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# EPR spectroscopy study of di-*o*-quinone bridged with $\pi$ -extended TTF: redox behavior and binding modes as a ligand

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The peculiarities of spin density distribution in the radical-anion forms of acceptor-donor-acceptor (A-D-A) system, consisting of two sterically hindered *o*-quinone moieties bridged with *p*-phenylene extended tetrathiafulvalene was studied. It was chemically reduced with alkali metals. The reduction proceeds through four one-electron stages. Radical-anion and radical-trianion species are paramagnetic, whereas dianion form was found to be EPR silent. Spin density distribution in the paramagnetic forms was studied. EPR and UV-vis spectra analysis and DFT calculations reveal that *p*-phenylene extended TTF fragment in the ligand in all studied redox forms acts as a conducting bridge providing electronic communication between two *o*-quinone moieties.

## Introduction

Sterically hindered *o*-quinones as ligands have been the subject of intense studies for nearly four decades. *o*-Quinones as a redox active ligands can interact in a cooperative fashion with the metal center to facilitate chemical transformations. Due to the appropriate energy values of their frontier orbitals, *o*-quinone ligands can be easily oxidized or reduced directly in the coordination sphere. Reversible bending of the crystal of rhodium semiquinonate complex on action of heat or light is one of the most interesting phenomena, which were discovered in study of semiquinonate complexes. This effect is based on the redox-isomerism mechanism.<sup>1,2</sup> An increasing attention to the quinone as acceptor chelating ligand origins from a conjunction of remarkable electronic properties and a versatile chemistry, allowing functionalization for a broad range of applications.<sup>3,4</sup> Rapid development of chemistry of tetrathiafulvalenes (TTF) happened in the same time period.<sup>5,6</sup> They display remarkable redox properties: a high  $\pi$ -donating ability and occurrence of three stable redox states. Investigation of systems combining donor and acceptor fragment in the single molecule has generated much interest, as these species could find use in applications such as information storage and processing, quantum computing, and spintronics.<sup>7</sup> Fused *o*-quinone-TTF-*o*-quinone triads were synthesized in order to

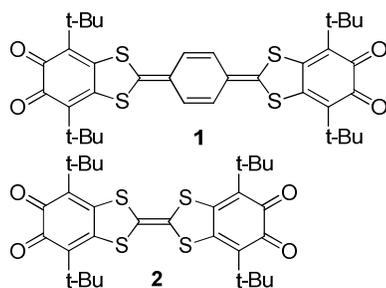
combine the features of donor and acceptor in the same molecule. Moreover, an occurrence of two chelating sites at the termini of the molecule gives additional opportunities to access different linear and spatially ordered structures using the triad as a bridge.

## Results and discussion

Recently we reported an acceptor-donor-acceptor (A-D-A) system containing two *o*-quinones bridged with  $\pi$ -extended tetrathiafulvalene moiety **1**.<sup>8</sup> (see Scheme 1) Similar to its homologue A-D-A triad **2**<sup>9</sup> the system **1** has a planar and rigid structure. Previous studies have shown that **2** can be chemically reduced by alkali metals to form dicatecholate finally. Reduction proceeds in four one-electron steps; mono- and trianion species found to be paramagnetic.<sup>10</sup> The nature of the EPR silence of dianion species was explained by the antiferromagnetic interaction of unpaired electrons via tetrathiafulvalene bridge. The first attempts to study complexes containing **2** as a ligand yielded promising results. It has been found that some complexes of **2** with lanthanides exhibit a single molecular magnet (SMM) behavior.<sup>11</sup> In the binuclear Yb(III) complex triad **2** acts as an antenna: the irradiation of the intraligand charge transfer (ILCT) band causes sensitization of Yb(III) NIR luminescence.<sup>12</sup> Unfortunately, the EPR

spectroscopy is not particularly effective in the study of the nature of the spin density distribution in the ligand **2**, since the structure of the ligand does not contain magnetic nuclei interacting with the unpaired electron spin.

