Supporting Information

Designing Inorganically Functionalized II-VI Magic-Size Clusters and Unraveling their Surface States

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EXPERIMENTAL SECTION

Materials and Reagents All chemicals were commercially available and used as received without further purification Zinc nitrate hydrate ($Zn(NO_3)_2·6H_2O$), zinc acetate hydrate ($Zn(OAc)_2·2H_2O$, AR,99.0%), indium nitrate ($In(NO_3)_3$), olaylamine (OLA, C18: 80-90%), n-octylamine (OTA, 99%) and tri-phenylphosphine (TPP, GC, >99.0%) were purchased from Aladdin Co., Ltd. (Shanghai, China). Zinc chloride ($ZnCl_2$, anhydrous, 99.95%), sulfur (99.999%) and selenourea (99.97%) were obtained from Alfa Aesar (Shanghai, China). Zinc trifluoromethanesulfonate ($Zn(OTf)_2$, 98%) and tri-n-octylphosphine (TOP) were obtained from Strem Chemical Co., Ltd. (Xi′an, China). Butylamine (BTA, AR, ≥99.0%), toluene (AR, ≥99.5%) and N,N-dimethylformamide (DMF, AR, ≥99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of $(CdS)_{34}$-OTA MSCs. The procedure for the synthesis of $(CdS)_{34}$-OTA was adapted from Hyeon group.[1] $CdCl_2$(octylamine)$_2$ complex was prepared by heating octylamine (10 mL) containing $CdCl_2$ (1.5 mmol) to 120 °C and aging at that temperature for 2 h under N_2. Sulfur-octylamine complex was prepared by dissolving elemental sulfur (4.5 mmol) in octylamine (5 mL) at room temperature. The resulting reddish-brown sulfur-octylamine complex solution was injected into $CdCl_2$(octylamine)$_2$ complex solution at room temperature and the color of the solution turned immediately to transparent light yellow. The reaction mixture was heated from room temperature to 40 °C. Finally, 1.5 mL of TOP was added to stop the reaction. The white precipitate was separated using a benchtop centrifuge (10000rpm, 30 s) at room temperature, and the colorless supernatant was discarded. The remaining white slush was re-dispersed into toluene or hexane to dilute 5 times.

Synthesis of $(CdS)_{34}$-BTA MSCs. $(CdS)_{34}$-BTA were synthesized under the same general conditions, except for the reaction solvent and temperature. In a glovebox, $CdCl_2$(butylamine)$_2$ complex was prepared by dissolving $CdCl_2$ (1.5 mmol) in butylamine (10 mL). Sulfur-butylamine complex was prepared by dissolving elemental sulfur (4.5 mmol) in butylamine (5 mL) at room temperature. The resulting reddish-brown sulfur-butylamine complex solution was injected into $CdCl_2$(butylamine)$_2$ complex solution at room temperature. The reaction mixture turned from clear to viscous yellow within 1 min. Finally, 1.5 mL of TOP was added to stop the reaction. The white precipitate was separated using a benchtop centrifuge (10000rpm, 30 s) at room temperature, and the colorless supernatant was discarded. The remaining white slush was re-dispersed into toluene or hexane to dilute 5 times.

Synthesis of $(CdSe)_{34}$-OTA_{16}/di-PTA_2 MSCs. The procedure for the synthesis of $(CdS)_{34}$-OTA was adapted from Buhro group.[2] In a typical procedure, $Cd(OAc)_2 \cdot 2H_2O$ (65 mg, 0.24 mmol) was dissolved in di-n-pentylamine (5.74 g, 36 mmol) and then was stored in an ice bath (0 °C) placed inside a refrigerator. In a glovebox, selenourea (50 mg, 0.41 mmol) was added to n-octylamine (1.2 g, 9.3 mmol), then removed from the glovebox and placed in a benchtop sonicating bath (10 min) to achieve dissolution of the selenourea. The selenourea solution was injected into the $Cd(OAc)_2 \cdot 2H_2O$ solution at 0 °C. The clear, colorless reaction mixture became viscous and light yellow within 6 h, cloudy and yellow within 8 h, and cloudy and green-yellow at longer times (0 °C). After 18 h at 0 °C, $(CdSe)_{34}$ was formed as a green-yellow precipitate mixed with colorless supernatant. TOP (0.25-0.50 mL) was injected to scavenge excess selenourea. The greenish-yellow precipitate was separated using a benchtop centrifuge (10000rpm, 30 s) at room temperature, and the colorless supernatant was discarded. The remaining greenish-yellow slush was re-dispersed into toluene or hexane to dilute 5 times.

