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# Facile detection of organophosphorus nerve agent mimic (DCP) through a new quinoline-based ratiometric switch

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## 1. Mole ratio plot

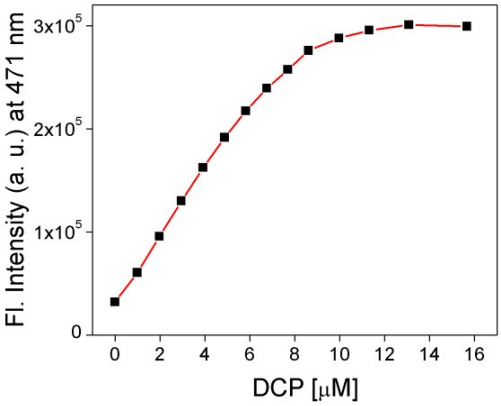



**Figure S1:** Plot of emission intensity at 471 nm of BIMQ (10 μM) depending upon the DCP concentration.

## 2. Determination of detection limit

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of BIMQ without DCP was measured by 10 times and the standard deviation of blank measurements was determined. The detection limit (DL) of BIMQ for DCP was determined from the following equation: DL = K × $Sb_1$/S, Where K = 2 or 3 (we take 3 in this case); $Sb_1$ is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph we get slope = $3.03\times10^{10}$, and $Sb_1$ value is 947.6 Thus using the formula we get the Detection Limit = $9.38\times10^{-8}$ M i.e. BIMQ can detect DCP in this minimum concentration by fluorescence techniques.

