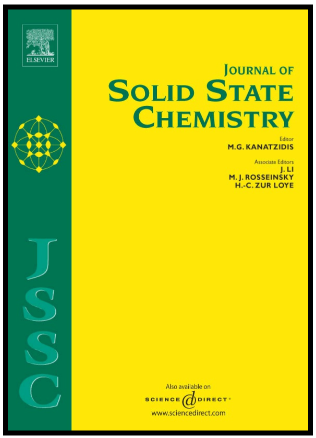

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Mesoporous aluminium organophosphonates: a reusable chemsensor for the detection of explosives

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Abstract

Rapid and sensitive detection of explosives is in high demand for homeland security and public safety. In this work, electron-rich of anthracene functionalized mesoporous aluminium organophosphonates (En-AlPs) were synthesized by a one-pot condensation process. The mesoporous structure and strong blue emission of En-AlPs were confirmed by the N_2 adsorption-desorption isotherms, transmission electron microscopy images and fluorescence spectra. The materials En-AlPs can serve as sensitive chemosensors for various electron deficient nitroderivatives, with the quenching constant and the detection limit up to 1.5×10^6 M^{-1} and 0.3 ppm in water solution. More importantly, the materials can be recycled for many times by simply washed with ethanol, showing potential applications in explosives detection.

Keywords: Explosives detection; Mesoporous; Aluminium phosphate; Recyclable

1. Introduction

The reliable and accurate detection of explosives has become increasingly important and urgent issue in modern society [1,2]. So far, many methods have been developed for the detection of explosives, such as trained canine teams, gas chromatography, ion mobility spectrometry (IMS), and surface-enhanced Raman spectroscopy, and so on [3-7]. However, none of them is ideal for the detection of explosives due to certain features such as more complicated, lack of selectivity, high cost, time-consuming. Fluorescence-based detection of nitroderivatives such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and picric acid (PA) by harnessing organic dyes have drawn much more attention owing to their high sensitivity, easy visualization and real-time monitoring with fast response time [8-12]. It is worth noting that nitroderivatives contain electron withdrawing nitro groups (–NO_2), which often act as good electron acceptors [13]. Thus using π-electron rich of fluorophores as sensors would significantly improve the sensitivity of explosives detection [14-16]. The fluorescence of electron-rich aromatic rings of anthracene is known to be rapidly quenched upon exposure to nitroderivatives based on electron-transfer and/or energy transfer mechanism [17,18]. However, few works are reported on the incorporation of anthracene into porous materials for the detection of explosives.

Porous materials have been widely used in various fields such as separation, catalysis, and sensors due to their structural stability, high surface areas, large pore volumes and controllable pore sizes [19-22]. As an important part of porous materials, mesoporous metal phosphates possess abundant potential applications in optics, magnetics, electronics, mechanics, and electron transfer [23-26]. So far, many organically functionalized mesoporous metal organophosphonates have been synthesized [27]. The materials can rapidly associate analytes and drugs inside the large pores via physical diffusion and/or chemical interaction, which can efficiently interact with the functional groups in/on the pore wall. In addition, the pore size of mesoporous materials generally lies in the working distances of photo-induced electron transfer and/or energy transfer. In this regard, organic fluorescent group functionalized mesoporous metal organophosphonates maybe served as a new generation of chemosensor for the detection of explosives.

The present work will contribute to the one-pot synthesis of mesoporous aluminium organophosphonates functionalized with anthracene groups (En-AlPs) and systematically investigated their application in explosives detection. The electron-rich of fluorophore anthracene will have donor-acceptor (D–A) interactions with the electron-deficient of nitroderivatives, resulting in a favorable photo-induced electron transfer, which accounts for the most of the fluorescence-based explosive detection. Furthermore, the large porous of En-AlPs would allow the explosives to enter and interact with anthracene groups, enhancing the fluorescence quenching process. Indeed, the En-AlPs show sensitive fluorescence quenching to PA in water solution, with the quenching constant up to 1.5×10^{6} M^{-1}. The materials can also be recycled for many times by simply washed with ethanol, showing potential application in explosives detection.

