Redox Properties of Linear and Cyclic Scaffolds Based on Di- and Tetraethynylethene

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A large selection of linear and cyclic acetylenic scaffolds based on functionalized di- and tetraethynylethenes (DEEs, TEEs) have been prepared during the past ten years, such as poly(triacetylene)s (PTAs), expanded dendralenes, or perethynylated expanded radialenes and dehydroannulenes. These carbon-rich oligoenynes are interesting for their electronic and advanced materials properties. In this account, we highlight their redox properties. Moreover, the electrochemistry of cyanoethynylethenes (CEEs), a class of powerful electron acceptors that have recently attracted our attention, since they combine the scaffolding potential of TEEs with the superior acceptor strength of tetracyanoethene (TCNE), will also be discussed.

1. Introduction

The acetylenic scaffolding of derivatized tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) and (*E*)-1,2-diethynylethene [DEE, (*E*)-hex-3-ene-1,5-diyne] modules has provided a large selection of extended, carbon-rich chromophores[1] that are formally derived from parent classes of linear and cyclic alkenes, such as the dendralenes, poly(acetylene)s (PAs), radialenes, and annulenes (Figure 1). These buta-1,3-diynediyl-expanded derivatives include *iso*-poly(triacetylene)s (expanded dendralenes), poly(triacetylene)s [PTAs, expanded poly(acetylene)s], perethynylated expanded radialenes, and dehydroannulenes. Both these derivatives and the related ethynediyl-expanded scaffolds[2] and "carbomer" structures[3] attract substantial interest for their electronic properties; in the case of annu-

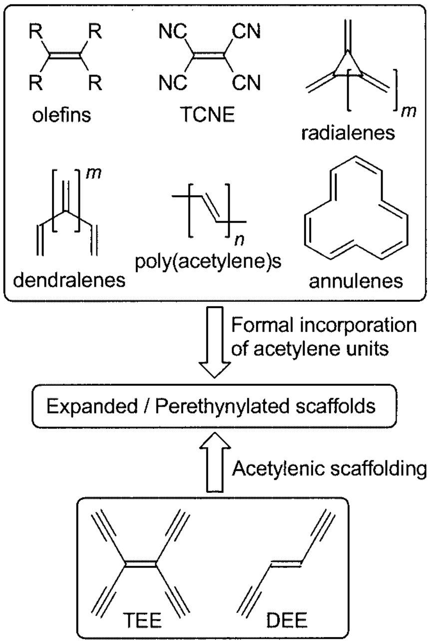

Figure 1. Parent classes of linear and cyclic olefins; formal incorporation of acetylene units affords perethynylated/expanded scaffolds, such as linear poly(triacetylene)s and cyclic expanded radialenes; synthetically, these can be obtained from suitably functionalized diethynylethene (DEE) and tetraethynylethene (TEE) building blocks[1]

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lene ring carbomers in particular with respect to the question of aromaticity.[4]

Systematic studies on TEE- and DEE-based scaffolds have contributed to a fundamental understanding of π-electron delocalization in systems where two or more conjugation pathways, linearly or crossed, can be operative or triggered. One of the most remarkable properties of these molecules is their readiness to accommodate electrons upon reduction. It is known that acetylenic C$\equiv$C triple bonds are not reducible electrochemically in organic solvents when they are isolated in molecules, whereas they may undergo reductive electron transfers when entering π-electron interactions with other multiple bonds or conjugated systems.[5] However, this electron-accepting behavior is strongly influenced by the true structure of the scaffold, be it a linear structure versus a cyclic one, or a cross-conjugated arrangement of triple and double bonds versus a linearly conjugated one. Moreover, the functional properties of the scaffolds are strongly enhanced by aryl substitution,[1f] providing advanced materials for photonics and electronics. Development of synthetic strategies[1a,1d] for targeting TEEs and DEEs of almost any desired substitution pattern has allowed a systematic investigation of the influence exerted by electron-donating and electron-withdrawing aryl substituents on the physico-chemical properties. A number of recent reviews summarize the synthetic protocols for obtaining functionalized modules based on TEE or DEE cores and their subsequent incorporation into large carbon-rich scaffolds.[1] In this review, we will focus attention on the exciting electrochemistry of these oligoenynes, which has previously not been reviewed. It should be mentioned that acetylene-extended tetrathiafulvalenes comprise another class of acetylenic scaffolds with an interesting electrochemistry that will not be covered in this account.[6] Comparisons will be made at the end of the present review between oligoenes, oligoynes, and oligoenynes to envisage the effects of acetylenic bonds on the electrochemical behavior. However, a direct comparison between oligoenes and oligoenynes containing the same number of multiple bonds is difficult, as similar structures with respect to substituent groups are rather scarce, or if comparable oligoene structures are available, electrochemically studies have often not been undertaken. If not otherwise stated, the redox potentials given in the tables and inside the text are measured under the following conditions:

Electrodes: Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl or Pt as pseudo reference. Potentials are referenced to the ferricinium/ferrocene (Fc$^+$/Fc) couple used as an internal standard. Potential window (accessible range of potentials): from -2.4 V to $+1.4$ V vs. Fc$^+$/Fc in CH$_2$Cl$_2$.

Cyclic voltammetry (CV): The CV experiments were carried out for scan rates ranging from 10 mV·s^{-1} to 10 V·s^{-1}. Each peak was analyzed by plotting E_p = f(log v) and I_p = f($v^{1/2}$), where E_p and I_p correspond to the peak potential and the peak current, respectively, and v is the scan rate. For reversible and quasi-reversible electron transfers the peak current ratio $I_\mathrm{pc}/I_\mathrm{pa}$ was unity at any scan rate and the peak potential difference $\Delta E_\mathrm{p} = E_\mathrm{pa} - E_\mathrm{pc}$ was either constant with the scan rates (reversible electron transfer) or increasing with the scan rates (quasi-reversible electron transfer). For reversible and quasi-reversible electron transfers, $E^\circ = (E_\mathrm{pa} - E_\mathrm{pc})/2$ assuming similar diffusion coefficients of the oxidized and reduced forms. Data are given at a scan rate

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Nicolle N. P. Moonen (left center), born in Tilburg, the Netherlands, in 1977, studied chemistry at the University of Nijmegen. In 2000, she received her M. Sc. degree for work on organometallic chemistry under the supervision of Dr. Peter H. M. Budzelaar and Professor Anton W. Gal. After an eight-month Socrates/Erasmus project on fullerene chemistry in the group of Professor François Diederich at ETH Zürich, she joined his group in September 2000 as a PhD student and is currently working on cyanoethynylethenes.

Corinne Boudon (left bottom), born in 1951 in Strasbourg, France, studied physical chemistry at the University of Strasbourg where she received in 1978 her Doctorat 3$^{\text{ème}}$ Cycle and in 1987 her Doctorat d'Etat. Since 1982 she has been Maître de Conférence at the chemical department of the University Institute of Technology Robert Schuman at Strasbourg. Her research interests are focused on topological effects on redox properties in superstructured porphyrins and on redox behavior of highly conjugated systems.

Mogens Brøndsted Nielsen (right top), born in Grenå, Denmark, in 1972, studied chemistry and physics at Odense University (University of Southern Denmark) and received his doctoral degree in 1999 under the supervision of Professor Jan Becher. During his Ph.D. studies, he spent one year in Professor J. Fraser Stoddart's group at the University of California, Los Angeles (UCLA), USA. Following postdoctoral studies on acetylenic scaffolding under Professor François Diederich at ETH Zürich from 2000−2002, he returned to the University of Southern Denmark where he became Associate Professor in 2003. In February 2004, he moved to an Associate Professorship at the University of Copenhagen.

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of 0.1 V·s^{-1}. The given potentials are uncorrected for ohmic drop.

Rotating Disk Voltammetry (RDV): $E_{1/2}$ = Half-wave potential. *Slope* = Slope of the linearized plot of E vs. log [I/($I_{\lim}$ − I)]; $I_{\lim}$ is the limiting current and I the current.

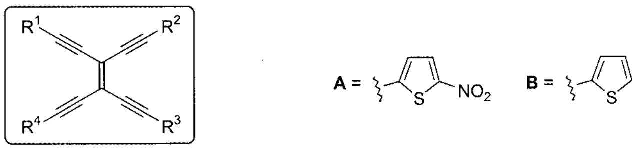
2. Tetraethynylethenes (TEEs)

Tetraethynylethene itself is an unstable compound,[7] the redox properties of which have never been reported, whereas silylated derivatives are stable compounds that can be subjected to an electrochemical investigation.[8] Thus, cyclic voltammetry of trimethylsilyl-substituted TEE **1** revealed a one-electron uptake at −1.96 V in THF (vs. the ferricinium/ferrocene couple, Fc$^+$/Fc; Table 1). Rotating disk voltammetry showed two further reductions at more negative potential (−2.50 and −2.74 V).

