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Charged Induced Formation of Crystalline Network Polymers†

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Order in purely organic network polymers is hard to achieve, as reversible, dynamic covalent bond formation is required. Strategies focused on thermodynamic controlled transformations, as kinetics would not seemingly favour reversibility. Herein, we report formation of crystalline network polymers under kinetically favoured conditions by using quaternary ammonium salt linked networks. Charged bulky bridges align, even under fast reaction times (20 minutes) if the rotational freedom is granted. Adding vicinal methyl substituents block the ordering, hence form amorphous networks. Raman experiments and SEM images reveal stacking of 2D layers.

Introduction

Nanoporous organic polymers,¹ ordered or not, offer significant promise in the fields of gas capture & storage,² optoelectronics³ and catalysis.⁴ Low density, high surface area, tunable pore size and structure, and ease of tailoring functionality made them⁵ an attractive alternative to inorganic/hybrid porous materials.⁶

The structural regularity in purely organic porous polymers⁷ is extremely difficult to control, owing to strong covalent bonding that tends to produce disordered materials.⁸ On the contrary, inorganic porous materials, like zeolites,⁹ and hybrid porous materials,¹⁰ such as metal-organic frameworks (MOFs) are usually crystalline and highly porous. Therefore, a challenge arises for the designed synthesis of organic network polymers, in order to meet the demands for both crystallinity and porosity. Even though a variety of rigid organic building units with different structural configurations are accessible and several synthetic schemes are developed,⁵ it is yet not straightforward to produce ordered porous organic polymers. While the permanent porosity requires rigid building units, reversible formation of covalent bonds under thermodynamic control is assumed to be required for crystallinity in organic network polymers. In 2005, Yaghi and co-workers introduced crystalline porous organic polymers,¹¹ namely covalent organic frameworks (COFs), by making use of reversible condensation reaction, and in 2007, they reported first synthesis of crystalline 3D COFs.¹² Almost similar 2D COFs

with a relatively mild synthetic route at ambient pressure was introduced in 2006 by Lavigne and co-workers.¹³ Whereas, Thomas and co-workers demonstrated¹⁴ that the structural regularity in the organic network polymers is not always guaranteed even if prerequisites for crystallinity have been well met; a match in shape and angles in rigid building units shall also be accounted for reversible formation of covalent bonds under controlled thermodynamic conditions.

Recently, new classes of charged porous organic polymers (CPOPs), with quaternary phosphonium cations¹⁵ and quaternary borate anions¹⁶ as centres for tetrahedral networks, have been introduced with high surface area but unordered network structure. The diamondoid framework topology, that is, imposed by the tetrahedral monomer could be the reason for high surface area, like inorganic zeolites with silica/alumina tetrahedral network. This is also the case of microporous organic polymers¹⁷ (MOPs) with tetrahedral networks¹⁸ containing carbon or adamantane centres.¹⁹ Unlike these CPOPs, we report here a simple design strategy for ordered, charged organic networks that rely on polymerization under kinetic (instead of thermodynamic) control. Surprisingly, quaternary ammonium based CPOPs have never been constructed whereas charged molecules of supramolecular nature that contain ammonium struts have been studied extensively for mechanochemical applications. Stoddart, a pioneer of molecules for nanoelectromechanical systems (NEMS), showed one step preparation of tetracationic receptors²⁰ from 1,4-bis(bromomethyl)benzene and 4,4'-bipyridine. More recently, he introduced a hydrocarbon scavenger 'ExBox',²¹ based on 1,4-bis(bromomethyl)benzene and 4,4'-(1,4-phenylene)-bipyridine, which led to a family of tetracationic cyclophanes.

In this work, we produced purely organic, charged networks, both crystalline and amorphous, termed as ionic covalent organic polymers, *i-COPs*, based on a cationic backbone with accompanying anions, via simple, catalyst free, room temperature,

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† Electronic Supplementary Information (ESI) available: For detailed synthesis for all polymers, their characterization, solid-state synthesis, screening for crystallinity, ion exchange. See DOI: 10.1039/b000000x/

open air, S_N2 (nucleophilic substitution) reaction, using commercially available monomers.

