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Carbazole-based diphenyl maleimides: Multi-functional smart fluorescent materials for data process and sensing for pressure, explosive and pH

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ABSTRACT

A series of carbazole-based diphenyl maleimide dyes with different N-substituent were synthesized through an Ullmann reaction in high yields. The dyes exhibit an intense emission in the solid state for their twisted conformation fixed by weak intermolecular interactions, resulting in the hindrance of the internal rotations. Their solid-stated emission wavelength and intensity are sensitive to external stimuli (like heat, pressure and vapor), due to a crystal-to-crystal or crystal-to-amorphous phase transition. Based on the multi-stimuli-responsive fluorescence properties of the *N*-benzyl analogue, two kinds of applications were explored. One is rewritable data recording processes including solvent writing and vapor writing. The other is sensing for low hydrostatic pressure (0–25 MPa). Interestingly, nanoparticles of the dyes formed in aqueous solution could effectively detect explosive and pH changes. A 15 ppm concentration of picric acid quenched the fluorescence of the *N*-methyl analogue with the detectable limit calculated to be 0.13 ppm. The *N*-methyl analogue also showed a different emission color and intensity over the pH range 12–14, which originated from the hydrolysis of the dye molecules in the strongly basic solution.

1. Introduction

Information processes including recording, storage and security technologies of data has become an integral part of our life. Recently, smart luminescent materials responsive to external stimuli have attracted increasing interest for their potential application in the processing of data record and storage [1–5]. Particularly, organic multi-stimuli-responsive smart materials showing piezochromic, vapochromic and thermochromic luminescence in the solid state can change their emission colors or intensity in response to an external grinding (or pressing, shearing), fuming and heating [6–16]. The tunable solid-state fluorescence makes them become good candidates for application as biological probes [17], chemical sensing [18–20] and optical devices [21,22], besides data processing. However, such smart organic materials are quite limited for the difficulties in changing the molecular structures and emission in the solid state.

It is generally known that an effective approach to control solid-state luminescence is to alter the molecular packing mode and/or conformation [23–29]. As a result, the factors affecting the aggregated state and conformation would impose a significant effect on the solid-state emission of materials. Three main factors should not be ignored: bulky aromatic groups, heteroatoms (N, O, S or F) and donor-acceptor (D-A) structure. Firstly, large and bulky groups can result in a twisted structure and restrict intramolecular rotation, which is positive for high fluorescent quantum yield [30–32]. Secondly, heteroatoms always generate weak intermolecular interactions rigidifying the molecular conformation and locking the molecular rotation, like hydrogen bonding and van der waals forces [33–35]. Lastly, intramolecular charge transfer caused by D-A structure of molecules can make their luminescent properties sensitive to the external environment [36]. However, the molecules simultaneously possessing these three features are very rare.

3,4-Disubstituted arylmaleimide dyes have attracted

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considerable attentions in organic light-emitting diode (OLED) [37–40] and anion sensing [41,42] for their good performance in luminescence. However, due to the interaction of dipole-dipole and π-π stacking, most of arylmaleimides show stronger fluorescence in solution than in solids. Regardless of the increasing interest in the photophysical properties of arylmaleimides [43–47], their solid-state fluorescence is rarely studied in the reported literature. Due to the electron-deficiency of maleimide, a pair of cross-intercepted dipoles would be formed, if the C (3) and C (4) positions of maleimide are symmetrically substituted by bulky aryl groups with an electron-releasing ability. Additionally, the heteroatoms in arylmaleimides, like O and N, are expected to dramatically affect the molecular packing modes by weak interactions. Following the strategy, we have recently reported a Λ-shaped and D-π-A-π-D type molecule, 3,4-bis(4-(9-carbazolyl) phenyl)-*N*-methylmaleimide (BCPMM) with strong AIEE and CIEE activity [48]. Its morphology-dependent fluorescence tuned by external stimulus, could be utilized to construct complex sequential logic systems. Therefore, arylmaleimides are potential stimuli-responsive materials with tunable solid-state fluorescence [49,50].

