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# Solvatochromism of catechol derivatives – solute/solvent interactions

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The solvatochromism of nine push-pull substituted catechol derivatives has been studied in a set of 39 various solvents. The influence of successive methyl substitution at the catechol OH groups on the extent of the solvatochromic shift has been investigated. The positive solvatochromism of 2-(3,4-dihydroxybenzylidene)-2*H*-indene-1,3-dione amounts 4360 cm<sup>-1</sup>, which ranges from toluene to hexamethyl-phosphoric triamide. To the best of our knowledge, it is one of the largest positive solvatochromic extent measured for a positive solvatochromic dye, comparable with Brooker's thiobarbituric acid with an extent of 4400 cm<sup>-1</sup>. The detailed analyses of the solvatochromism were carried out by alternatively using the Kamlet–Taft and Catalán solvent parameters to achieve information of dipolarity versus polarizability effects of solvent upon solvatochromic properties. In solvents with high  $\beta$  values such as alcohols (0.66 <  $\beta$  < 0.90), amides (0.48 <  $\beta$  < 0.80), dimethyl sulfoxide ( $\beta$  = 0.76), tetramethyl urea ( $\beta$  = 0.80) and hexamethyl-phosphoric triamide ( $\beta$  = 1.05) UV–Vis absorption spectra show two separate  $\lambda_{max}$ , which are caused by a deprotonation reaction. The solvatochromic behaviour of the anionic species is compared with those of the catechol derivatives. Copyright © 2012 John Wiley & Sons, Ltd.

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# INTRODUCTION

Solvatochromism is used to describe the pronounced change in position ( $\tilde{v}_{max}$ ) of an UV–Vis absorption band with a change in solvent polarity and has been established as a valuable tool to investigate the versatile properties of organic solvents.<sup>[1-10]</sup> Suitable solvatochromic probes for analytical application are highly dipolar push-pull aromatic systems or other types of those dyes. which contain polar or ionic groups.<sup>[1]</sup> Overall solvent polarity cannot be described quantitatively by a single physicochemical parameter. The extent of solvation is a function of several intermolecular forces between solute and solvent molecules.<sup>[5]</sup> These include nonspecific, dipole/induced dipole forces, dipole/ dipoleforces and ion/dipole forces and specific forces, hydrogen bond donating (HBD), hydrogen bond accepting (HBA), or charge transfer interactions.<sup>[7]</sup> Kamlet and colleagues have developed an LSE (linear solvation energy) model for characterizing manifold interactions between solutes and solvents.<sup>[11-17]</sup> The simplified Kamlet-Taft relationship, which is applied to solvatochromic UV–Vis shifts  $\tilde{v}_{max}$ , is shown in Eqn (1)<sup>[11–17]</sup>:

$$\tilde{v}_{\max} = \tilde{v}_{\max,0} + a \cdot \alpha + b \cdot \beta + s \cdot \pi *$$
(1)

 $\tilde{v}_{max,0}$  is the solute property of a reference system, the nonpolar solvent cyclohexane,  $\alpha$  represents the *HBD* ability,<sup>[11-14]</sup>  $\beta$  describes the *HBA* ability<sup>[14,15]</sup> and  $\pi^*$  describes the dipolarity/ polarizability<sup>[14,16,17]</sup> of the solvents. The contribution of the different solvent effects on the UV–Vis absorption shift  $\tilde{v}_{max}$  is expressed with solvent-independent correlation coefficients *a*, *b* and *s*. Disadvantageously, Kamlet–Taft's  $\pi^*$  parameter does not distinguish between dipolarity and polarizability. Furthermore, the whole empirical solvent parameter set is not based on well-defined reference processes because the solvent parameters were determined from an average of measurements using numerous data.

Catalán *et al.* published an array of alternative empirical solvent parameter scales relating to the Kamlet–Taft scales.<sup>[18–20]</sup> However, for this task well-defined reference systems were used to determine the solvent parameters. For this purpose a suitable pair of homomorph solvatochromic probes were used for each parameter.<sup>[18–20]</sup> In this context *SA* and *SB* correspond to the Kamlet–Taft parameter  $\alpha$  and  $\beta$ . The specific advantage of the new approach is the separate consideration of the polarizability *SP* and dipolarity *SdP* (Eqn (2)).

$$\tilde{v}_{\max} = \tilde{v}_{\max,0} + a \cdot SA + b \cdot SB + c \cdot SP + d \cdot SdP$$
(2)

The extreme sensitivity of the visible absorption spectrum to small changes in the surrounding medium has made several dyes as useful molecular probes. The extent of solvatochromism  $\Delta \tilde{v}$  is the difference between the measured  $\tilde{v}_{max}$  values of the dye in two solvents of widely different polarity. This actuality is attributed to the larger difference in the dipole moment between the electronic ground and the first excited state.

