

## $\pi$ -Dimerization of viologen subunits around the core of C<sub>60</sub> from twelve to six directions†

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Molecular reorganization around the core of C<sub>60</sub> has been achieved by electron transfer centered on  $\pi$ -dimerizable viologen subunits located in a restricted region of space. Fullerene C<sub>60</sub> hexaadducts, featuring 12 viologen subunits, have been prepared by using copper-mediated Huisgen 1,3-dipolar cycloaddition of azides with alkynes. Detailed electrochemical studies, supported by UV-Vis and EPR spectroscopic analyses, demonstrate that the linkers bearing the viologen subunits attached to specific positions around the all-carbon sphere, allow the formation of six intramolecular  $\pi$ -dimers. Theoretical calculations reveal that the close proximity of the orbitals of the viologen subunits attached to the C<sub>60</sub> facilitate the  $\pi$ -dimerization of the bis-radical species. These investigations support the fact that the motion of discrete peripheral groups oriented around the all-carbon sphere of C<sub>60</sub> can be controlled electrochemically using noncovalent reversible interactions.

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### Introduction

During the past decade, the development of artificial systems<sup>1</sup> has been discussed at some length and emerged as a grand important challenge in the field of nanoscience. In particular, molecular switches<sup>2</sup> and nanomachines,<sup>3</sup> able to trigger molecular motions, have been used to make responsive materials. Recently, much effort has been devoted to designing molecules<sup>4</sup> capable of converting electrical impulses into mechanical changes. This approach has been employed by Bucher and co-workers<sup>5</sup> to demonstrate the rotary motions of ferrocene derivatives by redox control. These rotational motions of ferrocene-based carousels have been achieved by electron transfer, centered on two  $\pi$ -dimerizable bipyridinium units. A rigid scaffold and linkers of an appropriate size allow an optimal orbital overlap between the two sets of singly occupied  $\pi$ -orbitals of the electrochemically generated bis-radical species.

Viologens (V<sup>2+</sup>) are known<sup>6</sup> for their facile one-electron reduction to radical cations, V<sup>(•+)</sup>. These radical cations are involved in  $\pi$ -dimerizations<sup>7</sup> at relatively high concentrations

and, more importantly, in confined environments.  $\pi$ -Dimer formation has also been shown to be greatly enhanced<sup>8</sup> by linking covalently two identical viologen derivatives. The electrostatic repulsion between the two charged entities leads to the formation of charge-separated geometries before reduction. At low concentrations, the ability of the two bipyridinium units to dimerize in their reduced forms results in a folded conformation of the molecule. Most of those compounds described in the literature to date are designed with two identical 4,4'-bipyridinium units connected together by flexible linkers to encourage intramolecular associations. More complex structures, featuring a large number of identical redox units, which are capable of multiple dimerizations are rare. Viologen-based dendrimers<sup>9</sup> have been shown to shrink upon reduction of the viologen units on account of partial dimerization where structural folding results in the encapsulation of a fraction of the viologen units, thereby preventing their reduction. Here, we describe a system in which 12 redox units are grafted onto a suitable rigid scaffold by means of flexible linkers, leading to  $\pi$ -dimerization and affording six viologen radical cation pairs.

Fullerene derivatives are attractive targets to achieve this goal. In particular, T<sub>h</sub>-symmetrical C<sub>60</sub> hexaadducts, with octahedral addition patterns that possess unique three-dimensional compact structures enable the design of nanoscale molecules with multiple identical peripheral groups located within a restricted space.<sup>10</sup> Recently, we have developed efficient synthetic methodologies<sup>11</sup> for the preparation of structurally complex hexasubstituted fullerene derivatives. They are based on the post-functionalization of easily accessible fullerene hexakisadduct building blocks. For this purpose, the copper-mediated Huisgen

