Supramolecular Chemistry

Construction and radical cation stabilisation of a supramolecular dyad by tetrathiafulvalene-modified β-cyclodextrin and cucurbit[7]uril

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A tetrathiafulvalene (TTF)-modified β-cyclodextrin derivative (**3**) was carefully designed and synthesised by the reaction of 2-(2-cycanoethylsulphanyl)-3,6,7-*tris*-(methylsulphanyl)tetrathiafulvalene (**1**) and mono-6-deoxy-6-iodo-β-cyclodextrin (**2**) in 49% yield, which was comprehensively characterised by ^{1}H NMR, mass spectra and elemental analysis. TTF-modified β-cyclodextrin (**3**) showed satisfactory water solubility up to *ca.* 1×10^{-3} M. Furthermore, the interactions between the radical cation of **3** and cucurbit[7]uril were investigated by means of UV–vis spectroscopy, electron paramagnetic resonance, kinetic experiment and cyclic voltammetry. The results indicated that the introduction of the cucurbit[7]uril and cyclodextrin unit could promote a remarkable effect on the stability of TTF radicals generated by 1 equiv. of Fe^{3+} in aqueous media, and the radical cations encapsulated in cucurbit[7]uril at this state could be considered as stable and persistent ones.

Keywords: cyclodextrin; cucurbit[7]uril; tetrathiafulvalene; radical cation

1. Introduction

Free radicals play an essential role in normal biological environments, and radical reactions are incorporated in a huge range of biological processes, such as photosynthesis and metastasis (*1*). Radical ions can be used as reporter molecules to obtain a wealth of information on the interdependencies between structures and their properties. Importantly, stable radicals have a much more selective and controllable nature than reactive radicals, and are widely applied in many fields such as *in vivo* electron paramagnetic resonance (EPR) imaging, conducting and magnetic materials, and polymer chemistry (*2*). Therefore, many endeavours, such as the introduction of bulky groups by chemical modification (*3*) or the formation of host–guest inclusion complexes between radical cations and cucurbit[*n*]urils (CBs, *n* = 5–8) (*4*), to prevent dimerisation/oligomerisation have been made to stabilise radicals. It was well documented that cucurbituril hosts have the ability to suppress and control the aggregation of some dyes (*5*). Anderson and co-workers (*6*) reported their research works on the radical cation stabilisation in a cucurbituril/oligoaniline rotaxane, where they found that the inclusion complexation with CB[7] could stabilise the radical cation of oligoaniline (*6*). In a recent publication, we constructed a pseudopolyrotaxane by capsulising a polyaniline chain with numerous CB[7] cavities (*7*). The results showed that, compared with free polyaniline, the CB[7]/polyaniline pseudopolyrotaxane presented higher water solubility and radical cation stability owing to the complexation of CB[7].

On the other hand, tetrathiafulvalene (TTF) and its derivatives are intensively studied owing to their unique π-electron donor with unusual and exciting electric and magnetic properties (*8*). As an electron-rich donor, TTF has a fast response to the external stimulus, such as electric signal, electron-accepting unit and metal ions. In the past decades, a number of functional groups including pyridine (*9*), anthracene (*10*), biphenyls (*11*), crown ether (*12*), cucurbituril (*13*), cyclophane (*14*), porphyrin (*15*), cyclodextrins (CDs) (*16*), phthalocyanine (*17*), calixarenes (*18*), C_{60} (*19*), self-assembly of synergic coordination nanotube (*20*) and carbon nanotubes (*21*) have been covalently or non-covalently introduced to the TTF system to construct TTF-based molecular sensors, molecular switches, molecular wires and molecular shuttles. However, it seems somewhat difficult to introduce TTF into the water phase directly, because of the instability of its radical cations in aqueous media (*22*). Therefore, the molecular recognition of the macrocyclic compound to radicals, especially in aqueous media, has not been well established in principle so far, although these studies are very important to understand the recognition mechanism and design new donor–accepter (D–A) system with unique photophysical and electrochemical properties.

