Photoinduced Charge Separation in Cyclohexylidene-Based Donor−(σ-Bridge)−Acceptor Compounds − Building Blocks for Materials

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We describe the syntheses and properties of five semi-rigid donor–(σ-bridge)–acceptor (D–σ–A) compounds. These compounds, which are candidates for incorporation in materials, have aniline-type donors and (mixed) cyano- and alkoxycarbonyl-1,1-difunctionalized vinyl acceptors that are separated by a four-σ-bond bridge. Their electronic properties were studied by means of photoelectron spectroscopy in combination with ab initio MO calculations, cyclic voltammetry, UV-Vis absorption spectroscopy, (time-resolved) fluorescence spectroscopy, and time-resolved microwave conductivity (TRMC). We found that these D–σ–A compounds exhibit a weak intramolecular charge-transfer absorption band that borrows its intensity from local transitions. Upon photoexcitation, a charge-separated state is generated in virtually quantitative yield. Conformational contraction or "folding" of this state takes place for the two D–σ–A compounds with a dicyanovinyl acceptor in apolar solvents. The absence of folding in compounds with an alkoxycarbonyl-functionalized acceptor is attributed to a reduced lifetime of the charge-separated state.

Introduction

Organic materials for application in molecular electronic and photonic devices receive considerable attention.[1] Examples are polymer-based light-emitting diodes (LEDs),[2] materials for nonlinear optics, and electronic components,[3] such as molecular wires, rectifiers[4−6] and switches.[7,8] In this field of research, our interest is mainly focussed on the role that can be played by donor−bridge−acceptor compounds (D−σ−A compounds) with saturated hydrocarbon bridges. These compounds have been proposed[9] and successfully applied[4] as molecular rectifiers. Some of them have been shown[10] or predicted[11−13] to possess an appreciable hyperpolarizability, which is needed for efficient frequency doubling of laser light (second harmonic generation). Upon electronic excitation of a D−σ−A compound, electron transfer from the donor to the acceptor can take place to produce a highly dipolar excited state. The fluorescence from these states can be tuned throughout the whole visible region[14] and highly fluorescent D−σ−A compounds have also been used in electroluminescent devices.[15]

One of our ultimate goals is the application of D−σ−A compounds as constituents for materials, such as monolayers, molecular assemblies, and polymers.[16] Therefore, the D−σ−A compounds should possess functionalities that can be used as anchoring points for (supramolecular noncovalent) interactions or further (covalent) functionalization.

In this article we report on the synthesis and photophysical properties of a set of D−σ−A compounds that are potential candidates for incorporation in materials. The parent compound of the set is **DA1** (Figure 1), which consists of an *N*,*N*-dimethylaniline donor and a dicyanovinyl acceptor that are separated by a cyclohexylidene-based spacer. Replacement of one (**DA2**) or both (**DA3** and **DA4**) cyano groups by alkoxycarbonyl groups provides the required attachment points for their incorporation in materials. In **DA2**, **DA3**, and **DA4**, the methyl and dodecyl groups occupy the anchoring points. Replacement of the two methyl

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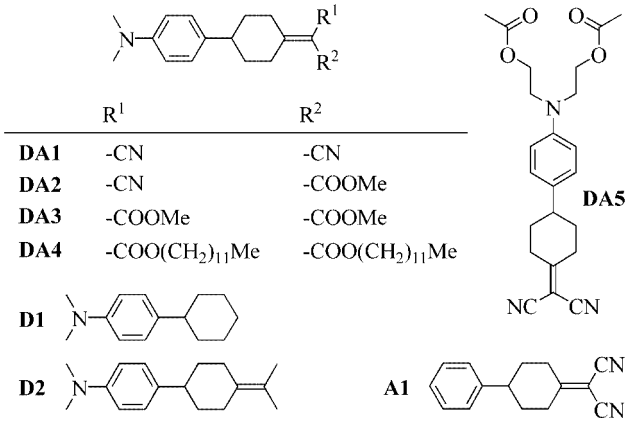


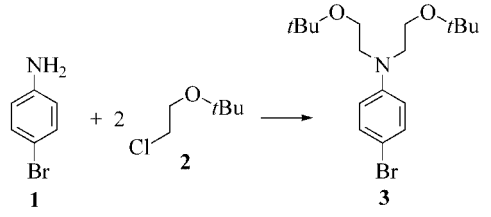
Figure 1. Donor−acceptor compounds and the model donor and model acceptor compounds studied

groups of the *N*,*N*-dimethylaniline donor of **DA1** by $-CH_2CH_2OH$ groups allows the incorporation of the functional entities in step-growth polymers, such as polyesters. The properties of model diacetyl ester **DA5** are reported. We show that modification of the donor (D) or acceptor (A) moieties does not lead to changes of their photophysical properties, i.e., their propensity to undergo photo-induced charge separation. We note that small structural modifications can markedly affect the excited-state properties of D−σ−A compounds.[17]

Results and Discussion

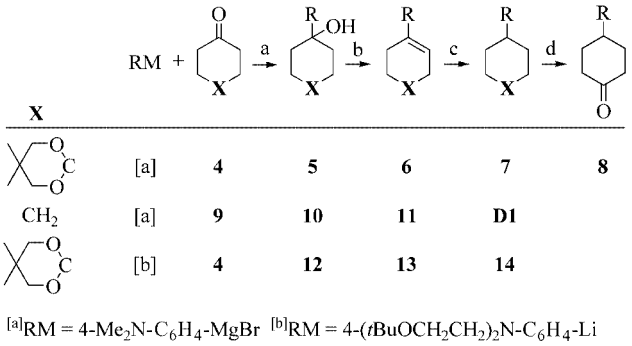
Synthesis

The syntheses of the donor model compounds **D1** and **D2**, the acceptor model compound **A1** and the D−σ−A compounds **DA1**−**DA5** are given in Schemes 1−5. First, the 4-bromoaniline derivative **3** was prepared by alkylation of 4-bromoaniline (**1**) with two equivalents of *tert*-butyl 2-chloroethyl ether (**2**) under conditions that minimize quaternization[18] (Scheme 1). *tert*-Butyl ether **2** was prepared by acid-catalysed *tert*-butylation of 2-chloroethanol with 2-methylpropene.[19,20]



Scheme 1. Synthesis of **3**. Conditions/reagents: K_2CO_3, KI, butanol

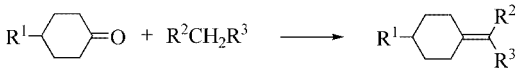
The syntheses of ketone **8** and **D1** are depicted in Scheme 2. In a broad sense, the synthetic route to **8** follows the route described by Kaiho et al.[21] The Grignard reagent of 4-bromo-*N*,*N*-dimethylaniline (prepared either by a dry-stirring method[22] or by application of ultrasound[21]) was added to cyclohexanone (**9**) and ketone **4**, to form **10** and **5**, respectively. These alcohols were dehydrated under acidic



Scheme 2. Syntheses of ketone **8**, **D1**, and **14**. Conditions/reagents: (a) THF; (b) for **5** and **12**: *p*-toluenesulfonic acid, toluene; for **10**: CF_3COOH; (c) 1 atm. H_2, Pd/C, THF/EtOH; (d) HCl, H_2O/THF

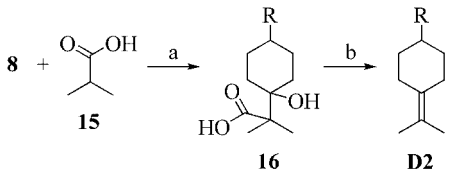
conditions to form **11** and **6**. Catalytic hydrogenation of **11** gave **D1** and hydrogenation of **6**, followed by deprotection with acid, afforded ketone **8**.

The carbonyl group of **8** was converted into several difunctionalized vinyl groups by means of Knoevenagel condensation reactions (Scheme 3). Reaction of **8** and 4-phenylcyclohexanone with malononitrile gave D−σ−A compound **DA1** and model acceptor (4-phenylcyclohexylidene)-malononitrile (**A1**), respectively. Methyl cyanoacetate, dimethyl malonate, and didodecyl malonate were used to convert **8** into **DA2**, **DA3**, and **DA4**, respectively. In the case of malononitrile, an apparent pH of 7.5−8.0 in an alcohol/water mixture is appropriate to readily accomplish the condensation,[23] but in the case of methyl cyanoacetate the reaction proceeds much slower. Dimethyl malonate and didodecyl malonate react only when utilizing $TiCl_4$ and pyridine in THF.[24]



R^1	R^2	R^3	
4-Me_2N-C_6H_4-	-CN	-CN	**DA1**
4-Me_2N-C_6H_4-	-CN	-COOMe	**DA2**
4-Me_2N-C_6H_4-	-COOMe	-COOMe	**DA3**
4-Me_2N-C_6H_4-	-$COO(CH_2)_{11}Me$	-$COO(CH_2)_{11}Me$	**DA4**
C_6H_5-	-CN	-CN	**A1**

Scheme 3. Synthesis of D−σ−A compounds and model acceptor compound **A1**. Conditions/reagents for **DA1**, **DA2**, and **A1**: β-alanine, EtOH/H_2O; for **DA3** and **DA4**: $TiCl_4$, pyridine, THF

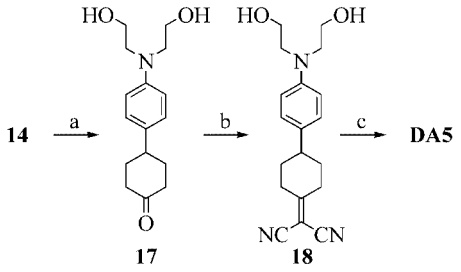


Scheme 4. Synthesis of **D2** (R = 4-$Me_2NC_6H_4$−). Conditions/reagents: (a) LDA, THF; (b) $Me_2NCH(OCH_2tBu)_2$, MeCN

Model donor **D2** was prepared according to Scheme 4. The dilithium salt of 2-methylpropanoic acid was added[25] to ketone **8** to form β-hydroxy acid **16**, which was sub-

sequently converted into **D2** by dehydrative decarboxylation.[26]

Although all our attempts to prepare a Grignard reagent from **3** failed,[27] lithiation of **3** with 2 equivalents of *n*-butyllithium in THF was successful. The lithiation product was coupled to ketone **4** in the same way as the Grignard reagent of 4-bromo-*N*,*N*-dimethylaniline (Scheme 2). A similar reaction sequence as followed for **5** gave ketal **14**. Deprotection of **14** under aqueous acidic conditions (Scheme 5) led to removal of both the *tert*-butyl groups and the ketal functionality to give **17**. Condensation of **17** with malononitrile gave **18**, which was converted into **DA5** by reaction with two equivalents of acetyl chloride.



