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Organogelators based on iodo 1,2,3-triazole functionalized with coumarin: properties and gelator-solvent interaction

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ABSTRACT

A new family of 1,2,3-triazole derivatives containing coumarin functional group with different alkyl chain lengths was synthesized and their gelation abilities and photochemistry properties were fully characterized. The main force for the self-assembly in gel state are π-π stacking and van der Waals interaction. Solubility parameters and Teas plots of the gelator and several single solvents were calculated to estimate the gelator-solvent interaction. The organogel in a binary solvent system was also characterized using various microscopic techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV−vis. Reversible and stereoselective [2+2] *cyclo*-addition of the gel was confirmed by ^{1}H NMR, UV absorption, fluorescence spectra and SEM. The gels formed were affected and destroyed by the addition of mercury ion.

1. Introduction

Organogels in which solvent molecules are immobilized by a limited amount of low-molecular mass organic gelators have attracted significant attention because of their broad range of applications in areas such as drug delivery,[1] functional nanoarchitectures,[2] stimuli-responsive materials[3] and other industrial applications.[4] Gels are thermally reversible materials that are primarily composed of a liquid, but display solid-like viscoelastic properties due to the presence of a gelator, which spontaneously self-assembles into elongated fibrillar structures in a wide variety of solvents.[5]

Gel properties depend on various factors, such as time, temperature, solvent, composition, structures of gelators.[6] For example, gelation behavior such as the gel transition temperatures or the range of solvents that are gelled can be changed dramatically by small variations in the structure by the different number of carbons in an *n*-alkyl chain or the introduction of branches.[7] Besides, realizing the role of the solvent is quite significant to gain a more detailed insight in developing a simple approach for estimating the gelling ability of a model gelator in a limited set of solvents. In a gel system, solvent-gelator interaction has a negative influence on gelator-gelator interaction. While strong solvent-gelator interaction helps to form thicker fibers, the fibrous structure will disappear if the interaction is too strong.[8] Several discoveries about the effect of solvents on gel morphology and properties have been reported. Wu et al. found the solvent could affect the structure, photoresponse and speed of gelation.[8] Niu et al. reported that the change of gel property can be easily realized by simply changing the properties of solvents.[9] Hansen solubility parameters are widely used to predict compatibility between two materials.[10] Undoubtedly, it also can be used to predict the compatibility between solvent and gelator. The Teas plot derived from Hansen solubility parameters can predict the behaviour of a gelator in untested solvents based on its known ability to gelate a range of more or less similar fluids and so can be used to select solvents for various applications.[11] Teas plot can intuitive indicate the behaviors of a gelator in different solvents through solubility parameters.

Photoresponsive materials, which can be modulated by light play essential roles in many areas such as medical and optoelectronic devices.[12] Coumarin is used as an important component of various functional materials because of the photochemical property. Coumarin derivatives can undergo a [2+2] photodimerization under UV irradiation with wavelengths longer than 300 nm and revert to starting monomeric states upon irradiation with light of shorter wavelengths. An enormous number of applications concerning coumarin derivatives have been developed as photoresists,[13] photo-controlled drug release[14] and photolabile protecting groups for biological systems.[15]

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1,2,3-Triazole ring is a stable structure and it can be constructed easily through the 'click reaction'. The research on 1,2,3-triazoles has been lively and ever-growing because of their wide applications in supramolecular and coordination chemistry[16] and they represent 'a few more bricks' on the road to carbon-rich functional materials.[17] Considering the unique properties of 1,2,3-triazole and coumarin, it is interesting to see what will happen after the combination of the two building blocks. Herein, we report the synthesis of a new series of 1,2,3-triazoles functionalized with coumarin group, as well as their gelation properties, supermolecular structures, and photochemistry. The interactions between gelators and solvents were also studied with Teas parameters and Teas plot.

