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Synthesis of yellow emitting bis-pyrimidine based purely organic phosphors

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ABSTRACT

Two organic phosphors 5,5′-(4-pyridinylmethylene)bis[1,3-dimethyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione] (BP) and 5,5′-(4-nitrophenylmethylene)bis[1,3-dimethyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione] (BP-NO_2) have been synthesized through a one pot reaction of *N*,*N*-dimethylbarbituric acid and pyridine aldehyde in acetonitrile at 80 °C. The synthesized phosphors were characterized by single-crystal X-ray crystallography, Fourier transform infrared spectroscopy, UV–vis spectroscopy, thermogravimetry analysis and photoluminescence (PL) spectroscopy. A broadband PL emission spectrum ranging from 400 to 800 nm was recorded from both phosphors. The BP showed a luminescence peak at ca. 560 nm (2.21 eV), while the BP-NO_2 exhibited a peak at 590 nm (2.1 eV), which reflect pure yellow emissions. The optimized geometry of the phosphors has been studied with a quantum chemical approach using the density functional theory. The highest occupied and lowest unoccupied molecular orbitals are predicted from the calculations.

1. Introduction

The generation of light by the electrical excitation of an organic molecule was first reported by Pope et al. [1] in 1963 by applying a voltage across a single crystal of anthracene immersed in an electrochemical cell. Vincett et al. [2] carried out organic electroluminescence using organic thin films. It is believed that the quantum efficiencies and life times of the organic phosphorescent compounds (OPs) were considerably lower than the OPs based on organometallic compounds. This can be explained in terms of the highly bonded nature of electrons in organic materials, which gives little freedom for emission from triplet states. The progress in organic light-emitting devices (OLEDs) based on organic materials started in the year 1987 with the synthesis of bilayers of low molecular weight organic molecules [3]. Burroughs et al. [4] in 1990 reported light emitting diodes based on conducting polymer poly(p-phenylenevinylene). Thereafter, OPs based on organic materials have generated considerable research interest due to their diverse properties such as biodegradability, ease of handling, low cost, excellent sensitivity and good specificity [5]. They have found tremendous applications in optoelectronic devices, viz. OLEDs, organic lasers and sensors [6–9]. Various authors have reported that organic materials are suitable hosts in highly efficient green and red phosphorescent OLEDs [10–12]. However, most of the reports to date are focused on luminescent materials based on organometallic compounds [13]. Additionally, metal containing compounds can be utilized as luminescent materials with superior emission efficiency as compared to organic phosphors.

One way to improve the fluorescent properties of the organic materials in the solid state is to modify the surface of the organic materials by attaching bulky substituents onto the molecular skeleton [14]. Bolton et al. [15] mentioned a phenomenon that uniquely combines three factors to initiate bright phosphorescence from purely organic materials i.e., aromatic carbonyl function, the heavy atom effect, and halogen bonding. The report states that the carbonyls exhibit a degree of spin orbital coupling, the heavy atom effect promotes singlet–triplet conversion and halogen bonding induces aromatic carbonyls. Chen et al. [16] fabricated the efficient white organic light-emitting diodes based on organic materials while Kohler et al. [17] described the latest advances in fluorescence and phosphorescence in organic materials. Pyridine based materials have been explored as electron transport materials (ETMs) and OLEDs [18,19] as well as utilized for the synthesis of luminescent materials [20]. Few reports exist in the literature on the synthesis and luminescent properties of different OPs [14,21,22] while bis-pyrimidine based luminescent material is under investigation. Pyrimidine has one kind of diazines isomers. Diazine is a future candidate for OLEDs [22–25]. Ge et al. [23] successfully synthesized highly efficient phosphorescent iridium (III) diazine complexes for OLEDs, whereas, Wang et al. [24] synthesized a new cyclometalated iridium (III) pyrimidine

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complex. They further reported that the PL spectrum of the synthesized complex exhibited a yellow emission at 560 nm. Zhang et al. [25] reported theoretical studies on structures and spectroscopic properties of highly efficient phosphorescent iridium (III) complexes with pyrazine and pyrimidine ligands. As a result the aim of this study was to synthesize organic phosphors based on bis-pyrimidine.

In this work, we report on an improved process to synthesize two OPs, i.e. 5,5′-(4-pyridinylmethylene)bis[1,3-dimethyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione] (BP) and 5,5′-(4-nitrophenylmethylene)bis[1,3-dimethyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione] (BP-NO_2). The structural, morphological, thermal and luminescent properties of the metal free OPs were investigated. Energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO) were also determined using the density functional theory (DFT/B3LYP/6-31G* (d) level of theory) in the gaseous phase and their energy gap showed that charge transfer occurred within the molecule.