Scheme 5. Synthesis of **DA5**. Conditions/reagents: (a) HCl, H_2O/dioxane; (b) malononitrile, β-alanine, EtOH/H_2O; (c) acetyl chloride, pyridine, CH_2Cl_2

Photoelectron Spectroscopy

To assess if ground-state electronic interactions[28−30] between the functionalities in the donor−acceptor compounds are present, He(I) photoelectron (PE) spectra of **DA1** and model donor compounds **D1** and **D2** were recorded and RHF/6-31G ab initio calculations were performed. The vertical ionization energies $I_{v,j}$ for **D1**, **D2**, and **DA1** are given in Table 1 together with RHF/6-31G orbital energies ε_j and their assignments. The PE spectra are given in Figure 1S (Supporting Information). The photoelectron spectra were analysed using the following procedure. Firstly, the PE bands of **D1**, **D2**, and **DA1** were correlated with those of model compounds. Secondly, the experimental ionization potentials $I_{v,j}$ were correlated with ab initio molecular orbital energies using Koopmans' theorem ($I_{v,j} = -\varepsilon_j$).[31]

The bands in the PE spectrum of **D1** can be readily correlated to those previously found for *N*,*N*-dimethylaniline (**DMA**).[32] The first and third band of **DMA** are assigned to the two linear combinations of one of the two degenerate $\pi(e_{1g})$ HOMOs of benzene with the nitrogen lone pair Lp (Lp-π_{ar} and π_{ar}-Lp). The second band is assigned to the benzene $\pi(e_{1g})$ MO, which has a nodal plane running through the nitrogen atom.[32] The PE spectrum of **D2** shows an additional band at 8.1 eV attributed to ionization from a MO centered on the olefinic bond. For isopropylidenecyclohexane, a value for $I_{v,j}$ of 8.34 eV has been reported.[33] The presence of the olefinic bond does not have a noticeable influence on the positions of the other bands.

Table 1. Vertical ionization energies ($I_{v,j}$) from PES, RHF/6-31G orbital energies ($-\varepsilon_j$), and assignments for **D1**, **D2**, **DA1**, and **DMA**

Compound	Band (*j*)	$I_{v,j}$/eV	$-\varepsilon_j$/eV	Assignment
D1	1	7.2	7.48	56a π_{ar}-Lp
	2	8.7	8.96	55a π_{ar}
	3	9.4	10.30	54a Lp-π_{ar}
	4	−	11.40	53a σ
D2	1	7.0	7.48	67a π_{ar}-Lp
	2	8.1	8.46	66a π
	3	8.7	8.96	65a π_{ar}
	4	9.3	10.31	64a Lp-π_{ar}
	5	−	11.31	63a σ
DA1	1	7.5	7.81	71a π_{ar}-Lp
	2	9.1	9.40	70a π_{ar}
	3	9.9[a]	10.24	69a π_{acc}
	4	9.9[a]	10.83	68a Lp-π_{ar}
	5	−	12.71	67a σ
DMA[32]	1	7.45	7.62	33a π_{ar}-Lp
	2	9.00	9.01	32a π_{ar}
	3	9.85	10.65	31a Lp-π_{ar}
	4	−	12.99	30a σ

[a] Overlap of bands.

Hence, within the resolution of the PES measurements, the ground-state electronic interaction between the olefinic bond and the aniline functionality is small.

The PE spectrum of **DA1** shows three bands of which the two with the lowest values of $I_{v,j}$ are assigned to the *N*,*N*-dimethylaniline donor. These bands are shifted to higher energy, relative to those in **D1**, by 0.3 and 0.4 eV, respectively (calculated shifts: 0.33 and 0.44 eV, respectively). This effect is attributed to an inductive shift resulting from the introduction of the acceptor moiety.[34] The third band is composed of two peaks, which are assigned to the π_{ar}-Lp MO and the $\pi[C{=}C(CN)_2]$ MO. The latter assignment is corroborated by the reported value for $I_{v,j}$ of 10.21 eV for the $\pi[C{=}C(CN)_2]$ MO in isopropylidenemalononitrile.[35] These results show that, besides inductive shifts, no clear-cut through-bond interactions are discernible between the donor and acceptor parts of **DA1**.

Cyclic Voltammetry

The oxidation and reduction potentials of the donor−acceptor compounds and model donor and acceptor compounds were determined by cyclic voltammetry. Data are given in Table 2. The electrochemical oxidation wave of the *N*,*N*-dimethylaniline donor in **D1**, **D2**, **DA1**, **DA2**, **DA3**, and **DA4** is followed by a back-reduction wave with a substantially smaller peak current. As this wave gains intensity upon increasing the scan rate (not shown), it is evident that oxidation is followed by an irreversible chemical reaction.[36] Using a scan rate of 0.5 $V{\cdot}s^{-1}$, a ratio of the cathodic peak current to the anodic peak current[37] (i_{pc}/i_{pa}) of 0.66 was obtained, allowing a reasonable estimate of E°_{ox}. It appears that the presence of an acceptor raises the value of E°_{ox} of the *N*,*N*-dimethylaniline donor by 0.02 V, to 0.05 V. The data suggest that the effect is more pronounced for stronger acceptors and that it is inductive in

nature (see above). In contrast to the compounds with an *N*,*N*-dimethylaniline donor, the oxidation of the donor in **DA5** is quasi-reversible (i_{pc}/i_{pa} = 0.94). Moreover, E°_{ox} is substantially higher (by 0.14 V, relative to **DA1**). Thus, the electron donating power of the donor in **DA5** is reduced relative to that of the other D−σ−A compounds. Presumably, this is due to an extra inductive effect exerted by the oxygen atoms of the ester.

Table 2. Redox potentials in V versus SCE as measured by cyclic voltammetry in acetonitrile. The term E°_{ox} denotes the half wave potential and ΔE^{p} the potential difference between the peak values of the forward and backward scans of the 0/+1 electrode process measured at a scan rate of 0.5 V·s^{-1}. The values of E^{p}_{ox} and E^{p}_{red} are the peak values of the first forward oxidation and reduction scans, respectively, measured at a scan rate of 50 mV·s^{-1}

Compound	E°_{ox} (ΔE^{p}/mV)	E^{p}_{ox}	E^{p}_{red}
D1	0.63 (150)	0.65	−
D2	0.63 (130)	0.65	−
A1	−	−	−1.85
DA1	0.68 (136)	0.71	−1.86
DA2	0.67 (135)	0.69	−2.02
DA3	0.65 (138)	0.69	< −2.1[a]
DA4	0.65 (149)	0.69	< −2.2[a]
DA5	0.82 (74)[b]	−	−1.86

[a] Outside potential window. [b] ΔE^{p} at 50 mV s^{-1} scan rate.

The reduction waves for all donor−acceptor compounds are irreversible, even at scan rates of 2 V·s^{-1}. In the case of an irreversible wave, the onset can be used to monitor differences in reduction potential.[38] For the investigated compounds, however, the differences in the onset of the reduction waves were identical to differences in the peak potentials. Therefore the latter are reported. The values show that the dicyanovinyl acceptor is the strongest acceptor and that replacement of a cyano group by an alkoxycarbonyl group reduces the reduction potential by 0.16 V. Thus, replacement of both cyano groups by alkoxycarbonyl groups, as in **DA3** and **DA4**, is expected to reduce the reduction potential even more. Unfortunately, the first reduction wave of **DA3** and **DA4** is positioned outside the potential window of the CV set-up that we used.

Electronic Absorption Spectra

Absorption spectra of **D1**, **D2**, **A1**, **DA1**, **DA2**, **DA3**, and **DA4** were recorded in cyclohexane. For solubility reasons, the spectrum of **DA5** was recorded in CH_2Cl_2. Absorption maxima and molar absorption coefficients are given in Table 3, while representative spectra are depicted in Figure 2. As discussed previously,[17] the *N*,*N*-dialkylaniline donor in **D1** and **D2** exhibits three absorption bands, in the region 195−350 nm, which are positioned near 204, 254, and 303 nm. The acceptor chromophore in **A1** displays an absorption at 234.0 nm [Figure 2(b); ε = 17.3·10^3 M^{-1}·cm^{-1}, almost identical to the value reported[39] for cyclohexylidenemalononitrile in cyclohexane (λ_{max} = 234 nm, ε = 18.2·10^3 M^{-1}·cm^{-1})]. This result shows that the absorption band of the dicyanovinyl acceptor in **A1** is not substantially influenced by the presence of the phenyl group. The acceptor absorptions of **DA1** (λ_{max} = 230 nm), **DA2** (λ_{max} = 230 nm), and **DA3** (λ_{max} = 218 nm) show up clearly in the difference spectra in Figure 2(b). The values of λ_{max} are in good agreement with those for compounds lacking a donor, i.e., **A1**, methyl cyano(cyclohexylidene)-acetate[39] (λ_{max} = 234 nm, ε = 14.7·10^3 M^{-1}·cm^{-1}) and diethyl isopropylidenemalonate[40] (λ_{max} = 218 nm, ε = 10.2·10^3 M^{-1}·cm^{-1} in 95% ethanol). The "peak" at ca. 260 nm in the difference spectra is attributed to the borrowing of intensity by the aniline ^1L_a transition from the acceptor π→π* transition.[17,39]

Table 3. Absorption maxima and molar absorption coefficients of the donor−acceptor compounds and their model chromophores in cyclohexane at 20 °C

Compound	λ_{max}/nm [ε/10^3 M^{-1}·cm^{-1}][a]		
D1[17]	203.5 [22.5]	253.5 [16.54]	302.0 [2.28]
D2[17]	204.0 [35.5]	253.0 [18.80]	302.5 [2.31]
A1	234.0 [17.3]		
DA1	203.0 [25.5]	255.0 [29.3]	304.5 [2.67]
DA2	203.5 [25.6]	254.5 [28.4]	302.5 [2.64]
DA3	204.5 [29.2]	253.5 [21.9]	302.5 [2.32]
DA4	205.0 [28.3]	253.5 [20.9]	302.5 [2.18]
DA5[b]		257.5 [26.2]	303.5 [2.53]

[a] Error in absorption coefficients is ca. 2% for maxima near 200 nm and ca. 1% for maxima near 250 and 300 nm. [b] Solvent: CH_2Cl_2.

