Journal of Materials Chemistry A

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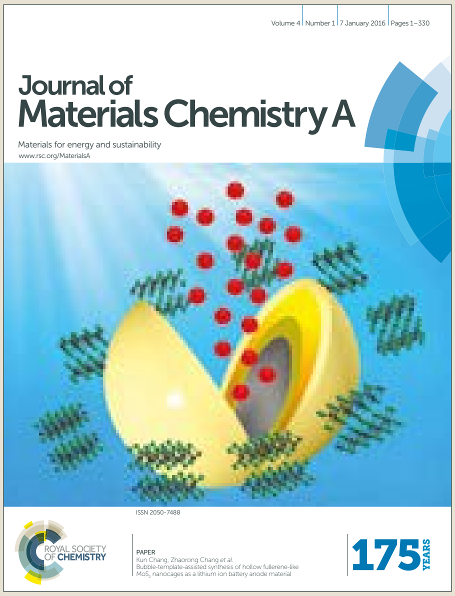

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ARTICLE

Layered 2D Triaminoguanidine-Glyoxal Polymer and Its Transition Metal Complexes, as Novel Insensitive Energetic Nanomaterials

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A new member of 2D carbon-nitrogen-rich family of nanomaterials was synthesized by polycondensation of triaminoguanidine hydrochloride with glyoxal. The obtained polymer (TAGP) has a carbon-to-nitrogen ratio of 3:4, identical to a ratio found in carbon nitrides. Our analysis showed that TAGP has a layered 2D network-type structure. TAGP is dispersible in polar organic solvents and forms stable complexes with various transition metal ions (TAGP-Ms). TAGP and most TAGP-Ms were found to exhibit properties of insensitive Energetic Materials (EMs), where TAGP shows a very low sensitivity to impact (I_m = 71.7 J) and to friction (> 352.8 N). TAGP has also higher nitrogen content than all currently-used energetic polymers, including glycidyl azide polymer [GAP], poly(3-nitrato-methyl-3-methyloxetane) [poly-NIMMO], and poly(glycidyl nitrate) [poly-GLYN]. Velocity of detonation of TAGP (6657 m·s^{-1}) was calculated to be significantly higher than of azide-containing GAP and comparable to the nitrate ester-based poly-GLYN. In our perspective, TAGP is also an example of a modular and combinatorial approach in which high nitrogen-content aminoguanidine derivatives, reacted with amine-reactive low-carbon-content or energetic crosslinkers, can produce novel energetic polymers with tuneable properties and performance. The properties of the aminoguanidine-based EPs could be even further modified and tuned by coordination of transition metal ions. Our novel TAGP and TAGP-M energetic nanomaterials have a great potential to be used in solid propellants and in energetic formulations and composites, as new generation energetic binders and combustion catalysts.

1. INTRODUCTION

Research in the field of Energetic Materials (EMs), such as explosives, propellants, and pyrotechnics, is very important, due to these materials broad range of civil and defence applications.[1] The effort in development of new EMs includes syntheses of new energetic molecules and nanomaterials, preparation of advanced energetic composites and formulation, as well as fabrication (including 3D printing and other advanced techniques) of unique energetic devices.[2] The new EMs span a wide variety of compounds and materials, such as nitrogen-rich polymers,[3] novel nitro-compounds,[4] energetic salts,[5] azole- and azine-based compounds,[6] energetic ionic liquids,[7] super-thermites,[8] poly-nitrogen compounds,[9] and energetic macromolecular structures, such as host-guest complexes, co-crystals, as well as energetic metal-organic frameworks (MOFs).[10] However, many of these new compounds and materials are facing difficulty in replacing currently-used EMs, due to various problems, related to the lack of their chemical compatibility with currently-used materials (energetic and non-energetic, such as binders and casing), low thermal stability, high sensitivity to impact and friction, toxicity and cost-effectiveness. Therefore, providing novel EMs with advanced capabilities of easily tuneable and adjustable properties, could be an important alternative approach to substantially alleviate many of the aforementioned problems.

One of possible approaches to tune and adjust chemical and physical properties of EMs, is to prepare Energetic Polymeric (EP) materials (polymers, co-polymers and grafted co-polymers). In this type of EMs, a selection of various building blocks (monomers, grafting moieties, accompanying anions or cations *etc*.), as well as an adjustment of a molecular weight and a degree of grafting, may greatly affect these materials properties and performance. In principle, such polymeric materials could be tuned to a certain level of hydrophobicity, acidity, plasticity, mechanical strength, mechanical sensitivity, detonability and many other desirable properties.

