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Preparation of efficient organogelators based on pyrazine-2,5-dicarboxylic acid showing room temperature mesophase

Yaodong Huang *, Yuqin Yuan, Wei Tu, Yan Zhang, Meijie Zhang, Hongmei Qu

Key Laboratory of Systems Bioengineering, Ministry of Education, Tianjin Key Laboratory of Biological and Pharmaceutical Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

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ABSTRACT

A new series of 3,6-dimethyl-pyrazine-2,5-dicarboxylic acid derivatives were synthesized and both their gelation abilities and thermotropic properties were studied. These compounds are efficient organogelators and easily form stable gels in many organic solvents. Moreover, they are room temperature liquid crystals, which all show hexagonal columnar mesophase. Results of ^{1}H nuclear magnetic resonance (^{1}H NMR), Fourier transform infrared spectroscopy (FTIR) and ultra-violet-visible spectroscopy (UV) showed the driving forces of gelation are intra-hydrogen bonding, π–π stacking and van der Waals interaction. On the other hand, the intra-hydrogen bonding may be essential to the formation of mesophase. A Teas plot was constructed to estimate the gel formation of four synthesized pyrazinecarboxamides in organic solvents.

1. Introduction

The spontaneous self-assembly of simple molecules is extremely attractive since it can produce complex supramolecular structures. Much attention has been paid on the development of functional soft materials through molecular self-assembly for many years. Among these self-assembly systems, supramolecular gel and liquid crystal are two kinds of important organized soft materials. Though the soft materials are not as durable as hard materials such as metals and plastics, they can easily respond to external stimuli such as temperature, electrical field, light, ultrasound and chemicals.[1] Low-molecular-weight organogels (LMOGs) are the materials in which three-dimensional networks are formed due to the self-assembling of low-molecular-weight compounds through non-covalent interactions such as hydrogen bonding, π–π stacking, and van der Waals interactions, and the networks can entrap and adhere a large amount of solvents therein. Liquid crystal is featured with its mobile and ordered states. It shares some of the properties of both isotropic liquids and crystalline solids. While the molecules in mesophases exhibit some positional and orientational order, they also behave as fluids. The formation of mesophases depends greatly on the ability of the mesogenic molecules to self-assemble into highly ordered structures. The same as to the LMOGs, liquid crystalline (LC) phases are formed also through either noncovalent interactions or hydrophobic–hydrophilic effects. Among these noncovalent interactions, hydrogen bond is considered as one of the most important interaction to construct supramolecular architecture because of its strength, directionality, reversibility, and selectivity.[2–9]

The report on the LC organogelators has increased in recent years.[10,11] These organic molecules can self-assemble themselves into LC structures as well as gel phases. Theoretically, a balance between the tendency of the gelator molecules to dissolve or to aggregate is essential to achieve gelation, and a balance between the tendency of the molecules to melt or to micro segregate into a noncrystalline state is required for the mesomorphic state. Though the application of the bifunctional LC organogelators has not yet obtained widely attention, it is no doubt to expect they will have more broad even some unique utilities. On the other hand, LC physical gels, formed by the mixing of liquid crystals and gelators, have been well studied and shown their use for functions, such as conductivity, ion transport, optics, and catalysis.[12] Their high performance in various functions derives from the formation of controlled phase-separated structures at the submicro and micrometer level.

A detailed literature survey shows that pyrazine dicarboxylic acids, their simple carboxylates and amides are elegant ligands but little attention has been paid to the self-assembly of their derivatives. In our previous report,[13] six synthesized pyrazinecarboxamides exhibited gelling ability and thermotropic

* Corresponding author. Fax: +86 22 27890166; e-mail address: huangyaodong@tju.edu.cn (Y. Huang).

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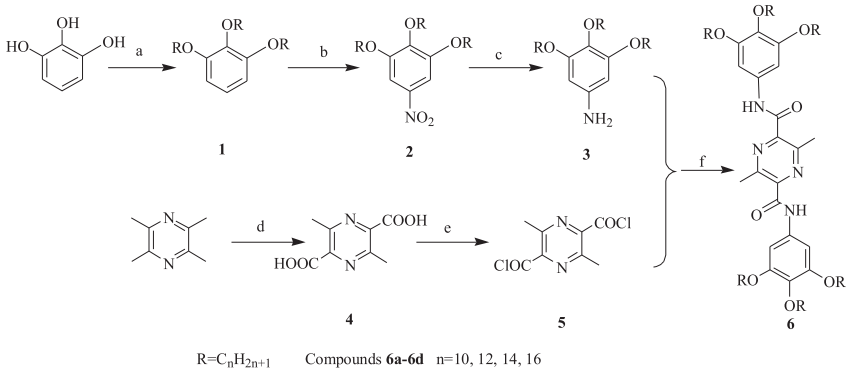
mesophase with narrow mesomorphic temperature domain (2–12 °C). As part of our ongoing research on the self-assembly of pyrazine-2,5-dicarboxylic acid derivatives, here we report a new series of pyrazinecarboxamides, which are both efficient gelators and room temperature liquid crystals. The interactions between gelators and solvents were also studied with Teas parameters and Teas plot.

2. Results and discussion

2.1. Synthesis

The compounds **1**–**3** and **4**–**6** were prepared according to the literatures.[13,14] The synthetic procedures were depicted in Scheme 1. Details of the synthesis and other experimental procedures can be found in the Supplementary data.



(a) RBr, DMF, K_2CO_3, reflux, 80%; (b) $SiO_2(HNO_3)$, CH_2Cl_2, 89%; (c) $N_2H_4{\cdot}H_2O$, C_2H_5OH, graphite, reflux, 90%; (d) $KMnO_4$, H_2O, H_2SO_4, reflux, 40%; (e) $SOCl_2$, reflux, 98%; (f) Et_3N, $CHCl_3$, 50%.

