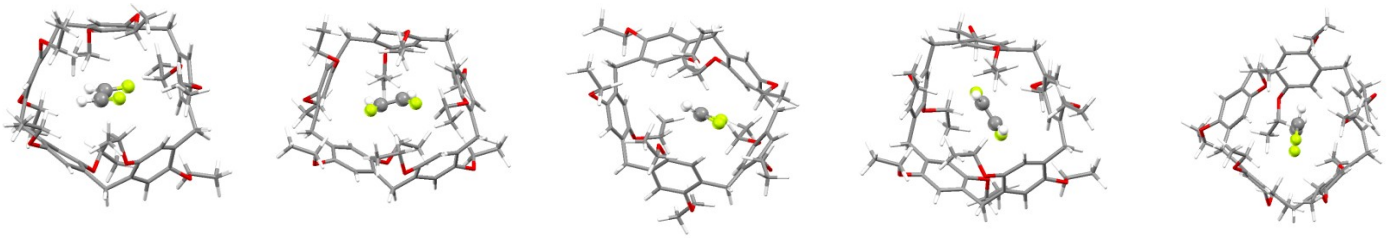
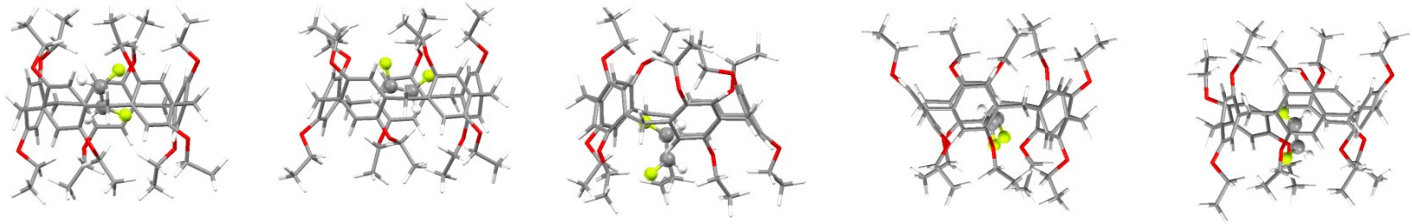
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Top view



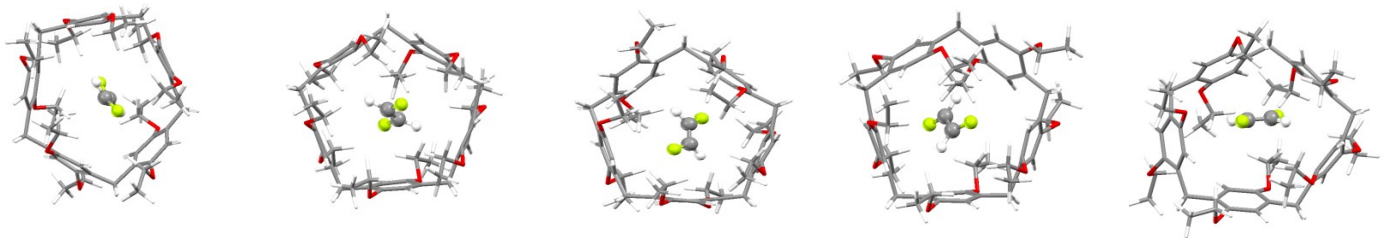
Side View



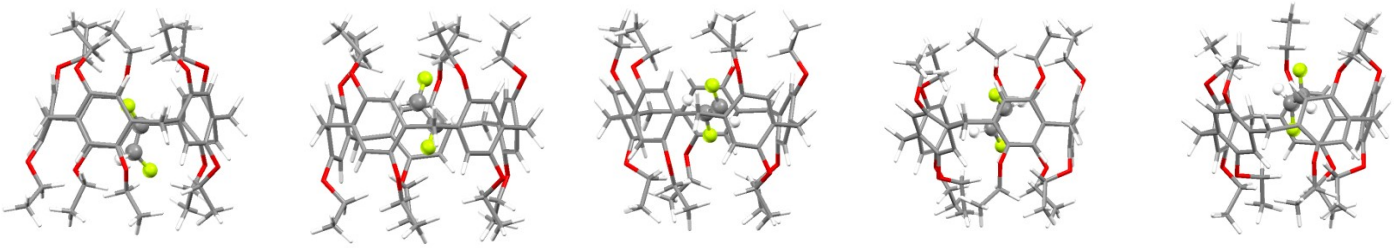
0 ps **2500 ps** **5000 ps** **7500 ps** **10000 ps**

Supporting information figure 1: MD Snapshots for every 2500 ps for cis-1,2-difluoroethene inside the EP5cavity.

Top view



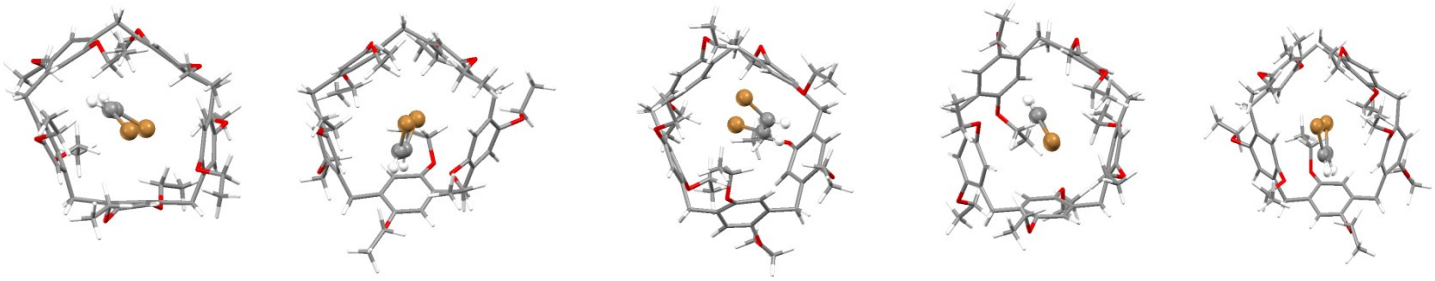
Side View



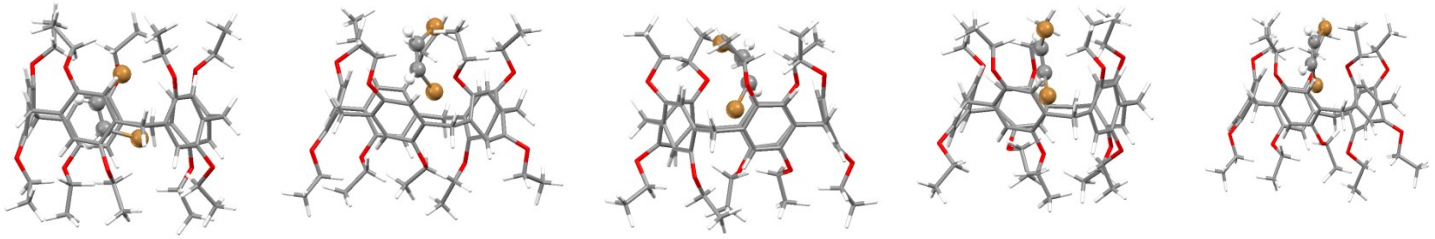
0 ps **2500 ps** **5000 ps** **7500 ps** **10000 ps**

Supporting information figure 2: MD Snapshots for every 2500 ps for trans-1,2-difluoroethene inside the EP5 cavity.

