

Nickel(II) Monobenzoporphyrins and Chlorins: Synthesis, Electrochemistry and Anion Sensing Properties

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EXPERIMENTAL SECTION

Materials

Methyl acrylate, triphenylphosphine, and pyrrole were purchased from Alfa Aesar UK and used as received. DriSolv Anhydrous dichloromethane (CH_2Cl_2 , $\geq 99.8\%$), anhydrous pyridine (99.8%), tetra-n-butyl-ammonium perchlorate (TBAP, $\geq 99.0\%$), palladium acetate, indane-1,3-dione, and liquid bromine, tetrabutylammonium cyanide (TBACN, $\geq 95.0\%$) were purchased from Sigma Aldrich and directly used without further purification. **Caution!** *Perchlorate salts are potentially explosive and should be handled with care.* Benzaldehyde, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, DDQ, K_2CO_3 , malononitrile and acetic acid were purchased from Hi-Media, India. All the solvents employed in the present work have been distilled or dried before use. NBS for bromination reaction was recrystallized from hot water and dried for 6-8 h at 70 °C under vacuum. Precoated silica-based TLC plates were purchased from E. Merck. All anions employed in this study are of tetrabutylammonium (TBA) salts which were obtained from Sigma-Aldrich or Alfa Aesar UK. Sodium azide, cyanate, and thiocyanates including 4-nitrophenyl thiocyanate (4-NP(SCN)) and two nitrophenyl isocyanate derivatives, 4-NP(OCN) and 3-NP(OCN) are obtained Alfa Aesar UK.

Instrumentation and Methods

The electronic absorption spectra were recorded on Agilent Cary 100 spectrophotometer using a pair of quartz cells of 10 mm path length with 3.5 ml volume. λ_{max} values are reported in nm and molar extinction coefficients (ϵ) are given in $\text{M}^{-1}\text{cm}^{-1}$. The emission spectra were recorded on Hitachi F-4600 spectrofluorometer using a quartz cell of 10 mm path length and 3.5 ml volume. The ^1H NMR spectra were recorded on JEOL ECX 400 MHz using CDCl_3 as a solvent at 298 K and reported in δ scale (ppm) value. The positive ion mode MALDI-TOF-MS spectra were obtained by Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer with 2-(4'-

hydroxyphenylazo)benzoic acid (HABA) as matrix. The geometry optimization of synthesized Ni(II) porphyrinoids in gas phase was carried out by DFT calculations using B3LYP functional and LANL2DZ basis set. The sensing studies were carried out in distilled CH₂Cl₂. Cyclic voltammetry (CV) measurements were carried out using an EG&G model 173 potentiostat/galvanostat coupled with an EG&G model 175 universal programmer, and current/voltage curves were plotted on an EG&G XY plotter in pyridine solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. A three electrode system composed of a glassy carbon working electrode, a platinum wire counter electrode, and a homemade saturated calomel reference electrode (SCE). The SCE reference electrode, tested in CH₂Cl₂ against ferrocene (0.48 V vs SCE), was separated from the bulk solution with a fritted glass bridge of low porosity filled with the solvent and supporting electrolyte. All solutions were degassed, and a blanket of N₂ was kept above the solution during electrochemical measurements. Low temperature CV measurements were made by immersing the cell in an appropriate dry ice/acetone mixture.

General Procedure for the Synthesis of *trans*-monobenzochlorins NiMBC(IND)₂ and NiMBC(MN)₂. 200 mg (0.227 mmol) of NiMBP(NO₂) was dissolved in 7 ml of DMSO. To this, 10 eq. of K₂CO₃ and 10 eq. of active methylene compound (malononitrile or indane-1,3-dione) were added and the reaction mixture was purged with argon for 10-15 min. The reaction mixture was stirred at 85 °C for 2.5-3.0 hrs. The completion of the reaction was monitored by thin layer chromatography and UV-visible spectroscopy. After completion, the reaction mixture was cooled to room temperature and diluted with 25 ml CHCl₃. The diluted reaction mixture was washed twice with brine solution and the organic layer was separated and passed over anhydrous sodium sulphate. The solvent was removed and the crude porphyrin mixture was purified by silica gel column chromatography. Trace of unreacted precursor was removed using CHCl₃ as an eluent and the desired compound was eluted using CHCl₃ to CHCl₃:acetone (95:5, v/v) mixture. The pure products were obtained by recrystallization utilizing a CHCl₃/CH₃OH mixture.

NiMBC(IND)₂: Yield: 76% (194 mg, 0.172 mmol). UV/vis (CH₂Cl₂): λ_{\max} (nm) (log ϵ): 230(5.04), 448(5.17), 527(3.96), 612(sh), 659(4.48). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.49(d, ³J_{H, H} = 4 Hz, 2H, β -H), 8.31(d, ³J_{H, H} = 4 Hz, 2H, β -H), 7.87-7.74(m, 14H, *meso*-Ph-H), 7.68(d, ³J_{H, H} = 8 Hz, 2H, *meso*-Ph-H), 7.58(t, ³J_{H, H} = 8 Hz, 2H, *meso*-Ph-H), 7.41(d, ³J_{H, H} = 8 Hz, 2H, *meso*-Ph-H), 7.35-7.35(m, 4H, IND-H), 7.22-7.19(m, 4H, IND-H), 6.88(d, ³J_{H, H} = 8 Hz, 2H, β -fused-H), 5.07(d, ³J_{H, H} = 4 Hz, 2H, β -H), 3.84(s, 6H, -CH₃), 3.00(d, ³J_{H, H} = 4 Hz, 2H, -CH(IND)). MALDI-TOF-MS (*m/z*): found 1127.627 [M+H]⁺, calcd 1127.259, found 1216.322 [M]⁺+THF+H₂O, calcd 1216.319. Anal. Calcd for C₇₀H₄₄N₄O₈Ni C, 74.55; H, 3.93; N, 4.97. Found C, 74.49; H, 3.90; N, 4.98.

NiMBC(MN)₂: Yield: 70% (154 mg, 0.159 mmol). UV/vis (CH₂Cl₂): λ_{\max} (nm) (log ϵ): 267(4.36), 442(5.00), 552(3.42), 662(sh), 651(4.32). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.45(d, ³J_{H,H} = 4 Hz, 4H, β -H), 8.27(s, 2H, *meso*-Ph-H), 7.91-7.86 (m, 5H, *meso*-Ph-H), 7.78(t, ³J_{H,H} = 8 Hz, 3H, *meso*-Ph-H), 7.71(t, ³J_{H,H} = 8 Hz, 2H, *meso*-Ph-H), 7.58(s, 2H, *meso*-Ph-H), 7.51(t, ³J_{H,H} = 8 Hz, 2H, *meso*-Ph-H), 7.35(s, 2H, *meso*-Ph-H), 7.18(s, 2H, *meso*-Ph-H), 7.06(d, ³J_{H,H} = 8 Hz, 2H, β -fused-H), 5.04(d, ³J_{H,H} = 4 Hz, 2H, β -H), 3.86-3.83(m, 8H, -CH(MN) & -CH₃). MALDI-TOF-MS (*m/z*): found 966.218 [M]⁺, calcd 966.221, found 837.306 [M+H]⁺-2MN, calcd 837.201. Anal. Calcd for C₅₈H₃₆N₈O₄Ni C, 71.99; H, 3.75; N, 11.58. Found: C, 72.01; H, 3.76; N, 11.39.

Synthetic Procedure for Oxidative Fusion of *trans*-monobenzochlorins into Difused monobenzoporphyrins NiMBP(IND)₂ and NiMBP(MN)₂. 70 mg of the respective *trans*-monobenzochlorins was treated with 6 eq. of DDQ in 20 ml of distilled CHCl₃. The reaction mixture was allowed to reflux for 2-3 hrs as the starting material was totally consumed. After completion, the reaction mixture was washed trice with distilled water to remove excess of DDQ. The organic layer was passed through anhydrous sodium sulphate and dried under reduced pressure. The crude porphyrins were purified by silica gel column chromatography using an initial CHCl₃ eluent followed by a 5-7% acetone in CHCl₃ eluent. The final solid product was washed with methanol to afford the pure product(s).

NiMBP(IND)₂: Yield: 69% (48 mg, 0.043 mmol). UV/vis (CH₂Cl₂): λ_{\max} (nm) (log ϵ): 229(4.90), 480(5.26), 596(4.28), 664(3.76). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.31(d, ³J_{H,H} = 4 Hz, 2H, β -H), 8.72(d, ³J_{H,H} = 4 Hz, 2H, β -H), 8.27(s, 2H, *meso*-Ph-H), 8.04-7.57(m, 16H, *meso*-Ph-H), 7.44(t, ³J_{H,H} = 4 Hz, 3H, IND-H), 7.31(s, 2H, IND-H), 7.01(t, ³J_{H,H} = 8 Hz, 3H, IND-H), 6.78(d, ³J_{H,H} = 8 Hz, 2H, fused-H), 3.87(s, 6H, -CH₃). MALDI-TOF-MS (*m/z*): found 1122.432 [M+H]⁺,

calcd 1122.774; found 1145.452 [M+H⁺+Na⁺], calcd 1145.762. Anal. Calcd for C₇₀H₃₈N₄O₈Ni C, 74.95; H, 3.41; N, 4.99. Found: C, 75.00; H, 3.42; N, 4.97.

NiMBP(MN)₂: Yield: 65% (45 mg, 0.047 mmol). UV/vis (CH₂Cl₂): λ_{max}(nm) (log ε): 277(4.40), 478(5.10), 599(4.07), 647(4.09). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.26(d, ³J_{H, H} = 4 Hz, 2H, β-H), 8.69(d, ³J_{H, H} = 8 Hz, 2H, β-H), 8.48(d, ³J_{H, H} = 8 Hz, 2H, *meso*-Ph-H), 8.00(d, ³J_{H, H} = 8 Hz, 2H, *meso*-Ph-H), 7.87-7.70(m, 14H, *meso*-Ph-H), 7.22(s, 2H, fused-H), 3.87(s, 6H, -CH₃). MALDI-TOF-MS (*m/z*): found 935.401 [M]⁺-CN calcd 935.179. Anal. Calcd for C₅₈H₃₀N₈O₄Ni•0.5CH₃OH C, 71.87; H, 3.30; N, 11.46. Found: C, 71.90; H, 3.33; N, 11.39.

Synthetic Procedure for NiMBC(IND)₂Br₄. 120 mg (0.106 mmol) of NiMBC(IND)₂ was dissolved in 25 ml distilled chloroform. To this, 16 q. of liq. Br₂ (87 μL, 1.7 mmol) dissolved in 10 ml of distilled CHCl₃ was added slowly. The resulted reaction mixture was stirred for 3-5 min at room temperature. The completeness of reaction was monitored by UV-vis spectroscopy with expected red shifts in the Soret and Q bands. After completion of reaction, the solution mixture was washed twice with 20% sodium metabisulphite (Na₂S₂O₅) solution and the organic layer was separated and dried over anhydrous sodium sulphate. The solvent was removed to dryness and the crude porphyrin was purified by silica gel column chromatography using s chloroform eluent.

NiMBC(IND)₂Br₄: Yield: 80% (122 mg, 0.08 mmol). UV/vis (CH₂Cl₂): λ_{max}(nm) (log ε): 230(5.05), 466(5.02), 549(3.85), 597(3.67), 650(sh), 706(4.60). ¹H NMR (400 MHz, CDCl₃) δ: 7.81-7.64(m, 13H, *meso*-Ph-H), 7.58-7.46(m, 5H, *meso*-Ph-H), 7.29-7.25(m, 3H, IND-H), 7.17-7.08(m, 3H, IND-H), 6.91(s, 2H, fused-H), 6.50(d, ³J_{H, H} = 8 Hz, 2H, IND-H), 5.29(d, ³J_{H, H} = 8 Hz, 2H, β-H), 3.84(d, ³J_{H, H} = 4 Hz, 6H, -CH₃), 2.72(d, ³J_{H, H} = 8 Hz, 2H, -CH(IND)). MALDI-TOF-MS (*m/z*): found 1443.598 [M]⁺ calcd 1443.398, found 1299.282 [M]⁺-IND calcd 1299.271. Anal. Calcd for C₇₀H₄₀Br₄N₄O₈Ni C, 58.28; H, 2.79; N, 3.88. Found: C, 58.25; H, 2.80; N, 3.90.

Synthesis of NiMBP(VCN)₂: 15 mg (0.016 mmol) of NiMBP(MN)₂ was dissolved in 5 mL distilled CHCl₃. To this, 6 equivalents (25 mg, 0.094 mmol) of tetrabutylammonium cyanide (TBACN) was added and the reaction mixture was stirred for 30 minutes at room temperature under aerobic conditions. The progress of the reaction was monitored by TLC and UV-vis spectroscopy. After completion, the reaction mixture was washed twice with distilled water. The organic layer was separated and dried over anhydrous Na₂SO₄ and evaporated to dryness. The crude porphyrin was purified by silica gel column chromatography using a chloroform eluent. The yield was found to be to 70% (10 mg, 0.011 mmol).

NiMBP(VCN)₂: UV/vis (CH₂Cl₂): λ_{\max} (nm) (log ϵ): 228(4.26), 326(3.80), 442(4.09), 520(3.89), 722(3.06), 780(2.30), 861(3.14). ¹H NMR (500 MHz, CDCl₃) δ : 9.96 (d, ³J_{H,H} = 5 Hz, 2H, fused-Ph-H), 8.74-8.72 (m, 4H, fused-Ph-H & β -H), 8.31 (d, ³J_{H,H} = 5 Hz, 2H, β -H), 7.97 (t, ³J_{H,H} = 10 Hz, 2H, fused-Ph-H), 7.88 (t, ³J_{H,H} = 10 Hz, 2H, fused-Ph-H), 7.79-7.72 (m, 10H, unfused *meso*-Ph-H) 6.94 (s, 2H, Benzo-H), 3.82 (s, 6H, -CH₃). ¹³C NMR (125 MHz, CDCl₃) δ : 168.1, 146.3, 139.5, 138.3, 138.0, 137.2, 137.0, 134.5, 132.1, 131.8, 130.9, 130.7, 129.8, 129.3, 129.1, 128.7, 127.8, 127.6, 126.5, 124.5, 117.2, 108.9, 107.7, 29.8. MALDI-TOF-MS (*m/z*): found 908.947 [M]⁺ calcd 908.168.

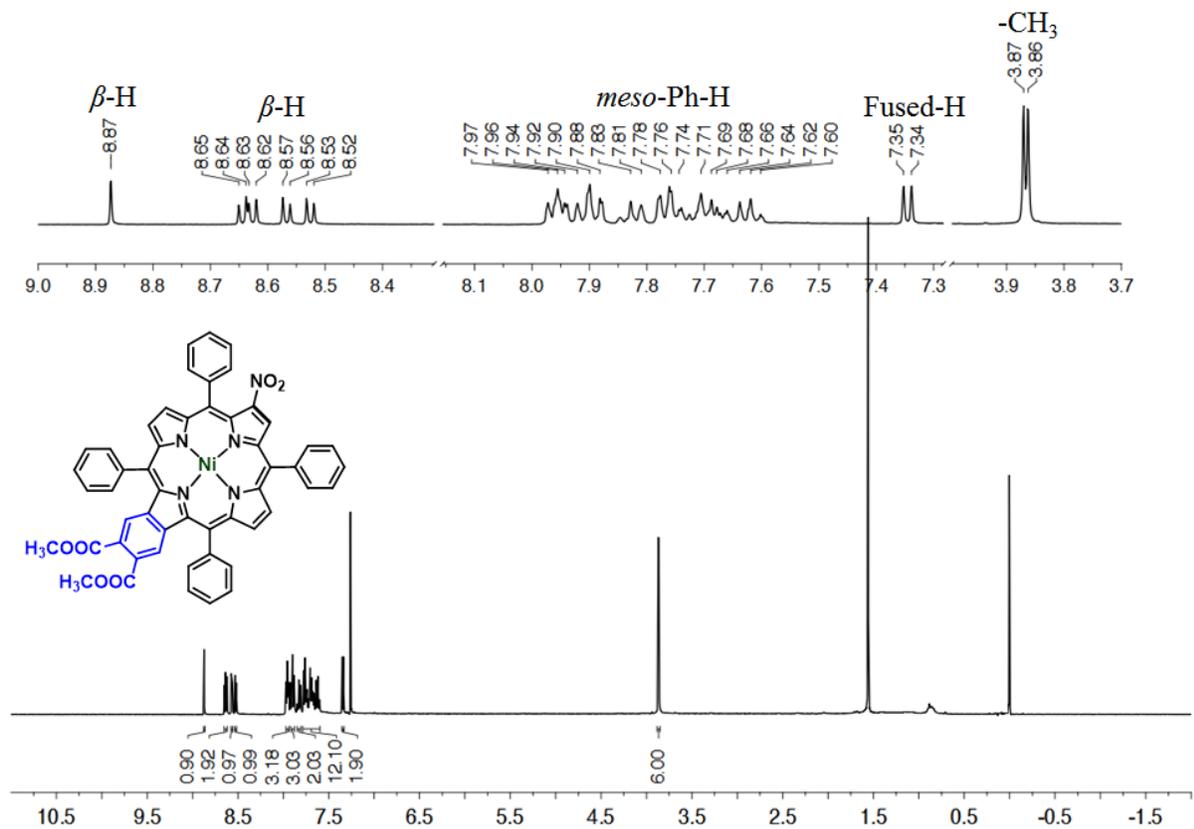


Figure S1. ^1H NMR spectrum of NiMBP(NO_2) in CDCl_3 at 298 K.

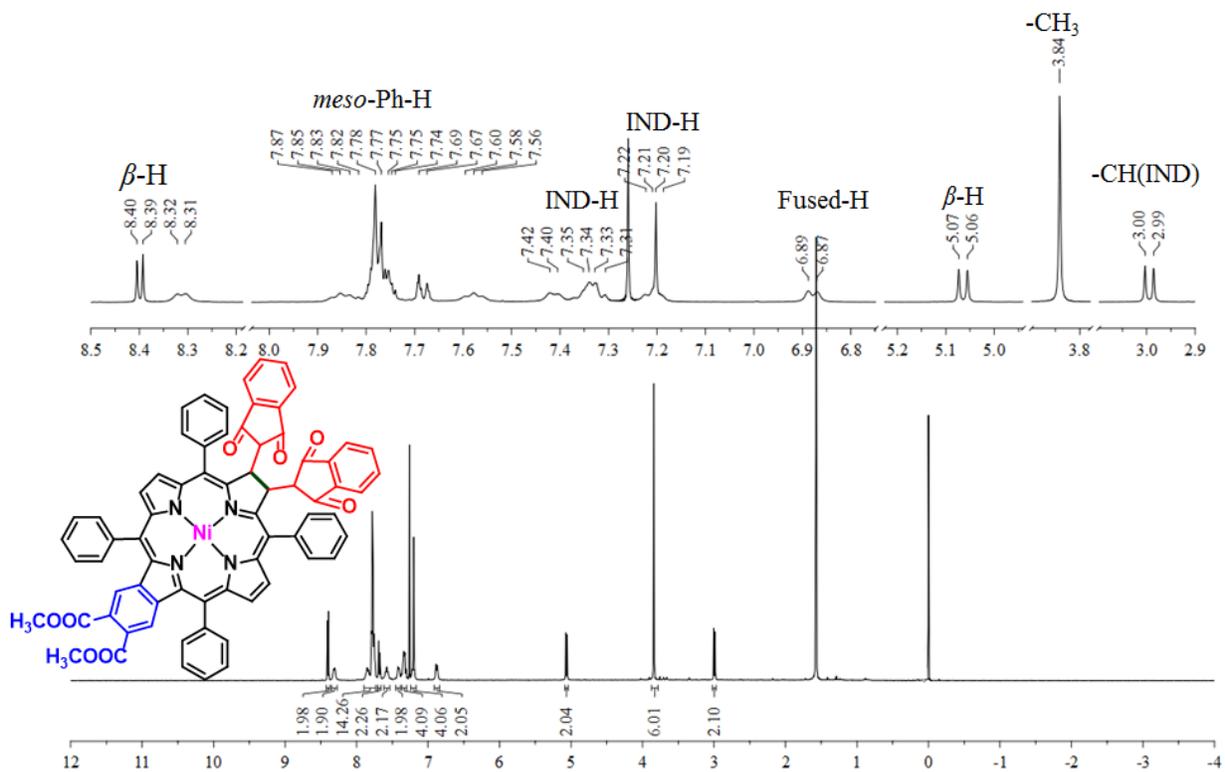


Figure S2. ^1H NMR spectrum of $\text{NiMBC}(\text{IND})_2$ in CDCl_3 at 298 K.

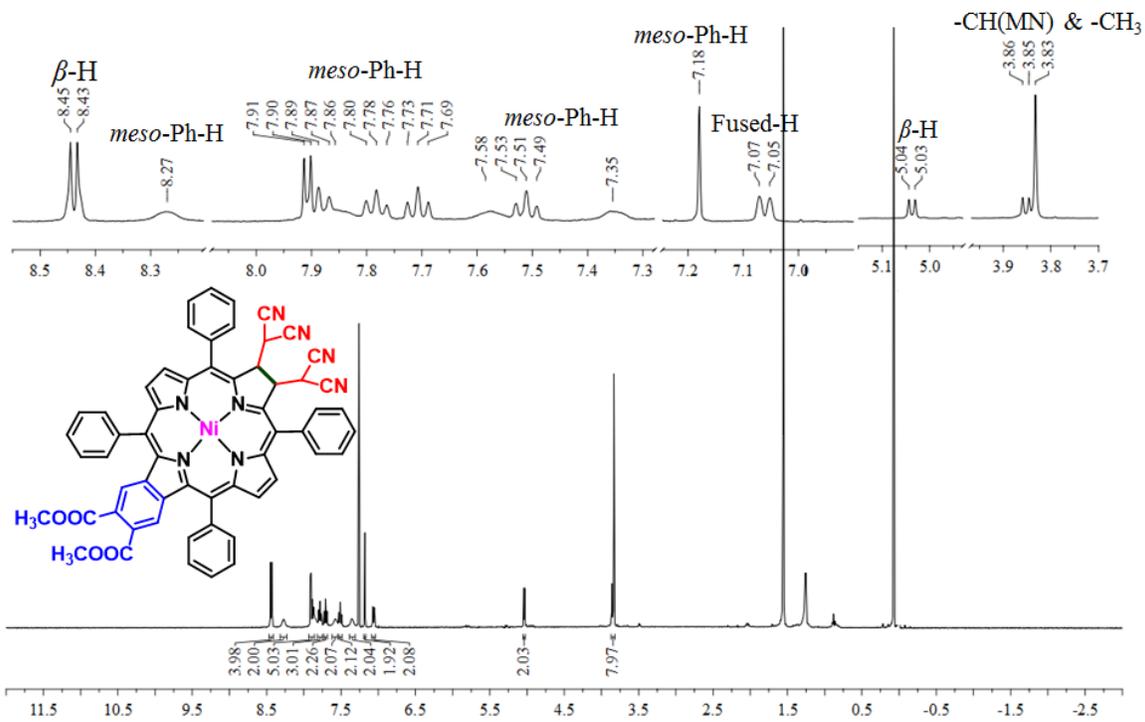


Figure S3. ^1H NMR spectrum of $\text{NiMBC}(\text{MN})_2$ in CDCl_3 at 298 K.

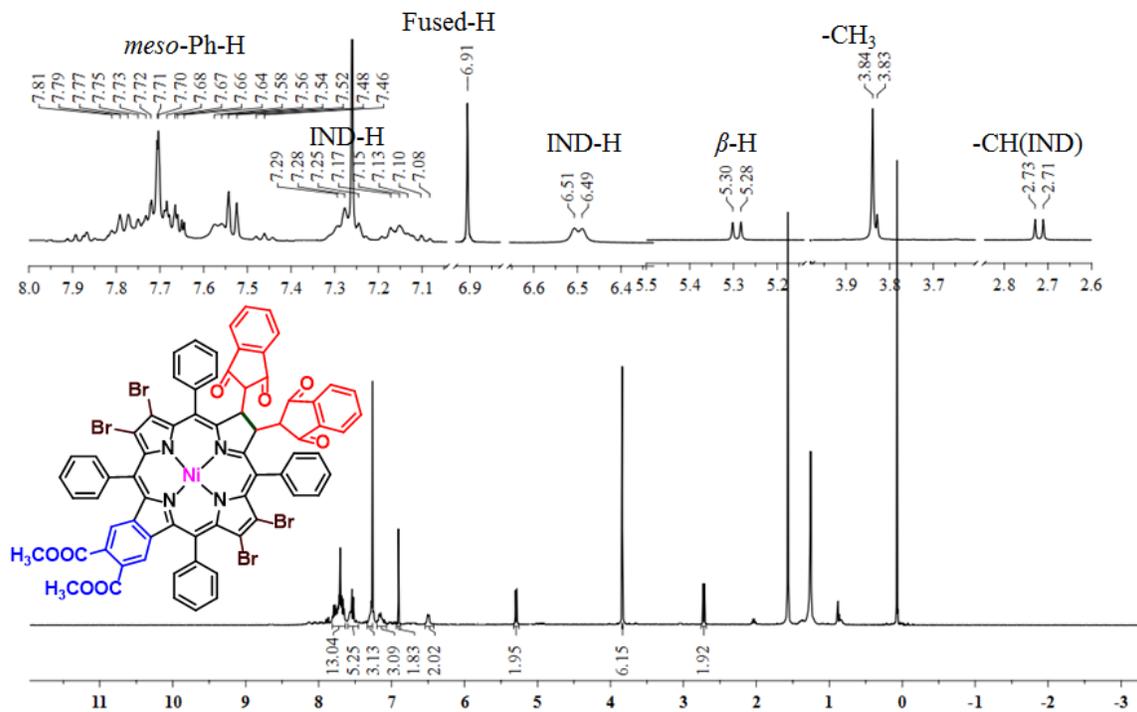


Figure S4. ^1H NMR spectrum of $\text{NiMBC}(\text{IND})_2\text{Br}_4$ in CDCl_3 at 298 K.

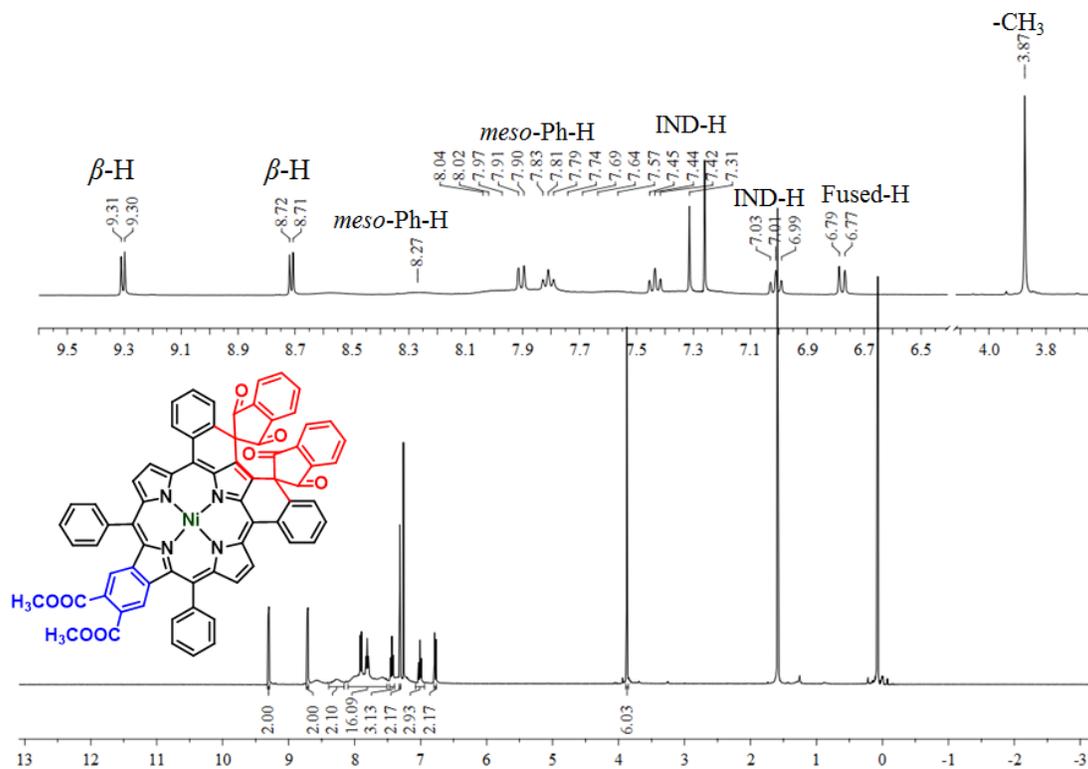


Figure S5. ^1H NMR spectrum of $\text{NiMBP}(\text{IND})_2$ in CDCl_3 at 298 K.

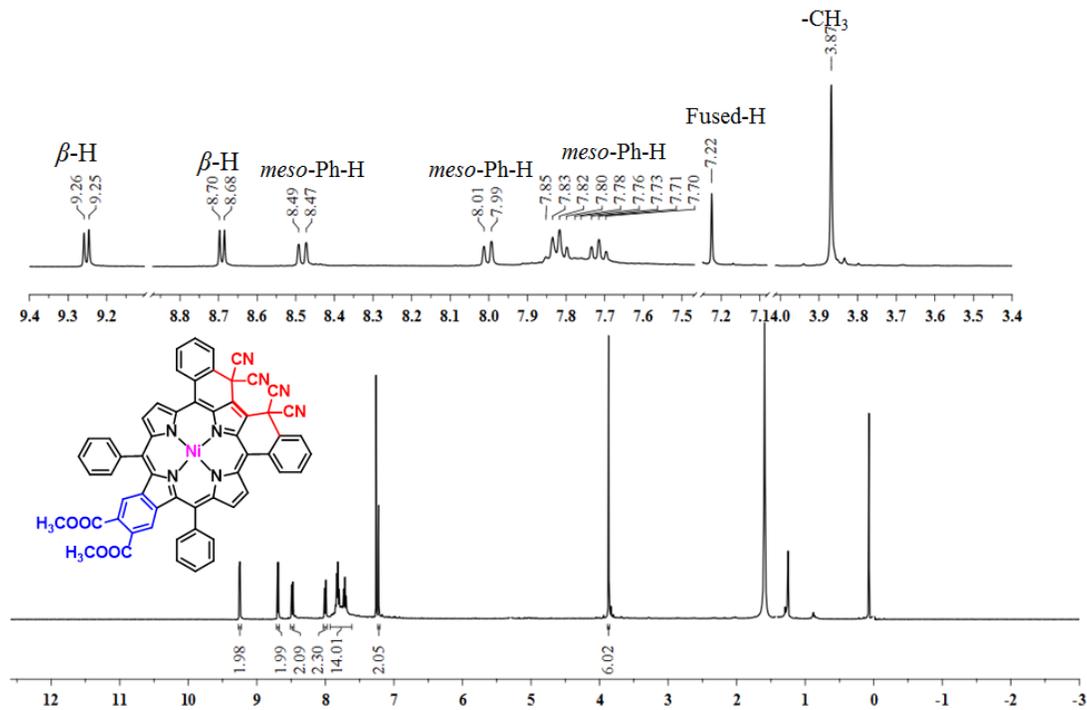


Figure S6. ^1H NMR spectrum of NiMBP(MN) $_2$ in CDCl_3 at 298 K.

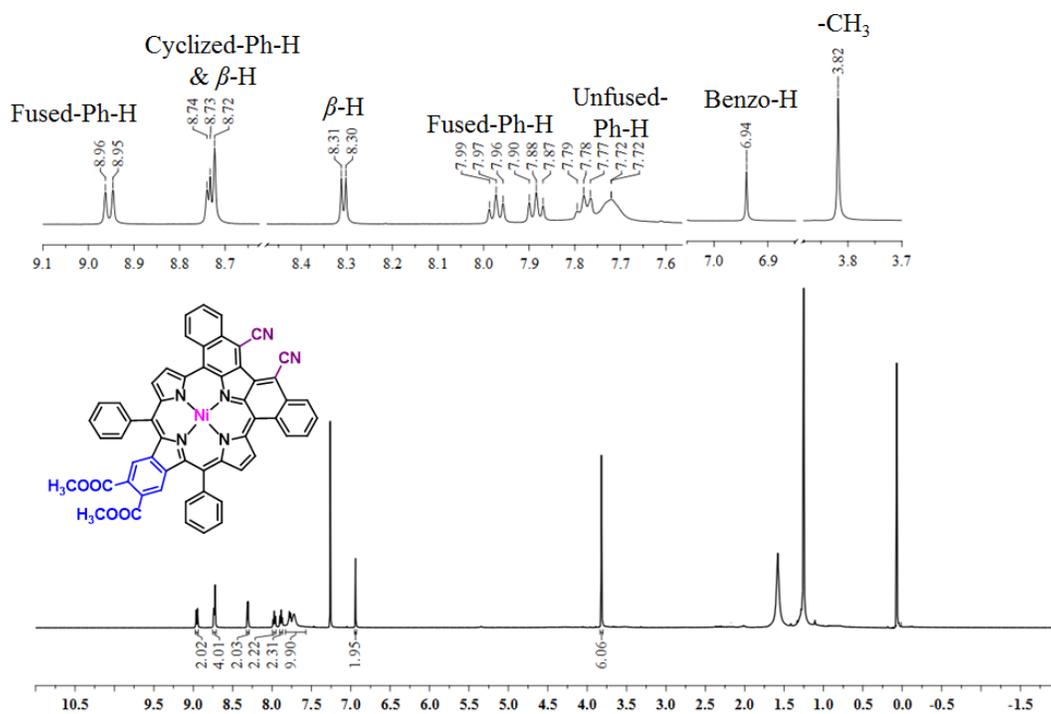


Figure S7. ^1H NMR spectrum of NiMBP(VCN) $_2$ in CDCl_3 at 298 K.

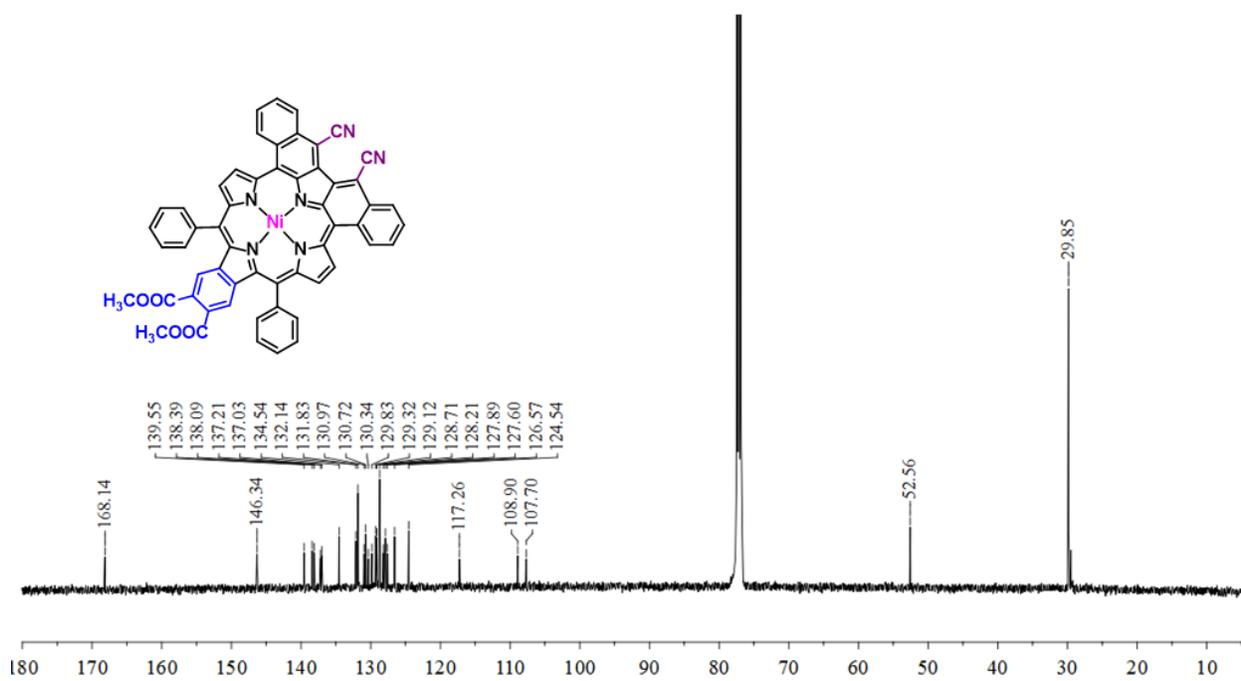


Figure S8. ¹³C NMR spectrum of NiMBP(VCN)₂ in CDCl₃ at 298 K.

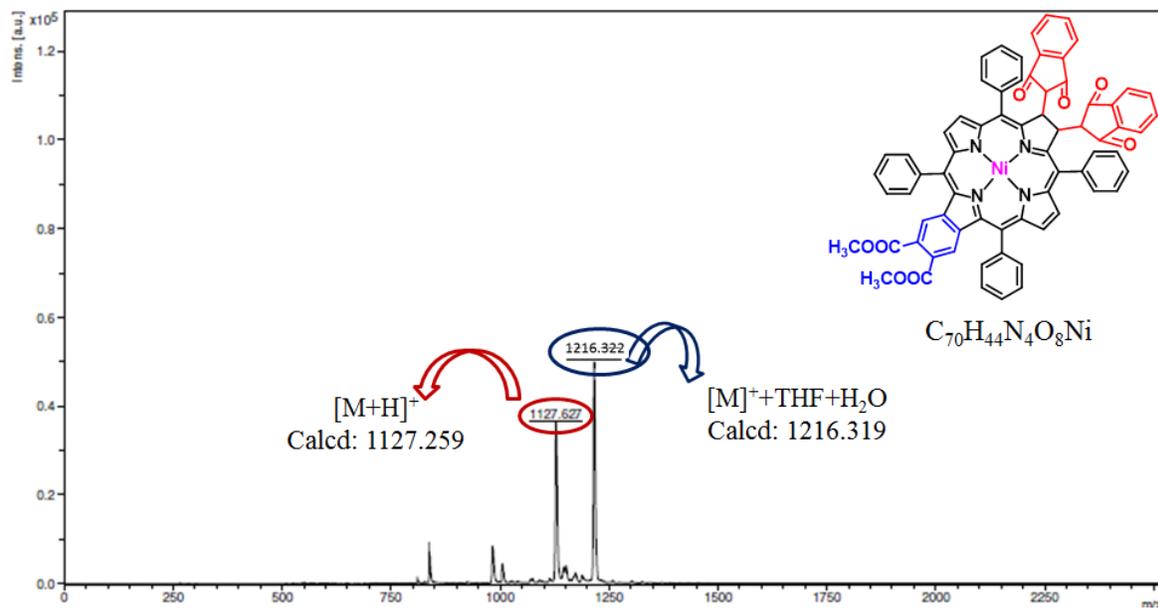


Figure S9. MALDI-TOF-MS spectrum of NiMBC(IND)₂ in CH₂Cl₂ at 298 K.

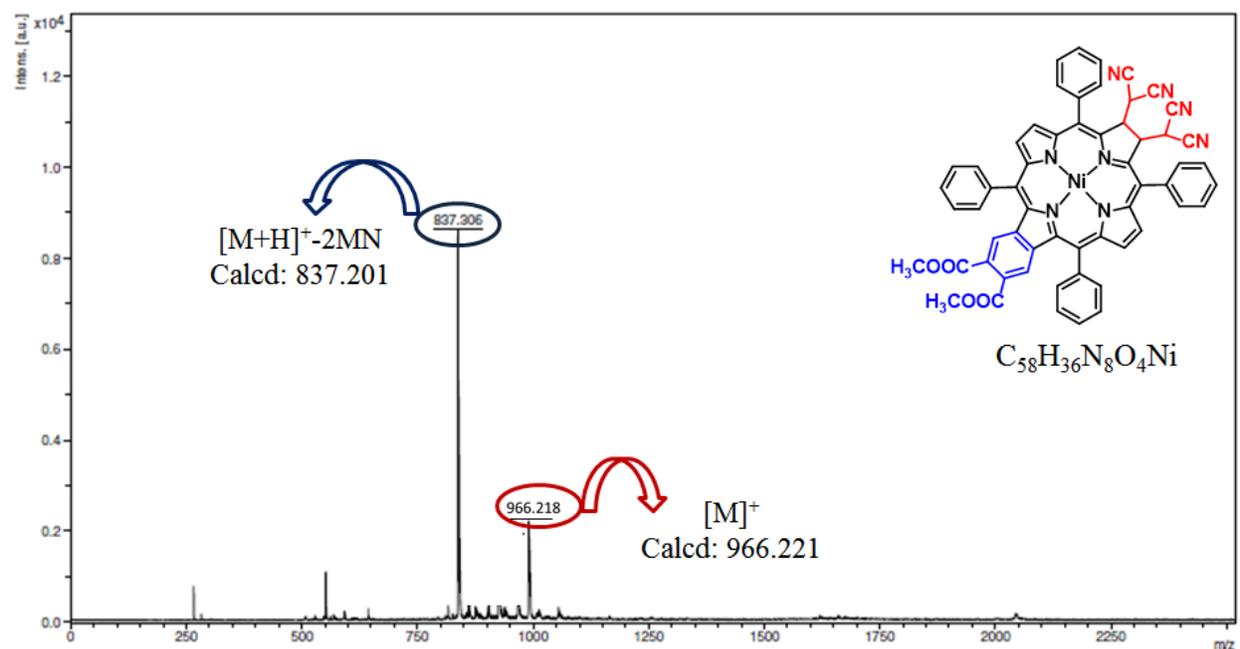


Figure S10. MALDI-TOF-MS spectrum of NiMBC(MN)₂ in CH₂Cl₂ at 298 K.

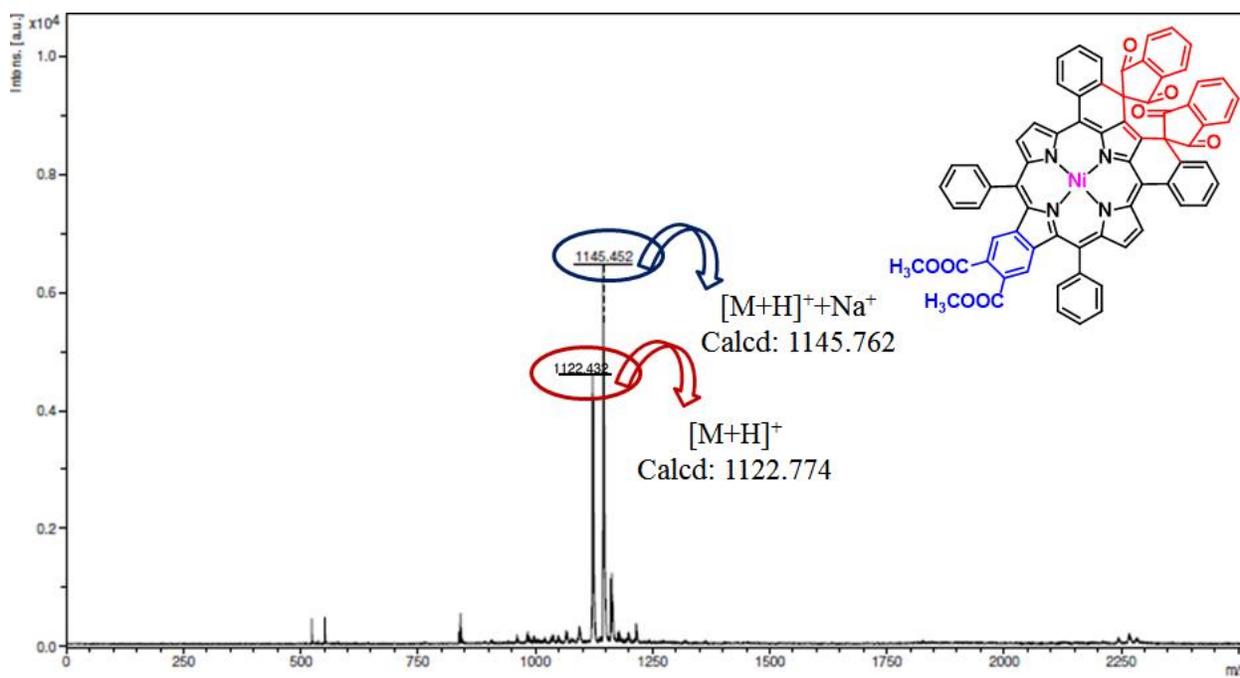


Figure S11. MALDI-TOF-MS spectrum of NiMBP(IND)₂ in CH₂Cl₂ at 298 K.

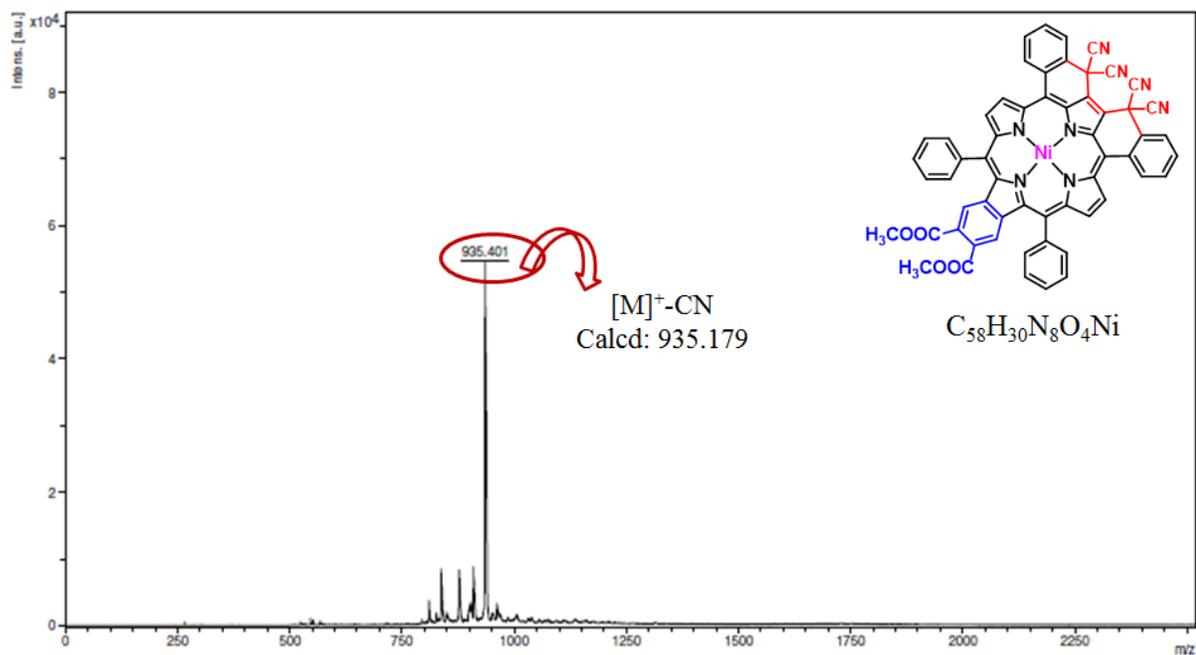


Figure S12. MALDI-TOF-MS spectrum of NiMBP(MN)₂ in CH₂Cl₂ at 298 K.

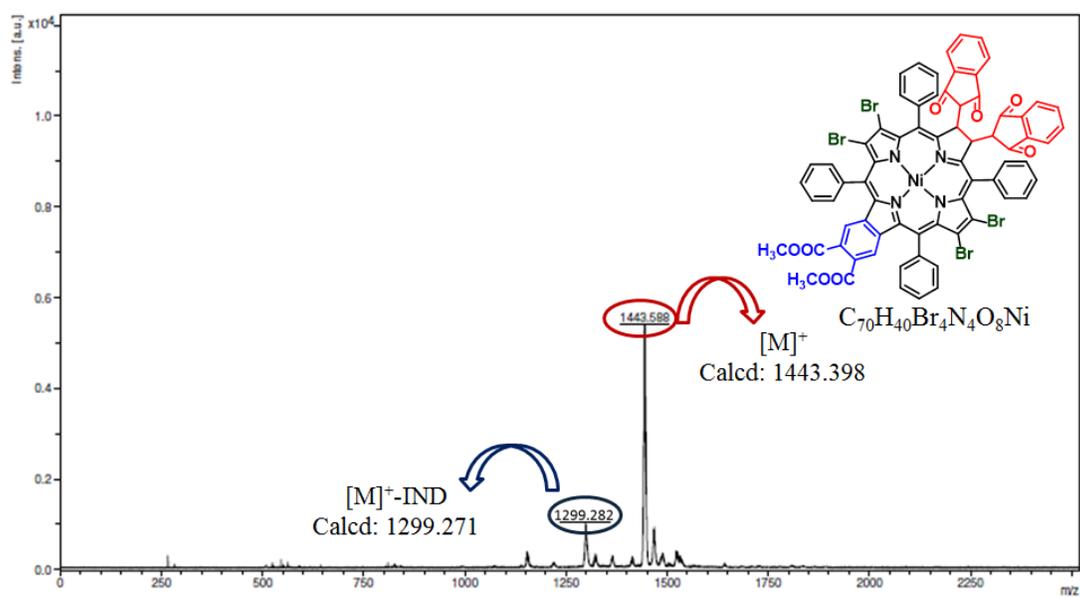


Figure S13. MALDI-TOF-MS spectrum of NiMBC(IND)₂Br₄ in CH₂Cl₂ at 298 K.

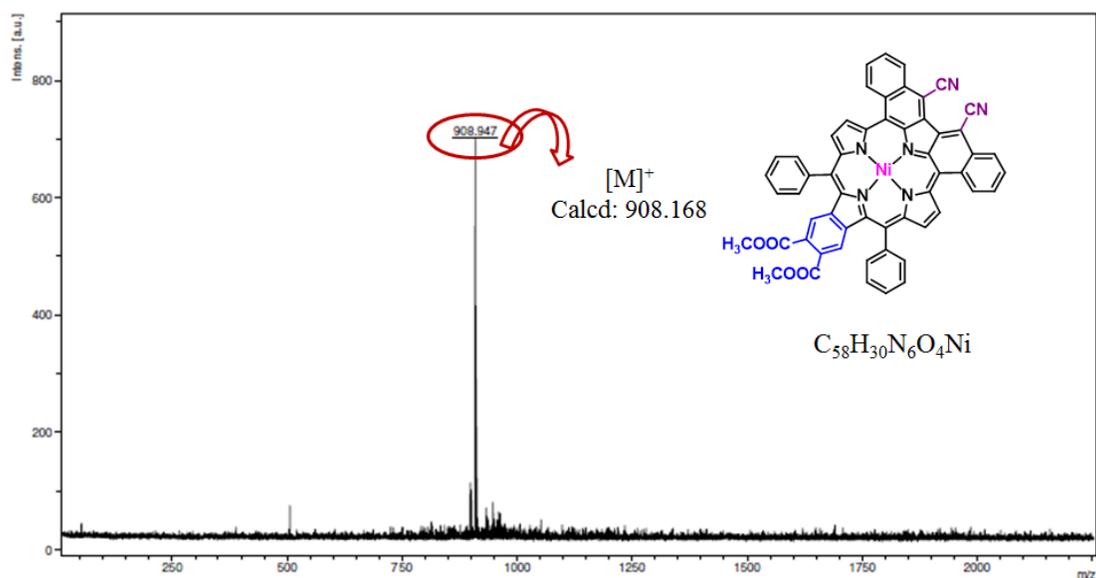
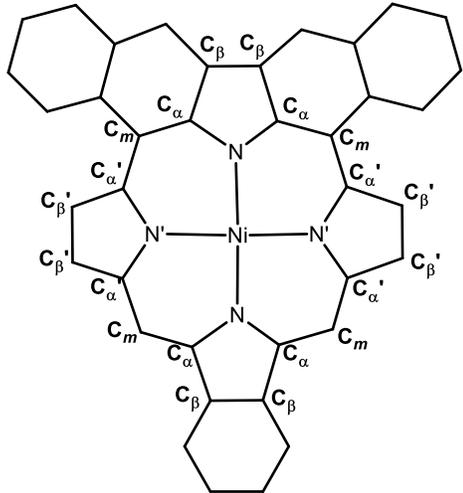
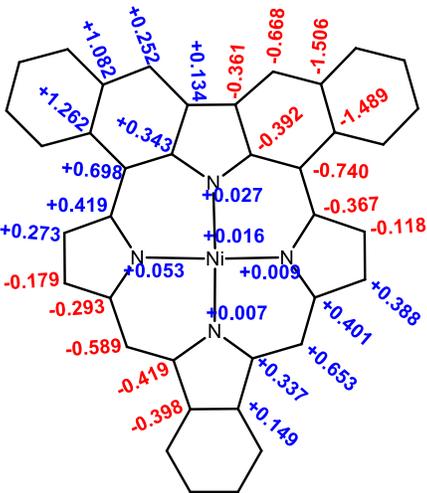


Figure S14. MALDI-TOF-MS spectrum of NiMBP(VCN)₂ in CH₂Cl₂ at 298 K.

Table S1. Crystallographic and structure refinement data for NiMBP(IND)₂.

Formula	C ₇₀ H ₃₈ N ₄ NiO ₈ .CHCl ₃
Formula weight	1241.12
crystal system	Monoclinic
space group	P2 ₁ /c
a (Å)	20.865(2)
b (Å)	18.0617(19)
c (Å)	14.9964(15)
α, degrees	90
β, degrees	95.788(4)
γ, degrees	90
Volume (Å ³)	5622.8(10)
D _{calc} , mg/m ³	1.466
Z	4
crystal size, mm	0.02×0.02×0.02
λ (Mo Kα) Å	0.71073
temperature, K	296 (2)
data collection range, θ, deg.	3.303 to 25.558
total reflections collected	13968
independent reflections	8745
quality-of-fit indicator	1.004
final R indices [I > 2σ(I)]	R1 = 0.0634, wR2 = 0.1785
R indices (all data)	R1 = 0.1125, wR2 = 0.2121
CCDC No.	2101149

Table S2. Selected average bond lengths and bond angles of NiMBP(IND)₂ where (a) is a structure showing notation (b) is the structure showing distance of each atom from mean plane.

			
Bond Lengths (Å)		Bond Angles (°)	
M-N	1.916 (3)	N-M-N	179.3 (1)
M-N'	1.914 (3)	N'-M-N'	178.5 (1)
N-C _α	1.377 (4)	M-N-C _α	126.9 (2)
N'-C _α '	1.374 (4)	M-N'-C _α '	127.1 (2)
C _α -C _β	1.446 (5)	N-C _α -C _m	124.9 (3)
C _α '-C _β '	1.434 (5)	N'-C _α '-C _m	125.0 (3)
C _β -C _β	1.384 (5)	N-C _α -C _β	110.6 (3)
C _β '-C _β '	1.344 (5)	N'-C _α '-C _β '	109.9 (3)
C _α -C _m	1.392 (4)	C _β -C _α -C _m	124.1 (3)
C _α '-C _m	1.394 (5)	C _β '-C _α '-C _m	124.6 (3)
ΔC_{β} ^a	0.250	C _α -C _β -C _β	106.3 (3)
$\Delta 24$ ^b	0.323	C _α '-C _β '-C _β '	107.2 (3)
ΔNi	0.016	C _α -N-C _α	106.0 (3)
		C _α '-N'-C _α '	105.7 (3)
		C _α -C _m -C _α	120.8 (3)

^a ΔC_{β} refers to the mean plane deviation of β -pyrrole carbons

^b $\Delta 24$ refers to the mean plane displacement of 24-atom core

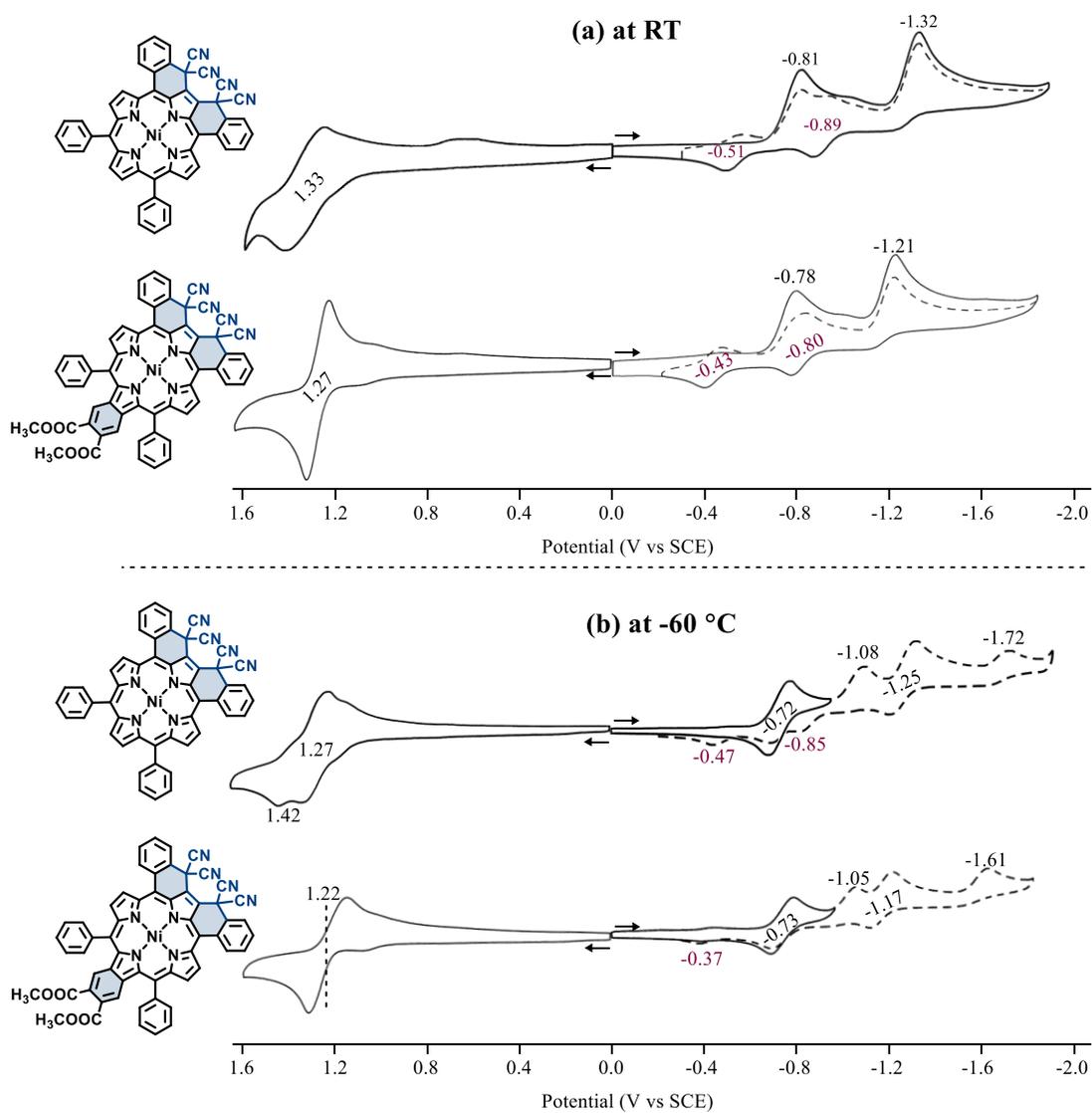


Figure S15. Cyclic voltammogram comparing the effect of β,β' -benzo fusion of NiTPP(MN)₂ and NiMBP(MN)₂ in CH₂Cl₂ containing 0.1 M TBAP at (a) room temperature and (b) low temperature (-60 °C). Scan rate = 0.1 V/s.

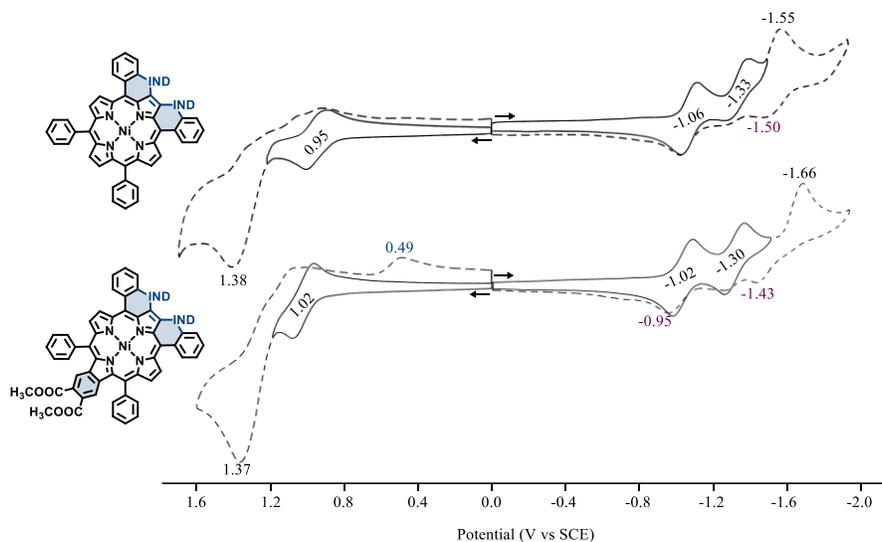


Figure S16. Cyclic voltammogram comparing the effect of β,β' -benzo fusion of NiTPP(IND)₂ and NiMBP(IND)₂ in CH₂Cl₂ containing 0.1 M TBAP. Scan rate = 0.1 V/s.

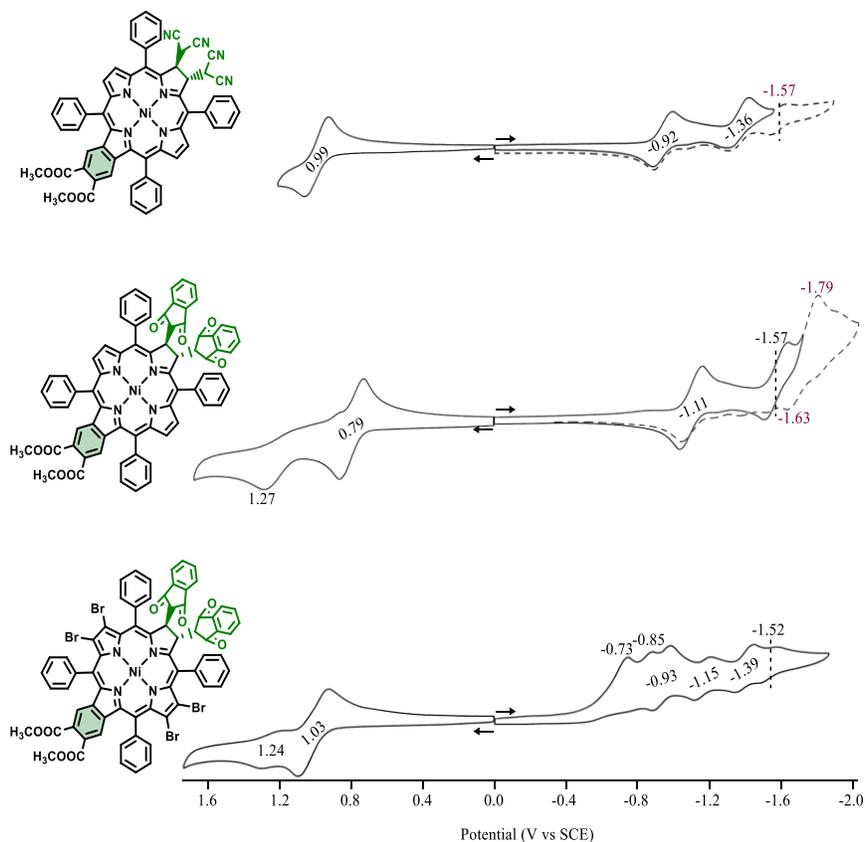


Figure S17. Cyclic voltammogram of NiMBC(MN)₂, NiMBC(IND)₂ and NiMBC(IND)₂Br₄ in CH₂Cl₂ containing 0.1 M TBAP at low temperature (-60 °C). Scan rate = 0.1 V/s.

