Supramolecular Chemistry 2nd Ed.

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Answers to Questions

Chapter 1

1.1 Log K = 19.7, 20.1, 24.8. Chelate and macrocyclic stabilisation. ($\Delta G^o = -RT \ln K$ and $\Delta G^o = \Delta H^o - T\Delta S^o$)

1.2 – 1.4 Essay and discussion questions based upon the material contained in the chapter.

Chapter 2

2.1 Recall $-\Delta G^o = nFE^o = RT \ln K$ in this case K represents the partition coefficient across the nerve cell (dimensionless);

$$K_{Na^+} = \frac{[Na^+]_{out}}{[Na^+]_{in}}$$

$$K_{K^+} = \frac{[K^+]_{out}}{[K^+]_{in}}$$

hence

$$E^o_{Na^+} = \frac{RT \ln K_{Na^+}}{nF} = \frac{8.314 \times 310 \times \ln \frac{440}{10}}{1 \times 96485} = 0.101\ V = 101\ mV$$

$$E^o_{K^+} = \frac{RT \ln K_{K^+}}{nF} = \frac{8.314 \times 310 \times \ln \frac{22}{330}}{1 \times 96485} = -0.072\ V = -72\ mV$$

so, net potential difference between outside and inside of cell = 101 - 72 = 29 mV

2.2

(a) Electrostatic energy = $\frac{q^+q^-}{4\pi\varepsilon_0 r} = -\frac{(1.602\times10^{-19})^2}{4\pi\varepsilon_0(5\times10^{-9})} = -4.62\times10^{-20}\ \text{J}$ for each pair of ions, hence 0.278 J for the sample.

(b) Electrostatic energy = $\frac{q^+q^-}{4\pi\varepsilon_0 r} = -\frac{(1.602\times10^{-19}\times6.022\times10^{23})^2}{4\pi\varepsilon_0(1\times10^{3})} = -8.37\times10^{13}\ \text{kJ}$

2.3 (a) Met(START)-Phe-His-Ser-Lys-STOP

(b) Cys-Ser-Ile-Ala-Ser

(c) Val-Pro-STOP

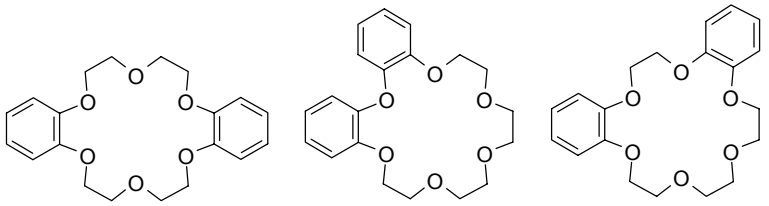
(d) Met(START)-Leu-Pro-STOP

2.4 Essay answer based on material in Section 2.1

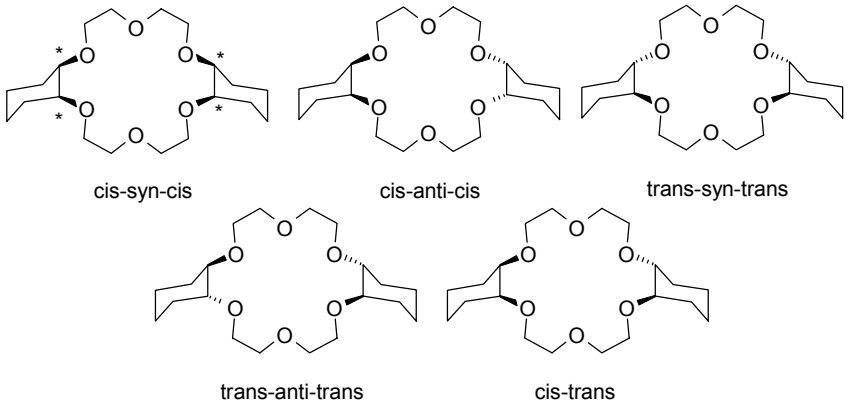
2.5 Na/K – bulk functions such as maintenance of electrolyte concentrations and membrne potential difference. Stabilisation of anionic proteins. Ca – bulk function in bone, messenger function in cellular signalling (*e.g.* proteins such as calmodulin in muscle contraction). Mg – catalysis of ATP hydrolysis. Fe – haemoglobin and FeS proteins. O_2 and electron transport and storage. Catalytic function. Co – B_{12} coenzyme. Small scale catalytic function.

