Supporting Information

Transformations Among Colloidal Semiconductor Magic-Size Clusters

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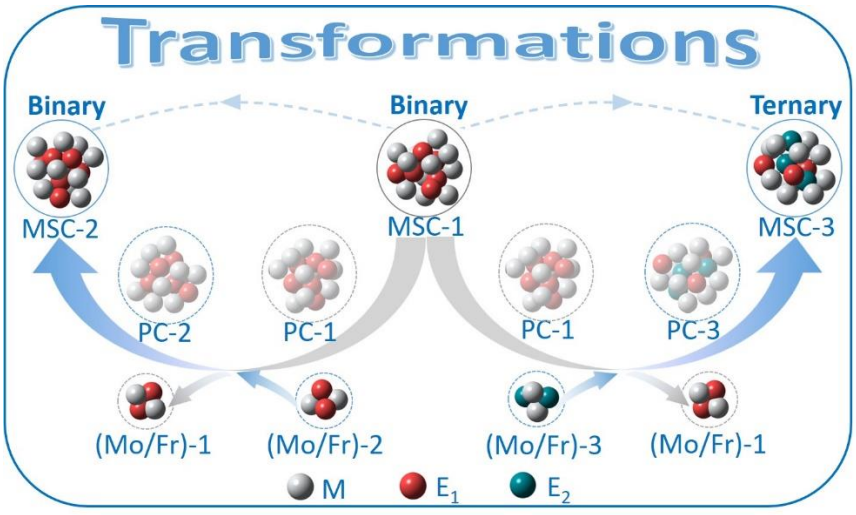

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Table S1. Summary of the acronyms used with their full names and explanations provided.

Acronym	Full name	Explanation
MSC	magic-size cluster	relatively stable, displaying sharp optical absorption
QD	quantum dot	zero-dimensional, with size-confinement effect
ME	metal chalcogenide	E = S, Se, Te
IP	induction period	prior to the nucleation and growth of QDs
PC	precursor compound	proposed to be a MSC counterpart, with no absorption at the absorption position of the MSC, existing in one IP sample usually
Mo/Fr	monomer/fragment	while a fragment is larger, a monomer was proposed to be M_2E_n, where n = 1 (Cu), 2 (Cd, Zn, Pb, Ge), 3 (In) they form via the reaction of M and E precursors or via PC fragmentation
--	quasi isomer	a concept proposed for a group of MSCs and their corresponding PCs (including as-synthesized and immediate ones); they have similar core compositions, slightly different configurations, and probably different (surface) ligands. While isomers usually refer to molecules with one identical molecular formula but different atomic arrangements, we have to point out unambiguously that for the PCs and MSCs, their composition information has not been obtained. MALDI-TOF-MS has been applied to study CdS PCs and MSCs, demonstrating that the PCs have a quite similar mass as their counterpart MSCs (Table S4).
--	counterpart	to describe corresponding PCs and MSCs.

Table S2. Summary of the key advance on the syntheses of binary semiconductor MSCs via either one-step (Refs 1 to 8) or two-step (Refs 9 to 11) approaches.

