

Electronic Supplementary Information

Formation and light-harvesting property of a self-assembled subphthalocyanine-porphyrin-phthalocyanine supramolecular complex

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Fig. S4 Plot of $I_0/(I_0-I)$ vs. $1/[TPPS]$. The concentrations of both SubPc(CD) and SiPc(CD)₂ were 5 μM, subsequently the mixture was titrated with TPPS. The slope of the linear regression determines the reciprocal value of the association constant K ; I denotes (*a*) the fluorescence of SiPc(CD)₂ upon excitation of TPPS, (*b*) the fluorescence of SubPc(CD) upon excitation of SubPc(CD), (*c*) the fluorescence of SiPc(CD)₂ upon excitation of SubPc(CD).

Material and Methods

SubPc, TPPS and SiPc(CD)₂ were prepared as described.^{1,2} All photophysical measurements were performed in distilled water (MilliQ).

Absorption and steady-state fluorescence spectroscopy

The ground-state absorption spectra were recorded using a commercial spectrophotometer Shimadzu UV-2501PC. Steady-state fluorescence spectra were measured in quartz cells (1 mm thickness) using a combination of a cw-Xenon lamp (XBO 150) and a monochromator (Lot-Oriel, bandwidth 10 nm) for excitation and a polychromator with a cooled CCD matrix as the detecting system (Lot-Oriel, Instaspec IV).³

Time-resolved fluorescence spectroscopy

Time-correlated single photon counting (TCSPC) technique was used to measure time-resolved fluorescence. The experimental setup was previously described.⁴ A pulsed, frequency doubled, linear polarised radiation of a Nd:VO₄ laser (Cougar, Time Bandwidth Products) with a wavelength of 532 nm, a pulse width of 12 ps, and a repetition rate of 60 MHz was used directly for excitation of the samples or to synchronously pump a dye laser (Model 599, Coherent) tunable in the range from 610 to 670 nm. Fluorescence was detected under a "magic" polarisation angle⁵ relative to excitation with a thermo electrical cooled micro channel plate (R3809-01, Hamamatsu). Detection wavelength was chosen by a computer-controlled monochromator (77200, Lot-Oriel). Electrical signals were processed by a PCI TCSPC controller card (SPC630, Becker & Hickl). The instrument response function

was 42 ps, as measured at an excitation wavelength with Ludox. Data were analysed by a home-made programme by applying a variable projection algorithm⁶ to the global fitting problem. The Nelder-Mead simplex algorithm⁷ was used for optimisation of the nonlinear parameters, and the support plane approach⁵ to compute error estimates of the decay times.

Picosecond transient absorption spectroscopy

To measure the transient absorption spectra, a white light continuum was generated as a test beam in a cell with D₂O/H₂O mixture using intense 25 ps pulses from a Nd³⁺:YAG laser (PL 2143A, Ekspla) at 1064 nm. Before passing through the sample, the continuum radiation was split to obtain a reference spectrum. The transmitted as well as the reference beams were focused into two optical fibres and were recorded simultaneously at different traces on a cooled CCD-matrix (Lot-Oriel, Instaspec IV). Tunable radiation from an OPG/OPA (Ekspla PG 401/SH, tuning range 200–2300 nm) pumped by third harmonic of the same laser was used as an excitation beam. The mechanical delay line allowed the measurement of light-induced changes of the absorption spectrum at different delays up to 15 ns after excitation. Analysis of experimental data was performed using the compensation method.⁸

References

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Table S1 Absorption and fluorescence data for SubPc(CD), TPPS and SiPc(CD)₂, and an equimolar mixture of these compounds in water. The fluorescence quantum yields of the complex were determined from the fluorescence spectra presented in Figs. 3 and S2.