A large selection of arylated TEEs containing either electron-withdrawing groups, such as 4-nitrophenyl, or electron-donating groups, such as 4-(dialkylamino)phenyl, or a combination of both, have been synthesized[9] and subsequently investigated electrochemically (**2**−**26**, Table 1).[8b][8c] As expected, introduction of the 4-nitrophenyl substituent shifts the first reduction anodically from −1.96 V in the silylated derivative **1** to −1.36 V in the mono(4-nitrophenyl) substituted TEE **5**. This first electron uptake by **5** occurs at the nitrophenyl group. Actually, the first reductions of mono- and bis(4-nitrophenyl)-substituted TEEs occur at similar potentials (around −1.35 to −1.38 V) and the reduction waves have amplitudes proportional to the number of nitrophenyl groups present. Wave and peak-shape analysis[10] of the first two-electron reduction of bis(4-nitrophenyl) derivatives clearly demonstrate a global exchange of two electrons resulting from two overlapping one-electron transfers occurring at close potentials (redox potential difference ranging from 36 to 80 mV). These results indicate that the two 4-nitrophenyl groups behave almost as non-interacting redox centers. Thus, for example, the first reduction of **5** is a one-electron transfer, whereas it occurs as two one-electron transfers for **7**. Moreover, this first reduction potential is not significantly affected by the presence of other aryl substituents, such as the anilino donor groups attached to the TEE frame in **19**. These findings suggest that mesomeric effects of the donor anilino group do not influence the nitrophenyl group through the conjugated backbone. Ineffective mesomeric effects may be due either to the distance between the substituents, to a non-planar structure in solution avoiding any interactions, or to structural changes occurring after the first electron transfer.

The tris(4-nitrophenyl) derivative **11** displays a specific behavior. It is noteworthy that the first reduction is only a global two-electron transfer occurring on the two nitrophenyl moieties[8c] and takes place at a potential about 100mV more positive than the average reduction potential of the mono- and bis(4-nitrophenyl) TEEs. Thus the third nitrophenyl moiety is reduced in a second one-electron step, which is ca. 50mV more negative than the average value for 4-nitrophenyl TEEs.

Table 1. Electrochemical data of TEEs measured in CH_2Cl_2 (if not otherwise stated) +0.1 M nBu$_4$NPF$_6$; all potentials vs. Fc$^+$/Fc[8,11,12]



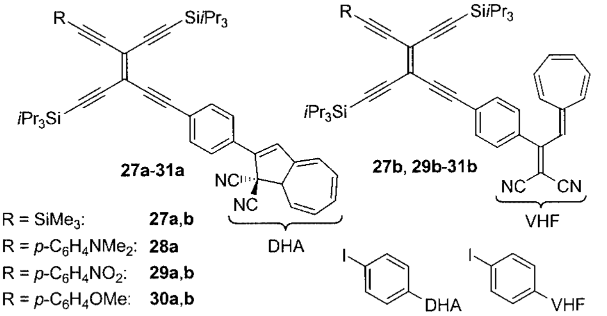
	R^1	R^2	R^3	R^4
1	SiMe$_3$	SiMe$_3$	SiMe$_3$	SiMe$_3$
2	Si*i*Pr$_3$	Si*i*Pr$_3$	SiMe$_3$	SiEt$_3$
3	Ph	Ph	Ph	Ph
4	3,5-di(*t*Bu)Ph	3,5-di(*t*Bu)Ph	3,5-di(*t*Bu)Ph	3,5-di(*t*Bu)Ph
5	p-$C_6H_4NO_2$	Si*i*Pr$_3$	SiMe$_3$	Si*i*Pr$_3$
6	p-$C_6H_4NO_2$	Ph	Ph	Ph
7	p-$C_6H_4NO_2$	p-$C_6H_4NO_2$	Si*i*Pr$_3$	Si*i*Pr$_3$
8	p-$C_6H_4NO_2$	Si*i*Pr$_3$	p-$C_6H_4NO_2$	Si*i*Pr$_3$
9	p-$C_6H_4NO_2$	p-$C_6H_4NO_2$	Ph	Ph
10	p-$C_6H_4NO_2$	Ph	p-$C_6H_4NO_2$	Ph
11	p-$C_6H_4NO_2$	p-$C_6H_4NO_2$	p-$C_6H_4NO_2$	Si*i*Pr$_3$
12	p-$C_6H_4NMe_2$	Si*i*Pr$_3$	SiMe$_3$	Si*i*Pr$_3$
13	p-$C_6H_4NMe_2$	p-$C_6H_4NMe_2$	Si*i*Pr$_3$	Si*i*Pr$_3$
14	p-$C_6H_4NMe_2$	Si*i*Pr$_3$	p-$C_6H_4NMe_2$	Si*i*Pr$_3$
15	p-$C_6H_4N(C_{12}H_{25})_2$	Si*i*Pr$_3$	p-$C_6H_4N(C_{12}H_{25})_2$	Si*i*Pr$_3$
16	p-C_6H_4OMe	p-C_6H_4OMe	SiMe$_3$	Si*i*Pr$_3$
17	p-$C_6H_4NMe_2$	p-$C_6H_4NO_2$	Si*i*Pr$_3$	Si*i*Pr$_3$
18	p-$C_6H_4NMe_2$	Si*i*Pr$_3$	p-$C_6H_4NO_2$	Si*i*Pr$_3$
19	p-$C_6H_4NMe_2$	p-$C_6H_4NMe_2$	p-$C_6H_4NO_2$	p-$C_6H_4NO_2$
20	p-$C_6H_4NMe_2$	p-$C_6H_4NO_2$	p-$C_6H_4NMe_2$	p-$C_6H_4NO_2$
21	p-C_6H_4OMe	p-C_6H_4OMe	p-$C_6H_4NO_2$	Si*i*Pr$_3$
22	p-$C_6H_4NMe_2$	Si*i*Pr$_3$	**A**	Si*i*Pr$_3$
23	p-$C_6H_4NMe_2$	p-$C_6H_4NMe_2$	**A**	Si*i*Pr$_3$
24	p-$C_6H_4NMe_2$	p-$C_6H_4NMe_2$	**A**	p-$C_6H_4NO_2$
25	p-$C_6H_4NMe_2$	p-$C_6H_4NMe_2$	**A**	**A**
26	3,5-di(*t*Bu)Ph	3,5-di(*t*Bu)Ph	**B**	**B**

Cyclic voltammetry							
Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)	Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)
1[a]	−1.96 (1 e$^-$)	320[b]		**17**	−1.37 (1 e$^-$)	80	
2[a]	−1.90 (1 e$^-$)	70[b]			−1.68 (1 e$^-$)	70	
			−2.55		+0.46 (1 e$^-$)	65	[c]
			−2.71	**18**	−1.40 (1 e$^-$)	85	
3[a]	−1.76 (1 e$^-$)	155[b]			−1.73 (1 e$^-$)	70	
4[a]	−1.90 (1 e$^-$)	230[b]			+0.47 (1 e$^-$)	75	
5	−1.36 (1 e$^-$)	75		**19**	−1.38 (2 e$^-$)	80	
	−1.65 (1 e$^-$)	75			−1.69 (1 e$^-$)	105	
6	−1.34 (1 e$^-$)	90					−2.11 (1 e$^-$)
	−1.53 (1 e$^-$)	85					+0.46 (2 e$^-$)
			+1.19	**20**	−1.38 (2 e$^-$)	95	
7	−1.38 (2 e$^-$)	100			−1.76 (1 e$^-$)	110	
	−1.65 (1 e$^-$)	73					−2.22
			−2.08				+0.40 (2 e$^-$)
8	−1.35 (2 e$^-$)	85		**21**	−1.38 (1 e$^-$)	80	
	−1.73 (1 e$^-$)	85			−1.65 (1 e$^-$)	80	
			−2.28				+0.96 (2 e$^-$)
9	−1.38 (2 e$^-$)	150		**22**	−1.23 (1 e$^-$)	90	
	−1.57 (1 e$^-$)	120			−1.63 (1 e$^-$)	80	
			−2.17		+0.47 (1 e$^-$)	76	
10	−1.29 (2 e$^-$)	84					+1.21 (1 e$^-$)
	−1.64 (1 e$^-$)	100		**23**	−1.23 (1 e$^-$)	105	
			−2.20		−1.63 (1 e$^-$)	104	
11	−1.26 (2 e$^-$)	84					+0.47 (2 e$^-$)
	−1.43 (1 e$^-$)	84		**24**	−1.22 (1 e$^-$)	80	
	−1.71 (1 e$^-$)	100			−1.40 (1 e$^-$)	75	
12	−1.94 (1 e$^-$)	70	[d]		−1.64 (1 e$^-$)	80	
	+0.44 (1 e$^-$)	65					+0.47
13	−1.99 (1 e$^-$)	70	[d]	**25**	−1.22 (2 e$^-$)	120	
	+0.42 (2 e$^-$)	160			−1.60 (1 e$^-$)	90	
14	−2.00 (1 e$^-$)	80	[d]				−2.14
	+0.35 (2 e$^-$)	88					+0.48
15	−2.00	65		**26**	−1.68 (1 e$^-$)	71	
	+0.32	100			+0.88 (2 e$^-$)	100	
16	−1.86	80					
			+0.98				

[a] Solvent: THF; working electrode: Hg. [b] Scan rate: 10 V·s^{-1}. [c] Reversible at scan rates above 2 V·s^{-1}. [d] Reversible at scan rates above 1 V·s^{-1}.

The behavior of (5-nitrothienyl)-substituted TEEs mirrors that of the nitrophenyl TEEs, since the nitrothienyl moieties also behave essentially as independent redox centers, as evidenced when comparing the first reduction of **25** and **22−24** (all at −1.22 or −1.23 V).[11] The second reduction of the "mixed" TEE **24** occurs at −1.40 V, that is, at the nitrophenyl group. The anilino- or methoxyphenyl-substituted TEEs **12−25**[12] also experience oxidations centered on the donor groups at about +0.3−0.5 V and about +1.0 V, respectively. The two donor groups present in TEEs **14**, **19−21**, and **23** are oxidized at similar potentials. However, the irreversible electron transfer avoids any detailed analysis, except for **14**, which is oxidized reversibly in two one-electron transfers separated by 80 mV. CV of **13** also showed a single unresolved overlapping two one-electron oxidation, whereas two separate one-electron oxidation steps were observed by RDV (at +0.40 and +0.52 V).

