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Design and Synthesis of Nitrogen-rich Carbonaceous Two-dimensional Polymer

Lei Liu,[ab] Yijie Xia,[b] Jie Zhang*[b]

Nitrogen-rich carbonaceous two-dimensional polymer was prepared through dynamic covalent chemistry under ionthermal condition. The synthesis is based on the formation of 2D polytriazine networks via the polytrimerization of nitriles of 2,4,6-tricyano-1,3,5-triazine (TCT) monomers from $ZnCl_2$ salt melts at 400 ºC. The formation of the 2D polymer was verified by detailed characterization.

Two-dimensional (2D) materials such as graphene, boron nitride, carbon nitride, transition metal dichalcogenides and complex oxides offer a variety of outstanding properties for fundamental scientific exploratory and practical application, ranging from nanoelectronics to biology.[1] However, the lack of general and robust methods to scale-up the polymer synthesis and produce high quality 2D materials have hindered their further investigation and application.[2] Currently, 2D polymers are being intensively investigated to address these challenges owing to their intrinsic properties of high chemical stability, low skeleton density, controllable molecular weight, outstanding functional group tolerance, easy industrial scale-up and the ability to be fine-tune their properties at the molecular level, allowing facile construction of 2D materials with desired functionalities by appropriate choice of building block.[3] Since the 1980s there have been a number of attempts to synthesize 2D polymer through polymerization of functional monomers, and theoretical studies have predicted unusual mechanical and folding behaviors of these 2D skeletons.[4] These 2D organic structures have flexibility by varying the design of the organic functional monomers and can effectively combine the organic synthetic methodologies with processability of the polymers, thus provide an unique opportunity for rational design and development of versatile 2D polymers for targeted applications. To date, numerous organic polymer based 2D materials have been developed, mainly using approaches of boronic acid condensation, carbonyl condensation, light induced polymerization of 2D supramolecular assemblies and 2D substrate assisted polymerization.[5] Nevertheless, it still remains a great challenge to synthesize 2D polymers with rational design at molecular level by using cost-effective and simple pathways for the polymerization.

Dynamic covalent chemistry has been an efficient and versatile approach in organic synthesis, specially aiming at synthesizing large complex molecular systems.[6] It relies on the use of covalent bonds that can be reversibly formed under the experimental conditions of equilibrium control. The reversible nature of the reactions introduces the prospects of "error checking" and "proof-reading" into synthetic processes where dynamic covalent chemistry could operate.[7] There have been many reports on the syntheses of crystalline inorganic materials employing dynamic covalent reaction, but only a few examples are known for the generation of crystalline organic frameworks.[8] Recently, Kuhn et al. introduced a new dynamic covalent reaction that allows the formation of porous crystalline triazine based 2D framework, through the reversible ionthermaltrimerization of aromatic polynitriles.[9] This dynamic polymerization reaction is moreover reversible as the retro-trimerization is also occurring at 300-400 ºC, thus opening the opportunities of dynamic self-optimization of the as formed 2D network structure, and could offer a broad variety of triazine-based 2D polymers in good yields by appropriate choices of reaction conditions including monomer architecture, reaction medium, reaction temperature, concentrations of reactants and catalysts. This polymerization method presents a successful example of building the 2D polymeric network cost-effectively, which is essential for the scale-up preparation of 2D materials for industry applications. To the best of our knowledge, there are only five reported syntheses of triazine-based 2D polymers by dynamic ionthermal trimerization of aromatic polynitriles.[9-10]

Herein, we report the synthesis of nitrogen-rich carbonaceous two-dimensional polymer by using dynamic polymerization reaction under one-pot catalytic ionthermal condition. Our design employs 2,4,6-Tricyano-1,3,5-triazine (TCT) as the building block. This monomer is a particularly interesting as it is nitrogen-rich, a trimer of cyanogens, and an interesting acceptor for the development of molecule-based magnets and conductors. Very different from the previous reported triazine-based 2D polymers, the present trimerization of TCTs will produce the triazine as the exclusive repeat unit of the 2D polymer as shown in scheme 1, thus significantly improving the nitrogen/carbon ratio. As we known, the electrical and optical properties of the organic polymeric material depend upon its electronic structure and ultimately on the chemical

constitution of its repeat unit; and the different nitrogen environment affects the electronic structure of doped carbon materials and results in different mechanisms of activity enhancement. [11]
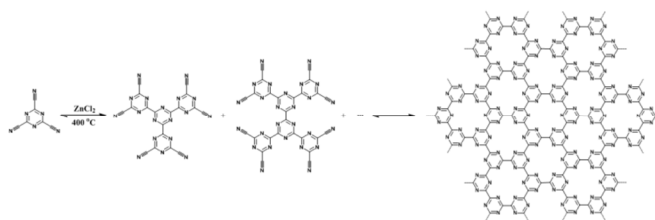
Scheme 1 Trimerization of TCTs in molten $ZnCl_2$ to trimers and oligomers and then to an idealized stiff polycyclic polymer architecture.

