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Self-Assembly and Self-Organization of Self-Recognizing Cyclophanes

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An analysis is presented of the different contributions that give rise to the packing observed in the crystal structures of a wide range of bipyridinium-based molecular assemblies and supramolecular arrays. It is demonstrated how the various interactions – electrostatic, van der Waals, and π-π interactions – that contribute to the solid-state arrangement of these molecules and supermolecules can be utilized in order to design a series of tetracationic cyclophanes that can potentially self-organize in a highly ordered way in the solid state by virtue of the fact that they contain π-electron donors as well as π-electron acceptors. The syntheses of these cyclophanes is outlined and the tunability of the self-assembly methodology in their construction is demonstrated. One of these tetracationic cyclophanes – comprising π-electron-rich hydroquinone rings and π-electron-deficient bipyridinium units – has been shown to pack as highly ordered two-dimensional, mosaic-like sheets in the solid state. Its dicationic precursor also forms extended π-π-stacked layers in the solid state. An analogous cyclophane – containing two π-electron-rich resorcinol rings in place of the two hydroquinone rings – forms, in the solid state, one-dimensional arrays wherein the component resorcinol rings interact through their parallel π-π stacking. It has also been established that the first of the aforementioned tetracationic cyclophanes forms a 1:1 adduct with ferrocene in both the solution and solid states. X-ray crystallography, performed on the 1:1 adduct, reveals that not only is the ferrocene molecule complexed in a π-π stacking sense within the tetracationic cyclophane, but the 1:1 adduct also packs in a manner that is remarkably similar to the supramolecular organization of the free cyclophane in the crystalline state.

Introduction

Self-assembly processes have been employed[1] successfully to build with accuracy molecular assemblies and supramolecular arrays formerly unattainable using conventional chemistry. Hydrogen bonding,[2] metal-ligand complexation[3] and π-π stacking[4] recognition motifs have been employed rationally to design and, to some extent, realize one-, two-, and three-dimensional solid-state arrays and networks.[5] The creation of a new generation of functioning materials depends ultimately on the development of molecular and supramolecular architectures exhibiting novel properties.[6] A more fundamental understanding of the molecular recognition phenomena leading to these proper-

ties is of the utmost importance to the chemist who wishes to develop new organic materials.

Figure 1. A generic cyclophane containing four recognition units that can act as both an *endo* and an *exo* receptor; the two black rectangles represents two identical interacting units; the white and grey rectangles represents two interacting units that can be either identical or different
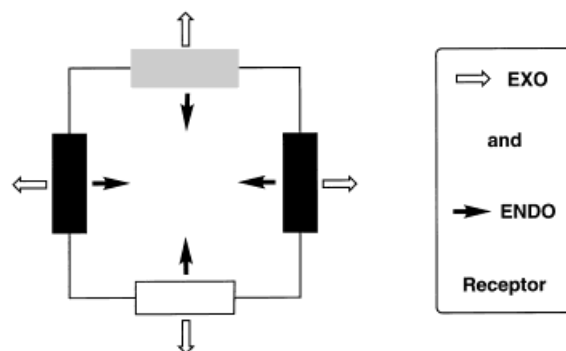
From a careful examination of the solid-state structures of a wide range of bipyridinum-based molecular compounds, we have been able to identify some of the major

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interactive patterns that govern their packing. Armed with this information, we have designed (Figure 1) a series of cyclophanes in which either two π-electron-rich or two π-electron-neutral rings, together with two π-electron-deficient bipyridinium units, are placed in diametrically opposite positions within the same molecule so as to create a box-like molecular geometry. These features give these cyclophanes the potential to form highly structured two-dimensional arrays of stacked π-π-interacting aromatic units after a mosaic-like fashion, while they still retain the ability to bind either π-electron-rich or π-electron-deficient substrates.

Here, we report on (i) the design and self-assembly of nine tetracationic cyclophanes $4-12 \cdot 4 \, \text{PF}_6$, (ii) the X-ray crystallographic characterization of two ($4 \cdot 4 \, \text{PF}_6$ and $8 \cdot 4 \, \text{PF}_6$) of them, as well as of one dicationic precursor $15 \cdot 2 \, \text{PF}_6$, and (iii) the ability of the cyclophane $4 \cdot 4 \, \text{PF}_6$ to form a 1:1 adduct with ferrocene which has been characterized in both the solid and solution states.

Results and Discussion

Design

In order to design, as rationally as possible, cyclophanes with the potential for self-recognition, a knowledge of the interactions that control their self-organization in the solid state is required.

(E) = *Electrostatic Interactions*

The compounds we will be considering are all salts and therefore the first, strong, short contact interactions that govern their packing are electrostatic. These interactions are probably the major contributors to the primary structures in the packing of most of the charged species, synthesized and characterized in our own research laboratories during the last decade.

(CP) = *Close Packing Considerations*

The visualization of a molecule as a collection of spherical atoms, with their characteristic radii, results inevitably in the concept of close packing of molecules in a crystal. This model, described in 1945 by Kitaigorodskii,[7] is based on the fact that the number of intermolecular contacts in a crystal tends to a maximum, and that these contacts cluster around distances associated with energy minima in the various atom-atom potential curves. The close packing principle applies to a far lesser extent than do the electrostatic interactions in the case of the ionic species we are considering, but it certainly does contribute to their secondary structure along with the other interactions described below.

(π) = *π-π Interactions*

Many different types of aromatic units have been incorporated into bipyridinium-based molecular systems. In Figure 2, we list all the different types of π-π interactions encountered to date and comment on their effect on packing. We identify the dioxy-substituted aromatic ring systems as

being π-electron-rich, the dialkyl-substituted ones as π-neutral, and the bipyridinium units as π-electron-deficient.

(π-1) *π-Electron-Rich−π-Electron-Deficient:* The interaction between a π-electron-deficient aromatic unit, such as the 4,4′-bipyridinium dication, and a π-electron-rich moiety, such as a hydroquinone or 1,5-dioxynaphthalene ring system, is (Figure 2b) the most recurrent form of aromatic-aromatic stacking observed in solid-state structures of bipyridinium-based molecular compounds.[8][9][10] This interaction is responsible for the formation, in the solid state, of both one-[8][9] and two-[10]dimensional superstructures. To date, the presence of counterions has rendered impossible the making of three-dimensional networks, comprising solely π-π interacting units.

(π-2) *π-Electron-Rich−π-Electron-Rich:* Close packing has been observed between benzofuran-based ring systems[11], as well as between hydroquinone or 1,5-dioxynaphthalene aromatic rings.[12] This interaction alone has been found to be responsible for the formation, in the solid state, of zero-[11] and one-[12]dimensional structures.

(π-3) *π-Electron-Deficient−π-Electron-Deficient:* This type of interaction has been found in two different contexts: (i) when the bipyridinium units of two adjacent molecules are aligned and facing each other,[13] and (ii) when one of the pyridinium rings of a 4,4′-bipyridinium unit in one molecule is (Figure 2a) π-π interacting with another one in an adjacent molecule in a parallel fashion.[14] π-π Interactions between bipyridinium units is, at first glance, a rather surprising phenomenon since it implies the close contact between two positively charged species.

(π-4) *π-Electron-Rich−π-Neutral:* The solid-state structures of some catenanes[10a] and pseudorotaxanes[10b] reveal (Figure 2a) a close packing between the π-neutral spacer of a tetracationic cyclophane and a π-electron-rich aromatic unit in an adjacent molecule.

(π-5) *π-Neutral−π-Neutral:* In several cases, when the spacers of a tetracationic cyclophane are either 4,4′-[13] or 3,3′-[14]biphenyl units, π-neutral−π-neutral interactions have been observed (Figure 2b) between adjacent tetracationic cyclophanes. The same two interaction patterns, analogous to the ones described in π-3 for the case of the π-electron deficient−π-electron deficient interaction, have been found in the solid state.

(π-6) *CH−π:* These interactions have been described (Figure 2c), for example, in bipyridinium-based systems and this was in the case of a [2]catenane.[14]

In the knowledge of these interactive patterns, a series of tetracationic cyclophanes incorporating a variety of potentially interactive π-π units that, in all cases, contain two 4,4′-bipyridinium units located diametrically opposite one another, has been designed. The major contibutor to their packing − as stated above − is the electrostatic interaction **(E)**. Another contribution, which is not insignificant, concerns the shapes of the molecules that contribute to their arrangements in a close-packing **(CP)** sense. To illustrate this point, let us quote Desiraju,[5e] who wrote: "*...chemistry is not geometry, and the major challenge in the practice of crystal engineering is that a crystal structure is a compromise,*

