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New insights in ambipolar sensors through fine tuning in phthalocyanine complexes

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Summary:

In the present work, we successfully synthesised a series of phthalocyanine complexes with varying the number and nature of halogens (F_0, F_8, F_{16} and Cl_8) and the metal centre (Co, VO, Zn and Cu). By engaging these molecules as a sublayer, we fabricated bilayer heterojunction sensors with $LuPc_2$ as a top layer and investigated their sensing properties towards both oxidizing and reducing gaseous species (NH_3, NO_2 and O_3). The resulting heterojunction devices exhibit p-type, n-type or ambipolar (both p- and n-type) behaviours, depending on an external trigger.

Keywords: Heterojunction, ambipolar device, ammonia, nitrogen dioxide, ozone.

Introduction

Molecular semiconductors exhibiting ambipolar charge transport properties have become a focal point in recent years within the field of organic electronics. Optimising the frontier molecular orbitals, the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), relatively to the Fermi energy level of electrodes, can influence the polarity of the molecular material and also facilitate ambipolar charge transport. Ambipolarity is often referred to a physical balance, characterized by an infinite number of unbalanced positions but only one stable state. It is achieved when the densities of electrons (e^-) and holes (h^+) contribute equally to electrical conduction. Theoretically, this equilibrium is realized in intrinsic semiconductors, yet trapping effects and specific environmental interactions may impede its observation. Tuning the e^- and h^+ concentrations near equilibrium to a sufficiently high level and choosing the suitable external triggers are crucial to achieve ambipolar charge transport. Among ambipolar organic semiconducting materials, phthalocyanines have attracted considerable attention due to their unique electrical properties and chemical stability. Specifically, lutetium bis-phthalocyanine ($LuPc_2$) stands out for its radical nature and for its huge density of e^- and h^+ near equilibrium enabling ambipolar charge transport in OFETs and heterojunction gas sensors. A few years ago Prof. M. Bouvet et al. introduced a novel device that consist of two different conducting layers: a poor conducting sublayer covered by highly conducting molecular material $LuPc_2$ as top layer. This concept inspired us to explore the potential of different types of poor conducting molecular materials as sublayer in a bilayer organic heterojunction device combining it with $LuPc_2$. Since $LuPc_2$ has huge e^- and h^+ densities at near equilibrium, the polarity of the device is highly influenced by the nature of the sublayer. In current scenario, we investigated the electrical and sensing properties of octahalogeno-phthalocyanine-based heterojunction device under different conditions and delved into its ambipolar behaviour using different external triggers. For very first time, we reported the inversion in nature of majority charge carriers in conductometric sensors induced by an external trigger such as light, temperature and humidity exposure. Fig. 1 depicts the triggers utilized in this work to invert the nature of majority charge carriers in the ambipolar device.

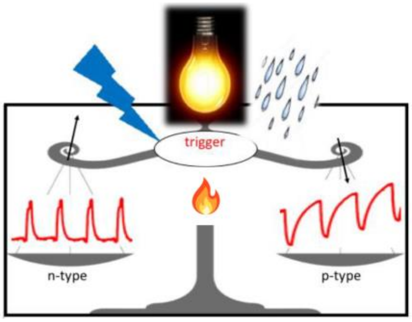

Fig. 1. schematic view of triggers (voltage, light, humidity and temperature) capable of changing from n-type to p-type.

