Nitrogen-Rich Tetraphenylethene-Based Luminescent Metal–Organic Framework for Efficient Detection of Carcinogens

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ABSTRACT: The introduction of nitrogen-rich functional groups into a luminescent metal–organic framework (LMOF) can enhance its fluorescent sensing ability. In this work, we designed and synthesized a triazole-containing tetracarboxyl-substituted tetraphenylethene (TPE) ligand, tetrakis[4-(4-carboxyphenyl)](1H-1,2,3-triazol-4,1-diyl)phenyl]ethene (H4TCPTAPE), featuring a prominent aggregation-induced emission (AIE). A highly porous TPE-based LMOF [Zn3(TCPTAPE)-(H2O)2(OH2)] (1) with large pores was successfully obtained via solvothermal assembly of the H4TCPTAPE ligand and Zn(II) ions, which showed a high fluorescence quantum yield of 54%. The activated 1 could selectively and sensitively detect aristolochic acid I with a high fluorescence quenching efficiency of 96% and a low detection limit of 1.02 μM, indicating that it has a potential application as a luminescence-based chemical sensor for carcinogens.

INTRODUCTION

Nitrogen-rich functional groups are a significant class of units that can be utilized in the fabrication of porous materials on the purposes of gas adsorption and separation,1–3 drug delivery,1 cancer therapy, and so forth.5 The versatile click chemistry copper(I)-catalyzed azide-alkyne cycloaddition is an extensively used method in the manufacture of various nitrogen-rich functional units for its mild conditions and high yield.6–10 In recent years, a few nitrogen-rich metal–organic frameworks (MOFs) have been pre-designed and constructed by introducing robust triazole functional groups through click chemistry, such as NTU-130,11 NU-140,12 Cu-ABTA,12 N3-MOF-5,14 etc. However, the luminescence performance of these MOFs containing nitrogen-rich functional groups is barely studied. Tetraphenylethene (TPE) is a typical aggregation-induced emission (AIE) lumogen and currently has emerged as a prevalent component to create efficient luminescent metal–organic frameworks (LMOFs).14–18 TPE-based LMOFs, as a new class of crystalline porous materials, have demonstrated excellent performance in sensing applications owing to their high emission efficiencies, large surface areas, and structural tenability.19–24 The host–guest interactions between TPE-based LMOF sensing materials and analyte species are generally determined by how the structural and chemical environments of the LMOF pores relate to the analyte.25

Aristolochic acids (AAs), which form a class of structurally related nitrophenanthrene carboxylic acids, can be found in natural medicinal plants.26 The aristolochic acid I (AA-I)-containing plants have long been utilized in Chinese herbal medicine to treat tumors, obstetrics, pneumonia, etc. However, due to the high nephrotoxicity and overbearing carcinogenicity, AA-I actually is one of the most potent carcinogens in the Carcinogenic Potency Database.27 In addition, carcinogens in Chinese herbs also include caffeic acid, anthrone, acrylamide, catechol, eugenol, coumarin, etc.28 Because of their bioaccumulation, persistency, and carcinogenicity on human health, numerous methods have been developed to analyze carcinogens in Chinese herbs, such as GLC,29 HPLC,30–32 CE–MS,33 CZE34 and LC–MS.35,36 However, these methods usually require costly apparatus and complicated pretreatments, toxic reagents, and long analysis time. Therefore, it is strongly demanded to develop a simple, accurate, time-saving, and low-cost method for carcinoen determination.

In this work, we designed and successfully synthesized a novel triazole-containing TPE-based ligand, tetrakis[4-(4-carboxyphenyl)](1H-1,2,3-triazol-4,1-diyl)phenyl]ethene (H4TCPTAPE) via a click reaction. Through chelation reactions between H4TCPTAPE and zinc ion, for the first time, a three-dimensional triazole-containing TPE-based LMOF [Zn3(TCPTAPE)(H2O)2(OH2)] (1) was obtained.

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Thanks to the efficient interactions between nitrogen-rich triazole and proton-containing analytes, activated 1 exhibited a high quenching efficiency of 96% and a low detection limit of 1.02 μM toward AA-I as well as other advantages such as a fast response, high selectivity, and good recyclability.

