Organometallic crystal engineering of [(1,4- and 1,3-hydroquinone)-Rh(P(OPh)₃)₂]BF₄ by charge assisted hydrogen bonding†

Seung Uk Son,[a] Jeffrey A. Reingold,[b] Gene B. Carpenter[b] and Dwight A. Sweigart*[b]

The ionic complexes [(1,4- and 1,3-hydroquinone)-Rh(P(OPh)₃)₂]BF₄ form porous organometallic structures dictated by charge assisted hydrogen bonding.

Organometallic crystal engineering has attracted significant recent attention due to potential catalytic and materials applications.[1,2] We recently reported a variety of inorganic–organometallic coordination polymers using $[\eta^4$-benzoquinone)Mn(CO)₃]⁻ as the fundamental building block connected to metallic nodes *via* the quinone oxygen atoms.[3] Braga and co-workers have reported the syntheses of hydrogen bond directed organometallic and organic–organometallic supramolecules based on ferrocene, cobaltocene and bis-benzene chromium units.[4] In the latter studies it was suggested that charge assisted hydrogen bonding, which is that occurring in ionic or zwitterionic systems in conjunction with inherent coulombic interactions, can be an effective strategy for fully utilizing the directional properties of hydrogen bonding mediated assembly.[5]

Herein, we present the structural consequences of hydrogen bonding within the ionic organometallic complexes [(1,4- and 1,3-hydroquinone)Rh(P(OPh)₃)₂]BF₄ (**1⁺BF₄⁻**, **2⁺BF₄⁻**). The relevant interactions occurring in these systems are illustrated in Fig. 1. The hydroquinone –OH groups, which are situated at angles of 180° and 120° for the 1,4- and 1,3-substituted complexes, respectively, are particularly strong H-bond donors when the carbocyclic ring is π-coordinated to the electrophilic transition metal fragment [Rh(P(OPh)₃)₂]⁺. The bulky phosphite ligands were introduced to minimize the probability of interpenetration in the solid state.[6]

Complexes **1⁺BF₄⁻** and **2⁺BF₄⁻** were prepared in 71 and 89% isolated yields, respectively.[7] The hydrogen bonding interaction

between the organometallic cation and the counter anion was studied in methylene chloride solution *via* FT-IR. (Table 1, Fig. 2) Free hydroquinone and resorcinol displayed v_{OH} bands at 3585 and 3580 cm⁻¹, respectively. The positions of these bands were found to be invariant over the concentration range utilized (3–11 mM), indicating the absence of hydrogen bonding at these concentrations.[8] As shown in Fig. 2, the hydroquinone –OH bands in solutions of **1⁺BF₄⁻** and **2⁺BF₄⁻** are shifted to 3330 and 3321 cm⁻¹, respectively. Concomitant with these –OH bands were two less shifted and smaller intensity bands labelled c and d in Fig. 2. Band c was found to occur at much higher intensity in the IR spectrum of **1⁺SbF₆⁻**. In view of the expected[9] weaker interaction of **1⁺** with SbF₆⁻ in comparison to BF₄⁻, it is concluded that band c corresponds to "free" **1⁺**, not hydrogen bonded to its counterion.

The shift of the v_{OH} bands in the IR can be used to estimate the strength of the H-bonding between the hydroquinone –OH groups and the counterion by application of Iogansen's equation.[10] The results, presented in Table 1, indicate that H-bonding between **1⁺**

Table 1 Summary of IR spectra[a]

	H-bonded OH/cm⁻¹	Free OH/cm⁻¹	Shift by HB/cm⁻¹	$-H°$[b]/ kJ mol⁻¹
1,4-Hydroquinone		3585[c]		
1,3-Hydroquinone		3580		
1⁺BF₄⁻	3330	3517	187	17.5
2⁺BF₄⁻	3321	3504	183	17.3

[a] The data were obtained using 11 mM solution in methylene chloride. [b] Calculated by Iogansen equation ($\Delta H° = -1.28(\Delta v)^{1/2}$).[10] [c] The same peak position was found for a 3 mM solution.
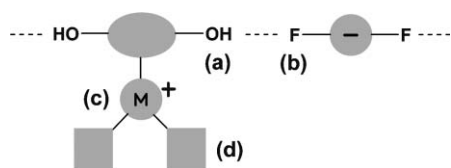

Fig. 1 (a) Hydrogen-bond donor activated by π-coordinated transition metal. (b) Negatively charged hydrogen bond acceptor. (c) Positively charged, π-coordinated transition metal. (d) Bulky ligands.

