Electron Transfer

Synthesis and Photophysics of a Neutral Organic Mixed-Valence Compound**

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Dedicated to Prof. Jörg Daub on the occation of his 65th birthday

Purely organic mixed-valence (MV) compounds are of great interest for the investigation of intramolecular electrontransfer (ET) processes.^[1-5] Usually these MV compounds are radical ions consisting of two redox centers connected by a saturated or unsaturated bridge. In this communication we present the synthesis and photophysical properties of the first organic MV compound that is neutral rather than charged.

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MV compounds are characterized by a so-called intervalence charge-transfer (IV-CT) band (usually in the near-IR (NIR) region) which is associated with the optically induced charge transfer from one redox center to the other. The electronic coupling V between the two diabatic (formally noninteracting) states (charge localized on the one and on the other redox center, respectively) is a measure for the electronic communication between these states and can be calculated from the IV-CT band by Equation (1), where μ_{eg}

$$V = \frac{\mu_{eg}}{\Delta \mu_{12}} \tilde{\nu}_{max} \tag{1}$$

and $\tilde{\nu}_{max}$ are the transition moment and the energy of the IV-CT band, respectively, and $\Delta \mu_{12}$ is the diabatic dipole moment difference between the two diabatic states mentioned above. The diabatic quantity $\Delta \mu_{12}$ can either be estimated by the effective electron-transfer distance e × r or can be traced back to purely adiabatic (measurable) quantities by Equation (2)

$$e r = \Delta \mu_{12} \sqrt{\Delta \mu_{eg}^2 + 4 \mu_{eg}^2}$$
⁽²⁾

(generalized Mulliken–Hush theory, GMH),^[6–8] where $\Delta \mu_{eg}$ is the difference between the adiabatic dipole moments of the ground and excited IV-CT state. However, while both the estimate of $e \times r$ by, for example, the distance of the redox centers r and the determination of $\Delta \mu_{eg}$ by quantum-chemical methods involves major inaccuracies,^[9] the experimental determination of $\Delta \mu_{eg}$ can be achieved by means of electrooptical absorption measurements (EOAM).^[10] Unfortunately, this method is complicated for charged species because of ion migration in the electric field, which can be circumvented by using glass matrices.^[11-13] Further disadvantages of charged MV compounds are the low solubility especially in nonpolar solvents^[14-16] and ion-pair effects.^[17,18] These disadvantages can be avoided by using neutral MV compounds, a class of compounds that has not been described and studied so far to the best of our knowledge,^[19] which is therefore the subject of this communication.

While MV radical cations based on two triarylamine centers^[20-22] and MV radical anions based on perchlorinated triarylmethyl radicals^[23,24] are well known, it was obvious to link the two redox centers by, for example, an ethylene bridge to create a neutral MV system. In the neutral, purely organic MV compound **1** a perchlorinated triarylmethyl radical center acts as the acceptor and a triarylamine redox center as the donor (Scheme 1).

The synthesis of compound **1** is outlined in Scheme 2. Compound **2** was prepared by a Pd-catalyzed Buchwald–Hartwig amination of the stilbene derivate $3^{[24]}$ and bis(4-methoxyphenyl)amine in 46% yield. Because of the low acidity of the α -*H* atom of **2**, KOtBu in DMSO was required to form the corresponding carbanion salt, which was subsequently oxidized with *p*-chloranil to obtain the air-stable radical **1** in 60% yield.

The cyclic voltammogram of **1** in dichloromethane/ tetrabutylammonium hexafluorophosphate (TBAH) solution shows one reversible oxidation process at $E_{1/2} = +240 \text{ mV}$ versus ferrocene (Fc), which is assigned to the oxidation of the



Scheme 1. Optically induced ET process in 1.



Scheme 2. Synthesis of the neutral radical 1.

