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A solvatochromic study of silicates and borate containing 4-nitrocatechol ligands

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Solvatochromism of 4-nitrocatechol (1), tetra-*n*-butylammonium 2-hydroxy-4-nitrophenolate (2), sodium tris(4-nitrobenzene-1,2-diolato)silicate (3a), tetra-*n*-butylammonium tris(4-nitrobenzene-1,2-diolato)silicate (3b), pyrrolidinium tris(4-nitrobenzene-1,2-diolato)silicate (3c), (3-amino-1-propyl)-bis(4-nitrobenzene-1,2-diolato)silicate (4a), and (*N,N*-diethyl-3-amino-1-propyl)-bis(4-nitrobenzene-1,2-diolato)silicate (4b) as well as potassium bis(4-nitrobenzene-1,2-diolato)borate (5) has been studied in a set of common solvents. The origin of the solvent-induced UV/vis band shifts of 1–3c, and 5 has been determined by means of Linear Solvation Energy Relationship (LSER) using the empirical Kamlet–Taft and Catalán solvent parameter sets, respectively. The solvent-induced UV/vis band shift of the negatively charged moiety of all solvatochromic dyes studied is mainly a function of the hydrogen-bond donor (HBD) strength and the dipolarity/polarizability of the solvent as shown by multiple regression analyses. HBD solvents cause a hypsochromic shift of the UV/vis band due to specific solvation of the anion site. Oppositely, increasing dipolarity/polarizability of the solvent induces a bathochromic shift of the UV/vis absorption band. The donor strength of the solvent has an influence on the UV/vis band shift since ion pair formation occurs in solvents of low relative permittivity. This is shown by the impact of the counter ion of sodium tris(4-nitrobenzene-1,2-diolato)silicate (3a) compared to tetra-*n*-butylammonium tris(4-nitrobenzene-1,2-diolato)silicate (3b). The influence of the counter ion on the position of the UV/vis absorption band occurs in the same way as HBD solvents do. Na^+ and the pyrrolidinium ion, respectively, have a stronger influence than the tetra-*n*-butylammonium ion on the solvatochromic band shift due to the stronger cation–anion interaction.

Supporting information may be found in the online version of this paper.

Keywords: chromophores; silicates; solvatochromism; solvent effects; ion pairs

INTRODUCTION

Solvatochromism has been established as a valuable tool to investigate the polarity of common organic solvents, solvent mixtures, ionic liquids, supercritical fluids, and salt solutions.[1–4] Furthermore, the use of solvatochromism to measure the polarity of an environment has been widely extended to inorganic surfaces, natural and synthetic polymers, colloids, micelles, and compositions of various materials.[5–14]

Ionic chromophores can cause different effects on the UV/vis band depending on the type of interaction and molecular structure of the dye. The occurrence of a solvatochromic UV/Vis band can be mainly attributed to three different sources.

Anion/cation interaction

The solvatochromic UV/vis band corresponds to a charge transfer (CT) transition from an anionic site to a cationic site due to HOMO–LUMO orbital interaction. These UV/vis bands derive either from an intramolecular CT transition as known for Reichardt's dye, Brooker's Merocyanine, and related compounds, or intermolecular CT transition as known for Kosower's *N*-Ethyl-4-methoxycarbonylpyridinium iodide, tropylium iodide, and various other anion–cation combinations.[15]

Solely cation

The UV/vis band originates from the cation, e.g., a solvatochromic triphenylmethylium dye.[16] The anion does not contribute to the chromophoric π-electron system by orbital interaction. Anion serves as electrostatic compensation which can have an effect because the solvent modifies the cation–anion separation. The solvatochromism of donor–cation CT complexes (pyrene–tropylium) can also be classified in this category.[17]

Solely anion

The UV/vis band originates from the anion, e.g., 4-nitrocatecholate.[18] The cation does not contribute to the chromophoric π-electron system by orbital interaction. Cation serves as electrostatic compensation which can have an effect due to the solvent or a complexating agent modifies the anion–cation separation. Solvatochromism of anion–acceptor CT complexes (bromide–tetracyanoethylene) can also be classified in this category.[19]

In this work, we report on the synthesis of salts containing a negatively charged solvatochromic moiety. Natural dyes often bear the catechol moiety rather than the dialkylamino group.[20,21] Surprisingly, solvatochromism of dyes possessing the catechol moiety is little known.[18]

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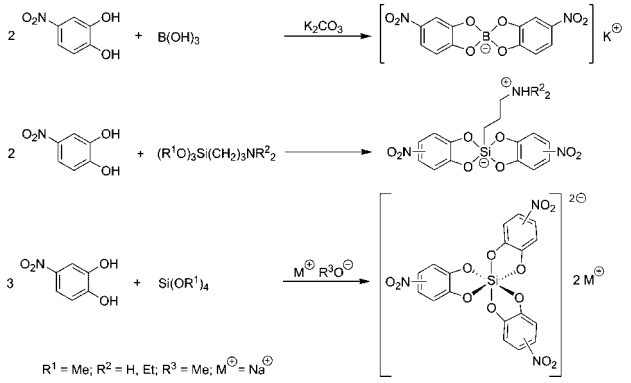

Scheme 1. Chemical functionalization of 4-nitrocatechol to boronic and silicon esters

Accordingly, the present work is concerned with the study of the solvatochromism of 4-nitrocatechol and its anionic derivatives. As shown below, the compounds employed were chosen in order to maintain the latter character.

Known and unknown λ^5*Si*-spirosilicates, hexacoordinate silicates, and one borate were synthesized by reaction of 4-nitrocatechol with different silanes and boric acid, respectively (Scheme 1), by means of established synthetic procedures (Fig. 1).

The main focus of this work is to investigate the influence of the solvents, complexation with boron and silicon, and ion pairing on the electron donor function of the catechol moiety of 4-nitrocatechol by using shifts of the position of the UV/vis absorption energy.

