Electronic Supplementary Material (ESI) for RSC Advances.

Synergistic effect of carboxylic and amine ligands on the synthesis of CdSe nanocrystals

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(a) (b)

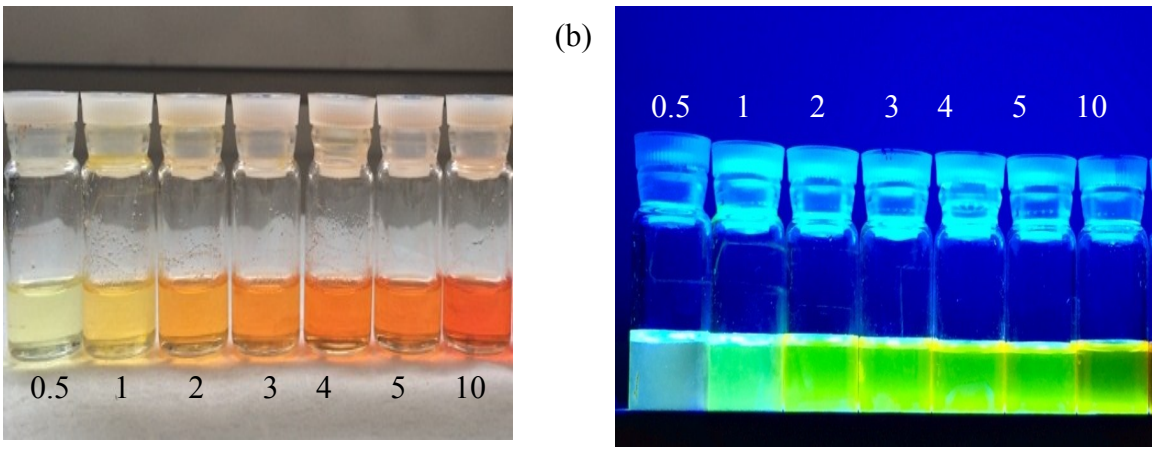

Figure S1: CdSe NCs prepared using $Cd(Ac)_2$ precursor with carboxylic acid and primary amine coordination ligands (SAc-ODAm) (a) under normal light (b) under UV illumination at 320-360 nm. The numbers indicate the synthesis time in minutes. Photograph (b) shows an increase in PL indicating an increase in NCs size with time.

Section 1: Preparation and characterisation of CdSe NCs

All the chemicals were purchased from Sigma-Aldrich and used after degassing under Ar atmosphere. CdSe NCs were synthesised using a hot-injection procedure at a relatively low temperature of 200 °C. A stock solution of selenium precursor solution (TOP-Se) (1 mol/L) was prepared by mixing trioctylphosphine (TOP) with selenium (Se) powder under Ar atmosphere. It was kept stirring for more than 12 hours to ensure complete dissolution and was finally stored in a refrigerator at 4 °C. The Cd precursor solution was prepared by adding 0.2 mmol of $Cd(Ac)_2$ and 1 mmol of a particular carboxylic acid into 5 mL of octadecene (ODE), followed by stirring at 200 °C under Ar. Afterwards, it was cooled down to room temperature and 1 mmol of primary amine was added to it. Finally, the solution was heated up and maintained at 200 °C. 1 mL of stock TOP-Se solution was rapidly injected into the Cd precursor solution and the reaction started immediately. After 0.5, 1, 2, 3, 4, 5 and 10 minutes, around 0.7 mL of the solution was withdrawn and quenched with 0.5 mL of chloroform. UV-visible absorbance spectroscopy of the diluted CdSe NCs (Dilution factor 17 times in chloroform) were performed on a Varian Cary 100 Scan UV-vis spectrophotometer. Photoluminescence (PL) spectra were measured by a two-fiber system attached with a USB2000 spectrometer (Ocean Optics). The size of CdSe QDs was obtained through their

absorbance peak based on the empirical formula proposed by Peng et al.(Peng, et al. Chem. Mater. 2003, 15, 2854 - 2860).

To facilitate the reproducibility of reaction, quantities and molar concentration of reaction precursors are summarized in the following table.

	Caboxylic Acid Ligand	Primary Amine Ligand	Cd(Ac)2	Se	TOP	ODE	NC Conc. Absorbance & Photoluminiscence (μmol/L)
Ligands	Amount (mmol)	Amount (mmol)	Amount (mmol)	Amount (mmol)	Amount (mL)	Amount (mL)	
No Ligand	0	0	0.2	1	1	5	*
OAm	0	1	0.2	1	1	5	*
DDAm	0	1	0.2	1	1	5	*
HDAm	0	1	0.2	1	1	5	*
ODAm	0	1	0.2	1	1	5	*
LA	1	0	0.2	1	1	5	1.9511
LA-OAm	1	1	0.2	1	1	5	3.5824
LA-DDAm	1	1	0.2	1	1	5	2.8408
LA-HDAm	1	1	0.2	1	1	5	3.0848
LA-ODAm	1	1	0.2	1	1	5	3.4041
MA	1	0	0.2	1	1	5	1.3346
MA-OAm	1	1	0.2	1	1	5	3.9840
MA-DDAm	1	1	0.2	1	1	5	2.8385
MA-HDAm	1	1	0.2	1	1	5	2.2655
MA-ODAm	1	1	0.2	1	1	5	3.4226
SA	1	0	0.2	1	1	5	2.3971
SA-OAm	1	1	0.2	1	1	5	3.5762
SA-DDAm	1	1	0.2	1	1	5	3.9876
SA-HDAm	1	1	0.2	1	1	5	3.6294
SA-ODAm	1	1	0.2	1	1	5	3.8990
OA	1	0	0.2	1	1	5	2.1328
OA-OAm	1	1	0.2	1	1	5	3.4496
OA-DDAm	1	1	0.2	1	1	5	3.6084
OA-HDAm	1	1	0.2	1	1	5	3.1468
OA-ODAm	1	1	0.2	1	1	5	3.3013

Table 1: Precursors and ligands amount used in the preparation of CdSe nanocrystals along with NC concentration in chloroform solution used for the absorbance and photoluminescence measurements of reaction products.

