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The 4-amino-1,8-naphthalimide Tröger’s base functionalised triazine covalent organic polymer TB-TZ-COP was synthesised and employed as a “turn-on” fluorescent and a colorimetric sensor for the discriminative sensing of volatile organic compounds; the TB-TZ-COP displaying the largest fluorescence enhancement and high sensitivity for 1,4-dioxane, a harmful environmental pollutant classified as a Group 2B carcinogen.

Discovery of suitable chemosensors for the fast and selective sensing of hazardous substances and organic pollutants has attracted increasing attention in recent years to mitigate environmental pollutions.1,2 Among the various known pollutants, the volatile organic compounds (VOCs) have become a major source of environmental contaminants due to their mass use in manufacturing industries, as well as in scientific research laboratories.3 The continuous exposure to VOCs is toxic to human health, causing a wide range of serious infinctions and chronic diseases like asthma, kidney failure, neurological damage, cystic fibrosis, and cancer.4-5 Therefore, the design and the development of suitable chemical sensors for VOCs is highly desirable for the betterment of human health and to get rid of environmental pollution.6 Several sophisticated instrumental techniques are currently available for VOCs detection and analysis, including gas-chromatography, high-performance liquid chromatography, ion chromatography, and mass spectrometry.3,4,6-7 Despite the high selectivity, the real-time use of these traditional techniques is limited due to their expensive apparatuses, lack of portability, time-consuming detection process, and complicated instrument standardization.6-7 Recently, fluorescence quenching/enhancement-based sensing has become an effective and alternative detection method to the above, owing to its simplicity, high sensitivity, easy visualization and short response time;1,2,8-9 where the initial emission intensity of the fluorophore is perturbed, in one way or the other, by the presence of analytes.10 A wide variety of fluorescent sensors have been developed and used for the detection of VOCs through fluorescence quenching based mechanism; however, background interference has been known to limits their practical use.11 Furthermore, their real-life application has also been restricted due to low sensitivity, non-reusability and lack of specificity among VOCs.12 Hence, there currently exists a need for developing alternative analytical/sensing methods for VOCs. In general, the use of ‘turn-on’ (also known as ‘switch-on’) fluorescence sensing is particularly appealing because the sensing event can be easily detected, sometimes, even by the naked eye.13 However, unlike ‘turn-off’ sensing, which can simply operate via static or dynamic quenching mechanisms, the design of turn-on fluorescence sensing, is more challenging.14 We thus considered if the use of solvatochromic fluorescent sensing, might be a simple and an effective alternative and an effective approach for the discriminative sensing of VOCs.15-16 With this in mind, we set out to develop an efficient fluorescent sensor suitable for selective and discriminative sensing of structurally related-VOCs, based on amino-1,8-naphthalimide Tröger’s bases (TBNaps).

Over the past few years, we are interested in developing novel luminescent structures and materials of 3- and 4-amino-TBNaps motifs for their application in supramolecular material and medicinal chemistry.17 TBNaps are fascinating chiral cleft-shaped supramolecular scaffolds (with ca. 90° angle between the two Nap structures) that are strongly colored and fluorescent due to their internal charge-transfer (ICT) excited state transition; which are solvent polarity dependent.2,17 Furthermore, TBNaps display significant Strokes shifts in different solvents and thus they can be used as a potential...
luminescent sensor for the discriminative sensing of structurally similar VOCs of varied polarity. Here we report the synthesis and fluorescence sensing properties of a new TBNap functionalized triazine covalent organic polymer, TB-TZ-COP, Scheme 1. We foreshow that the polyimide part of TB-TZ-COP would structurally facilitate the solvent polarity dependent emission properties, and thus TB-TZ-COP could act as a potential fluorescence sensor for the discriminative sensing of volatile organic pollutants.\(^2\)\(^9\)

