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Self-assembling and photophysical properties of the organogelators based on cyanostyryl-substituted carbazoles

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ABSTRACT

Four cyanostyryl-substituted carbazole derivatives (CN-ODEC1, CN-ODEC2, CN-DDEC1, and CN-DDEC) were synthesized and their self-assembly properties have been studied. It was found that they could form organogels especially in aromatic solvents. Scanning electron microscopy and light microscopy images show that the xerogels formed from monosubstituted derivatives (CN-O/DDEC1) gave well-organized tapes, and those from disubstituted derivatives (CN-O/DDEC2) exhibited heavy entangled three-dimensional structures. The UV–vis absorption and fluorescence emission spectra, as well as X-ray diffraction patterns, suggest that carbazole derivatives underwent J-type π -stacking. Meanwhile, we suggested that strong H-bonding and moderate π - π interactions were the key driving force for the gelation of the monosubstituted derivatives, and head-to-tail "ladder-type" J-aggregates were formed in the gel state. On the other hand, strong π - π interaction might be considered as the main driving force for the gelation of disubstituted derivatives, and J-aggregates with no well-organized packing mode of molecules were obtained in the gel phase. It should be noticed that aggregation-induced emission was observed during the gelation processes.

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1. Introduction

Low molecular weight gelators are one of the most interesting and promising examples of self-assembled soft matter [1]. It is believed that secondary forces, such as van der Waals, hydrogen bonding, hydrophobic, electrostatic, dipole–dipole, and π - π interactions, directed the monomers to self-assemble into the noncovalently bonded network that retains an organic solvent, exhibiting gel-like physical properties [1–3]. Although molecular self-assembly is not fully understood so far, researchers have

found that the organogelation processes are affected by the molecular structures, solvents, temperature and the stimulus of ultrasound, and so on [4]. The rapid development on functional gelators with π -conjugated systems has been achieved due to the potential applications in optoelectronic devices, chemical sensors, and so on [5,6]. In particular, fluorescent π -organogels have attracted increasing interest and are extensively studied in the fields of sensors, organic light-emitting diode (OLED) and organic thin-film transistor (OTFT) [7]. It is well known that carbazole is a typical π -conjugated system [8] and a promising candidate for optoelectronic materials because of its intense luminescence and electron donating ability [9]. The first organogelator based on carbazole was synthesized by our group

