## **FULL PAPER**

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## 1,1-Dicyano-4-[4-(diethylamino)phenyl]buta-1,3-dienes: Structure–Property Relationships

Francesca Tancini,<sup>[a]</sup> Yi-Lin Wu,<sup>[a]</sup> W. Bernd Schweizer,<sup>[a]</sup> Jean-Paul Gisselbrecht,<sup>[b]</sup> Corinne Boudon,<sup>[b]</sup> Peter D. Jarowski,<sup>[c]</sup> Marten T. Beels,<sup>[d]</sup> Ivan Biaggio,<sup>[d]</sup> and François Diederich<sup>\*[a]</sup>

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We report the synthesis and physical study of a series of 1,1dicyano-4-[4-(diethylamino)phenyl]buta-1,3-dienes in which the number and position of additional CN substituents along the 1,1-dicyanobuta-1,3-dienyl fragment is systematically varied. While X-ray analysis provided unambiguous information about molecular geometries in the crystal, UV/Vis and electrochemical measurements, by cyclic voltammetry (CV) and rotating disk voltammetry (RDV), revealed that introduction of additional cyano groups in the C2- and C4-positions most affected the optical properties of these molecules in solution, in terms of intramolecular charge-transfer ab-

## Introduction

 $\pi$ -Conjugated donor-acceptor (D–A) chromophores have been investigated for quite some time,<sup>[1,2]</sup> but have recently attracted renewed interests for potential applications in the fabrication of opto-electronic materials.<sup>[2–4]</sup> The energy and intensity of their characteristic intramolecular charge-transfer (ICT) transitions depend on the strength of the electron donor and acceptor moieties and the nature of the  $\pi$ -conjugated spacer.<sup>[5–8]</sup> While the nature of the donor, acceptor, and  $\pi$ -conjugated spacer have been systematically varied,<sup>[9]</sup> the number and positioning of the push/pull substituents along the  $\pi$ -conjugated spacer backbone has only been addressed in a few cases.<sup>[10]</sup> Our group has observed strong electro-optical effects associated with the increasing number of cyano groups in push–pull chromophores;<sup>[10e,11]</sup> sorption energy and intensity. A comparison with structurally related chromophores indicates that the shift of the anilino donor from position 2/3 to 4 along the butadiene scaffold results in a remarkable bathochromic shift of the ICT absorption maxima, mainly due to the higher planarity in the present series. These findings are further corroborated by density functional theory calculations. Preliminary nonlinear optical (NLO) measurements confirm the promise of the new pushpull chromophores as third-order nonlinear-optical molecular materials.

however, a clear indication of the effective and/or superfluous outcome of each cyano substitution as a function of position is imperative for the further design and application of such systems.

The synthesis and optical properties of 4-[4-(dimethylamino)phenyl]buta-1,3-dienes with 1,1-dicyano  $(1)^{[12]}$  and 1,1,2-tricyano  $(2)^{[13]}$  substituents (Figure 1) had been previously reported. The additional cyano group in **2** produced a bathochromic shift of the ICT-band in the UV/Vis spectrum by 0.4 eV, accompanied by a modest increase of the molar extinction coefficient (see Table 2 below). Stimulated by these early findings, we decided to prepare the complete series of 1,1-dicyano-4-[4-(dialkylamino)phenyl]buta-1,3dienes **3–8**, with additional CN substituents in positions 2, 3, 4, and combinations thereof (Figure 1).

Herein, we report the synthesis, structural characterization, and opto-electronic properties of the new push-pull chromophores **3–8**. This systematic investigation would allow the identification of the relative importance of each position along the butadiene backbone on chromophoric properties. Identification of both the most and the least effective position was anticipated to be of importance. For the latter, such ineffective position(s) could then be used to further extend the chromophores by judicious functionalization or branching to optimally tune materials properties such as stability, sublimability, solubility, or self-assembly behavior without deleteriously affecting opto-electronic attributes.

 <sup>[</sup>a] Laboratorium für Organische Chemie, ETH Zürich, Hönggerberg, HCI, 8093 Zürich, Switzerland Fax: +41-44-632-1109
 E-mail: diederich@org.chem.ethz.ch

<sup>[</sup>b] Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide UMR 7177, CNRS, Université de Strasbourg, 4, rue Blaise Pascal, CS 90032, 67081 Strasbourg Cedex, France

 <sup>[</sup>c] Advanced Technology Institute and Department of Physics, University of Surrey, Stag Hill, Guildford GU2 7XH, Surrey, United Kingdom

Stag Hill, Guildford GU2 7XH, Surrey, United Kingdom
 [d] Department of Physics and Center for Optical Technologies, Lehigh University, 415 Lewis Lab,

<sup>16</sup> Memorial Dr. East, Bethlehem, PA 18015, USA Supporting information for this article is available on the

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Figure 1. a) Known<sup>[12,13]</sup> and b) new push-pull chromophores with a 1,1-dicyano-4-[4-(dialkylamino)phenyl]buta-1,3-diene scaffold.

#### **Results and Discussion**

#### **Synthesis**

Target chromophores **3–8** were prepared by short synthetic routes, starting from ethynyl- or ethenyl-*N*,*N*-diethylanilines (Scheme 1; for the synthesis of the aniline precursors, see the Supporting Information). The dimethylamino groups in **1** and **2** were replaced by diethylamino groups to enhance the solubility of the target dipolar chromophores without much sacrifice in their crystallinity.<sup>[14]</sup> To introduce the cyano functionality in position 4 in compounds **4**, **6**, **7**, and **8**, dicyanovinyl (**9**<sup>[15]</sup>) and tricyanovinyl chloride **10**<sup>[16]</sup> were heated with appropriate ethynylanilines **11**<sup>[17]</sup> and **12** to give the 4-chlorinated buta-1,3-diene precursors **13–16** in 46–93% yield. Substitution of the chloro substituent in **13–16** by cyano was achieved by Pd-catalyzed reaction with

CuCN/KCN<sup>[18]</sup> to give the target molecules in low yields (5-32%). In the case of **3** and **5**, heating **9** and **10** with 4-(diethylamino)cinnamonitrile  $(17)^{[19]}$  in acetonitrile gave the desired products in 47% and 41% yield, respectively.

A variety of dicyanovinyl (DCV) and tricyanovinyl (TCV) derivatives have been shown to react with *N*,*N*-dialkylanilino-substituted acetylenes in a formal [2+2] cycloaddition (CA) to give a common cyclobutene intermediate, which rapidly undergoes cycloreversion (CR) with complete torquoselectivity to provide 2-anilino-substituted 1,1-dicyanobuta-1,3-dienes (Scheme 2).<sup>[20]</sup> With DCV and TCV chlorides, however, this product formation via a CA–CR cascade is not observed; rather 4-anilino-4-chloro-1,1-dicyanobuta-1,3-dienes **13–16** are formed and isolated exclusively.<sup>[21]</sup> Their formation, which is proven by X-ray analysis (see the Supporting Information), points at a slightly dif-



Scheme 1. Synthesis of target chromophores **3–8**: a) i) CH<sub>3</sub>CN, 90 °C, 2 h, 93% [(*Z*)-**13**], 85% [(*E*)-**14** + (*Z*)-**14**], 65% [(*Z*)-**15**], 46% [(*Z*)-**16**]; ii) dry toluene/DMF (5:1), 18-crown-6, KCN, CuCN, [Pd(PPh<sub>3</sub>)<sub>4</sub>], 95 °C, overnight, 28% (**4**), 20% [**6** from (*E*)-**14** + (*Z*)-**14**], 32% (**7**), 5% (**8**); b) i) CH<sub>3</sub>CN, 90 °C, 3 h, 47% (**3**), 41% (**5**).



