

Electronic Supporting Information (ESI)

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

Qi-Long Yan^a, Adva Cohen^a, Ajay K. Chinnam^a, Natan Petrutik^a, Avital Shlomovich^a, Larisa Burstein^b,
Michael Gozin^{a*}

[a] School of Chemistry, Faculty of Exact Science, Tel Aviv University, Tel Aviv, 69978, Israel.

[b] Wolfson Applied Materials Research Center, Tel Aviv University, Tel Aviv, 69978, Israel.

1. Experimental

Characterization. The density of prepared materials was measured by Helium 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. Transmission electron microscopy (TEM) was used to observe the structure of TAGP, where the sample was prepared directly on a copper grid, by crosslinking reaction (of TAG·HCl with glyoxal) in water and dried under ambient condition for 3 days.

DSC analyses were carried out on TA Q20 instrument, at heating rate of 10 °C·min⁻¹, with 50 ml·min⁻¹ N₂ gas flow. A typical sample mass was about 0.5 mg. TGA analyses were carried out on TA Q500 TGA instrument at heating rate of 10 °C·min⁻¹, under N₂ gas flow. The heat of combustion was measured by bomb calorimetry (Parr), under O₂ pressure of 2 MPa, which was corrected by the determination of NO₂ formation.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed under UHV (2.5×10⁻¹⁰ Torr), using 5600 Multi-Technique System (PHI, USA). Samples were irradiated with 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). It provides an estimation of elements present on a sample surface and is taken at a low resolution. Utility Multiplex: spectra taken for different peaks at 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 bonding analysis. The powder X-Ray spectra were obtained by a Rigaku diffractometer, the sampling rate of 0.5 point·sec⁻¹ and scan rate of 0.01 deg·min⁻¹.

2. Supporting Figures and Tables

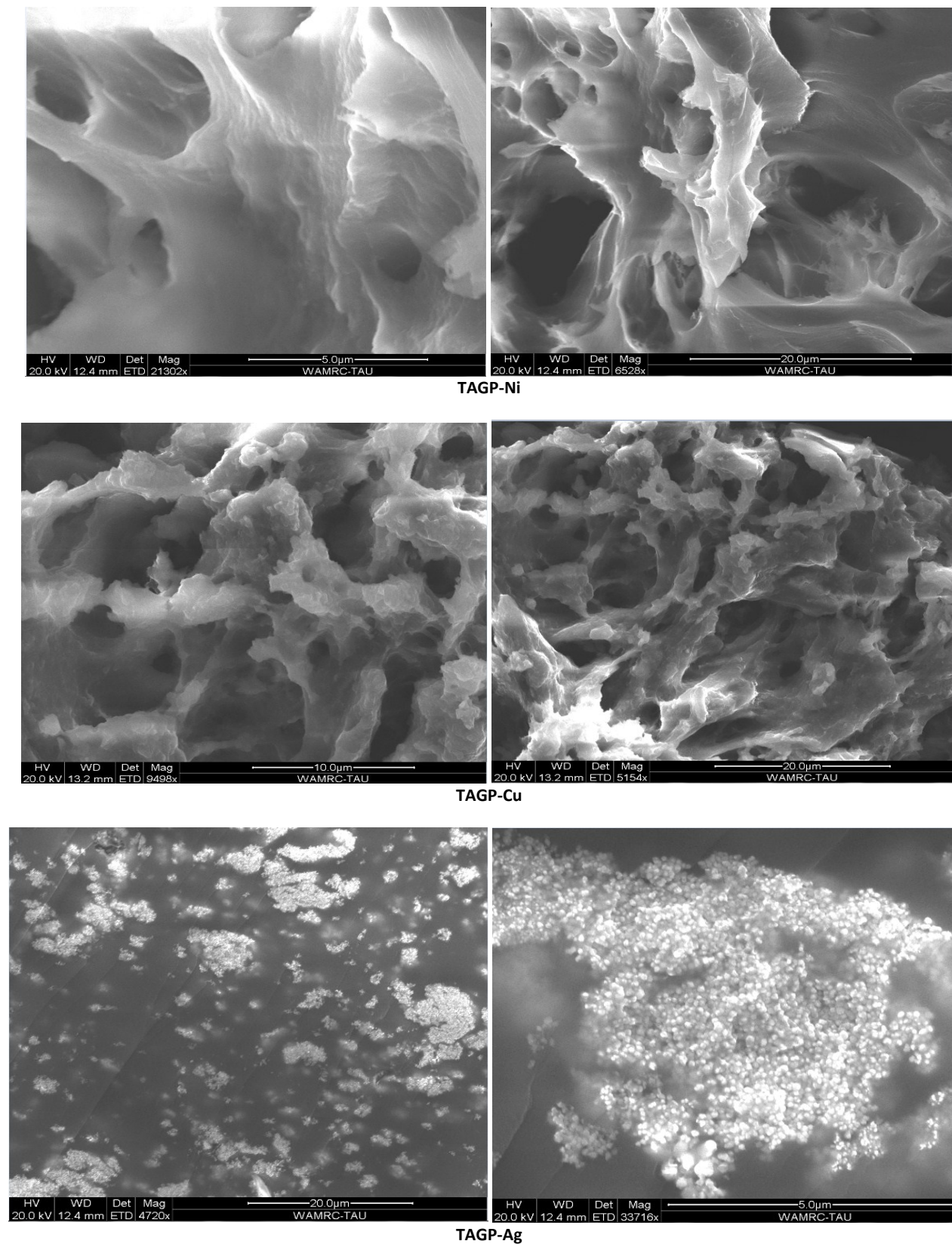
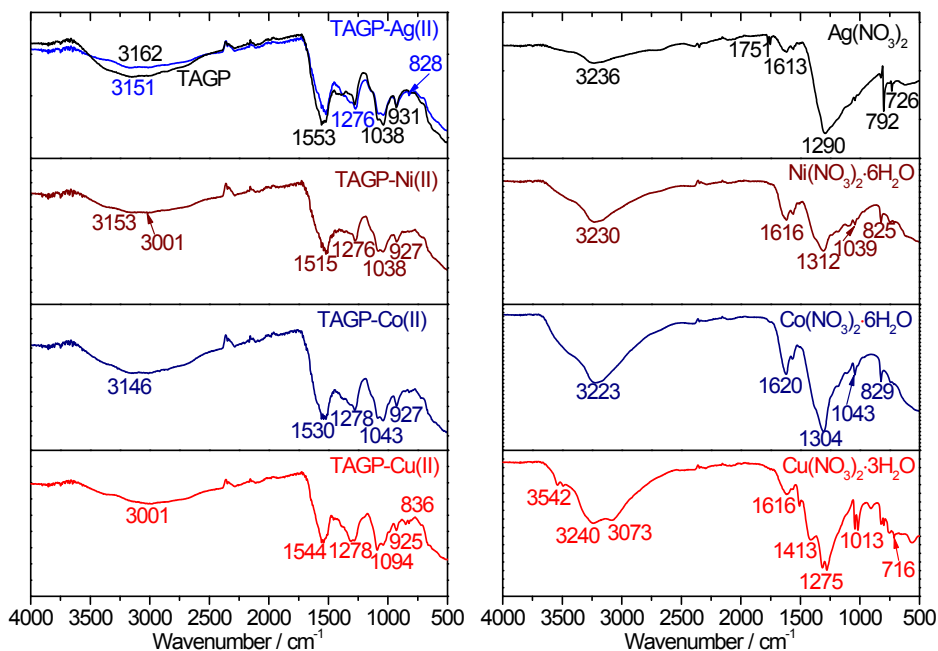


