Synthesis and Crystal Structure of Naphthalenediimide-based Coordination Polymers

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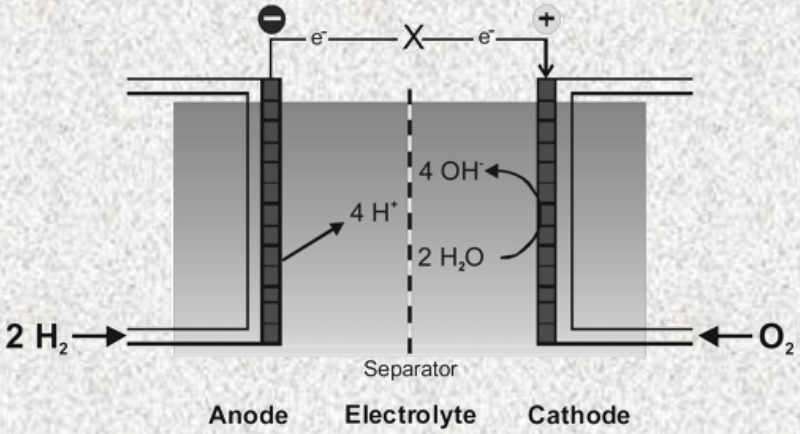
Motivation

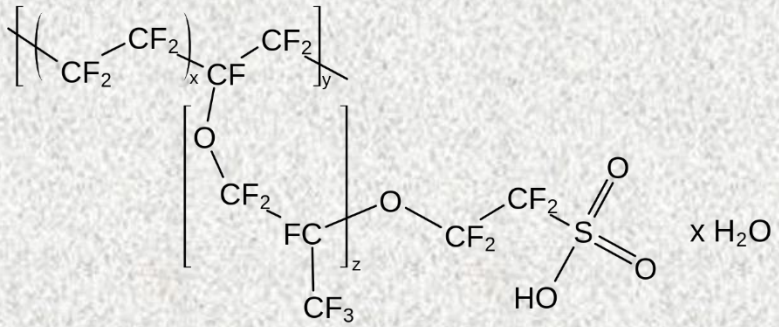
- Materials with high proton conductivity:
  - ✓ Proton-exchange membrane (PEM) fuel cells - “green” cells
  - ✓ Energy storage
  - ✓ Thermoelectrics
  - ✓ Sensing devices
  - ✓ Electrocatalysis



➢ **Figure 1: A hydrogen fuel cell depicting the continuous supply of reactants and redox reactions in the cell.**

DuPont's Nafion membranes

- Perfluorosulfonic acid polymer
- Sulfonate groups and
- Tetrafluoroethylene backbone (PTFE)



https://en.wikipedia.org/wiki/Nafion

Features

- Excellent thermal and mechanical stability
- Amorphous - inconsistent solubility and crystalline structure
- Conductivity is attributed to sulfonic acid groups & H_2O
- Protons on the SO_3H groups "hop" from one acid site to another
- Decline in proton conductivity (0.2 S/cm) at temperature above 80 ^{o}C
- It is a superacid catalyst

Goals: outline of specific aims

1) Porous metal-organic frameworks (MOFs)

2) Incorporate protogenic molecules: 1,2,4-triazole & imidazole

3) To illustrate the underlying proton conduction mechanism

- ✓ **The vehicular mechanism** - transport of protons through self-diffusion of proton carrier species
- ✓ Grotthuss or proton-hopping mechanism - conduction of protons within a hydrogen-bonded network of water molecules

Phosphonate-based metal-organic frameworks (MOFs)

- **Advantages**
- The geometry of RPO_3H_2, mimics that of the, RSO_3H, of Nafion
- RPO_3H_2 possesses two protonic acids rather than one on the sulfonate group.
- RPO_3H_2 has a higher charge and stronger coordination ability with oxophilic metal ions than sulfates