We chose nitrogen-rich 2,4,6-Tricyano-1,3,5-triazine (TCT) as the building block to take dynamic polymerization reaction under one-pot catalytic ionthermal condition. The as-prepared black powder is chemically stable, even when exposed to acidic or alkaline conditions, and also exhibits a high thermal stability ($T_{dec} > 400$ °C) as evidenced by thermogravimetric analysis (Figure S1 in the Supporting Information). The formation of the polymer was confirmed by the ^{13}C solid-state NMR, FT-IR, EA and XPS analyses. The ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectrum of the obtained polymer with the assignments of the resonances is shown in Fig. 1. The high-intensity broad-width peak around 161 ppm is ascribed to the carbon atoms present in the triazine rings of the polymer, while the signals around 154 ppm and 110 ppm assigned to the two kinds of carbons in TCT monomers are almost complete disappearance. In accordance with the results from the ^{13}C solid-state NMR analysis, the presence and absence of characteristic vibration bands in the FT-IR spectrum after the polymerization provide further insight into the efficiency of the dynamic polymerization reaction. As shown in Fig S2 (in the Supporting Information), the disappearance of the intense carbonitrile band at 2255 cm^{-1} is an evidence of a successful trimerization reaction, whereas the appearance of a strong broad absorption band around 1600 cm^{-1} point to the formation of triazine rings. Elemental analysis shows that the ratio of nitrogen/carbon is 1.13 that is as close to the theoretical values 1.16 as it can be expected for this kind of reaction mechanism.
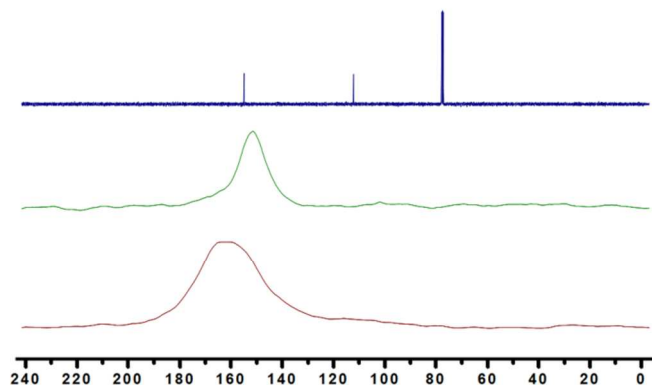

Fig. 1 ^{13}C-NMR spectrum of the TCT monomer and polymer: ^{13}C-NMR spectrum of TCT monomer in $CDCl_3$ (Top line), ^{13}C CP-MAS NMR spectrum of the TCT monomer (Middle line), ^{13}C CP-MAS NMR spectrum of the TCT based polymer (Down line)

To further confirm the dynamic polymerization, the structural measurements are carried out by X-ray photoelectron spectroscopy. The structures of the initial and final C and N species are of particular interests, as revealed by the C 1s and N 1s spectra in monomer and polymer respectively. Broad scan survey spectra are shown in supporting information, and there is no traceable zinc element residual which is consistent with the ICP test result. High-resolution spectra of the C 1s and N 1s regions are shown in Fig. 2(a-d). The distinct doublet around 287.9 eV and 284.0 eV are assigned to C species in TCT monomer, while the distorted broad peak centred at 285.4 eV is ascribed to the carbon atoms present in the triazine rings of the polymer. Similarly the N 1s signals in TCT monomer are located around 399.7 eV and 398.4 eV, whereas only one sharp peak is centred at 398.4 eV in polymer. Meanwhile, it has been noted that the carbonitrile group (EA/eV +0.68) possesses an electron affinity considerably larger than 1,3,5-triazine core (EA/eV +0.46) based on the previous theoretical calculation and experimental study,[12] thus our finding indicates that there is the successful trimerization reaction.
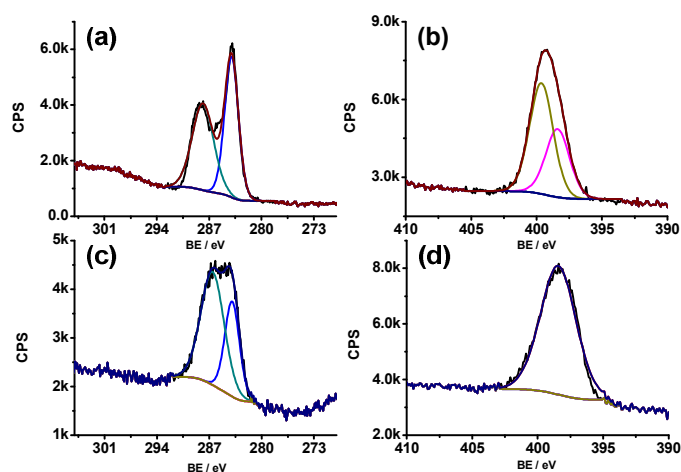

