Supporting Information

Tunable self-assembly of YF$_3$ nanoparticles by citrate mediated ionic bridges

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Characterization of YF$_3$ particles at 5 °C and 100 °C

Figure S1. DLS, TEM (with histogram) and XRD of as-synthesized YF$_3$ nanoparticles at 5 °C. XRD peaks identification agree with cubic phase of pattern reference (04-007-2483).
The size of the nanoparticles which are involved in the supraparticles assembly was also obtained using Scherrer equation,\(^1\)

\[
\tau = \frac{K \cdot \lambda}{\beta_{1/2} \cdot \cos \theta}
\]

Where \(\tau\) is the coherent crystal domain size (nm), \(K\) the shape factor (0.9 for spherical particles), \(\lambda\) is the used wavelength (nm), \(\beta_{1/2}\) is the full width at half maximum (FWHM) of the Bragg peak (rad) and \(\theta\) is the Bragg angle (rad).

Applying this equation, we obtain that supraparticles have a final crystal coherent domain of 6.5 nm while nanoparticles show a crystal coherent domain of 4.4 nm. Nanoparticles which are involved into supraparticles tend to create bigger crystal domains to reduce the final energy of the system stabilizing thermodynamically the crystals.\(^2,3\)

**Electrokinetic measurements**

Electrophoretic measurements made using the Zetasizer Nano Zs provide the electrophoretic mobility of the particles. These mobility measurements can be converted to values of the \(\zeta\)-potential but one should be careful in the conversion because the electrokinetic effects depend crucially on the size of the particles and the nature of the surface (e.g. metallic, organic). For details see for example the IUPAC guide for the calculation of \(\zeta\)-Potential.\(^4\) In the case of supraparticles, we employed the Smoluchowski
equation, which is the default equation implemented in the software of the apparatus as provided by Malvern to convert measured electrophoretic mobility to ζ-potential values. This equation is usually a reasonable approximation for particles with sizes in the order of 100 nm. In the case of nanoparticles, the basic approximations underlying the Smoluchowski equation are not fulfilled so we need to employ other methodologies. In our case, we have employed the Huckel equation, which is usually a good approximation for small particles (with sizes of the order of a few nanometers).

Values between -39 mV and -44 mV (Table S1) indicate a negative charge onto the surface of the particles and how stables the particles are. These results are enough higher to ensure the stability of these particles in water. Likewise, NPs are more stable than supraparticles as we can observe by their ζ-Potential values.

Table S1. Electrophoretic mobility of as-synthesized nanoparticles and supraparticles and their ζ-Potential using the corresponding equation.

|                  | Electrophoretic mobility | ζ-Potential | Equation  |
|------------------|--------------------------|------------|----------|
| Nanoparticles    | -3.074 μm cm / Vs        | -44.1 mV   | Huckel   |
| Supraparticles   | -2.311 μm cm / Vs        | -39.2 mV   | Smoluchowski |

Synthesis of YF₃ at different temperatures

Figure S3. DLS, TEM micrograph, TEM histogram and powder XRD of the obtained YF₃ supraparticles at 25 °C.
Cation role in fluorinated precursor

If we perform the synthesis of YF₃ particles at 100 °C using Bu₄NF instead of NH₄F, we obtain bigger supraparticles as shown in Figure S4.

![Figure S4. DLS, TEM micrograph, TEM histogram and powder XRD of the obtained YF₃ supraparticles using Bu₄NF precursor.](image)

The use of the ammonium cation affect the final size of nanoparticles and supraparticles. Bigger cations generate smaller nanoparticles forming bigger self-assembled supraparticles (Table S2).

| Precursor | DLS(vol.) | TEM histogram | Scherrer equation |
|-----------|-----------|---------------|-------------------|
| H₄NF      | 79 nm     | 72 ± 12 nm    | 6.5 nm            |
| Bu₄NF     | 190 nm    | 179 ± 26 nm   | 3.8 nm            |
Use of different metallic precursors in the synthesis of YF$_3$ supraparticles

The possible effect of acetate was studied using different metallic precursors. The use of yttrium (III) trifluoroacetate, acetate, chloride or nitrate produced similar supraparticles, as shown in Figure S5. Therefore, we conclude that the ligand introduced by the metal precursor is not crucial in the formation of supraparticles.

