Electronic Supplementary Information

Sequential energy and charge transfer processes in mixed host-guest complexes of subphthalocyanine, porphyrin and phthalocyanine chromophores

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Fig. S1 Change in UV/Vis spectra of SubPc+SiPc2 (***a***) and SubPc+SiPc3 (***b***) (2 µM for each component) in water upon addition of TPPS (from 0 to 4 µM). The inset of each figure shows the change in intensity of the SiPc Q-band with [TPPS]/[SiPc].

Fig. S2 Change in fluorescence spectrum of an equimolar mixture of SubPc and SiPc2 (***a***) and that of SubPc and SiPc3 (***b***) (1 µM for each component) in water upon addition of TPPS (from 0 to 2 µM). The SiPc part was selectively excited at 615 nm. The inset of each figure shows the change in SiPc-fluorescence intensity versus concentration of TPPS with [TPPS]/[SiPc].

Fig. S3 Change in fluorescence spectrum of an equimolar mixture of SubPc and SiPc3 (***a***) and that of SubPc and SiPc1 (***b***) (1 µM for each component) in water upon addition of TPPS (from 0 to 2 µM). The SubPc part was selectively excited at 532 nm.

Fig. S4 Fluorescence of the SubPc-TPPS-SiPc (black) and TPPS-SiPc (red) mixtures upon excitation at 532 nm for **1** (***a***) and **2** (***b***). The concentration of each component was fixed at 1 µM.

Fig. S5 Plot of $I_0/(I_0-I)$ vs. 1/[TPPS]. The slope of the linear regression determines the reciprocal value of the association constant K; I denotes (***a***) the fluorescence of SiPc upon excitation of TPPS, (***b***) the fluorescence of SubPc upon excitation of SubPc, (***c***) the fluorescence of SiPc upon excitation of SubPc.

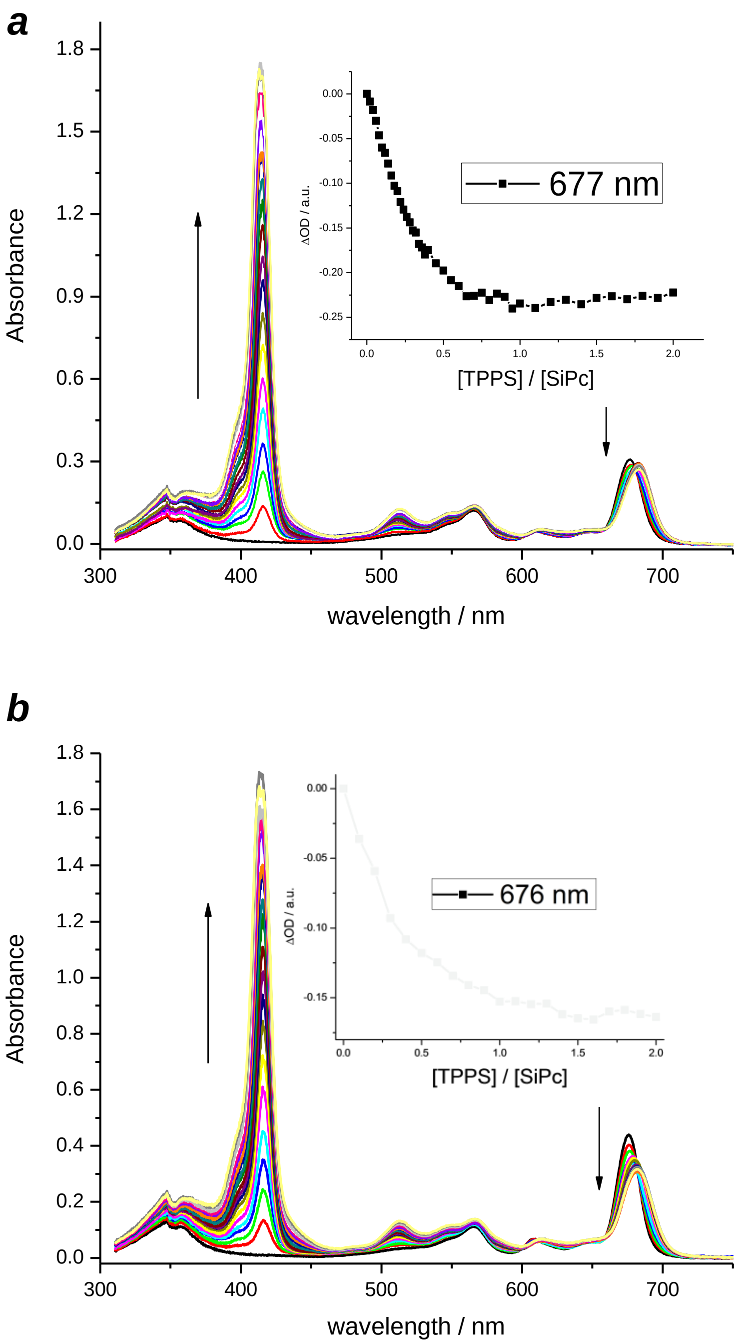
Fig. S6 DAF spectra of mixtures **1** (***a,b***) and **3** (***c,d***) upon excitation of SiPc (***a,c***) and TPPS (***b,d***). The concentration of each component in the supramolecular complexes was fixed at 1 µM.

