Directional charge transport in layered, two-dimensional triazine-based graphitic carbon nitride

Yu Noda,[a] Christoph Merschjann,[b,c], Ján Tarábek,[d] Patrick Amsalem,[e] Norbert Koch,[e] and Michael J. Bojdys*[a]

Abstract: Triazine-based graphitic carbon nitride (TGCN) is the most recent addition to the family of graphene-type, two-dimensional and metal-free materials. Although hailed as a promising low-bandgap semiconductor for electronic applications, so far, only its structure and optical properties have been known. Here, we combine direction-dependent electrical measurements and time-resolved optical spectroscopy to determine macroscopic conductivity and microscopic charge carrier mobilities in this layered material "beyond graphene". Electrical conductivity along the basal plane of TGCN is 65-times lower than through the stacked layers; as opposed to graphite. Furthermore, we develop a model for this charge transport behavior based on observed carrier dynamics and random-walk simulations. Our combined methods provide a path towards intrinsic charge transport in a direction-dependent, layered semi-conductor for applications in field-effect transistors (FETs) and sensors.

Until recently, only five members of the "graphene family" were known: graphene, hBN, BCN, fluorographene, and graphene oxide.[1] Common among them is their structure – *i.e.* covalent bonds along the basal plane and weak van der Waals (vdW) interactions in between layers – and their composition from light, non-metal atoms. Aside from graphene,[2] which is a semi-metal, all other members of this family are wide bandgap semiconductors (2-4 eV)[3] or insulators (>4 eV).[4] Hence, despite the great potential of two-dimensional (2D) materials as logic transistors,[5] or as integrated circuits,[6] the quest for a "post-silicon" semiconductor has focused predominantly on metal-containing systems such as molybdenum disulfide (MoS_2).[7] The availability or the recycling rates of most transition metals such as Mo and some of the main group elements that make up the bulk of 2D materials are low,[8] hence, it is highly desirable to have a 2D semiconductor composed of earth-abundant elements,

making organic materials more attractive. A recent, sixth addition to the graphene family is triazine-based graphitic carbon nitride (TGCN) based solely on nitrogen-linked triazine (C_3N_3) units.[9] Resonance forms of the structure are considered to be overall π-aromatic with carbons and nitrogens bonded in *sp²* fashion. Theory and spectroscopy suggest that few-layer TGCN has a bandgap between 1.6 and 2.0 eV,[9] close to that of silicon (1.1 eV) or GaAs (1.43 eV). This narrow bandgap, together with its metal-free composition, makes TGCN a great candidate for post-silicon electronics. However, very little is known about the charge transfer pathways or mechanism in this layered 2D material.
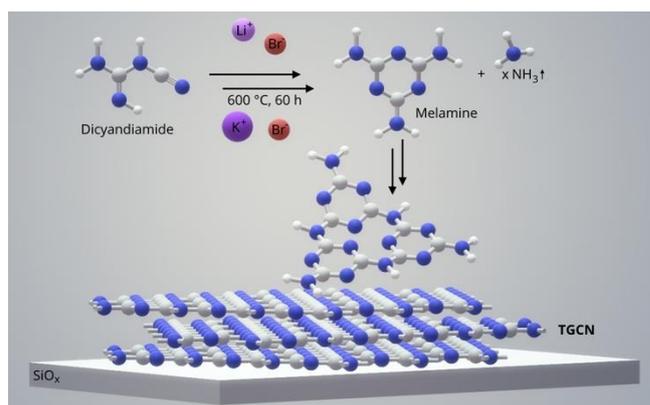
Scheme 1. Synthesis of thin films of semiconducting triazine-based carbon nitride (TGCN) on insulating quartz (SiO_x) glass. Dicyandiamide is ionothermally condensed in a eutectic salt-melt of LiBr/KBr. Cyclisation to the triazine (C_3N_3) motif and condensation under evolution of ammonia (NH_3) affords sheets of TGCN (stoichiometry of C_3N_4) at the solid-liquid interface on top of quartz glass slides.

