 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – APRIL 2012

# CH 4956 - ADVANCED COORDINATION CHEMISTRY

Date : 20-04-2012 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

**Part-A**

*Answer* ***all*** *questions. Each question carries* ***2*** *marks*

1. What is dendritic catalysis? Cite two reactions catalyzed by a dendritic catalyst.

2. Define relaxivity. Cite two FDA approved contrat agents for MRI.

3. How do you compute the field strength of low-spin octahedral complex of cobalt(III)?

4. Mention the different kinds of supramolecular interactions.

5. What is supramolecularself assembly? Cite an example.

6. How do you evaluate diffusion controlled process by cyclic voltammetry?

7. Octahedral complexes of high-spin*d*5 metal ions are feebly colored whereas octahedral complexes of low-spin *d*5 metal ions are intensely colored. Rationalize.

8. Encapsulated lanthanide complexes emit with high intensity. Comment.

9. Illustrate transmetalation reaction with an example.

10. What is quantum up-conversion?

**Part-B**

*Answer* ***eight*** *questions: Each question carries* ***5*** *marks*

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

12. Explain the method of constructing rotaxanes and pseudorotaxanes with examples.

13. What are catenanes? Explain the methods of synthesizing catenanes.

14. Illustrate a supramolecular assembly functioning like a molecular gear.

15. Explain the construction of two photochemical supramolecular assemblies.

16. Illustrate the importance of cation-cavity best fit in the synthesis of Schiff base macrocycles.

17. Explain the electronic spectral features of tetragonally distorted low-spin octahedral cobalt(III) complexes.

18. Explain the working principle of dye-sensitized photovoltaic cells.

19. Explain the biological roles and structural features of rubredoxins and ferredoxins.

20. Give an account of the photochemistry of lanthanide macrocyclic complexes. How do the photochemistry of lanthanides differ from that of ruthenium(II)?

21. Write a note on spectroelectrochemistry.

22. Write a note on the applications of dendrimers and metallodendrimers.

**Part-C**

*Answer* ***four*** *questions. Each question carries* ***10*** *marks*

23. A six-coordinate low-spin cobalt(III) complex of a quadridentate ligand with two thiocyanate ions exhibits electronic transitions at 660, 525, 415, and 290 nm. Assign these transitions, predict the geometry, and compute the field strength of the axial and equatorial ligands.

24a. The epr spectrum of a high-spin manganese(II) complex doped into a diamagnetic host consists of 30 lines (five sets of six lines each). Interpret the spectrum with the appropriate energy level diagram. (7)

b. Mention the causes of zero field splitting in transition metal complexes. (3)

25a. Explain the principle of cyclic voltammetry and the method of evaluating the reversibility of a redox couple. Mention the causes of electrochemical irreversibility of a redox couple.

b. The cyclic voltammogram of a pseudooctahedral cobalt(III) complex consists of two reduction waves at -0.34 and -1.22 V and two oxidation waves at -1.16 and -0.29 V versus Ag/Ag+. Explain the electrochemical behavior of this complex.

26a. Differentiate thermodynamic and kinetic coordination template effects. (3)

b. Explain the template synthesis of macrocyclic and compartmental macrocyclic ligands and their mono- and dinuclear complexes by coordination template effect. (7)

27. What are molecular shuttles? Explain their synthesis by chemical, electrochemical, and photochemical methods.

28a. Explain the mechanism of water proton relaxation by gadolinium(III)-based contrast enhancing agents for MRI.

b. Explain the synthetic strategies employed for the polyazacarboxylate ligands used for the development of contrast agents for MRI and diagnostic radiopharmaceuticals.

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