Supporting Information

Impact of aggregation on fluorescence sensitivity of molecular probes towards nitroaromatic compounds

Sana Sandhu[a], Rahul Kumar[a], Prabhpreet Singh[a]*, Subodh Kumar[a]*

Corresponding author. Address: Department of Chemistry, UGC Centre for Advanced Studies, Guru Nanak Dev University, Amritsar 143 005, India.

E-mail address: subodh_gndu@yahoo.com, Mobile: +91 9872361528

E-mail address: prabhpreet1979@gmail.com

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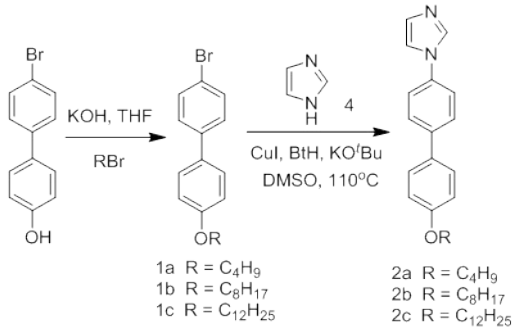
1. Experimental Details

1.1 General Remarks: All chemicals were obtained from common suppliers (Aldrich, Across, SDFCL, Spectrochem etc.) and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on BRUKER Bio spin AVANCE-III FT NMR HD-500 spectrophotometer using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are given in ppm; coupling constants in Hz. UV-Vis studies of compounds were performed on Shimadzu-2450 and fluorescence studies were carried out on BH-CHRONOS spectrophotometers. The SEM images were obtained with a FESEM JEOL JSM-6610LV. The TEM images were obtained with a JEOL JEM-2100 electron microscope. DLS experiments were performed on a Malvern zetasizer.

TIBP4, TIBP8 and TIBP12 coated paper strips. Whatman filter paper strips (1 cm x 1 cm) were dipped into solution of **TIBP4/ TIBP8/ TIBP12** (1 mM, DMSO) and were dried under vacuum at room temperature. **TIBP4** paper strips were used for naked eye (under 365 nm light) visualisation of 10^{-13} to 10^{-7} M PA solution. The 10^{-13}, 10^{-11}, 10^{-9} and 10^{-7} M solutions of PA were prepared in water and 10 µl aliquot of each of these solutions was added on separate paper strip. Similarly **TIBP8** paper strips were used for naked eye (under 365 nm light) visualisation of 10^{-17} to 10^{-11} M PA solution. For control experiment, drop of water alone was added on the **TIBP4/TIBP8** coated paper strip. The fluorescence spectrum of these paper strips was also recorded using front surface steady-state fluorescence on Chronos BH spectrophotometer.

SEM sample preparation. Solutions of **TIBP8**/**TIBP12** (1 µM, H_2O-2% DMSO) and its mixtures with varying concentrations of PA were prepared. These solutions were filtered through 0.02 micron filter membrane to remove interfering impurities. 10 µl of each of these solutions was added on the pre-cleaned surface of the separate glass slides and was allowed to dry in the incubator at 25^{o}C.

1.2 Synthesis of compound 2a-c



Scheme SI-1: Synthesis of **2a-c**

Synthesis of derivatives 1a-1c: 4'-Bromobiphenyl-4-ol (20 mmol, 4.9 g) was added to suspension of potassium hydroxide (crushed, 120 mmol, 6.7 g) in tetrahydrofuran (50 ml) at room temperature. The reaction mixture was allowed to stir for 30 minutes followed by the addition of 1-bromobutane /1-bromooctane /1-bromododecane (30 mmol). The reaction mixture was refluxed for 6 hrs. After the completion of the reaction, THF was distilled off. The residue was treated with water (100 ml) and was extracted with ethyl acetate. The solvent was distilled off and residue was crystallized from ethanol to get **1a-1c** as white solid.

Compound 1a: Yield 95 %, m.p. 100°C; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 0.99 (t, 3H, *J* = 7.5 Hz, CH_3), 1.49-1.55 (m, 4H, 2 x CH_2), 1.79 (quintet, *J* = 6.5 Hz, 2H, CH_2), 4.00 (t, 2H, *J* = 6.5 Hz, CH_2), 6.96 (d, 2H, *J* = 8.5 Hz, ArH), 7.40 (d, 2H, *J* = 8.5 Hz, ArH), 7.47 (d, 2H, *J* = 8.5 Hz, ArH), 7.52 (d, 2H, *J* = 8.5 Hz, ArH); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 13.8, 19.2, 31.3, 67.8, 114.9, 120.7, 127.9, 128.3, 131.8, 132.2, 139.8, 159.0.

Compound 1b: Yield 94 %, m.p. 110°C; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 0.89 (t, 3H, *J* = 7 Hz, CH_3), 1.26-1.34 (m, 8H, 4 x CH_2), 1.47 (quintet, 2H, *J* = 6.5 Hz, CH_2), 1.80 (quintet, 2H, *J* = 6.5 Hz, CH_2), 3.99 (t, 2H, *J* = 6.5 Hz, CH_2), 6.96 (d, 2H, *J* = 8.5 Hz, ArH), 7.40 (d, 2H, *J* = 8.5 Hz, ArH), 7.47 (d, 2H, *J* = 9 Hz, ArH), 7.52 (d, 2H, *J* = 8.5 Hz, ArH); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 31.8, 68.2, 114.9, 120.7, 127.9, 128.3, 131.8, 132.2, 139.8, 159.0.

Compound 1c: Yield 91 %, m.p. 120°C; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 0.89 (t, 3H, *J* = 7 Hz, CH_3), 1.19-1.37 (m, 16H, 8 x CH_2), 1.46 (quintet, 2H, *J* = 6.5 Hz, CH_2), 1.80 (quintet, 2H, *J* = 6.5 Hz, CH_2), 3.99 (t, 2H, *J* = 6.5 Hz, CH_2), 6.95 (d, 2H, *J* = 8.5 Hz, ArH), 7.40 (d, 2H, *J* = 8.5

Hz, ArH), 7.46 (d, 2H, *J* = 8.5 Hz, ArH), 7.52 (d, 2H, *J* = 8 Hz, ArH); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 14.1, 22.7, 26.2, 29.3, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9, 68.2, 114.9, 120.7, 127.9, 128.3, 131.7, 132.2, 139.8, 159.0.

Synthesis of imidazole derivatives 2a-2c: Cuprous iodide (0.6 mmol, 114 mg) and 1,2,3-benzotriazole (1.2 mmol, 143 mg) were dissolved in DMSO (6 ml) at room temperature. The solution was stirred for 10 min and **1a** (8 mmol, 2.4 g), imidazole (12 mmol, 817 mg) and potassium *t*-butoxide (13.2 mmol, 1.5 g) were added to this solution. The reaction mixture was stirred for 10 min and then was heated at 120^{o}C for 21 h. The completion of the reaction was monitored by TLC. The reaction mixture was allowed to cool at room temperature and was treated with aqueous EDTA (450 mg) and was heated on water bath for 30 minutes to ensure the decomplexation of copper complex. The reaction mixture was extracted with ethyl acetate, solvent was distilled off and the residue was purified by column chromatography. The compounds **2a** was isolated as light yellow solid (1.9 g). Similar reactions of imidazole with **1b** and **1c** gave respective compounds **2b** and **2c**.

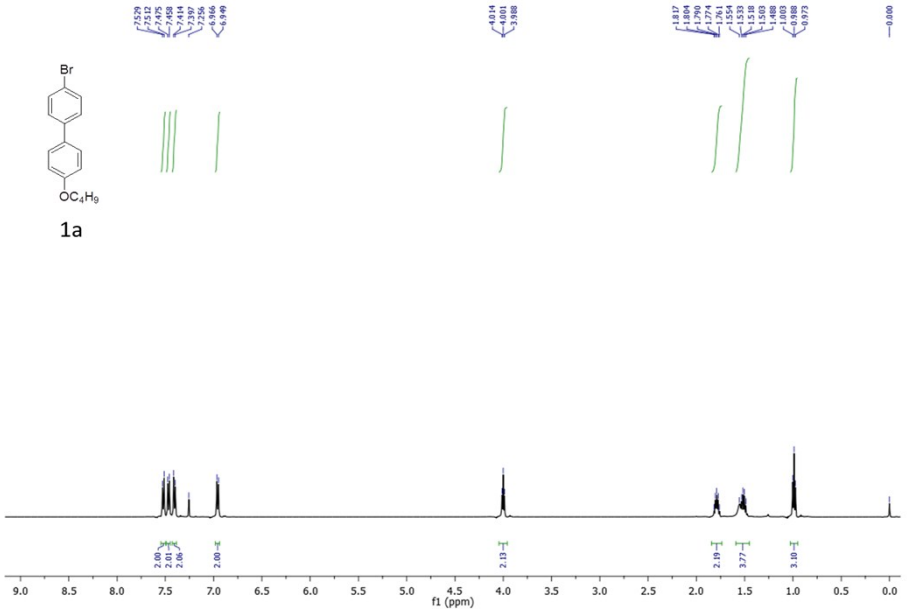
Compound 2a: Yield 83 %, m.p. 128^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 0.99 (t, 3H, *J* = 7.5 Hz, CH_3), 1.52 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 4.02 (t, 2H, *J* = 6.5 Hz, CH_2), 6.99 (d, 2H, *J* = 9 Hz, ArH), 7.22 (s, 1H, ArH), 7.31 (s, 1H, ArH), 7.43 (d, 2H, *J* = 9 Hz, ArH), 7.52 (d, 2H, *J* = 9 Hz, ArH), 7.64 (d, 2H, *J* = 8.5 Hz, ArH), 7.88 (s, 1H, Im-C2H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 13.8, 19.3, 31.3, 67.8, 115.0, 118.3, 121.8, 127.9, 128.0, 130.4, 132.0, 135.6, 135.9, 140.3, 159.1.

