SUPPORTING INFORMATION

Downconversion Luminescence-Based Nanosensor for Label-Free Detection of Explosives

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Figure S1. The chemical structures of the commonly used nitrocompounds.
Figure S2. XRD pattern of NaYF$_4$ doped with Gd$^{3+}$ and Tb$^{3+}$ ions (black line), calculated XRD curve after crystal structure refinement by Rietveld method (red line), $I_{\text{obs}}-I_{\text{cal}}$, difference curve (green line) and Bragg position (pink vertical line) is displayed.
Table S1. Rietveld refinement data of the as-synthesized product β-NaYF₄:Gd³⁺,Tb³⁺@PEI.

|          |        |          |          |       |
|----------|--------|----------|----------|-------|
| χ²       | 2.4    | wR_p (%) | 5.3      |       |
| R_p (%)  | 4.0    |          |          |       |
| Spacegroup | P62m  |          |          |       |
| a=b      | 5.96   | c        | 3.58     |       |

|        | x      | y        | z        | occupancy |
|--------|--------|----------|----------|-----------|
| Na⁺+1  | 0.333300 | 0.666700 | 0.500000 | 0.742401  |
| Y⁺³    | 0.333300 | 0.666700 | 0.500000 | 0.245310  |
| Y⁺³    | 0       | 0        | 0        | 0.714572  |
| Gd⁺³   | 0       | 0        | 0        | 0.246481  |
| Tb⁺³   | 0       | 0        | 0        | 0.091391  |
| F⁻¹    | 0.619858 | 0        | 0        | 0.979559  |
| F⁻¹    | 0.220950 | 0        | 0.500000 | 1.010779  |
Figure S3. The EDXA pattern showing the elemental composition consisting of Na, F, Y, Gd and Tb ions.
**Figure S4.** (a) The HRTEM image, (b) corresponding inverse fast Fourier transformation (IFFT) image of the square region marked red in figure (a), corresponding to (110) plane masked in the FFT pattern with red circles as shown in inset, (c) the line profile of the selected region in IFFT image for interplanar spacing of 0.30 nm, and (d) SAED pattern of $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI nanophosphors.
Figure S5. The TGA curve for branched polyethylenimine (PEI) showing decomposition temperature at ~ 400 °C.
Figure S6. The high-resolution XPS spectra of the elements present in β-NaYF₄:Gd³⁺, Tb³⁺@PEI showing the binding energy of (a) Na 1s, (b) Y 3d, and (c) F 1s revealing the core energy levels.
Figure S7. The Raman spectra of as-synthesized $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI excited under wavelength of 325 nm.
Table S2. The comparison of different methods and limit of detection for TNT (*NA= Not applicable).

| Detection technique | Probe                        | Detection rangea/linear rangeb | LOD   |
|---------------------|------------------------------|--------------------------------|-------|
| Electrochemical     | Graphene nanoribbons⁴        | 4.4 - 66 μMb                   | 4.4 μM|
| method              |                              |                                |       |
| Surface enhanced    | Molecularly imprinted        | NA*                            | 3 μM  |
| Raman spectroscopy  | polymers²                    |                                |       |
|                     |                              |                                |       |
| Fluorescence        | Mesoporous silica            | 1 - 25 μMa                     | 0.6 μM|
| method              | nanoparticles³               |                                |       |
|                     |                               |                                |       |
|                     | Graphene quantum             | 2.2 - 800 μMb                   | 2.2 μM|
| dots⁴               |                               |                                |       |
|                     | Polymer substrates and        | 0.1 - 5.5×10³ μMa⁶             | 1 μM  |
| fibres⁵             |                               |                                |       |
|                     | Pyrene derivatives⁶           | 1 - 14 μMa⁷                     | 1 μM  |
|                     |                               |                                |       |
|                     | Carbon quantum dots⁷          | 10⁻³ - 1 μMa⁸                   | 0.213 μM|
|                     | Downconverting                | 0.1 - 10 μMb⁹                   | 0.119 μM|
| phosphors           |                              |                                |       |
| (this work)         |                              |                                |       |
Figure S8. (a) Influence of pH on the luminescence intensity before and after the addition of TNT (300 μM). For pH 7-8, NaH₂PO₄-Na₂HPO₄, pH 9-11 NaHCO₃-Na₂CO₃-NaOH and pH 12-13 KCl-NaOH were used. (b) Effects on incubation time on the PL intensity at 544 nm due to the presence of TNT was studied at pH 7 in buffer solution at room temperature.
Figure S9. The comparison of static photoluminescence spectra of $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$ nanophosphors with and without PEI in presence and in absence of TNT in aqueous medium.
**Table S3.** The average lifetime of the $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI with different concentrations of TNT.

| S. No. | Sample                              | $\tau_1$ (ms) | Rel % | $\tau_2$ (ms) | Rel % | Average lifetime (ms) |
|-------|-------------------------------------|---------------|-------|---------------|-------|-----------------------|
| 1     | $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI | 0.35          | 18    | 2.50          | 82    | 2.11                  |
| 2     | $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI + 1 μM TNT | 0.42          | 22    | 2.34          | 78    | 1.91                  |
| 3     | $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI + 10 μM TNT | 0.21          | 27    | 2.17          | 73    | 1.72                  |
| 4     | $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI + 100 μM TNT | 0.24          | 24    | 1.89          | 76    | 1.49                  |
| 5     | $\beta$-NaYF$_4$:Gd$^{3+}$,Tb$^{3+}$@PEI + 300 μM TNT | 0.23          | 30    | 1.32          | 70    | 0.98                  |
Figure S10. The chemical structures of commonly used (A) amino acids, (B) pesticides, and (C) sugars.
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