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Selective Recognition of Fluoride Salts by Vasarenes: A Key Role of a Self-Assembled in situ Dimeric Entity Via an Exceptionally Short [O-H-O]$^-$ H-Bond

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A self-assembled supramolecular dimeric entity via an exceptionally short (2.404 Å) and strong (22.9 kcal mol^{-1}) [O-H-O]$^-$ hydrogen bond is the key to the special reactivity of vasarenes with fluoride salts. Vasarene is a self-assembled, vase-shaped compound, obtained by the reaction between ninhydrin and phloroglucinol. Analogous compounds are prepared by replacing the phloroglucinol with other polyhydroxy aromatics. Vasarenes show special affinity towards compounds of the type M$^+$F$^-$, where M being a large monovalent cation, producing ion-pairs-vasarene adducts. The first step in the proposed mechanism is the dissociation of the M$^+$F$^-$ salt releasing F$^-$ to the solution, which may provide an explanation as to why only MF salts, which include large monovalent cations, undergo this reaction. From a practical point of view, the ease of their preparation and their special affinity towards fluoride salts makes vasarenes potential means for salt separation. The readily formed dimeric structure with the very short [O-H-O]$^-$ *negative charge-assisted H-bond* (-CAHB) can also be further used as a model in theoretical studies of such systems and understanding their role in biological processes.

Introduction

Vasarene **1** (Fig. 1[a]) is a self-assembled vase-shaped compound obtained by the reaction between ninhydrin and phloroglucinol (1,3,5-benzenetriol)[1]. Analogous compounds are readily prepared by reacting ninhydrin with other polyhydroxy aromatics[2–4]. Previous work by our group[5] has revealed the special affinity of the vasarene towards compounds of the type M$^+$F$^-$ (MF), where M being a large monovalent cation. As a ligand, it was able to solubilize the fluoride salts in organic solvents as well as binding and precipitating them as ion-pair·vasarene adducts by a non-ditopic mechanism[5]. Its binding properties were found to be consistent with AND logic[6,7], displaying no affinity for either of the free cation or anion, yet binding the ion-pair strongly.

The principle of this supramolecular recognition is spatial collaboration between several rigid vasarene molecules, forming a "cage-like" assembly that hosts the heavy alkali fluorides, K, Rb and Cs. We had previously explained the inability to bind the lighter alkali fluorides, NaF or LiF, by the rigidity, and three-dimensional structure of the vasarene assembly, which confines a cavity incapable of constricting sufficiently to bind Li$^+$ and Na$^+$ that are apparently too small to span the distance required to form stable complexes[5].

Intrigued by the potential of this uncommon reaction, both from theoretical and practical aspects, we began to investigate the driving force for this process. Several analogues were prepared by replacing the phloroglucinol with other polyhydroxybenzenes: 1,3-benzenediol (resorcinol), 1,2-benzenediol (catechol), 1,2,3-benzenetriol (pyrogallol)[3], and 1,2,4,5-benzenetetrol. Their reactions with various ion-pairs, fluorides and others have been studied. All exhibited selective affinity to alkali fluorides, while some of the complexes are yet to be fully characterized by X-ray crystallography. Here we suggest a multistep mechanism for the complexation reaction in solution, which explains more systematically why only MF salts containing large M$^+$, can participate in this supramolecular process. The hypothesis is demonstrated within the reactions of one analogue, the bis ninhydrin-resorcinol.

Results and Discussion

Vasarene-analogue (Fig. 1[b-c]) was prepared according to

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† The research was supported by the Pazy Research Foundation.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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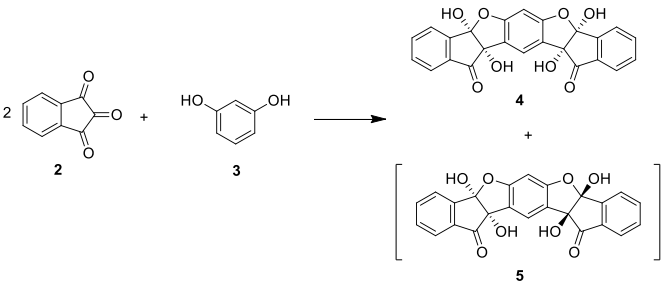
Table 1. Thermodynamic properties of monovalent fluoride salts and their complexations with **4**[a]