Compared to 4-nitrocatechol, the structurally related 4-nitrophenol has been widely used in solvatochromic analyses.[22] There exists a large number of substituted nitrophenol derivatives which were used as solvent-sensitive indicators for setting up polarity scales,[23–25] and as lipophilic trigger at physiological *p*H in micelles, bilayers, and biological membranes.[26–29]

Another objective of the experiments is to show how the free aromatic 1,2-diol function and that bonded to silicon and boron have an influence on the chromophoric π-electron system as a result of intermolecular interactions with the surrounding solvent molecules. The study of the influence of the counter cation and dye aggregation on the solvatochromic behavior of the silicates plays an important role. To separate the individual solvation

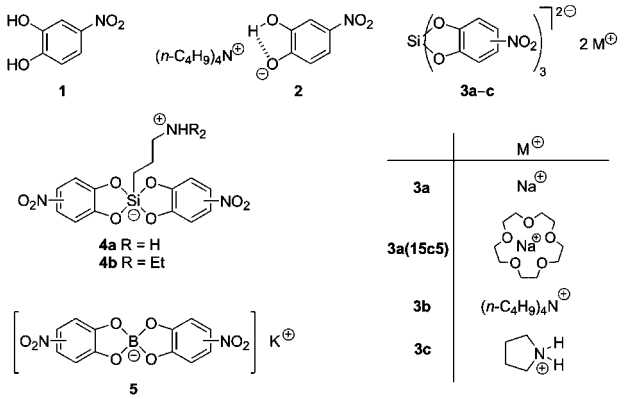

Figure 1. Solvatochromic compounds studied in this work

effects the simplified Kamlet–Taft Eqn (1)[2,30–33] was used

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

from which the coefficients of the individual interaction contributions can be determined by using multiple linear correlation analyses. $\tilde{\nu}_{max}$ is the longest-wavelength UV/vis absorption maximum of the compound measured in a given solvent, $\tilde{\nu}_{max,0}$ that of a reference solvent, α the solvent's hydrogen-bonding acidity, β describes the solvent's hydrogen-bonding basicity, and π^* the dipolarity/polarizability of the solvent. *a*, *b*, and *s* are solvent-independent regression coefficients. The knowledge of *a*, *b*, and *s* allows the interpretation of the influence of a particular solvent parameter on the solvatochromic response of the compound to be determined.

Alternatively to the well established Kamlet–Taft solvent parameter set, Catalán's *SA* (solvent acidity), *SB* (solvent basicity), *SPP* (solvent dipolarity/polarizability) scale (2) was also used for the multiple linear regression analyses of the solvatochromism of **1–5**.[34,35]

$$P = P_0 + a(SA) + b(SB) + c(SPP) \quad (2)$$

Catalán's parameter scales are based on well-defined reference processes in comparison to Kamlet–Taft's empirical polarity parameter set which has been derived from numerous chemical processes. For a systematic library of the solvatochromic results of our group, the comparison of results from the two related scales is of importance. Therefore, we apply two scales independent of each other and present the results.

RESULTS AND DISCUSSION

The hexacoordinate silicates (**3a–c**) were prepared according to Scheme 1, starting from tetramethoxysilane and 4-nitrocatechol with different bases (sodium methoxide, tetra-*n*-butylammonium hydroxide, and pyrrolidine, respectively).[36] The spirocyclic zwitterionic λ^5Si-silicates **4a** and **4b** were synthesized according to Tacke *et al.*,[37–43] starting from 3-amino-1-propyl-trimethoxysilane and (*N,N*-diethyl-3-amino-1-propyl)-trimethoxysilane, respectively. The reactions of the hexacoordinate silicates were performed in methanol (**3a**, **3a(15c5)**, **3b**) and tetrahydrofuran (**3c**). The zwitterionic silicates were synthesized in acetonitrile. Compound **5** was synthesized from boric acid, 4-nitrocatechol, and potassium carbonate in water. The stability of the hexacoordinate silicate **3b** in CD_3OD was investigated by ^{1}H NMR spectroscopy over a time period of 1 week. No decomposition or ligand splitting was observed (^{1}H NMR spectra are shown in the Supporting Information). The hexacoordinate silicates **3a** and **3b** (^{1}H) and the pentacoordinate silicates (^{1}H, ^{13}C) show double signals for the aromatic atoms, indicating the existence of two stereoisomers (Supporting Information). Compounds **4a** and **4b** are intermediate structures between an ideal trigonal bipyramid and an ideal square pyramid.[44–48]

Solvatochromic study of 4-nitrocatechol (1) and tetra-*n*-butylammonium 2-hydroxy-4-nitrophenolate (2)

UV/vis spectra of **1** ($\varepsilon_{CH_3CN} = 6300\,L \cdot mol^{-1} \cdot cm^{-1}$) and **2** ($\varepsilon_{CH3CN} = 18600\,L \cdot mol^{-1} \cdot cm^{-1}$) were measured in a set of 27 solvents (Table 1). The position of the UV/vis band is independent of the dye concentration in the range from 10^{-4} to 10^{-5} mol · L^{-1} which is an indication that dye aggregation has no noticeable

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Table 1. Long-wavelength solvatochromic UV/vis absorption maxima of **1** and **2**

	$\tilde{\nu}_{max}$ 10^{-3} [cm^{-1}]	
Solvent	(**1**)	(**2**)
toluene	30.77	25.58
chloroform	30.77	22.83
dichloromethane	30.77	23.20
diethyl ether	30.03	insoluble
1,4-dioxane	30.03	23.26
tetrahydrofuran	29.24	23.31
ethyl acetate	29.76	24.27
acetone	29.24	22.62
acetonitrile	29.59	22.42
benzonitrile	29.24	22.22
water	28.90	23.47
methanol	28.82	23.92
ethanol	28.99	23.64
1-propanol	28.99	23.53
1-butanol	28.90	23.42
tert-butanol	29.07	22.94
ethylene glycol	28.82	28.65
TFE	29.67	29.94
HFIP	29.85	29.76
triethylamine	28.90	insoluble
pyridine	27.93	22.03
DMSO	27.78	21.93
TMU	27.86	27.86
formamide	22.57	22.57
NMF	22.78	22.78
DMF	22.17	22.17
DMAA	22.17	22.17

TFE = 2,2,2-trifluoroethanol; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol; DMSO = dimethyl sulfoxide; NMF = *N*-methylformamide; DMF = *N,N*-dimethylformamide; DMAA = *N,N*-dimethylacetamide.

effect on the solvatochromic property. The solvatochromism of **1** can be well described by the Linear Solvation Energy Relationship (LSER) using the Kamlet–Taft parameter set (Eqn (1)). However, it should be mentioned that some solvents show effects which are not due to macroscopic behavior. These solvents are formamide, *N*-methylformamide, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and tetramethylurea (TMU). We suppose compound **1** dissociate into the monoanion form as can be seen by comparison of the UV/vis spectra of **1** and **2** in these solvents. Noticeable, **1** does not form the monoanion in hydrogen-bond acceptor (HBA) solvents with similar magnitude of β values such as DMSO, and pyridine. In the other solvents **1** shows solvatochromism because no chemical modification due to solvent molecules takes place. Therefore, the four amides and TMU were excluded from the multiple linear regression analyses.