Fig. S7 ΔOD spectra of **2** upon selective excitation of SiPc- (***a***), TPPS- (***b***) and SubPc- (***c***) parts at different delay times. The kinetics of the SiPc bleach is shown in (***d***). The concentration of each component was fixed at 10 µM.

Fig. S8 ΔOD spectra of **3** upon selective excitation of SiPc- (***a***), TPPS- (***b***) and SubPc- (***c***) parts at different delay times. The kinetics of the SiPc bleach is shown in (***d***). The concentration of each component was fixed at 10 µM.

Calculation of the degree of self-assembly

Table S1 Change in free energy ΔG_0 for different electron donor-acceptor pairs.



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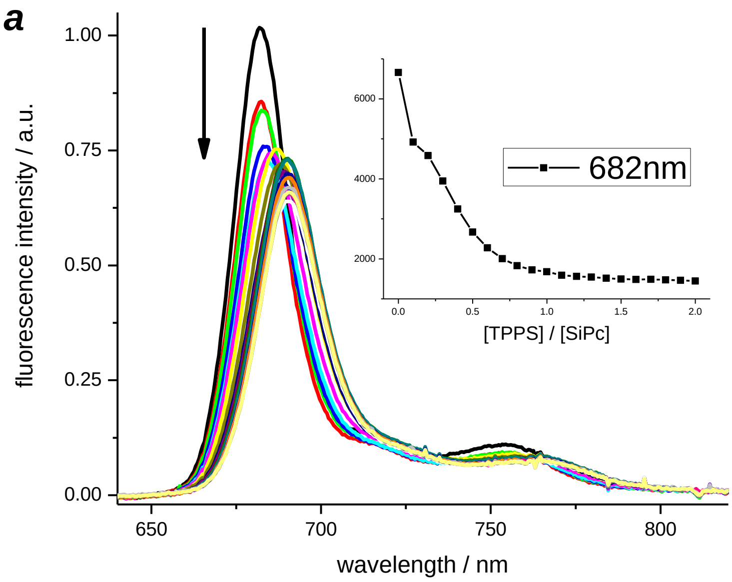

