

Triphenylene and Triptycene-Based MOFs as Chemiresistive Platforms for CO₂ and CH₄ Detection

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Summary:

Triphenylene-based metal-organic frameworks (MOFs) (Cu-HTAT and Ni-HTAT) show reproducible resistance responses to CO₂ and CH₄ under variable humidity. In parallel, triptycene-derived MOFs (HHTT, M = Cu, Ni, Zn, Co) are introduced as a complementary three-dimensional platform. The combined approach enables correlating ligand structure with gas accessibility and electrical response. Our results demonstrate measurable gas-induced modulation of conductivity, highlighting the potential of these MOFs for environmental sensing.

Keywords: metal-organic frameworks, triphenylene, triptycene, chemiresistive sensor, carbon dioxide, methane

Background, Motivation and Objective

Conductive metal-organic frameworks (MOFs) based on π -conjugated ligands (planar) have emerged as promising candidates for gas sensing due to their tunable porosity, accessible active sites, and intrinsic charge transport properties. Triphenylene-based MOFs have demonstrated chemiresistive responses toward polar analytes, although the detection of weakly interacting gases, such as CO₂ and CH₄ remains challenging, especially in the presence of water [1,2,3].

These conductive MOFs' sensors rely on planar aromatic linkers, however, the impact of ligand dimensionality on gas diffusion and adsorption remains underexplored [1].

In this work, we compare the performance of triphenylene-based MOFs (Cu- and Ni-HTAT) with a series of triptycene-derived frameworks (M-HHTT; M = Cu, Ni, Zn, Co). By introducing a rigid 3D scaffold with intrinsic free volume, we investigate how modifying the ligand dimensionality influences gas diffusion and adsorption. This comparative study will help clarifying the role of framework topology in modulating the electrical response to non-polar analytes in realistic environments.

Synthesis and fabrication Methods

Two complementary ligand systems were employed to construct conductive MOF platforms with distinct structural dimensionality. The triphenylene-based (HTAT) ligand was synthesized from triphenylene via bromination, followed by Pd-catalyzed Buchwald-Hartwig

amination with tert-butylamine. In parallel, the triptycene-derived hexahydroxy (HHTT) ligand was prepared through a two-step procedure involving Cu(I)-assisted methoxylation of a brominated triptycene precursor, followed by demethylation using boron tribromide to yield the corresponding hexahydroxy ligand [4,5,6]. Both ligands were obtained and characterized by NMR, ATR-FTIR, and ESI-MS.

MOFs based on HTAT (M-HTAT, M: Cu, Ni) and HHTT (M-HHTT, M: Cu, Ni, Zn, Co) were obtained by solvothermal coordination using the corresponding metal salts under mild conditions. The resulting powders were dispersed in H₂O/EtOH mixtures and deposited onto platinum or gold interdigitated electrodes by drop casting. These chips were next bonded on TO-8 packages for electrical characterization. Sensing experiments were carried out in a self-designed miniaturized chamber equipped with mass-flow controllers, enabling precise delivery of CO₂ and CH₄ pulses in synthetic air. Humidity was adjusted between 0 and 40% RH using a bubbler system. Electrical measurements were performed using a source-measure unit, recording resistance changes in real time under alternating gas exposure and purge cycles.

Results and discussion

PXRD confirms the formation of crystalline MOFs for both HTAT- and HHTT-based systems. Under CO₂ and CH₄ exposure, HTAT-based MOFs show a chemiresistive response that depends on relative humidity. As humidity increases, the baseline resistance decreases, in line with transport dominated by planar π -conjugated pathways. HHTT-based MOFs display a

similar trend, although some differences in signal modulation are observed, suggesting changes in gas accessibility and adsorption behavior associated to their three-dimensional structure. In both systems, the response is more pronounced at intermediate humidity levels, pointing to a combined effect of water and gas adsorption. Overall, these observations indicate that ligand topology plays a role in the sensing mechanism, with HTAT-based frameworks mainly governed by surface interactions, while HHTT-based systems introduce additional diffusion pathways that influence gas adsorption and electrical response.

