Triangular boron carbon nitrides: An unexplored family of chromophores with unique properties for photocatalysis and optoelectronics

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Abstract

It has recently been shown that heptazine (1,3,4,6,7,9,9b-heptaazaphenalene) and related azaphenalenenes exhibit inverted singlet and triplet states, that is, the energy of the lowest singlet excited state (S_1) is below the energy of the lowest triplet excited state (T_1). This feature is unique among all known aromatic chromophores and is of outstanding relevance for applications in photocatalysis and organic optoelectronics. Heptazine is the building block of the polymeric material graphitic carbon nitride which is an extensively explored photocatalyst in hydrogen evolution photocatalysis. Derivatives of heptazine have also been identified as highly efficient emitters in organic light emitting diodes (OLEDs). In both areas, the inverted singlet-triplet gap of heptazine is a highly beneficial feature. In photocatalysis, the absence of a long-lived triplet state eliminates the activation of atmospheric oxygen, which is favourable for long-term operational stability. In optoelectronics, singlet-triplet inversion implies the possibility of 100% fluorescence efficiency of electron-hole recombination. However, the absorption and luminescence wavelengths of heptazine and the S_1 - S_0 transition dipole moment are difficult to tune for optimal functionality. In this work, we employed high-level ab initio electronic structure theory to devise and characterize a large family of novel heteroaromatic chromophores, the triangular boron carbon nitrides. These novel heterocycles inherit essential spectroscopic features from heptazine, in particular the inverted singlet-triplet gap, while their absorption and luminescence spectra and transition dipole moments are widely tuneable. For applications in photocatalysis, the wavelength of the absorption maximum can be tuned to improve the overlap with the solar spectrum at the surface of earth. For applications in OLEDs, the colour of emission can be adjusted and the fluorescence yield can be enhanced.

1. Introduction

Heptazine (1, 3, 4, 6, 7, 9, 9b-heptaazaphenalene) is the building block of the polymer “melon” first prepared by Berzelius and Justus von Liebig in 1834.¹ Heptazine (Hz) is known as an isolated molecule since 1982.² Melem (triamino-Hz), cyameluric acid (trihydroxy-Hz) and cyameluric chloride (trichloro-heptazine) are well-known derivatives of Hz.³ More recently, new derivatives of Hz were synthesized⁴⁻⁶ and their use as emitters in organic light-emitting diodes (OLEDs)⁷⁻⁹ or as photoredox catalysts were explored.^{10, 11} A comprehensive up-to-date account of the literature on molecular (monomeric) Hz and derivatives thereof can be found in Ref.¹²

The polymer melon, also referred to as graphitic carbon nitride (g-C₃N₄), has found vast attention as a metal-free and photochemically highly stable photocatalyst for hydrogen evolution from water with sacrificial reagents.^{13, 14} Several thousand publications since 2009 mainly explored the effect of morphological modifications of melon or of various additives on the hydrogen evolution efficiency, see ¹⁵⁻¹⁸ for selected reviews. Despite this extensive body of research, the fundamental molecular mechanisms underlying photoinduced hydrogen evolution or pollutant oxidation could not be clarified, partly because the polymeric materials are chemically as well as structurally poorly defined.^{19, 20} Recently, a few studies investigated homogeneous water oxidation with molecular Hz-based photocatalysts in neat solvents.^{10, 21} These studies shed some light on the role of specific excited states of hydrogen-bonded Hz-H₂O complexes in the water-oxidation reaction.

An independent computational discovery, which was confirmed by spectroscopic studies, revealed that Hz chromophores exhibit the highly unusual property of inversion of the energies of the lowest singlet and triplet excited states, that is, the excitation energy of the T₁ state is higher than the excitation energy of the S₁ state in violation of Hund’s multiplicity rule.²² This inversion of S₁/T₁ energies was independently confirmed by calculations for the mono-aza phenalene [3.3.3]cyclazine,²³ referred to as cyclazine (Cz) in what follows, and other azaphenalenes.²⁴ It was pointed out that the S₁/T₁ inversion in Hz (by about 0.25 eV) appears to be very robust with respect to chemical modifications and oligomerization.²² The origin of the S₁/T₁ inversion in Cz and Hz can be traced to the spatially non-overlapping character of the highest occupied molecular orbital (HOMO) and the lowest unoccupied

molecular orbital (LUMO) and the nearly pure HOMO-LUMO excitation character of the S_1 and T_1 wave functions, which results in an exceptionally small exchange integral. Spin polarization in the singlet state, which is reflected in a higher admixture of double excitations in the singlet state than in the triplet state, can then lower the S_1 energy below the T_1 energy.^{22, 23}

The S_1/T_1 inversion in aza-phenalene chromophores has important implications for optoelectronics and photocatalysis. In OLEDs, the statistical recombination of electrons and holes results in 75% triplet excitons and 25% singlet excitons. When the energy of the S_1 state is below the energy of the T_1 state, a 100% yield of fluorescent singlet excitons is possible, since the triplet excitons may quantitatively convert to singlet excitons by intersystem crossing (ISC). This implies the possible existence of a new (fourth) generation of emitters with higher luminescence efficiencies and spectral qualities than delivered by previous generations.²⁵⁻²⁹ It is a disadvantage, however, that the transition dipole moment between the S_1 state and the S_0 state is very low in aza-phenalenes due to the non-overlapping character of HOMO and LUMO. In Cz and Hz, which exhibit D_{3h} symmetry, this transition is additionally forbidden by symmetry. The fluorescence rate of the S_1 state is therefore exceptionally low, which may result in a low fluorescence quantum yield despite the absence of S_1 quenching by ISC. This problem can be alleviated to some extent by lowering the molecular symmetry from D_{3h} to C_{2v} or C_s by asymmetric distribution of carbon and nitrogen atoms along the periphery of the phenalene frame or by asymmetric substitution of the H atoms at the three corners.³⁰ In early work by Wirz and coworkers and Leonard and coworkers, asymmetric tetra- and penta-aza-phenalenes were synthesized and spectroscopically characterized.^{31, 32} For more recent work, see Ref.³³. Adachi and coworkers synthesized several substituted heptazines and tested them for their light-emitting efficiencies.⁷⁻⁹

