Charge-Transfer Interactions in 4-Donor 4′-Acceptor Substituted 1,1-Diphenylethenes

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Two 1,1-diphenylethenes bearing either a 4-dimethylamino or 4-methoxy group as electron donor and a 4′-cyano group as electron acceptor, as well as compounds containing only a donor or acceptor functionality, were synthesized. The observation of strong fluorescence solvatochromism (originating from a biradicaloid twisted intramolecular charge-transfer state) of the donor-acceptor compounds reveals that photoinduced charge separation through the cross-conjugated 1,1-diphenylethene spacer occurs. The presence of weak charge-transfer absorption bands in the UV spectra reflects modest ground state donor-acceptor coupling. These results show that charge transport through a branched conjugation path is possible. 1-[4-(Dimethylamino)phenyl]-1-phenylethene was found to fluoresce from two different states. In nonpolar solvents the source is a local aniline-like state, whereas in polar solvents the fluorescence originates from a twisted intramolecular charge-transfer state.

Introduction

In the field of molecular electronics and optoelectronics, charge and electron transport play important roles as they form the foundation of a large number of (opto)electronic phenomena. Examples are nonlinear optics,[1,2] molecular rectification,[3,4] transport through molecular wires[5] and the photovoltaic effect.[6] One of the ways to generate charge transport is by photoinduced electron or charge transfer, which takes place in compounds consisting of an electron donor and an electron acceptor separated by a bridge. The types of bridges investigated include an abundant number of linear π-conjugated systems, but saturated σ-systems,[3,7–10] σ-π systems,[11,12] spiro-conjugated compounds[13] and monoatomic sp^3-hybridized spacers[14–16] have also been explored. Although linear π-conjugation is generally most beneficial for donor-acceptor interaction, photoinduced electron or charge transfer through the other type of bridges has been found to occur as well. It should be realised that strong interaction through a π-bridge results in substantial ground state donor-acceptor mixing and the appearance of a charge-transfer (CT) band in the electronic absorption spectrum. However, this also means that charge separation in the excited state is not complete. When a ground state donor-acceptor interaction is absent, no charge-transfer absorption band is observed, and the actual charge-separation process takes place from a locally excited donor or acceptor chromophore. In this case a full elementary charge is transferred from the donor to the acceptor site.

Hitherto, relatively little attention has been paid to compounds in which the donor and acceptor chromophores are separated by a single sp^2-hybridized carbon atom. Work on cross-conjugated donor-acceptor tetraethynylethenes[17–19] revealed that charge-transfer interactions and optical nonlinearities are substantially smaller than in linear π-conjugated systems. Eckert et al. reported intramolecular charge-transfer fluorescence of donor-acceptor 1,1-diarylethene derivatives.[20] Furthermore, a carbonyl spacer has been used in order to develop optically transparent second-order nonlinear optically active compounds.[21] Although it is clear that charge-transfer interactions in cross-conjugated systems are not particularly strong, it is of interest to gain more insight into their nature, since they reflect the tendency of charge carriers to take a nonlinear conjugated path during their transport, which may be of great value for the development of materials containing branched or multiple conduction channels.[22]

Here we report on the nature of charge-transfer interactions through a spacer consisting of a single sp^2-hybridized carbon atom. To this end, 1,1-diphenylethenes functionalized with an electron donor and/or an electron acceptor at the 4- and 4′-positions are studied. Dimethylamino and methoxy groups are used as electron donors, while a cyano group is applied as electron acceptor (Scheme 1). These functionalized 1,1-diphenylethenes can be regarded

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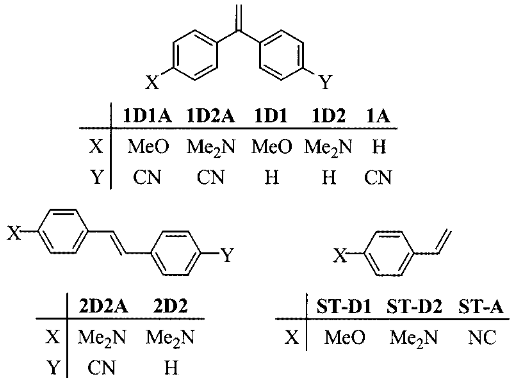
as cross-conjugated systems, in which the donor and acceptor moieties are both linearly conjugated to the vinylidenic double bond, but not to each other. This study gives an impression as to what extent a charge can be directed to follow such a cross-conjugated path instead of a linear conjugation path. In this picture, the interactions of the donor and acceptor chromophores with the vinylidene spacer and with the second phenyl group are also of interest, and so the properties of the 4-methoxy-, 4-dimethylamino- and 4-cyano-functionalized styrenes **ST-D1**, **ST-D2** and **ST-A** are taken into account. The degree of conjugation in a series of oligomers based on the 1,1-diphenylethene unit has recently been discussed.[23]



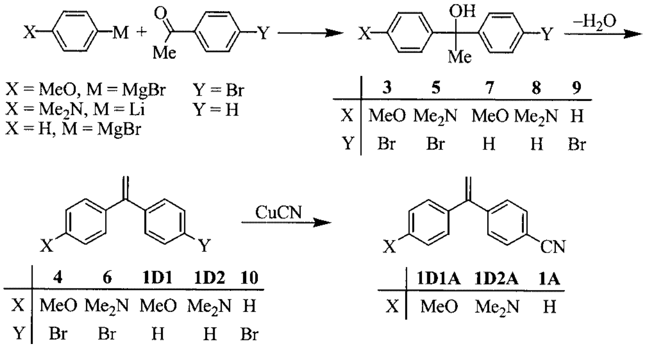
Scheme 1

The charge-transfer interactions in the substituted 1,1-diphenylethenes were examined by UV and fluorescence spectroscopy, and the experimentally obtained results have been interpreted by use of AM1 and PPP/SCF semi-empirical calculations. Investigation of the (steady-state) photophysics of the compounds under study is also relevant for another reason: although the photophysics of 1,1-diphenylethene is well documented, since the compound is frequently employed in photochemical studies,[24,25] knowledge of the photophysics and photochemistry of substituted 1,1-diphenylethenes is less well founded.[26] It is shown here that **1D2** exhibits intramolecular CT emission, and the nature of the emitting state is discussed.

Results and Discussion

Synthesis and Structure

The donor- and/or acceptor-substituted 1,1-diphenylethenes were synthesized in a few steps (Scheme 2). The appropriately substituted phenylmagnesium bromide or phenyllithium reagent was treated either with acetophenone or with 4-bromoacetophenone to give the 1,1-diphenylethanols **3**, **5**, **7**, **8** and **9**. Acid-catalysed dehydration of these compounds afforded the donor compounds **1D1** and **1D2**, as well as the bromides **4**, **6** and **10**. The bromides were converted into the corresponding cyanides **1D1A**, **1D2A** and **1A** through Rosenmund-von Braun reactions with copper(I) cyanide in DMF.[27]



Scheme 2

It is noteworthy that 1,1-diphenylethene derivatives are not planar, as a result of steric interactions between the hydrogen atoms *ortho* to the vinylidene bridge. An X-ray structure of 1,4-bis(1-phenylvinyl)benzene revealed torsion angles of 39.5° or 30.5° around the vinylidene-phenylene and vinylidene-phenyl carbon-carbon single bonds, respectively.[23] For all compounds under investigation, AM1 calculations gave torsion angles of approximately 39° around the vinylidene-phenylene/phenyl single bonds. It should be realized that the deviation from planarity is an intrinsic property of 1,1-diphenylethenes.