Chapter 3

3.1



3.2



3.3 The isomers all vary because of the different absolute configurations of the four chiral carbon atoms (marked with a star above) and are not interconvertable without bond breaking, *i.e.* they are diastereoisomers, not conformational isomers. Cis-syn-cis and trans-anti-trans have C_2 (rotational) symmetry and so are chiral, cis-anti-cis and trans-syn-trans have C_i (inversion) symmetry and so are not chiral, and cis-trans has no symmetry and so is chiral.

3.4 Binding constants are defined in section 1.4.1. The cyclohexenyl rings in dicyclohexy[18]crown-6 impose stringent constraints on the donor group orientations of the macrocycle – a kind of preorganisation. They also have a modest electronic effect on the basicity of the oxygen atoms making them slightly more electron rich. The small size of Na^+ means that 18-membered ring crown ethers have to distors significantly in order to optimized Na–O bind distances. The constraints placed upon conformation by the cyclohexenyl rings limits this process in different ways. The cis-syn-cis isomer is best suited to wrap around Na^+ but even this compound is less flexible than the unsubstituted crown ether and hence the fact that the dicyclohexyl compounds do not bind as strongly is a case of negative preorganisation despite their slightly better donor properties.

3.5 The cryptand, [2.2.1]cryptand, is preorganised and has 5 O donors complementary of alkali metal cations. Binding is reduced if you remove one O atom and introduce a CH_2 group because the CH_2 group is not a binding site and is repelled from the cation, however the hydrocarbon bridged species is still preorganised. The azacrown ether is much more flexible and less preorganised.

3.6 – 3.8 Notes based on the material in the chapter.

Chapter 4

4.1 Smaller anions have a higher density of negative charge and are hence more polarising. It is this feature that gives them a high solvation energy, however it also makes for strong charge-assisted hydrogen bonding or ion-dipolar interactions to hosts. Since the host is more organised than solvent the strong interactions are outweighed by strong, multiple, preorganised interactions to the host.

4.2 The key to enzyme activity is not high affinity in itself. An enzyme has the highest affinity for a reaction transition state and is poisoned by strong ground state binding. Thus enzymes exhibit *induced fit* binding. As far as **4.6**is concerned the binding process serves to bring the reactiove postions of the system to gether and hence the enzyme mimicry of the system is aided by the flexible nature of the corand.

4.3 The katapinand is most stable in an *out, out* conformation and hence is not preorganised. Anion binding free energy is reduced by the steric destabilisation that occurs on changing to an *in*, *in* conformation. The system thus illustrates the preorganisation principle. Moreover in this case the hydrocarbon chains that link the two sides of the host are much poorer hydrogen bond donors than the oxyethylene portions of bis(tren) and hence the complex is less stabilised.

4.4 For a rigid tetrahedron of edge length 4.65 Å the angle from the centre point (where the guest is located) to each N atom is 190.5°. The distance (*d*) from the middle point to any N atom can be calculated by making a right angle triangle from the middle point to the middle of any edge. Then $d = 4.65/(2\times\sin(109.5/2)) = 2.84$ Å. If the N–H bonds are 1.00 Å this just leaves 1.84 Å for the H···N hydrogen bonded distance in the NH_4 complex. This distance should be around 1.75 Å so the molecule is fairly preorganised; if anything a little large. The CSD does not contain the coordinates for the actual complex but the experimental N···N distance in [18]aneN_3O_3 is around 4.9 Å. Semiempirical models indicate a range of distances from 4.65 to 6.0 Å. In the chloride case the N···Cl^- distance of 2.84 is significantly less than the sum of their van der Waals radii (3.75 Å). An optimal hydrogen bond would therefore be around 3.25 Å suggesting that the "rigid" cage described in the question is a little small for Cl^- binding.

