A Molecular Elevator

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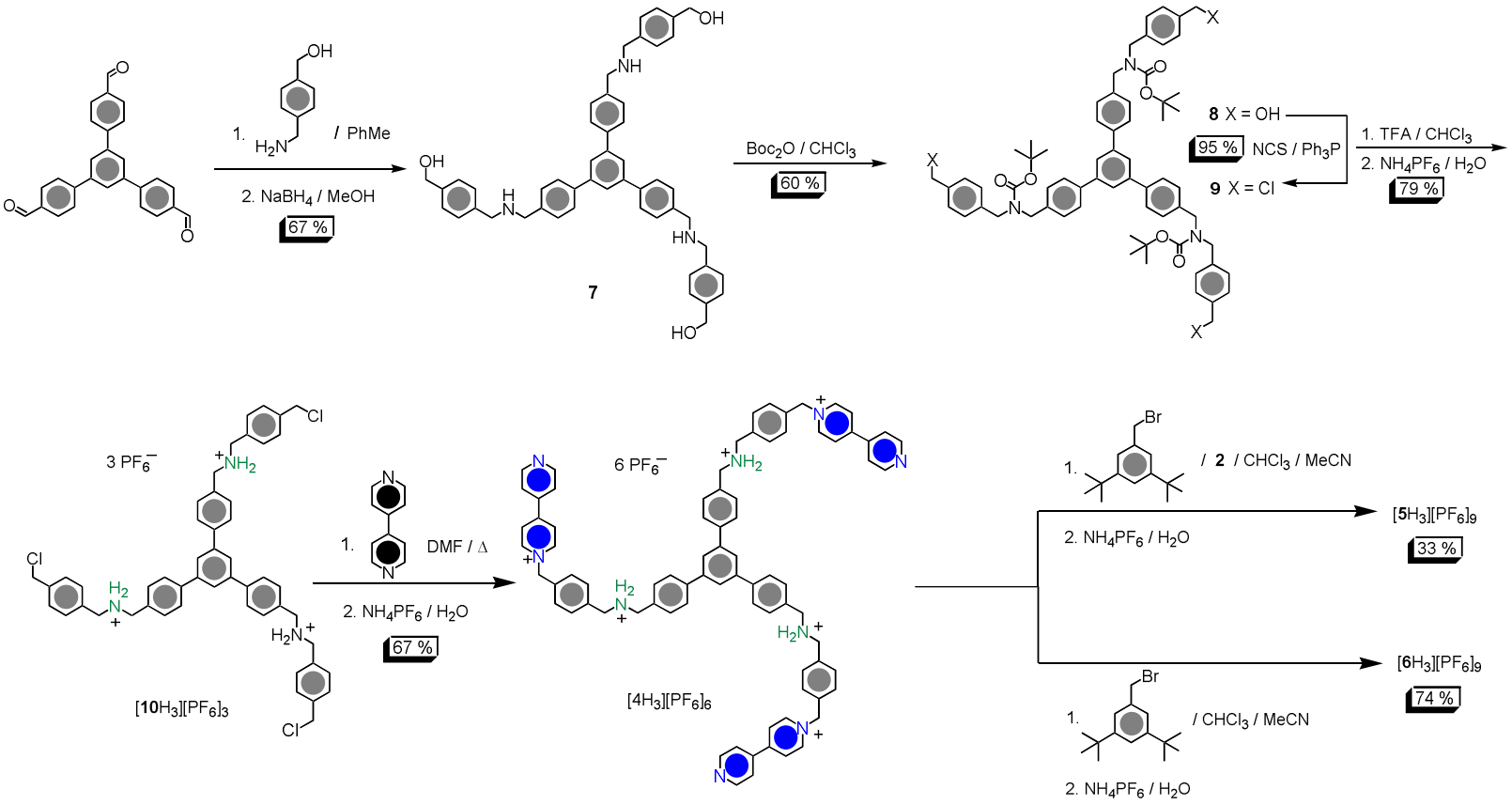
Supporting Material