In photocatalytic applications, the goals for optimization of aza-phenalene photocatalysts are largely complementary to the goals for optoelectronics. Since the S_1 state is nearly dark, the light is absorbed by the lowest bright $^1\pi\pi^*$ state (which is the S_4 state in Hz). The energy is transferred to the $S_1(\pi\pi^*)$ state by internal conversion on a sub-picosecond time scale.^{10, 34} The absence of a long-lived triplet state below the S_1 state eliminates the usual quenching channel of ISC and enables exceptionally long

lifetimes of the S_1 state if the fluorescence rate of the latter is very low. The energy of the absorbed photon can thereby be stored for long times with low losses, allowing useful photochemical transformations in the excited state. Moreover, the absence of a long-lived triplet state eliminates the activation of atmospheric oxygen to deleterious singlet oxygen, which solves a long-standing problem of artificial photosynthesis with organic or organometallic photocatalysts.^{35, 36}

The active sites for water oxidation photocatalysis are the peripheral N-atoms. They are the docking sites for hydrogen bonding and become extremely electron-deficient upon HOMO-LUMO excitation, because this excitation transfers the charge of one electron from the peripheral N-atoms to the peripheral C-atoms in Hz.³⁷ The rather high excitation energy of the bright $^1\pi\pi^*$ state of Hz, on the other hand, results in poor harvesting of solar radiation. The excitation energy of the S_1 state of Hz (≈ 2.60 eV) also is higher than the thermodynamic threshold for water splitting via the two-electron mechanism (1.76 eV, generating H_2 and H_2O_2) or the threshold for the four-electron mechanism (1.23 eV, generating H_2 and O_2).³⁸ Tuning the energy of the bright $^1\pi\pi^*$ state closer to the maximum of the solar spectrum and the energy of the S_1 state closer to the thermodynamic limits of the water-splitting reactions could result in a significant boost of the quantum efficiency of water splitting beyond the current value of $\approx 1\%$.³⁹

While modifications of the optical properties of the Hz chromophore by substitutions at the three CH groups have been explored in computational^{40, 41} and spectroscopic^{10, 21} studies, the range of tuning of the excitation energies is limited if the highly desirable S_1/T_1 inversion is to be preserved. In this communication, we propose a novel scenario for developing chromophores with tailored properties for optoelectronics as well as for photocatalysis. The basic concept is the systematic extension of the phenalene frame by inserting a rigid non-conjugated boron-nitride core, keeping the conjugated fused hexagonal rings along the triangular periphery. This novel concept offers the opportunity of constructing an essentially unlimited number of rigid chromophores with widely tuneable functionalities for optoelectronics or photocatalysis.

A number of recent publications reported the synthesis and investigation of boron-doped carbon nitrides or carbon-doped boron nitrides. Carbon-doped boron nitride nanosheets were employed in

photoredox catalysis⁴² and in photoelectrochemical water splitting.⁴³ Coordination complexes of boron atoms with carbon nitrides were synthesized and tested as emitters of OLEDs.^{44, 45} The absorption and luminescence spectra of a variety of planar BCN structures were investigated in the quest for improved OLED materials.^{28, 46-53} To the best of our knowledge, boron carbon nitride (BCN) compounds exhibiting the characteristic triangular shape of Cz or Hz and the associated robust inversion of the S_1 and T_1 states have remained unexplored so far.

2. Results and discussion

The ground-state equilibrium geometries of the compounds considered herein were determined with the second-order Møller-Plesset (MP2) *ab initio* method.⁵⁴ It was confirmed by the computation of the Hessian that the stationary points are minima. Vertical electronic excitation energies of singlet and triplet excited states were calculated with the algebraic-diagrammatic construction of second order (ADC(2)) method.⁵⁵⁻⁵⁷ ADC(2) is a computationally efficient single-reference propagator method which yields similar results as the simplified second-order coupled-cluster (CC2) method.⁵⁸ The accuracy of CC2 and ADC(2) for excitation energies of organic molecules was extensively benchmarked in comparison with more accurate methods, such as CC3 and CCSDT.⁵⁹⁻⁶² A mean absolute error of ≈ 0.22 eV for low-lying singlet states and ≈ 0.12 eV for low-lying triplet states has been estimated.⁵⁹ This accuracy is sufficient for the purposes of the present computational study. The correlation-consistent polarized valence-split double- ζ basis set (cc-pVDZ)⁶³ was employed. All calculations were performed with the TURBOMOLE program package (V. 6.3.1)⁶⁴ making use of the resolution-of-the-identity (RI) approximation.

Chart 1: Cyclazine (**1.1**) and the triangular BCNs derived from cyclazine (**2.1** and **3.1**).

The basic building principle of the triangular BCNs considered in this work is shown in Chart 1. We start from Cz (**1.1**). Cz was first synthesized by Faraquhar and Leaver⁶⁵ and its electronic absorption and emission spectra were measured by Leupin and Wirz.⁶⁶ Compound **2.1** is obtained by replacing the central N-atom of Cz by the BN₃ unit and extending the system from three fused hexagonal rings to six fused hexagonal rings, see Chart 1. This building principle can be continued, as illustrated by **3.1**. Here, the core consists of the triangular B₃N₆ unit and is surrounded by nine hexagons with conjugated bonds along the periphery. All three systems in Chart 1 are stable closed-shell molecules possessing D_{3h} symmetry.

