Supplementary Information

Role of the Hydrogen-Bond in Porphyrin

J-Aggregates

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Synthesis of 5,15-di[p-(ω-methoxy-polyethylenoxy) phenyl]-10,20-di[p-hydroxyphenyl] porphyrin (P-trans-OH)

5,15-di[p-(ω-methoxypolyethylenoxy)phenyl]-10,20-di[p-hydroxyphenyl]porphyrin (P-trans-OH) having an average molecular mass of about 2100 Da with a narrow polydispersity (M_w/M_n=1.01), was prepared by reaction between tetrakis(phydroxyphenyl)porphyrin (obtained from pyrrole and p-acetoxybenzaldheyde in boiling propionic acid[1]) and chlorinated poly(ethyleneglycol)methyl ether having an average molecular mass of about 750 Da (formed by reaction of poly(ethyleneglycol) methyl ether with thionyl chloride in tetrahydrofurane).[2] The reaction product, dissolved in $CHCl_3$, was fractionated by chromatographic column, using silica gel as a stationary phase and a solution of $CHCl_3/C_2H_5OH/N(C_2H_5)_3$ (96,5/2,0/1,5) as eluant. As indicated by MALDI-TOF (Figure 1)

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and ^{1}H-NMR analyses, the third colored compound eluted from the column was P-trans-OH.

^{1}H-NMR of P-Trans-OH (500MHz, CD_2Cl_2, 27°C), see Figure 2 for assignment: unresolved dou-
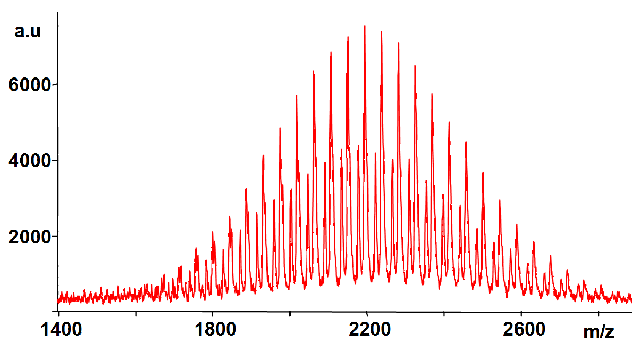

Figure 1: MALDI-TOF mass spectrum of P-trans-OH, consisting of two families of peaks due to species cationized by H^+ (m/z 1719 + n44) and Na^+ (m/z 1741+ n44).

blet at 8.87 ppm (4 H, C-H, pyrrolyc protons 2, 8, 12, 18); unresolved doublet at 8.70 ppm (4 H, C-H, pyrrolyc protons 3, 7, 13, 17); doublet at 8.01 ppm (4 H, C-H, phenyl protons a'); broad peak at 7.80 ppm (4 H, C-H, phenyl protons a); doublet at 7.26 (4 H, C-H, phenyl protons b'); broad peak at 6.96 ppm (4 H, C-H, phenyl protons b); broad peak at 4.12 ppm (4 H, C-H methylene protons c); broad peak at 3.89 ppm (4 H, C-H, methylene protons d); broad signals, range 3.75-3.55 ppm (128 H, C-H methylene protons of PEG); singlet at 3.46 ppm (6 H, C-H, methyl, ω); singlet at -2.859 ppm (2H, N-H pyrrole protons 21, 22).
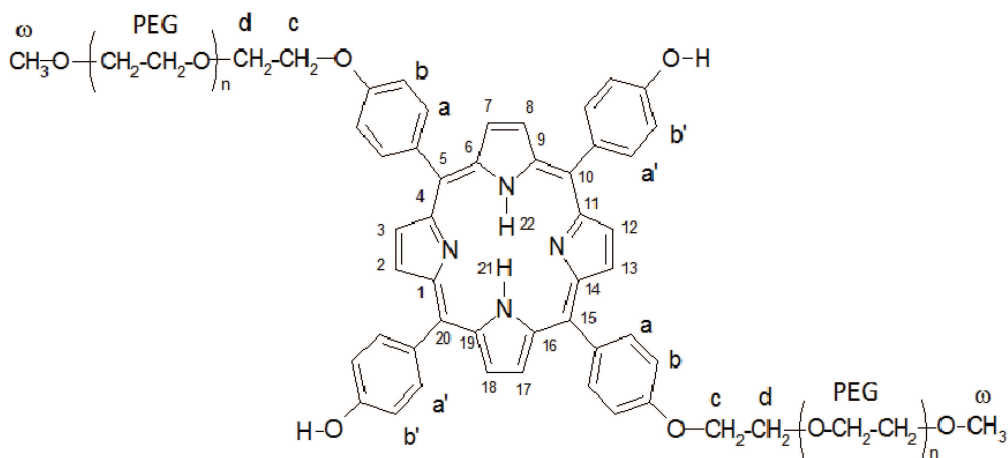

Figure 2: Structure and NMR assignments of P-Trans-OH.

