

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – MAY 2017, for Internal Students of the
Imperial College of Science, Technology and Medicine**

**This paper is also taken for the relevant examination for the
Associateship**

CHEM60001 ADVANCED CHEMISTRY

Paper 3

Tuesday 02nd May 2017, 14:00-15:30

**PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT
THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING
OF ANY PRIOR CORE COURSE.**

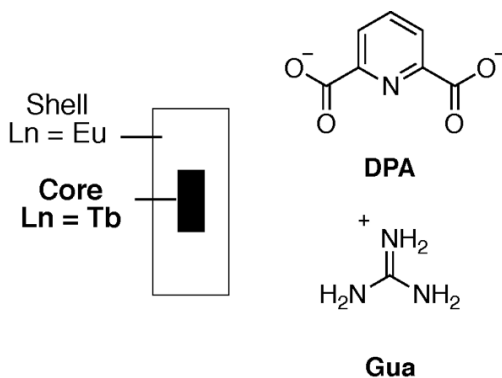
**USE A SEPARATE ANSWER BOOK FOR EACH
QUESTION. WRITE YOUR CANDIDATE NUMBER ON
EACH ANSWER BOOK.**

Q1, Lanthanides and Actinides

Answer part a) and **EITHER** part b) or part c) of this question.

a) Answer **ALL** parts of this question.

Recently two-colour luminescent crystals of the form $[\text{Gua}]_3[\text{Ln}(\text{DPA})_3]$ containing a core ($\text{Ln} = \text{Tb}$) and shell ($\text{Ln} = \text{Eu}$) have been reported.



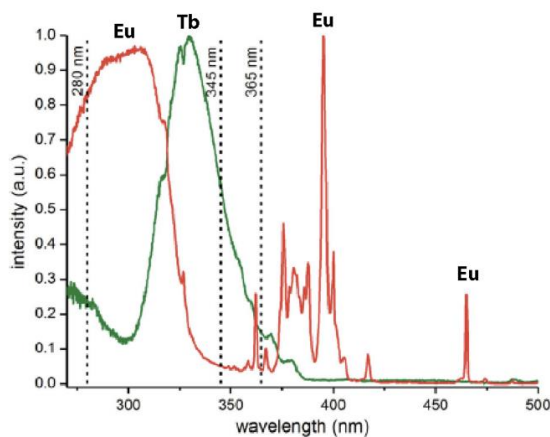
- Predict the coordination number and geometry of the lanthanide ion in $[\text{Gua}]_3[\text{Ln}(\text{DPA})_3]$.
(1 mark)
- Rationalise why core-shell crystals can be grown by taking a seed crystal of $[\text{Gua}]_3[\text{Tb}(\text{DPA})_3]$ and placing it in a solution of $[\text{Gua}]_3[\text{Eu}(\text{DPA})_3]$.
(3 marks)

Upon excitation of the organic ligand, characteristic green and red emissions of Tb^{3+} and Eu^{3+} are predicted due to emission from $^5\text{D}_4$ and $^5\text{D}_0$ states respectively.

- Determine the term symbols for the ground states of both Tb^{3+} and Eu^{3+} .
(4 marks)
- Draw a labelled diagram to explain the mechanism for Eu^{3+} luminescence.
(4 marks)

QUESTION CONTINUED OVERLEAF

Experimentally it was found that changing the wavelength of excitation ($\lambda_{\text{ex}} = 280 \text{ nm}$, 345 nm , or 365 nm) resulted in a change in the emission characteristics.

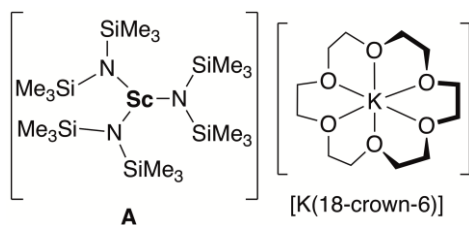


v) Explain why the fluorescence spectrum above contains sharp lines. (3 marks)

vi) Use this spectrum to rationalise why Eu@Tb core-shell crystals can be described as three-state luminescent materials. (3 marks)

b) Answer **ALL** parts of this question.

In 2017, **[A]**[K(18-crown-6)] the first complex containing Sc^{2+} was isolated.



i) Suggest the reagents and conditions to achieve the reduction of Sc^{3+} to Sc^{2+} . (2 marks)

ii) Determine the electronic configuration of Sc^{2+} and use it to suggest the nature of the HOMO in **A**. (1 mark)

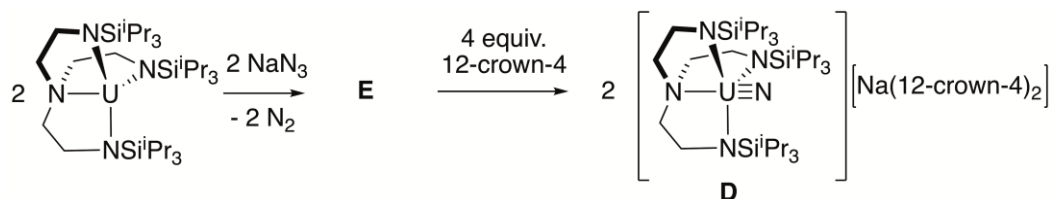
QUESTION CONTINUED OVERLEAF

- iii) $[\mathbf{A}][\text{K}(18\text{-crown-6})]$ reacts with CO_2 to form $[\mathbf{B}][\text{K}(18\text{-crown-6})]$ ($\nu_{\text{co}} = 2228 \text{ cm}^{-1}$) and $[\mathbf{C}][\text{K}_2(18\text{-crown-6})_3]$ ($\nu_{\text{co}} = 1671 \text{ cm}^{-1}$). Determine the structures of \mathbf{B} and \mathbf{C} .

