


## RESEARCH ARTICLE

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Cite this: DOI: 10.1039/c8qo00187a

# Synthesis and characterization of a doubly spin-labelled electrochemically driven molecular shuttle†

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Accepted 7th March 2018

DOI: 10.1039/c8qo00187a

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The EPR properties of novel nitroxide-spin-labelled rotaxanes containing a tetrathiafulvalene (TTF) unit and a cyclobis(paraquat-*p*-phenylene) ring are described. The rotaxanes were spin labelled both at the thread and the wheel. Single-electron oxidation of the TTF unit resulted in a significant through-space magnetic interaction between different radical units. In some cases, rotaxanation is proved to have dramatic effects on such magnetic interactions.

## Introduction

Mechanically interlocked molecules (MIMs), such as rotaxanes, are characterized by an interesting dynamic behaviour due to the lack of strong chemical bonds between their molecular parts that involve changes in the relative position of the components (co-conformation) in response to external stimuli (switching), such as variations in pH, absorption of light and removal or addition of electrons.<sup>1</sup> Switching at a molecular level offers huge opportunities for the development of a series of applications ranging from information and communication technology (ICT),<sup>2</sup> catalysis,<sup>3</sup> to medicine.<sup>4</sup>

The use of molecular movements to execute tasks, however, is still a difficult research challenge, and more studies are required to increase the range of viable functionalities that may be accessed through the control of motion at the nanoscale. In this context, a stimulating possibility is the incorporation of persistent radicals into the molecular components of MIMs. Tagging MIMs with specific radical labels makes possible not only to carry out EPR-based co-conformational investigations on interlocked systems,<sup>5</sup> but also to switch on/off magnetic interactions by chemically driven reversible mechanical effects.

As a notable example of the latter aspect, Tanaka and co-workers described a fourfold rotaxane where switchable spin-spin communication between mechanically interlocked paramagnetic Cu<sup>2+</sup> complexes could be induced by a change in

their relative distance and spatial arrangements in response to a change in pH.<sup>6</sup> More recently, we described the first example of a [2]rotaxane incorporating stable 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) radical units into both the ring (dibenzo [24]crown-8) and the dumbbell component in which a pH-dependent shuttling motion was exploited to reversibly modify the distance between the two spin centers and thus, enabling or preventing a through-space electron exchange between them.<sup>7</sup> Very recently, the synthesis of a rotaxane where the nitroxide unit is a part of the macrocycle ring which can be moved along a molecular thread has also been described.<sup>8</sup> In all the above examples radical centers are “transported” by changing the pH of the solution. However, redox-responsive bistable [2] rotaxanes are also of considerable interest because the redox switching process is usually rapid and precise and can be controlled within solid-state devices, as well as on surfaces.<sup>9</sup>

Thus, we decided to prepare a new spin-labelled rotaxane where the spin-exchange interaction could be switched on/off by redox-driven reversible mechanical effects. For this purpose, we prepared an interlocked structure based on a modified “Stoddart–Heath type” bistable [2]rotaxane which comprises a  $\pi$ -electron-deficient cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) ring and a tetrathiafulvalene (TTF) recognition unit in the thread (see Fig. 1).<sup>10</sup>

In TTF-CBPQT<sup>4+</sup>-based rotaxanes, shuttling of the ring along the thread from the TTF station to another recognition site (generally 1,5-dioxynaphthalene unit, DNP) is achieved by single-electron oxidation of the TTF moiety (at +0.43 V vs. Ag/AgCl in ACN) to the TTF<sup>•+</sup> radical cation (see Fig. 1).<sup>10</sup> The proposed rotaxanes were doubly spin labelled both at the ring and the dumbbell by introducing nitroxide units which represent the most well-known class of spin labels in supramolecular assemblies (see Fig. 2).<sup>11</sup>

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† Electronic supplementary information (ESI) available: General information on synthetic procedures and characterization, synthetic details and additional NMR and EPR data. See DOI: 10.1039/c8qo00187a

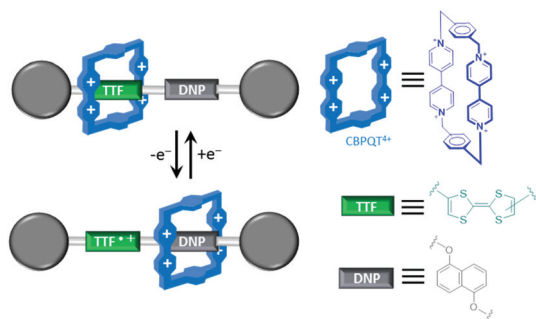


Fig. 1 Schematic representation of a Stoddart-Heath type bistable [2]rotaxane.