Synthesis of $(CdSe)_{34}$-Cys MSCs. The procedure for the synthesis of $(CdSe)_{34}$-Cys was adapted from reported literature.[3, 4] The Se precursor (Na_2SeSO_3, 0.05 M Se^{2-}) was prepared by heating a solution containing 100 mg Se powder, 478 mg Na_2SO_3, and 25 mL H_2O at 90 °C for 24 h under mild magnetic stirring. Colloidal solutions (50 mL) of $(CdSe)_{34}$-Cys were prepared by the sequential addition of 1 M NaOH (1.875 mL), Cys (0.08 g), 0.15 M $CdSO_4$ (0.5 mL), and 0.05 M Na_2SeSO_3 (0.375 mL) into single neck flask filled with H_2O (47.25 mL) at room temperature in the dark with mild magnetic stirring. After 12h, $(CdSe)_{34}$-Cys MSCs were formed and precipitated out of the reaction mixture by adding an equal volume of isopropanol, followed by repeated centrifugation and re-dispersed in 5mL H_2O (~4mg/mL).

L-Type Ligands to Metal Salts Ligand Exchange in $(CdS)_{34}$ or $(CdSe)_{34}$ or $(ZnSe)_{34}$ MSCs. Both one-phase and two-phase systems can be used for ligand exchange. In a two-phase system, 1 mL of (CdS)34-OTA MSCs dispersion in hexane were combined with 1 mL of N,N-dimethylformamide (DMF) solution of ZnCl2, Zn(NO3)2, Zn(OTf)2 or Zn(OAc)2 (10mg/mL) at room temperature. The resulting mixture was shaken vigorously until the (CdS)34-OTA MSCs were transferred from hexane into DMF, typically within 10 s. For sufficient exchange, vortex excessively for 10 minutes. The obtained (CdS)34-ZnCl2, (CdS)34-Zn(NO3)2, (CdS)34-Zn(OAc)2 and (CdS)34-Zn(OTf)$_2$ MSCs were purified twice with hexane and DMF respectively, and finally re-dispersed in 500 μL DMF for further experiments. In a one-phase system, 1 mL of $(CdS)_{34}$-BTA MSCs dispersion in toluene were combined with 300 μL of DMF solution of Zn(OTf)2 (6 mg/100 μL), Zn(NO3)2 (3 mg/100 μL), Zn(OAc)2 (6 mg/100 μL) or ZnCl2 (3 mg/100 μL) at room temperature. After vigorous shaking (10 min), (CdS)34-ZnCl2, (CdS)34-Zn(NO3)2, (CdS)34-Zn(OTf)2 and (CdS)34-Zn(OAc)2 MSCs were purified twice with toluene and DMF respectively, and finally re-dispersed in 500μL DMF for further experiments. The ligand exchange of (CdSe)34 MSCs used the same method, replacing (CdS)34 MSCs with (CdSe)34-OTA/di-PTA MSCs. The ligand exchange of (ZnSe)34 MSCs used the same method, replacing (CdS)34 MSCs with (ZnSe)34-OTA/di-PTA MSCs and metal salt with In(NO3)3.

L-Type Ligands to Metal Salts Ligand Exchange in $(CdSe)_{34}$-Cys MSCs. 100μL $ZnCl_2$ or $Zn(OAc)_2$ (5mg) aqueous solution was injected into 500μL $(CdSe)_{34}$-Cys MSCs at room temperature, and the aqueous solution was shaken for ten minutes. After purification twice with water, it was used for future characterization.

Reversible Ligand Exchange in $(CdS)_{34}$ or $(CdSe)_{34}$ MSCs. Back exchange was conducted using either the as-prepared $(CdS)_{34}$-$ZnCl_2$ or $(CdS)_{34}$-$Zn(OAc)_2$ MSCs. Addition of OLA (50μL) dispersion in hexane (500μL) to 500μL MSCs in DMF, a subsequent brief shaking (~10 s) led to the phase transfer of MSCs from the DMF layer to the hexane layer, indicating the successful binding of organic ligands to the MSCs surface. For sufficient exchange, vortex excessively for 10 minutes. The obtained $(CdS)_{34}$-OLA MSCs were purified twice with DMF and hexane respectively, and finally re-dispersed in 500μL hexane for further experiments.