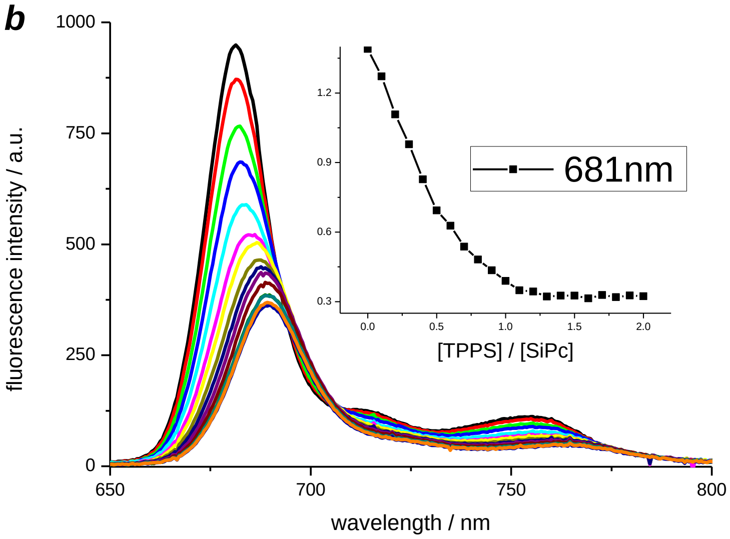

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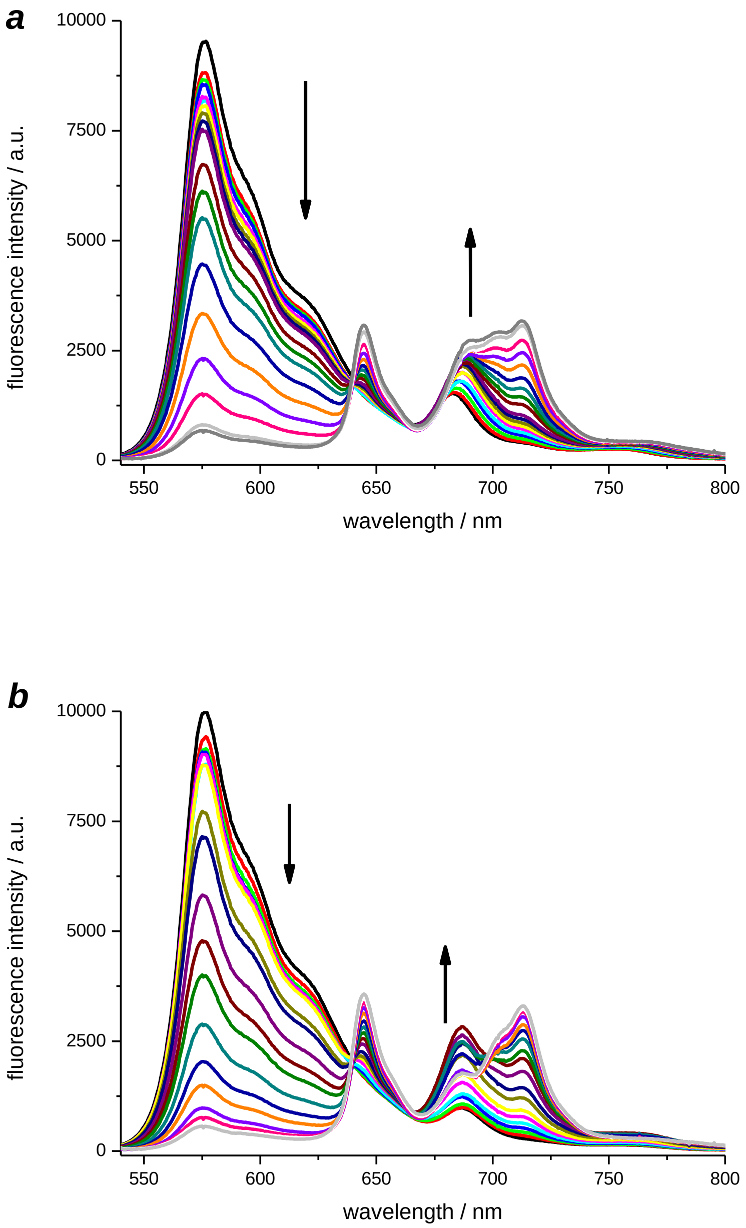

