Supporting Information

Understanding electron transfer process in ZnO-naphthol azobenzoic acid composites from photophysical characterisations

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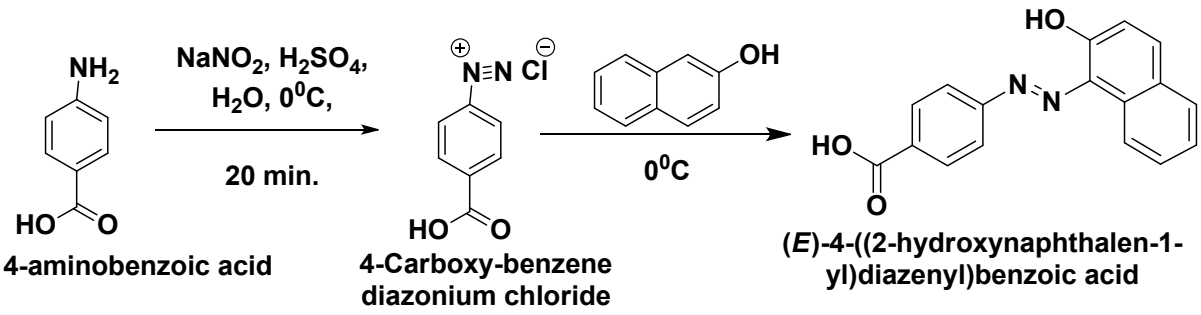
.

Supporting Information, SI-1

(4-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid (4ABBN))



4-aminobenzoic acid

4-Carboxy-benzene diazonium chloride

(*E*)-4-((2-hydroxynaphthalen-1-yl)diazenyl)benzoic acid

1H NMR (200 MHz, DMSO) δ ppm:

7.44-7.52 (1H,m), 7.59-7.66 (1H,m), 7.72-7.76 (1H,d, J=7.20Hz),7.83-7.87(2H, d, J=8.59 Hz), 7.92-7.97(1H, d, J=9.85 Hz), 8.03-8.07(2H, d, J=8.72Hz), 8.46-8.50 (1H,d, J=7.32Hz), 15.91 (1H, s).

13C (400 MHz, DMSO) δ ppm :

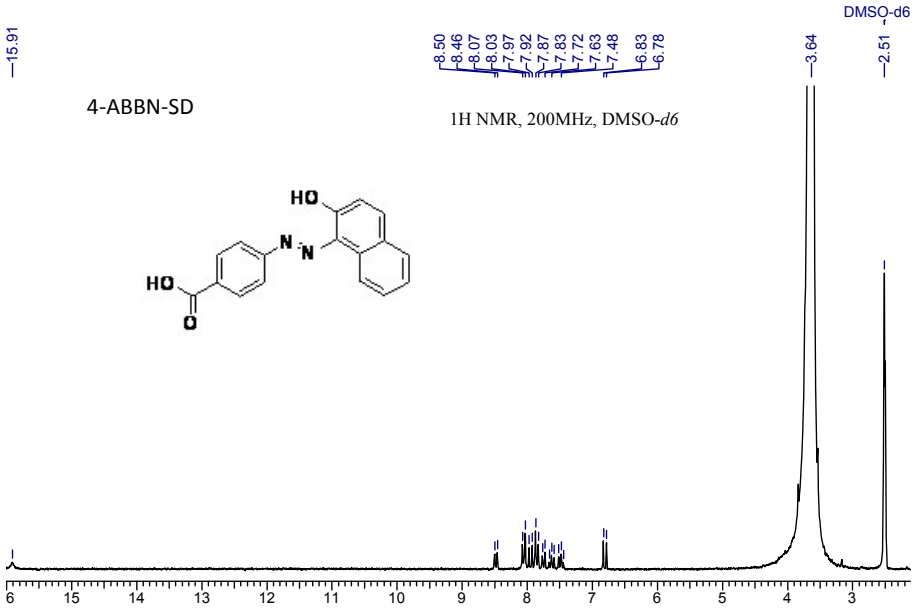
170.07,167.14,145.61,140.53,133.19,132.98,130.07,129.24,129.04,128.53,128.28,126.17, 124.15, 122.76, 121.59,119.56.

FTIR (cm-1): 3353, 2973,2894,1696,1389,1319,1207,1044 and 879 cm-1.

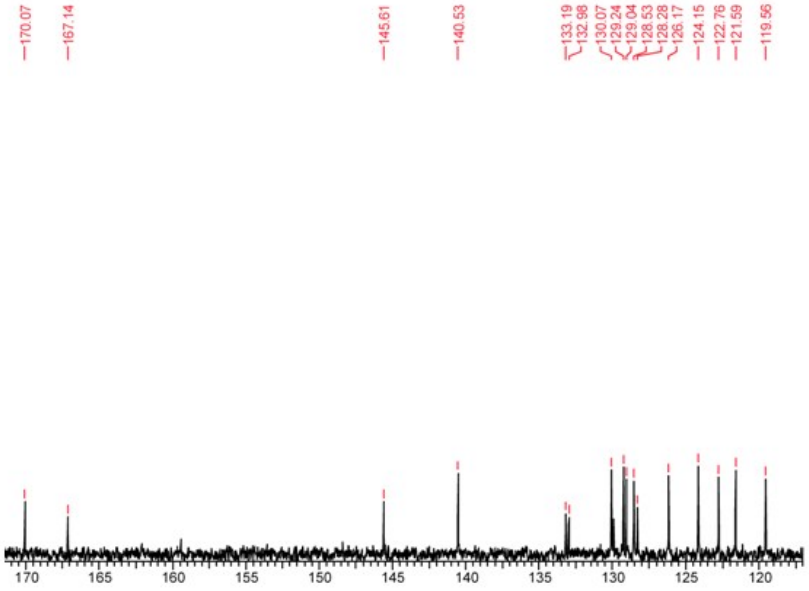
Raman (cm-1): 432, 498, 604, 710, 1255, 1382, 1658, 1700, 1769 cm-1.

Elemental Analysis: calcd(%): C 69.86, H 4.14, N 9.18; found (%): C 72.24, H 5.46, N 7.99.

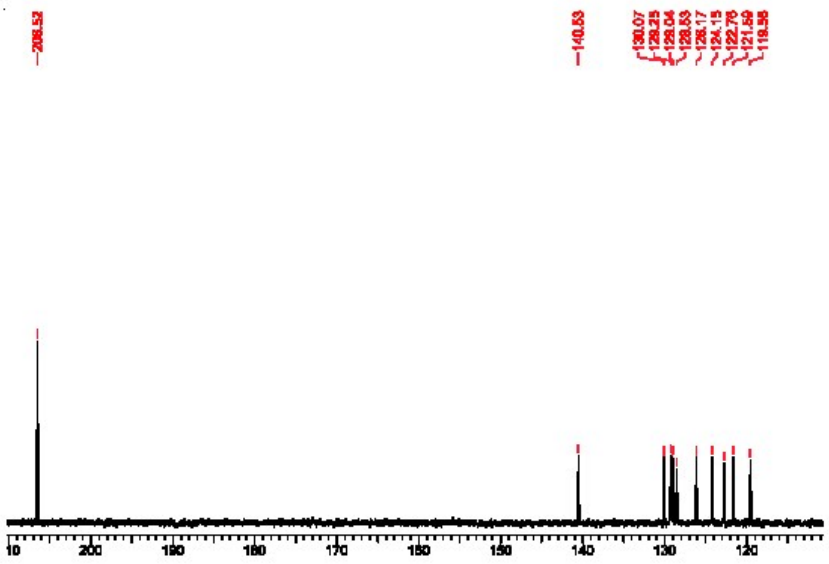
NMR


DMSO-d6
15.91
8.50
8.46
8.07
8.03
7.97
7.92
7.87
7.83
7.72
7.63
7.48
6.83
6.78
3.64
2.51
4-ABBN-SD
1H NMR, 200MHz, DMSO-d6
HO
N
N
HO
O
6
15
14
13
12
11
10
9
8
7
6
5
4
3

