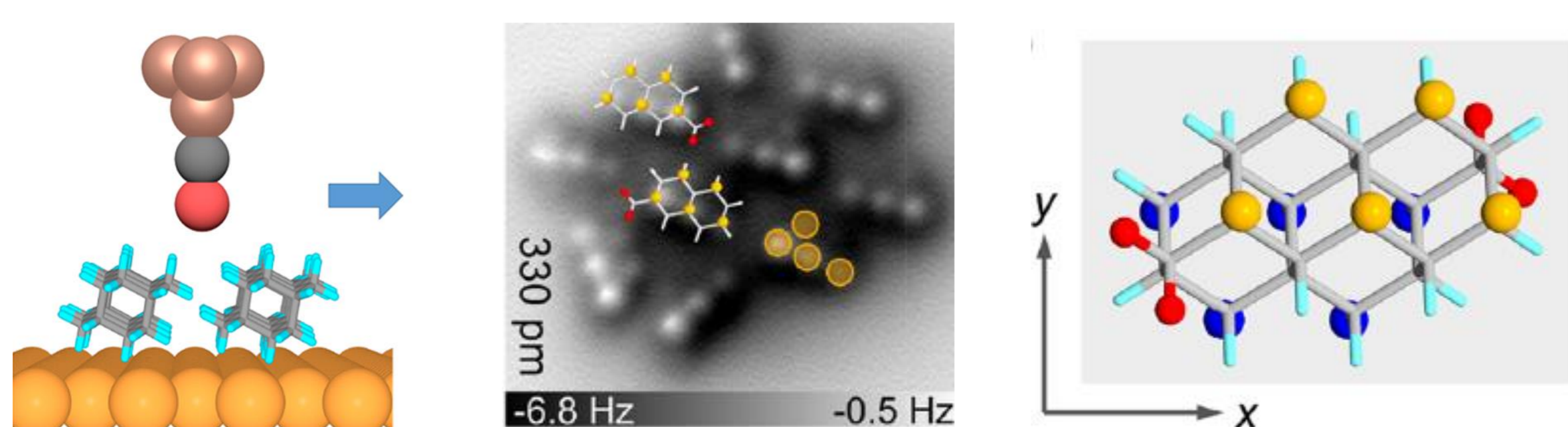


## Diamondoids

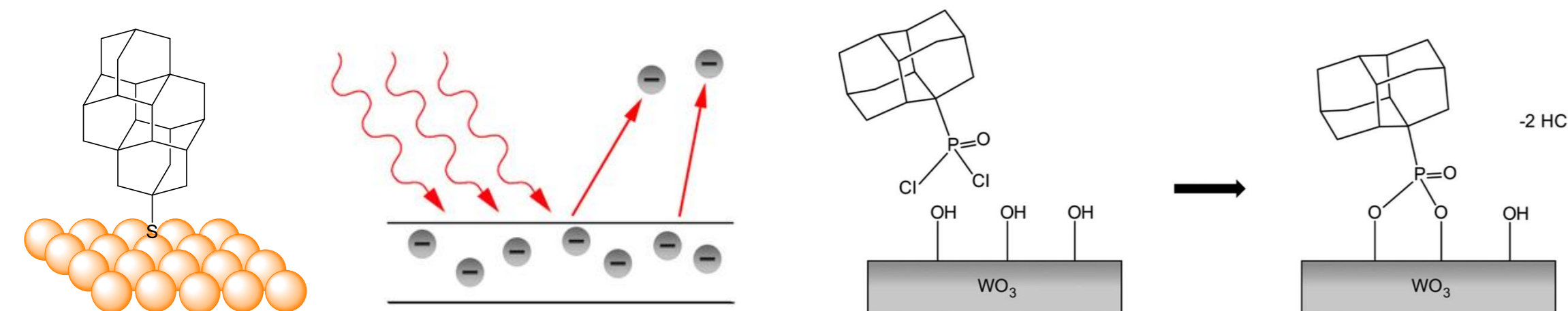
- Diamond-like cage hydrocarbons that can be functionalized (Figure 1)
- Bulky, rigid, non-polar, low strained, thermally and chemically stable
- Applications in medicine, material sciences, nanotechnology, supramolecular chemistry, etc.
- Promising candidates as molecular building blocks in nanotechnology (Figure 2) due to their exceptional properties [1,2]

**Diamondoids** can form highly-ordered self-assembled monolayers (SAMs) on metal surfaces driven by London dispersion (LD) interactions [3].

