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Unusual solvatochromism of the 4,4′-bis(dimethylamino)-benzophenone (Michler's ketone)–tetracyanoethene electron donor–acceptor complex

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ABSTRACT: The transition energy of the charge-transfer UV/Vis absorption maxima ($\nu_{\text{max, CT}}$) and the structure of the Michler's ketone (MK)–tetracyanoethene (TCNE) electron donor–acceptor (EDA) complex are remarkably solvent dependent. The UV/Vis spectra of the MK–TCNE complex were measured in 20 non-protic and seven protic solvents. In non-protic solvents, $\nu_{\text{max, CT}}$ of the EDA complex is quantitatively described by a multiple LSE relationship using the Kamlet–Taft dipolarity/polarizability (π^*) and basicity (β) parameters of the solvents. The influence of the two terms β and π^* on $\nu_{\text{max, CT}}$ is opposite, indicating a qualitatively different solvent-induced stabilization of the electronic ground and excited states of the complex. As expected, increasing dipolarity/dipolarizability of the solvent causes a bathochromic band shift (positive solvatochromism), whereas the basicity of solvents is responsible for a hypsochromic band shift due to specific solvation of the TCNE site. In protic solvents, the complex formation is associated with the formation of an ionic species ($\nu_{\text{max}} = 19\,800$ cm^{-1}) derived from Michler's ketone due to coordination of TCNE at the carbonyl oxygen of MK (called an n-complex). The solvent-induced switching of the π-complex into the n-complex is demonstrated for mixtures of DCE with protic solvents and for silica surfaces. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: Solvato chromism; Michler's ketone–tetracyanoethene; electron donor–acceptor complex

INTRODUCTION

Weak complexes between organic electron donors and acceptors often show a new absorption in the visible region of the UV/Vis spectrum, the so called intermolecular CT (charge-transfer) absorption.[1–3] The charge-transfer absorption process from the donor (D) to the acceptor (A) of an EDA (electron donor–acceptor) complex is attributed to the transition of an electron from the HOMO of the donor to the LUMO of the acceptor.[4] Corresponding to Mulliken's theory,[1b] this intermolecular electron transition process can be expressed by Eqn. (1),[1–5] where the mainly contributing resonance structure of each state is underlined.

$$\mathrm{A} + \mathrm{D} \xrightleftharpoons{\mathrm{K_C}} (\underline{\mathrm{A} \leftarrow \mathrm{D}} \leftrightarrow \mathrm{A}^{-\cdot}\mathrm{D}^{+\cdot}) \xrightarrow{h\nu_{\mathrm{CT}}} (\mathrm{A} \leftarrow \mathrm{D} \leftrightarrow \underline{\mathrm{A}^{-\cdot}\mathrm{D}^{+\cdot}}) \quad (1)$$

The charge-transfer absorption ($\nu_{\text{max, CT}}$, $h\nu_{\text{max, CT}}$) [Eqn. (2)] generally occurs in the UV/Vis region with

$$h\nu_{\text{max,CT}} = IP - EA - Ec \quad (2)$$

where *IP* is the ionization potential of the electron donor, *EA* is the electron affinity of the electron acceptor and *Ec* is the electrostatic energy (e^2/r_{DA}) of the radical ion pair $[\mathrm{A}^{-\cdot}\ \mathrm{D}^{+\cdot}]$.[4,5]

The appearance of new spectral bands arising from the CT transition between electron donors and electron acceptors is especially useful and easy to apply for several purposes. Accordingly, Rathore *et al.*[6] used weak EDA complexes for probing steric effects on the interactions of aromatic donors substituted with bulky alkyl groups and acceptors. Electrostatic repulsion arises between sterically substituted aromatic π donors and various π acceptor components.[6] This effect contributes to the value of the Coulomb term of Eqn. (2) and is detectable by a hypsochromic shift of the CT band because r_{DA} (the distance between $\mathrm{A}^{-\cdot}\ \mathrm{D}^{+\cdot}$) increases. Furthermore, TCNE has been established as a powerful reference acceptor towards a variety of structurally different donors for determining their ionization potential.[7]

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The UV/Vis absorption energy[2,3,5] and the corresponding emission energy[8] of EDA complexes are also remarkably solvent dependent.

The solvent influence on the position of the intermolecular CT absorption maxima of weak EDA complexes has been investigated for various electroneutral complexes[9] and also of EDA complexes with charged components, e.g. positively charged acceptors with neutral donors,[10] negatively charged donors with either positively charged acceptors[2,11] or neutral acceptors[12] and negatively charged acceptors with neutral donors.[13] For instance, the solvent-dependent CT absorption from the iodide ion to the 4-ethoxycarbonyl-*N*-ethylpyridinium cation was utilized in order to introduce the first empirical solvent polarity scale, the *Z*-scale, by Kosower in 1958.[11a,b]

According to the established theory of the CT mechanism of weak EDA complexes with electroneutral components [Eqn. (1)], a bathochromic shift of the CT absorption band is expected with increasing solvent polarity because the polarity of the excited state is larger than that of the ground state of the EDA complex. However, hypsochromic or poorly defined shifts of the CT absorption was found for some EDA complexes with increasing solvent polarity by using stronger polar solvents, e.g. the polarity of which is expressed by the dielectric constant or the $E_T(30)$ solvent parameter.[14] The solvent-induced shifts of the CT absorption maxima of various EDA complexes with charged components, e.g. the iodide–1,3,5-trinitrobenzene complex[12c] and other halide–acceptor complexes,[2,12] the pyrene–trophylium[10a,b] and other π donor–carbenium complexes[10] and coloured charge-transfer salts, e.g. tropylium iodide[11c] and 4-ethoxycarbonyl-*N*-ethylpyridinium iodide (*Z*-scale),[11a,b] can also be interpreted in terms of specific solvation using empirical solvent polarity parameters.[10e,12c,14b,15b,16]