One of the major challenges in this important field remains to be development of novel EPs that would have a series of superior properties, such as a sufficient mechanical strength, a high energy content, a good oxygen balance and a high nitrogen content, while being insensitive to impact and friction, as much as possible. Therefore, in recent years, a significant effort was made to develop novel high-nitrogen-content EPs, incorporating new building blocks, including azide-, azine-, and azole-based moieties.[11-14]

Guanidines and their monoamino-, diamino- and triamino-derivatives are excellent nitrogen-donors, with multiple nucleophilic functional groups. In principle, by using a matrix-type combination of various aminoguanidines, with a series of amine-reactive cross-linkers, it should be possible to generate a combinatorial library of

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Free online Electronic Supplementary Information (ESI) available: descriptions of the experimental details, characterization techniques; and figures on SEM images of involved 2D materials, FTIR of the explored materials, and DSC curves of guanidine-formaldehyde resin; Tables on summary of elemental analysis from EDS, and FTIR spectra. See DOI: 10.1039/x0xx00000x

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EPs, where some of the materials in this library would have the desired properties and performance.[15] Importantly, the properties of the aminoguanidine-based EPs could be even further modified and tuned (for example, for photo-chemical or for electrochemical ignition) by coordination of transition metal ions.

Various guanidine-based ligands were already utilized in bio-inorganic chemistry,[16] as well as for the preparation of Cu-containing catalysts for atom-transfer radical polymerization process (ATRP).[17] It was reported that the reaction between the $Cu(NO_3)_2$ and TAG·HNO_3 in acidic aqueous solution results in formation of Cu(TAG)$(NO_3)_2$ complex.[18a] Another TAG complex with copper was obtained by reaction of the $CuCl_2$ with TAG·HCl in concentrated aqueous HCl.[18c] Yet, the energetic properties of metal complexes of guanidine and guanidine derivatives were mostly overlooked, despite that various guanidine derivatives were widely used as cations in numerous energetic salts. For instance, nitrate and hydrochloride salts of triaminoguanidine[19] (TAG) were used as precursors for synthesis of energetic ionic liquids.[18] Surprisingly, triaminoguanidine-glyoxal polymer (TAGP) was never reported. In this work, we prepared, characterized and comprehensively studied a new TAGP and a series of its transition metal coordination (TAGP-M) compounds (Figure 1). We found that TAGP has a relatively-high nitrogen content of about 48% and possesses a unique structure on molecular and macromolecular levels.

TAGP was prepared by reacting TAG·HCl, as guanidine (high-nitrogen-content) building block, with glyoxal, as amine-reactive (low-carbon-content) crosslinker. TAGP was found to be an excellent chelator for binding of various transition metal ions, since after crosslinking, most binding sites of TAG moiety in the TAGP remained available for metal ions coordination. Both TAGP and TAGP-Ms exhibited properties of insensitive EMs.

2. EXPERIMENTAL SECTION

2.1 Preparation of TAGP. To aqueous solution of TAG·HCl[19] (96 mg in 30 ml of H_2O), aqueous solution of glyoxal (20 ml, 40% in H_2O) was added dropwise and room temperature. At the end of the addition, the reaction mixture was stirred for 30 min and was bath sonicated for 1 hr. Brown gelatinous precipitate was filtered, washed with water (2×20 ml) and vacuum dried, yielding a powder of TAGP material (112 mg).

2.2 Preparation of TAGP-Ms. Powder of TAGP (100 mg) was dispersed in isopropanol (30 ml) by bath sonication for 2 hr. To this dispersion, an aqueous solution of a metal salt (10 mM in 40 ml of H_2O; such as copper nitrate, cobalt nitrate, cobalt chloride, nickel nitrate or silver nitrate) was added dropwise at room temperature. After the end of the addition, the reaction mixture was stirred for 30 min and was bath sonicated for 2 hr. The product was filtered, washed with water (2×100 ml) and vacuum dried, yielding a powder of TAGP-M material. Resulted TAGP-Ms are called TAGP-Cu, TAGP-Co, TAGP-CoCl, TAGP-Ni, and TAGP-Ag, respectively.

3. RESULTS AND DISCUSSION

3.1 Morphology and Chemical Composition

We conducted a systematic and comprehensive study of TAGP's chemical composition and structure, using an array of advanced analytical techniques. Based on the reported chemistry of TAG with various mono-aldehydes,[20] solubility properties and chemical behaviour of TAGP, as well as its elemental composition ($C_3H_{5.3}N_4O_{1.2}$) that was measured by EDS/XPS (Figure S1; ESI), and TEM results (Figure 2), we hypothesize that TAGP has a two dimensional (2D) net-type structure, comprised of repeating 42-membered macrocyclic rings (Figures 1 and 5c).

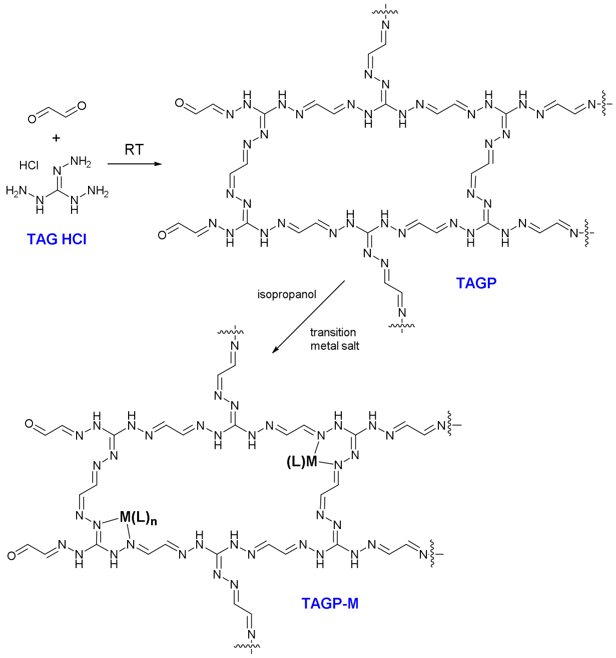

Figure 1. Preparation of TAGP and TAGP-M [M = Cu(II), Ag(I), Co(II) or Ni(II); L = Cl and H_2O].