2. Experimental

2.1. Materials

Aluminium isopropoxide (Al(*i*-PrO)$_4$, Beijing Beihua Chemical Co., Ltd.), Cetyl trimethyl ammonium chloride (CTAC, Beijing Beihua Chemical Co., Ltd.), Picric acid (PA, Xilong Chemical Co., Ltd.), Phosphoric acid (H_3PO_4, Tianjin Tiantai Fine Chemical Co., Ltd.), Tetramethylammonium hydroxide (TMAH, 25 wt%, Sigma-Aldrich). All chemicals used in the experiments were purchased and used as received without further purification. Organophosphonates 9,10-bis(dihydroxyphosphinylmethyl)anthracene (PAEn) was prepared by using a modified literature method [28,29].

2.2. Synthesis of mesoporous aluminium organophosphonates

Mesoporous aluminium organophosphonates was prepared as described previously with a modify [30], the process is as follows: 1.19 g CTAC and 0.13 g PAEn were added into 2.2 mL water containing 2.7 g TMAH (25 wt%), and 0.48 mL H_3PO_4. Then the solution was stirred at room temperature until completely dissolved. Subsequently, 1.53 g Al(*i*-PrO)$_4$ was added slowly, yielding a milky suspension after stirred for 24 h. The mixture was transferred to a Teflon-lined autoclave and crystallized statically at 130 °C under autogenous pressure for about 5 days. After cooling to room temperature, the obtained materials was certified and washed with deionized water and DMSO several times, and then refluxed in ethanol for 24 h to remove the template. After dried in the freezer dryer overnight, the materials functionalized with anthracene groups were obtained, marked as En-AlP2. Other loading levels were obtained with the same process just by varied the amount of

PAEn to 0.065g, 0.55g for En-AlP1, En-AlP3, respectively. The contents of anthracene loaded into the materials determined by CHN elemental analysis were 0.15, 0.31, and 0.92 mmol g^{-1}.

2.3. The detection of explosives with En-AlPs

3 mg En-AlPs were well dispersed into 3 mL water by ultrasonic. Certain amounts of explosives solution (10^{-4} M) was added into the system each time. Meanwhile, the fluorescence was recorded with the addition of different amounts of explosives in THF solution by spectrofluorometer under UV light illumination (365 nm).

2.4. Characterizations

The N_2 adsorption-desorption isotherms at 77 K were measured on a Micromeritics Gemini V analyzer. Transmission electron microscopy (TEM) images were recorded with a JEM-3010 electron microscope. UV-Vis adsorption spectra were obtained on a Shimadzu UV-2550 spectrophotometer. The UV/Vis excitation and emission spectra were obtained on a Shimadzu RF-5301PC spectrofluorometer. CHN elemental analyses were performed on a varioMICRO elemental analyzer.

3. Results and Discussion

The organophosphonates 9,10-bis(dihydroxyphosphinylmethyl)anthracene (PAEn) was prepared according to the synthetic route (Fig. 1). Then it was introduced into mesoporous aluminium organophosphonates through P-O-Al covalent bonds by a one-pot condensation process with the assistance of surfactant CTAC. After removing the surfactant by refluxed in ethanol, the materials functionalized with anthracene groups were obtained, marked as En-AlPs. The mesostructure of the En-AlPs were confirmed by N_2 sorption analysis and TEM observations. The N_2 adsorption–desorption isotherms of En-AlP1 and En-AlP2 showed type IV isotherms with distinct hysteresis loops in the 0.4–1.0 P/P_0 range, revealing the typical character of mesoporous materials (Fig. 2). One narrow peak around 2.4 nm were observed in the pore size distribution curve, and the respective Brunauer–Emmett–Teller (BET) surface area, pore volume are 132 m^2 g^{-1}, 0.24 cm^3 g^{-1}, and 172 m^2 g^{-1}, 0.28 cm^3 g^{-1}, respectively. When more PAEn was added during the preparation process, the N_2 adsorption–desorption isotherm of En-AlP3 becomes higher and shows a distinct hysteresis loop in the 0.7–0.95 P/P_0 range. Note that the pore size distribution of En-AlP3 contains a new broader pore range indicating the presence of newly formed larger mesopores. The reason can be contributed to the penetration of more bulky bridging groups PAEn into the mesopore walls. Furthermore, some PAEn molecules may also act as swelling agents incorporated in the formed CTAC micelles, leads to the formation of much larger diameter pores. All the textural parameters of the corresponding materials are summarized in Table 1. The wormlike pore structure of the En-AlPs could be clearly seen from Fig. 3, consistent with the result of N_2 sorption data.

