

[Electronic Supporting Information (ESI) to accompany]

Highly Insensitive and Thermostable Energetic Coordination Nanomaterials Based on Functionalized Graphene Oxides

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(1) Experimental Part

Materials: The commercial available graphene oxide (GO, 1-5 layers) was used as received from market with oxygen content over 42%. Guanidine (99%), diaminoguanidine (98%), copper nitrate trihydrate (99%), nickel nitrate (99%), cuprous chloride (98%), cobalt nitrate (98%), Iron(II) chloride tetrahydrate (99%) and hydrazine monohydrate (98%, N₂H₄ 64-65%) were obtained from Sigma-Aldrich and stored under nitrogen to discourage oxidation. Ultrapure deionized water (resistivity >18 MΩ) was obtained from a Mili-Q Biocel system. Whatman Anodisc™ membranes (0.2 μm pore size, 47 mm diameter) were used during filtration for support of fabricated papers.

Preparation of GO-DAG: the preparation procedure is the same as for GO-TAG in the mail text, and the difference is that only 250 mg of diaminoguanidine hydrochloride (DAG·HCl). The PH value of the filtrated liquid was in between 2.0~3.0 and the as prepared product (165 mg) is the DAG functionalized GO via a bridge of -CO-NH- (GO-DAG).

Preparation of GO-DAG-Copper Coordination Nanomaterials: 90 mg GO-DAG was dispersed in 25 ml H₂O, and then 10 ml aqueous solution of a certain amount of copper salts can be added to GO-DAG solution. The copper salts can be 200 mg of Cu(NO₃)₂, 121 mg of CuCl or a mixture of 100 mg Cu(NO₃)₂ with 50 mg CuCl. The mixture was reacted at a temperature of 75 °C for 5 hrs. The black precipitates were filtrated and washed by H₂O. The obtained filtrated liquids have different PH values (3.6 for Cu(NO₃)₂ 3.9 for CuCl and 4.1 for mixture of Cu(NO₃)₂ with CuCl. The as prepared products are coordination nanomaterials: GO-DAG-Cu(II), GO-DAG-Cu(I) and GO-DAG-Cu(I)/Cu(II), which are found to be energetic materials.

Preparation of TAG-Copper and DAG-Copper Complexes: 200 mg of TAG and 1000 mg of Cu(NO₃)₂ or 600 mg CuCl were dissolved in 40 ml H₂O and reacted under a temperature of 65 °C for 3 hrs. The reddish precipitates (TAG-Cu(II) and TAG-Cu(I) complexes) were filtrated and dried under vacuum. In case of DAG metal complexes, they are slightly soluble in H₂O. After reaction at 65 °C for 3 hrs, the H₂O needs to be evaporated to 20 ml and then the solution with excess copper salts was filtrated. The obtained solids are dried under vacuum and these amorphous materials are highly hygroscopic.

Characterization: The final density of the as-prepared materials was measured by gas pycnometer Micromeritics AccuPyc II 1340. The microstructure of the measured specimens was examined by field emission scanning electron microscopy (SEM, Quanta 200, using a field-emission gun electron source in an exceptionally high chamber pressure environment) and the elemental analysis was performed simultaneously by EDS technique coupled with SEM machine. The Raman spectra of the specimens were collected using LabRam HR spectrometer with 532 nm laser (Laser intensity was set to 3.0 mW). Elemental analysis (EA) on determination of C, H, and N is performed by the Perkin-Elmer 2400 series II