Experimental

Materials and methods

All the chemicals and compounds used were commercially available and used as received without further purification. 1,3,5-tris(bromomethyl)benzene, 4,4'-dipyridyl, 1,2-bis(4-pyridyl)ethane, 4,4'-trimethylenedipyridine, 1,2-bis(4-pyridyl)ethylene, Sodium tetrafluoroborate and Potassium trifluoromethanesulfonate were purchased from Sigma-Aldrich, USA. Ammonium hexafluorophosphate was bought from Acros Organics, USA. 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene was obtained from TCI, Japan. All the solvents purchased from SAMCHUN, South Korea were dried and stored in anhydrous conditions.

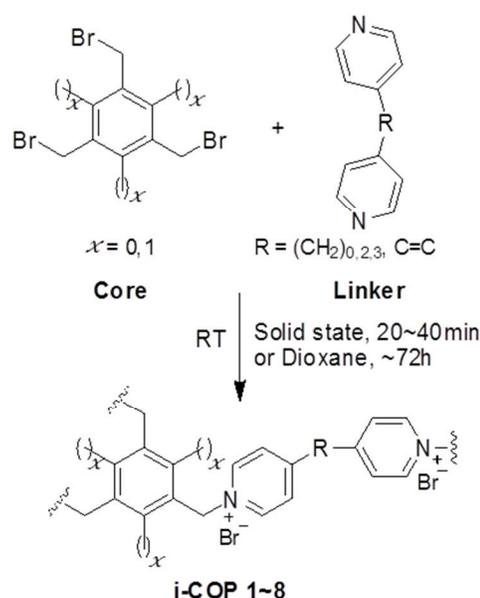
The elemental analyses (CHN) were performed on Flash 2000 CHNS analyzer, product of Thermo Scientific, USA. FT-IR spectra were recorded as KBr pellet using a Perkin-Elmer FT-IR spectrometer. Solid-state CP/MAS ^{13}C SSNMR spectra were recorded on a Agilent 400MHz, 54mm NMR DD2 spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH-TG 209 F3 instrument by heating the samples to 800°C at 10°C min⁻¹ in N₂ and air atmosphere. The graphitic nature of *i-COP_n* was evaluated from RAMAN spectrum between 1250~1700 cm⁻¹, measured by high resolution dispersive RAMAN microscope, ARAMIS by Horiba Jobin Yvon, France. N₂ physisorption isotherms for *i-COPs* were obtained with a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer at 77 K. Prior to analysis, the samples were degassed at 125 °C for 5 h under vacuum. The adsorption–desorption isotherms were evaluated to give the pore parameters, including BET and Langmuir surface area, pore size, and pore volume. CO₂ adsorption and desorption isotherms for *i-COPs* were measured at 273K and 298K by using isochoric system, ASAP 2020, Micromeritics Inc., USA. High power powder X-ray diffraction (PXRD) patterns of the samples were acquired from 2~80° by a Rigaku D/MAX-2500 (18 kW) Micro-area X-ray diffractometer. SEM images for samples, were taken on Field Emission SEM (Magellan400 by FEI Company, USA), that were prepared by dispersing the material onto a sticky carbon surface attached to a flat-circular aluminium sample holder. Osmium was coated on the samples under pressure of 0.06 mbar for 15 minutes via osmium coater (HPC-1SW, Vacuum Device Inc., Japan) before imaging.

Synthetic Procedure

The ionic covalent organic polymers, *i-COPs*, were synthesized using two different cores, 1,3,5-tris(bromomethyl) benzene and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene to study the effect of vicinal methyl substituent on the crystallinity. The enhanced ordered formation was achieved by increasing the distance between two connecting ends of linkers. The impact of various solvents and different reaction temperatures on the degree of crystallinity, for *i-COP_n*, $n = 1,3,5,7$ yielded from core, 1,3,5-tris(bromomethyl) benzene, is also studied. The solid-state synthesis also yielded crystalline *i-COP_n*, $n = 1,3,5,7$ and amorphous *i-COP_m*, $m = 2,4,6,8$ from core, 1,3,5-tris(bromomethyl) benzene and 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, respectively in 20~40 minutes only. Lastly, ion exchanged was employed to tune the characteristics of charged polymers, in addition to testify the existence of replaceable ions in the charged networks.