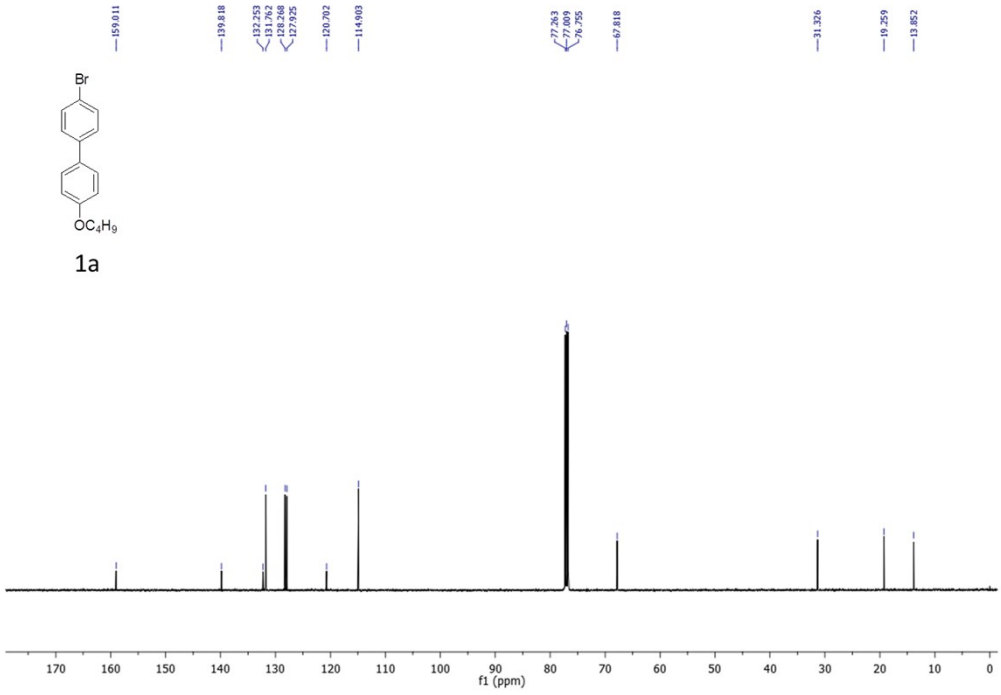
Compound 2b: Yield 71 %, m.p. 134^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 0.89 (t, 3H, *J* = 7 Hz, CH_3), 1.26-1.35 (m, 8H, 2 x CH_2), 1.48 (quintet, 2H, *J* = 6.5 Hz, CH_2), 1.81 (quintet, 2H, *J* = 6.5 Hz, CH_2), 4.00 (t, 2H, *J* = 6.5 Hz, CH_2), 6.99 (d, 2H, *J* = 8.5 Hz, ArH), 7.23 (s, 1H, ArH), 7.31 (bs, 1H, ArH), 7.43 (d, 2H, *J* = 8.5 Hz, ArH), 7.52 (d, 2H, *J* = 9 Hz, ArH), 7.64 (d, 2H, *J* = 8.5 Hz, ArH), 7.89 (s, 1H, Im-C2H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 14.1, 22.7, 26.1, 29.2, 29.3, 29.4, 31.8, 68.2, 115.0, 118.3, 121.8, 127.9, 128.0, 130.4, 132.0, 135.9, 140.3, 159.1.

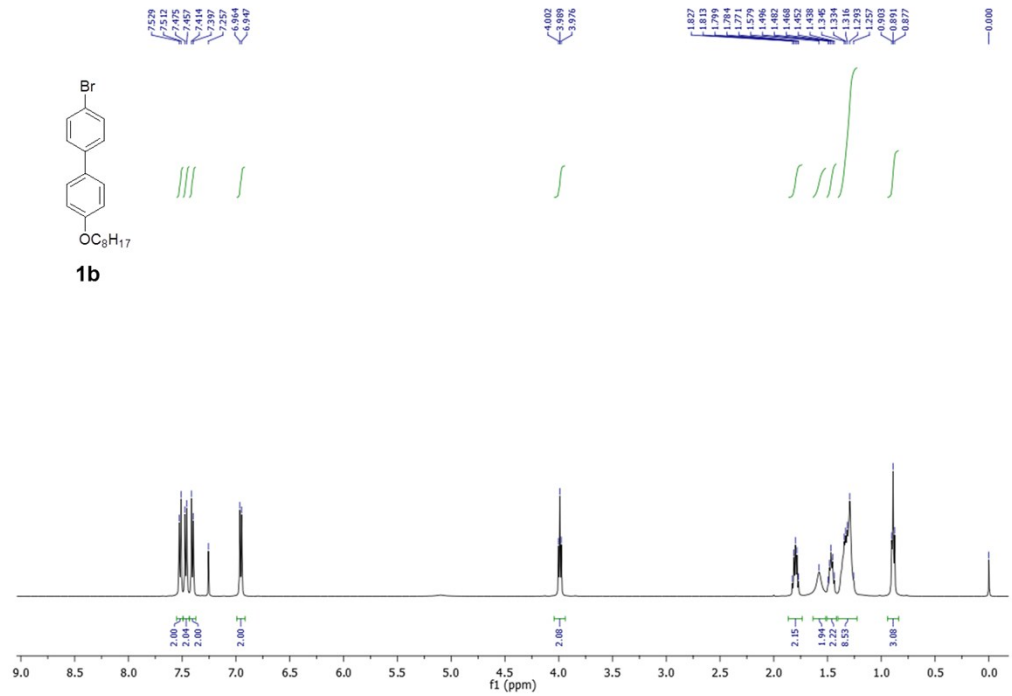
Compound 2c: Yield 65 %, m.p. 149^{o}C; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 0.88 (t, 3H, *J* = 7 Hz, CH_3), 1.27 (bs, 18H, CH_2), 1.47 (qunitet, 2H, *J* = 6.5 Hz, CH_2), 1.81 (quintet, 2H, *J* = 6.5 Hz, CH_2), 4.00 (t, 2H, *J* = 6.5 Hz, CH_2), 6.99 (d, 2H, *J* = 9 Hz, ArH), 7.22 (s, 1H, ArH), 7.31 (s, 1H, ArH), 7.43 (d, 2H, *J* = 8.5 Hz, ArH), 7.89 (s, 1H, Im-C2H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ

14.1, 22.6, 26.0, 29.2, 29.3, 29.3, 29.5, 29.5, 29.6, 29.6, 31.9, 68.1, 114.9, 118.2, 121.7, 127.9, 128.0, 130.3, 131.9, 135.5, 135.8, 140.3, 159.1.

2. ^{1}H and ^{13}C NMR spectra of 1a-c



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7.495
7.487
7.414
7.397
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6.964
6.947
4.002
3.989
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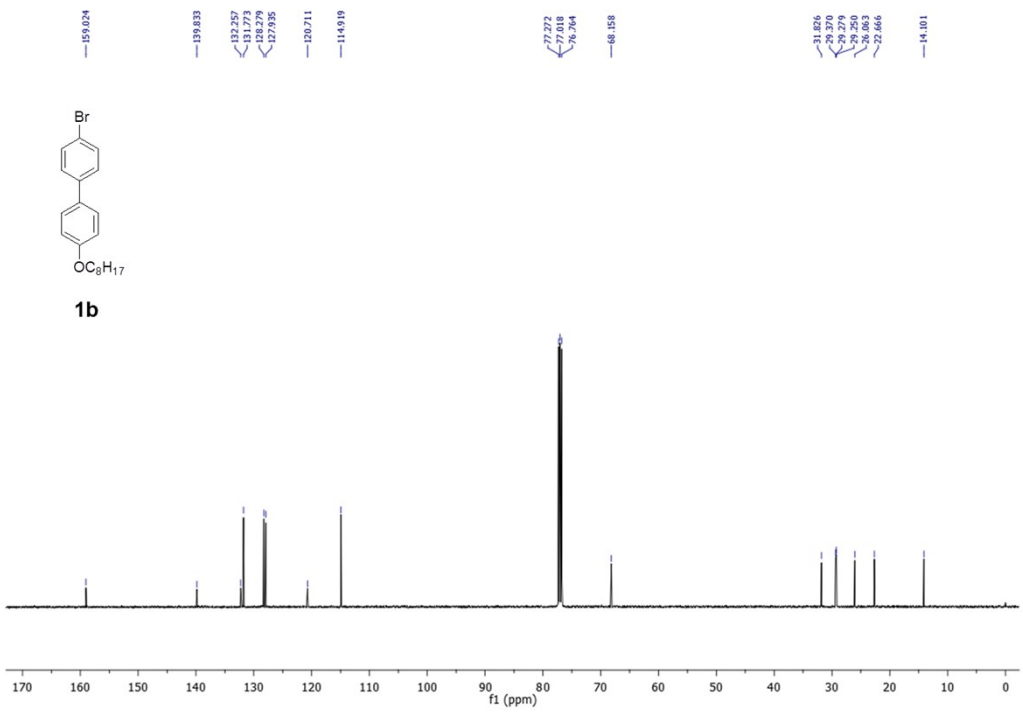
1.827
1.813
1.799
1.784
1.771
1.579
1.496
1.468
1.460
1.452
1.438
1.345
1.334
1.316
1.295
1.257
0.903
0.891
0.877
0.000
Br
OC8H17
2.00
2.04
2.00
2.00
2.08
2.15
1.94
2.22
8.53
3.08
f1 (ppm)

