Electronic Supplementary Material (ESI) for RSC Advances

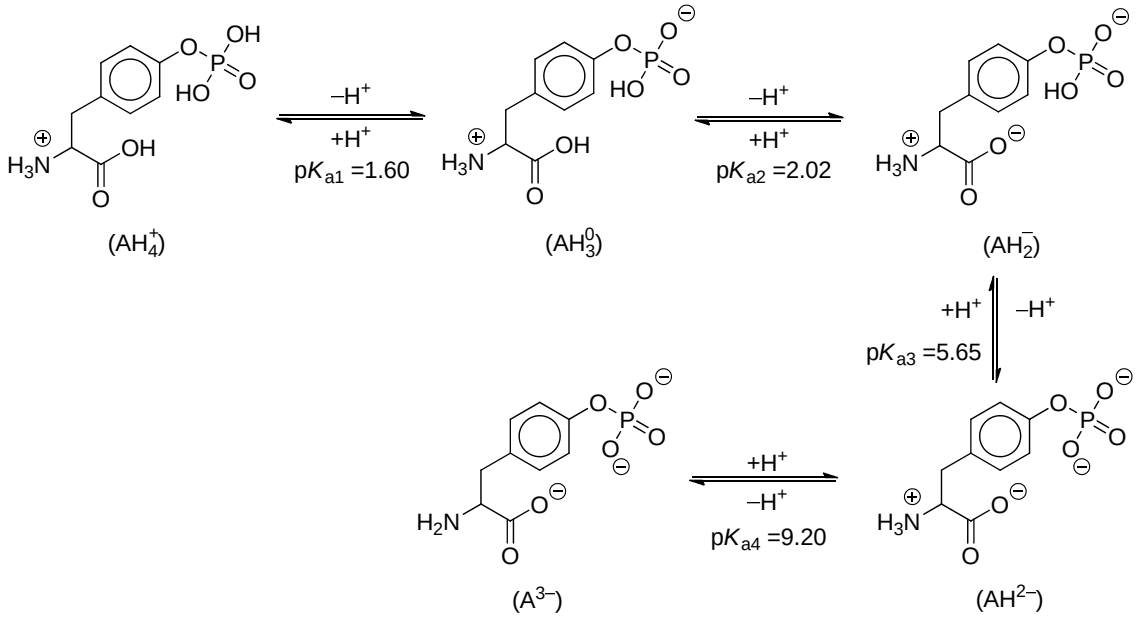
Direct experimental observation of the aggregation of α-amino acids into 100-200 nm clusters in aqueous solution

-Supporting Information-

Speciation Analysis of Tyrosine Phosphate in Aqueous Solution

(Figure 14 of the main text)

Aqueous tyrosine phosphate is an amphiprotic system where five differently charged species may be present in equilibrium (Scheme 1).



Scheme 1

Their molar fractions of the AH_4^+, AH_3^0, AH_2^-, AH^{2-} and A^{3-} at a given pH can be approximately predicted from the corresponding acidity constants, pK_{a1} = 1.60 (-PO_3H_2), pK_{a2} = 2.02 (-COOH), pK_{a3} = 5.65 (-PO_3H^-), pK_{a4} = 9.20 (-NH_3^+),[1] by using:[1]

$$x(AH_4^+) = \frac{[H^+]^4}{\alpha K_{a1}} \qquad (S1)$$

$$x(AH_3^0) = \frac{[H^+]^3}{\alpha K_{a2}} \quad (S2)$$

$$x(AH_2^-) = \frac{[H^+]^2}{\alpha K_{a3}} \quad (S4)$$

$$x(AH^{2-}) = \frac{[H^+]}{\alpha K_{a4}} \quad (S3)$$

$$x(A^{3-}) = 1 - x(AH_4^+) - x(AH_3^0) - x(AH_2^-) - x(AH^{2-}) \quad (S5)$$

where:

$$\alpha = \frac{[H^+]^4}{K_{a1}} + \frac{[H^+]^3}{K_{a2}} + \frac{[H^+]^2}{K_{a3}} + \frac{[H^+]}{K_{a4}} + 1 \quad (S6)$$

The obtained values and the corresponding overall charge in solution given by

$$z_{\text{over-all}} = x_{AH_4^+}(+1) + x_{AH_3^0}(0) + x_{AH_2^-}(-1) + x_{AH^{2-}}(-2) + x_{A^{3-}}(-3) \quad \text{(Table 1)}$$

are summarized in Table 1.

