Carbon- and Nitrogen-Based Organic Frameworks

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S *Supporting Information*

CONSPECTUS: This Account provides an overview of organic, covalent, porous frameworks and solid-state materials mainly composed of the elements carbon and nitrogen. The structures under consideration are rather diverse and cover a wide spectrum. This Account will summarize current works on the synthetic concepts leading toward those systems and cover the application side where emphasis is set on the exploration of those systems as candidates for unusual high-performance catalysis, electrocatalysis, electrochemical energy storage, and artificial photosynthesis.

These issues are motivated by the new global energy cycles and the fact that sustainable technologies should not be based on rare and expensive resources. We therefore present the strategic design of functionality in cost-effective, affordable artificial materials starting from a spectrum of simple synthetic options to end up with carbon- and nitrogen-based porous frameworks. Following the synthetic strategies, we demonstrate how the electronic structure of polymeric frameworks can be tuned and how this can modify property profiles in a very unexpected fashion. Covalent triazine-based frameworks (CTFs), for instance, showed both enormously high energy and high power density in lithium and sodium battery systems. Other C,N-based organic frameworks, such as triazine-based graphitic carbon nitride, are suggested to show promising band gaps for many (photo)electrochemical reactions. Nitrogen-rich carbonaceous frameworks, which are developed from C,N-based organic framework strategies, are highlighted in order to address their promising electrocatalytic properties, such as in the hydrogen evolution reaction, oxygen reduction reaction (ORR), and oxygen evolution reaction (OER). With careful design, those materials can be multifunctional catalysts, such as a bifunctional ORR/OER electrocatalyst.

Although the majority of new C,N-based materials are still not competitive with the best (usually nonsustainable candidates) for each application, the framework/N approach as such is still in its infancy and has already moved organic materials to regions where otherwise only traditional noble metals or special inorganic semiconductors are found. As one potential way to enhance the properties of polymeric frameworks, the idea of catalysts having unique active surfaces based on Mott−Schottky heterojunctions and related concepts are addressed.

In order to integrate all of the above versatile subjects from synthesis to applications on C,N-based organic frameworks, we begin the discussion with synthetic concepts and strategies for these frameworks to distinguish these systems from typical covalent organic frameworks based on boron oxide rings. Next we focus on the semiconducting properties of C,N-based organic frameworks in order to show a continuous transition between CTFs and other systems, such as graphitic carbon nitrides. At the end, applications of these materials are shown by highlighting their properties in electrochemical energy storage and photo- and electrocatalysis.
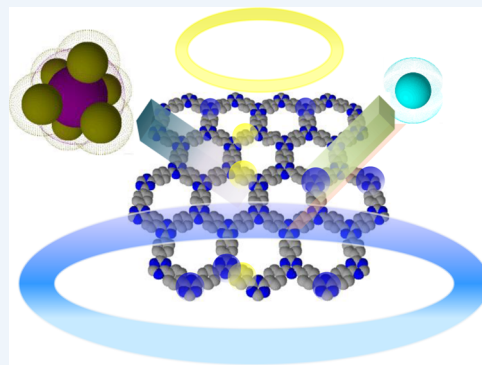
1. INTRODUCTION

Carbon- and nitrogen-based organic frameworks are attracting enormous attention because of the possibility to design materials having versatile and tunable functionality.[1] In that respect, they are very similar to highly popular inorganic two-dimensional (2D) materials such as graphene and transition-metal dichalcogenides, which show intriguing novel electronic/chemical functionality.[2,3] The design of a pore in a solid-state material is as exciting as the design of a new molecule, just that the problems of matter and surface are inverted. Pores, as we know them from zeolites or enzymatic pockets, can recognize and bind, are selective, transport information, or enable complex processes like catalysis. Porous materials are meanwhile classical ingredients in many applications, such as

membranes, electrodes, and sorption and storage devices, and obviously the composition of the wall matters. Classical choices include silica, inorganics, carbon, and more recently, metal complexes, as in metal−organic frameworks (MOFs).[4−6] Polymers have remained less explored because of their thermal instability and essentially hydrophobic character, but nevertheless have found massive applications in membrane science as chromatographic beads and ion exchange resins. It is a recent important development that pore design in polymers was made more rational in regard to size, architecture, and functionality, and classes such as the Davankov hyper-cross-linked polymers,[7]
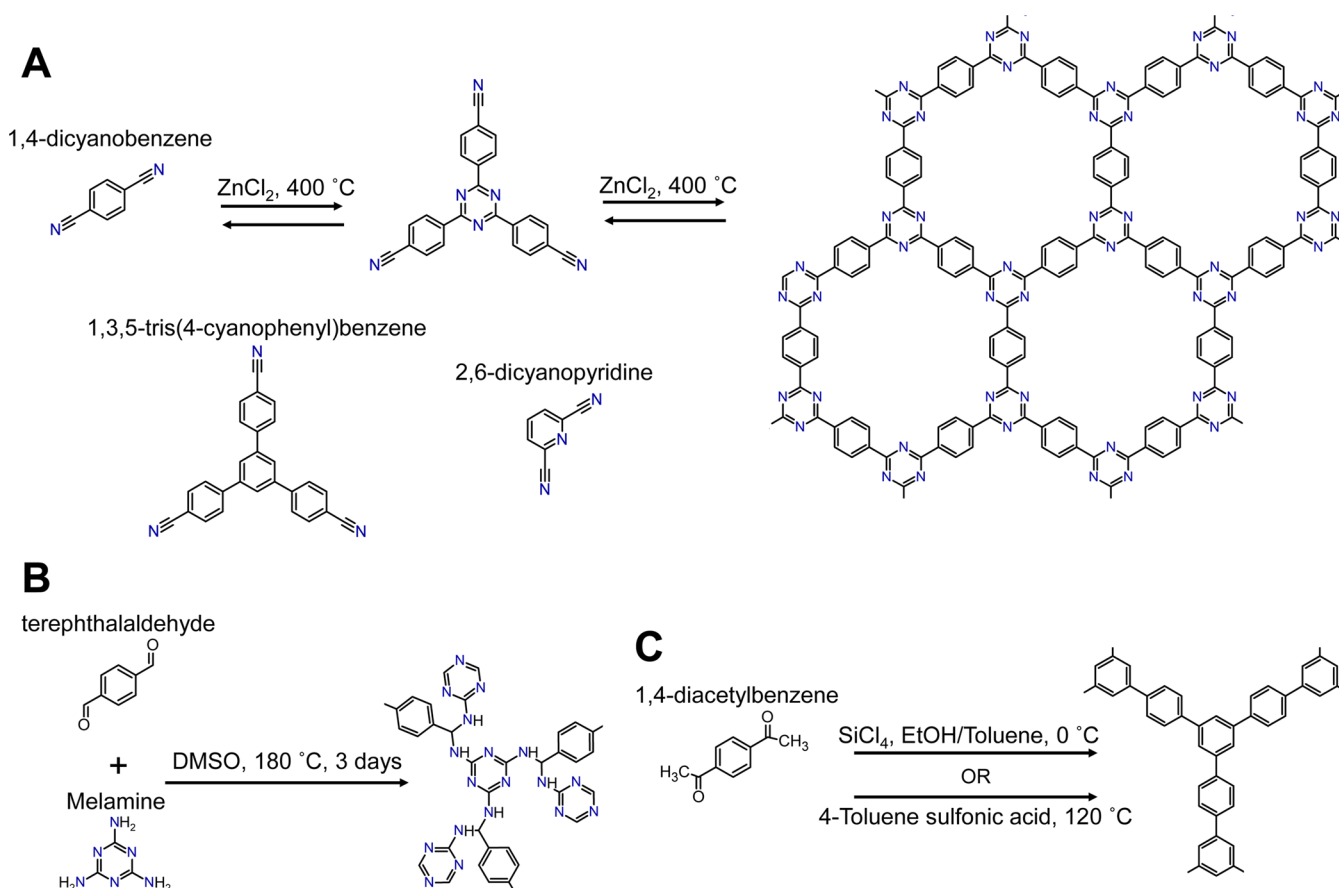
Figure 1. Synthetic routes for porous polymeric frameworks. (A) CTFs are synthesized from a variety of aromatic nitriles. (B) Schiff base networks as an example of imine-based frameworks. (C) Cyclotrimerization of bifunctional acetyl compounds as an alternative synthetic route to obtain porous polymeric frameworks.

polymers of intrinsic microporosity (PIMs),[8] conjugated microporous polymers,[9,10] and others[11] have been developed and already nicely reviewed.[12−14] To make the resulting pore structures persistent and able to withstand the capillary pressure and pore collapse, polymer systems must be composed of strong covalent linkages from shape-persistent molecules, and the cross-linking density (except in PIMs) must be very high.

