Polyhedron 116 (2016) 20–25

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Acyclic halogen and hydrogen bonding diquat-containing receptors for the electrochemical sensing of anions

Benjamin R. Mullaney [a], Matthew J. Cunningham [b], Jason J. Davis [b], Paul D. Beer [a,*]

[a] Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Rd, Oxford OX1 3TA, UK
[b] Physical & Theoretical Chemistry Laboratory, South Parks Rd, Oxford OX1 3QZ, UK

ARTICLE INFO

Article history:
Received 20 January 2016
Accepted 4 March 2016
Available online 10 March 2016

Keywords:
Diquat
Anion recognition
Sensing
Electrochemistry
Host–guest

ABSTRACT

The first examples of halogen and hydrogen bonding anion receptors containing the redox-active dicationic diquat motif and their anion recognition and electrochemical sensing properties are described. The acyclic receptors demonstrated strong binding affinities for halide anions in competitive solvents, with the most potent anion binding behaviour observed for the halogen bonding analogue. The redox-active diquat group is shown to be an effective electrochemical sensing probe, undergoing significant cathodic perturbations of the diquat^{2+}/diquat$^{+\cdot}$ redox couple upon the addition of halides.

1. Introduction

The critical importance of anions in Nature, the environment and medicine has stimulated considerable research towards exploring and developing synthetic anion receptors [1–6]. A range of complementary supramolecular interactions have been employed in the design of anion host systems, including electrostatics, hydrogen bonding (HB) [7], Lewis acid–base [8], and anion–π [9,10] interactions. A recent addition to the anion binding toolbox is halogen bonding (XB), the attractive interaction between an electrophilic halogen atom and a Lewis basic species [11–18]. Importantly, of the relatively few XB anion receptors reported to date [18–21], all exhibit contrasting, and in many cases significantly superior, anion recognition behaviour compared to HB analogues.

The integration of reporter/signalling groups into anion receptor host structural frameworks has been used to generate a multitude of colorimetric, luminescent [22–24], and electrochemical [25–28] sensors. The redox properties of ferrocene in particular have been exploited in order to electrochemically sense anions in HB acyclic [29–32], macrocyclic [33–35] and interlocked [36–38] structures. We recently reported the first redox-active ferrocene XB host systems which were demonstrated to exhibit enhanced recognition and sensitivity of halide electrochemical sensing in comparison to analogous ferrocene HB receptors [39].

Taking into account the positive charge and redox activity of the diquat motif, it is surprising that to the best of our knowledge, this motif has not been exploited in anion recognition and sensing applications. Herein, we describe the synthesis of novel acyclic XB and HB diquat-based receptors (Fig. 1), and investigate their halide binding and electrochemical sensing capabilities.

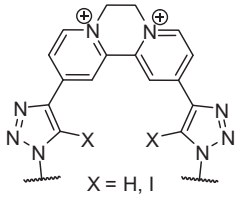

Fig. 1. Acyclic XB and HB diquat receptor design.

2. Experimental

2.1. Materials

Dry solvents were obtained by purging with nitrogen and then passing through an MBraun MPSP-800 column. H_2O was deionised and microfiltered using a Milli-Q® Millipore machine. $Cu(ClO_4)_2{\cdot}6H_2O$ was carefully dried *in vacuo* before use. Et_3N was distilled from, and stored over, KOH pellets. All other solvents and commercial reagents were used without further purification. Column chromatography was performed on silica gel (particle size: 40–63 μm). TBTA (tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine) [40], 4,4′–diethynyl-2,2′-dipyridine [41], 1-azido-4-(*tert*-butyl)

* Corresponding author.

http://dx.doi.org/10.1016/j.poly.2016.03.006
0277-5387/

benzene [42] and 1,2-bis(triflyl)ethane [43] were prepared according to literature procedures.

2.2. Characterisation

Routine NMR spectra were recorded on a Varian Mercury 300 spectrometer with ^{1}H operating at 300 MHz and ^{13}C at 75.5 MHz. Where the compound was insufficiently soluble to characterise properly on this instrument, ^{1}H data were recorded on a Bruker AVIII 500 MHz spectrometer, and ^{13}C data were recorded on a Bruker AVII 500 spectrometer with a 5 mm ^{13}C(^{1}H) dual cryoprobe operating at 126 MHz. Mass spectra were recorded on a Bruker microTOF spectrometer.

