Supporting Information for

A general strategy for colloidal stable ultrasmall amorphous mineral clusters in organic solvents

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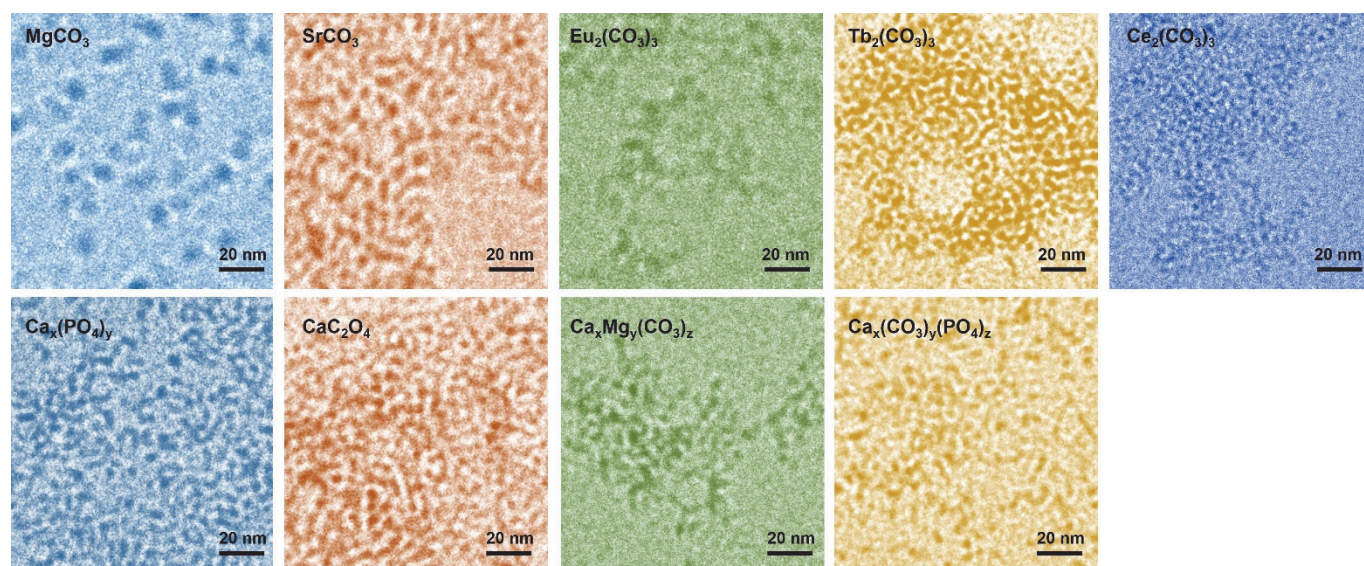
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Fig. S1 Enlarged TEM images of mineral clusters. All the images were colored to enhance visibility. A contrast decrease from the cluster center to the edge can be observed indicating a core-shell structure. However, no obvious boundary between the core and the shell can be distinguished in the TEM images due to the low contrast of the amorphous core. Similar case was also reported in the case of overbased $CaCO_3$ nanoparticles[1].
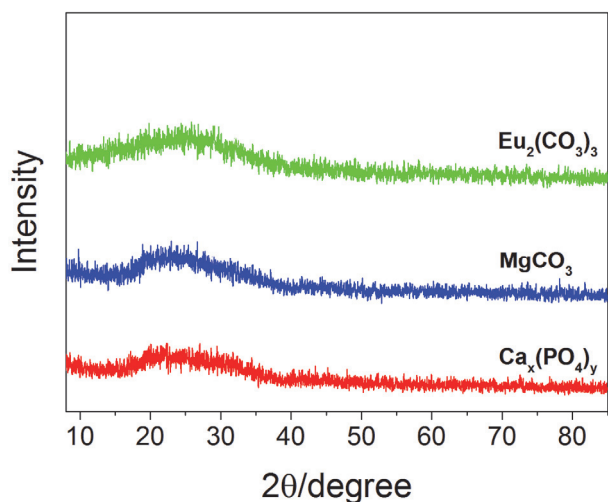
Fig. S2 XRD profiles of the dried $Ca_x(PO_4)_y$, $MgCO_3$ and $Eu_2(CO_3)_3$ clusters deposited on glass plates after one year storage in toluene indicating the stability of those clusters.
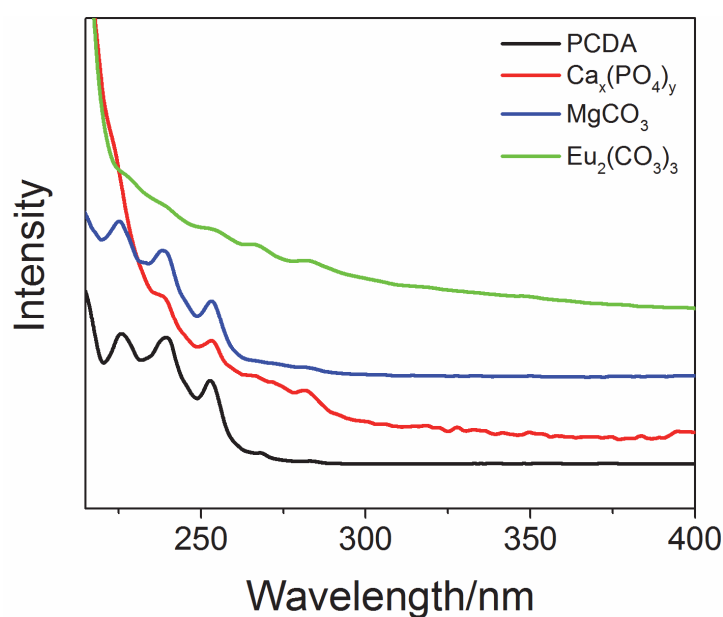

