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## Supporting Information

#### Tuning the shape anisotropy of loosely bound colloid-like ionic clusters in solution

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### **Preparing molar ratios**

Preparing the different molar ratios for the  $1^{4+}:2^{2-}$  ( $1^{4+}:3^{2-}$ , respectively) system started with producing following stock solutions in DMSO:glycerol:water 50:43:7 (v/v/v):

- $c(1^{4+}) = 6 \,\mathrm{mM}$  and
- $c(2^{2-}) = c(3^{2-}) = 6 \,\mathrm{mM}.$

The two stock solutions were then combined based on Table S.1 to receive the desired molar ratios.

Table S.1	Summary	of all	tested	molar	ratios	for	the	system	$1^{4+}:2^{2-}$	$(1^{4+}:3^2)$	,	respectively)	) in
	DMSO:gl	ycerol:	water 5	0:43:7	(v/v/v)	) cor	nbin	ed with	their calc	ulated i	oni	c ratio	

molar ratio	c(1 <sup>4+</sup> ) / mM	c( <b>2</b> <sup>2−</sup> / <b>3</b> <sup>2−</sup> ) / mM	$V(\mathbf{1^{4+}})$ / $\mu \mathrm{l}$	$V(2^{2-}/3^{2-})$ / $\mu l$	V(solvent) / µl	ionic ratio <sup>a</sup>
0:1	0.0	3.0	0	120	120	-
1:6	0.5	3.0	20	120	120	1/3
1:3	1.0	3.0	40	120	80	2/3
1:2	1.5	3.0	60	120	60	1
2:3	2.0	3.0	80	120	40	4/3
5:6	2.5	3.0	100	120	20	5/3
1:1	3.0	3.0	120	120	0	2

<sup>*a*</sup> calculating ionic ratio using equation (S.1)

Calculating the ionic ratio inside each  $1^{4+}:2^{2-}$  ( $1^{4+}:3^{2-}$ , respectively) system is based on equation (S.1)

ionic ratio = 
$$\left| \frac{z^+ \cdot c(\mathbf{1}^{4+})}{z^- \cdot c(\mathbf{2}^{2-}/\mathbf{3}^{2-})} \right|$$
, (S.1)

where  $c(1^{4+})$  and  $c(2^{2-}/3^{2-})$  represent the corresponding concentrations from **Table S.1**. Note that we assume a constant charge  $z^{\pm}$  for the cationic ( $z^{+} = +4$ ) and anionic ( $z^{-} = -2$ ) building block in all tested molar ratios.

### **Dynamic Light Scattering (DLS) measurements**

The Litesizer 500 with three different scattering angles (15°, 90°, 175°) uses a correlator, which can perform up to 248 auto/cross-correlations simultaneously over a time-range of 10 ns to 85 s. As result, we obtained the intensity time correlation function  $g_2(\tau)$ , which was directly fitted using a constrained regularization method incorporated inside the ALV software. The precise mathematical background of regularization DLS data is described in the CONTIN 2DP program by Provencher<sup>1,2</sup>. Equation (S.2) shows the ALV nonlinear fit model for calculating smooth distribution functions

$$g_2(\tau) - 1 = \left(\int_{\Gamma_{min}}^{\Gamma_{max}} e^{-\Gamma\tau} \mathbf{G}(\Gamma) \mathrm{d}\Gamma\right)^2 , \qquad (S.2)$$

where  $G(\Gamma)$  denotes the distribution function of the decay rate  $\Gamma$ . The decay rate itself coheres with the diffusion coefficient *D* through  $\Gamma = Dq^2$ , while  $q = \frac{4\pi n}{\lambda} \sin(\frac{\theta}{2})$  describes the scattering vector including the solvent refractive index (*n*) and the laser wavelength ( $\lambda$ ). Under the assumption that (i) scattering particles behave as hard spheres in dilute solution and (ii) Rayleigh-Debye theory is valid, the Stokes-Einstein-equation (see (S.3)) allows calculating the distribution of the hydrodynamic radius  $R_H$  based on

$$D = \frac{k_B T}{6\pi\eta R_H} , \qquad (S.3)$$

considering the Boltzmann constant  $k_B$ , the temperature *T* and the solvent viscosity  $\eta$ . The final 'mass weighted' particle radius distribution function results in adjusting the amplitudes of the decay rate in order to cut unphysically large contributions at small particle radii. All samples were measured with a quality setup of six runs, where each run took 30 s and all runs were averaged into one intensity time correlation function. The adjustments for the laser attenuation, which have direct impact on the mean scattering intensity, were carried out automatically in order to detect optimized count rate traces.