Fig. 4 shows the emission spectra of En-AlPs in water solution. Upon UV irradiation (365 nm), all of them exhibit strong blue emission, and their photoluminescence (PL) intensity is enhanced with the increased loading amounts of PAEn within a certain range. When the PAEn was 0.92 mmol g^{-1}, the PL intensity was not further increased, which maybe caused by the aggregation-caused quenching

(ACQ) effect. As anthracene is a well-known π-electron rich of fluorophores, the En-AlPs may show excellent sensoring performance to electron deficient nitroderivatives. We take commercially available picric acid (PA) as a model for the explosive detection in water solution.

The PL intensity of En-AlPs decreases significantly with the increasing loading amount of PA. Fig. 5 shows the fluorescence emission spectra of En-AlP2 with the addition of different amounts of PA in water solution. The PL quenching can be clearly discerned at a [PA] level as low as 1.4 μM or 0.3 ppm. When the PA concentration is increased to 33 μM, the quenching of fluorescence can clearly visible to the naked eye under the illumination of UV light at 365 nm. It is noting that the materials En-AlP1, En-AlP3 show similar quenching process, but slower than that of En-AlP2. The Stern–Volmer plots of relative PL intensity (I_0/I) of En-AlPs versus PA concentration are shown in Fig. 5B to further quantify the quenching efficiency, where I_0 and I are the PL intensities of the En-AlPs before and after adding PA, respectively. The I_0/I versus [PA] plots bend upwards quickly with quenching constants of about 0.4×10^6, 1.5×10^6, 1.3×10^6 M^{-1} for En-AlP1, En-AlP2, and En-AlP3, respectively. The sensitivity of them shows the sequence of En-AlP2 > En-AlP3 > En-AlP1, consistent with their fluorescence intensity.

The sensitive fluorescence quenching behaviors of En-AlPs to PA can be explained by the photoinduced electron transfer and/or energy transfer mechanism. From Fig. 6, it can be seen that the absorption of PA overlaps with the emission of En-AlPs from 380–500 nm in the water solution, which allows the energy transfer from the excited state of En-AlPs to the ground state of PA, leading to rapid fluorescence quenching response to the explosive PA. In addition, the large porous are convenient for electron acceptor PA to enter and interact with the electron-rich anthracene, improving the capacity of photo-induced electron transfer. Other electron deficient nitroderivatives such as 3-nitrophenol (NP), 2,4-dinitrotoluene (DNT), 4-nitrotoluene (NT), and 4-nitrobenzaldehyde (NBD) were also investigated for En-AlP2. As illustrated in Fig. 7, the En-AlP2 show lower sensing ability towards NP, DNT, NT and NBD in the systems compared to PA under the same conditions. The strong spectral overlap of PA with En-AlP2 is responsible for the high sensitivity. Furthermore, substitution of more electron-withdrawing nitro groups on the aromatic ring will also favor the fluorescence quenching of the materials. NP, NT and NBD only have one nitro group, but the NP behaves as a relatively stronger acid because of the –OH group affixed on benzene ring, which makes it can form hydrogen bond with the hydroxyl group on the surface of En-AlP2. While NT and NBD are hydrophobic in nature and the En-AlP2 are hydrophilic materials. It can be expected that the compatibility of the En-AlP2 to NT and NBD will be poor, resulting in lower quenching efficiencies.

The reusability of the anthracene functionalized mesoporous aluminium organophosphonates was further investigated by taking En-AlP2 as example. After the emission was quenched, the materials was certified, and washed with ethanol several times. Then the experimental procedure was repeated. It can be clearly seen from Fig. 8 that En-AlP2 could be regenerated and reused for at least five cycles without significant change of PL intensity, indicating that the materials can be used as environmentally friendly detectors for explosives.

4. Conclusion

In summary, electron-rich of anthracene functionalized mesoporous aluminium organophosphonates was prepared by a one-pot condensation process, which can be used for the detection of electron-deficient nitroderivatives in water solution based on the photo-induced electron and/or energy transfer mechanism. The large porous enable explosives to enter and interact with the anthracene chromophores, leading to rapid fluorescence quenching response to PA, with the quenching constant and the detection limit up to 1.5×10^{6} M^{-1} and 0.3 ppm, respectively. More importantly, the materials can be recycled for many times by simply washed with ethanol, proving that they can be used as an excellent fluorescence probe for future practical applications in explosives detection.

