Supporting Information

Piezochromic Luminescence in All-Inorganic Core-Shell InP/ZnS Nanocrystals via Pressure-Modulated Strain Engineering

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Experimental Section

Synthesis of InP QDs

InP NPs were synthesized based on the method described in the literature.[1] In a typical synthesis, 0.45 mmol $InCl_3$ and 2.2 mmol $ZnCl_2$ were mixed with 5 mL oleylamine (OLA) in a 50 mL three-neck flask. The reaction mixture was degassed under vacuum at 120 °C for 30 min and then heated to 180 °C. Next, 0.45 mL (1.6 mmol) tris(diethylamino)phosphine was quickly injected into the reaction flask, and the solution was continuously degassed and purged with nitrogen for 30 min. Afterward, the reaction solution was cooled to room temperature. The InP NCs were precipitated using acetone and centrifuged at 8000 rpm. The precipitate was re-dispersed in toluene and precipitated with acetone. This process was repeated a minimum of three times and the precipitation dried under vacuum for 1 h at 50 °C to get NC powders.

Synthesis of Core/Shell InP/ZnS NCs

An InP QDs synthesis is performed at 180 °C. Instead of cooling down the temperature, at 20 min: slow injection of 1 mL of saturated TOP-S (2.2 M). At 60 min: temperature is increased from 180 to 200 °C. At 120 min: slow injection of 1 g of $Zn(stearate)_2$ in 4 mL of octadecene (ODE). Temperature is increased from 200 to 220 °C. At 150 min: injection of 0.7 mL of stoichiometric TOP-S. Temperature is increased from 220 to 240 °C. At 180 min: slow injection of 0.5 g of $Zn(stearate)_2$ in 2 mL of ODE. Temperature is increased from 240 to 260 °C. At 210 min: end of reaction. At the end of the reaction, the temperature is cooled down. The washing and drying process was the same as that described for InP NCs.

In situ high-pressure measurements

In situ high-pressure experiments were implemented using symmetric DAC apparatus furnished with a pair of 400 μm culet diamonds at room temperature. A T301 stainless steel gasket was preindented by the diamonds and was drilled to generate a 130 μm diameter cavity for loading the samples. The prepared InP/ZnS NCs were enclosed in the gasket hole together with a ruby ball for determining the actual pressure through the standard ruby fluorescent technique.[2] Therein, silicon oil with a viscosity of 10 cSt was utilized as the pressure transmitting medium (PTM), which was purchased from Dow Corning Corporation (South Saginaw Road, Midland, MI, USA). In addition, when nitrogen is used as a pressure medium, a small piece of sample with thickness of 10 μm was loaded into the sample hole of the DAC with a preindented and drilled tungsten gasket. Nitrogen was loaded into the sample chamber using the gas-loading equipment.[3] *In situ* ADXRD patterns of samples under high pressure were recorded at beamline 15U1, Shanghai Synchrotron Radiation Facility (SSRF). Both of the beamline stations at SSRF exploited a monochromatic wavelength of

0.6199 Å. CeO_2 was utilized as the standard sample for the calibration. The pattern of intensity versus diffraction angle 2θ was plotted based on the FIT2D program, which integrated and analyzed the 2D images collected. *In situ* absorption and PL micrographs of the samples were obtained using a camera (Canon Eos 5D mark II) equipped on a microscope (Ecilipse TI-U, Nikon). The camera can record the photographs under the same conditions including exposure time and intensity. Absorption spectra were measured in the exciton absorption band region using a Deuterium-Halogen light source, and the excitation source, a 355 nm line of a UV DPSS laser with the power of 10 mW was used for PL measurements. The fiber spectrometer is an Ocean Optics QE65000 spectrometer. During experiments, we slowly raised pressure to begin the compression process, then release carefully to the ambient pressure. Each pressure point in the test is guaranteed to last more than 15 minutes.

TRPL measurements

The TRPL of InP/ZnS NCs in diamond anvil cell was measured by home-made setup. A 375 nm pulsed diode laser (LDH-P-C-375B, 40 ps) was used as excitation source. A 20× ultraviolet objective lens was used to project the incident laser onto the sample and collet the backscattered emission signal. The PL signal was directed into the 500 mm focal length grating spectrograph (HRS-500 MS), where a PMT together with a time correlated single photon counting electronics (TimeHarp 260 PICO) was used to detect the PL kinetics.