Fig. 2 High-resolution C 1s and N 1s XPS spectra: (a) C 1s spectrum of TCT monomer; (b) N 1s spectrum of TCT monomer; (c) C 1s spectrum of TCT based 2D polymer; (d) N 1s spectrum of TCT based 2D polymer.

Raman spectroscopy is used to fingerprint a material structure and layer-dependent changes of the vibrational structure, particularly for distinguishing ordered and disordered structures of carbon. But to the best of our knowledge, there is no report of the triazine based 2D frameworks characterized by Raman spectroscopy. Fig 3(a-d) compares the Raman spectra of the monomers and the nitrogen-rich carbonaceous two-dimensional polymers. As we known, the typical Raman spectra of carbon are: 1) the G line around 1580 cm^{-1} and the D line around 1350 cm^{-1} with the G line assigned to the E_{2g} phonon of C sp^2 atoms and the D line-as a breathing mode of κ-point phonons of A_{1g} symmetry; 2) the overtone of the D line at 2700 cm^{-1} and the G' line (the overtone of the G line, also called 2D line) at 3250 cm^{-1}.[13] As a reference, the DCB based 2D polymer is employed for comparing with TCT based 2D framework. It can be seen that DCB based 2D polymer displays the strong G line and D line at 1595 cm^{-1} and 1371 cm^{-1} respectively, and a band at ~ 2760 cm^{-1}. Similarly, the TCT based 2D polymer shows the strong G line and D line at 1590 cm^{-1} and 1370 cm^{-1} respectively, and a band at ~ 2700 cm^{-1}. These phenomena could indicate that both DCB and TCT based 2D polymers have the similar structure with graphene nanosheets.
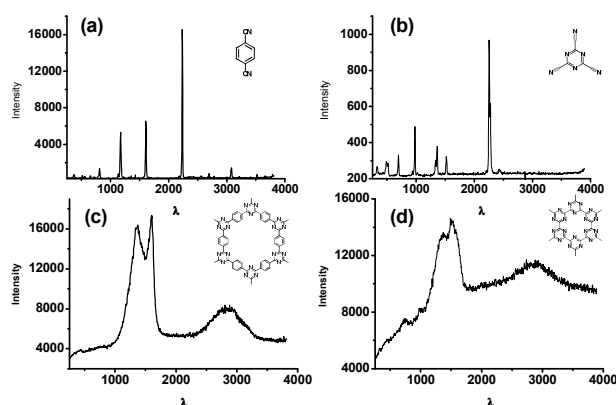
Fig. 3 Raman spectra of monomers and two-dimensional polymers: (a) Monomer DCB; (b) Monomer TCT; (c) DCB based 2D polymer; (d) TCT based 2D polymer.