General procedure for preparation of Ionic Covalent Organic Polymers (*i-COPs*)

1,3,5-tris(bromomethyl) benzene or 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene dissolved in solvent was added dropwise to flask containing either 4,4'-dipyridyl, 1,2-bis(4-pyridyl)ethane, 4,4'-trimethylenedipyridine or 1,2-bis(4-pyridyl)ethylene dissolved in solvent with continuous stirring at ambient temperature. The precipitates (*i-COP 1~8*) formed were stirred for 72 h before washing with THF. Finally, *i-COP 1* (light greenish to light yellowish precipitates), *i-COP 2* (dark yellow precipitates), *i-COP 3* (light pink precipitates), *i-COP 4* (light yellow precipitates), *i-COP 5* (mint green precipitates), *i-COP 6* (off white precipitates), *i-COP 7* (light cream precipitates) and *i-COP 8* (dark yellow precipitates) were recovered on Whatman® 1001-110 filter paper (using conical glass funnel), washed with THF and dried at room temperature for 8 h and then placed in an oven at 50°C under vacuum for 12 h. *i-COP 1, 2, 3, 4, 5, 6, 7* and *8* were obtained in 75, 82, 83, 86, 71, 93, 72 and 83 % yield, respectively (Scheme 1).



Scheme 1. Synthesis of ionic covalent organic polymers (*i-COPs*), at room temperature and ambient conditions

Results and Discussion

At first, the two nucleophilic nitrogens of all the linkers are distanced apart enough that there is no intramolecular cyclization using three binding nodes (electrophilic carbon). Insoluble powders^{22,23} precipitating (as early as 20 min.) are a clear indication for the network formation. Secondly, only the unsubstituted core, 1,3,5-tris(bromomethyl) benzene, leads to ordered polymer structures, *i-COP_n*, $n = 1,3,5$ and 7 (Figure 1). On the contrary, the presence of methyl groups in 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene rejects planar extension of network structure through highly unfavourable interaction of charged ammonium salts that form spontaneously, and the bulky, hydrophobic methyl substituents (*i-COPs 2,4,6,8*).

Effect of secondary species (e.g. solvents, bases) could become significant in hierarchical ordering.^{7c,24} Almost identical PXRD patterns are observed on the change of reaction solvents (Figure S1) and in the case of a solvent-free synthesis (a.k.a. green chemistry)²⁵

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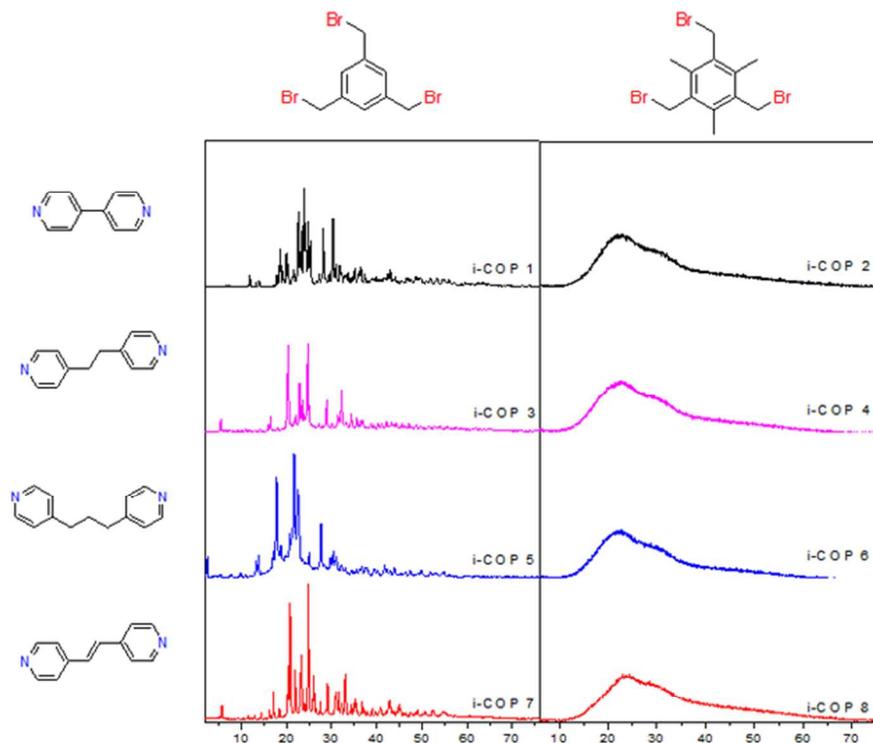


Figure 1. Powder X-ray diffraction patterns of *i-COPs* with variation of cores and linkers. Vicinal methyl substituents prevent ordering in *i-COPs*, showing steric effects due to charged spacers as the prime reasons.

no change in the ordered formation of network polymer structures (*i-COP_n*) is found (Figure S2). The ambient open air solid state synthesis,²⁶ at room temperature yielded same *i-COP* networks in much faster times, 20–40 minutes only. Solvent-less synthesis also show that ordering is unaffected by the use/lack of solvents, and more importantly the concentration of monomers.