The influence of different solvent properties upon the unprecedented solvatochromic shifts of various solvatochromic compounds have often been successfully analysed by employing the Kamlet–Taft solvent parameters,[15] which are recommended by several authors for this purpose.[17–19] For this application, the Kamlet–Taft linear solvation energy (LSE) relationship [Eqn. (3)] is used in the form[15,17a,18]

$$XYZ = (XYZ)_0 + (s + d\delta)\pi^* + a\alpha + b\beta \qquad (3)$$

where XYZ ($\nu_{\max}$) is the solvent-dependent absorption maximum of a solvatochromic compound, $(XYZ)_0$ [$\nu_{\max(0)}$] is the absorption maximum of the same solvatochromic compound measured in the reference system, e.g. in the gas phase or in an inert solvent, π^* is the dipolarity/polarizability of the solvent, δ is a polarizability adjustment term which for aromatic solvents is $\delta = 1$, for polyhalogenated solvents $\delta = 0.5$ and for all other solvents $\delta = 0$, α is the hydrogen-bond donating (HBD) capacity or acidity of the solvent, β is the hydrogen-bond acceptance (HBA) capacity or basicity of the solvent[18a,c] and *s*, *a*, *b* and *d* are solvent-independent coefficients reflecting the susceptibility of the terms π^*, α, β, and δ, respectively, upon ($\nu_{\max}$). Until now, only relatively weak or moderately polar solvents have been used for investigating the solvatochromism of neutral EDA complexes[2,3,5,9] because highly polar and strong donor solvents, e.g. alcohols, DMSO, DMF and trimethyl phosphate, prevent the formation of EDA complexes due to competing reactions with the acceptor component or radical ion pair formation occurs.[2,20]

The objective of this work was the investigation of the solvatochromism of the EDA complex formed between 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) and tetracyanoethene (MK–TCNE), taking into account also the stronger donor solvents as mentioned above. In spite of the fact that the UV/Vis spectral properties of the MK–TCNE EDA complex have not been reported in the literature,[21] it was chosen for different reasons. First, Michler's ketone, among other substituted benzophenones,[14a] is well known to be itself a solvatochromic compound.[17] Hence it is expected that related EDA complexes are also solvatochromic. Second, the CT absorption band of the MK–TCNE complex appears clearly separated from the expected disturbing radical-anion absorption of TCNE[20] by using stronger donor solvents. In order to detect with certainty the charge-transfer absorption of the MK–TCNE complex also in highly polar solvents, a special UV/Vis technique was employed (see Experimental section) because of the disturbing reactions of TCNE with these very strong HBA solvents.

RESULTS AND DISCUSSION

The UV/Vis absorption spectra of the MK–TCNE complex were measured in 21 non-protic and seven protic solvents. The complex was also measured adsorbed on silica particles from its 1,2-dichloroethane (DCE) solution. The striking observation is that the MK–TCNE complex exists in two different structures, accompanied by a characteristic colour change in the two different groups of solvents. It should be emphasized that the formation of two different kinds of complexes as a function of solvent property seems to be specific for 4,4′-bis(dialkylamino)benzophenone–TCNE complexes. For comparison, UV/Vis spectroscopic investigations of various other benzophenone–π acceptor complexes were carried out in DCE, protic solvents and solvent mixtures. Qualitative results are shown in Table 1.

None of the other investigated EDA complexes, excluding the unstable MK–TCNQ complex, show a new absorption maximum as the 4,4′-(dialkylamino)-benzophenone–TCNE complexes do in DCE by adding

Table 1. UV/Vis absorption maxima of 10 benzophenone–acceptor complexes, measured in 1,2-dichloroethane (DCE) and in binary DCE–alcohol mixtures

Benzophenone component	Acceptor	ν_{max} (cm^{-1}) In DCE (CT band)	In DCE–ROH
4,4′-Bis(methoxy)benzophenone	TCNE	22 000	-[c]
4-(*N*,*N*-dimethylamino)benzophenone	TCNE	15 000	-[c]
4-(*N*,*N*-Dimethylamino)-4′-methylbenzophenone	TCNE	14 920	-[c]
4-(*N*,*N*-Dimethylamino)-4′-methoxybenzophenone	TCNE	14 760	-[c]
MK	TCNE	14 880	19 600[d]
4,4′-Bis-(*N*,*N*-dimethylamino)benzophenone	TCNE	13 600	19 200[d]
MK	TNB[a]	21 000	-[c]
MK	TCQ[b]	16 000	-[c]
MK	TCNQ	14 000	19 600[e]
MK	$(C_6H_5)_3C^+AsF_6^-$	15 000	-[f]

[a] 1,3,5-Trinitrobenzene.
[b] Tetrachloro-1,4-benzoquinone.
[c] The intensity of the CT absorption band decreases with increasing concentration (5–10 cg g^{-1}) of added methanol or 2,2,2-trifluoroethanol (TFE). A novel UV/Vis absorption band or a shoulder is not observed.
[d] The intensity of this new absorption band increases with increasing concentration of methanol, ethanol, propan-2-ol, or cyclohexanol. Note that addition of TFE or 1,1,1,2,2,2-hexafluoropropan-2-ol to the benzophenone–acceptor complex does not cause this new absorption band.
[e] The MK–TCNQ complex remains unstable in the presence of protic solvents. Within minutes, radical ion pair formation occurs and side reactions take place. Therefore, this complex was not suitable for solvatochromic measurements.
[f] The common alcohols react with the carbenium salt.

methanol or other well behaved protic solvents (see the discussion on protic solvents).

However, TCNE is known to be a highly reactive species towards amines; with tertiary aromatic amines it yields intensely coloured 4-(tricyanovinyl)arylamine dyes[22] and with pyridine and water it yields pyridinium salts and HCN and CO_2 are generated.[22a,d] Experimental preliminaries by means of ^{1}H NMR spectroscopy of MK and TCNE mixtures showed that such reactions do not occur in the solvents studied provided that moisture is excluded. Also, other products were not detected such as expected from electrophilic *ortho*-substitution of the phenyl ring of MK with TCNE.[22c]

In each case, MK and TCNE give a stoichiometric (1:1) complex. The formation constant of the MK–TCNE complex in DCE was calculated as $K_c = 7.5$ (± 0.5) 1 mol^{-1} and the absorption coefficient as $\varepsilon = 1000$ (± 100) 1 mol^{-1} cm^{-1} at $\nu_{max,\ CT} = 14\,880$ cm^{-1} by means of the method of Scott.[23] Thus, the MK–TCNE complex accomplishes the condition for a weak intermolecular interaction according to the Mulliken theory.[1b]

Owing to its versatile UV/V is spectroscopic behaviour and its unexpectedly high stability in different classes of solvents, we investigated the solvatochromism of MK–TCNE in order to establish an indicator that may be suitable for detecting manifold microenvironmental polarities. First, we will present the results from measurements carried out in non-protic solvents.