Fig. S3 UV-vis spectra of PCDA, $Ca_x(PO_4)_y$, $MgCO_3$ and $Eu_2(CO_3)_3$ clusters in hexane. As PCDA's diacetylene group is easily polymerized by light irradiation[2], it is essential to assess whether the PCDA monolayer was polymerized during reaction and post-treatment. The similarity between the UV-vis absorption of mineral clusters and PCDA in hexane shows that the PCDA chains in the mineral clusters are still in their monomeric form after binding on the mineral core. No absorption in the visible region can be observed, corresponding to the good transparency of dispersions of mineral clusters due to their small size.
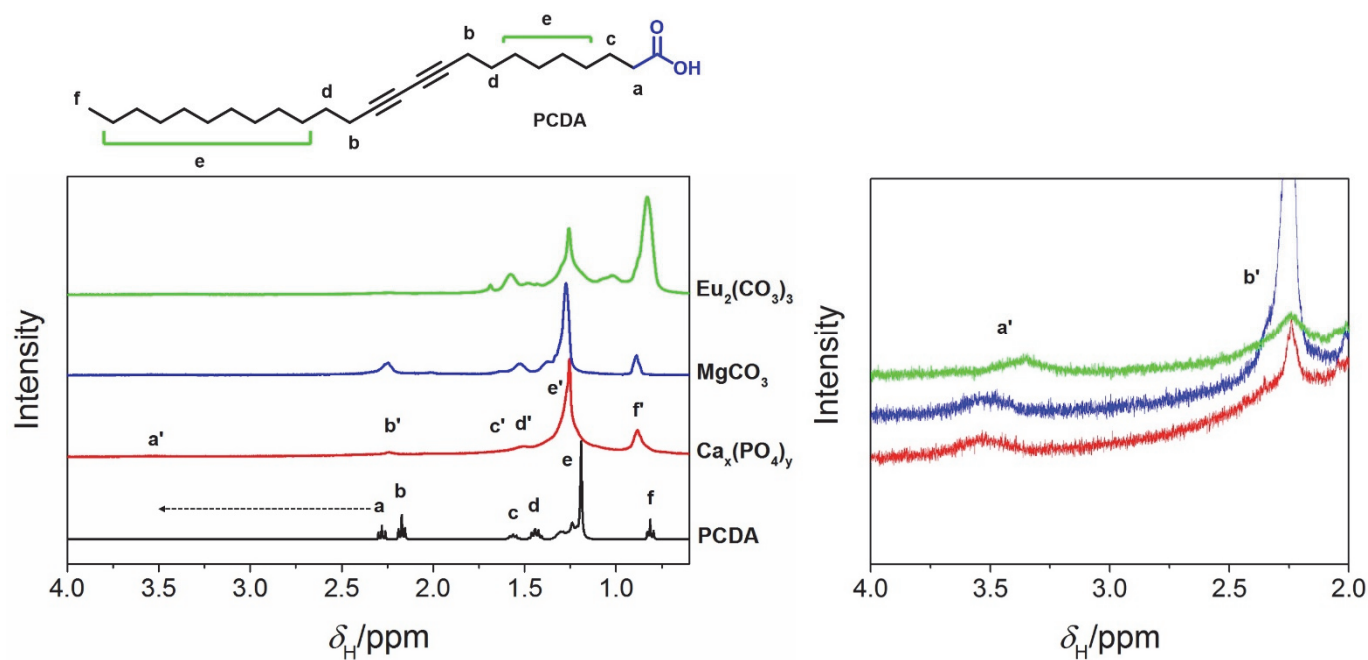
Fig. S4 ^{1}H NMR spectra and corresponding resonance assignments of PCDA, $Ca_x(PO_4)_y$, $MgCO_3$ and $Eu_2(CO_3)_3$ clusters in *d*-chloroform. a, b, c, … represent hydrogens in PCDA while a', b', c', … represent hydrogens in the mineral clusters. The right figure is an enlarged view of the area between 4.0 and 2.0 ppm showing the presence of a' peaks.
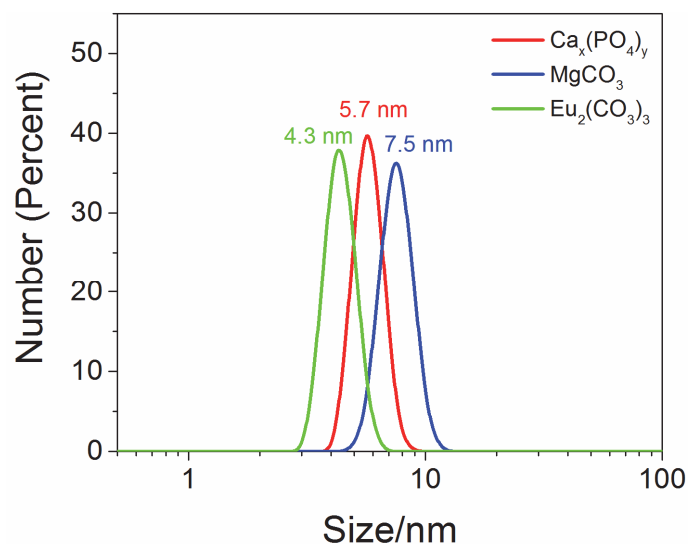

