Supplementary information for

Selectively Detecting of Trace Picric Acid by Reduced Perylene Bisimide with POSS Substituents and Their Nanoaggregates

Experimental section

Synthesis of POSS bisubstituted Perylene Bisimide (PDP-1).

Aminopropyllsobutyl-POSS (NH_2-POSS) 1.06g (1.2mmol), purified PBI 0.16 g (0.4mmol), 2.4 g Imidazole and 5ml Ortho-dichlorobenzene are added in a 50 mL three necked round-bottomed flask equipped with a cooling condenser, a temperature controller and a magnetic stirrer. The precursors are heated to 140 ℃ under N_2 and the reaction time is 12 h. After the reaction, the solution is cooled to room temperature and poured into a mixture of 50 ml acetic acid and 50ml 2M hydrochloric acid (HCl) and stirred. Then dichloromethane are used for extracting the solvents twice. The oil phase are rinsed to pH=7.0 by a saturated sodium bicarbonate solution and dried by anhydrous magnesium sulfate. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with n-hexane/ ethyl acetate (10:1) to afford in 75% yield.

Synthesis of reductive carbonylation of POSS bisubstituted Perylene Bisimide (PDP-2).

$LiAlH_4$ (0.0685 g) and $AlCl_3$ (0.2137 g) were prepared in a 50ml three necked round-bottomed flask and 10ml tetrahydrofuran (THF) were added under N_2 .The whole procedure are used ice-water bath to keep 0-4 ℃. Then removed bath, added 0.422 g PDP-1 and heated to 35 ℃ for 4h. After the reaction, 44ml 1M HCl were dripped dropwise into the flask and stirred for 1h before suction filtration. The residue was wash and dissolved by dichloromethane. With the extraction of the solvents with sodium hydroxide solution, the organic phase was dried by anhydrous magnesium sulfate. And the resultant solution was evaporated to remove solvents and the product was achieved with a yield of 55%.

Preparation of nanoaggregates of PDP-2.

About 1ml of 10^{-4}mol/L PDP-2 in trichloromethane was injected to a test tube, then an equal volume of methanol was added dropwise into the same tube and an interface could be observed between a binary liquid mixture and the mixture solution was then left to stand for 12h. And then nanoaggregates were formed in the mixture solution. The solution containing nanoaggregates was dripped on a sheet glass. After evaporating and drying in the vacuum oven samples for characterization were obtained.

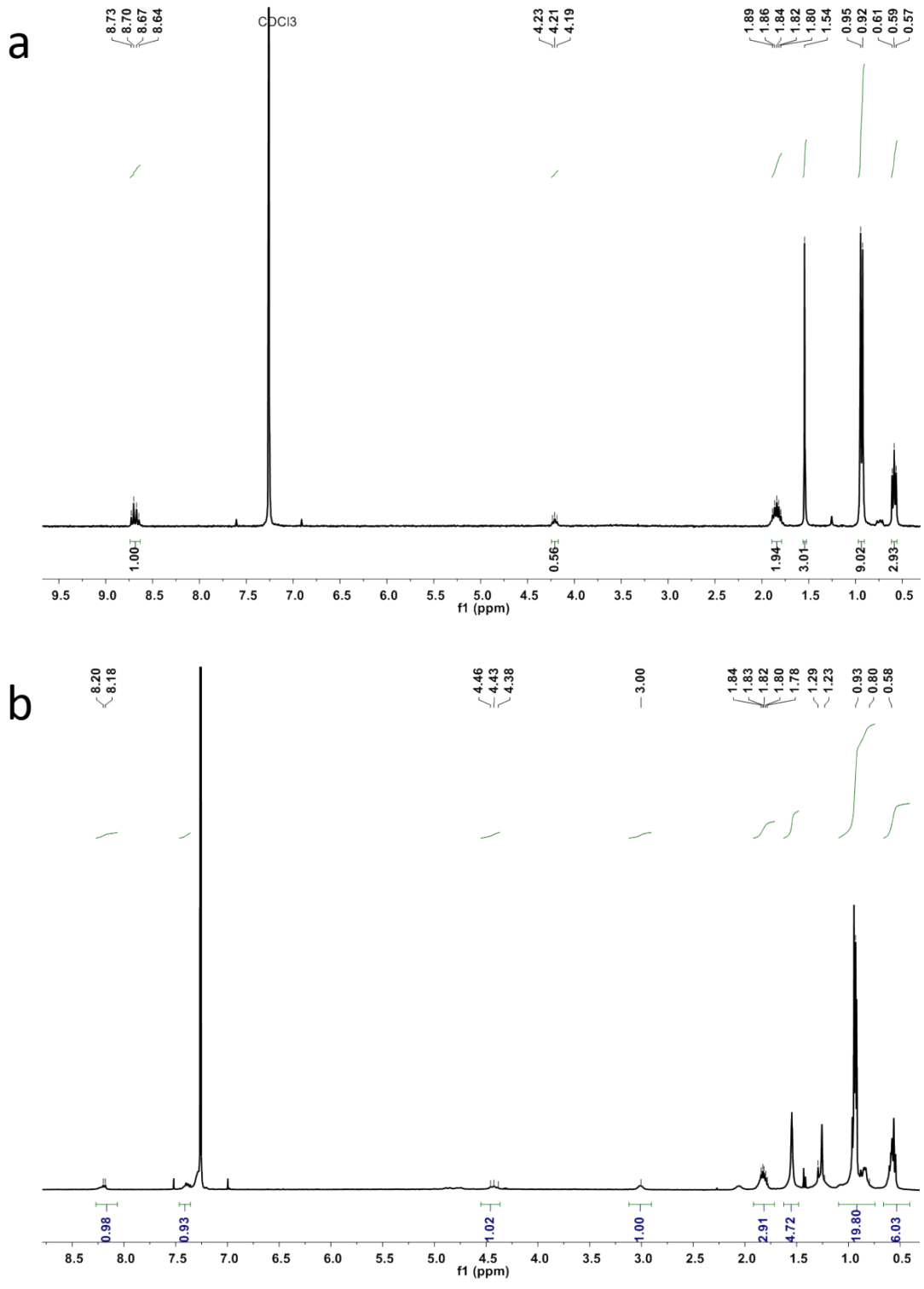

Fig. S1 ^{1}H NMR spectra of **PDP-1** (a) and **PDP-2** (b) in $CDCl_3$ at room temperature.