Ref, Year, Journal	Comment
[1] 1984, *88*, 969−977 Ber. Bunsenges. Phys. Chem.	CdS MSCs identified, including MSC-322 the term "magic agglomeration numbers" used
[2] 2002, *124*, 3343−3353 *J. Am. Chem. Soc.*	CdSe MSC-349 claimed as common nuclei for CdSe nanocrystals.
[3] 2004, *3*, 99−102 *Nat. Mater.*	CdSe MSC-415 with 1Cd to 1Se stoichiometry a core-cage structure of $(CdSe)_n$, n = 33, 34
[4] 2007, *19*, 548−552 *Adv. Mater.*	CdSe MSCs, with sharp absorption peaking at 330, 350-360, 384, 406, and 431 nm due to size growth
[5] 2008, *112*, 13805−13811 *J. Phys. Chem. C*	three types of CdSe MSCs, sharp absorption doublet and bandedge photoluminescence (PL)
[6] 2011, 7, 2250−2262 *Small*	PbSe MSCs with sharp absorption peak red shifting due to size growth
[7] 2014, *136*, 10645−10653 *J. Am. Chem. Soc.*	Non-stoichiometry CdSe clusters, sharp absorption peaking at 350, 380, and 408 nm, pyramidal structures
[8] 2015, *27*, 1432−1441 Chem. Mater.	InP MSCs sharp absorption peaking at 386 and 397 nm
[9] 2017, *8*, 15467 *Nat. Commun.*	CdTe MSCs sharp absorption peaking at 371, 417, and 448 nm the concept of the PC $\Rightarrow$ MSC transformation proposed
[10] 2017, *29*, 5727−5735 *Chem. Mater.*	CdS MSCs, sharp absorption peaking at 311 nm the concept of the PC $\Rightarrow$ MSC transformation proposed
[11] 2018, *30*, 1575−1584 *Chem. Mater.*	CdSe MSCs, sharp absorption doublet and bandedge photoluminescence (PL); similar optical static features demonstrated for 0D clusters and their self-assembled corresponding 2D platelets

Note: Semiconductor clusters can serve as building blocks or single-source precursors for advanced materials. Semiconductors have been widely used, such as in solar cells and light emitting diodes, and photocatalysis.

