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Solution and Solid-Phase Halogen and C–H Hydrogen Bonding to Perrhenate

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Abstract

^{1}H NMR spectroscopic and X-ray crystallographic investigations of a 1,3-bis(4-ethynyl-3-iodopyridinium)benzene scaffold with perrhenate reveal strong halogen bonding in solution, and bidentate association in the solid state. A nearly isostructural host molecule demonstrates significant C–H hydrogen bonding to perrhenate in the same phases.

With similar structural and electronic characteristics,[1] perrhenate (ReO_4^-) is a tractable surrogate[2] for the medically ubiquitous and environmentally pernicious[3] oxoanion, pertechnetate (TcO_4^-).[4] The metastable form of technetium[5] and its long half-life[6] decay product ^{99}Tc are standards for radiolabeling[7] and in situ radiotherapy. Considering the high mobility of $^{99}TcO_4^-$, its stability,[8] and increasing production,[9] the need for synthetic receptors to function as strong and selective chelating agents, liquid-liquid extractants,[2] and ion-exchange stationary phases[10] is pressing.

ReO_4^- and TcO_4^- are challenging targets due to their low hydration energies and diffuse charge densities.[11] To combat these difficulties, a number of hydrogen bonding (HB) scaffolds and hosts have been developed.[1, 11–12] Elegant HB examples include aza-cryptands with pH-tunable cavities,[12a–c] and charge neutral pyrrole-based macrocycles.[12d–e] In contrast, bidentate halogen bonding (XB) and unconventional C–H[13] HB receptors for ReO_4^- or TcO_4^- have not been reported. XB[14] in particular offers an exciting competitive[15]/cooperative[16] alternative with the benefit of soft-soft HSAB complementarity.[17] *Herein, we report the first two receptors that exhibit strong XB and C–H HB with ReO_4^- in solution, and the first bidentate and tridentate structures of each in the solid state.*

We have developed two bidentate receptor molecules based on a diethynyl benzene core (**1** and **2**, Scheme 1). **1** is designed to direct two XB donors towards one anionic guest in a planar conjugated conformation.[19] Molecule **2**—which lacks XB donors—was prepared to quantify C–H HB to ReO_4^-, and serve as a comparison. Both receptor scaffolds were synthesized by Sonogashira[20] cross-coupling of 1,3-diethynyl benzene with either 3-bromo-4-iodopyridine or 4-bromopyridine hydrochloride. The XB donor iodines of **1** were

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[†] Electronic supplementary information (ESI) available: synthesis and characterization of all novel compounds, ^{1}H NMR titration methods and data, and X-ray crystallographic data and crystal packing.

installed by lithium halogen exchange followed by quenching with I_2. Alkylation of the pyridines with octyl triflate activated the XB and HB donors of **1** and **2**, respectively, and enhanced solubility in organic solvents. To minimize competitive intramolecular interactions, triflate counteranions were exchanged by metathesis for non-coordinating $[BAr^F_4]^-$ anions.[21] Methyl derivatives **1b** and **2b** were synthesized in a similar manner for X-ray diffraction studies.

The crystal structure of $\mathbf{1b^{2+}}$•$2ReO_4^-$ represents the first bidentate XB[22] to ReO_4^- in the solid state. Yellow single crystals of $\mathbf{1b^{2+}}$•$2ReO_4^-$ suitable for X-ray diffraction were grown by diffusing DCM into a DMF/MeOH solution of receptor **1b** and tetra-*n*-butylammonium perrhenate ($TBA^+ReO_4^-$).[23] $\mathbf{1b^{2+}}$•$2ReO_4^-$ crystallized in space group $P2_1/c$, forming bidentate XB to separate oxygens of a ReO_4^- anion (Figure 1, top). The C–I···O^- distances 2.97 and 3.06 Å correspond to 84 and 86% of the Σ VdW radii, and corroborate strong XB interactions. To accommodate the size of ReO_4^-, both pyridinium rings rotate 11° from coplanarity. As a result, the observed C–I···O^- bond angles of 175 and 168° also confirm strong XB interactions. Examination of the crystal packing reveals C–H HB and electrostatic contacts between ReO_4^- and five additional molecules of **1b** (see ESI). The second ReO_4^- participates in seven C–H HB interactions, and two weak **σ** contacts with electron-deficient pyridinium rings.[24] A head-to-tail **π**-stacking dimer (3.4 Å) is also observed.[25] This arrangement produces columns of **1b** with each ReO_4^- on alternating sides of the receptor.