Not addressed by the present review but important for the context is the discovery of so-called covalent organic frameworks (COFs) by Yaghi and co-workers in 2005.[4] In this approach, usually polyboronic acids (e.g., 1,4-benzenediboronic acid in COF-1) are condensed with themselves or with polyhydroxy derivatives. However, to make COFs "crystalline" (i.e., with long-range-ordered pores), reversible covalent linkages had to be employed.[15] As this has been nicely reviewed,[16] we will not put further emphasis on that approach. Considering the groundbreaking character of those observations, we nevertheless want to mention that "finding suitable synthetic conditions for the COF synthesis is by no means a trivial issue", as is the fact that such reversible bonds are by definition chemically rather labile, i.e., apt to undergo solvolysis and hydrolysis, which to date has spoiled most real-life applications. In addition, it is not a minority opinion that the importance of pore regularity is for most applications overestimated,[17] and in fact reasons why disordered hierarchical systems are a more favorable choice have been discussed.[18] For instance, purposely destroying order in zeolites by etching

some of the walls away has brought a quantum jump in kinetic rates and novel applications.[19] Therefore, we will restrict ourselves in the following to more stable and application-oriented polymer frameworks that are mostly "noncrystalline". This by no means reduces our high opinion about regular COFs but allows to focus on less well covered aspects of the overall subject.

2. STRATEGIC DESIGN OF C,N-BASED POROUS ORGANIC FRAMEWORKS

Covalent Triazine Frameworks

The first reported alternatives to the boric acid scheme leading to conjugated, very stable nodes was the cyclotrimerization of nitriles, such as 1,4-dicyanobenzene (DCB), 1,3,5-tris(4-cyanophenyl)benzene (TCPB), and 2,6-dicyanopyridine (DCP) (Figure 1A). As this reaction (for reversibility) in principle relies on high temperature, Kuhn and co-workers applied the reaction in molten salt melts at 400 °C.[20−22] The applied ZnCl$_2$ played the role of both a solvent and a catalyst. For example, cyclotrimerization of DCB affords a covalent triazine framework (CTF) material called "CTF-1" with a Brunauer−Emmett−Teller (BET) surface area of 791 m^2 g^{-1} and a pore size of 1.2 nm. Analysis of the powder X-ray diffraction (PXRD) pattern suggested that CTF-1, like COF-1, possesses a hexagonal 2D structure. A higher ratio of ZnCl$_2$ to monomer (10:1) prohibits crystallization and gives amorphous polymers with a higher surface area. This is a general trend: crystalline species grow by the minimization of surface energy,

so they are "energetically minimal structures". There are meanwhile some other crystalline CTF species. For example, 2,6-dicyanonaphthaline was used to generate the highly crystalline material CTF-2.[23] The low surface area of CTF-2 (90 m^2 g^{-1}) was attributed to the partially staggered arrangement of the material layers.

A step toward purposely disordered materials was made by Kuhn and co-workers.[21,22] When CTF samples were heated to slightly above their decomposition temperature, denitrification set in, and the consecutive cycloaddition reactions gave disordered materials with ultrahigh surface areas (>3000 m^2 g^{-1}) and a very favorable combination of the original supermicroporosity and mesoporosity. These systems will be discussed in the applications section, but for instance, their dye sorption capacities exceeded 1 g/g of material, values which were not accessible by the crystalline materials. In comparison with boron-containing COFs, CTFs usually have lower crystallinity but really excellent thermal and chemical stability. Stability is also given for the disordered species.

Imine-Based Frameworks

Another well-known reversible covalent reaction is the formation of imines ($-C\equiv N-$), and several crystalline and noncrystalline networks have been synthesized along this route. The first imine-based COF was developed by Yaghi and co-workers.[24] The resulting material, COF-300, was obtained via the dehydration reaction of a rigid aldehyde and amine pair and possesses a 3D diamond-like structure with a BET surface area of 1360 m^2 g^{-1} and an average pore size of 7.8 Å.

Practically in parallel, Müllen and co-workers reported disordered frameworks based on Schiff base chemistry, made from melamine and various di- and trifunctional aldehydes, with BET surface areas of 1377 m^2 g^{-1} (Figure 1B).[25] These systems were conjugated and exhibited very high thermal and chemical stability while being composed mainly of carbon and 40 wt % nitrogen. Similarly, the crystalline material COF-LZU1 was made by cocondensation of 1,3,5-triformylbenzene and 1,4-diaminobenzene and possesses a 2D eclipsed structure with a layer distance of 3.7 Å.[26] Later, porphyrin-containing COF-366 was synthesized and used in optoelectronic applications.[27] Hydrazone-linked frameworks are made by the corresponding condensation reaction of aldehydes and hydrazides.[28] The resulting frameworks COF-42 and COF-43 possess 2D eclipsed layered structures with medium-range BET surface areas (710 and 620 m^2 g^{-1}, respectively). Contrary to simple expectations, the imine-based COFs are stable in most organic solvents and rather insensitive to water. Hydrazone-linked frameworks display excellent chemical and thermal stability. These structures bridge the ordered but sensitive boronic acid species and the chemically very stable but rather disordered CTF species.

Alternative, Related Cross-Linking Reactions

Staying in the family of $-C\equiv N-$ chemistry, Bojdys and co-workers[29] have applied the even more stable heptazine linkers. Although disordered, the product showed remarkable thermal stability exceeding 640 °C and a rather high specific surface area of >2200 m^2 g^{-1}. This chemistry was later extended to other dinitriles, which partly showed highly crystalline character but no accessible porosity.[29] Also relevant for the discussion of electronic properties, this is potentially due to donor–acceptor interactions between the very different tectonic units, resulting in a staggered layer arrangement that closes the pores.

Another very powerful but irreversible trimerization reaction was first described by Kaskel and co-workers (Figure 1C).[30] Cyclotrimerization of different bifunctional aromatic acetyl compounds gave benzene-linker-based organic frameworks with excellent stability and porosity. Although disordered, such materials are easily and cost-effectively accessed and show extraordinary suitability for gas sorption experiments and as catalytic supports.

3. APPLICATIONS OF C,N-BASED ORGANIC FRAMEWORKS

C,N-based purely organic polymeric frameworks (PFs) were first applied in gas storage and catalysis, very similar to covalent organic frameworks,[4,6] and we again can only point to the excellent reviews available.[16] The special charm of the boron oxide ring, its high reversibility for structural self-optimization, also turned into the weak link when corrosive conditions (including water) were applied. This is why part of the interest quickly switched back to the more stable regular 2D and 3D polymers, with systems based on carbon and nitrogen turning out to be especially stable and multifunctional.[12,20–22,31,32] CTFs are "neighbors" of graphitic carbon nitrides and N-rich carbonaceous frameworks, and some important functions of CTFs are similar. After a short resume on second-generation applications in gas storage and use in some illustrative and demanding catalytic reactions, we put the spotlight on electronic functions, which have opened a route toward metal-free semiconductors with tunable electronic properties and led to rather unexpected experimental possibilities. We will show a variety of functions of CTFs and other PFs for energy storage and conversion chemistry and as photo- or electro-catalysts.