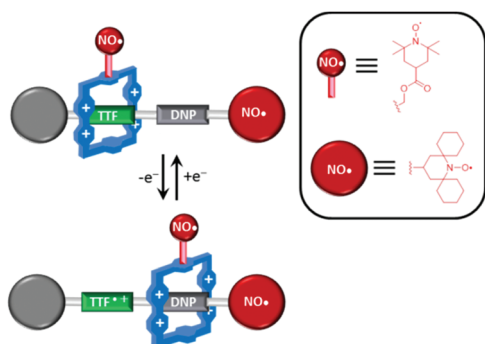


Fig. 2 Schematic representation of the switching process in the investigated [2]rotaxane.

It will be shown that the proposed molecular machines are capable of switching on/off magnetic interactions by electrochemically driven reversible mechanical effects.

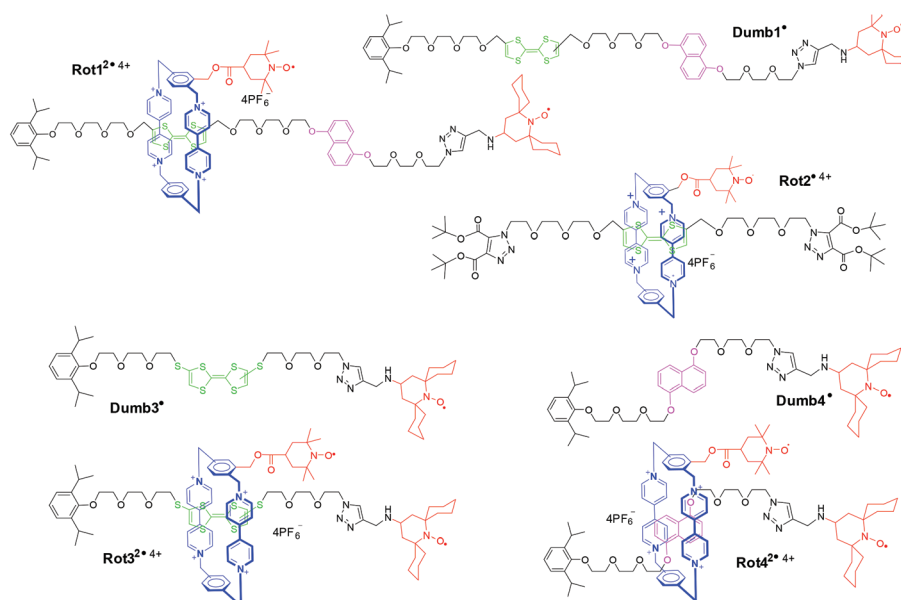
## Results and discussion

### Molecular design and synthesis

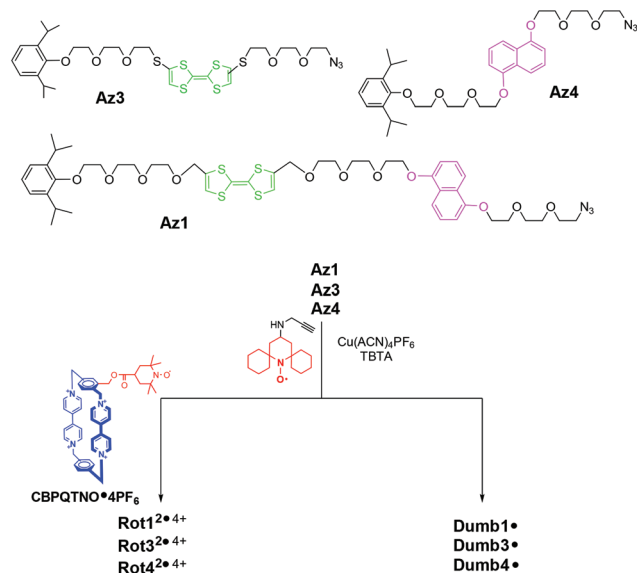
The structure of the proposed paramagnetic redox-active rotaxane (**Rot1**<sup>2•4+</sup>) is shown in Scheme 1. The electron-rich recognition units are represented by the redox active tetrathiafulvalene (TTF) group and the 1,5-dioxynaphthalene (DNP) component. The two nitroxide spin labels are located both at the wheel and the axle. One nitroxide unit is located at one end of the thread and also behaves as a stopper unit. Because the TEMPO unit is not large enough to be used as the end-cap group in CBPQT-based rotaxanes,<sup>12</sup> we introduced a sterically hindered nitroxide containing spirocyclohexyl substituents at 2 and 6 positions of the piperidine-*N*-oxyl ring as a terminal radical unit.<sup>13</sup>