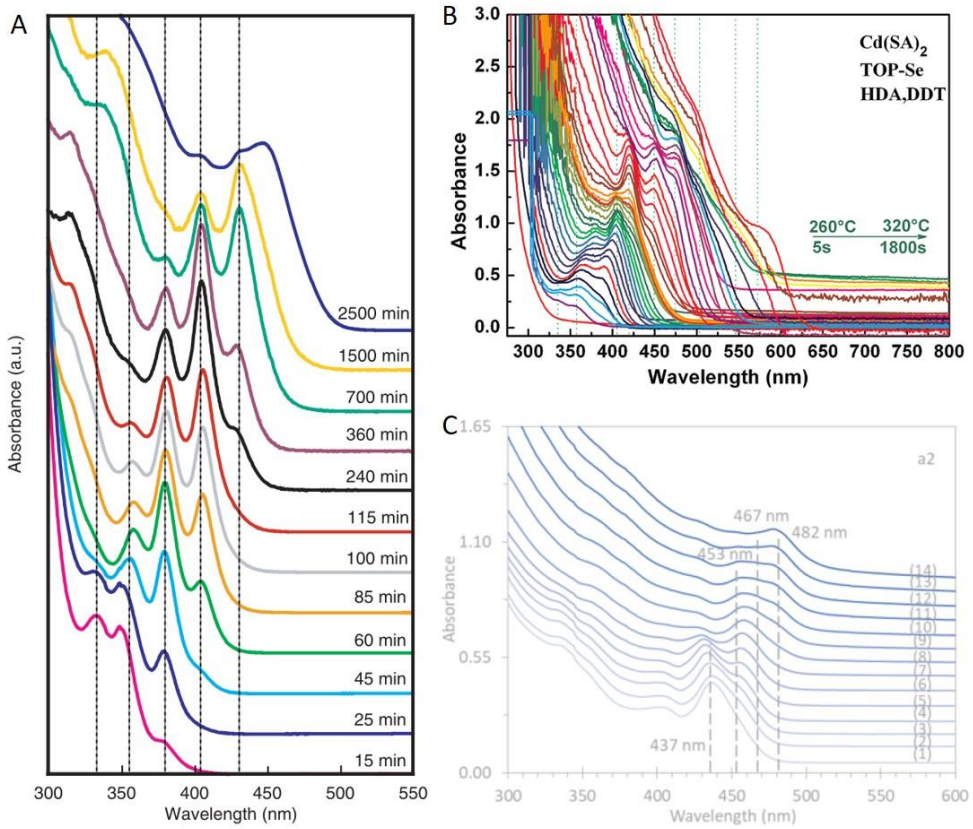


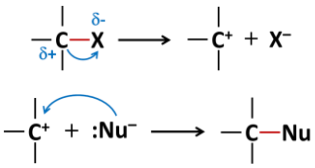
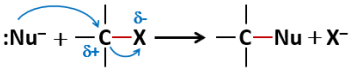
Figure S1. Temporal evolution of optical absorption properties from three reactions batches.[1-3] The redshift of the absorption peak positions has been attributed to size growth of these CdSe MSCs. (A) Fig 1 dealing with the reaction of a Cd precursor (made from CdO and dodecylamine and nonanoic acid) and SeTOP at constant temperature of 80 °C.[1] (B) Fig 8 concerning the reaction of $Cd(SA)_2$ + SeTOP in the temperature (period) of 260 (5 s) to 320 °C (1800 s). SA = stearic acid.[2] (C) Fig S4-3 addressing the reaction of $Cd(OA)_2$ + Se + $HPPh_2$ at 195 °C for 10 s (1), 2 (2), 4 (3), 6 (4), 8 (5), 10 (6), 15 (7), 20 (8), 30 (9), 45 (10), 60 (11), 90 (12), 120 (13), and 150 min (14). OA = oleic acid.[3] The present Account does not address this group but another group of MSCs, which are transformed from their counterpart PCs, such as CdSe MSC-415 (in Table S2 Ref 3).

(1) Kudera, S.; Zanella, M.; Giannini, C.; Rizzo, A.; Li, Y.; Gigli, G.; Cingolani, R.; Ciccarella, G.; Spahl, W.; Parak, W. J.; Manna, L. Sequential Growth of Magic-Size CdSe Nanocrystals. *Adv. Mater.* **2007**, *19*, 548−552.

(2) Sun, M.; Yang, X. Phosphine-Free Synthesis of High-Quality CdSe Nanocrystals in Noncoordination Solvents: "Activating Agent" and "Nucleating Agent" Controlled Nucleation and Growth. *J. Phys. Chem. C* **2009**, *113*, 8701−8709.

(3) Li, L.; Zhang, M.; Rowell, N.; Kreouzis, T.; Fan, H.; Yu, Q.; Huang, W.; Chen, X.; Yu, K. Identifying Clusters and/or Small-Size Quantum Dots in Colloidal CdSe Ensembles with Optical Spectroscopy. *J. Phys. Chem. Lett.* **2019**, *10*, 6399−6408.

Table S3. In-depth explanation of the pathway for the inter-molecular reaction proposed (Equations 1 and 2 in the main text).

Pathway	Organic chemical reaction	PC-1 to PC-2 intermolecular reaction
S_N1		PC-1—(Mo/Fr)-1 ⟶ PC-1 + (Mo/Fr)-1 PC-1 + (Mo/Fr)-2 ⟶ PC-2—(Mo/Fr)-2
S_N2		(Mo/Fr)-2 + PC-1—(Mo/Fr)-1 ⟶ PC-2—(Mo/Fr)-2 + (Mo/Fr)-1

In 1935, two reaction mechanisms were proposed, S_N1 and S_N2. S stands for chemical substitution, N for nucleophilic, and the number for the kinetic order of the reaction.[1]

For a S_N1 reaction, the carbocation forms first and is then attacked by a nucleophile. The first step of the dissociation of the leaving group from the substrate is rate-determining. Similarly, for a PC to PC transformation displaying a first-order reaction kinetics, we hypothesize that the group of CdE (Mo/Fr)-1 leaves the substrate CdE PC-1 first, which is rate-determining, and the addition of the substituent CdE (Mo/Fr)-2 to result in CdE PC-2 occurs.

For a S_N2 reaction, a nucleophile attacks the carbon atom of the substrate first and then the leaving group departs from the substrate. The first step of the addition is rate-determining. Correspondingly, for a PC to PC transformation without a first-order reaction kinetics, we hypothesize that the addition of the substituent CdE (Mo/Fr)-2 to the substrate CdE PC-1 takes place first and is rate-determining; then, the CdE (Mo/Fr)-1 group leaves to result in CdE PC-2.

(1) J. P. Clayden, N. Greeves, S. Warren, P. D. Wothers, *Organic Chemistry*, Oxford University Press, Oxford, UK, **2001**.