1b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139.833
132.257
131.773
128.279
127.935
120.711
114.919
77.272
77.018
76.764
68.158
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29.250
26.063
22.666
14.101
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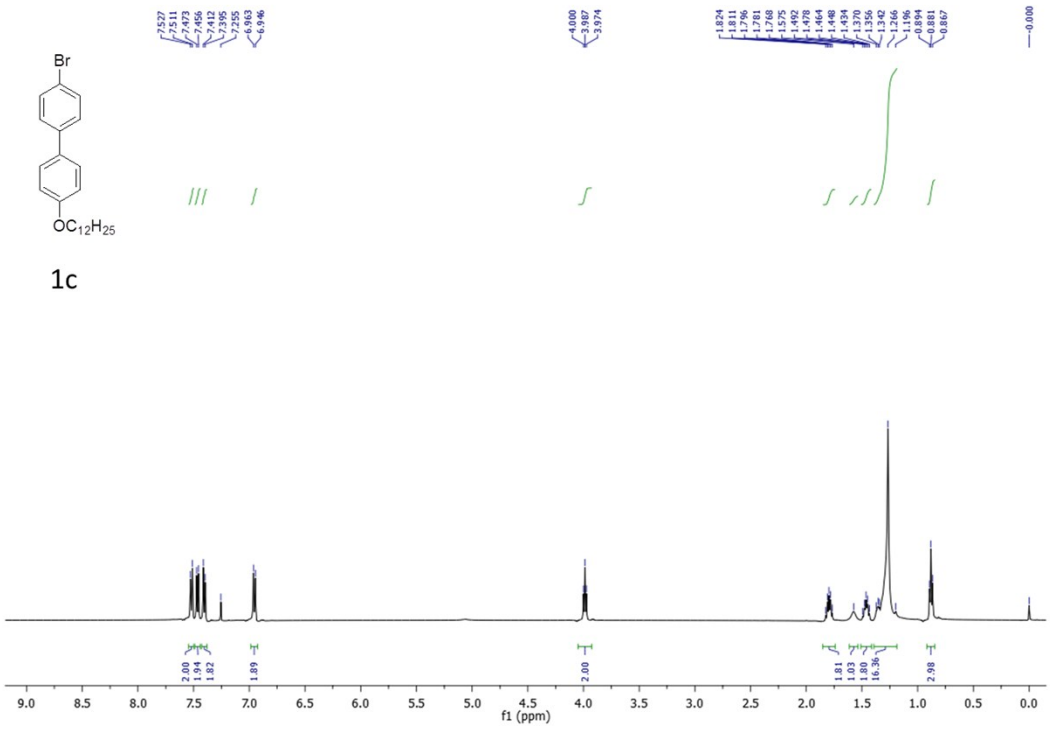
f1 (ppm)

1b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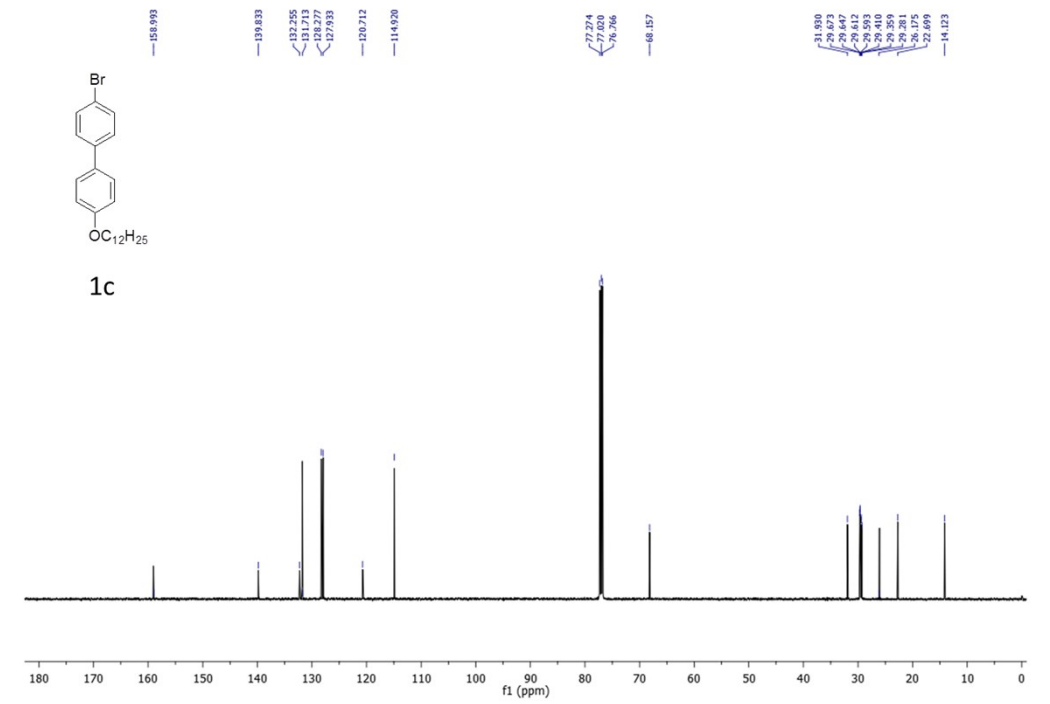
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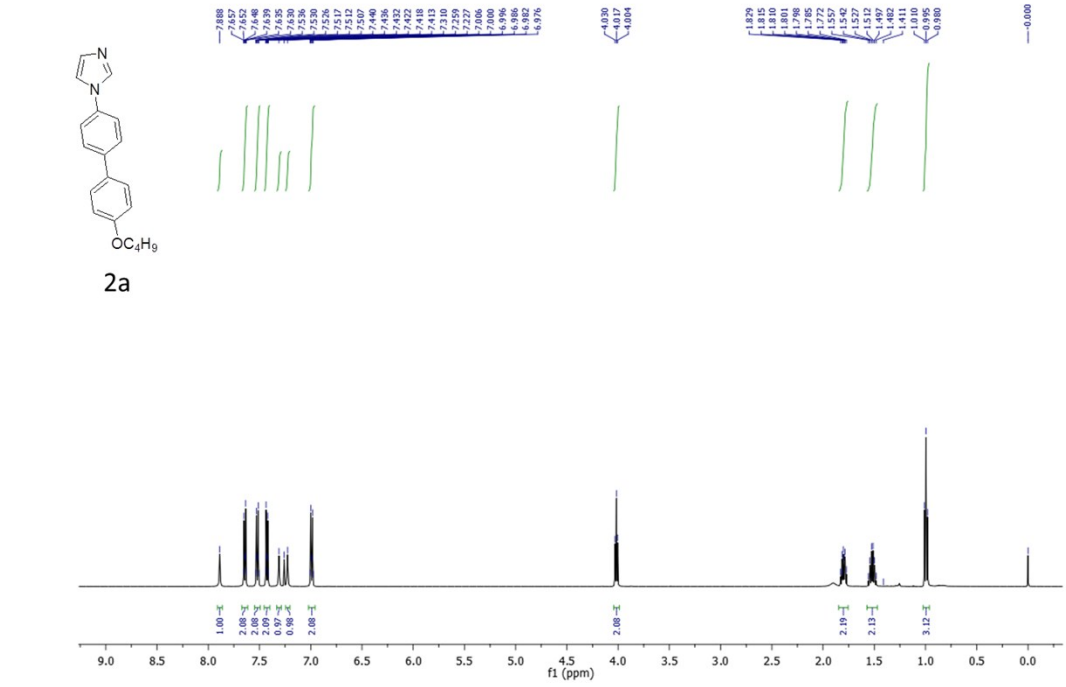
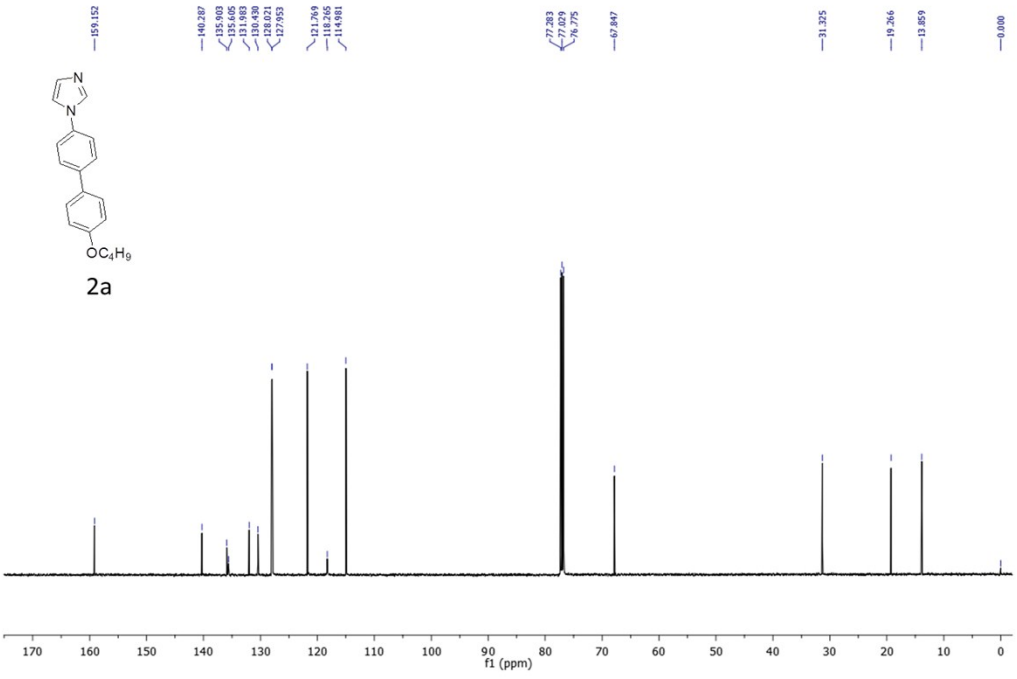
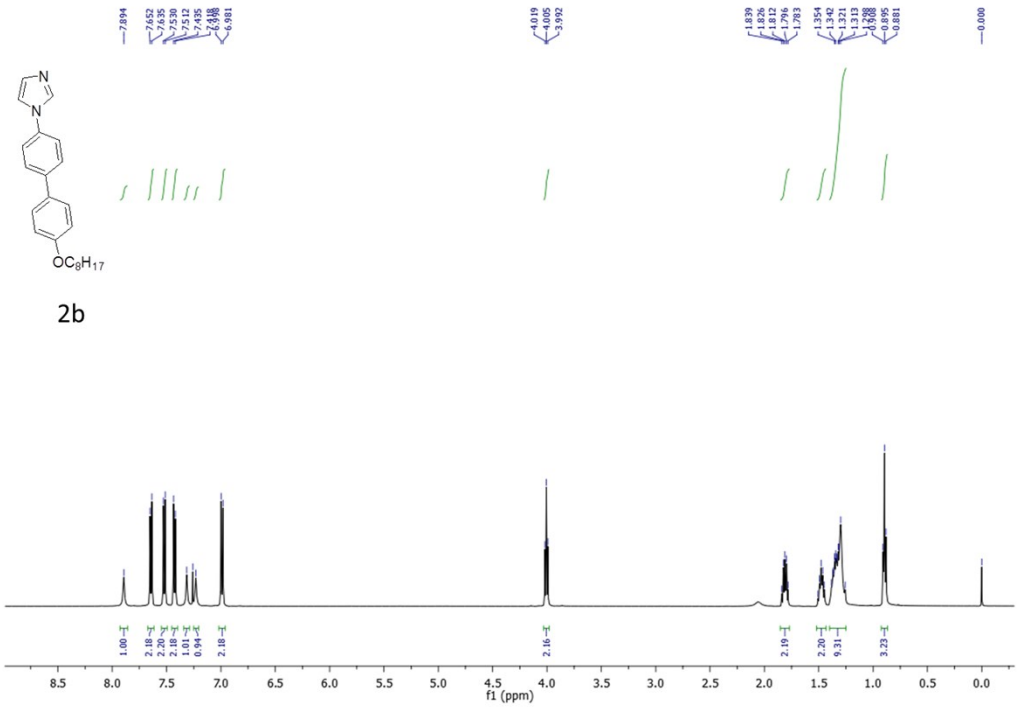
f1 (ppm)

