Supporting Information for

Helicity Control of a Perfluorinated Carbon Chain Confined in a Chiral Supramolecular Cage Monitored by VCD

Authors: Carlo Bravin,[a] Giuseppe Mazzeo,[b] Sergio Abbate,[b] Giulia Licini,[a] Giovanna Longhi,[*,b] and Cristiano Zonta[*,a]

a Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova

b Department of Molecular and Translational Medicine, Università di Brescia, Viale Europa 11, 25123 Brescia, BS, Italy.

*Correspondence to: cristiano.zonta@unipd.it

Correspondence to: giovanna.longhi@unibs.it

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1 General Methods

NMR spectra were recorded at 301 K on Bruker 400 Avance III BBi-z grad 5 mm and Bruker Avance-III 500MHz instruments. All the ^{1}H-NMR spectra were referenced to residual isotopic impurity of DMSO-d_6 (2.50 ppm). The following abbreviations are used in reporting the multiplicity for NMR resonances; s=single, d=doublet, t= triplet, and m=multiplet. The NMR data were processed using Bruker Topspin 3.5 pl2 and MestReNova 12.0.0.

High resolution electrospray ionization mass spectrometry HRMS (ESI-TOF) analyses were performed in positive mode with Waters Xevo G2-S QTof. The analysis was performed with Fast Flow Injection: 10 ul of sample injected ACN at 30 ul/min. Capillary: 3000V, Sample cone: 30V, Source temperature: 80 °C, Desolvation temperature: 250 °C. ECD spectra were recorded with a Jasco J-1500 spectrometer and processed with Spectra Manager Version 2.15.3.1

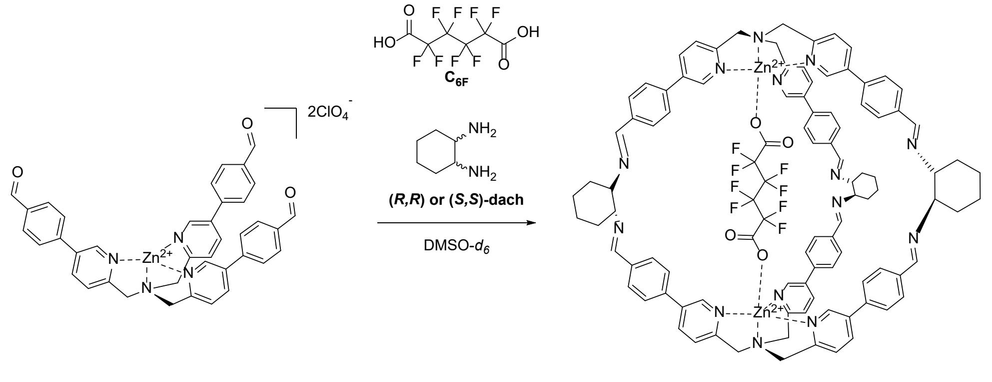
VCD and IR spectra were recorded on a Jasco FVS6000 instrument, equipped with a wire-grid linear polarizer, a ZnSe photo-elastic modulator at 50 kHz frequency and a liquid-N_2 cooled MCT detector. Spectra were recorded 10 mM/DMSO-d_6 solutions contained in 200 μm BaF_2 cells. 5000 scans per spectra were recorded. Solvent spectra were recorded in the same conditions and subtracted from the solution spectra.

DFT and TD-DFT calculations of the diastereomeric structures were carried out Gaussian 16 package[1] Revision B.01 and processed with GaussView 6.0.16[2] or CYL view BETA 1.0. The experimental/theoretical comparison of the ECD spectra were carried out with SpecDis Version 1.71[3]. Optimization and vibrational spectra have been calculated at B3LYP/6-31g(d,p) level with iefpcm solvent model, Lorentzian bandwidth of 16 cm^{-1} have been adopted with a wavenumber scaling factor of 0.97. ECD spectra have been calculated on the same structures adopting the cam-B3LYP functional and Gaussian bandwidth of 0.3 eV.

Chemicals were purchased from Merck, TCI, or Apollo Scientific and used without further purification.

2 Synthesis and Characterization

2.1 Synthesis of Cage C_6F@(*R*,*R*)-1



C_{6F}@(*R'R*)-1

To 500 µl (1.0 µmol) of a solution 0.002 M of complex **1** in DMSO-*d*$_6$, 100 µl (1.0 µmol) of a solution 0.01 M in DMSO-*d*$_6$ of octafluoroadipic acid $\mathbf{C_{6F}}$ and 75 µl (1.5 µmol) of a solution 0.02 M in DMSO-*d*$_6$ of (1*R*,2*R*)-cyclohexanediamine **(*R*,*R*)-dach** or (1*S*,2*S*)-cyclohexanediamine **(*S*,*S*)-dach** were added in a NMR tube. The mixture was left for 12 hour at room temperature and then other 50 µl (1.0 µmol) of chiral diamine solution 0.02 M in DMSO-*d*$_6$ of checked *via* ^{1}H NMR (NMR yield>90% determined with internal standard *p*-xylene).

The procedure is the same adopted for the preparation of higher concentration samples. The concentration of starting complex solution are 0.01, 0.02 and 0.03 mM respectively for cage 5 mM, 10 mM and 15 mM, and the stock solution for the chiral diamine and $\mathbf{C_{6F}}$ are respectively 0.2 M and 0.1 M.

^{1}H-NMR (400 MHz, (DMSO-*d*$_6$) δ (ppm): 9.12 (s, 6H, *J*=2.0 Hz PyrH), 8.48 (s, 6H, NH$_{imm}$), 8.43 (d, 6H, *J*=8.0 Hz, *J*=2.0 Hz, PyrH), 7.97 (d, 12H, *J*=8.5 Hz, ArH), 7.72 (m, 12H+6H, *J*=8.0 Hz, PyrH), 4.51 (s, 12H, CH$_2$), 3.18 (s, 6H, CH-dach) 1.76 (m, 12H, CH$_2$-dach), 1.38 (s, 6H, CH$_2$-dach). ESI-MS: *m/z*: calcd for $[C_{102}H_{90}F_8N_{14}Zn_2]^{2+}$ 929,7 $[M]^{2+}$ found 929,2 $[M]^{2+}$. FT-IR (optical path: 0,1 mm, DMSO-*d*$_6$): 1690 cm^{-1} ($\nu_{C=O}$, *s*), 1360 cm^{-1} ($\nu_{C\text{-}O}$, *w*), 1170 cm^{-1} ($\nu_{C\text{-}F}$, *m*). VCD (optical path: 0,1 mm, DMSO-*d*$_6$): 1700 cm^{-1} ($\nu_{C=O}$, *s*), 1370 cm^{-1} ($\nu_{C\text{-}O}$, *w*), 1160 cm^{-1} ($\nu_{C\text{-}F}$, *w*).

3 NMR and ESI-MS characterization

3.1 $C_6F@(\textbf{\textit{R}},\textbf{\textit{R}})$-1

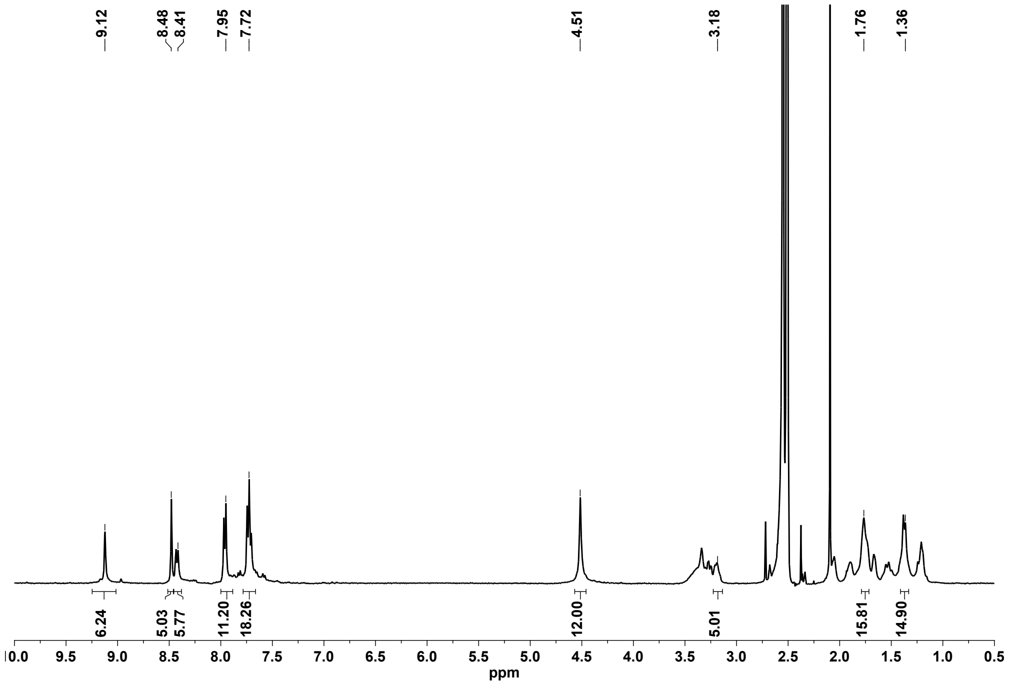


Figure S_3.1A ^{1}H-NMR spectrum (400 MHz, 301 K, DMSO-d_6) of cage $\mathbf{C_6F@(\textit{R},\textit{R})\text{-}1}$.