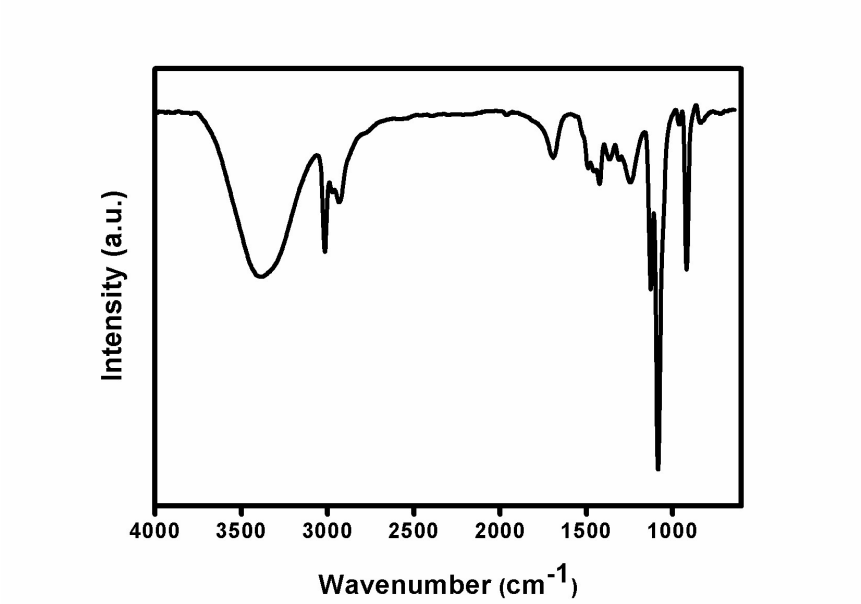
^{13}C


170.07
167.14
145.61
140.53
133.19
132.98
130.07
129.24
129.04
128.53
128.28
126.17
124.15
122.76
121.59
119.56
170
165
160
155
150
145
140
135
130
125
120

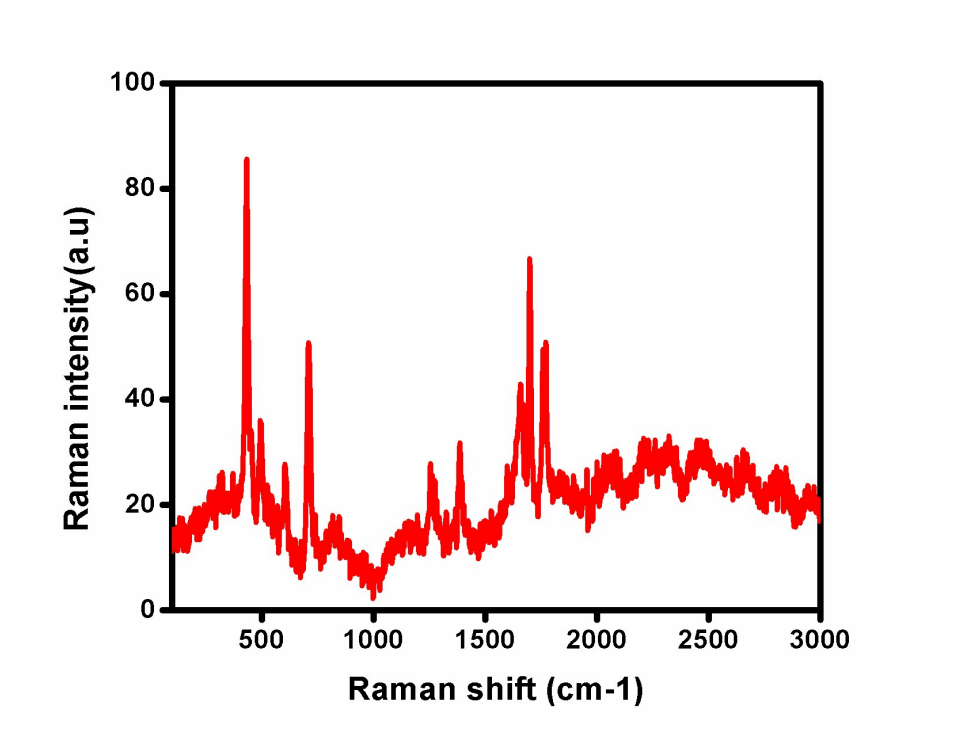
DEPT


208.52
140.53
130.07
129.25
129.04
128.53
128.17
124.15
122.76
121.59
119.56
10
200
190
180
170
160
150
140
130
120

IR


Intensity (a.u.)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

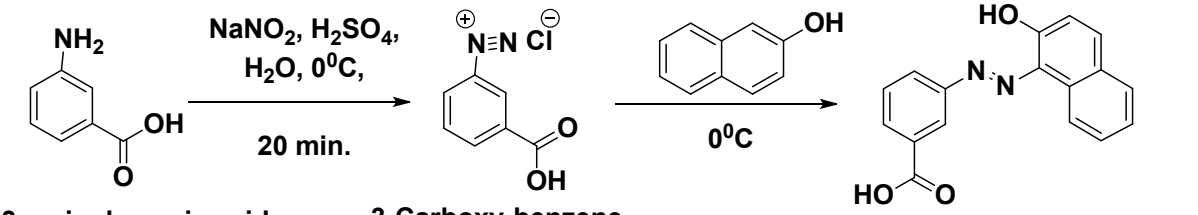
Raman



Figures.SI

Supporting Information, SI-2

3-(2-Hydroxy-naphthalen-1-ylazo)-benzoic acid (3ABBN)



3-aminobenzoic acid | **3-Carboxy-benzene diazonium chloride** | **(*E*)-3-((2-hydroxynaphthalen-1-yl)diazenyl)benzoic acid**

^{1}H NMR (200 MHz, DMSO) δ ppm:

7.43-7.53 (1H,m), 7.63-7.72 (2H,m), 7.79-7.90 (3H,m),7.97-8.02 (1H, d, J=9.47 Hz), 8.27(1H, s), 8.58-8.62(1H, d, J=7.96Hz), 15.91 (1H, s)

^{13}C (400 MHz, DMSO) δ ppm :

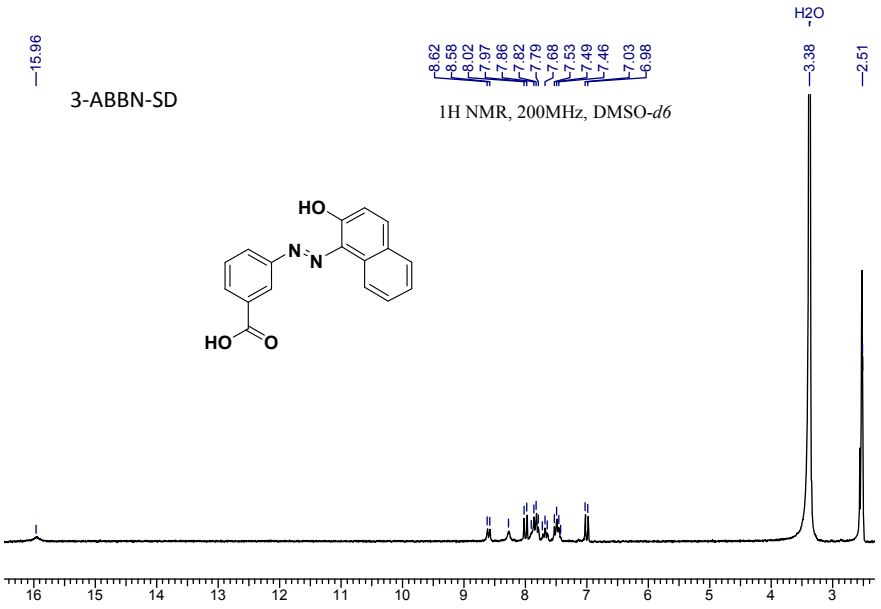
170.25,166.93,145.26,140.70,132.85,130.26,129.40,129.14,128.30,128.10,126.25,126.10,124.28,122.95,121.42,119.16.