Scheme 2. Proposed mechanisms for the reactions of DCV and TCV chlorides 9 and 10 with a) ethynylanilines 11 and 12 and b) 4-(diethylamino)cinnamonitrile (17).

ferent mechanism in the reaction with DCV and TCV chlorides (Scheme 2).

The formation of 13-16 may start with an addition-elimination process followed by conjugate re-addition of chloride to give the isolated products (route a, Scheme 2a). An alternative route b could involve formation of the cyclobutene, followed by 1,3-chloride migration<sup>[22,23]</sup> and cycloreversion. Likewise, the formation of 3 and 5 may occur through the ionic route a'[24] or involve a cyclobutane intermediate (route b'), from which elimination of HCl, followed CR, by generates the isolated buta-1,3-dienes (Scheme 2b).<sup>[13a]</sup> Given the strong polarization of the starting materials and the isolation of 14 as an (E)/(Z) mixture, the routes a and a' are conceivably likely; however, it is not clear at this stage whether these addition-elimination processes involve zwitterionic intermediates.

The (E) and (Z) configurations depicted in Scheme 1 are all supported by single-crystal X-ray analysis (see below and Supporting Information). Although a clear understanding of the observed stereoselectivity requires the knowledge about the reaction barriers, the geometries of the molecules isolated are in good agreement with theoretical calculations (see Supporting Information for details), confirming that each push-pull system adopts the energetically favored configuration. When the energy difference between (*E*) and (*Z*) isomers is low, as in the case of 14, both compounds were obtained from synthesis as an inseparable mixture. The final Pd-catalyzed substitution of Cl by CuCN/KCN occurs with retention of configuration. Interestingly buta-1,3-diene 6 was obtained exclusively as (*E*)isomer, even if a mixture of (*E*)-14 and (*Z*)-14 precursors was employed.

Target *N*,*N*-diethyl compounds **3–8** are soluble in the millimolar concentration range (0.1-20 mM) in common organic solvents, such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>CN, acetone, and toluene, giving rise to deeply colored solutions. These



solutions are stable for extended periods under normal laboratory conditions (3 months, at room temperature, under daylight exposure). They are thermally stable, with melting points ranging from 180 °C (for 8) to 220 °C (for 5).

#### X-ray Crystal Structures and Bond-Length Alternation

The target push-pull chromophores 3-8 and chloro-precursors 13-16 were all crystallized by slow diffusion of *n*pentane into a CH<sub>2</sub>Cl<sub>2</sub> solution. The crystal structures of 3-8 are depicted in Figure 2, whereas those of 13-16 are included in the Supporting Information.<sup>[25]</sup> Except for pentacyano derivatives **8** (torsion angle about C1–C2–C3–C4 153°), the buta-1,3-diene backbones in all other chromophores (**3**–7) are highly planar (torsion angles  $175-180^{\circ}$ ).

We evaluated the extent of donor-acceptor interactions in the ground state from the bond length alternation in the anilino rings.<sup>[26]</sup> Table 1 shows that these rings feature remarkably high quinoid character  $\delta r$  (for definition, see the caption to Figure 2) with  $\delta r$  values ranging from 0.043 for 4 to 0.072 for 8. These values are noticeably higher than



Figure 2. ORTEP plots of a) **3**, b) **4**, c) **5**, d) **6**, e) **7**, and f) **8** with vibrational ellipsoids shown at the 50% probability level, T = 100 K. Arbitrary numbering. Selected bond lengths [Å] and torsion angles [°]: **3**: C11–C16 1.414(3), C11–C12 1.422(3), C12–C13 1.372(3), C13–C14 1.417(3), C14–C15 1.425(3), C15–C16 1.365(3), C1–C2–C3–C4 –179.8(3); **4**: C1–C6 1.405(6), C1–C2 1.418(5), C2–C3 1.371(5), C3–C4 1.403(6), C4–C5 1.425(5), C5–C6 1.368(5), C7–C8–C9–C10 175.3(6); **5**: C5–C10 1.427(2), C5–C6 1.428(2), C6–C7 1.362(2), C7–C8 1.428(2), C8–C9 1.428(2), C9–C10 1.363(2), C1–C2–C3–C4 176.8(2); **6**: for one of the two different molecules in the unit cell: C6–C11 1.425(4), C6–C7 1.424(4), C7–C8 1.363(4), C8–C9 1.424(4), C9–C10 1.422(4), C10–C11 1.350(4), C2–C3–C4–C5 178.8(3); **7**: C5–C10 1.422(4), C5–C6 1.403(3), C6–C7 1.369(3), C7–C8 1.431(4), C8–C9 1.425(3), C9–C10 1.364(3), C1–C2–C3–C4 179.9(4); **8**: C6–C11 1.422(4), C6–C7 1.418(4), C7–C8 1.354(4), C8–C9 1.428(4), C9–C10 1.427(4), C10–C11 1.349(4), C2–C3–C4–C5 152.5(3). Quinoid character of the anilino rings  $\delta r = [(a - b) + (c - b)]/2 \approx [(a' - b') + (c' - b')]/2$ ; for the definition of bond lengths a, a', b, b', c, and c', see the figure. For benzene,  $\delta r = 0.00$ , for fully quinoid chromophores,  $\delta r = 0.10–0.12$  Å.

those of planar *N*,*N*-dialkylanilino-substituted cyanoethynylethenes<sup>[27]</sup> (up to 3 CN groups,  $\delta r$  values of 0.03–0.04) or highly non-planar 2-*N*,*N*-dialkylanilino-substituted di-, tri-, or tetracyanobuta-1,3-dienes<sup>[20,28,29]</sup> ( $\delta r$  values of 0.03– 0.063) indicating stronger intramolecular D–A interactions in **3–8**. The much higher planarity of the 4-anilino-substituted cyanobutadienes (Figure 1), as compared to 2(3)-anilino-substituted analogues, such as **18** and **19**,<sup>[2a,2b,20,28,29]</sup> evidently promotes more efficient intramolecular CT conjugation. According to the measured quinoid character, CT efficiency increases in the series **4** < **7** ≈ **3** < **5** ≈ **6** < **8**.

Table 1. Quinoid character ( $\delta r$ , standard uncertainties shown in parenthesis) of compounds **3–8** calculated from the experimental X-ray data, and <sup>1</sup>H NMR chemical shifts (300 MHz, CDCl<sub>3</sub>) for their H<sub>meta</sub> protons.

	δ <i>r</i> [Å]	$\delta_{meta}$ [ppm]	
3	0.051(3)	7.96	
4	0.043(4)	7.66	
5	0.065(2)	8.10	
6	0.067(3), 0.059(4)	8.24	
7	0.050(3)	7.75	
8	0.072(3)	7.85	

This polarization also causes downfield shifts of the anilino protons ( $\delta_{meta}$ ) in the *meta* position relative to the Et<sub>2</sub>N group.<sup>[27b]</sup> These shifts generally increase as the  $\delta r$  values increase, although local anisotropic effects of neighboring CN groups prevent a complete agreement between the two quantities (Table 1).