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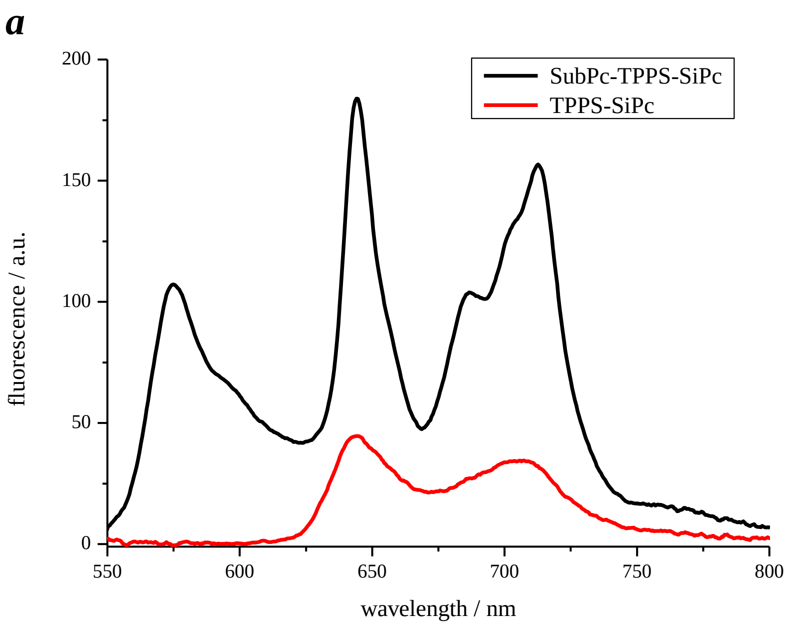

