

Synthesis and Electrochemical Properties of Tetrasubstituted Tetraphenylethenes

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Tetrakis(4-acetoxyphenyl and 4-benzoyloxyphenyl)ethenes **1f** and **1g** were obtained by acylation of tetrakis(4-hydroxyphenyl)ethene **1b**. Ullmann etherification of 4,4'-dihydroxybenzophenone **2b** and subsequent McMurry coupling yielded tetrakis(phenoxyphenyl)ethene **1i**. The tetrakis(acetamidophenyl)ethene **1h** was prepared in three steps from tetraphenylethene **1c** by nitration, Raney-Ni reduction and subsequent acetylation. Alternatively, trifluoroacetamide **1j**, 2-methylhexanamide **1k** and 2,4-dimethylbenzamide **1l**, with less tendency to form 2D hydrogen bonding networks and thus increased solubility as compared to **1h**, were prepared by acylation of 4,4'-diaminobenzophenone **2a** and subse-

quent McMurry coupling. Compounds **1f–l** were investigated by cyclic voltammetry. While the phenyl ether derivative **1i** displays single-electron processes during oxidation, a two-electron process was discovered for trifluoroacetamide **1j** as was also supposed for the esters **1f** and **1g**. In addition, compartmentation constants were shown to be dependent on the solvent. In situ IR spectroelectrochemistry provided evidence for quinoidal type substructures in the dioxidized forms of tetraphenylethenes **1**.

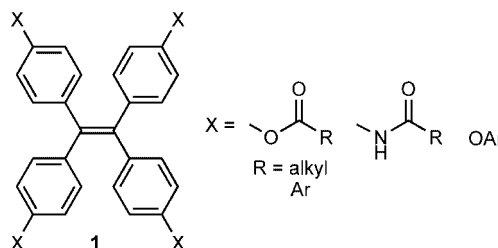
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Introduction

Tetraphenylethenes display interesting chemical and physical properties. For example, they can undergo photocyclization to the corresponding diphenylphenanthrenes.^[1–4] Upon oxidation tetraphenylethenes easily form radical cations and dications, respectively,^[5–7] while reduction with alkali metals leads to dianions.^[8] Both dianions^[8] and dications^[5,9] can be characterized by crystallography. Furthermore, tetraarylethenes provide three different conjugation modes: diagonal, lateral and cross conjugation and they may be used as two-dimensional molecular scaffolds for bichromophoric donor-acceptor dyads for energy transfer.^[10] Recently we have described novel liquid crystalline tetraphenylethene derivatives which form columnar mesophases.^[4,11] In an attempt to understand the redox properties of these compounds in solution, cyclic voltammetric (CV) studies were performed. However, preliminary results revealed a complex behavior. We therefore decided

to look for the redox properties of much simpler model systems. The unsubstituted tetraphenylethene,^[6,12,13] as well as the substituted analogues with methyl,^[5,6,12] trifluoromethyl,^[12] phenyl,^[12] hydroxy,^[14] methoxy,^[5,6,12] amino,^[12] *N,N*-dimethyl-,^[12,14,15] and diphenylamino,^[16] halogen,^[12] nitro,^[12] cyano^[6] and acetyl^[17] were investigated by cyclic voltammetry, spectroelectrochemistry and EPR in great detail.^[18]

According to these studies, tetraphenylethenes are generally oxidized and reduced in two successive one-electron steps. Functional groups at the *para* positions strongly influence the redox potentials and good correlations between the average reduction potential and the sum of the σ^- coefficients of the individual substituents have been observed.^[2] The arene substituents also affect the overall chemical stabilities of the oxidized and the reduced forms. Resonance stabilization by strongly electron-donating alkoxy groups has even allowed for the preparation and structural charac-



Scheme 1. Tetraphenylethene derivatives **1**.

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terization of the mono- and di-oxidized forms of tetra(4-anisyl)ethene (**1a**), giving valuable insight into the structural changes induced by electron transfer.^[5] Surprisingly, no information was available about tetraphenylethenes **1** with either acyloxy, acetamido, aryloxy or related substituents in the *para* position (Scheme 1).

As these derivatives **1**, however, are particularly interesting precursors for the synthesis of liquid crystalline compounds, we investigated their preparation and redox behavior. The results of this study are reported below.

Results and Discussion

Synthesis of Tetraphenylethenes **1**

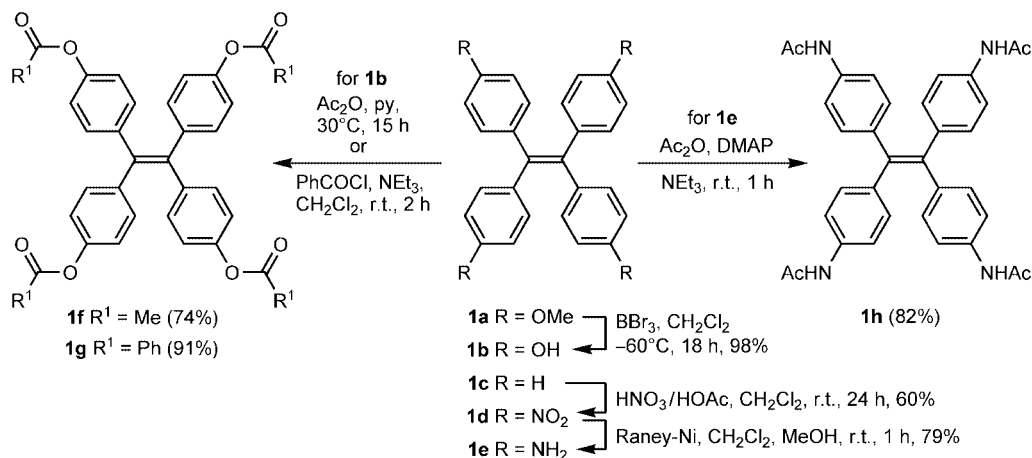
As shown in Scheme 2, tetrahydroxytetraphenylethene **1b**, which was obtained from tetrakis(4-methoxyphenyl)ethene **1a**,^[11,19] was acetylated with acetic anhydride in pyridine at 30 °C according to the procedure by Cid^[20] to cleanly afford the tetraacetate **1f** in 74% yield. Treatment of **1b** with benzoyl chloride in the presence of triethylamine in CH₂Cl₂ following a procedure by Lee^[21] yielded the tetrabenzoate **1g** in 91%.

Surprisingly no conversion was observed upon nitration of tetraphenylethene **1c** in neat conc. HNO₃ and HOAc or H₂SO₄.^[22] In contrast, **1c** was easily nitrated in CH₂Cl₂ to afford the desired tetrakis(nitrophenyl)ethene **1d** in 60% (Scheme 2). Attempts to reduce the nitro groups by using Pd/C, hydrazine,^[23] Sn/HCl or SnCl₄ and NaBH₄ in EtOH all failed.^[24] After considerable experimentation, reduction was successfully carried out using Raney-Ni in CH₂Cl₂/MeOH to give the tetraamine **1e** in 79% yield. The latter was treated with acetic anhydride in the presence of DMAP and NEt₃ to provide the acetamide derivative **1h** (82%). Unfortunately, the acetamide **1h** was insoluble in most com-