In contrast, the crystal structure of $\mathbf{2b^{2+}}$•$2ReO_4^-$ illustrates unique C–H HB to ReO_4^-. Colorless single crystals of $\mathbf{2b^{2+}}$•$2ReO_4^-$ were obtained by diffusing ether into a MeOH solution of receptor **2b** and $TBA^+ReO_4^-$.[26] $\mathbf{2b^{2+}}$•$2ReO_4^-$ crystallized in space group $P2_1/n$. Notably, tridentate C–H HB to ReO_4^- is formed using two Hc hydrogens and Hd (Figure 1, bottom), with C–H···O^- distances of 2.64, 2.71 and 2.31 Å. In addition, four intermolecular C–H[27] and two weak **σ**[28] contacts with ReO_4^- are present. The second ReO_4^- is involved in nine C–H HB and two weak **σ** interactions. To enable tridentate binding to ReO_4^-, both pyridinium rings adjust 9° from coplanarity, and one ethynyl spacer deviates 8° from linearity. An off-centered head-to-tail **π**-stacking dimer (3.3 Å) is also noted (see ESI).[25] Together, the crystal structures of $\mathbf{1b^{2+}}$•$2ReO_4^-$ and $\mathbf{2b^{2+}}$•$2ReO_4^-$ illustrate the importance of bidentate/tridentate XB and HB coordination to ReO_4^- in the solid state.

^1H NMR spectroscopic titrations involving **1a** and **2a** were conducted to probe their corresponding XB and C–H HB capabilities in solution. Both **1a**, **2a** and $TBA^+ReO_4^-$ were independently soluble in $CDCl_3$; however, precipitation of host-guest complexes necessitated a $CDCl_3/(CD_3)_2CO$ (3:2 v/v) mixed solvent. Titrating $TBA^+ReO_4^-$ produced noteworthy shifts for the pyridinium (Ha, Hb, and Hc) and phenyl (Hd) hydrogens for both **1a** and **2a** (Figure 2).[29]

The significant upfield shifting of Ha and Hb ($\Delta\delta = -0.099$ and -0.082 ppm, respectively) on **1a** is indicative of strong XB in solution.[30] The dominant XB conformation as suggested by the crystal structure of $\mathbf{1b^{2+}}$•$2ReO_4^-$ is distinctly bidentate (Figure 1, top). Further evidence of XB in solution can be seen in the downfield ^{13}C NMR shifting of **1a**'s C–X carbons ($\Delta\delta = 0.150$ ppm) upon titrating ReO_4^- (see ESI). Additionally, facile rotation of alkynyl-aromatic C–C bonds enables a second XB mode. Constructive bidentate XB-HB involving a single halogen and Hc/Hd is consistent with the downfield shifting of these hydrogens ($\Delta\delta$ = 0.038 and 0.154 ppm).[31] Taken together, the greater upfield (Ha and Hb) and greater downfield (Hc and Hd) shifting of **1a** is explained by strong bidentate XB in solution as well as XB-HB synergy.

For **2a**, C–H HB and electrostatic contacts are the prevailing interactions in solution. Specifically, a tridentate binding site involving two Hc hydrogens and Hd proves the most active as evidenced by the crystal structure of $\mathbf{2b}^{\mathbf{2+}}$•$2ReO_4^-$ and the downfield progression of these hydrogens ($\Delta\delta$ = 0.019 and 0.139 ppm, respectively). Upfield shifting of **2a**'s Ha/b ($\Delta\delta$ = −0.071 ppm) is indicative of anion-HB augmentation of ring electron density.[32]