[a]*Department of chemistry, Sungkyunkwan University, Suwon 440-746, Korea. E-mail: sson@skku.edu; Fax: +82-31-290-7075; Tel: +82-31-290-7065*
[b]*Department of chemistry, Brown University, Providence, Rhode Island 02912, USA. E-mail: dwight_sweigart@brown.edu; Fax: +1-401-863-9046; Tel: +1- 401-863-2767*

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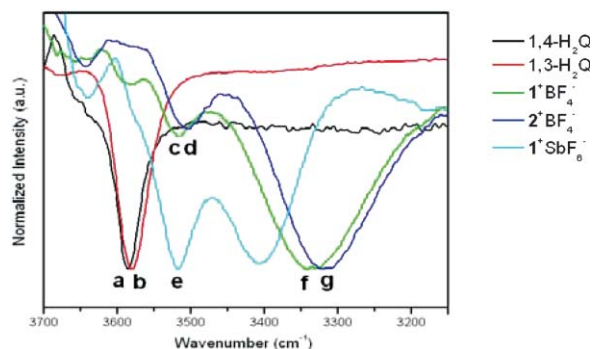

Fig. 2 IR spectra in the –OH stretch region (11 mM, CH₂Cl₂ solvent) for (a) free 1,4-hydroquinone, (b) free 1,3-hydroquinone, (c,d,e) –OH bands in **1⁺** and **2⁺** not H-bonded to counterion, (f) H-bonded –OH in **1⁺BF₄⁻** and (g) H-bonded –OH in **2⁺BF₄⁻**.

or $\mathbf{2}^+$ and BF_4^- is exothermic by *ca.* 17 kJ mol^{-1}. Fig. 2 shows that H-bonding in $\mathbf{1}^+BF_4^-$ is extensive, albeit not 100% complete, at 11 mM in CH_2Cl_2. In comparison to free 1,4-hydroquinone, enhanced H-bonding in $\mathbf{1}^+BF_4^-$ can be attributed to (1) the positive charge on the cation brought about by the electrophilic rhodium fragment and (2) the obligatory anionic counterion that can act as an H-bond acceptor. The charges on the species in $\mathbf{1}^+BF_4^-$ and the accompanying ionic interactions undoubtedly complement (or contribute to) the hydrogen bonding. The fact that the BF_4^- anion by itself is insufficient to guarantee H-bonding was indicated by experiments involving addition of Bu_4NBF_4 to a CH_2Cl_2 solution of 1,4-hydroquinone (11 mM). It was found, for example, that one equivalent of Bu_4NBF_4 had little effect on ν_{OH} and that five equivalents (55 mM) was needed to produce substantial H-bonding (ν_{OH} = 3466 cm^{-1}). We conclude that the H-bonding observed with $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4^-$ has as important components both ionic charge pairing and electrophilic activation imparted by coordination to the transition metal.

Given the fairly strong charge assisted hydrogen bonding observed for $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4^-$ in solution, it was anticipated that hydrogen bonding would also significantly influence the solid state structures. Additionally, H-bonding of the hydroquinone –OH groups to the BF_4^- counterions could be expected to increase the possibility of obtaining porous materials unclogged by counterions.