The reversible ligand exchange of $(CdSe)_{34}$ MSCs used the same method, replacing $(CdS)_{34}$-$ZnCl_2$ or $(CdS)_{34}$-$Zn(OAc)_2$ with $(CdSe)_{34}$-$ZnCl_2$ or $(CdSe)_{34}$-$Zn(OAc)_2$.

Treating $(CdS)_{34}$-OTA with AgOTf. In a typical process, different volumes (200μL, 100μL, 66μL, 33μL, 11μL) of AgOTf solution (1mg/100μL in toluene) was added to the purified $(CdS)_{34}$-OTA MSCs (1 mL), resulting in a small amount of brown-black precipitate and brown-yellow supernatant after 3 h. The supernatant was separated using a benchtop centrifuge (10000rpm, 30 s) at room temperature, and the precipitate was discarded. The supernatant was purified by precipitating with an equal volume of ethanol followed by centrifugation, and then re-dispersed into toluene.

Surface Modification of MSCs with TPP. Surface modification was performed inside a glovebox under N_2 atmosphere. Typically, 20 mg of purified $(CdS)_{34}$-BTA or $(CdS)_{34}$-$Zn(OTf)_2$ were dissolved in 500μL of dry N_2-purged toluene in a flask and stirred at room temperature until a homogeneous solution was attained. Then, 10 mg of solid TPP was added and stirred for 3 h. The product was washed with excess toluene to remove any unreacted TPP and finally re-dispersed into toluene for further experiments.

ECL Measurement. ECL detection experiments were carried out on MPI-E ECL analyzer (Remex Electronic Instrument Lt. Co., Xi'an, China) with three-electrode system containing a Pt wire as the counter electrode, Ag/AgCl (saturated KCl) as the reference electrode, and a glassy carbon electrode as the working electrode. All MSCs were modified to the surface of the glassy carbon electrode by drip coating then air-dry or vacuum dry. For (CdS)34 MSCs, the ECL signals were recorded in the presence of 50 mM TPrA in 1:1 acetonitrile:toluene containing 0.1 M TBAP during the potential scan from 0 to 1.5 V at 1000 V of the photomultiplier tube (PMT). For (CdSe)34 MSCs, the ECL signals were recorded in the presence of 5 mM BPO in 1:1 acetonitrile:toluene containing 0.1 M TBAP during the potential scan from 0 to -2.0 V at 900 V of the PMT. For (CdSe)34-Cys MSCs, the ECL signals were recorded in phosphate buffer solution (100 mM, pH 7.4) containing 50 mM $K_2S_2O_8$ during the potential scan from 0 to -2.0 V at 900 V of the PMT. Apart from this, we combined CHI760E electrochemical workstation and 3D fluorescence spectrometer (FL-3) to measure ECL spectra. The platinum sheet electrode was used as the working electrode, and the constant potential was 1.5 V or 0.9 V.

Raman Measurement. Laser confocal Raman spectra measurements were carried out using a Renishaw inVia-Reflex Raman system at room temperature. Excitation wavelengths of 488 nm (~20 mW) from a Ar-ion laser and 633 nm (~17 mW) from an He-Ne laser were selectively used to excite the $(CdS)_{34}$ and $(CdSe)_{34}$ MSCs, respectively.

LDI-MS Measurement. Laser-desorption-ionization (LDI) mass spectra were obtained on an Ultrafle Xtreme Workstation (Bruker Daltonics) in linear positive mode (LP-5-20 kDa). The $(CdS)_{34}$ or $(CdSe)_{34}$ MSCs sample were smeared directly onto a MALDI plate and left to air-dry or vacuum dry for several minutes, without a matrix.