4.5 Porphyrin-type tetrapyrroles are simply too small to host anions, indeed they exhibit 'doming' even with larger cations suchas as Fe(II) (as opposed to the smaller Fe(III)). The typical N···N distance across a porphyrin is around 4Å so the N···acceptor hydrogen bonds to a central anion (*e.g.*F^-) would have to be just 2 Å long – impossibly short. Even expanded porphyrins with five rings such as sapphyrin are relatively small and can only bind F^- in the marcocycle plane.

4.6 Podand complexation is relatively weak and so ^{1}H NMR spectroscopic titration which is effective up to binding constants of *ca.* 10^4 would be appropriate. For the strong complexation in hydride sponge fluorescence titration which works at much lower concentrations and is hence sensitive to larger binding constants might be effective, particularly since the napthalenyl group might be expected to fluoresce. As for a bicyclic zwitterion the complexation is likely to be very strong and there is no chromophore so potentiometric titration may be appropriate or if a suitable indicator can be identified that binds strongly then competitive indicator displacement assay, which will measure the difference in affinity for anion and indicator.

Chapter 5

5.1 The answers correspond to the data given in Table 5.1.

Chapter 6

6.1 Using equation 6.1 $K = K_{11}\ (1 + K_s[S])$ we find that the observed $130 = K_{11}\ (1+10[S])$. We can find [S] from the molecular mass of $CHCl_3$ = 119.378 g mol^{-1} and its density which tells us that 1 dm^3 contains 1480 g, hence [S] = 12.39 mol dm^{-3}. So, K_{11} = 130 / (1+123.9) = 1.04 M^{-1}. Significant solvent competition!

6.2 Occupancy factor is simply 28.5 / 120 = 0.238; the cavity is too large. A host volume of 42.5 $Å^3$ would be akin to solid methane. The ideal gas equation is PV = *n*RT. The number of moles, *n*, is 1 / 6.022×10^{23}, V = 42.5×10^{-30} m^3, R = 8.314 and we assume T = 298 K hence P = $8.314 \times 298 / (6.022 \times 10^{23} \times 42.5 \times 10^{-30})$ = 96.72 MPa or about 960 atm. Such a host would be too small to bind strongly to methane since the optimum occupancy factor is about 0.55.

6.3 Resorcarene carcerands are top-to-bottom symmetrical and hence while an unsymmetrical guest such as DMF will break this symmetry the two possible orientations give equivalent complexes. It is only where the two ends of the carcerand *and* the two ends of the guests are different coupled with restricted guest rotation that carcerism is observed.

6.4 The methyl groups prevent the cyclohexane chair framework from inverting *via* a boat intermediate. This motion would move the acid-derived substituents from being all axial to being a mixture of axial and equatorial hence removing the host preorganisation.

6.5 Formal names are Bicyclo[10.2.2]hexadeca-1(15),12(16),13-triene, Tricyclo[14.2.2.0*6,11*]icosa-1(19),6(11),7,9,16(20),17-hexaene and Tricyclo[14.2.2.1*3,7*]henicosa-1(19),3,5,7(21),16(20),17-hexaene. They can also be called [8]paracyclophane, [4.4]ortho-paracyclophane and [1.8]meta-paracyclophane.

6.6 The tri-ol is made from acid catalysed condensation of a mixture of pyrogallol (1,2,3-trihydroxy benzene) and resorcinol (1,3-dihydroxybenzene) and an aldehyde such as *n*-hexanal. This results in a mixture of [4]resorcarene type compounds containing pyrogallol and resorcarene derived units. The desired tri-ol must then be purified by chromatography. Fortunately it is formed in significant amounts!

