Electronic Supplementary Information

Discriminative Light-up Detection of Volatile Chlorinated Solvents and Dual-Phase Encrypted Security Ink

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1. Experimental Section

1.1. Materials and methods

All precursor materials and reagents (1,8-Diaminonaphthalene, phenylboronic acid, methyl boronic acid, benzaldehyde) were purchased from Sigma Aldrich (INDIA) and were of reagent grade. HPLC grade solvents were purchased from Zenith India and Northeast Chemicals. NMR (^{1}H, ^{13}C) spectra were recorded with a Varian-AS400 NMR spectrometer or Bruker Avance 600 MHz spectrometer. All solutions for ^{1}H and ^{13}C spectra were obtained taking residual solvent signal as internal reference. Electro spray ionization mass (ESI-MS) spectra were recorded on a Waters (Micro mass MS-Technologies) Q-Tof MS Analyzer spectrometer. Microbalance (± 0.1mg) and volumetric glassware were used for the preparation of solutions. UV/vis and PL spectra were recorded on a Perkin-Elmer Model Lambda-750 spectrophotometer and a Horiba Fluoromax-4 spectrofluorometer respectively using 4 mm quartz cuvettes at 298 K.

1.2. Syntheses of Compounds[1]
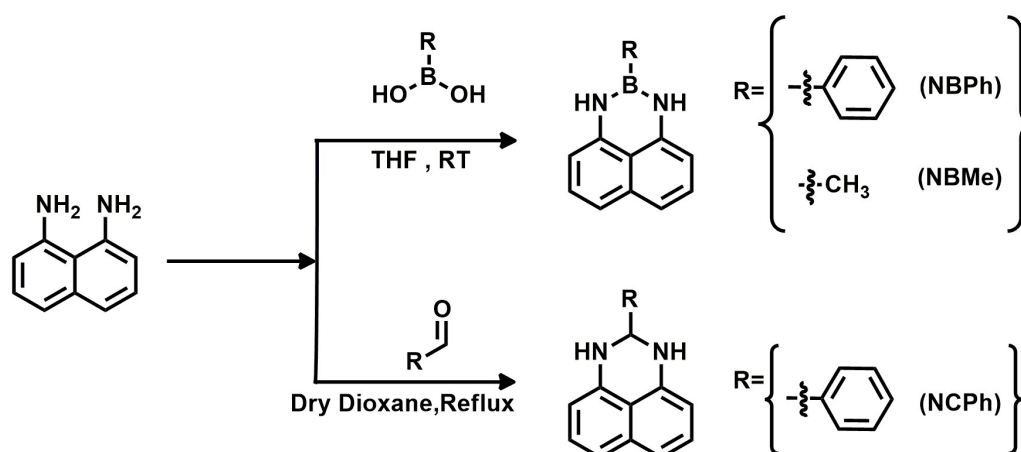
Scheme S1: Synthetic route for the preparation of **NCPh**, **NBMe**, **NBPh** molecules.

1.2.1. Syntheses of Compounds NBPh and NBMe

At room temperature naphthalene-1,8-diamine (100 mg, 0.633 m.mol) and phenylboronic acid (78 mg, 0.633 m.mol for **NBPh**) or methyl boronic acid (38 mg, 0.633 m.mol for **NBMe**) was taken in 50 mL round bottom flask and 10 mL THF was added as a solvent. Then the mixture was stirred for 15 hours at room temperature. After the reaction was over, the mixture was cooled to room temperature, solvent evaporated using rotatory evaporator under low pressure. The mixture was washed with water and extracted with ethyl acetate. The organic phase was dried over anhydrous sodium sulphate and dried using rotatory evaporator. The residue was purified by column chromatography over silica gel using 2% ethyl acetate in hexane to obtain the pure product.

Characterization Data of NBPh: Grey colored solid (105 mg, 68.08% yield), ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.66 (d, J = 7.1 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.16 (t, J = 7.7 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.43 (d, J = 7.3 Hz, 2H), 6.04 (s, 2H). 13C NMR (150 MHz, CDCl$_3$) δ 141.22, 136.53, 131.57,

130.42, 128.42, 127.76, 120.02, 118.00, 106.18. HRMS (+ ESI): Calculated for $C_{16}H_{13}BN_2$, 244.1182 [M] +.

Characterization Data of NBMe: Grey colored solid (84 mg, 73.04% yield), ^1H NMR (600 MHz, $CDCl_3$) δ 7.09 (t, J = 7.8 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.28 (d, J = 7.3 Hz, 2H), 5.62 (s, 2H), 0.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.36, 136.45, 127.68, 119.55, 117.48, 105.47, 8.70. HRMS (+ ESI): Calculated for $C_{16}H_{11}BN_2$, Found 183.1090 [M+H] +.

1.2.2. Syntheses of Compounds NCPh

Naphthalene-1,8-diamine (100 mg, 0.633 m.mol) and benzaldehyde (193 µL, 0.633) was taken in 50 mL round bottom flask and 10 mL dry dioxane was added as a solvent under inert condition. The reaction mixture was stirred for 24h at 90 °C temperature, followed by evaporation using rotatory evaporator under low pressure. The mixture was washed with water and extracted with ethyl acetate and the organic phase was dried over anhydrous sodium sulphate and evaporated using rotatory evaporator. The residue was purified by column chromatography over silica gel using 3% ethyl acetate in hexane to obtain the pure product.

Characterization Data of NCPh: Light yellow powder (70 mg, 44.96% yield), ^1H NMR (600 MHz, $CDCl_3$) δ 7.57 (dd, J = 6.4, 2.8 Hz, 2H), 7.38 (dd, J = 4.8, 1.6 Hz, 3H), 7.20 – 7.15 (m, 4H), 6.46 (dd, J = 7.1, 0.7 Hz, 2H), 5.40 (s, 1H), 4.51 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.17, 140.12, 135.01, 129.77, 128.99, 128.06, 127.01, 118.06, 113.58, 106.01, 68.56. HRMS (+ESI): Calculated for $C_{17}H_{14}N_2$, Found 247.1230 [M+H]+.

1.3. Sensing Studies

Stock solution for all the three probes (**NBMe**, **NBPh**, **NCPh**) were prepared at a concentration of 10 mM in 1 mL methanol and was diluted further into 20 µM solution in chloroform in a sealed cuvette at the time of sensing titration experiments and emission spectra was recorded under 330 nm excitation up to 15 min. The UV/visible spectra of the same solution was recorded before (at 0 min) and after (at 15 min) the 330 nm light excitation. For the interference study, the 10 mM methanol stock solution was diluted into 20 µM concentration in the corresponding solvents for all the probes and followed the same procedure of chloroform titration.

1.4. Fluorescence quantum yield calculation:

The change in fluorescence quantum yield of all the three probes (**NBMe, NBPh, NCPh**) were calculated using quinine sulfate (Φr = 0.52 in 0.1N H_2SO_4) as standard and it was determined by the below equation:

$$\Phi_s = \Phi_s(A_rE_s/A_sE_r)(\eta_s^2/\eta_r^2)$$

Where, Subscripts 'r' and 's' refer to the reference and sample fluorophore respectively. A and E denote Absorbance and Integrated fluorescence emission intensity. η is the refractive index of the used solvent.

2. Comparison table

Table S1: Represents a comparison of detection limit, detection method, selectivity of the probe, and discriminative features for existing material with the present work in chloroform detection

Publication	Material used	Detection limit	Selectivity	Method	Solvent Discrimication	Ref
Present Work	**Organic Small molecule**	**7.95 ppm**	**Yes**	Fluorometric & Colorimetric	Chloroform, carbon tetrachloride, chlorobenzene and 1,2-dichloromethane	-
Nat. Commun., **2013**, *4*, 2461	Polymer	-	Yes	Fluorometric & Colorimetric	Chloroform and 1,2-dichloromethane	2
ACS Appl. Mater. Interfaces, **2018**, *10*, 33730-33736	Organic phosphor	< 5 ppm	Yes	Phosphoresce nce	-	3
Molecules, **2017**, *22*, 1306	Copolymer	<150 ppm	NO	Fluorometric	-	4
Sensors and Actuators B, **2013**, *183*, 25-33	Nanocomposite	50 ppm	No	Electrical conductivity	-	5
Composites Part B, **2019** *173*, 106894	Nanocomposite	50 ppm	Yes	Electrical conductivity	-	6
J. Mater. Chem. A, **2013**, *1*, 10327	Composite material	30 ppm	Yes	Electrical conductivity	-	7
Chem. Commun., **2016**, *52*, 2095	Napthalimide based organic molecule	NO	Yes	Fluorometric	Halogenated and non-halogenated	8

|						
Chem. Eur. J., **2017**, *23*, 12559-12564	MOF	2.5×10^{-5} M	Yes	Colorimetric	-	9
RSC Adv., **2017**, *7*, 18132-18135	Pyridinium 5-aminothiazoles	-	Yes	Fluorometric And Colorimetric	Halogenated and non-halogenated	10
Macromolecules, **2017**, *50*, 4927-4934	Polymer	-	NO	FTIR	-	11
Sensors and Actuators B, **2018**, *261*, 97-105	Polyaniline	9.22 ppm	Yes	Bragg wavelength shift	-	12
Sensors and Actuators A, **2019**, *296*, 87-91	Graphene-polymer Nanocomposite	30 ppm	Yes	Visual Shape switching phenomena	NO	13

