

COMMUNICATION

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Cite this: *Polym. Chem.*, 2023, **14**, 4153

Received 22nd July 2023,
Accepted 2nd September 2023

DOI: 10.1039/d3py00857f

rsc.li/polymers

Tröger's base-containing fluorenone organic polymer for discriminative fluorescence sensing of sulfamethazine antibiotic at ppb level in the water medium†

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A new Tröger's base containing fluorenone organic polymer (TB-FL-COP) was synthesized and used as a fluorescence sensor for discriminative sensing of antibiotics in water. TB-FL-COP showed the highest fluorescence quenching, reversible sensing responses, and excellent sensitivity of 56 ppb level for sulfamethazine antibiotics. The Stern–Volmer quenching constant (K_{SV}) was calculated to be $1.2 \times 10^6 \text{ M}^{-1}$. The fluorescence sensing ability was also reflected by sharp visual color changes and further demonstrated in real water samples.

Introduction

Since their discovery in the early 20th century, antibiotics have been widely used to treat various bacterial infections in humans and animals.^{1,2} The excess use and improper disposal have made antibiotics an emerging organic contaminant and hazardous environmental pollutant.³ The large accumulation of antibiotics in waterbodies is a serious threat to human health and the ecosystem due to their wide dispersal, complex composition, and slow degradation.⁴ Sulfonamides are a class of synthetic antibiotics with exceptional characteristics such as low-cost synthesis, good water solubility, rapid adsorption, and ease of transport.^{5,6} Given their broad-spectrum activity and efficacy as a growth promoter, sulfonamide antibiotics are used in veterinary and animal husbandry.⁷ Sulfamethazine (SMZ, 4-amino-*N*-(4,6-dimethyl-2-pyrimidinyl) benzene sulfonamide, is an essential antibiotic frequently used to treat and prevent antimicrobial and various protozoan infections.⁸ SMZ is effective against chronic as well as acute bacterial infections in food-producing animals (cows, chickens, pigs, and so on).⁹

It is also used against Gram-positive and Gram-negative bacteria.¹⁰ The antibacterial property of SMZ emanates from their inhibition of *p*-aminobenzoic acid conversion, which interrupts folic acid synthesis and hence, restricts DNA replication.¹¹ Despite its effective bacteriostatic property, SMZ antibiotics do not completely metabolize in the living system.¹² Therefore, a large amount of SMZ antibiotic is excreted through urine or faeces and they can smoothly enter into the food chain through aquatic organisms and crops.¹³ Besides, the excess antibiotic-based treatments applied to livestock led to the presence of antibiotic residues in the slaughtered meat and other animal products that are consumed by humans. This could eventually lead to the development of drug resistance in the intestinal bacterial population.¹⁴ Furthermore, SMZ can cause severe allergic reactions as well as thyroid tumors in humans.¹⁵ In response to these hazardous problems, various countries and international institutions have established regulations to control SMZ. The allowed limit of sulfonamide antibiotics in animal-origin foodstuffs is 100 ng g^{−1} by the European Union and China.¹⁶ All these data alert the urgent need for an efficient sensing method for the trace detection of SMZ antibiotics.

Several instrumental techniques including Raman spectroscopy, capillary electrophoresis, and ion mobility spectrometry are currently used for the detection of antibiotics.^{17,18} However, massive instrumentation setup, high-maintenance cost and tedious instrument calibration, and required trained technician impair their practical utilization.¹⁹ On the other hand, fluorescence-based sensing has become an attractive method for trace analysis of antibiotics because of its high sensitivity, fast response time, and easy operational procedure.^{20,21} Given this, in recent years, a wide variety of fluorescence sensors such as luminescent metal-organic frameworks, fluorescent organic polymers, and small-molecule fluorescent sensors have been developed and employed for the detection of different kinds of antibiotics.^{1,22,23} Among the various fluorescence sensors known, luminescent covalent organic polymers (COPs) have become a popular sensor system

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†Electronic supplementary information (ESI) available: Solid-state CP-MAS ¹³C-NMR, thermogravimetric analysis, powder X-ray diffraction pattern, gas adsorption isotherm and fluorescence studies. See DOI: <https://doi.org/10.1039/d3py00857f>

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where I_0 is the initial emission intensity of **TB-FL-COP** in water and I is the intensity after the addition of antibiotics.

The relative changes (I_0/I) in emission intensity upon increasing the concentration $[Q]$ of antibiotics was demonstrated by the following Stern–Volmer equation:

$$I_0/I = K_{SV}[Q] + 1$$

The Stern–Volmer quenching constant (K_{SV}) was determined from the slope of the linear curve.