Similar to 4-nitrophenol,[49] the positive solvatochromic behavior of 4-nitrocatechol (**1**) is attributed to the hydrogen-bond accepting property of the solvent which induces a partial dissociation of the catechol moiety. Thus, an enhancement of the push–pull character of the π-electron system occurs as a function of the HBA strength of the solvent.

The negative sign of the coefficients *b*, *s*, and *c* (Table 2) indicates that with increase in solvent basicity (β, *SB*) and dipolarity/polarizability (π^*, *SPP*) the $\tilde{\nu}_{max}$ of **1** and **2** is shifted to lower frequencies. The solvatochromism of 4-nitrocatechol (**1**) is independent of the solvent's hydrogen-bond donor (HBD) strength α or *SA*. Contrary to the Kamlet–Taft parameters, the Catalán solvent parameters show for the dipolarity/polarizability SPP a greater effect than the solvent's HBA strength *SB*.

The comparison of the solvatochromism of tetra-*n*-butylammonium 2-hydroxy-4-nitrophenolate (**2**) with 4-nitrocatechol (**1**) clearly shows the effect of the negative charge. The phenolate group of **2** is a strong HBA. Therefore, the UV/vis band shift of compound **2** is significantly a function of the HBD strength α. With increase in α or *SA* a hypsochromic band shift for **2** was observed (coefficients *a* are positive). Thus, its electronic ground state is more stabilized than the excited state. Therefore, the difference of the UV/vis band shifts $\Delta\tilde{\nu} = \tilde{\nu}(1) - \tilde{\nu}(2)$ from the non-ionic to the ionic form of **1** can be used as a measure of the anionic character of the dyes as a function of interaction with the environment or a central ion.

Table 2. Values of the solvent-independent regression coefficient using the Kamlet–Taft's and Catalán's parameter sets for the solvatochromism of compound **1** and **2**

Kamlet–Taft regression analyses

Compd	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*n*	*r*	*f*	*sd*
(**1**)	31.684 ± 0.345	—	-2.600 ± 0.343	-1.605 ± 0.393	21	0.88	<0.0001	0.405
(**2**)	26.659 ± 1.218	2.499 ± 0.383	-4.421 ± 0.765	-2.521 ± 1.435	17	0.94	<0.0001	0.867

Catalán regression analyses

Compd	$\tilde{\nu}_{max,0}$	*a*	*b*	*c*	*n*	*r*	*f*	*sd*
(**1**)	33.924 ± 0.725	—	-2.370 ± 0.343	-4.021 ± 0.785	22	0.88	<0.0001	0.409
(**2**)	28.690 ± 2.861	6.671 ± 0.934	-2.641 ± 1.035	-5.781 ± 3.393	19	0.91	<0.0001	1.159

a, *b*, and *s* of the Kamlet–Taft parameters α, β, and π^*, and *a*, *b*, and *c* of the Catalán parameters *SA*, *SB*, and *SPP*, respectively; solute property of the reference system $\tilde{\nu}_{max,0}$, standard deviation (*sd*), correlation coefficient (*r*), number of solvents (*n*), and significance (*f*).

Solvent effects on the UV/vis absorption spectra and multiple regression analyses of compounds 3–5

Measurements were carried out for compounds **3a** (ε_{CH_3CN} = 12700 L · mol^{-1} · cm^{-1}), **3a(15c5)** (ε_{CH_3CN} = 28300 L · mol^{-1} · cm^{-1}), **3b** (ε_{CH_3CN} = 15300 L · mol^{-1} · cm^{-1}), **3c** (ε_{CH_3CN} = 27800 L · mol^{-1} · cm^{-1}), **4a** (ε_{CH_3CN} = 9500 L · mol^{-1} · cm^{-1}), **4b** (ε_{CH_3CN} = 18400 L · mol^{-1} · cm^{-1}), and **5** (ε_{CH_3CN} = 15000 L · mol^{-1} · cm^{-1}) in 22 organic solvents in order to investigate the manifold influence of the solvent properties on the UV/vis band shift. The concentrations used were in a range of 10^{-4}–10^{-5} mol L^{-1}. All compounds are insoluble in nonpolar or halogenated solvents (toluene, chloroform, dichloromethane, diethyl ether, triethylamine, etc.). The wavenumbers ($\tilde{\nu}_{max,0}$ 10^{-3} [cm^{-1}]) of the UV/vis absorption maxima measured in the various solvents are summarized in Table 3 for all compounds studied.

The results of the multiple linear regression analyses of $\tilde{\nu}_{max}$ (**3a–c**, **5**) with the empirical solvent parameters are shown in Table 4.

The negative sign of *s* and *c*, respectively, indicates that with increase in solvent dipolarity/polarizability (π^* and *SPP*) a bathochromic shift of $\tilde{\nu}_{max}$ takes place. This result demonstrates that the excited singlet state of these compounds becomes more stabilized when the solvent polarity increases. Regarding the HBD ability of the solvents, all hexacoordinate compounds show a hypsochromic UV/vis band shift (coefficient *a* is always positive). Regarding the HBA ability of the solvent, the hexacoordinate silicates, except compound **3b**, showed a bathochromic UV/visband shift (coefficient *b* is negative). This result was unexpected and not explicable by attenuation of the chromophoric push–pull system because both ss-OH groups of the catechol moiety are protected.

The four hexacoordinate silicates **3a–c** possess the same solvatochromic anionic moiety and differ only in the nature of the counter cation which is introduced through the base used in synthesis. The influence of the cation on the solvatochromic behavior has been found of importance because the cations in **3a** and **3c** are coordinating stronger than those of **3b** and **3a(15c5)**. The difference in the UV/vis absorption maxima of **3a** and **3b** ($\Delta\tilde{\nu}_{max}$ [cm^{-1}]), measured in 22 solvents as a function of the relative permittivity (ε_r) of the solvents is shown in Fig. 2.

