Supplementary Information (SI) for Analyst.

SUPPORTING INFORMATION

Sustainable, Biodegradable Paper Sensor Functionalized with Oxidized Bisindolylmethane for Temporal Discrimination of Hazardous Organophosphorus Simulants in Aqueous Media

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EXPERIMENTAL SECTION

1.1 General: All chemicals (solvents, reagents, and chemicals) were purchased from the best-known local chemical suppliers and used without further purification. Solvents were distilled and dried before use. FTIR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX system and were reported in wave numbers (cm^{-1}). On the other hand, ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance Neo spectrometer operating at 400 and 100 MHz for ^1H and ^{13}C NMR spectroscopy, respectively. Chemical shifts were reported in ppm downfield from the internal standard, tetramethyl silane (TMS). Mass spectra were recorded on Shimadzu LC-MS.

1.2 Spectroscopic studies. The UV-vis spectroscopic studies were recorded on a JASCO (model V-650) UV-Vis spectrophotometer. The slit-width for the experiment was kept at 5 nm. Sensing was carried out by adding requisite amounts of DCP/DCNP to aqueous solutions (pH 8) of probe 1 (10×10^{-6} M).

1.3 NMR studies: The ^1H-NMR titration studies of probe 1 were performed with DCNP (0.5 equiv) in DMSO-d_6/D_2O medium. All the spectra were recorded under similar experimental conditions with identical experimental parameters.

General Procedure for the synthesis of Oxidized Bis(indolyl)arylmethanes (1 and 2).

A mixture of 4-substituted benzaldehyde (1.0 equiv), indole (2.0 equiv), and iodine (0.05-0.10 equiv) in methanol (4 mL) was stirred at room temperature. To this mixture, a methanolic solution of DDQ (1.0 equiv) was added dropwise over 15-20 min. The reaction mixture was stirred until a precipitate formed, which was then allowed to settle. The resulting solid was collected by filtration, washed successively with methanol and ethyl acetate, and dried under vacuum to afford the corresponding oxidised di(indolyl)arylmethane derivatives (1 and 2).

Characterization data

Compound 1: ^{1}H NMR (400 MHz, DMSO-d6): δ 12.17 (bs, 1H), 8.21 (s, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.28 (t, J = 7.9 Hz, 2H), 7.05 (t, J = 7.4 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H); HRMS *m/z* calcd for $C_{23}H_{17}N_2O$ $(M+H)^+$ 337.1341, found 337.1339.

Compound 2: ^{1}H NMR (400 MHz, DMSO): δ 8.39 (s, 2H), 7.63 (dd, J = 15.9, 8.4 Hz, 4H), 7.37 - 7.30 (m, 2H), 7.21 (d, J = 8.8 Hz, 2H), 7.14 - 7.08 (m, 2H), 6.82 (d, J = 8.0 Hz, 2H). NH is not observed; HRMS *m/z* calcd for $C_{24}H_{19}N_2O$ $(M+H)^+$ 351.1497, found 351.1498.

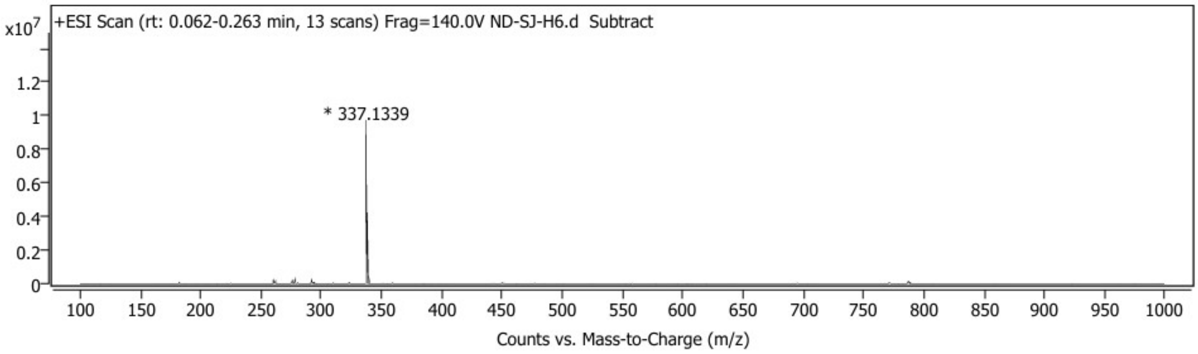


Figure. S1: HRMS of compound 1.