The studied substituted TEEs bearing electron-withdrawing groups (4-nitrophenyl) are reduced at similar potentials (−1.35 to −1.38 V) on the nitrophenyl moiety, as confirmed by spectroelectrochemical investigations.[8c] All mono- and bis(4-nitrophenyl)-substituted TEEs display a second reduction step at about −1.6 V, occurring on the TEE core. In contrast, the TEEs bearing electron-donating (4-dialkylamino)phenyl substituents are easily oxidized and have little effect on the reduction of the nitrophenyl group in donor/acceptor systems such as **18**, **19**.



27a-31a

27b, 29b-31b

32a

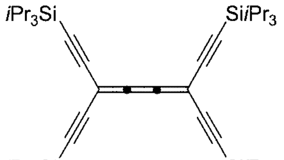
32b

R = SiMe$_3$: **27a,b**
R = *p*-C$_6$H$_4$NMe$_2$: **28a**
R = *p*-C$_6$H$_4$NO$_2$: **29a,b**
R = *p*-C$_6$H$_4$OMe: **30a,b**
R = Ph: **31a,b**

Taking advantage of the photochemically-driven dihydroazulene (DHA)-vinylheptafulvene (VHF) isomerization,[13] the photoswitchable TEE-DHA hybrid chromophores **27a−31a** were recently prepared and investigated electrochemically.[14] Thus, the electrochemistry of each isomer [TEE-DHA (**a**) versus TEE-VHF (**b**)] was studied for the series (see Table S1 in the Supporting Information). For **28a**, the TEE-VHF isomer was non-attainable by irradiation, which was explained by an efficient relaxation of the vertically excited singlet state to an emitting twisted intramolecular charge-transfer (TICT) state.[15] The DHA reference compound **32a** underwent irreversible electron transfers at −1.97 V, −2.07 V, and +1.16 V.[16] The VHF derivative **32b** was more readily reduced (−1.47 V) and oxidized (+0.84 V). All of the TEE-DHA compounds **27a**, **28a**, **30a**, and **31a** experience first a quasi-reversible or nonreversible reduction step between −1.6 and −1.8 V, which is centered on the photoactive DHA moiety, whereas the first reduction of nitrophenyl derivative **29a** occurs at −1.37 V and is centered at the nitrophenyl group. The conjugates **27a**, **28a**, **30a**, and **31a** are reduced at about 200−300 mV more positive potential than **32a** owing to the electron-withdrawing properties of the DHA-appended TEE group. Except for the anilino derivative **28a**, all TEE-DHA conjugates undergo a first oxidation step at about +1.10 V, corresponding to a small cathodic shift of about 60 mV relative to the oxidation of **32a**; the oxidation of **28a** at +0.40 V involves the anilino group.

3. Tetraethynylbutatriene

The silylated tetraethynylbutatriene **33**, a peralkynylated [3]cumulene, represents another acetylenic building module with a planar conformation, which is reduced reversibly at −1.30 and −1.84 V in THF.[17] It is more readily reduced than the corresponding TEE derivative **1** by as much as +660 mV.[8b] Another [3]cumulene bearing conjugated groups capable of stabilizing negative charges in the anionic species is 1,2-bis(fluoren-9-ylidene)ethane, which is reduced at −0.73 and −1.17 V vs. Ag/AgCl in DMF,[18] while tetraphenyl[3]cumulene is reduced at −1.30 and −1.63 V vs. SCE (standard calomel electrode) in DMF.[19]

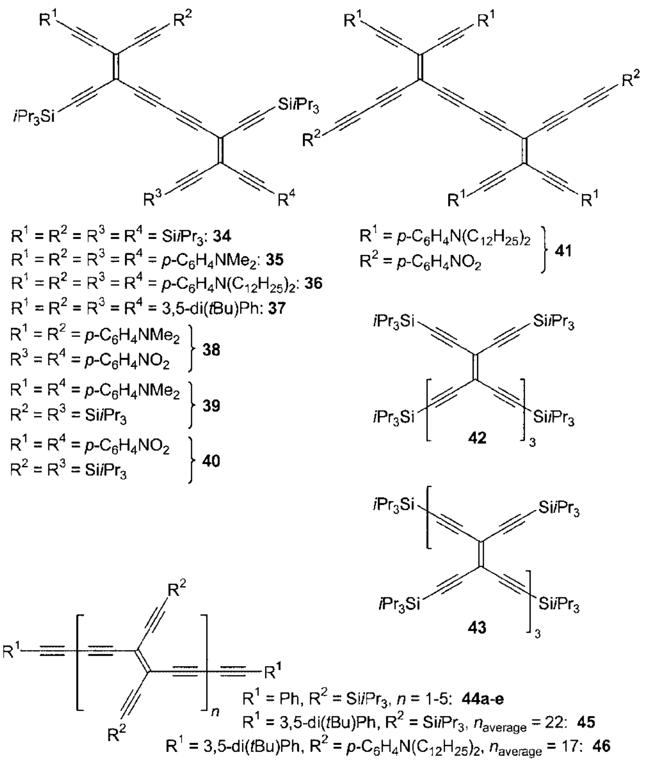


33

4. Oligomers of Tetraethynylethene: Expanded Dendralenes and Poly(triacetylene)s

From UV/Vis spectroscopic studies, it was deduced that linking two TEE units together to form a TEE dimer with a C_{20} carbon core enhances the electron-accepting strength considerably.[20] This observation was confirmed electrochemically in investigations of dimers **34−41**. The comparison of the first reduction potentials of **34** and **37** with those of **1** and **3**, respectively, shows that the dimers experience large anodic shifts of +460 mV and +400 mV, respectively (Table 2).[8a][8b,20] Attaching one more TEE unit as in the expanded [3]dendralene **42**,[8a] composed of three geminally silyl-substituted TEEs, shifts the first reduction anodically by a further +160 mV relative to **34**. The fact that π-electron delocalization along the acetylenic backbone is less effective by cross-conjugation than by linear conjugation is reflected in the further enhancement of acceptor strength when proceeding from cross-conjugated **42** to the poly(triacetylene) (PTA) **43**, containing the same number of TEE units but with a linear π-conjugation pathway along the entire oligomeric backbone.[8a] The less-efficient π-electron delocalization by cross-conjugation was furthermore estab-

Table 2. Electrochemical data of TEE oligomers measured in CH_2Cl_2 (if not otherwise stated) +0.1 M $n\mathrm{Bu_4NPF_6}$; all potentials vs. $\mathrm{Fc^+/Fc}$[8a][8b,12,20,22,23]



Cyclic voltammetry							
Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)	Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)
34[a]	−1.52 (1 e⁻)	80[b]		**42**[a]	−1.36 (1 e⁻)[c]	75	
	−1.89 (1 e⁻)	70[b]			−1.74 (1 e⁻)[c]	75	
			−2.90	**43**[a]	−1.23	80[b]	
35	−1.61 (1 e⁻)	60					−1.47
	−1.90	100		**44a**[a]	−1.57 (1 e⁻)	90[b]	
	+0.37 (2 e⁻)	70		**44b**[a]	−1.32 (1 e⁻)	100[b]	
	+0.54 (2 e⁻)	60			−1.60 (1 e⁻)	70[b]	
36	−1.63 (1 e⁻)	91		**44c**[a]	−1.17 (1 e⁻)	80[b]	
	+0.34 (2 e⁻)	70			−1.42 (1 e⁻)	80[b]	
	+0.60	83			−2.00 (1 e⁻)	80[b]	
37	−1.50 (1 e⁻)	70		**44d**[a]	−1.14 (1 e⁻)	80[b]	
	−1.72 (1 e⁻)	80			−1.32 (1 e⁻)	80[b]	
	+1.08 (1 e⁻)	80			−1.76 (1 e⁻)	70[b]	
	+1.19 (1 e⁻)	80			−1.99 (1 e⁻)	90[b]	
38	−1.28 (1 e⁻)	60		**44e**[a]	−1.07 (1 e⁻)		
	−1.35 (1 e⁻)	60			−1.24 (1 e⁻)		
	−1.49 (1 e⁻)	60			−1.55 (1 e⁻)		
			−2.10		−1.65 (1 e⁻)		
	+0.45 (1 e⁻)	60			−1.85		
			+0.56 (1 e⁻)	**45**[a] [d]	−0.70		
39	−1.59 (1 e⁻)	90		**46**			−1.30
			−1.93				+0.50
	+0.47 (2 e⁻)	85					
40	−1.29 (2 e⁻)	75					
	−1.45 (1 e⁻)	70					
	−1.86 (1 e⁻)[e]						
41	−1.37 (2 e⁻)	70					
	−1.53 (1 e⁻)	60					
	−1.73 (1 e⁻)	70					
			−2.15				
	+0.36 (2 e⁻)	60					
	+0.57 (2 e⁻)	70					

[a] Solvent: THF; working electrode: Hg. [b] Scan rate: 10 $\mathrm{V{\cdot}s^{-1}}$. [c] Pt working electrode. [d] Potentials determined by differental pulse polarography due to strong adsorption in polarography. [e] Reversible at scan rates above 1 $\mathrm{V{\cdot}s^{-1}}$.