Electronic Absorption Spectra

Electronic absorption spectra of **1D1**, **1D2** and **1A** in cyclohexane, along with the spectra of styrenes **ST-D1**, **ST-D2**, and **ST-A**, are shown in Figure 1, and maxima and molar absorption coefficients are compiled in Table 1. PPP/SCF calculations were performed in order to establish the nature of the observed transitions. Results are given in Table 2. Although the PPP/SCF calculated values, which should formally be regarded as gas-phase data, are not always accurate in their details, they provide a reliable and illustrative general picture.[28] The UV spectra of donor styrenes **ST-D1** and **ST-D2** exhibit weak bands located at the red edge of a more intense band. These weak bands are benzene ^1L_b-type transitions, which are perturbed by the presence of the donor functionality and the double bond.[29] The ^1L_b bands are partly obscured by ^1L_a-type transitions located at 259.5 (**ST-D1**) and 293.0 (**ST-D2**) nm. As can be inferred from the configuration interaction data in Table 2, the ^1L_a transitions of both **ST-D1** and **ST-D2** involve promotion of an electron from the HOMO to the LUMO. Both the HOMO and the LUMO of the donor-styrenes are delocalized over the entire compounds (not shown). However, the HOMO receives large contributions from the donor, while the LUMO has higher density at the double bond. Upon HOMO-LUMO excitation there is some net charge transfer from the donor to the double bond.

The UV spectra of **1D1** and **1D2** are in large part similar to those of **ST-D1** and **ST-D2**, respectively, but also exhibit additional features. New transitions are visible at 239.5 (**1D1**, calculated value 233 nm) and 259.0 nm (**1D2**, calcu-

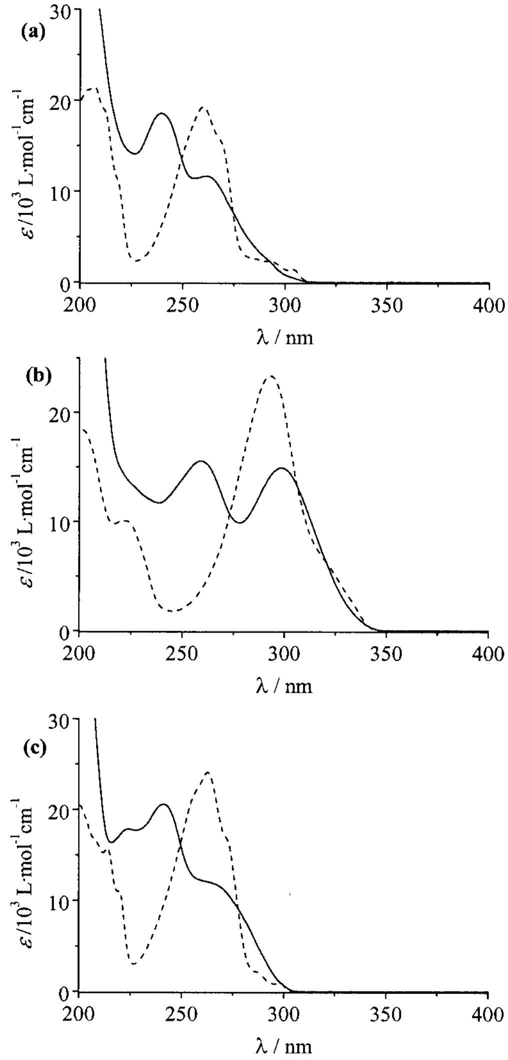


Figure 1. UV spectra of 4-donor- or 4-acceptor-functionalized 1,1-diphenylethenes and styrenes in cyclohexane; (a) methoxy-substituted compounds **1D1** and **ST-D1**, (b) dimethylamino-substituted compounds **1D2** and **ST-D2**, (c) cyano-substituted compounds **1A** and **ST-A**; in each graph the solid line represents the spectrum of the 1,1-diphenylethene and the dashed one the spectrum of the styrene

Table 1. Main UV maxima (in nm) of donor/acceptor-substituted styrenes and 1,1-diphenylethenes in cyclohexane; molar absorption coefficients, in 10^3 L·mol^{-1}cm^{-1}, are given between parentheses

		^1L_a	^1L_b
ST-D1		259.5 (19.3)	293.0, 304.5 (1.4)
ST-D2		293.0 (23.4)	325[a]
ST-A		263.5 (24.1)	288.0, 298.0 (1.0)
1D1	239.5 (18.6)	261.0 (11.6)	292[a]
1D2	259.0 (15.6)	298.5 (15.1)	[b]
1A	240.5 (20.7)	270[a]	283[a]
1D1A		255.0 (24.7)	294[a]
1D2A	257.0 (18.6)	280.0 (24.6)	339[a]

[a] Shoulder. [b] Hidden.

lated value 256 nm), which are reminiscent of the main transition in the UV spectrum of 1,1-diphenylethene.[23] For **1D1** this is confirmed by the fact that the 239.5 nm transition is predominantly based on the transition from the HOMO−1 to the LUMO, which bear a strong resemblance to the HOMO and LUMO of 1,1-diphenylethene.[23] However, the 259.0 nm transition of **1D2** corresponds to a HOMO → LUMO+3 transition and involves other types of orbitals. Furthermore, according to the calculations, forbidden 1,1-diphenylethene-type transitions are present at 262−263 nm.

In comparison to **ST-D1** and **ST-D2**, the HOMO → LUMO (^1L_a) transitions of **1D1** and **1D2** are slightly red-shifted and substantially less intensive (Figure 1, Table 1). As depicted for **1D2** in Figure 2, the HOMO is localized at the donor site and the vinylidenic double bond. The LUMO of **1D1** and **1D2**, resembling the LUMO of 1,1-diphenylethene,[23] is spread over the entire compound. Delocalization of the LUMO lowers its energy and explains why the ^1L_a transitions are red-shifted in relation to those of the styrenes. Although delocalized over the entire compound, the LUMO receives the largest contributions from the second phenyl group and, in particular, the vinylidenic double bond. The concentration of the HOMO and the LUMO in different parts of the molecules accounts for the decrease in ^1L_a transition dipole moment (and consequently oscillator strength). In addition, it shows that the ^1L_a transitions of the donor chromophores effectively involve charge transfer from the donor site to the double bond, and, to a lesser extent, to the second phenyl group.

4-Cyanostyrene **ST-A** exhibits an intensive ^1L_a band at 263.5 nm and a weak ^1L_a band at 288−298 nm (Figure 1, c). The former is the HOMO → LUMO transition.[30] On going from **ST-A** to 1,1-diphenylethene **1A**, a small bathochromic and a hypochromic shift of the HOMO → LUMO transition are again observed. As can be seen in Figure 2, the HOMO is 1,1-diphenylethene-like, while the LUMO is largely centred on the cyanophenyl moiety. The HOMO of **1A** is more spread out than that of **ST-A**, affecting the HOMO → LUMO transition in a way similar to that outlined above for **1D1** and **1D2**. From Figure 2 it can be seen that this transition involves charge transfer from the 1-phenylvinyl group to the cyano functionality. The 240.5 nm band in the spectrum of **1A** is based on a transition from the HOMO−1 to the LUMO.