In many technically important dyes the amino group or dialkylamino group is employed as a donor substituent.<sup>[21]</sup> Thus, 4-nitroaniline derivatives have been established as important

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solvatochromic dyes for measuring solvent polarity in terms of the Kamlet–Taft's  $\pi^*$  scale.<sup>[14]</sup> In contrast, in natural dyes the amino group serves as an electron-donating substituent only in few examples. Here, the more important substituent is the catechol moiety because of its ability to undergo deprotonation and simultaneous stabilisation of the negative charge by intramolecular hydrogen bonds (Scheme 1).<sup>[22]</sup> Deprotonation reactions are of interest in optical systems, for example, in their application as acid-base indicators.<sup>[23,24]</sup> In this case, dye molecules convert a chemical interaction into an optically detectable signal. Deprotonation of a hydroxy moiety in push-pull substituted chromophores induces a large bathochromic spectral shift because of electron delocalization of the phenoxide into the chromophore. Importantly, the phenolate oxygen atom is one of the strongest electron-donating substituent actually whose strength can be quantitatively described by its Hammett  $\sigma_n^+$ substituent constant. That is -4.27 compared with -1.70 of the N,N-dimethylamino substituent.[25]

Catechol derivatives are also of importance for surface functionalization.<sup>[26,27]</sup> Therefore, the understanding of the effect of the environment polarity on the UV–Vis absorption property is also of importance to adjust the molecular structure for specific application. Systematic studies on the solvatochromism of catechol derivatives are still lacking in spite of the importance of the catechol moiety in naturally occurring dyes. So far, 4-nitrocatechol and its silicon complexes and a phenolate betaine dye were only studied.<sup>[28,29]</sup>



**Scheme 1**. Protonation/deprotonation equilibrium of acceptor-substituted catechols (X = acceptor groups)

The objective of this study is the investigation of solvent effects on the position of the UV–Vis absorption band of a series of catechol derivatives to show which type of solvent interaction induces a significant shift on the position of the UV–Vis absorption band.

# **RESULTS AND DISCUSSION**

#### **Synthesis**

Compounds **2–4** were synthesized from 3,4-dihydroxybenzaldehyde, 4-hydroxy-3-methoxy-benzaldehyde and 3,4-dimethoxybenzaldehyde **1a–c**, respectively, with malononitrile, indandione and dicyanomethylene indanone in a condensation reaction according to Scheme 2. The catechol derivatives were received as yellow, orange and red solids in good yields.

#### Thermochromism

From thermodynamic investigations it is known that isoequilibrium behaviour can elucidate certain interaction mechanisms.<sup>[30,31]</sup>

The temperature dependence was investigated with chromophore **3a**, because of the most pronounced solvatochromic extent. At room temperature, compound **3a** shows two UV–Vis absorption maxima at  $\lambda_1 = 429 \text{ nm}$  ( $\tilde{v}_{\text{max}} = 23.31 \cdot 10^3 \text{ cm}^{-1}$ ) and  $\lambda_2 = 505 \text{ nm}$  $(\tilde{v}_{max} = 19.80 \cdot 10^3 \text{ cm}^{-1})$  in methanolic solution. The UV-Vis absorption maximum at  $\tilde{v}_{max} = 19.80 \cdot 10^3 \text{ cm}^{-1}$  is caused by the anionic compound (3a)<sup>-</sup>. On increasing temperature, the intensity of the UV–Vis absorption at  $\lambda_1 = 429 \text{ nm}$  ( $\tilde{v}_{\text{max}} = 23.31 \cdot 10^3 \text{ cm}^{-1}$ ) decreases while the intensity of the UV-Vis absorption at  $\lambda_2 = 505 \text{ nm}$  ( $\tilde{\nu}_{max} = 19.80 \cdot 10^3 \text{ cm}^{-1}$ ) increases showing an isosbestic point at 461 nm ( $\tilde{v}_{max} = 21.69 \cdot 10^3 \text{ cm}^{-1}$ , c(**3a**) = 6.1 \cdot 10^{-5} mol L<sup>-1</sup>). These changes are reversible and correspond to the temperature-dependent deprotonation equilibrium, **3a**  $\neq$  (**3a**)<sup>-</sup>. Shifts of the UV-Vis absorption maxima and changes in the band shape cannot be observed as a function of temperature.



Scheme 2. Synthesis of catechol-based dyes 2-4

In 1,4-dioxane and chloroform no temperature dependent shifts of the UV–Vis absorption maximum of **3a** is observed. Therefore, temperature dependent measurements give no indication on isokinetic relationships.

#### Solvent effects on the UV-Vis absorption spectra

The solvatochromism of **2–4** was studied in 39 various solvents of different *HBD* ability, *HBA* ability and dipolarity/polarizability.UV–Vis spectroscopic investigation of the 3,4-dihydroxybenzaldehyde **1a,b** shows one UV–Vis absorption band in nonpolar solvents such as toluene. With increasing solvent polarity a bathochromic shift and a splitting of the UV–Vis absorption band, caused by hydrogen bond formation and deprotonation, is observed. This illustrates very complex solvation behaviour of the catechol moiety as a function of the surrounding medium. The position of the UV–Vis absorption bands are independent of the dye concentration in the range of  $10^{-4}$  to  $10^{-5}$  mol L<sup>-1</sup>, which is an indication that dye aggregation has no noticeable effect on the solvatochromic properties.

Table 1 shows the UV-Vis absorption maxima of the compounds **2–4** and the extent of the solvatochromic shift  $\Delta \tilde{v}$ for selected solvents (the whole UV-Vis data set is given in supporting information). The catechol derivatives show the shortest wavelength in nonpolar solvents such as chloroform  $\lambda_{max}(2a) = 374 \text{ nm} (\tilde{v}_{max} = 26.74 \cdot 10^3 \text{ cm}^{-1})$ , benzene and toluene  $\lambda_{\text{max}}(3a) = 379 \text{ nm}$  ( $\tilde{\nu}_{\text{max}} = 26.39 \cdot 10^3 \text{ cm}^{-1}$ ), and dichloromethane  $\lambda_{max}$ (4a) = 450 nm ( $\tilde{\nu}_{max}$  = 22.22 $\cdot$ 10<sup>3</sup> cm<sup>-1</sup>). The largest bathochromic shift of the UV-Vis absorption maximum is observed in polar solvents dimethyl sulfoxide (DMSO),  $\lambda_{max}(2a) = 408 \text{ nm}$  $(\tilde{v}_{max} = 24.51 \cdot 10^3 \text{ cm}^{-1})$  and hexamethyl-phosphoric triamide (HMPA)  $\lambda_{max}(3a) = 454 \text{ nm}$  ( $\tilde{v}_{max} = 22.03 \cdot 10^3 \text{ cm}^{-1}$ ),  $\lambda_{max}(4a) =$ 525 nm ( $\tilde{v}_{max} = 19.05 \cdot 10^3 \text{ cm}^{-1}$ ). These shifts of the UV–Vis absorption bands correspond to a positive solvatochromism with solvatochromic ranges of  $\Delta \tilde{v} = 2230$  (**2a**) to 4360 cm<sup>-1</sup> (**3a**). The latter one is very high and comparable with the largest so far recorded red shift for a thiobarbituric acid derivative with  $4400 \text{ cm}^{-1}$ .<sup>[32,33]</sup>

