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Electrospinning Superassembled Mesoporous AlEgen–Organosilica Frameworks Featuring Diversified Forms and Superstability for Wearable and Washable Solid-State Fluorescence Smart Sensors

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intramolecular motion. The three-dimensional space of ordered porous materials provides abundant reaction sites, allowing rapid and sensitive monitoring of analytes. TPEPMOS exhibit good properties as acidic pH fluorescent sensors with a pK_a of 4.3. A flexible film is obtained by dispersing TPEPMO nanospheres in a poly(lactic-*co*-glycolic acid) (PLGA) and polyacrylonitrile (PAN) hybrid fibrous matrix (TPEPMO-CFs) using the electrospinning superassembly technique and is successfully served as an efficient fluorescent probe for the naked eye detection of ammonia gas and HCl vapor by emission changes. The fluorescence of TPEPMO-CFs can be reversed in the presence of volatile acidic/alkaline gas for more than five cycles, exhibiting excellent recyclability. In addition, TPEPMO-CF sensors show excellent washability and long-term photostability (fluorescence was maintained above 94% after washing 10 times). These stimuli-responsive AIEgen–organosilica frameworks featuring diversified forms and superstability for wearable and washable solid-state fluorescence exhibit great potential for smart gas sensors, wearable devices, and solid-state lighting applications.

INTRODUCTION

Flexible solid-state sensing materials have attracted enormous attention recently due to their use in wide application fields,^{1–} including wearable sensors,^{5,6} biochemical probes,⁷⁻¹¹ lightemitting diodes,^{12,13} and display devices.¹⁴ Fluorescent probes have been extensively explored for their facile and noninvasive operations using fluorescent molecules with desired optical properties.^{15,16} However, traditional organic fluorophores often suffer from aggregation-caused quenching (ACQ) in the solid state, which leads to severe negative effects on the stability and efficiency of the sensors.¹⁷ Promisingly, fluorogens demonstrating aggregation-induced emission (AIE) characteristics have drawn great attention, as they can overcome the drawbacks of ACQ of traditional dyes in the solid state.^{18–20} Restriction of intramolecular rotation (RIR) upon aggregation is proposed as the main cause of the AIE effect.²¹⁻²³ Based on this, many AIE fluorogens have been incorporated into inorganic materials to construct inorganic-organic hybrid materials, which exhibit excellent photoactive properties due to

linked into periodic mesoporous organosilica (PMO) frameworks with high fluorescent efficiency due to the restriction of

> the restriction of the intramolecular motion of AIE fluorogens by the inorganic matrix.^{24–27} Periodic mesoporous organosilica (PMO) is an interesting class of inorganic–organic hybrid materials,^{28–31} which possesses not only the excellent structural features of inorganic porous materials but also excellent optical properties that originate from the functional organic units embedded within the framework.^{32,33} Moreover, the density and fixation of the optical bridging groups within pore walls could be controlled by the molecular design of the precursors and the preparation conditions of materials, which creates a fascinating platform for hosting fluorogens.^{34,35} Nevertheless, most of the reported fluorescent PMO materials

Received:October 7, 2020Accepted:December 17, 2020Published:January 6, 2021



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Scheme 1. Illustration of the Construction of TPEPMOs and TPEPMO-CF Films for Sensing Applications



are mainly based on the ACQ bridging molecules, which results in relatively low fluorescence efficiency.³⁶ Thus, the design of PMO materials with highly efficient emission appropriate for solid-state optical applications is required.^{37–39}

Fluorescent pH indicators are indispensable tools for measuring changes in the immediate environment and intracellular proton concentrations.^{40,41} In addition, volatile acidic and alkaline gases, such as ammonia gas and hydrochloric acid gas, are common gases generated in the process of industrial production, causing great harm to the human body due to their toxic, hazardous, and corrosive nature.⁴ Therefore, the detection of acidic and alkali gases is equally important along with the measurements of the pH value in the solution. Although a variety of responsive sensors for pH levels in the solution or acid/alkali gases have been developed recently,⁴³ solid sensors with effective fluorescence emission that could detect solution pH values and acid/alkali gases simultaneously are rarely reported. For practical applications, solid-state sensors of acid-base monitoring are more worthwhile that can provide wearability, washability, operational simplicity, and good stability.⁴⁴