Figure S5. DLS and TEM of obtained yttrium (III) fluoride supraparticles using alternative metallic salts. (a) Y(CF$_3$COO)$_3$ precursor, (b) YCl$_3$ precursor and (c) Y(NO$_3$)$_3$ precursor.

Also, $\zeta$-potential measurements were carried out with the supraparticles obtained with the previous metallic precursors. The obtained results (Table S3) show similar $\zeta$-potential for all cases. Values between -36 to -40 mV reveal a clearly negative charge onto the supraparticles surfaces. In addition, TEM histograms show that the particles have no significant difference in size.
Table S3. \(\zeta\)-Potential measurements of the obtained supraparticles carried out in water with their size obtained by both DLS in volume and TEM histogram. \(\zeta\)-Potential was obtained from the electrophoretic mobility using Smoluchowski equation.

| Precursor         | \(\zeta\)-Potential | Size (volume) | TEM histogram |
|-------------------|----------------------|---------------|---------------|
| \(\text{Y(CH}_3\text{COO)}_3\) | -39.2 mV             | 79 nm         | 72 ± 12 nm    |
| \(\text{Y(CF}_3\text{COO)}_3\) | -37.6 mV             | 109 nm        | 82 ± 8 nm     |
| \(\text{YCl}_3\)    | -36.0 mV             | 102 nm        | 77 ± 10 nm    |
| \(\text{Y(NO}_3\text{)}_3\) | -39.0 mV             | 114 nm        | 85 ± 10 nm    |

In view of these results, we can conclude that the aggregation process is independent to the used anion.

**Effect of the free ions in the system**

We performed a simple synthetic approximation in order to understand the influence of free ions in our final colloidal system. The schematic representation of this procedure is illustrated in the Scheme S1. First, the standard procedure to synthesize \(\text{YF}_3\) nanoparticles at 5 °C was carried out (20 ml, \(\sim\)30 mM) (solution A). Then, the solution was divided into two different vessels (10 ml + 10 ml). The first 10 ml were washed twice with acetone and re-dispersed in 10 ml of water, then the colloidal solution was heated to 100 °C for two hours (solution B). The second 10 ml solution was heated to 100 °C directly without washing and maintained at this temperature also for two hours (solution C).

![Scheme S1](image.png)

Scheme S1. Representative illustration of the synthetic procedure performed to know the effect of the free ions in the system. (A) corresponds to the as-synthesized \(\text{YF}_3\) nanoparticles at 5 °C (solution A), (B) corresponds to the \(\text{YF}_3\) nanoparticles at 5 °C, washed twice with acetone and then heated up to 100 °C during 2 h (solution B) and (C) corresponds to the \(\text{YF}_3\) nanoparticles at 5 °C and then heated up to 100 °C during 2 h without wash (solution C).
In Figure S6, it can be observed the results from DLS in volume of solutions A, B and C. Washed NPs remained unaltered in the media upon rising the temperature (solution B), while non-washed NPs aggregated up to ~40 nm due to free ions in the media (solution C).

![DLS Measurement](image)

Figure S6. DLS measurements of YF$_3$ nanoparticles synthesized at 5 °C in water (black). YF$_3$ nanoparticles synthesized at 5 °C, washed twice and re-dispersed in 10 ml of water, then heated up to 100 °C for 2 hours (red). YF$_3$ nanoparticles synthesized at 5 °C, then heated up to 100 °C during 2 hours without wash (blue).

Note also that the final size of supraparticles is different if they are synthesized directly at 100 °C or if we synthesize them at 5 °C and then the temperature is increased up to 100 °C. This effect could be explained taking into account the different sizes of the nanoparticles observed by Scherrer equation. Different sizes of single nanoparticles could modify the final size of formed self-assembly.