Figure 2. Parts of the continuous two-dimensional stacks formed by the [2]catenanes **1**·4 PF$_6$, **2**·4 PF$_6$, and (*RS*)-**3**·4 PF$_6$ showing the interactive patterns a) π-3 and π-4, b) π-1 and π-5, and c) π-6 in the solid state and in a schematic way
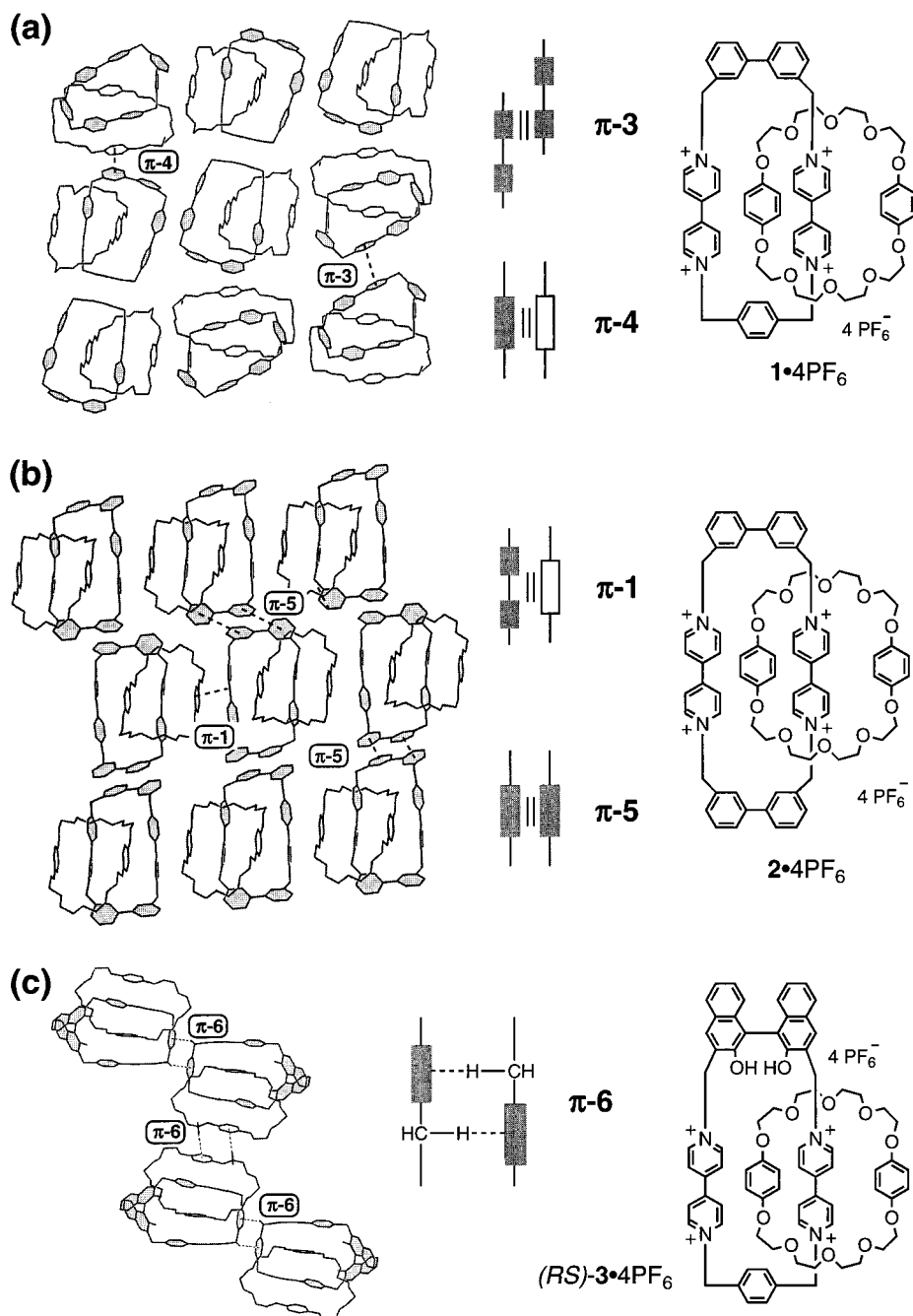

at times quite uneasy, between interactions of varying strengths, directionalities, and distance-dependent properties."

The incorporation of two π-electron-rich ring systems and two 4,4'-bipyridinium units located diametrically opposite each other in the same tetracationic cyclophane, creating a box-like geometry, provides the potential to form, in the solid state, a highly ordered two-dimensional array (Figure 3) wherein the superstructure would be sustained by the combination of **E**, **CP**, and π-2 interactions. The π-electron-rich units selected were hydroquinone in **4**·4 PF$_6$,

1,5-dioxynaphthalene in **5**·4 PF$_6$ and **6**·4 PF$_6$, and resorcinol in **7**·4 PF$_6$ and **8**·4 PF$_6$ on the basis of their known ability to stack with a π-electron-deficient unit present in another molecule. The length of the π-electron-rich spacer unit is such that the cyclophanes should adopt a near-square geometry in the solid state, a condition that is necessary in order to realize the mosaic-like array depicted in Figure 3.

A consideration of the cooperative effect between the four interactions **E**, **CP**, π-3, and π-4 led us to design the

Figure 3. Schematic representation of the anticipated solid-state packing of the tetracations incorporating both π-electron-rich and π-electron-deficient units in a crystalline salt
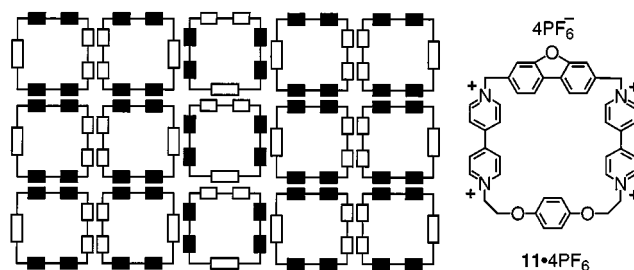
Figure 4. Schematic representation of the anticipated solid-state packing of the tetracations incorporating π-electron-rich, π-neutral, and π-electron-deficient units in a crystalline salt
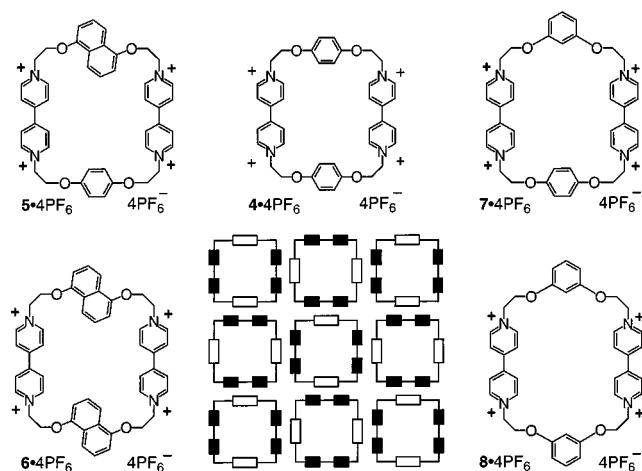
tetracationic cyclophanes **9**·4 PF$_6$ and **10**·4 PF$_6$ with the potential to pack as illustrated in Figure 4. It is anticipated that these cyclophanes will adopt a triangular shape since one of the π-electron-rich hydroquinone rings of the tetracationic cyclophane **4**·4 PF$_6$ has been modified to a shorter *p*-xylyl unit in **9**·4 PF$_6$ and an even shorter *m*-xylyl unit in **10**·4 PF$_6$.
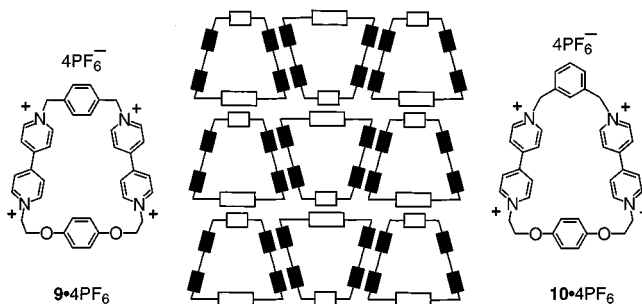
Dibenzofuran is well known to π-π stack with itself in the solid state.[11a][11b][11c] Two of these units have been incorporated into a tetracationic cyclophane containing also two bipyridinium units located diametrically opposite each other.[11d] The solid-state structure of this cyclophane revealed the formation of one-dimensional π-π stacks of dibenzofuran interacting units. In the tetracationic cyclophane **11**·4 PF$_6$, containing both dibenzofuran and hydroquinone units, the expected packing (Figure 5) relies on the combination of the interactions: **E**, **CP**, **π-1**, **π-3**, **π-4**, and **π-5**.

The idea of synthesizing the tetracationic cyclophane **12**·4 PF$_6$, in which one of the π-electron rich spacers of **4**·4 PF$_6$ has been replaced by the π-neutral biphenyl ring system, derives from the knowledge[13] of the solid-state structure of the cyclophane cyclobis(paraquat-4,4′-biphenylene) that forms highly ordered layered arrays. The expected

Figure 5. Schematic representation of the anticipated solid-state packing of the tetracation **11**$^{4+}$ in a crystalline salt

packing in the solid-state structure of **12**·4 PF$_6$ relies (Figure 6) on the combination of the interactions: **E**, **CP**, **π-1**, **π-2**, **π-3**, and **π-4**.

Figure 6. Schematic representation of the anticipated solid-state packing of the tetracation **12**$^{4+}$ in a crystalline salt
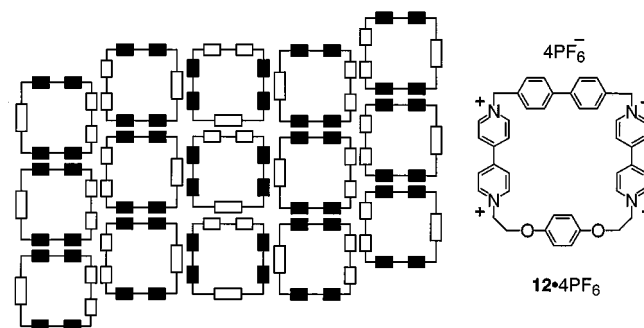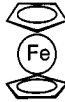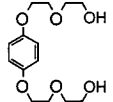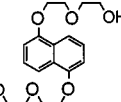
Synthesis

The tetracationic cyclophane **4**·4 PF$_6$ was prepared by the route shown in Scheme 1. The dibromide **13** was obtained by reaction[15] of the diol **14** with PPh$_3$Br$_2$ in MeCN. Portion-wise addition of **13** over 7 days to a ten-fold excess of 4,4′-bipyridine in MeCN afforded, after counterion exchange, the dicationic salt **15**·2 PF$_6$. Since the reported[16] synthesis of the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), employs 1,4-bis[2-(2-hydroxyethoxy)-ethoxy]benzene (**16**) (Table 1) as a template, at ultra high pressure (12 kbars) and yields 62% of this cyclophane, the synthesis (Scheme 1) of the cyclophane **4**·4 PF$_6$ was attempted[15] by mixing equimolar amounts of the dicationic salt **15**·2 PF$_6$ and the dibromide **13** in the presence of various π-electron-rich templates (Table 1) at both ambient and ultra high (12 kbar) pressures.

