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## **Supporting Information**

## Detection of nitroaromatic explosives by 3D hyperbranched $\sigma$ - $\pi$

## conjugated polymer on the basis of the POSS scaffold

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**Fig. S1** The fluorescence spectra of spin-coated films and polymers in THF (C = $10^{-3}$  g/L), with the excitation wavelengths of 347 nm, 330 nm, 310 nm and 324 nm for **PDMPS** film, **3D-HPs** film, **PDMPS** in THF and **3D-HPs** in THF, respectively.



Fig. S2 Restriction of intramolecular rotation (RIR) mechanism of PDMPS



Fig. S3 Emission spectra of PDMS with varied glycerol fraction in THF/glycerol mixture



Fig. S4 TGA (A) and DSC (B) curves of polymers with heating/cooling rate of 10 K/min



Fig. S5 Fluorescence quenching of PDMPS (A) and 3D-HPs (B) in TNT/THF solution.



**Fig. S6** Fluorescence quenching of **3D-HPs** (A), **PDMPS** (B) and **P** (C) in saturated DNT vapor



Fig. S7 The reversibility of **3D-HPs** film to saturated DNT vapor.



Fig. S8 Calculation on energy level diagram of models about polymers and DNT.