

Striking Effect of Intra- versus Intermolecular Hydrogen Bonding on Zwitterions: Physical and Electronic Properties

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S Supporting Information

ABSTRACT: We report the synthesis, characterization, and application of novel zwitterions. The zwitterionic structures consist of a positively charged cyanine and negatively charged dienolate moieties, confirmed by experimental observations and theoretical calculations. Single crystal X-ray studies revealed that **BIT-(NPh)₂** is a coplanar molecule that forms 1-D chains via π - π interactions. In contrast, **BIT-(NHexyl)₂** is a twisted molecule with a dihedral angle of 78° between the charged planes. In charge transport studies, thin films of the flat zwitterion show semiconducting properties, with a hole mobility of $2.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while the twisted zwitterion is a high resistivity insulator.

A zwitterion is an overall neutral molecule with a positive and a negative electrical charge at different locations within the molecule.¹ Amino acids are the best-known examples of zwitterions at a particular pH. Only a handful of aromatic zwitterions have been reported, such as quinonoid,^{2–5} bisdithiazolopyridone,⁶ hexaazaanthracene,^{7–10} and squaraine.¹¹ Among these zwitterions, only squaraine zwitterions have found their place in organic electronics such as solar cells.^{12–15} The remaining zwitterions have been less explored.¹⁶ In the quinonoid system presented here, the positive and negative charges are delocalized as a nitrogen cyanine and an oxygen cyanine, respectively. Routaboul et al. have demonstrated film formation of quinonoid zwitterions on a gold surface and suggested that a highly conductive interface with a metallic electrode can be formed, resulting in improved efficiency of carrier injection into an organic film.² A study has also shown that quinonoid zwitterions, as a few nanometer thin layer deposited on a metallic (gold) surface, have electronic properties close to those of a semimetal.¹⁷

The molecule [2,2'-Bi-1*H*-indene]-3,3'-dihydroxy-1,1'-dione (**BIT-OH₂**) was first synthesized and characterized over 100 years ago by Gabriel and Leupold,¹⁸ using inexpensive starting materials via a simple two-step reaction. The molecule has been considered as an analog of the well-known dye, Indigo. However, only a few **BIT-OH₂** derivatives have been synthesized and the liquid crystallinity as well as photochromism have been reported.^{19–21} Very recently, Dou et al.

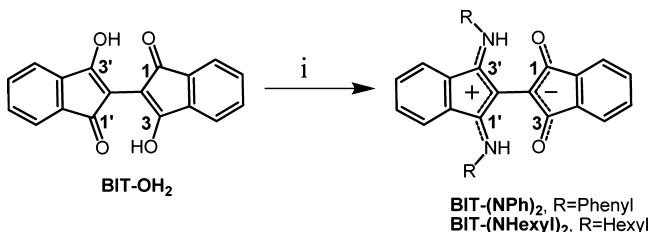
have discovered the formation of a single crystal polymer of a **BIT-diester**, through a highly efficient topochemical polymerization.²²

In this report, we functionalize the **BIT-OH₂** with aniline and 1-hexylamine in the 1' and 3' positions to form the zwitterions, [2,2'-Bi-1*H*-indene]-3',1'-dianiline-3,1-dione (**BIT-(NPh)₂**) and [2,2'-Bi-1*H*-indene]-3',1'-dihexylamine-3,1-dione (**BIT-(NHexyl)₂**), respectively. The zwitterionic structures are determined by experimental observations (Single X-ray diffraction, NMR, and ESR) and theoretical studies. In the zwitterionic form, the positive charge is delocalized on the cyanine moiety and the negative charge is delocalized as a dienolate. Single crystal X-ray studies showed that **BIT-(NPh)₂** is a coplanar molecule in contrast to a highly twisted **BIT-(NHexyl)₂**. The coplanar molecules are surrounded by neighboring molecules with the opposite charge. In contrast, the twisted zwitterion is organized by strong intermolecular hydrogen bonds to oxygen (1.980 Å) between adjacent zwitterions (within the chain) resulting in the formation of a well-organized 1-D helical structure with the enolate moieties in the molecule packed between the zwitterions in the adjacent column, resulting in head-to-tail arrangement and the formation of a well-organized 1-D ribbon structure. Density functional theory (DFT) calculations on these molecules showed that the zwitterionic structures are lower in energy by only ca. 1.0 kcal/mol than their nonzwitterionic isomers. Studies of an organic field-effect transistor (OFET) of the coplanar zwitterion show that it is a semiconductor, while the twisted molecule is a high resistivity insulator.