The UV spectra of the donor-acceptor compounds **1D1A** and **1D2A** are characterized by quite intensive bands at 255 and 280 nm, respectively, and absorption tails extending to well beyond 300 or 350 nm (Figure 3). Second derivative spectra indicate that actual peak maxima are situated at 258 and 294 nm for **1D1A** and at 256, 281 and 339 nm for **1D2A**. A difference spectrum (**1D1A** − **ST-1D** − **ST-A**) gives a maximum of 292 nm with ε = 2600 L·mol^{-1}cm^{-1} for the absorption tail of **1D1A**. For the low-energy band of **1D2A**, values of λ_{max} = 341 nm and ε = 2800 L·mol^{-1}cm^{-1} are obtained from the difference spectrum (**1D2A** − **ST-2D** − **ST-A**). These data are in fine agreement with the second derivative maxima. No significant solvent effect on the UV spectra of **1D1A** and **1D2A** was detected.

The experimentally recorded spectra of the donor-acceptor systems are satisfactorily reproduced by the PPP/

Table 2. PPP/SCF-calculated electronic transitions of donor/acceptor substituted styrenes and 1,1-diphenylethenes and donor-acceptor stilbene **2D2A**[a][b]

	λ_{max}/nm	*f* [c]	CI[d]
ST-D1	280	0.03	0.81(1-2′) − 0.53(2-1′) + 0.20(2−3′)
	257	0.82	0.98(1-1′)
ST-D2	311	0.08	0.93(1-2′) + 0.32(2-1′)
	299	0.91	0.98(1-1′)
ST-A	284	0.02	−0.56(1-2′) + 0.79(2-1′)
	282	1.07	0.98(1-1′)
1D1	274	0.02	0.79(1-3′) − 0.24(2-3′) + 0.37(3-1′) + 0.40(3-4′)
	262	0.00	−0.36(1-2′) − 0.59(2-2′) − 0.37(4-4′) + 0.58(4-1′)
	254	0.38	0.96(1-1′)
	233	0.55	−0.59(1-4′) + 0.75(2-1′)
1D2	307	0.08	0.93(1-3′) − 0.27(3-4′)
	302	0.48	0.31(1-4′) + 0.93(1-1′)
	263	0.00	0.32(1-2′) − 0.64(2-2′) − 0.30(4-4′) + 0.57(4-1′) +0.24(5−2′)
	256	0.48	0.88(1-4′) − 0.20(1-5′) − 0.29(1-1′) + 0.23(2-1′)
	241	0.01	0.92(1-2′) + 0.22(5-2′) − 0.25(4-1′)
	230	0.32	0.92(2-1′) − 0.19(1-4′)
1A	279	0.01	−0.42(1-3′) + 0.37(2-3′) + 0.80(4-1′)
	275	0.79	0.90(1-1′) − 0.38(2-1′)
	262	0.00	−0.54(1-4′) − 0.40(2-4′) + 0.23(3-1′) + 0.61(3-2′) − 0.24(3-5′)
	242	0.43	0.50(1-2′) + 0.33(1-1′) + 0.20(2-2′) + 0.73(2-1′)
1D1A	284	0.45	0.87(1-1′) + 0.43(2-1′)
	279	0.01	−0.25(1-3′) − 0.49(2-3′) + 0.79(4-1′)
	274	0.03	0.79(1-4′) − 0.21(2-4′) − 0.26(3-5′) − 0.47(3-2′)
	261	0.76	−0.48(1-2′) − 0.33(1-1′) + 0.77(2-1′)
	237	0.29	0.80(1-2′) + 0.38(2-1′) − 0.23(1-1′) + 0.28(1-5′)
1D2A	342	0.09	0.95(1-1′) + 0.23(1-2′)
	308	0.07	0.93(1-4′) − 0.24(3-2′)
	288	0.95	0.71(1-2′) + 0.31(1-3′) + 0.29(1-5′) + 0.50(2-1′) − 0.16(1-1′)
	280	0.03	0.20(1-3′) + 0.25(2-2′) − 0.45(2-3′) + 0.78(4-1′)
	266	0.58	−0.42(1-2′) + 0.81(2-1′) + 0.21(5-1′)
2D2A	382	1.33	0.90(1-1′) − 0.32(1-2′) − 0.26(2-1′)
	310	0.07	0.91(1-4′) + 0.26(3-2′)
	288	0.00	−0.45(1-3′) + 0.48(2-3′) + 0.71(4-1′)
	275	0.00	0.13(1-1′) + 0.78(1-2′) − 0.52(2-1′)
	264	0.53	0.36(1-1′) + 0.41(1-2′) + 0.75(2-1′)

[a] Calculations were run on geometries with torsion angles of 40° between the C=C and phenylene groups for the diphenylethenes and of 20° for stilbene **2D2A**; styrenes were assumed to be planar. [b] Only transitions above 230 nm are given. [c] Oscillator strength. [d] Configuration interaction data. With the exceptions of the 288 nm transition of **1D2A** and the 275 nm transition of **2D2A** (see text), only coefficients larger than 0.20 are listed. For all compounds a full CI treatment was applied.

SCF calculations. The lowest-energy bands are predicted to lie at 284 (**1D1A**) and 342 (**1D2A**) nm. This is in good agreement with the experimentally determined maxima of 294 nm and 339 nm, albeit that the intensity is overestimated for **1D1A**. The low-energy bands correspond to almost pure HOMO → LUMO transitions. It appears from Figure 2 that the HOMO of **1D2A** is very similar to the HOMO of donor compound **1D2**, while the LUMO is highly reminiscent of the LUMO of the acceptor chromophore **1A**. Evidently, the absorption tail represents a direct charge-transfer transition. Here it is interesting that the HOMO-LUMO mixing mediating the CT interaction occurs exclusively at the double bond. In this connection it is relevant to consider the frontier orbitals of donor-acceptor stilbene **2D2A** (Scheme 1) and related linear conjugated compounds.[31] PPP/SCF calculations for **2D2A** revealed that dimethylamino donor effects extend beyond the double bond, indicating that in cross-conjugated **1D2A** the delocalization is less pronounced. PPP/SCF orbitals calculated for **1D1A** are similar to those of **1D2A**.

According to the configuration interaction data in Table 2, the 255 and 280 nm bands (calculated values 261 and 288 nm, respectively) are for the major part composed of HOMO → LUMO+1 and HOMO−1 → LUMO transitions. In both **1D1A** and **1D2A** the LUMO+1 essentially corresponds to the LUMO of the donor compound, while the HOMO−1 strongly resembles the HOMO of **1A**. The 255 and 280 nm bands thus correspond to local ^1L_a transitions in the donor and acceptor chromophores. From the configuration interaction data it becomes clear that the CT bands steal intensity from these transitions. For **1D1A** this mainly seems to concern the acceptor ^1L_a transition (which is calculated at a lower energy than the anisole type ^1L_a transition),[32] while in **1D2A** intensity is taken from the anilino ^1L_a transition. Without configuration interaction the calculated CT transitions are λ_{max} = 277 nm, f = 0.17 for

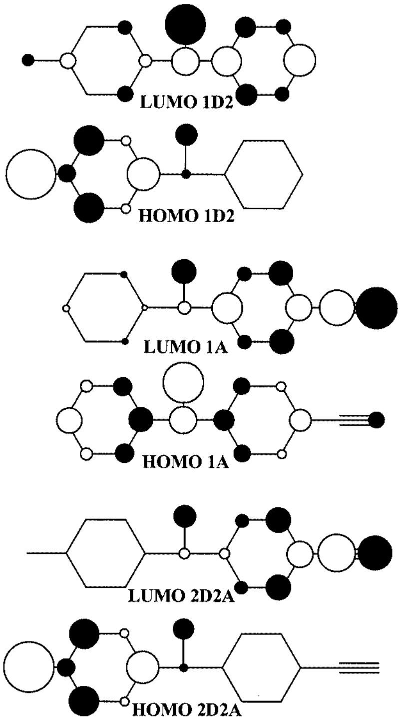


Figure 2. PPP/SCF-calculated HOMO and LUMO plots of compounds **1D2**, **1A** and **1D2A**; eigenvectors are scaled as the radii of the circles

