[Electronic Supporting Information (ESI) to accompany]

# Highly Thermostable and Insensitive Energetic Hybrid Coordination Polymers Based on Graphene Oxide-Cu(II) Complex

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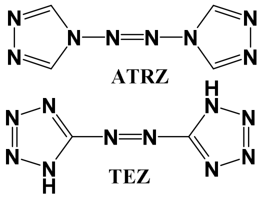
## (1) Experimental Part

***Materials:*** The commercial available graphene oxide (GO, 1-5 layers) was used as received from market with oxygen content over 42%. The copper nitrate trihydrate (99%), was 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 in diameter) were used in support of fabricated filtration papers. The ATRZ[1] and TEZ[2] (Scheme S1) were synthesized according to the literature.



**Scheme S1.** Molecular structure of ATRZ and TEZ

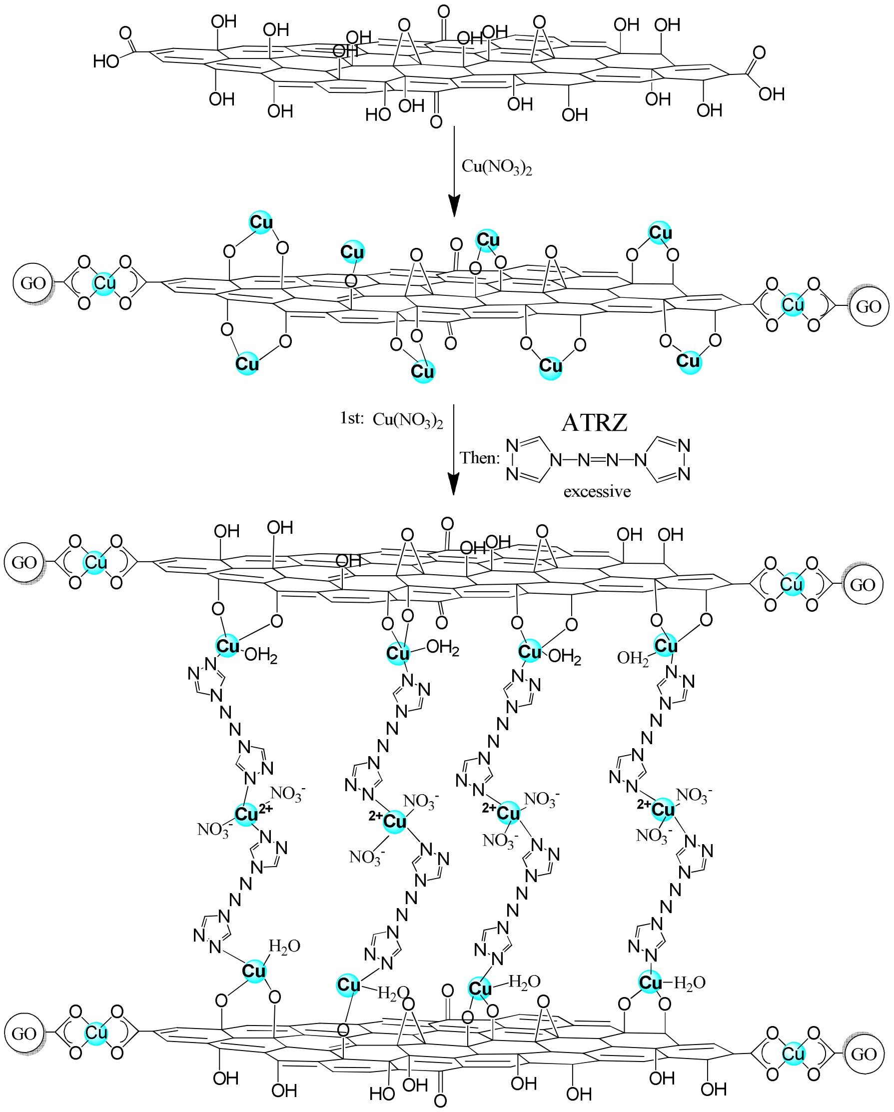
***Preparation of GO-Cu(II)-ATRZ ECP:*** 30 mg GO was dispersed in 50 ml $H_2O$ by a high power ultra-sonication in a glass reactor. 200 mg copper nitrate trihydrate was added and the mixture was further dispersed by high power ultra-sonication for 30 min. The reaction mixture was then heated and stirred for 12 hours at 60-65 °C. The Green–black solution was filtered and washed with 500 ml water. Afterwards, a solution of 100 mg of ATRZ in 25 ml hot water was added, and then the mixture was heated and stirred for 12 hours at 60-65 °C. The black product was filtered and washes with 500 ml hot water (60 °C). The pure GO-Cu(II)-ATRZ ECP was dried under vacuum (see Scheme s2).

***Preparation of GO-Cu(II)-TEZ ECP:*** 30 mg GO was dispersed in 50 ml $H_2O$ by high power ultra-sonication in a glass reactor. 200 mg copper nitrate trihydrate ware add and the mixture was further dispersed by high power ultra-sonication for 30 min. The reaction mixture was then heated and stirred for 12 hours at 60-65 °C. The Green–black solution was filtered and wash with 500 ml water. Then a solution of 100 mg of TEZ in 25 ml water was add and the mixture was heated and stirred for 12 hours at 60-65 °C. The black product was filtered and washes with 500 ml water. The pure GO-Cu(II)-TEZ CP was dried under vacuum.

***Preparation of GO/Cu(II)/ATRZ hybrid ECP:*** 30 mg GO was dispersed in 50 ml $H_2O$ by high power ultra-sonication in a glass reactor. 200 mg copper nitrate trihydrate was added and the mixture was further dispersed by high power ultra-sonication for 30 min. The green–black solution was filtered and washed with 500 ml water. The obtained GO-Cu complex was dispersed in water again and then 200 mg copper nitrate trihydrate was added to the dispersion and mixed for one hour. Afterwards, a solution of 300 mg of ATRZ in 25 ml hot water was added and the mixture was heated and stirred for 24 hr. The black

GO/Cu(II)/ATRZ hybrid ECP was filtrated and dried under vacuum. One has to note that the hybrid ECP is also a kind of coordination polymer, where the GO is covalently bonded to ATRZ-Cu(II) complex (see Scheme S2).