At ambient pressure in DMF, whatever the template chosen, formation of the cyclic product was not observed. When the reaction was carried out at high pressure in DMF without a template, only polymeric material was obtained. When either templates **16** or **17** were incorporated[17] into the reaction mixture, the tetracationic cyclophane **4**·4 PF$_6$ was isolated in 5 and 12% yields, respectively.

The self-assembly[13] of a similar tetracationic cyclophane — namely, cyclobis(paraquat-4,4′-biphenylene) — using ferrocene as a template, suggested an alternative route to us for templating the formation of tetracationic cyclophanes.

Scheme 1. Template-directed synthesis of the square tetracationic cyclophane **4**·4 PF$_6$
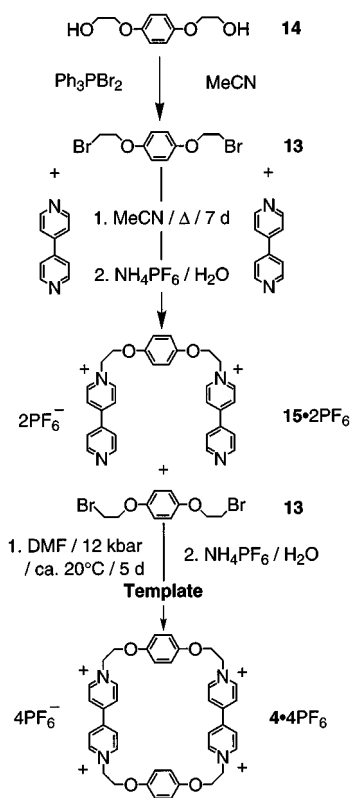
Table 1. Yields of formation of the tetracationic cyclophane **4**·4 PF$_6$ in different conditions

Template	—	Fc	16	17
Yield (%) at 1 bar	0	0	—	0
Yield (%) at 12 kbar	0	0	5	12

Therefore, we decided to use ferrocene as a templating agent for the synthesis of **4**·4 PF$_6$, and both surprisingly and unfortunately, we did not observe the formation of the tetracationic cyclophane **4**·4 PF$_6$ at either ambient or ultra high pressures.
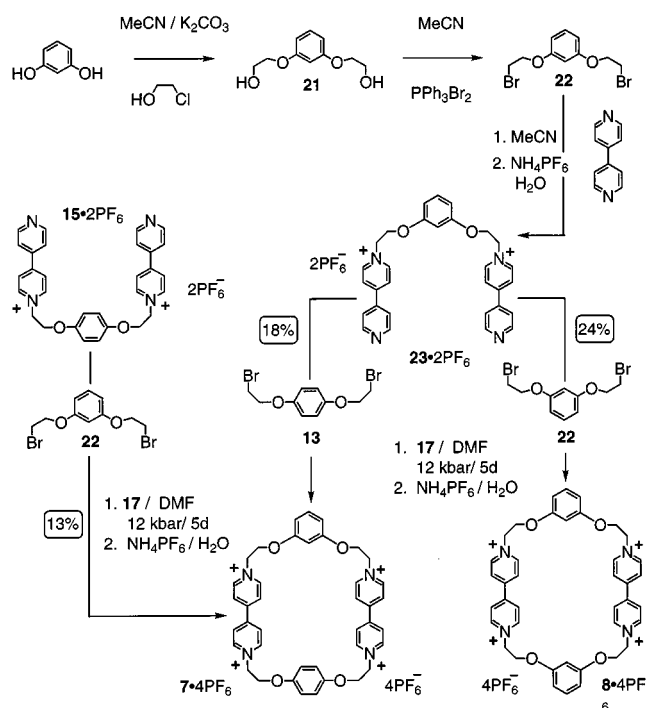
The naphthalene-containing tetracationic cyclophanes **5**·4 PF$_6$ and **6**·4 PF$_6$ were synthesized, following the synthetic scheme depicted in Scheme 2. The diol **18** was prepared in 56% yield by reaction of 2-chloroethanol with 1,5-naphthalenediol under basic conditions. The dibromide **19** was prepared in 57% yield as a result of reaction of the diol **18** with PPh$_3$Br$_2$ in MeCN. Portion-wise addition of the dibromide **19** to a 10-fold excess of 4,4′-bipyridine in MeCN afforded, after counterion exchange, the dicationic salt **20**·2 PF$_6$ in 51% yield. Reaction of this salt in turn with the dibromides **13** and **19** in DMF, at 12 kbar, using

1,5-bis[(2-hydroxyethoxy)ethoxy]naphthalene (**17**) as the template afforded, after counterion exchange, the desired tetracationic cyclophanes **5**·4 PF$_6$ and **6**·4 PF$_6$ in 9 and 6% yields, respectively. These very low yields may be a consequence of the lack of efficiency of the self-assembly process as a consequence of the distorted geometry of the naphthalene spacer unit in **20**·2 PF$_6$ with respect to **15**·2 PF$_6$ which contains a hydroquinone ring as a spacer.
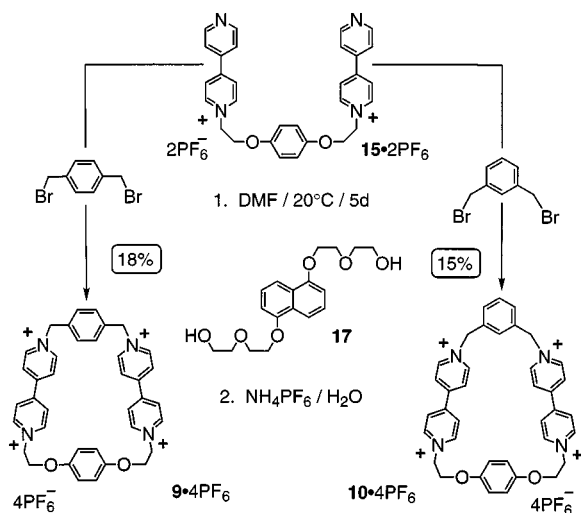
Scheme 2. Template-directed synthesis of the tetracationic cyclophanes **5**$^{4+}$ and **6**$^{4+}$
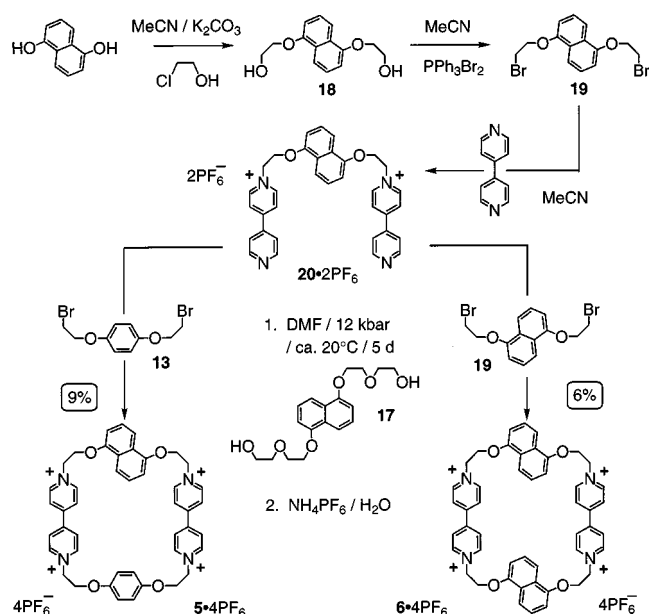
The synthetic strategy employed in the self-assembly of the tetracationic cyclophanes **7**·4 PF$_6$ and **8**·4 PF$_6$ relies Scheme 3) upon the same principles as those leading Schemes 1 and 2) to the salts **4−6**·4 PF$_6$. Subsequently, the diol **21**, which was prepared in 69% yield from the reaction of 2-chloroethanol with 1,5-naphthalenediol under basic conditions, was treated with PPh$_3$Br$_2$ in MeCN to afford the dibromide **22** in 66% yield.

Portion-wise addition of **22** to a 10-fold excess of 4,4′-bipyridine in MeCN afforded, after counterion exchange, the dicationic salt **23**·2 PF$_6$ in 62% yield. Reaction of this salt with **22** in DMF using **17** as a template afforded, after counterion exchange, the desired tetracationic cyclophane **8**·4 PF$_6$ in 24% yield. The other tetracationic cyclophane **7**·4 PF$_6$ was prepared in two different ways − both in the presence of the template **17** − (i) the first way involved the reaction between the dibromide **13** and the dicationic salt **23**·2 PF$_6$ and (ii) the second utilized the complementary components − namely the dibromide **22** and the dicationic salt **15**·2 PF$_6$. The former method afforded **7**·4 PF$_6$ in 18% yield and the latter, **7**·4 PF$_6$ in 13% yield. These results may reflect the better preorganization of **23**·2 PF$_6$ compared with **15**·2 PF$_6$ during the self-assembly process. This hypothesis gains some credence from the fact that, in the solid-state structure of the tetracationic salt **8**·4 PF$_6$ (vide infra), the cavity within the macrocycle is narrower than that within **4**·4 PF$_6$.