Theoretical Calculation. All calculations were performed using Gaussian 09[14] program package. Geometry optimizations and vibrational frequency analysis were performed at the TPSSh level of theory with the def2-SVP basis set.[5-7] The self-consistent reaction field (SCRF) method based on the universal solvation model SMD was adopted to evaluate the effect of solvent (toluene).[8] All single point calculations were carried out at the TPSSh/def2-TZVP level, and the solvation energy were performed at TM06-2X/def2-SVP level of theory.[9] The standard oxidation potentials relative to standard hydrogen electrode (SHE) were calculated with Gibbs free energy barriers (ΔG) of oxidation half-reaction.[10]

Principles of Ligand Exchange. The ligand exchange process is mainly determined by the binding affinity between original ligands and the foreign ligands. When the binding affinity of foreign ligands to the original ligands is larger than that of the original ligand to the inorganic core (Scenario I, Eq 1), the reaction tends to proceed in the direction of obtaining thermodynamically stable NCs-FL. If the binding affinity of foreign ligands to original ligands is close to that of the original ligand to the inorganic core (Scenario II, Eq 2), the ligand exchange process is reversible and the direction is determined by the concentration of foreign ligands. Once the binding affinity of foreign ligands to the original ligands is smaller than that of the original ligand to the inorganic core (Scenario III, Eq 3), then the surface treatment cannot be achieved.

$$\mathrm{FL + MSCs\text{-}OL} \rightleftharpoons \mathrm{MSCs\text{-}FL + OL\text{-}FL}\ (1)$$

$$\mathrm{FL + MSCs\text{-}OL} \rightleftharpoons \mathrm{MSCs\text{-}FL + OL\text{-}FL}\ (2)$$

$$\mathrm{FL + MSCs\text{-}OL} \cancel{\rightleftharpoons} \mathrm{MSCs\text{-}FL + OL\text{-}FL}\ (3)$$

(where FL is the foreign inorganic ligand, OL is the original organic ligand, and OL-FL is the complex product formed by stripping the original organic ligand from the MSC surface by inorganic ligands.)

In the first scenario, only a small amount of FL can trigger the ligand exchange process (X-type ligands such as S^{2-}, SCN^- and $Sn_2S_6^{4-}$ can be classified in this category). However, such a reaction is often violent, resulting in irreparable damage and defects on the surface of the inorganic core.[11, 12] Since MSCs are extremely sensitive to the environment, those changes may lead MSCs to aggregate or grow.[13] The binding affinity between the metal salt ligand and the original ligands is relatively weak, and ligand exchange can be classified into the second scenario. The relatively mild treatment results in less damage to the surface, making this process more suitable for the modification of MSCs. We should notice that according to Le Chatelier's principle, the balance will move in the direction of attenuated changes.

Supplementary Figures

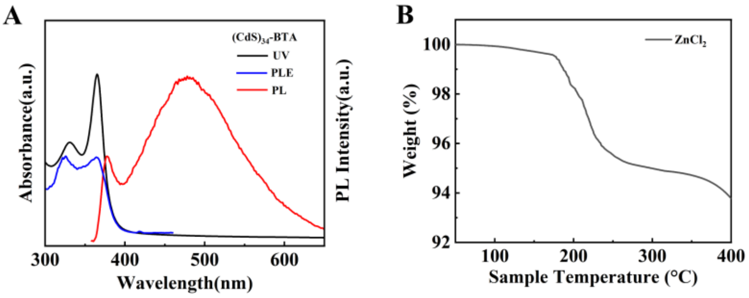


Figure S1 UV, PLE and PL spectra of $(CdS)_{34}$-BTA (a) and TGA of $ZnCl_2$(b).

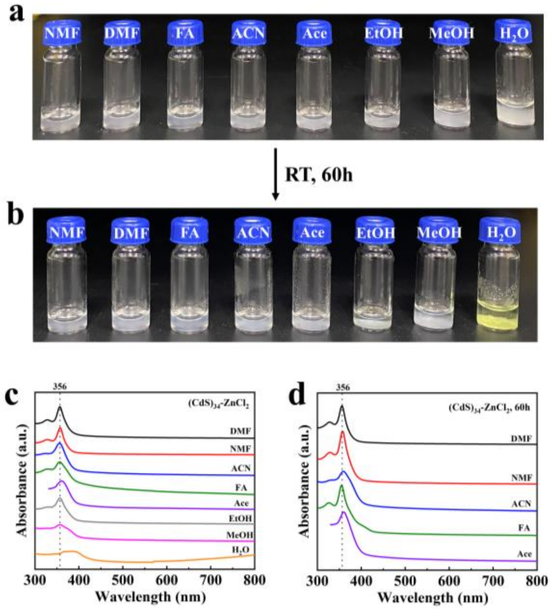


Figure S2 Stability of all-inorganic MSCs: Photographs of $(CdS)_{34}$-$ZnCl_2$ MSCs stable in various polar solvents for different times: (a) 0h (b) 60h. (c), (d) are the corresponding absorption spectra.

