# Predicted High-Energy Density MN<sub>8</sub> Containing Anionic 18-crown-6 Ring-based Polynitrogen Monolayers Acting as Cryptand

Sylvain Pitié,<sup>†,‡</sup> Busheng Wang,<sup>\*,†,‡</sup> Frédéric Guégan,<sup>†</sup> and Gilles Frapper<sup>\*,†</sup>

†Applied Quantum Chemistry Group, E4 Team, IC2MP UMR 7285, Université de Poitiers - CNRS, Poitiers 86073, France ‡Contributed equally to this work

E-mail: wangbs123@gmail.com; gilles.frapper@univ-poitiers.fr

#### Abstract

In this study, we investigate the potential of the 18-crown-6-like two-dimensional (2D)-N<sub>8</sub> structure to accommodate electrons from metals without compromising its covalent nitrogen network. To address this inquiry, a series of M@2D-N<sub>8</sub> complexes were examined, with M representing a metal likely to exhibit a range of oxidation states. Because of the layered structure of the parent bulk 2D-N<sub>8</sub> structure, several polymorphs were additionally studied to ensure the correct global minimum energy structures were located on their respective potential energy surface. Employing our crystal structure prediction enhanced by evolutionary algorithm and density functional theory methodology, we successfully predicted the existence of 16 layered M@2D-N<sub>8</sub> complexes from a total of 39 MN<sub>8</sub> systems investigated at 100 GPa (M = s-block Na-Cs, Be - Ba and d-block Ag, Au, Cd, Hg, Hf, W, and Y). Among those, there are 13 quenchable M@2D-N<sub>8</sub> compounds, which are dynamically stable at 1 atm. Orbital interactions and bonding analysis show that the 2D-N<sub>8</sub> presents a flat localized  $\pi^*$  band

that can accommodate one or two electrons without breaking the 2D covalent nitrogen network. Depending on the metal-to-polynitrogen charge transfer (formally 1 to 4 electrons), these N-rich phases are semiconducting or metallic at ambient conditions. Ab initio molecular dynamics simulations show that the  $K(I)@2D-N_8$  and  $Ca(II)@2D-N_8$ are thermally stable up to 600 K, while the  $Hf(IV)@2D-N_8$  compound is thermally not viable at 400 K because of the weakening of the N=N bonds due to a strong 4-electron reduction. These metal 18-crown-6 ring-based polynitrogen compounds, as expected due to their high nitrogen content (8 nitrogen atoms per metal), could potentially serve as new high-energy density materials. Metallic  $2D-N_8$  intercalation compounds, specifically  $K_x$ @2D-N<sub>8</sub> with x = 0.5 and 0.75, are predicted to be stable at ambient pressure. The stoichiometric number of alkali has the capability to modulate the Fermi level, thereby crossing a peak in the high density of states spectrum, which could indicate the potential presence of superconductivity. Finally, we show that the 2D 18crown-6 polynitrogen  $2D-N_8$  net functions as a cryptand which can stabilize oxonium  $H_3O^+$  and ammonium  $NH_4^+$  cations through hydrogen bonding, opening up possibilities for designing other intercalated guest-species within this  $\pi$ -conjugated layered 2D-N<sub>8</sub> allotrope.

#### **KEYWORDS**:

HEDM, polynitrogen, layered material, 2D cryptand, DFT, evolutionary algorithm, nanopore.

## 1 Introduction

Polynitrogen-containing materials have been extensively studied as high energy density materials due to the significant difference in average bond energy between N-N single or double bonds (160 and 418 kJ/mol, respectively) and triple bonds (954 kJ/mol) in the N<sub>2</sub> molecule, which contributes to an impressive energy content of polynitrogen compounds. While various theoretical studies predicted that pure nitrogen would have stable polymeric phases - see prior *in silico* extended covalent allotropes of nitrogen-<sup>1-4</sup> it was not until 2004 that the experimental synthesis of the cubic gauche structure (cg-N) took place at extremely

high pressures and temperatures (110 GPa, 2000 K).<sup>5</sup> This three-dimensional covalent material, composed of single-bonded tricoordinated nitrogen atoms, has a remarkable property: its estimated energy capacity is over five times greater than that of the most potent nonnuclear energetic substances. However, upon release of pressure to ambient conditions, cubic gauche nitrogen undergoes transition to the molecular phase. The weak N-N bonds do not hinder bond cleavage due to the low activation barrier. An effective method of increasing the stability of a polynitrogen compound is to establish a nitrogen network consisting of single and double bonds, and to form nitrogen-rich alloys with other elements. Stabilizing the bond between metal cations and anionic polynitrogen motifs allows the formation of new high-energy density materials (HEDMs). Linear double-bonded azide  $N_3^-$  and aromatic 5-ring pentazolate  $N_5^-$  are two experimental molecular motifs that illustrate this concept. Their salts are known to be viable under ambient conditions.<sup>6-8</sup> The quest of materials with a high nitrogen content remains a coveted goal in scientific research. This is due to their significant chemical value and potential as eco-friendly, HEDMs.

A fruitful approach to obtain "polymerized nitrogen" involves adjusting the pressure to overcome the significant kinetic barriers present in the reaction of metal M and N<sub>2</sub>, while also achieving thermodynamic stabilization of the resultant  $M_x N_y$  products.<sup>9</sup> A few examples of such high-pressure products containing polynitrogen units are  $K_2 N_6$ ,<sup>10</sup> YN<sub>6</sub>,<sup>11</sup> TaN<sub>5</sub>,<sup>12</sup> and TiN<sub>2</sub>.<sup>13</sup> Alongside these characterized polynitrogen anionic motifs, there is an expanding collection of proposed polynitrogen networks arising from thorough intensive crystal structure prediction (CSP) studies. A large number of metal-nitrogen binary systems under pressure have been studied in the last decade yielding new (meta)stable nitrogen-rich compounds, such as Ti-N,<sup>14</sup> Mg-N,<sup>15</sup> Ba-N,<sup>16</sup> and Sn-N,<sup>17</sup> from our research among others. Molecular, one-dimensional, and few two-dimensional polynitrogen networks have been predicted, with a few being successfully synthesized (e.g. TiN<sub>2</sub>,<sup>14</sup> MgN<sub>4</sub>,<sup>15</sup>), although most have not yet been investigated experimentally by high-temperature/high pressure (HT/HP) techniques.