#### UV/Vis Spectroscopy and Preliminary NLO Data

The UV/Vis spectra of compounds **3–8** in CH<sub>2</sub>Cl<sub>2</sub> feature ICT absorptions in the visible range with high molar extinction coefficients ( $\epsilon$ ), obtained by at least three independent measurements, between 24500 M<sup>-1</sup> cm<sup>-1</sup> and 105500 M<sup>-1</sup> cm<sup>-1</sup> (Figure 3). The ICT character of these

bands was corroborated by reversible protonation/deprotonation experiments, and the Lambert–Beer law was fully obeyed under the experimental concentration range (see Supporting Information). Table 2 summarizes the UV/Vis results including the data for the known derivatives  $1^{[12]}$  and  $2^{[13]}$  as well as those previously recorded for the related push–pull chromophores **18** and **19**.<sup>[11,28]</sup>

Table 2. UV/Vis data for 1-8 and 18 and 19.[a]

	$\lambda_{\rm max} \ [{\rm nm}] \ ({\rm eV})$	$\lambda_{\max} \text{ [nm] (eV)} \qquad \epsilon \text{ [M}^{-1} \text{ cm}^{-1} \text{]}$	
<b>1</b> <sup>[12]</sup>	490 (2.53)	46000	
<b>2</b> <sup>[13]</sup>	582 (2.13) <sup>[b]</sup>	63900 <sup>[b]</sup>	
3	524 (2.37)	105500	
4	567 (2.19)	54100	
5	594 (2.09)	97600	
6	610 (2.03)	64000	
7	678 (1.83)	70300	
8	698 (1.78)	24500	
<b>18</b> <sup>[28]</sup>	343 (3.61)	10200	
	481 (2.58)	7000	
<b>19</b> <sup>[11]</sup>	450 (2.76)	30000	
	643 (1.93)	3200	

[a] Except for 2, data were measured in CH<sub>2</sub>Cl<sub>2</sub>. [b] Measured in acetone;<sup>[13a,13b]</sup>  $\lambda_{max} = 585$  nm in CHCl<sub>3</sub>.<sup>[13c]</sup>



The energy of the single dominant ICT absorption in the spectra of 1–8 is clearly affected by the number of the CN groups along the butadienyl backbone. Moving from two (1,  $\lambda_{max}$ : 490 nm, 2.53 eV), to three (e.g. 3,  $\lambda_{max}$ : 524 nm, 2.37 eV), to four (e.g. 6,  $\lambda_{max}$ : 610 nm, 2.03 eV), and to five (8,  $\lambda_{max}$ : 698 nm, 1.78 eV) cyano groups results in a bathochromic shift of 208 nm (0.75 eV). The dependence of



Figure 3. UV/Vis spectra of 3-8 in CH<sub>2</sub>Cl<sub>2</sub>.

the ICT absorption maximum on the position of the CN groups is even more remarkable. Tricyano derivatives **2** ( $\lambda_{max}$ : 585 nm, 2.12 eV, in CHCl<sub>3</sub>), **3** ( $\lambda_{max}$ : 524 nm, 2.37 eV), or **4** ( $\lambda_{max}$ : 567 nm, 2.19 eV) show substantially different transition energies, and the same holds for the tetracyano derivatives **5** ( $\lambda_{max}$ : 594 nm, 2.09 eV), **6** ( $\lambda_{max}$ : 610 nm, 2.03 eV), and **7** ( $\lambda_{max}$ : 678 nm, 1.83 eV). This comparison shows that introduction of additional CN groups in positions 2 and 4 more effectively induce bathochromic shifts than in position 3 (compare **2**, **4** with **3**, or **7** with **5** and **6**).

The intensities of the ICT band are very high, except for the case of **8** ( $\varepsilon$ : 24500 m<sup>-1</sup> cm<sup>-1</sup>) which features stronger non-planarity in the buta-1,3-diene backbone. Substitution in position 3 results in particularly intense absorptions (**3**:  $\varepsilon = 105500 \text{ m}^{-1} \text{ cm}^{-1}$  and **5**:  $\varepsilon = 97600 \text{ m}^{-1} \text{ cm}^{-1}$ ).

The comparison between the absorption spectra of **3–8** and **18/19** reveals that moving the anilino donor substituent from position 2 (in **18**) or position 3 (in **19**) to position 4 (in **3–8**) leads to a strong bathochromic shift in the UV/Vis spectra (compare  $\lambda_{max}$  of the tetracyano derivatives **5–7** with **18**). This correlates well with the higher ground-state intramolecular CT interaction, as determined by the quinoid character (see above), and reflects the higher planarity of the  $\pi$ -conjugated butadiene backbone in 4-anilino-substituted **3–8** as compared to 2- or 3-anilino-substituted derivatives.<sup>[30]</sup>

A distinct positive solvatochromism was measured for all chromophores (see Supporting Information).<sup>[31,32]</sup> Upon changing from *n*-pentane to more polar nitrobenzene, the ICT band ( $\lambda_{max}$ ) of the tricyano derivatives shifts by 42–50 nm whereas the absorption maxima of compounds with four or five CN groups shift by 68–97 nm.

First experiments to determine the third-order optical nonlinearities of the new chromophores by degenerate fourwave mixing at wavelength of 1.5 µm were undertaken in CH<sub>2</sub>Cl<sub>2</sub> (see Supporting Information). For **4**, the rotational average of the third-order polarizability was determined as  $\gamma_{\rm rot} = (11 \pm 3) \times 10^{-48} \, {\rm m}^5 \, {\rm V}^{-2}$ , a value in line with those measured for 2(3)-anilino-substituted cyanobutadienes.<sup>[33]</sup>

#### Electrochemistry

Electrochemical measurements were carried out in  $CH_2Cl_2$  containing 0.1 M  $nBu_4NPF_6$  in a classical threeelectrode cell by cyclic voltammetry (CV) and rotating-disk voltammetry (RDV) (Table 3).

Chromophores 3–8 featured a reversible one-electron oxidation occurring on the *N*,*N*-diethylanilino moiety, whereas the reductions behave either as irreversible or reversible electron transfers. Increasing the number of CN substituents causes anodic shifts in both the oxidation and reduction potentials. These shifts are due to the electron-withdrawing effect as a result of the increasing CN-substitution and are more pronounced for the first reduction events [RDV (Table 3):  $E_{1/2} = -1.50$  V for 3 and -0.49 V for 8,  $\Delta E_{1/2} = 1.01$  V] than for the first, aniline-centered oxidation



Table 3. Electrochemical data observed by cyclic voltammetry (CV) at a scan rate of  $v = 0.1 \text{ V s}^{-1}$  and rotating disk voltammetry (RDV) in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>. All potentials are given vs. the ferricinium/ferrocene couple, used as internal standard.