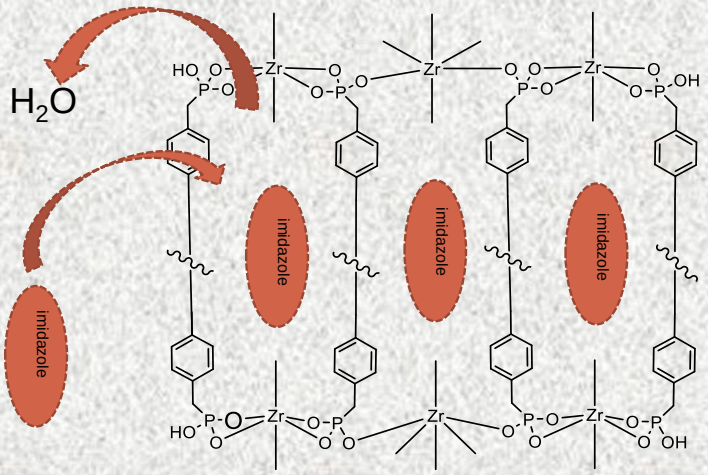
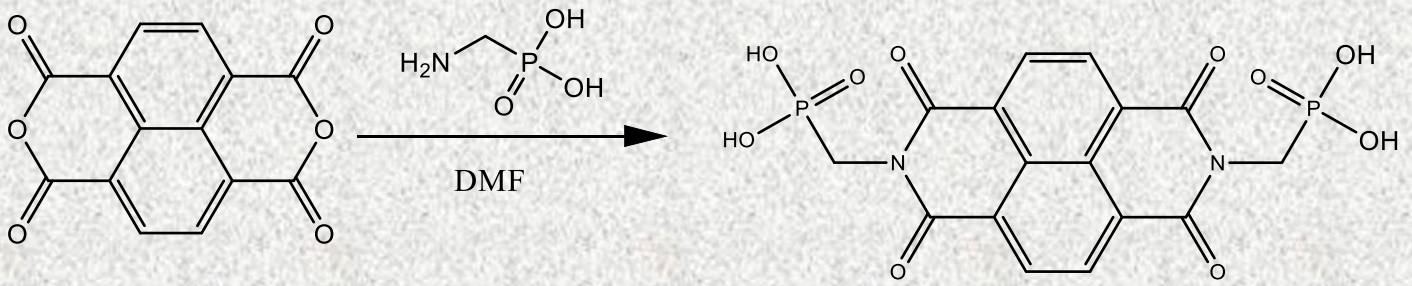


Fig. 2. Schematic of the processes whereby the lattice water molecule is replaced by imidazole molecule.

Synthesis of 1,4,5,8-naphthalenediimide bisphosphonic acid

- Reflux for 24 hours
- The reflux was performed at constant temperature. The selected temperature was between 130°C-160°C.



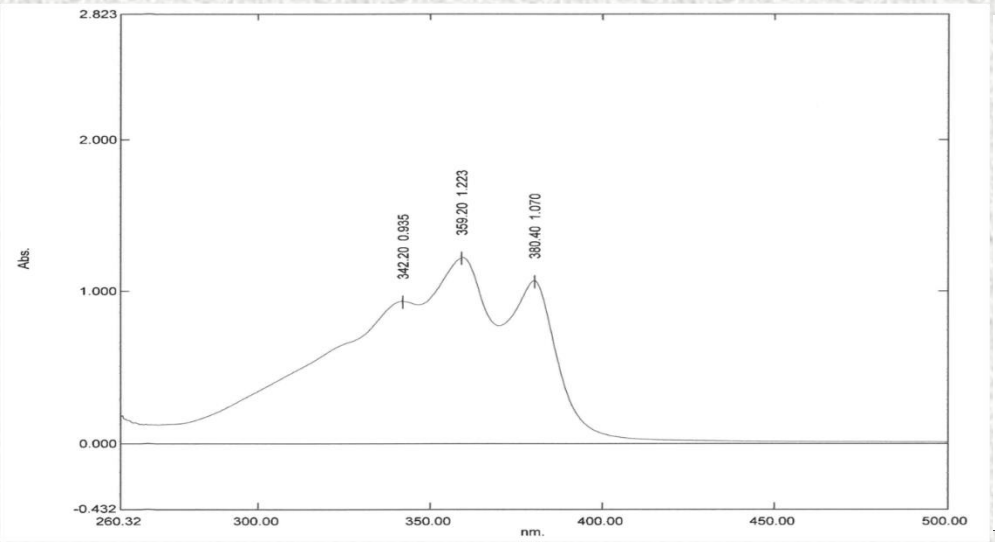
- **Fig. 2.** Condensation reaction of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and aminomethyl phosphonic acid to form 1,4,5,8-naphthalenediimide bisphosphonic acid