FTIR (cm^{-1}): 3420, 3052, 2921, 1693, 1386, 1207, 1111 and 986 cm^{-1}.

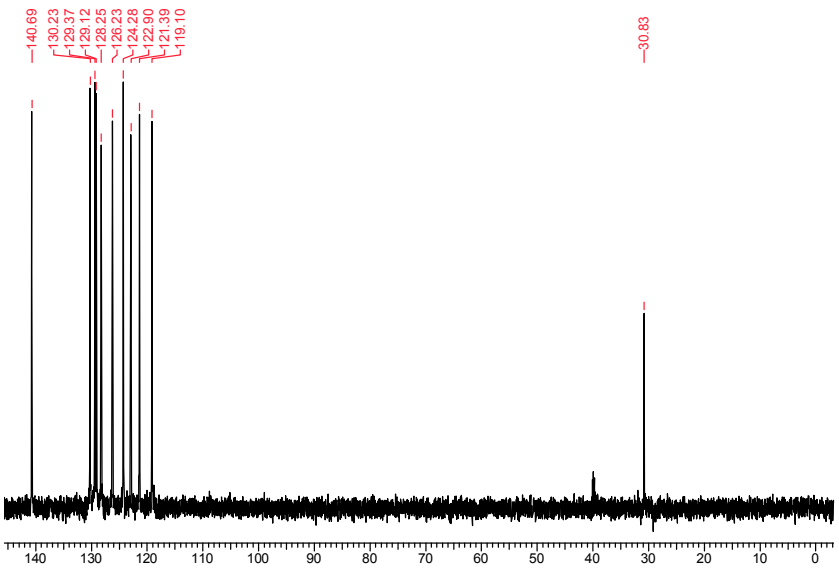
Raman (cm^{-1}): 432, 496, 607, 711, 1266, 1387, 1658, 1699, 1768 cm^{-1}.

Elemental Analysis: calcd(%): C 69.86, H 4.14, N 9.18; found (%): C 72.21, H 5.48, N 7.96.

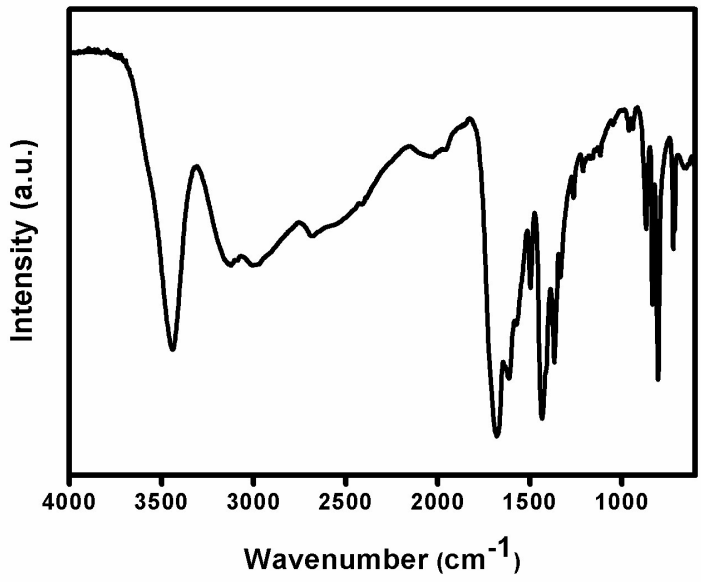
NMR


15.96
8.62
8.58
8.02
7.97
7.86
7.82
7.79
7.68
7.53
7.49
7.46
7.03
6.98
H2O
3.38
2.51
3-ABBN-SD
1H NMR, 200MHz, DMSO-d6
HO
N
N
HO
O
16
15
14
13
12
11
10
9
8
7
6
5
4
3

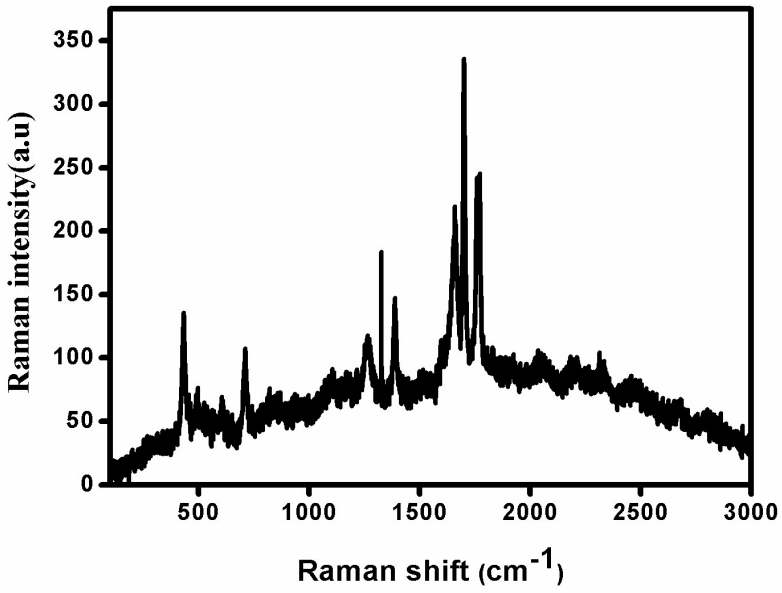
DEPT


140.69
130.23
129.37
129.12
128.25
126.23
124.28
122.90
121.39
119.10
30.83
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

IR


Intensity (a.u.)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

Raman


Raman intensity(a.u)
350
300
250
200
150
100
50
0
500
1000
1500
2000
2500
3000
Raman shift (cm-1)