Herein, we would like to report a novel chemically responsive supramolecular dyad constructed by TTF-modified CD (**3**) and CB[7]. It is significant that CB[7] can remarkably promote the stability of the radical cation of TTF in aqueous media in the presence of Fe^{3+} through

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the efficient binding of the TTF radical cation by CB[7] cavities. The introduction of the CD cavity as a bulk steric hindrance could also contribute to the stabilisation of the TTF radical cation. The present investigations will serve to further our understanding of this developing, but less investigated, area of optoelectronic nanometre-scale soft materials by molecular recognition strategy and supramolecular nanotechnology.

2. Experimental section

2.1 General

NMR spectra were recorded on Bruker AV300 and Varian Mercury Plus 400 instruments. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. UV–vis spectra were performed on a Shimadzu UV-3600 spectrophotometer. The UV–vis spectral data were recorded immediately in aqueous media in air at 25°C. The EPR spectrum was measured with a BRUKER EMX-6/1 spectrometer and recorded immediately in glass capillaries with an inner diameter of 1 mm for 83.886 s in aqueous media. The magnitude of the modulation was chosen to optimise the resolution and the signal-to-noise ratio of the observed spectra. In dynamic light scattering (DLS) measurements, a sample solution was prepared by filtering solutions (5 ml) through a 0.45 μm filter into a clean scintillation vial at a concentration of 7.1×10^{-4} M. The samples were examined on a laser light scattering spectrometer equipped with a digital correlator at 636 nm at a scattering angle of 90° at 25°C. The cyclic voltammetry (CV) measurements were carried out on a BAS Epsilon electrochemical analyser with a C3 cell stand. At the beginning of the electrochemistry experiment, the aqueous solution was deoxygenated by purging with dry nitrogen for at least 15 min. All the solutions were prepared in deionised water containing 0.1 M NaCl as a supporting electrolyte or in $NaHCO_3-Na_2CO_3$ buffer solution (pH = 10.72, 0.1 M) at 25°C. The glassy carbon electrode was polished with 0.05 μm BAS alumina suspension on a brown Texmet polishing pad, sonicated in distilled water for a few minutes to remove any residual alumina particles and then rinsed with ethanol before use. A platinum wire was used as the counter electrode. The measured potentials were recorded with respect to an Ag–AgCl reference electrode (immersed in a solution containing 3 M NaCl).

2.2 Materials

All the chemicals used were of reagent grade unless otherwise specified. Crude DMF was stirred in CaH_2 for 3 days and then distilled under reduced pressure prior to use. 2-(2-Cycanoethylsulphanyl)-3,6,7-*tris*(methylsulphanyl)te-trathiafulvalene (**1**) (23), mono-6-deoxy-6-iodo-β-cyclodex-trin (**2**) (24), 2-(3,6,7-trimethylsulphanyl tetrathiafulvalen-2-ylthio) acetic acid (**4**) (25) and cucurbit[7]uril were prepared according to the reported literatures (26).

2.3 Synthesis of 2-(6-deoxy-β-cyclodextrin-6-yl)-3,6,7-tris(methylsulphanyl)tetrathiafulvalene (3)

2-(2-Cycanoethylsulphanyl)-3,6,7-*tris*(methylsulphanyl)-tetrathiafulvalene (**1**) (0.6 mmol, 256.7 mg) was dissolved in dry DMF (17 ml) and degassed with N_2 for 15 min. A solution of caesium hydroxide monohydrate (0.78 mmol, 131.0 mg) in dry methanol (3.4 ml) was added dropwise to the mixture, and the colour of the solution became darker. After stirring for an additional 10 min, mono-6-deoxy-6-iodo-β-CDs (**2**) (0.5 mmol, 622.4 mg) dissolved in DMF (10 ml) was added dropwise to the solution mentioned above. The mixture was stirred at room temperature for about 2 h and then heated at 80°C for 1 day. After cooling to room temperature, stirring was kept overnight, and the brown-yellow solution was concentrated *in vacuo*. The residue was dissolved in a small amount of water, and washed with 300 ml acetone for at least three times. The crude product was purified on a column of Sephadex G-25, with water as the eluent. After drying under vacuum, **3** was obtained as a yellow solid in 49% yield (371.2 mg, 0.25 mmol). ^{1}H NMR (400 MHz, D_2O, ppm) δ 2.28–2.41 (m, 9H, $-SCH_3$ of TTF), 3.08–4.09 (m, 42H), 4.75–5.06 (m, 7H). Anal. Calcd for $C_{51}H_{78}O_{34}S_8 \cdot 9H_2O$: C, 37.04; H, 5.85; Found: C, 36.85; H, 5.63. MS (ESI): *m/z* 1513 $[M + Na]^+$, 1529 $[M + K]^+$. λ_{max} (log ε, H_2O) 331 (4.02), 308 (4.01) and 269 nm (4.03).

