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# A Pyrene-cored Conjugated Microporous

# Polycarbazole for Sensitive and Selective Detection

## of Hazardous Explosives

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KEYWORDS: CK-CMP, Polycarbazole; Conjugated microporous polymer; Detection of Hazardous Explosives

In this article, we report the synthesis and characterization of a highly luminescent conjugated microporous polycarbazole (CK-CMP) by FeCl<sub>3</sub>-induced oxidative polymerization of 1,3,6,8-tetrakis(4-(9H-carbazol-9-yl)phenyl)pyrene (L). The CK-CMP with small pore sizes exhibits good thermal stability and high luminescence when suspended in polar solvents upon irradiation by UV light. and , which can be applied to detect 2,4,6-trinitrophenol (PA) with good sensitivity and selectivity by fluorescence quenching.

#### Introduction

The detection of nitro explosives has become so important field because as it is closely related with national security, civilian safety and environmental protection. Nitro explosives, the highly explosive and dangerous energy sources, can be used as common ingredients of explosive devices<sup>1</sup> as well as Since it is often applied in TNP fireworks, leather and dye industries, which resulting in serious health and environmental problems-due to their being deposited into the soil and aquatic system. Among these high energy complexes, chemical sensing of 2,4,6-

trinitrophenol (PA) and 2,4,6-trinitrotoluene (TNT) is especially necessary as they are still highly explosive and toxic in extremely low concentrations.<sup>2</sup> However, conventional detecting techniques such as Surface-enhanced Raman spectroscopy, Cyclic Voltammetry, Capillary Electrophoresis and Gas Chromatography-Mass Spectrometry, are expensive and difficult to operate. Therefore, there is a compelling need to develop new porous materials that can be used to rapidly to detect nitro explosives. Since sensing based on by fluorescence quenching is a much simpler and highly sensitive technique, it has now been widely applied in fluorescent MOFs.<sup>2,3</sup>

Chemical sensing using MOFs has attracted considerable attention, but weak coordination bonds within MOFs can result in low stability and high water affinity. In sharp contrast, conjugated microporous polymers (CMPs) have emerged as a new kind of porous materials due to their applications in heterogeneous catalysis, gas separation and storage energy, electronic devices and chemical sensing.<sup>4</sup> CMPs are <del>a</del> purely organic frameworks, which exhibit high thermo stability, large surface areas, well-tuned pore structures, and can be readily functionalized.<sup>5</sup> In addition <del>to this</del>, commercial nitro explosives, such as PA or TNT all possess an electron deficient –NO<sub>2</sub> group, could interact with electron donating CMPs. resulting efficient excitation migration within the porous structures of CMPs to raise quenching sensitivity. Thus, these features of CMPs can make Porous Organic Frameworks (POFs) suitable for the detection of the hazardous explosives.<sup>5</sup>

As a class of CMPs, polycarbazoles possess the rigid conjugated framework, which is favorable for the formation of microporous polymer structures with permanent porosity, high surface areas, and excellent stability.<sup>6</sup> Due to oxidative sites of carbazoles, carbazole-functionalized monomers are readily polymerized into CMPs via FeCl<sub>3</sub> oxidative coupling. To date, pyrene-based porous materials have also been widely applied in photo-catalysis, photoelectric devices and chemical

sensing due to their excellent rigidity and photophysical properties.<sup>7</sup> Motivated by all the above, we designed and synthesized selected 1,3,6,8-tetrakis(4-(9H-carbazol-9-yl)phenyl)pyrene (L), a carbazole-functionalized monomer, as the building unit to construct a pyrene-cored Conjugated Microporous Polycarbazole (CK-CMP) by oxidative polymerization. Additionally, And the photophysical properties of the polymers were studied, followed by investigation of their application in <del>and</del> sensitive detection of hazardous explosives<del>.</del>



Scheme 1 The synthesis of CK-CMP

**Experimental Section** 

1,3,6,8-tetrakis(4-(9H-carbazol-9-yl)phenyl)pyrene (L) was synthesized according to the reported method.<sup>8</sup> (4-(9H-carbazol-9-yl)phenyl)boronic acid were purchased from Energy Chemical Technology (Shanghai) Co. Ltd. Tetrakis(triphenylphosphine)palladium(0) and 1,3,6,8-tetrabromopyrene was prepared <del>by</del> in our <del>own</del>-lab. All other reagents were of analytical grade and used without further purification.

