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Dipole moments of 4′-aminoflavonols determined using electro-optical absorption measurements or molecular Stark-effect spectroscopy

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Abstract

The electro-optical absorption measurements (EOAM) were used to measure the dipole moments of the normal form of 4′-(methoxy)-3-hydroxyflavone (FOM), 4′-(dimethylamino)-3-hydroxyflavone (FME), and 4′-*N*-(15-azacrown-5)-3-hydroxyflavone (FCR). For these probes the excited state intramolecular proton transfer (ESIPT) takes place. For comparison, the dipole moments of 4′-(dimethylamino)-3-methoxyflavone (FME3ME), for which ESIPT is lacking, were measured. In the case of FCR, FME, and FME3ME the equilibrated ground ($\boldsymbol{\mu}_g$) and excited Franck–Condon state ($\boldsymbol{\mu}_e^{FC}$) electrical dipole moments are parallel to each other and also parallel to the transition dipole moment. The electrical dipole moments of FCR, FME, and FME3ME in their ground state have values within the range $(14.1–17.7)\times10^{-30}$ C m. Upon optical excitation, the dipole moments increase by $(47.1–50.4) \times 10^{-30}$ C m. Among the studied flavonols, $\boldsymbol{\mu}_g$ and $\boldsymbol{\mu}_e^{FC}$ decrease in the order FME3ME > FCR > FME. This effect can be explained by the existence of an intramolecular H-bond for FCR and FME, which partly compensates a negative charge on the carbonyl oxygen in the ground state and thus diminishes the electron-donating ability of the amino-group in the excited Franck–Condon state. For FOM the equilibrated ground and excited Franck–Condon state dipole moments of the normal form have values of 9.4×10^{-30} C m and 26.3×10^{-30} C m, respectively. The smaller values of the dipole moments for FOM, in comparison with other flavonols, is caused by the absence in FOM of a strong electron-donating group, such as the amino-group. The dipole moments are not parallel and the angles between the different dipole moments are in the range 4–55°.

Keywords: Flavonols; Fluorescent probes; Dipole moments; Electro-optical absorption method

1. Introduction

Excited state intramolecular proton transfer (ESIPT) from the hydroxy-group to carbonyl oxygen is the reaction, which results in 3-hydroxyflavone and its derivatives in gigantic fluorescence Stokes shift of 7000–9000 cm^{-1} [1–6]. In 4′-*N*-alkylamino substituted flavones this reaction interplay with intramolecular charge transfer (ICT), which results in a fluorescence maximum at shorter wavelengths. The relative contribution of these two emission bands, one of which corresponds to the emission of the normal form (N*), and the other one to the flavonol phototautomer (T*), depends both on the substituents in the flavone molecule and on the nature of the solute's environment [7–13]. The latter effect is most beneficial for various biological applications through simple and convenient two-wavelength fluorescence detection [13–17]. From previous publications [7–13,18] it may be derived that the normal form has a large change of the dipole moment after transition to the excited state and that it is very sensitive to the medium polarity. This gives additional possibilities for monitoring the changes of physical properties of the probe surroundings, e.g. in biological membranes or in proteins.

Biological membranes are composed of the proteins and lipid bilayers. The local dielectric properties of membranes are of great importance for their function as they very much influence the electric forces between proteins or their segments. The lack of knowledge about the local dielectric constant of membranes has so far limited the progress in developing our understanding of the interactions between membrane proteins. The best known method for the estimation of the local dielectric constant in complex macromolecules is based on using standard equations, describing

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Abbreviations: FOM, 4′-(methoxy)-3-hydroxyflavone; FME, 4′-(dimethylamino)-3-hydroxyflavone; FME3ME, 4′-(dimethylamino)-3-methoxyflavone; FCR, 4′-*N*-(15-azacrown-5)-3-hydroxyflavone; ESIPT, excited state intramolecular proton transfer; ICT, intramolecular charge transfer; EOAM, electro-optical absorption measurements

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the dependence of the position of the electronic spectra of fluorescence probes on the dielectric constant and the refractive index of the solvent and on the dipole moments of the probe in its ground and excited states. If the dipole moments in the relevant electronic states are known, the local dielectric constant may be determined by these equations from the spectral position of the electronic spectra [19].