In this work, we report a flexible, wearable, and washable optical acid/alkali gas sensor fabricated by incorporating pHsensitive AIE performance PMOs (TPEPMOs) in polymerbased optical fibers (TPEPMO-CFs) via spinning superassembly. The TPEPMOs were made from TPE-Si₄ bridged organosilane precursors using a covalent linking strategy, which could avoid the typical fluorescence quenching suffered by conventional dyes (Scheme 1). The reactivity of TPE-Si₄ with OH⁻/H⁺ enables TPEPMOs to sense pH variations in the acidic range, meeting the desire of "acidic" probes. A linear relationship of its fluorescence intensity with pH is established in the pH range of 3.9-4.7 with a pK_a of 4.3, making it promising as a fluorescent indicator for pH sensing.⁴⁵ Flexible solid-state fluorescent sensors, by immobilization of a fluorescent functional group on solid substrates like fibrous membranes, can provide more advantages over fluorescent probes used only in solution, such as reusability and tailorability. Here, TPEPMOs are embedded into poly(lacticco-glycolic acid) nanofibers (TPEPMO-CF1) and polyacrylonitrile nanofibers (TPEPMO-CF2), separately, prepared using two different flexible electrospun fibers. Using the as-fabricated TPEPMO-CF1 as a free-standing solid sensor, the fluorescence of TPEPMO-CF1 increased immediately upon exposure to ammonia vapor. The TPEPMO-CF1 sensor shows a response with the concentration of ammonia as low as 30 mg/m^3 , which is the highest permissible concentration in air. Meanwhile, the TPEPMO-CF1 fluorescent sensor is capable of in situ responding to the amine vapors emitted from a shrimp sample. These results demonstrate that TPEPMO-CF1 can be used as

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an excellent solid-state sensor for the detection of volatile alkaline/acid gases for environmental and food spoilage monitoring. Furthermore, the TPEPMO-CF2 sensor shows excellent recyclability, optical stability, and washability. TPEPMO-CF2 can be reversed in the presence of volatile acidic/alkaline gas more than five cycles and it maintains up to 94% fluorescence performance even after washing 10 times. We construct sensing materials step by step using AIE molecules from nanoparticles (zero-dimensional (0D)), fibers (one-dimensional (1D)) to films (two-dimensional (2D)). This design strategy provides new perspectives for developing high-performance fluorescence materials by combinations of AIE characteristics and stimuli-responsive properties in chemosensors, bioprobes, and solid-state lighting.

EXPERIMENTAL SECTION

Chemicals and Reagents. 4,4'-Diaminobenzophenone, aniline, 3-(triethoxysilyl) propyl isocyanate, N,N'-dimethylformamide (DMF), granulated tin, and triethylamine were purchased from Shanghai Jingchun Reagent Company. Tetrahydrofuran (THF), dichloromethane, chloroform, methanol, and ethanol were obtained from Tianjin Fuyu Reagent Company. Tetraethoxy orthosilane (TEOS), polyacrylonitrile (PAN) (M_w = 150 000), methanal, poly(vinyl alcohol) (PVA), hexafluoro-2-propanol (HFIP), and aqueous ammonia were bought from Shanghai Macklin Biochemical Company. Hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, and acetone were obtained from Yantai Far East Fine Chemical Company. Poly(lactic-*co*-glycolic acid) (PLGA) (M_w = 88 000–117 000, 50:50) was purchased from Jinan Daigang Biomaterial Company.

Synthesis. *Preparation of TPE-A*₄. 4,4',4"',4"''-(Ethene-1,1,2,2-tetrayl)tetraaniline (TPE-A₄) was synthesized according to the literature procedures. 4,4'-Diaminobenzophenone (0.85 g, 4.0 mmol) was dissolved in concentrated hydrochloric acid (35 mL) and heated under reflux for 24 h with granulated tin (3.3 g, 28.0 mmol). After cooling, the mixture was vacuumfiltrated and washed with water. After drying overnight at room temperature, a grayish product was obtained (yield 62%). Spectral data for ¹H NMR (400 MHz, DMSO-*d*₆, δ) were as follows: 7.10 (2H, ArH), 7.07 (2H, ArH), and 3.85 (2H, NH₂) (Figure S1). ¹³C NMR (400 MHz, DMSO-*d*₆, δ): 121.49, 132.39, 137.10, 132.79, 139.59, and 140.70 (Figure S2).