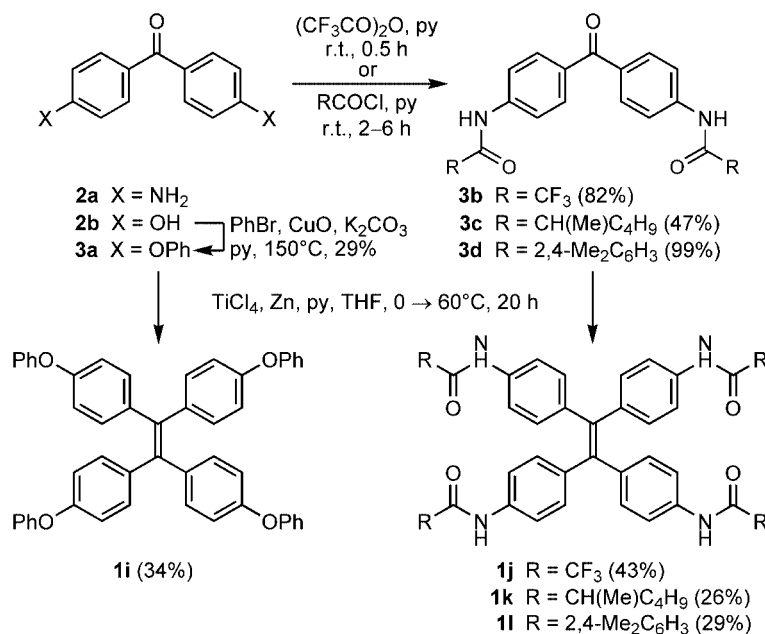
mon organic solvents, thus, suitable NMR spectra were obtained in DMSO only at 60 °C. Presumably, extensive hydrogen bonding of the four amide groups leads to a two dimensional network with very low solubility.^[25] As further solubility problems were expected for tetrakis(benzamido-phenyl)ethene, this target compound was completely abandoned and we looked for alternative amides. Trifluoroacetic acid derived amides are assumed to be less prone to hydrogen bonding. As depicted in Scheme 3, 4,4'-diaminobenzophenone **2a** was treated with (CF₃CO)₂O in pyridine at room temperature to give the bisamide **3b** in 82% yield. The latter was converted via McMurry coupling to the tetraphenylethene derivative **1j** (43%), which, indeed displays a much better solubility than the acetamide **1h**.

Additionally, based on previous observations with branched side chains,^[26] 4,4'-diaminobenzophenone **2a** was *N*-acylated with 2-methylhexanoyl chloride and 2,4-dimethylbenzoyl chloride to give the corresponding amides **3c** and **3d** in 47% and 99% yield, respectively. Coupling of **3c** and **3d** under the usual McMurry conditions^[19] gave the desired tetraphenylethenes **1k** and **1l** in 26% and 29% yields, respectively (Scheme 3). The rather low yields result from difficulties encountered in their chromatographic purification.

Scheme 3 shows the synthesis of the tetrakis(4-phenoxyphenyl)ethene **1i**, which was obtained from 4,4'-dihydroxybenzophenone **2b** which underwent an Ullmann etherification^[27] in the presence of bromobenzene, CuO and K₂CO₃ in pyridine to give the benzophenone derivative **3a** in 29% yield. Subsequent McMurry coupling under the usual conditions^[19] yielded the target ether **1i** in 34%. Alternatively, in order to improve the overall yield, hydroxy-substituted phenylethene **1b** was directly converted into the tetraphenyl ether **1i** under Ullmann etherification conditions albeit with a lower overall yield (19%). The long reaction times of 7 days may be taken as evidence that the fourfold etherification suffers from increasing steric hindrance during the course of the reaction.



Scheme 2. Preparation of tetraphenylethene derivatives **1b**,^[11] **1d**, **1e** using slightly modified known protocols and preparation of novel derivatives **1f**–**h**.

Scheme 3. Preparation of ethene derivatives **1i–l** starting from benzophenones **2a,b**.

Electrochemistry of Tetraphenylethenes **1**

We studied the electrochemical properties of the new tetraphenylethenes **1f–l**, along with those of reference compounds **1d** and tetrakis(bromophenyl)ethene (**1-Br**) in different solvents than in the original report.^[12] The known behavior of tetra(4-anisyl)ethene (**1a**) in CH₂Cl₂/NBu₄PF₆^[5] was completely reproducible under our conditions. As all other previously reported tetraphenylethenes, compounds **1f–l** undergo at least two sequential one-electron oxidation and reduction events. The first oxidation and reduction potentials differ by more than 3 V. Therefore, most compounds require different solvents for monitoring the anodic and the cathodic processes. The data are summarized in Table 1 and Table 2.

The chemical stabilities of the electrogenerated oxidized forms of the tetraarylethenes depend on both the *para*-substituents and the solvent. The best anodic responses were usually obtained when using the CH₂Cl₂/NBu₄PF₆ electrolyte system. As can be seen from Table 1, in this medium ethers **1a**, **1i** and benzoate **1g** (entries 2, 5 and 8) display chemically reversible waves even at sweep rates as low as 0.05 V s⁻¹ and at room temperature. Their oxidized forms are thus chemically stable, at least on the time scale of the voltammetric experiments. The amides, however, were insoluble in CH₂Cl₂. Thus, the more polar CH₃CN and/or DMF had to be used. In order to probe for solvent effects on the voltammetric behavior, amide **1k** was studied in three different electrolyte systems. While in THF/NBu₄PF₆ and CH₃CN/NBu₄PF₆ a single, chemically reversible anodic wave was observed (entries 11, 12), **1k** showed irreversible behavior in DMF/NBu₄PF₆ (entry 13). The oxidation of **1l** is completely irreversible in CH₃CN/NBu₄PF₆ under all conditions (entry 14). For amides **1j** and **1h** and for the ester **1f** voltammetric responses were found to depend on

Table 1. Electrochemical data for the oxidation of substituted tetraphenylethenes **1** at 295 K. Potentials are calibrated against the internal ferrocene/ferrocenium standard. NBu₄PF₆ (0.2 M) was used as supporting electrolyte.

Entry	Compd.	Solvent	$E_{1/2}^{0/+}$ [V]	$E_{1/2}^{+/2+}$ [V]	$\Delta E_{1/2}$ [V]	K_{comp} ^[28]
1	1-Br ^[a]	CH ₃ CN	1.08	1.25 ^[b]	0.18	975
2	1a	CH ₂ Cl ₂	0.41	0.53 ^[c]	0.12	112
3	1d	CH ₂ Cl ₂	1.72	2.02	n. a.	n. a.
4	1f ^[d]	CH ₂ Cl ₂	0.93	1.05	0.12	935
5	1g	CH ₂ Cl ₂	0.93	1.06 ^[e]	0.13	136
6	1h	CH ₃ CN	0.56 ^[f]	n. a.	n. a.	n. a.
7	1h	DMF	0.47 ^[g]	n. a.	n. a.	n. a.
8	1i	CH ₂ Cl ₂	0.58	0.65	0.07 ^[h]	13
9	1i	DMF	0.68 ^[i]	0.59 ^[i]	-0.09 ^[h]	0.03
10	1j	CH ₃ CN	0.84 ^[i]	0.86 ^[i]	0.02 ^[h]	2.70
11	1k	CH ₃ CN	0.53	<0.53	<0 ^[h]	<1
12	1k	THF	0.48	<0.48	<0 ^[h]	<1
13	1k	DMF	0.56 ^[g]	n. a.	n. a.	n. a.
14	1l	CH ₃ CN	1.15 ^[g]	n. a.	n. a.	n. a.

[a] Tetrakis(4-bromophenyl)ethene. [b] Second wave is associated with a significantly larger ΔE_p than the first one (quasireversible behavior); additional irreversible oxidation at 1.63 V. [c] Additional irreversible multi-electron oxidation peak at 1.73 V. [d] At 195 K. [e] Additional irreversible oxidation at 1.94 V. [f] Potential of a partially reversible wave at 233 K. See text for behavior at 295 K. [g] Irreversible peak under all conditions employed. [h] $E_{1/2}$ and $\Delta E_{1/2}$ values are based on digital simulations. [i] Irreversible peak. Partially reversible at 233 K. n. a. = not applicable.

temperature and sweep rate. Compound **1j** displayed reverse to forward peak current ratios $i_{p,\text{rev}}/i_{p,\text{forw}}$ slightly lower than unity at low sweep rates and at room temperature. The underlying chemical process is suppressed at higher sweep rates or by lowering the temperature resulting in full chemical reversibility (entry 10).