M^+F^- salt	Cationic radius (Å)[b]	Lattice Enthalpy, ΔH_L°[c] (kcal mol^{-1})	Hydration Enthalpy of Cation, ΔH_h°[d] (kcal mol^{-1})	Total Enthalpy $\Delta H_L^\circ+\Delta H_h^\circ(F^-+M^+)$[e] (kcal mol^{-1})	Indication for reaction from UV-vis Spectra
LiF	0.76	250.1	-134.8	+5.9	-
NaF	1.02	221.8	-107.3	+5.1	-
KF	1.38	197.5	-87.5	+0.6	+
RbF	1.52	189.4	-81.5	-1.5	+
CsF	1.67	180.8	-75.5	-4.1	+
NH_4F	1.61	201.5	-88.2	+3.9	-
Me_4NF	2.79	131.1	-60.0	-38.3	+
Et_4NF	3.36	116.2	-57.1	-50.3	+
Bu_4NF	4.13	110.8	-62.1	-60.7	+

[a] Conditions for all reactions: EtOH containing 1% of dist. H_2O at approx. 40˚C. [b] LiF-AF data for cationic radii from R. D. Shannon et al[8], TMAF-TBAF from Y. Marcus[9]. [c] ΔH_L° data for LiF-AF was obtained from S.W. Benson et al[10], for TMAF-TBAF it was calculated using the Kapustinskii equation[11], [d] ΔH_h° data was obtained from Y. Nagano et al[12,13] [e] ΔH_h° for F^- was taken as -109.4 kcal mol^{-1}[14]

Kim's procedure[1] using a stoichiometric ratio of 2:1 ninhydrin-**2**:resorcinol-**3** (Scheme 1). Crystallization (EtOH) showed the formation of both "boat" and "chair" configurations (Fig. 1) with the "boat" **4** as the major product, accompanied by **5** (less than 2%), precipitating later from the filtrate. The calculated ΔE between the two does not exceed 0.2 kcal mol^{-1} (Table S2), which may explain the formation of both configurational isomers.



Scheme 1. The reaction between ninhydrin **2** and resorcinol **3** (2D projections) to form the "boat" configuration **4** and the "chair" configuration **5** (constitutes less than 2% of the product).

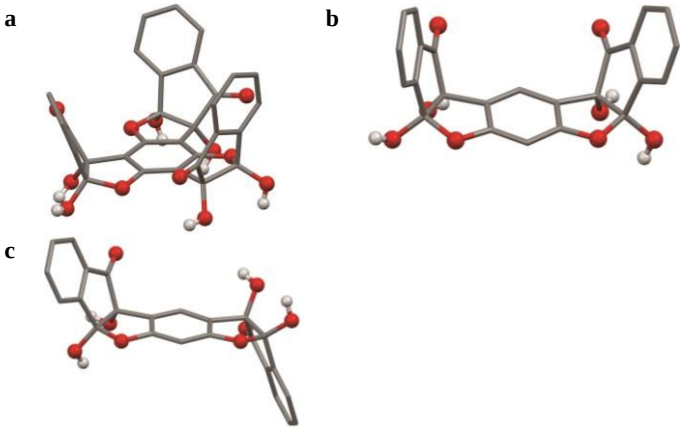


Fig. 1. Molecular X-ray structures of bis ninhydrin resorcinol analogue compared to the original vasarene: [a] vasarene **1**; [b] analogue-"boat" isomer **4**; [c] analogue-"chair" isomer **5**. In all structures, aromatic H atoms and solvent molecules have been removed for clarity.

Similar to **1**[5], **4** has shown no affinity to the lighter alkali fluorides or any other non-fluoride halide salt, while exhibiting a selective affinity for the heavier alkali fluorides RbF and CsF. Also, **4** readily binds and precipitates quaternary ammonium fluorides (R_4NF) that possess even larger monovalent cations (**Table 1**). It was effective in binding both Me_4NF (TMAF) and Et_4NF (TEAF) salts. The still larger $^nBu_4NF$ (TBAF) reacted similarly with **4** as indicated by a UV-vis absorption spectrum, but so far a pure crystalline product for X-ray analysis could not be isolated. However, NH_4F (AF), with a cationic radius close to that of Cs^+, did not produce any observable reaction with **4**. The results are summarized in **Table 1** and the crystallographic structures of the complexes are shown in **Fig. 2**.

