Supporting Information

A Prototype Device of Microliter Volume Voltammetric pH Sensor Based on Carbazole-Quinone Redox-Probe Tethered MWCNT Modified Three-in-One Screen-Printed Electrode

Sakthivel Srinivas,[a,b] *Krishnan Ashokkumar,*[b] *Kamaraj Sriraghavan,*[b*] *Annamalai Senthil Kumar* [a,b]*

[a] Nano and Bioelectrochemistry Research Laboratory, Carbon dioxide Research and Green Technology Centre, Vellore Institute of Technology, Vellore-632 014, India

[b]Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore-632 014, India

1. Synthesis and characterization of phenyl substituted Car-HQ[40,41]

1.2 Synthesis of (Z)-3-(2-phenylhydrazono)cyclohexan-1-one

To a solution of cyclohexane-1,3-dione (2.00 g, 17.84 mmol) in H_2O (25 mL) was added a filtered solution of phenyl hydrazine hydrochloride (2.58 g, 17.84 mmol) dissolved in combination of H_2O (25 mL) and aqueous solution of NaOH (5 N, 4 mL, 19.62 mmol) slowly over the period of 0.5 h and stirred at r.t. for another 5 h. Then the mixture was quenched with ice-water (200 mL) fine solid was obtained it was filtered off and dried. It affords 3-(2-phenylhydrazono)cyclohexan-1-one as a pale brown solid (3.43 g, 16.94 mmol, 95%).

1.3. Synthesis of 1,2,3,9-tetrahydro-4H-carbazol-4-one

To a solution of zinc chloride (15.16 g, 111.24 mmol) in AcOH (15 mL) was added cyclohexane-1,3-dione monophenylhydrazone (3.00 g, 14.83 mmol) in small portions over 5 min at 70 °C stirring, after completion of addition the reaction mixture was heated at 105 °C for 5 h. Then the mixture was cooled to room temperature and poured into chopped ice fine solid was obtained it was filtered off and dried. It affords 1,2,3,9-tetrahydro-4H-carbazol-4-one as a pale green solid (2.56 g, 13.79 mmol, 93%).

1.4. Synthesis of 9-benzyl-1,2,3,9-tetrahydro-4H-carbazol-4-one

To a solution of 1,2,3,9-tetrahydro-4H-carbazol-4-one (2.50 g, 13.49 mmol) in dry DMF (30 mL) was added NaH (60% dispersion in mineral oil, 0.81 g, 20.25 mmol) in small portions at 0 °C and the mixture was stirred for another 30 min at the same temperature. And the reaction mixture was allowed to warm to the room temperature then benzyl bromide (1.76 mL, 2.54 g, 14.84 mmol) was added and it was stirred for another 12 h and quenched with ice-water (300 mL) fine solid obtained it was filtered, washed with excess amount of water and dried. To afford 9-Benzyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one as a brown solid (3.31 g, 12.01 mmol, 89%).

1.5. Synthesis of 9-benzyl-9H-carbazol-4-ol

To a solution of 9-Benzyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one (3.00 g, 10.89 mmol) in dry THF (50 mL) was added NaH (60% dispersion in mineral oil, 1.09 g, 27.24 mmol) in argon atmosphere at r.t. And the mixture was stirred for 30 min and then freshly prepared methyl benzenesulfinate (2.14 mL, 2.55 g, 16.34 mmol) was added. Then the reaction mixture was refluxed for 4 h and cooled to the room temperature and subsequently quenched with water (30 mL) and aqueous solution sat. NH_4Cl (15 mL) the mixture was extracted with EtOAc (5 X 50 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated. The residue was re-dissolved in 1,4-dioxane (30 mL) and it was refluxed for overnight. Then the mixture was cooled to room temperature, the solution was concentrated and the residue was purified by flash chromatography it provides 9-Benzyl-3-bromo-9*H*-carbazol-4-ol as a colorless solid (2.03 g, 7.43 mmol, 68%).

