CRYSTAL GROWTH & DESIGN

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Protonation and Alkylation Induced Multidentate C−H···Anion Binding to Perrhenate

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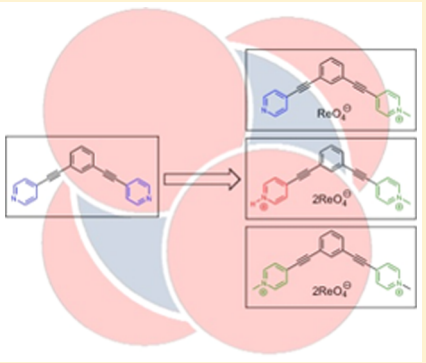
Supporting Information

ABSTRACT: A family of pyridyl-functionalized arylacetylene C−H hydrogen bonding (HB) receptors were synthesized and binding interactions to perrhenate (ReO_4^-) studied in the solid state. The protonation and alkylation state of the pyridine nitrogen dictate the location and denticity of the interactions. X-ray structures of neutral **1** and singly charged **2a**$^+$·ReO_4^- reveal the formation of favorable self-complementary dimers, owing to the presence of nitrogen HB acceptor sites. Dismissal of these dimers upon elimination of nitrogen HB acceptors on the receptor result in an array of multidentate C−H HB receptor−guest contacts.



INTRODUCTION

The design and application of synthetic receptors for anions remains a captivating and challenging area of chemistry. A common motivation driving these efforts is the detection and remediation of environmentally noxious anions. Pertechnetate (TcO_4^-) is a contemporary example, which has entered the environment as a product from nuclear processing plants in the past few decades.[1] Technetium-99 (^{99}Tc) becomes the mobile TcO_4^- when oxidized in the environment making it a particularly dangerous radioactive compound.

Due to the challenges of working with TcO_4^-, perrhenate (ReO_4^-) is often employed as a manageable surrogate with comparable structural and electronic characteristics.[2] However, both anions are elusive targets as a result of low hydration energies and diffuse charge densities.[3] Efforts to address these problematic features with noncovalent interactions has included elegant hydrogen bonding (HB) systems such as aza-thioether macrocycles,[4] amino-azacryptands,[5] tripodal aminopyridinium-based receptors,[6] and lipophilic guanidinium receptors.[7] Additionally, the first solution and solid-state investigations of bidentate halogen bonding (XB) to ReO_4^- were reported.[8] Complementing these studies, a XB receptor was recently shown to extract ReO_4^- from water in a solvent extraction process.[9] In contrast, nontraditional C−H HB receptors are underrepresented with only one investigation of ReO_4^- binding.[8]

Herein, we report crystal structures for a family of pyridyl-functionalized arylacetylene C−H HB receptors where ReO_4^- binding is dictated by alkylation and protonation of the receptors in the solid state. The neutral receptor forms self-complementary dimers whereas elimination of the nitrogen HB acceptor ensures the receptor binding pocket interacts with ReO_4^- resulting in an array of multidentate C−H HB receptor−guest contacts.

RESULTS AND DISCUSSION

In supramolecular chemistry the phenyl acetylene group has been effectively employed to impart direction and rigidity.[10] Rotation around the alkyne bonds allow for receptors to be conformationally flexible and adaptable for guest species to induce a specific host conformation. A diverse collection of phenyl acetylene receptors exhibiting induced-fit binding include the following: bis(2-anilinoethynyl) sulfonamide receptors,[11] resorcin[4]arene cavitand-based molecular switches,[12] and fluorophoric alkyne-linked bis-urea chemosensors.[13] Consequently, aryl C−H protons often frequent the binding pocket of the host, yet, despite this proximity, their role in anion binding is rarely discussed.

The receptors that we are developing incorporate both arylacetylene and pyridine functionalities. The pyridine ring is an appealing and established structural motif for the design of tunable anion receptors, as the chemistry at the pyridine nitrogen[14] dictates HB functionality; the neutral species can accept HBs through the nitrogen lone pair. Protonation of the pyridine ring establishes a strong HB donor while alkylation silences HB at this site.