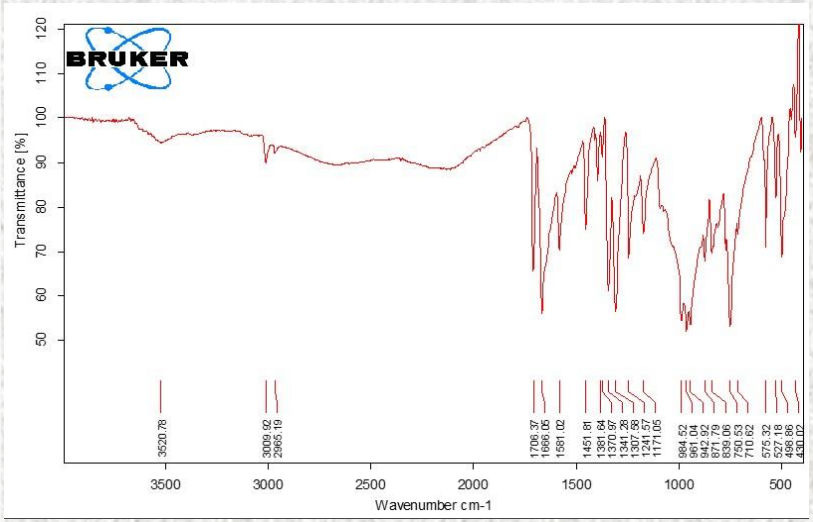
Synthesis and apparatus

Set-up diagram for the refluxing apparatus

UV-VIS and FT-IR

- **1,4,5,8-naphthalenediimide bisphosphonic acid**



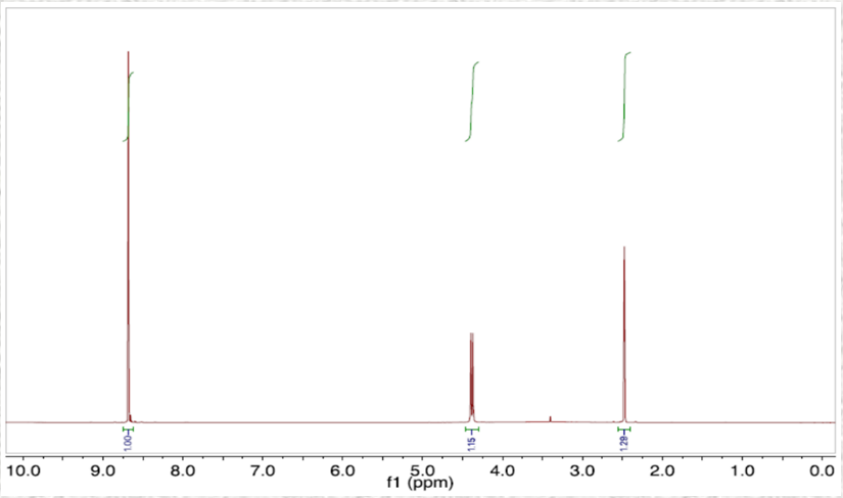


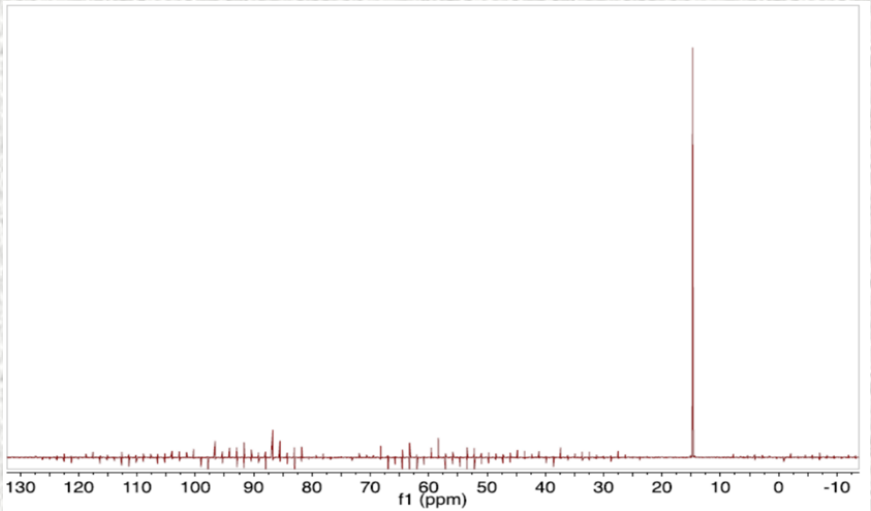
UV-Vis spectrum reveals the characteristic absorbance peaks for naphthalene backbone.

The C-N-C stretching vibrations of the imide ring are observed.

^{1}H-NMR and ^{31}P-NMR

1,4,5,8-naphthalenediimide bisphosphonic acid