Caution! Nitro-explosives are highly explosive and should be used carefully and in a small scale amounts. The explosives were handled as dilute solutions and with safety measures to avoid explosion

Preparation of 1,3,6,8-tetrakis(4-(9H-carbazol-9-yl)phenyl)pyrene (L)

In a 250 mL three-necked round-bottomed flask, 1,3,6,8-Ttetrabromo-Ppyrene (1.0356 g, 2 mmol) and 4-(9H-Ccarbozol-9yl)phenylboronic acid (2.8712 g, 10 mmol) was were dissolved in dioxane (100 mL) and then an aqueous solution of potassium carbonate (3.15 g, 23 mmol) in water (10 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (0.6 g, 0.50 mmol) was were added to the reaction mixture and it was stirred under N<sub>2</sub> at 100°C for 3 days. After cooling to room temperature, the yellow reaction mixture was transferred to dilute hydrochloric acid solution (100 mL). The precipitate was collected by filtration and then washed with water (3×40 mL). The solid was transferred to a Soxhlet and continuously extracted with CHCl<sub>3</sub> for 48 h. The CHCl<sub>3</sub> extracts were was evaporated under reduced pressure. The crude product L was further purified by silica-gel column chromatography using CHCl<sub>2</sub> as mobile phase to afford a bright yellow solid (0.5 g, 22%). 1H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 8.51(4H), 8.32(2H), 8.22(8H), 8.03(8H), 7.84 (8H), 7.61(8H), 7.51(8H), 7.35(8H). FT-IR (ATR4000–400 cm-1) 3418, 3047, 2910, 1600, 1514, 1493, 1451, 1359, 1338, 1312, 1223, 1164, 1004, 839, 746, 717, 628, 561, 533. MS(ESI): m/z for C<sub>88</sub>H<sub>54</sub>N<sub>4</sub> cacld 1166, M<sup>+</sup>, 1166.02.

#### The Synthesis of CK-CMP

The monomer L (300 mg, 0.52 mmol) was dispersed in anhydrous chloroform (30 mL), and then transferred dropwise to a suspension of FeCl<sub>3</sub> (415 mg, 2.5 mmol) in anhydrous chloroform (15 mL). The mixture was stirred for 24 h<del>ours</del> under  $N_2$  at 60 °C, and then 100 mL of methanol was added to the reaction mixture. The resulting mixture was kept stirring for another hour and the precipitate was collected by filtration. After being washed with methanol, the obtained solid was stirred vigorously in hydrochloric acid solution for 1 h. The suspension was then filtered and

washed with water and methanol, and then extracted using a Soxhlet extractor with THF for 24 h. The resulting product was dried at 120 °C on vacuum for 24 h to obtain a yellow powder (yield: 78%).

Preparation of CK-CMP Suspension

Finely ground samples of CK-CMP were was dispersed in ethanol solution to form a suspension solution with concentration of 1 mg/mL, which were was ultrasonically agitated for 15 min before testing.

Preparation of CK-CMP Ffilm

Finely ground samples of CK-CMP (3 mg) was dispersed in 0.5 mL ethanol solution to form a suspension solution, which were was ultrasonically agitated for 15 min. Then, the suspension was uniformly added dropwise onto a clean quartz plate and dried at 50  $^{\circ}$ C at vacuum for 3 hours to obtain the CK-CMP film.

Detection of PA Vapor

The 300 mg of PA was placed in a vacuum glass vial (150 mL) for 1 week to obtain saturated vapour of PA, and the CK-CMP film on quartz plate was placed into a vacuum cuvette (4 mL). They were connected by the rubber tube with valve. When the valve is opened, the PA saturated vapor will pass into the quartz cuvette. In repeatability test, the CK-CMP film was vacuumed at 25  $^{\circ}$ C for 1 hour to remove the absorbed PA.

