The Voltammetry of Triarylmethane Dyes in Acetonitrile and an Attempt to Correlate their Half-Wave Potentials with Quantum Chemical Characteristics

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The voltammetric behaviour of triarylmethane compounds in a non-aqueous medium of acetonitrile was studied. It was found that substances undergo one-electron oxidation and reduction forming radical-cation or radical, respectively. The fate of products was followed. The half-wave potential values obtained were correlated with the corresponding energies of the highest occupied and lowest free molecular orbitals obtained by the simple method of molecular orbitals (HMO).

After the original chemical oxidation of triarylmethane dyes [1—3], works on the electrochemical oxidation and reduction of several basic triarylmethane dyes also appeared. These experiments were carried out in buffered aqueous solutions. It has been found [4] that two-electron oxidation of a protonated, hydrated form [5] of dyes takes place first, followed by an oxidation of the non-hydrated form with an undetermined mechanism. The two-electron reduction proceeds in one or two steps depending on the nature of the substance, its concentration, and the pH of the solution [6—15].

Because of the disadvantages of aqueous solutions [16] various organic aprotic solvents, in combination with convenient indication electrodes, started to be used. At the voltammetric oxidation of several basic triarylmethane compounds in a non-aqueous medium of liquid sulfur dioxide [17] a one-electron process has been supposed but it has not been further studied. A stepwise reduction of several non-substituted triarylmethyl cations [18, 19] and simply substituted triarylmethane dyes [9] through a radical and an anion has been supposed in various organic solvents.

Relations between polarographic and spectrophotometric behaviour of triarylmethane dyes were also discussed [20].
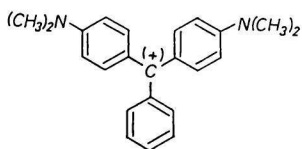
From the brief survey given it is evident that the polarographic investigation in aqueous solutions is complicated by simultaneous presence of several protonated and hydrated forms and that research in non-aqueous media has up to now been scarce. For this reason voltammetric oxidations and reductions of triarylmethane dyes were carried out in water-free acetonitrile in this study, using a rotating platinum indication electrode.

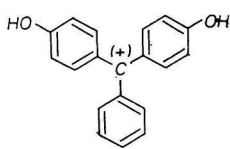## Experimental

The substances studied

For formulas of the substances *I—XII* see Table 1. Most of them are frequently used chemical indicators. In most cases the substances were commercial preparations (Merck, Geigy, Chemo Puro, Spolana). They were purified either by converting to perchlorates
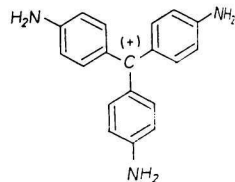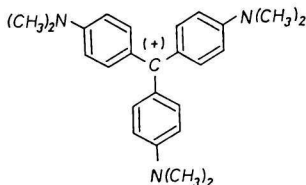
Table 1

I	*II*	*III*
malachite green	benzaurin	pararosaniline
IV	*V*	*VI*
crystal violet	aurin	setoglaucine
VII	*VIII*	*IX*
eriogreen B	aniline blue	erioglaucine A
X	*XI*	*XII*
rhodamine B	9(2,6-dimethoxyphenyl)-1,8-dimethoxyxanthium	sesquixanthium
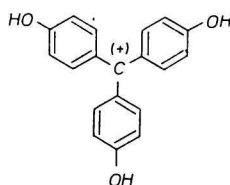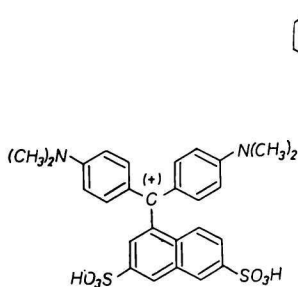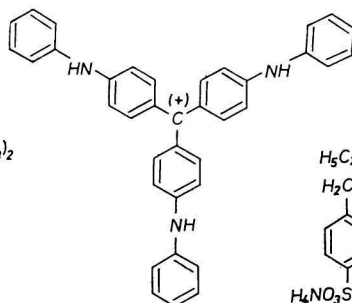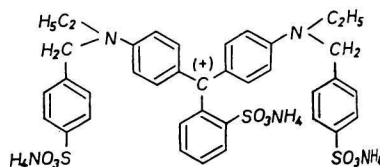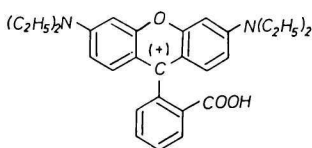
and by repeated crystallization (substances *I*, *IV*, *V*, *VI*, *X*), or by the crystallization from alcohol (substances *III*, *VII*, *VIII*, *IX*)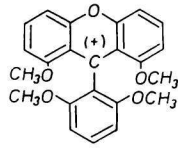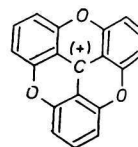. The substance *II* was prepared by *Hansson* [21], substances *XI* and *XII* by *Martin* and *Smith* [22]. The last two substances were converted to perchlorates by dissolving in acetonitrile and mixing with an equivalent amount of 70% perchloric acid. The purity of the substances was controlled by elemental analysis and by chromatography. The substances *V*, *VII*, *VIII*, *IX* were not obtained in a completely pure state even after many repeated purifications. They were, therefore, used only for a rough measurement of values needed.

