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Tetraphenylethylene Tetracylhydrazine Macrocycle with Ability for Discrimination of *n*-Propanol from *i*-Propanol and Highly Sensitive/Selective Detection of Nitrobenzene

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Novel tetraphenylethylene tetracylhydrazine macrocycle with aggregation-induced emission effect was synthesized. Due to cyclization at ortho position of phenyl ring, two TPE units that composed the macrocycle were almost folded and offered a deep V-like cavity. By grinding, powder of the macrocycle could turn to emit yellow-green fluorescence from blue-green one. Interestingly, methanol, ethanol or *n*-propanol could make the ground powder that emitted yellow-green fluorescence become blue light emission while other conventional solvents including *i*-propanol did not cause this solvatochromism. Therefore, the macrocycle could give discrimination between *n*-propanol and *i*-propanol. Moreover, the fluorescence of suspension of the macrocycle in H₂O/THF mixed solvent was more easily quenched by nitrobenzene than other nitroaromatic compounds probably due to smaller size of nitrobenzene instead of more electron-deficiency. The detection limit for measurement of nitrobenzene was low to 3.99 ug/L, which had potential for usage in analysis of nitrobenzene in potable water sources. Moreover, a solid film of the macrocycle showed sensitive response to the nitrobenzene vapour low to 1.01 femtogram per mL of air.

Introduction

emission (AIE) phenomenon Aggregation-induced have optoelectronic in colossal potential materials and chemo/biosensors, and attracts more and more attentions.¹⁻⁸ As sensors, AIE molecules could easily be utilized to analyze nitroaromatic explosives in water and in air,⁹⁻¹¹ detect harmful gas,^{12–14} monitor toxic volatile organic compounds,¹⁵ and so on. But as sensors, AIE molecules have generally displayed low selectivity.¹⁻⁸ Furthermore, such as how to make difference between *n*-propanol and *i*-propanol using AIE sensor, no report is seen. Propanol is odor compound and some methods have been developed to analyze and discriminate its isomers.¹⁶⁻¹⁹ But these methods depend expensive instruments.

Nitroaromatic compounds are a class of important explosives and conventional pollutants. For needs of antiterrorism and environmental protection, the detection of the nitroaromatics both in water and in air is paid to intensive attention.^{9–11,20–27} A large number of research works using AIE compounds as sensors for detecting them have been reported. The detection principle for nitroaromatics is often to explore the electronattracting property of nitroaromatics, which leads to fluorescence quenching of AIE sensor that is electron-donating due to D-A electron interaction.^{9–11,20–27} Therefore, aromatics bearing more nitro groups such as 2,4,6-trinitrotoluene and

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2,4,6-trinitrophenol usually display the largest quenching effect. To selectively recognize other nitromatics bearing less nitro groups is difficult although the identification of certain aromatic compound is helpful for determining the source of it. Recently, it was reported that 2,4-dinitrophenol could be made out from a lot of nitroaromatics including trinitroaromatics.²⁵ However, the excellent research result like this for selective detection of nitroaromatics is still very rare.

Due to confined size and polarity of inherent cavity, organic macrocycles such as crown ether, cyclodextrine, and calixarene can selectively include guest molecules. Therefore, these macrocycles are usually exploited in materials separation, transfer, catalysis, sensing, and so on. Tetraphenylethylene (TPE) and its derivatives are the most studied and most easily modified AIE compounds. if TPE possesses inherent cavity that can include guest molecule, TPE will display excellent performance in supramolecular chemistry owing to the control of the dimension, topology, polarity and functionality of the cavity over the guest entrance. Moreover, with formation of cycle(s), the TPE fluorophore will have less conformation numbers and less intramolecular rotations. According to AIE mechanism of restriction of intermolecular motion (RIM),¹ this will strengthen the AIE effect of the TPE unit and improve the functionality and sensitivity of TPE fluorophore as solid emitters and sensors. In our group, some TPE macrocycles have been synthesized and showed excellent properties of molecular recognition.²⁵⁻²⁹ Here, we report that a novel TPE tetracylhydrazine macrocycles is prepared in up to 52% yield in cyclization step and exhibits excellent alcohol-chromism which even can be used to discriminate *n*-propanol from *i*-propanol in

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addition to highly sensitive and selective detection of nitrobenzene.

