### SUPPORTING INFORMATION

Electrochemical Determination of TNT, DNT, RDX and HMX with Gold Nanoparticles/Poly(Carbazole-Aniline) Film–Modified Glassy Carbon Sensor Electrodes Imprinted for Molecular Recognition of Nitroaromatics and Nitramines

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Supporting information contains; (i) Optimization of electropolymerization for energetic material–carbazole-aniline mixtures, (ii) Fabrication of energetic material memory-Cz-ANI copolymer film on GCE, (iii) Impedance measurements of the modified electrodes, (iv) SEM image of the developed sensor electrode, (v) Electrochemical determination of TNT with GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> electrode, (vi) Slope, intercept, correlation coefficient of TNT, DNT, RDX and HMX determination, (vii) Analytical results of synthetic mixtures of energetic materials, (viii) Interference studies for electroactive compounds, (ix) calibration equations for TNT and RDX with using LC-MS, (x) Statistical comparison of the developed method with reference (LC-MS) method.

# **Optimization for Electropolymerization of Carbazole-Aniline Mixtures Containing Energetic Materials at Different Proportions**

When the GC working electrode was modified with only carbazole, the coated material was cracked and spilled from the electrode surface after several measurements in ACN media. In order to prevent this, aniline –added to the medium– could be easily coated on the surface of the GC electrode and formed a stable layer enduring for a long time (aniline may not function singly because it does not respond to energetic materials). Coating was made by using carbazole-aniline mixtures at 1:1, 2.5:1, 5:1 and 10:1 mole ratios. Electropolymerization with a 1:1 mixture decreased the sensitivity because of the relatively high ratio of aniline. On the other hand, the coatings prepared from 10:1 and 5:1 mixtures continued to spill from the electrode surface and reproducible results could not be obtained. Optimal results were obtained with a 2.5-1 mixture of Cz-ANI, which was used in further experiments.

Energetic material was added to the monomer mixture in order to provide energetic materialmemory capability for the GC/P(Cz-*co*-ANI) electrode. The energetic material was added to the Cz-ANI monomer mixture at 10 mg L<sup>-1</sup>, 50 mg L<sup>-1</sup>, 100 mg L<sup>-1</sup> and 250 mg L<sup>-1</sup> concentrations for optimizing the energetic material-memory electrode after electropolymerization. Then, the determination of the relevant energetic material was performed by using this modified electrode. The sensitivity obtained for mixtures containing the energetic material at 10 mg L<sup>-1</sup> and 50 mg L<sup>-1</sup> concentrations was lower than that obtained for 100 mg L<sup>-1</sup>, and the mixture prepared at 250 mg L<sup>-1</sup> of energetic material did not cause a rise in sensitivity. Thus, 100 mg L<sup>-1</sup> of energetic material was chosen as the optimal concentration in the monomer mixture.

**Fabrication of Energetic Material Memory-Cz-ANI Copolymer Film on GCE.** Electrochemical polymerization of carbazole-aniline monomer mixture (containing the energetic material) was carried out by cyclic voltammetry using a potential interval between - 1.2 V and 1.4 V, scanning speed of 20 mV s<sup>-1</sup>, and 5 cycles.



**Figure S-1.** The cyclic voltammograms for polymerization of  $(2 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ Cz} + 1 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ ANI})$  mixture containing 100 mg L<sup>-1</sup> energetic material in solution.

#### **Impedance Measurements of the Modified Electrodes**

Impedance measurements were made for the TNT memory–GC/P(Cz-co-ANI) ve TNT memory–GC/P(Cz-co-ANI)-Au<sub>nano</sub> electrodes in monomer-free solution media with Potentiostat EIS method; frequency range was 10 mHz – 1 MHz, and points/decade 10 mV.



**Figure S-2.** Impedance measurements on the TNT memory–GC/P(Cz-*co*-ANI) and TNT memory–GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> electrodes using the Potentiostat EIS method in monomer-free solution media.

Electrochemical impedance spectroscopy provides information on electrode modification in each step of the electrochemical process. Figure S-2 shows the impedance spectra of TNT memory–GC/P(Cz-*co*-ANI) and TNT memory–GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> modified electrodes. The high frequency region on the left hand side (beginning) of the spectrum identifies the electrolyte properties, while mid-frequency region corresponds to the

electrode/electrolyte interface process. The relaxation effect is represented by a semicircle whose intersections with the real axis are the electrolyte and the charge transfer resistances. In the low frequency region, the impedance is controlled by the diffusion of the counterions inside the polymer electrode: the impedance response, a  $45^{\circ}$  straight line (Warburg impedance)<sup>1</sup>. It can be observed from Figure S-2 that the radius of the semicircle for TNT memory–GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> is smaller than the corresponding value for the TNT memory–GC/P(Cz-*co*-ANI) electrode, indicating a lower charge-transfer resistance (R<sub>CT</sub>) and a higher electroactivity for the gold-coated electrode. This may result from the higher thickness of TNT memory–GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> on the same Z'/Z'' graph enabled the comparison of the electron-transfer capabilities of different (bare and modified) electrodes<sup>2</sup> where Aunanoparticles may show an important role in the electrode matrix, for the enhancement of conductivity by increasing the electron transfer<sup>3</sup>.