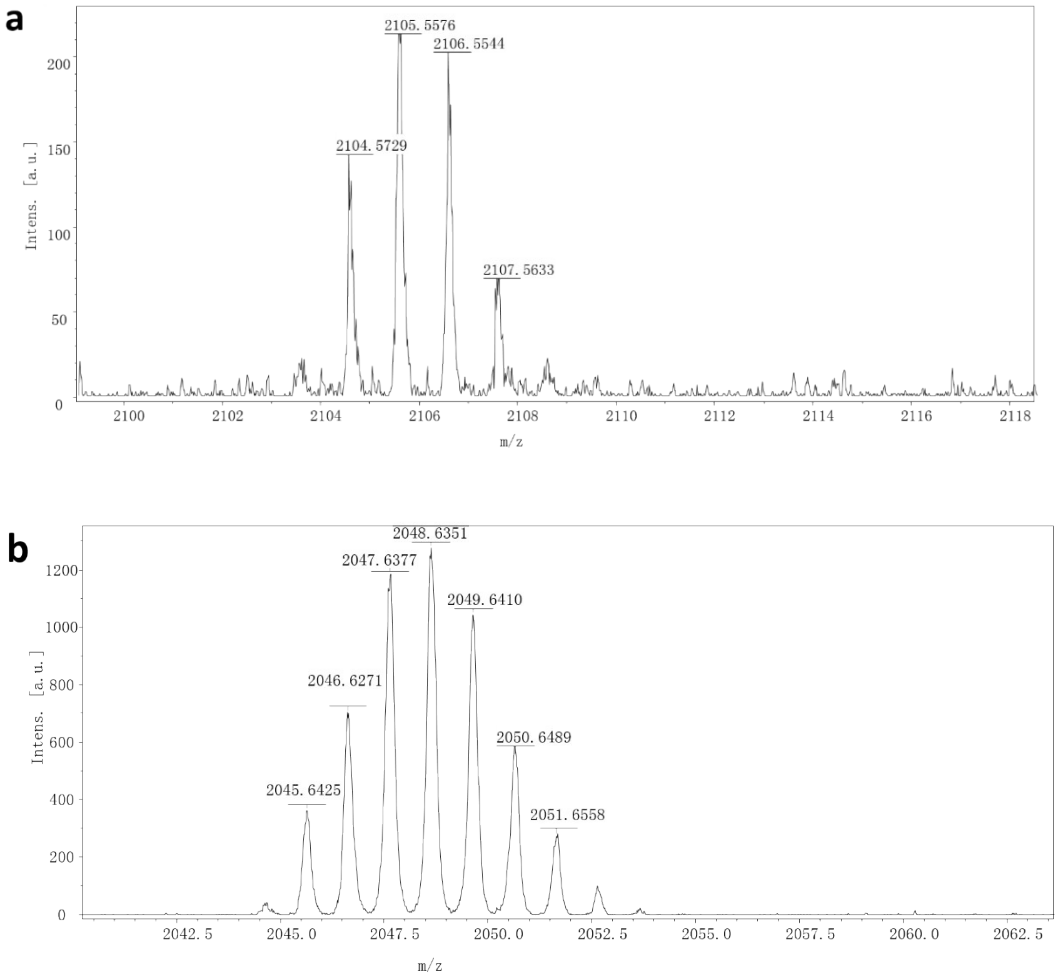

Fig. S2 Mass spectrogram of **PDP-1** (a) and **PDP-2** (b).

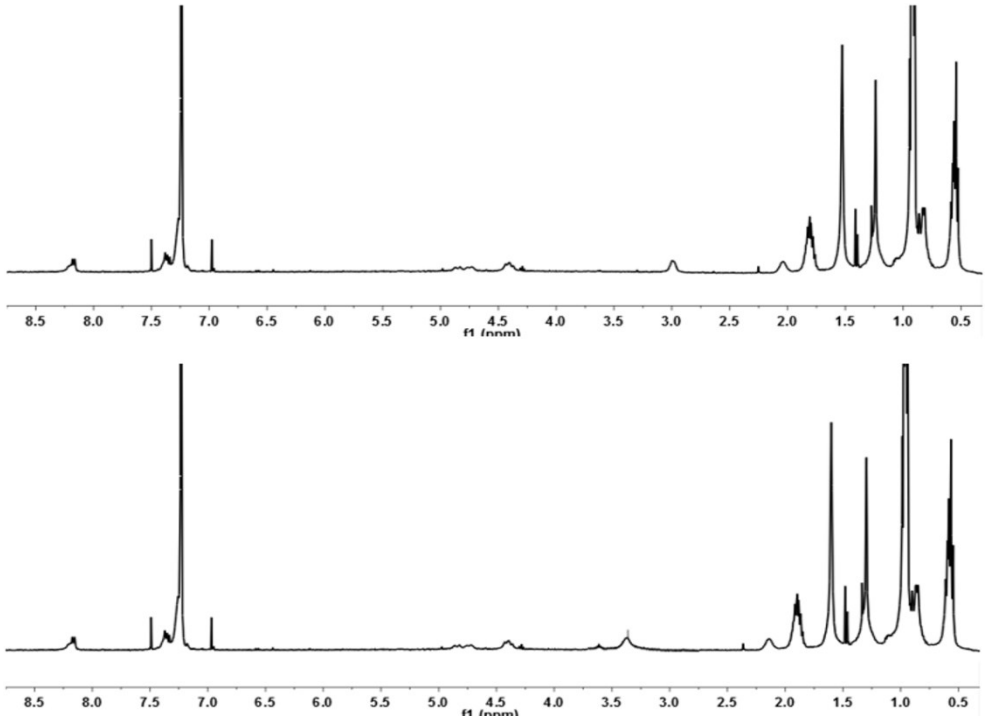

Fig. S3 The change of ^{1}H NMR for **PDP-2** with addition to trace PA.

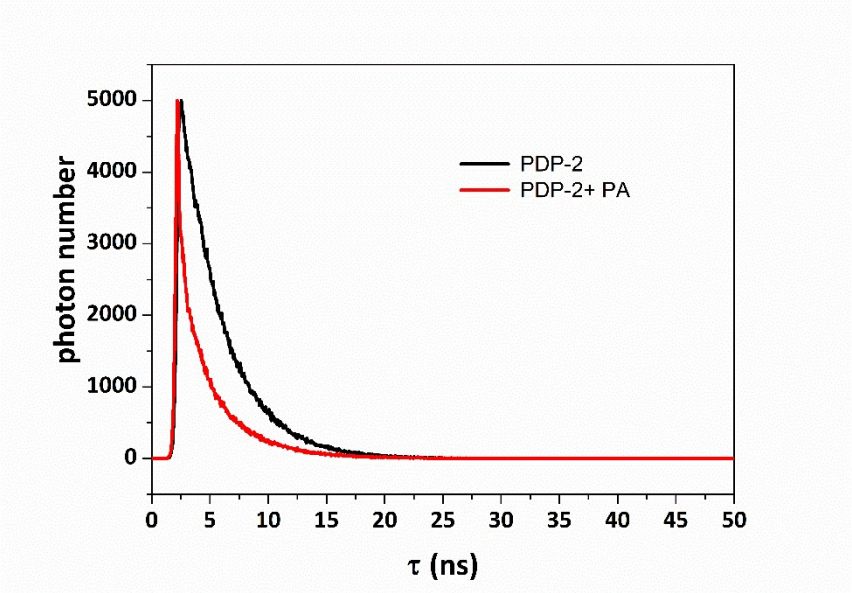

Fig. S4 The change of fluorescence lifetime with (red line) or without addition to trace PA (black line).