$\pi$ -Extended ligand **1** has been synthesized in order to i) decrease the energy gap between the frontier orbitals; ii) get visualization of electronic distribution on the molecule by means of the EPR spectroscopy study. Hyperfine constant (HFS) values due to splitting on four hydrogen atoms on the central *p*-phenylene ring should depend on the situation at the coordination sites of the ligand. It should be noted, that EPR spectroscopy is very informative technique for the study of paramagnetic semiquinone complexes. *o*-Semiquinone is paramagnetic ligand which fully consistent with the concept of the spin label.<sup>13,14,15</sup> spin density distribution on the ligand atoms substantially depends on the nature of the configuration of the coordination sphere at the metal ion. Moreover, the dynamic processes in the coordination sphere of the metal ion are also reflected on the shape of the EPR spectrum.<sup>15,16,17</sup> At the same time, the orbital, containing unpaired electron, usually by more than 99% is semiquinone-based. It means that, bearing information on the coordination sphere, this orbital only weakly affects on it. So, being a spin label, the semiquinone reports information, but not creates it.



Scheme 1. An acceptor-donor-acceptor systems built from annelated *o*-quinone and TTF units.

Obviously, *o*-quinone moiety in the triad **1** is regarded as a chelating site for binding of metal ions. We tried to investigate the coordination and redox abilities of new ligand using chemical reduction with alkali metals as a model. Since an isolation of individual species and growth of their crystals suitable for the structural analysis is a non-trivial task due to the preparative difficulties we tried to combine EPR and electronic spectroscopies to interpret the processes taking place upon chemical reduction of **1**. It has been established previously that the quinone **1** can't be isolated in a solid form due to its instability, but it can exist in the diluted solutions for a quite long time.<sup>8</sup> On the other hand, its direduced diprotonated form **1**<sup>2-</sup>H<sub>2</sub> is quite stable and could be easily oxidized in solution yielding **1**. So, for experimental purposes di-*o*-quinone **1** was generated directly in the solution before mixing with reducing agent.

Behavior of the triad **1** upon the chemical reduction appears to be the similar to the compound **2**. Chemical reduction of the di-*o*-quinone **1** proceeds through four one-electron stages (Scheme 2). We have performed interaction of **1** with Li, Na and K. The process of chemical reduction is similar for all studied metals. It should be noted that all alkali metal derivatives of **1** were studied only in the solution. Their isolation in the crystal phase were failed due to disproportionation processes which take place upon concentration.<sup>10</sup>

Similar to almost all *o*-quinones, **1** readily reacts with alkali metals in solution to give corresponding semiquinonates; this process is accompanied with a color change of solution from green to violet. Since reduced derivatives of the quinone **1** are extremely air-sensitive, all reactions with metals were conducted in evacuated ampoules equipped with a side thin tube, which could be placed into the EPR spectrometer cavity (see supporting materials). A piece of alkali metal (in excess amount) was added into the ampoule. The reaction proceeds under vigorous agitation and requires a considerable time to complete. So, it is easy to monitor intermediate stages by EPR spectroscopy. The initial EPR spectrum, which was captured in short time after the mixing of the reagents, corresponds to the radical-anion **1**<sup>•-</sup>. The corresponding spectrum of **1**<sup>•-</sup>-K consisted of triplet of triplets arising from two pairs of equivalent protons of *p*-phenylene ring (Fig. 1, top). The EPR spectra of Li (Fig. 2, top) and Na species indicate additional coupling constants with the metal ion. Although Li, Na and K possess a nuclear spin 3/2 for most abundant isotope, hyperfine splitting on the metal nuclei was observed only for Li and Na derivatives. The lack of splitting on the metal ion is frequently observed in the case of the potassium semiquinonates,<sup>10,18</sup> since the small magnetogyric ratio of the potassium <sup>39</sup>K nucleus ( $\gamma_K = 1.25006 \times 10^{-7} \text{ rad T}^{-1} \text{ s}^{-1}$ ) ordinarily renders  $a_K$  too small to be resolved.<sup>19,20</sup> The values of splitting constants on metal ion in Li and Na species are typical of their semiquinonates.<sup>10,21,22</sup> Two triplet splittings corresponding to \* and # protons of the central ring (see scheme 2) as well as the splitting on the metal ion in the EPR spectrum signs of different redox states of the dioxolene moieties at the termini of **1**<sup>•-</sup>. In other words, one side of the molecule is regarded as semiquinone with coordinated alkali metal ion, whereas another one remains a quinone. The shape of the spectrum does not undergo significant changes within the temperature range of 220-320K. The lack of the temperature dependence of this spectrum can be considered as the signature of the absence of the dynamic process of inter(intra)molecular cation exchange observed in the EPR time scale.