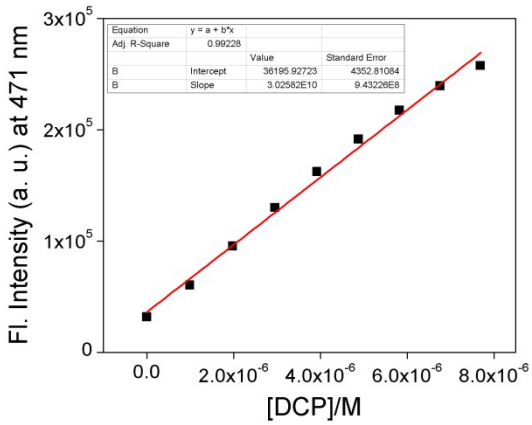



**Figure S2:** The linear response curve of at emission intensity at 471 nm of BIMQ depending on DCP concentration.

## 3. Lifetime decay profile

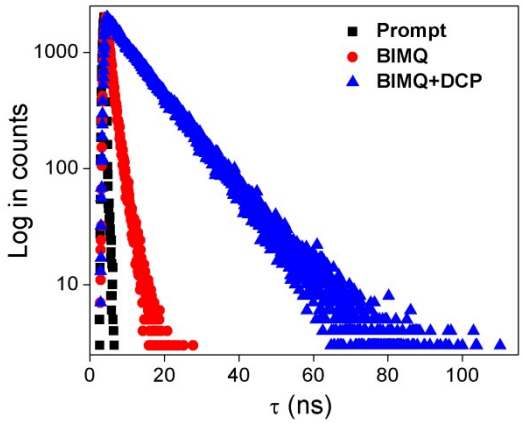



**Figure S3:** Lifetime decay profile of BIMQ and BIMQ-DCP

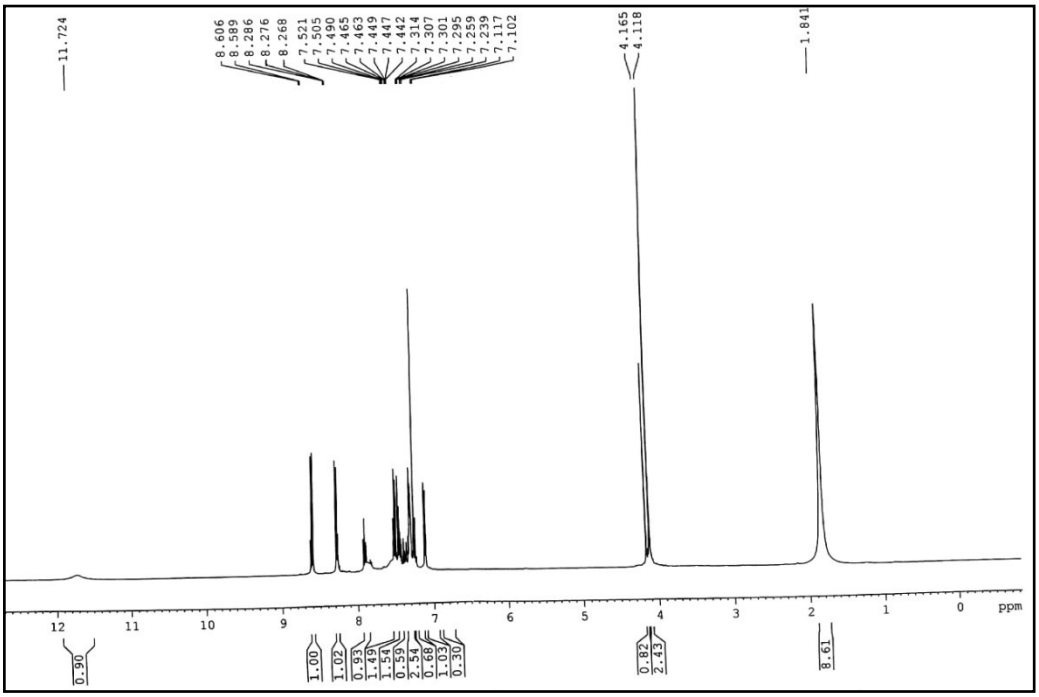
## 4. Determination of Quantum yield of BIMQ

For measurement of the quantum yields of BIMQ and its reaction product with DCP (BIMQ-DCP), we recorded the absorbance of the compounds in $CHCl_3$ solution. The emission spectra were recorded using the maximal excitation wavelengths and the integrated areas of the emission-corrected spectra were measured. The quantum yields were then calculated by comparison with quinine sulfate ($\varphi_s$ = 0.54 in 0.5M $H_2SO_4$) as reference using the following equation:

$$\Phi_x = \Phi_s \times \left(\frac{Ix}{Is}\right) \times \left(\frac{As}{Ax}\right) \times \left(\frac{nx}{ns}\right)^2$$

Where, x & s indicate the unknown and standard solution respectively, Φ is the quantum yield, I is the integrated area under the fluorescence spectra, A is the absorbance and n is the refractive index of the solvent. We calculated the quantum yields of BIMQ and BIMQ-DCP using the above equation and the values are 0.31 and 0.48 respectively.