3. Results and discussion

3.1 Synthesis and conformational analysis of 3

Considering that the caesium TTF-thiolate was unstable and decomposes rapidly in air, an atmosphere of N_2 and a gradual heating were necessary to get a smooth reaction (Scheme 1). In order to demonstrate the role of CB[7] and CD moieties clearly, the compound 2-(3,6,7-trimethyl-sulphanyl tetrathiafulvalen-2-ylthio) acetic acid (**4**) was synthesised as a reference. In addition to the corresponding signals assigned to the CD protons, the ^{1}H NMR of **3** also presented four signals at 2.37, 2.44, 2.46 and 2.50 ppm assigned to the protons of methylsulphanyl groups (Figure 1). The possible reason for the splitting of $-SCH_3$ protons may be the partial inclusion of the TTF group into the CD cavity, because the guest molecules in the CD cavity were widely reported to have led to the split of NMR signals of the included molecule (27). To study the original conformation of **3** in aqueous solution, the ROESY experiment was performed in D_2O at 25°C. As shown in Figure 2, the NOE correlations between the $-SCH_3$ protons and the interior protons (H3/H5) of the β-CD cavity were clearly observed. These NOE correlations indicated that the TTF moiety was included
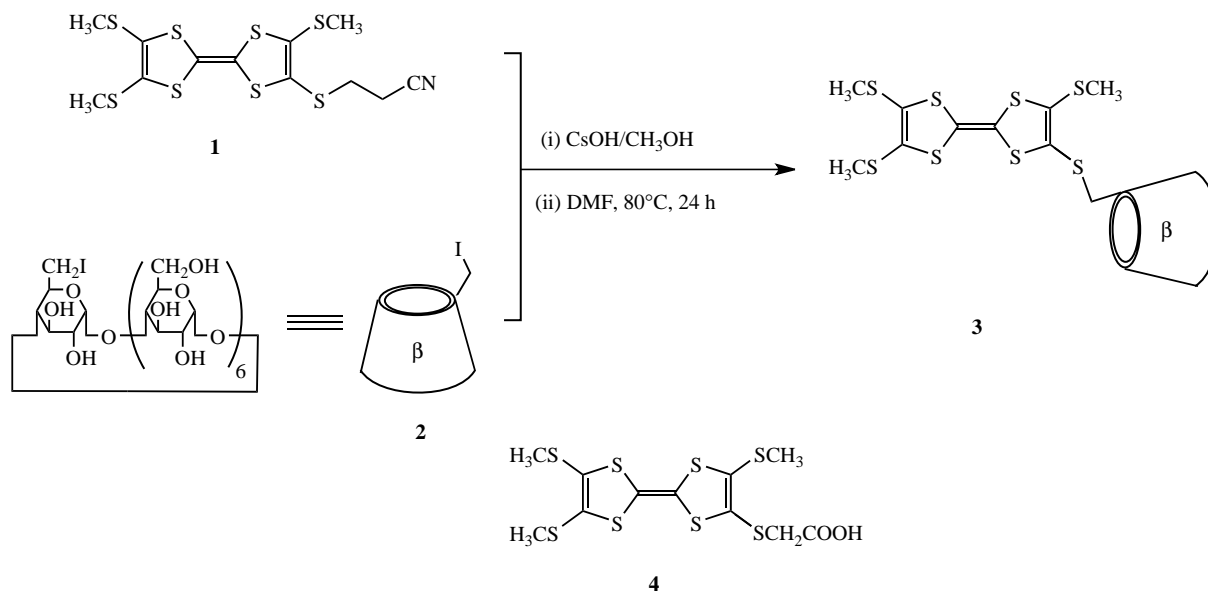
Scheme 1. Synthesis of **3** and the reference compound **4**.

