Supporting Information

Polynorbornene Derived 8-Hydroxyquinoline Paper Strips for Ultrasensitive Chemical Nerve Agent Surrogate Sensing

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Experimental section:

Materials:

8-hydroxyquinoline, glycine, *cis*-5-norbornene-*exo*-2, 3-dicarboxylic anhydride, 11-bromoundecanol, propergyl bromide, sodium azide, triethylamine (TEA), potassium carbonate, dicyclohexyl carbodiimde (DCC), triethylamine, dichloromethane (DCM), methanol (MeOH), toluene, $CDCl_3$ were purchased as reagent grade from Aldrich, Acros, Merck and used as received. Dichloromethane (DCM) was distilled over calcium hydride and used for reactions. The stock solutions of metal salts used were $CdCl_2$, $HgCl_2$, $Pb(No_3)_2$, $FeCl_2$. $4H_2O$, $CuSO_4.5H_2O$, NaCl, $MgCl_2$, $Ba(NO_3)_2$, $MnSO_4$, $NiCl_2.6H_2O$, $CdCl_2$, $ZnCl_2$. Deionized water was used.

Methods:

NMR Characterization: NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent. NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H 0.00).

Fluorescence Measurements: Fluorescence emission spectra were recorded on a Fluorescence spectrometer (Horiba Jobin Yvon, Fluromax-4, 250-900 nm). Emission spectra for all solutions were measured with an excitation wavelength of 310 nm. Typically the slit widths were 5 mm and the scan rate was 400 nm/min. Slit widths and scan rates were adjusted to allow adequate intensity, if needed.

UV-Vis experiments: UV-visible absorption measurements were carried out on Perkin-Elmer Lambda-35 UV-Vis spectrometer, with a scan rate of 480 nm/min. The absorption spectra for all solutions were measured in a quartz cell at concentrations so that the total absorbance was less than 1 abs. units.

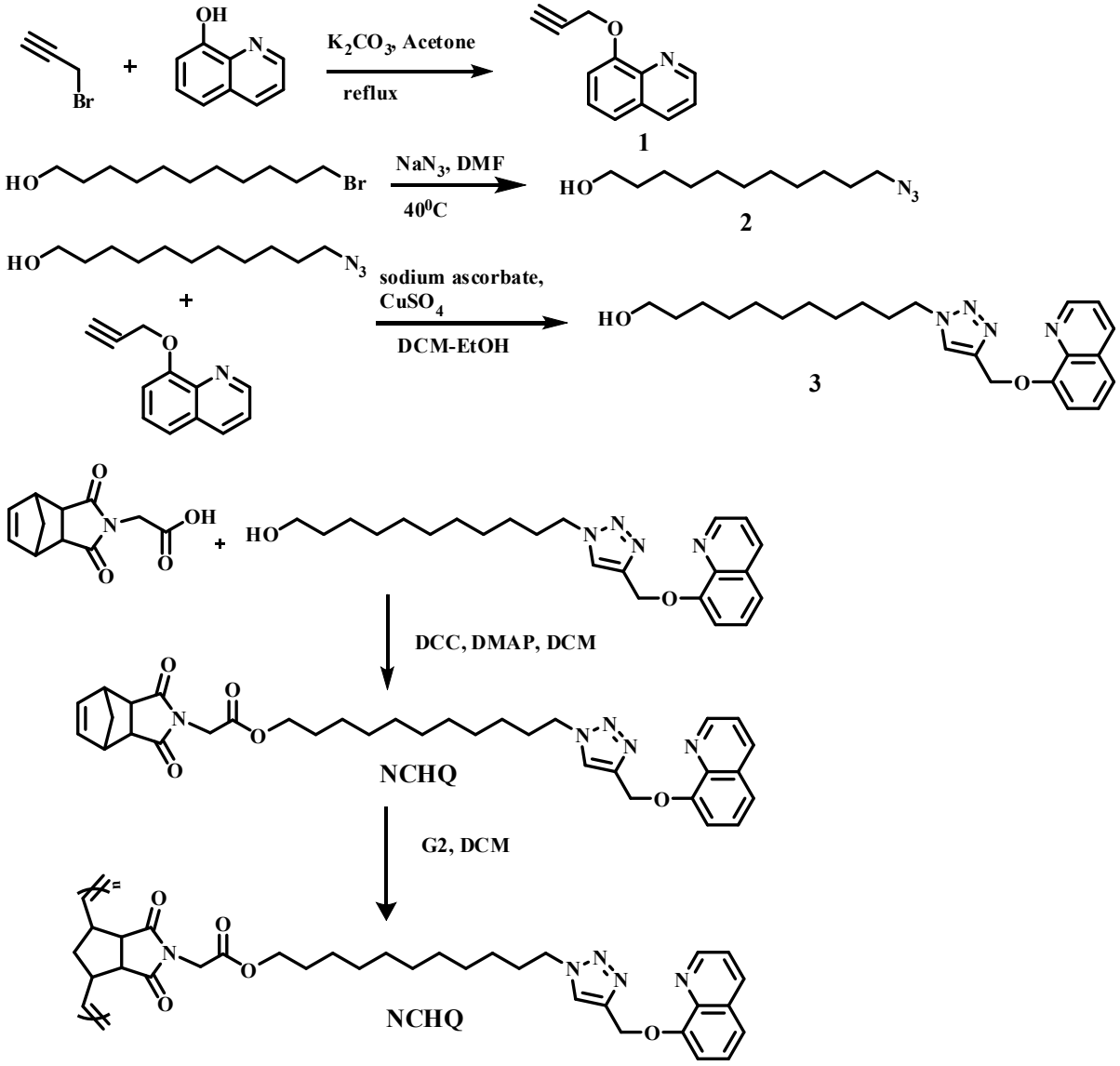
Mass Analysis: HRMS analyses were performed with Q-TOF YA263 high resolution (Waters Corporation) instruments by +ve mode electrospray ionization.

Synthetic Procedure:

Synthesis of **1**: Compound **1** was synthesised following a literature procedure.[1] In brief, to a dry round bottom flask 8-hydroxyquinoline (1gm, 0.006 mol) was taken and dissolved in dry acetone. Potassium carbonate (4.7 gm, 0.034) was added to it and refluxed for 1 hour. Propergyl bromide (0.82 gm, 0.006 mol) was then added slowly with time and continued refluxing. After complete addition the reaction mixture was refluxed for 24 hours. After cooling down to room temperature, the mixture was filtered and the filtrate was evaporated to get a brown liquid. The residue was dissolve in DCM and washed with water. Crude product was purified through column chromatography on silica gel using hexane-ethyl acetate as eluent. Pure product appeared as brown solid with 75% yield. . ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.9 (d, 1H), 8.2 (d, 1H), 7.6-7.7 (m, 3H), 7.3 (d, 1H), 5.0 (d, 2H), 2.5 (d, 1H). ^{13}C NMR (400MHz, $CDCl_3$): δ 153.1, 149.4, 140.3, 135.9, 129.5, 126.4, 121.7, 120.7, 110.0, 78.3, 76.1, 56.5. MS (ESI): m/z 183.87 [M^+].

Synthesis of **2**: 11- bromo undecanol (0.5gm, 0.002mol) was taken in a round bottom flask with a magnetic bar and was dissolved in 7 ml of dry DMF. Sodium azide (0.4 gm, 0.006 mol) was charged into the reaction mixture and stirred at 40^0C for 16 hours. After that, reaction mixture was cooled to room temperature and washed with ethyl acetate and water. Evaporating of ethyl acetate provided compound **2** in pure form as colourless liquid with 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.6 (t, 2H), 3.2 (t, 2H), 1.4-1.5 (6H, m), 1.2-1.3 (10H, m). ^{13}C NMR (400MHz, $CDCl_3$): δ 63.8, 51, 32.8, 30.8, 30.5, 27.3, 25.4. MS (ESI): m/z 214.4 (M+H).

Synthesis of **3**: To carry out 1, 3 dipolar cycloaddition reaction between compound **1** & **2** a highly dried round bottom flask with magnetic bar was taken. **1** (0.128gm, 0.7mmol) & **2** (0.1 gm, 0.47 mmol) was charged into the flask and dissolved in DCM-Ethanol (1:1). The flask was vacuum dried and purged with nitrogen several times. Sodium ascorbate (5.5mg, 0.028 mmol) was added to the reaction mixture and purged with nitrogen. Same condition was followed after addition of copper sulphate pentahydrate (1.17mg, 0.0047mmol).[2] The reaction mixture was stirred at room temperature for 24 hours. TLC showed formation of new compound. Solvent from the reaction mixture was evaporated. The residue was dissolved in DCM and washed with brine. Crude product was purified through column chromatography using DCM-Methanol as eluent. Product appeared as yellowish brown with 40% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.9 (d, 1H), 8.2 (d, 1H), 7.8 (s, 1H), 7.6-7.7 (m, 3H), 7.3 (d, 1H), 5.5 (s, 2H), 4.3 (m, 2H), 3.6 (m, 2H), 1.8 (m, 2H), 1.7 (m, 2H), 1.6 (m, 2H), 1.2-1.3 (m, 12H). ^{13}C NMR (400MHz, $CDCl_3$): δ 153.7, 149.2, 143.9, 140.1, 135.9, 129.4, 126.6, 122.9, 121.5, 120.0, 109.8, 62.9, 62.7, 50.3, 32.6, 30.0, 29.5, 29.2, 26.2, 25.6. MS (ESI): m/z 397.39 (M+H).