A series of pyridine-functionalized arylacetylene-based receptors demonstrate the influence of alkylation and protonation when binding to ReO_4^-. Receptors capable of accepting a HB prefer to form self-complementary dimers. As a result ReO_4^- molecules interact with the backbone of the

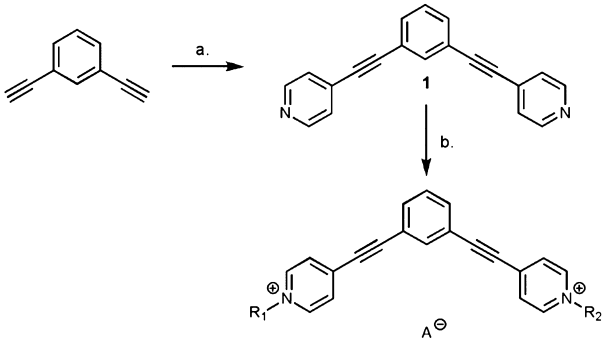
Received: October 28, 2015
Revised: December 21, 2015
Published: December 22, 2015

DOI: 10.1021/acs.cgd.5b01524
Cryst. Growth Des. 2016, 16, 974−980

receptor. Alkylation or protonation of the pyridine ring disrupts dimer formation, thus permitting favorable multidentate interactions between the receptor and ReO_4^- in the binding pocket.

Receptor Synthesis. Three bidentate HB receptor molecules based on a bis-ethynyl benzene core were prepared (Scheme 1). The synthesis of pyridyl arylacetylene scaffolds **1** and **2c** have been described previously.[8] Compound **2a** was isolated as a byproduct of the alkylation of neutral scaffold **1** (Scheme 1, step b).[15] Finally, anion exchange of triflate (OTf^-) with ReO_4^- was accomplished through vapor diffusion crystallization using tetra-*n*-butylammonium perrhenate ($TBA^+ReO_4^-$). This afforded a family of pyridyl-functionalized arylacetylene-based receptor molecules, where the electronic nature of the pyridine ring and C−H HB ability was tuned; all of the key crystal details and structure parameters are compiled in Table 1.

Scheme 1. Synthesis of Compounds 1, 2a, 2b, and 2c[a]



2a. $R_1 = CH_3$; R_2 = neutral; A = $[OTf]^-$
2b. R_1 = H; $R_2 = CH_3$; A = $2[OTf]^-$
2c. $R_1 = R_2 = CH_3$; A = $2[OTf]^-$

[a]Step a: 4-Iodopyridine, CuI, $Pd(PPh_3)_2Cl_2$, DMF, DIPEA, rt, 24 h, 22%. Step b: Methyl triflate (2 equiv), DCM, rt, 24 h, 98%.

Neutral Bis-Ethynyl Benzene Core Crystal Structure 1. To compare structural characteristics between scaffolds, it was crucial to evaluate the packing features of the neutral receptor without ReO_4^-. Crystals of the unmodified scaffold (**1**) were grown by slow evaporation of an MeCN/H_2O (9:1) solution of **1**. Scaffold **1** crystallized in space group $P\bar{1}$ with two independent molecules in the asymmetric unit as shown in Figure 1a.

The crystal structure of **1** reveals that each receptor forms two unique self-complementary HB dimers (Figure 1b) between the pyridine nitrogens and the hydrogens that are ortho to the alkynes on an adjacent pyridine. Receptors from each dimer reside out-of-plane (blue dimer interplanar distance of 0.279(9) Å and orange dimer interplanar distance of 0.968(9) Å) to minimize steric interactions between benzene and pyridyl hydrogens on independent receptors. As a result the alkynes distort 4−5° from linearity to accommodate the C−H···N HB. Interestingly, sheets of dimers are created by medium strength HBs (C−H···N distances, angles of 2.5055(16) Å, 159.88(11)° and 2.4988(19) Å, 160.22(11)°) that form between two self-complementary dimer systems (Figure 2a). Parallel sheets of dimers are supported by $\pi-\pi$ interactions that display interplanar distances of 3.116(6) and 3.450(6) Å. The crystal lattice of **1** exhibits herringbone