For compounds with 4-hydroxy-3-methoxy moieties (**2b**, **3b**, **4b**) the most hypsochromic UV–Vis absorption maxima are observed in benzene  $\lambda_{max}(\mathbf{2b}) = 363 \text{ nm}$  ( $\tilde{v}_{max} = 27.55 \cdot 10^3 \text{ cm}^{-1}$ ),  $\lambda_{max}(\mathbf{3b}) = 410 \text{ nm}$  ( $\tilde{v}_{max} = 24.39 \cdot 10^3 \text{ cm}^{-1}$ ) and 1,1,2,2-tetrachloroethane  $\lambda_{max}(\mathbf{4b}) = 464 \text{ nm}$  ( $\tilde{v}_{max} = 21.55 \cdot 10^3 \text{ cm}^{-1}$ ). The largest bathochromic shift is found in polar solvents tetramethyl urea (TMU)  $\lambda_{max}$   $(2b) = 385 \text{ nm} (\tilde{v}_{\text{max}} = 25.97 \cdot 10^3 \text{ cm}^{-1}), \ \lambda_{\text{max}}(3b) = 436 \text{ nm} (\tilde{v}_{\text{max}} = 10^{-1})$ 22.94 · 10<sup>3</sup> cm<sup>-1</sup>) and formamide  $\lambda_{max}$  (4b) = 526 nm ( $\tilde{\nu}_{max}$  = 19.01  $\cdot$  10<sup>3</sup> cm<sup>-1</sup>). From this a solvatochromic shift of  $\Delta \tilde{v} = 1450$  (**3b**) to  $2540 \text{ cm}^{-1}$  (**4b**) can be observed. Compounds with CH<sub>3</sub>protected OH-group 2c, 3c and 4c show that the UV-Vis absorption maximum is blue-shifted and the solvatochromic shift becomes very small (Table 1) because hydroxy groups are not available for interactions with HBA solvents. The most hypsochromic shifts are observed in hexane,  $\lambda_{max}(2c) = 360 \text{ nm}$  ( $\tilde{v}_{max} = 27.78 \cdot 10^3 \text{ cm}^{-1}$ ),  $\lambda_{\text{max}}(3c) = 408 \text{ nm}$  ( $\tilde{v}_{\text{max}} = 24.51 \cdot 10^3 \text{ cm}^{-1}$ ) and  $\lambda_{\text{max}}(4c) = 455 \text{ nm}$  $(\tilde{\nu}_{max} = 21.98 \cdot 10^3 \text{ cm}^{-1})$ . In benzonitrile,  $\lambda_{max}(2c) = 380 \text{ nm}$   $(\tilde{\nu}_{max} = 1.00 \text{ cm}^{-1})$ 26.32  $\cdot 10^3$  cm<sup>-1</sup>), and HMPA,  $\lambda_{max}(3c) = 420$  nm ( $\tilde{\nu}_{max} = 23.81 \cdot 10^3$  cm<sup>-1</sup>),  $\lambda_{max}(4c) = 480 \text{ nm} (\tilde{v}_{max} = 20.83 \cdot 10^3 \text{ cm}^{-1})$ , the most bathochromic UV-Vis absorption maxima are observed. It is clearly seen that an extension of the conjugated  $\pi$ -system from **2** to **4** is caused in a bathochromic shift of the UV-Vis absorption maxima. Catechol-based chromophores 2-4a and compounds 2-4b containing one hydroxy group show in alcohols, carbonic acid amides, DMSO, TMU and HMPA two separated UV-Vis absorption maxima. Exemplary, Fig. 1 shows the UV-Vis absorption spectra of **3a** in selected solvents.



**Figure 1**. UV–Vis absorption spectra of **3a** in selected solvents. In DMSO and HMPA two absorption maxima are observed (see text)

Solvent	$\tilde{v}_{max}[10^3 \mathrm{cm}^{-1}]$								
	2a	2b	2c	3a	3b	3c	4a	4b	4c
Dichloromethane	26.41	26.81	26.67	25.51	23.98	24.15	22.22 <sup>c</sup>	21.14	21.32
Toluene	а	27.47	27.03	26.39 <sup>c</sup>	24.21	24.45	а	а	21.60
Diethyl ether	26.74	26.88	27.17	а	а	24.39	21.05	21.37	21.51
1,4-Dioxane	26.39	26.88	26.95	24.63	23.81	24.27	21.46	20.70	21.32
Dimethylformamide	24.63	26.11	26.74	22.88	22.99	23.87	19.38	19.42	20.96
DMSO	24.51 <sup>b</sup>	26.11	26.53	22.94	22.99	23.81 <sup>b</sup>	19.46	19.46	20.92
$\Delta \tilde{v}[\text{cm}^{-1}]$	2230	1570	1460	4360	1450	700	3170	2540	1150
<sup>a</sup> Insoluble.									