Compound	λ_{abs} (nm)	λ_{em} (nm)	Φ_{fl}		
			SubPc-part excitation	Por-part excitation	Pc-part excitation
SubPc(CD)	566.0 ^a	575	0.10	-	-
TPPS	413.0 ^b	643, 704	-	0.09	-
SiPc(CD) ₂	676.0 ^c	682	-	-	0.40
SubPc(CD)-TPPS-	566.0 ^a	575 ^d	0.011 ^d	0.029 ^e	0.32 ^f
SiPc(CD) ₂	415.5 ^b	645 ^e	0.020 ^e	0.16 ^f	
	683.5 ^c	691 ^f	0.027 ^f		

^aQ band of SubPc(CD). ^bSoret band of TPPS. ^cQ band of SiPc(CD)₂. ^dFor SubPc part, ^eFor Por part, ^fFor Pc part.

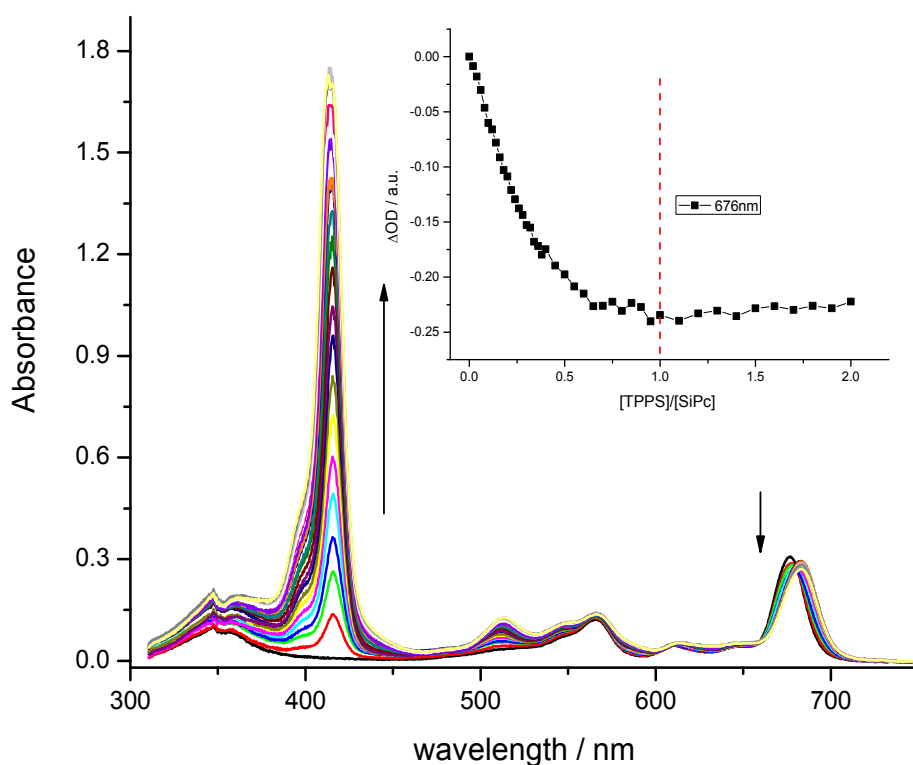


Fig. S1 Change of the UV-Vis spectrum of a mixture of SubPc(CD) and SiPc(CD)₂ (both at 2 μM) upon addition of TPPS (from 0 μM up to 4 μM) in water. For each measurement, a new sample was prepared in order to keep the concentrations of SubPc(CD) and SiPc(CD)₂ fixed. The inset shows the change of optical density for the Pc-Q-band at 676.0 nm with rising concentration of TPPS; the concentration of SubPc(CD) and SiPc(CD)₂ was fixed at 5 μM, while the concentration of TPPS was varied from 0 μM up to 10 μM.