The polyimide TB-TZ-COP was synthesized using a one-step metal-free polycondensation reaction, Scheme 1, between triazine-based triamine (TAPT, 2.0 eq.) and the 4-amino-1,8-naphthalic anhydride derived Tröger’s base (TBNap, 3.0 eq.) in a mixture of toluene and m-cresol as a reaction medium and isoquinoline as a catalyst under a stepwise increase of the reaction temperature (for details see ESI).\(^8\)\(^9\) The TB-TZ-COP polymer was isolated as a bright yellow solid and was found to be insoluble in common organic solvents. The successful formation of TB-TZ-COP was fully characterized at the molecular level by using CP/MAS \(^{13}\)C-NMR and FT-IR spectroscopy. The solid-state \(^{13}\)C-NMR spectrum of TB-TZ-COP showed the expected characteristic carbonyl carbon resonances at 164 ppm, which is slightly down-field shifted (~2 ppm) compared to the TBNap monomer due to the imide ring formation (Fig. 1).\(^9\)\(^2\)\(^0\) The signal corresponding to the triazine unit was clearly observed at 171 ppm, while the two \(^{13}\)C resonances of Tröger’s base linkage were located at 67 and 57 ppm.\(^2\)\(^0\) The chemical shifts corresponding to the other aromatic carbons were observed as a hampered overlapping signal in the range of 118 to 150 ppm (Fig. 1). In the FT-IR spectrum, the appearance of a new broad band at 1353 cm\(^{-1}\) corresponding to the stretching vibration of C-N-C linkage of the imide ring and the complete disappearance of NH\(_2\) stretching vibrations around 3314 cm\(^{-1}\) of TAPT monomer confirms the successful formation of polyimide network in the isolated material (ESI).\(^2\)\(^1\)

The characteristics carbonyl symmetric and asymmetric stretching vibrations of six-membered imide ring were observed at 1707 cm\(^{-1}\) and 1666 cm\(^{-1}\), respectively. The FT-IR spectra also showed several intense bands at 1240 cm\(^{-1}\) and 1503 cm\(^{-1}\) accounting for C-N and N-C-N stretching, respectively which confirms the successful incorporation of Tröger’s base and triazine functional groups into the isolated material (ESI). The elemental analysis of TB-TZ-COP indicated that the calculated elemental composition is consistent with the experimentally measured values. The thermogravimetric analysis (TGA) under N\(_2\) atmosphere showed an initial weight loss of ~4% at low temperature due to the loss of trapped solvent molecules and the desolvated TB-TZ-COP was stable up to 410°C, indicating its high thermal stability (ESI). The powder X-ray diffraction (PXRD) measurement shows that TB-TZ-COP was amorphous in nature (ESI). The morphology of TB-TZ-COP, as observed by FESEM, is composed of particles with a rough surface and in a disorganized pattern (Scheme 1 and ESI). The surface area and porosity of TB-TZ-COP were verified by N\(_2\) adsorption isotherm. The N\(_2\) uptake measurement at 77 K of activated TB-TZ-COP displayed steep and reversible adsorption of 139 cm\(^3\) g\(^{-1}\) at 1 bar (ESI), The Brunauer-Emmett-Teller (BET) surface was calculated to be 198 m\(^2\) g\(^{-1}\). The DFT pore size distribution confirms the presence of microporosity. Notably, the uptake capacity of TB-TZ-COP for CO\(_2\) was moderate while the uptake capacity for H\(_2\) was almost negligible (ESI). The presence of high surface area and micropores suggests that TB-TZ-COP can, in addition to the surface interactions, efficiently adsorb the analytes inside the voids space and thus it can show superior sensing capability.\(^2\)

Having successfully synthesized and characterized TB-TZ-COP, we next looked into the fluorescence sensing characteristics of TB-TZ-COP towards VOCs. These experiments were performed by dispersing TB-TZ-COP in various common organic solvents with varying polarities, such as toluene, CH\(_2\)Cl\(_2\), THF, acetone, CH\(_3\)OH, CH\(_2\)CH\(_2\)OH, CH\(_3\)CN, diethyl ether, glycol, 1,4-dioxane, DMF, DMSO and then measured the fluorescence emission intensity of TB-TZ-COP in these solvents. As expected, the suspension of TB-TZ-COP displayed different fluorescent emission characteristics in these solvents and thus discriminative sensing ability for the rapid detection of VOCs. Notably, the suspension of TB-TZ-COP in 1,4-dioxane displayed...
a dramatic enhancement in the fluorescence intensity in comparison to other organic solvents tested for. Furthermore, the discriminative sensing ability of TB-TZ-COP was found to be highly sensitive and reversible.