For the functionality of these chromophores in OLEDs or in photocatalysts, only the lowest triplet state and the two lowest singlet states of $\pi\pi^*$ character are of relevance. The vertical excitation energies of these states for **1.1**, **2.1** and **3.1** are listed in the upper part of Table 1. In addition, the S₁-T₁ energy gap, $\Delta_{ST} = E_S - E_T$, is listed. A more complete list of excitation energies of these compounds is provided in Tables S1-S3 in the ESI. In all three systems of Chart 1, the lowest excited state is a nondegenerate $^1\pi\pi^*$ state ($^1A_2'$), while the next higher excited $^1\pi\pi^*$ state is a degenerate state ($^1E'$). A negative Δ_{ST} implies that the vertical excitation energy of the T₁ state is higher than the vertical excitation energy of the S₁ state. For **1.1**, $\Delta_{ST} = -0.16$ eV, confirming the prediction of de Silva²³ with the same computational method.

State	1.1	2.1	3.1
$^1A_2'$	1.02 (0.000)	1.63 (0.000)	1.19 (0.000)
$^3A_2'$	1.18	1.91	1.42
$^1E'$	3.14 (0.520)	2.37 (0.586)	2.27 (1.262)
Δ_{ST}	-0.16	-0.28	-0.23

State	1.2	2.2	3.2
$^1A_2'$	2.57 (0.000)	2.22 (0.000)	1.91 (0.000)
$^3A_2'$	2.85	2.57	2.22
$^1E'$	4.43 (0.538)	2.98 (0.446)	2.69 (0.966)
Δ_{ST}	-0.28	-0.35	-0.31

Table 1: Vertical excitation energies (in eV), oscillator strengths (in parentheses) and S_1 - T_1 energy gap (Δ_{ST}) of the compounds in Chart 1 (upper part) and Chart 2 (lower part).

For **2.1** and **3.1**, the magnitude of Δ_{ST} is somewhat larger. While the $S_1 \leftarrow S_0$ radiative transition is forbidden, the oscillator strength of the bright degenerate $^1\pi\pi^*$ state is substantial and increases with the size of the molecular frame from 0.52 for **1.1** to 1.26 for **3.1**. The excitation energies of the S_1 state of **1.1**, **2.1** and **3.1** do not show a clear trend, while the energies of the $^1E'$ state exhibit the expected lowering with increasing size of the molecular frame, from 3.14 eV for **1.1** to 2.27 eV for **3.1**. It should be noted that for **2.1** and **3.1**, the energy of the bright state is quite low and is close to the maximum of the solar spectrum at the surface of earth. **2.1**, **3.1** or larger BCNs therefore represent excellent antennas for the harvesting of solar light as well as excellent emitters of visible light.

In all BCNs, the S_1 and T_1 excited states are nearly pure HOMO-to-LUMO excitations. To understand their peculiar properties, it is instructive to look at these molecular orbitals in some detail. The HOMOs and LUMOs of **1.1**, **2.1** and **3.1** are displayed in Fig. 1. For **1.1** and **3.1**, HOMO and LUMO are nondegenerate. For **2.1**, HOMO and LUMO are degenerate. This trend is systematic. For an even number of conjugated hexagons (Hz, Dz, ...), HOMO and LUMO are nondegenerate. For an odd number of conjugated hexagons (Nz, ...) HOMO and LUMO are degenerate.

The nondegenerate HOMO and LUMO of **1.1** and **3.1** are shown in the uppermost row (a, b) and the lowest row (g, h) of Fig. 1, respectively. The four molecular orbitals representing HOMO and LUMO of **2.1** are displayed in the two middle rows of Fig. 1 (c, d, e, f). As has been pointed out previously for **1.1**²³, HOMO and LUMO are spatially non-overlapping, see Fig 1a,b. Along the outer rim, HOMO

and LUMO are localized on complementary atoms. The LUMO has electron density on the central N-atom, but the HOMO has not. An analogous pattern can be seen for HOMO and LUMO of **3.1**. For the degenerate orbitals of **2.1**, the mutual exclusion of electron density on the atoms is less strict, see Figs. 1c-f. It should also be noted that for the BCNs **2.1** and **3.1** HOMO and LUMO are exclusively located on the conjugated rim and not on the boron-nitride core. The electron density on the catalytically active peripheral N-atoms therefore scales linearly rather than quadratically with the linear dimension of the molecule. For the case of nondegenerate HOMO and LUMO, the singlet-triplet splitting is given in first order by the exchange matrix element of HOMO and LUMO. For **2.1** with degenerate HOMO and LUMO, the expression for Δ_{ST} is more complicated.⁶⁷ The S_1/T_1 inversion arises from the combination of a small exchange matrix element with enhanced weight of double excitations in the singlet state.^{22, 23} The magnitude of Δ_{ST} in **1.1** – **3.1** is of the order of 0.2 eV and does not exhibit a clear trend with increasing system size, see Table 1.

Chart 2 illustrates the corresponding construction principle for BCNs starting from Hz (**1.2**). The Hz molecule was first synthesized by Hosmane et al.² and its chemical and spectroscopic properties were studied by Shahbaz et al.⁶⁸ Hz hydrolyzes rapidly in the presence of light and traces of water and is therefore difficult to handle in the laboratory. As the building block of polymeric carbon nitride (melon), this molecule nevertheless is of outstanding interest in water-oxidation photocatalysis. Hz derivatives or charge-transfer complexes containing Hz derivatives have been under investigation as improved emitters for OLEDs.⁷⁻⁹

Chart 2: Heptazine (**1.2**) and the triangular BCNs **2.2** and **3.2** derived from heptazine.

