Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

Chemical equilibria studies using multivariate analysis methods

Joaquim Jaumot, Ramon Eritja and Raimundo Gargallo

Table S1. Dissimilarity values obtained for the acid-base simulated data sets.

		Dissimilarity values					
		Hard-modeling		Soft-modeling		Hybrid-modeling	
		Conc.	Spectra	Conc.	Spectra	Conc.	Spectra
D1	Species 1	0.0009	0.0144	0.0351	0.0934	0.0023	0.0146
	Species 2	0.0010	0.0114	0.0932	0.0496	0.0022	0.0115
	Species 3	0.0010	0.0072	0.0440	0.0134	0.0023	0.0071
	Species 4	0.0005	0.0093	0.0308	0.0200	0.0013	0.0094
D2	Species 1	0.0021	0.0146	0.1009	0.0925	0.0034	0.0148
	Species 2	0.0020	0.0133	0.0881	0.0516	0.0038	0.0121
	Species 3	0.0146	0.0143	0.0856	0.0440	0.0007	0.0201
	Species 4	0.0138	0.2129	0.4522	0.3115	0.0005	0.1429
	Interference	-	-	0.8065	0.9640	0.4625	0.0916
D3	Species 1	0.0002	0.0100	0.0434	0.0960	0.0051	0.0101
	Species 2	0.0006	0.0076	0.0941	0.0195	0.0086	0.0078
	Species 3	-	-	-	-	-	-
	Species 4	0.0002	0.0058	0.0137	0.0075	0.0086	0.0056
D4	Species 1	0.0040	0.0118	0.1645	0.0931	0.0014	0.0122
	Species 2	0.0037	0.0114	0.0989	0.0160	0.0129	0.0103
	Species 3	-	-	-	-	-	-
	Species 4	0.0244	0.2121	0.0244	0.2364	0.0122	0.1925
	Interference	-	-	0.9025	0.2737	0.8153	0.0908

Table S2. Dissimilarity values obtained for the complexation simulated data sets.

|		Dissimilarity					
		Hard-modeling		Soft-modeling		Hybrid-modeling	
		Conc.	Spectra	Conc.	Conc.	Spectra	Conc.
	Species D	0.0009	0.0403	0.0302	0.0659	0.0008	0.0209
D7	Species L	0.0001	0.0052	0.0157	0.2474	0.0001	0.0043
	Species DL	0.0009	0.0110	0.9630	0.0382	0.0008	0.0093
	Species D	0.0014	0.0333	0.4076	0.0970	0.0003	0.0194
D8	Species L	0.0005	0.0086	0.0370	0.2342	0.0005	0.0074
	Species DL	0.0020	0.0257	0.1772	0.3962	0.0023	0.0203
	Species DL2	0.0013	0.0181	0.8258	0.3228	0.0011	0.0153
	Species D	-	-	-	-	-	-
D9	Species L	0.0005	0.0088	0.0651	0.2374	0.0036	0.0089
	Species DL	0.0019	0.0277	0.2064	0.0553	0.0136	0.0214
	Species DL2	0.0014	0.0182	0.8306	0.2514	0.0078	0.0233
	Species D	0.0110	0.0619	0.0344	0.0577	0.0004	0.0321
D10	Species L	0.2738	0.0308	0.9488	0.4580	0.0001	0.0126
	Species DL	0.2276	0.0296	0.9997	0.0415	0.0004	0.0215
	Interference	-	-	0.0125	0.4192	0.0084	0.0184

Figure S1. Building up of the simulated acid-base data sets. (a) Simulated concentration and (b) Spectra profiles for data set D1. (c) D1 simulated data after the addition of noise. (d) Simulated concentration and (e) Spectra profiles for data set D2. (f) D2 simulated data after the addition of noise. (g) Simulated concentration and (h) Spectra profiles for data set D3. (i) D3 simulated data after the addition of noise. (j) Simulated concentration and (k) Spectra profiles for data set D4. (l) D4 simulated data after the addition of noise. Legend: (solid lines) simulated profiles of spectroscopically active species, (dashed lines) simulated profiles of spectroscopically inactive species.