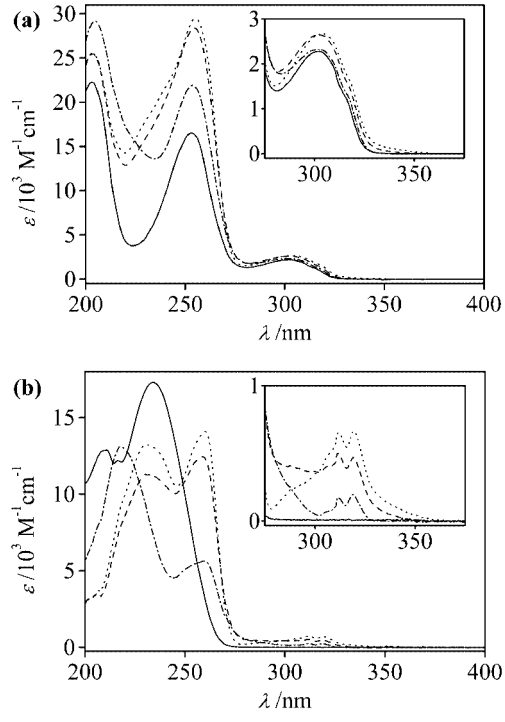


Figure 2. (a) Absorption spectra of **D1** (−), **DA1** (···), **DA2** (− − −), and **DA3** (−·−) in cyclohexane at 20 °C. The inset shows a magnification of the region 275−375 nm. (b) Absorption spectrum of **A1** (−) in cyclohexane at 20 °C and difference spectra obtained upon subtraction of the absorption spectrum of **D1** from that of **DA1** (···), **DA2** (− − −) and **DA3** (−·−). The inset shows a magnification of the region 275−375 nm

In the spectrum of **DA1**, a weak tail is discernible between 325 and 350 nm, which is absent in the spectrum of **D1** [see also the inset of Figure 2(b)] its occurrence was independent of concentration. Moreover, the intensity maximum at 304.5 nm is slightly red-shifted to that of **D1** (302.0 nm) and it has a significantly higher absorption coefficient. These results reveal that a very weak absorption band is present in the spectrum of **DA1**, which can be attributed to a charge-transfer (CT) transition involving electron transfer from the *N*,*N*-dialkylaniline donor to the dicyanovinyl acceptor.[41] These results are in line with those obtained by Pasman et al.[33,39,42] and others.[43]

Previous work has shown[44,45] that, for D−σ−A compounds with bridges of up to six σ-bonds, the CT absorption arises from intensity borrowing from transitions localized in the D and/or A chromophores; local excited-state character is mixed in the CT state to a degree governed by the coupling energy V^*. In compounds with bridges of up to six σ-bonds, V^* is dominant over the coupling V of the CT state with the ground state. Thus, the value of V^* can be estimated by:[44]

$$|V^*|^2 = \frac{f \cdot \nu_A^*}{f^* \cdot \nu_A} \cdot (\nu_A^* - \nu_A)^2 \quad (1)$$

In this equation f and ν_A denote the oscillator strength and the transition energy of the CT absorption, respectively, while f^* and ν^*_A represent the same quantities for the local transition. We take the absorption of aniline at 253.5 nm as the local excitation that donates intensity to the CT absorption. This absorption has the correct symmetry for mixing with the acceptor π−π* absorption[17] and, hence, also for mixing with the CT absorption. The maximum ν_A (32,300 cm^{-1}), absorption coefficient ε (400 $cm^{-1}\cdot M^{-1}$) and width at half height $\Delta\nu_{1/2}$ (4000 cm^{-1}) of the CT absorption of **DA1** in cyclohexane were estimated from the inset of Figure 2(b). This process gives for the oscillator strength $f = 4.32\cdot10^{-9} \cdot\varepsilon\cdot\Delta\nu_{1/2} = 0.0069$. The data for the aniline absorption at 253.5 nm ($\nu_A^* = 39450\ cm^{-1}$) were taken from those of 4-cyclohexyl-*N*,*N*-dimethylaniline[17] and give $f^* = 4.32\cdot10^{-9} \cdot 16540\ cm^{-1}\cdot M^{-1} \cdot 4100\ cm^{-1} = 0.29$. Application of Equation (1) then gives $V^* = 1200\ cm^{-1}$. This value compares favorably with that of 1080 cm^{-1} for another four-σ-bond-bridged compound.[44] The magnitude of this coupling denotes that, for **DA1** in cyclohexane, ET occurs in the adiabatic regime. Unfortunately, assessment of V is not possible, since the radiative rate constants for CT fluorescence in a set of solvents with different polarity are not available.

The absorption spectrum of **DA2** does not exhibit such a clear absorption tail as does that of **DA1**, but the band at 302.5 nm again has a significantly higher absorption coefficient than that of **D1**. In the difference spectrum of **DA2** and **D1** [inset of Figure 2(b)], this peak shows up as a weak CT absorption that is blue-shifted relative to the CT absorption in **DA1** by ca. 0.1 eV as judged from the onsets. This absorption finds its origin in the weaker electron-accepting power of the (alkoxycarbonyl)cyanovinyl acceptor in **DA2** as compared to the dicyanovinyl acceptor in **DA1**, as shown by CV (see above). For **DA3** and **DA4** (not shown), an even more hypsochromically shifted CT absorption band with an onset near 300 nm is distinguished in the difference spectrum. This observation confirms that the di(alkoxycarbonyl)vinyl group is a weaker acceptor than the (alkoxycarbonyl)cyanovinyl group. The absorption spectrum of **DA4** is virtually identical to that of **DA3** and the absorption spectrum of **DA5** exhibits a weak CT absorption tail similar in appearance to that in **DA1**.

Fluorescence Spectroscopy and Time-Resolved Measurements

The fluorescence spectra of **DA1**, **DA2**, **DA3**, **DA4**, and **DA5** were recorded in solvents of different polarity. For all compounds the donor fluorescence, which for **D1** in cyclohexane is located at 335 nm,[17] is strongly quenched. Instead, a broad fluorescence band is visible of which the maximum displays a strong bathochromic shift with increasing solvent polarity (Table 4). This effect is characteristic for charge-transfer (CT) fluorescence.[39,42,46−48] In addition, dual CT fluorescence is observed for **DA1** and **DA5** in cyclohexane (Table 4). Upon lowering the temperature of a solution of **DA1** in hexanes from 275 to 190 K the

Table 4. CT fluorescence maxima ν_{CT} in nm (quantum yield $\Phi_{CT}/10^{-3}$) of **DA1**−**DA5** in various solvents at 20 °C together with the results of the solvatochromic fits

Solvent	Δ*f*	DA1	DA2	DA3	DA4	DA5
cyclohexane	0.101	491[a,b] (46)	411 (5.9)	[c]	[c]	470[b,d](30)
benzene[b]	0.117	533 (36)	531 (14)	527 (0.68)	516 (0.90)	508 (56)
di-*n*-pentyl ether	0.173	516[b] (52)	498 (22)	486 (0.48)	477 (0.87)	492[b] (37)
di-*n*-butyl ether	0.193	516[b] (48)	509 (19)	498 (0.51)	489 (0.71)	500[b] (26)
diisopropyl ether	0.234	535 (14)	530 (6.9)	531 (0.61)	519 (0.89)	513 (29)
diethyl ether	0.254	566 (5.0)	562 (2.7)	556 (0.48)	542 (0.79)	529 (19)
THF	0.308	665 (≤ 0.1)	655 (≤ 0.1)	[c]	615 (≤ 0.1)	[e]
$\nu_{CT}(0)/10^3\ cm^{-1}$		28.2±0.5	28.0±0.8	26.1±0.4	27.2±0.5	29.1±0.3
slope/$10^3\ cm^{-1}$		−41.7±2.0	−41.1±3.6	−31.7±2.0	−34.8±2.0	−40.4±1.3
corr. coeff.		0.998	0.985	0.996	0.995	0.999

[a] A low-intensity shoulder with an estimated maximum of 420 nm is observed. [b] Value not used in solvatochromic fit. [c] No CT fluorescence observed. [d] A low-intensity shoulder with an estimated maximum of 400 nm is observed. [e] Could not be measured.

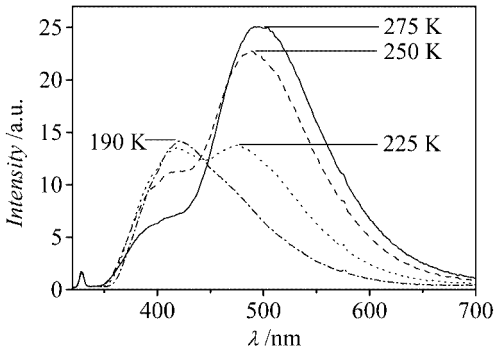


Figure 3. Fluorescence of **DA1** in hexanes at different temperatures. Excitation at 300 nm

fluorescence band at 496 nm gradually disappears while the band at 420 nm gains intensity (Figure 3). This behaviour is rationalized by the occurrence of folding of the initially extended CT (ECT) species to a more compact CT (CCT) species.[49−52] Lowering the temperature suppresses this folding process. The occurrence of the folding process in **DA1** was confirmed by time-resolved measurements (see below). We note that folding has been reported for related compounds that have an identical four-σ-bond bridge, but with their donor and acceptor units having changed positions. These compounds have a (substituted) 1-phenylpiperidine donor and a (substituted) naphthyl acceptor.[52−55] CCT emission is not observed for **DA2**, **DA3**, and **DA4**. Since it is believed that, for these compounds, the Coulombic attraction between the charges in the excited state is not substantially different from that in **DA1**, the absence of CCT emission is presumably related to a shorter lifetime of the ECT state.

The overall CT fluorescence quantum yields Φ_{CT} are low for all D−σ−A compounds under study ($\Phi_{CT} < 0.06$). As indicated by the low intensity of the CT absorption, which is largely dependent on the electronic coupling between $D^{\cdot+}-\sigma-A^{\cdot-}$ and locally excited states, the radiative rate constant for CT emission is expected to be small. It has been observed for related D−σ−A systems that the dicyanovinyl and the (alkoxycarbonyl)cyanovinyl acceptor groups provide a dark decay channel that enhances internal conversion of the CT state. This feature has been proposed to be due to strong coupling of the CT state with non-emissive locally excited singlet and triplet acceptor states through torsional motion around the C=C bond.[14,39]

Replacement of one dicyanovinyl cyano group by an alkoxycarbonyl group, namely going from **DA1** to **DA2**, reduces the value of Φ_{CT} by a factor of 2−3. An identical reduction in the value of Φ_{CT} was observed by Hermant et al. and might be ascribed to a larger rotational freedom of the alkoxycarbonyl group, providing an additional dark process.[14] Replacement of both cyano groups by alkoxycarbonyl groups (from **DA1** to **DA3** or **DA4**) reduces the value of Φ_{CT} by a factor of 10−110. No CT fluorescence is detected for **DA3** and **DA4** in cyclohexane, although the local donor emission is still quenched. This observation suggests rapid crossing to a state localized on the acceptor, which is close in energy to the CT state. The decrease in the value of Φ_{CT} in solvents with highest polarity is attributed to the small energy gap separating the CT and ground states. A small gap will increase the rate of internal conversion.[56]

On the assumption that the excited-state dipole moment (μ_e) is large relative to that of the ground state, the Lippert−Mataga relationship[57−59] [Equation (2)] predicts a linear relationship between the fluorescence maximum ν_{CT} of a CT state with dipole moment μ_e and the solvent polarity parameter Δf:

$$\nu_{CT} = \nu_{CT}(0) - \frac{2\mu_e^2}{hc\rho^3}\Delta f, \quad (2)$$

$$\Delta f = \frac{\varepsilon_s - 1}{2\varepsilon_s + 1} - \frac{n^2 - 1}{4n^2 + 2}. \quad (3)$$

In Equations (2) and (3), which are in CGS units, h is Planck's constant, c is the velocity of light, $\nu_{CT}(0)$ is the gas-phase position of ν_{CT}, ε_s is the solvent dielectric constant, and n is the solvent refractive index. Furthermore, ρ denotes the effective radius of the solvent cavity enclosing the CT species. In Figure 4, the fluorescence maxima ν_{CT} found for **DA1** to **DA5** are plotted versus Δf. A good fit to Equation (2) is obtained for the (ECT) emission maxima of **DA2**, **DA3**, and **DA4**. For **DA1** and **DA5**, fitting of the fluorescence maxima to Equation (2) is complicated by the presence of two emitting species. The fluorescence of ECT and CCT species for these compounds in cyclohexane only partly overlaps and, hence, the maxima of the ECT and CCT fluorescence bands can be obtained with reasonable accuracy. In di-*n*-pentyl and di-*n*-butyl ether as solvents, emission from CCT and ECT species is anticipated to overlap considerably more, making it impossible to extract proper maxima without the use of time-resolved methods. Since the driving force for folding decreases with solvent polarity, it can be expected (and has been observed[60]) that the CCT emission intensity decreases correspondingly. Based upon results for similar compounds,[50,60] we believe that the maxima in diisopropyl ether and the more polar

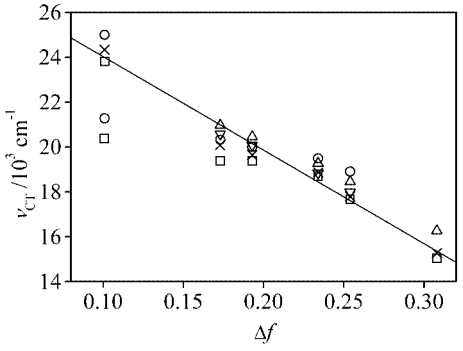


Figure 4. Plot of charge-transfer fluorescence maxima ν_{CT} versus the solvent polarity parameter Δf; □ **DA1**; × **DA2**; ▽ **DA3**; Δ **DA4**; O **DA5**. The fit (—) to the ECT maxima of **DA1** is given as well

solvents are representative for ECT fluorescence and can be used as such in the fitting procedure.