The triangular BCN **2.2** contains six N-atoms on the periphery, like Hz, and nine N-atoms altogether. We call it nonazine (Nz). The BCN **3.2** also contains six peripheral N-atoms and 12 N-atoms altogether. We call it dodecazine (Dz). While Hz has three free CH groups for substitution, Nz has six free CH groups and Dz has nine free CH groups. Nz and Dz therefore offer ample possibilities for chemical modification.

Hz (**1.2**), Nz (**2.2**) and Dz (**3.2**) possess, like **1.1**, **2.1** and **3.1**, a low-lying nondegenerate and dipole-forbidden $^1A_2'(\pi\pi^*)$ state and a strongly dipole-allowed $^1E'(\pi\pi^*)$ state, see the lower part of Table 1. A more complete list of excited states of **1.2**, **2.2** and **3.2** is given in Tables S4-S6 in the ESI. In Hz, two $\pi\pi^*$ states are located below the bright $^1E'(\pi\pi^*)$ state, while in the larger systems, the bright $^1\pi\pi^*$ state becomes the S_2 state. The energies of both $^1\pi\pi^*$ states decrease with the system size, the energy of the S_1 state by about 0.6 eV from **1.2** to **3.2**, the energy of the S_2 state by about 0.9 eV. The magnitude of Δ_{ST} of the Hz-derived compounds is about 0.1 eV larger than Δ_{ST} of the Cz-derived compounds. It should also be noted that the magnitude of Δ_{ST} increases with increasing size of the triangular BCNs, whereas the magnitude of Δ_{ST} decreases when Hz is substituted with pendants and the S_1/T_1 inversion can be lost for somewhat larger aromatic substituents at the CH positions.⁴¹

Comparing the singlet excitation energies of **1.2**, **2.2** and **3.2** with the singlet excitation energies of **1.1**, **2.1** and **3.1**, one notices that the substitution of peripheral CH groups by N-atoms increases all excitation energies. This effect is particularly strong for the smallest systems, **1.1** and **1.2**, and becomes less pronounced for the larger systems, **3.1** and **3.2**. The HOMOs and LUMOs of **1.2**, **2.2** and **3.2** are very similar to those of **1.1**, **2.1** and **3.1** discussed above and are displayed in Fig. S1 of the ESI.

The BCNs **2.1** and **3.1** obviously offer many possibilities for CH $\rightarrow$ N substitution along the rim. A comprehensive study of all possible structures is beyond the scope of the present work. Instead, we report results for three representative asymmetrically CH $\rightarrow$ N substituted exemplars of **2.1**, designated **2.3**, **2.4**, **2.5** and shown in Chart 3. The excitation energies and oscillator strengths are given in the upper part of Table 2. When the energies of these asymmetrically substituted systems are compared with the energies of the D_{3h} symmetric species **2.1** and **2.2**, it is seen that the magnitude of

Δ_{ST} is somewhat reduced and a S_1 - S_0 oscillator strength up to 0.02 can be realized, which corresponds to a fluorescence rate of $3.6 \times 10^6 \text{ s}^{-1}$. The degeneracy of the $^1E'$ state is lifted by about 0.1 eV in the asymmetric systems. The S_1 and S_2 excitation energies are in between those of **2.1** and **2.2**. Analogous data for asymmetrically CH $\rightarrow$ N substituted variants of Dz (**3.1**) can be found in Chart S2 and Table S8 in the ESI.

Chart 3: Selected asymmetrically CH $\rightarrow$ N substituted analogues of **2.1**.

Substitutions at the CH groups of BCNs open a wide chemical design space. A comprehensive investigation of substitution effects at CH positions of triangular BCNs is beyond the scope of the present work. To illustrate some of the effects, we consider a simple atomic substituent (fluorine) and present results for the Nz-derived structures **2.6**, **2.7** and **2.8** shown in Chart 4. The excitation energies and oscillator strengths are given in the lower part of Table 2. Symmetric tri-fluorination increases the energies of the S_1 and S_2 states by 0.35 eV. The blue-shift of the S_1 state may be useful for tuning the emission colour of OLEDs towards blue light. The magnitude of Δ_{ST} in the tri-fluoride **2.8** is 0.48 eV and is one of the largest Δ_{ST} found in the present exploratory study. Asymmetric di-fluorination of **2.2** generates an oscillator strength of 0.009, which corresponds to a fluorescence rate of $2.3 \times 10^6 \text{ s}^{-1}$. Overall, asymmetric CH $\rightarrow$ N substitution seems to be more effective in generating an S_1 - S_0 transition moment than asymmetric fluorination. Larger, for example aromatic, substituents can of course have significantly more pronounced effects on the excitation spectrum and the S_1 - S_0 transition moment.

State	2.3	2.4	2.5
$^1A'$	1.80 (0.011)	1.90 (0.023)	1.99 (0.015)
$^3A'$	1.99	2.01	2.18
$^1A'$	2.39 (0.115)	2.67 (0.192)	2.68 (0.137)
$^1A'$	2.58 (0.252)	2.77 (0.103)	2.77 (0.239)
Δ_{ST}	-0.19	-0.11	-0.19

State	2.6	2.7	2.8
1B_2	2.31 (0.007)	2.42 (0.009)	2.57 (0.000)
3B_2	2.59	2.68	3.05
1A_1	3.07 (0.259)	3.22 (0.179)	3.33 (0.444)
1B_2	3.14 (0.178)	3.22 (0.255)	-
Δ_{ST}	-0.28	-0.26	-0.48

Table 2: Vertical excitation energies (in eV), oscillator strengths (in parentheses) and S_1 - T_1 energy gap (Δ_{ST}) of the compounds in Chart 3 (upper part) and Chart 4 (lower part).