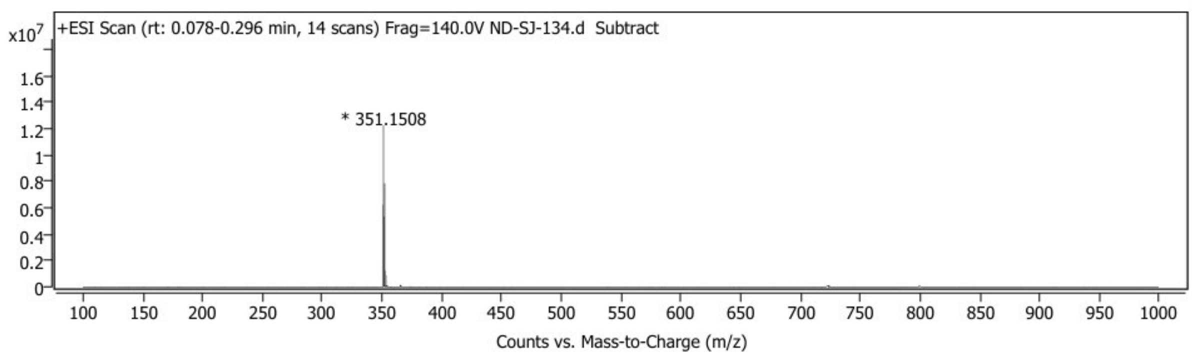


Figure. S2: HRMS of compound 2.

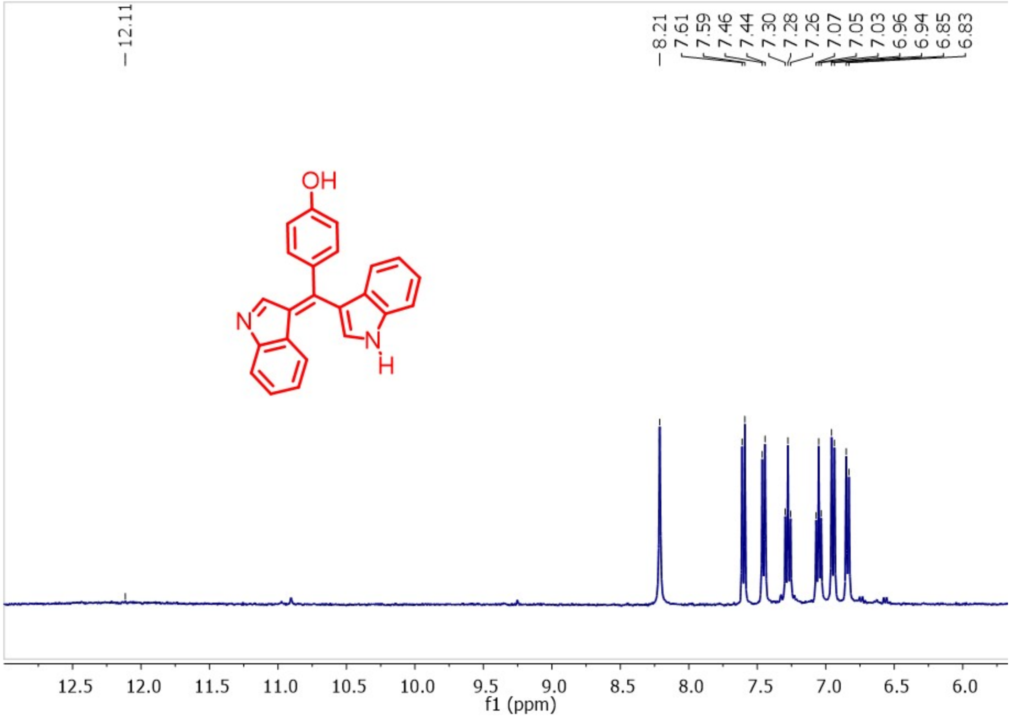


Figure. S3: Partial ^{1}H-NMR of compound 1 in DMSO-d_6.

