# Solvatochromism, Crystallochromism, and Solid State Structures of Hydrophilically Functionalized Aromatic Amino Ketones Containing Furan and Thiophene Rings

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[4-Di(2-acetoxyethyl)aminophenyl]-2-furylmethanone [Fur(OAc)$_2$], [4-di(2-hydroxyethyl)-aminophenyl]-2-furylmethanone [Fur(OH)$_2$], and their thiophene analogues, [4-di(2-acetoxy-ethyl)aminophenyl]-2-thienylmethanone [Thi(OAc)$_2$] and [4-di(2-hydroxyethyl)aminophenyl]-2-thienylmethanone [Thi(OH)$_2$], have been synthesized as model compounds for the study of molecular interactions in the solid-state and liquid environments with different polarity. The UV/Vis absorption spectra of these compounds have been studied in 30 solvents of different polarity and hydrogen bonding ability. The solvent dependent UV/Vis spectroscopic band shifts $\nu_{max}$ are analyzed using the empirical Kamlet−Taft solvent parameters $\pi^*$ (dipolarity/polarizability), α (hydrogen bond donating capacity), and $\beta$ (hydrogen bond accepting ability) in terms of the well-established linear solvation energy relationship (LSErs): $\nu_{max} = (\nu_{max})_0 + s\pi^* + a\alpha + b\beta$. The solvent independent coefficients *s*, *a*, and *b* and $(\nu_{max})_0$ have been determined. To evaluate the environmental effects for Fur(OH)$_2$ and Thi(OH)$_2$, the UV/Vis spectroscopic behavior of these compounds was also investigated as pure crystal powders and as a guest in ormosil sol−gel glasses. The solid-state structures of the latter compounds were determined by single-crystal X-ray diffraction techniques. The X-ray investigations confirm the existence of qualitatively different intermolecular hydrogen bonds in Fur(OH)$_2$ and Thi(OH)$_2$, which are additionally reflected by the UV/Vis reflectance absorption spectra and are related to the solvatochromism result.

## Introduction

The color change of a compound induced by external influences, e.g., by solvents (solvatochromism), applied stress (mechanochromism), salts (halochromisms), and temperature (thermochromism) was intensively studied over the past decades.[1−9] In this context, solvatochromic dyes have been established as empirical polarity indicators for solvents, solvent mixtures, and solutions of several solutes in various liquids.[1,10−13] This empirically derived concept for volume effects has been widely applied to evaluate the internal and external polarities of surfaces of macromolecular and related materials.[14−24] Because a chromophore is covalently functionalized by a polar group or another suitable moiety for molecular recognition in its periphery, manifold influences on the

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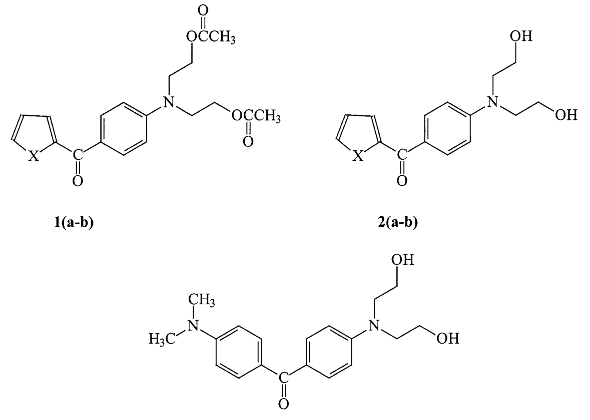
UV/Vis spectra can result from the intermolecular interactions in the solid-state (crystal) or in molecular aggregates of the dye.[25−29] Thus, quantum size effects have been observed for organic nano-crystals[26] and carotenoid dye nanoparticles.[27] However, two different influences, the supra-molecular structure and the quantity of accumulated dye molecules in the nano-crystal, seem to be of importance for the resulting UV/Vis spectroscopic properties. Because both influences are associated properties, a reasonable interpretation of the UV/Vis spectra of such nanosized dye aggregates is still complicated and requires further experimental and theoretical studies.

However, the probing of the nanosize of dye aggregates and supra-molecular structures associated by means of UV/Vis spectroscopy is an experimental challenge and of importance for both academic research and practical application in nanoscience technology. For this objective, the exact knowledge of solid-state structures is necessary, and the respective UV/Vis spectra have to be significantly different as a function of structure variation. This requires the choice of suitable model systems that show color changes as a function of the nature of accumulation processes. Until now, there exists no widely accepted relationship between the type of intermolecular interactions and the resulting color in crystalline materials. Recently, we have shown that, a hydrophilically substituted solvatochromic compound of the Michler's ketone type 4-(dimethylamino)-4′-[di-(2-hydroxyethyl)amino]benzophenone $MK(OH)_2$ bears a significant crystallo-chromism, which is well explained in terms of the intermolecular interaction between the polar hydrogen bond donating (HBD) substituents at the periphery and the polar hydrogen bond accepting (HBA) group in the chromophore.[30]

This type of compound shows sufficient solvatochromic and crystallochromic effects depending on structure variation and environmental influences.[28−35] In this context, we here report on the solid-state structures of related compounds, which are functionalized with furan and thiophene heterocyclic rings (Chart 1).

Similar compounds found a wide range of application in the field of nonlinear optic materials and nanotechnology devices.[36−38] Because the ground-state aromaticity of thiophene or furan is lower than that of 4-*N*,*N*-dimethylaminophenyl, and the solubility of thiophene or furan derivatives is usually higher than that of the parent benzene compounds, much attention has recently been paid to chromophoric and solvatochromic compounds that contain thiophene moieties.[25,36−39]

**Chart 1. Compounds Studied in This Work**


1(a-b)

2(a-b)

3

| No | Name | Substituent | Abbreviation |
|---|---|---|---|
| **1a** | [4-Di(2-acetoxyethyl)aminophenyl]-2-furylmethanone | X = O | $Fur(OAc)_2$ |
| **1b** | [4-Di(2-acetoxyethyl)aminophenyl]-2-thienylmethanone | X = S | $Thi(OAc)_2$ |
| **2a** | [4-Di(2-hydroxyethyl)amino-phenyl]-2-furylmethanone | X = O | $Fur(OH)_2$ |
| **2b** | [4-Di(2-hydroxyethyl)aminophenyl]-2-thienylmethanone | X = S | $Thi(OH)_2$ |
| **3** | 4-Dimethylamino-4'-[di(2-hydroxyethyl)amino]benzophenone | ---------- | $MK(OH)_2$ |

The specific object is to study the solvent influence on the UV/Vis absorption spectra of four novel heteroaryl aminophenyl ketone derivatives (Chart 1), and to evaluate the contribution of the different types of solute−solvent interaction on their solvatochromic properties using the Kamlet−Taft linear solvation energy relationship (LSErs).[1,10,40] The influence of solvent effects on a single solute is shown in eq 1, where XYZ represents the property to be correlated.

$$\mathrm{XYZ} = (\mathrm{XYZ})_0 + h\delta^2_{\mathrm{H}} + s(\pi^* + \mathrm{d}\delta) + a\alpha + b\beta \quad (1)$$

$(XYZ)_0$ is a property relating to a standard process, $\delta^2_H$ is the solvent cohesive energy density ($\delta_H$ is the Hildebrand solubility parameter), $\pi^*$ is the dipolarity/polarizability, $\delta$ represents a polarizability correction term, $\alpha$ is the HBD capacity, and $\beta$ is the HBA capacity.[40] This LSErs is suitable for experimental elucidation of manifold solvent effects because it simply allows the separation of "dipolarity/polarizability" from other solvent−solute interactions such as hydrogen bonding by a multiple square correlation analysis. However, the parameters used in multi-parameter LSE relationships are not seldom interrelated, featuring just different blends of fundamental intermolecular forces. This makes the interpretation of individual polarity parameters relating to nonspecific or specific interaction mechanism in special cases ambiguous.

