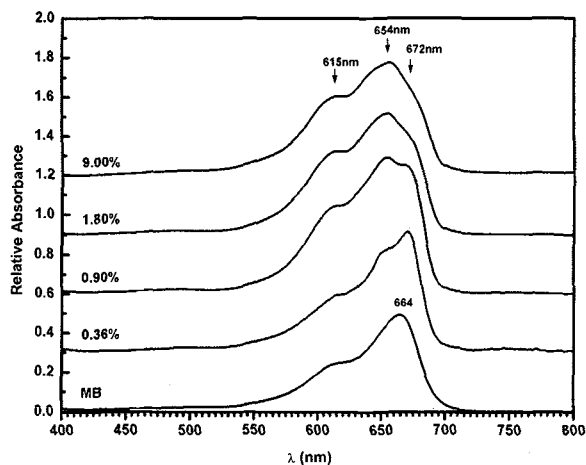


Figure 2. Relative absorption of individual MB molecules and those adsorbed onto laponite as functions of wavelength λ . The measurements were performed in aqueous solutions and suspensions, respectively. The laponite plots are labeled by the degree of loading. All spectra are essentially monomeric. In agreement with earlier results (Cenens and Schoonheydt 1988), 2 types of adsorbed MB molecules occur in the clay environment: one with absorption maximum at 672 nm and the other with maximum at 654 nm. The relative amounts of the 2 types depend on loading.

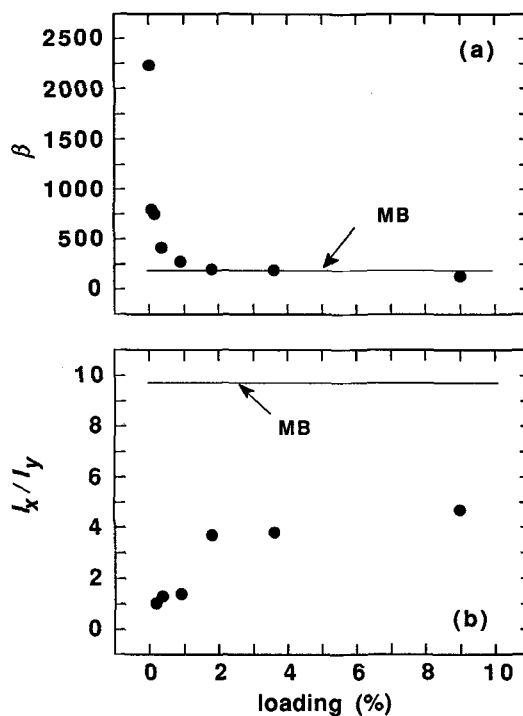


Figure 3. Hyperpolarizability β in 10^{-30} esu (a) and depolarization ratio of HRS (b) as functions of the degree of loading of MB molecules on laponite. The depolarization ratio I_x/I_y is the ratio of the intensities of the 2nd-harmonic field that are polarized parallel and perpendicular with respect to the linear polarization of the fundamental beam. The values for individual MB molecules are shown by horizontal lines.

onstrate that the properties of MB are changed upon adsorption. These changes may be caused by the strong electrostatic field at the surface of the laponite particles (Bleam 1990) or, alternatively, by the asymmetric distortion (Theng 1974) of the MB molecules associated with the surface interaction. Both types of surface effects in nonlinear optics are well known (Heinz et al. 1981; Heinz et al. 1982; Munn 1995). In addition, MB is particularly susceptible to the surface enhancement of the 2nd-order nonlinearity as it is near-centrosymmetric, with centrosymmetry broken in the direction orthogonal to π conjugation.

As the loading increases, the 654-nm band becomes dominant and the hyperpolarizability drops close to its solution value. The 654-nm band therefore represents adsorbed molecules relatively undistorted by the surface. The blue shift with respect to the aqueous solution band maximum (664 nm \rightarrow 654 nm) is analogous to a solvent shift, the clay environment in an aqueous suspension being somewhat less polar than a purely aqueous environment.

CONCLUSIONS

In conclusion, we have presented the 1st results on the nonlinear optical properties of dye (MB) molecules adsorbed onto clay (laponite) particles. Our linear (Figure 2) and nonlinear (Figure 3) results regarding the changes in the properties of the adsorbed MB molecules are mutually compatible; however, the sensitivity of the nonlinear results is much higher. Hence, nonlinear optical techniques could provide a new tool for clay science to probe clay and solvent dependence of molecular organization on the surface. Such studies will address the debate about whether specific clay-dye interactions exist or whether clay is a nonspecific medium (Cenens and Schoonheydt 1988; Garfunkel-Shweky et al. 1995). The present results indicate specific interactions at the lowest loadings only. Work on other types of clays will reveal the generality of the present observations.

To take advantage of the present results in clay-based materials for nonlinear optical applications, future work must develop ways to control the organization of dye molecules on clay surfaces and to organize the clay particles on a macroscopic level. However, the present results are very encouraging and warrant further research on clay-based nonlinear optical materials.

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