The results of linear fits of the proper (ECT) fluorescence maxima to Equation (2) are given in Table 4. From the slope, $-2\mu_e^2/hc\rho^3$, the value of μ_e can be determined. For **DA1**, an estimate of ρ as 0.4 times the molecular length [14 Å according to molecular mechanics (MM2 force field) calculations] yields a value for μ_e of 27 D. This value corresponds to a unit charge separation over 5.6 Å, which is in reasonable agreement with the distance of 7.1 Å between the aniline nitrogen atom and the carbon atom of the acceptor that is incorporated in the ring. For **DA2** and **DA5**, slopes similar to that found for **DA1** were obtained, indicating that charge separation occurs over a similar distance. The slopes for **DA3** and **DA4** are somewhat smaller than those of **DA1** and **DA5**. Fluorescence maxima for these compounds, however, could be obtained only in a limited range of solvent polarities. Hence, the smaller slopes for **DA3** and **DA4** may point to a smaller excited-state dipole moment and/or a larger solvent cavity, ρ.[61]

To verify the results of the steady-state measurements, time-resolved measurements were performed on **DA1**. Fluorescence lifetimes from single-photon counting (SPC) and excited-state dipole moments obtained by time-resolved microwave conductivity (TRMC)[62,63] of **DA1** are given in Table 5. The fluorescence lifetimes were used to fit the TRMC transients. Two fluorescence lifetimes were found for **DA1** in cyclohexane and benzene. In both cases, the long lifetime describes the decay of the low-energy band, while the short lifetime describes the decay of a high-energy band and the rise of a low-energy band. This feature shows that the species emitting at low energy is formed out of the species emitting at high energy. Thus, electron transfer in an extended conformation produces an extended charge-transfer (ECT) species and is followed by folding of the ECT species to a more compact charge-transfer (CCT) species ("harpooning").[49−52] The TRMC excited-state dipole moment associated with the ECT species of **DA1** (31 D; corresponding to unity charge separation over a range of 6.5 Å) is in reasonable agreement with the value obtained from solvatochromism (27 D). The TRMC dipole moments for the CCT species (about 5 and 11 D) represent lower limits since they were obtained by assuming a quantum yield of CCT formation of 1. Nevertheless, as expected, they are smaller than those for ECT emission. Only fluorescence decay was observed in diethyl ether, indicating that only ECT emission is present.

Table 5. Fluorescence lifetimes τ from SPC and excited-state dipole moments μ_e of the ECT and CCT species of **DA1** as obtained by TRMC

	ECT[a]		CCT[a]	
Solvent	τ/ns	μ_e/D	τ/ns	μ_e/D
cyclohexane	3.7	31	6.5	~5
benzene	7	31	17	11
diethyl ether	0.5	[b]		

[a] Cylindrical and spherical geometries were used in the calculation of the ECT and CCT dipole moments, respectively. [b] Not measured.

Conclusion

Photoelectron spectroscopy, in combination with RHF/6-31G MO calculations, do not reveal any ground-state, through-bond interactions between the donor and acceptor in **DA1**. Nevertheless, a substantial (0.3 to 0.4 eV) inductive effect of the dicyanovinyl acceptor on the *N*,*N*-dimethylaniline π-type MOs is present. This effect translates in cyclic voltammetry to a 0.05 V higher oxidation potential of the *N*,*N*-dimethylaniline donor. By means of electronic absorption spectroscopy, however, a weak charge-transfer absorption band can be distinguished for all D−σ−A compounds, which arises from intensity borrowing from transitions localized on the individual chromophores. An excited state interaction between the locally excited and the CT state of about 1200 cm^{-1} was deduced from the characteristics of this band. This value places ET for these compounds in the adiabatic regime.

Electron transfer occurs for all D−σ−A compounds upon photoexcitation, as was confirmed by the quenching of the local donor fluorescence and the appearance of a broad solvatochromic fluorescence band. Even for the weakest electron acceptor, the di(alkoxycarbonyl)vinyl acceptor, charge transfer is still feasible in cyclohexane, the most-apolar solvent studied.

Furthermore, conformational contraction or "folding" was found to occur upon photoexcitation of **DA1** and **DA5** in cyclohexane and, presumably, in slightly more polar solvents as well. The absence of folding in the case of the other D−σ−A compounds is attributed to the short lifetime of the intramolecular CT state of these compounds.

The results show that modification of both the electron donor and the electron acceptor is achieved without major changes of their characteristic photophysical properties. This feature renders **DA2**−**DA5** as suitable building blocks for the preparation of organized D−σ−A arrays (self-assembled monolayers) as well as D−σ−A polymers formed by either supramolecular non-covalent interaction or further covalent modifications.[16]

Experimental Section

General Remarks: All reactions and distillations were carried out under an atmosphere of dry nitrogen unless stated otherwise. Commercially available reagents were used without further purification. 4-Phenylcyclohexanone was obtained from Acros. THF and diethyl ether were distilled from Na/benzophenone prior to use. MeCN and pyridine were distilled from CaH_2. CH_2Cl_2 was distilled from P_2O_5. EtOH was stored on molecular sieves (3 Å). Column chromatography was performed using Acros silica gel 0.035−0.070 mm, pore diameter ca. 6 nm. Thin layer chromatography was performed on Merck silica gel 60 F_{254}. Spots were detected by the use of iodine vapor and/or UV light. Melting points were determined on a home-made melting point apparatus and are uncorrected. Gas chroma-

tography was performed on a Varian 3350 instrument equipped with a DB-5 (ID, 0.309 mm, 25 m) capillary liquid-phase column and an FID using nitrogen as the carrier gas. NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300.13 MHz for ^{1}H NMR and at 75.47 MHz for ^{13}C NMR spectroscopy. Samples were dissolved in $CDCl_3$ unless stated otherwise. Chemical shifts (in ppm) are given relative to internal TMS (δ = 0 ppm) in the case of ^{1}H NMR spectra and relative to $CDCl_3$ (δ = 77.00 ppm) in the case of ^{13}C NMR spectra. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 5000 operating with 2 cm^{-1} resolution (indicated by "FT-IR") or on a Perkin−Elmer 283 spectrophotometer (indicated by "IR"); solids were measured in KBr pellets and liquids were measured as a thin film between NaCl plates. Peak maxima are given in cm^{-1}. Peaks intensities are designated as s (strong), m (medium), or w (weak). Elemental analyses were performed by the Microanalytical Laboratory H. Kolbe, Mülheim an der Ruhr, Germany. For compounds **A1**, **D2**, and **DA1**, which are composed of the elements C, H, and N, the elements C and H were determined independently. For compounds **DA2**−**DA5**, which are composed of the elements C, H, N, and O, the elements C, H, and O were determined independently.

Photophysics: UV-Vis absorption and fluorescence spectroscopy were performed using the equipment and procedures described in ref.[17] For low-temperature fluorescence measurements, we used an Oxford Instruments Optistat DN liquid nitrogen cryostat regulated with an Oxford Instruments ITC 502 temperature controller. At each temperature, the sample was thermally equilibrated for 20 min before data collection. The sample was not degassed.

Fluorescence quantum yields[64] were determined relative to a reference solution [quinine bisulfate in 1 N H_2SO_4 (ϕ = 0.546)[65] or naphthalene in cyclohexane (ϕ = 0.23±0.02)].[64] Spectroscopic-grade solvents were used throughout, with the following exceptions. Diisopropyl ether (Acros 99.5+%) and di-*n*-butyl ether (Fluka, p. a.; low in aromatic compounds; ≥ 99.5%) were stirred with $LiAlH_4$ for at least one day and then distilled from $LiAlH_4$. Di-*n*-pentyl ether (Fluka, 99%) was purified as follows. Five parts of the ether were stirred with one part of sulfuric acid (Merck, p. a. 95−97%) for 1 d. The brown mixture was poured into 2.5 parts of water and the layers were separated. The organic layer was washed with water, saturated $NaHCO_3$ solution and water (similar volumes), dried with $MgSO_4$, and filtered. This procedure was repeated until a brown color did not develop anymore upon stirring with sulfuric acid. Subsequently, the ether was treated as described for diisopropyl and di-*n*-butyl ether. Hexanes, spectrophotometric grade (≥ 93%; generally a mixture of several isomers of hexane, predominantly *n*-hexane, and methylcyclopentane) was obtained from Acros.

Picosecond single-photon counting (SPC) fluorescence decay was measured using the set-up and fit programs described in ref.[66]. The samples were degassed by purging with Ar for 10 to 15 min and were excited at 310−320 nm.

Cyclic Voltammetry: Cyclic voltammetry (CV) measurements were performed with an EG&G Potentiostat/Galvanostat Model 263A in MeCN (Acros p. a. grade, freshly distilled from CaH_2) containing 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) as the supporting electrolyte at scanning rates of 50 $mV{\cdot}s^{-1}$ to 1.5 $V{\cdot}s^{-1}$. The solute concentration was 1 to 2 mM. The solution was purged with N_2 for at least 10 min prior to the measurement. Redox potentials were determined relative to an Ag/$AgNO_3$ (0.1 M in MeCN) reference electrode and were referenced to SCE by regularly measuring the oxidation potential of the $FeCp_2$/$FeCp_2^{+\cdot}$ couple (E°_{ox} = 0.31 V versus SCE).[67] Since we obtained typically a value E°_{ox} = 0.08 V versus Ag/$AgNO_3$ for the $FeCp_2$/$FeCp_2^{+\cdot}$ couple, we added 0.23 to our values to reference them to SCE. A value of ΔE^p of 74 mV at 50 $mV{\cdot}s^{-1}$ was obtained for ferrocene.

Calculations: All quantum mechanical calculations were run on a Silicon Graphics Power Challenge and Origin 2000 computer using GAMESS-UK.[68] Geometries were optimized at the RHF/6-31G level of theory [cartesian coordinates files are available upon request (L. W. J.)]. All optimized structures possess C_1 symmetry. The total RHF/6-31G energies (in hartree) were: **DA1**: −817.801775; **D1**: −596.592471; **D2**: −712.459898; **DMA**: −363.640788.