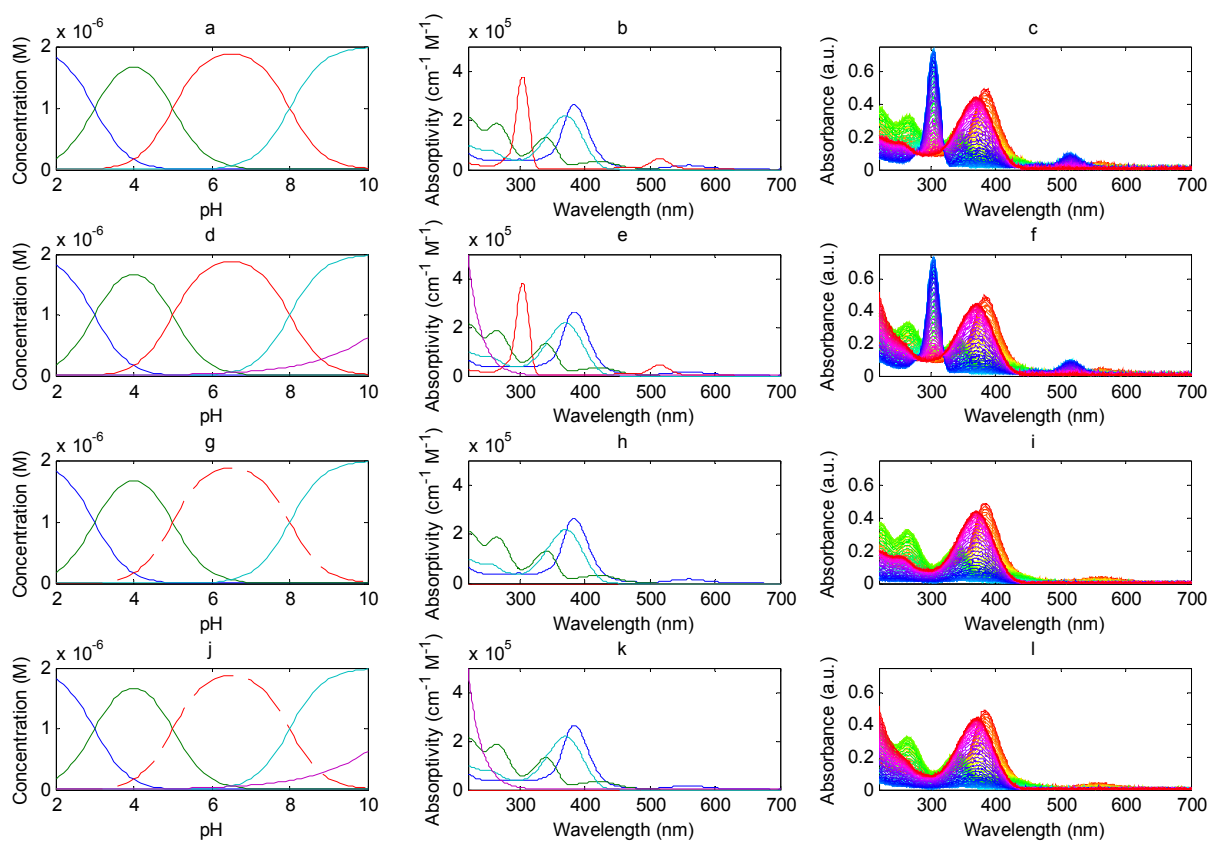
Figure S2. Building up of the simulated ligand-DNA complexation data. (a) Simulated concentration and (b) Spectra profiles for data set D7. (c) D7 simulated data after the addition of noise. (d) Simulated concentration and (e) Spectra profiles for data set D8. (f) D8 simulated data after the addition of noise. (g) Simulated concentration and (h) Spectra profiles for data set D9. (i) D9 simulated data after the addition of noise. (j) Simulated concentration and (k) Spectra profiles for data set D10. (l) D10 simulated data after the addition of noise. Legend: (solid lines) simulated profiles of spectroscopically active species, (dashed lines) simulated profiles of spectroscopically inactive species.