3. Effect of 365 nm light exposure
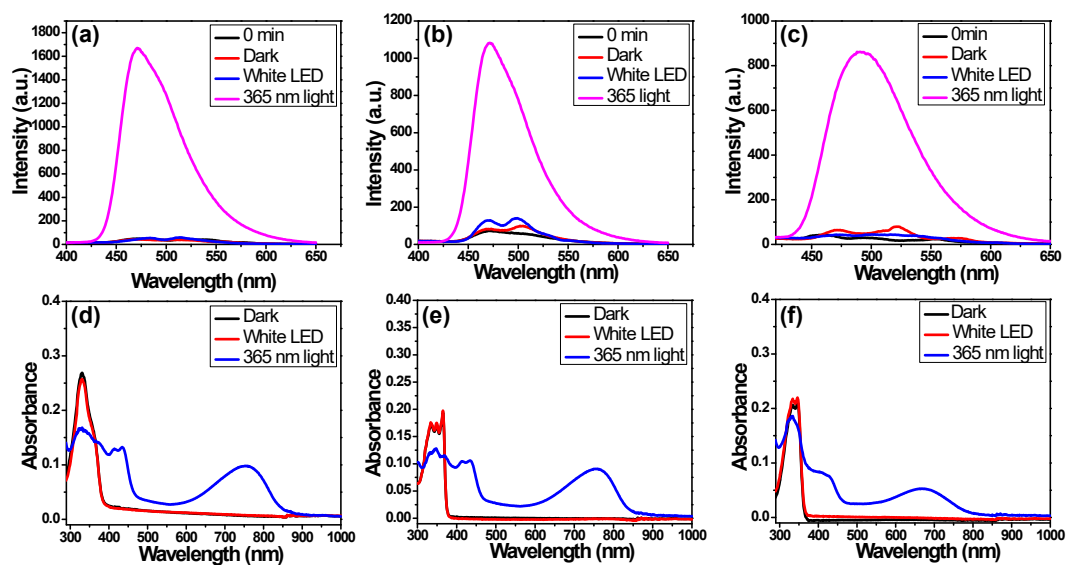
Fig. S1: Fluorescence spectra of (a) **NBPh** (b) **NBMe** (c) **NCPh** in chloroform (20 *μ*M) in dark and on exposure to different light sources for 15 min. UV/visible spectra of (d) **NBPh** (e) **NBMe** (f) **NCPh** in dark conditions and on exposure to different light sources for 15 min.
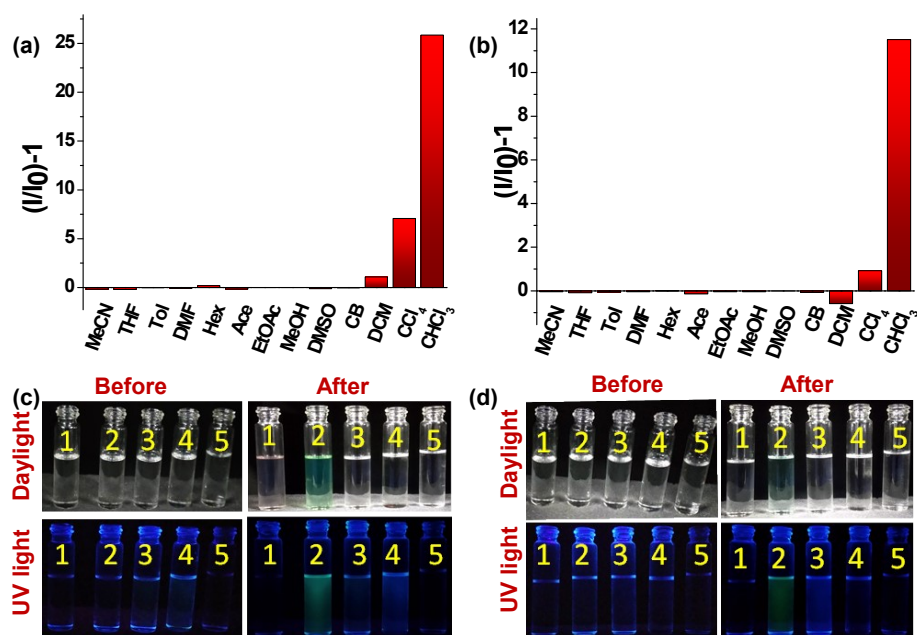
4.   Selectivity studies in liquid phase

Fig. S2: Selectivity study of (a) **NBPh** and (b) **NCPh** molecule (20 µM) in the presence of other common solvents such as acetonitrile, tetrahydrofuran, toluene, dimethylformamide, hexane, acetone, ethyl acetate, methanol, dimethyl sulfoxide, chlorobenzene, 1,2 dichloroethane, carbon tetrachloride, chloroform (from left to right). Digital photograph of (c) **NBPh** and (d) **NCPh** in different solvents (inset 1. carbon tetrachloride, 2. chloroform, 3. 1,2-dichloromethane, 4. chlorobenzene, 5. methanol) before and after irradiation for 15 min under 365 nm light.

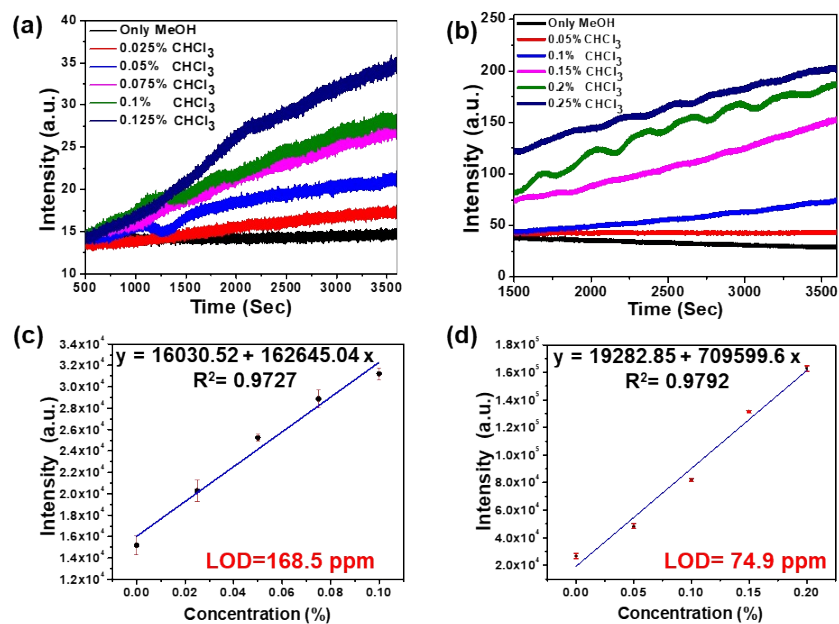## 5. Photoluminescence kinetics spectra

Fig. S3: Photo-luminescence kinetics spectra of (a) **NBPh** and (b) **NCPh** (20 µM) with increasing percentage of chloroform recorded up to 1 hour in methanol at room temperature. Fluorescence response of (c) **NBPh** and (d) **NCPh** (20 µM) taken in methanol as a function of chloroform percentage.

6. UV/Visible spectra
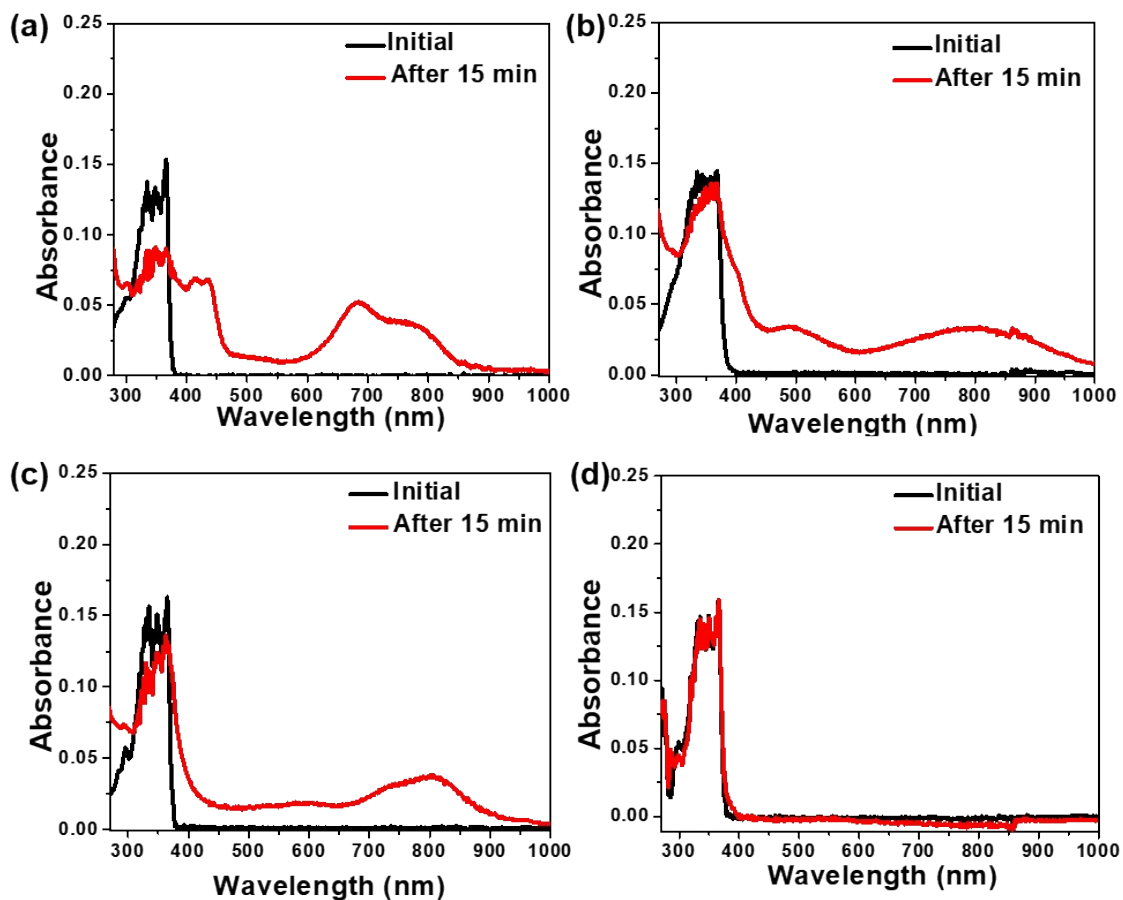
Fig. S4: UV/Visible spectra of NBMe in (a) $CHCl_3$, (b) CCl_4, (c) CH_2Cl_2 (d) PhCl before and after UV irradiation.