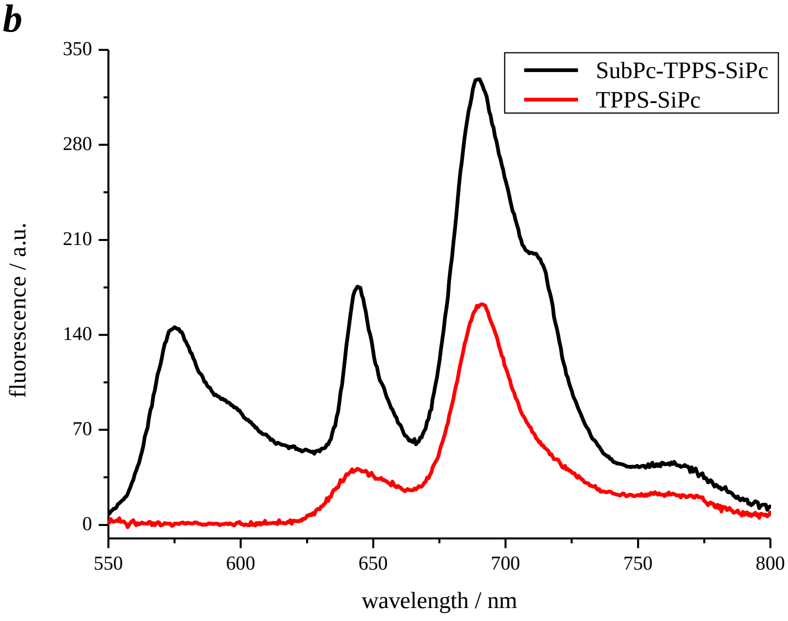

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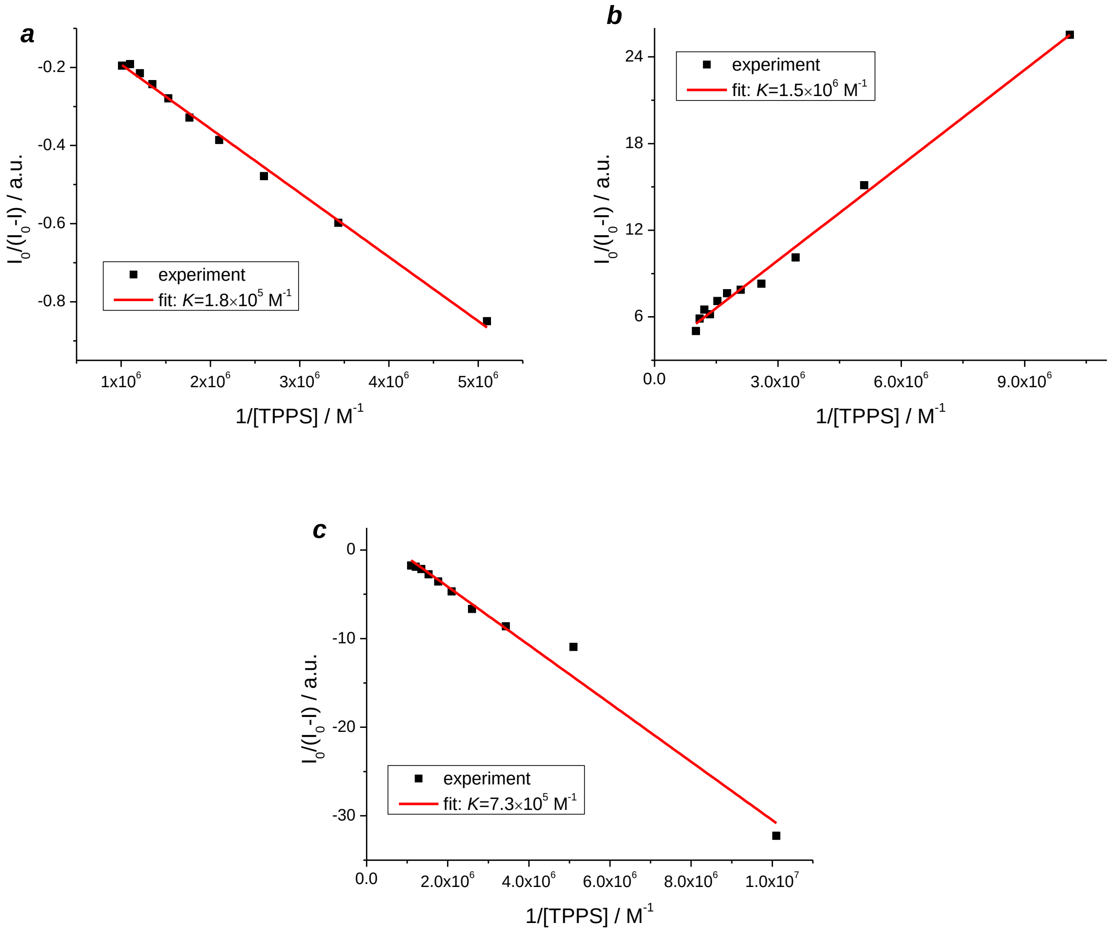
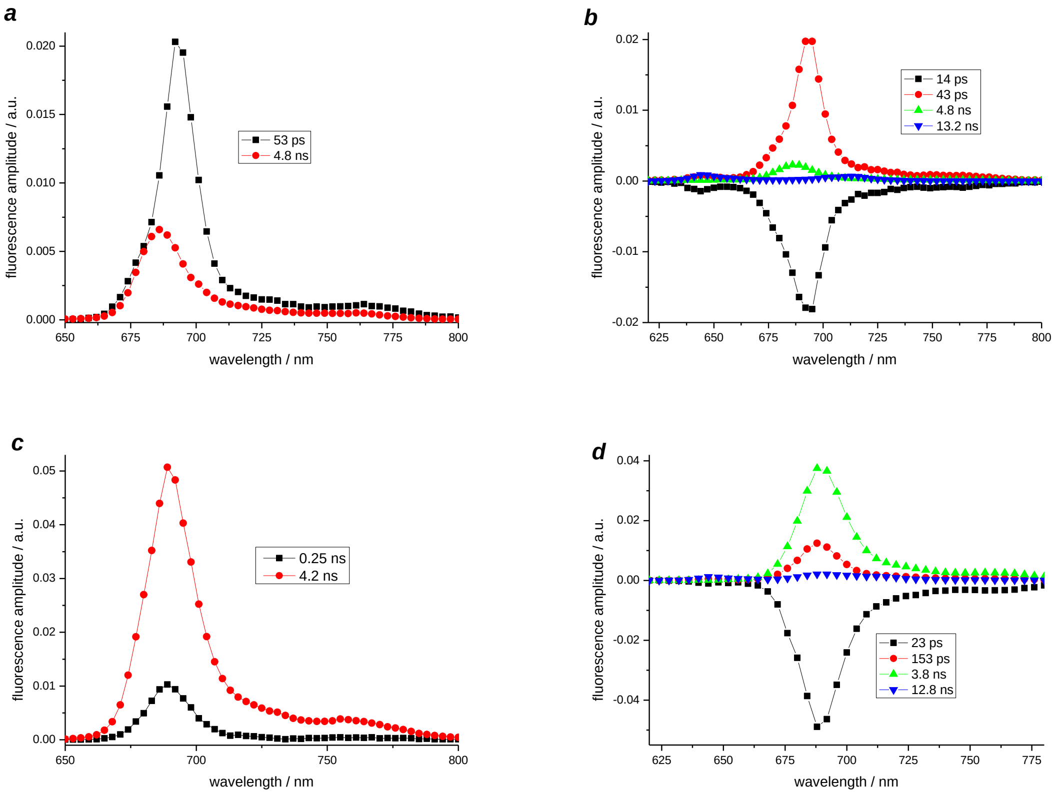


