

## Accepted Article

**Title:** New Meets Old: Accelerating Membrane-based CO<sub>2</sub> Separation by Soluble Nanoporous Polymer Networks Produced Via Mechanochemical Oxidative Coupling

**Authors:** Xiang Zhu, Yinying Hua, Chengcheng Tian, Carter W. Abney, Peng Zhang, Tian Jin, Gongping Liu, Katie L. Browning, Robert L. Sacci, Gabriel M. Veith, Hong-Cai Zhou, Wanqin Jin, and Sheng Dai

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## COMMUNICATION

# New Meets Old: Accelerating Membrane-based CO<sub>2</sub> Separation by Soluble Nanoporous Polymer Networks Produced Via Mechanochemical Oxidative Coupling

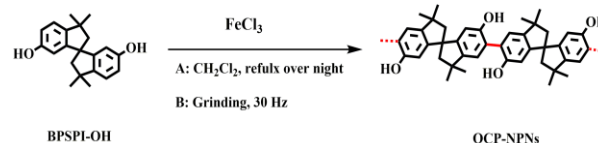
Xiang Zhu, Yinying Hua, Chengcheng Tian,\* Carter W. Abney, Peng Zhang, Tian Jin, Gongping Liu,\* Katie L. Browning, Robert L. Sacci, Gabriel M. Veith, Hong-Cai Zhou, Wanqin Jin\* and Sheng Dai\*

**Abstract:** Achieving homogeneous dispersion of nanoporous fillers within membrane architectures remains a great challenge for mixed-matrix membrane (MMMs) technology. Imparting solution processability of nanoporous materials would help advance the development of MMMs for membrane-based gas separations. For the first time, we report a novel mechanochemical-assisted oxidative coupling polymerization strategy to create a new family of soluble nanoporous polymer networks. The solid-state ball-milling methodology affords inherent molecular weight control over polymer growth and therefore provides unexpected solubility for the resulting nanoporous frameworks. MMM-based CO<sub>2</sub>/CH<sub>4</sub> separation performance was significantly accelerated by these new soluble fillers. We anticipate this facile protocol will facilitate new possibilities for the rational design and synthesis of soluble nanoporous polymer networks and promote their applications in membrane-based gas separations.

The interest in curtailing greenhouse gas emissions through capture of CO<sub>2</sub> from flue gas and removal of CO<sub>2</sub> from synthesis gas (mainly CH<sub>4</sub> and H<sub>2</sub>) has inspired an extensive search for novel methodologies capable of efficient separation of CO<sub>2</sub>.<sup>[1]</sup> Membrane-based CO<sub>2</sub> separation technology has gained significant attention as a promising solution, due to its lower energy costs and reduced environmental impact.<sup>[2]</sup> Among the various types of CO<sub>2</sub>-selective membranes, polymeric membranes have been the most widely studied, whereas they suffer from a well-known compromise between the permeability and selectivity as shown in the upper bound Robeson curves.<sup>[3]</sup> Coupling polymer matrices with nanoporous filler particles, for

example nanoporous organic networks (NPNs), could lead to synergistic improvements in membrane-based CO<sub>2</sub> separation performance, but difficulties are encountered in achieving homogeneous dispersion of these nanoporous fillers within MMMs.<sup>[4]</sup>

Although significant progresses have been made in the synthesis of NPNs by linking multidentate organic scaffolds towards a wide variety of potential applications,<sup>[5]</sup> it remains a great challenge to fabricate soluble nanoporous organic networks (SNPNs) through a rapid and straightforward method, mainly because it is very difficult to control the growth of polymeric architectures.<sup>[6]</sup> Ladder-like NPNs as a family of soluble porous polymers and successfully utilized in membrane-based gas separations.<sup>[7]</sup> Recently, Cooper et al. pioneered another successful synthesis of soluble porous polymer using a hyperbranching-based approach based on Suzuki-catalyzed aryl-aryl coupling copolymerization.<sup>[6a]</sup> The obvious downside is the use of the costly Pd-containing catalyst and necessity of complicated organic synthetic processes, significantly limiting the potential for practical implementation. In this regard, the search for novel techniques that are capable of efficient and facile synthesis of SNPNs is of great interest, importance, and urgency. Imparting solution processability would help advance development of NPNs and enable the combination of unique features such as intrinsically high porosity towards MMM-based CO<sub>2</sub> separations.