**Table 1.** UV–Vis absorption maxima of compounds **2–4** in various solvents and the extent of the solvatochromic shift

<sup>b</sup>Solvent with the highest bathochromic shift.

<sup>c</sup>Solvent with the highest hypsochromic shift.

It could be proved that the longer wavelength absorption band is associated with the monoanionic species of the dyes by means of UV–Vis spectroscopic investigations and nuclear magnetic resonance (NMR) experiments using 1,8-diazabicyclo [5.4.0]-undec-7-ene (DBU) as base for deprotonation. The reaction between the dyes **2–4a,b** and DBU in toluene was used as the reference system esteeming a first indication of the existence of deprotonated species in other solvents (supporting information).

#### Linear solvation energy correlation analyses

The influence of the solvent properties on the shift of  $\tilde{v}_{max}$  has been determined by means of multiple correlation analyses using the solvent polarity parameter sets of Kamlet–Taft and Catalán. The best correlation results are summarized in Tables 2 and 3. The correlation coefficients *r* are about 0.90 for LSE relationships, which indicates a high validity of the multiparameter equations and allow significant conclusions. Specific solvent–solute interactions through hydrogen bonding are expressed by the solvent acidity  $\alpha$  or SA, and by the solvent basicity  $\beta$  or SB.

The preferential location of the negative charge can be evaluated and discussed by knowledge of the solvent-independent coefficients, which are calculated by means of multiple correlation analyses. The algebraic sign of coefficient *a* provides information about the solvent interactions with the appropriate donor fragment of the respective dye. A positive sign indicates a hypsochromic shift and a negative sign a bathochromic shift. The latter occurrence is associated with an enhancement of the push–pull character of the dye. Otherwise, the coefficient *a* would be negative if the mesomeric structure **II** with the negatively charged acceptor group is predominant. In this case the *HBD* attack would increase the acceptor strength of this group.

However, the parameter of more significance for these compounds is b. The distinct magnitude of the coefficient of the b term is caused by the specific solvation of the catechol moiety by hydrogen bonding to the HBA-site of the solvent. Compounds 2a-c, 3b,c and 4c formally show no dependence on solvent acidity (a = 0). HBD solvents can interact both with oxygen atoms of the hydroxy groups (donor) and carbonyl/cyano groups (acceptor). Preferentially, protic solvents act with the oxygen atom of the carbonyl groups and/or the cyano groups (a < 0). Interactions of these kinds of solvents with the electron donor fragment caused in a hypsochromic shift of the UV–Vis absorption maxima (a > 0), the interactions with the electron acceptor moiety lead to a bathochromic shift. If both effects provide a similar contribution the coefficient a can be zero. The interactions of HBD solvents with the acceptor moieties reduce their electron density, consequentially the push-pull characters of the dyes increase. Compounds 3a and 4a,b have a negative sign for coefficient a. Thus, HBD solvents preferentially interact with the electron acceptor moiety of the dye. Furthermore, the correlation analyses show a negative sign of the coefficient b, which means that HBA solvents interact with the acidic hydrogen atom of the hydroxy groups. The solvent basicity provides the largest contributions.

**Table 2.** Values of the solvent-independent correlation coefficients *a*, *b* and *s* for the Kamlet–Taft Eqn (1); wavenumber of the reference system cyclohexane  $\tilde{v}_{max,0}$ , number of solvents *n*, correlation coefficient *r*, standard deviation *sd*, and significance *f* for compounds **2–4** 

	$\widetilde{v}_{\max,0}$	а	b	S	n	r	sd	f
2a	27.797	0	-2.669	-1.494	28	0.874	0.434	< 0.0001
2b	27.775	0	-1.215	-0.929	29	0.884	0.205	< 0.0001
2c	27.621	0	0	-1.190	36	0.933	0.116	< 0.0001
3a	27.002	-0.464	-3.317	-1.807	28	0.911	0.484	< 0.0001
3b	24.853	0	-1.260	-0.936	29	0.967	0.108	< 0.0001
3c	24.618	0	-0.264	-0.576	36	0.932	0.073	< 0.0001
4a	22.851	-0.427	-3.510	-0.731	33	0.944	0.385	< 0.0001
4b	23.051	-0.865	-4.975	-1.465	29	0.990	0.218	< 0.0001
4c	21.859	0	-0.656	-0.496	36	0.938	0.101	< 0.0001

**Table 3.** Values of the solvent-independent correlation coefficients *a*, *b*, *c* and *d* for Catalán Eqn (2); wavenumber of a reference system (gas phase)  $\tilde{v}_{max,0}$ , number of solvents *n*, correlation coefficient *r*, standard deviation *sd*, and significance *f* for compounds **2–4** 

	$\tilde{v}_{\max,0}$	а	Ь	С	d	c/d	п	r	sd	f
2a	30.236	0	-3.242	-2.121	-1.922	1.10	26	0.922	0.342	< 0.0001
2b	27.895	+0.339	-1.129	0	-1.164	0	29	0.979	0.093	< 0.0001
2c	28.821	0	0	-1.989	-0.841	2.37	34	0.944	0.109	< 0.0001
3a	27.361	0	-3.327	0	-2.355	0	27	0.949	0.377	< 0.0001
3b	25.894	0	-1.264	-1.710	-0.655	2.61	28	0.924	0.159	< 0.0001
3c	25.075	0	-0.171	-0.737	-0.507	1.45	34	0.943	0.068	< 0.0001
4a	25.950	-1.790	-4.088	-3.881	-0.624	6.22	31	0.943	0.379	< 0.0001
4b	23.769	-0.961	-2.982	-2.168	-0.863	2.51	27	0.941	0.295	< 0.0001
4c	22.976	-0.179	-0.744	-1.633	-0.308	5.30	34	0.945	0.095	< 0.0001

Compounds **2c**, **3c** and **4c** do not have classical hydrogen bond donors, which results in a smaller amount of coefficient *b*. The influence regarding the interaction of compounds **2c**, **3c** and **4c** with *HBA* solvents is negligible because the catechol moiety is protected. The UV–Vis absorption maxima are also shifted to higher wavelength with increasing solvent dipolarity and polarizability (s < 0).