The influence of the relative permittivity of the solvent on the position of the UV/vis absorption band shows whether ion pairs or dissociated ions are present. Contact ion pairs (■ in Fig. 2, **A** in Scheme 2) of **3a** and **3b** were formed in solvents with a low relative permittivity (tetrahydrofuran, 1,4-dioxane, ethyl acetate).

Formation of solvent-separated ion pairs (SSIPs) (○ in Fig. 2, **B** in Scheme 2) in which the anion and the cation are separated only by their solvent shells is determined by the competition between the solvation of the cation and the electrostatic stabilization of the anion by the counter ion. The more delocalized the charge on the anion, the weaker is the anion–cation interaction. This means that the more polar the solvent the stronger the cation–solvent interaction, and the formation of SSIPs is

Table 3. UV/vis absorption maxima ($\tilde{\nu}_{max}$ 10^{-3} [cm^{-1}]) of **3–5**, measured in 22 solvents at 25°C

Solvent	$\tilde{\nu}_{max}$ 10^{-3} [cm^{-1}]						
	(**3a**)	(**3a**(**15c5**))	(**3b**)	(**3c**)	(**4a**)	(**4b**)	(**5**)
methanol	25.45	25.38	25.51	25.38	27.70	28.65	27.55
ethanol	25.06	24.69	24.88	25.06	27.55	28.74	27.55
1-propanol	25.38	24.51	25.00	25.19	23.87	[b]	27.47
1-butanol	25.51	24.51	25.32	25.32	23.58	[b]	27.55
tert-butanol	26.04	24.10	24.57	25.38	[a]	27.55	26.95
TFE	25.97	25.84	25.77	25.84	[a]	27.47	27.86
HFIP	26.88	26.53	26.25	28.09	[a]	27.40	28.01
ethylene glycol	25.13	25.25	25.25	25.25	27.78	28.25	27.25
tetrahydrofuran	26.32	24.88	24.21	25.64	26.88	27.17	26.95
1,4-dioxane	26.67	25.38	24.57	26.04	[a]	27.25	27.86
acetonitrile	24.51	24.10	24.10	24.21	26.39	26.95	27.10
benzonitrile	24.69	24.10	23.47	24.45	[a]	26.81	26.53
nitromethane	25.19	24.33	24.15	24.57	[a]	25.97	26.11
ethyl acetate	26.46	25.19	24.39	25.97	[a]	27.47	27.55
acetone	24.63	23.64	23.53	24.63	27.03	27.47	26.81
pyridine	24.81	23.75	23.47	24.45	26.53	26.88	26.67
DMSO	23.53	23.36	23.47	23.47	26.04	26.39	26.46
formamide	25.00	24.75	25.00	25.06	25.00	26.46	26.81
NMF	24.94	25.00	25.13	24.94	26.04	26.95	27.03
DMF	23.53	23.31	23.47	23.42	25.84	26.53	26.67
DMAA	23.37	23.26	23.31	23.37	26.46	26.53	26.81
TMU	23.75	23.70	23.64	23.70	26.39	26.60	26.67

[a] insoluble.
[b] concentration effects.

Table 4. Values of the solvent-independent regression coefficient using Kamlet–Taft's and Catalán's parameter sets according to Eqns (1) and (2) for the solvatochromism of compounds **3a–c**, and **5**

Kamlet–Taft regression analyses

Compd	$\tilde{\nu}_{max,0}$	*a*	*b*	*s*	*n*	*r*	*f*	*sd*
(**3a**)	29.255 ± 0.616	—	−1.898 ± 0.456	−4.216 ± 0.703	22	0.84	<0.0001	0.682
(**3a(15c5)**)	25.572 ± 0.689	0.941 ± 0.236	−1.139 ± 0.468	−1.136 ± 0.705	22	0.83	<0.0001	0.546
(**3b**)	24.545 ± 0.328	1.340 ± 0.132	—	−0.939 ± 0.411	22	0.93	<0.0001	0.855
(**3c**)	27.821 ± 0.683	0.621 ± 0.235	−1.366 ± 0.460	−3.329 ± 0.721	21	0.88	<0.0001	0.517
(**5**)	27.855 ± 0.263	0.489 ± 0.106	—	−1.297 ± 0.333	21	0.85	<0.0001	0.692

Catalán regression analyses

Compd	$\tilde{\nu}_{max,0}$	*a*	*b*	*c*	*n*	*r*	*f*	*sd*
(**3a**)	34.774 ± 1.277	0.992 ± 0.364	—	−11.194 ± 1.445	19	0.90	<0.0001	0.427
(**3a(15c5)**)	29.677 ± 1.224	2.070 ± 0.305	−1.204 ± 0.447	−5.683 ± 1.287	22	0.91	<0.0001	0.412
(**3b**)	27.824 ± 0.644	2.576 ± 0.165	—	−4.531 ± 0.728	22	0.96	<0.0001	0.239
(**3c**)	32.259 ± 1.693	1.763 ± 0.422	−1.139 ± 0.619	−8.090 ± 1.782	22	0.84	<0.0001	0.570
(**5**)	30.527 ± 0.603	1.165 ± 0.157	—	−4.110 ± 0.682	20	0.90	<0.0001	0.218

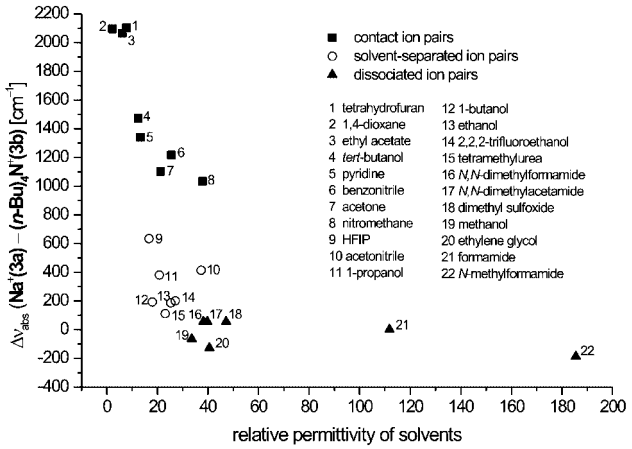
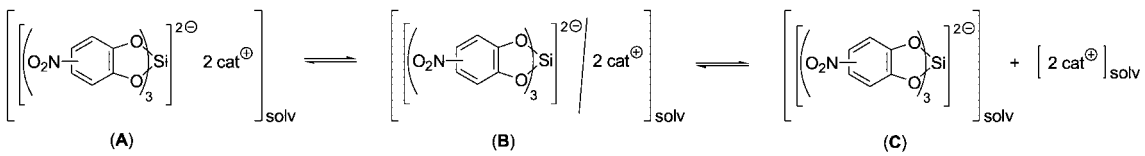


