Supplementary Material (ESI) for Chemical Communications

Supporting Information

Evaluation of Planarity and Aromaticity in Sapphyrin and Inverted Sapphyrin Using a Bidirectional NICS (Nucleus-Independent Chemical Shift) Scan Method

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Experimental Section

Steady-state absorption and emission. Steady-state absorption spectra were acquired using an UV-VIS-NIR spectrometer (Varian, Cary5000). Steady-state fluorescence spectra were recorded on a fluorescence spectrometer (Hitachi, FL2500). For the observation of near-infrared (NIR) emission spectra, a photomultiplier (Hamamatsu, R5108), a lock-in amplifier (EG&G, 5210), combined with a chopper after laser excitation at 442 nm from a CW He-Cd laser (Melles Griot, Omnichrome 74) were used.

Time-correlated Single Photon Counting. Time-resolved fluorescence was detected using a time-correlated single-photon-counting (TCSPC) technique. A home-made cavity dumped Ti:Sapphire oscillator pumped by a CW Nd-YVO_4 laser (Coherent, Verdi) was used as the excitation light source; this provided ultrashort pulses (100 fs at full width half maximum) and allowed for a high repetition rate (200 ~ 400 kHz). The output pulse of the oscillator was frequency-doubled with a second harmonic crystal. The TCSPC detection system consisted of a multichannel plate photomultiplier (Hamamatsu, R3809U-51) with a cooler (Hamamatsu, C4878), a TAC (time-to-amplitude converter) (EG&G Ortec, 457), two discriminators (EG&G Ortec, 584 (signal) and Canberra, 2126 (trigger)), and two wideband amplifiers (Philip Scientific (signal) and a Mini Circuit (trigger)). A personal computer with a multichannel analyzer (Canberra, PCA3) was used for data storage and processing. The overall instrumental response function was about 60 ps (fwhm). A sheet polarizer, set at an angle complementary to the magic angle (54.7°), was placed in the fluorescence collection system. The decay fittings were determined using a least-squares deconvolution process (LIFETIME program with an iterative nonlinear least-squares deconvolution procedure developed at the University of Pennsylvania).

Femtosecond Transient Absorption. Measurements were made using a set-up involving a dual-beam femtosecond time-resolved transient absorption spectrometer consisting of two independently-tunable home-made optical parametric amplifiers (OPA) pumped by a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane X) operating at 5 kHz repetition rate and an optical detection system. The OPA were based on non-collinearly phase-matching geometry and easily color-tuned by controlling the delay between the white light continuum pulses and pump pulses. The generated visible OPA pulses had a pulse width of ~35 fs and an average power of 10 mW at 5 kHz repetition rate in the range 500-700 nm. The probe beam was split into two parts. One part of the probe beam was configured to overlap with the pump beam at the sample to monitor the transient (signal), while the other part of the probe beam was passed through the sample without overlapping the pump beam to compensate the fluctuation in the probe beam (reference). The time delay between the pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). To obtain the time-resolved transient absorption difference signal at specific wavelength, the monitoring wavelength was selected by using an interference filter. By chopping the pump pulses at 47 Hz, the modulated probe pulses as well as the reference pulses could be detected by two separate photodiodes. The modulated signals of the probe pulses were measured by a gated-integrator (SRS, SR250) and a lock-in amplifier (EG&G, DSP7265) and stored in a personal computer for further signal processing. The polarization angle between the pump and probe beams was set to the magic angle (54.7°) in order to obviate polarization-dependent signals.

