Supporting Information

Revealing Highly Unbalanced Energy Barriers in Extension and Contraction of the Muscle-like Motion of a [c2]Daisy Chain

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Figure and Table Captions

Figure S1. Equilibrated structures in acid and base by SCC-DFTB-D optimizations: (a) Side view of ext^{4+}; (b) Central part of ext^{4+}; (c) Left half of ext^{4+}; (d) Right half of ext^{4+}; (e) Top view of ext^{4+}; (f) Side view of $cont^{2+}$; (g) One ring of $cont^{2+}$; (h) Left half of $cont^{2+}$; (i) Right half of $cont^{2+}$; (j) Top view of $cont^{2+}$. Selected atoms are labeled (some also magnified) and referred to in the text. Gray, white, red, and blue atom colors represent C, H, O, and N, respectively. To clearly illustrate the geometries in the enlarged sections, hydrogen atoms are omitted except for those forming hydrogen bonds and those on amino N. Lengths are given in nm. (Note that the terpyridine and benzene groups in the bulky stoppers are connected by –C≡C– groups, which in this representation incorrectly look like abnormally long single bonds.)

Figure S2. Selected frames in side and top views by SCC-DFTB-D constrained geometry optimizations during the contraction in basic environment (shown with a blue background) and during the extension in acidic environment (pink background). Frame labels 1_b, 1_a, etc., refer to Tables S1 and S2.

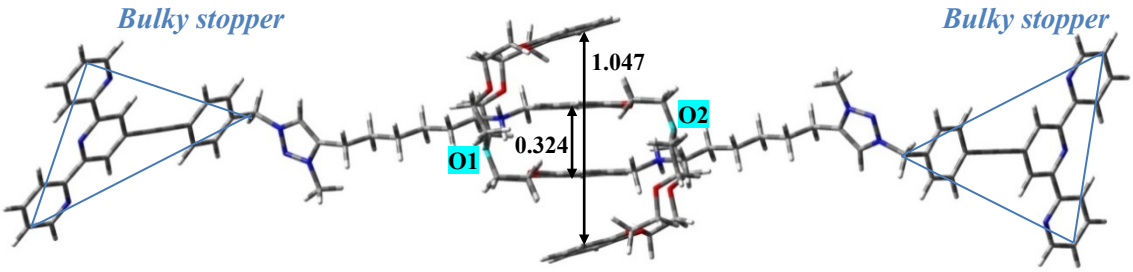
Figure S3. Configurations of (panels a-h) $PF_6^-(CH_3CN)_n$ (n=1-8) and (panels i-p) $PF_6^-(CHCl_3)_n$ (n=1-8) complexes, calculated by ωB97XD/6-31G**. Grey, white, blue, orange, light blue, and green colors represent C, H, N, P, F, and Cl atoms, respectively. To avoid overloading the figures, distances are only labeled when shorter than 3 Å between F of PF_6^- and H/Cl of $CH_3CN/CHCl_3$ in $PF_6^-(CH_3CN)_n/PF_6^-(CHCl_3)_n$ (n=1-4).

Table S1. Relative total energy and dihedral angle during the contraction in basic environment, as a function of the O1- O2 distance.

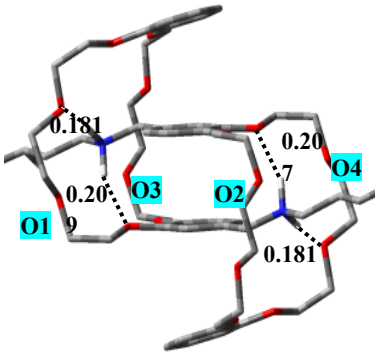
Table S2. As Table S1, but for stretching in acidic environment.

Table S3. Average potential energy E_{pot}, temperature T and their root mean square deviations (RMSD) in the time period of 900-1000 fs during SCC-DFTB-D/MD simulations in solution.

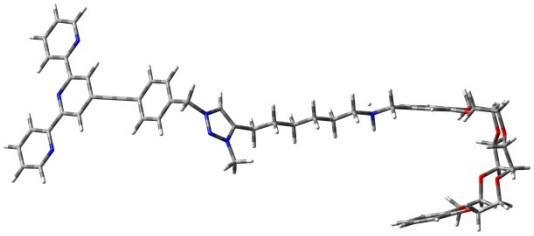
Movie S1. An animation is provided of the detailed model of the full contraction and elongation cycle of the [c2] daisy chain.



