

## Article

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## Acetylene-Derived Strong Organic Acceptors for Planar and Nonplanar Push–Pull Chromophores

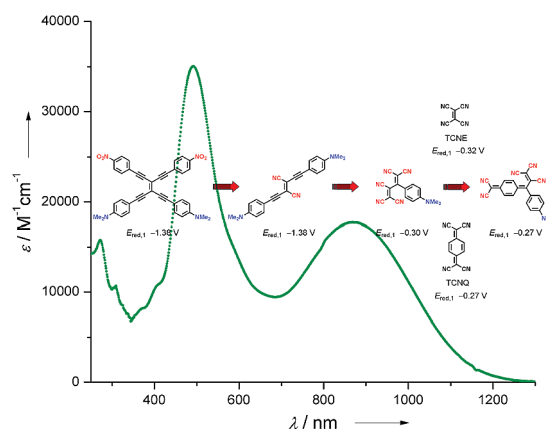
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### CONSPICUOUS

Though investigated for decades, interest in push–pull chromophores (D– $\pi$ –A), strong electron donors (D) connected by  $\pi$ -conjugating spacers to strong electron acceptors (A), continues to grow. Such chromophores are of substantial interest for optoelectronic devices such as waveguides. Also, strong donors and acceptors form bimolecular charge-transfer (CT) complexes and salts, some of which exhibit electrical conductivity and magnetic behavior. Furthermore, strong organic acceptors are increasingly explored as dopants in the fabrication of organic light-emitting diodes (OLEDs) and solar cells. This Account describes systematic efforts pursued over the past decade in our laboratory to generate new families of organic electron acceptors (A) and conjugate them via  $\pi$ -spacers to electron donors (D) under formation of push–pull systems with intense intramolecular CT interactions and high third-order optical nonlinearities.



First, we describe donor–acceptor-substituted tetraethynylethenes (TEEs). In these chromophores, the peripherally attached *p*-nitrophenyl acceptors and *N,N*-dimethylanilino donors behave as nearly independent redox centers. Acetylenic scaffolding using TEE building blocks produces large all-carbon sheets, such as perethynylated dehydroannulenes, expanded radialenes, and radiaannulenes with potent electron-acceptor properties. Arylated TEEs act as molecular switches allowing two-way photochemical interconversion that is not perturbed by thermal isomerization pathways.

Upon sequential substitution of the acetylene moieties in TEEs, we formed another family of potent acceptors, the cyanoethynylethenes (CEEs). Donor-substituted CEEs are planar CT chromophores with very high third-order optical nonlinearities. Their high environmental stability allows for the formation of thin films by vapor-phase deposition. Through careful analysis of the physicochemical properties of CEEs, we established useful guidelines for evaluating and tuning the optical gap in strong push–pull chromophores: increasing the length of the  $\pi$ -spacer in D– $\pi$ –A systems reduces ground-state D–A conjugation and lowers the HOMO–LUMO gap.

By taking advantage of “click-chemistry”-type [2 + 2] cycloadditions of tetracyanoethene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) with appropriately activated alkynes, followed by retro-electrocyclization, the formation of donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs), 1,1,2,4,4-pentacyanobuta-1,3-dienes (PCBDs), and novel TCNQ adducts is possible. Some of these stable, nonplanar CT chromophores form high optical quality amorphous thin films by vapor-phase deposition. Despite donor substitution, the new acceptors (TCBDs, PCBDs, and the TCNQ adducts) rival TCNE and TCNQ in their ease for reversible electron uptake. High-yielding cycloaddition/retro-electrocyclization cascades provide access to multivalent, dendritic chromophores acting as “molecular batteries” with a remarkable capacity for multiple electron uptake in a narrow potential range. Finally, we used a one-pot protocol for electronically controlled consecutive TCNE and tetrathiafulvalene (TTF) additions to end-capped polyynes to form [AB]-type oligomers with a dendralene-type backbone.

## 1. Introduction

Push–pull chromophores (D– $\pi$ –A), with strong electron donors (D) connected by  $\pi$ -conjugating spacers to strong electron acceptors (A), have been investigated for decades.<sup>1</sup> Nevertheless, interest in such systems is still growing, in view of their promising optoelectronic properties, such as large second-<sup>2,3</sup> and third-order nonlinear optical (NLO) effects,<sup>4</sup> and their potential for application as advanced functional materials in molecular devices.<sup>5</sup> New strong organic electron donors and acceptors are continuously being developed and conjugated into D– $\pi$ –A systems featuring low-energy charge-transfer (CT) bands.<sup>6</sup> Strong intermolecular D–A interactions are known to produce bimolecular CT complexes and salts, some of which exhibit high electric conductivity<sup>7</sup> or interesting magnetic properties.<sup>8</sup> Furthermore, stable strong organic acceptors attract interest as *p*-type dopants to improve the performance of organic light-emitting diodes (OLEDs) and organic solar cells.<sup>9</sup>

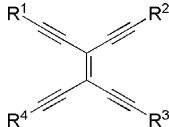
This Account summarizes ongoing efforts to develop new acetylene-derived electron acceptors and D– $\pi$ –A push–pull systems and explore their optoelectronic properties. The synthesis-driven program was initiated in the mid-1990s with the preparation of a library of D–A-substituted tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) derivatives to establish predictive structure–property relationships for third-order optical nonlinearity. Replacement of individual ethynyl moieties in TEEs by cyano groups afforded another class of potent, planar electron acceptors, the cyanoethynylethenes (CEEs). Nonplanar intramolecular CT chromophores such as donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs), 1,1,2,4,4-pentacyanobuta-1,3-dienes (PCBDs), and novel 7,7,8,8-tetracyanoquinodimethane (TCNQ) adducts became recently available in single-step, high-yielding cycloadditions of tetracyanoethene (TCNE) and TCNQ to appropriately activated alkynes, followed by retro-electrocyclization. These efficient, “click-chemistry”-type<sup>10</sup> transformations also provided access to dendritic, multivalent CT chromophores and [AB]-type oligomers with alternating donor and acceptor moieties. Throughout this Account, guidelines for evaluating and tuning the HOMO–LUMO gap in strong push–pull chromophores will be provided. Whereas chromophore design, synthesis, and UV/vis measurements took place at the ETH, electrochemical study and the determination of nonlinear optical properties were performed in the laboratories of outstanding collaborators whose names are found in the various references.

## 2. Donor–Acceptor-Substituted Tetraethynylethenes

A large variety of TEE derivatives have been prepared and their synthesis,<sup>11</sup> electrochemical,<sup>12</sup> and nonlinear optical properties<sup>4</sup> comprehensively reviewed. With its eight sp<sup>2</sup>-hybridized C-atoms, tetrakis(trimethylsilyl)ethynyl]ethene (**1**, Table 1) is a moderate electron acceptor and undergoes a reversible 1e<sup>−</sup> reduction at  $E_{\text{red},1} = -1.96$  V (in THF + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>; all electrochemical data in this Account are obtained by cyclic voltammetry (CV) and are referenced against the ferricinium/ferrocene (Fc<sup>+</sup>/Fc) couple). Decoration with a *p*-nitrophenyl acceptor moiety as in **2** shifts the first reduction potential anodically to  $-1.36$  V. The electron uptake is now centered on the *p*-nitrophenyl group. Remarkably, this potential is hardly affected by the presence of other aryl substituents, such as additional *p*-nitrophenyl or *N,N*-dimethylanilino (DMA) groups, as in **4** and **6–8**.<sup>13,14</sup> Similarly, the potential for the DMA-centered oxidation around  $E_{\text{ox},1} = +0.44$  V (in **3**) is not affected by other donor or acceptor groups (as in **5–8**). Clearly, donor–acceptor conjugation across the central TEE scaffold is not very efficient and the peripheral donor and acceptor groups behave almost as noninteracting redox centers. Note that the first 1e<sup>−</sup> reduction of *p*-nitrophenylacetylene in MeCN occurs at  $-1.38$  V<sup>15</sup> and the oxidation of *N,N*-dimethylaniline in MeCN at  $+0.40$  V.<sup>16</sup> The longest wavelength absorption band in the UV/vis spectra (in CHCl<sub>3</sub>) is an intramolecular CT band not only in the case of donor–acceptor chromophores **6–8** but also in the case of bis-donor-substituted **5**, reflecting the electron acceptor character of the TEE moiety. Upon protonation of the DMA moiety, the longest-wavelength CT band disappears, while it is regained by neutralization.

