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

Interlocked Benzenes in Triangular π-architectures:

Anchoring Groups Dictate Ion Binding and Transmission

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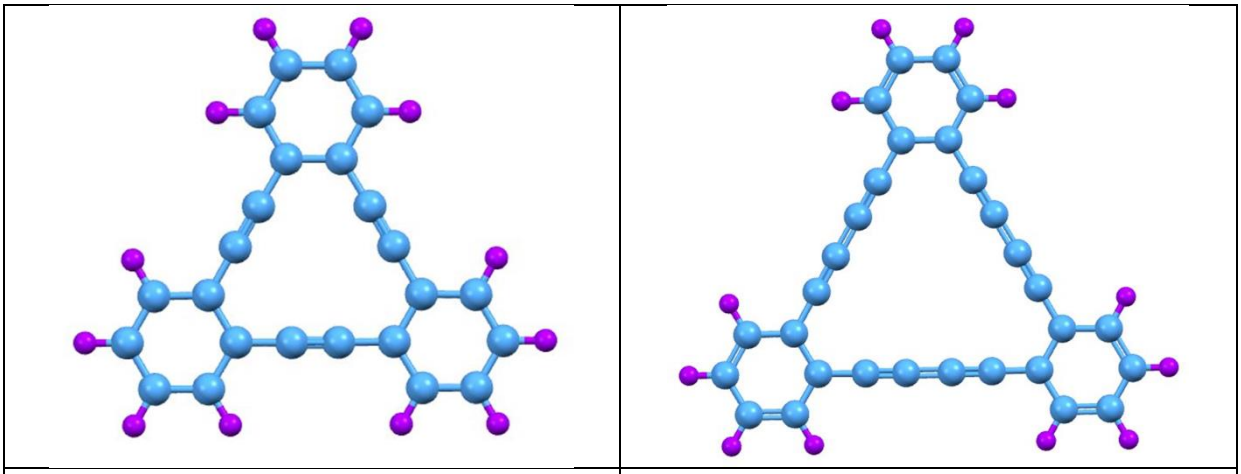


DBA-12	DBA-18

Figure S1: Optimized geometries of dehydrobenzoannulenes, DBA-12 and DBA-18, model compounds of graphyne and graphdiyne respectively.

Table S1: Interaction energies of the cation-π complexes of [2.2.2]PCP-ane, [2.2.2]PCP-ene, CHP and $(C_6H_6)_3$ calculated at the MP2/6-311G(d,p)//ωB97XD/6-311G(d,p) level.

	Interaction energies (kcal mol^{-1})			
	[2.2.2]PCP-ane	[2.2.2]PCP-ene	CHP	$(C_6H_6)_3$
Li^+	-70.10	-62.02	-65.66	-59.31
Na^+	-53.14	-43.86	-47.77	-42.09
K^+	-39.21	-34.12	-37.27	-35.70

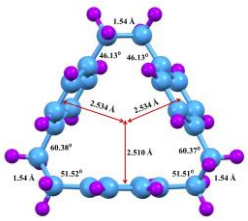
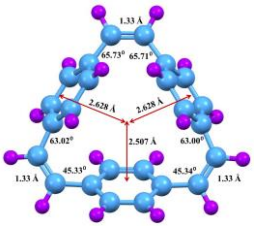
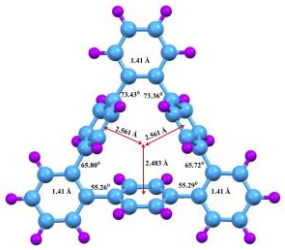
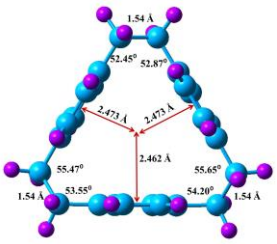
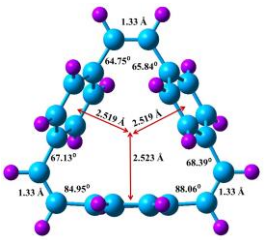
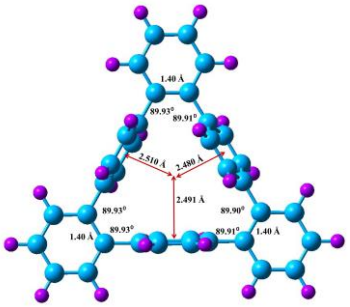
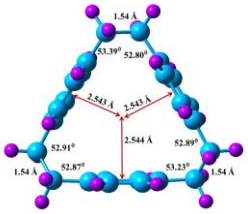
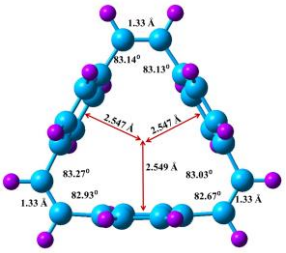
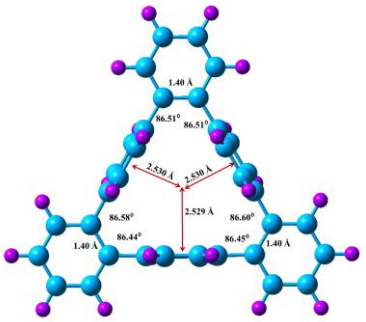
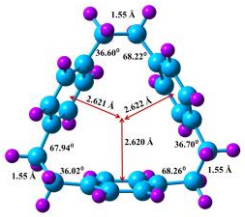
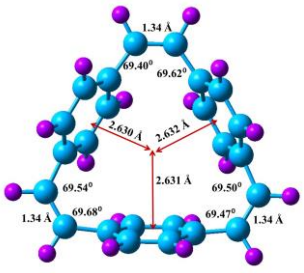
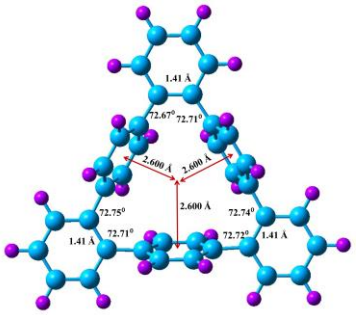
	[2.2.2]PCP-ane	[2.2.2]PCP-ene	CHP
Parent			
Li^+			
Na^+			
K^+			