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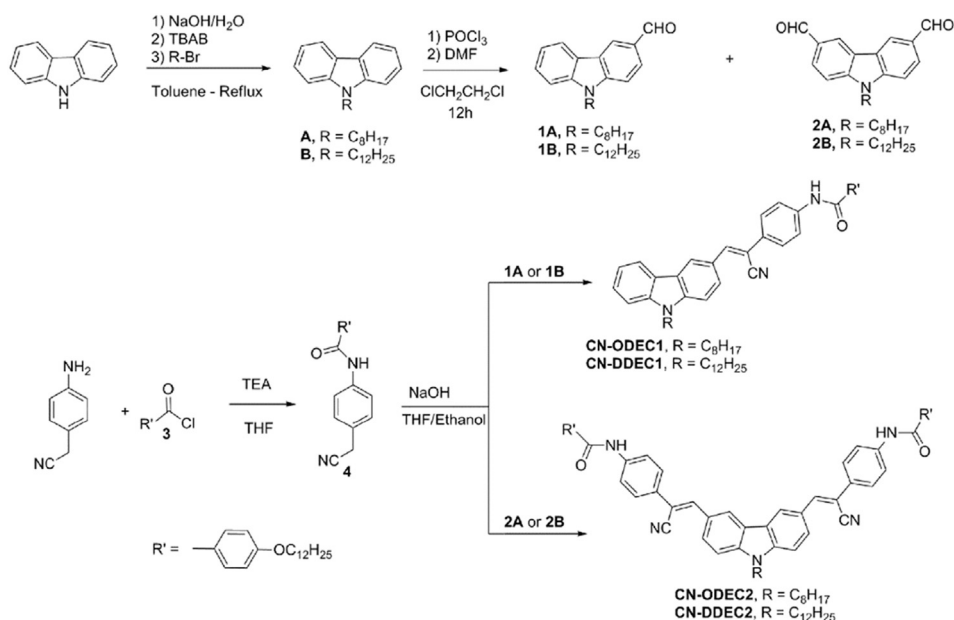
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[8c]. Since then, many organogels based on carbazole derivatives with potential applications in sensors, photonics, switch, and soft optical materials were successively developed [8a,8c,10]. To generate new functional gels, we went on to extend the carbazole-based π -conjugated system and synthesized new fluorescent molecules in which *N*-phenylbenzamide was linked at 3-position or 3,6-position of carbazole via the spacer of cyanovinyl (CN-ODEC1, CN-DDEC1, CN-ODEC2, and CN-DDEC2; Scheme 1). It is interesting that the new synthesized carbazole derivatives can form stable gels in many aromatic solvents and in DMSO, and the molecular structures affected their gelation abilities. For instance, the DMSO gels formed from CN-ODEC1 and CN-DDEC1 could be stable for several months, and their critical gelation concentration values were of 0.8 w/v %. However, the unstable gels were formed from CN-ODEC2 and CN-DDEC2 in DMSO. In most aromatic solvents, the critical gelation concentrations of CN-ODEC1 and CN-DDEC1 were as high as 5.0 w/v %, whereas those for CN-ODEC2 and CN-DDEC2 were only 0.2 w/v %. Besides, it was found that H-bonding in gels of CN-ODEC1 and CN-DDEC1 was stronger than those in gels of CN-ODEC2 and CN-DDEC2. Notably, the photophysical properties of the organogelators depend on the molecular structures, and aggregation-induced emission (AIE) was observed during the self-assembling processes of CN-ODEC1 and CN-DDEC1, whereas this development for CN-ODEC2 and CN-DDEC2 was accompanied with a notable redshift in the emission band.

2. Results and discussion

2.1. Synthesis

Compounds CN-ODEC1 and CN-DDEC1 were synthesized via Knoevenagel reactions of 2-(4-(4-



Scheme 1. Synthetic route for CN-O/DDECn ($n = 1, 2$).

dodecyloxybenzoylamino)phenyl)-1-acetonitrile (4) with formylcarbazoles **1A** and **1B**, respectively. Similarly, CN-ODEC2 and CN-DDEC2 were prepared from diformylcarbazoles **2A** and **2B**, respectively (Scheme 1).

It is worth to note that aldehydes **1A** and **2A** or **1B** and **2B** were synthesized [8c] in a one-step reaction from the 9-octylcarbazole (**A**) or 9-dodecylcarbazole (**B**), respectively, and the purification process via the silica gel column chromatography enabled as well in a one-step to separate the monoformylcarbazole and diformylcarbazole derivatives. The new compounds were characterized by ¹H NMR, MALDI-TOF MS (matrix-assisted laser desorption ionization/time-of-flight mass spectrometry), FT-IR spectrometry, and elemental analysis.

2.2. Gelation abilities of CN-O/DDECn

The gelation abilities of CN-ODEC1, CN-DDEC1, CN-ODEC2, and CN-DDEC2 were evaluated in selected organic solvents (Table 1). It was found that they showed good gelation abilities in aromatic solvents (benzene, toluene, *p*-xylene, 1,2-dichlorobenzene, and bromobenzene) and DMSO. So, the carbazole derivatives were insoluble in the gelling solvents at room temperature, and clear yellow solutions appeared when heating to ca. 100 °C. Upon cooling to room temperature, immobile light-yellow or deep-yellow rigid gel phases were readily formed (Fig. S4 in the Supplementary Material). Even so, the gelation abilities were found to be different between mono-substituted (CN-ODEC1 and CN-DDEC1) and disubstituted (CN-ODEC2 and CN-DDEC2) carbazole derivatives. First, the onset gelation concentration (OGC) [4b] for mono-substituted derivatives in aromatic solvents was as high as 5.0 w/v % except for 1.0 w/v % in benzene, whereas that for disubstituted carbazole derivatives were as low as 0.2 w/v %. For DMSO gels, OGC for CN-ODEC1 and CN-DDEC1 was

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