Electronic Supporting Information for

FITC-modified PPy Nanotubes embedded in Nanoporous AAO membrane can Detect Trace PCB20 via Fluorescence Ratiometric measurement

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The Supporting Information includes:

Part S1 Detailed fabrication of the FITC@PPyNTs@NPAAO dual-fluorophore membrane.

In a typical experiment of synthesizing FITC@PPyNTs@NPAAO dual-fluorophore membrane, 30 μL of 0.5 mol/L pyrrole in 1:1 (v/v) ethanol/deionized (DI)-water, and the same volume of 1 mol/L $FeCl_3$ in DI-water were titrated onto the NPAAO membrane in turn and pumped via a vacuum extracter (setup shown in Fig. S1) at ambient temperature. Pyrrole monomers both on the top planar surface and the channel walls of NPAAO would be oxidized to PPy. Then the NPAAO template loaded with PPy was rinsed with DI-water and ethanol respectively by ultrasonication to remove remaining pyrrole monomers and Fe^{3+}. For loading FITC, the PPyNTs@NPAAO complex membrane was immersed in 10^{-4} mol/L FITC/ethanol for 2 h, then rinsed with ethanol for several times to remove superfluous FITC molecules on its surface, and dried for characterization.

Part S2 Fluorescence spectra measurement conditions of the FITC@PPyNTs@NPAAO fluorescence ratiometric sensor membrane.

Fluorescence spectra measurements were carried out on a FL 4500 Fluorescence Spectrophotometer. The detection of PCB20 was carried out by measuring the fluorescence ratio changes. For effective comparison, only one FITC@PPyNTs@NPAAO dual-fluorophore membrane was used for successive fluorescence measurements in order to avoid the influence of different membranes. For the fluorescence measurements, the membrane was inserted into the quartz cell with its surface facing the excitation light source and the cell was fixed on the sample holder of the instrument. The position of the membrane was kept constant during each set of measurements to ensure the detection without interference of sample angle-change. 2 ml n-hexane or varied concentrations of PCB20 was added, and the fluorescence spectra were recorded every 5 min until the intensity was steady and the system reached equilibrium. After each measurement, higher concentration of PCB20 solution was used. Excitation and emission slits were all set at 5.0 nm with excitation at 280 nm and 420 nm for PPy and FITC, respectively.

Part S3 Calculation of the Stern-Volmer constant

As the quenching results from the interaction between PPy and PCB20, the association capability can be evaluated. Under optimal measurement conditions, the fluorescence quenching efficiency of the dual-fluorophore membrane is 0.07 (with PCB20 concentration expressed in ppb). In the proper range of PCB20 concentration where the fluorescence intensity of FITC is approximately constant, the change of PPy fluorescence intensity can be described by the Stern-Volmer equation as follows:

$$\frac{I_0}{I} = 1 + K_{sv}[Q] \quad (1)$$

where I_0 and I are the fluorescence intensities of PPy when the dual-fluorophore membrane is immersed in n-hexane and varied concentrations of PCB20/n-hexane, respectively; [Q] is the PCB20 concentration, i.e., [PCB20].

Part S4 Preparation of the PPy@glass membrane for control experiments.

A piece of glass (0.8 cm × 0.8 cm) with about the same area as that of the NPAAO template (diameter=1 cm) was rinsed with ethanol and DI-water by ultrasonication respectively. 30 μL 0.5 mol/L pyrrole in 1:1 (v/v) ethanol/deionized (DI)-water, and the same volume of 1 mol/L $FeCl_3$ in DI-water were slowly titrated onto the glass in turn. Then the pyrrole on the glass surface would be oxidized to PPy quickly (denoted as PPy@glass). The as-prepared PPy@glass membrane was dried at ambient temperature, and rinsed with DI-water and ethanol to remove superfluous molecules on the surface before characterization.