Apparatus

Voltammetry was carried out by means of a Polariter PO-4 (Radiometer). A rotating platinum electrode (RPE) served as an indication and calomel electrode containing saturated solution of sodium chloride as a reference electrode. A 0.1 M solution of sodium perchlorate in acetonitrile was used as a base electrolyte for both oxidation and reduction. The experimental apparatus has already been described [23]. Half-wave potentials were obtained graphically and a correction for iR was taken. Half-wave potentials were recalculated with respect to the saturated calomel electrode.

Constant-potential coulometry was carried out in the same way as in the previous paper [23], at a concentration of 1.98×10^{-5} M.

The ESR spectra measurements were carried out on a JES-3BX spectrometer (Japan). Generation of oxidation and reduction products of the substances was carried out directly in the measuring cell at a potential corresponding to the limiting diffusion current. Electronic absorption spectra were recorded on a Unicam SP-800 spectrophotometer.

Calculations

Calculations of energy values were carried out by the simple Hückel method of molecular orbitals (HMO) [24]. The parameters used are the same as in the paper [25]. The energy characteristics obtained are summarized in Table 2.

Table 2

HMO-energy characteristics and experimental data of substances studied[a]

Substance	k_1 [β]	k_{-1} [β]	$E_{1/2}$ anod. [mV]	$E_{1/2}$ cathod. [mV]
I	0.504	−0.129	970	−640
II	0.827	−0.048	—	−195
III	0.504	−0.185	680	−750
IV	0.504	−0.185	980	−805
V	0.827	−0.071	—	−320
VI	0.504	−0.134	965	−620
VII	0.504	−0.115	950	−640
VIII	0.368	−0.170	—	−610
IX	0.504[b]	−0.115[b]	990	−670
X	0.504	−0.131	1075	−950
XI	0.374	−0.382	—	−275
XII	0.667	−0.258	—	−385

a) k_1 (k_{-1}) — the energy of the highest occupied (the lowest free) π-molecular orbital; $E_{1/2}$ anod. ($E_{1/2}$ cathod.) — half-wave potentials of anodic (cathodic) waves.

b) The results were obtained by the perturbation method.

Table 3

Survey of the polarographic data of the substance studied[a]

Substance	Oxidation					Reduction				
	$c \times 10^5$ [mole l^{-1}]	$E_{1/2}$ [mV]	$i_d/c \times 10^{-4}$ [μA l mole^{-1}]		q [%/deg]	$c \times 10^5$ [mole l^{-1}]	$E_{1/2}$ [mV]	$i_d/c \times 10^{-4}$ [μA l mole^{-1}]	n	q [%/deg]
I	0.50	960	8.4			0.50	−645	9.0		
	1.98	980	8.0	1.50	2.0	1.98	−650	9.2	1.30	2.0
	7.69	965	8.4			7.69	−645	9.6		
	14.8	970	8.2			14.8	−635	8.6		
	30.5	975	8.5			30.5	−640	8.1		
	43.7	980	8.4			43.7	−640	7.9		
II	b					1.98	—	—		
						3.92	−195	0.6		
						7.69	−205	3.0		
						14.8	−195	5.0		
						30.5	−190	6.6		
						43.7	−185	13.9		
III	0.50	670^d	8.0			1.96	−740	1.5		
	1.96	680	7.8	1.27	f	3.84	−760	1.3	g	6.3
	3.84	685	5.3			7.41	−755	1.0		
	7.41	690	3.8			15.2	−750	1.1		
	e					21.8	−745	1.0		
IV	0.50	970	15.4			0.50	−820	18.8		
	1.98	975	14.7	2.90	1.3	1.98	−810	10.2	g	h
	7.69	980	14.4			7.69	−795	5.1		
	14.8	995	15.7			14.8	−790	3.6		
	43.7	990	14.6			e				
V	b					≃2.0−40	≃ −320		—	f
VI	0.50	970	7.6			0.50	−620	7.8		
	1.98	980	8.1	1.60	2.0	1.98	−625	8.0	1.8	h
	7.69	965	8.3			7.69	−625	8.0		
	16.5	965	8.7			16.5	−615	7.8		
	38.7	960	8.5			e				