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**Table 1. UV/Vis Absorption Maxima of [Fur(OAc)$_2$], 1a, [Fur(OH)$_2$], 2a, [Thi(OAc)$_2$], 1b, and [Thi(OH)$_2$], 2b Measured in 30 Solvents[a]**

| solvent | $\nu_{max}$ **1a** $10^3$cm$^{-1}$ | $\nu_{max}$ **2a** $10^3$cm$^{-1}$ | $\nu_{max}$ **1b** $10^3$cm$^{-1}$ | $\nu_{max}$ **2b** $10^3$cm$^{-1}$ | α | $\beta$ | $\pi^*$ |
|---|---|---|---|---|---|---|---|
| cyclohexane | 29.41 | 28.82 | 29.76 | 29.24 | 0.00 | 0.00 | 0.00 |
| triethylamine | 29.24 | 28.01 | 29.50 | 28.25 | 0.00 | 0.71 | 0.14 |
| tetrachloromethane | 28.82 | 28.41 | 29.07 | 28.82 | 0.00 | 0.10 | 0.28 |
| diethyl ether | 29.07 | 28.25 | 29.33 | 28.41 | 0.00 | 0.47 | 0.27 |
| *p*-xylene | 28.74 | 28.09 | 28.99 | 28.41 | 0.00 | 0.12 | 0.43 |
| toluene | 28.65 | 28.09 | 28.99 | 28.33 | 0.00 | 0.11 | 0.54 |
| ethyl acetate | 28.65 | 27.93 | 28.82 | 28.09 | 0.00 | 0.45 | 0.55 |
| 1,4-dioxane | 28.57 | 27.78 | 28.82 | 28.01 | 0.00 | 0.37 | 0.55 |
| benzene | 28.57 | 27.93 | 28.74 | 28.25 | 0.00 | 0.10 | 0.59 |
| tetrahydrofuran | 28.49 | 27.70 | 28.57 | 27.93 | 0.00 | 0.55 | 0.58 |
| dimethoxyethane | 28.49 | 27.70 | 28.74 | 27.86 | 0.00 | 0.41 | 0.53 |
| acetone | 28.33 | 27.55 | 28.49 | 27.62 | 0.08 | 0.43 | 0.71 |
| chloroform | 28.17 | 27.70 | 28.49 | 28.01 | 0.20 | 0.10 | 0.58 |
| dichloromethane | 28.17 | 27.70 | 28.41 | 27.93 | 0.13 | 0.10 | 0.82 |
| 1,2-dichloroethane | 28.17 | 27.70 | 28.41 | 27.86 | 0.00 | 0.10 | 0.81 |
| 1,1,2,2-tetrachloroethane | 27.78 | 27.47 | 28.09 | 27.62 | 0.00 | 0.00 | 0.95 |
| acetonitrile | 28.17 | 27.47 | 28.33 | 27.47 | 0.19 | 0.40 | 0.75 |
| benzonitrile | 27.78 | 27.10 | 27.93 | 27.17 | 0.00 | 0.37 | 0.90 |
| *N*,*N*-dimethylformamide | 27.93 | 27.03 | 28.01 | 27.03 | 0.00 | 0.69 | 0.88 |
| pyridine | 27.86 | 26.95 | 28.01 | 26.88 | 0.00 | 0.64 | 0.87 |
| ethanol | 27.55 | 26.81 | 27.86 | 27.03 | 0.86 | 0.75 | 0.54 |
| methanol | 27.40 | 26.81 | 27.70 | 26.95 | 0.98 | 0.66 | 0.60 |
| 1-butanol | 27.47 | 26.67 | 27.78 | 26.88 | 0.84 | 0.84 | 0.47 |
| dimethyl sulfoxide | 27.47 | 26.74 | 27.62 | 26.67 | 0.00 | 0.76 | 1.00 |
| acetic acid | 27.17 | 26.60 | 27.55 | 26.88 | 1.12 | 0.45 | 0.64 |
| formamide | 27.03 | 26.25 | 27.10 | 26.39 | 0.71 | 0.48 | 0.97 |
| 1,2-ethanediol | 26.88 | 26.25 | 27.03 | 26.39 | 0.90 | 0.52 | 0.92 |
| 2,2,2-trifluoroethanol | 26.81 | 26.53 | 27.10 | 26.81 | 1.51 | 0.00 | 0.73 |
| water | 26.53 | 25.97 | 26.67 | 26.11 | 1.71 | 0.47 | 1.09 |
| 1,1,1,3,3,3-hexafluoro-2-propanol | 26.18 | 26.04 | 26.46 | 26.39 | 1.96 | 0.00 | 0.65 |

[a] α, $\beta$, and $\pi^*$ values for all solvents were taken from ref 10.

The simplified Kamlet–Taft equation applied to single solvatochromic shifts, XYZ = $\nu_{max}$(probe)[1,10] is given in eq 2.

$$\mathrm{XYZ} = (\mathrm{XYZ})_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (2)$$

The above presumptions will be tested by the expected solvatochromic UV/Vis shifts of the four compounds studied.

A complementary point of investigations is the study of structurally different environmental effects (e.g., solvents, sol–gel glasses, neighboring goups of molecules in solid state) on UV/Vis spectra of solvatochromic molecules. Sol–gel chemistry has been developed for encapsulation of single mobile organic molecules to avoid migration by immobilization.[41–47] This method has been applied in order to study MK(OH)$_2$, Fur(OH)$_2$, and Thi(OH)$_2$ under the conditions of nonaggregation and large polarity, because probing the micro-environment of sol–gel materials is another area of interest.[23,48–55] It is expected that intermolecular interactions between the large polar probes are suppressed in the polar silicatic ormosil environment.

## Results and Discussion

**Solvent Effects on the UV/Vis Absorption Spectra.** The UV/Vis absorption spectra of Fur(OAc)$_2$, Fur(OH)$_2$, and their thiophene analogues, Thi(OAc)$_2$ and Thi(OH)$_2$, have been investigated in various solvents of different dipolarity/polarizability and HBD ability. The $\nu_{max}$ values (in cm$^{-1}$) of Fur(OAc)$_2$, Fur(OH)$_2$, Thi(OAc)$_2$, and Thi(OH)$_2$ and solvent parameters used are summarized in Table 1.

A representative collection of solvent-dependent UV/Vis spectra of Thi(OAc)$_2$ and Thi(OH)$_2$ are shown in Figure 1.

As expected,[30,31,34,35] with increasing the solvent polarity from cyclohexane to water, the UV/Vis absorp-

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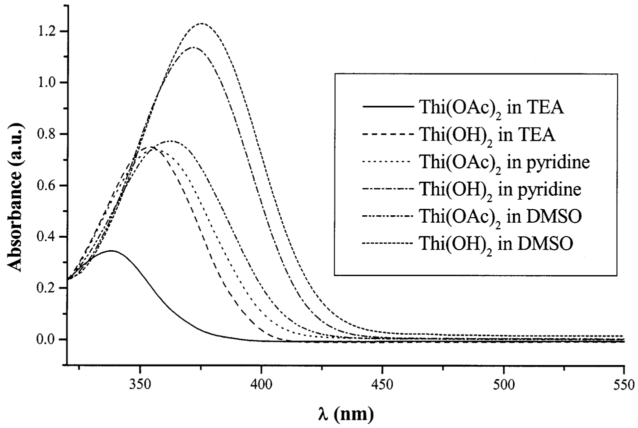

**Figure 1.** UV/Vis absorption spectra of Thi(OAc)$_2$ **1b**, and Thi(OH)$_2$ **2b**, in triethylamine (TEA), pyridine, and dimethyl sulfoxide (DMSO).

