

IMPERIAL COLLEGE LONDON

**BSc and MSci DEGREES – MAY 2014, for Internal Students of the
Imperial College of Science, Technology and Medicine**

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

ADVANCED CHEMISTRY THEORY IIIB

Paper 1

Thursday 08th May 2014, 09:30-11:45

**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.**

3.I5 – Bioinorganic Chemistry

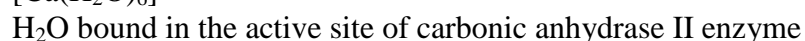
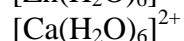
Answer part a) and **EITHER** part b) **OR** c) of this question.

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

- i) Briefly describe and illustrate the coordination sphere of the iron centre in the haem ring of the deoxy form of haemoglobin and myoglobin. State the oxidation state of the iron in this deoxy form, and state its d-electron configuration. (4 marks)
- ii) Describe how dioxygen can bind to the iron centre in Myoglobin. Include in your answer a full description of what the orbitals are used on both the dioxygen and iron centre and discuss any changes in the d-electron configuration of the iron upon O₂ binding. (5 marks)
- iii) Which, if any, of the following small molecules would also bind in the active site of deoxymyoglobin: carbon monoxide, carbon dioxide, water? Explain your reasoning and comment on the strength and reversibility of any binding. (4 marks)

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

- i) Arrange the four compounds/complexes listed below in increasing order of pK_a. Explain your reasoning.



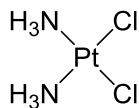
(4 marks)

- ii) Draw the full catalytic cycle for the hydration of CO₂ by the zinc containing carbonic anhydrase II enzyme. (5 marks)
- iii) In zinc enzymes 'spectroscopically silent' Zn(II) can often be replaced by Co(II) with high retention of activity. Explain the principles by which this substitution can be exploited to obtain structural and mechanistic information. (3 marks)

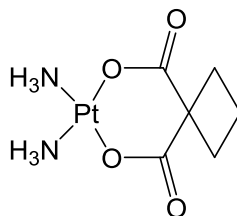
QUESTION CONTINUED OVERLEAF

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

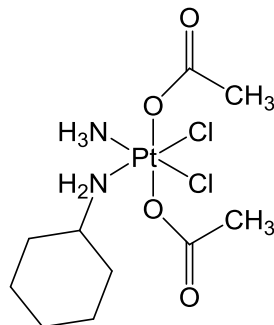
- i) Discuss the relative advantages and disadvantages of the Pt containing pharmaceuticals *cis*-platin (**A**), carboplatin (**B**) and satraplatin(JM216) (**C**) for the treatment of tumours in cancer therapy.



A



B



C

(6 marks)

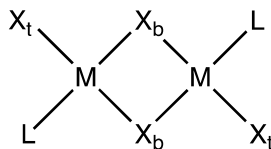
- ii) Suggest a synthetic route for the preparation of high purity satraplatin from *cis*-platin.

(6 marks)

3.I6 – Symmetry and Spectroscopy

Answer **BOTH** parts of this question.

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



- i) Determine Γ_{vib} for the C_{2h} point group *trans*-planar halogen bridging compound $M_2X_4L_2$. Show your working. (7 marks)

- ii) The *cis*-planar isomer of $M_2X_4L_2$ has C_{2v} point group symmetry and Γ_{vib} is given below.

$$\Gamma_{\text{vib}} = 7A_1(\text{pol, IR}) + 6B_1(\text{depol, IR}) + 2A_2(\text{depol, IR}) + 3B_u(\text{depol, IR})$$

Compare and contrast the expected IR and Raman spectra for the *cis* and *trans* isomers.

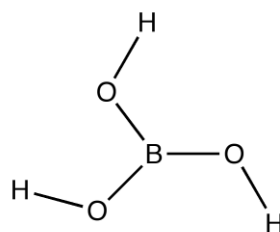
How could the experimental spectra be used to distinguish the isomers? (4 marks)

b) Answer any **TWO** parts of i), ii) or iii) of this question.

- i) Show, using a representation table, how the direct product $E \otimes E$ is determined for the D_{2d} point group. Using an expression for the transition dipole moment determine if the B_1 vibrational modes of D_{2d} point group are IR active. Show your working. (7 marks)

- ii) Identify the components **A** and **B** for the C_{3h} point group multiplication table shown below. Explain how this group multiplication table illustrates the fundamental axioms that define groups, provide specific examples using this table.