Figure S2: The key structural parameters (bond lengths, dihedral angles and distances from the centres of the cavities to the centres of the three benzenes) of [2.2.2]PCP-ane, [2.2.2]PCP-ene, CHP and their respective cation-π complexes.

Table S2: Partial charges on the alkali metal ions in various cationic complexes obtained from NBO analysis.

Partial charges (e)				
	[2.2.2]PCP-ane	[2.2.2]PCP-ene	CHP	$(C_6H_6)_3$
Li^+	0.923	0.930	0.933	0.923
Na^+	0.941	0.941	0.943	0.951
K^+	0.954	0.954	0.954	0.957

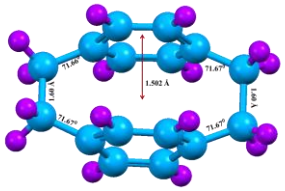
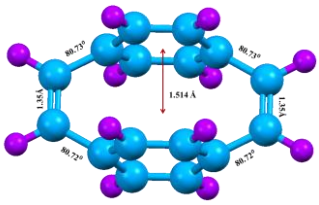
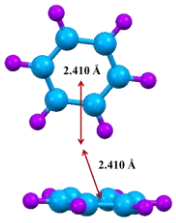
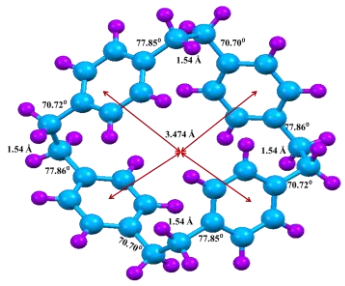
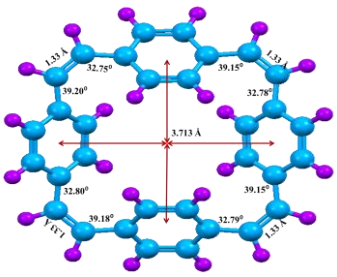
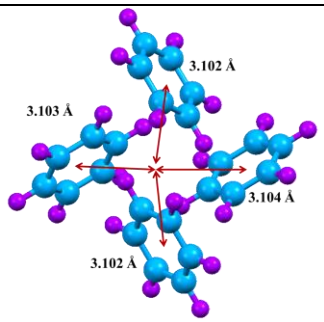
Paracyclophanes	Paracyclophenes	$(C_6H_6)_n$
		
[2.2]PCP-ane ($C_{16}H_{16}$)	[2.2]PCP-ene ($C_{16}H_{12}$)	$(C_6H_6)_2$
		
[2.2.2.2]PCP-ane ($C_{32}H_{32}$)	[2.2.2.2]PCP-ene ($C_{32}H_{24}$)	$(C_6H_6)_4$

Figure S3: The key structural parameters (bond lengths, dihedral angles and distances from the centres of the cavities to the centres of the benzenes) of [2.2], [2.2.2.2]PCP-anes, [2.2], [2.2.2.2]PCP-enes and benzene clusters.

