Research Plan

The purpose of the first joint project is to study geometric and electronic interactions between oligonucleotide aptamers and target molecules for biosensor applications. Particular emphasis will be given to the DNA aptamers to detect adenosine triphosphate (ATP). DNA aptamers that target ATP exhibit distinct binding site sequences. In particular 27-mer DNA aptamer shown in Fig. 1a that binds ATP contains two guanine-rich regions. This DNA aptamer has two nonequivalent ATP-binding sites labeled as A_I and A_{II} in Fig. 1b. One part of the work will focus on the molecular modeling of these complex structures of DNA aptamer and ATP molecule to mimic geometric and electronic interactions.

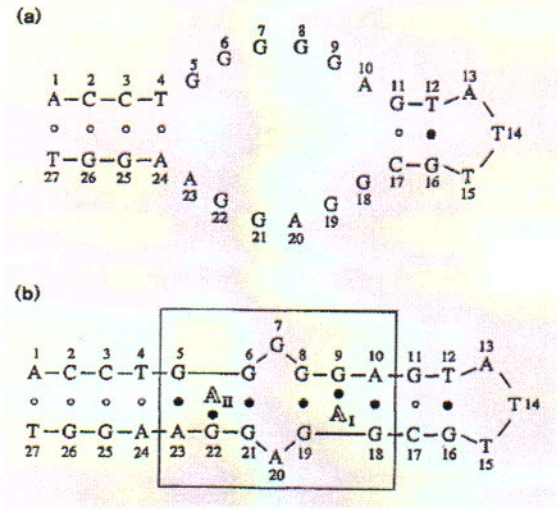

Figure 1. **(a)** The base sequence of the ATP-binding 27-mer DNA aptamer **(b)** The structure between target ATP and 27-mer DNA-aptamer complex showing two ATP-binding sites (A_I and A_{II}). Figure adapted from Ref.1.

Another strategy for ATP recognition is based on the idea of Target-Responsive Electrochemical Aptamer Switch (TREAS) strategy. In this case, initially, the ATP aptamer forms a duplex as illustrated in Figure 2. A label molecule (signaling element) such as a metallic nanoparticle is attached to the duplex and is positioned far away from the electrode surface so that initially there is no electron transfer with the electrode. After reaction with ATP, the DNA aptamer forms a stable tertiary structure with ATP and liberates its complementary strand. In this latter case, the label molecule becomes in close proximity to the electrode surface and an electron transfer reaction takes place generating an electrochemical signal.

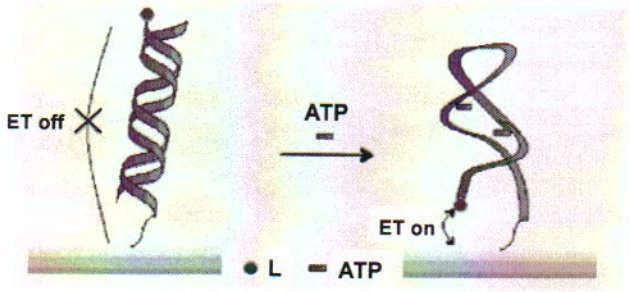

Figure 2. Schematic of TREAS strategy for ATP detection. Figure adapted from Ref.2.

In summary, comparison of interaction energies between the DNA duplex, duplex with mismatches and single strand DNA oligonucleotide with the target (in this case, ATP) complex structures will be made feasible through molecular modeling. The expertise of the experimental group governed by Dr. Philippe Banet at the Laboratory of Physico-Chemistry of Polymers and Interfaces at University of Cergy-Pontoise will be extremely useful and complementary to theoretical modeling.

As a second joint project, we will concentrate on the theoretical characterization of charge mobility in carbazole-based oligomers. Carbazole-based materials have received special attention for their excellent hole-transport properties, well-positioned ionization potential, and high triplet energy.[3] Thus, in this study, we aim to investigate the charge-transport properties of a series of methoxy-substituted carbazole oligomers by means of density functional theory calculations. Calculations of the frontier molecular orbitals, ionization energies and intermolecular electronic couplings between model dimers will be used to understand the role of methoxy groups on the charge-transport parameters of these materials.

References:

1. Chin H Lin and Dinshaw J Patel, Chemistry & Biology 1997, 4, 817-832.
2. X. Zuo, S. Song, J. Zhang, D. Pan, L. Wang, and C. Fan, J. Am. Chem. Soc. 2007, 129, 1042-1043.
3. S. Salman, D. Kim, V. Coropceanu, andJ-L Bredas, Chem. Mater. 2011, 23, 5223−5230.