TABLE S1: Molar Fractions of Tyrosine Phosphate Species and Their Overall Charge, $z_{over\text{-}all}$, in Aqueous Solution, at 298.15 K.

pH	$x(AH_4^+)$	$x(AH_3)$	$x(AH_2^-)$	$x(AH^{2-})$	$x(A^{3-})$	$z_{over\text{-}all}$
0.0	9.75E-01	2.45E-02	2.34E-04	5.24E-10	6.42E-17	0.98
0.2	9.61E-01	3.83E-02	5.79E-04	2.05E-09	4.24E-18	0.96
0.4	9.39E-01	5.93E-02	1.42E-03	7.99E-09	-5.50E-17	0.94
0.6	9.06E-01	9.06E-02	3.44E-03	3.07E-08	7.31E-17	0.90
0.8	8.56E-01	1.36E-01	8.18E-03	1.15E-07	4.50E-16	0.85
1.0	7.84E-01	1.97E-01	1.88E-02	4.21E-07	2.68E-15	0.77
1.2	6.86E-01	2.73E-01	4.13E-02	1.47E-06	1.46E-14	0.64
1.4	5.61E-01	3.54E-01	8.49E-02	4.78E-06	7.58E-14	0.48
1.6	4.20E-01	4.20E-01	1.60E-01	1.42E-05	3.58E-13	0.26
1.8	2.82E-01	4.48E-01	2.70E-01	3.81E-05	1.52E-12	0.01
2.0	1.69E-01	4.25E-01	4.06E-01	9.08E-05	5.73E-12	-0.24
2.2	9.08E-02	3.62E-01	5.47E-01	1.94E-04	1.94E-11	-0.46
2.4	4.45E-02	2.81E-01	6.74E-01	3.79E-04	6.01E-11	-0.63
2.6	2.04E-02	2.04E-01	7.75E-01	6.91E-04	1.74E-10	-0.76
2.8	8.89E-03	1.41E-01	8.49E-01	1.20E-03	4.77E-10	-0.84
3.0	3.75E-03	9.42E-02	9.00E-01	2.01E-03	1.27E-09	-0.90
3.2	1.55E-03	6.17E-02	9.33E-01	3.31E-03	3.31E-09	-0.94
3.4	6.30E-04	3.98E-02	9.54E-01	5.37E-03	8.50E-09	-0.96
3.6	2.54E-04	2.54E-02	9.66E-01	8.61E-03	2.16E-08	-0.98
3.8	1.02E-04	1.61E-02	9.70E-01	1.37E-02	5.46E-08	-1.00
4.0	4.04E-05	1.01E-02	9.68E-01	2.17E-02	1.37E-07	-1.01
4.2	1.59E-05	6.34E-03	9.60E-01	3.40E-02	3.40E-07	-1.03
4.4	6.23E-06	3.93E-03	9.43E-01	5.30E-02	8.40E-07	-1.05
4.6	2.41E-06	2.41E-03	9.16E-01	8.16E-02	2.05E-06	-1.08
4.8	9.16E-07	1.45E-03	8.75E-01	1.24E-01	4.92E-06	-1.12
5.0	3.40E-07	8.55E-04	8.16E-01	1.83E-01	1.15E-05	-1.18
5.2	1.22E-07	4.87E-04	7.38E-01	2.62E-01	2.62E-05	-1.26
5.4	4.23E-08	2.67E-04	6.40E-01	3.60E-01	5.70E-05	-1.36
5.6	1.39E-08	1.39E-04	5.29E-01	4.71E-01	1.18E-04	-1.47
5.8	4.34E-09	6.88E-05	4.14E-01	5.85E-01	2.33E-04	-1.59
6.0	1.29E-09	3.23E-05	3.09E-01	6.91E-01	4.36E-04	-1.69
6.2	3.65E-10	1.45E-05	2.20E-01	7.80E-01	7.80E-04	-1.78
6.4	9.96E-11	6.29E-06	1.51E-01	8.48E-01	1.34E-03	-1.85
6.6	2.65E-11	2.65E-06	1.01E-01	8.97E-01	2.25E-03	-1.90