The other spin label is positioned on the CBPQT host. We have already described the synthetic procedure for the introduction of one or two TEMPO paramagnetic side-arms into the aromatic ring of the CBPQT<sup>4+</sup> moiety.<sup>14</sup> In the same work, we have also shown that the complexation ability of the spin-labelled CBPQT<sup>4+</sup> macrocycle toward electron-rich molecules, such as 1,5-dimethoxynaphthalene, is maintained in the presence of the spin label.

For complete characterization of the system, single station [2]rotaxanes containing TTF (**Rot2**<sup>2•4+</sup> and **Rot3**<sup>2•4+</sup>) or DNP (**Rot4**<sup>2•4+</sup>) were also prepared (see Scheme 1). The general strategy adopted for the preparation of the bis-labelled rotaxanes **Rot3**<sup>2•4+</sup> and **Rot4**<sup>2•4+</sup> followed the approach reported by Stoddart *et al.*<sup>15</sup> based on the formation of CBPQT<sup>4+</sup> donor-acceptor pseudorotaxanes with TTF or DNP-containing axial derivatives. The axial derivatives included an azide group at one edge and the 2,6-diisopropyl phenyl diamagnetic stopper unit at the other end. Once the pseudorotaxane was formed, it



Scheme 1 Structures of the investigated [2]rotaxanes and the corresponding dumbbells.



**Scheme 2** General scheme for the preparation of rotaxanes **Rot1,3,4<sup>2•4+</sup>** and the corresponding radical dumbbells.

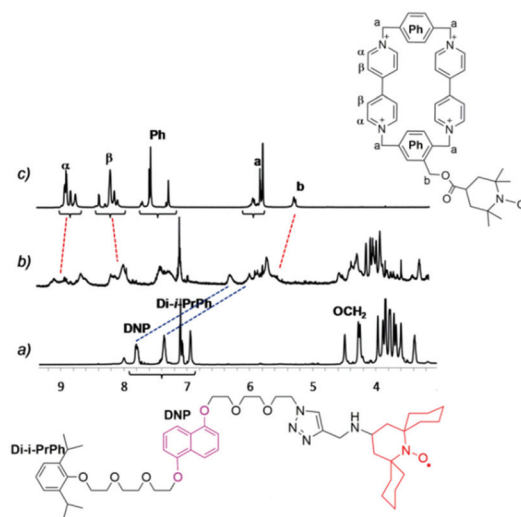
was reacted in the presence of Cu(I) (click conditions) with an alkyne spirocyclic nitroxide radical (see Scheme 2).

In a typical experiment, rotaxation was achieved when the spin labelled host (CBPQTNO•) was incubated with the axle in DMF at  $-10^{\circ}\text{C}$  for ten minutes.

The bulky stopper alkyne spirocyclic nitroxide was then added to ensure the interlocking of the thread as a result of Huisgen cycloaddition catalyzed by [Cu(MeCN)<sub>4</sub>]PF<sub>6</sub> in the presence of (benzyltriazolylmethyl)amine (TBTA) as a stabilizer. The desired rotaxanes were obtained in a non-optimized 22–26% yield, in some cases along with a small amount of the corresponding dumbbell (see synthetic procedures in the ESI†).