***Preparation of GO/Cu(II)/TEZ hybrid ECP:*** the preparation of GO-Cu(II) is the same as above, after that this complex was dispersed again in water and then 200 mg copper nitrate trihydrate was added to the dispersion and mixed for one hour. Afterwards, a solution of 350 mg of TEZ in 35 ml water was added and the mixture was heated and stirred for 24 hr. The black GO/Cu/ATRZ hybrid ECP was washed and filtrated, then dried under vacuum. One has to note that this hybrid ECP is also a kind of coordination polymer, where the GO is covalently bonded to TEZ-Cu(II) complex.



**Scheme S2.** The scheme of the preparation process that leads to formation of GO/Cu(II)/ATRZ hybrid ECP, which is also the case for GO/Cu(II)/TEZ hybrid ECP, where the $NO_3^-$ will be replaced by water molecules since TEZ would be negatively charged.

***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) 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). Transmission electron microscopy (TEM) was used to observe the interphase structure of the hybrid ECPs, where the samples were dispersed in the ethanol with concentration of 0.5 mg/mL, and two drops of 0.5 ml solution were put on the copper substrate mesh and dried under ambient condition for one day; 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 $min^{-1}$ $N_2$ 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 $N_2$ gas flow. The heat of combustion was tested by a bomb calorimeter under $O_2$ with pressure of 2 MPa, which was corrected by the determination of $NO_2$ 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 $K_\alpha$ mono-chromated 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.

## (2) Supporting Figures and Tables

### 2.1 Solvent effects on dispersion of GO and its reactivity with Cu(II) ions

Due to their high polarity, GO based materials could be well-dispersed in solvents such as water, N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).[s1] This dispersion is of great importance to this work, since a well-dispersed material would result in a better intercalation of the metal ions and the following coordination of the energetic ligands between the GO sheets with covalent bonding. In order to determine the most suitable solvent for our work, we tested the dispensability of GO and reactivity with $Cu(NO_3)_2 \cdot 3H_2O$ in various common solvents. The general experimental procedures include the dispersion by ultrasonic bath of ~20 mg GO in 20 mL of the tested solvents. The resulted GO dispersions were photographed every 3 hours, to monitor its precipitation process and final dispersions were shown in Figure S1. The $Cu(NO_3)_2 \cdot 3H_2O$ (600 mg) was dissolved in 6 ml of the solvent was then added and the mixture was sonicated for 20 min. The resulted GO/Cu(II) dispersions were photographed every 3 hours. The solvents were removed by centrifugation, and washed several times with water to remove the excessive Cu(II) ions and dried under vacuum. These dispersions were found to be high for polar solvents such as water, DMF, DMSO, EDA and sulpholane. The solvent pyridine showed a medium dispersion. Urea and Guanidine solutions resulted in the precipitation of the GO and $Cu(NO_3)_2$ as powders.