## 5. $^{1}$H NMR spectrum of BIMQ



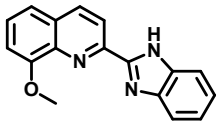




**Figure S4:** $^{1}$H NMR (400 MHz) spectrum of the probe (BIMQ) in $CDCl_3$

## $^{13}$C NMR spectrum of BIMQ

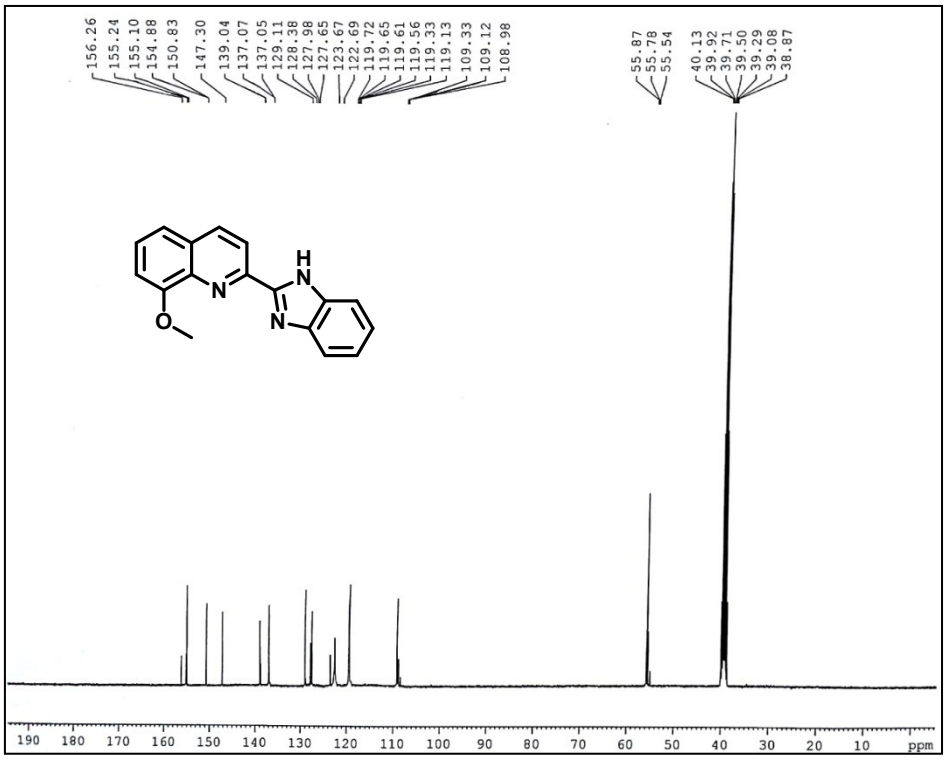