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triarylamine center to the radical cation (Figure 1).^[25] Furthermore, a reversible reduction wave at $E_{1/2} = -670 \text{ mV}$ can be observed, which corresponds to the reduction of the carbon radical center to the carbanion.^[24] The large splitting of the two redox processes reflects the pronounced nondegeneracy of the two redox centers in contrast to the degenerate bis(triarylamine) and bis(perchlorotriphenylmethyl) MV compounds mentioned above.

The excellent solubility of neutral 1 gave us the unique chance to investigate the UV/Vis/NIR

absorption spectra in thirteen different solvents ranging from totally apolar (n-

hexane) to strongly polar (acetonitrile).

The electronic absorption spectrum of 1 (Figure 2) shows an intense band at $25\,500 \text{ cm}^{-1}$, which is typical of perchlorinated benzene derivatives^[26-28] and a weaker band at 24900 cm⁻¹, which is assigned to methoxy-substituted triarylamine systems.^[29] Furthermore, two weak absorption bands at 19000 cm⁻¹ and 17500 cm⁻¹ can be observed which are characteristic for perchlorinated triarylmethyl radical systems.^[26] Even more interesting is the observation of a weak absorption band in the NIR region at about 12000 cm^{-1} which can be assigned to an

IV-CT associated with an intramolecular

electron transfer from the triarylamine to

the radical unit (Scheme 1).

To our surprise the absorption maximum $\tilde{\nu}_{max}$ of the IV-CT band of 1 shows a weak and superficially nonsystematical dependence on the solvent polarity (Table 1). The extinction coefficient of the IV-CT band is larger and the band width at half-height is smaller in nonpolar solvents such as *n*-hexane than in polar solvents like acetonitrile (Figure 3). To explain this unexpected behavior we used the Jortner model^[30-32] to simulate the IV-CT band in each solvent. In this calculation an average molecular vibration is treated quantum-mechan-

Table 1: Absorption maxima, extinction coefficients, and other parameters^[a] for 1 in solvents of different polarity.

Solvent	$\tilde{\nu}_{\max} [\mathrm{cm}^{-1}]$	$\varepsilon \left[M^{-1} \operatorname{cm}^{-1} \right]$	$\Delta \textit{G}^{\rm 00}[\rm{cm}^{-1}]^{[\rm{b,c}]}$	$\lambda_0 [\text{cm}^{-1}]^{[b,d]}$	$\lambda_v [\text{cm}^{-1}]^{[b,e]}$	$\tilde{\nu}_{v} [\mathrm{cm}^{-1}]^{[\mathrm{b},\mathrm{f}]}$
<i>n</i> -hexane	12300	4700	10400	950	1500	1100
cyclohexane	11900	4600	10300	1000	1350	1150
1,4-dioxane	12200	3900	9450	1850	1650	1400
dibutyl ether	11900	4200	9400	1700	1500	1400
diethyl ether	11900	4100	9000	2050	1650	1450
MTBE ^[g]	12000	3700	8900	2200	1600	1450
ethyl acetate	12000	3900	8250	2900	1600	1650
THF	11 600	3500	7900	3200	1400	1700
dichloromethane	12200	3600	8350	3000	1750	1550
benzonitrile	11 700	3600	7500	3550	1400	1800
2-propanol	11800	3900	8300	2750	1500	1650
acetone	12100	3600	7450	4000	1550	1850
acetonitrile	12600	3400	7500	4350	1600	1850

[a] Parameters obtained from the least squares fit of the IV-CT bands. [b] All values were determined with a maximum error of \pm 50 cm⁻¹ except for the λ_{o} value of 2-propanol (\pm 100 cm⁻¹). [c] Difference in the free energy between the diabatic ground and excited states. [d] Outer-sphere reorganization energy. [e] Inner-sphere reorganization energy. [f] Mean molecular vibration mode. [g] Methyl tert-butyl ether.



Figure 1. Cyclic voltammogram of radical 1 in CH₂Cl₂/0.1 м ТВАН. Scan rate $\nu = 250 \text{ mV s}^{-1}$.



