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Unsymmetric 1,3,4-oxa(thia)diazoles of quinoxaline–naphthalene conjugates

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ABSTRACT

Two new series of unsymmetric 1,3,4-oxa(thia)diazoles **1a**,**b** containing both quinoxaline and naphthalene moieties were prepared and their mesomorphic properties were investigated. The mesomorphic behavior of compounds **1a**,**b** and **2** was studied by DSC analysis and polarized optical microscopy. All compounds **1a** and **2** exhibited hexagonal columnar phases (Col$_h$), which were also confirmed by powder XRD diffractometer. N_{cell} and R_{ar} values equal to 5.23 and 22.73 Å^2 within a slice of 9.0 Å thick were also obtained for **1a** (n=16), indicating that a more disc-like structure constructed by two molecules lying side-by-side was correlated in Col$_h$ phases. In contrast, all compounds **1b** were not mesogenic, and the lack of mesomorphic properties in **1b** might be due to their unfavorable conformations. The PL spectra of all compounds **1a**,**b** showed one intense peak at λ_{max}=509–512 nm, and these photoluminescent emissions originated from quinoxaline moiety.

1. Introduction

1,3,4-Oxadiazole (OXD), considered as one of a few important compounds among five-membered ring heterocycles has been paid more attention in the field of materials chemistry due to their excellent thermal and chemical stabilities. 1,3,4-Oxadiazoles are structurally interesting; they are bent-shaped structures, electron-deficient rings, and good electron-acceptors. They were excellent candidates as blue emitters, and have applications[1] in OLED devices. Numerous known 1,3,4-oxadiazoles with a variety of novel structures were studied as electron transporting materials in OLED and widely applied as organic electron conductors. The first mesogenic asymmetric 1,3,4-oxadiazole was reported[2] by Dimitrowa et al. Thereafter more examples of mesogenic 1,3,4-oxadiazoles[3] with either symmetrical or asymmetrical structures were prepared and studied. Furthermore, a few mesogenic bi(1,3,4-oxadiazoles)[4] or tri(1,3,4-oxadiazoles)[5] were also reported. Nematic or layer smectic phases formed by these linear-shaped or bent-shaped molecules were commonly observed. In contrast, lesser examples exhibiting columnar phases[5b,6] were also known. 1,3,4-Oxadiazole is structurally nonlinear and has a larger exocyclic bond angle[7] ($\varepsilon \sim 135°$), which often resulted in a dramatic lowering both in melting or/and clearing points. This was an important key factor in processing commercial display technology. Hydrogen-bonded mesogenic oxadiazoles[8] mixed with pyridines or acids were reported. A few examples[9a] 1,3,4-oxadiazoles **I** and their metallomesogens **II**[3p,9b] were previously reported by this group. In contrast, their homologue 1,3,4-thiadiazoles showed an apparently different mesomorphic behavior. The replacement of oxygen atom by sulfur atom often led to an improved mesomorphic behavior.[9a] The reason might be twofold; (1) the larger sulfur atom incorporated in heterocyclic rings was more easily polarized and better induced in the mesophases. (2) The longer C–S bond distance[10] and larger C–S–C angle facilitated its formation of a more rod-like or better linear conformation, compared to the bent-shaped 1,3,4-oxadiazoles.

Quinoxalines were also called benzopyrazines. They were highly π-conjugated backbones and were potentially useful in many applications such as dyes, organic light-emitting diodes, electroluminescence, organic thin film transistors (TFT), and organic photovoltaics when incorporated with an electron-donor and electron-acceptor units via π-bridge(s). They were also considered as half-disc, elliptical or round molecules, which could easily or spontaneously self-assemble into columns when π–π interaction or dipole–dipole interactions are accessible between neighboring molecules. These molecules capable of forming columnar stacking arrangements might have a dramatic impact propensity. A few promising materials, such as liquid crystals, light-emitting diodes,

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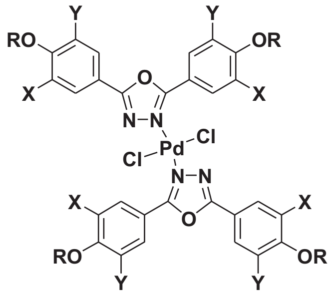
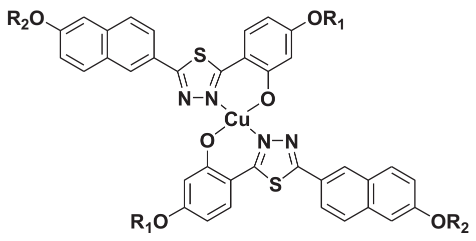
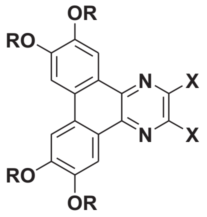
and photovoltaic devices have been explored and studied. Some known examples[11] derived from mesogenic quinoxalines **III**–**V**[12] were studied and were investigated. Compounds **III** derived from dibenzo[*a*,*c*]phenazine exhibited an improved mesomorphic behavior than compounds **IV** due to their better coplanarity. Some quinoxalines had a higher charge carrier mobility due to their highly conjugated structures. Substitutions and/or substituents positions incorporated were found to play an important role on the formation of mesophases.