The synthetic route for both molecules is shown in Scheme 1. It was, indeed, an unexpected synthetic result from an attempt to prepare the 3,3' Bisamine adducts. These **BIT** derivatives were obtained in acceptable yields, on the order of ca. 50%. Both compounds were easily isolated by standard techniques. Proton and ¹³C NMR spectra supported our claim that these molecules are zwitterions, based on the observation of the chemical shifts for a symmetric molecule in solution NMR spectra for both cases. In contrast, the NMR spectra of the nonzwitterionic tautomer (one of the NH proton transfers

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Scheme 1. Synthetic Route for the Zwitterions^a

^a(i) Aniline or *n*-hexylamine (3.0 equiv), acetic acid (3.0 equiv), and a mixture of *n*-butyl alcohol and isopropyl alcohol (50:50), reflux for 6 h.

to the oxygen) would be expected to be much more complicated.

We obtained a single crystal of both molecules for X-ray diffraction characterization by slow evaporation of a mixture of a dichloromethane (DCM)/hexane solution. **BIT-(NPh)₂** crystallizes in a monoclinic unit cell, space group *P2(1)/n*. On the other hand, **BIT-(NHExyl)₂** crystallizes in a tetragonal unit cell, space group *I4(1)/acd*, suggesting that the molecules are highly ordered in the solid state. The *R*-factor values for **BIT-(NPh)₂** and **BIT-(NHExyl)₂** are 12.7% and 3.8%, respectively. The reason for the relatively poor crystal structure of **BIT-(NPh)₂** can be attributed to the poor quality crystals, resulting in weak diffracting power. We have failed to obtain a good quality crystal after many attempts. Therefore, the theoretical calculations (DFT as implemented in the VASP code)²³ on the crystal structures were carried out for a better understanding of the geometry, and especially the hydrogen bonding. Details of the calculations are given in the Supporting Information.

The carbon–carbon bond (C9–C10 for **BIT-(NPh)₂** and C5–C6 for **BIT-(NHExyl)₂**) between the cyanine and the dienolate units is a typical C–C single bond with a bond length of 1.476 Å (see Figure 1). More importantly, the bond lengths of

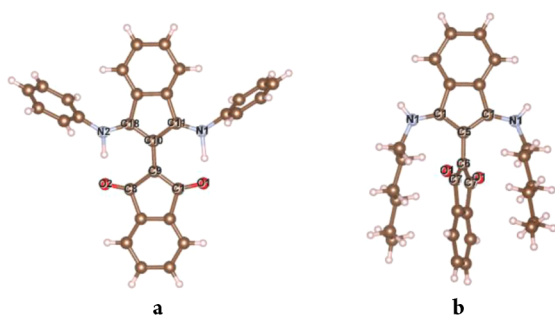


Figure 1. Molecular structures of both zwitterions: (a) molecule of **BIT-(NPh)₂**; (b) molecule of **BIT-(NHExyl)₂** (blue and red colors represent nitrogen and oxygen atom, respectively).

of the carbon–nitrogen bonds in both molecules are slightly shorter than the typical carbon (*sp*²)-nitrogen (*sp*²) single bond (1.34 Å),²⁴ due to delocalization of the charge over the cyanine. For the same reason, the carbon–oxygen bond lengths in both molecules are slightly longer than a carbon (*sp*²)-oxygen double bond in ketones (1.20–1.23 Å).²⁴ Since the theoretical results on the **BIT-(NHExyl)₂** crystal structure are consistent with the X-ray data and the crystal structure is quite accurate (*R* = 3.8%), the accuracy of the theoretical calculations on this new zwitterionic system is reliable to support the zwitterionic structure of **BIT-(NPh)₂**. Finally, the selected bond lengths of

both molecules from experimental results and theoretical calculations (in red) are shown on Table S1.