Figure 2. Difference of the UV/vis absorption energies of **3a** and **3b** [$\Delta\tilde{\nu} = \tilde{\nu}_{max}$(**3a**) − $\tilde{\nu}_{max}$(**3b**)] as a function of the solvent's relative permittivity

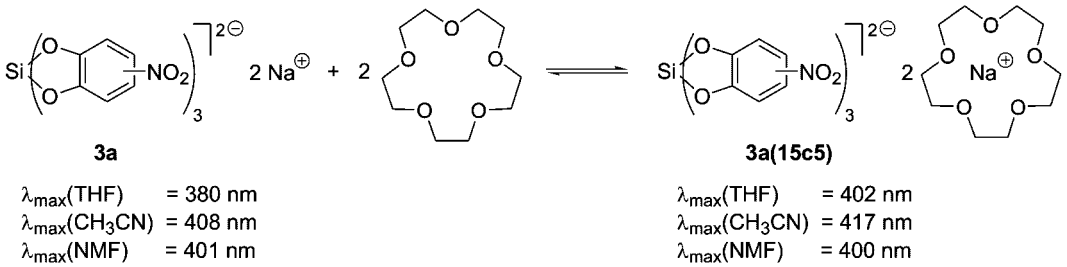
preferred. In solvents with a high relative permittivity and HBA property (dimethyl sulfoxide, formamide, *N*-methylformamide, *N,N*-dimethylformamide, *N,N*-dimethylacetamide) the counter ion effect on the UV/vis absorption band is negligible (▲ in Fig. 2, **C** in Scheme 2). Solvents with a high relative permittivity would favor dissociated ions more than separated ion pairs, as the latter process is less dependent on the relative permittivity. UV/vis spectral changes are only observed when ion pairs are present, due to the perturbation caused by the counter ion. The extent of this perturbation depends on the nature of the counter ion and its solvation.

To have an independent support for these interpretation, the sodium cation of **3a** was complexed by 15-crown-5 (**3a(15c5)**, Scheme 3). In tetrahydrofuran the UV/vis absorption maximum of **3a** shifts from $\lambda_{max} = 380$ nm to 402 nm in **3a(15c5)** ($\Delta\tilde{\nu} = 1440\ cm^{-1}$). In acetonitrile, the UV/vis absorption maximum shifts from λ_{max}(**3a**) = 408 nm to λ_{max}(**3a(15c5)**) = 417 nm ($\Delta\tilde{\nu} = 530\ cm^{-1}$). No UV/vis shift occurs between **3a** and **3a(15c5)** in *N*-methylformamide, a solvent with both a high donor strength and relative permittivity (Fig. 3). We conclude that the equilibration of **3a** in tetrahydrofuran after 15-crown-5 complexation is displaced from contact ion pairs for **3a** to solvent-separated ion pairs (SSIPs). The same process takes place in acetonitrile from SSIPs to dissociated ion pairs.

The investigation of the solvatochromic property of the λ^5*Si*-spirosilicate **4a** is not widely possible, because this compound is insoluble in many organic solvents. Therefore, compound **4b**, which contains a —$NH(C_2H_5)_2^+$ group instead of —NH_3^+ has been investigated, too. Compound **4b** shows two UV/vis absorption maxima in 1-propanol and 1-butanol. The intensity of the hypsochromic UV/vis band increases stronger compared to the band at longer wavelengths which indicates dye aggregation. An isosbestic point was not observed (Supporting Information).



Scheme 2. Contact ion pairs (**A**), solvent-separated ion pairs (SSIPs, **B**), and dissociated ion pairs (**C**) of **3a** and **3b**, respectively, cat^+ for **3a**: Na^+ and for **3b**: $(n\text{-}Bu)_4N^+$



Scheme 3. UV/vis absorption maxima of **3a** and **3a(15c5)**, measured in tetrahydrofuran (THF), acetonitrile, and *N*-methylformamide (NMF)

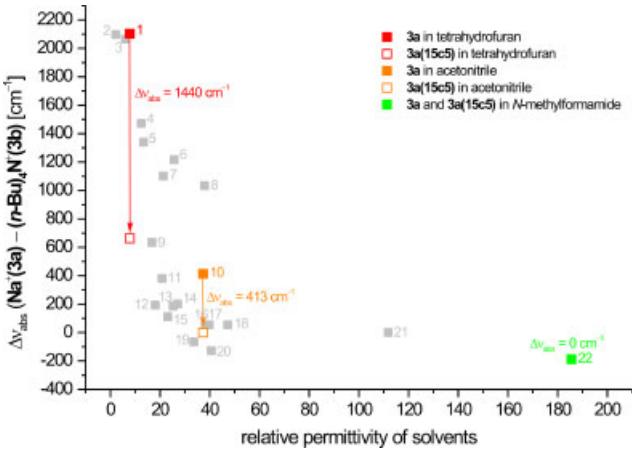


Figure 3. Impact of 15-crown-5 complexation of the sodium cation on the UV/vis shift of **3a**, measured in tetrahydrofuran (■), acetonitrile (■), and *N*-methylformamide (■). The numbering of the solvents is analogous to Fig. 2. This figure is available in colour online at www.interscience.wiley.com/journal/poc