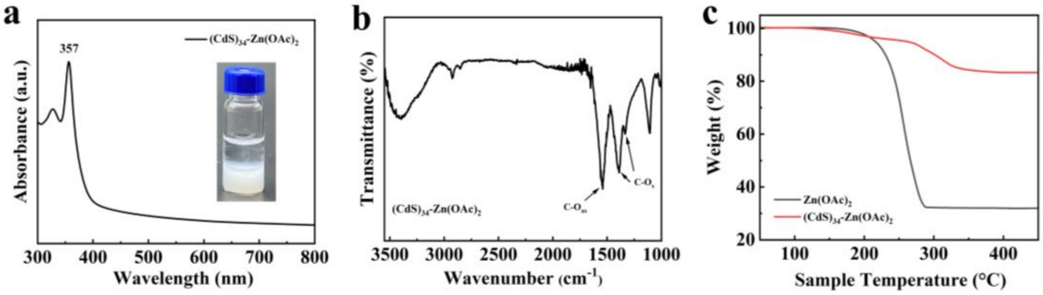


Figure S3 Characterization of $(CdS)_{34}$-$Zn(OAc)_2$: Absorption spectrum (a) and IR spectrum (b) of $(CdS)_{34}$-$Zn(OAc)_2$. (c) TGA data of $(CdS)_{34}$-$Zn(OAc)_2$ and $Zn(OAc)_2$.The inset in a is the photograph after phase transfer.

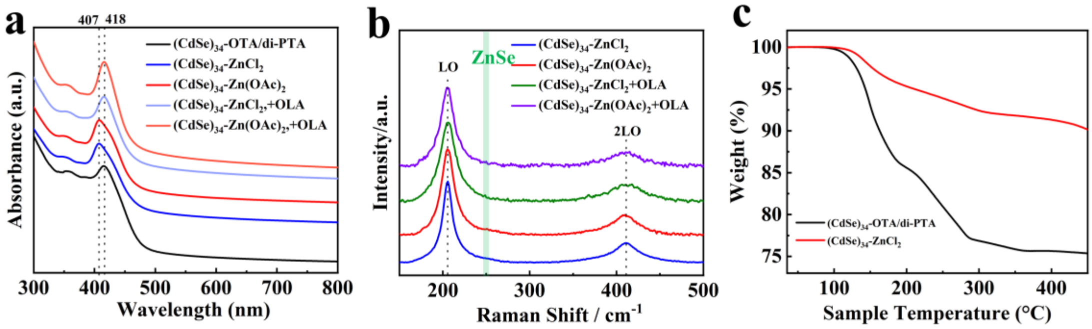


Figure S4 Additional data on reversible ligand exchange in $(CdSe)_{34}$ MSCs: (a) Absorption, (b) Raman spectra of $(CdS)_{34}$-BTA, $(CdS)_{34}$-$ZnCl_2$, $(CdS)_{34}$-OLA MSCs and back exchanged product with OLA. (c) TGA of $(CdSe)_{34}$ and $(CdSe)_{34}$-$ZnCl_2$.

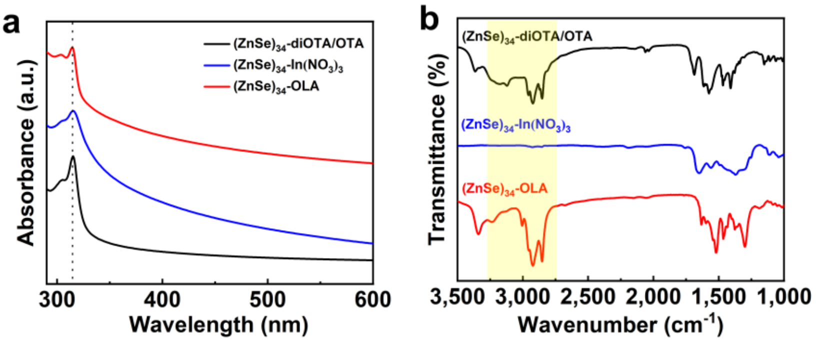


Figure S5 Ligand exchange of $(ZnSe)_{34}$ MSCs by $In(NO_3)_3$. (a) Absorption spectra and (b) IR spectra of $(ZnSe)_{34}$ MSCs during the ligand exchange process.