### Characterization of molecular structures

ESI-MS analysis and NMR and EPR spectroscopy techniques were used to provide evidence for the formation of the interlocked structures. Although NMR studies are hampered by the presence of paramagnetic centers which are responsible for severe signal broadening, we found significant differences upon comparing the <sup>1</sup>H NMR data of the rotaxane and the corresponding free dumbbell. This allowed us to provide a good assignment of the interlocked structure despite the bi-radical nature of the rotaxanes. In principle, to render the paramagnetic compound more suitable for NMR analysis it could quantitatively be converted into the corresponding hydroxylamine derivative by adding a stoichiometric amount of phenylhydrazine.<sup>16</sup> In the present case, however, phenylhydrazine is not a good additive as it gives rise to several signals in the aromatic region that overlap with those due to the TTF and DNP units making the analysis even more difficult.



**Fig. 3** Partial <sup>1</sup>H NMR spectra (600 MHz, CD<sub>3</sub>CN, 298 K) of (a) dumbbell **Dumb4•**; (b) rotaxane **Rot4<sup>2•4+</sup>**; and (c) **CBPQTNO•** host. Red dashed lines evidence the broadening and splitting of the macrocyclic signals and the deshielding of protons **b** caused by the complexation with the guest **Dumb4•**. Blue dashed lines evidence the shielding of some DNP protons. α, β = bipyridinium α and β protons; Ph = host *p*-phenylene protons; a = host benzyl protons, b = CH<sub>2</sub>O linker; DNP = naphthalene aromatic protons.

The <sup>1</sup>H NMR spectrum of the single station rotaxane **Rot4<sup>2•4+</sup>** (shown in Fig. 3 along with those of the dumbbell **Dumb4•** and the **CBPQTNO•** ring) clarifies the presence of the macrocycle on the DNP recognition unit.

An upfield shift was observed for the peaks corresponding to the DNP protons when passing from the free dumbbell to the corresponding rotaxane, indicating the presence of the macrocycle around the electron donor naphthalene station. In addition, the paramagnetic host exhibited a marked change in signals displaying a substantial broadening as a consequence of both the decrease in the tumbling rate in the rotaxane structure and the presence of the additional stopper paramagnetic unit.

Similar arguments also apply to the NMR analysis of the single station rotaxane **Rot3<sup>2•4+</sup>**: a significant upfield shift of TTF proton signals (*ca.* 6.8 ppm in the dumbbell, below 6.3 ppm‡ in the rotaxane in CD<sub>3</sub>COCD<sub>3</sub>) gives indication of the position of the **CBPQTNO•** ring over the electron-rich recognition unit (see the ESI†).

Fig. 4 compares the EPR spectra recorded at 328 K in ACN of the bis-labelled rotaxanes **Rot3<sup>2•4+</sup>** and **Rot4<sup>2•4+</sup>** with those of the thread (**Dumb3•**) and the **CBPQTNO•** wheel interlocked by a diamagnetic dumbbell (**Rot2<sup>4+</sup>**).

Because of a larger contribution to the line width from the unresolved coupling with the cyclohexyl hydrogen atoms, the EPR line shape of both dumbbells (the spectrum of **Dumb3•** is

‡ The signals of TTF overlap with the benzyl proton peaks of the paramagnetic host.