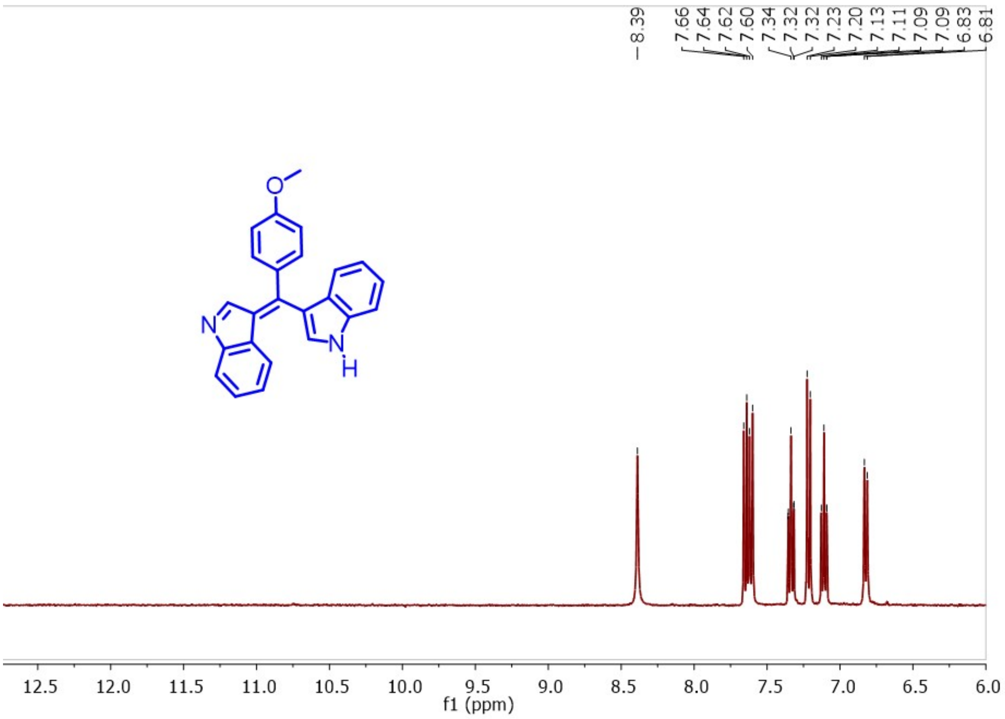


Figure. S4: Partial ^{1}H-NMR of compound 2 in DMSO-d_6.