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5
E	E	C_3	C_3^2	σ_h	S_3	S_3^5
C_3	C_3	C_3^2	E	S_3	S_3^5	σ_h
C_3^2	C_3^2	E	C_3	S_3^5	A	C_3
σ_h	σ_h	S_3	S_3^5	E	C_3	B
S_3	S_3	S_3^5	A	C_3	C_3^2	E
S_3^5	S_3^5	σ_h	C_3	B	E	C_3



Boric Acid has C_{3h} symmetry

(7 marks)

QUESTION CONTINUED OVERLEAF

- iii) The probability (ρ) of finding a molecule in a higher vibrational state is given below, show how perturbation theory is used to derive an expression for the coefficients a_k .

$$r = \int \psi dt = \sum_k \hat{a}_k a_k^2$$

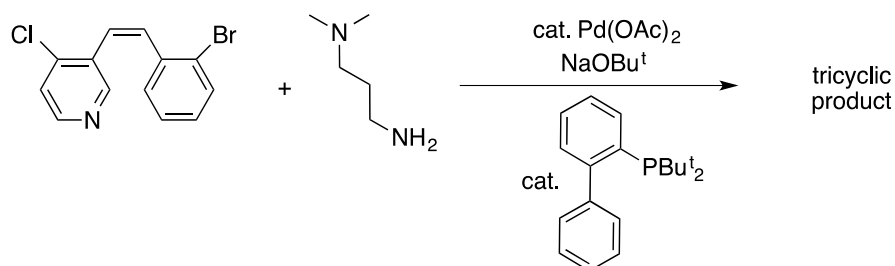
$$\text{where } \psi^{(1)} = \sum_n \hat{a}_n a_n \psi_n^{(0)} = a_0 \psi_0^{(0)} + \sum_{k, k \neq 0} \hat{a}_k a_k^2 \psi_k^{(0)}$$

(7 marks)

3.O1 – Organometallic Complexes in Organic Synthesis

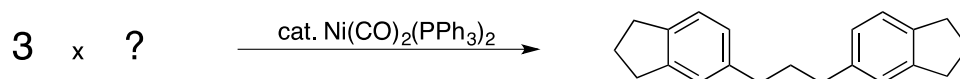
Answer any **FIVE** of the six parts a)-f) of this question.

a) Write down the structure of the product of the following reaction.



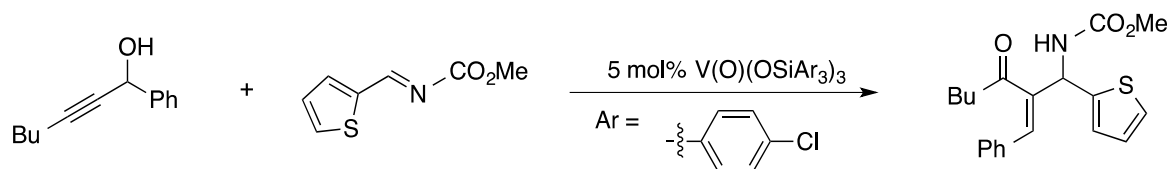
(5 marks)

b) Write down the structure of the starting material used in the reaction depicted below.



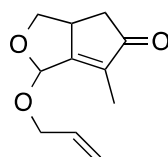
(5 marks)

c) Draw a catalytic cycle to explain the following transformation.



(5 marks)

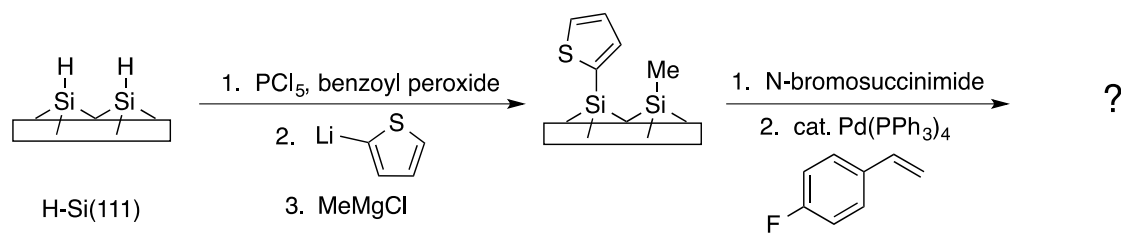
d) The molecule shown below was synthesised in one step from a symmetrical precursor. Write down the structure of the precursor, and suggest how it might be transformed into the compound shown below.