Acknowledgements

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Captions:

Fig. 1 The synthetic route of PAEn.

Fig. 2 (A) N_2 adsorption/desorption isotherms of (a) En-AlP1, (b) En-AlP2, (c) En-AlP3, respectively. (b) Corresponding pore size distributions based on the adsorption branch of the isotherm with the Barrett-Joyner-Halenda (BJH) method.

Fig. 3 TEM images of (a) En-AlP1, (b) En-AlP2, (c) En-AlP3.

Fig. 4 Fluorescence spectra of (a) En-AlP1, (b) En-AlP2, (c) En-AlP3 in water. Excitation wavelength: 365 nm.

Fig. 5 (A) Fluorescence emission spectra of En-AlP2 with the addition of different amounts of PA in water solution. (B) Stern–Volmer plots of I_0/I versus [PA] in water (a) En-AlP2; (b) En-AlP3; (c) En-AlP1.

Fig. 6 Absorption spectrum of (a) PA, (b) NT, (c) DNT, (d) NP, (e) NBD; the PL spectra of (f) En-AlP1, (g) En-AlP2, and (h) En-AlP3 in water.

Fig. 7 Fluorescence quenching efficiencies of En-AlP2 toward different analytes. The samples are ordered as PA (1), NP (2), DNT (3), NT (4), NBD (5).

Fig. 8 The quenching and recovery test of En-AlP2 in water solution. The inset shows fluorescence images in the water solution with [PA] of 0 and 33 µM, which are taken under UV light illumination (365 nm).

Table 1 Textural parameters of En-AlPs.

Sample	S_{BET} (m^2/g)	D_{BJH} (nm)	Pore Volume (cm^3/g)	Anthracene loading (mmol/g)
En-AlP1	132	2.4	0.24	0.15
En-AlP2	172	2.4	0.28	0.31
En-AlP3	104	15.0	0.34	0.92

