Photoinduced Intramolecular Charge Transfer in 4-Donor, 4′-Acceptor Substituted Dimethyldiphenylsilanes

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Photoinduced intramolecular charge-transfer fluorescence occurs in (4-*N*,*N*-dimethylaminophenyl)(4′-cyanophenyl)- (**1**) and (4-methoxyphenyl)(4′-cyanophenyl)dimethylsilane (**2**); the X-ray structure of **1** shows that the donor and acceptor chromophores are positioned orthogonally, hence, charge transfer is mediated *via* the $-SiMe_2-$spacer.

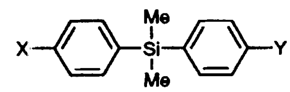
Recently, DσA compounds consisting of π-type electron donor (D) and electron acceptor (A) chromophores linked *via* an (oligo)silane $[-(SiMe_2)_n-$ (n = 1,2 and 6)] spacer have been proposed as second-order nonlinear optical compounds with improved transparency in the visible and near UV range.[1] However for n = 1, UV–VIS spectroscopy and hyperpolarizability (β) measurements (EFISH) indicated that D–A coupling *via* the σ-type $-SiMe_2-$ spacer is extremely weak; no discrete charge-transfer absorption band was found and β could be approximated by a vectorial addition of β values of the separate chromophores [β(DσA) = β(Dσ) + β(Aσ)]. Hence concomitant with the absorptive properties of these DσA compounds, initial excitation leads to either a D*σA or DσA* local excited state (LE).[2] An intriguing question then remains to what extent the LE deactivates by populating a dipolar excited state $(D^{\cdot +}\sigma A^{\cdot -})^*$ *via* rapid intramolecular charge transfer.

Here we present evidence based on the fluorescence solvatochromicity of (4-*N*,*N*-dimethylaminophenyl)(4′-cyanophenyl)- (**1**) and (4-methoxyphenyl)(4′-cyanophenyl)dimethylsilane (**2**) that photoinduced intramolecular charge-transfer takes place after initial excitation to a D*σA or DσA* LE.†

At first sight, the UV—VIS spectrum of **1** only shows local transitions of the separate D (33 330 and 37 590 cm^{-1}) and A (37 040 and 42 740 cm^{-1}) chromophores, respectively (Fig. 1). However as indicated by moderate intensity differences between related bands in a series Dσ, Aσ and DσA, respectively, difference spectroscopy unequivocally reveals the presence of a new, weak absorption band centred at 35 100 cm^{-1} (log ε 3.32) which borrows intensity from the short wavelength D and A bands. Similar results are also obtained for **2** [new, weak absorption at 40 000 cm^{-1} (log ε 3.53)]. Thus, some weak coupling between the D and A parts in **1** and **2** already occurs in their ground state.

Solvent dependent, continuous fluorescence spectroscopy of **1** gave only one broad emission band which shifted bathochromically with increasing solvent polarity and possesses no concentration dependence (Table 1). For **2** a similar behaviour was found except in cyclohexane, where only a superposition of local emissions of the related Dσ (**5**) and Aσ (**4**) chromophores was observed.‡ These results suggest that in the majority of solvents fluorescence occurs from a relaxed dipolar excited state $(D^{\cdot +}\sigma A^{\cdot -})^*$ which is populated *via* intramolecular charge transfer from the initial LE.[2] Application of the Weller equation[3] [eqn. (1)], which gives an estimate of the driving force (ΔG^0) for photoinduced charge transfer, reveals that ΔG^0 will become positive in going from **1** (ΔG^0 −0.44 eV) to **2** (ΔG^0 0.03 eV) in cyclohexane. Thus in the case of **2**, charge-transfer will be hampered in the latter solvent.§ We note in passing that for **1** in acetonitrile the CT emission band is only observed upon long-wavelength excitation (<33 330 cm^{-1}). Furthermore, besides CT emission, an additional local emission band (25 640 cm^{-1}) is found in

$$\Delta G^0 = [E_{ox}(D) - E_{red}(A)] - E_{00} + C \qquad (1)$$



	X	Y
1	Me_2N	CN
2	MeO	CN
3	Me_2N	H
4	H	CN
5	MeO	H

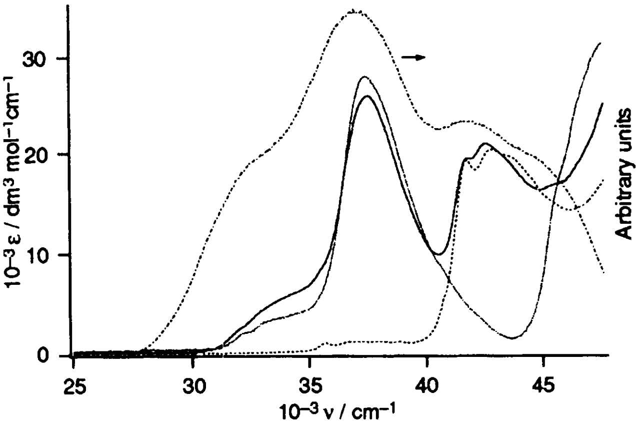


Fig. 1 Equimolar solution (cyclohexane) UV–VIS spectra of **1** (—), **3** (···) and **4** (---), and the solid-state UV–VIS spectrum of **1** [KBr matrix; (-·-·-·) in arbitrary units]

