Department of
Pure and Applied Chemistry

Examination for the degree of BSc

BSc Hons Chemistry

CH479 BSc Chemistry Core Paper A

Section A. Key Reactions in Organic Chemistry (CH485)
Section B. Chemistry in the Excited State (CH703)

Wednesday 6th December **Start: 14:00** **Duration:1 h 40 min**

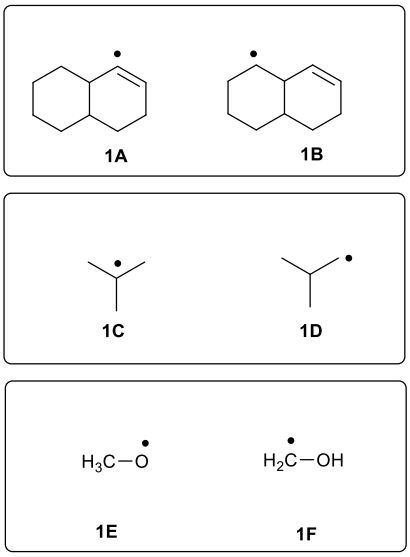
You must answer **ONE** question from **EACH** of the sections, **A** and **B**
Answer **TWO** questions in total.

A Periodic Table is included on the final page.

Section A: Key Reactions in Organic Chemistry (CH485)

1. Answer **ALL THREE** parts (a) – (c).

(a) (i) For all **THREE** of the following pairs of isomeric radical structures, indicate which radical within each pair is more reactive and give reasons for your choice.

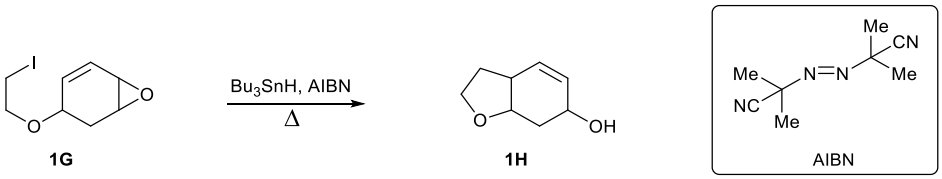


[2,2,2]

(ii) For each of the radicals **1A-1F**, identify the type of orbital (s, p, sp^3, sp^2, sp, π) containing the unpaired electron.

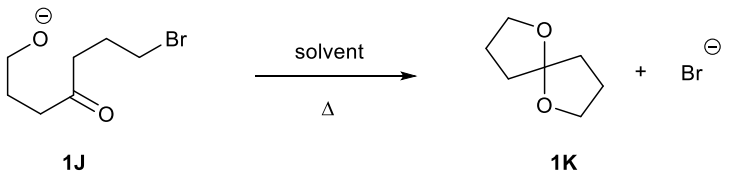
[6]

(b) Propose a mechanism for the formation of product **1H** in the reaction below. Include all the mechanistic (curly) arrows needed to represent the reaction.



[4]

(c) In the conversion of **1J** to **1K** below, two cyclisation steps are encountered. Use appropriate transition state diagrams to classify both reaction steps according to Baldwin's rules terminology.



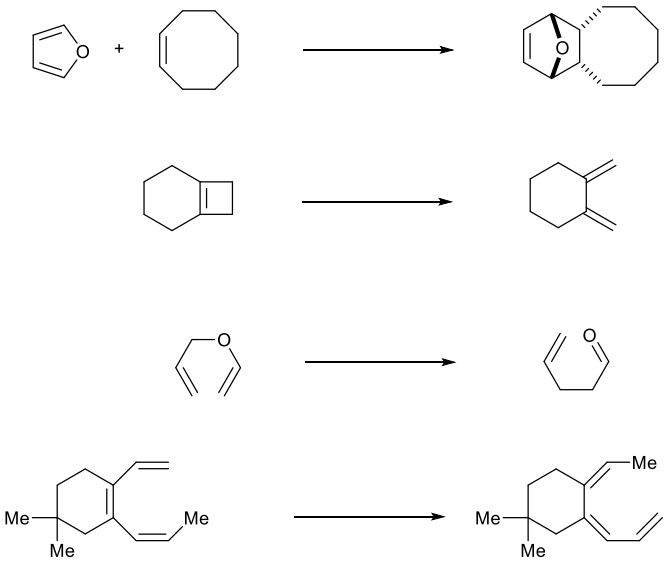
[2 x 2]

2. Answer **ALL FOUR** parts (a) – (d).

(a) Draw the structure of the major product in the following Diels-Alder reaction. With the help of drawings of the relevant orbitals, predict the regiochemistry of the reaction and its stereochemistry.

[1,2,4]

(b) Indicate whether each of the following reactions is a cycloaddition, an electrocyclic reaction or a sigmatropic reaction.