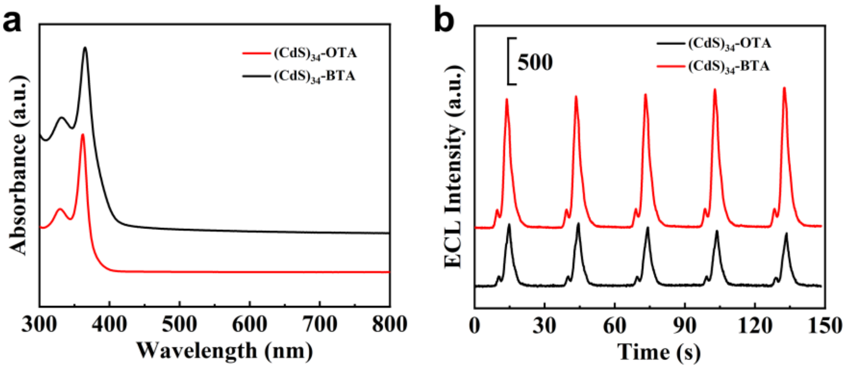


Figure S6 Assisted characterization of different organic chain lengths: (a) absorption spectra (b) and ECL-Time curve of (CdS)$_{34}$ MSCs with different ligand chain lengths.

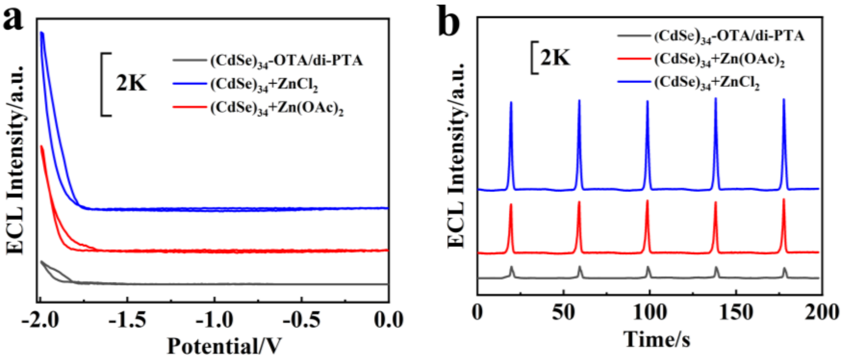


Figure S7 ECL performance of all-inorganic (CdSe)$_{34}$ MSCs: (a) ECL-V curves (b) and ECL-Time curves of (CdS)$_{34}$-OTA/di-PTA, (CdS)$_{34}$-ZnCl$_2$ and (CdS)$_{34}$-Zn(OAc)$_2$ MSCs.

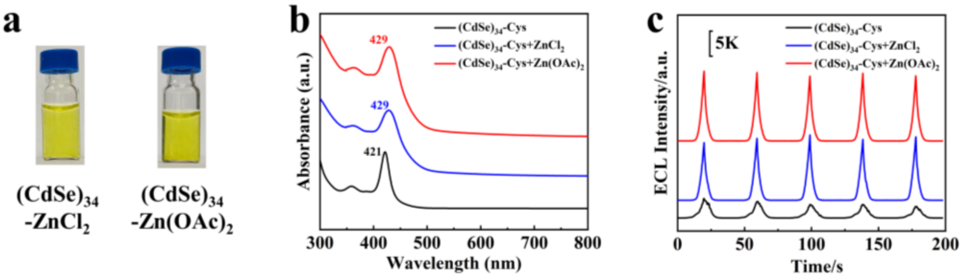


Figure S8 ECL performance of aqueous (CdSe)$_{34}$ MSCs: photograph (a), Absorption spectra (b) and ECL-Time curve (c) of (CdSe)$_{34}$-ZnCl$_2$ and (CdSe)$_{34}$-Zn(OAc)$_2$ in H$_2$O.