Scheme 3. Template-directed synthesis of the tetracationic cyclo-
phanes 7^{4+} and 8^{4+}

The tetracationic cyclophanes $11 \cdot 4 \ PF_6$ and $12 \cdot 4 \ PF_6$ were synthesized (Scheme 5) in 12 and 32% yields, respectively, by treating the dicationic salt $15 \cdot 2 \ PF_6$ in turn with the dibromides 24 and 25, in DMF at ambient pressure in the presence of ferrocene as a template.
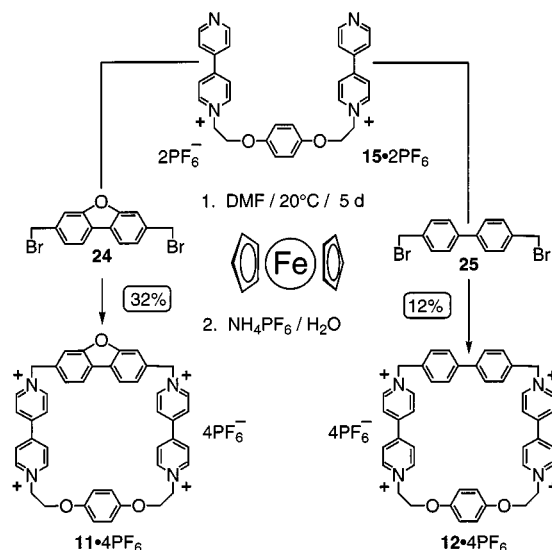
Scheme 5. Template-directed synthesis of the tetracationic cyclo-
phanes 11^{4+} and 12^{4+}

The tetracationic cyclophanes $9 \cdot 4 \ PF_6$ and $10 \cdot 4 \ PF_6$ were synthesized (Scheme 4) at atmospheric pressure by allowing the dicationic salt $15 \cdot 2 \ PF_6$ to react with dibromo-*p*-xylene and dibromo-*m*-xylene, respectively in MeCN in the presence of the template 17, giving yields of 18 and 15%.

Scheme 4. Template-directed synthesis of the tetracationic cyclo-
phanes 9^{4+} and 10^{4+}

The choice of ambient conditions, as opposed to the use of high pressure, relies on the fact that, in this situation, the reactivities of dibromo-*p*-xylene and dibromo-*m*-xylene are much greater than those of the dibromides 13, 19, and 22 employed in the previous ring closures.

Once again, the benzylic dibromides 24 and 25 are sufficiently reactive to allow the ring closure to occur at atmospheric pressure. By comparison with the results described above, in which ferrocene was shown not to template the ring closure in the synthesis of $4 \cdot 4 \ PF_6$ even at high pressure, here, at normal pressure, a saturated solution of ferrocene enhances the formation of the cyclophanes $11 \cdot 4 \ PF_6$ and $12 \cdot 4 \ PF_6$, resulting in yields of 32 and 12%, respectively.

X-ray Crystallography of $4 \cdot 4 PF_6$, $8 \cdot 4 PF_6$, and $15 \cdot 2 PF_6$

The solid-state structure[15] of $15 \cdot 2 \ PF_6$ was confirmed by X-ray crystallography. The dicationic salt $15 \cdot 2 \ PF_6$ exhibits (Figure 7) a partially extended skewed horseshoe conformation. The central phenoxymethylene groups are in a *syn* relationship and the OCH_2CH_2N groups adopt *gauche* geometries, both of which are in the same sense. The pyridylpyridinium units are non-planar and exhibit twist angles about the central C−C bond linkages between rings **A** and **B**, and **D** and **E** of 9 and 16°, respectively; there is no noticeable "bowing" of either unit. The skew angle, as defined by the molecular torsional angle N(**A**)−N(**B**)/N(**D**)−N(**E**), is 80°.

The packing (Figure 8) of the elongated dications is complex, involving extensive intermolecular π-π stacking interactions. The pyridylpyridinium units at each end of the molecule pack in a parallel (**AB,BA** and **DE,ED**) overlapping relationship with their centrosymmetrically related counterparts creating zig-zag chains (depicted with closed and open bonds, respectively, in Figure 8) that extend in the crystallographic (011) direction. Adjacent chains within the crystal are offset with respect to each other such that the

Figure 7. Ball-and-stick representation of the dicationic salt **15**·2 PF$_6$ in the solid state
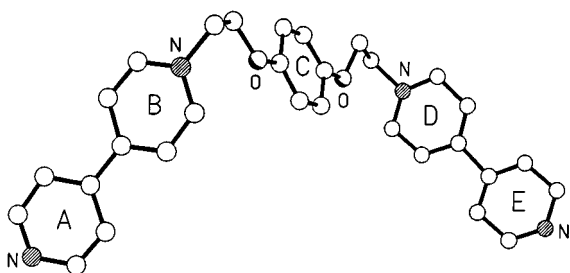
pyridyl ring **A** within one chain is positioned directly above and orthogonally oriented with respect to the pyridyl ring **E** in the next chain. The result of this packing relationship is the formation of extended π-π-stacked sheets (Figure 8) that propagate in the crystallographic *c* direction with a **BAED-DEAB** stepped sequence.

two-dimensional sheets are not planar, there being a slightly stepped relationship between adjacent macrocycles. Despite this terraced arrangement of molecules, there is a retention of a proximal relationship between one of the bipyridinium rings in one tetracation and a hydroquinone ring in the next and vice versa. The separation between the centroids of these rings in adjacent cyclophanes is 4.0 Å and the planes of the rings are inclined by 22°.

Adjacent sheets, although separated by layers of disordered PF$_6$$^-$ anions and MeCN molecules, are in register and form nanotubes that extend through the crystal. The distance between the cyclophane layers is 9.8 Å, so that two consecutive cyclophanes in adjacent layers form (Figure 10) a cube of ca. 1 nm side.

The X-ray structural analysis of **8**·4 PF$_6$ reveals (Figure 11) the cyclophane to have a C_i-symmetric chair-like conformation, with the resorcinol units inclined by ca. 45° to the mean plane of the macrocycle, and with a ca. 42° twist

Figure 8. Ball-and-stick (top) and schematic (bottom) representation of the packing in the solid-state structure of the dicationic salt **15**·2 PF$_6$
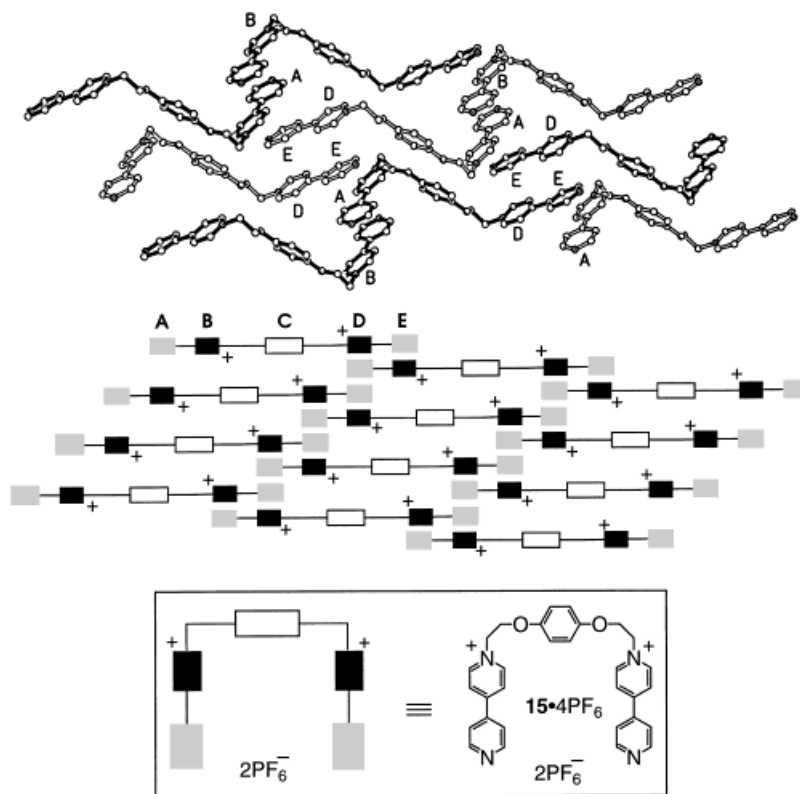
In the solid state the tetracationic cyclophane **4**$^{4+}$ has (Figure 9) an almost square, open, C_2-symmetric geometry, the distances between the corner NCH$_2$ methylene carbon atoms being 9.88 and 9.94 Å, respectively, the longer distance corresponding to the sides containing the hydroquinone rings. Although these sides of the cyclophane have a planarity that extends to include their adjacent oxybismethylene units, there are quite large twists (20°) between the pyridinium rings in the bipyridinium units.

The tetracations **4**$^{4+}$ pack to form a close-packed two-dimensional π-donor/π-acceptor mosaic (Figure 9). These

between the pyridinium rings within each bipyridinium unit. The profile of the molecule is rectangular with the distances between the corner NCH$_2$ methylene carbon atoms of 9.97 and 8.83 Å for the sides incorporating the bipyridinium units and the resorcinol rings, respectively. The vectors joining these four carbon atoms form a parallelogram with angles of 88 and 92° (angles identical to those observed in **4**$^{4+}$).