Results and Discussion

Synthesis and crystal structure of TPE tetracylhydrazine macrocycle 9

The tetracylhydrazine macrocycle 9 was synthesized according to the synthetic route shown in Scheme 1. By MucMurry dibromobenzophenone condensation of 1 and dihydroxybenzophenone 2 that are commercially available, dihydroxydibromo TPE 3 was obtained. Using 3 as starting material, dipentoxydibromo TPE 4 was prepared by etherification reaction. Treated by bis(pinacolato)diboron in the presence of Pd catalyst, dipentoxydibromo TPE 4 was transferred into dipentoxy TPE diborate ester 5, which could give dipentoxy TPE dibezoate 6 by Suzuki reaction. With dipentoxy TPE dibezoate in hand, both dipentoxy TPE dibezoic acid 7 and dipentoxy TPE dibezoylhydrazine 8 were obtained by reaction with hydrazine and hydrolysis reaction, respectively. Finally, TPE tetracylhydrazine macrocycle 9 was synthesized by condensation of the TPE acylhydrazine 8 and TPE benzoic acid 7 in 52% yield. Macrocycle 9 was very stable and no any change was found in more than two years at room temperature.











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Fig. 1. Crystal structure of 9. (A) Structure viewed from OB axis. (B) Structure viewed from near OC axis. (C) Stacking of two molecules of 9 from cavity to cavity. (D) 1D channel formed by stacking from cavity to cavity. (E) The channel structure in crystal. (F) Inclusion of ethanol molecule in the side of macrocycle 9. For clarity, solvents were omitted in A–E and hydrogen atoms were removed in A–B.

Fortunately, single crystal of 9 suitable for X-ray diffraction analysis was obtained by slow evaporating its solution in a mixed solvent of chloroform and ethanol.³⁰ The crystal structure of 9 confirmed that it was macrocyclic compound formed by condensation of one TPE carboxylic acid and one TPE acylhydrazine (Fig. 1A). Interestingly, the two TPE units were not in one plane but were folded into V-like structure due to acyl groups that connected at ortho-position of one phenyl ring (Fig. 1B). In the V-like structure, two of four benzoyl rings were almost cofacially parallel with a small dihedral angle of 13.7° but distance between them was 7.418 Å. As a result, the macrocycle possessed a deep V-like cavity with a smallest cross area of 6.4×5.4 Å and a depth of up to 13.7 Å. Because of long rigid tether bibenzene and short flexible linker acylhydrazine, the V-like cavity was rigid and avoided close π - π stacking that easily led to aggregation-caused quenching. In fact, only CH- π , CH-O interactions were found in crystal structure of 9.

Moreover, due to V-like cavity, one molecule of **9** was easy to insert by its small rim into bigger rim of another molecule and gave four CH- π interactions (2.878 Å and 2.898 Å, Fig. 1C). A large number of molecules stacked from cavity to cavity like this to form 1D channels with cross area of 6.4×5.4 Å in crystal (Fig. 1D–E), which had potential to load materials such as carbon dioxide.

It was also noted that one ethanol molecule was included into the side of the macrocyclic molecule by OH-O=C hydrogen bond (1.954 Å), OH- π interaction (2.810Å) and CH-HC van der Waals attractions of alkyl groups (2.188 Å) between ethanol and macrocycle (Fig. 1F). The inclusion of ethanol made the conjugation of benzoyl ring with TPE phenyl ring decrease, which shifted the emission of the macrocycle to shorter wavelength.

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Aggregation and photophysical properties of macrocycle 9



Fig. 2. (A) Change in the emission spectra of 9 in a mixed solvent of THF and H₂O with water fraction. Insets, curve of the fluorescent intensity at 488 nm vs water fraction. (B) TEM images of suspension of 9 in 95:5 H₂O/THF (V/V). $\lambda_{ex} = 386$ nm, ex/em slit widths = 1.5/3.0, [9] = 5.0×10⁻⁵ M.