HypNMR 2008[33] was used to fit changes in shift to a stepwise association model:

$$\mathbf{H+G \rightleftharpoons HG,\ K_1=\frac{[HG]}{[H][G]}} \quad (1)$$

$$\mathbf{HG+G \rightleftharpoons HG_2,\ K_2=\frac{[HG_2]}{[HG][G]}} \quad (2)$$

Iterative and simultaneous refinement of multiple isotherms provided stability constants (K_a) for both **1a** and **2a** with ReO_4^-.[34] For receptor **1a**, the K_1 of 8990 M^{-1} represents the first quantification of XB to ReO_4^- in solution, highlighting XB's effectiveness at targeting this challenging oxoanion.[35] Alternatively, **2a** exhibits C–H HB and electrostatic interactions with ReO_4^-, which result in a K_1 of 7390 M^{-1}. Both **1a** and **2a** display modest K_2 values of 172 and 145 M^{-1}, respectively, that likely result from a combination of weak mono- and bidentate HB, and weak σ bonding.

The earliest quantification of XB and C–H HB to ReO_4^- in solution, and their corresponding bidentate/tridentate complexation in the solid state have been reported. The enhanced association of **1a** to ReO_4^- when compared directly to a nearly isostructural and potent C–H HB molecule validates XB's place alongside HB in an ongoing effort to design rational and selective receptors for ReO_4^- and TcO_4^-. Future work with **1a** and **2a** will include liquid-liquid extraction of ReO_4^- from aqueous phase, and exploration of XB and C–H HB with other anionic guests.

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Notes and references

1. Katayev EA, Kolesnikov GV, Sessler JL. Chem Soc Rev. 2009; 38:1572. [PubMed: 19587953]
2. Clark JF, Clark DL, Whitener GD, Schroeder NC, Strauss SH. Environ Sci Technol. 1996; 30:3124.
3. Gu B, Brown GM, Bonnesen PV, Liang L, Moyer BA, Ober R, Alexandratos SD. Environ Sci Technol. 2000; 34:1075.
4. (a) Dilworth JR, Parrott SJ. Chem Soc Rev. 1998; 27:43.(b) Zuckier LS, Dohan O, Li Y, Chang CJ, Carrasco N, Dadachova E. J Nucl Med. 2004; 45:500. [PubMed: 15001694] (c) Finlay IG, Mason

MD, Shelley M. Lancet Oncol. 2005; 6:392–400. [PubMed: 15925817] (d) Jaubert F. Appl Radiat Isot. 2008; 66:960. [PubMed: 18378156]