**Figure S5:** $^{13}C$ NMR (100 MHz) spectrum of the probe (BIMQ) in DMSO-$d_6$

## Mass spectrum (HRMS) of BIMQ

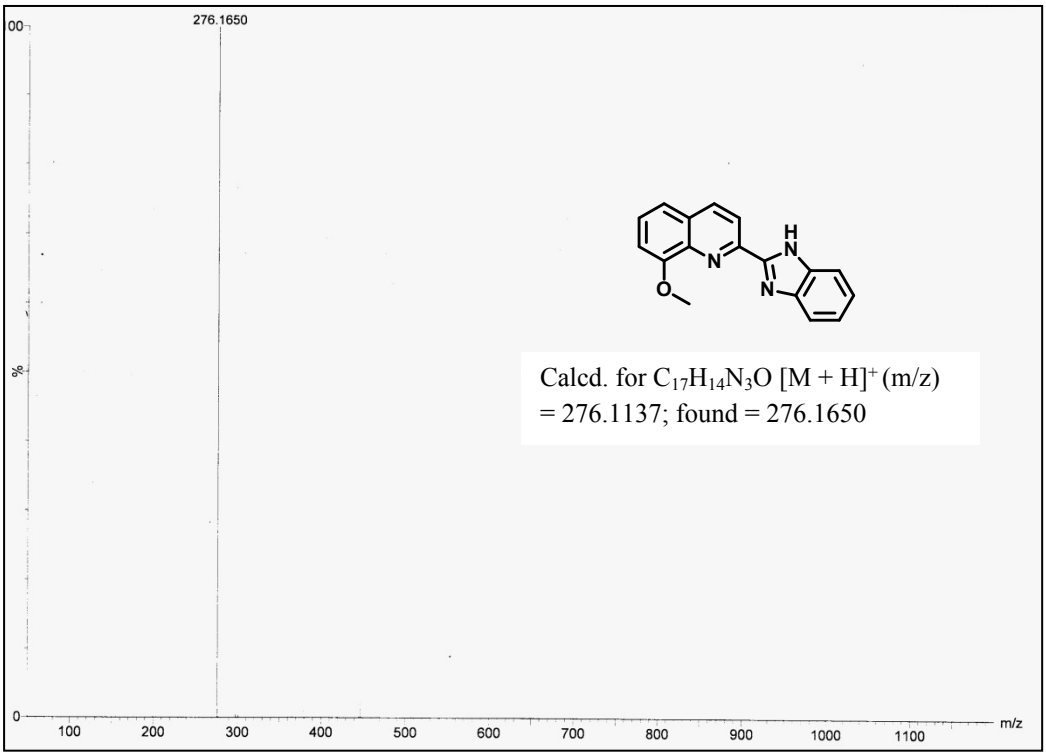
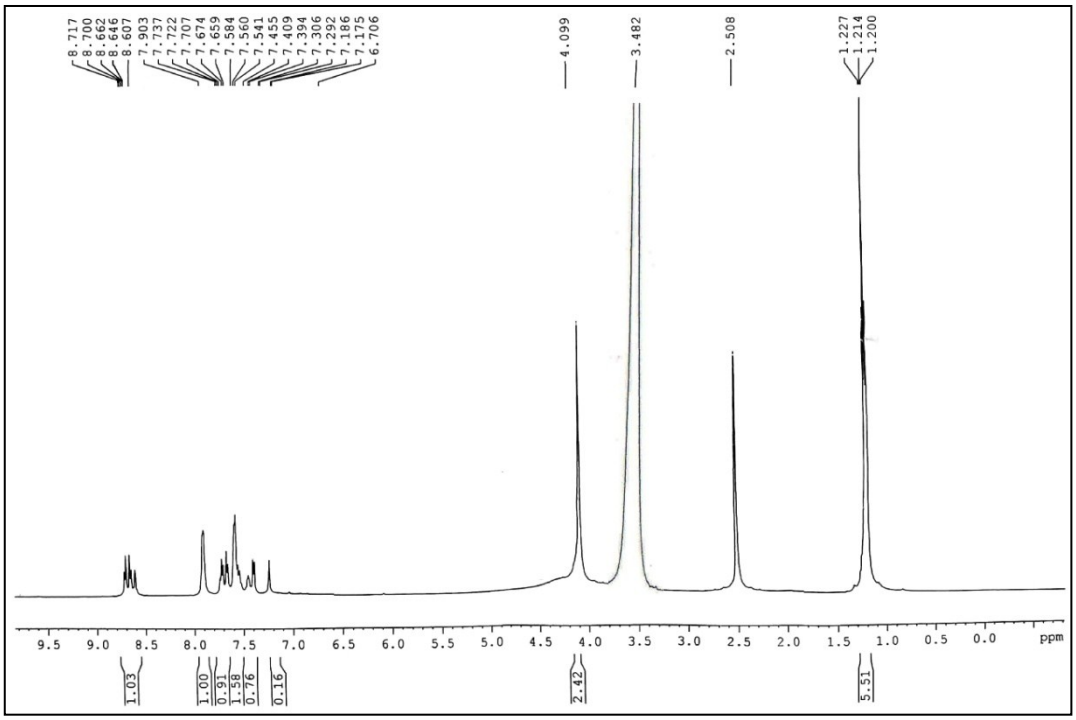