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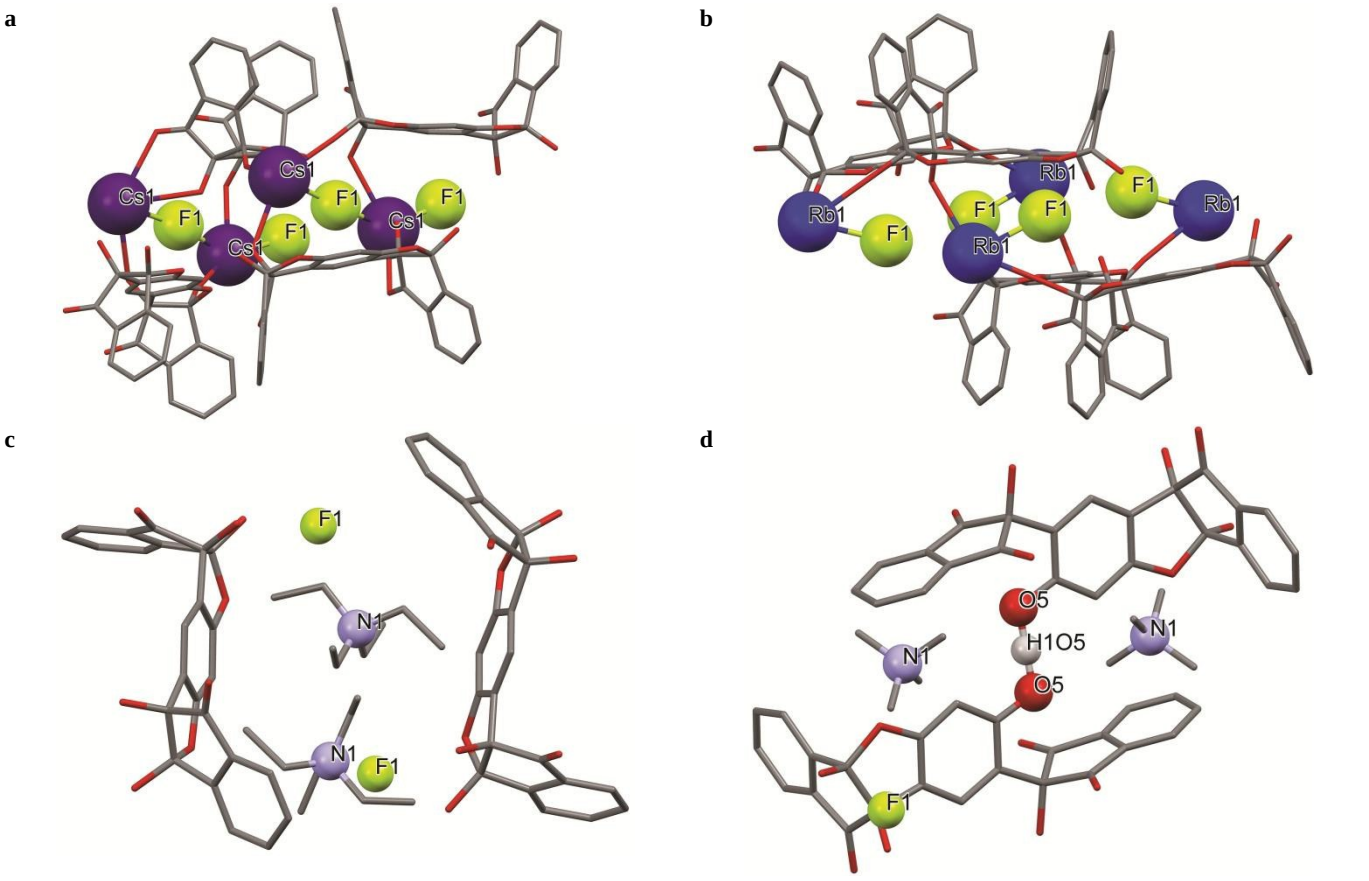


Fig. 2. X-ray structures of the complexes of: [a] **6** (**4**·CsF), [b] **7** (**4**·RbF), [c] **8** (**4**·TEAF), [d] **9** (**4**·TMAF); (shown are fragments of crystal packing in which H atoms and alternative disorder sites have been removed for clarity).