The elemental composition analysis of TAGP showed that this material has a carbon-to-nitrogen ratio of 3:4, which is found in a carbon-nitride family of compounds. The presence of oxygen atoms in TAGP, could be mostly attributed to unreacted aldehyde carbonyl groups, located at edges of TAGP's 2D sheets and to strongly-bound water molecules. The edges of TAGP's sheets could be also partially terminated with amine moieties of TAG monomer, as was shown by the FTIR analysis of this material (Figure S2, Table S2; ESI). TEM imaging of TAGP revealed fascinating details about this new nanomaterial assembly (Figure 2). It was shown that TAGP has a layered structure, with large oval holes (50-250 nm in diameter) in each layer, while the thickness of each individual layer of TAGP is about 5 nm. TEM results corroborated data obtained from the powder XRD (PXRD) studies of TAGP, which showed wide diffraction peak for this material (Figure 5a).

Although obviously very different in their structures and overall chemical and physical properties, we would like to make a general comparison between the layered structure of TAGP and the structure of another layered nanomaterial, with carbon-to-nitrogen ratio of 3:4, namely graphitic carbon nitride (g-C_3N_4).

The differences between TAGP and g-C_3N_4 nanomaterials are in their chemical bonding, *in-layer* molecular structures, layer-to-layer interactions, morphology and many other parameters. Nano-sheets of g-C_3N_4 have a thickness of 2-4 nm and typically don't have intrinsic large defects in their structure.[21] Nano-sheets of g-C_3N_4 are also highly-rigid, in contrast to a flexible and hollow structure of nano-sheets of TAGP. We observed that free-standing films of TAGP underwent self-curling during their drying process, most probably due to evaporation of water that was trapped between hydrophilic layers of TAGP. Yet, some of water molecules were bound much stronger to the structure of TAGP, as was found by the elemental analysis and FTIR spectroscopy.

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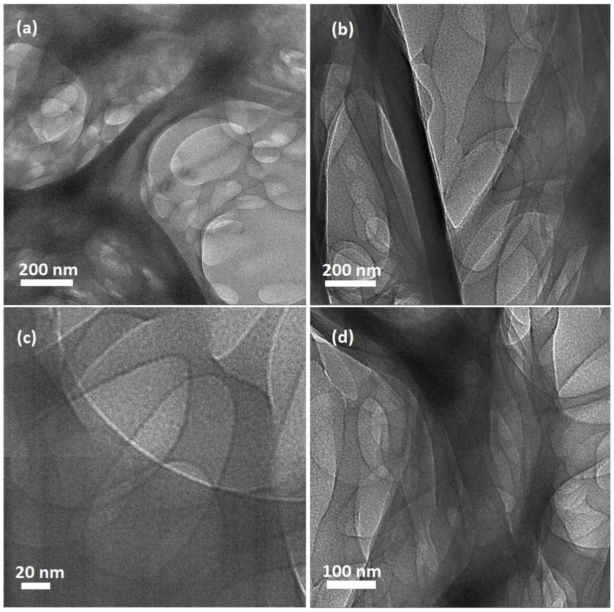

Figure 2. TEM images of TAGP at different magnifications. Stacked assembly, with oval holes in each of individual TAGP's layers, could be seen. TAGP sample was deposited on a copper substrate.

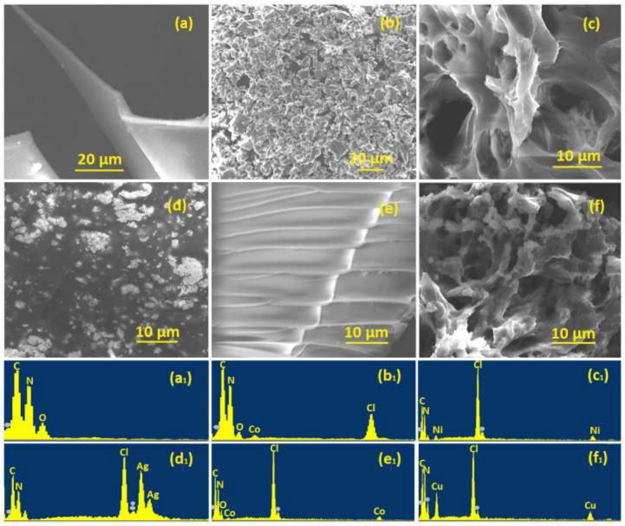

Figure 3. SEM images (**a**-**f**) and corresponding EDS spectra (**a$_1$**-**f$_1$**) of TAGP and TAGP-Ms. A thin film of TAGP (**a**); amorphous powder-like TAGP-CoCl has an irregular shape with a rough surface (**b**), chloride-free TAGP-Co has homogeneous block structure, with a smooth wave-shaped surface (**e**); TAGP-Ni (**c**) and TAGP-Cu (**f**) show similar porous morphologies; TAGP-Ag (**d**).