lished spectroscopically by HOMO−LUMO gap measurements on expanded dendralenes.[8a,21] Proceeding along the PTA series **44a−e** causes a continuous shift of the first reduction to less-negative potentials.[8b,22] Thus, the 5 nm long pentamer **44e** is a very strong electron acceptor with the first electron uptake occurring at −1.07 V. For polymer **45**, containing an average of 22 linearly π-conjugated TEE units, the first reduction occurs already at −0.70 V.[23] For an infinite polymer, we estimate the limit to be around −0.60 V. For the related anilino-appended polymer **46**, with an average length of 17 TEEs, an anodic shift of 350 mV relative to the corresponding TEE dimer **36** is observed.[12] Looking in more detail at the series **44a−e**, it is recognized that each oligomer exhibits a number of reversible or quasi-reversible reduction steps that is equal to the number of TEE moieties that it contains. Figure 2 shows the changes in the reduction potentials along the series. A plot of the first reduction potentials versus the number *n* of TEE repeat units fits an exponential curve. The second reduction step (only observed for the dimer and beyond) follows qualitatively the same trend with *n*. The third reduction potential also becomes less negative when proceeding from the trimer to the tetramer. These results indicate that increasing the number of TEE repeat units in the oligomers promotes an increase in the number of electrons that can be injected into the oligomeric backbone as observed previously for oligo(*p*-phenylene)s and oligo(*p*-phenylenevinylene)s.[24]

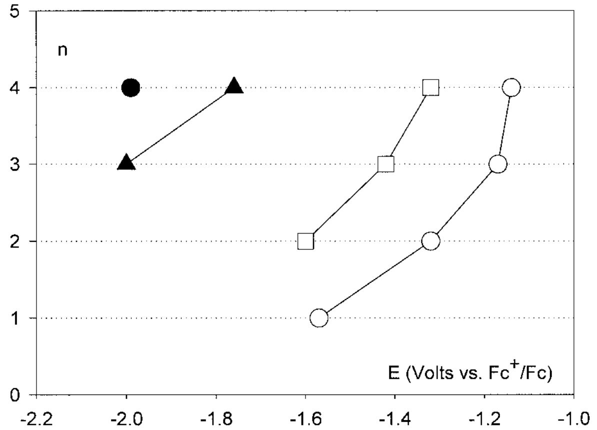


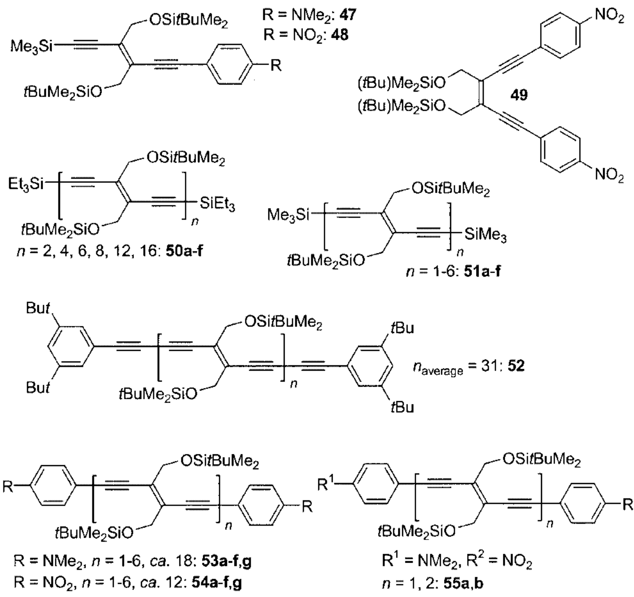
Figure 2. Changes in the reduction potentials measured for the monomer and oligomers of PTAs **44a−d** in THF +0.1 M $\mathrm{Bu_4NPF_6}$: first (○), second (□), third (▲), and fourth (●) reduction step[8b,22b]

The di(*tert*-butyl)phenyl-substituted TEE dimer **37** also gave aryl-centered one-electron oxidations at +1.08 V and +1.19 V.[20] TEE dimer **35** was oxidized in two steps at +0.37 and +0.54 V, each step being a two-electron step centered on two out of four dimethylanilino groups.[20] The reduction at −1.61 V is a reversible one-electron transfer occurring on the central carbon core; the same reduction potential was measured for TEE dimer **39** bearing two dimethylanilino groups. A similar redox behavior is expectedly found for **36** with four $(C_{12}H_{25})_2NC_6H_4$ groups. The electron-donating anilino groups present in **35** and **36** make the first reduction more difficult by about 100 mV relative to the dimers **34** and **37**. The "push-pull" donor-acceptor dimer **38** is reduced in two one-electron steps, centered on the two nitrophenyl groups,[20] whose potentials (−1.35 and −1.28 V) are separated by 70 mV. Similarly, the oxidation of its two dialkylanilino groups occurs in two distinct one-electron oxidation steps at +0.45 and +0.56 V. In the extended chromophore **41**, the four dialkylanilino groups are oxidized in two steps, similar to **36**.[20] The reduction of the nitrophenyl groups occurs in a single two one-electron step at −1.37 V; the peak shape in CV as well as the slope in RDV, however, clearly indicate that the two nitro groups behave as independent redox centers. The second reduction (one electron) occurs at −1.53 V on the central carbon core.

5. Oligomers of (*E*)-1,2-Diethynylethene: Poly(triacetylene)s

Non-arylated DEE monomers are difficult to reduce or oxidize. Oxidation is only observed upon introduction of an anilino group in **47**, whereas reduction is promoted by a nitrophenyl group as in **48** or **49** (Table 3).[25] However, when two or more DEEs are linked together, they become good electron acceptors, as revealed by the PTA series **50a−f** and **51a−f**.[26] When comparing DEE di- and trimers **51b**,**c** with TEE di- and trimers **34** and **43**, we recognize that the lateral acetylenes in the TEE-based PTAs contribute considerably to the stabilization of the reduced forms; that is, TEE-based PTAs are much stronger electron acceptors that are reduced at much less negative potentials. The first reduction step in the DEE oligomer series shifts anodically until about −1.71 V, corresponding to the hexamers **50c** and **51f**, after which saturation seems to be reached. However, the first reduction of hexadecamer **50f** deviates from the saturation value, which might be a consequence of rather high uncertainty resulting from poor resolution of the reduction wave and its irreversible behavior. For the polymer **52**, which has an average number of DEE units of 31 and elongated arylacetylene end-groups, the first reduction occurs at −0.65 V. It seems that this end-group elongation has quite a remarkable effect on the saturation value. There are two striking differences between the PTA series **50a−f**/**51a−f** and the TEE-based PTAs **44a−e**. The number of reversible one-electron reduction steps for the TEE oligomers corresponds directly to the number of TEE moieties in each rod, whereas in the DEE oligomers only a second, irreversible reduction step is observed for the trimer and beyond due to the high chemical reactivity of the generated dianion, avoiding the observation of further reductions. Secondly, in contrast to the TEE oligomers, the DEE oligomers can be oxidized at potentials more positive than +1.23 V. The general reluctance of both the DEE- and TEE-based PTA series to undergo oxidation explains their amazing stability in air over periods of months. The evolution of the first reduction and oxidation potentials along the DEE oligomer series is illustrated in Figure 3.

Table 3. Electrochemical data of DEE mono- and oligomers measured in CH_2Cl_2 +0.1 M nBu_4NPF_6 (if not otherwise stated); all potentials vs. Fc^+/Fc[8c][22b,25,26]



Cyclic voltammetry							
Compound	E° (V)	ΔE_p (mV)	E_p (V)	Compound	E° (V)	ΔE_p (mV)	E_p (V)
47	+0.40 (1 e^-)	88[a]		**53e**	−1.79 (2 e^-)	175	
48	−1.41 (1 e^-)	90					−2.37
			−2.00		+0.43 (2 e^-)	80	
49	−1.40 (2 e^-)	100		**53f**	−1.74 (2 e^-)	130	
	−2.09 (1 e^-)						−2.18
50a	−2.10 (1 e^-)	102			+0.42 (2 e^-)	75	
50b	−1.76 (1 e^-)	95					+1.02
	−1.90(1 e^-)	63		**53g**	−1.70 (2 e^-)	125	
50c	−1.71 (1 e^-)	90			+0.41 (2 e^-)	95	
50d	−1.69 (1 e^-)	80		**54a**	−1.42 (2 e^-)	120	
			+1.20				−2.16 (1 e^-)
50e	−1.72 (1 e^-)	160		**54b**	−1.39 (2 e^-)	95	
50f			−1.79[b]				−1.90 (1 e^-)
51a[c]	−2.68	100					−2.30 (2 e^-)
51b	−2.10 (1 e^-)	130[d]		**54c**	−1.39 (2 e^-)	95	
			+1.29		−1.74 (1 e^-)	95	
51c	−1.88 (1 e^-)	80[d]			−1.95 (2 e^-)	105	
			−2.09				+1.30
			+1.25	**54d**	−1.38 (2 e^-)	110	
51d	−1.80 (1 e^-)	90			−1.73 (1 e^-)	110[a]	
			−1.95		−1.88 (1 e^-)	140[a]	
			+1.23				−2.04
51e	−1.75 (1 e^-)	110					+1.24
			−2.30	**54e**	−1.38 (2 e^-)	105	
			+1.23				−1.79
51f	−1.71 (1 e^-)	130					−2.05
			−2.30				+1.24
			+1.23	**54f**	−1.38 (2 e^-)	100	
52[c]	−0.65						−1.80
53a	+0.31 (2 e^-)	85[a]					−1.93
53b	+0.41 (2 e^-)	74[e]					+1.22
			+0.99	**54g**	−1.41 (2 e^-)	70	
53c	−1.93 (1 e^-)	85			−1.71 (2 e^-)	150	
			−2.19	**55a**	−1.43 (1 e^-)	80	
	+0.42 (2 e^-)	75					−2.02
			+0.97		+0.42 (1 e^-)	70[a]	
53d	−1.80 (1 e^-)	110		**55b**	−1.40 (1 e^-)	85	
			−2.02 (1 e^-)				−1.90
	+0.42 (2 e^-)	90			+0.43 (1 e^-)	66[a]	
			+1.02				

[a] Reversible electron transfer at scan rates above 0.2 $V \cdot s^{-1}$. [b] Peak potential poorly resolved. [c] Solvent: THF; working electrode: Hg; RDV data. [d] Reversible electron transfer at scan rates above 0.5 $V \cdot s^{-1}$. [e] Reversible electron transfer at a scan rate of 1.0 $V \cdot s^{-1}$.

