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Fluorescence-enhanced organogelators with mesomorphic and piezofluorochromic properties based on tetraphenylethylene and gallic acid derivatives

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ABSTRACT

Two novel aggregation-induced emission compounds derived from tetraphenylethylene and gallic acid were synthesized and characterized. Both of the emission compounds possessed mesomorphic properties and exhibited mesomorphic phases over a wide temperature range and the thermal-induced mesomorphic transition from metastable to stable phases accompanied by a change of the luminescent color. The mesomorphic transition may be ascribed to liquid crystalline phase transition. The emission compounds possess different gelation behavior in organic solvents. The emission intensities of the emission compounds can be reversibly changed with the gel–solution transition by alternate cooling and heating. Moreover, the color and emission of these organogelators can be repeatedly switched by various external stimuli including pressing, heating and solvent-fuming. These new compounds may offer potential as external stimuli-responsive materials.

1. Introduction

In recent years, low-molecular mass organogelators (LMOGs) have drawn immense interest because of their potential applications in cosmetics, catalysis, drug delivery systems, sensors, switches and other related fields [1,2]. LMOGs can self-assemble into fibers, rods, ribbons or other aggregates in suitable solvents via a combination of noncovalent interactions, such as hydrogen bonding, π–π stacking, electrostatic forces, donor–acceptor interactions, metal coordination, solvophobic forces and van der Waals forces, to form entangled networks and gel solvents [3,4]. Most LMOGs, called “smart” or “intelligent” gels, show reversible changes in morphology and/or physical properties in response to various external stimuli, such as temperature, electrical pulse and light [5,6]. But most of chromophores exhibit aggregation-induced quenching in the gel states or in the solid states [7].

Recently, aggregation-induced emission (AIE) organogelators have attracted considerable research attention because of their strong gel emission [8]. For example, an AIE organogelator, 1-cyano-*trans*-1,2-bis-(3′,5-bis-trifluoromethylbiphenyl) ethylene (CN-TFMBE) (Scheme 1), was practically nonfluorescent in the solution state, but highly fluorescent in the gel state, with a more than 100-fold enhancement in the fluorescence intensity [9,10]. In 2008, Chen et al. [11] reported a thermochromic gel generated from a cholesterol-containing salen-based organogelator, which exhibited obvious AIE properties in the gel state. The fluorescence quantum yield of the gel was approximately 600 times greater than that in solution.

Mechano- or piezo-fluorochromic materials have also drawn a great deal of attention because of their fundamental research and practical applications in sensors, optical recording and strain- or pressure-sensing systems [12–29]. These materials generate a fluorescent color in response to external force stimuli, such as grinding, smearing and pressing, and then revert to the original color by heating, recrystallization or exposure to solvent vapor. To date, only a few liquid crystalline materials displaying piezofluorochromic property have been reported [30–32]. LMOGs that

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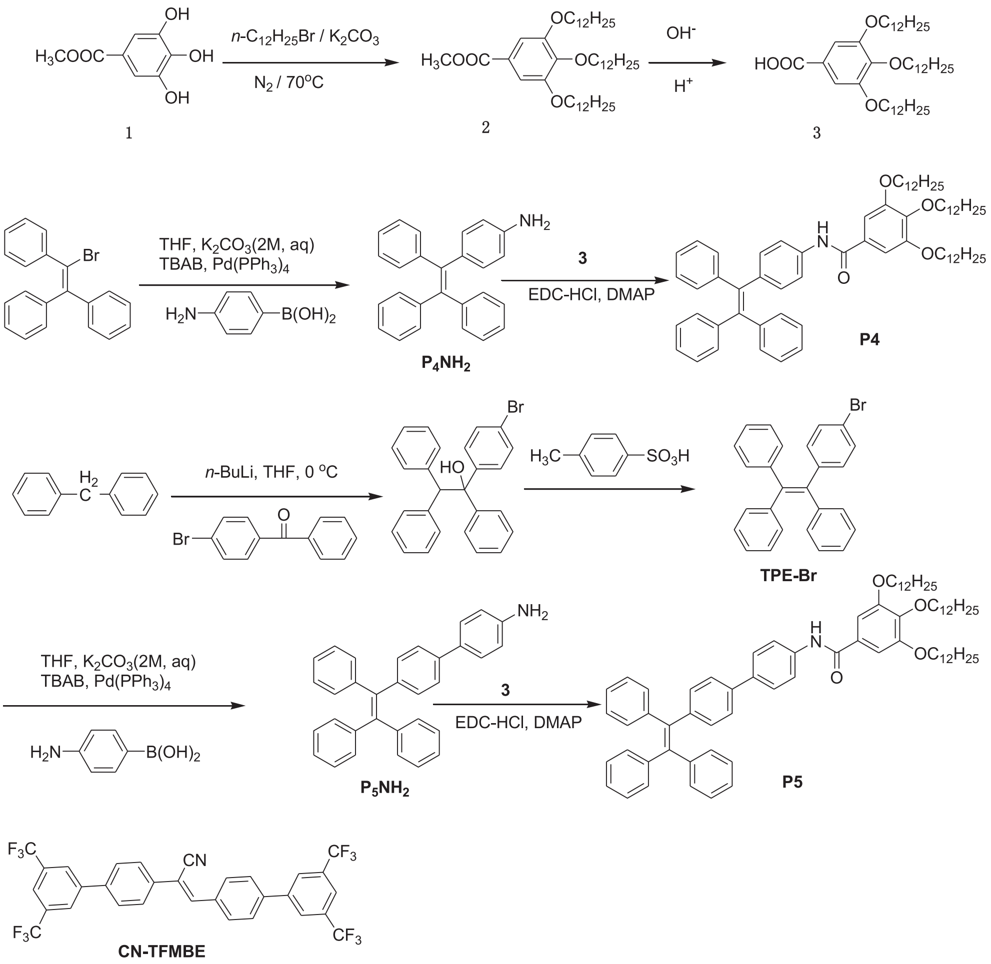