The limit of detection was calculated using the following equation:

$$\text{Limit of detection (LoD)} = 3\sigma/K$$

where σ is the standard deviation and K is the slope of the linear plot.

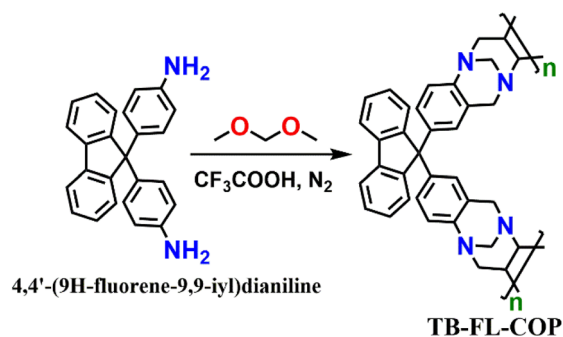
Results and discussion

Synthesis and characterization of TB-FL-COP

As shown in Scheme 1, Tröger's base-containing fluorenone organic polymer **TB-FL-COP** was synthesized by a simple acid-catalyzed one-pot cyclization reaction using the aromatic diamine, 4,4'-(9H-fluorene-9,9-diyl)dianiline, and dimethoxymethane in TFA under N_2 atmosphere at room temperature. The expected Tröger's base polymer **TB-FL-COP** was isolated as an off-white powder in 40% yield and found to be insoluble in most of the common organic solvents.²⁷

The chemical structure of **TB-FL-COP** was characterized by FT-IR and solid-state cross-polarization magic-angle spinning (CP/MAS) ^{13}C NMR. In the FT-IR spectrum of **TB-FL-COP**, a new stretching band appeared at 1273 cm^{-1} corresponding to the C–N stretching vibrations of Tröger's base unit. Upon polymer formation, the intense broadband observed at 3348 cm^{-1} corresponding to the N–H stretching frequency of NH_2 groups of monomers nearly disappeared (Fig. 1A). In the CP-MAS ^{13}C -NMR spectrum, two peaks appeared at $\delta = 34.00$ and 32.98 ppm corresponding to the C atoms of Tröger's base unit. These results strongly support the presence of Tröger's base moiety in the isolated **TB-FL-COP** polymer.

Thermogravimetric analysis (TGA) of **TB-FL-COP** under an N_2 atmosphere revealed that the as-synthesized polymer was



Scheme 1 The synthesis of polymer **TB-FL-COP**.

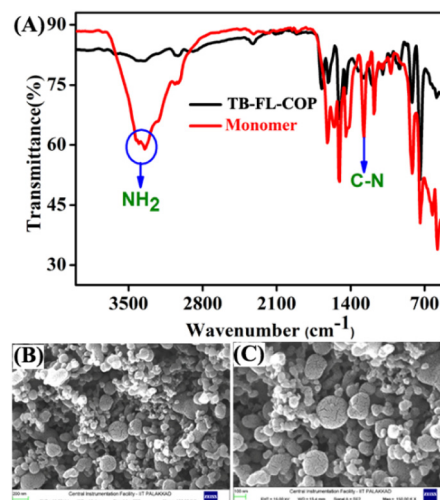


Fig. 1 (A) The FT-IR spectrum of polymer **TB-FL-COP** and monomer. The FESEM images of **TB-FL-COP** were imaged at (B) 100 and (C) 200 nm resolutions.

stable up to $400\text{ }^{\circ}C$ indicating its high thermal stability (Fig. S1, ESI†). The powder X-ray diffraction pattern of **TB-FL-COP** displayed a broad band with no obvious peaks which confirms the amorphous nature of **TB-FL-COP** (Fig. S2, ESI†). The amorphous form of **TB-FL-COP** facilitates its solution processability for sensing applications. The field-emission scanning electron microscopy (FESEM) imaging of **TB-FL-COP** showed that the polymer particles were aggregated to form a morphology of non-homogeneous sphere-shaped units on the solid surface (see Fig. 1B and C). The surface property of **TB-FL-COP** was evaluated using physisorption studies. Adsorption isotherm of N_2 intake was recorded at 77 K , which revealed that the **TB-FL-COP** has an average pore radius of 2.79 \AA , and a pore volume of 0.571 cc g^{-1} (Fig. S3, ESI†). The Brunauer–Emmett–Teller (BET) surface area of the polymer was calculated to be $41\text{ m}^2\text{ g}^{-1}$ and hence, **TB-FL-COP** can be a potential molecular adsorbent for guest encapsulation.