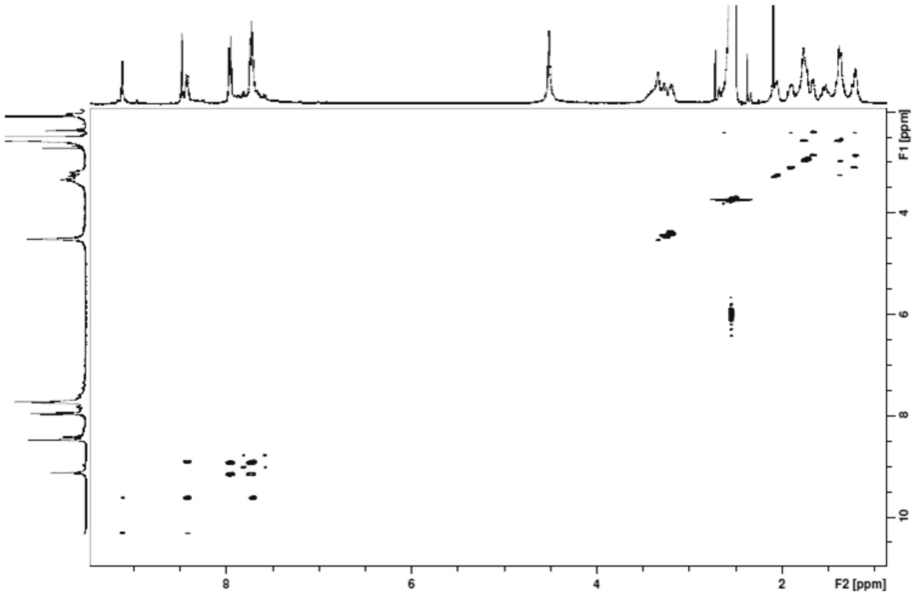


Figure S_3.1B ^{1}H-^{1}H COSY spectrum (500 MHz, 301 K, DMSO-d_6) of cage $\mathbf{C_6F@(\textit{R},\textit{R})\text{-}1}$.

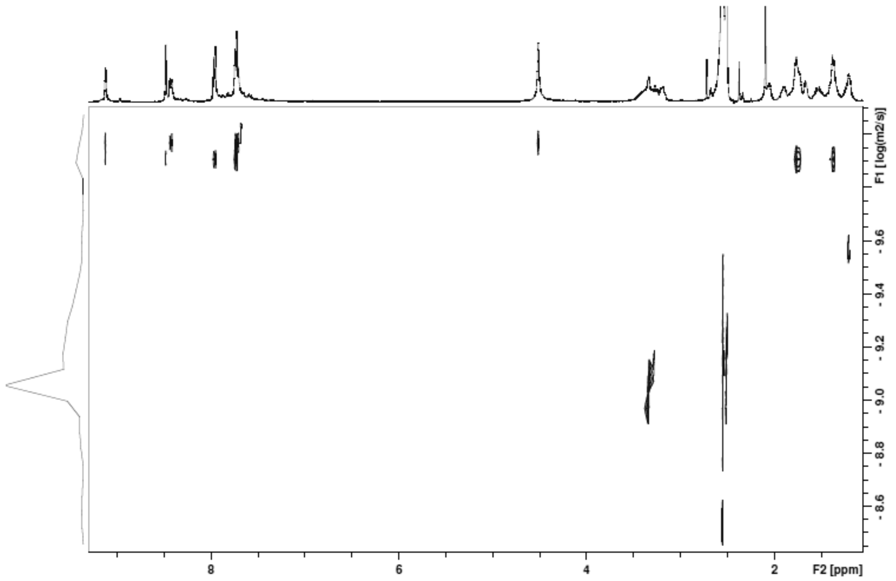


Figure S_3.1C DOSY spectrum (400 MHz, 301 K, DMSO-d_6) of cage **C_6F@(*R*,*R*)-1**. The diffusion coefficient corresponding hydrodynamic radius (r_H) was calculated to be 9.5±0.4 Å by using the Stokes-Einstein equation.[4,5]

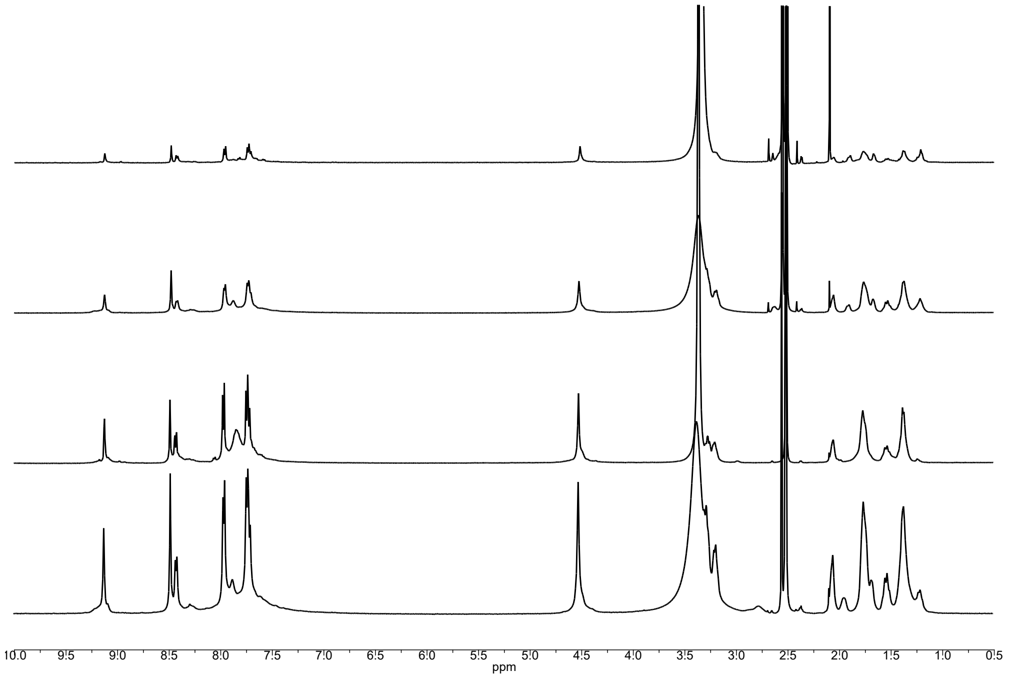


Figure S_3.1D ^{1}H NMR (400 MHz, 301 K, DMSO-d_6) of cage **C_6F@(*R*,*R*)-1**. The cage was synthesized at different final concentrations (a top, d bottom). a) 1 mM, b) 5 mM c) 10 mM d) 15 mM. The cage formation and the characteristic peaks are confirmed in each synthesis attempt.

