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Switchable Self-assembly of Prussian Blue Analogs Nano-tiles Triggered by Salt Stimulus

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Prussian blue analogs (PBAs) are materials well known for their bulk physical and (electro)-chemical properties, with an outstanding selectivity for caesium in ion exchange processes. Crystalline nano-tiles, made of copper based PBA, are produced and dispersed in water by tuning their electrostatic interactions. The shape and size of the nano-crystals are determined by combining scattering, microscopic and spectral techniques. We show here that Cu-PBA nano-tiles form planar superstructures by an edge to edge self-assembly process controlled by specific cation effect and ionic strength. Sedimentation and (re-)dispersion of the nano-tiles are found to be fully reversible. This switchable anisotropic self-assembly triggered by salt stimulus makes PBA nanocrystals potentially interesting for applications.

Introduction

Superparticles and superlattices formed by the self-assembly of facetted building blocks represent a new class of functional materials with enhanced performances.¹ The need to tune their structural conformation turned out to be of prime importance for their applications. The superior properties of these complex structures arise from the combination of physical and chemical characteristics of constituent particles, with the new interfaces/interactions formed in their superstructures. Cubical or multifaceted shaped particles are of particular interest because of the well-defined atomic arrangement of their surface provided by this morphology. Faceted nanoparticles (fNPs) show for example superior catalytic activity as compared to that of the spherical ones of the same composition.²⁻⁴ Other examples underscore the fact that faceted units allow a large contact area between the nanoparticles (NPs) in a superstructure. A new coupling mode was detected between collinear plasmonic nano-cubes, resulting in the advanced optical characteristic of this assembly compared to the one formed with spherical particles.⁵ The presence of metal-metal oxide interfaces with a large contact area in platinum and cerium oxide nano-cubes assembly allows the catalysis of two subsequent reactions with enhanced activity and selectivity.⁶ Metals, metal alloys and metal oxides have been used for the fabrication of cubical nanomaterials due to their specific optical,^{5, 7, 8} magnetic,⁹ electrical¹⁰ and catalytic^{2, 6} properties that can be enhanced by their multiple scale ordering. The finetuning of the fNPs arrangement in superlattices can help to

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refine the properties of functional materials. Various types of nano-cube packing, i.e. side to side or edge to edge, were obtained by means of controlled solvent evaporation,¹¹ tuning of the solvent composition,^{5, 12} functionalization of the nanoparticles with short and long chain ligands and polymers⁸ as well as through the selective modification of some sides of the cubes.¹³ For anisotropic fNPs, such as nano-tiles or nanoplatelets, self-assembly can lead to the formation of either pillar structures, due to strong stacking interaction,¹⁴ or a scale-like type structure, due to edge-interactions, for example when a substrate (hard or soft) helps the mesoscopic organization.¹⁵ However, self-assembly of nanoparticles typically requires ligand functionalization and use of organic solvents, whereas water could be a more suitable solvent for numerous potential applications.

Prussian blue analogs (PBA) are coordination polymers constituted by transition metals cyanides, known to form cubic nanocrystals. These cheap to produce and non-toxic materials have drawn attention of a large scientific community due to their outstanding electric,¹⁶⁻¹⁹ magnetic,²⁰⁻²² and photonic²³ properties, including their ability to sorb heavy and radioactive metals such as caesium (137Cs) and thallium (201Tl).24-26 Due to their low solubility, PBA are essentially used as bulk materials and therefore mainly their bulk properties have been well studied. Recent advances in the chemistry of PBA make it now possible to obtain cubical nanoparticles with precise control of their sizes and size distributions.²⁷ Stabilization of PBA cubic nanoparticles dispersions in organic^{28, 29} and aqueous media^{30, 31} has been achieved by using dispersants such as poly-vinylpyrrolidone, chemical functionalization of their surface or through the electrostatic repulsion of diluted colloids.³² Nevertheless, very few studies report on the investigation of stable aqueous dispersions of fNPs, when surface properties of nanoparticles (compared to the bulk) become important. Moreover, self-assembly of cubic PBA NPs in periodic

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arrangement has been made so far exclusively by using a solvent evaporation process. 30

Here, we present a straightforward synthesis of a highly stable concentrated aqueous dispersion of crystalline copper-based PBA (denoted as Cu-PBA) fNPs with a nano-tile (or nanoplatelet) shape. This material, with the general formula K₂CuFe(CN)₆·3H₂O, is formed in water and is stabilized through electrostatic interactions without the need of surface functionalization nor the use of dispersants. We show here that these nano-tiles self-assemble in aqueous solutions by salt addition, i.e. by tuning electrostatic interactions. The selfassembly occurs through an edge to edge process, to form larger planar super-structures. Interestingly, the specificity of the native Cu-PBA compound towards cation ($Cs^+ >> Na^+ > Li^+$) was reflected on the colloidal stability and on the growth of the super-structures by addition of nitrate salts. Moreover, it was shown that this self-assembly can be switched-on and -off on demand by a specific salt stimulus.