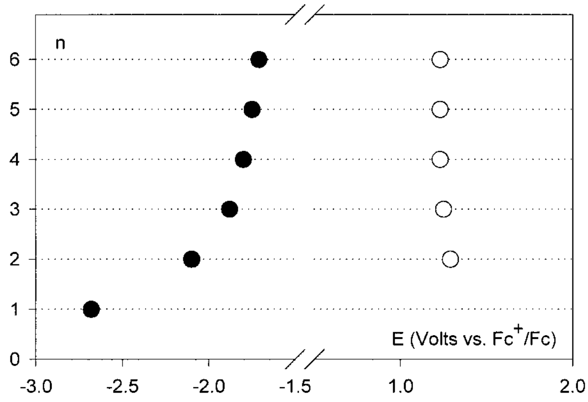
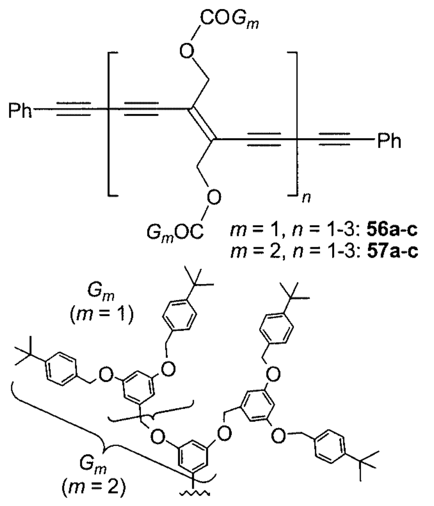


Figure 3. Changes in the first reduction (●) and oxidation (○) potentials measured for the monomer and oligomers of PTAs **51a−f** in CH_2Cl_2 +0.1 M Bu_4NPF_6 [22b]

The effect of donor-acceptor substitution at the end groups is demonstrated by comparing the series **53a−g**, **54a−g**, and **55a**,**b** (Table 3).[25] The presence of two donor end-groups in **53a−f** renders the reduction more difficult. Indeed, reduction was not observed until three DEEs were linked together (**53c**) and then it took place at a cathodically shifted potential relative to trimer **51c** lacking the donor end-groups. Several discrete reduction steps were obtained for the acceptor-acceptor oligomers **54a−g**, for which the first one was reversible and involved two overlapping one-electron transfers occurring at close potentials (redox potential difference ranging from 36 to 90 mV). For all compounds **54a−g**, the first reversible electron-transfer process occurred at about −1.40 V, whereas the magnitude of the second reduction potential varied linearly with the reciprocal of the number of DEE units. This result suggests that the first reduction occurred on both terminal 4-nitrophenyl groups, which are acting nearly as independent redox centers. However, ab initio calculations on the related TEE **8** suggest some degree of communication between the 4-nitrophenyl end-groups.[8c] Experimental support for a cumulenic-type dianion was furthermore established by the electrochemical isomerization of *cis*-enediyne **49** to *trans*-enediyne **54a** upon two-electron uptake.[8c] Indeed, conversion of the central double bond to a single bond, after formation of a cumulenic dianion, allows rotation about this bond and consequently *cis-trans* isomerization.

The effect of dendritic encapsulation in PTAs **56a−c** and **57a−c** with Fréchet-type[27] dendrons was studied (see Table S2 in the Supporting Information).[28] All oligomers were reduced in several irreversible steps, the electrons being transferred to the PTA backbone. The irreversibility increases with the dendritic generation ($m = 1 \rightarrow 2$), which might be explained by a decrease in the electron-transfer rates with increasing dendritic shielding.[29]

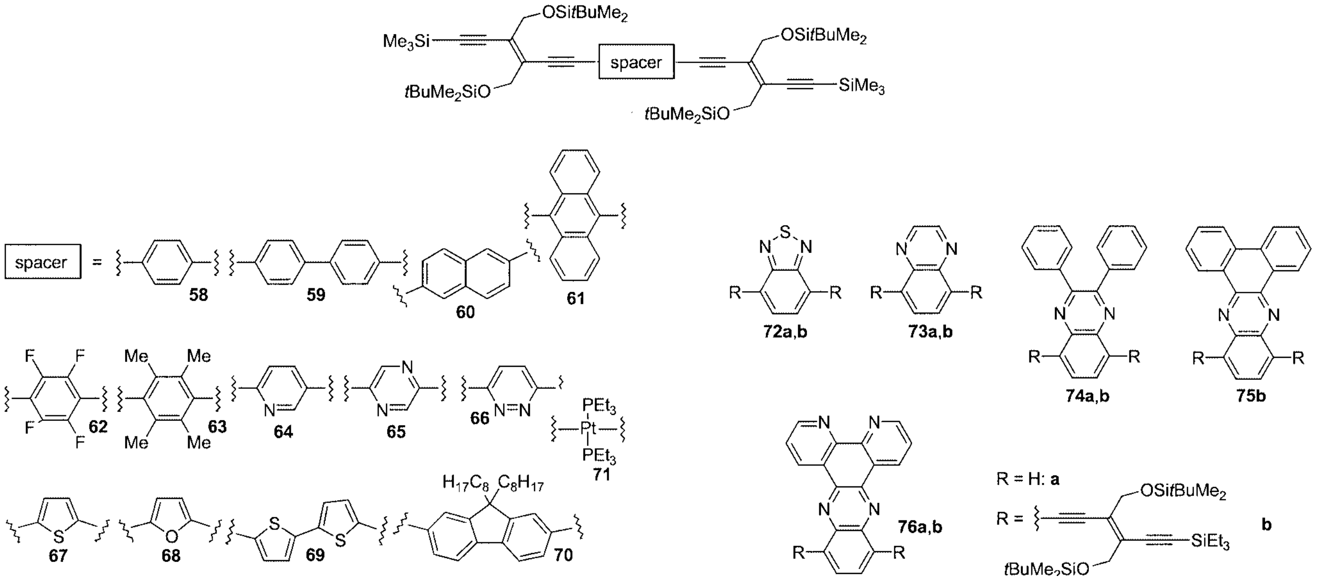
The series of hybrid oligomers **58−76**, containing a central spacer between two DEE units, was investigated in order to gain an understanding of the transmission of π-electron delocalization across this spacer (Table 4).[30] It turns out that the aromatic or heteroaromatic compounds **58−60**, **63**, **64**, and **67−70** were all reduced at more negative potentials than the DEE homo-dimer **51b**, whereas the derivatives containing anthracene (**61**), 2,3,5,6-tetrafluorobenzene (**62**), pyrazine (**65**), and pyridazine (**66**) spacers have less-negative first reduction potentials. These results signal that only weak π-electron delocalization exists along the conjugated backbone via the spacer unit. In contrast, the first reduction of the quinoxaline derivatives **72b−76b** is substantially facilitated (by 130−420 mV) relative to the DEE homo-trimer **51c**. It is interesting to compare the reduction potentials of these hetero-oligomers with those of the pure spacer compounds **72a−74a** and **76a**. Indeed, the first reduction step in **72b−76b** is likely to take place at the spacer rather than at the DEE units. Thus, **72b** is reversibly reduced in a one-electron step at −1.47 V, corresponding to an anodic shift of 490 mV relative to the reduction potential of the free benzothiadiazole spacer **72a**. The first reduction step in the quinoxaline-derived series, involving one electron, is a quasi-reversible electron transfer with a potential shift to less-negative values following the sequence **73b** → **74b** → **75b** → **76b**. These potentials are all significantly shifted to more positive values relative to the free spacers. We explain these large anodic shifts by predominantly inductive effects of the two strongly electron-withdrawing DEE substituents on the central spacer chromophore rather than by an effect resulting from extended π-electron conjugation along the oligomeric backbone. This interpretation is supported by the UV/Vis absorption spectra since these do not feature shapes and bands characteristic of DEE oligomers. The three tetrahedral transition metal complexes $[Zn(\mathbf{76b})_2(OTf)_2]$ (OTf = triflate), $[Ni(\mathbf{76b})_2(ClO_4)_2]$, and $[Cu(\mathbf{76b})_2(PF_6)]$ experience almost the same electrochemical behavior, namely a first irreversible reduction, assigned to adsorption, and two reduction steps.



m = 1, *n* = 1-3: **56a-c**
m = 2, *n* = 1-3: **57a-c**

The strong electron-withdrawing effect of the DEE unit was also confirmed by its ability to alter the electrochemistry of porphyrins, such as **77**, in porphyrin arrays (see Table S3 in the Supporting Information).[31] Compounds **78** and **79a**,**b** showed two one-electron oxidation and two one-elec-