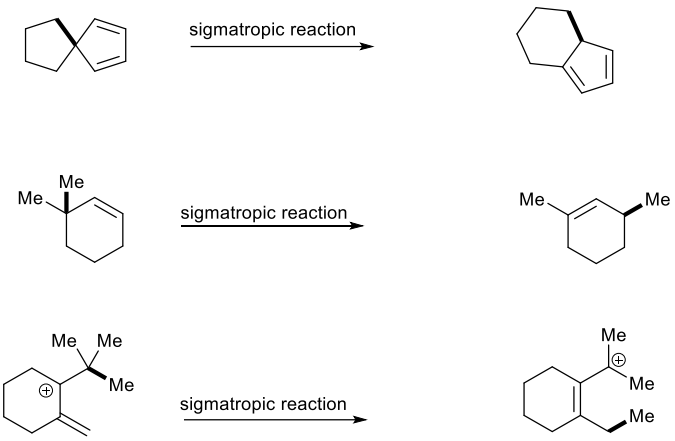


[4]

Question 2 continues on page 5

Question 2 continued…

(c) In each of the **THREE** cases below, show the curly arrows involved in the reactions, and classify the order of the sigmatropic reactions according to the [i,j] convention.



[3 x 2]

(d) Take **ONE** of the reactions in part (c) and use the aromatic transition state approach to establish whether it is thermally allowed.

[3]

Section B. Chemistry in the Excited State (CH703)

3. Answer **BOTH** parts (a) and (b).

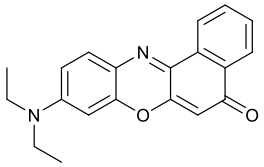
(a) (i) Name **FOUR** of the fundamental processes that occur during photocatalytic water splitting.

[4]

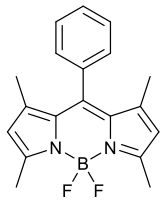
(ii) How do the fundamental processes for photovoltaic cells differ?

[2]

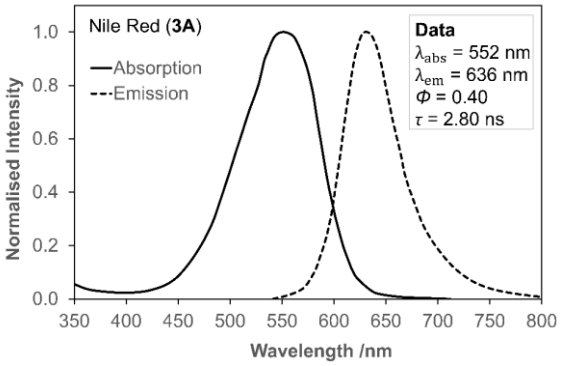
(b) The dyes Nile Red (**3A**) and BODIPY (**3B**) have the following optical properties in chloroform solution:

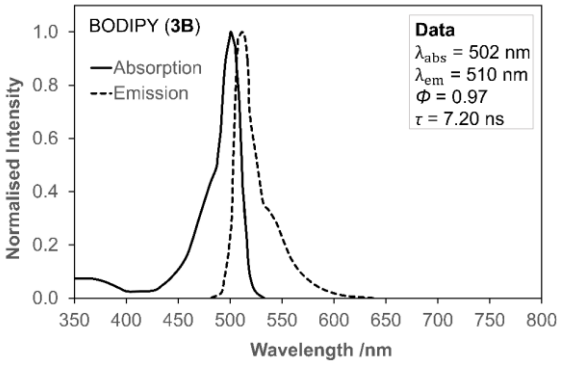


Nile Red (3A)



BODIPY (3B)





(i) Define the term Stokes shift and calculate the Stokes shift for Nile Red in energy units.

[3]

(ii) Calculate the radiative and non-radiative rates for Nile Red in chloroform. Show your working.

[4]

(iii) Nile Red shows positive emission solvatochromism. Define the term emission solvatochromism and explain its origin. Sketch how the emission spectrum of Nile Red may change in cyclohexane and methanol solutions relative to that in chloroform solution.

[3]

(iv) Nile Red and BODIPY can act as a FRET pair. Explain what is meant by FRET and give the requirements for FRET to occur. Identify the roles of the two dyes in this process.

[4]

4. Answer **BOTH** parts (a) and (b).

(a) Consider the data below about a series of photocatalysts **4A**–**4D**.

Photocatalyst	**Valence Band** ***E*** **/ V *vs* NHE**	**Conduction Band** ***E*** **/ V *vs* NHE**
4A	0.8	–2.1
4B	1.40	–0.6
4C	2.58	0.05
4D	2.2	–1.05

(i) Draw an energy diagram for **4A**–**4D** that includes water oxidation and proton reduction potentials at pH 0.

[3]

(ii) Which of the photocatalysts **4A**–**4D** can facilitate water splitting and which cannot? Explain your reasoning for each photocatalyst.

[8]

(b) Sketch a labelled Jablonski diagram for an organic dye showing **SIX** distinct photophysical processes. For each process, indicate a typical timescale range and whether it is radiative or non-radiative.

[9]

END OF PAPER

JAM, RE, SS

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.933	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.732	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.922	34 **Se** Selenium 78.09	35 **Br** Bromine 79.904	36 **Kr** Krypton 84.80
37 **Rb** Rubidium 84.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molibdenum 95.94	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.327	57-71 Lanthanides	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.967	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103 Actinides	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [269]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicium [277]	113 **Uut** Ununtrium unknown	114 **Fl** Flerovium [289]	115 **Uup** Ununpentium unknown	116 **Lv** Livermorium [298]	117 **Uus** Ununseptium unknown	118 **Uuo** Ununoctium unknown

57 **La** Lanthanum 138.906	58 **Ce** Cerium 140.115	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.24	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.966	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]