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Supporting Information

Hierarchical Self-Organization of Perylene Bisimide-Melamine Assemblies to Fluorescent Mesoscopic Superstructures

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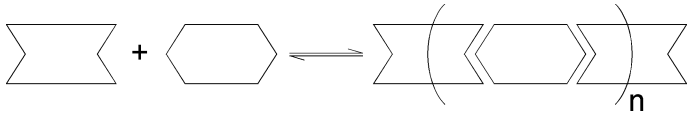
Derivation of a General Formula to Estimate the Chain Length of Supramolecular [··AA····BB··]$_n$ Type Polymers

For the estimation of the chain length of a supramolecular [··AA····BB··]$_n$ type polymer let us consider a mixture of ditopic receptors AA and BB where each receptor functionality A may associate with the complementary receptor B with a microscopic association constant K_μ and no competing association processes between A····A or B····B have to be taken into account.



AA BB [··AA····BB··]$_n$

From the law of mass action (Eq. 1), we derive the concentration of bound receptors [AB] (Eq. 2), where c_A^0 and c_B^0 are the total concentrations of the respective receptor units (i.e. $c_A^0 = 2 \cdot c_{AA}^0$ and $c_B^0 = 2 \cdot c_{BB}^0$). Thus, the probability p for a receptor to be bound is given by Eq. 3, where the factor 2 results from the fact that the complex [AB] involves two bound receptors, one of type A and one of type B.

$$[\mathrm{AB}] = K_\mu [\mathrm{A}][\mathrm{B}] = K_\mu \left(c_\mathrm{A}^0 - [\mathrm{AB}]\right)\left(c_\mathrm{B}^0 - [\mathrm{AB}]\right) \tag{1}$$

$$[\mathrm{AB}] = \frac{\left(c_\mathrm{A}^0 + c_\mathrm{B}^0 + \frac{1}{K_\mu}\right) - \sqrt{\left(c_\mathrm{A}^0 + c_\mathrm{B}^0 + \frac{1}{K_\mu}\right)^2 - 4c_\mathrm{A}^0 c_\mathrm{B}^0}}{2} \tag{2}$$

$$p = \frac{2[\mathrm{AB}]}{c_\mathrm{A}^0 + c_\mathrm{B}^0} = 1 + \frac{\frac{1}{K_\mu} - \sqrt{\left(c_\mathrm{A}^0 + c_\mathrm{B}^0 + \frac{1}{K_\mu}\right)^2 - 4c_\mathrm{A}^0 c_\mathrm{B}^0}}{c_\mathrm{A}^0 + c_\mathrm{B}^0} \tag{3}$$

Assuming a system containing an excess of B, we calculate the concentration of chain-terminating free receptors c_F according to Eq. 4:

$$c_F = 2c_A^0(1-p) + \underbrace{(c_B^0 - c_A^0)}_{Excess\ of\ B} \tag{4}$$

Using the definition of the Degree of Polymerization ($\overline{DP}$)[21] a general formula for the mean chain length of the supramolecular [··AA····BB··]$_n$ polymer is derived with Eq. 5. For exact stoichiometries $c_A^0 = c_B^0$, Eq. 5 simplifies into Eq. 6, which is the supramolecular version of the well-known Carothers' equation of condensation polymer chemistry:

$$\overline{DP} = \frac{\text{number of monomers}}{\text{number of assemblies}} = \frac{\left(c_A^0 + c_B^0\right)^2}{2c_A^0\left(-\frac{1}{K_\mu} + \sqrt{\left(c_A^0 + c_B^0 + \frac{1}{K_\mu}\right)^2 - 4c_A^0 c_B^0}\right) + \left(c_B^0\right)^2 - \left(c_A^0\right)^2} \quad (5)$$

$$\overline{DP} = \frac{1}{1-p} = \frac{2c_A^0}{-\frac{1}{K_\mu} + \sqrt{\left(2c_A^0 + \frac{1}{K_\mu}\right)^2 - 4\left(c_A^0\right)^2}} \quad (6)$$

If we plot the degree of polymerization as a function of the receptor concentrations c_A^0, c_B^0 for a given binding constant K_μ according to Eq. 5, we obtain the three-dimensional plot depicted in Figure 1.