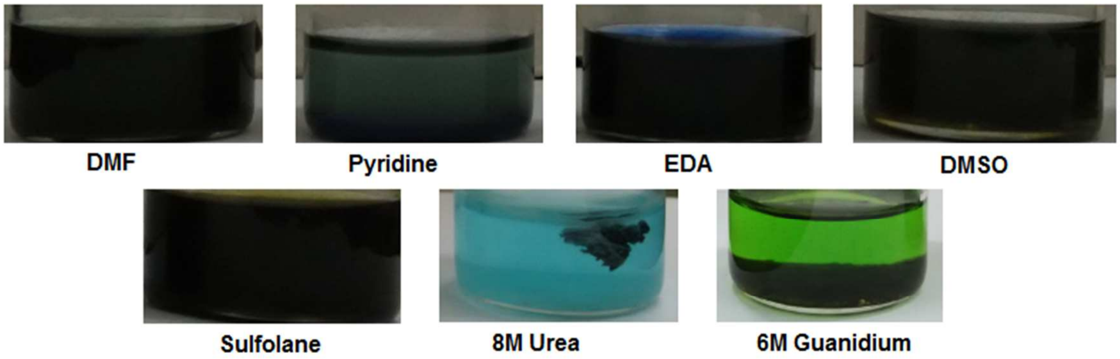


**Figure S1.** The dispersions of GO and $Cu(NO_3)_2$ in selected solvents

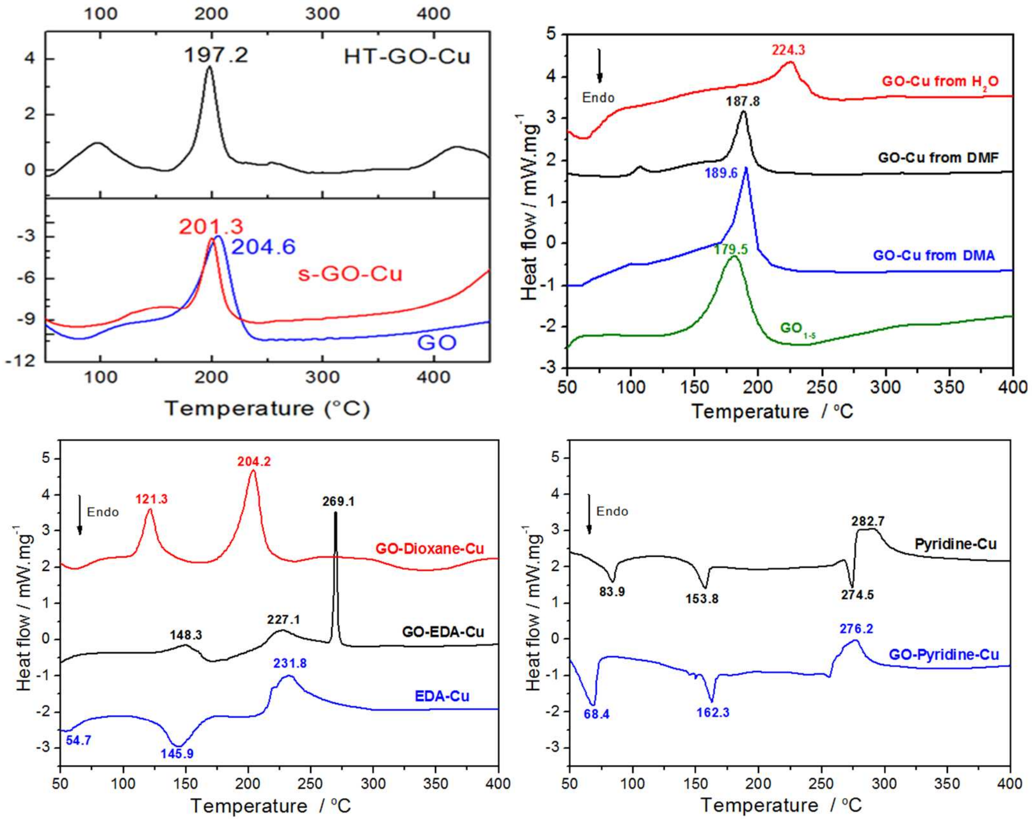


**Figure S2.** DSC curves of GO, HT GO-Cu (high temperature treated GO-Cu complex), s-GO-Cu(II) (Sonication treated GO-Cu complex), GO-Cu complexes prepared in different solvents where in most cases the solvents acted as the ligands ($GO_{1\text{-}5}$, means stacked GO with 1-5 layers, 10 °C $min^{-1}$).

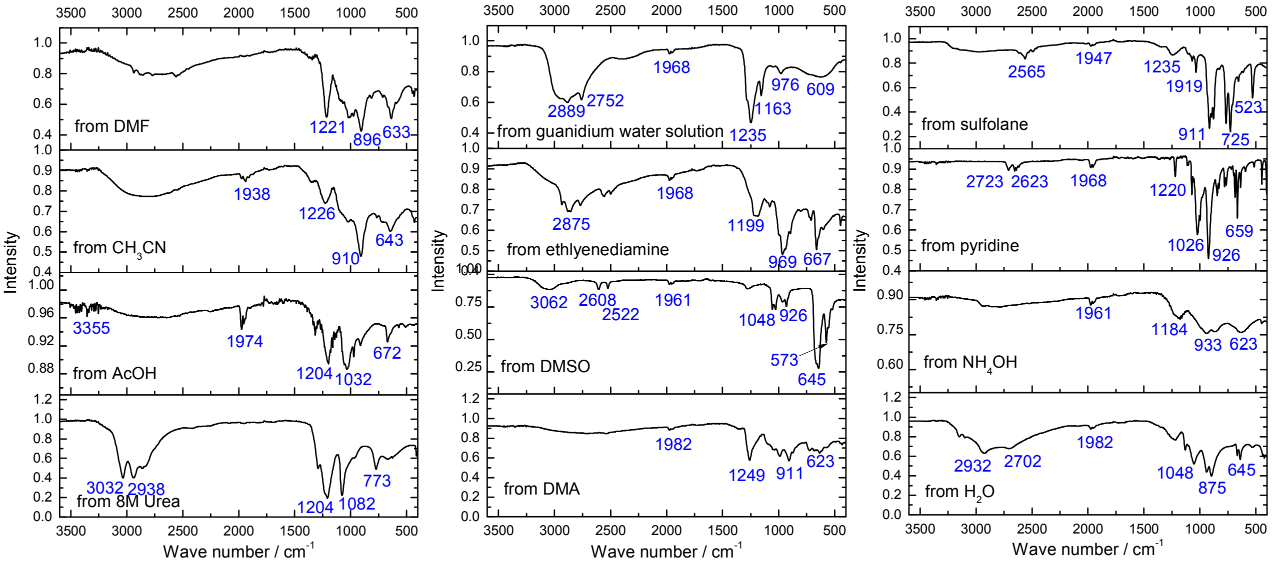


**Figure S3.** The FTIR spectra of GO-Cu(II) complex prepared from different solvents.

**Table S1:** IR peaks and peak assignments for GO-Cu complexes prepare from different solvents.

| **Sample/Solvent** | **FTIR absorption peak (in $cm^{-1}$)** | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3000-3600 | 1700-1750 | 1580-1620 | 1200-1400 | 1000- 1110 | 500-750 | impurity |
| comments | stretching vibration of O-H | stretching of C=O | bending vibration of O-H | stretching of C-O in carboxyl group C-O-C stretching vibration for epoxy group | stretching of C-OH bond | stretching of Cu-O | special peak from solvent |
| GO | 3211 | 1720 | 1611 | 1371 (1264) | 1048 | - | - |
| In $H_2O$ | 2932 | | | 1184 | 1048 | 875/645 | |
| GO-EDA-Cu complex | 3270 | - | 1580 | 1340 | 1042 | 525 | 829 |
| GO-Pyridine-Cu complex | 3106 | - | 1612 | 1389/1303 | 1041 | 504 | 700/2351 |
| GO-Cu from $H_2O$ | 3221/3329 | 1732 | 1606 | 1265/1282 | 1009-1030 | 690-730 | - |
| GO-Cu from DMA | 2700 | | | 1221 | | 896 | |
| GO-Cu from $CH_3CN$ | | | | 1204 | 1032 | 643 | 1974 |
| GO-Cu from AcOH | 3032/2938 | | | 1204 | 1082 | 673 | |
| GO-Cu from 8M_Urea | 3032/2938 | | | 1204 | 1082 | 773 | |
| GO-Cu from water solution of Guanidinium | 2889/2757 | | | 1235 | 1163 | 609 | 976 |
| GO-Cu from $NH_4OH$ | | | | | 1184 | | 933 |
| GO-Cu from DMSO | 3062 | | | | 1048 | 645 | 2608/2522/1961/945 |
| GO-Cu from DMF | | | | 1249 | | 623 | 1982/911 |
| GO-Cu from Sulfolane | 2565 | | | 1235 | 1019 | 725 | 1947/911 |