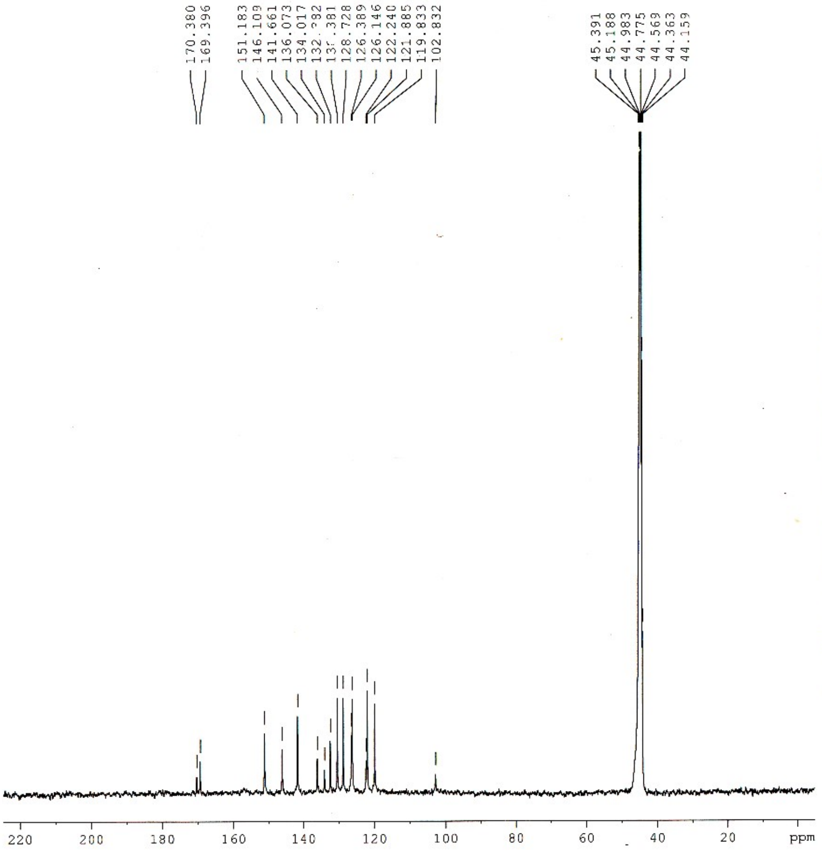


Figure. S5: ^{13}C-NMR of compound 1 in DMSO-d_6.

ADDITIONAL SPECTROSCOPIC DATA

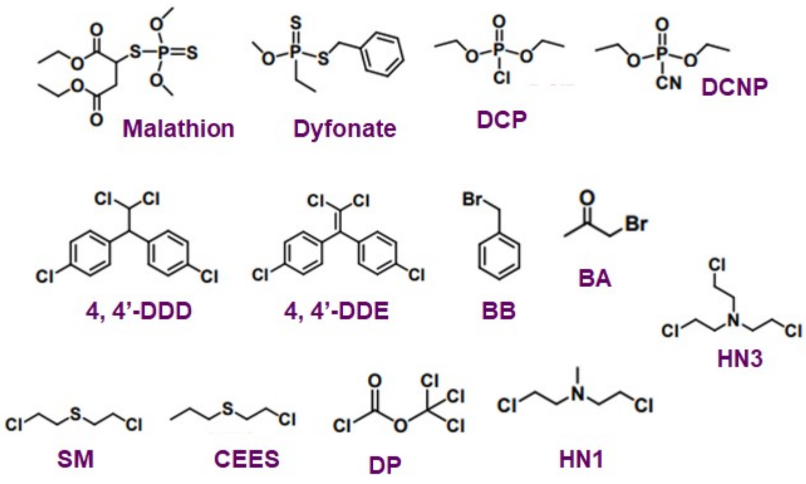


Figure. S6: Structure of different analytes involved in the present study

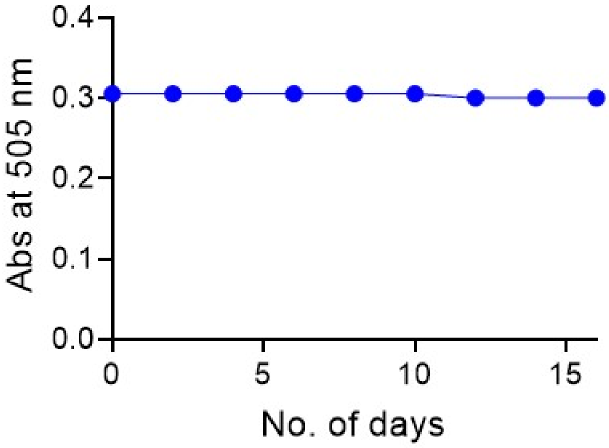


Figure. S7: Absorbance of comp 1 (at 505 nm) over 16 days.

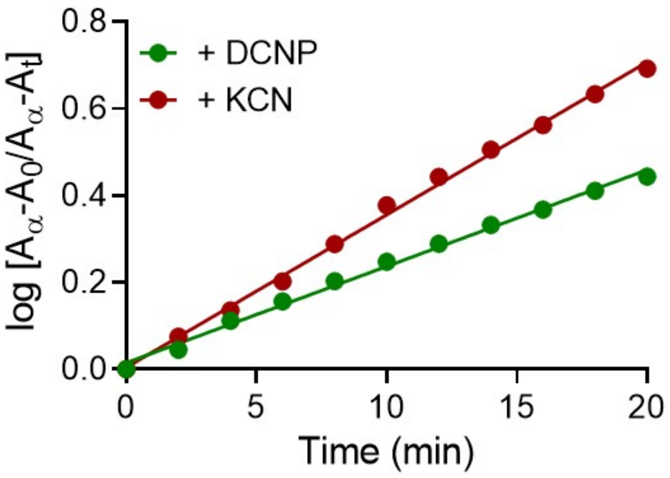


Figure. S8: Comparative kinetic profiles for the reaction of probe 1 with DCNP and KCN in pH 8 buffer medium.

