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ARTICLE TYPE

Emission Enhancement of Coplanar π -conjugated Gelator without Any Auxiliary Substituents

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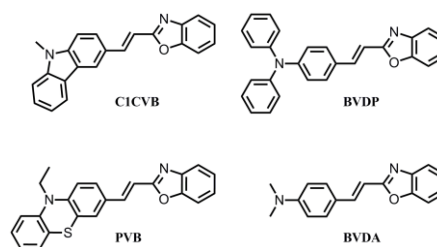
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A linear coplanar carbazole-based benzoxazole derivative without any auxiliary moieties could gelatinize organic solvents, and exhibited emission enhancement owing to the J-aggregate formation.

Organogels formed by a π -conjugated gelator in solvent is attracting increased attention because of their innovative optoelectronic applications.¹ In gel phase, the π -conjugated chromophores of gelators can self-assemble to form ordered 1D aggregates. Accordingly, numerous practical applications of π -organogels such as photovoltaics, field-effect transistors, sensors, and various stimuli-responsive materials have been developed.²

As we know, typical gelators contain amide, amino acid, or urea moieties, long alkyl chain, sugar, and cholesterol units as auxiliary groups.³ However, these auxiliary groups have a negative effect considering atom economy. For π -conjugated organic molecules without the aforementioned auxiliary groups to gelatinize solvents, considerable design strategies have been developed. One design concept is to introduce nonplanar or contortive units into a molecular structure. For example, our group and Han found that nonplanar tert-butyl and triphenylamine groups can replace long alkyl chains to adjust intermolecular interaction and prevent neat crystallization.⁴ Würthner found a contortive perylene bisimide-based gelator lacking flexible alkyl chains.⁵ Sambri and Stulz reported a few nonplanar tetraarylcyclopentadienone and terpyridine derivatives that gelatinize in different solvents.⁶ Park et al. revealed another efficient method involving the incorporation of CN or/and CF₃ into chromophores. This technique helps molecules self-assemble into nanowires through CN \cdots F and π - π interactions.⁷ Langford et al. found that some nonplanar and flexible cyclic compounds can form 1D fibers and prevent solvents from flowing.⁸ Considering the aforementioned molecular structures, we can summarize that the nonplanar molecular conformation of these molecules without typical auxiliary groups plays a key role in solvent gelation.

Moreover, the planarity of π -conjugated organic molecules is very important in electronic devices because the planar structure is favorable to enhancing intermolecular interaction and then increasing device performance. So, coplanar π -conjugated gelator without auxiliary groups should be developed. Miyata et al. found that two small methyl ester groups as auxiliary group could induce coplanar cyclic dehydrobenzoannulene derivatives to have boomerang-shaped structures, which lead to molecules to be gelator because of the existence of the dipole-dipole interaction



Scheme 1 Molecular structures of C1CVB, BVDP, PVB, and BVDA.

boomerang-shaped structures, which lead to molecules to be gelator because of the existence of the dipole-dipole interaction between methyl ester groups and the π - π interaction between aromatic rings.⁹ Whether it is possible for simple linear coplanar molecules without any auxiliary group to self-assemble into 1D aggregates and then form a 3D nanofibrous network to gelate a solvent remains unknown. In this communication, a strategy of introducing asymmetric planar carbazole moiety was considered to find non-traditional π -conjugated gelator. An asymmetric and linear coplanar benzoxazole derivative containing N-methyl carbazole moiety (C1CVB) was designed and synthesized. It was found that it indeed gelled some solvent and possessed enhanced emission property during gelation process. Moreover, to the best of our knowledge, C1CVB is a π -conjugated gelator with smallest molecular weight and no auxiliary groups ever reported.

C1CVB as a colorless needle-like crystal was synthesized through a one-step reaction (Scheme S1) with 85% yield. Three other molecules (BVDP, PVB, and BVDA) were synthesized under similar reaction conditions for comparison.¹⁰ C1CVB was found to easily dissolve in CH₂Cl₂, benzene, toluene, THF, and DMF (Table S1) but exhibited low solubility in cyclohexane, hexane, and polar alcohols at room temperature. Meanwhile, white deposition was observed when the hot solutions of C1CVB in hexane, octane, cyclohexane, ethanol, butanol, acetone, DMSO, and bromocyclohexane were slowly cooled to room temperature. These deposits were composed of straight and wide ribbons (Fig. 1a). Fortunately, transparent isobutanol, CHCl₃, and cyclopentanol hot solutions transformed into a translucent gel after natural cooling to room temperature. Moreover, turbid white gels were formed when the cyclohexane, acetone, DMSO, butanol, and pentanol solutions were rapidly cooled in an ice-water bath (0 °C, Fig. 1d). A large amount of thin and long fibers

