The spectral manifestations of heavy atom effect on pi-electron system of tryptanthrin as a part of new effective drug

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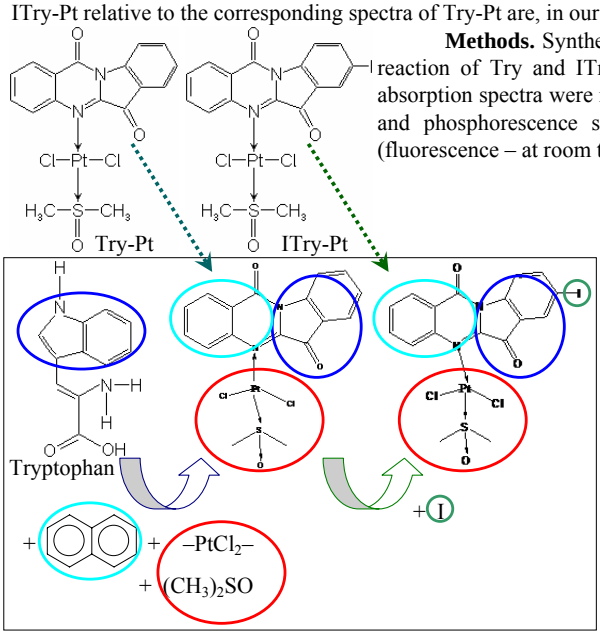
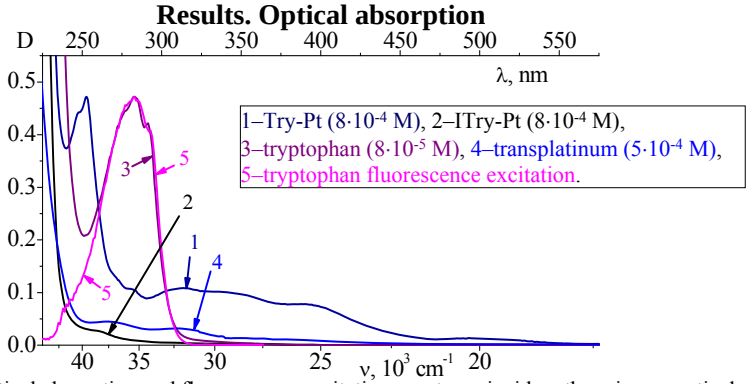
Tryptanthrin is a naturally occurring yellow indoloquinazoline alkaloid, the well-known pi-electron-containing compound. Tryptanthrin and its derivatives possess broad "spectrum" of health-care activities including anti-pathogenic, antibacterial, anticancer and anti-inflammatory due to its unique feature of binding to telomeric G4 DNA and stabilizing it. In particular, complexes based on iodo-tryptanthrin and bromo-tryptanthrin possess the higher anticancer activity than other tryptanthrin derivatives. The feature of tryptanthrin binding to G4 DNA can be used in nanobiotechnology for the development of new antitumor drugs.

Comparative investigations of optical absorption (at room temperature), fluorescence (at room temperature and T=78K) and phosphorescence (at T=78K) of the molecular complexes based on tryptanthrin (Try-Pt) and 8-iodo-tryptanthrin (ITry-Pt) with platinum chloride and DMSO were done. The positions of the first excited singlet (S_1) and triplet (T_1) energy levels of these complexes were obtained. The existence of two optical absorption centers in Try-Pt molecule was confirmed. The short-wave shift of optical absorption spectrum of ITry-Pt compared to the corresponding spectrum of Try-Pt as well as the appearance of new bands, the significant decrease of fluorescence intensity of ITry-Pt in contrast to the corresponding fluorescence intensity of Try-Pt, the short-wave shift of fluorescence and phosphorescence spectra of ITry-Pt relative to the corresponding spectra of Try-Pt are, in our opinion, the spectral manifestations of the effect of iodine atom on the pi-electron system of tryptanthrin.



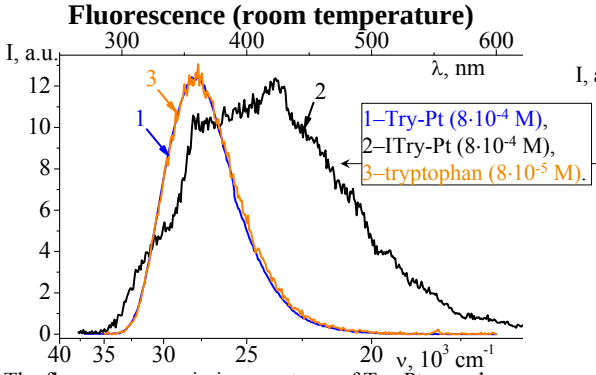
Methods. Synthesis and characterization of Try-Pt and ITry-Pt were performed as Tan and coworkers reported [2]. The reaction of Try and ITry with cis-$Pt(DMSO)_2Cl_2$ in CH_3OH and $CHCl_3$ (v:v= 5mL:5mL) at 55C afforded Try-Pt. Optical absorption spectra were recorded on a Cary 60 UV-Vis (Varian, Australia) spectrophotometer at room temperature. Fluorescence and phosphorescence spectra (emission and excitation) were recorded on a Horiba FluoroMax Plus spectrofluorometer (fluorescence – at room temperature and T=78K, phosphorescence at T=78K).