Fig. 2 shows a similar complex formation to that of **1** with alkali-fluorides[5]. There is an alternating arrangement of ligand and salt "layers", where the salt "chains" are held together by intermolecular interactions of hydrogen bonding and coordination to the oxygen groups of the ligands. The cell unit is made of a mirror image of single recurring unit creating π-π interactions between the rings of the ligands, thus, stabilizing the lattice. In the TEAF complex **8**, the ligands best stabilize the ion-pair complex in their "chair" configuration, requiring opening of one hemiketal bond and ring closure from opposite side[2]. However, **9** does not follow the same pattern of complex formation. In this case also, one hemiketal bond opens, but instead of ring closure, it forms a dimer with a second partially open ligand via an exceptionally short[15,16] and strong [O-H-O]$^-$ hydrogen bond[17], with O···O distance of 2.404(3)Å, corresponding to a *negative charge-assisted H-bond* (-CAHB) as defined by Gilli et al[18,19]. There are only few reported X-ray structures of organic compounds containing a similar motif of a linear [O-H-O]$^-$. Among them the O···O distances specified – e.g. 2.46[16], 2.45Å[15], 2.44Å[20] and even the shortest 2.43Å[21] – are all longer than the one found in structure **9**.

An intriguing observation during the complexation reactions was an immediate color change to intense yellow upon addition of MF to the **4** solution in EtOH/H_2O. This color was greatly intensified and red-shifted when carried out in a polar aprotic solvent system as DMSO. From the UV-vis absorption spectra, we could clearly spot a pattern as the reaction mixture of all the MF salts with large M^+ absorbed at the same range of 450-460 nm, while the smaller LiF, NaF and also NH_4F showed no significant absorbance (**Fig. 3**). The same peak was characteristic also to a solution of the pure crystalline adducts, both the colorless **6**-**8** and intense yellow **9**. This observation has led us to suggest that a single common complex structure in situ is shared by all the salts, prior to the formation of the final diverse arrangements in the solid state.

The key to understanding the common complex structure in solution was the unique dimer formation of **9**, for which we proposed a possible 5-step mechanism (**Scheme 2**), assumed to be a model to all

the others. At first, a dissociation of MF occurs with the release of free F^- to solution. The F^- acts as a Broensted base[22] removing a proton from the OH of the hemiketal group, which triggers a ring opening. Then, as HF is also capable of forming strong H-bonds[23], we suggest that HF thus produced remains attached to the phenolate oxygen via an $[O\text{-}H\text{-}F]^-$ H-bond with M^+ as counter-ion. This structure can react with another to form a dimer via $[O\text{-}H\text{-}O]^-$ (-)CAHB. The energetically favored symmetrical dimer formation, as calculated by DFT (E_{HB} =22.9 kcal mol^{-1}), is believed to be the driving force to this mechanism. Also, both aromatic entities on the two sides of the $[OHO]^-$ bond that form a plane, as well as the overlapping between the other two aromatic rings, all help stabilizing the dimer thus formed. We assume that this planarity along with the very strong and short H-bond may hold the key to the color formation[16], though its exact origin is still to be investigated. The missing links to the formation of the crystalline structures after the dimer falls apart as well as understanding why the TMAF complex **9** is the only one to also precipitate as its in situ dimeric entity are currently under study.