Top view



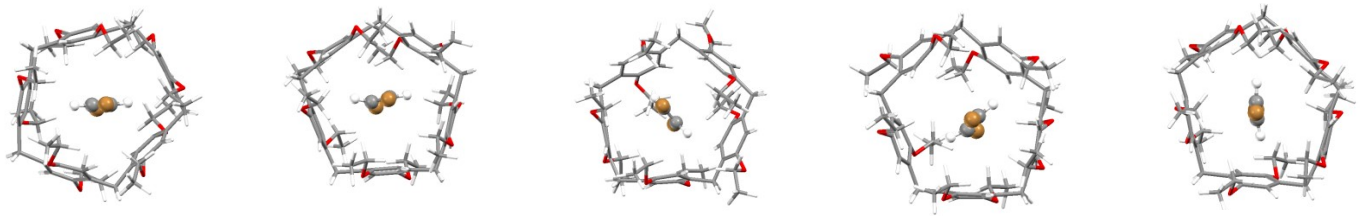
Side View



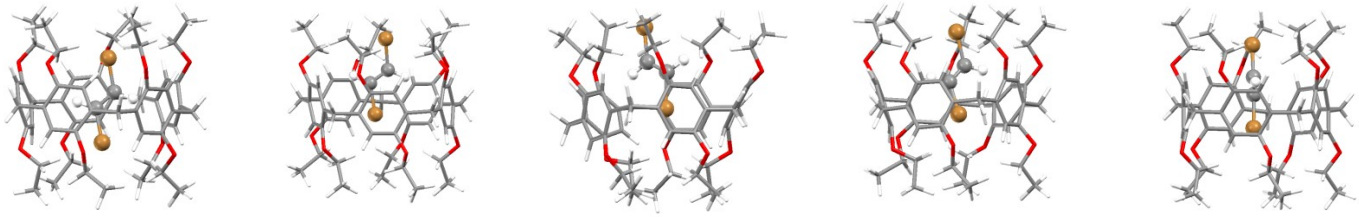
0 ps **2500 ps** **5000 ps** **7500 ps** **10000 ps**

Supporting information figure 3: MD Snapshots for every 2500 ps for cis-1,2-dibromoethene inside the EP5 cavity

Top view



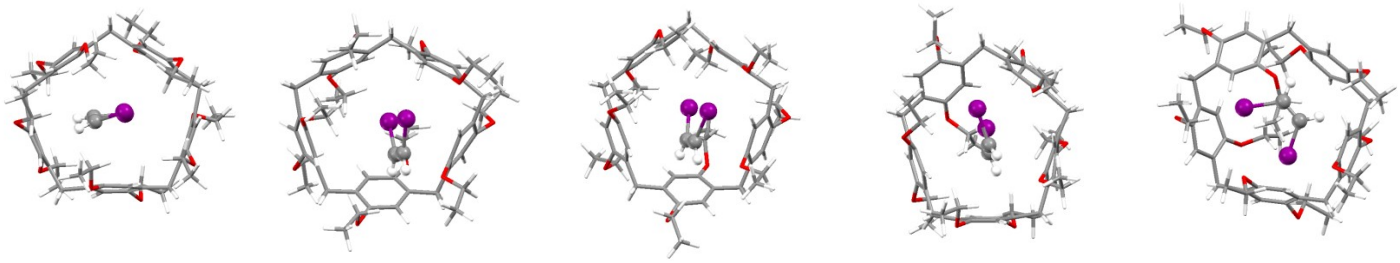
Side View



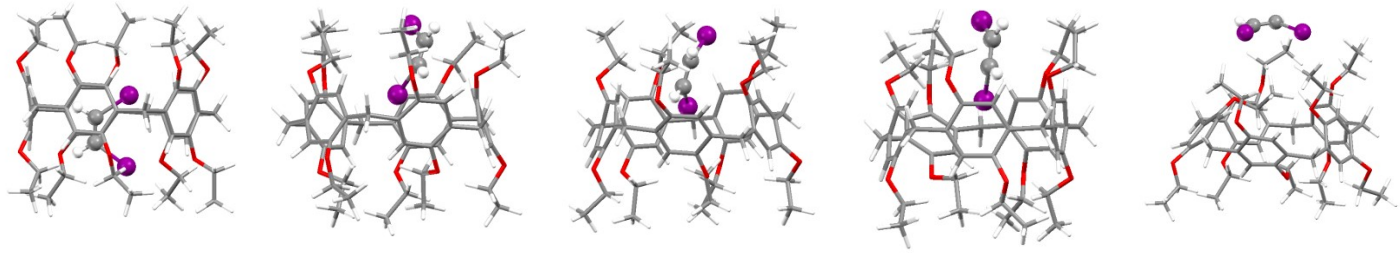
0 ps **2500 ps** **5000 ps** **7500 ps** **10000 ps**

Supporting information figure 4: MD Snapshots for every 2500 ps for trans-1,2-dibromoethene inside the EP5 cavity.

Top view



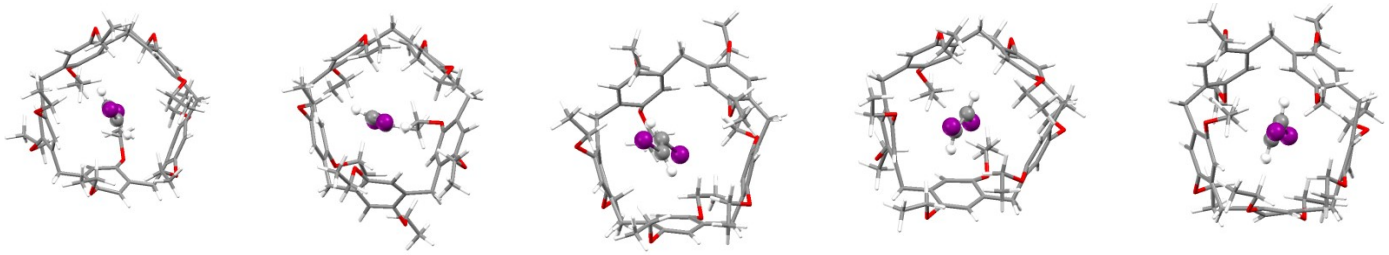
Side View



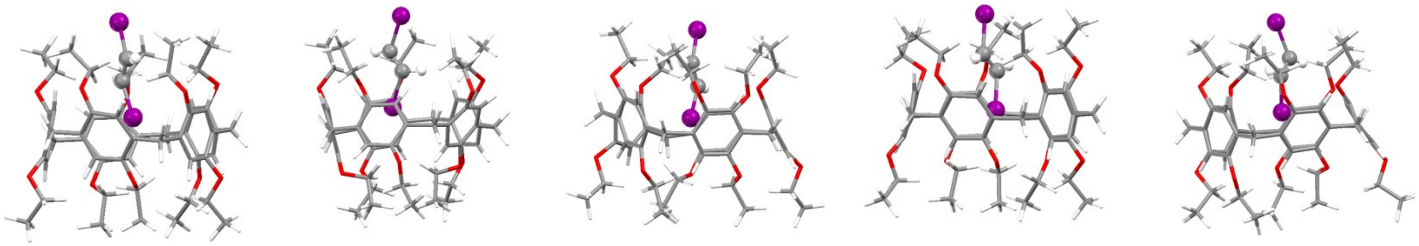
0 ps **2500 ps** **5000 ps** **7500 ps** **10000 ps**

Supporting information figure 5: MD Snapshots for every 2500 ps for cis-1,2-diiodoethene inside the EP5 cavity.

Top view



Side View

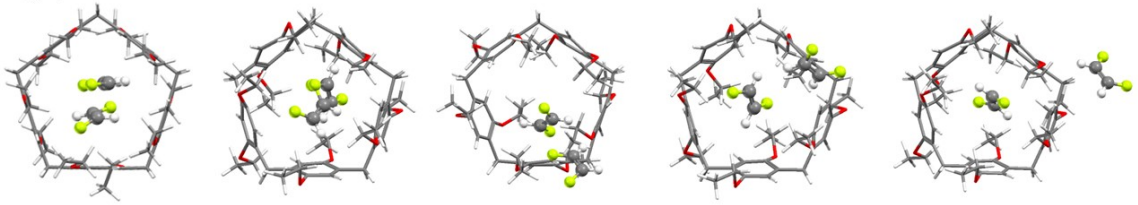


0 ps **2500 ps** **5000 ps** **7500 ps** **10000 ps**

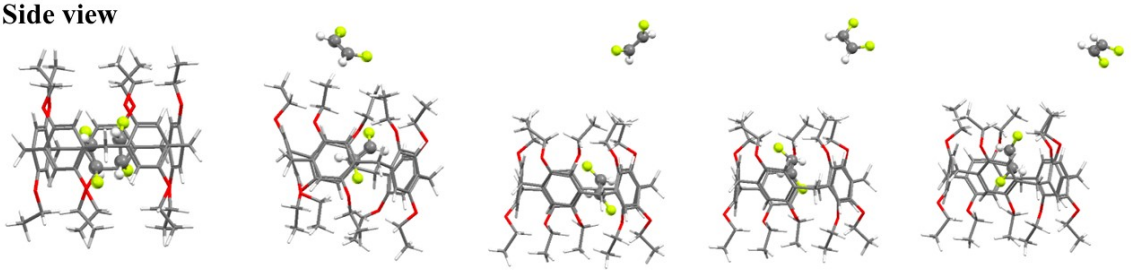
Supporting information figure 6: MD Snapshots for every 2500 ps for trans-1,2-diiodoethene inside the EP5 cavity.