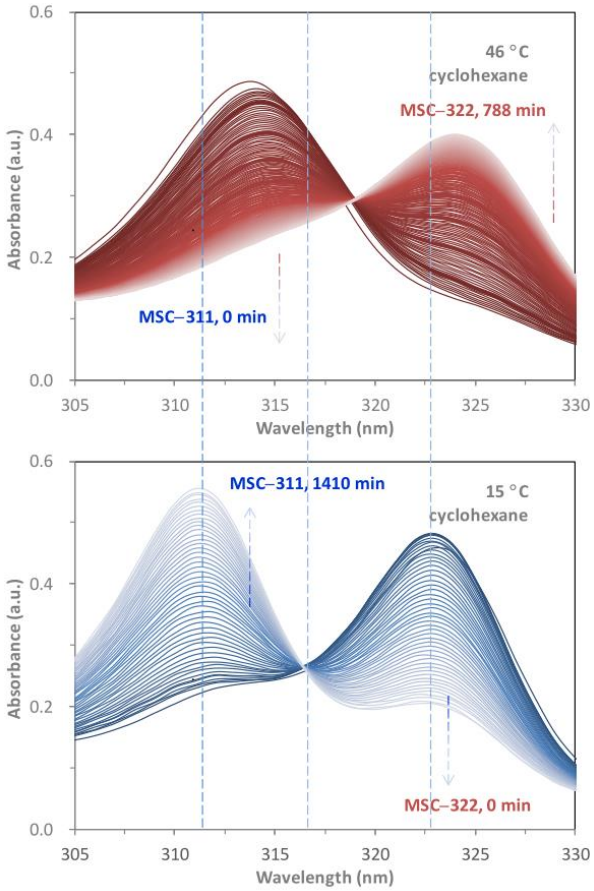


Figure S2. Expanded views in the range of 305 to 330 nm of Figures 1a and 1b. As indicated by the three vertical dashed lines, the absorption peak positions of CdS MSC-311 and MSC-322 are affected by temperature. Thus, it is easy to understand that the position of the isosbestic point changes as well with temperature, which are at about 319 nm at 46 °C (top) and at 316 nm at 15 °C (bottom).

Note S1. Additional discussion of the rate-determining step

For the MSC-311 to MSC-322 transformation, the barrier energy was about 276.8 kJ • mol^{-1} in toluene and 269.3 kJ • mol^{-1} in cyclohexane, while the transformation occurred slower in the former dispersion. Although the dissociation energy of the Cd–O and Cd–S bonds are respectively 236 ± 84 and 208.5 ± 20.9 kJ/mol,[1] the similar value of the energy barrier had guided us to propose that the rate-determining step involves the breaking of the Cd–S bond.[2] This is in agreement with the PC-enabled transformation model shown in Scheme 1. It is still challenging to provide a conclusive answer about the change of the surface ligand (–Cd–O bonds) during the whole MSC-311 to MSC-322 transformation.

(1) Haynes, W. M. *CRC Handbook of Chemistry and Physics*. **2017**; p 9-74 CRC Press: Boca Raton 97 ed.

(2) Zhang, B.; Zhu, T.; Ou, M.; Rowell, N.; Fan, H.; Han, J.; Tan, L.; Dove, M. T.; Ren, Y.; Zuo, X.; Han, S.; Zeng, J.; Yu, K. Thermally-Induced Reversible Structural Isomerization in Colloidal Semiconductor CdS Magic-Size Clusters. *Nat. Commun.* **2018**, *9*, 2499.

Table S4. Summary of the MALDI-TOF MS characterization of CdS PCs and MSCs.