Porous Polymeric Frameworks for Gas Storage and Catalytic Reactions

Since some porous PFs have enormously high specific surface areas and are also synthesized from affordable building blocks, a breakthrough for storing H_2 and CH_4 was expected. A theoretical study suggested that the 3D COF-108 could have a H_2 uptake of 18.9 wt % at 100 bar and 77 K.[33] To date, the highest H_2 storage was realized by the 3D COF-102, which showed a H_2 uptake of 7.24 wt % at ~35 bar and 77 K (Figure S1 in the Supporting Information).[34] The 3D COF-102 is also one of the best materials for CH_4 and CO_2 storage, with a CH_4 uptake of 187 mg g^{-1} and a CO_2 uptake of 1200 mg g^{-1}. A considerable performance for both CO_2 and CH_4 uptake was reported for PPN-4.[35]

The second generation of experiments instrumentalized the specific advantages of polymer frameworks, focusing in addition to high capacity on high chemical selectivity and high "swing effects". Katsoulidis and Kanatzidis[36] cross-linked phloroglucinols with benzaldehyde derivates and obtained disordered polymer frameworks with, however, "as-crystalline" micropores and very high CO_2 sorption capacities. Further on the way, a series of papers by Yavuz described the use of polymer-specific functionalities to induce "N_2 phobicity" (which is useful because most sorption problems are performed in competition with atmospheric N_2), enormous high-pressure CO_2 adsorption (up to 5.6 g/g of sorbent), and rather high temperature effects to enable pressure- and temperature-dependent sorption cycles for continuous operation under industrially relevant conditions.[37,38]
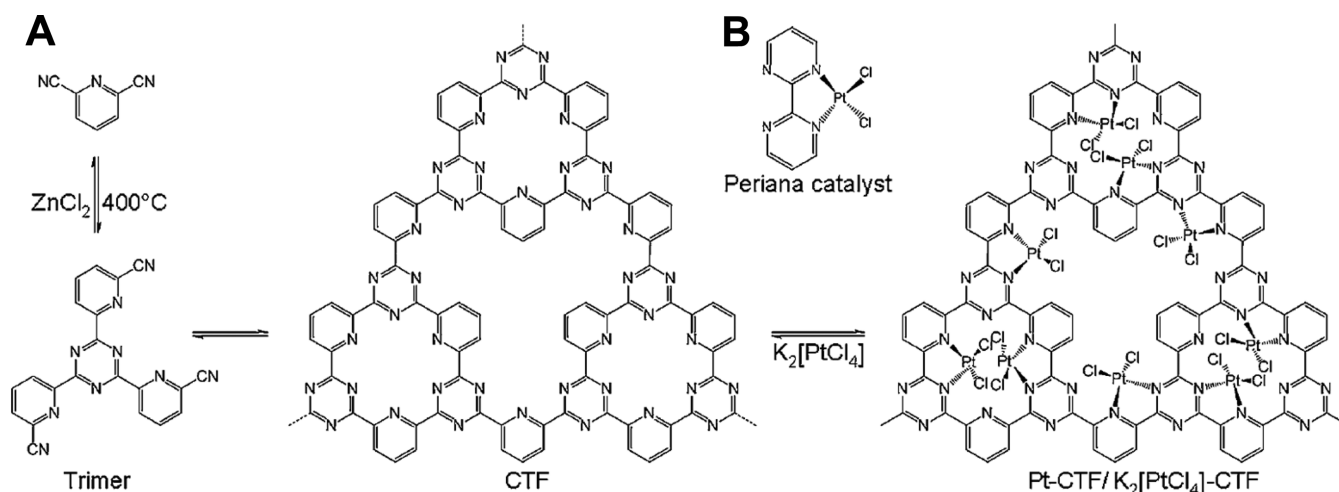
Figure 2. (A) Trimerization of DCP in molten $ZnCl_2$, conversion to a CTF, and subsequent platinum coordination to afford Pt-CTF. (B) Periana's platinum bipyrimidine complex. Reprinted with permission from ref 39. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

The extreme stability of C,N-based porous PFs with large surface areas was also used for next-generation heterogeneous catalysis. For instance, Pt was coordinated along a pyridine-bridged covalent triazine framework (Pt-CTF) to constitute a heterogeneous Periana catalyst for "low-temperature" methane oxidation to methanol (Figure 2).[39] This proceeds in boiling SO_3 containing sulfuric acid under high pressures of gaseous oxygen, and there was previously no classical heterogeneous support material surviving those strongly oxidizing conditions. The Pt-CTF catalyst, however, showed a higher turnover number even when compared with typical low-molecular-weight Periana catalysts, together with a high thermal stability up to 400 °C and high oxidation stability (no decline of activity in the examined window of conditions).

A related example is palladium particles supported in a CTF (Pd@CTF), which showed a much higher stability compared with the references for the oxidation reaction of glycerol.[40] Similarly, Pd(II)-containing COF-LZU1 (Pd/COF-LZU1) was reported as an excellent catalyst for the Suzuki–Miyaura coupling reaction with a variety of applicable reactants and yields of 96–98%.[26] More recent work generalized this by using phosphorus-containing PFs with very high transport porosity, which then were employed to immobilize rhodium and palladium complexes for highly efficient transfer hydrogenation reactions.[41] These selected cases just illustrate a much broader applicability of such structures.

C,N-Based Polymeric Frameworks as Organic Semiconductors

Successful improvement of photovoltaics and photocatalysts relies on the availability of new types of semiconductors that are simple to make and process.[32] Photo- and electronic functions in devices are determined by the electronic structures of the applied materials, such as the Fermi level, valence-band maximum, and conduction-band minimum.[42] From this point of view, PFs are promising materials because both the molecular binding schemes and packing in space can be controlled and enter the semiconductor properties. The tunable electronic structure of 2D materials has been well-studied in the field of inorganic materials,[2,3,43] but there has been little research on PFs in this direction.

A recent study by Sakaushi and co-workers that used first-principles calculations and electrochemistry to confirm the

density of states of triazine-based frameworks proved the above concept (Figure 3).[44] In that work, their electronic structures of
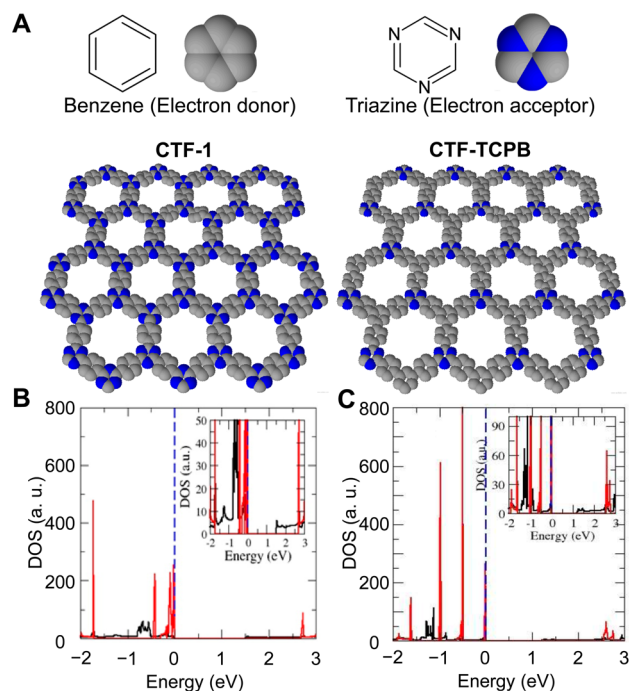

Figure 3. (A) Structures of CTF-1 and CTF-TCPB. Black and blue balls show carbon and nitrogen atoms, respectively. (B, C) Theoretically calculated densities of states (DOS) of (B) CTF-1 and (C) CTF-TCPB. The experimentally obtained DOS of CTFs were compared with these theoretical calculated values and showed a good agreement.[44] Panels (B) and (C) are reprinted from ref 44. Copyright 2013 American Chemical Society.

