Semiconductive Microporous Hydrogen-Bonded Organophosphonic Acid Frameworks

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Abstract: We report the first semiconductive, proton-conductive, microporous hydrogen-bonded organic framework (HOF) derived from phenylphosphonic acid and 5,10,15,20-tetrakis[p-phenylphosphonic acid] porphyrin (known as GTUB5). The structure of GTUB5 was characterized using single crystal X-ray diffraction (XRD). A narrow band gap of 1.56 eV was extracted from a UV-Vis spectrum of pure GTUB5 crystals, in excellent agreement with the 1.65 eV band gap obtained from density functional theory calculations. The same band gap was also measured for GTUB5 in DMSO.

The proton conductivity of GTUB5 was measured to be 3.00 × 10⁻⁶ S cm⁻¹ at 75 °C and 75 % relative humidity. The surface area of GTUB5’s hexagonal voids were estimated to be 422 m² g⁻¹ from grand
canonical Monte Carlo simulations. XRD showed that GTUB5 is thermally stable under relative humidities of up to 90 % at 90 °C. These findings pave the way for a new family of microporous, organic, semiconducting materials with high surface areas and high thermal stabilities. Such materials could find applications in printed electronics, optoelectronics, and electrodes in supercapacitors.

**One Sentence Summary:** We report a new family of thermally stable, proton-conductive, microporous, organic semiconductors with high surface areas.

**Main Text:** Metal organic frameworks (MOFs) emerged as revolutionary microporous materials at the beginning of the 21st century[1-3]. Owing to their well-ordered pores, which are surrounded by inorganic and organic components, MOFs have been used in a wide range of applications, such as gas storage/separation[4-7], catalysis[8-13], magnetism[14-16], electric conductivity[17-19], proton conductivity[20-22], and drug delivery[23-25]. In parallel to MOF research, another closely related family of supramolecular architectures known as hydrogen-bonded organic frameworks (HOFs) has attracted immense interest in recent years[26-28]. In HOFs, the linker connectivity is achieved via hydrogen-bonded networks rather than inorganic building units (IBUs)[29-33]. Hydrogen bonds provide simpler connectivity options compared to the complex molecular, one-, two-, and three-dimensional IBUs of MOFs[34]. Therefore, the design and synthesis of stable hydrogen-bonded supramolecular networks can be more easily achieved compared to that of MOFs. HOFs are also more convenient to recycle and are free of heavy metal ions, providing environmentally friendly solutions. The recent interest in HOFs has resulted in several review articles[34-37] summarizing their applications in CO₂ capture[38-40] and proton conductivity[41, 42]. However, to date, no semiconducting HOFs have been reported in the literature. Thermally stable and permanently microporous semiconducting HOFs could revolutionize the design of supercapacitors and electrodes due to their simpler chemistry compared to MOFs. In this communication, we present the first example of a HOF (known as GTUB5), synthesized using phosphonic acid functional groups R-PO₃H₂, which exhibits electrical conductivity, proton conductivity, and high thermal stability.
The phosphonic acid functional group has two protons and one oxygen from the P=O bond, which allow it to form multiple hydrogen bonds with other phosphonic acid groups and thereby stabilize the resulting HOF. Interestingly, the unique structure and multiple metal binding modes of the phosphonic acid functional group have led to some of the most thermally stable[34, 43-46] and chemically stable[34, 47-49] MOFs in the literature. The phosphonic acid functional group R-PO₃H₂ involves two deprotonation modes with pKa values of 1.7 and 7.4, respectively. Therefore, in order to create the first phosphonate HOF in the literature, we have adopted a novel crystallization method at pH’s between 1.7 and 7.4 with mixed phosphonic acid linkers of phenylphosphonic acid (PPA) and 5,10,15,20-tetrakis[p-phenylphosphonic acid] porphyrin (H₈-TPPA) to ensure that at least one of the phosphonic acid moieties is not fully

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Fig. 1: A) Portion of hydrogen-bonded network of GTUB5. B) Depiction of hexagonal void spaces in GTUB5. C) Tauc plot from the solid-state UV-Vis spectrum of GTUB5, showing a band gap of 1.56 eV. The second jump at 2.88 eV corresponds to the Soret band of the porphyrin core at 430 nm. D) Layer structure of GTUB5. E) One-dimensional hydrogen-bonded building unit of GTUB5. F) XRD pattern before and after the proton conductivity measurements.
deprotonated. H$_8$-TPPA exhibits a planar tetratopic geometry with a 90° angle between the phenylphosphonate tethers\cite{49-51}. Therefore, it is expected that within the mixed linker strategy H$_8$-TPPA and PPA could produce two-dimensional HOFs with hexagonal void channels.