in the β-CD cavity. Considering that the spacer between the β-CD and TTF moiety was the methylene group, DLS measurements were carried out to investigate the possible self-aggregation of compound **3**. The result of the DLS experiment showed that the hydrodynamic diameter of the aggregates was 138.7 nm, indicating the formation of the large-scaled assembly in aqueous media (see Figure S1 of the Supplementary Information, available online). In addition, a possible optimised molecule modulation of **3** is presented in Figure S2 (Supplementary Information, available online) and the distance between two adjacent

CD units was estimated to be 11.2 Å. Therefore, we can deduce that the self-assembly chain was composed of *ca.* 124 units of **3**. Benefiting from the good solubilisation effect of β-CD, **3** exhibited a satisfactory water solubility up to 1.0×10^{-3} M.
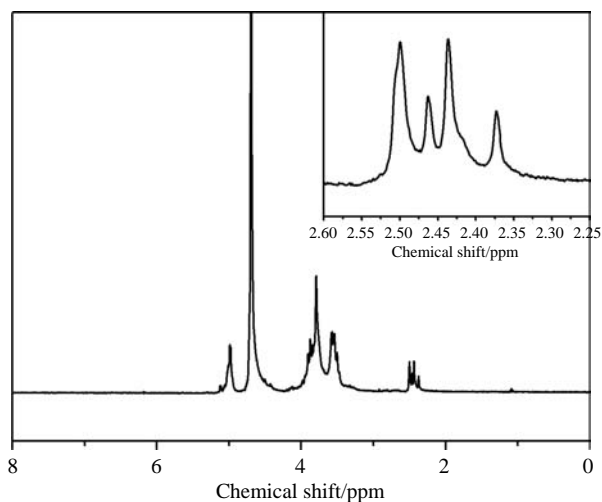

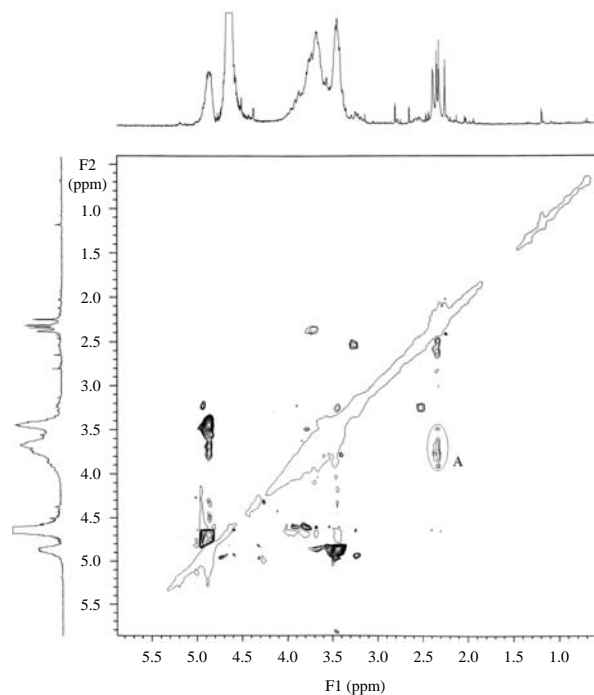Figure 1. ^{1}H NMR (D$_2$O, 400 MHz, ppm) spectrum of **3**. Inset: magnified area of $-$SCH$_3$ protons.

Figure 2. ROESY spectrum of **3** in D$_2$O at 25°C ([**3**] $= 1.0 \times 10^{-3}$ M). Peak A was assigned to the NOE correlations between $-$SCH$_3$ protons and the interior protons of the CD cavity.

