Calculations of circular dichroism and circularly polarized luminscence spectra of biologically relevant chromophors.

Anna Pikulska[1], Magdalena Pecul[1]
[1]Faculty of Chemistry, University of Warsaw, Poland

Circularly polarized luminscence (CPL) measures the differential emission of left and right circularly polarized light by a chiral sample, and can therefore be regarded as the emission spectroscopic counterpart to electronic circular dichroism (CD). When the equilibrium structure of the electronically excited state differs significantly from the ground state geometry and the excited state has a lifetime long enough to allow the molecule to structurally relax, the CD and CPL bands are dissimilar, even to the extent of having opposite signs. Thus, a comparison of CPL and CD spectra allows to investigate the molecular dynamics following the electronic excitation. After the period of significant developements in the 1980s CPL spectroscopy has fallen into relative obscurity, but nowadays a renewed interest in it can be observed, boosted by the recently emerged possibility of quantum chemical calculations of the CPL spectra for chemically interesting molecules [1,2].

We have carried out calculations of CD and CPL spectra for several biologically relevant chromphores, including several variants of green fluorescen protein chromophors: blue fluorescent protein (BFP), enhanced cyan fluorescent protein, (CFP), enhanced green fluorescent protein (GFP), yellow fluorescent protein (YFP). Our main aim has been to check how the protonation and deprotonation processes, and the presence of protein environment, influence the CD and CPL spectra and therefore to investigate the potential of CPL as a structural probe of electronic excited states. The presence of environment has been modeled employing polarizable embedding density functional theory (PE-DFT) method [3], in fully polarizable QM/MM/PCM model [4].

The CPL spectrum has also been calculated for thioflavin-T. Fluorescence spectroscopy of thioflavin-T intercalated in proteins is a well-known method of investigation of protein misfolding. Thioflavin-T is achiral, but it exhibits an induced CD effect in a chiral environment (for example when intercalated in a protein) [5]. We have therefore decided to carry out quantum chemical calculations of HOMO-LUMO excited state potential energy surface of thioflavin-T in different environments and of the associated CPL spectra, in order to investigate what are the capabilities of induced CPL of thioflavin-T in protein structural studies.

[1] Pritchard B., and Autschbach, J., ChemPhysChem 11, 2409-2415, 2010.
[2] Pecul, M., and Ruud, K., Phys. Chem. Chem. Phys. 11, 643-650, 2011.
[3] Olsen, J. M., Aidas K., and Kongsted, J., J. Chem. Theor. Comput., 6, 3721-3734, 2010.
[4] Steindal, A.H., Ruud, K., Frediani, L., Aidas, K., and Kongsted, J., J. Phys. Chem. B, 115, 3027-3037.
[5] Dzwolak, W., Pecul, M., FEBS Letters 579, 6601-6603, 2005.