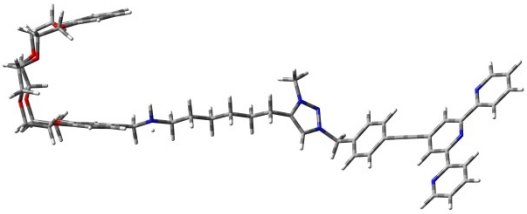
(a) Side view of ext^{4+}



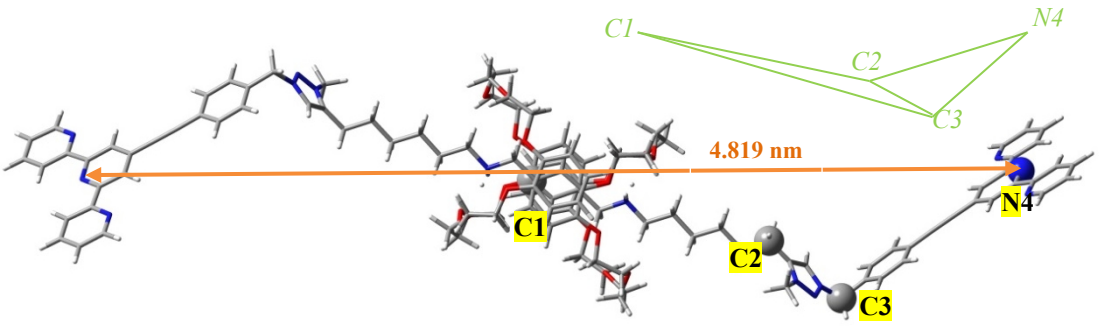
(b) Central part of ext^{4+}



(c) Left half of ext^{4+}

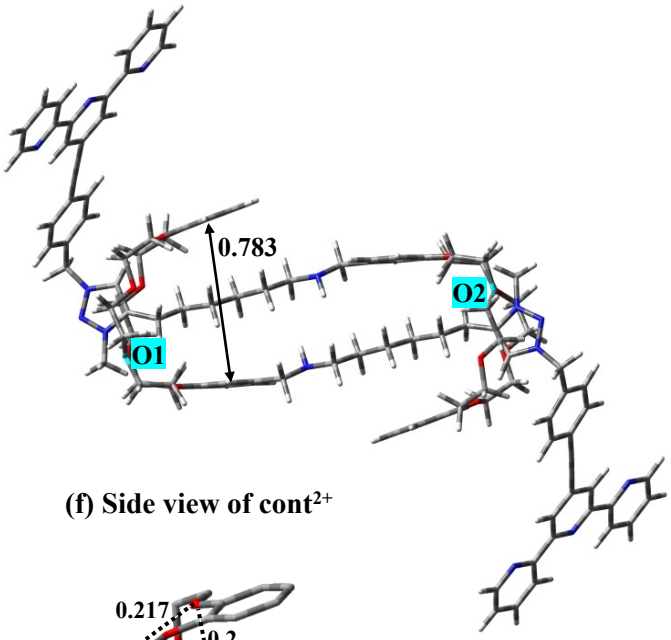


(d) Right half of ext^{4+}

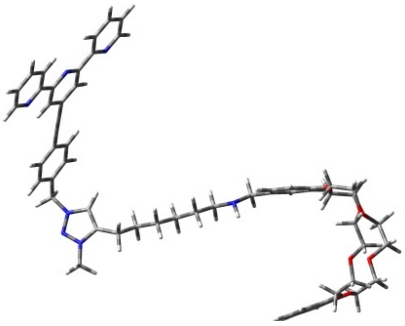


Dihedral angle of C1-C2-C3-N4: 139.6°

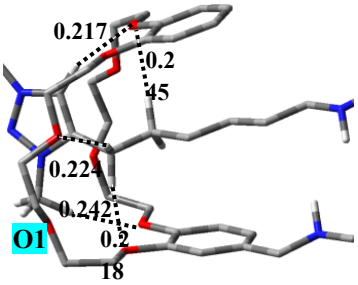
(e) Top view of ext^{4+}



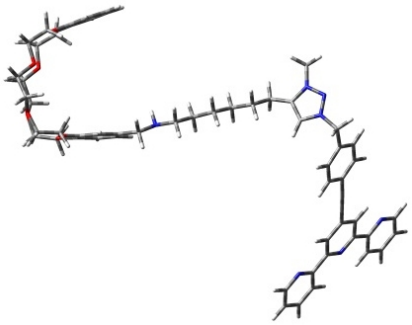
(f) Side view of cont^{2+}



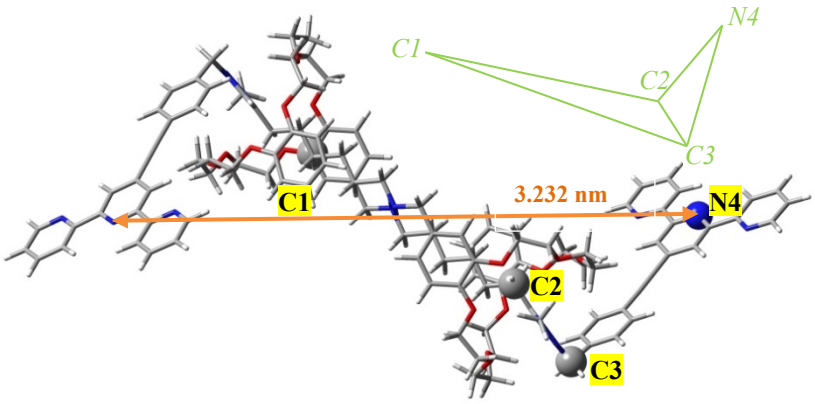
