



In-situ photoisomerization for aggregation-induced emission of dibiphenyl fumaronitrile



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ARTICLE INFO

Article history:

Received 6 April 2015

Received in revised form 1 June 2015

Accepted 10 June 2015

Available online 16 June 2015

Keywords:

Aggregation
Fumaronitrile
Photoisomerization
Emission
Quenching

ABSTRACT

The synthesis and photochemical characteristics of a fumaronitrile (FN)-based π -conjugated molecule, dibiphenyl fumaronitrile (**BP-FN**), comprising two biphenyl aggregation-induced emission (AIE) activators linked by an FN core were investigated. Upon illumination with a UV light, the emission from the *Z*-isomer, (**Z**)BP-FN, was more intense than that of the *E*-isomer, (**E**)BP-FN, due to conformational restriction of the former. (**E**)BP-FN exhibited *J*-aggregation behavior in mixed THF–H₂O solvents when the H₂O content exceeded 70 vol%, illustrative of typical AIE characteristics. (**Z**)BP-FN presented significant aggregation causing quenching in emission when the H₂O content exceeded 80 vol%. In-situ photoisomerization of (**E**)BP-FN to (**Z**)BP-FN proceeded successfully even in the H₂O-induced aggregated state in THF solution; however, the emission of the in-situ photoisomerized (**Z**)BP-FN aggregates was significantly quenched in solutions with high H₂O contents of above 80 vol%.

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1. Introduction

The fascinating and unprecedented optical phenomena derived from aggregation-induced emission (AIE) of π -conjugated organic molecules have fueled interest in these systems in the field of organic optoelectronics [1,2]. Despite the fact that π - π stacking between π -conjugated molecules generally leads to photoluminescence (PL) quenching, several specific π -conjugated organic molecules such as tetraphenylethylene (TPE) and cyanostilbene have demonstrated anomalous properties in which emission is enhanced in concentrated solution or solid-state but is quenched in solution [1–4]. It has been reported that these AIE features originated from the restricted intramolecular rotation in aggregated state of π -conjugated molecules. Over the past few years, many attempts have been made to develop efficient AIE-active materials having extraordinary properties for various applications geared toward organic semiconducting lasers, photochromic optical memory, fluorescence chemo/biosensors, organic light-emitting diodes, and organic transistors [5–8].

AIE-active π -conjugated organic molecules are often based on the diarylalkene structural motif. These molecules exhibit twisted structures due to internal steric repulsion between larger aryl groups in dilute solution, while present planar structures due to

tight π - π intermolecular packing in concentrated solution or in the solid state [1–4]. Among the various diarylalkene motifs, our interest lies in AIE-active molecules having unsymmetrically aryl-substituted alkene units, such as cyanostilbene [9]. These molecules may undergo typical *E/Z* isomerization under ultraviolet (UV) or visible irradiation. Recently, we also reported π -conjugated organic molecules with the fumaronitrile (FN) skeleton, in which the bis-bithiophenyl fumaronitrile unit exhibited facile photoisomerization upon illumination with visible light [10]. It has also been reported that FN-based π -conjugated molecules exhibit AIE phenomena, similar to cyanostilbene derivatives [5]. Motivated by these precedents, we investigated the effects of photoisomerization of the fumaronitrile (FN) skeleton on the AIE properties. Herein, we report the synthesis and photochemical characteristics of FN-based π -conjugated molecules, i.e., dibiphenyl-fumaronitrile (**BP-FN**) comprising two biphenyl AIE activators linked via the FN core. In addition, we study the effect of in situ photoisomerization between the *E/Z* **BP-FN** isomers on AIE in solution.