[a] Dr. Y. Noda, Dr. M. J. Bojdys
Department of Chemistry & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany
E-mail: m.j.bojdys@daad-alumni.de
Website: http://bojdyslab.org
[b] Dr. C. Merschjann
Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
[c] Dr. C. Merschjann
Institute of Methods for Material Development, Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin, Germany.
[d] Dr. J. Tarábek
Institute of Organic Chemistry and Biochemistry ASCR V.V.I., Flemingovo nám. 2, 16610 Prague 6, Czech Republic
[e] Dr. P. Amsalem, Prof. Dr. N. Koch
Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 6, 12489 Berlin, Germany

Supporting information for this article is given via a link at the end of the document.

The hitherto reported synthetic protocol for TGCN relies on surface-assisted growth of the material at flat interfaces, such as reactor walls or the liquid-gas interface,[9] while the bulk of the reaction medium – a eutectic salt melt of LiBr and KBr – yields a pre-form of TGCN, polytriazine imide (PTI);[10] a poly-crystalline powder that contains intercalated Li⁺ and Br⁻ ions that are partially sitting in the voids or in between the planes of the not-fully formed C, N-network.

In this work, we improve the yield and quality of TGCN flakes by growing them on top of quartz glass (SiO_x) slides submerged in the eutectic reaction mixture (Scheme 1). We are able to measure the conductivity of these crystalline, flat films of TGCN in out-of-plane and in-plane directions. In distinct contrast to common 2D layered compounds such as graphite and transition metal chalcogenides, the out-of-plane conductivity of 1.01×10^{-4} S m⁻¹ is almost two orders of magnitude higher than

in-plane conductivity at 1.55×10^{-6} S m^{-1}. Transient absorption (TA) spectroscopy provides kinetic information for the charge transport in TGCN films. We propose a zig-zag hopping charge-transport model that accounts for the high out-of-plane conductivity. This quantitative information and the theoretical models we develop also allow us to view TGCN in the context of other, dimensionally confined, directional (semi-)conductors such as single-walled carbon nanotubes,[11] or 2D systems,[12] which serves as the basis to further optimize devices based on this "post-silicon" semiconductor.
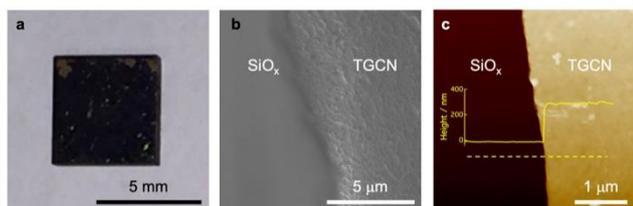
Figure 1. TGCN film grown on SiO$_x$. **a**: photograph. **b**: Scanning electron microscopy (SEM) image showing TGCN (right) on SiO$_x$ (left). **c**: Atomic force microscopy (AFM) height image collected at the edge of the TGCN film. The inset shows the sectional height profile (~ 301 nm) corresponding to the dotted line in the image.

TGCN layers grow as an opaque, dark brown film on SiO$_x$ slide (Figure 1a), covering most of the surface. The film can be removed by scratching or by application of any adhesive such as a scotch or dicing tape. The flat arrangement of TGCN at the interface is consistent with the previous report,[9] and it is advantageous in optical spectroscopic studies and in designing electrical devices. Fourier-transform infrared (FTIR) spectra confirm the formation of triazine units with their characteristic breathing mode at 828 cm^{-1} (Figure S3). X-ray photoelectron spectroscopy (XPS) shows C 1s, N 1s, and valence band spectra expected for TGCN (Figure S4). Elemental analysis confirmed C/N atomic ratio of 0.77 (Table S1). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) both confirm uniform and continuous morphology of the TGCN film with sub-micron thickness (Figures 1b, 1c, S5, and S6). The average thickness of the films is 306 ± 30 nm as determined by AFM (Figure 1, c).