Molecule **BIT-(NPh)₂** is coplanar, with strong intramolecular O⋯H bonds of 1.28 and 1.44 Å length. Furthermore, the experimental N–H bond lengths (1.12 and 1.31 Å) are longer than the theoretical results (1.082 and 1.084 Å) for N–H covalent bonds. This suggests that the molecule in the solid state may not be the zwitterionic tautomer (one hydrogen is bonded to oxygen and the other weakly to nitrogen) or that there is a rapid equilibrium between the zwitterionic and nonionic form. However, the solid state ¹⁵N CP/MAS NMR of a polycrystalline sample of **BIT-(NPh)₂** shows only one signal at –220.13 ppm (Figure S7), indicating only one kind of a protonated Schiff base nitrogen. The nitrogen atom of a protonated Schiff base appears in the range –200 to –240 ppm.²⁵ Therefore, this result strongly supports that the zwitterionic form is the only tautomer for **BIT-(NPh)₂**. In the crystal packing, the molecules form 1-D chains via π – π interactions in which the molecules are related by translation along the *b*-axis with the closest interplanar distance of 3.518 Å and an angle of 37°. Along the 1-D chain, positive and negative charges of the molecules alternate (see Figure 2a). These close intermolecular interactions could favor charge transport in organic electronic applications.

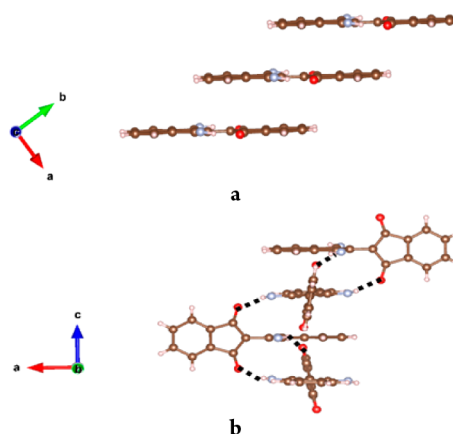


Figure 2. Crystallographic views of both zwitterions: (a) selected packing view of **BIT-(NPh)₂**; (b) selected packing view of **BIT-(NHExyl)₂** along the *b* axis (black dash lines represent the example of intermolecular hydrogen bonding). All the phenyl in **BIT-(NPh)₂** and hexyl in **BIT-(NHExyl)₂** groups are removed for clarity.

This is not the case for zwitterion **BIT-(NHExyl)₂**, where, within a chain of molecules, positive charges are adjacent to each other. This zwitterion is a twisted molecule with a dihedral angle of 78°, due to the presence of strong intermolecular hydrogen bonds to oxygen (1.980 Å) between adjacent zwitterions (within the column) resulting in the formation of a well-organized 1-D helical structure. Every molecule is 90° rotated along the *c* axis, relative to the neighboring molecules. All the positive charges are tightly packed into columns via π – π interactions. Similar molecular packing of twisted zwitterions was reported by Haddon et al.²⁶ The experimental nitrogen–hydrogen bond length (0.882 Å) is shorter than the theoretical result (1.041 Å). From the optimized crystal structure, the intermolecular O⋯H bond length is 1.823 Å. The closest distance between the cyanine units within the column is 3.283 Å (see Figure 2b). Moreover, the dienolate moieties are packed between the zwitterions within the adjacent column, resulting

in a head-to-tail arrangement and the formation of a well-organized 1-D ribbon structure (see Figure S3c). In conclusion, all these experimental and theoretical results for both zwitterions suggest that the nitrogen–hydrogen covalent bonding is more favorable over oxygen–hydrogen covalent bonding.