tion spectra of these compounds show a bathochromic shift of the solvatochromic long-wavelength symmetric UV/Vis band, the shape of which is independent of the solvent used. These bathochromic displacements are in agreement with an increased delocalization due to the conjugation of the lone pair of electrons of the [$-N(CH_2CH_2OH)_2$] or [$-N(CH_2CH_2O-CO-CH_3)_2$] donors with the aromatic $\pi$-electron system and the carbonyl group, respectively. The extent of the solvatochromic shift as a function of solvent polarity of the hydroxyl functionalized derivate is lower than that of the acetoxy functionalized one, which is likely caused by a competing influence of the polar substituent with the solvent molecules. As a result, Fur(OAc)$_2$ and Thi(OAc)$_2$ absorb hypsochromically dissolved in any solvent in comparison to Fur(OH)$_2$ and Thi(OH)$_2$, respectively. This is attributed to the electron withdrawing influence of the acetyl group, which lowers the electron density at the nitrogen atom. Thus, the delocalization ability of the lone pair of electrons at the nitrogen atom is slightly decreased. The extent of the hypsochromic shift, for example from Fur(OH)$_2$ to Fur(OAc)$_2$, occurs more strongly in HBA solvents such as triethylamine ($\Delta\nu = 1203$ cm$^{-1}$) than in HBD solvents such as water ($\Delta\nu = 533$ cm$^{-1}$) or HFIP ($\Delta\nu = 140$ cm$^{-1}$) indicating an additional electron pushing influence of HBA solvents upon the $-N(CH_2CH_2OH)_2$ substituent.

UV/Vis measurements of Thi(OH)$_2$ as a function of its concentration show no significant indication of probe aggregation in the concentration interval studied for the solvatochromic measurement. The long-wavelength UV/Vis absorption maximum ranges from $\lambda = 353 \pm 1$ nm to $\lambda = 355 \pm 1$ nm with increasing concentrations of Thi(OH)$_2$ from $c = 1.59 \times 10^{-5}$ to $c = 42.86 \times 10^{-5}$ M in toluene as solvent. Because the concentration exceeded $1.20 \times 10^{-3}$ M, a new bathochromically shifted UV/Vis absorption appears as a shoulder at $\lambda = 392$ nm. Thus, dye dimerization as the simplest case of aggregation in solutions [eq 3] is observed only at large dye concentration.

$$2\,\mathrm{Thi(OH)_2} \rightleftharpoons [\mathrm{Thi(OH)_2}]_2 \qquad (3)$$

$$\begin{array}{ll} \lambda_{max} = 353 \text{ nm (toluene)} & \lambda_{max} = 392 \text{ nm (toluene)} \\ \text{low concentration} & \text{high concentration} \\ (c < 10^{-3}\text{ M}) & (c > 10^{-3}\text{ M}) \end{array}$$

**LSE Correlation Analyses.** To determine the respective contributions of solvent properties on $\nu_{max}$, the simplified form of the Kamlet–Taft LSErs was used [eq 2]. The solvatochromic parameters α, $\beta$, and $\pi^*$ for the square multiple correlation analyses were taken from reference 10. The results of a multiple square correlation analysis are summarized in Table 2.

The correlations statistically provide a solid base to understanding the manifold solvent effects on the solvatochromic long-wavelength UV/Vis absorption band of these molecules. The LSErs shows a high quality in particular as indicated by correlation coefficients larger than 0.90 for special mathematical functions of $\nu_{max}$ with α, $\beta$, and $\pi^*$, respectively (Figure 2).

The qualitatively best regression fits obtained for the key compounds Fur(OH)$_2$ and Thi(OH)$_2$ are represented by eqs 4 and 5, respectively.

$$\nu_{max}{*}10^{-3}\,[\mathrm{Fur(OH)_2}] = 28.851 - 1.404\,\pi^* - 0.840\,\alpha - 0.801\,\beta \quad (n = 30;\ r = 0.979;\ \mathrm{SD} = 0.161) \qquad (4)$$

$$\nu_{max}{*}10^{-3}\,[\mathrm{Thi(OH)_2}] = 29.311 - 1.730\,\pi^* - 0.762\,\alpha - 1.045\,\beta \quad (n = 30;\ r = 0.980;\ \mathrm{SD} = 0.167) \qquad (5)$$

For Fur(OAc)$_2$ and Thi(OAc)$_2$ it can be concluded that the influence of the $\beta$ term of the solvent upon $\nu_{max}$ plays no role. It seems that the HBA property of the solvent affects the $-N(CH_2CH_2OH)_2$ substituent of Thi(OH)$_2$ to a greater extent than the HBD property of the carbonyl oxygen, because the value of coefficient $b = 1.045$ is larger than that of $a = 0.762$ [from eq 5]. The influence of the $\beta$ ($b = 0.801$) and α ($a = 0.840$) term, respectively, makes no difference on $\nu_{max}$ for [Fur(OH)$_2$] as shown by eq 4. However, the results of the correlation analyses show that the influence of the HBA property arises exclusively from the formation of hydrogen bonds donated from the hydroxyl group of the probe to the lone pair of electrons of the solvent molecule.

The negative sign of *s* coefficients indicates that the singlet excited state of these molecules becomes more stabilized when the solvents' dipolarity increases, which is well in agreement with previous results of these type of compounds.[30,31]

The negative sign of coefficient *a* of the LSErs in Table 2 indicates the formation of solute–solvent hydrogen bonds between the carbonyl oxygen and the HBD site of the solvent.[30] According to Novaki, Soeud[12] and Spange et al.,[35] coefficient *a* should increase with increasing basicity of the solvatochromic probe, because acid–base interaction of the solute with the HBD solvent becomes more dominant. Therefore, a correlation of the carbonyl–oxygen basicity, which may be expressed by the chemical shift of the $^{13}$C NMR signal of the corresponding carbonyl C atom, with *a* is expected. Coefficient *a* decreases in the order of MK(OH)$_2$ [$a = 1.66$, $\delta$ $^{13}$C (CO) = 197.1 ppm][30] > MK(OAc)$_2$ [$a = 1.656$, $\delta$ $^{13}$C (CO) = 192.9 ppm] > MK(OH)$_4$ [$a = 1.47$, $\delta$ $^{13}$C (CO) = 192.9 ppm][30] > Fur(OAc)$_2$ [$a = 0.991$, $\delta$ $^{13}$C (CO) = 180.8 ppm] > Thi(OAc)$_2$ [$a = 0.836$, $\delta$ $^{13}$C (CO) = 181.3 ppm] > Fur(OH)$_2$ [$a = 0.942$, $\delta$ $^{13}$C (CO) = 171.3 ppm] > Thi(OH)$_2$ [ $a = 0.757$, $\delta$ $^{13}$C (CO) = 187.2 ppm] [the $\delta$ $^{13}$C (CO) values in parentheses are taken from the

**Table 2. Solvent-Independent Correlation Coefficients *a*, *b*, and *s* of the Kamlet− Taft Parameters α, *β*, and *π**, Respectively, Solute Property of a Reference System (XYZ)$_0$, Standard Deviation (SD), Number of Solvents (*n*) Correlation Coefficient (*r*), and Significance (*F*) Calculated for the Solvatochromism of Fur(OAc)$_2$ 1a, Fur(OH)$_2$ 2a, Thi(OAc)$_2$ 1b, and Thi(OH)$_2$ 2b; *n* is the Number of Solvents**