Electro-optical absorption and emission measurements in solution (molecular Stark-effect spectroscopy in terminology of [20,21]) provide valuable information about the values and directions of the dipole moments in the ground and excited states of solute molecules [19,22–26]. The strong advantage of the electro-optical measurements in comparison with the various existing solvent shift variants is that the dipole moments are determined in a single solvent, and hence it is possible to study the influence of the solvent on the process of intramolecular charge redistribution in the ground and excited electronic states. In addition, all solvent shift methods require an estimate of the probe cavity radius.

In this paper we present the results from electro-optical absorption measurements (EOAM) of the equilibrated ground and excited Franck–Condon state dipole moments of the normal form of 4′-(methoxy)-3-hydroxyflavone (FOM), 4′-(dimethylamino)-3-hydroxyflavone (FME), and 4′-*N*-(15-azacrown-5)-3-hydroxyflavone (FCR). For comparison, we also measured the dipole moments of 4′-(dimethylamino)-3-methoxyflavone (FME3ME), for which ESIPT is lacking.

2. Experimental

2.1. Flavonol synthesis

The flavonols (Fig. 1) have been synthesized from 2-hydroxyacetophenone and the corresponding benzaldehydes by the Algar–Flynn–Oyamada reaction [27,28] and purified by means of repeated recrystallization or column chromatography. All flavonols were homogeneous at thin-layer chromatography on Silufol UV-254 plates in chloroform–methanol (98:2, 95:5, 9:1 or 85:15, v/v) with following detection by UV excitation at 254 and 360 nm wavelengths. Their structures have been confirmed by quantitative elemental analysis, proton magnetic resonance (PMR), UV–Vis and infrared (IR) spectrometry.

The basic physical–chemical characteristics of flavonols correspond to those presented previously [10,11].

2.2. Other chemical procedures and sample preparation

All solvents and reagents were obtained from Merck and some of them were additionally purified by the methods described in [29]. The purified solvents were thoroughly dried prior to use in the electro-optical measurements. The purity of the solvents was checked by UV absorption measurements (1 cm cell; reference air).

3. Electro-optical absorption measurements

To determine the ground and excited state dipole moments of the normal form, we used EOAM. Experimental details on the electro-optical methods have been reviewed extensively [30,31]. Using Liptay's formalism [32] the effect of an external electric field E_f on the molar absorption coefficient $\kappa(\tilde{\nu})$ can be described by a quantity L, which is defined by

$$L = L(\tilde{\nu}, \chi) = \frac{\kappa^\mathrm{E}(\tilde{\nu}, \chi) - \kappa(\tilde{\nu})}{\kappa(\tilde{\nu}) E_\mathrm{f}^2} \qquad (1)$$

where κ^E is the molar absorption coefficient in presence of an applied electric field, κ the same without applied electric field, χ the angle between the direction of E_f and the electric field vector of the incident light and $\tilde{\nu}$ the wavenumber. For

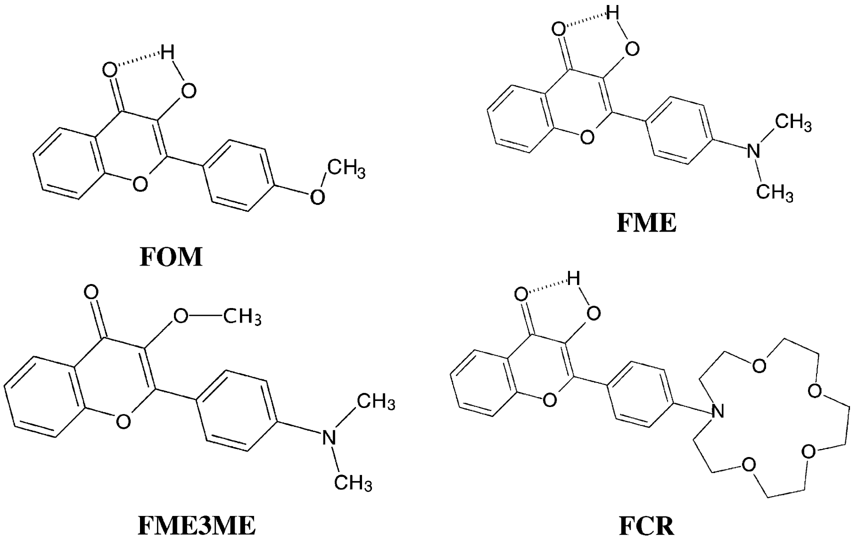

Fig. 1. Fluorescence probes studied in this work.