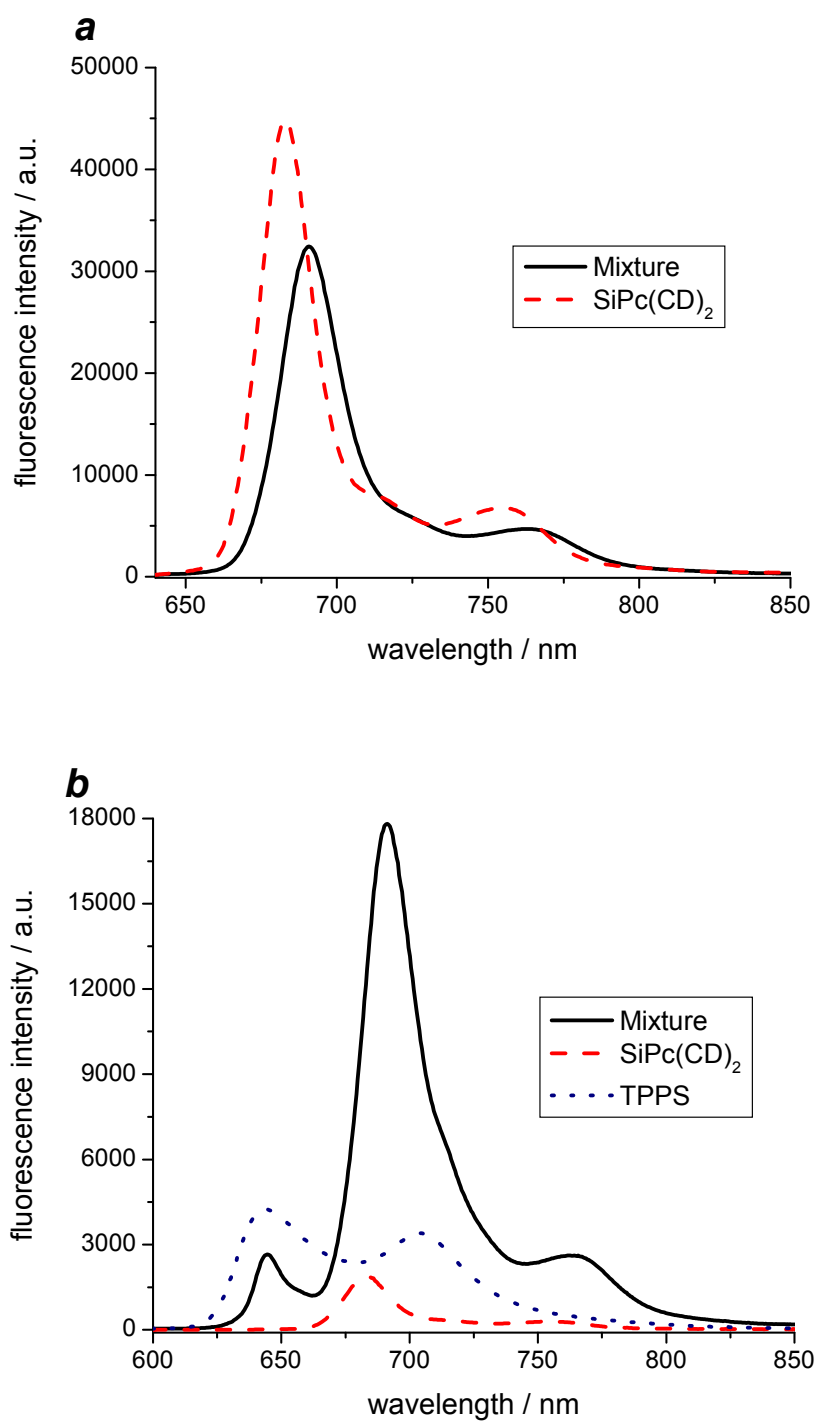


Fig. S2 Steady-state fluorescence spectrum of an equimolar (1 μ M each) mixture of SubPc(CD), TPPS and SiPc(CD)₂ in water upon selective excitation at the (a) Pc or (b) Por part. The spectra of the corresponding components are shown for comparison.