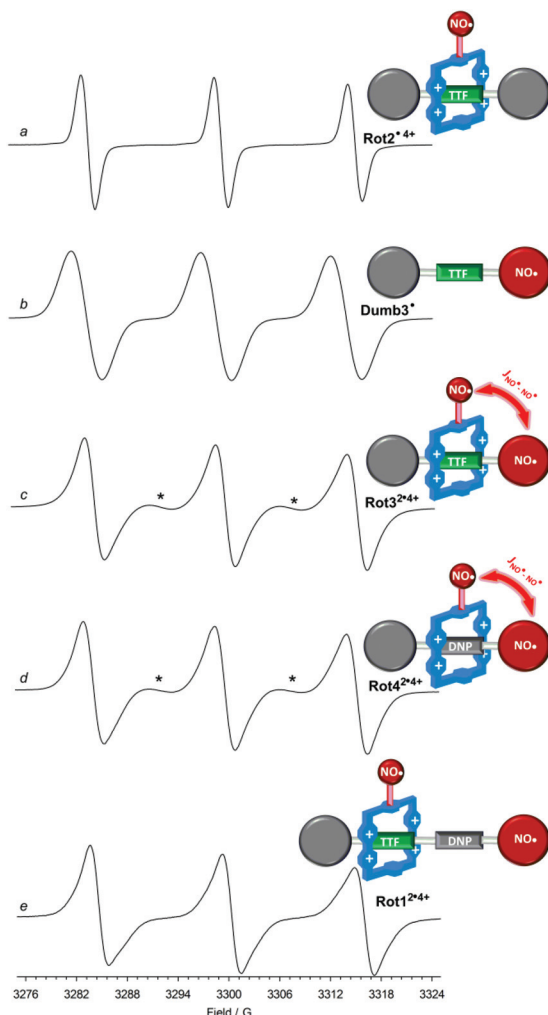


Fig. 4 EPR spectra of the investigated rotaxanes and **Dumb3<sup>\*</sup>** recorded in ACN at 328 K. Stars symbols specify the exchange lines.

shown in Fig. 4b) is quite different from that of the **CBPQTNO<sup>•</sup>** wheel (see Fig. 4a) where the paramagnetic label is a tetramethyl piperidinyll derivative. Also the nitrogen hyperfine splitting constant ( $a_N$ ) measured for the two dumbbells ( $a_N = 15.40$  G) is significantly different from that measured in the spin-labelled wheel ( $a_N = 15.82$  G). It is important to remark that these spectral features allow us to distinguish the EPR signals derived from the two kinds of nitroxide labels.

The EPR spectra of bis-labelled rotaxanes **Rot3<sup>2+4+</sup>** and **Rot4<sup>2+4+</sup>** (Fig. 4c and d, respectively) are characterized by the presence of the five-line pattern which clearly demonstrates a strong spin exchange between the two nitroxide units ( $J_{NO^{\bullet}-NO^{\bullet}}$ ). The broadening of the second and fourth lines (labelled with star) suggests that the exchange coupling,  $J$ , is modulated by conformational dynamics. In principle,  $J$ -coupling can be operative by the through-bond or through-space mechanism or both. Because of the mechanical linkage between the two nitroxide units, the through-bond mechanism can be obviously excluded and the interaction must be related exclusively to through-space interaction. To discard inter-

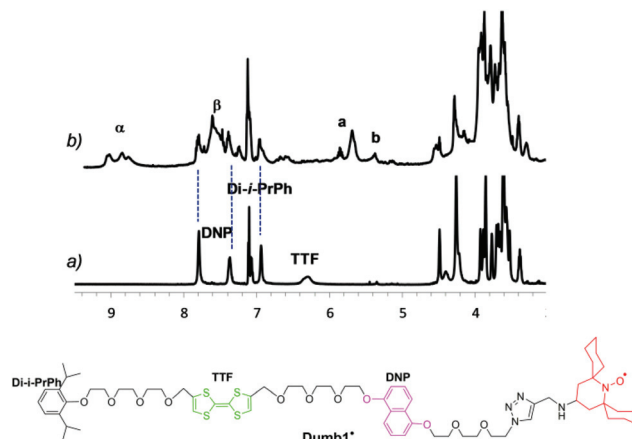


Fig. 5 Partial  $^1\text{H}$  NMR spectra (600 MHz,  $\text{CD}_3\text{CN}$ , 298 K) of (a) dumbbell **Dumb1<sup>\*</sup>** and (b) rotaxane **Rot1<sup>2+4+</sup>**. Blue dashed lines evidence the signals of DNP protons ( $\alpha$ ,  $\beta$  = host bipyridinium  $\alpha$  and  $\beta$  protons;  $a$  = host benzyl protons,  $b$  = host  $\text{CH}_2\text{O}$  linker).

molecular  $J$ -coupling between the nitroxide labels of two different rotaxane molecules, we recorded the EPR spectrum of a mixture containing both the dumbbell and the spin-labelled cyclophane under the same conditions. As expected, this spectrum is characterized by  $J = 0$ .