Table 3 (Continued)

	c	$E_{1/2}$	i_d	n	q	c	$E_{1/2}$	i_d	n	q
VII	≃0.5—40	≃950	i	—	1.7	≃0.5—40	≃−640	i	—	2.8
VIII	j					≃2.0—40	≃−610		—	—
IX	≃5.0—40	≃990		—	—	≃5.0—40	≃−670		—	—
X	0.50	1050	8.0			0.50	−930	22.8		
	1.98	1070	7.8	g	1.3	1.98	−950	19.8	g	2.4
	7.69	1085	6.9			7.69	−955	12.5		
	16.5	1075	6.5			e				
	38.7	1080	6.6							
XI	b					0.50	−275	7.8		
						1.96	−280	7.9		
						3.84	−275	7.9	1.05	f
						7.41	−275	8.2		
						15.2	−270	8.0		
XII	b					0.50	−395	8.0		
						1.96	−385	8.2		
						3.84	−385	7.9	1.01	h
						7.41	−380	8.3		
						15.2	−380	8.2		

a) c — concentration, $E_{1/2}$ — half-wave potential of the first wave, i_d — limiting diffusion current, n — number of electrons exchanged in the electrode reaction, q — the temperature quotient of the limiting diffusion current.

b) Substance does not yield an anodic wave.

c) Up to the concentration of 1.5×10^{-4} M another wave appeared with an average $E_{1/2}$ value of 950 mV. The ratio i_d/c is not constant and for this reason n and q were not determined.

d) Another wave of $E_{1/2}$ of about 1090 mV appeared on the anodic curve.

e) The electrode is passivated by the electrolytic products at higher concentrations.

f) Limiting diffusion current decreases with increasing temperature.

g) Very unstable product is formed by electrolysis; the number of electrons exchanged cannot be determined.

h) Limiting diffusion current increases irregularly with increasing temperature.

i) The wave-height proportional to the concentration.

j) Several waves appear, depending on the degree of purity of the substance; it cannot be decided which wave corresponds to the substance studied.

Results and Discussion

Results of measurement are given in Table 3. For an illustration, the anodic and cathodic polarographic curves of malachite green (*I*) are given in Fig. 1; polarographic curves of other substances are given in another paper [26].
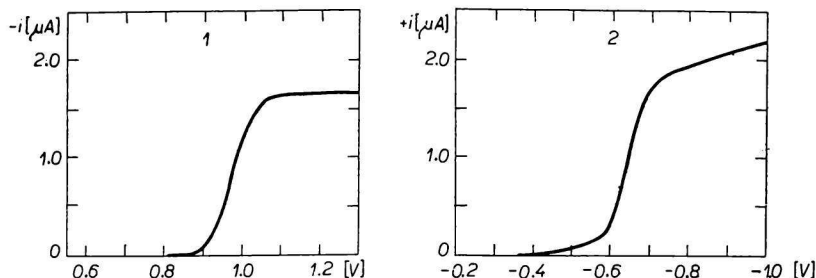

Fig. 1. Polarographic curves of malachite green (*I*) at the RPE; $c = 1.98 \times 10^{-5}$ M.
1. oxidation; *2.* reduction.

Logarithmic analysis was carried out for well developed polarographic waves. In the cases of linear logarithmic plot the following reciprocal slopes were obtained: *I* oxidation 0.063 V; *IV* oxidation 0.068 V, reduction 0.051 V; *VI* oxidation 0.073 V, reduction 0.064 V; *XII* reduction 0.066 V.