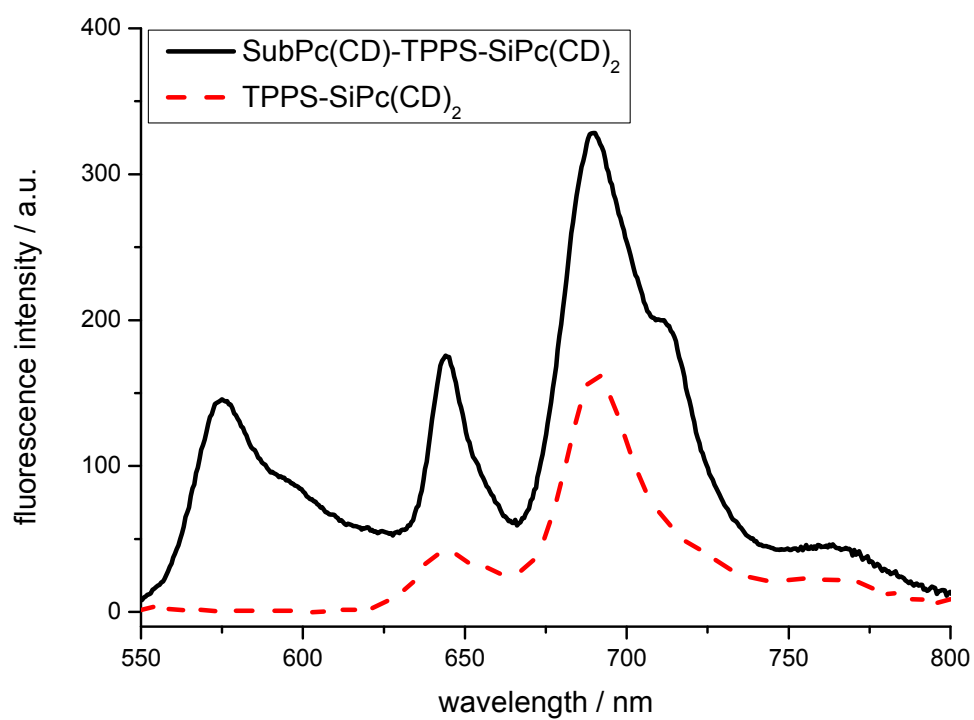


Fig. S3 Comparison of the fluorescence spectra of equimolar SubPc(CD):TPPS:SiPc(CD)₂ (black) and TPPS:SiPc(CD)₂ (red) mixtures in water upon excitation at 532 nm. The concentration of the chromophores was kept at 1 μ M.

Analysis of spectral titration data

Since several association equilibria are involved in ternary supramolecular complex formation, it is very difficult to carry out exact calculation of its association constant. However, some approximations could be done in order to demonstrate that the formation of a ternary complex is likely to occur. The fluorescence spectra of SubPc(CD) and SiPc(CD)₂ upon titration of TPPS were analysed to determine the association constants *K* by using the Benesi-Hildebrand equation⁹:

$$\frac{I_0}{I_0 - I} = \frac{1}{AK} \frac{1}{[x]} + \frac{1}{A},$$

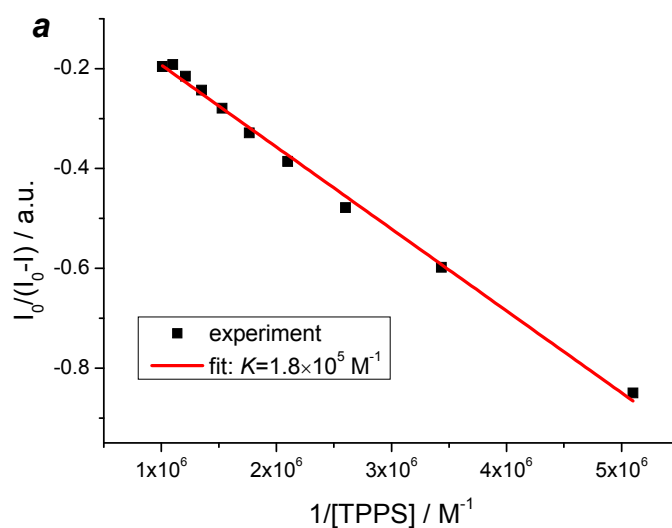
where [x] stands for TPPS concentration, *I*₀ and *I* represent the fluorescence intensities of SubPc(CD) or SiPc(CD)₂ without and upon addition of TPPS, respectively, and *A* is a constant related to the difference in the emission quantum yield of the complexed and the uncomplexed moieties. The concentration of TPPS was kept low with respect to the concentrations of SubPc(CD) and SiPc(CD)₂. When *I*₀/(*I*₀-*I*) vs 1/[x] was plotted, straight lines were obtained from which the different association constants *K* could be determined (see figure S4). The values of *K* are listed in table S2.