Table 1

cryst param	**1**	$\mathbf{2a}^+\cdot ReO_4^-$	$\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$	$\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot 2DCM$	$\mathbf{2c}^{2+}\cdot 2ReO_4^-$
CCDC	1433000	1433002	1433001	1433003	1028025
empirical formula	$C_{20}H_{12}N_2$	$C_{21}H_{15}N_2O_4Re$	$C_{21}H_{18}N_2O_9Re_2$	$C_{24}H_{22}Cl_4N_2O_8Re_2$	$C_{22}H_{18}N_2O_8Re_2$
fw	280.32	545.55	814.77	980.63	810.78
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
cryst size (mm)	0.25 × 0.2 × 0.05	0.35 × 0.05 × 0.02	0.35 × 0.15 × 0.05	0.3 × 0.3 × 0.04	0.2 × 0.1 × 0.01
cryst syst	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	5.8402(5)	45.388(4)	7.6357(4)	7.6734(6)	15.5756(10)
b (Å)	11.4802(10)	5.5199(5)	8.0400(4)	10.7002(8)	7.6106(5)
c (Å)	22.2886(19)	15.4046(15)	18.3333(9)	18.7453(14)	19.6042(13)
α (deg)	76.511(2)	90	82.310(2)	101.0830(19)	90
β (deg)	83.385(3)	95.401(4)	83.902(2)	91.6380(19)	100.084(2)
γ (deg)	89.692(3)	90	80.681(2)	103.1300(19)	90
V (Å^3)	1443.1(2)	3842.3(6)	1096.54(10)	1466.72(19)	2288.0(3)
Z	4	8	2	2	4
D_c (Mg m^{-3})	1.29	1.886	2.468	2.22	2.354
μ (mm^{-1})	0.077	6.355	11.087	8.659	10.623
F(000)	587	2096	760	924	1512
$2\theta_{max}$ (deg)	54.97	55.236	61.214	55.75	56.56
no. of reflns	48397	42312	70337	38575	40497
no. of indepen reflns	6623	4459	6731	6987	5583
R_{int}	0.0507	0.092	0.05	0.362	0.0706
R1 ($I > 2\sigma(I)$)	0.0532	0.0511	0.0289	0.024	0.0286
wR2 ($I > 2\sigma(I)$)	0.1261	0.0948	0.0614	0.0548	0.0563
GOF	1.026	1.163	1.162	1.246	1.000
max/min residual e$^-$ density (e Å^3)	0.37/-0.19	3.0/-3.5	2.88/-2.24	0.94/-0.94	2.88/-1.52

DOI: 10.1021/acs.cgd.5b01524
Cryst. Growth Des. 2016, 16, 974−980

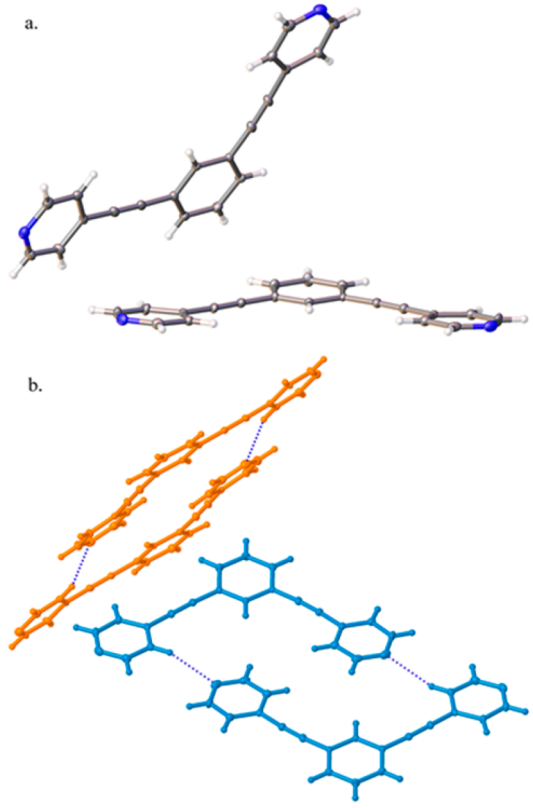


Figure 1. (a) Asymmetric unit of neutral pyridine-functionalized arylacetylene scaffold **1**. (b) Display of two unique self-complementary dimers of **1** (blue dimer C−H···N distance of 2.5932(19) Å and angle of 159.12(11)°; orange dimer C−H···N distance of 2.6269(16) Å and angle of 161.98(12)°).

packing (Figure 2c), when viewed along [110], between two independent receptor units, intersecting at 63.75(6)°.

The crystal structure of **1** is highlighted by C−H···N HB dimerization, emphasizing the critical role of the pyridine nitrogen. Dimerization and lack of charge suggests that this neutral molecule is an inadequate receptor for ReO_4^-. Elucidation of the neutral scaffold, however, establishes a baseline for the investigation of the modified receptors with ReO_4^-.

Crystal Structure of $2a^+ \cdot ReO_4^-$. Colorless single crystals of the monoalkylated pyridyl arylacetelyene complex $2a^+ \cdot ReO_4^-$ suitable for X-ray diffraction were grown by vapor diffusion of ether into an MeCN solution of ligand **2a** and $TBA^+ReO_4^-$. Complex $2a^+ \cdot ReO_4^-$ crystallized in space group *C*2/*c* with one singly charged receptor and one ReO_4^- anion per asymmetric unit (Figure 3).