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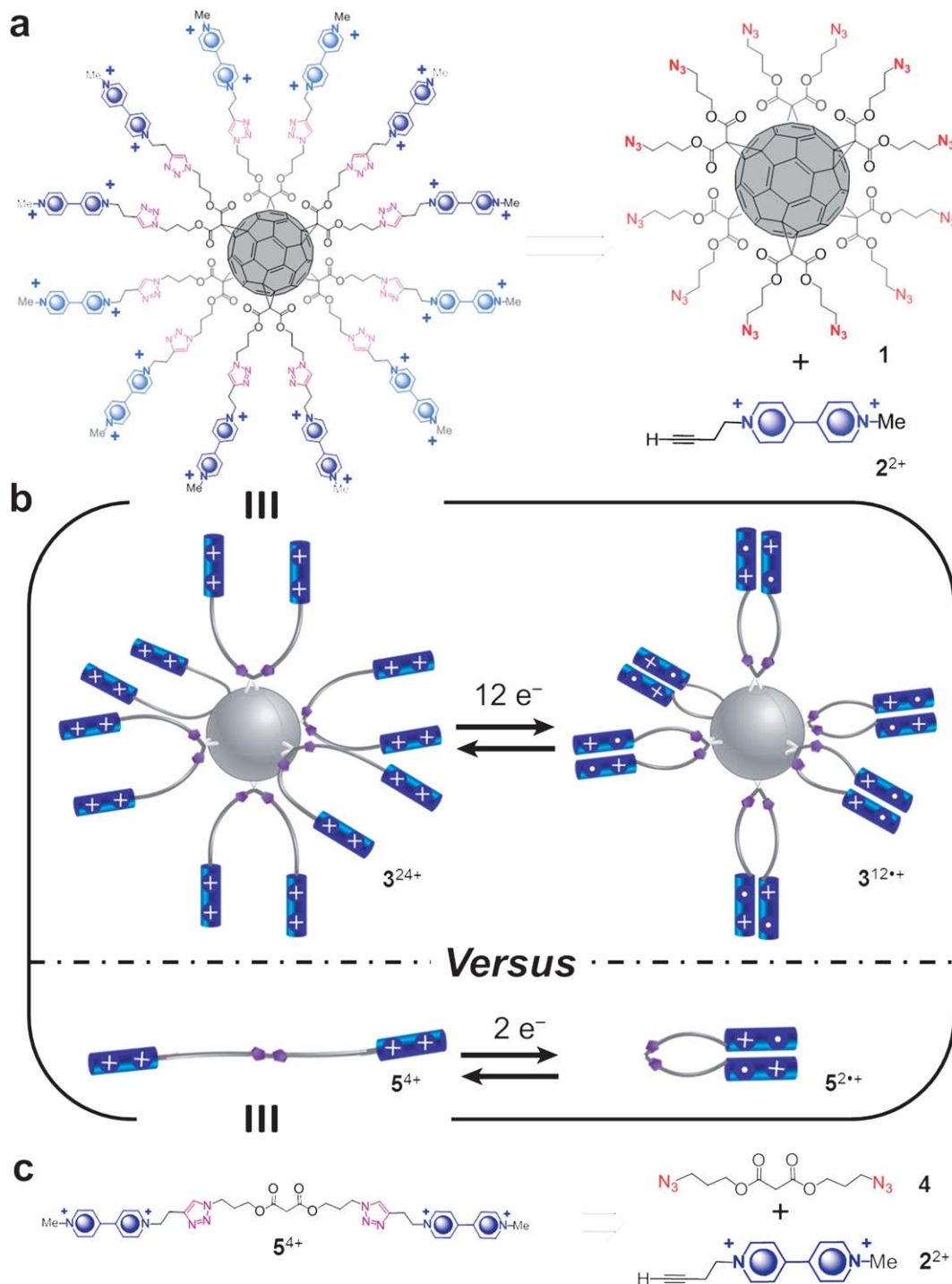
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1,3-dipolar cycloaddition of azides with alkynes resulting<sup>12</sup> in 1,2,3-triazoles was found to be a particularly useful synthetic tool, since it allows for the incorporation of almost any functional group around the fullerene core.<sup>10f,13</sup> In this article, we show that this synthetic approach is well suited to the synthesis of a redox-switchable fullerene hexa-adduct. In particular, 12 viologen

subunits have been attached to the C<sub>60</sub> core, leading to a unique three-dimensional, highly charged system. The formation of six intramolecular  $\pi$ -dimers has been demonstrated and the reversible conversion between an “open” charge-repelled form (12 arms) and a “close” state (6 arms) has been investigated. This example provides a unique case of a C<sub>60</sub> derivative able to change



**Scheme 1** (a) Retrosynthesis of the hexaadduct **3**·24PF<sub>6</sub> of C<sub>60</sub> bearing 12 4,4'-bipyridinium subunits. (b) Schematic representation of the reversible conversion between an “open” charge-repelled form of the hexaadduct **3**<sup>24+</sup> (12 directions) of C<sub>60</sub> and the “close” state of **3**<sup>12(++)</sup> (6 directions) upon reduction (−12e<sup>−</sup>) and comparison with the dimerization of the reference compound **5**·4PF<sub>6</sub> (−2e<sup>−</sup>). (c) Retrosynthesis of the malonate **5**·4PF<sub>6</sub> (viologen unit ≡ blue rod and C<sub>60</sub> ≡ grey sphere).

reversibly the number of peripheral groups around its all-carbon periphery.