a homogeneously broadened absorption band L is given by the following equation:

$$L = Dr + \tfrac{1}{6}Es + Frt + Gst + Hru + Isu \qquad (2)$$

where the parameters r and s are determined by the angle χ, and the quantities t and u depend on the first and second derivatives of the absorption spectrum:

$$r = \tfrac{1}{5}(2 - \cos^2\chi) \qquad (3)$$

$$s = \tfrac{1}{5}(3\cos^2\chi - 1) \qquad (4)$$

$$t = \left(\frac{1}{hc}\right)\left(\frac{\kappa}{\tilde{\nu}}\right)^{-1}\frac{\mathrm{d}(\kappa/\tilde{\nu})}{\mathrm{d}\tilde{\nu}} \qquad (5)$$

$$u = \left(\frac{1}{2h^2c^2}\right)\left(\frac{\kappa}{\tilde{\nu}}\right)^{-1}\frac{\mathrm{d}^2(k/\tilde{\nu})}{\mathrm{d}\tilde{\nu}^2} \qquad (6)$$

The coefficients D, E, F, G, H, I are connected with intrinsic properties of the solute molecules. Neglecting explicit polarizability terms D to I can be written as

$$D = \left(\frac{f_\mathrm{e}^2}{kT}\right)\mathbf{R}^{(1)}\boldsymbol{\mu}_\mathrm{g} \qquad (7)$$

$$E = \left(\frac{f_\mathrm{e}}{kT}\right)^2[3(m_\mathrm{a}\boldsymbol{\mu}_\mathrm{g}) - \boldsymbol{\mu}_\mathrm{g}^2] + \left(\frac{f_\mathrm{e}^2}{kT}\right)(3\mathbf{R}^{(2)} - 2\mathbf{R}^{(1)})\boldsymbol{\mu}_\mathrm{g} \qquad (8)$$

$$F = \left(\frac{f_\mathrm{e}^2}{kT}\right)(\boldsymbol{\mu}_\mathrm{g}\Delta^\mathrm{a}\boldsymbol{\mu}) + f_\mathrm{e}^2\mathbf{R}^{(1)}\Delta^\mathrm{a}\boldsymbol{\mu} \qquad (9)$$

$$G = \left(\frac{f_\mathrm{e}^2}{kT}\right)(\mathbf{m}_\mathrm{a}\boldsymbol{\mu}_\mathrm{g})(\mathbf{m}_\mathrm{a}\Delta^\mathrm{a}\boldsymbol{\mu}) + \left(\frac{f_\mathrm{e}^2}{2}\right)\mathbf{R}^{(2)}\Delta^\mathrm{a}\boldsymbol{\mu} \qquad (10)$$

$$H = f_\mathrm{e}^2(\Delta^\mathrm{a}\boldsymbol{\mu})^2 \qquad (11)$$

$$I = f_\mathrm{e}^2(\mathbf{m}_\mathrm{a}\Delta^\mathrm{a}\boldsymbol{\mu})^2 \qquad (12)$$

where k is the Boltzman constant, T the temperature, $\mathbf{m}_\mathrm{a}$ the unit vector in the direction of the transition moment for absorption, $\boldsymbol{\mu}_\mathrm{g}$ the equilibrated ground state dipole moment vector, $\Delta^\mathrm{a}\boldsymbol{\mu}$ the change of the dipole moment vector upon excitation to the considered Franck–Condon excited state. The vectors $\mathbf{R}^{(1)}$ and $\mathbf{R}^{(2)}$ are related to the transition polarizability of the considered transition and describe the effects due to the electric field dependence of the transition moment. The field correction is done by the cavity field factor f_e [32] which in the case of the 1,4-dioxane used in this work amounts to 1.22.