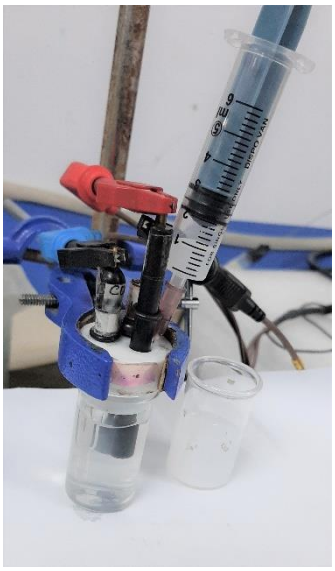
1.6 Synthesis of 9-benzyl-3-bromo-9H-carbazol-4-ol

To a solution of 9-Benzyl-9*H*-carbazol-4-ol (2.00 g, 7.32 mmol) in dry CH_3CN (40 mL) was added a freshly recrystallized NBS (977 mg, 5.50 mmol) at 0 °C and stirred for 0.5 h at the same temperature. And the reaction mixture was concentrated in vacuo and the residue obtained was purified over flash chromatography using hexane-ethyl acetate (80:20) as an eluant to afford 9-Benzyl-3-bromo-1*H*-carbazole-1,4(9*H*)-dione as a colorless solid (2.40 g, 6.80 mmol, 93%).

1.7 Synthesis of 9-benzyl-3-bromo-1H-carbazole-1,4(9H)-dione (1, Car-HQ)

To a solution of 9-Benzyl-3-bromo-9*H*-carbazol-4-ol (2.40 g, 6.81 mmol) in a 9:1 mixture of AcOH and H_2O (30 mL) was added PIFA (7.33 g, 17.0 mmol) in one portion and stirred at 50 °C for 0.5 h. Then, to this MeOH (30 mL) was added and stirring was continued for an additional 0.5 h at the same temperature after that the reaction mixture was quenched with ice-water and extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography to afford 9-benzyl-3-bromo-1H-carbazole-1,4(9H)-dione as red needles (2.27 g, 6.20 mmol, 91%). Mp: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.0 Hz, 1H), 7.45-7.36 (m, 3H), 7.29-7.23 (m, 3H), 7.15-7.10 (m, 3H)5.82 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 178.0, 175.0, 140.2, 139.1, 137.2, 135.9, 133.1, 128.8, 128.0, 127.5, 126.7, 125.1, 124.3, 123.2, 116.2, 111.7, 48.2; IR (neat) 1643, 1516, 1249, 1155, 748, 698 cm^{-1}.

A. B.



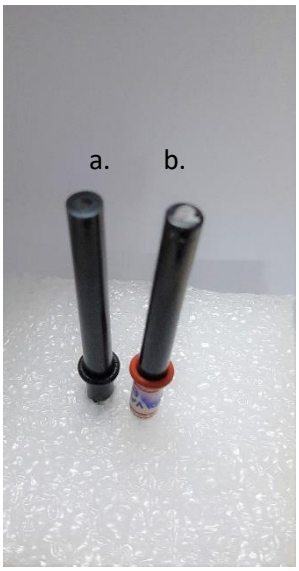


Figure S1. Photographs of (A) a conventional three-electrode system used in this work and (B) GCE/MWCNT@Car-HQ before (a) and after exposure (b) with a 100 µM $AgNO_2$ in the pH 7 PBS. White color precipitate obtained with case (b) electrode indicates liberation of Br- in the reaction medium due to an electrochemical reaction.