5. ^{99m}TC has an ideal half-life (6 h) and γ-ray emission energy (141 keV).
6. 2.15×10^5 years.
7. (a) Koizumi K, Kobayashi K, Oba H, Umeda Y. Ann Nucl Med. 2001; 15:439. [PubMed: 11758949] (b) Kidokoro-Kunii Y, Emoto N, Cho K, Oikawa S. J Nippon Med Sch. 2006; 73:10. [PubMed: 16538017]
8. (a) Wakoff B, Nagy KL. Environ Sci Technol. 2004; 38:1765. [PubMed: 15074687] (b) Maksin D, Hercigonja R, Lazarević M, Žunić M, Nastasović A. Polym Bull. 2012; 68:507.
9. Large scale production of ^{99}Tc as a by-product of uranium-235 fission poses the biggest environmental concern. See: Schulte EH, Scoppa P. Sci Total Environ. 1987; 64:163. [PubMed: 3589660]
10. Banerjee D, Rao MA, Joseph A, Manjrekar A, Singh I, Wattal PK. Desalin Water Treat. 2012; 38:332.
11. Katayev EA, Boev NV, Khrustalev VN, Ustynyuk YA, Tananaev IG, Sessler JL. J Org Chem. 2007; 72:2886. [PubMed: 17362041]
12. For examples of aza-cryptands, see: Farrell D, Gloe K, Gloe K, Goretzki G, McKee V, Nelson J, Nieuwenhuyzen M, Pal I, Stephan H, Town RM, Wichmann K. Dalton Trans. 2003:1961.McKee V, Nelson J, Town RM. Chem Soc Rev. 2003; 32:309. [PubMed: 14518184] Amendola V, Alberti G, Bergamaschi G, Biesuz R, Boiocchi M, Ferrito S, Schmidtchen FP. Eur J Inorg Chem. 2012; 2012:3410.for pyrrole-based macrocycles, see: Kolesnikov GV, German KE, Kirakosyan G, Tananaev IG, Ustynyuk YA, Khrustalev VN, Katayev EA. Org Biomol Chem. 2011; 9:7358. [PubMed: 21894302] Rambo BM, Sessler JL. Chem Eur J. 2011; 17:4946. [PubMed: 21465591] ; for pH-controllable polycationic dendrimers, see: Stephan H, Spies H, Johannsen B, Kauffmann C, Vögtle F. Org Lett. 2000; 2:2343. [PubMed: 10930279] ; for noteworthy non-HB hydrophobic π-metalated cyclotriveratrylenes, see: Steed JW, Junk PC, Atwood JL, Barnes MJ, Raston CL, Burkhalter RS. J Am Chem Soc. 1994; 116:10346.
13. **2a** solely employs C–H HB. Many receptors that utilize concerted N–H and C–H HB have been reported (see footnotes 1 and 11). For literature on unconventional C–H HB, see: Vargas R, Garza J, Dixon DA, Hay BP. J Am Chem Soc. 2000; 122:4750.Juwarker H, Lenhardt JM, Pham DM, Craig SL. Angew Chem Int Ed. 2008; 47:3740.Hua Y, Flood AH. Chem Soc Rev. 2010; 39:1262. [PubMed: 20349532]
14. (a) De Santis A, Forni A, Liantonio R, Metrangolo P, Pilati T, Resnati G. Chem Eur J. 2003; 9:3974. [PubMed: 12916124] (b) Auffinger P, Hays FA, Westhof E, Ho PS. Proc of the Natl Acad of Sci, U S A. 2004; 101:16789.(c) Glaser R, Chen N, Wu H, Knotts N, Kaupp M. J Am Chem Soc. 2004; 126:4412. [PubMed: 15053631] (d) Rosokha SV, Neretin IS, Rosokha TY, Hecht J, Kochi JK. Heteroat Chem. 2006; 17:449.(e) Metrangolo P, Meyer F, Pilati T, Resnati G, Terraneo G. Chem Commun. 2008:1635.(f) Cabot R, Hunter CA. Chem Commun. 2009; 2005Kilah NL, Wise MD, Serpell CJ, Thompson AL, White NG, Christensen KE, Beer PD. J Am Chem Soc. 2010; 132:11893. [PubMed: 20687599] (g) Legon AC. Phys Chem Chem Phys. 2010; 12:7736. [PubMed: 20495729] Sarwar MG, Dragisic B, Sagoo S, Taylor MS. Angew Chem Int Ed. 2010; 49:1674.(h) Erdelyi M. Chem Soc Rev. 2012; 41:3547. [PubMed: 22334193] (i) Zapata F, Caballero A, White NG, Claridge TDW, Costa PJ, Félix Vt, Beer PD. J Am Chem Soc. 2012; 134:11533. [PubMed: 22703526] (j) Beale TM, Chudzinski MG, Sarwar MG, Taylor MS. Chem Soc Rev. 2013; 42:1667. [PubMed: 22858664] (k) Desiraju Gautam R, Ho PS, Kloo L, Legon Anthony C, Marquardt R, Metrangolo P, Politzer P, Resnati G, Rissanen K. Pure Appl Chem. 2013; 85:1711.(l) Kniep F, Jungbauer SH, Zhang Q, Walter SM, Schindler S, Schnapperelle I, Herdtweck E, Huber SM. Angew Chem Int Ed. 2013; 52:7028.(m) Priimagi A, Cavallo G, Metrangolo P, Resnati G. Acc Chem Res. 2013; 46:2686. [PubMed: 23805801] (n) Vargas Jentzsch A, Hennig A, Mareda J, Matile S. Acc Chem Res. 2013; 46:2791. [PubMed: 23547885] (o) Mukherjee A, Tothadi S, Desiraju GR. Acc Chem Res. 2014; 47:2514. [PubMed: 25134974]
15. (a) Corradi E, Meille SV, Messina MT, Metrangolo P, Resnati G. Angew Chem Int Ed. 2000; 39:1782.(b) Aakeröy CB, Fasulo M, Schultheiss N, Desper J, Moore C. J Am Chem Soc. 2007; 129:13772. [PubMed: 17956090]

