

Electronic Supporting Information for

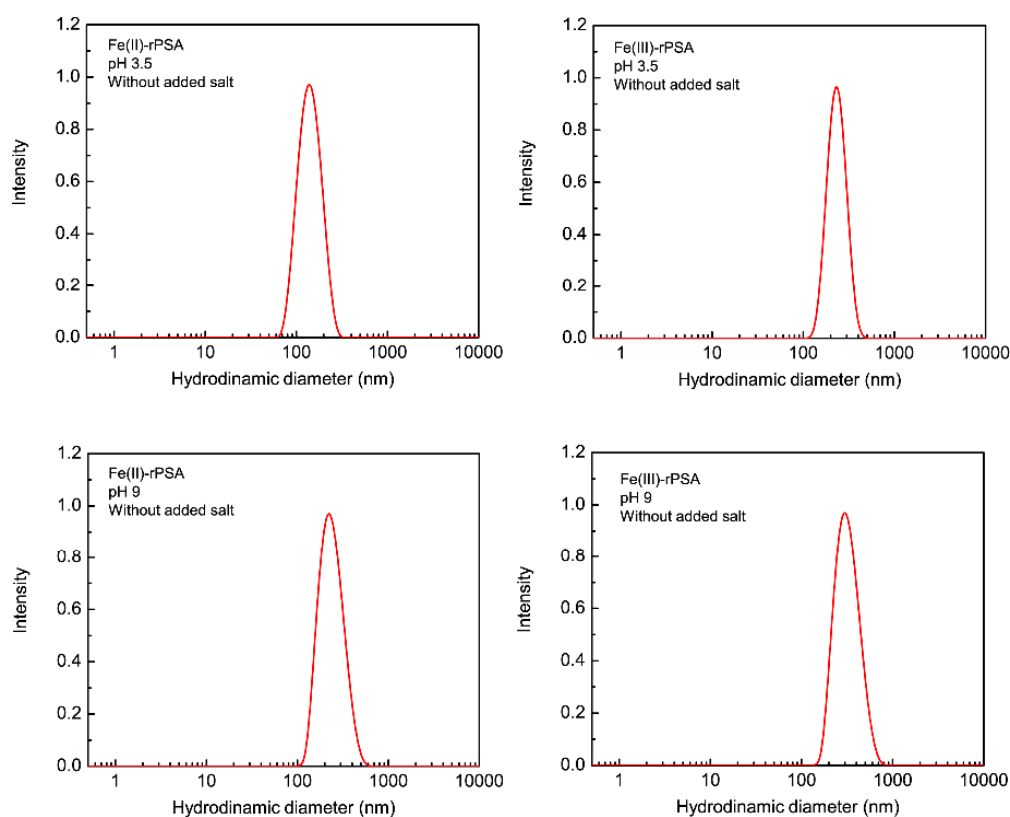
## Redox-Active Polyamine-Salt Aggregates as Multistimuli-Responsive Soft Nanoparticles

