Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

A novel mechanism for red emission carbon dots: hydrogen bond dominated molecular states emission

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Solvents and parameters.

For the simplicity, the organic solvents acronyms and the parameters was used as follows:

No.	Solvents	Solvents acronyms	[a] Solvents Δf	[b] Parameter $E_{30}(T)$	[c] HB index	[d] Kamlet-Taft Parameters		
						π*	α	β
1	Chloroform	TCM	0.1459	39.1	1.5	0.58	0.44	0.00
2	1,4-Dioxane	DX	0.0204	36.0	9.7	0.55	0.00	0.37
3	Dichloromethane	DCM	0.2185	40.7	1.5	0.73	0.30	0.00
4	Ethyl acetate	EAC	0.2002	38.1	8.4	0.55	0.00	0.45
5	Acetone	DMK	0.2846	42.2	9.7	0.71	0.08	0.48
6	Acetonitrile	ACN	0.3046	45.6	13	0.75	0.19	0.31
7	Dimethylformamide	DMF	0.2744	43.2	11.7	0.88	0.00	0.69
8	Dimethylsulfoxide	DMSO	0.2630	45.1	7.7	1.00	0.00	0.76
9	Formamide	FA	0.2822	55.8	-	0.97	0.71	0.48
10	Methanol	MA	0.3086	55.4	18.7	0.60	0.93	0.62
11	Ethanol	EA	0.2887	51.9	18.7	0.54	0.83	0.77
12	n-Propanol	NPA	0.2741	50.7	18.7	0.52	0.78	0.80
13	n-Butyl alcohol	NBA	0.2619	49.7	18.7	0.47	0.79	0.88
14	n-Amyl alcohol	NAA	0.1987	49.1	18.7	-	-	-
15	n-Hexyl alcohol	NHA	0.2033	48.8	-	-	-	-
16	Ethylene glycol	EG	0.2745	56.3	20.6	0.92	0.90	0.52

*[a] solvents Δf: calculated using the following formula:

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

the used parameter n and ε is obtained from the George Wypych , *Databook of Green Solvents*, 1st Edition, 2014, ChemTec Publishing.

*[b] Parameter $E_T(30)$: The same as *a.

*[c] HB index: Dwight G. Weldon, *Failure Analysis of Paints and Coatings*, 3rd Edition, 2009, John Wiley & Sons, Page 60-62,

*[d] Kamlet –Taft parameter: *J. org. Chem*, 1983, 48(17): 2877-2887.

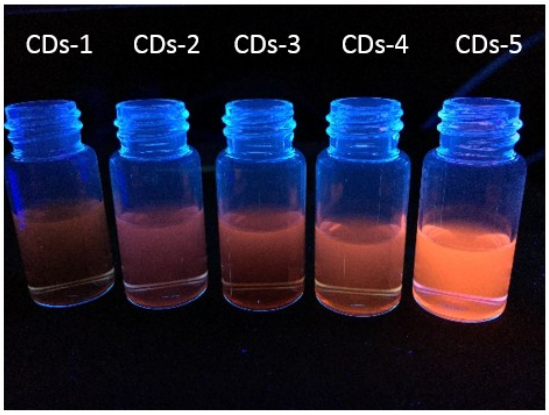

Figure S1. Digital photograph of different CDs samples under UV lamp (365 nm excitation).

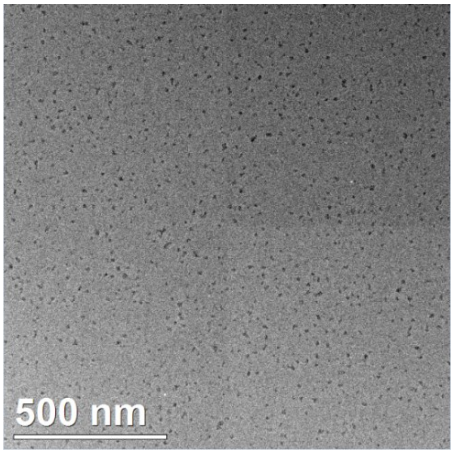

Figure S2. The TEM images of the CDs prepared in toluene (CDs-5) at lower magnification.