Scheme 1. Schematic representation of the synthesis process of **NCHQ** and **PNCHQ**.

Synthesis of **NCHQ**: Compound **3** was attached to norbornene acid through coupling reaction. Norbornene acid (106 mg, 0.48 mmol) was taken in a dry round bottom flask and 5 ml of dry DCM was added to it to dissolve. DCC (148.5 mg, 0.72 mmol) was charged to form white ppt. After 15 minutes of stirring at room temperature, compound **3** with catalytic amount of DMAP was added to it and continued stirring for 24 hours. TLC confirmed formation of product. DCU was filtered off and the filtrate was washed with saturated bicarbonate solution. Organic layer was separated and evaporated to dryness to get crude product. Crude product was purified through column chromatography using DCM-Methanol as eluent. Sticky whitish product appeared with 40% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.9 (d, 1H), 8.2 (d, 1H), 7.8 (s, 1H), 7.6-7.7 (m, 3H), 7.3 (d, 1H), 6.3 (d, 2H), 5.5 (s, 2H), 4.3 (m, 2H), 4.2 (s, 2H), 3.6 (m, 2H), 3.3 (m, 2H), 2.7 (m, 2H) 1.8 (m, 2H), 1.75 (dd,

1H), 1.7 (m, 2H), 1.6 (m, 2H), 1.5 (s, 1H), 1.2-1.3 (m, 12H). ^{13}C NMR (400MHz, $CDCl_3$): δ 177.5, 166.9, 153.7, 149.2, 143.9, 140.1, 136.0, 135.9, 129.4, 126.6, 122.9, 121.5, 120.0, 109.8, 62.9, 62.7, 50.5, 50.3, 49.7, 47.2, 39.2, 32.6, 30.0, 29.5, 29.2, 26.2, 25.6. MS (ESI): m/z 600.13 (M+H).

Synthesis of **PNCHQ**: Polymerization of **NCHQ** was carried out using Grubbs' second generation catalyst. Compound 4 (30 mg, 0.05 mmol) was taken in a 10 ml round bottom flask and purged with nitrogen after applying vacuum. Dry DCM-Methanol (1:1) mixture 1 ml was added to dissolve. Grubbs catalyst (0.7 mg) was charged and stirred vigorously for 20 mins. Ethyl vinyl ether (0.5 ml) was added to quench the polymerization. In ^1H NMR spectroscopy new peak at 5.5 confirmed formation of product.

Characterization:

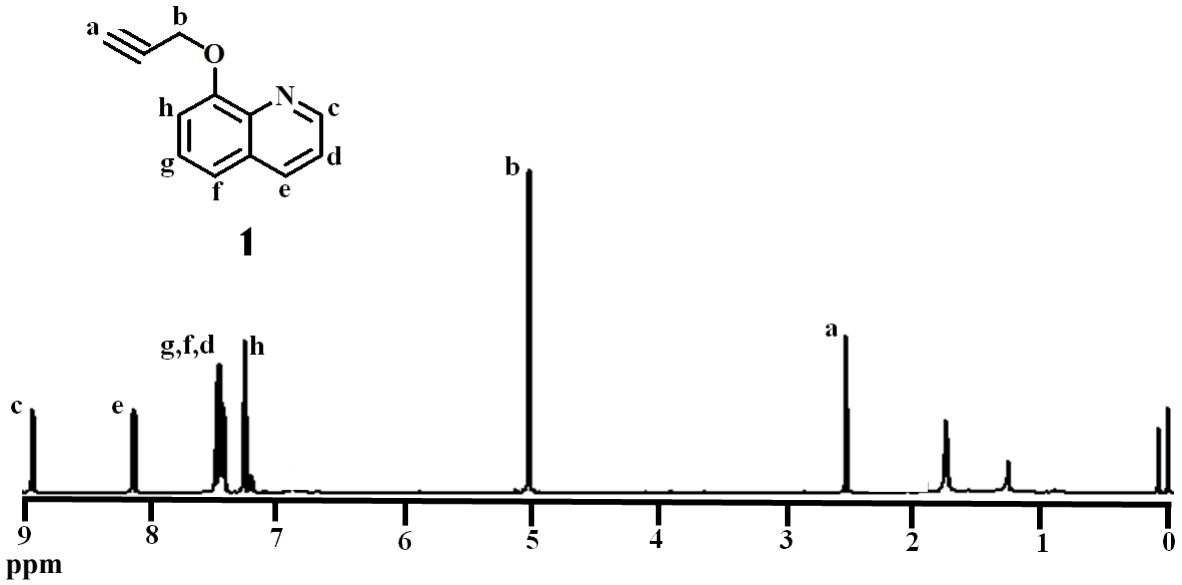


Fig. S1 ^1H NMR spectrum of **1** in $CDCl_3$

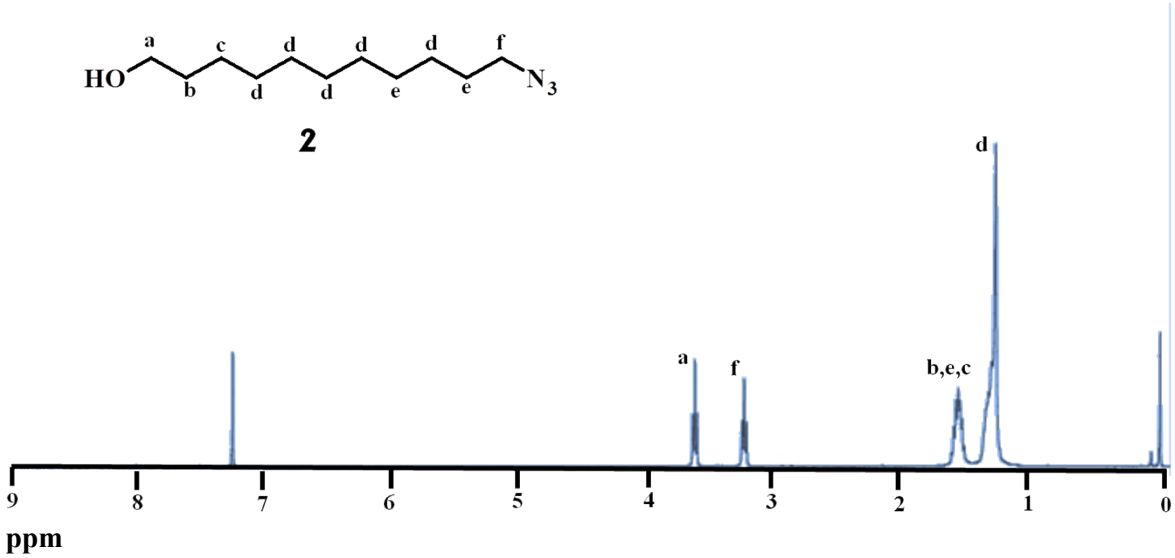


Fig. S2 ^{1}H NMR spectrum of **2** in $CDCl_3$

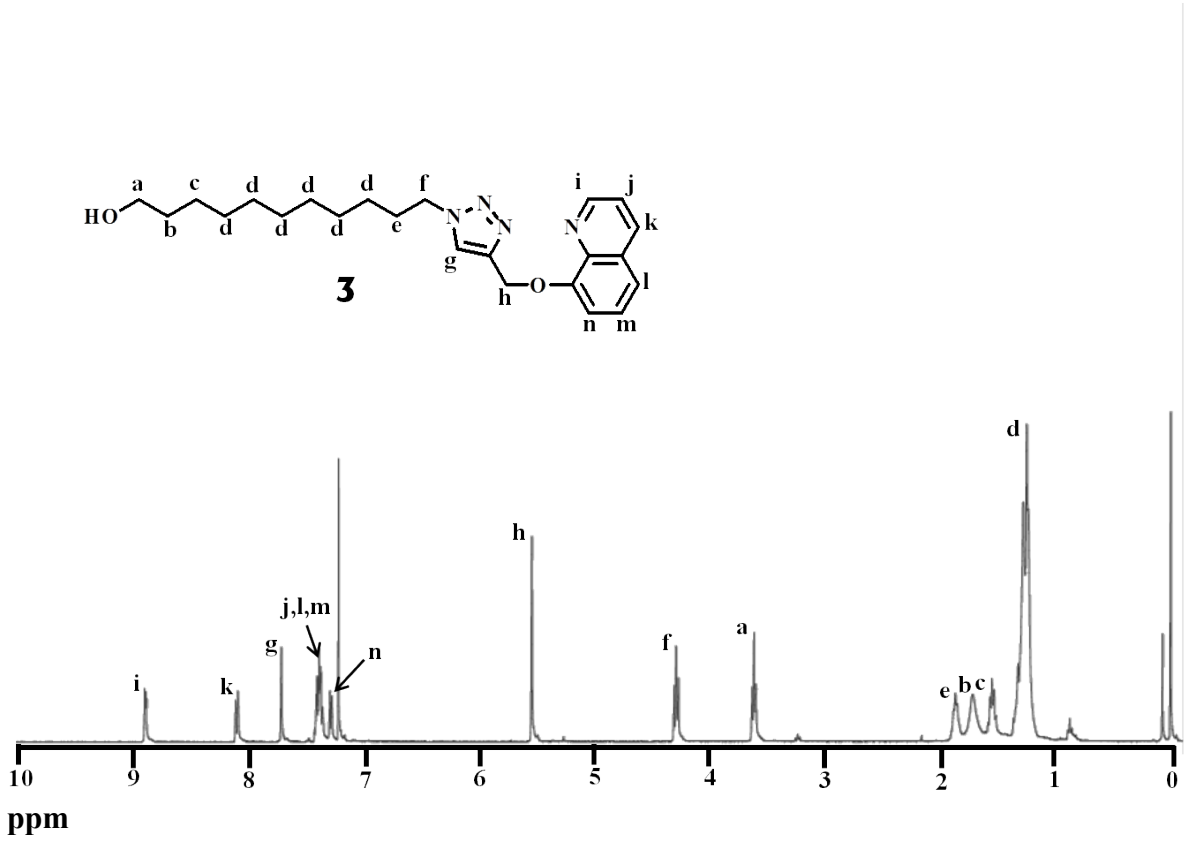


Fig. S3 ^{1}H NMR spectrum of **3** in $CDCl_3$

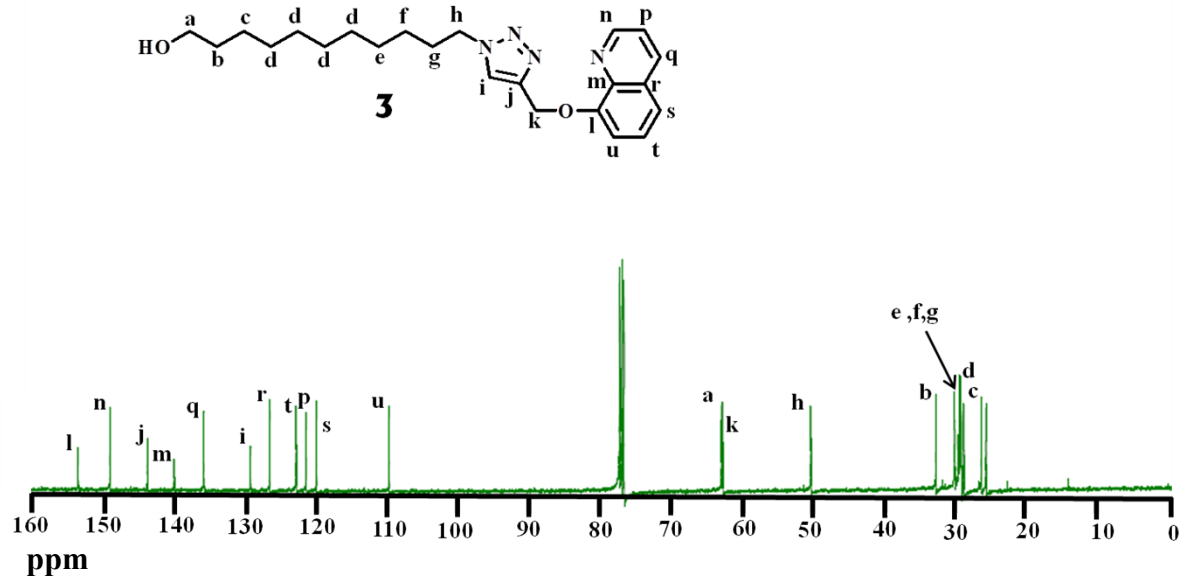


Fig. S4 ^{13}C NMR spectrum of **3** in $CDCl_3$

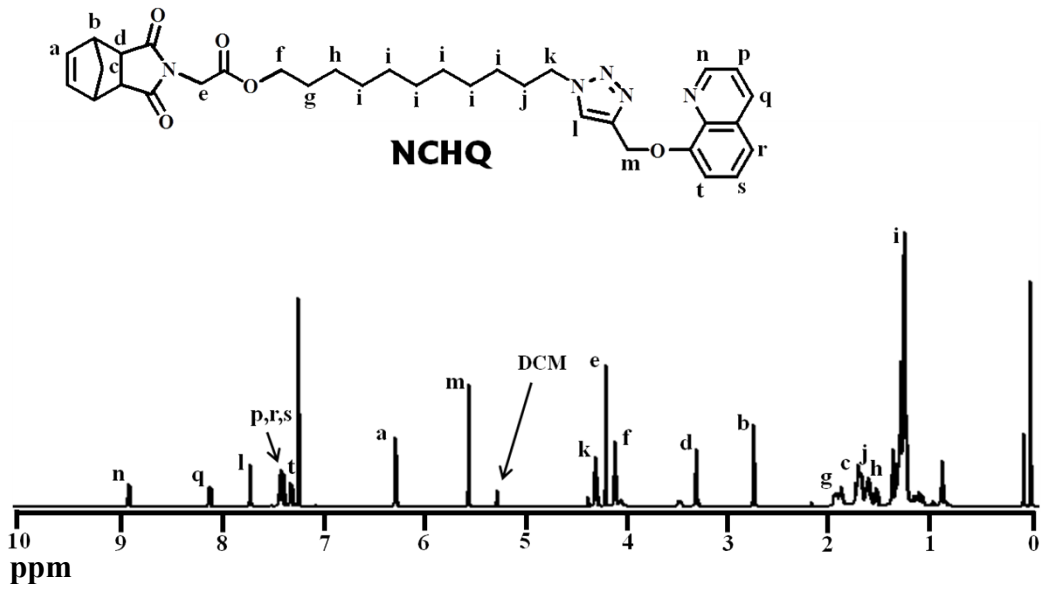