Abbreviations used in the tables are lauric acid (LAc), myristic acid (MAc), stearic acid (SAc) oleic acid (OAc), octyl amine (OAm), dodecyl amine (DDAm), hexadecyl amine (HDAm) , octadecyl amine (ODAm), Trioctyl Phosphine (TOP), Octadecene (ODE) cadmium acetate ($Cd(Ac)_2$) , Selenium (Se) and Nanocrystals concentration (NC Conc.).

The most prominent feature obtained from all following spectra is the peak wavelength, which is the reason why the spectra are not normalized to a uniform y-scale. The temporal evolution of these spectra generally indicates a red shift, *i.e.* the size of the CdSe NCs, which is proportional to the PL peak wavelength, increases with reaction time.

Section 2: Effect of only acid ligands of $Cd(Ac)_2$ towards reaction to TOP-Se.

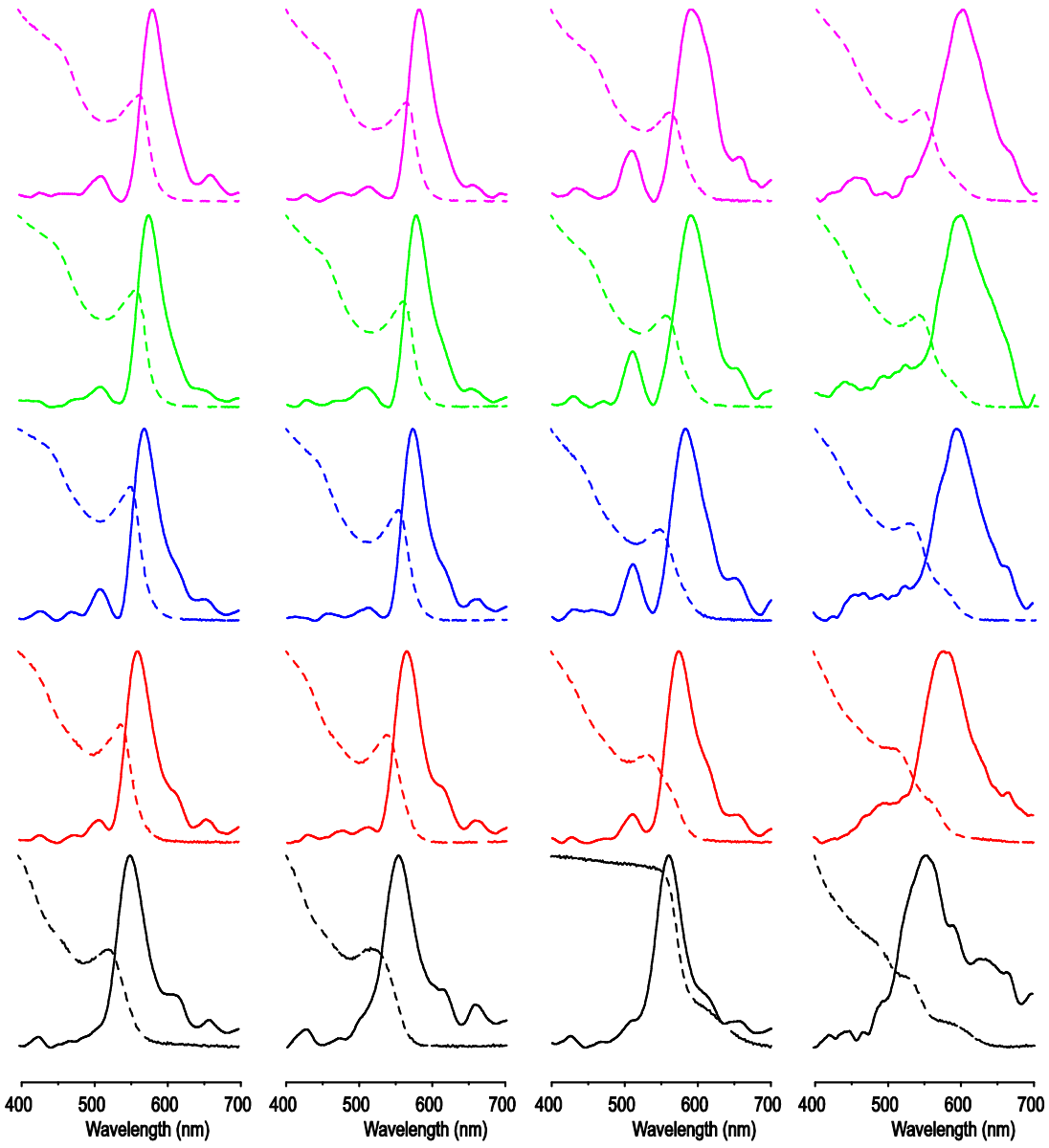

Figure S2: UV-VIS (dashed lines) and PL (continuous lines) spectra of the temporal evolution of CdSe NCs synthesized during the reaction between acid-coordinated $Cd(Ac)_2$ to TOP-Se. Various acids LAc (column a), MAc (column b), SAc (column c) and OAc (column d) ligands were used to coordinate to $Cd(Ac)_2$. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min). (column "a" to "d" from left to right)

Section 3: Effect of combined use of an amine ligand and various acid ligands on the synthesis of CdSe NCs and their UV-VIS absorbance and PL properties.