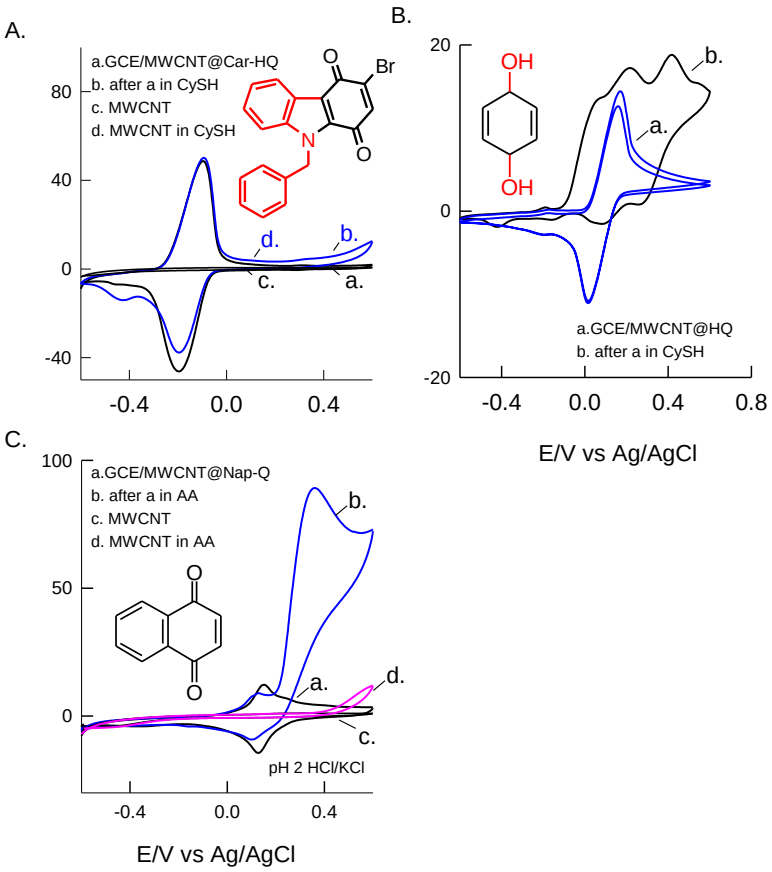
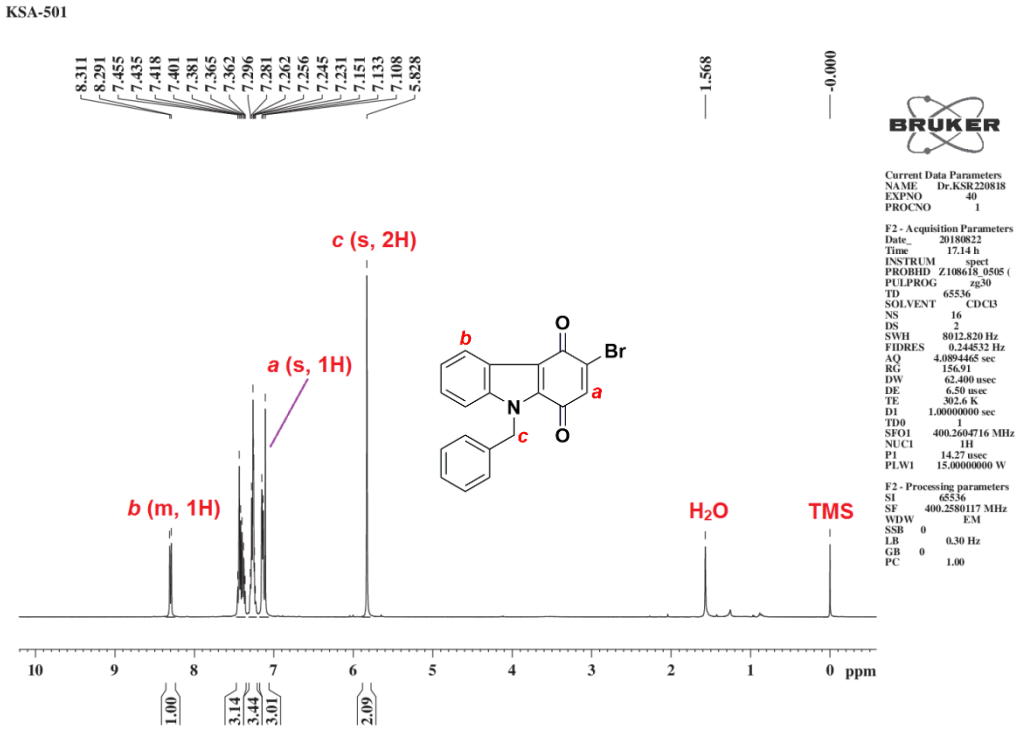