2. Results and discussion

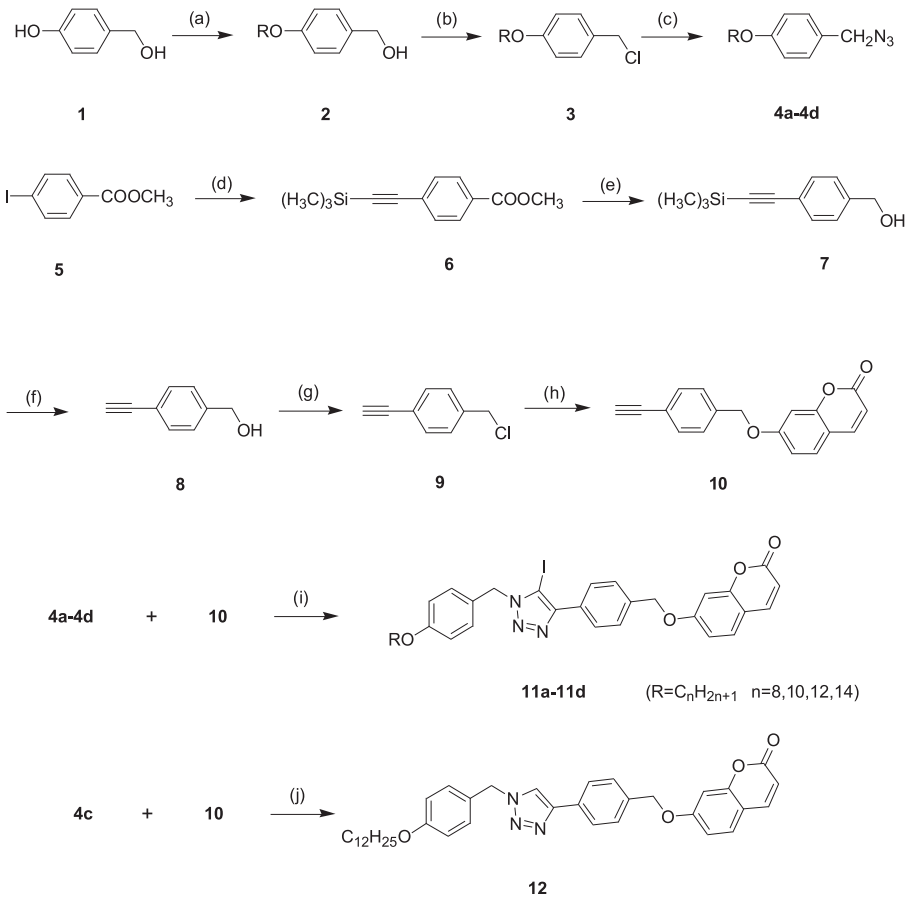
2.1. Synthesis

The synthetic routes for **11a**–**11d** and **12** are depicted in Scheme 1. 4-ethinyl benzyl alcohol (**8**) was obtained according to the literature.[18] Details of the synthesis and other experimental procedures can be found in the Supplementary data. The new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

method described in literatures.[19] The results are summarized in Table 1.

It was found that **11a**–**11d** could not dissolve in nonpolar solvents such as petroleum ether and cyclohexane. However, gels could be well formed in both the aromatic solvents (benzene, toluene, chlorobenzene and xylene) and the alcohols (ethanol, cyclohexanol, and isopropanol). They could even form super gels (MGC<5 mg/mL) in some solvents. The molecular structure of compounds **11a**–**11d** were similar except for the length of alkoxy chains and the compound with longer chains could gelate solvents with lower MGC than that with shorter side chains, which resulted from the enhancement of dispersive interaction of the alkoxy chains. These gels were thermo-reversible even after many cycles of heating-cooling and they were found to be stable for months at room temperature. Table 2

It is difficult to predict a priori, which molecular structures will contribute toward a good gelator molecule, and usually the gelling ability of very closely related molecules is affected by slight modifications. A small structural modification of compound **11c**, i.e. the replacement of iodine by hydrogen in triazole ring, resulted in the loss of gelation ability completely. The yielding compound **12** did not gel anyone of the tested solvents at all (see Table 1), indicating



Scheme 1. Synthetic route for compound **11a**–**11d** and **12**. (a) RBr, K_2CO_3, DMF, 70–80 °C, 6 h, ~99%; (b) $SOCl_2$, DMF, 5 h, ~98%; (c) NaN_3, DMF, 3 h, ~98%; (d) TMSA, $Pd(Ph_3P)_2Cl_2$, CuI, THF, TEA, 80 °C, 8 h, ~99%; (e) LiCl, KBH_4, THF, 80 °C, 8 h, ~50%; (f) K_2CO_3, THF, methanol, 24 h, ~70%; (g) $SOCl_2$, DMF, CH_2Cl_2, 5 h, ~98%; (h) 7-hydroxycoumarin, K_2CO_3, KI, DMF, 70–80 °C, 6 h, ~99%; (i) DIPEA, NBS, CuI, THF, 48 h, ~95%; (j) $CuSO_4 \cdot 5H_20$, ascorbic acid, THF, ethanol, 24 h, ~96%.

2.2. Gelation properties

The gelation properties of compounds **11a**–**11d** were investigated in a range of solvents including protic/aprotic, polar/apolar and some mixed solvents by means of inverted test-tube

the iodine atom in the 5-position played a crucial role in the gelating ability of the gelator. This might be due to the iodine atom in the 5-position changed the charge distribution of molecules, increased the polarity of molecules and enhanced the dipole-dipole interactions between molecules. In addition, another possible