## Results and discussion

### Design and synthesis

The preparation of compound  $3 \cdot 24\text{PF}_6$  featuring six pairs of viologen subunits is depicted in Scheme 1. The hexasubstituted fullerene building block<sup>11a</sup> **1** bearing 12 azide groups and the viologen derivative<sup>14</sup>  $2 \cdot 2\text{PF}_6$  with a terminal alkyne were prepared according to reported procedures. Copper-mediated Huisgen 1,3-dipolar cycloaddition was used to graft 12 viologen subunits onto the fullerene core. A mixture of freshly prepared **1** (1 equiv.),  $2 \cdot 2\text{PF}_6$  (13 equiv.),  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (0.1 equiv.), and  $\text{tris}[(1\text{-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine$  (0.1 equiv.) was stirred in DMF at room temperature for 24 h. After workup and purification, compound  $3 \cdot 24\text{PF}_6$  was obtained in 78% yield. IR spectroscopy confirmed the absence of azide groups in the isolated product. The resulting dodeca-viologen derivative was fully characterized (see ESI†) by UV-Vis, FT-IR, and NMR spectroscopies, as well as by mass spectrometry.

### NMR spectroscopy

The  $^{13}\text{C}$  NMR spectrum (Fig. 1) of the fullerene hexakis-adduct  $3 \cdot 24\text{PF}_6$  can be interpreted fully in terms of its  $T_h$ -symmetrical structure. It shows the three expected fullerene resonances ( $\delta = 70.11$  ppm for the  $\text{sp}^3$  C atom, and at 142.1 and 146.5 ppm for the two different  $\text{sp}^2$  C atoms), a signal ( $\delta = 46.7$  ppm) for the bridgehead C atom, a resonance ( $\delta = 164.3$  ppm) for the carbonyl carbon, and three signals ( $\delta = 29.7$ , 47.7 and 65.3 ppm) for the  $(\text{CH}_2)_3$  linkers. In addition, resonances corresponding to the  $\text{sp}^3$  C atom detected at  $\delta = 74.9$  and 78.8 ppm for compound  $2^{2+}$  are not present anymore, whereas two additional resonances can be identified at  $\delta = 124.3$  and 142.7 ppm in the spectrum of  $3 \cdot 24\text{PF}_6$ .

These resonances can be attributed to the  $\text{sp}^2$  C atoms of the 12 equivalent 1,2,3-triazole units. The water-soluble compound  $3 \cdot 24\text{Cl}$  was obtained in 94% yield from  $3 \cdot 24\text{PF}_6$  after counterion exchange with a saturated solution of tetrabutylammonium chloride (TBACl) in MeCN. The constitution of  $3 \cdot 24\text{Cl}$  was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic analysis. See the ESI† For comparison purposes, a model bis(bipyridinium) malonate was also prepared. The synthesis of  $5 \cdot 4\text{PF}_6$  is described in the ESI† Using click chemistry under the same experimental conditions as those employed in the synthesis of  $3 \cdot 24\text{PF}_6$ , two 4,4'-bipyridinium units were attached to the malonate<sup>11a</sup> **4** to give  $5 \cdot 4\text{PF}_6$  in 92% yield. The water-soluble  $5 \cdot 4\text{Cl}$  was isolated by anion metathesis after addition of TBACl to  $5 \cdot 4\text{PF}_6$  dissolved in MeCN. Following filtration, the water-soluble  $5 \cdot 4\text{Cl}$  which was obtained in 90% yield has been used as a reference compound in the following investigations.

