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Full Length Article

Fluorescence sensing based on phenylenediacetonitrile doped into polymer host

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ABSTRACT

Solution-processible phenylenediacetonitrile compounds featuring reduced and extended conjugation backbone were investigated for application in fluorescence sensing. Utilization of phenylenediacetonitrile-doped polymer films (at the concentration of 5 wt%) prepared by the simple spin-coating method was demonstrated to have a potential in sensing of volatile organic vapor as well as elevated temperatures, i.e., those exceeding glass transition temperature of the polymer. The sensing by the solution-processed films was accomplished via the distinct change in emission color (from blue to green) followed by emission intensity enhancement. The sensing mechanism was found to rely on diffusion-induced crystalline aggregate formation as proved by optical and atomic force microscopies as well as optical spectroscopy. The compound with the reduced conjugation demonstrated the superiority over the extended-backbone compound imposing greater twisted geometry, which along with dihexyl-type of side-groups facilitated the assembly of the molecules into ordered (crystalline) nanoaggregates as confirmed by polarized optical microscopy. A minute-time response to THF vapor or thermal stimulus implied potential for phenylenediacetonitrile doped into polymer host in fluorescence sensing application.

1. Introduction

Over the last years highly fluorescent molecules have received considerable attention not only in optoelectronic applications such as organic light emitting diodes (OLEDs) or organic lasers, but also in biological imaging and sensing [1–7]. In the case of fluorescence sensing, particularly based on the naked eye detection, it is important to have strong reaction signal (intense fluorescence) in response to the applied stimulus. To this end, compounds expressing high emission efficiency in the solid state (usually in the solid films), which is considered as the best suited for practical sensing applications, are highly desirable. Unfortunately, in the condensed (or aggregated) state most of the emissive fluorophores are quenched due to the concentration quenching effect, or the so-called aggregation-caused quenching [8], thereby severely limiting utilization of the majority of fluorophores for sensing application. Therefore, utilization of compounds capable of delivering high emission efficiency in the aggregated form may actually benefit with enhanced detection sensitivity, and thus, capability for the sensing applications [9]. Unveiling of aggregation-induced emission enhancement (AIEE) phenomenon showed that it is indeed possible to have high fluorescence quantum yield (Φ_F) in organic crystals or nanoparticles [10,11]. Formation of molecular aggregates can result in a change of Φ_F and fluorescence spectra as compared to those of isolated molecules [10,12]. The induced contrast of fluorescence properties between the two molecular phases enables various applications in sensing, where external stimuli (such as mechanic, thermal or important target molecules/ions, metal ions, proteins, DNA or sugar) provoke an occurrence of one phase or another [13–17]. Fluorescence sensors based on this phenomena were also employed in detection of volatile and toxic organic solvent vapor [18], and explosives like picric acid or trinitrotoluene [19,20].

Change of the phase (from molecular to aggregated) can be promoted, e.g., by diffusion of molecularly dispersed dye in the dye/polymer blend induced by the thermal annealing of blend (above the glass transition temperature (T_g) of the polymer) [21]. Such mechanism allowed demonstration of fluorescent threshold temperature and deformation sensors based on bis(benzoxazolyl)stilbene/ and bis(cyano-styryl)benzene/polymer blends obtained by a melt-processing technique [22,23]. Formation of aggregates triggers the redshift of fluorescence spectra, which is easily visible by a naked eye. A similar diffusion-induced aggregation of molecules was also

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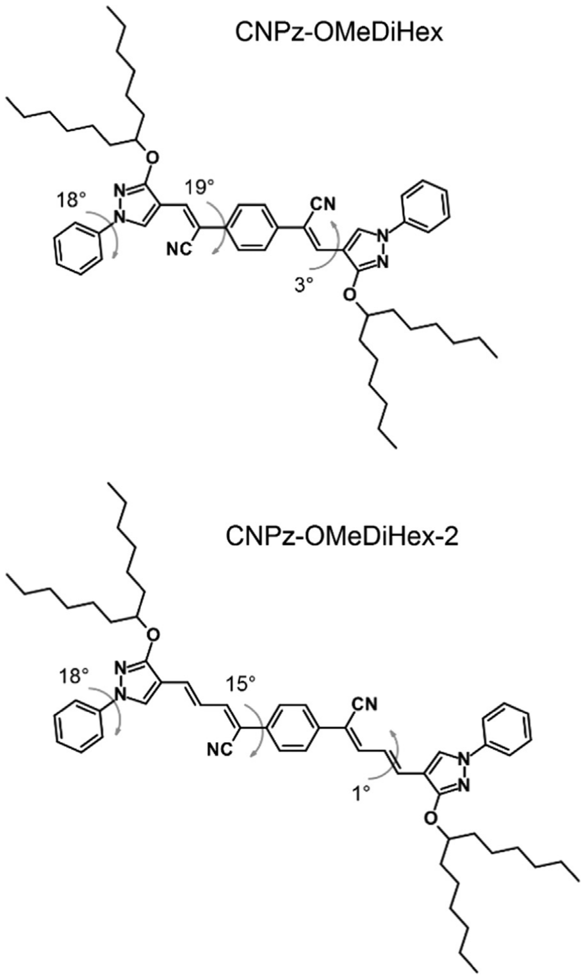

Fig. 1. Chemical structures of the phenylenediacetonitrile compounds CNPz-OMeDiHex and CNPz-OMeDiHex-2. Dihedral angles of the backbone are indicated.

observed via exposure of dye-doped polymer matrices to organic solvent vapor [24–26].