CTF-1 and the CTF synthesized using TCPB (CTF-TCPB) were measured by electrochemical methods and compared with the results of first-principles calculations. Because CTFs are composed of triazine rings as electron acceptors (A) having an electron affinity of +0.46 eV and benzene rings as electron donors (D) having an electron affinity of −1.15 eV,[45] this group of materials has a huge potential to act as organic semiconductors with a variety of electronic functions (Figure
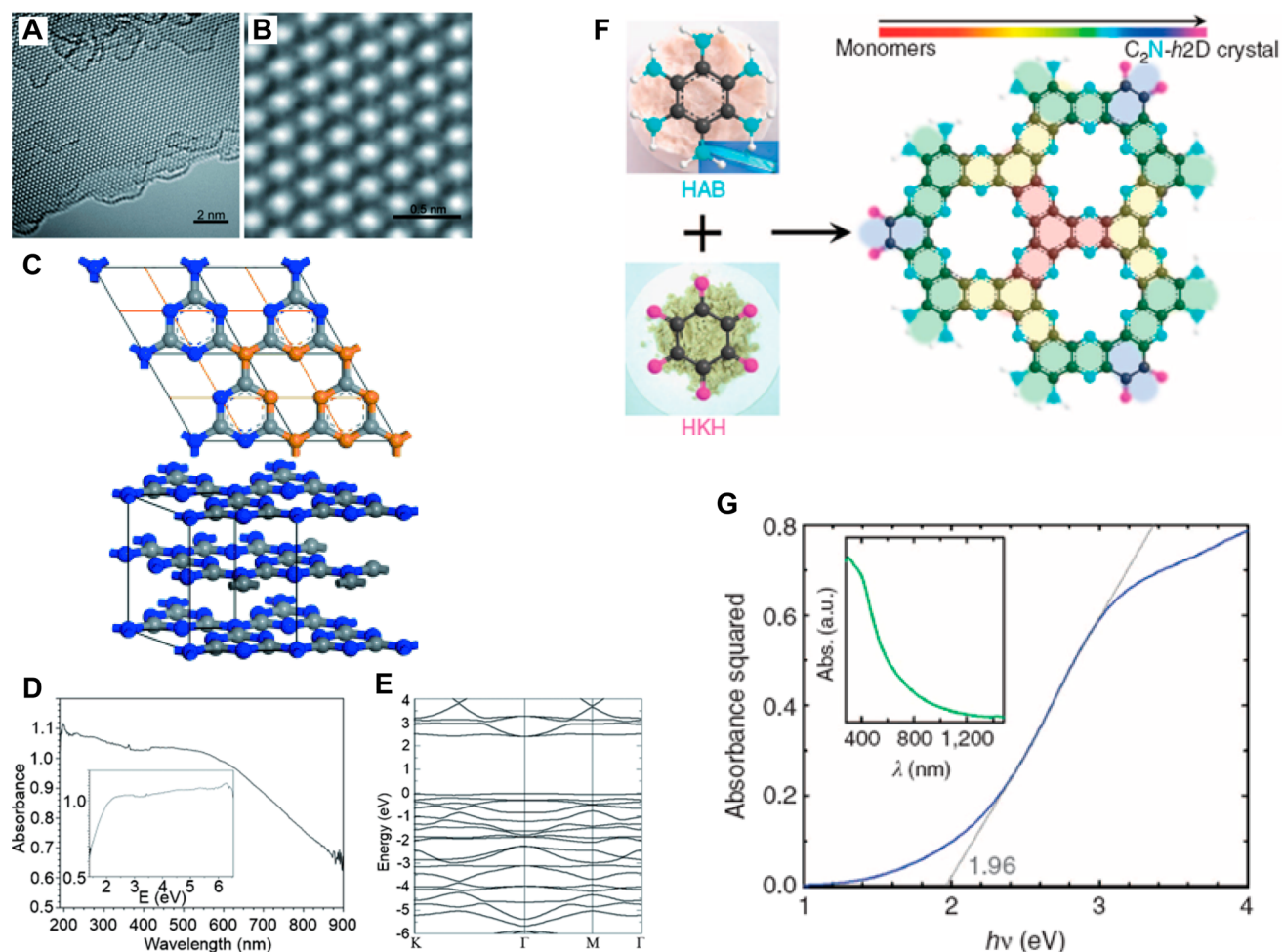
Figure 4. Characterization of C,N-based organic frameworks: (A−E) Triazine-based graphitic carbon nitride (TGCN) and (F, G) C_2N holey 2D crystal (C_2N-h2D).[50,51] (A, B) HRTEM images, (C) crystal structure, (D) optical characterizations, and (E) theoretically predicted band structure of TGCN (the band structure is assumed to be a monolayer). (F) Synthetic scheme and (G) optical characterization of C_2N-h2D. Panels (A−E) are reprinted with permission from ref 50. Copyright 2014 Wiley-VCH Verlag GmbH & Co. KGaA. Panels (F) and (G) are reprinted with permission from ref 51. Copyright 2015 Macmillan Publishers Limited.

3A), as confirmed by measuring their electrochemical and photochemical properties.[46,47] It was suggested that the electronic structures of these two CTFs depend on both the number of stacking layers and the ratio of the different aromatic rings (Figure 3B,C). This result suggests that one can start to control the electronic properties of PFs in a wider range than previously expected.

Using just molecular features and ignoring solid-state packing, Vilela and co-workers described a porous PF composed of benzene (D) and benzothiadiazole (A) units and showed that the system indeed acted as a highly efficient photosensitizer, enabling the very efficient formation of singlet oxygen while staying intact under those strongly oxidizing conditions. Photocatalytic production of singlet oxygen for the complete and selective conversion of α-terpinene to ascaridole was shown.[48] The use of such conjugated frameworks in energy applications was recently discussed in more detail,[49] and we mention this work to illustrate the complementary roles of "solid state packing" and "molecular design".

Recently, carbon nitride allotropes similar to CTFs possessing high crystallinity have been reported (Figure 4A−C,F).[50,51] Combined experimental and theoretical data suggest that they are metal-free semiconductors and have optical band gaps with a spectrally very interesting range (Figure 4D,E,G). As meanwhile carbon nitride chemistry is getting very rich,[20,23,25,26,29−31,39,48,50,51] and transitions between CTFs and all of these similar systems are—by the rules of polymer chemistry—rather continuous, we expect many other porous organic semiconducting species to be designed rather soon.