3.2 UV–vis spectroscopy

The binding mode of **3** and CB[7] in the presence of Fe^{3+} was investigated by spectrophotometric method at 25°C in aqueous solution. In the previous literatures, Kim et al. (*13*) reported the first stable π-dimer of a TTF cation radical encapsulated in the cavity of CB[8] and then a chemically or electrochemically controlled supramolecular switch based on the interconversion from $TTF^{\cdot+}$/ viologen$^{\cdot+}$ pair to $(TTF^{\cdot+})_2$ or (viologen$^{\cdot+})_2$ pair inside CB[8]. As seen in Figure 3, the UV–vis spectrum of **3** exhibited three absorption peaks centred at 269, 308 and 331 nm, respectively, and no appreciable absorption could be found in the long wavelength region, indicating that the TTF moiety of **3** existed in the neutral state. It was widely reported that TTF derivatives could be quantitatively oxidised to their corresponding radical cations by 1 equiv. of Fe^{3+} and even to dications by 2 equiv. of Fe^{3+} (*28*). In our case, two new peaks appeared at 442 and 854 nm in the UV–vis spectrum of **3** when 1 equiv. of Fe^{3+} was added to the solution, which were assigned to an intramolecular transition of the radical cation ($TTF^{\cdot+}$) and the formation of its π-dimer species $(TTF)_2^{2+}$ resulting in an inter-molecular charge transfer process, respectively (*29*). Significantly, after the addition of 4 equiv. of CB[7] to the **3**/Fe^{3+} system, the absorption peak at 442 nm showed no appreciable shift, but the peak at 854 nm disappeared, accompanied by the appearance of a new peak at 721 nm. With the further addition of CB[7], the absorption peak at 442 nm corresponding to the free TTF radical cation gradually declined, and the absorption peak at 721 nm
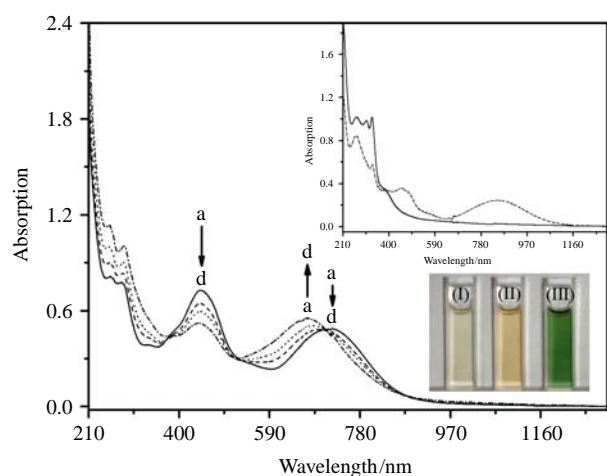
gradually enhanced, accompanied by an obvious hypso-chromic shift of 60 nm. Moreover, two isosbestic points were also observed at 522 and 707 nm. These phenomena jointly indicated the conversion of the free TTF radical cation to the **3**$^{\cdot+}$/CB[7] complex. This conversion could be readily distinguished not only by UV–vis spectroscopy but also by naked eyes through the colour change of the solution. That is, the slight yellow solution of **3** turned orange upon addition of 1 equiv. of Fe^{3+}, and then changed from orange to green with the further addition of 4 equiv. of CB[7] (Figure 3, inset photos). Without Fe^{3+}, the TTF group existed in a reductive state. The oxidation of Fe^{3+} led to the transformation of the TTF group from the reductive state (slight yellow) to the radical cation and its oligomers (orange). Then, the binding of CB[7] not only destroyed the oligomerisation of TTF radical cations to produce the free **3**$^{\cdot+}$ but also led to the formation of the **3**$^{\cdot+}$/CB[7] complex (green). Additionally, the absorption response was fit to a Hill coefficient of 1 (0.9), which corresponded to the formation of a 1:1 stoichiometry for the **3**$^{\cdot+}$/CB [7] complex in aqueous solution, and the binding constant ($\log K_s$) between **3**$^{\cdot+}$ and CB[7] was calculated to be 2.3 (Figure 4) (*30*). Interestingly, the stabilising effect could be reversible upon addition of N,N'-dimethyl-4,4'-bipyridinium (MV^{2+}) as a competitor. Due to the strong affinity between MV^{2+} and the cavity of CB[7] (*31*), the colour of the **3**$^{\cdot+}$/CB[7] complex turned to orange in the presence of 10 equiv. of MV^{2+}, accompanied by the appearance of the absorption peak at 854 nm (see Figure S3 of the Supplementary Information, available online).