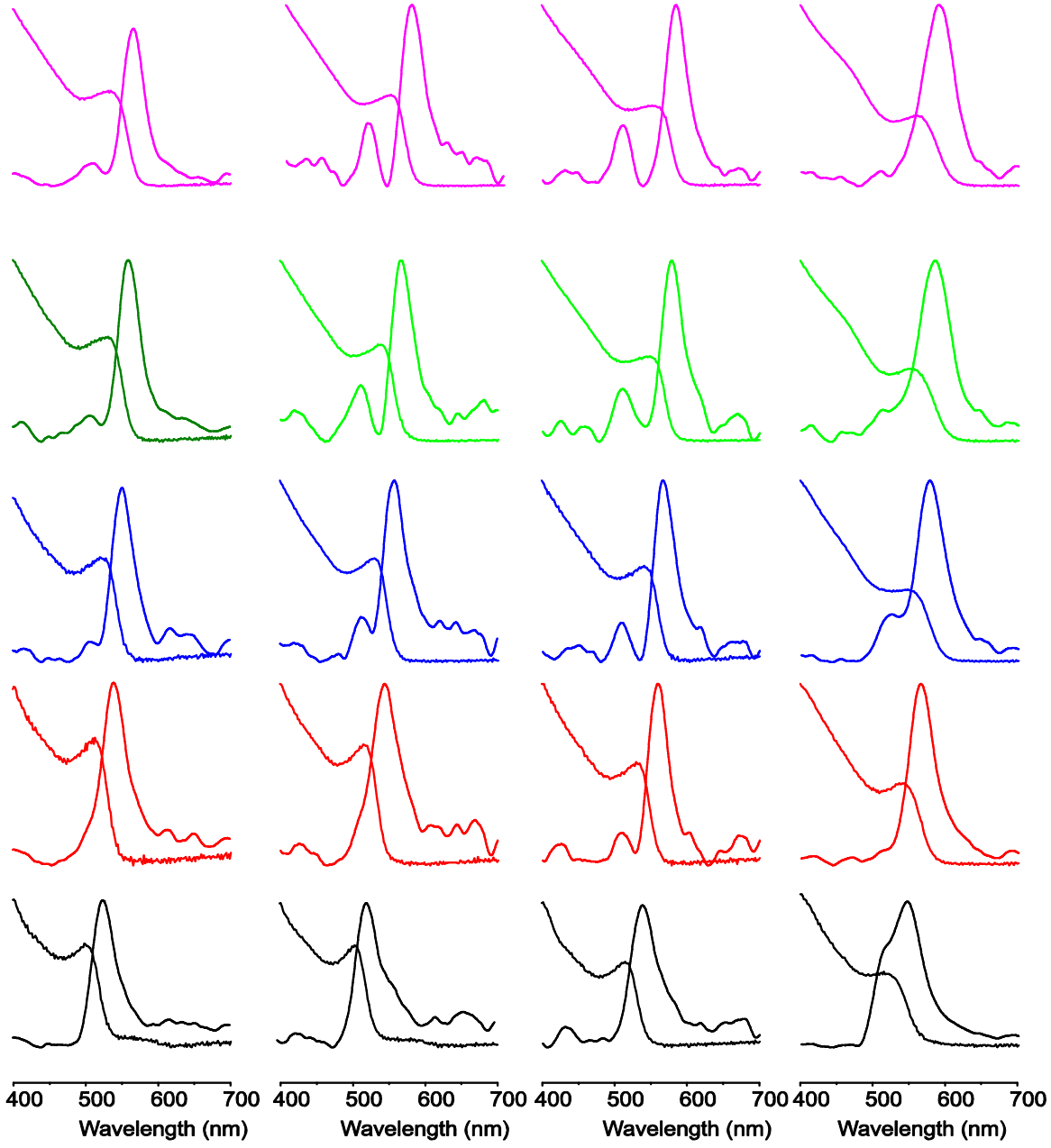

Figure S3: The temporal evolution of the UV-VIS and PL spectra of CdSe NCs produced using various acids, (LAc (column a), MAc (column b), SAc (column c) and OAc (column d)) ligands combined with OAm amine ligand. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column "a" to "d" from left to right).