Porous Polymeric Frameworks as Energy Storage Materials

Rechargeable electrochemical energy storage devices (REESs), such as batteries and supercapacitors, are necessary for the new energy cycles based on sunlight and wind.[32] Electrochemical energy storage devices show a higher specific energy but a lower power density compared to traditional capacitors, where the energy is stored only in the compression of electric double layers at the electrode−electrolyte interface without Faradaic reactions.[52] However, research has found ways to build a mixed form of a battery and supercapacitor having both high specific capacity and high power, and the border between batteries and supercapacitors is vanishing.[53] From this point of view, the use of porous PFs in REESs has a huge potential to establish a "new battery roadmap" to obtain tailored electrode materials, for example, electrode materials showing higher redox potential for higher energy density combined with a high specific power
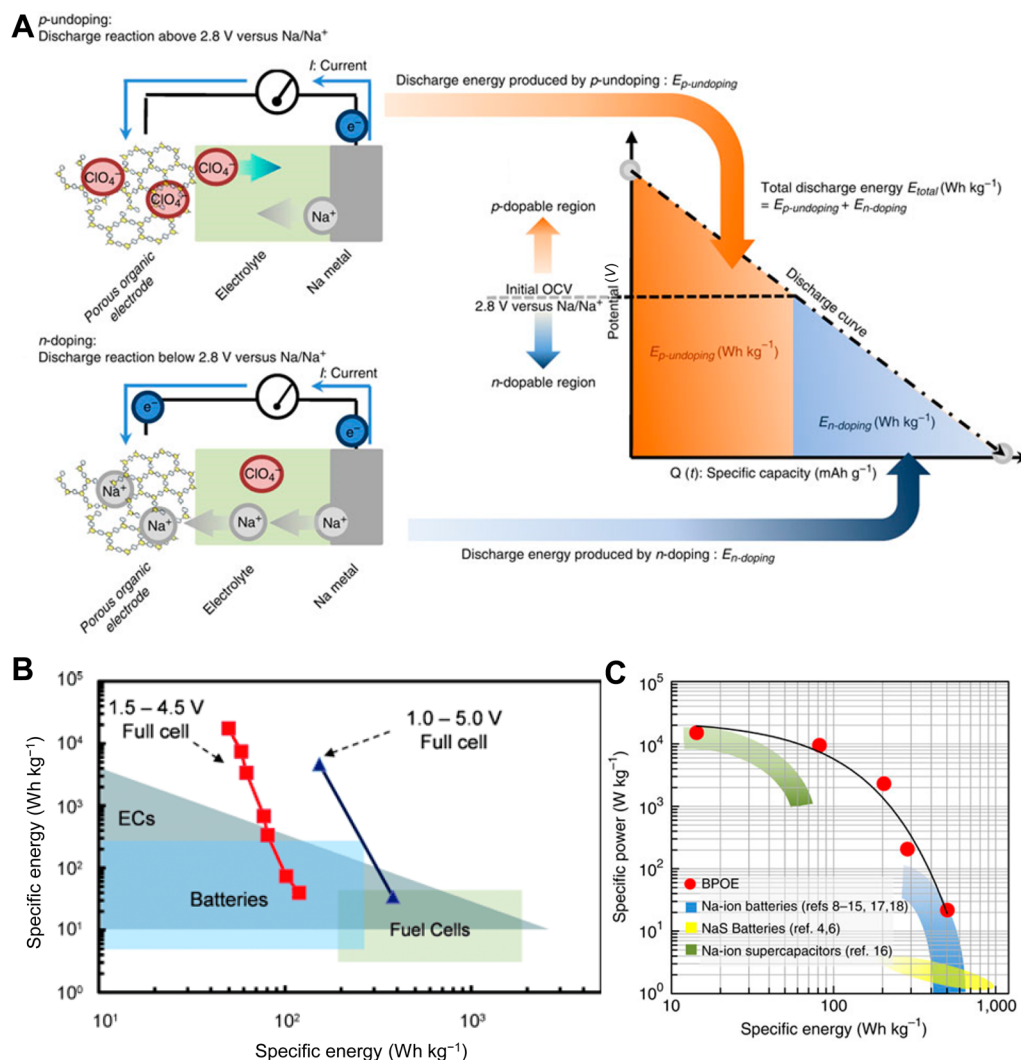
Figure 5. Energy storage principle using CTFs.[46,54] (A) The energy storage principle of CTFs is based on both anion and cation insertion/deinsertion as charge carriers. (B, C) Ragone plots for rechargeable (B) lithium and (C) sodium battery systems. Panel (B) is reprinted with permission from ref 46. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA. Panels (A) and (C) are reprinted with permission from ref 54. Copyright 2013 Macmillan Publishers Limited.

originating from their special electrochemical/electrophysical properties and highly porous structures.

The first report on the use of porous PFs in REESs employed CTF-1 (Figure 5)[46] and showed that it is an ambipolar organic material that can both accept and donate electrons in an interesting electrochemical window, while because of its polar porous character it can also incorporate anions and cations into the structure to enable electroneutrality (Figure 5A).[46,54] This unique energy storage principle is in general similar to redox-driven intercalation into inorganic solid-state materials but at the same time is very different from typical battery materials as both anion and cation intercalation can be used for energy storage in the same material. Additionally, CTF-1 showed a sloping charge−discharge curve and a high-power character due to short-range ordering. Thus, REESs using a disordered (and only the disordered) CTF-1 electrode showed a high specific energy of 379 W h kg_{cell}^{-1} at a specific power of 4633 W kg_{cell}^{-1} under a wide operating potential range of 1.0 to 5.0 V vs Li/Li$^+$ with stable cycling up to 50 cycles (Figure 5B). This electrochemical performance was calculated on the basis of the assumption of a full-cell configuration. When a smaller

operating potential of 1.5 to 4.5 V vs Li/Li$^+$ was applied, CTF-1 showed a lower specific energy (119 W h kg_{cell}^{-1}) but long-time stable cycling up to 1000 cycles.

Although this porous PF shows promising electrochemical properties, especially in the high-voltage region, the other battery components are not ready for such high voltages, and further studies are necessary to expand this energy storage mechanism to lower ranges by developing other porous PFs as electrode materials. Interestingly, crystalline CTF-1 shows only low electrochemical activity, and this importance of disorder was confirmed by other reports.[55] From this point of view, crystalline CTF-1 might not intercalate enough counterions into its layered structure, whereas the disordered form can host all charges as well as the corresponding counterions.[46]