Synthesis of 5,15-di[p-(ω-methoxy-polyethylenoxy) phenyl]-10,20-di[p-(ethyleneoxy)phenyl] porphyrin (P-trans-Et)

5,15-di[p(ω-methoxy-polyethylenoxy)phenyl]-10,20-di[p-(ethylenoxy)phenyl]porphyrin (P-trans-Et), having ethylenoxy groups instead of hydroxyl ones, was prepared by reaction between 5,15-di[p(ω-methoxy-polyethylenoxy)phenyl]-10,20-di[p-hydroxyphenyl]porphyrin and bromoethane. Briefly, 5,15-di[p(ω-methoxy-polyethylenoxy)phenyl]-10,20-di[p-hydroxyphenyl]porphyrin (15 mg,
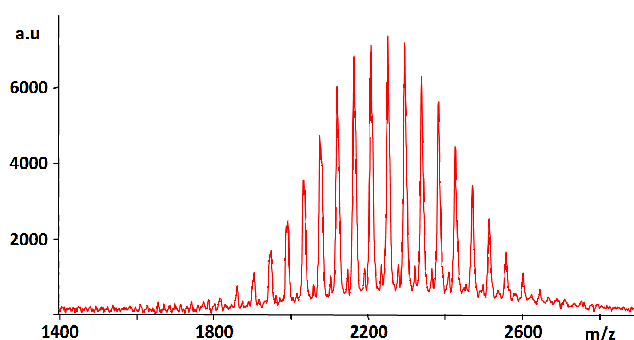

Figure 3: MALDI-TOF mass spectrum of P-trans-Et, consisting of two families of peaks due to species cationized by Na^+ (m/z 1797+ n44) and K^+ (m/z 1813+ n44).

0.00714 mmol), bromoethane (1.5 ml, 0.02 mol) and K_2CO_3 (140 mg, 0.001 mol) were placed in 2 ml of acetone at reflux for 4 hours.

The reaction product was rotoevaporated to dryness. The residue, dissolved in CH_2Cl_2 and filtered to eliminate the formed inorganic salts, was then fractionated by column chromatography by using silica gel as a stationary phase and a solution of $CHCl_3/C_2H_5OH$ (97/3) as an eluent (yield almost quantitative). The MALDI-TOF of the reaction product is shown in Figure 3.

Extinction spectra deconvolution bands

The deconvolution of the extinction spectra was performed by using Gaussian profiles, taking into account the inhomogeneous broadening due to the disorder. The presence of the monomer band did not allow for assessing the expected asymmetry of the P-trans-OH J-band (Gaussian shape at the red-edge and Lorentzian shape at the blu-edge) caused by energy static disorder.

The dotted Gaussian band for both the derivatives was added to improve the fit result.
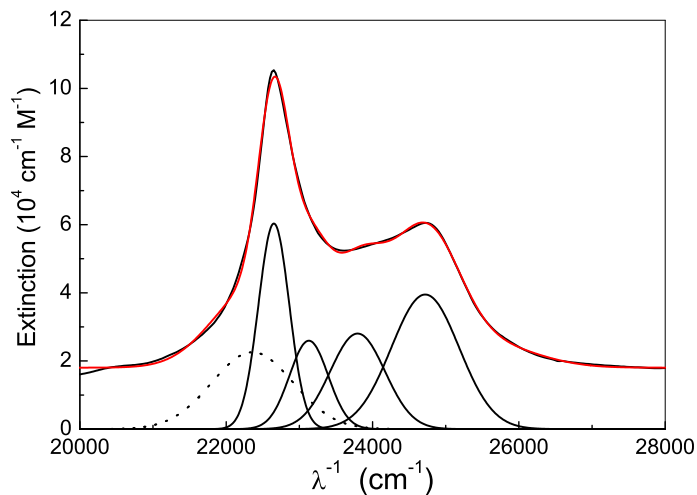

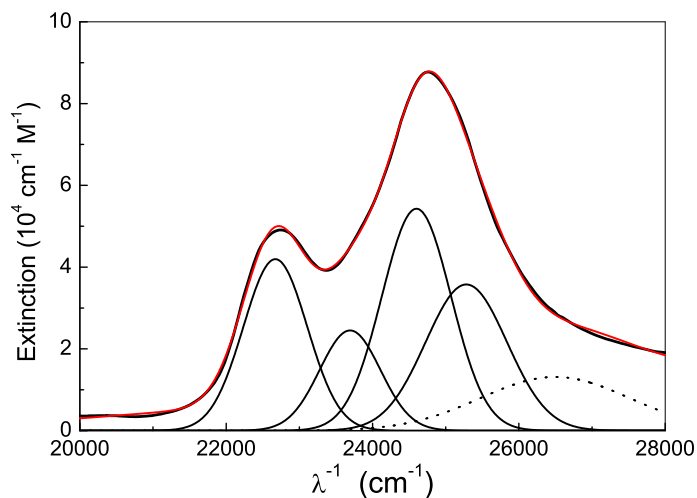Figure 4: Extinction spectrum of P-trans-OH in water with deconvolution bands.

Figure 5: Extinction spectrum of P-trans-Et in water with deconvolution bands.

Steady-state and time-resolved fluorescence anisotropy

A rather simple relation exists between the steady-state fluorescence anisotropy r_S and the time-resolved one r(t):

$$r_S = \frac{\int_0^\infty r(t)I(t)dt}{\int_0^\infty I(t)dt} \tag{1}$$

where $\int_0^\infty I(t)dt = I_S$ is the steady-state fluorescence intensity. If time-resolved fluorescence anisotropy is represented by a single exponential decay, $r(t) = r_0 exp\left(-t/\tau_R\right)$, and time-resolved fluorescence intensity by a bi-exponential one, $I(t) = A_1 exp\left(-t/\tau_1\right) + A_2 exp\left(-t/\tau_2\right)$, steady-state fluorescence anisotropy can be written as:

$$r_S = \frac{r_0 \tau_R}{\tau_1 A_1 + \tau_2 A_2}\left[\frac{\tau_1 A_1}{\tau_1 + \tau_R} + \frac{\tau_2 A_2}{\tau_2 + \tau_R}\right] \qquad (2)$$

This relation was used to estimate τ_R of P-trans-OH from the other measured quantities.

References

(1) Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 1625–1632.

(2) Mineo, P.; Vitalini, D.; Scamporrino, E. *Macromol. Rapid Commun.* **2002**, *23*, 681–687.