Fig. S5 Plot of $I_0/(I_0\text{-}I)$ vs. 1/[TPPS]. The concentrations of both SubPc and SiPc were 5 μM, subsequently the mixture was titrated with TPPS. The slope of the linear regression determines the reciprocal value of the association constant *K*; I denotes (***a***) the fluorescence of SiPc upon excitation of TPPS, (***b***) the fluorescence of SubPc upon excitation of SubPc, (***c***) the fluorescence of SiPc upon excitation of SubPc.



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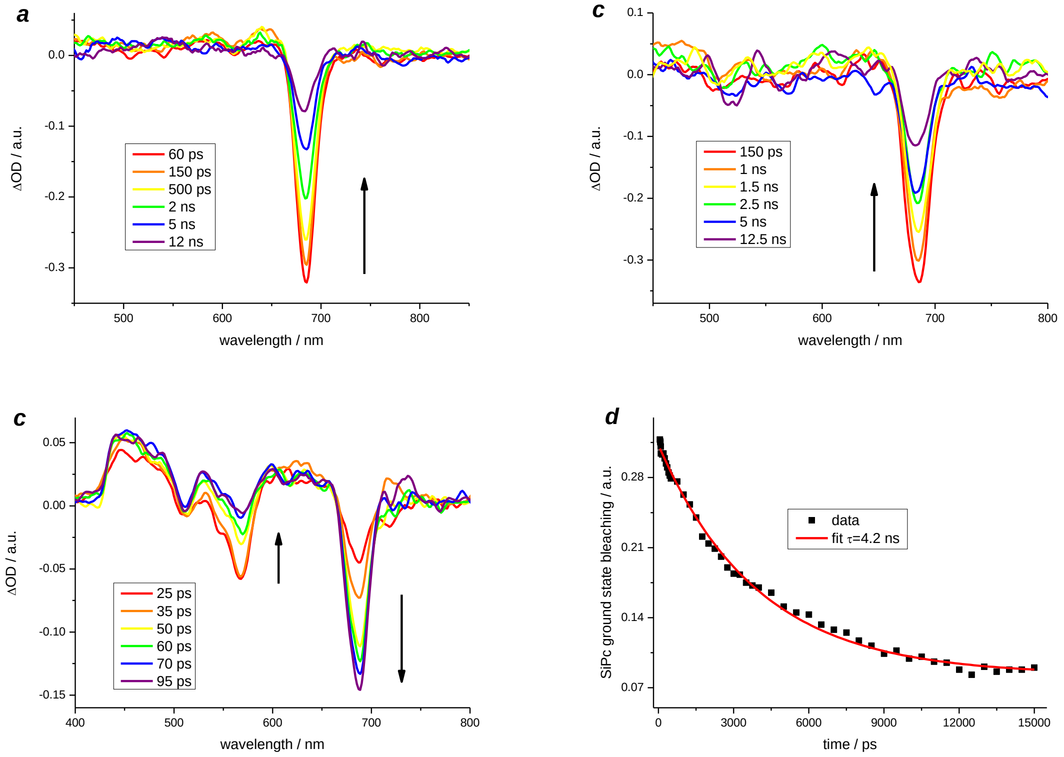

