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Supporting Information

The Key to Control Morphologies of Quantum Nanocrystals: Spherical Carborane Ligands

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Experimental Procedures

Chemicals Used

Cadmium oxide (CdO, ≥99.99%, trace metal basis, Sigma Aldrich), Selenium powder (Se, 100 mesh ≥99.5%, trace metal basis, Sigma Aldrich), 1-Octadecene (90%, Technical Grade, Sigma Aldrich), Tri-n-octylphosphine (90%, technical grade, Alfa Aesar), 1-Adamantanethiol (95%, Sigma Aldrich), ortho-carboranethiol (o-CarbSH), 1-methyl-ortho-¬2-carboranethiol (m-o-CarbSH), meta-carboranelthiol (m-CarbSH), meta-carboranylphosphinic acid (CarbPhos). and meta-carboranylcarboxylic acid (m-CarbCarboxylic).

Synthesis

This method is a modification of the method proposed by Ubani et al.[1] The pyrolysis reaction was inspired by the QDs organic preparation procedure as reported by Ubani et al, utilizing the same type of solvent, the same source of selenium, the same source of Cd, the same temperature and the same sampling method, but using the carborane ligands indicated above.

First step: Synthesis of Selenium precursor: 60mg of Se powder (0.04mmol) and 0.4mL Tri-n-octylphosphine were added to 10mL of 1-Octadecene. To dissolve the Se powder the mixture was heated to 60^{o}C and stirred for two hours until all the Se powder dissolved. This Se precursor solution was sealed and stored in room temperature for 1 week to allow the precursor to form. The precursor solution should not be disturbed over the period of 1 week.

Second step (for QNCs): Synthesis of CdSe QDs with o-CarbSH, m-o-CarbSH and m-CarbSH: 13 mg of CdO was mixed ~~dissolved~~ in 10mL of 1-Octadecene. CdO and the required carborane derivative was taken in a molar ratio of 1:2. The appropriate amount of Carborane derivative (depending on the molar mass of the derivative) was taken and dissolved in 6mL of 1-Octadecene. Then this mixture of Carborane derivative in 1-Octadecene was added to the CdO solution and then it was heated stepwise till 150^{o}C (1^{o}C/min) using a heating mantle. To synthsize the different QNCs, a temperature ramp for the final 40-45^{o}C was needed. The temperature of the CdO/carborane ligand solution was increased stepwise up until 150^{o}C (1^{o}C/min) and then the temperature was augmented abruptly till it reached 195^{o}C (10^{o}C/min). At this point the selenium precursor was added. This represented time zero. The samples were then removed at time intervals of 20s, 30s, 45s, 1 min, and 5 min. Of notable importance is the sudden rise in temperature of the CdO/Carborane ligand solution to give the NCs their final appearance, particularly for the QRs and QRods. Upon reaching 195^{o}C, 1 ml of the preformed Se precursor was injected into the CdO/Carborane derivative mixture. The addition of the Se precursor lead to evolution of smoke which is due to the rapid formation of the CdSe QDs. The samples were then removed at time intervals of 20s, 30s, 45s, 1 min, 5 min after the addition of the Selenium precursor. After pipetting out of the samples, a 0.2 μm PTFE microfilter was used to remove any unreacted reagents or particles greater than 200 nm from the colloidal samples.

Results and Discussion

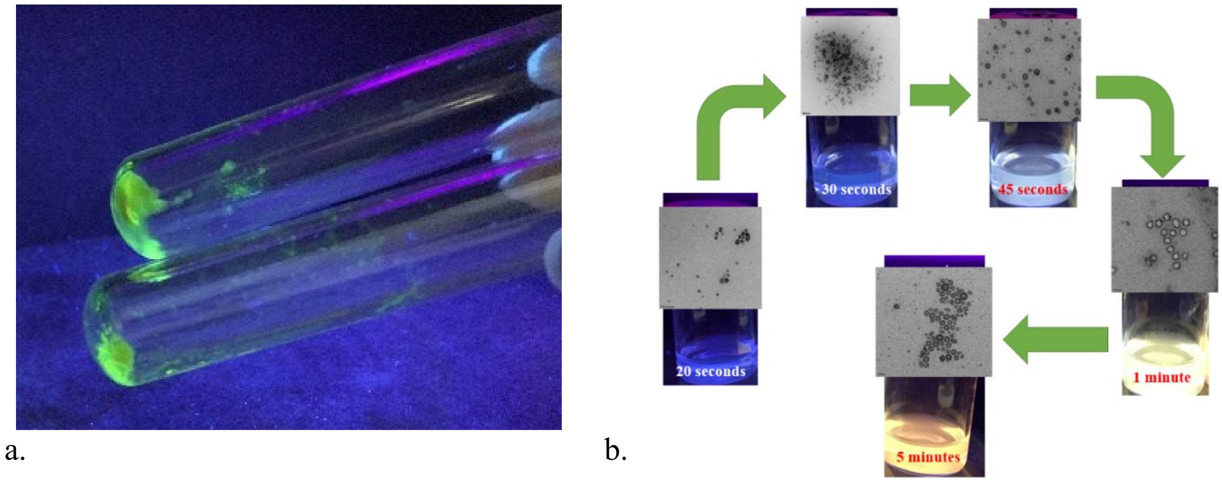


Figure S2. (a) The separated QNCs obtained through centrifugation as viewed under UV lamp. (b) Schematic depicting the formation of QRs over time. The time written corresponds to the time elapsed after the addition of Se precursor to the reaction mixture. The fluorescence (or lack of) observed under UV light corresponds to the different stages of the reaction procedure. The initial samples at 20 and 30 seconds do not emit any luminescence and the blue colour is from the UV lamp used to excite the samples. The sample at 45 seconds shows some luminescence but the intensity is considerably low to be recorded by the fluorometer.

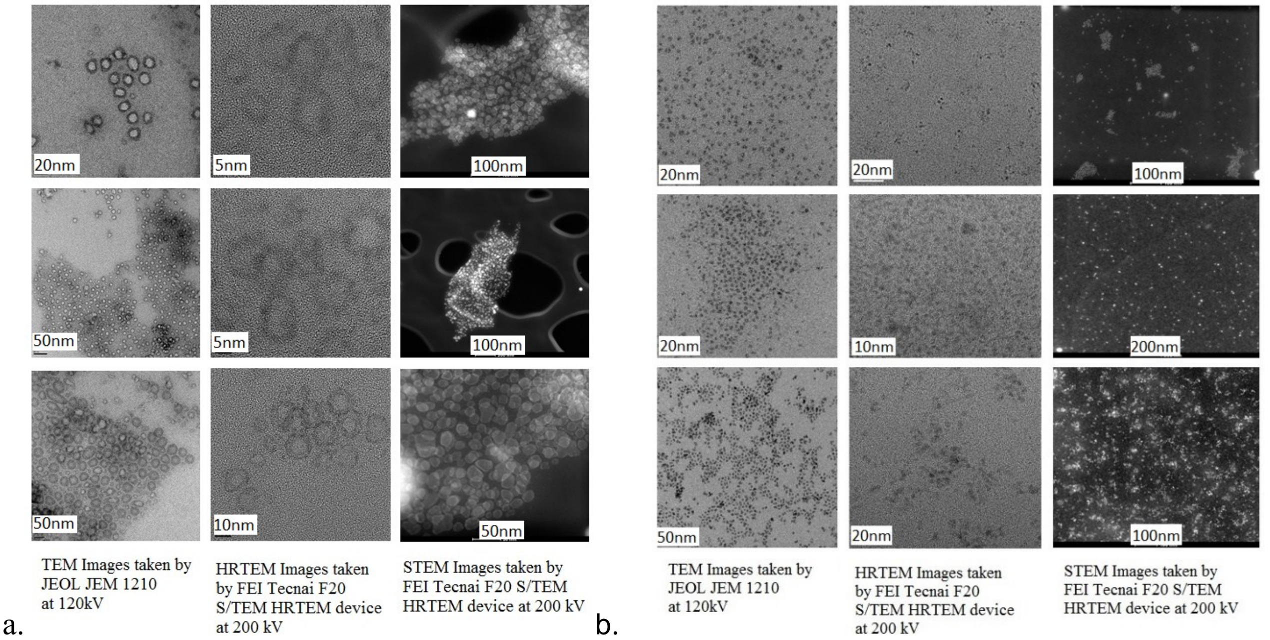


Figure S3 (a) TEM (left), HRTEM (centre) and STEM (right) images of the quantum rings are shown in the above figure. **(b)** TEM (left), HRTEM (centre) and STEM (right) images of the quantum dots are shown in the above figure.