*Preparation of TPE-Si*₄. TPE-A₄ (0.39 g, 1.0 mmol) and 3isocyanatopropyltriethoxysilane (1.28 g, 5.2 mmol) were dissolved in 50 mL of anhydrous THF. Then, triethylamine (0.6 g, 6.0 mmol) was added followed by 24 h reflux under a nitrogen atmosphere. After cooling to room temperature, the solvent was concentrated under reduced pressure and the solid was washed by *n*-hexane to afford the TPE-Si₄ product (yield, 68%). Spectral data for ¹H NMR (400 MHz, DMSO-*d*₆, δ) were as follows: 8.54 (4H, PhNHCO), 7.11 (8H, ArH), 6.75 (8H, ArH), 6.29 (4H, NHCH₂), 3.73 (24H, ethoxy CH₂), 2.99 (8H, CH₂NH), 1.45 (8H, CH₂CH₂Si), 1.14 (36H, ethoxy CH₃), and 0.56 (8H, Si–CH₂) (Figure S3). ¹³C NMR (400 MHz, DMSO-*d*₆, δ): 7.73, 18.67, 23.80, 46.27, 58.18, 117.22, 131.70, 137.11, 138.54, 138.98, and 155.55 (Figure S4).

Synthesis of TPE-Bridged Periodic Mesoporous Organosilicas (TPEPMOS). A mixture of cetyltrimethylammonium bromide (CTAB) (200 mg), NaOH (700 μ L, 2 M), and distilled water (100 mL) was stirred at 80 °C for 30 min in a 250 mL round bottom flask. Then, TEOS (1.0 mL) was added along with TPE-Si₄ (0.1 g in 1 mL ethanol). The resulting mixture was stirred at 80 $^{\circ}$ C for 1 h and then left to cool to room temperature with stirring. The precipitate was collected by centrifugation before being washed with water and ethanol several times. To remove CTAB, the as-synthesized samples were extracted with a methanol solution for 48 h.

Fabrication of Composite Electrospun Nanofibers. PLGA scaffold nanocomposites were fabricated by the electrospinning technique. PLGA (0.85 g) was dissolved in HFIP (5 mL) under magnetic stirring for 12 h. Then, TPEPMOs (0.25 g) were added into the mixture and ultrasonicated for 30 min to obtain a homogeneous precursor sol for further electrospinning. The distance between the spinneret (metallic needle) and the collector (grounded conductor) was fixed at 13 cm, and a high-voltage supply was maintained at 14 kV. The spinning rate was controlled at 0.5 mL/h.⁴⁶ The resulting samples are denoted as TPEPMO-CF1.

PAN fiber membranes were fabricated through a facile electrospinning method. PAN (15 wt %, $M_w = 150\,000$) was dissolved in 5 mL of *N*,*N*-dimethylformamide (DMF) under stirring at 70 °C for 6 h. Then, TPEPMOs (0.25 g) were added into the mixture, followed by ultrasonic treatment for 1 h. The PAN solution was electrospun onto the rotating collector with a spinning rate of 1.0 mL/h. The obtained PAN fibers were dried at 60 °C for 4 h.⁴⁷ The resulting samples are denoted as TPEPMO-CF2. The synthetic method of TPE-CF2 was the same as that of TPEPMO-CF2, except that TPEPMOs were replaced by TPE-Si₄ (25 mg).

Immobilization of TPEPMO-CF2 Membranes onto Various Substrates. TPEPMO-CF2 membranes were immobilized onto various substrates using a polydopamine (PDA)-mediated surface coating method.⁴⁸ Dopamine hydro-chloride (100 mg) was dissolved in 1 mL of PVA aqueous solutions (10 wt %) under stirring. After polydopamine formation, coating these solutions onto the surfaces of spinning membranes and film sensors can be immobilized onto a variety of substrates, including gloves, papers, leaves, masks, and clothes.

Response Measurements of Nanofibers to Vapors. For the response measurements of electrospinning films to vapors, the films were fixed in the sample cell and put into a closed container filled with ammonia and hydrochloric acid vapors. The fluorescence changes in the films were recorded by fluorescence spectroscopy, keeping the test angle of the sample cell consistent before and after exposure to the gas. The timedependent fluorescence of films was tested by sticking the films to the cover of the quartz cell. Hydrochloric acid and ammonia were added into the cell. After the vapors were saturated, the film samples were put back into the cell. It was made sure that the film did not touch any liquid and that the same point was tested before and after exposure to vapors. The fluorescence intensity was recorded at different times.⁴² For selective experiments, films were exposed to different vapors generated from their corresponding solvents for 10 min. For the fluorescence change tests toward different concentrations of vapors, ammonia and hydrochloric acid vapors are produced using a water bath at 333 K. The films were fixed in the sample cell. Then, a certain volume of the vapors was extracted using a syringe and immediately injected into the sealed bottle (500 mL) containing the sensing films (in the sample cell). After 10 min, the films with the sample cell were taken out for fluorescence measurement.