Species	Preparation	Matrix	*m* *(z = 1)*	Ref
CdS PC-311	180 °C/20 min in toluene	DCTB	5166.7 Da	1
CdS MSC-311	180 °C/20 min 3-day storage then in toluene	DCTB	5166.7 Da	1
CdS MSC-311	180 °C/20 min 4 °C stored 20 h then in toluene	DCTB or CHCA	5160 Da	2
CdS MSC-322	180 °C/20 min 60 °C stored 20 h then in toluene	DCTB or CHCA	5160 Da	2
CdS PCs	160 °C/30 min in toluene	DHAP	4855 Da 5008 Da	3

DCTB: trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene] malononitrile
CHCA: α-Cyano-4-hydroxycinnamic acid
DHAP: 2-6-Dihydroxyacetophenone

(1) Zhu, T.; Zhang, B.; Zhang, J.; Lu, J.; Fan, H.; Rowell, N.; Ripmeester, J. A.; Han, S.; Yu, K. Two-Step Nucleation of CdS Magic-Size Nanocluster MSC-311. *Chem. Mater.* **2017**, *29*, 5727−5735.

(2) Zhang, B.; Zhu, T.; Ou, M.; Rowell, N.; Fan, H.; Han, J.; Tan, L.; Dove, M. T.; Ren, Y.; Zuo, X.; Han, S.; Zeng, J.; Yu, K. Thermally-Induced Reversible Structural Isomerization in Colloidal Semiconductor CdS Magic-Size Clusters. *Nat. Commun.* **2018**, *9*, 2499.

(3) Li, L.; Zhang, J.; Zhang, M.; Rowell, N.; Zhang, C.; Wang, S.; Lu, J.; Fan, H.; Huang, W.; Chen, X.; Yu, K. Fragmentation of Magic-Size Cluster Precursor Compounds into Ultrasmall CdS Quantum Dots with Enhanced Particle Yield at Low Temperatures. *Angew. Chem. Int. Ed.* **2020**, *59*, 12013−12021.

Note S2. Additional discussion of MS

It was reported that both CdSe bulk and CdSe nanoparticles prepared in reverse micelles (referred to as MSC-415 in Table S2) produced similar $(CdSe)_n$ clusters by a time-of-flight mass spectrometer, where n = 13, 33, and 34.[1]

Afterwards, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) demonstrated the coexistence of InP intermediates (with a constant mass of ~10 kDa) and InP QDs (from 60−90 kDa) in InP synthetic samples. The InP intermediates displayed optical absorption peaking around 350 nm.[2] Such an experimental observation can also be elucidated that InP PCs and/or counterpart MSCs (with a mass of ~10 kDa) were present in the InP samples with/without InP QDs. See Figure S4.

We have used MALDI-TOF MS to study CdS PCs and counterparts MSCs.[3,4] Both CdS PCs and MSC-311 displayed peaks at ~5167 Da,[3] while both CdS MSC-311 and MSC-322 showed peaks at ~5160 Da.[4] See Table S4.

(1) Kasuya, A.; Sivamohan, R.; Barnakov, Y. A.; Dmitruk, I. M.; Nirasawa, T.; Romanyuk, V. R.; Kumar, V.; Mamykin, S. V.; Tohji, K.; Jeyadevan, B.; Shinoda, K.; Kudo, T.; Terasaki, O.; Liu, Z.; Belosludov, R. V.; Sundararajan, V.; Kawazoe, Y. Ultra-Stable Nanoparticles of CdSe Revealed from Mass Spectrometry. *Nat. Mater.* **2004**, *3*, 99−102.

(2) Xie, L.; Shen, Y.; Franke, D.; Sebastian, V.; Bawendi, M. G.; Jensen, K. F. Characterization of Indium Phosphide Quantum Dot Growth Intermediates Using MALDI-TOF Mass Spectrometry. *J. Am. Chem. Soc.* **2016**, *138*, 13469−13472.

(3) Zhu, T.; Zhang, B.; Zhang, J.; Lu, J.; Fan, H.; Rowell, N.; Ripmeester, J. A.; Han, S.; Yu, K. Two-Step Nucleation of CdS Magic-Size Nanocluster MSC-311. *Chem. Mater.* **2017**, *29*, 5727−5735.

(4) Zhang, B.; Zhu, T.; Ou, M.; Rowell, N.; Fan, H.; Han, J.; Tan, L.; Dove, M. T.; Ren, Y.; Zuo, X.; Han, S.; Zeng, J.; Yu, K. Thermally-Induced Reversible Structural Isomerization in Colloidal Semiconductor CdS Magic-Size Clusters. *Nat. Commun.* **2018**, *9*, 2499.

