# Electronic supplementary information for

# Detection of TNT based on conjugated polymer encapsulated in mesoporous silica nanoparticles through FRET

## 1. Materials and methods

**Reagents.** Tetraethoxysilane (TEOS), 3-aminopropyltrimethoxysilane (APTES), triethanolamine (TEA), cetyltrimethyl ammonium chloride (CTACl), 1-octadecene and 2,4,6-trinitrotoluene (TNT) in methanol (1000 μg·mL$^{-1}$) were obtained from Aladdin. 2,4-Dinitrotolene (DNT) was purchased from TCI. p-Phenylenedimethylene bis-(tetramethylene sulfonium chloride) was synthesized according to previously reported literature.[1] All the solvents used in this study were not purified before using.

**Instrumentation.** UV–vis absorption spectra were recorded by using SHIMADZU UV-2550 UV–visible spectrophotometer. The fluorescence properties of all samples were recorded by using Varian Cary Eclipse spectrofluorometer. The emission spectra were recorded in the wavelength range of 400-600 nm with an excitation at 373 nm and slit widths for excitation and emission of 20 nm. $^{13}$C NMR spectra were recorded on a Bruker Avance 500 MHz NMR. XRD diffraction data were collected on a Siemens D-5005 X-ray diffractometer using Cu Kα radiation. Nitrogen adsorption and desorption isotherm, surface area and median pore diameter were measured using a Micromeritics ASAP 2020 sorptometer. Transmission electron microscopy (TEM) images were gained using a JEM-2100F transmission electron microscopy operated at 200 KV. FT-IR spectra were measured using Magna 560 FT-IR spectra. Thermogravimetic analysis (TGA) were conducted by using Perkin-Elmer TGA7 thermal analyzer. The samples were heated from 40 to 900 $^{o}$C with a heating rate of 10 $^{o}$C /min under atmosphere.

**Synthesis of p-phenylenedimethylene bis-(tetramethylene sulfonium chloride).** This compound was prepared according to Lenz's description.[1] Briefly, added α,α'-dichloroxylene (14.0g, 0.08 mol) to the methanol (80 mL) solution of tetrahydrothiophene (21.2 mL) which was stirred at 50 $^{o}$C for 12 h. After which the solution was concentrated, and 250 mL of acetone was poured to precipitate the bis-sulfonium salt. Then the mixture was stirred in an ice-bath for 0.5 h before filtration. The white solid was washed with acetone and dried under vacuum at room temperature.

