Notes

Linearity relationship between solvatochromic shifts of stilbazolium-like dyes and modified reaction field function

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We analyzed statistically the linear correlation of the solvatochromic shifts of the stilbazolium-like dyes in the nonselected solvents with the reaction field function, $L(\varepsilon_r) - bL(n^2)$, and the solvent polarity parameter, E_T^N, respectively, and observed that there were not perfectly linearity relationships between them, so we introduced E_T^N into $L(\varepsilon_r) - bL(n^2)$ to form a new reaction field function, $L(\varepsilon_r) - bL(n^2) + g E_T^N$, called as the modified reaction field function, which can be perfectly linearly correlated with the solvatochromic shifts of the stilbazolium-like dyes in the nonselected solvents.

Keywords   Stilbazolium-like dye, solvatochromic shift, modified reaction field function

Introduction

Lots of interests have been put on the solvatochromic shifts, *e. g.*, the absorption maxima, the fluorescence emission maxima and the Stockes shifts in the last decade. The McRae-Bayliss model[1,2] and its analogs[3-7] are very popular for treating the solvatochromic shifts, because of their relatively simple equations and the calculation processes, but these models may usually only satisfy the solvatochromic shifts of a solute bearing charge transfer (CT) transition in some selected solvents other than in the nonselected solvents.[8-11]

The $E_T(30)$[12,13]-value, the Reichardt's solvent polarity scale, defined by the transition energy of the standard dye[12] in different solvents, or its normalized scale E_T^N-value,[13] have been introduced for correlating

the solvatochromic shifts of some solutes. Reichardt *et al.* reported that the absorption maxima of the derivatives of the pyridinium-N-phenoxide betaine dye,[12] so called the standard dye, could be perfectly in a linear reationship correlated with the E_T^N-values.[14] Ravi *et al.* have also reported that the absorption maxima of stilbene derivatives and dicyanovinyl-substituted aromatics in some selected solvents can be also in a good linear reationshipcorrelated with the E_T^N-values.[15] The above two cases mean that the solvatochromic shifts of the solute with CT transition could be better correlated with the E_T^N-values than with the reaction function based on the McRae-Bayliss model and its analogs.

The experiments have shown that the solvatochromic shifts of the stilbazolium-like dyes, bearing strong CT transition, are of a low-grade correlation with the solvent reaction field function, but could be better also correlated with the E_T^N-values, in which all of the solvents used are obviously divided into two groups in the linear correlations with relatively high linear fitting coefficients, which are the first experimental results best to our knowledge. So we assume that the E_T^N-value plays another important role in the solvent influence on the solvatochromic shifts of the stilbazolium-like dyes besides the bulk static relative permittivity and refractive index of the solvent.

In this note, we analyzed statistically the linear correlation of the solvatochromic shifts of the stilbazolium-like dyes in the nonselected solvents with the reac-

tion field function, $L(\varepsilon_r) - b\,L(n^2)$, and the E_T^N, respectively, and introduced E_T^N into $L(\varepsilon_r) - b\,L(n^2)$ to form a new reaction field function, $L(\varepsilon_r) - b\,L(n^2) + g\,E_T^N$, called as the modified reaction field function, which could be perfectly linearly correlated with the solvatochromic shifts of the stilbazolium-like dyes in the nonselected solvents.

Experimental

The stilbazolium-like dyes, which are trans-R-(4-N-methylpyridinio)-stilbazolium iodide, and named as DAPSI, MPSI, PSI, MPPSI, PPSI, FPSI and TPSI, where the corresponding substitutes are R = 4-N, N-dimethylaminobenzenyl, 4-methylbenzenyl, benzenyl, N-methyl-pyrrol-2-yl, pyrrol-2-yl, furan-2-yl and thiophen-2-yl, respectively, were synthesized in our laboratory and characterized by using UV-vis, fluorescence and ^{1}H NMR spectroscopy and elemental analysis.