Fig. S5 ^{1}H NMR spectrum of **NCHQ** in $CDCl_3$

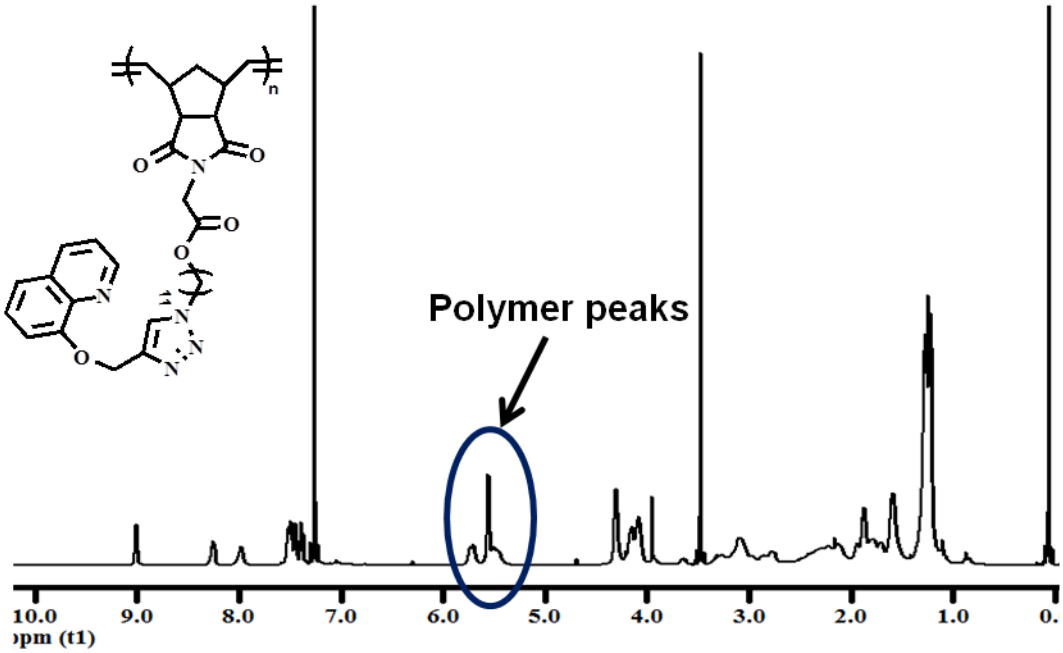


Fig. S6 ^{1}H NMR spectrum of **PNCHQ** in $CDCl_3$

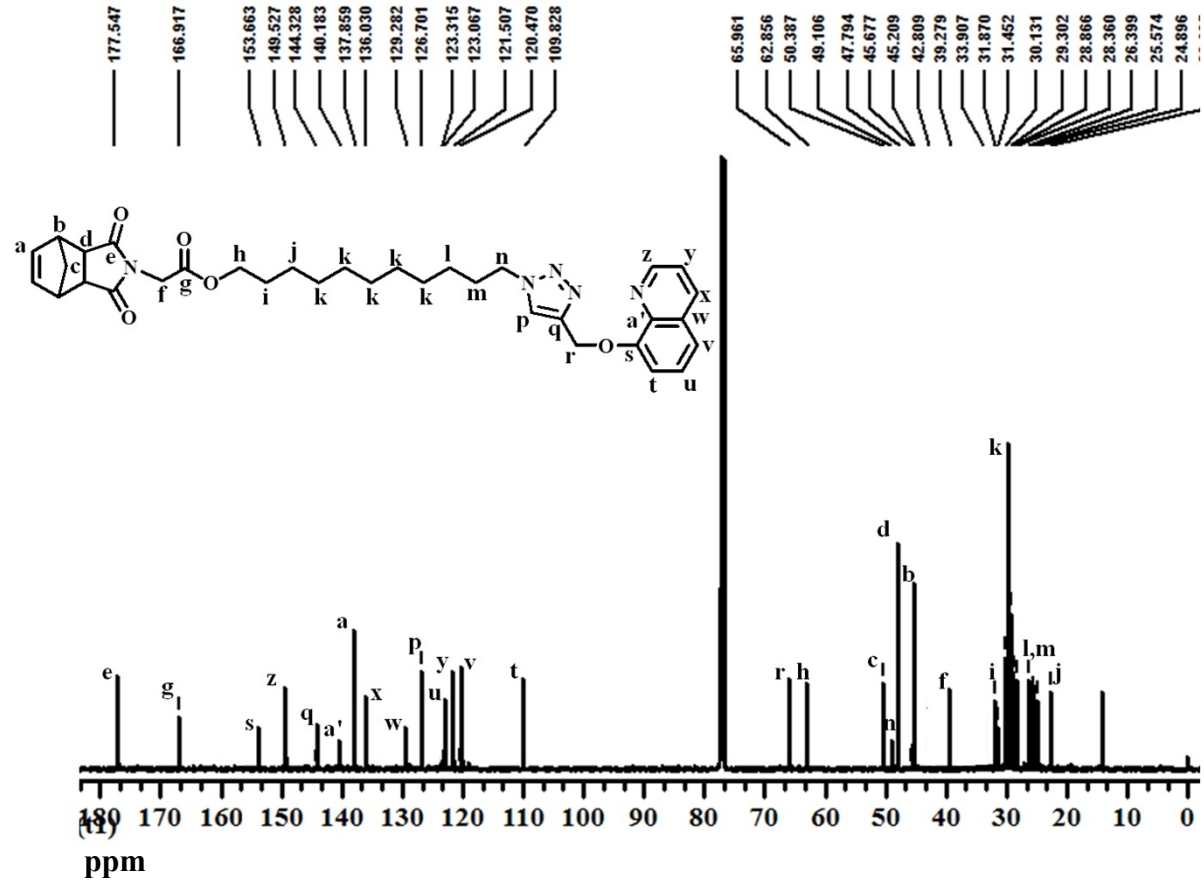


Fig. S7 ^{13}C NMR spectrum of **NCHQ** in $CDCl_3$

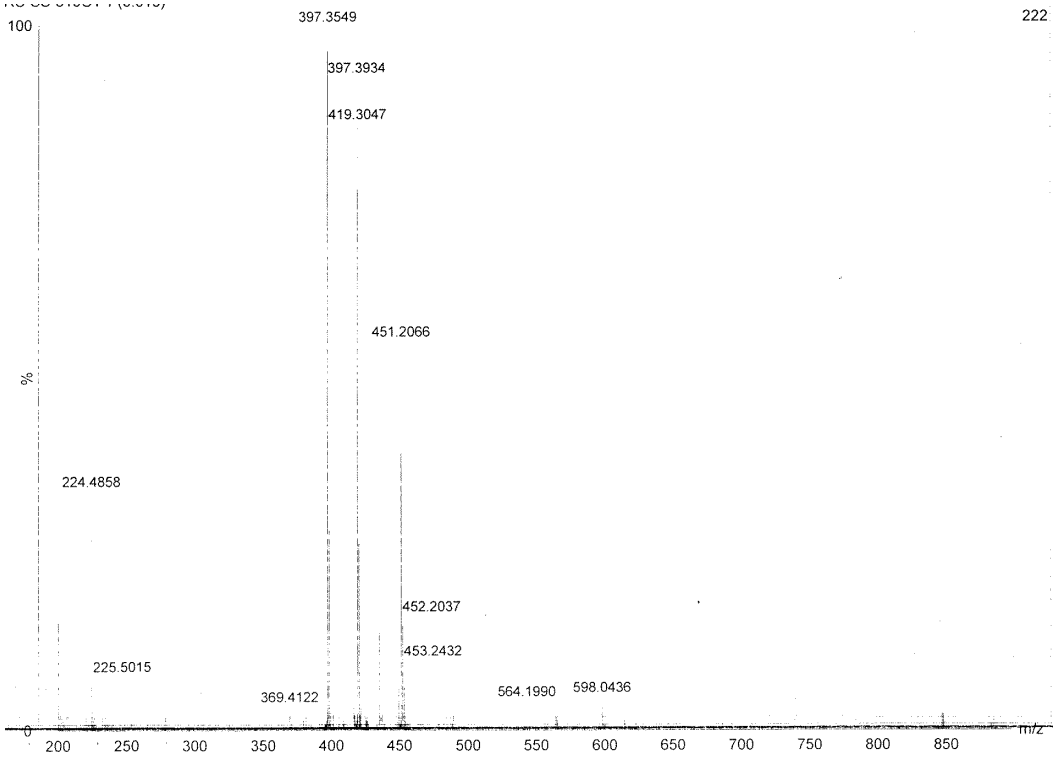


Fig. S8 ESI-MS spectrum of **3**.

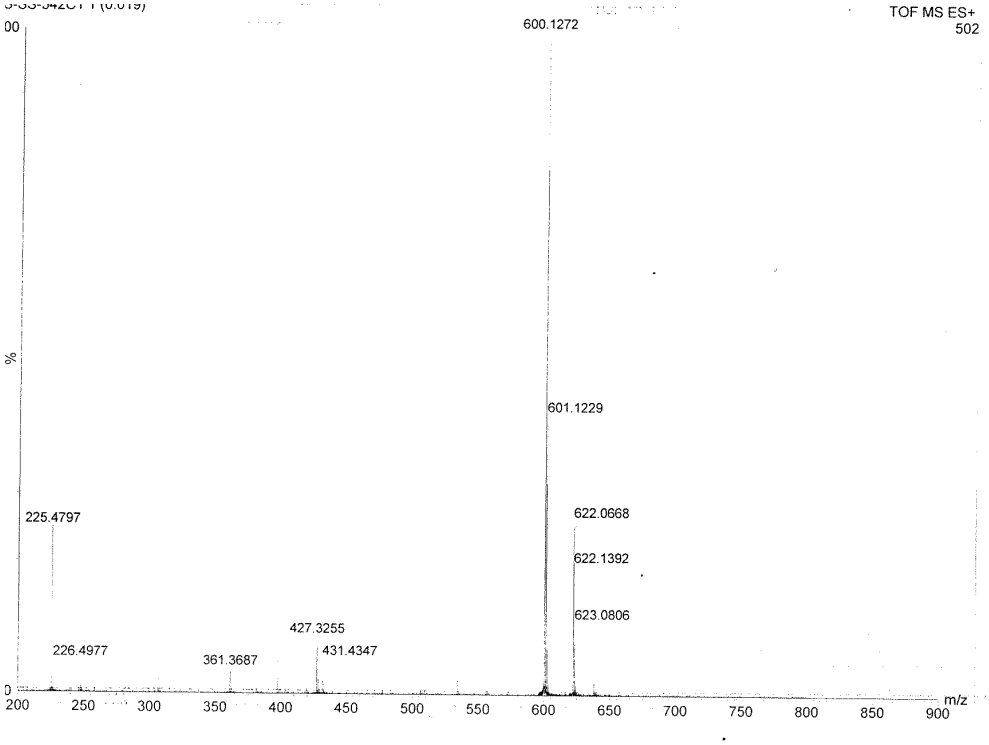


Fig S9. ESI-MS spectrum of **NCHQ**.