(5 marks)

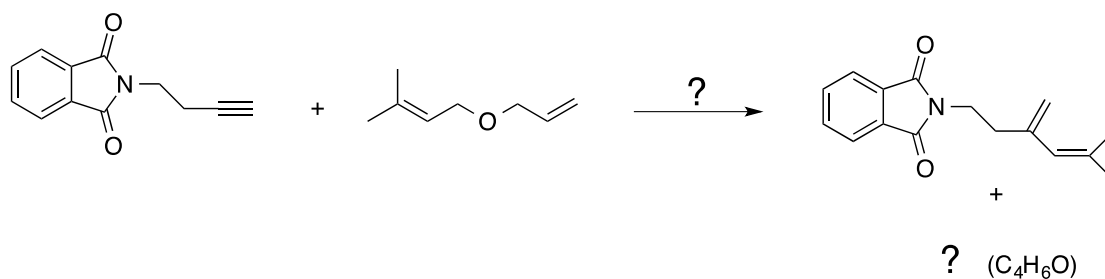
QUESTION CONTINUED OVERLEAF

- e) Write down the structure of the product obtained at the end of the reaction sequence depicted below.



(5 marks)

- f) Suggest a catalyst for the following transformation and write down the structure of the byproduct with formula $\text{C}_4\text{H}_6\text{O}$.



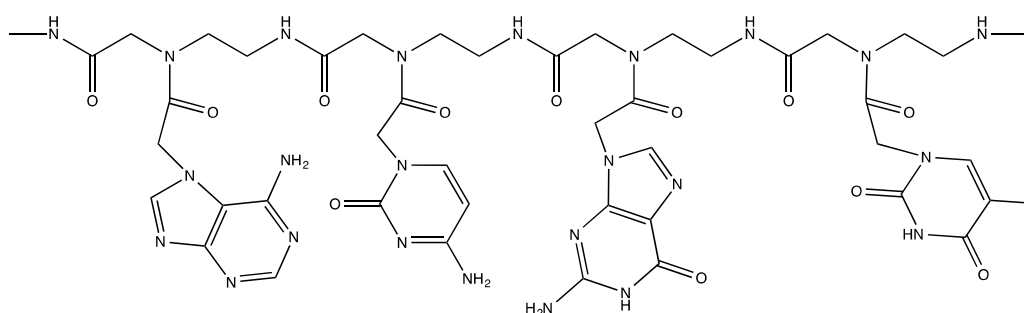
(5 marks)

3.O2 – Biological Chemistry

Answer **EITHER** part a) **OR** part b) of this question.

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

Some years ago the class of compounds known as peptide nucleic acid (PNA) was synthesized with the general structure:



A 14 base PNA was synthesized with a sequence complementary to the following DNA sequence: 3' ACGGTTAGACCTAG 5'

i) Write out the base sequence of the PNA.

(1 mark)

ii) A PNA molecule and a DNA oligonucleotide, with the same sequence at the same concentration, were hybridized to a DNA molecule with a complementary sequence and the melting curves of the duplexes measured by following the change in the absorbance at 254nm the following results were obtained:

Change in absorbance in both cases: -0.17

T_m (PNA) 68⁰C T_m (DNA) 62⁰C

Why does the absorbance at 254nm decrease when the duplexes melt?

(3 marks)

iii) Account for the higher melting temperature of the PNA.DNA duplex.

(7 marks)

iv) Predict the effect of increasing the ionic strength on the melting temperature of the PNA.DNA duplex.