Two-dimensional acetylenic scaffolding, using TEEs, generates families of much more potent all-carbon acceptors. Upon decoration of perethynylated dehydroannulenes (such as **9–12**),<sup>17</sup> expanded radialenes (such as **13**),<sup>18</sup> and radiannulenes (such as **14**)<sup>19</sup> with peripheral *N,N*-dialkylanilino (DAA) donors, chromophores featuring intense and strongly bathochromically shifted intramolecular CT bands are obtained (Figure 1). Functionalization by the peripheral donor groups provides two additional advantages: they increase the solubility of the large carbon sheets and, most importantly, stabilize the electron-accepting cores dramatically against attack by nucleophiles. In fact, the synthesis of hexadecadehydro[20]annulenes, such as **10**, and tetracosade-

TABLE 1. Cyclic Voltammetry and UV/Vis Data for Arylated TEEs



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	$E_{\text{ox},1}^a$ [V]	$E_{\text{red},1}^a$ [V]	$\lambda_{\text{max}}^b$ [nm (eV)]
<b>1</b>	SiMe <sub>3</sub>	SiMe <sub>3</sub>	SiMe <sub>3</sub>	SiMe <sub>3</sub>		−1.96	350 (3.54)
<b>2</b>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>	SiMe <sub>3</sub>	Si( <i>i</i> Pr) <sub>3</sub>		−1.36	382 (3.25)
<b>3</b>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>	SiMe <sub>3</sub>	Si( <i>i</i> Pr) <sub>3</sub>	+0.44	−1.94	433 (2.87)
<b>4</b>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>		−1.35	403 (3.08)
<b>5</b>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>	Si( <i>i</i> Pr) <sub>3</sub>	+0.42	−1.99	428 (2.90)
<b>6</b>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>	+0.47	−1.40	468 (2.65)
<b>7</b>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	Si( <i>i</i> Pr) <sub>3</sub>	Si( <i>i</i> Pr) <sub>3</sub>	+0.46	−1.37	447 (2.78)
<b>8</b>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	<i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub>	+0.46 <sup>c</sup>	−1.38	486 (2.55)

<sup>a</sup> In THF + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>; Fc<sup>+</sup>/Fc reference. <sup>b</sup> In CHCl<sub>3</sub>, 298 K. <sup>c</sup> Peak potential,  $E_{\text{pc}}$ , for irreversible oxidation.

hydro<sup>30</sup>annulenes, such as **12**, is not possible without such stabilizing groups.

The optical HOMO–LUMO gaps, extrapolated from either the end absorption or the maximum of the longest-wavelength UV/vis band, correlate well with the electrochemical gaps. This suggests that in both quantities the same orbitals (HOMO and LUMO) are involved. Particularly noteworthy is the ease of reduction of the bicyclic radiannulene chromophore **14**: it undergoes three reversible electron uptakes in THF, the first one occurring at −0.99 V. If the dialkylanilino groups are replaced by 3,5-di(*tert*-butyl)phenyl moieties, the first electron uptake by the C<sub>50</sub> core of **14** occurs at −0.83 V. These first reduction potentials are lower than that for the first reduction of buckminsterfullerene (C<sub>60</sub>, −1.02 V under comparable conditions), which is touted as a very good electron acceptor.

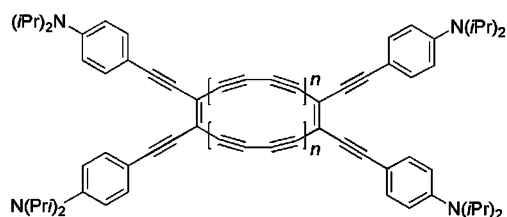
Arylated TEEs act as molecular switches<sup>20–22</sup> possessing two bistable states and undergoing switching exclusively under photoirradiation.<sup>23</sup> Thus, photochemical  $E \rightarrow Z$  isomerization provided access to (*Z*)-bis-DAA-substituted TEEs, such as **15** (Figure 2), which are precursors in the synthesis of dehydroannulenes **9–12**.<sup>17,19</sup> The fully reversible, optically active photoswitch (*R,R*)-**16**/*(R,R)*-**17** represents one of the rare systems allowing two-way photochemical interconversion not perturbed by thermal isomerization pathways and with good resistance against photofatigue.<sup>24</sup> Irradiation at  $\lambda = 398$  nm converts *trans*-isomer (*R,R*)-**16** into *cis*-isomer (*R,R*)-**17**, whereas switching in the opposite direction occurs upon irradiation at 323 nm. Compound **18** consists of three addressable subunits that can undergo individual, reversible switching cycles.<sup>25,26</sup> The TEE core can be reversibly photoisomerized between its *cis* and *trans* forms, the dihydroazulene unit can be transformed into a vinylheptafulvene moiety (**19**) upon irradiation,<sup>27</sup> and the electron-donating effect of the DMA group can be revers-

ibly eliminated by protonation/neutralization. By various pH- and light-controlled switching cycles, six out of the eight possible states of this elaborate system could be individually addressed.

### 3. Cyanoethynylethenes

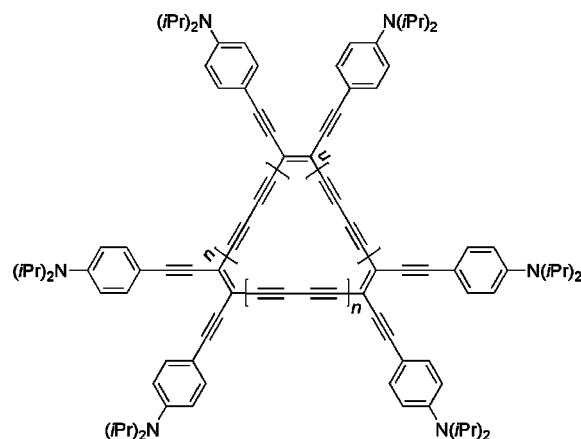
Replacement of acetylene moieties in TEEs by C≡N groups afforded the cyanoethynylethenes (CEEs, Figure 3), of which only two derivatives had been previously reported.<sup>28,29</sup> CEEs, such as **20–23**, are much stronger electron acceptors than their TEE analogues, and their first reduction potentials shift strongly anodically with increasing number of cyano groups.<sup>30</sup> Replacement of one RC≡C– by a N≡C– group moves the first reduction potential anodically by 380 mV, whereas substitution of RC≡C–C–C≡CR by NC–C–CN moieties produces an average anodic shift of this potential by 830 mV. Thus, dimeric **23** ( $E_{\text{red},1} = -0.57$  V in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>, vs Fc<sup>+</sup>/Fc) approaches the electron-accepting power of TCNE ( $E_{\text{red},1} = -0.32$  V).<sup>31,32</sup> On the other hand, the silylated CEE derivatives are much more delicate chromophores. While many TEE derivatives (Table 1) are thermally (up to 200 °C) and environmentally stable molecules that can be stored as solids for months in the air at room temperature, the silylated CEEs are highly reactive, strongly electrophilic chromophores that readily undergo conjugate additions with nucleophiles such as amines and alcohols.