First-principles calculations

First-principles calculations were performed using the plane-wave pseudopotential method within the framework of density functional theory as implemented in the Vienna ab initio Simulation Package.[4] The electron-ion interactions were described by the projected augmented wave pseudopotentials with Zn $3d^{10}4s^2$, S $3s^23p^4$, In $5s^25p^1$ and P $3s^23p^3$, as valence electrons. We used the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) as exchange-correlation functional.[5] We employed a kinetic energy cutoff of 510 eV and a $2\pi\times0.03$ $Å^{-1}$ Monkhorst-Pack *k*-point mesh spacing for electronic Brillouin zone integration. Geometry optimizations (including cell parameters and internal atomic positions) under different pressure were performed by using the conjugate gradient technique, until the residual forces on the atoms were less than 10^{-3} eV/Å. Considering a core-shell InP/ZnS nanocrystal with ~10^4 atoms (5.1 nm diameter), we used the bulk phases of InP and ZnS (space group $F\bar{4}3m$) to simulate the actual structure under high pressure.

References

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[2] H. K. Mao, J. Xu, P. M. Bell, *J. Geophys. Res.*, 1986, **91**, 4673.

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Author contributions

H.L., X.Z., X.Y., Y.W., M.W. and B.Z. designed and performed experiments and analyzed data. J.J., G.W., K.Y. and L.S. fabricated TRPL testing and analyzed data. X.Y., L.S., and B.Z. supervised the work.

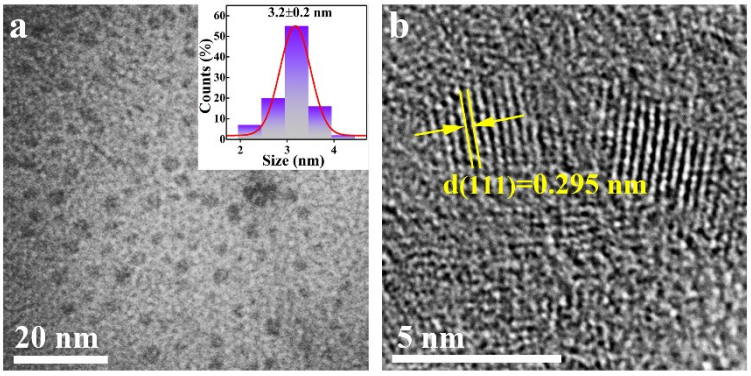

Fig. S1 Representative TEM and HRTEM images of InP core NCs. (a) The TEM image depicts the high uniformity nature of the as-prepared InP nanoparticles, with a size of 3.2 ± 0.2 nm, based on the analysis of 100 nanoparticles. **(b)** HRTEM image with well-defined lattice fringes demonstrate that the synthesized InP QDs possess good crystallinity. The interplanar distance of 0.295 nm exhibited by HRTEM is consistent with the (111) crystallographic facet of cubic InP NCs.

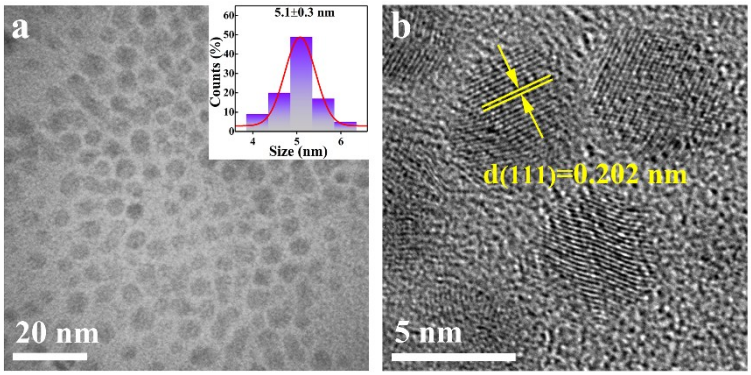

Fig. S2 Representative TEM and HRTEM images of InP/ZnS core/shell NCs. (a) The TEM image depicts the high uniformity nature of the as-prepared InP/ZnS nanoparticles, with a size of 5.1 ± 0.3 nm, based on the analysis of 100 nanoparticles. **(b)** HRTEM image with well-defined lattice fringes demonstrate that the synthesized InP/ZnS QDs possess good crystallinity. The interplanar distance of 0.202 nm exhibited by HRTEM is consistent with the (220) crystallographic facet of cubic InP NCs.