Figure S2. CV responses of various organic compounds immobilized MWCNT modified glassy carbon electrodes without and with added ascorbic acid (AA) and cysteine (CySH) in pH 7 PBS at v=10 mV s^{-1}.

A.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7.362
7.296
7.281
7.262
7.256
7.245
7.231
7.151
7.133
7.108
5.828
1.568
-0.000
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a (s, 1H)
b (m, 1H)
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TMS
b
a
c
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Br
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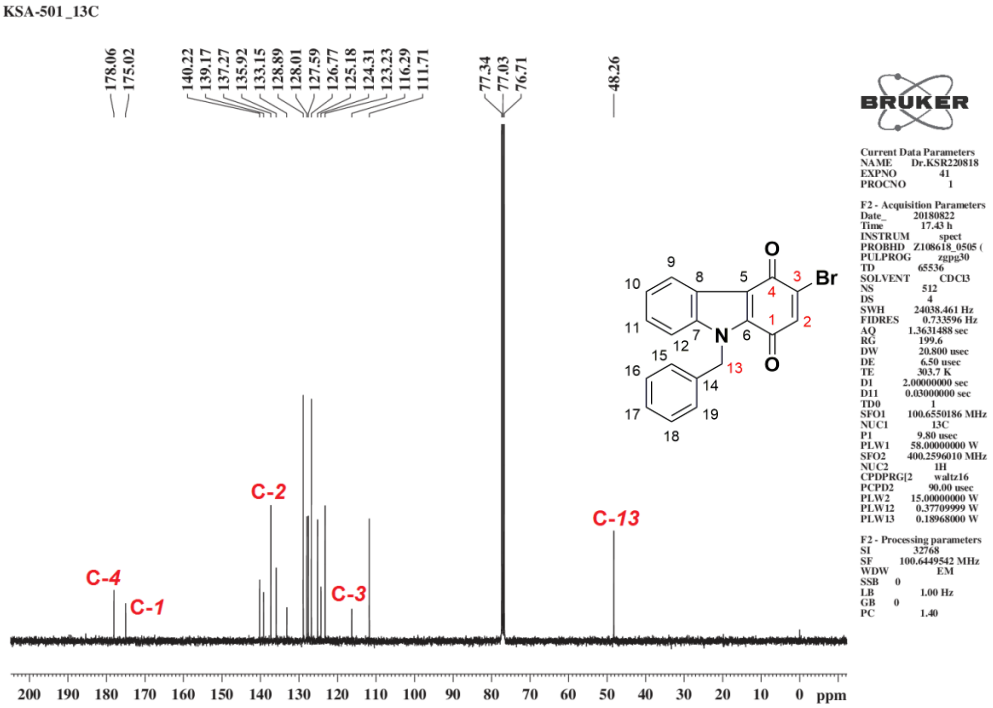
B.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C-1
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PLW13 0.18968000 W
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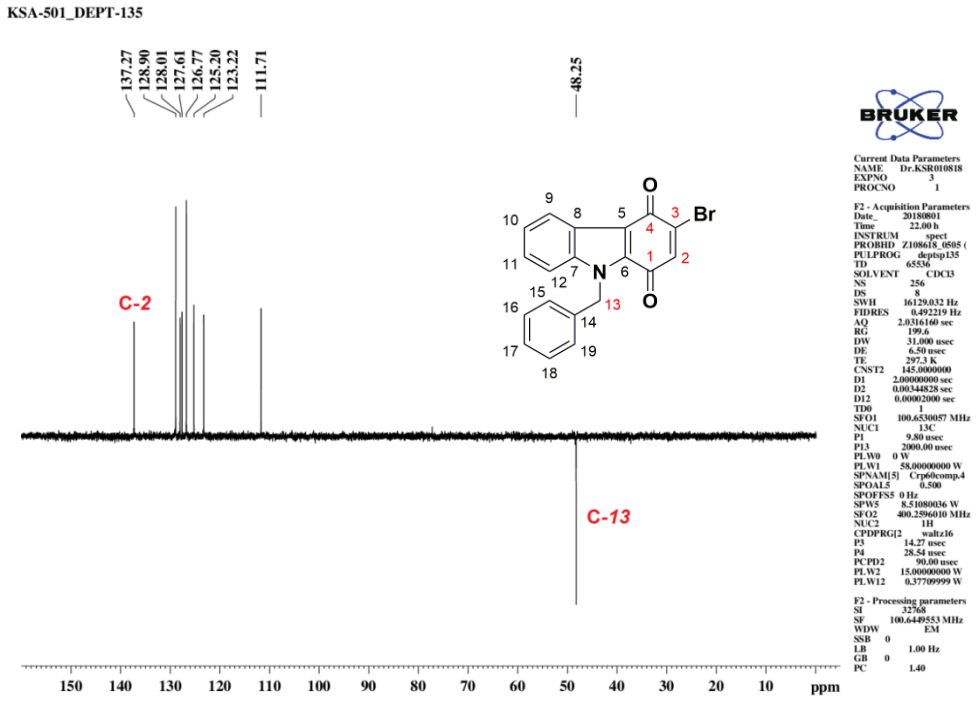
C.