Clean, flat areas of a TGCN flake with no visible cracks were selected *via* SEM and AFM for electrical conductivity measurements. Areas of ~200×200 μm were selected to accommodate four probes (Figure S2). In-plane I-V measurements with four-probes, up to 20 pA was observed at 12 V (Figure 2a). We estimate the in-plane electrical conductivity ($\sigma_{in-p.}$) as $1.55 \pm 0.19 \times 10^{-6}$ S m^{-1} based on a thin-film assumption.[13] In contrast, substantially higher currents in the μA range were recorded for out-of-plane measurements (60 μA at 1 V, Figure 2b). The out-of-plane electrical conductivity σ_{out-p} was estimated as $1.01 \pm 0.15 \times 10^{-4}$ S m^{-1}, which is 65 times higher than the in-plane conductivity (Figure 3a). This conductivity value is comparable to some conjugated covalent organic frameworks (COFs),[14] and two-orders of magnitude lower than MoS$_2$, a 2D semiconducting material (Table S2).[15] Compared to the thin layers, a well-ground TGCN powder pressed into a pellet shows

the lowest conductivity $\sigma_{pow.}$ of $8.06 \pm 0.34 \times 10^{-7}$ S m^{-1} (2.7 nA at 50 V, Figures 2c). We attribute the lower conductivity of the powder to a large number of grain boundaries and, accordingly, an increased contact resistance. Additionally, out-of-plane conductivity was verified with tunneling AFM, a mode of conductive AFM measurements (Figure S7). Electron paramagnetic resonance (EPR) spectra of TGCN show a single, nearly symmetrical Lorentzian line (g factor 2.0035, linewidth 0.43 mT, Figure S8). This g factor is attributed to unpaired electrons in sp^2 aromatic π-bonds, similar to other organic semiconductors (g factor 2.0028 – 2.0034),[16] and our recent triazine-core framework (g factor 2.0036).[17]
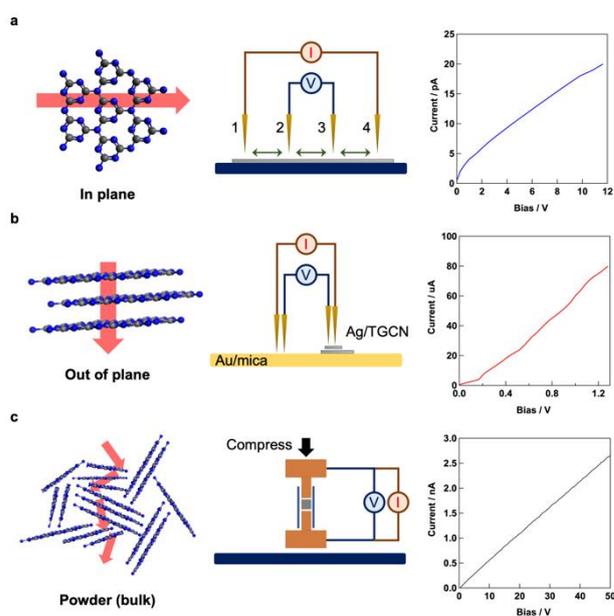
Figure 2. Electrical conductivity measurements of TGCN. **a**: model of in-plane charge transport; four-probe measurement setup; a typical I-V profile (averaged in-plane electrical conductivity σ_{in-p}: 1.55×10^{-6} S m^{-1}). **b**: model of out-of-plane charge transport; modified two-probe measurement setup with a top-electrode on TGCN; a typical I-V profile (averaged out-of-plane electrical conductivity σ_{out-p}: 1.01×10^{-4} S m^{-1}). **c**: model of charge transport in bulk powder; two-probe
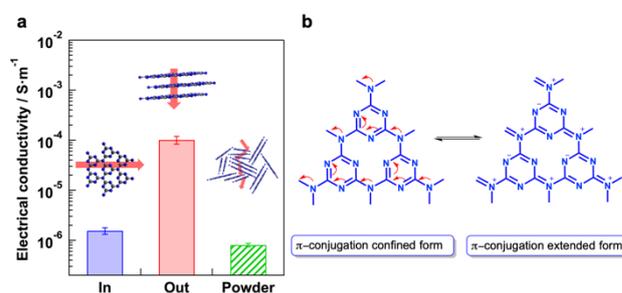
measurement setup with a press; a typical I-V profile (averaged bulk powder electrical conductivity $\sigma_{pow.}$ of 8.06×10^{-7} S m^{-1})

Figure 3. **a**: Directional-dependent electrical conductivity in TGCN. **b**: Resonance structures of TGCN showing a confined π-conjugation on the left and overall π-conjugation on the right.

