Progress Towards the Synthesis of Quinone-based Cathode Materials for New Rechargeable Battery Architectures

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Objective

- To develop a metal-organic framework (MOF) with built-in quinones that will serve as a porous cathode material for Mg ion batteries to trap electrons from electrolytes and make such electrons available during the charge-discharge process in an electrochemical cell reaction.

Overview

- Lithium metal batteries have limitations, but research on carbon composites offers a hopeful path forward for battery development. (Barbosa *et al.*, 2021).

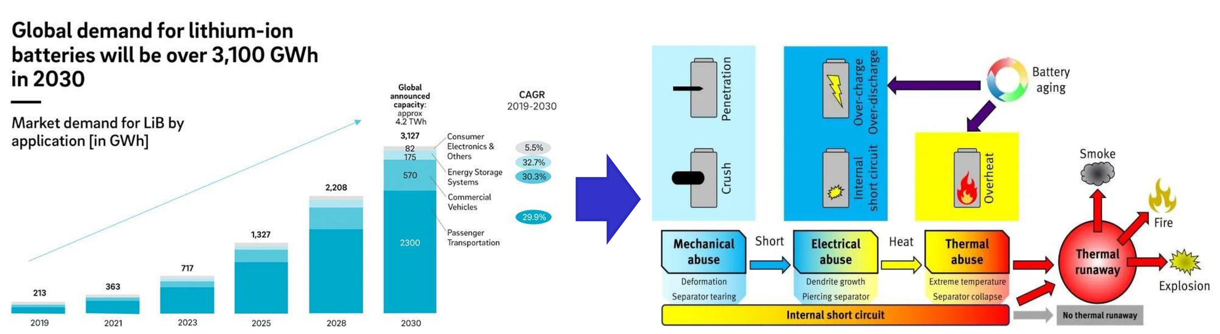

Fig 1: Global demand for Li-ion batteries (LIBs) and Lithium batteries failure mechanism (Wang et al., 2019)

- Rechargeable magnesium batteries (RMBs) are vital for sustainable energy, with improved performance and safety over lithium batteries, though facing challenges like low cathode intercalation rates and electrolyte issues.

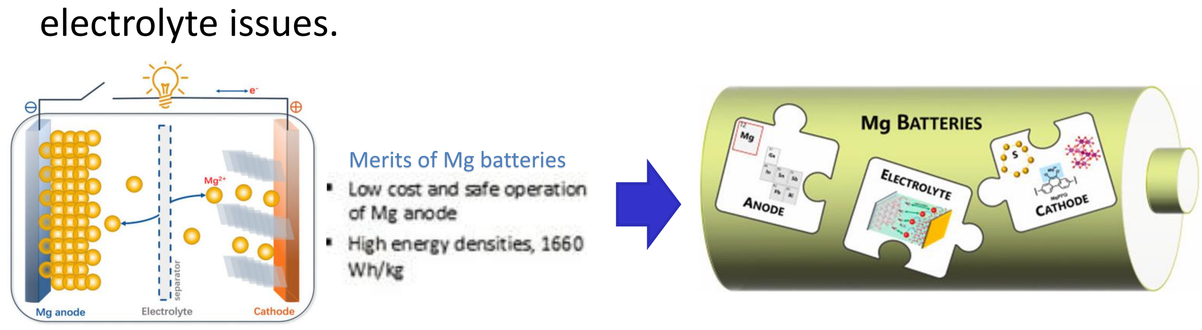

Fig 2: Advantages of Magnesium batteries over Lithium batteries as well as magnesium battery's current picture and missing pieces of the puzzle (Dominko et al., 2020).

- For the realization of high-performance batteries, the search for suitable cathode materials and their optimization is of crucial importance.
- Quinones are of special interest for application as cathode material due to their multi-electron redox activity, high energy density, and electronic stability.
- Pyrene-4,5,9,10-tetraone (PTO) is an outstanding quinone, as all four carbonyl positions can be utilized for the redox process for the uptake of four metal ions (e.g. Mg^{2+}) ions with a high operating voltage and a theoretical capacity as high as 409 mA h g^{-1}.