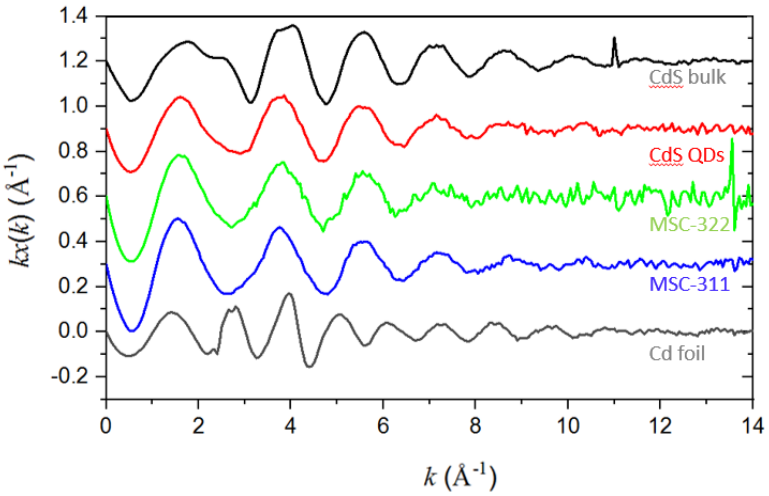


Figure S3. Corresponding Cd K-edge X-ray absorption fine structure (XAFS, Figure 2C) presented in k-space.

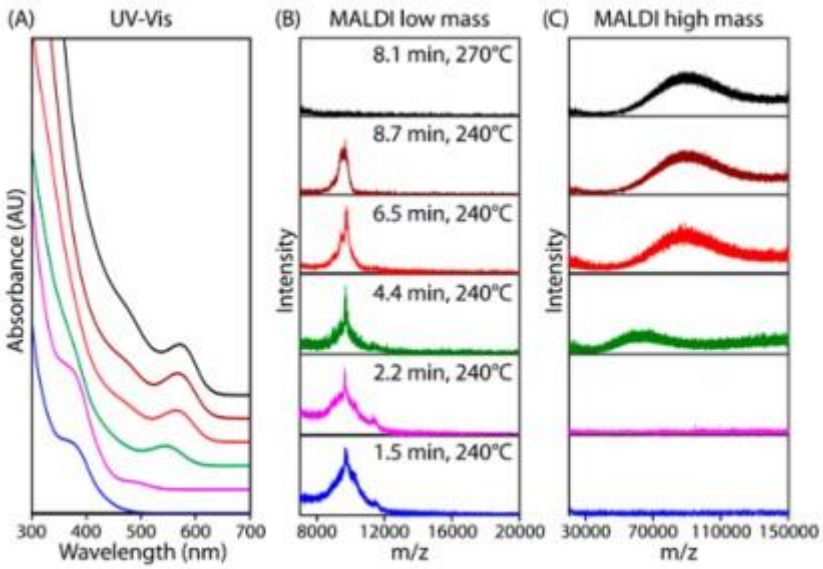


Figure S4. Reproduced from Figure 2 of Ref 48 (in the main text) and Ref 2 of Note S2. (A) UV−vis absorbance spectra and the corresponding, (B) low-mass, and (C) high-mass MALDI spectra of GPC-purified InP growth mixtures synthesized in a tube reactor. The growth time and temperature are provided in the middle panel for each condition. According to our PC concept advanced, we now argue that the first two samples are IP samples containing the InP PCs and/or counterpart MSCs. As the reaction proceeded with the growth of the InP QDs in size, the PC/MSC disappeared progressively.

