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Tetrathiafulvalene Radical Cation Dimerization in a Bistable Tripodal [4]Rotaxane

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Abstract: The template-directed synthesis of a bistable tripodal [4]rotaxane, which has cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) as the π-electron-deficient rings, and tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene units as the pairs of π-electron-rich recognition sites located on all three legs of the tripodal dumbbell, is described. The chemical and electrochemical oxidation of the [4]rotaxane and its tripodal dumbbell have allowed us to unravel an unprecedented $TTF^{\bullet+}$ radical cation dimerization. In fact, two types of TTF dimers, namely, the radical cation dimer $[TTF^{\bullet+}]_2$ and the mixed-valence one $[(TTF)_2]^{\bullet+}$, have been observed at room temperature for the tripodal dumbbell, whereas, in the case of the [4]rotaxane, only the radical cation dimer $[TTF^{\bullet+}]_2$ is formed. This anomaly can be explained if it is accepted that most of the neutral TTF units in the [4]rotaxane are encircled by $CBPQT^{4+}$ rings, which renders the formation of the mixed-valence dimer $[(TTF)_2]^{\bullet+}$ highly unfavorable.

Keywords: bistability · click chemistry · dimerization · rotaxanes · template synthesis

Introduction

The past few years have witnessed[1] a surge in the use of the Cu^{I}-catalyzed Huisgen[2] 1,3-dipolar cycloadditions[3] between alkynes and azides in the synthesis of mechanically interlocked compounds.[4] The convergent "click chemistry" approach[5] is an attractive one because it affords catenanes and [*n*]rotaxanes in high yields.[2] The power of this synthetic approach lies in the fact that we can now prepare higher order [*n*]rotaxanes,[4c,d] and "unstable" [2]rotaxanes[4a] that were previously unattainable. Moreover, the introduction of 1,2,3-triazole rings into the dumbbell-shaped component of bistable [2]rotaxanes,[6] does not alter the kinetics or thermodynamics of the switching process.[4g] This fact is a crucial one because mechanically interlocked compounds of this type are destined to be incorporated into the next generation of molecular machines.[7,8] Herein, we report the template-directed synthesis[9] of a bistable, tripodal [4]rotaxane, **1**·12 PF_6, which incorporates cyclobis(paraquat-*p*-phenylene)[10] ($CBPQT^{4+}$) as the π-electron-deficient rings, and tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) units located on all three legs of the tripodal dumbbell **2** as the pairs of π-electron-rich recognition sites.[6]

These two compounds were prepared with the aim of investigating the effect of bringing three bistable [2]rotaxanes and their three dumbbell components into close contact with each other. These covalently linked entities can be looked upon as models at the molecular level of the supramolecular counterparts that exist in 1) Langmuir monolayers,[11] 2) self-assembled monolayers,[12] and 3) molecular-switch tunnel junctions[13] in memory devices, all composed of some kind of bistable [2]rotaxane or its dumbbell precursor. In the context of these condensed phases, the importance of the investigations reported herein is evident in so far as the chemical and electrochemical properties reveal evidence of emergent phenomena,[14] namely, the observation that in both $\mathbf{1}^{12+}$ and **2** the $TTF^{\bullet+}$ radical cation dimerizes.[15] Whereas, in the case of $\mathbf{1}^{12+}$, only the radical cation dimer $(TTF^{\bullet+})_2$ can be detected, in the case of **2**, both $(TTF^{\bullet+})_2$ and the mixed-valence dimer $[(TTF)_2]^{\bullet+}$ have been identified.

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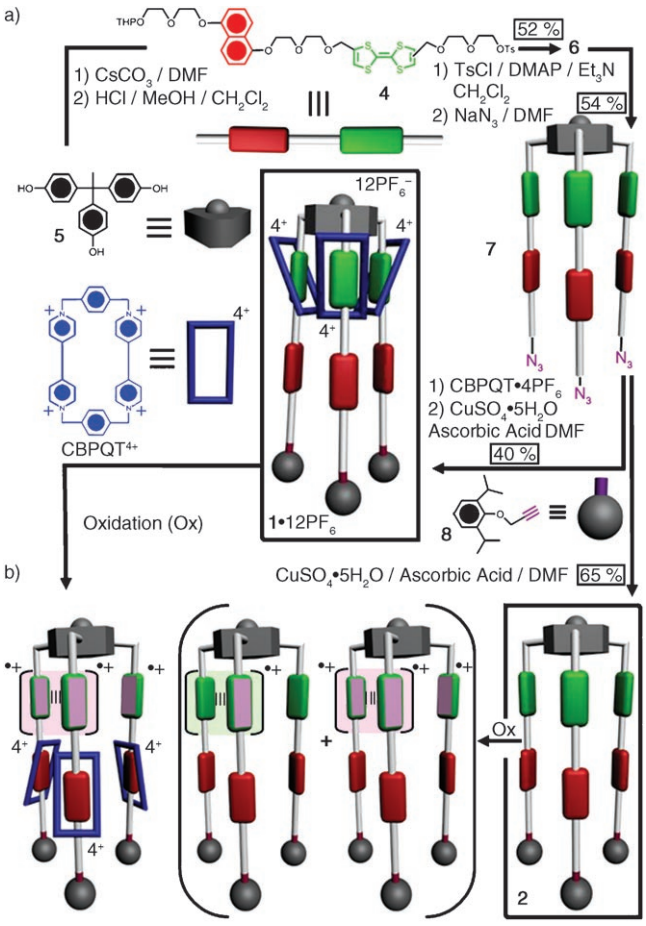
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains synthetic schemes; ^{1}H NMR spectra of **1**·12 PF_6; and spectroelectrochemistry, cyclic voltammetry, and titration data.