These are the values for one of the parameters characterizing the degree of reversibility of the electrode process. The degree of reversibility was further evaluated by a study of the electrolytic products at a potential corresponding to the limiting diffusion current. The electrolysis was not, however, performed with the substances which were not perfectly pure, *i.e.* *V*, *VII*, *VIII*, and *IX*. It was found that the electrode oxidation of *I*, *IV*, and *VI* is reversible (the electrolytic products yielded cathodic waves with half--wave potentials differing by less than ± 10 mV from those of the anodic waves of the original substances). The electrolytic products had a limited stability. Cathodic waves shifted to the anodic region with time and absorption spectra of the original substances appeared again. As an example, the absorption spectra of malachite green oxidation product are given in Fig. 2 with their dependence on time. The electrolytic product apparently undergoes a consecutive reaction with formation of the original substance. The electrolysis of *III* yielded a polarographically inactive product. The product of *X* did not yield a reversible cathodic wave either, but only a flat-shaped anodic curve so that the degree of reversibility of these substances could not be found.

The electroreduction of *I* is reversible. The electrolytic product was also unstable and its anodic wave shifted with time to the cathodic region and the initial absorption spectrum reappeared. The electrolytic currents of *III*, *IV*, and *X* reached a constant value (about 10% of the initial current) after a certain time of electrolysis. The electrolytic products yielded the original cathodic waves and their absorption spectra were also practically identical with those of the original substances. Apparently, immediate consecutive reactions proceed in which the original substance is reformed. The electrolytic product of *VI* yielded neither a corresponding anodic wave nor the wave of the original substance but only a flat anodic wave with a half-wave potential of about 700 mV. Polarographically inactive products were formed by the electrolysis of *XI* and *XII*.

The number of electrons exchanged during the electrode reactions was determined by constant-potential coulometry. It is evident from Table 3 that the values close to 1 were obtained, with the exception of the oxidation of IV and the reduction of VI. Also the limiting diffusion current values at a concentration of 1.98×10^{-5} M conform with the literature values [27] for one-electron waves of tris(4-dimethylaminophenyl)amine which may be assumed to have the same value for the diffusion coefficient.
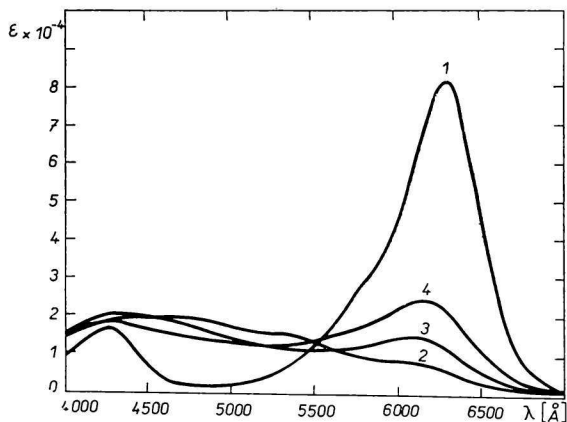

Fig. 2. Electron absorption spectra of malachite green (*I*).
1. initial substance; *2.* an oxidation product immediately measured; *3.* the oxidation product after 1 hour; *4.* the oxidation product after 24 hours.

It can, therefore, be assumed that most of the substances studied undergo one-electron reduction and oxidation under the given conditions; the products should be radicals, or radical-cations in the case of the oxidation of substances containing amino or dimethylamino groups. The existence of these radicals was proved by the measurement of ESR
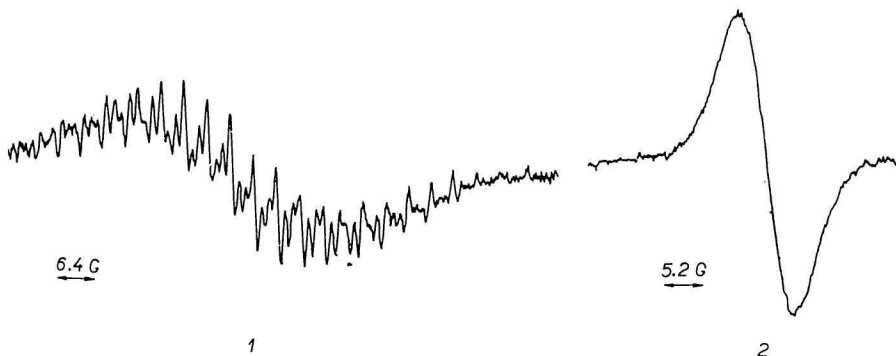

