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Threshold concentration in nonlinear absorbance law

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1. UV/Vis spectra

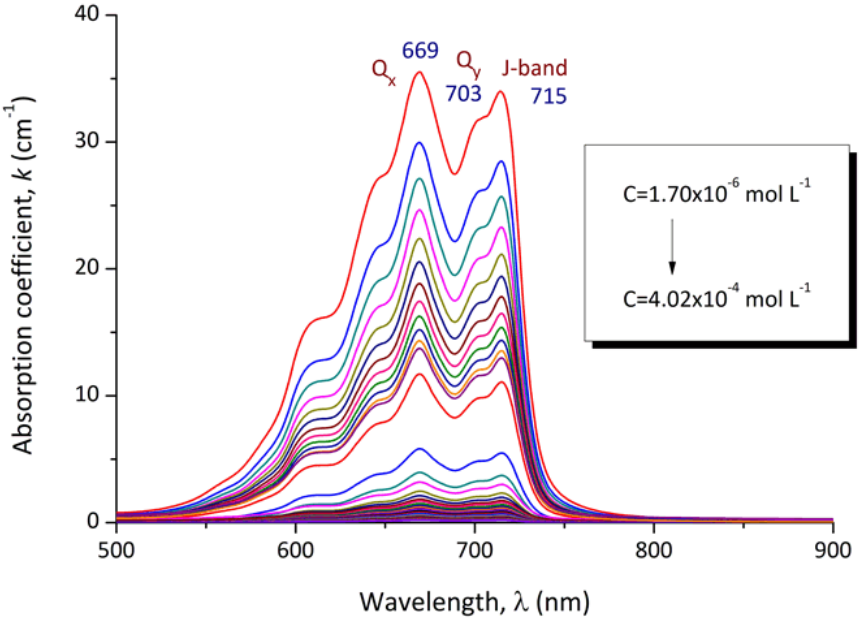

Fig. S1. UV/Vis spectrum (Q-band area) of J-dimer **1** in THF (concentration range of 1.7×10^{-6} – 4.02×10^{-4} mol L^{-1}).

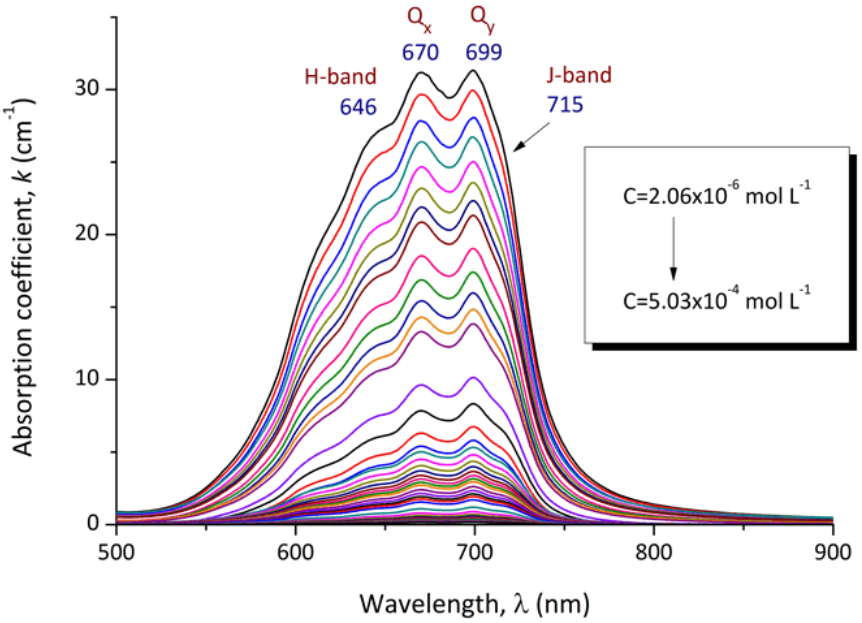

Fig. S2. UV/Vis spectrum (Q-band area) of J-dimer **1** in $CHCl_3$ (concentration range of 2.06×10^{-6} – 5.03×10^{-4} mol L^{-1}).

