



Pyrrole-Based Conjugated Microporous Polymers as Efficient Heterogeneous Catalysts for Knoevenagel Condensation

Ruidong Gao¹, Guang Zhang^{1*}, Fanli Lu¹, Long Chen¹ and Yang Li^{1,2*}

¹Department of Chemistry, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin, China, ²College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen, China

OPEN ACCESS

Edited by:

Mengmeng Li,
Institute of Microelectronics, China

Reviewed by:

San-Yuan Ding,
Lanzhou University, China
Shijie Ren,
Sichuan University, China
Jia-Xing Jiang, Shaanxi Normal
University, China

*Correspondence:

Guang Zhang
zhangg@tju.edu.cn
Yang Li
liyang2014@szu.edu.cn

Specialty section:

This article was submitted to
Supramolecular Chemistry,
a section of the journal
Frontiers in Chemistry

Received: 29 March 2021

Accepted: 26 April 2021

Published: 10 May 2021

Citation:

Gao R, Zhang G, Lu F, Chen L and Li Y
(2021) Pyrrole-Based Conjugated
Microporous Polymers as Efficient
Heterogeneous Catalysts for
Knoevenagel Condensation.
Front. Chem. 9:687183.
doi: 10.3389/fchem.2021.687183

Conjugated microporous polymers (CMPs) with robust architectures, facilely tunable pore sizes and large specific surface areas have emerged as an important class of porous materials due to their demonstrated prospects in various fields, e.g. gas storage/separation and heterogeneous catalysis. Herein, two new pyrrole-based CMPs with large specific surface areas and good stabilities were successfully prepared by one-step oxidative self-polycondensation of 1,2,4,5-tetra (pyrrol-2-yl)benzene or 1,3,5-tri (pyrrol-2-yl)benzene, respectively. Interestingly, both CMPs showed very high catalytic activity toward Knoevenagel condensation reaction, which was attributed to the inherent pore channels, high specific surface areas and abundant nitrogen sites within CMPs. Additionally, both CMPs displayed excellent recyclability with negligible degradation after 10 cycles. This work provides new possibilities into designing novel nitrogen-rich high-performance heterogeneous catalysts.

Keywords: heterogeneous catalysis, pyrrole, knoevenagel condensation, conjugated microporous polymers, photocatalysis

INTRODUCTION

Porous materials play significantly important roles in many fields of science and technology and have resurged with great popularity within last two decades. This, in part, is due to the emerging several kinds of unprecedented architectures with intriguing properties, e.g. metal-organic frameworks (Jiao et al., 2019), covalent organic frameworks (Cote et al., 2005) and conjugated microporous polymers (CMPs) (Cooper, 2009). CMPs are conjugated 2-dimensional or 3-dimensional polymers in contrast to many other porous materials and therefore are rigid and shape-persistent. Different from COFs, CMPs (Yue et al., 2020; Xu et al., 2021) are synthesized under kinetic control and are generally amorphous; thereby CMPs are more stable and obtained easier than COFs due to the much more kinds of reactions available for construction of CMPs, such as Sonogashira-Hagihara coupling reaction (Jiang et al., 2007) and Buchwald-Hartwig coupling reaction (Liao et al., 2018). Besides extended conjugation and high flexibility in structural design, CMPs also bear the merits of permanent porosity and tunable pore sizes. These characteristics of CMPs confer them with diverse potential applications (Lee and Cooper, 2020). For example, their π -conjugation has endowed CMPs with abundant electronic properties which have been employed to develop photocatalysts (Zhao et al., 2018) and light harvesting materials (Chen et al., 2010a). In addition, CMPs also exhibit promising prospects in heterogeneous catalysis (Chen et al., 2010a; Jiang et al., 2011), gas adsorption (Dawson et al., 2011; Lu et al., 2012), light emission (Xu et al., 2011),

chemical sensors (Liu et al., 2012), energy storage (Kou et al., 2011; Xu et al., 2014; Yue et al., 2020), and biosensing (Gu et al., 2014; Ding and Han, 2015; Tan et al., 2015; Rengaraj et al., 2016).

Catalyst is an indispensable part of organic synthesis. Unfortunately, thus far, many catalysts used in industry are still non recyclable. For a sustainable future, developing reusable heterogeneous catalysts is regarded as an environmentally benign approach due to their easy separation and cleaning processes after reactions (Sartori et al., 2004). In this regard, porous materials, e.g. MOFs (Huang et al., 2020), COFs (Zhao et al., 2020) and CMPs (Tantisriyanurak et al., 2020; Xu et al., 2021) have been demonstrated as promising platforms to develop recyclable heterogeneous catalysts in part due to their large specific surface areas which could accommodate abundant guest molecules and afford many nanoreactors. In particular, researchers have been actively studying CMP-based heterogeneous catalysts over the last decade due to their insolubility in common organic solvents, high stability, inherent porosity and tailor-made functionality through facile structural design. For example, CMPs could serve as the nanoporous scaffolds for metals support to mediate catalysis (Schmidt et al., 2009; Chan-Thaw et al., 2010; Hasell et al., 2010; Gu et al., 2014). In addition, CMPs could also function as catalysts for various chemical transformations, e.g. CO₂ reduction reaction (Hou et al., 2020), water splitting for hydrogen production (Zhao et al., 2018), aerobic oxidations (Jiang et al., 2020), α -alkylation of aldehydes (Luo et al., 2015), Knoevenagel condensation (Feng et al., 2017) and singlet oxygen generation (Zhang et al., 2013). However, the cost-effective CMP based heterogeneous catalysts with excellent catalytic performances is still very rare. Thus, the development of CMP based heterogeneous catalysts is highly desired and continuously attracting growing research interests.