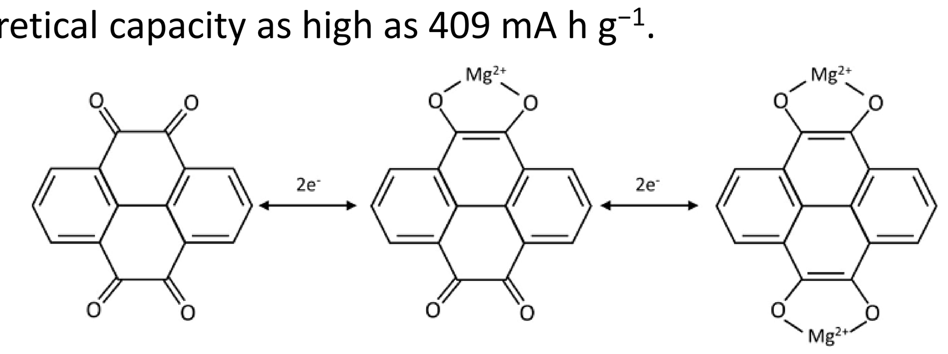

Fig 3: Reaction of PTO with Mg^{2+} (Ding *et al.*, 2022).

- Pyrene quinones are crucial for creating important fused-ring polyaromatic compounds.
- By harnessing the unique redox property of PTO, this study aims to immobilize PTO by investigating synthetic strategies for new pyrene tetraone derivatives that will serve as a porous cathode material for Mg ion batteries to trap electrons from electrolytes and make such electrons available during the charge-discharge process in an electrochemical cell reaction.
- We present a synthetic method for producing highly brominated PTO (i.e. tetra- to hexa- bromo pyrenetetraone) which are expected intermediate compound in the synthetic pathway for the proposed quinone-based metal-organic framework (MOF).