In this active field, our team has recently proposed a new two-dimensional (2D) nitrogen allotrope, henceforth referred to as  $2D-N_8$ , a phase derived from the predicted high-pressure stable layered  $Xe@N_8$  compound at 100 GPa.<sup>18</sup> Figure 1 displays the covalent network of this 2D nitrogen structure. Within the extended covalent nitrogen monolayer, each 18-ring unit contains six N=N moieties and six 3-coordinated  $sp^3$  nitrogen atoms, which can be formally reduced via an oxidizing agent. Furthermore, the approximately 5 Å hole has the capacity to accommodate a cation, which is stabilized by the bonding of lone pairs from the nearest  $\mathrm{sp}^2$  nitrogen atoms. In M@2D-N\_8, each 18-crown-6 moieties can play the role of a cryptand that is able to complex a cation (electropositive metal M). Additionally, the layered nature of the bulk  $N_8$  structure enables cation intercalation between monoatomic nitrogen layers. This opens up possibilities for tuning the electronic properties of  $M@2D-N_8$  materials through charge transfer from M to the nitrogen network. Moreover, the anisotropy of the binding forces in these layered materials may provide intriguing characteristics. Finally, it is conceivable that a sea of cations could stabilize  $2D-N_8$ . The imbalance caused by the reduction of the N=N units in  $M@N_8$  could be compensated for by the ionic bonding between cations and anionic polynitrogen sheets. Ultimately, the existence of  $M@2D-N_8$  can boost the feasibility of such a nitrogen-rich systems and expand the hypothetical HEDMs.



Figure 1: Schematic structure of the  $2D-N_8$  monolayer. N<sup>d</sup> and N<sup>t</sup> refer to 2- and 3- coordinated nitrogen atoms, respectively.

## 2 Methodology

To address these hypotheses, we have conducted an *in silico* investigation of M@2D-N<sub>8</sub> using *ab initio* crystal structure prediction (CSP) searches. From the only knowledge of the composition (1 M, 8 N), the lowest energy phase on the potential energy surface (PES), i.e., global minimum, is determined using the evolutionary algorithm (EA) method implemented in the USPEX code,<sup>19–21</sup> as well as metastable phases, i.e., local minima. This CSP technique has demonstrated success in predicting a vast range of chemical systems (e.g., clusters, polymers, surfaces, 2D and bulk materials).<sup>22</sup> We then extensively conducted EA-DFT CSP searches for the MN<sub>8</sub> compounds at 100 GPa, where M represents alkali (Li to Cs), alkaline earth (Be to Ba), and 29 d-block (Sc to Zn, Y to Cd, and Hf to Hg) elements, utilizing the fixed-composition (FC) EA combined with DFT calculations at the Perdew-Burke-Ernzerhof (PBE) gradient-corrected exchange and correlation functional.<sup>23</sup> The total number of atoms included in the primitive cell is up to 36 for FC-EA searches (Z = 1-4), unless otherwise stated. Find detailed information in Section S1 regarding to the CSP-EA DFT methodology, including the different levels of theory applied to fully explore the potential energy surfaces.

All structure relaxations (shape, volume, and atomic positions) and energy calculations were carried out using the the Vienna Ab Initio Simulation Package (VASP).<sup>24,25</sup> We carefully checked the viability - thermodynamic, dynamic, and thermal stabilities- of selected predicted compounds, and the methodological details to optimize chosen low-energy M@2D-N<sub>8</sub> candidates, determine their electronic and bonding properties, and the M@2D-N<sub>8</sub> kinetic and thermal stabilities through *ab initio* molecular dynamics (AIMD) simulations are given in the Supporting Information (SI). In the following, the structural parameters and enthalpies are presented at the r<sup>2</sup>SCAN+rVV10 level of theory.<sup>26–29</sup> The r<sup>2</sup>SCAN revision of the strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation (meta-GGA) coupled with rVV10 for dispersion forces is recommended as stable, general-purpose meta-GGAs for materials discovery. Meanwhile, the band structure and energy gap are determined using the hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional level of theory.<sup>30</sup> Dynamic stability of the structures is established by the absence of imaginary phonon frequencies, which are computed using the finite displacement method implemented in the PHONOPY code.<sup>31</sup> To perform chemical bonding analysis, we carry out crystal orbital bond index<sup>32</sup> (COBI), crystal overlap Hamilton population (COHP), using the LOBSTER package<sup>33</sup>), and electron localization function<sup>34</sup> (ELF) from the optimized geometries obtained from VASP. Finally, images of the crystalline structures are produced using VESTA software.<sup>35</sup> Additional details for the USPEX, VASP, and PHONOPY calculations are provided in Section S1 of the SI.

# 3 Results and discussion

We start our discussion on novel predicted  $MN_8$  with M being a s-block element. The global minima for  $MN_8$  all contain the extended 2D network of 18-crown-6 with M representing an alkali or alkaline-earth metal, with the exception of LiN<sub>8</sub> and BeN<sub>8</sub> that exhibit alternative ground-state structures, i.e., a one-dimensional anionic polynitrogen chain,  $-(N=N-N_6^-)_n$  (see Figure S2). The ground-state structures of high-pressure LiN<sub>8</sub> and BeN<sub>8</sub> phases are discussed in Section S5.1. The smaller size of the Li<sup>+</sup> and Be<sup>2+</sup> cations can explain the dynamical instability of the 18-ring-based *R*-3 LiN<sub>8</sub> and *Cc* BeN<sub>8</sub> stationary points on the 1:8 MN<sub>8</sub> PES at 100 GPa, but also the more compact volume of their ground-state phases; 5.642 Å<sup>3</sup>/atom for *R*-3 Li@2D-N<sub>8</sub> vs 5.468 Å<sup>3</sup>/atom for ground-state *P*-1 LiN<sub>8</sub> and 5.653 Å<sup>3</sup>/atom for *Cc* Be@2D-N<sub>8</sub> vs 5.357 Å<sup>3</sup>/atom for ground-state *P*-1 BeN<sub>8</sub> (see figure S2).

Table 1 summarizes the dynamically stable ground-sate  $M@2D-N_8$  systems discovered at 1 atm and 100 GPa (T = 0 K). All these 18-ring-based phases exhibit no imaginary frequencies in their complete phonon dispersion curves, as demonstrated in the Section S6.

Over 80000 different structures of bulk  $MN_8$  were examined at 100 GPa through extensive EA-DFT CSP searches resulting in the identification of 11 different low-lying layered  $M@N_8$ 

Table 1: Predicted M@2D-N<sub>8</sub> Phases at 0 and 100 GPa. The Calculated Enthalpy of Formation ( $\Delta H_f$ ) and the Velocity of Detonation (VoD) for Predicted M@2D-N<sub>8</sub> Phases at 0 and 100 GPa. The  $\Delta H_f$  and VoD Are Given in meV/atom and km.s<sup>-1</sup>, Respectively, at the r<sup>2</sup>SCAN+rVV10 Level of Theory.