The OH stretching vibration is very important; as it is the most common vibration in GO. The disappearance of this vibration with Cu(II) ions and DMF indicates a chemical reaction with the GO. In this paper are going to investigate the energetic properties of a GO-Cu(II) complex based ECP or hybrid ECP in comparison with GO-Cu complex and energetic ligands (TEZ and ATRZ). First of all, the solvent effects on formation of GO-Cu complex are very important. Figure S2 and S3 shows the results of the samples from Raman, FTIR and DSC experiments. IR shows that the solvents such as DMF, DMSO, Pyridine, sulfolane and $NH_4OH$ are unsuitable for this purpose, since they could also react with copper, forming a GO-Solvent-Cu complex, making it impossible to form a pure GO-Cu complex. In general, the wavelength at 3000-3700 $cm^{-1}$ belongs to $H_2O$ absorbed by GO molecule. At 2930 and 2850 $cm^{-1}$ the absorption corresponds to inversely symmetrical and symmetrical stretching vibration of $CH_2$. In the middle range, the peak at 1720 cm$^{-1}$ is caused by stretching of C=O in carboxyl and carbonyl groups. Accordingly, the bending vibration of OH at 1634 cm$^{-1}$ is relatively intensive. At 1380 cm$^{-1}$ the peak is due to stretching of C-O in carboxyl group, while at 1264 is the result of C-O-C stretching vibration. The appearance of new bands in the 470-450 cm$^{-1}$ and 390-380 cm$^{-1}$ region due to v(Cu-O) and v(Cu-N) respectively. The IR of GO-Cu shows a weak broad band within the range 3350-3250 cm$^{-1}$ corresponding to v(O-H). The Cu(II) ion could be complexed with GO by either sonication or heat treatment in water.

## 2.2 The formation of GO-Cu(II) complex in water solution

We have successfully reacted GO with $Cu(NO_3)_2$ by two different methods: sonication and heat treatment. In the two methods GO reacts with the oxygen groups on top however the amount of Cu bounded is different. Figure S4 presents the Raman of GO and HT-GO (GO after heat treatment), FTIR of s-GO-Cu (GO-complex prepared by sonication), HT-GO-Cu (GO-complex prepared under heating), GO and $Cu(NO_3)_2$. Peak assignments are shown in Table S2. The DSC curves are shown in Figure S5. It has been shown that little in decomposition heat after GO was complexed with Cu(II) by each of the methods.

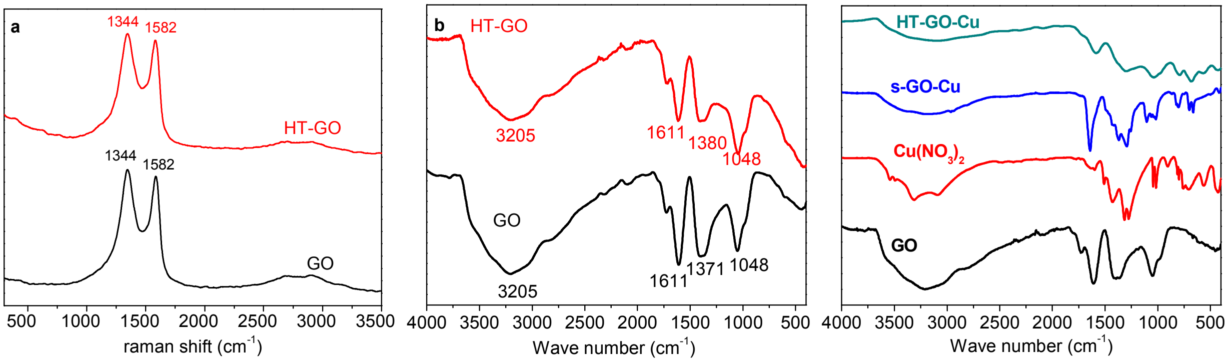


**Figure S4.** a, Raman analysis of HT-GO *vs.* GO; b, FTIR analysis of s-GO-Cu (GO-Cu prepared under sonication), HT-GO-Cu (GO-Cu complex prepared under heating), GO and $Cu(NO_3)_2$.

**Table S2.** FTIR and Raman data for GO and HT-GO

| Sample | **FTIR absorption peak** (in cm$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3000-3600 | 1700-1750 | 1580-1620 | 1200-1400 | 1000- 1110 | 500-750 | impurity |
| comments | stretching vibration of O-H | stretching of C=O | bending vibration of O-H | stretching of C-O in carboxyl group<br>C-O-C stretching vibration for epoxy group | stretching of C-OH bond | stretching of Cu-O | Special peak from solvent |
| GO | 3205 | 1720 | 1611 | 1371 | 1048 | - | - |
| HT-GO | 3205 | 1720 | 1611 | 13380 | 1048 | | |
| S-GO-Cu | | | 1633 | 1369/1288 | 1095/1019 | 791/700 | |
| HT-GO-Cu | 3118 | | 1597 | 1298 | 1039 | 796/675 | |
| **Raman shifts** | | | | | | | |
| | d-band peak | | G-band peak | | $I_D/I_G$ | | |
| sample | shift | FWHM | shift | FWHM | | | |
| GO | 1344 | 229 | 1582 | 91 | 0.99 | | |
| HT-GO | 1344 | 223 | 1582 | 89 | 0.99 | | |

