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Effect of connecting links on self-assembly and mechanofluorochromism of cyanostyrylanthracene derivatives with aggregation-induced emission

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ABSTRACT

Two cyanostyrylanthracene derivatives linked with *N*-dodecyl-L-phenylalaninamide by succinyl (PC2AN) and glutaryl (PC3AN) groups were successfully synthesized. The self-assembly and mechanofluorochromism (MFC) were investigated. Results showed the presence of cyano groups induced two compounds emitted weak fluorescence in solution and possessed strong fluorescence in the aggregated state, exhibiting typical aggregation-induced emission. The two compounds formed gels in certain solvents and also exhibited gelation-induced emission enhancement. The circular dichroism spectra of the gels suggested that chromophores of two gelators in gel phases were stacked into chiral aggregates. Moreover, PC3AN possessed better gel abilities than PC2AN. The gel-to-sol phase transition temperatures (T_{gel}) of PC2AN are higher than those of PC3AN in *o*-dichlorobenzene under the same concentrations. UV−visible absorption and infrared spectra showed that the hydrogen bonding between aromatic amide groups and the π−π interaction in the PC3AN gel are stronger than those in the PC2AN gel. Solid PC3AN did not change its emission color after applying mechanical force. Interestingly, PC2AN exhibited significant MFC. The PC2AN emitted blue-green fluorescence, which turned into yellow upon grinding. Thus, only one methylene group has significant effects on gelation ability and MFC.

1. Introduction

Molecules with aggregation-induced emission (AIE) properties have been widely developed because of their wide applications in biological probes, chemical sensing, and optoelectronic devices [1–4]. Such molecules have very weak emission in the solution state and emit enhanced fluorescence in their aggregated states. Many AIE molecules exhibit change in their fluorescence color or intensity by applying mechanical force (such as grinding, crushing, and rubbing) owing to the change in molecular stacking and then recovery to the original state upon solvent or thermal annealing. This phenomenon, which involves the restoration of molecular packing modes, is called mechanofluorochromism (MFC) [5–10]. These functional smart molecules have potential applications in sensors, memory chips, and security inks [11–17]. The derivatives of tetraphenylethene [18,19], 9,10-divinylanthracene [20,21], triphenylamine [22,23], phenothiazine [24,25], and β-diketone boron complexes [26–28] exhibit MFC activities. A number of studies have elucidated the MFC behavior in several AIE molecule systems. Slight differences in molecular structures usually induce distinct MFC behavior because of the difference in molecular stacking in the solid state.

Recently, low-molecular-weight gelators (LMWGs), which have an ability to immobilize organic solvents or water at low concentrations, have attracted significant attention [29–31]. In gel phases, LMWGs self-assemble into different one-dimensional nanostructures, such as fibers, rods, tubes, and ribbons, with the help of weak intermolecular interactions, including hydrogen bonding, van der Waals force, π−π stacking, and hydrophobic effect. Gels formed by LMWGs have been used in various sensors [32–34] drug releases systems [35,36], medical treatments [37,38], stimuli-responsive soft materials [39–41], solar cell [42], molecular recognition [43],

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field effect transistors [44], and dyes absorbing [45]. However, developing molecules with AIE, gelation, and MFC properties remains a challenge. Cyano-substituted diphenylethene derivatives usually show weak emission or are non-emissive in solution and emit enhanced fluorescence in the aggregated state because of the large steric hindrance of the cyano group [46,47]. Moreover, some cyano-substituted diphenylethene derivatives exhibit changes in their fluorescence colors upon application of mechanical force [48–50]. In the present study, two cyanostyrylanthracene derivatives linked with *N*-dodecyl-L-phenylalaninamide by succinyl (PC2AN) and glutaryl (PC3AN) groups were designed and synthesized. The self-assemblies and AIE properties in the gel phases, as well as MFC behavior in several solid states, were investigated. Results suggested that their gelation abilities, gel-to-sol phase transition temperature (T_{gel}), and intermolecular interactions were different, although the two compounds could form organogels in certain organic solvents and the two compounds possessed enhanced fluorescence after gelation relative to their solutions. Moreover, the MFC behavior of the two compounds are different. PC2AN exhibited a change in fluorescence color from blue-green to yellow after grinding and could revert to the original state after thermal annealing. By contrast, its analogue, solid PC3AN maintained a yellow fluorescence upon application of mechanical force. Thus, a molecule with AIE, MFC, and gelation properties was successfully obtained.