Part S5 Relationship between probing time and surface-to-mass ratio

As shown in Eq. (2), where k_q and τ_0 are the bimolecular quenching rate constant and fluorescence lifetime of the PPy on the dual-fluorophore membrane, higher K_{sv} means higher k_q and shorter probing-time. On the other hand, enhanced quencher diffusion rate resulted from the ultrahigh surface-to-mass ratio of the porous FITC@PPyNTs@NPAAO dual-fluorophore membrane can bring on shorter probing-time and ultrahigh sensitivity.

$$K_{sv} = k_q \tau_0 \quad (2)$$

Figures S1 to S6

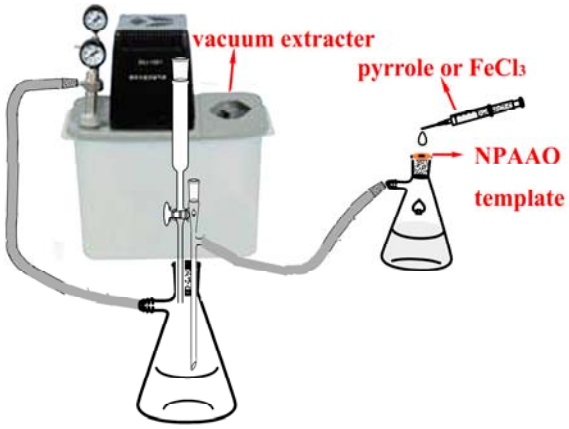

Fig. S1. Schematic showing the negative pressure deposition (NPD) setup.

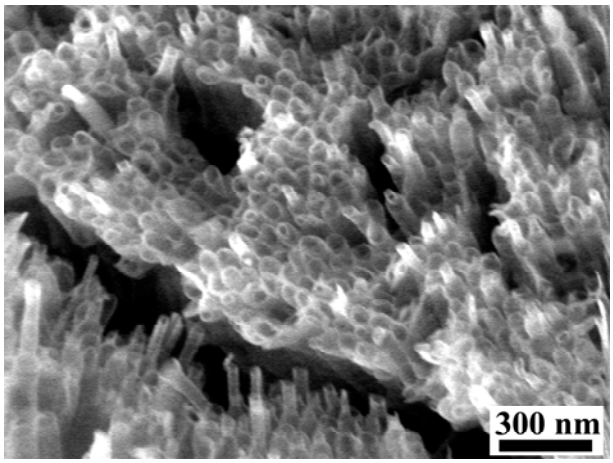

Fig. S2. SEM image showing a large amount of PPy nanotubes released from the NPAAO template.

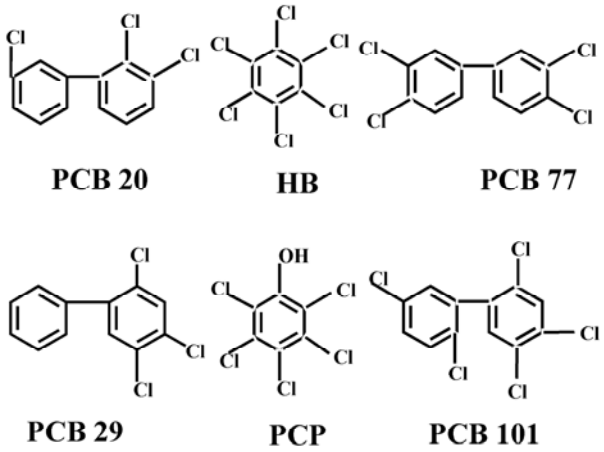

Fig. S3. Structural formulas of the compounds used.

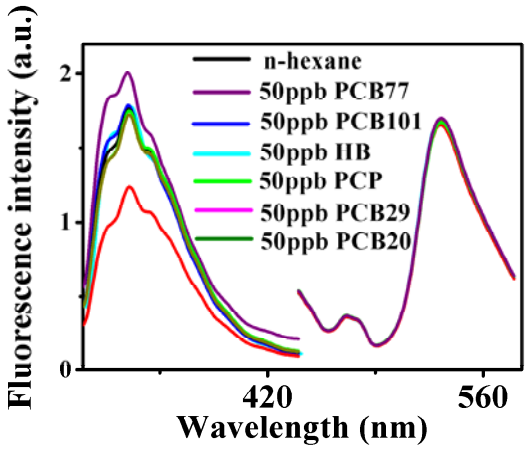

Fig. S4. Fluorescence spectra of the FITC@PPyNTs@NPAAO fluorescence ratiometric sensor membrane after being immerged in 50 ppb PCB101, HB, PCB29, PCP, PCB20, and PCB77, respectively. λ_{ex}=280, 420 nm for PPy and FITC respectively.

