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Letter to the Editors

Theoretical analysis of the fluorescence spectrum of hypocrellin A

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Hypocrellin A (HA) is a perylenequinonoid type photosensitizer that has attracted much attention owing to its excellent photosensitization properties [1–3]. Although considerable information pertaining to the photochemical and photobiological properties of HA have been obtained, some fundamental questions about its photophysics remain. For instance, the explanation for the fluorescence spectrum of HA is still under discussion. The fluorescence spectrum of HA consists of two peaks (~605 and ~655 nm) [4]. Diwu and co-workers attributed the peak at 605nm to neutral molecules of HA and the peak at 655nm to the zwitterionic form [1,2,5]; however, these assignments have not been confirmed experimentally.

It is known that the dipole moment of neutral molecules increases in excited state, while the dipole moment of zwitterions decreases [6]. Consequently in polar solvents, the fluorescence peak of the neutral molecules undergoes a red shift, and the peak for the zwitterionic molecules shifts towards the blue region. While Diwu and co-workers have measured the fluorescence spectrum of HA in different solvents, a quantitative analysis of the experimental data is lacking [4]. In view of this we deemed it worthwhile to analyse the results of Diwu and co-workers, in order to determine the molecular states corresponding to the two fluorescence peaks. Eq. (1) defines the dependence of fluorescence spectra on solvent polarity [7]:

$$\begin{aligned}\Delta\nu &= \nu^{\mathrm{sol(a)}} - \nu^{\mathrm{sol(f)}} \\ &= \nu^{0(\mathrm{a})} - \nu^{0(\mathrm{f})} \\ &\quad + 2\left[(\varepsilon_\mathrm{r}-1)/(2\varepsilon_\mathrm{r}+1) - \left(n^2-1\right)/\left(2n^2+1\right)\right] \\ &\quad \times \left|\mu_\mathrm{e}-\mu_\mathrm{g}\right|^2/\left(4\pi\varepsilon_0 hcaa_\mathrm{w}^3\right)\end{aligned} \tag{1}$$

where $\nu^{\mathrm{sol(a)}}$ and $\nu^{\mathrm{sol(f)}}$ are the wave numbers for the solvent-based electronic transitions corresponding to absorption and fluorescence, respectively; $\nu^{0(\mathrm{a})}$ and $\nu^{0(\mathrm{f})}$ are the corresponding wave numbers in the gas phase; ε_r and n are the bulk static relative permittivity and refractive index of the solvent, respectively; μ_g and μ_e are the permanent dipole moments of the ground state and excited-state molecule; a_w is the solvent cavity radius; ε_0 is the permittivity of the vacuum; a is a conversion constant; i.e. 100 cm m^{-1}; c is speed of light in a vacuum; h is Plank's constant. Since the lifetime of HA in the excited state, approximately 1 ns [8], is much longer than the relaxation time

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Table 1
Solvent dependence of the fluorescence spectrum of HA

Solvents	ε_r[a]	n[b]	$(\varepsilon_r-1)/(2\varepsilon_r+1)-(n^2-1)/(2n^2+1)$	$\Delta\nu_1$[c] (cm^{-1})	$\Delta\nu_2$[d] (cm^{-1})
Chloroform	4.81	1.4459	0.1495	676	1856
Tetrahydrofuran	7.58	1.4072	0.2124	797	1957
Methanol	32.66	1.3284	0.3112	890	2077
Dimethyl formamide	36.71	1.4305	0.2745	794	2021
Dimethyl sulfoxide	46.45	1.4793	0.2590	762	1985

[a] The bulk static relative permittivity of the solvent [9].

[b] The bulk static refractive index of the solvent [9].

[c] The Stoke's shift of 605nm peak [4].

[d] The Stoke's shift of 655nm peak [4].

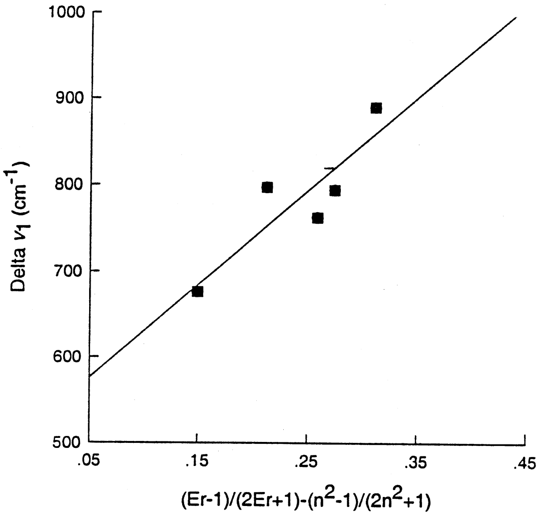

Fig. 1. Solvent dependence of 605 nm peak of the fluorescence spectrum of HA. $\Delta\nu_1$ is the Stoke's shift of 605 nm peak. In the calculation of $\mu_e-\mu_g$, a_w is 0.6 nm.

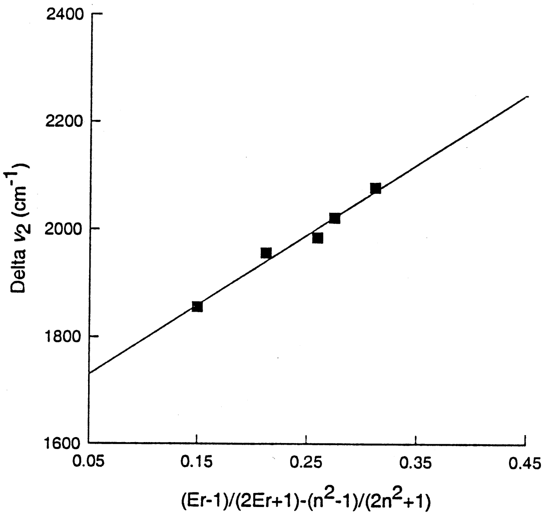

Fig. 2. Solvent dependence of 655 nm peak of the fluorescence spectrum of HA. $\Delta\nu_2$ is the Stoke's shift of 655 nm peak. In the calculation of $\mu_e-\mu_g$, a_w is 0.6 nm.

for the rearrangement of the solvent molecules, Eq. (1) would apply.

It can be seen from Table 1 that both peaks in the fluorescence spectrum of HA undergo a red shift in polar solvents, and Figs. 1 and 2 that there is a linear relationship between the Stoke's shifts of the two peaks and the solvent polarity. Accordingly, the $|\mu_e-\mu_g|$ of HA can be calculated to be 4.83 D for the peak at 605 nm and 5.29 D for the peak at 655nm. In view of the positive slopes in the two figures, we know $|\mu_e-\mu_g|=\mu_e-\mu_g$ for the two peaks. Since $\mu_e>\mu_g$ for both peaks, the two states must neutral molecules rather than zwitterions.

Acknowledgements

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