The dye's absorption maxima ν_a^{sol} and fluorescence emission maxima ν_f^{sol} were measured with Hitachi 557 UV-vis spectrophotometer and Hitachi 850 fluorescence spectrophotometer with a maximum wavelength uncertainty of ± 0.1 nm in nonselected solvents, which were analytical grade reagents and purchased from Beijing Chemi-

cal Factory of China, including 1. chloroform, 2. p-methylpyridine, 3. cyclopentanone, 4. cyclohexanone, 5. 2-butanone, 6. acetic acid, 7. acetone, 8. butanitrile, 9. N, N-dimethylacetamide (DMAC), 10. N, N-dimethylformamide (DMF), 11. dimethyl sulfoxide (DMSO), 12. acetonitrile, 13. dichloromethane, 14. 1,2-dichloroethane, 15. nitrobenzene, 16. ethyl acetoacetate, 17. acetylacetone, 18. ethanol, 19. formic acid, 20. methanol, 21. formamide, 22. water. Here the word "nonselected" means that the above twenty-two solvents are selected randomly.

Because the absorption maxima of the dyes variate from about 480 nm for DAPSI to 340 nm for PSI with variating the electron-donating ability of the donor, so some of solvents whose absorption bands overlap with those of dye in these solvents will be omitted. For examples, nitrobenzene is omitted for the dyes except DAPSI, and cyclopentanone, cyclohexanone, ethyl acetoacetate, and acetylacetone are omitted for FPSI, TPSI, PSI, and MPSI, formic acid is omitted for PSI, MPSI and DAPSI.

Theoretical background

According to the McRae-Bayliss model, the transition energy of the solute molecule in solution is given by

$$\nu_a^{sol} = \nu_a^{gas} - \left[(\mu_g\,\mu_e\,\cos\phi - \mu_g^2)/a_w^3\right]\cdot\left[L(\varepsilon_r) - L(n^2)\right] - \left[(\mu_e^2 - \mu_g^2)/a_w^3\right]\cdot\left[L(n^2)\right] \tag{1}$$

where ν_a is the transition energy (cm^{-1}) in solution (sol) and in gas phase (gas), μ_g and μ_e are the ground state and the excited state dipole moments (C·m), respectively, and ϕ is the angle between them, a_w is the solute cavity radius (m^3). $L(\varepsilon_r)$ and $L(n^2)$ are reaction field functions defined by $L(x) = 2(x-1)/(2x+1)$ with $x = \varepsilon_r$, n^2, where ε_r and n are the bulk static relative permittivity and refractiveindex of the solvent, respectively.

It is informative to rewrite Eq. (1) by taking out the common terms to form Eq. (2):

$$\nu_a^{sol} = \nu_a^{gas} + K_a\left[(L(\varepsilon_r) - b\,L(n^2)\right] \tag{2}$$

where $L(\varepsilon_r) - b\,L(n^2)$ is named as reaction field function and $K_a = (\mu_g^2 - \mu_g\,\mu_e\,\cos\phi)/a_w^3$, $b = (\mu_e^2 - \mu_g\mu_e\cos\phi)/(\mu_g^2 - \mu_g\mu_e\,\cos\phi)$. In general, the b and

K_a-values were determined when the maximal correlation coefficient (γ) was obtained for the correlation of the experimental data of ν_a^{sol} and $L(\varepsilon_r) - b\,L(n^2)$.