Experimental details

Materials

High purity K_4 Fe(CN)₆·3H₂O, CsNO₃, KNO₃, LiNO₃ and tetramethylammonium bromide (TMAB; 98%) were purchased from Sigma Aldrich. Cu(NO₃)₂·3H₂O was supplied by Fisher Scientific. Ultrapure water (18.2M Ω) from Merck Millipore Milli-Q Direct 8 system was used for the preparation of samples.

Prussian blue analogue nanoparticles synthesis

Copper-based Prussian blue analogue nanoparticles (Cu-PBA) were synthesized according to the previously reported protocol.³³ Briefly, 400 mL of 0.0776 M Cu(NO₃)₂ solution (pH = 4.7) (see Fig. 1a) were added under vigorous stirring to the same amount of 0.1 M K_4 Fe(CN)₆ solution (pH = 9.3) (see Fig. 1b). Burgundy precipitate was formed instantaneously which re-suspended in 10-30 seconds (see Fig. 1c). Then stirring was continued for another 5 minutes. The pH of the suspension was measured to be 9.5. It was transferred into 50 mL conical sample tubes and centrifuged (Sigma 3-16PK centrifuge with 11180 swing-out rotor) at 4500 rpm (3893 g) for 5 minutes. Red precipitate (\approx 7 mL) and orange supernatant were formed (see Fig. 1d). Supernatant was removed by decantation and 10 mL of MilliQ H₂O were added in each tube. After re-dispersion of the precipitate, centrifugation was repeated. Finally, the new precipitate was redispersed in water to obtain 1376 mL of stable red suspension (see Fig. 1e) with a particles weight fraction of 0.85% (20 mM). The Cu-PBA concentrations are expressed in millimolar of iron (II). It is worth mentioning that for the formation of a stable colloidal suspension, the order in which precursors are mixed is important. If potassium ferrocyanide is added to the copper salt solution then, insoluble Cu₂Fe(CN)₆ coordination polymer is formed as a main product.

This was taken care of in the experimental section.

The solubility of the PBAs is very low does not depend on the type of counter-ions used. Therefore it can be assumed that no

dissolution-crystallization phenomenon take place during the experiments. This assumption was checked in previous works.²⁴



Fig. 1 Photos of precursors (a and b), of product before (c) and after centrifugation (d), and of final and stable copper hexacyanoferrate dispersion (d).

X-Ray fluorescence (XRF)

The elementary composition of synthesized copper hexacyanoferrate colloidal system was determined with a SPECTRO XEPOS EDXRF spectrometer. For the measurement, 4 mL of nanoparticles suspension were introduced into the standard disposable cell for liquid samples. Spectra were recorded in helium atmosphere and analyzed by X-LabPro software. The calibration curve was built by serial dilution of nanoparticles suspension for which element composition is known.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was used for the determination of element composition of copper hexacyanoferrate nanocrystals. Spectra of diluted nanoparticles suspension in 1% nitric acid were recorded on a SPECTRO ACROS ICP-OES spectrometer.

Thermo-Gravimetric Analysis (TGA)

The amount of crystallization water was estimated by Setaram instrumentation with SetSys Evolution instrument on approximately 20–50 mg of solid samples at heating rate of 10° C min⁻¹. The analysis was performed in argon atmosphere from room temperature to 300°C.

X-ray diffraction (XRD)

Powder of PBA-NPs was obtained by evaporation of the water at room temperature. Powder x-ray diffraction diagrams were obtained using a Bruker® D8 Advance diffractometer in Bragg-Brentano geometry with Ni-filtered and Cu-K α radiation, between 2 θ = 5° and 80°, step size 0.01° and one second per step.

NP Size and Zeta Potential Determination in Diluted Suspension

Size and zeta potential of Cu-PBA suspension was measured as a function of salt addition (Fig. 4 and 6) by dynamic light scattering with a Nano ZS Zetasizer system from Malvern Instruments Ltd. Stock solution of dispersions was diluted with MilliQ water and filtered through the 0.45 μ m Whatman Syringe Filter. Then 10 mL of the suspension was introduced in the automatic titration unit MPT-2 equipped with the disposable plastic cell and titrated with 0.8 M solution of selected salt. The pH and conductivity of mixture were monitored as well in-situ (Fig. S5 in supporting information).