Two-photon Absorption Cross-Section ($\sigma^{(2)}$). The TPA experiments were performed using the open-aperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a 5 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). The laser beam was divided into two parts. One was monitored by a Ge/PN photodiode (New Focus) as intensity reference, and the other was used for the transmittance studies. After passing through an f = 10 cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction (z-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell was 1 mm. The transmitted laser beam from the sample cell was then probed using the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0, ranged from 40 to 60 GW/cm. Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open aperture traces with the following equation:

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)},$$

where α_0 is the linear absorption coefficient, l the sample length, and z_0 the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient β, the TPA cross-section $\sigma^{(2)}$ (in units of 1 GM = 10^{-50} cm^4·s/photon·molecule) of a single solute molecule sample can be determined by using the following relationship:

$$\beta = \frac{\delta N_A d \times 10^{-3}}{h\nu},$$

where N_A is the Avogadro constant, d the concentration of the TPA compound in solution, h is Planck's constant, and υ is the frequency of the incident laser beam. So as to satisfy the condition of $\alpha_0 l \ll 1$, which allows the pure TPA $\sigma^{(2)}$ values to be determined using a simulation procedure, the TPA cross-section value of AF-50 was measured as a reference compound; this control was found to exhibit a TPA value of 50 GM at 800 nm.

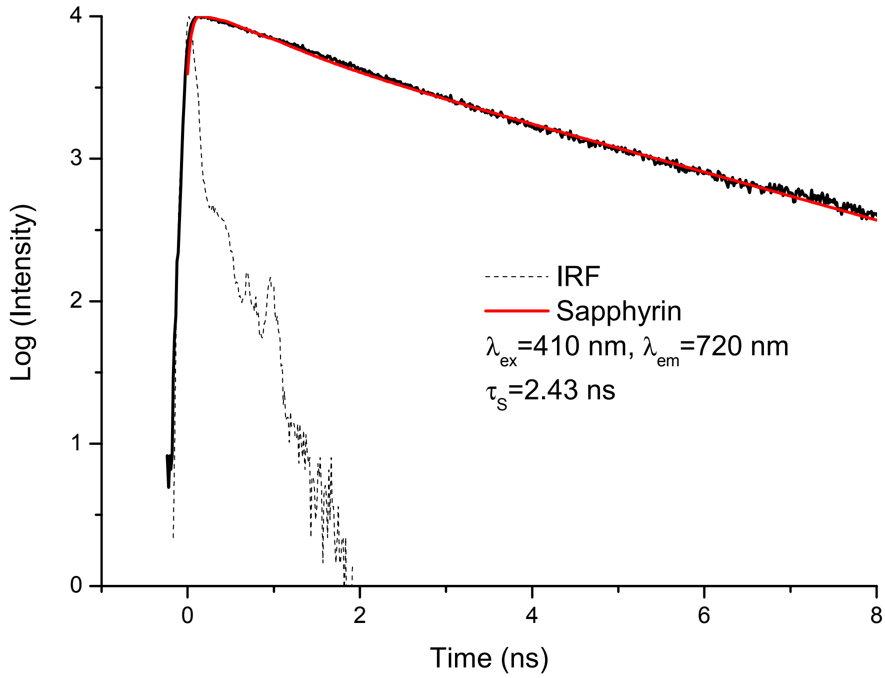

Figure S1. S_1-state fluorescence decay profile of Sap in CH_2Cl_2 measured by time-correlated single photon counting (TCSPC) method. The time-resolved fluorescence was monitored at 720 nm, after excitation at 410 nm.