Results and Discussion

The tetrahydropyranyl (THP)-protected acyclic polyether **3** (see the Supporting Information), which incorporates both TTF and DNP units,[4g] allows the synthesis of rotaxanes with different stoppers to be performed by using click chemistry. Compound **3** was tosylated (tosylchloride (TsCl)/4-dimethylaminopyridine (DMAP)/Et_3N/CH_2Cl_2) to give **4** in a yield of 85% (see the Supporting Information). Alkylation (Cs_2CO_3/DMF) of 1,1,1-tris(4-hydroxyphenyl)ethane (**5**) with **4**, followed by deprotection (HCl/MeOH/CH_2Cl_2) afforded the tripodal triol **6** in a yield of 52% (Scheme 1a; for further information see the Supporting Information). Tosylation of **6**, followed by reaction of the tritosylate with NaN_3 in DMF at 80°C for one day gave the triazide **7** (54%). When **7** was mixed with CBPQT·4PF_6 (3.1 equiv) in DMF, an intense green color was generated immediately, indicating the formation of [**7**⊂3CBPQT]·12PF_6. This [4]pseudorotaxane was stirred for two days in the presence of



Scheme 1. a) Template-directed synthesis of the bistable [4]rotaxane **1**·12PF_6 and the synthesis of its tripodal dumbbell precursor **2**. b) A schematic representation of the products resulting from oxidation (Ox = chemical and/or by SEC) of **1**·12PF_6 and **2** in argon-purged MeCN/CH_2Cl_2 (1:1) at 298 K. The different $TTF^{\bullet+}$ radical cation dimers are indicated by using different highlights, light pink for the radical cation dimer $(TTF^{\bullet+})_2$ and light green for the mixed-valence dimer $[(TTF)_2]^{\bullet+}$.

1) the propargyl ether **8** (3.3 equiv; see the Supporting Information) carrying a 2,6-diisopropylphenyl stopper and 2) a catalytic amount of $CuSO_4$·5H_2O with ascorbic acid as an in situ reductant. Chromatographic purification (SiO_2: 1% w/v NH_4PF_6/Me_2CO) of the crude product from the reaction mixture afforded **1**·12PF_6 as a green solid in a yield of 40%. Electrospray ionization mass spectroscopy (ESI-MS) revealed peaks at *m*/*z* 1951.7, 1427.7, 1113.2, 903.4, and 753.5, which correspond to the loss of three, four, five, six, and seven PF_6^- counterions, respectively. Following the same procedure in the absence of CBPQT·4PF_6, provided the model tripodal dumbbell **2** (65%) as a yellow oil.

The ^1H NMR spectrum (Figure S1a in the Supporting Information) of **1**·12PF_6 in CD_3CN recorded at RT is complicated by 1) the presence of multiple isomers stemming from the *cis*/*trans* isomerism of the TTF units and 2) the dynamic processes associated with the $CBPQT^{4+}$ ring.[10b] Heating the sample to 350 K yields a much simpler spectrum (Figure S1b in the Supporting Information) in which the characteristic signals of bistable [2]rotaxanes can be observed. COSY Experiments, conducted at both RT and high temperature, indicate the presence in solution of predominantly (>90%) a single translational isomer, namely, the one in which the $CBPQT^{4+}$ ring encircles the TTF unit.[6c] This conclusion is based on the absence of any high-field DNP resonances.

The mechanical switching of $\mathbf{1}^{12+}$ and the electrochemical response of **2** were studied by using cyclic voltammetry (CV), differential pulse voltammetry (DPV), and UV/Vis spectroelectrochemistry (SEC). Chemical oxidation was also used to monitor the electronic transitions in the near-IR (NIR) region.

In typical SEC measurements[6] of bistable [2]rotaxanes, the band centered around 840 nm in the ground state, which originates from the charge-transfer (CT) interaction between the TTF and $CBPQT^{4+}$ units,[10b,6b] starts bleaching as the voltage is raised and new absorption bands emerge at λ_{max} = 445 and 595 nm that correspond to the $TTF^{\bullet+}$ radical cation. This behavior is not evident in the case of **1**·12PF_6. When the voltage is raised, the band at 840 nm, instead of bleaching, undergoes a hypsochromic shift (λ_{max} = 820 nm; Figure 1). Moreover, four absorption bands, centered at λ_{max} = 595, 527, 445, and 405 nm, start to grow in their relative intensities. A similar kind of behavior is observed for **2** (Figure S2 in the Supporting Information), except that a new absorption band centered at λ_{max} = 790 nm started to emerge as the potential was raised, that is, a process is happening that is independent of the $CBPQT^{4+}$ rings.