**Scheme 1.** The synthesis route of soluble NPNs based on the oxidative coupling polymerization (OCP).

In this work, we report a novel strategy for the rationally-designed synthesis of a novel family of SNPNs. The key to our approach lies in the use of a mechanochemical (MC)-assisted FeCl<sub>3</sub>-mediated oxidative coupling polymerization (OCP).<sup>[8]</sup> MC synthesis strategy has been demonstrated as a versatile alternative technique that enables the preparation of nanoporous materials through sustainable solid-state assembly pathways. By using mechanochemistry to promote the oxidative polymerization, the molecular weight of the resulting materials can be controlled. Their homogeneous dispersion within membrane architectures were readily realized, and MMM-based CO<sub>2</sub>/CH<sub>4</sub> separation performance was significantly accelerated. A high CO<sub>2</sub> permeability of 675 barrer together with a CO<sub>2</sub>/CH<sub>4</sub> selectivity of

[\*] Dr. X. Zhu, Dr. C.C. Tian, T. Jin, Prof. S. Dai  
Department of chemistry,  
The University of Tennessee, Knoxville, Tennessee 37996-1600  
Email: tiachengcheng.ecust@gmail.com

Dr. C. W. Abney, Prof. S. Dai  
Chemical Sciences Division, Oak Ridge National Laboratory  
Oak Ridge, Tennessee, TN 37831-6009  
Email: dais@ornl.gov

Dr. X. Zhu, Dr. P. Zhang, Prof. H.-C. Zhou  
Department of chemistry, Texas A&M University, College Station, TX

Dr. K.L. Browning, Dr. R. L. Sacci, Dr. G. M. Veith  
Materials Science and Technology Division,  
Oak Ridge National Laboratory, Oak Ridge, United States

Y.Y. Hua, Prof. G.P. Liu, Prof. W.Q. Jin  
State Key Laboratory of Materials-Oriented Chemical Engineering  
Jiangsu National Synergetic Innovation Center for Advanced materials  
Nanjing Tech University, Nanjing 210009, China.  
Email: gpiliu@njtech.edu.cn; wqjin@njtech.edu.cn

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## COMMUNICATION

25 was achieved. This innovative solvent-free assemble approach not only provides a means to achieve SNPNs in a rapid and straightforward fashion, but also enables us to achieve high-performance MMMs for CO<sub>2</sub> separation.

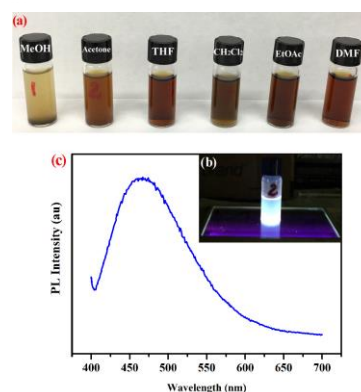
Our synthetic strategy is shown in **Scheme 1**. We first started by pursuing a NPN prepared by a novel solvent-mediated FeCl<sub>3</sub>-initiated oxidative coupling reaction<sup>[6]</sup> (method **A**, details can be found in the found in the supporting information). We reasoned that a ladder-like scaffold plays a crucial role in achieving high porosity, as have been extensively studied in the context of PIM chemistry.<sup>[7a]</sup> Accordingly, 3,3',3',3'-tetramethyl-2,2',3,3'-tetrahydro-1,1'-pirobi[indene]-6,6'-diol (**BPSPI-OH**) was selected and prepared for use due to possessing the desired ladder-like structure. Following reflux overnight, a brown solid (**OCP-NPN-1**) was obtained possessing a high Brunauer-Emmett-Teller (BET) surface area (~ 834 m<sup>2</sup> g<sup>-1</sup>), evaluated by nitrogen adsorption-desorption isotherms (Figure S1). The BET surface area is comparable to that of many previously-reported porous organic polymers, for example crystalline covalent-triazine-framework-1<sup>[9]</sup> (CTF-1, S<sub>BET</sub> = 791 m<sup>2</sup> g<sup>-1</sup>) and amorphous conjugated microporous polymer-1<sup>[10]</sup> (CMP-1, S<sub>BET</sub> = 834 m<sup>2</sup> g<sup>-1</sup>), thus confirming the feasibility of our **OCP** methodology for the construction of nanoporous polymers.