Pyrrole is a widely used monomer for constructing various functional materials. For example, polypyrrole represents as one of the state-of-the-art conductive polymer (Vernitskaya and Efimov, 1997), and three-dimensional polypyrroles were developed due to their enhanced performances in supercapacitors, sensors, etc. compared with linear polypyrroles. Porphyrin as a 4-fold pyrrole analog serves as a versatile monomer to construct all kinds of architectures like porphyrin-based belts (Minotto et al., 2021), polymers (Day et al., 2015), MOFs (Zhang et al., 2015), COFs (Hao et al., 2019) and CMPs (Chen et al., 2010b) for diverse applications. On account of the many functions and broad prospects of pyrrole-based materials, it is interesting to develop new kind of pyrrole-based architectures and explore their properties and applications. In this respect, even though several porphyrin-based CMPs have been reported (Chen et al., 2010b; Modak et al., 2013; Liu et al., 2014; Xu et al., 2019; Zhu et al., 2020), to the best of our knowledge, pyrrole-based CMPs are very rare (Lee and Cooper, 2020).

Herein, we designed and synthesized two new pyrrole-based CMPs (TrPB-CMP and TePB-CMP) through a simple FeCl₃-oxidized self-condensation of multitopic pyrrole monomers (Scheme 1). We further characterized the structures and explored the properties of both CMPs with different

techniques and then evaluated their catalytic performances toward Knoevenagel condensation reaction. Remarkably, both CMPs exhibit excellent catalytic activity and show superior recyclability.

EXPERIMENTAL

Synthesis of Pyrrole-Based Monomers and CMPs

The corresponding pyrrole-based monomers, i.e. 1,3,5-tri (pyrrol-2-yl) benzene and 1,2,4,5-tetra (pyrrol-2-yl) benzene (Xue et al., 2019) (Scheme 1) were readily prepared by one-step Suzuki coupling reaction between 1-(tert-butoxycarbonyl)-pyrrole-2-boronic acid and 1,3,5-tribromobenzene or 1,2,4,5-tetra-bromobenzene respectively (supporting information). Subsequently, both CMPs were synthesized by oxidative self-polymerization within chloroform at room temperature (Supplementary, ESI).

RESULTS AND DISCUSSION

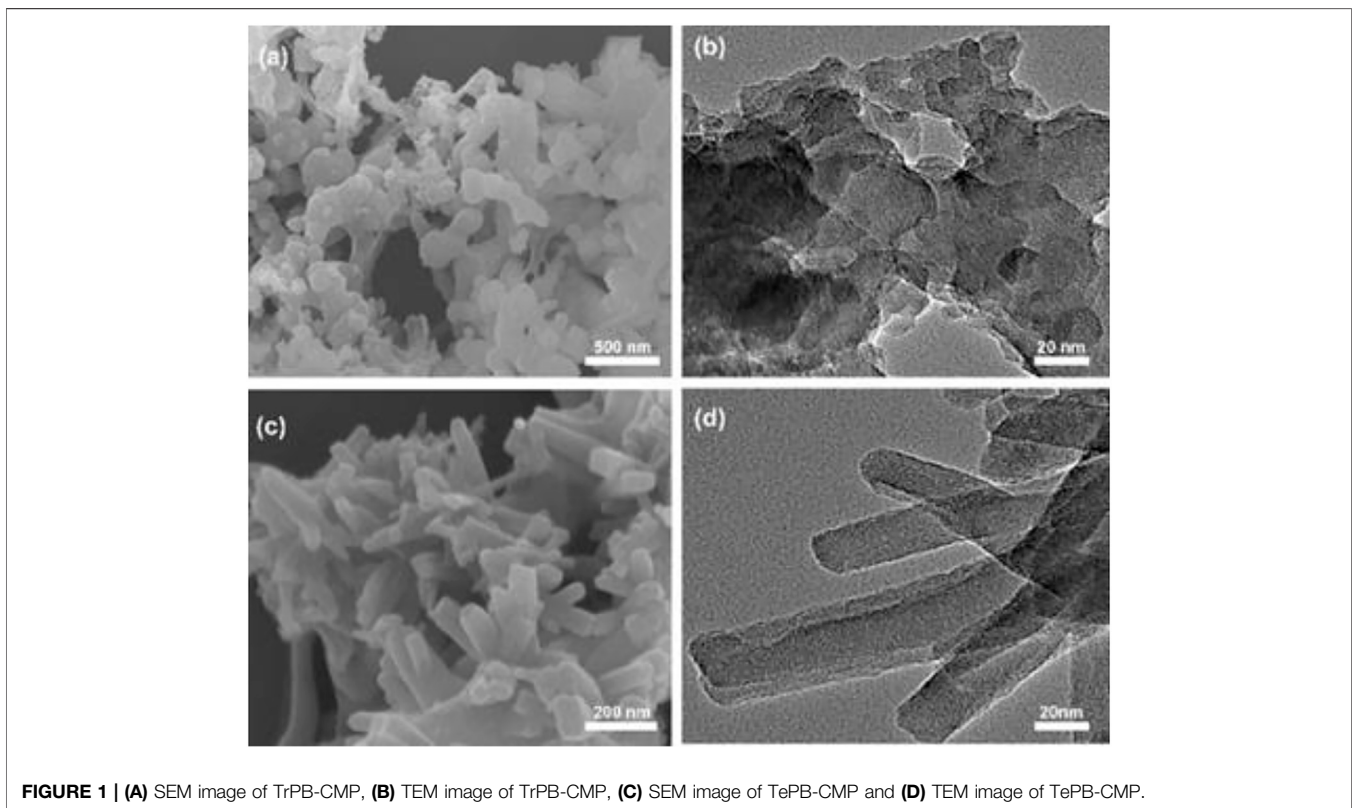
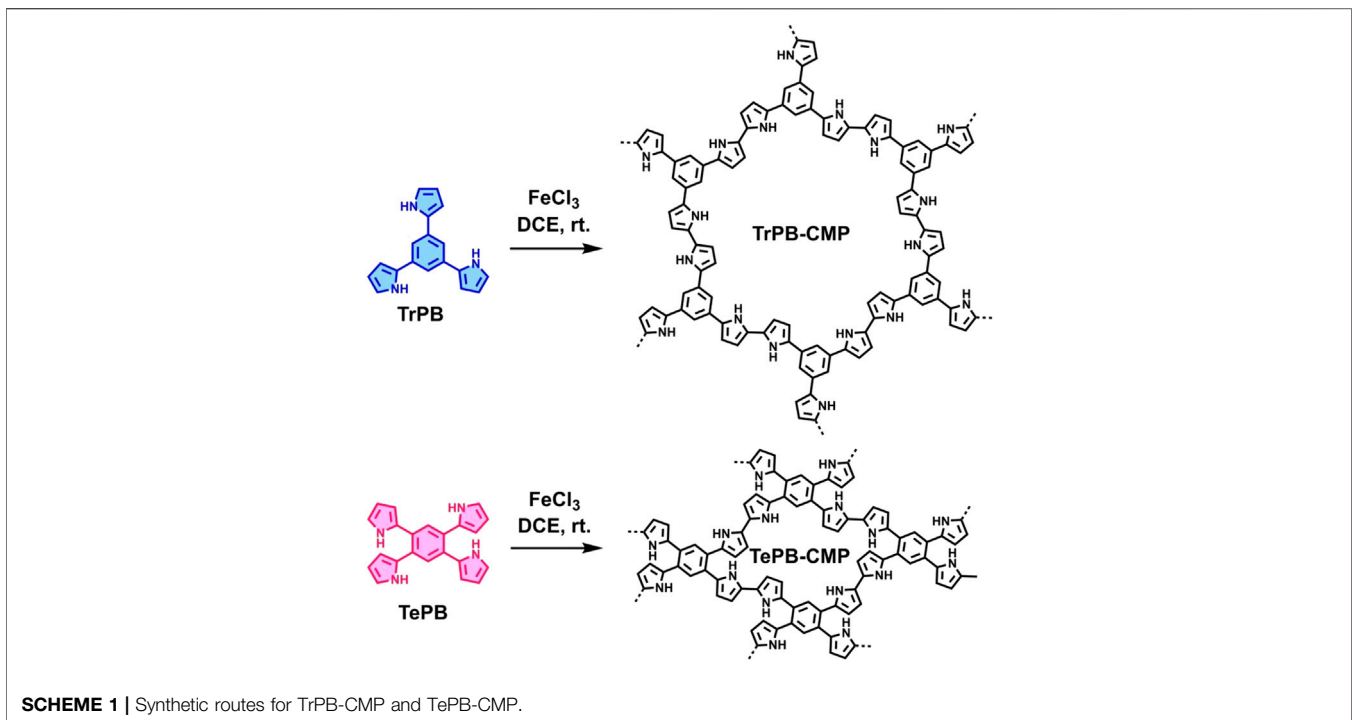
Structural Characterizations