The additional bands (λ_{max} = 820/790, 527, and 405 nm) are, in fact, characteristic[15e,f] of radical cation dimer $(TTF^{\bullet+})_2$ formation (Scheme 1b) in both **1**·12PF_6 and **2**.[16] Overall, the spectra reflect the presence of a mixture of the $TTF^{\bullet+}$ radical cation monomer (λ_{max} = 595 and 445 nm) and the $(TTF^{\bullet+})_2$ dimer in solution at room temperature.[17] This mixture is very stable in air and shows no appreciable spectral decay over a period of one day at RT. When the applied potential is increased above +0.80 V, the absorption bands

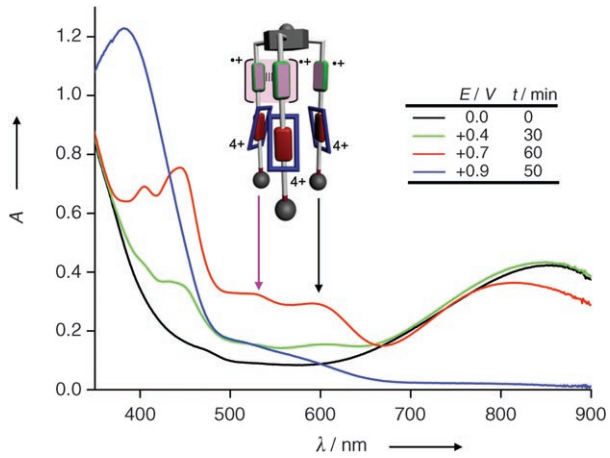


Figure 1. The changes in the UV/Vis spectrum during the SEC measurements conducted on **1**·12 PF_6. The applied potential changes from $E=0$ to 0.9 V. All data were recorded at 0.25 mV s^{-1} in argon-purged MeCN/CH_2Cl_2 (1:1) at 298 K. The concentrations of the sample and supporting electrolyte were 0.5 mM and 0.1 M, respectively. The UV/Vis spectra recorded at different applied potentials (E) are differentiated by the use of four different colors, namely, black, green, red, and blue.

of the $TTF^{\bullet+}$ radical cation on its own, and as the dimer, begin to bleach and a new peak ($\lambda_{max}=380$ nm) emerges (Figure 1 and Figure S2 in the Supporting Information) for the TTF^{2+} dication. In **1**·12 PF_6, a small absorption peak at 530 nm, associated with the CT band between DNP and the $CBPQT^{4+}$ ring, can also be detected. When the applied potential is switched off, the spectrum gradually changes back to its original form, in keeping with the fully reversible nature of the electrochemical reaction.

The chemical oxidation of **2** with $Fe(ClO_4)_3$ led to the observation (Figure 2) of a new broad absorption band ($\lambda_{max}=$ 1870 nm) in the NIR region.[18] This band is characteristic of another type of dimer,[15e] that is, the mixed-valence dimer $[(TTF)_2]^{\bullet+}$, which is also stable over a long period of time at RT, between the $TTF^{\bullet+}$ radical cation and a neutral TTF unit (Scheme 1). When **1**·12 PF_6 was titrated with $Fe(ClO_4)_3$ (Figure S3 in the Supporting Information) only the absorption bands of the $TTF^{\bullet+}$ radical cation monomer and dimer $(TTF^{\bullet+})_2$ were observed. This observation can be attributed to the fact that most of the TTF units are encircled by $CBPQT^{4+}$ rings in $\mathbf{1}^{12+}$. Only a small fraction of TTF units in $\mathbf{1}^{12+}$ are "free"[19] and so the chances of forming the mixed-valence dimer $[(TTF)_2]^{\bullet+}$ are low.[20] This situation is consistent with the results obtained by NMR spectroscopy, which indicates that most of the TTF units are encircled by $CBPQT^{4+}$ rings.

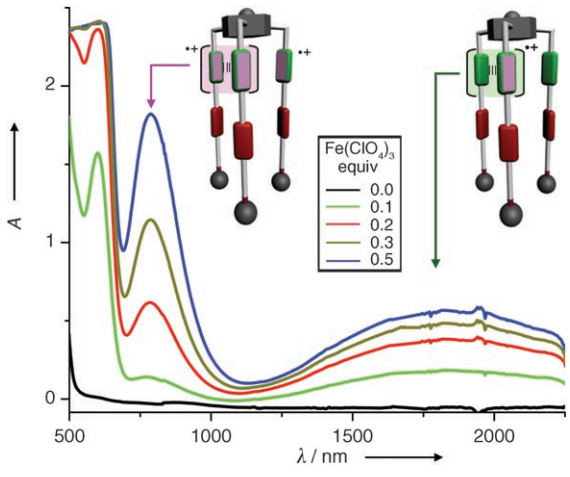


Figure 2. The change in the UV/Vis-NIR spectrum during the titration of **2** with $Fe(ClO_4)_3$. All data were recorded in argon-purged MeCN/CH_2Cl_2 (1:1) at 298 K. The concentrations of the sample and oxidant were 5.1 and 30.0 mM, respectively. The UV/Vis-NIR spectra recorded at different equivalents of $Fe(ClO_4)_3$ are differentiated by the use of five different colors, namely, black, green, red, brown, and blue.