Fig. 1

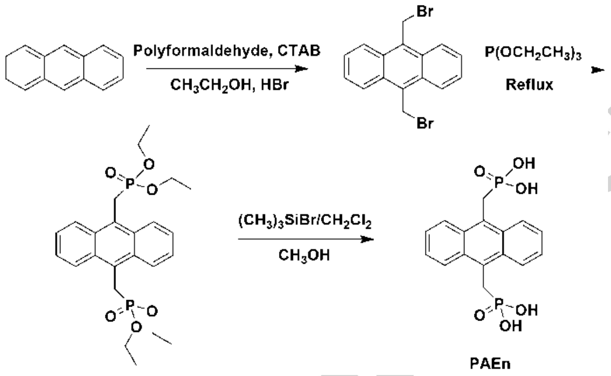


Fig. 2

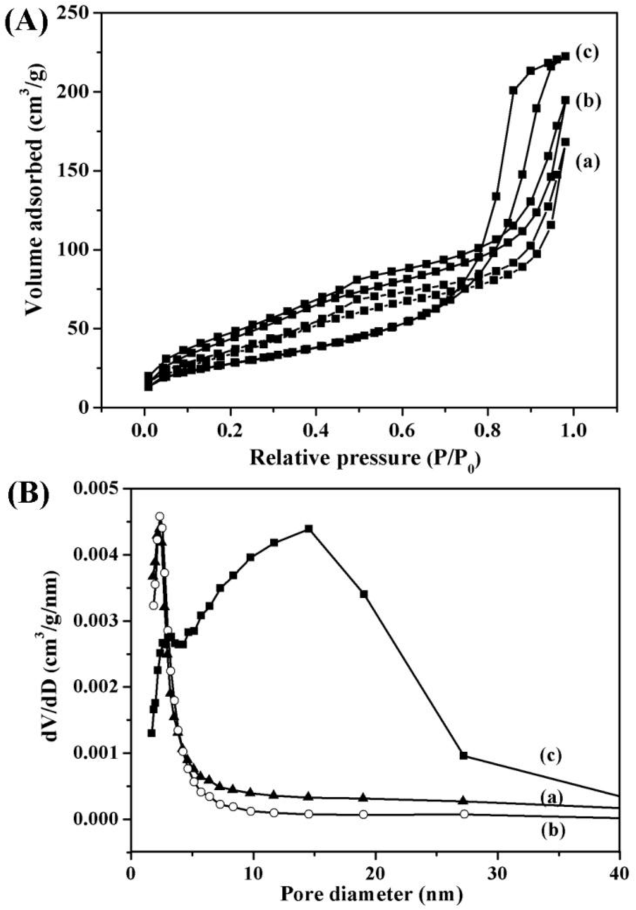

(A)
Volume adsorbed (cm^3/g)
Relative pressure (P/P$_0$)
0
50
100
150
200
250
0.0
0.2
0.4
0.6
0.8
1.0
(c)
(b)
(a)
(B)
dV/dD (cm^3/g/nm)
Pore diameter (nm)
0.000
0.001
0.002
0.003
0.004
0.005
0
10
20
30
40
(c)
(a)
(b)

Fig. 3

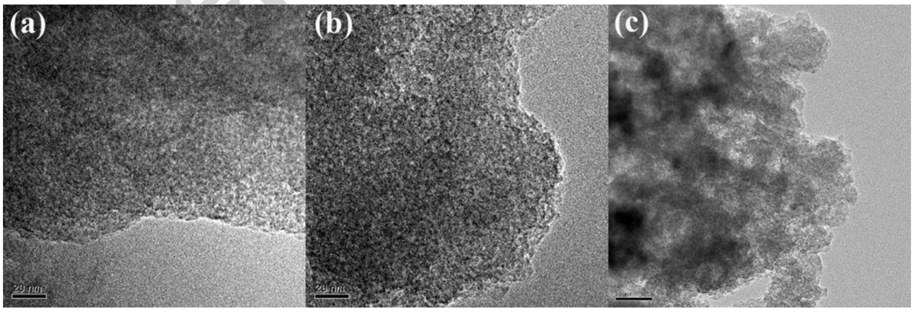

(a)
(b)
(c)
20 nm
20 nm

Fig. 4

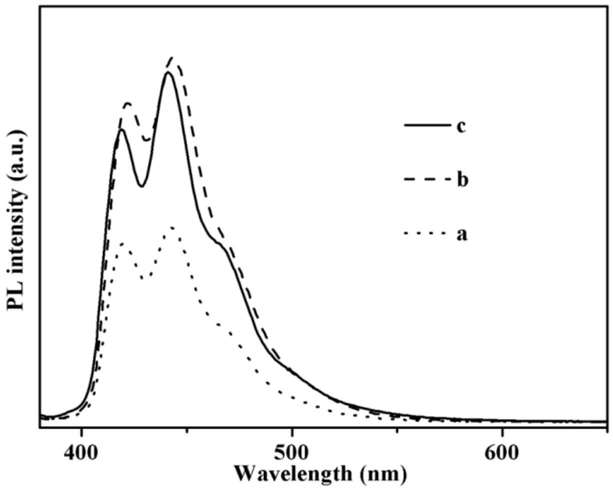

PL intensity (a.u.)
c
b
a
400
500
600
Wavelength (nm)