Crystals of $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4^-$ were obtained by slow diffusion of diethyl ether or toluene into methylene chloride solutions.‡ The differing bifunctional H-bond donor geometries of $\mathbf{1}^+$ and $\mathbf{2}^+$ (180°, 120°, respectively) are likely to be responsible for the observed substantial structural differences in the solids, shown in Fig. 3. $\mathbf{1}^+BF_4^-$ forms an interesting C_3 symmetric helical chain by hydrogen bonding of the –OHs with the BF_4^- anions (left in Fig. 3(a)). The O···F hydrogen bonding distances are 2.51 and 2.66 Å. In contrast, $\mathbf{2}^+BF_4^-$ forms a discrete hydrogen bonded dimer involving the –OHs and BF_4^- anions, with O···F distances of 2.76 and 2.86 Å (right in Fig. 3(a)). These supramolecular subunits, although fundamentally different, pack to form very intriguing isostructural motifs containing porous channels. In $\mathbf{1}^+BF_4^-$, six C_3 helices assemble as shown in Fig. 3(b) to generate hexagonal channels. The rotation directions of the helices alternate around the channels and the structure belongs to the centrosymmetric space group $R\bar{3}$ (Fig. 3(b) left). In $\mathbf{2}^+BF_4^-$, the discrete dimers pack in a manner complementary to that in $\mathbf{1}^+BF_4^-$ and form a similar channel structure. Not surprisingly, the rhombohedral unit cell dimensions for $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4^-$ are very similar, with almost identical unit cell volumes (19125 Å^3 and 19037 Å^3, respectively). It is noteworthy that the network topology in $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4^-$ is equivalent to that recently reported for the rhombohedral polymorph of Me_3In.[11]

In crystal engineering, it is common for slight modifications in ligand geometry and/or reaction conditions to result in supramolecular isomerization. This is typically the reason it is difficult to rationally design or predict supramolecular structures. In the case of $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4^-$ it is interesting that two isostructures can be obtained from the self-assembly of geometrically different building blocks. This suggests that the bulky triphenyl phosphite groups, which are common to both $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4^-$, play a major role in the supramolecular construction. This hypothesis is
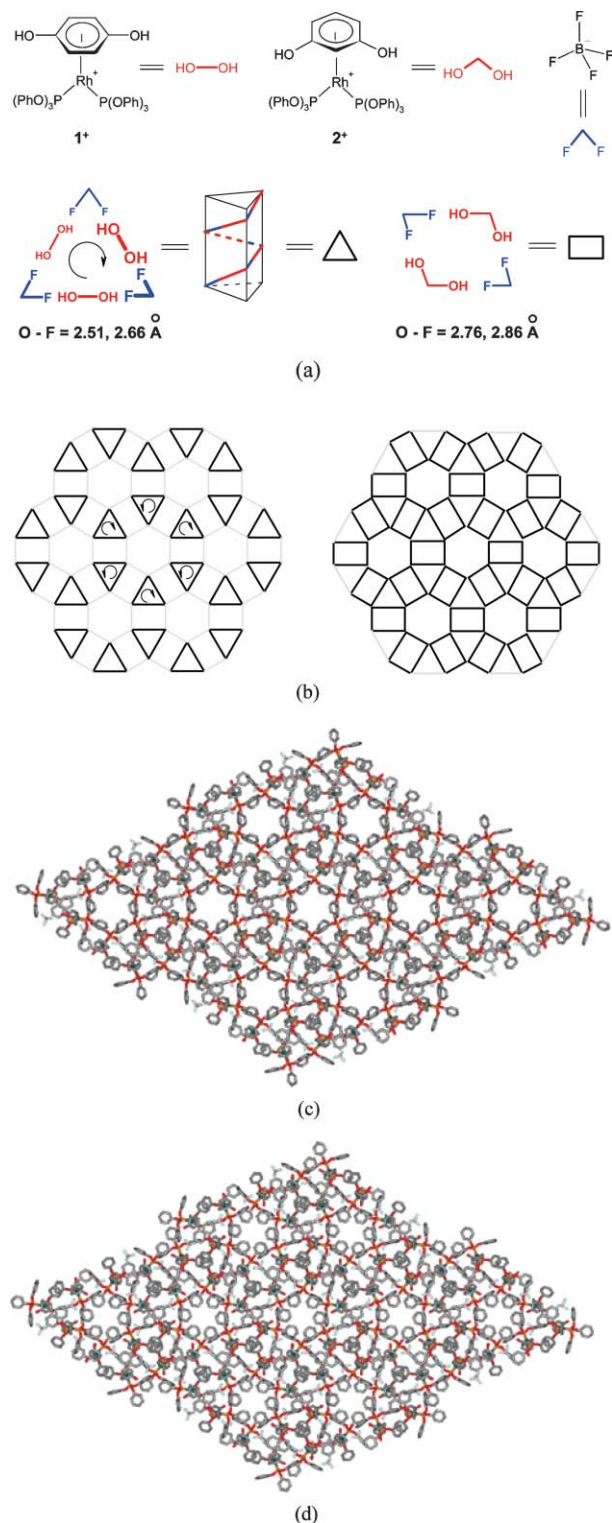