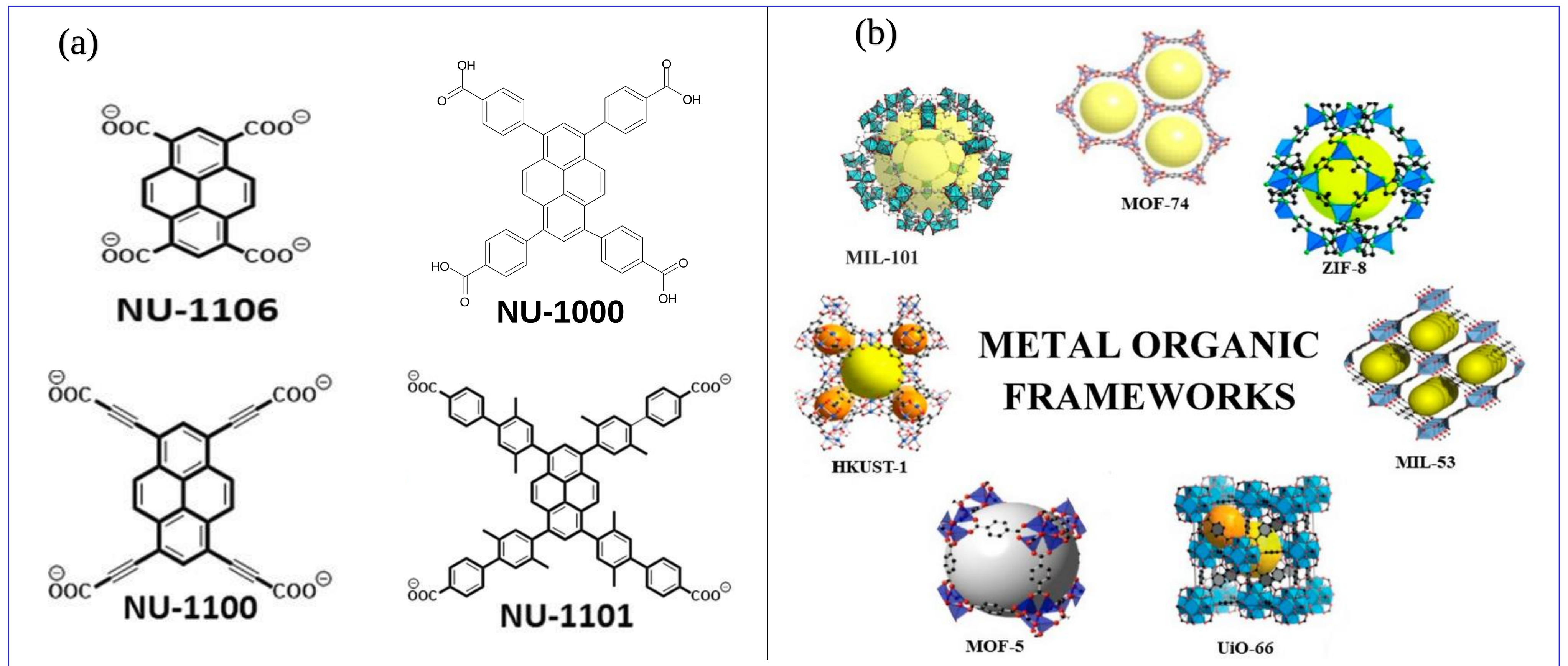

Fig 4: Examples of (a) Pyrene-based organic frameworks (Maldonado *et al.*, 2020) & (b) metal-organic frameworks (MOFs) (Bhakat et al., 2023).

Methods

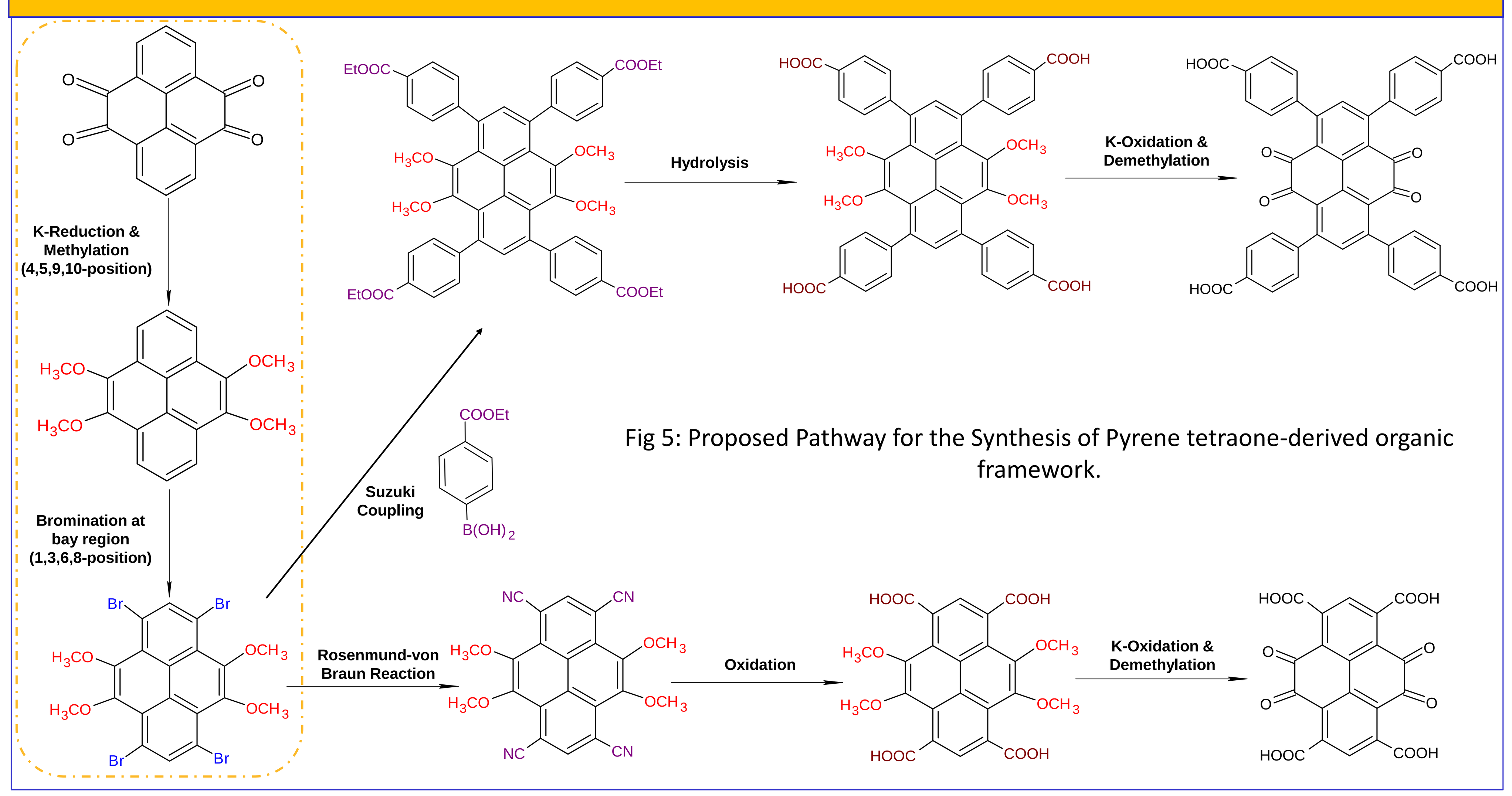

Fig 5: Proposed Pathway for the Synthesis of Pyrene tetraone-derived organic framework.