Fig. 5

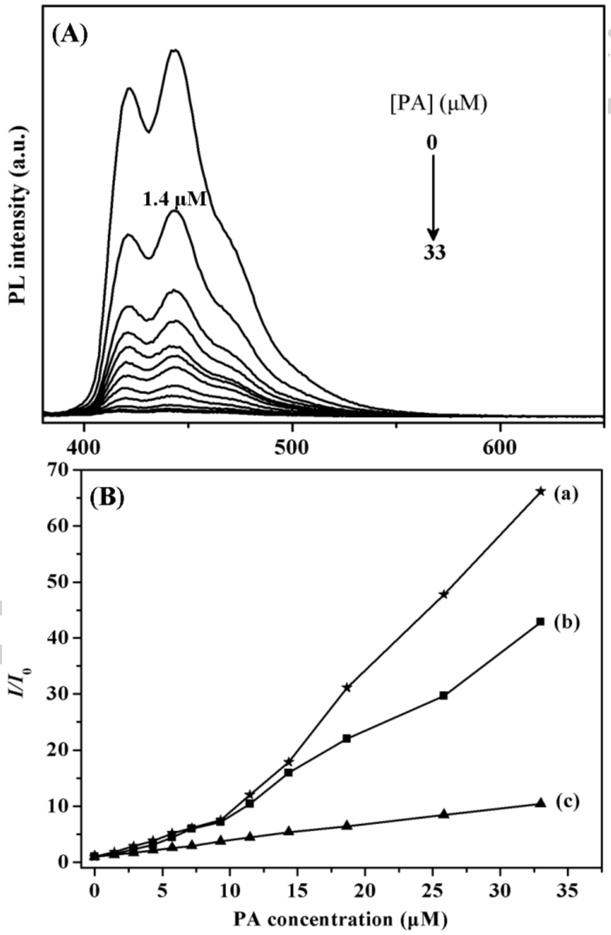

(A)
PL intensity (a.u.)
[PA] (μM)
0
33
1.4 μM
400
500
600
(B)
I/I0
(a)
(b)
(c)
0
10
20
30
40
50
60
70
0
5
10
15
20
25
30
35
PA concentration (μM)

Fig. 6

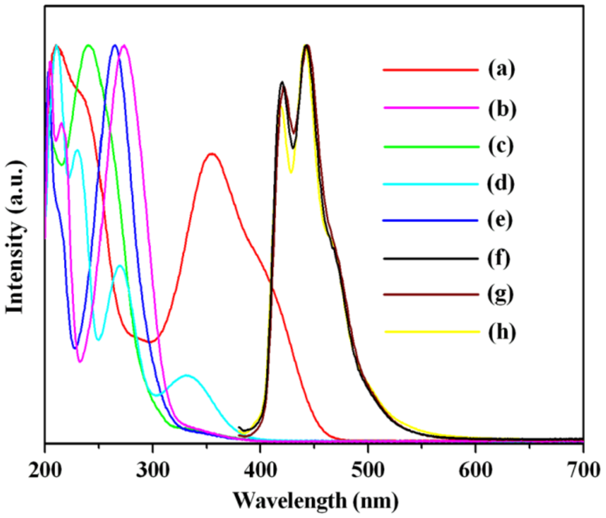

Intensity (a.u.)
Wavelength (nm)
200
300
400
500
600
700
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)

Fig. 7

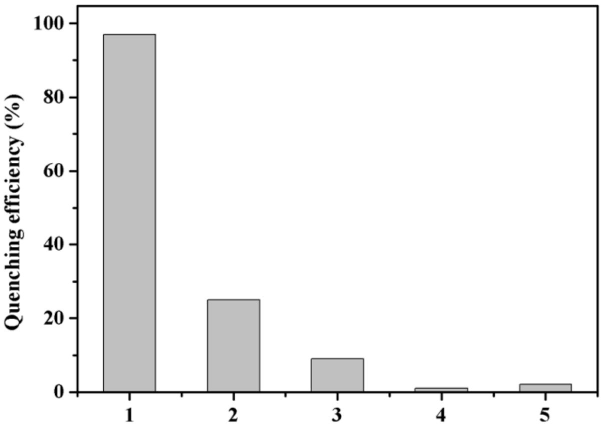
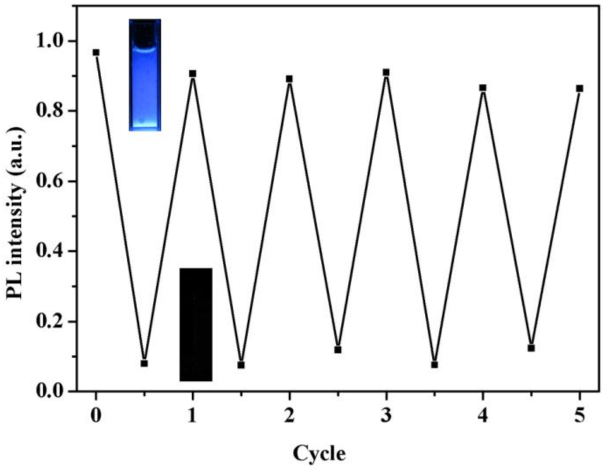

Quenching efficiency (%)
100
80
60
40
20
0
1
2
3
4
5

Fig. 8



Highlights

- Anthracene functionalized mesoporous aluminium organophosphonates were synthesized.
- The materials serve as sensitive chemosensors for nitroderivatives.
- The materials can be recycled for many times by simply washed with ethanol.
- The materials show potential applications in explosives detection.

Graphical abstract

Electron-rich of anthracene functionalized mesoporous aluminium organophosphonates can serve as sensitive and recycled chemosensors for nitroderivatives with the quenching constant up to 1.5×10^{6} M^{-1} in water solution.