Melatonin-Directed Micellization: A Case for Tryptophan Metabolites and their Classical Bioisosteres as Templates for the Self-Assembly of Bipyridinium-Based Supramolecular Amphiphiles in Water

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Electronic Supporting Information

Additional Spectroscopic Characterization

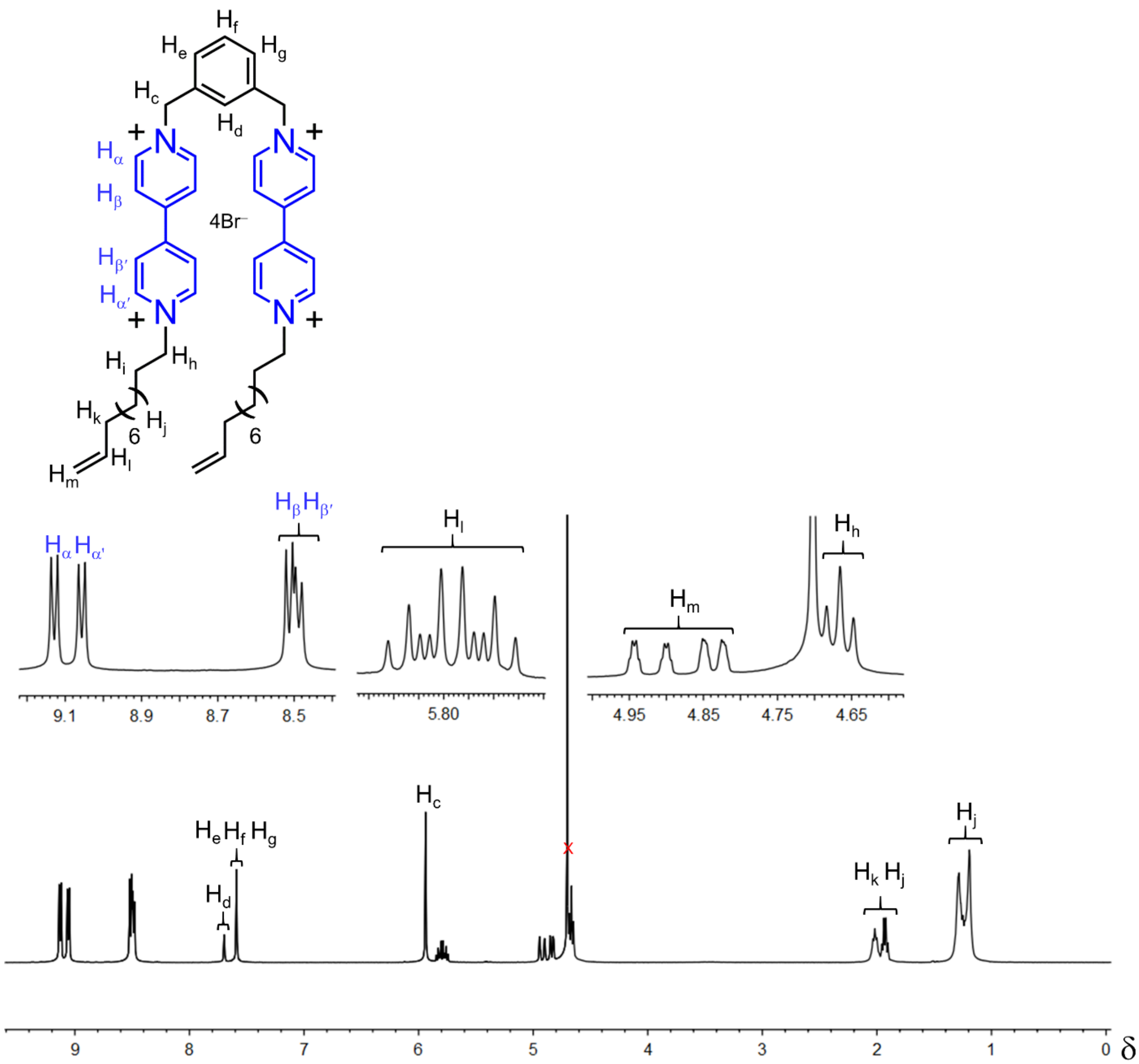

Figure S1: ^{1}H NMR spectrum of **1**·4Br in D_2O at 298 K (300 MHz)