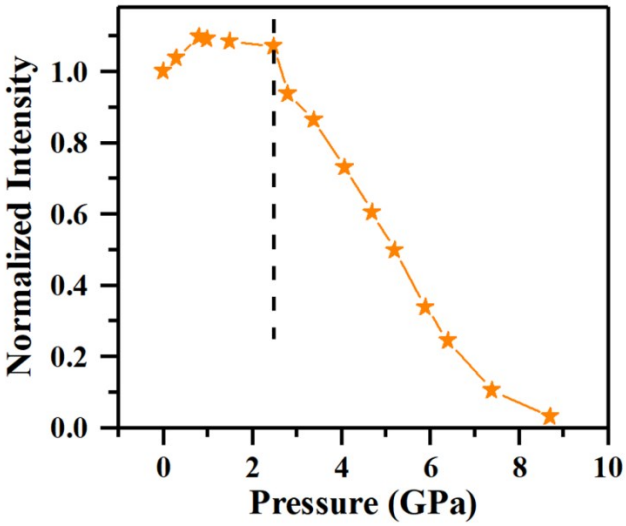

Fig. S3 Normalized PL intensity of InP/ZnS core/shell NCs as a function of pressure. The PL intensity increases slightly before ~2.5 GPa, consistenting with the PL images. When the pressure exceeds a certain threshold (~2.5 GPa), the PL intensity started to decrease until disappeared.

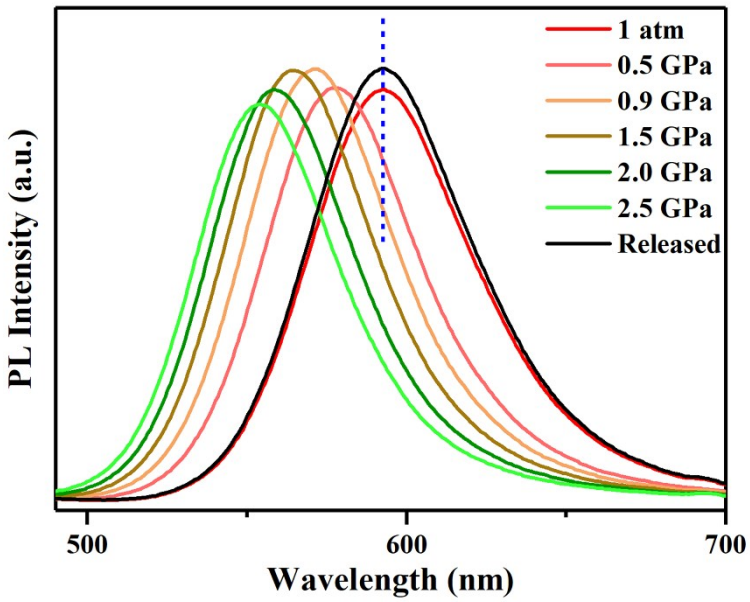

Fig. S4 Changes in the PL spectra of InP/ZnS core/shell QDs under pressure within 2.5 GPa. The PL peaks of InP/ZnS NCs exhibited a continuous blue-shift from 597 nm (1 atm) to 549 nm (2.5 GPa). The PL peak position and intensity returns to its initial state when the pressure is released from 2.5 GPa. In the same sample, we put pressure on it again to explore its optical properties under higher pressure.