(h) Left half of cont^{2+}



(g) One ring of cont^{2+}



(i) Right half of cont^{2+}

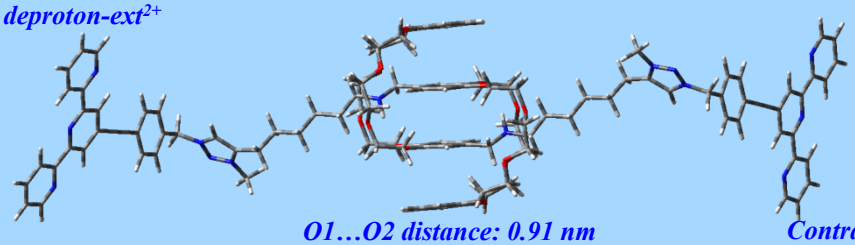


Dihedral angle of C1-C2-C3-N4: 85.0°

(j) Top view of cont^{2+}

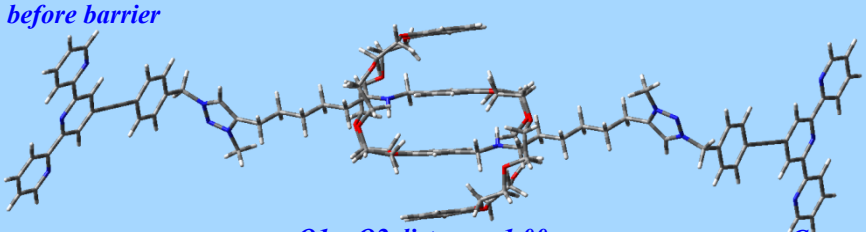
Figure S1

Frame 1_b: deproton-ext^{2+}



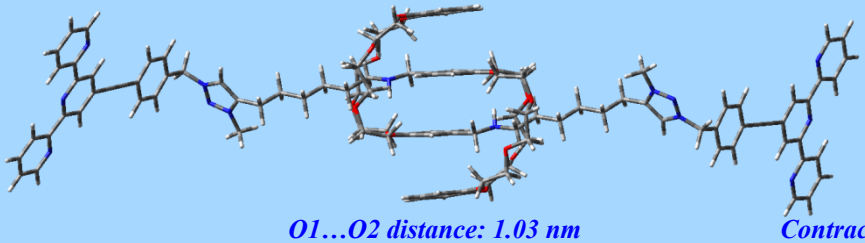
O1…O2 distance: 0.91 nm *Contraction in base*

Frame 4_b: before barrier



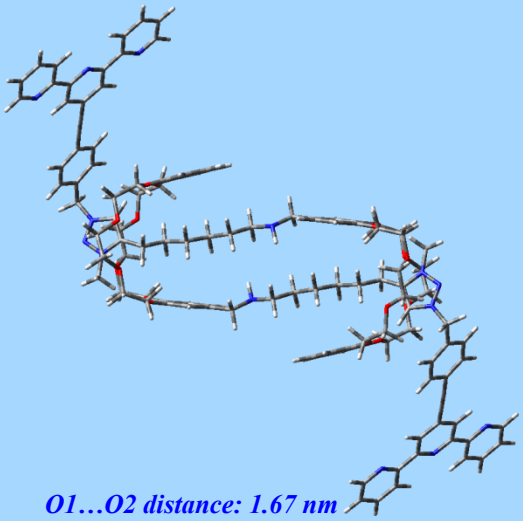
O1…O2 distance: 1.00 nm *Contraction in base*