Fig. 3. Electron spin resonance spectra of malachite green (*I*); $c = 2 \times 10^{-3}$ M.
*1.* oxidation product; *2.* reduction product.

spectra (measurements were carried out only with perfectly pure substances). It was found that an ESR signal is yielded by the oxidized forms of *I*, *IV*, *VI*, and *X*, which contain dimethylamino groups and undergo oxidation under the given conditions. *III* yields no signal. The reduced forms of *I*, *II*, *III*, *IV*, *VI*, *X*, and *XI* yield an ESR signal but *XII* yields none. The ESR spectra obtained have practically no hyperfine splitting and so their analysis could not be done. In Fig. 3 there are given the ESR spectra of the oxidation and the reduction product of malachite green; the spectra of other substances are given in the paper [26].

During the oxidation of cations studied, the reaction
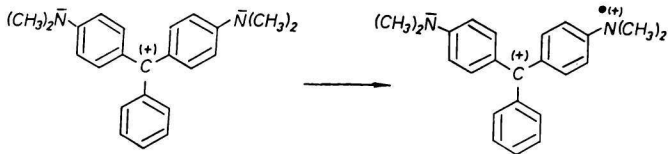
occurs.

Hanousek and *Matrka* [28] found that during the chemical oxidation of malachite green, the radical-cation apparently disproportionates
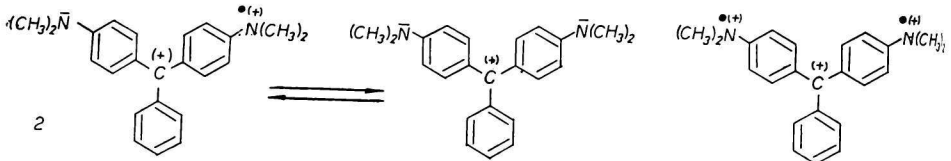
This fact could explain the higher numbers of electrons involved in the electrode process (the cation formed by disproportionation participates in the electrode reaction again and the gradual reappearance of the absorption spectrum and the anodic curve of the initial substance. Another explanation could be the existence of a reaction of the radical-cation formed with acetonitrile under the formation of the initial substance.

The substance *III* behaves in a different way and forms a polarographically inactive product. It is possible that here the radical-cation formed immediately undergoes a consecutive reaction forming a polarographically inactive product *e.g.* by dimerization which occurs frequently with triarylmethyl radicals [29, 30] and which is presumed in polarographic studies by other authors [9, 15]. In the case of *X*, the initial one-electron process (which is indicated also by the value of the limiting diffusion current) is probably followed by a deeper disintegrating of the dye molecule and by the formation of further oxidizable products because of the higher number of electrons exchanged (about 4) determined coulometrically. Substance *IV* undergoes, in all probability, a two-electron oxidation as follows from the limiting diffusion current value and the number of electrons exchanged. The oxidation product is again unstable and the initial substance is formed.

In the reduction of the triarylmethyl cations studied, the reaction

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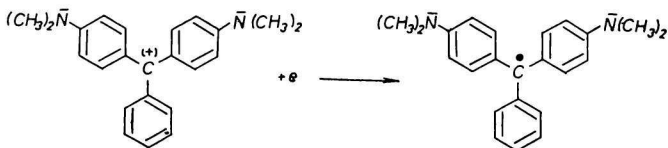
takes place. The radicals thus formed from *I*, *III*, *IV*, and *VI*, evidently disproportionate again: *I* disproportionates very slowly, the disproportionation of *III* and *IV* reaches an equilibrium after a certain time, and *VI* disproportionates practically completely already during the electrolysis so that the number of electrons exchanged is close to two and there are no voltammetric signs of the presence either of the radical or of the initial cation. The radicals of *XI* and *XII* apparently dimerize; this reaction of *XII* is probably very fast because the electrolytic product does not yield any ESR signal although, from the number of electrons exchanged and from the values of the limiting diffusion currents, it is evident that there is a one-electron reduction leading to a radical. An exception to this reaction mechanism is *X*, the limiting diffusion current of which suggests a two- -electron reduction; its product is, however, probably very unstable.