2.3. Electrochemistry

Cyclic voltammetry (CV) experiments were performed on an Autolab PGSTAT-12 system, and all data was analysed using General Purpose Electrochemical Software (GPES) v 4.9. All experiments were undertaken in anhydrous acetonitrile, with a supporting electrolyte of 0.1 M $TBAPF_6$. The electrodes used were: a 3 mm diameter glassy carbon working electrode (BASi), a platinum counter electrode, and a Ag/AgCl reference electrode. The surfaces of the carbon and platinum electrodes were cleaned thoroughly before each measurement. All solutions were degassed with dry nitrogen prior to the recording of each CV.

2.4. Synthesis

2.4.1. 4,4′-Bis(1-(4-tert-butyl)phenyl)-5-iodo-1H-1,2,3-triazol-4-yl)-2,2′-bipyridine, **1**

1-Azido-4-(*tert*-butyl)benzene (160 mg, 0.913 mmol) was dissolved in THF (2 mL). Sodium iodide (0.480 g, 3.20 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.600 g, 1.62 mmol) were added to the reaction, which was covered in aluminium foil and stirred at RT for 3–5 min. TBTA (42 mg, 0.079 mmol) was added, then DBU (122 mg, 0.801 mmol) dissolved in THF (1 mL) was also added. 4,4′-diethynyl-2,2′-dipyridine (82 mg, 0.40 mmol) was added to the reaction last, then the mixture was stirred in the dark at RT overnight. The reaction was then diluted with CH_2Cl_2 (200 mL), then washed with $NH_4OH_{(aq.)}$ (25%, 2 × 25 mL), then brine (50 mL). The organic layer was separated, dried ($MgSO_4$) and the solvent removed *in vacuo*. The residue was then suspended in CH_3CN (25 mL) and heated at reflux for 1 h. The mixture was cooled to RT, the solid filtered off and washed with CH_3CN (20 mL) then Et_2O (20 mL), and air-dried to give the product **1** as a white powder (0.247 g, 77%); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 9.23 (s, 2H, py*H*), 8.86 (d, ^3J = 4.69 Hz, 2H, py*H*), 8.07 (dd, ^3J = 4.98, ^4J = 1.47 Hz, 2H, py*H*), 7.63 (d, ^3J = 8.80 Hz, 4H, Ar*H*), 7.51 (d, ^3J = 8.21 Hz, 4H, Ar*H*), 1.41 (s, 18H, CCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm: 153.90, 149.73, 147.52, 134.11, 126.41, 126.03, 121.77, 119.01, 35.04, 31.27; HRMS (ESI+) *m/z*: 807.0911 ([M+H]$^+$, Calc. for $[C_{34}H_{33}I_2N_8]^+$ = 807.0912).

2.4.2. 4,4′-Bis(1-(4-tert-butyl)phenyl)-1H-1,2,3-triazol-4-yl)-2,2′-bipyridine, **2**

4,4′-Diethynyl-2,2′-dipyridine (41 mg, 0.20 mmol) and 1-azido-4-(*tert*-butyl)benzene (79 mg, 0.45 mmol) were dissolved in dry CH_2Cl_2 (20 mL). TBTA (0.116 g, 0.22 mmol), $[Cu(CH_3CN)_4](PF_6)$ (82 mg, 0.22 mmol) and DIPEA (64 mg, 0.5 mmol) were added and the solution stirred at RT under N_2 for 3 days. The reaction was then washed with $NH_4OH_{(aq.)}$ (25% w/w, 15 mL), brine (2 × 15 mL) and dried ($MgSO_4$), then the solvent removed *in vacuo*. The residue was then suspended in CH_3CN (25 mL) and heated at reflux for 1 h, then cooled to RT and the solid filtered off, washed with CH_3CN (10 mL), and diethyl ether (10 mL), then dried under vacuum to give the product **2** as a white solid (91.4 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.94 (br. s, 2H, py*H*), 8.84 (d, ^3J = 4.58 Hz, 2H, py*H*), 8.65 (br. s, 2H, py*H*), 8.16 (s, 2H, trz*H*), 7.78 (d, ^3J = 8.54 Hz, 4H, Ar*H*), 7.61 (d, ^3J = 8.54 Hz, 4H, Ar*H*), 1.40 (s, 18H, CCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm: 152.62, 145.68, 134.32, 126.82, 120.51, 120.25, 120.02, 117.90, 34.87, 31.26; HRMS (ESI+) *m/z*: 555.2982 ([M+H]$^+$, Calc. for $[C_{34}H_{36}N_8]^+$ = 555.2979.