Figure S1. SEM images of TAGP-Ms.

Table S1. Elemental Analysis results for TAGP and TAGP-Ms obtained from EDS/XPS experiments.

Elements	TAGP (w/a)%		TAGP-Cu (w/a)%		TAGP-Co (w/a)%		TAGP-Ni (w/a)%		TAGP-Ag (w/a)%	
C	26.30	22.22	30.74	26.55	30.87	26.55	34.53	28.30	21.49	24.79
N	40.90	29.63	47.81	35.40	48.02	35.40	53.70	37.74	36.77	36.36
O	14.02	8.89	9.56	6.19	9.60	6.19	0.00	0.00	8.59	7.44
Cl	-	-	12.10	3.54	12.15	3.54	13.59	3.77	8.46	3.31
Metal	-	-	10.84	1.77	10.10	1.77	11.25	1.89	25.73	3.31
C/H	3/5.3		1/1		1/1		1/1		1/1	
Formula	$C_3H_{5.3}N_4O_{1.2}$		$C_3H_3O_{0.7}N_4Cl_{0.4}Cu_{0.2}$		$C_3H_3O_{0.7}N_4Cl_{0.4}Co_{0.2}$		$C_3H_3N_4Cl_{0.4}Ni_{0.2}$		$C_3H_3O_{0.9}N_{4.4}Cl_{0.4}Ag_{0.4}$	

Note: w, weight percentage; a, atomic percentage; 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.

**Figure S2.** FTIR spectra of TAGP, TAGP-Ag, TAGP-Ni, TAGP-Co and TAGP-Cu (all samples were measured in KBr pellets).**Table S2.** Assignments of FTIR spectra measured for TAG-HCl, metal nitrates, TAGP and TAGP-Ms.