М	Pressure	Space group	$\Delta H_f{}^a$	VoD
	(GPa)		(meV/atom)	$(\mathrm{km.s}^{-1})$
Na	0	Cc	526	13.1
	100	Cc	-624	/
Κ	0	P6/m	495	12.4
	100	P6/mcc	-598	/
Rb	0	P6/mcc	502	11.5
	100	P6/mcc	-487	/
Cs	0	P/6m	516	10.4
	100	P/6m	-202	/
Mg	0	Cc	462	13.9
	100	Cc	-729	/
Ca	0	Cc	219	10.9
	100	Cc	-1033	/
Sr	0	Cc	243	10.2
	100	Cc	-998	/
Ba	0	Cc	256	10.1
	100	Cc	-655	/
Au	0	<i>P</i> -1	991	16.0
	100	<i>P</i> -1	200	/
Cd	0	$P2_1$	757	14.9
	100	Cc	-313	/
Hf	0	$P2_1$	311	13.8
	100	$P2_1$	-655	/
Hg	0	Pm	868	14.7
	100	<i>P</i> -1	-55	/
W	0	<i>P</i> -1	881	17.9
	100	Cc	-303	/

<sup>a</sup> See Section S4.1 and Table S5.

prototypes which constitute our  $M@N_8$  database. In each prototype, M is substituted by the desired metal either from the s- or d-block elements. Those structures were fully optimized using different functionals (refer to Table S5).

Among the 11 optimized prototypes, the 5 low-energy phases of M@2D-N<sub>8</sub> are lying in an energy window of 7 kJ.mol<sup>-1</sup> and 9 kJ.mol<sup>-1</sup>, at 0 and 100 GPa, respectively. The difference in weak forces related to e.g., the layer stacking, cation intercalation sites, cation-cation interatomic separation, should govern the thermodynamic stability of M@2D-N<sub>8</sub>. Therefore, depending on the experimental conditions of their synthesis, e.g., temperature, crystallization process, reactants, it can be expected that M@2D-N<sub>8</sub> can crystallize in different space groups, but all exhibiting the 18-crown-6 topology for the two-dimensional covalent nitrogen network. We note that our EA-DFT CSP searches successfully recovered the P6/mcc KN<sub>8</sub> at 70 GPa as previously reported by Steele and Oleynik.<sup>36</sup> However, no information regarding the quenchability of this high-pressure phase K@2D-N<sub>8</sub> under ambient pressure was provided.

Let start our structural, energetic, and electronic density analysis on M@2D-N8 with M an alkali or alkaline earth metal. The calculated enthalpy of formation ( $\Delta H_f$ ) and the velocity of detonation (VoD) for predicted s-block M@2D-N<sub>8</sub> phases at 0 and 100 GPa are presented in Table 1. Their low-energy phases crystallize into three different space groups, namely P6/m (Z = 1), P6/mcc (Z = 2), and Cc (Z = 2). These phases differ mainly by the oxydation state of the metal and the repulsive cation-cation interactions; for the alkaline earth dications (Cc phases) the larger M-M separations are the more stable is the phase. We note that the ground-sate M@2D-N<sub>8</sub> is not found by 'direct'' USPEX CSP EA-DFT searches, but from our collected 11 prototypes (See Section S3). Nevertheless, the energy difference between USPEX-based phase and polytypes-based one is tiny (< 0.030 eV/atm, 3 kJ/mol at PBE level of theory).



Figure 2: Crystal structures at 0 GPa of (a) P6/m K@N<sub>8</sub> and (b) Cc Ca@N<sub>8</sub> at the r<sup>2</sup>SCAN+rVV10 level of theory. Distances are given in Angströms. Nitrogen, potassium, and calcium atoms are represented in grey or darkblue, purple, and green spheres, respectively.

These structures exhibit notable distinctions in comparison to the stacking of  $2D-N_8$  monolayers, specifically regarding the positioning of the cations. They can either be found within the hole of 18-crown-6 moieties (referred to as an intralayer position) or situated between two layers (as depicted in Figure 2). As a result, the separation between cations is greater in the *Cc* phase compared to the *P6/m* phase. For instance in Ca@2D-N<sub>8</sub> at 0 GPa, the cation-cation separation measures 4.10 Å in the *Cc* phase compared to 3.17 Å in the *P6/m* phase . Similarly, at 100 GPa, these distances are 2.97 Å and 2.33 Å, respectively. Such a characteristic elucidates the slight energy variation observed in the studied s-block M@2D-N<sub>8</sub> phases.

Following the Zintl-Klemm concept,<sup>37</sup> when electropositive M is intercalated in bulk 3D- $N_8$ , the electropositive element gives one electron (alkali cation) or two electrons (alkaline earth dication) to the polynitrogen network  $N_8$  (See our ELF analysis in Section S8). The

closest M—N interatomic separations of  $\sim 2.4$  Å (M = Mg) - 3.2 Å (M = Cs) are calculated in M@2D-N<sub>8</sub> phases at 0 GPa at the  $r^2SCAN+rVV10$  level of theory, an expected range of such ionic bonds.<sup>38</sup> The cation  $M^{n+}$  (n = 1, 2) is eventually stabilized through ionic bonding to polynitride  $(N_8)^{n-}$  network in alkali/alkaline earth-based M@2D-N<sub>8</sub>. Thus, due to this charge transfer, one can expect a structural modification of the two-dimensional covalent polynitrogen framework. The main structural feature that happens is related to the elongation of the six  $N^d = N^d$  units of the 18-ring, as expected for the reduction of a double-bond molecular unit. The  $N^d$ - $N^d$  bond distance is going from 1.26 Å in pure 2D- $N_8$  to, e.g., 1.31 Å in K@2D-N<sub>8</sub> and 1.36 Å in Ca@2D-N<sub>8</sub>. This bonding effect is well reflected by the crystal orbital bond index (COBI)? analysis. From pure 2D-N $_8$  to K@N $_8$ , the averaged ICOBI of  $N^d$ - $N^d$  bond are 1.64 and 1.30, illustrating the  $N^d$ - $N^d$  elongation upon one electron transfer from K to 2D-N<sub>8</sub>. In the alkali series, Na to Cs, the N<sup>d</sup>-N<sup>d</sup> ICOBI values do not significantly vary, a signature of the full electron transfer from electropositive metal to the polynitrogen 2D network. Furthermore, the  $N^t-N^d$  ICOBI – formally the single N-N bond depicted in a resonant structure - are 1.09 (pure  $N_8$ ) and 1.15 (K@2D-N<sub>8</sub>). The  $\pi$ delocalization, represented by the symbol  $\delta$ , indicates the variance between the N<sup>d</sup>-N<sup>d</sup> and  $\mathrm{N}^t\text{-}\mathrm{N}^d$  COBIs values. The pure 2D-N\_8 structure displays a  $\delta$  value of 0.55, while the K@2D- $N_8$  structure exhibits a lower  $\delta$  value of 0.15. The introduction of K atoms into the layers of 2D-N<sub>8</sub> promotes enhanced delocalization of the  $\pi$  electrons within the 18-ring layer.