Further reduction is accompanied by the gradual decrease in intensity of the signal corresponding to the radical anion **1**<sup>•-</sup>. After full disappearance of the first signal, we observed the appearance of a new spectrum. It was ascribed to the trianion radical species **1**<sup>3•-</sup>. The spectrum of the **1**<sup>3•-</sup>-K (Fig. 1, bottom) is quite similar to the spectrum from **1**<sup>•-</sup>-K in character. It also consisted of triplet of triplets arising from the hyperfine coupling of the electronic spin with the two non-equivalent pairs of protons of the central six-membered ring. The HFS constant values are slightly different from those observed in the **1**<sup>•-</sup>, besides of the spectrum is shifted to a higher *g*-factor values. (See Table 1) In order to assign the constants in the EPR spectra of **1**<sup>•-</sup> and **1**<sup>3•-</sup> DFT calculations at the UB3LYP/6-311++G(d,p) level of theory have been performed. According to these calculations (see supporting information) the larger splitting values were attributed to the hydrogens which localized at the *meta* positions with respect to semiquinone ring (H\* at the Scheme 2). The calculated spin density distribution plots for paramagnetic products **1**<sup>•-</sup> and **1**<sup>3•-</sup> are shown in the supplementary materials.

Upon further reduction **1**<sup>3•-</sup> converts into the dicatecholate tetraanion species **1**<sup>4-</sup>; this is accompanied by full disappearing of the EPR signal. It should be mentioned that all reduced species **1**<sup>•-</sup> - **1**<sup>4-</sup> are quite air sensitive, but they may be stored in solution in absence of oxygen for a long time.

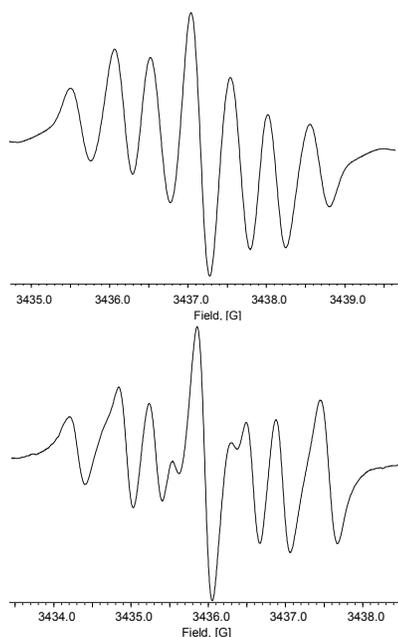


Figure 1 EPR spectrum of  $1^{\bullet}\text{K}$  (top) and  $1^{3\bullet}\text{K}_3$  (bottom) in THF, 298 K

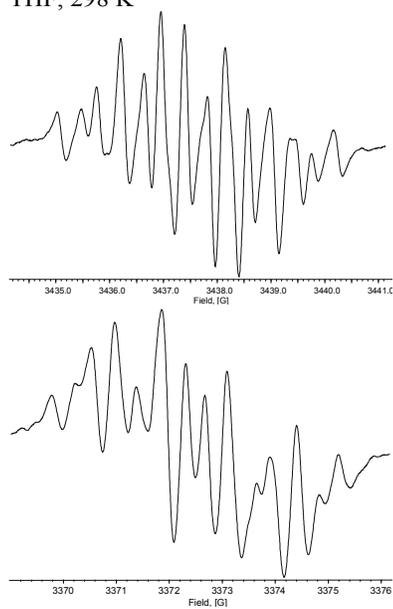


Figure 2. EPR spectrum of  $1^{\bullet}\text{Li}$  (top) and  $1^{3\bullet}\text{Li}_3$  (bottom) in THF, 298 K

Table 1. Hyperfine splitting constants and  $g$ -factors of observed paramagnetic species

Complex	$a_{\text{H}^*}$ , G	$a_{\text{H}^\#}$ , G	$a_{\text{M}}$ , G	$g$ factor
$1^{\bullet}\text{Li}$	1.18	0.77	0.43	2.00450
$1^{\bullet}\text{Na}$	1.02	0.59	0.33	2.00437
$1^{\bullet}\text{K}$	0.96	0.55	-	2.00421
$1^{3\bullet}\text{Li}_3$	1.31	0.76	0.41	2.00524
$1^{3\bullet}\text{Na}_3$	1.08	0.65	0.32	2.00504
$1^{3\bullet}\text{K}_3$	1.00	0.61	-	2.00482