D.

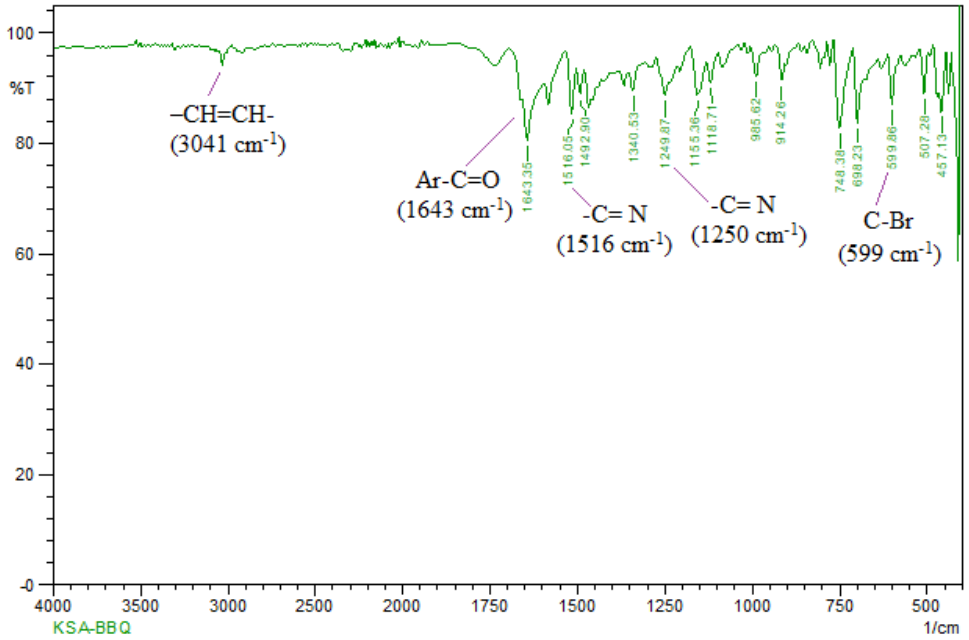


Figure S3. (A-B) are the ^{1}H,^{13}C ,DEPT NMR and (D) FT-IR spectra of the compound 9-benzyl-3-bromo-iH-carbazole-1,4(9H)-dione

References

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