

Electronic Supplementary Information

Highly efficient fluorescent multi-walled carbon nanotubes functionalized with diamines and amides

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1. **Figure S1: UV-Vis spectra of P-MWCNTs, O-MWCNTs and O-MWCNTs-E**
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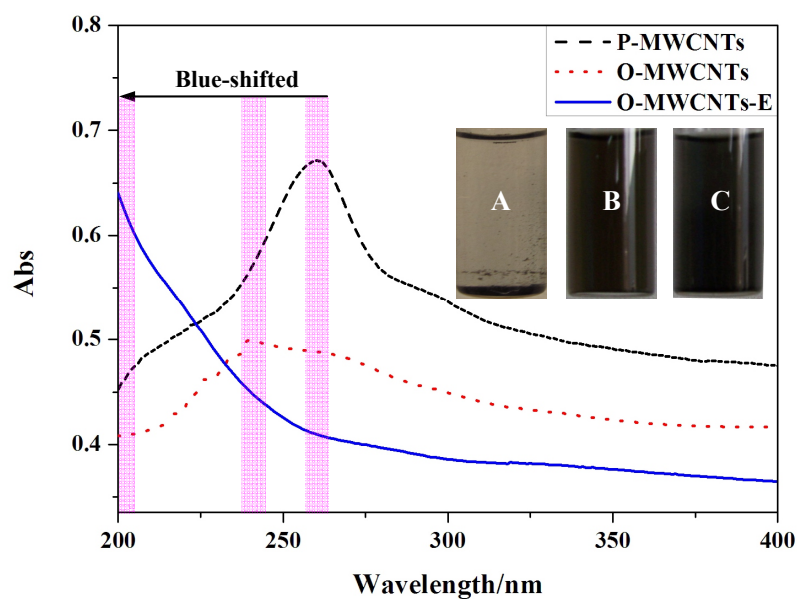


Fig. S1 UV-Vis spectra of P-MWCNTs, O-MWCNTS and O-MWCNTs-E. The absorbance of R-MWCNTs was recorded by the suspension of R-MWCNTs in ethanol, and the others dispersed in water. Inset: photographs of their dispersions in water after ultrasonication for 10 min followed standing for 1 h (A represents P-MWCNTs, B represents O-MWCNTs and C represents O-MWCNTs-E).

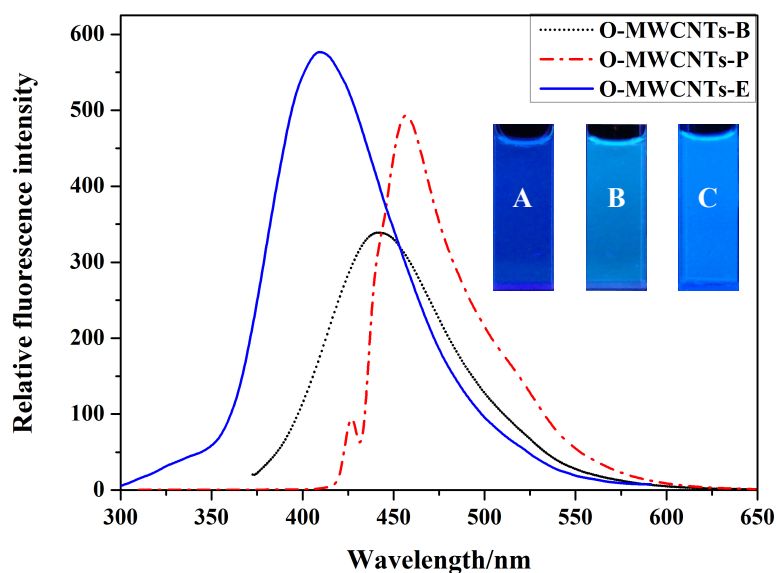


Fig. S2 The emission spectra for O-MWCNTs-B, O-MWCNTs-P, and O-MWCNTs-E. Inset: Digital photographs of O-MWCNTs-E (A), O-MWCNTs-P (B) and O-MWCNTs-B (C) in water respectively illuminated by an UV lamp.

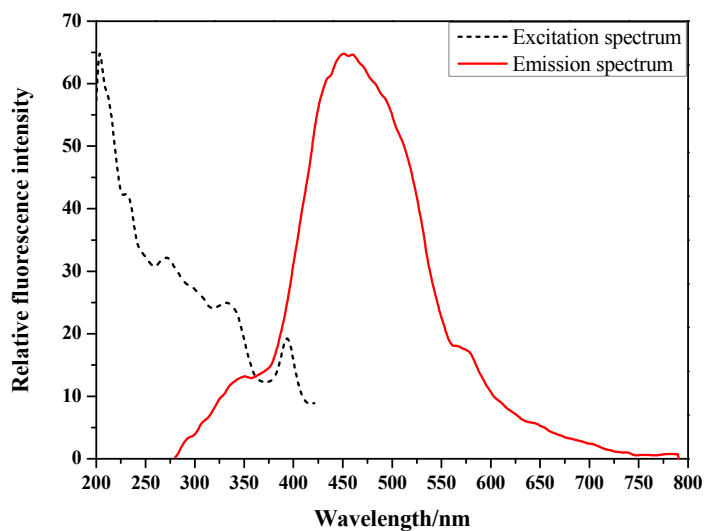


Fig. S3 The excitation and emission spectra for O-MWCNTs.