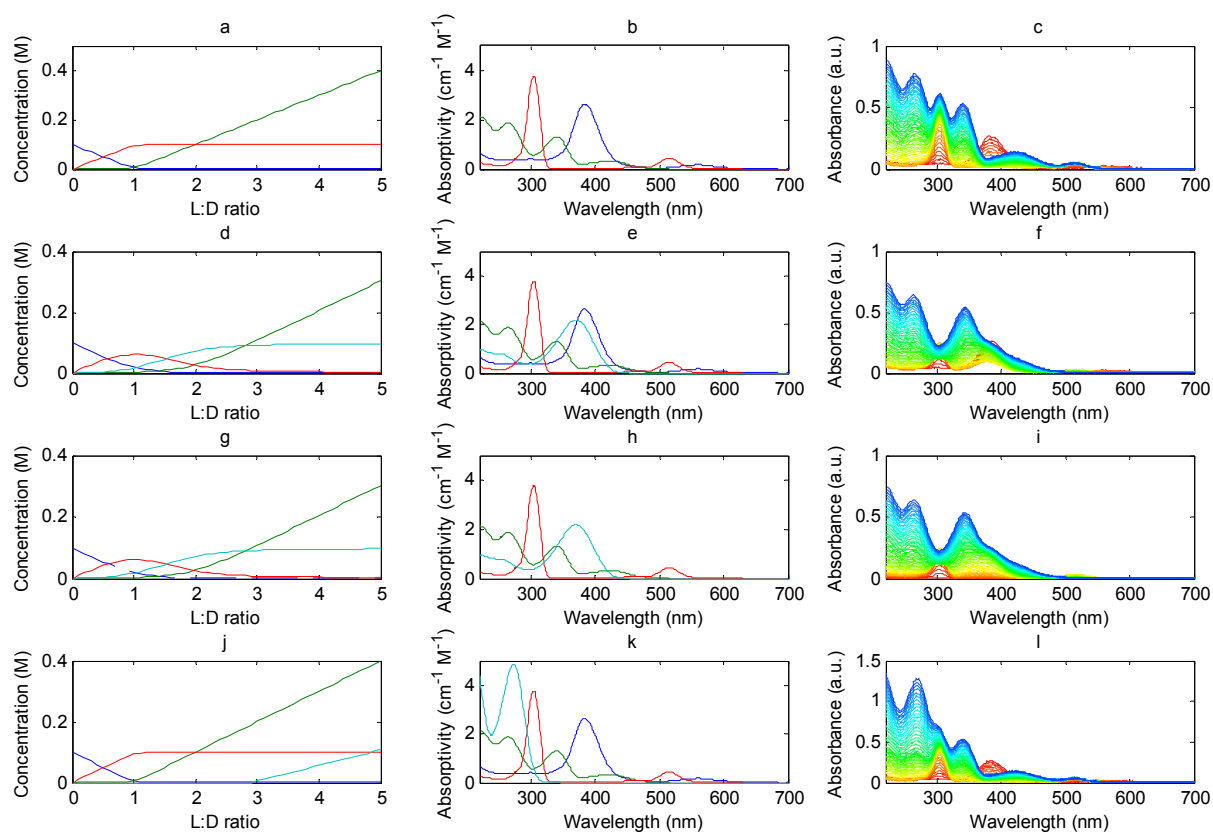
Figure S3. Band boundaries of the MCR-ALS resolved profiles in the analysis of data set D1. (a) Concentration profiles and (b) Spectra. Legend: (solid lines) resolved MCR-ALS profiles, (dashed lines) minimum and maximum band boundaries of the resolved profiles.
