Effect of Structure and Medium on Photostability of Halogenated Boron(III), Zinc(II), and Cadmium(II) Dipyrromethenates

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Abstract—Photostability of B(III), Zn(II), Cd(II) complexes with monoiodo- and dibromosubstituted dipyrromethenes $[BF_2L]$ and $[ML_2]$ in benzene and cyclohexane solutions is studied. It is found that the mechanism of destruction of the dyes under UV radiation is based on participation of singlet oxygen generated by the excited triplet state of the dye. Singlet oxygen enters the oxidation reactions of the pigment molecules leading to accumulation of colorless products based on di-, monopyrrol, and smaller fragments. Initial stages of the process include the reactions of dehalogenation of the dye molecules and are accompanied by enhancement of the fluorescence of the formed alkyl-substituted dipyrromethenates. The photostability of boron complexes $[BF_2L]$ is up to 32 times higher as compared to that of $[ZnL_2]$ and $[CdL_2]$. The replacement of 4-iodo-dipyrromethene ligands in $[BF_2L]$ and $[ML_2]$ by 5,5'- or 4,4'-dibromo-substituted ligands increases photostability of the dyes. The stability of the dyes against UV irradiation substantially decreases in benzene with respect to cyclohexane due to enhancement of polarization of the chromophore systems of dipyrromethene ligands because of their solvation with benzene (π–π-stacking).

Keywords: boron(III), zinc(II), cadmium(II) dipyrromethenates, UV irradiation, photostability, mechanism, self-sensibilization, structural and solvation effects

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