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Facilitation of amine-bridged covalent triazine framework synthesis by microwave irradiation

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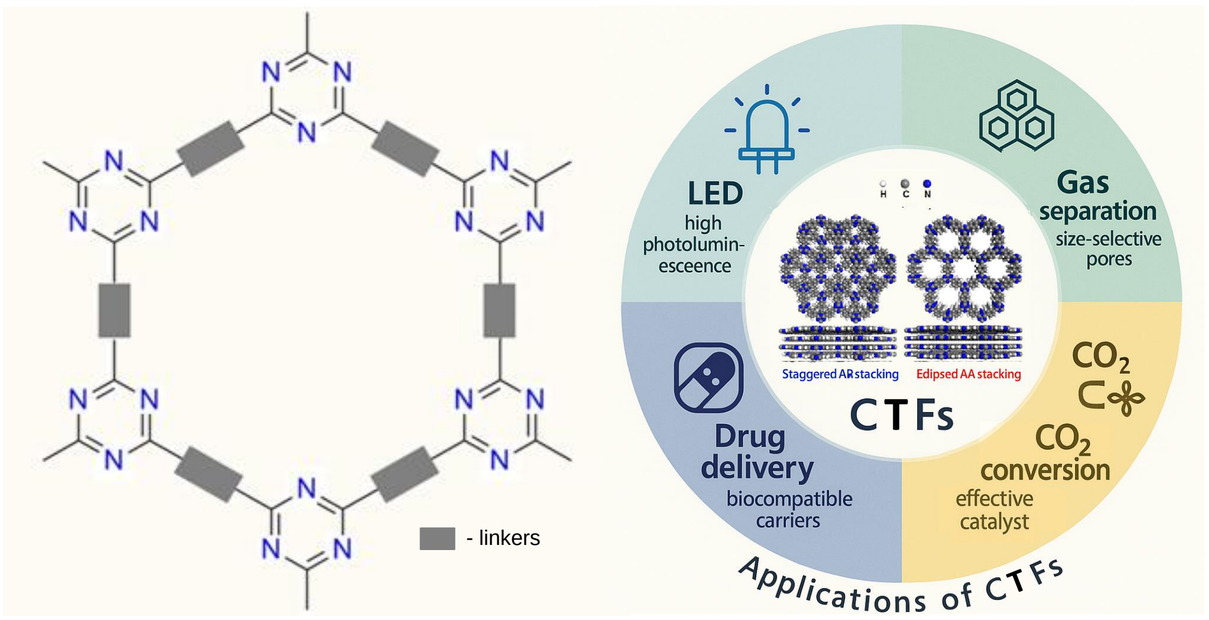
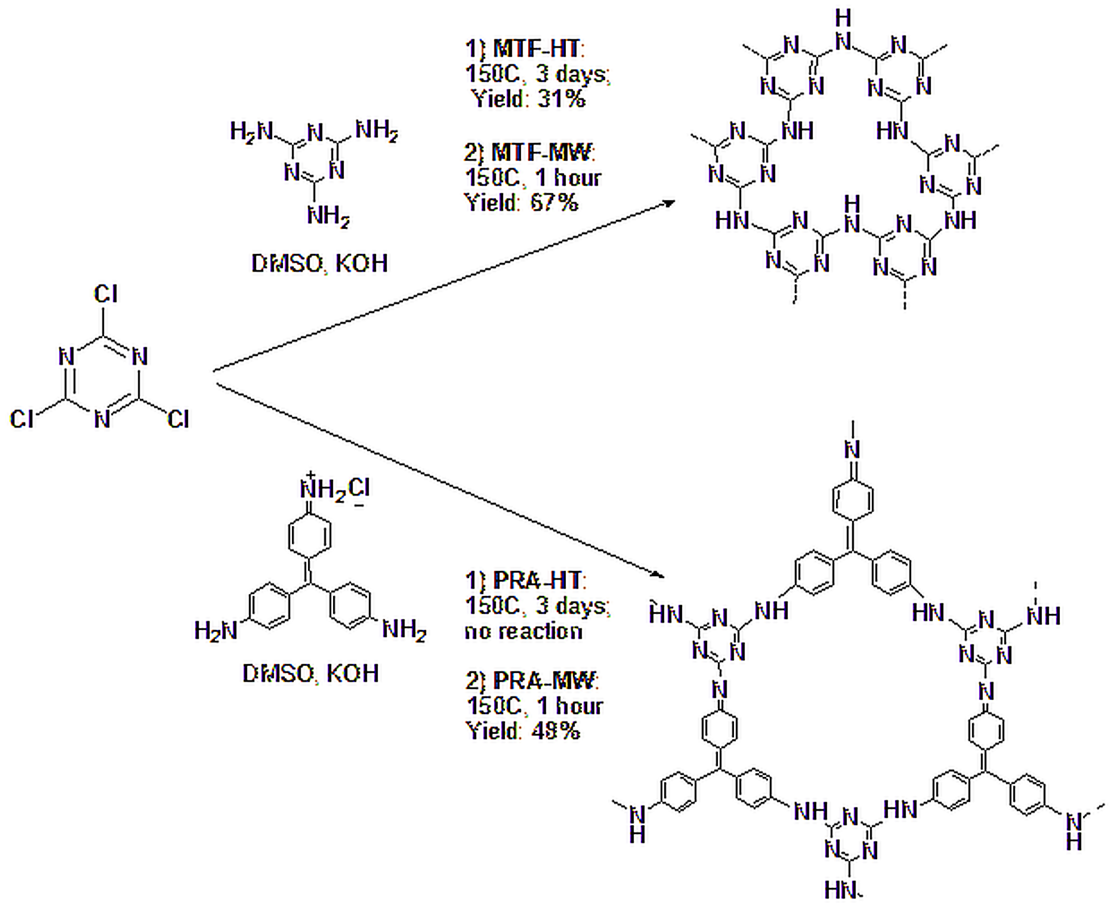
INTRODUCTION & AIM