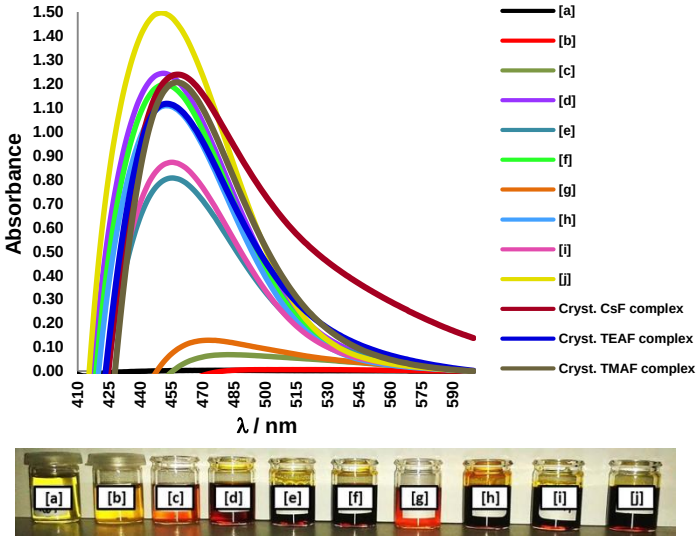
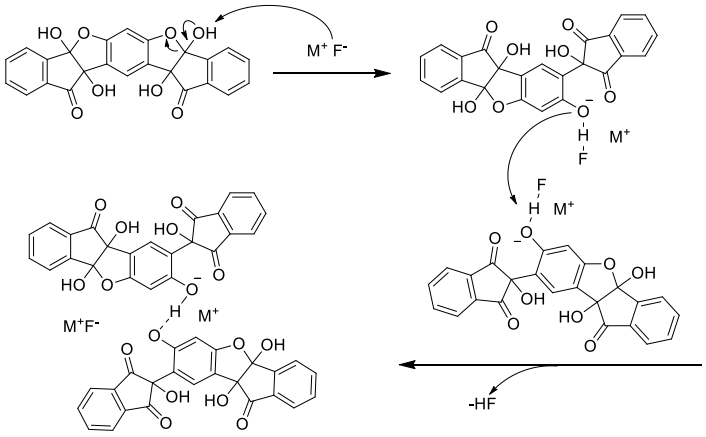


Fig. 3. Reduced UV-vis absorption spectra of **4** with different fluoride salts in DMSO: [a] **4** reference; [b] **4**·LiF; [c] **4**·NaF; [d] **4**·KF; [e] **4**·RbF; [f] **4**·CsF; [g] **4**·NH_4F; [h] **4**·Me_4NF; [i] **4**·Et_4NF; [j] **4**·Bu_4NF.



Scheme 2. The proposed mechanism for a complex formation in solution.

In this mechanism, F^- plays a dual role, with its presence and unique characteristics being essential for the formation of a complex. Firstly, by its ability to act as a base[22] that triggers the dimer formation, and secondly, by forming strong H-bonds with the vasarene and remaining attached contrarily to a regular acid-base reaction. Hence, for a complex formation, the F^- has to be easily separated from its counter M^+. This can be achieved under two conditions: 1. The lattice enthalpy, ΔH_L°, of the MF must be low (endothermic) – this is directly proportional to the M^+ radius that has to be sufficiently large, 2. The hydration/solvation enthalpy, ΔH_h°, must exceed the absolute value of ΔH_L°, thus, ensuring a spontaneous process (**Table 1**). It is clear from Table 1 that our empirical observations coincide precisely with the theoretical values. We can see that the anomalous AF has, in fact, a higher ΔH_L°, as a result of additional H-bonding between the F^- and the NH[13], so despite its large M^+ radius, is a poor source for F^-. It is also observed that KF is right on the boundary between being a non-spontaneous to a spontaneous process, which may provide an explanation to the difficulty encountered in achieving a well-defined complex.

To support our proposed mechanism in solution we have dissolved a pure crystalline TMAF complex **9** in DMSO-d_6 for ^{1}H-NMR. The spectrum clearly revealed the downfield broad signal[16] at 16.5ppm corresponding to 1H, characteristic to a low barrier H-bond[24,25]. This signal did not originate from the TMAF itself, as its reference ^{1}H-NMR showed no signal in the 12-20 ppm range. ^{1}H-NMR spectra of the other crystalline and in-situ complexes in DMSO-d_6 have all revealed this characteristic downfield signal at 16-18ppm.

In an attempt to further examine our hypothesis, we have looked at the removal of H^+ from the hemiketal OH by F^- (**Scheme 2**). Our assumption was that when selectively blocking these two OH groups, no reaction with MF will take place. An O,O'-dimethyl derivative of **4** was synthesized (**10**) using MeOH/I_2[26] and reacted with CsF in DMSO (**Scheme S1**). No reaction could be observed, supporting our proposed mechanism (Fig. S7).

The selective affinity towards the heavier alkali fluorides and the ability of **4** to solubilize the otherwise insoluble CsF in DMSO was also reinforced by performing ^{133}Cs and ^{19}F multinuclear NMR measurements to complex **6** in DMSO-d_6 (Fig. S8-9). Clear signals for Cs^+ (71.9 ppm), F^- (-138.9 ppm) and HF (-146.8 ppm) were observed, while the reference insoluble CsF in DMSO-d_6 showed none[5]. Referring to Popov's study[27], we can evidently see that the Cs^+ is solubilized by **4** as its signal is dramatically shifted by approx. 100 ppm to the range of an alcohol environment from a pure DMSO surrounding at ~ -70 ppm.

