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 ($PMTEMNa_2$) 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).

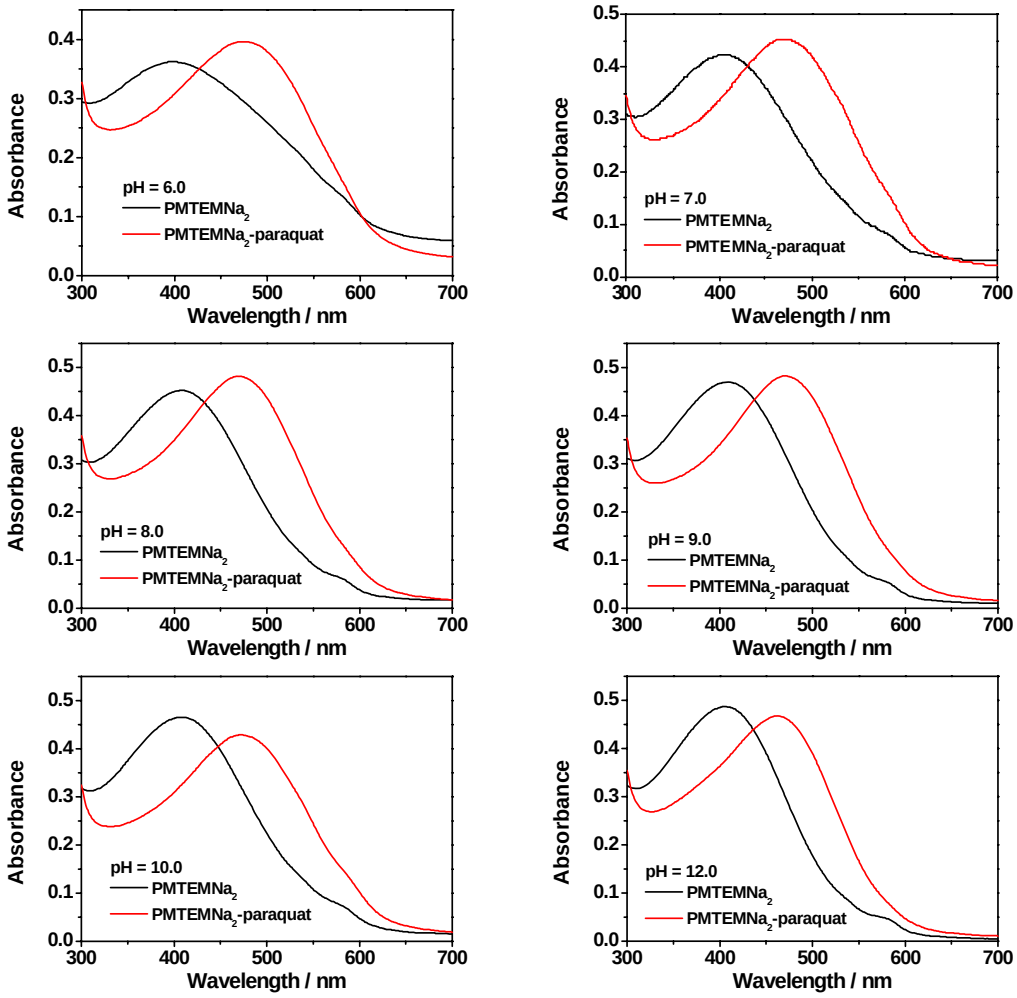

Fig. S1 Absorption spectra of $PMTEMNa_2$ in the absence and presence of paraquat at different pH values as indicated. [$PMTEMNa_2$] = 1.0×10^{-4} M, [paraquat] = 5.0×10^{-5} M.

Fig. S2 Changes in the colour of $PMTEMNa_2$ (1.0×10^{-4} M) solutions in the presence of increasing concentrations of paraquat as indicated (μM).