The morphology and elemental composition in TAGP and TAGP-Ms were studied by SEM/EDS (Figure 3, Figure S1 and Table S1; ESI). SEM images of TAGP show that this material has a smooth surface and can exist in a form of thin films, with a typical thickness of about 5-10 µm (Figure 3a), supporting TEM observations and proposed layered structure of TAGP. In contrast, most of the examined TAGP-Ms show irregularly-shaped structures and surfaces, except for TAGP-Co that has a smooth wave-shape surface (Figure 3e). Differently from all other TAP-Ms, TAGP-Ag has a form of inhomogeneous particle-reinforced composite (Figure 3d and Figure S1; ESI), indicating that the complexation of Ag^+ may take place *via* a nucleation mechanism. We found that TAGP-Ag powder has much larger specific area than the other TAGP-Ms. TAGP-Ag has also a very high density of 3.21 $g{\cdot}cm^{-3}$. EDS analysis of TAGP-Ms samples showed that they contain significant amounts of chlorine atoms (Figure 3b$_1$–3f$_1$, Table S1; ESI), where presently it is not completely clear whether all these chlorides are bound to metal centers or some present as counter anions.

3.2 Structures and Chemical Bonding

FTIR spectra of TAGP-Ms exhibited broad absorption bands (Figure S2, Table S2; ESI). Bands located at 3201-3251 cm^{-1} were assigned to the stretching modes of OH groups of water molecules, present in TAGP-Ms.

Absorption in 3070-3240 cm^{-1} region was also assigned to bound water molecules, present in the examined parent metal nitrate salts. TAG·HCl has several very strong bands. One of these bands appears in 1680-1580 cm^{-1} region and was assigned to ν(C=N) of guanidine group, in which one of the N atoms is protonated.[22] The coordination of metal centers in TAGP-Ms may have a resemblance to the reported complexes, based on TAG ligands and corresponding supramolecular cage compounds.[23]

Further analysis of chemical bonds, present in TAGP and TAGP-Ms, was performed by XPS (Figure 4). Figure 4 presents data obtained for TAGP, TAGP-Cu and TAGP-Co materials. C 1s spectra of all these compounds show typical C-N, C=C, C=N and C=O bonds. In the case of TAGP, the C-N bond content is higher than in TAGP-Co and TAGP-Cu, while the C-C bond content in TAGP-Cu is the lowest.

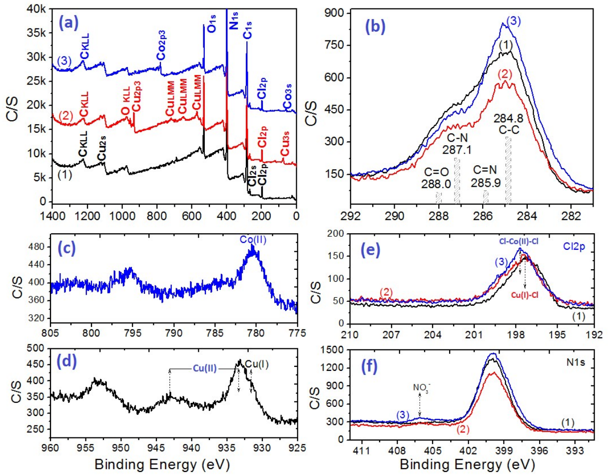

Figure 4. XPS of TAGP and TAGP-Ms. (**a**): overlaid spectra; (**b**): C 1s spectra; (**c**) TAGP-Co; (**d**) TAGP-Cu; (**e**) Cl 2p spectra and N 1s spectra for TAGP (**1**), TAGP-Cu (**2**) and TAGP-Co (**f**).

TAG and its oxidized products, as ligands, usually show C1s peaks for either C-N (285.7-286.0 eV) and C=N (286.5-286.7 eV) bonds, and N 1s peak for =N– (398.4 eV) and –NH– (399.7 eV) bonds. It was reported that the peak intensity depends on the oxidation state of the ligand.[24] The observed by us N 1s bonding energy for –NH– (at 400.1 eV) is well in agreement with the reported values for organic amines, coordinated with transition metal centers.[24c]

Based on XPS results of atomic concentrations, we found that metal-to-Cl ratio is about 1:2 for TAGP-Co and about 1:1 for TAGP-Cu. These findings are in a good agreement with the measured Co

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2p spectra, revealing the Co(II) state of Co $2p^{3/2}$ peak (780.8 eV; Figure 4c). No reference data was found for Co or Cl position in $CoCl_2$, yet the Co-to-Cl ratio in TAGP-Co indicates presence of bonds between Co and N, as no change in the N 1s shape was observed for TAGP-Co, as compared to the spectrum of pristine TAGP (Figure 4f).