In this paper, to examine whether the multi-stimuli-responsive fluorescence is a general phenomenon for 3,4-bis(4-(9-carbazolyl) phenyl)maleimides, to investigate how the different substituted groups affect the emission, and to explore sensing application of their nanoparticles, a new route was adopted to synthesize a series of 3,4-bis(4-(9-carbazolyl)phenyl) maleimide dyes (**5a-d**, Scheme 1) with different N-substituent groups in high yields. Considering that the size, rigidity, heteroatom and electronic effect of *N*-substituents would affect the packing structure and properties of solids, methyl, benzyl, pentafluoro benzyl and *tert*-butoxycarbonyl group were chosen as *N*-substituents. The solid-state luminescence properties of **5** and the pH and explosive sensing of **5a** nanoparticles were studied thoroughly. The results revealed that **5** exhibited morphology-dependent fluorescence that could be tuned by external stimulus, and good sensing for pH and explosive, and that their luminescent and sensing properties were influenced by groups of different bulk and by heteroatoms. To the best of our knowledge, smart fluorescent materials with responsiveness to heat, vapor, pH, explosives and low hydrostatic pressure are rarely reported.

2. Experimental section

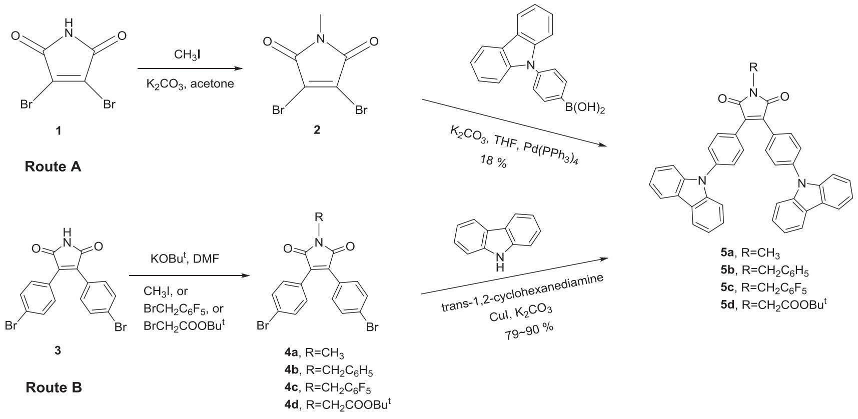
2.1. General information

All of the reagents and solvents used, except for 3,4-dibromophenylmaleimide, were obtained from commercial suppliers and were used without further purification unless otherwise noted. 3,4-Dibromophenylmaleimide was synthesized according to a previously reported method [40]. Thin layer chromatography was performed on G254 plates of Qingdao Haiyang Chemical. Column chromatography was performed on Sorbent Technologies brand silica gel (40–63 mm, Standard grade).

High resolution MALDI and ESI mass spectra were recorded on Bruker microflex LRF and micrOTOF II spectrometer, respectively. NMR spectra were measured in $CDCl_3$ on a Bruker Ascend 400 FT-NMR spectrometer; ^1H and ^{13}C chemical shifts were quoted relative to the internal standard tetramethylsilane. Melting points were measured using a SGW X-4 melting point apparatus. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 FT-IR spectrometer. Differential scanning calorimetry was done on a Perkin-Elmer DCS-7 instrument in the temperature range of 30–310 °C under flowing N_2 gas at a heating rate of 10 °C/min. UV–vis spectra were obtained on a Shimadzu UV-2600 spectrophotometer. The PL spectra were probed on a Shimadzu RF-5301PC fluorescence spectrophotometer. The thermal annealing processes were carried out in an oven. All photographs were recorded on a Canon Powershot G7 digital camera under UV light (365 nm). Powder X-ray diffraction (PXRD) data were collected using a PANalytical X-ray Diffractometer (X'Pert3 Powder) with Cu *Kα* radiation. The simulated patterns were obtained from single-crystal X-ray analysis. The fluorescence lifetime and absolute Φ_F values of solution and solid were measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere. The surface morphology of materials was analyzed by high voltage transmission electron microscope on a JEM-2010 (JEOL).

The single crystals of **5b** and **5c** were mounted on a glass fiber for the X-ray diffraction analysis. Data sets were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer equipped with graphite monochromatic Cu-*Kα* radiation ($\lambda = 1.54184$ Å). The single crystals were kept at 290.3 K for **5b** and 100.0 K for **5c** during data collection. The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package. All non-hydrogen atoms were refined anisotropically displacement parameters, and all hydrogen atoms in the ideal positions attached to their parent atoms.

Molecular Simulations were performed on Gaussian 09 program. Geometry at ground state was fully optimized by the density functional theory (DFT) method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G* basis set.



Scheme 1. Synthetic routes of **5**.