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Synthesis, spectral and electrochemical properties of novel 1,5-diphenyl-3-spirobifluorenyl pyrazoline derivatives

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ABSTRACT

A series of novel 1,5-diphenyl-3-spirobifluorenyl pyrazoline derivatives have been synthesized and characterized by ^{1}H NMR, X-ray crystallography, UV–vis and fluorescence spectroscopy and mass spectrometry. Their maximum UV–vis absorption wavelengths were between 386 and 395 nm, and the fluorescence emission wavelengths were between 459 and 469 nm, which belongs to the typical blue light emission. All compounds exhibited excellent absolute fluorescence quantum efficiency (AFQE) (>90%) in solution. Moreover, at solid phase, compound **4f** also displayed good AFQE (54%). The energy gaps of these derivatives were between 2.8 and 3.0 eV, typical for the blue light emission. Molecular orbital calculations revealed that the HOMO and LUMO energy levels were close to 1,3-diphenyl-5-(9-phenanthryl)-4,5-dihydro-1H-pyrazole (DPPhP). The high fluorescence quantum efficiency, appropriate energy gaps and HOMO and LUMO energy levels prove that 1,5-diphenyl- 3-spirobifluorenyl pyrazoline derivatives have the potential to be used as blue light emitting materials.

1. Introduction

Significant progress has been made recently since the discovery of multi-layered organic light-emitting diodes (OLEDs) by Tang and VanSlyke [1]. More and more researchers have focused on the development of OLEDs using small organic molecules for the potential application in lighting, back light, and flat panel displays [2–4]. There has been some progress in the blue phosphorescent OLEDs, however, achieving highly efficient and stable blue light emission is still a challenge [5].

As candidates for OLEDs, pyrazoline derivatives have drawn significant attention due to their high quantum yield in the blue light emission. Pyrazoline derivatives represent an important class of organic photonic materials [7,8]. It is known that the 1-nitrogen atom and 3-carbon atom on the pyrazoline ring are electron donor and acceptor, respectively [6]. Upon excitation, pyrazolines with twisted intramolecular charge transfer will form an electron donor–acceptor system, which makes them ideal hole and electron-transporting and emitting materials [9,10]. Recently, pyrazoline derivatives with good luminescence properties were synthesized and characterized [11,12]. However, these compounds tend to recrystallize easily, causing shortened lifetime and poor durability of OLEDs. A possible solution is to incorporate them into polymer matrix.

Materials with spirobifluorene can improve the morphological stability significantly and prevent crystallization effectively below the glass transition temperature [13]. Yin et al. synthesized a spirobifluorene-bridged donor/donor chromophore, 2,7-bis-(4-(*N*, *N*-diphenylamino)phen-1-yl)-9,9-spirobifluorene (SPF-TP) with high thermal stability (Td = 501 °C) and high fluorescence quantum yield (0.90, in THF) [14]. What is more, new spiro[benzotetraphene-fluorene] derivatives were synthesized and applied in sky-blue fluorescent host materials by Cha et al. [15]. Thiery et al. synthesized a series of pyridine-substituted spirobifluorene (SBF) dyes with high triplet energy levels (ET around 2.7 eV), resulting in their application as hosts for green and sky-blue phosphorescent organic light emitting diodes (PhOLEDs) [16]. Based on the ideal properties of spirobifluorene, we decided to incorporate it with pyrazoline. Our goal is to develop blue-emitting materials superior to current OLEDs. In this study, we designed, synthesized, and characterized a series of novel spirobifluorenyl substituted pyrazoline derivatives as shown in Fig. 1.

2. Results and discussion

The synthetic routes for the pyrazoline derivatives are summarized in Scheme 1. Spirobifluorene was reacted with acetyl

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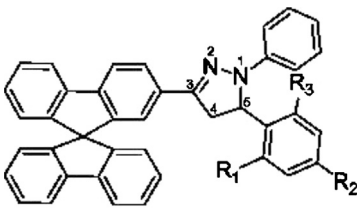


Fig. 1. The structure of the designed compounds.

chloride to afford spirobifluorenyl methyl ketone **2**, which was condensed with different substituted benzaldehyde via aldol condensation reaction to yield compounds **3a–f**. The spirobifluorenyl substituted pyrazoline derivatives were prepared from compounds **3a–f** and phenylhydrazine via a cyclization reaction. Afterwards, the products **4a–f** were purified by column chromatography and characterized by ^{1}H NMR, and ESI mass spectrometry.