| compound | (XYZ)$_0$ | *a* | *b* | *s* | *r* | SD | *n* | *F* |
|---|---|---|---|---|---|---|---|---|
| Fur(OAc)$_2$ | 29.424 | −0.991 | −0.169 | −1.562 | 0.977 | 0.183 | 30 | < 0.0001 |
| Fur(OAc)$_2$ | 29.375 | −0.991 | | −1.584 | 0.975 | 0.186 | 30 | < 0.0001 |
| Fur(OH)$_2$ | 28.851 | −0.840 | −0.801 | −1.404 | 0.979 | 0.161 | 30 | < 0.0001 |
| Fur(OH)$_2$ | 28.619 | −0.836 | | −1.508 | 0.937 | 0.270 | 30 | < 0.0001 |
| Thi(OAc)$_2$ | 29.792 | −0.944 | −0.261 | −1.753 | 0.979 | 0.177 | 30 | < 0.0001 |
| Thi(OAc)$_2$ | 29.716 | −0.942 | | −1.788 | 0.976 | 0.188 | 30 | < 0.0001 |
| Thi(OH)$_2$ | 29.311 | −0.762 | −1.045 | 1.730 | 0.980 | 0.167 | 30 | < 0.0001 |
| Thi(OH)$_2$ | 29.008 | −0.757 | | −1.866 | 0.918 | 0.329 | 30 | < 0.0001 |
| Fur(OAc)$_2$ | 29.513 | | | −1.827 | 0.980 | 0.111 | 17[a] | < 0.0001 |
| Thi(OAc)$_2$ | 29.816 | | | −1.972 | 0.976 | 0.134 | 17[a] | < 0.0001 |
| Fur(OH)$_2$ | 28.730 | | | −1.694 | 0.903 | 0.245 | 17[a] | < 0.0001 |
| Thi(OH)$_2$ | 29.138 | | | −2.078 | 0.891 | 0.322 | 17[a] | < 0.0001 |

[a] Solvents with α > 0 are excluded.

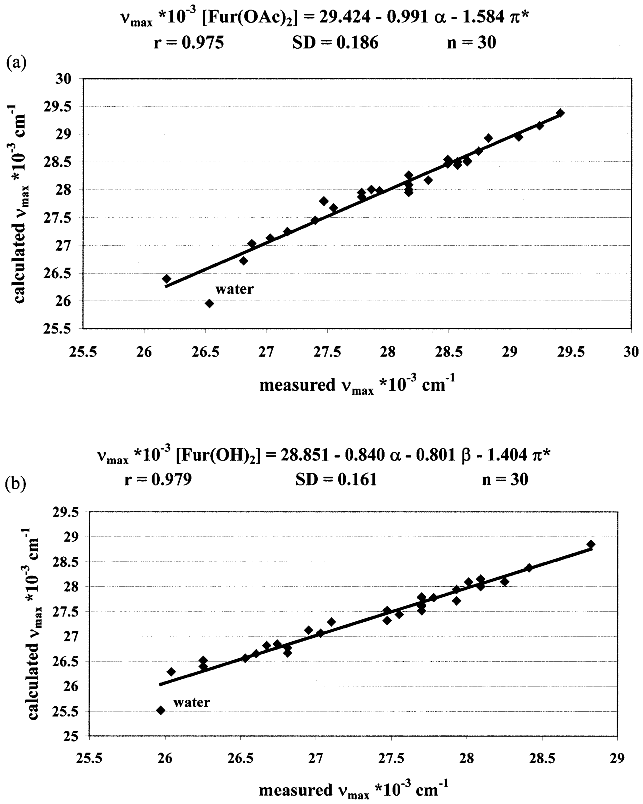

**Figure 2.** Relationships between calculated and measured $\nu_{max}$ values for (a) Fur(OAc)$_2$ **1a**, and (b) Fur(OH)$_2$ **2a** in 30 different solvents.

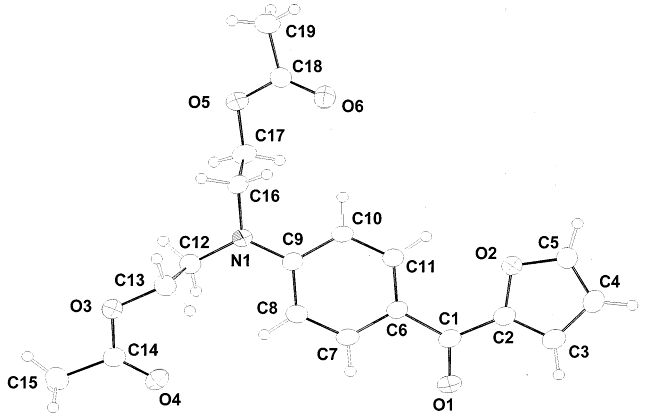

**Figure 3.** ZORTEP drawing (50% probability level) of Fur(OAc)$_2$ **1a**.

experimental part and reference 30]. Because *a* correlates only poorly with the chemical shift of *δ* $^{13}$C (CO), we presume that the HBD solvent also competes with the −N(CH$_2$CH$_2$OH)$_2$ substituent among solvation of the carbonyl group of the solute.

The value of *s* significantly increases from Fur(OAc)$_2$ (*s* = 1.58) to Thi(OAc)$_2$ (*s* = 1.79) and from Fur(OH)$_2$ (*s* = 1.51) to Thi(OH)$_2$ (*s* = 1.87), which indicates that the dipolarity/polarizability of the solvent becomes a greater influence in the case of the thiophene derivatives. A highly polar solvation shell is likely induced by interacting solvent molecules at the −N(CH$_2$CH$_2$OH)$_2$ substituent, which is responsible for the effect observed for Thi(OH)$_2$.

Altogether, the *a* values are significantly smaller than the *s* coefficients for the calculated LSErs. This demonstrates that the ability of the solvent to donate hydrogen bonds is much weaker than solute−solvent dipole−dipole interactions for Fur(OH)$_2$, Thi(OH)$_2$, Fur(OAc)$_2$, and Thi(OAc)$_2$.

**X-ray Crystal Structure Analyses.** *[4-Di(2-acetoxyethyl)aminophenyl]-2-furylmethanone, Fur(OAc)$_2$.* Fur(OAc)$_2$ crystallizes from ethyl acetate at 25 °C as yellow plates (Experimental Section) which are orthorhombic, *Pbca*, and contain 8 molecules within the unit cell (Figure 3).

*[4-Di(2-hydroxyethyl)amino-phenyl]-2-furylmethanone Fur(OH)$_2$.* Fur(OH)$_2$ can be also obtained from ethyl acetate at 25 °C as yellow plates (Experimental Section) Single crystals are monoclinic, space group $P2_1/c$, with $Z = 4$. (Figure 4).

The dotted lines in Figure 4B represent distances of 277.84(16) and 278.26(16) pm for the O3....O4 and O4....O3 interactions, respectively (see below). With respect to these separations, compound Fur(OH)$_2$ interacts with four nearest neighbors, which results in a zigzag motif, as depicted in Figure 4B. The O3....O4 and O4....O3 distances are less than 280 pm, and thus, correspond to a strong hydrogen bond interaction according to Emsley et al.[56] C13−O3−H(1O4) and C15−O4−H(1O3) angles of 106.4(12)°, and 107.7(14)° in Fur(OH)$_2$ indicate that the direction of the −OH....O4 and −OH....O3 bonds are toward the sp$^3$-hybridized lone pairs of electrons of O4 and O3. The N1−C9 distance

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(56) Emsley, J.; Jones, D. J.; Lucas, J. *Rev. Inorg. Chem.* **1981**, *3*, 1.