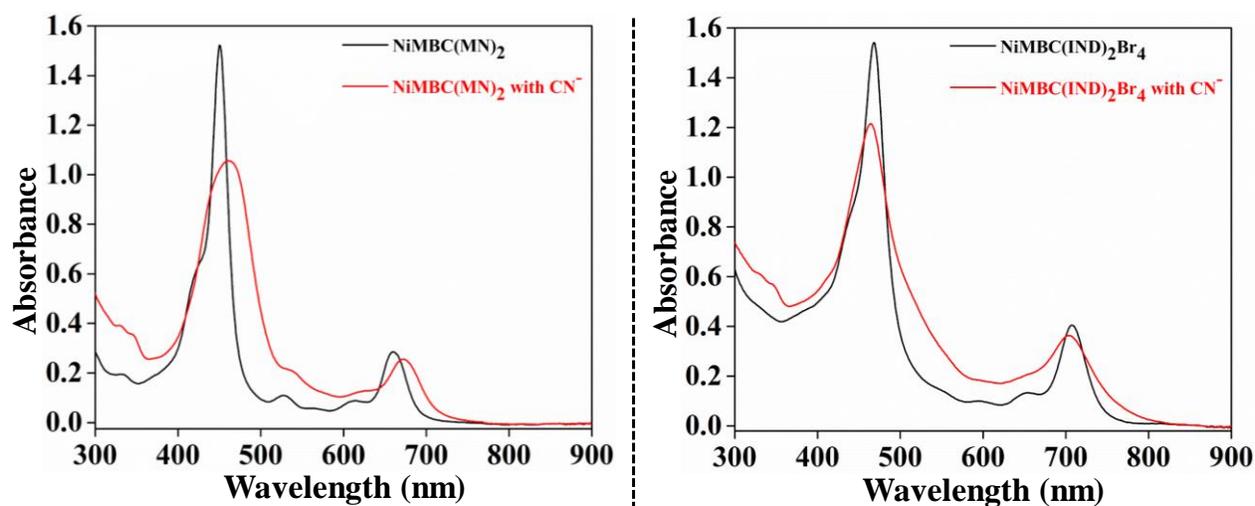


Figure S18. UV-Visible spectral changes of (a) NiMBC(MN)₂ with CN⁻ ion; (b) NiMBC(IND)₂Br₄ with cyanide ion in CH₂Cl₂ at 298 K.

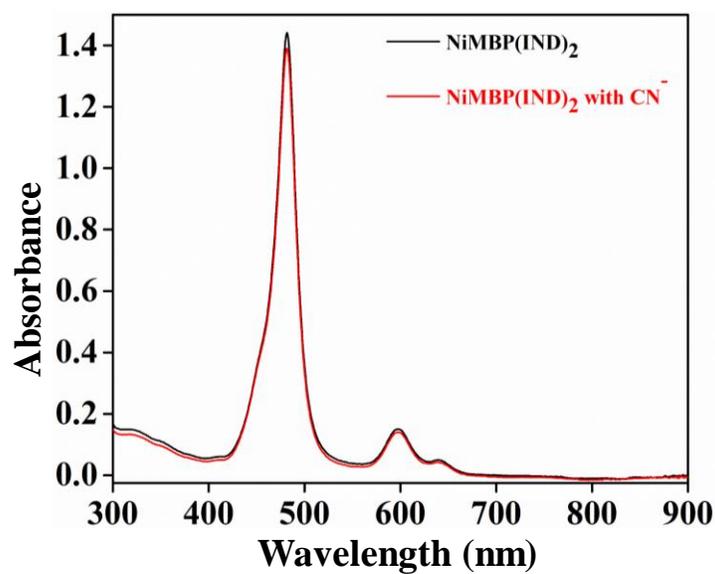


Figure S19. Comparative UV-visible spectra of NiMBP(IND)₂ with and without cyanide ions in CH₂Cl₂ at 298 K. The concentration of CN⁻ anions range from 0 to 1.12×10^{-3} M.

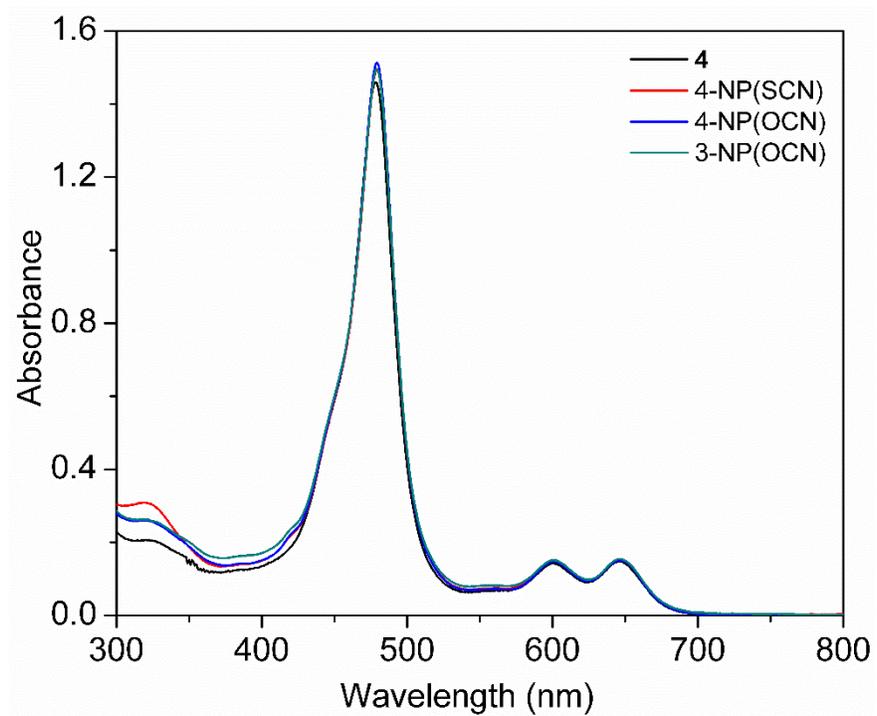


Figure S20. UV-Vis Spectral Changes of NiMBP(MN)₂ (1.08×10^{-5} M) upon Addition of 10 eq. of Tested Isocyanate and Isothiocyanate derivatives in CH₂Cl₂ 298 K.

Detection Limit

Detection limits of NiMBP(MN)₂ in CH₂Cl₂ were obtained according to the reported literature method.¹ NiMBP(MN)₂ was dissolved in CH₂Cl₂ (1.08×10^{-5} M) and the absorbance changes during the titration with CN⁻ ions (from 0 to 119 μM). Figure S21 shows a plot of the $\log(A_n - A_0)/(A_f - A_n)$ versus $\log[\text{CN}^-]$; where A_n = absorbance at after each addition of n aliquots of CN⁻ ions, A_0 = absorbance of NiMBP(MN)₂ without CN⁻ ions (reference conc.), A_f = absorbance at addition of final aliquot of CN⁻ ions. A linear regression curve was fitted to the plot and the x-intercept axis shows the lowest concentrations of [CN⁻] which can be detected for the respective compound (*i.e.* LOD in mol/L)

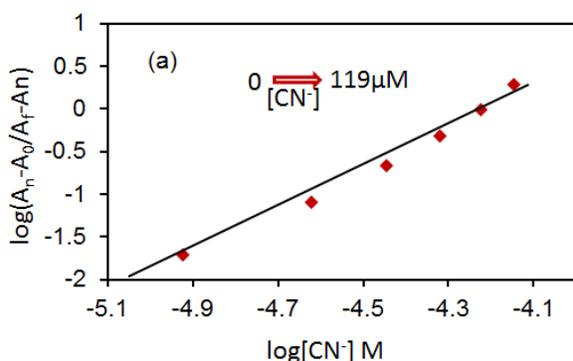


Figure S21. Plot of $\log(A_n - A_0)/(A_f - A_n)$ versus $\log[\text{CN}^-]$ to determine the limit of detection for NiMBP(MN)₂ in CH₂Cl₂.

For the plot above, the x-Intercept is $\log(-5.08)$. Antilog of this gives us the molar conc. *i.e.* 8.31×10^{-6} mol/L. Thus, multiplying this value with molecular weight of TBACN (268.5 g/mol) gives the actual limit of detection (LOD) value. Thus the LOD for non-aqueous media is 2.23 mg/L (2.23 ppm).

References.

1. Shortreed, M.; Kopelman, R.; Kuhn, M.; Hoyland, B., Fluorescent Fiber-Optic Calcium Sensor for Physiological Measurements. *Anal. Chem.* **1996**, *68*, 1414-1418.