**Figure S6:** HRMS of the probe (BIMQ)

## $^{1}$H NMR spectrum of BIMQ-DCP



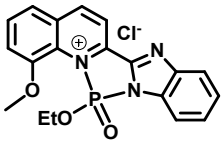




**Figure S7:** $^{1}$H NMR (400 MHz) spectrum of the BIMQ-DCP in DMSO-$d_6$

## $^{13}$C NMR spectrum of BIMQ-DCP

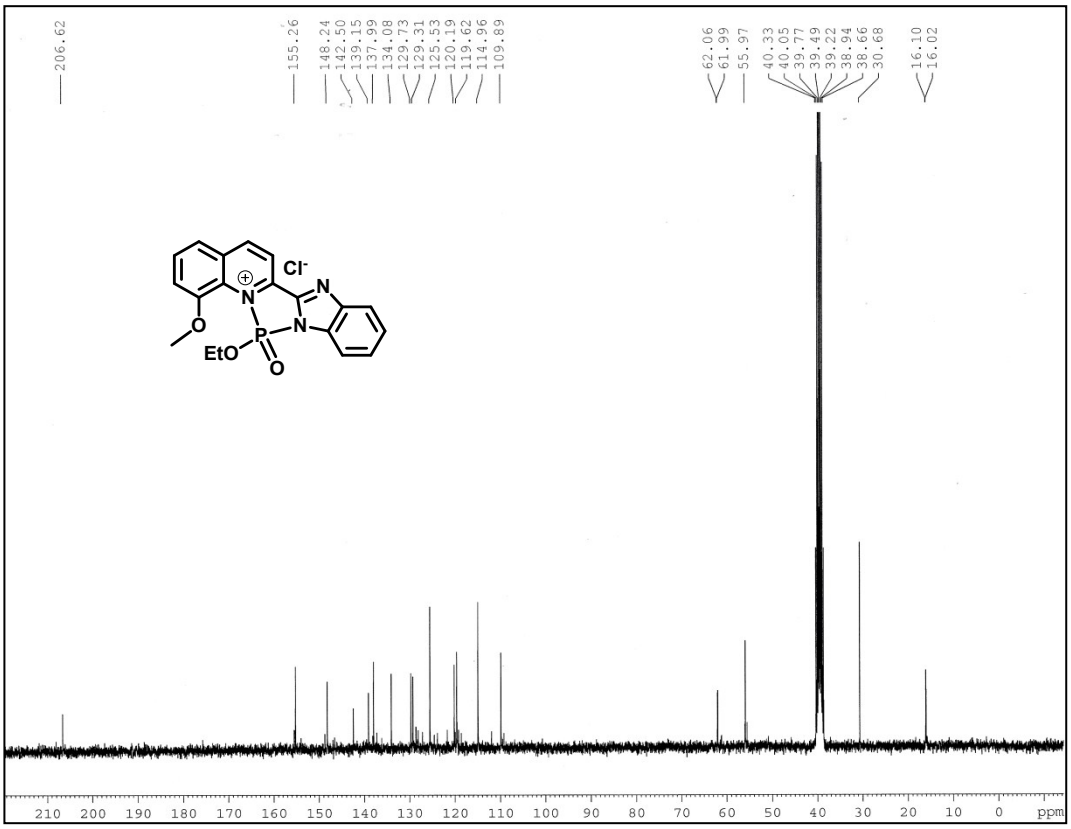
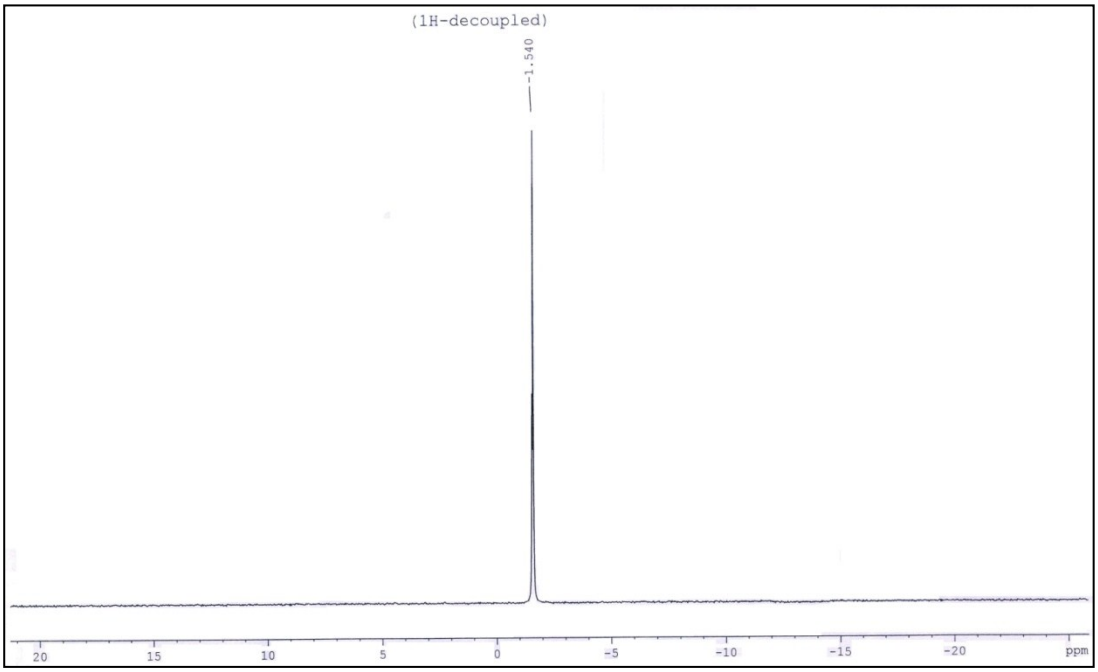