In order to explain and correlate the directional-dependent behavior of electrical charges, we investigated the transport of photoinduced charge carriers in TGCN films using optical spectroscopy (Figure S9). First, ultraviolet-visible-near-infrared (UV-Vis-NIR) transmittance/reflectance spectroscopy reveals a direct optical gap of 2.026(4) eV (612 nm), supporting the initial study.[9] Transient photoluminescence (TRPL) spectroscopy shows no measurable signal in the range between 350-950 nm. This strong suppression of radiative decay channels is in sharp contrast to other polymeric CNs, such as melon[10d, 18] or PTI.[19] This contrast indicates that the photophysics of triazine and heptazine networks is determined not only by their moieties, but also by their specific crystal structure.
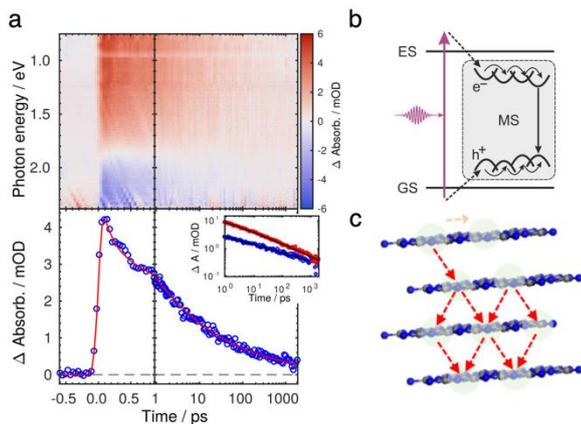
Figure 4. Transient-absorption (TA) spectroscopy results. **a**: transient signal for a pump pulse energy of 0.32 μJ, after chirp correction (top) and spectrally averaged data and fit result in the region between 800 to 1250 nm (bottom); the inset shows a double-logarithmic plot of the long-time evolution for two datasets, recorded at 0.32 μJ and 1.60 μJ pulse energy, respectively. **b**: Charge-transport model used for fitting the data. **c**: Proposed out-of-plane hopping transport of charge carriers.

We then performed TA spectroscopy to obtain kinetic information. In the two-dimensional spectro-temporal map (Figure 4a, top), the emergence of transient excited states is seen as positive absorbance changes (red colour code, λ >650 nm). The temporal development of the TA signal (Figure 4a, bottom) shows an ultrafast build-up of the signal within 200 fs, followed by a non-exponential decay over the course of a few nanoseconds. To show this in more detail, the long-time behaviour is plotted on a double-logarithmic scale in the inset of Figure 4a (bottom), together with another TA experiment at a higher excitation pulse energy. The convergence of the two traces towards long times is typical for a bimolecular recombination scenario.

With these observations, we suggest the following excitation-transport-recombination model (Figure 4b). Here, we assume a one-photon excitation from the ground state (GS) to an initial excited state (ES), which may be of excitonic nature. From there, ultrafast relaxation (<< 1 ps) towards a metastable charge-separated state (MS) takes place. In analogy to other semiconducting polymers, we identify the metastable state as an ensemble of electron and hole polarons.[18e] Both partners of such a polaron pair are initially localised at different, neighbouring triazine units. The subsequent charge transport is governed by