In order to investigate heat treatment experimental condition on the stability of the pristine GO, the GO was heated in water for 6 h at 80 °C. A comparison between GO and heat-treated GO (HT-GO) could show the functional group changes in GO. When comparing HT-GO to GO, the stretching of C-OH (1000-1100 $cm^{-1}$) bond is larger as compared to C=O starching (1700-1750 $cm^{-1}$) in HT-GO than GO. The stretching vibration of O-H (3000-3600 $cm^{-1}$), stretching of C=O (1700-1750 $cm^{-1}$), bending vibration of O-H (1580-1620 $cm^{-1}$) and stretching of C-O in carboxyl group, C-O-C stretching vibration for (1200-1400 $cm^{-1}$) all remain at the same concentrations. The analysis of GO *vs.* HT-GO, including IR, Raman and DSC, are shown in Figures S3 and S5. Overall, the change in GO as a result of heat treatment at 60-65 °C for less than 48 hrs was minor and can be neglected.

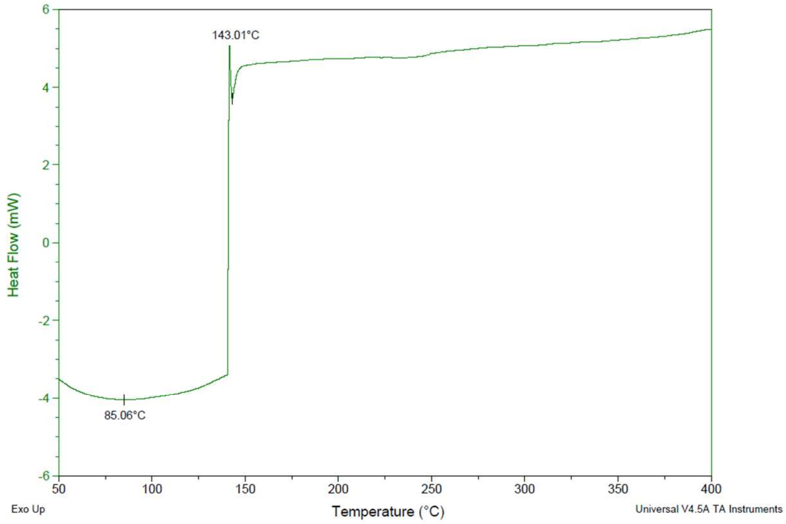


**Figure S5.** DSC curve of TEZ-Cu(II) complex under heating rate of 10 °C $min^{-1}$ with sample mass 0.21 mg: after 143 °C, the sample was ignited and run-away chemical reaction occurred, with the broken Al crucible left and the measurement was no longer valid.

**Table S3:** Raman data of GO and functionalized GO samples

| Samples | D-band peak | | G-band peak | | $I_D/I_G$ |
|---|---|---|---|---|---|
| | Shift | FWHM | Shift | FWHM | |
| GO | 1344 | 229 | 1582 | 91 | 0.99 |
| GO-Cu(II)-TEZ MOF | 1357 | 218 | 1598 | 138 | 1.12 |
| GO/Cu(II)/TEZ hybrid ECP | 1357 | 222 | 1586 | 146 | 1.02 |
| GO-Cu(II)-TRZ MOF | 1372 | 186 | 1614 | 121 | 1.27 |
| GO/Cu(II)/TRZ hybrid ECP | 1366 | 145 | 1620 | 104 | 1.08 |