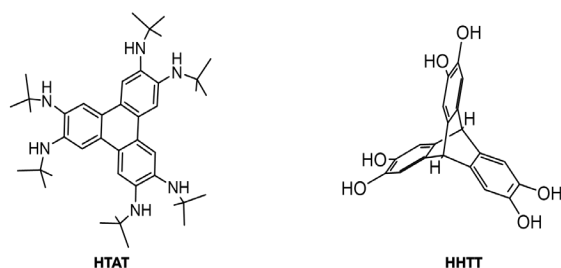


Figure 1. Chemical structures of the triphenylene-based (HTAT) and triptycene-based (HHTT) ligands

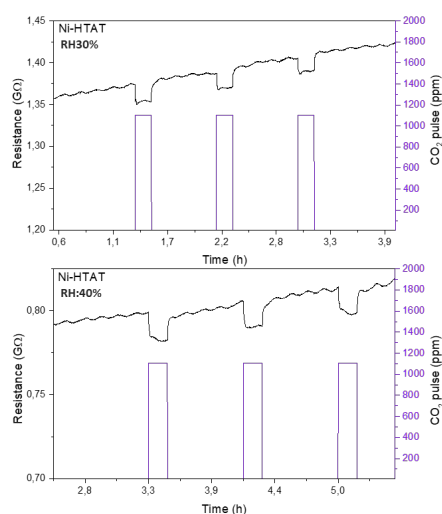


Figure 2 Chemiresistive response of Ni-HTAT to CO₂ pulses at 30% and 40% relative humidity.

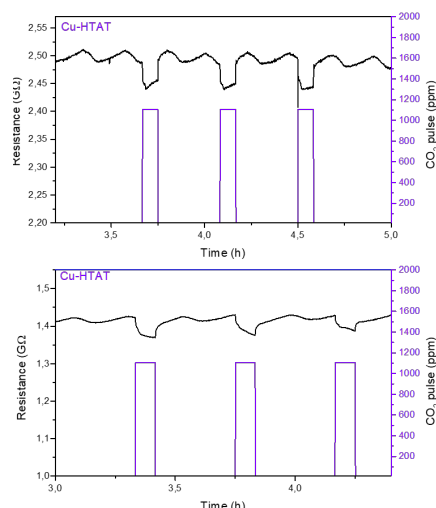


Figure 3 Chemiresistive response of Cu-HTAT to CO₂ pulses at 30% and 40% relative humidity.

In this work, we will describe the ligand synthesis, the MOF formation and characterization, and discuss their chemiresistive response upon greenhouse gas exposure, with particular emphasis on the role of humidity.

References

- [1] M. G. Campbell, S. F. Liu, T. M. Swager, M. Dincă, Chemiresistive Sensor Arrays from Conductive 2D Metal-Organic Frameworks, *J. Am. Chem. Soc.* **137**, 13780-13783 (2015); doi: 10.1021/jacs.5b09600
- [2] I. Fort-Grandas, M. Martínez-Belmonte, J. Benet-Buchholz, R. M. Gomila, A. Frontera, A. Romano-Rodríguez, A. Vidal-Ferran, Layered Nickel-HHTP Networks for Efficient Chemiresistive Sensing of Greenhouse Gases, *ACS Small* (2026, under review)
- [3] T. Chen, J.-H. Dou, L. Yang, C. Sun, N. J. Libretto, G. Skorupskii, J. T. Miller, M. Dincă, Continuous Electrical Conductivity Variation in M3(hexaiminotriphenylene)₂ (M = Co, Ni, Cu) MOF Alloys, *J. Am. Chem. Soc.* **142**, 12367-12373 (2020); doi: 10.1021/jacs.0c04458
- [4] S. Gonell, M. Poyatos, E. Peris, Triphenylene-Based Trinuclear Mercury N-Heterocyclic Carbene Complexes, *Angew. Chem. Int. Ed.* **52**, 7009-7013 (2013); doi: 10.1002/anie.201302686
- [5] Q. Chen, A. Afugu, Y. Shuku, Z.-F. Liu, K. Awaga, Z. Zhang, Triptycene-Based 2.5-Dimensional Metal-Organic Frameworks: Atomically Accurate Structures and Anisotropic Physical Properties from Hydrogen-Bonding Bridged Protonated Building Units, *J. Am. Chem. Soc.* **147**, 28215-28225 (2025); doi: 10.1021/jacs.5c08703
- [6] Y. Lin, C. Kong, L. Chen, Amine-functionalized metal-organic frameworks: structure, synthesis and applications, *RSC Adv.* **6**, 32598-32614 (2016); doi: 10.1039/C6RA01536K