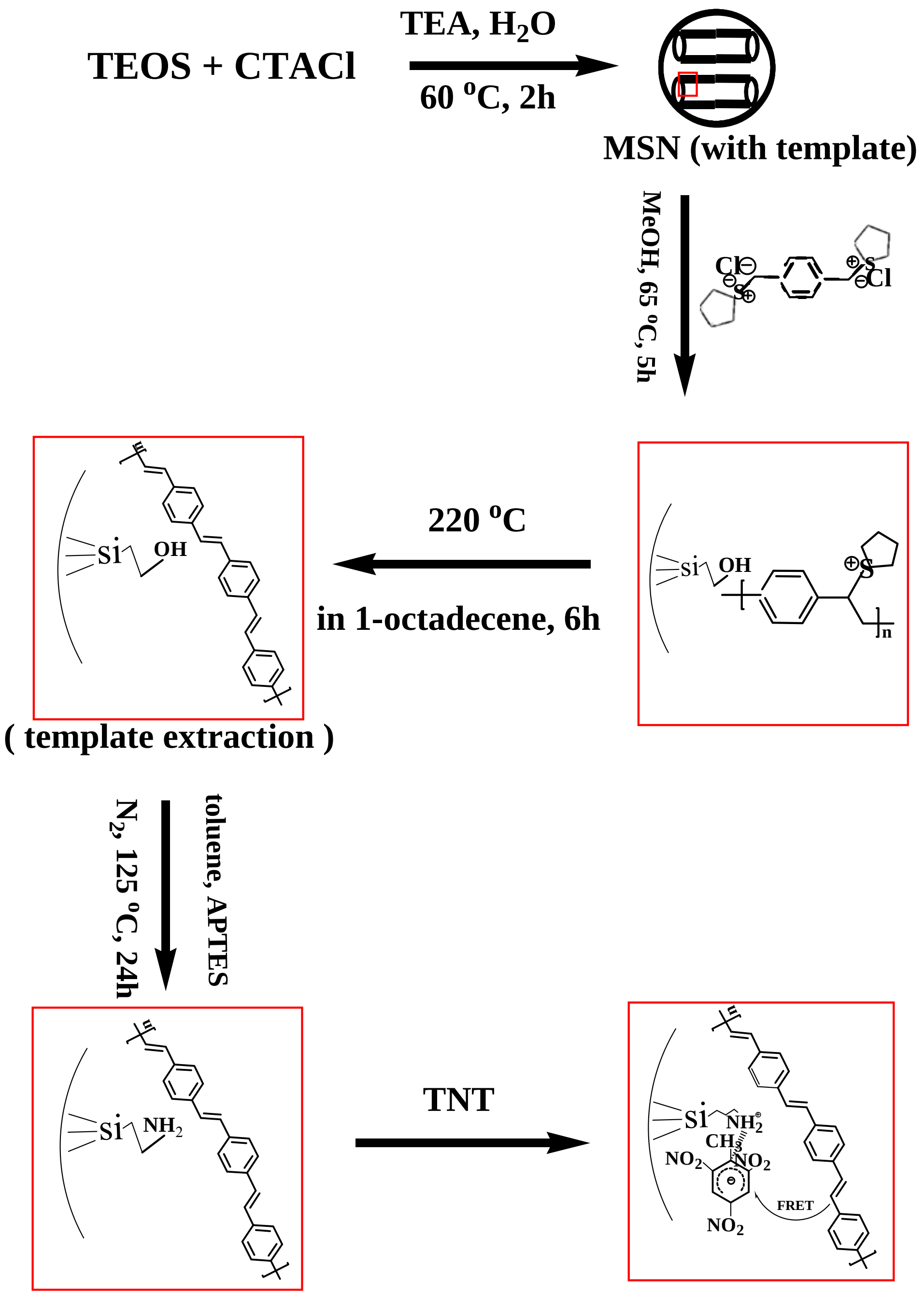
**Synthesis of mesoporous silica nanoparticles (MSN).** The synthesis procedure of mesoporous silica nanoparticles (about 100 nm) was similar to that reported in literature.[2] 64 mL water, 10.5 mL ethanol and 10.4 mL cetyltrimethyl ammonium chloride (CTACl) aqueous solution (25 wt%, 7.86 mmol) were mixed and stirred for 10 min at room temperature. Then triethanolamine (4.13 mL, TEA) was subsequently added to the above solution, and further stirred until all TEA was dissolved, resulting in pH values of 11.3 to 11.6. Usually, 60 mL of above solution was heated to 60 $^{o}$C in water bath. When the temperature stabilized, 4.3 mL Tetraethoxysilane (19.52 mmol, TEOS) was added dropwise within 2–3 min under stirring. A white solution was formed after 10 min. After 2 h, the solution was cooled to room temperature, at which time the pH had decreased to 9.3. The resulting nanoparticles were separated by centrifugation (9500 $r\cdot min^{-1}$, 15 min), washed with distilled water and methanol twice respectively, and preserved in methanol at last (the concentration of MSN is 29.18 $mg\cdot mL^{-1}$).

**Synthesis of PPV encapsulated mesoporous silica nanoparticles (PPV@MSN).**[3] 30 mL MSN was added in 50 mL methanol solution, then added 0.283 g p-phenylenedimethylene bis-(tetramethylene sulfonium chloride) to the above solution, and the mixture was rapidly heated to reflux. After 5 h, the solid was isolated by centrifugation, and subsequently washed by redispersion/centrifugation cycles with methanol three times (3×50 mL). The azury solid was dispersed in 1-octadecene liquor (about 10 mL). The mixture was heated to 220 $^{o}$C under nitrogen atmosphere. After 6 h, the reaction mixture was cooled to room temperature. Before centrifugal separating, added 3 mL of cyclohexane in the cool reaction to reduce the viscosity of the solution. Washed with ethanol twice, and dispersed in methanol at last.

Template extraction was carried as follows: one gram of sample was treated three times with 100 mL of extraction solution (15 mL conc. HCl in 120 mL ethanol) by ultrasonic in ice bath for 30 min. Subsequent washing was performed as described above.

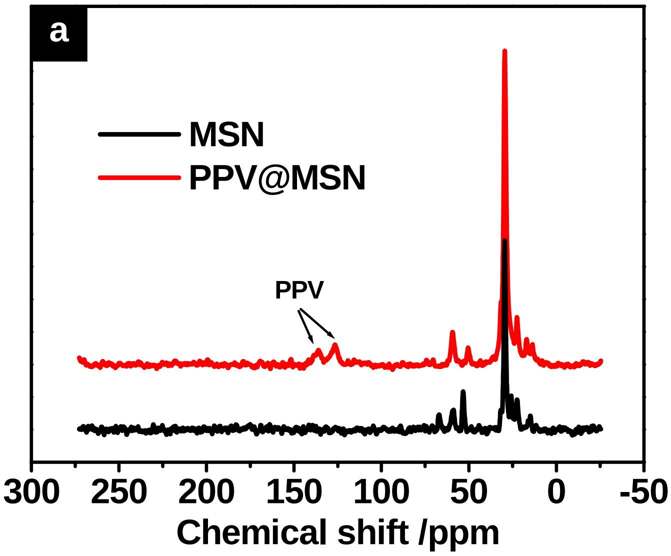
**Synthesis of amino-functionalized PPV@MSN (PPV@MSN-$NH_2$).**[4] The above dried PPV@MSN powder was dispersed in toluene by ultrasonic for 5 min before 3-aminopropyltrimethoxysilane (APTES) was added to the suspension. The molar ratio of PPV@MSN (calculated as $SiO_2$), APTES and toluene was fixed at 5:0.8:500, and the suspension was heated under reflux (125 $^{o}$C) for 24 h under dry nitrogen protection. The amine-functionalized PPV@MSN nanoparticles were filtered from the solution by centrifugation, and washed in toluene and ethanol twice, respectively. Finally, the nanoparticles were dispersed in ethanol solution, and the concentration of PPV@MSN-$NH_2$ is 45.63 mg·$mL^{-1}$, Yield: 90% (Si at %).