Analyzer, using a combustion method (950-1000 °C) to convert the sample elements to simple gases. The system uses a steady-state, wave front chromatographic approach to separate the controlled gases. They are detected as a function of their thermal conductivity. DSC curves were recorded by TA instrument Q20 under the heating rate of 10 °C min⁻¹ with 50 ml min⁻¹ N₂ gas flow, and the sample mass was about 0.5 mg. Thermogravimetric analysis (TGA) was carried out on a TA instrument Q500 TGA instrument with a heating rate of 10 °C min⁻¹ under N₂ gas flow. The heat of combustion was tested by a bomb calorimeter under O₂ with pressure of 2 MPa, which was corrected by the determination of NO₂ formation. The X-ray Photoelectron Spectroscopy (XPS) measurements were performed in UHV (2.5x10⁻¹⁰ Torr base pressure) using 5600 Multi-Technique System (PHI, USA). The samples were irradiated with an Al K_α monochromated source (1486.6 eV) and the outcome electrons were analyzed by a Spherical Capacitor Analyzer using the slit aperture of 0.8 mm. Sample charging was compensated with a charge Neutralizer (C1s at 284.6 eV was taken as an energy reference). Survey: spectrum in a wide energy range (0 - 1400 eV). It gives an estimation of the elements present on the sample surface and is taken at a low resolution. Utility Multiplex: spectra taken for different peaks in a low energy range window at an Intermediate (Utility) Resolution. It is taken for all the elements present for the atomic concentration (AC%) calculation. An AC table is given as an output of these measurements. High Resolution Multiplex: spectra taken for different peaks in a low energy range window at a High Resolution (PE = 11.75 eV, 0.05 eV/step). These measurements allow precise energy position and peak shape determination, necessary for bond bonding analysis. The powder X-Ray spectra were obtained by a Rigaku diffractometer, the sampling rate of 0.5 point per second and scan rate of 0.01 deg. per min.

Supporting Discussions

Analysis of FT-IR Spectra: The FT-IR spectra of all samples (Figure S1) exhibit peaks for oxygen-containing functionalities in the form of $\nu(\text{C}=\text{O})$, $\delta(\text{O}-\text{H})$, $\nu(\text{C}-\text{O})$ epoxide, and $\nu(\text{C}-\text{O})$ hydroxyl bending and stretching frequencies. A peak at near 1590 cm⁻¹ is also present, which we attribute to C=C stretching from residual graphene sheet regions in graphene oxide. If hydrogen bonding were present between an alkylammonium species and the graphene oxide, a weak peak would be present near 1525 cm⁻¹; however, it would be lost in the strong absorption of the C=C bonds. The spectrum for graphene paper does not exhibit any significant spectral features. Consistent with our XPS data (see Figure 3 in the main text), the FT-IR spectrum for GO-TAG exhibited absorption bands for the C-N stretch and N-H deformations of bound amine, C-H stretches and bends of the alkyl chain, and all expected stretches for graphene oxide. The FT-IR spectrum of GO-TAG also had most of the peaks for oxygen containing functionalities, which, however, are significantly weaker with the bands associated with CO-OH groups nearly disappearing. This is expected after ammonization, whereby the -OH was replaced by TAG groups, which is consistent with the C1s XPS spectrum for this material (Figure 3 in main text). Interestingly, the C-N stretch appeared significantly stronger in intensity in this FT-IR spectrum compared to that for the GO-TAG. This is also due to TAG incorporation and removal of the -OH in COOH groups (Figure 1 in main text), even though the amount of amine is expected to decrease after reduction. The IR spectrum of TAG·HCl shows two peaks at 3340 and 3220 cm⁻¹ over the -NH- range while the absorptions at 1690 and 1620 cm⁻¹ are due to stretching of C-N and bending of -NH₂ vibrations.

The wavelength at 3430 cm⁻¹ attributes, while 3000-3700 cm⁻¹ belongs to H₂O absorbed by GO molecule. At 2930 and 2850 cm⁻¹ the absorption corresponds to inversely symmetrical and symmetrical stretching vibration of CH₂. The absorption peak at 2300-2400 cm⁻¹ is due to stretching of C=N bond. In the middle range, the peak at 1720 cm⁻¹ is caused by stretching of C=O in carboxy and carbonyl groups. With the functionalization by amine group, this peak was disappeared, revealing that the amination was taken place on the carboxy group. Accordingly, the bending vibration of OH at 1634 cm⁻¹ is relatively intensive.