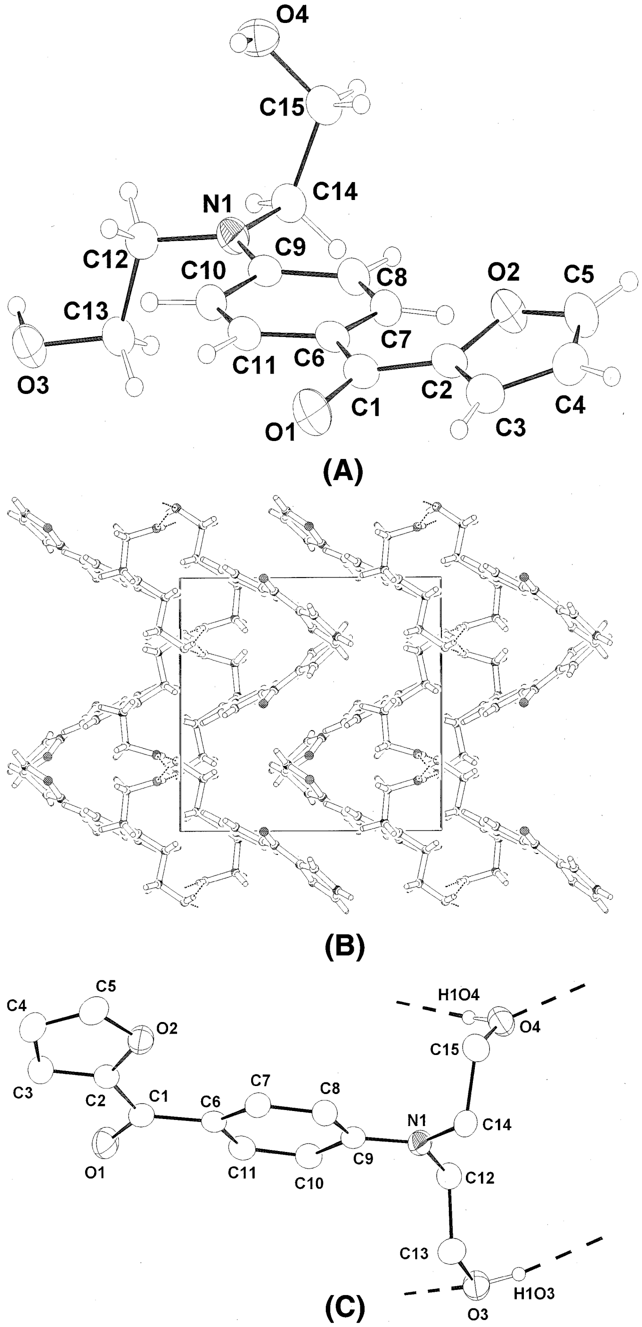


**Figure 4.** Crystal structure of Fur(OH)$_2$ **2a**.

in Fur(OH)$_2$ is smaller (136.65(18) pm) than the N1−C9 interatomic distance in Fur(OAc)$_2$ (137.75(17) pm), indicating a stronger conjugation of the lone pair of electrons at the nitrogen atom and the benzene ring in Fur(OH)$_2$.

*[4-Di(2-hydroxyethyl)aminophenyl]-2-thienylmethanone Thi(OH)$_2$.* Thi(OH)$_2$ crystallizes from ethyl acetate at 25 °C as yellow plates (Experimental Section) Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ (Figure 5).

The dotted lines in Figure 5B represent distances of 277.43(13) and 285.52(13) pm between the O2....O1 and O3....O1 separations. Thi(OH)$_2$ interacts with three nearest neighboring molecules. The two O−H groups deriving from one molecule form two hydrogen bonds with the carbonyl oxygen atom of two other Thi(OH)$_2$ molecules. These two hydrogen bonds are different in strength. The strong participation of the carbonyl group in two hydrogen bonds results in an elongation of the C = O distance in Thi(OH)$_2$ ($d_{C=O}$ = 124.76(14) pm) in comparison to Fur(OH)$_2$ ($d_{C=O}$ = 123.44(16) pm), where no hydrogen bond to the oxygen atom of the carbonyl group occurs. In Thi(OH)$_2$ the C6−C1−C2 angle ($\gamma$ = 120.63(10)°) is less than that in Fur(OH)$_2$ ($\gamma$ = 123.19(12)°). This difference is due to a conformation change, induced by hydrogen bonds to the carbonyl oxygen atoms as shown in Figure 6B. Also, the difference between the two distinct structures of **2a** and **2b** reflects the hydrogen-bond-acceptor directed properties of the sp$^3$- (the oxygen atom of the hydroxyl group in **2a**) versus the sp$^2$- (the carbonyl oxygen atom in Thi(OH)$_2$) hybridized oxygen atoms.

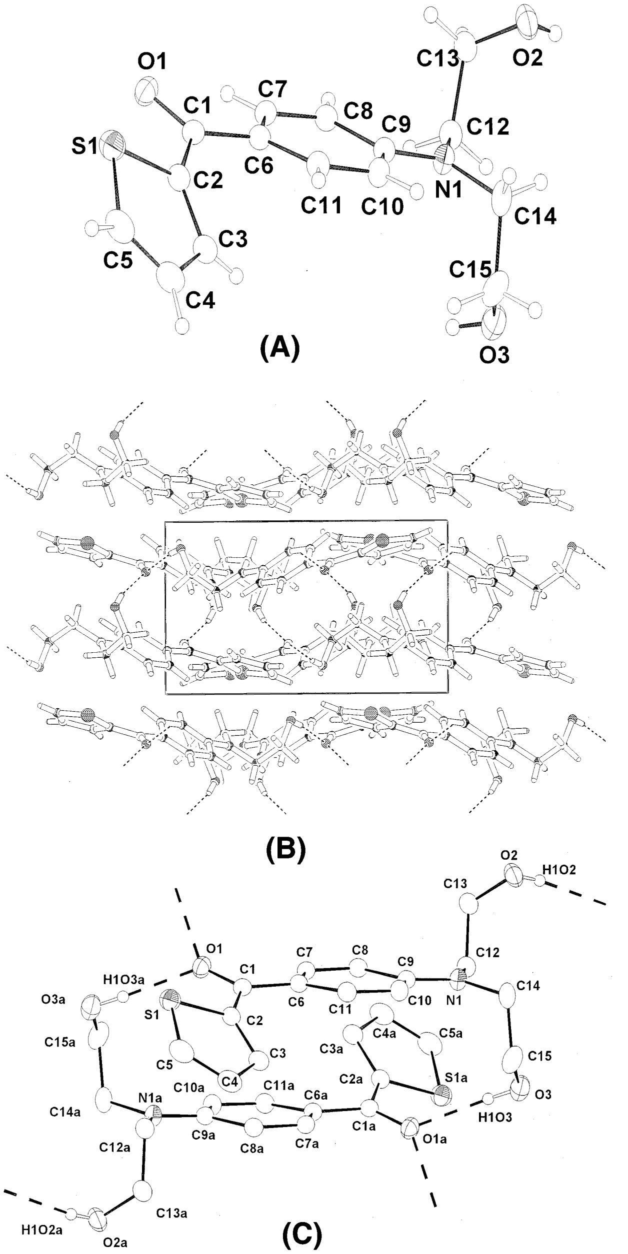


**Figure 5.** Crystal structure of Thi(OH)$_2$ **2b**.

**Summary Discussion on Environmental Effects on UV/Vis Absorption Spectra of Fur(OH)$_2$, Thi(OH)$_2$, and MK(OH)$_2$.** UV/Vis absorption spectra of MK(OH)$_2$ (for comparison to the solid-state structure)[30] Fur(OH)$_2$, and Thi(OH)$_2$ when entrapped in sol−gel