Synthesis and characterization

The syntheses of the molecular elevator [**5**H_3][PF_6]$_9$ and the control compound [**6**H_3][PF_6]$_9$ were completed (Scheme S1) in seven steps in 7 and 15 % yields, respectively, overall. 1,3,5-Tris(*p*-formylphenyl)benzene was condensed with (4-aminomethyl-phenyl)-methanol and the imine reduced ($NaBH_4$/MeOH) to the trisamine **7**, which was Boc-protected to afford the triol **8** that was subsequently converted (NCS/Ph_3P/THF) to the trischloride **9**, followed by TFA deprotection in $CHCl_3$ and counterion exchange (NH_4PF_6/MeOH/H_2O) to yield [**10**H_3][PF_6]$_9$. Reacting [**10**H_3][PF_6]$_9$ with 4,4'-bipyridine, followed by counterion exchange (NH_4PF_6/MeOH/H_2O), yielded the trifurcated salt [**4**H_3][PF_6]$_9$, which with and without the crown ether host **2** was converted into the mechanically interlocked molecular elevator [**5**H_3][PF_6]$_9$ and the control compound [**6**H_3][PF_6]$_9$, respectively, on reaction with bulky 3,5-di-*tert*-butylbenzenylbromide.


1. / PhMe
2. NaBH4 / MeOH
67 %
7
Boc2O / CHCl3
60 %
8 X = OH
95 % NCS / Ph3P
9 X = Cl
1. TFA / CHCl3
2. NH4PF6 / H2O
79 %
3 PF6−
[10H3][PF6]3
1. DMF / Δ
2. NH4PF6 / H2O
67 %
6 PF6−
[4H3][PF6]6
1. / 2 / CHCl3 / MeCN
2. NH4PF6 / H2O
[5H3][PF6]9
33 %
[6H3][PF6]9
74 %
1. / CHCl3 / MeCN
2. NH4PF6 / H2O

Scheme S1

General. All chemicals were purchased from Aldrich and were used without further purification. Column chromatography was performed on silica gel 60 (Merck 40-60 nm, 230-400 mesh). Melting points were determined on an Electrothermal 9200 apparatus and reported uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 MHz and Bruker Avance-500 at 500 and 125 MHz. The chemical shift values were expressed as δ values, and the coupling constants values (J) are in hertz. The following abbreviations were used for signal multiplicities: s, singlet; d doublet; t triplet; m multiplet. Fast atom bombardment mass spectrometry (FABMS) was performed on a VG ZAB-SE mass spectrometer equipped with a krypton primary atom beam using a 3-nitrobenzyl alcohol matrix. Electron impact mass spectra (EI-MS) were obtained from a VG Prospec mass spectrometer. Matrix-assisted laser desorption ionization spectra (MALDIMS) were recorded on a PerSeptives Biosystems instrument.

7: A mixture of 4-(aminomethyl)benzyl-alcohol (3.2 g, 23.3 mmol) and 1,3,5-tris(*p*-formylphenyl)benzene (3.0g, 7.7 mmol) was heated in PhMe (100 mL) under reflux overnight, while H_2O was removed through a Dean-Stark trap. The reaction mixture was cooled down in a freezer to –10 ˚C and the resulting suspension filtered to give the imine as a white solid (4.02 g, 74 %). Mp 166 – 168 ˚C; ^{1}H NMR (500 MHz, CD_3SOCD_3) δ 4.50 (d, J = 4.5 Hz, 6H), 4.81 (s, 6H), 5.17 (br, 3H), 7.32 (m, 12 H), 7.92 (d, J = 8.0 Hz, 6H), 8.01 (m, 9H), 8.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 64.7, 65.0, 125.4, 127.1, 127.4, 128.1, 128.8, 135.4, 138.6, 139.6, 141.7, 143.0, 161.5; HRMS (MALDI) *m/z* calcd for $C_{51}H_{46}N_3O_3$ 748.3534 $[M + H]^+$, found 748.3578. $NaBH_4$ (1.02 g, 26.8 mmol) was added portionwise to a solution of this white solid in dry MeOH (100 mL) and dry THF (100