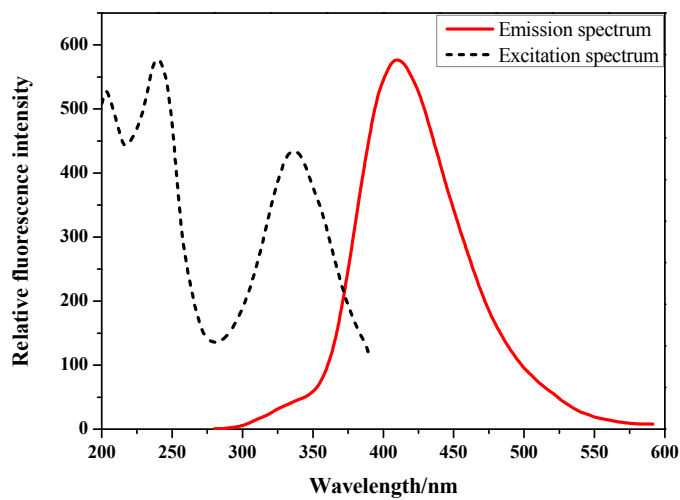


Fig. S4 The excitation and emission spectra for O-MWCNTs-E.

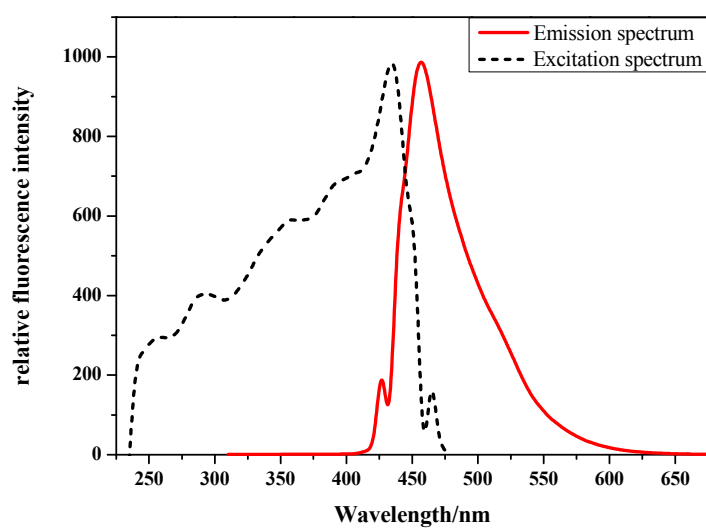


Fig. S5 The excitation and emission spectra for O-MWCNTs-P.

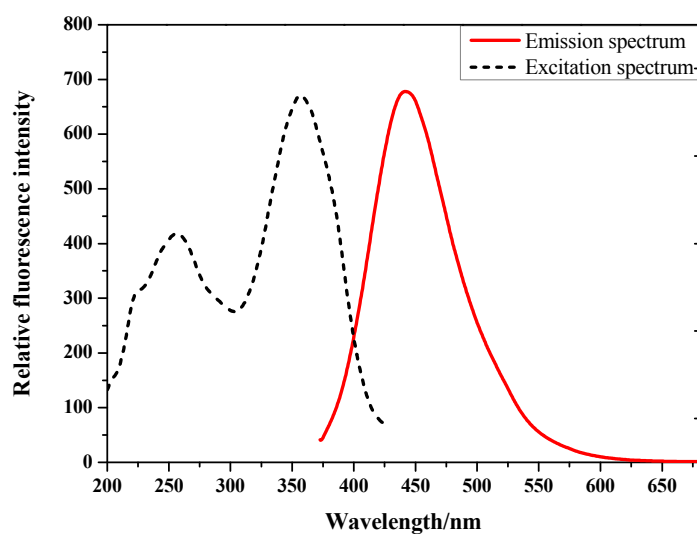


Fig. S6 The excitation and emission spectra for O-MWCNTs-B.