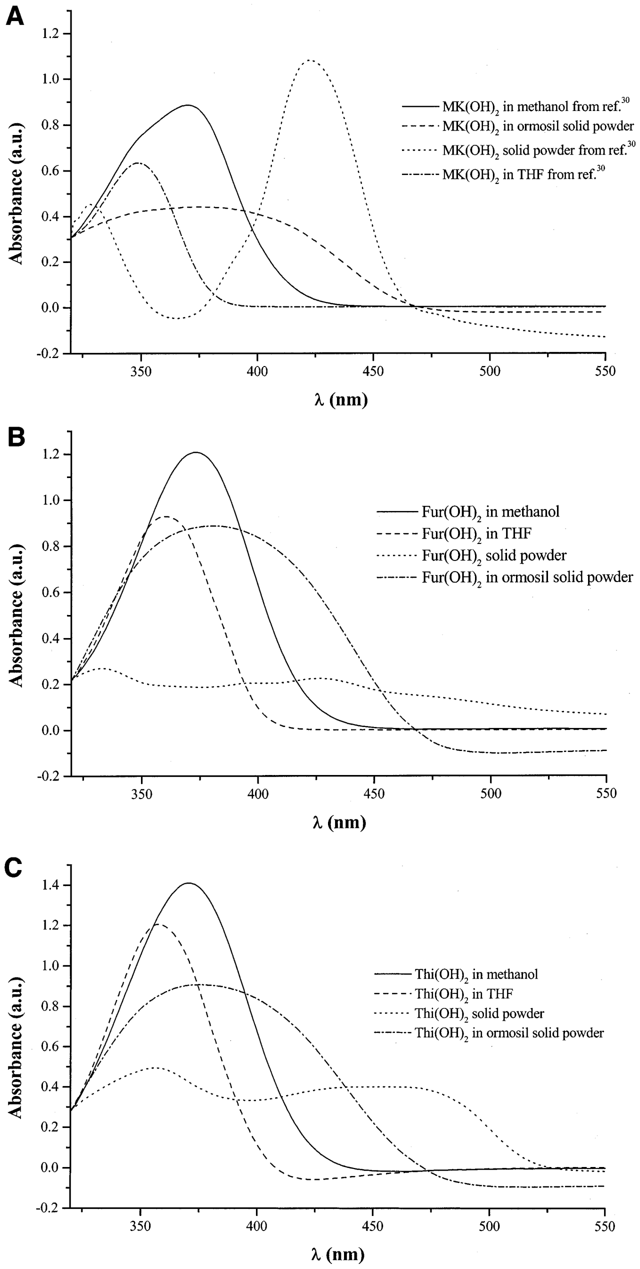
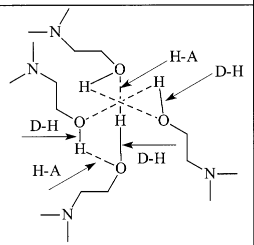
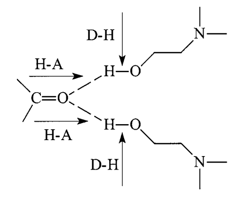
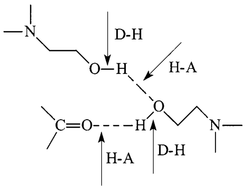


**Figure 6.** UV/Vis absorption spectra of [A] MK(OH)$_2$ **3**, [B] Fur(OH)$_2$ **2a**, and [C] Thi(OH)$_2$ **2b** as crystal powder and when entrapped in a sol−gel glass in the solid state, and dissolved in methanol and tetrahydrofuran (THF).

ormosil (organic modified silicate) glasses have been measured by means of diffuse reflectance spectroscopy. Ormosil was chosen because its internal polarity is close to that of methanol, thereby avoiding strong protonation of the probe at both the carbonyl oxygen and dimethylamino nitrogen atom. The silicatic material accomplishing this requirement was synthesized from a 1:1 mixture of tetramethoxysilane (TMOS) and methyl trimethoxysilane (MTMOS) according to an established sol−gel procedure[48] (Experimental Section). Representative UV/Vis spectra of MK(OH)$_2$, Fur(OH)$_2$, and Thi(OH)$_2$, measured as powders, encapsulated in sol−gel glasses, and dissolved in two solvents of different polarities (methanol and THF) for comparison are shown in Figure 6[A−C].

Generally, the half-width of the UV/Vis absorption band of the respective compounds in the sol−gel glasses are broader than those in well-behaved regular solvents, e.g., THF and methanol. This results indicates a wider polarity distribution compared to that of a solvent.

**Chart 2. Classification of the Intermolecular Hydrogen Bonds in the Solid State of MK(OH)$_2$ 3, Fur(OH)$_2$ 2a, and Thi(OH)$_2$ 2b**

| No | Abb. formula | structure unit | nature of the hydrogen bond |
|---|---|---|---|
| **2a** | Fur(OH)$_2$ |  | In the crystal lattice, each hydroxyl group form two types of hydrogen bonds with another two hydroxyl groups of two Fur(OH)$_2$ molecules. |
| **2b** | Thi(OH)$_2$ |  | In the crystal lattice, there are two qualitatively different types of hydrogen bonds between the two –CH$_2$CH$_2$OH substituents of two different Thi(OH)$_2$ molecules with one carbonyl oxygen of the third. |
| **3** | MK(OH)$_2$ |  | In the crystal lattice, the molecules are bridged by two kinds of hydrogen bonds, one of them between the hydroxyl hydrogen atom and the carbonyl oxygen atom and the other between the two hydroxyl groups of neighboring molecules. |

As seen from Figure 6[B−C], both Fur(OH)$_2$ and Thi(OH)$_2$ exhibit red-shifted UV/Vis absorption maxima when entrapped within the solid ormosil hosts [$\lambda_{\max}$ = 381 nm for entrapped Fur(OH)$_2$ and $\lambda_{\max}$ = 376 nm for entrapped Thi(OH)$_2$ as compared to their solution in THF]. The extent of the red-shift of $\lambda_{\max}$ of Fur(OH)$_2$ or Thi(OH)$_2$ doped glasses is similar to the effect of MK(OH)$_2$ ($\lambda_{\max}$ at 366 nm) when encapsulated in the sol−gel glass, indicating similar behavior.

The diffuse reflectance spectra of the MK(OH)$_2$ crystal powder revealed two separated UV/Vis absorption bands: one at $\lambda_{\max}$ = 329 nm and another more intense at $\lambda_{\max}$ = 423 nm.[30] The Fur(OH)$_2$ crystal powder shows only a broad UV/Vis absorption in the diffuse reflectance spectrum with three small poorly resolved peaks at $\lambda_{\max}$ = 333, 400, and 427 nm (Figure 6B).

Two new long-wavelength UV/Vis absorption bands at $\lambda_{\max}$ = 357 and 447 nm are clearly detectable in the Thi(OH)$_2$ crystal powder (Figure 6C).

It is obvious that the UV/Vis data obtained in well-behaved regular solvents and in sol−gel ormosil glasses fit well in the concept derived from the solution chemistry (vide supra) pointing to the existence of an underlying feature. Because two or three OH-functionalized probes interact simultaneously in the solid-state, the UV/Vis spectrum is modified depending on the structure formed. According to the UV/Vis results, three different mechanisms of hydrogen bond formation in the solid-state can be clearly recognized, as presented visually in Chart 2.

**Table 3. Intermolecular Hydrogen Bond Distances [Pm] and Angles [°] of the Participating Moieties of $MK(OH)_2$[a] 3, $Fur(OH)_2$ 2a, and $Thi(OH)_2$ 2b, According to Chart 2**

| compound | D−H | H···A | D···A | < (DHA) | D−H···A |
|---|---|---|---|---|---|
| $MK(OH)_2$ | 94.0 (3) | 174.0 (3) | 267.1 (2) | 168.0 (3) | O2−H2O2···O1 |
| | 90.0 (3) | 180.0 (3) | 269.9 (2) | 176.0 (3) | O3−H3O3···O2 |
| $Fur(OH)_2$ | 89.0 (2) | 190.0 (2) | 277.84 (16) | 168.5 (18) | O3−H1O3···O4 |
| | 85.0 (2) | 193.0 (2) | 278.26 (16) | 176 (2) | O4−H1O4···O3 |
| $Thi(OH)_2$ | 74.0 (2) | 204.0 (2) | 277.43 (13) | 173 (2) | O2−H1O2···O1 |
| | 85.0 (2) | 202.0 (2) | 285.52 (13) | 166.7 (19) | O3−H1O3···O1 |

[a] Data for $MK(OH)_2$ were taken from ref 30.