3.2 $C_6F@(\mathit{S,S})$-1

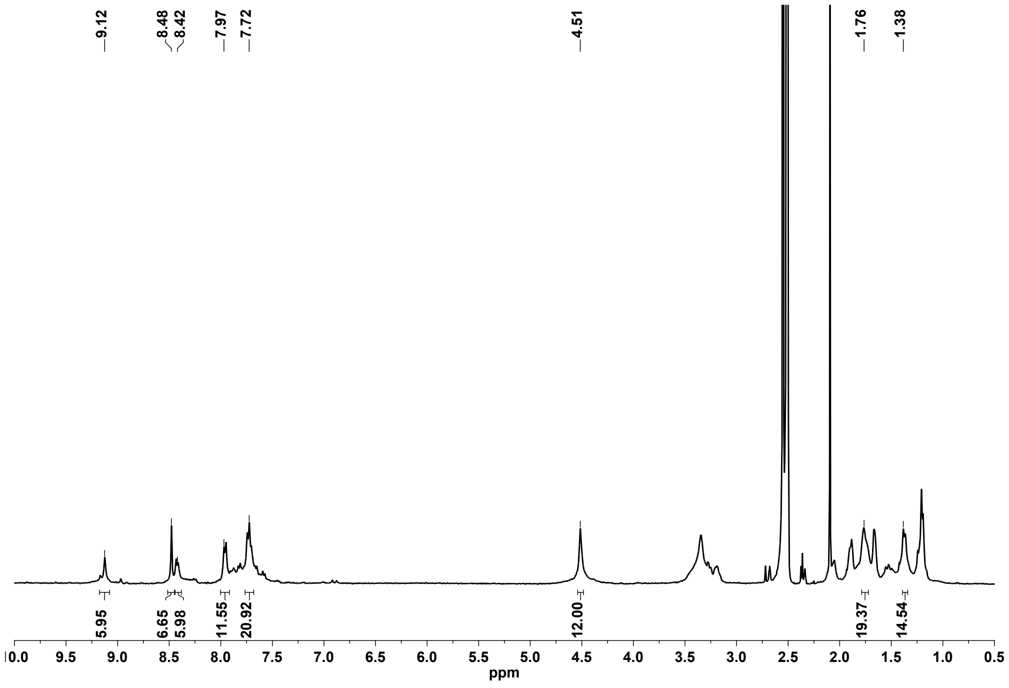


Figure S_3.2A ^{1}H-NMR spectrum (500 MHz, 301 K, DMSO-d_6) of cage **$C_6F@(\mathit{S,S})$-1**.

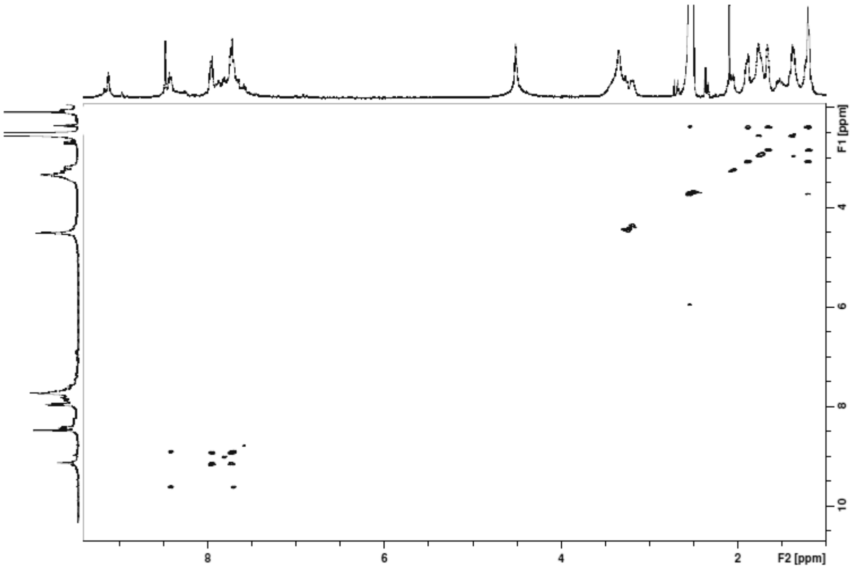


Figure S_3.2B ^{1}H-^{1}H COSY spectrum (500 MHz, 301 K, DMSO-d_6) of cage **$C_6F@(\mathit{S,S})$-1**.

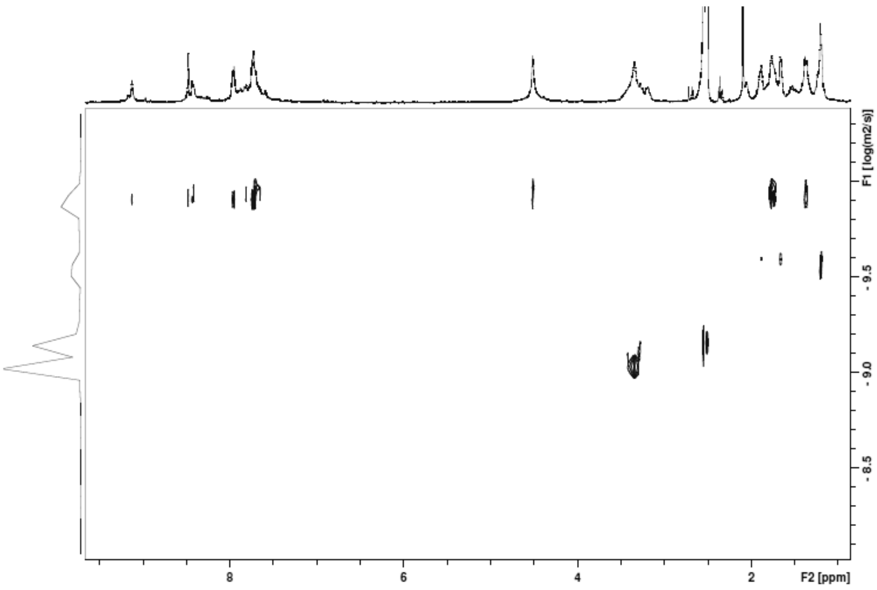


Figure S_3.2C DOSY spectrum (400 MHz, 301 K, DMSO-*d_6*) of cage **C_6F@(*S,S*)-1**. The diffusion coefficient corresponding hydrodynamic radius (r_H) was calculated to be 9.5±0.2 Å by using the Stokes-Einstein equation.[7,8]

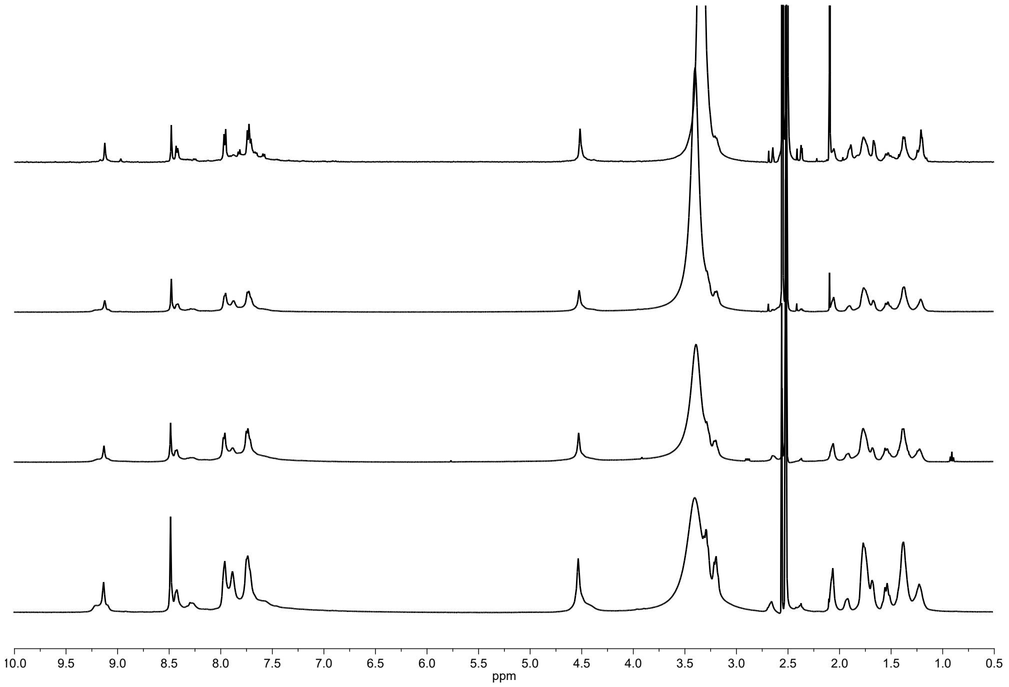


Figure S_3.2D ^{1}H NMR (400 MHz, 301 K, DMSO-*d_6*) of cage **C_6F@(*S,S*)-1**. The cage was synthesized at different final concentrations (a top, d bottom). a) 1 mM, b) 5 mM c) 10 mM d) 15 mM. The cage formation and the characteristic peaks are confirmed in each synthesis attempt.