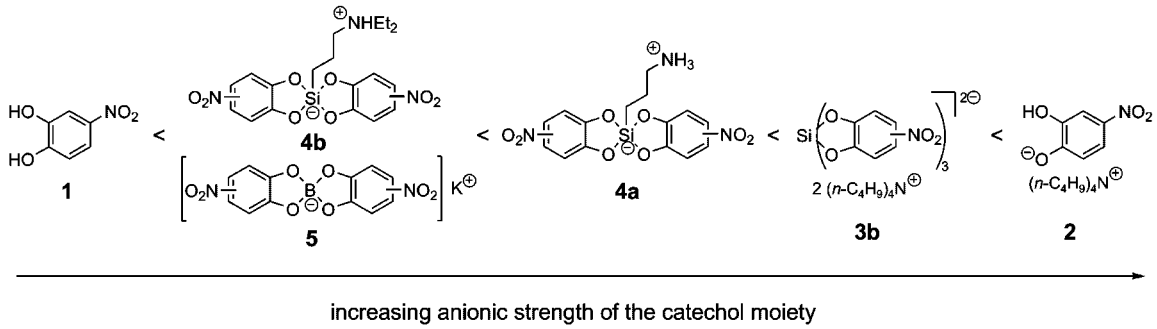
The UV/vis spectra are interpreted using the exciton model.[50] The observed spectral shift of the UV/vis absorption maximum, which is hypsochromically shifted indicates the existence of the H-type aggregate.[50] Thus, dye aggregate formation has an influence on the UV/vis absorption which makes the interpretation in terms of specific solvation effects impossible.

The UV/vis spectrum of compound **5** showed no dependence on its concentration, in the range from 1.3×10^{-4} to 3.2×10^{-5} mol · L^{-1}, indicating a negligible effect of the potassium cation. In agreement with the silicates studied, the borate ester **5** shows a bathochromic band shift with increase in solvent dipolarity (*s* and *c* are negative). Solvents which act as HBDs and electron-pair acceptors (EPA) interact with the negatively charged dye (*a* is positive).

As mentioned, use of the parameter sets of Kamlet–Taft and Catalán adds up to different factors of the correlation coefficients of the multiple linear regression analyses. However, on the basis of available data, there is no difference concerning the qualitative conclusion drawn from the determined solvent independent correlation coefficients.

The UV/vis data of **1–5** have been consulted to discuss the impact of complexation of the catechol moiety by silicon and boron compounds on the anionic character of the dye. For this comparison, UV/Vis data in acetonitrile as the reference solvent were selected because all compounds are well soluble, stable, and compound **1** is not ionic in this solvent. The largest bathochromic shift is observed for the monoanion **2** at $\lambda_{max}(\mathbf{2}_{CH3CN}) = 446$ nm showing the complete anionic limit. Thus, the order of the UV/vis absorption energy for the compounds measured in acetonitrile can be used as an indication of the anionic character of the catechol moiety of these compounds. It increases with decrease in absorption energy in the following order shown in Scheme 4.

The order of the anionic character is supported by the determined coefficients *a* which increase with the interaction strength of the chromophore with HBD solvents. This result shows that the anionic character of the catechol moiety is a function of the central ion used for protection. UV/vis spectroscopic results of the pentacoordinate silicates **4a** and **4b** point to the excistence of aggregated species in alcohols in concentrations greater than 9×10^{-5} mol L^{-1}.



Scheme 4. Anionic character of the catechol moiety

CONCLUSION

The solvatochromism of anionic solvatochromic dyes studied in this work can be characterized by means of LSER using the empirical Kamlet–Taft and Catalán solvent parameter sets. The positive solvatochromism regarding the solvent polarity and polarizability indicates that with increase in dipolarity/polarizability of the solvent (π^* or *SPP* values) a bathochromic shift of the UV/vis band occurs as shown by the negative sign of the coefficients *s* and *c*, respectively, which is typical for *para*-nitrosubstituted aromatics. For the charged dyes, with increase in HBD strength of the solvent a hypsochromic shift of the UV/vis band takes place as shown by the positive sign of the coefficient *a*. This effect is due to specific solvation of the anion by hydrogen bonds which results in a stabilization of the electronic ground state of the molecule. For compound **3a**, the LSER analysis using the Kamlet–Taft parameter set gives a reasonable result, because the negative sign of the coefficient *b* indicates that the HBA property of the solvent is responsible for the bathochromic UV/vis shift observed. This effect can be explained by specific solvation of the sodium cation by HBA solvents.

EXPERIMENTAL SECTION

All reactions were performed under argon atmosphere. The organic solvents used for solvatochromic studies were dried and purified according to standard procedures and stored under argon. Pyrrolidine was distilled before used.

Materials

4-nitrocatechol was purchased from FLUKA, tetra-*n*- butylammonium hydroxide and (*N*,*N*-diethyl-3-amino-1-propyl)trimethoxysilane from ABCR, 3-amino-1-propyltrimethoxy-silane and sodium methoxide from Lancaster, tetramethyl orthosilicate, boric acid, and pyrrolidine from Merck and potassium carbonate from Acros.

Instrumentation

The melting point was determined with a Mikro-Heiztisch System from Wagner & Munz and is uncorrected. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded with a Bruker Avance 250 NMR spectrometer at 250, 80.2, and 69.9 MHz, respectively. ^{29}Si{^{1}H}-CP-MAS NMR spectra were measured on a Bruker Avance 400 NMR spectrometer (external standard: kaolin ($\delta = -92.5$ ppm); spinning rate: 5 kHz; contact time: 3 ms; 90° ^{1}H transmitter pulse length: 5.50 μs; repetition time: 3 s). All NMR spectra were recorded at room temperature, the solvents employed were either CD_3OD (compounds **2**, **3a**, **3a(15c5)**, **3b**, **3c**) or DMSO-d_6 (compounds **4a**, **4b**, **5**). Quantitative elemental analyses were determined with a Vario-EL analysis. The UV/vis absorption spectra of freshly prepared solutions were measured by means of the MCS 400 diode-array spectrometer from Carl Zeiss Jena. Regression analyses were performed with the Origin 5.0 statistical program.