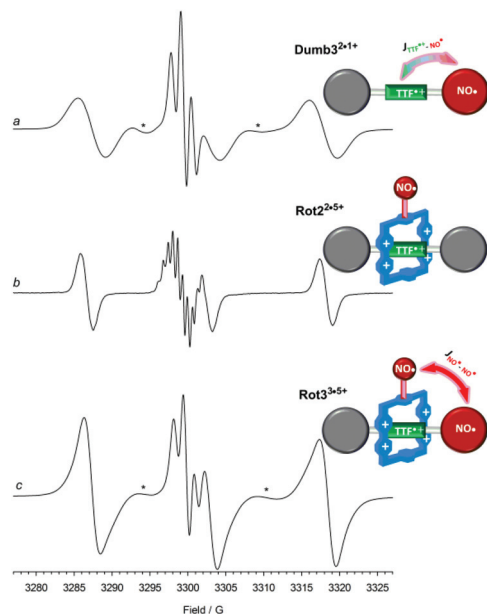
The  $^1\text{H}$  NMR spectrum of the two station rotaxane **Rot1<sup>2+4+</sup>** in  $\text{CD}_3\text{CN}$  is shown in Fig. 5b. Generally a marked shielding of TTF protons indicates that the host encircles the electron donor heterocycle station.<sup>12</sup> Indeed we detected a shift in the TTF signal in the spectrum of **Rot1<sup>2+4+</sup>** (ca. 6.5 ppm in the dumbbell; around 6 ppm in the rotaxane) that falls in a crowded spectral region due to overlapping with the benzyl proton peaks of the paramagnetic host (signals labelled with **a** in trace b, Fig. 5). The spectrum of the two station rotaxane **Rot1<sup>2+4+</sup>** does not show signal displacements of the DNP protons (blue dashed lines in trace a) which is instead observed in the NMR spectrum of the single station DNP rotaxane **Rot4<sup>2+4+</sup>**. Both these observations suggest that the paramagnetic host resides preferentially on the TTF recognition unit.

In contrast to what is observed in the single station rotaxanes **Rot3<sup>2+4+</sup>** and **Rot4<sup>2+4+</sup>**, the EPR spectrum of the two station rotaxane **Rot1<sup>2+4+</sup>** (see Fig. 4e) shows a three-line pattern. This clearly demonstrates the absence of a spin exchange between two different nitroxide fragments. Because of the different spectroscopic parameters in the EPR spectra of the two nitroxides (line width and  $a_N$ ), the external lines are not symmetric. They can be well reproduced by assuming the superposition (in a 1 : 1 ratio) of the signals derived from the two nitroxide labels.

### Switching process

As mentioned in the Introduction, the switching process in TTF-CBPQT<sup>4+</sup>-based rotaxanes is performed by the oxidation of TTF to the corresponding TTF<sup>•+</sup> radical cation. This process destabilizes the mechanically interlocked molecule and hence lowers the effective barrier to shuttling of the CBPQT<sup>4+</sup> ring





**Fig. 6** EPR spectra recorded in ACN at 328 K of (a) **Dumb3**<sup>2+1+</sup>, (b) **Rot2**<sup>2+4+</sup> and (c) **Rot3**<sup>2+4+</sup> after the addition of 1 equiv. of Fe(ClO<sub>4</sub>)<sub>3</sub>. Stars symbols specify the exchange lines.

onto the DNP recognition unit. Thus, we decided to investigate the behaviour of dumbbells and rotaxanes containing a redox-active TTF unit by EPR after its one-electron oxidation with Fe(ClO<sub>4</sub>)<sub>3</sub>. The EPR spectrum of the dumbbell **Dumb3**<sup>•</sup> in ACN at 328 K after addition of 1 equivalent of Fe(ClO<sub>4</sub>)<sub>3</sub> is shown in Fig. 6a. New lines due to the biradical **Dumb3**<sup>2+1+</sup>, together with those of the starting nitroxide and TTF<sup>•+</sup> monoradical ( $a_{2H} = 1.30$  G),§ were clearly detected.