Interestingly, this new principle using porous PFs is also easily extended to a sodium battery system.[54] Since the cost of sodium is much lower than that of lithium, affordable batteries with performances comparable to lithium batteries can be envisaged, and affordability will soon become the most important issue for REESs. To date there are only few organic compounds that are active in sodium battery systems, and
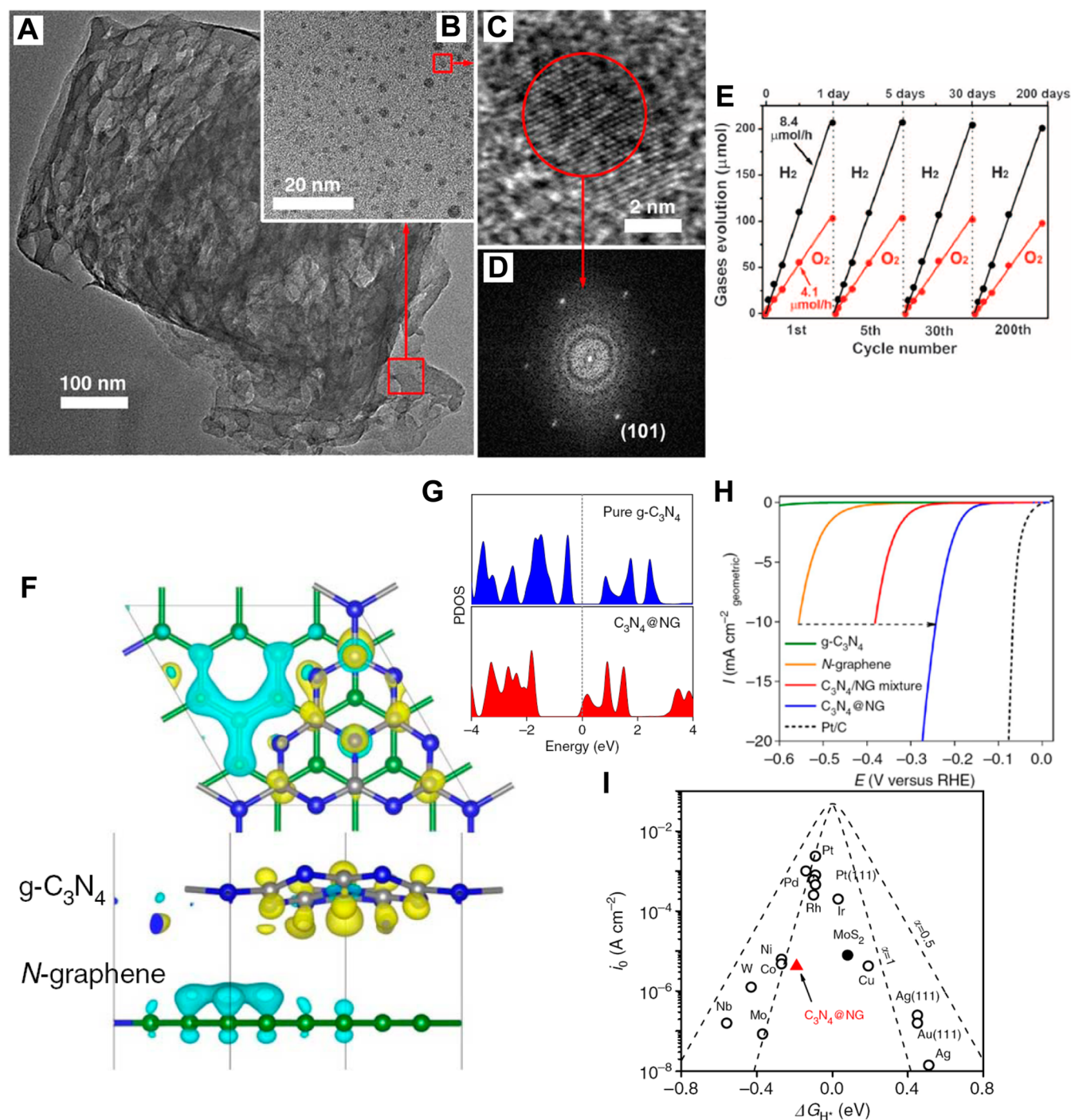
Figure 6. Unique surface of C,N-based hybrid materials for electrocatalysts: (A–E) a metal-free carbon nanodot–C_3N_4 nanocomposite (CDots–C_3N_4)[59] and (F–I) a nitrogen-rich carbonaceous framework/g-C_3N_4 hybrid (C_3N_4@NG).[61] (A–D) TEM images and (E) visible-light-driven water splitting of CDots–C_3N_4. (F) Interfacial electron transfer in C_3N_4@NG. The yellow and cyan isosurfaces represent electron accumulation and depletion, respectively; the isosurface value is 0.005 e $Å^{-3}$. (G) Projected density of states (PDOS) on pure g-C_3N_4 (top) and C_3N_4@NG (bottom). (H) HER polarization curves for four metal-free electrocatalysts and Pt/C. (I) Volcano plots for C_3N_4@NG and other typical catalysts. Panels (A–E) are reprinted by permission from ref 59. Copyright 2015 American Association for the Advancement of Science. Panels (F–I) are reprinted with permission from ref 61. Copyright 2014 Macmillan Publishers Limited.

CTF-1 is one of these exceptional cases. The CTF-1 electrode in a sodium battery system showed both a high specific energy of ~500 W h kg_{cell}^{-1} and a high specific power of ~10 kW kg_{cell}^{-1} (Figure 5C). Since CTF-1 is ambipolar, it can be used as both a cathode and an anode, i.e., an all-organic battery.[56] Although there are several issues to be overcome, this recent development again illustrates the high potential of thermally and electrochemically stable polymer frameworks in these applications.

C,N-Frameworks as Photo- and Electrocatalysts

The application of graphitic carbon nitride (g-C_3N_4) as an organic semiconductor to drive a variety of photocatalytic reactions is a role model for the search for new organic

frameworks for this purpose.[1,32,57] As indicated in the previous sections, PFs are rather flexible with respect to both molecular structure and supramolecular packing, and thus, electronic functions can be quite flexibly arranged.

Poly(triazine imide), the bridging entity between carbon nitrides and CTFs incorporated with Li^+ and Cl^- (PTI/Li^+Cl^-), was investigated as a photocatayst by Domen and co-workers.[58] Although PTI/Li^+Cl^- requires cocatalysts and UV light, both H_2 and O_2 could be photocatalytically produced from the valence and conduction bands of PTI/Li^+Cl^-, respectively. This indicates a suitable electronic structure of PTI/Li^+Cl^- for overall water splitting. Although there are just a few examples of PFs used as photocatalysts, we are sure that a PF with improved photocatalytic properties can be found, and very recently a metal-free carbon nanodot−C_3N_4 nano-composite (CDots−C_3N_4) exhibited very impressive perform-ance (Figure 6A−E).[59]

The hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and oxygen evolution reaction (OER) are central reactions in electrolyzers, metal−air batteries, and fuel cell technologies.[32] Recent reports have already proven that C,N-based materials are highly promising electrocatalysts for electrodes in the HER, ORR, and OER,[60,61] and current data are mainly gained by application of nitrogen-rich carboneous frameworks (NCFs), which are synthesized by thermal decomposition of PFs and partial fusion of their aromatic rings. For example, distinct ionic liquids having nitrile functions are promising precursors for NCF synthesis, going through triazine frameworks as an intermediate state.[62]

The chemical structure of nitrogen in these frameworks has quite a strong influence on the electronic structure, and some NCFs are very active in electrocatalytic reactions.[32] Qiao and co-workers delineated an important step for further improve-ment in the electrocatalytic activities of PF-based materials by hybridization of g-C_3N_4 and NCFs to form active C,N-based heterojunctions that possess a unique catalytically active surface (Figure 6F−I).[61] Together with CDots−C_3N_4,[59] these are examples of Schottky-type catalysts.[63] We expect that many C,N-frameworks can be hybridized in this fashion to develop their full catalytic potential when coupled to a conductive substrate with charge transfer properties.[63,64]

4. SUMMARY

We have provided an overview of a subclass of organic, covalent, porous frameworks that are mainly built from the elements carbon and nitrogen. The structures under consid-eration are conjugated and extremely stable, and thereby tightly related in their properties and applications, but the diverse systems have previously been discussed only separately. We have presented the synthetic concepts behind this approach for the case of covalent triazine frameworks, but it is clear that the options are broader and their exploration is only in its infancy. On the application side, those systems are candidates for very unusual high-performance catalysis and electrocatalysis because of their extreme thermal, electrochemical, and oxidation stability. The data presented on electrochemical energy storage indicate that the structures possess, for instance, a reversible ambipolar character, the adjustment of which might result in new, simple organic energy storage materials with currently unparalleled performance in both rate behavior and energy density. As the elemental physical principles behind them are tightly related, we expect similar possibilities for those systems

in electrocatalysis and artificial photosynthesis to be explored in the near future.

■ ASSOCIATED CONTENT

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Notes

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Markus Antonietti studied chemistry in Mainz, where he also received his Ph.D. in 1985 and his Habilitation in 1990. Since 1993 he has been the director of the Max Planck Institute of Colloids and Interfaces. His work deals with modern materials chemistry, energy materials, and sustainability issues within those topics. Besides being a devoted chemist, he loves cooking and loud music.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Wang, Y.; Wang, X.; Antonietti, M. Polymeric Graphitic Carbon Nitride as a Heterogeneous Organocatalyst: From Photochemistry to Multipurpose Catalysis to Sustainable Chemistry. *Angew. Chem., Int. Ed.* **2012**, *51*, 68−89.

(2) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. Two-Dimensional Atomic Crystals. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10451−10453.

(3) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* **2012**, *7*, 699−712.

(4) Côté, A. P.; Benin, A.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. Porous, Crystalline, Covalent Organic Frameworks. *Science* **2005**, *310*, 1166−1170.

(5) Tilford, R. W.; Gemmill, W. R.; zur Loye, H. C.; Lavigne, J. J. Facile Synthesis of a Highly Crystalline, Covalently Linked Porous Boronate Network. *Chem. Mater.* **2006**, *18*, 5296−5301.

(6) El-Kaderi, H. M.; Hunt, J. R.; Mendoza-Cortés, J. L.; Côté, A. P.; Taylor, R. E.; O'Keeffe, M.; Yaghi, O. M. Designed Synthesis of 3D Covalent Organic Frameworks. *Science* **2007**, *316*, 268−272.