16. (a) Voth AR, Khuu P, Oishi K, Ho PS. Nat Chem. 2009; 1:74. [PubMed: 21378804] (b) Chudzinski MG, McClary CA, Taylor MS. J Am Chem Soc. 2011; 133:10559. [PubMed: 21667941]
17. (a) Pinter B, Nagels N, Herrebout WA, De Proft F. Chem Eur J. 2013; 19:519. [PubMed: 23169478] b) Nagels N, Geboes Y, Pinter B, De Proft F, Herrebout WA. Chem Eur J. 2014; 20:8433. [PubMed: 24898290]
18. Kaae BH, Harpsøe K, Kvist T, Mathiesen JM, Mølck C, Gloriam D, Jimenez HN, Uberti MA, Nielsen SM, Nielsen B, Bräuner-Osborne H, Sauerberg P, Clausen RP, Madsen U. ChemMedChem. 2012; 7:440. [PubMed: 22267204]
19. Facile rotation of alkynyl-aromatic C–C bonds provides interconversion between mono- and bidentate receptor conformations.
20. Sonogashira K, Tohda Y, Hagihara N. Tetrahedron Lett. 1975; 16:4467.
21. Reger DL, Wright TD, Little CA, Lamba JJS, Smith MD. Inorg Chem. 2001; 40:3810. [PubMed: 11442381]
22. There are two known examples of solid-state XB to ReO_4^-. One is a serendipitous monodentate XB between $CHCl_3$ and ReO_4^-, see: Cowley AR, Dilworth JR, Salichou M. Dalton Trans. 2007:1621. [PubMed: 17426864] The other is a trifurcated monodentate XB to three 1,4-diiodotetrafluorobenzene molecules, see: Abate A, Martí-Rujas J, Metrangolo P, Pilati T, Resnati G, Terraneo G. Cryst Growth Des. 2011; 11:4220.
23. Crystal data for **1b** $C_{22}H_{16}I_2N_2O_8Re_2$, M = 1062.57, monoclinic, $P2_1/c$, a = 6.9841(5), b = 34.338(3), c = 11.4497(9), β = 99.704(2), V = 2706.6(4), Z = 4, T = 150 K, $\mu(\text{MoK}\alpha)$ = 11.265 mm^{-1}, ρ_{calcd} = 2.608 ml^{-1}, $2\theta_{max}$ = 52.74°, 65752 reflections collected, 5485 unique (R_{int} = 0.0505, R_{sigma} = 0.0250) R1 = 0.0477 (I > 2σ(I)) and wR2 = 0.1108 (all data). CCDC 1028026 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
24. There is one weak σ and one anion-π interaction. Interestingly, the anion-π oxygen-centroid distance is 3.22 Å with an oxygen-centroid-nitrogen angle of 89°. For literature on weak σ and anion-π interactions, see: Berryman OB, Bryantsev VS, Stay DP, Johnson DW, Hay BP. J Am Chem Soc. 2006; 129:48.Berryman OB, Hof F, Hynes MJ, Johnson DW. Chem Commun. 2006:506.Berryman OB, Sather AC, Hay BP, Meisner JS, Johnson DW. J Am Chem Soc. 2008; 130:10895. [PubMed: 18661980] ; for additional reviews on this growing subject, see: Gamez P, Mooibroek TJ, Teat SJ, Reedijk J. Acc Chem Res. 2007; 40:435. [PubMed: 17439191] Hay BP, Bryantsev VS. Chem Commun. 2008:2417.Schottel BL, Chifotides HT, Dunbar KR. Chem Soc Rev. 2008; 37:68. [PubMed: 18197334]
25. No solution dimer is observed in the current solvent system. See ESI for crystal packing.
26. Crystal Data for **2b** $C_{22}H_{18}N_2O_8Re_2$, M = 810.78, monoclinic, $P2_1/n$, a = 15.5756(10), b = 7.6106(5) c = 19.6042(13), β = 100.084(2), V = 2288.0(3), Z = 4, T = 100.0 K, $\mu(\text{MoK}\alpha)$ = 10.623 mm^{-1}, ρ_{calcd} = 2.354 g ml^{-1}, $2\theta_{max}$ = 56.56°, 40497 reflections collected, 5583 unique (R_{int} = 0.0706, R_{sigma} = 0.0467), R1 = 0.0286 (I > 2σ(I)), wR2 = 0.0604 (all data). CCDC 1028025 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
27. One interaction is bidentate (Hc and He). The $C–H\cdots O^-$ distances of 2.53 and 2.55 Å correspond to weak HB interactions.
28. Both weak σ interactions occur over the same electron-deficient pyridinium ring (*ortho* and *meta* carbons; oxygen-carbon distances 3.18 and 2.92 Å, respectively), and involve separate oxygens of a ReO_4^- anion. For literature on weak σ and anion-π interactions, see footnote 24.
29. Hydrogens He and the sole phenyl core triplet were not followed due to limited shifting and/or residual solvent peak ($CHCl_3$) obstruction.
30. Cametti M, Raatikainen K, Metrangolo P, Pilati T, Terraneo G, Resnati G. Org Biomol Chem. 2012; 10:1329. [PubMed: 22218406]
31. An ancillary Hc and Hd binding mode may also contribute to solution stability. See the crystal structure of $\mathbf{2b}^{2+}\bullet 2ReO_4^-$.