Synthesis of tetra-n-butylammonium 2-hydroxy-4-nitrophenolate (2)

To a 5 mL methanol solution of 4-nitrocatechol (310 mg, 2 mmol) was added tetra-*n*-butylammonium hydroxide (1 mL, 2 mmol, 40% solution in methanol). The solvent was then evaporated to give **2** as a yellow-orange solid (663 mg, 1.7 mmol, 84% yield). M.p. 67°C. ^{1}H NMR: $\delta = 0.82$ (t, $^{3}J_{H,H} = 7.3$ Hz, 12H, CH_3), 1.21 (sext, $^{3}J_{H,H} = 7.3$ Hz, 8H, CH_2), 1.44 (m, 8H, CH_2), 3.00 (m, 8H, CH_2), 6.40 (d, $^{3}J_{H,H} = 9.0$ Hz, 1H, ArH), 7.36 (d, $^{4}J_{H,H} = 2.8$ Hz, 1H, ArH), 7.50 (dd, $^{3}J_{H,H} = 9.0$ Hz, $^{4}J_{H,H} = 2.8$ Hz, 1H, ArH). ^{13}C NMR: $\delta = 163.9$, 148.9, 136.9, 120.1, 116.2, 109.5, 59.7, 25.0, 20.9, 14.2. Anal. Calcd for $C_{22}H_{40}N_2O_4$: C, 66.63; H, 10.17; N, 7.06. Found: C, 66.14; H, 9.84; N, 6.82.

Synthesis of sodium tris(4-nitrobenzene-1,2-diolato)silicate (3a)

A solution of sodium methoxide (1.08 g, 20 mmol) in 40 mL methanol was added to a solution of 4-nitrocatechol (4.65 g, 30 mmol) and tetramethyl orthosilicate (1.52 g, 10 mmol) in 20 mL methanol. The mixture was stirred for 2 hours, the solvent was evaporated under reduced pressure, and the residue washed with diethyl ether, filtered, and dried under reduced pressure, to give **3a** as a yellow solid (3.58 g, 6.71 mmol, 67% yield). M.p. > 350°C (dec.). ^{1}H NMR: $\delta = 6.57/6.60$ (m, $^{3}J_{H,H} = 8.5$ Hz, $^{4}J_{H,H} = 1.7$ Hz, 3H, ArH), 7.40 (m, $^{4}J_{H,H} = 1.7$ Hz, 3H, ArH), 7.60/7.64 (m, 3H, ArH). ^{13}C NMR: $\delta = 160.0$, 151.7, 140.4, 117.9, 110.7, 106.7. ^{29}Si{^{1}H}-CP-MAS NMR: $\delta = -138.79$. Anal. Calcd for $C_{18}H_9N_3O_{12}SiNa_2$: C, 40.54; H, 1.70; N, 7.88. Found: C, 40.12; H, 1.91; N, 7.75.

Synthesis of 3a(15c5)

To a solution of 4-nitrocatechol (2.33 g, 15 mmol) in 10 mL methanol was first added sodium methoxide (0.54 g, 10 mmol) dissolved in 20 mL methanol, then 15-crown-5 (2.20 g, 10 mmol), and tetramethyl orthosilicate (0.76 g, 5 mmol). The mixture was stirred for 4 hours at room temperature, the solvent was evaporated under reduced pressure and the residue was washed with diethyl ether, filtered and dried under reduced pressure, to give **3a(15c5)** as orange solid (4.22 g, 4.33 mmol, 86% yield). M.p. 159°C. ^{1}H NMR: $\delta = 3.63$ (s, 40H, CH_2), 6.56 (d, $^{3}J_{H,H} = 8.7$ Hz, 3H, ArH), 7.37 (d, $^{4}J_{H,H} = 2.7$ Hz, 3H, ArH), 7.61 (dd, $^{3}J_{H,H} = 8.7$ Hz, $^{4}J_{H,H} = 2.7$ Hz, 3H, ArH). ^{13}C NMR: $\delta = 160.6$, 152.2, 140.4, 117.9, 110.7, 106.6, 70.3. ^{29}Si{^{1}H}-CP-MAS NMR: $\delta = -138.19$. Anal. Calcd for $C_{38}H_{49}N_3Na_2O_{22}Si$: C, 46.87; H, 5.07; N, 4.31. Found: C, 46.26; H, 5.31; N, 4.31.

Synthesis of tetra-*n*-butylammonium tris(4-nitrobenzene-1,2-diolato)silicate (3b)

A solution of tetra-*n*-butylammonium hydroxide (20 mmol, 40% solution in methanol) was added to a solution of 4-nitrocatechol (4.65 g, 30 mmol) and tetramethyl orthosilicate (1.52 g, 10 mmol) in 20 mL methanol. The mixture was stirred for 2 hours, methanol was then evaporated, and the residue was dissolved in ethyl acetate. After evaporation the yellow solid was dried under reduced pressure to give **3b** (5.15 g, 5.3 mmol, 53% yield). M.p. 213°C. ^{1}H NMR: $\delta = 1.03$ (t, $^{3}J_{H,H} = 7.3$ Hz, 24H, CH_3), 1.28 (m, 16H, CH_2), 1.55 (m, 16H, CH_2), 3.14 (m, 16H, CH_2), 6.34 (d, $^{3}J_{H,H} = 8.5$ Hz, 3H, ArH), 7.01/7.02 (d, $^{4}J_{H,H} = 2.7$ Hz, 3H, ArH), 7.45/7.48 (dd, $^{3}J_{H,H} = 8.5$ Hz, $^{4}J_{H,H} = 2.7$ Hz, 3H, ArH). ^{13}C NMR: $\delta = 160.9$, 151.9, 137.4, 116.1, 108.3, 103.4, 57.9, 23.4, 19.6, 13.8. ^{29}Si{^{1}H}-CP-MAS NMR: $\delta = -137.01$. Anal. Calcd for $C_{50}H_{81}N_5O_{12}Si$: C, 61.77; H, 8.40; N, 7.20. Found: C, 61.36; H, 8.01; N, 6.97.

Synthesis of pyrrolidinium tris(4-nitrobenzene-1,2-diolato)silicate (3c)

Pyrrolidine (0.85 g, 12 mmol) was added to tetramethyl orthosilicate (0.91 g, 6 mmol) and 4-nitrocatechol (2.79 g, 18 mmol) dissolved in 20 mL tetrahydrofuran. This solution was refluxed for 2 hours. After 5 minutes an orange precipitate was obtained. The mixture was cooled to room temperature, the precipitate was filtered off, and dried under reduced pressure to give **3c** as a yellow solid (3.58 g, 5.7 mmol, 94% yield). M.p. $>300^{\circ}$C (dec.). ^{1}H NMR: $\delta = 0.63$ (t, $^{3}J_{H,H} = 7.0$ Hz, 8H, CH_2), 1.89 (t, $^{3}J_{H,H} = 7.0$ Hz, 8H, CH_2), 5.22 (m, 3H, ArH), 6.02 (m, 3H, ArH), 6.27 (m, 3H, ArH). ^{13}C NMR: $\delta = 160.2$, 151.9, 140.6, 118.1, 110.7, 106.6, 47.2, 25.5. ^{29}Si{^{1}H}-CP-MAS NMR: $\delta = -138.84$. Anal. Calcd for $C_{26}H_{29}N_5O_{12}Si$: C, 49.44; H, 4.63; N, 11.09. Found: C, 49.56; H, 5.11; N, 10.54.