(7) Davankov, V. A.; Tsyurupa, M. P. Structure and Properties of Hypercrosslinked Polystyrene—The First Representative of a New Class of Polymer Networks. *React. Polym.* **1990**, *13*, 27−42.

(8) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. Polymers of Intrinsic Microporosity (PIMs): Robust, Solution-Processable, Organic Nanoporous Materials. *Chem. Commun.* **2004**, 230−231.

(9) Cooper, A. I. Conjugated Microporous Polymers. *Adv. Mater.* **2009**, *21*, 1291−1295.

(10) Jiang, J. X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z.; Cooper, A. I. Conjugated Microporous Poly(aryleneethynylene) Networks. *Angew. Chem., Int. Ed.* **2007**, *46*, 8574−8578.

(11) Ben, T.; Ren, H.; Ma, S.; Cao, D.; Lan, J.; Jing, X.; Wang, W.; Xu, J.; Deng, F.; Simmons, J. M.; Qiu, S.; Zhu, G. Targeted Synthesis of a Porous Aromatic Framework with High Stability and Exceptionally High Surface Area. *Angew. Chem., Int. Ed.* **2009**, *48*, 9457−9460.

(12) Thomas, A.; Kuhn, P.; Weber, J.; Titirici, M.; Antonietti, M. Porous Polymers: Enabling Solutions for Energy Applications. *Macromol. Rapid Commun.* **2009**, *30*, 221−236.

(13) Xu, Y.; Jin, S. B.; Xu, H.; Nagai, A.; Jiang, D. Conjugated Microporous Polymers: Design, Synthesis and Application. *Chem. Soc. Rev.* **2013**, *42*, 8012−8031.

(14) Dawson, R.; Cooper, A. I.; Adams, D. J. Nanoporous Organic Polymer Networks. *Prog. Polym. Sci.* **2012**, *37*, 530−563.

(15) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. Dynamic Covalent Chemistry. *Angew. Chem., Int. Ed.* **2002**, *41*, 898−952.

(16) Ding, S. Y.; Wang, W. Covalent Organic Frameworks (COFs): From Design to Applications. *Chem. Soc. Rev.* **2013**, *42*, 548−568.

(17) Rolison, D. R. Catalytic Nanoarchitectures—The Importance of Nothing and the Unimportance of Periodicity. *Science* **2003**, *299*, 1698−1701.

(18) Antonietti, M.; Ozin, G. A. Promises and Problems of Mesoscale Materials Chemistry or Why Meso? *Chem.—Eur. J.* **2004**, *10*, 28−41.

(19) Perez-Ramirez, J.; Christensen, C. H.; Egeblad, K.; Christensen, C. H.; Groen, J. C. Hierarchical Zeolites: Enhanced Utilisation of Microporous Crystals in Catalysis by Advances in Materials Design. *Chem. Soc. Rev.* **2008**, *37*, 2530−2542.

(20) Kuhn, P.; Antonietti, M.; Thomas, A. Porous, Covalent Triazine-Based Frameworks Prepared by Ionothermal Synthesis. *Angew. Chem., Int. Ed.* **2008**, *47*, 3450−3453.

(21) Kuhn, P.; Forget, A.; Su, D.; Thomas, A.; Antonietti, M. From Microporous Regular Frameworks to Mesoporous Materials with Ultrahigh Surface Area: Dynamic Reorganization of Porous Polymer Networks. *J. Am. Chem. Soc.* **2008**, *130*, 13333−13337.

(22) Kuhn, P.; Krueger, K.; Thomas, A.; Antonietti, M. "Everything is Surface": Tunable Polymer Organic Frameworks with Ultrahigh Dye Sorption Capacity. *Chem. Commun.* **2008**, 5815−5817.

(23) Bojdys, M.; Jeromenok, J.; Thomas, A.; Antonietti, M. Rational Extension of the Family of Layered, Covalent, Triazine-Based Frameworks with Regular Porosity. *Adv. Mater.* **2010**, *22*, 2202−2205.

(24) Uribe-Romo, F. J.; Hunt, J. R.; Furukawa, H.; Klöck, C.; O'Keeffe, M.; Yaghi, O. M. A Crystalline Imine-Linked 3-D Porous Covalent Organic Framework. *J. Am. Chem. Soc.* **2009**, *131*, 4570−4571.

(25) Schwab, M. G.; Fassbender, B.; Spiess, H. W.; Thomas, A.; Feng, X.; Müllen, K. Catalyst-Free Preparation of Melamine-Based Microporous Polymer Networks through Schiff Base Chemistry. *J. Am. Chem. Soc.* **2009**, *131*, 7216−7217.

(26) Ding, S. Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W. G.; Su, C. Y.; Wang, W. Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki−Miyaura Coupling Reaction. *J. Am. Chem. Soc.* **2011**, *133*, 19816−19822.

(27) Wan, S.; Gandara, F.; Asano, A.; Furukawa, H.; Saeki, A.; Dey, S. K.; Liao, L.; Ambrogio, M. W.; Botros, Y. Y.; Duan, X.; Seki, S.; Stoddart, J. F.; Yaghi, O. M. Covalent Organic Frameworks with High Charge Carrier Mobility. *Chem. Mater.* **2011**, *23*, 4094−4097.

(28) Uribe-Romo, F. J.; Doonan, C. J.; Furukawa, H.; Oisaki, K.; Yaghi, O. M. Crystalline Covalent Organic Frameworks with Hydrazone Linkages. *J. Am. Chem. Soc.* **2011**, *133*, 11478−14481.

(29) Bojdys, M.; Wohlgemuth, S.; Thomas, A.; Antonietti, M. Ionothermal Route to Layered Two-Dimensional Polymer-Frameworks Based on Heptazine Linkers. *Macromolecules* **2010**, *43*, 6639−6645.

(30) Rose, M.; Klein, N.; Senkovska, I.; Schrage, C.; Fichtner, S.; Kaskel, S. A New Route to Porous Monolithic Organic Frameworks via Cyclotrimerization. *J. Mater. Chem.* **2011**, *21*, 711−716.

(31) Kuhn, P.; Thomas, A.; Antonietti, M. Toward Tailorable Porous Organic Polymer Networks: A High-Temperature Dynamic Polymerization Scheme Based on Aromatic Nitriles. *Macromolecules* **2009**, *42*, 319−326.

(32) Sakaushi, K.; Antonietti, M. Carbon-and-Nitrogen-Based Porous Solids: A Recently Emerging Class of Materials. *Bull. Chem. Soc. Jpn.* **2015**, *3*, 386−398.

(33) Han, S. S.; Furukawa, H.; Yaghi, O. M.; Goddard, W. A., III. Covalent Organic Frameworks as Exceptional Hydrogen Storage Materials. *J. Am. Chem. Soc.* **2008**, *130*, 11580−11581.

(34) Furukawa, H.; Yaghi, O. M. Storage of Hydrogen, Methane, and Carbon Dioxide in Highly Porous Covalent Organic Frameworks for Clean Energy Applications. *J. Am. Chem. Soc.* **2009**, *131*, 8875−8883.

(35) Yuan, D.; Lu, W.; Zhao, D.; Zhou, H.-C. Highly Stable Porous Polymer Networks with Exceptionally High Gas-Uptake Capacities. *Adv. Mater.* **2011**, *23*, 3723−3725.

(36) Katsoulidis, A. P.; Kanatzidis, M. G. Phloroglucinol Based Microporous Polymeric Organic Frameworks with −OH Functional Groups and High CO_2 Capture Capacity. *Chem. Mater.* **2011**, *23*, 1818−1824.