Non-protic solvents

The solvent-dependent CT absorption maxima of the MK–TCNE complex as measured in 21 non-protic solvents are compiled in Table 2.

In each case, the typical CT absorption band of the MK–TCNE complex could be detected in non-protic solvents. In the strong donor solvents DMF and DMSO, the CT absorption was immediately recorded after mixing the components (see footnotes to Table 2). During the first few seconds after complex formation, no disturbing influences were detected. The observed bathochromic band shift observed for the MK–TCNE complex ($\Delta\nu = 3100$ cm^{-1}) ranges from trimethyl phosphate (No. 21, highest observed $\nu_{max,\ CT}$) to 1,1,2,2-tetrachloroethane (No. 1, lowest observed $\nu_{max,\ CT}$).

The results of multiple correlation analyses of the CT maxima with various empirical solvent parameters are summarized in Table 3.

Polarity scales which are based on a single reference process, e.g. the DN (donor number) or AN parameter (acceptor number) of Gutmann[16] and the $E_T(30)$ parameter of Reichardt,[14] are not suitable to explain sufficiently the solvatochromism of the MK–TCNE complex. Advantageously, it can be shown that a multiple correlation according to Eqn. (3) by using the Kamlet–Taft solvent parameters β and π^* is very suitable in describing the solvatochromism of this EDA complex in non-protic solvents (Fig. 1):

$$\nu_{max,CT} \times 10^{-3}/\mathrm{cm}^{-1} = 16.667 - 2.426\,\pi^* + 3.028\,\beta \tag{4}$$

It is interesting that the respective influences of the β and π^* terms of the solvent on the value of $\nu_{max,\ CT}$ are opposite. An increase in the dipolarity/polarizability of the solvent, as measured by π^*, causes a bathochromic band shift due to a stronger solvation of the larger dipolar and more polarizable excited state ($D^{+\cdot}\ A^{-\cdot}$) of the EDA

Table 2. Charge-transfer UV/Vis absorption maxima of the MK–TCNE complex, measured in 21 non-protic solvents of different polarity, and the solvent parameters used in the correlation analysis (taken from Refs [15,16] and [18b])

No.	Solvent	$\nu_{\max,\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	π^*	β	α	*DN*[b]	*AN*[b]
1	1,1,2,2-Tetrachloroethane	14.30	0.95	0.00	0.00	—	—
2	Dichloromethane	14.87	0.82	0.10	0.13	1.0	20.4
3	1,2-Dichloroethane	14.88	0.81	0.10	0.00	0.0	16.7
4	Nitrobenzene	15.05	1.01	0.30	0.00	4.4	14.8
5	1,1-Dichloroethane	15.36	0.48	0.10	0.10	—	16.2
6	Acetonitrile	15.64	0.75	0.40	0.19	1.1	18.9
7	1,1,1-Trichloroethane	15.72	0.49	0.00	0.00	—	—
8	Benzene	15.80	0.59	0.10	0.00	0.1	8.2
9	Acetophenone	15.84	0.90	0.49	0.04	15.0	—
10	4-Butyrolactone	15.90	0.87	0.49	0.00	18.0	17.3
11	Toluene	16.12	0.54	0.11	0.00	0.1	—
12	Ethyl benzoate	16.30	0.74	0.41	0.00	15.0	—
13	1,4-Dioxane	16.32	0.55	0.37	0.00	14.3	10.3
14	Cyclohexanone	16.44	0.76	0.53	0.00	18.0	—
15	Dimethyl sulphoxide	16.69[a]	1.00	0.76	0.00	29.8	19.3
16	Butan-2-one	16.72	0.67	0.48	0.06	17.4	—
17	*N*,*N*-Dimethylformamide	16.75[a]	0.88	0.69	0.00	26.6	16.0
18	Isobutyl acetate	16.76	0.46	0.45	0.00	15.0	—
19	Ethyl acetate	16.80	0.55	0.45	0.00	17.1	9.3
20	Tetrahydrofuran	16.92	0.58	0.55	0.00	20.0	8.0
21	Triethyl phosphate	17.26[a]	0.72	0.77	0.00	26.0	—

[a] The radical anion of TCNE is immediately formed.
[b] *DN* = donor number; *AN* = acceptor number.

Table 3. Correlation equations for the correlation of the solvent-dependent UV/Vis absorption maxima ($\nu_{\max,\,\mathrm{CT}}$) with the solvent parameters *AN* (acceptor number), β, π^* and *DN* (donor number): $XYZ = XYZ_0 + a\,AN + b\,\beta + s\,\pi^* + d\,DN$

XYZ	XYZ_0	*a*	*b*	*s*	*d*	r^2[a]	*SD*[a]
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	17.623	−0.113	—	—	—	0.360	0.678
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	14.997	—	2.733	—	—	0.663	0.645
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	17.248	—	—	−1.720	—	0.137	0.780
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	15.178	—	—	—	0.067	0.666	0.450
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	16.667	—	3.028	−2.426	—	0.930	0.232
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	16.900	—	—	−2.340	0.070	0.920	0.231
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	17.322	−0.135	—	0.852	—	0.382	0.702
$\nu_{\mathrm{CT}} \times 10^{-3}$ (cm^{-1})	16.063	−0.072	2.546	—	—	0.881	0.308

[a] r^2 = Correlation coefficient squared; SD = standard deviation.

complex. This result is expected and agrees very well with the theory.[1,2,3,5] The hypsochromic shift of the CT band on increasing the Lewis basicity of the solvents, as measured by β, hints at a specific solvation of the electronic ground state of the EDA complex. Because the solvatochromic shift of pure MK is not affected by the solvent's basicity,[17] the specific solvation of the TCNE component should to be responsible for this effect, which is observed for the whole MK–TCNE complex. A similar explanation was also used in interpreting the hypsochromic shift of the CT band of five different alkylbenzene–TCNE complexes which have been investigated in the two solvents, 1,2-DCE ($\beta = 0.1$) and acetonitrile ($\beta = 0.40$).[9c,d] It is also well established that TCNE interacts weakly with n donors.[5,7,9d] Therefore, we conclude that the influence of the β term upon $\nu_{\max,\,\mathrm{CT}}$ is due to a specific solvation of the TCNE component site in the ground state of the EDA complex. It should be noted that the good linear correlation shown in Fig. 1 is only valid for non-HBD solvents.

