



## Phthalocyanine- and porphyrin-based GUMBOS for rapid and sensitive detection of organic vapors



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### ABSTRACT

Metal complexes of porphyrins and phthalocyanines are attractive materials for designing recognition elements for chemical sensors, and hence they have been the focus of intense research. An interesting feature of these materials is that they can be functionalized at multiple positions to create sensors having slightly different selectivities. Considering the importance of these materials, herein, we report the synthesis and vapor-sensing characteristics of novel porphyrin- and phthalocyanine-based GUMBOS. More specifically, sodium counterions of copper (II) meso-tetra (4-carboxyphenyl) porphyrin (CuTCPP) and copper phthalocyanine-3,4',4''-tetrasulfonic acid (CuPcS<sub>4</sub>) were replaced by trihexyl(tetradecyl)phosphonium cations to respectively produce the GUMBOS compounds, [P66614]<sub>4</sub>[CuTCPP] and [P66614]<sub>4</sub>[CuPcS<sub>4</sub>]. The resulting compounds were found to be solids with considerably lower melting points. These GUMBOS were then coated on the surface of a quartz crystal resonator, and the vapor sensing characteristics were evaluated by exposing the sensors to 11 different organic vapors. These materials exhibited excellent sensing characteristics; moreover, the two sensors exhibited cross-reactive response patterns, making these compounds very promising candidates for array-based vapor-sensing applications.

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## 1. Introduction

Cyclic tetrapyrroles such as phthalocyanines and porphyrins are an interesting class of materials that have attracted considerable attention because of their unique properties and flexible synthesis. These macrocyclic compounds are particularly noted for their high thermal, chemical, and photochemical stabilities and have thus found diverse uses in various fields. Such uses include, but are not limited to, as sensing materials for chemical sensors [1–4], photosensitizers for dye sensitized solar cells [5–7], photoconductors [8,9], light emitting materials [10], photosensitizers in photodynamic therapy [11,12], and many other uses [13]. In particular, these macrocycles and their metal complexes have been shown to interact with a large number of gases and vapors, and hence they have been widely employed as molecular recognition elements for gas-phase detection of a wide range of analytes

through implementation of different transduction principles [1–4]. To clarify, the interaction of vapors with these macrocycles, and the resulting changes in mass, optical, or electrical properties can be measured by a suitable transducer in order to obtain qualitative and/or quantitative information about the target chemical species. Among previously used transducers, the quartz crystal microbalance (QCM) has been particularly attractive, and in this regard, cyclic tetrapyrroles and their metalloderivatives have been shown to be very promising coating materials for sensitive detection of a wide array of organic vapors [14–27].

The key component of a sensor system is the sensing material since it determines the selectivity and sensitivity of a chemical sensor. Therefore, much attention has been focused on the design and evaluation of novel or improved sensing materials. Two approaches have been commonly employed to design sensing materials [28,29]. The conventional approach involves the development of highly selective materials such as molecularly imprinted polymers, zeolites, and cavitands which strongly bind to an analyte of interest [28]. However, the synthesis of a highly selective material for each analyte is challenging, and at the same time this approach

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is not useful for analyses of complex mixtures [29]. A more modern approach involves development of materials that show broad and partial selectivity toward a wide range of analytes. A group of cross-reactive sensors is then used to obtain a response pattern specific to an analyte or complex mixture. The collection of such sensors is known as a sensor array or electronic nose, and the first electronic nose to discriminate between complex odorant mixtures was reported by Persaud and Dodd in 1982 [30]. Phthalocyanine and porphyrin derivatives are ideally suited for sensor array applications because they absorb a large number of chemical species; moreover, the selectivity of these materials can be finely tuned by altering the central metal atom as well as the peripheral substitution pattern [17,19,22,23]. As an illustration, Di Natale et al. [24] have developed an electronic nose comprising eight QCM sensors, each coated with a different metalloporphyrin derivative, and have demonstrated with high accuracy that the breath of lung cancer patients is different from that of healthy individuals. Although cyclic tetrapyrroles have been demonstrated as excellent sensing materials for QCM sensors, some aspects of this class of materials still require further improvement. For example, imperfect adhesion of the film to the transducer surface, low sensitivity, complex deposition procedures, and slow response times are major limitations associated with such materials [15–20].

The QCM is a common mass-sensitive transducer whose operating principle is based on the converse piezoelectric effect. It comprises a thin circular plate of AT-cut quartz crystal sandwiched between two circular metallic electrodes. Applying an AC voltage across the electrodes causes the quartz crystal to undergo thickness shear mode (TSM) oscillations with resonance frequencies in the megahertz (MHz) region. The resonance frequency of the crystal is the central parameter that provides important information regarding analytical measurements. The use of the QCM transducer as a sensor, however, requires immobilization of a thin film of suitable sensing material on the surface of the crystal. The frequency and amplitude of the shear wave are then altered as it propagates through the film. Interaction of an analyte with the coating material causes a change in mass and/or viscoelastic properties of the coating; as a result, further alterations in the wave characteristics will occur. The relationship between the frequency shift ( $\Delta f$ ) and the surface mass was first derived by Sauerbrey, which is mathematically expressed as [31]:

$$\Delta f = -\frac{n}{C} \Delta m = -\frac{n}{C} \rho_f t_f \quad (1)$$

where  $\Delta m$  is mass per unit area of the film (in air or vacuum),  $\rho_f$  the density of the film,  $t_f$  the thickness of the film,  $n$  the harmonic number which can only be an odd integer, and  $C$  is the mass sensitivity or Sauerbrey constant which depends on the fundamental resonance frequency and properties of the quartz ( $C = 17.7 \text{ ng cm}^{-2} \text{ Hz}^{-1}$  for a 5 MHz AT-cut quartz crystal). It should be noted that this relationship is applicable only for a small mass which is rigidly and uniformly deposited on the surface. For viscous and viscoelastic films, some modifications to the Sauerbrey equation have been proposed [32–34]. In addition, for such films, the wave also undergoes attenuation which can be estimated by measuring another parameter known as motional resistance ( $R$ ) or dissipation ( $D$ ) [33,34].

