



## Fluorescence and physical properties of the organic salt 2-chloro-4-nitrobenzoate–3-ammonium-phenol



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### ABSTRACT

Organic salt 2-chloro-4-nitrobenzoate (CNBA<sup>−</sup>) 3-ammonium-phenol (AP<sup>+</sup>) exhibits fluorescence at 338 nm in solution and frontier molecular orbitals generated from TDDFT calculations indicate that the ground state and the excited state are physically separated on AP<sup>+</sup> and CNBA<sup>−</sup>. The crystal structure and physical–chemical properties of the CNBA<sup>−</sup> · AP<sup>+</sup> were investigated using X-ray single crystal and powder diffraction, SEM, FTIR, UV–Vis–NIR, and fluorescence spectrometry. X-ray diffraction demonstrates that the two molecules are linked via N<sup>+</sup>–H ··· O<sup>−</sup> ammonium–carboxylate interactions, as expected considering their interaction propensities. Proton transfer has been confirmed by FTIR analysis. The melting point of CNBA<sup>−</sup> · AP<sup>+</sup> was observed at 186 °C, which is higher than pure CNBA (140 °C) or AP (120 °C). The observation of a spatially separated HOMO and LUMO possessing a narrow  $\Delta E_{ST} = 73.3$  meV and an emission in the blue region is promising as an alternative method for the production of OLED materials.

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### 1. Introduction

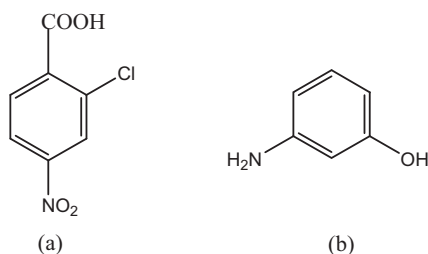
Highly efficient and long lasting organic light emitting diodes (OLEDs) remain an important research subject. In addition, thermally activated delayed fluorescence (TADF) is a promising property that merits further development in the field of organic electronics and photonics [1]. One of the key approach to achieve TADF in organic materials is to reduce the spatial overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which produces a narrow singlet to triplet ( $\Delta E_{ST}$ ) energy gap suitable for reverse intersystem crossing ( $T_1 \rightarrow S_1$ ) [2–6]. Donor and acceptor interaction in a single molecule and ionic or electrostatic interaction between them in a salt can give rise to a narrow  $\Delta E_{ST}$  for molecular electronics. Donor and acceptor interaction in organic salts is relatively uncommon for TADF and further investigation may lead to better materials for OLED applications. A well-separated HOMO and LUMO level with a narrow singlet to triplet energy gap has been obtained in the form of the 2-chloro-4-nitrobenzoate

3-ammonium-phenol (CNBA<sup>−</sup> · AP<sup>+</sup>) salt. Its crystal structure, fluorescence and physical properties are discussed in the present paper.

The active pharmaceutical ingredient (API) 2-chloro-4-nitrobenzoic acid (CNBA, Fig. 1) is a potential new drug against immunodeficiency diseases including HIV infections [7]. Structural and thermal characteristics of CNBA have been reported [8]. It exhibits dimorphism (two different crystal structures for CNBA i.e. form I and form II) and a hydrate [8,9]. Both forms crystallize in space group  $P2_1/c$  and an asymmetric unit comprised of  $Z = 1$  and  $Z = 4$  for form I and form II respectively. The crystal forms are visually distinguishable as form I tends to form blocks whereas form II is needlelike. The transition between form II and form I is reportedly found between 60 and 100 °C, with a melting point of form I at 136–140 °C [8,10,11]. The crystal structures of the two polymorphs have different conformations and can therefore be distinguished by infrared spectroscopy [8,11]. In recent years, an increasing number of reports have appeared discussing the improvement of the physicochemical properties of CNBA with different molecules such as isonicotinic acid [12], isonicotinohydrazide [12], 3-cyanopyridine [13], 4-benzoylpyridine [14], p-anisidine [15], quinoline [16], ethenzamide [11], nicotinamide [7], pyrazine [17], mesitylene [9], p-xylene [9], acetophenone [9],

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**Fig. 1.** Chemical structure of (a) 2-chloro-4-nitrobenzoic acid (CNBA) and (b) 3-aminophenol (AP).

dimethylsulfoxide [9], dioxane [9], 1,2,3 benzotriazole [18], including two salts: 3,5-dimethylpyridinium [19] and N'-isopropylideneisonicotinohydrazidinium [12] and another compound with proton exchange in the liquid state: collidine [20]. Charge densities and other properties have also been studied for CNBA [21,22]. It is clear from the literature that interactions involving hydrogen bonds between the CNBA carboxyl group and pyridine compounds occur often [23]. Additionally, it is observed that the melting point of CNBA cocrystals decreases in comparison to the pure CNBA (140 °C) except for the cocrystal with nicotinamide [7], which possesses a melting point of 158 °C. The recent report on the salt formation of 3,5-dinitrobenzoic acid with 2-aminophenol and 2-amino-4-chlorophenol [24] demonstrated that AP is a versatile cofomer for supramolecular structures with N-H...O, C-H...O and N-H... $\pi$  interactions.

