

MOLECULAR CRYSTALS LIOUID CRYSTALS Guest Editors:

Taylor & Franci

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: https://www.tandfonline.com/loi/gmcl20

Synthesis of conjugated microporous polymerbased fluorescent "turn-off" sensor for selective detection of picric acid

Jeong Jun Lee & Taek Seung Lee

To cite this article: Jeong Jun Lee & Taek Seung Lee (2019) Synthesis of conjugated microporous polymer-based fluorescent "turn-off" sensor for selective detection of picric acid, Molecular Crystals and Liquid Crystals, 686:1, 1-8, DOI: 10.1080/15421406.2019.1645471

To link to this article: <u>https://doi.org/10.1080/15421406.2019.1645471</u>

Molecular Crystals and Liquid Crystals



Published online: 10 Oct 2019.



🖉 Submit your article to this journal 🕑





View related articles 🗹



🌔 View Crossmark data 🗹



Check for updates

Synthesis of conjugated microporous polymer-based fluorescent "turn-off" sensor for selective detection of picric acid

Jeong Jun Lee and Taek Seung Lee

Organic and Optoelectronic Materials Laboratory, Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 34134, Korea

ABSTRACT

Various structures of conjugated microporous polymers (CMPs) were synthesized via the Suzuki cross-coupling reaction to detect the explosive compound, picric acid (PA). One of the CMP, CMP-3 showed high fluorescence in the solid state because of the presence of repeat unit with aggregation-induced emission (AIE). Upon exposure to PA, the fluorescence of CMP-3 was noticeably quenched (190.10-fold) compared to other CMPs. The addition of other nitroaromatic compounds such as 2,4-dinitrotoluene (2,4-DNT) or 2,6-dinitrotoluene(2,6-DNT), which were similar in structure to PA, did not affect the fluorescence of CMP-3, indicative high selectivity of the sensing material.

KEYWORDS

conjugated microporous polymers; picric acid; fluorescence; sensors

1. Introduction

Since nitroaromatic explosives greatly affect security and environmental pollution, the need for immediate and selective detection techniques for nitroaromatic explosives have been received much attention in recent years [1,2]. One of the various nitroaromatic explosives, PA is being used in a variety of fields, including pharmaceuticals and dye-stuffs, as well as rocket fuel [3–5]. Because of the versatile use in various applications, PA is regarded as an environmental pollutant, and thus interest in detection of PA is increasing [6,7].

Most organic fluorescent molecules are highly luminescent in solution, while they are not fluorescent in the solid state because of π - π stacking-induced, aggregation-caused quenching (ACQ) [8,9]. In contrast to ACQ, a phenomenon of nonfluorescence in solution but strong fluorescence in the aggregated or solid state has been reported, which is called AIE [10,11]. Typically, tetraphenylethylene (TPE) has been well-known as for an AIE-active compound, and various investigations have been carried out to detect various substances using TPE moiety [12,13].

Herein, we synthesized CMPs using TPE with AIE property. CMPs are amorphous porous materials connected by long π -bonds. CMPs are used in various applications such as gas storage [14] and catalysis [15], because they have the advantage of easy control of their properties including pore sizes and fluorescence according to the structure design. The fluorescence of CMPs was not quenched even in the solid state because of the TPE.

It is expected that the introduction of the AIE functionality to the porous CMP substrate can provide more effective fluorescent-sensing abilities. The changes in fluorescence of the CMPs could be used as a sensing signal upon exposure to nitrobenzene derivatives.

2. Experimental

2.1. Materials and Instruments

All chemicals were purchased from Sigma-Aldrich (U.S.A.) and solvents were purchased from Samchun Chemicals (Korea). All reagents were used without further purification unless otherwise noted. ¹H NMR spectra were recorded on a Bruker Fourier-300 spectrometer at Korea Basic Science Institute. Solid phase ¹³C-NMR data were acquired on 400MHz Solid stat NMR spectrometer (AVANCE III HD) at the Korea Basic Science Institute. FT-IR spectra were obtained from a Bruker Tensor 27 spectrometer. UV-vis absorption spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Photoluminescence spectra were taken using a Varian Cary Eclipse spectrometer. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 instrument. The Brunauer-Emmett-Teller (BET) method was used to obtain the specific surface area of the sample (BELSORP-max).