In spite of the positive solvatochromism of pure MK in HBD solvents, which is well documented by a multiple LSE relationship including the π^* and α term of the solvents,[17] a different behaviour is observed for the solvatochromism of the MK–TCNE complex in protic solvents.

Protic solvents

The characteristic broad CT absorption maximum of MK–TCNE is not observed in all pure protic solvents. A

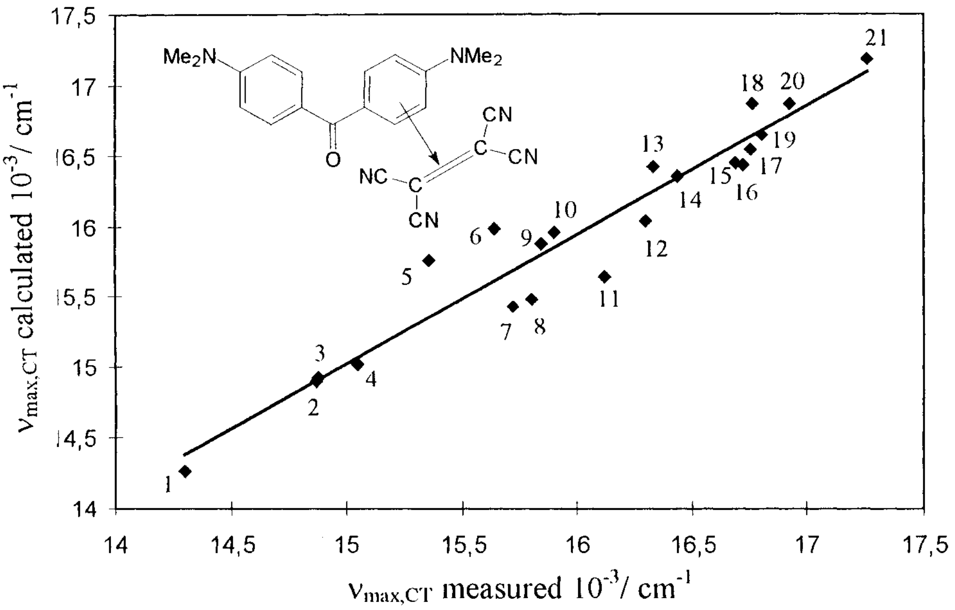


Figure 1. Linear correlation of the experimental UV/Vis absorption maxima of MK–TCNE and the values predicted according to Eqn. (3). The inset shows the structure of MK–TCNE

new visible absorption band appears at about $\nu = 19800\ cm^{-1}$ in methanol, ethanol, propan-2-ol, cyclohexanol, 2,2,2-trichloroethanol and benzyl alcohol as solvents. The same new band is observed in the UV/Vis spectrum of the MK–TCNE complex, measured in DCE by successively adding methanol. Figure 2(a) shows that the characteristic CT absorption band of the MK–TCNE complex at $\nu_{max,\ CT} = 14880\ cm^{-1}$ ($\lambda_{max} = 672$ nm) decreases and a new absorption maximum at $\nu_{max} = 19800\ cm^{-1}$ ($\lambda_{max} = 505$ nm) simultaneously increases. On increasing the amount of methanol added, the appearance of an isosbestic point at $\nu = 18900\ cm^{-1}$ ($\lambda = 530$ nm) is clearly detectable in the UV/Vis absorption spectrum.

Obviously, the MK–TCNE complex in DCE is converted stoichiometrically into another species by protic solvents, as indicated by the appearance of the isosbestic point as seen in Fig. 2(a). The new species is fluorescent, as shown in Fig. 2(b); the fluorescence intensity of the emission at $\lambda = 560$ nm increases with increasing methanol content in the mixture corresponding to the increase in the absorption intensity of the carboxenium zwitterion formed (for an explanation, see later) at $\lambda = 505$ nm.

Identical spectra series, as shown in Fig. 2(a) and Fig 2(b), are also obtained by titrating the MK–TCNE complex in DCE with ethanol, propan-2-ol, cyclohexanol or benzyl alcohol. The UV/Vis spectrum of the last example shows no isosbestic point because benzyl alcohol and TCNE also form a typical π-complex.

In protic solvents, MK undergoes complex formation with TCNE via the non-bonding electron pair of the carbonyl oxygen atom because a strong interaction of an electrophile towards the carbonyl oxygen of MK causes the formation of a carboxenium zwitterion that absorbs in the UV/Vis region at about $\lambda = 500$ nm.[17b,24] $[4\text{-}(CH_3)_2NC_6H_4)]_2COR^+$ species can also be formed by complexing MK with methyl triflate (MTF), bromotriphenylmethane (TPMB) or trimethylsilyl triflate (TMSTF) in DCE or CD_2Cl_2. The formation of *O*-substituted oxeniums $[4\text{-}(CH_3)_2NC_6H_4)]_2COR^+$ is usually associated with a typical UV/Vis absorption maximum at about $\lambda_{max} = 500$ nm. The UV/Vis absorption maximum of the oxenium of MK is slightly dependent on the *O*-fixed substituent: R = —CH_3, $\nu_{max} = 18900\ cm^{-1}$; R = —$Si(CH_3)_3$, $\nu_{max} = 19700\ cm^{-1}$; and R = —$C(C_6H_5)_3$, $\nu_{max} = 19960\ cm^{-1}$. A hypsochromic band shift is observed in the order R = —CH_3 <—$Si(CH_3)_3$ <—$C(C_6H_5)_3$. This effect is due to the fact that the conjugation along the π-electron system is disturbed by the *O*-fixed substituent because a growing steric demand of the substituent R causes an increasing twisting of the phenyl—C^+ bond.[17b] All attempts to isolate the novel red $[4\text{-}(CH_3)_2NC_6H_4)]_2COR^+$ compounds as pure crystalline solids have failed so far.[26] Structural data and UV/Vis spectroscopic results for analogous compounds are particularly reported for adducts of MK with substituted phenols and trifluoromethanesulphonic acid.[24]