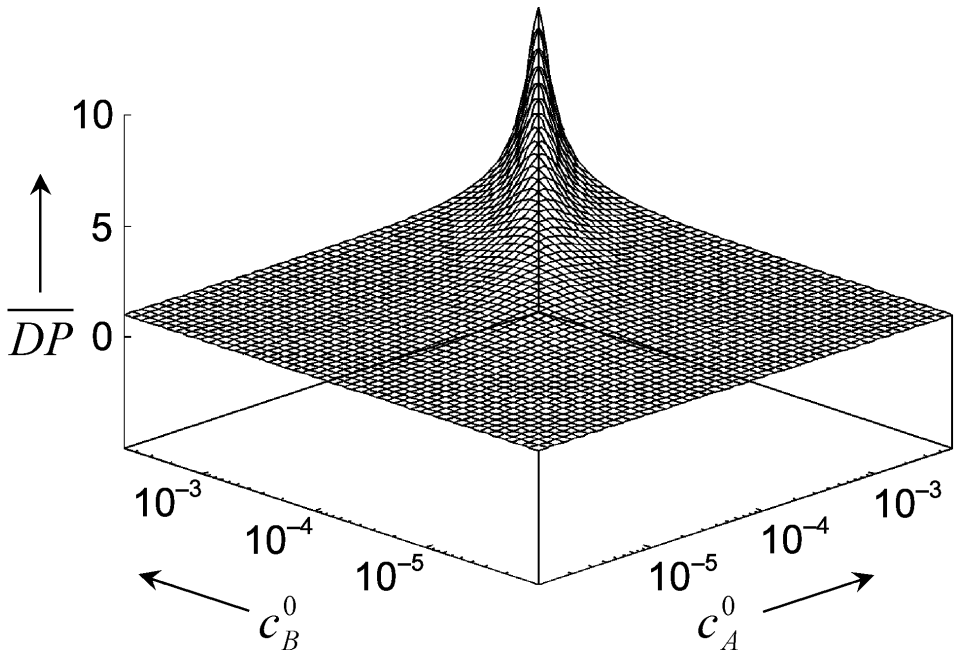


Figure 1. Plot of the mean chain length of an [··AA····BB··]$_n$-type supramolecular polymer as a function of the concentrations of the receptors A, B for a binding constant of 13500 L mol^{-1} (Eq. 5). For the plot, one has to take into account that also receptor A may prevail in excess. This can be done by using the absolute value of (c_B^0–c_A^0) in Eq. 5.

As shown in the three-dimensional plot of Eq. 5 given in Figure 1, long-chain assemblies are only predicted for an exact stoichiometry of the two receptors A and B, whereas for unequal stoichiometry the chain length drops rapidly to one. For example, a solution of two ditopic receptors AA and BB at a stoichiometric concentration of $c_{AA}^{0} = c_{BB}^{0} = 10^{-2}$ mol L^{-1} affords a $\overline{}$,*DP* of 16.9 for a binding constant $K_{\mu} = 13\,500$ L mol^{-1}. However, if c_{AA}^{0} is only $0.99 \cdot 10^{-2}$ mol L^{-1} and c_{BB}^{0} is $1.01 \cdot 10^{-2}$ mol L^{-1}, the calculated $\overline{}$,*DP* drops to only 10.8.

Even for an exact stoichiometry long chains of associated molecules are only obtained at high concentrations and for high binding constants. The vertex ridge of the three-dimensional plot describes this situation of the stoichiometric case when $c_{AA}^{0} = c_{BB}^{0}$ leads to the longest possible supramolecular chain at a given concentration for a given binding constant. Accordingly, for $K_{\mu} = 13\,500$ L mol^{-1} at least concentrations $c_{AA}^{0} = c_{BB}^{0} > 10^{-2}$ mol L^{-1} ($\approx 100 \cdot K_{\mu}^{-1}$) are required to overcome the entropic cost of the association process and to afford polymer-like species. This curve may be also calculated by the simpler Eq. 6, which describes stoichiometric $[\cdot\cdot AA\cdots BB\cdot\cdot]_n$ (nylon-type) and $[\cdot\cdot AB\cdots AB\cdot\cdot]_n$ (perlon-type) supramolecular polymers. As with perlon these association polymers are easier to prepare because the problem of exact stoichiometries, e.g. errors in weighing of the compounds, is not given.