### Electrochemical investigations

The electrochemical properties of  $3^{24+}$  and  $5^{4+}$  have been investigated in argon-purged DMF (0.1 M TBAP) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The redox signature of  $3^{24+}$ , which features two consecutive reversible one-electron waves at  $E_{1/2}^1 = -0.300$  and  $E_{1/2}^2 = -0.761$  V (vs. Ag/AgCl), exhibits close similarities with compounds having two identical viologen units separated by organic bridges reported in the literature.<sup>8</sup> The dodecaviologen  $3^{24+}$  shows (Fig. 2) a cathodic wave (I) at  $-0.340$  V, corresponding to the formation of the 12 radical cations around the all-carbon sphere. The second reduction peak (II) observed at  $-0.805$  V can be attributed to the formation of the neutral species  $3^{12(0)}$  where all 12 viologen subunits are in their fully reduced forms  $\text{MV}^{(0)}$ . An additional irreversible cathodic process, which was observed at  $-1.39$  V (vs. Ag/AgCl) by DPV (see ESI†) corresponds to the reduction of the  $\text{C}_{60}$  core. Concerning the reoxidation processes, the anodic peak

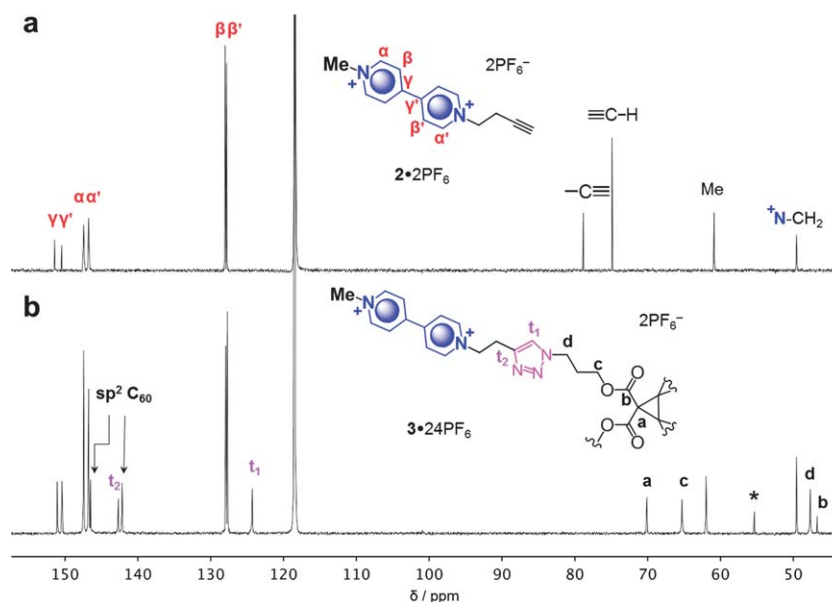
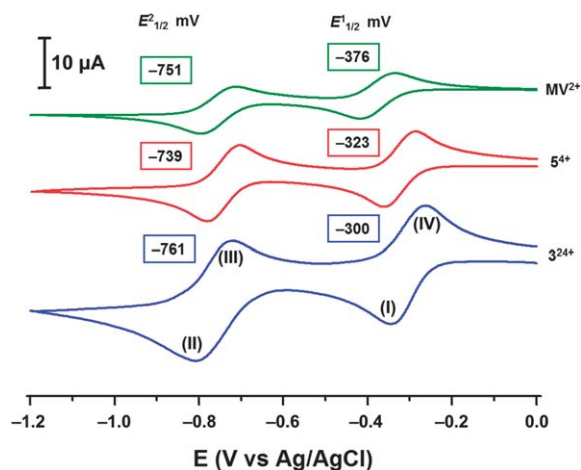


Fig. 1  $^{13}\text{C}$  NMR Spectra ( $\text{CD}_3\text{CN}$ , 125 MHz) of (a) the starting material  $2 \cdot 2\text{PF}_6$  and (b) the hexaadduct  $3 \cdot 24\text{PF}_6$  of  $\text{C}_{60}$ .