In K@2D-N<sub>8</sub>, the polynitrogen ring is flat, while the 2D covalent N<sub>8</sub> monolayer, P-3 phase, is slightly buckled (as well in bulk 3D-N<sub>8</sub>) at atmospheric pressure with a calculated layer thickness of 0.2 Å (0.2 Å in bulk *R*-3). This buckling is related to the expected pyramidalization of sp<sup>3</sup>-N, as encountered for instance in the mixing of symmetry-allowed s/p orbitals when NH<sub>3</sub> goes from planar to pyramidal trigonal configurations.<sup>39</sup> This known Jahn-Teller effect stabilizes the buckled structure and opens a band energy gap (1.4 eV in P-3 2D-N<sub>8</sub> at HSE06//r<sup>2</sup>SCAN+rVV10 level of theory). In the formal intercalation of K atoms into the layered 3D-N<sub>8</sub> compound, a notable change occurs in the structure of each

nitrogen layer, specifically the 2D-N<sub>8</sub>. The originally trigonal pyramidal N<sup>t</sup> atom becomes trigonal planar, resulting in a flat configuration. The energy difference between these two structures is relatively small, approximately 30 meV/atom, as denoted by  $\Delta$ H(buckled *P*-3 - planar *P*6/*m*). This observed buckled-to-planar phenomenon appears to be linked to the chemical precompression induced by K.



Figure 3: A scheme of the  $\pi^*$  at  $\Gamma$  k-point is indicated in (a). The p<sub>z</sub> denotes the 2p<sub>z</sub>(N)  $\pi$  orbital that is perpendicular to the N<sub>8</sub> monolayer. The calculated projected band structures at the HSE06//r<sup>2</sup>SCAN+rVV10 level of theory for (b) P6/m 2D-N<sub>8</sub>, (c) P6/m 3D-N<sub>8</sub>, (d) P6/m K@2D-N<sub>8</sub>,(e) Cc Ca@2D-N<sub>8</sub> and (f) P2/m K<sub>0.5</sub>@2D-N<sub>8</sub> at 0 GPa.

In order to comprehend the effects of M-to-N charge transfer on the structural and electronic characteristics of  $M@2D-N_8$ , a thorough examination of the electronic structures of pure hexagonal P6/m 2D-N<sub>8</sub> followed by P6/m M@N<sub>8</sub> was conducted. In the manuscript, M = K was chosen as a case study, utilizing the rigid band model. The HSE06 band structure of the hypothetical high-symmetry P6/m 2D-N<sub>8</sub> is shown in Figure 3 (b). In 2D-N<sub>8</sub>, there are 8  $\pi$  bands per unit cell, and 5 are fully occupied. This electron count of 10  $\pi$  electrons per unit cell follows the 4n+2 Hückel aromaticity rule. From the band structure of P6/m $2D-N_8$ , one can see a flat band at approximately 0.25 eV, not dispersed in energy along the entire K-paths, and  $\pi$  (2p<sub>z</sub> N) in character. This 6th  $\pi$  band, lowest unoccupied orbital, is mainly based on the molecular  $\pi^*(N_2)$  orbital of each  $N_2$  unit. Its localized antibonding character is demonstrated by the analysis of the COBI curve (see Section S8). Due to the symmetry property of the P6/m space group, i.e., the presence of a 2<sub>1</sub> glide plane, no 2p(N) atomic contribution can appear on each tri-coordinated sp<sup>2</sup> nitrogen N<sup>t</sup> of 2D-N<sub>8</sub>, as illustrated in the Bloch orbital displayed in Figure 3 (a). Therefore, the localization of the  $\pi_6$ band on the N<sub>2</sub> units elucidates the non-delocalized nature of the band, thereby providing a comprehensive explanation for the principal structural effect observed in  $K@2D-N_8$  and Ca@2D-N\_8. Occupancy of this 6th  $\pi^*$  band by one and two electrons in K@2D-N\_8 and Ca@2D-N<sub>8</sub>, respectively, is predicted to result in an elongation of the  $N^d$ - $N^d$  bond length, consistent with our observations of the transition from pure 2D-N $_8$  (1.28 Å) to Ca@2D-N $_8$ (1.37 Å). In layered bulk 2D-N<sub>8</sub>, the staking of the nitrogen monolayers leads to a weak but significant  $\pi - \pi$  overlapping along the {c}-axis, as shown in its band structure (see  $\Gamma$ -A dispersion band by roughly 1.8 eV at HSE06 level of theory). This  $\pi_6^*$  band leads to a sharp spike in the calculated density of states (DOS) diagram of P6/m K@2D-N<sub>8</sub> (see Figure S5). The Fermi level cuts this high density of states peak, conferring a metallic property to this compound, in perfect agreement with previous findings at 80 GPa.  $^{36}$  All alkali-based phases  $M@2D-N_8$  demonstrate intrinsic metallicity with several bands crossing the Fermi level at both 0 and 100 GPa (see their HSE06 band structures in Figure S5).

In Ca@2D-N<sub>8</sub> (1 atm), Ca atom gives two electrons to the N<sub>8</sub> monolayer that fully occupy this  $\pi_6^*$  band. An indirect energy gap of 0.30 eV is calculated between the valence ( $\pi_6^*$ ) and conduction ( $\pi_7^*$ ) bands at the HSE06 level of theory (see Figure S5). To summarize, the lowermost conduction bands have the potential to accommodate one or two electrons from the electropositive s-block M element without breaking the polynitrogen 2D-N<sub>8</sub> network.