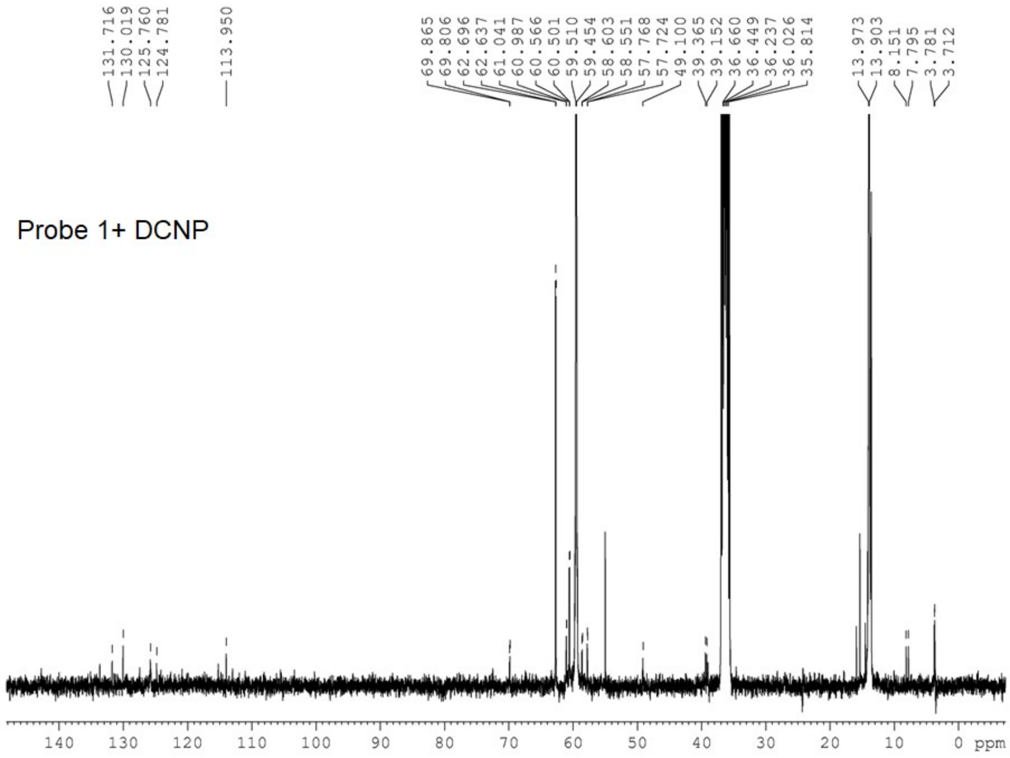


Figure. S9: ^{13}C-NMR of the probe 1 in the presence of DCNP in DMSO-d_6/D_2O (1:1) mixture (Incubation time: 30 mins).