In order to corroborate the DLS measurements and observe the aggregation process, we employed TEM microscopy (Figure S7). After the synthesis of YF$_3$ nanoparticles, if they are not washed and heated to 100 °C, supraparticles are clearly formed in the colloidal solution. Size of formed supraparticles (30-40 nm) agree quite well with the information obtained by DLS.

![TEM Images](image)

Figure S7. TEM images of free ions test. YF$_3$ nanoparticles synthesized at 5 °C in water (a, solution (A)). YF$_3$ nanoparticles synthesized at 5 °C, washed one time and re-dispersed in the same volume of water, then heated up 100 °C for two hours (b, solution (B)). YF$_3$ nanoparticles synthesized at 5 °C, then heated up 100 °C during two hours without wash (c, solution (C)).
Noting that the self-assembly is only observed if we did not wash the system, we can state that the main reason for the formation of big assembled particles is the presence of free ions (e.g. citrate). When the free ions are not removed, these interact with the ions adsorbed onto NPs surface forming supra-particles when we increase the temperature. Results suggest that the self-assembly process is mediated by free ions in the unwashed colloidal system. This study also shows that the aggregation is not only formed during the synthetic process. If the nanoparticles are formed under kinetic control (5 °C) and then heated up to 100 °C without removing the excess of ions, the self-assembly is also observed.

**Infrared spectroscopy study**

Firstly, we performed the IR spectroscopy of the used ions in the synthesis to have a reference pattern to be compared, to this aim we used sodium citrate, sodium acetate, tetramethylammonium hydroxide and ammonium fluoride as it can be observed in the Figure S8.

![IR spectroscopy reference patterns of the ions used during the synthetic procedure. Carboxylate-based anions on the left and nitrogen-based cations on the right.](image)

Figure S8. IR spectroscopy reference patterns of the ions used during the synthetic procedure. Carboxylate-based anions on the left and nitrogen-based cations on the right.

If we observe first the nitrogen based cations, we could observe as they present bands at 1500 cm\(^{-1}\) and the N-H str around 3000 cm\(^{-1}\). Considering the results of NMR and their integration we do not expect to see tetramethylammonium fluoride because it is present at small amounts, see Table S5 (five washing steps). On the other hand, the low relative intensity of ammonium bands compared with the carboxylic bands makes difficult their identification by IR spectroscopy.

Concerning the carboxylic moieties (citrate and acetate), we could observe that the \(v_{\text{asym}}(\text{OCO})\) and \(v_{\text{sym}}(\text{OCO})\) are approximately in the same position in both ions. Considering the NMR integration values (see Table S5), we observe that with a ratio citrate:acetate of 7:1, we only could observe the citrate bands in IR spectroscopy, due to the small amount of acetate. Considering all these effects, we performed IR spectroscopy to YF\(_3\) nanoparticles and supraparticles (Figure S9).
Figure S9. IR spectroscopy of five steps washed YF$_3$ nanoparticles (synthesized at 5 °C) and supraparticles (synthesized at 100 °C).

The most representative bands of carboxylate-based compounds are the symmetric and asymmetric stretching of carboxylates (OCO), in the table below we represent the wavenumber of each band and the ∆ between them (Table S4).

| Particles       | $\nu_{\text{asym}}$(OCO) (cm$^{-1}$) | $\nu_{\text{sym}}$(OCO) (cm$^{-1}$) | ∆ ($\nu_{\text{asym}}$ - $\nu_{\text{sym}}$) (cm$^{-1}$) |
|-----------------|-------------------------------------|-------------------------------------|-----------------------------------------------|
| YF$_3$ at 5 °C  | 1581                                | 1421                                | 160                                           |
| YF$_3$ at 100 °C| 1588                                | 1423                                | 165                                           |