With respect to photocatalysis, it is interesting to note that that the S_1 excitation energy of the trifluoride **2.8** is essentially the same as that of Hz (**1.2**), while the energy of the bright $^1\pi\pi^*$ state of **2.8** is 1.1 eV lower than the energy of the bright state of Hz. This example shows that the relative energies of the states involved in water-oxidation photocatalysis can be widely tuned with these new compounds, which may be useful for the development of a systematic mechanistic understanding of the photocatalytic mechanisms. Results for fluorinated derivatives of Dz (**3.1**) can be found in Chart S3 and Table S9 in the ESI.

Chart 4: Selected fluorinated derivatives of **2.2**.

For the functionality of triangular BCNs in organic optoelectronics, only the S_1 and T_1 states are of relevance. By the robust inversion of the energies of the S_1 and T_1 states, all BCNs are predestinated as chromophores for improved OLEDs. The so-called third generation OLEDs^{27, 29, 69} rely on the mechanism of TADF⁷⁰, exploiting thermally activated inverse intersystem crossing from long-lived triplet excitons to nearly degenerate singlet excitons. The essential requirement for TADF is a small ($\approx k_B T$) positive Δ_{ST} , such that population of the long-lived triplet state can be thermally activated to the singlet state, from which fluorescence occurs. Numerous molecules tailored for TADF were synthesized and tested as OLED emitters.^{25-29, 69}

The existence of a large family of organic emitters with inverted S_1/T_1 states provides the basis for the development of a novel fourth generation of OLEDs. In materials with S_1/T_1 inversion, triplet excitons formed by recombination of electrons and holes readily convert to singlet excitons by ISC. Together with the directly formed singlet excitons, 100% internal quantum efficiency can be achieved. The intrinsically low fluorescence rate of the S_1 state of aza-phenalenes and BCNs is a certain drawback. However, the BCNs allow a wider pattern of substitutions than Hz and define a vast chemical design space which can be explored by computation and/or synthesis for the development of fourth-generation OLED materials.

For photocatalysis, especially water-oxidation photocatalysis, the peripheral N-atoms of Hz (**1.2**) and the BCN analogues Nz (**2.2**) and Dz (**3.2**) are essential. They are the docking sites for hydrogen bonding with water molecules or other protic substrate molecules. The hydrogen bonding is essential

for the excited-state PCET reaction which leads to the abstraction of an H-atom from the substrate molecule.^{37, 41, 71} In contrast to optoelectronics, the energy and the properties of the lowest bright $^1\pi\pi^*$ state play a decisive role, in addition to the properties of the $S_1(\pi\pi^*)$ state. The photon is absorbed by the bright $^1\pi\pi^*$ state which then rapidly (on sub-picosecond time scales) decays to the S_1 state by internal conversion. The electronic population in the S_1 state survives for tens or hundreds of nanoseconds due to the low fluorescence rate and the absence of S_1 quenching by ISC.^{10, 34, 72} A substantial fraction of the energy of the absorbed photon can thus be stored in the S_1 state and is available for excited-state PCET reactions with the substrate.

An important criterion for solar-driven photocatalysis is the wavelength of the absorption maximum, given approximately by the vertical excitation energy of the bright $^1\pi\pi^*$ state. According to Table 1, the energy (wavelength) of the absorption maximum decreases from 4.43 eV (280 nm) for Hz (**1.2**) via 2.98 eV (416 nm) for Nz (**2.2**) to 2.69 eV (461 nm) for Dz (**3.2**). It has to be kept in mind that ADC(2) tends to overestimate excitation energies of $^1\pi\pi^*$ states by a few tenth of an eV and solvation effects or oligomerization effects, not considered here, will lead to further redshifts of the absorption maximum. The extension of the BCN frame shifts the absorption maximum of the bright $^1\pi\pi^*$ state deep into the solar spectrum at the surface on earth and the absorption intensity increases substantially (see the oscillator strengths in Table 1). In addition, the energy of the bright $^1\pi\pi^*$ state is quite sensitive to substituents. As has been computationally demonstrated for Hz (**1.2**), aromatic substituents such as benzene or toluene or oligomers thereof reduce the excitation energy substantially.^{40, 41} There exist thus ample possibilities to tune the peak absorption of triangular BCN chromophores to a desired value.

While the energy of the S_1 state of Hz molecules and Hz polymers is very robust and therefore difficult to tune, the BCNs Nz (**2.2**) and Dz (**3.2**) open promising opportunities of tuning the S_1 energy. The S_1 energy of Nz (**2.2**) is 0.35 eV lower than that of Hz (**1.2**) and the S_1 energy of Dz (**3.2**) is again lower by 0.32 eV. With a value of 1.91 eV, the S_1 excitation energy of Dz is close to the thermodynamic threshold (1.76 eV) of the two-electron water-splitting reaction.³⁸ This example shows

that the wide tunability of the excitation energies of triangular BCNs opens very promising opportunities for a systematic improvement of water-oxidation photocatalysts.

The S_1/T_1 inversion in Hz and triangular BCN chromophores is also of crucial importance for photocatalysis, although the T_1 state is not directly involved in the photocatalytic transformations. The S_1/T_1 inversion in Hz and in triangular BCNs eliminates a long-standing problem of artificial photosynthesis with organic materials. The population of long-lived triplet states, which exist in nearly all organic as well as organometallic photosynthesizers, readily activates atmospheric oxygen to reactive singlet oxygen which destroys organic materials.^{35, 36, 73} It was observed that polymeric carbon nitrides generate extremely low levels of singlet oxygen under irradiation⁷⁴⁻⁷⁶ which presumably is one of the reasons for their surprising photostability. It is expected that the BCNs will exhibit a similarly high level of photostability, both as free molecules and as polymers.