2. Results and discussion

2.1. Synthesis and characterization

The **BP-FN** could be effectively synthesized from 4-phenylbenzylcyanide by modification of previously reported procedures [10]. Fig. 1a shows that the synthesized **BP-FN** skeleton presented interesting photochemical properties, especially *E–Z*

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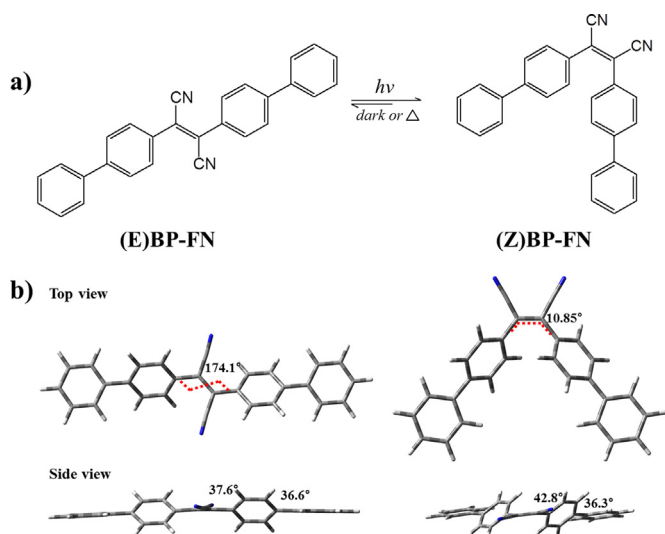


Fig. 1. (a) Schematic depicts of photoisomerization and (b) Optimized molecular structures of (*E/Z*)-BP-FNs using the B3LYP functional/6-31G* basis set.

photoisomerization. Furthermore, molecular calculations using time-dependent density functional theory (TD-DFT) with the B3LYP functional/6-31G* basis set were used to gain further insight into the spatial structures of the (*E/Z*)-BP-FN species. Fig. 1b shows the optimized structures of the (*E/Z*)-BP-FN species in vacuo, calculated with TD-DFT using the B3LYP functional/6-31G* basis set. As shown in Fig. 1b, in (*E*)-BP-FN, the dihedral angle between the phenyl groups bonded in fumaronitrile was 174.1°. This value might permit free intramolecular rotation of the phenyl groups. In comparison, the dihedral angle was 10.9° in the (*Z*)-BP-FN

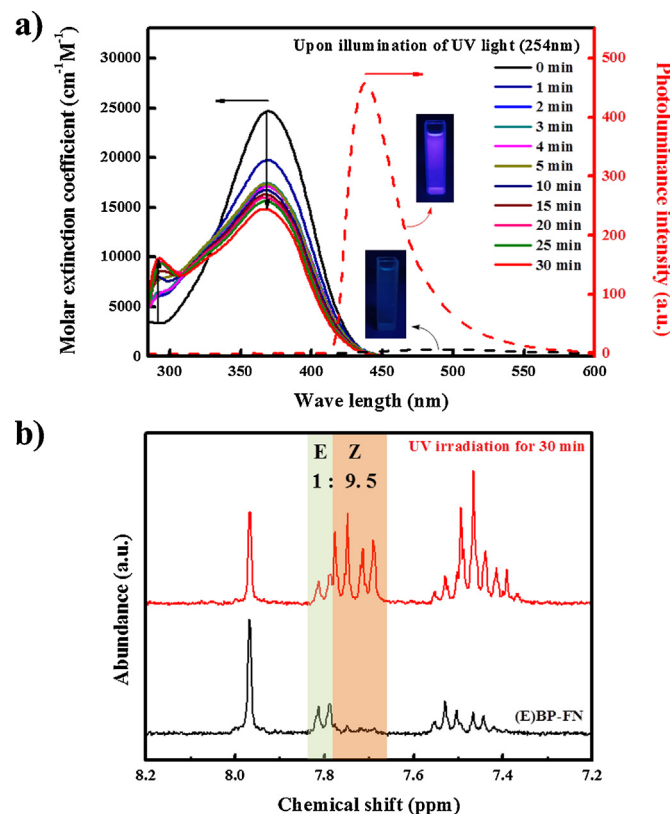


Fig. 2. (a) UV-visible absorption spectra and PL spectra, and (b) ¹H NMR spectra for the E to Z photoisomerization of BP-FN in solution.

congener; thus, rotation of these phenyl groups was conformationally restricted compared to the case of (*E*)-BP-FN [9]. These features could affect the photochemical properties of the (*E/Z*)-BP-FN species in concentrated solution as discussed below.