Table S2 Association constants of the formed supramolecular complexes

Complex	Association constant <i>K</i> (M ⁻¹)±10%
SubPc(CD)-TPPS	1.5×10 ⁶
TPPS-SiPc(CD) ₂	1.8×10 ⁵
SubPc(CD)-TPPS-SiPc(CD) ₂	7.3×10 ⁵

Upon excitation of SubPc(CD) and by monitoring the fluorescence of SubPc(CD) at different concentrations of TPPS, an association constant of 1.5×10⁶ M⁻¹ was obtained. The stability constant represents the association of SubPc(CD) with TPPS. The association of SiPc(CD)₂

with TPPS was determined by selective excitation of TPPS and monitoring the SiPc(CD)₂ fluorescence. The corresponding stability constant was calculated to be $K=1.8\times 10^5 \text{ M}^{-1}$. Finally, SubPc(CD) was selectively excited and the fluorescence of SiPc(CD)₂ was monitored. An association constant of $7.3\times 10^5 \text{ M}^{-1}$ was obtained. The latter describes association of SubPc(CD) with SiPc(CD)₂, which is only possible in the presence of TPPS. Hence it is an indicator for the formation of the ternary complex. For all the association combinations SubPc(CD)-TPPS, TPPS-SiPc(CD)₂ and SubPc(CD)-SiPc(CD)₂, high values of K were found, indicating that a ternary complex consisting of all the three molecules is formed in the mixture.