2. Experimental section

2.1. General information

Infrared spectra of the gel films were measured using a Nicolet-360 FT-IR spectrophotometer. The films were prepared by casting wet gel in KBr single crystal and then drying under vacuum. The UV-vis absorption spectra were determined on a Mapada UV-1800pc spectrophotometer. Different temperature absorption spectra were obtained through heating mixture and then natural cooling. C, H, and N elemental analyses were performed on a PerkineElmer 240C elemental analyzer. Photoluminescence measurements were taken on a Cary Eclipse Luminescence Spectrophotometer. NMR spectra were carried out on a Mercury plus 400 MHz instrument. Mass spectra were obtained with Agilent 1100 MS series and AXIMA CFR MALDI-TOF (Compact) mass spectrometers. TEM images were achieved on a JEM-2100F electron microscope. X-ray diffraction (XRD) patterns were obtained on a PANayltical Empyrean powder X-ray diffractometer, by employing a scanning rate of 0.05°/s in the 2θ from 1.1 to 30°.

2.2. Gelation measurement

The mixture of weighed compound and organic solvent was heated in a sealed bottle with 0.5 cm diameter by a heating panel until the solid was dissolved. After the solution was put at room temperature for 6 h, the state of the mixture was evaluated by the "stable to inversion of a test tube" method.

2.3. T_{gel} measurement

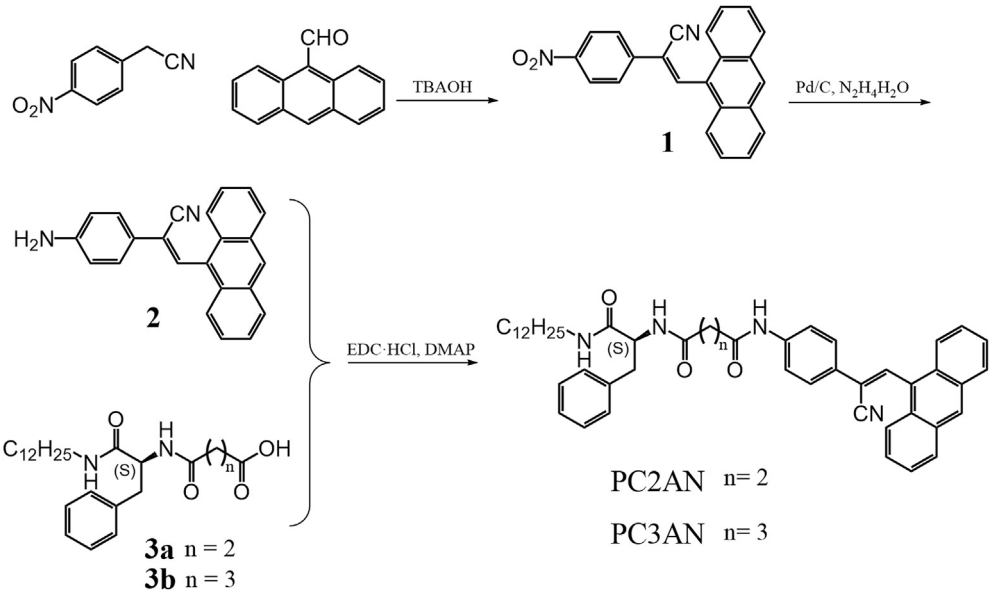
The bottle with a gel was firstly maintained at room temperature for 6 h, and then was inverted and immersed in an oil bath. The oil bath was heated at rate of 0.5 °C/min. Corresponding temperature was set as T_{gel} when the gel started to flow.

2.4. Synthetic procedures and characterizations

The synthesis route of compounds was shown in Scheme 1. Compound **3a** and **3b** were synthesized by the procedures reported previously [50,51].

2.4.1. (Z)-3-(anthracen-9-yl)-2-(4-nitrophenyl)acrylonitrile (**1**)

2-(4-nitrophenyl)acetonitrile (0.78 g, 4.8 mmol) and anthracene-9-carbaldehyde (0.98 g, 4.8 mmol) were dissolved in ethanol (30 mL). The mixture was heated to reflux for 1 h, and then a few drops of tetrabutylammonium hydroxide (TBAOH, 2 M solution in water) were added. After the mixture was further refluxed for 12 h, yellow solid was obtained after filtration and washing by ethanol (3 × 10 mL). After dried under vacuum, yellow solid was obtained in a 77% yield. Melting point (m.p.): 269–271 °C. Elemental analysis (%): calculated for $C_{23}H_{14}N_2O_2$: C 78.84; H 4.03; N 8.00; found: C



Scheme 1. Synthesis route of PC2AN and PC3AN.