Graphdiyne (GDY), a two dimensional (2D) carbon allotrope, is supposed to have excellent mechanical, electronic, optical, and magnetic properties.\(^1\)\(^-\)\(^4\) Since GDY was proposed in 1997 (ref. 5) and the first GDY film was fabricated on copper foil in 2010,\(^6\) many researchers have been dedicated to the study of GDY mainly focussing on the realization of an ideal structure\(^7\)\(^-\)\(^9\) and the expansion of its application area.\(^10\)\(^-\)\(^15\) Fundamental building units, consisting of three phenyl rings crosslinked by butadiyne linkages, endow GDY with uniformly distributed pores and an extended π-conjugated system, which were usually considered advantages for gas adsorption and separation as high surface area and selective binding sites. Based on uniform pore size, the superior performance of a monolayer graphdiyne membrane for hydrogen purification from syngas was predicted through computational simulation,\(^16\)\(^-\)\(^17\) as well as the separation of oxygen from harmful gases.\(^18\) The AB stacking of multilayer graphdiyne\(^19\) and short interlayer distance resulting from strong interlayer interaction prevented the extension of the pore structure. Recently, Li \textit{et al.}\(^20\)\(^,\)\(^21\) adjusted the pore size of graphdiyne through introducing substituted hydrogen or chlorine atoms. Guo \textit{et al.}\(^22\) constructed a series of porous carbon materials through stacking functionalized graphdiyne units in a disordered mode, and proved their outstanding CO\(_2\) capture and separation capacity by computational simulation. Concluding from the research of porous polymers, introducing three dimensional rigid building blocks into GDY could reduce the stacking effect between layers and improve its pore performance, so as to expand its application field like gas storage and separation. But so far there have been few relevant reports.

Light hydrocarbons comprised of only carbon and hydrogen like ethylene and acetylene were important chemical feedstock for manufacture plastic and other industrial products. However, their similar molecular weight and polarizability led to difficulties in separation of the gas mixture, and furthermore, the utilization of the pure gas. The common industrial separation methods relied on cryogenic distillation – an energy intensive process need high pressure and ultralow temperature – and resulted in tremendous energy cost and carbon emission.\(^23\)\(^-\)\(^24\) In contrast, adsorptive separation, as an alternative to distillation, did not require phase change of the mixture and possesses improved energy efficiency. Therefore, many researchers have been attracted to the development of new adsorbents with better separation performance in recent years.\(^25\)\(^-\)\(^30\) For acetylene adsorption and separation from ethylene, it was proved that adjusting the pore size and shape could be an effective way to improve the performance.\(^31\)\(^-\)\(^34\) However, the precise control of pore size and shape was still a challenge, especially for porous organic polymers. Since the electrostatic potential distribution of acetylene and ethylene were different, introducing proper surface functional groups to obtain selective adsorption sites in...
porous adsorbents could represent another efficient method. Up to now, some chemical groups like amine groups, imidazolium functional groups, hexafluorosilicate and pigment orange-71 have been demonstrated to exhibit preferential affinity to acetylene.\textsuperscript{25–28} And more examples were under research and still made sense for providing new design Scheme 1 protocols to obtain adsorbents with better acetylene adsorption and separation performance.

Triptycene,\textsuperscript{40–42} with three-dimensional rigid paddlewheel-like structure, has been successfully used as building blocks to construct supramolecular systems,\textsuperscript{43–48} polymeric materials\textsuperscript{49,50} and organic porous materials.\textsuperscript{51–53} In this work, triptycene was introduced into GDY scaffold to prevent the closer packing of two-dimensional layers, so that obtain a three dimensional graphdiyne-like porous triptycene network (G-PTN). Its pore structure and high surface area were characterized, while the selective adsorption capacity toward acetylene over ethylene was also detected and proved by experiments and computation simulation. Which represented a credible way to expand the application of GDY into adsorptive separation of light hydrocarbons, as well as offered a new selective binding site for acetylene over ethylene.