3. ^{1}H and ^{13}C NMR spectra of 2a-c



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7.495
7.485
7.478
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4.010
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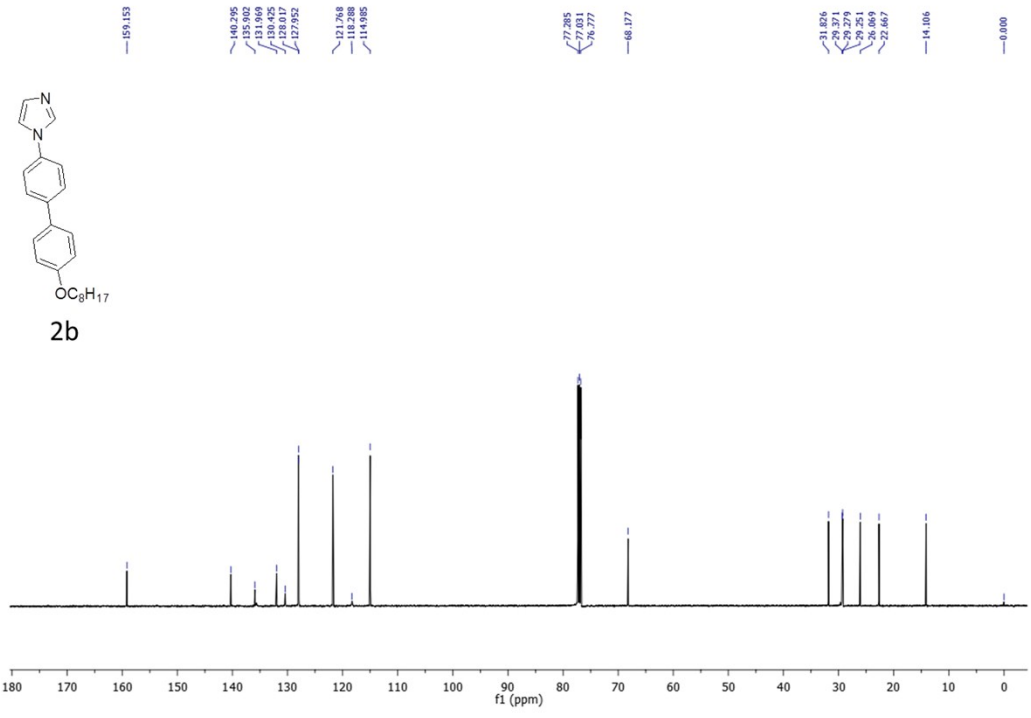
1.839
1.826
1.812
1.796
1.783
1.354
1.342
1.321
1.313
1.128
0.908
0.895
0.881
0.000
1.00
2.18
2.20
2.18
1.01
6.94
2.18
2.16
2.19
2.20
9.31
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2b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121.768
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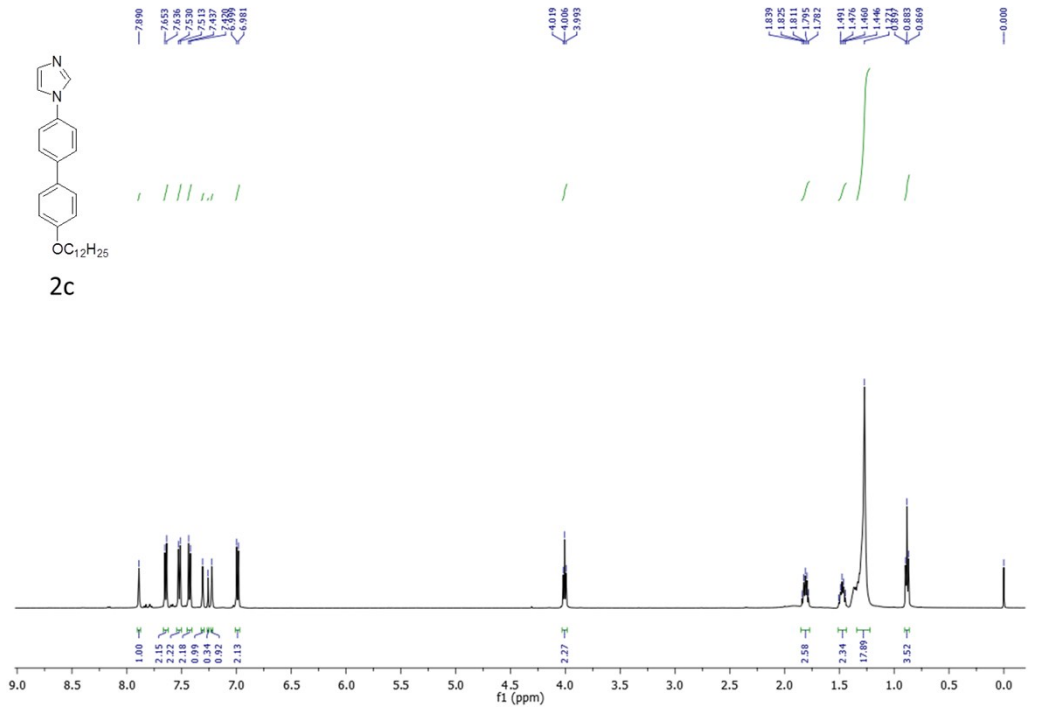
76.777
68.177
31.826
29.371
29.279
29.251
26.069
22.667
14.106
0.000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2b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1.825
1.811
1.795
1.782
1.491
1.476
1.460
1.446
1.271
0.889
0.869
0.000
1.00
2.15
2.22
2.18
0.99
0.94
0.92
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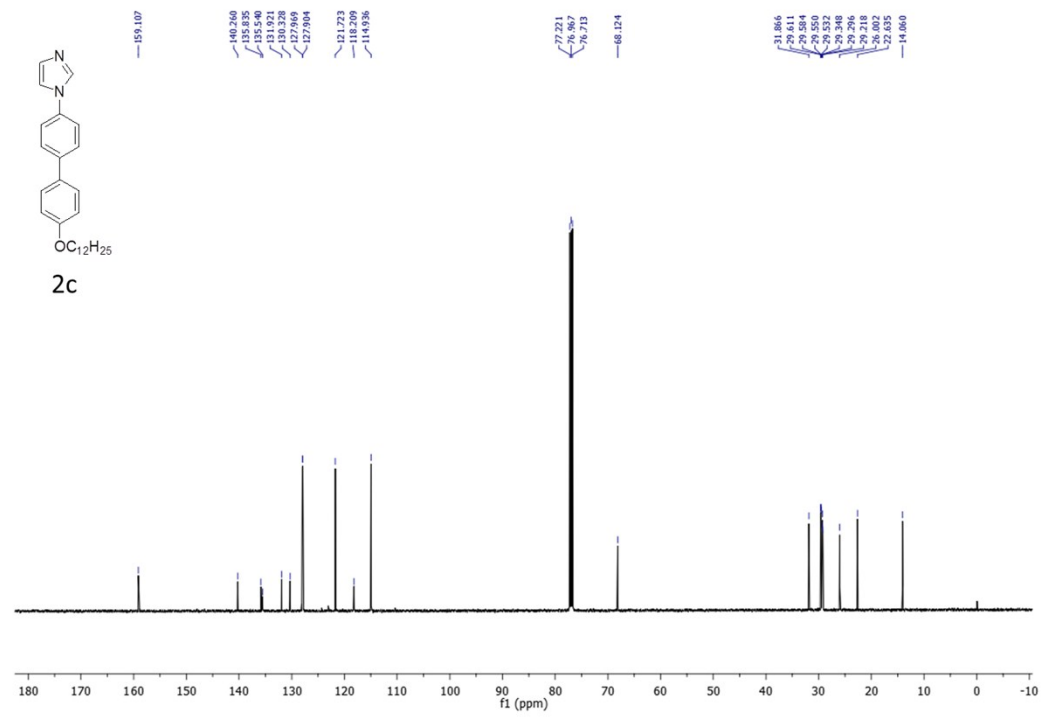
2.27
2.58
2.34
17.89
3.52
f1 (ppm)