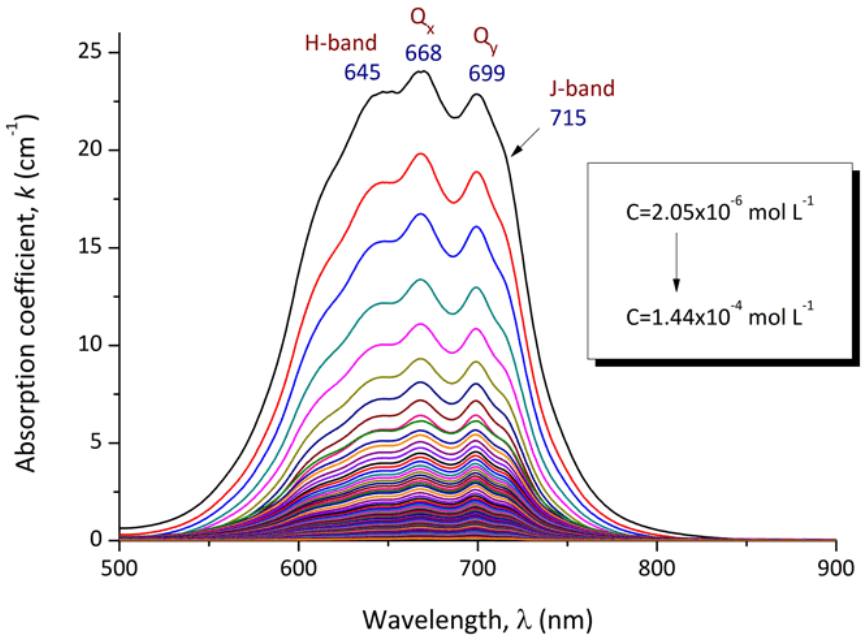

Fig. S3. UV/Vis spectrum (Q-band area) of J-dimer **1** in CCl_4 (concentration range of 2.05×10^{-6} – 1.44×10^{-4} mol L^{-1}).

2. Aggregation study

Thermodynamics of aggregation was studied according to Mataga's approach [1]. It is assumed that only monomeric and aggregated forms are in equilibrium, with the intermediate stages being proceeded quickly and not influncing the overall process. The proposed equation was modified by changing the linear extinction coefficient ε to an effective κ:

$$ln\left[\left(1-\frac{\kappa}{\kappa_0}\right)C\right] = n\,ln\left[\left(\frac{\kappa}{\kappa_n}-\frac{\kappa_n}{n\kappa_0}\right)C\right] + ln\left[\left(\frac{K_n}{n^n(n-(\kappa_n/\kappa_0))^{n-1}}\right)\right],$$

in which κ_n and κ_0 are referred to effective extinction of the most concentrated and diluted solutions respectively, κ and C are the extinction and concentration of each solution under investigation, n is the aggregation number, and K_n is the overall equilibrium constant. Initially, it is assumed that $\frac{\kappa_n}{n\kappa_0} \ll \frac{\kappa}{\kappa_n}$. From the first plot (Fig. S4) n is being calculated. Next, the defined value of n is substituted to the general equation, and the second plot allows to compute the K_n value.