**Figure S8:** $^{13C}$ NMR (100 MHz) spectrum of the BIMQ-DCP in DMSO-$d_6$

## $^{31}$P NMR spectrum of BIMQ-DCP



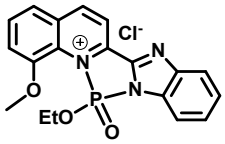



**Figure S9:** $^{31}P$ NMR (100 MHz) spectrum of the BIMQ-DCP in $CDCl_3$

## Mass spectrum (HRMS) of BIMQ-DCP

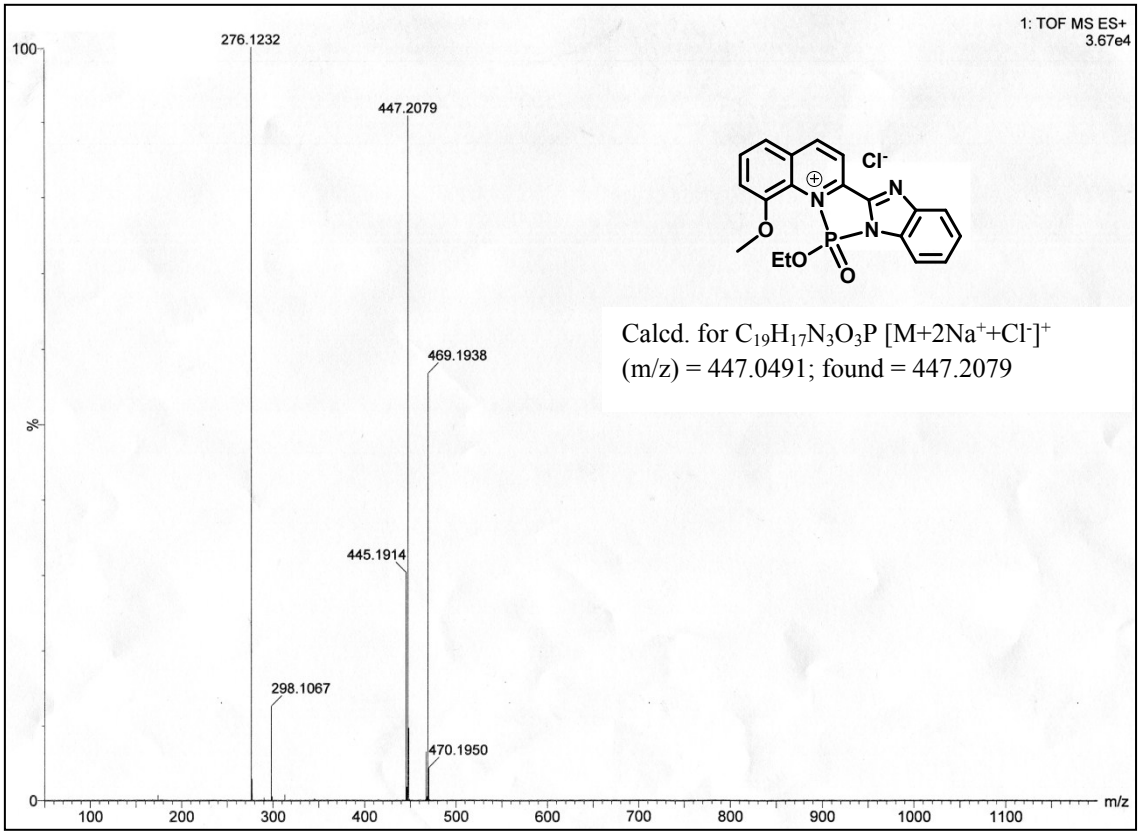



**Figure S10:** HRMS of BIMQ-DCP

## 6. Computational Study

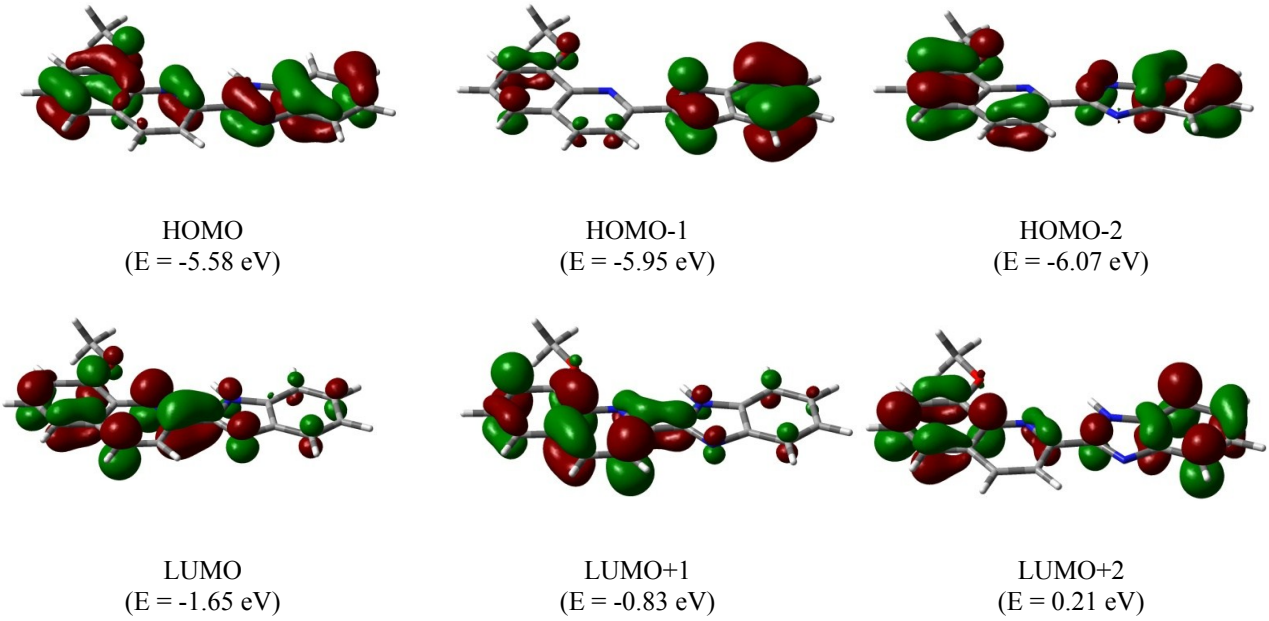



**Figure S11:** Contour plots of some selected molecular orbitals of BIMQ

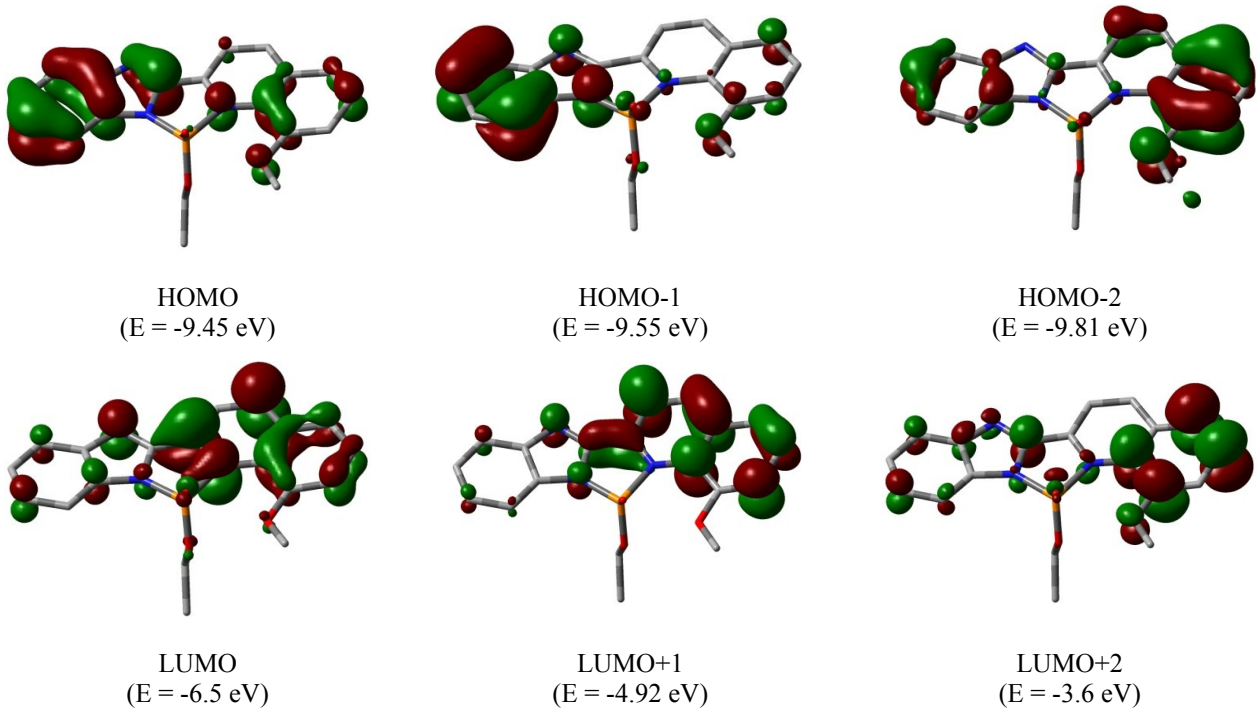



**Figure S12:** Contour plots of some selected molecular orbitals of BIMQ-DCP

Table S1: Vertical electronic transition of BIMQ and BIMQ-DCP calculated by TDDFT/CPCM method

| Compd. | Wavelength (nm) | Energy (eV) | Osc. Strength (f) | Key transitions | Character |