As we have known that the McRae-Bayliss model and its analogs were used for describing the interactions between the neutral or weak-dipole solute and solvents, so they were only valid for the neutral or weak-dipole solutes and some limited strong-dipole solutes in some selected solvents,[8-11] and usually we were not able to obtain a satisfied correlation coefficient from Eq. (2) in the nonselected solvents, especially for the strong-dipole solutes and ion-type solutes, as proved by many experiments. In addition, it was observed by us and other groups[14,15] that the solvatochromic shifts of some solutes bearing strong CT transition, including the stilbazolium-like dyes, were of relatively good linear correlation with the E_T^N-values. This is because that the E_T^N-values

mainly describe the interactions of the strong dipole-dipole, and dipole-induced-dipole as well as ion-dipole and ion-induced-dipole between the standard dye and solvent. So we next turn to correlate the differences between the calculated values from Eq. (2), $(\nu_a^{sol})^{calcd}$, and the observed values, ν_a^{sol}, e. g., $\Delta(\nu_a^{sol}) = \nu_a^{sol} - (\nu_a^{sol})^{calcd}$ with E_T^N-values, if there is a good enough linear correlation, Eq. (3) could be given:

$$\nu_a^{sol} = \nu_a^{gas} + L_1{}^a + K_a[L(\epsilon_r) - b\ L(n^2)] + L_2{}^a\ E_T^N =$$

where $A_a = \nu_a^{gas} + L_1{}^a$ is the intercept, $g_a = L_2{}^a/\ K_a$, $L(\epsilon_r) - b\ L(n^2) + g_a E_T^N$ is called modified reaction field function, here "a" denotes the absorption. Similarly, the similar equations for the fluorescence emission maxima and the Stockes shifts can be given out by replacing ν_a with ν_f and $(\nu_a - \nu_f)$ and replacing the down mark "a" with "f" and "s", where "f" and "s" denote the fluorescence emission maxima and the Stockes shifts, respectively.

In this paper, the b and g-values, including g_a, g_f and g_s-values which are relative to the absorption, fluorescence maxima and Stockes shifts, are determined as the following process: At first, a set of selected b-values give out a set of $L(\epsilon_r) - bL(n^2)$, then the best correlation coefficient (γ) and the best fitting b-value will be obtained from the correlation between the $L(\epsilon_r) - bL(n^2)$ and the solvatochromic shifts. Sequentially, a set of selected g-values also give out a set of $L(\epsilon_r) - bL(n^2) + gE_T^N$, from the correlation between the modified reaction field function and the solvatochromic shifts, the best linear relationship and the best fitting g-value will be obtained.

Results and discussion

Correlation with reaction field function $L(\epsilon_r) - bL(n^2)$

After selecting a set of b-values as 0.10, 0.20, 0.30···, we could obtain a set of γ-values for all of the experimental data ν_a^{sol}-values in the nonselected solvents according to Eq. (2). A plot of γ-values vs. the b-values (not shown) indicates that the best fitting γ-value can be obtained for DAPSI, PPSI and FPSI when b-val-

$$\Delta(\nu_a^{sol}) = L_1{}^a + L_2{}^a E_T^N \tag{3}$$

where $L_1{}^a$ and $L_2{}^a$ are the intercept and slope. In general, they were also determined when the maximal correlation coefficient (γ) was obtained for the correlation of the $\Delta(\nu_a^{sol})$ and E_T^N. Then, the sum of Eqs. (2) and (3) gives

$$A_a + K_a[L(\epsilon_r) - b\ L(n^2) + g_a E_T^N] \tag{4}$$

ue is about 0.50, which is used for other dyes in this paper, but all of the γ-values are below 0.922.

As an example, we give out plots of the ν_a^{sol} or ν_f^{sol} of DAPSI vs. the reaction field function, L ($\epsilon_r - b$ L (n^2), in Fig. 1 (a) and (b), respectively, from which we can see that a dispersed distribution appears for all of the experimental points, and the linear correlation coefficients are 0.625 and 0.733 (the first and second lines in Table 1), respectively. This means that such plots are in a very low-grade linear correlation. The similar results can be also obtained for the other dyes (Table 1). Such experimental facts indicate that we can not obtain the satisfied linear correlation between the solvatochromic shifts and the reaction field function according to Eqs. (1) or (2).