3. Conclusions

Using *ab initio* electronic-structure methods, we have explored the structural, electronic and optical properties of a new class of organic chromophores, the triangular boron carbon nitrides. These compounds are conceptually derived from Cz (**1.1**) or Hz (**1.2**). While Cz may be considered as a somewhat exotic aza-aromatic molecule and indeed has received little attention in the literature, the unique photocatalytic and optoelectronic functionalities of Hz are nowadays widely appreciated. The extended family of BCNs defined in the present work as extensions of Cz and Hz constitutes a vast chemical space of chromophores with exceptional and widely tuneable properties. The primary signature of the triangular BCNs is the robust inversion of the energies of the S_1 and T_1 states, which predestinate them as chromophores for organic optoelectronics. The BCNs also inherit the photocatalytic potency of Hz, which exhibits one of the highest excited-state oxidation potentials in organic chemistry. In contrast to Hz, the electronic and spectroscopic properties of the triangular BCNs are widely tuneable. The BCNs therefore offer access to parameter regions (such as excitation energies or oscillator strengths) which are inaccessible with chemically modified Hz molecules.

While Hz was prepared (without knowing its structure) by Berzelius and Justus von Liebig 187 years ago, the family of triangular BCNs has remained untouched by organic synthetic chemists. Albeit a

general synthesis protocol for triangular BCNs currently does not exist, the protocols existing for derivatives of Cz, Hz or various planar boron-containing carbon nitrides can possibly be adapted. The opportunity of discovering chromophores with hitherto unavailable optoelectronic and photocatalytic functionalities should stimulate work in this direction. Future more comprehensive computational screening studies should address the optimization of the emission efficiency, the coverage of the visible spectrum as well as colour purity of optoelectronic emitters. For photocatalytic applications, the excited-state PCET reactivity of BCNs in protic solvent environments should be explored. The optimization of photocatalytic water-oxidation catalysts sampled from a wide and so far unexplored chemical space may lead to transformative discoveries in the chemistry of solar energy harvesting.

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Figure 1: HOMO (left) and LUMO (right) for the molecules **1.1** (a, b), **2.1** (c, d, e, f) and **3.1** (g, h), respectively, at the ground-state equilibrium geometry.

Triangular boron carbon nitrides: An unexplored family of chromophores with unique properties for photocatalysis and optoelectronics

Supporting Information

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Table S1: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **1.1**.

Singlet		Triplet	
A_2'	1.02 (0.000)	A_2'	1.18
E'	3.14 (0.520)	E'	2.25
A_1''	4.84 (0.000)	E'	4.27
E'	5.07 (0.768)	A_1''	4.84

Table S2: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **2.1**.

Singlet		Triplet	
A_2'	1.63 (0.000)	E'	1.91
A_1'	2.25 (0.000)	A_1'	1.93
E'	2.37 (0.586)	A_2'	1.94
E'	3.16 (0.110)	E'	2.88

Table S3: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **3.1**.

Singlet		Triplet	
A_2'	1.19 (0.000)	A_2'	1.42
E'	2.27 (1.262)	E'	1.89
E'	2.51 (0.000)	E'	2.36

Table S4: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **1.2**.

Singlet		Triplet	
A_2'	2.57 (0.000)	A_2'	2.85
A_1''	3.76 (0.000)	E'	3.67
E''	3.84 (0.000)	A_1''	3.76
E'	4.43 (0.538)	E''	3.82

Table S5: Vertical excitation energies (in eV) and oscillator strengths (in parantheses) of **2.2**.

Singlet		Triplet	
A_2'	2.22 (0.000)	A_2'	2.57
E'	2.98 (0.446)	E'	2.67
A_1'	3.21 (0.000)	A_1'	2.99
A_1''	3.92 (0.000)	E'	3.49

Table S2: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **3.2**.

Singlet		Triplet	
A_2'	1.91 (0.000)	A_2'	2.22
E'	2.69 (0.966)	E'	2.36
E'	3.14 (0.077)	A_1'	2.92

Table S3: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) for selected fluorinated derivatives of Nz (**2.2**). **2.9** exhibits the lowest S_1 energy, while **2.10** and **2.11** exhibit highest oscillator strength of the S_1 state. The corresponding structures are shown in Chart S1.

State	2.9	2.10	2.11
$S_1 A'$	1.86 (0.000)	2.14 (0.022)	2.26 (0.022)
$S_2 A'$	2.61 (0.350)	2.92 (0.199)	3.06 (0.168)
$S_3 A'$	-	3.07 (0.162)	3.14 (0.189)
$S_4 A'$	2.80 (0.000)	3.20 (0.011)	3.33 (0.016)
$T_1 A'$	2.18	2.29	2.41
$T_2 A'$	2.27	2.64	2.75
$T_3 A'$	-	2.82	2.90
$T_4 A'$	3.14	2.97	3.10

Table S4: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) for two selected asymmetrically CH $\rightarrow$ N substituted derivatives of **3.1**. The corresponding structures are shown in Chart S2.

State	3.3	3.4
$S_1 A'$	1.63 (0.020)	1.68 (0.010)
$S_2 A'$	2.46 (0.429)	2.44 (0.350)
$S_3 A'$	2.65 (0.645)	2.63 (0.646)
$S_4 A'$	2.80 (0.084)	2.92 (0.201)
$T_1 A'$	1.79	1.93
$T_2 A'$	2.13	2.19
$T_3 A'$	2.22	2.26
$T_4 A'$	2.63	2.63

Table S5: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) for selected fluorinated derivatives of Dz (**3.2**). The corresponding structures are shown in Chart S3.