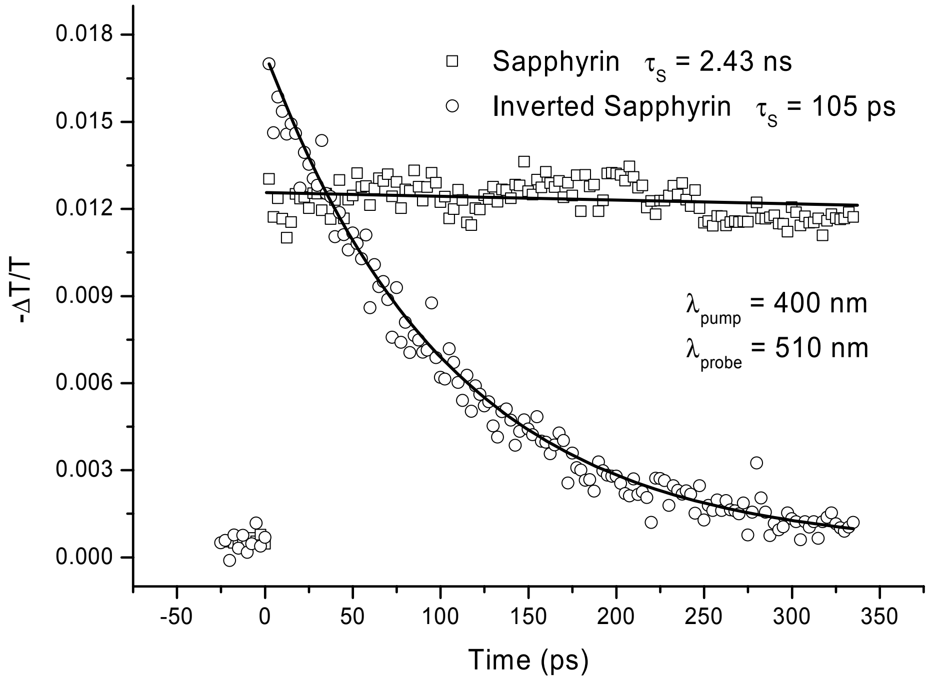

Figure S2. S_1-state decay profiles of sapphyrin (Sap) and inverted sapphyrin (InSap) in CH_2Cl_2 measured by femtosecond transient absorption spectroscopy, where the pump and the probe wavelengths are 400 and 510 nm, respectively. This was true for both samples.

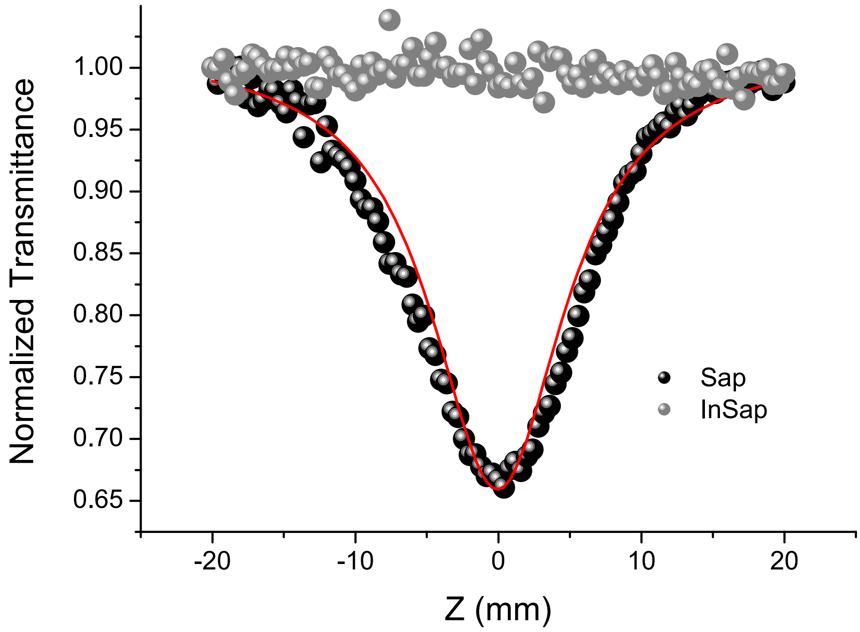

Figure S3. Open-aperture femtosecond Z-scan traces for Sap and InSap as recorded in CH_2Cl_2. The sample concentrations are 0.10 mM. The peak irradiance at the focal point is 80 GW/cm^2. The solid line for Sap is the best-fit curve for the experimental data under conditions of excitation at 1220 nm. The two-photon absorption coefficient of InSap could not be measured.