Altogether, the compounds **2–4** show positive solvatochromism with regard to the parameter  $\pi^*$ , which correlates with a higher dipole moment of the electronically excited state.

The correlation analyses, which use the solvent parameter of Catalán, provide regression results with almost the same parameter coefficient signs but allow a differentiation of the solvent polarity in the two terms *SP* and *SdP*.

The regression analyses with the more recent parameter set of Catalán were received with better correlation coefficients r, shown in Table 3. The coefficient a shows a positive value for compound **2b**; coefficient *a* is negative for **4a–c**. Hence, the enhancement of the push-pull character is due to both the preferential solvation of the acceptor substituent by HBD solvents and the catechol moiety by HBA solvents. For compounds 2a, 2c and 3a-c the term a is formally zero, which shows that the preferential solvation of the oxygen atom of the catechol and dimethoxy groups, respectively, or of the carbonyl/cyano groups by HBD solvents is equally. The substituent change from hydroxy groups to methoxy groups leads gradually in smaller b values because with the introduction of methoxy groups there are no more hydrogen bond donor fragments in the molecules. Because of separated consideration of polarizability SP and dipolarity SdP, more detailed information about nonspecific interactions between solute and solvent can be drawn. A bathochromic shift of  $\lambda_{max}$  is observed caused by the induced polarizability of the  $\pi$ -system through the solvent molecules. It can be seen that the magnitude of the polarizability SP (coefficient c) is higher than that of the dipolarity SdP (coefficient d), excluding compounds **2b** and **3a** (c = 0). Otherwise, negative signs for the terms c and d were observed, showing a higher dipole moment of the electronically excited state. Catalán et al. figured out that the Kamlet–Taft parameter  $\pi^*$  reflects a

mixture of solvent polarizability *SP* and dipolarity *SdP* in a relation of 2:1.<sup>[19]</sup> This relation is not given for the discussed chromophores, showing the *c/d*-value in Table 3, and can explain the differences between the LSER of Kamlet–Taft and Catalán. In comparison with catechol-based chromophores **2–4a**, it is striking that for **3a**, with the least polarizable carbonyl group, the largest solvatochromic extent and the largest *d* coefficient has been measured. With increasing of absolute value of coefficient *c* (influence of polarizability) from **3a**–**2a**–**4a** the absolute values of coefficient *d* (influence of dipolarity) decreases.

The plot of calculated wavenumbers as a function of measured wavenumbers for **3a** using the parameter set of Catalán is shown in Fig. 2.

As mentioned above, in some solvent compounds with hydroxy groups two UV–Vis absorption bands can be observed. Generally, for catechol derivatives two aspects with regard to solvatochromism and reaction with solvent molecules have to be taken into account. On the one hand, the solvent basicity can cause a deprotonation and on the other hand the acceptor strength of the chromophore is important, because the rate of possible deprotonation in a respective solvent increases with increasing electron accepting ability. The longer wavelength UV–Vis absorption maxima of the anionic species are summarized in Table 4.

UV–Vis experiments of the compounds using the base DBU in toluene clearly show that the UV–Vis absorption maximum after dye deprotonation is observed in the same region of the longer-wavelength absorption of the dyes as measured in DMSO, for example (supporting information). Generally, for the anionic species a smaller solvatochromic effect on  $\tilde{\nu}_{max}$  is observed. The linear multiple regression analyses of the monoanions show also high correlation coefficients *r* (Table 5), which allows significant conclusions about the solvatochromic behaviour of these compounds.

For anionic species a positive sign is determined for the coefficient *a*. The UV–Vis absorption maximum undergoes a hypschromic shift with increasing solvent acidity. Hydrogen bond donating and electron pair accepting solvents interact preferentially with the chromophore donor moiety (a > 0).



Figure 2. Results of the multiple correlation analyses of 3a (=) and (3a)<sup>-</sup> (O) using Catalán's solvent parameter set

are observed									
Solvent	$\tilde{\nu}_{max}$ [10 <sup>3</sup> cm <sup>-1</sup> ]								
	(2a) <sup>−</sup>	(2b) <sup>−</sup>	(3a) <sup>−</sup>	(3b) <sup>-</sup>	(4a) <sup>−</sup>	(4b) <sup>−</sup>			
Methanol	22.42	22.47	19.80	19.69	17.73	17.73			
Ethanol	23.32	22.08	19.57	19.42	17.70	17.73			
1-Propanol	22.22	21.88	19.49	19.34	17.83	17.64			
2-Propanol	22.22	21.74	19.49	19.38	17.79	17.64			
1-Butanol	22.17	21.79	19.53	19.31	17.79	а			
Water	22.32	а	а	а	а	а			
1,2-Ethanediol	22.32	22.37	19.46	а	а	17.86			
НМРА	а	22.52	18.73	а	17.61	а			
Formamide	22.03	a	19.42	20.37	17.27	17.79			
NMF	21.93	а	а	19.34	а	17.70			
Dimethylformamide	21.69	21.60	19.16	19.31	17.30	17.61			
DMSO	21.55	21.51	19.01	19.42	17.30	17.61			
DMAA	21.69	21.51	19.05	19.27	17.45	17.57			
TMU	21.69	21.60	19.23	19.31	17.51	17.54			
$\Delta \tilde{v}$ [cm <sup>-1</sup> ]	1760	1020	1080	1100	550	310			
<sup>a</sup> Solvent is not considered in multiple regression analysis (Table 5).									

