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## A Novel Triazine-Based Analog of Graphyne: Scalable Synthesis and Applications in Photocatalytic Dye Degradation and Bacterial Inactivation

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Graphyne, a theorized carbon allotrope possessing only sp- and  $sp^2$ -hybridized carbon atoms, holds great potentials in many fields, especially in catalysis, energy transfer/storage devices. Using a bottom-up strategy, we synthesized a new N-doped graphyne analog, triazine- and 1,4-diethynylbenzene-based graphyne **TA-BGY**, in solution in gram-scale. The unique  $sp/sp^2$ carbon-conjugated **TA-BGY** possesses an extended porous network structure with a BET surface area of ca. 300 m<sup>2</sup>g<sup>-1</sup>. Owing to its low optical band gap (1.44 eV), **TA-BGY** was expected to have many applications which were exemplified by the photodegradation of methyl orange and photocatalytic bacterial inactivation.

#### 1. Introduction

Graphyne (GY), a theorized one-atom thick carbon allotrope consist of  $sp^2$  hybridized carbons (benzene rings) bridged by ethylenic groups (*sp* carbons), is expected to possess twodimensional  $\pi$ -conjugated networks, uniformly distributed pores and unique mechanical and electronic properties.<sup>[1]</sup> Different from graphene which does not have an electronic bandgap because the valence and conduction bands are slightly overlapped, GY is predicted to be a natural semiconductor with intrinsic band gap (0.5 - 0.6 eV) owing to the special acetylenic  $-C \equiv C$ - bridges between the benzene rings.<sup>[2]</sup> Therefore, GY and its analogs are considered

to be potentially useful in various fields owing to their unique band gap properties.<sup>[3]</sup> So far, the true GY, in which only one acetylenic bond between adjacent benzene rings, has not been created due to the synthetic challenge, thus, it has only been studied through various computational simulations, and the exact properties of this theoretical material remains unknown. Despite the unsuccessfulness in the synthesis of true graphyne, some analogous structures of GY have been created during the past years.<sup>[4]</sup> For example, graphdiyne (GDY), in which its benzene rings are connected by diacetylenic bonds, was synthesized on the surface of copper *via* a cross-coupling reaction by Li's group in 2010.<sup>[4a]</sup> Ever since, several synthetic methods of GDY have been developed, and various applications of this new material have been explored (Figure 1).<sup>[5]</sup> In 2017, Li, Xiao and co-workers described a preparation of a carbon-rich network whose structure was close to hydrogen substituted graphyne (H-GY) through alkyne metathesis polymerization (Figure 1).<sup>[4b]</sup> Very recently, Yang, Huang and co-worked reported the synthesis of three graphyne analogs, hydrogen substituted graphyne (F-GY) at a liquid/liquid interface (Figure 1).<sup>[41]</sup> Nonetheless, the true GY material

is yet to be made. On the other hand, "more synthetically approachable" heteroatom-doped GY, especially N-doped GY, could hold similar importance in designing GY analogs potentially useful in photocatalysis and electronics as introducing heteroatoms is an efficient and essential method to adjust the band gaps and electronic structures of carbon materials.<sup>[6]</sup> Nitrogen-doping of carbon-based materials is usually implemented though three different strategies, such as chemical vapor deposition, pyrolysis of N-rich precursors, and post heating with N-containing substances. However, these approaches suffer drawbacks, such as varieties of species of N-containing substructures, randomness of the positions of N atoms as well as uncontrolled N percentage. Therefore, homogeneous 2D carbon materials have to be synthesized through a strategy which ensures N atoms to be in specific type and at specific locations in controllable percentage. One example was the bottom-up synthesis of triazinegraphdiyne (TA-GDY) reported by Hou, Huang and co-workers in 2018 (Figure 1).<sup>[4g]</sup> Herein, we report a gram-scale synthesis of triazine and 1,4-diethynylbenzene-based analog of graphyne (TA-BGY) through a bottom-up strategy in which C-C bonds were formed through aromatic nucleophilic substitution reactions (S<sub>N</sub>Ar) of cyanuric chloride with 1,4diethynyllithium benzene. TA-BGY was found to possess a low optical band gap of 1.44 eV, and demonstrated high efficiency in photodegradation of methyl orange (99%) and photocatalytic bacterial inactivation (no detectable bacteria after 1 h irradiation).