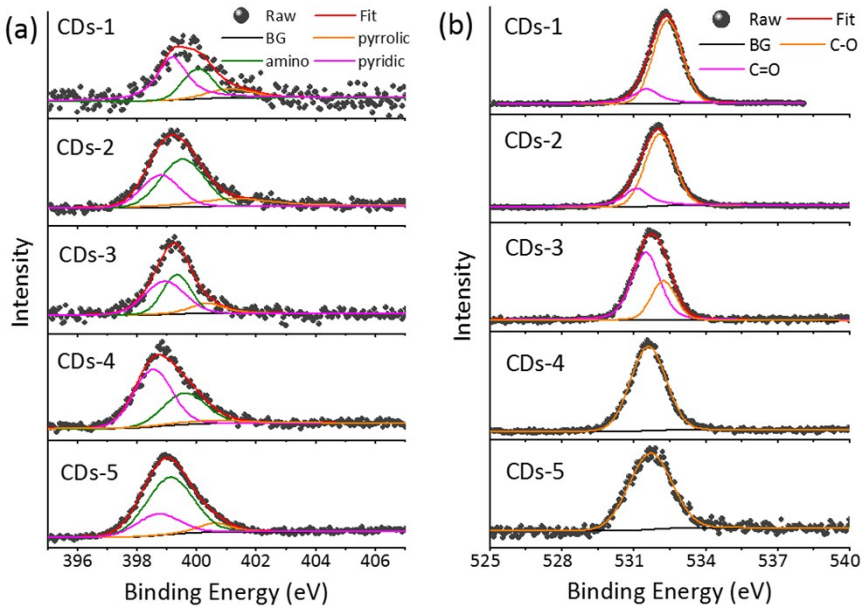

Figure S3. (a) The high resolution (a) N1s spectrum and (b) O1s spectrum for CDs-1 to CDs-5.

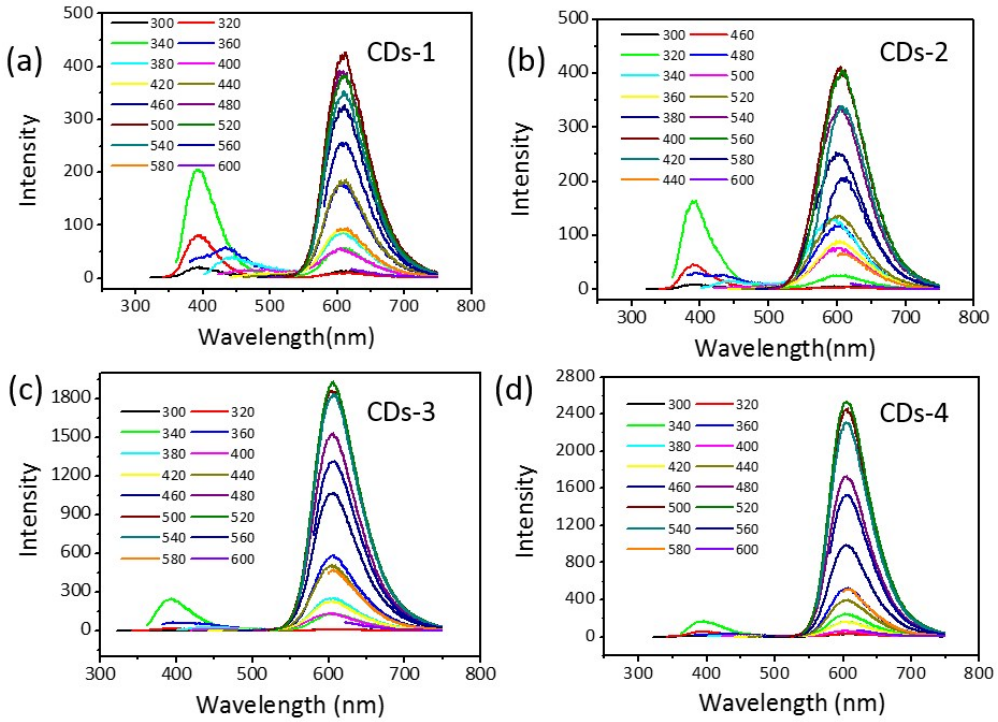

Figure S4. (a-d) The emission spectra for CDs-1 to CDs-4 under different excitation wavelength from 300 nm to 600 nm.

