#### Conjugated Microporous Polymers via Solvent-Free Ionothermal Cyclotrimerization of Methyl Ketones

Jaehwan Kim,<sup>*a*,‡</sup> Casandra M. Moisanu,<sup>*a*,‡</sup> Cara Gannett,<sup>*a*</sup> Arjun Halder, <sup>*a*</sup> José J. Fuentes-Rivera, <sup>*a*</sup> Sean H. Majer, <sup>*a*</sup> Kyle M. Lancaster, <sup>*a*</sup> Alexander C. Forse,<sup>*b*</sup> Héctor D. Abruña,<sup>*a*</sup> Phillip J. Milner<sup>*a*,\*</sup>

<sup>a</sup>Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY, 14850, United States <sup>b</sup>Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, U.K. \*pjm347@cornell.edu <sup>‡</sup>These authors contributed equally.

# Abstract

Conjugated microporous polymers (CMPs) are porous organic materials that display (semi)conducting behavior due to their highly  $\pi$ -conjugated structures. As such, they are promising next-generation materials for applications requiring both conductivity and porosity, such as supercapacitive energy storage and electrochemical sensing. However, most CMPs and related porous aromatic frameworks (PAFs) are currently prepared using expensive transition metal-based catalysts under solvothermal conditions, significantly increasing their manufacturing costs. Herein, we demonstrate that the ionothermal cyclotrimerization of methyl ketones via the aldol reaction represents a new strategy for the solvent-free synthesis of CMPs and PAFs. Specifically, we show that 1,3,5-triacetylbenzene and tetrakis(4-acetylphenyl)methane can be polymerized in molten zinc chloride to produce highly conjugated and microporous materials, as confirmed by 77 K N<sub>2</sub> adsorption measurements in conjunction with UV-Vis, Raman, and solid-state NMR spectroscopies. The CMP prepared from 1,3,5-triacetylbenzene demonstrates higher charge storage capacities (up to 172 F/g) than a commercially available supercapacitor carbon, reflecting the promise of cyclotrimerized CMPs for electrical energy storage applications.

# Introduction

Microporous organic polymers are promising for applications in catalysis, gas separations, and energy storage due to their high surface areas, chemical stabilities, and flexible structures.<sup>1–4</sup> In particular, conjugated microporous polymers (CMPs) are a subclass of porous organic materials that feature extended  $\pi$ -conjugation, leading to (semi)conducting behavior.<sup>5–7</sup> The combination of relatively high conductivity and tunable microporosity make CMPs prospective next-generation materials for organic electronics, chemiresistive sensing, and energy storage.<sup>5</sup> However, many current methods for synthesizing CMPs, such as the Sonogashira-Hagihara coupling, Suzuki-Miyaura coupling, Yamamoto coupling, and Buchwald-Hartwig coupling, require expensive palladium- or nickel-based catalysts.<sup>5,8,9</sup> Beyond their high cost, these residual metals can alter the fundamental electrochemical and catalytic behaviors of the resulting materials.<sup>10,11</sup> In addition, the majority of CMPs are prepared under solvothermal conditions using organic solvents, greatly increasing their manufacturing costs at large scale.<sup>12</sup> Thus, there is a compelling need to develop

new, solvent-free methods for the synthesis of high-quality CMPs using inexpensive catalysts and/or reagents.

**a** Previous work:



**Figure 1.** Synthesis of polymeric materials via cyclotrimerization. a) Solvothermal Brønsted acid (H<sup>+</sup>) or Lewis acid (LA) mediated dimerization/trimerization of methyl ketones. b) Ionothermal trimerization of nitriles to prepare covalent triazine frameworks (CTFs). c) Ionothermal trimerization of methyl ketones to prepare conjugated microporous polymers (CMPs) such as **TAB-CMP** (this work). The idealized structure of **TAB-CMP** is shown.