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Figure 1. (a) Fluorescence emission spectra of TPE-Si₄ in THF-water mixtures with different water fractions. (b) Plot of relative fluorescence intensities and the corresponding photographs under a UV lamp of TPE-Si₄ in THF-water mixtures. Excitation wavelength: 365 nm and concentration: 0.2 mM. (c) UV-vis absorption spectra of TPE-Si₄ and TPEPMO in THF. (d) Fluorescence emission spectra of TPE-Si₄ and TPEPMO in THF. Excitation wavelength: 360 nm.

Characterization. ¹H NMR spectra were acquired on a Bruker AVANCE III 400 MHz nuclear magnetic resonance (NMR) spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 710 FT-IR spectrometer (Thermo Nicolet Corporation) with samples prepared as KBr compressing tablets. Small-angle X-ray scattering (SAXS) was carried out using SAXSess mc² by Anton Paar. Brunauer-Emmet-Teller (BET) surface areas were tested using an SSA 6000 instrument. The powder PMO sample was pretreatment at 150 °C for 5 h in vacuum. Scanning electron microscopy (SEM) images were recorded on a SUPRATM55 scanning electron microscope with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) observations were obtained from an FEI Talos F200S electron microscope. Prior to the TEM measurement, the sample was first dispersed in ethanol and then deposited on a copper grid. Ultravioletvisible (UV-vis) spectra were measured using a PerkinElmer Lambda 750 UV/vis/near-infrared (NIR) spectrometer. Fluorescence spectra were obtained using an FS5 fluorescence spectrofluorometer. Using quinine sulfate in 0.1 M H₂SO₄ as a standard, fluorescence quantum yields were calculated according to the formula $\Phi u = \Phi s(Fu/Fs)(As/Au)$, where Φ , F, and A are the fluorescence quantum yield, integral fluorescence intensity, and absorbance at a fixed wavelength, respectively.

RESULTS AND DISCUSSION

Optical Properties. The TPE-bridged precursor (TPE-Si₄) with four polymerizable silyl groups was synthesized by the reaction of 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetraaniline with 3-isocyanatopropyltriethoxysilane (Figure S5). The com-

pounds were confirmed using nuclear magnetic resonance (NMR) and the spectra are given in the Supporting Information. The observed AIE properties of TPE-Si₄ were supported by the fluorescence studies of TPE-Si₄ in H_2O/THF mixtures with different contents of water (Figure 1a,b). The pure THF solution of TPE-Si₄ is weakly emissive, while the fluorescence intensity increases dramatically when the volume fraction of water is higher than 70%. Significantly fluorescence enhancements were observed with a further increase in the water fraction, and TPE-Si₄ displays its maximal emission intensities with a water fraction of 90%.

The TPE molecules were introduced into PMOs through covalent interaction by a one-pot condensation process using CTAB as the template. After removing the surfactant, TPEPMOs functionalized with AIE luminogen was obtained. The UV-vis spectrum of TPE-Si₄ in solution exhibits two absorption bands at 280 and 350 nm (Figure 1c), corresponding to C=C and aromatic and the π - π * transition of the TPE-Si₄ molecule structure, respectively.⁴⁹ A slight red shift occurs for the π - π * transition after TPE-Si₄ was incorporated into the PMO materials, which could be due to a higher conjugation or coplanarity degree of the molecules. In addition, the broadened band could be attributed to the light scattering against the TPEPMO particles.

The fluorescence spectrum is applied to understand the origin of the fluorescence behaviors of TPE groups in the PMOs. TPEPMOs exhibited strong fluorescence centered at approximately 495 nm (Figure 1d), which has a 10 nm red shift compared with that of TPE-Si₄ in solution. The possible interpretation for this phenomenon is that the immobilization effect of the framework induces the formation of a more planar

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Figure 2. (a) SAXS pattern of TPEPMOs and the inset showing the enlarged region. (b) N_2 adsorption-desorption isotherms of TPEPMOs and its corresponding pore-size distributions (inset). (c) TEM and (d) SEM images of TPEPMOs.

and rigid structure.⁵⁰ When TPE-Si₄ bonded with the rigid skeleton of the mesostructure, a highly emissive signal could be achieved by the restriction of the intramolecular rotation (RIR) mechanism.⁵¹ To further contrast the fluorescence emission efficiency of TPE-Si₄ and TPEPMOs, their relative fluorescence quantum yields were measured using quinine sulfate in 0.1 M H_2SO_4 as a standard (Table S1). Specifically, the fluorescence quantum yield of TPE-Si₄ in solution is 0.30, whereas the fluorescence quantum yields increased to 0.54 for TPEPMOs. As the TPE units are incorporated into the silica framework of the mesoporous materials, the internal rotation is restricted by the silica framework walls of the hybrid materials, significantly enhancing the fluorescence emission.