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NP Size Determination in Concentrated Suspension

Particle size determination in concentrated solution was obtained using the Acoustosizer II equipment from Colloidal Dynamics. The acoustic attenuation was measured between 1 and 20 MHz and converted to diameters by using the particle volume fraction, the solvent and particle density as input parameters.

Small angle x-ray scattering and static light scattering (SAXS and SLS)

Small angle X-Ray spectra of the suspension of copper hexacyanoferrate nanoparticles and their mixtures with salts of monovalent cations were recorded on the SWING beam line of the SOLEIL synchrotron in Saclay (France). Measurement was performed using fixed glass capillaries with the diameter of 1.5 mm. Spectra were obtained by averaging 5 individual 2Dspectra for each sample and recorded for an x-ray wavelength of 0.8 Å and for a sample to detector distance of 5 m. Scattering intensities versus Q-value, the scattering vector, were plotted over 2 decades after an azimuthal averaging of the 2D-data. SASview 3.0.0 software was used to fit the SAXS data.

SLS data were collected using an ALV-CGS3 goniometer equipped with a 22 mW HeNe Laser (632.8 nm), APD-based single photon detector and ALV/LSE-5004 Electronics. The accessible q-range was $5 \, 10^{-4}$ to $2 \, 10-3$ Å⁻¹.

Transmission electron microscopy (TEM)

Samples were prepared on 400 mesh carbon coated copper grids. First the grids were coated by cationic polyelectrolyte (polydiallyldimethylammonium chloride, $MW = 200\ 000 - 350\ 000\ g/mol$, Sigma Aldrich) through the dipping in polymer solution and rinsing with water. Then 5 μ L of nanoparticles suspension (20mM) were drop casted on the grid, excess water was removed by filter paper and by drying. TEM observations were performed on JEM-1400 microscope operating at 120kV.

Atomic force microscopy (AFM)

AFM imaging was performed in air using ScanAsyst (in contact mode 0.9 N/m) with a multimode AFM (Bruker AXS, Santa Barbara, USA) operated by a NanoScope V controller. The only parameter controlled by ScanAsyst software was the gain; all other ScanAsyst parameters were manually controlled. A silicon tip was attached to the silicon nitride lever (SNL, Bruker AFM Probes, Santa Barbara, USA) for probing the sample surface.

Results and Discussion

Copper hexacyanoferrate dispersion characterization.

The chemical composition of the Cu-PBA, synthetized according to the experimental procedure, was analyzed by X-Ray Fluorescence (XRF) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with both techniques giving similar results within the experimental error. The formula of the Cu-PBA was determined by chemical analysis as $K_{1.79}Cu_{1.13}Fe(CN)_{6}$ ·3H₂O which slightly differs from the ideal

stoichiometry expected, $K_2CuFe(CN)_6$. This discrepancy can be explained by the presence of some defects (around 10%), such as the presence of $Cu_2Fe(CN)_6$ units, in the crystalline structure. The amount of crystallization water was determined by thermogravimetry (TGA) from the weight loss of an airdried sample upon heating up to 200°C in nitrogen atmosphere (supporting information Fig. S1).³¹ The room temperature powder diffraction pattern (supporting information Fig. S2) of synthesized Cu-PBA compound corresponds to the face centered cubic structure with the lattice parameter a = 10.1 Å, typical value for Prussian blue and its analogs.¹⁸ The application of the Debye-Scherrer equation on the (200), (220) and (400) reflection peaks gives a size of crystalline domain of 107, 89 and 106 Å respectively.