### EXPERIMENTAL SECTION

**Materials and Methods.** All purchased starting materials and solvents were used without further purification. Proton nuclear magnetic resonance spectra (1H NMR) were obtained using a Bruker Avance 500 MHz spectrometer. All 1H NMR spectra were reported as chemical shift δ in units of parts per million (ppm) downfield with reference to the deuterated solvent (2.50 ppm for DMSO-d6 and 7.26 ppm for CDCl3) or TMS (0.00 ppm). Multiplicities were presented as s (singlet), d (doublet), t (triplet), and m (multiplet). Coupling constant values were expressed in hertz, and the number of protons was expressed as nH. 13C NMR spectra were reported as chemical shift δ in units of parts per million (ppm) downfield with reference to deuterated solvent (39.81 ppm for DMSO-d6 or 77.16 ppm for CDCl3 or DMSO-d6) expressed as ppm.

NMR spectra could not be collected because of the very low solubility of the product. The isolated product was used directly in the following step without further purification.

**Synthesis of 4,4′,4″,4‴-((Ethene-1,1,2,2-tetrayl-tetrakis(benzene-4,1-diyl))tetrakis(1H-1,2,3-triazole-4,1-diyl))tetrabenzoic acid (H₄TCPTAPE).** In a 250 mL round-bottom flask, Me₄TCPTAPE (240 mg, 0.2 mmol) was suspended in THF (20 mL) and an aqueous solution of KOH (1.9 g, 33.9 mmol) was added. After the resulting suspension was refluxed for 24 h at 90 °C, THF was removed using a rotary evaporator and the remaining aqueous solution was acidified to pH = 1 using concentrated HCl. The resulting precipitate was collected via centrifugation, washed with H₂O, and dried under high vacuum to yield H₄TCPTAPE (205 mg, 90% yield). NMR spectra could not be collected.

**Synthesis of Complex 1.** Zn(NO₃)₂·6H₂O (2 mg, 6.7 μmol), H₄TCPTAPE (2 mg, 1.8 μmol), dimethylacetamide (DMAC) (1.8 mL), H₂O (0.1 mL), and ethanol (0.1 mL) were added into a vial. The reaction mixture was kept under nitrogen for 3 days. Transparent colorless complex 1 was carefully separated from amorphous phase and washed with DMAC. Yield: 52%. IR: (KBr pellet, cm⁻¹): 3417 (s), 1606 (s), 1557 (m), 1291 (m), 1251 (m), 1200 (s), 1036 (s), 994 (m), 844 (m), 783 (s).

**Preparing of Activated 1.** The as-synthesized crystals of complex 1 were immersed in dried CHCl₃ (5 mL) for 3 days, during which time, CHCl₃ was replaced several times. The activated 1 sample was moved into a sample cell and dried under vacuum at 60 °C by using an outgassing function for 6 h. IR: (KBr pellet, cm⁻¹): 3417 (s), 1344 (s), 1232 (s), 1124 (s), 1009 (s), 994 (s), 844 (m), 783 (s).

**Procedure for Sensing Experiments.** A suspension of activated 1 dispersed in water or methanol (0.25 mg/mL) was used to detect different kinds of carcinogens. Fluorescent tests were performed by adding multifarious concentrations of carcinogens into the suspension of activated 1, and the emission spectra were recorded on a PerkinElmer LS 55 spectrophluorometer. Before each fluorescence measurement, the suspension was vortexed for 30 s to form a homogeneous phase. The excitation wavelength was 365 nm, while the slit widths of both the source and detector for the excitation and the emission were kept at 10 nm to maintain consistency.