Conclusions

In this work, we wished to substantiate the supramolecular process involved in the in situ complexation of MF salts by vasarenes. The proposed mechanism involves a common supramolecular dimeric entity shared by all complexes, providing the key to understanding the selective affinity of vasarenes towards MF salts with large M^+. This mechanism and dimer formation was supported by X-ray

crystallography, the presence of a broad downfield (16-18ppm) characteristic signal in ^{1}H-NMR, ^{133}Cs and ^{19}F-NMR indicating the solubilization of otherwise insoluble CsF as a **4**·CsF complex in DMSO[27] (Figs S8-9), a FT-IR strong broad band at 600-800 cm^{-1} characteristic to proton vibrations of a short and symmetrical homo-conjugated [O-H-O]$^{-}$[16] (Fig. S10), DFT calculations of E_{HB} as well as UV-vis absorption at ~455nm shared by all complexes that coincides precisely with the thermodynamic properties of the MF salts, and, finally, the fact that no color change was observed for the protected analogue **10**. We also believe that this easily formed dimeric structure with an exceptionally short[15,16] [O-H-O]$^{-}$ (-)CAHB can be further used as a model in theoretical studies of such systems and understanding their role in biological processes[28].

Experimental section

Ligand synthesis

Ninhydrin, **2** (6479 mg, 36.38 mmol) and resorcinol, **3** (2000 mg, 18.17 mmol) were stirred at 70-80°C in glacial acetic acid (50 mL) for 24h. During that time the mixture turned clear dark blue followed by formation of a white precipitate. The reaction mixture was allowed to cool to RT and the solid was collected by vacuum filtration. The product was washed with glacial acetic acid followed by cold diethyl ether to produce a white powdery solid (6913 mg, 88%). Crystallization (EtOH) afforded colorless crystals of **4**. Occasionally, from the filtrate precipitated less than 2% of **5**, which was crystallized from EtOH.

Bis ninhydrin resorcinol – "boat" configuration 4: (4*R*,12*R*,18*S*,26*S*)-4,12,18,26-Tetrahydroxy-13.17-dioxaheptacyclo[14.10.0.0^{3,14}.0^{4,12}.0^{6,11}.0^{18,26}.0^{19,24}]hexacosa-1,3(14),6(11),7,9,15,19(24),20,22-nonaene-5,25-dione

M.P > 278ºC (decomp.); Anal. Calcd. For $C_{24}H_{14}O_8$+H_2O: C, 64.28; H, 3.57 Found: C, 64.17; H, 3.84; ^{1}H-NMR (MeOD) δ (ppm): 6.19 (s, 1H), 7.60 (s, 1H), 7.78 (m, 8H), UV/Vis (DMSO): λ_{max}= 347, 368, 394 nm; IR: ν= 535, 608, 715, 771, 861, 932, 1033, 1124, 1222, 1428, 1471, 1605, 1706, 2071, 2352, 2674, 3304, 3468 cm^{-1}; MS/MS positive mode ESI (m/z): 414.07 [(M+H)-H_2O]$^{+}$, 449.11 [M+NH_4]$^{+}$ 453.06 [M+Na]$^{+}$, 883.13 [2M+Na]$^{+}$; Crystallographic data: $C_{24}H_{14}O_8$, M_W = 430.35, P$\bar{1}$ a =7.5394(6) Å, b=10.6149(9) Å, c=12.1610(1) Å, α = 84.000(1)°, β = 75.382(1)°, γ = 86.891(2)°, V=936.2(1) Å^3, Z=2, T=173(1) K, R_1 = 6.06%;

Bis ninhydrin resorcinol – "chair" configuration 5: (4*S*,12*S*,18*S*,26*S*)-4,12,18,26-Tetrahydroxy-13.17-dioxaheptacyclo[14.10.0.0^{3,14}.0^{4,12}.0^{6,11}.0^{18,26}.0^{19,24}]hexacosa-1,3(14),6,8,10,15,19,21,23-nonaene-5,25-dione

Crystallographic data: $C_{24}H_{14}O_8$•CH_3CH_2OH, M_W = 476.42, P2$_1$/c, a = 10.811(1) Å, b =7.8640(8) Å, c=26.025(3) Å, β = 99.560(2)°, V=2181.8(4) Å^3, Z=4, T=173(1) K, R_1 = 9.77%

Complexation reactions

4•MF (M = Rb, Cs) complexes: Bis ninhydrin resorcinol **4** (430 mg, 1 mmol) was dissolved in hot ethanol (15 mL). MF (1 mmol; 106 and 150 mg for RbF and CsF respectively) was dissolved in hot ethanol (3 mL). Upon addition of the MF solution to the solution of **4** an immediate color change to intense yellow was observed. Crystalline precipitate was formed after ~24h at RT, filtered and washed with cold ethanol.

