Supplementary information for:

**Colorimetric and Fluorescent Dual Detection of Paraquat and Diquat Based on a Novel Anionic Polythiophene Derivative**

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**Materials.** All chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Aladdin, and Beijing chem. Reagents Co. (Beijing, China) and were used as received. Water-soluble polythiophene derivative (PMTEMNa₂) were synthesized and purified as reported previously. S1

**Sample preparation.** The stock solution of paraquat, diquat and PMTEMNa2 were prepared in pure water. The stock solution of other pesticides was initially dissolved in methanol to a relatively high concentration, which was later diluted at least 20-fold with water. Stock solutions of paraquat and PMTPS were mixed directly to give a mixture with the desired concentration and then measured by UV-visible spectrometer immediately. Control experiments for addressing the selectivity of the sensor toward paraquat and diquat were carried out under the identical conditions. For real sample preparation, 1.0 g vegetable samples which were purchased from supermarket were mashed and dissolved in 1 mL water. After ultrasonic extraction, the mixture was centrifuged and then filtered through a ultrafiltration membrane (MWCO 3000). To avoid the influence of low pH values and some metal ions in certain vegetables, the filtrate was diluted by 20 mM phosphate buffer (pH 7.0) containing 2.0 mM EDTA.
The following detection procedures for these samples spiked with varying levels of paraquat were similar to those conducted in water stated above.

**Spectral measurements.** Absorption and emission spectra were collected by using a HITACHI U-3900 UV-VIS spectrophotometer and a HORIBA Scientific Fluorolog®-3 spectrofluorometer, respectively. $^1$H-NMR spectra were carried out on a Bruker DPX300 spectrometer and a JNM-ECA600 spectrometer, respectively. The photographs of the sensing solution color change were taken using a camera (Nikon).

![Absorption spectra of PMTEMNa$_2$ in the absence and presence of paraquat at different pH values as indicated.](image)

**Fig. S1** Absorption spectra of PMTEMNa$_2$ in the absence and presence of paraquat at different pH values as indicated. [PMTEMNa$_2$] = $1.0 \times 10^{-4}$ M, [paraquat] = $5.0 \times 10^{-5}$ M.
**Fig. S2** Changes in the colour of PMTEMNa$_2$ ($1.0 \times 10^{-4}$ M) solutions in the presence of increasing concentrations of paraquat as indicated (μM).

**Fig. S3** Absorption spectra of PMTEMNa$_2$ ($1.0 \times 10^{-4}$ M) in the presence of increasing amounts of pesticides in aqueous media. The concentrations of each pesticide were indicated on each spectrum.
**Fig. S4** Absorption spectra of PMTEMNa₂ (1.0 × 10⁻⁴ M) in the presence of increasing amounts of 4,4’-bipyridine in aqueous media.

**Fig. S5** Absorption spectra of PMTEMNa₂ (1.0 × 10⁻⁴ M) in the presence of increasing amounts of 1-ethylpyridinium bromide in aqueous media.

**Fig. S6** ¹H-NMR spectra of the PMTEMNa₂/paraquat complex along with the ¹H-NMR spectra of paraquat (solvent: D₂O).
**Fig. S7** Emission spectra of PMTEMNa$_2$ ($1.0 \times 10^{-5}$ M) in the presence of increasing amounts of paraquat in aqueous media.

**Fig. S8** Emission spectra of PMTEMNa$_2$ ($1.0 \times 10^{-5}$ M) in the presence of increasing amounts of diquat in aqueous media.
**Fig. S9** Emission spectra of PMTEMNa$_2$ in the absence and presence of various analytes as indicated in aqueous media. [PMTEMNa$_2$] = 1.0 × 10$^{-5}$ M, [analytes] = 1.0 × 10$^{-5}$ M.

**Fig. S10** Relative fluorescence intensity ($I/I_0$ @ 535 nm) of PMTEMNa$_2$ solutions in the presence of various analytes as indicated. [PMTEMNa$_2$] = 1.0 × 10$^{-5}$ M, [analytes] = 1.0 × 10$^{-5}$ M.
Fig. S11 Absorption spectra of PMTEMNa₂ (1.0 × 10⁻⁴ M) in the presence of increasing amounts of paraquat in 20 mM phosphate buffer (pH 7.0). Inset: the relationship between $A_{480}/A_{404}$ and the concentration of paraquat from 0.5 to 10 μM.

Fig. S12 Emission spectra of PMTEMNa₂ (1.0 × 10⁻⁵ M) in the presence of increasing amounts of paraquat in 20 mM phosphate buffer (pH 7.0).

Fig. S13 Absorption spectra of PMTEMNa₂ (1.0 × 10⁻⁴ M) in the presence of increasing amounts of diquat in 20 mM phosphate buffer (pH 7.0).
Fig. S14 Emission spectra of PMTEMNa₂ (1.0 × 10⁻⁵ M) in the presence of increasing amounts of diquat in 20 mM phosphate buffer (pH = 7.0).

Fig. S15 The relationship between $A_{480}/A_{404}$ and the concentration of paraquat from 0.5 to 10 μM in Chinese cabbage sample.

Fig. S16 Emission spectra of PMTEMNa₂ (1.0 × 10⁻⁵ M) in the presence of increasing amounts of paraquat in Chinese cabbage sample.
**Fig. S17** Absorption spectra of PMTEMNa₂ (1.0 × 10⁻⁵ M) in the presence of increasing amounts of paraquat in cole sample.

**Fig. S18** The relationship between $A_{480}/A_{404}$ and the concentration of paraquat from 0.5 to 10 μM in cole sample.

**Fig. S19** Fluorescence quenching of PMTEMNa₂ (1.0×10⁻⁵ M) by paraquat at various concentrations in Chinese cabbage (●) and cole (■) samples. The fluorescence quenching $QI = [(I₀-I)/I₀] × 100$%; $I₀$ and $I$ are the fluorescence intensity at 535 nm of a solution of PMTEMNa₂ in the absence and presence of different amounts of analytes, respectively. $λ_{ex} = 459$ nm.
Reference: