

Supporting Information

Design and synthesis of Co^{II}HMTAA-14/16 macrocycles and their nano-composites for oxygen reduction electrocatalysis

Experimental Section

General Methods

The 3,4-diaminotoluene (3,4-DAT), 2,4-diaminotoluene (2,4-DAT), acetylacetone (AA) and the solvents like ethanol, methanol, xylene, Sod. Hydroxide and Nafion solution (0.5 % wt in alcohol) were procured from Sigma Aldrich, India. All AR grade for synthesis was utilized as such without any pretreatment.

Specification of the instruments used is as follow:

- (i) **FT-IR:** Nicolet 730 FT-IR Spectrometer with an ATR-crystal.
- (ii) **UV-Vis:** Perkin Elmer Lambda 900.
- (iii) **Mass Spectrometric measurement:** FD Mass spectra of complexes and ligand were recorded on a VG (Instruments) ZAB2-SE-FPD. For MALDI-TOF spectra a Bruker Reflex spectrometer III was used.
- (iv) **TEM:** TEM (FEI Tecnai G2 20).
- (v) **XRD:** Shimadzu XRD-6000 with Cu K α radiation (40kV, 30mA, λ = 1.5418 Å) recorded with 2 θ ranging from 5 to 90.
- (vi) **XPS:** PHI Quantera II XPS scanning microprobe.

Preparation of macrocycles and nanocomposites

The macrocycles Co^{II}-HMTAA-14 and Co^{II}-HMTAA-16 (HMTAA-14=6,13-Dihydro-Me₆-dibenzo[b,i][1,4,8,11]-tetraazacyclotetradec-4,7,11,14-tetraene and HMTAA-16=7,15-Dihydro-Me₆-dibenzo[b,j][1,5,9,13]-tetraazacyclohexadec-5,8,13,16-tetraene) were prepared by microwave-assisted method. Typically, acetylacetone (2 moles, 0.400 g), cobalt(II) chloride hexahydrate (1 mole, 0.476 g) and 2,4-/3,4-diamino toluene (2 moles, 0.488 g) were dissolved in 50-60 ml methanol and the reaction mixture was transferred in microwave autoclave under 350W, 4MPa, 70 °C, microwave reaction conditions for 10 mins. The resulting solution was concentrated in a rotary evaporator and dried in vacuum. Dark magenta and dark brown colored crystals were washed with ethanol and recrystallized in methanol, assigned as Co^{II}-HMTAA-14 and Co^{II}-HMTAA-16 respectively. The prepared macrocycles were characterized by various techniques like elemental analysis, UV-VIS, IR and mass spectrometry etc and the micro-analytical data are given in Table 1. Further, their nanocomposites Co^{II}-HMTAA-14@C and Co^{II}-HMTAA-16@C were synthesized using similar above method, the ethanolic suspension of 0.005g of each macrocycle and 0.01g carbon black (C) transferred into microwave autoclave, operated at 350W, 4MPa irradiation for 30 min at 120 °C temperature [1-2].

Table 1 Micro-analytical data for Co^{II}HMTAA-14 and Co^{II}HMTAA-16 macrocycles

Macrocycles	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)	M.P (°C)	Mol Wt.	C* (%)	H* (%)	N* (%)
Co ^{II} HMTAA-14	49	246	502	57.13 (57.38)	5.92 (5.62)	11.34 (11.15)
Co ^{II} HMTAA-16	47	235	502	57.29 (57.38)	5.13 (5.62)	11.19 (11.15)

* Theoretical values of microanalysis are given in parenthesis.

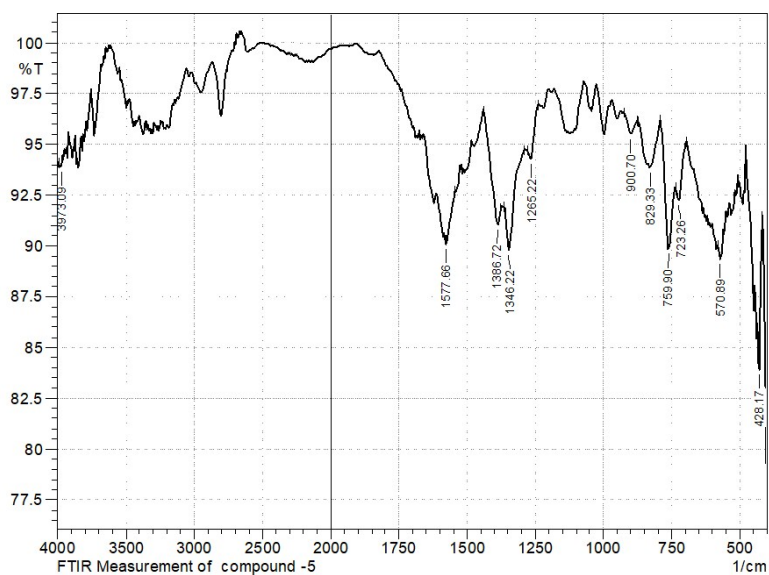


Figure S1: FTIR spectra of Co^{II}HMTAA-14 macrocyclic complex

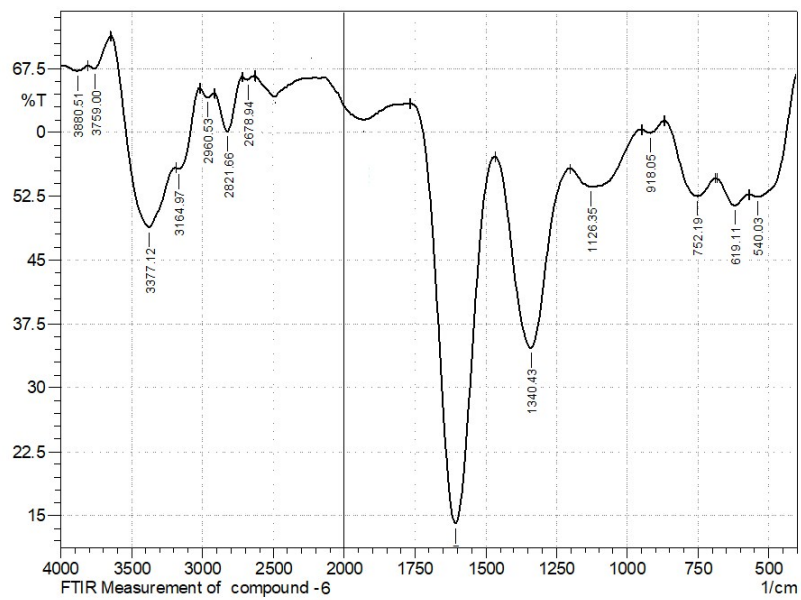


Figure S2: FTIR spectra of Co^{II}HMTAA-16 macrocyclic complex

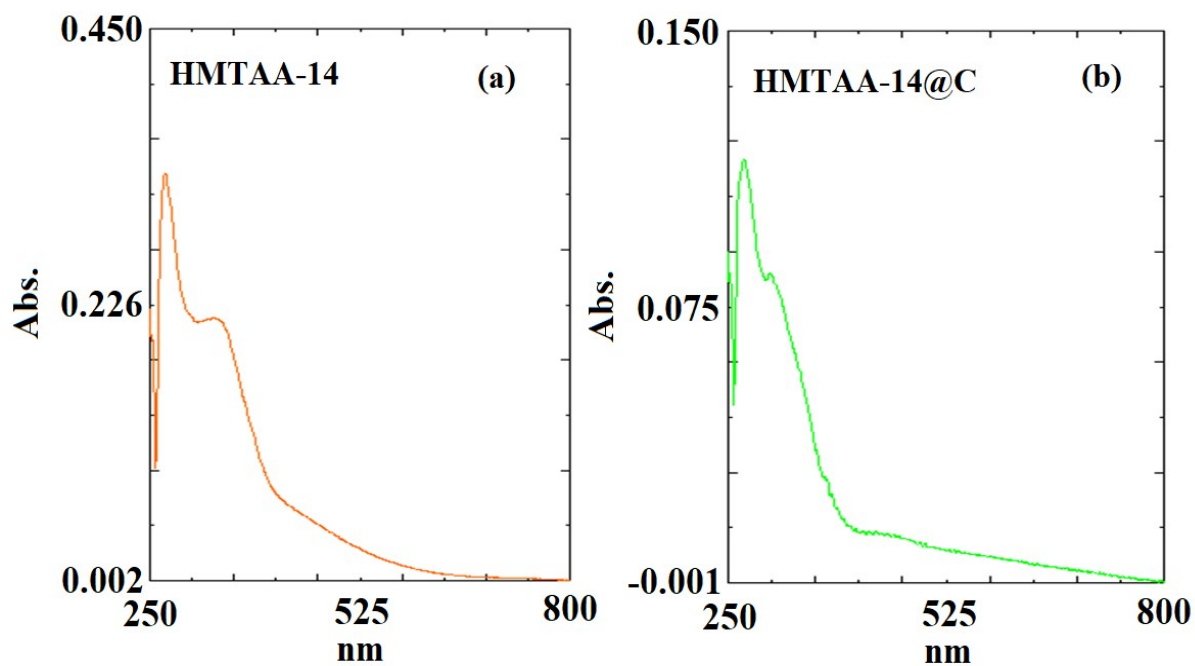


Figure S3: UV-vis spectra of (a) Co^{II}HMTAA-14 and (b) Co^{II}HMTAA-14@C macrocyclic complex