Using 2,2,2-trichloroethanol as solvent, the MK–TCNE complex was obtainable as a red oil. This oil was suitable for investigation by ^1H NMR spectroscopy in $CDCl_3$. Besides the signals of the two *N*,*N*-dimethylamino groups of unreacted MK at $\delta = 2.95$ ppm, only one new single signal of the dimethylamino groups at $\delta = 3.13$ ppm appeared, indicating the single coordination of an electrophile at the oxygen atom of the carbonyl

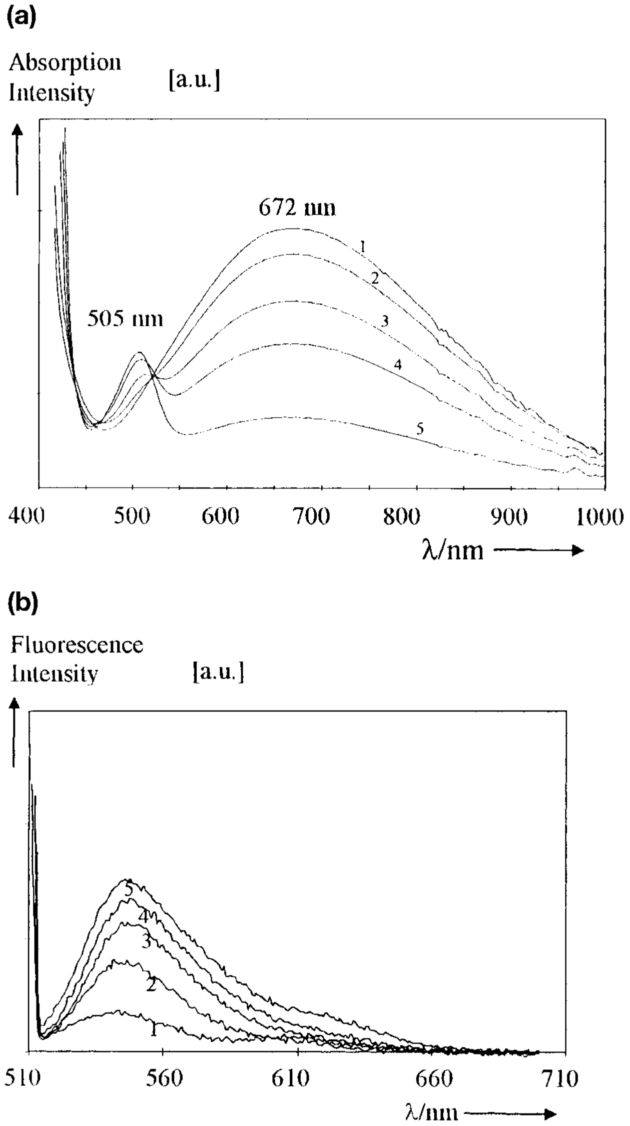


Figure 2. (a) UV/Vis absorption spectra series of the MK–TCNE complex as obtained with successive additions of methanol. Conditions: [TCNE] = 8.6 mmol l^{-1}; [MK] = 20 mmol l^{-1}; solvents, 1,2-dichloroethane (12 ml). Addition of methanol: (1) MK–TCNE in 1,2-DCE (without methanol); (2) addition of 0.012 mol l^{-1} methanol; (3) 0.363 mol l^{-1}; (4) 0.722 mol l^{-1}; (5) 2.061 mol l^{-1}. (6) Corresponding emission spectra series of the MK–TCNE complex. Excitation wavelength: $\lambda = 505$ nm

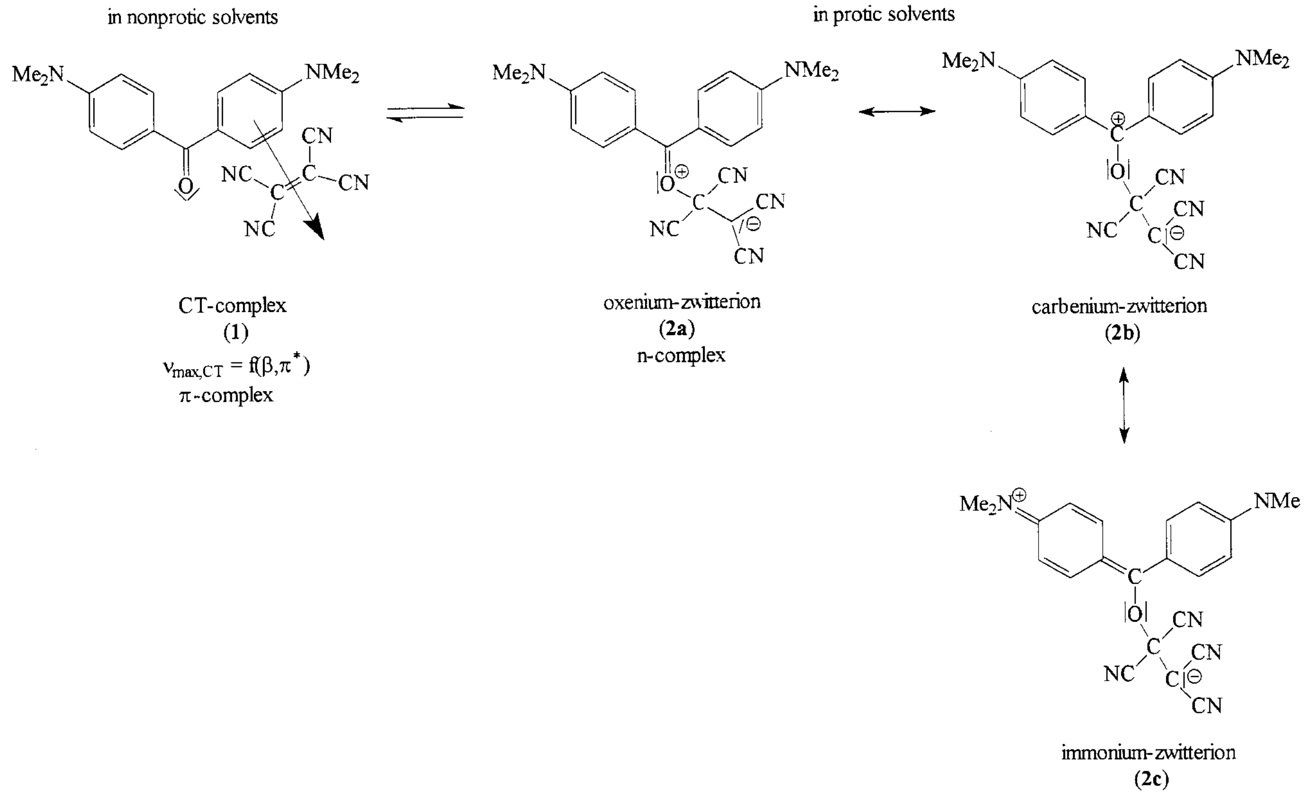
group. Correspondingly, the model compound $[4\text{-}(CH_3)_2NC_6H_4]_2COSi(CH_3)_3{}^+$ $CF_3SO_3{}^-$ shows the single ^{1}H signal of the dimethylamino groups at $\delta = 3.25$ ppm.[26]