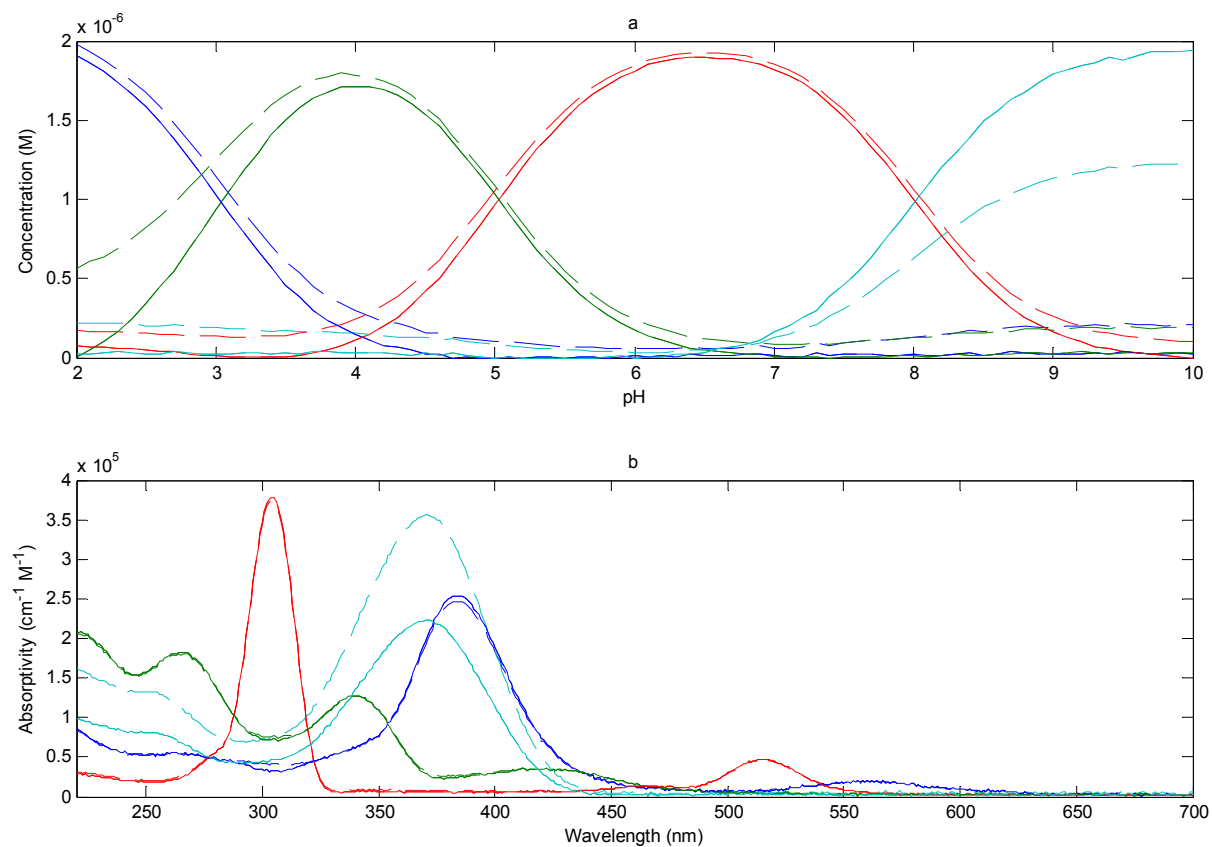
Figure S4. Fitting of the experimental acid-base data by means of the hard-modelling method. (a) Spectra obtained upon the pH titration of the krasG1 sequence. (b) Fitting of the experimental data by the proposed model at 295 nm. (c) Spectra obtained upon the titration of the krasC1 sequence. (d) Fitting of the experimental data by the proposed model at 295 nm. Legend: (x symbol) measured value of absorbance at the selected wavelength, (solid lines) fitted value of absorbance at the selected wavelength.