Chapter 7

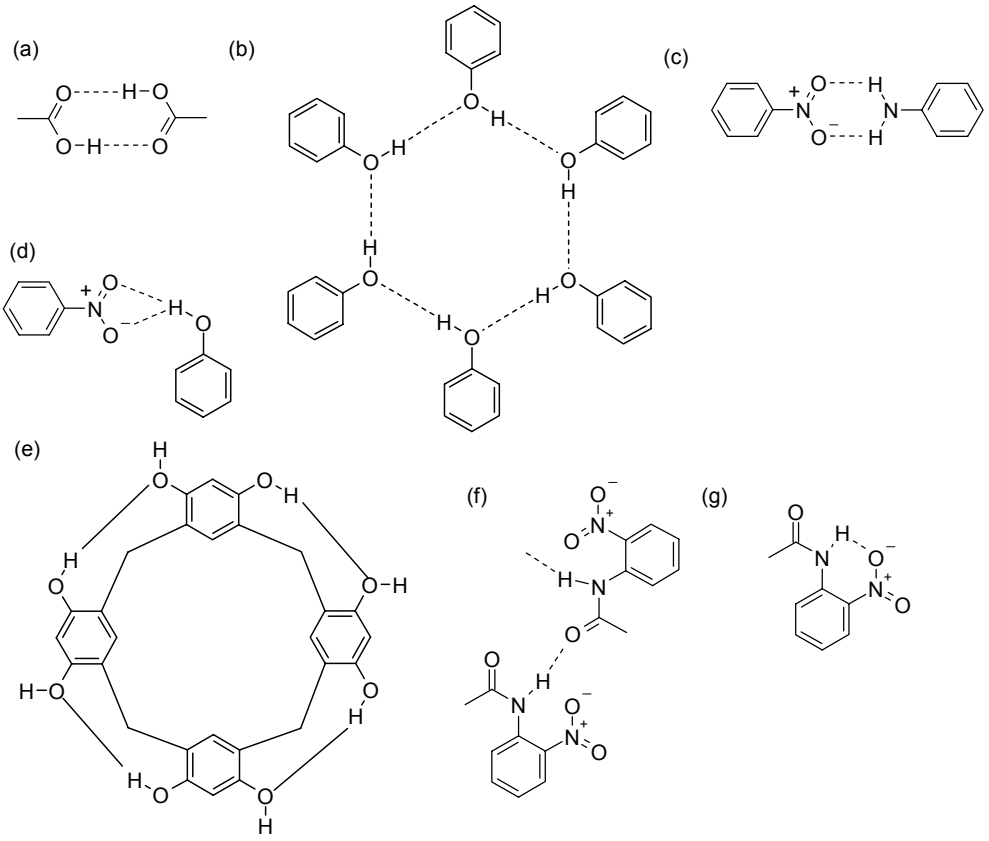
7.1 Cavity volume $v = 4/3\ \pi\ r^3$ = 250 $Å^3$ for the smaller cavity and 340 $Å^3$ for the larger cavity. The van der Waals volume of methane from question 6.2 is 28 $Å^3$ so occupancy factors are 0.112 and 0.082, respectively. Pressures can be calculated as in question 6.2. There is plenty of room for methane in both cavities and hence it will occupy the smaller one to maximise van der Waals interactions with the host framework.

7.2 Host molecular masses are 304.39, 60.06 and 648.93 g mol^{-1}, respectively. For an (unlikely!) 1:1 urea hydrate the complex molecular mass would be 60.06+18.02 = 78.08 and hence loss of one water molecule would

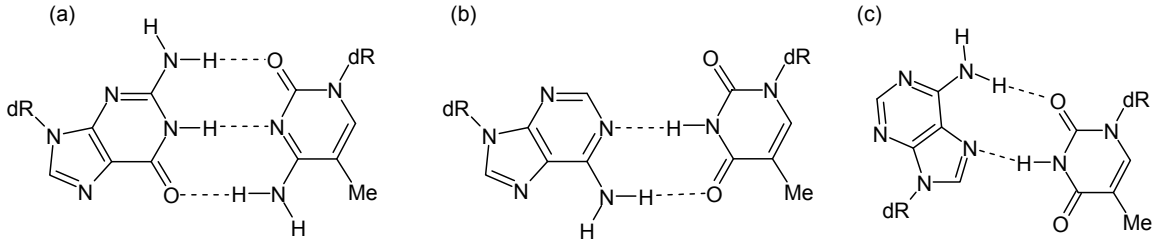
represent a loss of 23.1 % of the mass. In contrast a 1:1 complex of water and the calixarene would have a formula mass of 666.95 g mol^{-1} of which just 2.7 % is water. TGA can detect weight loss of $< 1\%$ but at these low levels it is sensitive to interference from loss of surface moisture, particularly if the weight loss occurs over a considerable time period.