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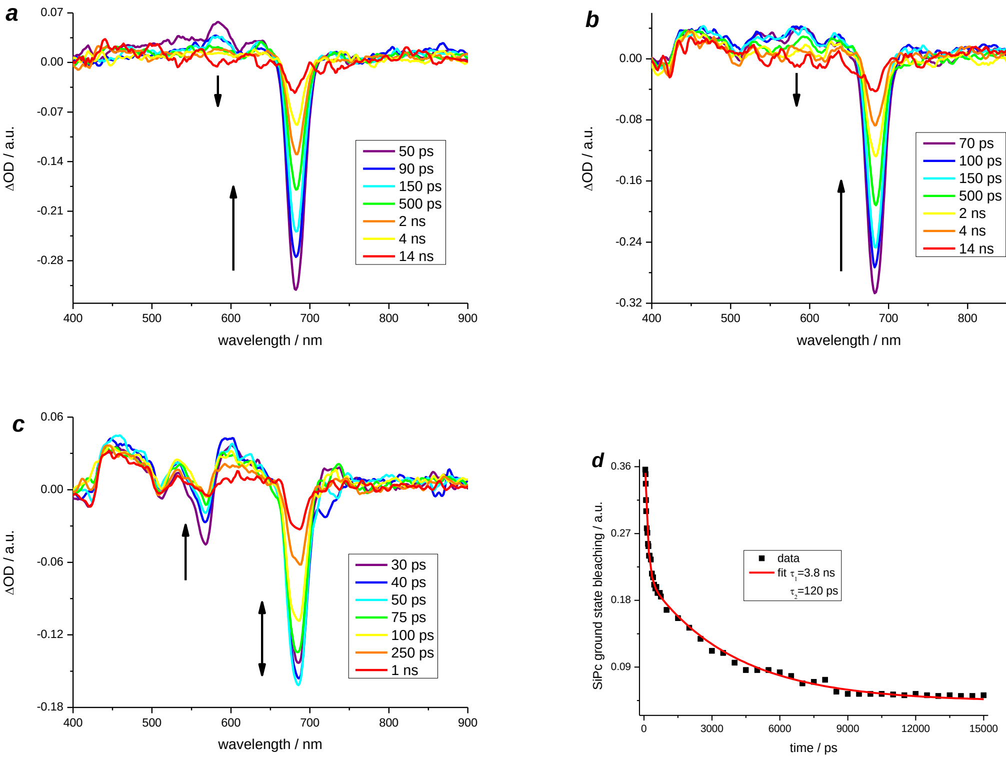

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Calculation of the degree of self-assembly

The fluorescence lifetime of SiPc2 incorporated in **2** is slightly reduced compared to the decay time of free SiPc2. It is caused by weak interactions between TPPS and SiPc2 in the self-assembled complex. In fact one can carry out some estimations:[1,2]

$$\Phi_{fl}^{x}(complex) = \Phi_{fl}^{x}(free) \cdot \frac{\tau_{fl}^{x}(complex)}{\tau_{fl}^{x}(free)}, \qquad (1.1)$$

where $\Phi_{fl}^{x}(complex)$ is the calculated fluorescence quantum yield of the complexed x and $\Phi_{fl}^{x}(free)$ is the fluorescence of free x, $\tau_{fl}^{x}(complex)$ and $\tau_{fl}^{x}(free)$ are fluorescence lifetimes of moiety x in the supramolecular complex and free form in water, respectively.

With $\tau_{fl}(complex)$ = 4.2ns, $\tau_{fl}(free)$ = 5.35ns and $\Phi_{fl}(free) = 0.40$, the fluorescence quantum yield of complexed SiPc is estimated to be 0.31. This is in accord with the measured value of 0.32 obtained by steady-state fluorescence spectroscopy. A similar reduction was found for the intersystem crossing quantum yield: Φ_{ISC} = 0.38 for free SiPc2, Φ_{ISC} = 0.27 for the complexed SiPc2. This indicates enhanced probability of radiationless transitions from the excited singlet state to the ground state $S_1 \rightarrow S_0$, since both fluorescence and intersystem crossing are affected roughly in the same way. The same behaviour is observed for SiPc3 moiety: the ISC quantum yield and the fluorescence quantum yield of the SiPc3 in the complex **3** are 0.10 and 0.21, respectively, compared to Φ_{ISC} = 0.40 and Φ_{fl} = 0.49 for free SiPc3. This means that charge recombination SubPc-TPPS$^{\bullet+}$-SiPc3$^{\bullet-}$ → SubPc-TPPS-SiPc3 occurs without “touching” a triplet state, since Φ_{fl} and Φ_{ISC} are quenched similarly.