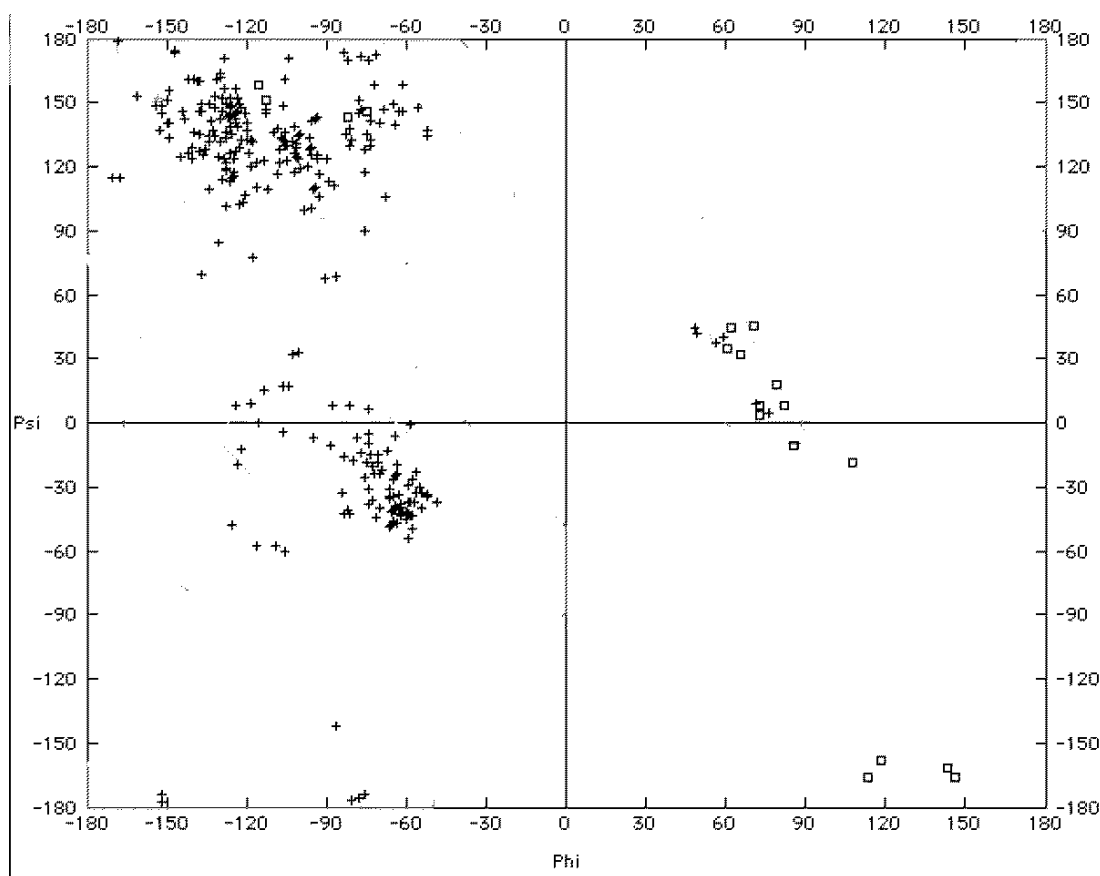
(7 marks)

v) A protein that binds in a sequence specific manner to the DNA.DNA duplex is investigated with the PNA.DNA duplex. It is found that whilst the sequence specificity of the protein binding is unaffected, the affinity of the protein for the PNA.DNA duplex is much reduced. Account for this observation based on what is known about protein-DNA interactions.

(7 marks)

QUESTION CONTINUED OVERLEAF

- b) A newly discovered lectin that binds specifically to the polysaccharide chitin has had its 3-dimensional structure elucidated and the Ramachandran plot for the protein is shown below:



It is found that the protein also binds a short disaccharide ligand derived from chitin.

Referring to the Ramachandran plot

- Draw the structure of an amino acid residue in a protein to illustrate the nature of the phi and psi angles. (3 marks)
- What is the major element of secondary structure in this protein? (3 marks)
- The binding of a chitin derived ligand was measured by isothermal titration calorimetry (ITC) and the following values derived from the thermograms:

Standard enthalpy of binding: $+7.5 \text{ kJ mol}^{-1}$ and equilibrium binding constant $2 \times 10^5 \text{ M}^{-1}$ (at 25°C)

Use these data to calculate the standard entropy of binding of the ligand to the protein.

(3 marks)

QUESTION CONTINUED OVERLEAF

iv) Assuming the rate of association is diffusion limited (i.e. $k_{on} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) calculate the dissociation rate
(2 marks)

v) Inspection of the 3-D structure of the protein-ligand complex revealed a binding pocket lined on one side by 2 tryptophan, 1 phenylalanine and 1 isoleucine residue and on the other by 2 aspartate residues. Using this information along with the results of the calculation in part (iii) above comment on the molecular driving forces that determine the protein-ligand affinity
(7 marks)

vi) To further probe the interaction of the protein with its ligands, 2 separate mutations were made in the binding pocket:

Mutation (a): One of the tryptophan residues was replaced by an alanine residue

Mutation (b): One of the aspartate residues was replaced by a glutamine residue.