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**Figure 1.** Graphyne and its analogs: Graphyne (GY), graphdiyne (GDY), triazine-graphdiyne (TA-GDY), hydrogen-substituted graphyne (H-GY), fluorine-substituted graphyne (F-GY), methyl-substituted graphyne (Me-GY), and triazine- and 1,4-diethynylbenzene-based graphyne (**TA-BGY**, this work). Gray, carbon (C); blue; nitrogen (N); green, fluorine(F).

#### 2. Results and Discussion

Our group previously reported a method to synthesize covalent triazine networks (CTNs) through aromatic nucleophilic substitution reaction of cyanuric chloride and *para*-dilithiumaromatic reagents under mild conditions.<sup>[7]</sup> We designed a triazine and 1,4-diethynylbenzene-based analog of graphyne (**TA-BGY**) which, we envisioned, could be

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synthesized by using the similar strategy - aromatic nucleophilic substitution reaction of cyanuric chloride and 1,4-diethynyllithium benzene (S<sub>N</sub>Ar). In light of this idea, a model reaction of cyanuric chloride and phenylethynyl lithium was carried out, and the resulting product 2,4,6-tris(phenylethynyl)-1,3,5-triazine was confirmed by NMR spectroscopy and mass spectrometry (**Supporting Information**). Under very similar reaction conditions used in the optimized model reaction, **TA-BGY** was successfully synthesized through the reaction of cyanuric chloride and 1,4-diethynyllithium benzene in a yield of 75% (**Scheme 1,** and **Supporting Information**). The as-synthesized **TA-BGY** was characterized by solid-state <sup>13</sup>C cross polarization magic angle spinning nuclear magnetic resonance spectroscopy (<sup>13</sup>C CP/MAS NMR), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TG), powder X-ray diffraction analysis (PXRD), field emission scanning electron microscopy (FE-SEM), field emission transmission electron microscopy (FE-TEM, TEM-Mapping) and atomic force microscopy (AFM).



Scheme 1. Synthesis of TA-BGY

The solid-state <sup>13</sup>C-NMR spectrum of **TA-BGY** showed the presence of *sp*-hybridized carbon of the triple bond (~ 80 ppm) and sp<sup>2</sup>-hybridized carbon of the benzene unit (120 - 150 ppm) and the triazine unit (~ 170 ppm), similar to the reference compound [2,4,6tris(phenylethynyl)-1,3,5-triazine] which showed corresponding signals at 80-100 ppm, 120-150 ppm, and 160-170 ppm, respectively (Figure 2A and Figure S5, Supporting Information).<sup>[8]</sup> In the Fourier transform infrared (FTIR) spectrum (Figure 2B-2C), the disappearance of characteristic carbon-chloro bond of cyanuric chloride at 850 cm<sup>-1</sup> as well as terminal ethynyl carbon-proton stretch vibration of 1,4-dithynylbenzene at 3277 cm<sup>-1</sup> of the starting materials, together with the appearance of vibrational band of triazine unit at 1510 cm<sup>-1</sup> (carbon-nitrogen stretching), benzene unit at 1360 cm<sup>-1</sup> (benzene ring breathing), and carbon-carbon triple bond unit at 836 cm<sup>-1</sup> and ca. 2200 cm<sup>-1</sup> (carbon-carbon triple bond stretching), implied the formation of TA-BGY.<sup>[8-9]</sup> In the XPS spectrum of the TA-BGY (Figure 3), the emergence of the peaks with binding energies of 398.8 eV (N 1s of the triazine ring), 284.3 eV (C 1s of benzene unit), 285.2 eV (C 1s of ethynyl unit) and 286.8 eV (C1s of triazine ring) provided additional evidence of the formation of TA-BGY. Meanwhile, the ratio of Ctriazine:Cphenyl:Cethynyl in the XPS spectrum of TA-BGY was 1:3.1:1.7, which was close to its theoretical value of 1:3:2 (an infinitely extended two-dimensional TA-BGY plane).<sup>[8]</sup> Scarcely any chloride peaks were found either in the survey spectrum or in Cl 2p scan (Table S1, Supporting Information), indicating a complete substitution of chloro atoms in cyanuric chloride by the 1,4-diethynylbenzene function.<sup>[7]</sup> The O 1s peaks found in the XPS spectrum could come from physically adsorbed oxygen or water molecules, which are typical for most carbon-based materials.<sup>[10]</sup> All of the data listed above confirmed the formation of TA-BGY unambiguously. In addition, TG analysis indicated that TA-BGY started decomposition at ~ 300 °C and experienced ~ 60% weight loss at 1000 °C in nitrogen atmosphere (Figure 2D).