## 2. Supporting Scheme



**Scheme S1.** Synthetic scheme for PPV@MSN-NH$_2$.

## 3. Supporting Figures



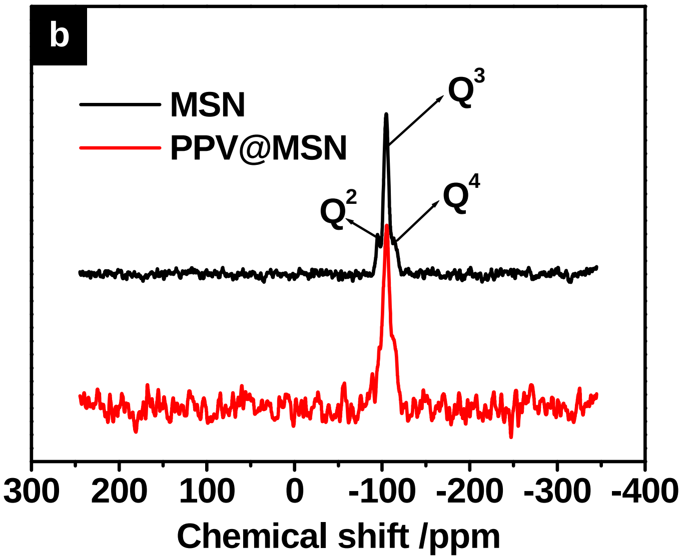


**Fig S1.** $^{13}$C(a) and $^{29}$Si(b) cross-polarization MAS-NMR spectra of MSN and PPV@MSN (without template extraction). $^{13}$C NMR (a): δ126.5 and 136.0 ppm are consistent with the resonances of PPV. $^{29}$Si (b): δ -94.8 ppm ($Q^2$, $Si(O\text{-}Si)_2(OH)_2$), δ -104.7 ppm ($Q^3$, $Si(O\text{-}Si)_3(OH)$), δ -110.9 ppm ($Q^4$, $Si(O\text{-}Si)_4$)

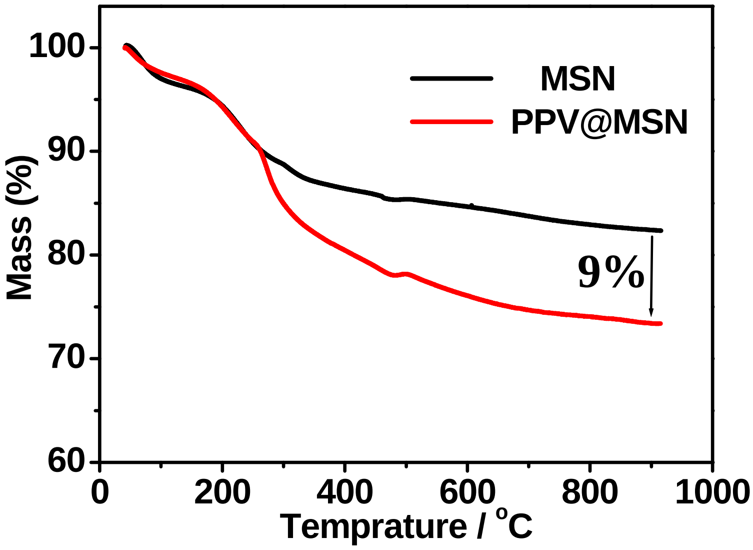


Fig S2. TGA curves of the synthesized MSN and PPV@MSN. The mass loss at 900 $^{o}$C is 82.42% for MSN and 73.42% for PPV@MSN. The loading amount of PPV in MSNs can be estimated as approximately 9% (w/w).

