

Supporting Information

Detection of TNT Explosives with New Fluorescent Conjugated Polycarbazole Polymer†

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1. General details

All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen. All reagents, unless otherwise specified, were obtained from Aldrich, Acros and TCI Chemical Co. and used as received. All the solvents used were further purified before use. The ¹H-NMR spectra were recorded on AVANCZ 500 spectrometers at 298 K by utilizing deuterated chloroform as solvent and tetramethylsilane (TMS) as standard. The molecular weights and polydispersity indexes (PDI) of the coupling products were determined by GPC using a HPLC Waters 510 pump using a series of monodisperse polystyrenes. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a model UV-3100 spectrophotometer. Fluorescence spectra (77K) were performed using a model RF-5301PC spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETSCH (DSC-204) unit at a heating rate of 10°C/min under nitrogen. Thermal gravimetric analysis (TGA) was Pyris1 TGA thermal analysis system at heating rate of 20°C/min under nitrogen.

2. Synthesis and Characterization

The monomers of **PCZ** were synthesized following the literatures (Chem. Commun., 2007, 1704.).

PCZ: Bis(cyclooctadiene)nickel (2.4 equiv), cyclooctadiene (2.4 equiv), and 2,2'-bipyridine (2.4 equiv) were dissolved in dry toluene (5 mL) and dry N,N-dimethylformamide (5 mL) in a Schlenk flask within a glovebox. The mixture was heated at 60 °C with stirring under argon for 20 min to generate the catalyst, and then a solution of the 2,7-dibromo-9-(4-(tris(4-(octyloxy)phenyl)methyl)phenyl)-9H-carbazole (200 mg) in dry toluene (7-10 mL) was added. The reaction was heated at 75 °C for 2 days. Then a mixture of toluene (4 mL) and bromobenzene (0.10 mL) was added and the mixture was heated at 75 °C for an additional 12 h. The mixture was then poured into a mixture of methanol and concentrated hydrochloric acid (1:1, 300 mL) and stirred for 4 h. The precipitated white solid was redissolved in THF (10 mL) and added dropwise to methanol (200 mL). The resulting solid was filtered off and subjected Soxhlet extraction for 2 days in acetone. The residue was then redissolved in THF and precipitated again from methanol, filtered, washed with methanol, and dried, yield 65%. ¹H-NMR (500 MHz, CDCl₃): δ 8.23-8.21 (m, 2H, Ar-H), δ 7.72 (s, 2H, Ar-H), δ 7.59-7.51 (m, 4H, Ar-H), δ 7.41 (m, 2H, Ar-H), δ 7.12-7.10 (m, 6H, Ar-H), 6.77-6.75 (m, 6H, Ar-H), δ 3.89 (m, 6H, OCH₂), δ 1.75-1.72 (m, 6H, CH₂), δ 1.28-1.24 (m, 6H, CH₂), δ 0.85-0.83 (m, 9H, CH₃). GPC analysis: M_n=4.0 x 10⁴ g mol⁻¹, D= 2.2.

3. The fluorescence and absorption spectra in film and solution

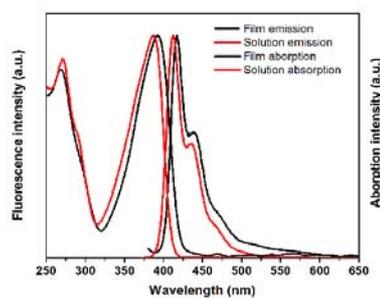


Fig. S1 The fluorescence and absorption spectra of **PCZ** film and in CHCl_3 solution.

Fig. S1 is the fluorescence and absorption spectra **PCZ** film and in CHCl_3 solution. From that, we found that the red shift between the absorption and emission spectra in solution and in solid state is only 5 and 4 nm, respectively.

4. The DSC property

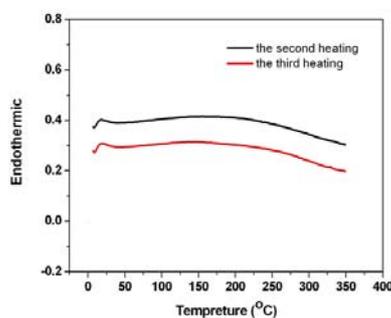


Fig. S2 The DSC spectrum of **PCZ**

Fig. S2 is the DSC spectrum of **PCZ**. As can be seen that there are no distinct peaks till 340 °C, which might mainly due to the bulky side chains of **PCZ** hindering the rotation or twist of the polymers backbones.