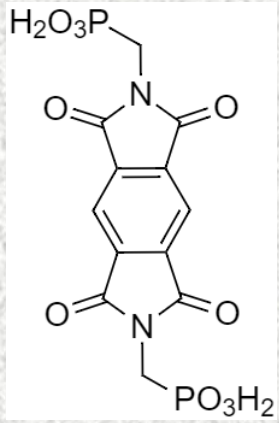




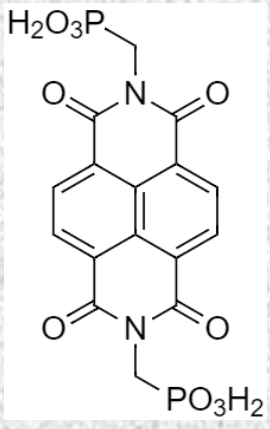
The peak at 8.7 ppm in the proton NMR confirms the aromatic hydrogens belonging to the naphthalene moiety.

^{31}P-NMR spectrum in indicates the presence of a singlet.

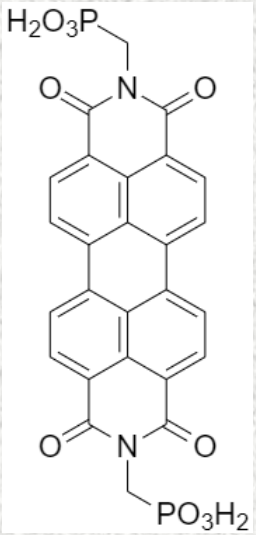
Chemical structure of ligands synthesized



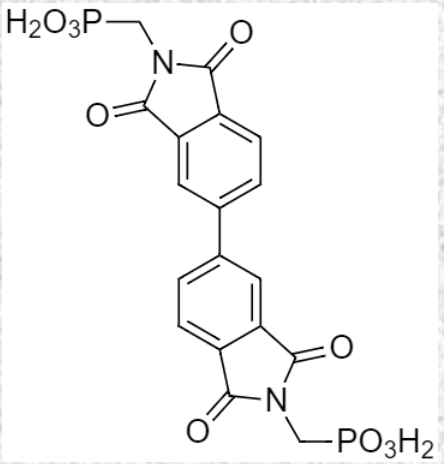
N,N´-bis (phosphonomethyl)-pyromellitimide (PPMI)



N,N´-bis (phosphonomethyl)-1,4,5,8-naphthalenediimide (PNDI)