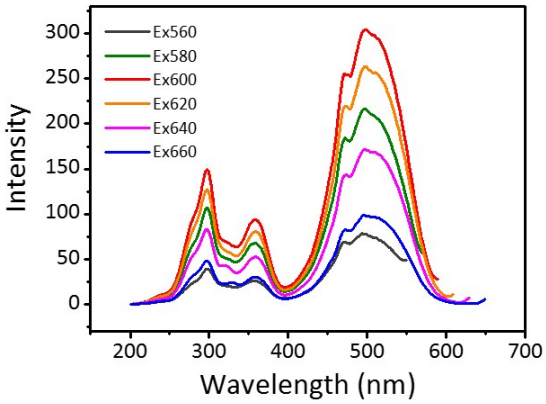

Figure S5. The PLE spectra for CDs-5 monitored at different wavelength from 300 nm to 600 nm.

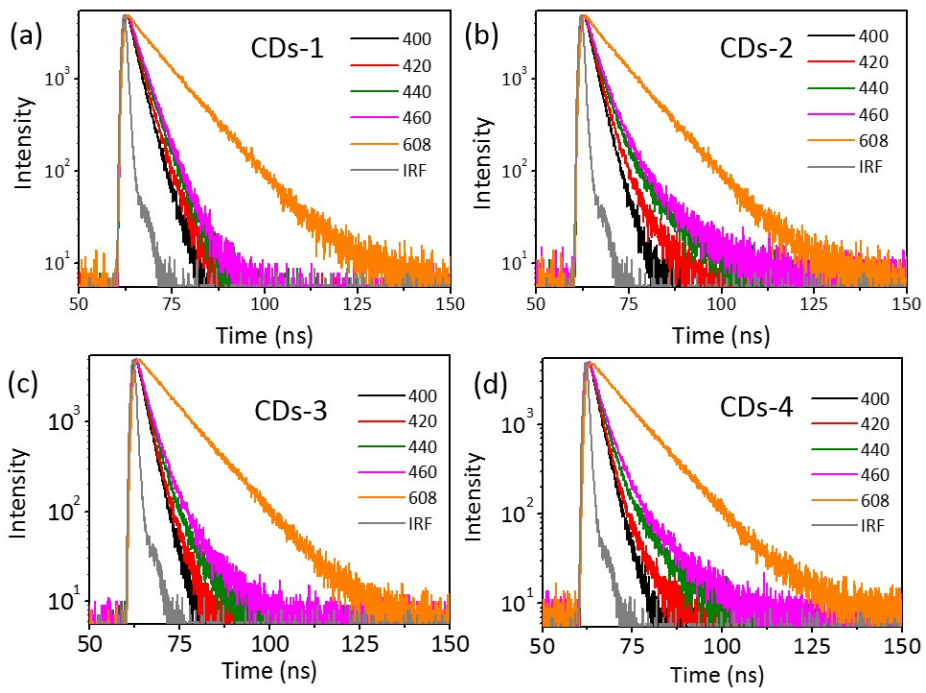

Figure S6. (a-d) The decay of from CDs1 to CDs-4 monitored at different emission wavelength.