7. Table S2: Representation of CIE coordinates for the final emission of **NBMe** probe after 15 min of exposure at 330 nm light excitation in the corresponding solvent.

Name of the Solvent	X Coordinate	Y coordinate
$CHCl_3$ (a_1)	0.153401	0.255429
CCl_4 (b_1)	0.19652	0.185147
DCM (c_1)	0.158929	0.191955
PhCl (d_1)	0.15774	0.043031

8.   Time-resolved fluorescence spectra

Fig. S5: Time-resolved fluorescence spectra of (a) **NBPh** (b) **NBMe** (c) **NCPh** (20 µM) in chloroform with irradiation (WI) and without irradiation of UV light.
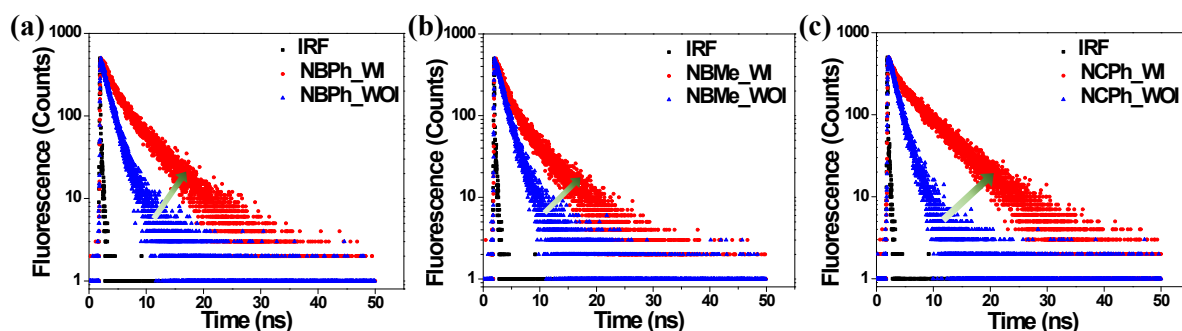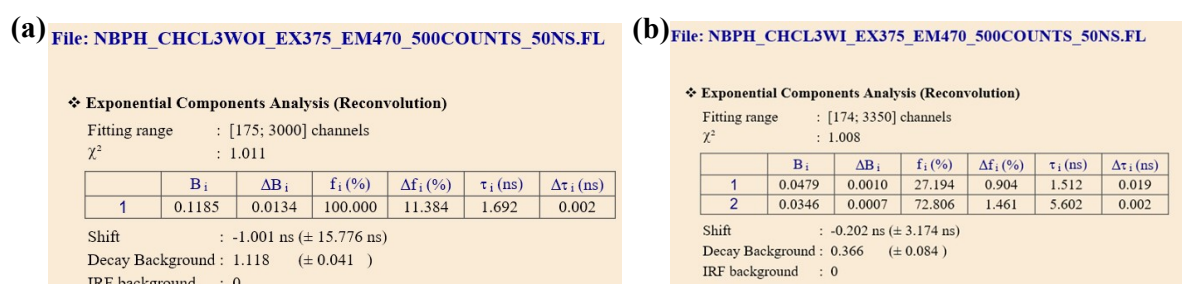
(a) File: NBPH_CHCL3WOI_EX375_EM470_500COUNTS_50NS.FL

❖ **Exponential Components Analysis (Reconvolution)**

Fitting range   : [175; 3000] channels
χ^2 : 1.011

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.1185	0.0134	100.000	11.384	1.692	0.002

Shift   : -1.001 ns (± 15.776 ns)
Decay Background : 1.118   (± 0.041)
IRF background   : 0

(b) File: NBPH_CHCL3WI_EX375_EM470_500COUNTS_50NS.FL

❖ **Exponential Components Analysis (Reconvolution)**

Fitting range   : [174; 3350] channels
χ^2 : 1.008

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0479	0.0010	27.194	0.904	1.512	0.019
2	0.0346	0.0007	72.806	1.461	5.602	0.002

Shift   : -0.202 ns (± 3.174 ns)
Decay Background : 0.366   (± 0.084)
IRF background   : 0

Fig. S6: Fitting parameters and IRF values correspond to lifetime measurements of **NBPh** probe in chloroform (a) Without irradiation (WOI), (b) With irradiation (WI)
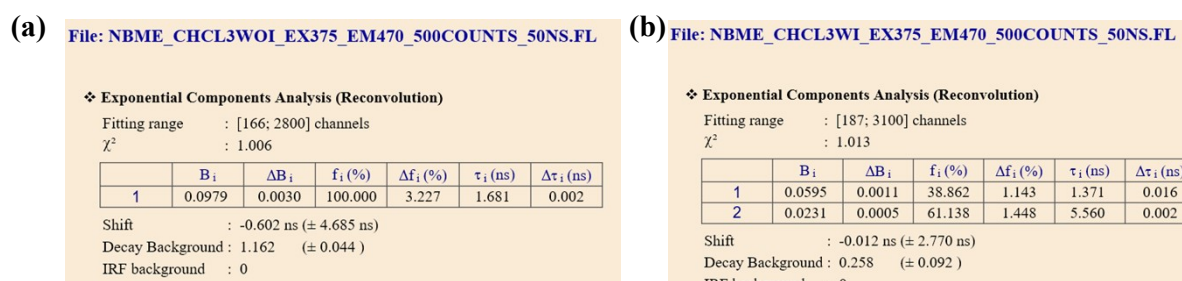
(a) File: NBME_CHCL3WOI_EX375_EM470_500COUNTS_50NS.FL

❖ **Exponential Components Analysis (Reconvolution)**

Fitting range   : [166; 2800] channels
χ^2 : 1.006

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0979	0.0030	100.000	3.227	1.681	0.002

Shift   : -0.602 ns (± 4.685 ns)
Decay Background : 1.162   (± 0.044)
IRF background   : 0

(b) File: NBME_CHCL3WI_EX375_EM470_500COUNTS_50NS.FL

❖ **Exponential Components Analysis (Reconvolution)**

Fitting range   : [187; 3100] channels
χ^2 : 1.013

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0595	0.0011	38.862	1.143	1.371	0.016
2	0.0231	0.0005	61.138	1.448	5.560	0.002

Shift   : -0.012 ns (± 2.770 ns)
Decay Background : 0.258   (± 0.092)
IRF background   : 0

Fig. S7: Fitting parameters and IRF values correspond to lifetime measurements of **NBMe** probe in chloroform (a) Without irradiation (WOI), (b) With irradiation (WI)
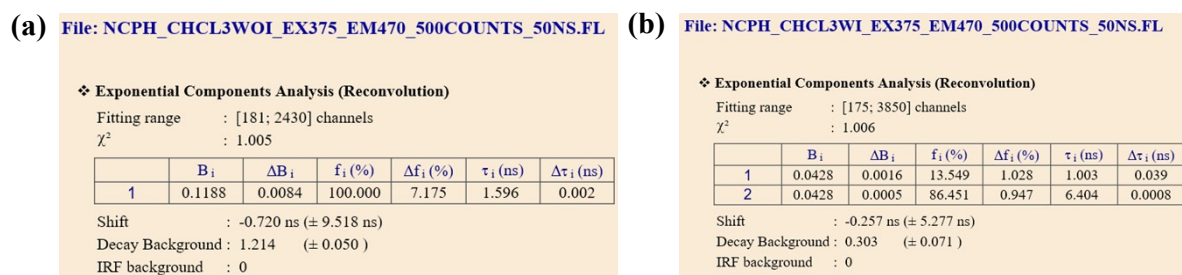
(a) File: NCPH_CHCL3WOI_EX375_EM470_500COUNTS_50NS.FL

❖ **Exponential Components Analysis (Reconvolution)**

Fitting range   : [181; 2430] channels
χ^2 : 1.005

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.1188	0.0084	100.000	7.175	1.596	0.002

Shift   : -0.720 ns (± 9.518 ns)
Decay Background : 1.214   (± 0.050)
IRF background   : 0

(b) File: NCPH_CHCL3WI_EX375_EM470_500COUNTS_50NS.FL

❖ **Exponential Components Analysis (Reconvolution)**

Fitting range   : [175; 3850] channels
χ^2 : 1.006

	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta\tau_i$ (ns)
1	0.0428	0.0016	13.549	1.028	1.003	0.039
2	0.0428	0.0005	86.451	0.947	6.404	0.0008

Shift   : -0.257 ns (± 5.277 ns)
Decay Background : 0.303   (± 0.071)
IRF background   : 0