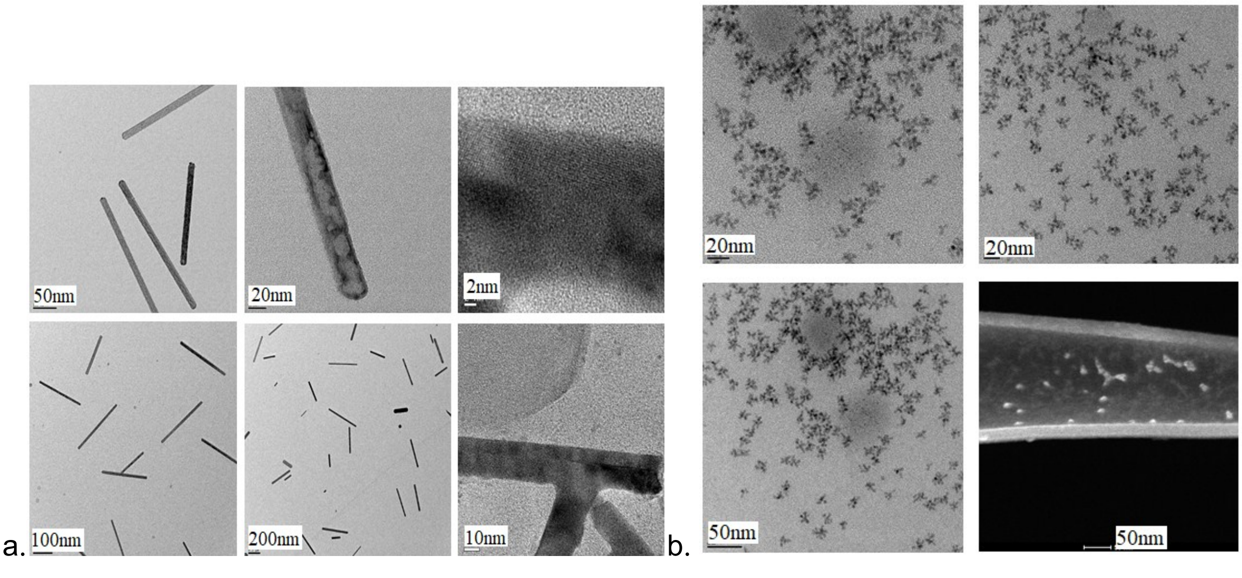


Figure S4: (a) TEM images (First two rows) and HRTEM images (Last row) of the QR_{ods} are shown in the above figure. **(b)** TEM (left top, bottom and right top), and STEM (right bottom) images of the QTDs are shown in the above figure. The QTDs have maintained their size over the period of three months as seen by the TEM images here.

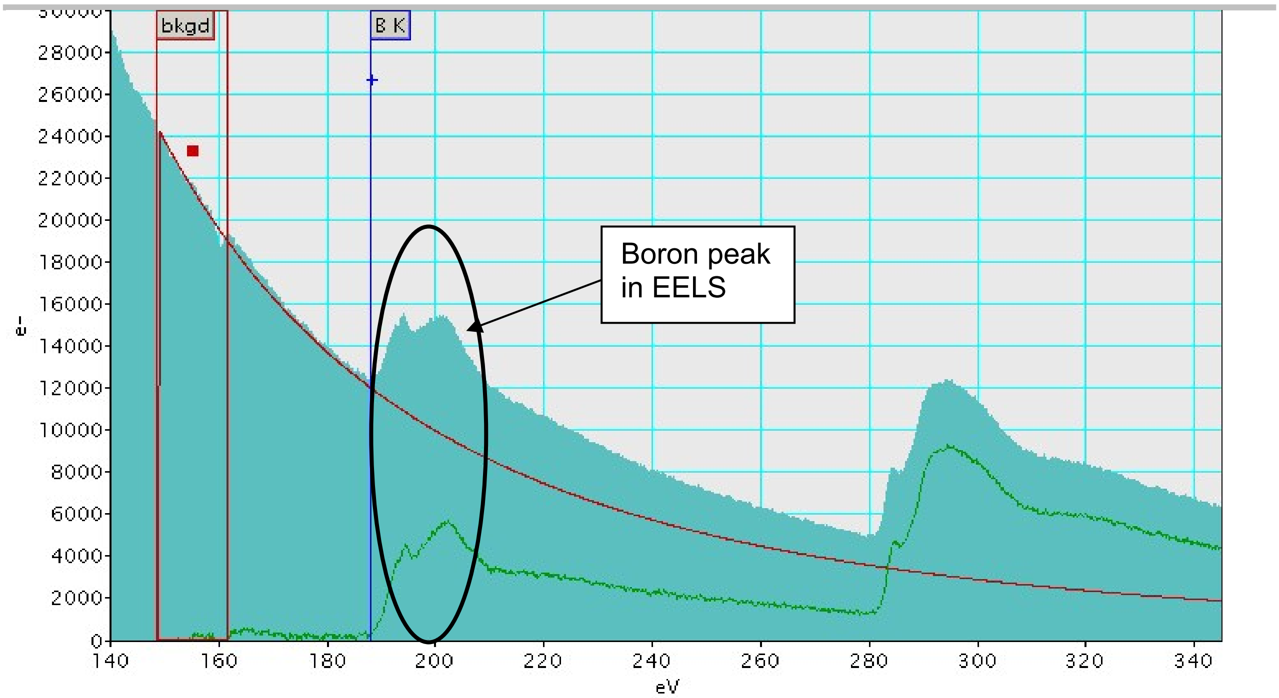


Figure S5: EELS of QRs with m-o-CarbSH. The EELS of the sample show the presence of boron in the sample thus proving that these rings are formed by the capping of m-o-CarbSH.

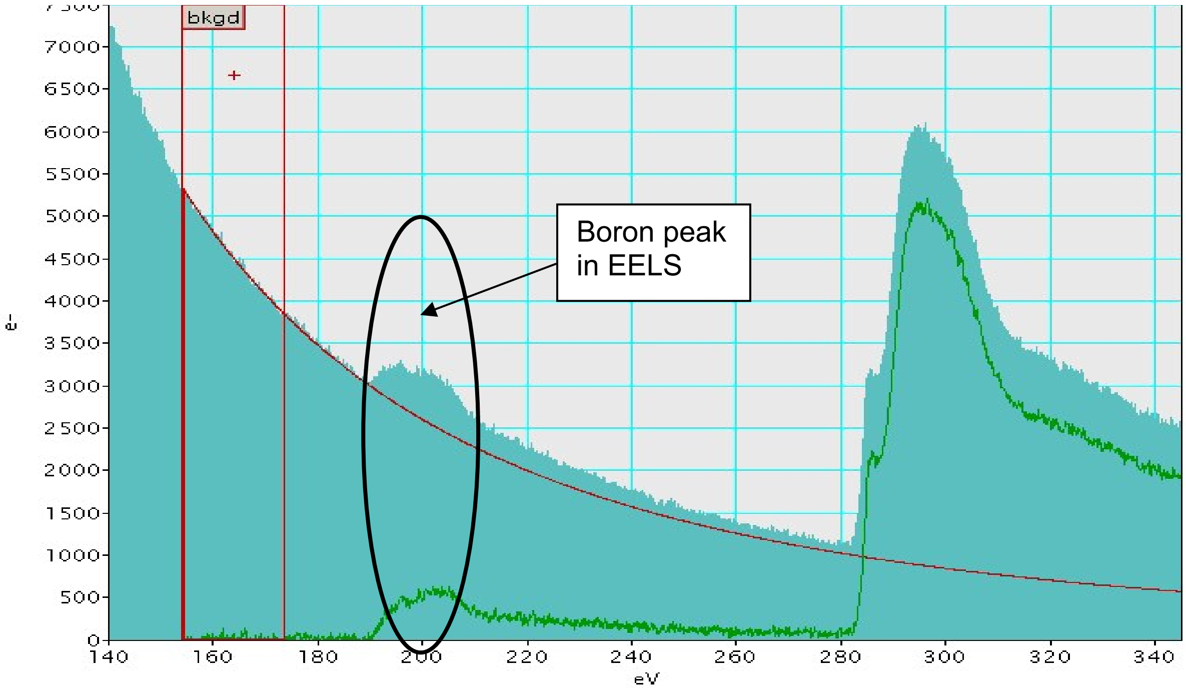


Figure S6: EELS of QR_{ods} with o-CarbSH. The EELS of the sample show the presence of boron in the sample thus proving that these rods are formed by the capping of o-CarbSH.