A classic C–C bond-forming reaction that potentially fulfills these criteria is the aldol reaction, which can be mediated using but inexpensive catalysts remains underutilized for the synthesis of polymeric materials.<sup>13–19</sup> For example, in the presence of Lewis or Brønsted acids, methyl ketones first dimerize to produce  $\alpha,\beta$ -unsaturated ketones with concomitant loss of water, followed by subsequent cyclotrimerization under more driving conditions to produce 1.3.5substituted arenes (Figure 1a). While this cyclotrimerization reaction has been widely used to prepare molecular arenes such as truxenes,  $\frac{20-22}{10}$  its application for the synthesis of extended solids such as CMPs remains limited. Seminal work by Kaskel and coworkers demonstrated that molten ptoluenesulfonic acid and SiCl<sub>4</sub> (under solvothermal conditions) can be used to polymerize diacetylarenes to produce porous organic frameworks by the cyclotrimerization reaction (OFCs).<sup>23</sup> These and related methods have subsequently been employed to prepare a range of porous organic materials.<sup>24-34</sup> However, these polymers likely contain dimerized mixtures of  $\alpha,\beta$ -unsaturated ketones and cyclotrimerized 1,3,5-substituted arenes (Figure 1a), as evidenced by residual carbonyl stretches in their Infrared (IR) spectra.<sup>31</sup> Likewise, the polymerization of

triacetylarenes on Ag(111) surfaces was found to produce mixtures of dimers and cyclic trimers.<sup>35</sup> Thus, a reliable method for driving these cyclotrimerization reactions to completion would potentially enable the low-cost synthesis of more uniform CMPs.

In contrast to the cyclotrimerization of methyl ketones, the cyclotrimerization of nitriles to produce covalent triazine frameworks (CTFs) is well-established (Figure 1b).<sup>36,37</sup> As first reported by Kuhn, Antonietti, and Thomas, CTFs can be prepared by driving cyclotrimerizations to high conversions using a molten Lewis acidic salt, such as ZnCl<sub>2</sub>, as the reaction solvent.<sup>38</sup> In addition to producing highly porous CTFs, this method bypasses the need for organic solvent during materials synthesis. Based on this precedent, we hypothesized that the cyclotrimerization of methyl ketones under ionothermal conditions, for example using ZnCl<sub>2</sub> as the solvent, should yield more uniform CMPs as well (Figure 1c).<sup>39</sup> Here, we demonstrate that CMPs and related porous aromatic frameworks (PAFs) can indeed be obtained by the cyclotrimerization of tri- and tetra-acetylated monomers under strongly Lewis acidic conditions, leading to nearly complete conversion of

ketones into 1,3,5-substituted arenes. In particular, the monomer 1,3,5-triacetylbenzene (**TAB**) produced a CMP with Brunauer–Emmett–Teller (BET) and Langmuir surface areas as high as 929 and 1990  $m^2/g$ , respectively. The combination of high surface area and extended conjugation makes some of CMPs prepared herein promising for supercapacitive energy storage.<sup>40–42</sup> Overall, the ionothermal cyclotrimerization of methyl ketones should prove useful for the synthesis of novel CMPs from simple monomers under solvent-free conditions.