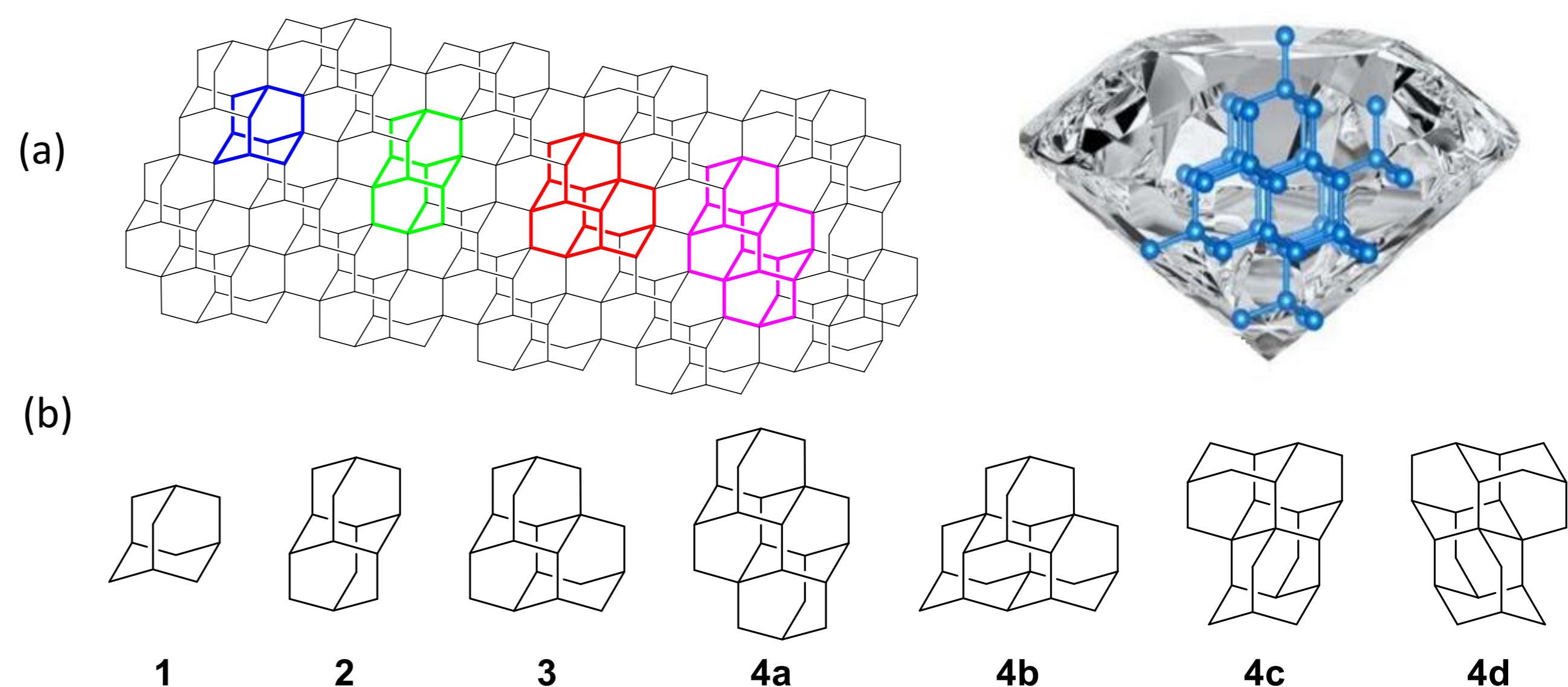
Recent investigation using molecular dynamic (MD) simulations indicates that differences in conformational entropy (Figure 3) can be an important factor governing the behavior of adamantyl substituents during self-assembly processes [4].