The emission intensity in H$_2$O was used as a reference to determine the relative number-fold emission enhancement of TB-TZ-COP in different organic solvents. The fluorescent study results implied that TB-TZ-COP was capable of discriminatively sense VOCs through a change in the TBNap fluorescence intensity, either via luminescent quenching or through luminescent enhancement. As alluded to above, then among different VOCs, the largest emission enhancement of 44% was observed at 502 nm for 1,4-dioxane, while THF, showed a moderate fluorescence enhancement (~16%) upon exciting at 360 nm. In high polar solvents such as DMF and DMSO, TB-TZ-COP displayed an average emission enhancement, which was significantly red-shifted to around 534 nm with a large Stokes shift; this shift is accompanied by TBNap spectral broadening. This can be accounted for because the excited state of the TBNap fluorophore is more stabilized in highly polar solvents and as a precursor in various manufacturing industries. However, the emission intensity in glycol increased significantly, which would facilitate the energy transfer that gives rise to the fluorescence emission. This can be accounted for because the excited state of the TBNap fluorophore is more stabilized in highly polar solvents and as a precursor in various manufacturing industries. However, the emission intensity in glycol increased significantly, which would facilitate the energy transfer that gives rise to the fluorescence emission.

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Fig. 4 (A) The reaction scheme for the condensation of glycol to 1,4-dioxane. (C) Emission spectra of TB-TZ-COP in glycol/1,4-dioxane mixture with different volume ratios of 1,4-dioxane and (B) corresponding photographs taken under UV light illumination ($\lambda_{ex}$ = 365 nm).
After exposure to dioxane vapours.

![Fig. 5](image)

Fig. 5. (A) Change in emission intensity of TB-TZ-COP upon addition of dioxane (µL) in glycol. (B) Recycling test in glycol and in dioxane. (C) Emission spectra of thin film of TB-TZ-COP before and after exposure to dioxane vapors.

To meet the practical application of the TB-TZ-COP polymer as a reversible fluorescence sensor, we next verified the reproducibility of the sensing process of TB-TZ-COP towards 1,4-dioxane. The emission intensity of TB-TZ-COP in both glycol and 1,4-dioxane was first recorded, and after each measurement, the polymer was isolated by centrifugation and subsequently reused in the next emission study (cycle). As shown in Fig. 5B, the emission intensity of TB-TZ-COP in glycol (cyan bar) and 1,4-dioxane (violet bar), was retained even after five cycles of repetitions. This study demonstrates the excellent reproducibility, the recyclability sensing and the high photo-stability of TB-TZ-COP over several sensing cycles. To further explore the vapor phase sensing propensity of TB-TZ-COP, the emission intensity of a freshly made thin film of TB-TZ-COP exposed to the saturated vapours of 1,4-dioxane was monitored as a function of exposure time. As can be seen in Fig. 5C, the initial emission intensity of TB-TZ-COP at 537 nm increased dramatically upon exposing the film to the saturated vapours of 1,4-dioxane at room temperature, indicating the strong binding interactions between analytes and polymer. For instance, the emission was enhanced by 17% after just 30 minutes of exposure time; reaching 33% within 120 minutes, as demonstrated in Fig. 5D. Furthermore, a noticeable visual colour change was observed upon exposing the film to 1,4-dioxane vapours, as presented as an inset in Fig. 5D, demonstrating the potential application of TB-TZ-COP as a naked eye sensor for both solution and vapor phase detection of VOCs.

In summary, we have synthesized a new TBNaP functionalized triazine covalent organic polymer, TB-TZ-COP, and demonstrated its application in the discriminative fluorescence sensing of VOCs. Notably, the ability of TB-TZ-COP to distinguish between structurally and chemically close related VOCs, such as glycol and 1,4-dioxane, was demonstrated. Such a system is highly attractive, the sensing being achieved in both solution and in the vapor phase using thin films using either colorimetric or fluorescent sensing. We are currently exploring the properties of such sensors in greater detail.

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**

Graphical Abstract

“Turn-on” fluorescence sensing of volatile organic compounds using a 4-amino-1,8-naphthalimide Tröger’s base functionalised triazine organic polymer

Sankarasekaran Shanmugaraju,* Deivasigamani Umadevi, Luis M. González-Barcia, Jason M. Delente, Kevin Byrne, Wolfgang Schmitt, Graeme W. Watson, and Thorfinnur Gunlaugsson*

The 4-amino-1,8-naphthalimide Tröger’s base functionalized triazine covalent organic polymer was synthesised and employed as a “turn-on” fluorescent sensor for the discriminative sensing of volatile organic compounds (VOCs).