Supporting Information

A Novel Fluorescent Polymer Brushes Film as A Device for Ultrasensitive Detection of TNT

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Figure S1. The UV absorption spectra of d-TPE solution before $(1 \times 10^{-3} \text{ mol/L}, 3 \text{ mL})$ (solid line) and after (dotted line) interacting with the PAA brushes film. The absorbance were 0.97262 and 0.94525, respectively. According to the Bouguer–Lambert–Beer law:A=lg(1/T)=Kbc, A₁/A₂=C₁/C₂, C₂=9.719×10⁻⁴ mol/L. C=C₁-C₂=2.814×10⁻⁵ mol/L, the amounts of d-TPE molecular self-assemble on the brushes film was 8.442×10⁻⁸ mol. (2.814×10⁻⁵ mol/L×0.003 L)



Figure S2. The structure of tetraphenylethene derivate (d-TPE) was confirmed by ¹H NMR spectroscopy in D₂O. The proton chemical shift at 7.21 ppm was assigned to the phenyl ring and the shift at 4.34 ppm could be attributed to the chemical shift of -CH₂- in 1-methoxy-4-methylbenzene. The proton chemical shift at 3.196 ppm was attributed to the -CH₂- in methylethanaminium bromide and the shift at 1.36 ppm assigned to the proton in methyl groups. All structures indicates the origin of monomer tetraphenylethene derivate (d-TPE).



Figure S3. The excitation (EX) and emission (EM) spectra of d-TPE molecules aqueous solution. Insert shows the structure of d-TPE molecule.

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Figure S4.The emission spectra of d-TPE/PAA brushes film (blue line) and d-TPE molecules aqueous solution (10^{-3} M) (black line), ($\lambda ex = 340$ nm).



Figure S5. The normalized fluorescence recovery cycles of free d-TPE molecules with TNT concentration between 0 and 1 ppb. Compared with the d-TPE combining with PAA brushes, the free d-TPE molecules can be washed off easily from the substrate, which indicated that the free d-TPE molecules cannot show a good recovery cycles character.



Figure S6. The normalized emission spectra of d-TPE/PAA brushes film with different TNT concentration of 0 ppb and 1 ppb. Each cycle is corresponding to the brushes film washed by methanol and annealed in vacuum at 60 °C for 2 hours after immersed in TNT aqueous solution. The measurements are 10 cycles, (λ ex = 340 nm).



Figure S7. The normalized emission spectra of d-TPE/PAA brushes film with water, varying concentrations of NaCl aqueous solution $(10^{-3} \text{ M}, 10^{-2} \text{ M}, 10^{-1} \text{ M})$. The d-TPE/PAA brushes film exhibited a stable fluorescence to varying NaCl concentrations.



Figure S8. The normalized emission spectra of d-TPE/PAA brushes film with water, aqueous solution of NaCl (10^{-2} M) and various concentrations of TNT (0-200 ppb) in aqueous solution of NaCl (10^{-2} M) (λ ex = 340 nm). The brushes film shows good fluorescence stability and highly sensitive to TNT in NaCl aqueous solution.



Figure S9. Plot of normalized PL intensities of d-TPE/PAA brushes film versus various TNT concentrations (0 – 0.5 ppb) in aqueous solution of NaCl (10^{-2} M). It shows a linear relationship (R=-0.99101) between PL intensity and TNT concentration.