Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Classical and Non-Classical Melatonin Receptor Agonist-Directed Micellization of Bipyridinium-Based Supramolecular Amphiphiles in Water

*Zhimin Sun, Lihui Xi, Kai Zheng, Zhao Zhang, Kim K. Baldridge and Mark A. Olson**

Institute for Molecular Design and Synthesis, School of Pharmaceutical Science and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, 300072, P. R. China. Email: molson@tju.edu.cn

Additional Spectroscopic Data

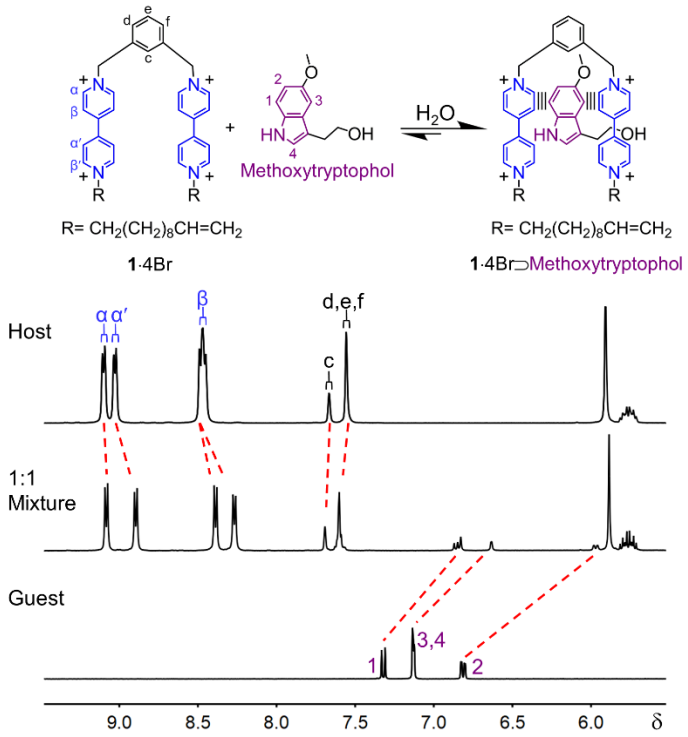

Figure S1. Stacked ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of a 1×10^{-2} M solution of **1**·4Br (top), 1:1 equivalent mixture of **1**·4Br and **MT** (middle), and template **MT** (bottom).

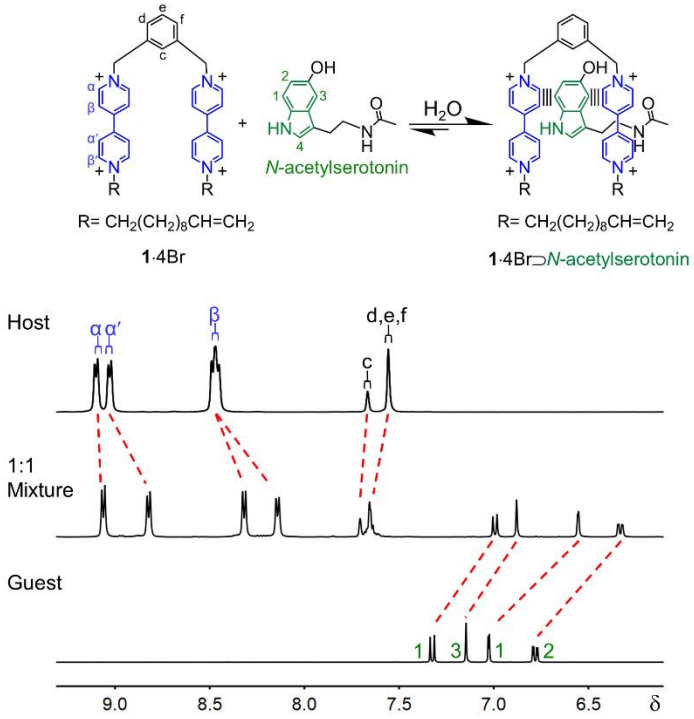

Figure S2. Stacked ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of a 1×10^{-2} M solution of **1**·4Br (top), 1:1 equivalent mixture of **1**·4Br and ***N*-AS** (middle), and template ***N*-AS** (bottom).