The H$_8$-TPPA linker was synthesized according to our previously reported method involving a Pd-catalyzed Arbuzov reaction\cite{50}, in order to avoid the porphyrin core being occupied by Ni(II) after a Ni-catalyzed Arbuzov reaction\cite{49,51}. The synthesized metal-free H$_8$TPPA linker eliminated the possibility of metal-ligand interactions that could have triggered the formation of MOFs. GTUB5 was synthesized following a conventional MOF crystallization method in scintillation vials in DMF/EtOH at a pH between 1.7 and 7.44 to ensure the presence of protonated phosphonic acid functional groups\cite{32}. The synthesis of GTUB5 is quite facile, giving dark purple 1-2 mm long needle-shaped crystals in high yield (see supplementary materials for synthesis details). The dark purple color of GTUB5 is an indication of its semiconductive nature. The structure of GTUB5 was characterized using single crystal X-ray diffraction. As seen in Figures 1A and 1B, GTUB5 is composed of two-dimensional sheets of hydrogen-bonded H$_8$-TPPA and PPA moieties. The structure contains two different hydrogen bonding patterns, which are observed between different H$_8$-TPPA units and between H$_8$-TPPA and PPA (see Figure 1E). In the first pattern, the P=O bond from the H$_8$-TPPA unit is exclusively involved in creating the (almost linear) double hydrogen bonding pattern between each unit. In the second pattern, the hydrogen bond forms between the second protonated hydroxyl group of the H$_8$-TPPA and deprotonated PPA$^{2-}$. The four DMF solvent molecules in the HOF structure act as a Lewis base acquiring the PPAs’ protons. The Brunauer-Emmett-Teller (BET) surface area of GTUB5 was estimated to be 422 m$^2$ g$^{-1}$ from a simulated N$_2$ adsorption isotherm at 77 K (see Figure S2) obtained using the grand canonical Monte Carlo method (see supplementary materials for simulation details).
The band gap was estimated from a solid-state diffuse reflectance UV-Vis spectrum of the GTUB5 crystals (see Figure S7). As seen in Figure 1C, the Tauc plot derived from the spectrum yields a narrow band gap of 1.56 eV. The second jump at ca. 2.88 eV corresponds to the Soret band of the porphyrin core at 430 nm. A similar band gap was also obtained from a UV-Vis spectrum of a dissolved sample of GTUB5 in DMSO (see Figure S6), suggesting that the hydrogen-bonded supramolecular structure is not disrupted in a polar aprotic solvent. From a cyclic voltammetry measurement on GTUB5 in DMSO (see Figure S8), the first oxidation and reduction potentials were measured to be 0.42 V and -1.23 V, respectively, yielding a HOMO-LUMO gap of 1.65 eV, thereby supporting this hypothesis.

To gain insight into the semiconductive nature of GTUB5, we performed density functional theory (DFT) calculations. The details of the calculations, employing hybrid Gaussian plane-wave (GPW) and Slater-Type Orbital (STO) basis sets, can be found in the supplementary materials. Figure 2 shows a periodic representation of the optimized geometry, which is in close agreement with the experimental crystal structure (see Table S3 and Figures S3-S6). A single point calculation on the optimized structure yields a band gap of 1.65 eV, in very good agreement with the experimental result of 1.56 eV. As seen in Figure 2, the HOMO and LUMO are predominantly localized on some of the porphyrins within the supercell (in which, a single unit cell is delineated by the black rectangle), but not all of them; with the LUMO localized on the same porphyrins as the HOMO. The fact that the HOMO and LUMO are aligned along the axis perpendicular to the plane of the page within the supercell suggests that GTUB5 is only conductive along this direction.
Focusing in on the portions of the structure that have significant HOMO and LUMO density, we see that the HOMO and LUMO are indeed localized on the same porphyrin (see Figure 3). Moreover, they are mostly confined to a subset of the carbons and nitrogens. The HOMO is composed of $\pi$ orbitals mostly on sp$^2$ hybridized carbons and nitrogens, while the LUMO is composed of $\pi^*$ orbitals on some of the sp$^2$ carbons and nitrogens. As shown in Table 1, $\sim$75% of the HOMO and LUMO orbital contributions are from the carbon and nitrogen 2p orbitals of the porphyrin. Table 1 also shows that a HOMO-LUMO transition would lead to an increase in the carbon 2p$_x$ orbital population, a slight decrease in the carbon 2p$_y$ population, and a slight increase in the carbon 2p$_z$ population; while the nitrogen 2p$_x$ and 2p$_z$ populations both decrease (the 2p$_y$ population remains negligible). These results suggest that the semiconductive nature of GTUB5 is predominantly determined by $\pi$-$\pi^*$ transitions involving orbitals localized on some of the porphyrin carbons and nitrogens. Inspection of the projected density of states
(pDOS) confirms that the HOMO-LUMO gap is predominantly due to orbitals localized on carbons and nitrogens (see Figure 4).