Figures.S2

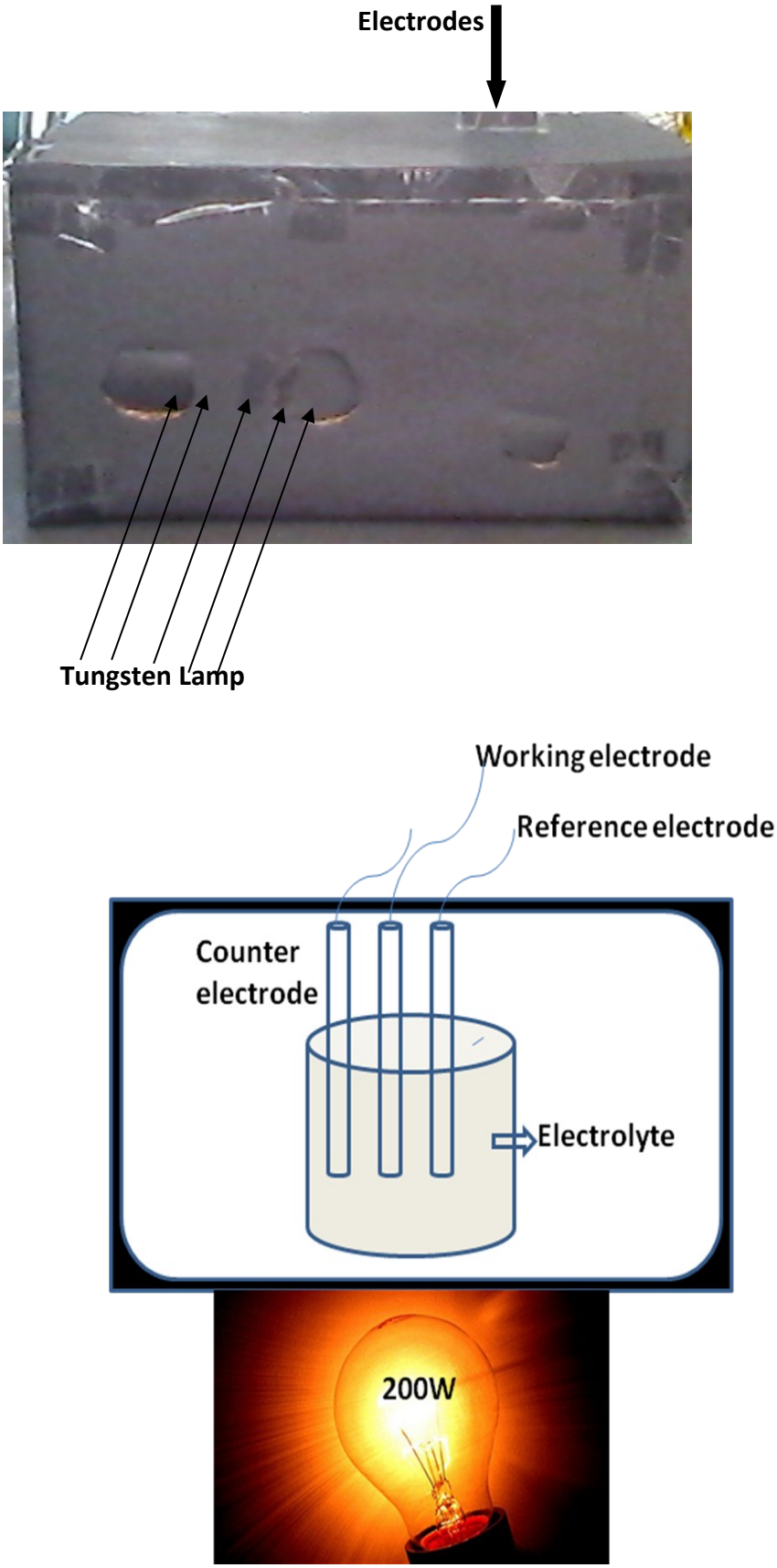


Figure. S3 Photoelectrochemical set up for the comparison of photocurrent with potential

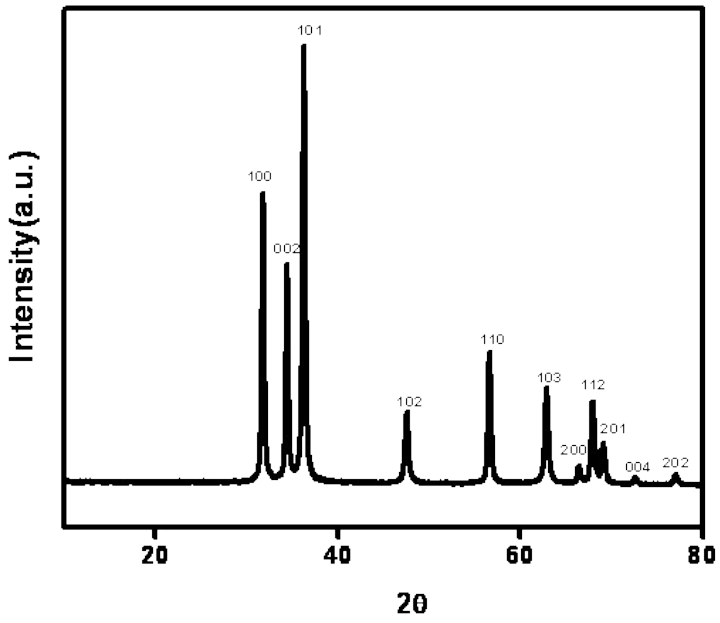


Figure. S4 Powder XRD pattern of ZnO NPs

Supporting Information, SI-5

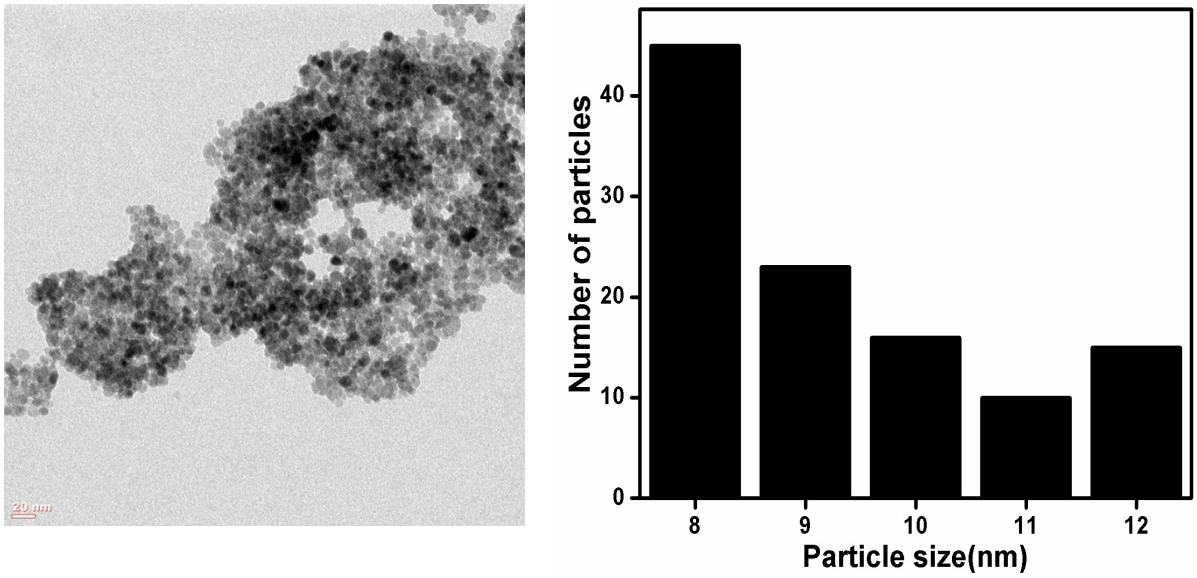
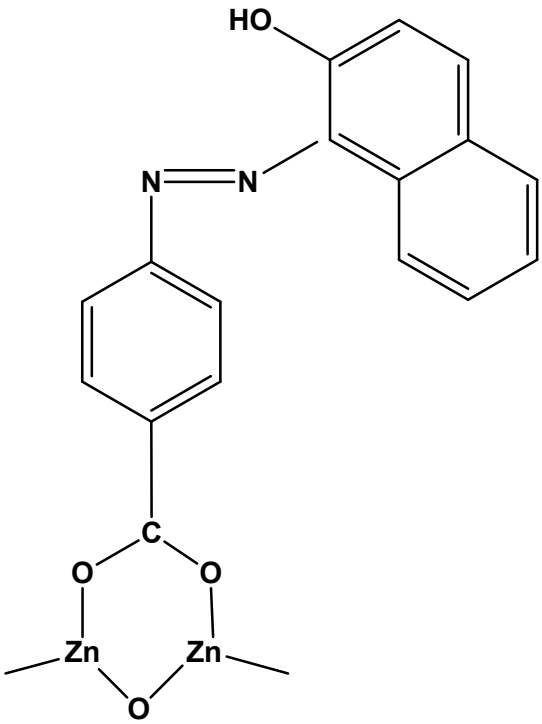


Figure.S5 TEM image and the corresponding histogram of ZnONPs

Supporting Information, SI-6



Details of calculations of the amount of 4ABBN to be used based on the number of ZnO on the surface of the particles.