The corresponding bond distances and angles of the participating functional groups are summarized in Table 3. Additionally, Table 3 contains results of $MK(OH)_2$ for comparison.[30] The small D−A (donor−acceptor) distances of 267.1(2) and 269.9(2) pm for $MK(OH)_2$ indicate the presence of a strong intermolecular hydrogen bond between these molecules.

The directed specific interaction between the carbonyl oxygen of the probe and one $HO-CH_2CH_2-$ moiety [specifically observed for $MK(OH)_2$] causes a significant bathochromic UV/Vis shift, which is associated with a new sharp UV/Vis absorption band in the UV/Vis spectrum of the crystal. This effect is related to the interaction of the probe with strong HBD solvents such as HFIP. A broad nonresolved UV/Vis absorption band with weaker intensity is observed when specific interactions between the carbonyl oxygen and the $HO-CH_2-CH_2-$ group do not occur in the solid-state, as is the case for $Fur(OH)_2$. However, the broad and poorly resolved UV/Vis absorption bands in the visible spectrum of $Fur(OH)_2$ indicate nonspecific $\pi-\pi$ and long-ranging dipolar interactions.

The UV/Vis diffuse reflectance spectrum of the $Thi(OH)_2$ powder shows a new long wavelength absorption at $\lambda = 447$ nm due to the strong interaction of two $-CH_2CH_2OH$ substituents of two different $Thi(OH)_2$ molecules with one carbonyl oxygen of a third $Thi(OH)_2$ species. The unprecedented bathochromic UV/Vis shift of the solid observed is in agreement with the strong influence of the $\beta$ term (of the solvent) on $\nu_{max}$ in solution and that especially the $-CH_2CH_2OH$ substituents of $Thi(OH)_2$ bear the highest HBD capacity of the compounds studied. The other UV/Vis band at $\lambda = 357$ nm relates to the single chromophoric system.

## Conclusion and Outlook

Hydrophilic functionalities as substituents at the periphery of heterocyclic aromatic aminoketones such as [4-di(2-hydroxyethyl)aminophenyl], 2-furyl, or 2-thienyl methanone derivate can be used to achieve information on aggregation versus solvatochromic properties of polar compounds. Occurrence of specific and nonspecific interactions of hydrophilically substituted genuine solvatochromic aromatic amino ketones in various solvents, sol−gel glasses, and in the solid-state can be monitored by UV/Vis spectroscopy. In organic solvents and ormosil glasses single molecule solvation is observed. This can be interpreted in terms of empirically derived LSErs using the Kamlet−Taft solvents parameter set. Depending on the nature of the aromatic moiety, furan, thiophene, or 4-(N, N-dimethylamino)phenyl, significant differences in the solid-state structures and solvatochromic properties are observed which are attributed to the modified HBD capacity of the $-N(CH_2CH_2OH)_2$ group and their ability to interact with other species. With increasing the HBD capacity of the solvent or the $-N(CH_2CH_2OH)_2$ substituent, or both, indicated by an increase of *b* from eq 2 (Kamlet−Taft LSErs) from [4-(*N*,*N*-dimethylamino)phenyl][30] < 2-furyl < 2-thienyl, a bathochromic shift of the solvatochromic and crystallochromic, respectively, long-wave UV/Vis $\pi-\pi^*$ transition is monitored. Thus, UV/Vis spectroscopic properties of organic dye crystals can be adjusted not only by the chromophore itself but also by interacting polar group in its periphery. This is promising to develop a concept for producing tailor-made organic crystals for optical materials and devices.

## Experimental Section

**Materials and Methods.** The reagents were of analytical grade and purchased from Lancaster and Acros. The solvents were redistilled over appropriate drying agents prior to use. Merck silica gel 60 (70−230 mesh ASTM) was used for column chromatography.

Elemental analyses were determined with a Vario-EL analysis apparatus. NMR measurements were recorded at 293 K on a Varian Gemini 300 FT NMR spectrometer, operating at 300 MHz for $^1H$ and at 75 MHz for $^{13}C$. The signals of the solvents ($CDCl_3$ or $CD_3OD$) were used as internal standards.

The UV/Vis absorption spectra of freshly prepared solutions were obtained by means of a MCS 400 diode-array spectrometer from Carl Zeiss Jena, connected with an immersion cell (TSM 5) via glass-fiber optics. A diffuse reflectance accessory was attached to the spectrometer for diffuse reflectance measurements, which were carried out with properly characterized powdered samples using $BaSO_4$ as a reference.

The multiple regression analysis of the long-wavelength UV/Vis absorption maxima was performed with the Origin 5.0 statistic program.

**Structure Determination.** Crystal structures of $Fur(OAc)_2$, $Fur(OH)_2$, and $Thi(OH)_2$ were determined using single-crystal X-ray diffraction methods. Data collection for these compounds were performed at 173 K using graphite monochromatized MoKα ($\lambda = 71.073$ pm) radiation on a Bruker axs Smart 1K CCD area detector. The complete data collection parameters and details of the structure solution and refinement are deposited in the Cambridge Crystallographic Data Centre. Further details of the crystal structure investigation (without structural factors) are available from the Cambridge Crystallographic Data Centre on quoting the depository numbers CCDC 197620 $Fur(OAc)_2$, CCDC 197621 $Fur(OH)_2$, and CCDC 197622 $Thi(OH)_2$. The unit cell was determined with the program SMART.[57] For data integration and refinement of the unit cell the program SAINT[57] was used. The space group was determined using the programs XPREP[57] for $Fur(OAc)_2$ and ABSEN[58] for $Fur(OH)_2$ and $Thi(OH)_2$. The empirical absorption correction was carried out with SADABS.[59] The structures were solved using direct methods with the programs SHELXL-97[60] for $Fur(OAc)_2$ and SIR97[61] for $Fur(OH)_2$ and Thi-

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(57) Bruker AXS Inc.: Madison, WI, 1998.

(58) McArdle, P. *J. Appl. Crystallogr.* **1996**, *29*, 306.

$(OH)_2$. The structure refinement by least-squares methods based on $F^2$ was done with SHELXL-97.[60]

All non-hydrogen atoms were fully refined in the calculated positions, the hydrogen atoms were taken from the electron density difference map, and in both their position and their thermal parameters refined freely.

The plots of the molecular structures were visualized using the programs ZORTEP[62] or PLATON.[63]

**[4-Di(2-acetoxyethyl)aminophenyl]-2-furylmethanone Fur(OAc)$_2$ and [4-di(2-acetoxyethyl)aminophenyl]-2-thienylmethanone Thi(OAc)$_2$.** The synthesis of [di(2-acetoxyethyl)amino]benzene was described previously.[64]

A solution of furyl-2-carbonyl chloride (6.85 g, 5.19 cm$^3$, 52.50 mmol) or thienyl-2-carbonyl chloride (7.33 g, 5.34 cm$^3$, 52.50 mmol) in 30 cm$^3$ of 1,2-dichloroethane was gradually added to a suspension of anhydrous $AlCl_3$ (8.00 g, 60 mmol) in 20 cm$^3$ of 1,2-dichloroethane at room temperature. The reaction mixture was stirred for 1 h and then treated with a solution of [di(2-acetoxyethyl)amino]benzene (9.64 g, 50 mmol) in 20 cm$^3$ of 1,2-dichloroethane for 1 h at 25 °C and kept stirring for 4 h at the same temperature. Then the reaction mixture was poured into water, acidified with 1 N HCl, and extracted with ethyl acetate. The ethyl acetate extract was washed with water, dried over $Na_2SO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel 60 with a mixture from ethyl acetate and *n*-hexane (2:1) as eluant, affording [Fur(OAc)$_2$] or [Thi-(OAc)$_2$].

*[4-Di(2-acetoxyethyl)aminophenyl]-2-furylmethanone Fur-(OAc)$_2$* ***1a***. Yield (8.62 g, 48%), mp 72 °C (ethyl acetate), pale-yellow crystals.