The molecules pack (Figure 12) head-to-tail with the resorcinol rings in one molecule parallelly π-stacked with those in the next (mean interplanar separation: 3.50 Å, centroid-

Figure 9. Plan view of the packing of 4^{4+} in the solid state (ball-and-stick representation)
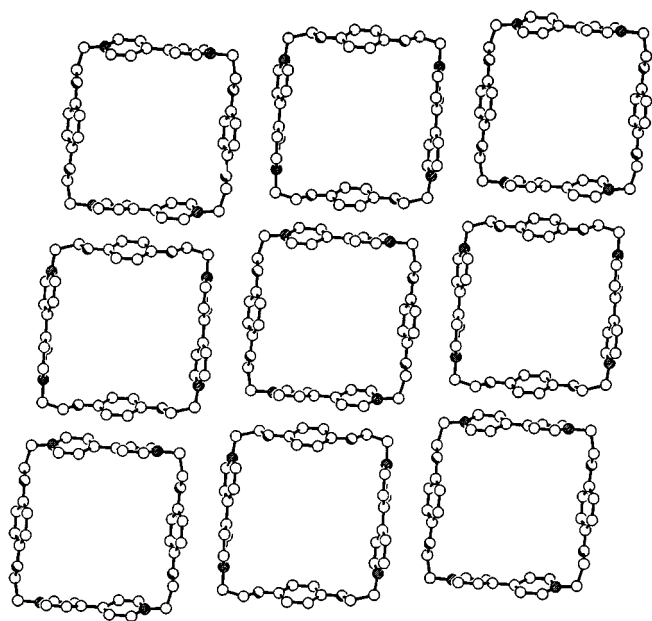
Figure 10. Schematic representation of the channels formed by the tetracations 4^{4+} in the solid state

Figure 11. Ball-and-stick representation of 8^{4+} in the X-ray structure of $8 \cdot 4 \, PF_6$
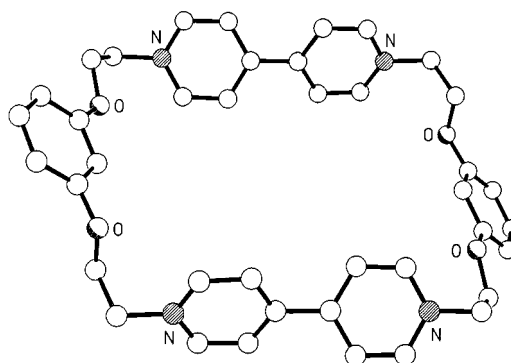
Figure 12. Representation of the packing in the solid-state structure of $8 \cdot 4 \, PF_6$ showing the resorcinol−resorcinol interaction
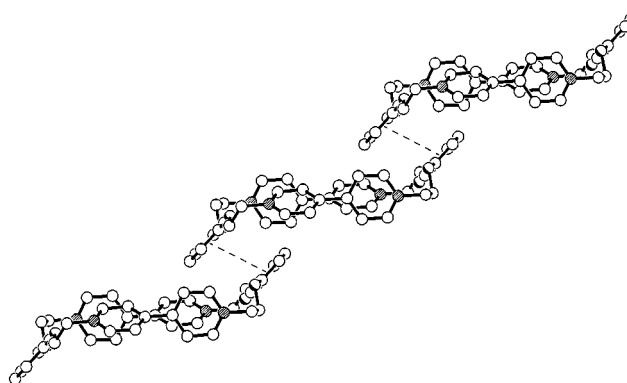
Figure 13. Representation of the packing in the solid-state structure of $8 \cdot 4 \, PF_6$ showing the one-dimensional arrays of π-π-stacked cyclophanes

−centroid distance: 3.64 Å). Adjacent chains in the crystal are oriented orthogonally with respect to each other to form the pseudo close-packed array illustrated in Figure 13. The regions bounded by the confluences of the corners of four adjacent molecules form channels that contain the PF_6^- anions.

Association Constants

The bright green color of a 1:1 molar solution of $4 \cdot 4 \, PF_6$ and ferrocene (**Fc**) in MeCN indicates the formation of a 1:1 adduct $4/Fc \cdot 4 \, PF_6$ of the inclusion complex type that also displays a charge transfer (CT) interaction.[19] A UV-spectrophotometric titration, using the CT band centered

on 602 nm as the probe, yields an association constant (K_a) of 44 ± 3 dm^3 mol^{-1} for the 1:1 adduct **4/Fc**·4 PF$_6$ in MeCN at 25°C. This K_a value corresponds to a free energy of adduct formation of −2.2 kcal mol^{-1}.

Figure 14. Schematic representation of the anticipated structure of the 1:1 adduct **4/Fc**$^{4+}$ in a crystalline state
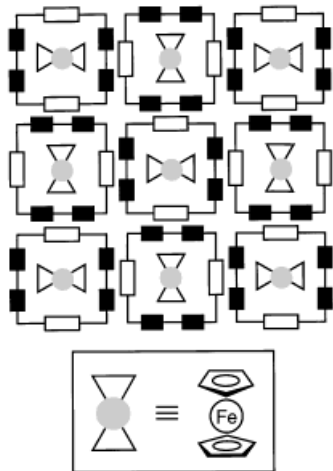
^{1}H-NMR-spectroscopic investigations, carried out on a 5.5·10^{-3} M solution of **4/Fc**·4 PF$_6$ in CD$_3$CN, indicate that the ferrocene molecule resides within the tetracationic cyclophane with its cyclopentadienyl rings oriented parallel to the planes of the two bipyridinium units in the tetracation. This relative geometry explains the significant upfield shifts (−0.29 ppm) observed for the cyclopentadienyl ring proton resonances of **Fc** and also (−0.08 ppm) for the β-CH bipyridinium signals of **4**$^{4+}$. Consequently, it was anticipated that inclusion of ferrocene in this manner should permit the retention (Figure 14) of the mosaic-like array proposed (Figure 3) and observed (Figure 9) in the solid state for **4**·4 PF$_6$.

All attempts to determine the binding constants between **4**·4 PF$_6$ and the π-electron-rich guests tetrathiafulvalene (TTF), 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene (**16**), 1,5-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene (**17**), and the π-electron-deficient guest tetracyanoquinodimethane (TCNQ) were unsuccessful, as indicated by UV-spectrophotometric or ^{1}H-NMR-spectrometric titration methods. Although the changes in absorption intensities and chemical shifts were too small to yield any reliable quantitative information, it is obvious from this study that the binding constants must be less than 10 M^{-1}.

The tetracationic cyclophanes **5**−**12**·4 PF$_6$ were tested for complexation with ferrocene on its own. The cyclophanes **5**−**10**·4 PF$_6$ did not form any stable adducts with ferrocene since no chemical shift changes were observed in the ^{1}H-NMR spectra of 1:1 mixtures of the two components: also, no charge transfer bands were detected by UV spectrophotometry. When the cyclophanes **11**·4 PF$_6$ and **12**·4 PF$_6$ were mixed in a 1:1 ratio with ferrocene, a light green color was observed and could be associated with charge transfer bands centered on 610 and 606 nm, respectively. Once again, however, the absorption changes, moni-

tored by UV spectrophotometry using the tritration procedure between ferrocene and **11**·4 PF$_6$ and **12**·4 PF$_6$, were far too small to yield any reliable K_a values: again, these binding constants must be less than 10 M^{-1}.

X-ray Crystallography of 4/Fc·4 PF$_6$

The X-ray structure[15] of the C_i-symmetric 1:1 adduct formed between the cyclophane **4**$^{4+}$ and ferrocene revealed (Figure 15) the total achievement of the supramolecular design strategy (Figure 14) in that the tetracationic cyclophane includes, via π-π stacking interactions with the bipyridinium units, a ferrocene molecule.[18] Furthermore, the tetracations self-assemble to form (Figure 16) a π-donor/π-acceptor two-dimensional mosaic directly analogous to that formed by the free macrocycle. The entrapping of the ferrocene molecule within the tetracationic cyclophane produces only very minor perturbations in its geometry. The lengths of the two sides between the corner NCH$_2$○carbon atoms are essentially unchanged at 9.83 and 9.95 Å, respectively, and there is only a small reduction, ca. 2°, in the twist angle between the two pyridinium rings of the bipyridinium units. The π-π stacking within the two-dimensional mosaic in the 1:1 adduct is improved with respect to that observed for the free macrocycle. The centroid−centroid separation between the hydroquinone ring in one molecule and one of the pyridinium rings of the next is reduced to 3.8 Å and the rings are closer to parallel, being inclined by only 6° (cf. 22° in **4**$^{4+}$). The two-dimensional mosaic sheets are again stacked in register with a mean intersheet separation of 9.8 Å, the PF$_6^-$ anions and included solvent molecules being intercalated between the layers.