**Table 4.** UV–Vis absorption maxima of the anionic species of **2–4a,b** in solvents in which two separated UV–Vis absorption bands are observed

**Table 5.** Values of the solvent-independent correlation coefficients *a*, *b*, *c* and *d* for Catalán Eqn (2); wavenumber of a reference system  $\tilde{v}_{max,0}$ , number of solvents *n*, correlation coefficient *r*, standard deviation *sd*, and significance *f* for anionic species (2–4a,b)<sup>-</sup>

	$\widetilde{v}_{\max,0}$	а	b	С	d	n	r	sd	f
(2a) <sup>−</sup>	22.246	+0.974	-1.756	-1.339	0	12	0.977	0.066	< 0.0001
(2b) <sup>−</sup>	23.802	+1.000	-0.687	-0.978	-0.407	11	0.986	0.065	< 0.0001
(3a) <sup>−</sup>	21.170	+0.438	-0.413	-1.916	-0.308	12	0.964	0.065	< 0.0001
(3b) <sup>-</sup>	16.506	+1.670	0	+3.522	0	10	0.953	0.102	< 0.0001
(4a) <sup>−</sup>	18.637	+0.184	-0.593	-2.039	0	11	0.936	0.075	< 0.0001
(4b) <sup>-</sup>	17.351	+0.389	0	+0.281	0	11	0.953	0.029	< 0.0001

Solvents with hydrogen bond acceptor and electron pair donating ability show interactions with the hydroxy group in  $(2-4a)^-$  (b < 0). The negative charge of the phenoxide is stabilized through an intramolecular hydrogen bond and a fast proton exchange. With the deprotonated hydroxy group in 4-position and 3-OMe-functionalization $(2-4b)^-$ , expectedly, the absolute value of *b* is zero or at least smaller compared with that of the catechol derivatives. The comparison of polarizability *SP* (coefficient *d*) and dipolarity *SdP* (coefficient *e*) shows, that *SdP* only has a marginal influence. Figure 2 presents the result of the determined regression plot of  $(3a)^-$  ( $\bigcirc$ ).

# CONCLUSIONS

Various donor-acceptor  $\pi$ -conjugated compounds bearing the catechol moiety were presented. The evaluation of the solvatochromic properties of these catechol derivatives has been carried out using alternatively the Kamlet–Taft and Catalán solvent parameter scales. It can be clearly shown that Catalán's improved empirically determined solvents parameter set allows a differentiation of polarizability versus dipolar effects on solvatochromism of complex dyes and seem to be a valuable tool for quantitative separation of these effects. Advantageously, the square correlation analyses of the solvatochromism of the catechol derivatives using Catalán's solvent parameter show that the influence of dipolarity rather than polarizability of solvent on solvatochromic probe are crucial that a large solvatochromic extend is achieved. Thus, the recent four empirical solvent scales of Catalán allow a more comprehensive interpretation of solvent effects on solvatochromism compared with the established Kamlet–Taft solvent parameters. UV–Vis absorption measurements of **3a** in methanol show temperature dependence caused by the protonation/deprotonation equilibrium between **3a** and (**3a**)<sup>–</sup>.

As can be seen, the coefficient *a* (influence of *HBD* solvents) of the anionic species ( $(2-4a,b)^{-}$ ) is obtained with a positive value, which indicates that the negative charge concentration is mostly located on the catechol moiety of the dyes.

# **EXPERIMENTAL SECTION**

#### General

Solvents for UV–Vis measurements were dried and distilled according to standard procedures prior to use. Compounds **2–4** were synthesized in a

Knoevenagel condensation reaction using the aldehydes 1. NMRspectroscopical data for compounds 2a-c were published elsewhere.[34-36] 2-(3-Oxo-2,3-dihydroinden-1-ylidene)-malononitrile was prepared according to a known procedure.<sup>[37]</sup> All other compounds were commercially available and used as received. NMR spectra were recorded with a Bruker Avance 250 (Bruker Biospin GmbH, Silberstreifen 4, 76287 Rheinstetten, Germany) spectrometer using the solvent residue as the internal standard. Infrared (IR) spectra were obtained with a BioRad FT-IR Spectrometer FTS 165. Elemental analyses were measured using a Vario EL from Elementaranalysensysteme GmbH Hanau. UV-Vis spectra were obtained with a MCS 400 diode-array spectrometer from Carl Zeiss Jena with freshly prepared dye solutions  $(c \approx 10^{-5} \text{ mol L}^{-1})$ . Multiple regression analyses were performed with the statistical program ORIGINPRO 8G (OriginLab Corporation, One Roundhouse Plaza, Northampton, MA 01060 USA). For temperature-dependent measurements 40 mL of a methanolic solution of compound **3a**  $(6.1 \cdot 10^{-5} \text{ mol L}^{-1})$ was kept in a thermostated bath at different temperatures (267-333 K). The UV-Vis spectrum at each temperature was measured using a UV-Vis immersion cell with a path length of d = 0.5 nm.