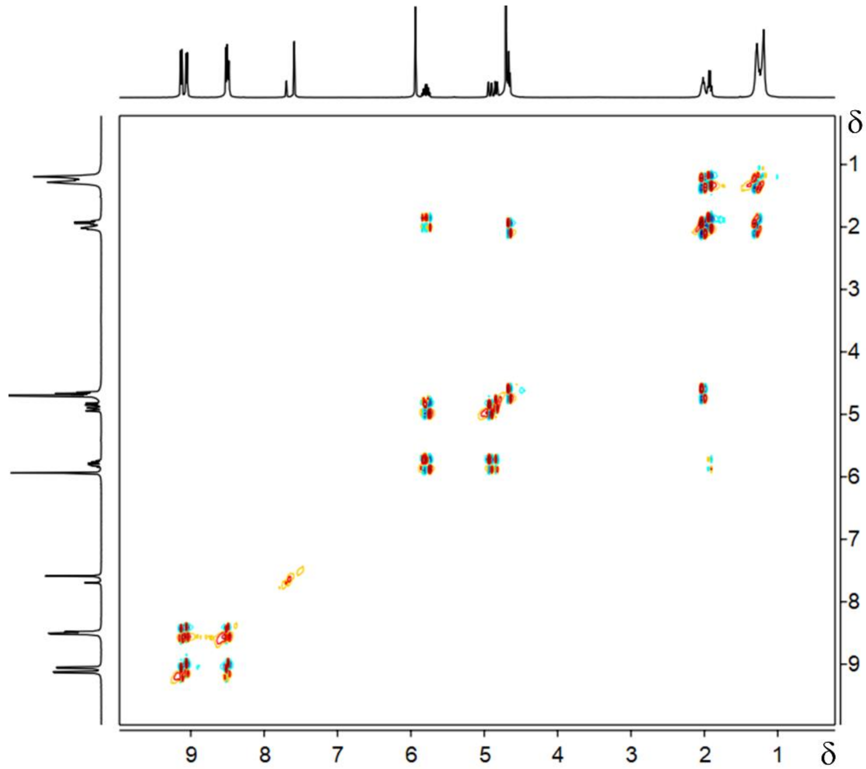

Figure S2: ^{13}C NMR spectrum of **1**·4Br in D_2O at 298 K (300 MHz)