3.3 ESI-MS spectrum $C_6F@(\textbf{\textit{R,R}})$-1

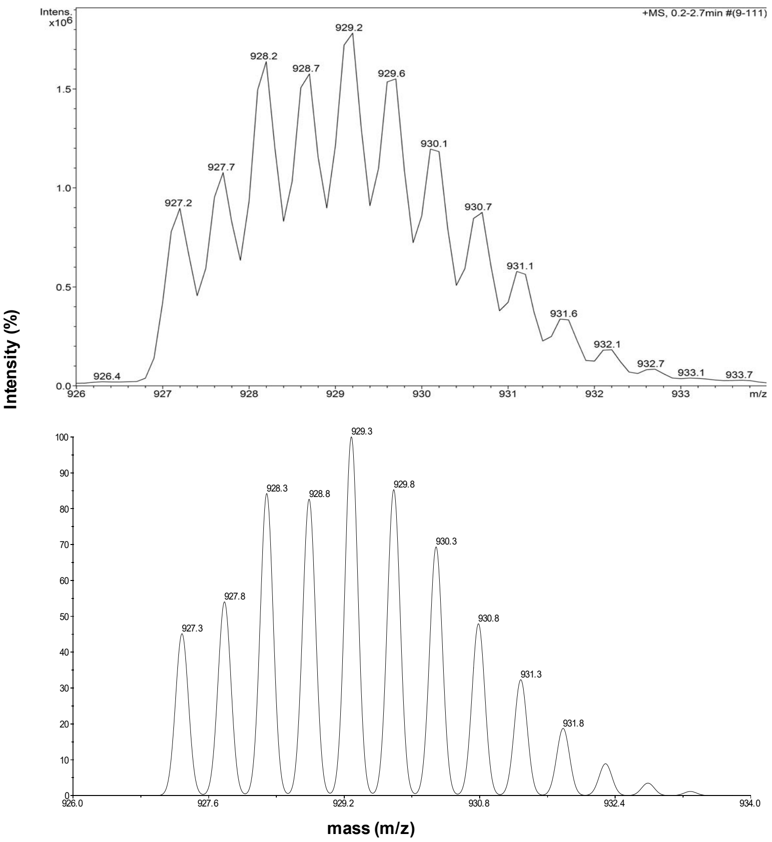


Figure S_3.3A Experimental (top), and calculated (bottom) MS (ESI-TOF) pattern of **$C_6F@(\textbf{\textit{R,R}})$-1** corresponding to $[C_{102}H_{90}F_8N_{14}O_4Zn_2]^{2+}$.

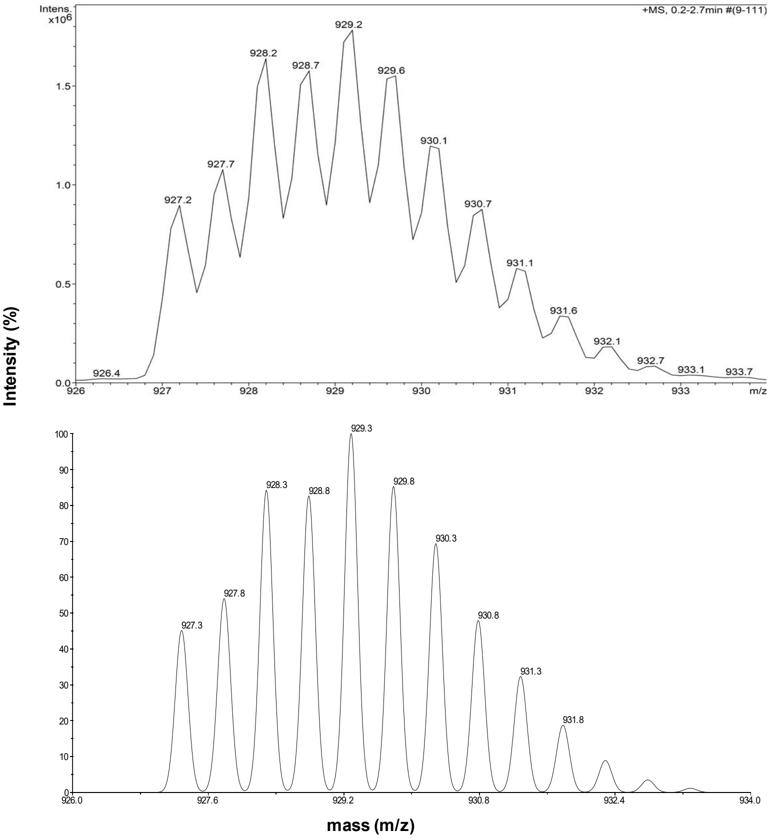


Figure S_3.3B Experimental (top), and calculated (bottom) MS (ESI-TOF) pattern of **C_6F@(*S*,*S*)-1** corresponding to $[C_{102}H_{90}F_8N_{14}O_4Zn_2]^{2+}$.

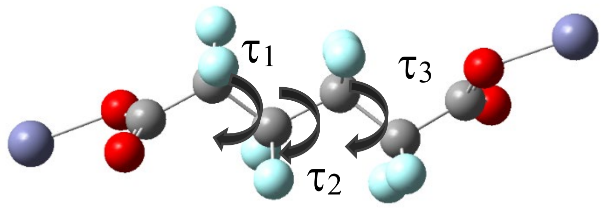
4 Computational section

4.1 Conformational Analysis

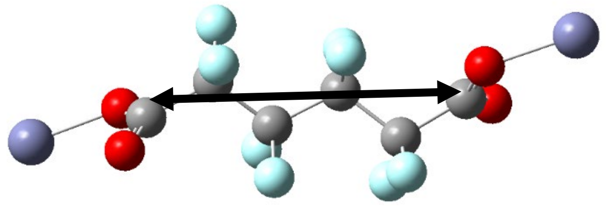
The diastereomeric conformers have been optimized with Gaussian 16 package at B3LYP/6-31G(d,p) level taking into account DMSO solvent within iefpcm frame, applying default grids and loose convergence criteria[1]. Three stereogenic elements have been varied to generate six different starting structures for the conformational search. In particular, the **TPMA** helix helicity sense and the helicity of the perfluorocarbonchain

Cage	**RRPP**	**RRPP**	**RRMP**	**RRMP**	**RRMM**	**RRMM**	**Zn-CO_2-$(CF_2)_4CO_2$-Zn**
Perfluorinated chain	**P**	**M**	**P**	**M**	**P**	**M**	
E (kcal(mol)	0.0	0.9	2.3	4.4	5.0	5.6	
N-C-C-N	29	29	-30	-34	-27	-23	
	24	26	-32	-33	-27	-29	
	29	29	-35	-35	-26	-25	
	23	26	29	31	-30	-27	
	29	27	26	28	-28	-28	
	27	29	25	30	-26	-27	
Biaryl torsions	M	M	M	M	P	P	
Zn…[O-O…O-O]…Zn	136	-127	113	-140	109	-167	
O=C..C=O	138	-127	114	-140	110	-164	
O_2C-C-C-CO_2	155	-151	139	-158	143	-160	141
τ1 [C-C-C-C]	173	-174	164	180	168	-175	164
τ2 [C-C-C-C]	169	-167	167	-168	166	-162	164
τ3 [C-C-C-C]	168	-164	164	-163	164	-169	167
C-C distance	6.524	6.512	6.476	6.539	6.514	6.594	6.464

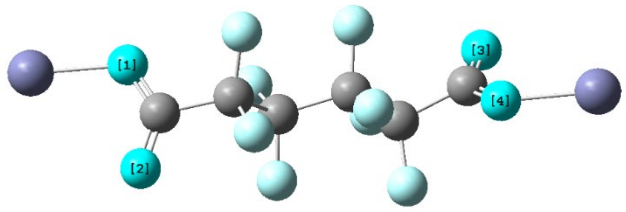
Table S_4.1 Geometric characteristics of the optimised structures for **C_6F@(*R*,*R*)-1**. Last column reports characteristics for a Zn_2-perfluoroalkyl dicarboxylate chain. See **figure S_4.1** for dihedral angle definitions.