The structures of both CMPs were characterized by Fourier transform infrared (FT-IR) and solid-state ¹³C cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopies. As for FT-IR spectra of both pyrrole-based CMPs (Supplementary Figures S5, S6, ESI), the bands between 3450 and 3200 cm⁻¹ correspond to the stretching vibrations of amino moieties (-NH-) originated from pyrroles (Soliman et al., 2007; Mohamed et al., 2008; Karabacak and Cinar, 2012). In addition, the bands at 1250 cm⁻¹ are attributed to the -C-N- stretching vibrations (Zhang et al., 2004; Cai et al., 2011). The peaks at 1408 cm⁻¹ for both CMPs are assignable to the stretching vibrations of -C=C- in the aromatic rings (Svatos and Attygalle, 1997; Samran et al., 2004). ¹³CP-MAS NMR spectra display broad signals between 100 and 140 ppm, which are attributed to the carbon signals from pyrrole and benzene rings (Supplementary Figures S13, S14, ESI) and the positions of these peaks are also in accordance with those of the monomers.

Properties of CMPs

The crystallinities of these polymers were determined by powder X-ray diffraction (PXRD) measurements (Supplementary Figure S10, ESI). Both materials show merely a broad diffraction band between 15° and 35°, which suggests both TrPB-CMP and TePB-CMP are amorphous in nature.

To gauge the thermal stabilities of the CMPs, thermal gravimetric analysis (TGA) under nitrogen atmosphere were carried out for both materials. The curves indicate that the weights remain 97% for TrPB-CMP at 221°C and TePB-CMP at 234°C respectively (Supplementary Figure S11, ESI), further increasing the temperature renders rapid weight losses with 69% of the initial weights at 800°C, which corresponds to the degradation of the materials. To probe the photophysical



properties of the CMPs, solid state diffuse reflectance UV-vis spectra of the TrPB-CMP and TePB-CMP were measured (**Supplementary Figure S12**, ESI). Both TrPB-CMP and TePB-CMP exhibited broad absorption band centered at 572 and 526 nm, respectively, which is assignable to the π - π^* transitions of pyrrole-based conjugated networks within CMPs. Remarkably, the absorption edges of both CMPs extend to the short-wavelength infrared region (up to 2000 nm). Moreover, the morphologies of both microporous polymers were investigated by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). SEM images reveal TrPB-CMP consists of submicrometer-sized spheres while TePB-CMP is composed of submicrometer-sized flakes (**Figure 1**). In addition, TEM images show that the pore does not produce a specific texture which verify the amorphous nature of both CMPs.

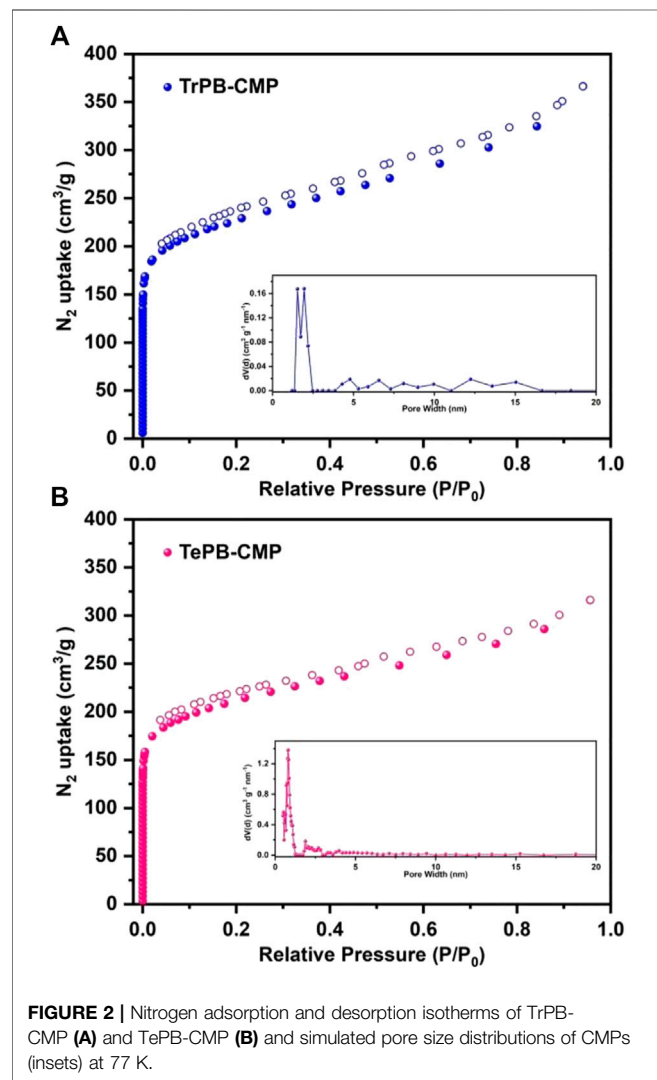
The porosities of CMPs were evaluated by nitrogen (N_2) sorption measurements. As shown in **Figure 2**, the nitrogen adsorption rate is extremely fast in the low relative pressure range, which indicates CMPs possess micropores. The hysteresis

