Metric engineering of supramolecular borromean rings†

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Electronic Supplementary Information
Experimental Methods

General. IR spectra were recorded with a Perkin-Elmer 2000 FT-IR spectrophotometer. Melting points were established with a Reichert instrument. Commercially available chemicals were used without further purification. $^1$H and $^{19}$F NMR spectra were recorded on a Bruker ADV 500 spectrometer at 25 °C. TMS and CFCl$_3$ were used as internal standards. Chemicals were purchased from Sigma-Aldrich and Apollo Scientific.

X-ray diffraction analysis. X-ray structures at room temperature were determined using a Bruker P4 diffractometer. X-ray structures at low temperature were determined using a Bruker SMART-APEX CCDC area detector diffractometer, equipped with a Bruker KRIOFLEX low temperature devices able to work until 90 K with a thermal stability of ±0.5 K.

General procedure for the synthesis of the complexes 7 and 9: Complexes 7 and 9 were obtained by dissolving, in a vial of clear borosilicate glass and at room temperature, the three starting materials 1, 2 and 3 or 5 in a 1:1:1.5 ratio, respectively. Ethanol was used as solvent. The open vial was closed in a cylindrical wide-mouth bottle containing vaseline oil. The solvent was allowed to diffuse at low temperature for 3 and at room temperature for 5. After a period ranging from three to five days colorless crystals were isolated.

7: Mp (ethanol) 127-130 °C (dec.); FT IR (KBr/ν cm$^{-1}$, selected bands): 2974(m), 280(m), 1487(w), 1447(w), 1364(m), 1355(m), 1301(m), 1135(s), 1105(vs), 1087(vs), 706(s), 691(s). $^1$H NMR (CDCl$_3$, 0,046 M): δ 2.58 (t, 12H), 3.57 (t, 12H), 3.64 (s, 12H); $^{19}$F NMR (CDCl$_3$, 0,069 M): δ -53.65 (s, 4F).

9: Mp (ethanol) 107-110 °C (dec.); FT IR (KBr/ν cm$^{-1}$, selected bands): 2969(m), 2890(s), 2830(m), 1485 (w), 1448(m), 1364(s), 1209(vs), 1146(vs), 1106(vs), 1085(vs), 947(s), 832(w), 586(m). $^1$H NMR (CDCl$_3$, 0.028 M): δ 2.58 (t, 12 H), 3.57 (t, 12 H), 3.64 (s, 12H); $^{19}$F NMR (CDCl$_3$, 0.041 M): δ -61.37 (br s, 4F), -114,25 (br s, 4F), -121,98 (br s, 4F).
Figure S1: Complex 7: Projection along the $c$ axis (A) and along the $b$ axis (B) of one fluorinated weave showing how it shapes up as an “eggs tray” where supercational “eggs”, namely K.2.2.2. ⊂ K+ ions, are accommodated (only two supercational “eggs” are represented here). Supercations K.2.2.2. ⊂ K’ are represented only by K’. The height of the tray corresponds to the fluorous layer thickness, namely to the separation between the two triangles defined by the alternating I’ (see text, Fig. 1). This height is 9.638 Å. Colours are as follows: K’ blue, I’ light brown, I violet, F green, C gray.
Figure S2: Complex 8: Projection along the c axis (A) and along the b axis (B) of one fluorinated weave. The close similarity with the packing of 7 is apparent. The (6,3) network forms an “eggs tray” where supercationic “eggs”, namely K.2.2.2.⊂K⁺ ions, are accommodated (only two supercationic “eggs” are represented here). Supercations K.2.2.2.⊂K⁺ are represented only by K⁺. The starting module 4 being longer than 3, the height of the tray (corresponding to the fluorous layer thickness, namely to the separation between the two triangles defined by the alternating I⁻, see text, Fig. 1), is 10.207 Å, namely greater than in 7. Colours are as in Figure 1S.
Figure S3: Complex 9: Projection along the \( c \) axis (A) and along the \( b \) axis (B) of one fluorinated weave. The similarity of this packing with 7 and 8 is apparent. The three interpenetrated (6,3) networks of a fluorinated layer form an “eggs tray” where K.2.2.2. \( \subset \) K’ ions are accommodated (only two supercations “eggs” are represented here). Supercations K.2.2.2. \( \subset \) K’ are represented only by K’. The starting module 5 being longer than 4 and 3, the height of the tray (corresponding to the fluorous layer thickness, namely to the separation between the two triangles defined by the alternating I’, see text, Fig. 1), is 12.384 Å, namely greater than in 8 and 7. Colours are as in Figure S1.
Figure S4: Complex 10: Projection along the c axis (A) and along the b axis (B) of one fluorinated weave. The close similarity with 7, 8 and even more with 9 is apparent. The three interpenetrated (6,3) networks of a fluorinated layer form an “eggs tray” where K.2.2.2. ⊂ K⁺ ions are accommodated (only two supercationic “eggs” are represented here). Supercations K.2.2.2. ⊂ K⁺ are represented only by K⁺. The starting module 6 being the longest among the studied diidoPFAs 3-6, the height of the tray (corresponding to the fluorous layer thickness, namely to the separation between the two triangles defined by the alternating I⁻, see text, Fig. 1), is 15.529 Å, namely the greatest in series. Colours are as in Figure S1.
Figure S5: Complex 7: The supercation $\text{K}_{2.2.2}.c.\text{K}^+$, here represented only by $\text{K}^+$, and its surrounding poliiodide anion. The fluorine atoms are omitted and only one of the two disordered models of $\text{C}_2\text{F}_4\text{I}_2$ molecules are shown. The six iodide anions around the cation are the vertices of a trigonal prism having basal edge and height of 11.748 and 4.534 Å, respectively (this height correspond to the thicknesses of the cation layers). The anions form a vessel closed at the bottom by another iodide anion. A) Side view; B) View from the top (along the $c^*$ axis); C) View from the bottom. Colours as in Figure 1S.
Figure S6: Compound 8: The supercation K\textsubscript{2.2.2.} \( \subset \) K\textsuperscript{+} (represented only by K\textsuperscript{+}) and its surrounding poliodide anion. A) Side view; B) View from the top (along the \( c^* \) axis); C) View from the bottom. The six iodide ions around the cation are the vertices of a deformed trigonal prism having basal edge and height of 11.740 - 11.775 and 4.702 Å, respectively (this height correspond to the thicknesses of the cation layers). As in 7, the anions form partially opened vessels.
Figure S7: Compound 9: The supercation K\textsubscript{2.2.2.}⊂K' (represented only by K') and its surrounding poliiodide anion. A) Side view; B) View from the top. The six iodide anions around the cation are the vertices of a trigonal prism having basal edge and height of 11.861 and 4.935 Å, respectively (this height correspond to the thicknesses of the cation layers). In this structure the anionic capsule is formed by two equivalent holes, each one defined by C\textsubscript{6}F\textsubscript{12}I\textsubscript{2} molecules of three different, not linked each other, poliiodide networks. The particularly close structural similarity of compounds 9 and 10 is confirmed by the fact that they crystallize in the same space group (P-3) with a variation of the c axis dependent of the diiodoperfluorocarbon chain length (17.719 and 20.294 Å for 9 and 10, respectively).
Figure S8: Compound 10: The supercation $K.2.2.2. \subset K^+$ (represented only by $K^+$) and its surrounding poliiodide anion. A) Side view; B) View from the top. The six iodide anions around the cation are the vertices of a trigonal prism having basal edge and height of 11.828 and 4.136 Å, respectively (this height correspond to the thicknesses of the cation layers). The anionic shell is similar to 9, but here the two valves are closer.