mL),. After the reaction had been left to stir overnight, the solvent was removed in vacuo. The resulting solid was partitioned between THF (150 mL) and brine (100 mL). The aqueous phase was washed with THF (100 mL). The organic phases were combined, dried ($MgSO_4$) and the solvent removed in vacuo to give **7** as a yellow liquid (3.6 g, 90 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.74 (s, 6H), 3.77 (s, 6H), 4.50 (s, 6H), 7.22 (d, J = 8 Hz, 6H), 7.43 (d, J = 8 Hz, 6H), 7.67 (d, J = 8 Hz, 6H), 7.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 50.7, 50.9, 61.9, 123.3, 124.2, 124.9, 125.7, 126.5, 129.1, 137.6, 138.6, 139.4, 140.2; HRMS(MALDI) *m/z* calcd for $C_{51}H_{52}N_3O_3$ 754.4003 $[M + H]^+$, found 754.3147.

8: The tris-amine **7** (2.7 g, 3.6 mmol) was dissolved in $CHCl_3$ (450 mL) and then di-*tert*-butyl dicarbonate (7.9 g, 36.1 mmol) was added. The reaction mixture was left to stir for 24 h, before being washed with 2M HCl aqueous solution (2 x 200 mL), and H_2O (200 mL). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to yield crude product that was subsequently purified by column chromatography (SiO_2: CH_2Cl_2/MeOH, 95:5) to yield **8** (2.3 g, 60 %). Mp 68 – 70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (s, 27H), 4.45 (br., 12H), 4.71 (s, 6H), 7.20 – 7.34 (m, 6H), 7.35 (d, J = 8 Hz, 6H), 7.66 (d, J = 8 Hz, 6H), 7.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.4, 48.7, 48.9, 65.0, 80.2, 124.8, 127.2, 127.4, 127.6, 127.9, 128.2, 128.4, 137.2, 139.9, 141.9, 155.9; HRMS(MALDI) *m/z* calcd for $C_{66}H_{75}N_3O_9Na^+$ 1076.5401 $[M + Na]^+$, found 1076.5425.

9: Tiphenylphosphine (4.1 g, 15.8 mmol) in THF (100 mL) was added to *N*-chlorosuccinimide (2.4 g, 18.1 mmol) in THF (100 mL) under an argon atmosphere, to form a white suspension. The tris-alcohol **3** (2.0 g, 1.9 mmol) dissolved in THF (40 mL) was then slowly added, and the reaction mixture was left to stir overnight. The solvent was

evaporated and the product purified by column chromatography (SiO_2: hexanes/EtOAc, 7:3). The product **9** was obtained as an off-white solid (2.0 g, 95 %). Mp 62 – 64 ˚C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57 (s, 27H), 4.45 (s, 6H), 4.52 (s, 6H), 4.65 (s, 6H), 7.22 – 7.40 (m, 12H), 7.42 (d, J = 8 Hz, 6H), 7.71 (d, J = 8 Hz, 6H), 7.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.5, 46.0, 48.9, 49.2, 80.3, 125.0, 127.5, 127.8, 128.5, 128.9, 136.6, 137.4, 138.4, 140.1, 142.0, 156.0; HRMS(MALDI) *m/z* calcd for $C_{66}H_{72}N_3O_6Cl_3Na^+$ 1130.4384 $[M + Na]^+$, found 1130.4398.

$[10H_3][PF_6]_3$: Trifluoroacetic acid (20 mL) was added to the *tert*-boc-protected amine **9** (0.9 g, 0.8 mmol) in $CHCl_3$ (120 mL), and the reaction mixture was stirred at the room temperature for 16 h. The solvent was evaporated off under vacuum, and the residue dissolved in MeOH/Me_2CO (15 mL, 1:1). A saturated solution of NH_4PF_6 in H_2O was added dropwise, followed by H_2O (50 mL). The aqueous phase was extracted with CH_2Cl_2/$MeNO_2$ (100 mL, 5:1), and the organic phase washed with H_2O (3 x 100 mL), dried (Na_2SO_4), and evaporated to yield **$[10H_3][PF_6]_3$** (0.8 g, 79 %) as a white solid. Mp 142 – 145 ˚C; ^{1}H NMR (500 MHz, CD_3CN) δ 4.31 (s, 6H), 4.33 (s, 6H), 4.71 (s, 6H), 7.52 (m, 12H), 7.61 (d, J = 8 Hz, 6H), 7.92 (d, J = 8 Hz, 6H), 7.97 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 45.3, 50.9, 51.0, 125.2, 127.8, 129.2, 130.0, 130.5, 130.6, 130.7, 139.4, 141.3, 141.4; HRMS(MALDI) *m/z* calcd for $C_{51}H_{49}N_3Cl_3^+$ 808.2992 $[M - PF_6 - 2HPF_6]^+$, found 808.3099.