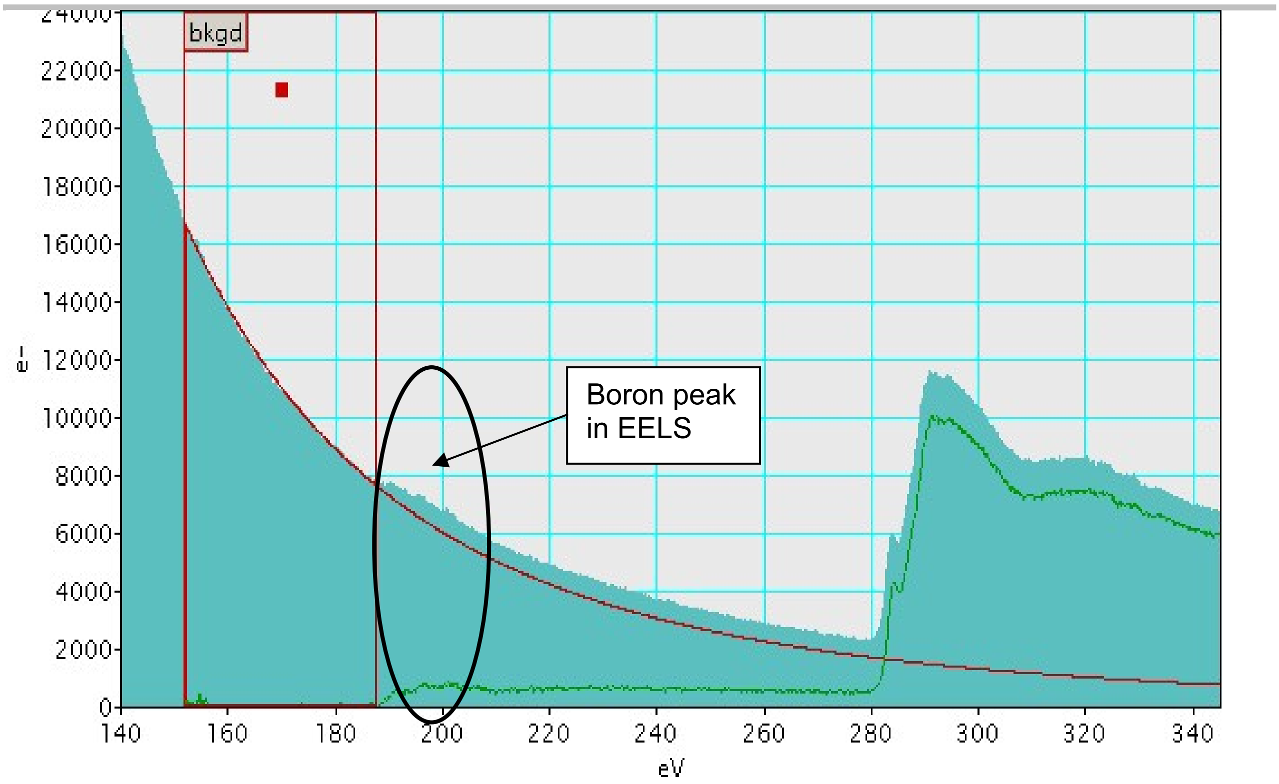


Figure S7: EELS of QDs with m-CarbSH. The EELS of the sample show the presence of boron in the sample thus proving that these dots are formed by the capping of m-CarbSH.

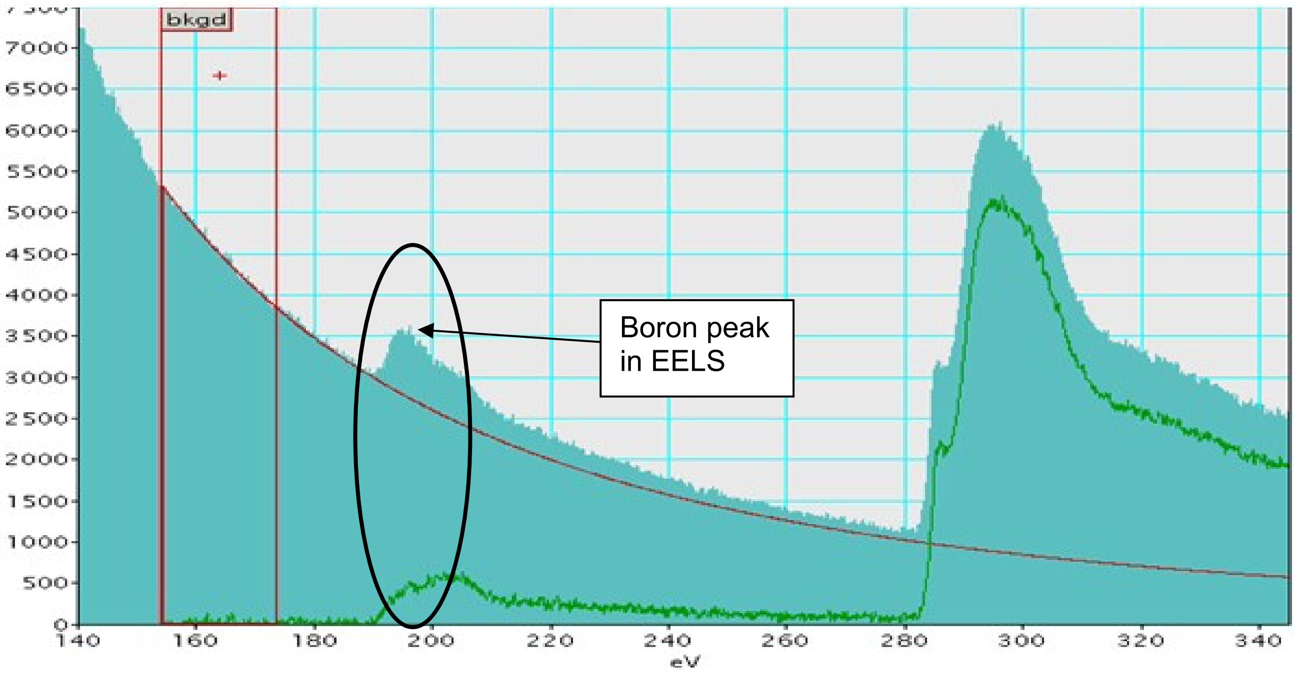


Figure S8: EELS of QTDs with m-CarbCarboxylic. The EELS of the sample show the presence of boron in the sample thus proving that these tetrapods are formed by the capping of m-CarbCarboxylic.

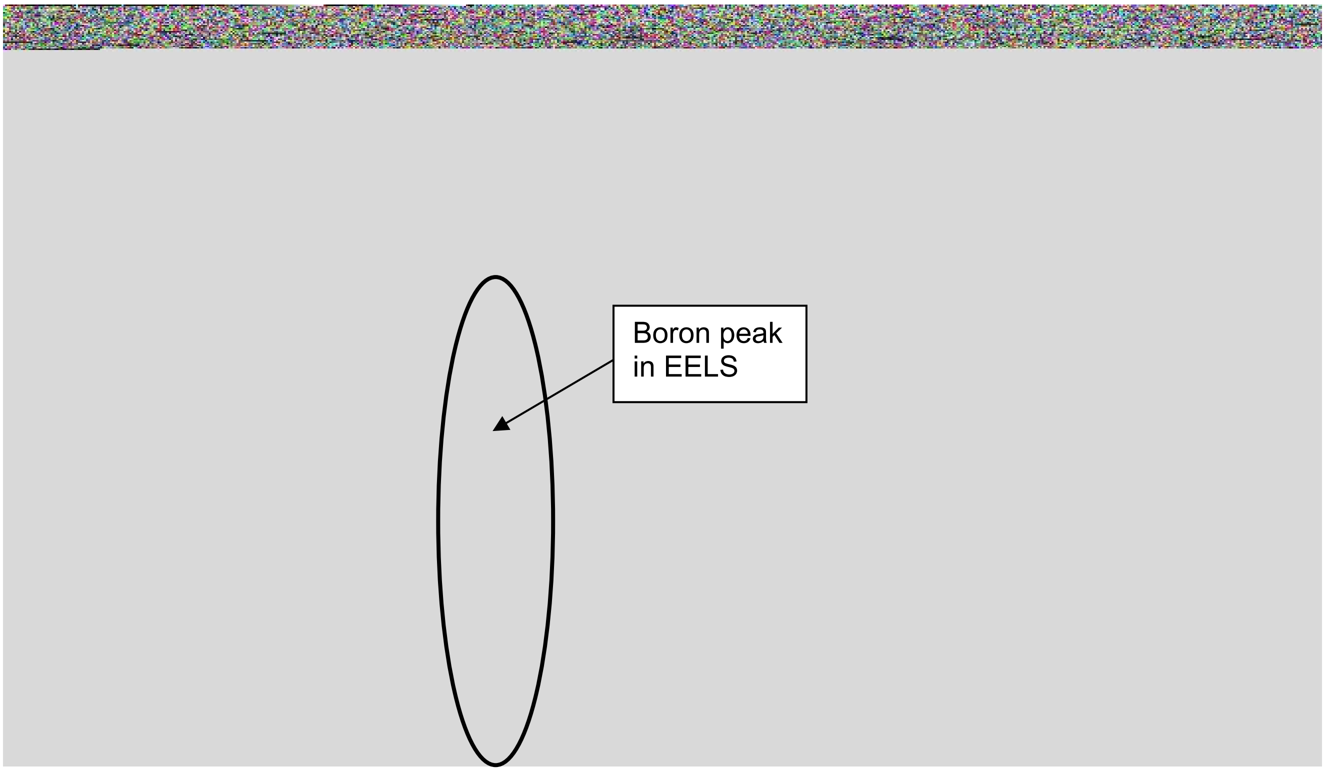


Figure S9: EELS of QR$_{ods}$ with m-Carbdithiol. The EELS of the sample show the presence of boron in the sample thus proving that these rods are formed by the capping of m-Carbdithiol.

. **Figure S10:** EELS of QRs with CarbPhos. The EELS of the sample show the presence of boron in the sample thus proving that these rings are formed by the capping of CarbPhos.