The absorption spectra of both zwitterions in DCM solution and as film are shown in Figure S1a. Both molecules have similar absorption in solution, exhibiting bands in the UV and visible region with an onset at 970 and 870 nm, respectively. This suggests that the most stable configuration of the two molecules in solution is essentially the same. In contrast, drop-cast films exhibit the onset of absorption in different regions. The **BIT-(NPh)₂** films show a much broader absorption than the twisted zwitterion, due to the different molecular conformation in the solid state (coplanar vs perpendicular). Cyclic voltammetry (CV) of both molecules (Figure S2) in DCM (0.1 M tetrabutylammonium hexafluorophosphate) reveals two one-electron reversible oxidation steps (0 and 0.5 V vs Ag/Ag⁺) and an irreversible reduction observed at ca. -0.3 V vs Ag/Ag⁺. The highest occupied molecular orbital (HOMO) values, calculated from CV (a ferrocene-ferrocenium (Fc/Fc⁺) redox couple was used as an internal standard (4.80 eV below the vacuum level)), are almost identical, ca. -4.7 eV. Meanwhile, the lowest unoccupied molecular orbital (LUMO) values of **BIT-(NPh)₂** and **BIT-(NHexyl)₂**, calculated from its optical band gap, are -3.4 and -3.3 eV, respectively. Finally, an electron spin resonance (ESR) signal for both zwitterions was not observed in either solution or the solid state, suggesting the absence of radical character in both molecules.

The geometry of the isolated molecules was optimized by the Gaussian program,²⁷ in which the wave functions are expanded by a Gaussian basis. The 6-31G(d,p) basis set was used, and the exchange-correlation potential and energy are described by a hybrid functional (B3LYP).^{28,29} The energy levels and the wave functions of the HOMO and the LUMO are calculated for the optimized geometry. The HOMO–LUMO maps of both zwitterions are shown in Figure 3. The LUMO orbitals of both

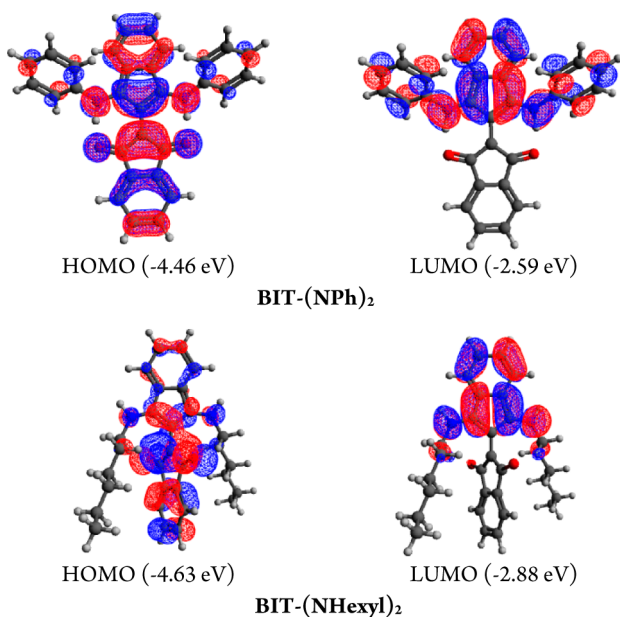


Figure 3. HOMO–LUMO maps of both zwitterions.

molecules are almost fully located on the cyanine moiety. For the planar structure **BIT-(NPh)₂**, the HOMO orbital is distributed all over the positive and negative parts. In contrast, the HOMO orbital of **BIT-(NHexyl)₂** is localized mainly on the enolate moiety. The HOMO–LUMO energy gaps for **BIT-(NPh)₂** and **BIT-(NHexyl)₂** are 1.88 and 1.75 eV, respectively. We have also calculated the energies of the nonzwitterionic tautomers (hydrogen covalently bonded to oxygen) for both zwitterions (see Figure S5 for the HOMO–LUMO map). The results suggest that the zwitterionic structures are lower in energy.