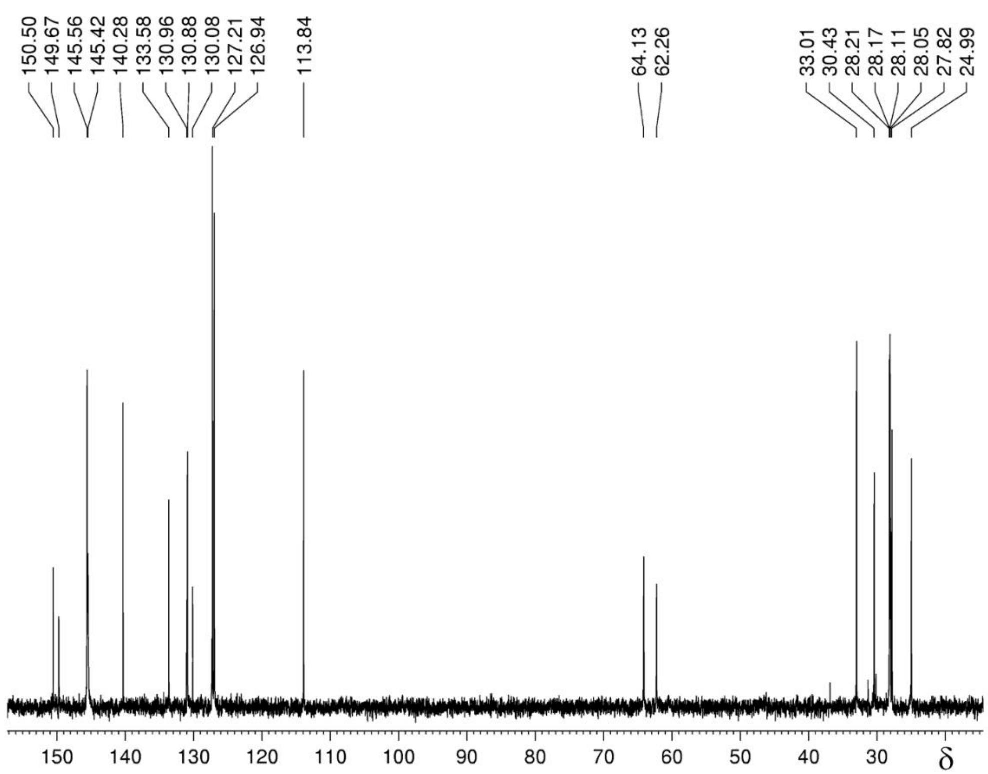

Figure S3: ^{13}C NMR spectrum of **1**·4Br in D_2O at 298 K (300 MHz)

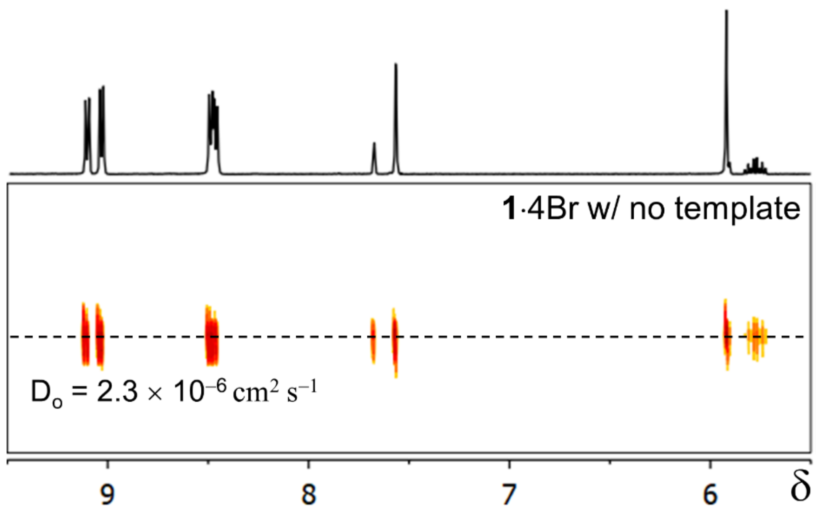

Figure S4: Diffusion ordered spectrum (400 MHz, D2O, 298 K) of a 1×10−2 M solution of **1**·4Br with no added template