# Continuous Wave Electron Paramagnetic Resonance (CW EPR) spectroscopy measurements

X-band CW EPR measurements, which were performed with the Miniscope MS400, made use of a sweep width of 100 G, a modulation amplitude of 600 mG and microwave attenuation of 20 dB. Note that the modulation amplitude surpassed the standard limit of  $\leq 0.5 B_{pp}$  ( $B_{pp}$  as peak-to-peak line width) to gain spectra with an improved phase resolution. Q-band CW EPR measurements were carried out with the Bruker EMX-plus spectrometer. We applied the same microwave attenuation as written before, but used a sweep width of 130 G and a modulation amplitude of 1000 mG. The important step for our simulation approach, which is based on the slow-motion theory developed by Schneider and Freed<sup>3</sup>, was to choose suitable starting parameters for the Fremy's salt *g*-tensor and hyperfine coupling tensor A. The spectral simulations were performed in Matlab (R2016a, v. 9.0) exploiting the EasySpin package (v. 5.2.11)<sup>4</sup>. Based on literature data<sup>5</sup> we took the following parameter sets:

- g-tensor:  $g_{xx} = 2.0086$ ,  $g_{yy} = 2.0064$ ,  $g_{xx} = 2.0029$
- hyperfine-tensor (X-band):  $A_{xx} = 5.3 \text{ G}, A_{yy} = 5.5 \text{ G}, A_{zz} = 28.3 \text{ G}$

• hyperfine-tensor (Q-band):  $A_{xx} = 5.5 \text{ G}, A_{yy} = 5.6 \text{ G}, A_{zz} = 28.3 \text{ G}$ 

Other values like line broadening and rotational diffusion rates that have to be implied into the simulation routine, depend on the discussed system and will be characterized while analyzing the CW EPR spectra. For calculating the rotational correlation time  $\tau_c$  (see equation (S.4)), we sticked to a simple model of Brownian diffusion with an axial rotational diffusion tensor containing the values  $D_{\parallel}$ (unique axis) and  $D_{\perp}$  (perpendicular to the unique axis)<sup>6</sup>

$$\tau_c = \frac{1}{6 \sqrt[3]{D_{\perp}^2 D_{\parallel}}} \,. \tag{S.4}$$

The discussed information about the line width of all measured CW EPR spectra (see main text) are based on isotropic broadening, which is implemented in the EasySpin program package. Note that this method does not assume any physical model causing the broadening. Instead we observed the changes of the full width at half maximum (FWHM) values of Fremy's salt with increasing concentration of the cationic component to describe the electrostatic interactions between both ions. Furthermore, we established a routine to analyze the present anisotropy of the rotational diffusion tensor. Note that even paramagnetic molecules in the 'fast-motion regime' significantly reflect deviations from the isotropic case through their CW EPR spectra<sup>6</sup>. Based on the values of the rotational diffusion tensor, we calculated its anisotropy *T* using equation (S.5)

$$T = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} \,. \tag{S.5}$$

A larger *T*-value indicates stronger separation between  $D_{\parallel}$  and  $D_{\perp}$ , while smaller *T*-values reflect more isotropic tumbling, which can be attributed to weaker electrostatic interactions in the direct vicinity. For ion clouds with later self-assembly into *globular ionoids* the right balance between attractive and repulsive electrostatic forces is important, which translates into an anisotropy *T* that must be situated in a specific range. As reference we took the values based on the established molar ratio  $\mathbf{1}^{4+}:\mathbf{3}^{2-}$  1:3. Finally, we had to imply so-called Euler angles  $\alpha$ ,  $\beta$  and  $\gamma$  to simulate CW EPR spectra at both frequencies with the EasySpin package. The entire set of Euler angles is made out of:

- pure  $3^{2-}$ :  $\alpha = 65^{\circ}$ ,  $\beta = 90^{\circ}$ ,  $\gamma = 15^{\circ}$  and
- $1^{4+}:3^{2-}: \alpha = 85^{\circ}, \beta = 90^{\circ}, \gamma = 15^{\circ}.$

### Analyzing ionic ratio dependence with DLS



Fig. S.1: Intensity time correlation functions at measurement day 79 with a) side and b) back scattering for the cluster system  $1^{4+}:2^{2-}$  in DMSO:glycerol:water 50:43:7 (v/v/v) depending on the molar ratio of cationic and anionic component. The well-known 1:3-ratio is highlighted with a slightly thicker red line.

Based on the intensity time correlation functions at measurement day 79 (see **Fig. S.1**) one can clearly state that the molar ratios  $1^{4+}:2^{2-}$  1:3 to 5:6 show almost the same decay. The small deviations, which are present, provide the shifts in the hydrodynamic radius for the self-assembled ionic structures. In contrary, the molar ratios 1:6 and 1:1 do not show a pronounced autocorrelation function, indicating the abscence of highly defined structures. **Fig. S.2** confirms this by displaying the autocorrelation functions for the 79 days old samples after filtering them.



Fig. S.2: Intensity time correlation functions after sample filtration with a) side and b) back scattering for the cluster system  $1^{4+}:2^{2-}$  in DMSO:glycerol:water 50:43:7 (v/v/v) depending on the molar ratio of cationic and anionic component. The well-known 1:3-ratio is highlighted with a slightly thicker red line.

### Analyzing ionic ratio dependence with CW EPR

Fig. S.3 displays all measured and simulated CW EPR spectra at both X- and Q-band frequencies for the system  $1^{4+}:3^{2-}$  in DMSO:glycerol:water 50:43:7 (v/v/v) depending on the molar ratio. One can clearly state that with increasing concentration of the 'Texas-sized molecular box' the rotational mobility of Fremy's salt continuously decreases (see also Fig. S.4 a)). This is also visible in the rising FWHM values, which are described in the main text. The coordination between both components shifts with higher ionic ratios from relatively free to a more fixed one, which distrubs the following self-assembly process into highly defined, globular structures.



Fig. S.3: a) X-band and b) Q-band CW EPR spectra for system 1<sup>4+</sup>:3<sup>2-</sup> in DMSO:glycerol:water 50:43:7 (v/v/v) depending on the molar ratio. Both graphs show for each mixture the measured spectrum (black line) as well as the simulated spectrum (red line).

While rotational correlation time  $\tau_c$  and line width show the same tendencies at X- and Q-band frequencies, we detect significant differences in their anisotropy values (see **Fig. S.4 b**)). At X-band frequencies, we mainly observe the drop of  $D_{\perp}$  with higher concentration, resulting in increasing *T*-values. However, higher frequencies display the formation of fixed coordinations between  $1^{4+}$  and  $3^{2-}$ , which decrease  $D_{\perp}$  as well as  $D_{\parallel}$  and keeps *T* at a constant lower value. It seems that X-band data show the existing electrostatic interactions in the total ion cloud state, while Q-band spectra highlight the direct coordination behavior of Fremy's salt.



Fig. S.4: a) Rotational correlation time  $\tau_c$  and b) anisotropy *T* of the system  $1^{4+}:3^{2-}$  versus the concentration of  $1^{4+}$  in DMSO:glycerol:water 50:43:7 (v/v/v).

Table S.2 summarizes the simulation results for both frequencies.