In order to study the coordination of carboxylates we need to observe its ∆ ($\nu_{\text{asym}}$ - $\nu_{\text{sym}}$). A value of ~160 cm$^{-1}$ clearly indicate an ionic coordination, in agreement with the results obtained by NMR and those predicted by MD simulations. The conclusions of NMR and MD for citrate interactions are summarized in Figure S10. At 5 °C, the main coordination of citrate with the NP is by one carboxylic group, while the other citrates interact with the NP with two carboxylic groups. On the other hand, the expected main interactions at 100 °C (from MD simulations) are: (i) citrate mediated bridge and (ii) coordination by one (bidentate) or two (monodentate) carboxylic group. All these interactions, observed at 100 °C, show a ratio of 6:1:2 (ionic:bidentate:monodentate).
Figure S10: Postulated interaction between citrate and NP at both temperatures, as deduced from NMR experiments and MD simulations. Carboxylates in black are those attached to the NP surface, red carboxylates are those interacting with cations (which are shown in blue).

**X-ray photoelectron spectroscopy (XPS)**

Figure S11. X-ray photoelectron spectroscopy (XPS) complete spectra with all assigned elements that are present in final powder YF$_3$ supraparticles.

**Effect of the washing process in YF$_3$ supraparticles obtained at 100 °C**

Generally, how one decides to wash the colloidal solution is a relevant factor in NPs design. If particles are washed too much, ligands anchored onto the surface are released and particles tend to coagulate. Likewise, if NPs are not washed enough, free ligand and by-products are present in the colloidal solution, giving us a non-real image of the surface of NPs. To study how many times, it is required to wash the NPs, we performed the study of this process with YF$_3$ supraparticles synthesized at 100 °C. The study englobes $^1$H NMR, DLS and $\zeta$-Potential measurements to see the capping agents, the size, the charge and the conductivity of the system.
$^1$H NMR spectra show the different surface composition of the ionic ligands on the synthesized supraparticles after one washing step (Figure S12a) and after five steps (Figure S12b). Results reveal different integrations in citrate and tetramethylammonium signals while acetate was used as reference in this study, giving an integration value of 3.

The relative amounts obtained by the integration of the peaks showed the presence of an excess of tetramethylammonium and citrate, compatible with the combination of attached ions and free ones. After five washing steps, a considerable number of citrate remains onto surface while most of the tetramethylammonium was washed away. We must consider a neutral system, so the negatively charged nanoparticles should have cations in the diffusion layer to neutralize the colloidal system. We have a negative formal charge of $-71e$ in one washing step that needs to be neutralized by the presence of ammonium onto particles surface or free in the system. After several washing steps, the nanoparticle’s surface become neutral (Stern layer) and they did not need tetramethylammonium as counter ion (Table S5). In Figure S13a it is clearly shown how nanoparticles start from a $\zeta$-Potential value of $-32$ mV which is keep in the first washing-up step. After five washing-ups, this $\zeta$-Potential value became $\sim 0$ mV, considering only the Stern layer. NPs, after several washing steps, reorganize their surface and become neutral. These measurements are compatible with the release of tetramethylammonium postulated by analysis of $^1$H NMR spectra. In this case, we have also detected the presence of ammonium anchored onto the particles surface due to the necessity to achieve a neutral system. The formal charge of $-43e$ after five washing steps inspire to propose the presence of 43 ammoniums onto the particles surface to produce a neutral system.
Table S5. Results obtained by the integration of the $^1$H NMR of Figure S12 and the corresponding relative number of molecules referenced with acetate.

| Molecule              | One washing step | Five washing steps |
|-----------------------|------------------|--------------------|
|                       | Integration | Rel. amount | Integration | Rel. amount |
| Acetate               | 3           | 1           | 3           | 1           |
| Tetramethylammonium   | 365.10      | 30          | 5.47        | 0.5         |
| Citrate               | 140.28      | 35          | 27.12       | 7           |

The last study performed in this section was the measurement of the supraparticles size by DLS to observe their stability during the washing processes (Figure S13b). We could observe that one washing step did not change the size of the supraparticles and produce a narrower signal compared with the unwashed NPs. After one washing step, supraparticles start to aggregate increasing in size. These results are compatible with $\zeta$-Potential measurements, where it is observed after one washing step supraparticles start to destabilize releasing the ions attached onto their surface. This produces the aggregation of the colloidal system due to the high reactivity of the uncoordinated surface.