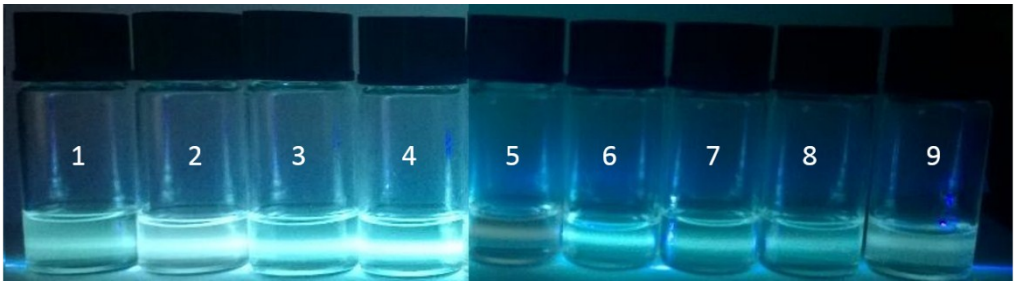

Fig. S5 Colour changes of **PDP-2** (1 μM) to PA (10 μM) and other nitro compounds (100 μM) interfering with colormetric detection of PA (1-none, 2-NB, 3-NA, 4-NBA, 5-PA, 6-NP, 7-DNT, 8-DNB, 9-TNT).

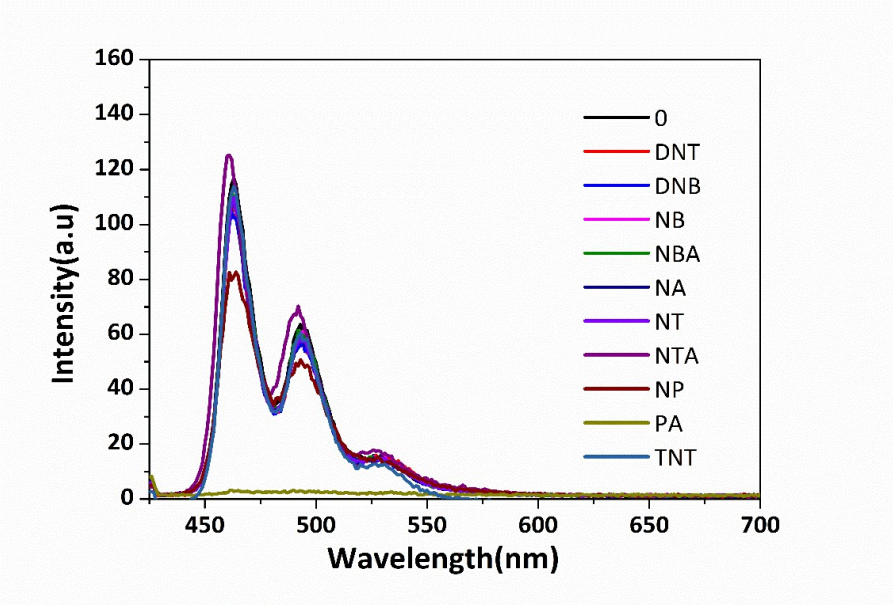

Fig. S6 Fluorescence spectra of **PDP-2** (1 μM) upon addition of PA (10 μM) and other nitro compounds (100 μM) in THF solution.

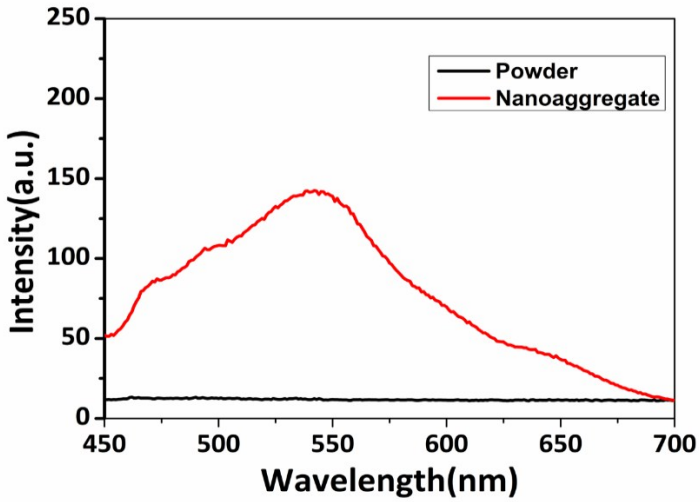

Fig.S7 The fluorescent emission of the powder (black line) by concentrating solution and the nanoaggregates of the **PDP-2** (red line).