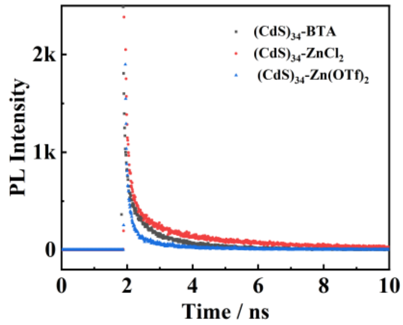


Figure S9 The fluorescence lifetime of $(CdS)_{34}$-BTA, $(CdS)_{34}$-$ZnCl_2$ and $(CdS)_{34}$-$Zn(OTf)_2$ MSCs.

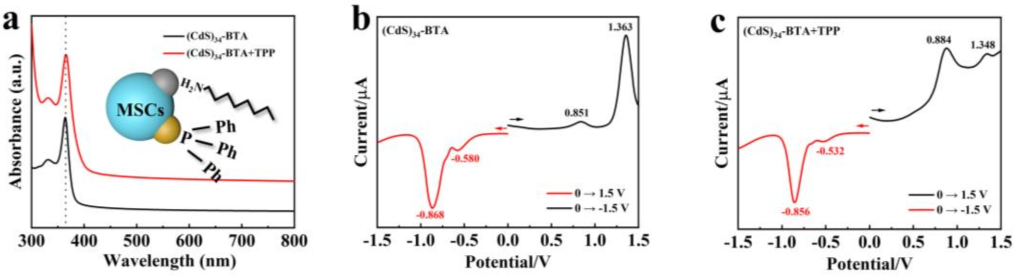


Figure S10 DPV related research: (a) Absorption spectra of $(CdS)_{34}$-BTA and $(CdS)_{34}$-BTA/TPP, DPV of (b) $(CdS)_{34}$-BTA and (c) $(CdS)_{34}$-BTA/TPP.

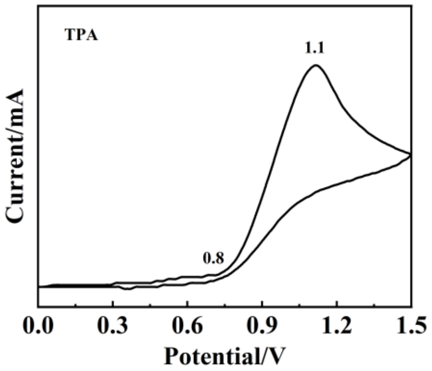


Figure S11 CV of TPA.

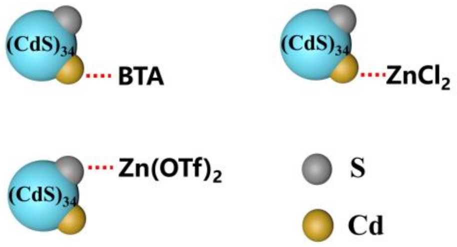
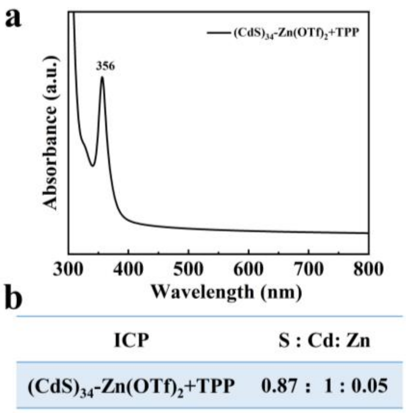


Figure S12 Surface passivation of $(CdS)_{34}$ MSCs with three different ligands.



ICP	S : Cd: Zn
$(CdS)_{34}$-Zn$(OTf)_2$+TPP	0.87 : 1 : 0.05

Figure S13 Characterization of $(CdS)_{34}$-Zn$(OTf)_2$+TPP: Absorption spectra (a) and ICP-OES (b).

Table S1. ICP-OES Data for $(CdS)_{34}$ Corresponding to Ligand Exchange

	S (mg/L)	Cd (mg/L)	Zn (mg/L)	S: Cd: Zn
$(CdS)_{34}$-BTA	3.244	12.44	----	1: 1.09
$(CdS)_{34}$-$ZnCl_2$	0.556	2.03	0.26	0.96: 1: 0.22
$(CdS)_{34}$-Zn$(OTf)_2$	1.71	6.52	3.16	0.93: 1: 0.82
$(CdS)_{34}$-Zn$(OAc)_2$	1.23	4.37	0.78	0.98: 1: 0.30
$(CdS)_{34}$-$ZnCl_2$+OLA	0.802	2.8	0.13	1: 1: 0.08
$(CdS)_{34}$-Zn$(OAc)_2$+OLA	1.24	4.24	0.183	1.02: 1: 0.07
$(CdS)_{34}$-Zn$(OTf)_2$+OLA	1.48	6.64	2.97	0.91: 1: 0.83

