



Research paper

Large refractive index variations induced by accumulating triplet excitons under photoexcitation at low power

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ABSTRACT

Herein, we present a method for the modification of the refractive index (n), based on employing an organic molecule with a long triplet excited-state lifetime. A host-guest material composed of a cyclic aromatic as the guest and an amorphous steroidal compound as the host was used to modulate n . The guest material exhibited a triplet lifetime longer than 1 s, and a high-density triplet excited-state population was obtained upon excitation with blue-violet light. The refractive index could be changed by 0.002, even when using a relatively low excitation power level of 100 mW cm^{-2} .

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1. Introduction

The ability to tune the refractive index (n) of a material is useful in various fields, such as digital data and 3-D image recording [1–3]. This tuning is also especially important in the development of information technology systems, and refractive index control as a means of optical switching has been intensively investigated [4–11]. Several methods have been reported for modulating n based on the Kerr effect [12–14], the expansion of materials upon heating [15–20], and the photoisomerization of photochromic molecules [21–31]. Organic molecules having different orbital energy levels will also exhibit very different optical properties, including n . Utilizing these molecules in different states, such as the ground and excited states, is therefore a potential means of refractive index switching. However, the lifetime of the excited state (τ) in such compounds is typically small (on the order of 10^{-9} s) and high-intensity irradiation is required to maintain this state. In organic molecules, the two lowest excited states are the singlet excited state (S_1) and triplet excited state (T_1), and the relaxation rates from S_1 and T_1 to the ground state (S_0) are generally very fast. Despite this, because the relaxation pathway from T_1 to S_0 involves a spin-forbidden transition, there is the possibility of reducing the relaxation rate for this path. Normally, the T_1 state is readily deactivated by oxygen under ambient conditions in which thermal diffusion occurs. However, it has been reported that the dispersion of

cyclic aromatic molecules in rigid materials such as steroidal compounds can prevent the deactivation of the T_1 state of the guest molecule because both oxygen transport and thermal diffusion are drastically restricted. As a result, the T_1 lifetime becomes approximately equal to that at low temperatures in the absence of air [32]. Under these conditions, the T_1 population can be increased by more than three orders of magnitude compared to the population obtained by dispersing the guest compound in a standard polymer matrix such as polymethyl methacrylate (PMMA). Therefore, a host-guest system composed of a steroidal compound and a cyclic aromatic could potentially be used to generate a significant T_1 population, thus reducing the degree of irradiation required to induce refractive index changes.

Herein, we report a method of controlling the refractive index under relatively low light excitation, employing materials with long T_1 lifetimes under ambient conditions. Specifically, a host-guest system comprising a cyclic aromatic as the guest and an amorphous steroidal compound as the host was used to modulate the refractive index of the guest. The guest in this composite material exhibited a T_1 lifetime of longer than 1 s at room temperature in air. As a result, T_1 excitons were accumulated in the composite material upon photoexcitation at a wavelength corresponding to visible blue-violet light. This effect decreased n of the composite in the 10^{-3} order when the material was irradiated at 100 mW cm^{-2} . Theoretical calculations suggest that the reduced polarizability of the guest molecule in the T_1 compared with that in the S_0 produces the decrease in the refractive index with increasing excitation power.

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2. Materials and methods

2.1. Materials and sample preparation

The host material β -estradiol, having a rigid molecular frame, and the guest material 3-(diphenylamino) dibenzo[g,p]chrysenes (3-DPADBC) (both purchased from Tokyo Chemical Industry) were used as the amorphous low molecular weight matrix and refractive index tuning compound, respectively. The molecular structures of these chemicals are shown in Fig. 1(a). A mixture consisting of 97 wt% β -estradiol and 3 wt% 3-DPADBC was melted at 200 °C and then cooled, to obtain a glass-like product. This material was ground, remelted at 200 °C, then sandwiched between two cover glasses, applying sufficient pressure to obtain a film thickness of several μm . Finally, the film was rapidly cooled to obtain a transparent composite sample consisting of two layers of glass and a β -estradiol/3-DPADBC layer.