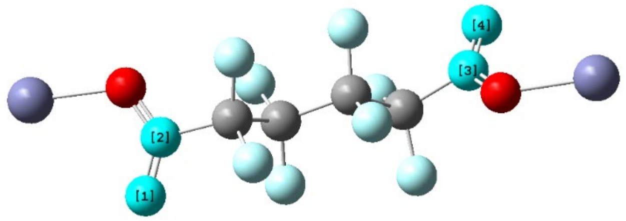


backbone C-C-C-C dihedral angles



C-C distance





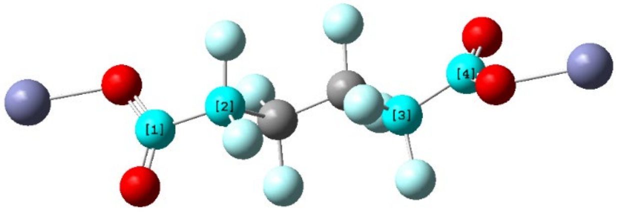


Figure S_4.1 Grafical definition of dihedral angles reported in **Table S_4.1**

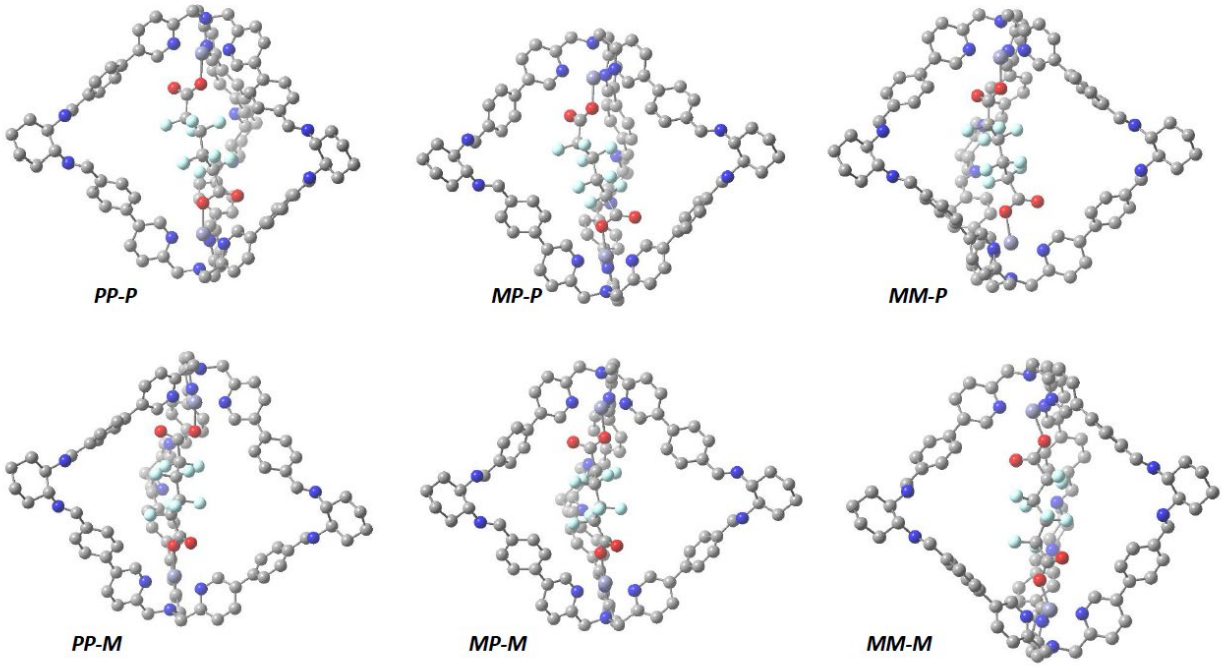


Figure S_4.2 Optimized structures used to calculate VCD and ECD spectra.

5 VCD Calculations

Table S_5.1 mid-IR intense normal modes. The evidenced ones involve vibrations located in the perfluoroalkyl dicarbocxylate guest.

RRPP-P

#	cm^{-1}	D	R	assignment
384	1182	510	20	CF2
385	1190	143	-262	CF2
386	1196	493	314	CF2
479	1402	640	710	o.p. COOsym
480	1403	62	-27	
481	1403	80	-69	
482	1406	9	-72	
483	1407	7	74	
484	1417	59	33	
485	1418	89	140	
486	1419	20	18	
487	1419	33	232	
488	1420	56	-156	
489	1421	9	-46	
490	1422	8	-46	
491	1425	0	-3	
492	1427	1	-5	
493	1428	3	-16	
494	1428	50	-228	i.p. COOsym

RRMP-P

#	cm^{-1}	D	R	assignment
384	1181	626	508	CF2
385	1190	82	-283	CF2
386	1197	389	55	CF2
480	1402	486	452	o.p. COOsym
481	1403	394	177	o.p. COOsym
482	1405	11	10	
483	1407	15	22	
484	1416	45	-36	
485	1416	51	181	
486	1418	18	320	
487	1418	53	-34	
488	1419	57	-58	
489	1419	10	-69	
490	1421	13	-69	
491	1422	1	6	
492	1424	2	-14	
493	1425	1	-14	
494	1428	74	-305	i.p. COOsym

RRMM-P

#	cm^{-1}	D	R	assignment
384	1182	712	497	CF2
385	1187	145	-357	CF2
386	1194	261	67	CF2
477	1399	482	64	o.p. COOsym
479	1401	185	346	
480	1402	21	73	
481	1403	56	58	
482	1406	23	-91	
483	1406	23	-120	
484	1419	85	-193	
485	1419	106	-152	
486	1420	28	199	
487	1421	33	183	
488	1423	3	-252	
489	1425	33	122	
490	1425	27	136	
491	1428	131	-214	i.p. COOsym
492	1431	0	-3	
493	1434	6	40	
494	1439	2	-6	

Table S_5.1-cont.

RRPP-M

#	cm^{-1}	D	R	assignment
384	1180	494	-125	CF2
385	1189	190	431	CF2
386	1198	487	-381	CF2
477	1399	776	-13	o.p. COOsym
478	1401	37	151	
479	1401	88	-384	
480	1402	40	-67	
481	1402	106	-118	
482	1406	3	9	
483	1406	30	134	
484	1418	80	58	
485	1418	51	148	
486	1419	65	-174	
487	1419	8	316	
488	1419	33	-129	
489	1421	22	-76	
492	1426	13	40	i.p. COOsym
493	1427	39	204	i.p. COOsym

RRMP-M

#	cm^{-1}	D	R	assignment
384	1178	414	318	CF2
385	1185	95	243	CF2
386	1200	614	-418	CF2
477	1395	885	-173	o.p. COOsym
478	1400	24	76	
479	1400	74	-212	
480	1402	44	25	
481	1404	48	-76	
482	1406	26	69	
483	1407	52	114	
484	1417	52	-29	
485	1417	44	-22	
486	1418	20	433	
487	1418	43	-23	
488	1419	42	-69	
489	1420	16	-49	
490	1420	11	-11	
491	1422	19	230	i.p. COOsym

RRMM-M

#	cm^{-1}	D	R	assignment
384	1179	110	29	CF2
385	1185	551	-184	CF2
386	1199	108	-62	CF2
481	1405	240	-335	
482	1406	105	-131	
483	1414	650	222	o.p. COOsym
484	1418	99	-259	
485	1418	18	86	
486	1419	118	-73	
487	1420	23	165	
488	1422	6	-316	
489	1425	44	209	
490	1425	31	153	
491	1428	23	27	i.p. COOsym