Conclusion

Consideration of the interactive patterns present in the solid-state structures of 4,4′-bipyridinium-based salts has led us to the design of a series of nine tetracationic cyclophanes **4**−**12**·4 PF$_6$ with the potential to form highly ordered arrays of extended π-π-stacked sheets in the solid state. The syntheses of these tetracationic cyclophanes were made possible by carefully tuning the reaction conditions and also by employing, in each case, a template adapted to the target cyclophane. The information present in the molecular structures of the tetracationic cyclophanes **4**−**12**·4 PF$_6$ not only facilitated their efficient self-assembly, but also allowed the formation in the solid state of (i) a regular repeating two-dimensional supramolecular array in the case of **4**·4 PF$_6$, and (ii) linear π-π stacks in the case of **8**·4 PF$_6$. The solid-state structure of the dicationic salt **15**·2 PF$_6$ displayed an unusual stucture in which pyridylpyridinium units are π-π-interacting with each other in two different ways so as to create two-dimensional π-π stacks. The symmetrically oriented molecular recognition elements of the cyclophane **4**·4 PF$_6$ have also allowed the directionally specific inclusion of ferrocene (**Fc**) within its cavity to form the 1:1 adduct **4/Fc**·4 PF$_6$ in both the solid and solution states. We believe that this research should be of relevance to chemists who wish to design novel organic materials with

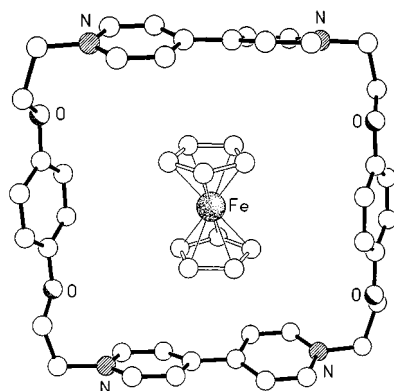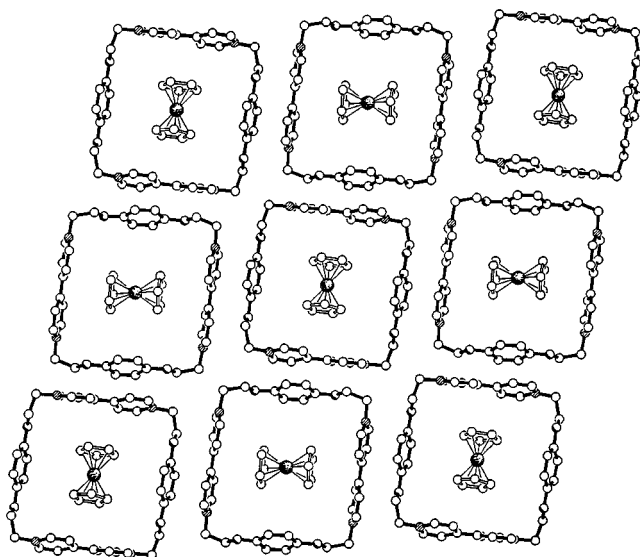Figure 15. Ball-and-stick representation of **4/Fc**$^{4+}$ in the X-ray structure of **4/Fc**·4 PF$_6$

Figure 16. View of the packing of the 1:1 adduct **4/Fc**$^{4+}$ in the solid state (ball-and-stick representation)

interesting physical properties, in a way that is reminiscent to the encoding procedure described by the late Margaret Etter[5b] for hydrogen-bonding interactions.

Experimental Section

Materials and Methods: Chemicals were purchased from Aldrich and used without further purification. Solvents were either used as purchased or dried (DMF from KOH, MeCN from CaH$_2$), according to procedures described in the literature.[20] The reactions requiring ultra high pressure were carried out in a Teflon vessel, using a custom-built reactor, manufactured by PSIKA Pressure Systems Limited of Glossop in the UK. − Thin-layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel 60F (Merck 5554). The plates were inspected by UV light and developed with a dilute solution of I$_2$ in CHCl$_3$. − Column chro-

matography was carried out using silica gel 60F (Merck 9385, 230−400 mesh). − Melting points were determined with an Electrothermal 9200 apparatus and are not corrected. − Low-resolution mass spectra were performed using a Kratos Profile spectrometer, operating in electron impact (EIMS) mode. Fast-atom bombardment mass spectra (FABMS) were recorded with a Kratos MS80 spectrometer operating at 8 keV using a xenon primary atom beam. The matrix used was 3-nitrobenzyl alcohol (NOBA). Liquid Secondary Ion Mass Spectra (LSIMS) were recorded with a VG ZabSpec mass spectrometer, using an *m*-nitrobenzyl alcohol matrix and a scan speed of 10 s per decade.

Tetracationic Cyclophane **4**·4 PF$_6$: The dibromide **13** (32.4 mg, 0.1 mmol), the dicationic salt **15**·2 PF$_6$ (76.6 mg, 0.1 mmol), and the diol **17** (100.9 mg, 0.3 mmol) were dissolved in dry DMF (10 ml). The reaction mixture was transferred to a high-pressure reaction Teflon tube, which was then compressed (12 kbars) at room temperature for 5 d. The precipitate, which resulted on addition of Et$_2$O (150 ml), was filtered off and purified by column chromatography [SiO$_2$; MeOH/2 N aqueous NH$_4$Cl/MeNO$_2$ (7:2:1)] to yield, after counterion exchange, **4**·4 PF$_6$ as a deep yellow solid (15 mg, 12%); m.p. > 260°C. − FABMS; *m/z*: 1075 [M − PF$_6$]$^+$. − ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 8.94 (d, 8 H), 8.36 (d, 8H), 6.71 (s, 8 H), 4.98 (t, 8H), 4.31 (t, 8 H). − ^{13}C NMR (75.5 MHz, CD$_3$CN, 25°C): δ = 153.5, 150.8, 147.3, 127.6, 116.3, 67.5, 62.3. − HRLSIMS: calcd. for C$_{40}$H$_{40}$F$_{12}$N$_4$O$_4$P$_2$ [M − 2 PF$_6$]$^+$: *m/z* 930.2333; found: *m/z* 930.2375. − Single crystals, suitable for X-ray crystallography, were grown by vapor diffusion of *i*Pr$_2$O into a solution of **4**·4 PF$_6$ in MeCN.

1,5-Bis(2-hydroxyethoxy)naphthalene (**18**): 2-Chloroethanol (8.68 g, 108 mmol) was added during 1 h to a refluxing solution of 1,5-naphthalenediol (5.76 g, 36 mmol) and K$_2$CO$_3$ (30 g, 217.7 mmol) in MeCN (200 ml) under N$_2$. The reaction mixture was kept under reflux for 48 h and filtered. The filtrate was concentrated and the residue was dissolved in CH$_2$Cl$_2$ (100 ml). The solution was washed with H$_2$O (2× 30 ml) and brine (30 ml), dried (MgSO$_4$), concentrated in vacuo, and the resulting dark brown residue was extracted with hot EtOAc (5 × 50ml). The solution was then concentrated in vacuo and the brown residue was crystallized from Me$_2$CO to yield the diol **18** as a brown solid (5.0 g, 56%); m.p. 180−181°C. − EIMS; *m/z*: 248 [M]$^+$. − ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 7.81 (d, *J* = 8.5 Hz, 2 H), 7.38 (t, *J* = 8.0 Hz, 2 H), 6.98 (d, *J* = 8.0 Hz, 2 H), 4.99 (t, *J* = 5.0 Hz, 2 H), 4.14 (t, *J* = 5.0 Hz, 4 H), 3.87−3.83 (m, 4 H). − ^{13}C NMR (CD$_3$CN, 75 MHz, 25°C): δ = 154.1, 126.1, 125.3, 114.0, 105.8, 70.0, 59.8.

1,5-Bis(2-bromoethoxy)naphthalene (**19**): Br$_2$ (2.28 g, 8.0 mmol) was added to a mechanically stirred suspension of Ph$_3$P (2.11 g, 8.0 mmol) in dry MeCN (100 ml) at 5°C at such a rate that the supernatant solution remained colorless. The solution was then allowed to warm up to room temperature and powdered 1,5-bis(2-hydroxyethoxy)naphthalene (1.00 g, 4.0 mmol) was added in one portion. After 48 h, the precipitate which formed was collected and crystallized from MeOH to obtain the dibromide **19** as a beige solid (850 mg, 57%); m.p. 146°C. − EIMS; *m/z*: 374 [M]$^+$. − ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 7.87 (d, *J* = 8.0 Hz, 2 H), 7.41 (t, *J* = 7.7 Hz, 2 H), 6.95 (d, *J* = 7.7 Hz, 2 H), 4.47 (t, *J* = 5.5 Hz, 4 H), 3.85 (t, *J* = 5.5 Hz, 4 H). − ^{13}C NMR (CD$_3$CN, 75 MHz, 25°C): δ = 154.3, 126.2, 125.2, 114.8, 105.7, 69.1, 31.6.

Dicationic Salt **20**·2 PF$_6$: The dibromide **19** (0.50 g, 1.3 mmol) was added portion-wise during 7 d, three times per d (24 mg per portion), to a refluxing solution of 4,4′-bipyridine (2.09 g, 13.4 mmol) in dry MeCN (50 ml) under nitrogen. The reaction mixture was maintained under reflux for a further 48 h before it was al-

lowed to cool down to room temperature, whereupon the brown precipitate was filtered and dissolved in a mixture of Me_2CO and H_2O, before being purified by column chromatography [SiO_2; MeOH/2 N aqueous NH_4Cl/$MeNO_2$ (7:2:1)] to yield, after counterion exchange, the dicationic salt **20**·2 PF_6 as a yellow-green solid (556 mg, 51%); m.p. > 240°C. − FABMS; *m/z*: 671 [M − PF_6]$^+$. − ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 8.95 (d, *J* = 7.0 Hz, 4 H), 8.81 (d, *J* = 7.0 Hz, 4 H), 8.34 (d, *J* = 7.0 Hz, 4 H), 7.76−7.71 (m, 6 H), 7.40 (t, 7.7 Hz, 2 H), 6.96 (d, *J* = 7.35 Hz, 2 H), 5.07 (t, *J* = 4.8 Hz, 4 H), 4.62 (t, *J* = 4.8 Hz, 4 H). − ^{13}C NMR (CD_3CN, 75 MHz, 25°C): δ = 155.5, 153.9, 151.9, 146.4, 141.9, 126.7, 126.5, 122.6, 118.5, 115.6, 67.2, 61.4.

