Effects of Modulators and Solvent Conditions on Model COF-300 Crystallinity

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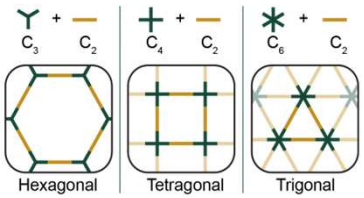
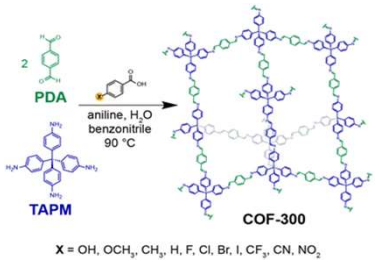
Background



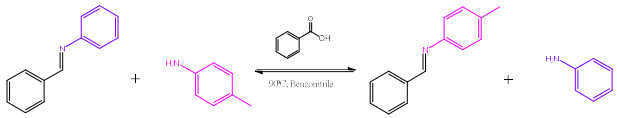
- Covalent organic frameworks (COFs) are crystalline, porous polymers
- Their pore size and shape are determined by monomer geometry
- COF-300 is formed by an imine condensation reaction between tetrakis(4-aminophenyl)methane (TAPM) and terephthaldehyde (PDA) with a benzoic acid catalyst and aniline modulator[1]
- Small molecule studies allow us to analyze the reaction kinetics and equilibrium of representative imine condensation reactions
- COFs have applications in molecular separation, gas storage, and water purification[2]



Scheme 1. COF-300 colloidal synthesis.

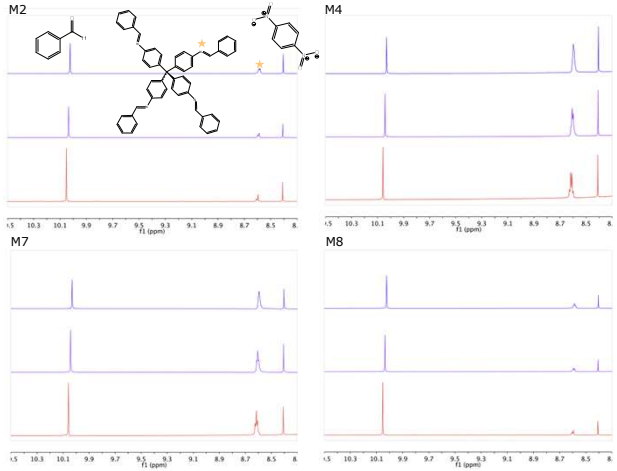
- To study the kinetics and analyze the effect of the solvent and temperature on the equilibrium, the compounds were synthesized with different additions to the reaction and run at three temperatures, and analyzed using Nuclear Magnetic Resonance (NMR)
- For this study, only TAPM was used
- The trials M2, M4, M7, and M8 run in acetonitrile-d3, while trials M3 and M6 were run in benzonitrile-d5

Key		
M2	acetonitrile-d3	aniline+water
M3	benzonitrile-d5	none
M4	acetonitrile-d3	none
M6	benzonitrile-d5	aniline
M7	acetonitrile-d3	water
M8	acetonitrile-d3	aniline



Scheme 2. Model compound reaction scheme catalyzed by benzoic acid with an aniline modulator.

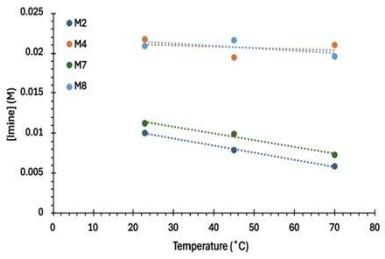
Reaction in Acetonitrile



- NMRs were run at room temperature (RT) or 23° C (blue), 45° C (purple), and 70° C (red)
- Once temperature was reached, the solution was equilibrated for 15 minutes before running
- Integrations of the benzaldehyde, imine (star), and dinitrobenzene (DNB) as an internal standard were taken and used to calculate the % Error compared to the expected ratio of benzaldehyde + imine integration

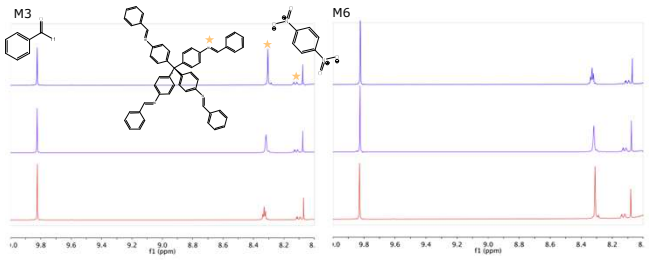
	Aldehyde	Imine	DNB	% Error
AM2 RT	308.98	198.57	100	14.49
AM2 45C	356.39	155.27	100	13.80
AM2 70C	389.15	115.35	100	15.01
AM4 RT	197.86	432.45	100	39.83
AM4 45C	199.52	386.11	100	29.92
AM4 70C	234.49	416.84	100	44.49
AM7 RT	400.04	223.03	100	38.22
AM7 45C	450.77	195.79	100	43.43
AM7 70C	489.61	144.44	100	40.66
AM8 RT	118.56	415.93	100	9.95
AM8 45C	142.3	428.5	100	3.84
AM8 70C	171.61	389.06	100	5.54

- Results indicate that there is only a small amount of deviation from expected behavior and that trials run with aniline have much lower deviations from expected values



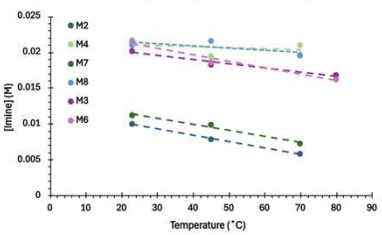
- Using the integration data from the NMRs and expected imine concentrations, the amount of imine was determined
- That value was then plotted against temperature
- Results consistent with % Error

Reaction in Benzonitrile



- NMRs were run at room temperature or 23° C (blue), 45° C (purple), and 80° C (red) in benzonitrile-d5
- Once temperature was reached, solution was equilibrated for 15 minutes before running
- The % Error was determined the same way as before

	Aldehyde	Imine	DNB	% Error
M3 RT	267.37	400.89	100	12.58
M3 45C	318.46	362.73	100	14.76
M3 80C	428.43	333.18	100	28.31
M6 RT	300.86	426.26	100	22.50
M6 45C	347.31	369.5	100	20.76
M6 80C	412.52	322.09	100	23.76



- The M6 and M3 data were plotted in the same way as the previous plots to observe the results
- Results show that M3 and M6 follow a similar pattern to the previous trials

Conclusions and Future Work

- Addition of water promotes hydrolysis, decreasing amount of imine produced.
- Future work will include performing model compound studies with PDA
- Running more trials with benzonitrile-d5 as solvent

References

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