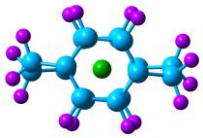
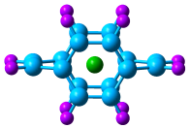
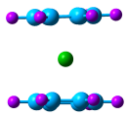
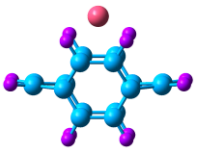
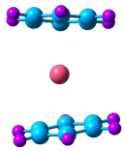
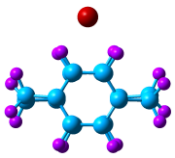
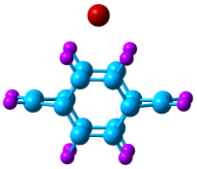
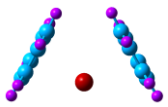
	[2.2]PCP-ane	[2.2]PCP-ene	$(C_6H_6)_2$
Li^+			
	-45.92	-40.97	-63.36
Na^+			
	-21.81	-21.21	-42.64
K^+			
	-11.32	-10.87	-31.45

Figure S4: Optimized geometries and interaction energies (in kcal mol^{-1}) of the cation-π complexes of Li^+, Na^+ and K^+ with [2.2]PCP-ane, [2.2]PCP-ene and $(C_6H_6)_2$.

Table S3: Vertical positions of the ions from the centres of the cavities and (in parentheses) the distances from the ions to the centres of the two benzene rings (in Å) in various complexes of the ions with [2.2]PCPs and $(C_6H_6)_2$. Note that, in case of parent macrocycles, $(C_6H_6)_2$ and complexed $(C_6H_6)_2$, only the distances to the centres of the benzenes are reported.

	Vertical offset distances from the centres of the cavities (Distances from the ions to the centres of the benzene rings) (in Å)		
	[2.2]PCP-ane	[2.2]PCP-ene	$(C_6H_6)_2$
Parent	(1.502, 1.502)	(1.514, 1.514)	(2.410, 2.410)
Li^+	0.0 (1.608, 1.608)	0.0 (1.608, 1.608)	(2.034, 2.035)
Na^+	2.760 (3.416, 3.415)	2.674 (3.368, 3.362)	(2.537, 2.537)
K^+	3.169 (4.019, 4.019)	3.126 (4.00, 4.00)	(2.920, 2.919)

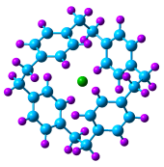
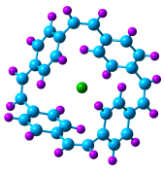
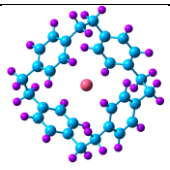
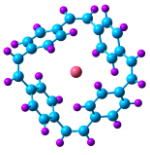
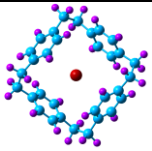
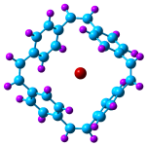
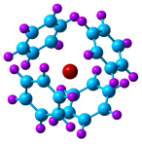
	[2.2.2.2]PCP-ane	[2.2.2.2]PCP-ene	$(C_6H_6)_4$
Li^+			
	-67.05	-57.32	-69.46
Na^+			
	-57.06	-48.91	-56.48
K^+			
	-47.93	-38.38	-45.65

Figure S5: Optimized geometries and interaction energies (in kcal mol^{-1}) of the cation-π complexes of Li^+, Na^+ and K^+ with [2.2.2.2]PCP-ane, [2.2.2.2]PCP-ene and $(C_6H_6)_4$.

Table S4: Vertical positions of the ions from the centres of the cavities and (in parentheses) the distances from the ions to the centres of the four benzene rings (in Å) in various complexes of the ions with [2.2.2.2]PCPs and $(C_6H_6)_4$. Note that, in case of parent macrocycles, $(C_6H_6)_4$ and complexed $(C_6H_6)_4$, only the distances to the centres of the benzenes are reported.