Owing to the very low concentration of the MK–TCNE complex in DCE–alcohol mixtures (below 1% of the total amount of the MK component used), NMR and IR measurements were unsuccessful in elucidating the structure in solution.

According to the experimental results, we suggest the following explanation. The former EDA π complex of MK–TCNE (in 1,2-dichloroethane) is transformed into a zwitterionic complex by protic solvents (Scheme 1). For instance, the formation of similar zwitterions between phenazine donors and TCNE was suggested by Dietz *et al.*[27] In the present paper, the zwitterionic form is designated as an n-complex because the interaction between the non-bonding electron pair of the oxygen atom of MK and the antibonding π^* orbital of TCNE is the dominant step, and the oxenium zwitterion (**2a**) should be the main contributing resonance structure. The contributions of the mesomeric carbenium (**2b**) and immonium (**2c**) (quinoid form) structures stabilize the n-complex. Since not only the n-electrons at the oxygen atom are involved, but also the π^*-electrons of the carbonyl bond, it is not a pure n-complex. This discussion shows that a well defined assignment of the complex type is not possible.

According to the exact definition of solvatochromism,[14] it should be noted that the formation of the zwitterion, associated with the UV/Vis absorption at $\lambda_{max} = 500$ nm, does not fit well in this accurate description because the observed UV/Vis absorption maxima are attributed to species of different constitutions and, therefore, are due to qualitatively different electronic transitions.

It is conceivable that the negatively charged site of the MK–TCNE zwitterionic species is either stabilized by specific solvation with the HBD solvent or even becomes protonated. Considering the pK_a values of 15–19 and 0–12 of the corresponding protic acids ROH (protic solvents) and $C(CN)_3H$ to $C(CN)_2H_2$ (cyanomethane derivatives),[22b,28] respectively, the zwitterionic form should be the dominant species in the protic solvents methanol, ethanol, propan-2-ol, cyclohexanol and benzyl alcohol. Oxenium formation is not observed on titrating the MK–TCNE complex (in DCE) with extremely polar protic solvents such as 2,2,2-trifluoroethanol [TFE, $E_T(30) = 59.8$, p$K_a = 12.4$][14,28] or 1,1,1,3,3,3-hexafluoropropanol [HFI, $E_T(30) = 65.3$, p$K_a = 9.3$].[14,28] The absorption intensity of the CT band of the MK–TCNE complex at $v = 14880$ cm^{-1} in DCE decreases drastically with increasing concentration of added TFE or HFI; this change is evidently larger as observed with methanol or the other alcohols. The two strong HBD solvents TFE and HFI strongly solvate the MK component itself and compete with the TCNE component. The latter effect does not occur in protic solvents possessing pK_a values ranging from 15 to 19, i.e. from methanol to propan-2-ol. Furthermore, the positively charged site of the zwitterion requires the stabilization by two dialkylamino groups in the *para* position of the phenyl rings. It appears that the electrophilic strength of TCNE is not sufficient to generate an oxenium species of such benzophenone components[25] with weaker donor substituents than dialkylamino groups in the *para* position of the phenyl rings (see Table 1). However, an electrophilic attack of the TCNE upon one of the dimethylamino groups of MK is also conceivable. However, the latter effect would not



Scheme 1. Occurrence of the MK–TCNE complex in non-protic and protic solvents

cause a bathochromic shift of the UV/Vis absorption of MK as observed. In contrast, a hypsochromic effect would be expected in this case. The results of the fluorescence measurements of the $[4\text{-}(CH_3)_2NC_6H_4]_2COR^+$ species support our suggestion. The Stokesshift observed for the positively charged part of the MK–TCNE zwitterionic complex ($\Delta\nu = 1620\ cm^{-1}$) is much smaller than that for $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+$ ($\Delta\nu = 2100\ cm^{-1}$). As a consequence of this result, a smaller difference in the dipole moment between the electronic ground and excited states of the oxenium part of the MK–TCNE zwitterion would be expected compared with $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+$. This can also be explained as being due to the larger steric effect of the TCNE substituent compared with the methyl group. Hence the TCNE substituent causes a stronger twisting between the phenyl rings and the central carbon atom.