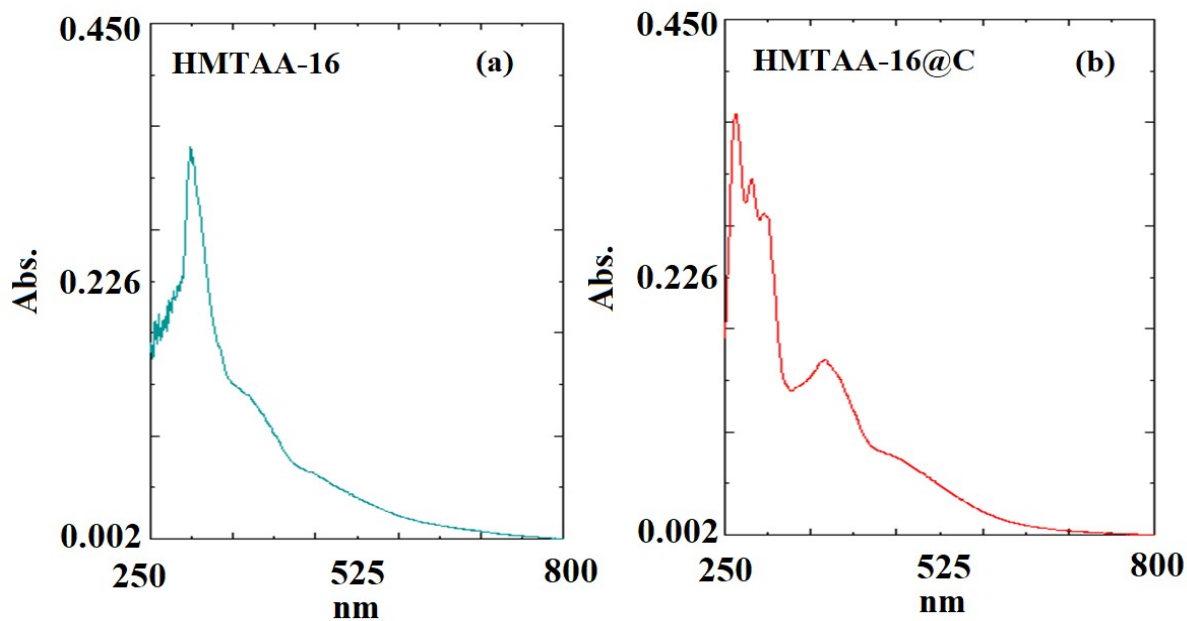


Figure S4: UV-vis spectra of (a) Co^{II}HMTAA-16 and (b) Co^{II}HMTAA-16@C macrocyclic complex