2.4.3. 2,11-Bis(1-(4-tert-butyl)phenyl)-5-iodo-1H-1,2,3-triazol-4-yl)-6,7-dihydrodipyrido[1,2-a:2′,1′-c]pyrazinediium Hexafluorophosphate, **3**·2PF_6

Bis-iodotriazole bipyridyl precursor **1** (30 mg, 0.037 mmol) was dissolved in $CHCl_3$ (10 mL). 1,2-Bis(triflyl)ethane (33 mg, 0.10 mmol) was added, and the solution stirred under N_2 in the dark at 40 °C for 3 days. The solvent was then removed, and the residue suspended in MeOH (20 mL) and stirred vigorously for 5 min. The solid was filtered off and the filtrate collected and reduced to ~5 mL. $NH_4PF_{6(sat.\ aq.)}$ (0.5 mL), then H_2O (10 mL) were slowly added, forming a precipitate which was filtered and washed with H_2O (3 × 10 mL), before being extracted with acetone (3 × 10 mL). The solvent was then removed *in vacuo*, giving the product **3**·2PF_6 as a brown solid (27 mg, 65%); ^{1}H NMR (300 MHz, d_6-acetone) δ ppm: 9.85 (s, 2H, py$^+$*H*), 9.57 (d, ^3J = 6.45 Hz, 2H, py$^+$*H*), 9.23 (d, ^3J = 6.45 Hz, 2H, py$^+$*H*), 7.77 (d, ^3J = 8.40 Hz, 4H, Ar*H*), 7.65 (d, ^3J = 8.21 Hz, 4H, Ar*H*), 5.72 (s, 4H, –CH_2–), 1.42 (s, 18H, CCH_3); ^{13}C NMR (126 MHz, d_6-acetone) δ ppm: 155.42, 149.82, 149.07, 144.45, 141.75, 135.04, 127.67, 127.28, 126.16, 125.49, 88.96, 53.78, 35.76, 31.53; HRMS (ESI+) *m/z*: 833.1078 ([M−2(PF_6)−H]$^+$, Calc. for $[C_{36}H_{35}I_2N_8]^+$ = 833.1069).

2.4.4. 2,11-Bis(1-(4-tert-butyl)phenyl)-1H-1,2,3-triazol-4-yl)-6,7-dihydrodipyrido[1,2-a:2′,1′-c]pyrazinediium Hexafluorophosphate, **4**·2PF_6

Bis-triazole bipyridyl precursor **2** (40 mg, 0.072 mmol) was dissolved in $CHCl_3$ (20 mL). 1,2-Bis(triflyl)ethane (64 mg, 0.20 mmol) was added, and the solution stirred under N_2 in the dark at 40 °C for 5 days. The solvent was then removed, and the residue suspended in MeOH (20 mL) and stirred vigorously for 5 min. The solid was filtered off and the filtrate collected and reduced to ~5 mL. $NH_4PF_{6(sat.\ aq.)}$ (0.5 mL), then H_2O (10 mL) were slowly added, forming a precipitate which was filtered and washed with H_2O (3 × 10 mL), before being extracted with acetone (3 × 10 mL). The solvent was then removed *in vacuo*, giving the product **4**·2PF_6 as a brown solid (25 mg, 40%); ^{1}H NMR (300 MHz, d_6-acetone) δ ppm: 9.68–9.73 (m, 4H, py$^+$*H*, trz*H*), 9.51 (d, ^3J = 6.45 Hz, 2H, py$^+$*H*), 9.01 (d, ^3J = 5.87 Hz, 2H, py$^+$*H*), 7.94 (d, ^3J = 8.80 Hz, 4H, Ar*H*), 7.75 (d, ^3J = 8.80 Hz, 4H, Ar*H*), 5.69 (s, 4H, –CH_2–), 1.40 (s, 18H, CCH_3); ^{13}C NMR (76 MHz, d_6-acetone) δ ppm: 154.10, 149.65, 148.92, 142.98, 141.93, 135.05, 127.97, 126.60, 125.49, 124.47, 121.32, 53.61, 35.58; MS (MALDI+) *m/z*: 582.51 ([M]$^+$, Calc. for $[C_{36}H_{38}N_8]^+$ = 582.32).

2.5. Supporting information

NMR and UV/vis titration protocols, electrochemical anion binding experimental methods and NMR spectra for new compounds are included in the Supporting information.

3. Results and discussion

3.1. Synthesis

The synthetic procedure for the target XB bis-iodotriazole **3** and HB proto-triazole **4** diquat receptors is shown in Scheme 1. Reaction of 4,4′-diethynyl-2,2′-dipyridine with two equivalents of