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

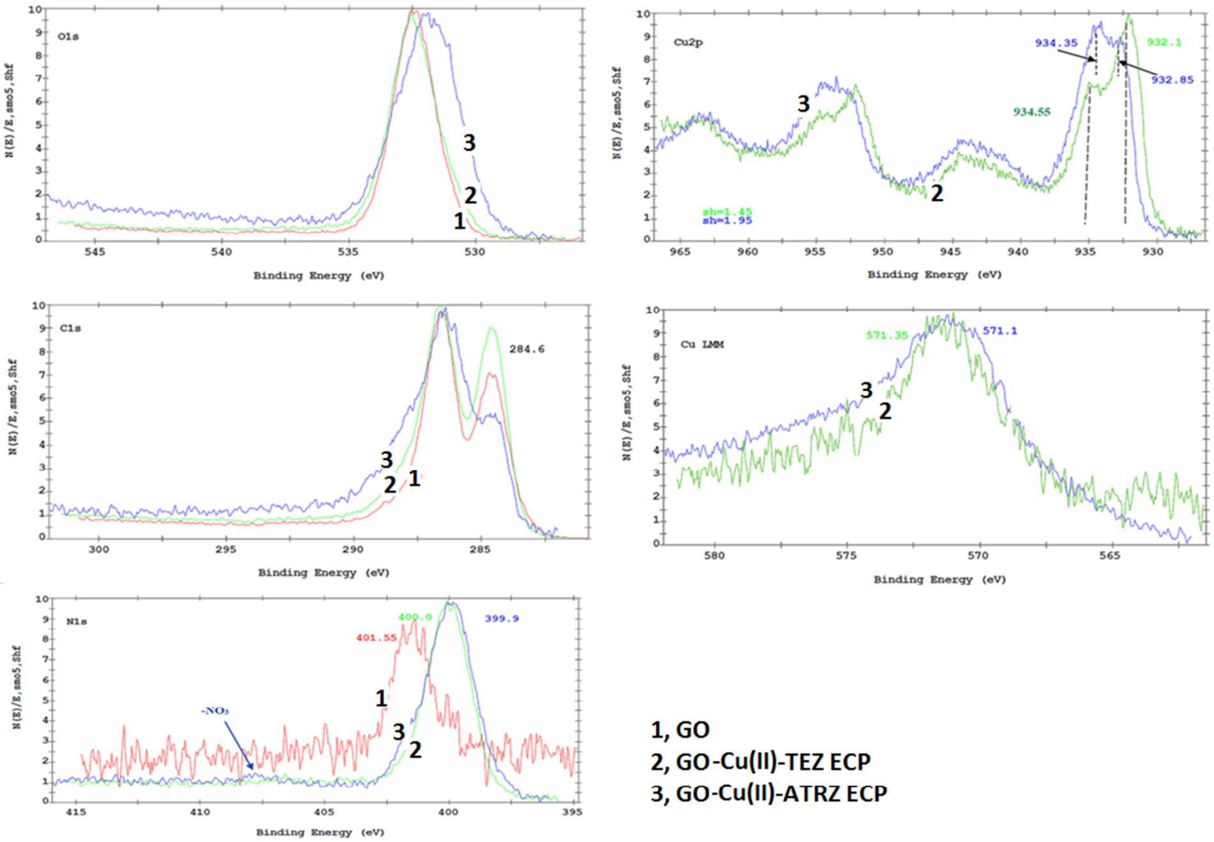


**Figure S4.** The chemical binding energy of C 1s, N 1s, O 1s and Cu 2p in GO (**1**), GO-Cu(II)-TEZ ECP (**2**) and GO-Cu(II)-ATRZ ECP (**3**) using XPS peak analysis.

**Table S4.** XPS data of GO and GO-based ECPs

| GO | Peak BE (eV) | atomic concentration | Bond |
|---|---|---|---|
| C1s | 284.57 | 42.5% | C-C |
| C1s | 286.59 | 48.7% | C-O / O-C-O |
| C1s | 288.05 | 8.8% | C=O |
| GO-Cu(II)-TEZ ECP | Peak BE (eV) | Atomic concentration | Bond |
| C1s | 284.57 | 43.3% | C-C |
| C1s | 285.62 | 3.2% | C-N |
| C1s | 286.59 | 40.3% | C-O/O-C-O |
| C1s | 287.47 | 2.6% | C-O-Cu |
| C1s | 288.05 | 10.6% | C=O |
| N1s | 398.9 | 11.7% | =N- |
| N1s | 399.89 | 61.7% | NH-/-N-N- |
| N1s | 400.8 | 24.2% | NHC=O/-N-C=O |
| N1s | 401.75 | 2.4% | N+ |
| Cu 2p3/2 | 932.1 |  | Cu-N |
| Cu 2p3/2 | 934.55 |  | C-O-Cu |
| GO-Cu(II)-ATRZ ECP | Peak BE (eV) | atomic concentration | Bond |
| C1s | 284.57 | 21.8% | C-C |
| C1s | 285.62 | 17.9% | C-N |
| C1s | 286.59 | 32.5% | C-O/O-C-O |
| C1s | 287.47 | 13.6% | C-O-Cu |
| C1s | 288.05 | 14.2% | C=O |
| N1s | 398.9 | 17.8% | =N- |
| N1s | 399.89 | 55.1% | NH-/-N-N- |
| N1s | 400.8 | 12.8% | NHC=O/-N-C=O |
| N1s | 401.75 | 14.3% | N+ |
| Cu 2p3/2 | 932.85 |  | Cu-N |
| Cu 2p3/2 | 934.35 |  | C-O-Cu |

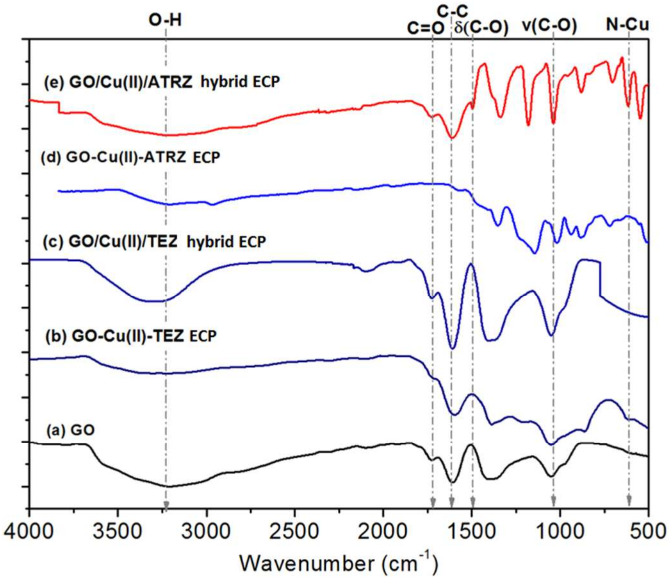


**Figure S7**. the FTIR spectra of (**a**) pristine GO, (**b**) GO-Cu(II)-TEZ ECP, (**c**) GO/Cu(II)/TEZ hybrid ECP, (**d**) GO-Cu(II)-ATRZ ECP, and (**e**) GO/Cu(II)/ ATRZ hybrid ECP.

**Table S5.** The assignments of the FTIR spectra for GO and the energetic coordination nanomaterials based on TEZ and ATRZ functionalized GO