### **Results and discussion**

**Cyclotrimerization of 1,3,5-triacetylbenzene.** We commenced our investigation into the ionothermal cyclotrimerization of methyl ketones using TAB as a monomer to prepare a CMP designated as CORN-CMP-1 (CORN = Cornell University) and referred to herein as TAB-CMP for consistency (Figure 1c; see Supporting Information or SI Section 4a for details).<sup>43</sup> Ionothermal cyclotrimerizations were carried out by combining mixtures of TAB and anhydrous ZnCl<sub>2</sub> in 8 mm diameter borosilicate glass tubes that were subsequently flame-sealed under vacuum (<50 mTorr) using a custom-built apparatus (SI Figure S13). In order to identify the optimal conditions for preparing CMPs, we evaluated the effects of both temperature and ZnCl<sub>2</sub>:TAB ratio on CMP formation. Following the standard ionothermal conditions used to prepare CTFs,<sup>37–39</sup> 10:1 molar ratios of ZnCl<sub>2</sub> and TAB were combined and heated in sealed tubes to 300 °C (TAB-CMP-300 °C, 10 eq.), 400 °C (TAB-CMP-400 °C, 10 eq.), or 500 °C (TAB-CMP-500 °C, 10 eq.) for 72 h. In addition, samples of TAB-CMP were prepared using 5:1 (TAB-CMP-400 °C, 5.0 eq.) and 1:1 (TAB-CMP-400 °C, 1.0 eq.) ratios of ZnCl<sub>2</sub>:TAB at 400 °C. Consistent with the formation of highly conjugated polymeric materials, insoluble shiny black solids were obtained in all cases, although partial graphitization under these conditions cannot be completely ruled out.<sup>44</sup> After isolation, the solids were subsequently soaked in aqueous hydrochloric acid to remove residual zinc salts followed by extended soaking in tetrahydrofuran and acetone to remove soluble organic impurities (see SI Section 3 for details). The samples were dried at 120 °C for 6 h in air prior to analysis. Notably, polymeric materials were obtained after only 24 h of reaction time, but 72 h



**Figure 2.** ATR IR spectra of **TAB** and **TAB-CMP** prepared under a range of ionothermal conditions. The C=O stretch of **TAB** is highlighted in orange, and the aromatic C=C stretches of **TAB-CMP** materials are highlighted in gray.

reaction times were employed herein to ensure that reactions proceeded to full conversion in all cases (SI Figure S40). Control experiments in which either **TAB** or ZnCl<sub>2</sub> alone were heated in sealed tubes at 400 °C for 72 h did not yield any isolable solids, indicating that both reaction components are required to prepare insoluble polymeric materials.

Analysis of the polymeric samples by Attenuated Total Reflectance (ATR) IR spectroscopy revealed that significant conversion of TAB occurred under all tested conditions (Figure 2). Specifically, the C=O stretch of TAB (1687 cm<sup>-1</sup>, highlighted in orange) was largely absent in all of the polymerized samples, consistent with significant conversion of the ketone groups into aromatic rings. Notably, aromatic C=C

stretches (1565 cm<sup>-1</sup>, highlighted in gray) were retained in the polymerized samples. In addition, the energy dispersive X-ray scattering (EDS) spectrum of desolvated **TAB-CMP-400** °**C**, **5.0** eq. revealed that this material contains less than 5 atomic % O (24 atomic % O for TAB) and only 0.3 atomic % Zn from residual Zn salts (SI Figure S16, Table S2). Similarly, the X-ray photoelectron spectrum (XPS) of **TAB-CMP-400** °**C**, **5.0** eq. supports the low O (4.40%) and Zn (0.01%) content of this material (SI Figure S18, Table S3). This is in contrast to the cyclotrimerizations of 1,4-diacetylbenzene (**DAB**) in molten *p*-toluenesulfonic acid and **TAB** in methanesulfonic acid, which yield insoluble polymeric materials (**OFC-1b** and *tri-PPN*, respectively) that contain significant residual carbonyl groups (see SI Sections 6–7 for details).<sup>23,25,31</sup> These IR, EDS, and XPS spectra suggest that significant cyclotrimerization of **TAB** was employed. This finding represents an advantage over the ionothermal synthesis of CTFs, where excess ZnCl<sub>2</sub> is typically required to serve as both the reaction mediator and solvent.<sup>44</sup>

The 77 K N<sub>2</sub> adsorption and desorption isotherms of the **TAB-CMP** materials were measured in order to validate the successful formation of porous organic materials (Figure 3a, Table 1). All five samples were found to be microporous, as evidenced by steep N<sub>2</sub> uptake at  $P/P_0 \approx 0$ . The BET surface areas of the samples fell into a relatively narrow range, from 756 to 929 m<sup>2</sup>/g, with the highest BET surface area belonging to **TAB-CMP-400** °C, **5.0 eq.** Although no clear trend in the BET surface areas as a function of temperature or ZnCl<sub>2</sub>:TAB ratio could be discerned, the Langmuir surface areas and pore volumes calculated at  $P/P_0 \approx 0.9$  reflected clearer trends. Increasing the reaction temperature from 300 °C to 400 °C or 500 °C led to an increase in N<sub>2</sub> adsorption at higher pressures. Meanwhile, intermediate equivalents of ZnCl<sub>2</sub> maximized the porosity at a constant reaction temperature of 400 °C (5.0 eq. > 10 eq. > 1.0 eq.), likely by balancing cyclotrimerization and partial graphitization under harsher conditions. Overall, **TAB-CMP-400** °C, **5.0 eq.** was found to exhibit the highest