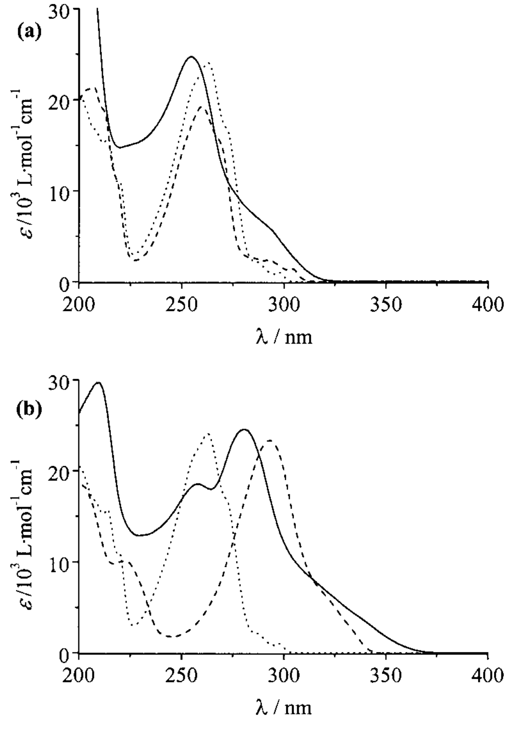


Figure 3. (a) UV spectrum of **1D1A** (−) and its reference chromophores **ST-D1** (− − −) and **ST-A** (···); (b) UV spectrum of **1D2A** (−) and its reference chromophores **ST-D2** (− − −) and **ST-A** (···)

1D1A and λ_{max} = 315 nm, f = 0.04 for **1D2A**, suggesting that in both cases about 60% of the CT band intensity is taken from the local transitions.

Although the presence of CT bands in the UV spectra of **1D1A** and **1D2A** demonstrates that ground state donor-acceptor interactions are operative, the interactions are not very strong. This is illustrated by comparison of the intensities of the CT bands with those of linear conjugated donor-acceptor substituted stilbenes. The CT band in **2D2A** is found at 380 nm in diethyl ether and at 383 nm in acetonitrile, with ε = 28500−31000 L·mol^{-1}cm^{-1}.[33] Although this shows directly that the probability of photoinduced charge transfer is much larger in stilbene **2D2A** than in **1D2A**, it is formally more appropriate to consider the oscillator strength f of the CT absorptions, which is obtained from [Equation (1)]

$$f = 4.32 \times 10^{-9}\,\varepsilon_{max}\Delta\nu_{1/2} \qquad (1)$$

in which ε_{max} is the absorption coefficient at the band maximum and $\Delta\nu_{1/2}$ is the band width at half height. Taking ε_{max} = 2800 L·mol^{-1}cm^{-1} and $\Delta\nu_{1/2}$ = 1960 cm^{-1} from the difference spectrum, f = 0.024 is obtained for **1D2A**. Here it should be born in mind that the band width is rather small for a CT band, which suggests that the difference spectrum does not uncover the complete CT band. From the spectrum of **2D2A**, values of ε_{max} = 28500 L·mol^{-1}cm^{-1} and $\Delta\nu_{1/2}$ = 4320 cm^{-1} were extracted,[33] so f = 0.53. The difference in oscillator strength reflects the difference in electronic coupling between the ground and the CT states in the two compounds. Unfortunately, a more thorough treatment is complicated by the facts that quantitative expressions are not available for systems with such different CT band intensities and that the CT transitions borrow intensity from the local transitions. While it was seen above that for **1D2A** 60% of the CT band intensity is stolen from the local transitions, for **2D2A** this amounts to 40%.

It is worthwhile to relate the intensity of the CT band of **1D2A** with those of compounds containing an dimethylamino-cyanophenyl donor-acceptor combination and a monoatomic sp^3-hybridized carbon or silicon spacer.[15] The intensities were 2100 (Si) and 2400 (C) L·mol^{-1}cm^{-1}, not very much smaller than that of **1D2A**. Apparently the hybridization of a monoatomic spacer does not affect the magnitude of the CT interaction very strongly.

Fluorescence

The fluorescence maximum of compound **1A** in cyclohexane is situated at 329 nm, while in acetonitrile it is at 360 nm. This small but distinct solvatochromism indicates that the lowest excited state is slightly dipolar in nature and that a limited extent of charge separation occurs. This was already deduced from the UV spectrum of **1A**. With quantum yields of 9 × 10^{-4} in cyclohexane and 2.0 × 10^{-3} in acetonitrile, the fluorescence of **1A** is weak. The fluorescence maximum of **1D1** varies from 332 nm in cyclohexane to 358 nm in THF (with a vibrational spacing of ca. 1300 cm^{-1}) to 360 nm in acetonitrile. Here as well, a small degree of charge separation occurs. The fluorescence quantum yield is an order of magnitude higher than for **1A**. In cyclohexane it is 9.4×10^{-3}, while in acetonitrile it is 8.6×10^{-3}. The fluorescence quantum yields of **1D1** and **1A** are much lower than those of cyanobenzene (0.23 in cyclohexane[15]) and anisole (0.45 in cyclohexane[15]), respectively. This can be explained by the presence of excited states localized at the double bond which are close in energy to the emitting ^1L_b state. Rapid radiationless deactivation, as in 1,1-diphenylethene,[23,34] then occurs through twisting of the double bond. For 4-cyanostilbene similar reasoning has been used.[35]

The fluorescence behaviour of **1D2** is quite complex. As can be seen from the data in Table 3 and the Supplementary Information, the fluorescence is fairly solvatochromic; upon going from cyclohexane to acetonitrile a bathochromic shift of 6090 cm^{-1} is observed. Figure 4 displays a plot in which the wavenumber at maximum fluorescence ν_{fl} is plotted against the solvent polarity parameter Δf. A linear relationship is expected according to the Lippert−Mataga relation [Equation (2) and Equation (3)][36]

$$\nu_{fl} = \nu_{fl}(0) - \frac{2\mu_e^2}{hc\rho^3} \times \Delta f \qquad (2)$$

with

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \qquad (3)$$

Here $\nu_{fl}(0)$ represents the (hypothetical) gas-phase fluorescence wavenumber, μ_e the excited state dipole moment, h the Planck constant, c the velocity of light and ρ the solute cavity radius. The solvent polarity parameter Δf is a function of the dielectric constant ε and the refractive index n.[37] In the case of **1D2** two separate linear relationships are found. One holds for the nonpolar solvents cyclohexane to diethyl ether, the other is valid for the polar solvents ethyl acetate, THF, butyronitrile and acetonitrile. For the nonpolar solvents a linear regression analysis to Equations (2) and (3) resulted in a slope $2\mu_e^2/\rho^3$ of $-5.8 \pm 1.0 \times 10^3$ cm^{-1}, an intercept $\nu_{fl}(0)$ of $28.4 \pm 0.2 \times 10^3$ cm^{-1} and a correlation coefficient of −0.974. For the polar solvents, the best-fit results were: slope $-26.4 \pm 5.0 \times 10^3$ cm^{-1}, intercept $32.4 \pm 1.7 \times 10^3$ cm^{-1} and correlation coefficient −0.967. Fluorescence band widths $\Delta\nu_{1/2}$ (Table 3) also suggest differences between nonpolar and polar solvents. In the former they range from 3580 to 4130 cm^{-1}, whereas in the latter the bands abruptly become much broader, with widths between 4810 and 5310 cm^{-1}. The small increase in the band width on going from dibutyl ether to diethyl ether suggests that a second band gradually emerges. This is corroborated by close inspection of the spectral shape, which indicates a broadening at the red side (see Supporting Information).