#### Preparation

An ethanolic solution of one equivalent of the acceptor was slowly added to a stirred solution of one equivalent of the respective aldehyde. The mixture was refluxed for 2 h. In case of compounds **2a–c**, two drops of piperidine were used as a catalyst. After precipitation the dye was filtered, washed with cold ethanol and dried under reduced pressure.

#### 2-(3,4-dihydroxybenzylidene)-2H-indene-1,3-dione, 3a

Yellow solid, Yield: 74%. Mp: 259–261 °C.  $C_{16}H_{10}O_4$  (266.25) Anal. Found: C 72.35; H 3.83. Calcd: C 72.18; H 3.79. IR: 3460  $\nu$ (OH) (H-bonds), 3235  $\nu$ (OH), 3093, 3041  $\nu$ (C–H), 1721  $\nu$ (C=O), 1665, 1594  $\nu$ (C=C), 1551, 1530, 1381, 1295, 1244, 1185, 1161, 1094 cm<sup>-1</sup>. <sup>1</sup> H NMR ( $\delta$ ,  $d_6$ -DMSO, 250 MHz): 6.90 (1H, d, <sup>3</sup>*J* = 8.4 Hz, ArH), 7.65 (1H, s, CH), 7.84 (1H, dd, <sup>3</sup>*J* = 8.4 Hz, <sup>4</sup>*J* = 2.0 Hz, ArH), 7.90 (4H, m, ArH), 8.34 (1H, d, <sup>4</sup>*J* = 2.0 Hz, ArH), 9.57 (1H, bs, OH), 10.49 (1H, bs, OH). <sup>13</sup>C NMR ( $\delta$ ,  $d_6$ -DMSO, 62.9 MHz): 116.1, 121.0, 122.9, 125.1, 125.4, 130.6, 135.6, 135.7, 139.5, 141.9, 145.5, 147.2, 152.9, 175.2, 189.3, 190.3.  $\varepsilon$ (DCM,  $\lambda_{max}$  = 392 nm): 38,000 L mol<sup>-1</sup> cm<sup>-1</sup>.

#### 2-(4-hydroxy-3-methoxybenzylidene)-2H-indene-1,3-dione, 3b

Yellow solid, Yield: 85%. Mp: 209–210 °C.  $C_{17}H_{12}O_4$  (280.27) Anal. Found: C 73.35; H 4.33. Calcd: C 72.85; H 4.32. IR: 3091  $\nu$ (C–H), 1721  $\nu$ (C=O), 1680, 1573  $\nu$ (C=C), 1509, 1437, 1389, 1279, 1177, 1158, 1019 cm<sup>-1</sup>. <sup>1</sup> H NMR ( $\delta$ ,  $d_6$ -DMSO, 250 MHz): 3.19 (3H, s, OCH<sub>3</sub>), 6.93 (1H, d, <sup>3</sup>J=8.3 Hz, ArH), 7.74 (1H, s, CH), 7.91 (5H, m, ArH), 8.70 (1H, d, <sup>4</sup>J=1.8 Hz, ArH), 10.61 (1H, bs, OH). <sup>13</sup> C NMR ( $\delta$ ,  $d_6$ -DMSO, 62.9 MHz): 55.2, 116.5, 121.4, 123.2, 125.9, 126.4, 130.1, 135.3, 135.9, 139.6, 142.1, 145.4, 147.3, 153.3, 175.6, 189.8, 191.3.  $\epsilon$ (DCM,  $\lambda_{max}$ =417 nm): 39,300 L mol<sup>-1</sup> cm<sup>-1</sup>.

#### 2-(3,4-dimethoxybenzylidene)-2H-indene-1,3-dione, 3c

Yellow solid, Yield: 87%. Mp: 203–204 °C.  $C_{18}H_{14}O_4$  (294.30) Anal. Found: C73.51; H 4.82. Calcd: C 73.46; H 4.79. IR: 3087, 3010  $\nu$ (C–H), 2975, 2846  $\nu$ (CH<sub>3</sub>), 1713  $\nu$ (C=O), 1673, 1561  $\nu$ (C=C), 1509, 1428, 1275, 1248, 1144, 1019 cm<sup>-1</sup>. <sup>1</sup> H NMR ( $\delta$ ,  $d_6$ -DMSO, 250 MHz): 3.89 (3H, s, OCH<sub>3</sub>), 3.90 (3H, s, OCH<sub>3</sub>), 7.16 (1H, d, <sup>3</sup>*J*=8.5 Hz, ArH), 7.80 (1H, s, CH), 7.94 (4H, m, ArH), 8.04 (1H, dd, <sup>3</sup>*J*=8.5 Hz, <sup>4</sup>*J*=1.8 Hz, ArH), 8.69 (1H, d, <sup>4</sup>*J*=1.8 Hz, ArH). <sup>13</sup> C NMR ( $\delta$ ,  $d_6$ -DMSO, 62.9 MHz): 55.8, 56.8, 117.1, 122.9, 123.0, 125.2, 125.3, 131.9, 135.6, 136.0, 139.4, 141.9, 147.1, 147.6, 153.5, 176.1, 189.5, 190.2.  $\varepsilon$ (DCM,  $\lambda_{max}$ =414 nm): 39,000 L mol<sup>-1</sup> cm<sup>-1</sup>.