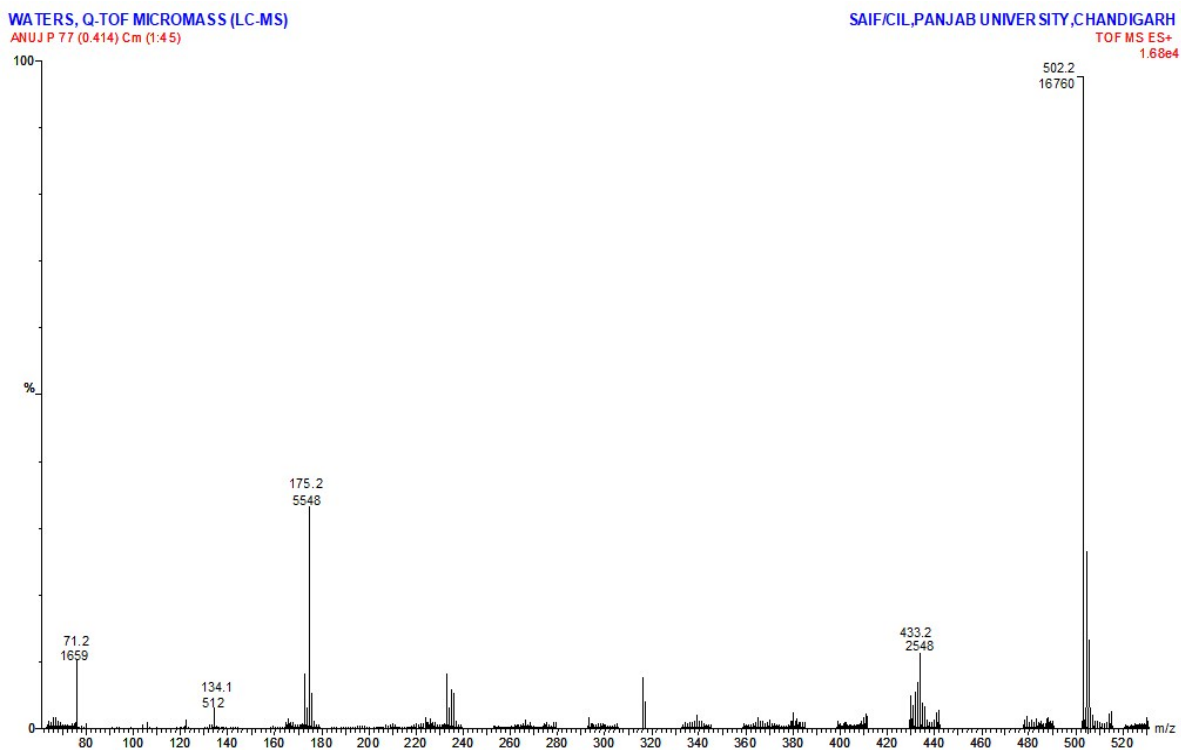


Figure S5: Mass spectra of Co^{II}HMTAA-14 macrocyclic complex

Electrochemical Measurements

RDE Voltammetric electrochemical measurements were conducted using a multi-potentiostat (Bio-Logic SP150) and a rotating RDE Pine instrument. A three-electrode cell consists of (i) glass carbon RDE as a working electrode, (ii) an Ag/AgCl, 3 M KCl electrode as a reference, and (iii) a Pt-electrode as a counter electrode was employed. All the studies were carried out in the range between 0 to -1.0 V vs. reference

electrode. ORR current-voltage curves were obtained at a scan rate of 50 mV/s at 1600 rpm. Oxygen was passed directly into the cell for about 30 min before the test.

Preparation of the electrode of RDE

The procedure of pre-treatment and modification glassy carbon electrode (5 mm in diameter) is as follows: the working electrode was cleaned mechanically with 0.5 μm diamond down to 0.05 μm alumina slurry. After getting a mirror-like an appearance on the electrode surface, the electrode was washed initially with Mill-Q water and then with acetone and dried. A mixture of 15 mg of M^{II}HMTAA-14/16@C and 10 mg carbon black (Vulcan XC-72R) was ultra-sonicated for 15 min. To this mixture added 10 μL of 0.5 wt% Nafion solution and sonicated for 15 min. Also, a suspension of 15 mg/ml Pt/C was obtained by using 20 wt% Pt-supported on carbon black. 1.8 μL Co^{II}HMTAA-14/16@C or Pt/C suspension was taken at the glassy carbon electrode. This resulted a catalyst (Co^{II}HMTAA-14/16@C or Pt/C) loading 0.25 $\mu\text{g}/\text{cm}^2$.

The measured potentials vs Ag/AgCl reference electrode was transformed to the reversible hydrogen electrode (RHE) scale using the Nernst equation³:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E^{\circ}_{\text{Ag/AgCl}}$$

Where, E_{RHE} = transformed potential vs reversible hydrogen electrode (RHE). $E_{\text{Ag/AgCl}}$ = experimental potential measured with respect to the Ag/AgCl reference electrode, and $E^{\circ}_{\text{Ag/AgCl}}$ is the standard potential of Ag/AgCl at 25 °C (0.1976 V).

References

1. K. Sakata, Y. Saitoh, K. Kawakami, N. Nakamura, T. Hori, Y. Nakano and M. Hashimoto, *Synth. React. Inorg. M.*, 2006, **26**, 1267.
2. M Shakir, K.S. Islam, A.K. Mohamed, M.Shagufta and S.S. Hasan, *Transit. Metal Chem.*, 1999, **24**, 577.
3. Baitao Li, X. Zhou, X. Wang, B. Liu and B. Li, Hybrid binuclear-cobalt-phthalocyanine as oxygen reduction reaction catalyst in single chamber microbial fuel cells. *J. Power Sources*, 2014, **272**, 320.