At 1340-1390 cm^{-1} the peak is due to stretching of C-O in carboxy group, while at 1264 is the result of C-O-C stretching vibration. The new bands shown in the 450-900 cm^{-1} region are due to stretching of Metal-O and Metal-N bonds.

Chemical Bonding Analysis from XPS Spectra: The N1s XPS spectrum for HA-graphene oxide paper (Figure 2B) shows N-C (399.5 eV) and N-C(O) (400.6 eV) peaks,[S13, S14] corresponding with the C1s spectrum in the main article. Additionally, it contains a third peak near 401.8 eV due to RNH_3^+ groups, which would only be observed in the hydrogen bonding scheme proposed by Matsuo et al.[S1] These alkylammonium ions most likely interact electrostatically with deprotonated carboxylic acid groups along the sheet edge; however, they may also form hydrogen bonds with hydroxyl groups on the basal plane. The N1s and C1s spectra for unmodified graphene (Figure 2D) show the presence of both N-N bonds and C-N bonds, which suggests the incorporation of hydrazine during reduction, as C-N bonds could only form via covalent reactions between hydrazine and the epoxide groups on graphene oxide. Additionally, we observe a significant presence of C(O)-N bonds in both spectra that can be attributed to amide groups formed between hydrazine and the edge carboxylic acid groups. We note that the N1s spectrum does not contain any feature that would suggest the presence of alkylammonium ions.

(2) Supporting Figures and Tables

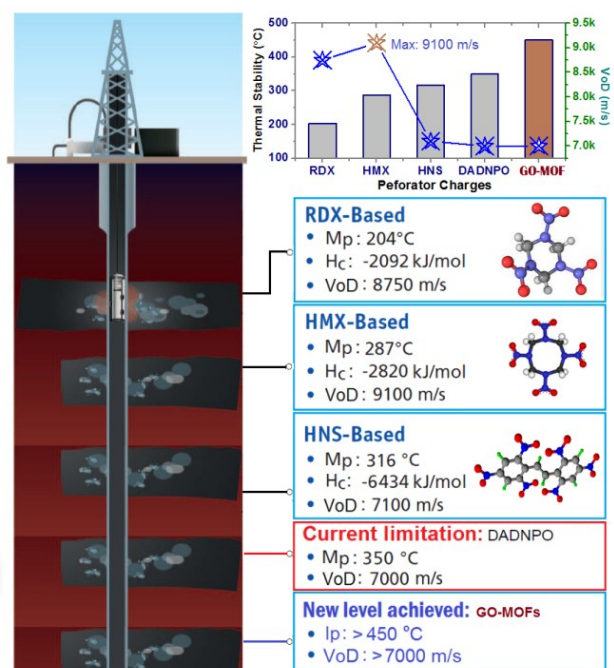


Figure S1. A comparison of the downhole exploration capacity by current industrial perforator explosives and the new level that would be achieved by our novel energetic GO-Based MOF materials, where DADNPO (2,6-dinitro-3,5-diamino pyridine-N-oxide) is industrial available the most stable explosive material with ignition temperature above 350 °C (H_c, Heat of combustion; M_p, melting point; I_p, ignition temperature; VoD, detonation velocity; this figure was adapted from the website of *EURENCO* company: <http://www.eurenco.com/content/explosives/oil-gas-extraction>). Heat resistance is an important characteristic of the explosives used for perforating deep oil wells, since the temperature in a drilled hole increases with the depth, which is also the case for the gas industry.