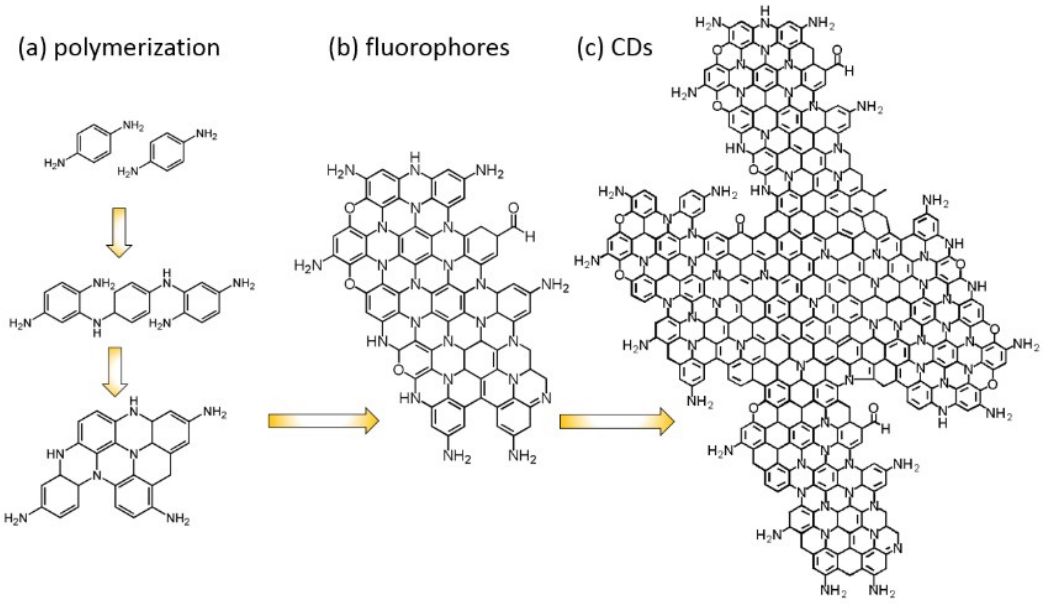

Figure S7. Illustration of the formation process of CDs based on polymerization of PPD. (a) polymerization of PPD, (b) formation of nitrogen contained fluorophores and (c) possible structure of CDs.

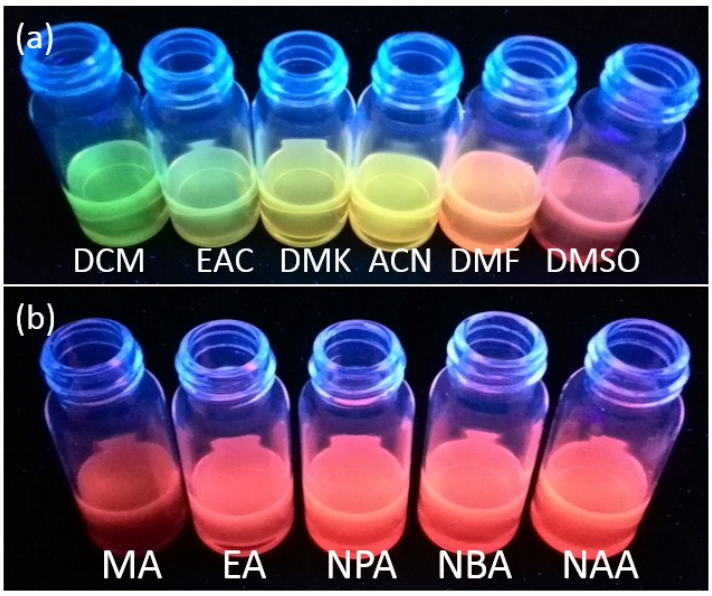

Figure S8. The digital photos of CDs-5 in different solvents excited under 365 UV lamp. (a) The images of CDs-5 in aprotic solvents and (b) in protic solvents.