The electrochemical behavior of **1**·12 PF_6, as suggested by CV measurements (Figure 3), is similar to that reported previously for TTF/DNP bistable [2]rotaxanes,[6] which indicates that the dimerization of TTF does not affect the switching process. The only difference is in the first oxidation peak for the TTF unit. It is usually observed[4g,7c] near +0.5 V for free TTF, and now is shifted to around +0.3 V[16c] as a result of the formation of the radical cation dimers.

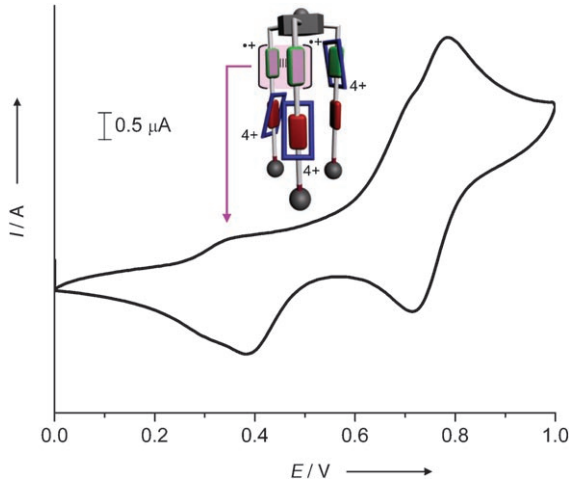


Figure 3. CV of **1**·12 PF_6. The cyclic voltammogram was recorded at 200 mV s^{-1} in argon-purged MeCN/CH_2Cl_2 (1:1) at 298 K. The concentrations of the sample and the supporting electrolyte were 0.5 mM and 0.1 M, respectively. The peak at around +0.3 V is ascribed to the oxidation of free TTF to the $TTF^{\bullet+}$ radical cation monomer and dimers. A schematic representation of the radical cation dimer $(TTF^{\bullet+})_2$ is shown.

DPV shows (Figure 4) the small peak in the CV trace more clearly as a peak with a maximum at +0.30 V. The first substantial TTF oxidation peak is shifted to higher potential and overlaps (Figure 3) with the second one. In DPV, the peak maxima for the first and second oxidations were located (Figure 4) at +0.66 and +0.73 V,[21] respectively. In the cathodic scan, two well-separated CV peaks are observed that correspond to the reduction of the $TTF^{\bullet+}$ radical cation and the TTF^{2+} dication. The positions of these peaks are consistent with those for free TTF units, which indicates that the $CBPQT^{4+}$ ring remains on the DNP unit during the

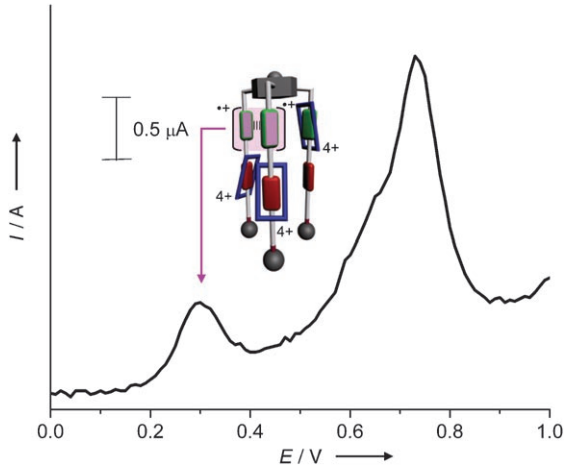


Figure 4. DPV results of **1**·12 PF_6. The data were recorded in argon-purged $MeCN/CH_2Cl_2$ (1:1) at 298 K. The peak at around +0.3 V is ascribed to the oxidation of free TTF to the $TTF^{\bullet+}$ radical cation monomer and dimers. A schematic representation of the radical cation dimer $(TTF^{\bullet+})_2$ is shown.

process. The CV peak of the $TTF^{\bullet+}$ radical cation is broadened as a result of the presence of a mixture of the $TTF^{\bullet+}$ radical cation as both a monomer and a dimer. The CV and DPV measurements carried out on **2** reveal (Figures S4 and S5 in the Supporting Information) the formation of the radical cation monomer $TTF^{\bullet+}$ and dimer with a peak maximum of +0.30 V.[22]