2.2. Synthesis of 1,1,2,2-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)ethene (2)

Mixture of 1 (3 g, 4.63 mmol), potassium acetate (4.56 g, 46.50 mmol), bis(pinacolato)diboron (5.30 g, 20.4 mmol), and anhydrous dioxane (90 mL) was put into a three-necked flask and argon gas was bubbled for 30 min. [1,1'-Bis(diphenylphosphino)ferrocene] dichloropalladium (II) in dichloromethane (180 mg, 0.22 mmol) were added to the flask under argon. The mixture was charged with argon gas for 30 min and then stirred at 110 °C for 3 days. After cooling to room temperature, the reaction mixture was poured into cold water. The precipitate was isolated by filtration and dried in a vacuum oven. The residue was dissolved in chloroform and purified by column chromatography (eluent: chloroform: ethyl acetate = 1:1). The resulting white solid was washed with methanol and dried (yield 3.16 g, 82%). ¹H NMR (300 MHz, CDCl₃) 7.5 (8H, d), 7.0 (8H, d) ppm, 1.3 (24H, s) ppm. FT-IR (KBr pellet, cm⁻¹): 2981 (C-H), 1606 (C = C), 1359 (B-O).

2.3. General procedure for the synthesis of CMPs

Monomers, N,N-dimethylformamide (DMF), 2 M K₂CO₃ aqueous solution were three-necked flask and bubbled by charged in а argon for 30 min. Tetrakis(triphenylphosphine)palladium(0) was added and the flask was charged with argon gas for 30 min. The mixture was stirred at 120 °C for 48 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was isolated by filtration and then washed with water. Further purification was performed by Soxhlet extraction with THF for 2 days and the product was dried in a vacuum oven.

CMP-1: 1,2,4,5-Tetrabromobenzene (394 mg, 1 mmol), 1,4-benzene diboronic acid bis(pinacol)ester (660 mg, 2 mmol), tetrakis(triphenylphosphine)palladium(0) (28 mg, 0.024 mmol), DMF (60 mL), and 2M K_2CO_3 aqueous solution (10 mL) were used.



Figure 1. Synthesis of CMP-1, CMP-2, and CMP-3.

225 mg of gray powder was obtained. ¹³C NMR: 139.8 (m), 128.7 (m) ppm. Anal. Calcd for $(C_6H_4)_n$: C,94.70; H, 5.30%; Found C, 84.4; H, 4.5%. FT-IR (KBr pellet, cm⁻¹): 3026 (C-H), 1606 (C = C).

CMP-2: 1 (648 mg, 1 mmol), 1,4-benzene diboronic acid bis(pinacol)ester (660 mg, 2 mmol), tetrakis(triphenylphosphine)palladium(0) (28 mg, 0.024 mmol), DMF (60 mL), and 2M K₂CO₃ aqueous solution (10 mL) were used. 500 mg of yellow powder was obtained. ¹³C NMR: 138.4 (m), 129.5 (m), 125.2 (m) ppm. Anal. Calcd for $(C_{36}H_{24})_n$: C,94.97; H, 5.03%; Found C, 83.3; H, 4.8%. FT-IR (KBr pellet, cm⁻¹): 3026 (C-H), 1606 (C = C).

CMP-3: 1 (648 mg, 1 mmol), 2 (836 mg, 1 mmol), tetrakis(triphenylphosphine)palladium(0) (28 mg, 0.024 mmol), DMF (60 mL), and 2M K₂CO₃ aqueous solution (10 mL) were used. 225 mg of yellow powder was obtained. ¹³C NMR: 140.1 (m), 130.9 (m), 126.8 (m) ppm. Anal. Calcd for $(C_{26}H_{16})_n$: C,95.09; H, 4.91%; Found C, 80.4; H, 4.6%%. FT-IR (KBr pellet, cm⁻¹): 3026 (C-H), 1605 (C = C).

2.4. Detection of nitrobenzene derivatives

2,4-Dinitrotoluene (2,4-DNT), 2,6-Dinitrotoluene (2,6-DNT) and picric acid (PA) were dissolved in acetonitrile at various concentrations and exposed to CMP-1,



Figure 2. SEM images of (a) CMP-1, (b) CMP-2, and (c) CMP-3.

CMP-2, and CMP-3 (0.375 mg/mL) dispersed in acetonitrile. The changes in the fluorescence of CMPs were investigated after 5 min with fluorescence spectroscope. The Stern-Volmer constant (K_{sv}) was evaluated using the changes in the fluorescence intensity accoding to the concentration of the nitrobenzene compounds added.

3. Results and discussion

Monomers 1 and 2 were synthesized according to previous literature method [16] and the chemical structures were identified with FT-IR and ¹H NMR spectra. Various structures of TPE and phenylene derivatives were used to observe the effects



Figure 3. Excitation (empty) fluorescence (filled) spectra of CMP-1 (\square, \blacksquare), CMP-2 ($\bigcirc, ●$), and CMP-3 ($\triangle, \blacktriangle$). Excitation wavelength: 332 nm.