a)

Top view



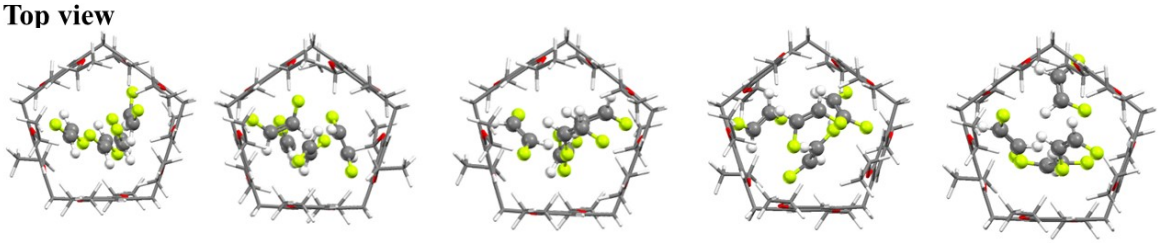
Side view



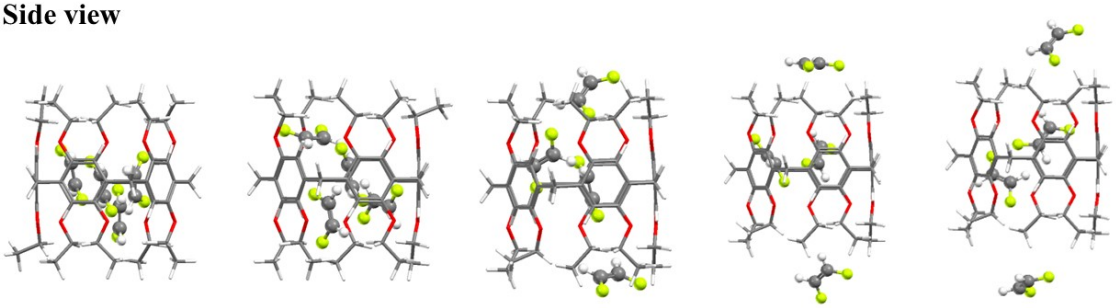
0 ps 2500 ps 5000 ps 7500 ps 10000 ps

b)

Top view



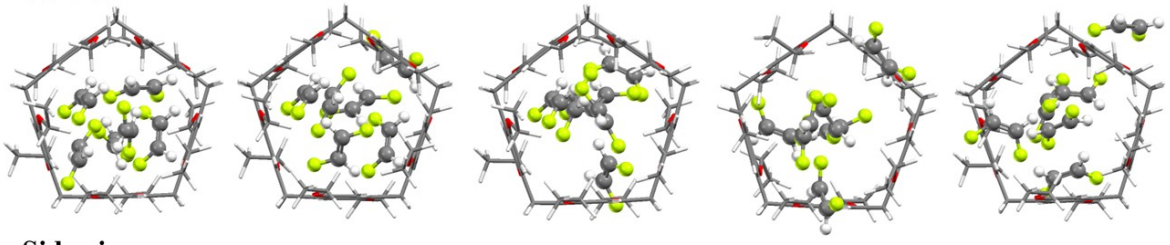
Side view



0 ps 2500 ps 5000 ps 7500 ps 10000 ps

c)

Top view



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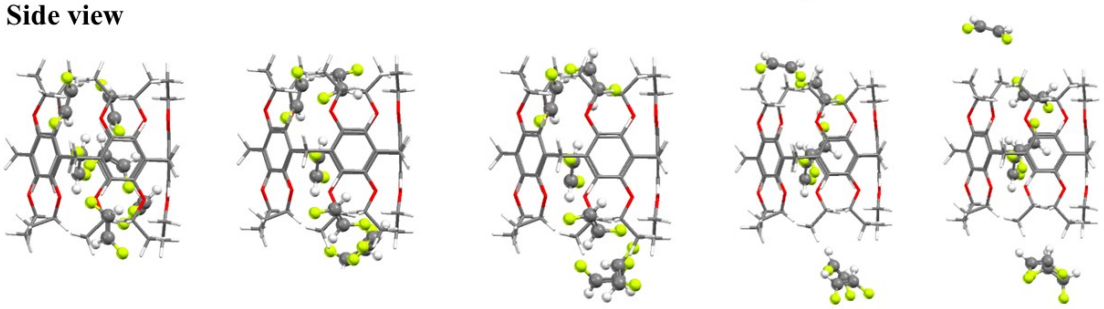
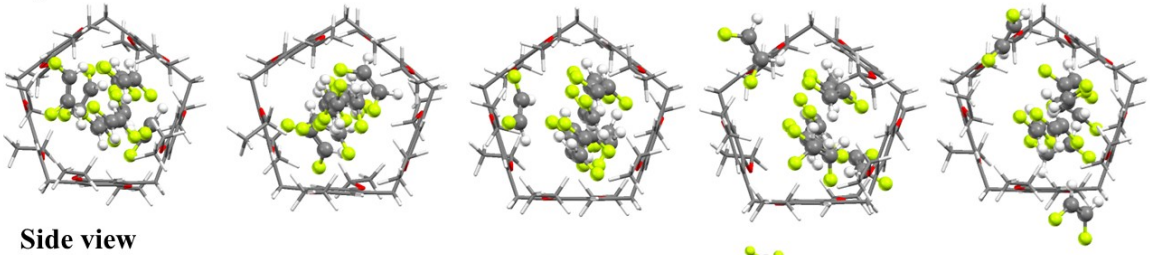


0 ps 2500 ps 5000 ps 7500 ps 10000 ps

d)

Top view



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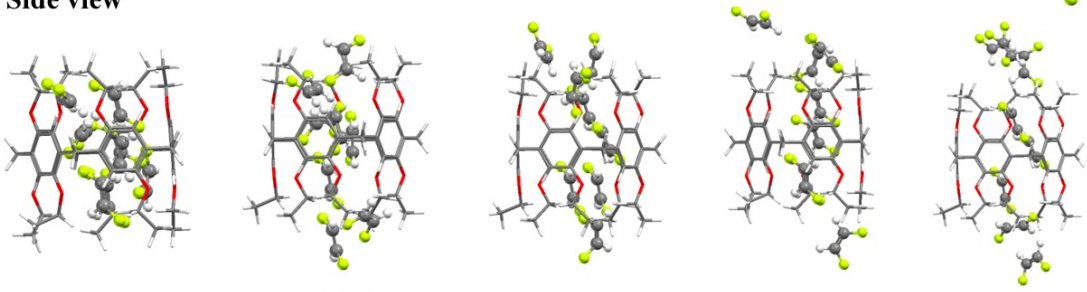
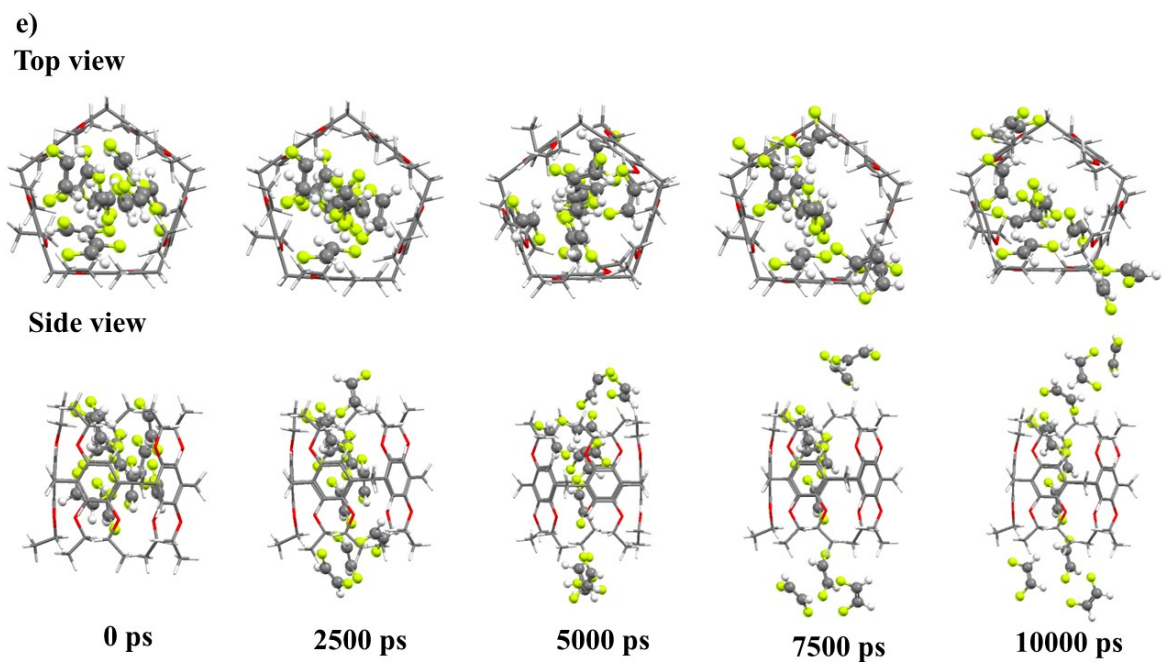


