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Motivation

Per- and polyfluoroalkyl substances (**PFAS**) are a class of compounds that is known for their hydrophobicity and oleophobicity. These properties make them useful in many consumer products, including non-stick coatings, firefighting foams, and food packaging. However, their extremely high stability and mobilization by water, cause them to accumulate in biological systems and humans. Despite low environmental concentrations (ng/L), they cause immune disorders, cancers, and birth defects in humans. [1]

PFAS cleanup can be performed by adsorption from water. Currently, water treatment plants adsorb **PFAS** using Granular Activated Carbon (GAC), because it is cheap. However, GAC is non-selective, breaks through quickly, and requires thermal, off-site regeneration. Non-selectivity is detrimental, because it results in competition with natural organic matter. [2] Thus, there is a need for highly specific **PFAS** adsorbents.

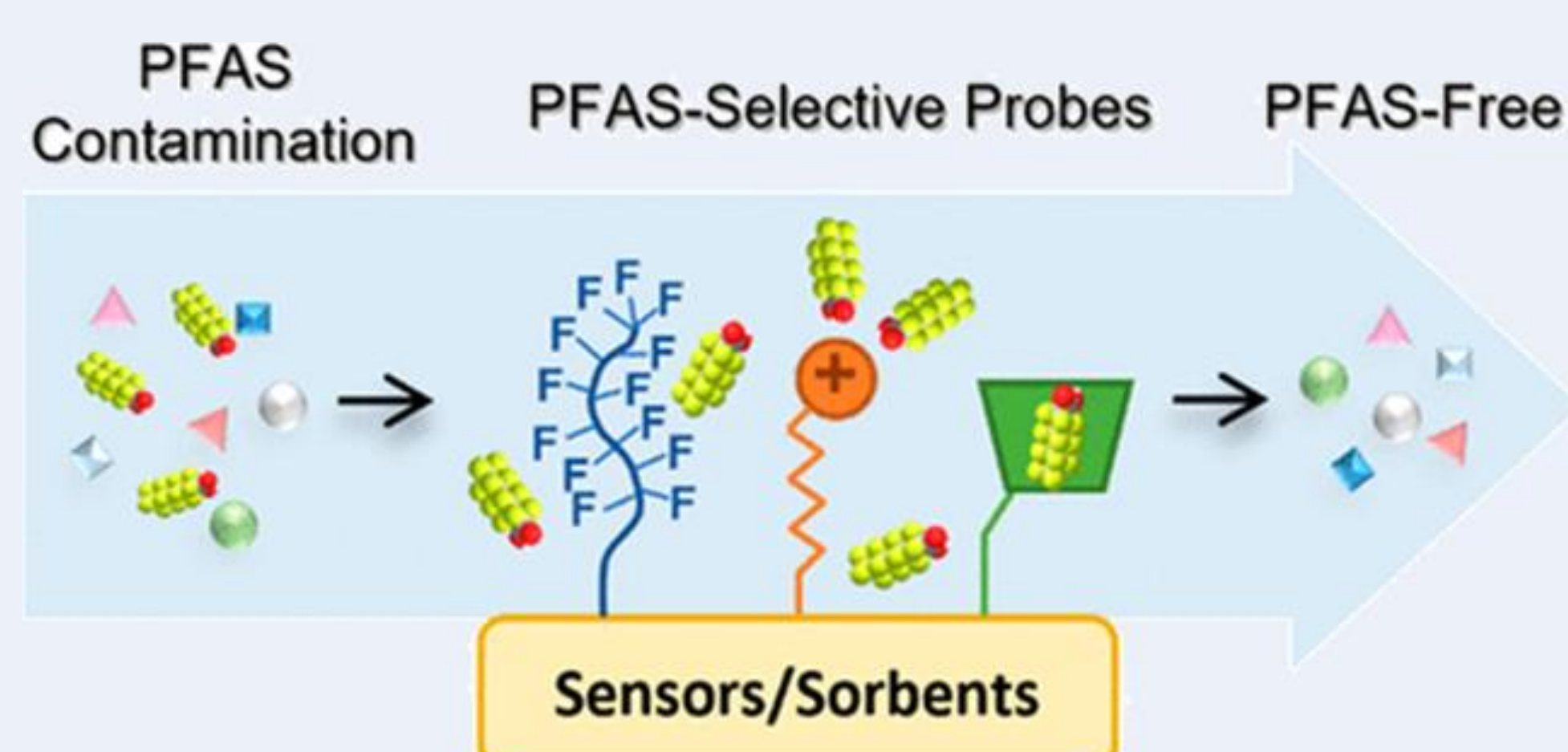


Figure 1. A **PFAS** adsorbent should be compatible with environmental water, which means that natural organic matter adsorption should be prevented. [3]

