Azide ion recognition in water/$CHCl_3$ using a chelating phosphonium borane as a receptor.

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Supplementary Information

General Considerations. [**1**]I was synthesized as described in *J. Am. Chem. Soc.*, 2008, **130**, 10890. Sodium fluoride was purchased from MCB manufacturing chemists Inc., sodium azide and sodium hydroxide from Fisher scientific company. Solvents were dried by passing through an alumina column (Hexanes, dichloromethane), refluxing under N_2 over Na/K (diethyl ether). Methanol and chloroform (ACS reagent grade) were used as provided. UV-vis and emission spectra were recorded on an Ocean Optics USB4000 spectrometer with a Ocean Optics ISS light source. pH Measurements were carried out with a Radiometer PHM290 pH meter equipped with a VWR SympHony electrode. IR spectra were obtained using a ATI Mattson Genesis Series FT infrared spectrophotometer. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). NMR spectra were recorded on Varian Unity Inova 400 FT NMR (399.59 MHz for ^{1}H, 128.19 MHz for ^{11}B, 100.45 MHz for ^{13}C, 161.75 MHz for ^{31}P) and Varian Inova 500 FT NMR (499.88 MHz for ^{1}H) spectrometers at ambient temperature. Chemical shifts are given in ppm, and are referenced against external $BF_3{\cdot}Et_2O$ (^{11}B) and H_3PO_4 (^{31}P).

Crystallography. The crystallographic measurements were performed using a Bruker APEX-II CCD area detector diffractometer (Mo-K_α radiation, λ= 0.71073 Å). A specimen of suitable size and quality was selected and mounted onto a nylon loop. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

Formation of 1-OH under biphasic conditions

This experiment was carried out by sonicating a biphasic mixture consisting of [**1**]I in $CDCl_3$ (0.0087 M, 0.6 mL) and NaOH in water (0.1 mL, 0.063 M). Conversion into **1**-OH was complete after 1h 30 min as shown by the detection of a single ^{31}P-NMR resonance at δ 20.8 ppm.

Reversibility of the reaction of [1]I with NaOH

In order to test the stability of [**1**]I and the reversibility of its reaction with hydroxide ions, a solution into [**1**]I in H_2O:MeOH 9/1 vol. (3 mL, 6.7×10^{-5} M; 9 mM phosphoric acid buffer, pH 2.29) was placed in a UV cell and analyzed by UV-vis spectroscopy (Figure S1). This pH of the solution was adjusted to 4.86 (with NaOH) which resulted in quenching of the broad band centered at 330 nm (due to hydroxide binding to the boron center) as well as a shift of the baseline caused by precipitation of **1**-OH (Figure S2). The pH of the solution was then adjusted to 2.39 (with HCl) which resulted in revival of the band at 330 nm (Figure S3) indicating conversation of **1**-OH back into [**1**]$^{+}$.

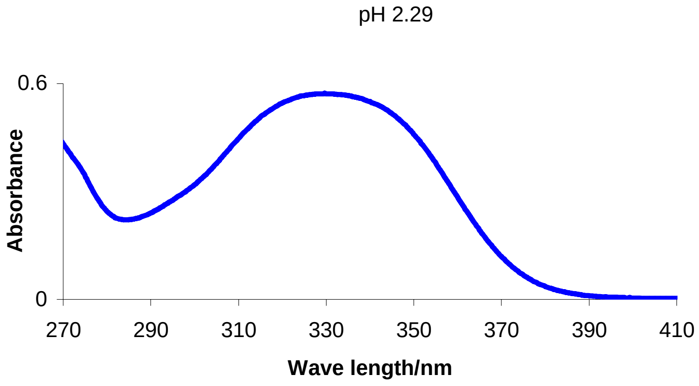


Figure S1. UV-Vis spectrum of a solution of [**1**]I in H_2O/MeOH 9/1 vol. (3 mL, 6.7 × 10^{-5} M; 9 mM phosphate buffer) at pH 2.29.