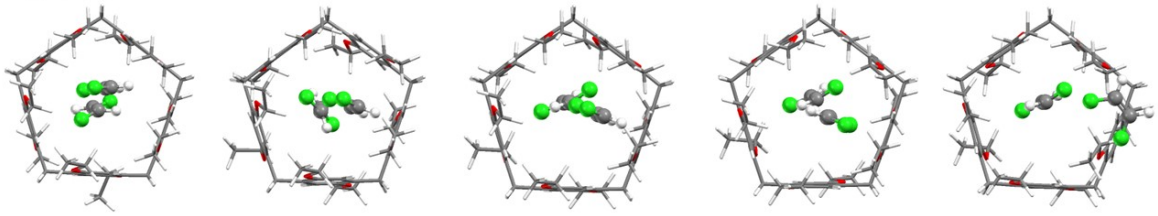
0 ps 2500 ps 5000 ps 7500 ps 10000 ps



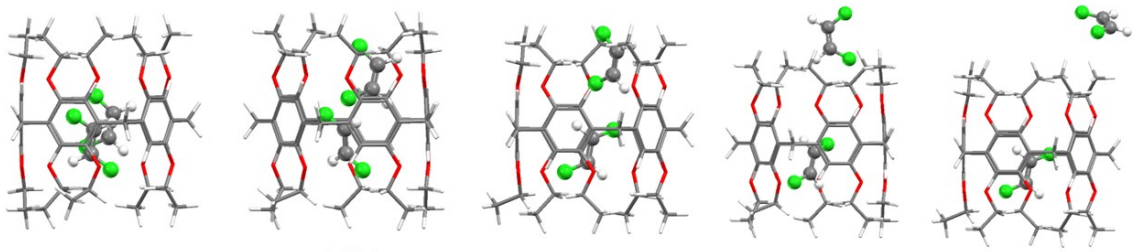
Supporting information figure 7: MD Snapshots for every 2500 ps for cis/trans-1,2-difluoroethene mixtures with a) 1:1; b) 2:2; c) 3:3; d) 4:4; and e) 5:5 ratio inside the EP5cavity.

a)

Top view



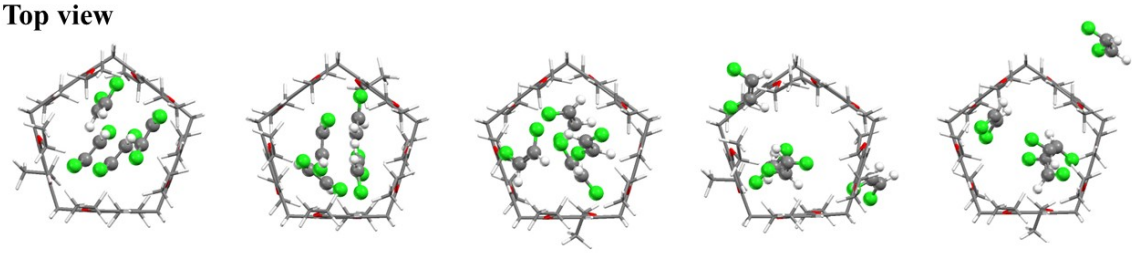
Side view



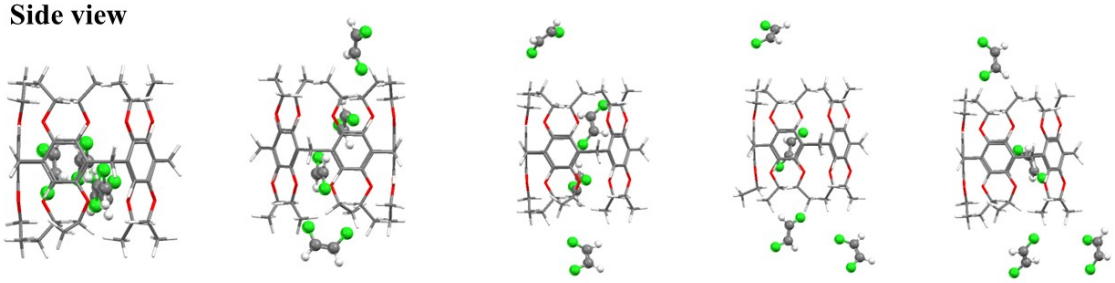
0 ps 2500 ps 5000 ps 7500 ps 10000 ps

b)

Top view



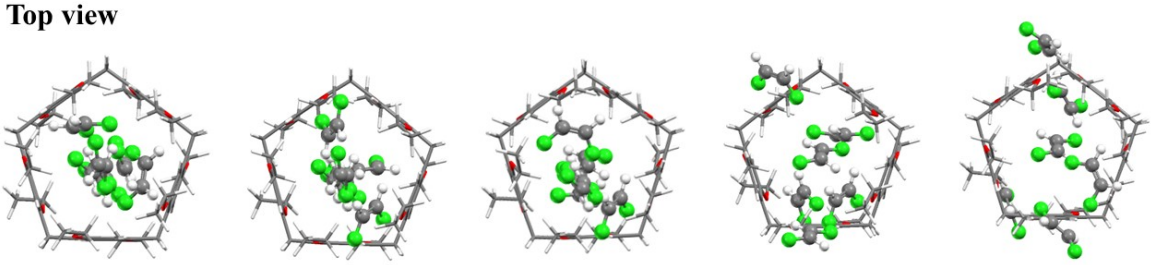
Side view



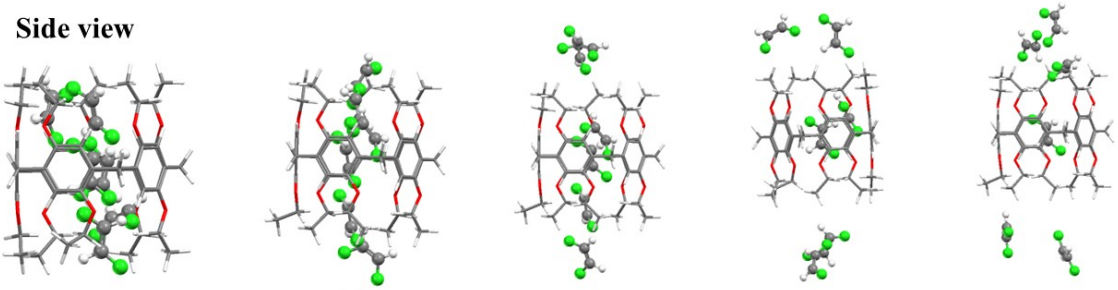
0 ps 2500 ps 5000 ps 7500 ps 10000 ps

c)