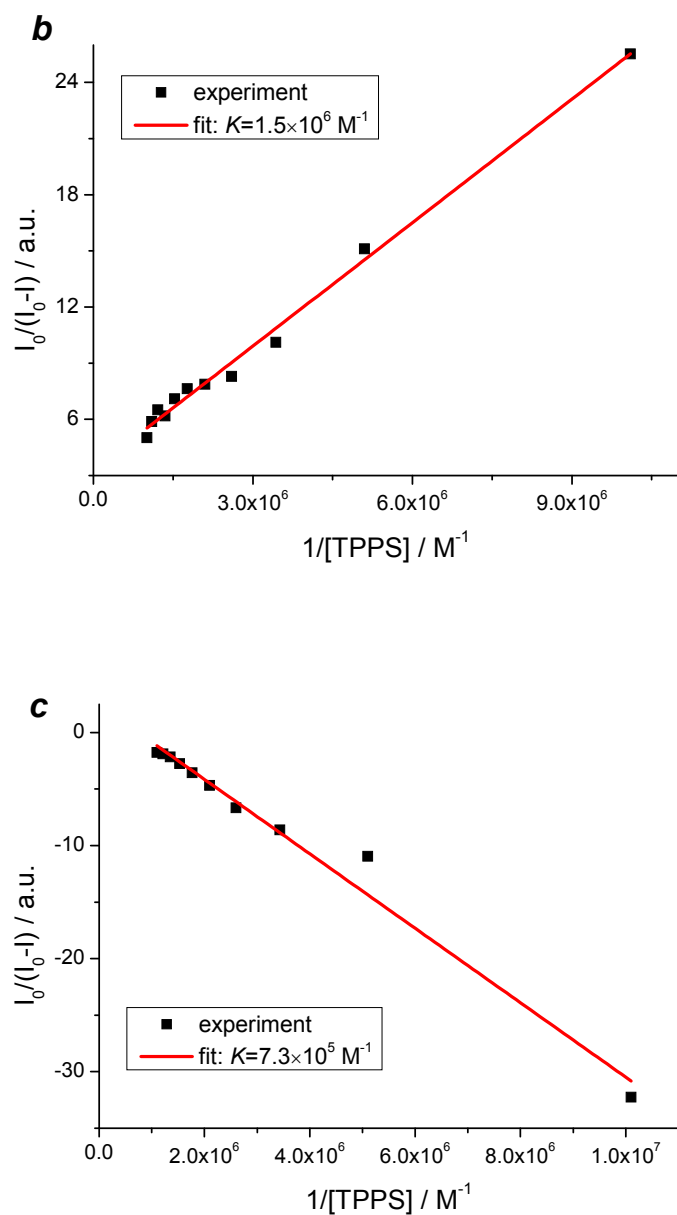


Fig. S4 Plot of $I_0/(I_0-I)$ vs. $1/[\text{TPPS}]$. The concentrations of both SubPc(CD) and SiPc(CD)₂ were 5 μM , subsequently the mixture was titrated with TPPS. The slope of the linear regression determines the reciprocal value of the association constant K ; I denotes (a) the fluorescence of SiPc(CD)₂ upon excitation of TPPS, (b) the fluorescence of SubPc(CD) upon excitation of SubPc(CD), (c) the fluorescence of SiPc(CD)₂ upon excitation of SubPc(CD).

Calculation of degree of self-assembly

The degree of complexation, q , was calculated by comparing the results of steady-state and time-resolved fluorescence experiments:

$$\Phi_{fl}^x(\textit{measured}) = q \cdot \Phi_{fl}^x(\textit{complex}) + (1 - q) \cdot \Phi_{fl}^x(\textit{free})$$

where x is the moiety being monitored (either SubPc(CD) or SiPc(CD)₂), $\Phi_{fl}^x(\textit{measured})$, $\Phi_{fl}^x(\textit{complex})$ and $\Phi_{fl}^x(\textit{free})$ are the fluorescence quantum yields measured, for the complex and for the free species respectively. The fluorescence quantum yield of the complex can be calculated using

$$\Phi_{fl}^x(\textit{complex}) = \Phi_{fl}^x(\textit{free}) \cdot \frac{\tau_{fl}^x(\textit{complex})}{\tau_{fl}^x(\textit{free})}$$

where $\tau_{fl}^x(\textit{complex})$ and $\tau_{fl}^x(\textit{free})$ are the fluorescence lifetimes of the x moiety in the supramolecular complex and in uncomplexed form respectively. For SubPc the following values have been used: $\tau_{fl}^x(\textit{complex}) = 0.046\text{ns}$; $\tau_{fl}^x(\textit{free}) = 2.1\text{ns}$; $\Phi_{fl}^x(\textit{measured}) = 0.011$; $\Phi_{fl}^x(\textit{free}) = 0.10$; and hence $\Phi_{fl}^x(\textit{complex}) = 0.002$. As result, the value of the complexation degree, q , was calculated to be 0.91. For SiPc the following values have been used: $\tau_{fl}^x(\textit{complex}) = 4.2\text{ns}$; $\tau_{fl}^x(\textit{free}) = 5.4\text{ns}$; $\Phi_{fl}^x(\textit{measured}) = 0.32$; $\Phi_{fl}^x(\textit{free}) = 0.40$; and hence $\Phi_{fl}^x(\textit{complex}) = 0.31$. It follows, $q = 0.89$. The total degree of self-assembly is calculated by multiplication of 0.89 and 0.91; and thus $0.89 \times 0.91 = 0.81$.