### RESULTS AND DISCUSSION

**X-ray Crystal Structure Determination of Complex 1.** Colorless rod crystals of complex 1 were synthesized through a
solvolothermal reaction of zinc nitrate and H₄TCPTAPE in DMAC, ethanol, and H₂O at 80 °C for 3 days. Single-crystal X-ray diffraction revealed that complex 1 was crystallized in the monoclinic space group P2₁/c (Table S1). Each asymmetric unit contains three zinc ions with independent coordination geometries, one TCPTAPE⁴⁻ ligand, two hydroxyls, and two coordination water molecules (Figure 1A). The Zn1 ion is six-coordinated with a distorted octahedral geometry, and its coordination positions were occupied by three carboxylate oxygen atoms, two hydroxyl oxygen atoms, and one coordination water molecule. The Zn2 ion is four-coordinated with a distorted octahedral geometry, and its coordination positions were occupied by three carboxylate oxygen atoms, two hydroxyl oxygen atoms, and one carboxylate oxygen atom. The Zn3 ion is four-coordinated with a distorted tetrahedral geometry, and its coordination positions were occupied by two carboxylate oxygen atoms, two hydroxyl oxygen atoms, and one carboxylate oxygen atom.

Figure 1. (A) Molecular structure of three zinc atoms in the asymmetric unit coordinated by the individual ligand atoms. (B) Chain formed along the c axis alternating rings. (C) Polyhedral representation of the SBU as an infinite rod. (D) H₄TCPTAPE ligand that is simplified as a butterfly shape. (E) Overall simplified structure of complex 1 with 1D rod SBUs and 1D open channels along the c axis. Hydrogen atoms are in gray and white in (B) and (D), respectively. Carbon atoms are in black and dark gray in (B) and (D), respectively. Oxygen atoms are in red. Nitrogen atoms are in blue. Zinc atoms are in light blue. Hydrogen atoms are omitted for clarity in (C) and (E).

Thermogravimetric analysis (TGA) of H₄TCPTAPE, complex 1, and activated 1 was done in the temperature range of 30 to 650 °C under a nitrogen atmosphere (Figure S3). Complex 1 showed a weight loss of 31.05 wt% from 30 to 230 °C, which corresponded to the elimination of DMAC solvent molecules in the pores. Further heating induced a weight loss of 4.68 wt% from 230 to 320 °C due to the release of a two coordinated water molecule. Then, a sharp weight loss recorded from 320 °C to 650 °C was attributed to the decomposition of the framework.

Luminescent Properties. H₄TCPTAPE, like most TPE derivatives, was emissive in the solid state, showing an AIE property. An absolute fluorescence quantum yield of 17% was measured by a calibrated integrating sphere. As depicted in Figure 3A, it was soluble in DMF (with little emission), and upon addition of a large amount of water, it formed emissive aggregates. Its emission intensity was enhanced when the water fraction was more than 80%. The immobilization of the TPE-based H₄TCPTAPE ligand into a rigid framework had an advantage, which was that the rotation and torsion of phenyl rings could be further inhibited, leading to an increased fluorescence quantum yield. Solid-state luminescent properties of complex 1 and activated 1 were investigated at room temperature (Figure 3B). The complex 1 showed strong blue emission peaking at 493 nm upon excitation at 365 nm, owing to the AIE effect of TPE units. The activated 1 exhibited slightly red-shifted emission located at 525 nm with a red shift of 32 nm, probably owing to increased intermolecular electronic coupling without the interference of highly disordered solvent guest molecules. The fluorescence lifetimes of H₄TCPTAPE solid, complex 1, and activated 1 were 2.6, 4.1, and 4.8 ns, respectively. The absolute fluorescence quantum yield of activated 1 is 38%, slightly lower than that of complex 1 (54%), which was similar to the previous findings of other TPE-based MOFs (PCN-94). The enhanced fluorescence quantum yield and fluorescence lifetimes of complex 1 were probably attributed to the immobilization of H₄TCPTAPE within a rigid framework via construction of coordination bonds to metal centers.

Response of Activated 1 to Carcinogens in Chinese Herbs. The wide permanent porosity and efficient solid-state emission of activated 1 encouraged us to examine its
fluorescence sensing ability for carcinogens in Chinese herbs, such as AA-I, caffeic acid, anthrone, coumarin, catechol, acrylamide, and eugenol. The finely ground activated 1 sample was uniformly dispersed in corresponding solutions to detect these carcinogens in Chinese herbs.