Conclusion

The existence in solution of only the radical cation dimer $(TTF^{\bullet+})_2$ of tetrathiafulvalene in the bistable tripodal [4]rotaxane, and of the mixed-valence dimer $[(TTF)_2]^{\bullet+}$ as well as $(TTF^{\bullet+})_2$ in its tripodal dumbbell precursor, are not insignificant observations, given the fact that neither dimer has so far been observed[6] in analogous bistable [2]rotaxanes or their precursor dumbbell compounds in solution. Note that, although they are rare,[23] both types of radical cation dimers occur at room temperature in solution in the case of other tethered molecules.[16] Our observations reported herein, coupled with those already present in the literature, beg the very important question from the point of view of fabricating devices with molecular monolayers (and multilayers) of bistable [2]rotaxanes containing tetrathiafulvalene units. What is happening in these condensed phases? Could it be that the radical cation and/or mixed-valence dimers of TTF are present when these condensed phases are oxidized? It is certainly a scenario not beyond the realms of possibility and will have to be considered as a serious possibility when investigating devices fabricated from bistable [2]rotaxanes containing tetrathiafulvalene units.

Experimental Section

General: All reagents and starting materials were purchased from Aldrich and used without further purification. CBPQT·4 PF_6,[10c] 5-(2-(2-(tetrahydro-2*H*-pyran-2-yloxy)ethoxy)ethoxynaphthalene-1-ol (**S1**),[6c] and the monotosylated tetrathiafulvalene derivative (**S3**)[6d] were prepared according to literature procedures. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). Column chromatography was carried out on silica gel 60F (Merck 9385, 0.040–0.063 mm). Deuterated solvents (Cambridge Isotope Laboratories) for NMR spectroscopic analyses were used as received. NMR spectra were recorded on Bruker Avance 500 and 600 spectrometers, with working frequencies of 500.13 and 600.13 MHz for ^1H nuclei, and 125.70 and 150.90 MHz for ^{13}C nuclei, respectively. Chemical shifts are quoted in ppm relative to tetramethylsilane with the residual solvent peak as a reference standard. Low-resolution ESI mass spectra were measured on an IonSpec FT-ICR mass spectrometer. GC-MS spectra were recorded on a Shimadzu GCMS-QP2010S Spectrometer. High-resolution mass spectra were measured either on an Applied Biosystems Voyager DE-PRO MALDI TOF mass spectrometer (HR-TOF), or on a Finnigan LCQ ion-trap mass spectrometer (HR-ESI).

Electrochemical and SEC experiments were carried out at room temperature in argon-purged solutions in $MeCN/CH_2Cl_2$ (1:1) with a Princeton Applied Research 263 A Multipurpose instrument interfaced to a PC. CV experiments were performed by using a glassy carbon working electrode (0.018 cm^2, Cypress Systems). Its surface was polished routinely with 0.05 μm alumina-water slurry on a felt surface immediately before use. The counter electrode was a Pt coil and the reference electrode was a standard calomel electrode (SCE). The concentration of the sample and supporting electrolyte (tetrabutylammonium hexafluorophosphate (TBA·PF_6)) were 0.5 mM and 0.1 M, respectively. The scan rate was set to 200 $mV\,s^{-1}$. In the DPV experiment, the pulse height, pulse width, step height, and step time were set to 50 mV, 50 ms, 5 mV, 500 ms, respectively. The peak top potentials for the overlapped peaks were determined by using the curve-fitting operation of the IGOR Pro software (Version 5.04B, Wavemetrix).

Spectroelectrochemical experiments were carried out in a custom-built optically transparent thin-layer electrochemical (OTTLE) cell with an optical path of 1 mm by using a Pt grid as working electrode, a Pt wire as counter electrode and a Ag wire pseudoreference electrode. Experimental errors: potential values, ±10 mV; absorption maxima, ±2 nm. The scan rate was set to 0.25 $mV\,s^{-1}$ and the UV/Vis spectra were recorded every 2 min.

The near-IR measurements were carried on a Shimadzu UV/Vis-NIR scanning spectrophotometer by using a cell with an optical path of 1 mm. The argon-purged solutions ($MeCN/CH_2Cl_2$ (1:1)) of the [4]rotaxane **1**·12 PF_6, and dumbbell-shaped component **2** (0.5 and 5.1 mM, respectively) were titrated with $Fe(ClO_4)_3$ (30 mM) at RT. The UV/Vis-NIR spectra were recorded after each addition of $Fe(ClO_4)_3$.