Results. Optical absorption



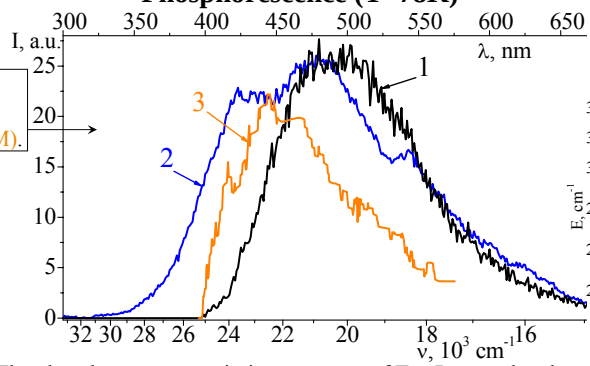
Tryptophan: optical absorption and fluorescence excitation spectra coincide – there is one optical center.
Try-Pt: there are two centers in optical absorption.
ITry-Pt: new bands appearing and the short-wave bands optical density significantly decreasing (compared to the Try-Pt) are the influence of iodine atom.

Fluorescence (room temperature)



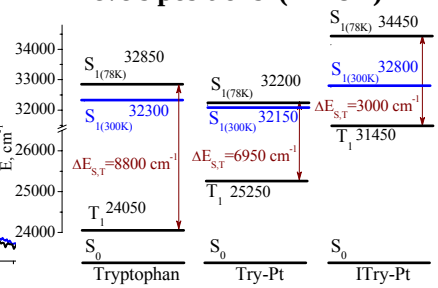
The fluorescence emission spectrum of Try-Pt complex coincides with fluorescence emission spectrum of Tryptophan – there is only one optical center (Tryptophan-like group).
ITry-Pt: A significant decrease in the fluorescence intensity and new bands appearing (compared to the Try-Pt) are the influence of iodine atom.
The same is for T=78K.

Phosphorescence (T=78K)



The phosphorescence emission spectrum of Try-Pt complex doesn't coincide with phosphorescence emission spectrum of Tryptophan – possibly: a few optical centers or excimers / some other complexes.
ITry-Pt: An phosphorescence / fluorescence intensities ratio increase and a shift of the short-wavelength edge of the phosphorescence spectrum to shorter wavelengths (compared to the Try-Pt) are the influence of iodine atom.

The scheme of the first excited singlet (S_1) and triplet (T_1) energy levels positions (T=78K)



The position of S_1 was estimated on the intersection of curves of the optical absorption and fluorescence spectra (for both T=300K and T=78K)
The position of T_1 was estimated on the shortwave edge of the phosphorescence spectrum curve.

Conclusions

1. The existence of two optical absorption centers in the Try-Pt molecule was confirmed.

2. A shift to the short-wavelength side and a decrease in the value of the optical density of the short-wave bands (related to the absorption of the pi-electron system) of the optical absorption spectrum of ITry-Pt in comparison with the corresponding spectrum of Try-Pt, as well as the appearance of new bands with maxima at wavelengths of 288 and 350 nm (related to the absorption of the iodine atom) are the spectral manifestation in the optical absorption of the effect of a "heavy atom" of iodine on the pi-electron system of tryptanthrin.

3. A significant decrease in the fluorescence intensity of ITry-Pt (~25 times) in relation to the corresponding fluorescence intensity of Try-Pt and the shift of the short-wavelength edge of the fluorescence spectrum of ITry-Pt towards shorter wavelengths relative to the corresponding spectrum of Try-Pt is a fluorescent manifestation of the known effect of a "heavy atom" of iodine on the pi-electron system of tryptanthrin.

4. An increase in the ratio of phosphorescence intensity to fluorescence intensity when an iodine atom is attached to the pi-electron system and a shift of the short-wavelength edge of the phosphorescence spectrum of the ITry-Pt complex to shorter wavelengths relative to the short-wavelength edge of the corresponding Try-Pt spectrum (as a result of a decrease in the energy difference between the singlet (S) and triplet (T) levels and an increase in the probability of the S-T transition) is a phosphorescent manifestation of the effect of the iodine atom on the pi-electron system of tryptanthrine.