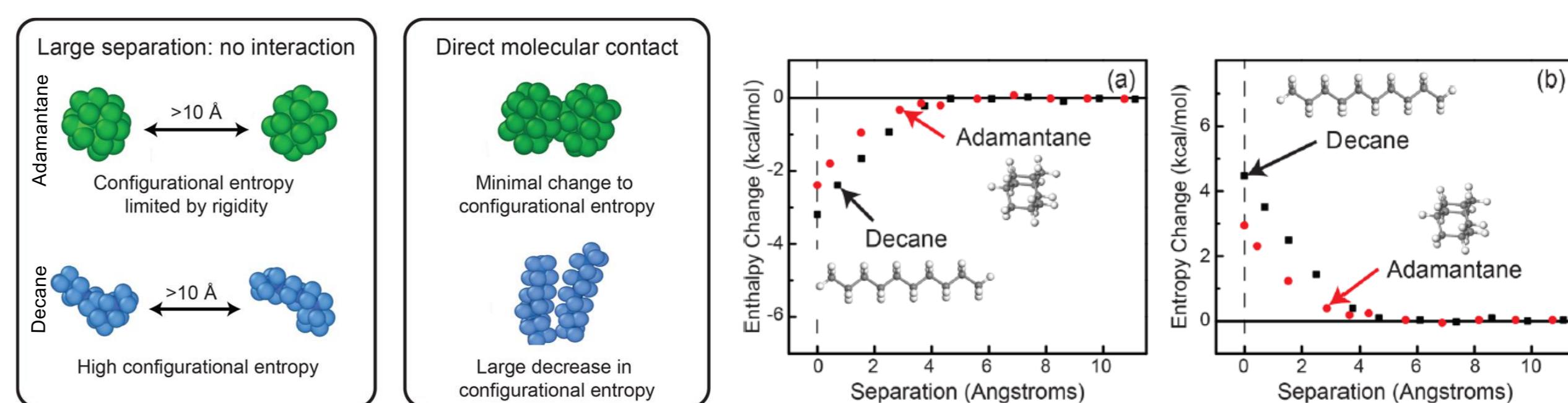
**Figure 2.** [121]Tetramantane (**4a**) clusters on Au(111) substrate observed by an atomic force microscope (AFM) with a CO-functionalized tip; each molecule is arranged in an Olympic ring-like pattern.



**Figure 4.** The process of monochromatic photoemission from diamondoid monolayers capable of forming on various carriers.



**Figure 1.** (a) Structural similarity between diamond crystal lattice and diamondoids; (b) Structures of adamantane (**1**), diamantane (**2**), triamantane (**3**) and four tetramantane isomers (**4a-c**).