State	3.5	3.6	3.7
$S_1 A'$	1.98 (0.006)	2.17 (0.000)	1.91 (0.015)
$S_2 A'$	2.70 (0.468)	2.93 (1.040)	2.60 (0.547)
$S_3 A'$	2.85 (0.514)	-	2.79 (0.326)
$S_4 A'$	3.17 (0.017)	3.35 (0.252)	2.96 (0.003)
$T_1 A'$	2.27	2.48	1.98
$T_2 A'$	2.39	2.50	2.32
$T_3 A'$	2.45	-	2.79
$T_4 A'$	2.94	3.12	2.95

Chart S2: Selected fluorinated derivatives of Nz (**2.2**).

Chart S3: Selected asymmetrically CH $\rightarrow$ N substituted derivatives of (3.1).

Chart S4: Selected fluorinated derivatives of Dz (3.2).

Figure S2: HOMO and LUMO for the molecules **1.2** (a and b), **2.2** (c, d and e, f) and **3.2** (g and h) respectively at their ground-state equilibrium structure.

Cartesian coordinates in Angstrom of Cz (**1.1**) at the MP2/cc-pVDZ level.

C	-2.1261712	-1.2025280	0.0000000
C	-0.7073599	-1.2251833	0.0000000
N	0.0000000	0.0000000	0.0000000
C	-0.7073599	1.2251833	0.0000000
C	-2.1261712	1.2025280	0.0000000
C	-2.8275277	0.0000000	0.0000000
C	1.4147198	0.0000000	0.0000000
C	2.1045054	1.2400543	0.0000000
C	1.4137639	2.4487108	0.0000000
C	0.0216658	2.4425823	0.0000000
C	0.0216658	-2.4425823	0.0000000
C	1.4137639	-2.4487108	0.0000000
C	2.1045054	-1.2400543	0.0000000
H	-2.6372860	2.1682456	0.0000000
H	-0.5591128	3.3680794	0.0000000
H	3.1963988	1.1998339	0.0000000
H	3.1963988	-1.1998339	0.0000000
H	-0.5591128	-3.3680794	0.0000000
H	-2.6372860	-2.1682456	0.0000000
H	-3.9229787	0.0000000	0.0000000
H	1.9614894	-3.3973992	0.0000000
H	1.9614894	3.3973992	0.0000000

Cartesian coordinates in Angstrom of Hz (**1.2**) at the MP2/cc-pVDZ level.

N	-2.3770694	0.0167866	0.0000000
C	-1.2302088	-0.6816424	0.0000000
N	-0.0000035	0.0000018	0.0000000
C	0.0247821	1.4061780	0.0000000
N	-1.1300922	2.0913252	0.0000000

C	-2.2459412	1.3500242	0.0000000
C	1.2054004	-0.7245397	0.0000000
N	2.3761902	-0.0669661	0.0000000
C	2.2921121	1.2700625	0.0000000
N	1.2030653	2.0502198	0.0000000
N	-1.2460863	-2.0243537	0.0000000
C	-0.0461543	-2.6200497	0.0000000
N	1.1740040	-2.0669785	0.0000000
H	-3.1857918	1.9149024	0.0000000
H	-0.0655010	-3.7164210	0.0000000
H	3.2512947	1.8014504	0.0000000

Cartesian coordinates in Angstrom of **2.1** at the MP2/cc-pVDZ level.

C	-0.7292978	3.6862196	0.0000000
C	-0.0040452	2.4749592	0.0000000
N	-0.7261856	1.2577904	0.0000000
C	-2.1413550	1.2409829	0.0000000
C	-2.8277109	2.4747002	0.0000000
C	-2.1263455	3.6829384	0.0000000
C	-2.7962504	0.0000000	0.0000000
C	-2.1413550	-1.2409829	0.0000000
N	-0.7261856	-1.2577904	0.0000000
C	-0.0040452	-2.4749592	0.0000000
C	-0.7292978	-3.6862196	0.0000000
C	-2.1263455	-3.6829384	0.0000000
C	-2.8277109	-2.4747002	0.0000000
C	1.3981252	-2.4216239	0.0000000
C	2.1454002	-1.2339764	0.0000000
N	1.4523712	0.0000000	0.0000000
C	2.1454002	1.2339764	0.0000000
C	3.5570087	1.2115194	0.0000000
C	4.2526910	0.0000000	0.0000000
C	3.5570087	-1.2115194	0.0000000

B	0.0000000	0.0000000	0.0000000
C	1.3981252	2.4216239	0.0000000
H	-2.6741502	-4.6317640	0.0000000
H	-3.8889339	0.0000000	0.0000000
H	-2.6741502	4.6317640	0.0000000
H	1.9444670	3.3679156	0.0000000
H	1.9444670	-3.3679156	0.0000000
H	5.3483004	0.0000000	0.0000000
H	-3.9207361	-2.4500906	0.0000000
H	-3.9207361	2.4500906	0.0000000
H	-0.1614726	4.6205024	0.0000000
H	4.0822088	2.1704118	0.0000000
H	4.0822088	-2.1704118	0.0000000
H	-0.1614726	-4.6205024	0.0000000

Cartesian coordinates in Angstrom of Nz (**2.2**) at the MP2/cc-pVDZ level.