32. For examples in the literature of this spectroscopic phenomenon, see: Lee CH, Na HK, Yoon DW, Won DH, Cho WS, Lynch VM, Shevchuk SV, Sessler JL. J Am Chem Soc. 2003; 125:7301. [PubMed: 12797804] Amendola V, Boiocchi M, Fabbrizzi L, Palchetti A. Chem Eur J. 2005; 11:5648. [PubMed: 16021647] Gomez DE, Fabbrizzi L, Licchelli M, Monzani E. Org Biomol Chem. 2005; 3:1495. [PubMed: 15827647] Shao J, Lin H, Yu M, Cai Z, Lin H. Talanta. 2008; 75:551. [PubMed: 18371920] Wang Y, Lin H, Shao J, Cai ZS, Lin HK. Talanta. 2008; 74:1122. [PubMed: 18371759] . Upfield shifting could also arise in part from weak σ interactions, see: Gil-Ramírez G, Escudero-Adán EC, Benet-Buchholz J, Ballester P. Angew Chem Int Ed. 2008; 47:4114.Caballero A, Zapata F, Gonzalez L, Molina P, Alkorta I, Elguero J. Chem Commun. 2014; 50:4680.Giese M, Albrecht M, Repenko T, Sackmann J, Valkonen A, Rissanen K. Eur J Org Chem. 2014; 2014:2435.

33. Frassineti C, Ghelli S, Gans P, Sabatini A, Moruzzi MS, Vacca A. Anal Biochem. 1995; 231:374. [PubMed: 8594988]

34. Reported K_as are the average of triplicate data sets. Errors are estimated at 10%. Full details of the titration experiments including σs, SDs, and model determination are contained in the ESI. Titrations were conducted at 290 K.

35. **2a**'s tridentate C–H HB site is active regardless of conformational changes. By comparison, **1a** can oscillate between bidentate, monodentate, and inactive XB modes. Given these differences, **1a**'s superior association to ReO_4^- establishes XB's effectiveness at targeting charge diffuse anions.