Molecular Mechanics (MM2) calculations were performed using the MM2 Force Field as implemented in CambridgeSoft Chem3D Pro, version 4.0 (1997).

***tert*-Butyl 2-Chloroethyl Ether (2):** A 500-mL pressure flask was charged with 2-chloroethanol (84.8 g, 1.05 mol) and dry CH_2Cl_2 (150 mL). The magnetically stirred solution was cooled to −10 °C. Separately condensed 2-methylpropene (150 g, 2.67 mol), cooled to −20 °C, and concentrated H_2SO_4 (5 mL) were added. The flask was stoppered and the mixture was stirred for 60 h at room temperature. After cooling the mixture to −10 °C, the flask was opened and the mixture was poured into a saturated $NaHCO_3$ solution (400 mL). The layers were separated and the water layer was extracted with *n*-pentane (2 × 100 mL). The combined organic layers were washed with water (100 mL) and dried with $MgSO_4$. After filtration, the solvent was carefully evaporated under reduced pressure. To remove most of the CH_2Cl_2, *n*-pentane (50 mL) was added and evaporated again at the rotary evaporator. The remaining colorless oil (127.5 g, 89%) was essentially pure *tert*-butyl 2-chloroethyl ether. ^{1}H NMR: δ = 1.21 (s, 9 H), 3.56 and 3.61 (A_2B_2, J = 6.3 Hz, 4 H) ppm. ^{13}C NMR: δ = 27.4, 43.6, 62.4, 73.5 ppm (in accordance with ref.[69]). FT-IR: $\tilde{\nu}_{max}$ = 2976, 2935, 2877, 1392, 1364, 1249, 1235, 1200, 1106, 1084, 669 cm^{-1} (in accordance with ref.[70]).

4-Bromo-*N*,*N*-bis(2-*tert*-butoxyethyl)aniline (3): A stirred mixture of *tert*-butyl ether **2** (63.7 g, 0.466 mol), 4-bromoaniline (39.6 g, 0.230 mol), K_2CO_3 (64.3 g, 0.465 mol) and KI (4.16 g, 25.1 mmol) in butanol (120 mL) was heated under reflux for 6 d. TLC (*n*-hexane/acetone, 10:1 v/v) showed that most of the starting compound had reacted. The mixture was filtered through a glass frit and the residue washed with *n*-butanol (2 × 50 mL). The filtrate was concentrated under reduced pressure and the remaining oil was subjected to vacuum distillation using a 10 cm Vigreux column. Two fractions were collected, one (I, 42.9 g) boiling at 50−142 °C (0.01 Torr) and another (II, 22.3 g of a viscous colorless oil) at 142−146 °C (0.01 Torr). Fraction II proved to be pure product **3** (yield: 26%). According to ^{1}H NMR spectroscopy, fraction I consisted of 4-bromoaniline (8%), monoalkylated product (71%) and dialkylated product **3** (21%). To this mixture were added **2** (25.6 g, 0.187 mol), K_2CO_3 (26.0 g, 0.188 mol), KI (6.21 g, 37.4 mmol), and butanol (40 mL) and then the mixture was treated in the same manner as the original reaction mixture. Vacuum distillation yielded, after some first runnings (13.6 g), a colorless oil (37.1 g) collected at 134−146 °C (0.01 Torr) which, according to ^{1}H NMR spectroscopy, consisted of **3** (91%) and monoalkyl product (9%). This fraction was further purified as follows. The mixture was heated with acetic acid anhydride (2.00 g, 19.6 mmol) at 120 °C for 15 min. TLC (*n*-hexane/acetone, 10:1 v/v) showed that all the monoalkylated product had reacted to give the acetylated product. Column chromatography (eluent: petroleum ether/diethyl ether, 4:1 v/v)

yielded an additional amount (34.6 g, 40%) of pure **3**. Total yield: 66% with respect to 4-bromoaniline. ^{1}H NMR: δ = 1.16 (s, 18 H), 3.47 and 3.48 (A_2B_2, 8 H), 6.54−6.60 (AA′BB′, 2 H), 7.22−7.27 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 27.5, 52.2, 58.6, 73.1, 107.3, 113.2, 131.8, 147.0 ppm. FT-IR: $\tilde{\nu}_{max}$ = 3090, 3043, 2972, 2932, 2904, 2871, 1591, 1498, 1472 (sh), 1383, 1363, 1272−1196, 1130−1083, 881, 806, 738 cm^{-1}.

9-[4-(Dimethylamino)phenyl]-3,3-dimethyl-1,5-dioxaspiro[5.5]-undecan-9-ol (5): A solution of 4-bromo-*N*,*N*-dimethylaniline (40.4 g, 202 mmol) in THF (200 mL) was added to magnesium (5.16 g, 212 mmol), which had been activated by dry-stirring[22] for 2 d. The mixture began to boil and the reaction was kept under control by occasional cooling with an ice-bath. Stirring was continued overnight at room temperature. The mixture was cooled to −30 °C and a solution of 3,3-dimethyl-1,5-dioxaspiro[5.5]undecan-9-one (**4**)[71] (36.0 g, 182 mmol) in THF (120 mL) was added dropwise, while maintaining the temperature of the reaction mixture below −30 °C. Stirring was continued for 1 h at −30 °C and then overnight at room temperature. The reaction mixture was poured into a saturated NH_4Cl solution (140 mL) and extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layers were dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure afforded a dark-green solid, which was subjected to column chromatography [SiO_2 (400 g); eluent: *n*-hexane/ethyl acetate, 3:1 v/v, followed by ethyl acetate when the *N*,*N*-dimethylaniline impurity had been collected]. This procedure afforded **5** (37.3 g, 64%) as an off-white solid. An analytically pure sample was prepared by recrystallization from diethyl ether to yield **5** as a colorless solid (m.p. 137−138 °C). ^{1}H NMR: δ = 0.98 (s, 6 H), 1.52 (s, OH), 1.69−1.74 (m, 2 H), 1.84−1.95 (m, 2 H), 2.00−2.15 (2 × m, 4 H), 2.92 (s, 6 H), 3.49 (s, 2 H), 3.56 (s, 2 H), 6.68−6.73 (AA′BB′, 2 H), 7.34−7.39 (AA′BB′, 2 H) ppm. ^{13}C NMR: (APT): δ = 22.7, 40.6 (CH_3); 112.3, 125.4 (CH); 30.2, 72.2, 97.3, 136.4, 149.5 (q); 28.2, 35.2, 70.0 (CH_2) ppm. FT-IR: $\tilde{\nu}_{max}$ = 3534 (sharp, OH), 3238 (broad, OH), 2966, 2947, 2939, 2921, 2864, 2850, 2808, 1610, 1516, 1505, 1368, 1361, 1247, 1145, 1102, 987, 937, 842, 825, 819, 573, 549, 541 cm^{-1}.

9-[4-(Dimethylamino)phenyl]-3,3-dimethyl-1,5-dioxaspiro[5.5]undec-8-ene (6): A solution of **5** (37.1 g, 116 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg) was heated under reflux in toluene (400 mL) in a Dean−Stark apparatus until the theoretical amount of water had separated (30 min). TLC (*n*-hexane/ethyl acetate, 3:1 v/v) showed that all starting compound had disappeared. Ethyl acetate (150 mL) was added and the catalyst was removed by flash chromatography over a short silica column [6 × 2 cm (cross section)]. Evaporation of the solvent under reduced pressure afforded crude **6** as an off-white solid (34.8 g, 99%). An analytically pure sample of **6** was prepared by recrystallization from MeOH (80 mg mL^{-1}) yielding colorless needles (m.p. 113−114 °C). ^{1}H NMR: δ = 0.98 (s, 3 H), 1.07 (s, 3 H), 2.11−2.15 (m, 2 H), 2.52−2.57 (2 × m, 4 H), 2.95 (s, 6 H), 3.55 and 3.64 (AB, J_{AB} = 11.3 Hz, 2 × 2 H), 5.84−5.87 (m, 1 H), 6.68−6.73 (AA′BB′, 2 H), 7.30−7.35 (AA′BB′, 2 H) ppm. ^{13}C NMR (APT): δ = 22.5, 22.8, 40.6 (CH_3); 25.5, 27.9, 35.0, 70.3 (CH_2); 30.2, 97.1, 129.8, 135.5, 149.5 (q); 112.3, 117.2, 125.7 (CH) ppm. FT-IR: $\tilde{\nu}_{max}$ = 2944, 2923, 2899, 2863, 2801, 1869 (w), 1611, 1524, 1395, 1246, 1229, 1203, 1166, 1113 (s), 860, 819, 798 cm^{-1}.

4-(3,3-Dimethyl-1,5-dioxaspiro[5.5]undec-9-yl)-*N*,*N*-dimethylaniline (7): A solution of **6** (34.5 g, 114 mmol) in THF (500 mL) was stirred with a catalytic amount of 10% Pd on carbon under 1 atm of H_2 until, after 2 d, the uptake of hydrogen had ceased. GC showed a conversion of over 99.9%. The solution was filtered through Celite and then evaporation of the solvent yielded **7** as an off-white solid (34.1 g, 98%). A small sample was purified by charcoal treatment and subsequent crystallization (60 mg mL^{-1}) from *n*-hexane/ethyl acetate (10:1 v/v) to yield **7** as colorless needles (m.p. 102−104 °C). ^{1}H NMR: δ = 0.98 (s, 6 H), 1.40−1.51 (m, 2 H), 1.61−1.77 (two overlapping m, 4 H), 2.34−2.39 (m, 2 H), 2.42−2.53 (m, 1 H), 2.91 (s, 6 H), 3.52 (s, 2 H), 2.55 (s, 2 H), 6.71−6.73 (m, 2 H), 7.10−7.13 (m, 2 H) ppm. ^{13}C NMR (APT): δ = 22.7, 40.7, 42.8, 112.8, 127.3 (CH and CH_3); 30.1, 97.2, 134.9, 149.0 (q); 30.2, 32.5, 69.8, 70.0 (CH_2) ppm. FT-IR: $\tilde{\nu}_{max}$ = 2950, 2929, 2859, 2797, 1866 (w), 1617, 1523, 1395, 1292, 1242−1209, 1168, 1137−1103, 916, 873, 814, 797, 544, 495 cm^{-1}.

4-[4-(Dimethylamino)phenyl]cyclohexanone (8): A solution of **7** (32.9 g, 108 mmol) in 2 M HCl solution (180 mL) and THF (180 mL) was heated under reflux for 1 h. The hot solution was poured into a large Erlenmeyer flask containing solid $NaHCO_3$ (35.4 g, 421 mmol) while stirring vigorously. When all the CO_2 had evolved, most of the THF was evaporated under reduced pressure. The white suspension was extracted with CH_2Cl_2 (5 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (25 mL), water (25 mL), and dried with $MgSO_4$. Filtration and then concentration of the filtrate under reduced pressure gave **7** (21.5 g, 91%) as an off-white solid, which was used in following reactions without purification. A sample was treated with charcoal in *n*-hexane. Subsequent crystallization from *n*-hexane (25 mg mL^{-1}) gave analytically pure **7** as colorless crystals (m.p. 57.5−58 °C). ^{1}H NMR: δ = 1.83−1.97 (m, 2 H), 2.17−2.22 (m, 2 H), 2.46−2.56 (m, 4 H), 2.89−2.99 (m, 1 H), 2.92 (s, 6 H), 6.69−6.74 (AA′BB′, 2 H), 7.10−7.14 (AA′BB′, 2 H) ppm. ^{13}C NMR (APT): δ = 34.2, 41.4 (CH_2); 40.7, 41.7, 112.9, 127.2 (CH and CH_3); 132.7, 149.4, 211.6 (q) ppm. IR: $\tilde{\nu}_{max}$ = 2970, 2950, 2870, 2805, 1720, 1620, 1525, 1350, 1330, 1160, 1060, 925, 945, 825, 795, 525, 495 cm^{-1}.