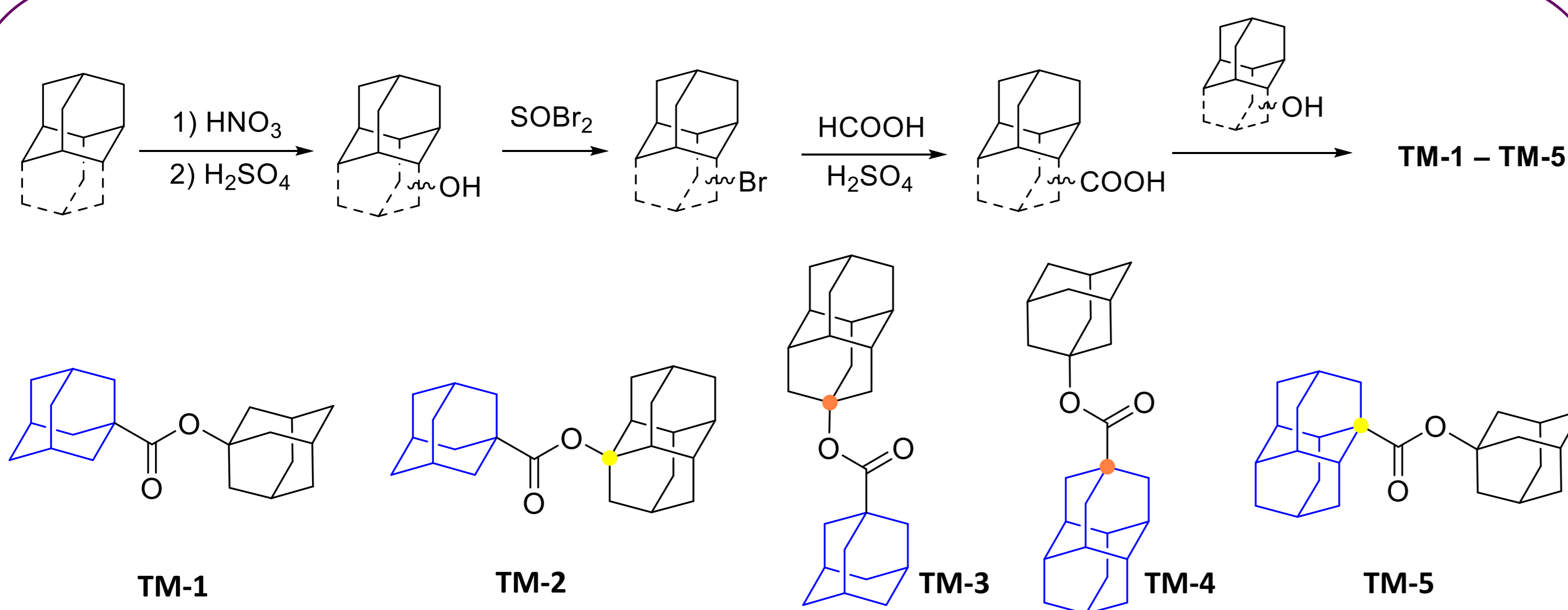
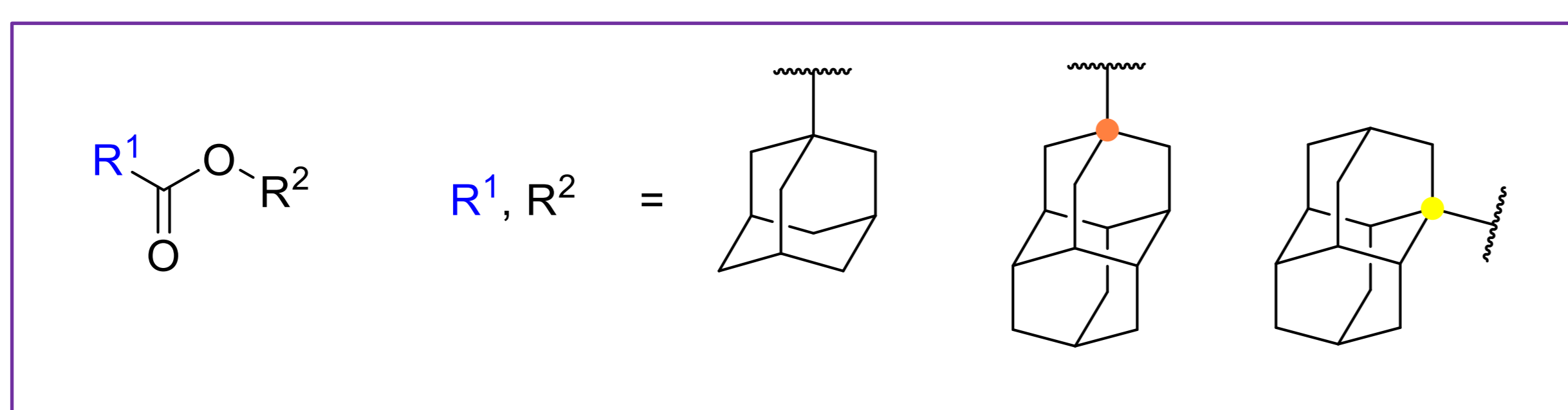
**Figure 3.** Distance-dependent contributions of entropy and enthalpy to assembly for a pair of rigid adamantanes (**1**) and a pair of flexible decane molecules. Entropy changes for the adamantane pair upon contact overcome more favorable enthalpic interactions acting in the decane pair.