## Results and discussion

The synthesis of G-PTN was conducted via a copper-catalyzed cross-coupling reaction of 2,3,6,7,14,15-hexakis[(4-ethynylphenyl) ethynyl] triptycene (Scheme S1,Fig. S1–S4†). Fourier-transform infrared (FT-IR) and \textsuperscript{13}C cross-polarization magic-angle spinning (CP/MAS) NMR experiments were utilized to confirm the formation of diacetylenic linkages. As shown in Fig. S5,† the several signal peaks in NMR spectrum with chemical shifts around 54 ppm, 79 ppm, 94 ppm, 127 ppm and 143 ppm were assigned to the bridgehead carbons of triptycene, diacetylene units and aromatic carbons of triptycene, respectively.\textsuperscript{20,21} While the oxidation of terminal alkyne could result in the signals around 178 ppm and 194 ppm. In FT-IR spectrum of G-PTN in Fig. S6,† the typical \textsuperscript{13}C=C stretching vibration was marked at 2189 cm\textsuperscript{-1}, proving the existence of alkyne groups.

Fig. S7† exhibited the scanning electron microscope (SEM) and transmission electron microscope (TEM) images of G-PTN, which appeared to be interconnected tiny particles as other amorphous porous organic polymers. The amorphous nature of G-PTN was also demonstrated by a broad peak at 2θ = 20° in powder X-ray diffraction pattern (Fig. S8†). Thermogravimetric analysis (TGA) was employed to test the thermal stability of G-PTN, in Fig. S9,† the material begin to degradation at about 350 °C under nitrogen.

The ideal structure of G-PTN was presented as Fig. 1, which suggested the porous nature of such cage-like material. For verification, nitrogen adsorption isotherm was obtained at 77 K. As shown in Fig. 2a, the curve accorded with type I(b) reversible sorption profile with type H4 hysteresis loop, implying the existence of abundant micropores. The pore size distribution calculated by NLDFT method exhibited two main pore sizes of 0.59 nm and 1.27 nm in Fig. 2b. The Brunauer–Emmett–Teller (BET) surface area (Fig. S10†) of G-PTN was calculated to be 1046 m\textsuperscript{2} g\textsuperscript{-1} (Langmuir surface area was 1396 m\textsuperscript{2} g\textsuperscript{-1}), and the single point adsorption total pore volume of pores less than 320.5 nm diameter at P/P\textsubscript{0} = 0.993 was determined to be 0.53 cm\textsuperscript{3} g\textsuperscript{-1}. The microporous structure of G-PTN was suitable for small gas molecule adsorption. As a typical greenhouse gas, the capture and storage of CO\textsubscript{2} was essential in face of global warming and abnormal climate change. The CO\textsubscript{2} adsorption capacity of G-PTN was then obtained as 80.7 cm\textsuperscript{3} g\textsuperscript{-1} (15.8 wt%) at 273 K and 1 bar and 51.5 cm\textsuperscript{3} g\textsuperscript{-1} (10.1 wt%) at 298 K (Fig. S11a and b†), which were comparable with other triptycene-based nitrogen-rich porous organic polymer.\textsuperscript{60,62}

The C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} adsorption isotherms were collected at 273 K and 298 K to estimate the light hydrocarbons adsorption and separation capacities of G-PTN. As shown in Fig. 2c, the values of 81.1 cm\textsuperscript{3} g\textsuperscript{-1} and 66.1 cm\textsuperscript{3} g\textsuperscript{-1} were obtained at 273 K and 1 bar for C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}, respectively, exhibiting manifest acetylene selectivity of G-PTN. Under ambient condition, the gas uptake capacities slightly decreased to 59.6 cm\textsuperscript{3} g\textsuperscript{-1} (C\textsubscript{2}H\textsubscript{2}) and 44.7 cm\textsuperscript{3} g\textsuperscript{-1} (C\textsubscript{2}H\textsubscript{4}), approximately remaining the same ratio (Fig. 2d). Since G-PTN hardly exhibited uniform distributed pores, and the primary pore sizes calculated (5.9 Å and 12.7 Å) were wider than both kinetic diameter of C\textsubscript{2}H\textsubscript{2} (3.3 Å) and C\textsubscript{2}H\textsubscript{4} (4.2 Å). It seemed that the acetylene selectivity of G-PTN more likely originated from the stronger affinity of polymer framework toward acetylene.