were found in the SEM images of cyclohexane gel (Fig. 1b). When temperature of cold bath was above 10 °C, white deposition was observed. This suggests that the rapid cooling may have resulted in a large amount of small seed crystals that can promote the growth of thin fibers. Meanwhile, ultrasound treatment is a common and efficient means of breaking and dispersing particles or cells and preparing an emulsion. Accordingly, we attempted to prepare **C1CVB** gel by treating hot solutions in an ultrasound cleaner.¹¹ Indeed, ultrasound waves can promote the gelation of cyclohexane, acetone, DMSO, butanol, and pentanol solutions. The thin and long fibers in gel phase were confirmed by the microscope image of the ultrasound-formed cyclohexane gel (Fig. 1c). This result indicated that the rapid growth of aggregates benefited gel formation. Notably, **C1CVB** is the smallest π -conjugated gelator without auxiliary groups ever reported because the molecular weight of **C1CVB** is only 324.1 g/mol.

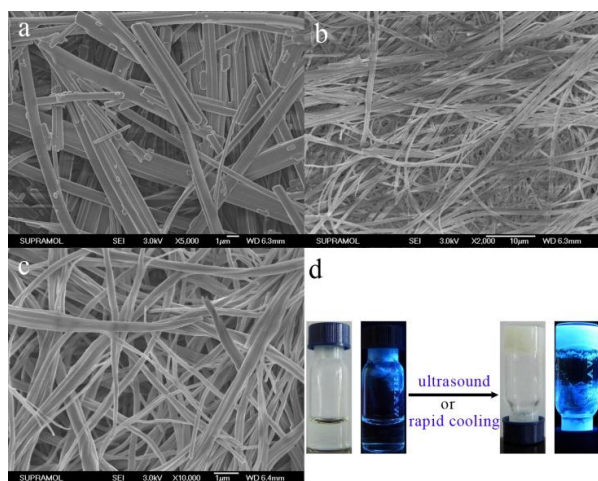


Fig. 1 SEM images of **C1CVB** aggregates from a hot solution of cyclohexane after (a) slowing, (b) rapid cooling, and (c) ultrasound bathing. (d) Photos of **C1CVB** in cyclohexane hot solution (left) and gel (right) under natural light and 365 nm light.

Three analogs of **C1CVB** were synthesized for comparison. **BVDP** and **PVB** have a nonplanar triphenylamine and phenothiazine moieties, and **BVDA** has a coplanar dimethylaniline unit. Their gelation abilities were also studied (Table S1). Results showed that none of the three analogs was a gelator for selected solvents even by ultrasound stimulus or rapid cooling, and nonplanar **BVDP** and **PVB** had larger solubility relative to that of **BVDA**. For example, **BVDP** and **PVB** formed clear solutions in acetone and DOSO, but only deposits of **BVDA** were observed in these two solvents.

To determine why only **C1CVB** could gelate solvents, single crystals of four compounds were grown by slow solvent-diffusion method for X-ray diffraction (XRD) analysis. Crystal structures of all compounds were obtained, although good **C1CVB** crystals were difficultly formed because of their tendency to form into long and thin fibrous crystals. Crystallographic analysis revealed that the dihedral torsional angles between the vinyl unit and phenyl group, the oxazole ring were 3.3° and 5.8°, respectively (Fig. 2a), indicating that **C1CVB** indeed possessed a virtually planar conformation. In the crystal, 1D π - π molecular packing occurred; the distance between two adjacent **C1CVB** molecules

was 3.56 Å, and the sliding angle (the angle between the line of centers of two molecules and the long axes of any one of the parallel molecules) was 34.4°. This result clearly indicated the formation of a J-aggregate in the crystal.¹² The XRD pattern of the xerogel of **C1CVB** from cyclohexane was similar to the stimulated XRD pattern of the **C1CVB** single-crystal structure (Fig. S3), suggesting that **C1CVB** molecules in gel phase also adopted the same packing as that in crystal. Therefore, 1D packing was responsible for the long fibrous aggregate and gel formation.

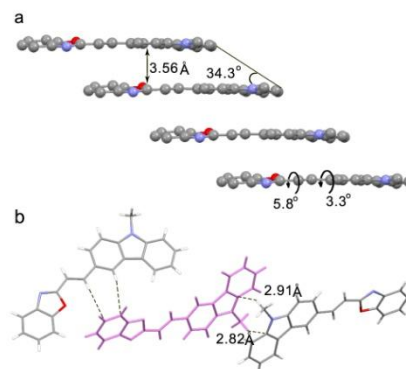


Fig. 2 Crystal structure of **C1CVB**. Molecular packing diagrams for J-aggregate (a) and C-H... π interactions (b). Hydrogen atoms are omitted for clarity in (a).