Our group discovered that a type of macrocycle (called pillararenes) strongly and specifically binds the two most common **PFAS** compounds, PFOS and PFOA. This results in a Pillararene-**PFAS** complex (PiP), see Figure 2. Immobilization of pillararenes onto a commercial resin resulted in a **PFAS** adsorbent with high breakthrough capacity for PFOS (90 mg/g) and PFOA (80 mg/g). Crucially, the resin can be regenerated using salty (0.1 g/L) methanol. [4]

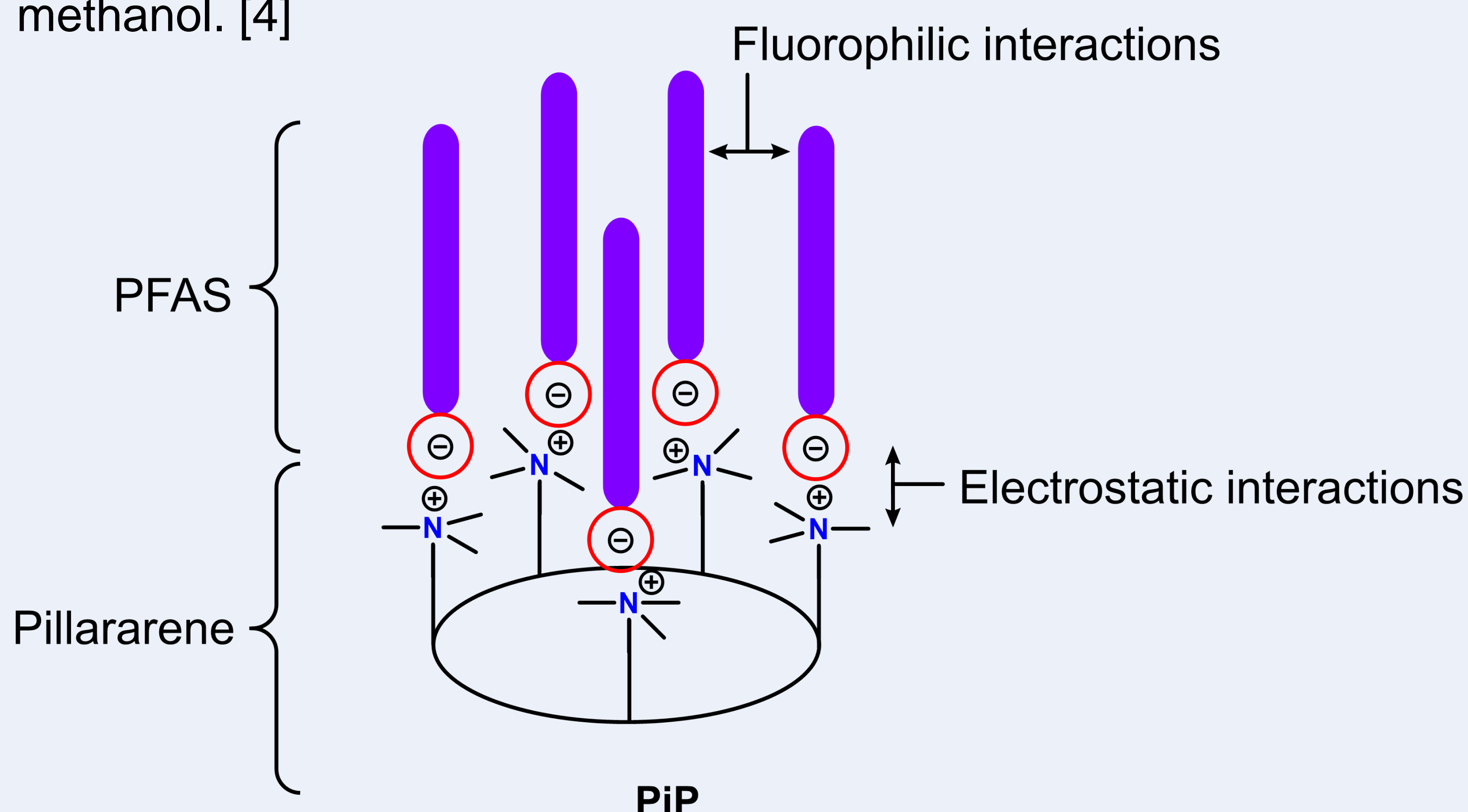


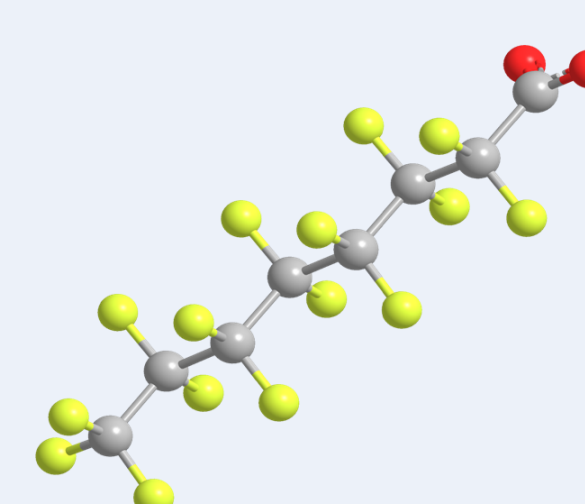
Figure 2. Electrostatic and fluorophilic interactions allow five **PFAS** molecules to bind on the rim of a pillararene.

Research goals

Fundamentals of PiP formation are poorly understood. This understanding is paramount for the design of a next generation of **PFAS**-adsorbing pillararenes. These pillararenes should have an extensive **PFAS** scope and increased **PFAS** binding strength, while retaining **PFAS** selectivity and regenerability.

We have formulated the following objectives for our work:

- Design and synthesize new pillararenes and evaluate their binding strengths towards different **PFAS**.
- Perform computational studies on PiP binding mechanisms to discover what interactions are responsible for PiP formation.
- Implement knowledge on PiP mechanism to design a next generation of **PFAS** adsorbents.