Fig. 3 Building blocks used in this study. (a) Two supramolecular subunits based on the different hydrogen bonding modes. (b) Assembly of subunits into supramolecular isostructures. (c,d) 3-D supramolecular structures of $\mathbf{1}^+BF_4^-$ and $\mathbf{2}^+BF_4$.

strengthened by an examination of the chemical composition of the channels.

The channels or pores located at the core of the six helices in $\mathbf{1}^+BF_4^-$ consist of hydrophobic phosphite phenyl groups. Two of
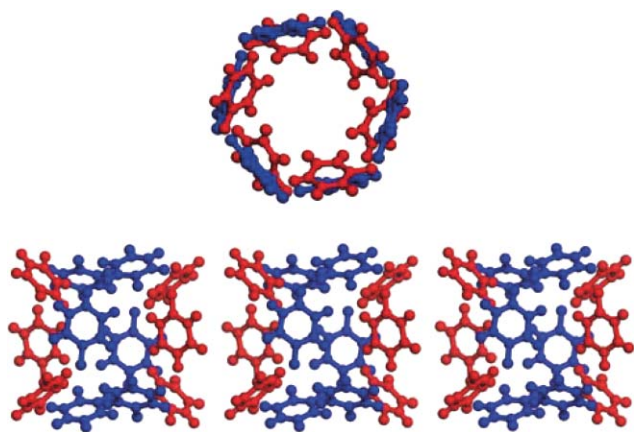
Fig. 4 Views perpendicular and parallel to the channel axis in **1**$^+$BF$_4$$^-$. Two types of phenyl groups are shown in red and blue.

the three phenyl groups from each P(OPh)$_3$ ligand contribute to the channels. Fig. 4 illustrates the view perpendicular and parallel to the channel axis. There are two types of phenyl groups present: half (blue) are situated parallel to the channel axis and define a pore diameter of *ca.* 10.5 Å; the other half (red) are inclined by *ca.* 45° to the axis, reducing the effective pore diameter to *ca.* 6 Å. These two subgroups together form interesting sphere like units (red) linked by linear units (blue). In **2**$^+$BF$_4$$^-$ completely analogous channels exist with the difference that the "red" phenyl groups are more inclined (*ca.* 75°), with the result that the channels are much more blocked in comparison to the situation in **1**$^+$BF$_4$$^-$.

The micropores in **1**$^+$BF$_4$$^-$ are likely to be robust because the hydrogen bonding is "charge-assisted" by coulombic interactions. Complementing this is the relatively small pore size and the large distance of *ca.* 23 Å between successive pore centers.[6c] Metal–organic networks with pores in the size range reported herein have recently been found to be excellent hosts for suitably small guest molecules (*e.g.*, acetylene[12]). Aside from size, the important factor influencing adsorption is the chemical environment of the pore interior. In the case of **1**$^+$BF$_4$$^-$, the channels or pores consist of aromatic rings, which may make the material a particularly useful model for hydrogen adsorption.[13]

In summary, the complexes [(1,4- and 1,3-hydroquinone)Rh(P(OPh)$_3$)$_2$]BF$_4$ (**1**$^+$BF$_4$$^-$, **2**$^+BF_4$$^-$) were found to exhibit charge assisted hydrogen bonding between the –OH groups and the BF$_4$$^-$ counterion. In the solid state, this hydrogen bonding interaction gives rise to isostructural supramolecular networks containing hydrophobic channels that consist of phenyl groups from the triphenyl phosphite ligands. Applications of these materials to guest–host chemistry are being examined.

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