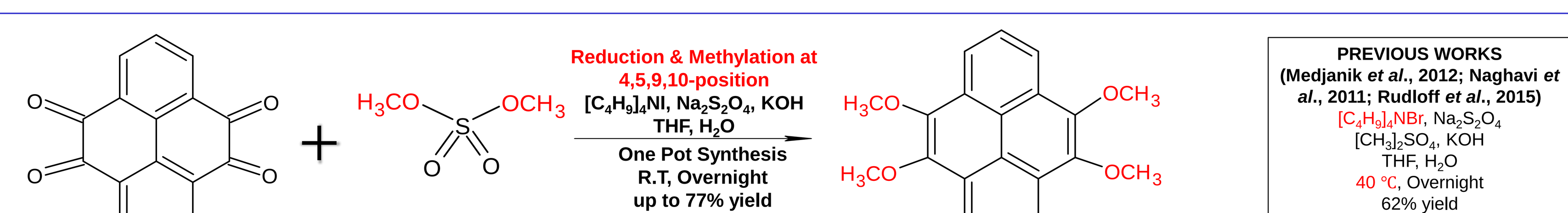

Fig 6: Synthesis of 4,5,9,10-tetramethoxypyrene (TMP).

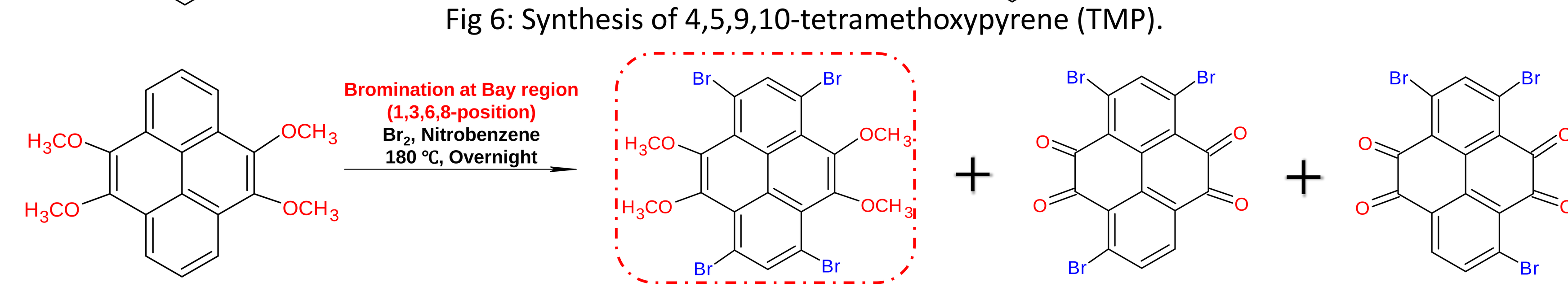

Fig 7: Synthesis of 1,3,6-tribromo-; 1,3,8-tribromo-; & 1,3,6,8-tetrabromopyrene-4,5,9,10-tetraone (TBPT).

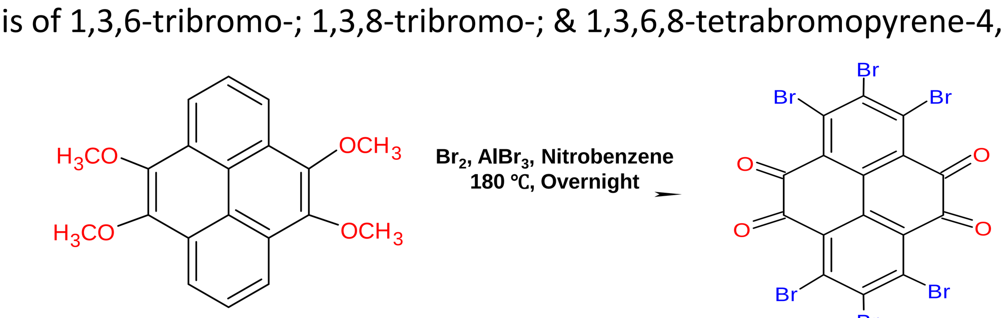

Fig 8: Synthesis of 1,2,3,6,7,8-hexabromopyrene-4,5,9,10-tetraone.