6.8	6.90E-12	1.09E-06	6.59E-02	9.30E-01	3.70E-03	-1.94
7.0	1.77E-12	4.45E-07	4.25E-02	9.51E-01	6.00E-03	-1.96
7.2	4.51E-13	1.79E-07	2.71E-02	9.63E-01	9.63E-03	-1.98
7.4	1.14E-13	7.17E-08	1.72E-02	9.67E-01	1.53E-02	-2.00
7.6	2.85E-14	2.85E-08	1.08E-02	9.65E-01	2.42E-02	-2.01
7.8	7.08E-15	1.12E-08	6.76E-03	9.55E-01	3.80E-02	-2.03
8.0	1.74E-15	4.38E-09	4.18E-03	9.37E-01	5.91E-02	-2.05
8.2	4.24E-16	1.69E-09	2.56E-03	9.07E-01	9.07E-02	-2.09
8.4	1.01E-16	6.39E-10	1.53E-03	8.62E-01	1.37E-01	-2.14
8.6	2.36E-17	2.36E-10	8.96E-04	7.99E-01	2.01E-01	-2.20
8.8	5.30E-18	8.40E-11	5.06E-04	7.15E-01	2.85E-01	-2.28
9.0	1.14E-18	2.87E-11	2.74E-04	6.13E-01	3.87E-01	-2.39
9.2	2.34E-19	9.31E-12	1.41E-04	5.00E-01	5.00E-01	-2.50
9.4	4.54E-20	2.87E-12	6.88E-05	3.87E-01	6.13E-01	-2.61
9.6	8.40E-21	8.40E-13	3.19E-05	2.85E-01	7.15E-01	-2.72
9.8	1.49E-21	2.36E-13	1.42E-05	2.01E-01	7.99E-01	-2.80
10.0	2.55E-22	6.40E-14	6.11E-06	1.37E-01	8.63E-01	-2.86
10.2	4.25E-23	1.69E-14	2.56E-06	9.09E-02	9.09E-01	-2.91
10.4	6.97E-24	4.40E-15	1.06E-06	5.94E-02	9.41E-01	-2.94
10.6	1.13E-24	1.13E-15	4.30E-07	3.83E-02	9.62E-01	-2.96
10.8	1.82E-25	2.88E-16	1.73E-07	2.45E-02	9.75E-01	-2.98
11.0	2.91E-26	7.30E-17	6.97E-08	1.56E-02	9.84E-01	-2.98
11.2	4.63E-27	1.84E-17	2.79E-08	9.90E-03	9.90E-01	-2.99
11.4	7.37E-28	4.65E-18	1.11E-08	6.27E-03	9.94E-01	-2.99
11.6	1.17E-28	1.17E-18	4.45E-09	3.97E-03	9.96E-01	-3.00
11.8	1.86E-29	2.94E-19	1.77E-09	2.51E-03	9.97E-01	-3.00
12.0	2.95E-30	7.40E-20	7.07E-10	1.58E-03	9.98E-01	-3.00
12.2	4.67E-31	1.86E-20	2.82E-10	9.99E-04	9.99E-01	-3.00
12.4	7.41E-32	4.67E-21	1.12E-10	6.31E-04	9.99E-01	-3.00
12.6	1.17E-32	1.17E-21	4.47E-11	3.98E-04	1.00E+00	-3.00
12.8	1.86E-33	2.95E-22	1.78E-11	2.51E-04	1.00E+00	-3.00
13.0	2.95E-34	7.41E-23	7.08E-12	1.58E-04	1.00E+00	-3.00
13.2	4.68E-35	1.86E-23	2.82E-12	1.00E-04	1.00E+00	-3.00
13.4	7.41E-36	4.68E-24	1.12E-12	6.31E-05	1.00E+00	-3.00
13.6	1.17E-36	1.17E-24	4.47E-13	3.98E-05	1.00E+00	-3.00
13.8	1.86E-37	2.95E-25	1.78E-13	2.51E-05	1.00E+00	-3.00
14.0	2.95E-38	7.41E-26	7.08E-14	1.58E-05	1.00E+00	-3.00

1. P. W. Atkins and J. de Paula, *Physical Chemistry for the Life Sciences*, Oxford University Press, Oxford, 2006.