In order to attain structure–electronic properties correlations for both molecules, the charge transport was investigated by OFET devices with a bottom gate–bottom electrodes configuration. In the **BIT-(NPh)₂** devices, the source–drain current (I_{ds}) displays a linear response to low drain voltages (V_d) and saturates beyond certain V_d (Figure 4a). Moreover the

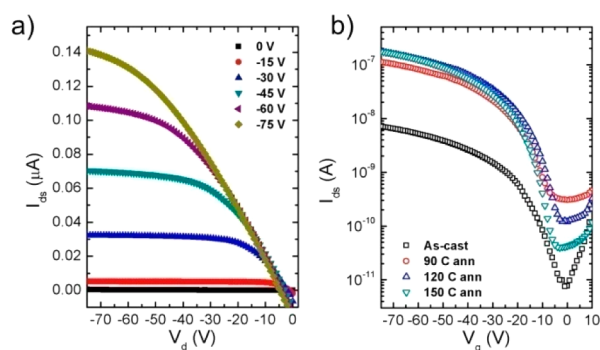


Figure 4. (a) Output characteristics of **BIT-(NPh)₂** OFETs annealed at 150 °C. (b) Transfer characteristics of **BIT-(NPh)₂** OFETs when annealed at various temperatures with $V_d = -70$ V.

I_{ds} proportionally increases with the gate bias (V_g). All these behaviors confirm the semiconductive property of the coplanar molecule, exhibiting a regular FET transport. On the other hand, when referring to FET characteristics based on **BIT-(NHexyl)₂**, the I_{ds} is reduced by orders of magnitude over that of the just described device and it remains nearly unchanged with different V_g (results not shown here). Since electronic conduction cannot be modulated by V_g , this implies that the twisted zwitterion is an insulator. Why do the two zwitterions have such different electronic properties? Although both zwitterions form 1-D chains, the orientation of orbital overlap are remarkably different. The HOMO orbital of the coplanar molecule is distributed over the whole molecule and the crystal packing maximizes the face-to-face orbital overlap, leading to the observed hole transport. In contrast, the LUMO orbital of **BIT-(NHexyl)₂** is located on the cyanine part and the 1-D helix should favor electron transport. However, the molecule is an insulator, possibly due to the poor face-to-face orbital overlap (every molecule is 90° rotated relative to the neighboring molecules). However, Haddon et al. showed that perpendicular, zwitterionic π -systems with an unpaired electron can lead to interesting electronic and magnetic properties.²⁶ Figure 4b shows transfer characteristics of **BIT-(NPh)₂** OFETs as a function of thermal annealing. Noticeably annealing leads to a 2 orders of magnitude enhancement of the hole mobility (μ_p), e.g. from $2.3 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $2.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when annealed at 150 °C. This increase can be primarily ascribed to the enhanced structural order and crystallinity. In addition, atomic force microscopy (AFM) studies of **BIT-**

(NPh)₂ and BIT-(NHExyl)₂ films show almost identical morphology, being very smooth with a roughness of 0.2 nm (Figure S6).

In this report, we have presented the synthesis and characterization of a novel class of aromatic zwitterions. The zwitterionic structures are confirmed by the experimental observations and the theoretical calculations. Single crystal X-ray studies have demonstrated that BIT-(NPh)₂ is a coplanar molecule with close intermolecular interactions. In contrast, BIT-(NHExyl)₂ is a twisted molecule with the two charged planes almost perpendicular to each other. Due to the presence of strong intermolecular hydrogen bonds to oxygen between adjacent zwitterions (within the column), a well-organized 1-D helical structure along the cyanine moieties is formed. Furthermore, DFT calculations on these molecules confirmed the zwitterionic structures are lower in energy by ca. 1.0 kcal/mol than the nonzwitterionic isomers. In charge transport studies, thin films of the coplanar structure show a hole mobility of $2.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, the twisted zwitterion does not exhibit any FET transport, behaving as an insulator. The orientation of orbital overlap in these zwitterions is responsible for the observed FET properties. To the best of our knowledge, this is the first observation of the profound effect on the electronic properties of zwitterions as a function of hydrogen bond interactions.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic procedures; absorption spectra; cyclic voltammetry; X-ray crystal structure, ¹⁵N NMR, DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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