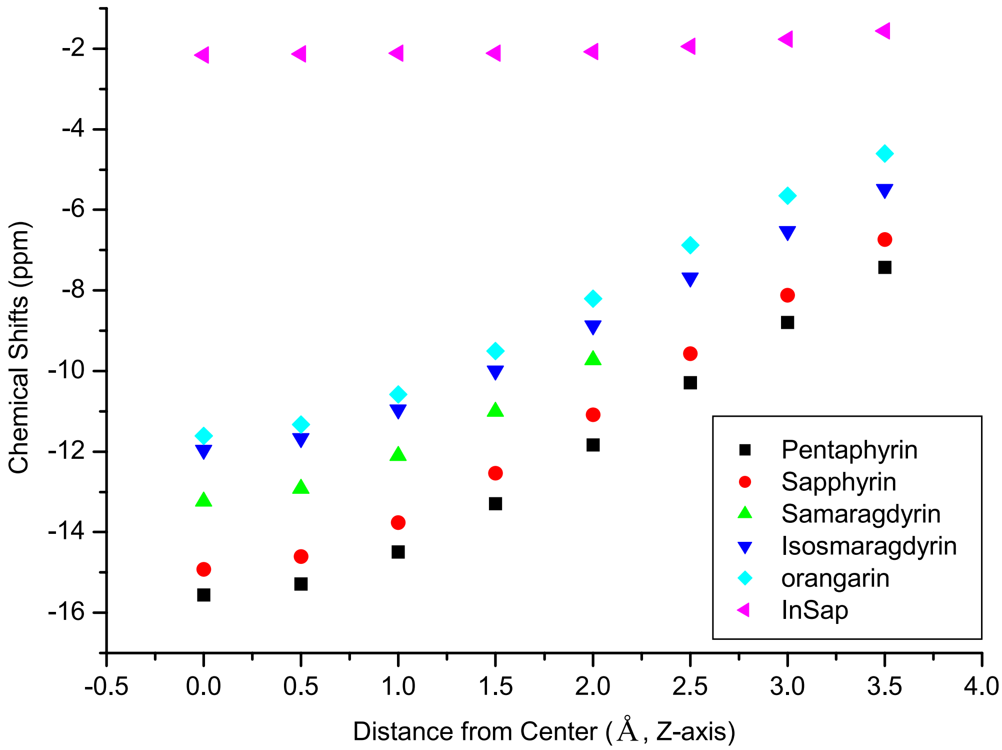

Figure S4. Isotropic chemical shifts for six pentapyrrolic systems; pentaphyrin, sapphyrin, smaragdyrin, isosmaragdyrin, orangarin, and inverted sapphyrin.

Optimized XYZ coordination in Sap using B3LYP/6-311+G* for NICS calculation:

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

N	0.01543	0.00462	-0.01061
N	0.02635	-0.0042	2.9168
N	3.37928	-0.00634	3.59586
N	5.01638	0.00363	0.59288
N	2.78166	0.00953	-1.2996
C	-1.34833	0.00405	0.19245
C	0.29553	0.00918	-1.35401
C	-1.95432	0.00819	-1.09004
C	-0.95146	0.01131	-2.03423
C	0.1571	-0.00844	4.26641
C	-1.32857	-0.00355	2.68791
C	-1.14758	-0.01023	4.9224
C	-2.07214	-0.00738	3.93641
C	2.68172	-0.01018	4.7904
C	4.74253	-0.00725	3.83056
C	3.66934	-0.01365	5.83061
C	4.9032	-0.01193	5.25587
C	5.71221	0.00814	-0.59209
C	5.96581	0.00041	1.56084
C	7.14649	0.00748	-0.3586

C	7.3071	0.00267	0.98349
C	1.57284	0.01161	-1.94923
C	3.81445	0.01346	-2.21297
C	1.85423	0.017	-3.34146
C	3.22226	0.01818	-3.5019
C	-1.95618	0.00019	1.44698
C	1.32042	-0.01097	5.05307
C	5.8196	-0.00445	2.95754
C	5.16586	0.01268	-1.87091
H	-3.02004	0.00872	-1.2672
H	-1.07054	0.01473	-3.1069
H	-1.30793	-0.0134	5.99242
H	-3.15047	-0.00765	4.0242
H	5.86373	-0.01364	5.75071
H	3.43032	-0.01706	6.88436
H	7.90736	0.01037	-1.12774
H	8.22973	0.00079	1.54864
H	1.10957	0.01971	-4.12263
H	3.77204	0.022	-4.4319
H	-3.04111	0.00021	1.4464
H	1.11426	-0.01434	6.11933
H	6.76837	-0.0063	3.48598
H	5.86361	0.01598	-2.70173
H	2.98822	0.00587	-0.30578