Fig. S8: Fitting parameters and IRF values correspond to lifetime measurements of **NCPh** probe in chloroform (a) Without irradiation (WOI), (b) With irradiation (WI)
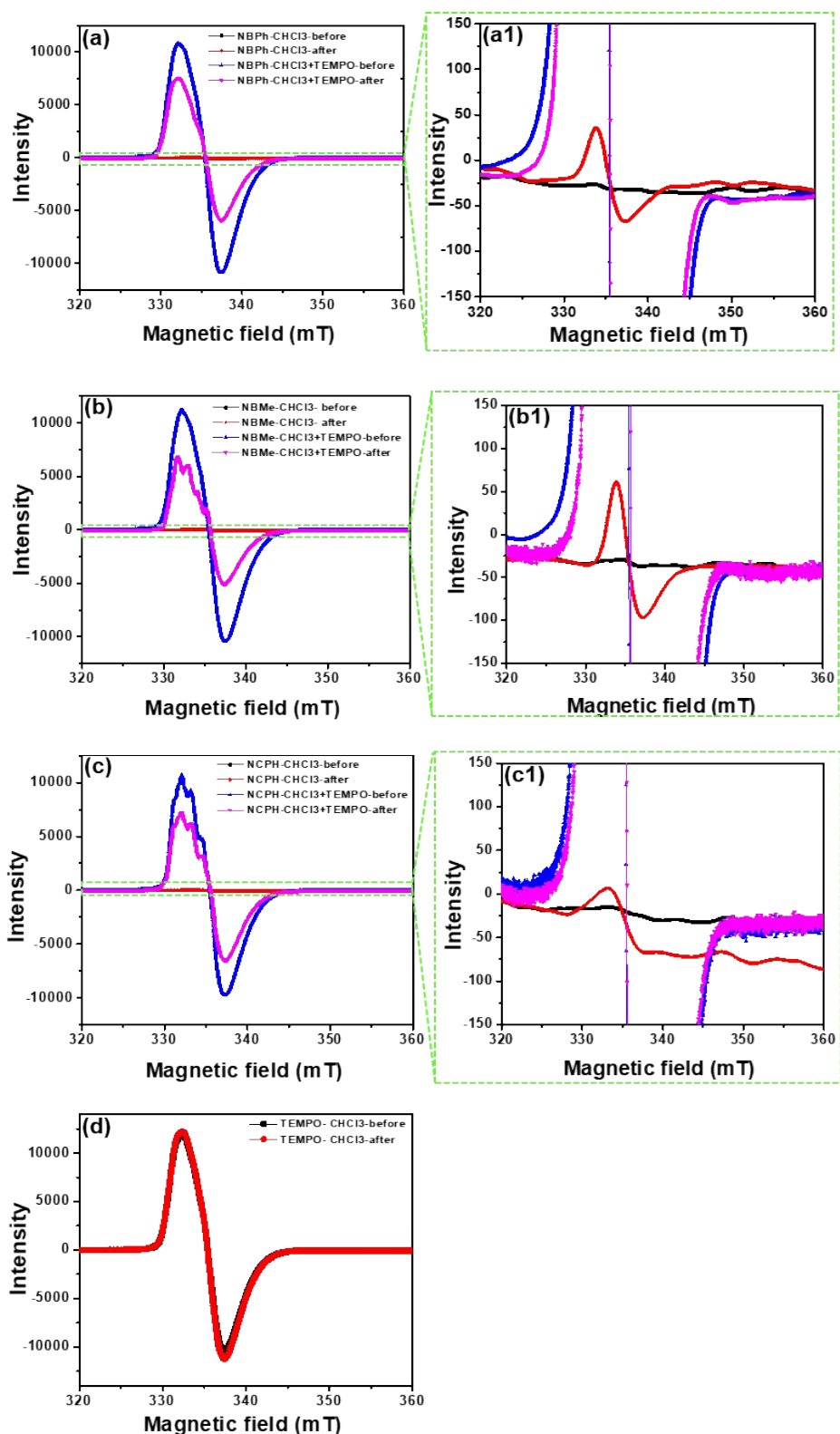
9. ESR Spectra

Fig. S9: ESR spectra of (a) **NBPh** (b) **NBMe** (c) **NCPh** with and without 1 equivalent of TEMPO in chloroform (10mM) before and after the exposure to 365 nm sources for 5 min (left). (a1), (b1), and (c1) represents the magnified portion of the corresponding ESR spectra (right).

10. Fluorescence change in presence of radical scavenger

Fig. S10: Bar diagram represents fluorescence intensity of **NBPh**, **NBMe**, **NCPh** with 1 equivalent and 5 equivalent of TEMPO in chloroform (20 µM) before and after the exposure to 365 nm sources for 15 min at room temperature.

11. Temperature dependent luminescence spectra

Fig. S11: Fluorescence spectra of (a) NBPh (b) NBMe (c) NCPh in chloroform (20 µM) on exposure to 365 nm sources for 15 min at different temperature.

12.   NMR and FTIR Titration

For NMR titration, 1 mg of the probe (**NBMe**, **NBPh**, **NCPh**) was dissolved in 500 μL CDCl$_3$ solution and NMR spectra was recorded instantly under dark condition. Then the same solution was kept under 365 nm UV light and spectra was recorded with the mentioned time. For FTIR titration, 1 mg of the probe (**NBMe**, **NBPh**, **NCPh**) was dissolved in 500 μL chloroform solution and followed the same procedure of NMR titration.
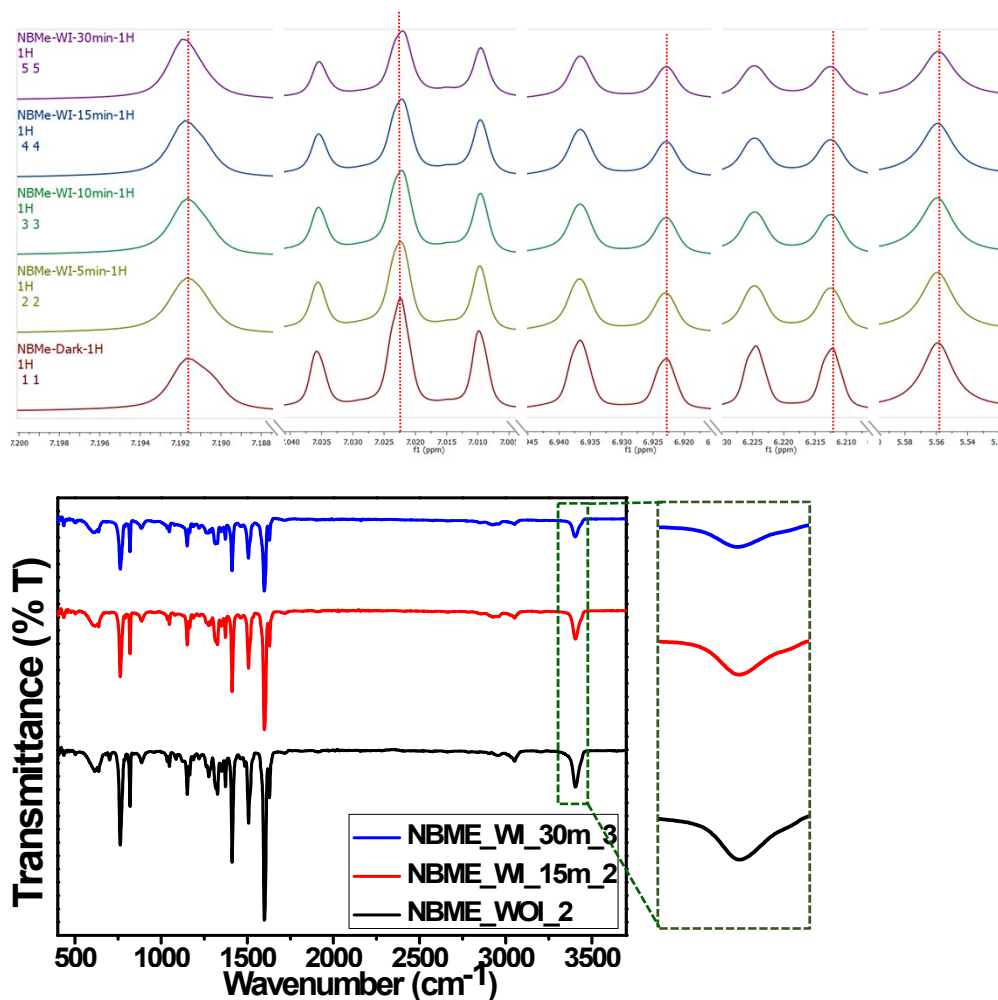
Fig. S12: (above) Partial ^{1}H-NMR spectra for the titration of **NBMe** molecules in the presence of deuterated chloroform under dark state and with irradiation (WI) of 365 nm UV light with time up to 30 min. (below) FTIR spectra of **NBMe** molecules in chloroform without irradiation (WOI), with irradiation (WI) after 15 min and 30 min.
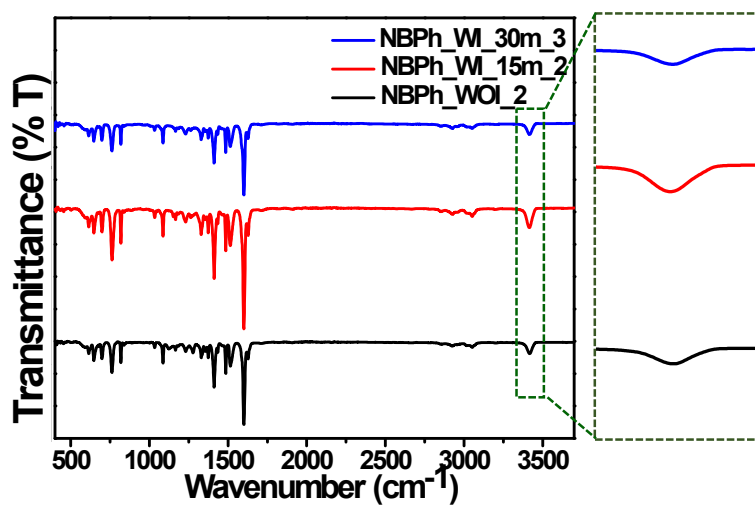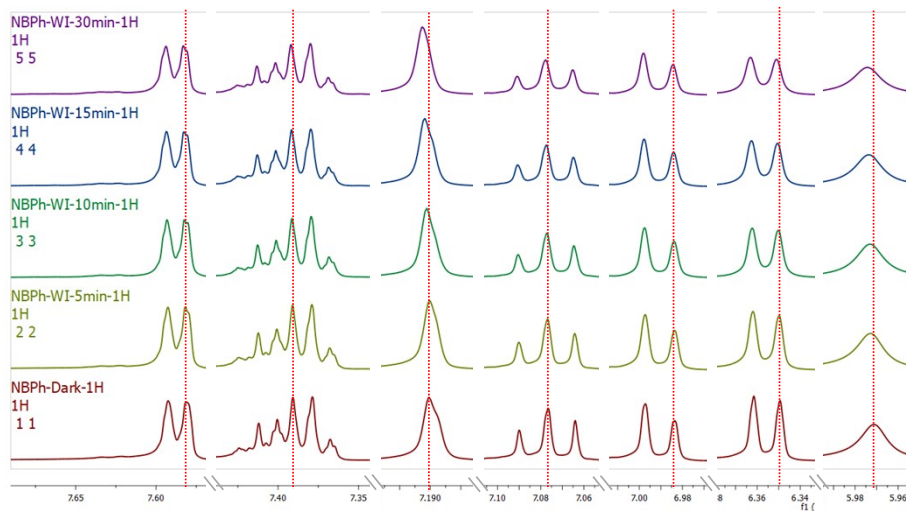
Fig. S13: (above) Partial ^{1}H-NMR spectra for the titration of **NBPh** molecules in presence of deuterated chloroform under dark state and with irradiation (WI) of 365 nm UV light with time up to 30 min. (below) FTIR spectra of **NBPh** molecules in chloroform without irradiation (WOI), with irradiation (WI) after 15 min and 30 min.