Figure 2. UV/Vis/NIR absorption spectrum of 1 in CH₂Cl₂.

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Figure 3. IV-CT bands of 1 measured in solvents of different polarity.

ically, and a classical solvent coordinate is used.^[5] An excellent least squares fit of the IV-CT band of 1 in each solvent was achieved by varying the parameters for the innersphere reorganization energy λ_v and the outer-sphere reorganization energy λ_o as well as the parameters for the difference of the free energy between the diabatic ground and excited state ΔG^{00} and for the average molecular vibrational mode $\tilde{\nu}_{v}$ in Equation (3). In Figure 4 the fits of

$$\varepsilon = \frac{8 N \pi^3}{3000 h \ln 10} n \tilde{\nu} \mu_{eg}^2 \sum_{j=0}^{\infty} \frac{e^{-s} S^j}{j!} \sqrt{\frac{1}{4 \pi \lambda_o R T}} \exp\left[-\frac{(j \tilde{\nu}_v + \lambda_0 - \tilde{\nu} + \Delta G^{00})^2}{4 \pi \lambda_o R T}\right] (3)$$
with the Huang-Rhys factor $S = \frac{\lambda_v}{2}$

v,

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Figure 4. Least squares fit of the IV-CT bands of 1 (experimental data —) in *n*-hexane (\bullet), benzonitrile (\blacksquare), and acetonitrile (\bullet) according to the method of Jortner.

the IV-CT band in *n*-hexane, benzonitrile and acetonitrile are shown. The results of all fits are also summarized in Table 1. From these data it becomes apparent that the surprisingly low total reorganization energy is dominated by the solvent part λ_0 in all solvents with exception of the hexanes.^[33]

A plot of each parameter against a term describing the solvent polarity $(D-1)/(2D+1)-0.5(n^2-1)/(2n^2+1)$, where D is the permittivity and n is the refractive index, reveals linear correlations for both ΔG^{00} and λ_{o} (Figure 5 a and b).^[34] As initially expected from Marcus' theory,^[35] an increase of the solvent reorganization energy λ_0 with solvent polarity is found. The solvent reorganization energy approaches zero for totally apolar environments. Concomitantly, ΔG^{00} decreases due to the fact that the excited state has zwitterionic character while the ground state is apolar (see below). Therefore, the usually observed negative solvatochromism of degenerate ionic compounds is covered (compensated for) by the positive solvatochromism of ΔG^{00} which leads to the weak solvent dependence of the IV-CT band described above. The analysis yields directly ΔG^{00} in CH₂Cl₂ (8350 cm⁻¹) which is in reasonable agreement with the redox potential difference in CH₂Cl₂/0.1M TBAH ($\Delta E = 910 \text{ mV} \cong 7340 \text{ cm}^{-1}$). As expected, the inner-sphere reorganization energy λ_{v} is independent on the solvent polarity (Figure 5c). We also recorded a weak but systematic solvent dependence of $\tilde{\nu}_{v}$ (Figure 5d), which could be due to the varying importance of different molecular modes contributing to the averaged mode \tilde{v}_{v} . On the other hand, this shift may also compensate for inaccuracies of the theory in general.

Furthermore, the adiabatic dipole moment of the ground state ($\mu_g = 13 \pm 2 \times 10^{-30}$ Cm = 3.9 ± 0.6 D) and the difference between the adiabatic ground and excited state ($\Delta \mu_{eg} = 64 \pm 4 \times 10^{-30}$ Cm = 19 ± 1 D), and the transition moment ($\mu_{eg} = 11.0 \times 10^{-30}$ Cm = 3.30 D) of **1** were determined by EOAM in 1,4-dioxane as previously described.^[10] With these values and Equation (2) the diabatic dipole moment ($\Delta \mu_{12} = 67.8 \times 10^{-30}$ Cm = 20 D) was calculated, which corresponds to an effective diabatic ET distance of 4.2 Å; this is significantly less than the C–N distance between the redox centers (12.3 Å). With these transition moments the electronic coupling V was calculated with Equations (1) and (2). Given the rather short effective ET distance, the transition dipole moment $\mu_{eg} = 11.0 \times 10^{-30}$ Cm = 3.30 D and consequently the electronic