Monoalkylation of the scaffold eliminates the HB accepting ability of one nitrogen; however, dimerization similar to **1** is conserved. The preservation of the self-complementary dimer results in C−H HB interactions with ReO_4^- occurring with the receptor backbone (Figure 4). Examination of the environment around the anion reveals that one ReO_4^- accepts nine HBs from six different receptor molecules (distances, 2.341(6)−2.741(5) Å; C−H···O^- angles, 126.5(5)−168.5(5)°) and one anion-π contact.[16] Further investigation reveals a self-complementary dimer (C−H···N distance of 2.353(7) Å and angle of 172.0(5)°) similar to **1**; each receptor molecule sits slightly out-of-plane (interplanar distance of 0.60(4) Å). Additionally, both pyridine rings rotate out of planarity

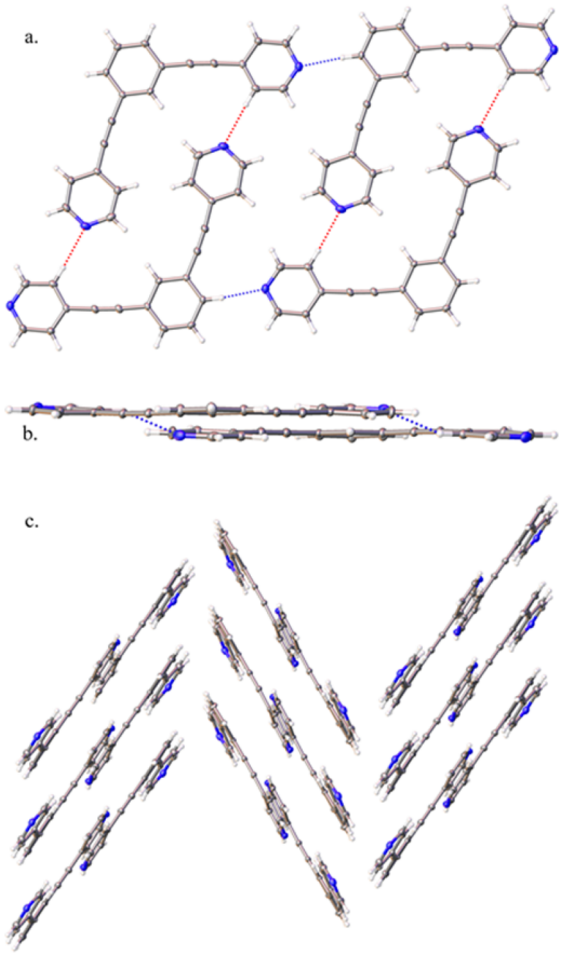


Figure 2. (a) Self-complementary dimer formed by **1** (red dashed lines) and dimers forming sheets of dimers through HB (blue dashed lines). (b) Side view of one dimer highlighting the offset dimerization. (c) Herringbone packing displayed when viewed along [110].

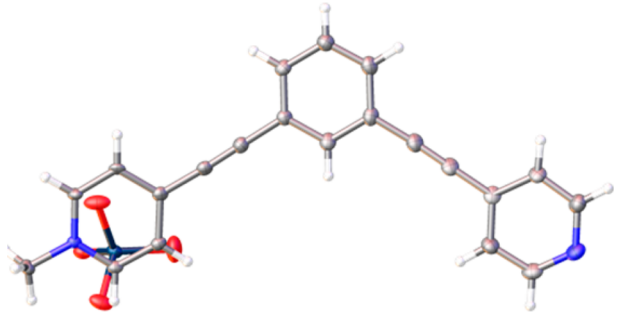


Figure 3. Asymmetric unit of monoalkylated complex $2a^+ \cdot ReO_4^-$.

(pyridinium ring rotates 10.1(3)° and neutral pyridine ring rotates 2.5(3)°) with the center benzene ring to reduce steric contacts between hydrogens on independent receptors in the dimer.

A self-complementary dimer is present in $2a^+ \cdot ReO_4^-$ due to the availability of a HB accepting lone pair. However, the second pyridine nitrogen is not available in this capacity; thus, anion−π interactions contribute to assemble these HB dimers in the solid state. Crystal packing of $2a^+ \cdot ReO_4^-$ displays a herringbone type pattern, similar to **1**, when viewed down the crystallographic *c* axis, with two independent receptors intersecting at an angle of 55.7(4)°. Parallel sheets of dimers

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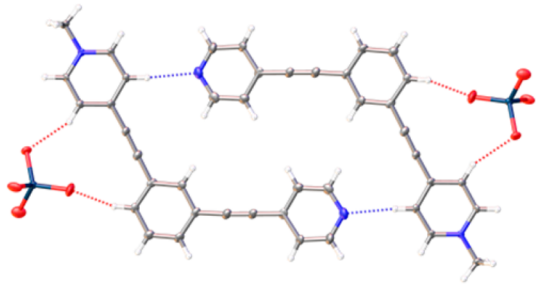

Figure 4. Complex $\mathbf{2a}^{+}\cdot ReO_4^{-}$ formation of a self-complementary dimer.

are supported by $\pi-\pi$-stacking interactions that display an interplanar distance of 3.18(3) Å. In contrast to **1**, the crystal packing is altered due to the presence of ReO_4^{-} in this crystal—the lattice of $\mathbf{2a}^{+}\cdot ReO_4^{-}$ is held together by C−H HB, $\pi-\pi$ stacking, and anion−π contacts between receptor and ReO_4^{-} (Figure 5).