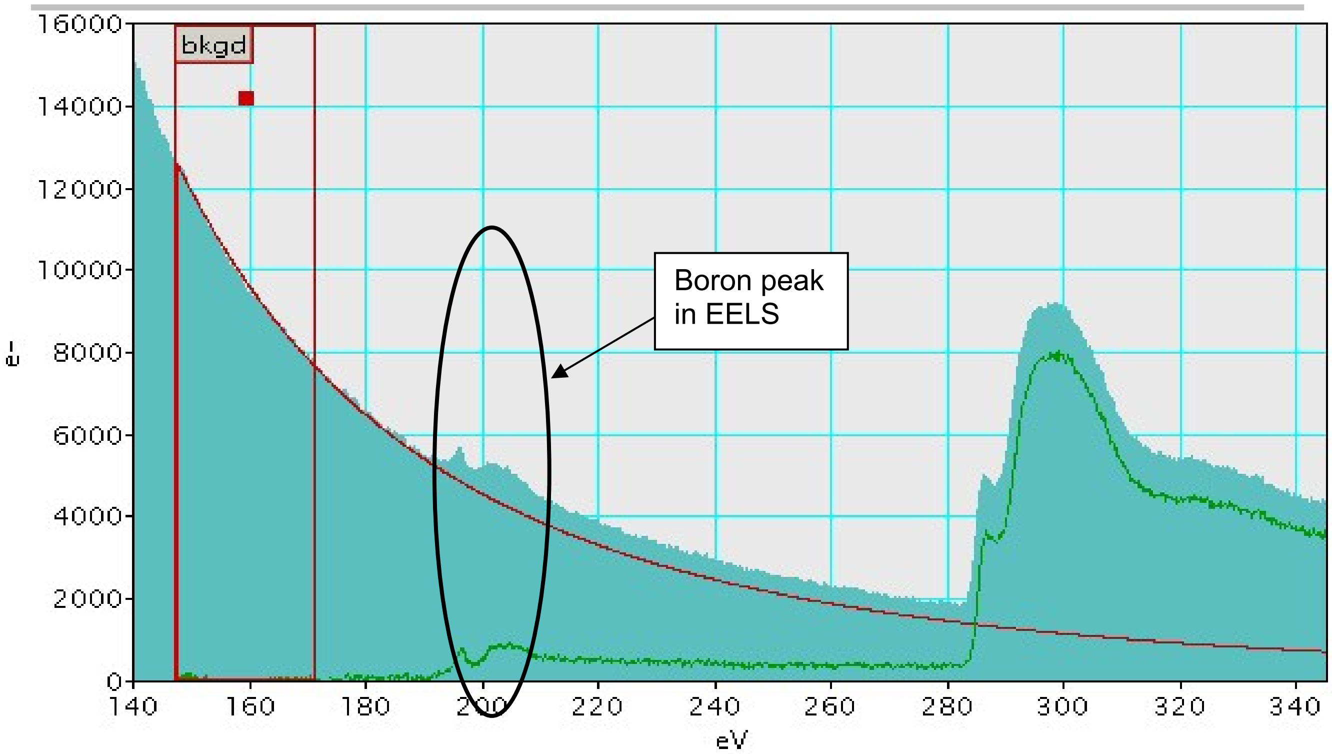


Figure S11: EELS of QRs with m-Carbdiphosphinic. The EELS of the sample show the presence of boron in the sample thus proving that these rings are formed by the capping of m-Carbdiphosphinic.

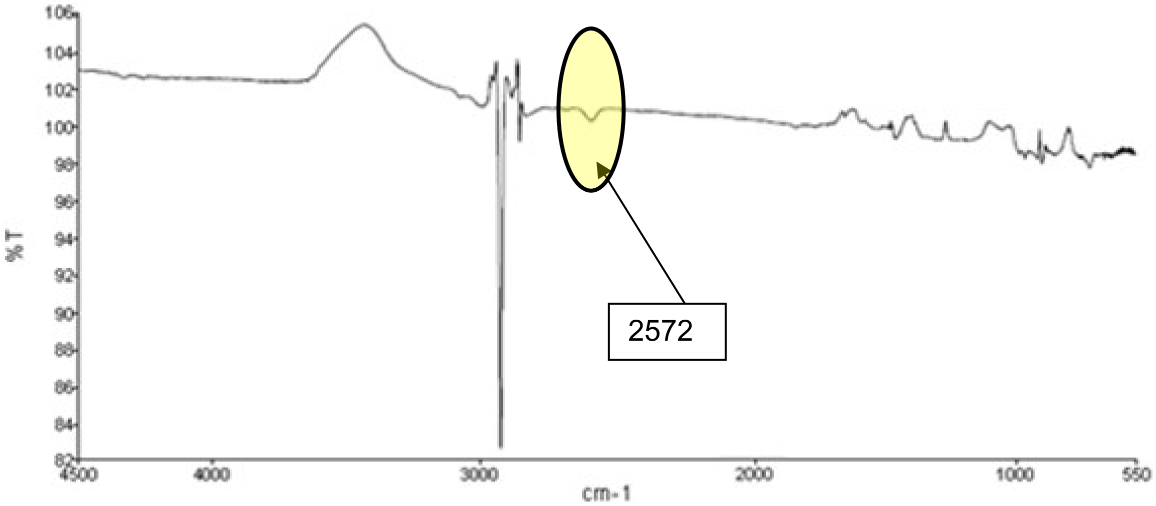


Figure S12 (a): Infrared Spectrum of QRs with m-o-CarbSH. The IR of the sample shows the B-H bond stretching from m-o-CarbSH used to cap QRs

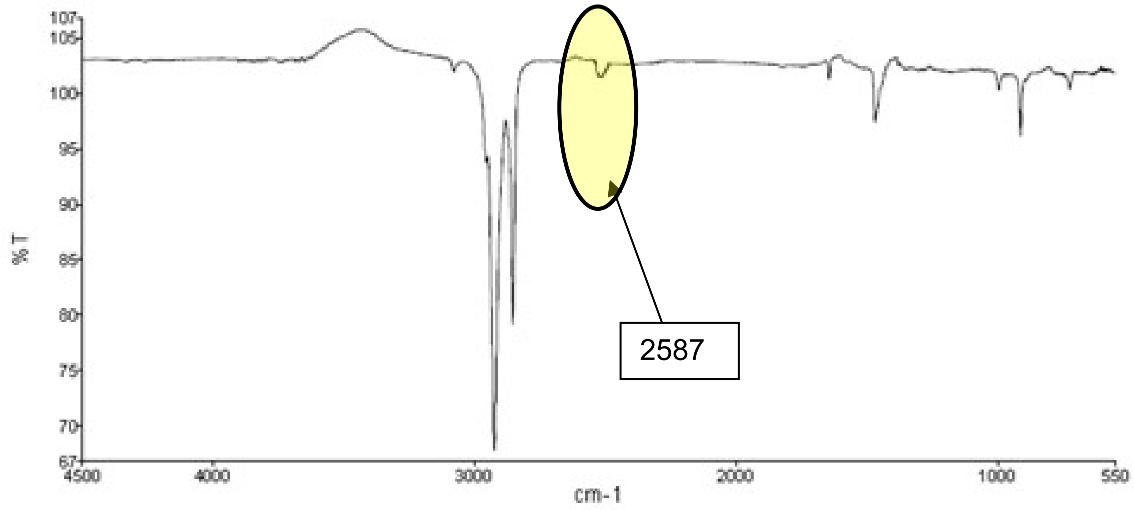


Figure S13: Infrared Spectrum of QR_{ods} with o-CarbSH. The IR of the sample shows the B-H bond stretching from o-CarbSH used to cap QR_{ods}.

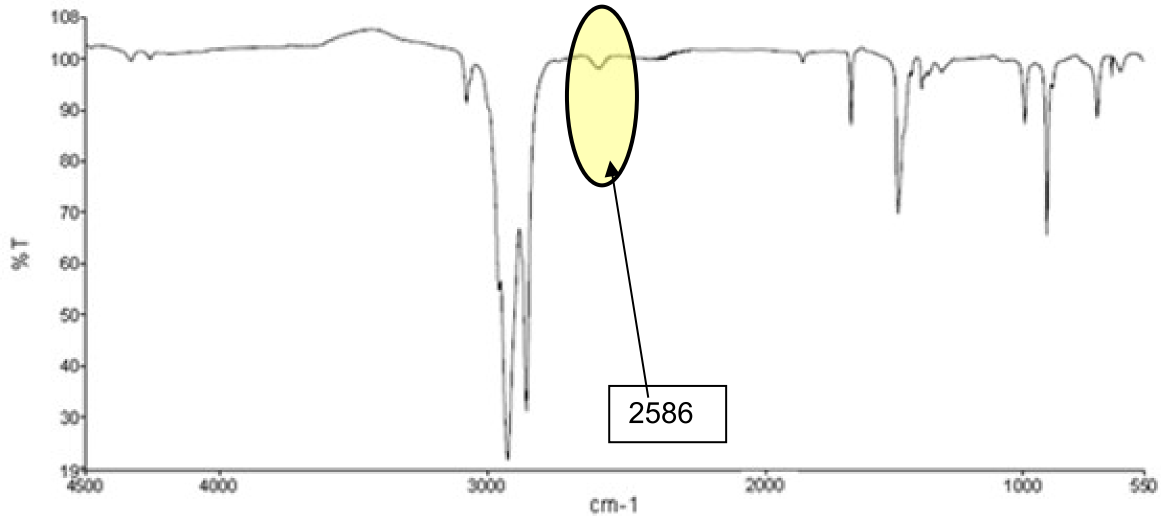


Figure S14: Infrared Spectrum of QDs with m-CarbSH. The IR of the sample shows the B-H bond stretching from m-CarbSH used to cap QDs.