Figure S13. The study of the washing process by Zeta-sizer. (a) $\zeta$-Potential and conductivity measurements of YF$_3$ supraparticles after each washing process (b) DLS measurements of YF$_3$ supraparticles after each washing process performed in water.
Testing the citrate mediated bridges in other NPs

Figure S14. TEM images and XRD patterns obtained for a set of LnF$_3$ NPs at 5 °C and 100 °C. (a) SmF$_3$, (b) EuF$_3$ and (c) LuF$_3$ NPs/supraparticles. In all cases, NPs are obtained at 5 °C and supraparticles at 100 °C. SmF$_3$ shows typical hexagonal crystalline structure (00-012-0792), EuF$_3$ shows orthorhombic structure (00-033-0542) and LuF$_3$ is cubic (isostructural with YF$_3$). At 5 °C, SmF$_3$ and EuF$_3$ show a mixture of orthorhombic and hexagonal structure due to their close lattice energies and their small size, while LuF$_3$ remains stable in the cubic crystalline structure. Scale bars in all images are the same to be compared easily.

Methods for Molecular Dynamics Simulations

- Initial conditions and preparation of simulation systems

Preparation of Sim1. We prepared two different systems for MD simulations, summarized in Table S6. The first simulation system (denoted as Sim1 in Table S6) corresponds to an YF$_3$ particle in ionic solution with an excess of ions. We considered 20 citrate trivalent anions with 60 tetramethylammonium monovalent counter ions and 40 monovalent acetate anions with 40 ammonium monovalent counter ions. These numbers were selected after trials with smaller number of ions, with the goal of obtaining a
NP saturated of ions while at the same time, having ions in solution with a high concentration similar to that of the experimental conditions. The ions were randomly placed in the simulation box containing a NP (initial conditions in which NP is unprotected onto its surface) and the whole system was solvated with water using the VMD program. In this way, we generated a big simulation box (~10 nm size in each direction) containing about ~10^5 atoms. This system (Sim1) was suitable for the study of ion-NP interaction.

**Preparation of Sim2.** We also wished to study the interaction between NPs in the presence of ions, but the direct simulation of many NPs in ionic solution is unfeasible with current computational resources. However, it is still possible to obtain information about NP-NP interaction by considering an infinite array of NPs with a given separation by employing periodic boundary conditions. To do this, we modified the simulation box of Sim1 to prepare a system which effectively correspond to an infinite bidimensional square lattice of NPs with different lattice constant. The initial configuration is build up as in the case of Sim1 but using a simulation box with shorter length in the x and y axis and larger length in the z axis, see system Sim2 in Table S6. In this way, we obtain effective lattices with particle center-to-center distances of ~3.7 nm (Sim2), and surface-to-surface of ~7 Å. During this work, more simulation boxes were prepared (at different distances). To summarize the computational details, we hereby will only show the most relevant simulations, those with essential information to describe our system.

Table S6. Number of organic molecules and total number of atoms (including nanoparticle atoms), distance between nanoparticles in simulations. In Sim1 we considered a large distance where particle can be considered alone in system. Box water size in each simulation is also described. In all cases we used a spherical nanoparticle of 3 nm formed by 1162 atoms (240 of Y and 922 of F).

|          | Number of molecules | NPs distance (Å) | Atoms (total) | Box size (Å) |
|----------|---------------------|------------------|---------------|--------------|
| **Sim1** | 20/40/40/60/33,173  | 73.86            | 102,541       | 102.9 x 108.1 x 99.0 |
| **Sim2** | 20/40/40/60/12,520  | 6.78             | 40,582        | 35.0 x 35.0 x 380  |