2c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68.124
31.866
29.611
29.584
29.550
29.532
29.348
29.306
29.218
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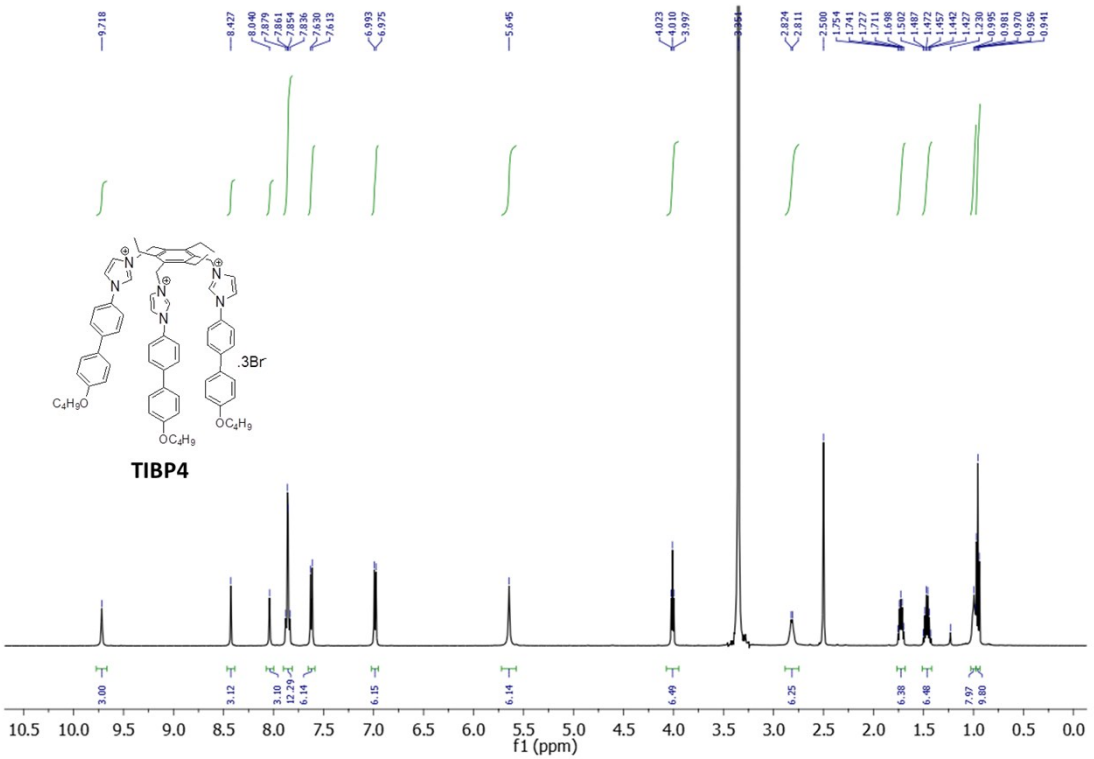
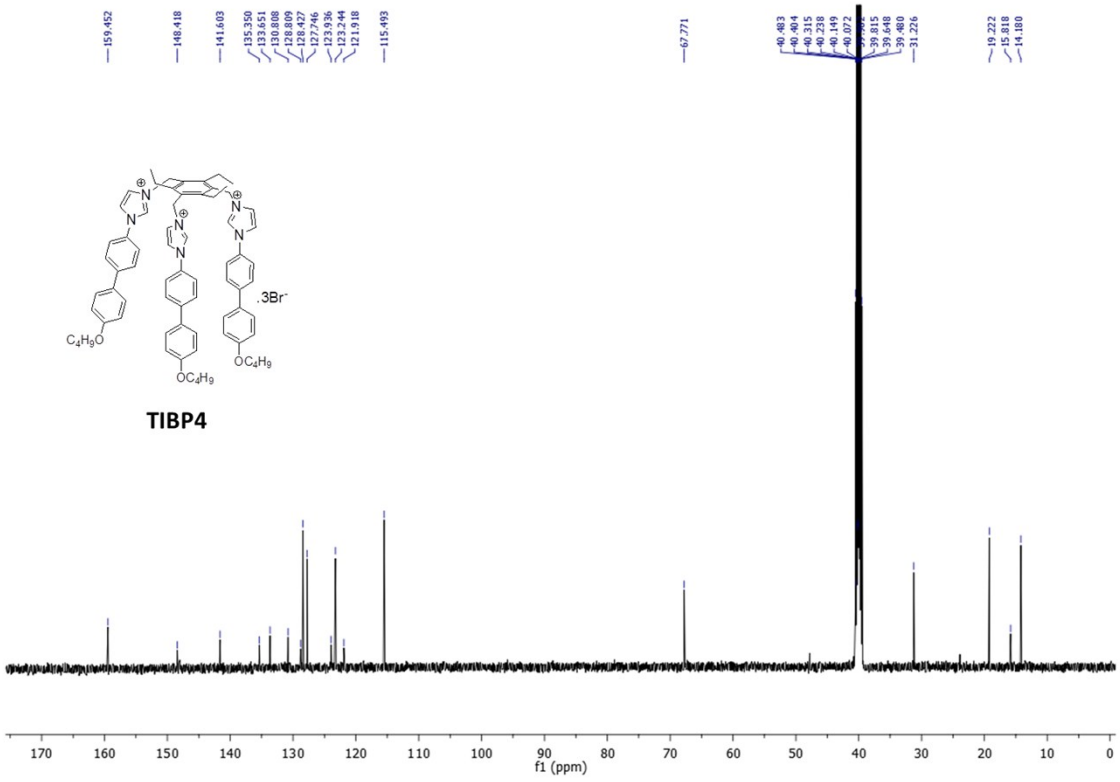
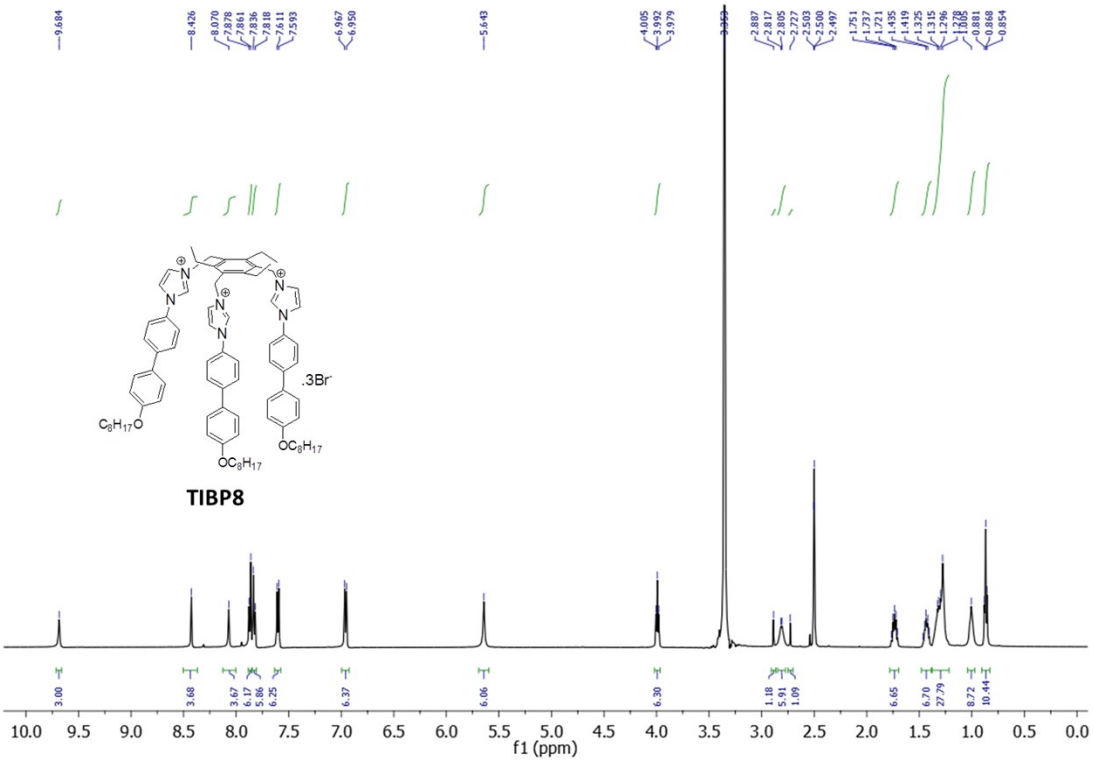
14.060
f1 (ppm)