The measured fluorescence quantum yield is a superposition of the fluorescence quantum yields of free SiPc and complexed SiPc:

$$\Phi_{fl}^{x}(measured) = q \cdot \Phi_{fl}^{x}(complex) + (1-q) \cdot \Phi_{fl}^{x}(free), \qquad (1.2)$$

where q is the ratio of complexation, x is the complexed moiety, $\Phi_{fl}^{x}(measured)$ is the measured fluorescence quantum yield in a complex and $\Phi_{fl}^{x}(free)$ is the fluorescence quantum yield of free moiety x.

By using the values obtained for the SiPc-moieties, the degree of self-assembly was found to be 0.89 and 0.94 for **1** and **2**, respectively. This means that 89% of all SiPc1 molecules and 94% of all SiPc2 molecules are incorporated in the supramolecular complex with TPPS.

For **3**, the estimation of $\Phi_{fl}^{SiPc3}(complex)$ is more complicated since two fluorescence lifetimes of the SiPc3 moiety appear in the supramolecular complex: 0.15 ns and 3.8 ns. By using equation **Error! Reference source not found.** with $\Phi_{fl}^{SiPc3}(free) = 0.49$, $\tau_{fl}^{SiPc3}(complex) =$ 3.8ns and $\tau_{fl}^{SiPc3}(free) =$ 5.58ns, one obtains the fluorescence quantum yield $\Phi_{fl}^{SiPc3}(complex) =$ 0.33. However, this does not take into account the ET process that is responsible for the reduced fluorescence lifetime of 0.15 ns. Assuming on the other hand that only electron transfer occurs, then the fluorescence quantum yield calculated with equation **Error! Reference source not found.** turns out to be $\Phi_{fl}^{SiPc3}(complex) = 0.013$. The measured fluorescence quantum yield is 0.21. Apparently, both processes occur at the same time and compete with each other. For this reason, equation **Error! Reference source not found.** is extended to

$$\Phi_{fl}^{complex} = \Phi_{fl}^{free} \cdot \left(r \frac{3.8ns}{\tau_{fl}^{free}} + (1-r) \frac{0.15ns}{\tau_{fl}^{free}} \right), \tag{1.3}$$

1 – *r* is the percentage of SiPc3 molecules that participate in charge transfer reaction and *r* can be taken from results obtained in ps-TAS experiments, namely *r* = 0.5. This yields a complexation probability of 0.88 and correlates very well the values obtained for SiPc1 and SiPc2 containing complexes.

The same calculations can be performed for the other incorporated moiety, namely SubPc. It follows that the SubPc-TPPS complexation is also very efficient. The probability of complexation of SubPc-TPPS varies from 0.81 (**3**) to 0.91 (**2**) and 0.95 (**1**).

Table S1 Changes in free energy (ΔG_0) for different electron donor-acceptor pairs calculated with the Rehm-Weller approach[3] and the electrochemical data as obtained earlier.[1,4] $E_{0,0}$ denotes the energy of the first excited singlet state of the initially excited moiety (SubPc, TPPS or SiPc).

Charge-separated Species	$\Delta G_0 \pm 0.05$ [eV]		
	$E_{0,0}$(SubPc)	$E_{0,0}$(TPPS)	$E_{0,0}$(SiPc)
SubPc$^{•+}$-TPPS$^{•-}$	-0.20	0.03	
TPPS$^{•+}$-SiPc1$^{•-}$		-0.34	-0.22
TPPS$^{•+}$-SiPc2$^{•-}$		-0.40	-0.28
TPPS$^{•+}$-SiPc3$^{•-}$		-0.42	-0.30
SubPc$^{•+}$-SiPc1$^{•-}$	-0.64		-0.29
SubPc$^{•+}$-SiPc2$^{•-}$	-0.70		-0.35
SubPc$^{•+}$-SiPc3$^{•-}$	-0.72		-0.37

References

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