The quantity $L(\tilde{\nu}, \chi)$ in the present work was determined for two values of the angle χ ($\chi = 0$ and $\chi = \pi/2$) and for a set of wavenumbers within the first absorption band. Then the coefficients (8)–(12) and their standard deviations were obtained by the program SYSTAT, Version 7.0.

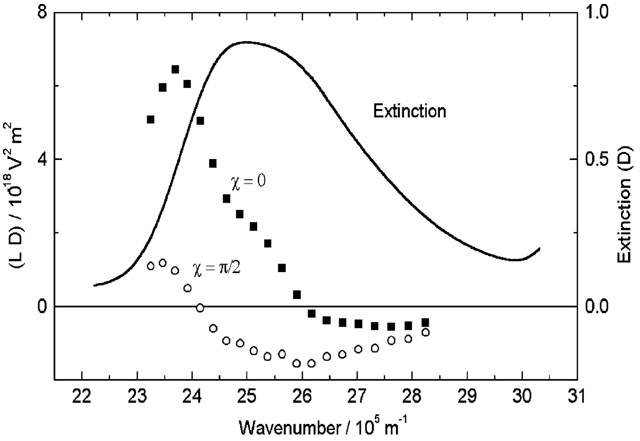

Fig. 2. Absorption and electro-optical absorption spectra of FCR in 1,4-dioxane at $T = 298$ K.

4. Results and discussion

The electro-optical absorption spectra of all four flavonols are accurately reproducible, and have the maximum at the red edge of the absorption spectrum. As an example, the experimental data points of the electro-optical absorption spectra of FCR in 1,4-dioxane are shown in Fig. 2.

In the case of FCR, FME, and FME3ME follows from our measurements that the coefficient F equals G and coefficient H equals I, within the experimental error. This means that $\mathbf{m}_\mathrm{a}||\boldsymbol{\mu}_\mathrm{g}||\Delta^\mathrm{a}\boldsymbol{\mu}$. The same result follows from the slope of the linear function $L(\nu, \chi = 0) = f[L(\nu, \chi = \pi/2)]$ which for solute molecules with C_n—symmetry is given in good approximation by the simple linear relationship [33–35]:

$$L(\nu, \chi = 0) = AL\left(\nu, \chi = \frac{\pi}{2}\right) + \frac{Bf_\mathrm{e}^2\mu_\mathrm{g}^2}{6k^2T^2} \qquad (13)$$

where $A = (1 + 2\cos^2\theta)/(2 - \cos^2\theta)$; $B = (3\cos^2\theta - 1)/(2 - \cos^2\theta)$ and θ is the angle between $\mathbf{m}_\mathrm{a}$ and $\boldsymbol{\mu}_\mathrm{g}$.

Fig. 3 shows the respective plot of $L(\nu, \chi = 0)$ versus $L(\nu, \chi = \pi/2)$ for FCR in 1,4-dioxane. The points represent the experimental data and the line is their approximation by a linear regression. From the linearity of the function $L(\nu, \chi = 0) = f[L(\nu\chi = \pi/2)]$ for FCR, FME, and FME3ME follows that the first absorption band of the studied probes is sufficiently homogeneous and that the angle between the vectors $\mathbf{m}_\mathrm{a}$ and $\boldsymbol{\mu}_\mathrm{g}$ is constant over the measured wavenumber interval in according with Eq. (13). From the slope of the function $L(\nu, \chi = 0) = f[L(\nu\chi = \pi/2)]$ for FCR, FME, and FME3ME we found that the coefficient $A \cong 3$. From Eq. (13) follows that in this case $\mathbf{m}_\mathrm{a}||\boldsymbol{\mu}_\mathrm{g}||\Delta^\mathrm{a}\boldsymbol{\mu}$.

As an example in Table 1 the results of three independent electro-optical absorption measurements on FCR in 1,4-dioxane solutions at $T = 298$ K are presented. As follows from the table, the reproducibility of measurements is fine. The coefficients (7)–(12) and their standard deviations were obtained with the assumption $F = G$ and $H = I$.