Chapter 8

8.1



8.2



(a) N_1 = DDD, N_2 = $R_2^2(8)$, $R_2^2(8)$ and $R_2^2(12)$

(b) N_1 = DD, N_2 = $R_2^2(8)$

(c) N_1 = DD, N_2 = $R_2^2(9)$ – the Hoogstein pairing is clearly different at the second level graph set.

8.3 Use the information in Table 1.5. The compounds involving moderate strength hydrogen bonds have significant synthetic versatility but are still strong, directional and chemically stable.

8.4 The packing motif is related to the ratio of H to C. benzene has a relatively high ratio of 1:1 and is hydrogen rich, favouring the edge-to-face CH···π interactions. The packing factors in these compounds is explained in section 8.10.1

8.5 The librational effects giving rise to this phenomenon are explained in Figure 8.4. Make a right angle triangle with hypotenuse 0.92 Å and adjacent side 0.85 Å. The angle at the oxygen atom (θ) is civen by cos $\theta = 0.85 / 0.92$, hence $\theta = 22.5^{o}$ and the total angle swept out by the libration is twice that, *i.e.* 45 ^{o}. Neutron diffraction at very low temperature (*ca.* 4 K is perfectly feasible using a displex) would give an accurate hydrogen atom nucleus location with essentially zero librational shortening and no shortening arising from the fact that the hydrogen electron density is drawn towards the electronegative oxygen atom.

8.6 $H_3O^+ > Me_2NH_2^+ > RCO_2H > CF_3OH > Me_2P(O)OH > PhOH > MeOH > PhNH_2 > MeNH_2 > Me_2NH > MeSH > CHCl_3 > CH_2Cl_2 > C_6H_6 > MeOMe > Me(CH_2)_4Me$. Consider factors such as the electronegativity of the atoms to which the H atom is attached (O > N > S > C), the presence of activating substituents (CF_3OH > MeOH), steric bulk ($MeNH_2 > Me_2NH$), and charge ($Me_2NH_2^+ > MeNH_2$).

8.7 An agostic C–H bond shows Reduced $^{1}J_{CH}$ ^{13}C NMR coupling constant (which is related to the C—H σ-bonding electron density), high field ^{1}H NMR chemical shift as a result of shielding by the electropositive metal centre (about 0–10 ppm like that of a metal hydride), reduced ν(CH) IR or Raman vibrational frequency as a consequence of lowered vibrational force constant and short T_1 (spin lattice) NMR relaxation time, since spin polarisation may be readily transferred on to the metal centre. A free C–H bond will have a high IR frequency, and 'normal' C–H coupling constant, relaxation time and chemical shift. The IPA interaction is much more electrostatic in nature and is a three-centre four-electron interaction in which a metal lone pair or metal electron density interacts with a D–H dipole. Agostic bonds are three-centre two electon interactions. IPA interactions thus have the characteristics of a hydrogen bond (*cf.* Table 1.5). A discussion of the differences between agostic and IPA interactions based on experimental data can fe found in Thakur, T. S.; Desiraju, G. R., "Misassigned C–HCu agostic interaction in a copper(II) ephedrine derivative is actually a weak, multicentred hydrogen bond", *Chem. Commun.* 2006, 552-554.

8.8 (a) static: H^1 is a singlet broadene by the quadrupolar N nucleus, H^2 is a triplet and H^3 and H^4 are a doublet from coupling to H^1

(b) Rotation aboit the Ir–C_5 vector makes H^1, H^2 and H^3 all equivalent to one another since the hydrogen bond is breaking and re-forming rapidly with eah of them thus there will be two singlet resonances, one for $H^{1–3}$ and one for H^4.

(c) The final process allows all of the protons to exchange with one another giving a single resonance.