H	0.64352	0.0023	0.78685
H	2.95424	-0.00327	2.68289
Bq	2.27535	4.00208	1.23928
Bq	2.27528	3.90208	1.23948
Bq	2.27522	3.80208	1.23968
Bq	2.27515	3.70208	1.23989
Bq	2.27509	3.60208	1.24009
Bq	2.27502	3.50208	1.24029
Bq	2.27496	3.40208	1.24049
Bq	2.27489	3.30208	1.24069
Bq	2.27482	3.20208	1.24089
Bq	2.27476	3.10208	1.2411
Bq	2.27469	3.00208	1.2413
Bq	2.27463	2.90208	1.2415
Bq	2.27456	2.80208	1.2417
Bq	2.27449	2.70208	1.2419
Bq	2.27443	2.60208	1.2421
Bq	2.27436	2.50208	1.24231
Bq	2.2743	2.40208	1.24251
Bq	2.27423	2.30208	1.24271
Bq	2.27417	2.20208	1.24291
Bq	2.2741	2.10208	1.24311
Bq	2.27403	2.00208	1.24331
Bq	2.27397	1.90208	1.24352

Bq	2.2739	1.80208	1.24372
Bq	2.27384	1.70208	1.24392
Bq	2.27377	1.60208	1.24412
Bq	2.2737	1.50208	1.24432
Bq	2.27364	1.40208	1.24452
Bq	2.27357	1.30208	1.24473
Bq	2.27351	1.20208	1.24493
Bq	2.27344	1.10208	1.24513
Bq	2.27338	1.00208	1.24533
Bq	2.27331	0.90208	1.24553
Bq	2.27324	0.80208	1.24573
Bq	2.27318	0.70208	1.24594
Bq	2.27311	0.60208	1.24614
Bq	2.27305	0.50208	1.24634
Bq	2.27298	0.40208	1.24654
Bq	2.27291	0.30208	1.24674
Bq	2.27285	0.20208	1.24694
Bq	2.27278	0.10208	1.24715
Bq	2.27272	0.00208	1.24735
Bq	2.27265	-0.09792	1.24755
Bq	2.27259	-0.19792	1.24775
Bq	2.27252	-0.29792	1.24795
Bq	2.27245	-0.39792	1.24816
Bq	2.27239	-0.49792	1.24836

Bq	2.27232	-0.59792	1.24856
Bq	2.27226	-0.69792	1.24876
Bq	2.27219	-0.79792	1.24896
Bq	2.27213	-0.89792	1.24916
Bq	2.27206	-0.99792	1.24937
Bq	2.27199	-1.09792	1.24957
Bq	2.27193	-1.19792	1.24977
Bq	2.27186	-1.29792	1.24997
Bq	2.2718	-1.39792	1.25017
Bq	2.27173	-1.49792	1.25037
Bq	2.27166	-1.59792	1.25058
Bq	2.2716	-1.69792	1.25078
Bq	2.27153	-1.79792	1.25098
Bq	2.27147	-1.89792	1.25118
Bq	2.2714	-1.99792	1.25138
Bq	2.27134	-2.09792	1.25158
Bq	2.27127	-2.19792	1.25179
Bq	2.2712	-2.29792	1.25199
Bq	2.27114	-2.39792	1.25219
Bq	2.27107	-2.49792	1.25239
Bq	2.27101	-2.59792	1.25259
Bq	2.27094	-2.69792	1.25279
Bq	2.27087	-2.79792	1.253
Bq	2.27081	-2.89792	1.2532