13. Electrostatic potential diagram

Ground state geometry were optimized by density functional theory (DFT) method using the B3LYP/6-31G basis set in Gaussian 09 software.[14] Then the electrostatic potential diagram was evaluated via using the optimized structure.
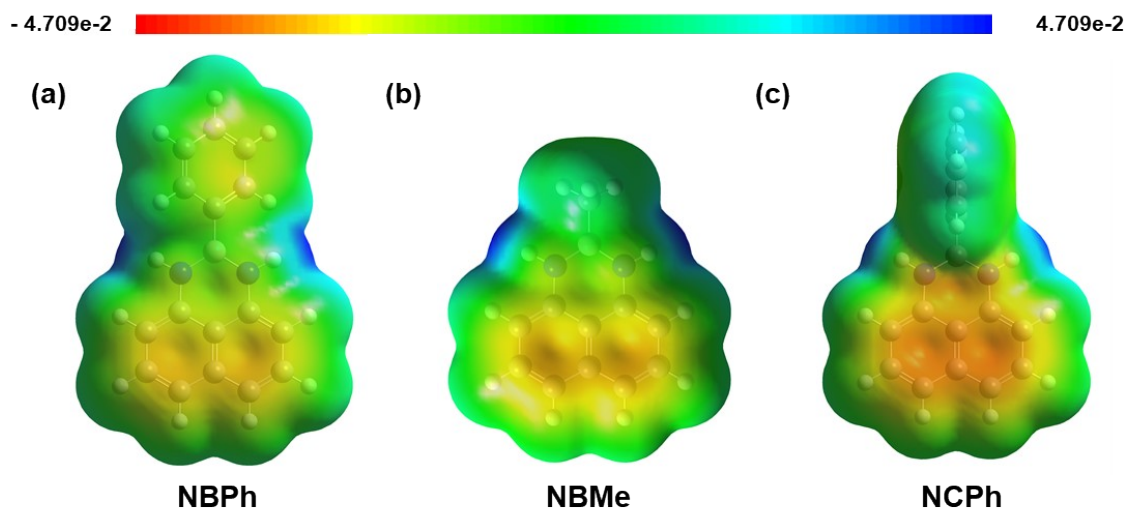
Fig. S14: Electrostatic potential diagram (ESP) of (a) **NBPh** (b) **NBMe** (c) **NCPh** calculated at B3LYP/6-31G.