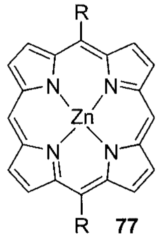
Table 4. Electrochemical data of hybrid DEE-oligomers and reference compounds measured in CH_2Cl_2 +0.1 M $n$$Bu_4NPF_6$; OTf = triflate; all potentials vs. Fc^+/Fc[30]

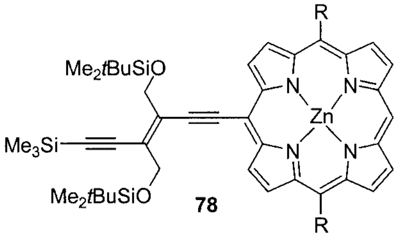


Cyclic voltammetry							
Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)	Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)
58			−2.44	**72a**	−1.96 (1 e^-)	80	
			+1.24	**72b**	−1.47 (1 e^-)	90	
59			−2.37				−2.15[a]
			−2.45				−2.33
			+1.18				+1.18
60			−2.28	**73a**			−2.15[a]
			−2.38	**73b**	−1.75 (1 e^-)	100	
			+1.17				−2.12
61	−1.72 (1 e^-)	85					+1.17
			−2.13	**74a**	−2.09 (1 e^-)	75	
	+0.72 (1 e^-)	90		**74b**	−1.72 (1 e^-)	100	
			+1.22				−2.08
62	−1.90 (1 e^-)	130					+1.16
			−2.23	**75b**	−1.54 (1 e^-)	90	
63			−2.35		−1.98 (1 e^-)	80	
	+1.02 (1 e^-)	115[a]					+1.15
64			−2.25	**76a**	−1.70 (1 e^-)	70	
			−2.43				−2.13
			+1.43	**76b**	−1.46 (1 e^-)	90	
65	−1.80 (1 e^-)	105			−1.92 (1 e^-)	90	
			−2.20				+1.16 (1 e^-)
66	−1.86 (1 e^-)	70		Zn(**76b**)$_2$(OTf)$_2$			−1.19[b]
			−2.15		−1.44 (1 e^-)	60	
67			−2.16		−1.90 (1 e^-)	75	
	+1.04 (1 e^-)	150[a]					+1.15
68			−2.40	Ni(**76b**)$_2$(ClO_4)$_2$			−1.26[b]
	+1.00 (1 e^-)	130			−1.47 (1 e^-)		
69			−2.12		−1.88 (1 e^-)		
	+0.80 (1 e^-)	75	+1.09 (1 e^-)				+1.23
70			−2.35	Cu(**76b**)$_2$(PF_6)			−1.24[b]
	+1.05 (1 e^-)[a]	100			−1.44 (1 e^-)	60	
71	+0.72 (1 e^-)	75			−1.87 (1 e^-)	125	
			+1.16				+1.15

[a] Reversible electron transfer at scan rates above 1 V·s^{-1}. [b] Adsorption peak.

tron reduction waves, all of which were porphyrin-based as evidenced by comparison with the porphyrin derivative **77**. Whereas all three compounds were reversibly oxidized at similar potentials (+0.35−0.36 V), reductions became significantly facilitated upon increasing DEE substitution. Thus, attachment of two DEE moieties to the porphyrin core in **79a** shifts the first one-electron reduction anodically by 350 mV when compared with **77** (−1.85 V), which lacks these substituents. It is clear from the data in Table 3 (Supporting Information) and from facilitated reduction of species **77**−**79** that DEEs are powerful electron-withdrawing substituents that mediate, as additional salient features, a strong increase in the solubility and in the fluorescence quantum yield of the resulting hybrid chromophores.[30b]


77


78

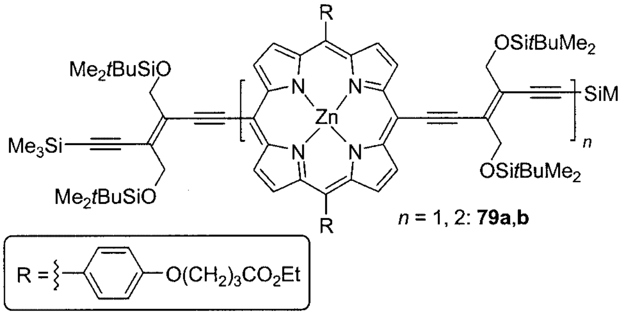
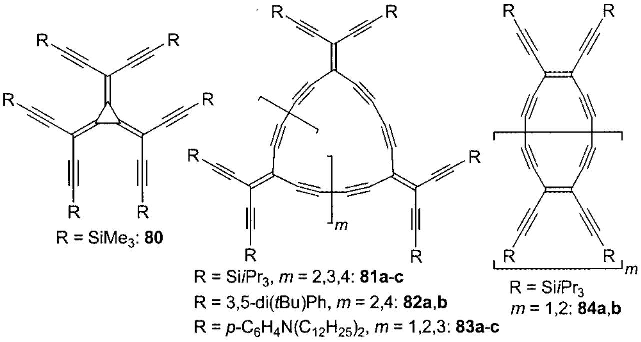

n = 1, 2: **79a,b**

Table 5. Electrochemical data for cyclic compounds measured in CH_2Cl_2 +0.1 M nBu_4NPF_6 (if not otherwise stated); all potentials vs. Fc^+/Fc[8b,12,20,34,35]



Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)	Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)
80[a]	−0.96 (1 e^-)	115		**83a**[b]	−1.30 (1 e^-)	90	
	−1.51 (1 e^-)[c]	115			−1.60 (1 e^-)	100	
81a[a]	−1.08 (1 e^-)	61			+0.35 (2 e^-)	56	
	−1.28 (1 e^-)	73					+0.68
81b[a]	−1.35 (1 e^-)	100		**83b**[b]	−1.28 (1 e^-)	65	
	−1.64 (1 e^-)	80			−1.46 (1 e^-)	90	
			−1.94		+0.32 (2 e^-)	55	
81c[a]	−1.27 (2 e^-)	95		**83c**[b]	−1.37 (1 e^-)	60	
	−1.67 (1 e^-)	95			−1.50 (1 e^-)	60	
	−1.81 (1 e^-)	95			−1.71 (1 e^-)	127	
	−1.98 (1 e^-)	95			+0.30 (2 e^-)	65	
82a[b]	−1.17 (1 e^-)	70			+0.61 (>2 e^-)	126	
	−1.33 (1 e^-)	70		**84a**[d]	−0.99 (1 e^-)	80[e]	
	−1.71 (1 e^-)	70			−1.46 (1 e^-)	80[e]	
			+1.00 (1 e^-)	**84b**[a]	−1.12 (1 e^-)	85[e]	
82b[b]	−1.29 (2 e^-)	140			−1.52 (1 e^-)	90[e]	
	−1.52 (1 e^-)	70			−1.91 (1 e^-)	140[e]	
	−1.68 (1 e^-)	70					
	−1.84 (1 e^-)	80					
			+1.02				

[a] Working electrode: Pt; solvent: THF. [b] Working electrode: glassy carbon. [c] Reversible at a scan rate above 0.1 V·s^{-1}. [d] Working electrode: Hg; solvent: THF. [e] Scan rate: 10 V·s^{-1}.

7. All-Carbon Cores: Expanded Radialenes and Dehydroannulenes

Radialenes are a series of all-methylidene-substituted cycloalkanes.[32] The redox properties of the parent class of radialenes are strongly dependent on the nature of the substituents at the double bonds. Thus, derivatives with alkyl substituents are generally difficult to reduce, whereas those with either cyano or methoxycarbonyl substituents are reducible to the corresponding anions and subsequently to the dianions.[33] The effect of perethynylation is elucidated by studying the radialene **80**, which in its protonated form (R = H) is isoelectronic with hexacyano[3]radialene (Table 5).[34] In analogy to the latter, radialene **80** also underwent two reduction steps, at potentials of −0.94 V and −1.51 V in CH_2Cl_2.

The high acceptor strength was maintained in the perethynylated expanded radialenes **81a**−**c**, **82a**,**b**, and **83a**−**c** (Table 5).[12,20,35] Indeed, the reduction of the macrocyclic perimeters in these three series is greatly facilitated relative to the comparison TEE dimers featuring identical longest linear π-conjugation pathways and containing peripheral substituents of different donor strength. Thus, large anodic shifts in the first reduction potential are observed: +170−440 mV for **81a**−**c** relative to **34**, +210−330 mV for **82a**,**b** relative to **37**, and +240−320 mV for **83a**−**c** relative to **36**. These data clearly indicate an increased capacity of the macrocyclic π-systems to stabilize the radical anions formed upon electron uptake. In particular, the expanded [3]- and [4]radialenes, presumably adopting planar conformations, were able to accommodate an electron very readily. This ability has recently been explained by calculations by a gain of aromaticity upon reduction.[36] An X-ray crystal structure analysis showed that the expanded [6]radialene **82b** takes a chair-like conformation.[20] The first reduction potentials are plotted in Figure 4 in comparison to the TEE dimers and some other oligomers.

The expanded radialenes **83a**−**c** undergo reversible oxidation steps centered on the dialkylanilino groups.[12,20] All individual *p*-$C_6H_4N(C_{12}H_{25})_2$ moieties were not oxidized at the same potential, however, and the sums of the wave amplitudes corresponding to the successive oxidations were in the expected ratio (6:1 for **83a**, 8:1 for **83b**, and 10:1 for **83c**), in agreement with the numbers of oxidizable anilino groups present in each series. One oxidation step close to the electrolyte discharge was observed for the expanded radialenes **82a**,**b**, presumably centered on a di(*tert*-butyl)phenyl group.