The molecular structure of the resultant sphere-like polymer was characterized using <sup>1</sup>H-<sup>13</sup>C cross-polarization magic-angle spinning (CP-MAS) <sup>13</sup>C NMR (Figure S2). The aliphatic carbons in the backbone were clearly revealed by the resolved resonance at ~ 30, 43 and 58 ppm, respectively, while the signal peak at ~ 157 ppm corresponds to the substituted phenyl carbons binding with the oxygen atom (Figure S2b). High thermal stability was observed for the resultant network (Figure S3). However, the amorphous network **OCP-NPN-1** (Figure S4) was insoluble in common organic solvents, like tetrahydrofuran (THF, Figure S5) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>).

Motivated by the aforementioned results, we subsequently initiated a novel mechanochemical (**MC**)-assisted solid-state **OCP** of **BPSPI-OH** to attempt the fabrication of soluble nanoporous networks (method **B**, **Scheme 1**). Recent work has demonstrated mechanochemical methods efficiently enable facile generation of soluble porous coordination polymers<sup>[11]</sup> and hold great promise for the synthesis of nanoporous organic frameworks.<sup>[12]</sup> However, the direct synthesis of SNPNs using the mechanochemistry is rarely reported. We anticipated that this innovative methodology could enable a rapid growth of polymer networks and therefore provide solution processability for the resultant materials through limiting the inherent molecular weight.

In our initial attempt at solid-state **OCP** promoted by ball-milling, the white **BPSPI-OH** moiety (150 mg, 0.49 mmol) and two mass equivalents of FeCl<sub>3</sub> (300 mg, 1.85 mmol) were mixed in a zirconium oxide milling jar with a stainless steel ball and subjected to vibrational ball-milling in a Retsch mixer-mill 400 at 30 Hz for 0.5 h (Figure S6). The obtained black solid was carefully washed with a mixed solution of ethanol and dilute HCl to remove the FeCl<sub>3</sub>. According to the x-ray photoelectron spectroscopy (XPS) result, only 0.1 at.% content of Fe was detected, where a high O-doping content of 26.4 at.% was achieved. The binding energy of O1s at 532.0 eV (Figure S7) was assigned to O-<sup>δ-</sup>CH<sub>2</sub>-<sup>δ+</sup>Ar<sup>δ+</sup>H<sup>δ+</sup> (19.7 %). These active sites could facilitate CO<sub>2</sub> binding inside the framework. The BET surface

area of the resulting material (**MC-OCP-NPN-1**) (Figure S8) is lower than that of solvent-mediated **OCP-NPN-1** (470 vs 834 m<sup>2</sup> g<sup>-1</sup>). Nevertheless, this value is comparable to that of the soluble CMP (SCMP1) reported by Cooper et al. (S<sub>BET</sub> = 505 m<sup>2</sup> g<sup>-1</sup>).<sup>[6a]</sup> The pore size distribution (PSD), calculated from the CO<sub>2</sub> isotherm at 273 K, indicates the intrinsic microporous nature (Figure S9).<sup>[6a]</sup> More importantly, **MC-OCP-NPN-1** can be dissolved in many common organic solvents, like THF, ethyl acetate and dimethylformamide (**Figure 1**), which may give a rise to homogeneously disperse these nanoporous particles within a membrane architecture. No Tyndall effect was observed for the dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution of **MC-OCP-NPN-1**, further confirming the formation of a homogeneous solution (Figure S10). Interestingly, when dissolving and re-precipitating the polymer from CH<sub>2</sub>Cl<sub>2</sub>, a significant decrease in BET surface area was observed (205 vs 470 m<sup>2</sup> g<sup>-1</sup>, Figure S8). Nonetheless, this value can be further enhanced to be 319 m<sup>2</sup> g<sup>-1</sup> when we repeated the dissolution and re-precipitating process using CH<sub>2</sub>Cl<sub>2</sub>/EtOH (volume ratio: 1 to 4) instead. We reasoned that the swelling of **MC-OCP-NPN-1** in different solvents may account for this BET difference.<sup>[13]</sup> In addition, upon lamination under UV irradiation, the dissolved **MC-OCP-NPN-1** affords a bright blue-luminescent solution (**Figure 1**). As shown in the photoluminescence spectrum, **MC-OCP-NPN-1** exhibits a maximum emission at ~ 470 nm (**Figure 1c**), suggesting an inherently conjugated architecture.<sup>[6a]</sup> This is rarely observed for conventional soluble PIMs. Additionally, the <sup>13</sup>C NMR spectra matches well with that of **OCP-NPN-1** (Figure S11).



**Figure 1.** (a) Photographs of soluble performance of **MC-OCP-NPN-1** in various solvents; (b) THF solution of **MC-OCP-NPN-1** shows bright blue luminescence under UV light; (c) Photoluminescence spectrum of **MC-OCP-NPN-1**.