Physical characterization of CK-CMP

Fourier transform infrared (FT-IR) spectra of the samples was recorded using a Bruker Vector 22 spectrophotometer. Solid-state <sup>13</sup>CP/MAS NMR spectra was performed on a Bruker Advance II WB 400MHz NMR spectrometer. The Thermogravimetric Analysis (TGA) was performed in a nitrogen atmosphere using Seiko Extar 6000 TG/DTA equipment at the heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) was carried out on a Bruker D8 ADVANCE X-ray diffractometer with Cu-Ka radiation. The morphology and microstructure were observed on a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Gas adsorptiondesorption isotherms were tested on a ASAP 2020 HD88 instrument after the samples were degassesed under dynamic vacuum at 423 K for 12 hours. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and pore size distribution (PSD) was evaluated by non-local density functional theory (NLDFT). Photoluminescence spectra was were measured using a PerkinElmer LS55 Fluorescence Spectrometer. Fluorescence decay curves were measured with Edinburgh FLS920P spectrophotometer with double xenon lamp houses, one was with 450 W for steady state measurement and another was 60 W microsecond flash lamp for dynamic spectrum recording). Electrochemical behaviour was investigated by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell in a 0.1 M tetra-nbutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in nonaqueous acetonitrile at room temperature under nitrogen with a scanning rate of 50 mV/s. A platinum working electrode, a glassy carbon electrode, and an Ag/AgNO<sub>3</sub> (0.1 M) reference electrode was were used. The CV curves were calibrated using ferrocene/ferrocenium (Fc/Fc+) redox couple (4.8 eV below the vacuum level) as the internal standard. The formal potential of Fc/Fc+ was measured as 0.04 V against Ag/Ag+. Thus, the lowest unoccupied molecular orbital (LUMO) energy levels could be calculated according to: ELUMO =  $-e(E_{red} + 4.76 \text{ V})$ .

Results and discussion

Oxidative coupling of the carbazole-functionalized monomers with FeCl<sub>3</sub> resulted in the formation of the bulk polymer as a yellow fine powder in high yields. The method has-various advantages in building microporous polycarbazoles, such as using low-priced catalysts, under the mild reaction conditions and with high yields. In addition to this, the rigid fused rings of carbazoles also facilitates the formation of polymers with high porosity and good stability. It is well-known that pyrene itself is electrically neutral and so the electric properties of this polycarbazole depends on those of the carbazole based monomers through p-conjugation. The carbazoles is an electron-donating group, but and the pyrene moiety is considered as an acceptor. Therefore, electron-donating CMP containing carbazole units could attract the electronegative – NO<sub>2</sub> groups by means of coulombic interactions. In this work, we ehoose designed and synthesized 1,3,6,8-tetrakis(4-(9H-carbazol-9-yl)phenyl)pyrene to obtain this highly luminescent CK-CMP by FeCl<sub>3</sub>-induced oxidative polymerization due to its high lifetime and quantum yield of the pyrene core. (Scheme 1). CK-CMP is chemically stable, even in dilute solutions of acid and or base. Scheme 1 shows the chemical structure of the polycarbazole (CK-CMP).

Thermal analysis indicates that its thermal decomposition temperature is stable up to 500 °C under  $N_2$  atmosphere due to its cross-linking structures (Figure S1). Scanning electron microscopy images showed the similar amorphous aggregated morphologies of that CK-CMP (Figure S2) Powder X-ray diffraction (PXRD) pattern of CK-CMP did not show any diffraction signals, which further confirms the formation of a porous amorphous structure (Figure S3). Nitrogen adsorption measurement at 77 K over this activated sample shows a typical type I behavior, suggesting the presence of microporous structures in CK – CMP (Figure S4). The

structure of CK-CMP was further confirmed at the molecular level by <sup>13</sup>C CP/MAS NMR spectrum. The <sup>13</sup>C NMR spectrum for the obtained polymer with assignment of the resonances is shown in Figure 1. The high-intensity peak at 123 ppm is ascribed to the signal peak of substituted phenyl carbons. Signal peak at 137 ppm corresponds to the substituted phenyl carbons binding with nitrogen atom. The signal peak for unsubstituted phenyl carbons is located at 123 and 107 ppm, respectively. In addition, CK-CMP exhibited a rather broad absorption band in the range of 200 to 500 nm, indicating the formation of the highly conjugated polymer (Figure S4). The main peaks of CK-CMP are similar to those of the previously reported results<sup>[9]</sup>, which also confirms the formation of this polycarbazole.



Figure 1 Solid-state <sup>13</sup>C CP/MAS NMR spectrum of CK-CMP.

#### **Fluorescence Properties**

The photoluminescence spectra of solid monomer and CK-CMP are shown in Figure 1. Upon excitation at 380 nm, CK-CMP exhibited an emission band with the emission maximum at 513

nm, which was red-shifted by 6 nm from that of monomer. The CK-CMP suspension exhibited an emission band with the emission maximum at 535 nm, which was red-shifted by 22 nm from that of solid CK-CMP (Figure S6).