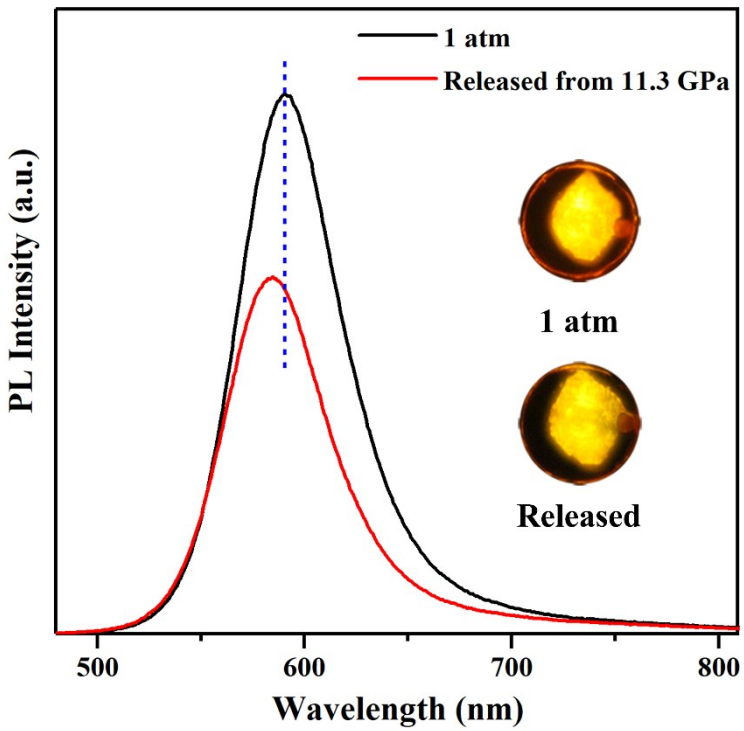

Fig. S5 Comparison of the PL spectra and image of InP/ZnS NCs under the initial ambient condition with that released from 11.3 GPa. The PL peak position and intensity not returns to its initial state when the pressure is released from 11.3 GPa. The inset fluorescent microscopic images directly reveal the differences in PL color and intensity.

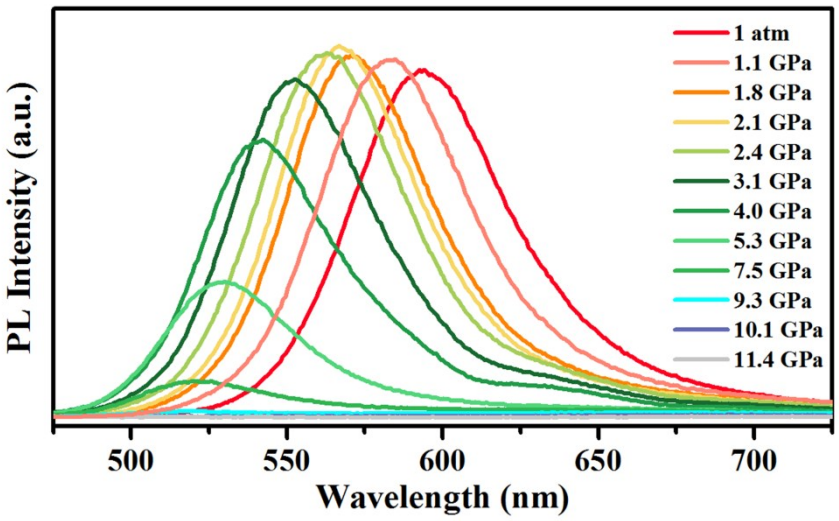

Fig. S6 Changes in the PL spectra of InP/ZnS NCs under pressure with nitrogen as the pressure transmitting medium.

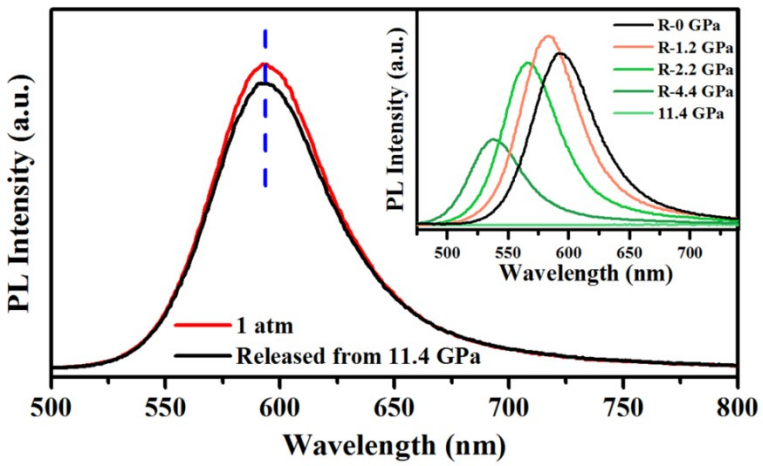

Fig. S7 Compare the PL spectrum of initial InP/ZnS NCs with that released from 11.4 GPa by using nitrogen as the pressure transmitting medium. The PL peak position and intensity almost returns to its initial state when the pressure is released from 11.4 GPa. Inset: the PL spectra of InP/ZnS NCs during decompression from 11.4 GPa.

