Please read Buck, Matthew R.; Bondi, James F.; Schaak, Raymond E. “A total-synthesis framework for the construction of high-order colloidal hybrid nanoparticles” *Nature Chemistry* **2012**, *4*, 37-44. Below are 6 problems related to this publication.  With your knowledge of inorganic chemistry and after reading the paper, please answer the following:

1.  What do you consider to be key characteristics of colloidal hybrid nanoparticles?  Look up the first reference cited in the paper (Cozzoli, Pellegrino, & Manna, *Chem. Soc. Rev.* **2006**, *35*, 1195) and read the introduction.  How would you modify your list of characteristics based on the Cozzoli paper?

2.  This paper refers to several analytical techniques to characterize their hybrid nanoparticles.  TEM techniques and XRD feature prominently in the work.  List as many pieces of information as you can that the authors obtained from the following:

* + TEM
  + TEM-EDS
  + HR- XRD

Why should both HR-TEM *and* XRD be used to provide a more complete argument about structures and composition (as opposed to just one technique *or* the other)?

3. In this article, heterotrimers of M-Pt-Fe3O4 (M= Au, Ag, Ni, Pd) were synthesized.  In the supplementary information figure S1, the TEM image shows the coherent (111) interfaces in Au-Pt-Fe3O4.  The images labels the d-spacings of the Au, Pt, and Fe3O4 (111) phases to be 2.37 Å, 2.26 Å, and 4.86 Å, respectively.

The formula for lattice mismatch is:

The substrate is the original material and the epitaxial layer is grown upon that.

a)     Calculate the (111) lattice mismatch for Pt-Fe3O4 and Au-Pt.  For Fe3O4, use half the lattice spacing. (Note that the convention in this paper is to list the substrate first).

b)      Look up the lattice spacings for (111) planes of Ag, Pd, Ni and calculate the lattice mismatch Ag-Pt, Pd-Pt and Ni-Pt. One place you can get this data is from the MinCryst database: <http://database.iem.ac.ru/mincryst/search.php?select=Formula>

c)      What percent lattice mismatch is possible for these heterotrimers M-Pt-Fe3O4 to form?  Do you think lattice mismatch is the only contributing factor to the formation of M-Pt-Fe3O4?

4. The author states that the research described demonstrates “a rational and stepwise approach for constructing hybrid nanoparticle oligomers that conceptually parallels the total synthesis framework used by organic chemists to construct large organic molecules.” One of the most extensively utilized strategies used in organic synthesis is cross-coupling reactions. An example of a cross coupling reaction used in organic synthesis is the Cadiot-Chodkiewicz Coupling shown below.



Look through the reactions shown in the paper and identify a reaction showing the construction of hybrid nanoparticle oligomers that would be conceptually similar to the cross coupling reaction.

5.  Figure 3 summarizes a series of experiments that tests how silver crystallizes with Fe3O4 or Pt. Experiment C in Figure 3 examined a combination of Fe3O4 and Pt nanoparticles with an excess of silver.

a) Suggest the possible outcomes of experiment c if only one equivalent of silver was used for the reaction along with one equivalent of Fe3O4 and one equivalent of Pt.

b) Consider the titration of a diprotic base such as the fully basic form of glycine (NH2CH2COO-) with only one equivalent of a strong acid such as HCl or the redox titration of a mixture of Fe2+ and Cr2+ by an oxidizing agent such as Ce4+ as analogy to these reactions where the metal particles react. Based on these analogies, do you expect silver is likely to bind to both of the nanoparticles (Pt and Fe3O4) or only one of the nanoparticles for the reaction described in part a above. Justify your choice.

c) If you performed the limited silver experiment described above in part a, suggest a way to identify the product(s) that you made and what your results would look like.

6.   Gold, platinum, and Fe3O4 all adopt specific crystal structures in the solid state.

a) What are these structures (space group, and descriptive name of the packing)?

b) What are the dimensions of the unit cell?

c) Can you sketch them and draw an arrow to indicate (100) (110) directions?

d) Can you render the crystal structure to show the (11-1) plane.

e) Why are platinum and gold are thought of as “noble metals”?  

f) At the nanoscale, Pt and Au appear to combine to make an interface. From reading this paper, how do you think Pt and Au fuse with each other? Such a combination of Au-Pt is either an *alloy* (a solid solution) or an *intermetallic* species.  What is the difference between these?