Top view



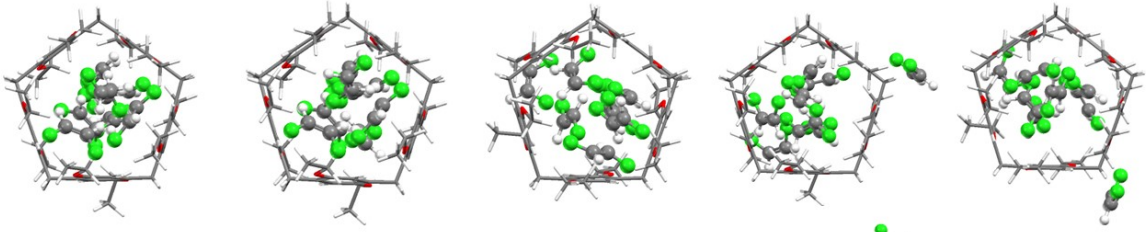
Side view



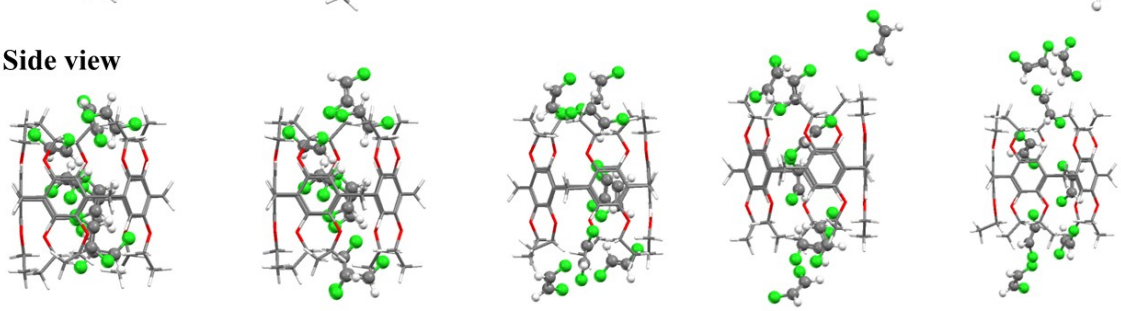
0 ps 2500 ps 5000 ps 7500 ps 10000 ps

d)

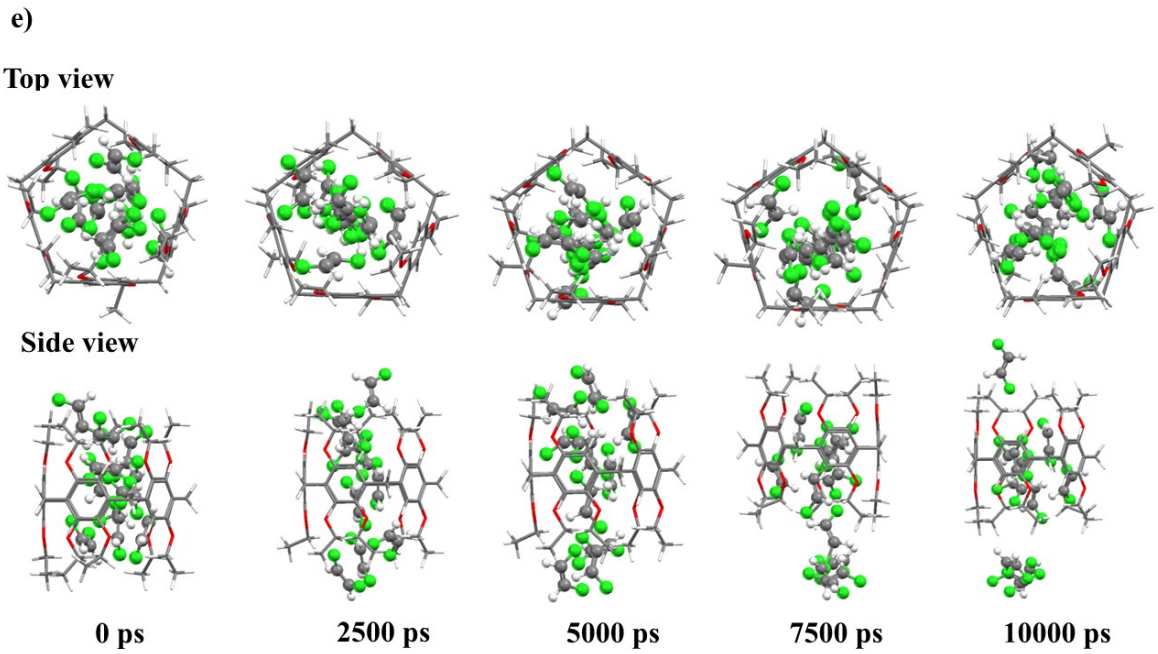
Top view



Side view



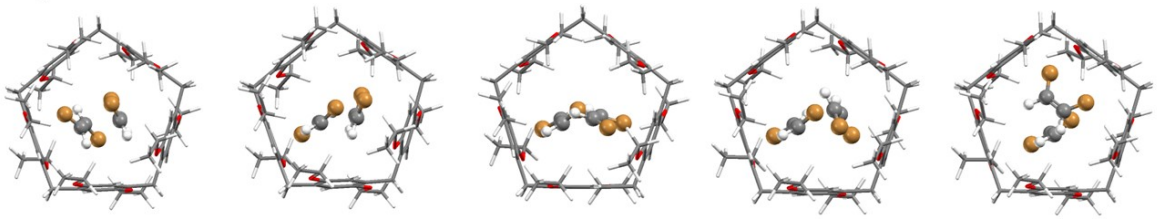
0 ps 2500 ps 5000 ps 7500 ps 10000 ps



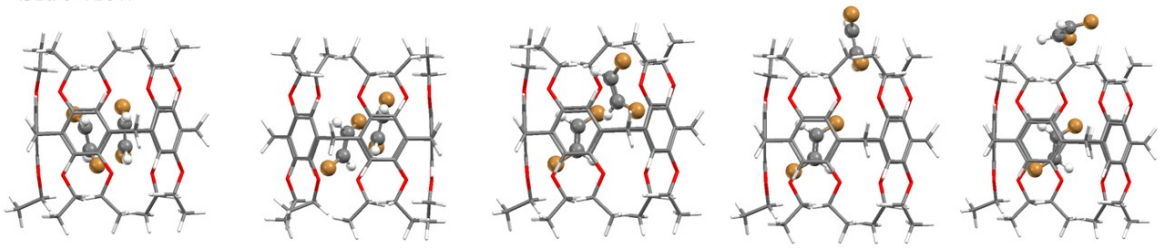
Supporting information figure 8: MD Snapshots for every 2500 ps for cis/trans-1,2-dichloroethene mixtures with a) 1:1; b) 2:2; c) 3:3; d) 4:4; and e) 5:5 ratio inside the EP5cavity.

a)

Top view



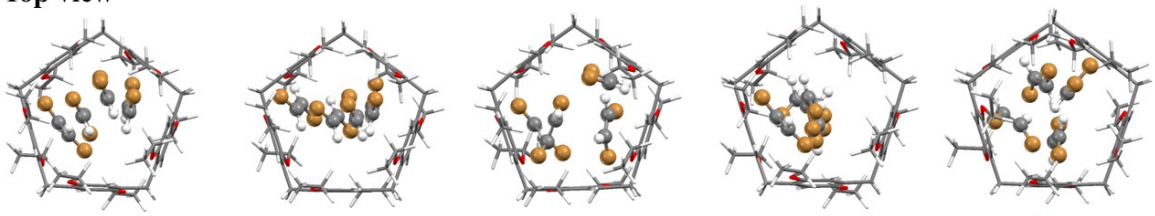
Side view



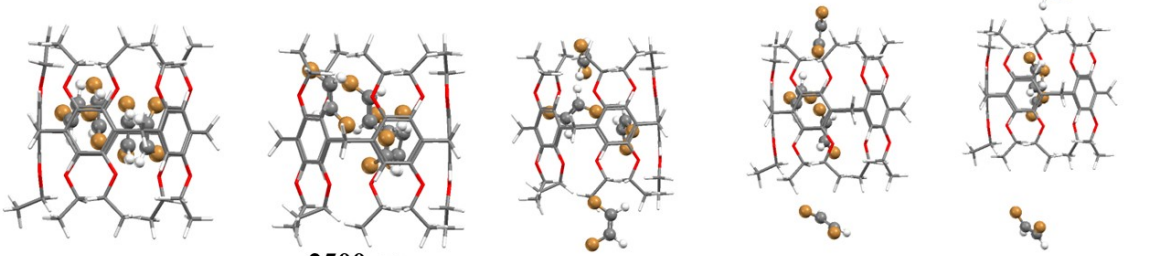
0 ps 2500 ps 5000 ps 7500 ps 10000 ps

b)