Fig. S5 Number weighted DLS size distributions of $Ca_x(PO_4)_y$, $MgCO_3$ and $Eu_2(CO_3)_3$ clusters in chloroform showing the cluster sizes consistent with TEM observations (a little larger than the sizes from TEM due to the solvation).
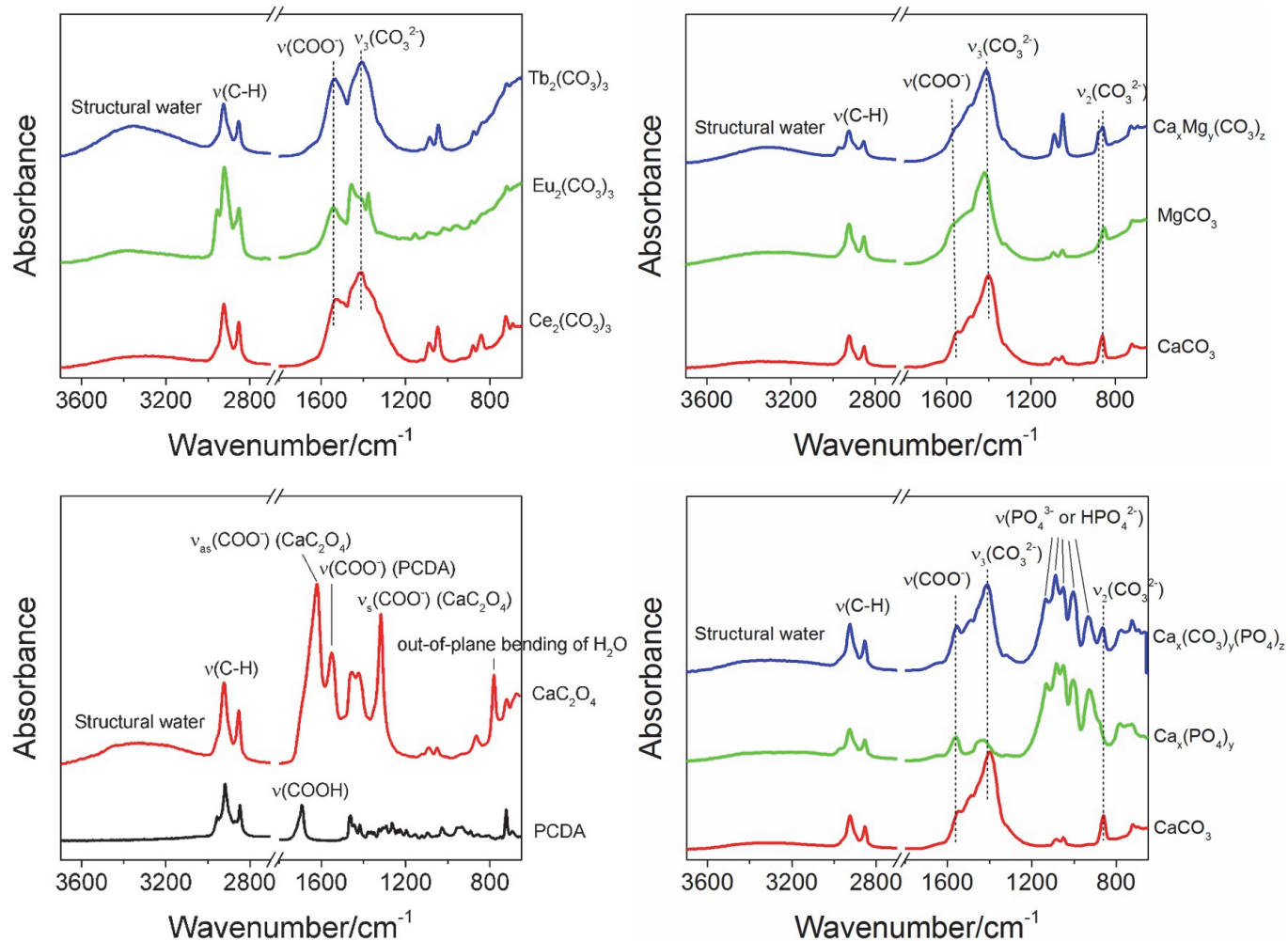
Fig. S6 ATR-FTIR spectra of various dried mineral clusters stabilized by PCDA. Corresponding assignments are also labeled in the figure. Note that the IR spectrum of the $SrCO_3$ cluster is not shown here because the pure $SrCO_3$ cluster could not be obtained even after ten times washing by precipitation in ethanol and dissolution in toluene, and contaminant Sr-PCDA salts always existed.
