Supplementary Information
‘Metal Free’ fluorescent Supramolecular Assemblies for Distinct Detection of Organophosphate/Organochlorine Pesticides

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**Experimental Section**

1. **General Experimental Methods and Instrumentations**

1.1 **Physical Measurements**  
UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length: 1 cm). The cell holder was thermostat 25°C. The fluorescence spectra were recorded with HORIBA Scientific Fluoromax-4 spectrofluorometer and one of the fluorescence spectra was recorded with SHIMADZU-5301 PC spectrofluorometer. TEM images were recorded from Transmission Electron Microscope HR-TEM-JEOL 2100. The time-resolved fluorescence spectra were recorded with a HORIBA time-resolved fluorescence spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on a JOELFT NMR-AL 400 MHz and BRUKER-AVANCE-II FT-NMR-AL 500 MHz spectrophotometer using CDCl$_3$, DMSO and D$_2$O as solvent and tetramethyl silane, SiMe$_4$ as internal standards. Data are reported as follows: chemical shifts in ppm, multiplicity (s = singlet, br = broad signal, d = doublet, t = triplet, m = multiplet), coupling constants $J$ (Hz), integration, and interpretation. Silica gel 60 (60-120 mesh) was used for column chromatography.

1.2 **UV-vis and Fluorescence Titrations**  
For UV-vis and fluorescence titrations stock solutions (10$^{-4}$ M) of derivative 2 was freshly prepared in DMSO while the stock solutions (10$^{-4}$ M) of derivatives 1, 3, 4 and 5 were prepared in THF. For each experiment, titrations were performed with solutions of all the derivatives in H$_2$O prepared by mixing 300 µl of stock solution with 2700 µl distilled H$_2$O. Typically, aliquots of freshly prepared standard solutions (10$^{-2}$ M) of metal ions such as Fe$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Ag$^+$ and Al$^{3+}$ ions as their perchlorate salt. In titration experiments, each time a 3 ml solution of derivative 2 was filled in a quartz cuvette (path length, 1 cm) and spectra were recorded.
Biomolecules such as spermine, spermidine, glutathione, cysteine, homocysteine, hydrazine, H$_2$O$_2$, ClO$^-$ and amines were freshly prepared in distilled water. In each titration experiments, 3 mL, 1µM solutions of derivative 2 were filled in a quartz cuvette (path length, 1 cm) and biomolecules were added into the quartz cuvette by using a micro-pipette.

1.3 Calculation of detection limit

The calculations of detection limit was based on the fluorescence titrations. To determine S/N ratio, the emission intensity of all the derivatives (2, 3, 4 and 5) without additions of pesticides (CPF and DCN) was measured 10 times and standard deviations of blank measurements was determined. The detection limit was calculated by using following equation:

\[
DL = 3 \times \frac{SD}{S}
\]

Where SD is the standard deviation of blank solution measured by 10 times and S is slope of the calibration curve.

1.4 Analysis in real samples

Apples and grapes were chosen for evaluating potential of CPF and DCN in real samples. After washing with water, these were chopped and crushed to make a homogenate. The 10g of homogenate was mixed with 10 ml of methanol and was filtered twice using fine paper to remove the insoluble particles. Then different volumes (0, 10, 30, 50, 70 and 100 µl) of CPF and DCN solution was mixed with 1ml solution of above homogenate of apple and grapes juice respectively and their fluorescence spectra was recorded.

1.5 Determination of residues of DCN in real samples
Grapes were used to measure the residue level of DCN with time. For this, solution of DCN ($10^{-2}$M) was used was spiked on skin of grapes and stored for overnight at room temperature. Then samples were prepared by using method outlined above. The samples were prepared each day for four consecutive days and their fluorescence spectra was recorded every day.

2. Synthesis and Characterization

2.1 Synthesis of derivative 2

9, 10-dibromoanthracene 6 and 4-formyl phenyl boronic acid 7 in dioxane were added in a two neck rbf followed by addition of K$_2$CO$_3$ in distilled water (1mL) and Pd (0) and reaction was refluxed under nitrogen for overnight. Then after evaporating solvent under vacuum residue was extracted using CHCl$_3$/water and dried over anhydrous Na$_2$SO$_4$. Then after removing organic layer under pressure, residue was purified using column chromatography using hexane/CHCl$_3$, 1:9 to furnish derivative 2 as yellow solid in 50% yield. $^1$H NMR (400 MHZ, CDCl$_3$): $\delta$ (ppm) = 7.36-7.40 (m, 4H, Ar-H), 7.60-7.64 (m, 4H, Ar-H), 7.68 (d, $J = 10$ Hz, 4H, Ar-H), 8.16 (d, $J = 10.4$ Hz, 4H, Ar-H) and 10.2 (s, 2H, CHO). $^{13}$C NMR (100 MHZ, CDCl$_3$): $\delta$ = 125.69, 126.51, 129.38, 129.92, 132.12, 135.75, 136.15, 145.77, 192.10. ESI-MS calculated for C$_{26}$H$_{18}$O$_2$: 386.131; Found: 387. 15 for [M+H]$^+$. 