**Table 1.** Effects of amounts of FeCl<sub>3</sub> and grinding time on N<sub>2</sub> adsorption property and molecular weight of **OCP-CNPs**.

Sample	FeCl <sub>3</sub> (mass eq.)	Time (h)	Yield (%)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	M <sub>n</sub> (kDa)	M <sub>w</sub> (kDa)	PDI
<b>OCP-NPN-1</b>	2	12	95	834	N/A	N/A	N/A
<b>MC-OCP-NPN-1</b>	2	0.5	35	470	3.7	6.9	1.85
<b>MC-OCP-NPN-2</b>	1	0.5	16	430	3.0	5.8	1.94
<b>MC-OCP-NPN-3</b>	4	0.5	65	733	N/A	N/A	N/A
<b>MC-OCP-NPN-4</b>	2	0.25	36	448	3.0	6.1	2.03





## COMMUNICATION

nanoporous **MC-OCP-NPN-1**, and gradually improved as the increase of filler containing within the membrane. Interestingly, when 60 wt% **MC-OCP-NPN-1** was loaded, the resultant MMM exhibits 2-fold higher CO<sub>2</sub> permeability than that of pure polyimide membrane (675 vs 322 barrer, **Figure 3a**). To our delight, the obtained CO<sub>2</sub>/CH<sub>4</sub> selectivity maintained very well and was slightly decreased from 29 to 25. It should be noted that all the measured permeabilities and selectivities of MMMs agree well with the predicted values based on the Maxwell model, suggesting an ideal mixed-matrix morphology was formed (**Figure 3a**).<sup>[2]</sup> As a result, the permeation performance of pure **MC-OCP-NPN-1**-based membrane could be predicted (CO<sub>2</sub> permeability of 1095 barrer and CO<sub>2</sub>/CH<sub>4</sub> selectivity of ~ 23), which is very promising for CO<sub>2</sub>/CH<sub>4</sub> separation.<sup>[2a,c]</sup> We reasoned that the intrinsic adsorption affinity of CO<sub>2</sub> over CH<sub>4</sub> on **MC-OCP-NPN-1** may account for this efficient membrane-based separation performance. As such, the CO<sub>2</sub> and CH<sub>4</sub> adsorption isotherm was recorded at 25 °C and 1.0 bar, respectively, to get a better understanding. As shown in **Figure 3b**, **MC-OCP-NPN-1** can adsorb 20.9 cm<sup>3</sup> g<sup>-1</sup> of CO<sub>2</sub>, whereas only 5.8 cm<sup>3</sup> g<sup>-1</sup> of CH<sub>4</sub> uptake was obtained. Clearly, **MC-OCP-NPN-1** exhibits a much higher CO<sub>2</sub> binding affinity and high-performance membrane-based CO<sub>2</sub>/CH<sub>4</sub> separation could be expected for **MC-OCP-NPN-1**-based MMMs.

In summary, a mechanochemical-assisted oxidative coupling polymerization strategy has been implemented for the first time to create a novel family of soluble fluorescent nanoporous polymer networks. The uniqueness of the solid-state ball-milling methodology accommodates facile polymer growth and therefore gives rise to unexpected solubilities for the resulting nanoporous frameworks. This innovative protocol not only provides a means to achieve soluble porous polymers in a rapid and straightforward fashion, but also enables us to achieve a homogeneous dispersion of porous polymers within membrane architectures. The resulting mixed-matrix membrane exhibits an efficient membrane-based CO<sub>2</sub>/CH<sub>4</sub> separation with a high CO<sub>2</sub> permeability of 675 barrer and a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 25. In general, the concept presented here can provide new opportunities for the synthesis of more soluble nanoporous organic frameworks and promote the membrane-based applications of these new nanoporous materials.