For ester **1f** and amide **1h** (entries 4, 6, 7) temperature effects are even more pronounced. At room temperature

Table 2. Peak potentials of the main feature for the reduction of substituted tetraphenylethenes **1** at 295 K, sweep rate $\nu = 0.1 \text{ V s}^{-1}$. Potentials are calibrated against the internal ferrocene/ferrocenium standard. NBu_4PF_6 (0.2 M) was used as the supporting electrolyte.

Entry	Compd.	Solvent	E [V] (n)
1	1-Br ^[a]	DMF	-2.45 ($2e^-$, irrev.) ^[b]
2	1d	CH_2Cl_2	-1.33 ($2e^-$, rev.); -1.61 ($2e^-$, quasirev.)
3	1f	THF	-2.69 ^[c] ($2e^-$, irrev.)
4	1g	THF	-2.62 ^[d] ($1e^-$, p.rev.); -2.73 ^[d] ($1e^-$, irrev.)
5	1h	DMF	-2.39 ($2e^-$, irrev.)
6	1i	DMF	-2.55 ($2e^-$, p.rev.)
7	1l	DMF	-2.80 ($2e^-$, irrev.)

[a] Tetrakis(4-bromophenyl)ethene. For comparison see ref.^[12] [b] CVs show a discernible shoulder at ca. -2.26 V. Digital simulations indicate a peak composed of two individual reduction processes with a difference of intrinsic half-wave potentials of about 150 $\pm$ 30 mV; additional partially reversible reduction peak at -2.57 V. [c] Additional peaks due to the formation of electroactive products following reduction: $E_{p,c} = -3.04 \text{ V}$, $E_{p,a} = -0.92, -0.53, -0.135$, and -0.015 V . [d] Data by digital simulation of voltammograms recorded at 273 K. n. a. = not applicable, irrev. = irreversible, rev. = reversible, quasirev. = quasireversible and p.rev. = partially reversible.

amide **1h** is oxidized in a single irreversible wave at 0.485 V (peak A in Figure 1, parts a and b). The corresponding oxidized form rapidly converts to a secondary species which undergoes further oxidation at a more anodic potential (Figure 1, parts a and b). The symmetric shape of this additional anodic peak (peak B) suggests an adsorption of the underlying species onto the surface of the working electrode. Upon reversal of the initial sweep direction a cathodic return peak associated with the secondary oxidation product (peak C) and the absence of such a return peak for the primary one indicates that this transformation is complete even on the voltammetric time scale. The half-wave potential of this secondary couple was determined as 0.535 V. As the sweep rate is increased, the peak current of peak B diminishes with respect to peak A but still no further return peak as peak C is observed (Figure 1, parts a and b). However, upon cooling to 233 K the primary oxidation wave is observed as a partially reversible couple at $E_{1/2} = 0.56 \text{ V}$ with a peak current ratio of about 0.55 along with a small peak due to the subsequently formed product (c in Figure 1 and Table 1, entry 6).

When the sweep rate is increased above 0.4 V s^{-1} , the reverse peak continuously broadens with a concomitant decrease in the reverse to forward peak current ratio, obviously as a result of slow electron transfer kinetics. In DMF/ NBu_4PF_6 the behavior of amide **1h** was qualitatively similar. However, the cathodic return peak was absent even at low temperature (Table 1, entry 7).

The room temperature oxidation of acetate **1f** in CH_2Cl_2 / NBu_4PF_6 occurs as a broad irreversible composite peak (Figure 2, part b, peak A). The appearance of additional anodic (peak B) and cathodic (couple C/C' and D/D') features of the immediate oxidation peak indicates that the degradation of the oxidized form(s) gives rise to subsequently

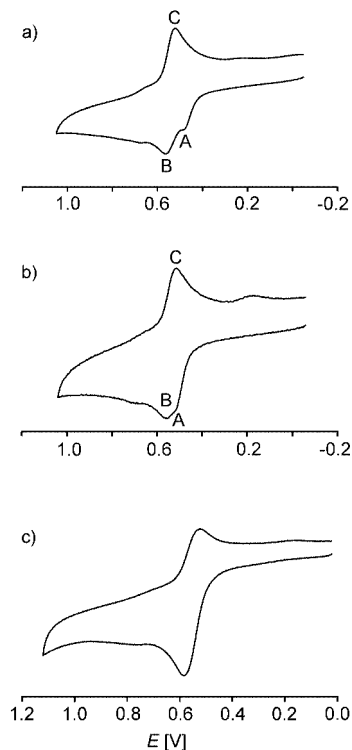


Figure 1. Cyclic voltammetric studies of compound **1h** in $\text{CH}_3\text{CN}/\text{NBu}_4\text{PF}_6$ (0.2 M). a) At $\nu = 0.1 \text{ V s}^{-1}$ (295 K), b) at $\nu = 0.8 \text{ V s}^{-1}$ (295 K), and c) at $\nu = 0.1 \text{ V s}^{-1}$ (233 K).

formed electroactive products. These newly formed species collect in the vicinity of the working electrode upon repetitive scanning. This is accompanied by a decrease of the height of peak A during the second scan (see Figure 2, b). At 195 K under identical conditions two fully reversible, consecutive one-electron oxidation waves are observed instead (c in Figure 2, Table 1, entry 4).

The appearance of two consecutive one-electron oxidation waves in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ is typical of the tetraphenylethene derivatives in our study (see also part c in Figure 2, part a in Figure 3, and part a in Figure 4). Wave splittings, $\Delta E_{1/2}$,^[28] were either determined from the voltammograms or were simulated on the basis of the peak-to-peak separations and the half-widths of the forward waves when the individual anodic peaks were too close to be sufficiently resolved. Values of $\Delta E_{1/2}$ in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ vary between 70 and 130 mV (Table 1) and show that the intermediate monocations are only moderately stable with respect to disproportionation. The redox splittings reflect, at least on a qualitative level, trends in the relative thermodynamic stabilities of the monocations as the supporting electrolyte and temperature are kept constant in this series. Medium and ion pairing have also a strong bearing on $\Delta E_{1/2}$ and thus on the relative stabilities of the monooxidized vs. the dioxidized and the neutral forms. The phenyl ether **1i** provides an instructive example for such medium effects.

Whereas K_{comp} assumes a value of 13 in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ (Table 1, entry 8, Figure 3, a), it is even lower than 1 in the more polar DMF/ NBu_4PF_6 system (Table 1,

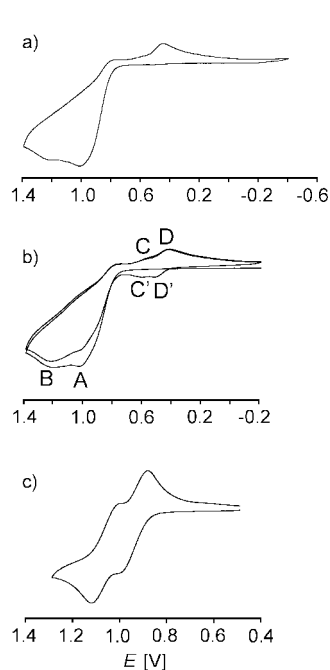


Figure 2. Cyclic voltammetric studies of compound **1f** in $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ (0.2 M). a) At $v = 0.05 \text{ V s}^{-1}$ (295 K), b) two repetitive scans at $v = 0.1 \text{ V s}^{-1}$ (295 K), and c) at 0.1 V s^{-1} (195 K).