diffusive hopping of the individual polarons, leading to the observed non-exponential recombination kinetics.[18e, 18g] Typically, such bimolecular reactions manifest as power-law decays with two crucial parameters: the combined electron-hole hopping rate coefficient k, and the characteristic exponent α (Equation S1). The results of the global fit for low and high excitation fluence are shown in Table S3 (see also Figures S10 and S11), indicating an over-all faster recombination process at higher initial concentration of excited states. Using the lowest obtained rate coefficient $k = 62(4)$ ps^{-1}, the diffusive hopping mobility of the involved polarons can be estimated as $\mu = ed^2 k/(2Dk_\mathrm{B}T)$, where e is the elementary charge and D is the dimensionality of the diffusion process. We further assume an isotropic transport with an average hopping distance d = 4.5 Å. This roughly corresponds to the co-facial distance of two triazine units along the stacking direction. With these numbers, we obtain mobilities between 2.43 cm^2 V^{-1} s^{-1} for 1D diffusion and 0.81 cm^2 V^{-1} s^{-1} for 3D diffusion. This range of mobility is comparable to other 2D semiconducting materials such as borocarbonitride (BCNs; 5-20 cm^2 V^{-1} s^{-1})[20] and MoS$_2$ (1-8 cm^2 V^{-1} s^{-1}),[21] and substantially higher than that of typical undoped polymers like MEH-PPV (10^{-4} to 10^{-6} cm^{2}V^{-1}s^{-1}).[22]

The characteristic exponent varies between α = 0.318(4) and α = 0.424(4) for low and high fluence, respectively, and mirrors the effective dimensionality of the transport. For diffusive bimolecular kinetics without disorder, an exponent $\alpha = D/4$ is expected due to spatial segregation of electrons and holes with time.[23] For a purely 1D transport with additional drift of both carriers in the same direction, an exponent α of 1/3 was found.[24] Such a situation might occur due to concentration gradients along the vertical axis, caused by gradual attenuation of the pump pulse. On the other hand, bias voltages (e.g., due to potential charging of surfaces by the strong pump light) would force carriers in opposite directions, and lead to $\alpha = (D + 1)/4$.[24] We therefore expect 0.25 ≤ α ≤ 0.5 for purely 1D, and α > 0.5 for D ≥ 2, respectively. Our result thus favours a scenario with moderately confined 1D pathways. The increase of α may indicate a higher effective dimensionality at higher carrier concentrations, potentially induced by stronger in-plane cross-talk between the pathways. One should mention that for melon, even lower characteristic exponents α ≤ 0.22 were found in TA studies,[18g] and assigned to exponential band tails, disregarding hopping transport completely. This shows again that the photophysics in the different CN networks is far from subtle and needs further investigation.

The electrical measurement results indicate a preferred transport along the stacking direction, and TA measurements and modelling suggest a confinement of charge carriers within a low-dimensional subspace. While many reported 2D materials feature strongly anisotropic charge transport, they usually favor the in-plane conductivity by a factor of 10^3 (MoS$_2$),[25] or 10^4 (graphite).[26] In a case of polyporphyrin-linked COF, in-plane conductivity was 30 times higher than out-of-plane conductivity.[14a] The same relation is also known in organic molecular crystals.[27]

The favored in-plane conductance in these materials is in obvious contrast to the high out-of-plane conductivity in TGCN. In graphene or intrinsically conducting polymers, delocalised orbitals facilitate a high in-plane mobility. Similarly, resonance forms can be considered for TGCN (Figure 3b). In such a case, the

conjugated triazine moieties are bridged with N atoms in sp^2 configurations, extending the π-conjugated system to the entire network that would lead to high in-plane conductivity. Our results, however, contradict this expectation, with preference for the co-facial transport between triazine cores rather than in-plane. This suggests that TGCN is not likely to be overall π-aromatic under ambient conditions.

Because the triazine moieties do not stack directly on top of each other in TGCN, a co-facial hopping transport would inevitably follow a zig-zag route. This partially confined, low-dimensional charge transport out-of-plane in TGCN is depicted in Figure 4c. To further examine this, we have estimated the probabilities for all possible transitions in the three conceivable stacking modes of TGCN:[9] AB-stacking and two ABC-stacking modes (Figure S12). In case of AB-type stacking, we see that the preferred mode of transport is indeed along 1D paths in between individual layers, with only minor in-plane contributions. On the other hand, an ABC structure exhibits a more isotropic distribution of transitions in 3D. We also performed random-walk simulations of single carriers in each of the structures (Figure S13). From these, one may estimate a mobility anisotropy of up to 3:1 in favor of out-of-plane transport. This apparently weaker theoretical prediction for the anisotropy – as compared to the experimental results – merits further exploration.