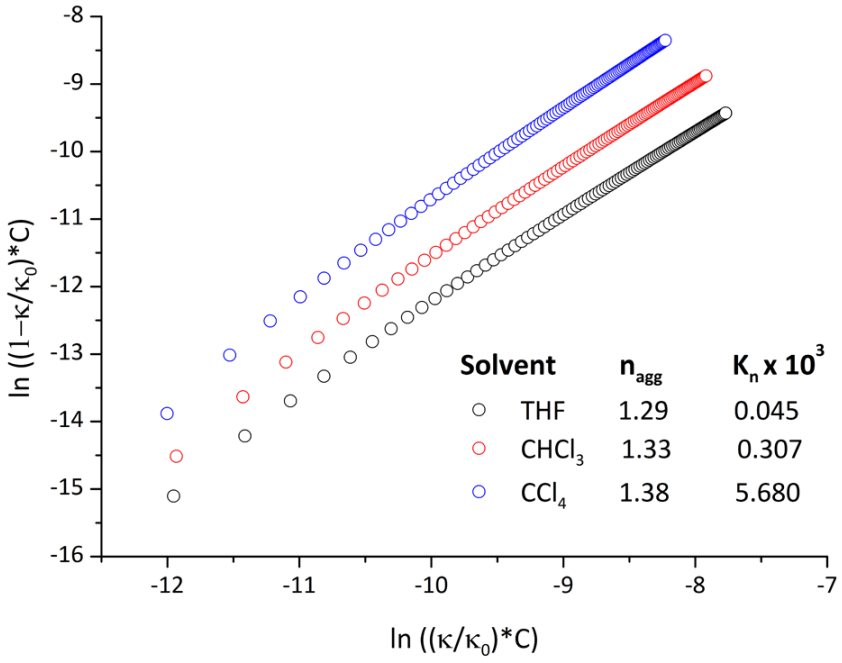

Fig. S4. Computing the thermodynamics of aggregation for J-dimer **1** in THF, $CHCl_3$ and CCl_4. The concentration range is of 1.7×10^{-6} – 5.0×10^{-6} mol dm^3.

Effective molar extinction is the generalized absorption characteristic, driving from diluted to concentrated solutions (Fig. S5). It represents a compromise between a linear and a polynomial functions

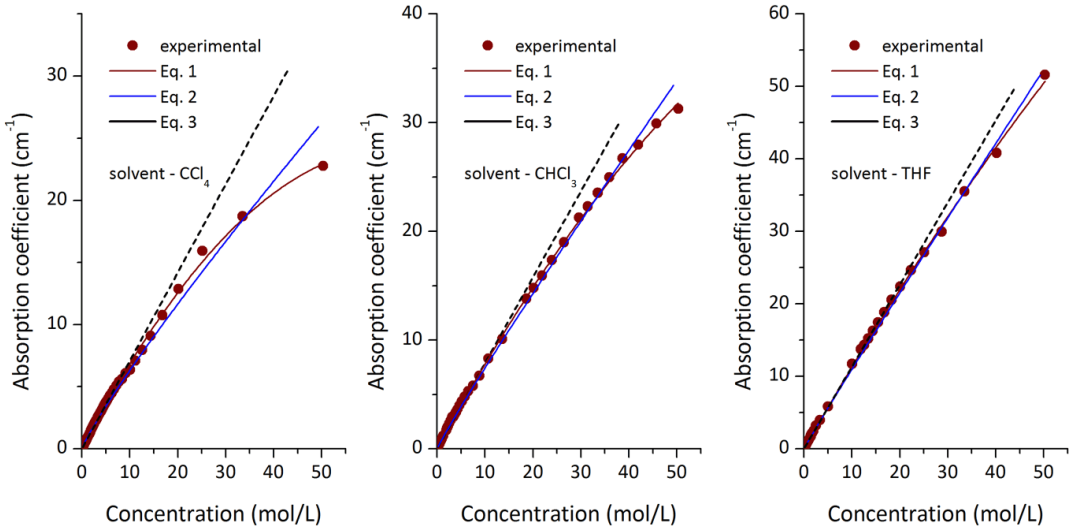

Fig. S5. Approximation of experimental absorbance with polynomial (Eq.1), power (Eq.2) and linear (Eq.3) functions. For the equations the reader is referred to the original text.

3. References

1. N. Mataga, *Bulletin of the Chemical Society of Japan*, 1957, **30**, 375-379.