Frame 5_b: barrier geometry

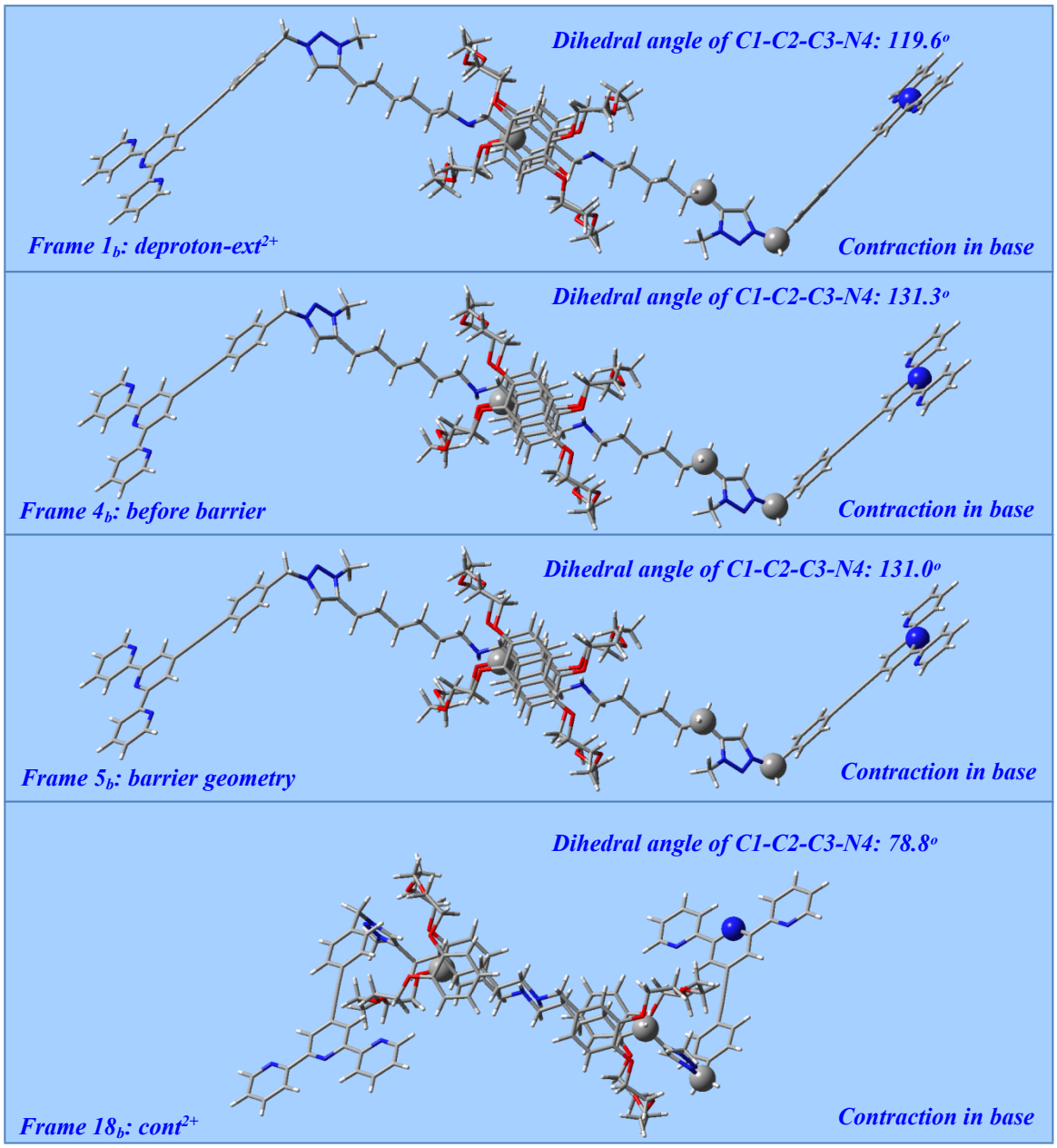


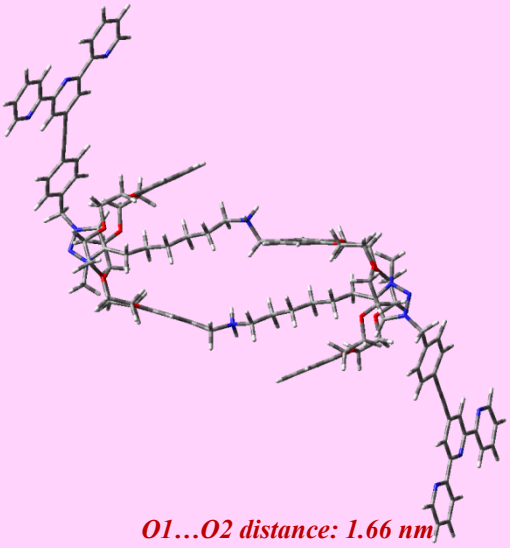
O1…O2 distance: 1.03 nm *Contraction in base*

Frame 18_b: cont^{2+}

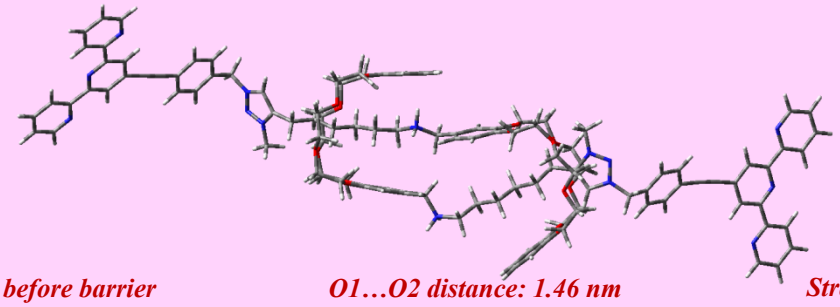


O1…O2 distance: 1.67 nm *Contraction in base*

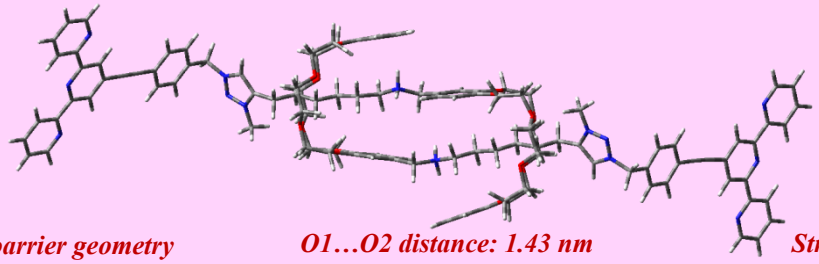

Dihedral angle of C1-C2-C3-N4: 119.6°
Frame 1b: deproton-ext2+
Contraction in base
Dihedral angle of C1-C2-C3-N4: 131.3°
Frame 4b: before barrier
Contraction in base
Dihedral angle of C1-C2-C3-N4: 131.0°
Frame 5b: barrier geometry
Contraction in base
Dihedral angle of C1-C2-C3-N4: 78.8°
Frame 18b: cont2+
Contraction in base



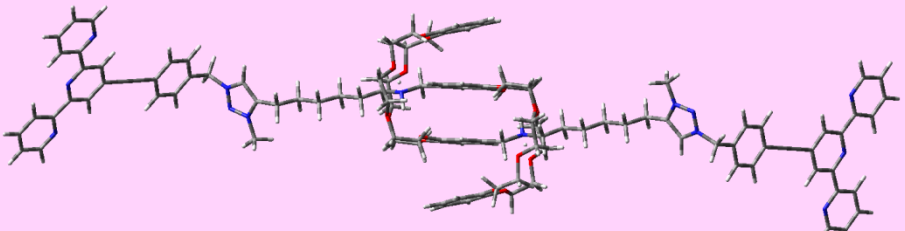
Frame 1_a: proton-cont^{4+} *O1…O2 distance: 1.66 nm* *Stretching in acid*