As already described for the extended macrocyclic chromophores obtained by TEE scaffolding (Figure 1), introduction of DMA donor groups greatly enhances the stability of the CEEs and the DMA-substituted derivatives **24–28** shown in Figure 3 feature high environmental and thermal stability, some of them up to 250 °C.<sup>30,33,34</sup> In contrast to D–A-substi-



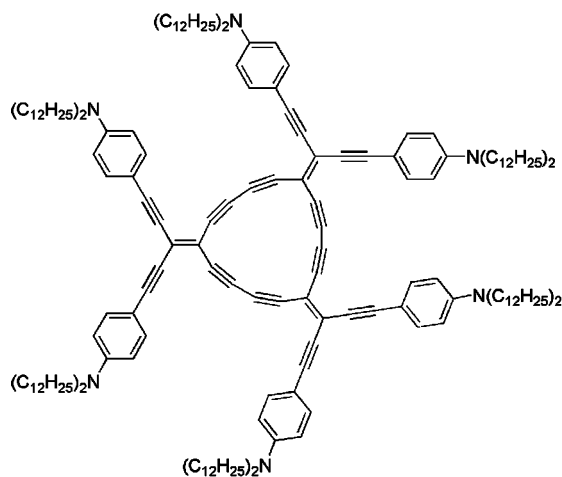
**9**  $n = 1$   $\lambda_{\max}$  600 nm (23 000 M<sup>-1</sup> cm<sup>-1</sup> (2.07 eV))  
 $E_{\text{ox},1}$  +0.24 V  
 $E_{\text{red},1}$  -1.14 V

**10**  $n = 2$   $\lambda_{\max}$  552 nm (41 100 M<sup>-1</sup> cm<sup>-1</sup> (2.25 eV))  
 $E_{\text{ox},1}$  +0.34 V  
 $E_{\text{red},1}$  -0.98 V

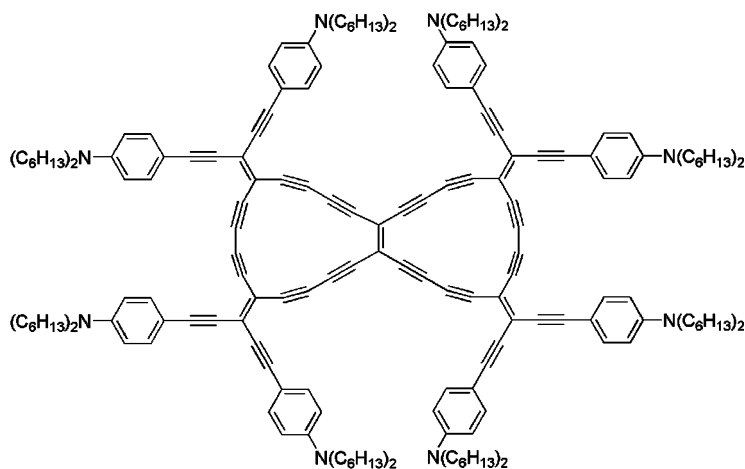


**11**  $n = 1$   $\lambda_{\max}$  573 nm (131 000 M<sup>-1</sup> cm<sup>-1</sup> (2.17 eV))  
 $E_{\text{ox},1}$  +0.37 V  
 $E_{\text{red},1}$  -1.31 V

**12**  $n = 2$   $\lambda_{\max}$  614 nm (76 400 M<sup>-1</sup> cm<sup>-1</sup> (2.02 eV))  
 $E_{\text{ox},1}$  +0.40 V  
 $E_{\text{red},1}$  -1.20 V



**13**  $\lambda_{\max}$  646 nm (171 000 M<sup>-1</sup> cm<sup>-1</sup> (1.92 eV))  
 $E_{\text{ox},1}$  +0.35 V  
 $E_{\text{red},1}$  -1.30 V



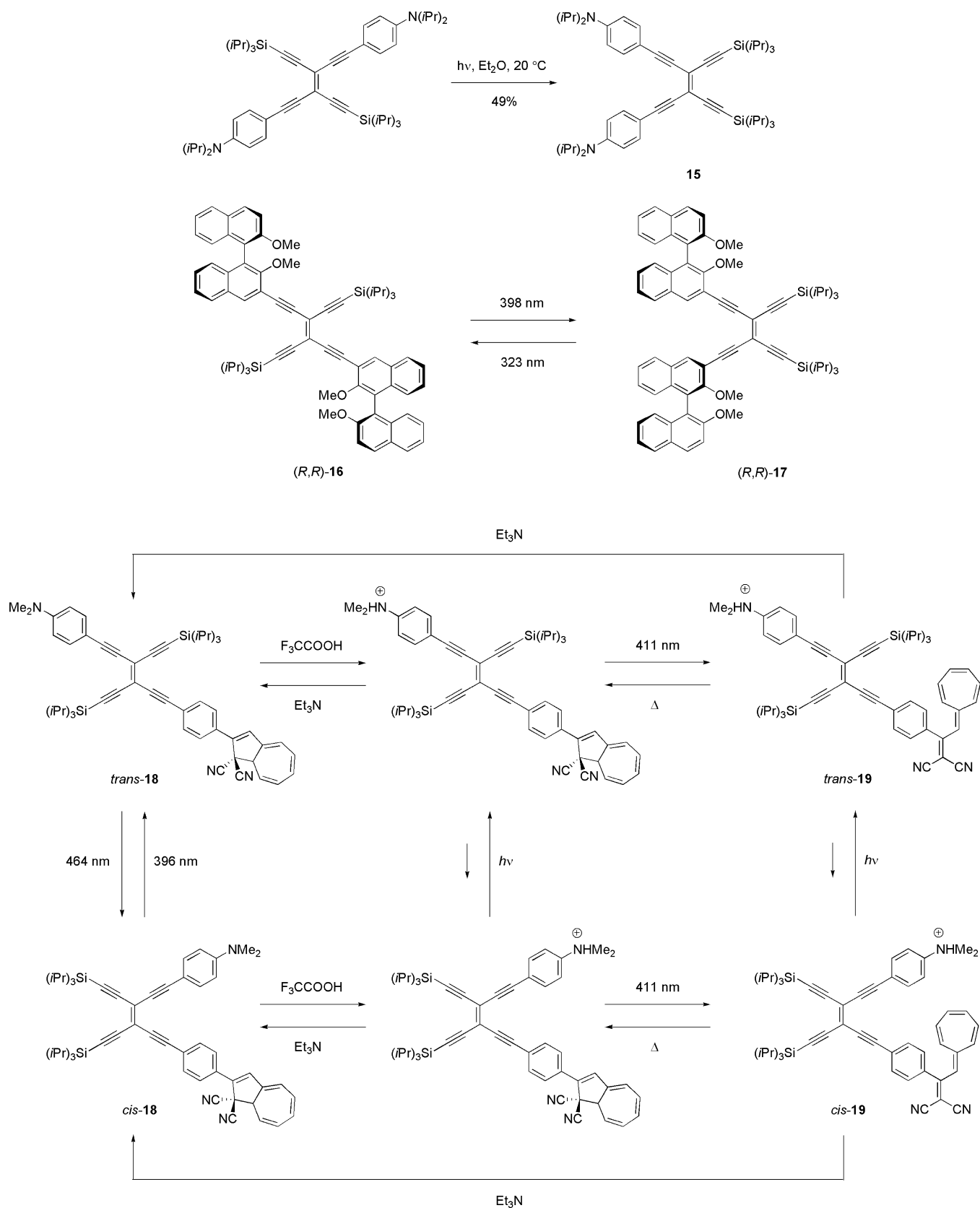
**14**  $\lambda_{\max}$  698 nm (85 900 M<sup>-1</sup> cm<sup>-1</sup> (1.78 eV))  
 $E_{\text{ox},1}$  +0.37 V  
 $E_{\text{red},1}$  -0.99 V