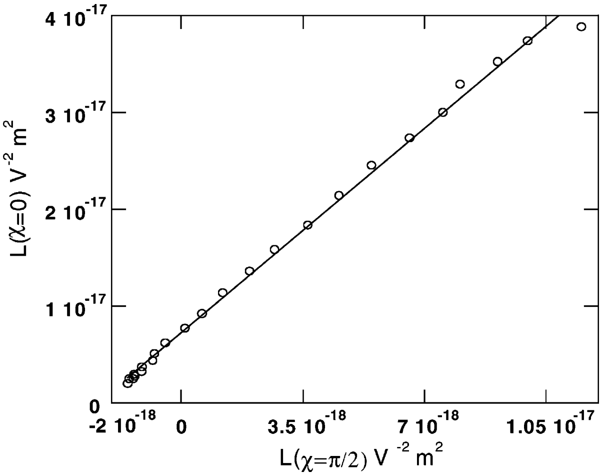

Fig. 3. Plot of $L(\nu, \chi = 0)$ versus $L(\nu, \chi = \pi/2)$ of FCR in 1,4-dioxane at $T = 298$ K. The points show the experimental data and the line is their approximation by a linear fit.

Using the symmetry condition $\mathbf{m}_a || \boldsymbol{\mu}_g || \Delta^a \boldsymbol{\mu}$ the values of the dipole moments $\boldsymbol{\mu}_g$ and $\Delta^a \boldsymbol{\mu}$ were calculated from

$$\boldsymbol{\mu}_g = \left(\frac{kT}{f_e}\right)\sqrt{\frac{E - 6D}{2}} \tag{14}$$

$$\Delta^a \boldsymbol{\mu} = \left(\frac{kT}{f_e^2}\right)\frac{F}{\boldsymbol{\mu}_g} \tag{15}$$

The dipole moment in the excited Franck–Condon state ($\boldsymbol{\mu}_e^{FC}$) was determined by the formula

$$\Delta^a \boldsymbol{\mu} = (\boldsymbol{\mu}_e^{FC} - \boldsymbol{\mu}_g) \tag{16}$$

Table 3
Electro-optical coefficients obtained by EOAM for FOM in 1,4-dioxane at $T = 298$ K for two independent measurements[a]

Coefficient	Measurements	
	First	Second
D ($\times 10^{-20}$ V^{-2} m^2)	17.3 ± 11.3	26.6 ± 6.2
E ($\times 10^{-20}$ V^{-2} m^2)	713.9 ± 48.2	753.6 ± 34.0
F ($\times 10^{-40}$ C V^{-1} m^2)	357.7 ± 30.8	384.1 ± 22.0
G ($\times 10^{-40}$ C V^{-1} m^2)	495.6 ± 20.7	552.7 ± 17.1
H ($\times 10^{-60}$ C2 m^2)	564.0 ± 63.4	619.4 ± 43.1
I ($\times 10^{-60}$ C^2 m^2)	527.2 ± 51.2	572.7 ± 37.2

[a] The coefficients and their standard deviations were obtained from fitting of the experimental L values by the program SYSTAT, Version 7.0 according to Eq. (2).

which is sufficiently valid for non-polar solvents. The dipole moments obtained as an average over several independent EOAM measurements in 1,4-dioxane at $T = 298$ K are shown in Table 2.

The amino-group in the side ring of 3-hydroxyflavone has a substantial influence on the π-electron density distribution in the ground state, and an even more stronger influence in the excited S_1-state [13]. From our results follows that the intramolecular H-bond between the hydroxy-group and carbonyl oxygen in the normal form (Fig. 1) also plays some role in the charge distribution. Among the studied flavonols (see Table 2), the value of the dipole moment $\boldsymbol{\mu}_g$ is lower for FCR and FME than in the case of FME3ME. This can be understood with the existence of an intramolecular H-bond in the case of FCR and FME, which partly compensates a negative charge on the carbonyl oxygen.