We have known that the stilbazolium-like dye's molecule is a kind of quasi one-dimensional ionic molecule, so the interactions of the dye and solvent molecules could be influenced by the presence of the cation, in which the ion-dipole, and ion-induced dipole as well as the strong dipole-dipole and dipole-induced dipole forces should be considered in the model. Thus, the McRae-Bayliss model and its analogs, in which the solute molecule is limited to sphere and the interactions between the solute and the surrounding medium are limited to the dipole-dipole and dipole-induced dipole forces,[1,2,16] are invalid in our cases, so Eqs. (1) and (2) can not satisfactorily interpret the solvatochromic shifts of the dyes.

Noted that the intercepts of the linear correlations between the solvatochromic shifts and the reaction field function represent the solvatochromic shifts in gas phase for each dye as given in Eqs. (1) and (2).
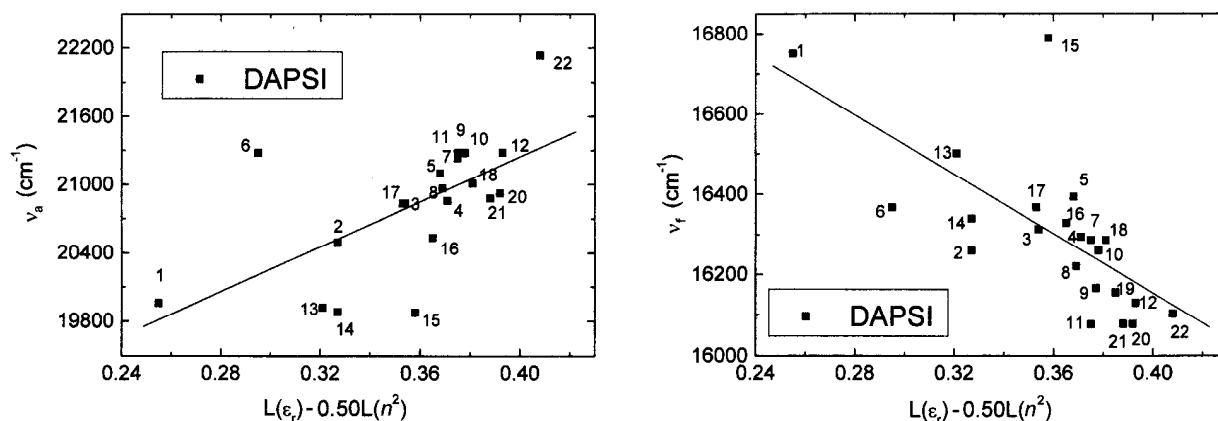
Fig. 1 Plots of the correlation between the absorption maxima (a) and fluorescence emission maxima (b) of DAPSI and the reaction field function, $L(\varepsilon_r) - b\ L(n^2)$, with $b = 0.50$. The number codes of the solvents are given in the experimental part.

Table 1 Linear correlation coefficients γ of the linear fitting between the absorption maxima ν_a^{sol} and fluorescence emission maxima ν_f^{sol} of seven dyes and the reaction field function in the nonselected solvents

Dyes	MPPSI		PPSI		FPSI		TPSI		PSI		MPSI		DAPSI	
	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}
γ	0.715	0.488	0.791	0.632	0.745	0.727	0.701	0.500	0.751	0.564	0.716	0.600	0.625	0.733
N	21	21	21	21	17	17	17	17	16	16	16	16	21	22[a]

[a] Including formic acid.