As further proof, the isosteric heats of adsorption (Q\textsubscript{st}) for C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} were calculated based on the Clausius–Clapeyron equation after fitting the adsorption curves at two different temperature utilizing the dual-site Langmuir model, and the specific values near zero-coverage region were 29.6 kJ mol\textsuperscript{-1} (C\textsubscript{2}H\textsubscript{2}) and 23.9 kJ mol\textsuperscript{-1} (C\textsubscript{2}H\textsubscript{4}) according to Fig. S12a,† which was in support of a stronger interaction between the framework of G-PTN and acetylene. Furthermore, the separation performance of G-PTN for the binary gas mixture of C\textsubscript{2}H\textsubscript{2}/C\textsubscript{2}H\textsubscript{4} (1 : 99 v/v) could be predicted via the adsorption isotherms of the pure component gas under the same condition utilizing ideal adsorbed solution theory (IAST).\textsuperscript{64,65} The data thus obtained were plotted in Fig. S12b,† at 298 K and 1 bar, the value of selectivity was 1.64.

For further understanding of the selective adsorption, the theoretical calculations were adopted to determine the binding
sites and the binding energies when G-PTN was utilized as adsorbent and acetylene or ethylene was utilized as adsorbate. A model molecule termed as M1 consisting the basic triangular unit of graphydeine and three triptycene groups (Fig. S13†) was separated out to represent G-PTN in the calculations. As shown in Fig. 3, the van der Waals surface of M1, acetylene and ethylene were coloured according to the value of molecular electrostatic potential (ESP) in BWR color mode and the extreme points were also exhibited. Generally, the intermolecular interactions based on electromagnetic forces could occur between the adsorbents with negative ESP and adsorbates with positive ESP, or the converse. Then two interaction models between acetylene and M1 were screened and optimized, as well as two for ethylene (Fig. S14,† named as M1-C2H21, M1-C2H22,

![Image](image1.png)

**Fig. 1** The ideal structure of G-PTN. (a) The three-dimensional structure image of G-PTN; (b) and (c), (d) and (e) the projection drawing of G-PTN from different view angles.

![Image](image2.png)

**Fig. 2** Gas sorption test of G-PTN. (a) Nitrogen sorption and desorption isotherms of G-PTN at 77 K; (b) pore size distribution calculated of G-PTN; C2H2 and C2H4 sorption isotherms of G-PTN at (c) 273 K and (d) 298 K. In (c) and (d), filled symbols denote gas adsorption and empty symbols denote desorption.
In configurations M1-C2H2 and M1-C2H4 (Fig. S14b and d†), the isolated graphdiyne unit could not afford the complete contact with adsorbates, which hindered it from becoming the primary adsorption site (the interaction energies of M1-C2H2 and M1-C2H4 were −13.9 kJ mol⁻¹ and −17.3 kJ mol⁻¹, respectively). For further investigation, two triangular units of graphdiyne and one adsorbate molecule were combined to construct new interaction configurations named as G2-C2H2 and G2-C2H4. The optimized structures were exhibited in Fig. S16.† In the case of acetylene, the triangular units were parallel to each other with a interlayer distance of 3.6 Å and acetylene molecule was perpendicular with the units at the center of the rings. As for G2-C2H4, the dihedral angle of two graphdiyne units was shown as 34.67° to realize the complete contact of the areas with the most positive ESP and the most negative ESP. When the graphdiyne units in G2-C2H4 were froze and the ethylene molecule was replaced with acetylene, a new configuration termed as G2-C2H2 was then obtained through constrained optimization (Fig. S17†) and the interaction energy was calculated using rSCAN-3c method as 104.2 kJ mol⁻¹. By contrast with the binding energy of G2-C2H4 (Fig. S17b, †−31.5 kJ mol⁻¹), it could be concluded that in order to realize the complete contact and high binding energy, the ideal three dimensional structures of graphdiyne were disparate for acetylene, ethylene or other gas molecules owing to the slight structural differences. Therefore, by judicious selection of three dimension rigid building blocks participating in the framework of graphdiyne, the selective adsorbents with excellent gas adsorption and separation capacities could be designed and constructed.

