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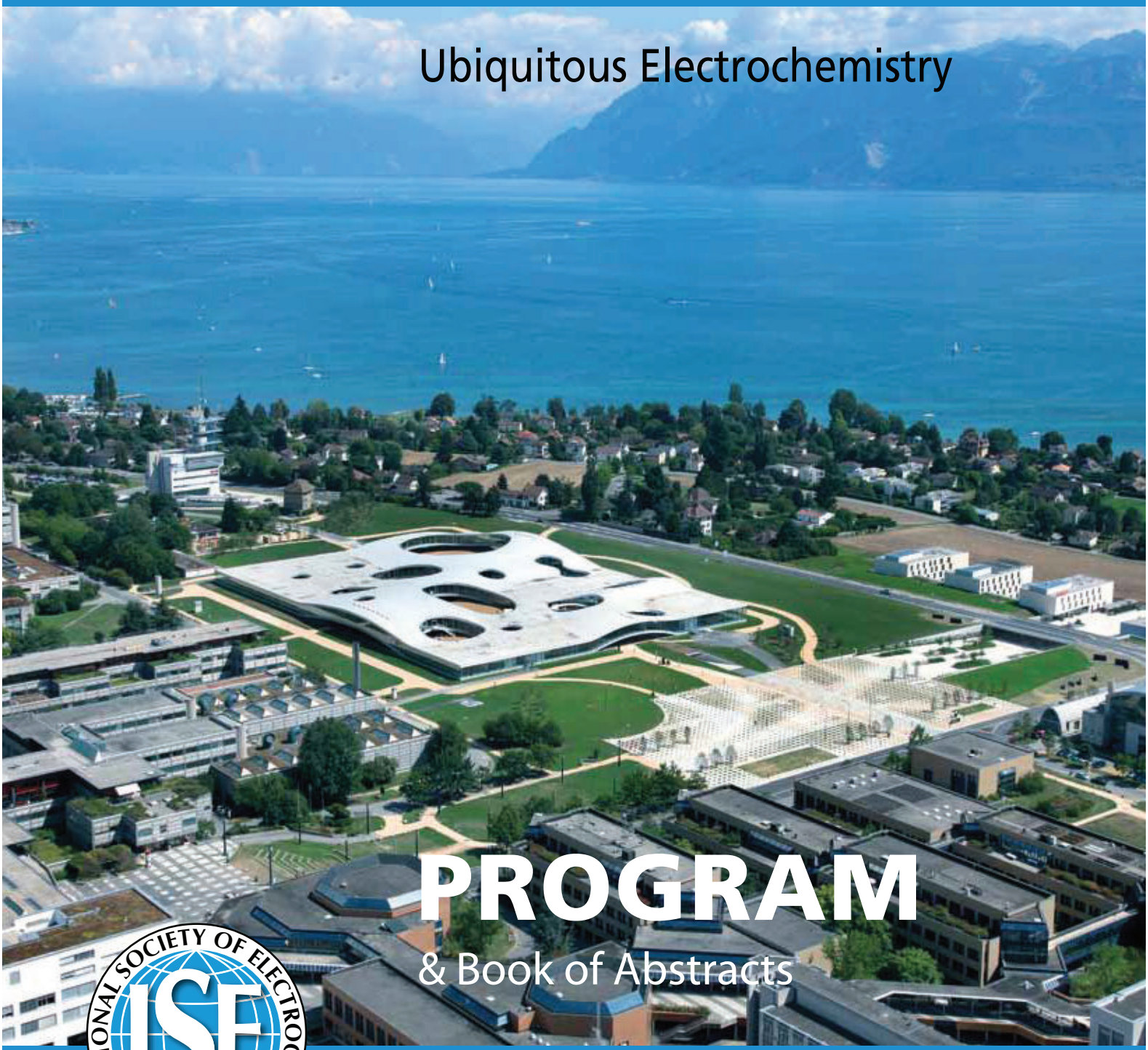

Ubiquitous Electrochemistry

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Determination of the TATAAA oligonucleotide via hybridization of the electrosynthesized molecularly imprinted polymer (MIP) bearing complementary adenine and thymine nucleobases

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A new method of selective determination of the TATAAA (T – thymine, A – adenine) oligonucleotide was developed for potential clinical analysis application. Towards that, a dedicated molecularly imprinted polymer (MIP) was devised and prepared by electropolimerization. For this MIP preparation, 4–{[bis–(2,2'–bithien–5–yl)]methane}phenyl 2–adenine ethyl ether and 4–{[bis–(2,2'–bithien–5–yl)]methane}phenyl thymine acetate were synthesized as electroactive functional monomers. These monomers, with their selective recognition adenine and thymine moieties, were able to form a pre-polymerization complex in solution with the TATAAA oligonucleotide target, initially used as a template for imprinting. Electropolymerization of this complex under potentiodynamic conditions in the presence of a selected cross-linking monomer, 4,4'-bisthiophene-3-yl-5,5'-bisthiophene-2-yl-3,3'-(2,2'-bithiophene), resulted in deposition of a thin porous MIP film on a gold electrode of the 10 MHz quartz resonator of a quartz crystal microbalance (QCM). The TATAAA imprinting was confirmed by X-ray photoelectron spectroscopy (XPS). Next, the TATAAA template was extracted from the MIP film with a strong base solution, thus emptying the imprinted cavities and making them sensitive to the TATAAA analyte. These cavities were compatible with respect to their size, shape, and orientation of recognizing sites to those of the TATAAA analyte molecule. With empty cavities, the film was ready for use as a recognition unit of a TATAAA chemical sensor. The detectability of this chemosensor under flow-injection analysis (FIA) conditions was determined using piezoelectric microgravimetry at QCM. The ab initio PM6/3-21G molecular modeling optimized geometry of the pre-polymerization complex.