Frame 6_a: before barrier *O1…O2 distance: 1.46 nm* *Stretching in acid*



Frame 7_a: barrier geometry *O1…O2 distance: 1.43 nm* *Stretching in acid*



Frame 18_a: ext^{4+} *O1…O2 distance: 0.91 nm* *Stretching in acid*

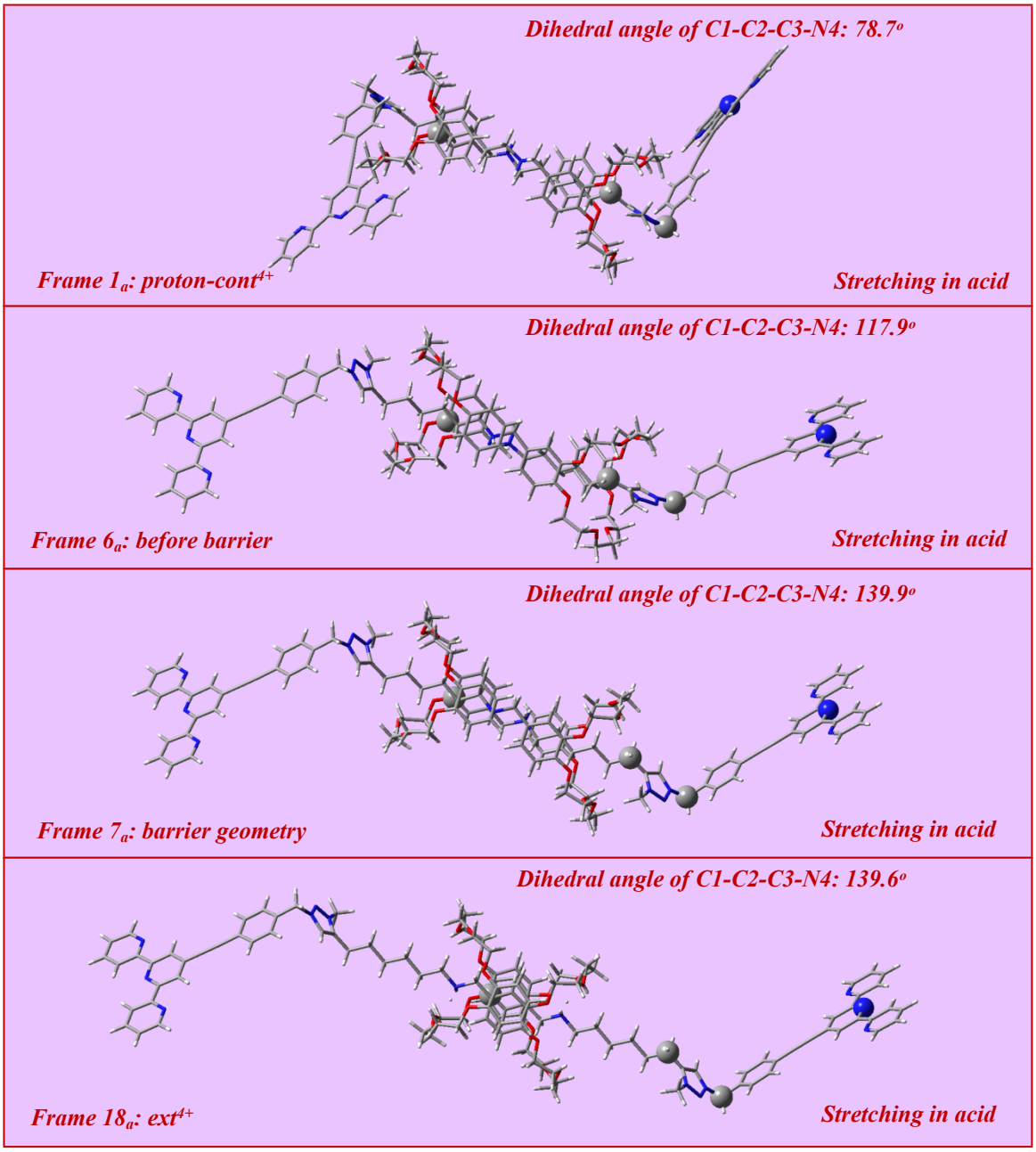
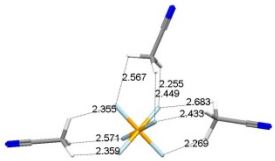