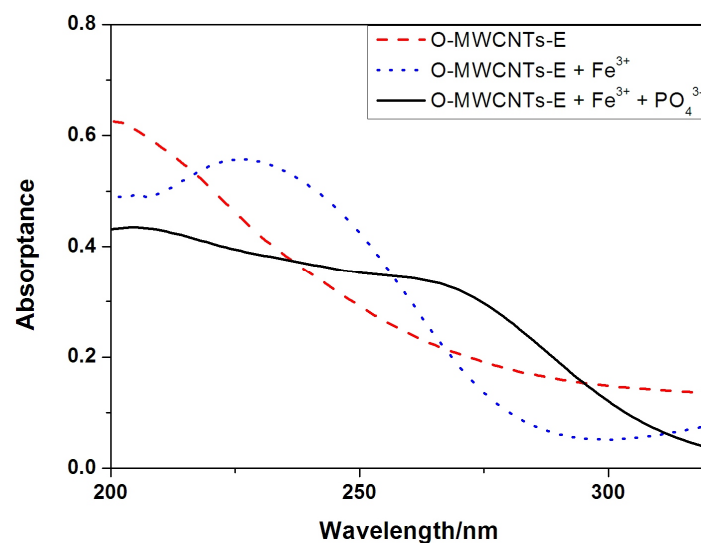


Fig. S7 The comparison of UV-Vis spectra of O-MWCNTs-E, O-MWCNTs-E + Fe³⁺ and O-MWCNTs-E + Fe³⁺ + PO₄³⁻.

The experimental details.

Oxidative treatment of MWCNTs. 0.1 g of MWCNTs were added in 10 ml of mixed acids (H₂SO₄:HNO₃, ratio 3:1), and then the resulting mixture was treated by sonication for 12 h with an additional standing time of 12 h. The products were washed by distilled water until the filtrate reaches to pH 7, and then dried at 100 °C. After washing and drying, the obtained products were O-MWCNTs.

Functionalization of O-MWCNTs. The dried O-MWCNTs (30 mg) and N,N-dimethylformamide (3 mL) were refluxed and stirred in dichlorosulfoxide (30 mL) at 80 °C for 40 h. After centrifugation, the supernatant was decanted and the remaining solid was washed with anhydrous tetrahydrofuran two times followed by drying in vacuum at room temperature. A mixture of the activated O-MWCNTs acyl chloride and 1,2-ethylenediamine was heated under nitrogen at 60 °C for 36 hours. The reaction mixture was removed from the heat source, allowed to cool to room temperature and dried by rotary evaporation. After being removed to a centrifuge tube by anhydrous ethanol, the product was centrifuged at 4000 rpm for 20 min. The supernatant was decanted and remaining solid was washed with anhydrous ethanol for another two times followed by rotary evaporation. The same procedure was used to prepare other diamines functionalized O-MWCNTs.

Characterization of MWCNTs, O-MWCNTs and O-MWCNTs-E. The UV-Vis spectra were recorded on a PerkinElmer Lambda 950 spectrometer, in which the products were dispersed in water. The Fourier transform infrared spectroscopy (FTIR) spectra were measured by a Thermo NEXUS 670 Fourier transform infrared spectrometer. Transmission electron microscopy (TEM)

images were obtained by using a TEM-3100F transmission electron microscopy with accelerating voltage of 200 KV. The fluorescence spectra measurements were performed on a PerkinElmer LS 55 spectrometer, in which the dispersions in water were used. Time-resolved fluorescence decays were recorded on a time-correlated single photon counting FLSP920 system. The data were fitted with a multi-exponential decay and χ^2 was less than 1.1. The X-ray photoelectron spectroscopy (XPS) analyses were conducted using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation came from monochromatic Al X-rays (1486.6 eV) at 225 W (15 kV, 3 mA). Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) higher resolution scans at a pass energy of 40 eV. Survey scans were carried out over a 1400–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow higher resolution scans were run with 0.05 eV steps and a 200 ms dwell time. Base pressure in the analysis chamber was 3.4×10^{-9} Torr and during sample analysis 6.1×10^{-9} Torr. Atomic concentrations were calculated using Vision XPS software and a Shirley baseline.

Determination of the quantum yields. Determination of the quantum yields of these oxidized produces was accomplished by comparison of the wavelength integrated intensity of these oxidized products to that of the standard quinine sulfate. The optical density is kept below 0.05 to avoid inner filter effects. The quantum yields of these oxidized products were calculated using

$$\Phi = \Phi_S [(I \cdot A_S \cdot n^2)/(I_S \cdot A \cdot n_s^2)]$$

where Φ is the quantum yield, I is the integrated intensity, A is the optical density and n is the refractive index of the solvent. The subscript S refers to the standard reference of known quantum yield. In this work, when determining O-MWCNTs, quinine sulfate was chosen as the standard, whose quantum yield is 0.577 for excitation from 200 nm to 400 nm. As for the diamines functionalized O-MWCNTs, the standard is Rhodamine 6G whose quantum yield is 0.95 for excitation from 248 nm to 528 nm in the solvent ethanol. The refractive indexes of water and ethanol are 1.333 and 1.3614 respectively.

Preparation of the solutions with additional ions. In order to eliminate the pH effect induced by metal ions, all the chosen ions solutions were adjusted to pH 1.0. The resulting ions solutions were added to the same amount of O-MWCNTs-E solutions respectively to obtain the series of mixed solutions, in which the concentrations of the ions in the mixed solutions keep identical. In all the mixed solutions, the concentration of O-MWCNTs-E was identical to raw solution with pure O-MWCNTs-E.