- **Protocols for Molecular Dynamics (MD) Simulations**

All MD simulations were performed using the NAMD program, version 1.9. In all cases, before running the actual MD simulations, we performed an energy minimization of the initial configurations using NAMD to solve possible bad contacts between atoms. We have performed MD simulations of all the systems described in Table S6, at two different temperatures 5 ºC and 100 ºC. The Newton equations of motion were solved using a time step of 2 fs in all simulations. Electrostatic interactions were computed using the PME method with the standard settings in NAMD (1 Å resolution, updated each 2 time steps). Lennard-Jones interactions were truncated at 1.2 nm employing a switching function starting at 1.0 nm. Periodic boundary conditions were employed in all directions. Temperature was fixed at the desired value (278K or 373K) using the Langevin thermostat (relaxation time 1 ps). Pressure was kept constant at 1 atm using the Nosé-Hoover-Langevin piston barostat (oscillation period of 100 fs and decay time of 50 fs). In Sim1, we employed the isotropic version of the barostat. In Sim2 we maintained the pressure constant by applying the barostat only in the Z direction.
For each case, simulation times were selected by checking that physical magnitudes of interest (energy, size of simulation box, number of adsorbed ions) were stable and that we have enough statistics to compute the reported results. The simulation times employed were: for Sim1 at 5 °C we use 56.7 ns, for Sim 1 at 100 °C: 55.4 ns, for Sim2 at 5 °C: 20.2 ns and for Sim2 at 100 °C: 20.2 ns.

**Additional details for the Results of Molecular Dynamics (MD) Simulations**

- **Calculation of adsorbed ions in simulation Sim1**

In order to study the binding of ions to the nanoparticle’s surface using MD simulations, we need to introduce a definition allowing us to distinguish between a bounded ion belonging to the Stern layer and a bulk ion, belonging to the diffuse layer. We employ a structural definition, assuming that ions are bound to a nanoparticle surface if they are found in the first coordination shell of the Y or F atoms of the nanoparticle. As usual in MD simulations, the identification of the first coordination shell is based on the radial distribution function (rdf). The rdfs obtained in simulation Sim1 are reported in Figure S15. In the case of anions (citrate and acetate), the rdf was computed between carboxylic oxygens of the anions with yttrium cations of the NP. In the case of cations (ammonium and tetramethylammonium) the rdf was computed using nitrogen atoms from ions and fluorides from the NP.

![Figure S15. Radial correlation function g(r) of ions with the nanoparticle element (Y or F) with opposite charge obtained in simulation Sim1. (a) Correlation function between yttrium and all carboxylic oxygens (acetate or citrate). (b) Correlation function between fluorine and the nitrogen of ammonium cation. (c) Correlation function between fluorine and the nitrogen of tetramethylammonium cation.](image)

Carboxylic oxygen atoms (from anions) and nitrogen atom (from cations) are assigned to the first coordination shell of the nanoparticle (yttrium or fluorine atoms) if their separation is smaller than the distance r corresponding to the first minimum of the g(r) function between these two types of atoms. Using this criterion, we have computed the number of ions adsorbed onto the NP in simulation Sim1 (see Table S6) averaged over all the production run. The results were given in Table S7.

In the case of citrate ions, we can also classify the adsorbed ions reported in Table S7 into two different types. At 100 °C, seven citrates are coordinated with two carboxylic groups onto two yttrium atoms while three citrates are attached with one carboxylic group onto one yttrium. At 5 °C, five citrate anions
are coordinated using two carboxylates onto two yttrium atoms while three citrates are attached with one carboxylic onto one yttrium atom.