### SEM image of TNT memory-GC/P(Cz-co-ANI)-Au<sub>nano</sub> electrode

The SEM image of TNT memory–GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> electrode was recorded with the aid of scanning electron microscopy (SEM; FEI Model Quanta 450 FEG, Hillsboro, OR, USA).

The SEM image of the produced Au<sub>nano</sub> was shown in Figure S-3.



**Figure S-3.** The SEM image of Au colloidal nanoparticles, the size of particles varying from 50 to 500 nm (with five thousand-fold zoom).

# Electrochemical Determination of TNT with GC/P(Cz-Co-ANI)-Au<sub>nano</sub> Electrode (nonimprinted electrode)

Electrochemical determination of TNT was achieved with using GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> modified electrode (non-imprinted electrode). Square wave voltammogram of TNT can be seen in Fig. S-4.



**Figure S-4**. Square wave voltammogram of TNT recorded with GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> electrode.

Calibration of TNT using GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> at -1.0 V reduction potential gave a linear dependence of current *versus* concentration;

$$I_{-1.0 V} = (5.0 \pm 0.74) \times 10^{-2} C_{TNT} + (2.19 \pm 0.24) (r = 0.997)$$
(1)

where I  $_{-1.0 \text{ V}}$  was the peak current ( $\mu$ A) at -1.0 V and C<sub>TNT</sub> the TNT concn. (mg L<sup>-1</sup>).

LOD and LOQ were calculated as 3 and 10 mg  $L^{-1}$ , respectively.

As pointed out in manuscript, the developed TNT-memory–GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> electrode was capable of decreasing the LOD level almost 100-fold compared to that of non-imprinted GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> electrode.

## Slope, Intercept, Correlation Coefficient of TNT, DNT, RDX and HMX Determination

**Table S-1.** Slope, intercept, correlation coefficient for the tested nitroaromatic and nitramine energetic materials.

| Calibration parameter                       | TNT       | DNT       | RDX       | HMX       |
|---|-----------|-----------|-----------|-----------|
| $\frac{\text{Slope}^{a}}{(\times 10^{-3})}$ | 6.1±0.70  | 5.2±0.86  | 7.9±0.81  | 5.1±0.47  |
| Intercept                                   | 4.56±0.42 | 6.40±0.53 | 3.23±0.46 | 4.16±0.27 |
| Correlation<br>coefficient<br>(r)           | 0.997     | 0.996     | 0.996     | 0.997     |

<sup>&</sup>lt;sup>a</sup>In  $\mu$ A**·**L**·** $\mu$ g<sup>-1</sup> units.

## Analytical Results for Synthetic Mixtures of Energetic Materials

One mg L<sup>-1</sup> of TNT was determined in the presence of 5-fold concentrations of DNT, RDX, HMX and (DNT+RDX+HMX) synthetic mixtures. Similar to TNT, binary and multi-component mixtures were prepared for DNT, RDX and HMX in ACN. Results were given in Tables S-2, S-3, S-4 and S-5.

| Table S-2 | . Recovery | (%) value | s of TNT | from synthe | etic mixtures | of energetic | materials. |
|-----------|------------|-----------|----------|-------------|---------------|--------------|------------|
|           |            |           |          |             |               |              |            |

| Sample (mg L <sup>-1</sup> )  | Average Current Intensity(µA) | Recovery (%) |  |  |
|---|-------------------------------|--------------|--|--|
|   | at -1.0 V (N=5)               |              |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ TNT}$   | 10.58                         | -            |  |  |
| 1 mg $L^{-1}$ TNT + 5 mg $L^{-1}$ DNT   | 11.12                         | 105          |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ TNT} + 5 \text{ mg } \text{L}^{-1} \text{ RDX}$   | 10.45                         | 98.8         |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ TNT} + 5 \text{ mg } \text{L}^{-1} \text{ HMX}$   | 10.51                         | 99.3         |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ TNT} + 5 \text{ mg } \text{L}^{-1} \text{ DNT} +$ | 11.20                         | 106          |  |  |
| JINGL KDA + JINGL HMA   |                               |              |  |  |