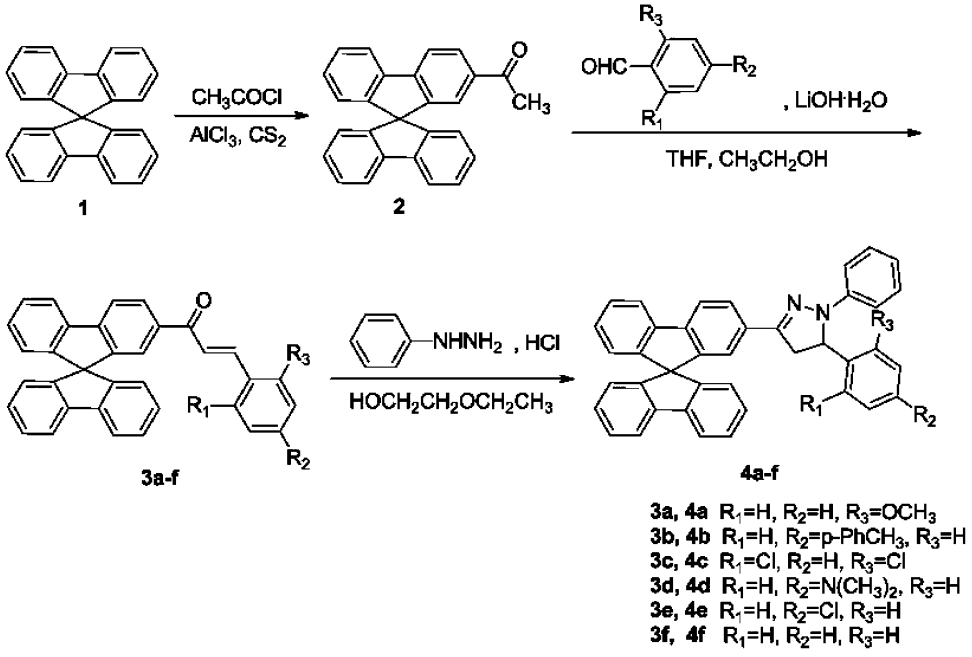
2.1. Single-crystal X-ray determination

Single crystals suitable for the X-ray structure analysis were grown by evaporating solution of **4c** in a mixture of CH_2Cl_2/*n*-hexane (1:3 v/v) at room temperature, and the crystallographic data were collected using a Rigaku Saturn 724+ CCD area detector. Single crystal diffraction experiment showed that compound **4c** belongs to a triclinic system, and P-1 space group. As shown in Fig. 2, the lattice of compound **4c** contains one **4c** molecule and two dichloromethane molecules. The two fluorene ring molecules share a carbon atom C25, and are almost vertical, the angle between the two planes is 89.99°. In the pyrazoline ring, the bond length of N1-C26 is 1.289 Å, indicating a carbon–nitrogen double bond, whereas the bond length of N2-C27 is 1.470 Å, typical for a carbon–nitrogen single bond. The pyrazoline ring and the 3-position phenyl ring share the C27 atom. The two rings are again almost vertical to each other with the dihedral angle of 85.56°. The pyrazoline, 2-position phenyl and the directly attached fluorene ring are nearly coplanar, with the dihedral angles 6.50° and 6.64°, respectively. Detailed crystallographic data and refinement are summarized in Table 1.

2.2. UV–vis absorption and fluorescence spectra

Fig. 3 shows the UV–vis absorption spectra of compounds **4a–f** in diluted solution of CH_2Cl_2. The corresponding photophysical data are listed in Table 2. As shown in Fig. 3, all compounds exhibit absorption bands at ca. 250–300 nm, which can be assigned to the π–π^* translation of the K band of the benzene ring. The bands at ca. 385–395 nm belong to the π–π^* transition of the conjugated backbone of the compounds. The difference of the UV–vis absorbance of these compounds is due to the different R groups at C-5 position. When an electron-withdrawing group is located at C-5 position, the wavelength of the absorption peak is longer than those of other pyrazoline compounds without electron-withdrawing group. Compound **4f,** which has no substituent on the benzene ring, shows the minimum λ_{max}, while compound **4d,** with electron-donating group, has the maximum λ_{max} and red-shifted significantly compared to **4f**. This demonstrates that the UV absorption λ_{max} for compounds with electron-donating groups has the tendency to red-shift. Moreover, the stronger the electron-donating ability of the substituent, the greater the red-shift.

Fig. 4 demonstrates that compounds **4a–f** give a strong fluorescence emission peak in dichloromethane. The emission bands of compounds **4a–f** appeared at 459–469 nm are smooth and pure blue emissions. **4c** shows the shortest emission wavelength (459 nm), while **4d** has the longest wavelength (469 nm). The difference in the fluorescence spectra of **4c** and **4d** may be related to the different electronic effect at the C-5 position. This provides evidence that the group at C-5 position affects the fluorescence emission of pyrazoline compounds.



Scheme 1. The synthetic route for the spirobifluorenyl substituted pyrazoline derivatives.