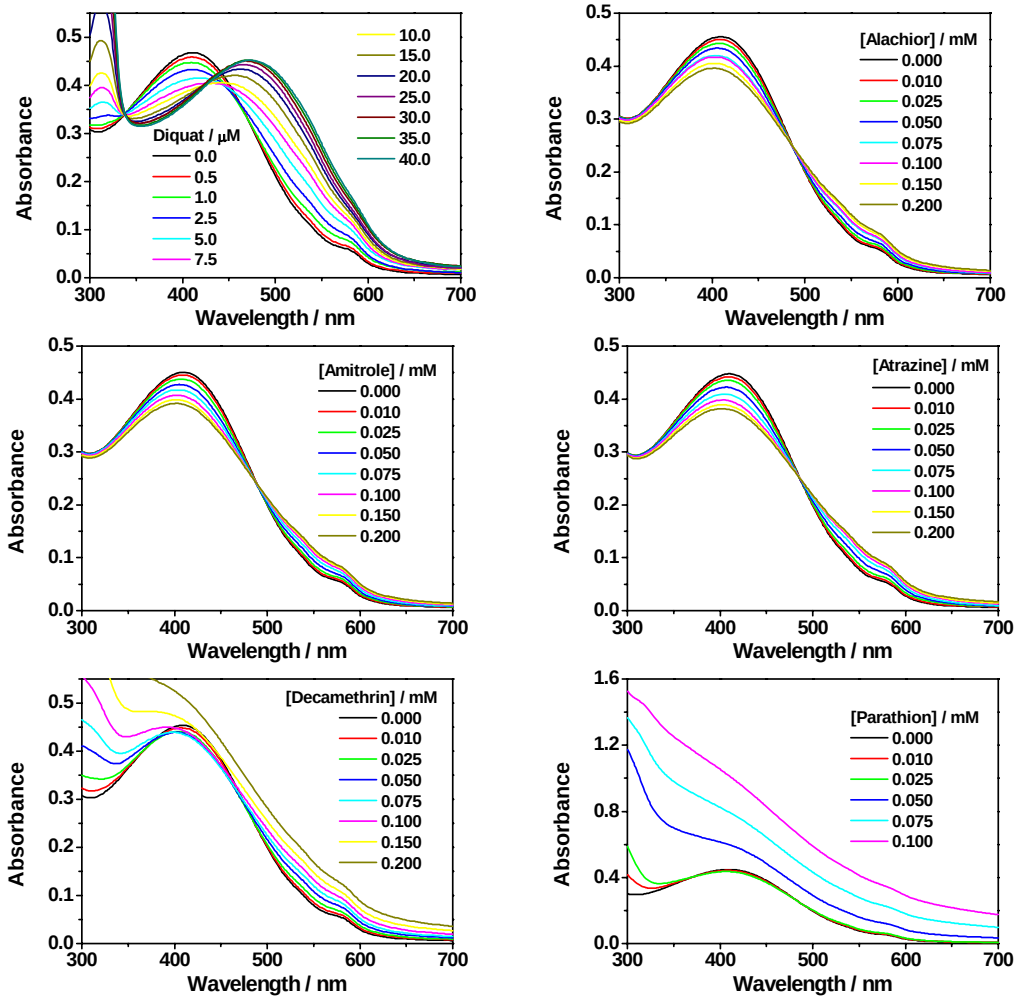

Fig. S3 Absorption spectra of $PMTEMNa_2$ (1.0×10^{-4} M) in the presence of increasing amounts of pesticides in aqueous media. The concentrations of each pesticide were indicated on each spectrum.

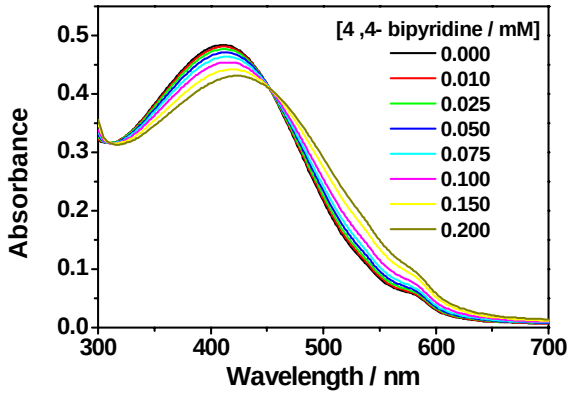

Fig. S4 Absorption spectra of $PMTEMNa_2$ (1.0×10^{-4} M) in the presence of increasing amounts of 4,4'-bipyridine in aqueous media.