Results

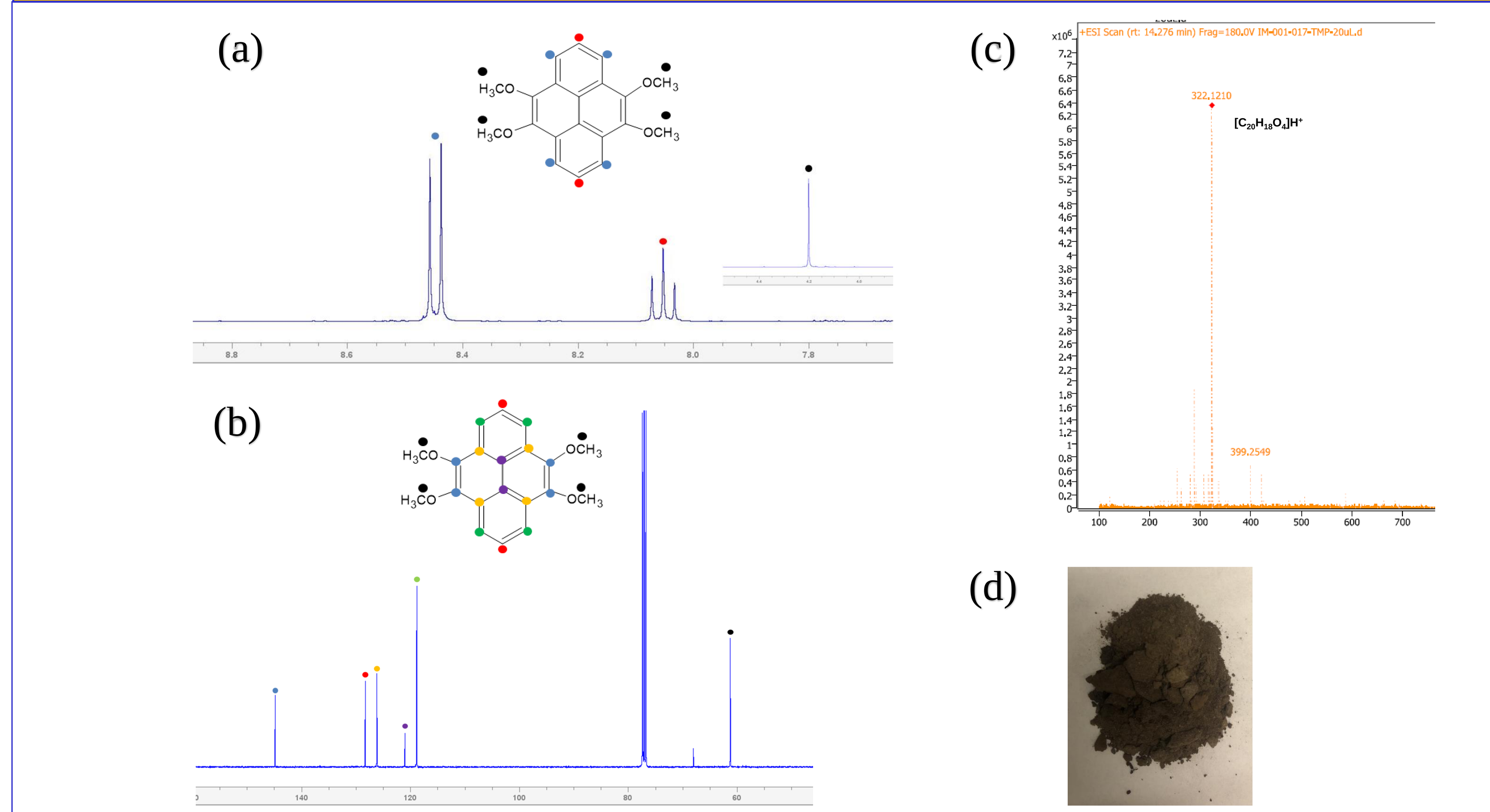

Fig 9: (a) ^{1}H NMR; (b) ^{13}C NMR; (c) LC-MS QTOF Analysis; and (d) Sample of 4,5,9,10-tetramethoxypyrene.