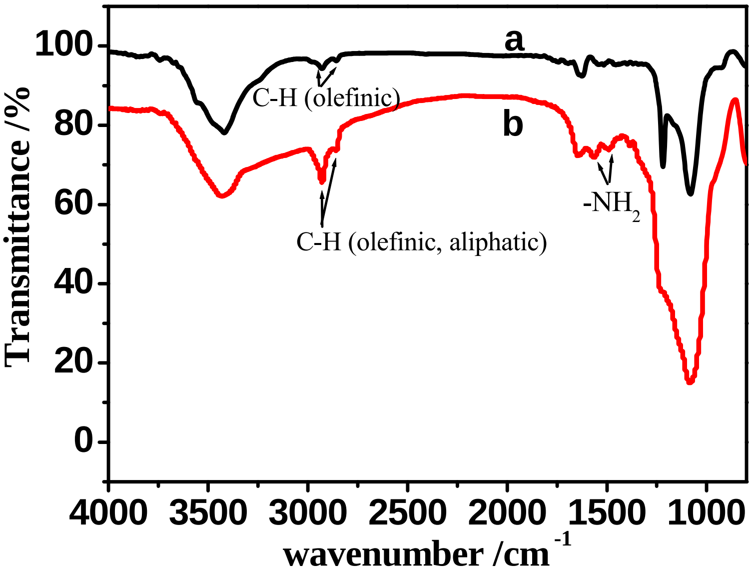


**Fig S3.** FTIR spectra of PPV@MSN (a) and PPV@MSN-$NH_2$ (b). FTIR: 2925 cm$^{-1}$ and 2858 cm$^{-1}$ (olefini C-H $\nu_{st}$, aliphatic –$CH_2$ $\nu_{st}$), [5, 6] 1560 cm$^{-1}$ and 1382 cm$^{-1}$ (–$NH_2$ $\nu_{\delta}$).

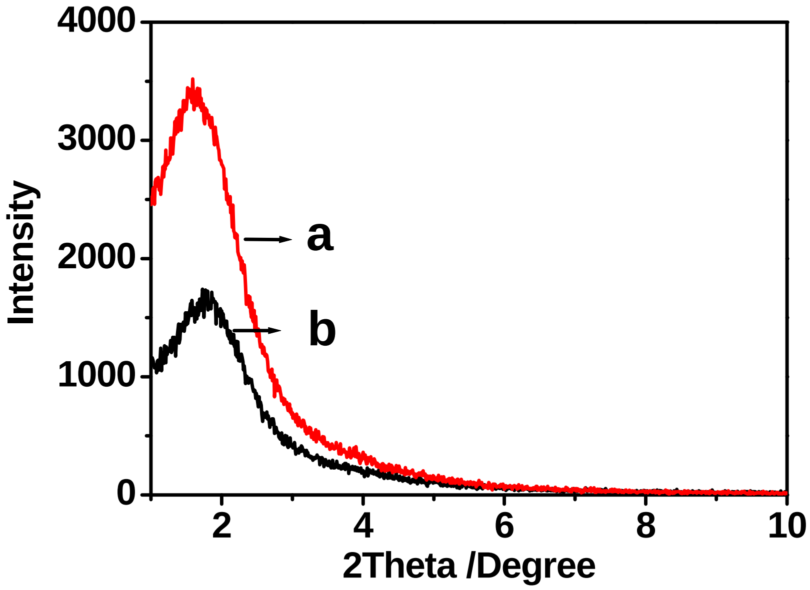


**Fig S4.** XRD patterns of MSN (a) and PPV@MSN (b).

## 4. Supporting Table

**Table S1.** Textural properties of PPV@MSN and PPV@MSN-$NH_2$.

| Sample | $S_{BET}$ [a] ($m^2.g^{-1}$) | $V_t$ [b] ($cm^3.g^{-1}$) | $D_{BJH}$ [c] (nm) |
|---|---|---|---|
| PPV@MSN | 768 | 0.70 | 2.19 |
| PPV@MSN-$NH_2$ | 580 | 0.49 | 1.87 |

[a] BET surface area. [b] Total pore volume. [c] Average pore diameter calculated using BJH method.

**Table S2.** Stern-Volmer equation, quenching constant and correlation coefficient.

| Sample | Quencher | Stern-Volmer equation | R |
|---|---|---|---|
| PPV@MSN | TNT | $(I_0/I)$-1= 0.003(+/-0.001)+[3.73(+/-0.09) ×$10^3$]$C_{TNT}$ | 0.9987 |
| PPV@MSN-$NH_2$ | DNT | $(I_0/I)$ -1= 0.017(+/-0.008)+[1.56(+/-0.07) ×$10^4$]$C_{DNT}$ | 0.9957 |
| PPV@MSN-$NH_2$ | TNT | $(I_0/I)$-1 = -0.03(+/- 0.02)+[7.42(+/- 0.15) ×$10^4$]$C_{TNT}$ | 0.9989 |

## References

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