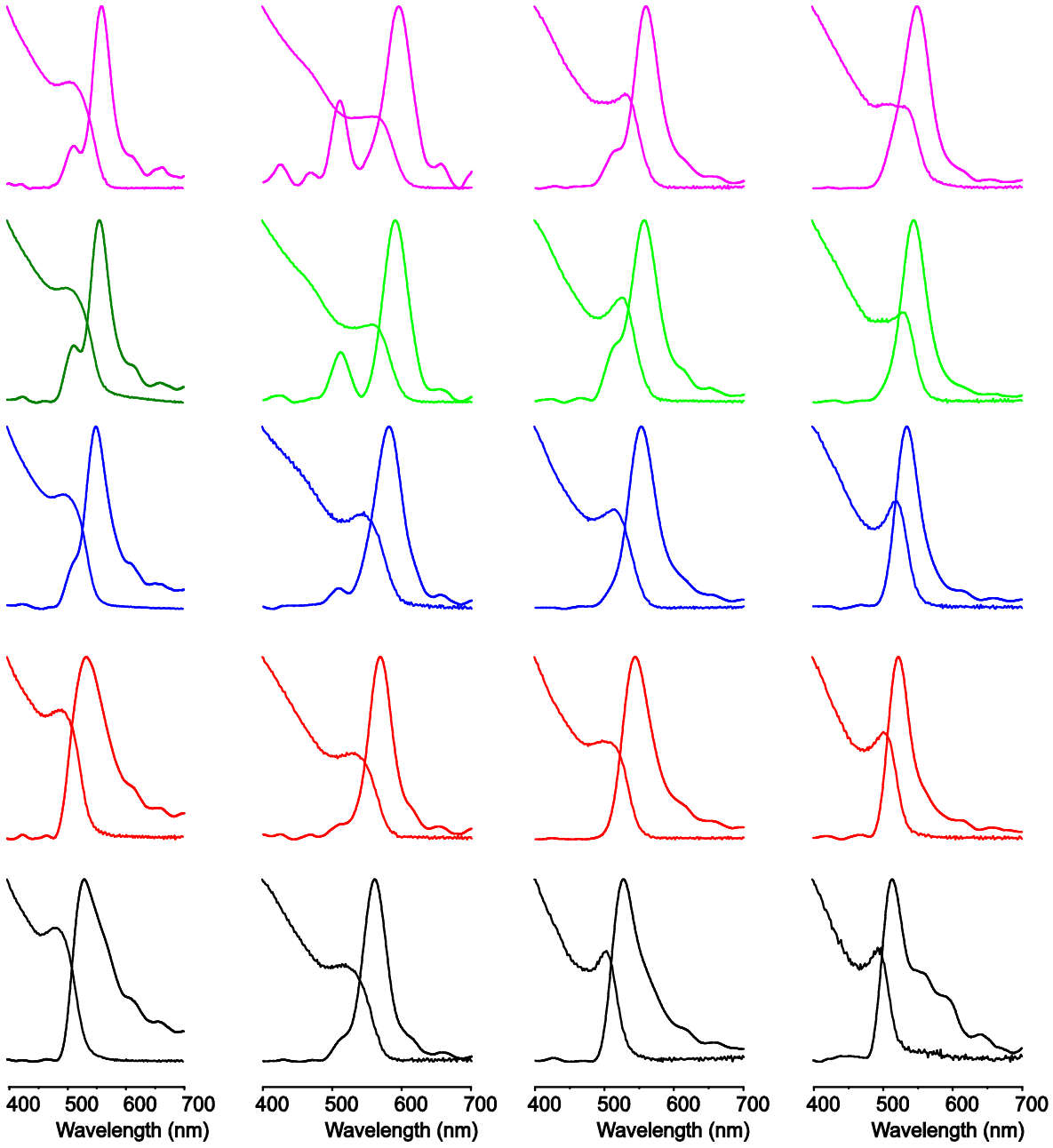

Figure S4: The temporal evolution of the UV-VIS and PL spectra of CdSe NCs produced using various acids, (LAc (column a), MAc (column b), SAc (column c) and OAc (column d) ligands combined with DDAm amine ligand. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column “a” to “d” from left to right).