Chapter 9

9.1 The primitive cubic unit cell contains $^1/_8$ of an SUB at each corner linked by twelve spacer ligands. If the spacer runs along a unit cell edge then ¼ of each ligand is within the unit cell. So the total volume occupied by the SBU is $8 \times {}^1/_8 \times 300$ Å^3 = 300 Å^3 and by the spacer is $12 \times {}^1/_4 \times 200$ Å^3 = 600 Å^3. Total occupied volume = 900 Å^3. The unit cell edge length is the length of the ligand plus twice the radius of the SBU = $10 + 2(300 \times 3/4\pi)^{1/3}$ = 18.31 Å. The total volume of the unit cell is the cube of the edge length, *i.e.* 6135 Å^3. So the percentage occupied volume = 900 / 6135 = 14.7 % (85.3 % void), *i.e.* 5353 Å^3 – space for about 350 H_2 molecules! Such a dense packing could not be achieved in practice because of the thermal motion of H_2 meaning its dynamic volume is much larger than its van der waals volume. (c) Expanding the framework yet further gives total volume occupied by the SBU is $8 \times {}^1/_8 \times 300$ Å^3 = 300 Å^3 and by the spacer is $12 \times {}^1/_4 \times 300$ Å^3 = 900 Å^3. Total occupied volume = 1200 Å^3. The unit cell edge length is the length of the ligand plus twice the radius of the SBU = $15 + 2(300 \times 3/4\pi)^{1/3}$ = 23.31 Å. The total volume of the unit cell is the cube of the edge length, *i.e.* 12666 Å^3. So the percentage occupied volume = 1200 / 12666 = 9.5 % (90.5 % void).

Chapter 10

10.1 The spectrum should show three peaks in the ratio 2:1:1. The complex formed is a 4×4 grid so there will be four ‘corner’ Ag ions, four central and eight in the middle of each edge. The ligand possesses four bidentate binding domains. It is unlikely to form helicates because it is too rigid and the binding domains are too close together.

For the ‘ladder’ we expect two signals in the ratio 2:1.

For the ‘office block’ complexes we expect two signals (ratio 2:1) for the triple decker compound and two signals in the ratio 1:1 for the tetra-decker.

10.2 For 8-component assemblies using these 2-connecting building blocks there are only two possibilities – a square and a linear chain hence the probability is 50 %. If we allow 4-component assemblies as well then we can also have a pair of M_2L_2 macrocycles and a pair of M_2L_2 chains so the M_4L_4 macrocycle is one of 4 possibilities, probability = 25 %. Allowing 2, 4 and 6. component assemblies brings in the possibility of an ML pair with an M_3L_3 ring or an ML pair with an M_3L_3 chain, probability of M_4L_4 macrocycle becomes 0.167. With eight components of each type the macrocycle is formed either in the case when all 8 metals and all 8 ligands react to give two M_4L_4 macrocycles or it represents half of the product in combination with any of the other species described in the first part of the question. In addition combinations of all of the other asembiles are possible. In total there are 21 possible combinations. The macrocycle is formed twice in one and once in 5 others so total possibility = 7 / 42 = 0.167 again. In reality it is statistically more likely that assemblies with fewer bonds will predominate since the more bonds in an assembly the more chance there is that one will break. The assembly tree for the tri(4-pyridyl)triazine example is given in section 10.4.5. Why not try the supramolecular cube made from $[Ru([9]ane\text{-}S_3)]^{2+}$ and 4,4′-bipyridyl?

10.3 $K = 100 = [MT] / [M]_{free}[T]_{free}$ at equilibrium.

let $[MT] = x$ then $100 = x / (0.1–x)(0.1–x)$.

rearranging gives $10000x^2 – 2001x+100 = 0$ which can be solved by the quadratic formula to give $x = 0.103$ or 0.0969. The former answer is unrealistic since x cannot exceed 0.1 so $x = 0.0969$. In other words 96.9 % of the thread T is bound when it undergoes reaction and hence the yield of [2]catenane will be 96.9 % and free macrocycle will be 3.1 %. This calculation shows that it does not take a large binding constant to give a respectable yield of macrocycle. If macrocycle M is actually being formed in the cyclisation reaction then its concentration will build up as the reaction proceeds, increasing the proportion of [MT] from initially zero to the dominant species when M is in excess over T.

10.4 Effective concentration in cavity is 2.76 mol dm^{-3} of both reactants.

Initial rate in solution = k x 0.1 x 0.1 = 0.01 k

Initial rate in cavity = k x 2.76 x 2.76 = 7.66 k

So, rate enhancement = factor of 766.

Unlikely to be achieved in practice because species in cavity are not freely diffusing and may be locked in an unfavourable mutual orientation. Also, no account is taken of complexation/decomplexation equilibria, particularly is the hemicarcerand is used as a catalyst (*i.e.* less than stoichiometric amount).