While the solid of TPEtetracylhydrazine macrocycle 9 emitted strong green-yellow fluorescence, the solution of them in THF were emissionless. By adding non-solvent water into the solution until turbidity appeared, the solution started to emit fluorescence. As more water was added and the solution became more turbid, the fluorescence was stronger (Fig. 2A). Therefore, they were typical AIE compounds. In addition, as water increased, the emission maximum wavelength displayed slow bathochromic shift from 483 nm to 490 nm. The phenomena should be attributed to the amorphous precipitates that formed by addition of water. As more water was added, the precipitates produced faster, which would be easier to give amorphous aggregates. TEM images of suspension of 9 in 95:5 H₂O/THF disclosed that the aggregates were nanospheres with diameter of 50-100 nm (Fig. 2B), demonstrating the amorphous structure of the precipitates. Amorphous precipitates often emitted bathochromic fluorescence due to loosely stacking of molecules while crystal solid showed hypsochromic emission due to a little closer stacking between molecules.

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Fig. 3. Photos of solid powder of 9. (A) As-prepared powder under room daylight. (B) the ground powder under room daylight. (C) As-prepared powder under 365 nm light. (D) The ground powder under 365 nm light.

Thanks to the propeller-like structure, AIE compounds do not stack very closely in solid. Therefore, imposed by external force such as grinding, the stacking will become closer which will arouse the change of molecule conformation and conjugation. Therefore, mechnochromic effect is usually observed in AIE compounds.^{1,31-36} Here, macrocycle 9 also showed mechanochromism. Under daylight, both the as-prepared solid powder and the ground powder of 9 were yellow. But under radiation of 365 nm UV light, the as-prepared solid powder emitted green-blue light while the ground powder exhibited yellow-green fluorescence (Fig. 3). By grinding, the conjugation of TPE phenyl rings with double bond increased, which led to emission bathochromic effect. Meanwhile, due to more conjugation, the repulsive forces between phenyl ring also increased. Therefore, macrocycle 9 resided on a conformation having higher internal energy upon grinding.



Fig. 4. (A) Photos of ground powder of **9** when it was fummed with methanol and then dried up in air. (B) Photos of ground powder of **9** when it was fumed with n-propanol and i-propanol, and then ground again. (C)

Photos of solid powder of **9** dispersed in hexane (right) and in hexane with 2.5% ethanol (V/V) under 365 nm UV light.

In addition, the macrocycle also showed obvious solvatochromic effect.^{1,35-38} By wetted with methanol, the ground powder turned to blue emission. After air drying up, the powder was recovered to yellow-green fluorescence. This process could be repeated for many times (Fig. 4A). Wetted with ethanol or npropanol, the very obvious solvatochromic effect were also observed. Test by other conventional solvents, including *i*-propanol, n-butanol, i-butanol, t-butanol, THF, chloroform, dichloromethane, acetonitrile, acetone, benzene, ethyl ether, petroleum ether, ethylacetate, DMF, DMSO, and so on, no distinct solvatochromic effect was observed. These solvents except for ethyl ether and petroleum ether could dissolve the powder and quench the fluorescence. Ethyl ether and petroleum ether did not dissolve the powder, but they aroused no color change on the emission of the ground powder. Therefore, macrocycle 9 not only could be exploited to recognize methanol, ethanol and n-propanol among other many solvents, but also was even able to discriminate n-propanol from ipropanol (Fig. 4B). This selectivity is very rare in reported solvatochromic studies based on AIE molecules. The probable reason is that n-propanol has smaller steric hindrance than i-propanol and is easier to enter the cavity of macrocycl 9 by hydrogen bonding interactions between hydroxyl group and acylhydrazine ones, which reduces the conjugation of phenyl rings with double bonds and leads to hypsochromic emission just as shown in Fig. 1F. The fluorescent quantum yields of the suspension of 95:5 H₂O/THF, 85.5:4.5:10 H₂O/THF/MeOH, 85.5:4.5:10 H₂O/THF/EtOH, 85.5:4.5:10 H₂O/THF/n-PrOH, and 85.5:4.5:10 H₂O/THF/i-PrOH were measured using quinine sulfate as fluorescence standard, and showed to be 7.60%, 2.35%, 2.62%, 2.03%, and 2.70%, respectively, also demonstrating the effect of alcohols on the fluorescence of 9.

More outstandingly, 9 could be utilized to recognize ethanol from mixture of ethanol and other solvents. As shown in Fig. 4C, solid powder of 9 dispersed in hexane emitted blue-green light while that dispersed in in hexane with 2.5% ethanol showed blue light under 365 nm light. This funding had potential for analyzing ethanol in gasoline.