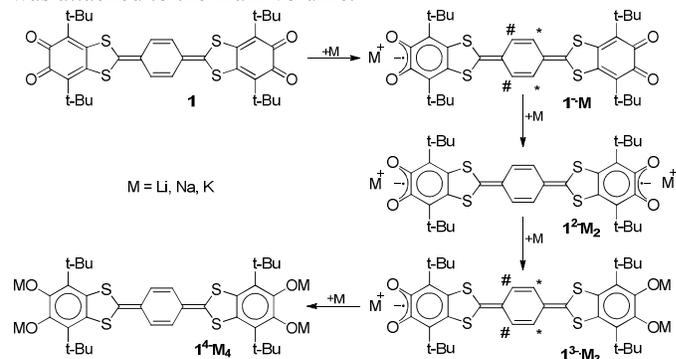
Actually, EPR study of chemical reduction of **1** led us to suggest that the reaction proceeds through four one-electron steps, as it shown on Scheme 2. Two species  $1^{\bullet}$  and  $1^{3\bullet}$  are paramagnetic, whereas direduced form  $1^{2\bullet}$  was found to be EPR silent.

The broken-symmetry (BS) state, which is a singlet biradical<sup>23</sup> according to the spin density distribution, corresponds to the global minimum of compound  $1^{2\bullet}\text{K}_2$ . The frontier orbitals plots for  $1^{2\bullet}\text{K}_2$  are shown in the supporting materials. The triplet state for K derivative is 1027  $\text{cm}^{-1}$  disfavored as compared to the singlet. Previously we have reported that  $1^{2\bullet}\text{H}_2$  also exists in singlet biradical state. The value of antiferromagnetic coupling in it was estimated as 1090  $\text{cm}^{-1}$ .<sup>8</sup>

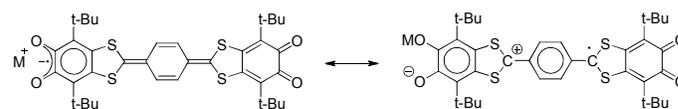
Di-catecholate product  $1^4\text{K}_4$  is strongly colored species, which is unusual for the catecholates. Obviously, the color is due to the central p-quinonoid chromophore fragment.

Since the di-quinone **1** itself and its reduced derivatives are colored species the reduction process can be easily monitored with UV-visible spectroscopy.

**Electronic spectra.** In order to obtain reference spectra corresponding to the intermediate redox forms of **1** (Fig. 3), a joint EPR and UV/Vis spectroscopic study was undertaken. It became possible due to the fact that the same concentration of **1** in the solution occurs to be in the best sensitivity window for both methods. The reaction was conducted in the ampoule equipped both with EPR tube and spectroscopic cuvette which was attached to the main volume.



Scheme 2. Reduction of triad **1** with alkali metals.



Scheme 3. Intramolecular electron transfer in  $1^{\bullet}\text{M}$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ).

It has been reported previously that there is an equilibrium between intermediate redox forms of di-o-quinones<sup>10</sup> are in a solution and a concentrating results in their disproportionation. The isolation of these forms as individual compounds becomes a non-trivial task. Due to the fact that reduction proceeds through alternate paramagnetic and EPR silent stages, the registration of the electronic spectra at the simultaneous control of the intensity and a shape of the EPR signal allows to get reference spectra for the intermediate redox forms.

Previously we have shown that two intense bands in the UV-vis spectrum of **1** at 735 nm and 450 nm correspond to the intramolecular charge transfer (HOMO-LUMO) and HOMO-LUMO+2 transitions respectively. According to the DFT data the transition at 450 nm is mostly localized on the central part

of the molecule, such bands are characteristic of the *p*-quinonoid compounds. An absorption in this region is absent in case of mono-, di- and tri-reduced species, but arises again in the tetra-reduced dicatocatechol derivative.

A pattern of intense line with a shoulder in range of 350-500 nm is characteristic of *p*-phenylene extended TTFs. Notably, saddle-like distorted systems exhibit absorption at a high energy border of this region,<sup>24</sup> whereas species with planar skeleton display absorption near 500 nm.<sup>25</sup> The dicatocatechol form **1**<sup>4+</sup> shows in THF an intense line at 570 nm ( $\epsilon = 95000 \text{ M}^{-1}\text{cm}^{-1}$ ) with a shoulder at 530 nm ( $\epsilon = 43000 \text{ M}^{-1}\text{cm}^{-1}$ ).