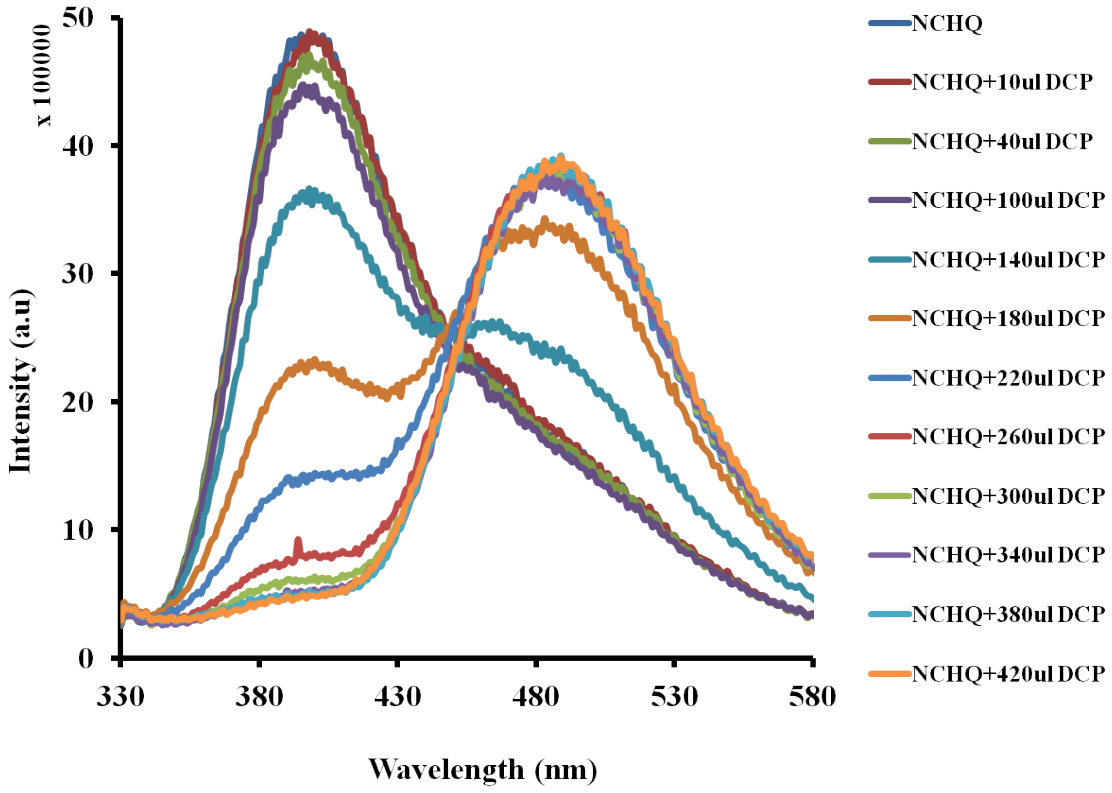


Fig. S10 Emission spectra of **NCHQ** with gradual addition of DCP in methanol (λ_{ex}=300 nm)

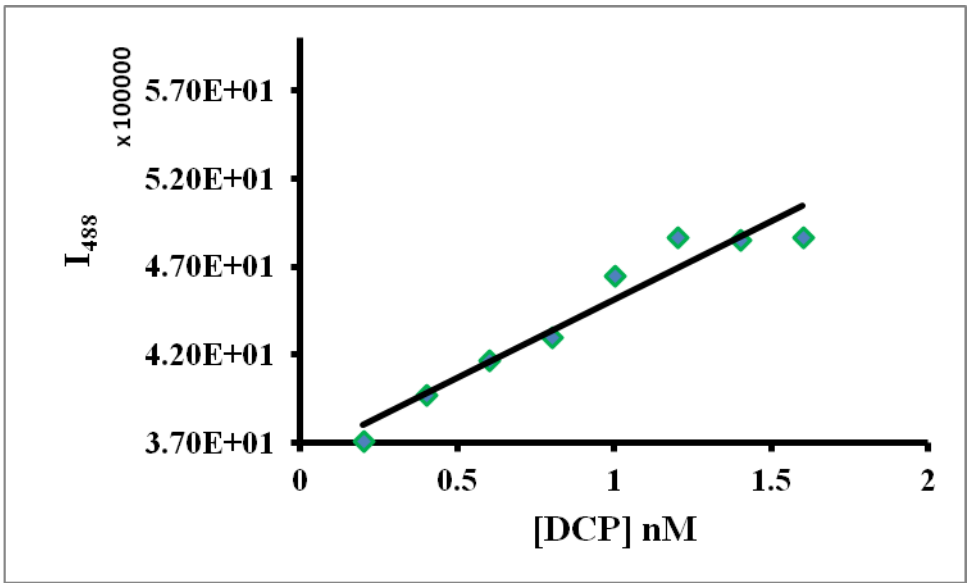


Fig. S11 Detection limit experiment by titration of **NCHQ** with DCP in nanomolar concentration.

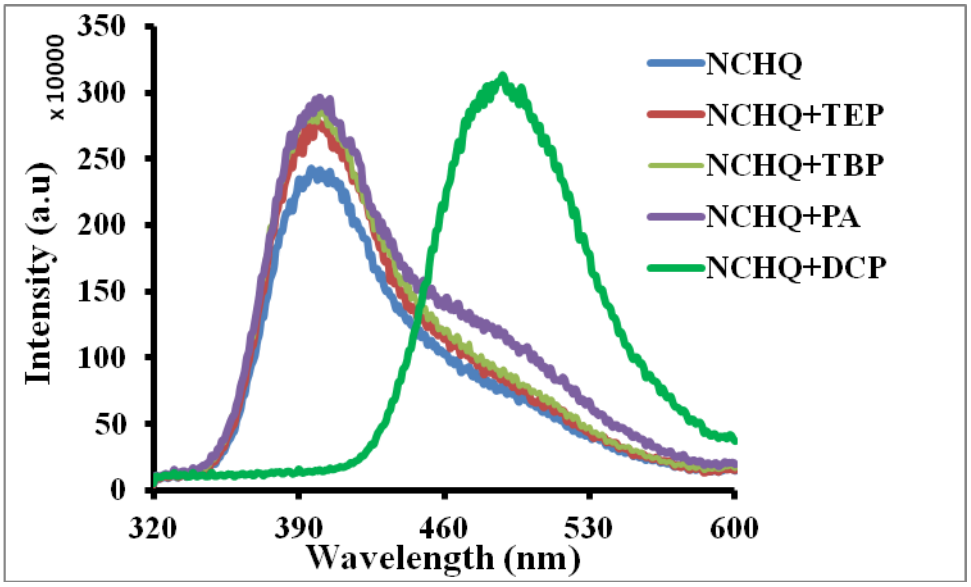


Fig. S12 Emission spectra of **NCHQ** in presence of DCP and other silimar phosphates (λ_{ex}=300 nm). TEP-triethylphosphate, TBP- tributyl phosphate, PA- Phosphoric acid.