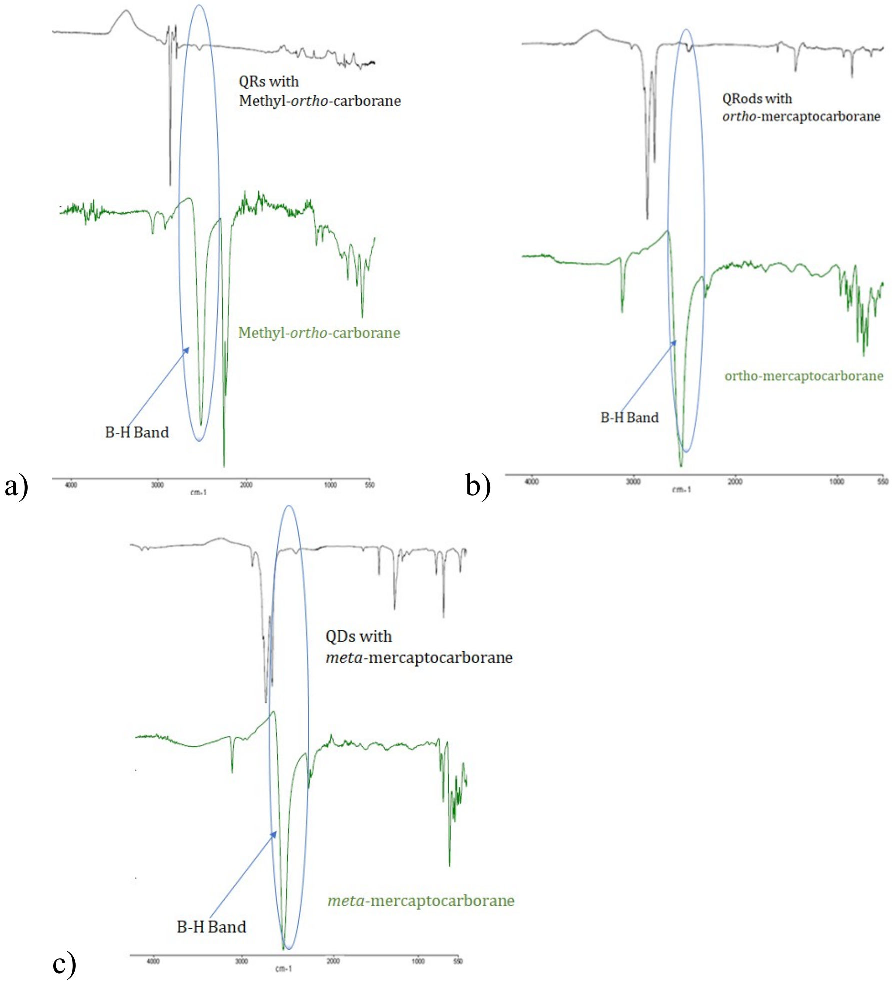
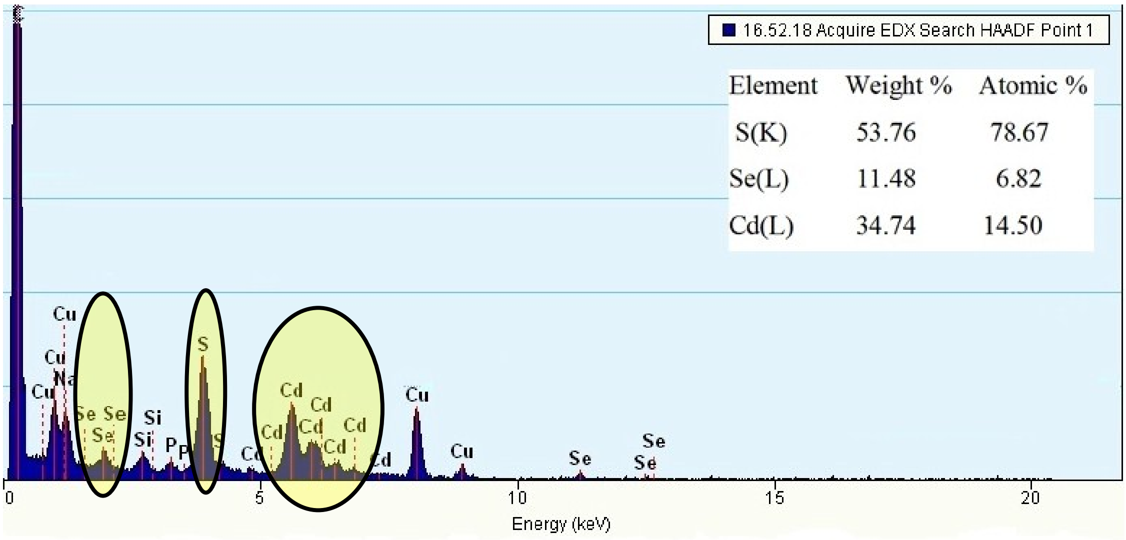
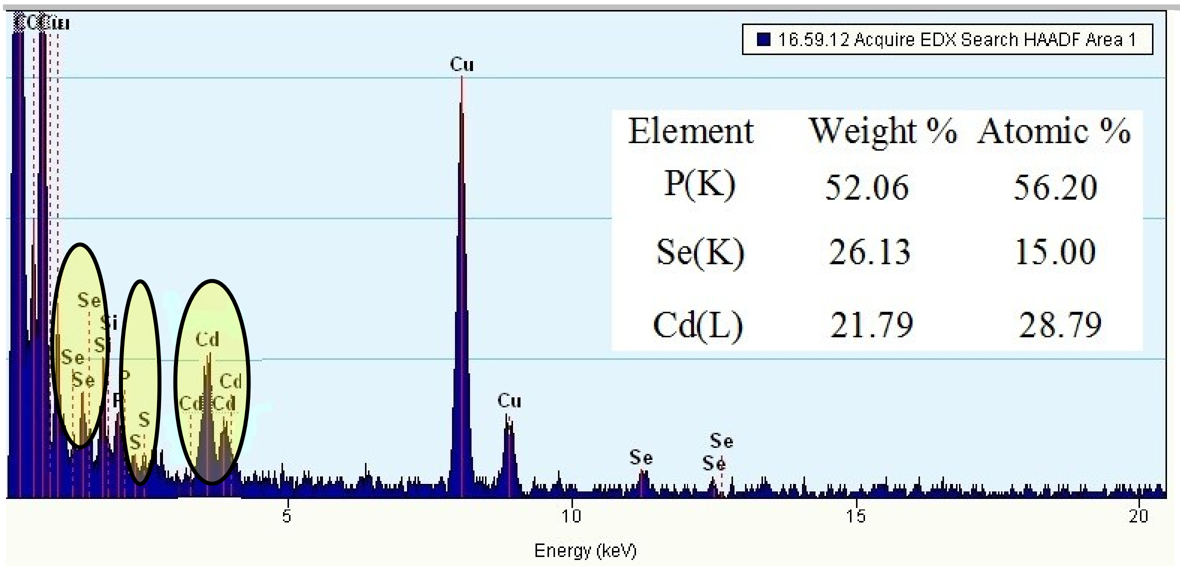


Fig. S15: (a)FTIR spectra of pristine ligand and QNCs capped with 1- methyl-2- *ortho*-carboranethiol. (b)FTIR spectra of pristine ligand and QNCs capped with *ortho*-carboranethiol.(c)FTIR spectra of pristine ligand and QNCs capped with *meta*- carbornaethiol.



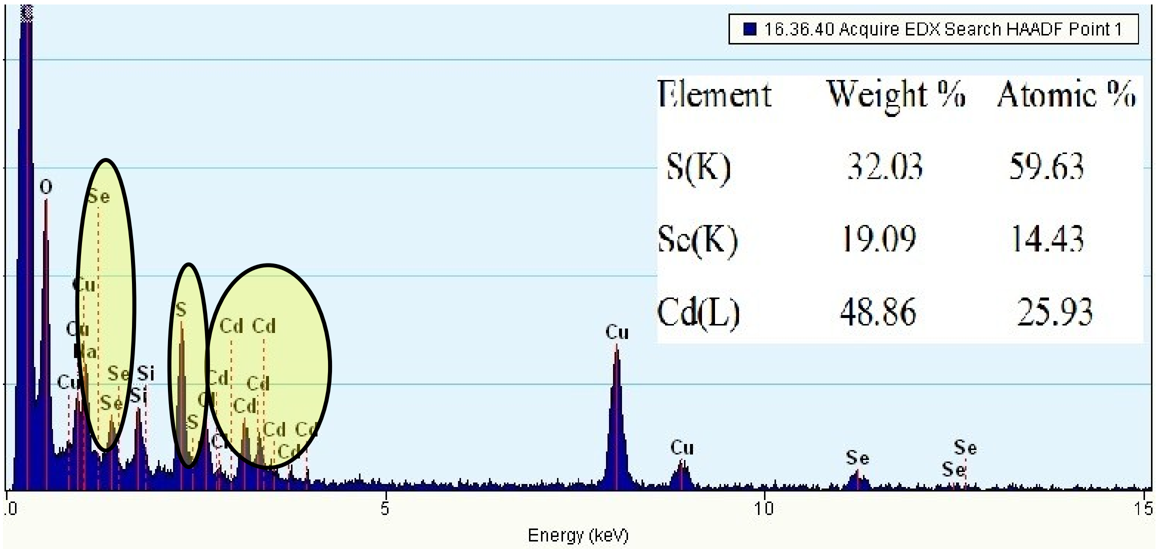
Element	Weight %	Atomic %
S(K)	53.76	78.67
Se(L)	11.48	6.82
Cd(L)	34.74	14.50

Figure S16: EDX of QRs with m-o-CarbSH. The EDX of the sample shows the ratio of Cd, Se and S present in the sample.