**Figure 3.** a) 77 K N<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms of **TAB-CMP** materials. b) N<sub>2</sub>-Tarazona NLDFT-calculated pore size distribution for **TAB-CMP** prepared at 400 °C with 5.0 equivalents of ZnCl<sub>2</sub>, assuming a cylindrical pore geometry.

Sample Name	<b>BET Surface Area</b>	Langmuir Surface Area	Pore Volume at
	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	$P/P_0 \approx 0.9 ~(\mathrm{cm}^3/\mathrm{g})$
TAB-CMP-300 °C, 10 eq.	$849 \pm 4$	$1344 \pm 8$	0.45
TAB-CMP-400 °C, 10 eq.	$756 \pm 5$	$1576 \pm 44$	0.57
TAB-CMP-500 °C, 10 eq.	$823 \pm 5$	$1588 \pm 32$	0.58
TAB-CMP-400 °C, 1.0 eq.	$801 \pm 3$	$1027 \pm 2$	0.35
TAB-CMP-400 °C, 5.0 eq.	$929 \pm 6$	$1990 \pm 22$	0.61

**Table 1.** 77 K N<sub>2</sub> Brunauer–Emmett–Teller (BET) surface areas, Langmuir surface areas, and pore volumes at  $P/P_0 \approx 0.9$  for **TAB-CMP** materials.

BET and Langmuir surface areas and the largest pore volume among all prepared **TAB-CMP** samples. The N<sub>2</sub>-Tarazona nonlocal density functional theory (NLDFT) calculated pore size distribution of **TAB-CMP-400** °C, **5.0** eq., assuming a cylindrical pore geometry, revealed a relatively narrow micropore regime with a maximum at 6.3 Å, along with pores in the 10–40 Å range (Figure 3b). The small micropores of this material are consistent with the likely non-planar structure (Figure S117–S118), whereas the larger mesopores could arise due to defects from residual ketones or due to void spaces between particles. This pore size distribution is similar to that determined for the previously reported material *tri-PPN* (SI Figure S112). Importantly, when 1,3,5-triethylbenzene was subjected to the same reaction conditions, a low yield of a non-porous solid was obtained, confirming that the acetyl groups of **TAB** are critical to the formation of a porous polymeric material (see SI section 8 for details). Given its superior porosity compared to the other **TAB-CMP** samples prepared herein, **TAB-CMP-400** °C, **5.0** eq. was selected for further characterization to validate the proposed structure for this material.