To the best of our knowledge, the fluorescence properties of CNBA have not been investigated. HOMO–LUMO analysis can be used to study luminescence properties of molecules facilitating the design of materials for OLED applications [1–6,25–27]. Stable organic molecules with high electroluminescence efficiency have been very attractive for fabricating OLED materials [28]. For materials possessing a narrow energy gap between its singlet and triplet excited states,  $\Delta E_{ST}$ , leads to reverse intersystem crossing,  $T_1 \rightarrow S_1$  wherein thermal energy is harvested from the surrounding [1–6]. Therefore, a molecular design with a narrow  $\Delta E_{ST}$  ( $\leq 100$  meV) and a reasonable decay rate of  $>10^6$  s<sup>-1</sup>, leads to highly efficient TADF materials. One pathway to achieve and control a narrow energy gap is creating spatially well-separated HOMO and LUMO levels.

The derivatives of metal-free carbazoyl dicyanobenzene (CDCBs) show excellent delayed fluorescence ranging from 470 nm to 600 nm [3]. The carbazoyl group acts as an electron donor and the dicyanobenzene group acts as an electron acceptor. 4CzIPN, a derivative of CDCB, exhibits spatially separated HOMO and LUMO on the carbazoyl and dicyanobenzene moieties respectively giving rise to a narrow energy gap of  $\Delta E_{ST} = 83$  meV. 2-biphenyl-4,6-bis(12-phenylindolo[2,3-a] carbazole-11-yl)-1,3,5-triazine (PIC-TRZ) contains an indolocarbazole donor unit and a triazine acceptor unit. The spatially localized HOMO and LUMO are located on the indolocarbazole and biphenyl triazole units respectively and a narrow band gap of  $\Delta E_{ST} = 110$  meV can be maintained due to significant steric hindrance between the indolocarbazole and biphenyl triazole groups [2]. The observed large Stokes shift indicates that the origin of the delayed fluorescence emission is based on intramolecular charge transfer between the donor and the acceptor units. The donor and acceptor in the above reports are chemical moieties, which are part of a single molecule. Recently a 50% phosphorescent yield was obtained for MTDATA:t-Bu-PBD thin film emitting at 540 nm. It is an organic salt with charge transfer occurs between the donor and acceptor moieties. Both MTDATA and t-Bu-PBD exhibits fluorescence emission around 370 and 440 nm respectively. The donor–acceptor system possesses spatially separated HOMO and LUMO and a high

electroluminescence efficiency with  $\Delta E_{ST} = 50$  meV [29]. The narrow value for  $\Delta E_{ST}$  can be maintained due to the intermolecular excited state or exciplex formation between the m-MTDATA and t-Bu-PBD. The thermal stability due to ionic interactions and the ease of preparation are advantages of an organic salt over a single molecule incorporating both the donor and acceptor. In this treatise, the fluorescence properties of the donor and acceptor system, CNBA<sup>-</sup> · AP<sup>+</sup> salt, in solution have been reported in combination with the crystal structure, morphology, FTIR, UV–Vis–NIR and thermal analyses. The energy levels of the HOMO, the LUMO as well as  $\Delta E_{ST}$  were calculated with a time dependent DFT method using Gaussian 03 software.

## 2. Experimental section

### 2.1. Crystal growth

Single crystals of CNBA<sup>-</sup> · AP<sup>+</sup> were grown from slow evaporation in ethanol solution. A calculated amount of 0.251 g of CNBA (1.25 mmol) and 0.136 g of AP (1.25 mmol) were dissolved in ethanol and the solution was stirred for one hour for complete dissolution. The obtained solution was filtered using Whatman filter paper. The filtered solution was covered with perforated foil and kept at room temperature for complete evaporation. Plate-like pale-yellow CNBA<sup>-</sup> · AP<sup>+</sup> crystals were obtained within 5 days. The crystals were recrystallized several times and a suitable transparent crystal was used for single crystal X-ray diffraction.

### 2.2. Single crystal X-ray diffraction and X-ray powder diffraction

X-ray diffraction data were collected on a Bruker Kappa APEXII single crystal X-ray diffractometer. Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation with graphite monochromator was used. Data were reduced using SAINT/XPREP (Bruker, 2004). Lorentz and polarization corrections were included. All non-hydrogen atoms were found using the direct method analysis in SHELX-97 [30] and after several cycles of refinement, the positions of the hydrogen atoms were calculated and added to the refinement process. Supplementary crystallographic data can be found in the Cambridge Crystallographic Data Centre at free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif/](http://www.ccdc.cam.ac.uk/data_request/cif/); CCDC ID 940688. Crystal data and structure refinement details can be found in Table 1.

X-ray Powder Diffraction (XRPD) data were collected on a Rigaku MiniFlex II diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) at 20 kV over a  $2\theta$  range of 10–60° at a scan rate of 5°/min. A gently ground crystalline sample of CNBA<sup>-</sup> · AP<sup>+</sup> was used for this measurement.

### 2.3. Scanning electron microscopy (SEM)

The morphology of the CNBA<sup>-</sup> · AP<sup>+</sup> crystals was examined using a JEOL JSM-5800 Scanning Electron Microscope (SEM). The samples were fixed on a metal stud using carbon tape and covered by approximately 10 nm gold coating. 15 kV was used to accelerate the electron beam and the secondary electrons were used to record the image.

### 2.4. Infrared spectroscopy

The FTIR spectrum was recorded in KBr in the frequency region of 400–4000 cm<sup>-1</sup> using a Bruker spectrometer with a resolution of 4 cm<sup>-1</sup>. For the sample preparation, about 3 mg of sample was ground with ~250 mg KBr using a mortar and pestle and pressed with a metal die to prepare the pellet.

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