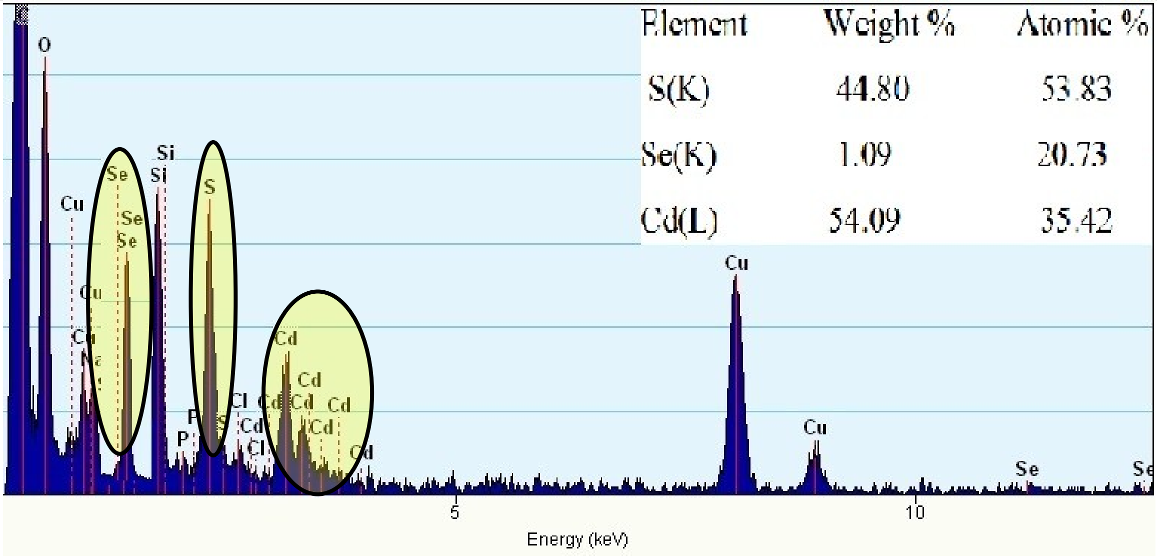
Element	Weight %	Atomic %
P(K)	52.06	56.20
Se(K)	26.13	15.00
Cd(L)	21.79	28.79

Figure S17: EDX of QRs with meta-CarbPhos. The EDX of the sample shows the ratio of Cd, Se and P present in the sample.



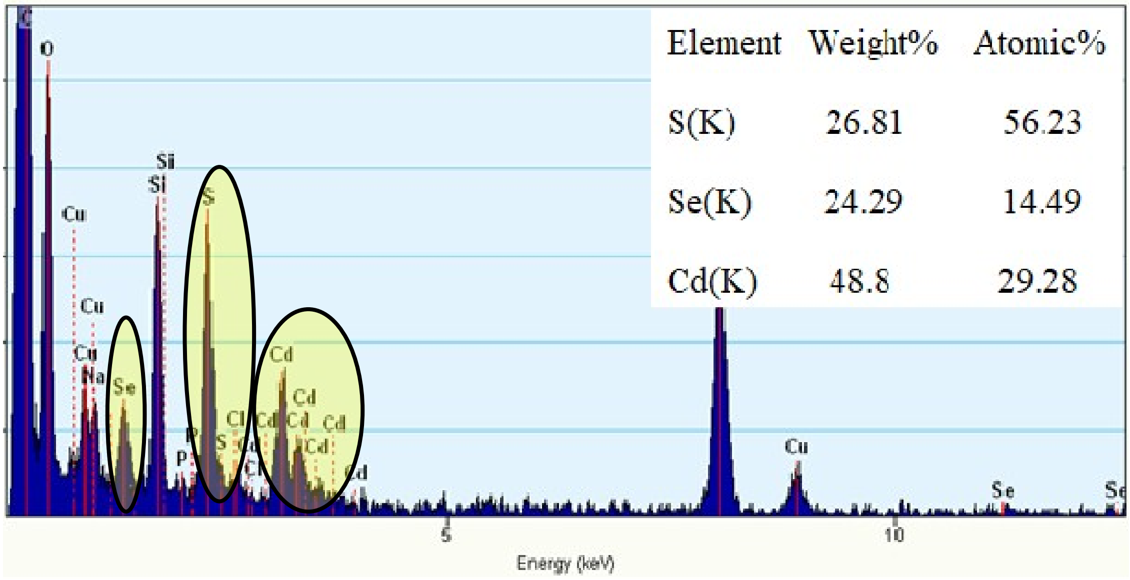
Element	Weight %	Atomic %
S(K)	32.03	59.63
Se(K)	19.09	14.43
Cd(L)	48.86	25.93

Figure S18: EDX of QR_{ods} with o-CarbSH. The EDX of the sample shows the ratio of Cd, Se and S present in the sample.



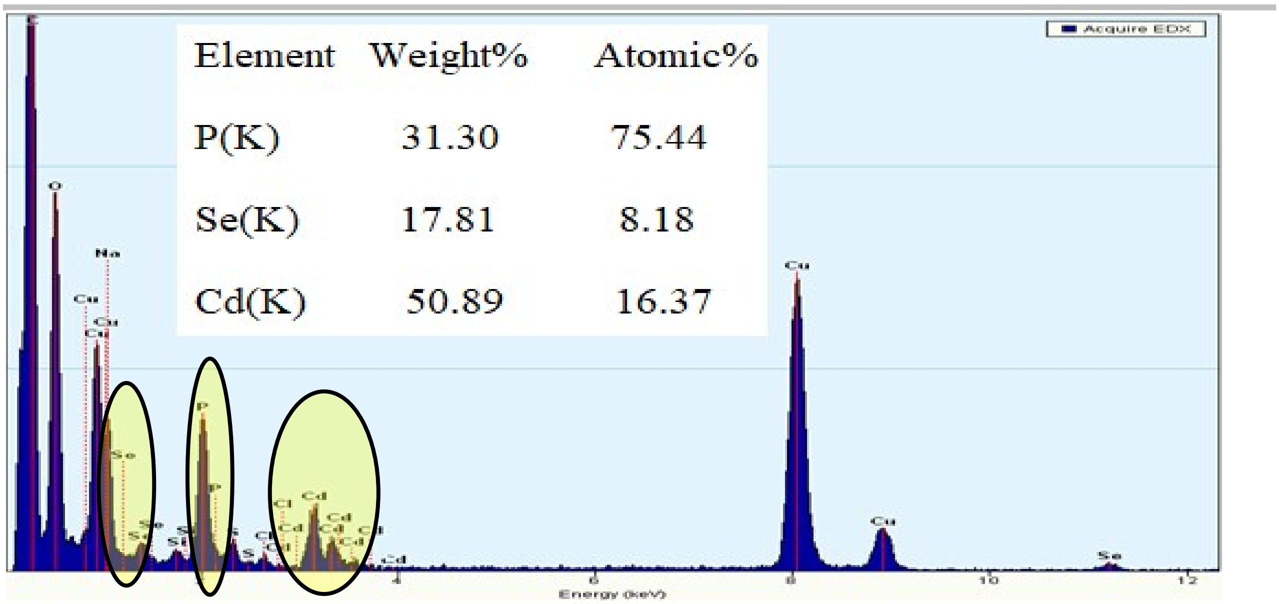
Element	Weight %	Atomic %
S(K)	44.80	53.83
Se(K)	1.09	20.73
Cd(L)	54.09	35.42

Figure S19: EDX of QDs with m-CarbSH. The EDX of the sample shows the ratio of Cd, Se and S present in the sample.