(a) Number of moles of Zinc acetate dihydrate (ZA) in y ml = **x moles**

Assuming 100% conversion of ZA to ZnONPs, no: of moles of ZnONPs = **t moles in y ml**

(b) Total radius of ZnO = **0.202 nm**

Volume of one ZnO molecule = $4/3\pi r^3$ = **0.034508 nm^3**

(c) Volume of one ZnONP of 'a' radius (from TEM) = $4/3\pi a^3$ = **b nm^3**

(d) Total no: of molecules which can be accommodated in one particle = b nm^3/ 0.034508 nm^3

= **c molecules**

(e) Total no: of ZnO molecules = t moles * N = **s molecules**

(f) Total no: of ZnO particles = s/c = **r particles**

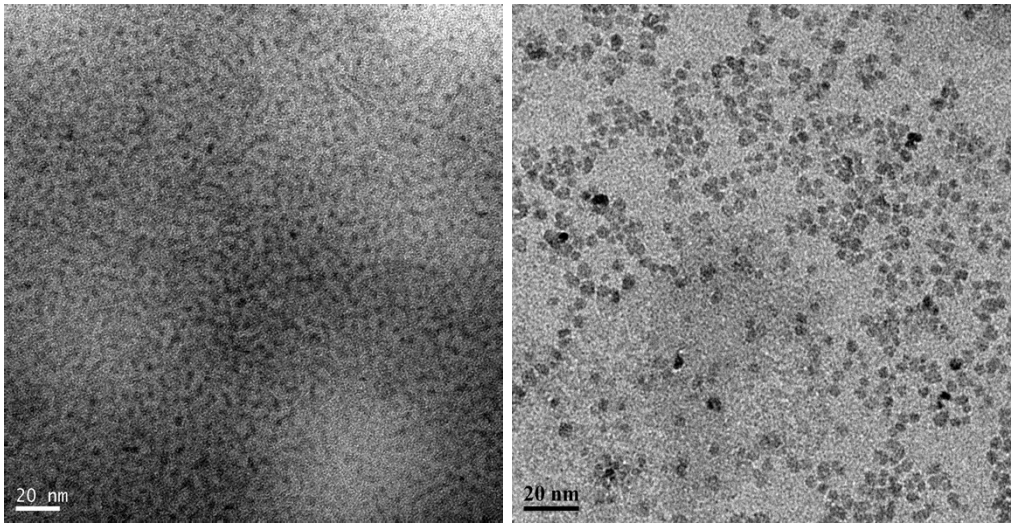
(g) Total no: of ZnO particles exposed on the surface = 4π (a nm^2)/ π (0.202 nm^2) = **e particles**

(h) Total no: of ZnO molecules exposed on the surface = e* r = **f molecules**

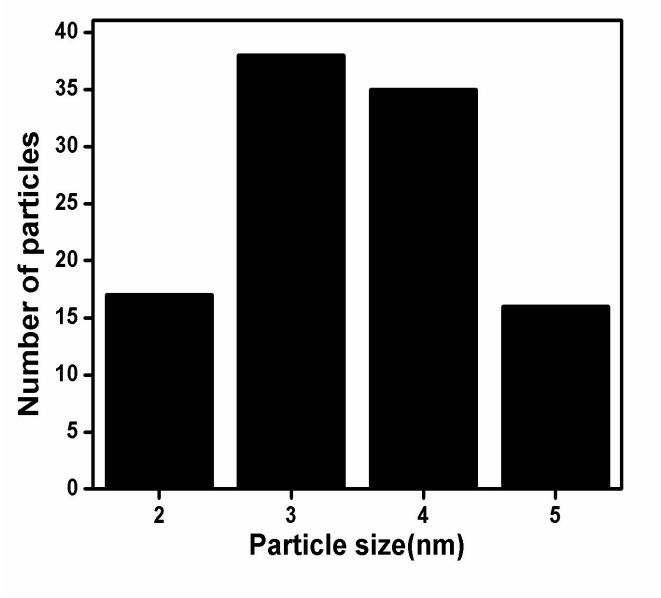
(i) Total no: of organic linkers required = f molecules/2 = **k molecules**

No: of moles of organic linker = k molecules/N = **m moles**

Supporting Information, SI-7



(a) (b)



(c)

Figure. S7 TEM images of (a) ZnO-3ABBN composite, (b) ZnO- 4ABBN composite and (c) corresponding histogram of the composites.

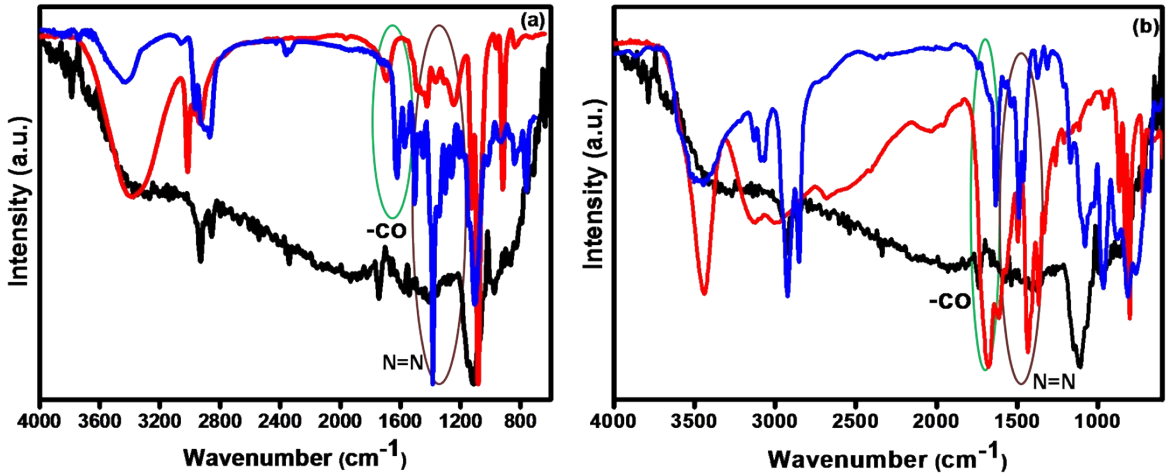


Figure. S8 IR spectra of (a) ZnO (black), 4ABBN (red) and ZnO-4ABBN composite (blue), left and (b) ZnO (black), 3ABBN (red) and ZnO-3ABBN composite (blue), right.

Supporting Information, SI-9

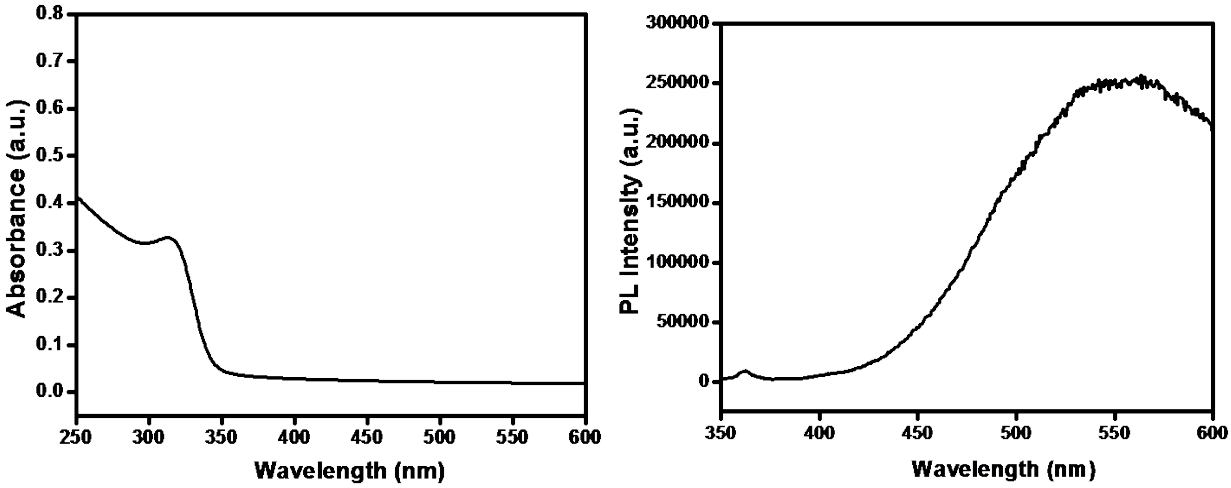


Figure. S9 UV-vis spectrum (left) and photoluminescence spectrum, λexc=325 nm (right) of pristine ZnO NPs (1.69 x 10^{-3} M).