2.2. Measurement of refractive index changes

Fig. 2(a) shows the experimental setup used to assess variations in the refractive index of specimens under excitation. A semiconductor laser emitting at 405.5 nm (B&WTEKT, Inc., BWB-405-40E) was employed for pumping (excitation of the samples), and a He-Ne laser emitting at 632.8 nm (MELLES GRIOT, 05-LHP-121) was used for probing (measurement of the refractive index changes). The pump laser was directed straight at the front of the sample (meaning at an angle of 0°), while the probe laser was incident at an angle of

16.1°. The probe laser beam was enlarged by a beam expander. The intensity of the pump laser was adjusted using a rotatory ND filter, and the irradiation power level was determined with a power meter (Coherent, OP-2VIS). The reflection of the probe laser from the sample was projected onto a screen, such that interference patterns could be readily observed and recorded by a digital video camera at 60 Hz. The shift of the interference stripes induced by turning the pump laser on and off was measured from still images, and associated refractive index variations (Δn) were calculated from this shift. The time-dependent nature of the shift following cessation of irradiation was also analyzed, allowing the relaxation rate constant for Δn (k_n) to be calculated. Changes in the absorbance (Δabs) of the probe laser beam by the excited sample were ascertained by placing an integrating sphere into the beam path and measuring the beam intensity with the CCD at ms intervals (Otsuka Electronics MCPD-7000) (Fig. S1). The intensity of the transmitted probe laser during excitation of the sample was normalized by the intensity of the transmitted probe laser without excitation, giving a value corresponding to the change in transmittance, and Δabs was obtained from the associated transmittance change. The variation in Δabs upon the cessation of excitation was also determined by tracking the time-dependent intensity of the probe laser, and the rate constant for the relaxation of Δabs (k_a) was calculated.

2.3. Measurement of the absolute value of n

The absolute value of n at 632.8 nm was determined by the m-line method. The sample used for the m-line method trial was pre-

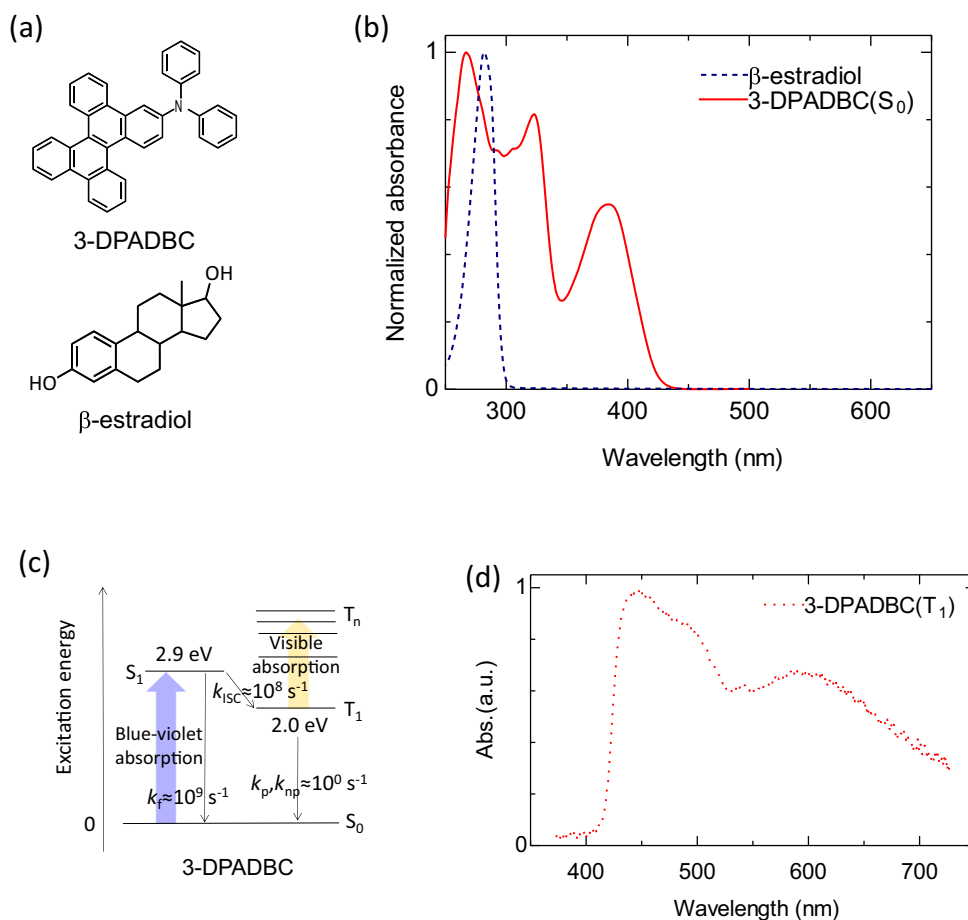


Fig. 1. Absorbance spectra and energy states. (a) The molecular structures of β -estradiol and 3-DPADBC. (b) The absorbance spectra of 3-DPADBC and β -estradiol. (c) The energy states and relaxation rate constants of 3-DPADBC. Here k_f , k_p and k_{np} are the rate constants for radiative relaxation from S₁, radiative relaxation from T₁, and non-radiative relaxation from T₁, respectively. (d) The absorbance spectrum of excited 3-DPADBC in the T₁.

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