Structural Properties. Fabrication of luminescent AIE PMOs was achieved by coassembly and covalent linking of TEOS and TPE-Si₄. Evidence for the incorporation of TPE groups into the frameworks of PMOs is further confirmed by FT-IR studies. The FT-IR spectrum of TPE-Si₄ shows the characteristic C==O stretching vibration of the imide group at 1695 cm⁻¹ and the C==C stretching vibration of aromatic rings at 1530 cm⁻¹ (Figure S6). The characteristic bands of TPE-Si₄ moieties remain in the spectrum of TPEPMOs, and the bands at 1350–870 cm⁻¹ corresponding to the stretching vibrations of the Si–OH and Si–O–Si frameworks are observed, which suggested that the TPE groups are incorporated into the pore walls of PMO materials.

The small-angle X-ray scattering (SAXS) pattern of TPEPMOs (Figure 2a) shows an intense diffraction peak in the low-angle region, indicating the formation of the ordered mesostructure. In addition, three peaks are shown at q = 1.42, 2.60, and 2.90 nm⁻¹, which could be indexed as (100), (110), and (200), belonging to a 2D hexagonal symmetry. The lattice parameter a_0 of the 2D hexagonal system is around 5.10 nm, which is calculated using $a_0 = 2d_{100}/\sqrt{3}$. Nitrogen adsorption/ desorption isotherms of TPEPMOs are shown in Figure 2b.

The curve belonged to the type IV isotherm with no hysteresis loops, indicating the existence of the mesostructure and uniform cylindrical pores in the hybrid materials. The pore-size distribution of TPEPMOs calculated with the BJH method is centered at 1.90 nm, and the BET surface area and the total pore volume are calculated to be 617 m²/g and 0.97 cm³/g, respectively (Table 1).

Table	1.	Structural	and	Textural	Data	for	TPEPMOs ⁴

	d_{100}	a_0	$D_{\rm BIH}$	S_{BET}	$V_{\rm t}$	Ь
sample	[nm]	[nm]	[nm]	$[m^2/g]$	$[cm^{3}/g]$	[nm]
TPEPMOs	4.42	5.10	1.90	617	0.97	3.20
${}^{a}d_{100}$ = interplanar distance between two (100) planes; a_{0} = lattice						
parameter; D_{BIH} = pore diameter, calculated from adsorption branches						
by the Barrett–Joyner–Halenda (BJH) method; $S_{BET} = BET$ surface						
area; $V_{\rm t}$ = total pore volume; wall thickness $b = a_0 - D_{\rm BIH}$.						

The formation of mesoscale porous structures is further confirmed by TEM images of the extracted TPEPMOs (Figure 2c), which show a highly ordered 2D hexagonal phase along the (110) lattice direction. The observed pore diameter is ca. 1.9 nm, and the thickness of the pore walls is about 2.8 nm, which are in good agreement with the nitrogen sorption results. A representative nanosphere morphology can be seen from the SEM observation, and the average particle size is about 87 nm (Figure 2d).

Sensing Properties. Herein, the pH-responsive TPEP-MOs are developed, which exhibit AIE features, overcoming the limitations exposed by the concentration quenching problem encountered by most conventional dyes. The reactivity of TPE-Si₄ with OH⁻/H⁺ enables TPEPMOs to sense pH in a meta-acid range. With reduction in pH values from 7 to 1, the TPEPMO emission peak intensity decreases (Figure 3a). However, the fluorescent intensity changed

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Intensity (a.u.)

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b 10000 5.00 12 . pH=2 4.70 pH=3 8000 Intensity (a.u) 4 52 pH=4 4.40 . pH=5 4.30 pH=6 600 4 22 4.15 4.10 400 4.05 4.00 200 500 550 600 Wavelength(nm) Wavelength(nm) С No FL

Figure 3. (a) Fluorescence spectra of TPEPMOs at pH values between 1 and 7. The inset is the photograph of the TPEPMO aqueous dispersion at different pH values in UV light. (b) Fluorescence spectra of TPEPMOs at pH values between 4 and 5. (c) Sensing mechanism of TPEPMOs.