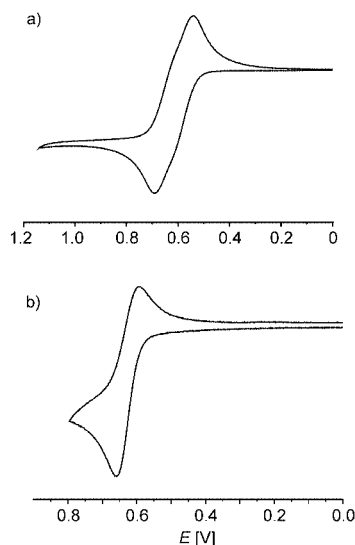


Figure 3. Cyclic voltammograms of the phenyl ether **1i** in a) $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ (0.2 M) and b) in $\text{DMF}/\text{NBu}_4\text{PF}_6$ (0.2 M) at $v = 0.05 \text{ V s}^{-1}$ (295 K).

entry 9, Figure 3, b). Hence, in the DMF-based electrolyte system the dication is thermodynamically more favoured than the monooxidized form. Such a situation may be encountered when the higher oxidized form enjoys some additional stabilization, e.g. by resonance. Similar observations are made for the amide **1k** in $\text{CH}_3\text{CN}/\text{NBu}_4\text{PF}_6$ or $\text{THF}/\text{NBu}_4\text{PF}_6$ solutions (Table 1, entries 11 and 12).

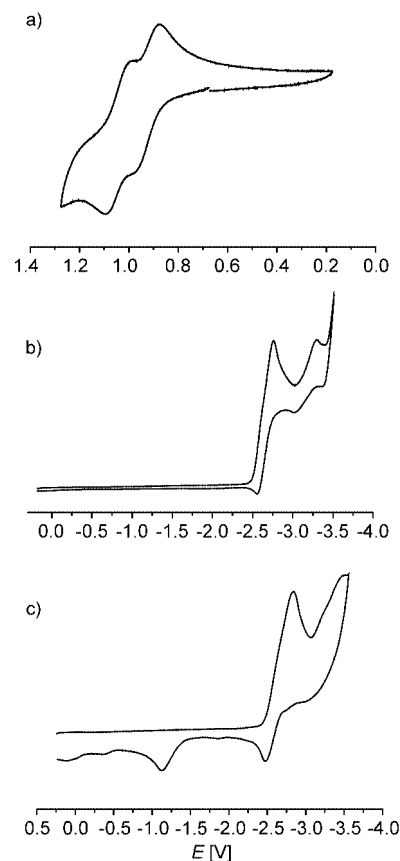


Figure 4. Cyclic voltammetry of benzoate **1g**. a) In $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ (0.2 M), $v = 0.1 \text{ V s}^{-1}$ (295 K), b) in $\text{THF}/\text{NBu}_4\text{PF}_6$ (0.2 M), $v = 0.05 \text{ V s}^{-1}$ (273 K), and c) $v = 0.6 \text{ V s}^{-1}$ (273 K).

The two-electron nature of the oxidation wave of the amide **1j** in $\text{CH}_3\text{CN}/\text{NBu}_4\text{PF}_6$ (Table 1, entry 10) was first established using the Baranski method,^[29] which gave an estimate of 1.7 electrons vs. the ferrocene standard. Bulk coulometry on a 0.05 mM solution of **1j** in $\text{CH}_3\text{CN}/\text{NBu}_4\text{PF}_6$ at ambient temperature finally confirmed the two-electron process. Upon electrolysis the solution turned intense purple-blue in color while 2.03 equivalents of charge were released. However, when the oxidation was complete, the color quickly faded along with the disappearance of the corresponding voltammetric wave of the $\mathbf{1j}^{2+}/\mathbf{1j}$ couple. This indicates that the dication has only limited stability on a more extended time-scale.

In $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ the nitro derivative **1d** is oxidized in two consecutive largely irreversible peaks close to the solvent discharge limit (Table 1, entry 3). Both peaks are associated with about the same peak currents as the reduction waves and, with reference to the known cathodic behavior of **1d**,^[12] are thus assigned as two-electron processes. Under the same conditions, **1d** is reduced at considerably less cathodic potentials than the other tetraphenylethene derivatives **1** (see below). This is because the reductions of **1d** involve the nitro substituents and not the tetraphenylethene core itself, as it has already been pointed out.^[12,30] As a consequence, two cathodic waves are observed as perfectly reversible and quasireversible features (Table 2, entry 2).

For all other tetraphenylethene derivatives described herein, the reductions are outside the potential window of the $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ electrolyte but were monitored in THF and DMF owing to their superior cathodic discharge limits (Table 2). For every new amide studied, ether and ester-substituted tetraphenylethene reductions are followed by chemical reactions, which are so fast under all conditions that the reductions appear as chemically irreversible composite peaks in their cyclic voltammograms. This prevents us from determining individual $E_{1/2}$ values.^[31] In most cases, a discernible shoulder at the anodic side of the main peak indicates the presence of separate redox processes and stepwise reduction to the mono- and dianions. Similar behavior has been reported for the tetraphenylethene itself and its methyl, *tert*-butyl, phenyl and amino derivatives.^[12]

In the case of benzoate **1g** and phenyl ether **1i**, a small anodic reverse peak was detected in DMF and THF, respectively. For **1i** the partially reversible wave broadened considerably as the sweep rate was increased or the temperature lowered, indicating that the reduction also suffers from slow electron transfer kinetics. In the case of **1g** the return peak intensified at higher sweep rates and lower temperatures (Table 2, entry 4, Figure 4, b and c). Monitoring this couple as a function of sweep rate allows us to derive the rate and equilibrium constants for the subsequent processes and reliable estimates of the $\Delta E_{1/2}$ of the first and second reductions. Although the values for the equilibrium constants and the rates of the subsequent processes may only be qualitatively correct, it is still clear that both the reduction steps are followed by chemical reactions and that the second reduction accelerates the rate of the subsequent process(es) by about a factor of 1000 with respect to the first one. There is also an additional, largely irreversible composite wave at more cathodic potentials. On the basis that the peak currents increase with increasing sweep rate and with decreasing temperature (see Figure 4, b and c), this wave is assigned to further reductions of the dianion of **1g** to the tri- and tetraanions with half-wave potentials of ca. -3.085 and -3.145 V, respectively. Additional peaks on the reverse scan after traversing the third and fourth reduction waves are attributed to the oxidations of the products of the subsequent reaction (Figure 4, c).

A comparison of the data listed in Table 1 and Table 2 demonstrates the influence of the *para* substituents on the oxidation and reduction potentials with the phenyl ether **1i** and nitro derivative **1d** as the extremes. Thus, **1i** displays the lowest oxidation potentials of all compounds in this study. Its reduction potential is even more negative than the cathodic discharge limit of the THF/ NBu_4PF_6 electrolyte system. Even within a series of chemically similar systems such as the ethers and amides, the influence of remote substituents is clearly observed. Replacing the methoxy by the phenoxy group (**1a** vs. **1i**) shifts the oxidation potentials to about 180 mV higher in value (Table 1, entries 2, 8). Substitution of $\text{CH}(\text{Me})\text{C}_4\text{H}_9$ by the CF_3 or by the $2,4\text{-Me}_2\text{C}_6\text{H}_3$ group in the amides **1j**–**l** has an even larger effect (Table 1, entries 10, 11, 14). Owing to the chemical irreversibility of

the reduction steps, the substituent effects on the reduction potentials are less clear cut as is the case for the oxidations.