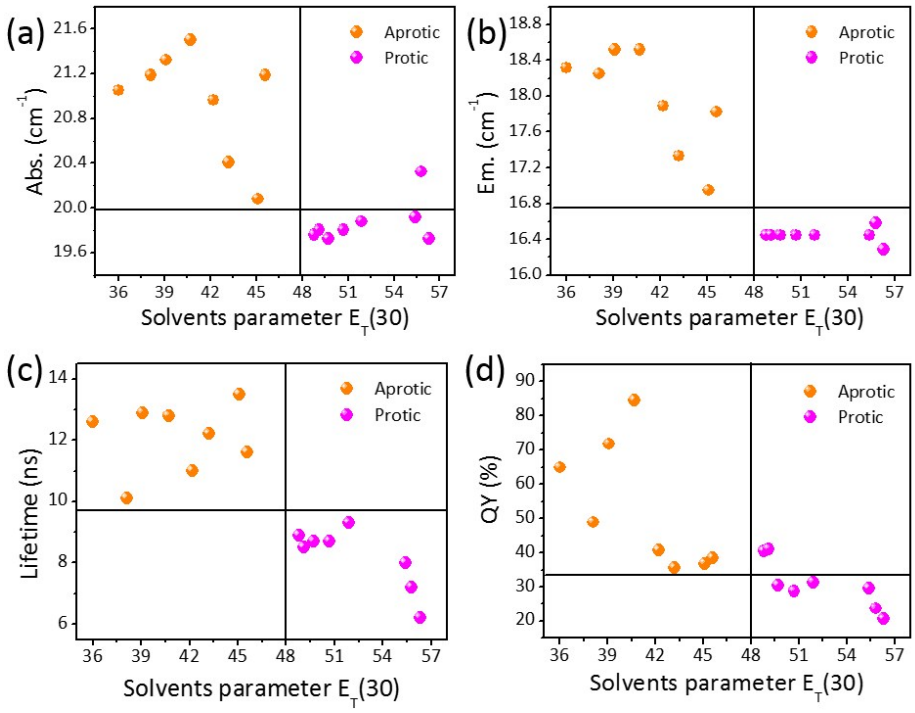

Figure S9: Dimroth-Reichard plot between classical solvents polarity parameter $E_T(30)$ and spectral parameters of CDs-5, specifically, (a) absorption, (b) emission wavenumber, (c) lifetime and (d) QY, respectively.

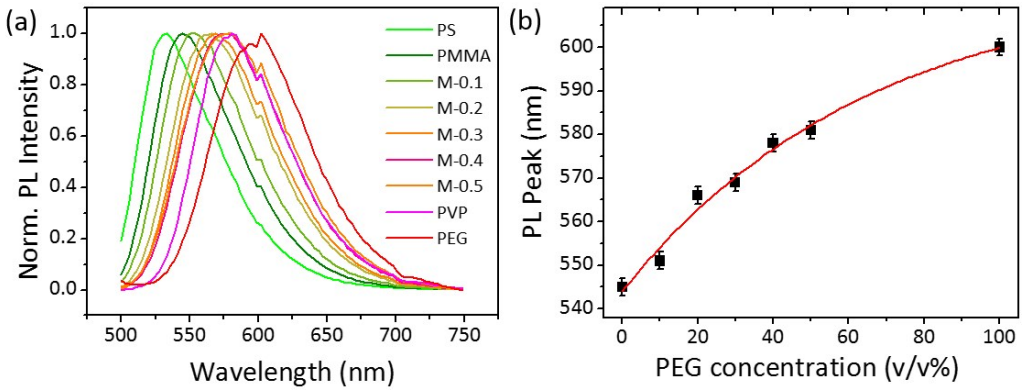

Figure S10: (a) The emission spectra of CDs-polymers. M-0.1 to M-0.5 was the abbreviation for CDs in PEG/PMMA mixture matrix with different proportion from 10% to 50%, respectively. (b) The relationship between emission peak and the volume proportion of PEG in PMMA.

Table S1. The elements proportion for different CDs samples.

Samples	C%	N%	O%
CDs-1	45.2	2.7	52.1
CDs-2	62.5	5.5	32.0
CDs-3	72.8	7.6	19.6
CDs-4	73.9	9.1	17.0
CDs-5	56.1	27.8	16.1

Table S2. The decay fitting parameter for different CDs samples at different wavelength.

CDs-1	t_1 /ns	f_1	t_2 /ns	f_2	<t> /ns	χ^2
400 nm	1.7	0.39	3.1	0.61	2.55	1.04
420 nm	2.0	0.45	3.9	0.55	3.05	1.09
440 nm	2.2	0.38	4.4	0.62	3.55	1.16
460 nm	2.4	0.38	4.6	0.62	3.76	1.19
608 nm	1.0	0.001	9.2	1.00	9.17	1.19
CDs-2	t_1 /ns	f_1	t_2 /ns	f_2	<t> /ns	χ^2
400 nm	1.8	0.59	3.4	0.41	2.46	1.04
420 nm	2.1	0.64	5.7	0.36	3.41	1.09
440 nm	2.4	0.53	7.6	0.47	4.83	1.25
460 nm	2.6	0.50	8.0	0.50	5.29	1.23
608 nm	1.3	0.001	9.2	0.99	9.13	1.22
CDs-3	t_1 /ns	f_1	t_2 /ns	f_2	<t> /ns	χ^2
400 nm	1.6	0.43	2.6	0.57	2.17	0.97
420 nm	1.9	0.71	4.4	0.29	2.63	1.07
440 nm	2.1	0.61	5.6	0.39	3.45	1.18
460 nm	2.2	0.52	6.0	0.48	4.03	1.18
608 nm	2.4	0.001	9.2	1.00	9.14	1.20
CDs-4	t_1 /ns	f_1	t_2 /ns	f_2	<t> /ns	χ^2
400 nm	1.7	0.59	3.0	0.41	2.23	1.10
420 nm	2.0	0.70	5.7	0.30	3.13	1.12
440 nm	2.2	0.55	7.3	0.45	4.51	1.18
460 nm	2.4	0.49	7.6	0.51	5.08	1.14
608 nm	2.1	0.001	9.3	0.99	9.25	1.17
CDs-5	t_1 /ns	f_1	t_2 /ns	f_2	<t> /ns	χ^2
400 nm	1.6	0.17	4.1	0.83	3.69	1.41
420 nm	2.8	0.51	6.4	0.49	4.58	1.19
440 nm	3.1	0.53	7.7	0.47	5.27	1.07
460 nm	3.2	0.55	7.6	0.45	5.16	1.11
608 nm	1.0	0.001	9.4	1.00	9.38	1.23