Complex 6: cesium fluoride complex of vasarene-analogue 4: Anal. Calcd. For $C_{26}H_{20}O_9CsF$ (**4•CsF**•CH_3CH_2OH): C, 49.65; H, 3.18; F, 3.02 Found: C, 49.55; H, 2.95; F, 2.53; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.10-8.26 (m, 20H), 16.68-17.50 (brs, 1H); ^{133}Cs-NMR (DMSO-d_6) δ(ppm): 71.90; ^{19}F-NMR (DMSO-d_6) δ(ppm): -138.9, -146.8; UV/Vis (DMSO): λ_{max}= 368, 371, 452 nm. IR (KBr) ν: 609, 714, 774, 829, 879, 889, 979, 1019, 1105, 1145, 1174, 1215, 1255, 1300, 1425, 1460, 1615, 1711, 2502, 2562, 2667, 2772, 3183, 3423 cm^{-1}; MS/MS positive mode ESI (m/z): 563.97 [M–H_2O]$^{+}$, 1146.91 [(2M+H)–H_2O]$^{+}$; Crystallographic data: $C_{24}H_{14}CsFO_8$•CH_3CH_2OH, M_W =628.33, Pbca, a = 12.2617(9) Å, b=15.379(1) Å, c = 25.646(2) Å, α = 90°, β=90°, γ = 90°,V=4836.1(6) Å^3, Z=8, T=173(1) K, R_1 = 2.54%

Complex 7: rubidium fluoride complex of vasarene-analogue 4: Anal. Calcd. For $C_{26}H_{20}O_9RbF$ (**4•RbF**•CH_3CH_2OH): C, 54.27; H, 3.47; F, 3.30 Found: C, 54.45; H, 3.18; F, 2.24; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.06-8.37 (m, 20H), 16.10 (brs, 1H); UV/Vis (DMSO): λ_{max}= 359, 370, 455 nm . IR (KBr) ν: 609, 654, 709, 769, 884, 939, 969, 1004, 1029, 1089, 1174, 1215, 1280, 1470, 1600, 1721, 1841, 2542, 2973, 3423 cm^{-1}; MS/MS positive mode ESI (m/z): 516.97 [(M+H)–H_2O]$^{+}$; Crystallographic data: $C_{24}H_{14}FO_8Rb$•CH_3CH_2OH (in disorder), M_W =574.84, Pbca, a =12.194(1) Å, b =15.536(2) Å, c =25.299(2) Å, α= 90°, β= 90°, γ= 90°, V=4792.7(8) Å^3, Z=8, T=295(1) K, R_1 = 6.26%

4•R_4NF (R = Me, Et) complex: Bis ninhydrin resorcinol **4** (220 mg, 0.5 mmol) was dissolved in hot ethanol (15 mL). R_4NF (0.5 mmol; 85 and 95 mg for Me_4NF•$4H_2O$ and Et_4NF•$2H_2O$ respectively) was dissolved in hot ethanol (3 mL) and few drops of distilled water. Upon addition of the R_4NF solution to the solution of **4** an immediate color change to intense yellow was observed. Crystalline precipitate (yellow and colorless crystals for **4•Me$_4$NF** and **4•Et$_4$NF** respectively) was formed after ~24h at RT, filtered and washed with cold ethanol.