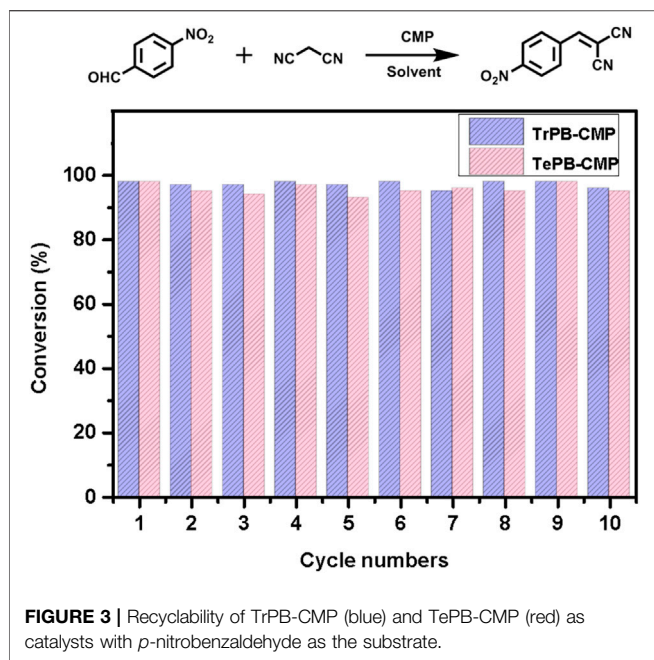
loop appeared in the middle pressure range of N_2 adsorption curves indicates the existence of mesopores in CMPs (Thommes et al., 2015). The Brunauer-Emmett-Teller (BET) specific surface areas of TrPB-CMP and TePB-CMP were calculated as 810 and $800 \text{ m}^2 \text{ g}^{-1}$ respectively. The pore size distributions (PSDs) of CMPs were computed based on the adsorption branch by nonlocal density functional theory (NLDFT) method, which showed the average pore sizes of TrPB-CMP and TePB-CMP were around 1.53 and 0.80 nm respectively. Interestingly, the pore size of TrPB-CMP obtained by theoretically modeling one hexagonal segment (**Supplementary Figure S18**, ESI) was around 1.51 nm, which was in good consistency with the experimental result. While the pore size of TePB-CMP obtained by theoretically modeling one hexagonal segment (**Supplementary Figure S19**, ESI) was around 0.7 nm, which was also close to the experimental result.

Catalytic Performances Toward Knoevenagel Condensation

Considering the presence of weakly basic pyrrole moieties within both CMPs, the CMPs might be used as heterogeneous catalysts for base-catalyzed reactions which are extremely important in catalyzing the synthesis of various small molecules for chemical and pharmaceutical industries (Perryman et al., 2013; Volchkov and Lee, 2013; Denmark et al., 2014). In this respect, base-catalyzed Knoevenagel condensation was selected as the model reaction to evaluate the catalytic activity of both CMPs. Knoevenagel condensation as a well-known and powerful reaction to formulate -C=C- bonds, exhibits broad applications in producing natural products, fine chemicals and pharmaceuticals (Knoevenagel and Dtsch, 1898; Khare et al., 2019). Recently, some representative exploratory researches on Knoevenagel condensation with porous materials as the catalysts were reported including benzimidazole-based porous organic polymers (Wang et al., 2015), 3D imine-linked COF (Fang et al., 2014), and porphyrin-based porous polymer (Modak et al., 2013).

Various reaction substrates were used to test the catalytic activities of the CMP catalysts under classical reaction conditions (Wang et al., 2015; Taher et al., 2020). In addition, the reaction temperature, solvent and reaction temperature were investigated in details to find the best conditions for the reaction (**Supplementary Table S2**, ESI). The yields of the substrates in the Knoevenagel condensation reaction were summarized in **Table 1**. As displayed in **Table 1**, remarkably, the reactions were completed after 1 h and the yields for all substrates under the catalysis of CMPs were quite high, which was much higher than that without addition of CMPs (44%) (**Supplementary Table S3**, entry 1, ESI). As for benzaldehydes with strong electron-withdrawing substituents in the *para*-position, the catalytic efficiency of both TrPB-CMP and TePB-CMP are basically the same with nearly quantitative conversions (entries 4, 5). The catalytic effects of both CMPs proved to be obviously different when the electron-withdrawing strength of the *para*-substituent on benzaldehyde was weakened (entries 2 and 3). It suggests TrPB-CMP renders higher conversions than





TePB-CMP for the benzaldehyde substrates, which is probably due to more adequate interactions between the substrates and the basic sites within the pores of TrPB-CMP than those of TePB-CMP rendered by the bigger pore size of TrPB-CMP (entries 1 and 2). Moreover, for larger size molecules, there is a significant difference in catalytic efficiency, probably because the steric hindrance of the larger substrate molecules is not

conducive to entering the micropores (entry 7). When using benzaldehyde substrates with electron-donating substituents, the catalytic yields of both TrPB-CMP and TePB-CMP were lower (entries 8 and 9). In addition, compared with the results reported in the previous literatures, the reaction conditions of the current work have advantages over others, e.g., metal-free catalysis and shorter reaction time (**Supplementary Table S4**, ESI).