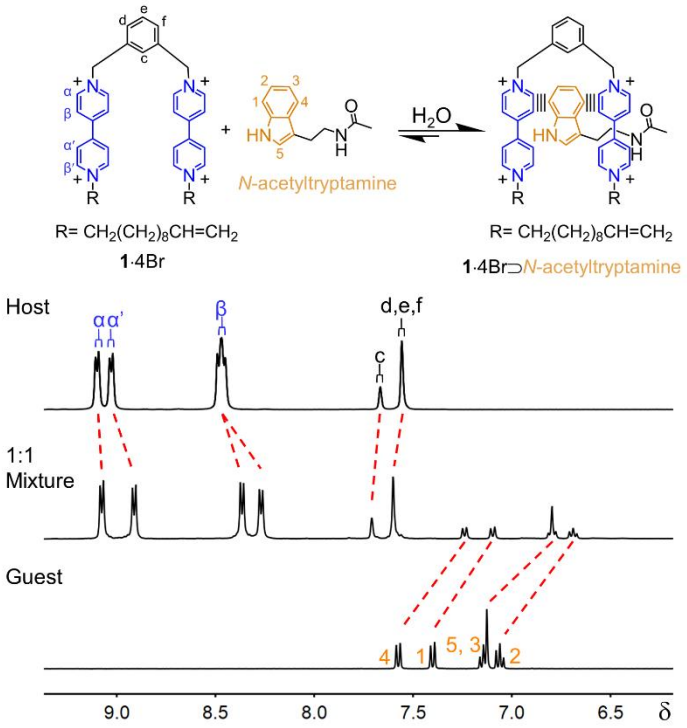

Figure S3. Stacked ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of a 1×10^{-2} M solution of **1**·4Br (top), 1:1 equivalent mixture of **1**·4Br and ***N*-AT** (middle), and template ***N*-AT** (bottom).

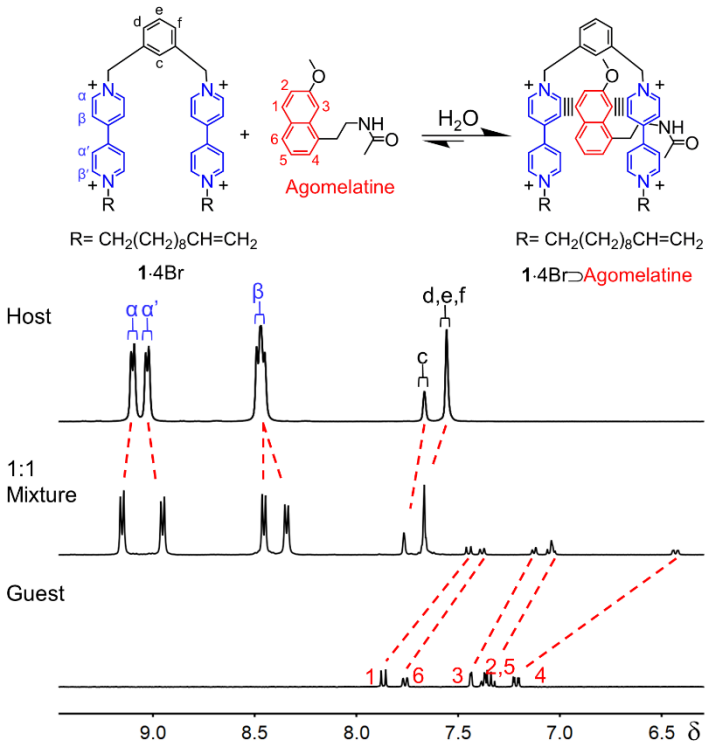

Figure S4. Stacked ^{1}H NMR spectra (400 MHz, D_2O, 298 K) of a 1×10^{-2} M solution of **1**·4Br (top), 1:1 equivalent mixture of **1**·4Br and **AM**(middle), and template **AM** (bottom).