Synthesis of 3: A solution of **S1** (62 mg, 0.18 mmol; see the Supporting Information),[6c] **S2** (100 mg, 0.17 mmol; see the Supporting Information),[6d] K_2CO_3 (92 mg, 0.68 mmol), and [18]crown-6 (5 mg) in dry MeCN (30 mL) was heated under reflux for 16 h. After cooling to RT, the reaction mixture was filtered and the residue was washed with MeCN (5 mL). The combined organic solution was concentrated in vacuo to obtain the crude THP-protected compound as a yellow oil, which was extracted with CH_2Cl_2 (3×20 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 99:1) to give **3** as a yellow oil (113 mg, 88%). ^1H NMR (500 MHz, CD_2Cl_2): δ = 7.86 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 6.87 (d, J = 7.5 Hz, 2H), 6.24, 6.22, 6.20, 6.19 (4×s, 2H; TTF), 4.61 (t, J = 2.7 Hz, 1H), 4.29–4.24 (m, 8H), 3.97–3.55 (m, 20H), 2.23 (t, J = 2.7 Hz, 1H), 1.75–0.88 ppm (m, 7H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 154.8, 154.7, 135.1, 135.0, 134.9, 134.8, 127.1, 127.0, 125.6, 125.5, 116.8, 116.7, 116.7, 116.6, 114.8, 114.7, 111.0, 110.7, 106.1, 106.0, 99.3, 72.8, 71.3, 71.2, 70.6, 70.2, 70.1, 69.9 (×2), 69.8, 68.6, 68.5 (×2), 68.4 (×2), 67.1, 62.5, 62.0, 31.0, 25.9, 19.9 ppm;[24] HRMS (HR-TOF): m/z calcd for $C_{35}H_{46}O_{10}S_4$: 754.1974; found: 754.1967.

Synthesis of 4: A solution of TsCl (37 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was added dropwise with stirring to a solution of **3** (100 mg, 0.13 mmol), Et_3N (0.05 mL, 0.39 mmol), and DMAP (5 mg) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was then stirred for 16 h at RT. After removal of the solvent, the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 99:1) to give the tosylate **4** as a yellow oil (100 mg, 85 %). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.91 (dd, J = 8.4, 4.7 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.44–7.38 (m, 4H), 6.91 (d, J = 7.7 Hz, 2H), 6.24 (s, 2H), 4.67 (t, J = 3.5 Hz, 1H), 4.33 (m, 6H), 4.25 (br s, 2H), 4.16 (m, 2H), 4.00 (m, 4H), 3.86–3.46 (m, 15H), 2.43 (s, 3H), 1.79–1.48 ppm (m, 7H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 154.8, 154.7, 145.5, 135.1, 135.0, 134.9, 134.8, 133.3, 130.3, 128.3, 127.1 (×2), 125.6, 125.5, 116.8, 116.7 (×2), 116.6, 114.8, 114.7, 110.9 (×2), 110.7, 106.1, 106.0, 99.3, 71.3, 71.2, 71.0, 70.2, 70.1, 69.9, 69.8, 69.7, 69.0, 68.6 (×2), 68.5 (×3), 68.4, 67.1, 62.5, 31.0, 25.9, 21.8, 19.9 ppm;[24] HRMS (HR-TOF): m/z calcd for $C_{42}H_{52}O_{12}S_5$: 908.2062; found: 908.2056.

Synthesis of 6: A solution of **4** (2.04 g, 2.24 mmol), compound **5** (0.21 mg, 6.7 mmol), and $CsCO_3$ (4.38 g, 13.44 mmol) in dry DMF (50 mL) was heated at 80 °C for 1 d. After cooling to RT, the reaction mixture was filtered and the residue was washed with MeCN (20 mL). The combined organic solution was concentrated in vacuo to obtain the crude THP-protected compound as a yellow oil, which was redissolved in MeOH/CH_2Cl_2 (1:1, 100 mL). A concentrated aqueous solution of HCl (0.5 mL) was added and the reaction mixture was stirred at RT for 1 h. A 1 N aqueous solution of NaOH (100 mL) was added to the reaction mixture, which was extracted with CH_2Cl_2 (3×100 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 99:1) to give the triol **6** as a yellow oil (879 mg, 52 %). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.84 (t, J = 8.0 Hz, 6H), 7.36 (t, J = 8.0 Hz, 6H), 6.97 (d, J = 8.0 Hz, 6H), 6.86 (d, J = 7.9 Hz, 6H), 6.78 (d, J = 7.9 Hz, 6H), 6.24, 6.22, 6.20, 6.19 (4×s, 6H; TTF), 4.27 (m, 24H), 4.06 (m, 6H), 3.95 (m, 12H), 3.78–3.58 (m, 42H), 2.07 ppm (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 156.7, 154.2, 154.1, 152.4, 143.1, 134.5 (×2), 134.4 (×2), 129.4, 126.5 (×2), 125.1, 125.0, 116.2, 116.1 (×2), 116.0, 114.3, 114.1, 113.5, 105.6, 72.6, 70.7, 70.5, 69.6, 69.5 (×2), 69.3 (×2), 68.0 (br s), 67.9, 67.8, 67.3, 61.5, 50.9, 29.9 ppm;[24] MS (ESI): m/z calcd for $C_{110}H_{126}O_{27}S_{12}$: 2262.51; found: 2262.35.