In both cases the affinity was reduced 100-fold but for mutation (a) the enthalpy of binding remained approximately the same whilst for mutation (b) the enthalpy of binding became negative. Assuming that the protein is not significantly destabilized by the mutations interpret the above changes in the context of the forces that determine the protein-ligand interactions.

(7 marks)

3.P1 – Modern Analytical Instrumental Techniques

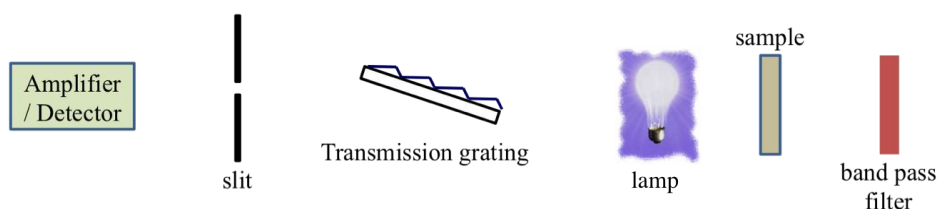
Answer part a) and **EITHER** part b) **OR** part c) of this question.

Useful equations that might be needed to answer questions a), b), and c)

$n\lambda = d(\sin\alpha + \sin\beta)$	$t_f = \frac{1}{k_r + k_{nr}}$	$\tau_q = \frac{1}{k_r + k_q[Q] + k_{nr}}$	$f_f = \frac{k_r}{k_r + k_{nr}}$
$A = -\log T = \log \frac{P_0}{P}$	$A = \frac{k_{FRET}}{k_r + k_{nr} + k_{FRET}}$	$\frac{\ddot{S}}{N\ddot{\theta}_n} = \sqrt{n} \frac{\ddot{S}_i}{N_i\ddot{\theta}}$	$A = \frac{d\beta}{d\lambda} = \frac{n}{d \cos(\beta)}$
$F = kf_f P_0 2.303 \epsilon bc$	$\frac{n_{upper}}{n_{lower}} = \exp(-\Delta E/kT)$	$S = kP + k_d$	$r = \frac{\lambda f}{n\pi R}$
$A_{total} = \log \left(\frac{P'_0 + P''_0}{P'_0 10^{-\epsilon' bc} + P''_0 10^{-\epsilon'' bc}} \right)$		$F_{total} = 2.303 k f_f bc (P'_0 \epsilon' + P''_0 \epsilon'')$	

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

i) Dr. Bloggs has been hunting through his lab and found the following components.



Using only these components, suggest how Dr. Bloggs can build a fluorescence spectrometer. In your response justify your design and the optical path. (7 marks)

ii) List 3 key limitations with the design in your answer to i).

(3 marks)

iii) Five of the following sentences are wrong. Find the statements that are in error and correct them.

- The passage of an electron from the excited state T_1 to the excited state S_1 is called intersystem crossing.
- The phosphorescence lifetime goes from the ns to the ms range.
- The fluorescence lifetime typically goes from the ps to the ns range.
- The radiative lifetime is defined as $1/(k_r + k_{nr})$
- Increasing the sample temperature decreases the fluorescence quantum yield.
- The fluorescence lifetime is independent of concentration, excitation intensity, and the presence of oxygen.
- The fluorescence lifetime decreases when quenched.
- The natural lifetime is greater than the fluorescence lifetime.

(5 marks)

QUESTION CONTINUED OVERLEAF

- iv) The fluorescence intensity and lifetime of a tryptophan (amino acid) residue of a protein in either the native or denatured state has been measured at three temperatures 5, 17 and 44 °C.

Measurement	1	2	3	4	5	6
τ_f /ns	0.1	0.3	0.5	1	3	5
I /au	5	10	20	40	80	100

Assign to each measurement the likely temperature and state of the protein.

(Hint: tryptophan residues in close proximity to other amino acids result in energy transfer and as a consequence reduced quantum efficiency).

(2 marks)

- b) Answer **BOTH** parts of this question.

- i) Given the following table

Species	Absorbance (1 cm cell)	
	475 nm	700 nm
A (7.5×10^{-5} M)	0.155	0.755
B (4.25×10^{-5} M)	0.702	0.091

Calculate the concentrations of A and B in a mixed solution that yielded an absorbance of 0.439 at 475 nm and 1.025 at 700 nm in a 2.50 cm cell.

(5 marks)

- ii) List 6 assumptions that need to be taken into account when using the Beer-Lambert law.