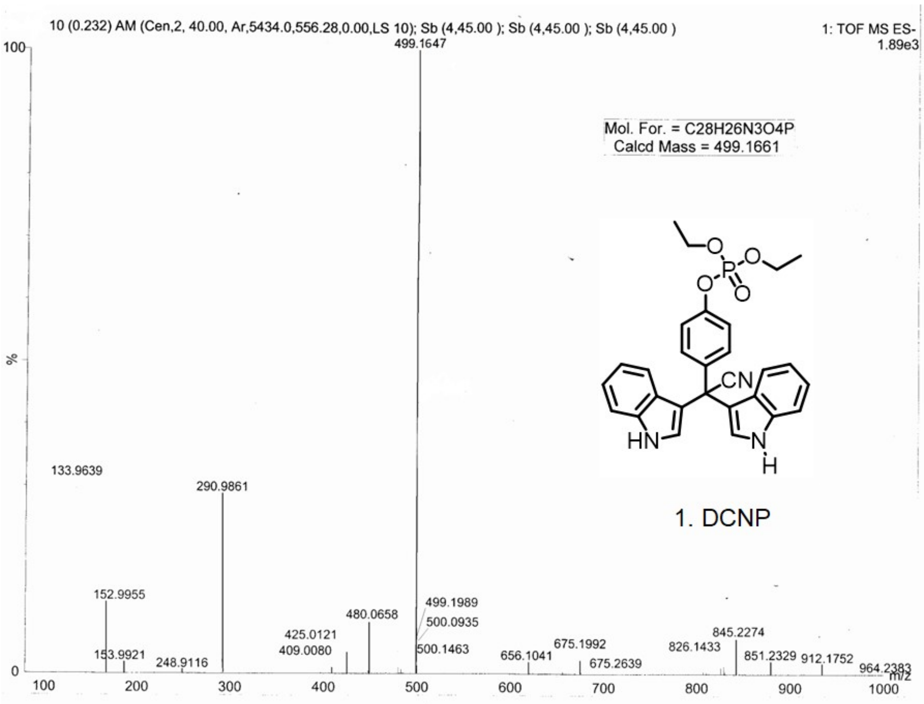


Figure. S10: Mass spectra of 1. DCNP.

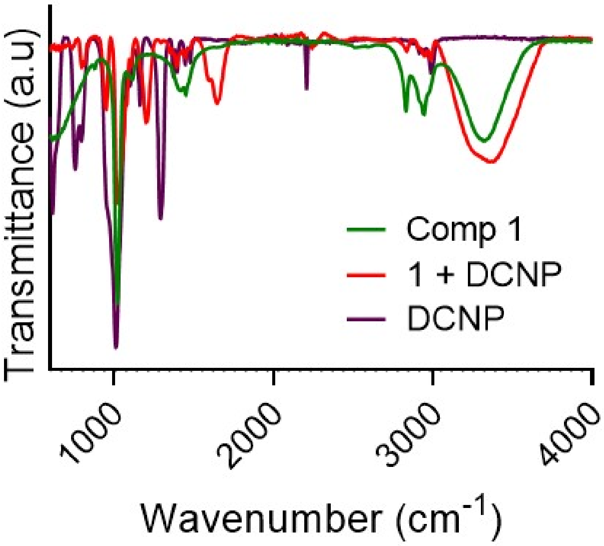


Figure. S11: FTIR spectra of 1. DCNP.