Correlation with solvent polarity parameter E_T^N

The solvent polarity parameter E_T^N gives a signifi-

cant influence on the solvatochromic shifts of the stil-bazolium-like dyes. Fig. 2 shows plots of ν_a^{sol} or ν_f^{sol} of DAPSI vs. E_T^N, from which we can see that all of the
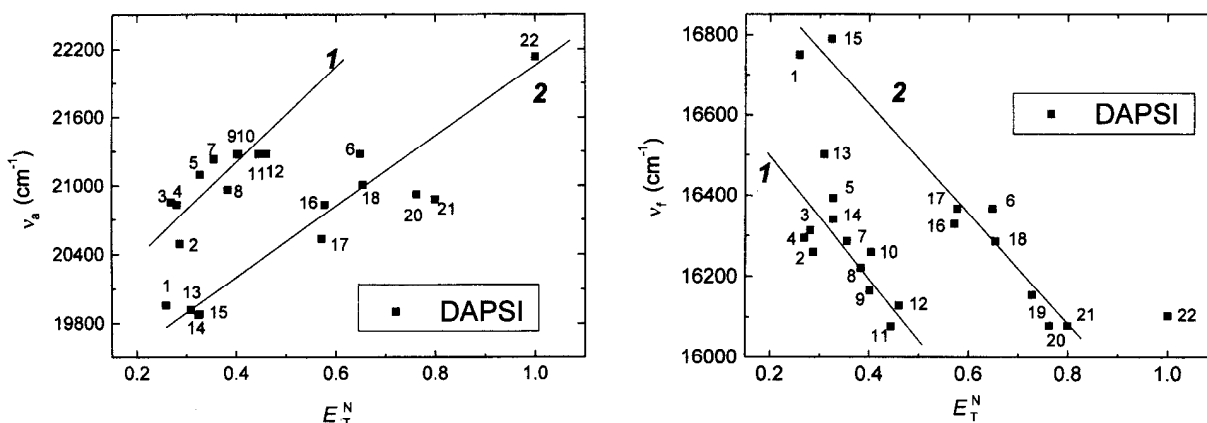

Fig. 2 Plots of the linear correlations of ν_a^{sol}(a) and ν_f^{sol}(b) of DAPSI vs. E_T^N in the nonselected solvents. The number codes of the solvents are given in the experimental part.

Table 2 Linear correlation coefficients γ of the linear fitting between the absorption maxima ν_a^{sol} (a) and fluorescence emission maxima ν_f^{sol} (γ_f) of seven dyes and the solvent polarity parameter E_T^N in the nonselected solvents

Groups	MPPSI		PPSI		FPSI		TPSI		PSI		MPSI		DAPSI	
	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}	ν_a^{sol}	ν_f^{sol}
1	0.936	-0.687	0.789	0.889	0.882	-0.977	0.830	-0.975	0.929	-0.973	0.673	-0.933	0.802	-0.726
N	10	13[a]	9	8	8	11	8	10	8	7	8	10	10	12
2	0.960	-0.854	0.920	0.969	0.929	-0.966	0.910	-0.957	0.916	-0.939	0.965	-0.939	0.941	-0.956
N	11	7	12	11[b]	9	6	9	7	8	9	8	6	11	9[c]

[a] out of line in methylpyridine, [b] out of line in formamide and water, [c] out of line in water and including formic acid.

experimental points are divided into two groups and fitted to form two lines labeled by 1 and 2, in which Group 1 includes the aprotic solvents containing n-electron carbonyl and nitrile compounds, and Group 2 includes the protic solvents, alkane chloride and π-type solvents. The similar results are also obtained for the other dyes and listed in Table 2, from which one can see that the linear correlations for both two lines of all of the dyes give out improved γ-values, especially for the lines of Group 2. This means that there is a relative good linear correlation between the absorption or fluorescence emission maxima and the E_T^N in some selected solvents for some solutes bearing strong CT transition.

Noted that the intercepts of the linear correlations between the solvatochromic shifts and the E_T^N represent the solvatochromic shifts in the solvent with $E_T^N = 0$ for each dye.