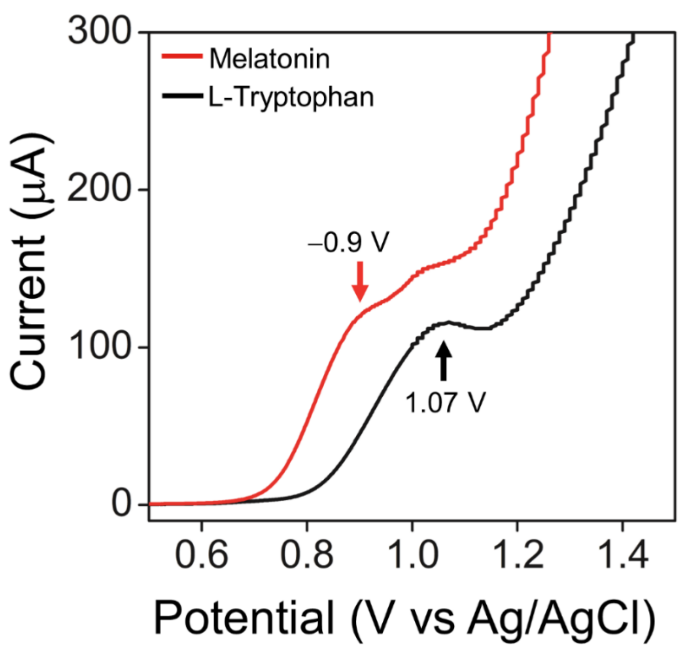

Figure S5: Stacked linear sweep voltammograms measured at 100 mV/s of 5×10^{-3} M and 2.5×10^{-2} M solutions of melatonin (red) and L-tryptophan (black) respectively in H_2O with 3×10^{-2} M NaBr as supporting electrolyte.