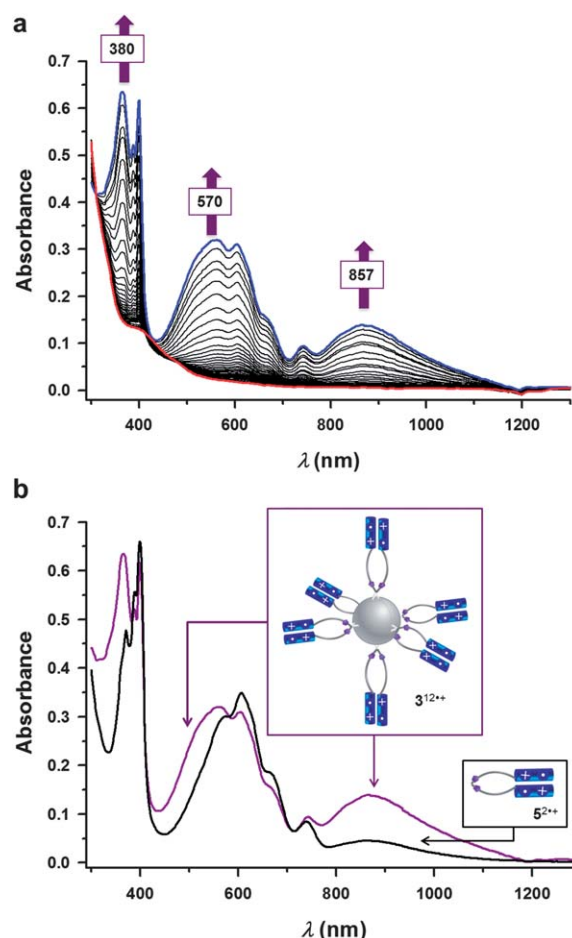
**Fig. 2** Cyclic voltammograms of methylviologen  $MV^{2+}$  (green trace),  $5^{4+}$  (red trace) and  $3^{24+}$  (blue trace) recorded in DMF (TBAPF<sub>6</sub> 0.1 M) solutions at 0.3 mM at a stationary platinum working electrode ( $E$  vs. Ag/AgCl,  $\nu = 0.050$  V s<sup>-1</sup>).

(III) at  $-0.723$  V is attributed to the first oxidation of the 12  $MV^0$  units, and the peak (IV) at  $-0.264$  V to the second oxidation of the resulting radical species. It appears both viologen-centered processes are reversible with  $\Delta E_p^1 = 79$  mV (first redox process) and  $\Delta E_p^2 = 76$  mV (second redox process). The cyclic voltammogram recorded for the diviologen  $5 \cdot 4PF_6$  exhibits a similar pattern with two reversible waves at  $E_{1/2}^1 = -0.323$  and  $E_{1/2}^2 = -0.739$  V (vs. Ag/AgCl). It should be noted that the first reduction process for both  $3 \cdot 24PF_6$  and  $5 \cdot 4PF_6$  proceeds at significantly less negative potential values than that for methylviologen ( $MV^{2+}$ ) used as a reference in these investigations. These shifts result<sup>8</sup> unambiguously from the intramolecular dimerization between bipyridinium radicals. More importantly, the cathodic shift is pronounced for  $3 \cdot 24PF_6$  when compared to that of  $5 \cdot 4PF_6$ , an observation which can be explained by a stronger association (dimerization) in the case of the dodecaviologen. This observation was corroborated by investigating the electrochemical activity of  $3 \cdot 24PF_6$  and  $3 \cdot 24Cl$ , respectively, in argon-purged MeCN and H<sub>2</sub>O (see ESI†) where the intramolecular dimerization of radical viologen subunits is known to be stronger. The first reduction is reversible and exhibits Nernstian behavior in all cases, whereas the second reduction is affected by the adsorption of the reduced species on the electrode. In particular, in the case of the water-soluble hexa-adduct of C<sub>60</sub>  $3 \cdot 24Cl$ , the reduction to radical cation occurs at a less negative potential value than that for  $3 \cdot 24PF_6$  in DMF, as a consequence of the stabilizing influence of the radical coupling involved in the  $\pi$ -dimerization in aqueous medium.<sup>8</sup> The electrochemical data support the notion that the geometric and structural features of the dodeca(bipyridinium) derivative system  $3^{24+}$  allow an efficient redox-triggered motion of the C<sub>60</sub> derivative driven by the formation of six intramolecular  $\pi$ -dimers around the carbon sphere irrespective of the solvent.

### Spectroelectrochemical investigations

The UV-Vis absorption data of the dodecaviologen are illustrated in Fig. 3. Compound  $3^{24+}$  exhibits an intense viologen-

centered  $\pi$ - $\pi^*$  transition<sup>15</sup> in the UV spectrum, between 260 and 280 nm (see ESI†), while the characteristic bands from a hexa-adduct of C<sub>60</sub> derivative<sup>10d</sup> are observed at 320 and 337 nm in DMF. We carried out a spectroelectrochemical investigation on compound  $3 \cdot 24PF_6$  in DMF to gain further insights into the nature of the electrogenerated species (Fig. 3a). The adsorption spectra of the radical cation species were performed in the range of  $\sim 5 \times 10^{-6}$  to  $2 \times 10^{-4}$  M in order to verify the absence of intermolecular radical-radical interactions between viologen units attached to different C<sub>60</sub> cores. The electrochemical reduction of  $3 \cdot 24PF_6$ , carried out at  $E_{ap} = -0.50$  V ( $E_{ap}$ : potential applied at the working electrode) produced a large decrease in intensity of the initial  $\pi$ - $\pi^*$  absorption band and led to the growth of new bands at 380 nm ( $\epsilon = 127\,000$  L mol<sup>-1</sup> cm<sup>-1</sup>) and 570 nm ( $\epsilon = 63\,800$  L mol<sup>-1</sup> cm<sup>-1</sup>), which can be attributed to  $3^{12+}$  (Fig. 3a and b). Importantly, the diagnostic signature for the formation of  $\pi$ -dimers is observed very clearly at 857 nm ( $\epsilon = 27\,800$  L mol<sup>-1</sup> cm<sup>-1</sup>). This assignment is based on the good matching found (see ESI†) between these bands and those