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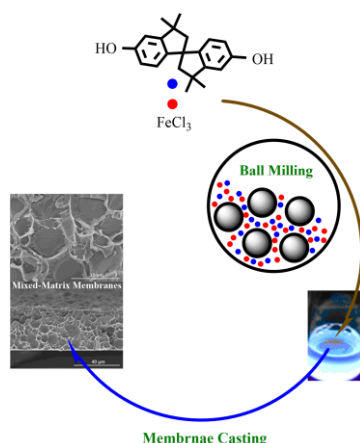
**Keywords:** mechanochemical oxidative coupling polymerization fluorescent nanoporous polymer networks CO<sub>2</sub>/CH<sub>4</sub> separation

- [1] a) D. M. D'Alessandro, B. Smit, J. R. Long, *Angew. Chem. Int. Ed.* **2010**, *49*, 6058-6082; b) T. M. McDonald, J. A. Mason, X. Kong, E. D. Bloch, D. Gygi, A. Dani, V. Crocella, F. Giordanino, S. O. Odoh, W. S. Drisdell, B. Vlasisavljevich, A. L. Dzubak, R. Poloni, S. K. Schnell, N. Planas, K. Lee, T. Pascal, L. F. Wan, D. Prendergast, J. B. Neaton, B. Smit, J. B. Kortright, L. Gagliardi, S. Bordiga, J. A. Reimer, J. R. Long, *Nature* **2015**, *519*, 303-308; c) Y. Zeng, R. Zou, Y. Zhao, *Adv. Mater.* **2016**, *28*, 2855-2873; d) X. Zhu, C. Tian, G. M. Veith, C. W. Abney, J. Dehaut, S. Dai, *J. Am. Chem. Soc.* **2016**, *138*, 11497-11500; e) L. Zou, Y. Sun, S. Che, X. Yang, X. Wang, M. Bosch, Q. Wang, H. Li, M. Smith, S. Yuan, Z. Perry, H.-C. Zhou,