**FIGURE 1.** Donor-substituted expanded all-carbon sheets. Given are the electrochemical data in CH<sub>2</sub>Cl<sub>2</sub> (**9–12**, **13**) or THF (**14**) + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> vs Fc<sup>+</sup>/Fc and the maxima of the longest-wavelength CT bands,  $\lambda_{\max}$ , in CH<sub>2</sub>Cl<sub>2</sub> (**9–12**) or CHCl<sub>3</sub> (**13**, **14**) at 298 K.

tuted TEEs, DMA-substituted CEEs, such as **24** and **25**, can be sublimed undecomposed.

Donor-substituted CEEs display strong intramolecular CT character, resulting in intense, strongly bathochromically shifted CT bands in their UV/vis spectra. The spectrum of compound **28** in CH<sub>2</sub>Cl<sub>2</sub> features a maximum of the CT band at

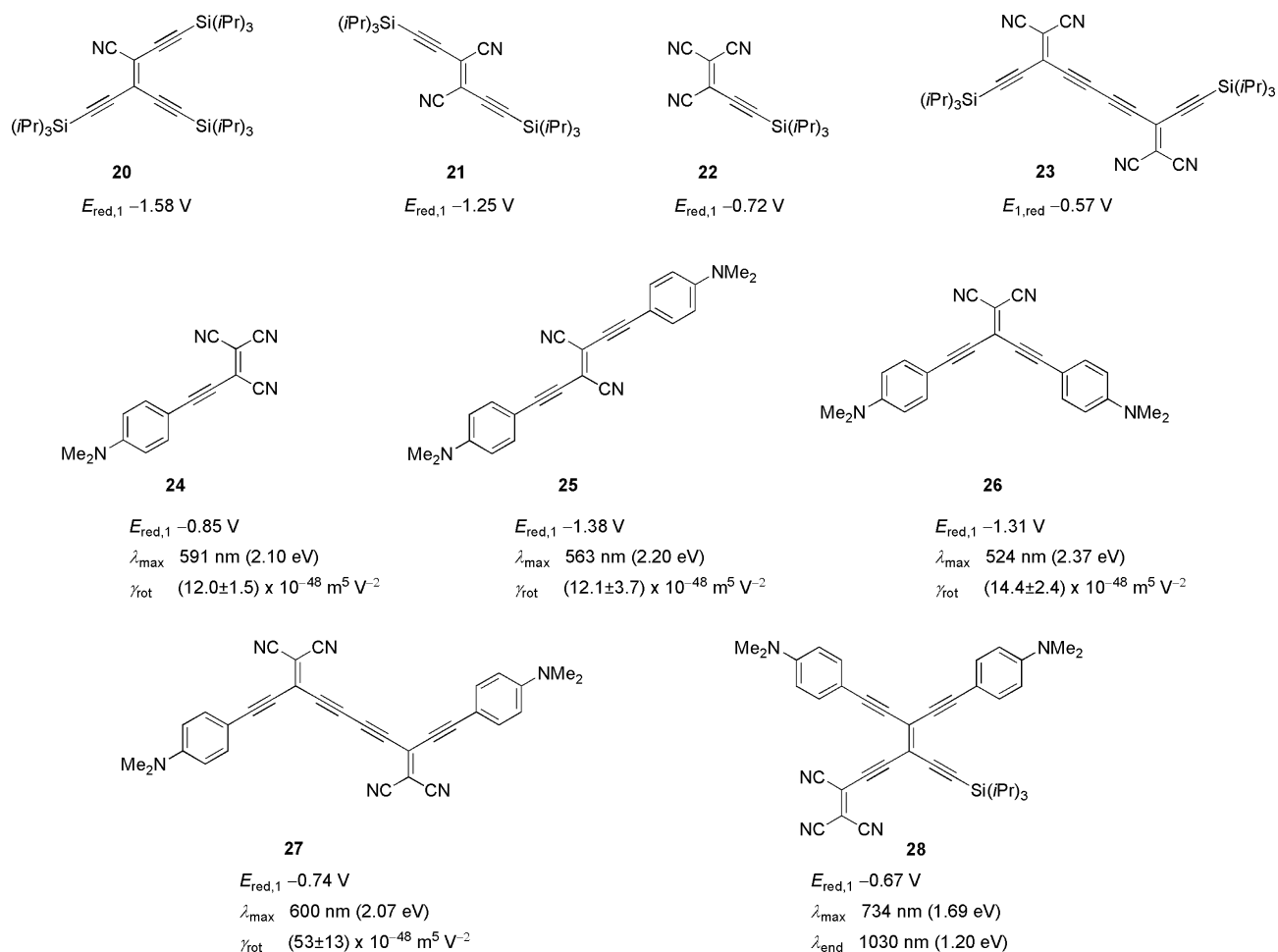
734 nm (1.69 eV) and an end absorption extending to 1030 nm (1.20 eV). X-ray crystal structures of **24** and **25** revealed a pronounced quinoid character of the DMA rings. The chromophores feature large solvatochromic effects both in their absorption and in their emission spectra.<sup>34</sup> Remarkable are the solvatochromic properties of centrosymmetric **25**: the CT band



**FIGURE 2.** Molecular photoswitches based on arylated TEEs.

shifts from 524 nm (2.37 eV) in hexane/ $\text{CHCl}_3$  to 563 nm (2.20 eV) in pure  $\text{CHCl}_3$ , while the Stokes shift of the fluores-

cence band increases from  $1540\text{ cm}^{-1}$  (0.19 eV) to  $2219\text{ cm}^{-1}$  (0.27 eV). In the absence of a dipole moment, these



**FIGURE 3.** Silylated and donor-substituted CEEs. Given are the first reduction potentials  $E_{\text{red},1}$  in  $\text{CH}_2\text{Cl}_2$  + 0.1 M  $n\text{Bu}_4\text{NPF}_6$  vs  $\text{Fc}^+/\text{Fc}$  and, for the donor-substituted derivatives, the maxima of the CT bands  $\lambda_{\text{max}}$  in  $\text{CHCl}_3$  at 298 K and the third-order molecular polarizability  $\gamma_{\text{rot}}$  measured by DFWM experiments in  $\text{CH}_2\text{Cl}_2$ . The end absorption  $\lambda_{\text{end}}$  of **28** is also shown.

findings seem to violate the Franck–Condon principle. We therefore explain the solvatochromism of **25** by an increase in the electric moment from the ground to the excited state resulting from a change in the quadrupole moment, with partial positive charges on the two DMA donors and partial negative charges on the two cyano moieties.<sup>35</sup> From the optical spectra, large transition dipole moments, up to 9.8 D (for **24**) were calculated.