| Sample (mg L <sup>-1</sup> )  | Average Current Intensity(µA) | Recovery (%) |  |  |
|---|-------------------------------|--------------|--|--|
|   | at -1.0 V (N=5)               |              |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ DNT}$   | 11.52                         | -            |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ DNT} + 5 \text{ mg } \text{L}^{-1} \text{ TNT}$ | 11.21                         | 97.3         |  |  |
| $1 \text{ mg } L^{-1} \text{ DNT} + 5 \text{ mg } L^{-1} \text{ RDX}$               | 11.38                         | 98.8         |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ DNT} + 5 \text{ mg } \text{L}^{-1} \text{ HMX}$ | 11.65                         | 101          |  |  |
| $1 \text{ mg } L^{-1} \text{ DNT} + 5 \text{ mg } L^{-1} \text{ TNT} +$             | 11.30                         | 98.1         |  |  |
| $5 \text{ mg } \text{L}^{-1} \text{ RDX} + 5 \text{ mg } \text{L}^{-1} \text{ HMX}$ |                               |              |  |  |

**Table S-3.** Recovery (%) values of DNT from synthetic energetic material mixtures.

**Table S-4.** Recovery (%) values of RDX from synthetic mixtures of energetic materials.

| Sample (mg L <sup>-1</sup> )  | Average Current Intensity(µA) | Recovery (%) |  |  |
|---|-------------------------------|--------------|--|--|
|   | at -1.03 V (N=5)              |              |  |  |
| $1 \text{ mg L}^{-1} \text{ RDX}$   | 10.89                         | -            |  |  |
| $1 \text{ mg } L^{-1} \text{ RDX} + 5 \text{ mg } L^{-1} \text{ TNT}$               | 10.67                         | 98.0         |  |  |
| $1 \text{ mg } L^{-1} \text{ RDX} + 5 \text{ mg } L^{-1} \text{ DNT}$               | 10.57                         | 97.1         |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ RDX} + 5 \text{ mg } \text{L}^{-1} \text{ HMX}$ | 10.48                         | 96.2         |  |  |
| 1 mg $L^{-1}$ RDX + 5 mg $L^{-1}$ TNT +<br>5 mg $L^{-1}$ DNT + 5 mg $L^{-1}$ HMX    | 10.35                         | 95.0         |  |  |

| Sample (mg L <sup>-1</sup> )  | Average Current Intensity(µA) | Recovery (%) |  |  |
|---|-------------------------------|--------------|--|--|
|   | at -1.05 V (N=5)              |              |  |  |
| 1 mg L <sup>-1</sup> HMX  | 9.14                          | -            |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ HMX} + 5 \text{ mg } \text{L}^{-1} \text{ TNT}$ | 9.12                          | 99.8         |  |  |
| $1 \text{ mg } \text{L}^{-1} \text{ HMX} + 5 \text{ mg } \text{L}^{-1} \text{ DNT}$ | 9.17                          | 100          |  |  |
| $1 \text{ mg L}^{-1} \text{ HMX} + 5 \text{ mg L}^{-1} \text{ RDX}$                 | 9.55                          | 104          |  |  |
| 1 mg $L^{-1}$ HMX + 5 mg $L^{-1}$ TNT +<br>5 mg $L^{-1}$ DNT + 5 mg $L^{-1}$ RDX    | 9.61                          | 105          |  |  |

Table S-5. Recovery (%) values of HMX from synthetic mixtures of energetic materials.

# Interference of Electroactive Camouflage Materials to the Electrochemical Determination of Energetic Materials

Paracetamol and caffeine solutions were prepared using vermidon tablet. One tablet of vermidon (500 mg paracetamol and 30 mg caffeine) was taken into 100 mL ACN and dissolved in the ultrasonic bath for 15 min. The PTFE was then filtered through a 0.45  $\mu$ m filter and the solution was diluted to the mark in a 100 mL flask. The final concentrations in solution were 5000 mg L<sup>-1</sup> paracetamol and 300 mg L<sup>-1</sup> caffeine. One tablet of aspirin (500 mg acetylsalicylic acid), 28 tablets of canderel (504 mg aspartame) and 500 mg of D-glucose were used for preparation of the corresponding solutions with the same procedure followed for paracetamol and caffeine. The final concentrations in solution were 5000 mg L<sup>-1</sup> aspartame, and 5000 mg L<sup>-1</sup> D- glucose. All the solutions were diluted 5-fold with ACN before measurements.