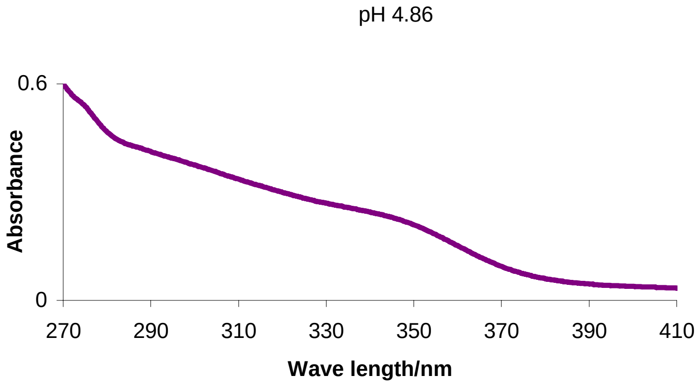


Figure S2. UV-Vis spectrum of a solution of [**1**]I in H_2O/MeOH 9/1 vol. (3 mL, 6.7 × 10^{-5} M; 9 mM phosphate buffer) at pH 4.86.

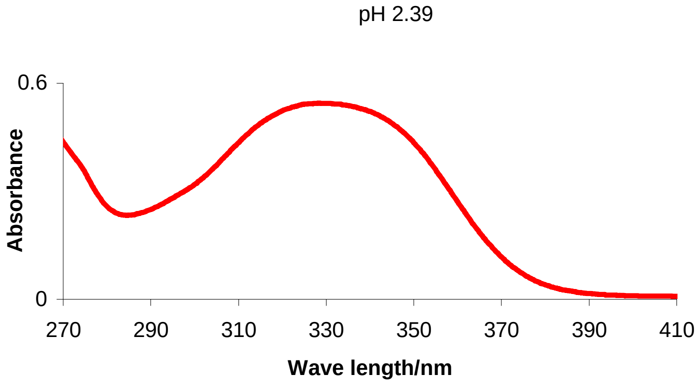
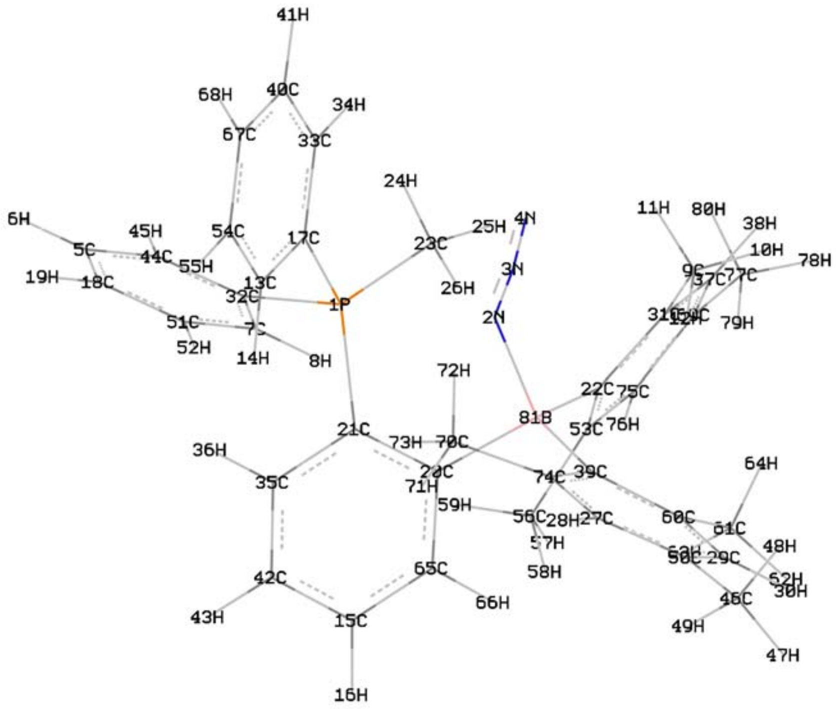


Figure S3. UV-Vis spectrum of a solution of [**1**]I in H_2O/MeOH 9/1 vol. (3 mL, 6.7 × 10^{-5} M; 9 mM phosphate buffer) at pH 2.39.

Computational details:

DFT calculations (full geometry optimization) were carried out with the Gaussian 03 program using the gradient-corrected Becke exchange functional (B3LYP) and the Lee-Yang-Parr correlation functional. Geometry optimization of **1**-N_3 was carried out with the following mixed basis set: 6-31+g(d’) for the boron, nitrogen, 6-31+g(d) for the phosphorus atom, 6-31g basis set was used for all carbon and hydrogen atoms. Frequency calculations, which were carried out on the optimized structures of the compounds, confirmed the absence of any imaginary frequencies. The Natural Bond Orbital (NBO) analysis was carried out using the stand along PC version of GENNBO 5.0 program.