There seems to be two possibilities remain in creating order for *i-COPs*: (1) chemical structures of cores and linkers, (2) temperature of the reaction. In the odd numbered *i-COPs*, it is evident that the quaternary ammonium centres with a large bromine anion sitting nearby would be able to repel each other to the lowest energy positions, the furthest away from each other (Br- size 3.7–3.9 Å vs. benzene 4–5 Å). And since there are only hydrogens to block their positioning, charged centres enjoy orienting with each other in the most energetically favourable fashion. This anticipation, in fact, drew us to test the substitution effect where bulky methyls are introduced to force the ammonium centres to not have rotational freedom. As expected, this resulted in *i-COP_m*, *m*=2,4,6 and 8, unordered network polymers (Figure S3). The selection of the cores, therefore, verified structural directing effects of substituent, leading to a conviction that lack of rotational space is very unpopular for

highly rigid building motif. Although it is highly desired, our attempts to resolve the XRD patterns with respect to finding the preferential crystal orientation have failed. Temperature of the reaction was screened next (Figure S4), only to find no observable change in the crystallographic patterns or intensities. Furthermore, the formation of an ordered morphology that is consistent with the crystalline nature of *i-COP_n* is evidenced by SEM, which reveals the formation of blocks that look mostly rectangular like wooden chips of variable sizes. On the other hand, SEM images for the amorphous polymers present agglomerates, which prove non-uniform morphology of *i-COP_m* (Figure 2).

i-COPs, by design, should produce two dimensional (2D) structures, if ordered. The planarity of the 2D systems like graphene are often studied with Raman spectroscopy, a widely used tool to identify *sp*² and *sp*³ hybridized atoms.²⁷ The Raman spectrum depends on the existence of *sp*² rings or chains, clustering of *sp*² phase, ratio of *sp*²/*sp*³ and bond disorder.²⁸ The crystal symmetries for pristine graphene only shows the G peak by Raman spectroscopy; as the disorder appears, D peak(s) appears and may be attributed to *sp*³ hybridized carbon atoms.²⁹ The polyaromatic materials show G band at ~1585 (attributed to E_{2g} mode) and

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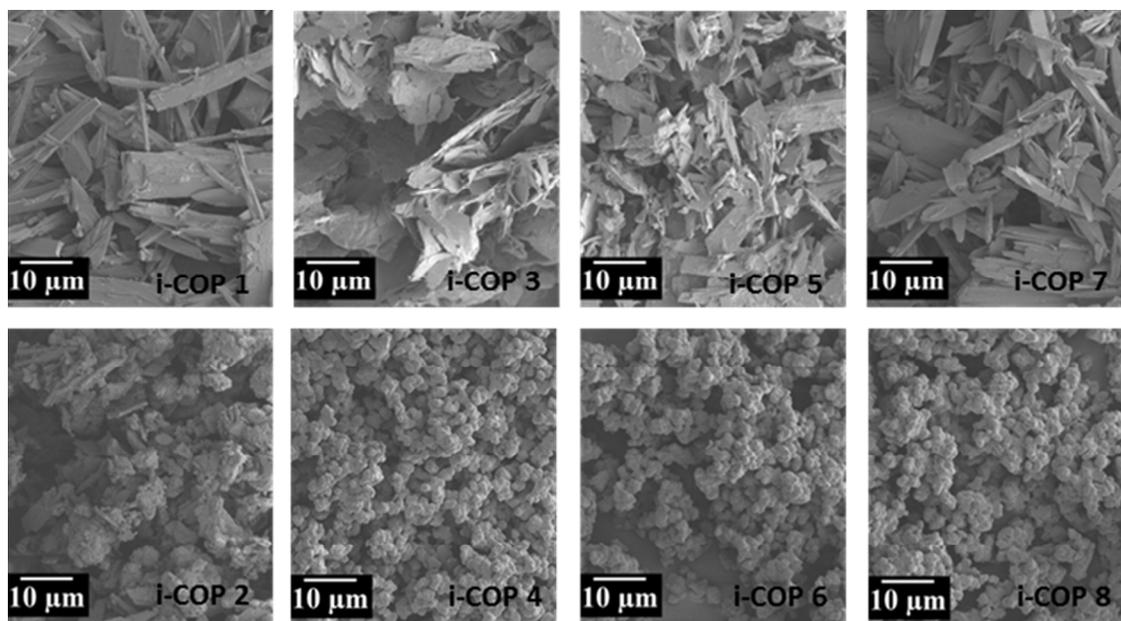


Figure 2. Scanning electron micrographs of i-COPs. Crystalline i-COPs (odd numbers) show plate like assemblies, showing a preferred planar orientation. The corresponding amorphous i-COPs (even numbers) are agglomerates of irregular geometry, a preferred alignment to minimize surface energy.