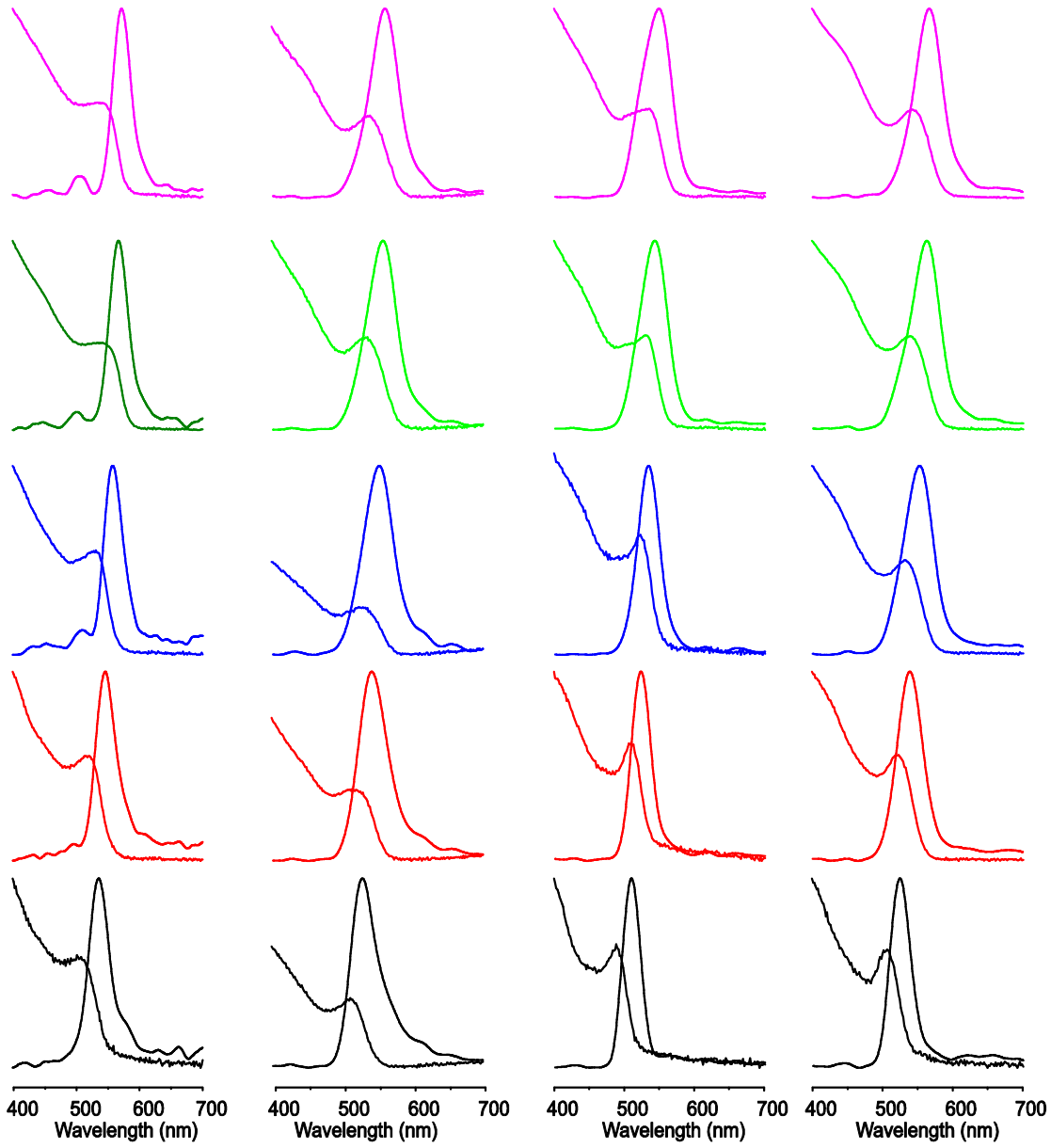

Figure S5: The temporal evolution of the UV-VIS and PL spectra of CdSe NCs produced using various acids, (LAc (column a), MAc (column b), SAc (column c) and OAc (column d)) ligands combined with HDAm amine ligand. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column "a" to "d" from left to right).

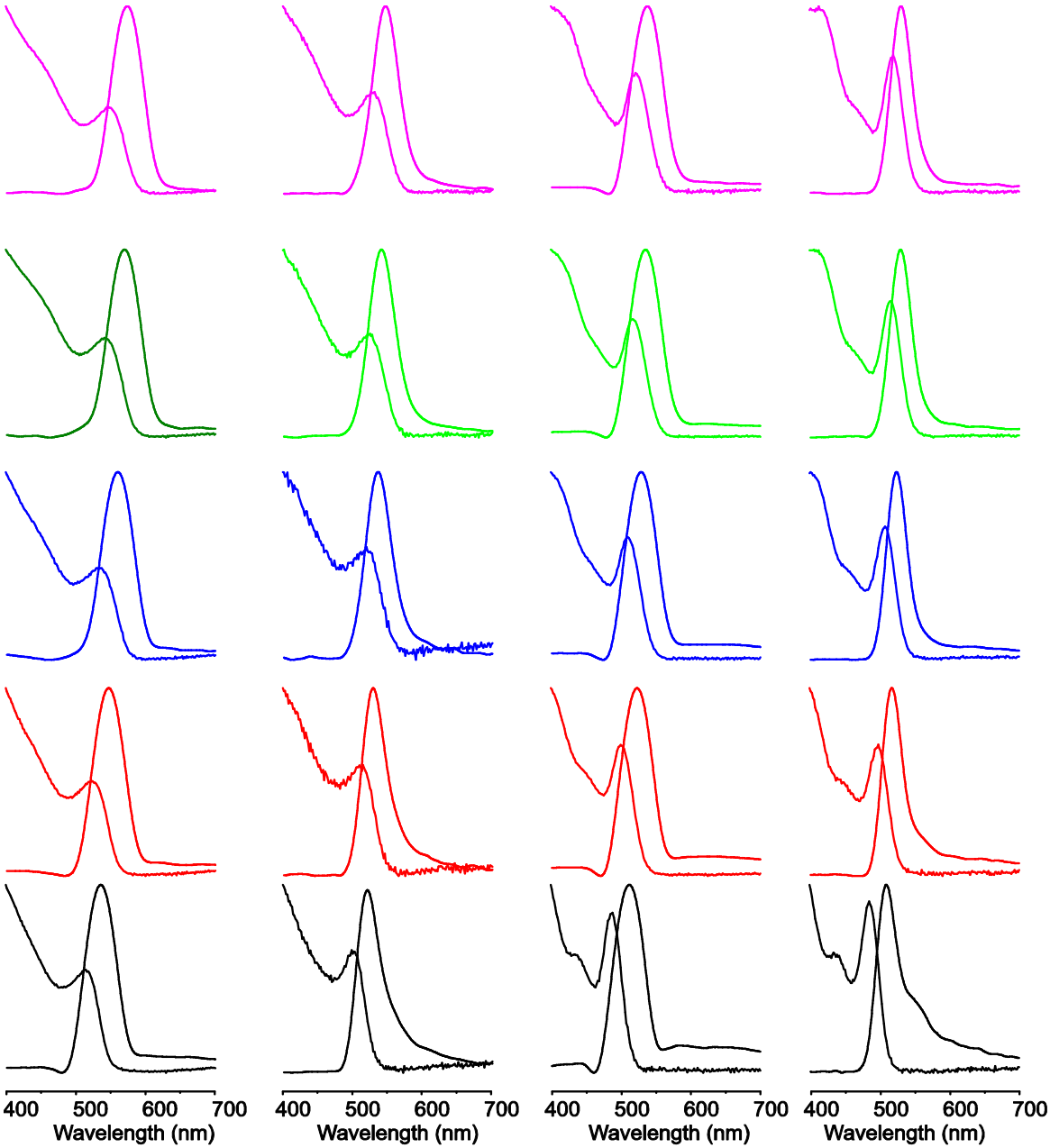

Figure S6: The temporal evolution of the UV-VIS and PL spectra of CdSe NCs produced using various acids, (LAc (column a), MAc (column b), SAc (column c) and OAc (column d)) ligands combined with ODAm amine ligand. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column "a" to "d" from left to right).

Section 4: Effect of combined use of an acid ligand and various amine ligands on the synthesis of CdSe NCs and their UV-VIS absorbance and PL properties.