Synthesis of S3: A solution of TsCl (118 mg, 0.60 mmol) in CH_2Cl_2 (2 mL) was added dropwise with stirring to a solution of **6** (234 mg, 0.10 mmol), Et_3N (0.13 mL, 0.90 mmol), and DMAP (10 mg) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was then stirred for 16 h at RT. After removal of the solvent, the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 99:1) to give the tritosylate **S3** as a yellow oil (231 mg, 85 %). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.88 (d, J = 8.5 Hz, 3H), 7.82 (d, J = 8.5 Hz, 3H), 7.77 (d, J = 8.0 Hz, 6H), 7.40 (m, 6H), 7.29 (d, J = 8.0 Hz, 6H), 7.01 (d, J = 8.5 Hz, 6H), 6.88 (d, J = 7.5 Hz, 3H), 6.85–6.81 (m, 9H), 6.23, 6.22, 6.21, 6.19 (4×s, 6H; TTF), 4.28 (m, 16H), 4.20 (m, 12H), 4.08 (m, 6H), 3.97 (m, 6H), 3.91 (m, 6H), 3.78 (m, 18H), 3.67–3.61 (m, 20H), 2.10 ppm (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 157.1, 154.7, 154.6, 145.4, 142.3, 135.0, 134.9 (×3), 133.2, 130.2, 129.9, 129.8, 128.1, 127.0, 126.9, 125.6, 125.5, 116.7, 116.6 (×2), 116.5, 114.8, 114.6, 114.1, 113.9, 110.7, 106.0 (×2), 71.2, 70.9, 70.1 (×2), 70.0, 69.9, 69.8 (×2), 69.2, 68.3, 68.2, 50.9, 30.9, 21.7 ppm;[24] MS (ESI): m/z calcd for $C_{131}H_{144}O_{33}S_{15}$: 2724.5400; found: 2724.5120.

Synthesis of 7: A solution of tritosylate **S3** (230 mg, 0.08 mmol) and NaN_3 (82 mg, 1.2 mmol) in dry DMF (20 mL) was heated at 80 °C for 2 d. After removal of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL) and then washed with a saturated aqueous solution of NH_4Cl (2×30 mL), followed by a saturated aqueous solution of K_2CO_3 (30 mL) and then finally dried ($MgSO_4$). The crude product, obtained after the removal of the solvent, was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 99:1) to give the triazide **7** as a yellow oil (124 mg, 63 %). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.85 (d, J = 8.4 Hz, 6H), 7.37 (t, J = 7.7 Hz, 6H), 6.99 (d, J = 8.0 Hz, 6H), 6.89 (d, J = 8.0 Hz, 6H), 6.80 (d, J = 8.4 Hz, 6H), 6.22, 6.21, 6.20, 6.19 (4×s, 6H; TTF), 4.27 (m, 24H), 4.08 (m, 6H), 3.99 (m, 12H), 3.81–3.61 (m, 36H), 3.43 (m, 6H), 2.09 ppm (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 157.1, 154.7, 154.6, 142.3, 135.0 (×2), 134.9 (×2), 129.9, 127.0 (×2), 125.6, 116.7, 116.6 (×2), 116.5, 114.8 (×2), 114.7, 113.9, 110.8, 110.7, 106.0 (×2), 71.2, 70.9, 70.6, 70.1, 70.0 (×2), 69.8, 69.7, 68.5 (×2), 68.4, 68.3, 67.7, 51.2, 50.9 ppm;[24] MS (ESI): m/z calcd for $C_{110}H_{123}N_9O_{24}S_{12}$: 2337.53; found: 2337.37.

Synthesis of 8: A solution of 2,6-diisopropylphenol (0.48 mL, 2.7 mmol), propargyl bromide (1.2 mL, 8.1 mmol), and K_2CO_3 (1.1 g, 8.1 mmol) in dry DMF (10 mL) was heated at 80 °C for 1 d. After removal of the solvent, the residue was extracted with CH_2Cl_2 (3×20 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2: hexane/EtOH 97:3) to give **8** as yellow oil (50 mg, 86 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (br s, 3H), 3.40, (m, 2H), 2.57 (s, 2H), 1.25 ppm (d, J = 6.8 Hz, 9H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 153.0, 142.2, 125.5, 124.4, 79.5, 75.4, 62.2, 26.9. 24.4 ppm; MS (GC-MS): m/z (%): 216 , (20 %) [M^+], 173 (100), 159 (65), 135 (95), 107 (95), 91 (55), 43 (65).