3.3 EPR studies

To further investigate the stabilisation of the radical cation **3**$^{\cdot+}$ by the complexation with CB[7], EPR spectroscopy was carried out. As a one-electron oxidised species, TTF

Figure 3. UV–vis spectral changes of **3** (1.0×10^{-4} M) in the presence of 1 equiv. of $Fe(ClO_4)_3 \cdot 6H_2O$ upon addition of CB[7] (4–10 equiv., from a to d) recorded immediately in aqueous media. Inset: UV–vis spectra of **3** (1.0×10^{-4} M) in the absence of (straight) and in the presence of (dot) 1 equiv. of Fe^{3+} in aqueous solution. Inset photos: colour changes of **3** (1.0×10^{-4} M, I), (I) in the presence of 1 equiv. of Fe^{3+} (II), and (II) in the presence of 4 equiv. of CB[7] (III), respectively.
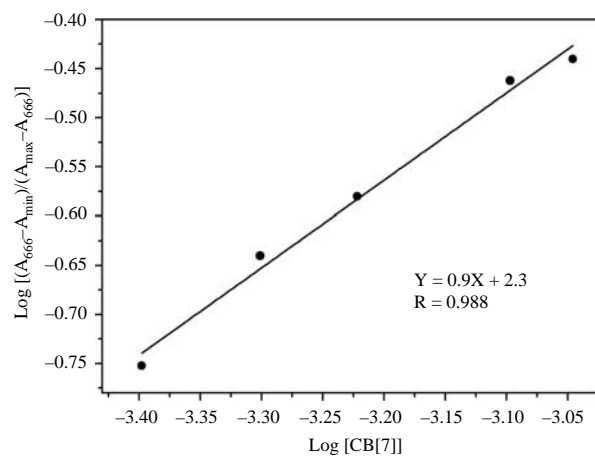

Figure 4. UV–vis spectral changes at 666 nm (A_{666}) of **3**$^{\cdot+}$ vs. increasing concentration of log[CB[7]] ([**3**] = 1.0×10^{-4} M).
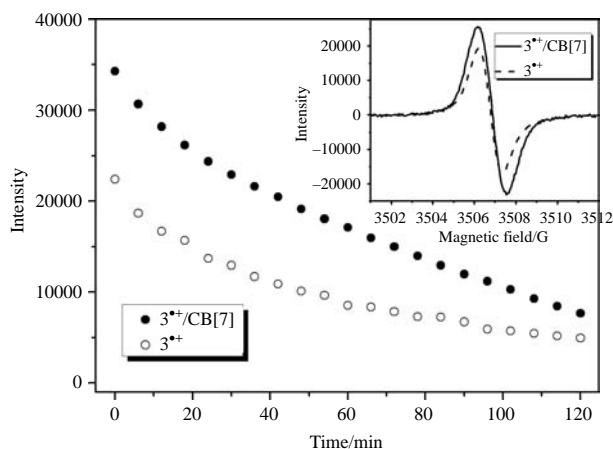
Figure 5.   EPR signal decay of **3** $(1.0 \times 10^{-4}\,\mathrm{M})$ oxidised by 1 equiv. of Fe^{3+} in the absence and presence of 4 equiv. of CB[7] in aqueous solution. Inset: EPR spectra of **3** oxidised by Fe^{3+} in the absence and presence of CB[7] at room temperature.

radical cations are known to exist as a paramagnetic monomer in solution at room temperature (*32*). As shown in Figure 5, the solution of both **3**/Fe^{3+} ($g = 2.0102$, $a = 0$) and **3**/Fe^{3+}/CB[7] ($g = 2.0101$, $a = 0$) systems exhibited strong singlet EPR signals, and these EPR signals gradually diminished within 2 h. However, as compared with that of **3**/Fe^{3+}, the EPR signals of **3**/Fe^{3+}/CB[7] exhibited a slower attenuation rate and a smaller attenuation ratio of the signal intensity. These results verified that the complexation with CB[7] efficiently improved the stability of **3**$^{\cdot+}$ in aqueous solution.