Complex 8: tetraethyl ammonium fluoride complex of vasarene-analogue 4: Anal. Calcd. For $C_{34}H_{40}O_9NF$ (**4•(CH$_3$CH$_2$)$_4$NF**•CH_3CH_2OH): C, 65.28; H, 6.14; N, 2.24; F, 3.04 Found: C, 65.45; H, 6.11; N, 2.13; F, 2.75; ^{1}H-NMR (DMSO-d_6) δ (ppm): 1.15 (t, 24H, TEA^{+}), 3.18 (q, 16H, TEA^{+}), 7.20-8.01 (m, 20H), 14-18 (brs, 1H); UV/Vis (DMSO): λ_{max}= 359, 369, 455 nm . IR (KBr) ν: 578, 609, 704, 774, 859, 904, 999, 1044, 1079, 1145, 1210, 1265, 1310, 1395, 1455, 1605, 1711, 2667, 2878, 2978, 3168, 3518 cm^{-1}. Crystallographic data: $C_{24}H_{14}O_8$•$(CH_3CH_2)_4NF$•CH_3CH_2OH, M_W =625.67, P2$_1$, a =9.5145(7) Å, b =16.6525(1) Å, c =9.5978(7) Å, β = 94.788(1)°, V=1515.37(2) Å^3, Z=2, T=173(1) K, R_1 = 5.27%

Complex 9: tetramethyl ammonium fluoride complex of vasarene-analogue 4: Anal. Calcd. For $C_{60}H_{65}FN_2O_{19}$ {[**2[4]•(CH$_3$)$_4$N]•(CH$_3$)$_4$NF**•2CH_3CH_2OH•H_2O}: C, 63.37; H, 5.76; N, 2.46; F, 1.67 Found: C, 63.63; H, 5.69; N, 2.23; F, 1.74; ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.07 (s, 24H, TMA^+), 7.08-8.28 (m, 20H), 16.10-18.24 (brs, 1H); UV/Vis (DMSO): λ_{max}= 354, 369, 452 nm. IR: ν= 577, 624, 685, 715, 767, 864, 941, 1119, 1207, 1224, 1486, 1608, 1702, 2335, 2607, 2746, 3035, 3165, 3269, 3616 cm^{-1}; MS/MS positive mode ESI (m/z) (for Dimer without salt): 883.12 $[M+Na]^+$; Crystallographic data: [$C_{48}H_{27}O_{16}$•$(CH_3)_4N$] •$(CH_3)_4NF$• 2CH_3CH_2OH (in disorder), M_W = 1130.08, $P\bar{1}$, a = 9.749(1) Å, b =11.785(1) Å, c =14.738(2) Å, α= 70.446(2)°, β= 86.671(2)°, γ=71.563(2)°, V=1511.5(3) $Å^3$, Z=1, T=295(1) K, R_1 = 7.44%

Notes and references

‡ CCDC 1042999–1043004 contain all the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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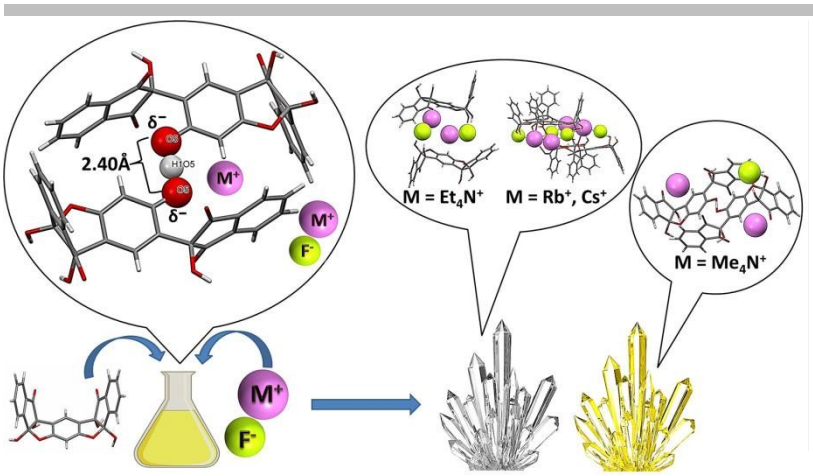
Graphical Abstract



A supra-molecular dimeric entity with an exceptionally short [O-H-O]$^-$ H-bond is the key for binding M$^+$F$^-$ ion-pairs by vasarenes.

*R. Bengiat, M. Gil, A. Klein, B. Bogoslavsky, S. Cohen, F. Dubnikova, G. Yardeni, I. Zilbermann and J. Almog**

Selective Recognition of Fluoride Salts by Vasarenes: A Key Role of a Self-Assembled in situ Dimeric Entity Via an Exceptionally Short [O-H-O]$^-$ H-Bond