The electronic spectra of mono-, di- and tri-reduced species are similar and show one intense broad peak in the UV-vis region. TD DFT calculations at the B3LYP/6-311++G(d,p) level performed for **1**<sup>2-</sup>**H**<sub>2</sub> reveal for this species a theoretical spectrum which is in a perfect consistence with an experimental one.<sup>8</sup> The position and the shape of the peak in the UV-vis spectrum does not substantially depends on the nature of the cation at the dioxolene coordination site. Taking into account these data this absorption was assigned to SOMO – LUMO transition and its maximum is shifted to longer wavelengths as the oxidation state of the ligand increases. From the other hand, the position of this absorption band does not substantially depend on the nature of the metal cation, this is an additional confirmation of ligand-based origin of this transition.

The absence of absorption band in range of 300-500 nm in spectra of intermediate redox forms of **1** indicates that the structure of the central part of the  $\pi$ -extended TTF is different from *p*-quinonoid. Previously we have reported that according with both structural and DFT calculations data for **1**<sup>2-</sup>**H**<sub>2</sub><sup>8</sup> the contribution of the zwitter-ionic form to the structure of the molecule is quite significant: the geometric features of *p*-phenylene extended TTF fragment in it are more characteristic of dication form, rather than neutral extended TTF. Moreover, the geometrical parameters of the optimized structure are in a good accordance with a structural data for the molecule. The DFT calculations performed for **1**<sup>1-</sup>**K**, **1**<sup>2-</sup>**K**<sub>2</sub>, and **1**<sup>3-</sup>**K**<sub>3</sub> show that the double bonds in the *p*-quinonoid pattern are slightly longer than would be expected for pure double bond (see Fig. 9-11 in supporting information). One possible explanation is a contribution of the zwitter-ionic form to the structure. (Scheme 3 illustrates a charge transfer by the example of the monoreduced derivative). The driving force for the charge transfer is formation of the aromatic system on the central six-membered ring. This transfer becomes possible in the case where at least one of dioxolene termini of the molecule exist in the monoreduced (semiquinone) state.

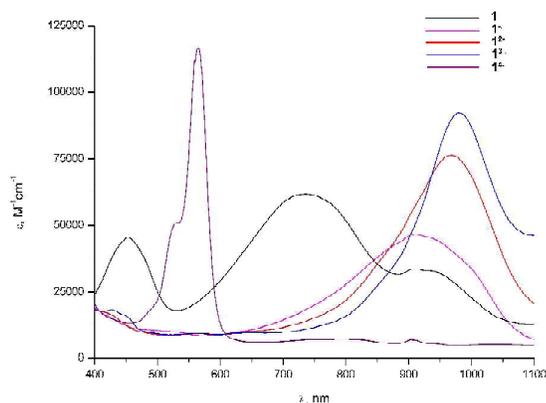


Figure 3. UV-vis spectra of **1** and its reduced species **1**<sup>•</sup>**K** - **1**<sup>4+</sup>**K**<sub>4</sub> in THF, 298 K

Notably, dicatocatechol species is stable to further chemical reduction in the presence of the excess of alkali metal. UV-vis study shown that the intensity of light absorption at the maximum of the peak remains constant for two days in the reaction mixture. It means that *p*-quinonoid fragment of the ligand is stable towards chemical reduction with alkali metal, but exhibits a redox activity and could be reduced electrochemically, as it has been described in our previous work.<sup>8</sup>

It has been found also that reduced species **1**<sup>•</sup> - **1**<sup>4+</sup> could be easily chemically oxidized with quinone **1** to give corresponding adducts in the reverse sequence. This feature can be used for preparation of species containing the ligand **1** in a required oxidation state. Measured amount of **1** is reduced with potassium to give dicatocatechol species and then **1**<sup>4+</sup>**K**<sub>4</sub> is added to stoichiometric amount of diquinone **1**.<sup>10</sup> This reaction is likely to be of practical value as a preparative since the alkali metal ion at semiquinone could be easily replaced with a numerous transition or non-transition metal.<sup>26,27</sup>

### The role of the extended tetrathiafulvalene insertion

The question is whether the acceptor and donor moieties which are being fused together in the same molecule are essentially the quinone and tetrathiafulvalene respectively? DFT calculations performed for **1** at the B3LYP/6-311++G(d,p) level reveal that HOMO is mostly localized on the extended TTF unit, whereas LUMO is mainly distributed between two *o*-quinone moieties.<sup>8</sup> The properties of *o*-quinone as an oxidant are determined by its ability to gain electrons. The similar assertion could be formulated concerning to the TTF. Features of the chemical reduction and spectroscopic study confirm that from this viewpoint donor and acceptor units in **1** could be referred as a TTF and *o*-quinone respectively.