The powder X-ray diffraction (XRD) patterns of the solid of 9 were measured. As shown in Fig. 5, while the as-prepared solid displayed intensive and sharp diffraction peaks, the ground one decreased to very weak peaks and some of them even disappeared, hinting transformation from crystal state to amorphous one after the as-prepared solid was ground. In amorphous state, the molecule of macrocycle 9 had more conjugation of the double bond with phenyl rings, which resulted in bathochromic shift in emission colour. When the ground powder was wetted by ethanol, the diffraction became more strong and sharp a little, and even some new diffraction peaks appeared, suggesting that crystal state was recovered in some degrees and new crystal structure was formed due to interaction of the solid with ethanol. This result was in accordance with the single crystal structure in which ethanol molecule was bound (Fig. 1F). Both the wetted solid and the single crystals grown in chloroform and ethanol emitted blue light.

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Fig. 5. Powder XRD pattern of solid of the macrocycle 9 that was asprepared, ground and wetted by ethanol.Selective and sensitive detection of nitrobenzene

Due to bearing electron-rich aromatic rings of pentoxyphenyl groups, the macrocycle 9 could interact with electron-deficient nitroaromatic compounds (NACs). Common NACs, including 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenol (TNP), 1,3,5trinitrobenzene (TNB), 2,4-dinitrotoluene (DNT). 2.4dinitrophenol (DNP), 1,3-dinitrobenzene (DNB), 2.4dinitrobenzoic acid (DNBA), p-nitrotoluene (PNT), pnitrophenol (PNP), nitrobenzene (NB), were taken to test. As shown in Fig. 6, when these NACs were added into the suspension of 9 in 95:5 H₂O/THF, nitrobenzene could quench the fluorescence of the suspension by 62%, which was the largest value. Trinitroaromatic compounds such as TNP and TNB only caused 17% and 23% quenching, respectively, while TNT had no effect on the fluorescence. Other NACs showed less quenching effect. In addition, nitrobenzene led to hypsochromic shift of the emission maximum wavelength from 490 nm to 486 nm, indicating the interaction of nitrobenzene with macrocycle 9. In general, fluorescence probes based on AIE effect more sensitively respond to NACs bearing more nitro groups due to stronger D-A interactions.^{20-27,39-41} Here, rather than trinitro or dinitroaromatic compounds, but nitrobenzene displayed the largest quenching effect. Probably with less size, nitrobenzene could enter the cavity of 9 more easily than other NACs, which favored interaction with the macrocycle. Therefore, nitrobenzene exhibited the largest quenching effect although it only possessed one nitro group and was not more electron-deficient.



Fig. 6. The fluorescence spectra of suspension of 9 in 95:5 H₂O/THF after

NAC was added. [9] =1.0×10 5 M, [NAC] = 5.0×10 5 M, λ_{ex} = 368 nm, ex/em slit widths = 1.5/3.0.

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To obtain the sensitivity of 9 as probe for analysis of nitrobenzene, the smaller concentration of 9 (1.0×10^{-6} M, for being completely interacted by nitrobenzene as few as possible) in H₂O-THF mixed solvent with higher fraction of H₂O (99:1, for enhancing aggregation and emission) was used. As nitrobenzene was added into the suspension of 9 in 99:1 H₂O-THF, the fluorescence intensity was gradually decreased (Fig. 7A). Even 0.050 molar equivalents of nitrobenzene also aroused obvious emission abatement. Meanwhile, the emission maximum wavelength showed hypsochromic shift of about 5 nm when 100 molar equivalents of nitrobenzene was added. which confirmed the interaction of 9 with nitrobenzene. In the concentration range less than 1 molar equivalent of nitrobenzene, the relationship between fluorescence intensity and concentration of nitrobenzene was linear, which was fitted by Origin 7.5 software to be straight line with R = 0.994 and slope of 1.28×10^8 (Fig. 7B). The fluorescent intensity of 9 at 0.050 molar equivalents of nitrobenzene was measured for 9 times and the calculated standard deviation was 1.18. According to detection limit = $3 \times \sigma/k$ (σ , standard deviation; k, slope of the fitted straight line),⁴²⁻⁴³ the detection limit was $3 \times 1.18/1.28 \times 10^8 = 2.76 \times 10^{-8}$ M, corresponding to 3.39 ug/L. In current national recommended water quality criteria (2015) released by United States Environmental Protection Agency in its website, the nitrobenzene content in water consumed by human people is 10 ug/L. Therefore, the macrocycle could be utilized for analysis of nitrobenzene in potable water, which was difficult to get by many published methods. 44-49