	CV			RDV		
	$E^{o[a]}$	$\Delta E_{\rm p}^{\rm [b]}$	$E_{p}^{[c]}$	$E_{1/2}$	Slope <sup>[d]</sup>	
	[V]	[mŶ]	[Ŷ]	[V]	[mV]	
3	+0.66	90		+0.70 (1 e <sup>-</sup> )	65	
			-1.49	-1.50	80	
4	+0.71	140		+0.75 (1 e <sup>-</sup> )	95	
	-1.19	140		-1.23 (1 e <sup>-</sup> )	100	
			-1.84	-1.95	70	
5	+0.91	60		+0.95 (1 e <sup>-</sup> )	70	
			-0.88	-0.88 (1 e <sup>-</sup> )	60	
				-1.57	90	
6	+0.93	70		+0.96 (1 e <sup>-</sup> )	70	
	-0.87	70		-0.89 (1 e <sup>-</sup> )	60	
			-1.51	-1.57	70	
7	+0.81	70		+0.82 (1 e <sup>-</sup> )	60	
	-0.70	70		-0.70 (1 e <sup>-</sup> )	60	
	-1.41	80		-1.42 (1 e <sup>-</sup> )	60	
8	+1.04	60		+1.06 (1 e <sup>-</sup> )	70	
	-0.47	70		-0.49 (1 e <sup>-</sup> )	60	
	-1.15	70		-1.17 (1 e <sup>-</sup> )	70	

[a]  $E^{\circ} = (E_{\rm pc} + E_{\rm pa})/2$ , where  $E_{\rm pc}$  and  $E_{\rm pa}$  correspond to the cathodic and anodic peak potentials, respectively. [b]  $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$ . [c]  $E_{\rm p}$  = Irreversible peak potential at sweep rate  $v = 0.1 \text{ Vs}^{-1}$ . [d] Logarithmic analysis of the wave obtained by plotting *E* vs. log[*I*/( $I_{lim} - I$ )].

 $(\Delta E_{1/2} = 0.36 \text{ V})$ , resulting in the overall decrease in the HOMO–LUMO gaps. While the first redox potentials for 1,1,2,3- and 1,1,3,4-tetracyano substituted **5** and **6** are practically identical ( $E_{1/2(\text{ox})} \approx +0.95 \text{ V}$  and  $E_{1/2(\text{red})} \approx -0.88 \text{ V}$ ), a significantly different redox behavior was observed for 1,1,2,4-tetracyano derivative **7** ( $E_{1/2(\text{ox})} +0.82 \text{ V}$  and  $E_{1/2(\text{red})} = -0.70 \text{ V}$ ). A similar difference was found in the UV/Vis and bond length alternation studies, and this is rationalized based on the computational studies reported below. Electrochemical data for the chlorinated series **13–16** and a brief discussion on their redox properties can be found in the Supporting Information.

#### Calculations

For the ease of computation, the *N*-ethyl substituents on the anilino moieties in **3–8** were changed to *N*-methyl groups. Vertical transition energies between  $S_0-S_1$  states were calculated by time-dependent density functional theory (TD-DFT) at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level; solvation in CH<sub>2</sub>Cl<sub>2</sub> was applied using the polarizable continuum model (PCM) (for details of the computational studies, see the Supporting Information).<sup>[34,35]</sup>

In all cases, the computed transition energies are slightly larger than the experimental values. Differences between computed excitation energies and experimental absorption maxima are in the range of 0.12–0.34 eV, well within the expected error.<sup>[35]</sup> A minor part of these differences results from the Et  $\rightarrow$  Me replacement, which should lead to small shifts of 4–6 nm.<sup>[30]</sup>



Figure 4. Visualization of the frontier molecular orbitals of a) 1, b) 2, c) the N,N-dimethyl analog of 3, and d) the N,N-dimethyl analog of 4, computed at the B3LYP/6-31G(d) level. The orientation of each molecule is according to Figure 1, and the HOMO is shown at the left- and the LUMO at the right-hand side in each graph.

The effect of the addition of CN groups along the butadienyl chain, in positions 2, 3 and/or 4, was regarded as a perturbation of compound 1, bearing two CN groups in position 1. Since the low-energy absorption bands of 1-8are characterized by a HOMO–LUMO transition, we focused on these two frontier MOs, where the HOMO of 1 has a large coefficient on C3, and the LUMO large coefficients on C2 and C4. The frontier MOs of 1 and 2, and the *N*,*N*-dimethyl derivatives of 3 and 4 are visualized in Figure 4; MO energies and the plots for 5-8 can be found in the Supporting Information.

While a ca. 90 nm (0.4 eV) bathochromic shift upon C2cyanation of 1 was found for 2, the C3-cyanation was estimated to have a relatively small effect on the  $S_0-S_1$  gap of 34 nm (or 0.16 eV); exptl.: 3 (524 nm) > 1 (490 nm); calcd. 3(458) < 1 (466 nm). Such findings reflect that both the HOMO and LUMO levels of 3 are stabilized to similar amounts by cyanation at C3. Our electrochemical studies for 3 ( $E_{1/2,ox}$  = +0.70,  $E_{1/2,red}$  = -1.50 V) and the previously reported data for 1 ( $E_{1/2,ox}$  = +0.55,  $E_{1/2,red}$  = -1.60 V under similar conditions)<sup>[12b]</sup> confirm this quantitatively. Also, the 3-substituted CN group has significant orbital coefficients in both the HOMO and LUMO levels. This additional spatial overlap results in the higher extinction coefficients when this position is CN-substituted: oscillator strength f for 3 (1.57) > 2 (1.29) and 4 (1.19), and 5 (1.29) and 6 (1.24) > 7 (1.13), almost parallel to the trend in  $\varepsilon$ , Table 2. For 2 and 4, there is little orbital coefficient on the additional CN group in the HOMO, whereas significant orbital coefficients are observed for these groups in the LUMO (Figure 4). This suggests that the LUMO levels have been perturbed to a greater extent than the HOMO levels. This unequal perturbation is clearly seen in the electrochemistry of 4 ( $E_{1/2,ox}$  = +0.75,  $E_{1/2,red}$  = -1.23 V), where the LUMO

level has dropped roughly by 0.4 eV and the HOMO level only by 0.2 eV, compared to 1. This results ultimately in a 79 nm red-shift of the absorption maximum of 4 relative to 1. A similar distortion of the orbital lobes in the C2 and C4 positions towards the attached CN groups was also found in the LUMO plots of 5-8 (see Supporting Information). The reduction in excitation energy, therefore, is found to be affected by the C2- and/or C4-cyanations, which lower the LUMO level to a larger extent than the HOMO level. Combining the discussed effects, we observed for the tricyano-substituted butadienes experimentally: 2 (585 nm) > 4 (567 nm) > 3 (524 nm), calculated: 4 (538 nm)  $\geq$  2 (537 nm) > 3 (459 nm); and for the tetracyano-substituted butadienes experimentally: 7 (678 nm) > 6 (610 nm) > 5 (594 nm), calculated: 7 (597 nm) > 6 (538 nm) > 5(522 nm).

### Conclusions

A complete series of 1,1-dicyano-4-(N,N-diethylanilino)substituted buta-1,3-dienes **3–8** was synthesized, and the configuration and geometry of each compound unambiguously determined by X-ray analysis. The quinoid character, calculated from the X-ray crystal data, of the new chromophores is high, reflecting the high planarity of their  $\pi$ -conjugated buta-1,3-diene backbone.