Correlation with the modified reaction field function

Due to that the interactions between a dye and the solvents include the ion-dipole, and ion-induced dipole as well as the strong dipole-dipole and dipole-induced dipole forces, sometimes, including the weak hydrogen-bonding force, which can be described with the E_T^N-value, we introduce the E_T^N into the reaction field function to form a new reaction field function $L(\varepsilon_r) - b\ L(n^2) + gE_T^N$, which is called as the modified reaction field function.
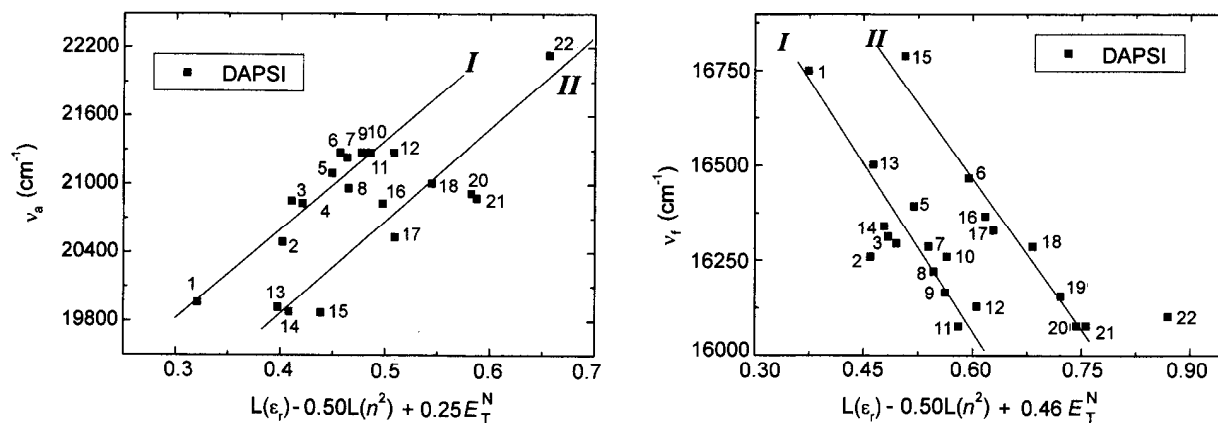

Fig. 3 Plots of the linear correlations between the ν_a^{sol} of DAPSI and $L(\varepsilon_r) - 0.50L(n^2) + 0.25\ E_T^N$(a) and ν_f^{sol} of DAPSI and $L(\varepsilon_r) - 0.50L(n^2) + 0.46\ E_T^N$(b) in nonselected solvents. The number codes of the solvents are given in the experimental part.

A series values of the $[L(\varepsilon_r) - b\ L(n^2) + g_a\ E_T^N]$ could be obtained, when $b = 0.50$ and $g_a = 0.10$, 0.15, 0.20, 0.25, 0.30, 0.35···, and then the correlation between the ν_a^{sol} and the $[L(\varepsilon_r) - b\ L(n^2) + g_a$

$E_T^N]$ in the nonselected solvents can be obtained for each dye. Fig. 3 (a) shows the best linearity relationship between the ν_a^{sol} and the $[L(\varepsilon_r) - b\ L(n^2) + g_a\ E_T^N]$ for DAPSI, here $b = 0.50$ and $g_a = 0.25$, in

which all of the solvents used are divided into two groups labeled by the symbols **I** and **II** with very high linear correlation coefficients 0 . 9 5 8 for Group **I** and 0.938 for group **II**. The division of the points is similar to that in Fig. 2 (a) except in chloroform. The similar results can be also obtained for the other dyes when b = 0.50 and $g_a = 0.25$ (Table 3).

Fig. 3 (b) shows the best linearity relationship between the v_f^{sol} and the $[L(\varepsilon_r) - b\ L(n^2) + g_f\ E_T^N]$ for DAPSI, here $b = 0.50$ and $g_f = 0.46$, in which all of the solvents used are divided into two groups labeled by the symbols **I** and **II** with very high linear correlation coefficients -0.952 for Group **I** and -0.977 for group **II**, respectively. The division of the points is similar to that in Fig. 2 (b) except in chloroform. The similar results can be also obtained for the other dyes when b =

0.50 and $g_f = 0.25$, 0.55, 0.55, 0.55, 0.75 and 0. 80 for PPSI, MPPSI, FPSI, MPSI, TPSI and PSI, respectively (Table 3).