In the pure solvent HFI, the MK–TCNE complex undergoes complete dissociation into the radical ion-pair salt ($MK^{+\cdot}TCNE^{-\cdot}$). The sharp visible absorption band of the $MK^{+\cdot}$ radical cation appears at $\nu = 15000\ cm^{-1}$. The favoured stabilization of radical cations in the extremely polar and high ionizing power solvent HFI has been reported recently by Eberson *et al.* in detail.[29] Our results are in complete agreement to the results gives by Eberson *et al.*[29] In pure TFE, MK and TCNE yield a mixture of both $MK^{+\cdot}TCNE^{-\cdot}$ and $[4\text{-}(CH_3)_2NC_6H_4]_2C^+\text{—}O\text{—}C(CN)_2\text{—}C(CN)_2^-$.

Silica surface

The π- and the n-complex of MK–TCNE each exhibit a characteristic UV/Vis spectrum. Both the influence of the solvent's dipolarity/polarizability and basicity on the charge-transfer energy and the influence of the HBD property on the switching of the EDA complex can be demonstrated by adsorption the MK–TCNE complex from DCE solution on the surface of different silica particles in suspension of DCE. The silica samples used were Aerosil 300 and KG 60. The surfaces of these materials are evidently polar ($\pi^* = 1 \pm 0.2$) and bear a large HBD capacity ($\alpha = 1 \pm 0.2$), whereas the HBA capacity is very low ($\beta = 0.2$ to -0.26). The polarity parameters of Aerosil 300 and KG 60 were also measured in DCE and taken from Ref. 30a.

Immediately after mixing the green MK–TCNE complex DCE solution with dried silica, the solution phase turns colourless and the EDA complex is adsorbed completely on the particle surface by using appropriate amounts of both components. According to the value of the polarity parameters of the silicas, the following effects are expected: a bathochromic shift of the CT band and the appearance of the oxenium species, but probably also of the protonated zwitterion because the pK_a value is about 2–3 for bare silicas.

The corresponding UV/Vis spectra before and after the adsorption of MK–TCNE on the two different silicas are shown in Fig. 3.

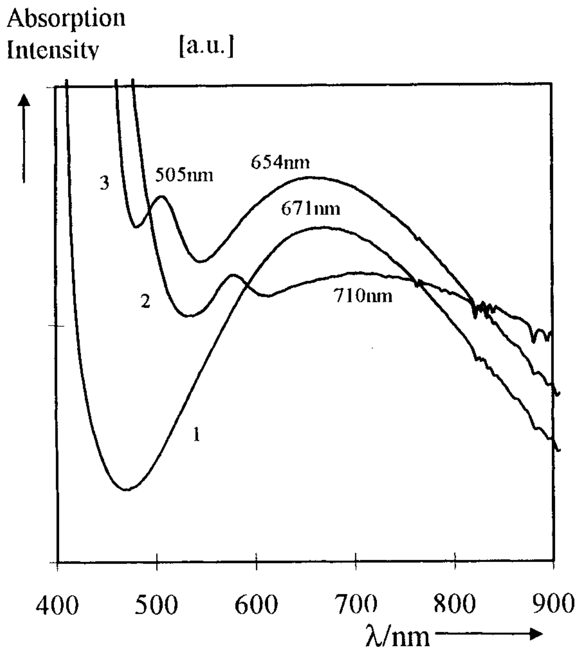


Figure 3. UV/Vis absorption spectra of the MK–TCNE complex (1) in 1,2-DCE, (2) adsorbed on the KG 60 surface and (3) adsorbed on the Aerosil surface

For KG 60, the characteristic broad charge-transfer absorption band of the adsorbed EDA complexes shifts bathochromically because the dipolarity of the silica surface is higher than that of DCE. The observed band shift correlates very well with the value expected according to Eqn. (3) if one considers only the π^* term. The basicity properties of bare silicas are difficult to analyse.[30c] Thus, the solvatochromism of the adsorbed MK–TCNE complex can be used to achieve additional information about surface polarity.[30b] As expected, the oxenium absorption maximum of MK at $\nu_{max} = 19800\ cm^{-1}$ ($\lambda = 505$ nm) appears on adsorption on silica. The ionic form is produced by the acidic silanol groups analogously as observed in protic solvents. It should be noted that the concentration of the oxenium species, which is generated on the silica surface, increases with time. After 1 day, a dark reddish suspension is obtained.

For comparison, the related model compound $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+$ can be generated quantitatively by chemisorption of the dimethylketal of MK on a silica surface. The corresponding UV/Vis absorption and emission spectra of $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+\ ^-O$-silica ($\nu_{max,abs} = 18860\ cm^{-1}$; $\nu_{max,em} = 16700\ cm^{-1}$) are shown in Fig. 4.

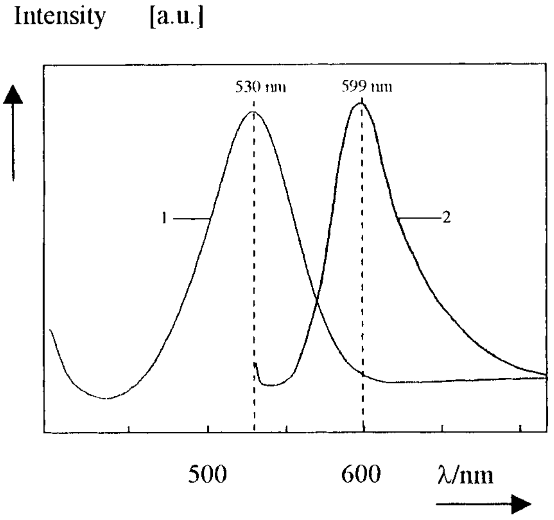
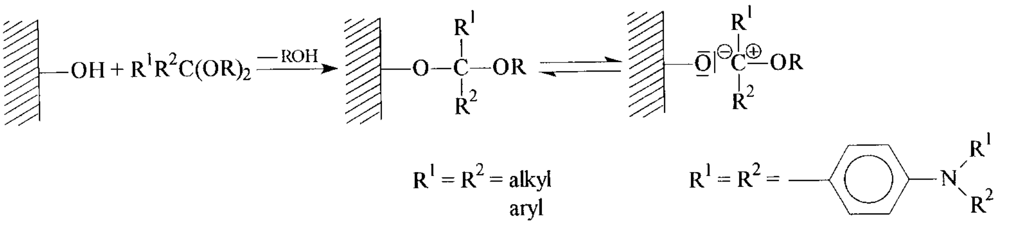