To illustrate the high catalytic performance and gain further insights into the catalytic mechanism, additional comparison experiments were performed to evaluate the catalytic activity of pyrrole-based small molecules, i.e. TrPB and TePB (**Scheme 1**) and linear polypyrrole toward Knoevenagel condensation under the same conditions as those of CMPs. As shown in **Supplementary Table S3**, the catalytic activity of TrPB, TePB and polypyrrole was not obvious, which was similar to without any catalyst. Consequently, compared with non-porous analogues, the open porous structure allows the reactants to easily enter the catalytic center. In addition, the larger the specific surface area of the pore, the better the catalytic performance. Due to the high specific surface area and microporous character, benzimidazole-based CMPs (BPOP-1 and BPOP-2) was favorable for the accessibility of substrates to catalytic active sites inside the framework (Wang et al., 2015), which make the heteroatoms on the pore wall fully exhibit catalytic activity. Moreover, Similar pore restriction effects also appeared in other catalytic reactions (Mackintosh et al., 2008; Hu et al., 2020; Yang et al., 2020).

As for testing the rates of the reactions, *p*-nitrobenzaldehyde was used as the substrate which catalyzed by both TrPB-CMP and

TABLE 1 | Catalytic activities of TrPB-CMP or TePB-CMP toward Knoevenagel condensation with different aromatic aldehyde substrates.

Entry	R	Substrates	Product	Yield (%) ^a	
				TrPB-CMP	TePB-CMP
1	H			74	66
2	Br			79	74
3	OH			95	89
4	NO ₂			99	99
5	CN			99	99
6	C(CH ₃) ₃			7	6
7	Ph			41	18
8	CH ₃			36	23
9	OCH ₃			17	12

^aReaction conditions: A (1 mmol), B (1.1 mmol), TrPB-CMP or TePB-CMP (0.1 mmol), H₂O (0.5 ml), toluene (1.5 ml). All reaction yields were obtained by the results of GC-MS.

TePB-CMP (**Supplementary Figures S15, S16**, ESI). The results suggested the substrates are quickly converted into the products within 30 min for both CMP-catalyzed reactions and reached the maximum conversion within 1 h. The conversion rate of TrPB-CMP is faster than that of TePB-CMP, which was probably benefited from the bigger pore size and specific surface area of TrPB-CMP. As to the recyclability of both CMP catalysts, as shown in **Figure 3**, the catalytic activities of both CMPs are basically unchanged within 10 cycles. After 10 cycles, FT-IR spectra of both recycled CMPs appeared the same as those of the pristine CMPs, which suggests the structures of both CMPs are robust and intact (**Supplementary Figures S7, S8**, ESI). In addition, after 10 cycles, the N₂ adsorption tests indicated the BET specific surface areas of TrPB-CMP and TePB-CMP were 800 and 781 m²g⁻¹, respectively, both of which were only slightly decreased compared with those of the pristine CMPs (**Supplementary Figures S17**, ESI). Consequently, it reveals both CMPs serve as efficient heterogeneous catalysts with excellent recyclability.

CONCLUSION

In summary, two new pyrrole-based conjugated microporous polymers were successfully synthesized by self-polymerization of 1,3,5-tri-(pyrrol-2-yl)benzene or 1,2,4,5-tetra (pyrrol-2-yl)benzene. These two CMPs effectively catalyzed Knoevenagel condensation reaction with diverse substrates and showed excellent recycling performance, which was attributed to the open pore channels, large specific surface area and abundant heteroatoms as active sites within CMPs. This work suggests a

REFERENCES

- Cai, Y.-m., Qin, Z.-y., and Chen, L. (2011). Effect of Electrolytes on Electrochemical Properties of Graphene Sheet Covered with Polypyrrole Thin Layer. *Prog. Nat. Sci. Mater. Int.* 21 (6), 460–466. doi:10.1016/S1002-0071(12)60083-5
- Chan-Thaw, C. E., Villa, A., Katekomol, P., Su, D., Thomas, A., and Prati, L. (2010). Covalent Triazine Framework as Catalytic Support for Liquid Phase Reaction. *Nano Lett.* 10 (2), 537–541. doi:10.1021/nl904082k
- Chen, L., Honsho, Y., Seki, S., and Jiang, D. (2010a). Light-harvesting Conjugated Microporous Polymers: Rapid and Highly Efficient Flow of Light Energy with a Porous Polyphenylene Framework as Antenna. *J. Am. Chem. Soc.* 132 (19), 6742–6748. doi:10.1021/ja100327h
- Chen, L., Yang, Y., and Jiang, D. (2010b). CMPs as Scaffolds for Constructing Porous Catalytic Frameworks: a Built-In Heterogeneous Catalyst with High Activity and Selectivity Based on Nanoporous Metalloporphyrin Polymers. *J. Am. Chem. Soc.* 132 (26), 9138–9143. doi:10.1021/ja1028556
- Cooper, A. I. (2009). Conjugated Microporous Polymers. *Adv. Mater.* 21 (12), 1291–1295. doi:10.1002/adma.200801971
- Cote, A. P., Benin, A. I., Ockwig, N. W., Koeffe, M., Matzger, A. J., and Yaghi, O. M. (2005). Porous, Crystalline, Covalent Organic Frameworks. *Science* 310 (5751), 1166–1170. doi:10.1126/science.1120411
- Dawson, R., Adams, D. J., and Cooper, A. I. (2011). Chemical Tuning of CO₂ Sorption in Robust Nanoporous Organic Polymers. *Chem. Sci.* 2 (6), 1173–1177. doi:10.1039/C1SC00100K
- Day, N. U., Wamser, C. C., and Walter, M. G. (2015). Porphyrin Polymers and Organic Frameworks. *Polym. Int.* 64 (7), 833–857. doi:10.1002/pi.4908
- Denmark, S. E., Wilson, T. W., and Burk, M. T. (2014). Enantioselective Construction of Quaternary Stereogenic Carbon Atoms by the Lewis Base new approach to fabricate pyrrole-based heterogeneous catalysts. Additionally, both CMPs exhibit broad absorptions between 250 and 2400 nm, which might promise application potentials in photocatalysis.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

GZ and YL designed the work. RG carried out the experimental part. RG, GZ, FL, and YL organized and wrote the manuscript.