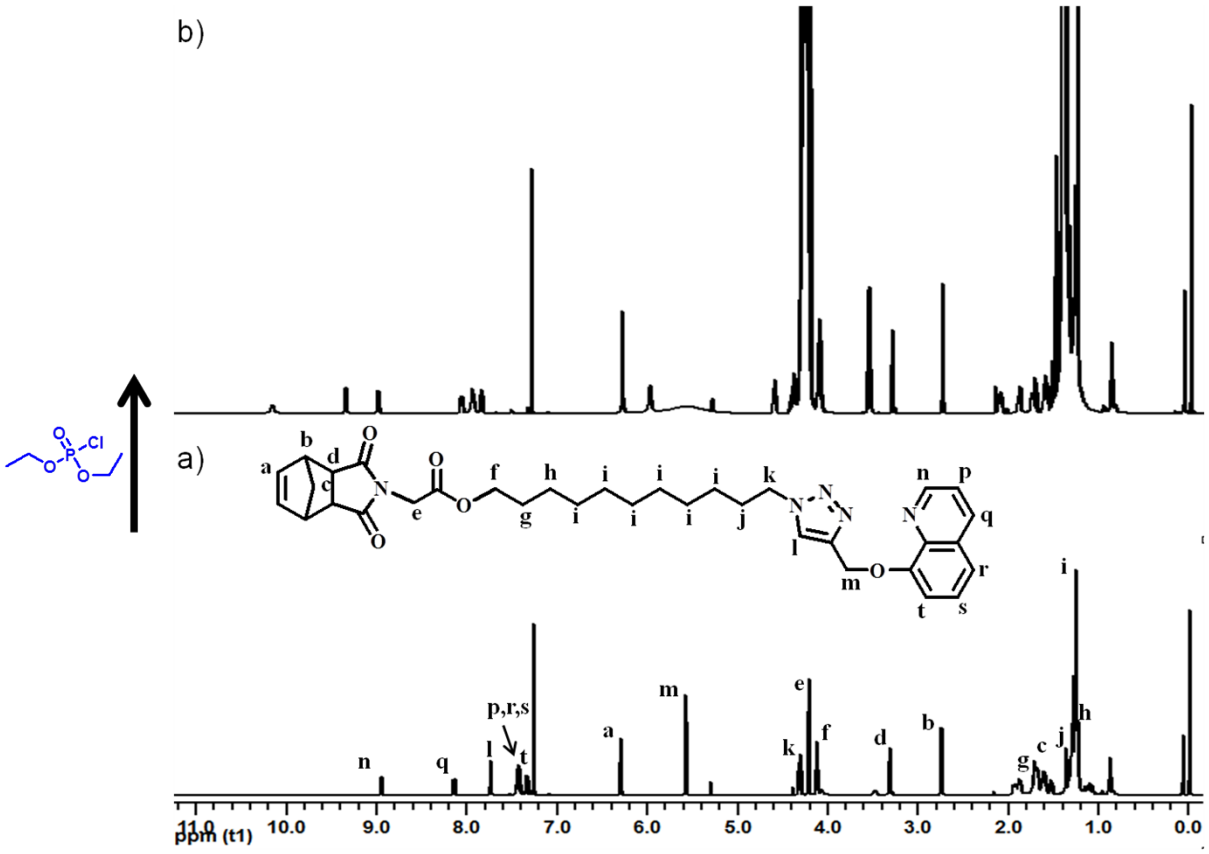


Fig. S13 Peak shifting in ^{1}H NMR spectra of **NCHQ** a) before and b) after the addition of DCP**.**

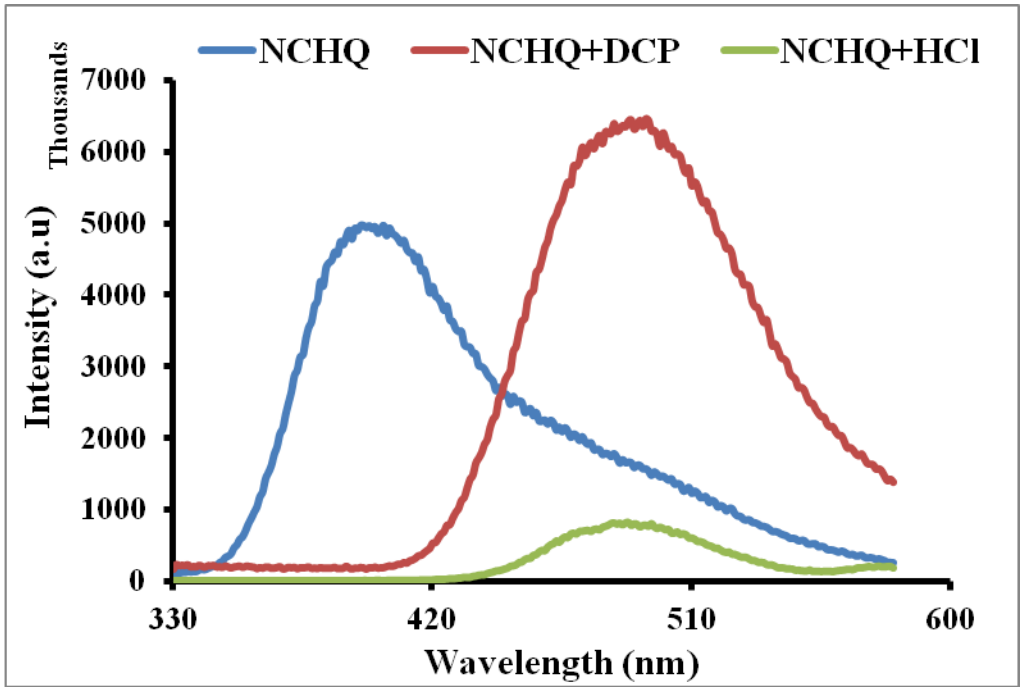


Fig. S14 Comparative emission spectra of **NCHQ** with DCP and HCl (λ_{ex}=300 nm).

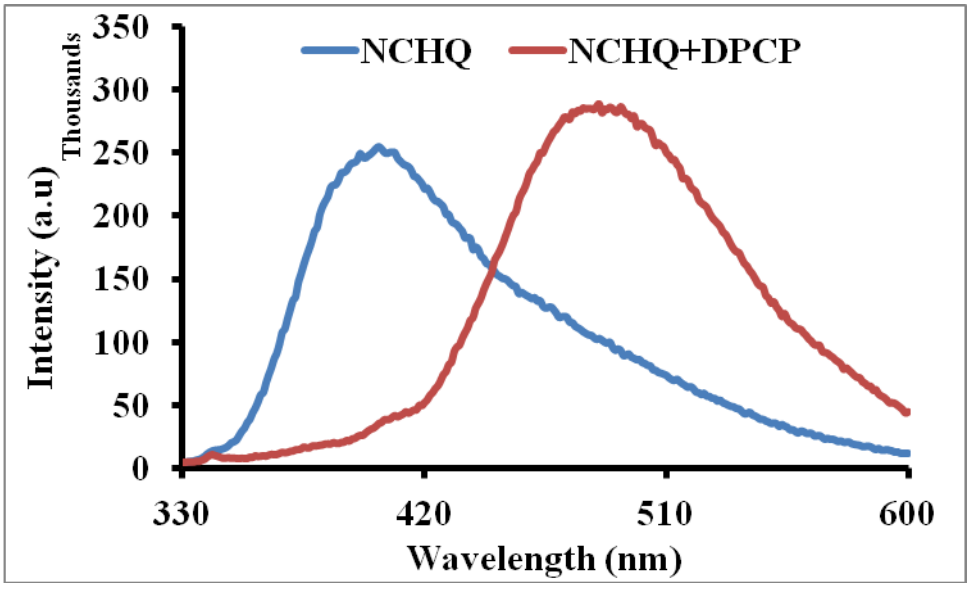


Fig. S15 Emission spectra of **NCHQ** with DPCP (λ_{ex}=300 nm).

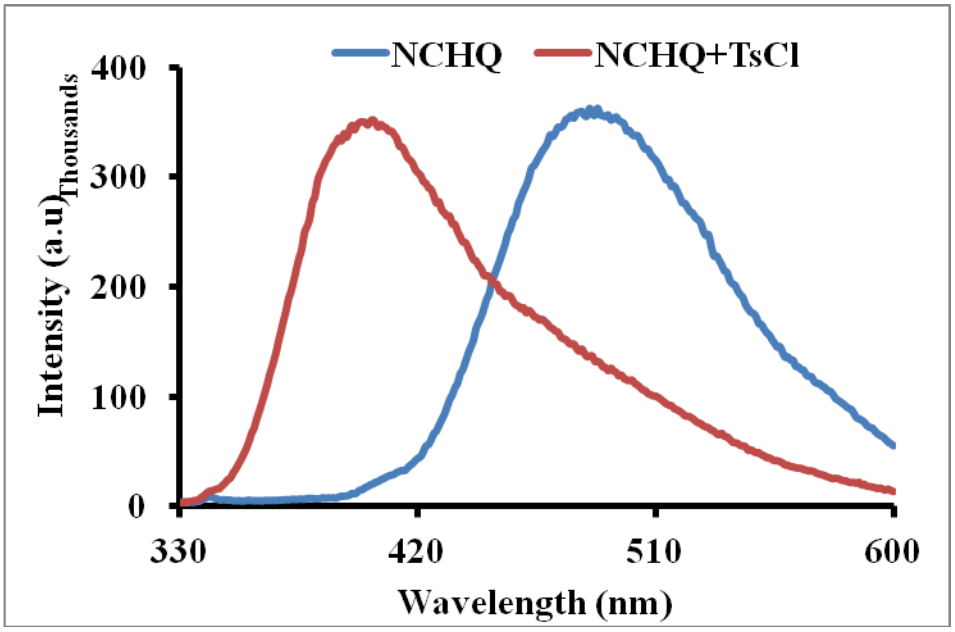


Fig. S16 Emission spectra of **NCHQ** before and after the addition of tosyl chloride (TsCl) (λ_{ex}=300 nm).