Additional Figures

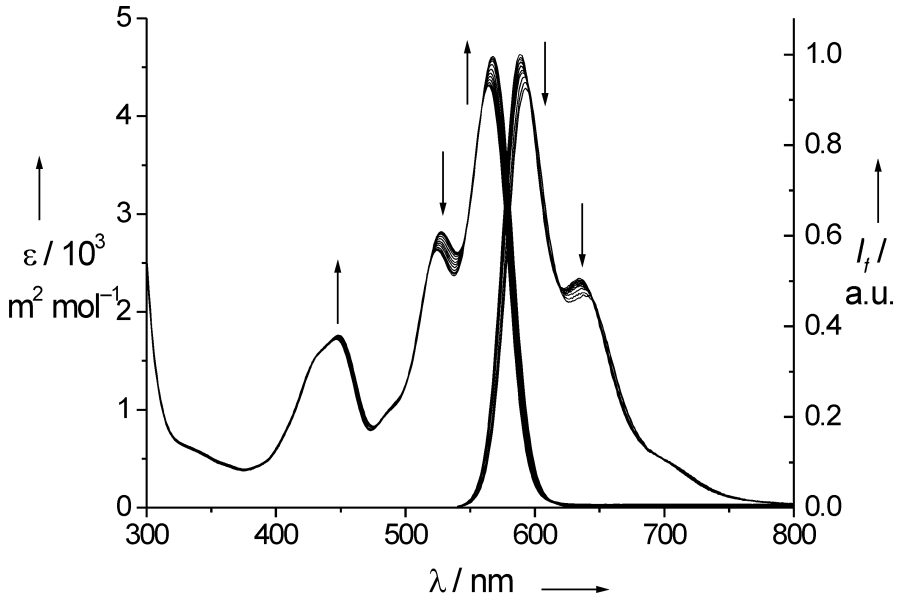


Figure 2. Absorption and Fluorescence spectra of perylene bisimide **5** (c = 10^{-6} mol L^{-1}) in methylcyclohexane in the presence of increasing amounts of melamine **9**. The fluorescence spectra are independent of the excitation wavelength. The excitation wavelength was 530 nm.

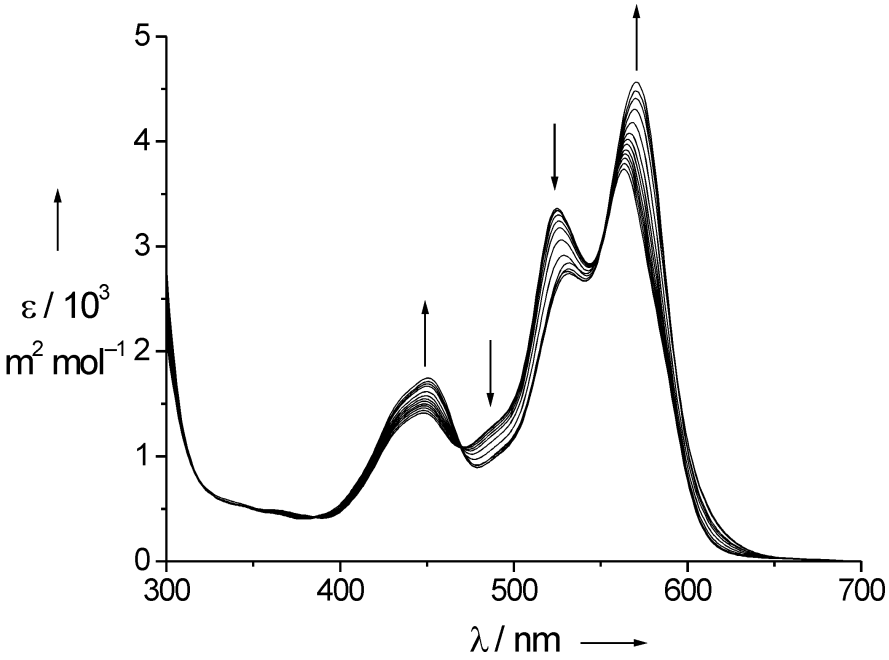


Figure 3. Changes in the UV/Vis absorption spectra of a $5 \cdot 10^{-5}$ mol L^{-1} solution of **3b·8c** in methylcyclohexane upon addition of monotopic melamine **9** (conc. up to $2.5 \cdot 10^{-4}$ mol L^{-1}). The concentration of **3b·8c** was kept constant. Arrows indicate changes upon increasing concentrations of **9**.