Covalent triazine frameworks (CTFs) are N-rich porous polymers built from 1,3,5-triazine rings connected by covalent linkers. Their rigid, heteroatom-dense backbones typically show high thermal stability, appreciable surface areas, and sites well-suited for gas capture and catalysis[1,2]. Here we target for obtaining of NH–linked CTFs from amines that react sluggishly under standard conditions by contrasting efficiency of conventional synthesis with microwave assisted, which delivers rapid, uniform energy input to accelerate substitution at milder conditions[3].



METHODS

Reactions were performed as nucleophilic substitutions of cyanuric chloride with melamine or pararosaniline hydrochloride. The reactions were conducted under conventional heating during 3 days at 150°C or under microwave irradiation (**50–200 W**) during 1 hour at the same temperature.

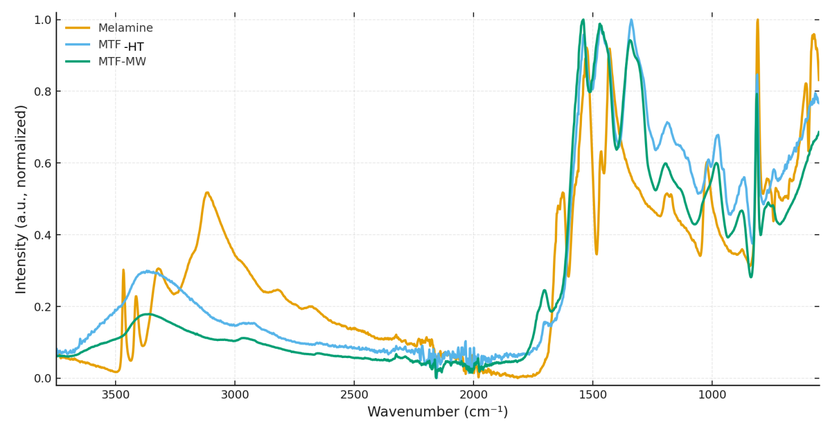


Characterization included FT-IR (linkage formation, triazine retention), TGA (to 600 °C with low-temperature desorption), N_2 sorption at 77 K with BJH pore-size analysis, and CO_2-uptake estimates from ≤150 °C TGA mass loss of preliminary CO_2-saturated CTF samples.

RESULTS & DISCUSSION

Conventional heating gave the –NH–linked framework **MTF-HT** with **31%** yield, whereas microwave irradiation raised the yield of **MTF-MW** more than twice (to **67**%). Moreover, the reaction of cyanuric chloride with pararosaniline failed under conventional conditions, but gave the **PRA-MW** in **48%** yield under microwave assistance.