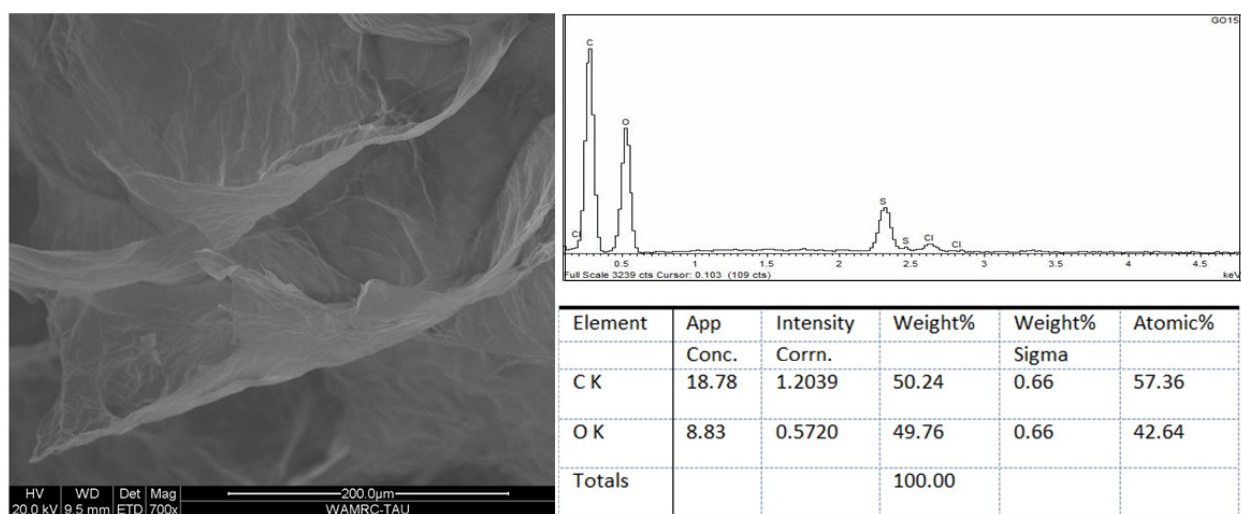


Figure S2. The SEM image and EDS spectrum of GO with 1-5 layers

