The ground and low-lying excited electronic states of isooloxazine, 10-methylisoalloxazine and lumiflavin, three flavin-related compounds, were investigated by means of quantum chemical methods. Minimum structures were determined employing (time-dependent) Kohn–Sham density functional theory. Spectral properties were computed utilizing a combined density functional and multi-reference configuration interaction (DFT/MRCI) method. Solvent effects were mimicked by a conductor like screening model and micro-hydration with four explicit water molecules. At selected points along a linearly interpolated path connecting the Franck–Condon region and the S1 minimum, spin–orbit interaction was computed employing a nonempirical mean-field Hamiltonian. For isoalloxazine, intersystem crossing (ISC) rate constants were computed, taking both direct and vibronic spin–orbit coupling into account.

On the basis of these calculations we suggest the following photo relaxation model. In the vacuum, efficient ISC ($k_{\text{ISC}} \approx 10^9 \text{s}^{-1}$) takes place between the primarily excited $1^1(n \rightarrow \pi^*)$ state ($S_1$) and the lowest $3^3(n \rightarrow \pi^*)$ state ($T_2$). The energetic proximity of the $1^1(n \rightarrow \pi^*)$ state ($S_2$) enhances the nonradiative relaxation of $S_1$ by internal conversion (IC). In aqueous solution these ISC and IC channels are energetically not accessible due to the blue shift of the $(n \rightarrow \pi^*)$ states. The high triplet quantum yield observed in experiment [J.T.M. Kennis, S. Crosson, M. Gauden, I.H.M. van Stokkum, K. Moffat, R. van Grondelle, Biochemistry 42 (2003) 3385–3392] is explained by the intersection between the $1^1(\pi \rightarrow \pi^*)$ state ($S_1$) potential energy hypersurface (PEH) and the second $3^3(\pi \rightarrow \pi^*)$ ($T_2$) PEH along the relaxation pathway and the strong enhancement of their spin–orbit coupling by vibronic interactions. The calculated ISC rate for this channel ($k_{\text{ISC}} \approx 10^4 \text{s}^{-1}$) is in good agreement with experimental results. According to our model, lack of an efficient IC channel leads to an increased fluorescence quantum yield in aqueous solution.