Experimental Reagents and chemicals

m-Phenylenediamine (mPDA >99%) was purchased from Acros Organics, ethylenediamine (EDA, Sigma Ultra) was obtained from Sigma Aldrich. ortho-Phosphoric acid (85%, ACS certified) was purchased from Fisher Scientific. All the other chemicals were of analytical grade. Buffer solutions with different pH were prepared using chemicals (such as sulphuric acid, citric acid, sodium phosphate dibasic, sodium phosphate monobasic, sodium carbonate, sodium bicarbonate and sodium hydroxide) dissolved in DI water.

Synthesis of fluorescent carbon dots

0.5 g of mPDA was dissolved in 2 ml deionized water, and then 1 ml of phosphoric acid and 0.5 ml of EDA were added into the prepared solution subsequently to form a homogeneous and transparent solution. The solution in an open glass vial was then heated in a domestic 800 W oven for 40 s (Caution: Please do not overheat the solution to avoid any potential explosion). After that, 3 ml deionized water was added to the resultant vial in order to dissolve the solid. An aqueous solution of the CDs was purified in a centrifuge (10,000 rpm/min for 20 min) to remove large or agglomerated particles.
**Characterization**

The high resolution transmission electron microscope (HRTEM, JEOL JEM-2010 FasTEM) at an operating voltage of 200 kV was used to observe the morphology and microstructures of CDs. The X-ray diffraction (XRD) patterns were obtained on a Bruker D2 Phaser X-ray diffractometer with Cu Kα radiation and operating at 30 kV and 10 mA. Fourier transform infrared (FTIR) spectra were collected on Nicolet 560 Fourier spectrometer with Diamond ATR accessory from 32 scans with resolution of 4 cm⁻¹ and data spacing of 1.928 cm⁻¹. In order to collect the X-ray photoelectron spectra (XPS) of the samples, a PHI model 590 spectrometer equipped with multiprobes (Φ Physical Electronics Industries Inc.), using a monochromatic Al Kα X-ray source (hv = 1486.6 eV) was employed. The absorption spectra were performed on a Cary 50 UV-vis spectrophotometer (Agilent Technologies). Fluorescence emission spectra and excitation spectra were measured using a Varian Cary Eclipse fluorescence spectrometer (Agilent Technologies) using the conditions listed in the figure captions.

**Quantum yield (QY) measurements**

Quantum yield of fluorescent CDs was calculated using standard reference fluorophore quinine sulphate (dissolved in 0.1 mol/l H₂SO₄, excited at 350 nm, QY = 0.58) and fluorescein (dissolved in 0.1 mol/l NaOH, excited at 440 nm, QY = 0.95) according to the following equation:

\[
QY_C = QY_R (I_C/I_R)(OD_R/OD_C)(n_C^2/n_R^2) (1)
\]

where the subscripts C and R refer to the carbon nanoparticle samples and the standard reference fluorophore, respectively; QY is the quantum yield; I is the integrated intensity, OD is the optical density of the samples at the excitation wavelength, and n is refractive index of the solutions.

**Results**

The XRD patterns (Fig. S1) of the carbon dots show several crystal peaks such as ~ 15.8°, ~ 23.2°, ~ 34.7°, corresponding to d lattice spacing of 5.16 Å, 3.83 Å and 2.58 Å, which are consistent very well with the d lattice obtained from HRTEM graphs in Fig. 1B-D. The XRD spectrum of CDs is similar to that of carbon materials.
IR spectroscopy is a powerful technique to characterise the surface functionality of the nanoparticles, and the results are shown as Fig. S2.

The presence of absorption bands at 687 cm\(^{-1}\) and 785 cm\(^{-1}\) are assigned to aromatic sp\(^2\) C-H bending from mPDA. The absorption band at 1541 cm\(^{-1}\) is related to the plane blending vibration and the stretching vibration of N-H from EDA or mPDA. In the spectrum of carbon dots, these groups are maintained. The appearance of 944 cm\(^{-1}\) and 878 cm\(^{-1}\) assigned to vibration of P=O phosphate group, suggests the presence of phosphoric acid. There are new peaks appearing in CDs compared with raw materials. Absorption band at 543 cm\(^{-1}\) emerges, which reflects the deformation vibration in plane of secondary amines -NH-; while the new appeared band at 1634 cm\(^{-1}\) are attributed to CX (X = C, N, or...
O) stretching vibration, while a new appeared peak at 1142 cm\(^{-1}\) in CDs are possibly assigned to the vibration of the -NH\(^+\) structure, or stretching of P-O, P=O or P=N groups. The results here suggest that a new product is formed after microwave heating.

The application of the as-prepared dual-fluorescence carbon dots for the differentiation of nitro-explosives (TNT and picric acid) was also demonstrated. The sensing experiments were carried out by monitoring the fluorescence quenching behaviour of carbon dots solution upon the addition of target explosives at room temperature through a fluorescence spectrometer, with the excitation and emission slit widths of 5 nm. Briefly, 3 ml of the diluted CDs solution in buffer solution (0.01 mol/l, pH=7.5) was placed in a disposal cuvette and then the target analyte was added successively. The fluorescence emission experiments were excited at 350 nm and 440 nm, while the emission data were collected in the wavelength range of 360-650 nm and 450-650 nm, respectively.

![Fig. S3 Explosives detection using diluted CDs solutions with incremental addition (0-50 μM) of (A) picric acid; and (B) TNT.](image)

The carbon dots have dual fluorescence emission under different excitations. Due to their dual emission and high quantum yield, the nanoparticles may have great potentials into the development of ratiometric sensors through using fluorescence changes of different emission peaks. Herein the detection/discrimination of nitro-explosives (picric acid and trinitrotoluene) is investigated through analysis of fluorescent intensities changes of different peaks. As shown in Fig. S3A, with incremental
addition of picric acid to diluted CDs solution in buffer solution (pH=7.50), the fluorescent intensities quench greatly for both blue and green emission. While TNT only quenches the green fluorescence emission, and the blue emission intensity keeps stable with increasing addition of TNT (0-50 μM) as shown in Fig. S3B. The detection limit (S/N=3) for PA and TNT are 1.5 μM and 5.2 μM, respectively. Through integration of blue and green emission quenching, differentiation and selective detection of picric acid and TNT was achieved. The blue emission quenching by picric acid is possibly due to the overlap of picric acid absorption and blue emission peak, which has been already investigated in detail in our other studies. The large overlap suggests the possibility of FRET process, which leads to the fluorescence quenching. While little overlap between blue emission and TNT absorption excludes the presence of FRET process, therefore almost no quenching to blue emission by TNT is observed. While for green emission, both TNT and Picric acid quench the emission peak at ~ 510 nm. The phenomena could be potentially attributed to the formation of Meisenheimer complex between NH₂ group on CDs and electron deficient compounds. It has been reported Meisenheimer complex has an absorption band at ~ 520 nm, which coincidently overlap with green emission greatly. The presence of FRET process is responsible for fluorescence quenching by both TNT and picric acid for green emission at ~ 510 nm.

Besides the ratiometric explosives detection, we anticipate that the synthesized CDs could be utilized in broad applications such as chemical sensing, biosensing, bioimaging, illumination, electronic devices, electrocatalysts, etc. For example, the CDs open the possibility for monitoring multiple analytes or species simultaneously because of dual fluorescence emission and high quantum yield. Especially in bio-imaging, the new green fluorescence CDs could decrease the “water window” effect, indicating the interference of blue emission light between cells and tissues with conventional CDs could be prevented. These new applications are currently under pursuing in our group.
References