2c

4. ^{1}H and ^{13}C NMR spectra of TIBP4, TIBP8 and TIBP12



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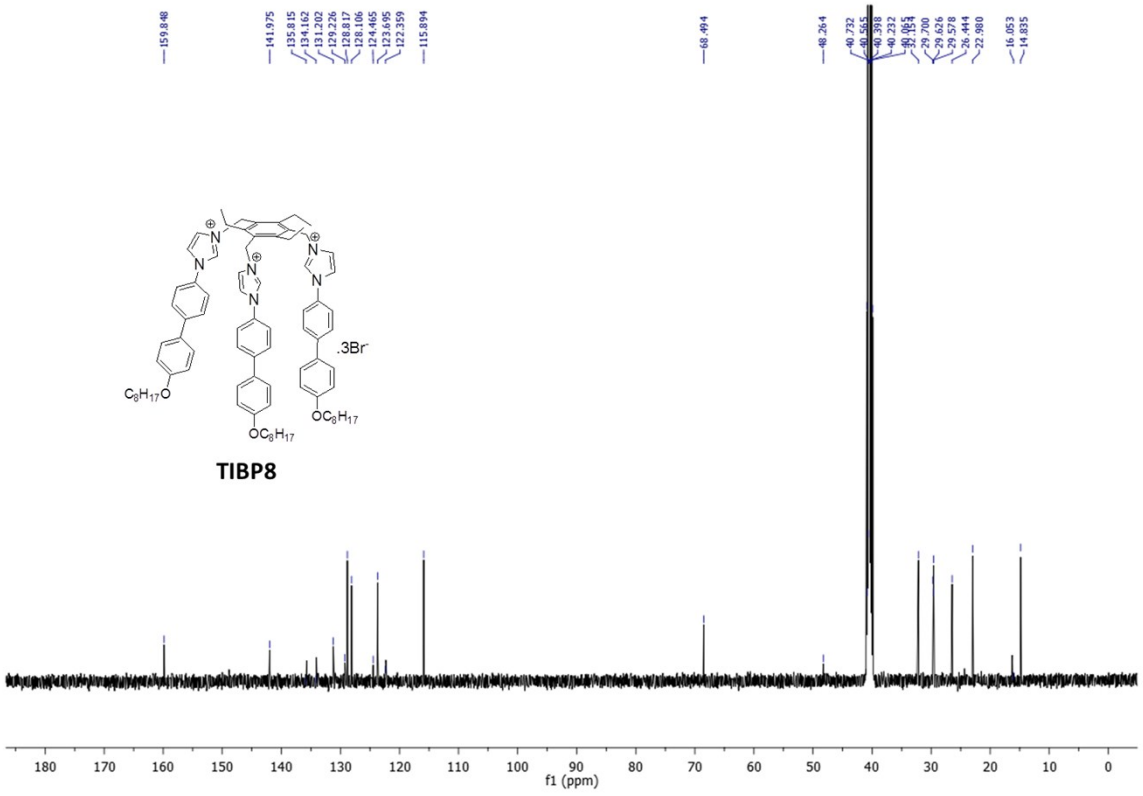
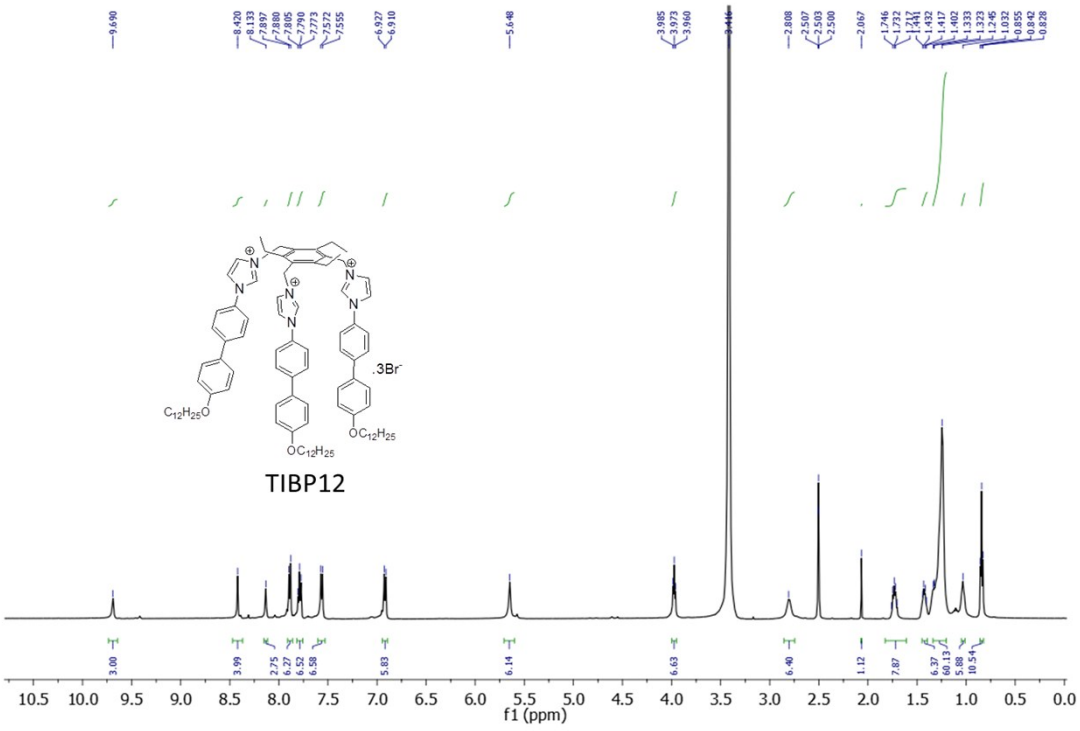
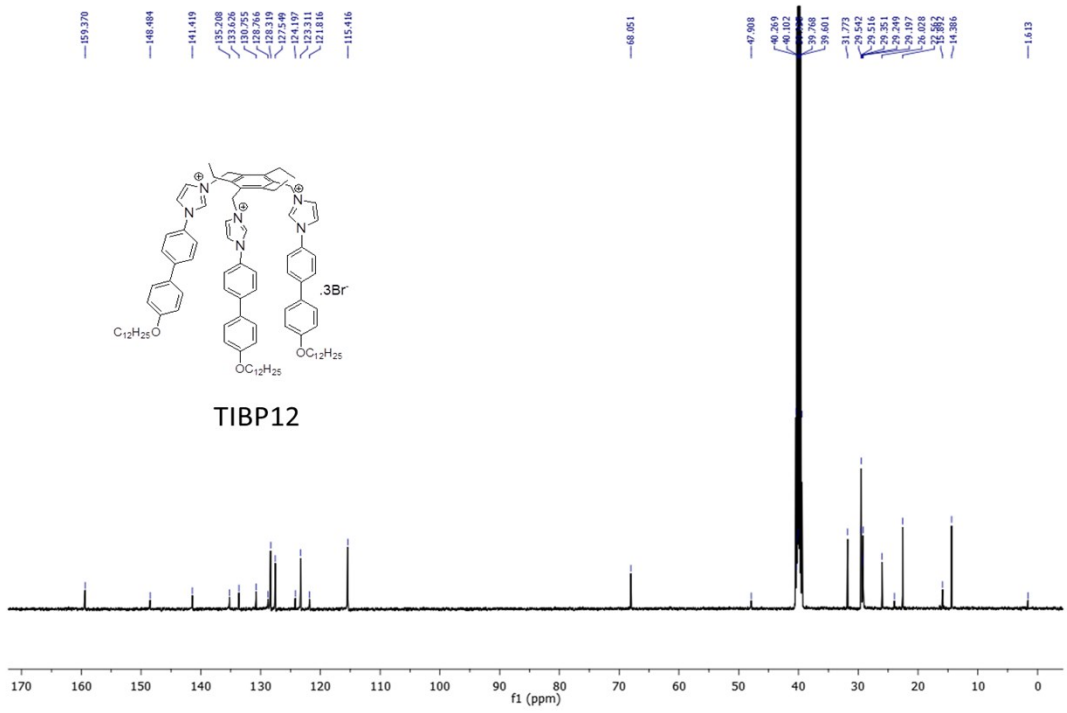
.3Br⁻
f1 (ppm)


TIBP8
.3Br⁻
f1 (ppm)