**Fig. 3** (a) UV-Vis spectra recorded every 3 min during one-electron reduction (per viologen) of  $3 \cdot 24PF_6$  in DMF (0.1 M TBAPF<sub>6</sub>) using a platinum grid working electrode ( $\sim 1$  cm<sup>2</sup>) whose potential was fixed at  $-0.50$  V (0.03 mM in viologen units, 1 mL,  $l = 1$  cm,  $t \sim 1$  h). (b) UV-Vis spectra recorded during the exhaustive one-electron reduction (per viologen) of  $3^{24+}$  (purple trace) and  $5^{4+}$  (black trace) in DMF (0.1 M TBAPF<sub>6</sub>) at 298 K.



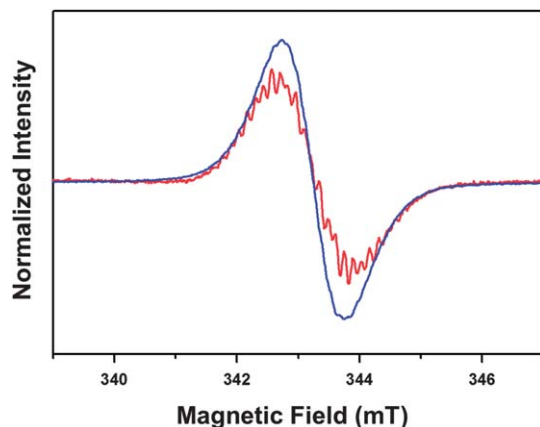


Fig. 4 EPR Spectra recorded at 298 K (blue trace) and 230 K (red trace) from MeCN solutions of  $3^{12+}$  0.2 mM obtained upon treatment of  $3^{24+}$  with Zn dust.

obtained upon chemical reduction of the same compound with zinc dust. The purple color and UV-Vis signature of the resulting solutions can be attributed to the formation of intramolecular dimers between the bipyridinium radicals. The reversibility of the reduction process was confirmed by the complete recovery of the UV-Vis absorption spectrum for the initial species after exposure to  $O_2$ . Electrochemical reduction of model compound  $5 \cdot 4PF_6$ , which produced similar spectroscopic patterns with a lower intensity associated with the band at 850 nm, supports the belief that the dimerization is stronger for the  $C_{60}$  derivative  $3^{24+}$  than for the malonate  $5^{4+}$  in DMF. These results draw attention to the capacity of the bipyridinium radicals in  $3^{12+}$  to self-assemble into  $\pi$ -dimer complexes in DMF, an outcome which was confirmed by spectroelectrochemical studies carried out on  $3 \cdot 24PF_6$  in MeCN and with the water-soluble compound  $3 \cdot 24Cl$  in buffer solution (see ESI†).

### EPR spectroscopy

The radical-cationic redox state of the hexaadduct  $3^{12+}$  of  $C_{60}$  was investigated (Fig. 4) by EPR spectroscopy in MeCN at 298 and 230 K. The EPR spectra were collected after full chemical

reduction of  $3 \cdot 24PF_6$  by zinc dust for 30 min. At 298 K,  $3^{12+}$  displays minimal hyperfine splitting in its EPR spectrum, indicating that it exists in a high spin-exchange regime on account of dimerization of the 12 BIPY $^{+}$  units. The lack of hyperfine splitting is completely consistent with previously reported results.<sup>4b</sup> By comparing the peak-to-peak intensity of  $3^{12+}$  to a calibration curve constructed with the tethered BIPY $^{+}$  dimer  $5^{2+}$ , the number of BIPY $^{+}$  dimers in  $3^{12+}$  was calculated to be four instead of the expected six. This discrepancy can be attributed to the rapid, dynamic interactions between multiple BIPY $^{+}$  units, both tethered and untethered. On cooling to 230 K,  $3^{12+}$  displays a well-resolved hyperfine splitting in its EPR spectrum superimposed on the original broad signal as a result of the slowing down the dynamic BIPY $^{+}$  interactions, which allows the observation of a single BIPY $^{+}$  unit in a low spin-exchange regime.