Figure 4. (a) SEM image of the flexible film of TPEPMO-CF1 hybrid nanofibers. (b) Fluorescence spectra and photograph of the TPEPMO-CF1 film after exposure to ammonia vapor (ca. 1.5 v %) for different times (excitation wavelength: 365 nm). (c) SEM image of the flexible film of TPEPMO-CF2 hybrid nanofibers. (d) Fluorescent recovery cycles of the TPEPMO-CF2 film. Points HCl and NH₃ are corresponding to MSNF films after exposure to HCl and NH₃ vapor alternatively.

remarkably in the pH range of 4-5. As shown in Figure 3b, an aqueous dispersion of TPEPMOs exhibits greatly intensified fluorescence emission once pH values increase from 4 to 5. The plots of peak fluorescence emission intensities against pH values are shown in Figure S7, and the sigmoidal fit to the data

indicates a pK_a of about 4.3 for the TPEPMO probe. The drastic change in the fluorescent intensity of the TPEPMO material is attributed to the protonation of the carbonyl of ureido units in TPE-Si₄ molecules (Figure 3c). Fluorescence quenching of TPE induced by protonation has been already

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discovered in previous reports.⁴² In addition, the pK_a values obtained here are consistent with the result in our previous studies for the similar urea groups.⁵² A linear relationship of its fluorescence intensity with pH is established in the pH range of 3.9–4.7 (Figure S8), which makes it promising as a fluorescent indicator for pH sensing and also suggests that TPEPMO probes could find potential applications as acidic cellular compartments and pH meters.

Flexible Sensor. Electrospinning is a facile and convenient technique to produce a flexible fibrous membrane in which functional nanoparticles can be embedded. First, we used the electrospinning technique to embed TPEPMOs into PLGA nanofibers, interweaving a flexible, free-standing, and tailorable composite fibrous membrane TPEPMO-CF1, which could be used as a solid sensor to detect alkaline/acidic gases. The morphology of the TPEPMO-CF1 nanofibrous membrane was evaluated using SEM (Figure 4a). The fibers of the membrane are randomly interconnected with diameters of about 320 nm. It is clear that TPEPMOs have been distributed almost uniformly in the electrospun nanofibers and without obvious agglomeration. Meanwhile, some of the spherical particles are observable on the nanofiber surfaces.⁵³ In addition, the BET surface area and the total pore volume of TPEPMO-CF1 are calculated to be 20.3 m²/g and 0.092 cc/g, respectively (Figure S9a). After assembly of the TPEPMOs into the PLAG nanofibers, the flexible membrane exhibited a weak fluorescence under UV light because the precursor sol of electrospun nanofibers is acidic. A reversible transition from the weakly emissive to highly emissive was achieved by exposure of the TPEPMO-CF1 membrane to ammonia vapor.

Upon exposing the TPEPMO-CF1 membrane to ammonia vapor, the fluorescence intensity of the membrane increases immediately; meanwhile, the corresponding fluorescence emission is brighter. The fluorescence enhancement ratio of the TPEPMO-CF1 membrane is measured with the increased exposure time to saturated ammonia vapor (Figure S10). Increased fluorescence changes can be quickly detected and a more than 2-fold higher light-up process is observed within 2 min. In addition, Figure 4b shows the fluorescence spectra of the TPEPMO-CF1 membrane upon exposure to ammonia vapor (ca. 1.5 v %) for different times. The as-synthesized TPEPMO-CF1 membrane was almost nonemissive under UV irradiation, but its fluorescence intensity gradually increased with time after exposure to ammonia vapor. The fluorescence in 10 min is 4-fold larger than that at the beginning. When TPEPMO-CF1 was exposed to a low concentration of ammonia vapor (30 mg/m³, the maximum allowed concentration at a working place), the fluorescence intensity increases nearly 3-fold after 6 h, which could be directly observed by the naked eye under a UV lamp (Figure S11). Furthermore, the detection limit $(3\sigma/S)$ for ammonia vapor is estimated to be 15 mg/m³ based on the signal-to-noise ratio method (Figure S12).

The safety and quality control of food attracted increasing attention due to health and economic concerns. In particular, the sensitive detection of the released ammonia and biogenic amines is crucial to the assessment of the safety and quality of seafood and meat products during storage and transportation. Accordingly, we investigated whether the TPEPMO-CF1 film can be used to detect ammonia gas generated by food spoilage. When TPEPMO-CF1 was sealed with shrimps and stored at room temperature (25 °C) for 24 h, a significantly enhanced fluorescent emission from TPEPMO-CF1 was observed.

However, it showed no remarkable fluorescence changes when TPEPMO-CF1 was kept at room temperature without the shrimps (Figure S13). This result highlights that the flexible fiber membrane is an appropriate sensing material for practical applications in monitoring food spoilage. The reproducibility and recycling are the outstanding advantages of solid sensors. The enhanced fluorescence of TPEPMO-CF by NH₃ could be quenched with the treatment of hydrochloric acid vapor (Figure S14). These results not only imply the excellent reproducibility of TPEPMO-CF1 but also indicate that the film can be used as an environmentally friendly detector for both ammonia and hydrochloric acid vapor.