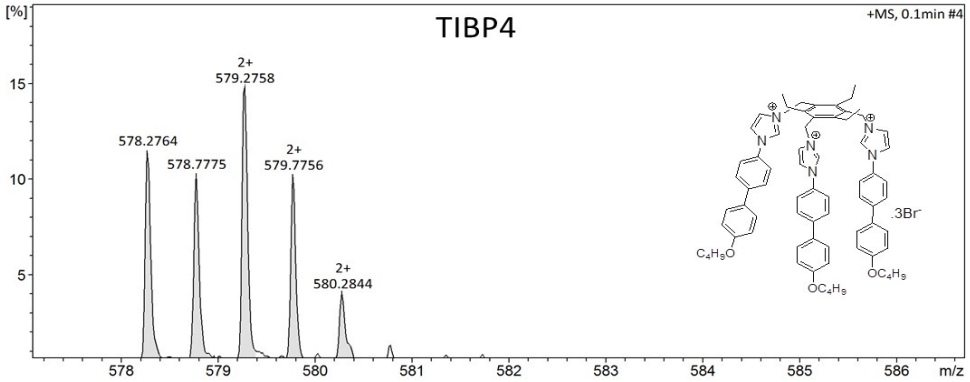


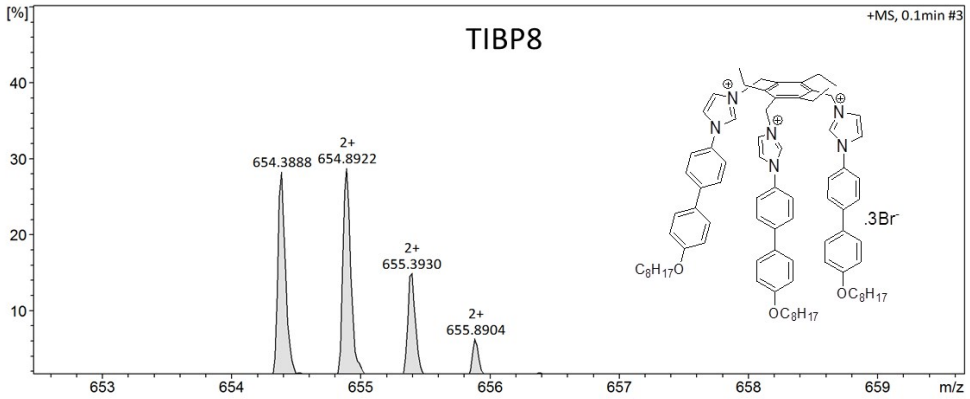
TIBP12

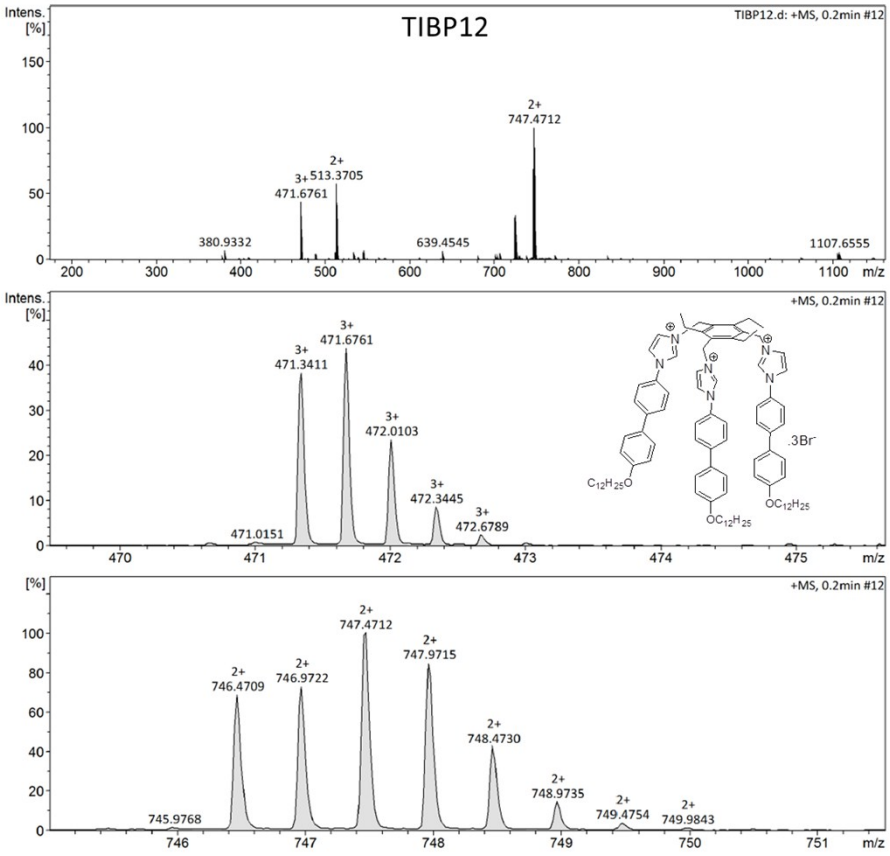


TIBP12

5. HRMS spectra of TIBP4, TIBP8 and TIBP12






TIBP12
TIBP12.d: +MS, 0.2min #12
Intens.
[%]
2+
747.4712
2+
513.3705
3+
471.6761
380.9332
639.4545
1107.6555
m/z
+MS, 0.2min #12
3+
471.6761
3+
471.3411
3+
472.0103
3+
472.3445
3+
472.6789
471.0151
.3Br-
C12H25O
OC12H25
OC12H25
+MS, 0.2min #12
2+
747.4712
2+
747.9715
2+
746.4709
2+
746.9722
2+
748.4730
2+
748.9735
2+
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2+
749.9843
745.9768

6. UV-VIS and Fluorescence studies of TIBP4, TIBP8 and TIBP12 in binary solvents

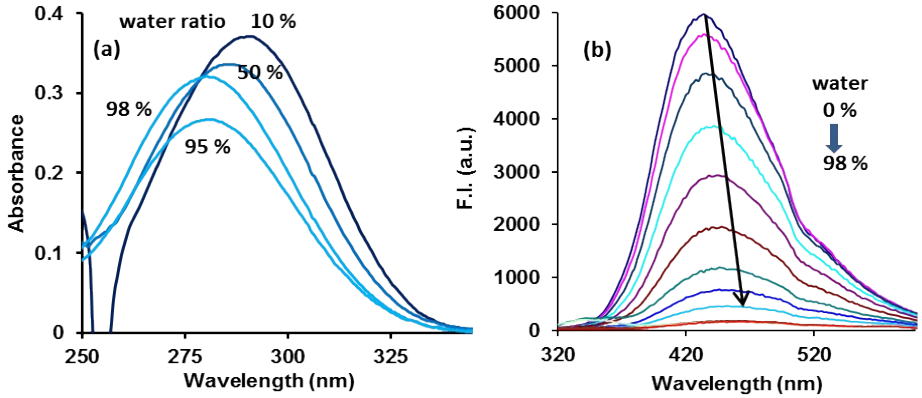

Figure SI-1: (a) UV-Vis and (b) fluorescence studies of **TIBP4** at 5 μM in binary mixtures with varying fractions of water in DMSO

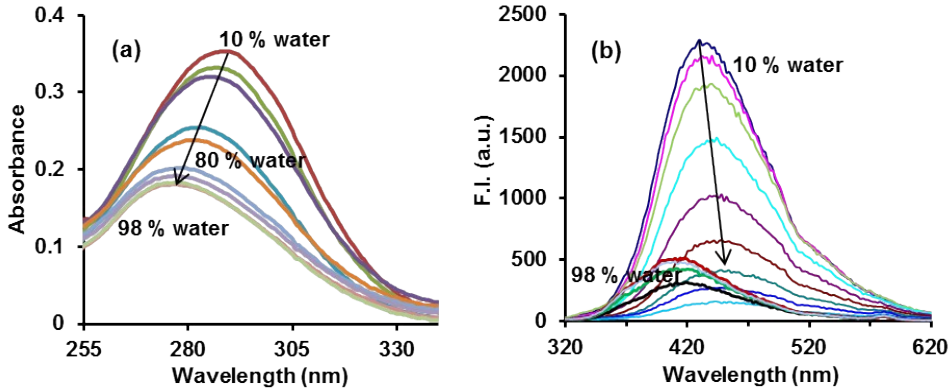

Figure SI-2: (a) UV-Vis and (b) fluorescence spectra of **TIBP8** (5 μM) in binary mixtures with different fractions of water in DMSO

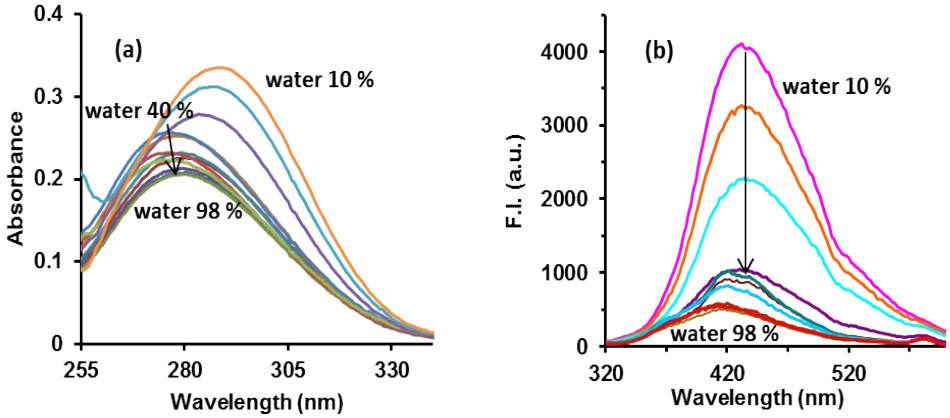

Figure SI-3: (a) UV-Vis and (b) fluorescence spectra of **TIBP12** (5 μM) in binary mixtures with different fractions of water in DMSO

7. Fluorescence titration of TIBP4, TIBP8 and TIBP12 with NACs

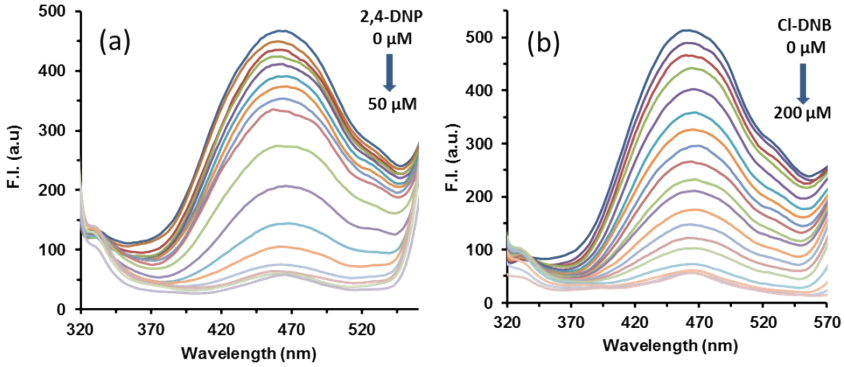

Figure SI-4: Emission spectra of fluorescence titration of **TIBP4** (5 µM) with 2,4-DNP and Cl-DNB (water + 2 % DMSO, λex = 290 nm)