The position of these new lines is consistent with a radical showing an electron spin exchange between the nitroxide terminal unit and the oxidised TTF unit ( $J_{NO-TTF^{•+}}$ ). The limit of very rapid exchange has not yet been achieved, as indicated by the different line widths of the exchanging lines. The different widths are a consequence of the diverse *g*-factors of the TTF<sup>•+</sup> radical cation and nitroxide exchanging species. Because of the large number of  $\sigma$  bonds in the linker between the two radical units, their principal exchange mechanism must have a through-space character.

The EPR spectrum of the single station rotaxane **Rot3**<sup>2+4+</sup> in ACN at 328 K after the addition of 1 equivalent of Fe(ClO<sub>4</sub>)<sub>3</sub> is shown in Fig. 6c. The EPR spectra of the oxidised rotaxane **Rot3**<sup>3+5+</sup> is characterized by the presence of exchange lines together with those of the starting nitroxides and TTF<sup>•+</sup> monoradical. The exchange lines show the same line width and resonate at magnetic field values symmetric with respect to nitroxide monoradical lines. These two spectral features suggest that the exchange lines originate from a strong spin exchange

between the two nitroxide units ( $J_{NO-NO}$ ). No evidence of the spin exchange between the TTF<sup>•+</sup> and nitroxide radical units was observed.

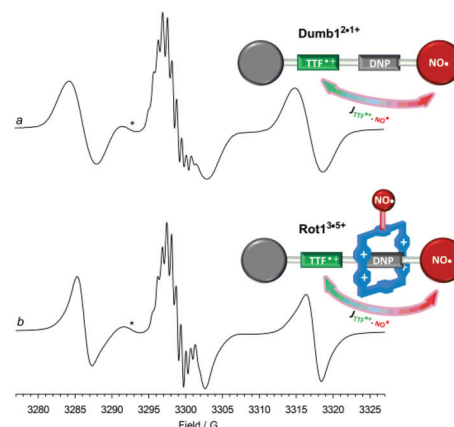
This last observation led to two conclusions: (i) the CBPQT<sup>4+</sup> ring is forced to remain in proximity to the TTF<sup>•+</sup> radical cation as no alternative binding site of the dumbbell is available for the ring to encircle; and (ii) the absence of the spin exchange can be explained by the ring acting as an 'attenuator', preventing the exchange interaction between the TTF<sup>•+</sup> and both nitroxide labels.

The absence of the spin exchange between the terminal nitroxide unit (stopper) and TTF<sup>•+</sup> when encircled by the CBPQT wheel is not surprising, as it has already been observed in an analogous rotaxane containing a diamagnetic CBPQT wheel.<sup>17</sup>

The absence of the spin exchange between the nitroxidic pendant and TTF<sup>•+</sup> when this is encircled by the **CBPQTNO**<sup>•</sup> wheel was confirmed by recording the EPR spectrum of the single station rotaxane **Rot2**<sup>•4+</sup> in ACN at 328 K after the addition of 1 equivalent of Fe(ClO<sub>4</sub>)<sub>3</sub>. Actually, the EPR spectrum of **Rot2**<sup>2+5+</sup>, shown in Fig. 6b, is simply due to the superposition of the signals derived from the non-exchanging nitroxide spin label (a 1 : 1 : 1 triplet with a line separation of  $a_N = 15.82$  G) and the TTF<sup>•+</sup> radical cation (a multiplet, with  $a_{2H} = 1.23$  G and  $a_{4H} = 0.63$  G).¶ No indication of spin-exchange lines was visible in this EPR spectrum.

Having fully characterized the model single station dumbbell, we proceeded to investigate the behaviour of the two station derivatives (dumbbell and rotaxane) after addition of Fe(ClO<sub>4</sub>)<sub>3</sub>. The EPR spectrum of **Dumb1**<sup>•</sup> in ACN at 328 K after the addition of 1 equivalent of Fe(ClO<sub>4</sub>)<sub>3</sub> is shown in Fig. 7a.