Bq	2.27074	-2.99792	1.2534
Bq	2.27068	-3.09792	1.2536
Bq	2.27061	-3.19792	1.2538
Bq	2.27055	-3.29792	1.254
Bq	2.27048	-3.39792	1.25421
Bq	2.27041	-3.49792	1.25441
Bq	2.27035	-3.59792	1.25461
Bq	2.27028	-3.69792	1.25481
Bq	2.27022	-3.79792	1.25501
Bq	2.27015	-3.89792	1.25521
Bq	2.27008	-3.99792	1.25542
Bq	2.27002	-4.09792	1.25562
Bq	2.26995	-4.19792	1.25582
Bq	2.26989	-4.29792	1.25602
Bq	2.26982	-4.39792	1.25622
Bq	2.26976	-4.49792	1.25642
Bq	2.26969	-4.59792	1.25663
Bq	2.26962	-4.69792	1.25683
Bq	2.26956	-4.79792	1.25703
Bq	2.26949	-4.89792	1.25723

Optimized XYZ coordination in InSap using B3LYP/6-311+G* for NICS calculation:

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-1.62596	-1.98408	-0.11966
H	-1.21982	-0.98615	-0.12944
C	-0.9604	-3.15727	-0.00574
C	0.47416	-3.26415	0.07771
C	1.35142	-2.18362	-0.21995
C	2.65303	-2.57249	0.05211
N	2.57566	-3.89124	0.48491
C	1.27504	-4.31407	0.51005
C	3.88287	-1.84921	-0.04584
C	3.97152	-0.48624	-0.14091
N	2.90728	0.42436	-0.08429
C	3.38219	1.73646	-0.14038
C	4.81083	1.62292	-0.32092
C	5.16036	0.31086	-0.32095
C	2.71032	2.9299	-0.06146
C	1.35921	3.36082	0.06921
N	0.15539	2.67092	0.03859
C	-0.90754	3.55369	0.16959
C	-0.3472	4.83664	0.31573
C	1.03012	4.72022	0.25232

C	-2.3017	3.30842	0.142
C	-3.09437	2.18731	0.03012
N	-2.71355	0.86131	-0.06836
C	-3.85682	0.15909	-0.13068
C	-5.02587	1.04068	-0.08748
C	-4.54977	2.30055	0.01732
C	-4.02914	-1.25858	-0.20298
C	-3.04214	-2.21099	-0.18713
N	-3.22894	-3.58514	-0.23034
C	-1.96653	-4.28577	0.01215
H	0.01385	1.69591	-0.17464
H	2.04696	0.17524	0.37928
H	-1.76758	-5.0334	-0.76549
H	-4.09162	-3.98455	0.10364
H	-1.97288	-4.81223	0.97866
H	-5.10716	3.22613	0.08069
H	-6.05748	0.71507	-0.12673
H	1.75969	5.51302	0.33426
H	-0.9234	5.74039	0.45248
H	6.1498	-0.10413	-0.45319
H	5.46558	2.47373	-0.44896
H	1.01883	-5.30312	0.85786
H	3.36013	-4.42875	0.81576
H	-5.06018	-1.59969	-0.25211

H	-2.86444	4.2341	0.22954
H	3.38313	3.78135	-0.09818
H	4.81591	-2.40368	-0.04812
H	1.05805	-1.26731	-0.70409
Bq	-0.02176	-0.05379	3.9
Bq	-0.02441	-0.05192	3.80005
Bq	-0.02707	-0.05004	3.70011
Bq	-0.02972	-0.04816	3.60016
Bq	-0.03238	-0.04629	3.50021
Bq	-0.03504	-0.04441	3.40027
Bq	-0.03769	-0.04253	3.30032
Bq	-0.04035	-0.04065	3.20037
Bq	-0.043	-0.03878	3.10042
Bq	-0.04566	-0.0369	3.00048
Bq	-0.04832	-0.03502	2.90053
Bq	-0.05097	-0.03315	2.80058
Bq	-0.05363	-0.03127	2.70064
Bq	-0.05628	-0.02939	2.60069
Bq	-0.05894	-0.02752	2.50074
Bq	-0.0616	-0.02564	2.4008
Bq	-0.06425	-0.02376	2.30085
Bq	-0.06691	-0.02188	2.2009
Bq	-0.06956	-0.02001	2.10095
Bq	-0.07222	-0.01813	2.00101