In summary, the improved synthetic protocol enables us to directly deposit macroscopically flat layers of semiconducting TGCN – a metal-free, 2D layered material – on insulating quartz glass. The film morphology allows direct determination of electrical conductivity in-plane and out-of-plane, and it facilitates spectroscopic analysis. Combined with numerical simulations, we can now qualitatively understand the mobilities and preferred pathways of charge carriers in TGCN. We revealed a unique anisotropic characteristic of the semiconductive TGCN film – more conductive out-of-plane (1.01×10^{-4} S m^{-1}) than in-plane (1.55×10^{-6} S m^{-1}). This indicates that at ambient conditions, the fully-conjugated resonance form of TGCN – one that encompasses the triazine moieties and the bridging N-atoms in one π-conjugated system – is not the preferred one. Likewise, kinetic information on the charge transport in films of TGCN derived from TA spectroscopy suggest the existence of moderately confined 1D transport pathways, which account for the higher out-of-plane conductivity. To the best of our knowledge, such a surprising relationship has not been reported for any known 2D material. This result makes TGCN an interesting candidate for the design of van der Waals heterostructures, demonstrating a working strategy for TGCN to be applied in organic electronics device fabrication.

Acknowledgements

[1] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proceedings of the National Academy of Sciences of the United States of America* **2005**, *102*, 10451-10453.

[2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature* **2005**, *438*, 197-200.

[3] aR. R. Nair, W. Ren, R. Jalil, I. Riaz, V. G. Kravets, L. Britnell, P. Blake, F. Schedin, A. S. Mayorov, S. Yuan, M. I. Katsnelson, H.-M. Cheng, W. Strupinski, L. G. Bulusheva, A. V. Okotrub, I. V. Grigorieva, A. N. Grigorenko, K. S. Novoselov, A. K. Geim, *Small* **2010**, *6*, 2877-2884; bW. Lei, D. Portehault, R. Dimova, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 7121-7127; cA. Mathkar, D. Tozier, P. Cox, P. Ong, C. Galande, K. Balakrishnan, A. Leela Mohana Reddy, P. M. Ajayan, *J. Phys. Chem. Lett.* **2012**, *3*, 986-991.

[4] K. Watanabe, T. Taniguchi, H. Kanda, *Nat. Mater.* **2004**, *3*, 404-409.

[5] B. Radisavljevic, A. Kis, *Nature Materials* **2013**, *12*, 815.

[6] S. Chuang, C. Battaglia, A. Azcatl, S. McDonnell, J. S. Kang, X. Yin, M. Tosun, R. Kapadia, H. Fang, R. M. Wallace, A. Javey, *Nano Letters* **2014**, *14*, 1337-1342.

[7] Z. Yu, Y. Pan, Y. Shen, Z. Wang, Z.-Y. Ong, T. Xu, R. Xin, L. Pan, B. Wang, L. Sun, J. Wang, G. Zhang, Y. W. Zhang, Y. Shi, X. Wang, *Nature Communications* **2014**, *5*, 5290.

[8] W. F. Sheehan, *Chemistry* **1976**, *49*, 17-18.

[9] G. Algara-Siller, N. Severin, S. Y. Chong, T. Bjorkman, R. G. Palgrave, A. Laybourn, M. Antonietti, Y. Z. Khimyak, A. V. Krasheninnikov, J. P. Rabe, U. Kaiser, A. I. Cooper, A. Thomas, M. J. Bojdys, *Angew. Chem. Int. Ed.* **2014**, *53*, 7450-7455.