The presence of charge-sensitive IR labels in the benzoate **1g** and trifluoroacetamide **1j**^[32] paired with the chemically reversible nature of their first and second oxidations in cyclic voltammetry prompted us to study these processes under the conditions of in situ IR spectroelectrochemistry. As is shown in part a of Figure 5 for the amide **1j**, the CONH band, which is originally located at 1730 cm^{-1} , gradually splits into two separate features at 1753 and 1733 cm^{-1} , respectively. From this observation we conclude that there are two kinds of differently charged amide groups at the dication stage. This finding nicely parallels the results of a structural study on the tetra(4-anisyl)ethene **1a**, where substantially different degrees of quinoidal distortions have been observed for the two geminal anisyl groups at each carbon atom.^[5] Such charge localization, on mainly one of the arenes at each of the central carbon atoms, is expressed by resonance form **B** in part b of Figure 5. The prominent feature that grows in at 1570 cm^{-1} is probably related to the quinone iminium type substructures of the dioxidized form (Figure 5, a). The subsequent reduction at a potential cathodic of the composite wave gave the reduced parent in nearly quantitative spectroscopic yield.

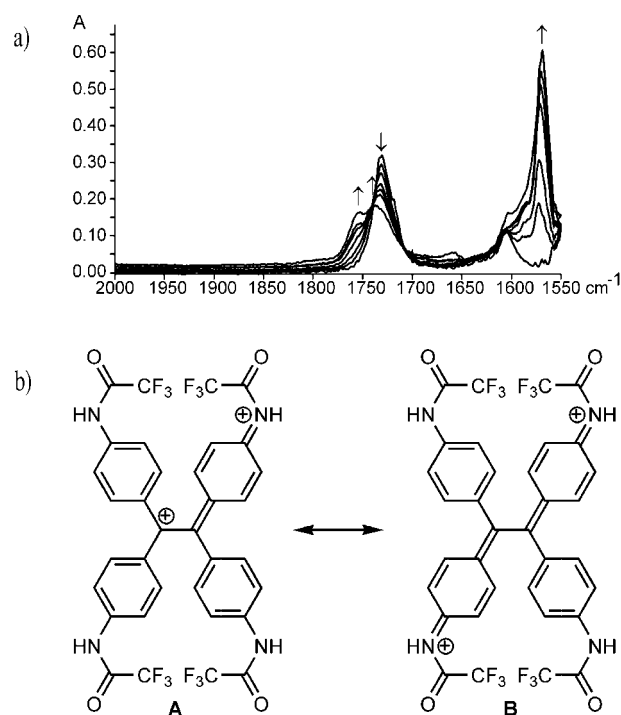


Figure 5. a) IR spectroelectrochemical traces recorded upon stepwise oxidation of the amide **1j**. The down and up arrows at 1730 , 1733 , and 1753 cm^{-1} indicate the CONH bands of the neutral starting material and of the dication, respectively, while the up arrow at 1570 cm^{-1} may indicate a quinoidal type substructure of the dioxidized form. b) Possible resonance forms of the trifluoroacetamide dication **1j**²⁺.

Qualitatively similar results were obtained for the benzoate **1g**, where the dioxidized form is of only fleeting existence and substantial degradation to a new species is ob-

served during the time required to effect complete consumption of the neutral starting compound (for details see Figure S1 in the Supporting Information).

Conclusions

We have synthesized novel tetraphenylethenes **1f–l** with various substituents in *para* positions and studied their electrochemical behavior by cyclic voltammetry. Our investigations extend the range of tetraphenylethenes studied by electrochemistry to amide, ester and phenyl ether functionalized derivatives **1f–l**. Additional studies include the nitro and bromo derivatives as references in solvents other than those employed in the previous work, such that the oxidation potentials of the nitro derivative **1d** are also available. This work also demonstrates the medium effects on the comproportionation constants. The two electron nature of the composite wave of a prototype amide derivative **1j** has been probed by a comparison of the results of potential sweep and potential step methods and finally by bulk electrolysis. In situ IR spectroelectrochemistry served to identify the presence of two differently charged (and thus structurally different) aryl groups at each of the central carbon atoms and has provided spectroscopic evidence for quinoidal type substructures in the dioxidized forms of tetraphenylethenes **1**.

Experimental Section

General: The following tetraphenylethenes **1a–e** are known in the literature.^[6,11–14,18] Melting points were measured using a differential scanning calorimeter Mettler–Toledo DSC 822. ¹H NMR spectra were recorded using a Bruker ARX 300 and ARX 500 with tetramethylsilane as the internal standard. ¹³C NMR multiplicities were assigned by DEPT experiments. IR spectra were recorded using a Bruker Vector 22 FT-IR spectrometer with ATR technique. Mass spectrometry was performed using a Varian MAT 711 mass spectrometer with EI ionization (70 eV). UV/Vis spectra were recorded using a Perkin–Elmer Lambda7 spectrometer. Column chromatography was performed using silica gel 60 (Fluka, mesh 40–63 μ m) with hexanes (boiling range 30–75 °C). Electrochemical data were acquired with a computer controlled EG&G model 273 potentiostat utilizing the EG&G 250 software package. Digital simulations of experimental CVs were performed with DigiSim[®] software (version 2.1) available from BAS. CH₂Cl₂ and 1,2-Dichloroethane (Fluka, Burdick&Jackson Brand) for electrochemical work and CH₃CN (Roth) were freshly distilled from CaH₂ prior to use. DMF (Fluka, Burdick&Jackson Brand) was stored over molecular sieves (4 Å) and purged with argon prior to use. THF was dried with potassium and freshly distilled from potassium/benzophenone.

Electrochemical Experiments: All electrochemical experiments were performed in a home-built cylindrical vacuum-tight one-compartment cell. A spiral shaped Pt wire and a Ag wire as the counter and reference electrodes, respectively, were sealed directly into opposite sides of the glass wall while the respective working electrode [Pt or glassy carbon, 1.1 mm, polished with 0.25 μ m diamond paste (Buehler–Wirtz) before each experiment] was introduced via a teflon screw cap with a suitable fitting. The cell was attached to a conventional Schlenk line via two side arms equipped with teflon

screw valves and allowed experiments to be performed under an atmosphere of argon with approximately 2.5 mL of analyte solution. Bulk electrolysis was performed in a vacuum type “H-cell” with a large surface Pt gauze working and a smaller size Pt gauze counter electrode and a silver wire as the reference directly welded into the side walls of the individual cell compartments. The compartments are separated from each other by medium porosity frits. The OTTE cell was also home built following the design of Hartl and co-workers^[33] and comprises a Pt-mesh working and counter electrode and a thin Ag wire as a pseudo-reference electrode sandwiched between the CaF₂ windows of a conventional liquid IR cell. The working electrode was positioned in the center of the spectrometer beam. In all experiments NBu₄PF₆ (0.2 M in the respective solvent) was used as the supporting electrolyte. For each compound cyclic voltammograms were run at sweep rates from 0.05 V s^{−1} to 10 V s^{−1} at both room temperature and at low temperature (195 K in CH₂Cl₂, 233 K in CH₃CN or DMF, 213 K in THF). Scans recorded at high sweep rates suffer, however, from distortions owing to Ohmic drop and somewhat slow electron transfer kinetics, especially at low temperatures.