**Fig. 3:** HOMO and LUMO iso-surfaces, corresponding to an electron density of 0.01 electrons per Å³. **A)** Top view. **B)** Side view. Red/blue correspond to the negative/positive phases. (O – red; N – blue; P – yellow; C – black; H – white)

| Carbon | 2px   | 2py   | 2pz   | Sum  |
|--------|-------|-------|-------|------|
| HOMO   | 0.366 | 0.042 | 0.134 | 0.541|
| LUMO   | 0.484 | 0.020 | 0.170 | 0.674|

| Nitrogen | 2px   | 2py       | 2pz  |
|----------|-------|-----------|------|
| HOMO     | 0.163 | 4.70x10⁻⁹⁷ | 0.053| 0.216|
| LUMO     | 0.048 | 5.22x10⁻⁴  | 0.020| 0.067|

**Table 1:** Contributions from the 2p orbitals on the porphyrin carbons and nitrogens to the HOMO and LUMO.
The thermal decomposition of GTUB5 was investigated via a thermogravimetric analysis (TGA) of hand-picked crystals up to 900°C. The TGA curve (see Figure S9) shows an initial 2% loss between 50 and 100°C, corresponding to the evaporation of the remaining MeOH on the crystal surface after the synthesis. The following ca. 12% step until 250°C corresponds to the loss of dimethylammonium cations (calculated to be 12.9 % based on the molecular formula). The remaining organic components of GTUB5 decompose in two steps at ca. 400°C and 900°C. The second large weight loss at ca. 900°C suggests the formation of phosphides above 400°C\textsuperscript{[52]}.

Given the presence of $–\text{PO}_3\text{H}_2$ groups in its hydrogen-bonded framework, the proton conductivity of GTUB5 was measured. Electrochemical impedance spectroscopy measurements were carried out at 75% and 90% relative humidity (%rh) and temperatures in the range of 25 to 75 °C (see supplementary materials and Ref. 53 for setup details). At 75% rh, we see that the proton conductivity of GTUB5...
increases from $8.29 \cdot 10^{-7}$ to $3.00 \cdot 10^{-6}$ S cm$^{-1}$ as the temperature is increased from 25 to 75°C, while a non-monotonic increase is observed at 90%rh (see Table 1 for full data set). Furthermore, at any given temperature, we observe an increase in the proton conductivity with increasing relative humidity. The activation energies, i.e., sum of the migration energy and the defect formation energy, were extracted from the slopes of the Arrhenius plots (see Figure S10) to be $E_A = 0.26$ eV and $E_A = 0.13$ eV at 75°C and 90°C, respectively. These low activation energy values suggest that a Grotthuss mechanism with high proton mobility (and therefore low migration energy) is the predominant mechanism for proton conduction through the framework. As seen in Figure 1F, the XRD pattern of the sample recorded before and after the proton conductivity experiments slightly changes, indicating that the structure was slightly affected by the humidified atmosphere and the applied temperatures up to 75°C during the measurements.

Table 1: Proton conductivities and activation energies ($E_a$) of GTUB5 at different relative humidities

| Relative humidity [%rh] | 75       | 90       |
|------------------------|----------|----------|
| 25 °C                  | $8.29 \cdot 10^{-7}$ | $3.55 \cdot 10^{-6}$ |
| Conductivity [S cm$^{-1}$] | 50 °C                  | $1.67 \cdot 10^{-6}$ | $3.26 \cdot 10^{-6}$ |
|                        | 75 °C                  | $3.00 \cdot 10^{-6}$ | $4.20 \cdot 10^{-6}$ |
| $E_A$ [eV]             |          | 0.26     | 0.13     |

Conclusion: In conclusion, we presented the first member, GTUB5, of a novel family of two-dimensional, microporous phosphonic acid HOFs (with a calculated surface area of 422 m$^2$/g). Given its low band gap (as confirmed by solid-state/solution measurements and DFT calculations), GTUB5 paves the way for the creation of new semiconductive microporous compounds. Within the context of semiconductive microporous compounds, GTUB5 is the first HOF in the literature exhibiting such a small band gap. The use of hydrogen bonds in constructing a framework comes with the advantages of
simpler connectivity options and no toxic metal ions (which could possibly lead to environmentally friendly solutions for capacitors and batteries). The hydrogen-bonded framework also renders GTUB5 proton-conductive (with proton conductivities on the order of $10^{-6}$ S cm$^{-1}$). Owing to its structure, the phosphonic acid group can give rise to structurally diverse frameworks, which could increase the number of potential HOF applications. GTUB5 has the same band gap of 1.65 eV in DMSO, suggesting that GTUB5 retains its hydrogen-bonded network in polar aprotic solvents. Therefore, phosphonate HOFs have the potential to revolutionize the semiconducting materials industry with applications in printed electronics, optoelectronics, photovoltaics, and electrodes in supercapacitors. Currently, we are focusing on different linker geometries and pH modulations to further optimize the pore sizes and conductive behavior of phosphonate HOFs.

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