The stable colloidal suspension of potassium copper hexacyanoferrate (II) was characterized by DLS. From the decay rate of the correlation functions, the intensity distribution and size distribution of the dispersed NPs was obtained (supporting information Fig. S3a, b and c). The presence of two populations of nanoparticles was observed: a small fraction of large crystals with a hydrodynamic size of about 110-120 nm and a larger fraction of smaller nanocrystals with an average size around 25-30 nm. Size determination by DLS at high particles concentrations can be affected by several effects, such as multiple scattering, high laser absorption, etc. Therefore, size determination was also performed by acoustic attenuation measurement which is more adapted to measure particle size of concentrated dispersions. The NPs size, determined by acoustic attenuation, was in the range from 20 to 35 nm which is in good agreement with the size of the small colloids estimated by DLS (supporting information Fig. S4). Only the small colloids were measured by acoustic attenuation, as this technique is highly sensitive to the particle volume fraction compared to DLS which is highly sensitive to the volume of the particles. This confirms that a significant proportion of the particles is composed of the small colloids. By increasing the ionic strength, i.e. by increasing salt concentration, the large NPs shift towards higher sizes and the small NPs contribution disappear (supporting information Fig. S3c). This indicates that the small and large particles are in equilibrium. The Z-potential of the NPs, measured by electrophoretic light scattering, indicates that they are negatively charged with an average value of -41 ± 3 mV on average for a 20 mM suspension (0.845 wt%). The negative charge of the NPs presumably arises from the K^{+} counterion dissociation at the PBA surface sites. The ζ -potential value decreases from -50 to -41 mV by increasing NPs concentration from 1 to 20 mM (supporting information Fig. S5). Nevertheless, the absolute value of the ζ -potential remains above 25 mV, ensuring the colloidal stability (as shown in Fig. 1e in the experimental section); indeed no sedimentation was observed even after several months in this concentration range.

To obtain more information on the structural aspect of the Cu-PBA NPs, the suspension was highly diluted and dried before investigation by transmission electronic microscopy (TEM). TEM pictures confirm the coexistence of two populations of

NPs, as observed by DLS experiments, and informs on their faceted structures (see Fig. 2a). A large fraction of faceted nanoparticles with an average size of 20-25 nm is detected, as confirmed by DLS and acoustic attenuation measurements. The size of PBA nanocrystals generally depends on the nucleation and growth kinetics, as it was shown by Li et al. for nickel based PBA:³⁴ faster addition and higher precursors concentration result in the formation of smaller particles. In the present experimental procedure both criteria are met, high precursors concentration (100mM) and fast mixing, in favor of the formation of small nanocrystals, here of around 25 nm. TEM images reveal also the presence of a small fraction of larger faceted crystals, with a platelet shape, that can result from the assembly of several small fNPs (see Fig. 2a insert). The presence of such large entities dispersed in aqueous solution was shown by static scattering experiments, using static light scattering (SLS) and small angle X-ray scattering (SAXS) (see Fig. 2b), where both data sets were plotted on a same graph. A large q^{-2} dependence in the scattered intensity is observed for q values ranging from about 3 10^{-3} to 6 10^{-2} Å⁻¹, indicating the presence of flat colloids with high aspect ratios. In order to estimate the characteristic sizes of these colloids, the scattering profile was simulated with a minimum number of parameters using a form factor (P) of a disk, $P(q, D, t)_{Disk}$ with D, the diameter of the disk, and t its thickness. The scattered intensity was scaled as $I(q) = \Phi V_{Cu-PBA} (\Delta \rho)^2 P(q, D, p)$ t)_{\it Disk} with ${\it \Phi}$, the volume fraction of the large particles (~ 0.0015), $\Delta \rho$, the scattering contrast between water and the particles, $\Delta \rho = \rho_{Cu-PBA} - \rho_{H2O} = [1.87 - 0.94] \times 10^{-5} \text{ Å}^{-2}$ and V, the volume of the disk expressed as $V = \pi (D/2)^2 t$. The scattering data can be well reproduced by the disk model with a diameter of about 160 nm and a thickness of around 4-5 nm. No polydispersity was taken into account for the thickness; this explains the difference between the scattering data and the model at high q-values, above 0.1 Å⁻¹. To compare these size parameters with the average hydrodynamic values (D_{H}) obtained from DLS measurements, a correction factor has to be taken into account due to the anisotropy of the particles. The expression of the correction factor for disk-shaped colloids was earlier described in the work of Mazer et al.³⁵ (supporting information, Eq. 1). Then using this expression for disk, a D_{H^-} value of about 120 nm was estimated, which is in good agreement with the size of the large particles obtained by DLS. The high value of the polydispersity index (PDI = 0.270) from the DLS experiment can therefore be attributed to the presence of anisotropic aggregates (supporting information Fig. S3b, c). Such a platelet shape is unusual for PBA nanoparticles which typically have cubic morphology. However, planar PBA particles have already been reported for Cu-PBA by using a local growth method.³⁶ In order to confirm the anisotropic shape of the large Cu-PBA nanoparticles, droplets of the suspension were dried on a silicon substrate which was then scanned by AFM. As shown in Fig. 2c, flat objects were detected with average sizes of roughly 100 nm in their large dimension and 10 nm in their thickness, these values are given without any tip geometry deconvolution. For techniques that require the aqueous dispersions to be dried,