D band at ~ 1360 (originated from A_{1g} mode) due to stretching of bond of sp^2 atoms in both rings and chains, and breathing modes (defect sites) of sp^2 atoms in rings, respectively.³⁰ For i-COP_n, Raman spectrum indicates the G peaks (1598 cm^{-1} for i-COP 1, 1607 cm^{-1} for i-COP 3, 1606 cm^{-1} for i-COP 5 and 1630 cm^{-1} for i-COP 7), which is characteristic of crystalline symmetry (Figure 3).

Even though low intensity D and D' peaks exist in i-COP 1, their intensities reduce as the space between two nucleophilic nitrogens of dipyrindyl based linker increase, which is in agreement with PXRD patterns (Figure 1). This is evident in i-COP 3 and 5, proving the reduction in disorders/defects and in i-COP 7 the π - π stacking prevent the twist in linker structure leading to ordered polymer that is nearly identical in symmetry to pristine graphene. The defects are generally quantified by the ratio of intensity of D to G peaks, I_D/I_G ; high ratio represents more defects.³¹ It is found that I_D/I_G ratio for i-COP 1 is 4.1 which goes down to 0.06 for i-COP 7, a value very similar to that of pristine graphene, $I_D/I_G \sim 0$ (Table S1).

Porosity³² in 2D systems often requires preventing dense packing; a good example is the polymers of intrinsic microporosity (PIM),³³ which has 90° kinks in every repeating unit leading to substantial porosity at the expense of crystallinity.³⁴ Weber et al. also synthesized aromatic polyamide and polyimide based on spirobifluorene with a 90° kink in repeating units further demonstrating that bent structures prevent efficient packing for a crystal order.³⁵ Since all the i-COPs are designed to favour dense

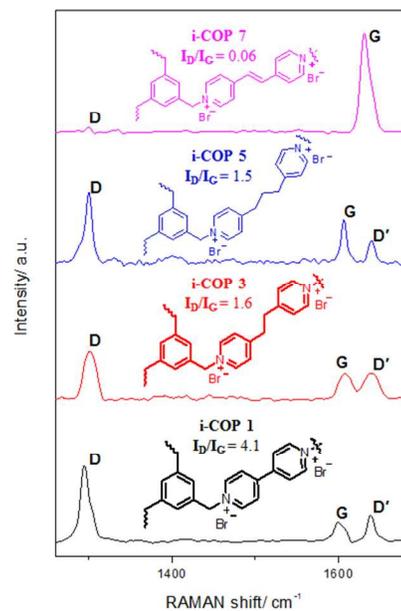


Figure 3. Raman spectrum for crystalline ionic covalent organic polymers (i-COP_n, n = 1, 3, 5 and 7), where I_D and I_G represents the intensity of D and G peak, respectively.

chain packing, low surface areas and pore sizes were observed from nitrogen physisorption isotherms (Figure S7 and Table S2) as well as low CO₂ capture capacities (Figure S8). Nevertheless, *i-COPs* showed moderate CO₂/N₂ selectivities (up to 145 in *i-COP* 4) mainly due to lack of the preferential binding of nitrogen at the few available pore openings.