$[4H_3][PF_6]_6$: 8· $3PF_6$ (0.5 g, 0.4 mmol), dissolved in DMF (10 mL), was added dropwise over 2 h to a solution of 4,4'-bipyridine (1.6 g, 10.0 mmol) in anhydrous DMF (43 mL) under argon atmosphere at 100 ˚C. The reaction mixture was then left to stir at 100 ˚C for

additional 70 h. The solvent was removed in vacuo, and the remaining solid was washed with hexanes/CH_2Cl_2 (5 x 100 mL, 1:1) and then dissolved in a small volume of MeOH (10 mL). A saturated solution of NH_4PF_6 in H_2O was added dropwise, followed by H_2O (100 mL). The aqueous phase was extracted with CH_2Cl_2/$MeNO_2$ (70 mL, 1:1), and the organic phase washed with H_2O (4 x 100 mL), dried (Na_2SO_4), and evaporated to yield **$[4H_3][PF_6]_6$** (0.6 g, 67 %) as a yellow solid. Mp 250 ˚C (decomposition); ^{1}H NMR (500 MHz, CD_3CN) δ 4.32 (s, 6H), 4.33 (s, 6H), 5.78 (s, 6H), 7.54 (d, J = 8.5 Hz, 6H), 7.59 (m, 12H), 7.78 (dd, J^1 = 1.5 Hz J^2 = 4.5Hz, 6H), 7.89 (d, J = 8.5 Hz, 6H), 7.95 (s, 3H), 8.32 (d, J = 7.0 Hz, 6H), 8.30 (m, 12H); ^{13}C NMR (125 MHz, CD_3CN) δ 50.8, 51.1, 63.4, 121.7, 125.2, 126.2, 127.7, 129.5, 129.9, 130.7, 131.1, 132.1, 134.3, 140.9, 141.3, 141.4, 144.9, 151.0, 154.7; HRMS(MALDI TOF) *m/z* calcd for $C_{81}H_{73}N_9F_{12}P_2$ 1461.5267 $[M - 2PF_6 - 2HPF_6]^+$, found 1461.1137.

$[6H_3][PF_6]_9$: 3,5-Di-*tert*-butyl benzylbromide (0.16g, 0.60 mmol) was added to **$[4H_3][PF_6]_6$** (0.05g, 0.02 mmol) in a $CHCl_3$/MeCN solution (3.5 mL, 4:3) under argon atmosphere. The temperature was raised to 75 ˚C and the reaction mixture subsequently stirred for additional 48 h. The solvent was evaporated off and the product purified by column chromatography (SiO_2: MeOH/2M NH_4Cl_{aq}/$MeNO_2$, 7:2:1). The excess of $MeNO_2$ and MeOH were then removed in vacuo, such that the product still remained in solution and a saturated aqueous solution of NH_4PF_6 was added dropwise. The aqueous phase was extracted with CH_2Cl_2/$MeNO_2$ (50 mL, 1:3), and the organic phase washed with H_2O (3 x 100 mL), dried (Na_2SO_4), and evaporated to yield **$[6H_3][PF_6]_9$** as a yellow solid. (0.75 g, 74 %). Mp 198 – 200 ˚C; ^{1}H NMR (500 MHz, CD_3CN) δ 1.32 (s, 54H), 4.31 (br., 12H), 5.76

(s, 6H), 5.86 (s, 6H), 7.41 (d, *J* = 1 Hz, 6H), 7.56 (d, *J* = 8 Hz, 6H), 7.59 (t, *J* = 1 Hz, 3H), 7.61 (m, 12H), 7.92 (d, *J* = 8 Hz, 6H), 7.97 (s, 3H), 8.36 (d, *J* = 7 Hz, 6H), 8.39 (d, *J* = 7 Hz, 6H), 8.96 (d, *J* = 7 Hz , 6H), 8.99 (d, *J* = 7 Hz , 6H); ^{13}C NMR (125 MHz, CD_3CN) δ 30.3, 34.6, 50.9, 51.2, 64.0, 65.3, 123.7, 124.0, 124.9, 127.4, 127.6, 127.7, 129.6, 130.6, 131.0, 132.3, 134.4, 141.3, 141.4, 145.6, 145.9, 150.2, 150.6, 152.3, (two aromatic signals are overlapping); MS(FAB) *m/z* $[M]^+$ 3087.7.