(3 marks)

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

- i) An absorption spectrometer lets exactly 2 wavelengths of light enter the sample, $\lambda = 254$ nm and $\lambda = 255$ nm, where the extinction coefficient is $\epsilon_{254} = 10,000 \text{ cm}^{-1}\text{M}^{-1}$ and $\epsilon_{255} = 5,000 \text{ cm}^{-1}\text{M}^{-1}$ respectively. Assuming that the incident power at both wavelengths is equal to one, plot the absorbance as a function of concentration for 1×10^{-6} M, 1×10^{-5} M, 1×10^{-4} M, and 1×10^{-3} M solutions. (Assume a sample path length of 1 cm).

(2.5 marks)

- ii) In all cases in i) what is the deviation from linearity assuming a monochromatic light source?

(2 marks)

- iii) Plot the absorbance versus concentration for all cases in i and ii.

(2 marks)

- iv) Using the graph plotted in iii) highlight the locations associated with the limit of linearity and the dynamic range.

(1.5 marks)

3.P6 – Molecular Electronic Materials

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

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

Figure 1 shows the current-voltage characteristics for a simple single-layer solar cell fabricated by sandwiching a 150 nm film of poly-3-hexylthiophene (P3HT) between indium tin oxide (ITO) and aluminium electrodes. You may assume the work-function of aluminium is 4.3 eV and the work-function of ITO is 4.9 eV. When the device is illuminated with light of 100 mW/cm^2 intensity a short-circuit current of $100 \mu\text{A/cm}^2$ is generated.

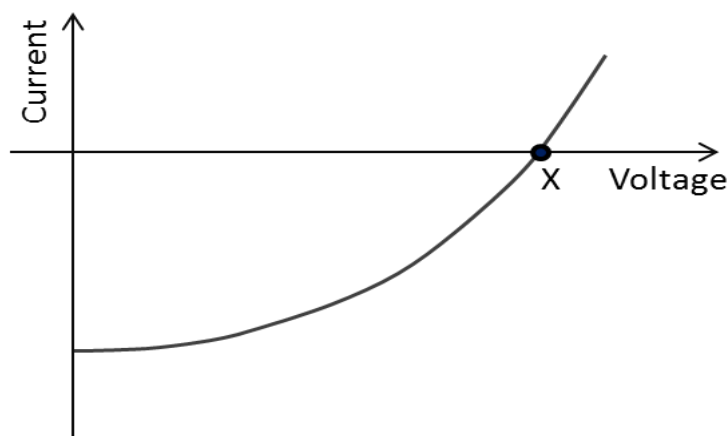


Figure 1

- i) What is the internal field strength when the device is in short circuit in the dark? (2 marks)
- ii) What is the potential difference across the electrodes at point X? (2 marks)
- iii) Estimate the power conversion efficiency (η) of the device. (4 marks)
- iv) What is the fill factor (FF) of the device? (2 marks)
- v) When the P3HT polymer film is doped with C_{60} molecules the short circuit current is found to increase from $100 \mu\text{A/cm}^2$ to 6.5 mA/cm^2 under the same illumination conditions stated above. Explain this observation. (5 marks)

QUESTION CONTINUED OVERLEAF

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

- i) A single layer organic light emitting diode is fabricated by sandwiching a 100nm film of poly p-phenylenevinylene (PPV) between calcium and indium tin oxide (ITO) electrodes. The work-functions of calcium and ITO are 2.8 and 4.9 eV respectively. The electron affinity (EA) and ionization potential (IP) of PPV are 2.7 eV and 5.1eV respectively. Describe the function of this light-emitting device detailing the mechanism of electroluminescence generation.

(5 marks)

- ii) Explain why multi-layered organic light emitting diode structures are often preferred over single layer structures.

(5 marks)

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

- i) Briefly explain what space charge limited current means.

(2 marks)

- ii) Show that the space charge limited current, J_{SCLC} , is given by

$$J_{SCLC} = \frac{\epsilon_r \epsilon_0 \mu V^2}{d^3}$$

where ϵ_r is the dielectric constant, ϵ_0 vacuum permittivity, V the voltage and d the thickness of the semiconductor layer. Clearly state any assumptions in your derivation.

(4 marks)

- iii) The time of flight technique was used to determine the charge carrier mobility in a particular organic semiconductor. In a typical experiment a 2.4 μ m thick film of the semiconductor was sandwiched between two electrodes. A transit time for holes was found to be 55 ns when 9 V was applied across the electrodes. From this data calculate the mobility of the electrons

(4 marks)