Fluorescence sensing of antibiotics

Having successfully synthesized and characterized, we then explored the fluorescence sensing properties of **TB-FL-COP** towards various antibiotics such as furazolidone (FZD), nitrofurazone (NFZ), chloramphenicol (CRP), nitrofurantoin (NFT), dimetridazole (DMZ), sulfamethazine (SMZ), and sulfadiazine (SDZ). Considering the practical use of polymer, all fluorescence sensing studies were performed in a water medium. The stock solution of **TB-FL-COP** was prepared by dispersing 2 mg in 10 mL of deionized water and $1.0 \times 10^{-3}\text{ M}$ stock solution of different antibiotics in deionized water was also prepared. To establish the sensing selectivity of **TB-FL-COP**, we first performed fluorescence titration studies using various antibiotics. The changes in fluorescence emission intensity of **TB-FL-COP** were measured before and after the addition of different antibiotics.



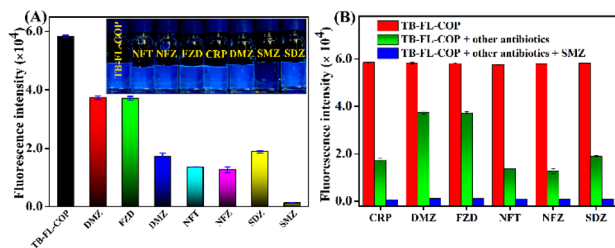


Fig. 2 (A) The extent of fluorescence quenching observed for TB-FL-COP after the addition of different antibiotics (Inset: observed visual color changes). (B) The relative changes in emission intensity of TB-FL-COP in the presence of various antibiotics along with or without SMZ antibiotics in the aqueous medium.

As shown in Fig. 2A, TB-FL-COP exhibited differential fluorescence quenching responses for different antibiotics. Among various antibiotics, SMZ antibiotics displayed the highest fluorescence quenching while other antibiotics such as FZD, CRP, NFT, DMZ, and SDZ showed moderate to poor fluorescence quenching responses. The high selectivity of TB-FL-COP for SMZ antibiotic was also reflected by a sharp visual color change (see Fig. 2A inset). The bright blue emission of TB-FL-COP become almost colorless upon the addition of SMZ while other antibiotics did not show any observable color changes. To further confirm the high selectivity of TB-FL-COP towards SMZ, competitive fluorescence titration studies were performed using SMZ in the presence of other competing antibiotics. As shown in Fig. 2B, the initial emission intensity of TB-FL-COP (red bar) was moderately quenched (green bar) upon the addition of various other antibiotics, however, the subsequent addition of SMZ antibiotic to the previous solution caused a strong fluorescence quenching (blue bar). These results demonstrate the preferential binding affinity and discriminative sensing propensity of TB-FL-COP towards SMZ even in the presence of other competing antibiotics.

To further probe the fluorescence sensing propensity of TB-FL-COP towards SMZ, a fluorescence titration study was carried out. The initial strong fluorescence emission at $\lambda = 526$ nm observed for TB-FL-COP was decreased in intensity upon the gradual increase in the concentration of SMZ (see Fig. 3A). From the fluorescence titration profile, a non-linear Stern-Volmer plot was obtained which indicates a complex fluorescence quenching mechanism involves in the overall quenching processes. The Stern-Volmer quenching constant $K_{SV} = 1.2 \times 10^6 \text{ M}^{-1}$ was determined from the slope of a linear plot obtained at a low concentration of SMZ. The relatively high K_{SV} value indicates a strong binding affinity of TB-FL-COP for SMZ antibiotics. The calculated K_{SV} value is comparable to other reported polymer-based fluorescence sensors for antibiotics.^{38,39} Similar fluorescence titration studies in a PBS buffer medium using TB-FL-COP displayed a strong fluorescence quenching in the presence of SMZ and thus TB-FL-COP is a practically more useful sensor for SMZ detection (Fig. S4, ESI†). Likewise, under identical spectroscopic conditions, fluorescence titration was carried out using other

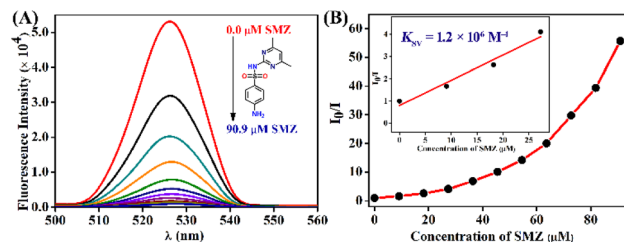


Fig. 3 (A) The observed changes in fluorescence emission intensity of TB-FL-COP at different concentrations of SMZ antibiotics and (B) corresponding Stern-Volmer plot (Inset: Stern-Volmer plot at low concentration of SMZ).

antibiotics. It was observed that the extent of fluorescence quenching was different for different antibiotics and from the titration profile, the fluorescence quenching constant was calculated to be in the order of $K_{SV} = 10^3$ – 10^4 M^{-1} , these values are lower than the quenching constant calculated for SMZ (see Table S1 in ESI†).