Top view

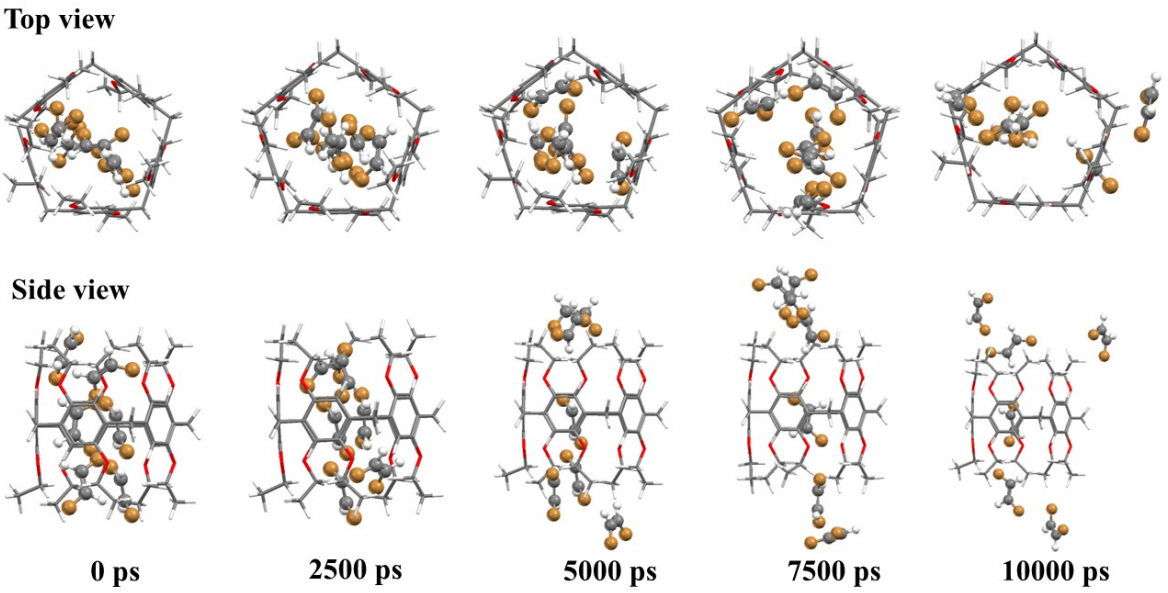


Side view

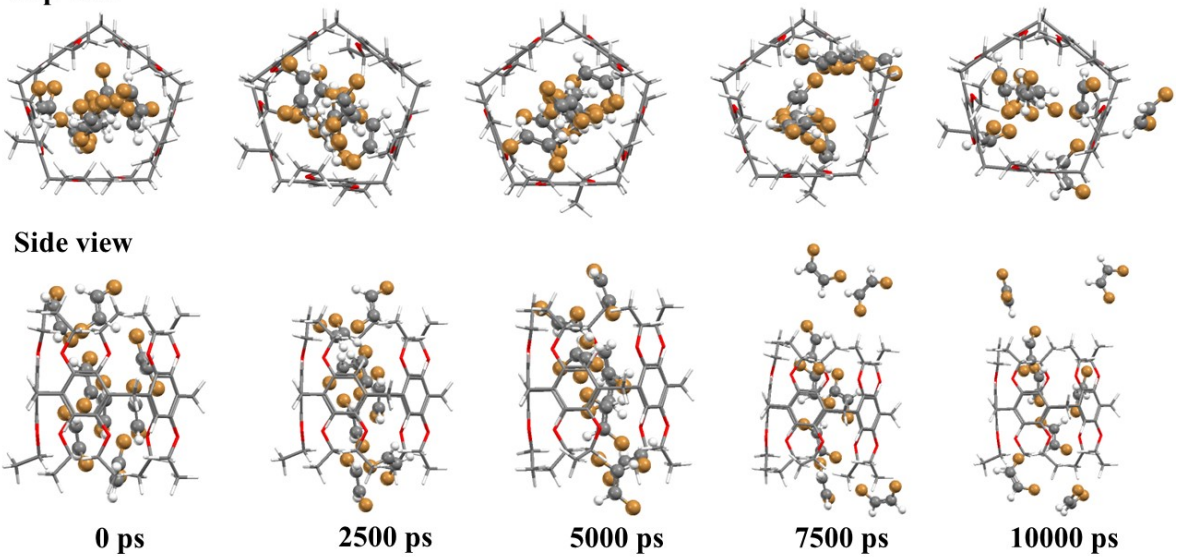


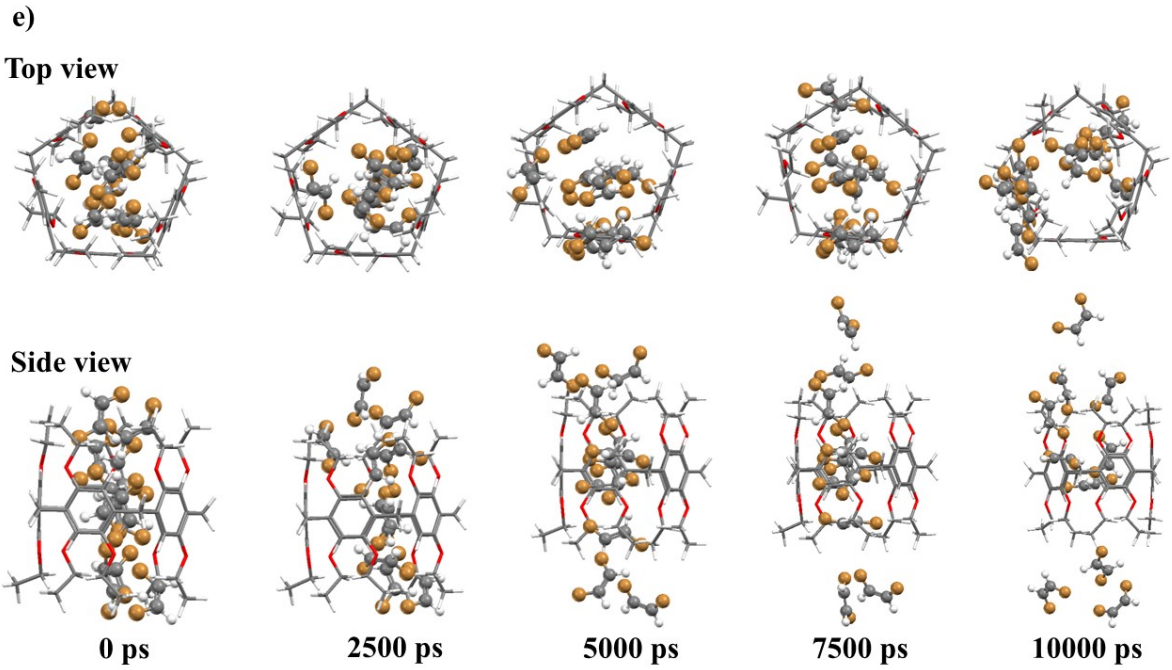
0 ps 2500 ps 5000 ps 7500 ps 10000 ps

c)