Table 1 Fluorescence data; emission wavenumbers (10^{-3} ν_{CT}/cm^{-1}) and quantum yields (Φ)[12] of **1** and **2**; Φ values were determined relative to naphthalene (Φ = 0.23; excitation 37 740 cm^{-1})

		1		**2**	
Solvent	Δ*f*	ν_{CT}	Φ	ν_{CT}	Φ
Cyclohexane	0.100	28.17	0.04		0.11
Di-*n*-butyl ether	0.193	23.98	[a]	29.76	[a]
Diethyl ether	0.251	22.60	0.10	28.17	0.04
Ethyl acetate	0.292	19.81	0.08	26.30	0.05
Tetrahydrofuran	0.308	19.77	0.07	26.21	0.04
Acetonitrile	0.392	16.67[b,c]	<0.001	23.27	0.13
$-2\mu e^2/hc\rho^3$ ($\times 10^{-3}$ cm^{-1})		39.55		32.98	
Corr. coeff.		0.994		0.996	

[a] Not determined due to solvent absorption at 37 740 cm^{-1}. Excitation wavelength 33 330 and 35 090 cm^{-1} for **1** and **2**, respectively. [b] Excitation wavelength 32 260 cm^{-1}; at 37 740 cm^{-1}, Φ < 0.001. [c] Local emission observed at 25 640 cm^{-1}.

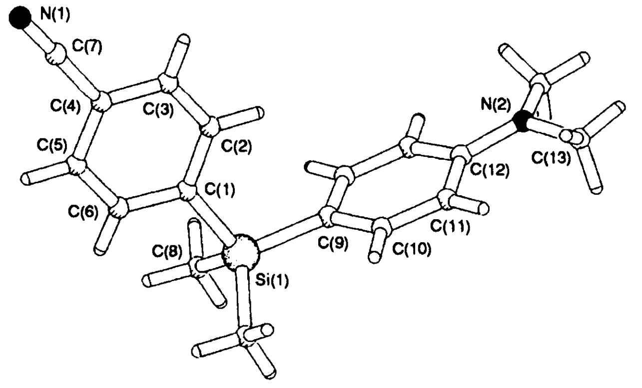


Fig. 2 X-Ray structure of **1**. The molecule is located on a crystallographic mirror plane.||

acetonitrile which is shifted with respect to the local emission of **3** in cyclohexane (29 940 cm^{-1}).‡

Solvatochromic sensitivities and excited-state dipole moments μ_e of **1** and **2**, respectively, were derived from their fluorescence solvatochromicity using the Lippert–Mataga equation [eqn. (2)] where $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(4n^2 + 2)$.[4,5]¶

$$\nu_{CT} = \nu_{CT}(0) - (2\mu_e^2/hc\rho^3)\Delta f \qquad (2)$$

Sensitivities of 39 550 and 32 980 cm^{-1} were found for **1** and **2**, respectively; both values fall in the range of the most sensitive polarity probes hitherto available (Table 1).[5] Although their fluorescence quantum yields Φ are rather low, they may find application as a fluorescent polarity probe.[6] Dipole moments μ_e of 18.9 D (**1**) and 17.3 D (**2**) are obtained for the $(D^{\cdot+}\sigma A^{\cdot-})^*$ state using ρ 4.5 Å¶ which correspond to a unit charge separation over 3.9 Å and 3.6 Å, respectively. Since the centre-to-centre distance between the D and A part of **1** and **2**, respectively, is estimated to be 5.4 Å,§,|| charge- rather than full-electron transfer (**1**, 72% and **2**, 67%) is involved. This is in line with theoretical calculations (Extended Hückel[7] and PM3[8]) which reveal that in the HOMO and LUMO of **1** and **2** some carbon atoms of the benzene core of the D and A part, respectively, possess considerable orbital coefficients.