*<t> average lifetime.

*χ^2 fitting Chi-squared.

Table S3. The decay fitting parameter for CDs-5 at different wavelength.

Wavelength	<t> /ns	χ^2
568 nm	9.36	1.09
588 nm	9.32	1.19
608 nm	9.34	1.13
628 nm	9.33	1.2
648 nm	9.35	1.2

Table S4. The decay parameter for CDs-5 in different solvents.

Solvents	Wavelength /nm	<t> /ns	χ^2
TCM	540	12.9	1.19
DX	546	12.6	1.23
DCM	540	12.8	1.25
EAC	548	10.1	1.16
DMK	559	11.0	1.11
ACN	561	11.6	1.14
DMF	577	12.2	1.21
DMSO	590	13.5	1.18
FA	603	7.2	1.17
MA	608	8.0	1.18
EA	608	9.3	1.13
NPA	608	8.7	1.18
NBA	608	8.7	1.21
NAA	608	8.5	1.18
NHA	608	8.9	1.14
EG	614	6.2	1.33

Table S5. The supplementary spectral parameter data of CDs-5 in differnet solvents.

No.	Solvents	acronyms	Absorption (cm^{-1}) ×1000	Emission (cm^{-1}) ×1000	Stokes shift (cm^{-1}) ×1000	k_r (10^{-9} s^{-1})	k_{nr} (10^{-9} s^{-1})
1	Chloroform	TCM	21.321	18.518	2.803	0.057	0.022
2	1,4-Dioxane	DX	21.052	18.315	2.737	0.052	0.028
3	Dichloromethane	DCM	21.505	18.518	2.987	0.066	0.012
4	Ethyl acetate	EAC	21.186	18.248	2.938	0.048	0.051
5	Acetone	DMK	20.964	17.889	3.075	0.037	0.054
6	Acetonitrile	ACN	21.186	17.825	3.361	0.033	0.053
7	Dimethylformamide	DMF	20.408	17.331	3.077	0.029	0.053
8	Dimethylsulfoxide	DMSO	20.080	16.949	3.131	0.027	0.047
9	Formamide	FA	20.325	16.584	3.741	0.033	0.106
10	Methanol	MA	19.920	16.447	3.473	0.037	0.088
11	Ethanol	EA	19.880	16.447	3.433	0.034	0.074
12	n-Propanol	NPA	19.801	16.447	3.354	0.033	0.082
13	n-Butyl alcohol	NBA	19.723	16.447	3.276	0.035	0.080
14	n-Amyl alcohol	NAA	19.801	16.447	3.354	0.048	0.069
15	n-Hexyl alcohol	NHA	19.762	16.447	3.315	0.045	0.067
16	Ethylene glycol	EG	19.723	16.287	3.436	0.033	0.128

* k_r is the abbrevation of radiation rate, which is calculated by $k_r=\Phi/\tau$, where Φ is the QY, and τ is the fluorescent average lifetime.

* k_{nr} is the abbrevation of non-radiation rate, which is calculated by $k_{nr}=(1-\Phi)/\tau$.

Table S6. The decay parameter for CDs-5 in DCM/ EA binary mixture solvents.

EA in DCM	Wavelength/nm	<t> /ns	χ^2
0.0%	540	12.13	1.31
0.5%	542	12.34	1.40
1.0%	548	11.70	1.41
2.0%	571	11.13	1.34
4.0%	583	10.29	1.53
9.0%	592	9.63	1.19