[10] aM. J. Bojdys, J. O. Muller, M. Antonietti, A. Thomas, *Chem. Eur. J.* **2008**, *14*, 8177-8182; bE. Wirnhier, M. Döblinger, D. Gunzelmann, J. Senker, B. V. Lotsch, W. Schnick, *Chemistry – A European Journal* **2011**, *17*, 3213-3221; cS. Y. Chong, J. T. A. Jones, Y. Z. Khimyak, A. I. Cooper, A. Thomas, M. Antonietti, M. J. Bojdys, *J. Mater. Chem. A* **2013**, *1*, 1102-1107; dF. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. C. Wang, M. J. Bojdys, *Nat. Rev. Mater.* **2017**, *2*.

[11] C. M. Voge, M. Kariolis, R. A. MacDonald, J. P. Stegemann, *Journal of Biomedical Materials Research Part A* **2008**, *86A*, 269-277.

[12] C. Glynn, D. Thompson, J. Paez, G. Collins, E. Benavente, V. Lavayen, N. Yutronic, J. D. Holmes, G. González, C. O'Dwyer, *Journal of Materials Chemistry C* **2013**, *1*, 5675-5684.

[13] I. Miccoli, F. Edler, H. Pfnur, C. Tegenkamp, *J Phys Condens Matter* **2015**, *27*, 223201.

[14] aH. Yang, S. L. Zhang, L. H. Han, Z. Zhang, Z. Xue, J. Gao, Y. J. Li, C. S. Huang, Y. P. Yi, H. B. Liu, Y. L. Li, *ACS Appl. Mater. Interfaces* **2016**, *8*, 5366-5375; bS.-L. Cai, Y.-B. Zhang, A. B. Pun, B. He, J. Yang, F. M. Toma, I. D. Sharp, O. M. Yaghi, J. Fan, S.-R. Zheng, W.-G. Zhang, Y. Liu, *Chem. Sci.* **2014**, *5*, 4693-4700; cH. Ding, Y. Li, H. Hu, Y. Sun, J. Wang, C. Wang, C. Wang, G. Zhang, B. Wang, W. Xu, D. Zhang, *Chem. - Eur. J.* **2014**, *20*, 14614-14618.

[15] O. El Beqqali, I. Zorkani, F. Rogemond, H. Chermette, R. B. Chaabane, M. Gamoudi, G. Guillaud, *Synth. Met.* **1997**, *90*, 165-172.

[16] aM. Tabbal, T. Christidis, S. Isber, P. Merel, M. A. El Khakani, M. Chaker, A. Amassian, L. Martinu, *J. Appl. Phys.* **2005**, *98*; bJ. S. Zhang, G. G. Zhang, X. F. Chen, S. Lin, L. Mohlmann, G. Dolega, G. Lipner, M.

Antonietti, S. Blechert, X. C. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 3183-3187; cJ. S. Zhang, M. W. Zhang, R. Q. Sun, X. C. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 10145-10149; dG. G. Zhang, M. W. Zhang, X. X. Ye, X. Q. Qiu, S. Lin, X. C. Wang, *Adv. Mater.* **2014**, *26*, 805-809.

[17] D. Schwarz, Y. Noda, J. Klouda, K. Schwarzova-Peckova, J. Tarabek, J. Rybacek, J. Janousek, F. Simon, M. V. Opanasenko, J. Cejka, A. Acharjya, J. Schmidt, S. Selve, V. Reiter-Scherer, N. Severin, J. P. Rabe, P. Ecorchard, J. J. He, M. Polozij, P. Nachtigall, M. J. Bojdys, *Adv. Mater.* **2017**, *29*.