Fig. 7. (A) Change in the fluorescence spectrum of suspension of **9** in 99:1 H_2O/THF with concentration of nitrobenzene, inset: curve of fluorescent intensity at 490 nm vs concentration of nitrobenzene from 0 to 1.0×10^{-4} M. (B) Fluorescent intensity at 490 nm changed with concentration of

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nitrobenzene from 0 to 1.0×10⁻⁶ M, the red straight line was fitting one by Origin 7.5. [9] = 1.0×10^{-6} M, λ_{ex} = 368 nm, ex/em slit widths = 5/5.

Furthermore, with film, as-prepared powder or ground one of 9 to test, their fluorescence also displayed sensitive response to vapour of nitrobenzene. The film was prepared by coating solution of 9 in THF onto surface of quartz slide and air up. As-prepared powder or ground one was prepared just by adhesive force themselves on the quartz slide. When the film was put into the saturated NB vapour, the fluorescence of the film was completely guenched in 1 minutes (Fig. 8A). As shown in Fig. 8B, when 20 mL of room air was slowly injected into the cell bottom in 1 minute, no fluorescence change was observed. But after 20 mL of air saturated with nitrobenzene vapour was injected in the same way, 75% fluorescence was quenched. As the nitrobenzene-saturating air was diluted with pure air, the quenching efficiency gradually decreased. Noticeably, even the nitrobenzene-saturating air was diluted with pure air for 1.0×10^6 times, 5.0% quenching efficiency was observed. This suggested that 1.01 femtogram of nitrobenzene per mL of air could be detected. Meanwhile, the emission wavelength appeared hypsochromic shift of about 14 nm from 484 nm to 470 nm, which was much larger than that in suspension and further demonstrated the interaction of 9 with nitrobenzene. More interestedly, after the film that was quenched by nitrobenzene vapour was put into room air, the fluorescence could be recovered to 95% of the original intensity in 5 minutes, indicating that the film could be repeatedly used for detection of nitrobenzene vapour.



Fig. 8. (A) Photos of film of 9 under 365 nm light in the absence and in the presence of NB vapour. (B) Change in the fluorescence spectrum of film of 9 with ratio of nitrobenzene-saturating air vs pure air. $\lambda_{ex} = 371$ nm, ex/em slit widths = 3/3.

Using ground powder for test, a similar result was obtained. While air had no effect on the fluorescence, the saturated nitrobenzene vapour quenched the fluorescence in 82.9% efficiency. Meanwhile, there was a large hypsochromic shift of 24 nm from 492 nm to 468 nm (Fig. S11). The higher quenching efficiency and larger shift should be ascribed to the finer powder and more unstable conformation of 9 after grinding. In the case of as-prepared powder of 9, the saturated nitrobenzene vapour led to 46.6% quenching efficiency and 8 nm hypsochromic shift from 476 nm to 468 nm (Fig. S12), which were less than that from both film and ground powder.

Conclusions

In conclusion, novel TPE tetracylhydrazine macrocycle, which possessed a deep V-like cavity and could stack into 1D channel structure in crystal state, was synthesized. The macrocycle exhibited mechanochromic and solvatochromic effect. By solvatochromism, the macrocycle could recognize methanol, ethanol and n-propanol among all other conventional solvents, especially having ability to discriminate *n*-propanol from *i*-propanol. Moreover, this novel TPE macrocycle displayed selective recognition of nitrobenzene among other NACs, and offered a very low detection limit of 3.39 ug/L for analysis of nitrobenzene, and its solid film could even detect nitrobenzene vapour low to femtogram per mL of air. This result demonstrated the potential for using macrocyclic AIE molecules to significantly enhance the selectivity and sensitivity of AIE probes.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgements

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Graphical Abstract



Novel tetraphenylethylene tetracylhydrazine macrocycle with aggregation-induced emission effect was synthesized. The Macrocycle could discriminate *n*-propanol from *i*-propanol and detect nitrobenzene in water at 3.99 ug/L. Moreover, a solid film of the macrocycle could sense nitrobenzene vapour at 1.01 femtogram per mL of air.