Top view
Side view
0 ps
2500 ps
5000 ps
7500 ps
10000 ps

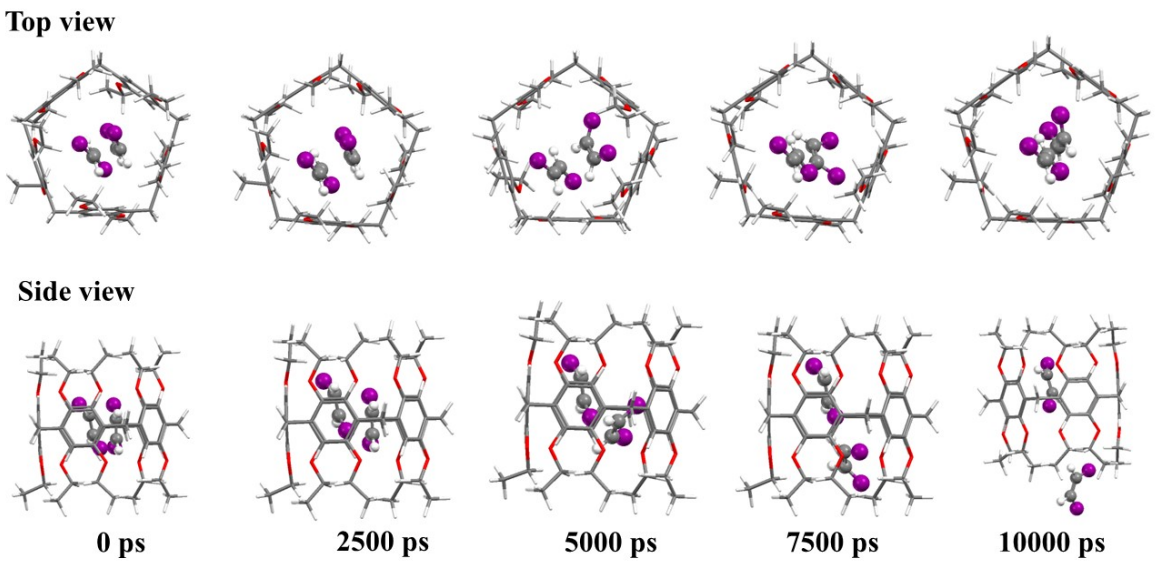
d)


Top view
Side view
0 ps
2500 ps
5000 ps
7500 ps
10000 ps

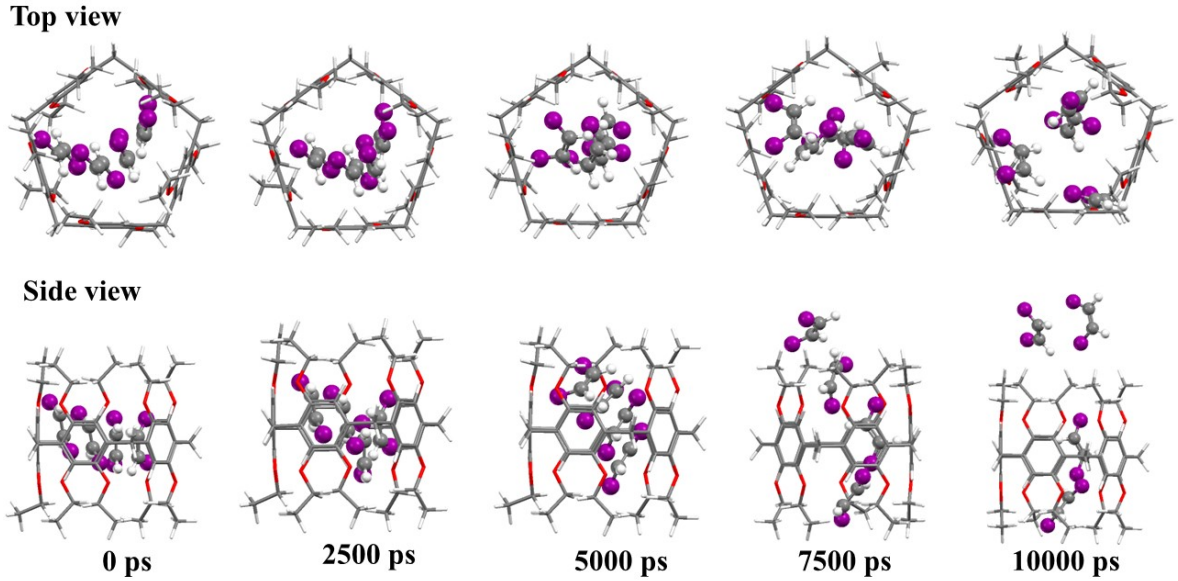


Supporting information figure 9: MD Snapshots for every 2500 ps for cis/trans-1,2-dibromoethene mixtures with a) 1:1; b) 2:2; c) 3:3; d) 4:4; and e) 5:5 ratio inside the EP5cavity.

a)

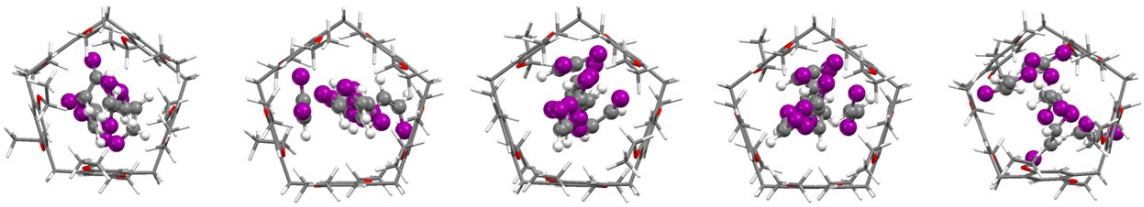

Top view
Side view
0 ps
2500 ps
5000 ps
7500 ps
10000 ps

b)

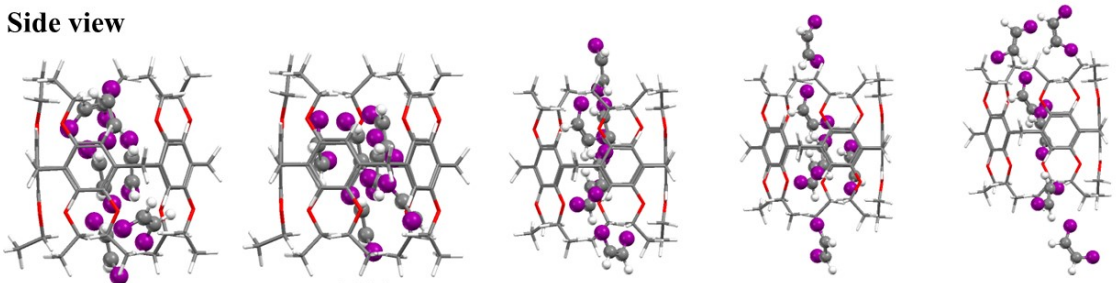

Top view
Side view
0 ps
2500 ps
5000 ps
7500 ps
10000 ps

c)

Top view



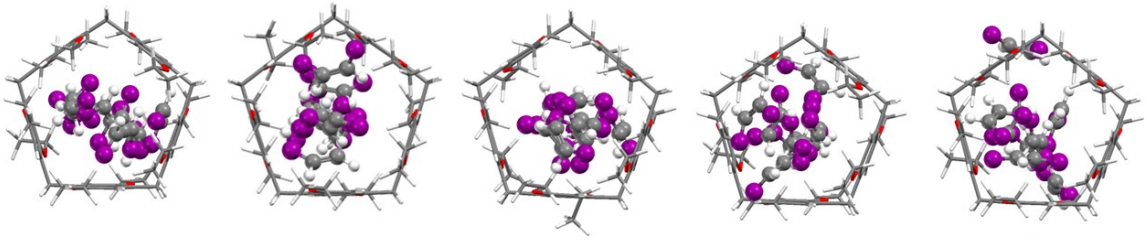
Side view



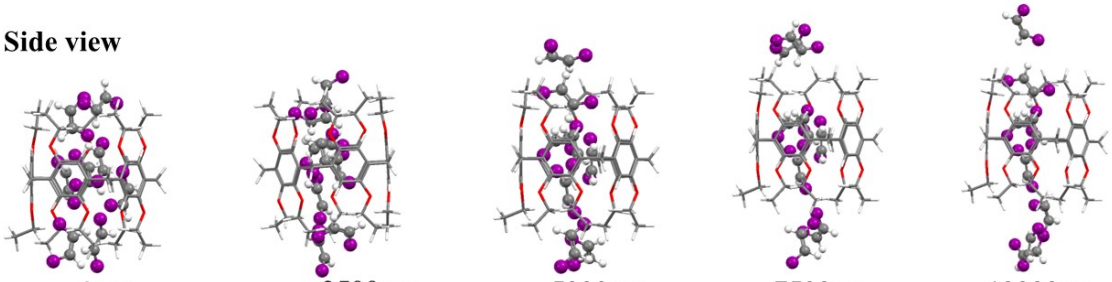
0 ps 2500 ps 5000 ps 7500 ps 10000 ps

d)