Supporting Information, SI-10

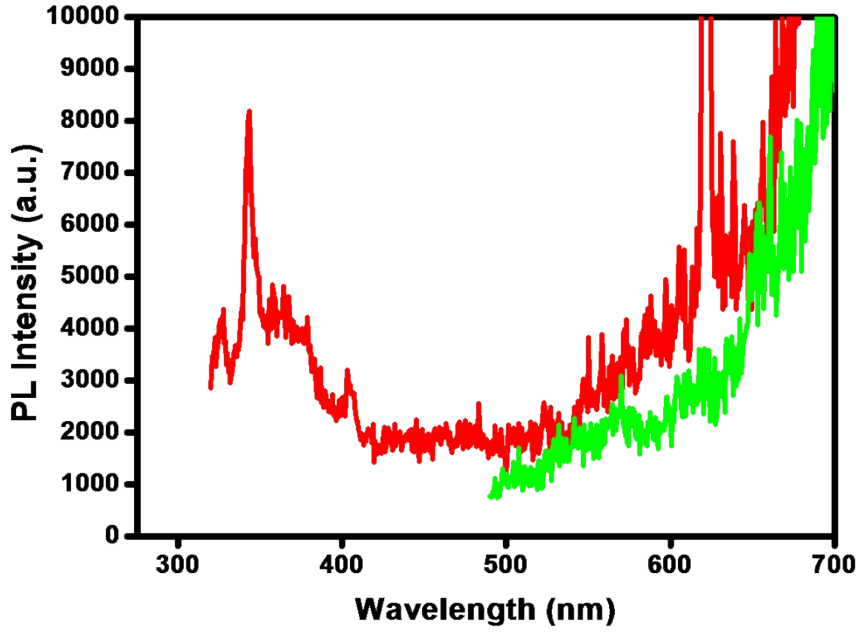


Figure. S10 PL spectrum of 3ABBN (9.04×10^{-4}M) at λexc=310 nm (red) and λexc=480 nm (green)

Supporting Information, SI-11

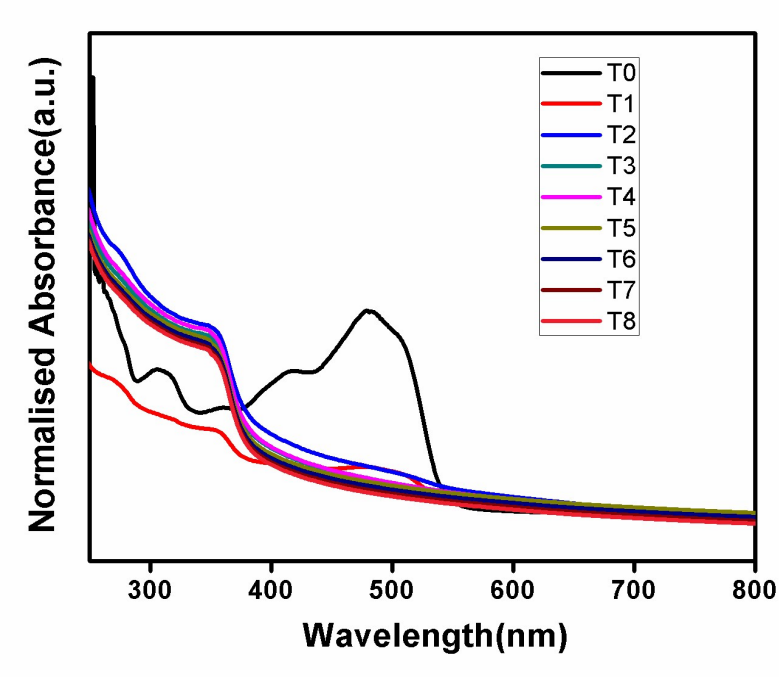


Figure. S11 UV-vis absorption spectra of 3ABBN after irradiating with visible light at different durations up to 8 h, denoted by T0 to T8

Supporting Information, SI-12

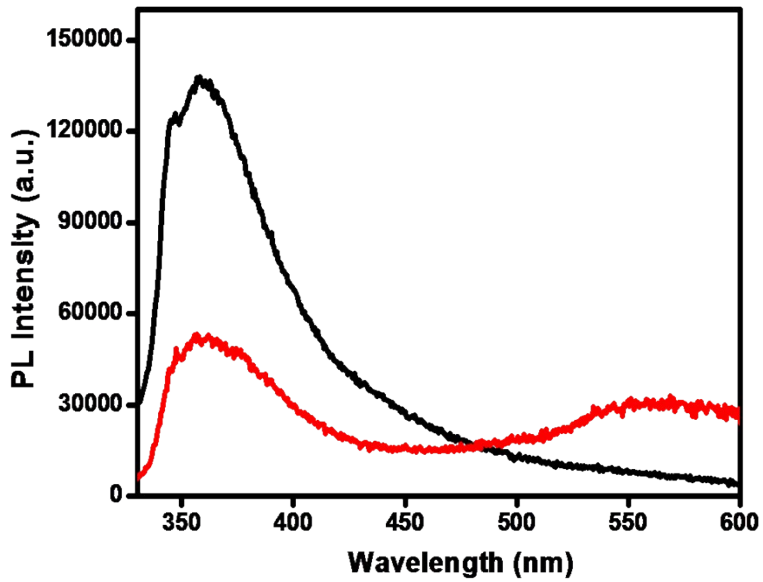


Figure. S12 PL spectrum of 4ABBN (9.04 x 10^{-4} M-black) and ZnO-4ABBN composite (1.69 x 10^{-3} +9.04 x 10^{-4} M- red), λexc=310 nm.

Supporting Information, SI-13

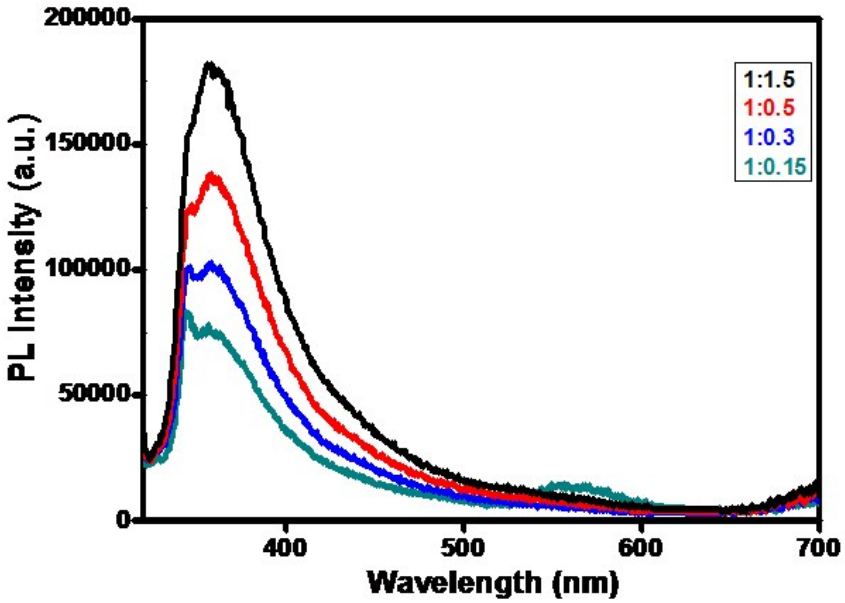


Figure. S13 PL spectrum of 4ABBN (13.56 x 10^{-4} M-black), (9.04 x 10^{-4} M-red), (7.23 x10^{-4}M-blue and (5.42 x 10^{-4} M-olive green), λexc=310 nm.