We have showed that M@2D-N<sub>8</sub> compounds with M = Na, K, Rb, Cs, Mg, Ca, Sr, and Baare thermodynamical stable phases at 100 GPa, and metastable compounds at atmospheric pressure. The peculiar existence of a localized  $\pi^*(N_2)$  band allows the transfer of one and two electrons from intercalated metals into  $2D-N_8$  layers without breaking the covalent polynitrogen 18-ring network at both 1 atm and up to at least 100 GPa. It is important to note that this statement is made under static DFT calculations (0 K), thus we also evaluated the kinetic and thermal stabilities of  $M@2D-N_8$  (M = K, Ca as illustration) by performing *ab initio* molecular dynamics simulations at temperatures in the range of 300 - 1000 K (see Section S9). All the nitrogen atoms in the 2D layers vibrate only slightly around their equilibrium positions during annealing at 300 K for 10 ps, indicating the stability of the layered structure at room temperature. Despite the fluctuation of the atoms positions, the whole structure is maintained at 800 K and 600 K for K@2D-N<sub>8</sub> and Ca@2D-N<sub>8</sub>, respectively, while the system exhibits nitrogen-nitrogen bond breaking at 1000 K and 800 K, respectively. This indicates that the dynamically stable  $M@2D-N_8$  (M = K, Ca) structures are definitely viable up to about 600 K: no structural transformations are observed in the nitrogen network, indicating the existence of substantial kinetic barriers leading to the trapping of this metastable layered  $M@2D-N_8$  compounds.

It has been shown that the intercalated s-block M(I or II)@2D-N<sub>8</sub> 1:8 compounds, which are predicted to exist at high pressure, can be quenchable to ambient conditions. Following the example of graphite intercalation compounds such as the superconducting CaC<sub>6</sub> at 1 atm,<sup>40</sup> we have investigated the stoichiometric modulation of the metal intercalant M into the interlayer spaces of  $M_x$ @2D-N<sub>8</sub> (x = 0.5 - 1; M = K as an example). We have chosen two K-doped 2D-N<sub>8</sub> polytypes with x = 0.5 and 0.75, both of which are dynamically stable and metallic, see Figures S14 and S16 for the optimized crystals and band structures of  $K_x@2D-N_8$ . We demonstrate the ability to tune the Fermi level crossing a high DOS peak by modulating the alkali concentration in conjugated layered  $M_x@2D-N_8$ . Whether this doping effect is beneficial for superconductivity in ambient pressure layered compounds needs to be further investigated in the future. Interestingly, we find that the  $\pi$ -electron concentration, i.e. the number of  $\pi$ -electron per atom in a 2D  $\pi$ -conjugated polymer, ranges from 1.31 to 1.34 in  $M_x@2D-N_8$  ( $0.5 \le x \le 0.75$ , M alkali) while it is 1.33 in superconducting CaC<sub>6</sub>. Simulation and analysis of the superconducting properties would be the next step in substantiating this ' $\pi$ -electron concentration' hypothesis and studying the doping-critical temperature (Tc) relationship in bulk 2D  $\pi$ -conjugated polymers in more detail.

Following our study of the stability of the 18-crown-6-like  $2D-N_8$  compound in a reduction process by embedded metals, we can ask wether this layered structure is capable of acepting more than 2 electrons without breaking its covalent nitrogen net? To answer this question, we have studied several  $M@2D-N_8$  where M is a transition metal because of their diversity of oxidation states, and the ability of the cation to be stabilized by a cryptand in different structural forms. We predicted 6  $M@2D-N_8$  as global minima of their respective  $MN_8$  PES over the investigated d-block based 29  $MN_8$  systems at 100 GPa using our CSP EA-DFT approach. M are Ag, Au, Cd, Hf, Hg, and Y. We note that the polynitrogen network in the predicted ground-state MN<sub>8</sub> phases (global minimum; M, d-block element; at 100 GPa) is mainly based on one-dimensional polynitrogen chains containing two-coordinated N atoms (anionic polyacetylene-like all-N chains). Nevertheless, our preliminary results show that 18rings  $2D-N_8$  motifs may show up in thermodynamically metastable but dynamically stable  $M@2D-N_8$  phases (local minima on the PES, such as  $W@2D-N_8$ ). These findings will be the subject of a dedicated publication. The crystal structure of each selected ground-state or metastable  $M@2D-N_8$  at 0 and 100 GPa is listed in Table S4. Beside the 7 selected dynamically (meta)stable high-pressure compounds (M = Ag, Au, Cd, Hf, Hg, and Y, global minima; W, local minima), only 2 are not quenchable to 1 atm, namely Ag and Y; Cc Ag@2D-N<sub>8</sub> and Cc Y@2D-N<sub>8</sub> present imaginary frequencies in their phonons dispersion curves at 1 atm (see Figure S4). In this study, we focus our discussion on two new dynamically stable M@2D-N<sub>8</sub> containing a transition metal with an oxidation state higher than 2, namely Hf@2D-N<sub>8</sub>, and W@2D-N<sub>8</sub>, both predicted at 0 and 100 GPa.

Hafnium and tungsten are known high oxidation transition metals, known to accept oxidation numbers up to +IV and +VI respectively. Bader charge were computed for both  $M@2D-N_8$  structures, and the charges obtained are comparable to those obtained for formal  $Hf^{4+}$  and  $W^{3+}$  ions in nitrides (see S8.4). This analysis allows us to state that 4 and 3 electrons from Hf and W, respectively, are transferred from M to  $\mathrm{N}_8$  network. These high-pressure phases present two-dimensional covalent polynitrogen monolayers containing 18-rings which are strongly buckled (see Figure S21 and S25). Their quenchable phases are also dynamically stable at ambient pressure and 0 K. Their structures, depicted in Figure 4, present non-planar nitrogen monolayers in which the metal sits in the void of each 18-ring. Adding more electrons than 2 to  $2D-N_8$  leads formally to the partial occupation of the disperse  $\pi^*$  bands as shown in the 2D-N<sub>8</sub> band structure in Figures 3 and S5. This hypothetical situation leads to an electronic instability that is elevated mainly through the pyramidalization of the tri-coordinated nitrogen atoms, i.e. a s/p orbital hybridization. This is what happens in Hf@2D-N $_8$  and W@2D-N $_8$  with a layer thickness of 0.9 and 1.0 Å, respectively. This deformation allows Hf to make bonds between the nitrogen net, as shown by the COBI and ELF calculations (see Section S8.5). Moreover, the ELF calculation of the  $W@2D-N_8$ illustrates the presence of a metallic bond between the tungsten atoms (see Figure 3(d) and Section S8.6 in SI). The interatomic distance between the tungsten atoms is observed to be 3.0 Å, which is in close proximity to the established distance of 2.8 Å in the W Im-3m crystal structure.<sup>41</sup> This suggests the formation of an infinite metallic chain denoted as  $(W)_n$ running across the pores of the  $2D-N_8$  monolayers.