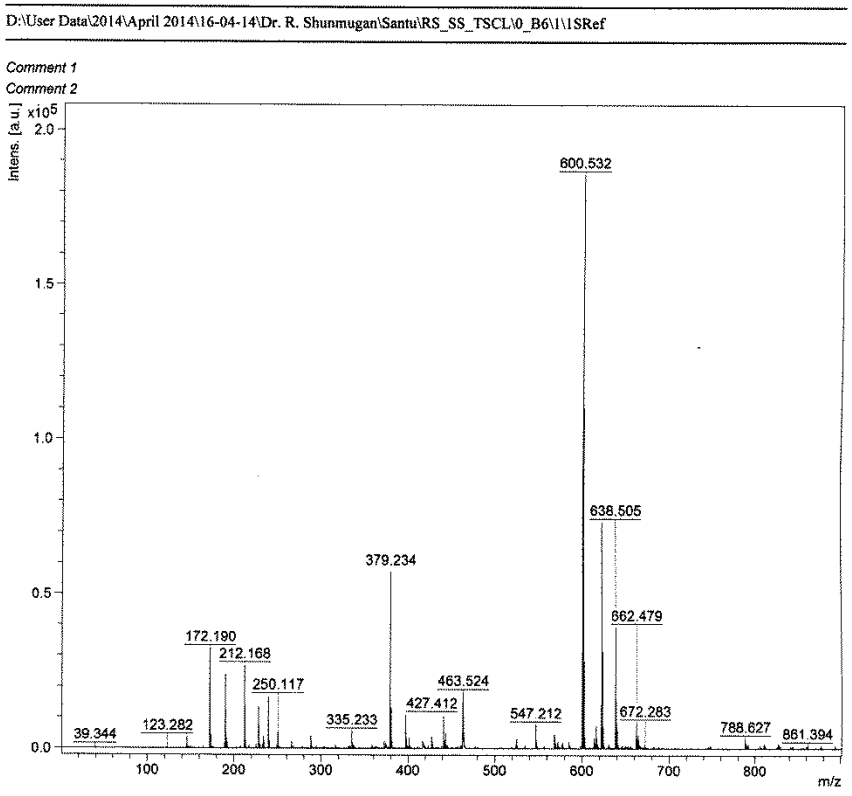


Fig. S17 MALDI analysis of **NCHQ**-TsCl mixture.

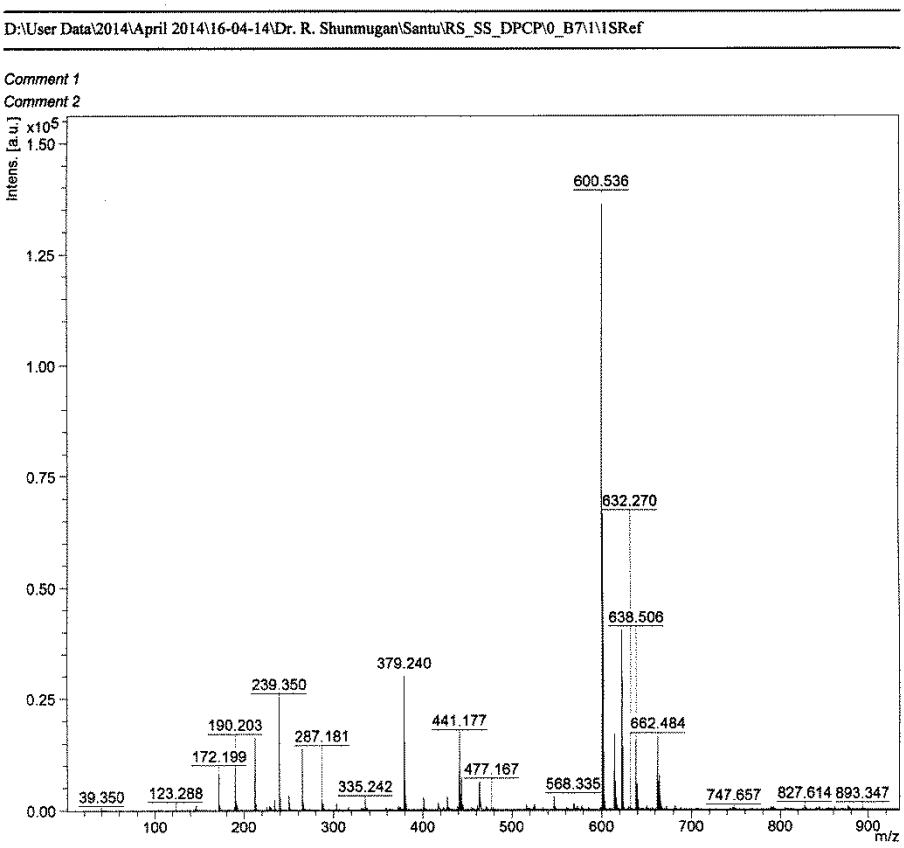


Fig. S18 MALDI analysis of **NCHQ**-DPCP mixture.

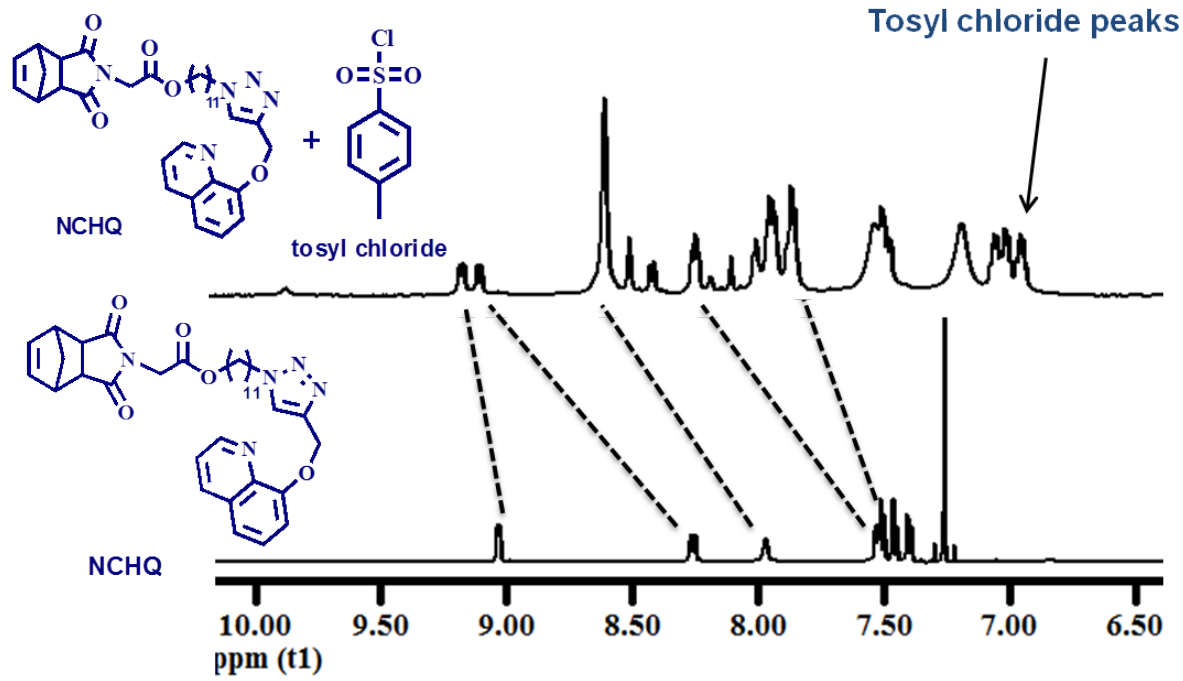


Fig. S19 Peak shifting in ^{1}H NMR spectra of **NCHQ** before and after the addition of tosyl chloride in $CDCl_3$.