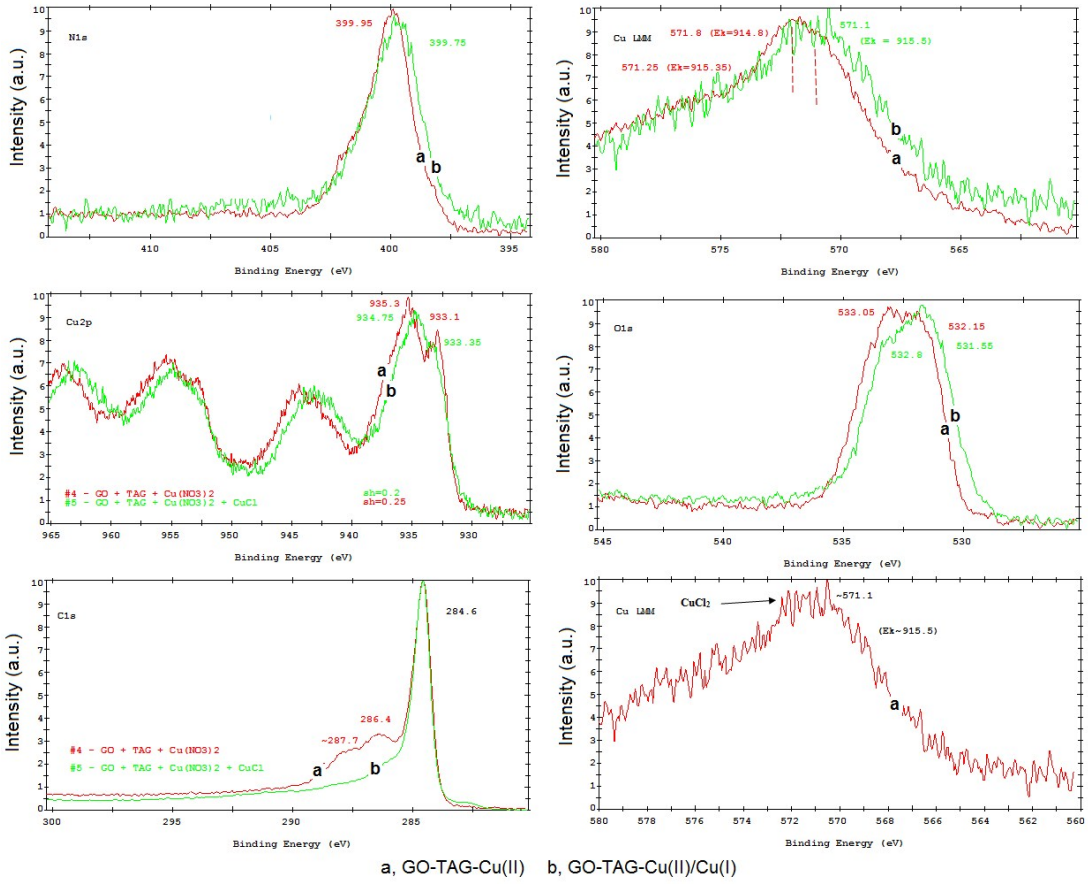
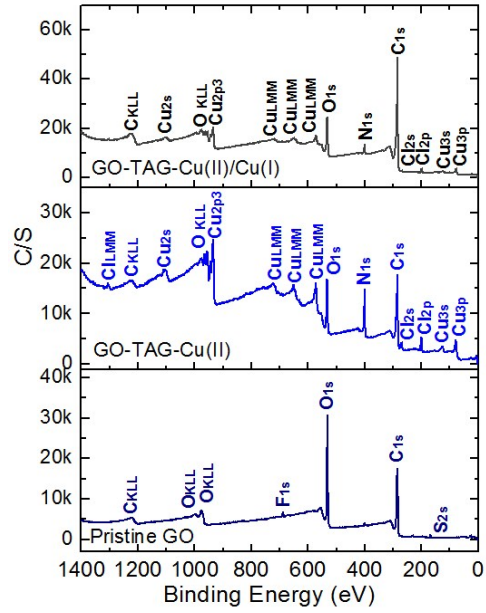