[18] aX. C. Wang, K. Maeda, X. F. Chen, K. Takanabe, K. Domen, Y. D. Hou, X. Z. Fu, M. Antonietti, *J. Am. Chem. Soc.* **2009**, *131*, 1680-1681; bS. B. Yang, Y. J. Gong, J. S. Zhang, L. Zhan, L. L. Ma, Z. Y. Fang, R. Vajtai, X. C. Wang, P. M. Ajayan, *Adv. Mater.* **2013**, *25*, 2452-2456; cS. Barman, M. Sadhukhan, *J. Mater. Chem.* **2012**, *22*, 21832-21837; dC. M. Cheng, Y. Huang, X. Q. Tian, B. Z. Zheng, Y. Li, H. Y. Yuan, D. Xiao, S. P. Xie, M. M. F. Choi, *Anal. Chem.* **2012**, *84*, 4754-4759; eC. Merschjann, S. Tschierlei, T. Tyborski, K. Kailasam, S. Orthmann, D. Hollmann, T. Schedel-Niedrig, A. Thomas, S. Lochbrunner, *Adv. Mater.* **2015**, *27*, 7993-7999; fH. Y. Zhang, Y. P. Chen, R. Lu, R. Y. Li, A. C. Yu, *Phys. Chem. Chem. Phys.* **2016**, *18*, 14904-14910; gR. Godin, Y. Wang, M. A. Zwijnenburg, J. W. Tang, J. R. Durrant, *J. Am. Chem. Soc.* **2017**, *139*, 5216-5224; hD. Hollmann, M. Karnahl, S. Tschierlei, K. Kailasam, M. Schneider, J. Radnik, K. Grabow, U. Bentrup, H. Junge, M. Beller, S. Lochbrunner, A. Thomas, A. Brückner, *Chem. Mater.* **2014**, *26*, 1727-1733.

[19] M. J. Bojdys, N. Severin, J. P. Rabe, A. I. Cooper, A. Thomas, M. Antonietti, *Macromol Rapid Comm* **2013**, *34*, 850-854.

[20] L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z. F. Wang, K. Storr, L. Balicas, F. Liu, P. M. Ajayan, *Nat. Mater.* **2010**, *9*, 430-435.

[21] A. M. van der Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G. H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, J. C. Hone, *Nat. Mater.* **2013**, *12*, 554-561.

[22] C. A. Amorim, M. R. Cavallari, G. Santos, F. J. Fonseca, A. M. Andrade, S. Mergulhão, *J. Non-Cryst. Solids.* **2012**, *358*, 484-491.

[23] D. Toussaint, F. Wilczek, *J. Chem. Phys.* **1983**, *78*, 2642-2647.

[24] S. A. Janowsky, *Phys. Rev. E* **1995**, *51*, 1858-1860.

[25] J. A. Wilson, A. D. Yoffe, *Adv. Phys.* **1969**, *18*, 193-335.

[26] K. S. Krishnan, N. Ganguli, *Nature* **1939**, *144*, 667.

[27] F. Ortmann, K. Hannewald, F. Bechstedt, *Appl. Phys. Lett.* **2008**, *93*, 222105.

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION
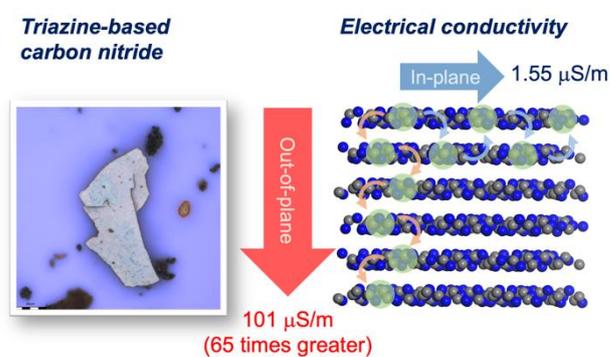
Yu Noda, Christoph Merschjann, Ján Tarábek, Patrick Amsalem, Norbert Koch, and Michael J. Bojdys*

Page No. – Page No.

Directional charge transport in layered, two-dimensional triazine-based graphitic carbon nitride

Beyond graphene, between layers. Triazine-based carbon nitride (TGCN) – a new member of graphene family of two-dimensional (2D) and metal-free materials – grows as in macroscopic thin films on glass substrate. In this organic, narrow-bandgap semiconductor, the electrical conductance is favored in out-of-plane direction, in contrast with other 2D materials. The hopping mechanism in between layers is supported by transient absorption spectroscopy and numerical calculations.