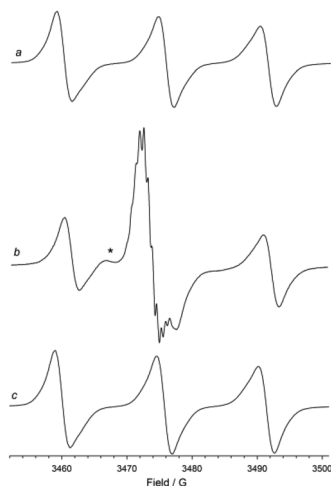
The low field exchange line (labelled with star) was clearly visible in the spectrum of **Dumb1**<sup>2+1+</sup>, while that resonating at a



**Fig. 7** EPR spectra recorded in ACN at 328 K of (a) **Dumb1**<sup>•</sup> and (b) **Rot1**<sup>2+4+</sup> after the addition of 1 equiv. of Fe(ClO<sub>4</sub>)<sub>3</sub>. Stars symbols specify the exchange lines.

§ In the presence of 1 equivalent of Fe(ClO<sub>4</sub>)<sub>3</sub> the nitroxide unit starts to oxidize to the corresponding EPR-silent oxammonium species leading to the formation of a TTF<sup>•+</sup> monoradical.

¶ The coupling of the unpaired electron with four equivalent protons in **Rot2**<sup>2+5+</sup> is due to the methylene groups of the two chains bound to the TTF unit.



**Fig. 8** EPR spectra at 328 K in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/ACN of the radical species electrogenerated from Rot1<sup>2+4+</sup> at the following potentials: (a)  $E_{\text{appl}} = 0$  V; (b)  $E_{\text{appl}} = +0.5$  V; and (c)  $E_{\text{appl}} = -0.5$  V. The potentials were applied on the same sample in the sequence a–b–c. Star symbol specifies the exchange line.

high field was more difficult to detect because of severe broadening. The position of this line is consistent with the occurrence of the electron spin exchange between the nitroxide terminal unit and the oxidised TTF unit ( $J_{\text{NO}^{\cdot-}\text{TTF}^{\cdot+}}$ ), irrespective of the large distance between the two radical centers. We attributed this unexpected behaviour to the high flexibility of the glycol chains which allows the terminal paramagnetic nitroxide unit to interact with TTF<sup>•+</sup> presumably by a charge–charge contact. The intensity of the exchange lines is however very low and the EPR spectrum is dominated by the lines due to the starting nitroxide and TTF<sup>•+</sup> monoradical. This suggests that only a reduced number of conformations have the two radical units sufficiently close to undergo an exchange coupling.

This exchange line is also present in the EPR spectrum of the two station rotaxane Rot1<sup>2+4+</sup> after oxidation with 1 equivalent of Fe(ClO<sub>4</sub>)<sub>3</sub> (see Fig. 7b). As observed in dumbbell Dumb1<sup>2+1+</sup>, this exchange line resonates at a magnetic field which corresponds to the symmetric centre between the resonance field of the TTF radical cation and that of the stopper nitroxide unit. The position of this line is thus consistent with the occurrence of the electron spin exchange between the nitroxide terminal unit and oxidised TTF unit. This interaction is possible because the ring moves to the DNP unit after the formation of TTF<sup>•+</sup> leaving it to interact with the nitroxidic stopper unit.

To verify the reversibility of the switching process, TTF<sup>•+</sup> was electrogenerated in deoxygenated acetonitrile inside the EPR cavity (see the ESI†). When the spectrum is recorded in a positive setting close to the first one electron oxidation process of the TTF unit (ca. +0.5 V), it shows the presence of the exchange line together with those of the starting nitroxides

and TTF<sup>•+</sup> monoradical (Fig. 8b). After the formation of TTF<sup>•+</sup> was complete the sign of the current can be reversed with the reduction of the TTF radical cation back to neutral TTF and obtain the starting EPR spectrum (Fig. 8c). The complete electrochemical switching cycle of the EPR pattern was repeated several times without an appreciable loss of signal, highlighting the reversibility of the process.

## Conclusions

The reported spin-labelled rotaxanes provide novel examples of polyradicals where the magnetic interactions can be tuned by removal or addition of electrons in a reversible manner. Through-space spin–spin interactions strongly depend on rotaxation, the movement of the wheel and the flexibility of the thread chain. Hence, spin labelled interlocked molecules represent an intriguing class of complex structures which may have interesting applications in magnetic materials. Experiments in this direction are underway in our laboratory.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the University of Bologna.

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