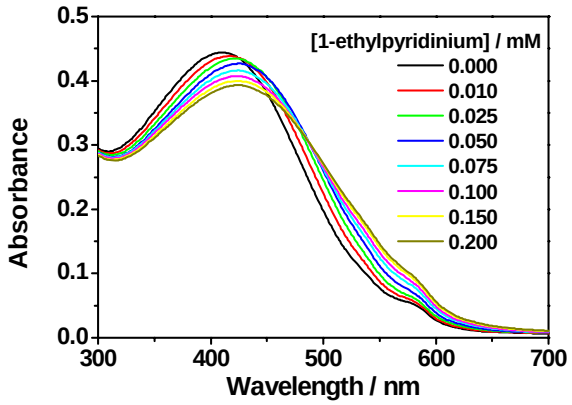

Fig. S5 Absorption spectra of $PMTEMNa_2$ (1.0×10^{-4} M) in the presence of increasing amounts of 1-ethylpyridinium bromide in aqueous media.

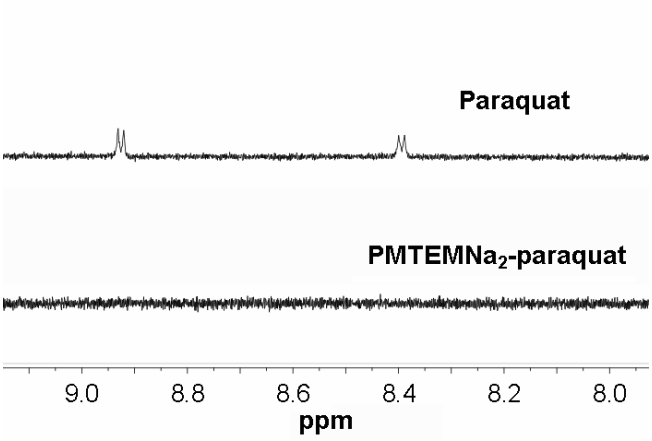

Fig. S6 ^{1}H-NMR spectra of the $PMTEMNa_2$/paraquat complex along with the ^{1}H-NMR spectra of paraquat (solvent: D_2O).

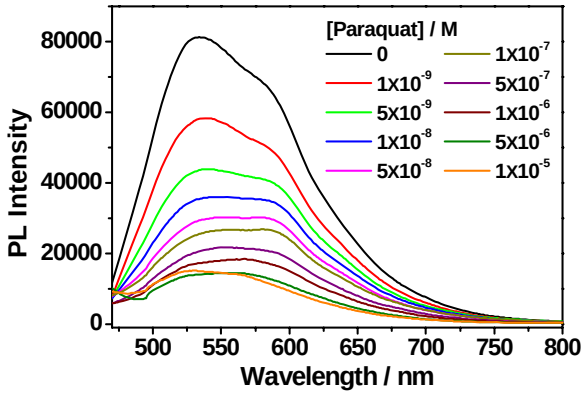

Fig. S7 Emission spectra of $PMTEMNa_2$ (1.0×10^{-5} M) in the presence of increasing amounts of paraquat in aqueous media.

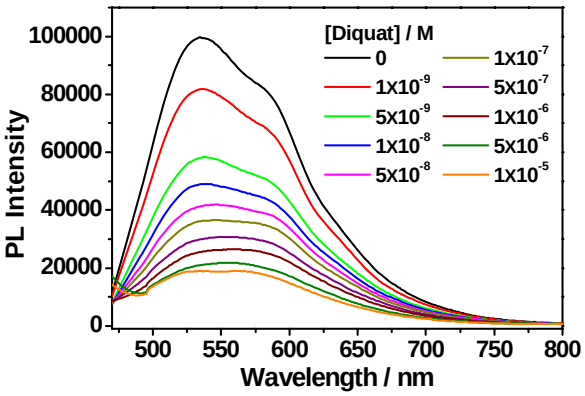

Fig. S8 Emission spectra of $PMTEMNa_2$ (1.0×10^{-5} M) in the presence of increasing amounts of diquat in aqueous media.

