CHEMPHYSCHEM

Supporting Information

Supporting Information for

Singlet-Singlet Annihilation Leading to a CT Intermediate in Chromophore End-Capped Pentaphenylenes

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Steady State Measurements of PI-(pPh)$_1$-PI and PI-(pPh)$_2$-PI in THF.

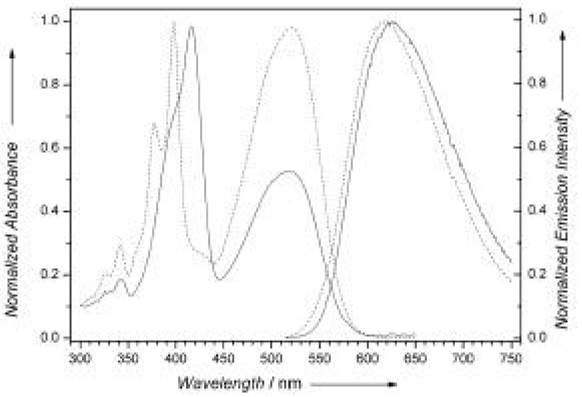

Figure 1 SI. Normalized absorption and emission spectra (excitation at 495 nm) of **PI-(pPh)$_1$-PI** (dashed) and **PI-(pPh)$_2$-PI** (solid) in THF.

Compound	**PI-(pPh)$_1$-PI**	**PI-(pPh)$_2$-PI**
Quantum Yield	0.30	0.28
Absorption maximum (nm)	520	519
Emission maximum (nm)	617	625

Table 1 SI. Fluorescence quantum yields, absorption and emission maxima of the compounds **PI-(pPh)$_1$-PI** and **PI-(pPh)$_2$-PI** in THF.

Excitation of the pPh moiety. After excitation with 395 nm femtosecond pulses the spectral characteristic of the **PI** chromophore are observed (see figure 2 SI) in the transient absorption experiments. A short separation distance between the two units and a large spectral overlap of the **pPh** emission and **PI** absorption (data not shown) provide the conditions for a fast and efficient energy transfer. Based on this experiments we can conclude that by exciting into the **pPh** unit, the excitation energy is rapidly transferred to the **PI** chromophore.

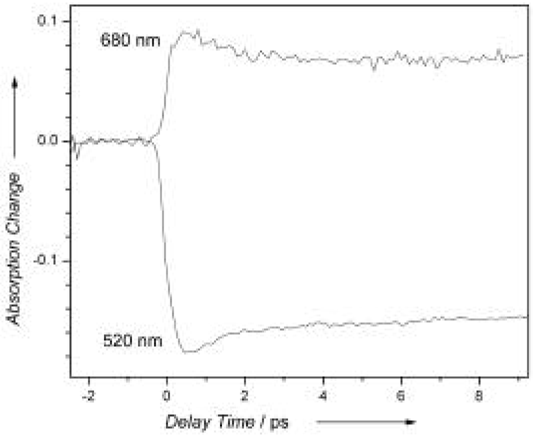

Figure 2 SI. Time-resolved monochromatic transient absorption traces of **PI-(pPh)$_1$** in MCH - 395 nm excitation wavelength, 400 µW excitation power.

Lippert-Mataga plot

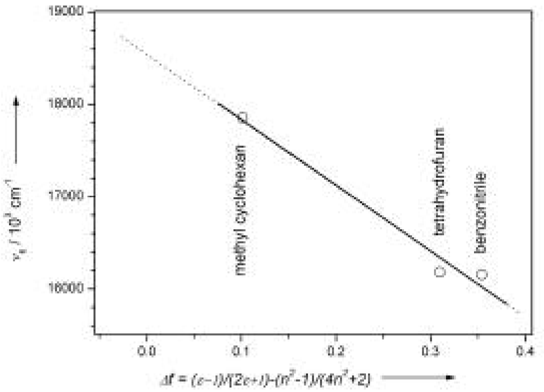

Figure 3 SI. Lippert-Mataga plot for **PI-(pPh)$_1$**.

The Lippert equation:

$$n_{fl} = n_{ab} - \frac{2\Delta f}{hca^3}(m_E - m_G)^2 + const. \qquad \text{Equation [1]}$$

where

$$\Delta f = \frac{e-1}{2e+1} - \frac{n^2-1}{4n^2+2} \qquad \text{Equation [2]}$$

While the slope is:

$$Slope = -\frac{2}{hca^3}(m_E - m_G)^2 \qquad \text{Equation [3]}$$

From the experimental data:

$$Slope_{\,PI\text{-}(pPh)1} = -7140\ cm^{-1}\ \ Þ\ \ (m_E - m_G) = 84\sqrt{\frac{hca^3}{2}}\ D \qquad \text{Equation [4]}$$

In the Lippert-Mataga equation [1], *a* denotes the radius of the solvent cavity, *n* and *e* the refractive index and the dielectric constant of the solvent, $?_{fl}$ and $?_{ab}$ the fluorescence and absorption wavelength (expressed in cm^{-1} units), μ_E and μ_G the dipole moment (expressed in Debye units) in the excited and the ground state, respectively. Based on the calculation performed above we can conclude that for the model **PI-(pPh)$_1$** the single excited state has a larger dipole moment than the ground state.

Quantum-Chemical Calculation

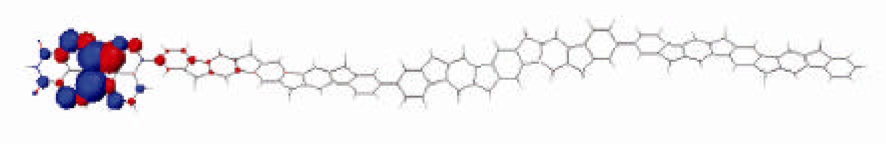

Figure 4 SI. Changes in atomic charge density when going from the ground-state S_0 to the lowest singlet excited-state S_1, as computed at the INDO/SCI (ZDO) level for **PI-(pPh)$_3$** for s =1.5 (on the basis of the AM1/CI gas-phase excited-state geometries).

The calculated displacement of the transition dipole moment amounts to about 0.3 nm for a s value corresponding to the dielectric constant of MCH. As a result the dipole-dipole separation is reduced to 4.8 nm.