Bq	-0.07488	-0.01625	1.90106
Bq	-0.07753	-0.01438	1.80111
Bq	-0.08019	-0.0125	1.70117
Bq	-0.08284	-0.01062	1.60122
Bq	-0.0855	-0.00874	1.50127
Bq	-0.08816	-0.00687	1.40132
Bq	-0.09081	-0.00499	1.30138
Bq	-0.09347	-0.00311	1.20143
Bq	-0.09612	-0.00124	1.10148
Bq	-0.09878	0.00064	1.00154
Bq	-0.10144	0.00252	0.90159
Bq	-0.10409	0.00439	0.80164
Bq	-0.10675	0.00627	0.7017
Bq	-0.1094	0.00815	0.60175
Bq	-0.11206	0.01002	0.5018
Bq	-0.11472	0.0119	0.40186
Bq	-0.11737	0.01378	0.30191
Bq	-0.12003	0.01566	0.20196
Bq	-0.12268	0.01753	0.10201
Bq	-0.12534	0.01941	0.00207
Bq	-0.128	0.02129	-0.09788
Bq	-0.13065	0.02316	-0.19783
Bq	-0.13331	0.02504	-0.29777
Bq	-0.13596	0.02692	-0.39772

Bq	-0.13862	0.0288	-0.49767
Bq	-0.14128	0.03067	-0.59762
Bq	-0.14393	0.03255	-0.69756
Bq	-0.14659	0.03443	-0.79751
Bq	-0.14924	0.0363	-0.89746
Bq	-0.1519	0.03818	-0.9974
Bq	-0.15456	0.04006	-1.09735
Bq	-0.15721	0.04193	-1.1973
Bq	-0.15987	0.04381	-1.29724
Bq	-0.16252	0.04569	-1.39719
Bq	-0.16518	0.04757	-1.49714
Bq	-0.16784	0.04944	-1.59708
Bq	-0.17049	0.05132	-1.69703
Bq	-0.17315	0.0532	-1.79698
Bq	-0.1758	0.05507	-1.89693
Bq	-0.17846	0.05695	-1.99687
Bq	-0.18112	0.05883	-2.09682
Bq	-0.18377	0.0607	-2.19677
Bq	-0.18643	0.06258	-2.29671
Bq	-0.18908	0.06446	-2.39666
Bq	-0.19174	0.06634	-2.49661
Bq	-0.1944	0.06821	-2.59655
Bq	-0.19705	0.07009	-2.6965
Bq	-0.19971	0.07197	-2.79645

Bq	-0.20236	0.07384	-2.8964
Bq	-0.20502	0.07572	-2.99634
Bq	-0.20768	0.0776	-3.09629
Bq	-0.21033	0.07947	-3.19624
Bq	-0.21299	0.08135	-3.29618
Bq	-0.21564	0.08323	-3.39613
Bq	-0.2183	0.08511	-3.49608
Bq	-0.22096	0.08698	-3.59603
Bq	-0.22361	0.08886	-3.69597
Bq	-0.22627	0.09074	-3.79592
Bq	-0.22892	0.09261	-3.89587
Bq	-0.23158	0.09449	-3.99581
Bq	-0.23424	0.09637	-4.09576
Bq	-0.23689	0.09824	-4.19571
Bq	-0.23955	0.10012	-4.29565
Bq	-0.2422	0.102	-4.3956
Bq	-0.24486	0.10388	-4.49555
Bq	-0.24752	0.10575	-4.59549
Bq	-0.25017	0.10763	-4.69544
Bq	-0.25283	0.10951	-4.79539
Bq	-0.25548	0.11138	-4.89534