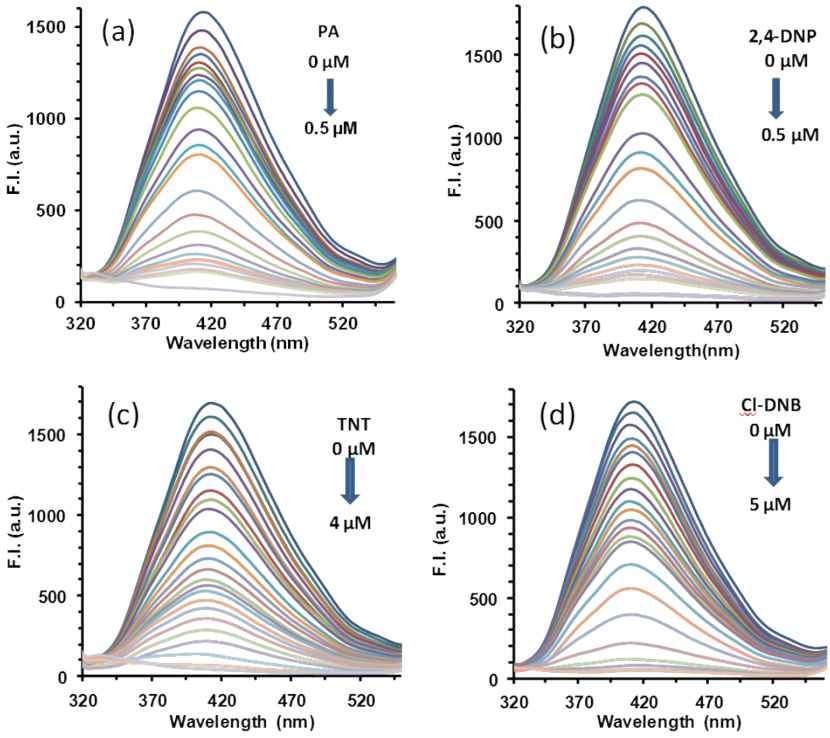

Figure SI-5: Fluorescence titration of **TIBP8** (5 µM, λex = 290 nm) with PA, 2,4-DNP, TNT and Cl-DNB (water + 2 % DMSO, λex = 290 nm)

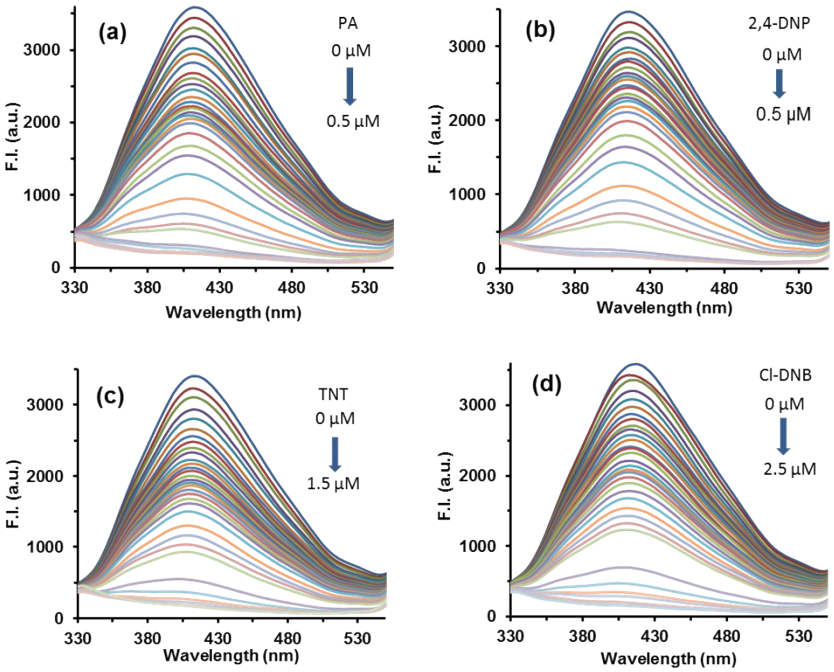

Figure SI-6: Fluorescence titration of **TIBP12** (5 µM, λ_{ex} = 290 nm) with (a) PA, (b) 2,4-DNP, (c) TNT and (d) Cl-DNB (water + 2 % DMSO, λex = 290 nm)

8. K_{SV} values for interaction of TIBP4, TIBP8 and TIBP12 with NACs (Table SI-1)

	PA	2,4-DNP	TNT	Cl-DNB
TIBP4*	6.25 x 10^5 M^{-1} 10^{-8}-20 µM R^2= 0.992	5.03 x 10^4 M^{-1} 10^{-8}-40 µM R^2= 0.991	1.84 x 10^4 M^{-1} 10^{-6}-20 µM R^2= 0.992	1.35 x 10^4 M^{-1} 10^{-6}-80 µM R^2= 0.989
TIBP8!	2.56 x 10^{11} M^{-1} 10^{-14} - 10^{-9} M R^2= 0.990	5.11 x 10^{10} M^{-1} 10^{-14} - 10^{-9} M R^2= 0.982	3.95 x 10^{10} M^{-1} 10^{-14} – 10^{-8} M R^2= 0.965	1.25 x 10^6 M^{-1} 10^{-8} – 10^{-6}M R^2= 0.949
TIBP12!	5.04 x 10^{11} M^{-1} 10^{-14} – 10^{-11}M R^2= 0.989	4.93 x 10^{11} M^{-1} 10^{-14} - 10^{-10}M R^2= 0.989	3.29 x 10^{11} M^{-1} 10^{-14} - 10^{-11}M R^2= 0.988	3.22 x 10^{11} M^{-1} 10^{-14} - 10^{-10}M R^2= 0.994

*determined using Stern-Volmer equation $I_o/I = 1 + K_{SV}[Q]$. !determined using exponential equation $I/I_o = Ae^{Ksv[Q]} + B$

9. Interaction of TIBP4 with PA at molecular level

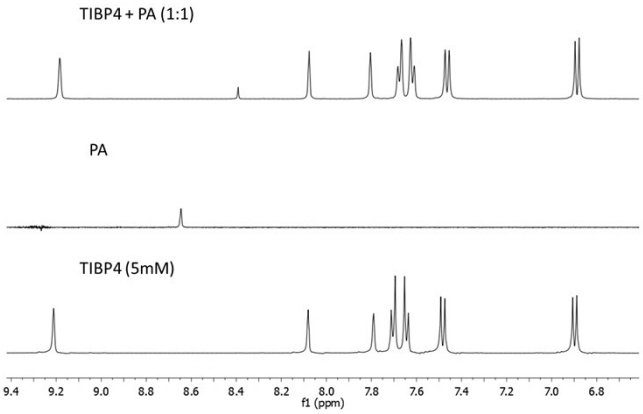

Figure SI-7: Effect of addition of PA on ^{1}H NMR spectrum of **TIBP4** (5 mM, DMSO:H_2O; 7:3)

10. Spectral overlap between TIBP4, TIBP8 and TIBP12 with NACs showing RET

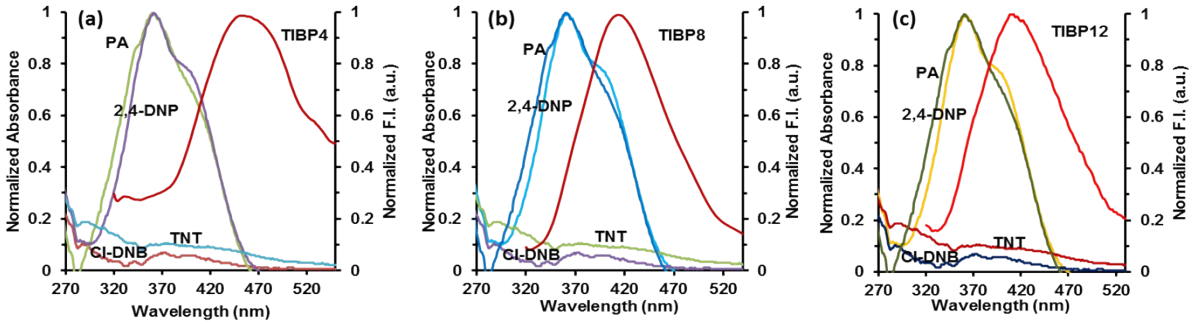

Figure SI-8: Normalized graph of fluorescence spectra (red lines) of **TIBP4, TIBP8** and **TIBP12** and UV-Vis spectrum of NACs (PA, 2,4-DNP, TNT, Cl-DNB)

11. Vapour phase detection of PA by TIBP8 and TIBP12

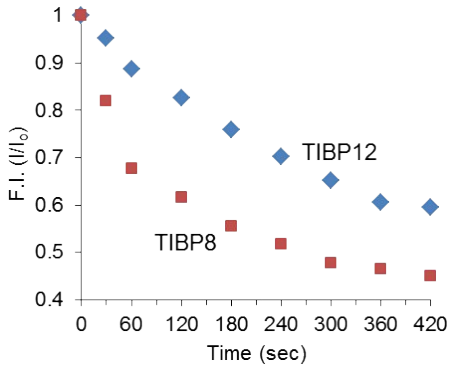

Figure SI-9: Plot of F.I. (I/I_o) of thin-films of **TIBP8** and **TIBP12** with time on exposure to saturated PA vapour