FUNDING

This work was financially supported by National Natural Science Foundation of China (21602154).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2021.687183/full#supplementary-material>

Catalyzed Additions of Silyl Ketene Imines to Aldehydes. *Chem. Eur. J.* 20 (30), 9268–9279. doi:10.1002/chem.201403342

Ding, X., and Han, B.-H. (2015). Metallophthalocyanine-based Conjugated Microporous Polymers as Highly Efficient Photosensitizers for Singlet Oxygen Generation. *Angew. Chem. Int. Ed.* 54 (22), 6536–6539. doi:10.1002/anie.201501732

Fang, Q., Gu, S., Zheng, J., Zhuang, Z., Qiu, S., and Yan, Y. (2014). 3D Microporous Base-Functionalized Covalent Organic Frameworks for Size-Selective Catalysis. *Angew. Chem. Int. Ed.* 53 (11), 2878–2882. doi:10.1002/anie.201310500

Feng, L.-J., Wang, M., Sun, Z.-Y., Hu, Y., and Deng, Z.-T. (2017). Hypercrosslinked Porous Polyporphyrin by Metal-free Protocol: Characterization, Uptake Performance, and Heterogeneous Catalysis. *Designed Monomers Polym.* 20, 344–350. doi:10.1080/15685551.2016.1259831

Gu, C., Huang, N., Gao, J., Xu, F., Xu, Y., and Jiang, D. (2014). Controlled Synthesis of Conjugated Microporous Polymer Films: Versatile Platforms for Highly Sensitive and Label-free Chemo- and Biosensing. *Angew. Chem. Int. Ed.* 53 (19), 4850–4855. doi:10.1002/anie.201402141

Hao, W., Chen, D., Li, Y., Yang, Z., Xing, G., Li, J., et al. (2019). Facile Synthesis of Porphyrin Based Covalent Organic Frameworks via an A2B2 Monomer for Highly Efficient Heterogeneous Catalysis. *Chem. Mater.* 31 (19), 8100–8105. doi:10.1021/acs.chemmater.9b02718

Hasell, T., Wood, C. D., Clowes, R., Jones, J. T. A., Khimyak, Y. Z., Adams, D. J., et al. (2010). Palladium Nanoparticle Incorporation in Conjugated Microporous Polymers by Supercritical Fluid Processing. *Chem. Mater.* 22 (2), 557–564. doi:10.1021/cm9030446

Hou, Y., Zhang, E., Gao, J., Zhang, S., Liu, P., Wang, J.-C., et al. (2020). Metal-free Azo-Bridged Porphyrin Porous Organic Polymers for Visible-Light-Driven CO₂ Reduction to CO with High Selectivity. *Dalton Trans.* 49 (22), 7592–7597. doi:10.1039/D0DT01436B