3.4   UV–vis kinetics

In addition to the EPR experiment, the kinetic experiments in aqueous solution were carried out to support the relative persistence of **3**/Fe^{3+}/CB[7] and **3**/Fe^{3+}. In this case, although the introduction of the metal oxidant Fe^{3+} could generate $TTF^{\cdot+}$ in these two systems, the initial value of the **3**/Fe^{3+}/CB[7] system was much higher than that of **3**/Fe^{3+} (about six times), mainly due to the strong affinity between $TTF^{\cdot+}$ and CB[7]. As shown in Figure 6, the intensity of radical cations in the **3**/Fe^{3+} system was attenuated to a plateau in 30 min. In sharp contrast, the TTF radical cations seemed much more stable in the presence of CB[7]. The intensity of the radical was readily detectable, and the colour of the solution remained dark orange, and no points of intersection with the **3**/Fe^{3+} system were observed in more than 3 h. Compared to the EPR study, the lifetime of radical cations was a little longer in UV–vis kinetic experiments. According to the general definition (*1b*), the radical cations at this state could be considered as persistent ones. Furthermore, the absorbance value decay experiments of **3**$^{\cdot+}$ at different concentrations of CB[7] were carried out to investigate the concentration dependence of the stability of the radical
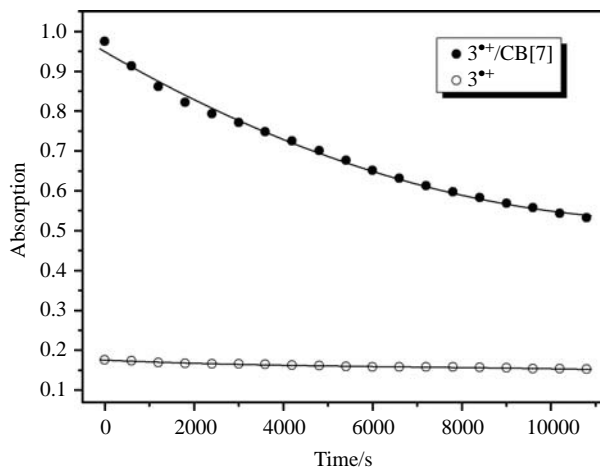

Figure 6.   Absorbance value decay of host compound **3** $(1.0 \times 10^{-4}\,\mathrm{M})$ and 1 equiv. Fe^{3+} in the absence and presence of 4 equiv. of CB[7] monitored at 442 nm with time in aqueous media.

cation (see Figure S4 of the Supplementary Information, available online). It was shown that the intensity of radical cations in the presence of 6, 8 and 10 equiv. of CB[7] was attenuated to a plateau in 2 h with a decrease in the initial value, which was consistent with the result of the UV–vis spectroscopic experiment.

3.5   Electrochemical studies

To investigate the oxidative process and high efficient stability between **3** and CB[7], the CV experiment was also carried out (Figure 7) (*33*). It is well known that TTF derivatives can undergo two successive reversible one-electron redox to the TTF^+ radical cation and TTF^{2+} species, respectively. The electrochemical behaviours of **3** and CB[7] were investigated in aqueous solution with NaCl as the supporting electrolyte. In our case, however,
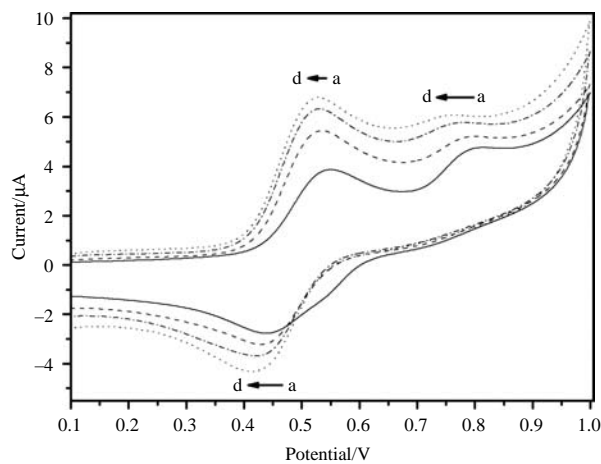