We subsequently determined why **C1CVB** molecules stack together in J-type model and the driving force behind J-aggregation. Dipole-dipole interactions may play an important role, as suggested by Hisaki and Park.^{9,13} The conformation of **C1CVB** in crystal was used to calculate the molecular dipole moment at ground state. Results showed that **C1CVB** has a dipole moment of 3.78 D, almost parallel to the molecular long axis. The slipped arrangement between two molecules can cancel the repulsive interaction of dipole moments in H-aggregate and enhance dipole-dipole interaction (Fig. S4).¹⁴ Therefore, the driving force for J-aggregate formation was confirmed to be the dipole-dipole interaction.

By solvent-diffusion method, block crystals of **BVDP** and **BVDA** and wide rod-like crystals of **PVB** were obtained. In the crystal structure of **BVDP**, no 1D packing was detected, and only a kind of antiparallel dimer was observed. This finding can be ascribed to the existence of a propeller-like triphenylamine unit (Fig. S5a).^{10a} Although **BVDA** had a coplanar conformation, 1D packing was also not found in crystal (Fig. S5b). However, nonplanar **PVB** molecules formed a unidirectionally slipped-stacked 1D structure in crystal (Figure S5c).^{10b} Moreover, the crystal growth of **PVB** was found to be very slow, which may be due to the presence of the nonplanar phenothiazine moiety. As previously discussed, rapid aggregate growth critically affected the molecule's ability to form 3D networks, so **PVB** was not a gelator. By comprising **C1CVB** and **BVDA**, coplanar conformation was not an exclusive requirement for molecules to self-assemble into 1D aggregate. The fact that **PVB** and **C1CVB** with unsymmetrically substituted phenothiazine and carbazole moieties, respectively, had 1D aggregates in crystal probably indicated that an asymmetric conformation was important for this series of molecules to form 1D packing and then promote solvent

gelation.¹⁵ Further studies are needed to confirm if asymmetric conformation is a common and effective strategy of identifying linear π -conjugated gelators without auxiliary groups.

The solutions were found to have very weak emission, and the gel emitted very strong blue fluorescence (Fig. 1d). The dilute cyclohexane solution emitted weak blue fluorescence with a maximum of 420 nm (Fig. S6). The fluorescence quantum yield (Φ) in cyclohexane solution was as low as 0.027. Such low Φ can be attributed to the intramolecular rotation of single bonds and the cis-trans isomerisation of double bond.¹⁶

In a hot cyclohexane solution, the maximal absorption peak of **C1CVB** was located at 356 nm, which gradually decreased and red shifted to 368 nm (Fig. S7a), indicating a head-to-tail arrangement,¹⁷ in accordance with the crystal structure. Concentration-dependent NMR spectra also confirm π - π interaction between **C1CVB** (Fig. S8). A weak emissive band with a maximum of 420 nm similar to that of dilute solution was observed for the hot cyclohexane solution. During gelation, the intensity of the emissive band was gradually enhanced, accompanied by a red shift of 25 nm (Fig. S7b). The emissive intensity of gel increased 16-fold, indicating that **C1CVB** was an aggregation-induced emission enhancement (AIEE) gelator.¹⁸ Moreover, the absolute fluorescence quantum yield of xerogel was obtained using an integrating sphere and reached as high as 0.71, which was an increase of more than 26 times relative to that in solution. In gel, the molecules stacked together in a J-aggregate model, and multiple C-H $\cdots\pi$ interactions were found between 1D aggregates (Fig. 2b). This molecular packing prevented the single bond from freely rotating and suppressed cis-trans isomerisation. Therefore, the restriction of intramolecular rotation and J-aggregate formation induced AIEE phenomenon.¹⁹ To further understand AIEE mechanism, the time-resolved emission spectra of solution and gel were measured and compared (Fig. S9). In toluene, the average lifetime was 0.95 ns, and the radiative (K_r) and nonradiative (K_{nr}) rates were found to be 0.012 and 1.4 ns⁻¹, respectively. After gelating cyclohexane, **C1CVB** had a longer life time of 2.2 ns, K_r increased to 0.32 ns⁻¹, and K_{nr} decreased by more than 10-fold (ultimately reaching 0.13 ns⁻¹). This result clearly revealed that the J-aggregate formation in gel accelerated the radiative relaxation because such transition from excited state to ground state was allowed, suppressing nonradiative transition.

In summary, a linear coplanar **C1CVB** was a gelator for some solvents. The crystal structures suggested that 1D arrangement was important for molecules to gelate a solvent. Furthermore, asymmetric conformation may play an important role in promoting gelation. π -Conjugated **C1CVB** is also an AIEE gelator with minimal molecular weight. This work tells us a design strategy of introducing asymmetric moiety to obtain simple and functional π -conjugated gelator.

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Notes and references

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