Table 3. Fluorescence properties of donor compound **1D2**

Solvent	Δf	ν_{fl} /10^3 cm^{-1}	Φ_{fl}[a]	$\Delta\nu_{1/2}$ /10^3 cm^{-1}
Cyclohexane	0.100	27.74	0.29	3.58
Di-*n*-butyl ether	0.193	27.36	[b]	3.58
Diisopropyl ether	0.234	27.03	[b]	3.96
Diethyl ether	0.251	26.81	0.21	4.13
Ethyl acetate	0.292	24.45	0.19	5.08
THF	0.308	24.39	0.21	4.81
Butyronitrile	0.376	22.83	[b]	5.14
Acetonitrile	0.392	21.65	0.23	5.31

[a] Fluorescence quantum yield. [b] Not determined.

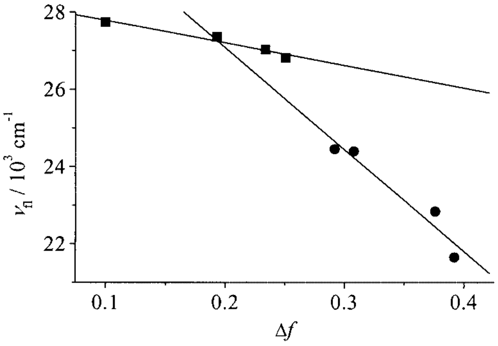


Figure 4. Lippert−Mataga plot of the fluorescence solvatochromism of **1D2**; squares, nonpolar solvents; circles, polar solvents; the lines are results of linear fits to Equation (2)

From the fluorescence data in polar solvents it can be concluded that **1D2** possesses a first excited state with a large dipole moment. The observation of different solvatochromic sensitivities $2\mu_e^2/hc\rho^3$ and different band widths for nonpolar and polar solvents moreover strongly suggests that different emitting species are present as a function of solvent polarity. In most solvents only a single species is present, but in diisopropyl ether and diethyl ether the two species coexist. This kind of behaviour is not unusual for a 4-substituted dimethylaniline; dual fluorescence has been observed for a large number of dialkylaniline derivatives.[35,38] The short-wavelength component emanates from a slightly polar locally excited (LE) aniline-^1L_b-like state, while the long-wavelength band originates from a highly polar intramolecular charge-transfer (ICT) state. In nonpolar solvents the LE state is lower in energy than the ICT state, whereas in polar solvents the ICT state is more stable. The exact nature of the ICT state such as observed for **1D1** has given rise to controversy. Neglecting some other opinions, one view is that the anilino group (or another moiety) is rotated 90° out of the conjugation plane by twisting along a ground state formal single bond. This is referred to as a twisted ICT (TICT) state.[35,38] Such a TICT state possesses biradicaloid character. According to the other point of view, a planar quinoid-like structure is adopted (a planar intramolecular CT or PICT state).[39,40] Convincing evidence for the former hypothesis has recently been put forward.[41]

Irrespective of the exact nature of the CT state, the fact that **1D2** populates this state clearly shows that photoinduced electron transport occurs. If a cavity radius ρ of 4.2 Å is used,[42] for the polar excited state a dipole moment of 13.9 D is obtained upon application of Equations (2) and (3). The dimethylamino group must function as an electron donor, while the 1-phenylvinyl group acts as an electron acceptor. Interestingly, 1,1-diphenylethene was previously found to behave as an electron donor in intermolecular photoinduced electron transfer reactions.[26,43] The redox activity of the 1,1-diphenylethene-based unit thus comprises both electron-donating and electron-accepting functions.

The question arises as to what extent the cross-conjugated phenyl group plays a role in the electron-accepting behaviour of the 1,1-diphenylethene spacer. To find an answer, a comparison with the fluorescent properties of 4-(dimethylamino)styrene **ST-D2** and 4-(dimethylamino)stilbene **2D2** is illustrative. The fluorescence maximum of **ST-D2** shows only a very limited shift with the solvent polarity. It is situated at 358 nm in cyclohexane, at 365 nm in both THF and ethyl acetate, and at 371 nm in acetonitrile. Hence, the presence of the second phenyl group in **1D2** is essential for photoinduced charge transfer to occur. Stilbene **2D2** exhibits fluorescence solvatochromism, but it is less pronounced than that of **1D2**. By fitting literature data[44] to Equations (2) and (3),[45] a single correlation with slope $-13.3 \pm 1.4 \times 10^3$ cm^{-1}, intercept $27.8 \pm 0.4 \times 10^3$ cm^{-1} and correlation coefficient −0.990 was obtained. This indicates that for the stilbene only a single excited species with a dipole moment substantially smaller than that of **1D2** is present. The presence of different emitting species for **1D2** and **2D2** is corroborated by the fluorescence band widths. For the polar excited state of **1D2** these are much larger than for the stilbene, which range from 3300 to 3690 cm^{-1}.[44] Hence, both the solvatochromic shift and larger band widths indicate that the degree of charge separation is larger in **1D2**. This is in line with the expectation that the degree of photoinduced charge separation is larger in the less conjugated system, something which can nicely be seen from comparison of the HOMOs and LUMOs of **1D2** and **2D2**.[31] In **1D2** the HOMO is entirely localized on the anilino site and the vinylidenic double bond, whereas in **2D2** it is also spread over the second phenyl group. The LUMO of **1D2** is slightly more centred at the unsubstituted phenyl group than the LUMO of **2D2**.

Fluorescence quantum yields of **1D2** are of the same order of magnitude as those of dimethylaniline (0.19 in cyclohexane[15]) and are much larger than the quantum yields of **1D1** and **1A**. In both nonpolar and polar solvents the fluorescence quantum yields of **1D2** are also an order of magnitude larger than those of **2D2**, which are about 0.03.[44] This shows that the deactivation process governing the decay of **2D2**, involving a twist of the double bond,[44] does not play a significant role in **1D2**. Apparently, the aniline-centred lowest excited state of **1D2** is so low in energy that radiationless deactivation through 1,1-diphenylethene-like states is prevented. It is furthermore remarkable that the fluorescence quantum yields of **1D2** are hardly affected by the nature of the solvent.

Strong fluorescence solvatochromism is also observed for donor-acceptor compounds **1D1A** and **1D2A**. This is illustrated for **1D2A** in Figure 5, while fluorescence data are given in Table 4. Unlike that of **1D2**, the fluorescence solvatochromism for both **1D1A** and **1D2A** obeys a single linear relationship; correlation coefficients are excellent (Table 4). For a given compound, in all solvents an identical emitting species of highly dipolar nature must be present. With use of cavity radii of 4.4 and 4.5 Å,[42] excited state dipole moments of 13.0 and 17.9 D are obtained for **1D1A** and **1D2A**, respectively. This shows that a larger degree of charge separation occurs in **1D2A** than in **1D1A**. In fact, the μ_e value of **1D1A** is even smaller than μ_e of the polar CT state of **1D2**. Apparently, the presence of a strong donor is of more importance for the generation of a large excited state dipole moment than the presence of both a donor and a acceptor. In spite of the reduced donor-acceptor distance (AM1 optimized geometries reveal that the N−N distance is 10.9 Å in **1D2A** vs. 13.4 Å in stilbene **2D2A**), the solvatochromic sensitivity $2\mu_e^2/\rho^3$ and the excited state dipole moment of **1D2A** are larger than those of **2D2A**.[33] This is in accordance with the less pronounced ground state donor-acceptor interaction in **1D2A**; the weaker the coupling in the ground state, the larger the degree of charge separation in the excited state.