(37) Patel, H. A.; Karadas, F.; Canlier, A.; Park, J.; Deniz, E.; Jung, Y.; Atilhan, M.; Yavuz, C. T. High Capacity Carbon Dioxide Adsorption by Inexpensive Covalent Organic Polymers. *J. Mater. Chem.* **2012**, *22*, 8431−8437.

(38) Patel, H. A.; Je, S. H.; Park, J.; Chen, D. P.; Jung, Y.; Yavuz, C. T.; Coskun, A. Unprecedented High-Temperature CO_2 Selectivity in N_2-Phobic Nanoporous Covalent Organic Polymers. *Nat. Commun.* **2013**, *4*, No. 1357.

(39) Palkovits, R.; Antonietti, M.; Kuhn, P.; Thomas, A.; Schüth, F. Solid Catalysts for the Selective Low-Temperature Oxidation of Methane to Methanol. *Angew. Chem., Int. Ed.* **2009**, *48*, 6909−6912.

(40) Chan-Thaw, C. E.; Villa, A.; Katekomol, P.; Su, D.; Thomas, A.; Prati, L. Covalent Triazine Framework as Catalytic Support for Liquid Phase Reaction. *Nano Lett.* **2010**, *10*, 537−541.

(41) Zhang, Y.; Riduan, S. N. Functional Porous Organic Polymers for Heterogeneous Catalysis. *Chem. Soc. Rev.* **2012**, *41*, 2083−2094.

(42) Hosono, H. Recent Progress in Transparent Oxide Semiconductors: Materials and Device Application. *Thin Solid Films* **2007**, *515*, 6000−6014.

(43) Thouless, D. J.; Kohmoto, M.; Nightingale, M. P.; den Nijs, M. Quantized Hall Conductance in a Two-Dimensional Periodic Potential. *Phys. Rev. Lett.* **1982**, *49*, 405−408.

(44) Sakaushi, K.; Nickerl, G.; Kandpal, H. C.; Cano-Cortés, L.; Gemming, T.; Eckert, J.; Kaskel, S.; van den Brink, J. Polymeric Frameworks as Organic Semiconductors with Controlled Electronic Properties. *J. Phys. Chem. Lett.* **2013**, *4*, 2977−2981.

(45) Yasuda, T.; Shimizu, T.; Liu, F.; Ungar, G.; Kato, T. Electro-Functional Octopolar π-Conjugated Columnar Liquid Crystals. *J. Am. Chem. Soc.* **2011**, *133*, 13437−13444.

(46) Sakaushi, K.; Nickerl, G.; Wisser, F. M.; Nishio-Hamane, D.; Hosono, E.; Zhou, H.; Kaskel, S.; Eckert, J. An Energy Storage Principle Using Bipolar Porous Polymeric Frameworks. *Angew. Chem., Int. Ed.* **2012**, *51*, 7850−7854.

(47) Ren, S.; Bojdys, M. J.; Dawson, R.; Laybourn, A.; Khimyak, Y. Z.; Adams, D. J.; Cooper, A. I. Porous, Fluorescent, Covalent Triazine-Based Frameworks via Room-Temperature and Microwave-Assisted Synthesis. *Adv. Mater.* **2012**, *24*, 2357−2361.

(48) Zhang, K.; Kopetzki, D.; Seeberger, P. H.; Antonietti, M.; Vilela, F. Surface Area Control and Photocatalytic Activity of Conjugated

Microporous Poly(benzothiadiazole) Networks. *Angew. Chem., Int. Ed.* **2013**, *52*, 1432−1436.

(49) Vilela, F.; Zhang, K.; Antonietti, M. Conjugated Porous Polymers for Energy Applications. *Energy Environ. Sci.* **2012**, *5*, 7819−7832.

(50) Algara-Siller, G.; Severin, N.; Chong, S. Y.; Björkman, T.; Palgrave, R. G.; Laybourn, A.; Antonietti, M.; Khimyak, Y. Z.; Krasheninnikov, A. V.; Rabe, J. P.; Kaiser, U.; Cooper, A. I.; Thomas, A.; Bojdys, M. J. Triazine-Based Graphitic Carbon Nitride: A Two-Dimensional Semiconductor. *Angew. Chem., Int. Ed.* **2014**, *53*, 7450−7455.

(51) Mahmood, J.; Lee, E. K.; Jung, M.; Shin, D.; Jeon, I.-Y.; Jung, S.-M.; Choi, H.-J.; Seo, J.-M.; Bae, S.-Y.; Sohn, S.-D.; Park, N.; Oh, J. H.; Shin, H.-J.; Baek, J.-B. Nitrogenated Holey Two-Dimensional Structures. *Nat. Commun.* **2015**, *6*, No. 6486.

(52) Winter, M.; Brodd, R. J. What Are Batteries, Fuel Cells, and Supercapacitors? *Chem. Rev.* **2004**, *104*, 4245−4269.

(53) Simon, P.; Gogotsi, Y.; Dunn, B. Where Do Batteries End and Supercapacitors Begin? *Science* **2014**, *343*, 1210−1211.

(54) Sakaushi, K.; Hosono, E.; Nickerl, G.; Gemming, T.; Zhou, H.; Kaskel, S.; Eckert, J. Aromatic Porous-Honeycomb Electrodes for a Sodium-Organic Energy Storage Device. *Nat. Commun.* **2013**, *4*, No. 1485.

(55) Su, Y.; Liu, Y.; Liu, P.; Wu, D.; Zhuang, X.; Zhang, F.; Feng, X. Compact Coupled Graphene and Porous Polyaryltriazine-Derived Frameworks as High Performance Cathodes for Lithium-Ion Batteries. *Angew. Chem., Int. Ed.* **2015**, *54*, 1812−1816.

(56) Sakaushi, K.; Hosono, E.; Nickerl, G.; Zhou, H.; Kaskel, S.; Eckert, J. Bipolar Porous Polymeric Frameworks for Low-Cost, High-Power, Long-Life All-Organic Energy Storage Devices. *J. Power Sources* **2014**, *245*, 553−556.

(57) Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light. *Nat. Mater.* **2009**, *8*, 76−80.

(58) Ham, Y.; Maeda, K.; Cha, D.; Takanabe, K.; Domen, K. Synthesis and Photocatalytic Activity of Poly(triazine imide). *Chem.—Asian J.* **2013**, *8*, 218−224.

(59) Liu, J.; Liu, Y.; Liu, N.; Han, Y.; Zhang, X.; Huang, H.; Lifshitz, Y.; Lee, S.-T.; Zhong, J.; Kang, Z. Metal-Free Efficient Photocatalyst for Stable Visible Water Splitting via a Two-Electron Pathway. *Science* **2015**, *347*, 970−974.

(60) Sakaushi, K.; Fellinger, T.-P.; Antonietti, M. Bifunctional Metal-Free Catalysis of Mesoporous Noble Carbons for Oxygen Reduction and Evolution Reactions. *ChemSusChem* **2015**, *8*, 1156−1160.

(61) Zheng, Y.; Jiao, Y.; Zhu, Y.; Li, L. H.; Han, Y.; Chen, Y.; Du, A.; Jaroniec, M.; Qiao, S. Z. Hydrogen Evolution by a Metal-Free Electrocatalyst. *Nat. Commun.* **2014**, *5*, No. 3783.

(62) Paraknowitsch, J. P.; Zhang, J.; Su, D.; Thomas, A.; Antonietti, M. Ionic Liquids as Precursors for Nitrogen-Doped Graphitic Carbon. *Adv. Mater.* **2010**, *22*, 87−92.

(63) Li, X.-H.; Antonietti, M. Metal Nanoparticles at Mesoporous N-Doped Carbons and Carbon Nitrides: Functional Mott−Schottky Heterojunctions for Catalysis. *Chem. Soc. Rev.* **2013**, *42*, 6593−6604.

(64) Sauer, J.; Freund, H.-J. Models in Catalysis. *Catal. Lett.* **2015**, *145*, 109−125.