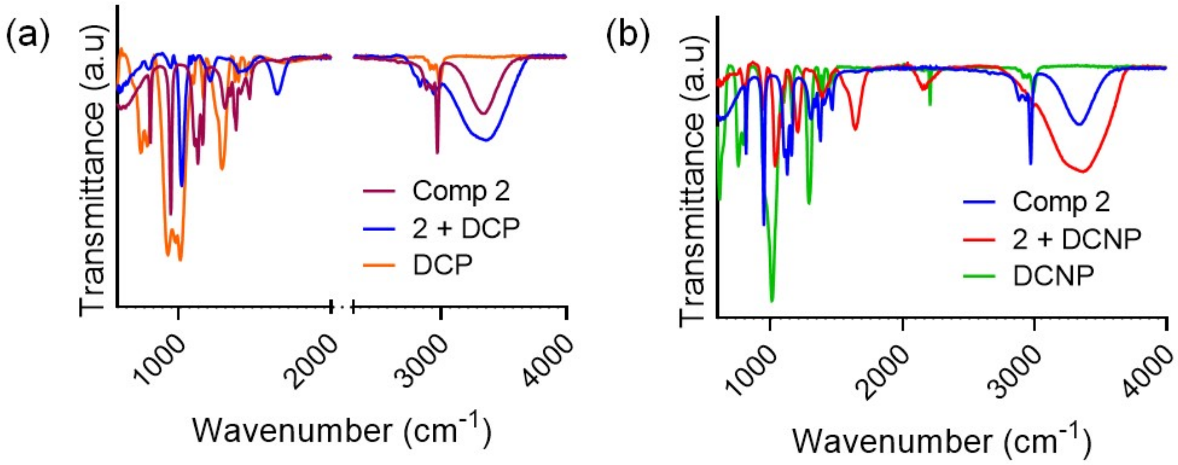


Figure. S12: FTIR spectra of 2. DCP and 2. DCNP

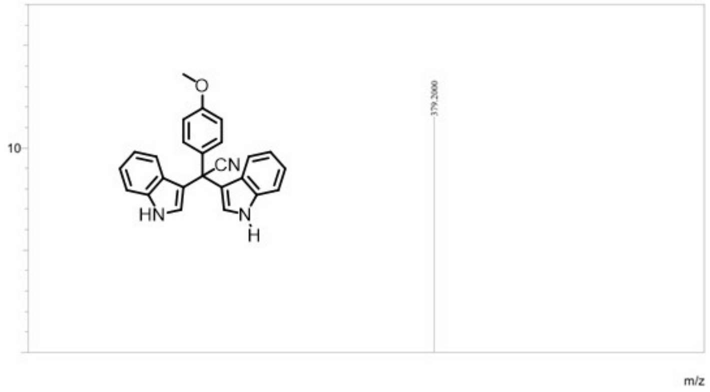


Figure. S13: Mass spectra of 2. DCNP

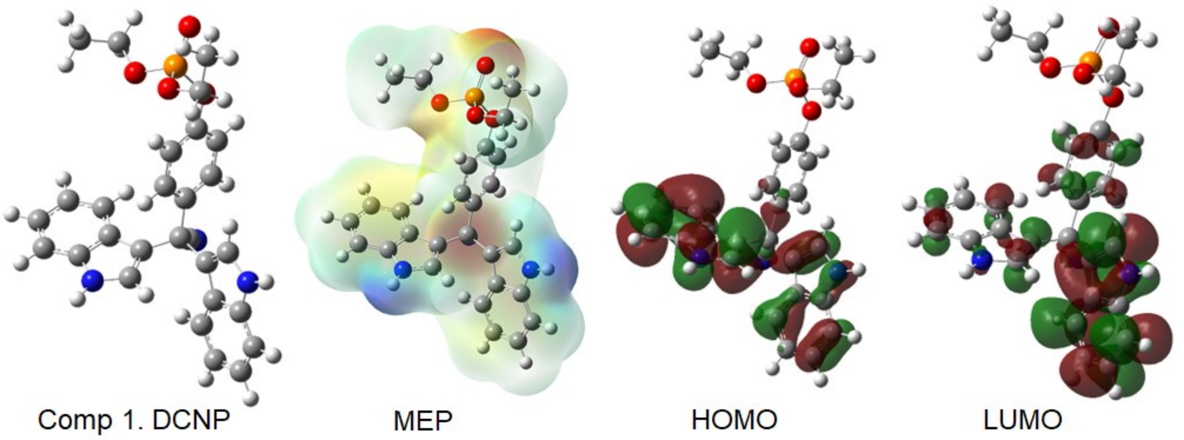
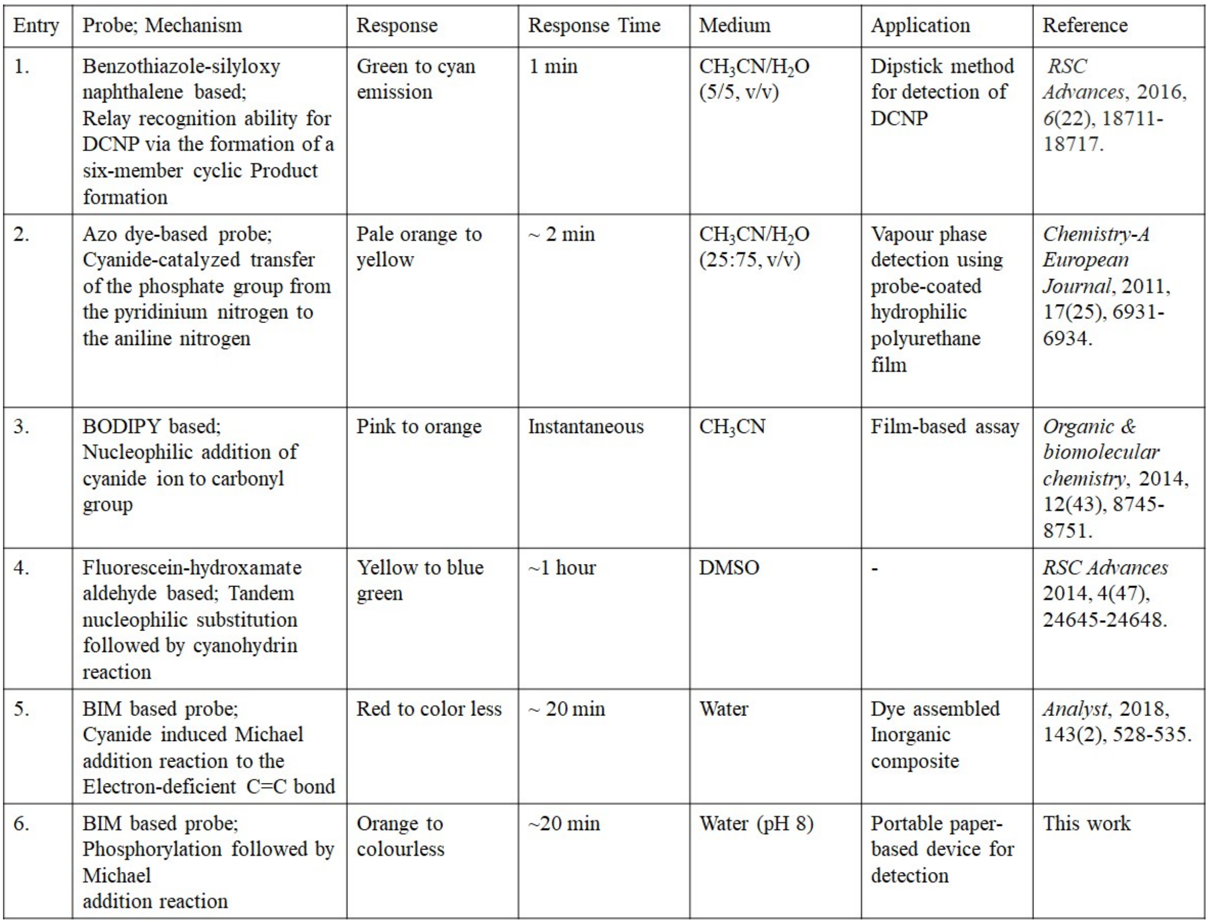