We can see that the g-value is the ratio of the contributions of the reaction field function and E_T^N to one of the solvatochromic shifts from the theoretical background, so it reflects the sensitivity of the ground or excited state to the E_T^N stronger than that of the reaction field function. Here, $g_f > g_a$ indicates that the fluorescence emission state (so called as E^* state) is more sensitive to E_T^N than the ground state. And this kind of sensitivity also occurs in the E^* state for each of stilbazolium-like dyes. The g_f-values increase in the order PPSI < DAPSI < MPPSI = FPSI = MPSI < TPSI < PSI which is related to the strength of the interactions between the dye and solvent molecules.

Table 3 Linear correlation coefficients γ of the linear fitting between the absorption maxima v_a^{sol} (γ_a) and fluorescence emission maxima v_f^{sol} (γ_f) of seven dyes and the modified reaction field function, $L(\varepsilon_r) - 0.50\ L(n^2) + gE_T^N$, with $g_a = 0.25$ for all of the dyes, and $g_f = 0.25$, 0.46, 0.55, 0.55, 0.55, 0.75, and 0.80 for PPSI, DAPSI, MPPSI, FPSI, MPSI, TPSI, and PSI, respectively

Groups	MPPSI		PPSI		FPSI		TPSI		PSI		MPSI		DAPSI	
	v_a^{sol}	v_f^{sol}	v_a^{sol}	v_f^{sol}	v_a^{sol}	v_f^{sol}	v_a^{sol}	v_f^{sol}	v_a^{sol}	v_f^{sol}	v_a^{sol}	v_f^{sol}	v_a^{sol}	v_f^{sol}
I	0.981	-0.939	0.980	0.994	0.941	-0.975	0.963	-0.968	0.941	-0.952	0.972	-0.938	0.958	-0.952
N	12	13[a]	12	7	10	10	11	8	12	10	10	10	12	12
II	0.949	-0.945	0.917	0.943	0.954	-0.990	0.963	-0.970	0.982	-0.952	0.987	-0.926	0.938	-0.977
N	9	7	9	12[b]	7	7	6	9	4	6	6	6	9	9[c]

[a] out of line in methylpyridine, [b] out of line in formamide and water, [c] out of line in water and including formic acid.

Noted that the intercepts of the linear correlations between the solvatochromic shifts and the modified reaction field function represent the sum of the solvatochromic shifts in gas phase and L_a^1 for each dye as given in Eq. (3).

Comparing Table 3 with Tables 1 and 2, one can see that the best linear correlations for both the absorption and fluorescence emission maxima of all the dyes are

obtained by using the modified reaction field function in the nonselected solvents, which means that the modified reaction field function could be valid in the nonselected solvents.

Similarly, a much better linearity correlation can be also obtained between the Stockes shifts for seven dyes and the modified reaction field function, whose linear fitting results (γ and N) are listed in Table 4.

Table 4 Linear correlation coefficients γ of the linear fitting between the Stockes shifts of seven dyes and the modified reaction field function with $b = 0.50$, $g_s = 0.25$

Groups		MPPSI	PPSI	FPSI	TPSI	PSI	MPSI	DAPSI
I	γ	0.922	0.916	0.993	0.979	0.949	0.989	0.979
N		12	14	8	8	9	9	12
II	γ	0.923	0.956	0.984	0.967	0.989	0.953	0.951
N		9	7	9	9	7	7	9

The above analyses indicate that the linear correlating ability of the $L(\varepsilon_r) - b\ L(n^2) + g\ E_T^N$ is stronger than that of the $L(\varepsilon_r) - b\ L(n^2)$ or E_T^N in the nonselected solvents.

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