Ion Exchange

In order to explore the charged nature of the *i-COPs* we turned to ion exchange, which is usually employed in charged structures to tune their properties according to the field of application. Fischer et al. exchanged lithium of ABNs with sodium and manganese ion, and also reported oxidation of styrene with a higher selectivity of 81% for [Mn(bpy)₂]²⁺-ABN catalyst.^{16,36} Ship-in-a-Bottle synthesis approach³⁷ enabled them to develop [Mn(bpy)₂]²⁺-ABN catalyst. To form porous hybrid gel materials, Coskun and coworkers presented the incorporation of imidazolium cation onto pyrene to interact to 'reduced graphene oxide'.³⁸ At first, 1-bromopyrenemethanol was synthesized and then functionalized with N-methylimidazole to yield a charged molecule. For ion exchange, the aqueous solutions of NH₄PF₆, KBF₄ and Li(CF₃SO₂)₂N were used to exchange (quantitatively) bromide ion with PF₆⁻, BF₄⁻ and (CF₃SO₂)₂N⁻, respectively. Among all the *i-COPs* synthesized herein, we succeeded to exchange (quantitatively) bromide counter ions of *i-COP* 1 with a variety of anions that include PF₆⁻, BF₄⁻ and CF₃SO₃⁻ by treating with aqueous solutions of NH₄PF₆ (Pf), NaBF₄(Bf) and CF₃SO₃K (Tf), respectively (Figure S9). Because of the aliphatic bridges between rigid aromatic rings of the other *i-COPs*, the exchanged anion slightly reorganized the order in the symmetric structure leading to minor shifts in PXRD patterns in the case of Pf and Tf and amorphous nature in Bf (Figure S10). Such structural flexibility was also observed in porous coordination polymers (PCPs),³⁹ metal-organic frameworks (MOFs)⁴⁰ and coordination polymer networks (CPNs)⁴¹ which was identified by slight differences in their PXRD patterns.

Conclusions

In conclusion, purely organic, charged, crystalline network polymers namely, ionic covalent organic polymers (*i-COPs*) were prepared via rapid nucleophilic substitutions under kinetic control. It was shown that the structural regularity is neither dependent on temperature nor on the solvent. We believe that this is because the limitation of binding motif to only pyridyl-bromomethyl coupling and the steric factors lead to restriction in structural freedom. The solid-state reaction turned to be extremely efficient without compromise on the ordered structures. By controlling and simplifying variation in reaction conditions and composition, we concluded that charged ammonium centres repel the vicinal methyl substituents, and bromines reject each other, leading to a maximal spacing and thus order in the super structure. As the dense chain packing was observed, *i-COPs* had low surface areas and did not show significant gas capture. The ordered network polymers were also found to have graphitic nature, which was further tuned by selecting non-twisting building unit to yield crystalline network polymer (*i-COP* 7) like pristine graphene. The synthesized materials contain free replaceable counter anions, which enable us to anticipate their use to wide variety of applications, for instance, ion exchange, catalysis, electrochemical applications, such as, Li⁺ batteries or Na⁺ batteries and DSSCs.^{15,16} We envision that the surface area could be adjusted

by tuning the nature of cationic polymer networks to achieve high gas capture.

Acknowledgements

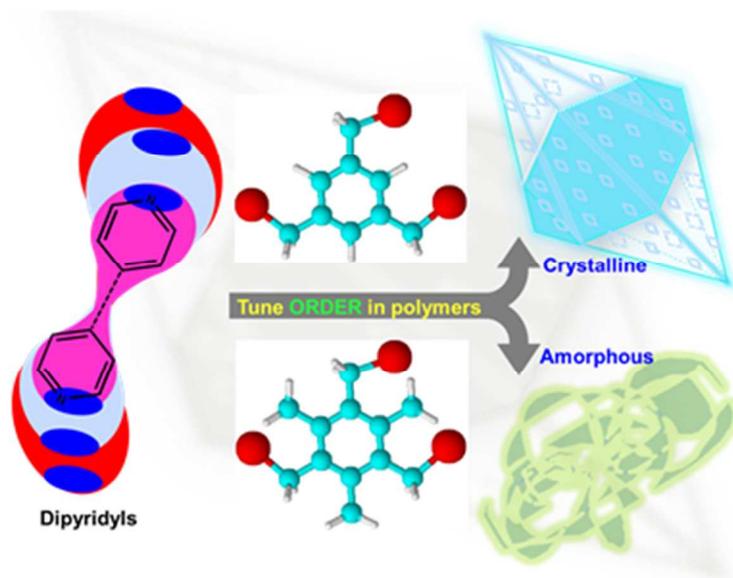
We acknowledge the financial support by Korea CCS R&D Centre, Basic Science Research Program through the National Research Foundation of Korea (NRF), ICT & Future Planning (2013R1A1A1012998), and IWT (NRF-2012-C1AAA001-M1A2A2026588).

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Graphical Abstract



Organic Crystals: Kinetic control on dynamic covalent bond formations is now possible through quaternary ammonium bridged crystalline network polymers.