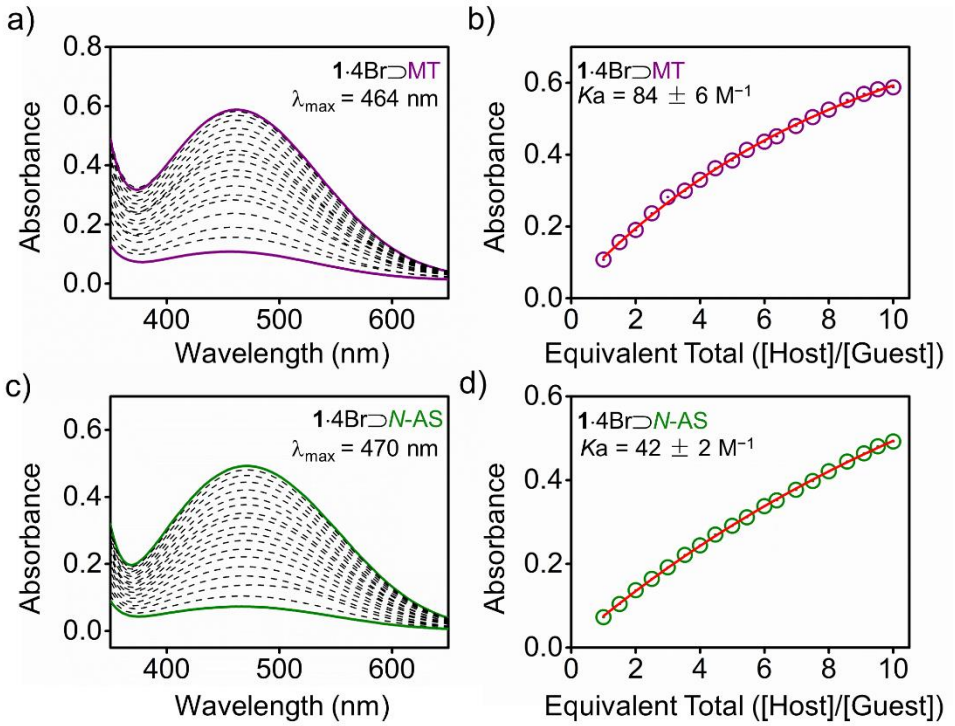

Figure S5. Example UV/Vis spectra recorded during a titration of **1**·4Br with templates **MT** (a) and ***N*-AS** (c). Example plots of the non-linear regression fits (b and d) from the titration data shown in (a) and (c) for a 1:1 host and guest complex.

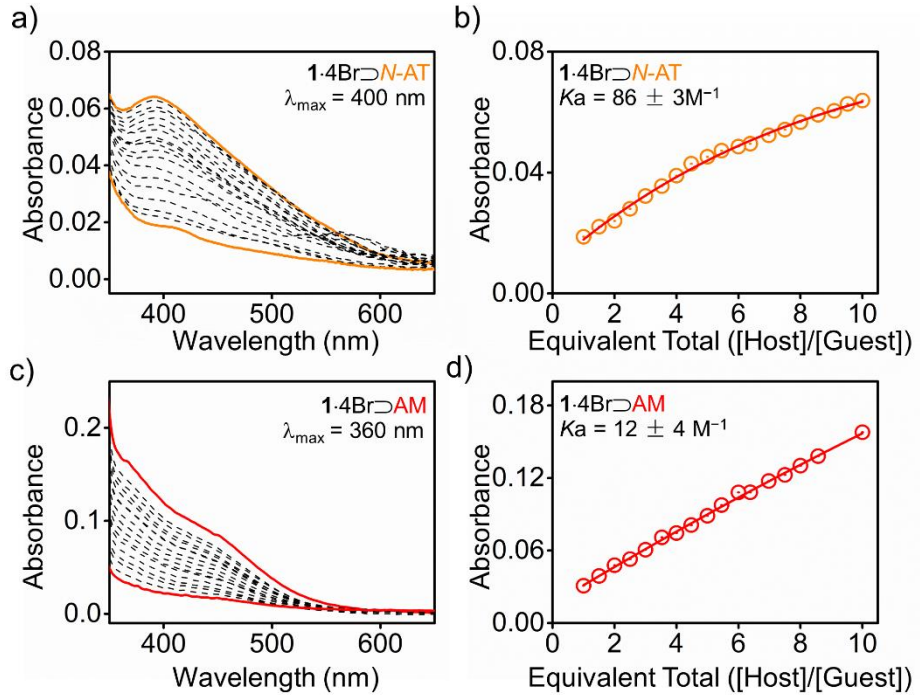

Figure S6. Example UV/Vis spectra recorded during a titration of **1**·4Br with templates ***N*-AT** (a) and **AM** (c). Example plots of the non-linear regression fits (b and d) from the titration data shown in (a) and (c) for a 1:1 host and guest complex.