6 VCD and ECD measurements of the two enantiomers.

6.1 VCD measurement for C6F@(R,R)-1 and C6F@(S,S)-1

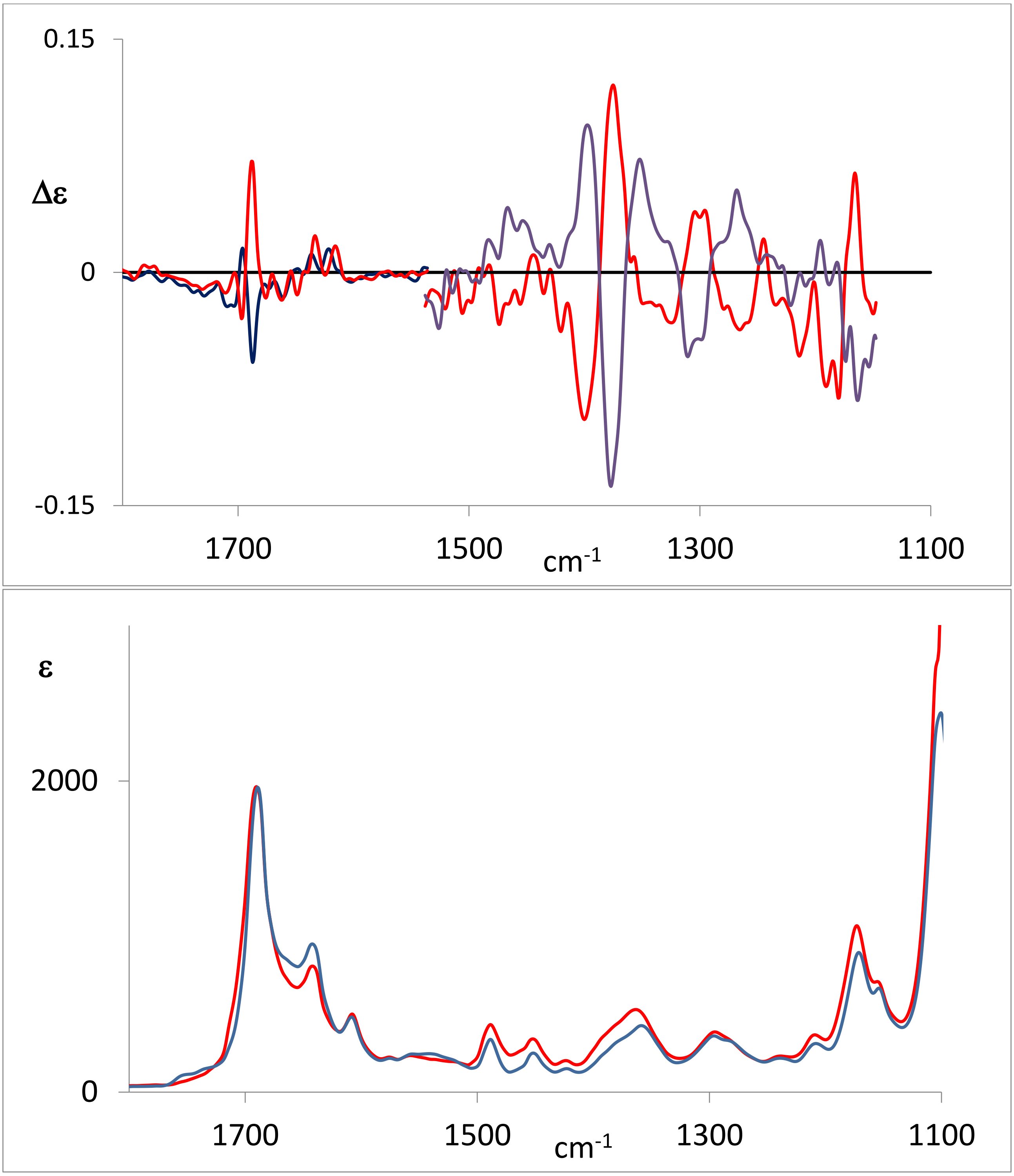


Figure S_6.1 Experimental VCD spectra of **C$_6$F@(*R*,*R*)-1** and **C$_6$F@(*S*,*S*)-1** (top) and IR absorption spectra of **C$_6$F@(*R*,*R*)-1** (see Scheme 1).

6.2 ECD measurement for C_6F@(*R*,*R*)-1 and C_6F@(*S*,*S*)-1

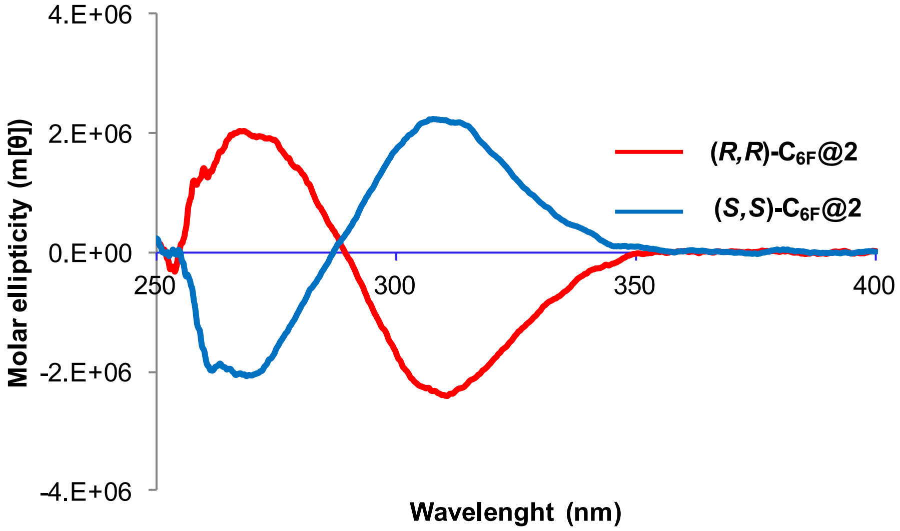


Figure S_S_6.2 Experimental CD spectra of **C_6F@(*R*,*R*)-1** and **C_6F@(*S*,*S*)-1.** (c=1*10^{-5} mM, *l*=0.1 mm. CD_3CN).

7 TD-DFT Calculations

Once obtained the energy distribution of the conformers, TD-DFT cam-B3LYP/6-31G(d) calculations were performed to simulate the CD spectrum. The calculations were carried out over 20 excited states for the optimized conformational structures of the different diasteroisomers of the supramolecular systems **C_6F@(R,R)-1**.

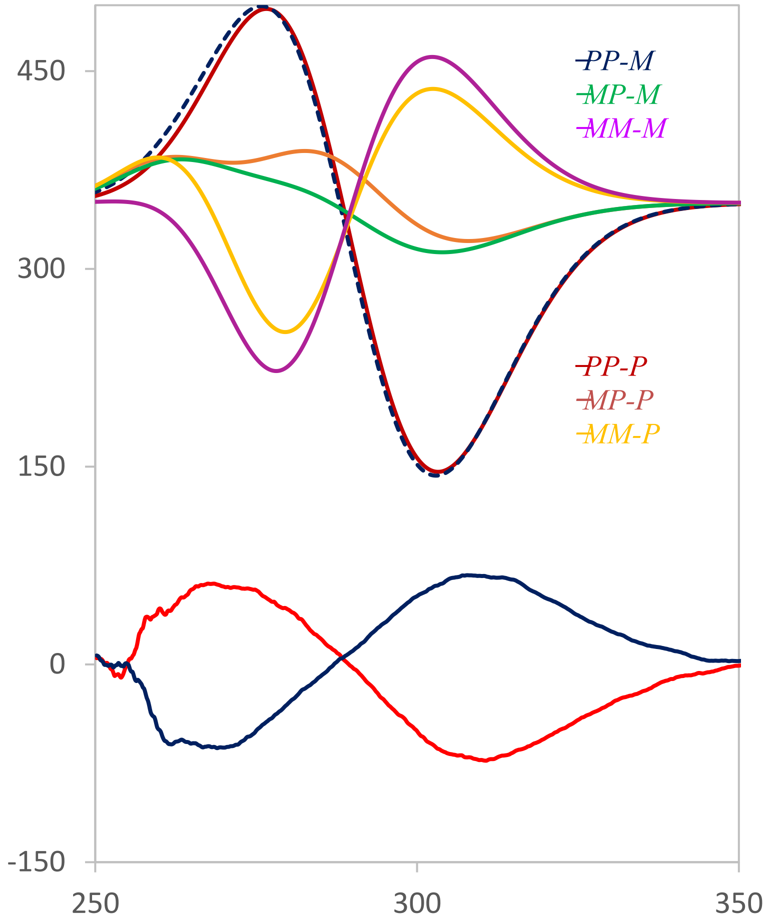


Figure S_7.1 Comparison of calculated ECD spectra of **C_6F@(*R*,*R*)-1** and head groups and fluorinated chains in all possible configurations (*P,P-M, P,P-P, M,M-M, M,M-P, M,P-M, M,P-P*) (top) with experimental ECD spectra of **C_6F@(*R*,*R*)-1** and **C_6F@(*S*,*S*)-1**. (Calculated transitions represented by Gaussian band 0.3 eV wide; spectral features shifted by 20 nm for ease of comparison)..