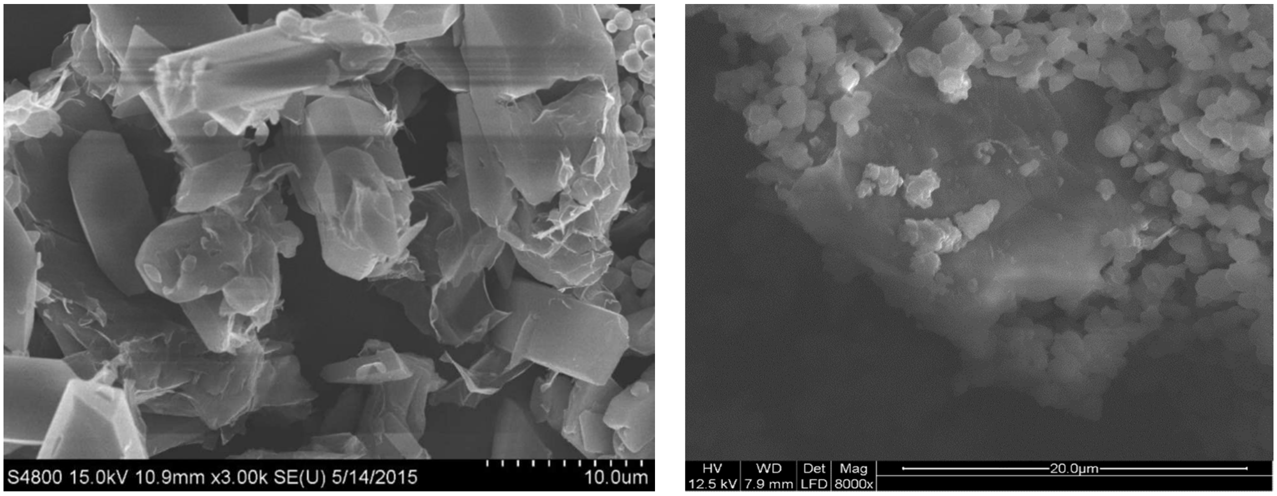
| Samples | FTIR absorption peak (in cm$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3000-3600 | 2300-2400 | 1700-1750 | 1500-1700 | 1200-1400 | 1100-1200 | 1000-1110 | 500-900 |
| GO | 3240 | - | 1740 | 1621 | 1371 | | 1048 | - |
| GO/Cu(II)/TEZ hybrid ECP | 3309 | - | 1740 | 1637 | 1373 | | 1080 | - |
| GO-Cu(II)-TEZ ECP | 3240 | - | 1740 | 1601 | 1384 | | 1053 | 872/622 |
| GO/Cu(II)/ATRZ hybrid ECP | 3211 | 2365 | 1747 | 1623 | 1353 | 1171 | 1041 | 878/618/550 |
| GO-Cu(II)-ATRZ ECP | 3240 | - | - | - | 1367 | 1134 | 1014 | 877/842 |
| assigments | stretching of O-H | stretching of C=N bond | streching of C=O | bending vibration of O-H | streching of C-O in carboxy group<br>C-O-C streching vibration for epoxy group | | streching of C-OH bond | stretching of Metal-oxygen bond |

**Table S6.** The weight percentage of the elemental compositions of the ECPs determined by EA, XPS and EDS analysis

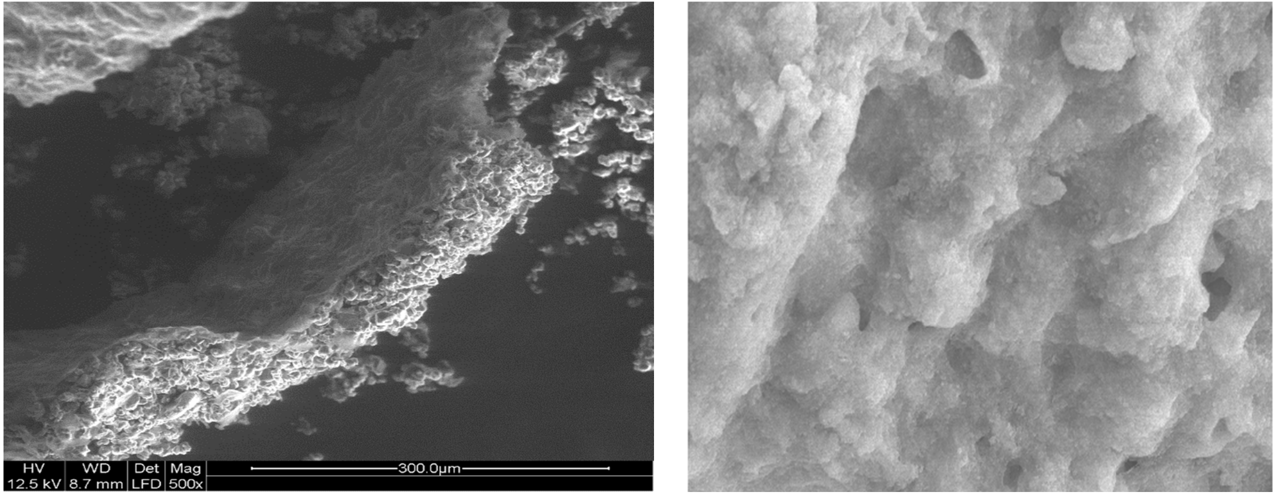
| | GO (Mean value of XPS and EDS in wt.%) | GO-Cu(II)-ATRZ ECP (Mean value of XPS and EDS in wt.%) | GO-Cu(II)-TEZ ECP (Mean value of XPS and EDS in wt.%) |
|---|---|---|---|
| **C** | 58.81 | 26.38 | 28.40 |
| **O** | 37.79 | 33.58 | 46.26 |
| **N** | 0.91 | 20.98 | 8.52 |
| **F** | 0.97 | - | - |
| **Cl** | 0.29 | - | 0.11 |
| **S** | 1.23 | - | - |
| **Cu** | - | 19.05 | 16.71 |
| **Atomic ratio of H/C (from EA)** | 0.54 | 0.74 | 0.52 |
| **Formula (FW)** | $C_{50}H_{27}O_{25}$ (1027.7) | $C_{22}H_{16}O_{21}N_{15}Cu_3$ (1017.09) | $C_{27}H_{21}N_7O_{33}Cu_3$ (1162.12) |
| | GO/Cu(II)/ATRZ hybrid ECP (only by EDS in wt.%) | GO/Cu(II)/TEZ hybrid ECP (only by EDS in wt.%) | |
| **C** | 16.05 | 12.57 | |
| **O** | 39.13 | 39.02 | |
| **N** | 24.95 | 28.72 | |
| **Cl** | 0.75 | 0.68 | |
| **Cu** | 19.12 | 19.01 | |
| **Atomic ratio of H/C (from EA)** | 0.81 | 1.23 | |
| **Formula (FW)** | $C_{27}H_{22}O_{49}N_{36}Cu_6$ (2015.3) | $C_{21}H_{26}O_{49}N_{42}Cu_6$ (2032.0) | |

The H/C ratio was determined by elemental analysis (EA) from combustion gaseous products; the determined theoretical formulae are based on exclusion of the impurity and average elemental content from both analyses. The final nitrogen contents listed in Table 1 are calculated based on the final theoretical formulae; the high content ratio of H/C in GO/Cu(II)/TEZ hybrid ECP is due to presence of chelating water instead of $NO_3^-$.