Synthesis of (3-amino-1-propyl)-bis(4-nitrobenzene-1, 2-diolato)silicate (4a)

A solution of 3-amino-1-propyl-trimethoxysilane (0.90 g, 5 mmol) in 2 mL acetonitrile was added at room temperature to a solution of 4-nitrocatechol (1.55 g, 10 mmol) in 20 mL acetonitrile. After being stirred for 2 hours, the reaction mixture was kept undisturbed for 2 days. The precipitate was filtered off, washed with acetonitrile, and then dried under reduced pressure to give **4a** as a orange solid (1.96 g, 5 mmol, 99% yield). M.p: $>300^{\circ}$C (dec.). ^{1}H NMR: $\delta = 0.61$ (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 2.62 (m, 2H, CH_2), 6.74 (d, $^{3}J_{H,H} = 8.6$ Hz, 2H, ArH), 6.76 (d, $^{3}J_{H,H} = 8.6$ Hz, 2H, ArH), 7.42 (d, $^{4}J_{H,H} = 2.3$ Hz, 2H), 7.46 (d, $^{4}J_{H,H} = 2.3$ Hz, 2H, ArH), 7.66 (dd, $^{3}J_{H,H} = 8.6$ Hz, $^{4}J_{H,H} = 2.3$ Hz, 2H, ArH), 7.70 (dd, $^{3}J_{H,H} = 8.6$ Hz, $^{4}J_{H,H} = 2.3$ Hz, 2H, ArH). ^{13}C NMR: $\delta = 158.6$, 157.7, 150.0, 149.1, 139.1, 138.4, 117.9, 116.9, 109.5, 109.3, 105.3, 104.9, 41.7, 22.6, 14.7. ^{29}Si{^{1}H}-CP-MAS NMR: $\delta = -71.06$. Anal. Calcd for $C_{15}H_{15}N_3O_8Si$: C, 45.80; H, 3.84; N, 10.68. Found: C, 45.51; H, 3.98; N, 11.00.

Synthesis of (N,N-diethyl-3- amino-1-propyl)-bis (4-nitrobenzene-1,2-diolato)silicate (4b)

A solution of (*N,N*-diethyl-3-amino-1-propyl)trimethoxysilane (1.18 g, 5 mmol) in 2 mL acetonitrile was added at room temperature to a solution of 4-nitrocatechol (1.55 g, 10 mmol) in 20 mL acetonitrile. After being stirred for 2 hours, the reaction mixture was kept undisturbed for 2 days. The precipitate was filtered off, washed with acetonitrile, and dried under reduced pressure to give **4b** as a yellow solid (1.23 g, 2.7 mmol, 55% yield). M.p. 254°C. ^{1}H NMR: $\delta = 0.66$ (m, 2H, CH_2), 1.07 (t, $^{3}J_{H,H} = 7.2$ Hz, 6H, CH_3), 1.52 (m, 2H, CH_2), 2.82 (m, 2H, CH_2), 2.93 (q, $^{3}J_{H,H} = 7.2$ Hz, 4H, CH_2), 6.76 (d, $^{3}J_{H,H} = 8.6$ Hz, 2H, ArH), 6.80 (d, $^{3}J_{H,H} = 8.6$ Hz, 2H, ArH), 7.45 (d, $^{3}J_{H,H} = 2.3$ Hz, 2H, ArH), 7.49 (d, $^{4}J_{H,H} = 3.1$ Hz, 2H, ArH), 7.67 (dd, $^{3}J_{H,H} = 8.6$ Hz, $^{4}J_{H,H} = 3.1$ Hz, 2H, ArH), 7.71 (dd, $^{3}J_{H,H} = 8.6$ Hz, $^{4}J_{H,H} = 2.3$ Hz, 2H, ArH). ^{13}C NMR: $\delta = 158.4$, 157.4, 149.9, 148.9, 139.2, 138.5, 118.0, 117.0, 109.6, 109.3, 105.4, 105.0, 53.7, 46.6, 19.1, 14.2, 8.7. ^{29}Si{^{1}H}-CP-MAS NMR: $\delta = -71.90$. Anal. Calcd for $C_{19}H_{23}N_3O_8Si$: C, 50.77; H, 5.16; N, 9.35. Found: C, 50.82; H, 5.09; N, 9.33.

Synthesis of potassium bis(4-nitrobenzene-1,2-diolato)borate (5)

A solution of boric acid (309 mg, 5 mmol) in 10 mL water was added to a solution of 4-nitrocatechol (1.55 g, 10 mmol) at 50°C. To the stirred mixture was added a solution of potassium carbonate (691 mg, 5 mmol) in 5 mL water. After stirring at 50°C for 2 hours the reaction mixture was cooled to room temperature. The precipitate was filtered off and dried under reduced pressure to give **5** as a yellow solid (1.15 g, 3.2 mmol, 64% yield). M.p. 325°C. ^{1}H NMR: $\delta = 6.76$ (d, $^{3}J_{H,H} = 8.6$ Hz, 2H, ArH), 7.39 (d, $^{4}J_{H,H} = 2.3$ Hz, 2H, ArH), 7.72 (dd, $^{3}J_{H,H} = 8.6$ Hz, $^{4}J_{H,H} = 3.1$ Hz, Hz, 2H, ArH). ^{13}C NMR (69.9 MHz, DMSO-d_6, 25°C): $\delta = 158.0$, 150.9, 139.4, 117.3, 107.2, 102.8: ^{11}B NMR: $\delta = 15.0$. Anal. Calcd for $C_{12}H_6BKN_2O_8$: C, 40.47; H, 1.70; N, 7.87. Found: C, 40.87; H, 1.75; N, 7.76.

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