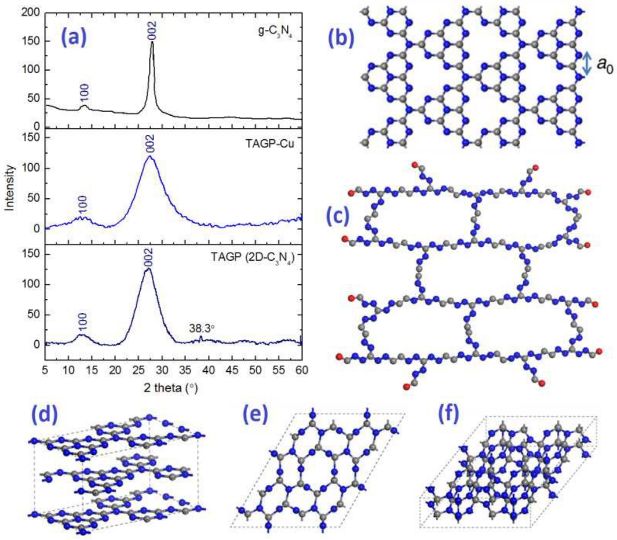

Figure 5. (**a**): PXRD patterns of g-C_3N_4, TAGP-Cu and TAGP; (**b**): molecular structure of single layer of g-C_3N_4; (**c**): proposed molecular structure of a single layer of TAGP; (**d**, **e** and **f**): β-form of g-C_3N_4, shown from different perspectives, where the blue and grey spheres represent N and C atoms, respectively; a_0 is the lattice parameter. It was set to be 3.172 for β-form, 2.379 for the sheet, and 2.383 for the stacked one, in our calculations.[24]

XPS spectrum of Cu 2p demonstrates a dominant Cu $2p^{3/2}$ peak (934.3 eV) that corresponds to Cu(II), while a smaller Cu $2p^{3/2}$ peak (932.6 eV) may indicate possible presence of Cu(I) (Figure 4d). The mixture of Cu(II) and Cu(I) in TAGP-Cu could be responsible for the deviation in measured Cu-to-Cl ratio from 1:1 to 1:1.3. The presence of Cu(I) in TAGP-Cu, suggests that TAGP was partially oxidized by Cu(II), resulting in appearance of N=N bonds and formation of Cu(I). References for Cu-Cl covalent bonds are: CuCl at 932.6 eV (198.4 eV for Cl 2p), $CuCl_2$, at 934 and 935 eV (199.4 eV for Cl 2p). A small shift in the Cl 2p spectrum of TAGP-Cu to slightly higher binding energy value was observed. We noticed that this shift was smaller than the shift in Cl 2p spectrum measured for TAGP-Co (Figure 4e). These observations provide an additional support to our previous conclusion that only a single chloride ligand is bound to the copper metal center in TAGP-Cu, while in case of TAGP-Co, two chloride ligands are bound the cobalt metal center. It is possible that the remaining coordination cites are occupied by water molecules.

Solid state forms of TAGP and TAGP-Cu were analysed by PXRD (Figure 5a). Only two broad peaks were found in the PXRD spectra of TAGP and TAGP-Cu, with no match to any known phase in the ICDD database. Then, we attempted to compare our experimental data with the reported PXRD patterns for carbon nitrides.

It was reported that the carbon nitride (C_3N_4) could exist in α, β, cubic, pseudo-cubic and g-C_3N_4 forms.[26] A single sheet of g-C_3N_4 is usually composed of either s-triazine or tri-s-triazine repeating units (Figure 5b), where the latter form is more energetically stable.[25] The preferred stacking method for g-C_3N_4 sheets is following a repeating unit in the *P6m2* symmetry group (Figure 5d), with distance of 3.29 Å between the layers.[27] Remarkably, measured PXRD pattern for TAGP (and for TAGP-Cu) exhibited a certain degree of resemblance to the reported pattern of g-C_3N_4, with 100 and 002 typical Miller planes.[25] These results are closely correlated with previously-described TEM observations, providing an additional confirmation to the 2D layered structure of TAGP.

3.3 Thermal Stability and Reactivity

DSC and TG analyses revealed that TAGP is an energetic material, with two major exothermic decomposition peaks at 193.4 and 244.9 °C (Figure 6a). In contrast, g-C_3N_4 is stable at temperatures above 500 °C, without any detectible exothermic decomposition. The exothermic peaks in thermograms of TAGP could be attributed to two-step decomposition process of this nanomaterial. A mechanism of this process probably includes a scission of crosslinking ethane-1,2-diimine units, in the first step (first exothermic peak), followed by a decomposition of amino-guanidine moiety of TAGP (second exothermic peak). The proposed hypothesis for the reactive center in the second step of the TAGP's decomposition mechanism (at 244.9 °C) is strongly supported by data obtained for decomposition of triaminoguanidine hydrochloride (TAG·HCl) and guanidine hydrochloride (AG), which exhibit single exothermic peaks at 242.4 and 238.7 °C, respectively (Figure 6a and Figure S3, ESI).