The monoalkylated receptor complex $\mathbf{2a}^{+}\cdot ReO_4^{-}$ highlights the importance of a pyridinium ring in the crystal lattice. Alkylation of the pyridine ring encourages C−H HB and electrostatic interactions between the scaffold and ReO_4^{-}. However, conservation of one neutral pyridine permits self-dimerization and prevents ReO_4^{-} from binding in the pocket. As a result, this alters the crystal lattice and induces herringbone type packing held together through C−H HB, $\pi-\pi$ stacking, and anion−π contacts between the receptor and ReO_4^{-}. This structure elucidates the competitive and energetically favorable nature of dimer formation despite the presence of anions.

Crystal Structure of $\mathbf{2b}^{2+}\cdot 2ReO_4^{-}\cdot H_2O$. Colorless single crystals of $\mathbf{2b}^{2+}\cdot 2ReO_4^{-}\cdot H_2O$ were grown by diffusing ether into an MeCN solution of the receptor and $TBA^{+}ReO_4^{-}$. Complex $\mathbf{2b}^{2+}\cdot 2ReO_4^{-}\cdot H_2O$ crystallized in space group $P\bar{1}$ with one receptor, two ReO_4^{-}, and one water molecule per asymmetric unit.

Protonation of **2a** eliminates the HB accepting functionality of the receptor, which prompts the disruption of previously observed dimers. This enables multidentate C−H HB to ReO_4^{-} in the receptor pocket. Complex $\mathbf{2b}^{2+}\cdot 2ReO_4^{-}\cdot H_2O$ exhibits tridentate C−H HB between ReO_4^{-} and the phenyl and pyridyl hydrogens ortho to the alkynyl group (C−H···O^{-} distances, angles of 2.480(3) Å, 161.0(3)°; 2.390(4) Å, 138.7(3)°; and 2.609(4) Å, 140.1(3)° (Figure 6). In addition, the same ReO_4^{-} participates in a medium strength HB with water (O−H···O^{-} distance of 2.15(7) Å and angle of 169(7)°), five intermolecular C−H HB (C−H···O^{-} distances, angles of 2.362(4)−2.615(3) Å, 151.7(3)−161.8(3)°) with three other receptor molecules, and two anion-π contacts. The second ReO_4^{-} participates in a medium strength HB with water (2.08(6) Å, 175(5)°), eight other C−H HB (2.344(3)−2.757(3) Å, C−H···O^{-} angles 121.1(3)−164.7(3)°) with four other receptor molecules and one anion−π contact.

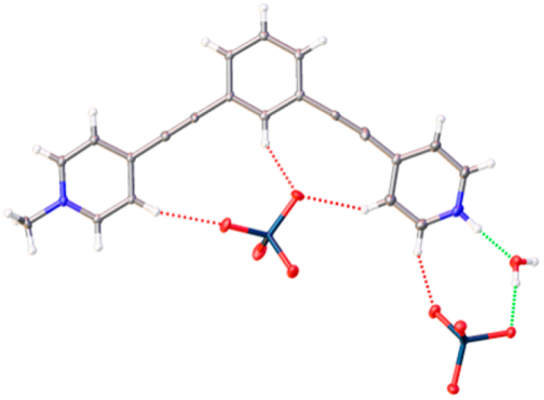

Figure 6. Asymmetric unit of monoalkylated/monoprotonated complex $\mathbf{2b}^{2+}\cdot 2ReO_4^{-}\cdot H_2O$ displaying a tridentate C−H HB to ReO_4^{-} in the receptor binding pocket.

Although protonation and alkylation of the receptor nullified the HB accepting abilities of the scaffold, the presence of water molecules presents a new HB acceptor within the crystal lattice. The water molecules aid in directing crystal growth by accepting a HB from the protonated pyridinium ring and donating two HBs to two ReO_4^{-} molecules. A strong N−H HB between a receptor and water molecule is observed (N−H···O^{-} distance of 1.74(7) Å and angle of 177(8)°). With the dimer absent both pyridine rings remain nearly planar with each other, rotated by 0.72(17)° out of co-planarity. An off-centered antiparallel π-stacking dimer is noted (Figure 7). These dimers are staggered in offset columns which are assisted by C−H and N−H HB interactions with ReO_4^{-} and water molecules (Figure 8).