Small optical HOMO–LUMO gaps, large transition dipole moments, and large changes in the electric moment from the ground to the excited state make the donor-substituted CEEs attractive for NLO applications.<sup>36,37</sup> The third-order NLO properties of donor-substituted CEEs **24**–**27** were investigated by degenerate four-wave mixing (DFWM) experiments.<sup>36</sup> Extraordinarily large third-order optical nonlinearities, relative to the small molecular mass of these molecules, that are within a factor of 50 from the predicted fundamental limit<sup>38</sup> were observed (Figure 3). The highest rotational average of the

third-order molecular polarizability ( $\gamma_{\text{rot}} = (53 \pm 13) \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$ ) was measured for dimeric CEE **27** at the off-resonance wavelength of 1.5  $\mu\text{m}$ .

A high-quality crystalline thin film (ca. 20 nm thickness) of donor-substituted CEE **24** was prepared by vacuum deposition on highly oriented pyrolytic graphite (HOPG).<sup>39</sup> In this film, planar molecules of **24** adopt a favorable antiparallel molecular dipole orientation at an intermolecular stacking distance of 3.44 Å. The structure of the crystalline thin film was solved by transmission electron microscopy (TEM) electron diffraction and shown to be identical to the previously determined X-ray crystal structure. Nanoscale data recording into the crystalline film by scanning tunneling microscopy (STM) afforded dots with an average diameter of 2.1 nm, which amounts to a possible storage density of  $10^{13}$  bits  $\text{cm}^{-2}$ . The formation of these dots is explained by intermolecular, electric field-induced CT in stacks of **24**.

**TABLE 2.** A Series of DMA-substituted CEEs **29–32** to Explore the D–A Conjugation and NLO Properties as a Function of the  $\pi$ -Spacer between Donor and Acceptor Moieties<sup>a</sup>

	$\lambda_{\text{end}}$ [nm (eV)]	$E_{\text{ox},1}$ [V]	$E_{\text{red},1}$ [V]	$\Delta(E_{\text{ox},1} - E_{\text{red},1})$ [V]	$\gamma_{\text{rot}} \times 10^{-48}$ [m <sup>5</sup> V <sup>-2</sup> ]
<b>29</b>	655 (1.89)	+0.60	-1.34	1.94	14 ± 3
<b>30</b>	695 (1.78)	+0.53	-1.25	1.78	18 ± 5
<b>31</b>	740 (1.68)	+0.40	-1.18	1.58	13 ± 3
<b>32</b>	785 (1.58)	+0.46	-1.07	1.53	33 ± 15

<sup>a</sup> Shown are the optical and electrochemical gaps and the third-order molecular polarizability measured by DFM experiments in CH<sub>2</sub>Cl<sub>2</sub>.

#### 4. Evaluation of the Efficiency of Intramolecular Charge-Transfer Interactions in the Ground State

It has become common practice in the literature to use UV/vis spectra as a measure for evaluating the effectiveness of different conjugation pathways in D–A systems, assuming that a more bathochromically shifted maximum ( $\lambda_{\text{max}}$ ) of the lowest-energy CT band reflects a better D–A  $\pi$ -conjugation. In contrast, we have found that this does not hold for push–pull chromophores formed from strong acceptors and donors separated by  $\pi$ -conjugated spacers, such as in donor-substituted CEEs. In a comprehensive study, supported by theoretical calculations, we identified a strong correlation between ground-state D–A conjugation and the length of the  $\pi$ -spacer, which provides useful guidelines for tuning the optical gap in strong push–pull systems.<sup>34,40</sup> Contrary to previously common opinion, efficient D–A conjugation leads to larger optical gaps. Smaller optical gaps, that is, more bathochromically shifted CT bands, are obtained by impairing D–A conjugation through introduction of  $\pi$ -spacers such as alkenes or alkynes.<sup>34,40,41</sup> At strong D–A conjugation, the HOMO (highest occupied molecular orbital) of the donor is lowered and the LUMO (lowest unoccupied molecular orbital) of the acceptor raised, resulting in a large optical (and electrochemical) gap. In the case of weaker ground-state D–A conjugation, that is, when donor and acceptor are separated by larger  $\pi$ -spacers, the energy levels of HOMO and LUMO resemble those in the free components, and a smaller optical gap (bathochromically shifted CT band) is observed. It is noteworthy that the introduction of extended  $\pi$ -spacers also strongly enhances the third-order optical nonlinearity of the push–pull chromophores, which correlates with the lower optical gap.<sup>36,37</sup>

These initial conclusions for donor-substituted CEEs were further supported by the study in a series of push–pull chromophores

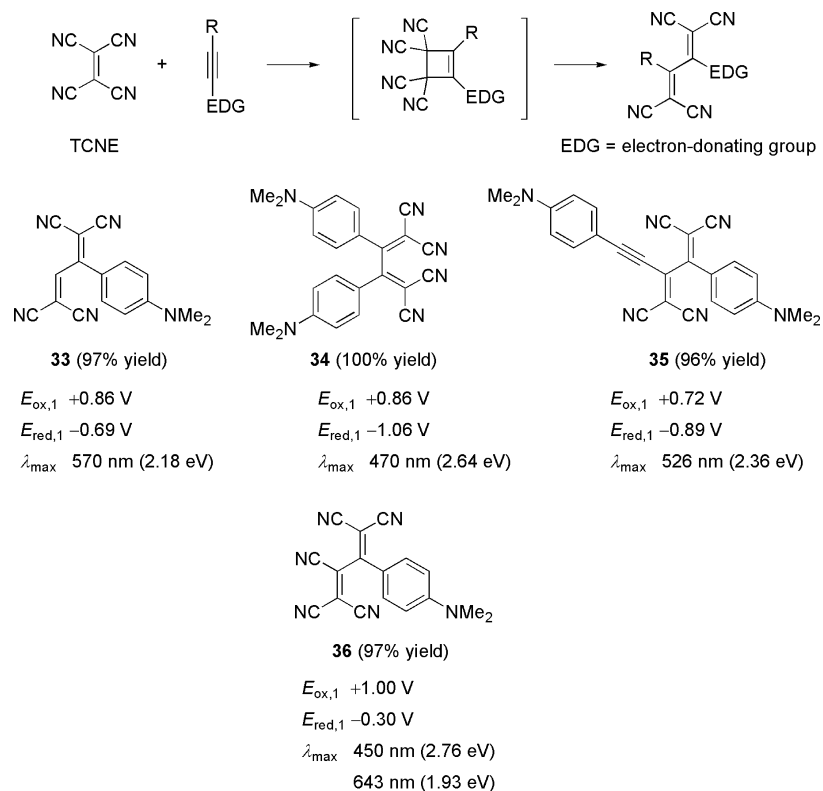
**29–32** in which the unsaturated spacer between DMA donor and C(CN)<sub>2</sub> acceptor moieties was gradually extended (Table 2).<sup>40</sup> The electrochemical HOMO–LUMO gap, calculated as the difference between first oxidation and reduction potentials ( $\Delta(E_{\text{ox},1} - E_{\text{red},1})$ ), decreases steadily from 1.94 (**29**) to 1.53 V (**32**) with increasing length of the  $\pi$ -spacer. At the same time, the optical gap, determined from the end absorption of the UV/vis spectra, changes from  $\lambda_{\text{end}} = 655$  nm (1.89 eV) in **29** to  $\lambda_{\text{end}} = 785$  nm (1.58 eV) in extended chromophore **32**. These changes in electrochemical and optical gaps result solely from the reduction in the D–A conjugation with increasing spacer length.<sup>40</sup>