As confirmed by scanning electron microscopy (SI Figure S15), tunneling electron microscopy (SI Figure S17), and powder X-ray diffraction (SI Figure S37), TAB-CMP-400 °C, 5.0 eq. is amorphous. This is likely due to the irreversible nature of the Lewis acid-mediated cyclotrimerization reaction resulting in the formation of an aromatic ring.<sup>5</sup> Therefore, the structure of this material was interrogated using solid-state Raman, UV-Vis absorption, and magic angle spinning (MAS) <sup>1</sup>H and <sup>13</sup>C solid-state nuclear magnetic resonance (SSNMR) spectroscopies (Figure 4). The Raman spectrum of TAB-CMP-400 °C, 5.0 eq. contains two primary peaks at 1611 and 1352 cm<sup>-1</sup>, which are similar to the G and disorder-induced D bands, respectively, of graphene-like materials,<sup>45,46</sup> including carbon-rich CMPs (Figure 4a).<sup>47</sup> Similarly, the solid-state UV-Vis absorption spectrum of TAB-CMP-400 °C, 5.0 eq. dispersed in BaSO<sub>4</sub> displayed broadband visible light absorption above 300 nm without a discernible optical band gap, consistent with the black color of this material and a high degree of conjugation (Figure 4b). The UV-Vis absorption profile of TAB-CMP-400 °C, 5.0 eq. directly contrasts with those of OFC materials, which typically do not display significant absorption at longer wavelengths (Figure S100).<sup>23</sup> While the Raman and UV-Vis absorption spectra of TAB-CMP-400 °C, 5.0 eq. are consistent with the proposed graphene-like structure, they could also be indicative of partial graphitization under the harsh ionothermal conditions.<sup>44</sup> Critically, the MAS <sup>1</sup>H SSNMR spectrum of desolvated TAB-CMP-400 °C, 5.0 eq. revealed a strong resonance centered at approximately 7.5 ppm, representing aromatic protons that would not be expected in a fully graphitized carbon material (Figure 4c). Consistently, the H/C ratio determined by combustion analysis (4.1%) was found to be similar to the predicted ratio (4.2%). Last, the cross-polarized (CP) MAS <sup>13</sup>C SSNMR spectrum of TAB-CMP-400 °C, 5.0 eq. contains two main aromatic resonances corresponding to C-H and quaternary carbons, as confirmed by experiments carried out with different <sup>1</sup>H-<sup>13</sup>C contact times (Figure 4d). Importantly, resonances corresponding to ketones (~200 ppm) were not observed,



**Figure 4.** Solid-state spectroscopic characterization of **TAB-CMP** prepared at 400 °C with 5.0 equivalents of ZnCl<sub>2</sub>. a) Raman spectrum with D and G bands resembling those of graphene-like materials indicated. b) Solid-state UV-Vis absorption spectrum. Inset: image of sample. c) MAS <sup>1</sup>H SSNMR (700 MHz) spectrum. d) CP MAS <sup>13</sup>C SSNMR (175 MHz) spectra with two different contact times. Inset: Fitted spectra and deconvolution, with the two main peaks at 124.5 and 126.7 ppm assigned to aromatic carbons with and without attached protons, respectively. Asterisks mark spinning sidebands. SSNMR spectra were collected at a spinning speed of 20 kHz.

consistent with the high degree of cyclotrimerization suggested by IR spectroscopy (Figure 2) and EDS (SI Figure S16). Similar spectra were obtained for an independently prepared sample from that shown in Figure 4 (SI Figure S23–S24). Overall, the 77 K N<sub>2</sub> uptake and spectroscopic and elemental analysis data presented herein are consistent with extensive cyclotrimerization during the synthesis of **TAB-CMP-400** °C, **5.0 eq.** 

**Generality of ionothermal cyclotrimerization.** Encouraged by the successful ionothermal cyclotrimerization of TAB, we next evaluated the generality of this method using several di-, tri-, and tetra-acetylated monomers (see SI Section 2 for synthesis of monomers). Cyclotrimerization reactions were carried out using 10 eq. of ZnCl<sub>2</sub> at 400 °C following the standard procedure for preparing **TAB-CMP**. Significant conversion of the monomers into polymeric materials occurred in every case, as confirmed by IR and Raman spectroscopies, EDS, PXRD, and SEM (see SI



Figure 5. Synthesis of TAPM-PAF via the ionothermal cyclotrimerization of TAPM. The idealized structure of TAPM-PAF is shown.