Herein, we report the synthesis and vapor-sensing characteristics of two representative GUMBOS, one derived from porphyrin and the other derived from phthalocyanine. GUMBOS, an acronym for a 'group of uniform materials based on organic salts', is a collective term that we use to refer to solid phase ionic liquids and related organic salts with melting points up to 250 °C, while ionic liquids (ILs) are defined as organic salts that melt below 100 °C [35,36]. Thus, GUMBOS are solids at room temperature and have a melting point range of 25–250 °C. Specifically, copper (II) meso-tetra(4-carboxyphenyl)porphyrin (CuTCPP) tetrasodium

salt was reacted with trihexyl(tetradecyl)phosphonium chloride ([P66614][Cl]) to produce [P66614]<sub>4</sub>[CuTCPP]. Similarly, copper phthalocyanine-3,4,4',4''-tetrasulfonic acid (CuPcS<sub>4</sub>) tetrasodium salt was reacted with [P66614][Cl] to obtain [P66614]<sub>4</sub>[CuPcS<sub>4</sub>]. Both of these compounds were found to be solids at room temperature. Thin films of these compounds were deposited on the surface of the quartz crystal resonator by dipping the crystal into a solvent/nonsolvent/GUMBOS ternary mixture, and subsequently evaporating the more volatile solvent. The vapor-sensing characteristics of these films were then evaluated by exposing each sensor to 11 different organic vapors over a wide range of concentrations. Each sensor exhibited high sensitivity, rapid response, and partial selectivity toward all vapors. Moreover, the two sensors exhibited cross-reactivity patterns, thereby making these materials promising candidates for array-based vapor sensing applications.

## 2. Experimental

### 2.1. Materials

Copper phthalocyanine-3,4,4',4''-tetrasulfonic acid (CuPcS<sub>4</sub>) tetrasodium salt, trihexyl(tetradecyl)phosphonium chloride ([P66614][Cl]), lithium *N,N*-bis-(trifluoromethane)sulfonimide (LiTFSI), heptane, acetonitrile, chloroform, toluene, methanol, 1-propanol, 2-propanol, 1-butanol, dichloromethane (DCM) and 3-methyl-1-butanol were obtained from Sigma–Aldrich (St. Louis, MO, USA). Copper (II) meso-tetra(4-carboxyphenyl)porphyrin was obtained from Frontier Scientific, Inc. (Logan, UT, USA). Acetone was obtained from Avantor Performance Materials, Inc. (Center Valley, PA, USA). Absolute ethanol was obtained from Pharmco Products, Inc. (Brookfield, CT, USA). All chemicals were used as received without any further purification.

In these studies, two different types of QCM instruments were employed. A QCM200 system and the associated AT-cut polished chromium/gold quartz crystals were purchased from Stanford Research Systems, Inc. (Sunnyvale, CA, USA). A quartz crystal microbalance with dissipation monitoring (QCM-D) E4 system and the associated gold-coated quartz crystals were obtained from Q-Sense AB (Gothenburg, Sweden). For both the instruments, AT-cut quartz crystals with the fundamental resonance frequency of 5 MHz were used. Mass flow controllers (Model 5850E), along with instrument control and read out equipment (Model 5878) were purchased from Brooks Instrument, LLC (Hatfield, PA, USA), and polytetrafluoroethylene (PTFE) containers were procured from SPI Supplies/Structure Probe, Inc. (West Chester, PA, USA).

### 2.2. Synthesis of GUMBOS and IL

The GUMBOS and IL were synthesized by using a metathesis reaction in a binary solvent mixture [37]. Briefly, copper (II) meso-tetra(4-carboxyphenyl)porphyrin (CuTCPP) was neutralized using an excess of sodium hydroxide in water to obtain the soluble tetrasodium salt. The other reactant [P66614][Cl] was dissolved in DCM, and subsequently these two solutions were mixed and stirred for 24–48 h to obtain [P66614]<sub>4</sub>[CuTCPP]. Likewise, [P66614]<sub>4</sub>[CuPcS<sub>4</sub>] was prepared by reacting CuPcS<sub>4</sub> and [P66614][Cl]. The ion exchange reactions are outlined in Fig. 1a and b. Tetrasodium salts of phthalocyanine and porphyrins are soluble in water, but insoluble in DCM. By contrast, [P66614][Cl] is soluble in DCM, but insoluble in water. Therefore the sodium salts of phthalocyanine and porphyrin were dissolved in water, and [P66614][Cl] was dissolved in DCM. The products [P66614]<sub>4</sub>[CuTCPP] and [P66614]<sub>4</sub>[CuPcS<sub>4</sub>] are soluble in DCM, but insoluble in water. Hence, these compounds were found in the DCM layer. While preparing these compounds, the water soluble reactant was used

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