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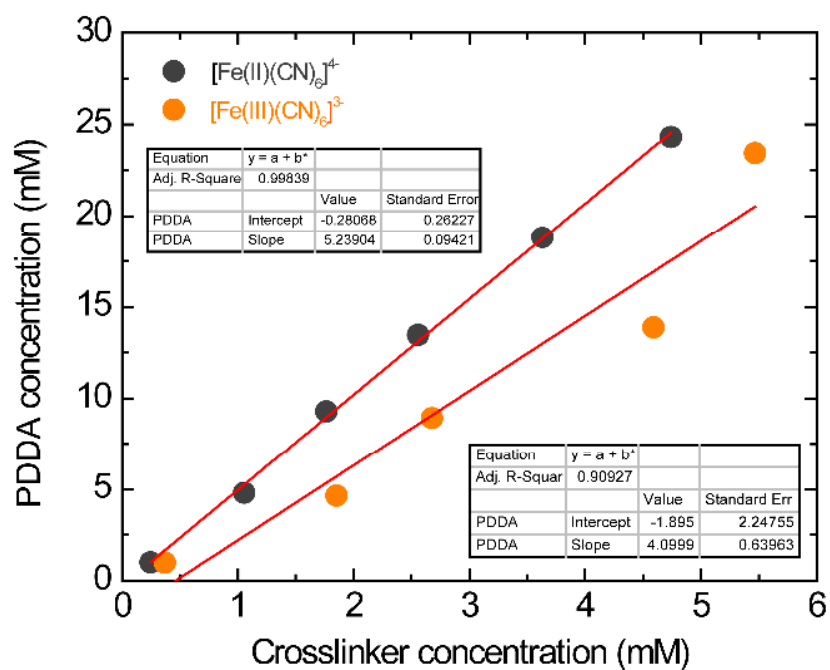
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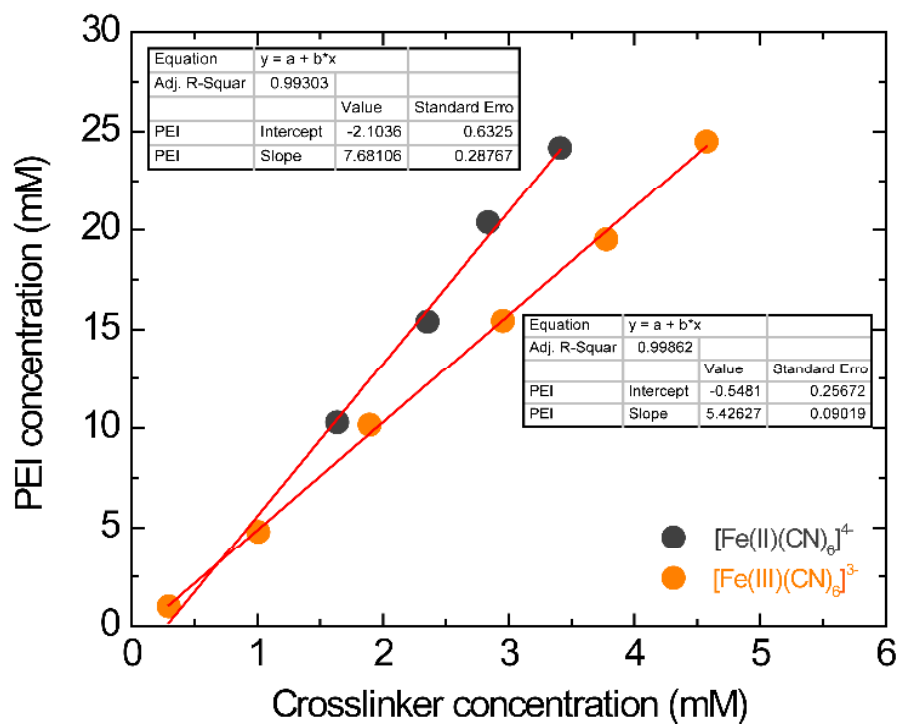
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**Figure S1:** Dynamic light scattering size distributions for Fe(II)- and Fe(III)-rPSAs formed at pH 3.5 (upper panel) and pH 9 (lower panel). In all cases, PEI concentration was fixed at 1 mM. Crosslinker concentration for each sample is displayed in Table 1 (main text).

