Development of Fluorescent Chemosensors: 
Mercury Sensing and Biological Molecules Sensing Probes

WANG Hao

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Principal Supervisor: Prof. CHAN Wing Hong

Hong Kong Baptist University

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Abstract

Cholic acid-based fluorescent photoinduced electron transfer (PET) sensor probes A, B and C, bearing a pair of dithiocarbamate pendants as the receptive site and an anthracene moiety as the signal displaying unit, were designed and synthesized via a sequence of high yield steps. The sensor probes not only show high selectivity and sensitivity to Hg$^{2+}$ in aqueous acetonitrile solution, but also respond moderately to MeHg$^+$. A distinctive OFF-ON type signaling of up to 10-fold enhancement was observed for the novel sensor probe A toward Hg$^{2+}$ in aqueous acetonitrile solutions.

Novel ditopic fluorescent PET chemosensor AS1 was designed and synthesized from cholic acid. On the basis of rational chemical design, an amidothiourea moiety and a cyclic diamino-chiral receptive site were introduced simultaneously to the chiral framework of cholic acid to confer the chemosensor with specific binding abilities. In acetonitrile, the sensor demonstrated differential binding toward trifunctional aminoacids like serine, lysine, threonine and tyrosine against other simple aminoacids. Moreover, high enantioselectivities ($K_D/K_L$) of up to 8.9 and sensitivities in the micromolar range with the sensor were observed for trifunctional aminoacids.

The interactions of chemosensor AS1 and phosphate, pyrophosphate, AMP, ADP, ATP, CTP, GTP, TTP have been investigated. Interestingly, the aminoacid chemosensing probe AS1 was also found to be an ideal selective ATP sensor. ATP could trigger significant quenching in fluorescence of AS1 in a 1:1 aqueous CH$_3$CN solution at pH 7.4, whereas other phosphorus containing guest molecules only showed a much smaller effect. The nature of the complex between AS1 and ATP was established through
combined UV, $^1$H NMR and $^{31}$P NMR spectroscopic methods. The uniqueness of the new sensor is that it binds with ATP 33-124 times more selectively than other nucleotides, as evidenced from the respective binding constants. **AS1** is an extremely sensitive sensing probe, as little as 30 nM ATP can cause 15% fluorescence quenching of the sensor.

![Chemical structures of sensor A, sensor B, sensor C, and AS1](image-url)
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