The morphology and microstructure of the as-prepared TCT based 2D polymer are investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM). As a reference, the microscopic analyses of DCB based 2D polymer have also been conducted. It can be clearly seen from Fig. 4 that the obtained sample TCT based 2D polymer is composed of stacked multi-layers, while DCB based 2D polymer exhibits as free-standing sheets with morphology similar to that of graphene. Atomic force microscopy (AFM) analysis is conducted on samples prepared from suspensions sonicated in N, N-Dimethylformamide. Figure 4c-4d reveals the same morphology as that observed from SEM and TEM images. Extended exfoliation of TCT based 2D polymer leads to 2D nanosheets mixed with some multiple-layer stacked particles. The thickness of TCT and DCB 2D nanosheets is determined from the AFM measurements (Fig. S8). Both of the 2D polymers have the thickness at ~3 nm. A high resolution TEM analysis is attempted. The thin nanosheets deposited on the lacy carbon-coated copper grid are sensitive to the TEM electron beam, as expected, particularly when higher-resolution imaging is attempted, therefore the structure of the 2D materials are not pronounced as expected from HTEM images in Fig. 4e-4f. The porous properties of these two 2D polymers are characterized from the N_2 sorption analysis at 77 K. As evidenced from Fig 5, N_2 isotherms for TCT based 2D polymer shows the type III isotherm, whereas the DCB based 2D polymer displays the type I isotherm. As measured by nitrogen sorption experiments, TCT based 2D polymer shows a surface area of 73 m^2g^{-1}, and DCB based 2D polymer exhibits 780 m^2g^{-1} which is consistent with previous reports.[9-10] These findings indicate that TCT based 2D polymer has the similar structure with graphitic carbon nitride.
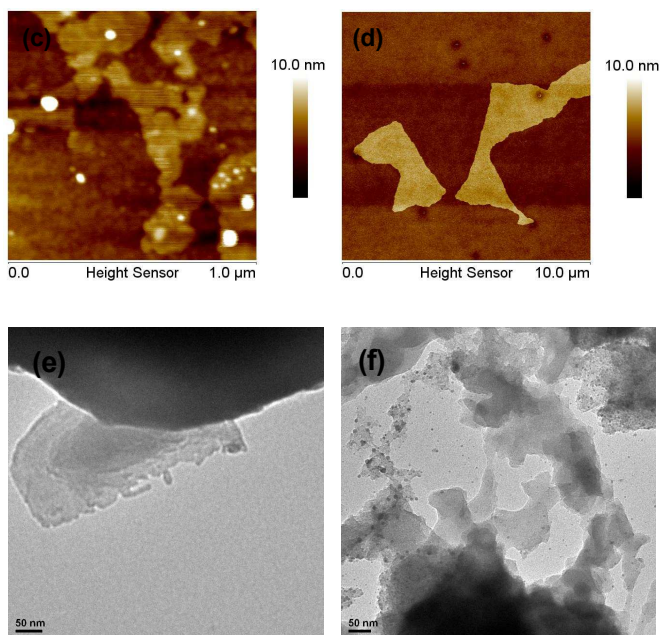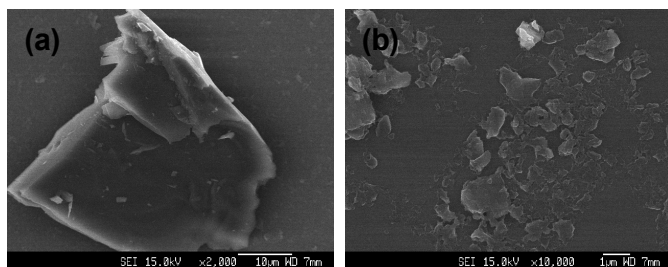

Fig. 4 SEM micrographs of two-dimensional polymers: (a) TCT based 2D polymer; (b) DCB based 2D polymer; AFM images of exfoliated two-dimensional polymers: (c) TCT based 2D polymer; (d) DCB based 2D polymer; TEM images of exfoliated two-dimensional polymers: (e) TCT based 2D polymer; (f) DCB based 2D polymer.
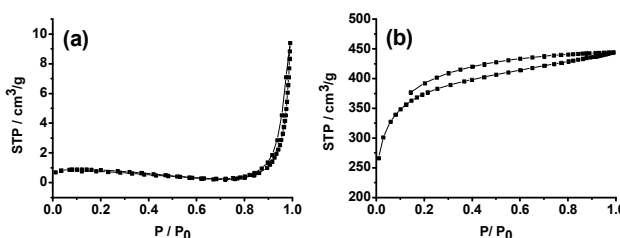

Fig. 5 N_2 sorption isotherms of (a) TCT based 2D polymer and (b) DCB based 2D polymer. P_0 is the saturated vapor pressure of the gas at 77 K.

In this work, we have synthesized TCT 2D polymer that is reminiscent of graphene in some aspects. The nitrogen-rich carbonaceous two-dimensional polymer has been synthesized through dynamic covalent chemistry under ionthermal condition. The synthesis is based on the formation of 2D polytriazine networks via the polytrimerization of nitriles of 2,4,6-tricyano-1,3,5-triazine (TCT) monomers from $ZnCl_2$ salt melts at 400 ^oC. The further study for their optical electrical and magnetic properties is undergoing.

Notes and references

[a]China Center for Modernization Research, Chinese Academy of Sciences, Zhongguancun Beijing, 100190, China

[b]Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 3 Research Link, 117602, Singapore

E-mail: zhangj@imre.a-star.edu.sg

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