Figure 5. Plots of a) λ_{o} , b) ΔG^{00} , c) λ_{v} and d) \tilde{v}_{v} versus the solvent polarity function $f(D) - 0.5 f(n^2)$ with f(D) = (D-1)/(2D+1) and $f(n^2) = (n^2-1)/(2n^2+1)$.

coupling $V = 2000 \text{ cm}^{-1}$ are noticeably small. This implies that the electronic interaction between the two redox centers in **1** is weak compared to that in an analogous MV compound consisting of two triarylamine redox centers.^[33] The AM1-UHF calculation of **1** shows the reason for the weak interaction between the two redox centers: steric interactions among the perchlorinated ring systems cause a twist of the π system.^[36] This effect and the fact that the β -LUMO is largely concentrated on the central triarylmethyl carbon p orbital while the β -HOMO is delocalized over the triarylamino group results in a weak conjugation of the aromatic redox centers (Figure 6).



Figure 6. AM1-UHF-optimized structure of radical 1; β -HOMO (bottom) and β -LUMO (top).

Using the diabatic parameters determined by Jortner's theory as well as the electronic coupling V determined by the GMH theory, we computed the adiabatic potential energy surfaces for *n*-hexane and acetonitrile (Figure 7). It is obvious from these curves that the solvent has a dominating influence on the shape of the potential surfaces and thus also has an impact on the deactivation pathways of the excited state.

In summary we have presented the synthesis and a detailed study of the photophysical properties of the first neutral organic MV compound. Only by using Jortner's one-



Figure 7. Adiabatic potential energy surfaces of 1 in *n*-hexane (—) and acetonitrile (----) calculated with Equation (3) of ref. [1] with $\mu_{eg} = 11.4 \times 10^{-30}$ Cm = 3.4 D and V = 2070 cm⁻¹ in *n*-hexane and $\mu_{eg} = 11.4 \times 10^{-30}$ Cm = 3.4 D and V = 2120 cm⁻¹ in acetonitrile. *x* = ET coordinate.

mode model were we able to analyze the IV-CT band and to reveal the compensating trends of the solvent reorganization energy λ_o and the free energy difference ΔG^{00} . Both effects are rather strong due to the highly zwitterionic character of the excited IV-CT state. The analysis demonstrates that a lack of solvatochromism is no indication for a negligible change of dipole moment upon excitation. This large change of dipole moment upon excitation was also directly proved by EOAM. These measurements also revealed that the effective diabatic ET distance is much smaller than the formal separation of the redox centers. The uncharged character of this prototypical neutral MV compound enabled us to perform the presented measurements quite easily. Our findings will be useful for the design of molecular storage and switching devices where a neutral character is of practical advantage.