Thus, it can be concluded that the bathochromic shift of the CT band in the UV/vis spectrum is not an appropriate measure for the efficiency of D–A conjugation in the ground state. For this purpose, ground-state data, such as <sup>13</sup>C NMR chemical shifts, bond length alternation, and quinoid character of aromatic rings in X-ray crystal structures, redox potentials, or theoretical calculations<sup>42,43</sup> need to be used instead. Similar conclusions have been reached by Meier and co-workers for D–A-substituted oligo(1,4-phenylene vinylene)s<sup>44</sup> and oligo(1,4-phenylene ethynylene)s,<sup>45</sup> and more recently by Haley and co-workers for fluorinated D–A-substituted tetrakis(phenylethynyl)benzenes and bis(dehydrobenzoannuleno)benzenes.<sup>46</sup>

#### 5. Donor-Substituted 1,1,4,4-Tetracyanobuta-1,3-dienes and 1,1,2,4,4-Pentacyanobuta-1,3-dienes

Thermal [2 + 2] cycloaddition of TCNE with electron-rich metal acetylides followed by electrocyclic ring opening of the initially formed cyclobutenes to give organometallic 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivatives had already been reported by Bruce and co-workers in the early 1980s.<sup>47</sup> Sub-



SCHEME 1. Donor-substituted TCBDs **33–35** and PCBD **36**<sup>a</sup>

<sup>a</sup> Given are the yields of the [2 + 2] cycloaddition of TCNE with donor-substituted alkynes, followed by retro-electrocyclization, the electrochemical data in  $\text{CH}_2\text{Cl}_2$  + 0.1 M  $n\text{Bu}_4\text{NPF}_6$  vs  $\text{Fc}^+/\text{Fc}$ , and the maxima of the longest-wavelength CT bands  $\lambda_{\text{max}}$  in  $\text{CH}_2\text{Cl}_2$  at 298 K.

sequently, a variety of organic and organometallic TCBDs have been prepared, and some of them have been investigated as second-order NLO materials.<sup>48–50</sup> Nevertheless, the corresponding reaction with electron-rich, organo-donor-substituted alkynes had not been systematically studied.

We found that a wide variety of donor-substituted alkynes readily undergo a high-yielding, atom-economic transformation, a formal [2 + 2] cycloaddition followed by retro-electrocyclization, with TCNE to yield a new class of potent CT chromophores, donor-substituted TCBDs, such as **33–35** (Scheme 1).<sup>51,52</sup> Very recently, we showed that even electronically confused alkynes bearing one electron-donating group and one electron-withdrawing group, such as DMA-substituted cyanoalkynes, reacted with TCNE to yield donor-substituted 1,1,2,4,4-pentacyanobuta-1,3-dienes (PCBDs), such as **36**.<sup>53</sup>

Although donor-substituted TCBDs show a high degree of nonplanarity, as revealed by extensive X-ray crystallographic studies, they feature efficient intramolecular CT interactions. The DMA rings in their crystal structures exhibit high quinoid character, and the UV/vis spectra display intense, low-energy intramolecular CT bands, with maxima varying between 450 nm (2.76 eV) and 700 nm (1.76 eV). DAA-substituted PCBDs,

such as **36**, display two intramolecular CT bands, with the one of lower energy being notably weaker (Scheme 1).

Donor-substituted TCBDs are thermally stable up to 300 °C and can be sublimed undecomposed. Large third-order optical nonlinearities, reaching  $\gamma_{\text{rot}}$  values of  $(12 \pm 2) \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$  for **35**,<sup>51</sup> accompanied by ready synthetic accessibility of larger compound quantities and high environmental stability make these chromophores ideal materials for device construction. Their nonplanarity enables the formation of high optical quality amorphous thin films<sup>54</sup> that have been introduced into highly nonlinear organic silicon-on-insulator waveguides for all-optical processing with excellent performance.

Despite the substitution with *N,N*-dialkylanilino, methoxyphenyl, or thienyl donors, the TCBD and PCBD moieties in these push–pull systems remain potent electron acceptors that undergo two reversible  $1\text{e}^-$  reduction steps. The introduction of the additional CN group when going from TCBD **33** ( $E_{\text{red},1} = -0.69 \text{ V}$ ) to PCBD **36** ( $E_{\text{red},1} = -0.30 \text{ V}$  in  $\text{CH}_2\text{Cl}_2$  vs  $\text{Fc}^+/\text{Fc}$ )<sup>53</sup> greatly facilitates the two electron uptakes. Gratifyingly, the first reduction of PCBD **36** occurs at very similar potential to those reported under identical conditions for TCNE ( $E_{\text{red},1} = -0.32 \text{ V}$ ) and TCNQ ( $E_{\text{red},1} = -0.25 \text{ V}$ ).<sup>55</sup>

## 6. Multivalent Charge-Transfer Chromophores

Particularly remarkable are the redox properties of oligomeric and dendritic, donor-substituted TCBDs that exhibit several reversible electron-transfer processes under electrochemical conditions. Thus, the trimeric DAA-substituted TCBD **37** undergoes six reversible  $1e^-$  reduction steps, each centered on a dicyanovinyl moiety, in the narrow potential range between  $-0.69$  and  $-1.69$  V in  $\text{CH}_2\text{Cl}_2$  (Figure 4).<sup>52</sup> For comparison, the six electron uptakes by fullerene  $\text{C}_{60}$  in MeCN/toluene occur in a much wider potential range between  $-0.98$  and  $-3.26$  V.<sup>56</sup>

Recently, we introduced extended multivalent CT systems, such as **38** and **39**,<sup>57</sup> acting as potent “molecular batteries”,<sup>58</sup> featuring exceptional electron uptake capacity (Figure 4). In contrast to the tris-TCBD derivative **37**, buta-1,3-diyne-1,4-diyl instead of ethyne-1,2-diyl linkers were used to attach the DAA substituents to the central core to (i) reduce steric crowding and (ii) increase the distance between pairs of the redox-active  $\text{C}(\text{CN})_2$  moieties in order to bring the individual reduction potentials even closer. The multivalent TCBD derivatives **38** and **39** were obtained as deep-colored, highly stable solids in excellent yields of 77% and 86%, respectively, by the “click-chemistry”-type TCNE addition to the corresponding oligoalkyne precursors. Electrochemical studies revealed that all DAA moieties in multivalent donor-substituted TCBDs are reversibly oxidized in a single multielectron transfer, suggesting that they all behave as independent electroactive centers;<sup>59</sup> for example, dendritic **39** undergoes a unique  $12e^-$  oxidation step at  $+0.87$  V. A similar behavior has previously been observed, among others, for ferrocenyl dendrimers by Astruc and co-workers.<sup>58</sup> A number of reversible reduction steps centered on the two-electron dicyanovinyl acceptors were observed. Thus, dendritic **39** accepts 24 electrons in two successive  $12e^-$  reduction steps within an exceptionally narrow potential range between  $-0.70$  and  $-1.10$  V. Research activities toward the preparation of very large multivalent TCBDs with further enhanced charge uptake and storage capacity are currently being pursued.