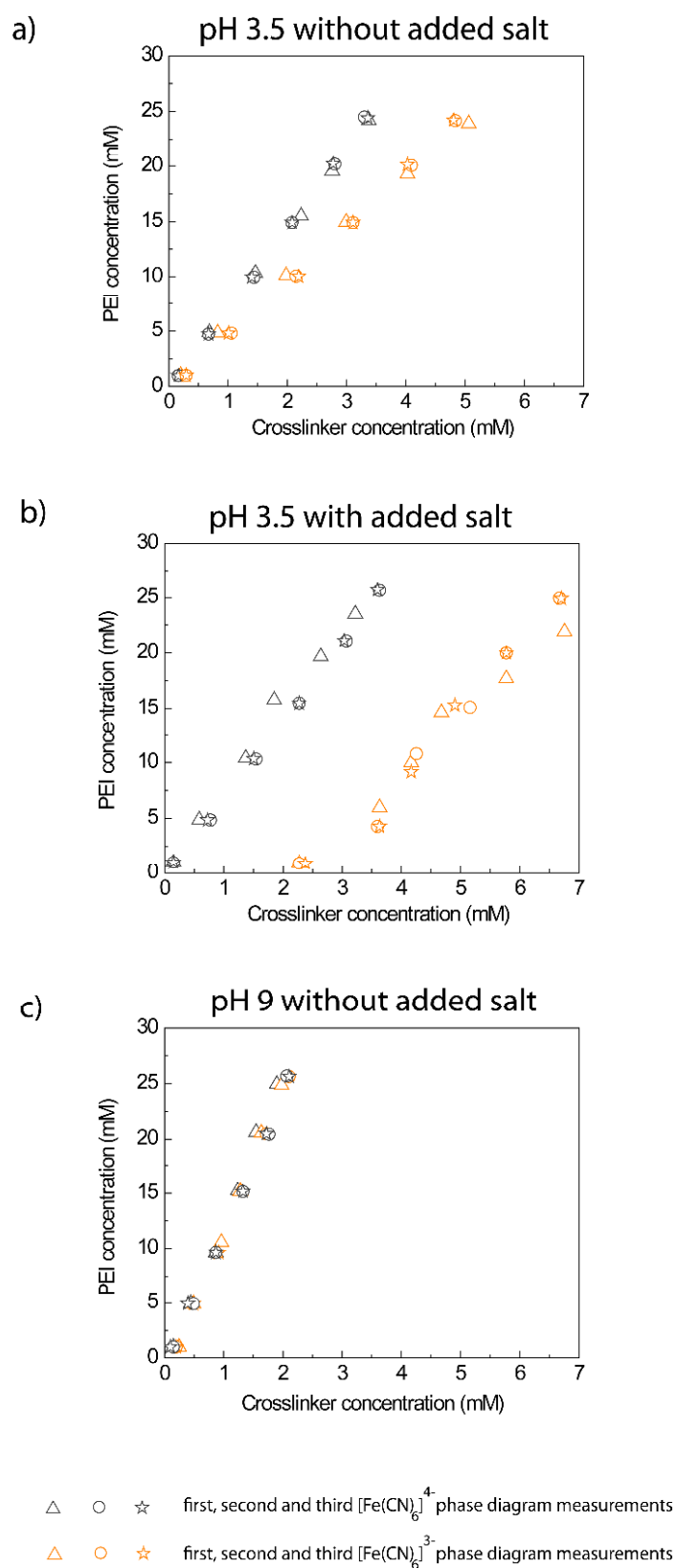


**Figure S2.** Overlaid Fe(II)- and Fe(III)-rPSA phase diagrams using poly(diallyldimethylammonium chloride) (PDDA, 100-200 kDa) as polyamine instead of PEI. Measurements were conducted at pH 3.5 (acetate buffer) without added salt. Red lines indicate linear regressions.



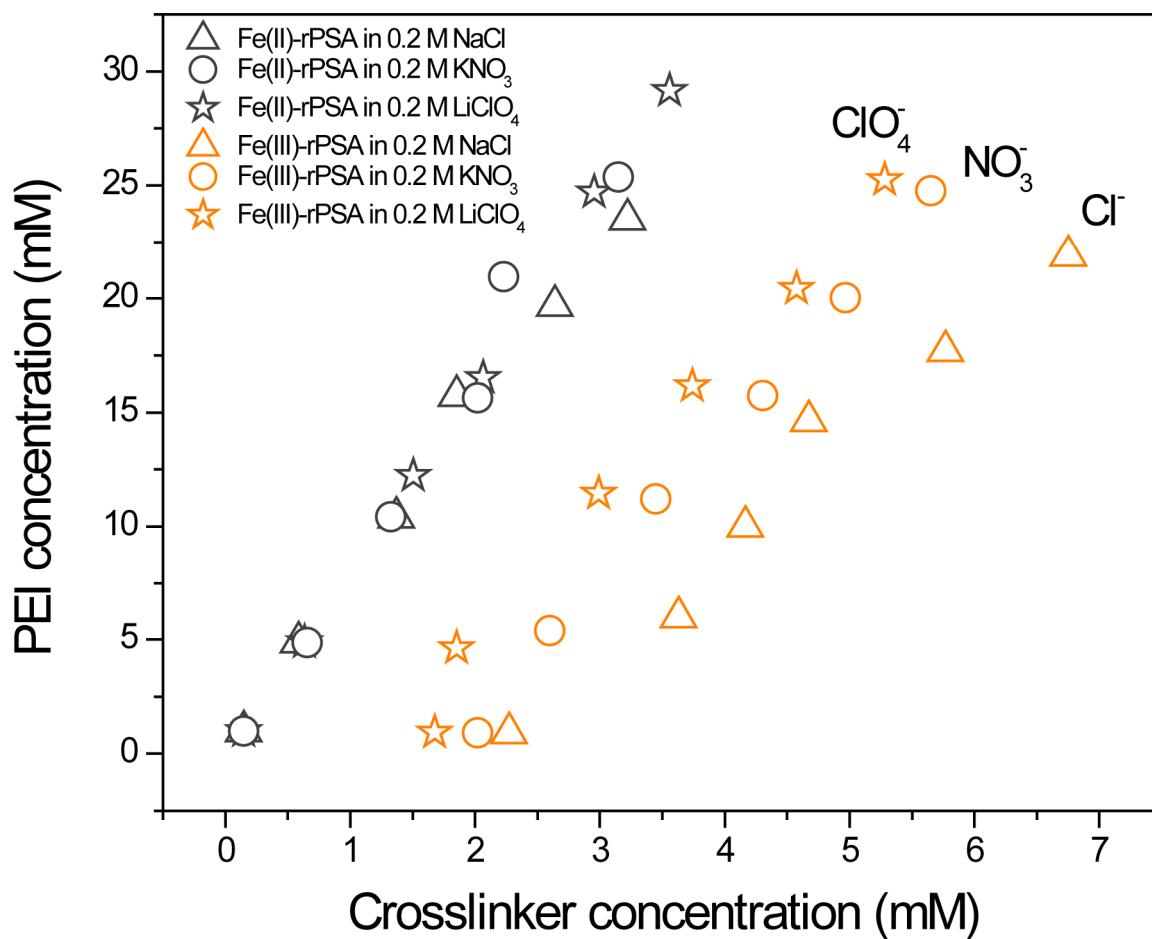
**Figure S3.** Overlaid Fe(II)- and Fe(III)-rPSA phase diagrams using PEI 750 kDa instead of PEI 10 kDa. Measurements were conducted at pH 3.5 (acetate buffer) without added salt. Red lines indicate linear regressions.