Experimental Section

2: Pd₂(dba)₃·CHCl₃ (74.0 mg, 71.5 µmol, 0.05 equiv), P(tBu)₃ (173 µL, 0.33 M in n-hexane, 57.2 µmol, 0.04 equiv), and NaOtBu (344 mg, 3.58 mmol, 2.50 equiv) were added to a solution of stilbene $\mathbf{3}^{[24]}$ (1.30 g, 1.43 mmol, 1.00 equiv) and bis(4-methoxyphenyl)amine (361 mg, 1.58 mmol, 1.10 equiv) in absolute toluene. The reaction mixture was stirred for 24 h under reflux in the dark under a nitrogen atmosphere. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (50 mL) and washed with water (2 × 50 mL). The organic layer was dried over MgSO4, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/CH₂Cl₂ 1:1). The crude product was precipitated by adding a concentrated solution of 2 in acetone dropwise to methanol which gave 690 mg (0.65 mmol, 46%) of a yellow solid, m.p. 174°C. ¹H NMR (400 MHz, [D₆]acetone, 295 K): $\delta = 7.47$ (AA', CH=CHCCHCH, 2H), 7.11 (s, 1H, (C_6Cl_5CH) , 7.10 (AA', NCCHCHCO, 4H), 7.08 (d, ${}^{3}J_{HH} = 16.5$ Hz, 1 H, C=CH), 7.01 (d, ${}^{3}J_{HH} = 16.5$ Hz, 1 H, C=CH), 6.94 (BB', OCCHCH, 4H), 6.85 (BB', CH=CHCCHCHCN, 2H), 3.80 ppm (s, 6H, OCH₃);¹³C NMR (151 MHz, [D₆]acetone, 295 K): $\delta = 157.6$ (q), 150.7 (q), 141.0 (q), 139.44 (HC=CH), 139.44 (2C, q), 137.79 (q), 137.77 (q), 136.3 (q), 135.9 (2C, q), 135.5 (q), 134.9 (q), 134.8 (q), 134.6 (q), 134.34 (q), 134.29 (q), 134.27 (q), 134.25 (q), 134.1 (q), 133.20 (q), 133.17 (q), 133.0 (q), 128.8 (CH=CHCCHCH), 128.1 (OCCHCH), 120.4 (HC=CH), 120.0 (CH=CHCCHCHCN), 115.7 (NCCHCHCO), 57.6 (C₆Cl₅-CH), 55.7 ppm (OCH3); IR (KBr): $\tilde{\nu} =$ 3037 (w), 2997 (w), 2929 (w), 2869 (vw), 2832 (w), 1599 (m), 1504 (vs), 1463 (w), 1323 (w), 1294 (w), 1241 (s), 1176 (w), 1105 (w), 1037 (m), 966 (w), 827 (m), 808 (m), 649 (w), 575 (w), 521 cm⁻¹ (w); MS (EI, 70 eV) [m/z, %]: 1055 (74, M^+), 1040 (8, M^+ -Me), 1021 (45, M^+ -Cl), 987 (20, M⁺-Cl-Me), 807 (36, M⁺-C₆Cl₅). Elemental analysis calculated for $C_{41}H_{21}Cl_{14}NO_2$: C 46.64, H 2.00, N 1.33; found: C 46.35, H 2.23, N 1.39.

1: Stilbene derivate 2 (50.0 mg, 47.4 µmol, 1.00 equiv) was dissolved in absolute DMSO (10 mL) under a nitrogen atmosphere. KOrBu (10.6 mg, 94.8 µmol, 2.00 equiv) was added, and the deep purple solution that formed immediately was stirred for 1.5 h in the dark at room temperature. Then *p*-chloranil (11.7 mg, 47.4 µmol, 1.00 equiv) was added, and the solution was stirred for further 1.5 h in the dark at room temperature. The deep brown suspension was purified by flash chromatography on silica gel (CH₂Cl₂/petroleum ether 4:1). The crude product was precipitated twice by adding a concentrated solution of **1** in acetone dropwise to methanol to obtain 30.0 mg (28.4 µmol, 60%) of a brown solid, m.p. 165 °C (decomp.). IR (KBr): $\bar{\nu} = 3040$ (w), 2999 (w), 2945 (w), 2930 (w), 2909 (w), 2832 (w), 1595 (s), 1504 (vs), 1463 (vw), 1440 (vw), 1322 (s), 1242 (vs), 1174 (m), 1105 (w), 1037 (m), 945 (w), 816 (m), 707 (w), 653 (w), 575 (w), 521 cm⁻¹ (w); MS (FAB, 70 eV, 2-(octyloxy)nitrobenzene) [*m*/*z*, %]:

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1054 (<1, M^+); Elemental analysis calculated for $C_{41}H_{20}Cl_{14}NO_2$: C 46.68, H 1.91, N 1.33; found: C 46.53 H 2.11 N 1.27.

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