### Computational chemistry

A computational study was carried out in order to predict the conformation adopted by  $3^{24+}$  in solution. Defining the position of the 12 viologen subunits is important in order to gain an understanding of the hexa-dimerization. The octahedral orientation of the six malonate substituents attached around the  $C_{60}$  generates a special environment for each pair of viologen subunits compared to the isolated malonate  $5^{4+}$ . The central  $5 \cdot 4PF_6$ , bearing two viologen subunits and being structurally similar to  $3 \cdot 24PF_6$ , has been used as a reference compound in the computational simulations. The conformations of the dodeca(bipyridinium)  $3^{24+}$  and of the isolated bis(bipyridinium) malonate  $5^{4+}$ , both fully charged, have been relaxed by means of simulated annealing molecular dynamics. These simulations were performed using Tinker 6.0<sup>16</sup> and the MM3 force field,<sup>17–21</sup> where both molecules were solvated in MeCN in the presence of  $PF_6^-$  counterions so as to neutralize the total charge. The minimum energy conformations obtained by simulated annealing (SA) were then used as the initial configuration for molecular dynamics (MD) simulation at room temperature to

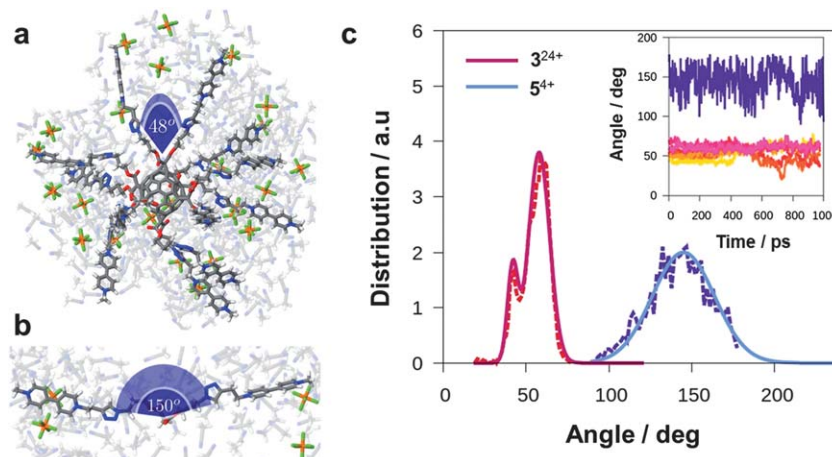


Fig. 5 Interbranch angle distribution of the isolated malonate  $5^{4+}$  (a) and the molecule  $3^{24+}$  (b) obtained as a result of MD simulations starting from their minimum energy configuration obtained by simulated annealing SA. (c) Minimum energy configuration of the isolated malonate  $5^{4+}$  and the molecule  $3^{24+}$  obtained by SA.

evaluate the flexibility of the two molecules (see ESI† for more details).

Fig. 5 illustrates the minimum energy conformation of the isolated malonate  $5 \cdot 4PF_6$  where the molecule adopts an elongated shape. On account of the electrostatic repulsions between the positive charges located formally on the nitrogen, the viologen subunits repel each other, leading to an angle of  $150^\circ$  between the two branches of the molecules. The MD simulations of the isolated malonate  $5^{4+}$ , summarized in Fig. 5, reveal a large distribution of this inter-branch angle ( $\alpha$ ) which fluctuates between  $90^\circ$  and  $180^\circ$ . This broad distribution indicates a significant flexibility of the molecule which allows it to adopt transiently bent conformations. On adding 12 viologen subunits to the  $C_{60}$  core, the steric hindrance generated by the electrostatic repulsion between the 24 positive charges on the 12 viologen subunits, prevents the six malonate residues from unfolding. Consequently, in the minimum energy conformations of the complex, the inter-branch angle ( $\alpha$ ) is reduced to *ca.*  $48^\circ$ . MD simulations reveal small transient variations of the angles  $\alpha$  leading to the narrow distribution of values represented in Fig. 5. The close proximity of the viologen subunits attached to the  $C_{60}$  in  $3^{24+}$  should facilitate their dimerization

following the formation of the bis(bipyridinium) radicals. The unfolded minimum energy conformation of the disubstituted malonate explains why the dimerization constant was observed experimentally to be lower for  $5^{4+}$  than for  $3^{24+}$ .