Table S2. ICP-OES Datas for $(CdSe)_{34}$ Corresponding to Ligand Exchange

	Se (mg/L)	Cd (mg/L)	Zn (mg/L)	Se:Cd:Zn
$(CdSe)_{34}$-OTA/di-PTA	0.96	1.24	----	1.09 : 1
$(CdSe)_{34}$-$ZnCl_2$	0.956	1.38	0.251	0.99 : 1 : 0.31
$(CdSe)_{34}$-Zn$(OAc)_2$	6.71	10.5	0.871	0.94 : 1 : 0.14
$(CdSe)_{34}$-$ZnCl_2$+OLA	0.728	1.02	0.052	1.01 : 1 : 0.08
$(CdSe)_{34}$-Zn$(OA)_2$+OLA	1.72	2.26	0.0421	1.09 : 1 : 0.03

Table S3. ICP-OES Datas for $(ZnSe)_{34}$ Corresponding to Ligand Exchange

	Se (mg/L)	Zn (mg/L)	In (mg/L)	Se:Cd:Zn
$(ZnSe)_{34}$+$In(NO_3)_3$	1.40	1.23	0.84	0.94 : 1 : 0.39

Table S4. The calculated redox potentials (V) and the experiment values

Species (M^+/M)	Calc. E (V vs Ag/AgCl)	Exp. E (V vs Ag/AgCl)
$(CdS)_{34}^{+}/(CdS)_{34}^{0}$	1.092	0.868
$(CdS)_{34}^{2+}/(CdS)_{34}^{+}$	1.635	1.363

References:

1. Son, J. S.; Park, K.; Kwon, S. G.; Yang, J.; Choi, M. K.; Kim, J.; Yu, J. H.; Joo, J.; Hyeon, T. *Small* **2012,** 8, (15), 2394-402.
2. Wang, Y.; Zhang, Y.; Wang, F.; Giblin, D. E.; Hoy, J.; Rohrs, H. W.; Loomis, R. A.; Buhro, W. E. *Chem Mater* **2014,** 26, (7), 2233-2243.
3. Park, Y. S.; Okamoto, Y.; Kaji, N.; Tokeshi, M.; Baba, Y. *J Nanosci Nanotechnol* **2012,** 12, (1), 539-46.
4. Park, Y. S.; Dmytruk, A.; Dmitruk, I.; Kasuya, A.; Takeda, M.; Ohuchi, N.; Okamoto, Y.; Kaji, N.; Tokeshi, M.; Baba, Y. *ACS Nano* **2010,** 4, (1), 121-8.
5. Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *The Journal of Chemical Physics* **2003,** 119, (23), 12129-12137.
6. Weigend, F.; Ahlrichs, R. *Phys Chem Chem Phys* **2005,** 7, (18), 3297-305.
7. Weigend, F. *Phys Chem Chem Phys* **2006,** 8, (9), 1057-65.
8. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J Phys Chem B* **2009,** 113, (18), 6378-96.
9. Zhao, Y.; Truhlar, D. G. *Theoretical Chemistry Accounts* **2007,** 120, (1-3), 215-241.
10. Marenich, A. V.; Ho, J.; Coote, M. L.; Cramer, C. J.; Truhlar, D. G. *Phys Chem Chem Phys* **2014,** 16, (29), 15068-106.
11. Kovalenko, M. V.; Scheele, M.; Talapin, D. V. *Science* **2009,** 324, (5933), 1417-20.
12. Nag, A.; Chung, D. S.; Dolzhnikov, D. S.; Dimitrijevic, N. M.; Chattopadhyay, S.; Shibata, T.; Talapin, D. V. *J Am Chem Soc* **2012,** 134, (33), 13604-15.
13. Zhou, Y.; Wang, F.; Buhro, W. E. *Chemistry of Materials* **2020,** 32, (19), 8350-8360.

14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Taroverov, T. Keith, R. Kobayashi,

J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox. Gaussian 09 (Revision D.01) I. Gaussian, Wallingford, CT, 2013.