## Reproducibility of the phase-diagrams

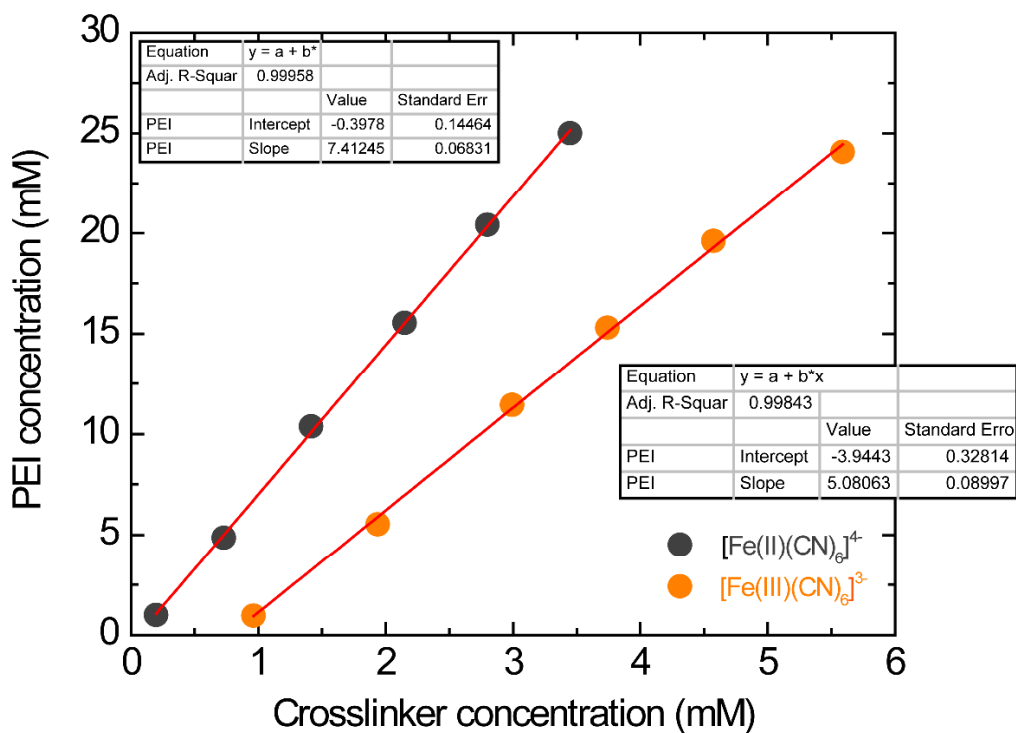


**Figure S4.** Overlaid phase diagrams of Fe(II)-rPSA (grey symbols) and Fe(III)-rPSA (orange symbols) for different conditions: pH 3.5 (acetate buffer) without added salt (a), pH 3.5 (acetate buffer) plus 0.2 M NaCl (b), and pH 9 (tris buffer) without added salt (c). Triangles, circles and stars represent three different measurements for each phase diagram.