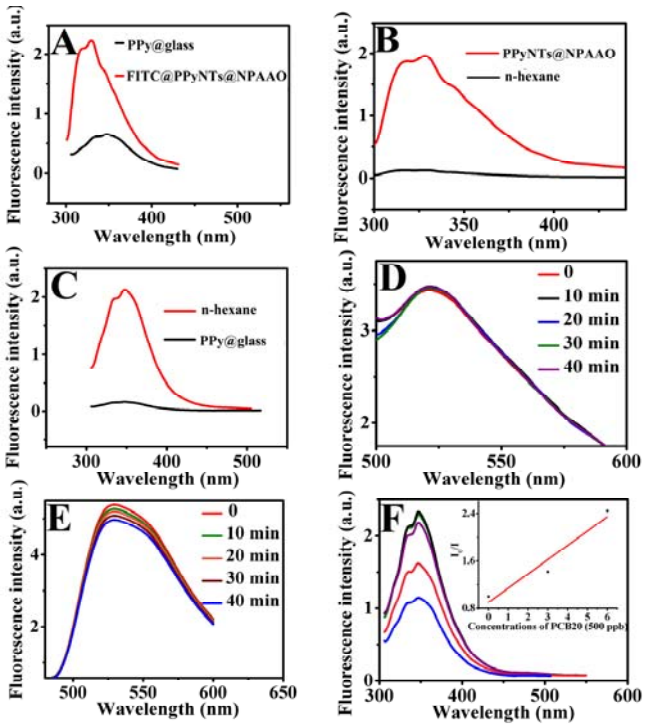

Fig. S5. (A) Fluorescence spectra of FITC@PPyNTs@NPAAO fluorescent membrane and PPy@glass after being immerged in n-hexane, respectively. (B) Fluorescence spectrum of the PPyNTs@NPAAO membrane after being dipped in n-hexane for 5 min, and fluorescence spectrum of the n-hexane after the PPyNTs@NPAAO membrane was taken out. (C) Fluorescence spectrum of the PPy@glass membrane after being dipped in n-hexane for 5 min, and fluorescence spectrum of the n-hexane after the PPy@glass membrane was taken out. λ_{ex}=280 nm. Fluorescence spectra of (D) FITC@PPyNTs@NPAAO fluorescent membrane immerged in n-hexane and (E) 10^{-5} mol/L FITC/ethanol irradiated for 0–40 min with excitation of 480 nm. (F) Fluorescence spectra of PPy@glass membrane immerged in n-hexane and varied concentrations of PCB20. Inset: Approximate Stern-Volmer plot of PPy@glass membrane as a function of different quencher concentrations. λ_{ex}=280 nm.

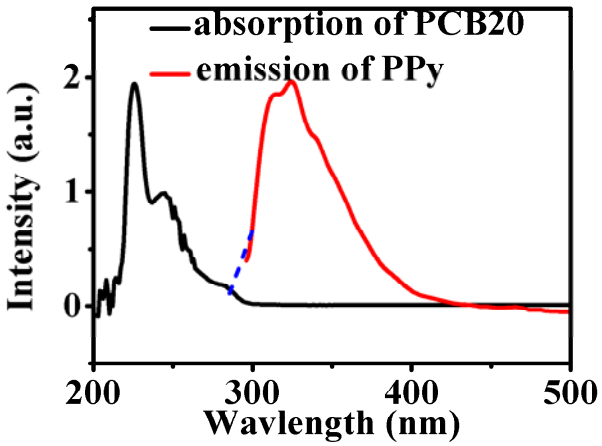

Fig. S6. Fluorescence and UV-vis absorption spectra of PPy and PCB20.