Although the preparation of analogous material to TAGP – guanidine-formaldehyde polymer (GP) was already described in 1968,[19,20] unfortunately, GP's energetic properties were overlooked and never reported. As a part of the present study, we prepared GP, as a reference material, and evaluated its thermostability. We found that GP has fast and intense exothermic decomposition, with peak temperature of 273.6 °C. This decomposition temperature is significantly higher than of the GP's parent guanidine hydrochloride (AG; 238.7 °C; Figure S3; ESI). The observations made for TAGP and GP support the validity of our idea of building a combinatorial array of energetic materials, based on nitrogen-rich guanidines and property-modifying amine-reactive linkers.

Metal complexes of TAGP also exhibited exothermic double-peak decomposition behaviour, in the temperature range of 175-365 °C. The lower temperature exothermic peaks in thermograms of TAGP-Co, TAGP-Ni and TAGP-Ag were found to be somewhat weaker than the higher temperature peaks. An opposite behaviour was observed in the case of TAGP-Cu. These results reflect influence of different coordinated metals on a thermostability of ethane-1,2-diimine and amino-guanidine reactive centers in various TAGP-Ms.

The main decomposition processes of TAGP, TAGP-Co, and TAGP-Ni are covered by very close energy release of 1434, 1426 and 1416 $J\cdot g^{-1}$, respectively; indicating that the decomposition effects induced by cobalt and nickel are very limited. The decomposition heat of TAGP-Ag was significantly lower (868 $J\cdot g^{-1}$), while in terms of energy density and decomposition heat, the heat release of TAGP-Cu was found to be the largest (2246 $J\cdot g^{-1}$) among all tested materials. Important to mention that many EMs on a basis of copper are known, indicating unique properties of this metal to promote exothermic reactions.

We think that TAGP has certain clear advantages in terms of thermostability and structural homogeneity over other commonly-used energetic polymers. For example, thermal decomposition of GAP begins already at 70 °C[28] and although GAP's thermostability could be improved by co-polymerization with 3,3-bis(3-azido-methyl)-oxetane (BAMO), the resulted co-polymer was found to contain crystalline domains inside a bulk of amorphous GAP29 Other reported EPs, such as poly-NIMMO and poly-GLYN, with

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relatively fast degradation below 190 °C, also exhibit lower thermostability than TAGP.

The decomposition of GAP starts by a loss of its azido groups,[30] while in cases of poly-NIMMO and poly-GLYN the degradation initiated *via* the breakage of nitrate ester groups.[31] We think that a good thermostability of TAGP could be attributed to the absence of azide or nitrate ester groups in TAGP's structure, allowing plausible initiation of the decomposition process in much less thermo-sensitive ethane-1,2-diimine bridging moieties.

3.4 Energetic Performance and Sensitivity

In order to assess energetic properties of the materials prepared in this study, we conducted bomb calorimetry measurements (to estimate the constant-volume heat of combustion, ΔH_c) and performed thermochemical calculations, using EXPLO-5 software. The ΔH_c values were corrected by determination of the content of the nitric acid formation during combustion of our nitrogen-rich compounds. The corresponding heats of formation (ΔH_f) were calculated on a basis of the experimental ΔH_c. Obtained thermosdynamic data, detonation and combustion parameters are summarized in Table 1.

Since we could not establish the average molecular weight (Mw) of TAGP-based nanomaterials, we used Mw and ΔH_f of a single repeating unit of each material in our EXPLO-5 calculations. Also, since it was reported that changes in the Mw of GAP are practically not affecting the ΔH_c value determined for this EP,[32] we assumed that the ΔH_f values for repeating units in TAGP could be also calculated on a basis of measured ΔH_c values for the latter material. We found that ΔH_c values for TAGP materials were found to be larger that of the poly-GLYN (Table 1). Overall, TAGP exhibited comparable ΔH_f value to its parent TAG·HCl compound, higher value than GAP and much higher ΔH_f value than poly-GLYN.

We calculated that the VoD of TAGP (6657 $m \cdot s^{-1}$) is also substantially higher than the VoD of GAP (5041 $m \cdot s^{-1}$) and comparable to the VoD of poly-GLYN (6755 $m \cdot s^{-1}$). In terms of combustion, oxygen deficient TAGP and its complexes should be used in formulations containing sufficient amounts of oxidizer, to achieve the best specific impulse. Thus, for comparison purposes, in our calculations, 70% of ammonium dinitramide (ADN) oxidant was used in combination with 30% of TAGP materials, and reference GAP and poly-GLYN energetic binders.

We discovered that TAGP, GAP and poly-GLYN have very close I_{sp} values (255-260 s), showing significant real-world application potential of TAGP. Among TAGP-Ms, the combustion performance of TAGP-Cu was predicted to be the highest, probably due to the catalytic nature of copper.

Unfortunately, calculations of detonation and combustion performance TAGP-Co and TAGP-Ag materials could not be included in the present work, as suitable thermochemical parameters for cobalt- and silver-containing compounds are not available in the EXPLO-5 software.