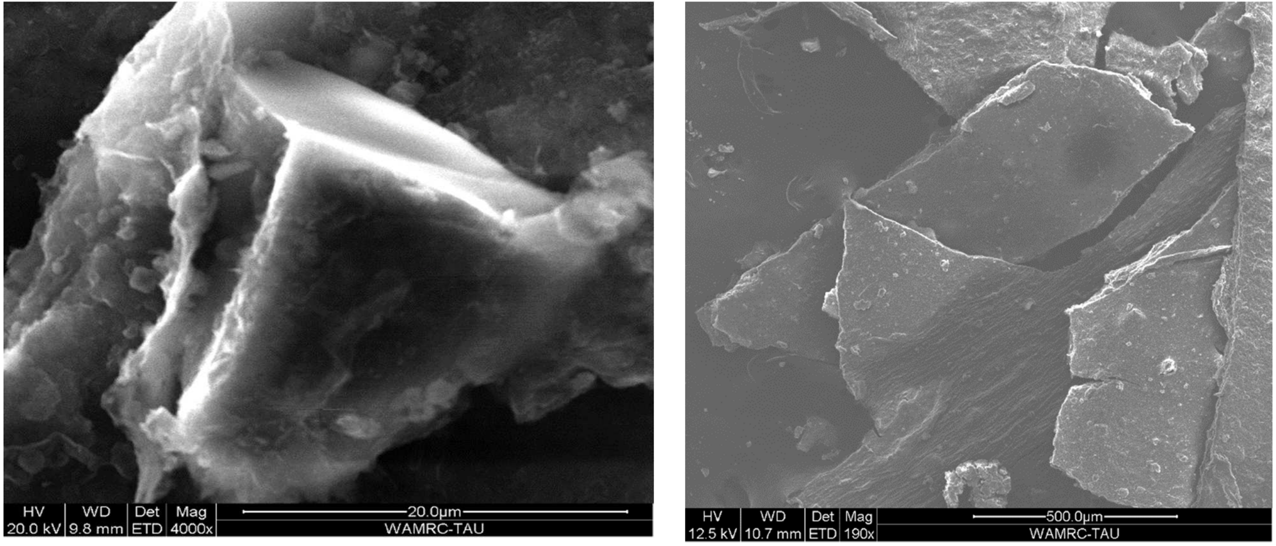
## 2.3 The morphology of different samples



**ATRZ-Cu MOF crystals mixed with GO in DMF** **ATRZ-Cu MOF crystals mixed with GO in water**



**GO-ATRZ MOF in DMF** **sonicated GO-Cu(II) complex (washed with water)**



**A large crystal of GO-ATRZ-Cu(II) hybrid ECP** **GO-TEZ-Cu(II) ECP**

**Figure S8.** the morphology of the several hybrid ECPs and mixture materials

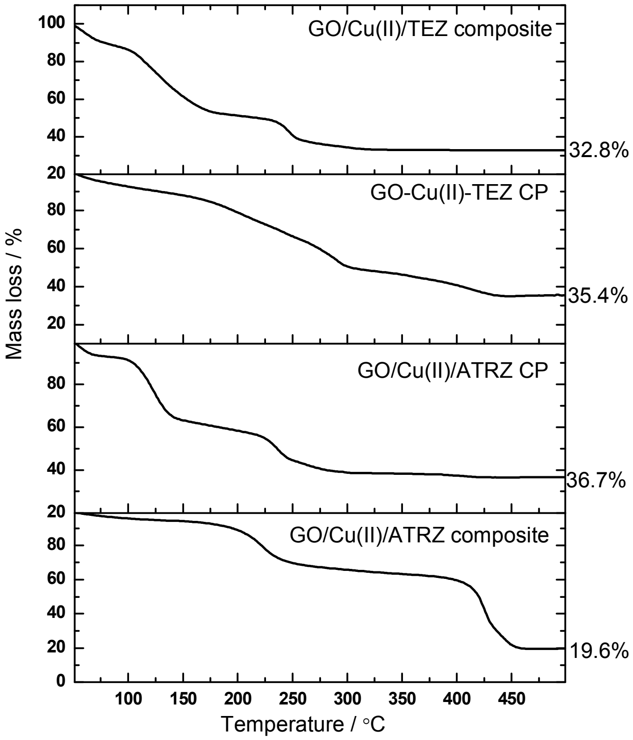


**Figure S9.** The TGA curves of involved materials.

## 2.4 Preparation of TEZ-Cu complex

**Caution!** This material is highly sensitive to external stimuli and should be synthesizes with the necessary precautions.

100 mg TEZ was dissolved in 5 ml water and 10 ml of 1 mol $L^{-1}$ $Cu(NO_3)_2$ solution was add dropwise during stirring. The brown precipitates ware collected and washed with water to remove all access Cu(II) ions. When tested for mp, the capillary blow away during the explosion of the material. DSC was performed with extreme caution, and results had to be repeated several times since the crucible did not stay in place, as can be seen in Figure S8), and the measurement was no longer valid. Since this material is highly dangerous, no further analysis was performed.

## (3) References

(s1) Yang, H. F.; Shan, C. S.; Li, F. H.; Han, D. X.; Zhang, Q. X.; Niu, L. Chem. Commun., 2009, 3880.