Furthermore, the UV-visible absorption titration study and time-dependent fluorescence lifetime measurement were carried out to probe the plausible mechanism for the observed fluorescence quenching. As shown in Fig. S5 (in ESI†), the initial absorption intensity of TB-FL-COP increases with increasing the concentration of SMZ (0.0 to $90.9 \times 10^{-6} \text{ M}$), which indicates that TB-FL-COP binds with SMZ in the ground-state. This was further supported by the time-dependent lifetime measurement. The lifetime of TB-FL-COP ($\tau = 0.1$ ns) remained almost unchanged after the addition of SMZ antibiotics ($90.9 \times 10^{-6} \text{ M}$), except for a slight increase to 0.15 ns (Fig. S6 in ESI†). All these results including sharp visual color changes of TB-FL-COP after the addition of SMZ (Fig. 2A inset) and obtained linear Stern-Volmer plot at low concentration (Fig. 3B inset) indicate that TB-FL-COP forms a donor-acceptor type of charge-transfer (CT) complex with SMZ in the ground state at low concentration, which resulted in strong fluorescence quenching *via* the static quenching mechanism. However, a non-linear plot at a high concentration of SMZ indicates that fluorescence quenching is due to both static and dynamic quenching mechanisms (Fig. 3B).

The highest fluorescence quenching of TB-FL-COP for SMZ antibiotic was further validated by computational modeling using Density Functional Theory (DFT) calculations. All computational analyses were performed at the B3LYP/6-311++G(d,p) level of theory using the Gaussian 16 program.⁴⁰ The frontier molecular orbitals (HOMO and LUMO) energies for various antibiotics were calculated and compared with the HOMO and LUMO energy values of the TB-FL-COP model system. The LUMO energy value for antibiotics was found to be lower in energy than TB-FL-COP and thus, they can readily form a donor-acceptor type of charge transfer complex sensor and subsequently result in fluorescence quenching (see Table S2 in ESI†). The observed difference in the extent of fluorescence for different antibiotics is presumably due to the difference in the extent of energy transfer between the sensor and analyte. The



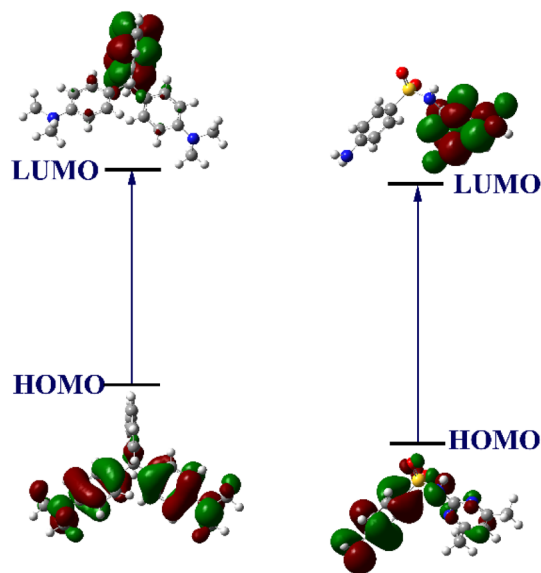


Fig. 4 The frontiers molecular orbitals (HOMO and LUMO) energy level diagram of TB-FL-COP and SMZ.

highest fluorescence quenching for SMZ was ascribed to its enhanced energy transfer from the sensor since the LUMO of SMZ is placed at lower energy and much closure to the LUMO of TB-FL-COP compared to the LUMO energy of all other antibiotics (Fig. 4).