Safety measurements that were conducted for TAGP revealed significant insensitivity of this EP to impact (10 kg hammer, I_m = 71.7 J) and to friction (36 kg, > 352.8 N, Table 1). Although all our TAGP-Ms showed insensitivity to friction (> 352.8 N), a range of sensitivity to impact was observed for these materials. More specifically, TAGP-Co was found to be the least sensitive (I_m = 81.1 J), while TAGP-Ag was the most sensitive (I_m = 9.7 J). Still, the latter metal complex significantly outperformed in its sensitivity RDX and formulations of GAP,[33] where sensitivity of TAGP-Ni and TAGP-Cu were found to be comparable to TNT.

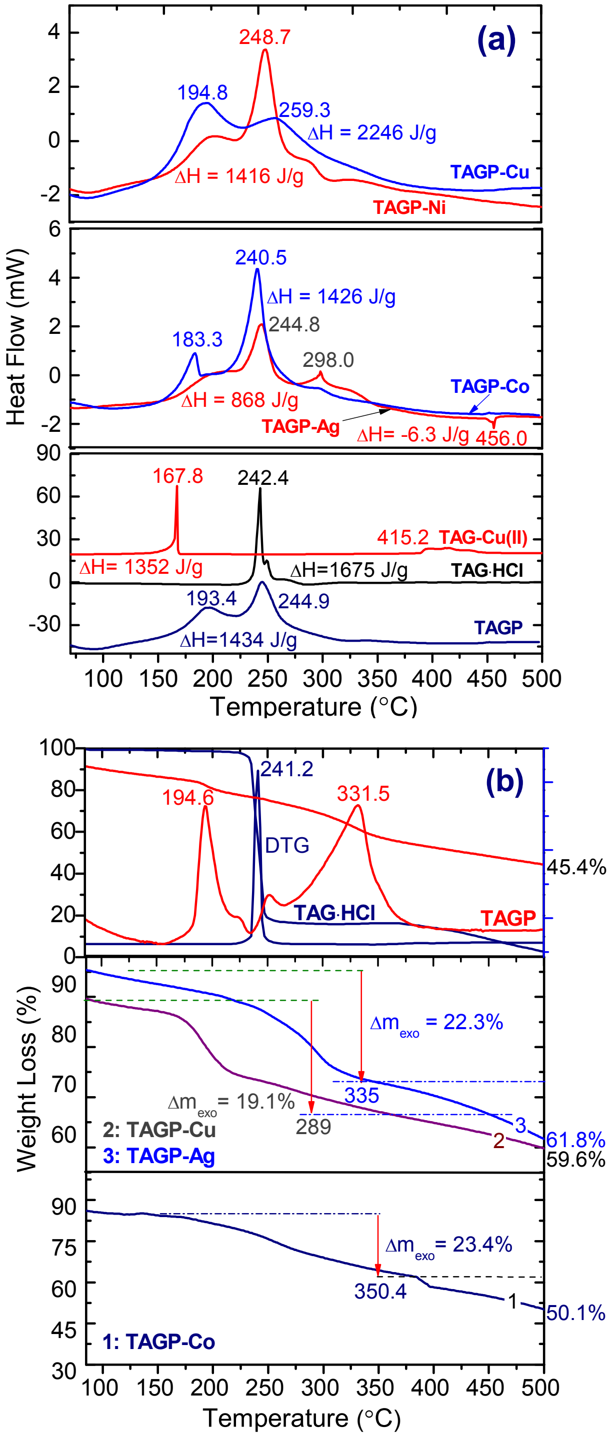

Figure 6. DSC (**a**) and TG/DTG (**b**) curves of TAG·HCl, TAGP and TAGP-Ms (at heating rate of 10 °C·min^{-1}). Pure TAG·HCl decomposes in one fast step, at about 241 °C (with mass loss of 84.3%), while TAGP and TAGP-M materials decompose in two distinct steps.

These results provide an important piece of information for construction of future databases and corresponding software, capable of predicting sensitivity to impact and friction for energetic metal complexes and metal coordinated polymers, as a function of the bound metal (where the same ligand is used).

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Table 1. Energetic properties of TAGP, TAGP-Ms, RDX explosive and reference EPs.