$C_{19}H_{21}NO_6$ (338) (cald. C, 63.51%; H, 5.85%; N, 3.90%; found C, 63.52%; H, 5.75%; N, 3.89%.). $^1H$ NMR ($CDCl_3$): $\delta$ 8.04 (d, $J$ = 9.16 Hz, 2H, ArH-2,6), 7.67 (s, 1H, FuH-5′), 7.22 (d, $J$ = 3.48 Hz, 1H, FuH-3′), 6.82 (d, $J$ = 9.16 Hz, 2H, ArH-3,5), 6.58 (dd, $J$ = 3.48, 1.74 Hz, 1H, FuH-4′), 4.30 (t, $J$ = 6.16 Hz 4H, $CH_2{-}O$), 3.73 (t, $J$ = 6.16 Hz, 4H, $CH_2{-}N$), 2.07 (s, 6H, $C{-}CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 180.8 ($C{=}O$), 171.2 ($C{=}O$ ester), 153.5 (FuC-2′), 151.3 (ArC-4), 146.4 (FuC-5′), 132.5 (ArC-2,6), 126.0 (ArC-1), 119.1 (FuC-3′), 112.3 (FuC-4′), 111.3 (ArC-3,5), 61.4 ($CH_2{-}O$), 49.9 ($CH_2{-}N$), 21.2 ($C{-}CH_3$).

*[4-Di(2-acetoxyethyl)aminophenyl]-2-thienylmethanone Thi-(OAc)$_2$* ***1b***. Yield (9.75 g, 52%), green oil.

$C_{19}H_{21}NO_5S$ (375) calcd. C, 60.80%; H, 5.60%; N, 3.73%; S, 8.53%; found C, 59.31%; H, 5.64%; N, 3.53%; S, 8.66%. MS (EI) *m*/*z* (relative abundance, %) 376 ($M^+$+1). $^1H$ NMR ($CDCl_3$): $\delta$ 7.90 (d, $J$ = 9.16 Hz, 2H, ArH-2,6), 7.65 (d, $J$ = 4.58 Hz, 2H, ThH-3′,4′), 7.15 (t, $J$ = 4,35 Hz, 1H, ThH-5′), 6.82 (d, $J$ = 9.16 Hz, 2H, ArH-3,5), 4.30 (t, $J$ = 6.16 Hz 4H, $CH_2{-}O$), 3.73 (t, $J$ = 6.16 Hz 4H, $CH_2{-}N$), 2.07 (s, 6H, $C{-}CH_3$). $^{13}C$ NMR ($CDCl_3$): $\delta$ 186.5 ($C{=}O$), 171.3 ($C{=}O$ ester), 151.2 (ThC-2′), 144.5 (ArC-4), 133.6 (ThC-4′), 133.0 (ThC-5′), 132.4 (ArC-2,6), 128.0 (ThC-3′), 126.8 (ArC-1), 111.3 (ArC-3,5), 61.5 ($CH_2{-}O$), 50.0 ($CH_2{-}N$), 21.2 ($C{-}CH_3$).

*[4-Di(2-hydroxyethyl)aminophenyl]-2-furylmethanone Fur-(OH)$_2$ and [4-Di(2-hydroxy-ethyl)aminophenyl]-2-thienylmethanone Thi(OH)$_2$.* [4-Di(2-acetoxyethyl)aminophenyl]-2-furylmethanone Fur(OAc)$_2$ (0.36 g, 1 mmol) or [4-di(2-acetoxyethyl)aminophenyl]-2-thienylmethanone Thi(OAc)$_2$ (0.38 g, 1 mmol) was added to a solution of potassium carbonate (0.28 g, 2 mmol) dissolved in 20 mL of methanol and water (1:1). The mixture was refluxed for 2 h at 80 °C in a water bath. After cooling to room temperature, the mixture was poured into ice water and neutralized with concentrated HCl. The precipitate was filtered off, washed with water, and crystallized from ethanol to give pure **2a** or **2b**.

*[4-Di(2-hydroxyethyl)aminophenyl]-2-furylmethanone Fur-(OH)$_2$* ***2a***. Yield (0.23 g, 0.85 mmol, 85%), mp 94 °C, yellow crystals.

$C_{15}H_{17}NO_4$ (275) calcd. C, 65.45%; H, 6.18%; N, 5.09%; found C, 65.21%; H, 6.16%; N, 5.07. %. $^1H$ NMR ($CD_3OD$): $\delta$ 7.97 (d, $J$ = 9.32 Hz, 2H, ArH-2,6), 7.85 (dd, 1H, $J$ = 1.74, 0.79 Hz FuH-5′), 7.29 (dd, $J$ = 3.63, 0.79 Hz, 1H, FuH-3′), 6.86 (d, $J$ = 9.32 Hz, 2H, ArH-3,5), 6.69 (dd, 3.63, 1.74 Hz, 1H, FuH-4′), 3.80 (t, $J$ = 6.16 Hz, 4H, $CH_2{-}O$), 3.68 (t, $J$ = 6.16 Hz, 4H, $CH_2{-}N$). $^{13}C$ NMR ($CD_3OD$): $\delta$ 181.3 ($C{=}O$), 153.2 (FuC-2′), 152.7 (ArC-4), 147.0 (FuC-5′), 132.2 (ArC-2,6), 124.1 (ArC-1), 119.4 (FuC-3′), 112.1 (FuC-4′), 111.2 (ArC-3,5), 59.2 ($CH_2{-}O$), 53.7 ($CH_2{-}N$).

*[4-Di(2-hydroxyethyl)aminophenyl]-2-thienylmethanone Thi-(OH)$_2$* ***2b***. Yield (0.26 g, 88%), mp 101 °C, canary-yellow crystals.

$C_{15}H_{17}NO_3S$ (291) calcd. C, 61.86%; H, 5.84%; N, 4.81%; S, 11.00%; found C, 61.69%; H, 5.84%; N, 4.73%; S, 11.32%. $^1H$ NMR ($CD_3OD$): $\delta$ 7.85 (d, $J$ = 9.32 Hz, 2H, ArH-2,6), 7.71 (dd, $J$ = 3.79, 1.1 Hz, 2H, ThH-3′,4′), 7.23 (dd, 3.79, 4.90 Hz, 1H, ThH-5′), 6.87 (d, $J$ = 9.32 Hz, 2H, ArH-3,5), 3.80 (t, $J$ = 6.16 Hz, 4H, $CH_2{-}O$), 3.68 (t, $J$ = 6.16 Hz, 4H, $CH_2{-}N$). $^{13}C$ NMR ($CD_3OD$): $\delta$ 187.2 ($C{=}O$), 152.5 (ThC-2′), 144.1 (ArC-4), 133.9 (ThC-4′), 133.1 (ThC-5′), 132.2 (ArC-2,6), 127.9 (ThC-3′), 124.9 (ArC-1), 111.2 (ArC-3,5), 59.2 ($CH_2{-}O$), 53.8 ($CH_2{-}N$).

**Preparation of Sol−Gel Materials.** A mixture of 1.24 cm$^3$ (8.40 mmol) of tetramethoxy silane, 1.20 cm$^3$ (8.41 mmol) of methyl trimethoxy silane (molar ratio of 0.5:0.5), and 2.20 cm$^3$ of methanol was sonicated for 10 min, and then 0.016 mmol of the appropriate solvatochromic compound (5.25 mg MK-(OH)$_2$, 4.40 mg Fur(OH)$_2$, or 4.66 mg Thi(OH)$_2$) dissolved in 0.8 cm$^3$ of methanol and 1.20 cm$^3$ of acidic deionized water (pH = 3) to reach $r = 4$ (molar ratio of $H_2O$/silanes) were added, followed by sonication with a time period of 10 min. The mixture was left in air at room temperature for 5 days and then at 60 °C for 2 days. The obtained solid was ground in a mortar, and the resulting powder was heated at 120 °C for 24 h to complete the sol−gel reaction.

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