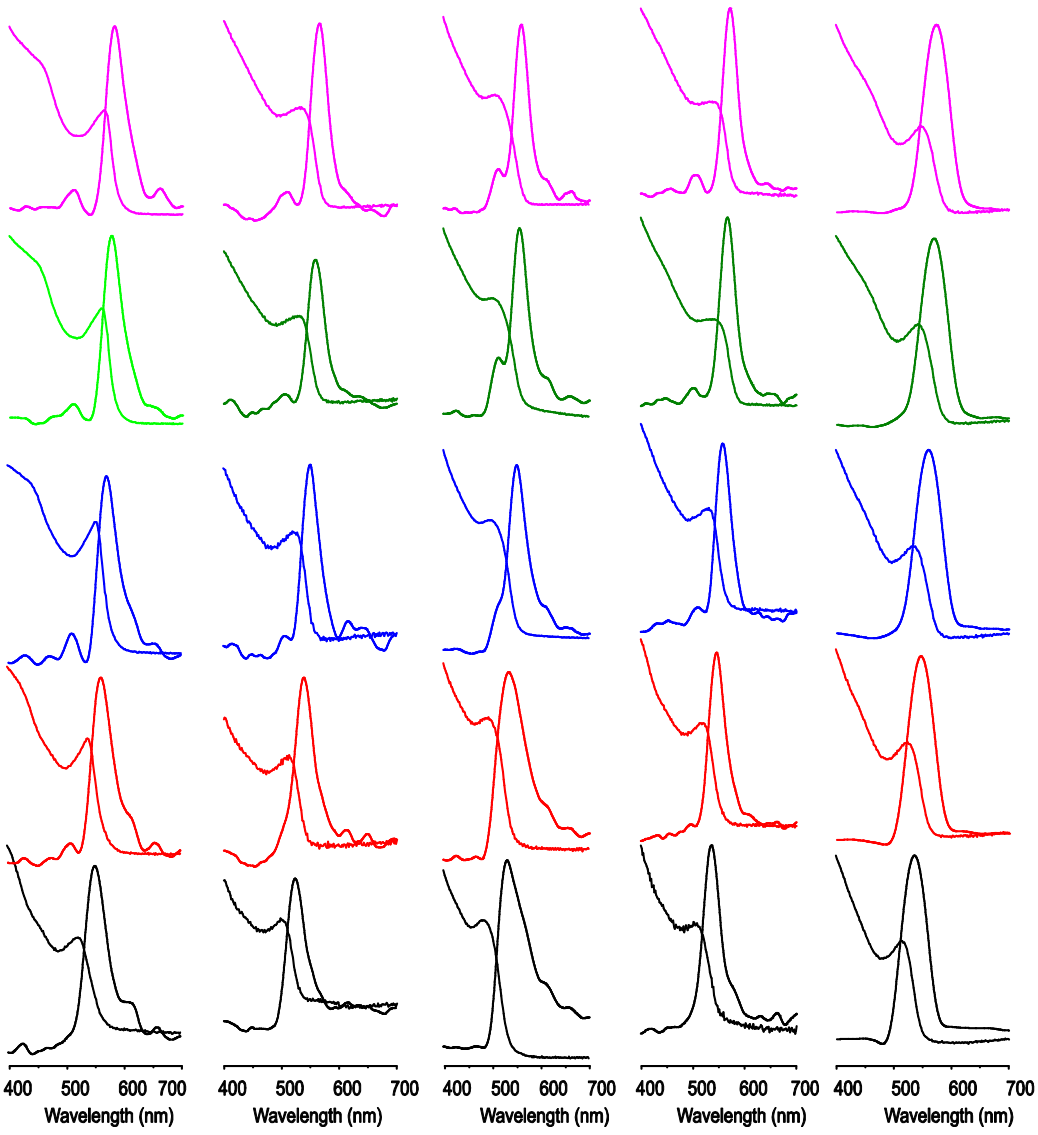

Figure S7: UV-VIS (dashed line) and PL (continuous line) spectra of the temporal evolution of CdSe NCs synthesized during the reaction of LAc and various amine-coordinated $Cd(Ac)_2$ and TOP-Se. Only acid without amine (column a) and with various amines OAm (column b), DDAm (column c), HDAm (column d) and ODAm (column e) ligands were used in combination with LAc to coordinate to $Cd(Ac)_2$. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column "a" to "e" from left to right).