14.   Vapour phase study
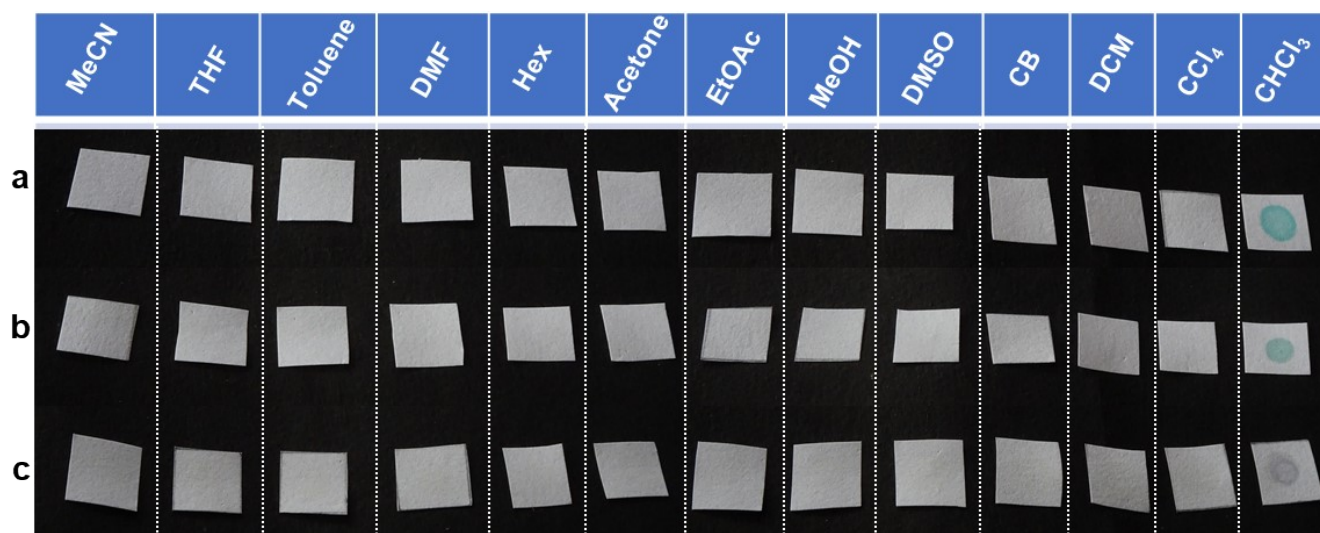
Fig. S15: Digital photographs illustrate the naked eye responses of (a) **NBMe**, (b) **NBPh**, (c) **NCPh** molecule in the presence of other common solvents such as acetonitrile, tetrahydrofuran, toluene, dimethylformamide, hexane, acetone, ethyl acetate, methanol, dimethyl sulfoxide, chlorobenzene, 1,2-dichloroethane, carbon tetrachloride, chloroform (from left to right).
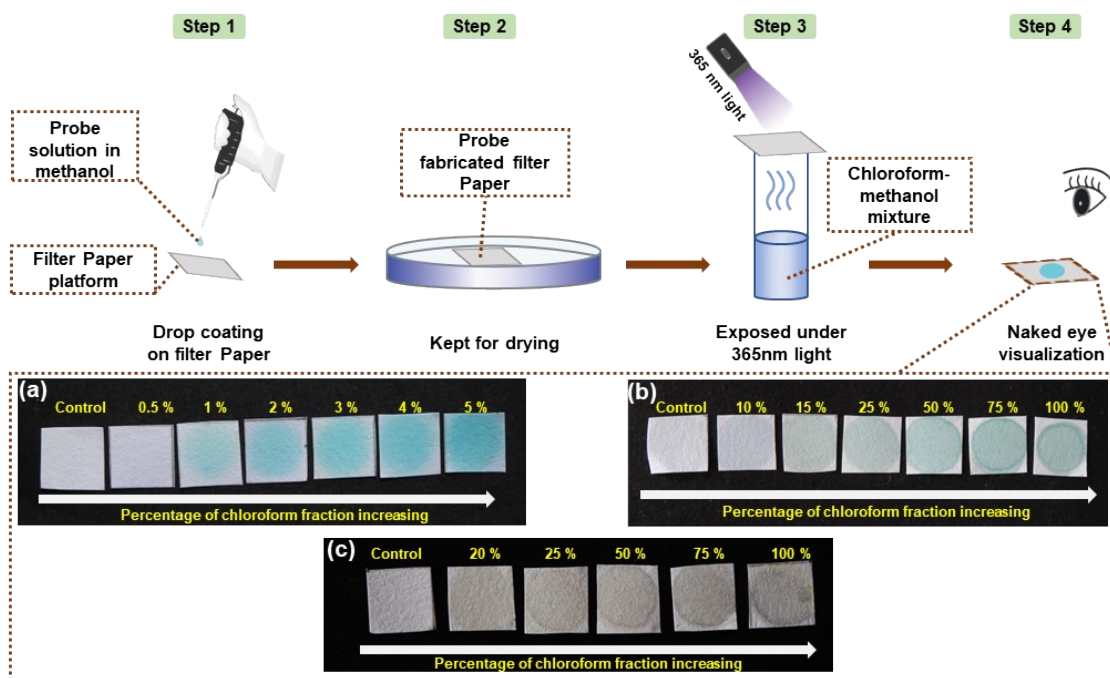
Fig. S16: Demonstrates a schematic representation for vapour phase chloroform detection process and the visual colour changes of the filter paper embedded with (a) NBMe, (b) NBPh, (c) NCPh up on increasing chloroform percentage.
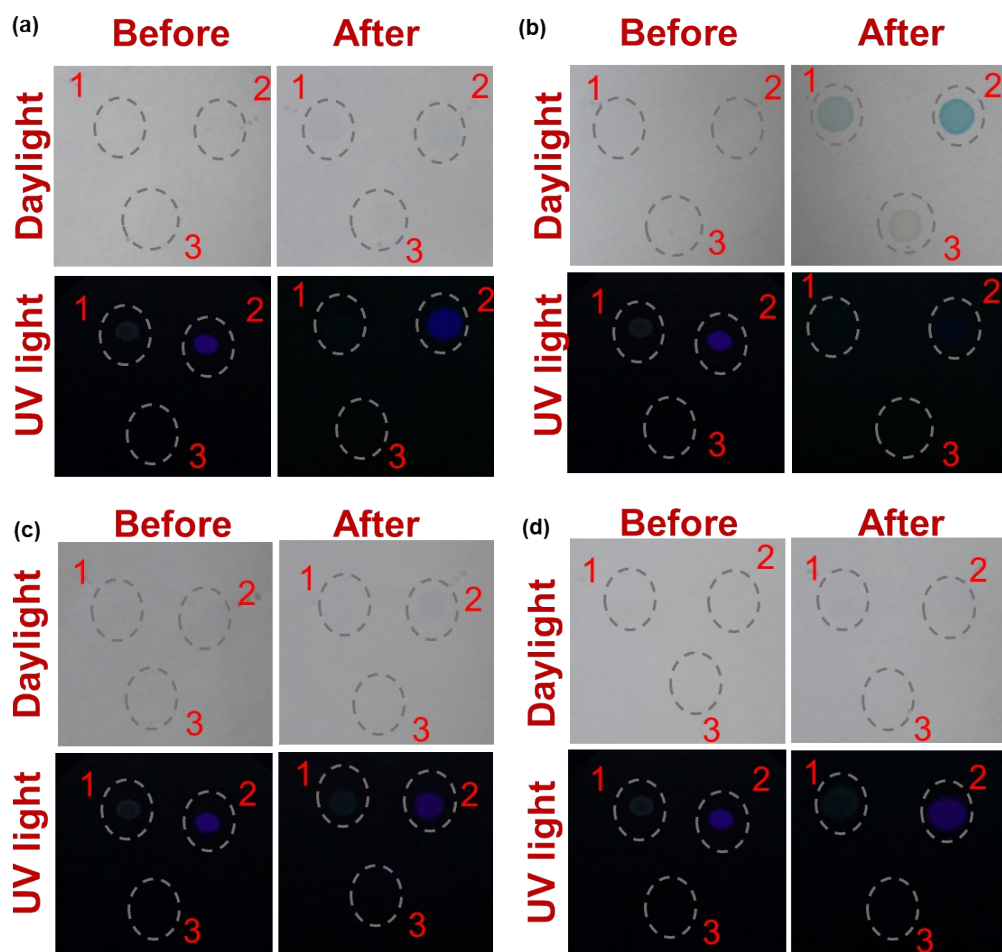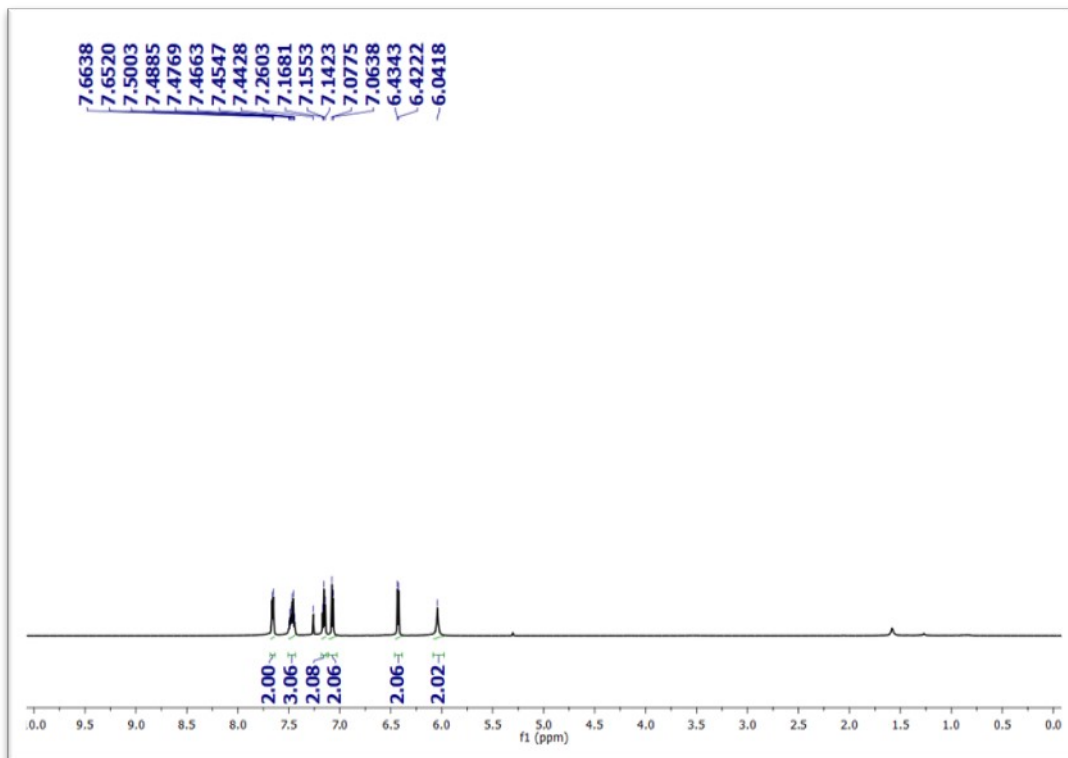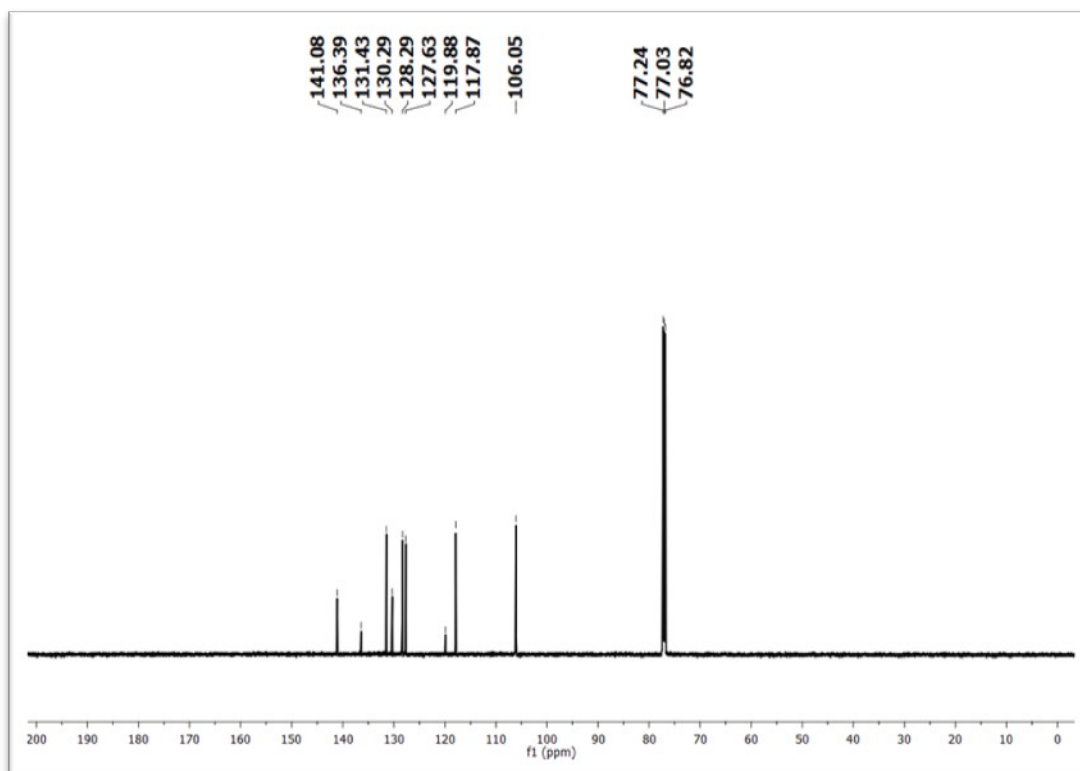
Fig. S17: Digital photographs depict the fluorescence and naked eye response of all three molecules (inset 1, **NBPh**; 2, **NBMe**; 3, **NCPh**) before and after the exposure of (a) carbon tetrachloride, (b) chloroform, (c) 1,2 dichloroethane, (d) chlorobenzene in presence of 365 nm light for 2 min.
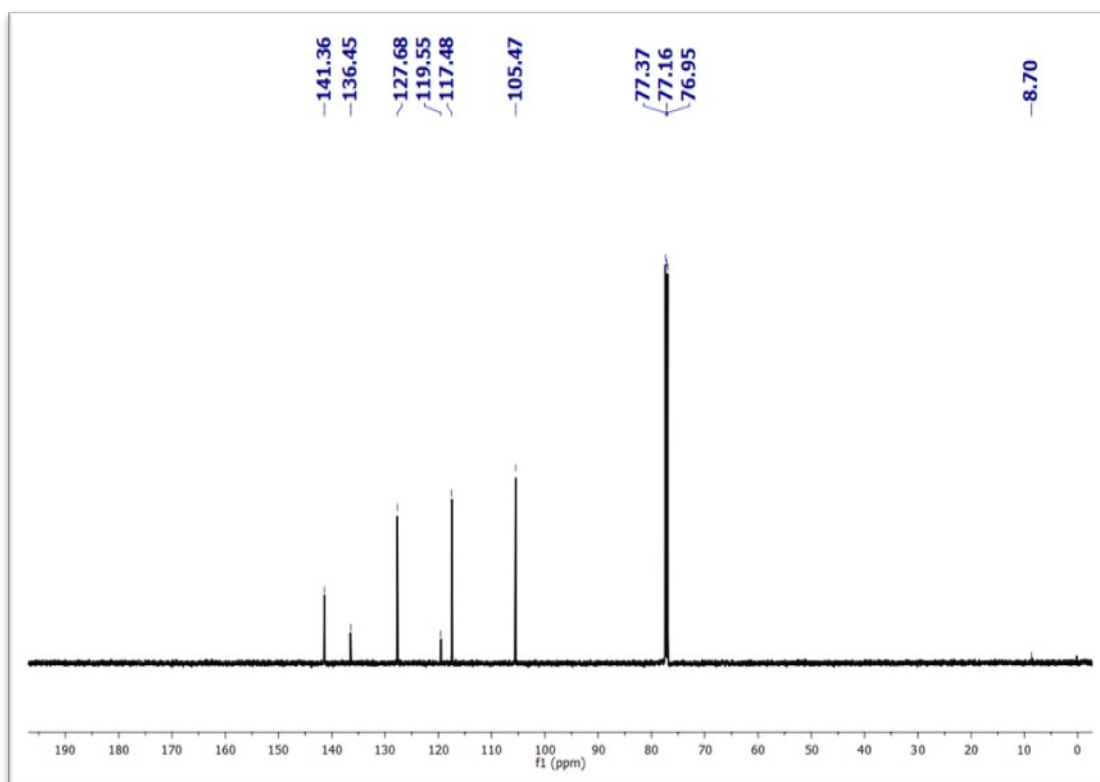
15. ¹H-NMR, ¹³C-NMR, and Mass Spectra