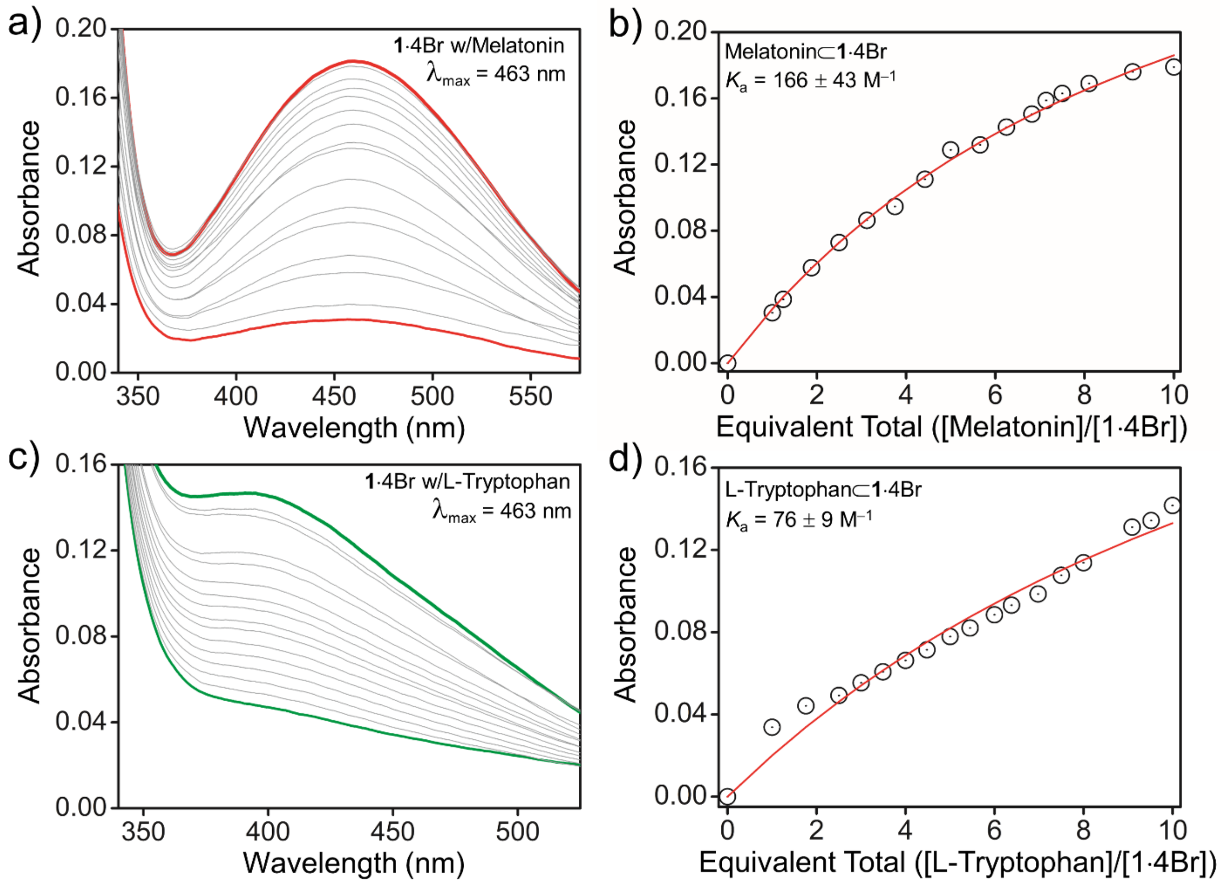

Figure S6: Example UV/Vis spectra obtained during a titration of **1**·4Br with π-electron donors melatonin (a) and L-tryptophan (c). Example plots of the non-linear regression fits (b and d) to data obtained from the titration shown in (a) and (c) for a 1:1 host-guest complex.

Table 1S: Binding Constant Data Calculated from Non-Linear Regression Fits of the Data Obtained from UV/Vis Titration Experiments Between **1**·4Br and Melatonin and L-Tryptophan Using a 1:1 Host-Guest Binding Model

	K_a for Melatonin (M^{-1})	Covariance of Fit	RMS of Regression	K_a for L-Tryptophan (M^{-1})	Covariance of Fit	RMS of Regression
	154.47	5.9171E-3	4.7858E-3	65.65	3.0368e-2	6.5221e-3
	12366	1.3623E-2	7.0875E-3	83.51	1.3242E-2	4.1951E-3
	213.16	3.4508E-3	3.2037E-3	78.60	1.9327E-2	6.3391E-3
Mean	**166.43**			**75.92**		
Stdev	43			9.23		

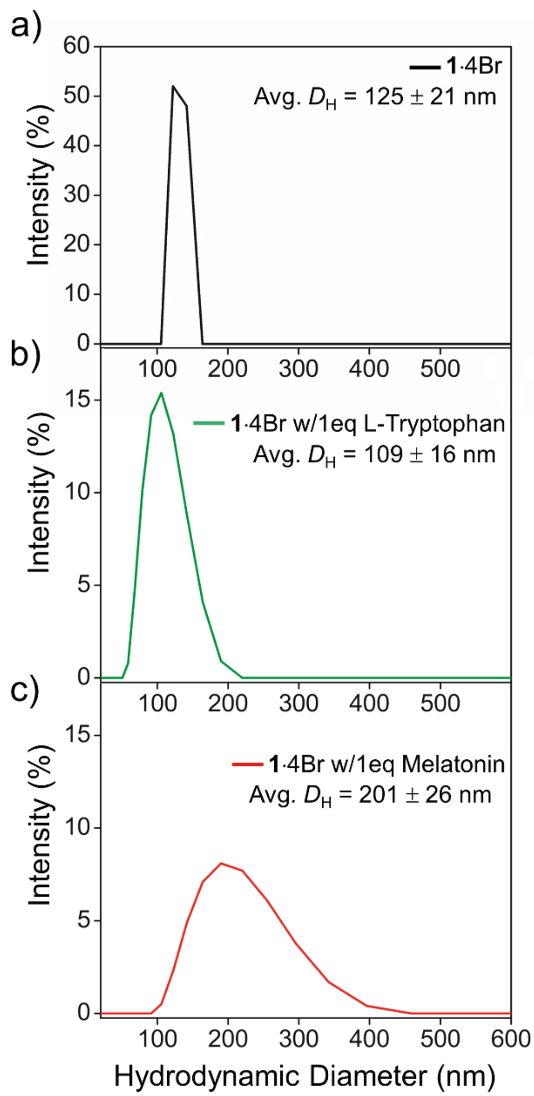

Figure S7: Hydrodynamic diameter (D_H) distributions measured for a 1×10^{-2} M aqueous solution of **1**·4Br (a) with 1 equivalent of L-tryptophan (b) and with 1 equivalent of melatonin (c) added using dynamic light scattering at 298 K.