10.5 One to try yourself!

Chapter 11

11.1 $\Delta G_A = -RT \ln K = 10$ kJ mol^{-1} so, ln K = –10,000 / –8.314 x 298 = 4.04; K = 56.6 M^{-1}.

For B: 4.84 and 127 M^{-1}

% complexed A

K = [H1·A] / [H1][A] at equilibrium.

Let x = extent of reaction, *i.e.* conc of host complexed with guest A

$[H1]_0 \approx [H1]_x = 10^{-2}$

$\therefore K = x / 10^{-2}(10^{-4}-x) = 1/0.566 = 1.77 = 10^{-4} - x / x$

So, $1.77x = 10^{-4}-x$ and $2.77x = 10^{-4}$

so $x = 3.61\text{x}10^{-5}$ and % of A complexed is $3.61\text{x}10^{-5}/10^{-4} = 0.361$ or 36 %

similarly, % complexed B = 56%

Selectivity factor = 56/36 = 1.56

For H2 a similar analysis gives K = 181,430 and 406,716 M^{-1}

% complexed for both = 99.9% and selectivity factor = 1.003, so in fat H1 is better at discriminating between the two analytes.

11.2 Reaction of $[RuCl_2(bpy)_2]$ with bypm would give $[Ru(bpym)(bpy)_2]^{2+}$ which could be used as a 'complex as a ligand' and reacted in a 3:1 ratio with Ru^{2+} to give $[Ru\{Ru(\mu\text{-bpym})(bpy)_2\}_3]^{8+}$ which would contain four chiral ruthenium centres and hence exist as $2^4 = 16$ isomers, listed below (central metal ion brackets). Each diastereoisomer will exist as an enantiomeric pair making eight possible disatereoisomers but of these, two are triply degenernate because of the overall triangular shape of the molecule and hence only differ by 120 ^{o} rotation. This leaves four distinct diastereoisomers.

1. (Λ)ΛΛΛ and (Δ)ΔΔΔ enantiomeric pair

2. (Λ)ΔΔΔ and (Δ)ΛΛΛ enantiomeric pair

3. (Λ)ΛΛΔ and (Δ)ΔΔΛ enantiomeric pair × 3

4. (Λ)ΛΔΔ and (Δ)ΔΛΛ enantiomeric pair × 3

11.3 $A_\lambda = -\log (I/I_0) = \varepsilon.c.l$, Φ = # photons out / # photons in.

Here $-\log (I/3.6\times10^{17}) = 15\,000 \times 2 \times 10^{-5} \times 1 = 0.3$ so $I = 3.6\times10^{17} \times 10^{-0.3} = 2.16\times10^{12}$. If 2.16×10^{12} quanta are absorbed and the quantum yield is 0.1 then 2.16×10^{11} quanta will be re-emitted.

For more information on quantum yield measurements see A. T. R. Williams, S. A. Winfield and J. N. Miller, "Relative fluorescence quantum yields using a computer controlled luminescence spectrometer", *Analyst*, 1983, **108**, 1067 and S. Dhami, A. J. de Mello, G. Rumbles, S. M. Bishop, D. Phillips and A. Beeby, "Phthalocyanine fluorescence at high concentration: dimers or reabsorption effect?", *Photochem.Photobiol.*, 1995, **61**, 341. The web site http://www.jobinyvon.com/read.asp?Docid=1546 is also useful.

Chapter 12

12.1 Characteristics of biological modesl are detailed in section 12.1.2

12.2 Enzyme / protein structure is discussed in section 2.6.1

12.3 Pauling's remark refers to the *entatic state* concept. By stabilising the transition state of the enzymatic reaction the enzyme lowers the reaction activation energy and hence dramatically enhances its rate.

12.4 These binding sites bind reasonably strongly to the substrates and position them close to the reactive functional groups of the system, however they are open enough to leave an exposed surface for reaction and flexible enough to bind all stages of the reaction from starting substrate, through transition state to product.

12.5 Doming is discussed in section 12.6.1 – crucially it is involved in the allosteric communication between four myoglobin units in haemoglobin (section 2.4 especially Figure 2.19).