¹H-NMR of NBPh

¹³C-NMR of NBPh
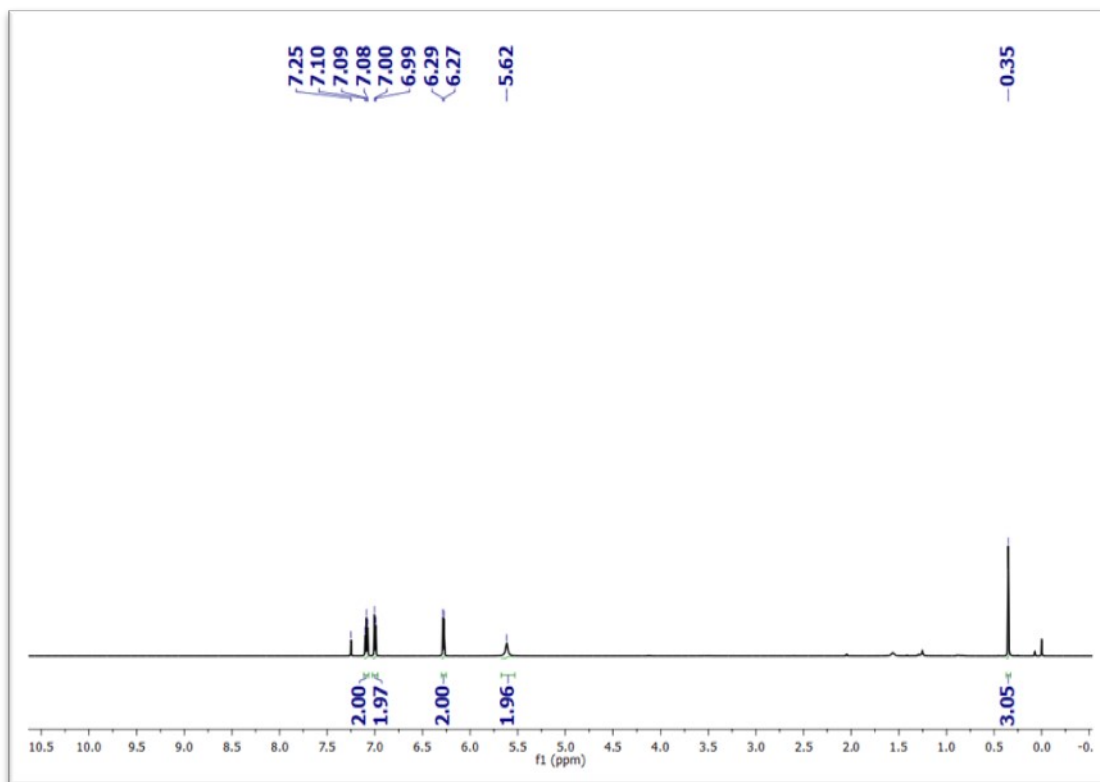
¹H-NMR of NBMe

¹³C-NMR of NBMe

¹H-NMR of NCPh

7.5801
7.5740
7.5679
7.5648
7.3812
7.3798
7.3743
7.3705
7.2037
7.1901
7.1785
7.1641
7.1632
7.1508
6.4633
6.4621
6.4515
6.4504
5.3967
4.5072

2.00
2.99
4.46
2.00
1.01
1.95

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)
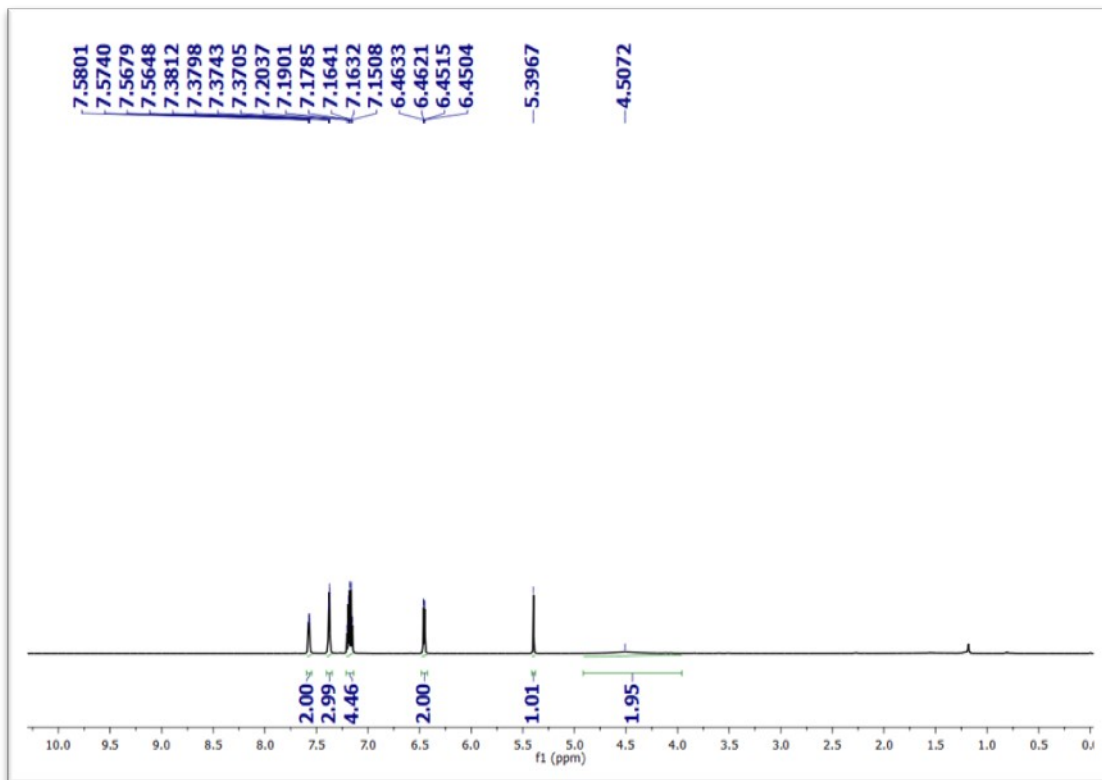
¹H-NMR of NCPh

¹³C-NMR of NCPh

142.17
140.12
135.01
129.77
128.99
128.06
127.01
118.06
113.58
106.01
77.37
77.16
76.95
68.56