$[5H_3][PF_6]_9$: 3,5-Di-*tert*-butyl benzylbromide (0.17g, 0.60 mmol) was added to a $CHCl_3$/MeCN (3 mL, 2:1) solution of **$[4H_3][PF_6]_6$** (0.05g, 0.02 mmol) and **2** (0.04g, 0.02mmol) under argon atmosphere. The temperature was then raised to 75 ˚C and the reaction mixture subsequently stirred for additional 48 h. The solvent was evaporated, and the crude product purified by column chromatography (SiO_2: MeOH/2M NH_4Cl_{aq}/$MeNO_2$, 7:2:1). The excess of $MeNO_2$ and MeOH was then removed in vacuo such that the product still remained dissolved and a saturated solution of NH_4PF_6 in H_2O was added dropwise. The aqueous phase was extracted with CH_2Cl_2/$MeNO_2$ (50 mL, 1:3), and the organic phase washed with water (3 x 100 mL), dried (Na_2SO_4), and evaporated to yield **$[5H_3][PF_6]_9$** (0.03 g, 33 %) as a dark greenish solid. ^{1}H NMR (500 MHz, CD_3CN) δ 1.31 (s, 54H), 3.63 – 4.32 (m, 66H), 4.58 (m, 6H), 4.80 (m, 6H), 4.93 (m, 6H), 5.74 (s, 6H), 5.77 (s, 6H), 6.86 (m, 6H), 6.90 (m, 6H), 7.38 (s, 6H), 7.39 (d, *J* = 1 Hz, 6H), 7.44 (s, 3H), 7.46 (d, *J* = 8 Hz, 6H), 7.57 (t, *J* = 1 Hz , 3H), 7.62 (m, 12H), 7.68 (d , *J* = 8.5 Hz, 6H), 8.36 (d, *J* = 7 Hz, 6H), 8.39 (t, *J* = 7 Hz , 6H), 8.91 (d, *J* = 7 Hz , 6H), 8.97 (d , *J* = 7 Hz, 6H); ^{13}C NMR (125 MHz, CD_3CN) δ 30.3, 34.6, 50.9, 51.0, 63.9, 65.3, 67.3, 67.4, 70.4, 70.4, 70.5, 71.7, 104.5, 112.2, 121.0, 121.1, 122.7, 123.7, 124.2, 125.8, 127.3, 127.4, 129.5, 129.7, 129.9, 130.2,

131.7, 133.2, 134.7, 137.3, 138.2, 145.2, 145.5, 146.2, 147.6, 149.9, 150.4, 152.4; HRMS(ESI) *m/z* calcd for $C_{198}H_{234}N_9O_{24}P_6F_{36}^{3+}$ 1330.5067 $[M - 3PF_6]^{3+}$, found 1330.5019.

Experimental Methods

Electrochemical measurements. Electrochemical experiments were carried out by employing cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques on argon-purged acetonitrile (Romil HiDry™) solutions at room temperature, with an Autolab 30 multipurpose instrument interfaced to a PC. The working electrode was a glassy carbon electrode (Amel; 0.07 cm^2); its surface was routinely polished with a 0.3 μm alumina-water slurry on a felt surface, immediately prior to use. The counter electrode was a Pt wire, separated from the solution by a frit; an Ag wire was employed as a quasi-reference electrode, and ferrocene was present as an internal standard. The concentration of the compounds examined was 4×10^{-4} M; tetraetylammonium hexafluorophosphate (TEAP) 0.04 M was added as supporting electrolyte. Cyclic voltammograms were obtained at sweep rates varying from 20 mV/s to 1 V/s; differential pulse voltammograms were recorded at sweep rates of 20 and 4 mV/s with a pulse height of 75 or 10 mV, respectively, and a duration of 40 ms. The potential window examined was from –2 to +2 V versus SCE. The experimental error on the potential values was estimated to be 10 mV. The diffusion coefficient and the number of exchanged electrons were determined by chronoamperometric experiments with the method reported by Bard et al. (*S1*). In such

experiments, a Pt disk ultramicroelectrode (25 μm radius) was employed as the working electrode.