1-[4-(Dimethylamino)phenyl]cyclohexanol (10): A mixture of 4-bromo-*N*,*N*-dimethylaniline (20.3 g, 101 mmol) and Mg (2.58 g, 106 mmol) in THF (100 mL) was treated with ultrasound (bath) for 2 h at room temperature until most of the magnesium had disappeared. ***Caution:*** Occasionally the reaction proceeded so fast that ice-cooling was necessary. A solution of cyclohexanone (**9**) (8.94 g, 91.1 mmol, which had been stored on 4 Å molecular sieves) in THF (60 mL) was added dropwise over 15 min, while keeping the temperature below −30 °C. The resulting suspension was stirred at −30 °C for 1 h and then overnight at room temperature. The mixture was subsequently poured in a saturated NH_4Cl solution (200 mL) and extracted with CH_2Cl_2 (2 × 100 mL). The combined extracts were dried with $MgSO_4$ and filtered. Evaporation of the solvent under reduced pressure afforded a brown oil (22.1 g) which was subjected to column chromatography (eluent: *n*-hexane/ethyl acetate, 10:1 v/v) to yield **10** (11.4 g, 57%) as an off-white solid. ^{1}H NMR: δ = 1.22−1.36 (m, 1 H), 1.48 (s, OH), 1.55−1.89 (m, 9 H), 2.93 (s, 6 H), 6.70−6.75 (AA′BB′, 2 H), 7.35−7.40 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 22.4, 25.6, 38.8, 40.6, 72.6, 112.4, 125.5, 137.3, 149.4 ppm. IR: $\tilde{\nu}_{max}$ = 3340 (broad), 2950, 2870, 2860, 2825, 1625, 1530, 1320, 1200, 1140, 965, 940, 850, 820, 800, 540 cm^{-1}.

4-(Cyclohex-1-enyl)-*N*,*N*-dimethylaniline (11): Solid **10** (11.4 g, 52.0 mmol) was added to trifluoroacetic acid (65 mL) whilst stirring at room temperature. After 10 min, the reaction mixture was slowly added to a saturated $NaHCO_3$ solution (800 mL). The resulting white suspension was extracted with diethyl ether (3 × 150 mL). The combined organic layers were dried with $MgSO_4$ and filtered. Evaporation of the solvent under reduced pressure yielded **11** (10.2 g, 97%) as an off-white solid [m.p. 53 °C (ref.[72] 54.5−55

°C)], which was used in the next step without further purification. ^{1}H NMR: δ = 1.60−1.69 (m, 2 H), 1.72−1.80 (m, 2 H), 2.15−2.22 (m, 2 H), 2.34−2.41 (m, 2 H), 2.93 (s, 6 H), 5.99−6.02 (m, 1 H), 6.71−6.76 (AA′BB′, 2 H), 7.27−7.32 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 22.3, 23.2, 25.8, 27.3, 41.0, 113.0, 121.9, 125.6, 132.0, 135.9, 149.0 ppm.

4-Cyclohexyl-*N*,*N*-dimethylaniline (D1): A solution of **11** (10.2 g, 50.7 mmol) in THF/EtOH (1:1 v/v, 150 mL) was stirred overnight in the presence of a catalytic amount of 10% Pd/C under 1 atm of H_2. The reaction mixture was filtered through Celite. After removal of most of the solvent under reduced pressure, the remaining oil was subjected to vacuum distillation using a 10 cm Vigreux column. **D1** (6.47 g, 63%) was collected as a colorless oil at 113 °C (0.02 Torr) (ref.[73] 162−164 °C; 11 Torr). ^{1}H NMR: δ = 1.16−1.45 (m, 5 H), 1.69−1.87 (m, 5 H), 2.35−2.44 (m, 1 H), 6.67−6.72 (AA′BB′, 2 H), 7.06−7.11 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 26.4, 27.0, 34.7, 40.9, 43.5, 113.0, 127.3, 136.6, 149.0 ppm.

3,3-Dimethyl-9-{4-[*N*,*N*-bis(2-*tert*-butoxyethyl)amino]phenyl}-1,5-dioxaspiro[5.5]undecan-9-ol (12): *n*-Butyllithium in hexanes (1.59 M, 190 mL, 302 mmol) was added to a stirred solution of **3** (56.3 g, 151 mmol) in THF (150 mL), while keeping the temperature below −70 °C. Stirring was continued for 2 h at −78 °C and then a solution of 3,3-dimethyl-1,5-dioxaspiro[5.5]undecan-9-one (**4**)[71] (30.0 g, 151 mmol) in THF (100 mL) was added dropwise over 10 min, while keeping the temperature below −60 °C. The mixture was stirred for another 2 h at −60 °C and was then warmed to room temperature overnight. The mixture was poured into a saturated NH_4Cl solution (110 mL) and the organic layer was separated from the water layer. The water layer was washed with diethyl ether (2 × 100 mL) and the combined organic layers were dried with $MgSO_4$. Filtration followed by removal of the solvent under reduced pressure afforded an oil that was subjected to column chromatography [SiO_2 (500 g); *n*-hexane/ethyl acetate, 10:1 v/v]. This procedure gave of a slightly yellow solid (46.0 g; 62% with respect to **3**) that mainly consisted of **12**, which was used in the next step without further purification. An analytically pure sample was obtained by recrystallization from *n*-hexane (50 mg mL^{-1}), which yielded colorless needles (71%; m.p. 112−115 °C). ^{1}H NMR: δ = 0.90 (s, 6 H), 1.18 (s, 18 H), 1.41 (s, OH), 1.43−1.72 (m, 2 H), 1.87−1.95 (m, 2 H), 2.00−2.06 (m, 2 H), 2.10−2.15 (m, 2 H), 3.49 (s, 2 H superposed on a singlet-like A_2B_2 system of 8 H), 3.57 (s, 2 H), 6.64−6.68 (AA′BB′, 2 H), 7.30−7.35 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 22.7, 27.5, 28.3, 30.2, 35.2, 52.1, 58.7, 70.1, 72.2, 73.0, 97.3, 111.0, 125.6, 135.3, 146.8 ppm. FT-IR: $\tilde{\nu}_{max}$ = 3486 (OH), 2974, 2922, 2867, 1614, 1521, 1390, 1364, 1197, 1111, 1065, 978, 814, 540 cm^{-1}.

***N*,*N*-Bis(2-*tert*-butoxyethyl)-4-(3,3-dimethyl-1,5-dioxaspiro[5.5]-undec-8-en-9-yl)aniline (13):** A solution of crude **12** (38.1 g) and a catalytic amount of *p*-toluenesulfonic acid monohydrate (9 mg, 0.05 mmol) in toluene (400 mL) was treated as described for **6** (using 130 mL of ethyl acetate in the workup). Crude **13** was afforded as an off-white solid (36.6 g). A pure sample was obtained in 100% yield from analytically pure **12** using the same procedure (m.p. 77−79 °C). ^{1}H NMR: δ = 0.95 (s, 3 H), 1.03 (s, 3 H), 1.17 (s, 18 H), 2.07−2.11 (m, 2 H), 2.49−2.53 (2 × m, 4 H), 3.49 (singlet-like A_2B_2 system, 8 H), 3.52 and 3.60 (AB, J_{AB} = 11.4 Hz, 2 × 2 H), 5.79−5.81 (m, 1 H), 6.61−6.64 (AA′BB′, 2 H), 7.24−7.27 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 22.6, 22.8, 25.5, 27.5, 28.1, 30.2, 34.9, 52.1, 58.8, 70.3, 73.0, 97.1, 111.1, 116.7, 125.9, 128.7, 135.4, 146.8 ppm. FT-IR: $\tilde{\nu}_{max}$ = 2973, 2954, 2941, 2891, 2868, 1608, 1522, 1393, 1380, 1364, 1359, 1200, 1116, 1089, 856, 814, 798, 790, 739, 533 cm^{-1}.

***N*,*N*-Bis(2-*tert*-butoxyethyl)-4-(3,3-dimethyl-1,5-dioxaspiro[5.5]-undecan-9-yl)aniline (14):** A solution of **13** (36.6 g) in EtOH/THF (1:1 v/v, 220 mL) was treated as described for **7**, yielding crude **14** (36.8 g, 100%). Crystallisation from MeOH (225 mL) afforded colorless needles of pure **14** (19.2 g). The mother liquor was concentrated under reduced pressure and further concentrated by Kugelrohr distillation at 0.001 Torr and 130 °C, yielding a brown oil (7.21 g), which was crystallized from MeOH (29 mL) to yield the pure product (5.29 g). Total yield: 24.5 g of **14** (m.p. 103−104 °C). This yield is 66% with respect to **12**. ^{1}H NMR: δ = 0.98 (s, 6 H), 1.18 (s, 18 H), 1.40−1.50 (m, 2 H), 1.60−1.76 (m, 4 H), 2.34−2.38 (m, 2 H), 2.40−2.50 (m, 1 H), 3.46 and 3.49 (A_2B_2, *J* = 7.2 Hz, 8 H), 3.51 (s, 2 H), 3.55 (s, 2 H), 6.61−6.64 (AA′BB′, 2 H), 7.05−7.08 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 22.8, 27.5, 30.2 (q), 30.4, 32.6, 42.8, 52.1, 58.8, 69.9, 70.1, 73.0, 97.4, 111.3, 127.6, 133.8, 146.3 ppm. FT-IR: $\tilde{\nu}_{max}$ = 2969, 2948, 2934, 2910, 2863, 2856, 1618, 1521, 1391, 1383, 1361, 1202, 1187, 1132, 1114, 1097, 1080, 955, 913, 814, 796, 537 cm^{-1}.