Supporting Information, SI-14

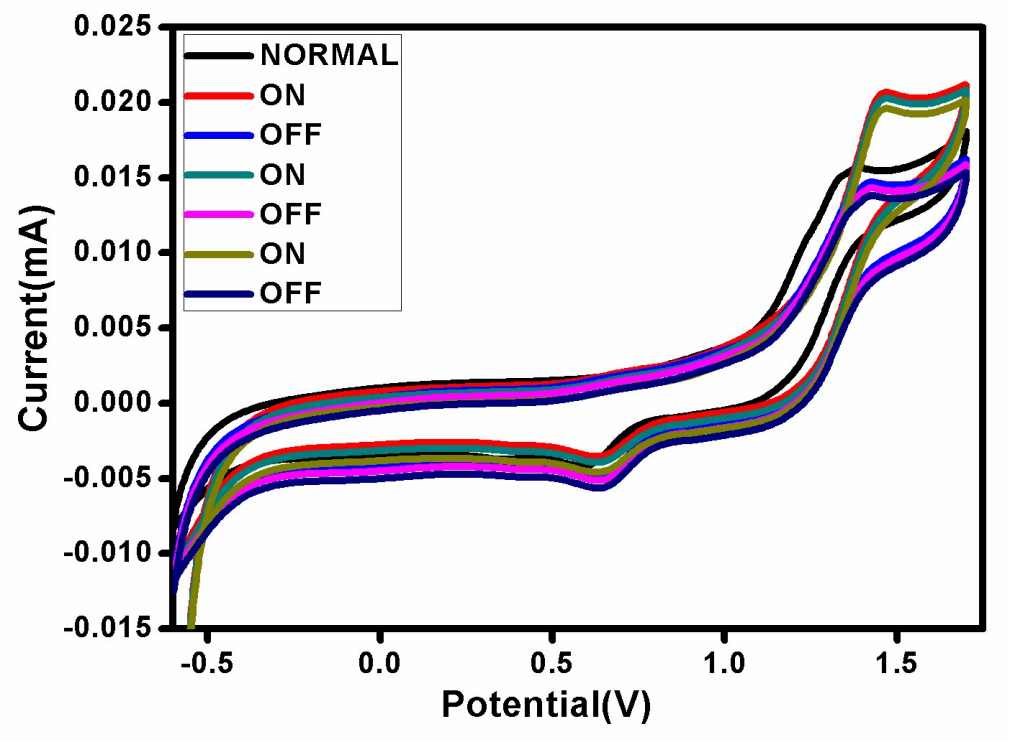
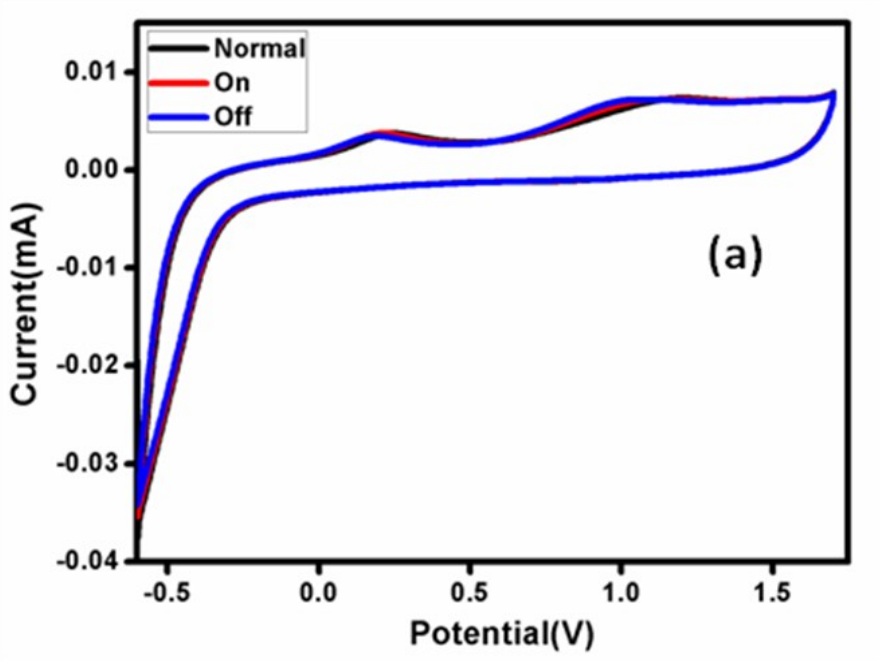


Figure. S14 Comparison of photocurrent with potential of ZnO-4ABBN composite upon turning on and off 200W tungsten lamp in three consecutive cycles by cyclic voltammetry.

Supporting Information, SI-15



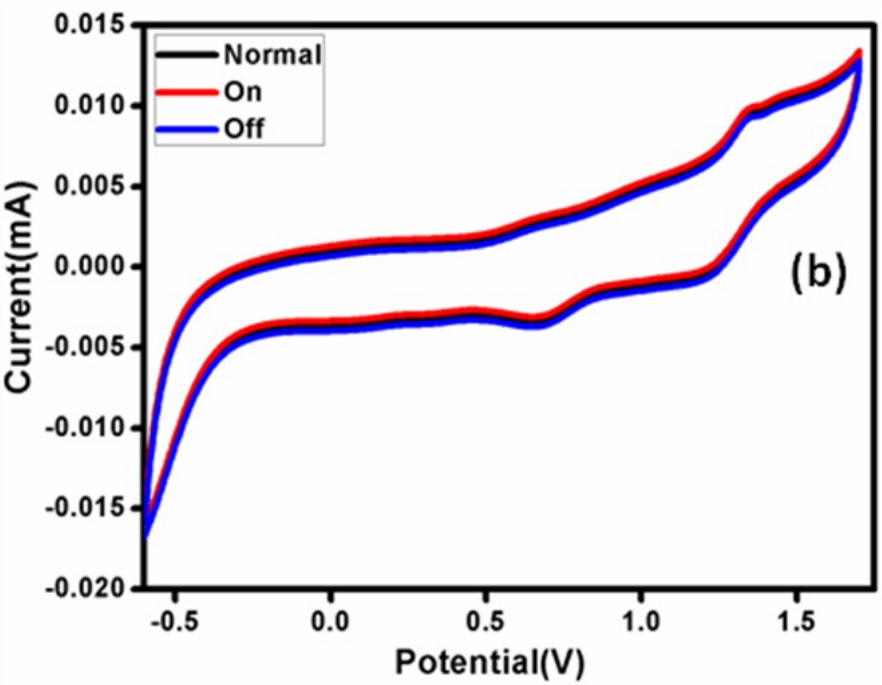


Figure. S15 Comparison of photocurrent with potential of (a) ZnO and (b) 4ABBN upon turning on and off 200W tungsten lamp by cyclic voltammetry.

Supporting Information, SI-16

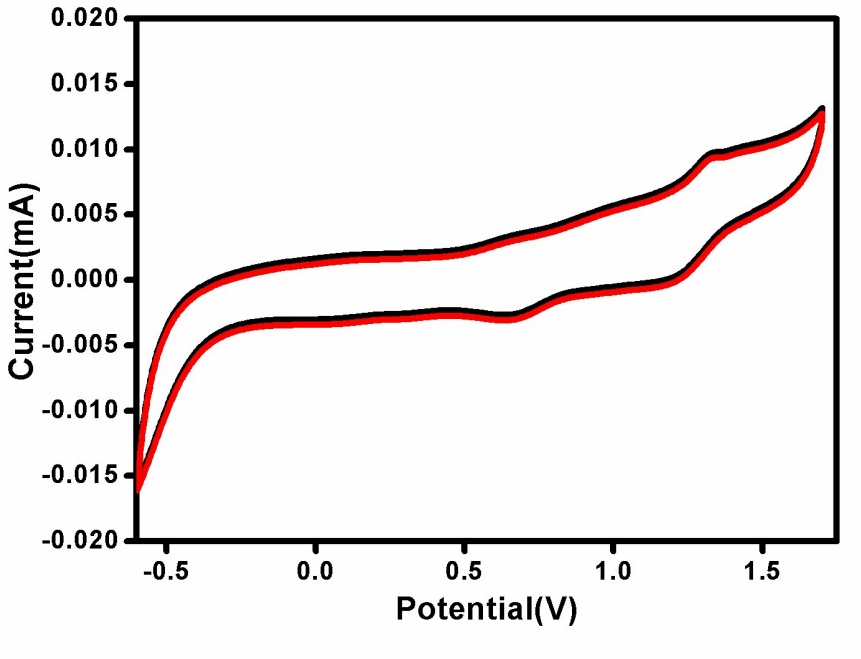


Figure. S16 Current–voltage data for photoelectrochemical cells employing 4ABBN (black) and 4ABBN-SiO_2 (red) by cyclic voltammetry.