For the practical application of wearable sensors, many polymer membrane-based sensor substrates suffer from low corrosion resistance, weak washability, and poor photostability. Polyacrylonitrile (PAN) is widely used as a support for the assembly of composite membranes due to its good lightfastness, good solvent resistance, and acid-alkali resistance. Therefore, the wearable sensor film TPEPMO-CF2 is fabricated by the incorporation of TPEPMOs in PAN-based fibers. Figure 4c shows a typical SEM image of the as-prepared TPEPMO-CF2. The diameter of the individual TPEPMO-CF2 fiber is about 250 nm. Some TPEPMOs are observed on nanofiber surfaces (Figure 4c, enlarged section). Besides, the BET surface area and total pore volume TPEPMO-CF2 are estimated to be 18.2 m^2/g and 0.085 cc/g, respectively (Figure S9b). The flexible TPEPMO-CF2 membrane exhibited a strong fluorescence due to the neutral precursor sol of electrospun, which is different from TPEPMO-CF1. As illustrated in Figure 4d, the TPEPMO-CF2 film could quench its fluorescence after exposure to hydrochloric acid vapor (ca. 0.025 v %), and the respective fluorescent spectra could coincide nicely during the treatment of hydrochloric acid. The time-dependent fluorescence response studies of TPEPMO-CF2 show that the fluorescence changes can be detected within 15 s, and 50% of fluorescence intensity is quenched in 90 s (Figure S15). The detection limit for hydrochloric acid vapor is estimated to be 32 mg/m³ (Figure S16). We have further examined the recovery of the TPEPMO-CF2 film for the successive detection of NH₃ gas. Upon exposing the TPEPMO-CF2 film to NH₃ gas, the fluorescence intensity of the film increases immediately. After NH₃ exposure, the TPEPMO-CF2 film exhibits stronger fluorescence than the original film because of the higher alkalinity of the film after ammonia treatment. After five cycles of quenching and recovery, the fluorescence property of the TPEPMO-CF2 was well maintained (Figure 4d), indicating that the film exhibits good acid-alkali resistance and reversibility, which could be used as a detector for harmful gases.

The detection ability of the TPEPMO-CF2 sensor toward various acids is then investigated (Figure S17a). The obvious fluorescence quenching for hydrochloric acid and nitric acid indicates that these volatile strong-acid vapors interact more efficiently with the sensor, whereas the TPEPMO-CF2 film reveals a low response to some weak volatile acids (H_3PO_4 and H_2SO_4). In addition, since ammonia is a volatile gas, different organic amines and volatile organic compounds are selected for the selective test of fluorescence-enhanced sensing (Figure S17b). After the TPEPMO-CF2 sensor is quenched by acid, ammonia vapor shows the most effective fluorescence enhancement sensing effect. Triethylamine also reveals a certain light-up effect. However, for aniline and various organic solvent vapors, almost no obvious fluorescence response is



Figure 5. (a) Illustration of TPEPMOs in the TPEPMO-CF film and their corresponding optical properties. (b) Dewashing experiment of TPEPMO-CF2, TPE-CF2, and soaked-CF for 10 times using 1/1 ethanol/PBS (7.4). (c) Photobleaching behaviors of TPEPMO-CF2 and TPE-CF2.

observed. Moreover, the stability of the sensor is estimated in different environments. The sensing properties of the TPEPMO-CF2 sensor at different temperatures are shown in Figure S18. The TPEPMO-CF2 film exhibits similar fluorescence quenching phenomena after exposure to hydrochloric acid vapor at 20, 30, and 40 $^{\circ}$ C. Moreover, the fluorescence could be effectively recovered by the effect of ammonia at different temperatures.

To further prove the practical values of TPEPMO-CF2 film sensors, their washability and photostability were thoroughly investigated. As shown in Figure 5b, the fluorescence emission intensity of the TPEPMO-CF2 film was well retained after continuous washing. Even after being washed 10 times, 94% of the fluorescence emission can still be maintained. However, for the reference sample TPE-CF2 in which TPE-derivative was assembled in PAN directly, only 85% of the fluorescence intensity was retained. In addition, for another control sample, which was prepared by the PAN film soaked in a TPE derivative solution, the fluorescent groups were rapidly removed during the washing process. After three and ten washing cycles, the film has only 79 and 64% of fluorescence left, respectively. These results suggest that the TPEPMO-CF2 sensor exhibits good washability. A salient advantage of PMOs as chemosensors is their high photostability. Figure 5c exhibits the emission intensity changes in TPEPMO-CF2 and TPE-CF2 with time against light irradiation ($\lambda = 365$ nm) over 100 min. The results showed that TPE-CF2 lost 23% of its initial fluorescence. However, TPEPMO-CF2 exhibited hardly any photobleaching under strong excitation. The high photostability of TPEPMO-CF2 could be attributed to the protective silica network, which can protect TPE groups from oxygen or other exoteric quenching factors.