The value of the change of the dipole moment vector after excitation to the Franck–Condon state $\Delta^a \boldsymbol{\mu}$ is somewhat

Table 1
Electro-optical coefficients obtained by EOAM for FCR in 1,4-dioxane at $T = 298$ K for three independent measurements[a]

Coefficient	Measurements		
	First	Second	Third
D ($\times 10^{-20}$ V^{-2} m^2)	69.7 ± 14.5	85.0 ± 24.4	177.1 ± 47.0
E ($\times 10^{-20}$ V^{-2} m^2)	4858.4 ± 79.3	4521.3 ± 116.2	5002.8 ± 170.0
$F = G$ ($\times 10^{-40}$ C V^{-1} m^2)	2596.2 ± 28.6	2664.5 ± 30.8	2601.8 ± 62.9
$H = I$ ($\times 10^{-60}$ C2 m^2)	2415.7 ± 94.2	2189.9 ± 166.6	2418.7 ± 169.1

[a] The coefficients and their standard deviations were obtained from fitting of the experimental L values by the program SYSTAT, Version 7.0 according to Eq. (2).

Table 2
The average values of the dipole moments of FCR, FME, and FME3ME in 1,4-dioxane at $T = 298$ K obtained from several independent EOAM measurements

Molecule	$\boldsymbol{\mu}_g$[a] ($\times 10^{-30}$ C m)	$\Delta^a \boldsymbol{\mu}$[b] ($\times 10^{-30}$ C m)	$\boldsymbol{\mu}_e^{FC}$ ($\times 10^{-30}$ C m)[c]
FCR	15.3 ± 0.4	47.1 ± 1.6	62.5 ± 1.2
FME	14.1 ± 0.1	45.1 ± 0.95	59.2 ± 0.95
FME3ME	17.7 ± 0.05	50.4 ± 1.6	68.1 ± 1.5

[a] The dipole moment in the equilibrium ground state.

[b] The change of the dipole moment vector after excitation to the Franck–Condon state.

[c] The dipole moment in the excited Franck–Condon state.

Table 4
The average values of the dipole moments of FOM in 1,4-dioxane at $T = 298\,\mathrm{K}$ obtained from two independent EOAM measurements

$\boldsymbol{\mu}_g$ ($\times 10^{-30}$ C m)[a]	$\Delta^a\boldsymbol{\mu}$ ($\times 10^{-30}$ C m)[b]	$\boldsymbol{\mu}_e^{FC}$ ($\times 10^{-30}$ C m)[c]	$\angle(\mathbf{m}a^{d}, \boldsymbol{\mu}_g)$	$\angle(\mathbf{m}a, \Delta^a\boldsymbol{\mu})$	$\angle(\mathbf{m}a, \boldsymbol{\mu}_e^{FC})$	$\angle(\boldsymbol{\Delta}^a\boldsymbol{\mu}, \boldsymbol{\mu}_g)$
9.4 ± 0.5	19.9 ± 0.5	26.3 ± 0.7	41 ± 1°	14 ± 1°	4 ± 1°	55 ± 2°

[a] The dipole moment in the equilibrium ground state.
[b] The change of the dipole moment vector after excitation to the Franck–Condon state.
[c] The dipole moment in the excited Franck–Condon state.
[d] The transition dipole moment.

larger for FME3ME than for FCR and FME. This means that the intramolecular H-bond diminishes the electron-donating ability of the different substituted-groups in 4′-position of the flavonols. On the contrary, in case of FME3ME, the OCH_3-group instead of OH in FME and FCR enhances the electron-accepting power of the carbonyl oxygen. Also, the comparably larger values of the dipole moment of FME3ME in the ground and excited Franck–Condon states as well indicates a planar conformation of the FME3ME molecule in these states, despite the sterical hindrance of the 3-OCH_3-group. Otherwise the values of the dipole moments would be much less.

In the case of FOM in 1,4-dioxane at $T = 298\,\mathrm{K}$ the situation is more complicated as compared to FCR, FME, and FME3ME. The electro-optical coefficients F and G, as well as H and I are not equal to each other (see Table 3) and the function $L(\nu, \chi = 0) = f[L(\nu\chi = \pi/2)]$ is not linear (see Fig. 4). In this case, Eq. (13) is no longer valid.