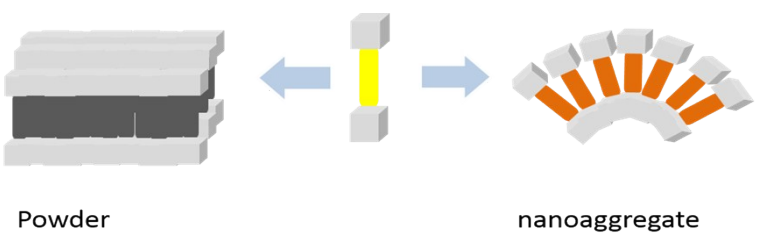

Fig.S8 Alignment structures of PDP-2 in powder formed by solution evaporating and in nanoaggregates formed by interfacial assembly.

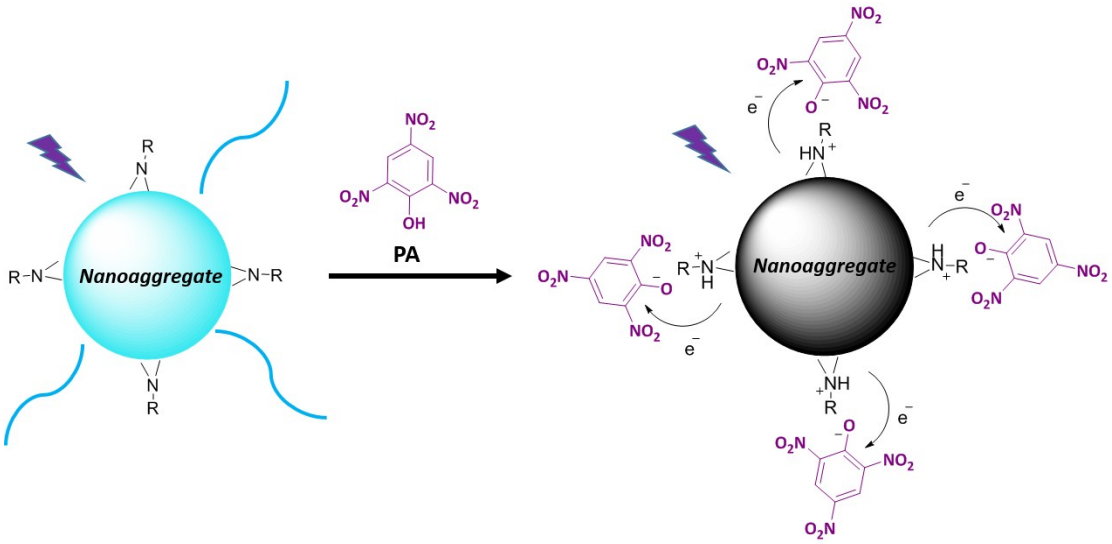

Fig.S9 The change of fluorescence intensity of nanoaggregates of **PDP-2** with dropwise addition of PA.

Table S1. Comparison of selectivity, K_{sv} and detection limit towards PA in comparison with previous literatures.

Publications	**Selectivity Towards PA**	**K sv (M^{-1})**	**Detection limit**	**Response with PA**
Our work	*high*	*$1.19*10^6$*	*80 ng*	**Turn-off**
Angew.Chem.Int.Ed. 2013, 52, 2881	*high*	*$3.5 * 10^4$*	---------	**Turn-off**
Chem.Commun. 2012, 48, 5007	*moderate*	*$9.9 * 10^4$*	*1.37 ng-13.7 ng*	**Turn-off**
J. Mater. Chem. 2012, 22, 11574	*moderate*	*$3.04 * 10^4$*	*0.15 ng*	**Turn-off**
J. Org. Chem. 2013, 78, 1306	*moderate*	*$3.8*10^4$*	*0.32 ug-0.23 ug*	**Turn-off**
J. Phys. Chem. C 2013, 117, 7236	*low*	*$2.405 * 10^5$*	*1.15 fg/cm^2*	**Turn-off**
J. Mater. Chem. A, 2013, 1, 8745	*high*	*$3.14 * 10^4$*	*55.64 ng*	**Turn-off**

Applied Materials & Interfaces, 2013, 5, 5373-5380.	*high*	*$2*10^6$*	--------	**Turn-off**