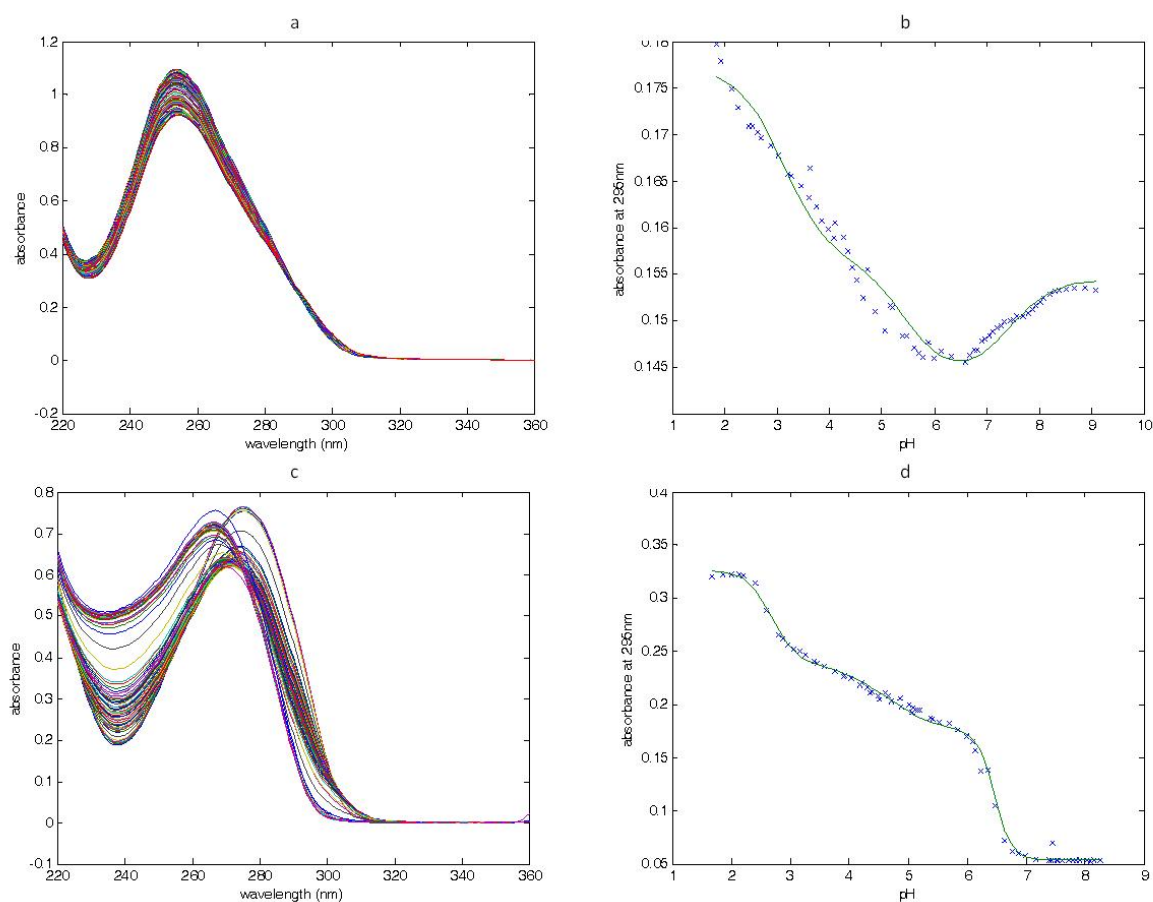
Figure S5. Fitting of the experimental complexation data by means of the hard-modelling method. (a) Spectra obtained upon the mole-ratio experiment between the krasG1 sequence and the TMPyP4 porphyrin. (b) Fitting of the experimental data by the proposed model at 445 nm. (c) Spectra obtained upon the mole-ratio experiment between the krasC1 sequence and the TMPyP4 porphyrin. (d) Fitting of the experimental data by the proposed model at 445 nm. Legend: (x symbol) measured value of absorbance at the selected wavelength, (solid lines) fitted value of absorbance at the selected wavelength.