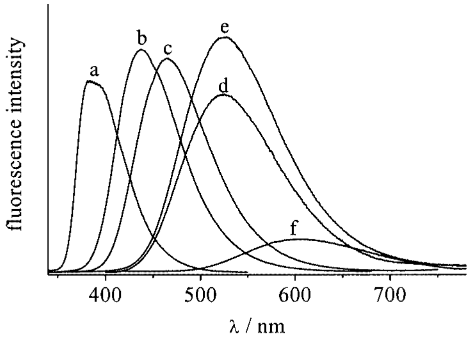


Figure 5. Fluorescence solvatochromism of **1D2A**: (a) cyclohexane, (b) di-*n*-butyl ether, (c) diethyl ether, (d) ethyl acetate, (e) THF, (f) acetonitrile

Table 4. Fluorescence properties of donor-acceptor compounds **1D1A** and **1D2A**

		1D1A			**1D2A**		
Solvent	Δf	ν_{fl}[a]	Φ_{fl}[b]	$\Delta\nu_{1/2}$[a]	ν_{fl}[a]	Φ_{fl}[b]	$\Delta\nu_{1/2}$[a]
Cyclohexane	0.100	29.45	0.016	3.79	25.71	0.087	3.66
Di-*n*-butyl ether	0.193	27.97	[c]	4.28	22.86	0.20	3.93
Diethyl ether	0.251	27.03	0.031	4.74	21.48	0.19	4.02
Ethyl acetate	0.292	25.91	0.053	4.97	19.03	0.082	4.38
THF	0.308	25.71	0.079	4.86	19.03	0.13	4.23
Acetonitrile	0.392	23.58	0.12	5.09	16.53	0.0018	4.67
$-2\mu_e^2/hcp^3$ [a]		20.0 ± 1.2			32.2 ± 1.8		
$\nu_{fl}(0)$[a]		31.7 ± 0.3			29.0 ± 0.5		
r		−0.993			−0.994		

[a] Units 10^3 cm^{-1}. [b] Fluorescence quantum yield. [c] Not determined.

Fluorescence quantum yields are larger for **1D1A** than for **1D1** and **1A**, which is in line with expectation when the energy of the emitting state becomes more distant from the 1,1-diphenylethene-like states. Nonetheless, in common with the trend for donor chromophores **1D1** and **1D2**, the quantum yields of **1D1A** are much lower than those of **1D2A**, except in acetonitrile. This means that in **1D1A** a prominent deactivation pathway is still present. Since fluorescence quantum yields of 2-(4-cyanophenyl)-2-(4′-methoxyphenyl)propane range from 0.25 to 0.58 in the same set of solvents,[15] the double bond must still play a role in the deactivation mechanism. Only in acetonitrile is the ICT state so stabilized that no double bond twisted state is within reach. For **1D2A** this is the case in all solvents (cyclohexane possibly being an exception), meaning that fluorescence quantum yields reach their maximum in medium polarity solvents. This trend has been observed before when intensity stealing is involved.[15,46]

It is of interest to speculate on the structure of the fluorescent CT state of **1D2A** and **1D1A**. Although in principle the negative charge could find itself at the double bond, there is in practice little doubt that the negative charge is located on the strong cyanophenyl acceptor. This is indicated both by the larger dipole moment and the much lower energy of the CT state of **1D2A** vs. that of **1D2** and by the fact that strong fluorescence solvatochromism is observed for **1D1A** but not for **1D1**. A bona fide quinoid resonance structure with a positive charge at the amino group and a negative charge at the cyano group cannot be drawn, because of the cross-conjugated nature of the spacer. Consequently, the PICT model does not hold for donor-acceptor 1,1-diphenylethenes. The ICT state must have biradicaloid character (Figure 6), and **1D2A** and **1D1A** adopt a TICT structure. It is not certain which bond is twisted, since twisting around bonds other than the N−aryl bond can also be involved in the formation of TICT states.[35,38] By the same reasoning it is highly probable that the fluorescence of **1D2** in polar solvents also originates from a TICT state.

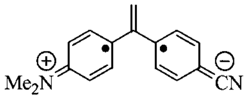


Figure 6. Biradicaloid structure of the CT state of **1D2A**; note that the radical sites can also be situated at other atoms in the rings or at the vinylidenic double bond

Conclusion

From the occurrence of strong fluorescence solvatochromism and the presence of an intramolecular charge-transfer absorption it is evident that photoinduced charge separation occurs in donor-acceptor substituted 1,1-diphenylethenes. In line with a few previous examples,[17−21] charge transport over a spacer consisting of a single sp^2-hybridized carbon atom, and hence in a branched conjugation path, proves to be possible. The electronic interaction is not as efficient as in an identically substituted stilbene with linear conjugation, but is still sizeable. As a consequence of the weaker ground state interaction, the degree of charge separation upon excitation is larger than in the stilbene. Because of the cross-conjugated nature of the spacer, compounds **1D1A** and **1D2A** must adopt biradicaloid TICT states. The occurrence of photoinduced charge separation is not, however, restricted to the donor-acceptor substituted 1,1-diphenylethenes; it is observed for **1D2** as well. This shows that the 1,1-diphenylethene moiety does not behave as a simple spacer. In addition to its already known electron-donating behaviour[26,43] it also exhibits electron-accepting behaviour.

Experimental Section

General: Reactions involving organolithium or Grignard reagents were conducted under a nitrogen atmosphere with use of standard Schlenk techniques. Starting materials and reagents were obtained from commercial sources and were used as received unless stated otherwise. Solvents were generally distilled before use; dry diethyl ether and toluene were obtained by distillation from sodium-benzophenone. Column chromatography was performed with Acros silica (0.035−0.070 mm, pore diameter ca. 6 nm). NMR spectra were obtained on Bruker AC 300 or Varian Unity Inova 300 spectrometers, operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C NMR spectroscopy. All NMR spectra were recorded in CDCl$_3$ and are referenced to TMS. Infrared spectra were recorded with a Mattson Galaxy Series FTIR 5000 instrument in diffuse reflectance mode on dispersions in KBr. Elemental analyses were carried out at the Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Since some of the diphenylethenes were found to be susceptible to oxidation,[47] all compounds were stored at −20 °C under nitrogen atmosphere.