Absorption and luminescence spectra. The absorption and luminescence spectra were recorded with a Perkin Elmer λ40 spectrophotometer and a LS 50 spectrofluorimeter, respectively, on air equilibrated acetonitrile (Merck Uvasol™) solutions at room temperature, with concentrations ranging from 4×10^{-6} to 1×10^{-4} M. Solutions were examined in 1-cm spectrofluorimetric and 4-cm spectrophotometric quartz cells. The experimental error on the wavelength values was estimated to be ±1 nm.

Molecular modeling. Molecular modeling was carried out both by inspection of a physical CPK model and molecular mechanics calculations. The latter were performed by employing the MM3 force field as implemented in the Tinker 4.0 package (Copyright 1990-2003 Dr. J.W. Ponder, Biochemistry and Molecular Biophysics, Washington University School of Medicine, St. Louis, MO). The model of the molecular elevator, $[\mathbf{5}H_3]^{9+}$, was constructed from the crystal structure of its parent supramolecular bundle, $[\mathbf{2}\cdot\mathbf{3}H_3]^{3+}$ (*S2*), by adding 4,4'-bipyridinium and 3,5-di-tert-butyl groups to each leg of the $[\mathbf{3}H_3]^{3+}$ component. Such a structure was then energy-minimized until a gradient lower than 0.1 kcal/mol/Å had been reached. The models of the various deprotonated forms of the molecular elevator were obtained from that of $[\mathbf{5}H_3]^{9+}$ after removal of the proton(s) from the ammonium unit(s) and manual displacement of the corresponding crown ether loop(s)

to surround the bipyridinium unit(s). The so-obtained structures were then energy-minimized as described above.

Mechanochemical Considerations

The energies and forces developed in the acid/base-controlled operation of the molecular elevator can be evaluated from the thermodynamic parameters determined experimentally with the voltammetric measurements.

In the forthcoming discussion, as well as in the main text, we refer to *upper* and *lower* positions of the platform of the molecular elevator. Since no fixed reference system can be identified for molecules in solution, only the relative position of the platform with respect to the rig component within the molecular elevator can be considered. If we arbitrarily take the 3,5-di-*tert*-butylbenzyl feet and the triphenylbenzene core of the rig component respectively as bottom and top of the molecular elevator, we can define the upper level as the one in which the platform is located at the maximum distance from the feet. Accordingly, the lower level is the one in which the platform is closer to the feet.

Base stroke (Upper-to-lower level motion). The driving force for the motion of the platform from the upper to the lower level upon deprotonation of the $–NH_2^+–$ centres of $[\mathbf{5}H_3]^{9+}$ is provided by the electron donor/acceptor interactions between the electron-donor units of the platform and the $BIPY^{2+}$ electron-acceptor units of the rig. A thermodynamic

cycle involving the reduction of the $BIPY^{2+}$ units in the *fully deprotonated elevator species* can be considered (Figure S1).