2. Experimental section

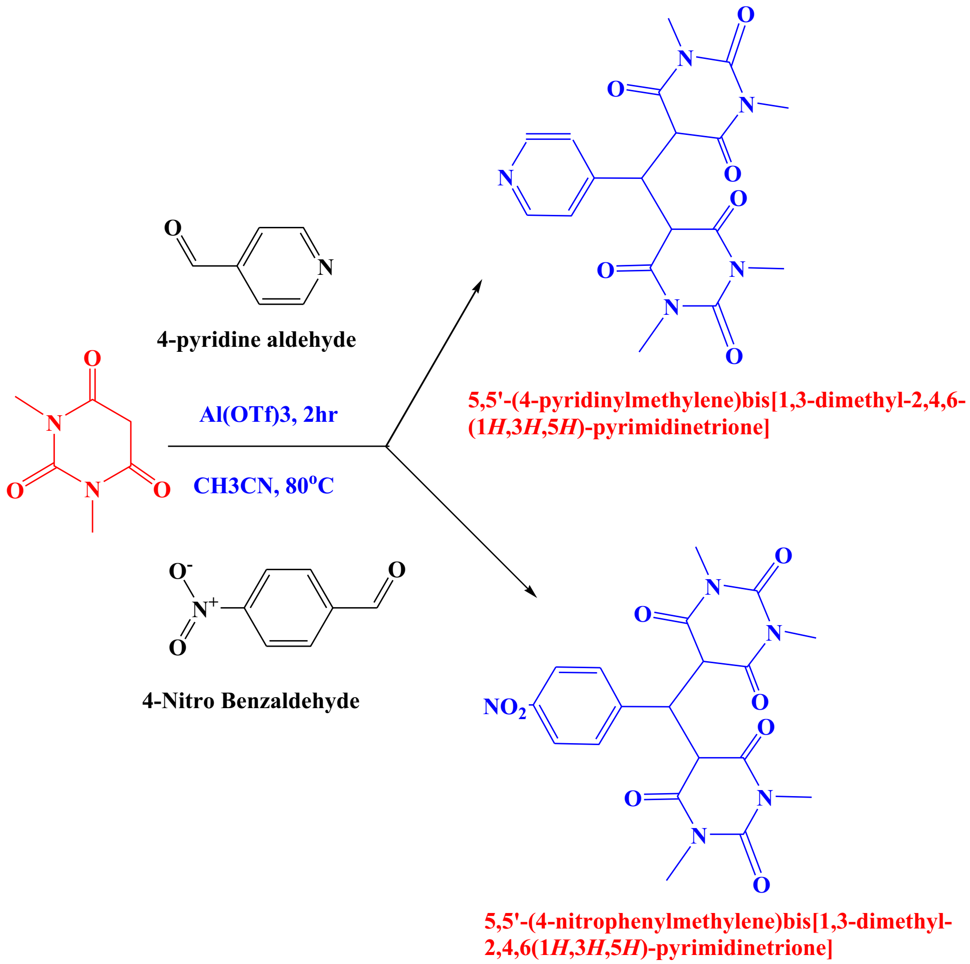
2.1. Sample synthesis

All the reagents and solvents used in the syntheses were purchased from Merck and were used without further purification. The synthesis of BP and BP-NO_2 were performed as illustrated in Scheme 1.

A 100 ml 2-neck round bottom flask containing 30 ml of acetonitrile was charged with *N*,*N*-dimethylbarbituric acid (10 mmol). To this reaction, a mixture of 4-pyridine aldehyde (10 mmol) and $Al(OTf)_3$ (5 mol%) was added and the resulting solution was heated to 80 °C using a magnetic stirrer with vigorous stirring for 2 h. After completion of the reaction the white solid precipitates were filtered off and washed three times with ethanol and then allowed to dry at room temperature in air. The pure 5,5′-(4-pyridinylmethylene)bis[1,3-dimethyl-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione] was obtained in 97% yield and had a melting point of 236 °C. The structure of the compound was analyzed by IR spectroscopy and single crystal XRD (CCDC no. 956426). The synthesis of the 4-nitrophenyl derivative was carried out in the same way by allowing 4-nitrobenzaldehyde to react with *N*,*N*-dimethylbarbituric acid in the presence of $Al(OTf)_3$. This integrity of this compound was confirmed by comparison with the corresponding compound reported by Jursic et al. [26].

2.2. Sample characterization

Single crystal diffraction data was collected at 100 K on a Bruker 111 × 8 ApexII 4 K diffractometer using monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The crystal structure was solved with the direct method [27,28] using the program SIR-97 [29] and refined by full-matrix least-squares refinement methods based on F^2, using SHELXL-97 program [30]. Molecular structures of the compound were drawn with the help of the ORTEP [31] and Mercury program [32]. The hydrogen bonding in the compound



Scheme 1. Synthesis of 5,5′-(4-pyridinylmethylene)bis[1,3-dimethyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione] and 5,5′-(4-nitrophenylmethylene)bis[1,3-dimethyl-2,4,6-(1*H*,3*H*,5*H*)-pyrimidinetrione].