- Hu, X., Sun, X., Song, Q., Zhu, Y., Long, Y., and Dong, Z. (2020). N,S Co-doped Hierarchically Porous Carbon Materials for Efficient Metal-free Catalysis. *Green. Chem.* 22 (3), 742–752. doi:10.1039/c9gc03863a
- Huang, S., Chen, G., Ye, N., Kou, X., Zhang, R., Shen, J., et al. (2020). Iron-mineralization-induced Mesoporous Metal-Organic Frameworks Enable High-Efficiency Synergistic Catalysis of Natural/nanomimic Enzymes. *ACS Appl. Mater. Inter.* 12 (51), 57343–57351. doi:10.1021/acsami.0c16689
- Jiang, J.-X., Su, F., Trewin, A., Wood, C. D., Campbell, N. L., Niu, H., et al. (2007). Conjugated Microporous Poly(aryleneethynylene) Networks. *Angew. Chem. Int. Ed.* 46 (45), 8574–8578. doi:10.1002/anie.200701595
- Jiang, J.-X., Wang, C., Laybourn, A., Hasell, T., Clowes, R., Khimyak, Y. Z., et al. (2011). Metal-organic Conjugated Microporous Polymers. *Angew. Chem. Int. Ed.* 50 (5), 1072–1075. doi:10.1002/anie.201005864
- Jiang, J., Liang, Z., Xiong, X., Zhou, X., and Ji, H. (2020). A Carbazolyl Porphyrin-Based Conjugated Microporous Polymer for Metal-Free Photocatalytic Aerobic Oxidation Reactions. *ChemCatChem* 12 (13), 3523–3529. doi:10.1002/cctc.202000199
- Jiao, L., and Jiang, H. L. (2019). Metal-Organic-Framework-Based Single-Atom Catalysts for Energy Applications. *Chem.* 5(4), 786–804. doi:10.1016/j.chempr.2018.12.011
- Karabacak, M., and Cinar, M. (2012). FT-IR, FT-Raman, UV Spectra and DFT Calculations on Monomeric and Dimeric Structure of 2-Amino-5-Bromobenzoic Acid. *Spectrochimica Acta A: Mol. Biomol. Spectrosc.* 86, 590–599. doi:10.1016/j.saa.2011.11.022
- Khare, R., Pandey, J., Smriti, S., and Ruchi, R. (2019). The Importance and Applications of Knoevenagel Reaction (Brief Review). *Orient. J. Chem.* 35 (1), 423–429. doi:10.13005/ojc/350154
- Knoevenagel, E., and Dtsch, Ber. (1898). Condensation zwischen malonester und aldehyden unter dem einfluss von ammoniak und organischen aminen. *Ber. Dtsch. Chem. Ges.* 31, 2585–2595. doi:10.1002/cber.18980310307
- Kou, Y., Xu, Y., Guo, Z., and Jiang, D. (2011). Supercapacitive Energy Storage and Electric Power Supply Using an Aza-Fused π -Conjugated Microporous Framework. *Angew. Chem. Int. Ed.* 50 (37), 8753–8757. doi:10.1002/anie.201103493
- Lee, J.-S. M., and Cooper, A. I. (2020). Advances in Conjugated Microporous Polymers. *Chem. Rev.* 120 (4), 2171–2214. doi:10.1021/acs.chemrev.9b00399
- Liao, Y., Wang, H., Zhu, M., and Thomas, A. (2018). Efficient Supercapacitor Energy Storage Using Conjugated Microporous Polymer Networks Synthesized from Buchwald-Hartwig Coupling. *Adv. Mater.* 30 (12), 1705710. doi:10.1002/adma.201705710
- Liu, X., A. S., Zhang, Y., Luo, X., Xia, H., Li, H., et al. (2014). A Porphyrin-Linked Conjugated Microporous Polymer with Selective Carbon Dioxide Adsorption and Heterogeneous Organocatalytic Performances. *RSC Adv.* 4 (13), 6447–6453. doi:10.1039/c3ra46988c
- Liu, X., Xu, Y., and Jiang, D. (2012). Conjugated Microporous Polymers as Molecular Sensing Devices: Microporous Architecture Enables Rapid Response and Enhances Sensitivity in Fluorescence-On and Fluorescence-Off Sensing. *J. Am. Chem. Soc.* 134 (21), 8738–8741. doi:10.1021/ja303448r
- Lu, W., Sculley, J. P., Yuan, D., Krishna, R., Wei, Z., and Zhou, H.-C. (2012). Polyamine-tethered Porous Polymer Networks for Carbon Dioxide Capture from Flue Gas. *Angew. Chem. Int. Ed.* 51 (30), 7480–7484. doi:10.1002/anie.201202176
- Luo, J., Zhang, X., and Zhang, J. (2015). Carbazolic Porous Organic Framework as an Efficient, Metal-free Visible-Light Photocatalyst for Organic Synthesis. *ACS Catal.* 5 (4), 2250–2254. doi:10.1021/acscatal.5b00025
- Mackintosh, H. J., Budd, P. M., and Mckeown, N. B. (2008). Catalysis by Microporous Phthalocyanine and Porphyrin Network Polymers. *J. Mater. Chem.* 18 (5), 573–578. doi:10.1039/b715660j
- Minotto, A., Bulut, I., Rapisarda, G., Carnicella, G., Patrini, M., Lunedei, E., et al. (2021). Towards Efficient Near-Infrared Fluorescent Organic Light-Emitting Diodes. *Light Sci. Appl.* 10 (1), 18. doi:10.1038/s41377-020-00456-8
- Modak, A., Mondal, J., and Bhaumik, A. (2013). Porphyrin Based Porous Organic Polymer as Bi-functional Catalyst for Selective Oxidation and Knoevenagel Condensation Reactions. *Appl. Catal. A: Gen.* 459, 41–51. doi:10.1016/j.apcata.2013.03.036
- Mohamed, T. A., Soliman, U. A., Hanafy, A. I., and Hassan, A. M. (2008). Conformational Stability, Barriers to Internal Rotation of 2-aminothiophenol (D0 and D3): A Combined Vibrational and Theoretical Approach. *J. Mol. Struct. THEOCHEM* 865 (1-3), 14–24. doi:10.1016/j.theochem.2008.06.021
- Perryman, M. S., Harris, M. E., Foster, J. L., Joshi, A., Clarkson, G. J., and Fox, D. J. (2013). Trichloromethyl Ketones: Asymmetric Transfer Hydrogenation and Subsequent Jovic-type Reactions with Amines. *Chem. Commun.* 49 (85), 10022–10024. doi:10.1039/C3CC46070C
- Rengaraj, A., Puthiaraj, P., Haldorai, Y., Heo, N. S., Hwang, S.-K., Han, Y.-K., et al. (2016). Porous Covalent Triazine Polymer as a Potential Nanocargo for Cancer Therapy and Imaging. *ACS Appl. Mater. Inter.* 8 (14), 8947–8955. doi:10.1021/acsami.6b00284
- Samran, J., Phinyocheep, P., Daniel, P., Derouet, D., and Buzaré, J.-Y. (2004). Raman Spectroscopic Study of Non-catalytic Hydrogenation of Unsaturated Rubbers. *J. Raman Spectrosc.* 35 (12), 1073–1080. doi:10.1002/jrs.1256
- Sartori, G., Ballini, R., Bigi, F., Bosica, G., Maggi, R., and Righi, P. (2004). Protection (And Deprotection) of Functional Groups in Organic Synthesis by Heterogeneous Catalysis. *Chem. Rev.* 104 (1), 199–250. doi:10.1021/cr0200769
- Schmidt, J., Weber, J., Epping, J. D., Antonietti, M., and Thomas, A. (2009). Microporous Conjugated Poly(thienylene Arylene) Networks. *Adv. Mater.* 21 (6), 702–705. doi:10.1002/adma.200802692
- Soliman, U. A., Hassan, A. M., and Mohamed, T. A. (2007). Conformational Stability, Vibrational Assignments, Barriers to Internal Rotations and Ab Initio Calculations of 2-aminophenol (D0 and D3). *Spectrochimica Acta Part A: Mol. Biomol. Spectrosc.* 68 (3), 688–700. doi:10.1016/j.saa.2006.12.047
- Svatos, A., and Attygalle, A. B. (1997). Characterization of Vinyl-Substituted, Carbon-Carbon Double Bonds by GC/FT-IR Analysis. *Anal. Chem.* 69 (10), 1827–1836. doi:10.1021/ac960890u
- Taher, A., Lumbiny, B. J., and Lee, I.-M. (2020). A Facile Microwave-Assisted Knoevenagel Condensation of Various Aldehydes and Ketones Using Amine-Functionalized Metal Organic Frameworks. *Inorg. Chem. Commun.* 119, 108092. doi:10.1016/j.inoche.2020.108092
- Tan, J., Wan, J., Guo, J., and Wang, C. (2015). Self-sacrificial Template-Induced Modulation of Conjugated Microporous Polymer Microcapsules and Shape-dependent Enhanced Photothermal Efficiency for Ablation of Cancer Cells. *Chem. Commun.* 51 (98), 17394–17397. doi:10.1039/C5CC05478H
- Tantisriyanurak, S., Duguid, H. N., Peattie, L., and Dawson, R. (2020). Acid Functionalized Conjugated Microporous Polymers as a Reusable Catalyst for Biodiesel Production. *ACS Appl. Polym. Mater.* 2 (9), 3908–3915. doi:10.1021/acscpm.0c00595
- Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., et al. (2015). Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* 87 (9-10), 1051–1069. doi:10.1515/pac-2014-1117
- Vernitskaya, T. y. V., and Efimov, O. N. (1997). Polypyrrole: a Conducting Polymer; its Synthesis, Properties and Applications. *Russ. Chem. Rev.* 66 (5), 443–457. doi:10.1070/rc1997v066n05abeh000261
- Volchkov, I., and Lee, D. (2013). Asymmetric Total Synthesis of (-)-Amphidinolide V through Effective Combinations of Catalytic Transformations. *J. Am. Chem. Soc.* 135 (14), 5324–5327. doi:10.1021/ja401717b
- Wang, Y., Wang, L., Liu, C., and Wang, R. (2015). Benzimidazole-containing Porous Organic Polymers as Highly Active Heterogeneous Solid-Base Catalysts. *Chemcatchem* 7 (10), 1559–1565. doi:10.1002/cctc.201500244
- Xu, F., Chen, X., Tang, Z., Wu, D., Fu, R., and Jiang, D. (2014). Redox-active Conjugated Microporous Polymers: a New Organic Platform for Highly Efficient Energy Storage. *Chem. Commun.* 50 (37), 4788–4790. doi:10.1039/C4CC01002G
- Xu, Y., Chen, L., Guo, Z., Nagai, A., and Jiang, D. (2011). Light-emitting Conjugated Polymers with Microporous Network Architecture: Interweaving Scaffold Promotes Electronic Conjugation, Facilitates Exciton Migration, and Improves Luminescence. *J. Am. Chem. Soc.* 133 (44), 17622–17625. doi:10.1021/ja208284t
- Xu, Y., Cui, D., Zhang, S., Xu, G., and Su, Z. (2019). Facile Synthesis of Conjugated Microporous Polymer-Based Porphyrin Units for Adsorption of CO₂ and Organic Vapors. *Polym. Chem.* 10 (7), 819–822. doi:10.1039/c8py01476k
- Xu, Y., Sprick, R. S., Brownbill, N. J., Blanc, F., Li, Q., Ward, J. W., et al. (2021). Bottom-up Wet-Chemical Synthesis of a Two-Dimensional Porous Carbon