Computed structure of 1-N_3



Cartesian coordinate

P1	2.087396	-0.09284	-0.13657	H10	-3.11489	1.642483	-3.23522
N2	-0.51783	-0.59198	-1.02889	H11	-1.67773	0.629553	-3.26434
N3	-0.87403	-1.32506	-1.91827	H12	-2.93651	0.334375	-2.06275
N4	-1.1146	-2.03057	-2.79724	C13	2.048502	-2.87538	-0.42972
C5	6.145506	-0.22296	0.726817	H14	1.711607	-2.90046	0.600752
H6	6.964828	-0.92451	0.608859	C15	-0.18696	-0.6976	3.843193
C7	4.024884	1.577374	1.027721	H16	-0.69428	-0.86194	4.789391
H8	3.210023	2.281549	1.163157	C17	2.264843	-1.6412	-1.06994
C9	-2.39562	1.118725	-2.59471	C18	6.37134	1.030965	1.302062

H19	7.36732	1.307155	1.632433
C20	-0.34327	-0.15248	1.434172
C21	1.078807	-0.27522	1.37728
C22	-1.32641	1.772949	-0.31931
C23	1.763805	1.307915	-1.26273
H24	2.662468	1.477446	-1.86358
H25	0.899182	1.106002	-1.88974
H26	1.54857	2.206408	-0.67907
C27	-4.18784	-2.61021	0.592134
H28	-4.22115	-3.69736	0.633901
C29	-5.27971	-0.49847	0.696283
H30	-6.18434	0.092815	0.822266
C31	-1.73006	2.10942	-1.65203
C32	3.7874	0.314906	0.443814
C33	2.664157	-1.62131	-2.41963
H34	2.8211	-0.68122	-2.93722
C35	1.831003	-0.60383	2.535822
H36	2.909311	-0.69461	2.484885
C37	-1.57247	3.409187	-2.15993
H38	-1.90072	3.61363	-3.17769
C39	-2.82762	-0.55206	0.392012
C40	2.850573	-2.8215	-3.11337
H41	3.146824	-2.79665	-4.15654
C42	1.204399	-0.81734	3.761332
H43	1.795228	-1.07379	4.634599
C44	4.860995	-0.58152	0.298452
H45	4.699341	-1.55626	-0.1469
C46	-6.72005	-2.58813	0.772745
H47	-7.44614	-1.99066	1.33583
H48	-7.14746	-2.76275	-0.22467
H49	-6.63214	-3.56492	1.262163
C50	-5.38053	-1.89141	0.682748
C51	5.307832	1.930671	1.452379
H52	5.476465	2.904279	1.900557
C53	-0.86322	2.865417	0.480185
C54	2.238678	-4.07079	-1.12959
H55	2.058553	-5.01737	-0.63146
C56	-0.56582	2.77267	1.971328
H57	-0.48939	3.780019	2.395294
H58	-1.35611	2.248186	2.515127
H59	0.368922	2.249238	2.199241
C60	-4.051	0.174071	0.56785
C61	-4.13988	1.689819	0.669347
H62	-5.13028	1.976153	1.040593
H63	-3.39728	2.107157	1.353718
H64	-3.99219	2.187585	-0.29367
C65	-0.92495	-0.37561	2.705209
H66	-2.00457	-0.30828	2.78061
C67	2.642401	-4.04635	-2.46975
H68	2.780157	-4.97525	-3.01283
C69	-1.03199	4.44884	-1.39708
C70	-1.75069	-2.93666	0.436483
H71	-1.97483	-3.81463	1.054033
H72	-1.54316	-3.3052	-0.57513
H73	-0.83726	-2.48618	0.821766
C74	-2.93791	-1.98068	0.461573
C75	-0.71172	4.154302	-0.06982
H76	-0.35527	4.956234	0.574114
C77	-0.83519	5.833683	-1.97384
H78	-1.69889	6.144995	-2.57361
H79	-0.68958	6.577913	-1.18333
H80	0.04393	5.877151	-2.63203
N81	-1.34777	0.167291	0.155773