Figure. S14: Energy-optimised structures (as well as MEP) using B3LYP/6-31G* level of theory, and Frontier molecular orbital analysis of probe 1. DCNP.

Table. S1: Comparison table between the previously reported sensors and the present work.



Entry	Probe; Mechanism	Response	Response Time	Medium	Application	Reference
1.	Benzothiazole-silyloxy naphthalene based; Relay recognition ability for DCNP via the formation of a six-member cyclic Product formation	Green to cyan emission	1 min	CH_3CN/H_2O (5/5, v/v)	Dipstick method for detection of DCNP	*RSC Advances*, 2016, *6*(22), 18711-18717.
2.	Azo dye-based probe; Cyanide-catalyzed transfer of the phosphate group from the pyridinium nitrogen to the aniline nitrogen	Pale orange to yellow	~ 2 min	CH_3CN/H_2O (25:75, v/v)	Vapour phase detection using probe-coated hydrophilic polyurethane film	*Chemistry-A European Journal*, 2011, 17(25), 6931-6934.
3.	BODIPY based; Nucleophilic addition of cyanide ion to carbonyl group	Pink to orange	Instantaneous	CH_3CN	Film-based assay	*Organic & biomolecular chemistry*, 2014, 12(43), 8745-8751.
4.	Fluorescein-hydroxamate aldehyde based; Tandem nucleophilic substitution followed by cyanohydrin reaction	Yellow to blue green	~1 hour	DMSO	-	*RSC Advances* 2014, 4(47), 24645-24648.
5.	BIM based probe; Cyanide induced Michael addition reaction to the Electron-deficient C=C bond	Red to color less	~ 20 min	Water	Dye assembled Inorganic composite	*Analyst*, 2018, 143(2), 528-535.
6.	BIM based probe; Phosphorylation followed by Michael addition reaction	Orange to colourless	~20 min	Water (pH 8)	Portable paper-based device for detection	This work