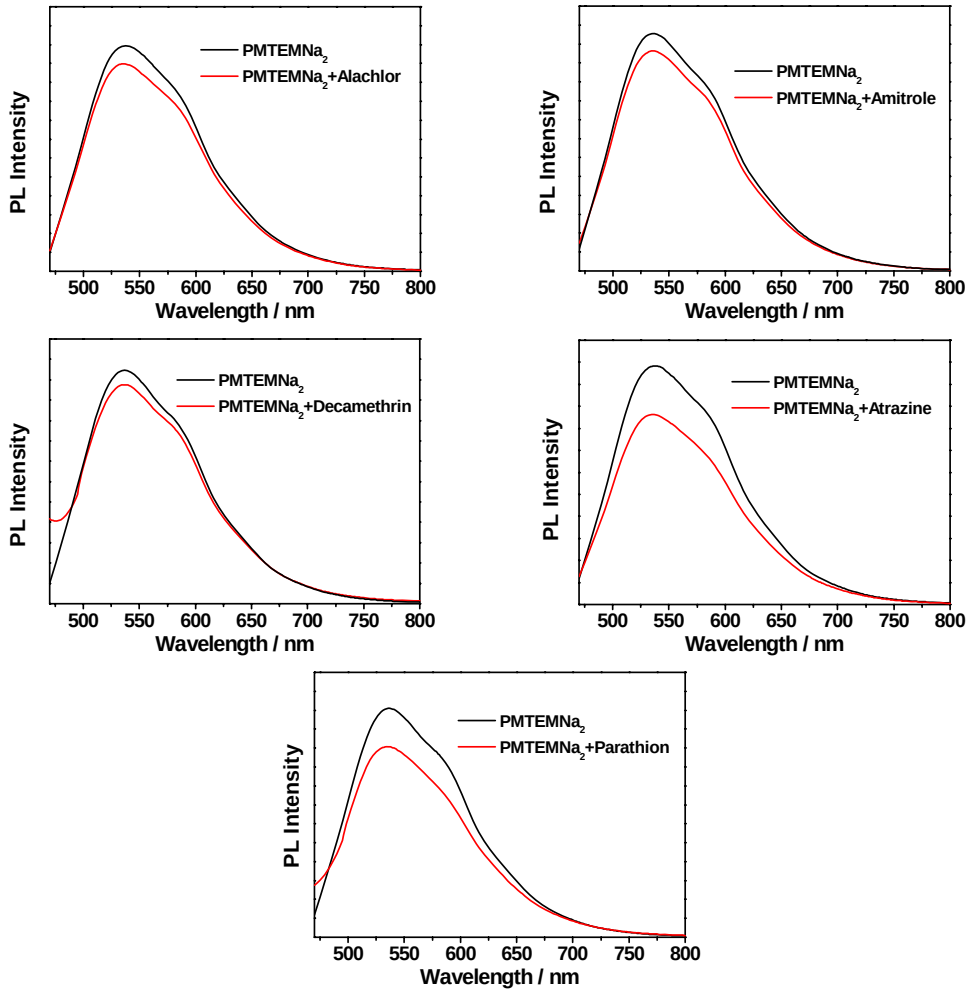

Fig. S9 Emission spectra of $PMTEMNa_2$ in the absence and presence of various analyes as indicated in aqueous media. [$PMTEMNa_2$] = 1.0×10^{-5} M, [analytes] = 1.0×10^{-5} M.

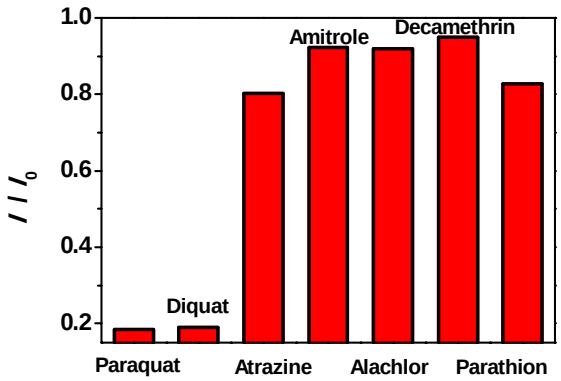

Fig. S10 Relative fluorescence intensity (I/I_0 @ 535 nm) of $PMTEMNa_2$ solutions in the presence of various analytes as indicated. [$PMTEMNa_2$] = 1.0×10^{-5} M, [analytes] = 1.0×10^{-5} M.

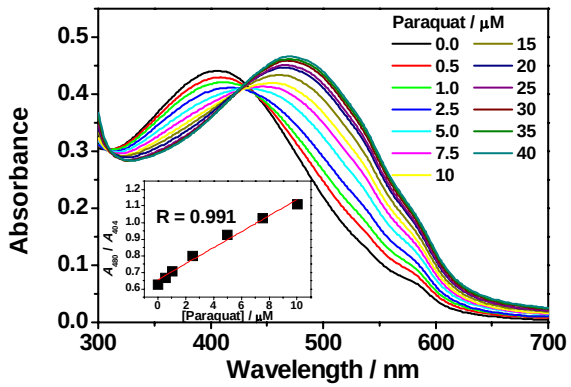

Fig. S11 Absorption spectra of $PMTEMNa_2$ (1.0×10^{-4} M) in the presence of increasing amounts of paraquat in 20 mM phosphate buffer (pH 7.0). Inset: the relationship between A_{480}/A_{404} and the concentration of paraquat from 0.5 to 10 μM.