From the above mentioned results follows that the vectors $\boldsymbol{\mu}_g$ and $\Delta^a\boldsymbol{\mu}$ are not parallel to each other, and both are not parallel to $\mathbf{m}_a$ in the case of FOM. This difference between FOM and another flavonols may be explained in the following way. As was mentioned above, in FME3ME, FCR, and FME the amino-group has a substantial influence on the π-electron density distribution, both in the ground and excited state. In contrast, in FOM, due to the absence of a strong electron-donating group, the charge distribution is not only determined by the methyl-group, but also by the heterocyclic oxygen and chromone part of the molecule. In this situation the vectors $\boldsymbol{\mu}_g$ and $\Delta^a\boldsymbol{\mu}$ may not be parallel to each other and to $\mathbf{m}_a$, too.

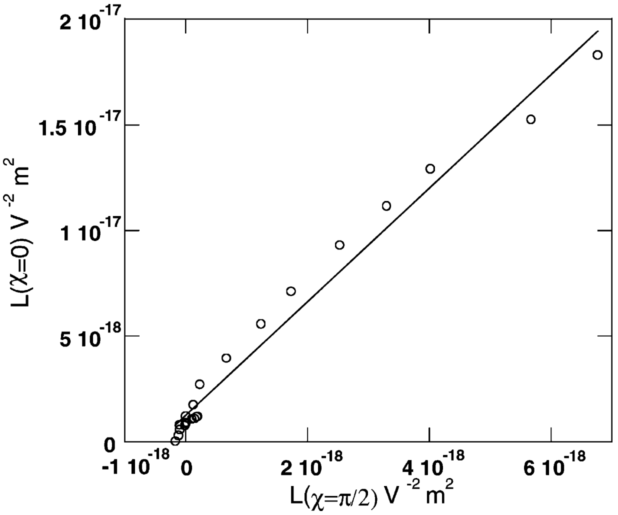

Fig. 4. Plot of $L(\nu, \chi = 0)$ versus $L(\nu, \chi = \pi/2)$ of FOM in 1,4-dioxane at $T = 298\,\mathrm{K}$. The points show the experimental data and the line is their approximation by a linear fit.

Assuming all vectors to lie in one plane and neglecting transition polarizability effects the values of the dipole moments and the angles between different vectors for FOM can be calculated using (8)–(12). The average values from two independent EOAM measurements are shown in Table 4. As follows from Table 4, the dipole moments of FOM in the ground state and especially in the excited Franck–Condon state are much less than for FME3ME, FCR, and FME.

5. Conclusions

As follows from our experiments in the case of FCR, FME, and FME3ME the equilibrated ground and excited Franck–Condon state electrical dipole moments are parallel to each other and also parallel to the transition dipole moment. The electrical dipole moments of the normal form of FCR, FME, and FME3ME in the ground state have values within the range $(14.1\text{–}17.7) \times 10^{-30}\,\mathrm{C\,m}$. Upon optical excitation the dipole moments increase by $(47.1\text{–}50.4) \times 10^{-30}\,\mathrm{C\,m}$. This increase of the dipole moments is much larger than in the case of the parent 3-hydroxyflavone [21] and can be explained by intramolecular charge transfer from the amino-group to the carbonyl-group. Among the studied flavonols, $\boldsymbol{\mu}_g$, $\Delta^a\boldsymbol{\mu}$, and $\boldsymbol{\mu}_e^{FC}$ of FME3ME are much larger then those of FCR and FME. This effect can be explained by the existence of an intramolecular H-bond in the case of FCR and FME, which partly compensates a negative charge on the carbonyl oxygen in the ground state and diminishes an electron-donating ability of the amino-group in the excited Franck–Condon state.

In the case of FOM the situation is unlike that for FCR, FME, and FME3ME. The equilibrated ground and excited Franck–Condon state electrical dipole moments of the normal form are smaller, only 9.4×10^{-30} and $26.3 \times 10^{-30}\,\mathrm{C\,m}$, respectively. The dipole moments are not parallel and the angles between the different dipole moments are in the range 4–55°. This effect can be explained by the different contribution of the methyl-group, the heterocyclic oxygen and chromone part of the molecule to the charge distribution in the ground and excited states.

From our results follows, that due to the large values of the electric dipole moments of the normal form of FCR, FME, and FME3ME, these fluorescent probes are very promising for studying the micropolarity in different systems.

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