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

¹³C-NMR of NCPh

Mass spectra of NBMe

+ESI Scan (rt: 0.676 min) Frag=175.0V RP-NCPH.d
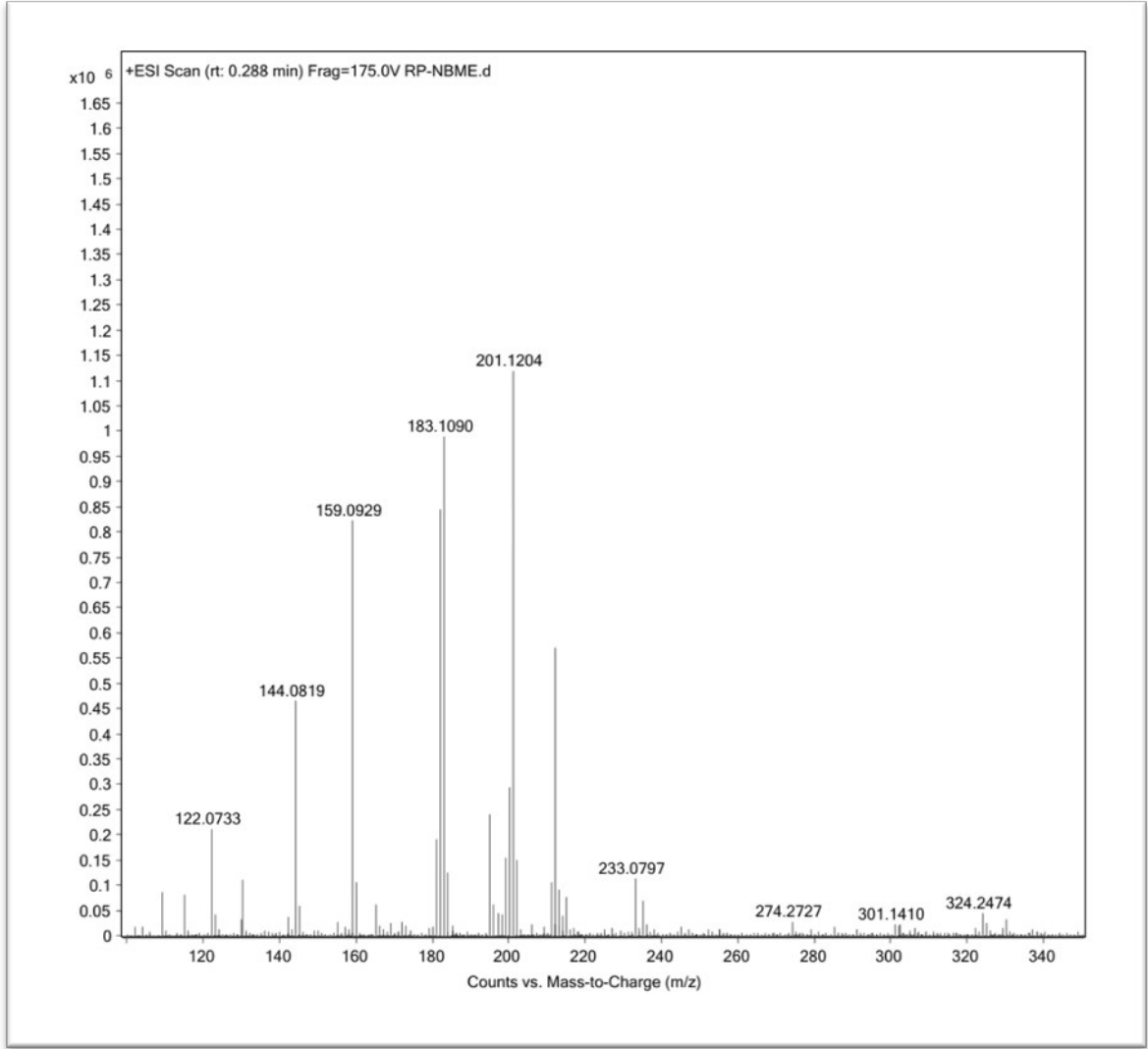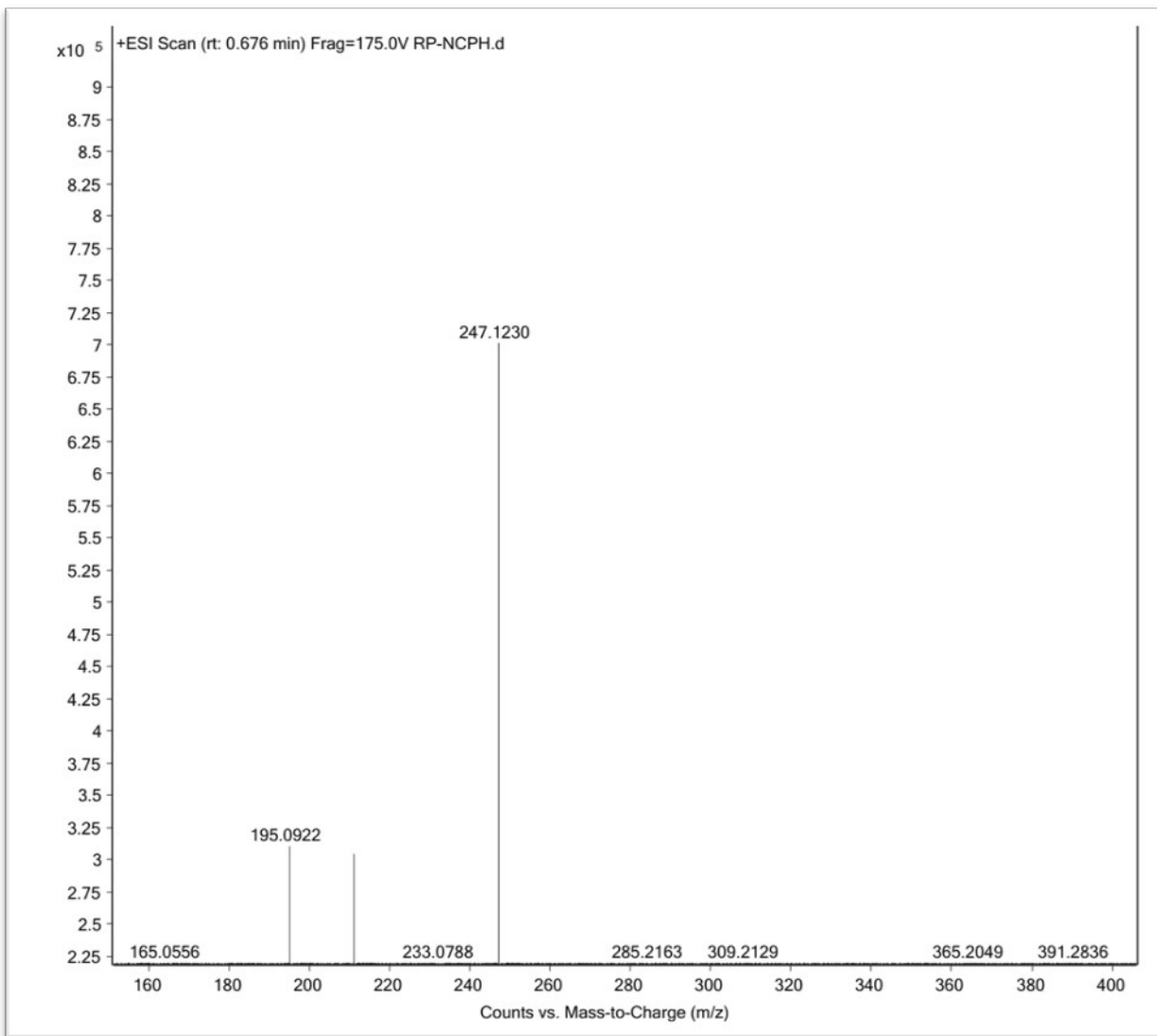
Mass spectra of NCPh
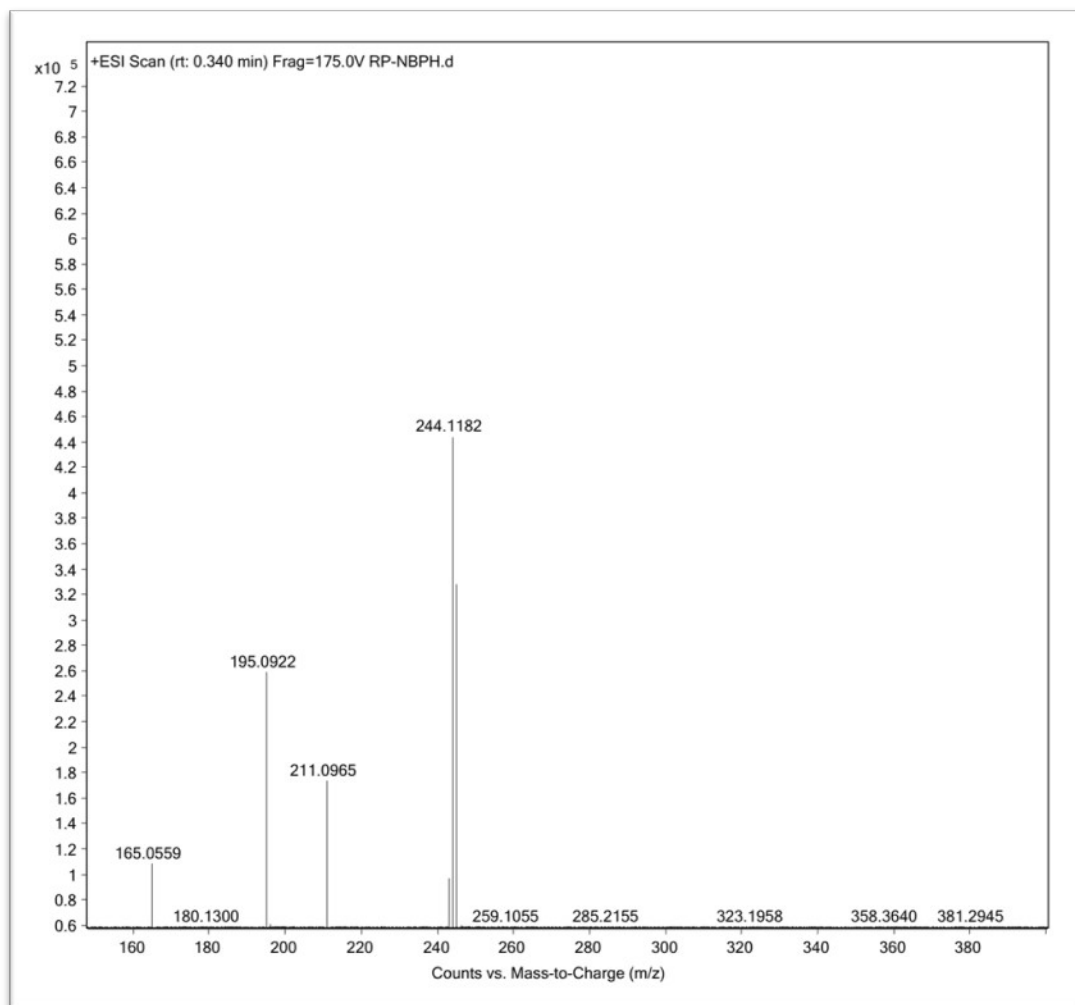
Mass spectra of NBPh

16. References:

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