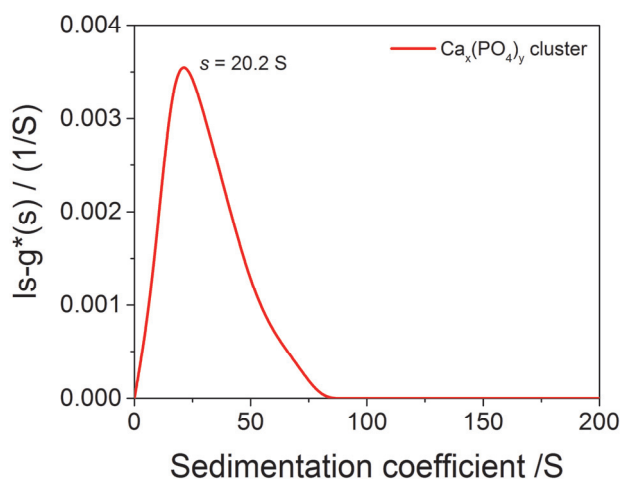
Fig. S7 AUC sedimentation coefficient distributions ls-g*(s) of $Ca_x(PO_4)_y$ cluster in toluene obtained form centrifugation at 20,000 rpm at 25 °C. The obtained quantities are the sedimentation coefficients, s (in units of S (Svedberg) = 10^{-13} s (seconds)), and apparent sedimentation coefficient distributions, ls-g*(s). The sedimentation coefficient is proportional to the size and density of a particle, and ls-g*(s) is the non-diffusion-corrected distribution of sedimenting species, which is an apparent measure of the concentration of the respective component.