The emission spectra of activated 1 dispersed in methanol suspension upon incremental addition of AA-I at room temperature and recorded in Figure 4A. The quenching efficiency (QE) was estimated using the formula \( \frac{I_0 - I}{I_0} \) where \( I_0 \) and \( I \) were the emission intensities of activated 1 before and after adding guest molecules.\(^{46} \) As shown in Figure 4B, the emission intensity of activated 1 was decreased drastically by 96% of the original intensity at 224.80 \( \mu \)M of AA-I and the \( K_{SV} \) (quenching constant (M\(^{-1}\))) value was calculated as \( 2.64 \times 10^4 \) M\(^{-1}\), which was among the highest values reported for known luminescent sensory materials. Based on the IUPAC criteria (\( 3\sigma/K_{SV} \)),\(^{47} \) the limit of detection (LOD) for AA-I was estimated to be 1.02 \( \mu \)M (Figure S7). In addition, the lowest concentrations for complete quenching were 5100 \( \mu \)M for caffeic acid and 26.70 mM for anthrone (Figures S5 and S6). The LODs of caffeic acid and anthrone were calculated to be 23.14 and 90.07 \( \mu \)M, respectively, which were confirmed by fluorescence titrations at low concentrations (Figures S8 and S9). In particular, the emission wavelength of activated 1 that was soaked in anthrone solution showed a slight blue shift of 28 nm, which might be caused by a conformational change of phenyl rings of TCPTAPE\(^{4-}\)ligands.\(^{48} \) Although different degrees of fluorescence quenching of activated 1 were obtained on addition of an identical amount of carcinogens (224.80 \( \mu \)M), except for AA-I, the QE of other carcinogens was less than 15% (Figure 5 and Figure S10). This evidently revealed that activated 1 has a high selectivity toward AA-I over all the other carcinogens analytes. To evaluate the practicability as a sensing material, recyclability is a very significant issue. Thus, the recycling performance of activated 1 was also investigated (Figure 4D). After sensing experiments, the activated 1 could be reused by centrifuging the suspension and washing with corresponding solvents several times. The good reusability of activated 1 without devastation of its structure and decrease of luminescence intensity endowed activated 1 with a promising practical application for sensing AA-I.

Mechanism of AA-I Sensing by Activated 1. In order to better comprehend the luminescent quenching effect of activated 1 toward carcinogens in Chinese herbs, the quenching mechanism was studied in detail. The luminescence quenching is typically attributed to either a photoinduced electron transfer (PET) or a fluorescence resonance energy transfer (FRET) mechanism.\(^{49-51} \) Since the absorption spectra of analyts and the emission spectrum of activated 1 barely overlapped, the FRET hardly contributed to the fluorescence quenching (Figure S11). To examine the possibility of the PET mechanism, the HOMO and LUMO energy levels of AA-I,
caffeic acid, anthrone, and H$_4$TCPTAPE were calculated by the density functional theory (DFT) method (Figure S12). The LUMO energy level of H$_4$TCPTAPE (−2.05 eV) (donor) was obviously higher than that of AA-I (−2.21 eV) (acceptor). This indicated that the PET process could be the main cause of luminescence quenching of AA-I toward activated 1. Furthermore, hydrogen-bonding interactions between activated 1 and AA-I, caffeic acid, and anthrone may also contribute to the fluorescence quenching.

### CONCLUSIONS

In summary, we designed and synthesized a nitrogen-rich tetracarboxyl-substituted ligand (H$_4$TCPTAPE) by artfully incorporating triazole functional groups into an AIE-active TPE core via click chemistry. A highly porous, three-dimensional TPE-based LMOF [Zn$_3$(TCTAPE)-\((\text{H}_2\text{O})_2(\text{OH})_2]\) (1) was successfully prepared based on the ligand and its luminescent properties as well as related applications in sensing for carcinogens were investigated. The activated 1 exhibited a high quenching efficiency of 96% and a low detection limit of 1.02 μM for AA-I. The high luminescence quenching effect, well-defined correlation between the luminescent intensity and concentration of AA-I, high selectivity toward AA-I, and exceptional reusability demonstrated that activated 1 was a promising luminescent sensor for carcinogens.

### ASSOCIATED CONTENT

- Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05457.

- Thermal analysis, absorption and emission spectra, geometrical structures, FTIR spectra, PXRD patterns, and fluorescence titration (PDF)
- Crystallographic data (CIF)

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- Notes

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