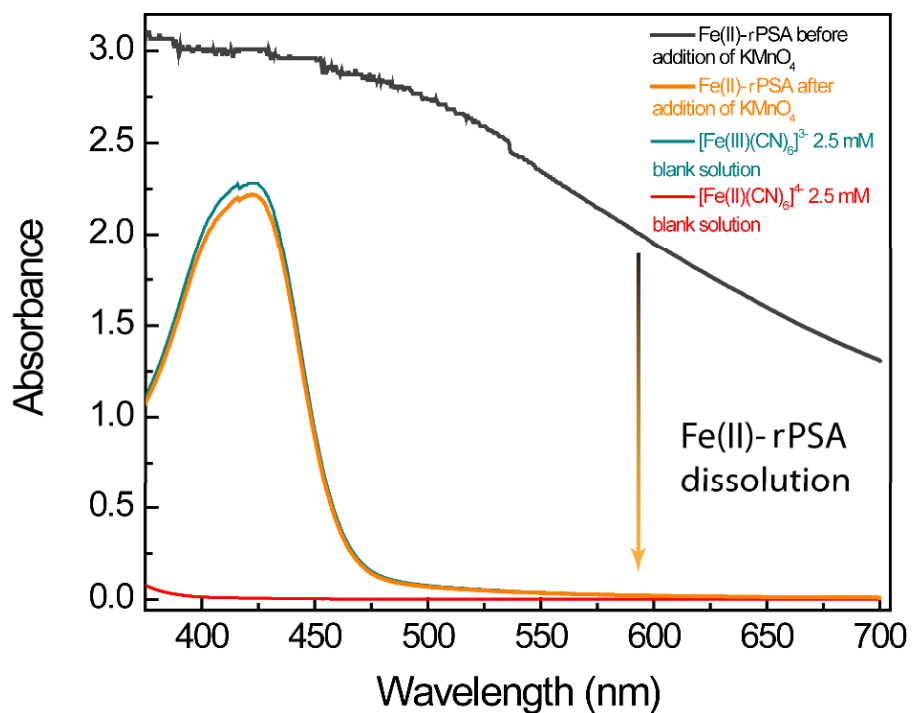
Hofmeister series:  $\text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^-$



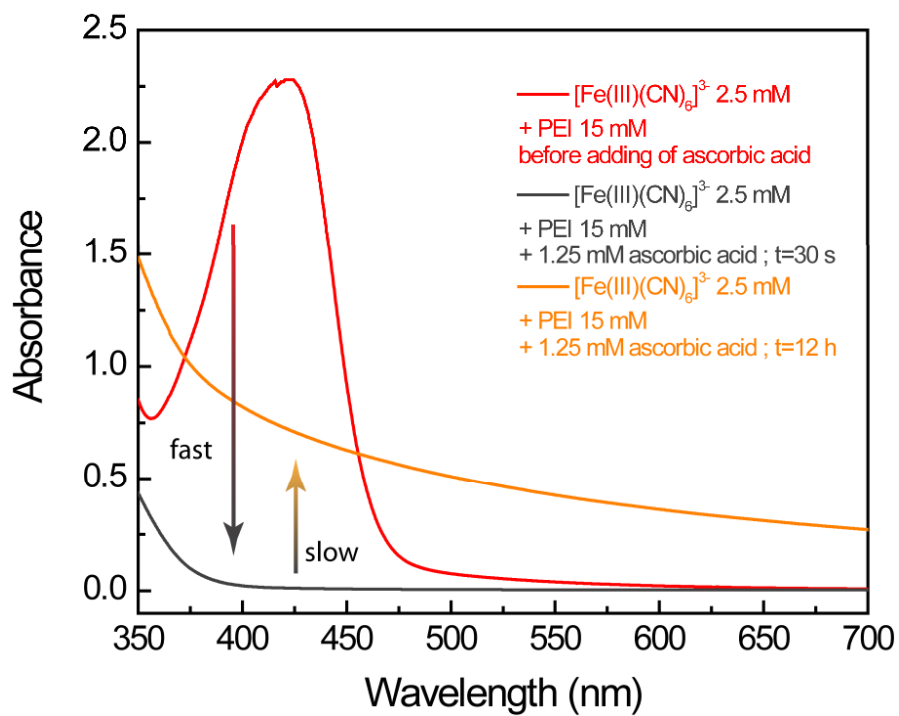
**Figure S5.** Overlaid Fe(II)- and Fe(III)-rPSA phase diagrams in presence of 0.2 M NaCl (triangles), 0.2 M KNO<sub>3</sub> (circles) and 0.2 M LiClO<sub>4</sub> (stars). Measurements were conducted at pH 3.5 (acetate buffer) using PEI 10 kDa.