The size of clusters can be determined by the equation

$d_{cluster} = \sqrt{\dfrac{18\eta_0 s_{cluster}}{\rho_{cluster} - \rho_0}}$, where η_0 the viscosity of solvent (0.005516 P), s the sedimentation coefficient of clusters (20.2 S), $(\rho_{cluster} - \rho_0)$ the density difference between cluster and solvent ($\rho_{toluene}$ = 0.87 g/ml).

Due to the core-shell structure of the $Ca_x(PO_4)_y$ cluster, it is difficult to know the exact density. However, it is clear that the cluster density ($\rho_{cluster}$) should be between that of amorphous calcium phosphate (1.75 g/mL) [3] and PCDA (0.93 g/mL for the solid state). Therefore, the cluster size at s = 20.2 S as calculated should be between 4.7 and 16.9 nm, in accordance with TEM and DLS measurements (~5.7 nm). If the above formula is used with the diameter from DLS (5.7 nm), the density of the clusters can be estimated to be 1.48 mg/ml. According to $\rho_{Cluster} = \rho_{ACP} w_{ACP} + \rho_{PCDA} w_{PCDA}$, this yields an ACP mass fraction of 0.67 in the clusters.
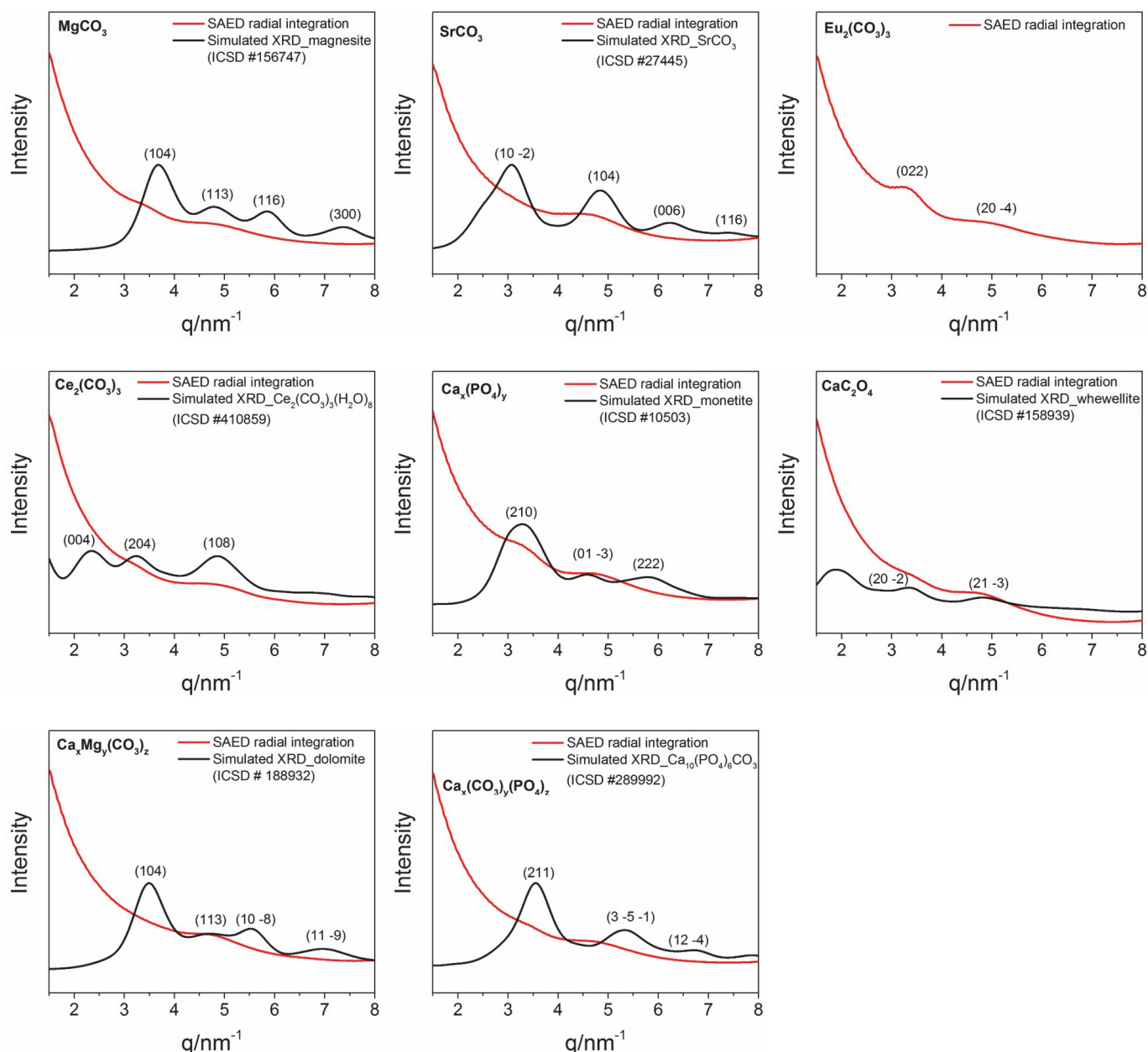
Fig. S8 Comparison of the radial integration plots of SAED patterns of mineral clusters with the simulated XRD curves of their corresponding crystalline phases with a size of 1.5 nm. Indices of the main peaks in simulated XRD curves are also labelled. The similar positions between mineral clusters and their corresponding nanocrystalline phases indicate the possible existence of short-range order in the amorphous cluster. Note that there are also some inconsistences that may be due to an inadequate selection of standard crystalline data. No data for crystalline $Tb_2(CO_3)_3$ can be found, and the indexing of crystalline $Eu_2(CO_3)_3$ was done according to the literature[4].

References

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