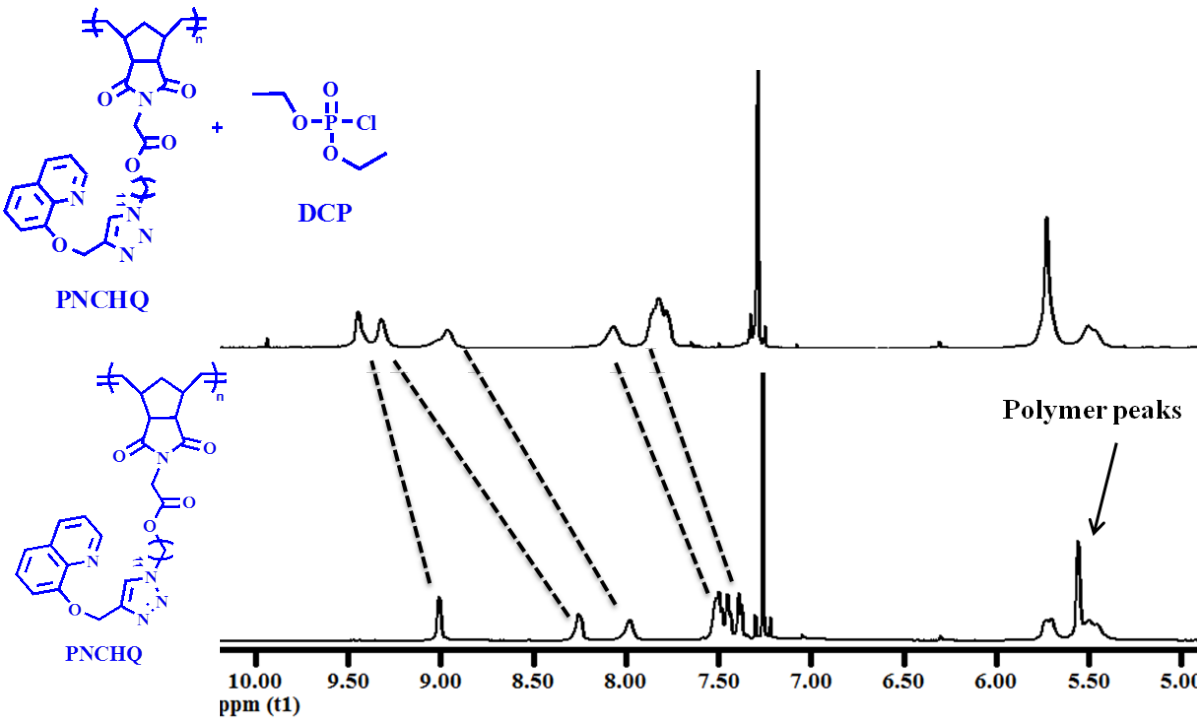


Fig. S20 ^{1}H NMR spectra of **PNCHQ** and **PNCHQ**-DCP in $CDCl_3$.

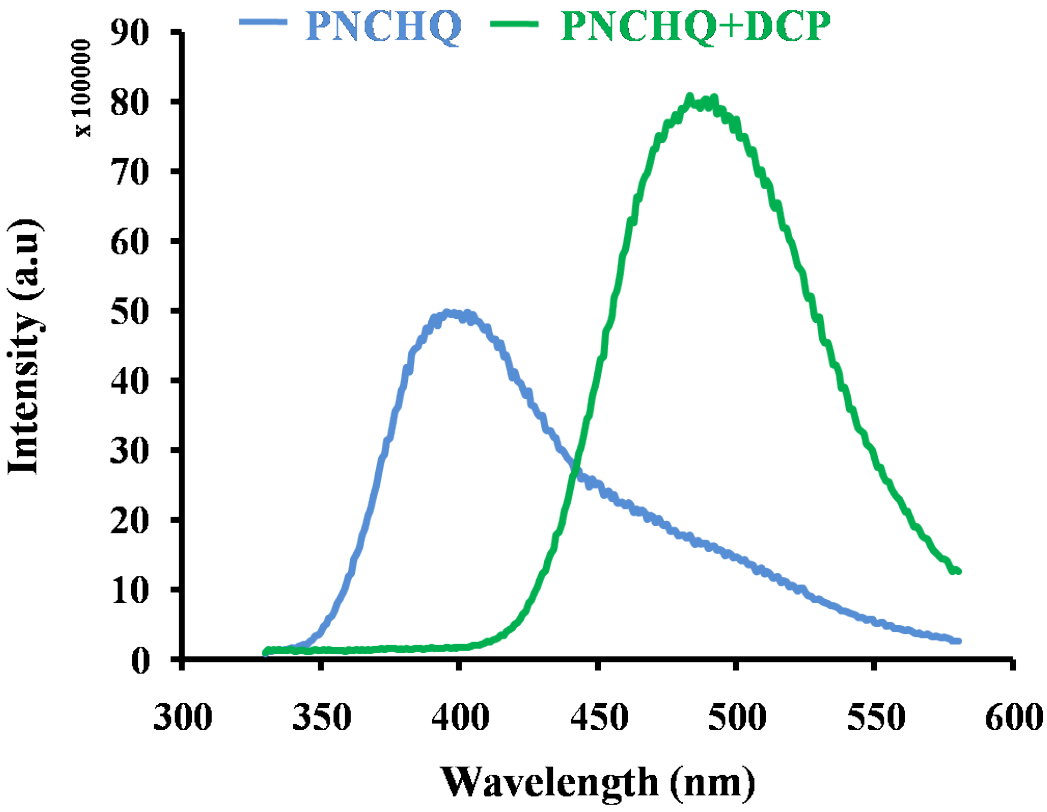


Fig. S21 Emission spectra of **PNCHQ** before and after the addition of DCP (λ_{ex}=300 nm).

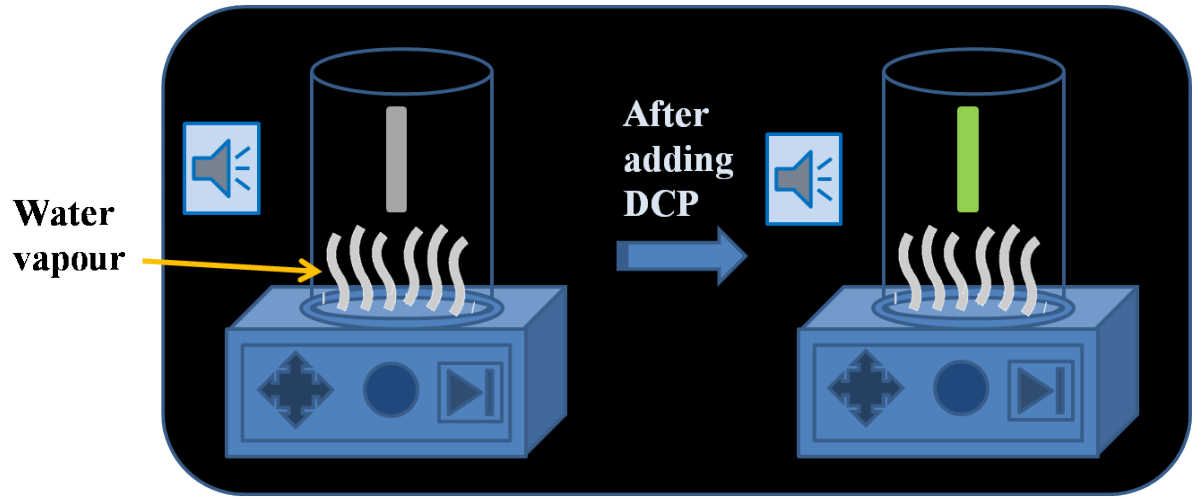


Fig. S22. A cartoon representation of **PNCHQ** coated paper strip sensing of DCP in presence of water vapour.

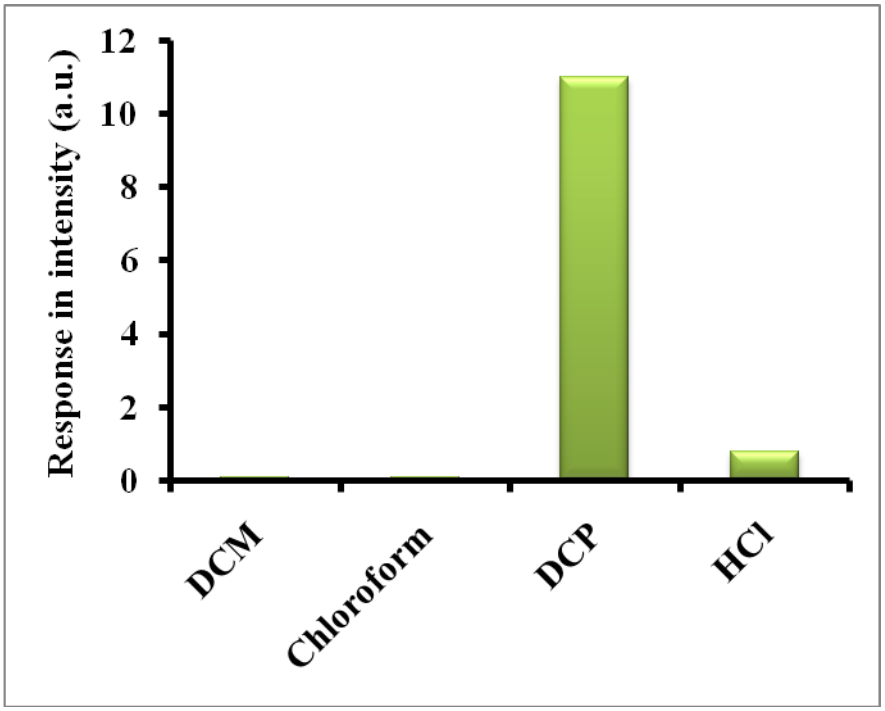


Fig. S23 Response of **PNCHQ** coated paper strip against other chlorine compounds.

References:

1. Zhang, Y. M.; Chen, Y.; Li, Z. -Q.; Li, N.; Liu, Y. *Bioorg. Med. Chem.* **2010,** *18*, 1415.

2. Bag, S. S.; Kundu, R. *J. Org. Chem.* **2011**, *76*, 3348.