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The weight loss around 100 °C could probably be attributed to the loss of physically adsorbed solvent and water molecules.



**Figure 2**. (A) Solid-state <sup>13</sup>C CP/MAS NMR spectrum of **TA-BGY**; (B) and (C) FTIR spectra of **TA-BGY** and its reaction precursors 2,4,6-trichloro-1,3,5-triazine and 1,4-diethynylbenzene; (D) TG analysis of **TA-BGY**.

Morphological details of **TA-BGY** were studied by field emission scanning electron microscope (FE-SEM), field emission transmission electron microscopy (FE-TEM), and atomic force microscopy (AFM). FE-TEM and FE-SEM images of **TA-BGY** showed extended porous network structures with branched morphologies (Figure 4A-4C). TEM-Mapping of **TA-BGY** indicated carbons and nitrogens were evenly distributed in the materials (Figure S1, **Supporting Information**). The FE-SEM and FE-TEM images of **TA-**

**BGY** also revealed its layered or stacked structures, which was confirmed by the observation of lamellar structures in its AFM images (Figure 4D, samples for AFM were prepared by sonication of **TA-BGY** in ethanol at a concentration of 0.1 mg/mL). The thickness of 3.4 nm with a lateral micrometre scale in AFM image indicated that the nano-sheets of **TA-BGY** were composed of less than 10 one-atom-thick layers (Figure 4D-4E).<sup>[11]</sup>



Figure 3. X-ray photoelectron spectroscopy of TA-BGY: (A) survey spectra; (B) N 1s scan;(C) C 1s scan.

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**Figure 4**. FE-TEM images of **TA-BGY**: (A) 200 nm scale; (B) 20 nm scale; (C) FE-SEM image of **TA-BGY**; (D) Atomic force microscopy topography of **TA-BGY**; (E) Height profile of the **TA-BGY** layers shown in D.

The porous property of **TA-BGY** was evaluated by nitrogen adsorption-desorption measurement at 77K (Figure 5A-5B), and a characteristic type IV adsorption isotherm was obtained, typical for materials with mesoporous porosity.<sup>[12]</sup> The Brunauer-Emmett-Teller

(BET) surface area of **TA-BGY** was ca. 300 m<sup>2</sup>g<sup>-1</sup>, and a broad pore diameter distribution (1.2 nm, 17 nm and 30~160 nm) was found by DFT method. The pore with a width of 1.2 nm is possibly attributed to hexagon pores formed from eclipsed stacking layers of **TA-BGY** (Figure S20, **Supporting Information**). Powder X-ray diffraction (PXRD) measurement of the **TA-BGY** showed no distinct sharp peaks, declaring its amorphous nature. The lack of long-range order for **TA-BGY** implied that its pore structures could be formed from its unordered curling and stacking.



**Figure 5**. (A) Nitrogen sorption isotherm of **TA-BGY**; (B) Pore size distributions of **TA-BGY**; (C) PXRD pattern of **TA-BGY**; (D) UV-Vis DRS spectrum of **TA-BGY** (insert: Kubelka-Munk transformed reflectance spectrum of **TA-BGY**).

DFT calculation indicated that **TA-BGY** possesses an optical band gap of 1.44 eV with a -5.94 eV (vs. vacuum) valence band, and a -4.50 eV (vs. vacuum) conduction band (**Support information**). In addition, the theoretical optical band gap of **TA-BGY** obtained by DFT calculation (1.44 eV) is pretty close to the experimental one (1.44 eV), extrapolated from **TA-BGY**'s Kubel-Munk transformed reflected spectrum (Figure 5D, insert),<sup>[13]</sup> the mathematical equivalent transformation of UV-Vis DRS (Figure 5D). The optical band gap of **TA-BGY** (1,4-diethynylphenyl linkage) is narrower than that of **CTF-1** (2.69 eV, phenyl linkages) and **CTF-2** (2.56 eV, biphenyl linkages), but broader than that of **GDY** (0.5-0.6 eV),<sup>[2b]</sup> Such a narrow band gap for **TA-BGY** implies its better electrical conductivity, and easier generation of electron/hole pairs under excitation of external energy.<sup>[14]</sup> The UV-Vis diffuse reflectance spectrum (UV-Vis-DRS, Figure 5D) of the dark-brown **TA-BGY** showed a broad intrinsic absorption (ranged in ultraviolet, visible light and infrared), which could be attributed to the  $\pi$ - $\pi$ \* electron transition of C<sub>sp2</sub> and N<sub>sp2</sub> in the polymeric networks.<sup>[9]</sup> Such a broad light absorption for **TA-BGY** unveiled its potential of being used in photocatalysis, such as in photocatalytic dye degradation and bacterial inactivation.<sup>[15]</sup>