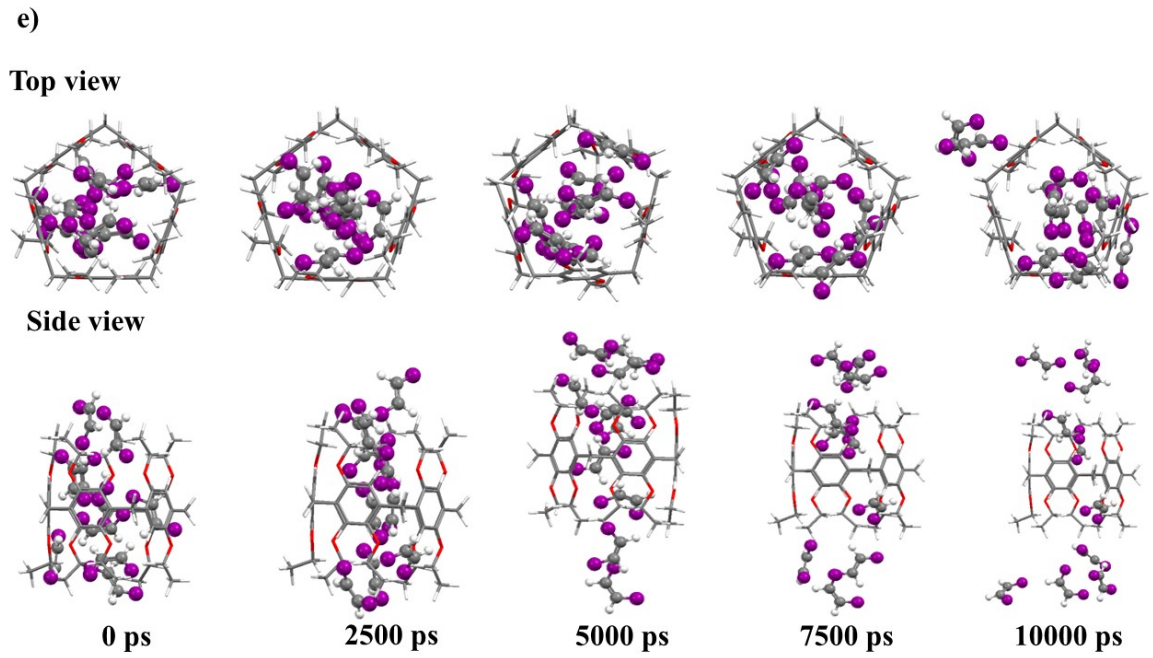
Top view



Side view



0 ps 2500 ps 5000 ps 7500 ps 10000 ps



Supporting information figure 10: MD Snapshots for every 2500 ps for cis/trans-1,2-diiodoethene mixtures with a) 1:1; b) 2:2; c) 3:3; d) 4:4; and e) 5:5 ratio inside the EP5cavity.

Supporting information table 1: Distance between the center of the guest and the center of the host obtained from the optimized geometry.

Complex	Distance (in Å)
EP5@cis-DFE	1.168
EP5@cis-DCE	1.868
EP5@cis-DBE	2.429
EP5@cis-DIE	4.273
EP5@trans-DFE	0.005
EP5@trans-DCE	0.711
EP5@trans-DBE	0.021
EP5@trans-DIE	0.018

Supporting information table 2: C-X bond lengths of the bare guest molecules

Bare guest	C_1-X_1	C_2-X_2
cis-DFE	1.354	1.354
cis-DCE	1.724	1.725
cis-DBE	1.882	1.884
cis-DIE	2.088	2.088
trans-DFE	1.361	1.362
trans-DCE	1.734	1.734
trans-DBE	1.895	1.895
trans-DIE	2.104	2.104

Supporting information table 3: C-X bond lengths of the guest molecule encapsulated in the host molecule

Guest encapsulated	C_1-X_1	C_2-X_2
EP5@cis-DFE	1.347	1.359
EP5@cis-DCE	1.714	1.735
EP5@cis-DBE	1.873	1.895
EP5@cis-DIE	2.084	2.097
EP5@trans-DFE	1.368	1.368
EP5@trans-DCE	1.740	1.740
EP5@trans-DBE	1.901	1.903
EP5@trans-DIE	2.111	2.112

Supporting information table 4: HOMO-LUMO analysis of the bare guest and the complex (energies are in eV)

Guest	HOMO	LUMO	GAP	Complexes	HOMO	LUMO	GAP
cis-DFE	-6.495	-0.961	5.535	EP5@cis-DFE	-4.552	-1.456	3.097
cis-DCE	-6.346	-1.649	4.697	EP5@cis-DCE	-1.864	-1.162	0.522
cis-DBE	-6.283	-1.750	4.533	EP5@cis-DBE	-1.733	1.448	3.181
cis-DIE	-6.000	-2.343	3.657	EP5@cis-DIE	-4.623	-2.321	2.302
trans-DFE	-6.460	-1.110	5.350	EP5@trans-DFE	-4.656	-1.469	3.186
trans-DCE	-6.324	-1.788	4.536	EP5@trans-DCE	-4.659	-1.478	3.181
trans-DBE	-6.261	-1.921	4.340	EP5@trans-DBE	-4.669	-1.785	2.884
trans-DIE	-5.973	-2.582	3.391	EP5@trans-DIE	-4.653	-2.716	1.937

Supporting information table 5: QTAIM analysis of the EP5 and the transDXE bond critical pints (ρ,$\nabla^2\rho$, G, V, H values are in atomic units)

Complex	Interactions	ρ	$\nabla^2\rho$	G	V	H	Ellipticity
EP5@trans-DFE	H2-C	0.005	-0.005	0.004	-0.003	0.001	3.300
	H1-C	0.005	-0.004	0.003	-0.002	0.001	1.272
	H1-C	0.004	-0.003	0.002	-0.002	0.001	1.473
EP5@trans-DCE	Cl1 -H	0.002	-0.002	0.001	-0.001	0.000	0.059
	H1-C	0.004	-0.003	0.003	-0.002	0.001	1.391
	H1 - C	0.005	-0.004	0.003	-0.002	0.001	0.990
	H2-C	0.006	-0.005	0.004	-0.003	0.001	3.761
EP5@trans-DBE	Br2 - H	0.002	-0.002	0.001	-0.001	0.000	0.018
	Br2 - H	0.002	-0.002	0.001	-0.001	0.000	0.059
	Br2 - H	0.003	-0.002	0.002	-0.001	0.001	0.029
	H2 -C	0.005	-0.005	0.004	-0.003	0.001	3.614
	Br1 - H	0.002	-0.002	0.001	-0.001	0.000	0.038
	Br1 - H	0.002	-0.002	0.001	-0.001	0.000	0.049
	Br1 - H	0.002	-0.002	0.001	-0.001	0.000	0.043
	H1 -C	0.005	-0.004	0.003	-0.002	0.001	0.773
	H1 -C	0.004	-0.003	0.003	-0.002	0.001	0.828
EP5@trans-DIE	I2 -H	0.005	-0.003	0.002	-0.002	0.001	0.074
	I2 -H	0.003	-0.002	0.002	-0.001	0.001	0.055
	I2 -H	0.004	-0.003	0.002	-0.002	0.001	0.075
	I2 -H	0.003	-0.002	0.002	-0.002	0.001	0.063

	I2 -H	0.003	-0.002	0.002	-0.001	0.001	0.064
	H2 -C	0.006	-0.005	0.004	-0.003	0.001	3.838
	H1 -C	0.005	-0.004	0.003	-0.002	0.001	1.002
	H1 -C	0.004	-0.003	0.003	-0.002	0.001	1.435
	I1 - H	0.004	-0.003	0.002	-0.002	0.001	0.899
	I1 - H	0.003	-0.002	0.002	-0.001	0.000	0.060
	I1 - H	0.005	-0.003	0.002	-0.002	0.001	0.123
	I1 - H	0.003	-0.002	0.002	-0.001	0.001	0.069
	I1 – H	0.004	-0.003	0.002	-0.002	0.001	0.070