	Vertical offset distances from the centres of the cavities (Distances from the ions to the centres of the benzene rings) (in Å)		
	[2.2.2.2]PCP-ane	[2.2.2.2]PCP-ene	$(C_6H_6)_4$
Parent	(3.474, 3.474, 3.474, 3.473)	(3.712, 3.712, 3.712, 3.712)	(3.102, 3.102, 3.103, 3.103)
Li^+	0.0 (3.294, 3.292, 3.292, 3.291)	0.0 (3.367, 3.362, 3.366, 3.368)	(3.320, 3.605, 2.233, 2.923)
Na^+	0.0 (3.398, 3.401, 3.399, 3.402)	0.0 (3.458, 3.448, 3.476, 3.483)	(2.659, 2.660, 3.440, 3.441)
K^+	0.0 (3.439, 3.439, 3.438, 3.440)	0.0 (3.311, 3.307, 3.307, 3.705)	(3.060, 3.061, 3.061, 3.062)

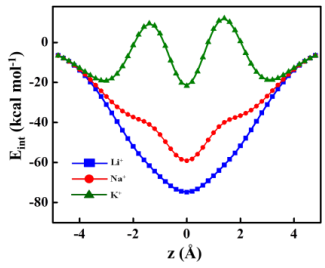
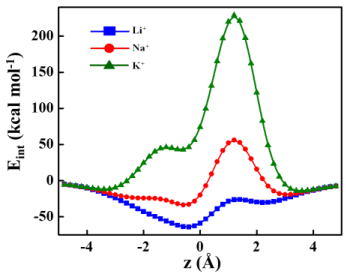
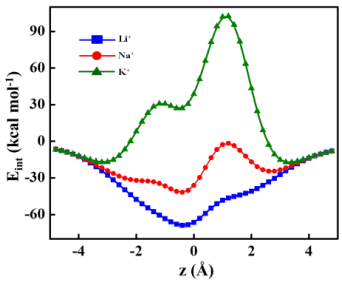
[2.2.2]PCP-ane	[2.2.2]PCP-ene	CHP
		

Figure S6: Energy scans for the passage of the alkali metal ions through the cavities of [2.2.2]PCP-ane, [2.2.2]PCP-ene and CHP calculated using the M06-2X/6-311G(d,p) level of theory.

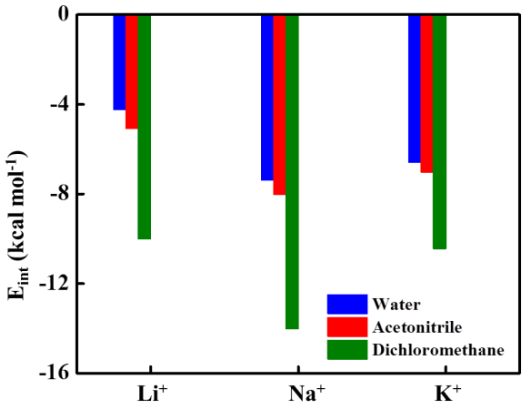


Figure S7: Cation-π interaction energies for the interaction of the alkali ions with [2.2.2]PCP-ane in various solvents calculated at the ωB97XD/6-31G(d,p) level.

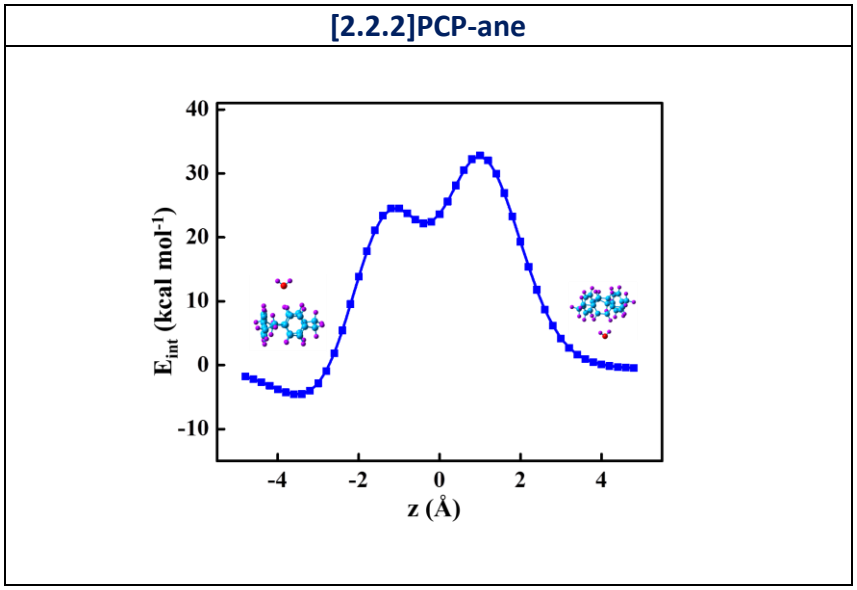


Figure S8: Energy scan for the passage of H_2O through the cavity of [2.2.2]PCP-ane.