To determine the sensitivity of TB-FL-COP for antibiotics detection, the fluorescence titration studies were performed by taking micromolar (μM) concentrations of SMZ. It was found that TB-FL-COP can detect the presence of SMZ even at the nanomolar (nm) level of concentrations and the LoD value was determined to be 56 ppb, this value of sensitivity is much lower than several other reported fluorescence and other types of sensors reported for antibiotic detection (see Table S3†).^{41,42} A time-dependent fluorescence titration study was also performed to know the fluorescence quenching response time of TB-FL-COP for SMZ. The emission intensity of TB-FL-COP was monitored at various time intervals and quenching efficiency was plotted against contact time. Upon the addition of a 90.9 μM concentration of SMZ, a quenching efficiency of 98% was reached within 30 seconds after the addition of SMZ (Fig. S5A†). The instantaneous increase in fluorescence quenching indicates that TB-FL-COP can be used as a fast fluorescence sensor for antibiotics detection. Furthermore, the effect of the pH of the sensing medium on the sensing performances of TB-FL-COP towards SMZ was studied. As shown in Fig. S7 in ESI†, TB-FL-COP was found to be highly emissive in basic pH > 8 and the highest fluorescence emission was observed at pH = 10. While in the acidic pH < 5 , TB-FL-COP was less emissive. Notably, the addition of SMZ antibiotics quenches the fluorescence emission of TB-FL-COP almost in all pH of the sensing medium. These results indicate that the effect of pH on the fluorescence sensing performance of TB-FL-COP is inconsequential.

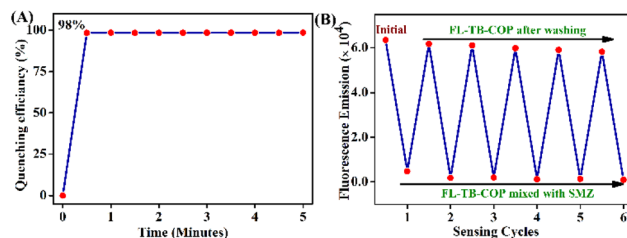


Fig. 5 (A) The percentage of fluorescence quenching was measured for TB-FL-COP after the addition of SMZ at a different time interval. (B) The reversible fluorescence sensing of TB-FL-COP for SMZ in water medium.

To check the reversibility, the fluorescent intensity of TB-FL-COP in water was measured before and after adding a 45.5 μM concentration of SMZ solution. After the measurement, the TB-FL-COP solution containing SMZ was washed several times with ethyl acetate to remove SMZ and subsequent fluorescence measurements indicate that TB-FL-COP regain the initial emission intensity. This procedure was repeated for several cycles and almost 91% of the initial emission intensity recovered even after six cycles. Thus, the recyclability of TB-FL-COP enriches its practical application of sensing antibiotics (see Fig. 5). To explore the sensor's usefulness in real-world applications, a fluorescence titration study with water samples was carried out. Water from a pond near Ahalia Hospital in Palakkad was used to make SMZ and TB-FL-COP stock solutions, which were then titrated to achieve high fluorescence quenching. Interestingly, TB-FL-COP exhibited a strong fluorescence quenching in the presence of SMZ in real-water samples (Fig. S8, ESI†). Despite the presence of many water contaminants and impurities in the pond water, the observed strong fluorescence quenching validates the potential application of TB-FL-COP for SMZ detection even in the real-water medium.

Conclusions

In conclusion, a new Tröger's base containing fluorenone organic polymer (TB-FL-COP) was developed and successfully used as a turn-off fluorescence sensor for the discriminative sensing of various antibiotics in an aqueous medium. Interestingly, TB-FL-COP showed a preferential binding affinity with the largest fluorescence quenching efficiency for sulfamethazine (SMZ) antibiotic and showed high selectivity, reversibility, and excellent sensitivity for SMZ detection. The selective sensing of SMZ antibiotic was also evident from the sharp visual color changes and thus TB-FL-COP can be a colorimetric probe. Further, we have demonstrated that TB-FL-COP can be employed to sense SMZ antibiotics in real-water samples. All the studies presented herein confirm that TB-FL-COP is a useful fluorescence sensor for selective, sensitive, and reversible sensing of SMZ antibiotics in water. As is given in Chart 1 (in ESI†), further works are in progress to explore the



applications of **TB-FL-COP** as a molecular filter for the efficient adsorption, removal, and conversion of different antibiotics from wastewater and device fabrications.

Author contributions

Ananthu Shanmughan: Data curation; formal Analysis; investigation; methodology; software; validation; writing – original draft. Mini Ajith Nithasha: Formal analysis; investigation; methodology; validation. Binduja Mohan: Data curation; investigation; writing – original draft. Deivasigamani Umadevi: Computational investigation and validation. Sankarasekaran Shanmugaraju: Conceptualization; funding acquisition; project administration; resources; supervision; validation; visualization; writing – original draft.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful to the Indian Institute of Technology Palakkad (ERG research grant 2023-168-CHY-SHS-ERG-SP to SS), India, for financial support and CIF at the Indian Institute of Technology Palakkad for the facility.

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