Figure 4. UV/Vis (1) absorption and (2) emission spectra of $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+$ chemisorbed on Aerosil 300 in DCE

$[4\text{-}(C_2H_5)CH_6H_4]_2COCH_3^+$ ($\nu_{max,abs} = 18500\ cm^{-1}$; $\nu_{max,em} = 16690\ cm^{-1}$) was generated by the same procedure. It should be emphasized that the process for generating the $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+$ is very sensitive to water impurities (see Experimental section). Figure 4 shows a successful experiment because in the region between $\lambda = 350$ and 420 nm there appear neither an additional band nor shoulders derived from MK impurities which are formed by reaction of the dimethyl ketal of MK with residual traces of water. The bathochromic shift of the UV/Vis absorption maximum of the oxenium ($\Delta\nu = 500\ cm^{-1}$) observed for the diethylamino as compared with the dimethylamino derivative is due to the stronger positive inductive effect of the ethyl groups.[17b]

Acetals and ketals usually react with silica in forming a functionalized surface (Scheme 2).[31]

The two strong n-donating dialkylamino groups in the *para* position of the phenyl ring significantly stabilize the



Scheme 2. Surface reaction of ketals with silanol groups

positive charge of the central carbon atom. Hence the nucleophilicity of the silanolate is too low to form a covalent bond in this case. The structure of the $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+$ present on the silica surface was proved by the surface reaction with tri-*n*-butylstannane as hydride donor. Tri-*n*-butylstannane is a strong nucleophile that reacts even with weak electrophilic cations[32] but not with the covalent precursor MK or its dimethylketal. $[4\text{-}(CH_3)_2NC_6H_4]_2CHOCH_3$ was obtained in moderate yield (see Experimental section). Surprisingly, a migration of the ortho-linked methyl group to the nitrogen atoms was not observed. Perhaps the two dialkylamino groups are protected by surface silanols.

CONCLUSION

The MK–TCNE EDA complex is suitable as a UV/Vis spectroscopic polarity probe for the investigation of environments possessing both HBD capacity and high dipolarity/polarizability properties. In non-protic solvents, the visible absorption maxima of the CT band correlates well with the Kamlet–Taft π^* and β parameters of the solvents. In moderate protic solvents, a zwitterionic species is formed due to coordination of TCNE at the carbonyl oxygen of MK. Furthermore, in the case of highly ionization power solvents with $E_T(30) > 58$, the EDA complex dissociates into its corresponding radical ion pair.

EXPERIMENTAL

Materials. TCNE was sublimed under reduced pressure before use. TCNQ, 1,3,5-trinitrobenzene and tetrachloro-1,4-benzoquinone were purchased from Fluka. MK from Merck was recrystallized twice from ethanol and dried carefully over CaH_2. Methyl triflate and trimethylsilyl triflate were purchased from Merck and used as received. Bromotriphenylmethane was purchased from Merck. It was recrystallized from toluene–hexane containing 2% of acetyl bromide.

The solvents were carefully dried and freshly distilled before use. The purity was checked by measuring the $E_T(30)$ solvent parameter. DCE was distilled freshly before use in each case and stored over alumina to avoid traces of HCl.

Aerosil 200 and silica (LC 1500, Grace) were dried at 400 °C for 12 h before use and allowed to cool to room temperature under dry argon.

The substituted benzophenones were commercially available products except 4-(*N*,*N*-dimethylamino)-4′-methoxy- and 4-(*N*,*N*-dimethylamino)-4′-methylbenzophenone. These two compounds were synthesized from the corresponding benzanilide component and *N*,*N*-dimethylaniline by a Friedel–Crafts reaction according to Ref. 33.

The dimethylketal of MK was obtained by a two-step synthesis from the MK dichloride and sodium methoxide in methanol according to Ref. 34. This procedure requires careful exclusion of traces of water to prevent unreacted MK remaining as impurity.

To prepare an Aerosil–dichloroethane suspension, about 0.5 g of Aerosil 200 was suspended in 15 ml of 1,2-dichloroethane.

Procedure for preparing $[4\text{-}(CH_3)_2NC_6H_4]_2COCH_3^+$ $^-$O-silica. A 0.8 g (2.3 mmol) amount of the dimethylketal of MK was added to a suspension of 9.8 g of silica (LC 1500) in 15 ml of 1,2-dichloroethane. A dark reddish suspension was immediately obtained. After adding 1.2 ml (4.5 mmol) of tri-*n*-butylstannane to the mixture, the reddish colour of the silica disappeared and it became colourless. A sample from the supernatant solution was taken for thin-layer chromatography [TLC plates from Merck, KG 60 F_{254}; mobile phase, cyclohexane–acetone (70:30, v/v)]. The chromatography showed $[4\text{-}(CH_3)_2NC_6H_4]_2CHOCH_3$ in addition to the dimethylketal of MK. $[4\text{-}(CH_3)_2NC_6H_4]_2CHOCH_3$ was assigned by using the methoxy ether of Michler's hydrol as a reference compound. The yield of $[4\text{-}(CH_3)_2NC_6H_4]_2CHOCH_3$ was 30–50%.

Spectra. The UV/Vis spectra were recorded by means of an MCS 400 diode-array spectrometer from Carl Zeiss Jena, connected with an immersion cell (TSM 5) via glass-fibre optics. In a typical experiment, MK and TCNE were dissolved in the pure solvent and the spectrum was immediately recorded as a function of time, after mixing the individual components in the reaction vessel. The concentration of MK was 20 mmol l^{-1} and that of TCNE was 8.6 mmol l^{-1}.

The fluorescence spectra were recorded with an RF-5001 PC fluorescence spectrometer (Shimadzu).

NMR spectra were recorded with a 300 MHz Gemini NMR spectrometer from Varian.

Correlation analysis. Multiple regression analysis was performed with the SPSS 6.1 statistic program.

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