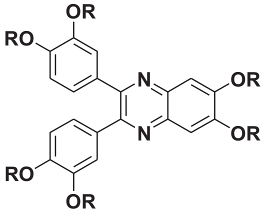
I; Cr (X = H)
Col (Y = OR)



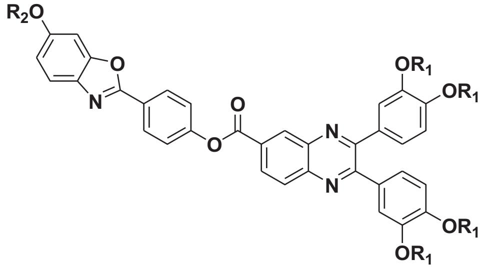
II; SmA/SmC



III: Cr (X = H),
Col (X = CN, OR)



IV: Cr



V; Col

In this work, we report the preparation and mesomorphic studies of two new series of unsymmetrical 1,3,4-oxa(thia)diazole **1a**,**b**. These were constructed by incorporating a lateral quinoxaline and naphthalene groups. Both lateral moieties were incorporated to enhance the molecular polarization and/or dipole needed to induce the mesophases. Also, π–π interactions might be also enhanced. All compounds **1a** and **2** exhibited hexagonal columnar phases (Col$_h$), which were also confirmed by powder XRD diffractometer. In contrast, all compounds **1b** were not mesogenic, and the lack of mesomorphic properties in **1b** might be due to their unfavorable conformation. The PL spectra of all compounds **1a**,**b** were examined.

2. Results and discussion

2.1. Synthesis and characterization

Two common synthetic routes were applied to prepare 1,3,4-oxadiazole derivatives. In this work the synthetic procedures of 1,3,4-oxa(thia)diazoles **1a**,**b** were given in Scheme 1. 1,2-Bis(3,4-didodecyloxy)phenyl)-1,2-ethanedione was obtained by the reaction of 1,2-bis (dodecyloxy)benzene with oxalyl chloride in the presence of AlCl$_3$ stirring in carbon disulfide at ice bath temperature, which was then condensed with 3,4-diaminobenzoic acid stirring in THF to give 2,3-bis-(3,4-bis(dodecyloxy)phenyl)quinoxaline-6-carboxylic acid **3**. On ^{1}H NMR spectrum, a characteristic broad peak often appeared at $\delta \sim 13.50$ ppm assigned for –COO*H* was not observed for acids **3** due to rapid exchange. However, a characteristic peak at ca. δ 170.92 ppm assigned for –*C*OOH was observed on its ^{13}C NMR spectrum. Then, 2,3-bis(3,4-bis(dodecyloxy) phenyl)-*N*′-(6-(alkoxy)-2-naphthoyl)quinoxaline-6-carbohydrazides **2** isolated as yellow-green solids were then obtained by condensation reactions of 6-(alkoxy)-2-naphthohydrazides and 2,3-bis-(3,4-bis(dodecyloxy)phenyl)quinoxaline-6-carboxylic acid **3** in stirring THF at room temperature. The reaction of 2,3-bis(3,4-bis(dodecyloxy)phenyl)-*N*′-(6-(alkoxy)-2-naphthoyl)-quinoxaline-6-carbohydrazides in refluxing phosphoryl chloride gave the 1,3,4-oxadiazoles **1a**. The products isolated as bright yellow solids were obtained after recrystallization from THF/methanol with a yield of 53–65%. In contrast, their analogue 1,3,4-thiadiazoles **1b** were prepared by the solutions of 2,3-bis(3, 4-bis(dodecyloxy)phenyl)-*N*′-(6-(alkoxy)-2-naphthoyl)-quinoxaline-6-carbohydrazides and phosphorous pentasulfide in refluxing pyridine for 24 h. The products isolated as yellow-green solids were obtained after recrystallization from THF/methanol. All final compounds **1a**,**b** and **2** were characterized by ^{1}H NMR, ^{13}C NMR, mass and elemental analysis. For instance, two characteristic broad singlet peaks occurred at δ 9.99–10.22 ppm and 10.26–10.48 ppm, assigned for amide-H (–CON*H*) of compounds **2** were appeared for the formation on the ^{1}H NMR spectra. On ^{13}C NMR spectra, observation of two peaks appeared, for example, at 163.84 and 165.52 ppm, and at 166.64 and 169.30 ppm was indicative of the formation of compounds **1a** (n=10) and **1b** (n=10), respectively. All data on mass and elemental analysis were well consistent with their structures and purities.

2.2. Phase transitions, mesomorphic behavior, and thermal stability

The mesomorphic behavior of compounds **1** and **2** was studied and characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The phase transitions and thermodynamic data for compounds **1** and **2** are summarized in Table 1. All compounds **2** (n=8, 10, 12, 14, 16) exhibited enantiotropic columnar phases based on observation under polarized microscope. Under POM, a typically pseudo focal-conic or more leaf-