|---|---|---|---|---|---|
| BIMQ | 357.9 | 3.4636 | 0.3933 | (94%)HOMO→LUMO | $\pi\rightarrow\pi^*$ |
| | 329.4 | 3.7641 | 0.3283 | (73%)HOMO-1→LUMO | $\pi\rightarrow\pi^*$ |
| | 316.6 | 3.9164 | 0.0264 | (85%)HOMO-2→LUMO | $\pi\rightarrow\pi^*$ |
| | 264.6 | 4.6850 | 0.0151 | (74%)HOMO-1→LUMO+1 | $\pi\rightarrow\pi^*$ |
| | 258.2 | 4.8018 | 0.0508 | (83%)HOMO-2→LUMO+1 | $\pi\rightarrow\pi^*$ |
| BIMQ-DCP | 496.6 | 2.4965 | 0.0257 | (74%)HOMO→LUMO | $\pi\rightarrow\pi^*$ |
| | 443.2 | 2.7972 | 0.3032 | (65%)HOMO-1→LUMO | $\pi\rightarrow\pi^*$ |
| | 439.2 | 2.8227 | 0.3346 | (80%)HOMO-2→LUMO | $\pi\rightarrow\pi^*$ |
| | 309.1 | 4.0110 | 0.0853 | (46%)HOMO→LUMO+1 | $\pi\rightarrow\pi^*$ |
| | 280.2 | 4.4240 | 0.0454 | (59%)HOMO-1→LUMO+1 | $\pi\rightarrow\pi^*$ |