Since CK-CMP exhibited porous structure and intense fluorescence, we are very interested in its fluorescent chemosensing behaviour for nitro compounds. The luminescent responses of CK-CMP suspension to 0.2 mM nitro compounds such as 2,3-dimethyl-2,3-dinitrobutane (DMNB), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 4-nitrotoluene (4-NT), 3,4-dinitrotoluene (3,4-DNT), 2-nitrotoluene (2-NT) and picric acid (PA) were measured (Figure2). Interestingly, PA exhibited drastic quenching effect on the fluorescence of CK-CMP suspension with the quenching percentage (QP =  $(I_0-I)/I_0 \times 100\%$ ,  $I_0$  and I are luminescence intensities of CK-CMP suspension before and after exposure to the nitro compounds, respectively) of 89.3 % by monitoring emission peak at 535 nm. However, other nitro compounds had almost no effect on the emission. It shows that CK-CMP possesses the extremely high selectivity towards PA among the nitro compounds.



Figure 2 The fluorescence spectra of CK-CMP suspension without and with different nitro compounds (0.2 mM).



Figure 3 Change in fluorescence intensities at 535 nm of CK-CMP suspension with different nitro compounds (0.2 mM).

To investigate the quenching behaviour of PA for CK-CMP suspension, the concentrationdependent luminescence measurement for PA was carried out in the concentration range of 0.01 to 0.4 mM (Figure 4 and 5). It was found that the luminescent intensities of the CK-CMP suspension rapidly decreased with the addition of PA. Moreover, the Stern–Volmer (SV) equation,  $I_0/I = K_{sv}[Q]+1$  ( $K_{sv}$  is the quenching constant, and [Q] is the concentration of the quencher) was used for the analysis of concentration-dependent luminescence data. As shown in Figure 5, the  $I_0/I$  exhibited a good linear dependence relation ( $I_0/I = 0.121 + 9.9 \times 10^4$  ′ [PA], R<sup>2</sup> = 0.974) with the concentrations of PA in the range of 0 ~ 0.1 mM, with slope  $K_{sv}$  of SV curve of 9.9×10<sup>4</sup> M<sup>-1</sup>. As far as we know, this  $K_{sv}$  is among the highest values for the detection of PA (Table 1).<sup>9</sup>

Material	Quenching constant (M <sup>-1</sup> )	Ref.	
СК-СМР	9.9×10 <sup>4</sup>	This work	
$[Gd_2L_{1.5}(NMP)_2]n$	$4.48 \times 10^4$	9a	
$[Zn_8(ad)_4(BPDC)_6O{\cdot}2Me_2NH_2]$	$4.6 \times 10^4$	9b	
${[Tb(L_1)_{1.5}(H_2O)] \cdot 3H_2O}_n$	$7.47 \times 10^4$	9c	
UiO-68@NH <sub>2</sub>	$5.8 \times 10^4$	9d	
$[NH_2(CH_3)_2][Zn_4O(bpt)_2(bdc-$	$6.19 \times 10^4$	9e	
NH <sub>2</sub> ) <sub>0.5</sub> ]·5DMF	S		
$[Zn_2(NH_2BDC)_2(dpNDI)]_n$	$7.3 \times 10^4$	9f	
1000- 1000- 000- 000- 000- 000- 000- 00	0.01 mM 0.02 mM 0.03 mM 0.04 mM 0.05 mM 0.06 mM 0.07 mM 0.08 mM 0.09 mM 0.09 mM 0.1 mM 0.2 mM 0.3 mM 0.3 mM		
Wavelength(nm)			

**Table 1.** Comparison of sensing performances of materials towards PA

Figure 4 Concentration-dependent luminescence quenching of CK-CMP suspension after adding different concentrations of PA.



Figure 5 Stern-Volmer plot for fluorescence quenching of CK-CMP suspension by PA.

The quenching behaviour of PA for CK-CMP suspension was further studied by fluorescence lifetime (Figure S7). As illustrated in Table S1, CK-CMP suspension had a lifetime value of 1.89 ns, and the lifetimes showed little decrease (1.88 to 1.78 ns) with addition of PA (0.01 to 0.1 mM). The linear Stern–Volmer relationship and minimal change in lifetimes indicate that a static quenching process is dominant.

The high sensitivity of CK-CMP suspension towards PA prompted us to investigate its ability for sensing PA vapour, which were was conducted by exposing CK-CMP film on the quartz plate to saturated PA vapour at room temperature. The photoluminescence spectra showed that after exposure to saturated PA vapour, the fluorescence of CK-CMP film was significantly quenched with quenching percentage of 55% (Figure 6). When there is air in the saturated PA vapour, the result is the same.