It has been shown [31, 32] that, in the case of a reversible one-electron process, when the potential determining step is the reaction

$$R + e \rightarrow R\dot{}$$

and the electron enters the lowest free molecular orbital, the cathodic half-wave potential is proportional to the difference between the total energy of the π-electrons of the reduced form formed and that of the initial substance. This difference equals the energy of the lowest free molecular orbital in the treatment of the system by means of the HMO method. Similarly, under the same assumptions for the electrode reaction in which the electron is removed from the highest occupied orbital, the anodic half-wave potential is proportional to the energy of the highest occupied molecular orbital [33]. In this way, the half-wave potentials of a number of organic compounds were correlated [34]. Although mostly these correlations are very close, only in a few cases all the conditions for their physical justification are fulfilled and therefore they must be regarded only as empirical correlations [34].
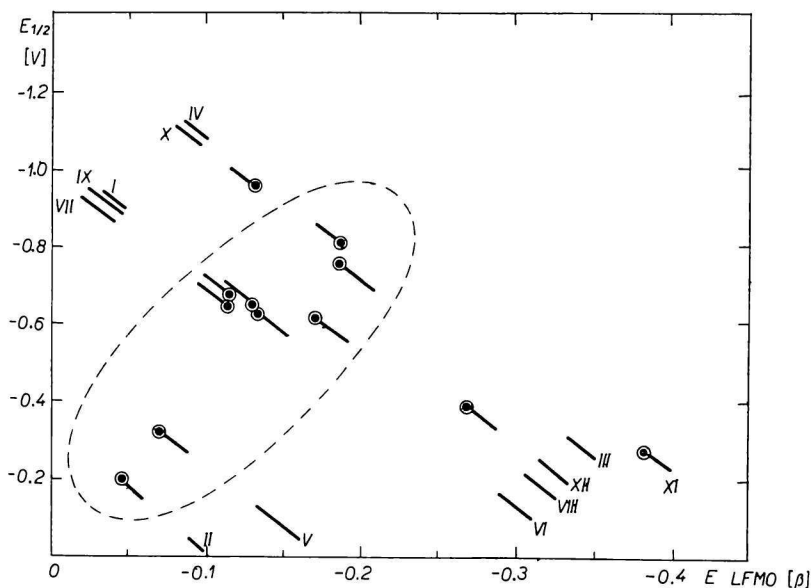

Fig. 4. The dependence of cathodic half-wave potentials on the energy of the lowest free molecular orbital (*cf.* the data in Table 2).

Because in the present work it also seems probable that a number of substances undergo one-electron reversible oxidations or reductions, these correlations have been attempted. The values of the anodic half-wave potentials were compared with the energies of the highest occupied molecular orbital (HOMO), and the cathodic half-wave potentials with the energies of the lowest free molecular orbital (LFMO). The correlated values are given in Table 2.

It is apparent from Table 2 that the values of the anodic half-wave potentials obtained differ little and that the HOMO energies have the same value for all substances undergoing the polarographic oxidation. Because all these substances contain the substituents $-NH_2$ and $-N(CH_3)_2$, it seems that the presence of further substituents does not practically influence the value of the half-wave potentials and not at all the HOMO. A rather dispersed field of points was obtained in the correlation of the cathodic half-wave potentials with LFMO energies (Fig. 4). It is interesting that substances *V*, *VII*, *VIII*, and *IX*, which were not perfectly purified and the values which we assumed to be only approximate, fulfil relatively well the correlation conditions; it could then be assumed that their reduction proceeds according to the one-electron mechanism. On the other hand, substances *XI* and *XII*, with which the one-electron reduction mechanism was proved, differ quite substantially; apparently the structure of these substances is so much different that they should not be included in the group of substances studied. The substance *X* deviates probably because of its two-electron reduction, too.

Generally, it can be said that, differing from the linear dependence obtained in the correlation of spectral data and the pseudobasicity of the triarylmethane dyes with their quantum chemical characteristics [25], their half-wave potentials correlate only very roughly with the energies of the HOMO and the LFMO. If we tried to draw a straight line through the experimental data in Fig. 4 we would find that its slope (approx. 3.50 eV/β) is higher than those which have been obtained in the published correlations of half-wave potentials (the slopes had values between 2.0 and 2.7 eV/β). The value obtained agrees, however, with the slopes of the relations of other experimental values (the excitation energies of the first absorption band of the electronic spectra and those of the charge-transfer band) with the corresponding theoretical values. In these cases, the slope varied between 2.3 and 3.7 eV/β [34].

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