8 Coordinates of optimized best structure

C_6F@(R,R)- *PP-P*

#	Z	Type	X	Y	Z
1	6	0	8.523446	6.464397	-0.917361
2	6	0	-1.528495	-5.886536	8.703054
3	6	0	-6.406175	-2.633766	-7.819069
4	7	0	8.327380	5.022004	-0.855539
5	7	0	-0.995218	-6.123994	7.368575
6	7	0	-4.996954	-2.674373	-7.448676
7	6	0	7.582979	4.450374	-1.718789
8	6	0	-4.661343	-3.154099	-6.315258
9	6	0	0.022219	-5.463401	6.974972
10	6	0	7.417450	2.983562	-1.751848
11	6	0	6.417906	2.403163	-2.545403
12	6	0	8.269759	2.142568	-1.016145
13	6	0	6.261062	1.019431	-2.592480
14	1	0	5.759646	3.038890	-3.131199
15	6	0	8.129061	0.763198	-1.078702
16	1	0	9.043042	2.591614	-0.402680
17	6	0	7.119075	0.178967	-1.865310
18	1	0	5.488540	0.588988	-3.222007
19	1	0	8.792398	0.129375	-0.497970
20	6	0	0.657208	-5.715806	5.666793
21	6	0	1.638678	-4.841519	5.178490
22	6	0	0.314434	-6.842549	4.900186
23	6	0	2.255729	-5.077300	3.951728
24	1	0	1.923130	-3.971814	5.764508
25	6	0	0.940966	-7.088959	3.686749
26	1	0	-0.445592	-7.518100	5.276978
27	6	0	1.921401	-6.209202	3.190881
28	1	0	3.018948	-4.392499	3.595510
29	1	0	0.655666	-7.959650	3.104179
30	6	0	-3.248105	-3.361437	-5.938897
31	6	0	-2.216812	-3.197354	-6.879706
32	6	0	-2.916756	-3.801172	-4.649006
33	6	0	-0.904216	-3.503711	-6.550630
34	1	0	-2.469620	-2.849564	-7.875231
35	6	0	-1.596375	-4.096609	-4.312364
36	1	0	-3.701322	-3.937391	-3.909663
37	6	0	-0.573022	-3.975469	-5.265797
38	1	0	-0.123209	-3.377477	-7.294236
39	1	0	-1.368707	-4.471190	-3.319162
40	6	0	2.578283	-6.479497	1.890514
41	6	0	2.962836	-7.771794	1.498498
42	6	0	2.833470	-5.442822	0.988208
43	6	0	3.573119	-7.972222	0.266084
44	1	0	2.807987	-8.612142	2.167207
45	1	0	2.582444	-4.413605	1.220346
46	6	0	3.774472	-6.884066	-0.581138
47	1	0	3.892369	-8.962200	-0.040694
48	6	0	0.815042	-4.401534	-4.964366

49	6	0	1.438923	-4.115035	-3.744821
50	6	0	1.558929	-5.145259	-5.895620
51	1	0	0.948751	-3.512839	-2.986785
52	6	0	2.840825	-5.578885	-5.582685
53	1	0	1.118867	-5.408731	-6.851577
54	6	0	3.379504	-5.260430	-4.338307
55	1	0	3.415567	-6.168785	-6.287999
56	6	0	6.969498	-1.294394	-1.916909
57	6	0	5.706317	-1.888111	-1.841765
58	6	0	8.069789	-2.159556	-2.028383
59	1	0	4.812363	-1.283667	-1.741975
60	6	0	7.872353	-3.535034	-2.082166
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62	6	0	6.576372	-4.040332	-1.996433
63	1	0	8.711678	-4.212369	-2.194301
64	1	0	-5.406057	-3.480597	-5.573380
65	1	0	0.490626	-4.682674	7.593296
66	7	0	2.680308	-4.535014	-3.444563
67	7	0	3.403332	-5.642927	-0.212994
68	7	0	5.519474	-3.216980	-1.866703
69	6	0	6.284088	-5.529009	-1.999694
70	6	0	4.355940	-7.057117	-1.971503
71	6	0	4.788397	-5.666969	-3.949641
72	1	0	5.076908	-6.584653	-4.476779
73	1	0	5.477464	-4.882855	-4.281894
74	1	0	3.545748	-7.364029	-2.641997
75	1	0	5.090476	-7.872092	-1.976170
76	1	0	7.046722	-6.064900	-2.578753
77	1	0	6.348588	-5.898975	-0.970318
78	7	0	4.922083	-5.801260	-2.489468
79	30	0	3.655175	-4.147060	-1.633141
80	1	0	7.038333	5.013525	-2.491649
81	6	0	7.884845	7.126659	0.332685
82	6	0	-6.842541	-1.167060	-8.073024
83	6	0	-2.959185	-5.297125	8.591292
84	7	0	6.432718	7.110409	0.209410
85	7	0	-6.925578	-0.460351	-6.801944
86	7	0	-2.885097	-3.920411	8.120445
87	6	0	5.738022	6.453268	1.053430
88	6	0	-3.440560	-3.606322	7.016011
89	6	0	-6.124405	0.504120	-6.570084
90	6	0	4.261782	6.501705	1.056877
91	6	0	3.566708	7.439846	0.274334
92	6	0	3.528145	5.646832	1.891892
93	6	0	2.184397	7.537487	0.348467
94	1	0	4.132651	8.098480	-0.375154
95	6	0	2.138288	5.731923	1.955018
96	1	0	4.049661	4.920539	2.509297
97	6	0	1.447036	6.690973	1.197768
98	1	0	1.665818	8.270891	-0.261490
99	1	0	1.592327	5.079288	2.629251
100	6	0	-6.198285	1.296578	-5.327343
101	6	0	-7.308854	1.205799	-4.470973
102	6	0	-5.152552	2.165930	-4.986792
103	6	0	-7.365665	1.956507	-3.304456
104	1	0	-8.119504	0.536208	-4.736626

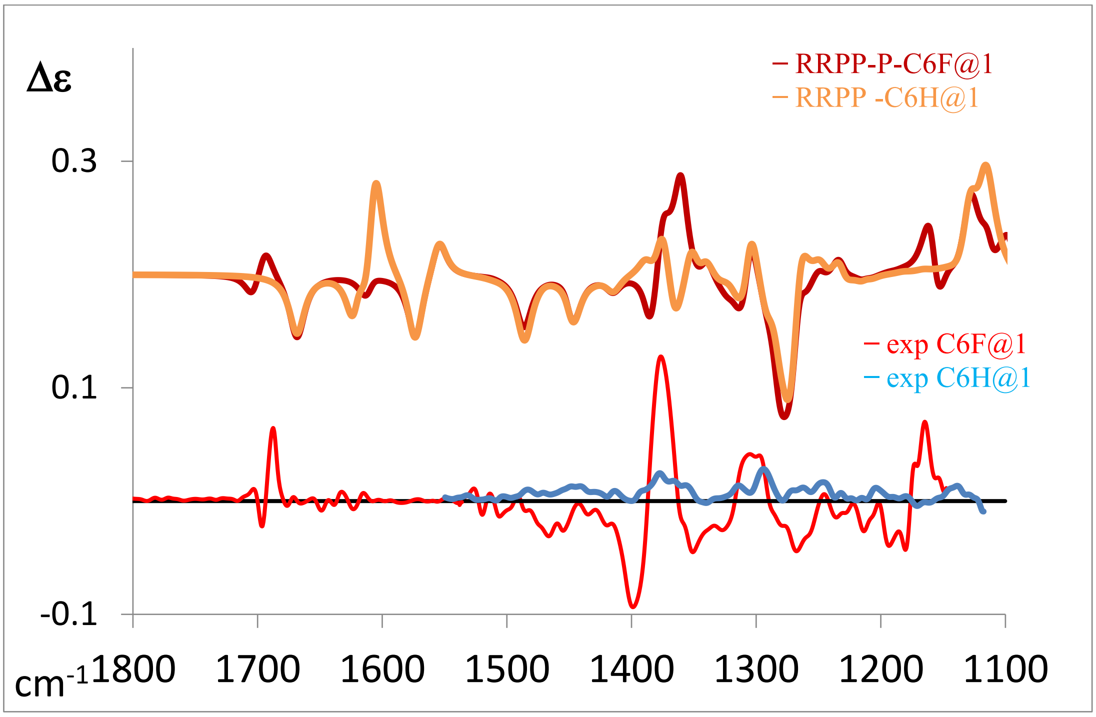
105	6	0	-5.197891	2.903578	-3.806315
106	1	0	-4.295043	2.260312	-5.647388
107	6	0	-6.304716	2.808776	-2.947334
108	1	0	-8.224884	1.863087	-2.647120
109	1	0	-4.378404	3.571615	-3.560205
110	6	0	-3.499686	-2.210353	6.538959
111	6	0	-3.092641	-1.145613	7.361138
112	6	0	-4.018585	-1.919360	5.269122
113	6	0	-3.228060	0.167926	6.935469
114	1	0	-2.685500	-1.369513	8.340948
115	6	0	-4.143526	-0.600809	4.834736
116	1	0	-4.344124	-2.730048	4.622911
117	6	0	-3.765984	0.463893	5.668320
118	1	0	-2.907804	0.976349	7.585628
119	1	0	-4.576881	-0.397436	3.860413
120	6	0	-6.341998	3.565201	-1.673815
121	6	0	-7.490255	4.221715	-1.204048
122	6	0	-5.202634	3.633264	-0.868529
123	6	0	-7.448102	4.913937	0.001310
124	1	0	-8.401769	4.213947	-1.792746
125	1	0	-4.280847	3.157344	-1.176666
126	6	0	-6.269005	4.921107	0.745649
127	1	0	-8.319468	5.447508	0.364746
128	6	0	-3.968714	1.872993	5.255405
129	6	0	-3.700447	2.307044	3.952463
130	6	0	-4.458077	2.834775	6.154573
131	1	0	-3.297505	1.635965	3.201736
132	6	0	-4.669851	4.142085	5.734188
133	1	0	-4.700870	2.549989	7.172880
134	6	0	-4.380708	4.485915	4.415638
135	1	0	-5.065772	4.887415	6.415071
136	6	0	-0.021720	6.850099	1.320840
137	6	0	-0.879692	5.747366	1.377166
138	6	0	-0.617443	8.119190	1.407923
139	1	0	-0.496938	4.736914	1.286905
140	6	0	-1.992409	8.237094	1.572195
141	1	0	0.001258	9.009983	1.381433
142	6	0	-2.770719	7.083354	1.633942
143	1	0	-2.459074	9.211345	1.666053
144	1	0	-3.933025	-4.352638	6.374210
145	1	0	-5.339828	0.800439	-7.282710
146	7	0	-3.899574	3.573562	3.550185
147	7	0	-5.169979	4.277635	0.309087
148	7	0	-2.209820	5.863766	1.524487
149	6	0	-4.279110	7.134259	1.786084
150	6	0	-6.179153	5.601902	2.098084
151	6	0	-4.539765	5.904407	3.902529
152	1	0	-5.326255	6.425871	4.461750
153	1	0	-3.606512	6.445743	4.092860
154	1	0	-6.567378	4.912300	2.855636
155	1	0	-6.824747	6.488879	2.120012
156	1	0	-4.576091	8.050437	2.311495
157	1	0	-4.727495	7.180797	0.787367
158	7	0	-4.786709	5.922289	2.451160
159	30	0	-3.525852	4.257016	1.603021
160	1	0	6.198797	5.843155	1.845107