The crystal structure of $\mathbf{2b}^{2+}\cdot 2ReO_4^{-}\cdot H_2O$ highlights the influence of two pyridinium rings on ReO_4^{-} binding. Alkylating and protonating both pyridine rings eliminates the HB accepting capacity of the receptor, thus inhibiting self-dimerization and enabling tridentate binding to ReO_4^{-}. The inclusion of water establishes a conventional HB that results in

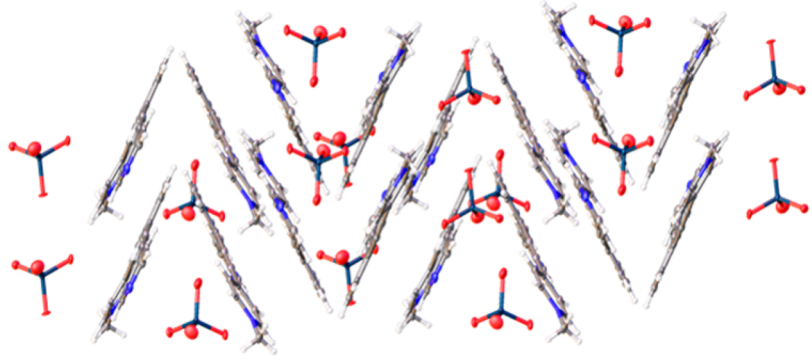

Figure 5. Complex $\mathbf{2a}^{+}\cdot ReO_4^{-}$ receptor interactions with ReO_4^{-}, showing dimer systems together held together and displaying herringbone type packing, similar to that of **1**.

DOI: 10.1021/acs.cgd.5b01524
Cryst. Growth Des. 2016, 16, 974−980

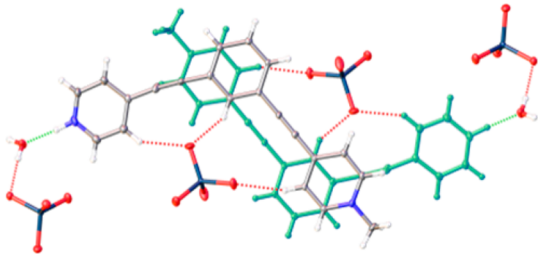

Figure 7. Off-centered antiparallel dimer of receptor−guest complex $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$ (interplanar distance of 3.086(13) Å).

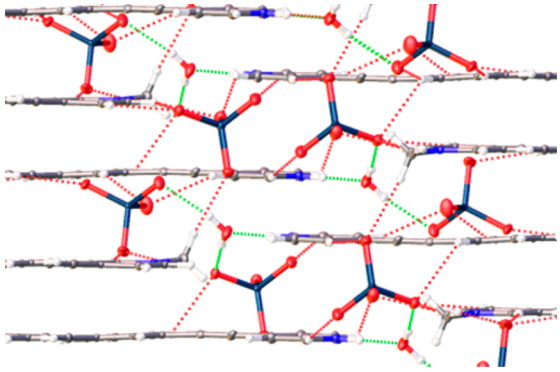

Figure 8. Close-in examination of staggered columns of receptors held together by interactions with molecules of water and ReO_4^-.

strong interactions with one symmetrically unique ReO_4^-, which allows binding to the other ReO_4^- to occur solely through aryl C−H HB. Similar to $\mathbf{2a}^+\cdot$ ReO_4^-, the alkylated pyridinium ring displays C−H HB and electrostatic anion−π contacts with ReO_4^-. Altering the electronic state of the pyridine rings and eliminating the HB acceptor drastically influences the receptor interactions with guests, creating a multidentate binding pocket.

Crystal Structure of $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot$2DCM. Two unique dialkylated receptor and ReO_4^- complexes were crystallized. Complex $\mathbf{2c}^{2+}\cdot 2ReO_4^-$ (Figure 9a) was previously reported.[7] Similar to $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$, $\mathbf{2c}^{2+}\cdot 2ReO_4^-$ exhibits tridentate binding to ReO_4^- in the binding pocket (2.714(3) Å, 160.3(3)°; 2.308(4) Å, 162.3(3)°; and 2.639(4) Å, 156.0(3)°). As a result, the pyridinium rings adjust 8.7341(5)° from co-planarity and one alkynyl spacer deviates 8.7211(7)° from linearity. In addition, an off-centered antiparallel dimer is noted.