- Adv. Mater.* **2017**, 1700229; f) R. W. Flaig, T. M. Osborn Popp, A. M. Fracaroli, E. A. Kapustin, M. J. Kalmutski, R. M. Altamimi, F. Fathieh, J. A. Reimer, O. M. Yaghi, *J. Am. Chem. Soc.* **2017**, *139*, 12125-12128.
- [2] a) N. Du, H. B. Park, M. M. Dal-Cin, M. D. Guiver, *Energy Environ. Sci.* **2012**, *5*, 7306-7322; b) B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn, J. Gascon, *Chem. Soc. Rev.* **2015**, *44*, 2421-2454; c) S. Wang, X. Li, H. Wu, Z. Tian, Q. Xin, G. He, D. Peng, S. Chen, Y. Yin, Z. Jiang, M. D. Guiver, *Energy Environ. Sci.* **2016**, *9*, 1863-1890; d) X. Zhu, C. Tian, C.-L. Do-Thanh, S. Dai, *ChemSusChem* **2017**, *10*, 3304-3316; e) X. Zhu, C. Tian, S. M. Mahurin, S.-H. Chai, C. Wang, S. Brown, G. M. Veith, H. Luo, H. Liu, S. Dai, *J. Am. Chem. Soc.* **2012**, *134*, 10478-10484; f) X. Zhu, C. Tian, S. Chai, K. Nelson, K. S. Han, E. W. Hagaman, G. M. Veith, S. M. Mahurin, H. Liu, S. Dai, *Adv. Mater.* **2013**, *25*, 4152-4158; g) J. Shen, G. Liu, K. Huang, W. Jin, K.-R. Lee, N. Xu, *Angew. Chem. Int. Ed.* **2015**, *54*, 578-582; h) G. Liu, W. Jin, N. Xu, *Angew. Chem. Int. Ed.* **2016**, *55*, 13384-13397; i) W. J. Koros, C. Zhang, *Nat. Mater.* **2017**, *16*, 289.
- [3] a) P. M. Budd, N. B. McKeown, *Polym. Chem.* **2010**, *1*, 63-68; b) Y. Yampolskii, *Macromolecules* **2012**, *45*, 3298-3311; c) D. F. Sanders, Z. P. Smith, R. Guo, L. M. Robeson, J. E. McGrath, D. R. Paul, B. D. Freeman, *Polymer* **2013**, *54*, 4729-4761.
- [4] a) T.-S. Chung, L. Y. Jiang, Y. Li, S. Kulprathipanja, *Prog. Polym. Sci.* **2007**, *32*, 483-507; b) A. F. Bushell, P. M. Budd, M. P. Attfield, J. T. A. Jones, T. Hasell, A. I. Cooper, P. Bernardo, F. Bazzarelli, G. Clarizia, J. C. Jansen, *Angew. Chem. Int. Ed.* **2013**, *52*, 1253-1256; c) M. Rezakazemi, A. Ebadi Amooghini, M. M. Montazer-Rahmati, A. F. Ismail, T. Matsuura, *Prog. Polym. Sci.* **2014**, *39*, 817-861; d) Y. Peng, Y. Li, Y. Ban, H. Jin, W. Jiao, X. Liu, W. Yang, *Science* **2014**, *346*, 1356-1359; e) C. H. Lau, K. Konstas, A. W. Thornton, A. C. Y. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* **2015**, *54*, 2669-2673; f) M. S. Denny Jr, J. C. Moreton, L. Benz, S. M. Cohen, *Nat. Rev. Mater.* **2016**, *1*, 16078; g) C. H. Lau, X. Mulet, K. Konstas, C. M. Doherty, M.-A. Sani, F. Separovic, M. R. Hill, C. D. Wood, *Angew. Chem. Int. Ed.* **2016**, *55*, 1998-2001; h) B. Ghalei, K. Sakurai, Y. Kinoshita, K. Wakimoto, Ali P. Isfahani, Q. Song, K. Doitomi, S. Furukawa, H. Hirao, H. Kusuda, S. Kitagawa, E. Sivaniah, *Nat. Energy* **2017**, *2*, 17086.
- [5] A. G. Slater, A. I. Cooper, *Science* **2015**, *348*, 8075.
- [6] a) G. Cheng, T. Hasell, A. Trewin, D. J. Adams, A. I. Cooper, *Angew. Chem. Int. Ed.* **2012**, *51*, 12727-12731; b) S. Deng, J. Zhi, X. Zhang, Q. Wu, Y. Ding, A. Hu, *Angew. Chem. Int. Ed.* **2014**, *53*, 14144-14148; c) G. Cheng, B. Bonillo, R. S. Sprick, D. J. Adams, T. Hasell, A. I. Cooper, *Adv. Funct. Mater.* **2014**, *24*, 5219-5224.
- [7] a) N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, *35*, 675-683; b) N. B. McKeown, P. M. Budd, K. J. Msayib, B. S. Ghanem, H. J. Kingston, C. E. Tattershall, S. Makhseed, K. J. Reynolds, D. Fritsch, *Chem. Eur. J.* **2005**, *11*, 2610-2620.
- [8] a) F. Toda, K. Tanaka, S. Iwata, *J. Org. Chem.* **1989**, *54*, 3007-3009; b) Q. Chen, M. Luo, P. Hammershøj, D. Zhou, Y. Han, B. W. Laursen, C.-G. Yan, B.-H. Han, *J. Am. Chem. Soc.* **2012**, *134*, 6084-6087; c) T. Jin, Y. Xiong, X. Zhu, Z. Tian, D.-J. Tao, J. Hu, D.-e. Jiang, H. Wang, H. Liu, S. Dai, *Chem. Commun.* **2016**, *52*, 4454-4457; d) F. Jiang, T. Jin, X. Zhu, Z. Tian, C.-L. Do-Thanh, J. Hu, D.-e. Jiang, H. Wang, H. Liu, S. Dai, *Macromolecules* **2016**, *49*, 5325-5330.
- [9] P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem. Int. Ed.* **2008**, *47*, 3450-3453.
- [10] J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem. Int. Ed.* **2007**, *46*, 8574-8578.
- [11] a) P. Zhang, H. Li, G. M. Veith, S. Dai, *Adv. Mater.* **2015**, *27*, 234-239; b) Y.-B. Huang, Q. Wang, J. Liang, X. Wang, R. Cao, *J. Am. Chem. Soc.* **2016**, *138*, 10104-10107.
- [12] a) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friscic, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413-447; b) J.-S. Park, S. H. Park, *ACS Cent. Sci.* **2017**, *3*, 13-19; c) B. P. Biswal, S. Chandra, S. Kandambeth, B. Lukose, T. Heine, R. Banerjee, *J. Am. Chem. Soc.* **2013**, *135*, 5328-5331; d) E. Troschke, S. Grätz, T. Lübken, L. Borchardt, *Angew. Chem. Int. Ed.* **2017**, *56*, 6859-6863; e) X. Zhu, C. Tian, T. Jin, K. L. Browning, R. L. Sacci, G. M. Veith, S. Dai, *ACS Macro Lett.* **2017**, 1056-1059.
- [13] K. E. Hart, J. M. Springmeier, N. B. McKeown, C. M. Colina, *Phys. Chem. Chem. Phys.* **2013**, *15*, 20161-20169.

## COMMUNICATION

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Page No. – Page No.

**New Meets Old: Accelerating Membrane-based CO<sub>2</sub> Separation by Soluble Nanoporous Polymer Networks Produced Via Mechanochemical Oxidative Coupling**