Table 1S: Binding Constant Data Calculated from Non-Linear Regression Fits of Data Obtained from UV-Vis Titration Experiments Between **1**·4Br and **MT**, ***N*-AS**, ***N*-AT**, and **AM** using a 1:1 Host-Guest Binding Model

	K_a for **MT** (M^{-1})	Covariance of Fit	RMS of Regression	K_a for ***N*-AS** (M^{-1})	Covariance of Fit	RMS of Regression
	82.07	8.8557E-4	4.3744E-3	40.79	1.9999E-4	1.8055E-3
	77.12	9.8079E-4	4.6540E-3	41.93	2.5654E-4	2.0407E-3
	92.12	1.6114E-4	5.8406E-3	44.30	1.4472E-4	1.5414E-3
Mean	**83.77**			**42.34**		
Stdev	6.24			1.46		
	K_a for ***N*-AT** (M^{-1})	Covariance of Fit	RMS of Regression	K_a for **AM** (M^{-1})	Covariance of Fit	RMS of Regression
	88.18	3.6496E-3	8.3728E-4	7.90	2.5186E-3	5.4805E-4
	87.59	5.2726E-3	1.0101E-3	17.39	5.9196E-3	8.3948E-4
	82.01	9.2188E-4	4.3888E-3	10.44	1.5868E-3	1.4452E-3
Mean	**85.93**			**11.91**		
Stdev	2.78			4.01		

The following general expression for the equilibrium constant for the 1:1 host-guest binding was used:

$$K_a = \frac{[HG]}{[H][G]}$$

The following expression for the free guest concentration was used:

$$[G] = \frac{1}{2}\left[\left(G_0 + H_0 - \frac{1}{K_a}\right) + \sqrt{\left(G_0 + H_0 + \frac{1}{K_a}\right)^2 + 4\frac{G_0}{K_a}}\right]$$

The following expression for the complexed guest concentration was used:

$$[HG] = \frac{1}{2}\left[\left(G_0 + H_0 + \frac{1}{K_a}\right) - \sqrt{\left(G_0 + H_0 + \frac{1}{K_a}\right)^2 - 4[H_0][G_0]}\right]$$

The above equations were used in relation to the following expression which relates [HG] to changes in UV-Vis absorption upon donor-acceptor titration:

$$\Delta A_{obs} = \varepsilon_{\Delta HG}([HG])$$

The above expressions were obtained from:

P. Thordarson, *Chem. Soc. Rev.*, **2011**, *40*, 1305-1323

The binding constant data was calculated using Bindfit at:

http://supramolecular.org

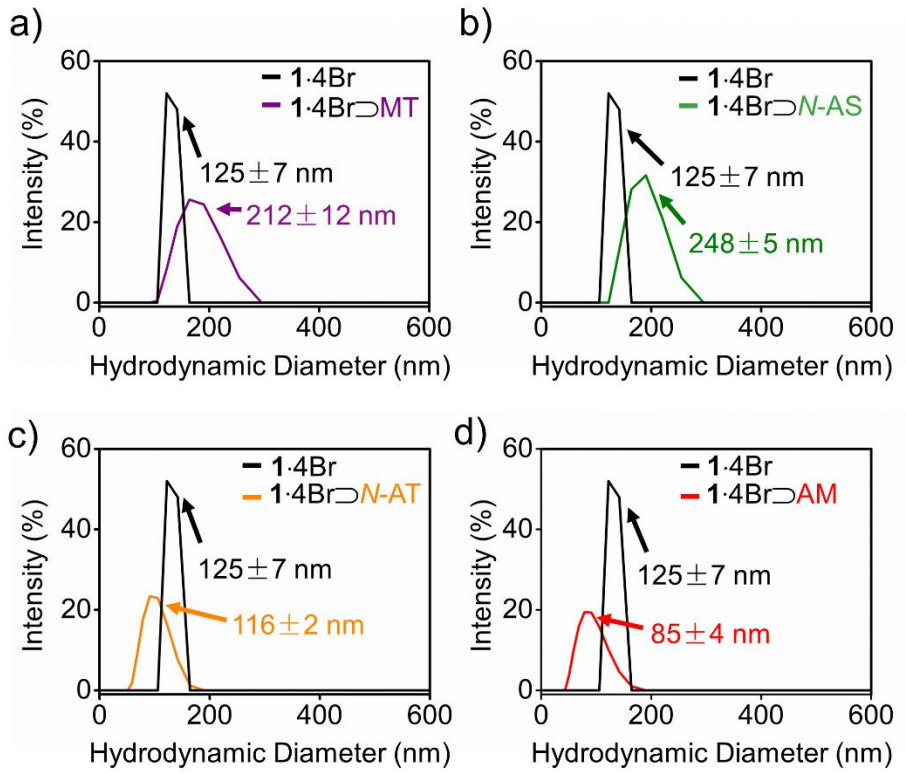

Figure S7. Hydrodynamic diameter (D_H) distributions measured for a 1×10^{-2} M aqueous solution of (a) **1**·4Br with 1 molar equivalent of **MT**, (b) ***N*-AS**, (c) ***N*-AT**, and (d) **AM** added using dynamic light scattering at 298 K.