Scheme S1: Synthesis of derivative 2
2.2 Synthesis of derivative 8

Derivative 8 was synthesized according to previous reported method.³

2.3 Synthesis of derivative 3

![Scheme S2: Synthesis of derivative 3.]

Derivative 8 and phenyl boronic acid 7 in Dioxane were added in a two neck rbf followed by addition of K$_2$CO$_3$ in distilled water (1mL) and Pd (0) and reaction was refluxed under nitrogen for overnight. Then after evaporating solvent under vacuum residue was extracted using CHCl$_3$/water and dried over anhydrous Na$_2$SO$_4$. Then after removing organic layer under pressure, residue was purified using column chromatography using hexane/CHCl$_3$, 1:8 to furnish derivative 3 as dark reddish solid in 52% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ = 0.85 (t, J = 8Hz, 6H), 1.16-1.30 (m, 36H), 1.65-1.72 (m, 4H), 4.16 (t, J = 8Hz, 4H), 7.42-7.53 (m, 10H, Ar-H), 7.75-7.81 (m, 2H, Ar-H), 8.11-8.15 (m, 2H, Ar-H), 8.61 (d, J = 4Hz, 2H, Ar-H).

Synthesis of derivative 4 and 5

Derivative 4 and 5 were also synthesized according to previous reported method.³
**Figure S1**: $^1$H NMR of derivative 2 in CDCl$_3$ as solvent (400MHz).
Figure S2: $^{13}$C NMR spectrum of derivative 2 (100MHz).
Figure S3: $^1$H NMR spectrum of derivative 3 (400MHz).
Figure S4: Mass spectrum of derivative 2.

Figure S5: UV-vis spectra of derivative 2 (10µM) in THF and water.
**Figure S6**: Fluorescence spectra of derivative 2 (10µM) in THF and water, λ<sub>ex</sub> = 380 nm, slit = 3-3.

**Figure S7**: Concentration dependent ¹H NMR of derivative 2 a) 3 mg b) 10 mg in CDCl<sub>3</sub>.
Figure S8: UV-vis spectra of derivative 2 (10µM) upon addition of Cu$^{2+}$ ions (0-150 equiv.) in 90% water.

Figure S9: XPS spectra of Cu 2p region of assemblies of derivative 2.

Figure S10: Fluorescence spectra of assemblies of derivative 2 (10µM) with addition of 150 equiv. of Cu$^{2+}$ ions, λex = 380 nm, slit = 3-3.
Figure S11: Bar diagram of derivative 2 (10µM) with different biomolecules in 90% water, λ<sub>ex</sub> = 380 nm, slit = 3-3.

Figure S12: Bar diagram of derivative 2 (10µM) with different metal ions in 90% water, λ<sub>ex</sub> = 380 nm, slit = 3-3.

Figure S13: Bar diagram of derivative 2 (10µM) with different amines in 90% water, λ<sub>ex</sub> = 380 nm, slit = 3-3.
Figure S14: UV-vis spectra of assemblies of derivative 2 (10µM) on addition of CPF (100 equiv.) in 90% water, $\lambda_{ex} = 380$ nm.

Figure S15: a) CIE coordinates of assemblies of derivative 2 (10µM) in aqueous solution b) in presence of CPF.

Figure S16: Calibration curve showing fluorescence intensity of derivative 2 (10µM) at 475 nm as a function of CPF concentration (equiv.) in 90% water, $\lambda_{ex} = 380$ nm.
From the graph, slope (S) = 806431 and standard deviation (SD) = 0.009
Then using the formula we get the detection limit = 3×0.009/806431 = 3.34×10⁻⁸ M

From the graph, slope (S) = 7×10^3 and standard deviation (SD) = 0.009
Then using the formula we get the detection limit = 3×0.009/7×10^3 = 3.85×10⁻⁶ M
**Figure S19**: UV-vis spectra of assemblies of derivative 2 on addition of DCN (150 equiv.) in 90% water, $\lambda_{ex} = 380$ nm, slit= 3-3.