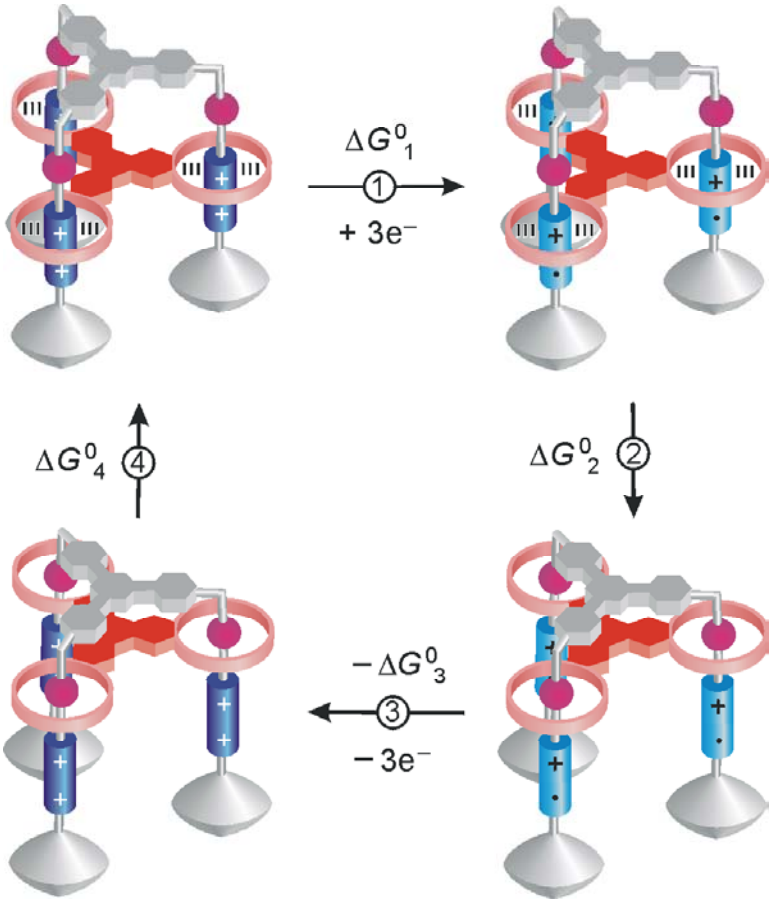


Figure S1. Thermodynamic cycle involving the first three-electron reduction process of the fully deprotonated molecular elevator, **5**$^{6+}$.

$$\Delta G^0_1 + \Delta G^0_2 - \Delta G^0_3 + \Delta G^0_4 = 0$$

Horizontal and vertical processes in Figure S1 correspond to redox reactions and co-conformational rearrangements (molecular motions), respectively. The thermodynamic quantity of interest is the free energy change for the upper-to-lower level motion (process 4), ΔG^0_4. Process 1 corresponds to the one-electron reduction of the three bipyridinium

units, each surrounded by a crown ether loop, while process 3 refers to the one-electron oxidation of the three "free" bipyridinium radical cation units, i.e., not surrounded by the crown ethers.

ΔG^0_1 can be easily determined from the halfwave redox potential for the reduction of the bipyridinium units in the fully deprotonated molecular elevator, $\mathbf{5}^{6+}$, whereas ΔG^0_3 can be calculated from the halfwave redox potential for the reduction of the bipyridinium units in the fully deprotonated model $\mathbf{6}^{6+}$:

$$\Delta G^0_1 = -nFE^0_{\text{elevator}} = -3 \cdot 9.648\times10^4 \text{ C/mol} \cdot (-0.53 \text{ V}) = 153 \text{ kJ/mol}$$

$$\Delta G^0_3 = -nFE^0_{\text{model}} = -3 \cdot 9.648\times10^4 \text{ C/mol} \cdot (-0.35 \text{ V}) = 101 \text{ kJ/mol}$$

Process 2 is related to the stabilization offered to the crown ether loops of the platform by the one-electron reduced bipyridinium units of the rig. Indeed, the electrochemical data for $\mathbf{5}^{6+}$ indicate that the $BIPY^{\bullet+}$ radical cations are still involved in electron donor/acceptor interactions, since the redox potential value for the uptake of a second electron by each of the $BIPY^{\bullet+}$ units is more negative than that for the same process in the model rig $\mathbf{6}^{6+}$ (Figure 3A). ΔG^0_2 can be estimated from a thermodynamic cycle identical to that described above, but involving the second one-electron reduction of the bipyridinium units. Since the fully reduced BIPY units are no longer electron acceptors, it is reasonable to assume that the free energy change corresponding to their interaction with the electron-donor units of the platform is negligible. It can thus be calculated that $-\Delta G^0_2 \approx -35$ kJ/mol, and that the energy available in the upper-to-lower level movement (base stroke) is

$$\Delta G^0_{\text{down}} = \Delta G^0_4 = -\Delta G^0_1 - \Delta G^0_2 + \Delta G^0_3 = -153 - 35 + 101 = -87 \text{ kJ/mol} = -21 \text{ kcal/mol}$$