Table S.2:	Summary	of	the	simulat	ted a	axial	rotation	al	diffu	sion	tensor	$D_{\perp}$	and	$D_{\parallel}$	as	well	as
	the calcul	ated	rot	ational	corr	elatio	n time	$ au_c$	and	anise	otropy	Τo	f sys	stem	144	-: <b>3</b> <sup>2</sup> -	in
	DMSO:gly	cer	ol:w	ater 50:	43:7	(v/v/	v) deper	ndiı	ng on	the r	nolar ra	atio					

ratio		X-ba	nd	Q-band					
	$D_{\perp}/\mathrm{s}^{-1}$	$D_{\parallel}/\mathrm{s}^{-1}$	$ au_c$ / ps	Т	$D_{\perp}/\mathrm{s}^{-1}$	$D_{\parallel}/\mathrm{s}^{-1}$	$ au_c$ / ps	Т	
0:1	9.5e8	3.5e10	52.72	0.923	1.0e9	5.0e10	45.24	0.942	
1:6	5.7e8	3.2e10	76.36	0.948	4.5e8	2.0e10	104.56	0.935	
1:3	3.1e8	3.2e10	114.61	0.971	3.0e8	1.0e10	172.62	0.915	
1:2	2.1e8	4.0e10	137.94	0.984	2.1e8	7.5e9	241.00	0.920	
2:3	1.8e8	4.0e10	152.87	0.987	1.8e8	7.0e9	273.30	0.927	
5:6	1.55e8	4.0e10	168.89	0.988	1.6e8	6.5e9	303.02	0.930	
1:1	1.4e8	3.5e10	188.98	0.988	1.5e8	6.0e9	324.89	0.929	

### Ionoid Evolution Diagram (IED)

In this section we want to highlight the idea as well as the crafting process for the so-called ionoid evolution diagrams (IEDs), which were introduced in the main text. Fig. S.5 displays on the one hand the IED for modifying the ionic ratio of  $1^{4+}:2^{2-}$  and on the other hand a Hertzsprung-Russell diagram (HRD) as inspirational foundation.



Fig. S.5: Comparison between a Hertzsprung-Russell diagram, which summarizes complex relationships of the properties of stars and stellar evolution during their complete lifetimes (here exemplary for our sun) and our ionoid evolution diagram for describing the dynamic ionic self-assembly process of for all tested molar ratios of  $1^{4+}:2^{2-}$ .

Hertzsprung-Russell diagrams display the classification of stars as well as stellar evolution during their complete lifetime through plotting the luminosity (often as relative value compared to our sun) on the y-axis against their surface temperature on the x-axis. Mass and time development are thus implicitely part of HRDs. Hence, these diagrams allow summarizing and displaying all stages of stellar development which is a remarkably large and complex set of data and we develop our IEDs to describe the dynamic ionic self-assembly process inside our solutions, which also comprises a wealth of complex data and long temporal evolution. To include important design elements like molar/ionic ratio, we need to define fitting parameters, which can represent the present electrostatic correlations between anionic and cationic component. Based on the fact that the source of electric fields lies in a charge or charge density<sup>7</sup>, we plot the volume charge density of our ionoic building blocks versus their respective diameter (without a solvation shell around them).

Both parameters, diameter as well as volume charge density, were determined using the YASARAstructure software<sup>8</sup>. After implementing the ionic building units into the software, we applied the already existing experiment 'Energy minimization'<sup>A</sup> to optimize their chemical structure at a temperature of T = 293 K. At the end we could (i) read off the diameter and (ii) calculate the volume V (based on the molecular surface) of each ionic building unit to finally obtain the volume charge density  $\rho$  using equation (S.6):

A This experiment creates a simulation box with periodic cell boundaries around the ionic building unit. Furthermore, it applies the AMBER03 forcefield to run the simulation.

$$\rho = \frac{z^{\pm} \cdot e}{V} \quad \text{with} \quad [\rho] = \frac{\text{As}}{\text{m}^3} , \qquad (S.6)$$

with  $z^{\pm}$  as charge for the cationic/anionic component and *e* for the elementary charge. **Table S.3** summarizes for each ionic building unit the derived information from the YASARA-structure software.