Table 2. Calculated energies and orbital density distribution on *o*-quinone and *p*-phenylene extended TTF parts in **1** for selected orbitals.

Orbital	E, eV	Orbital density distribution, %		
		Q	Ex-TTF	Q
LUMO+1	-3.066	37.1	21.8	37.1
LUMO	-3.462	38.9	18.2	38.9
HOMO	-5.148	11.5	77.0	11.5
HOMO-1	-6.284	35.6	17.8	35.6

DFT calculations conducted at B3LYP/6-311++G(d,p) level for mono-, di- and tri-reduced derivatives of **1** (**1**<sup>•</sup>, **1**<sup>2-</sup> and **1**<sup>3-</sup>) reveal that SOMO in these compounds do not display preferred distribution either on TTF or quinone units. EPR study of mono- and tri-reduced species display a significant spin density values on the central *p*-phenylene ring of the extended TTF. Very similar situation is observed in the case of di-reduced species. Both calculated SOMOs for dipotassium derivative are delocalized across whole molecule. In fact, *p*-phenylene extended TTF insertion acts as a conducting bridge providing interaction between two quinone moieties at the termini of the molecule.

### Conclusions

The peculiarities of chemical reduction of A-D-A triad consisting of two sterically hindered o-quinones bridged by *p*-phenylene extended TTF with alkali metals has been studied. It has been established that reduction proceeds through four one-electron stages. It was found that monoanion and trianion species are paramagnetic, whereas direduced derivative is EPR silent. A redox behavior of the studied triad indicating four distinct reduction states suggesting the considerable electronic communication between two terminal o-quinone units by through-bond and/or through-space interactions. Such a system is of particular interest for understanding electron-transfer processes for the design of molecular wires. Depending on the redox state, the A-D-A triad can bind the metal ion by only the one coordination site or act as a bridging ligand.

## Experimental

All reactants were of reagent grade. Solvents were purified by standard methods.<sup>28</sup>

UV-vis spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer.

The syntheses of reduced species as well as all spectroscopic investigations were carried out in the absence of oxygen and moisture. X-band cw EPR spectra were recorded on a Bruker EMX spectrometer. The standard for *g*-factor was DPPH (*g* = 2.0037).

The 2,2'-Benzene-1,4-diylbis(6-hydroxy-4,7-di-tert-butyl-1,3-benzodithiol-2-ylidene-5-olate) (**1**<sup>2-</sup>)H<sub>2</sub> has been prepared according to previously reported procedure.<sup>8</sup>

**General procedure for preparation of the solutions.** The solution of 16.7 mg (2.5\*10<sup>-5</sup> mol) 2,2'-Benzene-1,4-diylbis(6-hydroxy-4,7-di-tert-butyl-1,3-benzodithiol-2-ylidene-5-olate) in 100 ml of THF was stirred with 2 g MnO<sub>2</sub> for 10 min. Then green solution of 2,2'-cyclohexa-2,5-diene-1,4-diylidenebis(4,7-di-tert-butyl-1,3-benzodithiole-5,6-dione) (**1**) was filtered and 20 ml of filtrate was placed into the ampoule, containing a volume with 50 mg piece of potassium. This ampoule was additionally equipped with attached EPR tube and cuvette for UV-vis experiment. The solution was poured into the volume with metal, agitated and then returned into EPR tube and cuvette. After registration of the EPR and electronic spectra, the procedure was repeated again.

The reactions with sodium and lithium were conducted in the same manner.

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## Notes and references

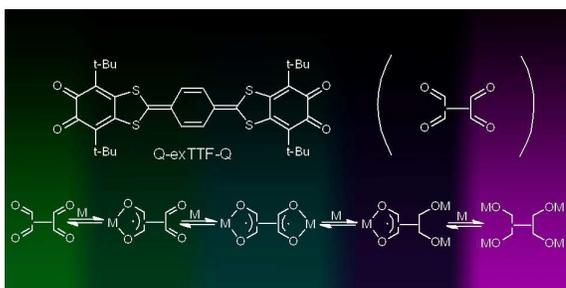
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