Scheme 1. Synthetic routes for **P4** and **P5**; the chemical structure of **CN-TFMBE**.

exhibit piezofluorochromic properties are exceedingly rare [33]. In 2012, Ren et al. reported several phosphole-lipids which formed highly fluorescent ionic organogels and their donor and acceptor doped systems exhibited piezofluorochromism. However, organic LMOGs with multimorphic and piezochromic luminescent properties have not been reported thus far to the best of our knowledge. In this article we report our recent results of two organogelators (**P4** and **P5**, Scheme 1) with AIE, multimorphic and piezofluorochromic properties, synthesized from tetraphenylethylene and gallic acid derivatives.

2. Experimental

2.1. Materials and measurements

4-Aminophenylboronic acid, 4-bromophenyl phenylmethanone, 2-bromo-1,1,2-triphenylethylene, 4-toluenesulfonic acid, diphenylmethane, 1-bromododecane, methyl 3,4,5-trihydroxybenzoate, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl), 4-dimethylamiopryidine (DMAP), *n*-butyllithium, tetrabutyl ammonium bromide (TBAB) and tetrakis(-triphenylphosphine) palladium (0) were purchased from Alfa-Aesar company and used as received. Ultra-pure water (18 MΩ.cm) was used in the experiments. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Company (China) and used without further purification. Methyl 3,4,5-tris(dodecyloxy)benzoate (**2**) [7], 3,4,5-tris(dodecyloxy) benzoic acid (**3**) [34] and 1-bromo-4-(1,2,2-triphenylvinyl)benzene (**TPE-Br**) [35,36] were prepared according to the literature methods.

Proton and carbon nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were measured on a Mercury-Plus 300 spectrometer [$CDCl_3$, tetramethylsilane (TMS) as the internal standard. For **P_5NH_2**, using DMSO-d_6 as solvent]. Mass spectra (MS) were measured on a Thermo DSQ EI-mass spectrometer. Elemental analyses were performed with an Elementar Vario EL elemental analyzer. Photoluminescence spectra (PL) were measured on a Shimadzu RF-5301pc spectrometer with 1.5 nm and 3.0 nm slit widths for excitation and emission, respectively. Ultraviolet–visible absorption spectra (UV–vis) were recorded on a Hitachi UV–vis spectrophotometer (U-3900). Wide-angle X-ray diffraction (WAXD) and small-angle X-ray diffraction (SAXD) measurements were performed by using a Bruker X-ray diffractometer (D8 ADVANCE, Germany) with an X-ray source of Cu Kα ($\lambda = 0.15406$ nm) at 40 kV and 40 mA, at scan rates of 4° and 0.6° per 1 min for WAXD and SAXD, respectively. Time-resolved emission decay behavior was measured on an Edinburgh Instruments Ltd. spectrometer (FLSP920). Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204 F1) at a heating rate of 10 °C/min under N_2 atmosphere. Transition temperatures and textures were determined using a Leitz Orthoplan Pol polarizing optical microscope (POM) equipped with a Likam heating stage system. The THF/water mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. Pressed samples were prepared by pressing in an IR