(4 marks)

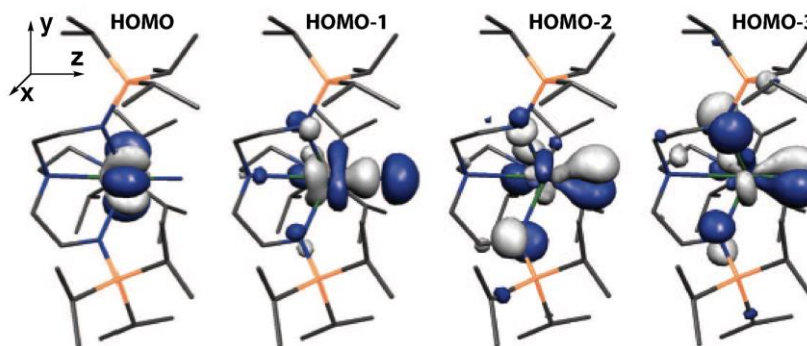
c) Answer **ALL** parts of this question.

In 2012, $[\mathbf{D}][\text{Na}(12\text{-crown-4})_2]$ the first uranium nitride was reported.



- i) Suggest a structure for the intermediate \mathbf{E} and assign oxidation states to all three uranium complexes.

(3 marks)



- ii) The calculated frontier molecular orbitals of the anion $[\mathbf{D}]$ are given above and account for the $\text{U} \equiv \text{N}$ bonding. Provide a qualitative description of the symmetry of these orbitals and use them to rationalise the bond order.

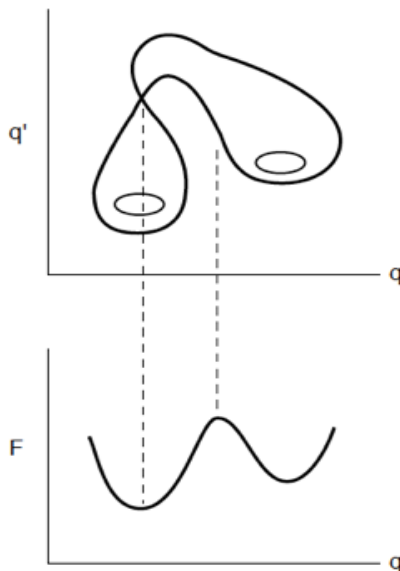
(4 marks)

Q2, Molecular Reaction Dynamics

Answer any **TWO** of the three parts a), b) and c) of this question.

a) Answer **ALL** parts of this question.

The figure below shows the potential energy surface $V(q,q')$ (upper graph) and the corresponding free energy graph, $F(q)$ (lower graph). Use the figure to answer parts (i-iii).



- i) Give an expression for $F(q)$ in terms of $V(q, q')$.
(2 marks)
- ii) Explain whether q is a good order parameter. Use the minima and/or maxima of the graphs to justify your answer.
(3 marks)
- iii) Explain whether q is a good reaction coordinate. Use the minima and/or maxima of the graphs to justify your answer.
(4 marks)
- iv) A diatomic molecule exhibits vibrational motion at wavenumber 2000 cm^{-1} . Estimate the duration of an optical pulse that would be required to create a vibrational wavepacket.
(3.5 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts of this question.

i) State and explain two assumptions behind Transition State Theory. (2 marks)

ii) Explain how the true rate of a barrier crossing process is different to the rate obtained by Transition State Theory. (2 marks)

iii) The rate of electron transfer in a donor-acceptor molecular wire is measured to be $6.17 \times 10^5 \text{ s}^{-1}$. The edge-to-edge distance between them is 1.13 nm. Assuming activationless electron transfer, estimate the electron tunnelling coefficient of the wire environment. Define each symbol used and explain any approximations you have made. (6.5 marks)

iv) Explain the difference between the time dependent behaviour of a vibrational eigenstate and a vibrational wavepacket. (2 marks)

c) Answer **ALL** parts of this question

i) State the time-dependent Schrodinger equation in one dimension. Define all terms and symbols used. (1.5 marks)

ii) Compute the expectation value of the position operator, $\langle x \rangle$, for the superposition of 2 states given by eigenstates $\phi_1(x)$ and $\phi_2(x)$

$$\Psi_{(x,t)} = \frac{1}{\sqrt{2}} \left[e^{-\frac{iE_1 t}{\hbar}} \phi_{1(x)} + e^{-\frac{iE_2 t}{\hbar}} \phi_{2(x)} \right]$$

(11 marks)