Table S7. Ions adsorbed to the NP computed from simulation Sim1. Number of ions directly attached onto the nanoparticle surface at both experimental temperatures and relative amount of each organic molecule. Citrate (Cit), Acetate (Acet), Ammonium (Amm) and Tetramethylammonium (Tma). The number of ions presented here corresponds to the obtained in the final step of Sim1.

| Temperature | Cit | Acet | Amm | Tma | Total | Observations |
|-------------|-----|------|-----|-----|-------|--------------|
| 5 °C        | 8   | 16   | 32  | 0   | 56    | Number of molecules |
|             | -24e | -16e | +32e | 0   | -8e   | Ionic charge   |
| 100 °C      | 10  | 19   | 39  | 0   | 68    | Number of molecules |
|             | -30e | -19e | +39e | 0   | -10e  | Ionic charge   |

- Additional details on the Self-assembly study (Sim2)

As reported in the main paper, the most relevant result of simulation Sim2 is the presence of a spontaneously self-assembled citrate bridge between two ammonium cations for the simulation Sim2 performed at 100 °C, which is not present in Sim2 performed at 5 °C. We provide a movie (Movie S1) for this simulation. Also, here we give additional snapshots of these results, Figure S16.

Figure S16. Interphase observed between YF$_3$ nanoparticles at different temperatures according to Sim2. (a) Snapshot of Sim2 at 5 °C where it can be observed that the ions are not close to the interphase. (b) Snapshot of Sim2 at 100 °C shows the formation of a citrate bridge. The atoms of the Np and the citrate and the two ammonium ions involved in the bridge are shown in Van der Waals size.
Free Energy Calculations using biased MD simulations with the ABF technique

To quantify the stabilization energy produced by the citrate bridge interaction in the aggregation process, we performed an Adaptive Biasing Force (ABF) MD simulation, with the algorithm implemented in NAMD\textsuperscript{10}. In this simulation (performed in the same NPT conditions as Sim2), we considered the separation of citrate as the reaction coordinate. We started from a configuration obtained in Sim2, with the citrate starting from its equilibrium position (by definition taken as 0 Å) and forced up to distances of to 50 Å (the reaction coordinate was divided in intervals of 0.5 Å). During these free energy simulations, only the citrate ion of the ionic bridge was restrained.

Additional MD simulations performed with implicit water

In order to identify the effect produced by solvation and the presence of explicit water molecules in our simulations, we performed additional MD simulations starting from the simulations of system Sim2 but removing all explicit water molecules and introducing a dielectric medium with a value of $\varepsilon = 80$. These new simulations were denoted as Sim2.b in Table S8. This computational approximation, using implicit water, was considered at both temperatures, 5 °C and 100 °C. Simulations were performed with times that ensure the equilibrium: Sim2.b at 5 ºC (22 ns) and Sim2.b at 100 ºC (22 ns). The results are shown in Figure S17.

Table S8. Number of organic molecules and total number of atoms (including nanoparticles atoms), distance between nanoparticles in simulations and box size in the simulation with implicit water. We used a spherical nanoparticle of 3 nm formed by 1162 atoms (240 of Y and 922 of F).

| Number of molecules CIT/ACET/AMM/TMA/water | NPs distance (Å) | Atoms (total) | Box size (Å) |
|--------------------------------------------|-----------------|---------------|--------------|
| Sim2.b                                     | 20/40/40/60/-   | 6.78          | 3,022        | 35.0 x 35.0 x 380 |

The first important conclusion of the results shown in Figure S17 is the high affinity of tetramethylammonium cation for the NP surface. In this case, we want to note that tetramethylammonium (the hydrophobic cation) had no affinity to the NP surface in the standard simulations performed with explicit water Sim2). We can conclude that adsorbed water protects the NP of a massive condensation onto its surface and could be considered as other stabilizer of this system.
Figure S17. MD simulations with implicit water. Snapshot of Sim2.b at 5 °C of the interface between two YF₃ where it is clearly observed the condensation of tetramethylammonium cations (ions and NP atoms are shown Van der Waals representation).

In addition, in simulation Sim2.b performed at 100 °C we found more condensation of all ionic species onto NP surface in all directions, while in the case of 5 °C the condensation is located in the interface between the different NPs.

Our results suggest that water is playing a double role in this system: (I) as solvent allowing the co-precipitation method by the insolubility of YF₃ in aqueous media and (II) as stabilizer onto NP surface protecting them to aggregation by the high condensation of hydrophilic cations.

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