Tetrakis(4-acetoxyphenyl)ethene (1f): Acetic anhydride (1.27 g, 1.17 mL, 12.4 mmol) was added to a solution of pyridine (3 mL) and **1b** (420 mg, 1.10 mmol) and the reaction mixture stirred at room temperature for 15 h. The solvent was removed under vacuum, the residue dissolved in CH₂Cl₂ (20 mL) and washed with diluted HCl (3 × 10 mL). Recrystallization from methanol gave compound **1f** as fine colorless crystals (457 mg, 0.8 mmol, 74%). M.p. 221 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.25 (s, 12 H, CH₃), 6.85 (d, ³J = 8.7 Hz, 8 H, 3-H, 5-H), 7.01 (d, ³J = 8.7 Hz, 8 H, 2-H, 6-H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 21.5 (CH₃), 121.3 (C-3, C-5), 132.7 (C-2, C-6), 140.0 (C=C), 140.9 (C-1), 149.7 (C-4), 169.5 (C=O) ppm. FTIR (ATR): $\tilde{\nu}$ = 3068 (w), 1750 (vs), 1600 (m), 1501 (s), 1367 (s), 1185 (vs), 1009 (s), 908 (m), 850 (m) cm^{−1}. UV/Vis (toluene) λ_{max} = 314 nm. MS (EI): *m/z* (%) = 654 (100) [M⁺], 522 (59), 480 (57), 438 (41), 396 (70), 43 (56). C₃₄H₂₈O₈ (564.58): calcd. C 72.33, H 5.00; found C 72.11, H 5.10.

Tetrakis(4-benzoyloxyphenyl)ethene (1g): Benzoyl chloride (0.59 g, 0.49 mL, 4.20 mmol) was added dropwise over 20 min to a solution of **1b** (414 mg, 1.00 mmol) and triethylamine (430 mg, 0.59 mL, 4.20 mmol) in CH₂Cl₂ (5 mL) at 0 °C. Then the reaction mixture was stirred at room temperature for 2 h and washed with 1 M HCl (3 × 2 mL). After removal of the solvent under vacuum, the residue was recrystallized from methanol/hexane (1:1) to give **1g** as fine colorless crystals (743 mg, 0.92 mmol, 91%). M.p. 306 °C. ¹H NMR (500 MHz, CDCl₃): δ = 7.05 (d, ³J = 8.6 Hz, 8 H, 3-H, 5-H), 7.16 (d, ³J = 8.6 Hz, 8 H, 2-H, 6-H), 7.50 (t, ³J = 7.8 Hz, 8 H, 3'-H, 5'-H), 7.63 (t, ³J = 7.4 Hz, 4 H, 4'-H), 8.19 (d, ³J = 7.3 Hz, 8 H, 2'-H, 6'-H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 121.2 (C-3, C-5), 128.6 (C-2', C-6'), 129.6 (C-1'), 130.2 (C-3', C-5'), 132.5 (C-2, C-6), 133.6 (C-4'), 139.9 (C=C), 140.9 (C-1), 149.1 (C-4), 165.0 (C=O) ppm. FTIR (ATR): $\tilde{\nu}$ = 3161 (w), 1730 (vs), 1598 (w), 1503 (m), 1260 (s), 1199 (s), 1163 (s), 1059 (s), 700 (vs) cm^{−1}. UV/Vis (toluene): λ_{max} = 308 nm. MS (EI): *m/z* (%) = 812 (47) [M⁺], 105 (100). C₅₄H₃₆O₈ (812.86): calcd. C 79.79, H 4.46; found C 80.12, H 4.48.

Tetrakis(4-acetylaminophenyl)ethene (1h): A solution of 4-(dimethylamino)pyridine (6.10 mg, 0.05 mmol), triethylamine (47 mg, 0.07 mL, 0.47 mmol) and acetic anhydride (130 mg, 0.12 mL, 1.30 mmol) in CH₂Cl₂ (5 mL) was added dropwise to a suspension of **1e** (61 mg, 0.16 mmol) in CH₂Cl₂ (5 mL) and the reaction mixture was stirred at room temperature for 16 h. A 0.1 N solution of NaOH (10 mL) was then added, the layers were separated and the

aqueous layer was extracted with CH_2Cl_2 (3×2 mL). The combined organic layers were washed with brine (3×5 mL). The solvent was removed under vacuum and the residue was washed with CH_2Cl_2 and dried to give **1h** as orange powder (71 mg, 0.13 mmol, 82%). M.p. $>230^\circ\text{C}$ (dec.). ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$, 60°C): δ = 1.99 (s, 12 H, CH_3), 6.86 (d, 3J = 7.7 Hz, 8 H, 3-H, 5-H), 7.32 (d, 3J = 7.7 Hz, 8 H, 2-H, 6-H), 9.71 (s, 4 H, NHCO) ppm. ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$): δ = 23.5 (CH_3), 118.1, 130.7 (C-2, C-3, C-5, C-6), 137.2, 138.0 (C-1, C-4), 138.8 (C=C) ppm. FTIR (ATR): $\tilde{\nu}$ = 3249 (m), 3102 (w), 3035 (w), 1663 (s), 1593 (s), 1511 (vs), 1403 (m), 1370 (m), 1313 (s), 1017 (m), 839 (s) cm^{-1} . UV/Vis (CH_3CN): λ_{max} = 273 nm. MS (EI): m/z (%) = 560 (1), 518 (2), 476 (3), 434 (3), 393 (1), 58 (30), 43 (100).

Bis[4-(phenyloxy)phenyl] Ketone (3a): Potassium carbonate (1.94 g, 14 mmol) was dried in a Schlenk flask, and in a N_2 atmosphere **2b** (1.50 g, 7.00 mmol), bromobenzene (2.20 g, 1.48 mL, 14.0 mmol), CuO (1.68 g, 21 mmol) and pyridine (30 mL) were added. The reaction mixture was stirred at 150°C for 7 d. After cooling to room temperature, CH_2Cl_2 (200 mL) was added and the solid filtered off. The filtrate was vigorously stirred with 10% HCl (2×200 mL) for 1 h, washed with a satd. solution of NaHCO_3 and H_2O (200 mL each) and dried (MgSO_4). The solvent was removed under vacuum and the residue purified by chromatography on SiO_2 with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (10:1) to give **3a** as yellowish crystals (700 mg, 2.00 mmol, 29%). ^1H NMR (300 MHz, CDCl_3): δ = 7.01–7.04 (m, 4 H, 3-H, 5-H), 7.08–7.43 (m, 10 H, 3-H, 2'-H, 3'-H, 4'-H, 5'-H, 6'-H), 7.78–7.81 (m, 4 H, 2-H, 6-H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 117.5 (C-3', C-5'), 120.5 (C-2', C-6'), 124.9 (C-4'), 130.4 (C-3, C-5), 132.5 (C-1), 132.6 (C-2, C-6), 155.9 (C-1'), 161.8 (C-4), 188.4 (C=O) ppm.

Tetrakis(4-phenyloxyphenyl)ethene (1i): a) In a Schlenk flask in an inert gas atmosphere TiCl_4 (390 mg, 0.23 mL, 2.00 mmol) was added to abs. THF (20 mL) at 0°C . Then Zn powder (265 mg), pyridine (0.14 mL) and a suspension of **3a** (690 mg, 1.90 mmol) in THF (10 mL) were slowly added and the reaction mixture stirred at 60°C for 18 h. A solution of $\text{K}_2\text{CO}_3/\text{H}_2\text{O}$ (10%, 20 mL) and H_2O (20 mL) were added, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried (MgSO_4) and concentrated. The residue was purified by chromatography on SiO_2 with hexanes/ EtOAc (15:1) to give **1i** as colorless crystals (460 mg, 0.60 mmol, 34%).