such as for AFM or TEM, results have to be analyzed with care because the stability of the dispersion strongly depends on the particle concentration and ionic strength that dramatically change during the drying process. Nevertheless the size of the large platelets obtained by AFM measurements (around 100nm) are, at the first order, in agreement with the sizes obtained by DLS (D_{H} = 110-120nm), combined SLS/SAXS (disk diameter = 160nm) and TEM (side of the squared platelets = 100-200nm). Moreover AFM measurements confirm the high anisotropy of the Cu-BPA colloids. For this type of dispersed system, all statistical analysis techniques, such as scattering methods, remain the most valuable ones.



Fig. 2 (a) TEM image Cu-PBA nanotiles; Insert shows platelet of about 150 by 180 nm formed by the assembly of nano-tiles; (b) combination of SLS (0.0005 Å-1 < q < 0.002 Å-1) and SAXS (0.002 Å-1 < q < 0.2 Å-1) spectra (red dots) for Cu-PBA dispersion superimposed by a disk-shape form factor model (blue line). (c) AFM image and the corresponding height profile obtained from one isolated self-assembled nanotile on a glass substrate.

From all these results, it can be concluded that the Cu-PBA colloids are nano-crystals with a square based tile (platelet) shape with sides of 25 ± 5 nm and with a thickness of 4-5 nm (see Fig. 3). A cubic unit cell representing the internal crystalline structure is shown on the right part of Fig. 3. On the one hand, the negative sites inside the lattice are counterbalanced by the potassium ions to produce an overall neutral structure. On the other hand, the surface cyano groups can be easily ionized, by hydration and dissociation of the potassium in the water phase, providing a negative charge at the particle surface which ensures the stability of the suspension through electrostatic repulsions. A fraction of the nano-tiles participates to the formation of larger platelets (top part in Fig. 3) by an edge to edge self-assembly process. It results in the coexistence of free and self-assembled nano-tiles with a partitioning that is governed by the concentration and/or the ionic strength.

An excess of salt was used for the synthesis of the particles, leading to the formation of an unstable dispersion that rapidly settles down, as shown in Fig. 1d in the Experimental section. The removal of the excess salt during the washing steps, i.e. where the supernatant is replaced by deionized water, leads to stabilize the dispersion. The ionic strength is therefore decreased during the washing process, suggesting that the excess salt screens the electrostatics repulsions between the charged particles. In the next section the effect of the ionic

strength on the dispersion stability as well as the nano-tile selfassembly was studied for different added salts.

Specific ion effect on the Cu-PBA dispersion

One of the major interests in PBA materials is their unconventional ion exchange properties which makes them attractive for analytical applications, fabrication of high capacity batteries and sorption of heavy and radioactive metals. However, Prussian blue and its analogs have mainly been used as bulk materials because of their low solubility limits. In the following, the ion exchange property is investigated on dispersion of Cu-PBA nanoparticles, which have much higher specific surfaces (S/V) compared to bulk materials. The nano size of the particles implies that potassium ions in the native-PBA are of two types: (i) the internal potassium ions, within the crystalline structure of the NPs, acting as charge compensators and (ii) the surface potassium ions whose (partial) dissociation in the water phase leads to charge and stabilize the particles. Both bulk and surface sites are expected to show cation selectivity typical of the Cu-PBA material.



Fig. 3 Schematic representations of (i) a Cu-PBA crystalline nano-tile, with its unit cell in the zoomed part (some cyano groups are omitted for clarity), and (ii) of the planar superstructure formed by the nano-tiles through an edge-by-edge self-assembly process in water (top part). The large double arrow highlights the equilibrium existing between the nano-tiles and their self-assembly in the native state.

Four nitrate salts with different monovalent cations were selected for this study. Tetramethyl ammonium (or Me_4N^+) was chosen in order to study "pure" electrostatics and surface effects as Me_4N^+ is too large, with an ionic radius of 3.22 Å, to be incorporated within the PBA bulk structure. On the other hand lithium, potassium and caesium, with ionic radii respectively of 0.76, 1.38 and 1.67 Å,³⁷ are exchangeable and can diffuse through the crystalline lattice of the PBA. Potassium is the "reference" cation as it is already present as charge compensator in the native of Cu-BPA. The investigation of lithium and caesium cations allows to estimate the effect of the cation selectivity in comparison to potassium since PBA are known to have a pronounced selectivity for cations in the

following order: $\text{Li}^{+} < \text{K}^{+} < \text{Cs}^{+}$.^{38, 39} Nitrate was kept as a counter anion due to the high solubility of all its salts.

Particle size and ζ -potential were measured for a 20 mM Cu-PBA suspension as a function of salt concentration, expressed as the mole ratio M⁺/Fe^{II}, where M⁺ and Fe^{II} correspond respectively to the added cation and to the iron (II) constituting the PBA structure. The results are collected for the four selected cations in Fig. 4. For the four added salts, a linear increase in the electrical conductivity was observed (supporting information Fig. S6a) whatever the nature of the cation. The pH of the system changed only slightly from 7 to 8 upon salts addition (supporting information Fig. S6b), indicating that the effect of this factor on the suspension stability can be omitted.

For the four salts, a decrease in the ζ-potential from -41 to -35 mV is observed for M^{+}/Fe^{II} ratios ranging from 0 to 0.5 (see red rhombs in Fig. 4 bottom, Phase I). This decrease is likely to arise from a compression of the electric double layer with an increase in the sorption of cations at the surface of the particles (see Fig. 4 top). For $M^+/Fe^{11} > 0.5$, ζ -potential remains constant at a value close to -35 mV for Me_4N^+ , Li^+ and K^+ (see Fig. 4 bottom, Phase II) whereas for $Cs^+ \zeta$ -potential further decreases (see the discussion on Phase III below). The particle size and the polydispersity index, PDI, are not strongly affected by the addition of Me_4N^+ or Li^+ salt (see Fig. 4 bottom and supporting information Fig. S7), indicating that the suspension remained stable. The overall evolution in the ζ -potential as a function of the M^+/Fe^{II} ratios is then similar for Me_4N^+ , Li^+ and K⁺ salts. Even though the charge of the NPs remains nearly constant in Phase II, the NPs aggregate to form larger structures for $M^+/Fe^{II} > 1$ in the case of K^+ , as observed by the increase in the average size (see dark circles in Fig. 4). Beyond two equivalents of potassium, i.e. $K^+/Fe^{II} > 2$, the suspension become unstable and flocculation occurs rapidly. The dashed line in Fig. 4 represents the concentration range where the suspension is un-stable. It can be assumed that an increase in K^{\dagger} concentration leads to (i) a dynamic exchange with the K^{\dagger} ions already inserted into the crystalline structure and to (ii) a partial neutralization by electrostatics screening of the Cu-PBA surface sites as observed when Me_4N^+ or Li^+ salts is added. K^+ differs here from $Me_4 N^{\dagger}$ and Li^{\dagger} only by its stronger interaction with PBA³⁸ which leads to the destabilization of the suspension presumably by a bridging effect of K^{+} ions between the particles. The effect of Li⁺ salt on the average size is intermediate between the ones of $K^{\!\!+}$ and $Me_4N^{\!\!+}$ salts. The average size shows only a slight increase at high M⁺/Fe^{II} ratios, i.e. $Li^{+}/Fe^{\parallel} > 1.6$ compared to 0.65 for the K⁺ salt (see red triangles in Fig. 4 bottom). This pronounced difference (2.5 times) can be attributed to the difference in the cation-PBA adsorption constant values, which approximately three times larger for K⁺ than for Li⁺.³⁸



Fig. 4 Top: a schematic representation of the ion exchange process. Bottom: the evolution of average aggregates size and ζ-potential as a function of ionic strength for 20 mM Cu-PBA suspension. Dashed lines represent conditions under which fast flocculation occurs (PDI >0.3) and are used to show general trend.

The titration with Cs⁺ shows a clear difference in the evolution of the ζ -potential for M⁺/Fe^{II} > 0.5, compared to K⁺, Li⁺ and Me₄N⁺. Indeed ζ -potential decreases further down to a value of -20mV for 0.5< Cs⁺/Fe^{II} <1.5 and remains constant for M⁺/Fe^{III} >1.5. The selectivity of PBA for Cs⁺ is about 270 times

higher than for $K^{+,38}$ Therefore in Phase I, i.e. $0 < Cs^{+}/Fe^{II} < 0.5$, caesium ions replace potassium ions in volume sites of the PBA. The number of K^{+} ions released from the PBA bulk to the surrounding solution equals the one of added Cs^{+} . In this part of the titration the suspension behaves exactly like upon the

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titration with potassium: ζ -potential linearly decreases down to -32 mV and the suspension remains stable with a constant measured size. For M⁺/Fe^{II} >0.5 the further decrease in the ζ potential can therefore be attributed to the particularly high affinity of PBA for Cs⁺ which leads to (i) a surface charge compensation by adsorption of Cs⁺ ions on the particles surface sites and to (ii) an increase in the size. Interestingly ζ potential becomes constant for Cs⁺/Fe^{II} >1.5 which is close to 1.8, the expected value for a full K⁺/Cs⁺ exchange (K_{1.79}Cu_{1.13}Fe(CN)₆·3H₂O).

Salt effect on the self-assembly of PBA nano-tiles

In the following the self-assembly of PBA nano-tiles upon salt addition is investigated further by scattering techniques. Potassium and caesium salts were added to a 20 mM Cu-PBA suspension (see Fig. 5 and supporting information Fig. S8) at M^*/Fe^{II} ratios from 0 to 4. In this concentration range, the assembly of PBA nano-tiles grows from an average size of 100 nm, obtained by DLS, up to several hundred nanometers.



Fig. 5 (a) SAXS spectra of 20 mM Cu-PBA suspension upon titration with CsNO₃. (b) Zoom of the region where curves show $q^{\cdot 2}$ dependence.

At $M^*/Fe^{II} = 0.2$, the SAXS spectra for Cs⁺ and K⁺ remain similar to the one without salt addition ($M^*/Fe^{II} = 0$) which was already discussed. This is in agreement with the DLS results in Fig. 4 (Phase I) showing no change in the average size. At higher M^*/Fe^{II} ratios, Phase II (and III) in Fig. 4, a significant extension in the q^{-2} dependence to the lower q region is observed. This indicates that the planar structures, constituted by the self-assembly of nano-tiles, become larger (>300 nm) by extending in two dimensions through an edge-to-edge process. The increase in the average size observed by DLS corresponds to the formation of larger platelets (Fig. 4 bottom). The fitting of the SAXS spectra by using a disk model, already described above, confirms the extension of the platelets by adding salt (supporting information Fig. S9).

Colloidal stability versus particles concentration and specific ion effect

The stability of charged dispersions depends on the ionic strength, the nature of cation and also on the nanoparticles concentration. The stability of the PBA suspension was investigated by addition of K⁺ and Cs⁺ salts at different particle concentrations (1, 2 and 20 mM). The average size measured by DLS was plotted as a function of the ionic strength (see Fig. 6a), which is equal to the concentration of the added 1:1 salt (KNO₃ or CsNO₃). The dashed lines indicate the region where the salt concentration is high enough to induce fast flocculation. This peculiar salt concentration, which leads to destabilize the dispersion, is usually referred to as the critical coagulation concentration (ccc). For K^+ , the higher the nanoparticles concentration the lower the ccc (see Fig. 6a), as it is expected for charged colloids dispersions when salt is added. The same conclusion can be made by plotting the PDI instead of the average size (see Fig. S10). Surprisingly an opposite tendency is found for caesium: the higher the particle concentration the higher the ccc. This means that for a given concentration of Cs^+ , for example for $[Cs^+] = IS = 10$ mM, the dispersion gets stabilized by increasing the particle concentrations from 2 to 20 mM. A fundamental distinction between the effect of K^{+} and Cs^{+} on the dispersion stability is highlighted here. The average size measured by DLS was plotted as a function of the M^+/Fe^{II} ratio (see Fig. 6b) in order to understand the difference observed between the opposite behaviours of K^{\dagger} and Cs^{\dagger} . Interestingly a similar evolution in the stability of the PBA dispersion (Fig. 6b) was observed for K^+ and Cs⁺: the M⁺/Fe^{II} ratio, where flocculation appears, decreases for both K^{+} and Cs^{+} when the particle concentration is increased. The comparison between Fig. 6a and 6b suggests that the destabilization of the dispersion, when salt is added, has a different origin for K^{+} and for Cs^{+} . With potassium ions, the aggregation of the particles is induced by a classical charge screening effect. In this case, the flocculation rate strongly increases with the particle concentration, as it is usually observed for most charged colloids.⁴⁰ On the other hand caesium is specifically absorbed in the Cu-PBA structure and replaces potassium. Moreover, we have shown that the strong interaction of caesium with the lattice of PBAs leads to decrease the effective charge of the nanoparticles, which is reflected by the ζ -potential values, see Fig. 4. Consequently the stability of the dispersion (or self-assembly of the PBA tiles) is controlled by the effective particle charge that is mainly influenced by (i) the M^+/Fe^{II} ratio for Cs^+ and (ii) by an electrostatic screening effect for K^{+} (Fig. 6a and 6b).