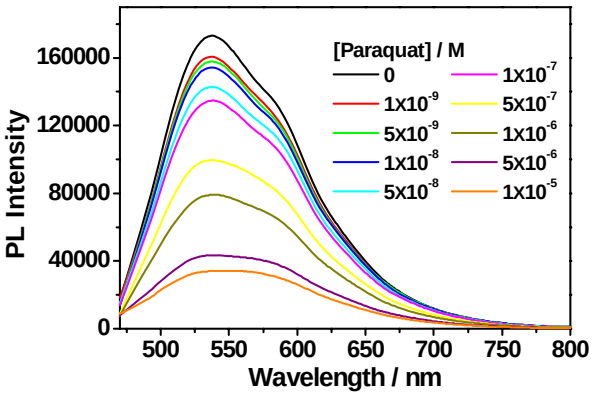

Fig. S12 Emission spectra of $PMTEMNa_2$ (1.0×10^{-5} M) in the presence of increasing amounts of paraquat in 20 mM phosphate buffer (pH 7.0).

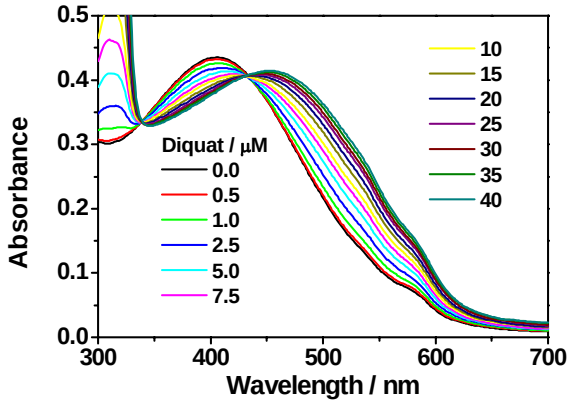

Fig. S13 Absorption spectra of $PMTEMNa_2$ (1.0×10^{-4} M) in the presence of increasing amounts of diquat in 20 mM phosphate buffer (pH 7.0).

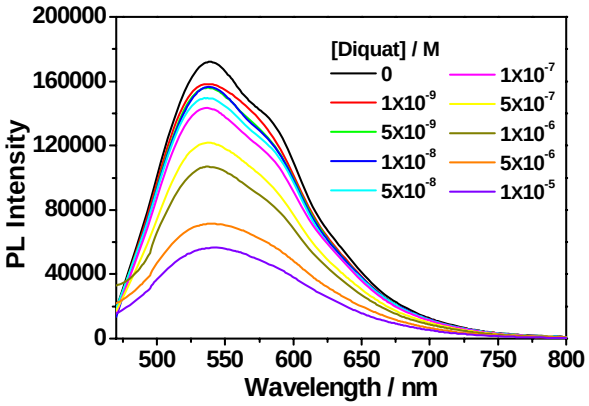

Fig. S14 Emission spectra of $PMTEMNa_2$ (1.0×10^{-5} M) in the presence of increasing amounts of diquat in 20 mM phosphate buffer (pH = 7.0).

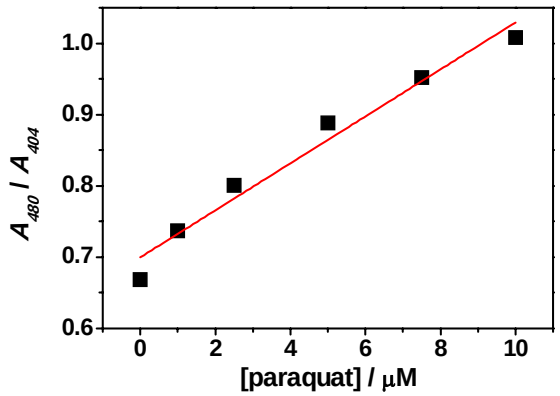

Fig. S15 The relationship between A_{480}/A_{404} and the concentration of paraquat from 0.5 to 10 μM in Chinese cabbage sample.