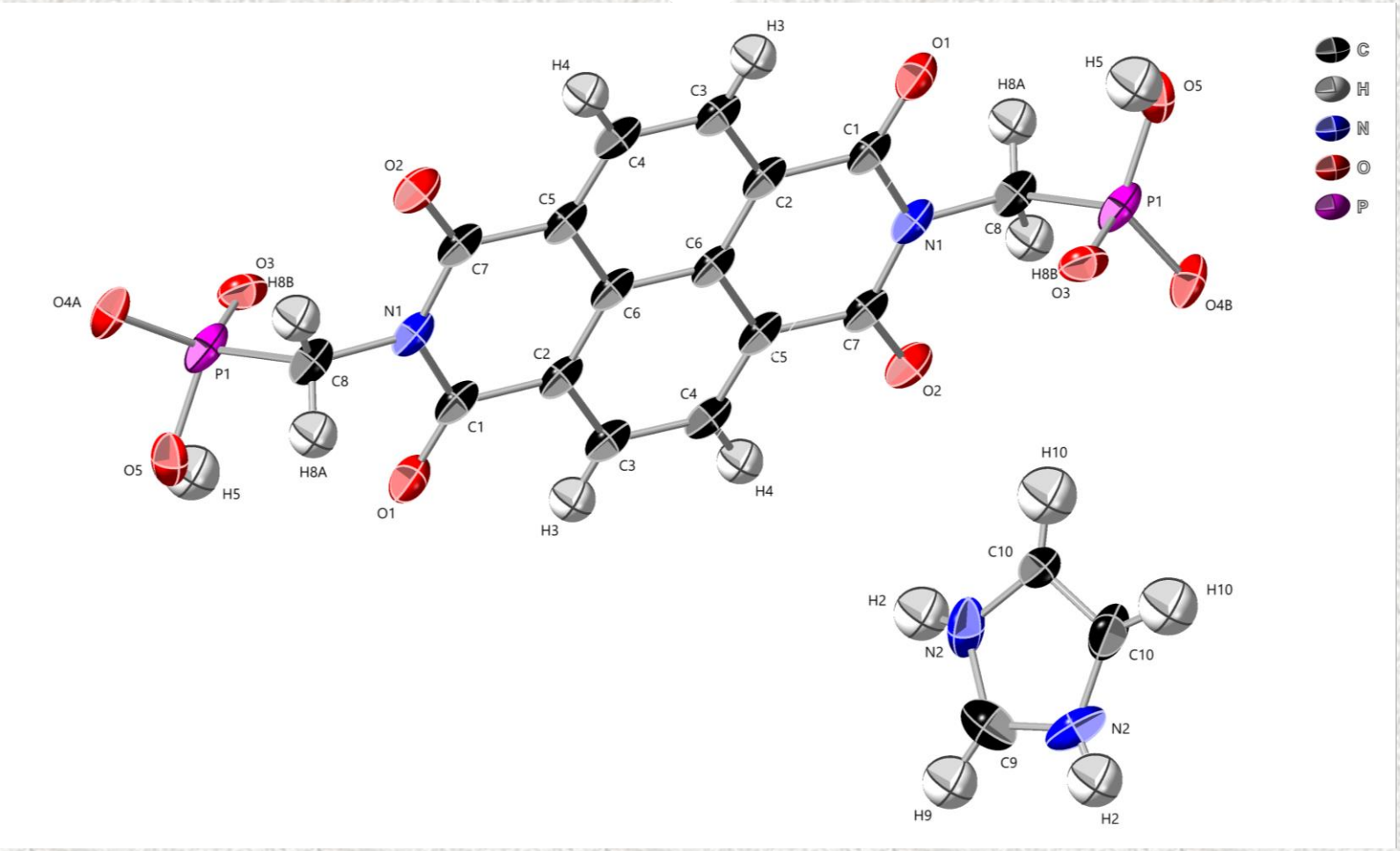


N,N´-bis (phosphonomethyl)-3,4,9,10-perylenediimide (PPDI)



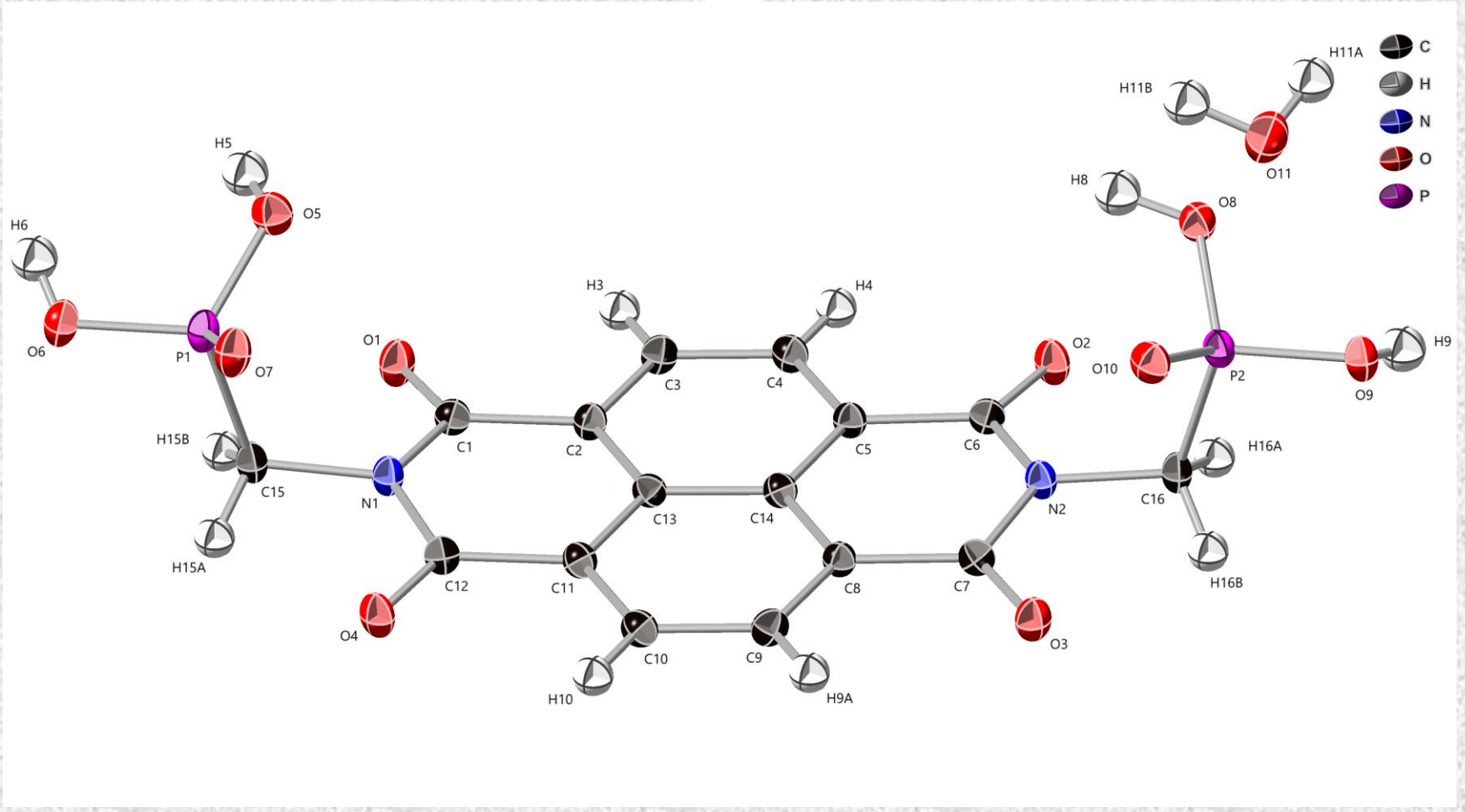
N,N´-bis (phosphonomethyl)-3,3′,4,4′-biphenylenediimide (PBDI)

The molecular structure of N,N´-bis (phosphonomethyl)-1,4,5,8-naphthalenediimide



Thermal ellipsoid are drawn at 50% probability level.