Scheme 1. Synthetic procedures for LC gelators **6a**–**6d**.

2.2. Characterization

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Bruker 400 spectrometer operated at 400 MHz and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Bruker 400 spectrometer operated at 100 MHz. Accurate mass data were obtained with a Bruker Technologies 10204 Accurate-Mass Q-TOF LC/MS instrument under ESI model. Element Analysis data were obtained with an Elementar Vario Micro cube instrument. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Bio-Rad FTS 6000 spectrometer. Ultraviolet-visible spectroscopy (UV) absorption spectra were recorded with a Lambda35 spectrometer. X-ray diffraction (XRD) were checked on a Bruker diffractometer (Cu Kα radiation k=1.54056 Å). Scanning electron microscopy (SEM) images were taken by Hitachi S-4800 microscope. Polarization optical microscopy (POM) was carried out using an Olympus BX51 microscope equipped with a Linkam LTS 350 platinum heating plate connected to a Linkam TMS 94 processor and the photographs were taken with a Fujix Digital camera HC-300Z. Differential scanning calorimetry (DSC) traces were recorded using a Mettler-Toledo DSC1/500 and the samples were placed in an aluminum crucible and analyzed, under a stream of helium and nitrogen, with a heating/cooling rate of 10 °C/min.

6a: Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.86 (s, 2H, −CONH); 7.02 (d, J=8.4 Hz, 4H, ArH); 4.07 (t, J=7.0 Hz, 8H, $-OCH_2$); 3.99 (t, J=6.9 Hz, 4H, $-OCH_2$); 3.11 (s, J=6.5 Hz, 6H, pyrazinee−CH_3); 1.91–1.28 (m, 96H, $-CH_2$); 0.92 (m, 18H, $-O(CH_2)_5CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.48, 153.69, 151.11, 143.18, 135.66, 133.33, 99.25, 77.34, 77.02, 73.88, 69.54, 32.25, 30.67, 30.00, 29.77, 26.45, 23.74, 23.02, 14.46. HRMS: calculated for $[M]^+$ $C_{80}H_{138}N_4O_8$ 1284.0587, found 1284.0585. EA: Calcd. C, 74.83; H, 10.83; N, 4.36, Found C, 74.88; H, 10.79; N, 4.33.

6b: Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.87 (s, 2H, −CONH); 7.03 (d, J=8.4 Hz, 4H, ArH); 4.04 (t, J=6.9 Hz, 8H, $-OCH_2$); 3.97 (t, J=6.9 Hz, 4H, $-OCH_2$); 3.12 (s, J=6.5 Hz, 6H, pyrazinee−CH_3); 1.90–1.26 (m, 120H, $-CH_2$); 0.88 (m, 18H, $-O(CH_2)_5CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.51, 153.76, 151.18, 143.24, 135.68, 133.36, 99.29, 77.34, 77.02, 73.94, 69.59, 32.34, 30.69, 30.03, 29.78, 26.51, 23.79, 23.07, 14.50. HRMS: calculated for $[M]^+$ $C_{92}H_{162}N_4O_8$ 1453.2499, found 1453.2501. EA: Calcd. C, 76.09; H, 11.24; N, 3.86, Found C, 76.13; H, 11.20; N, 3.80.

6c: Yield: 49%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.86 (s, 2H, −CONH); 7.02 (d, J=8.4 Hz, 4H, ArH); 4.06 (t, J=7.0 Hz, 8H, $-OCH_2$); 3.98 (t, J=7.0 Hz, 4H, $-OCH_2$); 3.11 (s, J=6.5 Hz, 6H, pyrazinee−CH_3); 1.90–1.28 (m, 144H, $-CH_2$); 0.92 (m, 18H, $-O(CH_2)_5CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.60, 152.85, 150.28, 142.31, 134.81, 132.50, 98.43, 76.48, 76.19, 73.04, 68.73, 31.41, 29.84, 29.17, 28.85, 25.62, 22.90, 22.19, 13.59. HRMS: calculated for $[M]^+$ $C_{104}H_{186}N_4O_8$ 1621.4377, found 1621.4381. EA: Calcd. C, 77.08; H, 11.57; N, 3.46, Found C, 77.16; H, 11.49; N, 3.41.

6d: Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 9.86 (s, 2H, −CONH); 7.01 (d, J=8.4 Hz, 4H, ArH); 4.04 (t, J=7.0 Hz, 8H, $-OCH_2$); 3.97 (t, J=6.9 Hz, 4H, $-OCH_2$); 3.12 (s, J=6.5 Hz, 6H, pyrazinee−CH_3); 1.90–1.27 (m, 168H, $-CH_2$); 0.89 (m, 18H, $-O(CH_2)_5CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.28, 154.44, 151.04, 143.96, 135.03, 132.00, 99.96, 78.14, 77.79, 74.65, 70.35, 33.00, 30.78, 30.45, 27.19, 26.40, 23.75, 23.23, 15.21. HRMS: calculated for $[M]^+$ $C_{116}H_{210}N_4O_8$ 1789.6255, found 1789.6258. EA: Calcd. C, 77.88; H, 11.83; N, 3.13, Found C, 77.97; H, 11.79; N, 3.10.

2.3. Gelation properties

The gelation abilities of the four synthesized compounds were detected for twenty-eight different organic solvents by means of inverted test-tube method described in literature,[15] and the minimum gel concentrations (MGC) are listed in Table 1. As shown in Table 1, compounds **6a**–**6d** can gel many kinds of solvents, such as