The repeatability of detection of CK-CMP film for saturated PA vapour was also studied. As shown in Figure 7, CK-CMP film exhibited the same degree of fluorescence quenching percentages after each cycle, and the fluorescence intensity recovered to a similar level when the PA vapour was removed. Therefore, CK-CMP film maintained high sensitivity to saturated PA vapour after repeated cycles.



Figure 6 The fluorescence spectra of CK-CMP film in the absence and presence of PA vapor.

According to previous reports<sup>7b,9</sup>, the fluorescent quenching of CK-CMP on addition of PA may be attributed to the following factors: (a) resonance energy transfer and/or (b) photo-induced electron transfer between CK-CMP and PA. Firstly, we checked the possibility of resonance energy transfer. As shown in Figure 8, it is evident that partial overlap exists between the absorption spectrum of PA and the emission spectrum of CK-CMP. Thus, resonance energy transfer may contribute to fluorescence quenching. Secondly, the possibility of photo-induced electron transfer was also checked by comparison of molecular orbital energy levels of CK-CMP and PA. The LUMO energy level of CK-CMP was evaluated by the cyclic voltammogram curve

of the monomer, because the CK-CMP is insoluble in common organic solvents (Figure S8). The result shows that the LUMO energy level of the monomer to be -3.74 eV, which is much higher than HOMO energy level of PA (-4.88 eV)<sup>7b</sup>, indicating the possible electron transfer from the HOMO of CK-CMP to the LUMO of PA upon photoexcitation. Thus, the fluorescent quenching of CK-CMP by PA is the result of two synergistic mechanisms.



Figure 7 Cycling test of CK-CMP film upon exposure to PA vapor.



Figure 8 Absorption spectrum of PA and emission spectrum of CK-CMP in EtOH.

#### Conclusions

We have successfully synthesised a pyrene-cored conjugated microporous polycarbazole CK-CMP via FeCl<sub>3</sub>-induced oxidative self-condensation of 1,3,6,8-tetrakis(4-(9H-carbazol-9yl)phenyl)pyrene (L). Particularly, owing to the introduction of pyrene into this threedimensional structure, CK-CMP exhibits high luminescence in various polar solvents upon irradiation with UV light. In addition to this, CK-CMP has high thermal stabilities and also features selective and sensitive detection of PA over other nitro-explosives. Thus, explosives detection experiments of CK-CMP exhibits that pyrene based polycarbazoles are a candidate for the detection of nitroaromatic explosives.

#### ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the

ACS Publications website at DOI: xxxxxxxxx.

FT-IR, TGA, PXRD, SEM of CK-CMP, the fluorescence spectra and The fluorescence decay curves.

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#### Notes

The authors declare no competing financial interest.

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#### ABBREVIATIONS

CMPs, conjugated microporous polymers; MOFs, metal-organic frameworks; L, 1,3,6,8tetrakis(4-(9H-carbazol-9-yl)phenyl)pyrene; CK-CMP, Pyrene-cored Conjugated Microporous Polycarbazole

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#### Graphical Abstract and image

Xiao-Li Yang<sup>a</sup>, Dai-Yu Hu<sup>a</sup>, Qiang Chen<sup>c</sup>, Liang Li<sup>c</sup>, Pei-Xian Li<sup>b</sup>, Shi-Bin Ren<sup>\*b</sup>, Marcus Bertuzzo<sup>d</sup>, Kai Chen<sup>b</sup>, and Xin-Hui Zhou<sup>\*c</sup>

A Pyrene-cored Conjugated Microporous Polycarbazole for Sensitive and Selective Detection of Hazardous Explosives



#### Graphical Abstract and image

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Marcus Bertuzzo<sup>e</sup>, Kai Chen<sup>b</sup>, De - Man Han<sup>b</sup>, Xin - Hui Zhou\*<sup>c</sup>, and Xing - Hua Xia<sup>d</sup>

A Pyrene – cored Conjugated Microporous Polycarbazole for Sensitive and Selective Detection of Hazardous Explosives



#### Highlights

1. A highly luminescent conjugated microporous polycarbazole (CK-CMP) was by FeCl<sub>3</sub>induced oxidative polymerization

2. CK-CMP with small pore sizes exhibits good thermal stability and high luminescence .

3. CK-CMP can detect 2,4,6-trinitrophenol (PA) with good sensitivity and selectivity by fluorescence quenching.

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