Dihedral angle of C1-C2-C3-N4: 78.7°
Frame 1a: proton-cont4+
Stretching in acid
Dihedral angle of C1-C2-C3-N4: 117.9°
Frame 6a: before barrier
Stretching in acid
Dihedral angle of C1-C2-C3-N4: 139.9°
Frame 7a: barrier geometry
Stretching in acid
Dihedral angle of C1-C2-C3-N4: 139.6°
Frame 18a: ext4+
Stretching in acid

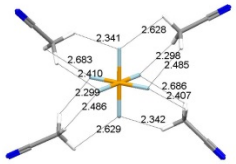
Figure S2

(a) $PF_6^-(CH_3CN)$

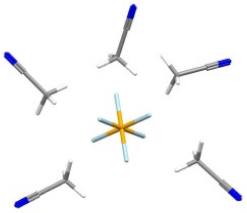
(b) $PF_6^-(CH_3CN)_2$



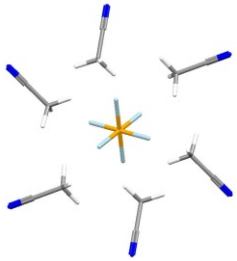
(c) $PF_6^-(CH_3CN)_3$



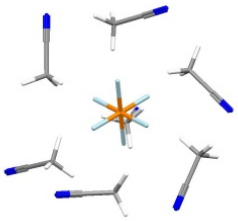
(d) $PF_6^-(CH_3CN)_4$



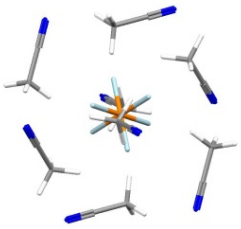
(e) $PF_6^-(CH_3CN)_5$



(f) $PF_6^-(CH_3CN)_6$

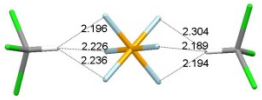


(g) $PF_6^-(CH_3CN)_7$

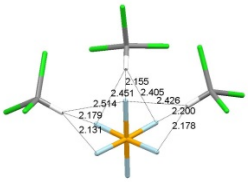


(h) $PF_6^-(CH_3CN)_8$

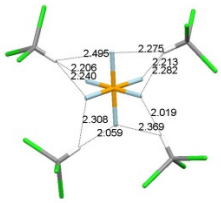
(i) $PF_6^-(CHCl_3)$



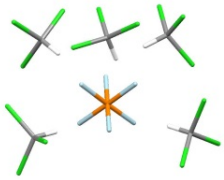
(j) $PF_6^-(CHCl_3)_2$



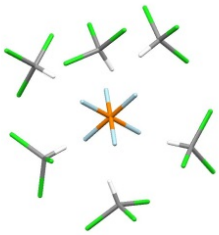
(k) $PF_6^-(CHCl_3)_3$



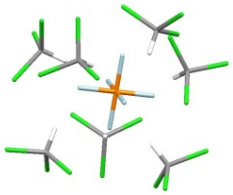
(l) $PF_6^-(CHCl_3)_4$



(m) $PF_6^-(CHCl_3)_5$



(n) $PF_6^-(CHCl_3)_6$



(o) $PF_6^-(CHCl_3)_7$

(p) $PF_6^-(CHCl_3)_8$

Figure S3

Table S1. Relative total energy and dihedral angle during the contraction in basic environment, as a function of the O1 - O2 distance. Energy barriers and reaction heats are shown in bold.

frames in base	O1 - O2 distance (nm)	ΔE_{tot} (kcal/mol)				dihedral angle of C1-C2-C3-N4 (°)
		SCC-DFTB-D	ωB97XD/6-31G**			
		in vac.	in vac.	in CH_3CN	in $CHCl_3$	
	0.85	0.48	1.25	-1.01	-0.65	116.8
	0.90	0.06	0.67	0.34	0.22	119.6
1_b	0.91	0.00	0.17	0.03	0.002	119.6
2_b	0.92	0.02	0.00	0.00	0.00	125.1
3_b	0.95	0.57	0.047	0.28	0.47	118.6
4_b	1.00	3.16	2.95	3.32	3.53	131.3
5_b	1.03	**5.33**	**6.95**	**6.16**	**6.74**	131.0
6_b	1.05	3.86	4.89	1.10	1.80	132.4
7_b	1.10	2.30	3.63	0.80	1.37	133.6
8_b	1.15	-0.48	-5.47	-2.86	-3.25	135.2
9_b	1.20	-2.77	-9.34	-3.20	-4.57	134.4
10_b	1.25	-3.48	-7.31	-0.43	-2.18	133.8
11_b	1.30	-6.84	-8.22	-3.19	-5.61	138.4
12_b	1.35	-10.92	-16.49	-12.55	-14.18	142.1
13_b	1.40	-13.69	-19.71	-15.87	-17.53	142.4
14_b	1.45	-21.80	-28.64	-19.44	-22.17	150.3
15_b	1.50	-25.91	-33.81	-23.66	-26.59	150.9
16_b	1.55	-33.42	-45.65	-28.76	-32.89	109.0
17_b	1.60	-36.83	-50.12	-33.54	-37.97	92.0
18_b	1.67	**-45.05**	**-62.17**	**-40.27**	**-46.19**	78.8
	1.68	-45.01	-61.83	-39.72	-45.71	78.8
	1.70	-44.66	-60.46	-37.93	-44.04	79.0