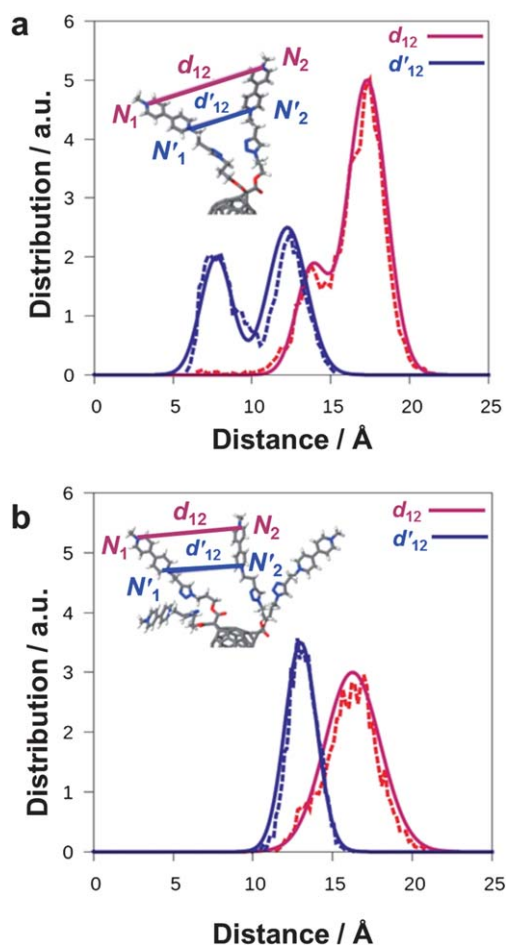
In the case of the  $C_{60}$  hexaadduct, viologen dimers can be obtained by the association of two redox-centers of the same malonate unit but also by the association of two viologens of two neighboring malonates. These two kinds of dimerization are referred to respectively, as self-dimerization and cross-dimerization in the following discussion. Since the isolated molecule  $5^{4+}$  presents an unfolded minimum energy conformation, the cross-dimerization is not limited by the flexibility of the malonate linkers and both dimerization mechanisms only depend on the distance between the neighboring viologens. It is to be expected that a viologen subunit will preferentially form a dimer with the closest viologen rather than with a remote one. Therefore, the relative amount of self- and cross-dimerization can be evaluated by computing the distances separating the bipyridinium units located on the same malonate – referred as self-distance – and ions located on neighboring malonates – referred as cross-distance. The fluctuations of these distances during the MD simulations are summarized in Fig. 6. The self-distances between the nitrogen atoms of the viologen subunits, labelled  $N$  and  $N'$ , present a bistable characteristic because of the two possible conformations of the malonates (see ESI† for the details). Fig. 6b presents the distribution of the cross-distance obtained during the MD simulations. In order to compute these distributions, we considered only the minimal distances separating each nitrogen from its closest neighbor. The self-distances are (Fig. 6) upwards to 50% shorter than the cross-distances. Consequently, one can expect more self-dimerization to occur than cross-dimerization.

## Conclusions

We have described an example of a three-dimensional redox-switchable system wherein molecular reorganization of discrete peripheral groups around the all-carbon sphere of  $C_{60}$  can be controlled electrochemically using noncovalent reversible interactions. We have shown that 12 viologen subunits can be grafted efficiently onto a hexasubstituted fullerene core to give a molecular system with multiple copies of  $\pi$ -dimerizable bipyridinium units, each located in a restricted space. Electrochemistry, along with UV-Vis and EPR spectroscopies, provide evidence for intramolecular dimerization. These multiple “open/close” molecular movements around the  $C_{60}$  core, triggered by electron-transfers centered on  $\pi$ -dimerizable bipyridinium units, have been shown to occur in organic solvents, and more importantly, in aqueous media. This system paves the way towards more elaborated redox-switchable structures where mechanically interlocked molecules<sup>22</sup> (MIMs) can be incorporated around the all-carbon sphere using a similar synthetic protocol.

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**Fig. 6** (a) Self and (b) cross distances between bipyridinium units obtained using MD simulations starting from their minimum energy configuration obtained by SA. The bistable characteristic of the self-distances could be a consequences of forming meta-stable  $\pi$ -stacks between the triazole rings.

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