Figure 7.   CV of **3** $(5.0 \times 10^{-4}\,\mathrm{M})$ upon addition of CB[7] (0–2.0 equiv., from a to d) at 150 mV/s recorded in the deionised water with NaCl (0.1 M) as the supporting electrolyte.

the reversibility was less favourable mainly due to the aqueous media and the steric hindrance of CDs. The curve of the free host compound showed two oxidation and one distinct reduction peaks at 548, 814 and 441 mV, respectively. Comparatively, the CV curve for the complex of **3** and 2 equiv. of CB[7] gave more negative oxidative potentials at 529 and 761 mV. Additionally, the reduction capability of TTF also displayed a distinct shift in the reduction peak from 441 to 412 mV. Consequently, it can be concluded that the oxidation of TTF in the presence of CB[7] was more favourable than that of the corresponding compound **3**. The results of CV offered the possibility to stabilise the radical cations by CB[7], which was not only a stabiliser but also an important mediator to adjust the oxidative potential of TTF. In the control experiment, the curve of free **4** showed only two oxidation peaks at 404 and 860 mV in the $NaHCO_3-Na_2CO_3$ buffer solution (pH = 10.72, 0.1 M). In contrast, the CV curve of **4** gave more positive oxidative potentials at 459 and 950 mV in the presence of 5.6 equiv. of native β-CD (see Figure S5 of the Supplementary Information, available online). Furthermore, only the first oxidative peak of **4** shifted to 387 mV upon addition of 2 equiv. of CB[7] ($\Delta E_{ox}^1 = -17$ mV), which was similar to those observed in the case of the **3**/CB[7] system ($\Delta E_{ox}^1 = -19$ mV) (see Figure S6 of the Supplementary Information, available online). These results indicated the different magnitudes of the complexation constants between the neutral species (**4**/β-CD and **4**/CB[7]) and the radical ones (**4**$^{\cdot+}$/β-CD and **4**$^{\cdot+}$/CB[7]).

Some possible reasons for the stabilisation of **3**$^{\cdot+}$ by CB[7] may be as follows. Firstly, different from other unstable radicals, the radical cation of TTF was a cyclic π-aromatic system. Delocalisation that could dilute the spin density on an atomic centre was an effective way to attenuate the reactivity. Secondly, many stable radicals contained electronegative heteroatoms. Compound **3** was heteroatom-based with eight sulphur atoms, which could make the radical cations considerably less reactive to molecular oxygen. These two factors make the radical cation of **3** much more stable than that of common carbon-centred ones. Thirdly, the incorporation of steric protection with bulky substituents, such as *t*-butyl group (*34*) and bicyclo[2.2.2]octane (BCO) (*35*), was the most universally reliable and popular approach of providing kinetic and thermodynamic stability to radical ions (*36*). In our case, the CD moiety could not only increase the solubility of TTF in water but also act as a bulky component surrounding the radical cation to make the system much more stable and rigid due to both thermodynamic and kinetic stabilisation effects. Moreover, CDs and CB[7], as sterically demanding substituents, could prohibit the formation of the self-associate dimers and prevent the cation of TTF from interacting with its environment. Consequently, the introduction of the CB[7] and CD unit

exhibited a remarkable effect on the stability of TTF radicals generated by the oxidant.

4. Conclusion

By virtue of the oxidative nature of Fe^{3+} and the redox property of TTF, we designed and synthesised the TTF-modified CD derivative **3**, which can introduce the TTF moiety into water without the need for any organic co-solvent. EPR, CV and UV–vis experiments revealed that CB[7] can stabilise and prolong the lifetime of the radical cation in aqueous media. The complexation in the cavity of **3** with guest molecules offers an opportunity to adjust and control photophysical and electrochemical properties of the accommodated guest. Taking advantage of the formation, recombination, and charge transport of radical cation complex and its intermolecular interaction, one can design a robust and efficient organic electronic device at nanometre levels.

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