b) In a Schlenk flask K_2CO_3 (710 mg, 5.00 mmol) was dried and in an inert gas atmosphere **1b** (500 mg, 1.26 mmol), CuO (605 mg, 7.60 mmol) and bromobenzene (801 mg, 0.54 mL, 5.00 mmol) were added. The reaction mixture was stirred at 150°C for 7 d and then cooled to room temperature. After addition of CH_2Cl_2 (50 mL), the reaction mixture was filtered. The filtrate was vigorously stirred with diluted HCl (2×50 mL) for 1 h, washed with a satd. solution of NaHCO_3 and H_2O (2×30 mL each) and dried (MgSO_4). The solvent was removed under vacuum and the residue was purified by flash chromatography on SiO_2 with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (15:1) to give **1i** (166 mg, 0.24 mmol, 19%). M.p. 196°C . ^1H NMR (500 MHz, CDCl_3): δ = 6.77–6.78 (m, 8 H, 3'-H, 5'-H), 6.96–7.03 (m, 20 H, 3-H, 5-H, 2'-H, 4'-H, 6'-H), 7.30–7.32 (m, 8 H, 2-H, 6-H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ = 118.4 (C-3', C-5'), 119.2 (C-3, C-5), 123.6 (C-4'), 130.6 (C-2, C-6), 133.1 (C-2', C-6'), 139.1 (C-1), 139.3 (C=C), 156.1 (C-1'), 157.4 (C-1) ppm. FTIR (ATR): $\tilde{\nu}$ = 3032 (w), 2963 (w), 1586 (s), 1503 (m), 1485 (vs), 1227 (vs), 1167 (m), 1158 (m), 1095 (m), 1070 (m), 1011 (m), 858 (m), 844 (m), 793 (s), 749 (s), 689 (s) cm^{-1} . UV/Vis (THF): λ_{max} = 324, 263, 259 nm. MS (EI): m/z (%) = 700 (100) [M^+], 514 (4), 350 (6), 28 (8), 18 (27). HRMS for $\text{C}_{50}\text{H}_{36}\text{O}_4$ (EI): calcd. 700.2614; found 700.2616.

4,4'-Bis(trifluoroacetylaminobenzophenone (3b): Trifluoroacetic anhydride (0.6 mL, 4 mmol) was slowly added dropwise to a solution of **2a** (200 mg, 0.93 mmol) in pyridine (15 mL) and the reaction mixture was stirred at room temperature for 30 min (tlc control). Pyridine was removed, the residue dissolved in CHCl_3 (10 mL) and successively washed with 1 N HCl (10 mL) and a satd. solution of NaHCO_3 (2×5 mL). After removal of the solvent, the residue was purified by flash chromatography with hexanes/acetone (5:1) and recrystallized from hexanes/acetone to give **3b** as white crystals (300 mg, 0.74 mmol, 82%). M.p. 241°C . ^1H NMR (500 MHz, $[\text{D}_6]$ -acetone): δ = 7.90 (d, J = 8.7 Hz, 4 H, 2-H, 6-H), 7.96 (d, J = 8.7 Hz, 4 H, 3-H, 5-H), 10.59 (s, 2 H, NHCO) ppm. ^{13}C NMR (125 MHz, $[\text{D}_6]$ -acetone): δ = 116.81 (q, 1J = 288.1 Hz, CF_3), 121.10, 131.85 (C-2, C-3, C-5, C-6), 135.43, 141.15 (C-1, C-4), 155.10 (q, 2J = 37.6 Hz, CF_3CO), 194.21 (C=O) ppm. FTIR (ATR): $\tilde{\nu}$ = 3279 (s), 1707 (s), 1642 (m), 1600 (m), 1536 (s), 1150 (s), 927 (m), 856 (m), 676 (s) cm^{-1} . UV/Vis (CH_3CN): λ_{max} = 291 nm. MS (EI): m/z (%) = 404 (76) [M^+], 292 (5), 216 (100), 168 (4), 146 (6), 28 (11). $\text{C}_{17}\text{H}_{10}\text{F}_6\text{N}_2\text{O}_3$ (404.27): calcd. C 50.51, H 2.49, N 6.93; found C 50.40, H 2.56, N 6.70.

4,4'-Bis(2-methylhexylamino)benzophenone (3c): 2-Methylhexanoyl chloride (2.1 g, 14 mmol) was added dropwise to a solution of **2a** (849 mg, 4 mmol) in pyridine (50 mL) and the reaction mixture stirred at room temperature for 2 h. Pyridine was removed, the residue dissolved in CHCl_3 (20 mL) and successively washed with 1 N HCl (10 mL) and a satd. solution of NaHCO_3 (2×10 mL). After removal of the solvent, the residue was purified by flash chromatography with hexanes/acetone (3:1) and recrystallized from hexanes/acetone to give **3c** as white crystals (825 mg, 1.9 mmol, 47%). M.p. 163°C . ^1H NMR (300 MHz, $[\text{D}_6]$ -acetone): δ = 0.90 (t, J = 7.1 Hz, 6 H, 5'-H), 1.20 (d, J = 6.8 Hz, 6 H, 6'-H), 1.27–1.58 (m, 9 H, 3'-H, 4'-H, 2'-H), 1.66–1.86 (m, 1 H, 2'-H), 2.55 (sext, J = 6.8 Hz, 1 H, 1'-H), 7.76 (d, J = 8.8 Hz, 4 H, 3-H, 5-H), 7.86 (d, J = 8.9 Hz, 4 H, 2-H, 6-H), 9.41 (s, 2 H, NHCO) ppm. ^{13}C NMR (75 MHz, $[\text{D}_6]$ -acetone): δ = 13.88 (C-5), 17.08 (C-6), 22.14 (C-4), 29.10 (C-3), 33.42 (C-2), 40.70 (C-1), 118.29, 130.84 (C-2, C-3, C-5, C-6), 131.71, 143.09 (C-1, C-4), 175.41 (NHCO), 193.39 (C=O) ppm. FTIR (ATR): $\tilde{\nu}$ = 3248 (s), 2926 (s), 2856 (w), 1651 (s), 1592 (s), 1521 (s), 1406 (m), 1306 (m), 1250 (m), 937 (m), 855 (m), 758 (w), 665 (w) cm^{-1} . UV/Vis (CH_3CN): λ_{max} = 306, 231 nm. MS (CI): m/z (%) = 437 (100) [M^+], 380 (28), 324 (47), 268 (7), 232 (8), 212 (22), 183 (5), 120 (5), 85 (16), 43 (16). $\text{C}_{27}\text{H}_{36}\text{N}_2\text{O}_3$ (436.59): calcd. C 74.28, H 8.31, N 6.42; found C 74.02, H 8.19, N 6.32.

4,4'-Bis(2,4-dimethylbenzylamino)benzophenone (3d): 2,4-Dimethylbenzoyl chloride (2.3 g, 13.6 mmol) was added dropwise to a solution of **2a** (724 mg, 3.4 mmol) in pyridine (40 mL) and the reaction mixture stirred at room temperature for 2 h. Pyridine was removed, the residue dissolved in CHCl_3 (50 mL) and successively washed with 1 N HCl (25 mL) and a satd. solution of NaHCO_3 (2×25 mL). After removal of the solvent, the residue was purified by flash chromatography with hexanes/acetone (3:1) and recrystallized from hexanes/acetone to give **3d** as white crystals (1.6 g, 3.5 mmol, 99%). M.p. 235°C . ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 2.34 (s, 6 H, 4'- CH_3), 2.38 (s, 6 H, 2'- CH_3), 7.10–7.20 (m, 4 H, 6'-H, 3'-H), 7.41 (d, J = 7.5 Hz, 2 H, 5'-H), 7.76 (d, J = 8.7 Hz, 4 H, 2-H, 6-H), 7.92 (d, J = 8.8 Hz, 4 H, 3-H, 5-H), 10.59 (s, 2 H, NHCO) ppm. ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$): δ = 19.33 (4'- CH_3), 20.80 (2'- CH_3), 118.82, 130.78 (C-2, C-3, C-4, C-5), 126.10, 127.48, 131.24 (C-3', C-5', C-6'), 132.13, 133.89, 135.54, 139.59, 143.15 (C-1, C-4, C-1', C-2', C-4'), 168.27 (NHCO), 193.48 (C=O) ppm. FTIR (ATR): $\tilde{\nu}$ = 3298 (s), 2964 (w), 2923 (w), 1707 (s), 1666 (w), 1600 (w), 1586 (s), 1507 (s), 1403 (m), 1309 (m), 1246 (m), 928 (w), 855 (w), 832 (w) cm^{-1} . UV/Vis (CH_3CN): λ_{max} = 309 nm. MS

(EI): m/z (%) = 404 (76) [M^+], 292 (5), 216 (100), 168 (4), 146 (6), 28 (11). $C_{31}H_{28}N_2O_3$ (476.57): calcd. C 78.13, H 5.92, N 5.88; found C 77.91, H 5.95, N 5.83.