Figure 4: Crystal structures at 0 GPa of  $P2_1$  Hf@2D-N<sub>8</sub> (a) and (b), and P-1 W@2D-N<sub>8</sub> (c) and (d) at the r<sup>2</sup>SCAN+rVV10 level of theory. On Figure (d) the ELF on the  $\bar{1}00$  plane is displayed, illustrating the delocalized bonding along the infinite W-W chains (dotted area). Distances are given in Angströms. Nitrogen, hafnium, and tungsten atoms are represented in grey or darkblue, yellow, and brown spheres, respectively.

As we mentioned in the introduction of this study, potentially all the compounds we investigated could be candidates for HEDMs. To quantify this, we evaluated the energy density and velocity of detonation (*VoD*) for all quenchable M@N<sub>8</sub> phases (M = Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Au, Cd, Hg, Hf, and W), which are dynamically stable at ambient pressure, using the Kamlet–Jacobs empirical equation<sup>42</sup> (details of the calculations and other detonation properties are given in S1.5 and S10, respectively). We assume that the decomposition products are M(s) and N<sub>2</sub>(g). All the unary phases are taken from the valuable Materials Project databank,<sup>43</sup> and fully optimized at the r<sup>2</sup>SCAN+rVV10 level of theory. From Table 1, one may see that the detonation velocity ranges from 10.1 to 17.9 km.s<sup>-1</sup>, which is higher than the experimentally determined range of the secondary explosive cyclotetra-methylene tetranitramine  $(CH_2)_4(NNO_2)_4$  HMX ( $VoD \sim 9.1 \text{ kms}^{-1}$ ), explosive 2,4,6-trinitrotoluene (TNT) ( $VoD \sim 6.9 \text{ kms}^{-1}$ ), and primary explosive lead azide  $Pb(N_3)_2$  ( $VoD \sim 3.8 \text{ kms}^{-1}$ ). The release of a large amount of gaseous N<sub>2</sub> during the decomposition reaction of M@2D-N<sub>8</sub> in confers to these layered polynitrogen compounds potential applications in propellants and explosives.



Figure 5: Crystal structures at 0 GPa of (a)  $P1 (H_3O^+)@2D-(N_8^-)$  and (b)  $Ccc2 (NH_4^+)@2D-(N_8^-)$  at the r<sup>2</sup>SCAN+rVV10 level of theory. Dashed lines illustrate the O(N)-H—N hydrogen bonds. Distances are given in Angströms. Nitrogen, oxygen, and hydrogen atoms are represented in grey, red, and white spheres, respectively.

Finally, we conducted a prospective study to investigate the stabilizing capability of 18crown-6 2D-N<sub>8</sub> towards molecular cations. Specifically, we focused on oxonium  $(H_3O^+)$  and ammonium  $(NH_4^+)$  cations as representative prototypes. It is noteworthy that both oxonium and ammonium ions, akin to alkali cations, possess a propensity to form stable complexes with crown ethers, cryptands, and other cyclic and polycyclic polyethers.<sup>44–46</sup>Therefore, we sought to explore the interaction between the 2D multidentate ligands 2D-N<sub>8</sub> and these molecular monocations. To achieve this, we first substituted M<sup>+</sup> with H<sub>3</sub>O<sup>+</sup> or NH<sub>4</sub><sup>+</sup> in various M(alkali)@2D-N<sub>8</sub> phases at pressures of 0 and 50 GPa. Subsequently, we examined different spatial arrangements of each molecular guest in the interlayer region and successfully located a dynamically stable phase for each cation on the PES. Detailed structures of these stable phases can be found in Figure 5 and Figure S38. The triclinic crystal structure of  $(H_3O^+)@2D-(N_8^-)$ , characterized by the P1 space group with a unit cell of Z = 1, reveals that an oxonium cation resides above each void of the 18-ring. Notably, the oxonium cation engages in O-H—N hydrogen bonds with three of its 2-coordinated nitrogen atoms. On the other hand, the orthorhombic crystal structure of  $(NH_4^+)@2D-(N_8^-)$  is described by the *Ccc2* space group with a unit cell of Z = 2. In this structure, an ammonium cation is linked to two monolayers via four N-H—N hydrogen bonds. This discovery provides a glimpse into the potential of the layered porous 2D-N<sub>8</sub> as a cryptand, which may have the ability to encapsulate various guest species.

## 4 Conclusions

In conclusion, our study reveals the remarkable capacity of the two-dimensional 18-crown-6-like 2D-N<sub>8</sub> structure to efficiently incorporate metal electrons and molecular species while preserving its covalent nitrogen network, consistent with conventional chemical principles governing the partial reduction of unsaturated systems. Through the examination of a series of  $M@2D-N_8$  complexes, we observed that different metals with a variety of oxidation states could be successfully incorporated into the framework. The stability of these complexes was also evaluated, with the use of a cryptand in different structural arrangements. By employing crystal structure prediction enhanced by evolutionary algorithm and density functional theory methodology, we predict the existence of 16 M@2D-N $_8$  complexes out of the 39 MN $_8$ systems investigated at high pressure conditions. Notably, 13 of these complexes (containing Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Au, Cd, Hg, Hf, and W metals) were found to be quenchable, i.e. dynamically stable at ambient pressure. These metal 18-crown-6 ring-based polynitrogen monolayer complexes, characterized by a high nitrogen content, hold promise as new high-energy density materials. We show that the stoichiometric modulation of the alkali element in metallic  $M@2D-N_8$  intercalation compounds, which are dynamically stable, can tune the Fermi level crossing a high density of states peak, i.e. the flat localized  $\pi^*(N_2)$ -based band  $\pi_6^*$ . This result hypothesizes the potential superconducting properties of these functionalized  $\pi$ -conjugated polynitrogen compounds  $M_x@2D-N_8$  (M, alkali; x < 1) at ambient pressure. As a prospect, we demonstrate the potential of the theoretical  $2D-N_8$  compound as a cryptand for stabilizing oxonium  $H_3O^+$  and ammonium  $NH_4^+$  cations through hydrogen bonding. This discovery not only paves the way for the exploration of other encapsulated molecular candidates, but also offers the opportunity to design bidimensional layers with adjustable polynitrogen ring size and pores.