Figure S3. XPS spectra, and the chemical bonding of N, O with copper ions for Cu_{2p} in GO-TAG-Cu(II) and GO-TAG-Cu(II)/Cu(I) using XPS peak analysis.

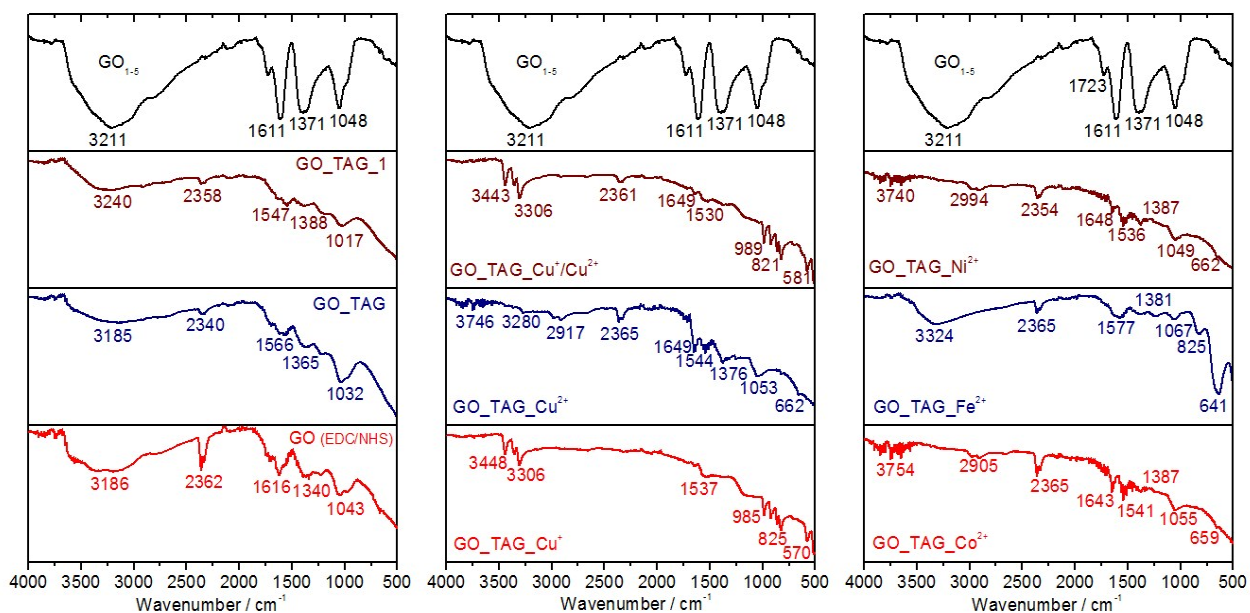


Figure S4. The FTIR spectra of GO-ligand complexes prepared from H₂O: GO_TAG_1 means the excessive coupling agent EDC/NHS has been used; the source of Cu⁺ is CuCl; the other metal ions are from their nitrate salts;

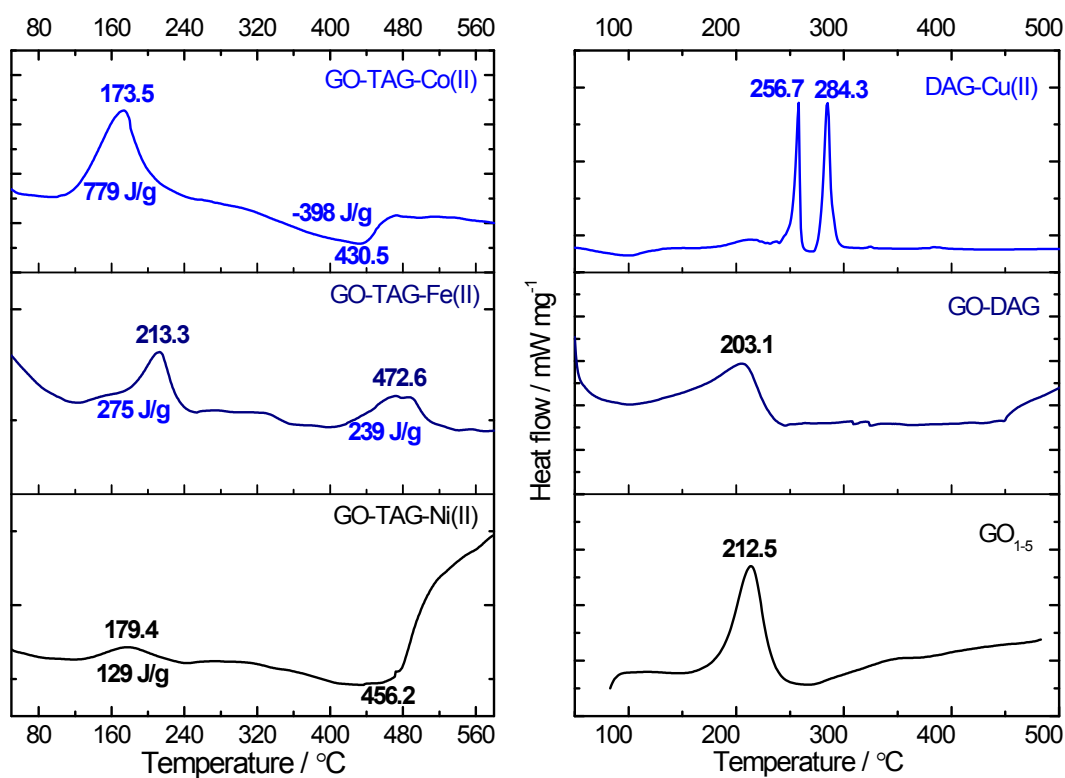


Figure S5. DSC curves of physical mixtures of GO-TAG/Fe(II), GO-TAG/Co(II) and GO-TAG/Ni(II)