UV/Vis measurements and theoretical calculations show that by increasing the number of electron-accepting CN groups along the  $\pi$ -conjugated bridge of these chromophores, remarkable red-shifts of the ICT absorption maxima can be achieved, and good control over the extinction coefficients of these transitions is possible. Particularly crucial are C2 and C4-cyanation, which result in the largest bathochromic shifts, as the LUMO level is more strongly lowered than the HOMO level. In contrast, cyanation at C3 lowers both HOMO and LUMO levels to a similar extent which explains why the smallest bathochromic shifts of the ICT band are observed. Consequently, position C3 is in future work best used for further functionalization and branching. Modification at this site, as an additional position to the anilino nitrogen, with alkyl or substituted ethynyl groups could improve physical and molecular materials properties, such as solubility, without considerably affecting the chromophore planarity and opto-electronic behavior. Preliminary NLO measurements for compound **4** suggest that this additional modification is worthwhile and holds promise for producing new advanced functional materials for optical device applications.<sup>[36]</sup>

### **Experimental Section**

Only the synthesis of the target chromophores **3–8** is reported here, whereas all other details and protocols can be found in the Supporting Information.

CCDC-863131 (for 3), -863132 (for 4), -863133 (for 5), -863134 (for 6), -863135 (for 7), -863136 (for 8), -863137 (for 13), -863138 (for 14), -863139 (for 15), -863140 (for 16) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

General Procedure A (Cl→CN Substitution): A solution of chlorinated buta-1,3-diene (1 equiv.) in dry toluene (20 mL) was treated with 18-crown-6 (1.3 equiv.), KCN (2.1 equiv.), and [Pd(PPh<sub>3</sub>)]<sub>4</sub> (0.07 equiv.). The mixture was stirred at 95 °C for 1.5 h, treated with a solution of CuCN (2.0 equiv.) in dry DMF (2 mL), stirred at 95 °C for 1 h, treated with another portion of CuCN (2.0 equiv.) in dry DMF (2 mL), and finally stirred at 95 °C overnight. After evaporation, a solution of the residue in CH<sub>2</sub>Cl<sub>2</sub> was filtered and the solvents evaporated. Flash chromatography (SiO<sub>2</sub>) gave the desired compound as a colored solid.

**General Procedure B [Reaction of 17 with Dicyanovinyl (DCV) or Tricyanovinyl (TCV) Chlorides]:** A solution of **17** (1.00 mmol) and cyanovinyl chloride (1.50 mmol) in acetonitrile (9 mL) was heated at 90 °C for 3 h and subsequently evaporated. Flash chromatography (SiO<sub>2</sub>) gave the desired compound as a colored solid.

(Z)-3: This compound was synthesized according to General Procedure B with 17 (200 mg, 1.01 mmol). Flash chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) gave (Z)-3 (130 mg, 47%) as a purple solid.  $R_{\rm f}$  = 0.55 (CH<sub>2</sub>Cl<sub>2</sub>); m.p. 208.0-209.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.27 [t, J = 7.2 Hz, 6 H, N(CH<sub>2</sub>Me)<sub>2</sub>], 3.52 [q, J = 7.2 Hz, 4 H, N( $CH_2Me$ )<sub>2</sub>], 6.73 (d, J = 9.3 Hz, 2 H, Ar $H_{ortho}$ ), 7.24 (s, 1 H, ArC=CH), 7.37 [s, 1 H, HC=C(CN)<sub>2</sub>], 7.96 (br. d, J = 9.3 Hz, 2 H, ArH<sub>meta</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 8:2, 25 °C): δ = 12.61, 45.26, 94.93, 111.29, 111.96, 115.02, 115.05, 119.29, 135.86, 153.04, 156.41, 157.80 ppm (one signal missing because of overlap with the CD<sub>3</sub>CN resonance at 116.52). IR (ATR):  $\tilde{v} = 2980$  (m), 2940 (m), 2217 (s), 1606 (s), 1532 (m), 1497 (m), 1470 (w), 1448 (w), 1411 (m), 1335 (w), 1281 (w), 1227 (w), 1186 (m), 1156 (m), 1082 (m), 1009 (w), 975 (w), 923 (w), 893 (m), 824 (s), 794 (m), 779 (m), 762 (m), 680 (m), 630 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ ) 289 (6500), 524 nm (105500 M<sup>-1</sup> cm<sup>-1</sup>). HR-ESI-MS: calcd. for  $C_{17}H_{20}N_5^+$  [M + NH<sub>4</sub>]<sup>+</sup> 294.1713; found 294.1704



m/z. C<sub>17</sub>H<sub>16</sub>N<sub>4</sub> (276.34): calcd. C 73.89, H 5.84, N 20.27; found C 73.68, H 5.86, N 20.08.

(Z)-4: This compound was synthesized according to General Procedure A with (Z)-13 (150 mg, 0.52 mmol). Flash chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/pentane, 8:2) gave (Z)-4 (40 mg, 28%) as a violet solid.  $R_{\rm f} = 0.57$  (CH<sub>2</sub>Cl<sub>2</sub>/pentane, 8:2); m.p. 204.1–205.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 1.25 [t, J = 7.2 Hz, 6 H,  $N(CH_2Me)_2$ ], 3.49 [q, J = 7.2 Hz, 4 H,  $N(CH_2Me)_2$ ], 6.70 (d, J = 9.3 Hz, 2 H,  $ArH_{ortho}$ ), 7.28 (d, J = 12.3 Hz, 1 H, ArClC=CH), 7.66 (d, J = 9.3 Hz, 2 H, Ar $H_{meta}$ ), 7.88 [d, J = 12.3 Hz, 1 H,  $HC=C(CN)_2$  ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 12.85, 45.16, 81.67, 111.96, 112.12, 113.81, 114.71, 118.16, 122.02, 127.84, 130.639 151.41, 153.84 ppm. IR (ATR):  $\tilde{v} = 2974$  (m), 2925 (m), 2211 (s), 1608 (s), 1543 (s), 1507 (m), 1471 (w), 1448 (w), 1414 (m), 1377 (w), 1357 (w), 1333 8 (w), 1291 (m), 1270 (m), 1195 (m), 1152 (m), 1093 (w), 1071 (m), 1009 (w), 972 (w), 926 (w), 902 (w), 880 (m), 820 (s), 794 (m), 754 (m), 729 (m)  $cm^{-1}$ . UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 294 (18000), 567 nm (54100 M<sup>-1</sup> cm<sup>-1</sup>). HR-ESI-MS: calcd. for  $C_{17}H_{17}N_4^+$  [M + H]<sup>+</sup> 277.1448; found 277.1445 m/z.  $C_{17}H_{16}N_4$ (276.34): calcd. C 73.89, H 5.84, N 20.27; found C 73.95, H 5.97, N 20.34.