Additional support for the occurrence of photoinduced intramolecular charge transfer after initial excitation to the LE is provided by a survey of the X-ray structure of **1**; the D and A chromophores are positioned orthogonally (Fig. 2).|| Moreover, as indicated by the solid-state UV–VIS spectrum of **1**, which resembles its solution spectrum, no intermolecular face-to-face interactions[9] occur between the D and A parts (Fig. 1). Consequently, ground-state spatial (*through-space*) overlap between the D- and A-type molecular orbitals is thwarted. Hence, our results strongly suggest that in compounds **1** and **2** photoinduced intramolecular charge-transfer is mediated through-bond *via* the $-SiMe_2-$ spacer. Nevertheless, the possible occurrence of geometry changes upon initial local excitation is subject of further investigations.

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Footnotes

† Compound **1** was obtained from (4-*N*,*N*-dimethylaminophenyl)-(4′-bromophenyl)dimethylsilane[1] by treatment with Cu^ICN in DMF;[10] **2** was prepared in an analogous way from the 4-methoxyphenyl derivative. Satisfactory analytical data (^1H-, ^{29}Si- and ^{13}C-NMR, IR and HPLC) were obtained for all compounds.

‡ The reference chromophores (**3–5**) possess only a non-solvatochromic emission band (cyclohexane; **3**, 29 940 cm^{-1}, Φ = 0.13, **4**, 32 790 and 33 670 cm^{-1}, Φ = 0.28, and **5**, 33 220 cm^{-1}, Φ = 0.09). Preliminary time-resolved fluorescence measurements (nanosecond timescale) of **1** (solvent acetonitrile) reveal that the local- and CT-emission derive from separate photophysical phenomena.

§ Redox potentials [E_{ox} (D) and E_{red} (A)] were determined with cyclic voltammetry (MeCN–0.1 mol dm^{-3} NBu_4 PF_6; *E vs.* SCE): **1**, E_{ox} (D) 0.79 V and E_{red}(A) −2.30 V; **2**, E_{ox}(D) 1.75 V, E_{red}(A) −2.29 V; **3**, E_{ox}(D) 0.74 V; **4**, E_{red}(A) −2.28 V and **5**, E_{ox}(D) 1.78 V. E_{00} is the zero–zero excitation energy (**1**, 3.71 eV and **2**, 4.19 eV) and *C* a constant containing a Coulomb attraction energy and a solvation free energy term [$C = -(e^2/\varepsilon_S R) - (e^2/2)(1/r_{d+} + 1/r_{a-})(1/37.5 - 1/\varepsilon_S)$ with *R* (5.4 Å)|| the centre-to-centre distance between the donor (D) and the acceptor (A) part, $r_{d}{}^{\cdot-} = r_{a}{}^{\cdot-}$ = 4.5 Å the effective radii of the D and A radical ions[11] and the dielectric constant ε_S(cyclohexane) = 2.015. For **2** the same values for *R*, $r_d{}^{\cdot+}$ and $r_a{}^{\cdot-}$ were used. 1 eV = 1.60218 × 10^{-19} *J* = 8065.7 cm^{-1}.

¶ $\nu_{CT}(0)$ represents the hypothetical gas phase emission, *h* is the Planck constant, *c* is the velocity of light, μ_e is the excited-state dipole moment, ρ the Onsager radius of the solute [$\rho = (3V/4\pi)^{1/3}$] with V (392.05 Å^3) taken from the X-ray structure of **1**;|| the same value was used for **2**, and ε and *n* are the solvent dielectric constant and refractive index. 1D (Debye) = 3.33564 × 10^{-30} C m.

|| *Crystal data* for compound **1**, $C_{17}H_{20}N_2Si$, M_r = 280.44, colourless block-shaped crystal (0.4 × 0.4 × 0.5 mm), orthorhombic, space group *Pnma* (no. 62) with a = 11.7053(5), b = 9.7903(10), c = 13.6840(14) Å, V = 1568.2(2) Å^3, Z = 4, D_c = 1.188 g cm^{-3}, $F(000)$ = 600, μ(Mo-Kα) = 1.4 cm^{-1}, 4153 reflections measured, 1900 independent ($1.49 < \theta < 27.50°$, T = 150 K, Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å) on an Enraf-Nonius CAD4 Turbo diffractometer on rotating anode. Data were corrected for L_p and for a linear decay of 2% of the reference reflections, but not for absorption. An empirical extinction correction was applied. The structure was solved by automatic direct methods (SHELXS86). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL93). Refinement converged at a final $wR2$ value of 0.098, $R1$ = 0.042 [for 1582 reflections with $F_o > 4\sigma(F_o)$] S = 1.06, for 142 parameters. Hydrogen atoms were located on a difference Fourier map. A final difference Fourier showed no residual density outside −0.68 and 0.40 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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