1,3-Bis(2-hydroxyethoxy)benzene (**21**): A solution of resorcinol (5 g, 45.4 mmol) in EtOH (70 ml) was added dropwise over 15 min to a stirred solution of NaOH (5.44 g, 136.2 mmol) in EtOH (70 ml) and H_2O (24 ml). A solution of 2-chloroethanol (11.00 g, 136.2 mmol) in EtOH (70 ml) was then added dropwise over 20 min and the reaction mixture was heated under reflux for 3 d. After cooling down to room temperature, the reaction mixture was filtered to afford the diol **21** as a white solid (2.0 g). The mother liquor was then concentrated in vacuo to leave a yellow oil which was partitioned between CH_2Cl_2 (150 ml) and brine (70 ml). The pH of the aqueous layer was adjusted to ca. 2 using 2 N HCl. The aqueous layer was extracted with CH_2Cl_2 (4 × 50 ml) and the combined organic layers were concentrated in vacuo to afford the diol **21** as a white solid (2.2 g, 4.2 g overall, 69%); m.p. 97°C. − EIMS; *m/z*: 198 [M]$^+$. − ^{1}H NMR (300 MHz, CD_3COCD_3, 25°C): δ = 7.18−7.12 (1 H, m), 6.55−6.50 (3 H, m), 4.08−4.00 (4 H, m), 3.95 (2 H, t, *J* = 5.0 Hz), 3.88−3.80 (4 H, m). − ^{13}C NMR (CD_3COCD_3, 75 MHz, 25°C): δ = 161.2, 130.6, 107.5, 102.1, 70.3, 61.3.

1,3-Bis(2-bromoethoxy)benzene (**22**): Br_2 (1.3 ml, 25.2 mmol) was added dropwise to a vigorously stirred suspension of Ph_3P (6.62 g, 25.2 mmol) in dry MeCN (25 ml). The reaction mixture was maintained at < 5°C during the addition and then allowed to warm up to room temperature before the diol **21** (2.5 g, 12.6 mmol) was added to it in one portion. The reaction mixture was stirred for 4 h at room temperature, after which time it was filtered, and the solvent removed under vacuum, giving a white solid which was crystallized from MeOH to afford the dibromide **22** as a white solid (2.7 g, 66%); m.p. 87°C. − EIMS; *m/z*: 324 [M]$^+$. − ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 7.22 (t, *J* = 7.5 Hz, 1 H), 6.57 (dd, *J* = 7.5 Hz, 2 H), 6.50 (t, *J* = 2.5 Hz, 1 H), 4.30 (t, *J* = 5.5 Hz, 4 H), 3.70 (t, *J* = 5.5 Hz, 4 H). − ^{13}C NMR (CD_3CN, 75 MHz, 25°C): δ = 160.8, 131.5, 108.8, 102.9, 69.3, 31.6.

Dicationic Salt **23**·2 PF_6: The dibromide **22** (1.05 g, 3.24 mmol) was added portion-wise every 8 h over 7 d to a refluxing solution of 4,4′-bipyridine (5.05 g, 3.24 mmol) in dry MeCN (100 ml). The reaction mixture was maintained under reflux for a further 48 h. Then, it was allowed to cool down to room temperature, whereupon the greenish-brown precipitate which formed was filtered off and dissolved in H_2O before being purified by column chromatography [SiO_2; MeOH/2 N aqueous NH_4Cl/$MeNO_2$ (7:2:1)]. The fractions containing the product were combined and concentrated under vacuum to give a residue which was dissolved in H_2O. The dicationic salt **23**·2 PF_6 was precipitated from this solution by addition of a saturated aqueous NH_4PF_6 solution. The dication was isolated as a beige solid (1.55 g, 62%); m.p. > 215°C. − FABMS; *m/z*: 621 [M − PF_6]$^+$. − ^{1}H NMR (300 MHz, CD_3COCD_3, 25°C): δ = 9.35 (d, *J* = 7.5 Hz, 4 H), 8.87 (d, *J* = 7.5 Hz, 4 H), 8.68 (d, *J* = 7.5 Hz, 4 H), 8.00 (d, *J* = 5 Hz, 4 H), 7.19 (t, *J* = 7.5 Hz, 1 H), 6.69−6.57 (m, 3 H), 5.30 (t, *J* = 5 Hz, 4 H), 4.67 (t, *J* = 5 Hz,

4 H). − ^{13}C NMR (CD_3COCD_3, 75 MHz, 25°C): δ = 159.9, 155.4, 152.2, 147.1, 142.0, 131.2, 126.7, 122.8, 108.6, 102.9, 67.2, 61.7.

General Procedure for the Syntheses of the Tetracationic Cyclophanes **5−8**·4 PF_6: The dibromide (0.1 mmol), the dicationic salt (0.1 mmol), and the diol **17** (100.9 mg, 0.3 mmol) were dissolved in dry DMF (10 ml). The reaction mixture was transferred to a high-pressure reaction Teflon tube, which was then compressed (12 kbars) at room temperature for 5 d. The precipitate, which resulted on addition of Et_2O (150 ml), was filtered off and purified by column chromatography [SiO_2; MeOH/2 N aqueous NH_4Cl/$MeNO_2$ (7:2:1)] to yield, after counterion exchange, the desired tetracationic cyclophane.

Tetracationic Cyclophane **5**·4 PF_6: Yield 9%; m.p. > 260°C. − FABMS; *m/z*: 1125 [M − PF_6]$^+$. − ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 9.05 (d, *J* = 7.0 Hz, 4 H), 8.88 (d, *J* = 7.0 Hz, 4 H), 8.35 (d, *J* = 7.0 Hz, 4 H), 8.30 (d, *J* = 7.0 Hz, 4 H), 7.86 (d, *J* = 8.4 Hz, 2 H), 7.37 (t, *J* = 7.7 Hz, 2 H), 6.82 (d, *J* = 7.7 Hz, 2 H), 6.64 (s, 4 H), 5.17 (t, *J* = 4.4 Hz, 4 H), 4.93 (t, *J* = 4.4 Hz, 4 H), 4.59 (t, *J* = 4.4 Hz, 4 H), 4.26 (t, *J* = 4.4 Hz, 4 H). − ^{13}C NMR (CD_3CN, 75 MHz, 25°C): δ = 153.4, 151.0, 147.3, 146.3, 145.0, 127.9, 127.6, 126.7, 116.5, 115.9, 107.2, 67.7, 67.5, 62.2. − HRLSIMS: calcd. for $C_{44}H_{42}F_{12}N_4O_4P_2$ [M − 2 PF_6]$^+$: *m/z* 980.2490; found: *m/z* 980.2487.

Tetracationic Cyclophane **6**·4 PF_6: Yield 6%; m.p. > 260°C. − FABMS; *m/z*: 1175 [M − PF_6]$^+$. − ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 9.01 (d, *J* = 7.0 Hz, 8 H), 8.30 (d, *J* = 7.0 Hz, 8 H), 7.77 (d, *J* = 8.4 Hz, 4 H), 7.32 (t, *J* = 7.7 Hz, 4 H), 6.78 (d, *J* = 7.7 Hz, 4 H), 5.14 (t, *J* = 4.4 Hz, 8 H), 4.52 (t, *J* = 4.4 Hz, 8 H). − ^{13}C NMR (CD_3CN, 75 MHz, 25°C): δ = 154.0, 150.6, 147.2, 126.9, 126.7, 115.6, 106.8, 67.7, 62.4. − $C_{48}H_{44}F_{24}N_4O_4P_4$ (1320.8): calcd. C 43.65, H 3.36, N 4.24; found C 43.60, H 3.39, N 4.26.

Tetracationic Cyclophane **7**·4 PF_6: Yield 13% from **15**·2 PF_6 and **22**, 18% from **13** and **23**·2 PF_6; m.p. > 225°C. − FABMS; *m/z*: 1075 [M − PF_6]$^+$. − ^{1}H NMR (CD_3CN, 300 MHz, 25°C): δ = 8.95 (d, *J* = 6.2 Hz, 4 H), 8.91 (d, *J* = 6.2 Hz, 4 H), 8.34−8.25 (m, 8 H), 7.23 (t, *J* = 8.5, 1 H), 6.72 (s, 4 H,), 6.61−6.54 (m, 2 H), 6.49 (s, 1 H), 4.99−4.92 (m, 8 H), 4.44−4.37 (m, 4 H), 4.36−4.29 (m, 4 H). − ^{13}C NMR (CD_3CN, 75 MHz, 25°C): δ = 159.6, 153.3, 151.2, 147.1, 131.3, 127.8, 127.7, 116.2, 107.1, 104.1, 67.5, 66.7, 62.2. − HRLSIMS: calcd. for $C_{40}H_{40}F_{12}N_4O_4P_2$ [M − 2 PF_6]$^+$: *m/z* 930.2333; found: *m/z* 930.2333.

Tetracationic Cyclophane **8**·4 PF_6: Yield 24%; m.p. > 230°C. − FABMS; *m/z*: 1075 [M − PF_6]$^+$. − ^{1}H NMR (300 MHz, CD_3CN, 25°C): δ = 8.99 (d, *J* = 7.0 Hz, 8 H), 8.38 (d, *J* = 7.0 Hz, 8 H), 7.23 (t, *J* = 8.45 Hz, 2 H), 6.60−6.50 (m, 6 H), 5.00 (t, *J* = 4.4 Hz, 8 H), 4.42 (t, *J* = 4.4 Hz, 8 H). − ^{13}C NMR (CD_3CN, 75 MHz, 25°C): δ = 159.7, 151.2, 147.3, 131.6, 127.9, 107.2, 104.9, 66.7, 62.2. − $C_{40}H_{40}F_{24}N_4O_4P_4$ (1220.6): calcd. C 39.36, H 3.30, N 4.59; found C 39.12, H 3.18, N 4.63. − Single crystals, suitable for X-ray crystallography, were grown by vapor diffusion of *i*Pr_2O into a solution of **8**·4 PF_6 in MeCN.