Synthesis of 1·12 PF$_6$: The triazide **7** (50 mg, 0.021 mmol), CBPQT·4 PF_6 (74 mg, 0.066 mmol), and the propargyl ether **8** (15 mg, 0.069 mmol) were dissolved in DMF (0.5 mL) at RT to afford a deep green solution. Stock solutions of $CuSO_4$·5 H_2O in DMF (20 μL, 0.006 mM) and ascorbic acid in DMF (20 μL, 0.012 mM) were added. The solution was stirred at RT for 48 h. The crude product, obtained after the removal of the solvent, was purified by column chromatography (SiO_2: Me_2CO followed by a 1 % w/v NH_4PF_6 solution in Me_2CO). The green compound present in this salt solution was concentrated to a small volume and the pure product was precipitated from this concentrate by adding an excess of cold water. The bistable tripodal [4]rotaxane **1**·12 PF_6 was isolated as a green solid (52 mg, 40 %). M.p. 140 °C (dec); ^{1}H NMR (500 MHz, CD_3CN): δ = 9.31–9.11 (m, 24H), 8.53–8.32 (m, 6H), 8.20–8.00 (m, 18H), 7.09–7.54 (m, 24H), 7.48–7.40 (m, 4H), 7.22 (m, 2H), 7.14–7.10 (m, 6H), 6.91–6.71 (m, 8H), 6.64 (br s, 5H), 6.50–6.40 (m, 3H), 6.33 (s, 1H), 6.28–6.19 (m, 4H), 6.14–6.03 (m, 4H), 5.99–5.93 (m, 4H), 5.82–5.80 (m, 4H), 5.72–5.68 (m, 4H), 4.95–4.85 (m, 6H), 4.56 (br s, 4H), 4.56–4.21 (m, 14H), 4.21–3.79 (m, 60), 3.45 (m, 6H), 3.15 (4H), 2.22 (s, 3H), 1.17–1.13 ppm (m, 36); MS (ESI): m/z: 1950 [M−3 PF_6]$^{3+}$, 1427 [M−4 PF^6]$^{4+}$, 1113 [M−5 PF_6]$^{5+}$, 903 [M−6 PF_6]$^{6+}$, 753 [M−7 PF_6]$^{7+}$; HRMS (HR-ESI): m/z calcd for $C_{263}H_{279}F_{54}N_{21}O_{27}P_9S_{12}$: 1950.4843; found: 1950.4875 [M−3 PF_6]$^{3+}$.

Synthesis of 2: The triazide **7** (50 mg, 0.021 mmol) and the propargyl ether **8** (15 mg, 0.069 mmol) were dissolved in DMF (1.0 mL) at RT. Stock solutions of $CuSO_4$·5 H_2O in DMF (100 μL, 0.006 M) and ascorbic acid in DMF (100 μL, 0.012 M) were added. The solution was stirred at RT for 2 d. After removal of the solvent, the residue was extracted with CH_2Cl_2 (3×10 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography (SiO_2: CH_2Cl_2/EtOH 98:2) to give **2** as a yellow oil (40.6 mg, 65 %). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.88 (d, J = 8.5 Hz, 2H), 7.84 (s, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.38 (m, 6H), 7.14 (s, 9H), 7.00 (d, J = 8.0 Hz, 6H), 6.89 (d, J = 7.0 Hz, 6H), 6.83 (d, J = 7.0 Hz, 6H), 6.25, 6.24, 6.23, 6.21 (4×s, 6H; TTF), 4.86 (s, 6H), 4.65 (t, J = 4.8 Hz, 6H), 4.29 (m, 21H), 4.15–4.06 (m, 12H), 3.99 (m, 13H), 3.81–3.61 (m, 32H), 3.38 (m, 6H), 2.11 ppm (s, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 157.2, 154.7, 154.6, 153.3, 144.6, 142.3, 135.0, 134.9, 129.9, 127.0, 126.9, 125.6, 125.5, 125.2, 124.4, 124.1, 116.7, 116.6 (×2), 116.5, 114.9, 114.5, 113.9, 110.7, 106.0 (×2), 71.2, 71.0, 70.2, 70.1, 70.0, 69.9, 69.8, 68.5, 68.4, 68.3, 68.2 (×2), 67.8, 50.8, 30.0, 26.9, 24.1 ppm; MS (MALDI-TOF): m/z calcd for $C_{153}H_{181}N_9O_{27}S_{12}$: 2985.9872; found: 2985.9567.

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[19] These free TTF units originate from the translational isomer (<10%) in which the $CBPQT^{4+}$ ring encircles the DNP unit.

[20] Another important point is the fact that the free TTF units will be oxidized before the encircled ones (see text and ref. [7b]), a situation that will lower the chances even more of getting mixed-valence dimers.

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[22] Moreover, both spectra show a minor oxidation peak at +0.5 V that could be attributed to the further oxidation of the various radical cationic $TTF^{\bullet+}$ species present in solution.

[23] The fact that $TTF^{\bullet+}$ radical cations do dimerize in the tripodal [4]rotaxane $\mathbf{1}^{12+}$, even though the molecule incorporates 12 positive charges, indicates that even an accumulation of so much charge—perhaps because it is shielded internally by counterions and solvent—does not prevent, in an appreciable amount, communication occurring between $TTF^{\bullet+}$ radical cations. Clearly what has been demonstrated to occur intramolecularly to $\mathbf{1}^{12+}$ could easily be happening in condensed phases of tetracationic bistable [2]rotaxanes.

[24] Some of the signals in the ^{13}C NMR spectrum are doubled up because of the *cis*/*trans* isomerism.

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