(Z)-5: This compound was synthesized according to General Procedure B with 17 (160 mg, 0.8 mmol). Flash chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) gave (Z)-5 (96 mg, 41%) as a blue-green solid.  $R_{\rm f} = 0.68$ (CH<sub>2</sub>Cl<sub>2</sub>); m.p. 231.0–232.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 1.31$  [t, J = 7.2 Hz, 6 H, N(CH<sub>2</sub>Me)<sub>2</sub>], 3.59 [q, J =7.2 Hz, 4 H, N( $CH_2Me_2$ ], 6.79 (d, J = 9.0 Hz, 2 H, Ar $H_{ortho}$ ), 7.81 (s, 1 H, C=CH), 8.10 (br. s, 2 H, Ar $H_{meta}$ ) ppm. <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{ CD}_3\text{CN}, 25 \text{ °C}): \delta = 1.24 \text{ [t, } J = 7.4 \text{ Hz}, 6 \text{ H},$  $N(CH_2Me)_2$ ], 3.61 [q, J = 7.4 Hz, 4 H,  $N(CH_2Me)_2$ ], 6.93 (d, J = 9.1 Hz, 2 H, ArHortho), 7.83 (s, 1 H, C=CH), 8.08 (br. s, 2 H, ArH<sub>meta</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN, 25 °C): poor quality spectrum because of solubility reasons. IR (ATR):  $\tilde{v} = 2971$  (m), 2930 (m), 2207 (s), 1606 (s), 1561 (m), 1514 (m), 1488 (w), 1457 (w), 1416 (m), 1367 (m), 1339 (w), 1302 (w), 1262 (w), 1188 (m), 1162 (m), 1006 (w), 918 (m), 830 (s), 809 (m), 795 (m), 784 (m), 737 (w), 676 (w), 616 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$ ) 293 (6900), 375 (8900), 398 (9100), 594 nm (97600  $M^{-1}$  cm<sup>-1</sup>). HR-MALDI-MS (3-HPA): calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>5</sub><sup>-</sup> [M]<sup>-</sup> 301.1333; found 301.1333 m/z. C<sub>18</sub>H<sub>15</sub>N<sub>5</sub> (301.35): calcd. C 71.74, H 5.02, N 23.24; found C 71.74, H 5.23, N 22.93.

(E)-6: This compound was synthesized from a mixture of (E)-14 and (Z)-14 (200 mg, 0.64 mmol) following General Procedure A. Flash chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) gave (E)-6 (38 mg, 28%) as a dark green solid.  $R_{\rm f} = 0.28$  (CH<sub>2</sub>Cl<sub>2</sub>); m.p. 188.3–189.7 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 1.32$  [t, J = 7.2 Hz, 6 H,  $N(CH_2Me)_2$ ], 3.58 [q, J = 7.2 Hz, 4 H,  $N(CH_2Me)_2$ ], 6.79 (d, J = 7.2 Hz, 2 H,  $ArH_{ortho}$ ), 7.81 (s, 1 H, C=CH), 8.23 (d, J = 7.2 Hz, 2 H, Ar*H<sub>meta</sub>*) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C): δ = 13.02, 45.91, 80.91, 99.54, 110.27, 112.83, 114.02, 114.42, 114.80, 132.72, 134.46, 150.34, 153.45 ppm. IR (ATR):  $\tilde{v} = 2971$  (m), 2923 (m), 2212 (s), 1606 (s), 1551 (s), 1492 (w), 1438 (s), 1347 (m), 1315 (m), 1260 (m), 1194 (m), 1158 (w), 1095 (w), 1070 (w), 1014 (w), 928 (w), 821 (s), 796 (m), 696 (m), 666 (m), 609 (m)  $cm^{-1}$ . UV/Vis  $(CH_2Cl_2)$ :  $\lambda_{max}$  ( $\varepsilon$ ) 262 (6400), 329 (7100), 610 nm (64000 m<sup>-1</sup> cm<sup>-1</sup>). HR-MALDI-MS (3-HPA): calcd. for  $C_{18}H_{15}N_5^-$  [M]<sup>-</sup> 301.1333; found 311.1328. C18H15N5 (301.35): calcd. C 71.74, H 5.02, N 23.24; found C 71.56, H 5.00, N 23.07.

(*Z*)-7: This compound was synthesized from (*Z*)-15 (130 mg, 0.42 mmol) following General Procedure A. Flash chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) gave (*Z*)-7 (40 mg, 32%) as a green solid.  $R_{\rm f}$  = 0.31 (CH<sub>2</sub>Cl<sub>2</sub>); m.p. 221.0–222.0 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,

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25 °C):  $\delta$  = 1.29 [t, *J* = 7.2 Hz, 6 H, N(CH<sub>2</sub>*Me*)<sub>2</sub>], 3.55 [q, *J* = 7.2 Hz, 4 H, N(CH<sub>2</sub>Me)<sub>2</sub>], 6.75 (d, *J* = 9.6 Hz, 2 H, Ar*H*<sub>ortho</sub>), 7.24 (s, 1 H, C=C*H*), 7.75 (d, *J* = 9.6 Hz, 2 H, Ar*H*<sub>meta</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 8:2, 25 °C):  $\delta$  = 12.79, 45.59, 85.51, 111.15, 111.58, 112.59, 112.88, 113.08, 120.68, 125.71, 131.56, 132.74, 152.75 ppm (one signal missing because overlapped with CD<sub>3</sub>CN resonances at 116.52). IR (ATR):  $\tilde{v}$  = 2972 (m), 2931 (m), 2210 (s), 1607 (s), 1508 (s), 1477 (m), 1420 (m), 1346 (m), 1312 (m), 1296 (m), 1276 (m), 1213 (m), 1192 (m), 1092 (w), 1077 (w), 1009 (w), 961 (m), 901 (m), 856 (m), 830 (s), 797 (m), 746 (m) cm<sup>-1</sup>. UV/ Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (ε) 341 (8800), 402 (5500), 442 (3000), 678 nm (70300 m<sup>-1</sup> cm<sup>-1</sup>). HR-MALDI-MS (3-HPA): calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>5</sub>-[M]<sup>-</sup> 301.1333; found: 301.1329 *m*/*z*. C<sub>18</sub>H<sub>15</sub>N<sub>5</sub> (301.35): calcd. C 71.74, H 5.02, N 23.24; found C 71.65, H 5.07, N 23.27.

(*Z*)-8: This compound was synthesized from (*Z*)-16 (170 mg, 0.51 mmol) following General Procedure A. Flash chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) gave (*Z*)-8 (9 mg, 9%) as a green solid.  $R_f = 0.13$  (CH<sub>2</sub>Cl<sub>2</sub>); m.p. 187.3–188.1 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 1.36$  [t, J = 7.2 Hz, 6 H, N(CH<sub>2</sub>*Me*)<sub>2</sub>], 3.65 [q, J = 7.2 Hz, 4 H, N(*CH*<sub>2</sub>*Me*)<sub>2</sub>], 6.86 (d, J = 9.6 Hz, 2 H, Ar*H*<sub>ortho</sub>), 7.85 (br. s, 2 H, Ar*H*<sub>meta</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>CN, 8:2, 25 °C): poor quality spectrum because of solubility reasons. IR (ATR):  $\tilde{v} = 2973$  (m), 2931 (m), 2212 (s), 1602 (s), 1508 (s), 1471 (w), 1416 (w), 1345 (w), 1308 (m), 1180 (m), 1157 (m), 1094 (w), 1076 (w), 1002 (w), 894 (m), 829 (s), 794 (m), 742 (m) cm<sup>-1</sup>. UV/ Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\hat{e}$ ) 259 (6100), 379 (5400), 431 (3800), 698 nm (24500 m<sup>-1</sup> cm<sup>-1</sup>). HR-MALDI-MS (3-HPA): calcd. for C<sub>19</sub>H<sub>14</sub>N<sub>6</sub>-[M]<sup>-</sup> 326.1285; found: 326.1278 *m*/*z*. C<sub>19</sub>H<sub>14</sub>N<sub>6</sub> (326.36): calcd. C 69.92, H 4.32, N 24.75; found C 69.51, H 4.31, N 24.65.