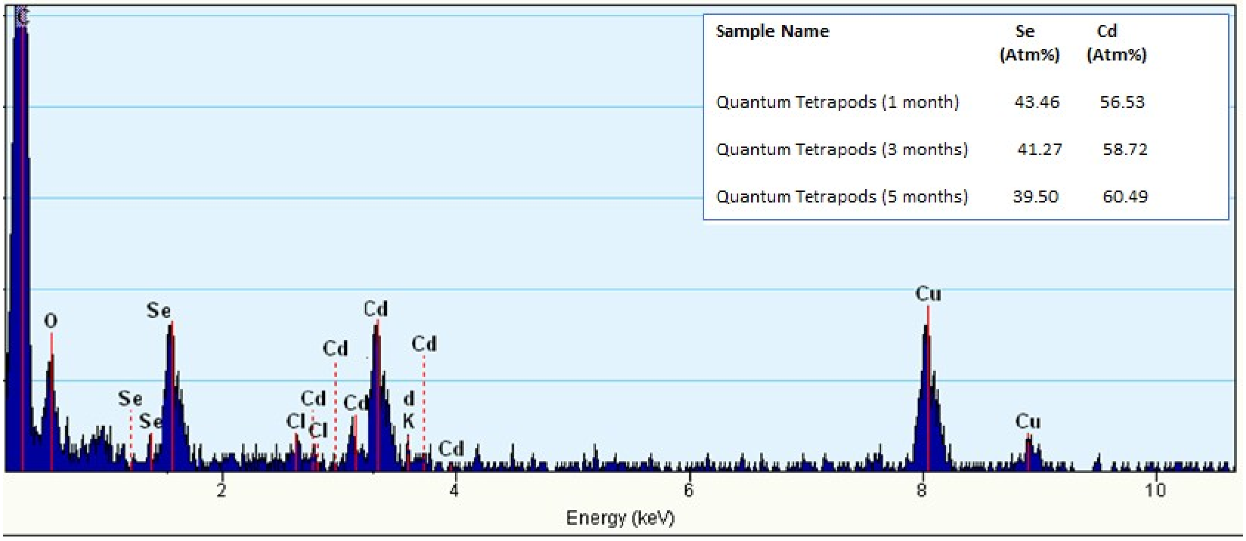
Element	Weight%	Atomic%
S(K)	26.81	56.23
Se(K)	24.29	14.49
Cd(K)	48.8	29.28

Figure S20: EDX of QR_{ods} with m-Carbdithiol. The EDX of the sample shows the ratio of Cd, Se and S present in the sample.



Element	Weight%	Atomic%
P(K)	31.30	75.44
Se(K)	17.81	8.18
Cd(K)	50.89	16.37

Figure S21: EDX of QRs with m-Carbdiphosphinic acid. The EDX of the sample shows the ratio of Cd, Se and P present in the sample.



Sample Name	Se (Atm%)	Cd (Atm%)
Quantum Tetrapods (1 month)	43.46	56.53
Quantum Tetrapods (3 months)	41.27	58.72
Quantum Tetrapods (5 months)	39.50	60.49

Figure S22: EDX of QTPs with m-CarbCarboxylic. The EDX of the sample shows the ratio of Cd and Se over different months and it remains almost comparable over the period of three months.

Sample Name	**Se (mg/l)**	**Cd (mg/l)**	**Molar ratio of Cd:Se**
Quantum Rings (QRs)	119	359	2.11:1
Quantum Dots (QDs)	112	340	2.13:1
Quantum Rods (QRods)	117	352	2.11:1
Quantum Tetrapods (QTDs)	121	312	1.81:1

Table S1: ICP-MS shows the ratio of Cd:Se in the samples to be around 2:1 for all the respective sample

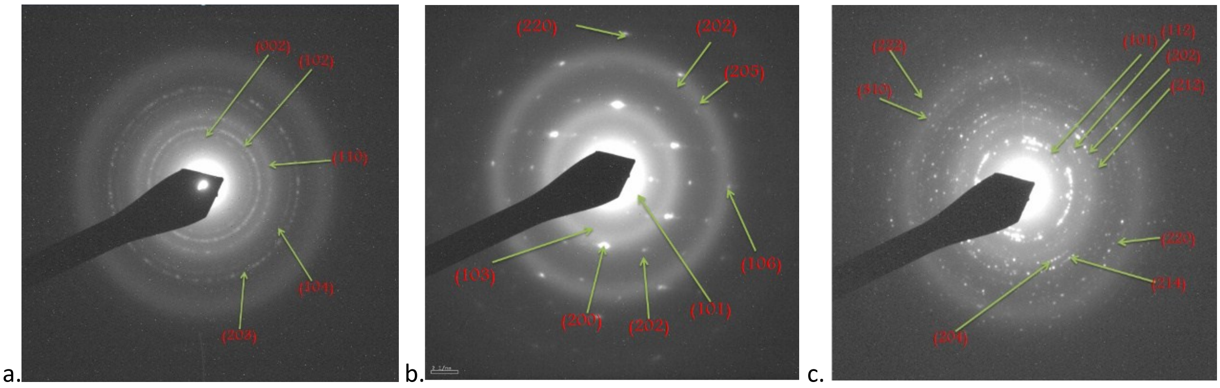


Figure S23: Electron diffraction of a) QRs capped with m-o-CarbSH, b) QR_{ods} capped with o-CarbSH and c) QDs capped with m-CarbSH. The electron diffraction pattern of the rods is more monocrystalline while that of the dots and rings are more polycrystalline. All confirm CdSe in hexagonal structure.

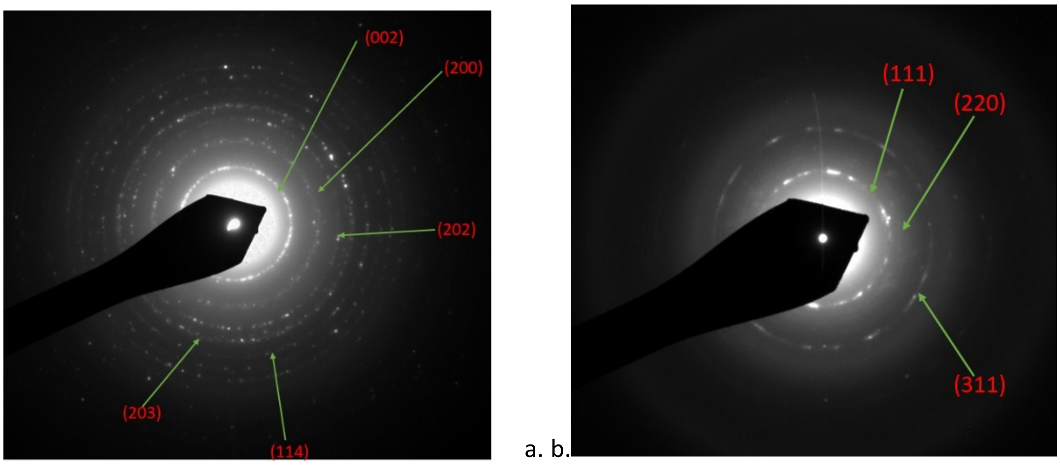


Figure S24: Electron diffraction of a) QTDs capped with m-CarbCarboxylic after 1 month confirms CdSe in hexagonal structure and b) QTDs capped with m-CarbCarboxylic after 5 months confirms CdSe in cubic structure. The diffraction pattern is polycrystalline in nature.

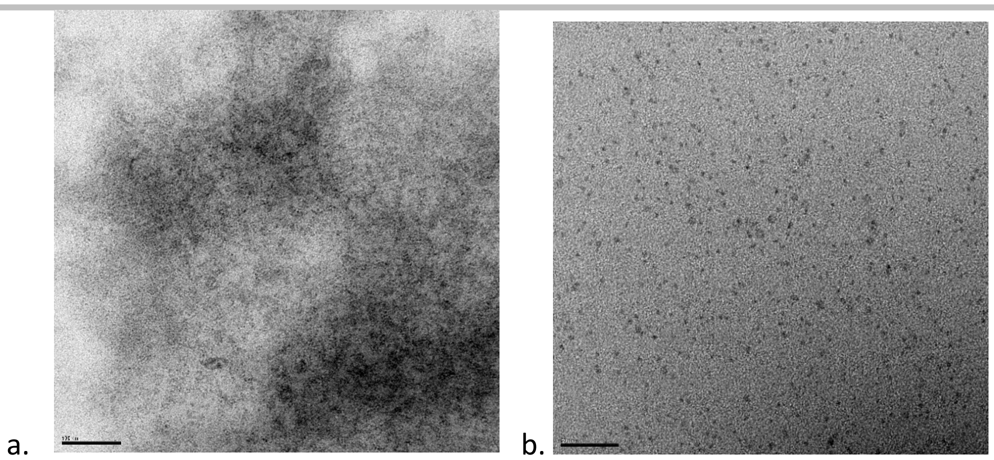


Figure S25: TEM images of QDs produced by 1-Adamantane thiol are shown here. The image on the left shows QDs produced without the temperature ramp. And the image on the right shows QDs are produced even when temperature ramp is done. No other QNCs were observed with temperature ramp using 1-Adamantane thiol.