For this study a solvate of the charged dialkylated pyridyl arylacetylene receptor and ReO_4^- complex ($\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot$ 2DCM) was isolated from vapor diffusion of DCM into an MeCN solution of **2c** and $TBA^+ReO_4^-$. Complex $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot$ 2DCM crystallized in space group $P\bar{1}$ with one receptor, two ReO_4^- anions, and two DCM molecules per asymmetric unit (Figure 9b).

A DCM molecule is observed occupying the binding pocket, inhibiting tridentate C−H HB to ReO_4^-. One ReO_4^- molecule participates in a weak C−H HB with a DCM molecule. Due to the inclusion of solvent molecules, receptor contacts with ReO_4^- were limited to mono- and bidentate interactions, unlike the crystal structures of $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$ and $\mathbf{2c}^{2+}\cdot 2ReO_4^-$. These results suggest that judicious choice of solvent will be important when designing these receptors to target ReO_4^- in solution.

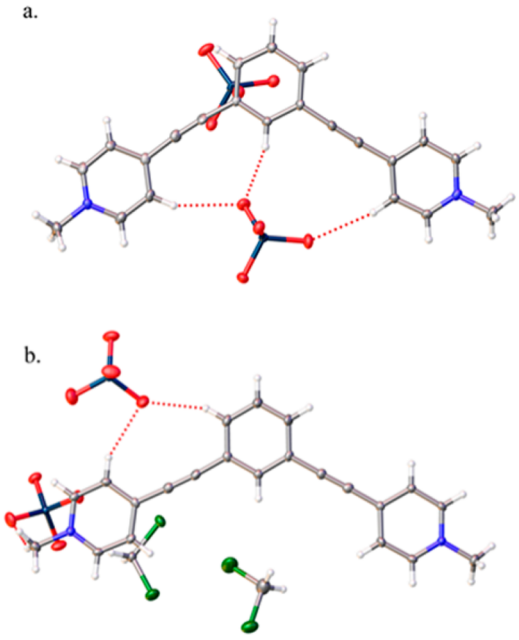

Figure 9. (a) Asymmetric unit of $\mathbf{2c}^{2+}\cdot 2ReO_4^-$ exhibiting tridentate binding to ReO_4^-. (b) Asymmetric unit of the solvate complex $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot$2DCM.

Complex $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot$2DCM displays bidentate HB interactions with the backbone of the receptor between hydrogens ortho to the alkynes and one ReO_4^- anion (C−H···O^- distances, angles of 2.499(3) Å, 156.2(3)° and 2.581(4) Å, 152.7(2)°). Additionally, the same ReO_4^- participates in three intermolecular C−H HB (C−H···O^- distances, angles of 2.568(4)−2.765(3) Å, 139.8(2)−157.9(2)°) with two other receptor molecules and one anion−π contact. The second ReO_4^- forms a monodentate C−H HB (2.513(3) Å, C−H···O^- angle of 149.9(3)°) and an anion−π contact, as well as eight additional C−H HBs (2.267(3)−2.637(4) Å, C−H···O^- angles of 130.0(2)−159.2(3)°) with five other receptors. To accommodate binding with both ReO_4^- anions, the pyridinium rings rotate 2.56(13)° and 8.27(13)° out of co-planarity with the central benzene ring.

Crystal packing displays staggered columns of offset antiparallel π-stacking dimers (interplanar distance of 3.174(9) Å). Columns of dimers are held together by HB interactions to ReO_4^- while DCM solvate molecules occupy the space in the binding pocket (Figure 10). Comparison of C−H···O^- distances between $\mathbf{2c}^{2+}\cdot 2ReO_4^-$ and $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot$ 2DCM reveals stronger C−H···anion interactions when tridentate binding occurs.

Similar to $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$, the two pyridinium rings do not contain HB acceptors. Introducing a second alkyl group on the receptor removed the HB abilities of the nitrogen, resulting in C−H HB interactions with ReO_4^-. Inclusion of a DCM solvate molecule in the crystal lattice, eliminates the tridentate interactions with ReO_4^- that were displayed in the crystals of $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$ and $\mathbf{2c}^{2+}\cdot 2ReO_4^-$. All three pyridyl arylacetylene dimer complexes, $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$, $\mathbf{2c}^{2+}\cdot 2ReO_4^-$, and $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot$2DCM, are held together through aryl C−H HB, $\pi-\pi$-stacking, and electrostatic interactions with ReO_4^-.