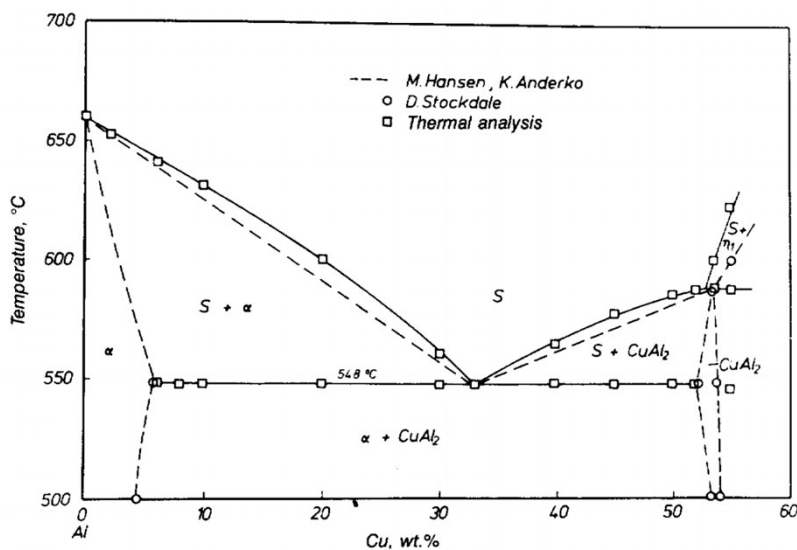


Figure S6. The Al-Cu phase diagram [s2]

Table S1. Raman data of GO and functionalized GO samples

Samples	D-band peak		G-band peak		I_D/I_G
	Shift	FWHM	Shift	FWHM	
GO	1348	229	1596	91	0.99
GO-TAG	1343	155	1575	83	1.02
GO-TAG-Cu(II)	1341	124	1589	73	1.17
GO-TAG-Cu(I)	1348	133	1585	84	1.15
GO-TAG-Cu(I)/Cu(II)	1348	144	1582	82	1.11
GO-TAG-Fe(II)	1344	128	1577	86	1.15
GO-TAG-Co(II)	1343	161	1584	83	1.06
GO-TAG-Ni(II)	1350	172	1588	84	0.98

Notes: Raman shifts are in cm^{-1} ; I_D/I_G is the integrated intensity ratio of D-band and G-band; L_a is the grain size; FWHM, the full width at half maximum, in cm^{-1} .

Table S2. The compositions and their mass content on the surface of the studied CNMs samples determined by EA, XPS and EDS analysis

	GO (XPS/EDS), theory	GO-TAG-Cu(II) (XPS/EDS)	GO-TAG-Cu(I)/Cu(II) (XPS/EDS)
C	62.25/57.37, (58.4%)	50.23/52.22, (51.5%)	60.95/60.49, (60.5%)
O	34.38/42.64, (38.92%)	16.60/12.99, (14.4%)	15.30/15.50, (15.3%)
N	0.91/-, (0%)	18.76/17.62, (16.8%)	10.03/10.15, (10.8%)
F	0.94/-, (0%)	-	-
Cl	0.29/-, (0%)	4.42/5.32, (5.3%)	4.35/4.07, (4.2%)
S	1.23/-, (0%)	-	-
Cu	-	9.98/11.85, (9.5%)	7.42/7.89, (7.6%)
H/C	0.54 (H content: 2.65%)	0.61, (H content: 2.61%)	0.42, (H content: 2.18%)
Formula (FW)	$\text{C}_{50}\text{H}_{27}\text{O}_{25}$ (1027.7)	$\text{C}_{41}\text{H}_{16}\text{O}_9(\text{C}_2\text{H}_{10}\text{N}_{12})\text{Cl}_{1.5}\text{Cu}_{1.5}$ (1003.2)	$\text{C}_{42}\text{H}_{13}\text{O}_8(\text{CH}_5\text{N}_6)\text{ClCu}$ (833.6)

Note: the H/C ratio was determined by elemental analysis (EA) from combustion gaseous products; the determined theoretical formula is based on exclusion of the impurity and average elemental content from both analyses.