UV spectra were collected on Cary 1 or Cary 5 spectrophotometers in spectrophotometric grade solvents. Fluorescence spectra were obtained on a Spex Fluorolog instrument, equipped with a Spex 1680 double excitation monochromator, a Spex 1681 emission monochromator and a Spex 1911F detector. Fluorescence emission spectra were corrected for the detector spectral response with the aid of a correction file provided by the manufacturer. Fluorescence quantum yields[48] were determined relative to anthracene (Φ_{fl} = 0.27, excitation wavelength 310 nm) or naphthalene (Φ_{fl} = 0.23, excitation wavelength 270 or 280 nm). An excitation wavelength of 310 nm was used for anilines, while 270 or 280 nm excitation was employed for other compounds. Solutions were degassed by purging with argon for 15 minutes. Cyclohexane, ethyl acetate, acetonitrile, diethyl ether and THF used for fluorescence measurements were of spectrophotometric grade (Acros) and were dried over molecular sieves prior to use. Butyronitrile (Fluka, 99 +%) was distilled from calcium hydride. Diisopropyl ether (Acros, 99 +%) and dibutyl ether (Fluka, p.a.) were purified as described elsewhere.[12]

PPP/SCF/CI calculations were performed with a home-adapted version of Griffiths' program.[49] Torsion angles of 40° around the C−C formal single bonds were introduced by correction of the bond resonance energy with cos40°. In all cases a full configuration interactions was performed. AM1 calculations were run with the Quantum CAChe package.[50] Geometries were optimized with the eigenvector following routine and the precise option.

4-Methoxystyrene (**ST-D1**) and 4-cyanostyrene (**ST-A**) were purchased from Acros and were used as received. 4-(Dimethylamino)styrene (**ST-D2**) was prepared as described by Hollywood et al.[51]

1-(4-Bromophenyl)-1-(4-methoxyphenyl)ethene (4): A solution of 4-(methoxyphenyl)magnesium bromide was prepared by allowing 4-bromoanisole (14.14 g, 75.6 mmol) and magnesium (2.19 g, 90.1 mmol) to react in diethyl ether (85 mL). A solution of 4-bromoacetophenone (14.97 g, 75.2 mmol) in diethyl ether (35 mL) was added dropwise to the Grignard reagent, after which the mixture was heated at reflux for 1.5 h. Subsequently, sulfuric acid (30%, 20 mL) was added, and the mixture was heated under reflux for another hour.[52] Water (30 mL) and diethyl ether (120 mL) were added, the layers were separated, and the aqueous layer was extracted with diethyl ether (2 × 50 mL). The combined organic extracts were dried with magnesium sulfate, filtered, and concentrated to dryness.

A ^{1}H NMR spectrum of the resulting product showed that dehydration of alcohol **3** to 1,1-diphenylethene derivative **4** was not complete. The product was therefore dissolved in toluene in the presence of a trace of *p*-toluenesulfonic acid and boiled for 3 hours in a flask fitted with a Dean−Stark separator. After removal of the toluene in a rotary evaporator, recrystallization of part (11.80 g) of the resulting solid from ethanol gave **4** (7.70 g, 26.6 mmol) as an off-white solid. M.p. 89 °C. ^{1}H NMR: δ = 3.82 (s, 3 H, OCH_3), 5.33 and 5.40 (AB, $^2J_{H,H}$ = 1.1 Hz, 2 × 1 H, $=CH_2$), 6.85 and 7.22 (AA′BB′, $^3J_{H,H}$ = 8.8 Hz, 2 × 2 H, Ar−H), 7.20 and 7.46 (AA′BB′, $^3J_{H,H}$ = 8.6 Hz, 2 × 2 H, Ar−H) ppm. ^{13}C NMR: δ = 55.4, 113.4, 113.7, 121.7, 129.4, 130.0, 131.3, 133.5, 140.8, 148.6, 159.6 ppm. IR: $\tilde{\nu}_{max}$ = 2835, 1604, 1508, 1246, 1027, 901, 829 cm^{-1}.

1-(4-Cyanophenyl)-1-(4-methoxyphenyl)ethene (1D1A): A mixture of **4** (7.60 g, 26.3 mmol), copper(I) cyanide (2.78 g, 31.0 mmol) and DMF (19 mL) was heated at reflux under nitrogen for 20 hours. Subsequent to cooling to room temperature the mixture was poured into ammonia (25%, 300 mL), after which air was passed through for 3 hours. The aqueous system was extracted three times with chloroform/hexane (90 mL, 1:1 v/v). The combined extracts were washed with water (200 mL) and dried on magnesium sulfate. Evaporation under reduced pressure gave a brown oil (5.75 g, 24.4 mmol, 93%). Purification of 3.0 g of the crude product by column chromatography on silica with chloroform as eluent afforded a yellow oil (2.18 g), which very slowly (weeks) solidified on standing. M.p. 48.5 °C. ^{1}H NMR: δ = 3.82 (s, 3 H, OCH_3), 5.42 and 5.51 (AB, $^2J_{H,H}$ = 0.8 Hz, 2 × 1 H, $=CH_2$), 6.88 and 7.21 (AA′BB′, $^3J_{H,H}$ = 8.9 Hz, 2 × 2 H, Ar−H), 7.43 and 7.61 (AA′BB′, $^3J_{H,H}$ = 8.6 Hz, 2 × 2 H, Ar−H) ppm. ^{13}C NMR: δ = 55.3, 111.3, 113.8, 115.3, 118.8, 128.9, 129.3, 132.0, 132.6, 146.4, 148.2, 159.7 ppm. IR: $\tilde{\nu}_{max}$ = 2837, 1256, 2230, 1603, 1510, 1030, 901, 839, 766 cm^{-1}. $C_{16}H_{13}NO$ (235.3): calcd. C 81.67, H 5.57, N 5.95, O 6.80; found C 81.50, H 5.47, N 5.84, O 6.95.

1-(4-Bromophenyl)-1-[4-(dimethylamino)phenyl]ethene (6): A solution of 4-bromo-dimethylaniline (5.05 g, 25.2 mmol) in diethyl ether (50 mL) was added dropwise to finely cut lithium pieces (0.60 g, 86.4 mmol) in diethyl ether (20 mL). After the mixture had been stirred overnight at room temperature, a solution of 4-bromoacetophenone (5.04 g, 25.3 mmol) in diethyl ether (50 mL) was added dropwise. The mixture was next heated at reflux for two hours and then allowed to cool down to room temperature. Ethanol (25 mL) and water (120 mL) were added successively and the layers were separated, upon which the ethereal layer was washed with water (3 × 25 mL). Drying over magnesium sulfate and concentration under reduced pressure afforded **5** (6.49 g, 20.3 mmol) as a yellowish oil. Subsequently, a solution of **5** (6.49 g, 20.3 mmol) in toluene (100 mL) was heated to reflux in a Dean-Stark apparatus for three hours in the presence of a catalytic amount of *p*-toluenesulfonic acid. After removal of the toluene, the remaining solid was recrystallized from methanol/chloroform, 10:1 v/v. Yield 4.50 g (14.9 mmol, 73% with respect to **5**). M.p. 127 °C. ^{1}H NMR: δ = 2.98 [s, 6 H, $N(CH_3)_2$], 5.23 and 5.38 (AB, $^2J_{H,H}$ = 1.2 Hz, 2 × 1 H, $=CH_2$), 6.7 and 7.2 (AA′BB′, $^3J_{H,H}$ = 8.8 Hz, 2 × 2 H, Ar−H), 7.24 and 7.45 (AA′BB′, $^3J_{H,H}$ = 8.5 Hz, 2 × 2 H, Ar−H) ppm. ^{13}C NMR: δ = 40.5, 111.8, 112.0, 121.4, 128.8, 128.9, 130.1, 131.2, 141.3, 148.8, 150.3 ppm. IR: $\tilde{\nu}_{max}$ = 2802, 1605, 1522, 1354, 897, 824 cm^{-1}.