#### Author Information

#### **Corresponding Author**

Busheng Wang - Applied Quantum Chemistry Group, E4 Team, IC2MP UMR 7285, Université de Poitiers - CNRS, Poitiers 86073, France; orcid.org/00000002-7743-9471; Email: wangbs123@gmail.com

Gilles Frapper - Applied Quantum Chemistry Group, E4 Team, IC2MP UMR 7285, Université de Poitiers - CNRS, Poitiers 86073, France; orcid.org/0000-0001-5177-6691; Email: gilles.frapper@univ-poitiers.fr

#### Authors

Sylvain Pitié - Applied Quantum Chemistry Group, E4 Team, IC2MP UMR 7285, Université de Poitiers - CNRS, Poitiers 86073, France; orcid.org/0000-0003-1920-193X
Frédéric Guégan - Applied Quantum Chemistry Group, E4 Team, IC2MP UMR 7285, Université de Poitiers - CNRS, Poitiers 86073, France; orcid.org/0000-0002-4932-8643

Complete contact information is available at :https://pubs.acs.org/XXX

#### Authors contribution

S. Pitié and B. Wang contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

# Acknowledgement

This research was made possible by two grants from the French National Research Agency (ANR) for postdoctoral fellowships for B.W. (PRCI Predict-2D-Nanomat) and S.P. (PRC TcPredictor). This work was partially supported by the European Union (ERDF), and

Région Nouvelle Aquitaine (France). The authors acknowledge the High-Performance Computing Centers (HPC) of Poitiers University (Mésocentre SPIN, France), Irène/TGCC, and Jean Zay/IDRIS of GENCI (France) under projects no. A0140807539 and "Grand Challenge 2023 TGCC" session A14 spe00040 for generous allocations of computing time. We would like to thank all the contributors of the Materials Project for their valuable open-source databank. G.F. wishes to thank Pr. John Akapulco for many hepful discussions.

## Supporting Information Available

The Supporting Information is available free of charge at https://pubs.acs.org/doi/XXX

Additionnal calculations details with computational methods; Discussion of several structures that were not analyzed in the main text; calculated crystal structures parameters and energies of the phases discussed; phonon dispersion curves; electronic band structures and DOSs of selected compounds at ambient and high pressures. Analysis of the COBIs, ELF, and Bader charges; band gaps for the P = 1 atm and 100 GPa phases; *ab initio* molecular dynamics simulations; simulated radial distribution function (RDF). Crystallographic Information Files (CIFs) of predicted dynamically stable crystal structures M@2D-N<sub>8</sub>.

# References

- Nosé, S.; Klein, M. L. Structural Transformations in Solid Nitrogen at High Pressure. Phys. Rev. Lett. 1983, 50, 1207–1210.
- (2) Mailhiot, C.; Yang, L. H.; McMahan, A. K. Polymeric Nitrogen. *Phys. Rev. B* 1992, 46, 14419–14435.
- (3) Pickard, C. J.; Needs, R. J. High-Pressure Phases of Nitrogen. Phys. Rev. Lett. 2009, 102.
- (4) Mattson, W. D.; Sanchez-Portal, D.; Chiesa, S.; Martin, R. M. Prediction of New Phases of Nitrogen at High Pressure from First-Principles Simulations. *Phys. Rev. Lett.* 2004, 93, 125501.
- (5) Eremets, M. I.; Gavriliuk, A. G.; Trojan, I. A.; Dzivenko, D. A.; Boehler, R. Single-Bonded Cubic Form of Nitrogen. *Nat. Mater.* 2004, *3*, 558–563.
- (6) Prasad, D. L. V. K.; Ashcroft, N. W.; Hoffmann, R. Evolving Structural Diversity and Metallicity in Compressed Lithium Azide. J. Phys. Chem. C 2013, 117, 20838–20846.
- (7) Liu, X.; George, J.; Maintz, S.; Dronskowski, R. β-CuN<sub>3</sub>: The Overlooked Ground-State Polymorph of Copper Azide with Heterographene-Like Layers. Angew. Chem. Int. Ed. 2014, 54, 1954–1959.
- (8) Huang, B.; Wang, B.; Wu, S.; Guégan, F.; Hu, W.; Frapper, G. Predicted Polymeric and Layered Covalent Networks in Transition Metal Pentazolate M(cyclo-N<sub>5</sub>)<sub>x</sub> Phases at Ambient and High Pressure: Up to 20 Nitrogen Atoms per Metal. Chem. Mater. 2021, 33, 5298–5307.
- (9) Grochala, W.; Hoffmann, R.; Feng, J.; Ashcroft, N. W. The Chemical Imagination at Work in Very Tight Places. Angew. Chem. Int. Ed. 2007, 46, 3620–3642.

- (10) Wang, Y.; Bykov, M.; Chepkasov, I.; Samtsevich, A.; Bykova, E.; Zhang, X.; Jiang, S.-q.; Greenberg, E.; Chariton, S.; Prakapenka, V. B.; Oganov, A. R.; Goncharov, A. F. Stabilization of Hexazine Rings in Potassium Polynitride at High Pressure. *Nat. Chem.* **2022**, *14*, 794–800.
- (11) Aslandukov, A.; Trybel, F.; Aslandukova, A.; Laniel, D.; Fedotenko, T.; Khandarkhaeva, S.; Aprilis, G.; Giacobbe, C.; Lawrence Bright, E.; Abrikosov, I. A.; Dubrovinsky, L.; Dubrovinskaia, N. Anionic N<sub>18</sub> Macrocycles and a Polynitrogen Double Helix in Novel Yttrium Polynitrides YN<sub>6</sub> and Y<sub>2</sub>N<sub>11</sub> at 100 GPa. Angew. Chem. Int. Ed. 2022, 61.
- (12) Bykov, M.; Bykova, E.; Ponomareva, A. V.; Abrikosov, I. A.; Chariton, S.; Prakapenka, V. B.; Mahmood, M. F.; Dubrovinsky, L.; Goncharov, A. F. Stabilization of Polynitrogen Anions in Tantalum–Nitrogen Compounds at High Pressure. *Angew. Chem. Int. Ed.* **2021**, *60*, 9003–9008.
- (13) Bhadram, V. S.; Kim, D. Y.; Strobel, T. A. High-Pressure Synthesis and Characterization of Incompressible Titanium Pernitride. *Chem. Mater.* **2016**, *28*, 1616–1620.
- (14) Yu, S.; Zeng, Q.; Oganov, A. R.; Frapper, G.; Zhang, L. Phase Stability, Chemical Bonding and Mechanical Properties of Titanium Nitrides: a First-Principles Study. *Phys. Chem. Chem. Phys.* 2015, 17, 11763–11769.
- (15) Yu, S.; Huang, B.; Zeng, Q.; Oganov, A. R.; Zhang, L.; Frapper, G. Emergence of Novel Polynitrogen Molecule-like Species, Covalent Chains, and Layers in Magnesium-Nitrogen Mg<sub>x</sub>N<sub>y</sub> Phases under High Pressure. J. Phys. Chem. C 2017, 121, 11037–11046.
- (16) Huang, B.; Frapper, G. Barium-Nitrogen Phases Under Pressure: Emergence of Structural Diversity and Nitrogen-Rich Compounds. *Chem. Mater.* **2018**, *30*, 7623–7636.