## 7. Novel Cascade Reactions

While exploring the reactivity of multivalent TCBD derivatives, we found  $\text{C}\equiv\text{C}$  bonds adjacent to the electron-accepting TCBD units to be activated for the  $[2 + 2]$  cycloaddition with tetrathiafulvalene (TTF), followed by retro-electrocyclization, to give substituted 1,2-di(1,3-dithiol-2-ylidene)ethane fragments, as previously observed by Hopf and co-workers and Hirsch and

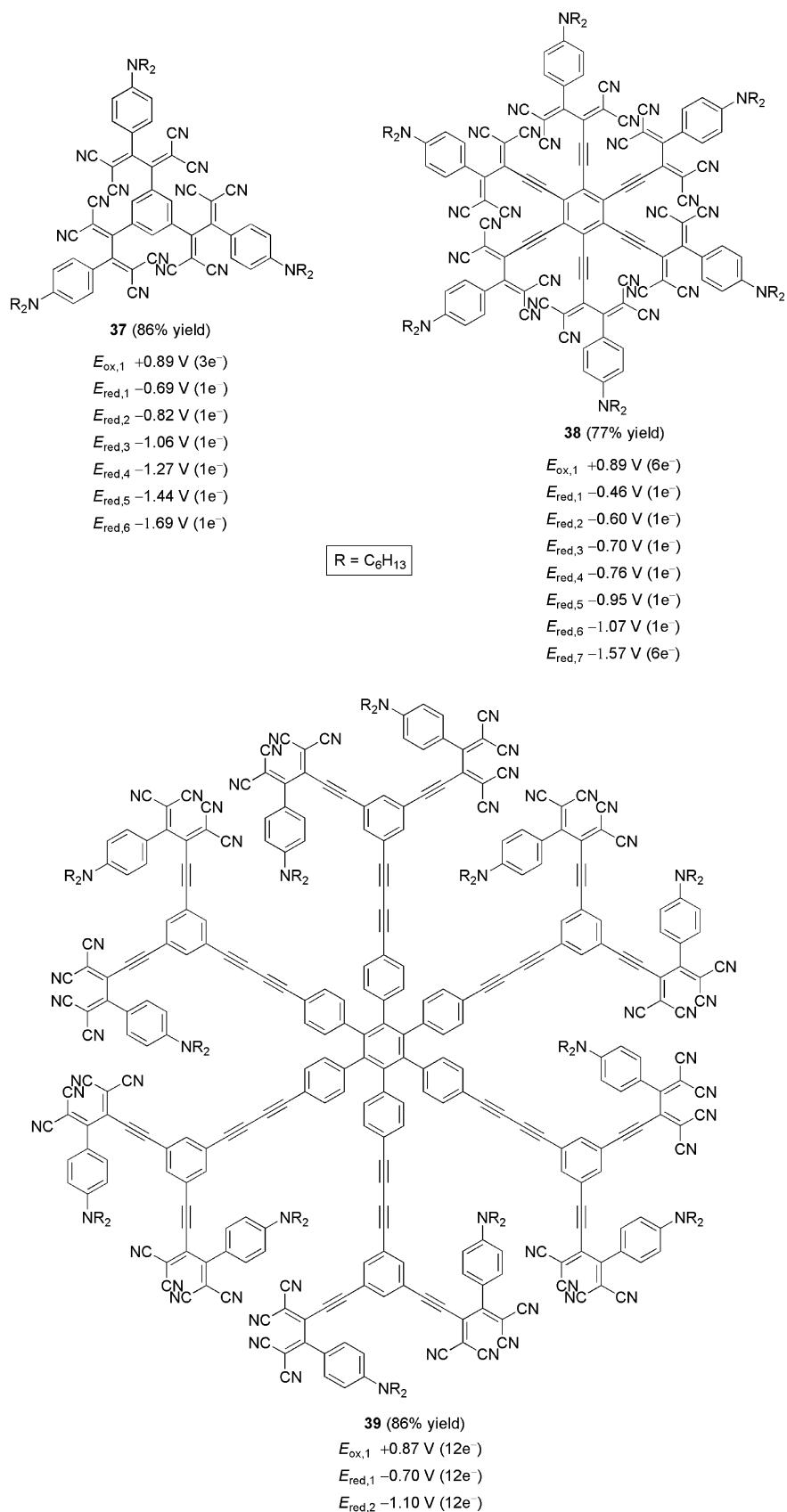
co-workers for cyanoethynylethenes<sup>60</sup> and  $\alpha,\omega$ -dicyanopolyynes,<sup>61</sup> respectively.

Based on this observation, we constructed a new family of [AB]-type oligomers with a dendralene-type backbone<sup>62,63</sup> by applying a cascade of sequential TCNE/TTF additions to appropriately end-capped polyynes.<sup>57</sup> In this cascade, TCBD moieties activate the adjacent acetylenic bonds electronically for the following reaction with TTF, whereas 1,2-di(1,3-dithiol-2-ylidene)ethane donors provide the activation for TCNE addition. Thus, upon alternating treatment of mono-DMA-, monophenyl-substituted tetrayne **40** with TCNE and TTF, the regular [AB]-type oligomer **41** was obtained as a thermally stable, black metallic solid (Scheme 2). Gratifyingly, the A–D–A–D chromophore **41** was also obtained as a single product in a five-component cascade reaction, by four successive  $[2 + 2]$  TCNE/TTF additions, followed by retro-electrocyclizations, to end-capped tetrayne **40**. Simply mixing a polyyne with appropriate acceptor (TCNE, TCNQ) and donor (TTF) components, which undergo these electronically controlled cascade additions, clearly opens up a new easy access to novel multivalent D–A chromophores.

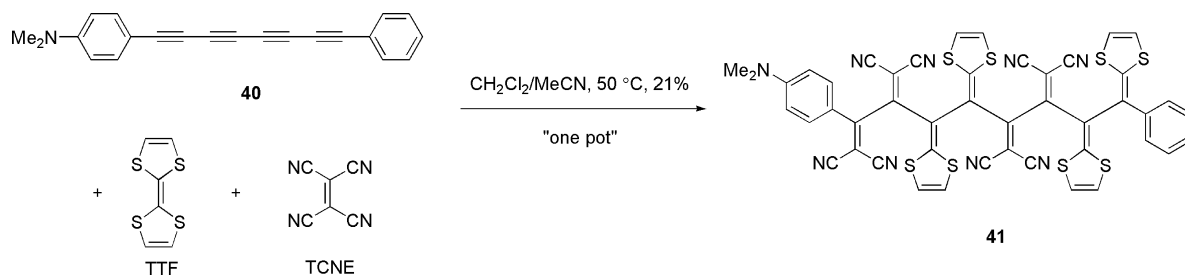
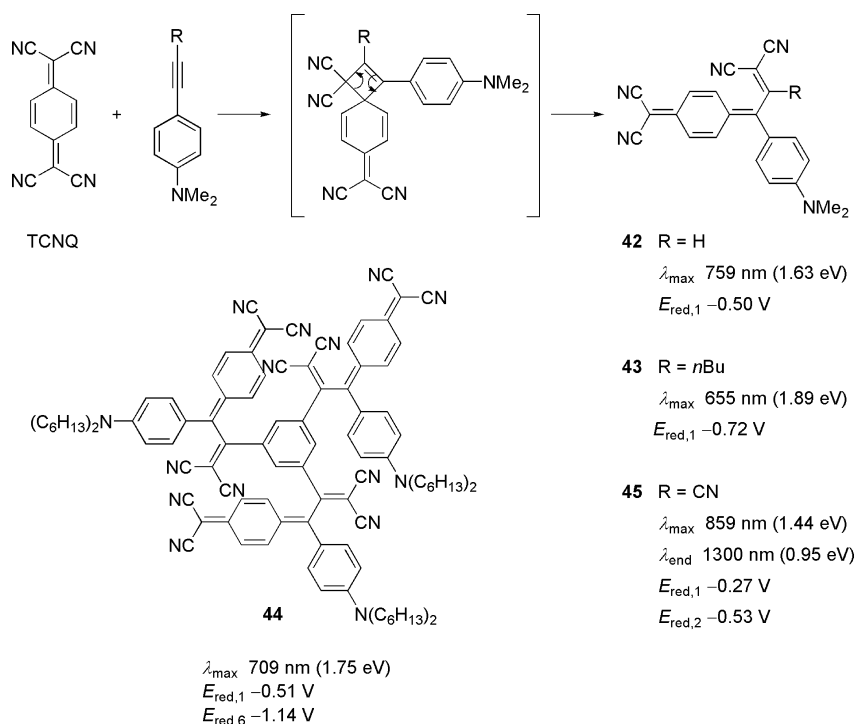
## 8. Charge-Transfer Chromophores by $[2 + 2]$ Cycloaddition of TCNQ with Alkynes