2-{4-[4-(Dimethylamino)phenyl]-1-hydroxycyclohexyl}-2-methylpropanoic Acid (16): *n*-Butyllithium in hexanes (1.6 M, 26 mL, 41.6 mmol) was added to a solution of *N*,*N*-diisopropylamine (4.22 g, 41.7 mmol, which had been stored over KOH) in THF (85 mL) at −40 °C. The mixture was warmed to 0 °C over 30 min and was then recooled to −40 °C. 2-Methylpropanoic acid (1.83 g, 20.8 mmol) in THF (4 mL) was added. The mixture was heated to 50 °C and after 2 h it was cooled to −40 °C, and then **8** (3.63 g, 16.7 mmol) was added. After stirring for another 2 h, the mixture was heated to 50 °C and kept at that temperature for 1 h. Subsequently, it was poured over ice (170 g) under vigorous stirring. The mixture was extracted with diethyl ether (4 × 40 mL) and the aqueous phase was acidified to pH 7 with 3 M HCl solution (13 mL) and then with 1 M HCl to pH 3−4. The resulting white suspension was extracted with CH_2Cl_2 (200 mL, followed by 3 × 50 mL). The combined organic layers were dried with $MgSO_4$ and filtered. Evaporation of the solvent under reduced pressure gave an off-white solid (4.34 g), which was extracted with *n*-pentane in a Soxhlett apparatus overnight to remove any starting compounds. The remaining solid (3.65 g, 72%) proved to be pure **16** (m.p. 189−191 °C, dec). ^{1}H NMR: δ = 1.29 (s, 6 H), 1.60−1.91 (m, 8 H), 2.33−2.43 (m, 1 H), 2.90 (s, 6 H), ca. 6.6 (broad, OH), 6.73−6.77 (AA′BB′, 2 H), 7.10−7.15 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 21.0, 29.3, 31.8, 41.2, 42.7, 50.0, 74.0, 113.6, 127.4, 135.9, 149.0, 182.0 ppm. FT-IR: $\tilde{\nu}_{max}$ = 3541 (sharp, OH), 3439 (br., OH), 3159 (br., OH), 2998, 2970, 2955, 2942, 2929, 2879, 2857, 2617 and 2502 (br., NH^+), 1941 (br), 1714, 1612, 1516, 1388, 1275, 1258, 1232, 1157, 1139, 1048, 962, 927, 830, 818, 802, 552 cm^{-1}.

***N*,*N*-Dimethyl-4-[4-(1-methylethylidene)cyclohexyl]aniline (D2):** *N*,*N*-Dimethyl-1,1-bis(neopentyloxy)methanamine (6.03 g, 26.1 mmol) was added to a suspension of **16** (3.58 g, 11.7 mmol) in MeCN (140 mL). After stirring for 30 min at room temperature, the clear solution was heated overnight under reflux. The solvent was evaporated under reduced pressure and the resulting brown oil was subjected to column chromatography [silica (100 g); eluent: CH_2Cl_2]. The light-brown solid obtained (2.60 g) was treated with charcoal (1 g) in *n*-hexane/CH_2Cl_2 (1:1 v/v, 60 mL) and then filtered through Celite. The solvent was evaporated under reduced pressure and the resulting solid was recrystallized under N_2 from deoxygenated MeOH (113 mg mL^{-1}, cooled from boiling to room temperature) twice. This procedure yielded colorless plate-shaped crystals (1.03 g, 36%) of **D2** (m.p. 59−60 °C). ^{1}H NMR: δ = 1.34−1.48 (m, 2 H), 1.69−1.70 (m, 6 H), 1.82−1.97 (m, 4 H), 2.53−2.64 (m, 1 H), 2.75−2.80 (m, 2 H), 2.89 (s, 6 H), 6.67−6.72 (AA′BB′, 2 H),

7.06−7.11 (AA′BB′, 2 H) ppm. ^{13}C NMR (APT): δ = 20.0, 40.9, 43.8, 112.9, 127.4 (CH and CH_3); 30.2, 35.5 (CH_2); 120.7, 131.1, 135.7, 149.1 (q) ppm. FT-IR: $\tilde{\nu}_{max}$ = 2988, 2958, 2921, 2848, 2793, 1615, 1522, 1443, 1339, 1224, 1060, 978, 946, 914, 819, 798, 552, 531 cm^{-1}. $C_{17}H_{25}N$ (243.4): calcd. C 83.89, H 10.35, N 5.75; found C 83.88, H 10.26.

{4-[4-(Dimethylamino)phenyl]cyclohexylidene}malononitrile (DA1): Malononitrile (1.43 g, 21.6 mmol) and β-alanine (123 mg, 1.38 mmol) were added to a solution of **8** (4.36 g, 20.1 mmol) in 85% EtOH (50 mL) stirred at room temperature. A precipitate began to form immediately. After 6 h the suspension was concentrated at the rotary evaporator without heating. Water (25 mL) was added and the mixture was filtered through a glass frit. The residue was washed with water (3 × 25 mL) and dried under vacuum. This crude product (4.64 g) was dissolved in *n*-hexane/ethyl acetate (1:1 v/v, 120 mL) and purified by flash chromatography over a short silica column [6 × 2 cm (cross section)]. Evaporation of the solvent under reduced pressure gave yellow crystals (4.61 g) that were purified by three crystallizations from boiling *n*-hexane/ethyl acetate (1:1 v/v, 46 mg·mL^{-1}). The purity of these crystals was checked after each crystallization by their fluorescence in diethyl ether. Yield: 1.39 g (26%) of light-yellow needles (m.p. 149−151 °C). ^{1}H NMR: δ = 1.65−1.79 (m, 2 H), 2.18−2.25 (m, 2 H), 2.43−2.54 (m, 2 H), 2.77−2.85 (m, 1 H), 2.94 (s, 6 H), 3.13−3.19 (m, 2 H), 6.71−6.74 (AA′BB′, 2 H), 7.05−7.10 (AA′BB′, 2 H) ppm. ^{13}C NMR (APT and CH correlation): δ = 34.3, 34.5 (CH_2); 40.4, 112.6, 127.0 (CH); 41.4 (CH_3); 82.7, 111.5, 131.3, 149.3, 183.9 (q) ppm. FT-IR: $\tilde{\nu}_{max}$ = 2953, 2939, 2888, 2864, 2802, 2230, 1615, 1602, 1598, 1523, 1444, 1357, 1345, 1332, 946, 822, 803, 544 cm^{-1}. $C_{17}H_{19}N_3$ (265.4): calcd. C 76.95, H 7.22, N 15.84; found C 77.08, H 7.31.

Methyl Cyano{4-[4-(dimethylamino)phenyl]cyclohexylidene}acetate (DA2): A mixture of β-alanine (0.111 g), methyl cyanoacetate (2.56 g, 25.8 mmol) and ketone **8** (4.34 g, 20.0 mmol) in MeOH/water (16:3 v/v, 47.5 mL) was stirred at room temperature. A precipitate began to form after ca. 1 d. After 100 h, most of the solvent was evaporated, using a rotary evaporator without external heating, and then CH_2Cl_2 (50 mL) was added to the residue. The water layer was separated and the organic layer was washed with water (3 × 50 mL), dried with $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure to afford an off-white solid. This solid was crystallized twice from diethyl ether to give off-white crystals (2.30 g) of **DA2**. The product was further purified by flash chromatography (eluent: *n*-hexane/ethyl acetate, 1:1 v/v) followed by two crystallizations from the same solvent mixture (115 mg·mL^{-1} and 333 mg·mL^{-1}). This procedure gave **DA2** (1.16 g, 19%) as colorless crystals (m.p. 109 °C). ^{1}H NMR: δ = 1.58−1.80 (m, 2 H), 2.11−2.28 (m, 3 H), 2.41−2.52 (m, 1 H), 2.75−2.85 (m, 1 H), 2.92 (s, 6 H), 3.14−3.23 (m, 1 H), 3.84 (s, 3 H), 4.03−4.09 (m, 1 H), 6.67−6.72 (AA′BB′, 2 H), 7.04−7.09 (AA′BB′, 2 H) ppm. ^{13}C NMR (APT): δ = 31.2, 35.1, 35.4, 36.6 (CH_2); 40.6, 42.2, 52.5 (CH and CH_3); 102.0, 115.4, 132.4, 149.4, 162.3, 179.3 (q); 112.8, 127.2 (CH) ppm. FT-IR: $\tilde{\nu}_{max}$ = 2954, 2937, 2916, 2898, 2874, 2813, 2223, 1731, 1616, 1592, 1523, 1430, 1288, 1241, 806, 788, 778, 539 cm^{-1}. $C_{18}H_{22}N_2O_2$ (298.4): calcd. C 72.46, H 7.43, N 9.39, O 10.72; found C 72.41, H 7.51, O 10.66.

Dimethyl {4-[4-(Dimethylamino)phenyl]cyclohexylidene}malonate (DA3): A solution of $TiCl_4$ (2.2 mL, 20 mmol) in dry CCl_4 (20 mL; stored over 4 Å molecular sieves) was slowly added to THF (40 mL), while maintaining the temperature below 0 °C. A solution of dimethyl malonate (1.27 g, 9.60 mmol) and ketone **8** (1.94 g, 8.93 mmol) in THF (20 mL) was added to this mixture. Subsequently, a solution of pyridine (2.90 g, 36.7 mmol; stored on 4 Å molecular sieves) in THF (20 mL) was added over ca. 10 min while maintaining the temperature between −5 and 0 °C. The resulting reaction mixture was stirred for 3 d at room temperature and then saturated aqueous Na_2CO_3 (200 mL) and *n*-hexane (200 mL) were added. The organic layer was separated and the aqueous layer was extracted with *n*-hexane (2 × 150 mL). The combined organic extracts were washed sequentially with saturated NaCl solution, saturated Na_2CO_3 solution, and saturated NaCl solution. The organic layer was dried with $MgSO_4$ and filtered. Evaporation of the solvent under reduced pressure yielded a brown oil (2.06 g), which was purified by column chromatography (eluent: petroleum ether/diethyl ether/chloroform, 4:1:1 v/v/v). The product was crystallized twice from MeOH and then from EtOH, yielding colorless needles (0.18 g, 6%; m.p. 91.0 °C). ^{1}H NMR: δ = 1.59−1.73 (m, 2 H), 2.04−2.22 (2 × m, 2 × 2 H), 2.68−2.78 (m, 1 H), 2.91 (s, 6 H), 3.16−3.20 (m, 2 H), 3.78 (s, 6 H), 6.67−6.72 (m, 2 H), 7.05−7.10 (m, 2 H) ppm. ^{13}C NMR: δ = 32.5, 35.3, 40.8, 42.8, 52.1, 112.9, 121.6, 127.3, 133.6, 149.3, 161.2, 166.1 ppm. FT-IR: $\tilde{\nu}_{max}$ = 2952, 2938, 2913, 2853, 2801, 1729, 1723, 1628, 1615, 1522, 1305, 1239, 1194, 1063, 810, 758, 539 cm^{-1}. $C_{19}H_{25}NO_4$ (331.4): calcd. C 68.86, H 7.60, N 4.23, O 19.31; found C 68.74, H 7.68, O 19.24.

Didodecyl Malonate: A solution of triethylamine (15.9 g, 157 mmol) and 1-dodecanol (28.0, 150 mmol) in diethyl ether (75 mL) was added dropwise to a stirred solution of malonoyl dichloride (10.5 g, 74.5 mmol) in diethyl ether (75 mL) while keeping the temperature between −5 and 0 °C. Subsequently, the reaction mixture was stirred overnight at room temperature. The mixture was washed with 0.1 M HCl solution (70 mL) and the aqueous layer was extracted with diethyl ether (50 mL). The combined organic layers were washed with water (50 mL) and dried with $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure. The remaining brown oil was dissolved in petroleum ether/diethyl ether (1:1 v/v; 200 mL) and subjected to flash column chromatography. The eluate was treated with active carbon, filtered and, after removal of the solvent, recrystallized from EtOH and petroleum ether to yield didodecyl malonate (11.7 g, 36%) as colorless crystals (m.p. 33.2 °C; ref.[74] 35 °C, ref.[75] 32.5 °C). ^{1}H NMR and ^{13}C NMR spectra were in accordance with those reported in ref.[76].