FT-IR analysis:

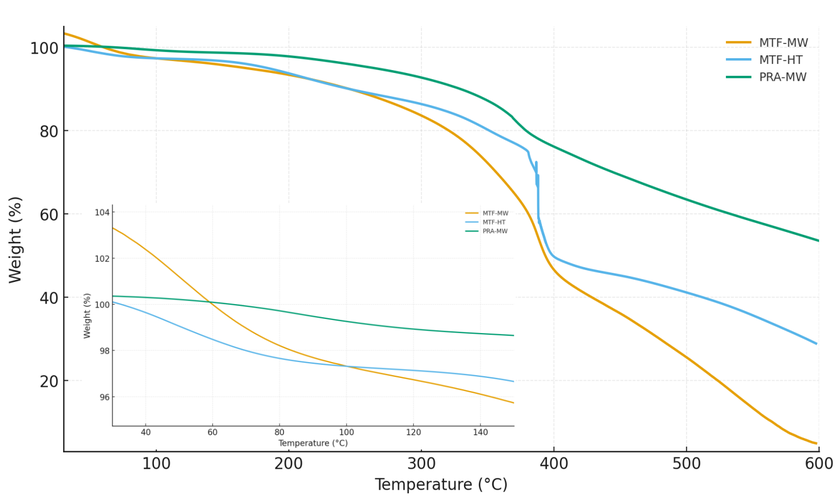


The formation of –NH– bridged CTFs was confirmed by FT-IR for both amines. More specifically, the collapse of the $–NH_2$ stretching multiplet of both amines (~3500–3250 cm^{-1}) into a broad peak at 3700–3100 cm^{-1}, signaling extensive H-bonding of bridging N–H groups. The given spectrum shows the case of the CTFs obtained from melamine.

BET and BJH measurements:

The results of BET and BJH measurements showed that all obtained frameworks have mesoporous structure. **MTF-HT** (BET surface area ~122.6 m^2/g) and **PRA-MW** (BET surface area ~25.4 m^2/g) have mesopores with wide size distribution and «bottle-like» forms, however, the latter has low total pore volume (0.1133 cm^3/g). **MTF-MW** (BET surface area ~14.1 m^2/g) has ordered, «net-like» structure and uniformly distributed mesopores.

TGA analysis:



We investigated thermal stability of obtained frameworks by TGA. All obtained frameworks are stable till 300°C. Thermal stability of synthesized frameworks adheres to the series MTF-MW ≥ MTF-HT > PRA-MW. Following the interest in CO_2-capture properties, we preliminary saturated the powders of these materials with CO_2 and then explored the substitution of CO_2 with N_2. The values of weight loss of CTFs preliminary saturated with CO_2, due to nitrogen displacement in 30–150°C temperature range, resulted for **MTF-MW** – 7.6 wt% (corresponds to CO_2 uptake ~4.7 mmol/g), **MTF-HT** – 3.5 wt% (~2.6 mmol/g), **PRA-MW** – 1.7 wt% (~1.1 mmol/g). The maximal weight loss corresponding for **MTF-MW** demonstrates the highest affinity of this framework to CO_2.

CONCLUSION

As a result of current investigation, it was demonstrated that synthesis of CTFs via microwave irradiation:

- Sharply decreases in CTF formation time and boosts yields;
- Facilitates the formation of ordered, «net-like» structures of CTFs;
- Leads to the formation of materials possessing uniformly distributed mesopores;
- Promotes increased CO_2 uptake by the framework.

FUTURE WORK / REFERENCES

FUTURE WORK:

The current work demonstrated the developed synthetic approach could be promising for further directions:

- Optimization and application of microwave synthesis conditions for upscaling of CTFs;
- Expansion of the scope of starting materials for CTF synthesis;
- Tests of functional properties of obtained CTFs for gas separation.

REFERENCES:

1. Liao L. et al., ACS Omega 2023, 8, 5, pp. 4527–4542
2. Silpa E. P. et al., Materials Advances 2024, 5, 23, pp. 9175–9209
3. Chaudhary M. and Mohanty P., New Journal of Chemistry 2018, 42, 15, pp. 12924–12928