CHAPTER VII

CONCLUSIONS

(i) The first excited energies of the acridine and aminoacidine derivatives calculated using semiempirical methods, the NDDO-G and AM1, are agreed well with those obtained from high level of theory and experiment values.

(ii) The NDDO-G and AM1 methods have an advantage for the calculation of the first excited state of molecules. This method is not only accurate enough, but also saves computational time. The qualitative conclusion would not be changed by the use of the sophisticated calculation. The solvent environment was found to influence weakly on the excitation energy.

(iii) The excitation energies of R6G at the TDDFT, AM1 and NDDO-G methods overestimate the experiment value. The best agreement was found for the AM1 which the difference is 72.4 nm. Therefore, AM1 method is recommended to be used to calculate the excitation energy of rhodamine-DNA complex. In addition, the electronic transition amount to 98% at the first excited state was found to take place only in xantylium ring of R6G.

(iv) MD simulations on P6G and R6G dimers do not fully support the computational findings of the previous work by Daré-Doyen (DD) et al. The simulations were opted for a different computational protocol and can be confirmed that short simulation time are not adequate for sampling the phase space of xantylium dimers and sheds some doubt on the possibility to compare short-time MD results with NMR data.

(v) Despite considerable effort, reconstruct the DD charges were not reproduced the value using standard recommended (referred to as STD) by the AMBER program. In addition, to the generation of the atomic net charge, pertinent minima differ by ~10° in the torsion angle for the rotation within the xantylium dimer.

(vi) An answer to the question why positively charged xantylium moieties form dimer (or even higher-order aggregates[4]) in aqueous solution was also proposed. A quantification of the straight forward argument which relies on the solvent-induced

energy gain as a consequence of the increased charge in the dimer results in dimerization energies of 60–70 kcal/mol. This energy is completely dominated by the electrostatic interaction of the solute with its aqueous environment.

(vii) A residue-based cutoff strategy and a PME procedure yield compatible values of the electrostatic energy, if a self-interaction correction is applied to PME results of AMBER8.

(viii) For P6G, an estimate of the solute-solvent entropy change during dimerization was proposed, accounting for the reorganization of the solvent in the vicinity of the solute. This entropy related contribution almost cancels the gain in electrostatic energy, as corroborated by a free energy calculation via thermodynamic integration which resulted in driving force for dimerization of about -7 kcal/mol.

(ix) The MD results for the chromophore-DNA complexes, Rho-5C, Rho-5G and Rho-5G', show that the distance between the planes of the stacked chromophore and the nearest GC base pair remains almost unchanged and fluctuates slightly around 3.6 Å, 3.8 Å and 3.8 Å for Rho-5C, Rho-5G and Rho-5G', respectively. The variations of the twist parameter indicate highly flexible of the rhodamine in DNA complexes. However, the stacking interaction with chromophore has a small effect on the second and third AA base pairs.

As it is know that the charge transfer rate is supposed to vary significantly with the position of the chromophore relative to the adjacent guanine. This mean that the electronic coupling and the charge transfer rate cannot be determined on the basis of averaged geometries. Therefore, the obtained MD trajectories for the three systems can be directly used for the further study.