**Figure S20**: Fluorescence spectra of solution of derivative 2 in presence of DCN (150 equiv.) with changing excitation wavelength from 310 nm to 400 nm.

**Figure S21**: Calibration curve showing fluorescence intensity of derivative 2 (10µM) at 475 nm as a function of DCN concentration (equiv.) in 90% water, $\lambda_{ex} = 380$ nm.
From the graph, slope (S) = 456832 and standard deviation (SD) = 0.009

Then using the formula we get the detection limit = \(3 \times 0.009 / 80000000 = 3.3 \times 10^{-10}\) M

Figure S22: Bar diagram of assemblies of derivative 2 (10µM) in 90% water in presence of different pesticides (CPF, DCN, BPA, dichlorvos, glyphosate and DCP).

Figure S23: Fluorescence life time spectra of derivative 2 (10µM) at 475 nm in 90% water and in presence of CPF.
Figure S24: Overlay $^1$H NMR spectra of a) derivative 2 b) CPF c) derivative 2 in presence of CPF in DMSO-d$_6$-D$_2$O (500 MHz).

Figure S25: XRD diffraction pattern of a) assemblies of derivative 2 b) in presence of CPF
Figure S26: DLS data of assemblies of derivative 2 (10µM) in 90% aqueous solution with average particle size of 365.1 nm

Figure S27: DLS data of assemblies of derivative 2 (10µM) in 90% water in presence of CPF with average particle size of 231.0 nm.
**Figure S28:** Fluorescence lifetime spectra of derivative 2 (10µM) at 475 nm in 90% water and in presence of DCN.

**Figure S29:** XRD diffraction pattern of assemblies of derivative 2 in presence of DCN.

**Figure S30:** DLS data of assemblies of derivative 2 (10µM) in 90% water in presence of DCN (150 equiv.) with average particle size of 542.5 nm.
Figure S31: Spectral overlapping graph of absorption spectrum of DCN and emission spectrum of assemblies of derivative 2 (10µM) in 90% water.

Figure S32: a) UV-vis spectrum b) fluorescence spectrum of derivative 3 (10µM) in 90% water.

Figure S33: Fluorescence spectrum of derivative 3 (10µM) in presence of DCN (150 equiv.) in 90% water, λex = 525 nm
From the graph, slope (S) = 725696 and standard deviation (SD) = 0.012

Then using the formula we get the detection limit = \(3 \times 0.012 / 725696 = 4.96 \times 10^{-8} \text{ M}\)
From the graph, slope (S) = $3 \times 10^{-6}$ and standard deviation (SD) = 0.011

Then using the formula we get the detection limit = $3 \times 0.011/3 \times 10^{-6} = 1.1 \times 10^{-8}$ M
From the graph, slope \((S) = 34531\) and standard deviation \((SD) = 0.012\)

Then using the formula we get the detection limit = \(3 \times 0.012/34531 = 1.04 \times 10^{-6}\) M
From the graph, slope \((S) = 2 \times 10^6\) and standard deviation \((SD) = 0.012\)

Then using the formula we get the detection limit \(= 3 \times 0.012/874788 = 1.8 \times 10^{-8}\) M

**Figure S42:** Calibration curve showing fluorescence intensity of derivative 5 (10µM) at 458 nm as a function of DCN concentration (equiv.) in 90% water, \(\lambda_{ex} = 320\) nm.

**Figure S43:** a) plot of \(F/F_0\) versus different concentrations of CPF in apple b) DCN in grapes juice.

**Figure S44:** Bar graph of \(F/F_0\) values for DCN residues in grapes juice in four consecutive days.
| No | Pesticide Class | Type of Detection | Type of Derivatives | Reaction-Mediated Change | Type of Response | Sensing Media | Real-time Application in | Design of MoF/Polyaminals | | |
|----|----------------|-------------------|-----------------|------------------------|-----------------|---------------|------------------------|---------------------------|---|---|
| 1  | Organochlorine | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 2  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 3  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 4  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 5  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 6  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 7  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 8  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 9  | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |
| 10 | Organophosphate | Fluorescence, UV  | Simple anthracene/PBI derivatives | Interaction between pesticide and MoF | "Turn off" | Ethanol, THF, DMF, CHCl₃ and water | Real-time in fruits/vegetables | Using PBI/hexaphenylbenzene based scaffolds | | |

Table S1: Comparison table for sensing of pesticides with other literature reports.
References

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