# Band Gap and $CO_2$ Capture Engineering in Porphyrin-Based Porous Organic Polymers

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The development of new sustainable materials for gas adsorption and photocatalytic transformations offers a promising strategy to address environmental challenges and energy scarcity. Porous organic polymers (POPs) are attractive candidates for photocatalytic applications because of their high porosity, physicochemical stability, and tunable structure. Previous research has shown that porphyrin-based POPs with azo linkages show great potential for $CO_2$ capture [1]. Furthermore, replacing azo linkages with ethynyl linkages can yield semiconducting polymers with low optical band gaps [2]. The electronic properties of POPs and the band gap can be further tuned through careful selection of linear spacers [3]. In this study, we computationally investigate how substituents (−H, $-CH_3$, −OH) on phenyl spacers influence the band gap and $CO_2$ adsorption properties of porphyrin-based POPs featuring azo and ethynyl linkages. Structurally, these POPs form 2D frameworks, whose crystal structures were optimized using periodic DFT calculations with the CRYSTAL23 program. The optimized structures were then subjected to grand canonical Monte Carlo (GCMC) simulations using RASPA program, and the resulting $CO_2$ adsorption isotherms were compared. Band gaps were determined from structures reoptimized using the hybrid PBE0 and B3LYP functionals, which can be particularly reliable for reproducing experimentally reported optical band gaps when no charge transfer excitation is involved [4]. The calculated $CO_2$ uptake and electronic properties were compared with experimental data obtained from UV-Vis diffuse reflectance measurements. These results demonstrate that periodic DFT can be used to investigate and optimize the adsorption and electronic properties of functionalized POPs.

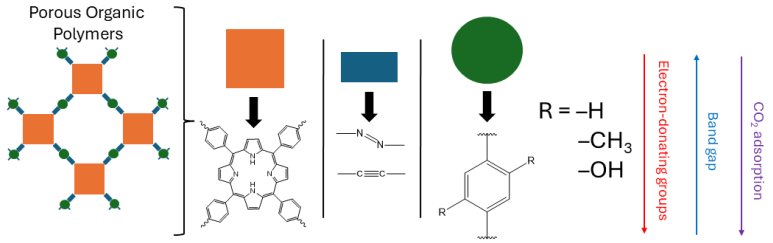


**Figure 1.** Porous organic polymers with tunable adsorption and electronic properties

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## References:

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