Figure 4. Photographs of CMP-1, CMP-2, and CMP-3 dispersions in ethanol (from left to right) (a) under ambient light; in the absence (b) and presence of PA (c) under UV light (365 nm) [PA] = 2.5 mM.

on the pore structure and fluorescence properties of CMPs (Figure 1). CMP-1, CMP-2, and CMP-3 were synthesized via the Suzuki coupling reaction, obtained as pale gray (CMP-1) and yellow powders (CMP-2 and 3), and were not soluble in common organic solvents such as chloroform, THF, acetone, and methanol, indicating the crosslinked, network structure. SEM was used to investigate the morphology of the CMPs (Figure 2). It was confirmed that CMP-1, CMP-2, and CMP-3 constituted aggregated structure of randomly-shaped beads. The average size of the beads was 120 nm for CMP-1, 414 nm for CMP-2, and 73 nm for CMP-3. The specific surface area was analyzed, obtaining the total pore volumes of CMP-1, CMP-2, and CMP-3 were 0.3855, 0.8612, and 0.8084 cm³g⁻¹ and the average pore diameter was 2.2508, 4.1704, and 4.8049 nm, respectively. The BET surface areas of CMP-1, CMP-2, and CMP-3 were found to be 825.99, 685.05, and 672.95 m²g⁻¹, respectively, indicating high specific surface areas.

CMP-1, CMP-2, and CMP-3 exhibited fluorescence at 441, 542, and 547 nm, respectively, when excited at 332 nm (Figure 3). The excitation spectra of CMPs showed that they had 332 nm absorption in common. CMP-2 and CMP-3 showed long wavelength absorption around 410 nm mainly because of the presence of TPE. Monomers 1 and 2 exhibited fluorescence at 481 and 476 nm, respectively, and the emission was not



Figure 5. Changes in the fluorescence of (a) CMP-1, (c) CMP-2, and (e) CMP-3 (0.375 mg/mL in MeCN) with various concentrations of PA. Arrow direction represents the PA concentration of 0, 1.56×10^{-4} , 3.13×10^{-4} , 6.25×10^{-4} , 1.25×10^{-3} , and 2.5×10^{-3} M. Exposure time 5 min. Excitation wavelength 332 nm. Stern-Volmer plots according to changes in the fluorescence of CMP-1 (b), CMP-2 (d), and CMP-3 (f). Inset plots in (b), (d) and (f) represent low PA concentration regions which had linearity with fluorescence. F₀ and F correspond to the fluorescence intensity of CMPs at 441 nm in the absence and presence of PA, respectively.

observed in the monomers containing benzene. However, CMP-1, an all-phenylene polymer, showed fluorescence in the visible region. CMP-2 and CMP-3 showed longer wavelength emission wavelength than that of monomers. These phenomena were

Table 1. Stern-Volmer Constants (M^{-1}) of CMPs

	CMP-1	CMP-2	CMP-3
PA	3880	8026	14890
2,4-DNT	289	583	891
2,6-DNT	228	228	1238



Figure 6. Changes in the fluorescence of CMP-1, CMP-2, and CMP-3. F_0 represent fluorescence intensity of CMPs in the absence of nitroaromatic compounds. $F_{2.5.}$ indicates the fluorescence intensity of CMPs in the presence of nitroaromatic compounds (2.5 mM). The wavelengths of $F_{2.5}$ is 478 nm for CMP-1 and 550 nm for CMP-2 and CMP-3.

probably because of extended conjugated length as a result of polymerization. Unlike CMP-1, which contained only phenylene units, the fluorescence wavelengths of CMP-2 and CMP-3 were similar, mainly because of the presence of TPE. The fluorescence of CMP-2 and CMP-3 was not quenched even in the aggregated forms, because of the AIE-active TPE, which would be useful in turn-off sensory material. The CMP-1, CMP-2 and CMP-3 were highly fluorescent so that the fluorescence was observed by the naked-eyes under UV irradiation (365 nm) (Figure 4a and b).