#### 2-(2-(3,4-Diyhdroxybenzylidene)-3-oxo-2,3-dihydroinden-1-ylidene)malononitrile, **4a**

Red solid, Yield: 86%. Mp: 252–254 °C.  $C_{19}H_{10}N_2O_3$  (314.29) Anal. Found: C72.65; H 3.32; N 8.93. Calcd: C 72.61; H 3.21; N 8.91. IR: 3318  $\nu$ (OH), 3083  $\nu$ (C–H), 2228, 2214  $\nu$ (CN), 1703  $\nu$ (C=O), 1527  $\nu$ (C=C), 1505, 1297,

1118 cm<sup>-1</sup>. <sup>1</sup> H NMR (δ, *d*<sub>6</sub>-DMSO, 250 MHz): 6.91 (1H, d, <sup>3</sup>*J* = 8.4 Hz, ArH), 7.64 (1H, dd, <sup>3</sup>*J* = 8.4 Hz, <sup>4</sup>*J* = 2.0 Hz, ArH), 7.93 (4H, m, ArH), 8.29 (1H, s, CH), 8.46 (1H, d, <sup>3</sup>*J* = 7.5 Hz, ArH), 9.63 (1H, bs, OH), 10.66 (1H, s, OH). <sup>13</sup>C NMR (δ, *d*<sub>6</sub>-DMSO, 62.9 MHz): 69.4, 114.7, 114.9, 115.9, 121.1, 123.8, 124.2, 124.8, 125.5, 130.6, 135.1, 135.5, 136.9, 139.0, 145.3, 147.7, 153.4, 163.0, 186.3.  $\varepsilon$ (DCM,  $\lambda_{max}$  = 450 nm): 36,500 L mol<sup>-1</sup> cm<sup>-1</sup>.

#### 2-(2-(4-Hydroxy-3-methoxybenzylidene)-3-oxo-2,3-dihydroinden-1yli-dene)malono-nitrile, **4b**

Wine solid, Yield: 84%. Mp: 239–240 °C.  $C_{20}H_{12}N_2O_3$  (328.32) Anal. Found: C73.29; H 3.70; N 8.70. Calcd: C 73.16; H 3.68; N 8.53. IR: 3401  $\nu$ (OH), 3088  $\nu$ (C–H), 2217, 2205  $\nu$ (CN), 1698  $\nu$ (C=O), 1555  $\nu$ (C=C), 1503, 1293, 1144 cm<sup>-1</sup>. <sup>1</sup> H NMR ( $\delta$ ,  $d_6$ -DMSO, 250 MHz): 3.89 (3H, s, OCH<sub>3</sub>), 6.95 (1H, d, <sup>3</sup>J=8.3 Hz, ArH), 7.57 (1H, dd, <sup>3</sup>J=8.3 Hz, <sup>4</sup>J=1.6 Hz, ArH), 7.91 (4H, m, H-2, ArH), 8.34 (1H, s, CH), 8.48(1H, d, <sup>3</sup>J=7.8 Hz, ArH), 10.82 (1H, bs, OH). <sup>13</sup>C NMR ( $\delta$ ,  $d_6$ -DMSO, 62.9 MHz): 56.0, 83.3, 102.6, 114.7, 115.1, 115.8, 116.2, 117.5, 124.1, 126.5, 135.4, 136.0, 137.4, 139.5, 147.7, 154.3, 163.6, 174.8, 177.7, 187.0.  $\varepsilon$ (DCM,  $\lambda_{max} = 473$  nm): 38,000 L mol<sup>-1</sup> cm<sup>-1</sup>.

#### 2-(2-(3,4-Dimethoxybenzylidene)-3-oxo-2,3-dihydroinden-1-ylidene)malononitrile, **4c**

Wine solid, Yield: 79%. Mp: 222–224 °C.  $C_{21}H_{14}N_2O_3$  (342.35) Anal. Found: C 73.67; H 4.11; N 8.18. Calcd: C 73.68; H 4.12; N 8.18. IR: 3098, 3004  $\nu$ (C–H), 2961, 2831  $\nu$ (CH<sub>3</sub>), 2218, 2207  $\nu$ (CN), 1692  $\nu$ (C=O), 1588, 1553  $\nu$ (C=C), 1503, 1433, 1352, 1283, 1235, 1154 cm<sup>-1</sup>. <sup>1</sup> H NMR ( $\delta$ ,  $d_6$ -DMSO, 250 MHz): 3.88 (3H, s, OCH<sub>3</sub>), 3.91 (3H, s, OCH<sub>3</sub>), 7.19 (1H, d, <sup>3</sup>*J*=8.8 Hz, ArH), 7.70 (1H, dd, <sup>3</sup>*J*=8.8 Hz, <sup>4</sup>*J*=2.3 Hz, ArH), 7.95 (4H, m, ArH), 8.36 (1H, s, CH), 8.51 (1H, d, <sup>3</sup>*J*=7.8 Hz, ArH). <sup>13</sup>C NMR ( $\delta$ ,  $d_6$ -DMSO, 62.9 MHz): 56.1, 56.3, 90.2, 110.6, 115.7, 116.1, 117.5, 122.4, 123.7, 124.1, 127.4, 135.9, 136.3, 139.4, 140.6, 145.7, 154.8, 164.6, 176.8, 176.3, 187.0.  $\epsilon$ (DCM,  $\lambda_{max}$ =469 nm): 38600 L mol<sup>-1</sup> cm<sup>-1</sup>.

## SUPPORTING INFORMATION

Kamlet–Taft's and Catalán's solvent parameters, UV–Vis absorption maxima of compound **2–4**, UV–Vis absorption spectra of **2–4a,b** in toluene, dimethyl sulfoxide and after addition of 1,8-diazabicyclo [5.4.0]-undec-7-ene, UV–Vis absorption maxima of **3a** in methanol at different temperatures.

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