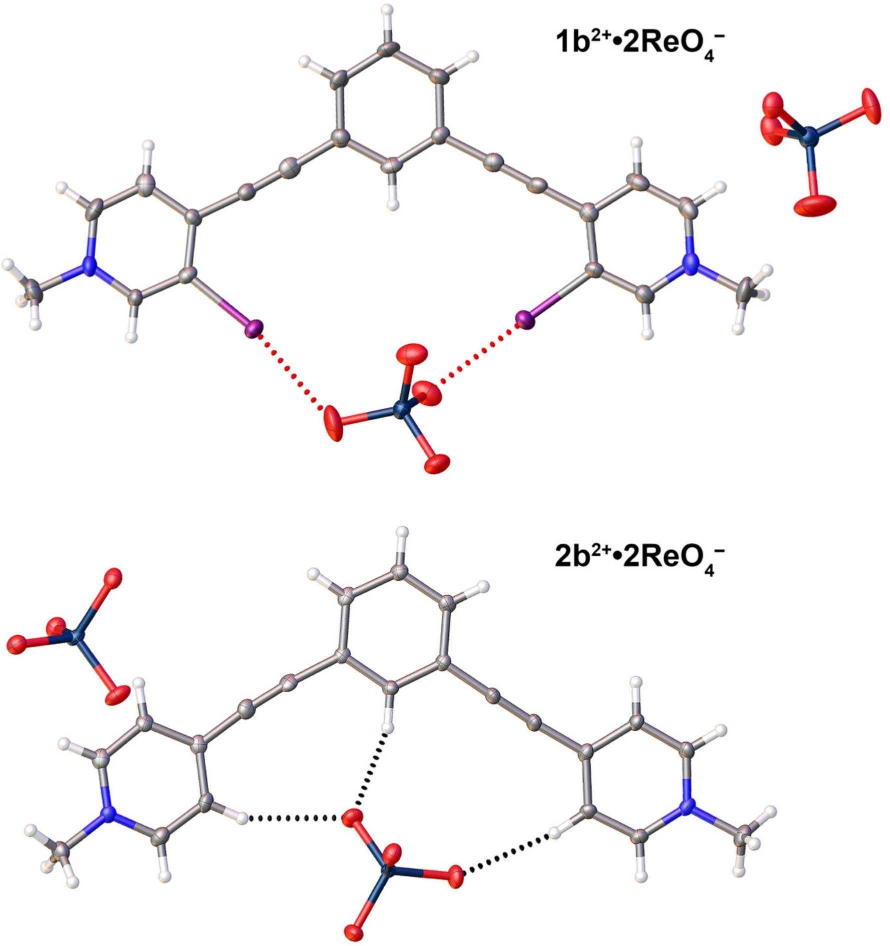


Figure 1.

X-ray crystal structures of **1b**$^{2+}$•2ReO$_4^-$ (top) highlighting bidentate XB to ReO$_4^-$ in the solid state (red). Crystal structure of **2b**$^{2+}$•2ReO$_4^-$ (bottom) illustrating tridentate C–H HB to ReO$_4^-$ (black).