N	3.4842312	1.2145238	0.0000000
C	2.1335374	1.2174790	0.0000000
N	1.4327146	0.0000000	0.0000000
C	2.1335374	-1.2174790	0.0000000
N	3.4842312	-1.2145238	0.0000000
C	4.0562904	0.0000000	0.0000000
C	1.3918435	-2.4107437	0.0000000
C	-0.0124010	-2.4564371	0.0000000
N	-0.7163573	-1.2407672	0.0000000
B	0.0000000	0.0000000	0.0000000
C	1.3918435	2.4107437	0.0000000
C	-0.0124010	2.4564371	0.0000000
N	-0.7163573	1.2407672	0.0000000
N	-0.6903071	-3.6246947	0.0000000
H	5.1533873	0.0000000	0.0000000
N	-0.6903071	3.6246947	0.0000000
C	-2.1211364	-1.2389581	0.0000000

C	-2.1211364	1.2389581	0.0000000
C	-2.0281452	3.5128505	0.0000000
C	-2.0281452	-3.5128505	0.0000000
N	-2.7939241	2.4101709	0.0000000
N	-2.7939241	-2.4101709	0.0000000
C	-2.7836870	0.0000000	0.0000000
H	1.9368801	-3.3547748	0.0000000
H	-2.5766936	-4.4629643	0.0000000
H	-3.8737602	0.0000000	0.0000000
H	1.9368801	3.3547748	0.0000000
H	-2.5766936	4.4629643	0.0000000

Cartesian coordinates in Angstrom of **3.1** at the MP2/cc-pVDZ level.

C	-1.2143575	0.0000000	4.9822765
C	-1.2349458	0.0000000	3.5690907
N	0.0000000	0.0000000	2.8873311
C	1.2349458	0.0000000	3.5690907
C	1.2143575	0.0000000	4.9822765
C	0.0000000	0.0000000	5.6737176
C	-2.4269998	0.0000000	2.8193792
C	-2.4782067	0.0000000	1.4179996
C	-3.6662591	0.0000000	0.6729879
C	-3.7195022	0.0000000	-0.7341992
N	-2.5115608	0.0000000	-1.4627794
C	-2.4844906	0.0000000	-2.8731675
C	-3.7186463	0.0000000	-3.5619464
C	-4.9246499	0.0000000	-2.8560505
C	-4.9330330	0.0000000	-1.4586714
B	-1.2527563	0.0000000	-0.7360746
N	-1.2497769	0.0000000	0.7087960
B	0.0000000	0.0000000	1.4337763
N	1.2497769	0.0000000	0.7087960
C	2.4782067	0.0000000	1.4179996

C	3.6662591	0.0000000	0.6729879
C	3.7195022	0.0000000	-0.7341992
N	2.5115608	0.0000000	-1.4627794
C	2.4844906	0.0000000	-2.8731675
C	3.7186463	0.0000000	-3.5619464
C	4.9246499	0.0000000	-2.8560505
C	4.9330330	0.0000000	-1.4586714
B	1.2527563	0.0000000	-0.7360746
N	0.0000000	0.0000000	-1.4559217
C	0.0000000	0.0000000	-2.8743701
C	-1.2392465	0.0000000	-3.5307117
C	1.2392465	0.0000000	-3.5307117
C	2.4269998	0.0000000	2.8193792
H	0.0000000	0.0000000	6.7696094
H	-5.8736764	0.0000000	-3.4040513
H	5.8736764	0.0000000	-3.4040513
H	-4.6164788	0.0000000	1.2130589
H	-3.3697978	0.0000000	3.3723073
H	3.3697978	0.0000000	3.3723073
H	4.6164788	0.0000000	1.2130589
H	-1.2467256	0.0000000	-4.6236588
H	1.2467256	0.0000000	-4.6236588
H	-3.6973354	0.0000000	-4.6547666
H	3.6973354	0.0000000	-4.6547666
H	-5.8687629	0.0000000	-0.8937602
H	5.8687629	0.0000000	-0.8937602
H	2.1713971	0.0000000	5.5102593
H	-2.1713971	0.0000000	5.5102593

Cartesian coordinates in Angstrom of Dz (**3.2**) at the MP2/cc-pVDZ level.

B	-0.7169416	1.2417793	0.0000000
N	-1.4439754	0.0000000	0.0000000
B	-0.7169416	-1.2417793	0.0000000

N	0.7219877	-1.2505193	0.0000000
B	1.4338832	0.0000000	0.0000000
N	0.7219877	1.2505193	0.0000000
N	2.8682226	0.0000000	0.0000000
N	-1.4341113	2.4839536	0.0000000
N	-1.4341113	-2.4839536	0.0000000
C	1.4275984	2.4726730	0.0000000
C	1.4275984	-2.4726730	0.0000000
C	-2.8551968	0.0000000	0.0000000
C	-2.8401170	2.4816614	0.0000000
C	-0.7291233	3.7004441	0.0000000
C	3.5692403	1.2187828	0.0000000
C	3.5692403	-1.2187828	0.0000000
C	-2.8401170	-2.4816614	0.0000000
C	-0.7291233	-3.7004441	0.0000000
N	-1.4084135	4.8701842	0.0000000
N	-3.5134965	3.6548140	0.0000000
C	-2.7463162	4.7567593	0.0000000
N	4.9219100	-1.2153703	0.0000000
N	4.9219100	1.2153703	0.0000000
C	5.4926325	0.0000000	0.0000000
N	-1.4084135	-4.8701842	0.0000000
N	-3.5134965	-3.6548140	0.0000000
C	-2.7463162	-4.7567593	0.0000000
C	0.6750714	3.6646625	0.0000000
C	2.8361552	2.4169602	0.0000000
C	0.6750714	-3.6646625	0.0000000
C	2.8361552	-2.4169602	0.0000000
C	-3.5112265	-1.2477023	0.0000000
C	-3.5112265	1.2477023	0.0000000
H	-3.2950197	5.7071415	0.0000000
H	6.5900394	0.0000000	0.0000000
H	-3.2950197	-5.7071415	0.0000000

H	3.4152579	3.3420343	0.0000000
H	1.1866576	4.6287172	0.0000000
H	-4.6019155	1.2866830	0.0000000
H	-4.6019155	-1.2866830	0.0000000
H	3.4152579	-3.3420343	0.0000000
H	1.1866576	-4.6287172	0.0000000