Table S2: The comparison of the present probe (BIMQ) with some previous probes for DCP

| **Fluorophore used** | **Type of response** | **Response Time (min or sec)** | **Test kit** | **Detection limit** | **Detection in gaseous phase** | **Reference** |
|---|---|---|---|---|---|---|
| Hybrid hydroxynaphthalene–hemicyanine | Colorimetric, fluorometric (ratiometric) | Within few minutes | Yes (Dip-stick method) | 18.86 nM | Yes | *Org. Biomol. Chem., 2017, 15, 5959* |
| No fluorophore; only malononitrile derivative | Colorimetric, fluorometric | Within minutes | Yes (Dip-stick method) | 0.10 μM | Yes | *Analyst, 2018, 143, 4171* |
| Diphenylamine-Tetraphenylethylene-pyridine (DPA-TPE-Py) | Aggregation based Fluorometric (ratiometric) | 30 sec | Yes (Dip-stick method) | 1.82 ppb | Yes | *J. Mater. Chem. C, 2016, 4, 10105* |
| Rhodamine B | Colorimetric, fluorometric (turn-on) | Few Sec | Not mentioned | $1.1\times10^{-7}$ M and $2.4\times10^{-8}$ M | Yes | *Chem. Commun.*, 2014, 50, 8640 |
| Napthothiazolium conjugated benzothiazole | Chromogenic, fluorogenic (ratiometric) | Within 1 minute | Yes (Dip-stick method) | 17 nM | Yes | *Chem. Commun., 2015,51, 9729* |

| | | | | | | |
|---|---|---|---|---|---|---|
| derivative | | | | | | |
| Coumarin-4-dimethyaminoaryl | Fluorometric (ratiometric) | 5 minutes | Not mentioned | $4.4\times10^{-8}$ M | Yes | *New J. Chem.*, 2017,41, 1653 |
| Triphenylamine | Colorimetric, fluorometric (ratiometric) | 100 Sec | Yes (Dip-stick method) | $6.99\times10^{-8}$ M | Yes | *New J. Chem., 2017,41, 12562* |
| Rhodamine B | Colorimetric, fluorometric (turn-on) | 60 Sec | Yes (Dip-stick method) | $5.5\times10^{-8}$ M | Yes | *RSC Adv.*, 2014, 4, 24881. |
| Combination of spirobenzopyran and naphthalene | Colorimetric, fluorometric (turn-on) | After 30 seconds | Yes (Dip-stick method) | $2.1\times10^{-8}$ M | Yes | *RSC Adv., 2015, 5, 28996* |
| Aminoquinolin oximes | Colorimetric, fluorometric (ratiometric) | Within 10 minutes | Yes (Dip-stick method) | 21 nM | Yes | *J. Mater. Chem. C, 2017,5, 7337* |
| No fluorophore in particular | Fluorometric (turn-on) | After 10 seconds | Yes (Test strip method) | 1.94 nM | Yes | *Anal. Methods*, *2018, 10, 1709* |
| No fluorophore; only hydroxybenzylidene-malononitrile derivative | Colorimetric, fluorometric (turn-on) | Within minutes | Yes (Test strip method) | 0.10, 0.11 and 0.20 µM | Yes | *Analyst, 2018, 143, 4171* |
| No fluorophore | Fluorometric (turn-off) | Almost 2 minutes | Yes (Spot Testing Device) | 0.023 and 0.092 mM | Yes | *New J. Chem., 2018, 42, 8756* |
| No fluorophore in particular; fluorene-pyrene copolymer | Fluorometric (turn-on) | Within 3 seconds | Yes (Test strip method) | 132 ppb | Yes | *Anal. Methods, 2017, 9, 1748* |
| No fluorophore | Fluorometric (ratiometric) | Within 1 minute | Yes (Test strip method) | 0-45 µM | Yes | *J. Mater. Chem. C, 2017, 5, 7337* |
| Quinoline | Fluorometric (ratiometric) | Almost 30 seconds | Yes (Dip-stick method) | $9.38 \times 10^{-8}$ M | Yes | Present Work |