To elucidate the responsiveness of CMPs toward nitroaromatic compounds, various concentrations of nitrobenzene derivatives were exposed to CMPs dispersed in acetonitrile and changes in the fluorescence were observed. Three CMPs were effectively quenched by the presence of PA (Figure 5). CMP-1 showed emission shift from 441 to 478 nm as well as fluorescence quenching upon exposure to PA. CMP-2 and CMP-3 did not show emission shift but emission quenching. The decrease in the fluorescence of CMPs resulted from a photoinduced electron transfer. Because PA is electron-deficient, the excited electrons of CMPs were transferred to PA when the CMPs were exposed to PA. The degree of quenching (F_o/F) can be quantified using Stern-Volmer constant (K_{sv}):

$$F_0/F = 1 + K_{sv}[Q]$$

where F_0 and F are the fluorescence intensity at 441 nm before and after exposure to PA, respectively, K_{sv} is a Stern-Volmer quenching constant, and [Q] is the concentration of the quencher. Among CMPs, CMP-3 was effectively quenched by PA to have K_{sv} values of 14890 M^{-1} , in which K_{sv} values for 2,4-DNT and 2,6-DNT were much lower than PA (Table 1). Moreover, CMP-1 and CMP-2 were not comparable to CMP-3 in terms of K_{sv} values for nitroaromatic sensing. The K_{sv} was obtained using

linear plot in low PA concentration region. When 2.5 mM PA was added to the CMP-3 dispersion, the fluorescence of CMP-3 was reduced by 190-fold compared to the initial fluorescence. At the same conditions, fluorescence was decreased by 26-fold for CMP-1 and 42-fold for CMP-2 (Figure 6). The decrease in the fluorescence of CMP-3 by addition of PA can be visually detected by the naked-eyes (Figure 4c). When a nitrobenzene derivatives such as 2,4-DNT or 2,6-DNT was added at the same concentration, significant decrease in fluorescence could not be observed with the naked-eyes (data not shown here).

4. Conclusion

We synthesized porous, fluorescent CMPs via Suzuki polymerization to use for PA detection. CMPs were prepared using various structures of monomers, phenylene and TPE derivatives. It was found that all-TPE polymer, CMP-3 synthesized using only TPE monomers, showed the high Stern-Volmer constant for PA, mainly because of higher fluorescence compared to CMP-1 and CMP-2. In addition, the addition of 2,4-DNT and 2,6-DNT that had structure similarity to PA resulted in a relatively small decrease in fluorescence (3.19-fold, 4.07-fold, respectively), because of HOMO-LUMO band gap difference. Through this, we confirmed that CMP-3 could be used as a fluorescent sensor that can selectively detect PA.

Acknowledgment

Financial support from the National Research Foundation (NRF) of Korean government through Basic Science Research Program (2018R1A2A2A14022019) and Nuclear R&D Project (2016M2B2B1945085) is gratefully acknowledged.

References

- [1] Y. Salinas, R. Martínez-Máñez, M. D. Marcos, F. Sancenón, A. M. Costero, M. Parra and S. Gil, *Chem. Soc. Rev.*, **41**, 1261–1296, (2012).
- [2] R. C. Stringer, S. Gangopadhyay and S. A. Grant, Anal. Chem., 82, 4015-4019, (2010).
- [3] J. Wyman, M. Serve, D. Hobson, L. Lee and J. Uddin, J. Toxicol. Environ. Health, Part A, 37, 313, (1992).
- [4] V. Pimienta, R. Etchenique and T. Buhse, J. Phys. Chem. A, 105, 10037–10044, (2001).
- [5] C. Beyer, U. Böhme, C. Pietzsch and G. Roewer, J. Organomet. Chem., 654, 187-201, (2002).
- [6] A. Chowdhury and P. S. Mukherjee, J. Org. Chem., 80, 4064–4075, (2015).
- [7] W. Wei, R. Lu, S. Tang and X. Liu, J. Mater. Chem. A, 3, 4604-4611, (2015).
- [8] G. v. Bünau, Ber. Bunsenges. Phys. Chem., 74, 1294-1295, (1970).
- [9] T. H. Kim, G. Jang and T. S. Lee, Polym. Korea, 41, 641-647, (2017).
- [10] Y. Hong, Methods Appl. Fluoresc., 4, 022003, (2016).
- [11] Y. Hong, J. W. Lam and B. Z. Tang, Chem. Soc. Rev., 40, 5361-5388, (2011).
- [12] C. Park and J.-I. Hong, Tetrahedron Lett., 51, 1960–1962, (2010).
- [13] F. Sun, G. Zhang, D. Zhang, L. Xue and H. Jiang, Org. Lett., 13, 6378–6381, (2011).
- [14] B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath and W. Lin, Angew. Chem., 117, 74–77, (2005).
- [15] C.-D. Wu, A. Hu, L. Zhang and W. Lin, J. Am. Chem. Soc., 127, 8940-8941, (2005).
- [16] S. Dalapati, E. Jin, M. Addicoat, T. Heine and D. Jiang, J. Am. Chem. Soc., 138, 5797–5800, (2016).