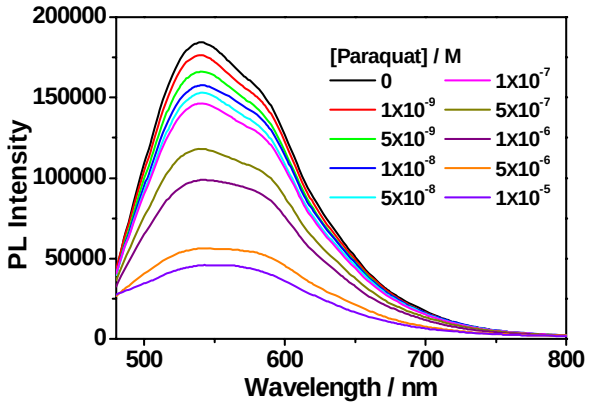

Fig. S16 Emission spectra of $PMTEMNa_2$ (1.0×10^{-5} M) in the presence of increasing amounts of paraquat in Chinese cabbage sample.

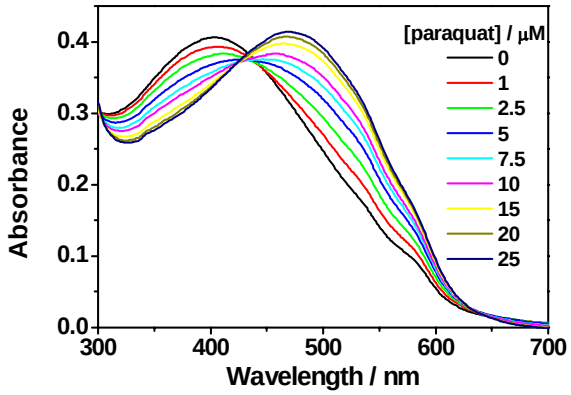

Fig. S17 Absorption spectra of $PMTEMNa_2$ (1.0×10^{-5} M) in the presence of increasing amounts of paraquat in cole sample.

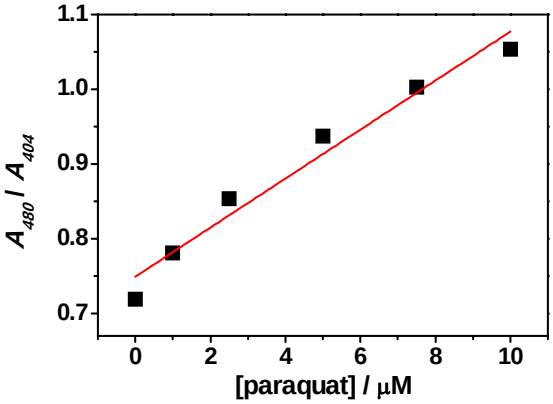

Fig. S18 The relationship between A_{480}/A_{404} and the concentration of paraquat from 0.5 to 10 μM in cole sample.

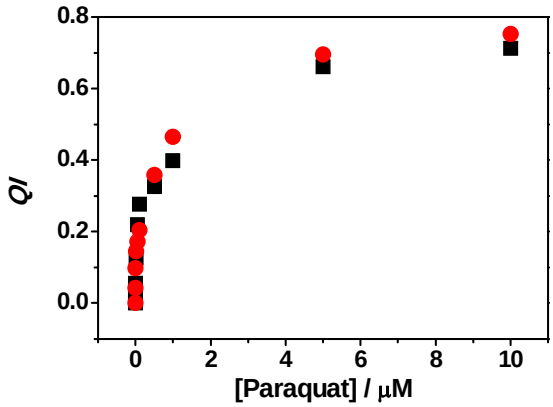

Fig. S19 Fluorescence quenching of $PMTEMNa_2$ (1.0×10^{-5} M) by paraquat at various concentrations in Chinese cabbage (●) and cole (■) samples. The fluorescence quenching $QI = [(I_0\text{-}I)/I_0] \times 100\%$; I_0 and I are the fluorescence intensity at 535 nm of a solution of $PMTEMNa_2$ in the absence and presence of different amounts of analytes, respectively. $\lambda_{ex} = 459$ nm.

Reference:

S1. Z. Y. Yao, X. P. Hu, B. H. Huang, L. Zhang, L. Liu, Y. L. Zhao and H.-C. Wu, *ACS Appl. Mater. Interfaces* 2013, **5**, 5783.