Samples	3200-3500	3200-3000	1500-1700	1200-1500	1000-1200	500-1000
TAG-HCl	3317	3190	1678/1613	1321	1128	604 (H-Cl)
$M(NO_3)_2 \cdot xH_2O$	3542/3240	3073	1508 $\nu(H-NO_3)$	1304-1312 /1274-1290	1013-1039	564
TAGP	3325	3251/3151	1553	1276	1038	931/828
TAGP-Ag	3332	3234/3162	1512	1276	1038	931
TAGP-Ni	3324	3233/3001	1515	1276	1043	927
TAGP-Co	3321	3226/3146	1530	1278	1043	927
TAGP-Cu	3313	3201/3001	1533	1278	1094	925/836
comments	$\nu(N-H)$ amines or amide	$\nu(O-H)$ in H_2O	1515-1618: $\delta(C=N)$ 1678: $\delta(C-N-)$	1319-1321: $\nu(N-O)$ 1277: $\nu(O-H)$ 1276-1278: in plane $\delta(N-H)$	1038-1043: $\nu(C-N)_t$ 1128: $\nu(C=N)$	925-931: $\nu(N-N)$ 836: $\nu(Cu-O-H)$ 564: $\nu(M-N)$

Notes: in range of 3500-3300 cm^{-1} , primary amines have two N-H stretch absorptions, secondary amides have only a single absorption; in spectra of TAGP-Ms, N-H stretching peak is overlapping with broad O-H peak;
w, weak; s, strong; ν , stretching; δ , bending; lowercase p, s and t, primary, secondary and tertiary amine;
M = Ag^+ , Cu^{2+} , Co^{2+} and Ni^{2+} , while x = 3 for Cu^{2+} and 6 for the others.

The FTIR spectra of all measured samples (Figure S2) exhibit peaks corresponding to a spectrum of TAGP, with absorption bands that could be assigned to the C-N bond stretch and N-H deformations of amine and C=C bond stretches. The FTIR 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} could be assigned to C-N bond stretching and bending. The absorption peak at 2300-2400 cm^{-1} is due to stretching of C=N bond. The new bands for TAGP-M complexes that appear in the 450-900 cm^{-1} region are most probably due to the stretching of Metal-O and Metal-N bonds. As a Nitrogen-donor ligand, TAG·HCl has several very strong bands, and one of them that appears in 1680-1580 cm^{-1} region, which could be assigned to $\nu(\text{C}=\text{N})$ of guanidine group (Figure S2, Table S1).

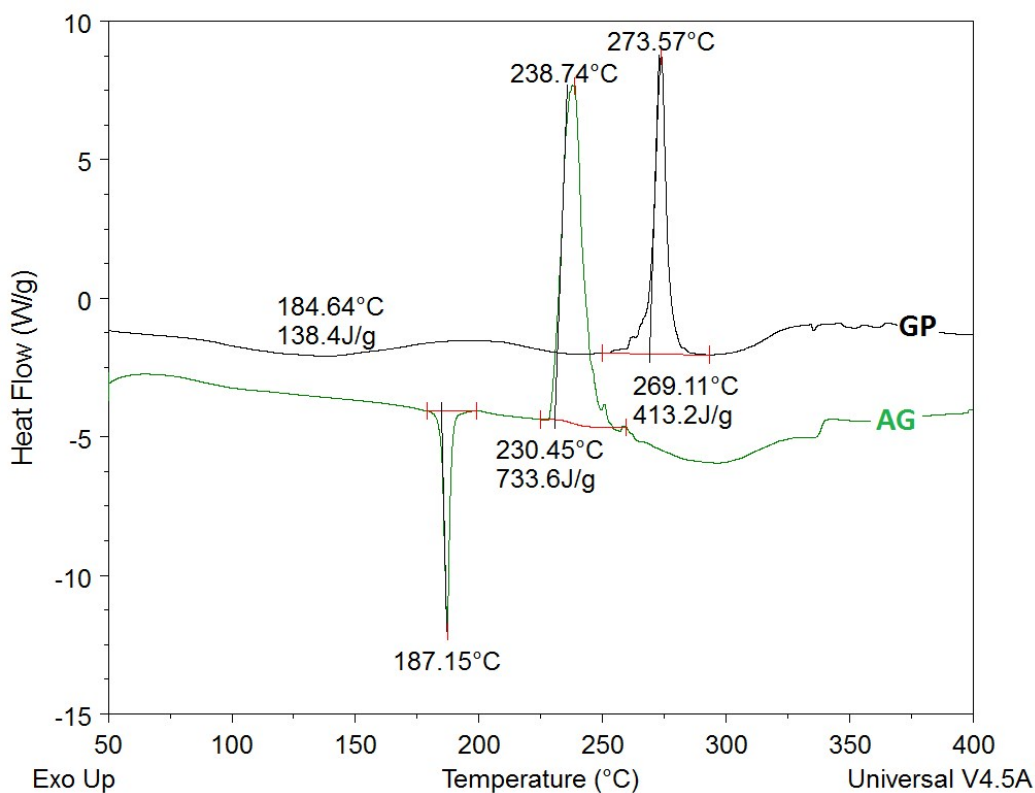


Figure S3. DSC thermograms of guanidine-formaldehyde polymer (**GP**) and of guanidine hydrochloride (**AG**).