161	6	0	-1.442151	1.172157	-0.493258
162	6	0	0.052213	1.052519	-0.104432
163	6	0	0.672564	-0.361373	-0.274566
164	6	0	2.215992	-0.425727	-0.155454
165	6	0	-2.025270	2.568107	-0.124217
166	6	0	2.737358	-1.890339	-0.045089
167	8	0	-2.546516	2.618447	1.042429
168	8	0	-1.932758	3.457650	-0.969724
169	8	0	3.194281	-2.270383	1.029688
170	8	0	2.623735	-2.520056	-1.154483
171	1	0	-3.528286	-5.936895	7.895137
172	1	0	-0.915884	-5.160493	9.264587
173	1	0	-7.050424	-3.038100	-7.019612
174	1	0	-6.095131	-0.712437	-8.745669
175	1	0	8.041463	6.905677	-1.806420
176	1	0	8.226696	6.561992	1.216888
177	6	0	10.044448	6.717391	-0.976733
178	6	0	8.312646	8.603487	0.469897
179	6	0	-1.533727	-7.238029	9.447159
180	6	0	-3.666219	-5.278143	9.963161
181	6	0	-6.567041	-3.494892	-9.090445
182	6	0	-8.235648	-1.099344	-8.732255
183	1	0	-2.041750	-7.974248	8.810854
184	1	0	-0.497680	-7.578780	9.554407
185	6	0	-2.230455	-7.168501	10.809980
186	6	0	-3.662514	-6.644234	10.657304
187	1	0	-2.229364	-8.160702	11.275440
188	1	0	-1.668661	-6.505135	11.481861
189	1	0	-4.150639	-6.561408	11.635064
190	1	0	-4.253064	-7.361192	10.070525
191	1	0	-3.157581	-4.541024	10.597894
192	1	0	-4.690251	-4.914996	9.820147
193	1	0	10.513062	6.155628	-0.158356
194	1	0	10.429971	6.290836	-1.909726
195	1	0	7.847277	9.168535	-0.348003
196	1	0	7.893673	8.999511	1.401899
197	6	0	10.414003	8.199330	-0.858395
198	6	0	9.831806	8.796950	0.427045
199	1	0	11.504248	8.309492	-0.877630
200	1	0	10.026532	8.751108	-1.725875
201	1	0	10.294303	8.311546	1.297426
202	1	0	10.068713	9.864514	0.500058
203	1	0	-6.310851	-4.530858	-8.841334
204	1	0	-5.825620	-3.156422	-9.825718
205	6	0	-7.970501	-3.409954	-9.699546
206	6	0	-8.341296	-1.953527	-9.999738
207	1	0	-8.012642	-4.016178	-10.611612
208	1	0	-8.704967	-3.837402	-9.003196
209	1	0	-9.357700	-1.888407	-10.404443
210	1	0	-7.668694	-1.557461	-10.772937
211	1	0	-8.466494	-0.049812	-8.947230
212	1	0	-8.976280	-1.438982	-7.996683
213	9	0	0.310127	-0.848984	-1.487583
214	9	0	0.157273	-1.170885	0.690407
215	9	0	0.176236	1.420193	1.198580
216	9	0	0.754374	1.929212	-0.868443

217	9	0	-2.127981	0.175808	0.134198
218	9	0	-1.555900	0.982806	-1.834504
219	9	0	2.590643	0.292538	0.934366
220	9	0	2.763834	0.167991	-1.258602

9 Preliminary studies of the perhydro diacid

As suggested by one of the reviewer of this paper, we report here also our initial attempts in the study of the perhydro diacid. It should be noted that for the cage with hexanedioic acid, **C6H@(*R,R*)-1**, we obtained a similar IR spectrum except for the 1160 cm^{-1} band (assigned to CF_2 vibrations). VCD spectrum is very weak and noisy with no clear features above noise. This is either due to higher conformational disorder or to the unoptimized cage formation conditions. However, a preliminary calculation, starting from the optimized PP-P **C6F@(R,R)-1** after substituting $(CF_2)_4$ with $(CH_2)_4$ gives spectra that do not show the 1350 cm^{-1} doublet, as shown in the plots below: the C=O…C=O dihedral angle is similar as in the case with fluorine, but the two symmetric COO stretchings are highly coupled with the (CH_2)-wagging normal modes of the aliphatic chain. The study on this system was not further pursued, due to low intensity signals combined with the higher number of possible conformations accessible by the perhydro compounds.



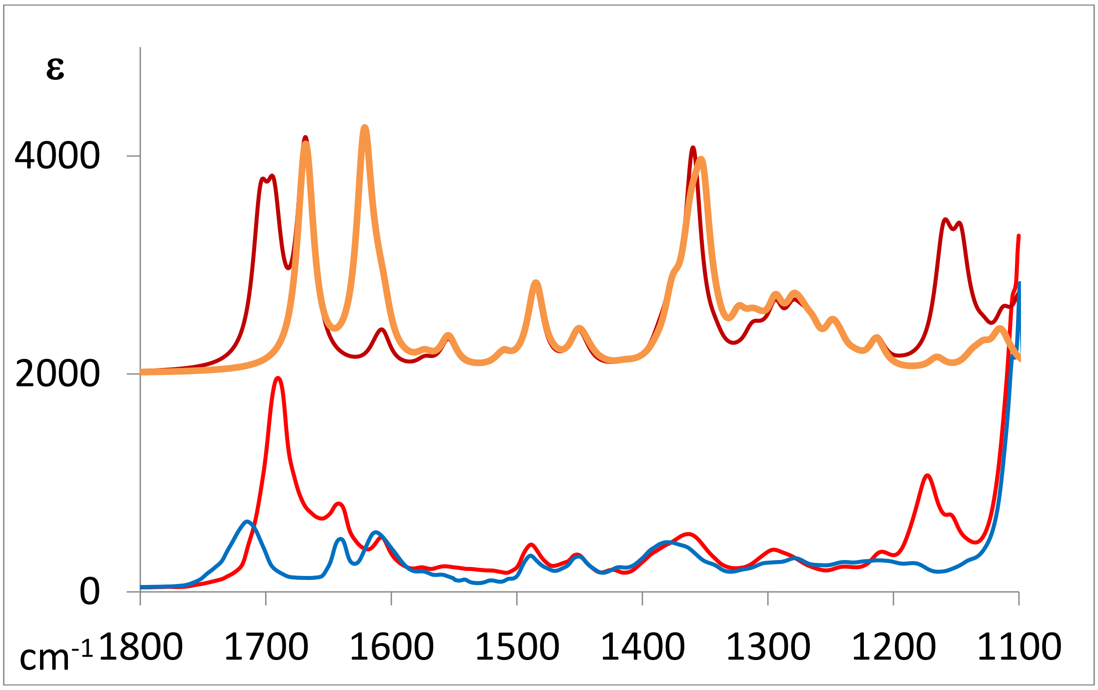


Figure S9.1 Comparison of experimental and calculated VCD (top) and IR (bottom) spectra for RRPP-P-C6F@1 and RRPP-P-C6H@1 systems.

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