**Figure S6.** Overlaid Fe(II)- and Fe(III)-rPSA phase diagrams using PEI 750 kDa instead of PEI 10 kDa. Measurements were conducted at pH 3.5 (acetate buffer) in presence of NaCl 0.2 M. Red lines indicate linear regressions.

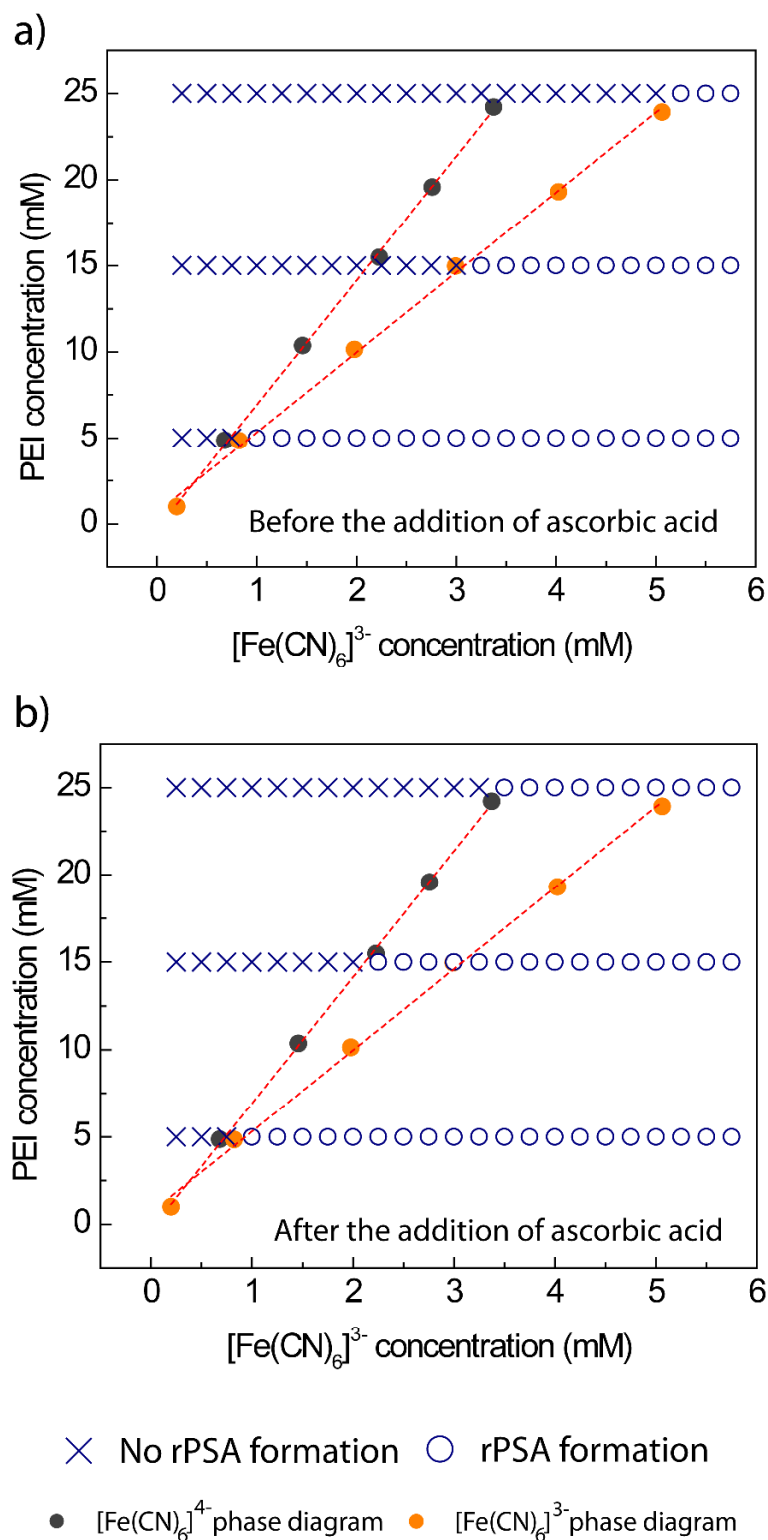


**Figure S7.** Redox-triggered Fe(II)-rPSA dissolution. UV-Vis spectra between 350 and 700 nm for an Fe(II)-rPSA solution at the initial state (before addition of  $\text{KMnO}_4$ , black curve) and after addition of  $\text{KMnO}_4$  (orange line). Blue-green and red lines correspond to blank spectra of  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  without PEI, respectively.

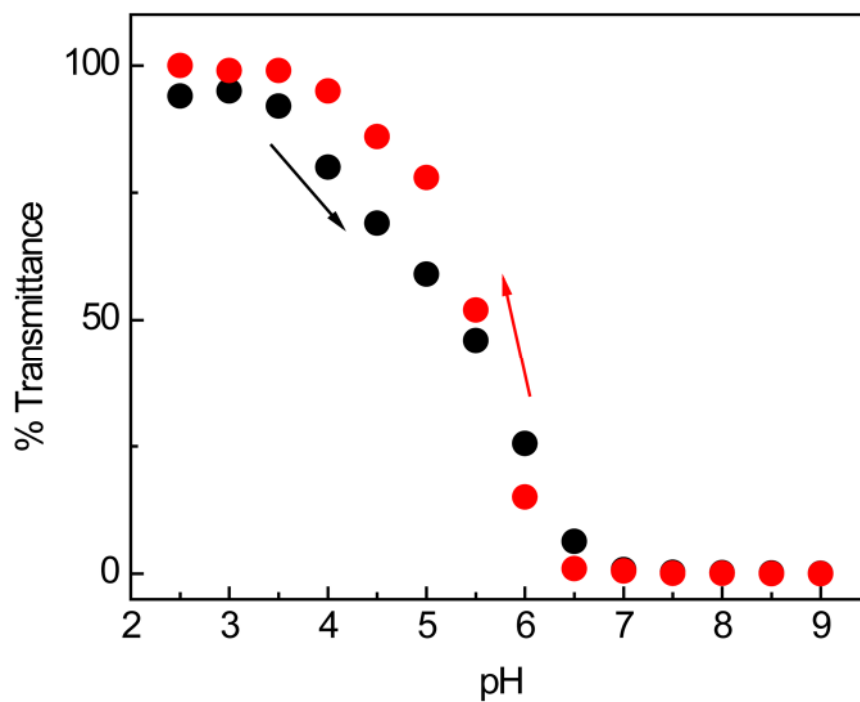


**Figure S8.** Redox-triggered Fe(II)-rPSA formation. UV-Vis spectra between 350 and 700 nm for a mixture of  $[\text{Fe}(\text{CN})_6]^{3-}$  2.5 mM and PEI 15 mM before adding ascorbic acid (red line), after 30 s of adding ascorbic acid (grey line), and after 12 h of adding ascorbic acid (orange line).





**Figure S9.** Redox-triggered Fe(II)-rPSA phase diagram. Each blue mark correspond to a 5 mL aqueous solution containing PEI and [Fe(CN)<sub>6</sub>]<sup>3-</sup> at certain concentrations. The aggregation state of each solution was registered before (a) and after (b) the addition of 50  $\mu$ L of ascorbic acid 0.3 M. X symbols represents translucent solutions. Circles represent rPSA colloidal dispersions. Measurements were conducted in acetate buffer at pH 3.5 (acetate buffer). For comparison, both Fe(II)- and Fe(III)-rPSA phase diagrams obtained by direct mixing of reagents are also displayed in the plots.



**Figure S10.** Reversible switching between solution region (pH 3.5) and rPSA region (pH 9) for an aqueous solution containing 20 mM PEI and 2 mM  $[\text{Fe}(\text{CN})_6]^{3-}$  without added salt. Black dots indicate a pH shifting from 3.5 to 9. Red dots indicate a pH shifting from 9 to 3.5. The turbidity of the solutions was expressed as % transmittance at  $\lambda=580$  nm.