Back in the early 1970s, Hagihara and co-workers reported the reactions of Pt(II) alkynyls with TCNQ to give intensely colored products that were described as intermolecular CT complexes.<sup>64</sup> However, one of these products was later shown to be a buta-1,3-dienyl derivative apparently resulting from  $[2 + 2]$  cycloaddition of TCNQ to the alkyne moiety.<sup>65</sup> Nevertheless, no special attention was paid to this result, and the reaction was not further investigated. While the chemistry of strongly electrophilic TCNQ has been thoroughly investigated since then,<sup>66–68</sup> its reactivity toward alkynes remained unexplored. Namely, it possesses two types of strongly electron-deficient CC double bonds that could, in analogy to TCNE, undergo thermal  $[2 + 2]$  cycloaddition with donor-substituted alkynes, followed by retro-electrocyclization.

Recently, we showed that a variety of DAA-substituted alkynes react with TCNQ in a uniform manner to afford a new class of stable monomeric and oligomeric D–A chromophores, such as **42–44**, in high to quantitative yields (Scheme 3).<sup>69</sup> The cyclohexa-2,5-diene-1,4-diyldiene-expanded PCBD **45** was obtained from the corresponding electronically confused DMA-substituted cyanoalkyne and TCNQ under forcing con-



**FIGURE 4.** Dendritic donor-substituted TCBDs **37–39** acting as a type of “molecular batteries”. Given are the yields of the [2 + 2] cycloaddition/retro-electrocyclization sequences of TCNE with alkyne precursors and the cyclic voltammetry data in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> vs Fc<sup>+</sup>/Fc.

**SCHEME 2.** Five-Component Cascade Reaction of Four Successive [2 + 2] TCNE/TTF Additions, Followed by Retro-electrocyclizations, to End-Capped Tetrayne **40** to Give [AB]<sub>4</sub>-Type Oligomer **41****SCHEME 3.** Thermal [2 + 2] Cycloaddition of TCNQ with Donor-substituted Alkynes to Give a New Class of Nonplanar, CT Chromophores<sup>a</sup>

<sup>a</sup> Given are the maxima of the intramolecular CT bands,  $\lambda_{\text{max}}$ , in CH<sub>2</sub>Cl<sub>2</sub> at 298 K and the cyclic voltammetry data in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> vs Fc<sup>+</sup>/Fc.

ditions.<sup>53</sup> The reactions are completely regioselective, with the alkynes adding exclusively to one dicyanovinyl moiety of TCNQ.

The resulting chromophores are nonplanar (X-ray), yet efficient intramolecular CT interactions are established. The UV/vis spectra of **42–44** feature intense, low-energy intramolecular CT bands with maxima between 655 nm (1.89 eV, **43**) and 759 nm (1.63 eV, **42**). The additional CN group in **45** shifts the CT band to even lower energy, with the maximum at  $\lambda_{\text{max}} = 859$  nm (1.44 eV) being accompanied by a tail reaching far into the near-infrared and an end absorption near 1300 nm (0.95 eV). This low optical gap is quite remarkable for such a small chromophore.<sup>70</sup>

Monomeric TCNQ adducts, such as **42** and **43**, are potent electron acceptors and display two reversible one-electron reduction steps, centered on the two C(CN)<sub>2</sub> moieties (Scheme

3). The stepwise reduction of trimeric **44**, undergoing six reversible one-electron reduction steps in the narrow potential range between -0.51 and -1.14 V, indicates electrostatic interactions between the electroactive dicyanovinyl moieties. The two one-electron reductions of the expanded PCBD derivative **45** at -0.27 and -0.53 V are greatly facilitated compared with those of **42** (-0.50 and -0.76 V) as a result of the additional CN group. The first reduction step of **45** occurs at similar potential to that of TCNQ (-0.25 V), whereas the second reduction is notably facilitated (-0.53 V (**45**) vs -0.81 V (TCNQ)). This can be explained by the enhanced distance between the charge-hosting C(CN)<sub>2</sub> and C(CN)<sub>3</sub> moieties in **45**, leading to the reduction of electrostatic repulsion. We are confident that even stronger electron acceptors than the parent TCNE and TCNQ are in reach upon (i) incorporation of particularly strong acceptor moieties, such as 2,3,5,6-tetrafluoro-

7,7,8,8-quinodimethane ( $F_4$ -TCNQ;  $E_{\text{red},1} = +0.03$  V in MeCN vs  $Fc^+/Fc$ ; for conversion to the  $Fc^+/Fc$  scale, see ref 12),<sup>71</sup> 2,5-dicyano-7,7,8,8-tetracyanoquinodimethane (TCNQ(CN)<sub>2</sub>,  $E_{\text{red},1} = +0.15$  V),<sup>71</sup> and 3,6-difluoro-2,5,7,7,8,8-hexacyanoquinodimethane ( $F_2$ -HCNQ,  $E_{\text{red},1} = +0.43$  V)<sup>72</sup> or (ii) attenuation of the donor moiety. Investigations in this direction are currently being pursued.

## 9. Conclusions

Our synthesis-driven search for new acetylene-derived strong electron acceptors and the exploration of the properties of their donor-substituted push–pull derivatives have been quite successful. Moving from TEEs to DEEs to TCBDs and PCDBs and ultimately to new expanded derivatives of TCNQ has increasingly facilitated reversible electron uptake, and first reduction potentials around  $E_{\text{red},1} \approx -0.25$  V in  $CH_2Cl_2$  (vs  $Fc^+/Fc$ ) are similar to those of the benchmark acceptors TCNE and TCNQ. Remarkable also are the acceptor properties of expanded all-carbon sheets: with their large number of  $\pi$ -conjugated sp-C-atoms, perethynylated dehydroannulenes, expanded radialenes, and radiaannulenes<sup>73</sup> feature first reduction potentials at values similar to those of fullerene  $C_{60}$ , which is touted to be a good electron acceptor. General rules for tuning optical (and electrochemical) gaps of strong push–pull systems could be established: Increasing the length of the  $\pi$ -spacer in D– $\pi$ –A systems reduces ground-state D–A conjugation and lowers the HOMO–LUMO gap. “Click-chemistry”-type, atom-economic, and near-quantitative [2 + 2] cycloadditions of TCNE and TCNQ to electron-rich alkynes, followed by retro-electrocyclization, generated not only new families of strong, nonplanar CT chromophores but also provided access to multivalent, dendritic derivatives with the character of “molecular batteries”, capable of multiple reversible electron uptakes in a narrow potential range. Controlled by the electronic character of the alkynes in polyynes oligomers, sequential TCNE and TTF cycloaddition/retro-electrocyclization cascades opened the way to new [AB]-type oligomers, with alternating donors and acceptors along the dendralene-type backbone. The exploitation of the remarkable optoelectronic properties of these, in most cases, highly stable push–pull chromophores is now underway. Easy and inexpensive access to large compound quantities, high third-order optical nonlinearities, and high optical quality film formation, as demonstrated for the nonplanar donor-substituted TCBDs, should make these chromophores useful components for future optical-processing device applications. It is also clear that there remains much room for synthesis-driven

discovery of new, even more potent acceptors and push–pull chromophores.

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## BIOGRAPHICAL INFORMATION

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## FOOTNOTES

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