Molecular Interactions Between Serum Albumin Proteins and Keggin Type Polyoxometalates Studied by Luminescence Spectroscopy

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Supporting Information



Figure S1. Excitation spectra of Eu-Keggin POM in absence and presence of BSA. Black line: blank Eu-Keggin solution (pH 6.25); red curve: 10:1 Eu-Keggin POM:BSA (pH 6.29) and blue curve: 1:1 Eu-Keggin POM:BSA (pH 5.70). The POM concentration was kept constant at 10⁻⁴ M. The emission was monitored at 613 nm.



Figure S2. Steady state emission spectra for the Eu-Keggin POM (10⁻⁴ M) upon increasing concentration of BSA (0-10⁻⁴ M) in aqueous solution. In the inset the relative intensity increase is depicted for the 3 main emission transitions: ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (593 nm, black squares), ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (619 nm, red dots) and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (700 nm, blue triangles).



Figure S3. Time-resolved decay data of the Eu-Keggin POM (10^{-4} M) with increasing concentration of BSA $(0-10^{-4} \text{ M})$ in aqueous solution considering a fixed lifetime of 0.22 ms for full decay analysis. Excitation took place at 291 nm while the emission was monitored at 613 nm.



Figure S4. Change of the species present in solution (in %) upon addition of BSA $(0-10^{-4} \text{ M})$ to a solution of Eu-Keggin POM (10^{-4} M) . The shorter-lived component (0.22 ms) corresponds to the lifetime of the free Eu-Keggin POM and was fixed in the measurement, while the longer-lived component (0.57 ms) corresponds to the lifetime of the formed POM/BSA complex.



Figure S5. Emission fluorescence spectra of HSA in the absence and presence of different concentrations of plenary Keggin POM ([HSA]=10⁻⁵ M, in pure water). From top to bottom, the concentration of plenary Keggin POM increased stepwise from 0 to 10^{-5} M with increments of 10^{-6} M. In the inset, the plot of the derived Stern-Volmer equation is given (with R² = 0.98). From the plot, K_q and n were calculated to be $1.4 \pm 0.6 \times 10^{6}$ M⁻¹ and 1.22 ± 0.05 , respectively.



Figure S6. Emission fluorescence spectra of HSA in the absence and presence of different concentrations of lacunary Keggin POM ([HSA]=10⁻⁵ M, in pure water). From top to bottom, the concentration of lacunary Keggin POM increased stepwise from 0 to 10^{-5} M with increments of 10^{-6} M. In the inset, the plot of the derived Stern-Volmer equation is given (with R² = 0.98). From the plot, K_q and n were calculated to be $2.9 \pm 0.8 \times 10^{5}$ M⁻¹ and 1.08 ± 0.05 , respectively.



Figure S7. Emission fluorescence spectra of HSA in the absence and presence of different concentrations of Eu-Keggin POM ([HSA]=10⁻⁵ M, in pure water). From top to bottom, the concentration of Eu-Keggin POM increased stepwise from 0 to 10^{-5} M with increments of 10^{-6} M. In the inset, the plot of the derived Stern-Volmer equation is given (with R² = 0.96). From the plot, K_q and n were calculated to be $6.1 \pm 1.0 \times 10^4$ M⁻¹ and 0.97 ± 0.07 , respectively.



Figure S8. Emission fluorescence spectra of BSA in the absence and presence of different concentrations of plenary Keggin POM ([BSA]=10⁻⁵ M, in pure water). From top to bottom, the concentration of plenary Keggin POM increased stepwise from 0 to 10^{-5} M with increments of 10^{-6} M. In the inset, the plot of the derived Stern-Volmer equation is given (with R² = 0.99). From the plot, K_q and n were calculated to be $4.9 \pm 0.3 \times 10^{6}$ M⁻¹ and 1.27 ± 0.03 , respectively.



Figure S9. Emission fluorescence spectra of BSA in the absence and presence of different concentrations of lacunary Keggin POM ([BSA]=10⁻⁵ M, in pure water). From top to bottom, the concentration of lacunary Keggin POM increased stepwise from 0 to 10^{-5} M with increments of 10^{-6} M. In the inset, the plot of the derived Stern-Volmer equation is given (with R² = 0.99). From the plot, K_q and n were calculated to be $5.0 \pm 0.5 \times 10^{6}$ M⁻¹ and 1.29 ± 0.04 , respectively.