Didodecyl {4-[4-(Dimethylamino)phenyl]cyclohexylidene}malonate (DA4): A solution of $TiCl_4$ (2.2 mL, 20 mmol) in dry CCl_4 (10 mL) was slowly added to THF (40 mL), while maintaining the temperature below 0 °C. A solution of didodecyl malonate (4.01 g, 9.10 mmol) and ketone **8** (1.97 g, 9.07 mmol) in THF (20 mL) was added to this mixture. Subsequently, a solution of pyridine (2.89 g, 36.5 mmol) in THF (20 mL) was added over ca. 20 min while maintaining the temperature just below 0 °C. The resulting reaction mixture was stirred for 3 d at room temperature. Water (60 mL) and diethyl ether (70 mL) were added, and then the water layer was extracted with diethyl ether (2 × 60 mL). The combined organic layers were washed sequentially with saturated NaCl solution (60 mL), saturated Na_2CO_3 solution (60 mL) and saturated NaCl solution solution (60 mL). The combined aqueous layers were extracted again as described above and all the organic phases were combined and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure afforded a residue that was subjected to flash chromatography (eluent: petroleum ether/diethyl ether, 2:1 v/v) and, after evaporation of the solvent, the product was recrystallized from MeOH, subjected to column chromatography (eluent: *n*-hexane/ethyl acetate, 20:1 v/v) and again recrystallized from MeOH, EtOH, and petroleum ether. This procedure yielded **DA4** (0.73 g, 13%) as a colorless solid (m.p. 48.1−49.3 °C). ^{1}H NMR: δ =

0.86−0.90 (m, 6 H), 1.26−1.30 (m, 40 H), 1.60−1.73 (2 × m, 6 H), 2.04−2.21 (2 × m, 4 H), 2.68−2.78 (m, 1 H), 2.91 (s, 6 H), 3.18−3.22 (m, 2 H), 4.14−4.19 (m, 4 H), 6.68−6.71 (m, 2 H), 7.06−7.09 (m, 2 H) ppm. ^{13}C NMR: δ = 14.1, 22.7, 26.0, 28.6, 29.3, 29.4, 29.6 (3 resolved signals), 29.7, 31.9, 32.4, 35.3, 40.8, 42.9, 65.1, 112.9, 122.4, 127.3, 133.7, 149.3, 160.2, 165.8 ppm. FT-IR: $\tilde{\nu}_{max}$ = 2956 (m); 2913, 2849, 1734, 1712 (s); 1616, 1521, 1470, 1344, 1300, 1070, 941, 821, 813, 719 cm^{-1}. $C_{41}H_{69}NO_4$ (640.0) calcd. C 76.94, H 10.87, N 2.19, O 10.00; found C 76.87 H 10.95, O 9.85.

(4-Phenylcyclohexylidene)malononitrile (A1): Malononitrile (1.37 g, 207 mmol) and β-alanine (115 mg) were added to a stirred solution of 4-phenylcyclohexanone (3.48 g, 200 mmol) in MeOH/water (16:3 v/v, 50 mL) at room temperature. After 10 min a white precipitate began to form. After 5 h, most of the solvent was evaporated at the rotary evaporator without heating. Water (25 mL) was added and the mixture was filtered through a glass frit. The solid was washed with water (2 × 25 mL) and dried under reduced pressure to give crude **A1** (4.35 g), which was purified by flash chromatography using *n*-hexane/ethyl acetate (1:1) as the eluent. Evaporation of the solvent under reduced pressure gave a white solid that was recrystallized from *n*-hexane/ethyl acetate (7:2 v/v; 87 mg·mL^{-1}) to give **A1** (3.19 g, 72%) as colorless crystals (m.p. 104.5−105.5 °C). ^{1}H NMR: δ = 1.68−1.82 (m, 2 H), 2.22−2.28 (m, 2 H), 2.44−2.55 (m, 2 H), 2.83−2.93 (m, 1 H), 3.16−3.20 (m, 2 H), 7.17−7.24 (m, 2 H), 7.25−7.27 (m, 1 H), 7.30−7.35 (m, 2 H) ppm. ^{13}C NMR: δ = 34.4 (2 overlapping signals), 42.8, 83.3, 111.5, 126.6, 126.9, 128.7, 143.5, 183.3 ppm. FT-IR: $\tilde{\nu}_{max}$ = 3086, 3063, 3032, 2963, 2952, 2929, 2877, 2865, 2228 (C≡N), 1593, 1495, 1445, 1431, 1427, 1370, 1339, 1021, 1003, 986, 759, 701, 533 cm^{-1}. $C_{15}H_{14}N_2$ (222.3) calcd. C 81.05, H 6.35, N 12.60; found C 80.96, H 6.35.

4-{4-[*N*,*N*-Bis(2-hydroxyethyl)amino]phenyl}cyclohexanone (17): A solution of **14** (28.4 g, 59.7 mmol) in dioxane/2 M HCl solution (1:1 v/v, 360 mL) was heated under reflux for 3.5 h. The hot mixture was poured over $NaHCO_3$ (35.2 g, 419 mmol) while stirring vigorously. After most of the CO_2 had evolved, the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried with $MgSO_4$. After filtration and removal of most of the solvent under reduced pressure, residual solvents and 2,2-dimethylpropane-1,3-diol were evaporated by kugelrohr distillation at 80 °C (0.001 Torr) yielding **17** (16.4 g, 99%). The product was further purified by column chromatography (eluent: *n*-hexane/EtOH, 4:1 v/v) to yield **17** (14.8 g, 89%) as a white solid. A sample was recrystallized from *n*-hexane/ethyl acetate (2:3 v/v, 22.8 mg·mL^{-1}) to yield analytically pure **17** as colorless crystals (m.p. 101 °C). ^{1}H NMR: δ = 1.82−1.96 (m, 2 H), 2.15−2.21 (m, 2 H), 2.46−2.56 (m, 4 H), 2.89−2.99 (m, 1 H), 3.07 (broad s, 2 H), 3.56 (t, *J* = 4.9 Hz, 2 H), 3.85 (t, *J* = 4.7 Hz, 2 H), 6.66−6.71 (AA′BB′, 2 H), 7.08−7.13 (AA′BB′, 2 H) ppm. ^{13}C NMR: δ = 34.2, 41.4, 41.6, 55.4, 60.8, 112.8, 127.4, 133.1, 146.6, 211.7 ppm. FT-IR: $\tilde{\nu}_{max}$ = 3229, 3144 (br., s); 2944, 2923, 2898, 2866, 2850, 1698, 1617, 1521, 1461, 1425, 1348, 1239, 1225, 1187, 1161, 1111, 1081, 1069, 1062, 1054, 802, 641 (br., w), 559, 549, 493, 470 cm^{-1}.

(4-{4-[Bis(2-hydroxyethyl)amino]phenyl}cyclohexylidene)malononitrile (18): β-Alanine (79 mg, 0.89 mmol) and malononitrile (0.618 g, 9.36 mmol) were added to a stirred solution of ketone **17** (2.47 g, 8.91 mmol) in 85% EtOH (25 mL). The mixture was stirred overnight at room temperature, after which time a precipitate had formed. The reaction mixture was stored at −20 °C for 12 h to allow more product to precipitate. Then mixture was filtered and the residue was washed with water (3 × 10 mL), dissolved in THF and purified with flash chromatography. Evaporation of the solvent under reduced pressure gave **18** (2.41 g, 83%) as an off-white solid. Pure **18** was obtained by repeated crystallization from THF/diethyl ether (1:1 v/v, 19 mg·mL^{-1}; dissolution in THF at room temperature followed by addition of diethyl ether and crystallization at −20 °C) followed each time by flash chromatography with THF. The fluorescence purity was monitored in diethyl ether. This procedure gave **18** (1.54 g, 53%) as slightly yellow crystals (m.p. 137−139 °C). ^{1}H NMR ($CDCl_3$ with some drops of [D$_6$]DMSO to enhance the solubility): δ = 1.63−1.77 (m, 2 H), 2.17−2.23 (m, 2 H), 2.46−2.56 (m, 2 H), 2.75−2.85 (m, 1 H), 3.11−3.16 (m, 2 H), 3.53 (apparent t, *J* = 5.0 Hz, 4 H), 3.78 (apparent q, *J* = 5.1 Hz, 4 H), 4.57 (apparent t, *J* = 5.4 Hz, 2 × OH), 6.67−6.70 (AA′BB′, 2 H), 7.01−7.07 (AA′BB′, 2 H) ppm. ^{13}C NMR ($CDCl_3$ with some drops of [D$_6$]DMSO): δ = 34.3, 34.6, 41.4, 55.1, 60.1, 82.7, 111.4, 112.5, 131.1, 146.9, 183.8 ppm. FT-IR: $\tilde{\nu}_{max}$ = 3204 (br., s), 2951, 2943, 2922, 2882, 2865, 2230 (s, C≡N), 1612, 1598, 1522, 1358, 1187, 1059, 1006, 823, 803, 656 (br., w), 561, 534, 526, 475 cm^{-1}.

[{(Acetyloxy)ethyl}{4-[4-(dicyanomethylene)cyclohexyl]phenyl}-amino]ethyl Acetate (DA5): Compound **18** (187 mg, 0.575 mmol) and dry pyridine (0.20 mL, 2.5 mmol) were added to an ice-cooled stirred solution of acetyl chloride (95.6 mg, 1.22 mmol) in dry CH_2Cl_2 (4.85 mL). A white precipitate formed immediately, which dissolved upon warming the mixture to room temperature. Stirring was continued for 8 d at room temperature (protected from light). The solvent was evaporated under reduced pressure and the residue was subjected to column chromatography (eluent: CH_2Cl_2/acetone, 20:1 v/v). Yield: 52 mg (43%) of a yellowish oil. ^{1}H NMR: δ = 1.62−1.83 (m, 2 H), 2.05 (s, 6 H), 2.17−2.23 (m, 2 H), 2.43−2.54 (m, 2 H), 2.74−2.84 (m, 1 H), 3.13−3.18 (m, 2 H), 3.60 (t, *J* = 6.3 Hz, 4 H), 4.22 (t, *J* = 6.3 Hz, 4 H), 6.70−6.74 (m, 2 H), 7.03−7.06 (m, 2 H) ppm. ^{13}C NMR (APT): δ = 34.5, 34.7, 49.9, 61.3 (CH_2); 41.7, 112.4, 127.5 (CH); 20.8 (CH_3); 83.1, 111.6, 132.1, 145.9, 170.9, 183.7 (q) ppm. FT-IR: $\tilde{\nu}_{max}$ = 2956, 2899, 2866, 2231 (C≡N), 1737, 1614, 1598, 1520, 1445, 1381, 1369, 1230, 1197, 1047, 822, 810 cm^{-1}. $C_{23}H_{27}N_3O_4$ (409.5) calcd. C 67.46, H 6.65, N 10.26, O 15.63; found C 67.40, H 6.58, O 15.71.

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