Fig. 2 shows (a) the UV-visible absorption spectra and photoluminescence (PL) spectra, and (b) the ¹H nuclear magnetic resonance (NMR) spectra acquired during E-Z photoisomerization of BP-FN in solution. The photoisomerizations of molecules containing stilbene or azobenzene motifs have long been the subject of intense research, and have been demonstrated to be affected by their substitution pattern, polarity and viscosity of the solvent, and temperature [11]. In solution, the *E*-isomer of BP-FN showed rapid E-Z photoisomerization under illumination with UV light, as shown in Fig. 2a. The UV-visible absorption spectrum of (*E*)-BP-FN acquired in tetrahydrofuran (THF) solution were characterized by absorption bands at wavelengths in the range of 300–420 nm, with peak maxima at 380 nm. Upon UV irradiation, the intensities of the absorption bands were significantly reduced with a slight blue shift of ~20 nm, and new peaks appeared with maxima at 290 nm. These new absorption bands could be assigned to (*Z*)-BP-FN, indicating facile E-Z photoisomerization of the BP-FN skeleton. The molar extinction coefficient of (*Z*)-BP-FN at 360 nm was nearly half that of (*E*)-BP-FN at 370 nm, probably because (*Z*)-BP-FN is more sterically hindered than (*E*)-BP-FN. This causes the phenyl rings to twist out of coplanarity, resulting in the ~20 nm blue-shifted absorption band of (*Z*)-BP-FN compared to that of (*E*)-BP-FN. Fig. 2a also shows that the intensity of the emission peaks in the PL spectra increased significantly during E-Z photoisomerization upon illumination with a UV light source. (*Z*)-BP-FN exhibited much more intense emission than (*E*)-BP-FN even in solutions of the same concentration, which is similar to phenomena observed with a previously reported cyanostilbene derivative. This difference in the emission intensity of the isomers may be caused by the increase in the conformational restriction of the intramolecular rotation of the phenyl groups during E-Z photoisomerization, as explained in relation to Fig. 1b. Investigation of the changes in the ¹H NMR spectra at different irradiation times indicated that, initially, only signals assigned to (*E*)-BP-FN were present. After irradiation, however, new signals appeared that stemmed from (*Z*)-BP-FN. As shown in Fig. 2b, the photoisomerization of (*E*)-BP-FN to (*Z*)-BP-FN after UV irradiation for 30 min could also be determined to proceed with 90% conversion with an (*E*)/(*Z*) ratio of 1/9.5.

2.2. Aggregation induced photochemical properties

Fig. 3 based on the observed photoisomerization, we investigated the AIE properties of the (*E/Z*)-BP-FN species. Fig. 3 shows (a, b) the UV-visible absorption spectra and the PL spectra, and (c) the AIE characteristics of (*E*)-BP-FN (a) and (*Z*)-BP-FN (b) acquired in THF solution with addition of H₂O (0–90%). As shown in Fig. 3a, addition of H₂O up to 50 vol% decreased the photo-absorption of (*E*)-BP-FN; however, the absorption bands were broadened and red-shifted with H₂O contents higher than 60 vol% compared to that without H₂O addition, indicative of *J*-aggregation behavior in THF-H₂O mixed solvents. Moreover, significantly enhanced emission was also observed in the presence of a high H₂O content, illustrative of typical AIE characteristics. Meanwhile, (*Z*)-BP-FN exhibited a significant increase in the photo-absorption during addition of H₂O up to 50 vol%, but this enhanced absorption subsequently declined without band-shifts in the presence of H₂O contents higher than 60 vol%. The *J*-aggregation of (*Z*)-BP-FN was only observed in the presence of H₂O contents higher than 80 vol% as shown in Fig. 3b. Interestingly, (*Z*)-BP-FN exhibited only slightly enhanced emission during addition of H₂O up to 70 vol%, but presented significantly quenched emission with the addition of

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