 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

 **M.Sc.** DEGREE EXAMINATION - **CHEMISTRY**

FOURTH SEMESTER – APRIL 2011

# CH 4956 - ADVANCED COORDINATION CHEMISTRY

 Date : 09-04-2011 Dept. No. Max. : 100 Marks

 Time : 9:00 - 12:00

**Part-A**

***Answer all questions. Each question carries two marks***

1. Define an A-ET-E device.

2. How does change in the angular orientation of a ligand with respect to the metal ions affect the magnitude of - and -bonding?

3. Give two examples of gadolinium-based contrast reagents for MRI.

4. Mention the prominent emission bands of europium(III) and terbium(III).

5. What are the different kinds of metallodendrimers.

6. How is the kinetic lability of alkali- and alkaline earth metal complexes of macrocycles exploited in the synthesis of the corresponding transition metal complexes?

7. How do you convert complex of a ring contracted macrocycle into that of the ring expanded one?

8. Mention the causes of electrochemical irreversibility in the case of transition metal complexes.

9. Define quantum down-conversion.

10. Complexes of *d10* metal ions are often spectroscopically silent. Comment

**Part-B**

***Answer eight questions. Each question carries five marks***

11. Illustrate a pH controlled molecular shuttle.

12. Construct a molecular break.

13. Explain the method of synthesizing dendrimers with examples.

14. Explain the synthesis of compartmental macrocyclic complexes by coordination template method with examples.

15. Explain acid/base driven threading and dethreading motions in supramolecular assemblies.

16. -Back bonding by ligands increases the magnitudes of 10*Dq* values. Explain with a qualitative MO energy level diagram.

17. What is cation-cavity “best fit”? Illustrate with examples.

18. Explain the electronic spectral features of low-spin transition metal ions in *Oh*and *Td* geometries.

19. Give a brief account of the photochemistry of lanthanides.

20. Explain the template synthesis of 2- and 3-catenanes.

21. Explain the principles of spectroelectrochemistry. Highlight the limitations of this technique.

22. Construct the Orgel diagram for high-spin *d*3 and *d*7 metal ions in *Oh* geometry. Explain the features of their Tanabe-Sugano diagrams.

**Part-C**

***Answer four questions. Each question carries ten marks***

23a. Explain the EPR spectrum of bis(salicylaldimine)copper(II) and justify your interpretation with experimental evidences. (7)

 b. What is zero field splitting? Mention its causes for transition metal complexes. (3)

24. Explain the different synthetic strategies employed for symmetric and unsymmetric compartmental macrocyclic ligands and their complexes.

25a. Explain the principle of angular overlap model. (3)

 b. With the help of angular overlap model show that *t* o 

26a. Explain the principle and methodology of cyclic voltammetry.

 b. The cyclic voltammogram of a dinuclear Cu(II)/Ni(II) complex consists of two cathodic waves at *E*pc = -0.56 and -0.34 V and two anodic waves at *E*pa = -0.5 and -0.25 V at the scan rate of 100 mV s-1 with *i*pc values of 25 and 19 **A, and *i*pa values of 23 and 19 **A. Compute the electrochemical parameters and explain the electrochemical behavior of the system.

27a. Explain the principle and methodology of constructing a dye sensitized solar cell. (6)

 b. Give an account of Ru(II) polypyridyl complexes used in the construction of solar cells. (4)

28a. Mention the different kinds of rotaxanes. (3)

 b. Explain the construction of such assemblies by various synthetic methods. (7)

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