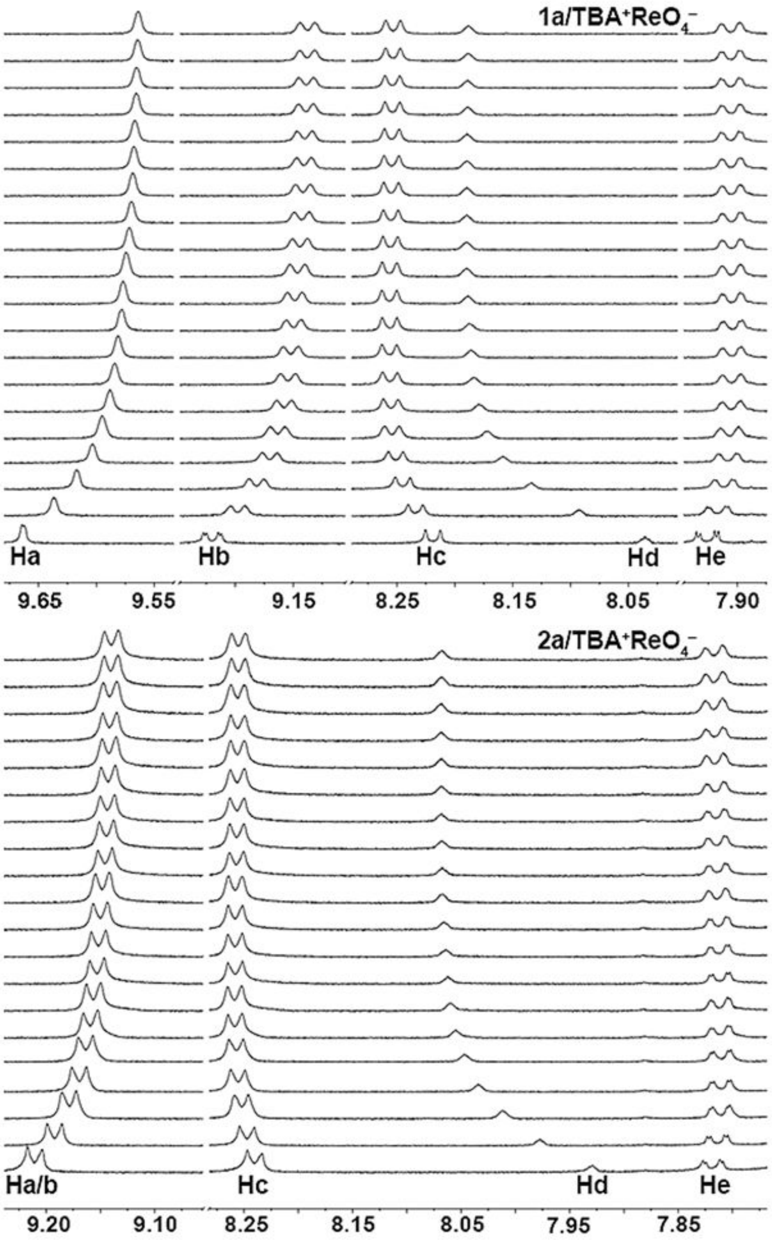
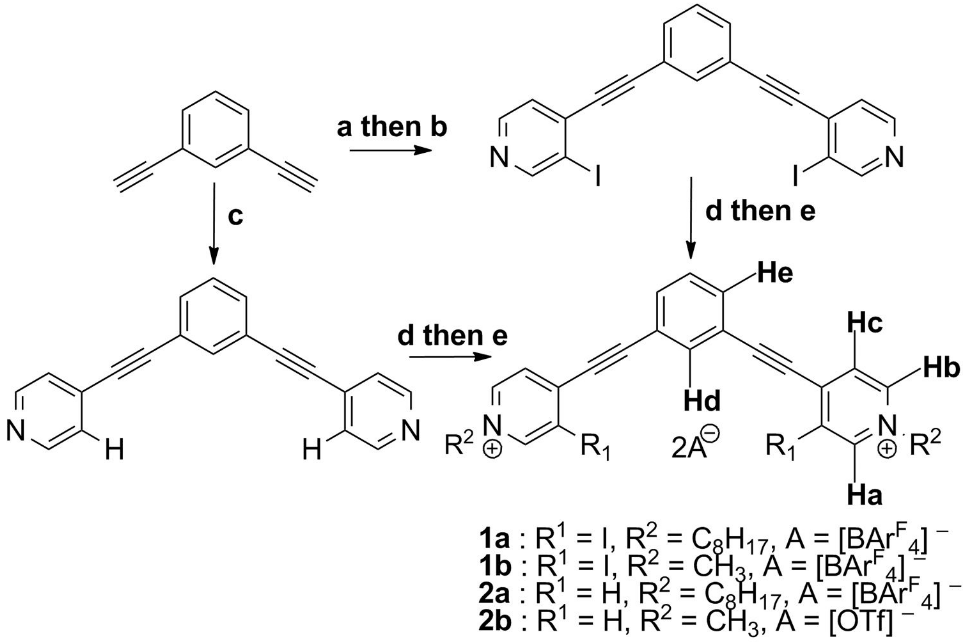


Figure 2.

Partial ^{1}H NMR spectra of **1a** (top, 0–4.78 equiv) and **2a** (bottom, 0–4.62 equiv) upon titrating $TBA^+ReO_4^-$ (equivalents from bottom to top).



Scheme 1.

a) 3-Bromo-4-iodopyridine, CuI, $Pd(PPh_3)_2Cl_2$, DMF, DIPEA, rt, 24 h, 88%; b) *n*-BuLi, THF, −78°C, I_2, 24 h, 41%; c) prepared according to literature procedure,[18] 22% d) octyl triflate or methyl triflate, DCM, rt, 24 h, 98%; e) vapor diffusion of ether into DCM solution of TBA^+Cl^-, 55–75%; $Na^+[BAr^F{}_4]^-$, DCM, rt, 30 min, 59–75%.