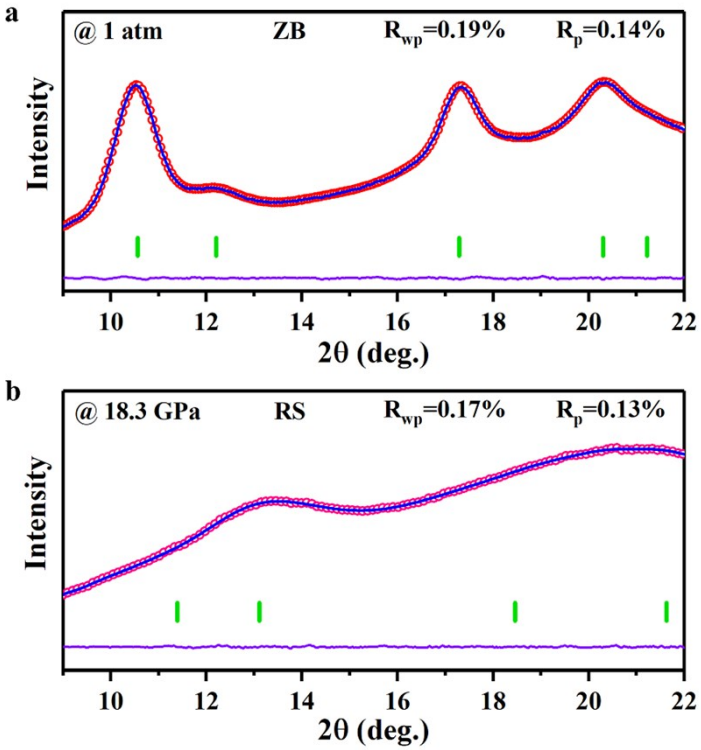

Fig. S8 Structure refinements. Rietveld refinements of the experimental (blue fork), simulated (Red profile), and difference (purple line) ADXRD patterns of ZB structure at 1 atm (**a**) and RS structure at the pressure of 18.3 GPa (**b**), Green vertical markers indicate the corresponding Bragg reflections.

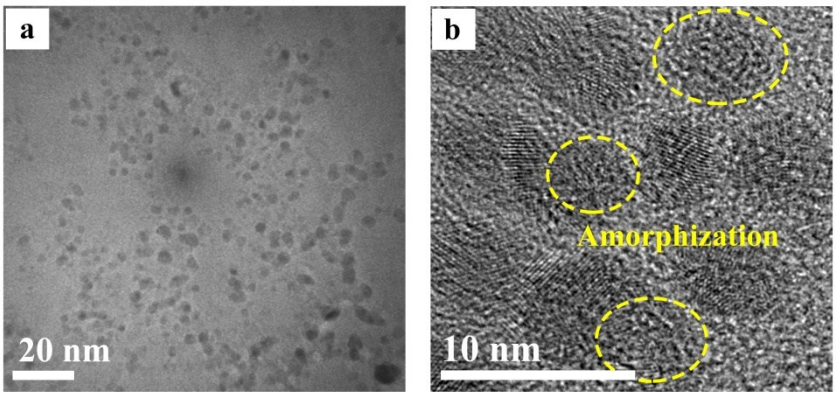

Fig. S9 The TEM (a) and HRTEM (b) images of InP/ZnS NCs after decompression from 26.5 GPa. The HRTEM image shows some irregular stripes and partial amorphization.