Section 4 for details). Only the PAF synthesized from tetrakis(4acetylphenyl)methane (TAPM, Figure 5), designated as CORN-PAF-1 and referred to herein as TAPM-PAF-400 °C, 10 eq., was found to be porous to N<sub>2</sub> at 77 K, which is likely due to significant graphitization or decomposition of the other monomers. Therefore, TAPM-PAF-400 °C, 10 eq. was characterized further. The 77 K N<sub>2</sub> BET and Langmuir surface areas of TAPM-PAF-400

°C, 10 eq. were  $133 \pm 1 \text{ m}^2/\text{g}$  and  $192 \pm 2 \text{ m}^2/\text{g}$ , respectively (Figure 6a). These values are lower than those obtained for TAB-CMP prepared under identical conditions (Figure 3), which may be due to interpenetration or a higher degree of graphitization or decomposition during the synthesis of TAPM-PAF. Consistent with the latter explanation, increasing the synthesis temperature to 500 °C (TAPM-PAF-500 °C, 10 eq.) significantly reduced the porosity of this material, whereas reducing the synthesis temperature to 300 °C (TAPM-PAF-300 °C, 10 eq.) greatly improved its porosity (BET surface area =  $361 \pm 3 \text{ m}^2/\text{g}$ , Langmuir surface area =  $627 \pm 13 \text{ m}^2/\text{g}$ ) with a narrow pore size distribution (Figure 6). Characterization by the spectroscopic methods outlined above confirmed significant conversion of the ketones from the monomer in both TAPM-PAF-400 °C, 10 eq. and TAPM-PAF-300 °C, 10 eq. (SI Figures S51-54). Although resonances corresponding to the expected aromatic and sp<sup>3</sup>-hybridized carbons in TAPM-PAF-300 °C, 10 eq. could be observed by CP MAS <sup>13</sup>C SSNMR, additional resonances due to defects or impurities were also observed, which likely account for its low surface area compared to TAB-CMP (SI Figure S54). Nonetheless, the <sup>1</sup>H SSNMR signal was significantly stronger than that of a commercially available carbon (SI Figure S114), confirming that this material did not undergo complete carbonization under the reaction conditions. Overall, the porosity of TAPM-PAF-300 °C, 10 eq. supports the potential generality of the ionothermal cyclotrimerization of methyl ketones as a route



**Figure 6.** a) 77 K N<sub>2</sub> adsorption (filled circles) and desorption (open circles) isotherms of **TAPM-PAF** prepared at various temperatures with 10 equivalents of ZnCl<sub>2</sub>. b) N<sub>2</sub>-Tarazona NLDFT-calculated pore size distribution of **TAPM-PAF** synthesized at 300 °C, assuming a cylindrical pore geometry.



**Figure 7.** Supercapacitor performance of **TAB-CMP-400** °C, **5.0** eq. a,b) CV measurements using different sweep rates. c) Galvanostatic charge-discharge measurements at different current densities. d) Capacitance values determined from charge-discharge measurements.

to prepare microporous polymers, but further work is required to identify milder reaction conditions that lead to reduced degradation of certain monomers.

**Supercapacitor performance of TAB-CMP.** Due to the microporosity and highly conjugated structure of **TAB-CMP-400** °**C**, **5.0 eq.**, we evaluated its potential for supercapacitive energy storage using standard electrochemical methods (Figure 7). A slurry consisting of 80% **TAB-CMP-400** °**C**, **5.0 eq.**, 10% Super P carbon, and 10% polytetrafluoroethylene (PTFE) binder was pressed into a nickel foam current collector and dried at 110 °C under vacuum overnight. The resulting electrode was subjected to cyclic voltammetry (CV) measurements in acetonitrile with 1.5 M tetraethylammonium tetrafluoroborate (Et<sub>4</sub>NBF<sub>4</sub>) as the supporting electrolyte (Figure 7a–b). **TAB-CMP-400** °**C**, **5.0 eq.** exhibited reversible supercapacitive charge storage by CV. The voltametric profiles appear as distorted rectangles, delivering higher currents at more cathodic potentials. The profiles become more rectangular at faster scan rates (Figure S93), indicating that the deviation from ideal capacitor behavior likely arises from diffusion-limited, pseudo-Faradaic processes such as the reduction of residual Zn<sup>2+</sup> ions or carbonyl groups in the CMP.<sup>48</sup> High

specific capacitance values, up to a maximum of approximately 120 F/g, were achieved at slow sweep rates (0.5–1 mV/s). Importantly, these maximum capacitance values are higher than those observed for a commercial supercapacitor activated carbon at the same sweep rates (SI Figure S94). However, a gradual drop in capacitance was observed for **TAB-CMP-400** °C, **5.0 eq.** at faster sweep rates (approximately 60 F/g at 20 mV/s), which is likely due to the small pores of this material limiting ion diffusion at faster sweep rates.<sup>49</sup>