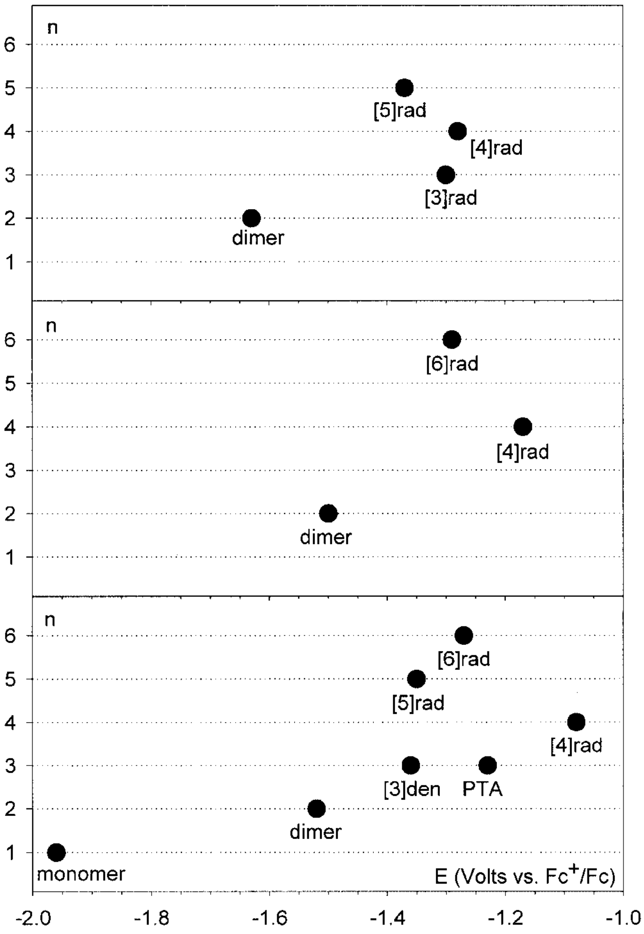


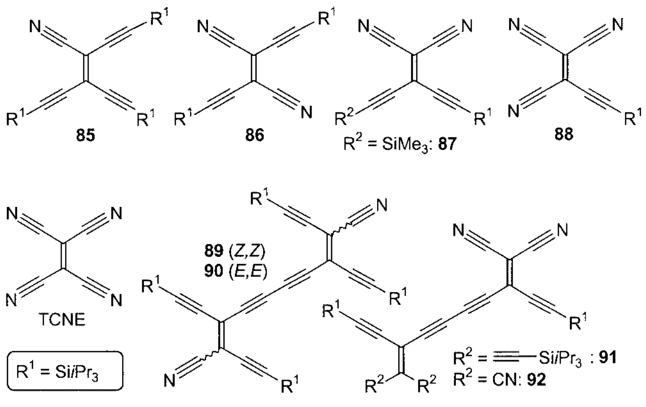
Figure 4. Comparison of first reduction potentials in three differently substituted expanded radialene series with their corresponding TEE dimers. Top: p-$C_6H_4N(C_{12}H_{25})_2$ substituted compounds **36**, **83a−c**; middle: 3,5-di(*tert*-butyl)Ph substituted compounds **37**, **82a**,**b**; bottom: trialkylsilyl-substituted compounds **1**, **34**, **42**, **43**, **81a−c**

The perethynylated dehydroannulenes **84a**,**b** are also strong electron acceptors (Table 5),[8b,35,37a] although the [12]annulene **84a** was more readily reduced (−0.99 V in THF) than the [18]annulene **84b** (−1.12 V in THF). Indeed, **84b** loses its Hückel aromaticity upon reduction, whereas **84a** gains aromaticity when converted into its dianion with 14 π-electrons. According to X-ray crystallography, both these dehydroannulenes possess fully planar carbon cores.[35,37] The effect of substituting the peripheral silyl groups by aromatic groups is currently being explored for these perethynylated dehydroannulenes.[37b]

8. Cyanoethynylethenes

An ultimate tuning of the acceptor strength, while maintaining the opportunity for acetylenic scaffolding, can be achieved with the cyanoethynylethenes (CEEs, **85−92**, Table 6),[38] which show first reduction potentials in the range between that of TEE derivative **1** (−1.96 V in THF) and tetracyanoethene (TCNE, −0.32 V in CH_2Cl_2).[39] In

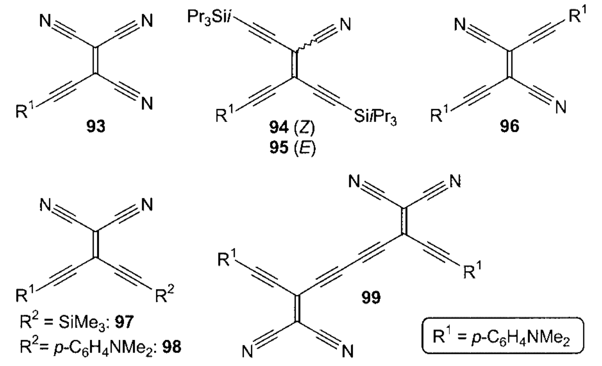
Table 6. Electrochemical data of CEEs measured in CH_2Cl_2 +0.1 M nBu_4NPF_6; all potentials vs. Fc^+/Fc[38d,39]



	Cyclic voltammetry						
Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)	Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)
85	−1.58 (1 e$^-$)	90		**89**	−1.07 (1 e$^-$)	75	
			−2.34		−1.37 (1 e$^-$)	75	
86	−1.25 (1 e$^-$)	100		**90**	−1.06 (1 e$^-$)	60	
			−2.05		−1.36 (1 e$^-$)	60	
87	−1.15 (1 e$^-$)	70		**91**	−0.90 (1 e$^-$)	80	
			−1.95		−1.44 (1 e$^-$)	70	
88	−0.72 (1 e$^-$)	85		**92**	−0.57 (1 e$^-$)	90	
			−1.69		−0.84 (1 e$^-$)	90	
TCNE[a]	−0.32 (1 e$^-$)						−2.24
	−1.35 (1 e$^-$)						

[a] Quasi-reversible electron transfers.[39]

Table 7. Electrochemical data for donor-substituted CEEs measured in CH_2Cl_2 +0.1 M nBu_4NPF_6; all potentials vs. Fc^+/Fc[38e]



	Cyclic voltammetry						
Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)	Compound	$E°$ (V)	ΔE_p (mV)	E_p (V)
93			−0.86	**97**	−1.24	125	
	+0.79	65			+0.67	125	
94	−1.63	75		**98**	−1.31	60	
			−2.25				−2.02
			−2.35				−2.20
	+0.56	75					+0.63
95	−1.64	90		**99**	−0.74	70	
			−2.26		−0.92	120	
			−2.37				−2.25
	+0.56	80			+0.69	60	
96	−1.38	70					
			−1.95				
			−2.05				
			−2.20				
	+0.50	70					
	+0.58	70					

substituted TEEs, the 4-nitrophenyl group essentially acts as an independent redox center, and an increase in the number of these substituents does not increase the acceptor strength of the chromophore (vide supra). In sharp contrast, the cyano group in CEEs is an integral part of the acetylene-based chromophores and the first reduction potential shifts strongly anodically with increasing number of cyano groups. This effect is evident when comparing the first reduction potentials of CEEs **85−88** (Table 6):[38d] the increase in electron-acceptor strength upon substituting one RC≡C− by one N≡C− group can be quantified to 380 mV, and upon replacing one NC−C−CN by one RC≡C−C−C≡CR fragment to 830 mV.[40] A strong linear correlation (R^2 = 0.996) was obtained between calculated electron affinities EA (B3LYP/6-31G**)[41] and the first reduction potentials for CEEs **85−88**, TCNE, and TEE.

A selection of extended CEEs (**89−92**) was also investigated (Table 6). The extended CEE **92** is an exceptionally good electron acceptor, approaching the strength of TCNE. A clear increase in acceptor strength with extension of π-electron conjugation was observed when proceeding from monomer **87** to dimer **92**, as was likewise found for the comparison between TEE monomer **1** and dimer **34** (vide supra). At present, we cannot yet quantify the individual effects resulting from adding cyano groups and extending the overall π-conjugation length.

Introduction of a donor group (**93** vs. **88**) results, as expected, in a decrease of the acceptor strength (Table 7).[38e] A similar behavior was observed by Dulog and co-workers[38b] in phenylated tricyanoethynylethenes, since the reduction of these chromophores experiences cathodic shifts after the introduction of two or three methoxy substituents into the phenyl ring. The oxidation of the anilino group in **93** occurs at a very anodically shifted potential (+0.79 V) as compared to an anilino group attached to a TEE core (+0.3−0.5 V), and this implies that the anilino moiety and the CEE core do not act as independent redox entities, but rather undergo strong electronic communication. This delocalization is also apparent from the UV/Vis spectrum, which features an intense charge-transfer band at λ_{max} = 591 nm (ε = 43800 $\text{M}^{-1}\cdot\text{cm}^{-1}$).[38d] A whole series of donor-substituted CEEs **93−99** have been prepared and their electrochemical properties are collected in Table 7.

9. Oligoenynes vs. Oligoenes vs. Oligoynes: Triple vs. Double Bonds

We have until now discussed different ene-diyne and ene-tetrayne mono- and oligomers in which the double bonds are either cross-conjugated to the acetylene backbone or linearly conjugated. It is interesting to compare these compounds with the series of pure oligoenes and pure oligoynes.