Graphene does not have an electronic bandgap, but GY is expected to be a natural semiconductor with intrinsic band gap (predicted 0.5 - 0.6 eV) owing to the special acetylenic  $-C \equiv C-$  bridges between the benzene rings.<sup>[2]</sup> With an even wider band gap (1.44 eV), **TA**-

**BGY**, as a N-doped analog of GY, was projected to be a good photocatalyst. Electron spin resonance (ESR) was employed to detect the generation of hydroxyl radicals in an aqueous solution containing **TA-BGY** under light irradiation with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a trapping agent for 'OH (Figure 6A). As expected, a clear four-line spectrum with peaks intensity ratio of 1:2:2:1 (g=2.001, aH = aN = 1.50 mT) was observed under the

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irradiation of simulated sunlight (AM 1.5G), and the intensity of the corresponding signal of DMPO- 'OH adduct increased along with the irradiation time, confirming the generation of hydroxyl radicals by TA-BGY under sunlight irradiation.<sup>[16]</sup> It has been well reported that hydroxyl radical possesses can break down dye compounds.<sup>[17]</sup> Subsequently, the oxidative ability of TA-BGY as a photocatalyst was examined through photodegradation of an azo dye - methyl orange (MO), which was widely used in industries of textile, leather, food and cosmetics, and therefore frequently found in waste water.<sup>[18]</sup> Using a Xe 500W lamp with an AM 1.5G cut-off filter as a light source, the decomposition of MO in water (30 mg/L) containing dispersed TA-BGY (2 mg/mL) was monitored. As shown in Figure 6B, MO is hardly degraded by light irradiation without a photocatalyst (blue curve), and slight decrease of MO concentration in the **TA-BGY** dispersed solution before irradiation could be attributed to the physical absorption of MO by the porous TA-BGY (black curve). After a 8 h of irradiation (125 mW/cm<sup>2</sup>), ca. 80% of MO was degraded (red curve). By increasing the power density of the irradiation light to 150 mW/cm<sup>2</sup>, 99% of MO was found to be degraded within 8 h (Figure 6C). This photocatalyst was found to be stable under light irradiation as evidenced by its repeated use in MO degradation without significant loss of its photocatalytic activity (Figure 6C), albeit the slight gradual decrease of photocatalytic activity possibly caused by its loss in recovery after every recycling.

Theoretically, the Highest Occupied Molecular Orbital (HOMO), the second highest HOMO (HOMO-1) and the Lowest Unoccupied Molecular Orbital (LUMO) of MO predicted at the DFT-B3LYP/6-31G level of theory are -2.6350 eV, -3.201 eV and 0.0158 eV (vs. vacuum), respectively.<sup>[19]</sup> Obviously, the energy level of MO's HOMO, or even HOMO-1, is higher than conduction band edge of **TA-BGY**, indicating photosensitization of MO is obstructed

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(Figure S18, **Supporting Information**).<sup>[20]</sup> Therefore, we concluded that the degradation of MO did not resulted from photosensitizer-assisted photocatalytic degradation.



**Figure 6**. (A) Electron spin resonance (ESR) spectra of **TA-BGY** in the dark, and under the light irradiation for 60s and 600s in an aqueous solution containing DMPO as a trapping agent for 'OH; (B) Photodegradation of MO irradiated under simulated sunlight (AM 1.5G, 125 mW/cm<sup>2</sup>); (C) Degradation rate of MO catalyzed by **TA-BGY** during the first 5 cycles; (D) The filtrate of a solution of MO and **TA-BGY** after 8 h of simulated sunlight irradiation (AM 1.5G, 150 mW/cm<sup>2</sup>) (b), an aqueous solution of MO (c) (3 mg/mL); and ultrapure water (a).