5. The TGA property

Fig. S3 is the TGA spectrum of **PCZ**. From this spectrum we could find that its thermal gravimetric temperature reach to 344 °C, which suggests it be a thermal

stable material for applications.

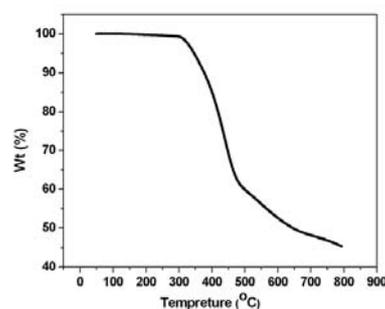


Fig. S3 The TGA spectrum of PCZ

6. The optimization of the PCZ film

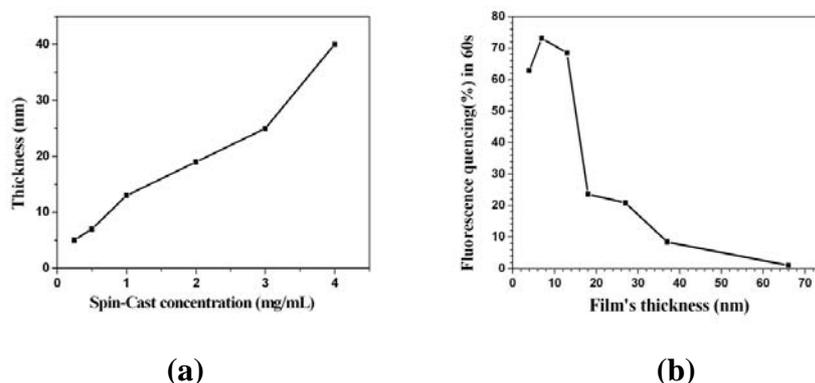


Fig. S4 (a) The thickness-concentration plot. (b) Film's fluorescence quenching (%) in 60 s is changed with its different thickness.

The film was fabricated by spin-coating with a spin rate of 1500 rpm on quartz substrates at room temperature. The **PCZ** concentrations in chloroform are 0.5mg/ml, 1 mg/ml, 2mg/ml, 3mg/ml and 4mg/ml, respectively. Then the prepared film was annealed in vacuum at 45 °C for 4 h in order to remove the chloroform. The thickness of the film was recorded by profiler, as shown in Fig.S4 (a).

The **PCZ** fluorescence quenching is dependent on the film thickness shown in Fig.S4 (b). The increased thickness leads to weaker response. However, if the thickness is too large, an integral film is hampered, which is crucial for its response.

This can be explained by the longer journey of TNT's molecules to diffuse costing more time and leading to slow response. Films formed from concentration of 0.5 mg/ml (thickness is 7 nm) displayed strongest response to the explosives.

7. The response of PCZ to DNT vapor

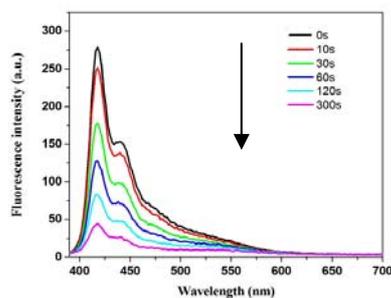


Fig. S5 Time-dependent fluorescence intensity of **PCZ** film (7 nm) in DNT vapor in 0s, 10 s, 30 s, 60 s, 120 s, and 300 s, respectively.

PCZ also shows response to DNT vapor. Fig. S5 shows the time-dependent fluorescence quenching of **PCZ** film (7 nm) exposed to DNT vapor at different time.

8. The response of PCZ to other interferential gases:

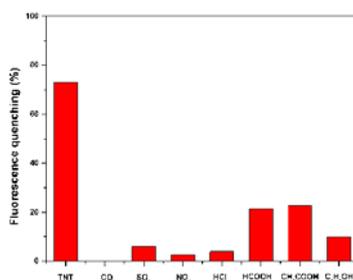


Fig. S6. **PCZ**'s fluorescence quenching (%) in 60 s toward CO_2 , SO_2 , NO_2 , HCl , HCOOH , CH_3COOH , and $\text{C}_2\text{H}_5\text{OH}$ gases.

Interferential gases to TNT, such as CO_2 , SO_2 , NO_2 , HCl , HCOOH , CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$ have been also tested by **PCZ**. As can be seen from Fig. S6, **PCZ**

fluorescence quenching sensitivities are weaker in these vapors than that in TNT,
which indicates the good selectivity of **PCZ** to TNT.