Results

The $ZnCl_8Pc$, CuF_8Pc, CoF_8Pc and VOF_8Pc-based heterojunction devices exhibit both p- and n-type (ambipolar) behaviour depending on humidity level, gas species, optical trigger, and temperature variations. The $ZnCl_8Pc/LuPc_2$ device exhibits p-type behaviour towards NH_3 exposure at high relative humidity (50% rh) values and turns to n-type behaviour at low humidity (30%), displaying the ambipolar transport mechanism within the device (Fig. 2a). This suggests that water molecules serve not only as e^- dopant in the top layer but also gradually diffuse into the sublayer. As a result, subsequent e^- doping in the sublayer reduces its electron affinity, inverts the charge hopping pathways at the interface [1]. Consequently, this transformation inversed the device polarity. On other hand, the $CuF_8Pc/LuPc_2$ device exhibits p-type behaviour in dark and n-type behaviour under visible light illumination towards NH_3. Light illumination on semiconducting devices is well known for facilitating oxygen desorption from the surface of sensing materials, which induces a detrapping of negative charges [2]. Upon light exposure the desorption of oxygen molecules is favoured. Hence, there is an inversion in nature of majority charge carriers, which leads to an inversion in gas response. Most surprisingly, $CoF_8Pc/LuPc_2$ sensor exhibits n-type behaviour under NH_3 exposure and p-type behaviour under NO_2 and O_3 exposure. This change in polarity depends on the nature of the target gases, exhibiting another type of the ambipolar behaviour, compared to the light effect mentioned above. Very recently, we discovered a novel application of temperature variation as an external trigger for ambipolar device. Under NO_2, the $VOF_8Pc/LuPc_2$ device exhibits p-type behaviour in ambient conditions (20 °C and 45% rh) and n-type under thermal condition (80 °C and 45% rh) (Fig 2b). At the same time, it is important to note that $LuPc_2$ is the only common top layer in all these sensors that can interact with gas molecules. Thus the electron transfer takes place between gas molecules and $LuPc_2$, which leads to a change in charge carrier density in the top layer. Since the charge densities of these sublayers were optimized to near equilibrium by tuning the macrocycle with a precise degree of halogenation and selecting a metal centre with suitable electronegativity, even a slight variation in the trapping effect or oxygen adsorption/desorption kinetics can inverse the nature of majority charge carrier density. However, facilitating oxygen desorption from the sensing materials remains a significant challenge, requiring appropriate external triggers. It is worthy to mention that all these ambipolar sensors exhibit high sensitivity even at low gas concentrations and display limit of detection (LOD) values in the ppb range. Comparison of all these sensors is given in Tab. 1.

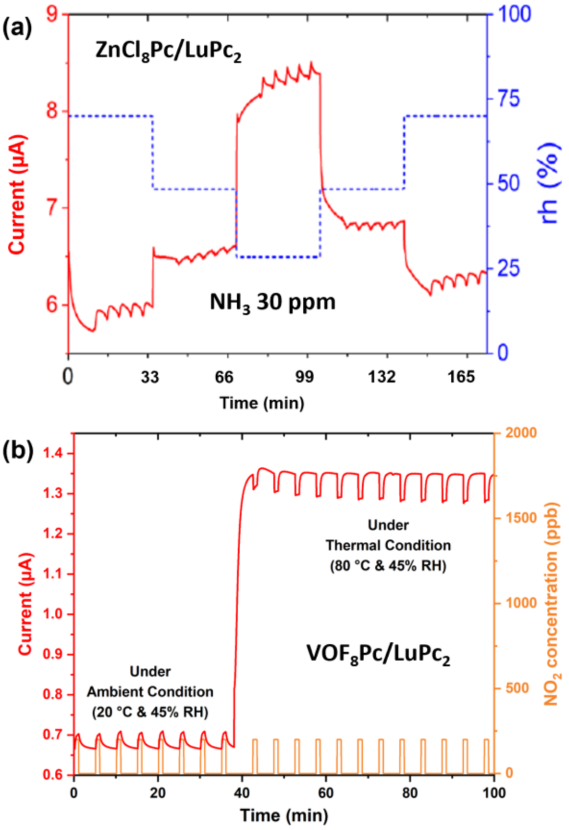

Fig. 2. Response of $ZnCl_8Pc/LuPc_2$ (a) and $VOF_8Pc/LuPc_2$ (b) heterojunction devices under NH_3 and NO_2, respectively, at different conditions.

Tab. 1: Change in current under different conditions. Upward arrows represent current increase and downward arrows represent current decrease.

Sensors	Ambipolar state	
$ZnCl_8Pc/LuPc_2$	NH_3: 50% rh – ▼	NH_3: 30% rh – ▲
$CuF_8Pc/LuPc_2$	NH_3: Dark – ▼	NH_3: Light – ▲
$CoF_8Pc/LuPc_2$	NH_3 – ▲	NO_2 and O_3 – ▲
$VOF_8Pc/LuPc_2$	NO_2 : 20 °C – ▲	NO_2 : 80 °C – ▼

References

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