Chapter 13

13.1 The key point about amphiphiles is that two regions of very different solubility are covalently linked together. This means that the molecule aggregate in such a way as to group together the polar regions in contact with an aqueous layer while hiding the fatty tails as a result of the hydrophobic effect. Depending on amphiphile concentration and shape this can be most efficiently achieven in a number of ways as shown in Figure 13.6. In each case the hydrophilic groups are stabilised by favourable solute colvent and mutual dipolar interctions while the clumping of the hydrophobic residues (*e.g.* in the interiour of a micelle) minimises the volume of 'hole' created in the solvent and maximises van der Waals interactions. When a hydrophobic guest enters a cyclophane hydrophobic cavity the number of holes in the water solvent is similarly reduced by one. The hydrophobic huest has no polar functionalit to create fabourable solute-water interactions.

13.2 Area = $6.022 \times 10^{23} \times 2 \times 10^{-5} \times 5$ å^2 = 6.022 m^2. To cover 10 cm^2 only 3.32×10^{-8} mol would be needed. If double the quantity were present a mixture of a monolayer and micelles might form or a surface multilayer. A large excess would result in the formation of suspended aggregates such as micelles or structures such as

extended bilayers or hexagonal mesophases / lyotropic liquid crystalline phases.

13.3 Mesogens have interactions with one another of different strongths in different directions. At lower temperatures these interactions can retain siginificant order, *e.g.* in a 2D smectic A phase. As the temperature increses thermal energy becomes larger relatively to some interactions before others and hence the weaker interactions break down reducing the degree of order. The nematic pahse is uaully last because it is the least ordered corresponding to only average orientational order. Here it is not so much htat there are strong interactions between the mesogens but rather their anisotropic shape means that they experience severe steric interactions that tend to co-align them. Eventually thermal energy becomes so great that molecular tumbling removes even this ordering and an isotropic melt is obtained.

Chapter 14

14.1 The dendrimer grows 10 Å in radius with every generation and its volume is approximated to that of a sphere. The filled volume is the volume of one sphere times the number of spheres present in total. We can thus obtain the void volume by subtracting filled volume from the total. We see that the dendrimer will have to distort or elongate before generation 7 to avoid running out of space.

Generation	# spheres	radius of dendrimer (Å)	volume of dendrimer (Å^3)	filled volume (Å^3)	empty volume (Å^3)	% yield from core
0	1	5	523	523	0	
1	5	15	14130	2617	11513	93.2
2	17	25	65417	8897	56520	74.0
3	53	35	179503	27737	151767	36.3
4	161	45	381510	84257	297253	4.2
5	485	55	696557	253817	442740	0.006
6	1457	65	1149763	762497	387267	2.2×10^{-11}
7	4373	75	1766250	2288537	Negative!	9.1×10^{-37}

14.2 Each generation (n) adds $3 \times (d_n - d_{n-1})$ dendrons, where d_n is the number of dendrons in generation n. Hence the yield for each generation = $0.995^{3\times(dn\,-\,dn-1)}$. As you can see from the table above trying to produce any material of generation 5 or above by a divergent approach is hopeless!

14.3 Dimer $(\mathbf{14.7})_2$ is linked by a total of four hydrogen bonds. In addition there is a total of four attractive secondary interactions and two repulsive secondary interactions (across the middle) so from the Schneider values the total free energy of association, $\Delta G_{\text{dim}} = -(4 \times 7.87) - (4 \times 2.93) + (2 \times 2.93) = -37.34$ kJ mol^{-1}. Since $\Delta G = -\text{RT} \ln K$, then at 25 °C we get $\ln K_{\text{dim}} = 15.07$ and hence $K_{\text{dim}} = 3.5 \times 10^6$. This is rather less than the observed value in toluene. The added stability could come from van der Waals interactions between the two molecules and solvophobic interactions arising from π-π interactions between toluene molecules. In wet

chloroform the water and to some extent chloroform solvates the hydrogen bonding sites, reducing the mutual affinity compared to the case in toluene, and the toluene solvophobic interactions will be absent. As a result the affinity goes down to $K_{dim} = 1 \times 10^7$, a value much closer to the predicted one.