Considering the requirement of wearable materials, it is better to assemble TPEPMO-CF sensors onto various material surfaces. To this end, the TPEPMO-embedded PAN polymer was coated onto a wide variety of material surfaces, including chemigum (gloves), masks, clothes, and papers (Figure S19). This kind of integrated gas-sensing sensor may not only ensure practical applications of wearable materials but also inspire the future development of wearable sensors with simpler preparation and wide applicability.

CONCLUSIONS

In summary, we have demonstrated a wearable and washable optical sensor for monitoring of NH₃ and HCl vapor based on AIEgen-organosilica framework (TPEPMO)-incorporated nanofibre composites. For effective light performance, a mesoporous nanoparticle TPEPMO with AIE characteristics was employed for the fabrication of TPEPMO-CF nanofibres. TPEPMOs exhibited pH sensing capability in solution due to the reactivity of TPE-Si₄ with OH^-/H^+ . The covalent linking strategy enables the fluorescence efficiency of TPEPMOs due to the restriction of intramolecular rotation of TPE-bridged groups, and the three-dimensional interface of the mesopores ensured the higher sensitivity for sensing. Stable and washable sensors were fabricated by embedding the TPEPMOs in superassembled electrospun nanofibres, which served as a flexible light-guiding platform for detecting environmental acidity/alkalinity. The fluorescence of the as-prepared TPEPMO-CF1 increased immediately and became brighter upon exposure to ammonia vapor, which renders them capable of monitoring the ammonia vapor with low concentrations in air and assessing the spoilage of food. Furthermore, the TPEPMO-CF2 sensor built from polyacrylonitrile as a substrate showed excellent reversibility and acid-alkali resistance in the presence of volatile acidic/alkaline gases for more than five cycles. The fluorescence performance of TPEPMO-CF2 was maintained up to 94% even after being washed 10 times, which is much higher than the TPE directassembled TPE-CF2. The covalent linking and electrospinning superassembly strategy provides better optical stability and washability for fabricating wearable sensors. In addition, the TPEPMO-embedded PAN polymer was coated onto a wide variety of material surfaces, including chemigum (gloves),

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masks, clothes, and papers, further proving the practical values of TPEPMO-CFs. These superassembled AIEgen—organosilica frameworks featuring diversified forms and superstability with wearable and washable solid-state fluorescence can be used as excellent solid-state sensors with solid-state lighting in various fields, which is environmentally friendly for future smart sensing applications.	 Shihai Miao – National Supercomputer Research Center of Advanced Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250014, P. R. China Wenlong Fu – National Supercomputer Research Center of Advanced Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250014, P. R. China 					
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 Supporting Information The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.0c04226. ¹H NMR and ¹³C NMR spectra; details of the synthesis of TPE-Si₄; fluorescence quantum yield of TPE-Si₄ and TPEPMOs; figures of FT-IR spectra and linear calibration plot of TPEPMOs; time-dependent fluorescence, selective test, regeneration test, and sensing stability of TPEPMO-CFs; and film sensors immobilized onto a variety of materials (PDF) 	 Kingsinaing Enang – National Supercomputer Research Center of Advanced Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250014, P. R. China Junjie Zhou – Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Department of Chemistry, Laboratory of Advanced Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China Xiaoping Jiang – National Supercomputer Research Center of Advanced Materials, Advanced Materials Institute, Qilu University of Technology (Shandong Academy of Sciences), Jinang 250014, P. P. China 					
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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (2019YFC1604601, 2019YFC1604600, 2018YFC1602301, 2017YFA0206901, and 2017YFA0206900), the National Natural Science Foundation of China (21705027, 22005160, 61903235, and 51808328), the Natural Science Foundation of Shanghai (18ZR1404700), the Natural Science Foundation of Shandong Province (ZR2017PEM004 and ZR2017LEM011), the Major Scientific and Technological Innovation Projects of Shandong Province (2018CXGC1406), the Australia National Health and Medical Research Council (NHMRC, APP1163786), the Australian Research Council (ARC, DP190101008), and the Recruitment Program of Global Experts of China and the Thousand Talent Plan of Shanghai.

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