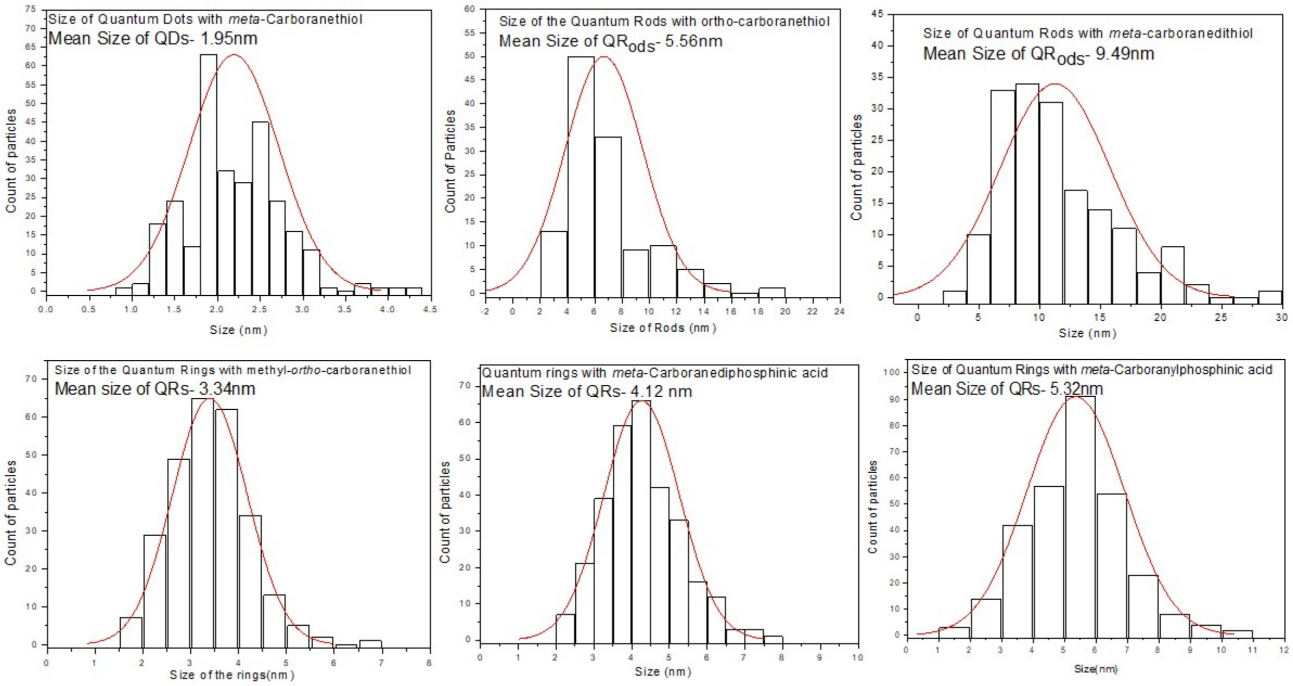
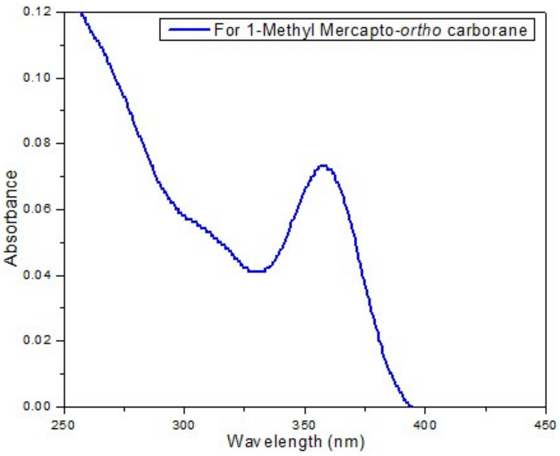


Figure S26. Gaussian size graphs of the QNCs made by different ligands.



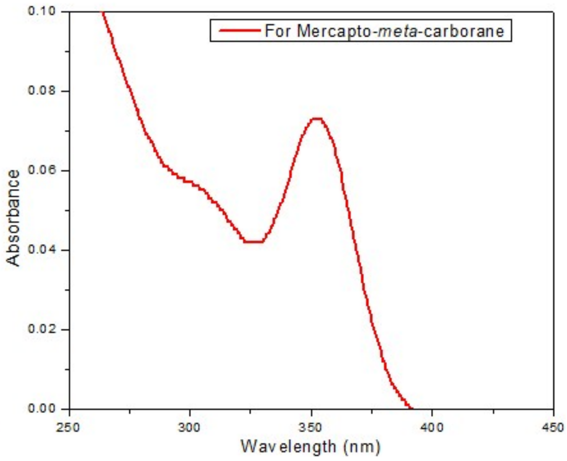


Figure S27: Absorption spectra (left) for Quantum rings formed by 1-methyl-mercapto-*ortho*-carborane and Absorption spectra (right) for Quantum dots formed by mercapto-*meta*-carborane.

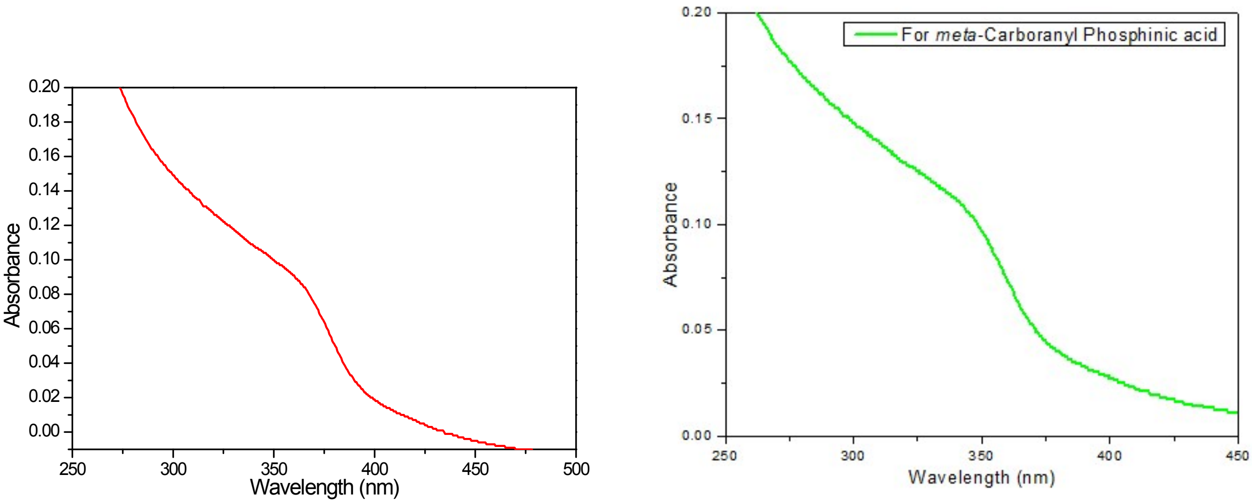


Figure S28: Absorption spectra (left) for Quantum rods formed by mercapto-*ortho*-carborane and Absorption spectra (right) for Quantum rings formed by carboranyl-*meta*-phosphinic acid.

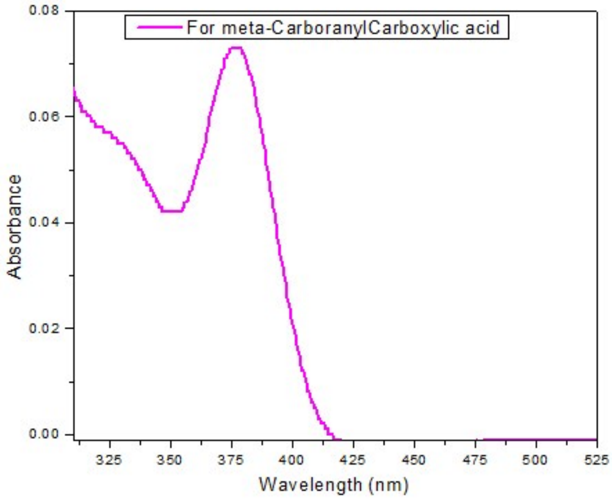


Figure S29: Absorption spectra for Quantum tetrapods formed by carboranyl-*meta*-carboxylic acid.

It is to be noted that with the size range, the absorption peak at around 360nm is difficult to imagine. We are not sure of the exact reason for this. One possible hypothesis revolves around the fact that the measured size contains the CdSe core along with the spherical ligands of carboranes. If we subtract the diameter the spherical carboranyl ligands which is 0.5nm (established from crystallographic data) and considering the thiol group it is 0.7nm, then from 3 or 4nm dimension we obtain a QD core of diameter of 1.6 or 2.6nm. The calculation is shown below:
3nm- (0.7x2)= 3nm-1.4nm=1.6nm
4nm- (0.7x2)= 4nm-1.4nm=2.6nm and so on
Now, for the QDs having a size range between 1-3nm are known to have an absorbance around 300nm to 400nm wavelength and perhaps that is why in these QDs we get to see the absorbance peak at this value.[2] Perhaps there could be other reasons as well due to which the absorbance is shifted to this range. But these types of QNCs with carboranyl capping have been produced for the first time and need further research to understand all the aspects of how these new spherical ligands affect the properties of these QNCs. Here we report the synthetic route that led us to obtain the different quantum nanostructures using these novel ligands. The detailed study about the consequence of the capping with these spherical ligands on the optical properties would need further study.

References

1. C. A. Ubani, M. Y. Sulaiman, Z. Ibarahim, N. B. Ibrahim and M.Y. Othman, *Journal of Modern Education Review*. 2011, **1,** 63.
2. [1]A. E. Vikraman, A. R. Jose, M. Jacob, K. G. Kumar, ***Anal. Methods***, 2015,**7**, 6791-6798.