The supercapacitor performance of TAB-CMP-400 °C, 5.0 eq. was further assessed using galvanostatic charge-discharge measurements carried out at a range of current densities over the potential window from -1.8 to -1.0 V vs. Ag/AgCl (Figure 7c-d). Notably, lower capacitance values were obtained using a wider potential range (-1.8 to -0.5 V vs. Ag/AgCl, SI Figure S95), and thus the narrower window was employed for all charge-discharge experiments. The chargedischarge curves were found to be relatively symmetrical at all current densities, indicating that supercapacitive charging is reversible in this material. As expected, the delivered capacitance varied inversely with current density, delivering the highest capacitance at the slowest rates of charge and discharge. Promisingly, at a current density of 0.1 A/g, a high capacitance of 172 F/g could be achieved using TAB-CMP-400 °C, 5.0 eq. This value is within the range of typical capacitance values for carbon nanomaterials (100-300 F/g).<sup>41,42</sup> When the current density was increased to 1 A/g, the material still delivered a capacitance of 113 F/g, which is comparable to that reported for other CMPs, 5,7,50 such as triazatruxene-based polymers (141 F/g at 1.0 A/g)<sup>51</sup> and porphyrin-based CMPs (142 F/g at 5 A/g),<sup>52</sup> but lower than that reported for larger-pore CMPs, such as aza-CMPs (300–400 F/g at 1.0 A/g)<sup>50,53</sup> and  $\beta$ -ketoenamine linked porous polymers (252 F/g at 1.0 A/g).<sup>54</sup> Consistent with the CV data, the drop in capacitance at higher current densities suggests restricted ion diffusion within the small pores of this material at fast rates.<sup>5,49,53</sup> Indeed, potentiostatic electrochemical impedance spectroscopy (PEIS) measurements further support that the charging process is limited by ion diffusion and not by electrochemical double layer formation, indicated by the absence of a vertical line at low frequencies in the Nyquist plot (SI Figure S96).<sup>55</sup> In addition, the relatively large magnitude of the impedance values in the Nyquist plot (SI Figure S96) suggests that TAB-CMP-400 °C, 5.0 eq. displays high electrical resistivity. Two-point probe measurements confirm that this material possesses a moderate intrinsic conductivity  $(5.7 \times 10^{-5})$ S/cm), which is a common challenge facing CMPs (SI Figure S98).<sup>5,53,56</sup> Nonetheless, the conductivity of TAB-CMP-400 °C, 5.0 eq. is significantly higher than those of both OFC-1b (2.2  $\times 10^{-7}$  S/cm, SI Figure S102) and tri-PPN (2.9  $\times 10^{-7}$  S/cm, SI Figure S109), confirming that more complete cyclotrimerization leads to materials with higher electronic conductivities. Overall, our results suggest that the narrow pore size distributions and high surface areas displayed by CMPs prepared by acetyl trimerization offer promise for the design of next-generation supercapacitor materials, but additional work is required to increase the pore size and electrical conductivity of these materials for optimal performance.

### Conclusion

This work demonstrates that the solvent-free cyclotrimerization of methyl ketones can be driven to high conversions using molten  $ZnCl_2$  as the reaction solvent, leading to highly-conjugated microporous organic materials. In particular, the amorphous CMP prepared from **TAB** possesses a low degree of residual carbonyl groups and a relatively narrow pore size distribution. As such, it is a promising platform for supercapacitive energy storage, although further work is required to prepare larger pore variants to increase their capacities at faster charge-discharge rates.

Future efforts will focus on broadening the monomer scope of this transformation in order to unlock ionothermal cyclotrimerization as a sustainable and general method for the preparation of microporous organic materials.