Water pollution is one of the most serious ecological threats today.<sup>[21]</sup> The ingestion of bacteria though drinking polluted water may lead sepsis and generalized infection.<sup>[22]</sup> Sunlight has been used for water disinfection *via* direct or indirect mechanisms. Direct mechanisms involve ultraviolet light to interact directly with essential biomacromolecule (protein, nucleic

acid, deoxyribonucleic acid etc.) in the microorganisms to cause inactivation.<sup>[15b, 23]</sup> Since ultraviolet part takes only 4% of the sunlight in terms of energy, disinfection of water through direct mechanisms is not efficient.<sup>[24]</sup> Indirect mechanisms involve photons that interact with chromophores either within the organism or external to the organism to create reactive oxygen species (ROS) that subsequently cause microorganism inactivation. Thus, developing new materials that can efficiently utilize visible light for water disinfection through indirect mechanisms is highly desirable. Given that highly active hydroxyl radicals could be generated by TA-BGY under simulated sunlight irradiation, we envisioned that TA-BGY could be used in disinfection of water, and had its photocatalytical antimicrobial activity evaluated (Supporting Information). The disinfection experiment was performed with using a aqueous suspension of Escheichia coli (E. coli) under irradiation of simulated sunlight with power density of 100 mW/cm<sup>2</sup>. TA-BGY and the irradiation of simulated sunlight were used as variables in the controlled experiment, and bacteria were measured by colony forming units (CFU/mL) (Figure 7A). Hardly any inactivation of E. coli was observed in the suspension in the presence of TA-BGY in the dark (black curve) or the one under the simulated irradiation without TA-BGY (red curve), but, in the suspension of E. coli in the presence of TA-BGY under irradiation, the numbers of live bacteria decreased sharply after 45 min, and showed a thorough elimination of live E. coli after 60 min (blue curve in Figure 7A and Figure S21, Supporting information), together with the incompleteness of the cell morphology (Figure 7B - 7C and Supporting Information). The free radicals in intracellular/extracellular locations of the bacterial cell and damaged the cell membrane and in turn the proteins, DNA and intracellular systems by increase the oxidative stress in the cell,<sup>[25]</sup> demonstrating strong photocatalytic disinfection activity of TA-BGY toward E. coli.



**Figure 7**. (A) Disinfection performance of **TA-BGY** (data were obtained five independent experiments, and the red circle mean no detectable level of bacteria (*E. coli*); Transmission Electron micrographs of *E. coli* treated with **TA-BGY** in the dark (B) and under the light (C).

#### 3. Conclusion

In summary, we have developed a bottom-up strategy to synthesize a N-doped graphyne analog, triazine- and 1,4-diethynylbenzene-based graphyne (TA-BGY), in gram-scale through aromatic nucleophilic substitution reactions ( $S_NAr$ ) of cyanuric chloride with 1,4-diethynyllithium benzene. The as-synthesized TA-BGY was found to possess an extended 2D porous network structure with a BET surface area of ca. 300 m<sup>2</sup>g<sup>-1</sup> and a narrow optical band

gap of 1.44 eV. The abilities of **TA-BGY** in photocatalytic dye degradation and antimicrobial disinfection have unveiled its potentials in photocatalytic water purification. The study on the design and synthesis of other novel hetero-doped graphyne analogs is underway in our laboratory.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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#### **Conflict of interest**

The authors declare no conflict of interest.

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A new N-doped graphyne analog, triazine- and 1,4-diethynylbenzene-based graphyne (TA-BGY), was synthesized through aromatic nucleophilic substitution reactions. TA-BGY was expected to have many applications which were exampled by the photodegradation of methyl orange (99%) and photocatalytic bacterial inactivation (*Escheichia coli*, under 1h irradiation of simulated sunlight, AM 1.5G, 100 mW/cm<sup>2</sup>, no live bacterium was detected).

**Keyword:** graphyne analog, aromatic nucleophilic substitution reaction, hydroxyl radical, photocatalytic dye degradation, antibiosis

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#### A Novel Triazine-Based Analog of Graphyne: Scalable Synthesis and Applications in

#### Photocatalytic Dye Degradation and Bacterial Inactivation

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