Note S3. Experimental condition and spectrum evolution for Figure 3

One dispersion was kept at a constant temperature of 30 °C (A and B); both MSC-391 and MSC-415 developed in the first 40 min (A), after which the former decreased while the latter increased in density for times up to 170 min (B). The other dispersion was monitored at various temperatures from 10 to 40 °C, with 120 min kept at each temperature and with a temperature increment of 10 °C (C to F). At 10 °C (C), MSC-361 evolved and stabilized, while MSC-391 kept increasing with time. At 20 °C (D), MSC-361 decreased a little, accompanied by an apparent increase for both MSC-391 and MSC-415. At 30 °C (E), both MSC-361 and MSC-391 declined, while MSC-415 increased continuously. At 40 °C (F), both MSC-361 and MSC-391 disappeared accompanied by a limited increase of MSC-415, the population of which seemed to be relatively stable at this temperature.

Note S4. Additional description of spectrum evolution for Figure 4

For the middle panel with an OTA amount of 0.40 mL (parts D to F), both a monotonic decrease of sMSC-371 and a synchronized increase of sMSC-417 occurred in the first 30 min (part D). In the period from 35 to 75 min, which followed the complete disappearance of sMSC-371 and was prior to the development of sMSC-448, sMSC-417 appeared to be relatively stable as its strength changed little (part E). From 80 to 480 min, sMSC-417 decreased monotonically accompanied by a coordinated increase of sMSC-448 (part F). When the OTA amount was 0.30 mL instead of 0.40 mL, similar sMSC-371 to sMSC-448 transformations via sMSC-417 were observed but at faster rates and with a shorter period of stability for sMSC-417, which was from 15 to 50 min.

For the bottom panel with the OTA amount of 0.075 mL (parts G to I), a monotonic increase of sMSC-448 was accompanied by a decrease for both sMSC-371 and sMSC-417 in the first 40 min (part G). During the period from 45 to 115 min which was after both sMSC-371 and sMSC-417 had disappeared and before the development of a significant amount of dMSC-371, the strength of sMSC-448 appeared to be constant (part H). Afterwards, sMSC-448 decreased monotonically accompanied by a coordinated increase of dMSC-371 from 120 and 480 min (part I).

Note S5. Experimental condition and spectrum evolution for Figure 5

The as-mixed samples with volumes of 15 (A and C) and 30 μL (B and D) were dispersed in 3.0 mL of a mixture of 2.0 mL Tol and 1.0 mL OTA (A and B) and of 2.0 mL Tol and 1.0 mL butylamine (BTA) (C and D). After a 24 h incubation, 30 μL of the incubated sample was dispersed in 2.3 mL of Tol (E), to which 0.7 mL of OTA was added after 20 h (F).

Table S5. Comparison of two studies on CdS MSC-311 and MSC-322.

	Ref [1] (*Nat. Commun.* 2018)	**Ref [2] (*Science* 2019)**
	The two MSCs are isomers, exhibiting reversible transformations	
Transformations	thermally-induced (Fig 1) the MSC-322 to MSC-311 transformation also chemically-induced	chemically-induced
Compositions and structures	Similar cluster masses (Fig 2a MALDI) Similar local structure (Fig 2b PDF, Fig 2c XAFS) Slightly different shapes (Fig 2b PDF, Fig 2d SAXS). SAXS showed that the center-to-center distance was 2.05 and 2.25 nm for MSC-311 and MSC-322, respectively. MSC-311 is more spherical than MSC-322, thus.	MSC-311, β-$Cd_{37}S_{20}$ a zinc blende-like structure MSC-322, α-$Cd_{37}S_{20}$ a wurtzite-like structure

(1) Zhang, B.; Zhu, T.; Ou, M.; Rowell, N.; Fan, H.; Han, J.; Tan, L.; Dove, M. T.; Ren, Y.; Zuo, X.; Han, S.; Zeng, J.; Yu, K. Thermally-Induced Reversible Structural Isomerization in Colloidal Semiconductor CdS Magic-Size Clusters. *Nat. Commun.* **2018**, *9*, 2499.

(2) Williamson, C. B.; Nevers, D. R.; Nelson, A.; Hadar, I.; Banin, U.; Hanrath, T.; Robinson, R. D. Chemically Reversible Isomerization of Inorganic Clusters. *Science* **2019**, *363*, 731−735.