- (17) Wang, B.; Larhlimi, R.; Valencia, H.; Guégan, F.; Frapper, G. Prediction of Novel Tin Nitride Sn<sub>x</sub>N<sub>y</sub> Phases Under Pressure. J. Phys. Chem. C 2020, 124, 8080–8093.
- (18) Wang, B.; Guégan, F.; Frapper, G. Putting Xenon and Nitrogen Under Pressure: Towards New Layered and Two-Dimensional Nitrogen Allotropes with Crown Ether-like Nanopores. J. Mater. Chem. C 2022, 10, 10374–10381.
- (19) Oganov, A. R.; Glass, C. W. Crystal Structure Prediction Using *Ab Initio* Evolutionary Techniques: Principles and Applications. J. Chem. Phys. 2006, 124, 244704.
- (20) Oganov, A. R.; Lyakhov, A. O.; Valle, M. How Evolutionary Crystal Structure Prediction Works—and Why. Acc. Chem. Res. 2011, 44, 227–237.
- (21) Lyakhov, A. O.; Oganov, A. R.; Stokes, H. T.; Zhu, Q. New Developments in Evolutionary Structure Prediction Algorithm USPEX. Comput. Phys. Commun. 2013, 184, 1172–1182.
- (22) Oganov, A.; G., S.; A.G., K. Computational Materials Discovery; The Royal Society of Chemistry, 2018.
- (23) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
- (24) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B 1996, 54, 11169–11186.
- (25) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. Comput. Mater. Sci. 1996, 6, 15–50.
- (26) Sabatini, R.; Gorni, T.; de Gironcoli, S. Nonlocal van der Waals density functional made simple and efficient. *Phys. Rev. B* 2013, *87*, 041108.

- (27) Peng, H.; Yang, Z.-H.; Perdew, J. P.; Sun, J. Versatile van der Waals Density Functional Based on a Meta-Generalized Gradient Approximation. *Phys. Rev. X* 2016, *6*, 041005.
- (28) Furness, J. W.; Kaplan, A. D.; Ning, J.; Perdew, J. P.; Sun, J. Accurate and Numerically Efficient r<sup>2</sup>SCAN Meta-Generalized Gradient Approximation. J. Phys. Chem. Lett. 2020, 11, 8208–8215.
- (29) Furness, J. W.; Kaplan, A. D.; Ning, J.; Perdew, J. P.; Sun, J. Correction to "Accurate and Numerically Efficient r<sup>2</sup>SCAN Meta-Generalized Gradient Approximation". J. Phys. Chem. Lett. **2020**, 11, 9248–9248.
- (30) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. J. Chem. Phys. 2003, 118, 8207–8215.
- (31) Togo, A.; Oba, F.; Tanaka, I. First-Principles Calculations of the Ferroelastic Transition between Rutile-type and CaCl<sub>2</sub>-type SiO<sub>2</sub> at High Pressures. *Phys. Rev. B* 2008, 78, 134106.
- Müller, P. C.; Ertural, C.; Hempelmann, J.; Dronskowski, R. Crystal Orbital Bond Index: Covalent Bond Orders in Solids. J. Phys. Chem. C 2021, 125, 7959–7970.
- (33) Maintz, S.; Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R. LOBSTER: A Tool to Extract Chemical Bonding from Plane-wave Based DFT. J. Comput. Chem. 2016, 37, 1030–1035.
- (34) Savin, A.; Nesper, R.; Wengert, S.; Fässler, T. F. ELF: The Electron Localization Function. Angew. Chem., Int. Ed. Engl. 1997, 36, 1808–1832.
- (35) Momma, K.; Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. J. Appl. Crystallogr. 2011, 44, 1272–1276.
- (36) Steele, B. A.; Oleynik, I. I. Novel Potassium Polynitrides at High Pressures. J. Phys. Chem. A 2017, 121, 8955–8961.

- (37) Nesper, R. The Zintl-Klemm Concept A Historical Survey. Z. Anorg. Allg. Chem.
  2014, 640, 2639–2648.
- (38) Fang, T.-T. Elements of Structures and Defects of Crystalline Materials; Elsevier, 2018; p 13–35.
- (39) Albright, T. A.; Burdett, J. K.; Whangbo, M. Orbital Interactions in Chemistry; Wiley, 2013.
- (40) Emery, N.; Hérold, C.; d'Astuto, M.; Garcia, V.; Bellin, C.; Marêché, J. F.; Lagrange, P.;
  Loupias, G. Superconductivity of Bulk CaC<sub>6</sub>. *Phys. Rev. Lett.* **2005**, *95*.
- (41) McMahon, M. I.; Nelmes, R. J. High-Pressure Structures and Phase Transformations in Elemental Metals. *Chem. Soc. Rev.* 2006, 35, 943.
- (42) Kamlet, M. J.; Jacobs, S. J. Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of C–H–N–O Explosives. J. Chem. Phys. 1968, 48, 23–35.
- (43) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. *APL Mater.* 2013, 1, 011002.
- (44) Gokel, G. W.; Leevy, W. M.; Weber, M. E. Crown Ethers: Sensors for Ions and Molecular Scaffolds for Materials and Biological Models. *Chem. Rev.* 2004, 104, 2723–2750.
- (45) Shi, Q.; Wang, X.; Liu, B.; Qiao, P.; Li, J.; Wang, L. Macrocyclic Host Molecules with Aromatic Building Blocks: the State of the Art and Progress. *Chem Comm.* 2021, 57, 12379–12405.
- (46) Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. Steering Molecular Organization and

Host–Guest Interactions Using Two-Dimensional Nanoporous Coordination Systems. Nat. Mater. 2004, 3, 229–233. For Table of Contents Only