Table S2. As Table S1, but for stretching in acidic environment.

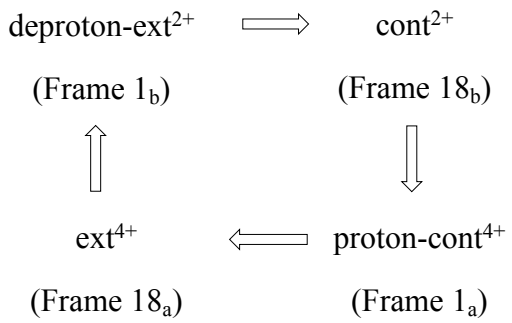
frames in acid	O1 - O2 distance (nm)	ΔE_{tot} (kcal/mol)				dihedral angle of C1-C2-C3-N4 (°)
		SCC-DFTB-D	ωB97XD/6-31G**			
		in vac.	in vac.	in CH_3CN	in $CHCl_3$	
	1.71	2.98	5.04	3.76	1.27	80.2
1_a	1.67	0.51	0.70	0.27	0.47	79.2
2_a	1.66	0.00	0.00	0.00	0.00	78.7
3_a	1.61	1.85	4.58	1.74	1.27	132.2
4_a	1.56	3.06	6.73	4.92	4.26	131.5
5_a	1.51	5.28	9.28	9.34	7.94	127.2
6_a	1.46	8.53	14.14	20.31	18.70	117.9
7_a	1.43	**10.28**	**14.59**	24.39	23.03	139.9
8_a	1.40	8.95	11.49	23.97	21.79	139.4
9_a	1.35	6.79	9.00	28.33	**24.15**	151.2
10_a	1.30	2.91	7.00	29.45	23.80	152.0
11_a	1.25	-10.03	-0.33	**33.12**	22.42	137.0
12_a	1.20	-17.95	-10.21	26.19	15.43	148.0
13_a	1.15	-28.05	-20.59	20.22	7.89	154.3
14_a	1.10	-36.54	-31.32	13.25	-0.39	158.1
15_a	1.05	-40.91	-39.25	7.17	-6.52	140.2
16_a	1.00	-49.25	-47.17	-0.88	-14.11	140.7
17_a	0.95	-53.92	-52.26	-5.59	**-18.61**	140.4
	0.92	-54.82	-52.77	**-6.03**	-18.50	139.6
18_a	0.91	**-54.85**	**-52.81**	-5.99	-18.44	139.6
	0.90	-54.70	-52.74	-5.91	-18.23	140.0
	0.85	-52.08	-49.97	-3.57	-15.73	140.9

Table S3. Average potential energy E_{pot}, temperature T and their root mean square deviations (RMSD) in the time period of 900-1000 fs during SCC-DFTB-D/MD simulations in solution.

rotaxanes in solution	E_{pot} (kcal/mol)	RMSD (E_{pot}) (kcal/mol)	T (K)	RMSD (T) (K)
ext^{4+}	-2001757.81	*27.93*	306.25	*3.96*
proton-$cont^{4+}$	-2001745.67	*30.94*	305.90	*3.86*
$cont^{2+}$	-2001585.15	*28.57*	306.78	*5.51*
deproton-ext^{2+}	-2001553.13	*25.29*	305.34	*5.22*

Movie S1

An animation is provided of the detailed model of the full contraction and elongation cycle of the [c2] daisy chain through four states, starting with deproton-ext^{2+}:



These correspond to the curves in Figure 3 in the main text and data in Table S1-S2 above. The blue/pink background color indicates a basic/acidic environment, respectively.