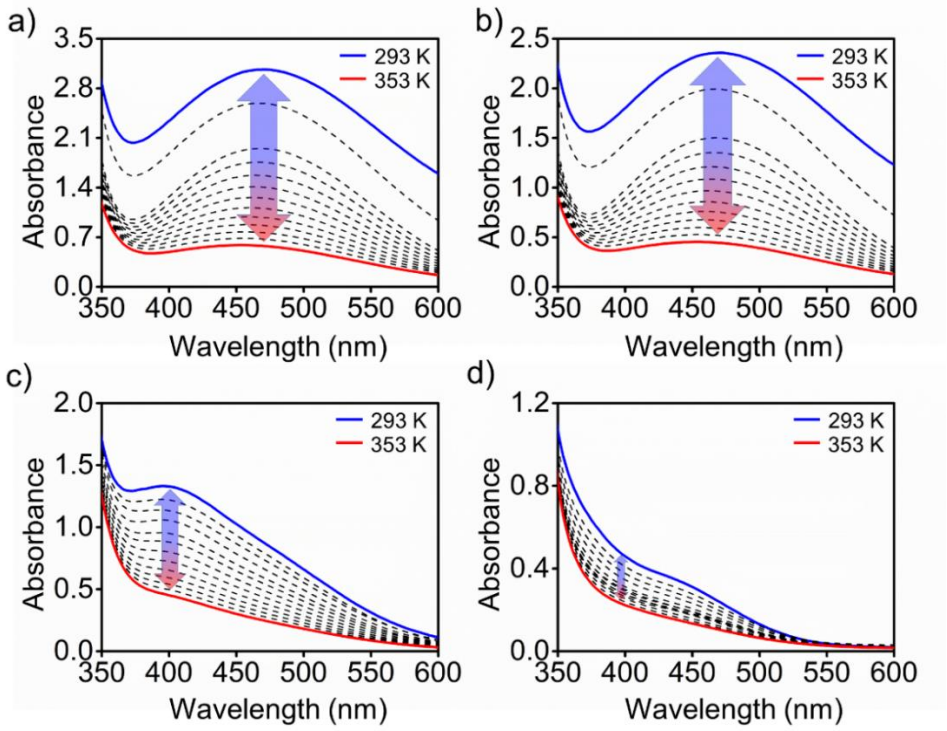

Figure S8. Variable temperature UV-Vis absorption spectra for (a) **1**·4Br with 1 molar equivalent of **MT**, (b) ***N*-AS**, (c) ***N*-AT**, and (d) **AM** recorded in H_2O at a concentration of 1×10^{-2} M from 293 K to 353 K (0.5 cm path length).

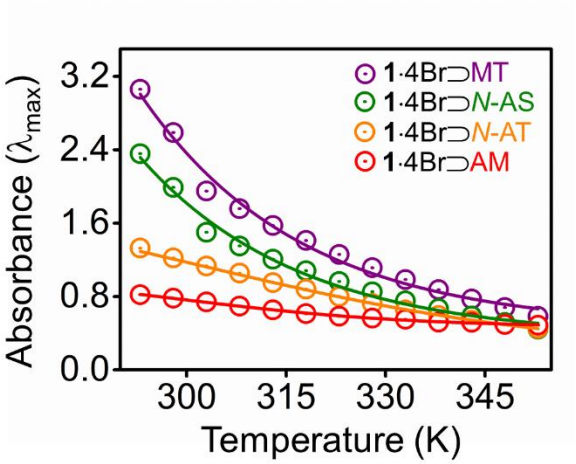

Figure S9. UV-Vis absorbance changes at λ_{max} as a function of temperature (293-353 K) for **1**·4Br with 1 molar equivalent of **MT** (purple trace), ***N*-AS** (green trace), ***N*-AT** (orange trace), and **AM** (red trace) recorded in H_2O at a concentration of 1×10^{-2} M (0.5 cm path length).