ionic	diameter /	charge $z^{\pm} \cdot e$	volume V /	volume charge density $\rho$ /
compound	nm	/ 10 <sup>-15</sup> As	$A^{\mathcal{I}}$	$10^{2} \frac{115}{m^{3}}$
1 <sup>4+</sup>	1.390	6.408	907.15	0.706
$2^{2-}$	0.278	-3.204	118.36	-2.710
<b>3</b> <sup>2</sup> -	0.285	-3.204	106.48	-3.010

 Table S.3: Summary of all derived informaton from the YASARA-structure software to construct the ionoid evolution diagrams

After characterizing the ionic building units based on the parameters in **Table S.3**, we can illustrate the studied system  $1^{4+}:2^{2-}$  in the IED by simply combining the two affected ionic compounds. Note that each possible molar/ionic ratio between both components can be highlighted as an intersection point along their connection line, as shown in **Fig. S.5**. In the next step, we want to analyze the dynamic ionic self-assembly process after the incubation time of ten days starting from the previously established intersection point. Therefore, we (i) extend the x-axis to incorporate the build up ionic structures and (ii) introduce a second y-axis that is able to describe the shape<sup>B</sup> of these formations. We utilize the so-called eccentricity *e*, which is known in mathematics as a measure of how much a conic section deviates from being circular, e. g. ellipses can be calculated through equation (S.7)

$$e = \sqrt{1 - \frac{b^2}{a^2}} \tag{S.7}$$

with a = length of its semi-major axis and b = length of its semi-minor axis. Circles have an eccentricity of e = 0, while ellipses strictly stay below the value of one. We adapt equation (S.7) to characterize our three-dimensional self-assembled structures by exchanging parameter a and b with our measured hydrodynamic radii at side and back scattering. If the particle size distribution shows two separate entities, we applied the values from the smaller ones into the IED, because we want to highlight the building process of the globular structures in the sample. Note that we had to establish the following 'rule': The higher value from DLS will be set as a (semi-major axis) independent from the scattering angle.

B Present deviations from a spherical structure are an important feature to distinguish between *globular ionoids* and anisotropic ionic clusters. DLS results based on different scattering angles can be used to derive these information. However, parameters like the particle form factor P(q) or the  $\rho$ -ratio, which are able to describe the morphology of our ionic structures more in detail, can be derived by measuring e. g. static light scattering.<sup>9</sup>

To further highlight the advantage of using the eccentricity as parameter to analyze the shape of our highly defined ionic clusters, we exemplary display simple two- and three-dimensional structures in **Fig. S.6** with e = 0, e = 0.25, e = 0.50 and e = 0.75. To generate these four eccentricities, we applied the following values (without a specific length unit) for the semi-major axis *a* and semi-minor axis *b*:

- (1) e = 0.00: a = 6.00 and b = 6.00,
- (2) e = 0.25: a = 6.20 and b = 6.00,
- (3) e = 0.50: a = 6.95 and b = 6.00 and
- (4) e = 0.75: a = 9.07 and b = 6.00.



Fig. S.6: Two- and three dimensional structures based on the eccentricity-values of e = 0, e = 0.25, e = 0.5 and e = 0.75 together with the transition from *globular ionoids* to anisotropic ionic clusters. The two-dimensional shapes contain the semi-major axis *a* and semi-minor axis *b*, which are directly embedded in equation (S.7).

The visual difference between the eccentricities e = 0 and e = 0.25 appears less significant compared to e = 0.25 and e = 0.5, which lead us to set the value of e = 0.25 as border *globular ionoids* to anisotropic ionic clusters. Note that this value is currently just valid for the  $1^{4+}:2^{2-}$  system and has to be verified with other ionic building blocks. Applying equation (S.7) to our DLS results, we are also able to analyze the time-dependent behavior of the self-assembled structures, e. g. in **Fig. S.5** the blue full dots show measurement day ten and the blue crossed dot day 79. The arrow between a pair of dots highlights the development over time and allows a better comparision between different molar/ionic ratios. At last, evolution with time is also emphasized in IEDs by the oval (or for *globular ionoids* more circular) frame.

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