- Material with High Supercapacitance Using a Cascade Coupling/cyclization Route. *J. Mater. Chem. A* 9 (6), 3303–3308. doi:10.1039/d0ta11649a
- Xue, S., Kuzuhara, D., Aratani, N., and Yamada, H. (2019). Synthesis of a porphyrin(2.1.2.1) Nanobelt and its Ability to Bind Fullerene. *Org. Lett.* 21 (7), 2069–2072. doi:10.1021/acs.orglett.9b00329
- Yang, F., Li, Y., Zhang, T., Zhao, Z., Xing, G., and Chen, L. (2020). Docking Site Modulation of Isostructural Covalent Organic Frameworks for CO₂ Fixation. *Chem. Eur. J.* 26 (20), 4510–4514. doi:10.1002/chem.202000552
- Yue, Y., Xu, Y., Kong, F., Li, Q., and Ren, S. (2020). Bulk-synthesis and Supercapacitive Energy Storage Applications of Nanoporous Triazine-Based Graphdiyne. *Carbon* 167, 202–208. doi:10.1016/j.carbon.2020.06.001
- Zhang, K., Kopetzki, D., Seeberger, P. H., Antonietti, M., and Vilela, F. (2013). Surface Area Control and Photocatalytic Activity of Conjugated Microporous Poly(benzothiadiazole) Networks. *Angew. Chem. Int. Ed.* 52 (5), 1432–1436. doi:10.1002/anie.201207163
- Zhang, W., Jiang, P., Wang, Y., Zhang, J., and Zhang, P. (2015). Synthesis of Two Metal-Porphyrin Frameworks Assembled from Porphyrin Building Motifs, 5, 10, 15, 20-tetrapyrrolylporphyrin and Their Base Catalyzed Property. *Inorg. Chem. Commun.* 61, 100–104. doi:10.1016/j.inoche.2015.09.002
- Zhang, X., Zhang, J., Liu, Z., and Robinson, C. (2004). Inorganic/organic Mesosstructure Directed Synthesis of Wire/ribbon-like Polypyrrole nanostructures. Electronic Supplementary Information (ESI) Available: FT-IR Spectra, Powder XRD Pattern and Conductivities of As-Made PPy Nanostructures. *Chem. Commun.* (16), 1852–1853. doi:10.1039/B405255B
- Zhao, Y., Ma, W., Xu, Y., Zhang, C., Wang, Q., Yang, T., et al. (2018). Effect of Linking Pattern of Dibenzothiophene-S,_s-Dioxide-Containing Conjugated Microporous Polymers on the Photocatalytic Performance. *Macromolecules* 51 (23), 9502–9508. doi:10.1021/acs.macromol.8b02023
- Zhao, Y., Zhao, Y., Qiu, J., Li, Z., Wang, H., and Wang, J. (2020). Facile Grafting of Imidazolium Salt in Covalent Organic Frameworks with Enhanced Catalytic Activity for CO₂ Fixation and the Knoevenagel Reaction. *ACS Sustain. Chem. Eng.* 8 (50), 18413–18419. doi:10.1021/acssuschemeng.0c05294
- Zhu, Z., Yang, Z., Fan, Y., Liu, C., Sun, H., Liang, W., et al. (2020). Calcination of Porphyrin-Based Conjugated Microporous Polymers Nanotubes as Nanoporous N-Rich Metal-free Electrocatalysts for Efficient Oxygen Reduction Reaction. *ACS Appl. Energ. Mater.* 3 (6), 5260–5268. doi:10.1021/acsaem.0c00079

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2021 Gao, Zhang, Lu, Chen and Li. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.