**Negative electron affinity (NEA)** is an important property for development of electron emitters, with applications in microscopy, electron beam lithography, field-emission flat panel displays, etc.

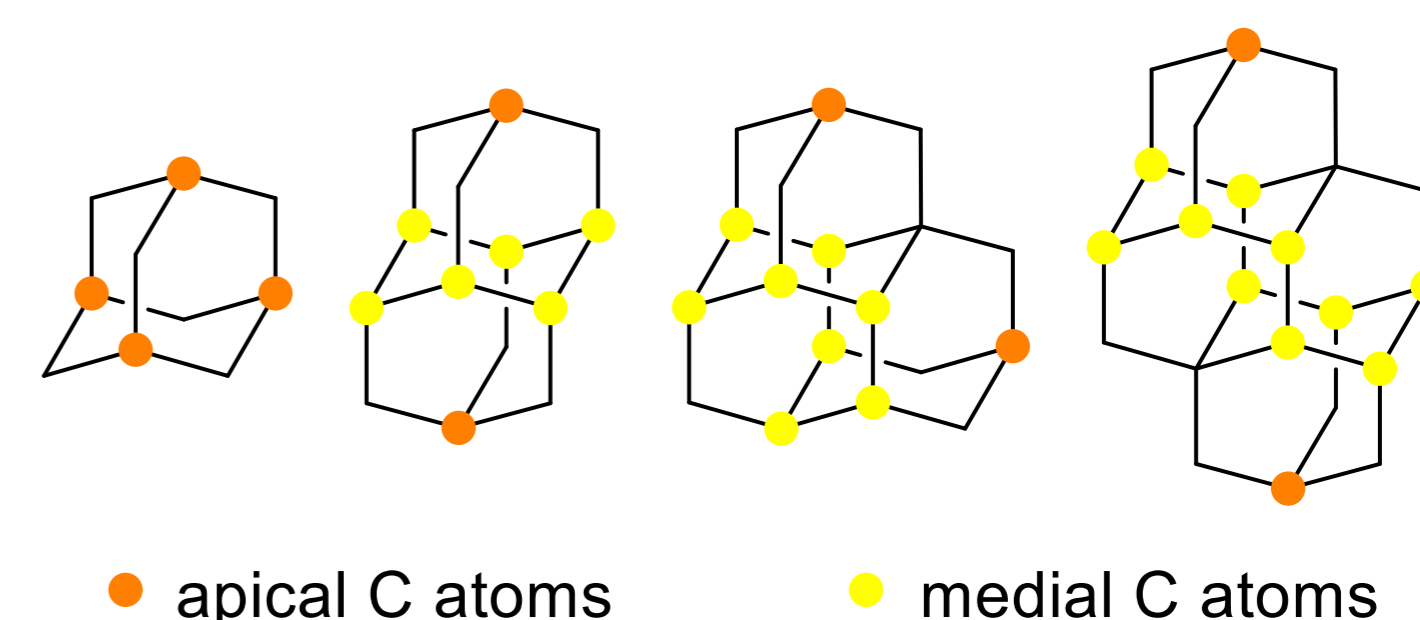
Efficient monochromatic photoemission from diamondoid monolayers (Figure 4) depends on the interplay between diamondoids and carrier surface:

**metal excitation => charge transfer to diamondoid LUMO => emission**

## This work => synthesis of new diamondoid ester derivatives



Diamantane and some other diamondoids have two chemically different bridgehead C–H positions that can be selectively functionalized [2]:



New diamondoid derivatives have been prepared by condensing two diamondoid cages *via* a carboxyl ester moiety. Thus, target esters (**TM-1 – TM-5**) incorporate differently bound combinations of adamantane (**1**) and diamantane (**2**) subunits.

All obtained diamondoid esters were fully characterized by standard spectroscopic techniques: gas chromatography with mass spectrometry detection (GC-MS), <sup>1</sup>H- and <sup>13</sup>C-NMR and IR.

Further investigation will include the use of atomic force microscopy (AFM) in order to study the self-assembly of the prepared esters on various carrier surface in combination with computational analysis.

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