Switchable self-assembly of PBA nano-tiles by salt stimulus

It was shown during the synthesis procedure (see experimental section) that aggregated Cu-PBA NPs can be redispersed by replacing the supernatant with deionized water, i.e. by decreasing ionic strength. This indicates that the nanoparticle aggregation is fully reversible and can therefore be easily tuned by washing or dialysis procedures. Moreover, we have shown that ionic strength, as well as specific ion-PBA interactions, controls the size of the nano-tiles self-assembly with a well-defined 2D structure. Therefore, the control of the ionic strength provides an elegant way of tuning the size of the 2D platelets and the dispersion stability. In order to go a step further in the control of the PBA NPs dispersions we propose a procedure to stabilize/destabilize on-demand suspensions by a specific salt stimulus (see Fig. 7). An example of such a switchable system is described in the following. One equivalent of concentrated barium chloride was added to a diluted suspension of Cu-PBA in native potassium form (1 mM). Due to the higher complexation constant for barium,³⁸ potassium was replaced by barium in the PBA lattice. During the K^+/Ba^{2+} exchange the ζ -potential drops from -42 mV down to -12.8 mV which leads to fast flocculation within minutes. In a second step, one equivalent of potassium sulfate is added, which leads the NPs to re-disperse after a short time (5-10 seconds) of sonication. The mechanism of this process can be described as follows: barium cation precipitates with sulfate anion (solubility of BaSO₄ in water of 2.448×10^{-3} g/L at 20°C). This enables to replace barium by potassium in the lattice of PBA. The Cu-PBA under its K⁺ form is therefore recovered and shows a ζ -potential (-39.2 mV) comparable to the one of the native particles (-42 mV). The slightly lower ζ -potential value can be attributed to the moderated increase in the ionic strength compared to the native stable dispersion. The on/off switchability of the dispersion stability can be performed several times up to the increase in the ionic strength prevents the re-dispersion. This procedure may be used to control of the dispersion stability as well as for the synthesis of nanoparticles containing cations with low affinity towards the PBA.



Fig. 6 Averaged diameters (hydrodynamic sizes) of Cu-PBA NPs, determined by DLS, as a function of (a) K^* or Cs⁺ concentration and of the (b) M^* /FeII ratio for different concentrations of Cu-PBA: 1, 2 and 20 mM. The red arrows show in which direction concentration of the nanoparticles increases in the case of caesium ions and blue arrows show the same tendency for potassium ions. Dashed lines represent the conditions under which fast flocculation occurs and are used to show general trend.



Fig. 7 Photos showing the reversibility of the Cu-PBA nanoparticles dispersion, triggered by specific salt stimulus.

Conclusions

Here we reported the synthesis of stable aqueous suspension of copper-based Prussian blue analogs stabilized by electrostatic repulsions in the absence of surface modifying agents. The nano-tiles obtained with this procedure have 25-30 nm-long sides, thickness of 4-5 nm and show high ζ potential (41±3 mV) which enables the stability of the dispersion. These NPs self-assemble in water to form larger (\approx 100 nm) planar superstructures made of nano-tiles, typically

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around 10, assembled by their edges. Increase in the ionic strength promotes this self-assembly process by forming even larger planar structures (> 100-200 nm), leading ultimately to the instability of the suspension. Upon salt addition, the increase in the size of the self-assembly, and the stability of the dispersion, depends on the type of the cation added. Interestingly this specific cation effect $(Cs^+ > K^+ > Li^+)$ is consistent with the adsorption constant values reported earlier for cations and bulk PBAs. On the one hand, cations being too large to intercalate within the PBA lattice, such as tetramethylammonium, and cations with a low affinity for PBAs, such as lithium, have no or only slight effects on the suspension stability. On the other hand, potassium and caesium adsorb on the particles surfaces and bridge the nanotiles by their edges. This mechanism can be described as an "ionic glue" operation which at the origin of the PBA nanocrystal self-assembly. The flocculation/dispersion process of the NPs was shown to be completely reversible and easily switchable by salt stimulus. This new procedure offers opportunities to control the synthesis of novel functional materials through the controlled self-assembly of faceted nanoparticles. Moreover, the switch-ability of anisotropic nanocrystals self-assembly triggered by salt stimulus can also be interesting for the control of optical/magnetic properties.⁷⁻⁹

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