- Collaborate with the Wetsus-WUR project of Rick Nooijen, in which we investigate what pillararene functionalized surfaces perform best as **PFAS** adsorbent.



$$K_{\text{binding}} = \frac{[\text{PiP}]}{[\text{Pillararene}] [\text{PFAS}]^{10}}$$

How do PFAS bind?

How to increase binding strength?

How to expand PFAS scope?

Figure 3. Questions related to our research objectives. We aim to understand the mechanism of PiP formation, and use this knowledge to design a next generation of pillararenes.

Technological challenges

The innovative aspects of this research include:

- Pillararenes as a **PFAS**-adsorbing technology.
- Synthesis of new functionalized pillararenes that improve stoichiometry and/or binding constant of the PiP complex.
- Investigation of the contribution of the fluorophilic interactions in PiP formation through computational chemistry.

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- [2] Roest, K.; ter Laak, T.; Huiting, H.; Siegers, W.; Meekel, N.; de Jong, C.; de Jong, M.; van Houten, M.; Pancras, T.; Plaisier, W.; Dalmijn, J.; *Concawe Report* **2021** 5/21.
- [3] Darling, S. B.; Chen, J.; Wang, Y.; *ACS Appl. Mater. Interfaces* **2021**, *13*, 60789-60814.
- [4] Gao, T.; Huang, S.; Nooijen, R.; Zhu, Y.; Kociok-Köhn, G.; Stuerzer, T.; Li, G.; Salentijn, G.; Chen, B.; Bitter, H.; Miloserdov, F. M.; Zuilhof, H.; *Angew. Chem. Int. Ed.* **2024**, *63*, e202403474.