In our previous work we revealed the possibility to tune the emissive and morphological properties of phenylenediacetonitrile-based nanoaggregates formed by a precipitation method [27]. One of the derivatives bearing dihexyl-type of side-groups (CNPz-OMeDiHex, shown in Fig. 1) showed a particularly strong optical response to the alteration of aggregate morphology. Variation of aggregate morphology (amorphous↔crystalline) resulted not only in the prominent change of fluorescence spectra, but also in a switching of fluorescence quantum yield (low↔high).

Here we demonstrate that CNPz-OMeDiHex-doped polystyrene films, which can be easily prepared by a simple spin-coating technique, can be utilized as fluorescent threshold temperature or organic solvent vapor sensors. Branchy dihexyl side-groups enable homogenous dispersion of compound molecules in the polystyrene film preventing their immediate crystallization during the processing at relatively high loads (upto 5 wt%). Annealing above T_g of host polymer or exposure to organic solvent vapor of such films results in the rapid formation of crystalline CNPz-OMeDiHex aggregates accompanied by the appearance of redshifted fluorescence spectrum and enhanced Φ_F. For comparison, a similar phenylenediacetonitrile derivative featuring extended conjugation backbone was synthesized and studied in regard to its ability to form fluorescent aggregates upon application of the mentioned external stimuli. Extention of the conjugation of the *p*-divinylbenze backbone is expected to affect the molecular geometry thereby influencing intermolecular interaction, packing morphology, and consequently, optical response to the stimuli.

2. Experimental

Synthesis and structure identification of the studied phenylenediacetonitrile compounds CNPz-OMeDiHex and CNPz-OMeDiHex-2 (see Fig. 1) are provided in Supplementary information (SI).

^{1}H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer equipped with a 5 mm double resonance broad band BBO z-gradient room temperature probe, and at 700 MHz on a Bruker Avance III spectrometer equipped with a 5 mm TCI 1H-13C/15N/D z-gradient cryoprobe. ^{13}C NMR spectra were collected using the same instruments at 100, and 176 MHz. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). The IR spectra of the samples in KBr pellets were recorded on a Bruker Tensor 27FT-IR System spectrometer. High-resolution ESI–TOF mass spectra were measured on a Bruker maXis spectrometer. The course of the reactions was monitored by TLC on Merck TLC aluminum Silica gel 60 F_{254} sheets and developed with I_2 or UV light. Silica gel (Merck, grade 9385, 230–400 mesh, pore size 60 Å) was used for column chromatography. Melting points were determined in capillary tubes on capillary melting point apparatus Büchi Melting Point M-565.

The PS films with CNPz-OMeDiHex or CNPz-OMeDiHex-2 dispersed at different concentrations were prepared by dissolving compound and PS at appropriate ratios in tetrahydrofuran (THF) solutions (70 mg/mL) and then spin-coating the solutions on pre-cleaned glass substrates at 2000 rpm for 40 s, which resulted in a film thickness of about 1 μm. Thermal annealing of the spin-coated films was carried out at 110 °C for 1, 2, 60 and 240 min. Exposure to THF vapor for 1, 10 and 120 min was accomplished by placing the films in a downward position on top of the vial filled with THF. Neat films were prepared by drop-casting THF solutions of the compound (10^{-2} mol/L) on pre-cleaned glass substrates. Absorption measurements were performed with UV–vis–NIR spectrophotometer Lambda 950 (Perkin-Elmer). Fluorescence of the investigated films was excited by a 365 nm wavelength light emitting diode (Nichia NSHU590-B) and recorded using a back-thinned CCD spectrometer PMA-11 (Hamamatsu). Fluorescence quantum yields (Φ_F) were determined by using the integrating sphere method [28]. Fluorescence transients were measured at fluorescence band maximum using a time-correlated single photon counting system PicoHarp 300 (PicoQuant), which utilized a semiconductor diode laser (repetition rate 1 MHz, pulse duration 70 ps, emission wavelength 370 nm) as an excitation source. Fluorescence microscopy images of the investigated films were obtained using optical fluorescence microscope Olympus BX51. Topographic images of the doped PS films with nanometer resolution were obtained by employing atomic force microscope MultiMode 8 (Bruker). Spectroscopic grade THF and PS (average molecular weight of 35,000) were purchased from Sigma-Aldrich and used without further purification. Preparation of the samples and all optical measurements were performed in ambient conditions unless stated otherwise.

3. Results and discussion

Ground state geometry optimization of the two phenylenediacetonitrile compounds carried out using density functional theory at the B3LYP/6-31G* level revealed some differences in the dihedral angles of the backbone. Namely, somewhat stronger twisted backbone (the larger angles) was obtained for CNPz-OMeDiHex as compared to that for CNPz-OMeDiHex-2 featuring