## **Experimental/Methods.**

General Procedures. All reagents were purchased from commercial vendors and used without additional purification unless noted otherwise in the SI. Infrared spectra were collected on a Bruker Tensor II IR spectrometer with a diamond Attenuated Total Reflectance (ATR) attachment. Surface area data were collected on a Micromeritics 3-flex gas sorption analyzer using ultrapure N<sub>2</sub> (99.999%) and a liquid N<sub>2</sub> bath. Brunauer-Emmett-Teller (BET) and Langmuir surface areas were determined by linear least squares regression analysis using the linearized forms of the BET and Langmuir equations, respectively. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Ultima IV diffractometer equipped with a Cu K<sub>a</sub> source ( $\lambda = 1.5406$  Å) and were baseline-corrected using OriginPro. Solution-state NMR data were collected on a Bruker INOVA 500 MHz spectrometer and were referenced to residual solvent. Mass spectral (MS) data were obtained on Advion Mass Spectrometer equipped with an APCI (Atmospheric Pressure Chemical Ionization) module. Solid-state UV-Vis absorption spectra were collected using a Shimadzu UV-2600i UV-Vis Spectrophotometer equipped with an ISR-2600 Plus Integrating Sphere. Thermogravimetric decomposition profiles were collected on a TA Instruments Q500 V6.7 thermogravimetric analyzer using a temperature ramp of 5.00  $^{\circ}$ C/min from room temperature to 600.00 °C. Energy dispersive X-ray scattering (EDS) data were collected at 10.0 kV using a Zeiss Gemini 500 scanning electron microscope equipped with an Oxford Instruments Ultima Max 170 detector (detector type X-max) and processed using the AZtec software. Idealized structural models were constructed using BIOVIA Materials Studio 2020 (extended structures) or Avogadro (molecular fragments). C/H combustion elemental analysis was performed by Atlantic Microlab Inc. Details of scanning electron microscopy (SEM), tunneling electron microscopy (TEM), magic angle spinning solid-state NMR (MAS SSNMR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and electrochemistry experiments are included in the SI.

**Example procedure for the synthesis of polymeric samples.** Three 8 mm diameter borosilicate glass tubes were each charged with monomer (40.0 mg) and anhydrous zinc chloride (1-10 molar eq.) that was freshly removed from a desiccator. The tubes were evacuated (<100 mTorr), and then flame-sealed under high vacuum using a natural gas torch and a custom-built apparatus (SI Figure S13). The tubes were placed in an oven and heated at 400 °C for 72 h (temperature sequence: ramp up to 400 °C over 6 h from room temperature, hold at 400 °C for 72 h, cool down to 23 °C over 6 h). The tubes were cooled to room temperature and were snapped into two pieces using a glass tube cutter. The black reaction mixture was scraped out of the tubes with a Hayman Style spatula, using water (10 mL) to help slide the mixture off the tube walls. The reaction mixtures from all three tubes were combined in a 100 mL jar and suspended in 3 M HCl (28 mL). The suspension was allowed to stir for 24 h. The heterogeneous mixture was filtered, and the resulting shiny black solid was rinsed with water  $(3 \times 5 \text{ mL})$  and THF  $(3 \times 5 \text{ mL})$ . The solid was transferred to a 20 mL scintillation vial filled with THF and allowed to stand for 24 h at room temperature, after which the THF was decanted off and replaced with fresh THF. This soaking process was repeated two more times for a total of three THF soaks. After the third THF soak, the THF was decanted from the solid and replaced with acetone. The vial was allowed to stand for 24 h at room temperature,

after which the acetone was decanted from the solid and replaced with fresh acetone. This soaking process was repeated two more times for a total of three acetone soaks. The acetone was decanted, and the solid was oven-dried at 120 °C for 6 h and then allowed to cool to room temperature prior to characterization.

## **Supporting Information.**

Synthetic procedures for preparing monomers and polymers, experimental characterization data for all polymeric samples, and details of electrochemistry experiments.

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