**Table S-6.** Recovery (%) values of energetic materials in the presence of various electroactive compounds.

| Electroactive                       | Recovery (%)                | Recovery (%)                | Recovery (%)                | Recovery (%)                |  |
|-------------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|--|
| Camouflage                          | for 1 mg L <sup>-1</sup> of |  |
| Materials                           | TNT                         | DNT                         | RDX                         | HMX                         |  |
| 1000 mg L <sup>-1</sup> of          |                             |                             |                             |                             |  |
| Paracetamol +                       | 106                         | 106                         | 106                         | 104                         |  |
| $60 \text{ mg L}^{-1} \text{ of}$   | 100                         | 100                         | 100                         | 104                         |  |
| Caffeine                            |                             |                             |                             |                             |  |
| 1                                   |                             |                             |                             |                             |  |
| $1000 \text{ mg L}^{-1} \text{ of}$ | 99.5                        | 96.4                        | 98.7                        | 99.1                        |  |
| Acetylsalicylic                     |                             |                             |                             |                             |  |
| acid                                |                             |                             |                             |                             |  |
|                                     |                             |                             |                             |                             |  |
| $1008 \text{ mg L}^{-1}$            | 106                         | 102                         | 105                         | 102                         |  |
| Aspartame                           |                             |                             |                             |                             |  |
|                                     |                             |                             |                             |                             |  |
| $1000 \text{ mg L}^{-1}$            | 96.7                        | 97.4                        | 96.3                        | 99.0                        |  |
| D-Glucose                           |                             |                             |                             |                             |  |
|                                     |                             |                             |                             |                             |  |



**Figure S-5.** Square wave voltammograms of 1 mg  $L^{-1}$  TNT, 1 mg  $L^{-1}$  TNT + 1008 mg  $L^{-1}$  Aspartame, 1 mg  $L^{-1}$  TNT + 1000 mg  $L^{-1}$  of Paracetamol + 60 mg  $L^{-1}$  of Caffeine, 1 mg  $L^{-1}$  TNT + 1000 mg  $L^{-1}$  D-Glucose, 1 mg  $L^{-1}$  TNT + 1000 mg  $L^{-1}$  of Acetylsalicylic acid, recorded with TNT-memory–GC/P(Cz-*co*-ANI)-Au<sub>nano</sub> electrode.

### Calibration equations for TNT and RDX with using LC-MS

The calibration equations for TNT and RDX (with LC-MS) between peak area and concentration were:

| Peak Area = $38.79 C_{TNT} - 299.0$        | (r = 0.9999) | (2) ( $C_{TNT}$ : TNT concn. in $\mu g L^{-1}$ )                |
|--|--------------|---|
| Peak Area = 66.12 C <sub>RDX</sub> – 664.9 | (r = 0.9999) | (3) (C <sub>RDX</sub> : RDX concn. in $\mu$ g L <sup>-1</sup> ) |

#### Statistical Comparison of the Developed Method with LC-MS

**Table S-7.** Statistical comparison of the developed method with LC-MS for TNT and RDX determinations in contaminated clay soil samples.

| Sample/Analyte | Method                                | Mean<br>conc.,<br>µg L <sup>-1</sup> | Std.<br>dev.<br>(σ) | S <sup>a,b</sup> | t <sup>a,b</sup> | t <sub>table</sub> b | $\mathbf{F}^{\mathbf{b}}$ | F <sub>table</sub> <sup>b</sup> |
|----------------|---------------------------------------|--------------------------------------|---------------------|------------------|------------------|----------------------|---------------------------|---------------------------------|
| TNT            | Developed<br>Method<br>(Voltammetric) | 396.1                                | 7.02                | -                | -                | -                    | -                         | -                               |
|                | LC-MS                                 | 397.6                                | 8.56                | 7.83             | 0.303            | 2.306                | 1.49                      | 6.39                            |
| RDX            | Developed<br>Method<br>(Voltammetric) | 593.9                                | 11.2                | -                | -                | -                    | -                         | -                               |
|                | LC-MS                                 | 597.4                                | 7.06                | 9.34             | 0.587            | 2.306                | 2.50                      | 6.39                            |

<sup>a</sup>  $S^2 = ((n_1 - 1)s_1^2 + (n_2 - 1)s_2^2)/(n_1 + n_2 - 2)$  and  $t = (\bar{a}_1 - \bar{a}_2)/(S(1/n_1 + 1/n_2)^{1/2})$ , where S is the pooled standard deviation,  $s_1$  and  $s_2$  are the standard deviations of the two populations with sample sizes of  $n_1$  and  $n_2$ , and sample means of  $\bar{a}_1$  and  $\bar{a}_2$  respectively (t has  $(n_1 + n_2 - 2)$  degrees of freedom); here,  $n_1 = n_2 = 5$ .

<sup>b</sup> Statistical comparison made on paired data produced with developed and reference methods; the results given only on the row of the reference method.

#### References

(1) Arbizzani, C.; Catellani, M.; Mastragostino, M.; Mingazzini, C. *Electrochim. Acta.* **1995**, 40, 1871–1876.

(2) Zhou, M.; Zhai, Y.; Dong, S. Anal. Chem. 2009, 81, 5603-5613.

(3) Guo, Z. Z.; Florea, A.; Cristea, C.; Bessueille, F.; Vocanson, F.; Goutaland, F.; Zhang, A.; Sandulescu, R., Lagarde, F.; Renault, N. J. *Sensor. Actuat. B: Chem.* **2015**, 207, 960–966.