Since the free energy change represents the amount of useful work, W, that can be obtained from a chemical process, and considering the motion of the platform as the one-dimensional displacement of a rigid component for a distance d (=0.7 nm, see the text), the maximum force that can be generated in the base stroke is given by the following equation (where N_A is Avogadro's constant):

$$F_{\text{max,down}} = \frac{W_{\text{max},down}}{d} = \frac{-\Delta G^0_{down}}{d} \cdot \frac{1}{N_A} = \frac{87 \times 10^3}{0.7 \times 10^{-9}} \cdot \frac{1}{6.022 \times 10^{23}} = 2.0 \times 10^{-10} \text{ N} = 200 \text{ pN}$$

Acid stroke (Lower-to-upper level motion). The driving force for the motion of the platform from the lower to the upper level after reprotonation of the amine centres of $\mathbf{5}^{6+}$ to give back $[\mathbf{5}H_3]^{9+}$ can be straightforwardly estimated by examining the equilibrium between the two co-conformations of the fully protonated molecular elevator, $[\mathbf{5}H_3]^{9+}$ (Figure S2).

As pointed out in the main text, $[\mathbf{5}H_3]^{9+}$ exists exclusively in the co-conformation in which the platform is located at the upper ($-NH_2^+-$) level. The alternative co-conformation, in which the platform is positioned at the lower ($BIPY^{2+}$) level, could not be evidenced either by NMR spectroscopy or by voltammetry. The presence of such a co-conformation would be easily detected in voltammetric experiments, owing to the shift of the redox potential of the BIPY units when surrounded by the crown ether loops of the platform. By pushing differential pulse voltammetric measurements to achieve the best sensitivity, we could

establish that the amount of the minoritary co-conformation cannot be larger than 0.1%. Therefore, the thermodynamic constant K for the equilibrium represented in Figure S2 must be larger than 10^3, and the driving force for the lower-to-upper motion is

$$\Delta G^0_{up} = -RT \ln K < -17 \text{ kJ/mol} \approx -4.1 \text{ kcal/mol}$$

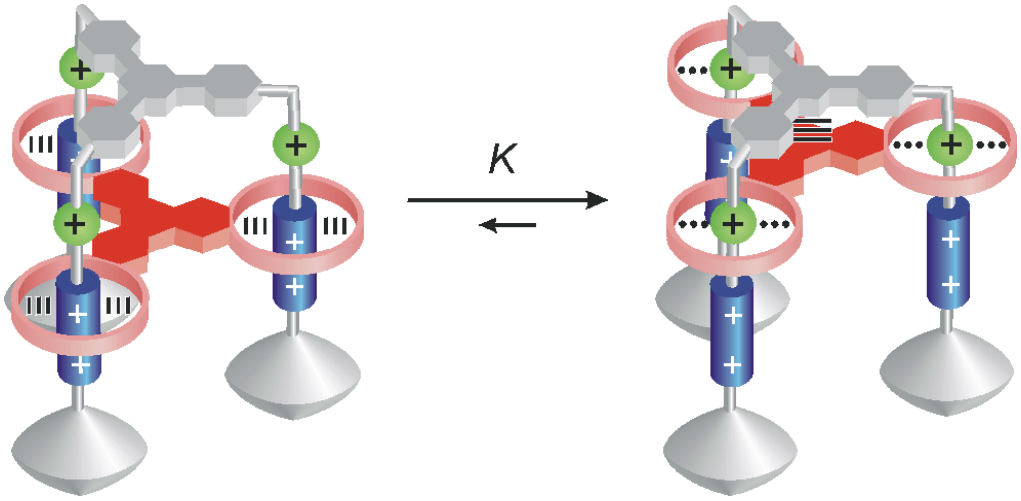


Figure S2. Schematical representation of the chemical equilibrium between the two co-conformations of the fully protonated molecular elevator, $[\mathbf{5}H_3]^{9+}$.

References

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S2. V. Balzani *et al*., *Chem. Eur. J.* **9**, 5348 (2003).