Solution Studies. Previously, ^{1}H NMR titration studies were completed to quantify the C−H HB interactions of an octylated derivative of $\mathbf{2c}^{2+}\cdot 2ReO_4^-$ in a $CDCl_3/(CD_3)_2CO$ (3:2 (v/v)) mixed solvent system, resulting in a stability

DOI: 10.1021/acs.cgd.5b01524
Cryst. Growth Des. 2016, 16, 974−980

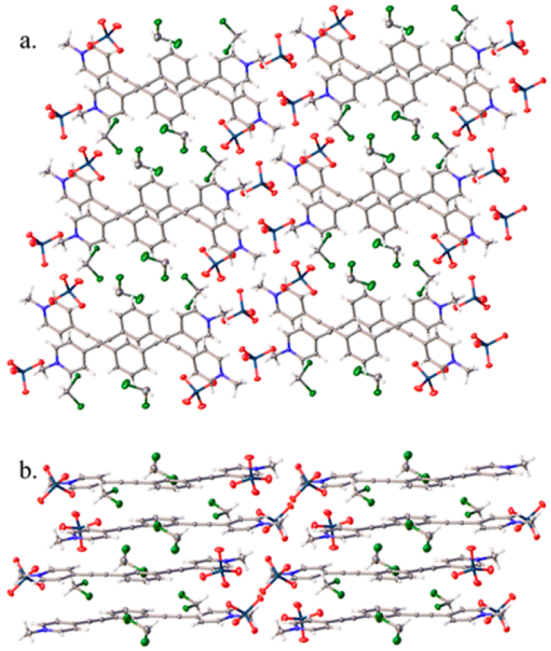

Figure 10. (a) View of crystal packing down crystallographic *a* axis for $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot 2DCM$ and (b) view of crystal packing down crystallographic *b* axis.

constant (K_a) with a K_1 of 7390 and K_2 of 145 M^{-1}. In contrast, the binding of the octylated derivatives of $\mathbf{2a}^+$ and $\mathbf{2b}^{2+}$ to ReO_4^- in solution has not been quantified. Due to the large electrostatic component of the interaction, it is likely that the doubly charged systems $\mathbf{2b}^{2+}$ and $\mathbf{2c}^{2+}$ will exhibit stronger binding than the singly charged $\mathbf{2a}^+$. The solid-state studies presented herein and the previous solution studies have inspired future experiments that will be used to evaluate the impact of protonation/alkylation on solution phase anion binding within this system.

CONCLUSION

In summary, a family of pyridyl-functionalized arylacetylene C−H HB receptors was prepared exhibiting various alkylation and protonation states. All ReO_4^- crystals were grown in competitive crystallization environments where C−H HB with this charge diffuse anion was preferred over the OTf^- counteranion.

The receptors display unique solid-state interactions with ReO_4^- through modification of the pyridine ring. Comparably, self-complementary dimers of neutral scaffold **1** and monoalkylated complex $\mathbf{2a}^+\cdot ReO_4^-$ were observed as a result of the HB accepting abilities of the pyridine nitrogen lone pair. Complex $\mathbf{2a}^+\cdot ReO_4^-$ exhibited bidentate binding to ReO_4^- with hydrogens ortho to the alkyne on the backbone of the receptor. Complexes $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$ and $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot 2DCM$ highlight the influence of two pyridinium rings on C−H HB to ReO_4^-. Both structures contained solvent molecules in the lattice, which aided crystal growth. The water molecule in $\mathbf{2b}^{2+}\cdot 2ReO_4^-\cdot H_2O$ displayed strong N−H HB with the protonated nitrogen, allowing for tridentate C−H HB to ReO_4^- in the binding pocket. The DCM in $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot 2DCM$ nullified C−H HB to ReO_4^- inside the binding pocket, which was previously observed. C−H HB interactions between receptor and ReO_4^- in complex $\mathbf{2c}^{2+}\cdot 2ReO_4^-\cdot 2DCM$ were only observed with the receptor backbone.

Through simple alkylation and protonation, the noncovalent interactions of the presented receptor system with ReO_4^- were directly affected. To prevent competitive self-dimerization and enhance electrostatic interactions with ReO_4^-, it is essential that the pyridine nitrogens be protonated or alkylated. This also facilitates multidentate binding from each arm of the receptor with ReO_4^- anions. We report evidence that underrepresented aryl C−H HB is a viable tool in the design of chelators for ReO_4^-. Optimization of the bis-ethynyl binding pocket is currently underway to increase selectivity for ReO_4^-.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b01524.

Experimental procedures for and copies of ^1H, ^{13}C, and ^{19}F NMR spectra of **2a** (PDF)

Accession Codes

CCDC 1028025 and 1433000−1433003 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Center for Biomolecular Structure and Dynamics CoBRE (National Institutes of Health (NIH), Grant NIGMS P 20GM103546), National Science Foundation (NSF)-MRI (Grant CHE-1337908), Montana University System (MREDI, Grant 51030-MUSRI2015-02) and the University of Montana (UM).

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