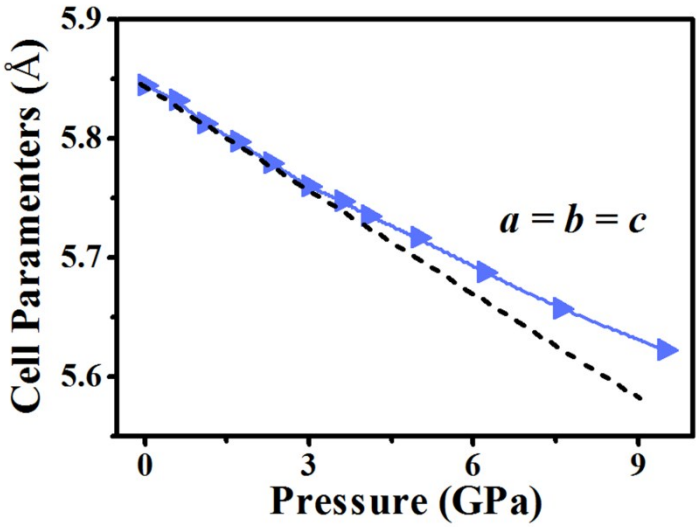

Fig. S10 Changes in the unit cell parameters at various pressure: *a* (= *b* = *c*). On increasing pressure, unit cell dimension of InP/ZnS NCs displayed a nolinear decrease. The rate of decline is more gradual as the value of pressure increasing.

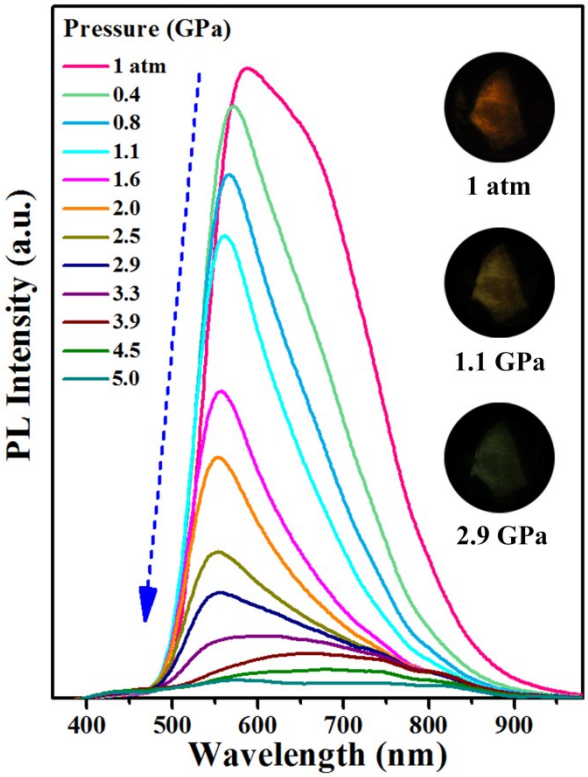

Fig. S11 Changes in the PL spectra of InP NCs under pressure. Inset: PL images under UV irradiation (λ_{ex} = 355 nm) showing PL color and intensity change at various pressure levels. At ambient conditions, the spectrum of InP NCs is composed of a peak located at 589 nm which corresponds to the band-to-band emission and a shoulder around 665 nm which originates from surface defect states. By applying pressure, the band-to-band PL intensity of the InP NCs exhibit continuously weakening and until disappearing at about 5.0 GPa.

Table S1. The fitting parameters of TRPL and calculated PL lifetime of InP/ZnS core/shell NCs.

P/GPa	τ_1/ns	A_1(%)	τ_2/ns	A_2(%)	τ_3/ns	A_3(%)	τ_{avg}/ns
0	39.053	45.9	12.378	30.6	4.186	23.5	33.090
0.55	37.286	46.6	11.600	30.2	4.010	23.2	31.741
0.75	35.907	47.4	11.527	29.5	3.967	23.1	30.656
1.02	33.912	48.4	10.951	29.3	3.712	22.2	29.092
1.28	32.383	50.7	10.456	28.2	3.617	21.1	28.080
1.52	31.957	51.7	10.257	27.6	3.386	20.6	27.896
1.87	31.454	53.5	9.916	27.3	3.049	19.2	27.729
2.14	30.631	55.4	9.272	26.5	2.472	18.1	27.359
2.55	30.064	56.7	9.106	25.3	2.153	18.0	27.071
3.06	31.192	57.2	8.755	24.7	1.603	18.2	28.380
3.62	32.620	56.5	8.601	23.6	1.540	19.9	29.810
4.02	33.343	56.5	8.629	22.6	1.297	20.9	30.639
4.47	34.302	54.3	8.323	22.6	0.999	23.1	31.577
5.11	39.002	49.6	8.093	21.8	0.645	28.6	36.109
6.16	43.012	44.3	7.628	21.4	0.416	34.3	39.954
7.11	53.311	33.1	7.544	18.3	0.339	48.7	49.565
8.10	72.717	26.7	6.648	14.7	0.277	58.7	69.000