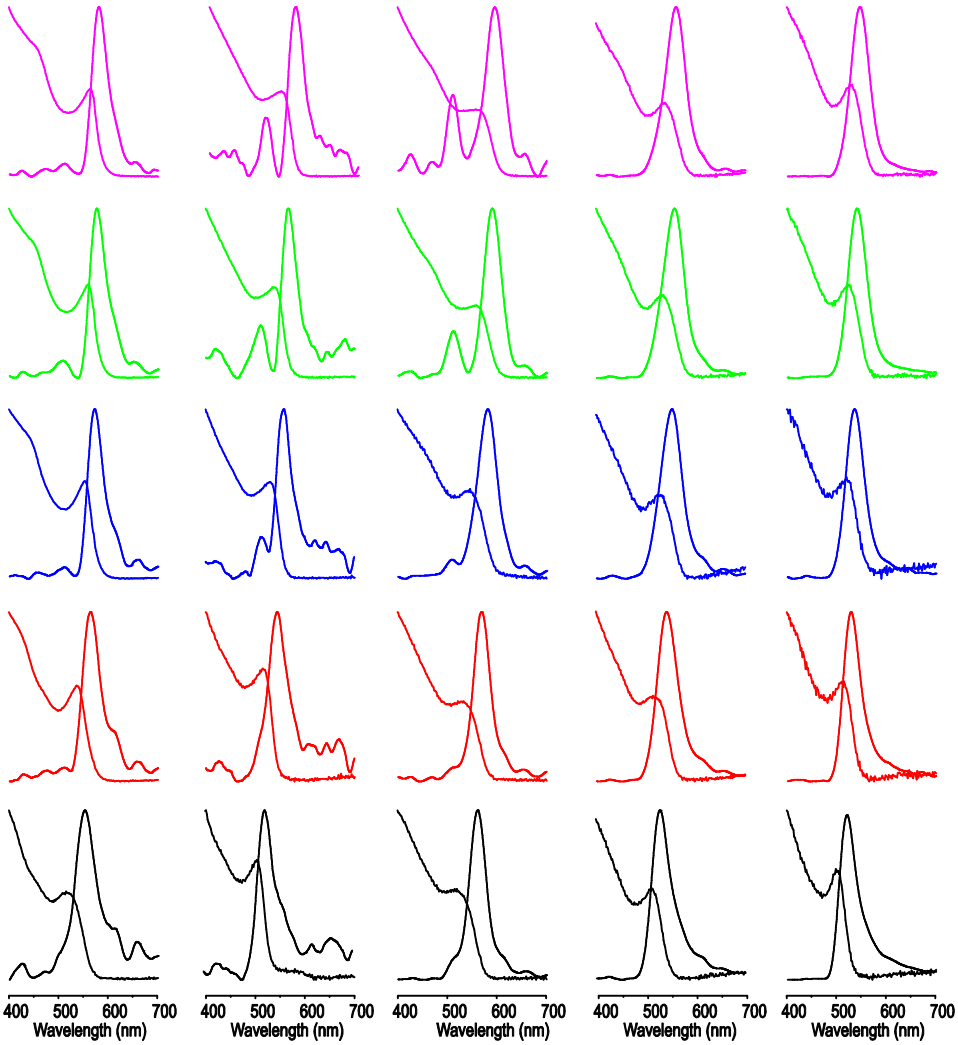

Figure S8: UV-VIS (dashed lines) and PL (continuous lines) spectra of the temporal evolution of CdSe NCs synthesized during the reaction of MAc and various amine-coordinated $Cd(Ac)_2$ and TOP-Se. Only acid without amine (column a) and with various amines OAm (column b), DDAm (column c), HDAm (column d) and ODAm (column e) ligands were used in combination with MAc to bind $Cd(Ac)_2$. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column "a" to "e" from left to right)..