Table S3. the assignments of the FTIR spectra for GO and the energetic coordination nanomaterials based on di-and tri-aminoguanidine functionalized GO.

Samples	FTIR absorption peak (in cm^{-1})						
	3000-3600	2300-2400	1700-1750	1500-1700	1200-1400	1000-1110	500-900
GO	3211	-	1720	1611	1371/1264	1048	-
GO (activated)	3186	2362	1720	1616	1340/1263	1043	-
GO-TAG	3185	2340	-	1566	1365/1264	1032	825
GO-TAG-Cu(I)	3448/3306	-	-	1537	-	985	570/825
GO-TAG-Cu(II)	3746/3280	2365	-	1544	1376/1264	1053	662
GO-TAG-Cu(I)/Cu(II)	3443/3306	2361	-	1530	-	989	581/821
GO-TAG-Fe(II)	3324	2365	-	1577	1381/1265	1067	641/825
GO-TAG-Co(II)	3754/2905	2365	-	1541	1387/1263	1055	659
GO-TAG-Ni(II)	3740/2994	2354	-	1536	1387/1261	1049	662
comments	stretching of O-H and amines or amide N-H stretch absorption	stretching of C=N bond	stretching of C=O	bending vibration of O-H	stretching of C-O in carboxy group C-O-C stretching vibration for epoxy group	stretching of C-OH bond	stretching of Metal-oxygen bond

Notes: in between 3500-3300 cm^{-1} , the primary amines produce two N-H stretch absorptions, secondary amides only one, and tertiary none; for GO-TAG, the peak for N-H stretching is overlapped with O-H broad peak.

As an *N*-donor ligand, TAG several very strong bands, and one of them appears in 1680–1580 cm^{-1} regions could be assigned to $\nu(\text{C}=\text{N})$ in guanidine group (Figure S5, Table S3), whose N atom was usually protonated by one proton preceding the N atom in C-N moiety. If Cu(II) ions are coordinated by TAG ligands in the absence of potentially capping coligands such as Cl^- , NO_3^- and H_2O , GO based coordination polymers (ECPs) could be formed through aggregation, which is the case for our starting materials. In fact, the trinuclear complexes based on tritopic triaminoguanidine ligands were employed as building blocks in the synthesis of various supramolecular cage compounds.^[53] It provides theoretical foundation for formation of ECP structure based on TAG ligand and Cu(II) ion. As shown in Figures S5, as well as Table S3. The spectra of the coordination compounds of Cu(II) with TAG ligand are very complicated and the entire assignment of all the absorption bands is very difficult. In order to interpret the vibrational spectra, attention should be paid to the featured absorption bands, such as $>\text{N}-\text{H}$ bending vibration bands, characteristic bands of $>\text{C}=\text{N}-$ group in the moiety of $-\text{N}_2\text{C}=\text{N}-$, stretching of Cu-X (X represents N, O and Cl) bands as well as bands of C-N stretching. The strong bands centered at 3236 cm^{-1} were assigned to the stretching modes of OH⁻ groups in water presented in the TAG-Cu(I) ECP structures or 3095 cm^{-1} for H₂O molecules with hydrogen bonds in copper nitrate.

(3) References

- [s1] N. A. Travlou et al., Cu-BTC MOF-graphene-based hybrid materials as low concentration ammonia sensors, *J. Mater. Chem. A*, 2015, 3, 11417-11429
- [s2] E. Schtirmann, H. Loblich, Phase boundaries and interlamellar spacing in solidification of the eutectic system Al-CuAl₂, *Metall.*, **1977**, 31, 610-614 (In German).
- [s3] Spielberg, E.T., Gilb, A., Plaul, D., Geibig, D., Hornig, D., Schuch, D., Buchholz, A., Ardavan, A., Plass, W. A spin-frustrated trinuclear copper complex based on triaminoguanidine with an energetically well-separated degenerate ground state (2015) *Inorganic Chemistry*, 54 (7), pp. 3432-3438.