General Procedure for the Preparation of Tetrakis(4-amidophenyl)-ethenes 1j–k: In a Schenk flask $TiCl_4$ was added to abs. THF in a N_2 atmosphere at 0 °C. Then Zn powder and pyridine were added followed by dropwise addition of a solution of the respective **3b–d** in THF/ CH_2Cl_2 . The reaction mixture was stirred at 60 °C for 20 h, cooled to room temperature and filtered through Celite. The filtrate was washed once with K_2CO_3/H_2O (10%) and H_2O . The aqueous layer was extracted three times with $CHCl_3$, and the combined organic layers were dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by flash chromatography with hexanes/acetone (3:1) and recrystallized from acetone/hexanes to give the products **1j–k** as yellowish solid.

Tetrakis(4-trifluoroacetamidophenyl)ethene (1j): According to the General Procedure from **3b** (0.606 g, 1.5 mmol) in THF (10 mL) and CH_2Cl_2 (5 mL), $TiCl_4$ (0.2 mL, 1.8 mmol), Zn (0.210 g, 3.2 mol), pyridine (0.11 mL, 1.4 mol), THF (15 mL). Yield: 0.257 mg, 0.32 mmol, 43%. M.p. 357 °C. 1H NMR (500 MHz, $[D_6]$ -acetone): δ = 6.97 (d, J = 8.7 Hz, 8 H, 2-H, 6-H), 7.42 (d, J = 8.7 Hz, 8 H, 3-H, 5-H), 10.09 (s, 4 H, NHCO) ppm. ^{13}C NMR (75 MHz, $[D_6]$ -acetone): δ = 116.88 (q, 1J = 287.9 Hz, CF_3), 120.99, 132.70 (C-2, C-3, C-5, C-6), 136.07, 141.67 (C-1, C-4), 140.96 (C=C), 155.55 (q, 2J = 37.2 Hz, CF_3CO) ppm. FTIR (ATR): $\tilde{\nu}$ = 3306 (s), 3127 (w), 2934 (w), 1703 (vs), 1596 (m), 1537 (s), 1279 (m), 1242 (m), 1186 (s), 1156 (vs), 915 (m), 823 (m) cm^{-1} . UV/Vis (CH_3CN): λ_{max} = 272 nm. MS (DEI): m/z (%) = 776 (100) [M^+], 706 (3), 338 (6). $C_{34}H_{20}F_{12}N_4O_4$ (776.53): calcd. C 52.59, H 2.60, N 7.22; found C 52.84, H 2.88, N 7.21.

Tetrakis[4-(2-methylhexylamido)phenyl]ethene (1k): According to the General Procedure from **3c** (0.5 g, 1.1 mmol) in THF (10 mL) and CH_2Cl_2 (3 mL), $TiCl_4$ (0.14 mL, 1.3 mmol), Zn (0.157 g, 2.4 mmol), pyridine (0.08 mL, 1 mol), THF (15 mL). Yield: 120 mg, 0.143 mmol, 26%. M.p. 296 °C. 1H NMR (500 MHz, $[D_6]$ -DMSO): δ = 0.86 (t, J = 7.1 Hz, 12 H, 5'-H), 1.06 (d, J = 6.8 Hz, 12 H, 6'-H), 1.27–1.58 (m, 9 H, 3'-H, 4'-H, 2'-H), 1.16–1.35 (m, 20 H, 2'-H, 3'-H, 4'-H), 1.55 (m, 4 H, 2'-H), 2.39 (sext, J = 6.6 Hz, 4 H, 1'-H), 6.87 (d, J = 8.6 Hz, 8 H, 3-H, 5-H), 7.38 (d, J = 8.6 Hz, 4 H, 2-H, 6-H), 9.77 (s, 4 H, NHCO) ppm. ^{13}C NMR (125 MHz, $[D_6]$ -DMSO): δ = 11.54 (C-5'), 15.57 (C-4'), 19.82 (C-6'), 26.82 (C-3), 31.10 (C-2), 38.22 (C-1), 116.14, 128.84 (C-2, C-3, C-5, C-6), 135.18, 136.02 (C-1, C-4), 136.04 (C=C), 172.33 (HNC=O) ppm. FTIR (ATR): $\tilde{\nu}$ = 3296 (s), 2928 (s), 2187 (w), 1979 (w), 1658 (vs), 1589 (s), 1511 (vs), 1402 (s), 1306 (m), 1242 (m), 1180 (m), 825 (s) cm^{-1} . UV/Vis (CH_3CN): λ_{max} = 338, 275, 240 nm. MS (EI): m/z (%) = 840 (100) [M^+], 729 (12), 616 (2), 112 (2), 85 (6), 74 (10), 43 (14).

Tetrakis[4-(2,4-dimethylbenzamido)phenyl]ethene (1l): According to the General Procedure from **3d** (1 g, 2.1 mmol) in THF (15 mL) and CH_2Cl_2 (10 mL), $TiCl_4$ (0.26 mL, 2.4 mmol), Zn (0.312 g, 4.8 mmol), pyridine (0.16 mL, 2 mmol), THF (20 mL). Yield: 210 mg, 0.23 mmol, 29%. M.p. 333 °C. 1H NMR (300 MHz, $[D_6]$ -DMSO): δ = 3.37 (br. s, 12 H, 2'-CH₃), 3.38 (br. s, 12, 4'-H), 7.09–7.13 (m, 8 H, 6'-H, 3'-H), 7.33 (d, J = 7.5 Hz, 4 H, 5'-H), 7.46 (d, J = 8.5 Hz, 8 H, 3-H, 5-H), 7.54 (d, J = 8.5 Hz, 8 H, 2-H, 6-H) ppm. ^{13}C NMR (125 MHz, $[D_6]$ -DMSO): δ = 19.29 (4'-CH₃), 20.76 (2'-CH₃), 119.44, 127.25, 128.16 (C-3', C-5', C-6'), 125.95, 131.05 (C-2, C-3, C-5, C-6), 134.39, 135.27, 136.84, 139.02, 139.83 (C-1, C-4, C-1', C-2', C-4'), 167.54 (NHCO) ppm. (The C=C signal was not detected.) FTIR (ATR): $\tilde{\nu}$ = 3295 (s), 2921 (s), 1656 (vs), 1596 (s), 1512 (vs), 1409 (s), 1319 (s), 1231 (s), 1081 (s), 818 (m), 778

(s) cm^{-1} . UV/Vis (CH_3CN): λ_{max} = 265 nm. $C_{62}H_{56}N_4O_4$ (921.15): calcd. C 80.84, H 6.13, N 6.08; found C 75.36, H 6.09, N 5.57.

Supporting Information (see also the footnote on the first page of this article): IR spectroelectrochemical spectra recorded during the oxidation of tetrakis(4-benzoyloxyphenyl)ethene (**1g**).

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