The homologous series of oligoenes **100a−c** was prepared and investigated by Müllen and co-workers.[42] The first reduction potential of these poly(acetylene) (PA) oligomers is plotted against the reciprocal number of multiple bonds (*m*) in Figure 5 and compared to the potentials of the PTA series **50a−e/51a−f**. A linear dependence is observed in both series (until saturation). The influence of the C≡C bonds becomes obvious from this comparison: the PTA oligomers are reduced at less-negative potential relative to PA oligomers containing the same number of multiple bonds. However, studies on longer PA derivatives by Grubbs, Lewis, and co-workers[43] reveal a limiting value for PA of about −1.9 V vs. Fc^+/Fc (−1.4 V vs. SCE) and hence close to the corresponding value of −1.7 V obtained for PTA. Studies by Hapiot et al.[44] show that replacement of the central double bond in β-carotene ($E°$ = −1.62 V vs. SCE in CH_2Cl_2, i.e. ca. −2.1 V vs. Fc^+/Fc) for a triple bond actually leads to a small lowering of the first reduction potential ($E°$ = −1.63 V vs. SCE for 15,15′-didehydro-β-carotene).[45] In other words, it seems that the effect of replacing double bonds with triple bonds is not so easily generalized. 1,6-Diphenylhexatriene was studied by Roncali and co-workers.[46] This compound gave an irreversible oxidation at +1.18 V vs. Ag/AgCl in CH_2Cl_2, whereas no reduction is mentioned. However, from the spectroscopic data (λ_{max} = 370 nm, 3.35 eV) it is clear that the reduction cannot be seen in CH_2Cl_2. The phenyl end-groups of this hexatriene do not allow any meaningful comparison to the present DEEs.[47]

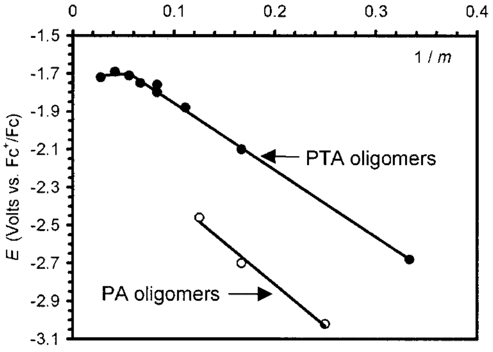


Figure 5. Plot of first reduction potential vs. the reciprocal of the number of multiple bonds (*m*) in the PTA series **50a−e/51a−f** and PA series **100a−c**;[42] the original potentials for **100a−c** (measured in THF) were converted, for the sake of comparison, from calibration against SCE to the Fc^+/Fc reference by subtracting a value of 0.5 V; this conversion represents an approximation

Hirsch and co-workers[48] have prepared the series of end-cap stabilized oligoynes **101a−c**, which were all reduced in one irreversible step at low sweep rates (0.1 $V\cdot s^{-1}$). However, at higher sweep rates, the reduction became more and more reversible. From this observation, it is concluded that the first reduction step involves a reversible one-electron reduction followed by an irreversible chemical reaction. Thus, in contrast to PTAs, these linear polyynes are not able to stabilize the electrogenerated radical anion. The dependence of the reduction potential on the reciprocal of the number of multiple bonds, including the aryl double bonds, is rep-

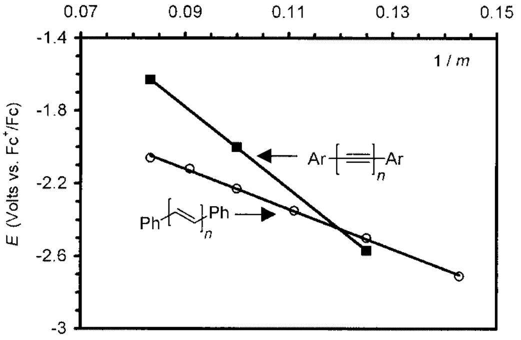
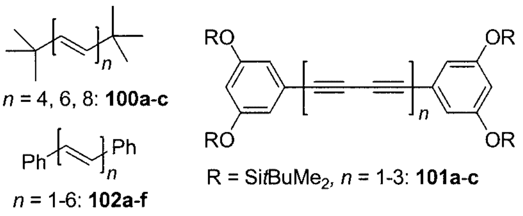


Figure 6. Plot of first reduction potential vs. the reciprocal of the number of multiple bonds (*m*) in the arylated oligoyne and oligoene series **101a−c**[48] and **102a−f**;[49a] the original potentials for **102a−f** (solvent: DMF) were converted from calibration against SCE to the Fc^+/Fc reference by subtracting a value of 0.5 V; this conversion represents an approximation; compounds **101a−c** were measured in CH_2Cl_2; note that *m* corresponds to the total number of multiple bonds, including the aryl rings, that is, $m = n + 6$

resented in Figure 6. These data also satisfy a linear relationship. This is also the case for the α,ω-diphenyloligoenes **102a−f** investigated by Aten and Hoijtink.[49] Direct comparison between these two series is prohibited by the very different experimental conditions, such as the solvent polarity. However, the slope of the lines describing the data deviates considerably, being larger for the oligoyne series. Thus, enhancement of the readiness of reduction upon increasing the number of multiple bonds seems to be more significant in the oligoyne series.


n = 4, 6, 8: **100a-c**

n = 1-6: **102a-f**

R = Si*t*BuMe₂, *n* = 1-3: **101a-c**

10. Tetraethynylethene vs. Ethene

Finally, it is worthwhile to note the different oxidation behavior of nitro- and anilino-substituted TEEs and ethenes. The lack of redox studies on similar structures only allows comparison with substituted ethenes. Indeed, 4-(dimethylamino)phenyl-substituted ethenes and tetra(*p*-anisyl)ethene have been studied extensively to explain why disubstituted ethenes bearing oxidizable substituents show electron transfers occurring either in two one-electron steps or in a unique two-electron step.[50] This point is of importance for many organic and organometallic species, as shown in a review by Evans et al.[51] and in several recent papers.[44,52] For example, tetrakis(4-dimethylaminophenyl)ethene is oxidized in three reversible steps with half-wave potentials of −0.303 V (two electrons), +0.634 V (one electron), and +0.701 V (one electron) vs. Fc^+/Fc in CH_2Cl_2.[53] Formation of two separate cyanine systems accounts for the extremely ready removal of the first two electrons. In comparison, the two anilino groups present in TEE **14** were oxidized in a single step and at a relatively high potential of +0.35 V, i.e. oxidation of **14** occurs without a cyanine as intermediate. All the above mentioned data demonstrate that the oxidation of (4-dimethylamino)phenyl moieties becomes more difficult in the presence of acetylenic bonds. However, as shown for the hybrid oligomers, the strong electron-attracting character of the DEE core may explain this anodic potential shift. In contrast to substituted ethenes characterized by two one-electron processes in which the second occurs more readily than the first, in the DEE and TEE series, the redox-potential difference between the two overlapping one-electron transfers is always between 36 and 90 mV, corresponding to almost non-interacting redox centers. The same is observed for the reduction of nitrophenyl-substituted TEE or DEE with a redox potential difference of between 36 and 80 mV. A similar redox potential separation was even observed in 2,2′-4,4′-tetranitrodiphenyl.[54]

11. Summary and Outlook

The systematic and extensive electrochemical studies which have been carried out on linear and cyclic DEE and TEE oligomers allow us to draw some very important conclusions:

i) Two overlapping one-electron reductions of bis(4-nitrophenyl)-substituted TEEs and DEEs allows electrochemical *cis-trans* isomerization (cf. **49/54a**), which is of potential use for constructing molecular switches, in combination with the well-established photochemical isomerization of arylated TEEs.[9]

ii) Linearly conjugated PTA backbones accommodate electrons more readily than cross-conjugated expanded dendralene backbones. Thus, the PTA-trimer **43** is reduced at less-negative potential than the expanded [3]dendralene **42**.

iii) PTAs based on TEE repeat units are more readily reduced than PTAs composed of DEE repeat units and can accommodate, at least until the pentamer, as many electrons as the number of TEE repeat units present. Moreover, the reduction potentials of TEE oligomers can be finely tuned by lateral substitution.

iv) Aromatic and heteroaromatic spacer groups disrupt the electron delocalization along the backbone of DEE oligomers. The effect of two DEE moieties attached to larger two-dimensional spacer chromophores is to strongly enhance, presumably via inductive effects, the acceptor strength of the spacer. Thus DEEs are an outstanding class of new substituents to tune the properties of advanced materials for optoelectronic applications: they enhance the solubility, strongly increase the electron-accepting capability, and, as shown extensively in other work,[9] may dramatically increase the fluorescence quantum yields of chromophores to which they are attached.

v) Perethynylated expanded radialenes exhibit a very strong ability to accommodate electrons, which provides good evidence for macrocyclic cross-conjugation, and, in part, for some gain in aromaticity upon reduction. This holds particularly for expanded [3]- and [4]radialenes that, presumably, are planar molecules.

vi) The readiness of reduction of perethynylated dehydroannulenes reflects the response towards gaining or losing aromaticity in the Hückel sense.

vii) Replacement of acetylene moieties in TEEs by cyano groups results in cyanoethynylethenes (CEEs) with a significantly enhanced acceptor strength. Addition of multiple cyano groups paired with an extension of the linear π-conjugation pattern increases the accepting power of a CEE-based chromophore further towards that of TCNE, the milestone in our investigations.

viii) PTA oligomers are stronger electron acceptors than PA oligomers of the same length.

Supporting Information for this article (electrochemical data for **27–32**, **56**, **57**, and **77–79**) is available (see also footnote on the first page of this article).

Acknowledgments

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