Supporting Information, SI-17

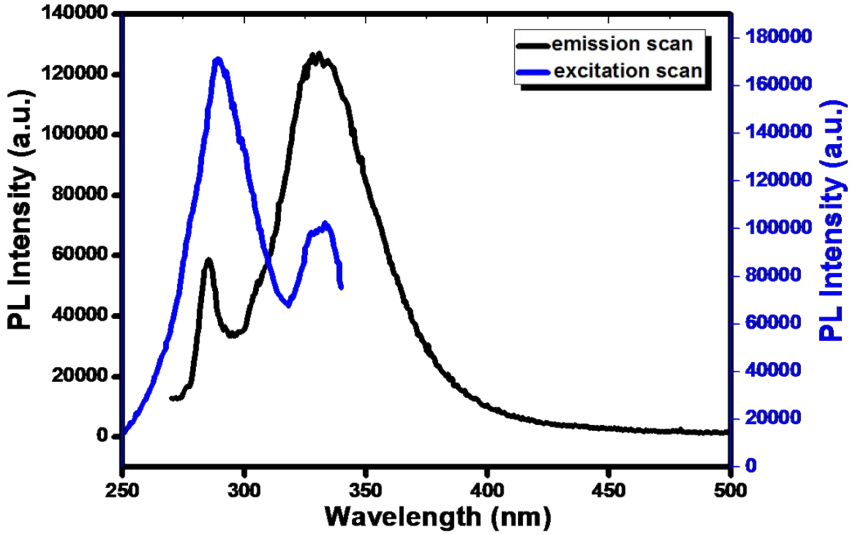


Figure. S17 PL spectrum of 4ABBN (9.04 x 10^{-4} M) at λexc=260 nm (black) and λem=350 nm (blue).

Supporting Information, SI-18

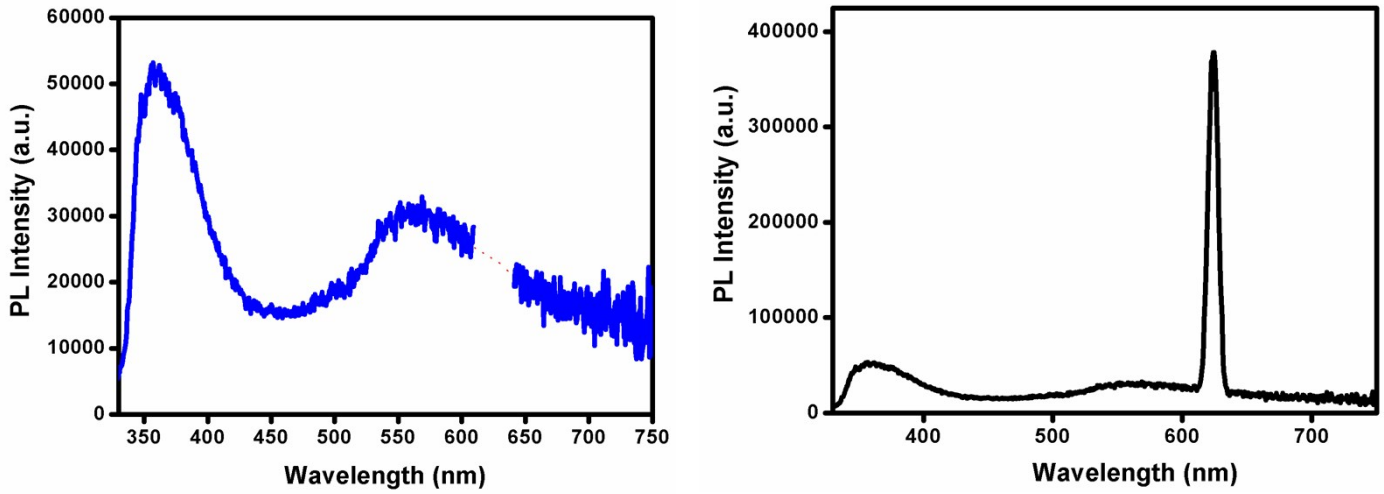


Figure. S18a Emission spectra of ZnO-4ABBN composite (1.69 x 10^{-3} M ZnO + 9.04 x 10^{-4} M 4ABBN; λ_{exc}=310 nm). Overtone at 620 nm ($2\lambda_{exc}$) is also shown in the figure.

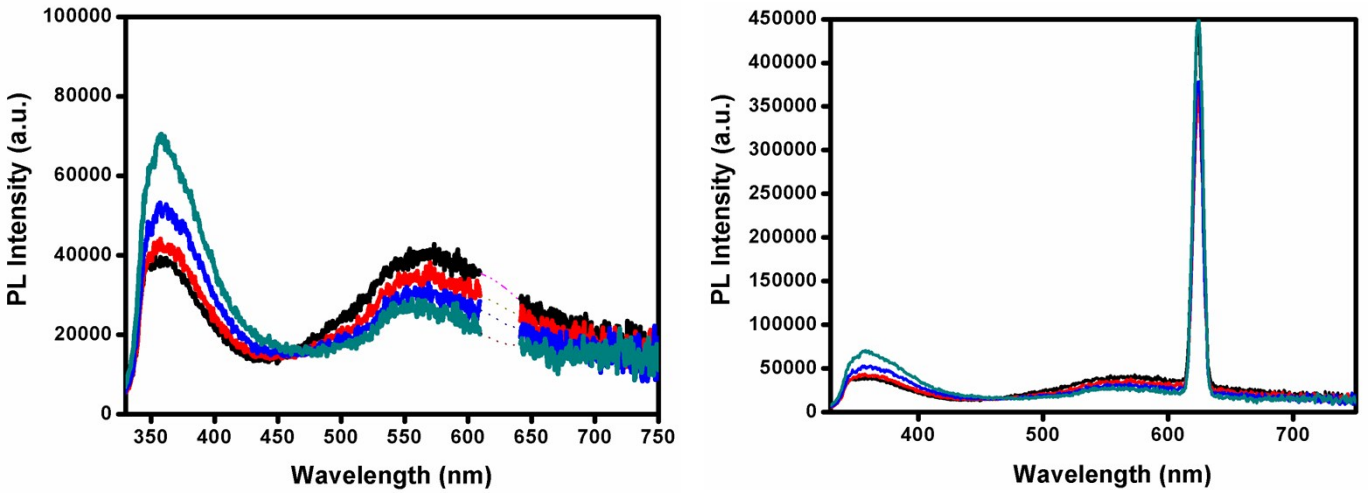


Figure. S18b Emission spectra of ZnO-4ABBN composite with different concentrations of 4ABBN indicating varying surface coverage of ZnO: (a) 1.69 x 10-3 +13.56 x 10-4 M; ZnO:dye = 1:1.5-black, (b) 1.69 x 10-3+9.04 x 10-4 M; ZnO:dye = 1:0.5- red, (c) 1.69 x 10-3+7.23 x10-4 M; ZnO:dye = 1:0.3- blue and (d) 1.69 x 10-3+5.42 x 10-4 M; ZnO:dye = 1:0.15 - cyan; λexc=310 nm. Overtone at 620 nm (2λexc) is also shown in the figure.

Reference ESI, SI-18

G. A. Beane, A. J. Morfa, A. M. Funston and P. Mulvaney, *J. Phys. Chem. C,* 2012 **116**, 3305-3310.