General Procedure for the Syntheses of the Cyclophanes **9−10**·4 PF_6: The dibromide (0.1 mmol), the dicationic salt (0.1 mmol), and the diol **17** (100.9 mg, 0.3 mmol) were dissolved in dry MeCN (10 ml). The reaction mixture was stirred at room temperature for 14 d and then concentrated in vacuo. The residue was purified by column chromatography [SiO_2; MeOH/2 N aqueous NH_4Cl/$MeNO_2$ (7:2:1)] to yield, after counterion exchange, the desired tetracationic cyclophane.

Tetracationic Cyclophane **9**·4 PF_6: Yield 18%; m.p. > 230°C. − FABMS; *m/z*: 1015 [M − PF_6]$^+$. − ^{1}H NMR (300 MHz, CD_3CN,

25°C): δ = 8.91−8.87 (m, 8 H), 8.28−8.24 (m, 8 H), 7.58 (s, 4 H), 6.58 (s, 4 H), 5.78 (s, 4 H), 4.93 (d, J = 4.4 Hz, 4 H), 4.24 (d, J = 4.8 Hz, 4 H). − ^{13}C NMR (75 MHz, CD$_3$CN, 25°C): δ = 153.5, 150.6, 150.5, 147.1, 146.2, 136.0, 131.3, 128.1, 127.4, 116.3, 68.0, 65.3, 62.1. − HRLSIMS: calcd. for C$_{38}$H$_{36}$F$_{12}$N$_4$O$_2$P$_2$ [M − 2 PF$_6$]$^+$: _m/z_ 870.2122; found: _m/z_ 870.2107.

Tetracationic Cyclophane **10** · 4 PF$_6$: Yield 15%; m.p. > 225°C. − FABMS; _m/z_: 1015 [M − PF$_6$]$^+$. − ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 8.90 (d, J = 7 Hz, 4 H), 8.82 (d, J = 7.0 Hz, 4 H), 8.27 (d, J = 7 Hz, 4 H), 8.22 (d, J = 7.0 Hz, 4 H), 7.57−7.84 (m, 4 H), 6.61 (s, 4 H), 5.78 (s, 4 H), 4.93 (t, J = 4.8 Hz, 4 H), 4.29 (t, J = 4.8 Hz, 4 H). − ^{13}C NMR (75 MHz, CD$_3$CN, 25°C): δ = 153.7, 151.0, 147.3, 146.1, 134.4, 133.5, 132.0, 131.9, 128.0, 127.5, 116.3, 68.2, 65.0, 62.4. − HRLSIMS: calcd. for C$_{38}$H$_{36}$F$_{12}$N$_4$O$_2$P$_2$ [M − 2 PF$_6$]$^+$: _m/z_ 870.2122; found: _m/z_ 870.2101.

General Procedure for the Syntheses of the Cyclophanes **11−12**·4 PF$_6$: The dibromide (0.1 mmol), the dicationic salt (0.1 mmol), and ferrocene (409 mg, 2.2 mmol) were dissolved in dry MeCN (10 ml). The reaction mixture was stirred at room temperature for 14 d and then concentrated in vacuo. The residue was purified by column chromatography [SiO$_2$; MeOH/2 N aqueous NH$_4$Cl/MeNO$_2$ (7:2:1)] to yield, after counterion exchange, the desired tetracationic cyclophane.

Tetracationic Cyclophane **11** · 4 PF$_6$: Yield 32%; m.p. > 250°C. − FABMS; _m/z_: 1105 [M − PF$_6$]$^+$. − ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 8.95−8.90 (m, 8 H), 8.31−8.28 (m, 8 H), 8.17 (d, J = 8.1 Hz, 2 H), 7.69 (d, J = 8.1 Hz, 2 H), 7.39 (s, 2 H), 6.68 (s, 4 H), 5.96 (s, 4 H), 4.96 (t, J = 5.0 Hz, 4 H), 4.26 (t, J = 5.0 Hz, 4 H). − ^{13}C NMR (75 MHz, CD$_3$CN, 25°C): δ = 157.9, 153.3, 150.9, 150.8, 147.2, 146.6, 135.2, 128.4, 127.7, 125.7, 123.5, 116.0, 112.6, 67.2, 66.0, 62.2. − C$_{44}$H$_{38}$F$_{24}$N$_4$O$_3$P$_4$ (1250.7): calcd. C 42.26, H 3.06, N 4.48; found C 41.95, H 3.08, N 4.34.

Tetracationic Cyclophane **12** · 4 PF$_6$: Yield 12%; m.p. > 245°C. − FABMS; _m/z_: 1091 [M − PF$_6$]$^+$. − ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 8.94−8.87 (m, 8 H), 8.29−8.25 (m, 8 H), 6.65 (s, 4H), 5.80 (s, 4 H), 4.94−4.91 (m, 4 H), 4.25−4.22 (m, 4 H). − ^{13}C NMR (75 MHz, CD$_3$CN, 25°C): δ = 157.7, 150.8, 147.2, 146.3, 15.3, 130.8, 128.9, 128.5, 127.7, 116.0, 67.1, 66.1, 62.2. − HRLSIMS: calcd. for C$_{44}$H$_{40}$F$_{12}$N$_4$O$_2$P$_2$ [M − 2 PF$_6$]$^+$: _m/z_ 946.2435; found: _m/z_ 946.2415.

The 1:1 Adduct **4/Fc**·4 PF$_6$: For the 1:1 adduct (5.5·10$^{−3}$ M): ^{1}H NMR (300 MHz, CD$_3$CN, 25°C): δ = 8.89 (d, 8 H), 8.28 (d, 8 H), 6.74 (s, 8 H), 4.96 (t, 8 H), 4.31 (t, 8 H), 3.87 (s, 10 H). − Single crystals, suitable for X-ray crystallography, were grown by vapor diffusion of _i_Pr$_2$O into a 1:1 solution of **4**·4 PF$_6$ and ferrocene (**Fc**) in MeCN.

X-ray Crystallography: The data for all compounds with the exception of **8**·4 PF$_6$ have already been deposited. Table 2 provides a summary of the crystal data, data collection, and refinement parameters for **8**·4 PF$_6$, and for comparison those for **15**·2 PF$_6$, **4**·4 PF$_6$, and **4/Fc**·4 PF$_6$.[15] The structure of **8**·4 PF$_6$ was solved by direct methods and the non-hydrogen atoms refined anisotropically. There was evidence for disorder in the PF$_6^-$ anions but this could not be resolved into alternate partial occupancy orientations. The positions of the hydrogen atoms were idealized, assigned as isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares based of F^2. Computations were carried out using the SHELXTL program system (version 5.03). The crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101398. Copies of the data can be obtained free of charge on application to

Table 2. Crystal data, data collection, and refinement parameters for **15**·2 PF$_6$, **4**·4 PF$_6$, **8**·4 PF$_6$, and **4/Fc**·4 PF$_6$[a]

Data	**15**·2 PF$_6$	**4**·4 PF$_6$[b]	**8**·4 PF$_6$[b]	**4/Fc**·4 PF$_6$[b]
Empirical formula	C$_{30}$H$_{30}$N$_4$O·2 PF$_6$	C$_{40}$H$_{40}$N$_4$O$_4$·4 PF$_6$	C$_{40}$H$_{40}$N$_4$O$_4$·4 PF$_6$	C$_{50}$H$_{50}$FeN$_4$O$_4$·4 PF$_6$
Solvent	0.5 H$_2$O	2.3 MeCN	−	2 MeCN/2 H$_2$O
M	777.5	1315.1	1220.6	1524.8
Colour, habit	clear prisms	yellow blocks	clear prisms	green blocks
Crystal size [mm]	0.67×0.63×0.50	0.23×0.27×0.33	0.17×0.17×0.10	0.20×0.20×0.23
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P1	C_2/c	$P2_1/n$	$P2_1/c$
Temperature [K]	291	293	203	293
a [Å]	10.459(7)	22.990(7)	11.308(1)	9.834(2)
b [Å]	11.811(8)	20.372(6)	13.902(1)	20.450(4)
c [Å]	14.522(12)	17.476(5)	15.265(1)	16.767(3)
α [°]	92.56(2)	−	−	−
β [°]	110.81(2)	124.00(2)	92.95(4)	103.09(2)
γ [°]	90.67(2)	−	−	−
V [Å^3]	1675(2)	6785(4)	2396.4(3)	3284(1)
Z	2	4[c]	2[c]	2[c]
D_c [g cm^{-3}]	1.542	1.287	1.692	1.542
$F(000)$	794	2666.4	2820	1552
μ [mm^{-1}]	2.14	1.99	1.47	3.85
2θ range [°]	3.0−110.0	3.0−110.0	8.6−110.0	3.0−120.0
Independent reflections	4216	4268	2995	4860
Observed reflections, $|F_o| > 4\sigma(|F_o|)$	2411	2512	2430	2348
Number of parameters	509	444	343	425
R_1[d]	0.138[e]	0.118[e]	0.090[f]	0.118[e]
R_w[g]	0.157	0.127	0.2352[h]	0.116
Largest difference peak, hole [eÅ^{-3}]	0.53, −0.37	0.55, −0.38	0.69, −0.66	0.60, −0.49

[a] Details in common: graphite-monochromated Cu-K_α radiation, ω-scans Siemens PA diffractometer). − [b] Rotating anode source. − [c] The molecule has crystallographic C_2 symmetry. − [d] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. − [e] Refinement based on F. − [f] Refinement based on F^2. − [g] $R_w = \Sigma[(|F_o|-|F_c|)w^{1/2}]/\Sigma[|F_o|w^{1/2}]$, $w^{-1} = \sigma^2(F) + 0.00050 F^2$. − [h] Value quoted is for $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.134 P)^2 + 9.500 P$.

FULL PAPER

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