The molecular structure of N,N´-bis (phosphonomethyl)-1,4,5,8-naphthalenediimide



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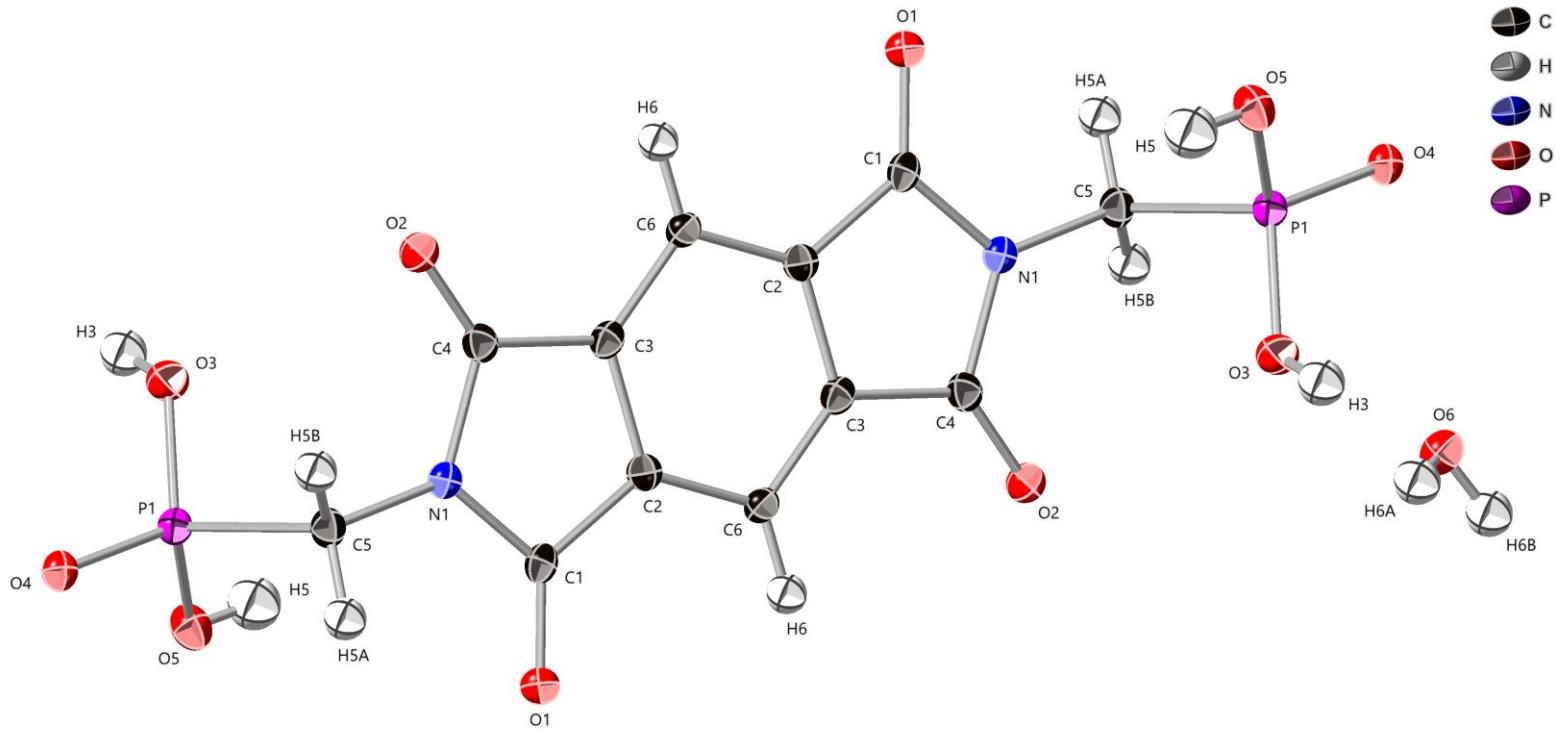
The molecular structure of N,N´-bis (phosphonomethyl)-pyromellitimide (PPMI)



Thermal ellipsoid are drawn at 50% probability level.

Conclusion and Future Work

- The spectroscopy data herein presented strongly suggests that and N,N´-bis(phosphonomethyl)-pyromellitimide and 1,4,5,8-naphthalene diimide bisphosphonic acid were successfully synthesized.
- High resolution mass spectrometry can be used to confirm the structure of our product.
- Future efforts will be geared towards the synthesis of other diimide bisphosphonic acids.
- The synthesis of MOFs based on diimides bisphosphonic acids.

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- Katia Campos

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Thanks