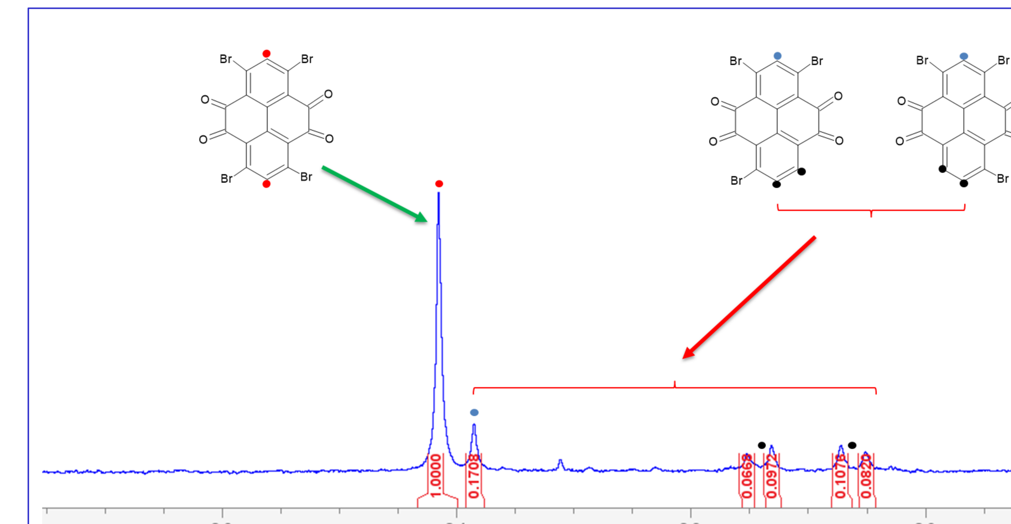

Fig 10: ^{1}H NMR Analysis of 1,3,6,8-tetrabromopyrene-4,5,9,10-tetraone

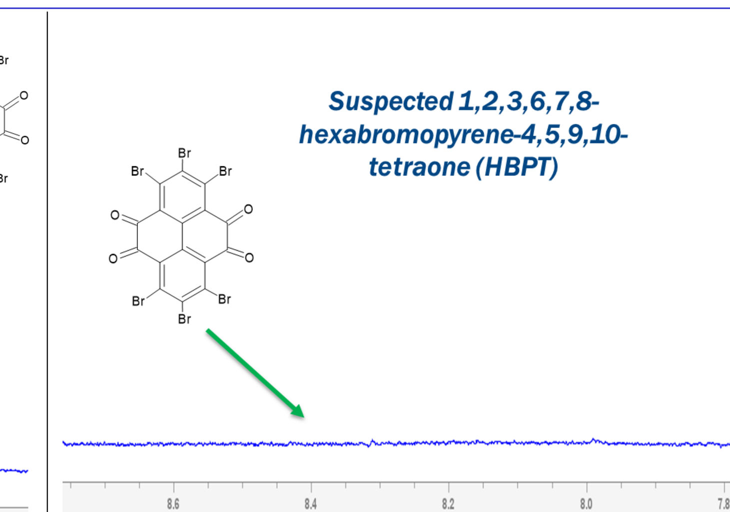

Fig 13: ^{1}H NMR Analysis of suspected 1,2,3,6,7,8-hexabromopyrene-4,5,9,10-tetraone

Conclusion & Future Directions

- Improved isolated yield (up to 77%) of 4,5,9,10-tetramethoxypyrene (TMP) with high purity product after a simple filtration process, without the need for extraction and column chromatography was achieved.
- Optimized purification process for 1,3,6,8-tetrabromopyrene-4,5,9,10-tetraone in progress.
- Synthesis of the other pyrene tetraone derivatives will be carried out and analyzed appropriately.
- The resulting pyrene tetraone derivatives can be further used as the building blocks in the synthesis of extended Polyaromatic Systems (e.g. proposed MOFs as cathode materials for Mg ion rechargeable batteries).

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