1-(4-Cyanophenyl)-1-[4-(dimethylamino)phenyl]ethene (1D2A): A mixture of **6** (4.00 g, 13.3 mmol), copper(I) cyanide (1.37 g, 15.3 mmol) and DMF (10 mL) was heated at reflux under a nitrogen atmosphere for six hours. After workup as described for **1D1A**, the crude product was purified by column chromatography (silica, eluent chloroform), giving a light yellow solid (1.33 g, 5.36 mmol, 40%). M.p. 161 °C. ^{1}H NMR: δ = 2.98 [s, 6 H, $N(CH_3)_2$], 5.31 and 5.48 (AB, $^2J_{H,H}$ = 1.1 Hz, 2 × 1 H, $=CH_2$), 6.68 and 7.16 (AA′BB′, $^3J_{H,H}$ = 8.9 Hz, 2 × 2 H, Ar−H), 7.45 and 7.62 (AA′BB′, $^3J_{H,H}$ = 8.5 Hz, 2 × 2 H, Ar−H) ppm. ^{13}C NMR: δ = 40.2, 110.8, 111.8, 113.3, 118.8, 127.7, 128.7, 128.9, 131.7, 146.9, 148.3, 150.2 ppm. IR: $\tilde{\nu}_{max}$ = 2810, 2226, 1607, 1523, 1358, 897, 856, 820 cm^{-1}. $C_{17}H_{16}N_2$ (248.3): calcd. C 82.23, H 6.49, N 11.28; found C 81.88, H 6.55, N 11.16.

1-(4-Methoxyphenyl)-1-phenylethene (1D1): A solution of 4-(methoxyphenyl)magnesium bromide was prepared by allowing 4-bromoanisole (9.35 g, 50.0 mmol) and magnesium (1.50 g, 61.7 mmol) to react in diethyl ether (50 mL). A solution of acetophenone (6.00 g, 50.0 mmol) in diethyl ether (15 mL) was added dropwise, and the mixture was heated at reflux for two hours. After the mixture had cooled to room temperature, water (100 mL) and hydrochloric acid (1 M, 50 mL) were added cautiously. After separation of the layers the organic one was washed with water (3 × 50 mL), dried over magnesium sulfate and filtered, and the solvents were evaporated to dryness. Yield 10.64 g (46.6 mmol, 93%) of **7** in the form of a yellow oil, which was used without further purification. Compound **1D1** was prepared from **7** by Dean-Stark dehydration as described for **6**. The crude product, which was obtained in quantitative yield, was recrystallized from methanol to afford white crystals in 53% yield. M.p. 73.6 °C. ^{1}H NMR: δ = 3.83 (s, 3 H, OCH_3), 5.36 and 5.40 (AB, $^2J_{H,H}$ = 1.4 Hz, 2 × 1 H, $=CH_2$), 6.86 and 7.26 (AA′BB′, $^3J_{H,H}$ = 8.8 Hz, 2 × 2 H, Ar−H), 7.32 (m, 5 H, Ar−H) ppm, in agreement with literature data.[53] ^{13}C NMR: δ = 55.3, 112.9, 113.5, 127.6, 128.1, 128.3, 129.4, 134.0, 141.8, 149.4, 159.3 ppm. IR: $\tilde{\nu}_{max}$ = 2836, 1607, 1510, 1252, 1028, 901, 841, 785, 708 cm^{-1}.

1-[4-(Dimethylamino)phenyl]-1-phenylethene (1D2): Firstly, 1-[4-(dimethylamino)phenyl]-1-phenylethanol (**8**) was synthesized from 4-(dimethylamino)phenyllithium (50.0 mmol) and acetophenone (6.00 g, 49.9 mmol) as described for **5**. Yield 10.38 g (43.0 mmol, 86%) of a yellowish oil. Subsequently **1D2** was obtained from **8** by the procedure given for **6**. Purification was accomplished by kugelrohr distillation. The fraction boiling at 110−150 °C at 0.25 Torr was collected. Yield 78% of a light yellow solid. M.p. 54 °C. ^{1}H NMR: δ = 2.98 [s, 6 H, $N(CH_3)_2$], 5.26 and 5.38 (AB, $^2J_{H,H}$ = 1.2 Hz, 2 × 1 H, $=CH_2$), 6.69 and 7.16 (AA′BB′, $^3J_{H,H}$ = 8.8 Hz, 2 × 2 H, Ar−H), 7.35 (m, 5 H, Ar−H) ppm, in agreement with literature data.[53] ^{13}C NMR: δ = 40.3, 111.2, 111.8, 127.2, 127.8, 128.3, 128.8, 129.3, 142.1, 149.7, 150.0 ppm. IR: $\tilde{\nu}_{max}$ = 2805, 1611, 1522, 1356, 889, 820, 777 cm^{-1}.

1-(4-Bromophenyl)-1-phenylethene (10): A solution of phenylmagnesium bromide was prepared by treatment of bromobenzene (4.35 g, 27.7 mmol) with magnesium (0.80 g, 32.9 mmol) in diethyl ether. A solution of 4-bromoacetophenone (5.01 g, 25.2 mmol) in diethyl ether (20 mL) was added dropwise. Subsequently, the mixture was heated at reflux temperature for three hours. After the mixture had cooled, water (100 mL) and hydrochloric acid (1 M, 25 mL) were added cautiously, after which the layers were separated. The organic one was washed with water (3 × 50 mL), dried over magnesium sulfate and filtered, and the solvents were evaporated to dryness to give **9** (6.93 g, 5.0 mmol, 99%). Ethene **10** was then prepared from **9** by the method described for **6**. Yield 82% of a yellow liquid. ^{1}H NMR: $\delta = 5.45$ and 5.47 (AB, $^{2}J_{\mathrm{H,H}} = 1.2$ Hz, 2×1 H, =CH$_2$), 7.21 and 7.46 (AA′BB′, $^{3}J_{\mathrm{H,H}} = 8.5$ Hz, 2×2 H, Ar−H), 7.35 (m, 5 H, Ar−H) ppm. ^{13}C NMR: $\delta = 114.7$, 121.8, 127.9, 128.2, 128.3, 129.9, 131.3, 140.4, 140.9, 149.0 ppm. IR: $\tilde{\nu}_{\max} = 1661$, 1588, 1485, 903, 1072, 1011, 831, 777 cm^{-1}.

1-(4-Cyanophenyl)-1-phenylethene (1A): This compound was prepared from **10** by the method described for **1D1A**. The crude product was purified by crystallization from methanol at −20 °C, column chromatography with chloroform as eluent and another crystallization from methanol at −20 °C. Yield 64% of white crystals. M.p. 42 °C. ^{1}H NMR: $\delta = 5.54$ and 5.58 (AB, $^{2}J_{\mathrm{H,H}} = 0.8$ Hz, 2×1 H, =CH$_2$), 7.26 (m, 2 H, Ar−H), 7.35 (m, 3 H, Ar−H), 7.42 and 7.62 (AA′BB′, $^{3}J_{\mathrm{H,H}} = 8.5$ Hz, 2×2 H, Ar−H) ppm, in agreement with literature data.[26] ^{13}C NMR: $\delta = 111.3$, 116.6, 118.8, 128.1, 128.2, 128.4, 128.8, 132.0, 140.2, 146.0, 148.7 ppm, in agreement with literature data.[26] IR: $\tilde{\nu}_{\max} = 2226$, 1605, 1502, 1491, 912, 853, 783, 706 cm^{-1}.

Supporting Information: Fluorescence spectra of **1D2** in different solvents (see also the footnote on the first page of this article).

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