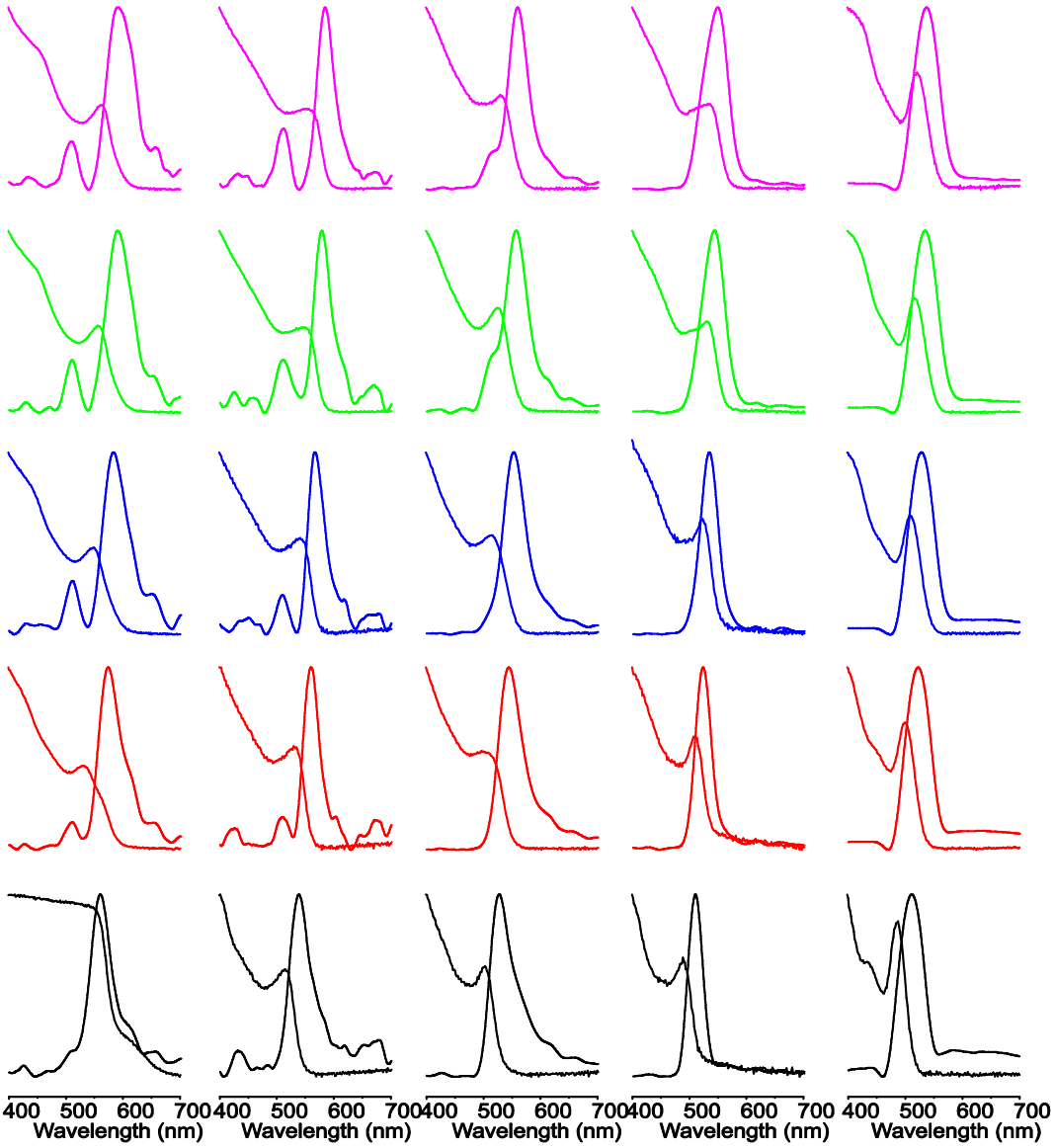

Figure S9: UV-VIS (dashed lines) and PL (continuous lines) spectra of the temporal evolution of CdSe NCs synthesized during the reaction of SAc and various amine-coordinated $Cd(Ac)_2$ and TOP-Se. Only acid without amine (column a) and with various amines OAm (column b), DDAm (column c), HDAm (column d) and ODAm (column e) ligands were used in combination with SAc to coordinate to $Cd(Ac)_2$. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column "a" to "e" from left to right)..

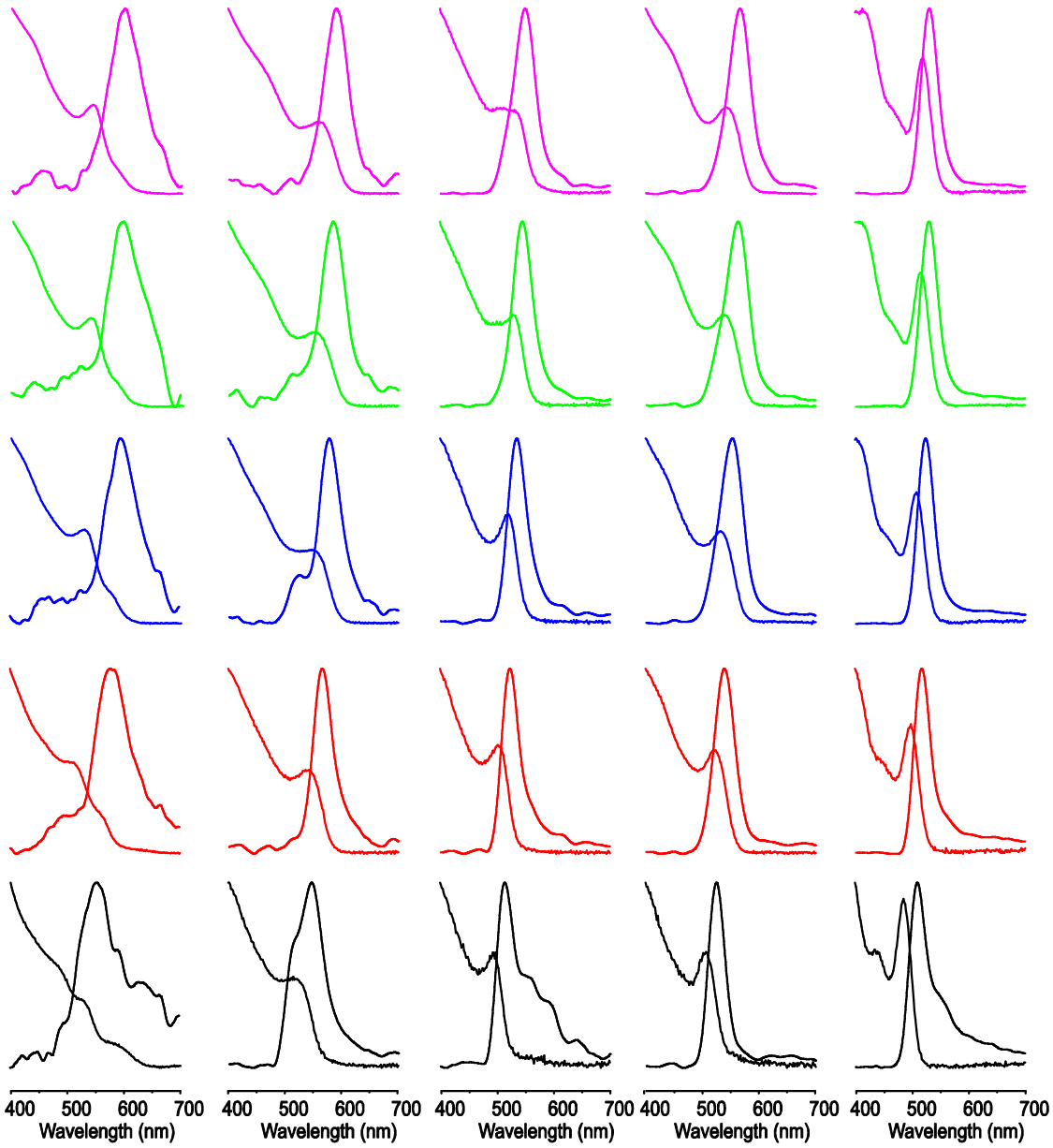

Figure S10: UV-VIS (dashed lines) and PL (continuous lines) spectra of the temporal evolution of CdSe NCs synthesized during the reaction of OAc and various amine-coordinated $Cd(Ac)_2$ and TOP-Se. Only acid without amine (column a) and with various amines OAm (column b), DDAm (column c), HDAm (column d) and ODAm (column e) ligands were used in combination with OAc to coordinate to $Cd(Ac)_2$. Colors indicate different reaction times (black: 0.5 min; red: 1 min, blue: 2 min; green: 3 min; magenta: 4 min) (column "a" to "e" from left to right)..