**Supporting Information** (see footnote on the first page of this article): Details of the syntheses (11–16), UV/Vis measurements (including oscillator strength and transition dipole moment), electrochemsitry (13–16), X-ray data, DFT calculations, and <sup>1</sup>H and <sup>13</sup>C NMR spectra of new compounds.

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- [1] R. Gompper, H.-U. Wagner, Angew. Chem. 1988, 100, 1492– 1511; Angew. Chem. Int. Ed. Engl. 1988, 27, 1437–1455.
- [2] a) M. Kivala, F. Diederich, Acc. Chem. Res. 2009, 42, 235–248;
  b) S.-i. Kato, F. Diederich, Chem. Commun. 2010, 46, 1994–2006;
  c) J. Roncali, P. Leriche, A. Cravino, Adv. Mater. 2007, 19, 2045–2060.
- [3] a) For a special issue on organic electronics, see: J. Mater. Res. 2004, 19, 1887–2203, edited by F. Faupel, C. Dimitrakopoulos, A. Kahn, C. Wöll; b) for a special issue on organic electronics and opto-electronics, see: Chem. Rev. 2007, 107, 923–1386, edited by S. R. Forrest, M. E. Thompson; c) for a special issue on materials for electronics, see: Chem. Rev. 2010, 110, 1–574, edited by R. D. Miller, E. A. Chandross.
- [4] S. Barlow, S. R. Marder, in: *Functional Organic Materials* (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, Germany, 2007, pp. 393–437.
- [5] L. R. Dalton, J. Phys. Condens. Matter 2003, 15, R897-R934.
- [6] a) D. M. Burland, R. D. Miller, O. Reiser, R. J. Twieg, C. A. Walsh, J. Appl. Phys. 1992, 71, 410–417; b) D. R. Kanis, M. A.

Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195–242; c) J. Y. Lee, K. S. Kim, B. J. Mhin, *J. Chem. Phys.* **2001**, *115*, 9484–9489.

- [7] a) S. R. Marder, J. W. Perry, G. Bourhill, C. B. Gorman, B. G. Tiemann, K. Mansour, Science 1993, 261, 186–189; b) S. R. Marder, L. T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchard-Desce, J. W. Perry, J. Skindhoj, Science 1994, 263, 511–514; c) F. Meyers, S. R. Marder, B. M. Pierce, J. L. Brédas, J. Am. Chem. Soc. 1994, 116, 10703–10714; d) R. R. Tykwinski, M. Schreiber, V. Gramlich, P. Seiler, F. Diederich, Adv. Mater. 1996, 8, 226–231; e) R. Spreiter, C. Bosshard, G. Knöpfle, P. Günter, R. R. Tykwinski, M. Schreiber, F. Diederich, J. Phys. Chem. B 1998, 102, 29–32; f) R. R. Tykwinski, U. Gubler, R. E. Martin, F. Diederich, C. Bosshard, P. Günter, J. Phys. Chem. B 1998, 102, 4451–4465; g) M. G. Kuzyk, J. Mater. Chem. 2009, 19, 7444–7465.
- [8] a) G. Archetti, A. Abbotto, R. Wortmann, *Chem. Eur. J.* 2006, *12*, 7151–7160; b) J. C. May, I. Biaggio, F. Bureš, F. Diederich, *Appl. Phys. Lett.* 2007, *90*, 251106/1–251106/3; c) E. L. Spitler, L. D. Shirtcliff, M. M. Haley, *J. Org. Chem.* 2007, *72*, 86–96; d) N. Hebbar, Y. Ramondenc, G. Plé, G. Dupas, N. Plé, *Tetrahedron* 2009, *65*, 4190–4200; e) J. Kulhánek, F. Bureš, O. Pytela, T. Mikysek, J. Ludvík, *Chem. Asian J.* 2011, *6*, 1604–1612.
- [9] a) P. Nguyen, G. Lesley, T. B. Marder, Chem. Mater. 1997, 9, 406–408; b) G. P. Bartholomew, G. C. Bazan, J. Am. Chem. Soc. 2002, 124, 5183–5196; c) H. Meier, J. Gerold, H. Kolshorn, B. Mühling, Chem. Eur. J. 2004, 10, 360–370; d) F. Bureš, W. B. Schweizer, J. C. May, C. Boudon, J.-P. Gisselbrecht, M. Gross, I. Biaggio, F. Diederich, Chem. Eur. J. 2007, 13, 5378–5387; e) A. S. Andersson, L. Kerndrup, A. Ø. Madsen, K. Kilså, M. B. Nielsen, P. R. La Porta, I. Biaggio, J. Org. Chem. 2009, 74, 375–382; f) Y.-L. Wu, F. Bureš, P. D. Jarowski, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, F. Diederich, Chem. Eur. J. 2010, 16, 9592–9605; g) J. Rotzler, D. Vonlanthen, A. Barsella, A. Boeglin, A. Fort, M. Mayor, Eur. J. Org. Chem. 2010, 1096–1110.
- [10] a) A. P. Chafin, G. A. Lindsay, J. Phys. Chem. C 2008, 112, 7829–7835; b) J. Hung, W. Liang, J. Luo, Z. Shi, A. K.-Y. Jen, X. Li, J. Phys. Chem. C 2010, 114, 22284–22288; c) J. Luo, S. Huang, Y.-J. Cheng, T.-D. Kim, Z. Shi, X.-H. Zhou, A. K.-Y. Jen, Org. Lett. 2007, 9, 4471–4474; d) Y.-J. Cheng, J. Luo, S. Huang, X. Zhou, Z. Shi, T.-D. Kim, D. H. Bale, S. Takahashi, A. Yick, B. M. Polishak, S.-H. Jang, L. R. Dalton, P. J. Reid, W. H. Steier, A. K.-Y. Jen, Chem. Mater. 2008, 20, 5047–5054; e) M. Kivala, C. Boudon, J.-P. Gisselbrecht, B. Enko, P. Seiler, I. B. Müller, N. Langer, P. D. Jarowski, G. Gescheidt, F. Diederich, Chem. Eur. J. 2009, 15, 4111–4123.
- [11] P. Reutenauer, M. Kivala, P. D. Jarowski, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Chem. Commun.* 2007, 4898– 4900.
- [12] a) E. Hertel, K. A. Hoffmann, Z. Physik. Chem. 1941, 50B, 382–402; b) K. Staub, G. A. Levina, S. Barlow, T. C. Kowal-czyk, H. S. Lackritz, M. Barzoukas, A. Fort, S. R. Marder, J. Mater. Chem. 2003, 13, 825–833.
- [13] a) J. K. Williams, D. W. Wiley, B. C. McKusick, J. Am. Chem. Soc. 1962, 84, 2216–2221; b) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, H. F. Mower, J. Am. Chem. Soc. 1958, 80, 2806–2815; c) P. Reutenauer, P. J. Boul, J.-M. Lehn, Eur. J. Org. Chem. 2009, 1691–1697.
- [14] The enhanced solubility is especially important for the synthesis of the strongly dipolar ICT chromophores, see: B. Breiten, Y.-L. Wu, P. D. Jarowski, J.-P. Gisselbrecht, C. Boudon, M. Griesser, C. Onitz, G. Gescheidt, W. B. Schweizer, N. Langer, C. Lennartz, F. Diederich, *Chem. Sci.* 2011, *2*, 88–93; however, as inferred from the quality of <sup>13</sup>C NMR, the solubility of some target molecules is still poor in chlorinated solvents.
- [15] A. D. Josey, C. L. Dickenson, K. C. Dewhirst, B. C. McKusic, J. Org. Chem. 1967, 32, 1941–1944.
- [16] a) W. J. Linn, Organic Syntheses 1973, Coll. Vol. 5, 1973, 1007– 1011; Org. Synth. 1969, 49, 103–107; b) C. L. Dickenson, D. W.