Another cage molecule named as M2 was also separated as a model to verify the theoretical calculation results above for the reason that all the phenyl rings of triptycene in G-PTN would participate in the π-conjugated system rather than being isolated in the ideal case. Fig. S18† exhibited the optimized structure of M2, there were two kinds of pores across the molecule with diameters of about 0.66 nm and 1.77 nm, respectively. Taking the atomic volume into account, such sizes were in line with the pore size distribution results calculated from nitrogen adsorption isotherm of G-PTN (5.9 Å and 12.7 Å). The most stable binding configuration of M2 and acetylene (M2-C2H2) was exhibited in Fig. S19a and b† with similar binding mode to M1-C2H2. Employing the same optimized method, M1-C2H2 was obtained for exact comparison with M2-C2H2 (Fig. S19c†). As shown in Fig. S19,† the angles between acetylene and phenyl rings were slightly different in these two configurations, which could result from the electron distribution change during phenyl ring getting involved in π-conjugated system. The binding energies then were calculated using rSCAN-3c method as −19.1 kJ mol⁻¹ for M2 and −20.0 kJ mol⁻¹ for M1. With extended three dimensional structure, it was clear that triptycene residues could be regarded as cross points of three graphdiyne units with dihedral angle of about 120°. For such three dimensional structure, acetylene molecules could more simply realize complete contact with two π-conjugated systems than ethylene, which could result in selective adsorption.
Experimental

The building unit 2,3,6,7,14,15-hexakis[(4-ethynylphenyl)ethynyl]triptycene was synthesized consulting the existing literature through the reaction route showed in Scheme S1.† All original reagents were purchased from commercial source without further purification.

Synthesis of G-PTN

In a 50 mL pyrex tube, 2,3,6,7,14,15-hexakis[(4-ethynylphenyl)ethyl]triptycene (310 mg, 0.78 mmol) and cuprous chloride (78 mg, 0.79 mmol) were dissolved in 20 mL pyridine. The mixture was heated to 60 °C, as the reaction processed, brown precipitate was gradually obtained. After 4 days, the reaction system was cooled to room temperature, and the precipitate was filtrated and washed sequentially by dichloromethane, tetrahydrofuran, acetone and ethanol. The product was then obtained after drying in vacuum as brown powder. (303 mg).

Computational details

The configurations M1-C2H21, M1-C2H22, M1-C2H41 and M1-C2H42 were screened out through molclus program using xtb 6.4.1 (GFN2-xtb method) for optimization and energy evaluation. Further constrained optimization were conducted using rSCAN-3c method by orca 5.0.3. The interaction energies were calculated using double-hybrid function PWPB95 in combination with the def2-QZVPP basis set, DFT-D3 dispersion correction and counterpoise correction. To save computational time, the resolution-of-identity (RI) technique and the auxiliary basis def2/j were used.

The configurations G2-C2H21 and G2-C2H41 were optimized with rSCAN-3c method in orca 5.0.3. The configuration G2-C2H2 was obtained through replacing the ethylene molecule in G2-C2H41 into acetylene with further constrained optimization freezing all atoms in graphdiyne units by rSCAN-3c method in orca 5.0.3. The binding energies of G2-C2H2 and G2-C2H4 were both determined at the same calculation level with optimization.

The configurations M2-C2H21 and M1-C2H2com were also screened out through molclus program utilizing xtb 6.4.1 (GFN2-xtb method), but did not go through further optimization by density functional theory calculations. The binding energies were evaluated through rSCAN-3c method in orca 5.0.3.

The ESP colored vdW surfaces were analysed by Multiwfn and visualised with the VMD visualisation program using
the wavefunction data obtained from DFT calculations, as well as the IRI isosurface.\textsuperscript{97}

**Conclusions**

In conclusion, a three dimensional graphdiyne-like porous tritycene network (G-PTN) was synthesized in this work. With high BET surface area of 1046 m\(^2\) g\(^{-1}\), its gas sorption capacities for CO\(_2\), C\(_2\)H\(_2\) and C\(_2\)H\(_4\) were measured as 51.5 cm\(^3\) g\(^{-1}\), 59.6 cm\(^3\) g\(^{-1}\) and 44.7 cm\(^3\) g\(^{-1}\) at 298 K, respectively, exhibiting selective adsorption capacity toward C\(_2\)H\(_2\) over C\(_2\)H\(_4\). Introducing graphdiyne units into selective adsorbents for C\(_2\)H\(_2\)/C\(_2\)H\(_4\) broadened the application potential of graphdiyne, while opened a new design protocol to obtain excellent gas separation materials. Upon adjusting pore size and three-dimensional structure, the separation performance of porous graphdiyne could be further improved and the related work was still under research.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**