	TAG·HCl	**TAGP**	**TAGP-Cu**	**TAGP-Co**	**TAGP-Ni**	**TAGP-Ag**	**RDX**	**GAP_{2900}**	**poly(GLYN)**
Formula	CH_9N_6Cl	$C_3H_{5.3}N_4O_{1.2}$	$TAGPCu_{0.2}$	$TAGPCo_{0.2}$	$TAGP_1Ni_{0.2}$	$TAGP_2Ag_{0.4}$	$C_3H_6N_6O_6$	$C_3H_5N_3O$	$C_3H_5NO_4$
M_w [g·mol^{-1}]	140.6	116.6	133.2	132.3	121.0	172.4	222.1	99.1	119.0
%N [wt.%]$^{(a)}$	59.78%	48.04%	42.07%	42.36%	46.30%	35.74%	37.84%	42.41%	9.3%
T_p [°C]$^{(b)}$	243.5	193.4/244.9	194.8/259.3	183.3/240.5	196.5/248.7	244.8/298.0	242.6	200.1	204.3
ρ [g·cm^{-1}]$^{(c)}$	1.55	1.50	1.69	1.61	1.59	3.21	1.82	1.30	1.46
Ω_{co2} [%]$^{(d)}$	-9.1%	-41.2%	-36.0%	-32.3%	-39.7%	-27.8%	-21.6%	-121%	-60.5%
ΔH_f [kJ·g^{-1}]$^{(e)}$	+1.42	-1.07	+0.85	+1.41	-0.01	-4.49	+0.38	+1.15	-2.71
ΔH_f [kJ·mol^{-1}]	+199.7	-125.7	+113.4	+186.1	-0.99	-773.6	+84.4	+113.8	-322.5
Impact [J]	25.0	71.7	15.2	81.1	21.6	9.7	7.5	4.2$^{(h)}$	-
Friction [N]	-	> 352.8	> 352.8	> 352.8	> 352.8	> 352.8	> 260	260$^{(h)}$	-
$P_{C\text{-}J}$ [kbar]$^{(f)}$	178.0	142.3	125.4	-	73.3	-	348.6	116.1	157.5
VoD [m·s^{-1}]$^{(g)}$	7198	6557	5760	-	4361	-	8817	5041	6755
I_{sp} [s]	253.0	256.1	248.2	-	234.1	-	246.1	255.5	260.4

Notes: superscripts **a**, nitrogen content; **b**, temperatures of two decomposition peak, measured by DSC (at heating rate of 10 °C·min^{-1}); **c**, density measured by Helium gas pycnometry (at 25°C); **d**, oxygen balance, for $C_aH_bN_cO_d$ compound, $\Omega = -1600\times(2a+0.5b-d)/M_w$; **e**, calculated enthalpy of formation; **f**, calculated detonation pressure; **g**, calculated detonation velocity; **h**, these values were calculated for formulations containing GAP EP (GAP/TMTEN/Carborn/AP/60%solid); I_{sp}, theoretical specific impulse (in sec), calculated at 7 MPa pressure, and compositions containing 30% of the examined compound and 70% of ammonium dinitramide (ADN); $TAGP = C_3H_3N_4O_{0.7}Cl_{0.4}$; $TAGP_1 = C_3H_3N_4Cl_{0.4}$; $TAGP_2 = C_3H_3N_{4.4}O_{0.9}Cl_{0.4}$.

4. CONCLUSIONS

In this work, a series of novel nitrogen-carbon rich energetic nanomaterials was synthesized on a basis of triaminoguanidine-glyoxal polymer (TAGP). Our analysis showed that TAGP has a layered 2D network-type structure, proposedly compiled of repeating 42-membered macrocyclic rings. TAGP is dispersible in polar organic solvents and forms stable complexes with various transition metal ions (TAGP-Ms). TAGP and TAGP-Ms (except of TAGP-Ag) have good thermostability (175-365 °C) and were found to exhibit properties of Insensitive Energetic Materials in sensitivity to impact and friction tests. Remarkably, TAGP-based EMs have higher nitrogen content than all currently-used energetic polymers, including GAP, poly-NIMMO, and poly-GLYN. Velocity of detonation of TAGP (6657 m·s^{-1}) was calculated to be significantly higher than of azide-containing GAP and comparable to the nitrate ester-based poly-GLYN. The decomposition heat of TAGP-Cu was found to be the largest (2246 J·g^{-1}) among all prepared nanomaterials in this study. For comparison, the heat release of TAGP is only 1434 J·g^{-1}, suggesting activity of a copper ions as combustion catalyst. Importantly, in our perspective, TAGP could be a very good example of a modular combinatorial approach in which nitrogen-rich amino-guanidine derivatives are reacted with amine-reactive low-carbon-content or energetic crosslinkers, forming a series of novel energetic polymers, with desirable and tuneable properties and performance. Our novel TAGP and TAGP-M energetic nanomaterials have a potential to be used in many civil and defence applications, as solid propellants and in energetic formulations and composites, as new generation of energetic binders and non-migrating combustion catalysts.

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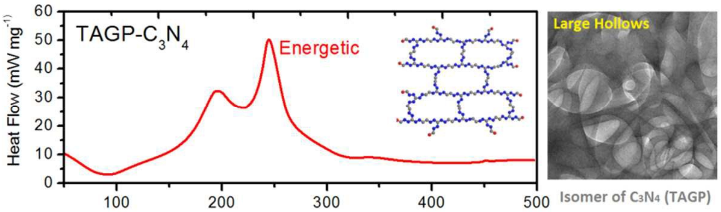
Graphical Abstract



A new member of 2D carbon-nitrogen-rich family of nanomaterials was synthesized by polycondensation of triaminoguanidine hydrochloride with glyoxal. This new polymer (TAGP) and its transition metal complexes (TAGP-Ms) were found to be thermostable and exhibited properties of Insensitive Energetic Materials. TAGP could be an example of a modular combinatorial approach for preparation of novel energetic polymers with tuneable properties and performance.