Wiley, B. C. McKusick, J. Am. Chem. Soc. 1960, 82, 6132-6136.

- [17] A. Elangovan, Y.-H. Wang, T.-I. Ho, Org. Lett. 2003, 5, 1841– 1844.
- [18] For the Sonogashira-like cyanation reaction of vinyl halides used here, see: a) K. Yamamura, S.-I. Murahashi, Tetrahedron Lett. 1977, 18, 4429–4430; b) M. Procházka, M. Široký, Collect. Czech. Chem. Commun. 1983, 48, 1765-1773. Cyanation with CuCN in DMF at various temperatures, with or without KCN additive, gave lower yields in the present cases, see: c) C. Wang, C. Wang, Q. Wang, Z. Wang, H. Sun, X. Guo, Z. Xi, Chem. Eur. J. 2007, 13, 6484-6494; d) J. Fitzgerald, W. Taylor, H. Owen, Synthesis 1991, 686-688. Other cyano agents, such as  $[K_4Fe(CN)_6]$  or  $Zn(CN)_2$ , applied in conjunction with Pd<sup>0</sup> catalysts have been examined in the literature and were especially successful in the cyanation of aryl halides, see: e) T. Schareina, A. Zapf, M. Beller, J. Organomet. Chem. 2004, 689, 4576-4583; f) R. Gerber, M. Oberholzer, C. M. Frech, Chem. Eur. J. 2012, 18, 2978-2986; g) P. E. Maligres, M. S. Waters, F. Fleitz, D. Askin, Tetrahedron Lett. 1999, 40, 8193-81956; h) M. T. Martin, B. Liu, B. E. Cooley, J. F. Eaddy, Tetrahedron Lett. 2007, 48, 2555–2557.
- [19] H. S. I. Chao, Synth. Commun. 1988, 18, 1641-1650.
- [20] a) P. D. Jarowski, Y.-L. Wu, C. Boudon, J.-P. Gisselbrecht, M. Gross, W. B. Schweizer, F. Diederich, *Org. Biomol. Chem.* 2009, 7, 1312–1322; b) Y.-L. Wu, P. D. Jarowski, W. B. Schweizer, F. Diederich, *Chem. Eur. J.* 2010, *16*, 202–211; c) F. Silvestri, M. Jordan, K. Howes, M. Kivala, P. Rivera-Fuentes, C. Boudon, J.-P. Gisselbrecht, W. B. Schweizer, P. Seiler, M. Chiu, F. Diederich, *Chem. Eur. J.* 2011, *17*, 6088–6097.
- [21] The structure of the product formed by 4-ethynyl-N,N-dimethylaniline and 11 reported in ref.<sup>[20a]</sup> is incorrect. The postulated 4-chloro-1,1-dicyano-2-[4-(dimethylamino)phenyl]buta-1,3diene was not formed; rather the 4-anilino-substituted regioisomer similar to 13 (Me<sub>2</sub>N instead of Et<sub>2</sub>N) was isolated as eventually revealed by X-ray analysis.
- [22] G. Himbert, S. Kosack, Chem. Ber. 1988, 121, 2053-2057.
- [23] J. Ø. Madsen, S. O. Lawesson, Tetrahedron 1974, 30, 3481– 3492.
- [24] a) K. C. Brannock, A. Bell, R. D. Burpitt, C. A. Kelly, J. Org. Chem. 1964, 29, 801–812; b) R. Huisgen, Acc. Chem. Res. 1977, 10, 117–124; c) T. Kim, H. Sarker, N. L. Bauld, J. Chem. Soc., Perkin Trans. 2 1995, 577–580; d) H. A. Clever, G. Wang, W. C. Mollberg, A. B. Padias, H. K. Hall Jr., J. Org. Chem. 1992, 57, 6837–6842; e) I. Nakamura, R. Nagata, T. Nemoto, M. Terada,

Y. Yamamoto, T. Späth, A. de Meijere, *Eur. J. Org. Chem.* 2007, 4479–4482.

- [25] Starting from a mixture of (*E*) and (*Z*) isomers, **14** crystallizes only in the (*E*) form. Dissolution of the crystals in CHCl<sub>3</sub> returns the inseparable mixture of (*E*) and (*Z*) isomers.
- [26] C. Dehu, F. Meyers, J. L. Brédas, J. Am. Chem. Soc. 1993, 115, 6198–6206.
- [27] a) N. N. P. Moonen, F. Diederich, *Org. Biomol. Chem.* 2004, *2*, 2263–2266; b) N. N. P. Moonen, W. C. Pomerantz, R. Gist, C. Boudon, J.-P. Gisselbrecht, T. Kawai, A. Kishioka, M. Gross, M. Irie, F. Diederich, *Chem. Eur. J.* 2005, *11*, 3325–3341.
- [28] T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* 2006, 12, 1889–1905.
- [29] G. Jayamurugan, J.-P. Gisselbrecht, C. Boudon, F. Schoenebeck, W. B. Schweizer, F. Diederich, *Chem. Commun.* 2011, 47, 4520–4522.
- [30] Changes from  $Me_2N$  to  $Et_2N$  donor substituents only have a minor effect; see the citation in ref.<sup>[14]</sup>
- [31] For the solvatochromism of 2- or 3-anilino-substituted cyanobuta-1,3-dienes, see: F. Bureš, O. Pytela, M. Kivala, F. Diederich, J. Phys. Org. Chem. 2011, 24, 274–278.
- [32] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH, Weinheim, Germany, 2004.
- [33] a) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* 2005, 737–739; b) B. B. Frank, P. R. Laporta, B. Breiten, M. C. Kuzyk, P. D. Jarowski, W. B. Schweizer, P. Seiler, I. Biaggio, C. Boudon, J.-P. Gisselbrecht, F. Diederich, *Eur. J. Org. Chem.* 2011, 4307–4317. Ref.<sup>[33b]</sup> describes experimental corrections to earlier reported data.
- [34] M. J. Frisch et al., *Gaussian 09*, revision A.02, Gaussian, Inc., Wallingford CT, 2009. See the Supporting Information for the full list of the authors.
- [35] a) C. J. Jödicke, H. P. Lüthi, J. Chem. Phys. 2002, 117, 4146–4156; b) C. J. Jödicke, H. P. Lüthi, J. Am. Chem. Soc. 2003, 125, 252–264; c) D. Jacquemin, V. Wathelet, E. A. Perpète, C. Adamo, J. Chem. Theory Comput. 2009, 5, 2420–2435.
- [36] a) B. Esembeson, M. L. Scimeca, I. Biaggio, T. Michinobu, F. Diederich, Adv. Mater. 2008, 20, 4584–4587; b) C. Koos, P. Vorreau, T. Vallaitis, P. Dumon, W. Boggerts, R. Baets, B. Esembeson, I. Biaggio, T. Michinobu, F. Diederich, W. Freude, J. Leuthold, Nat. Photonics 2009, 3, 216–227.

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