Supporting Information

Physicochemical characterization of octakis(alkyloxy)-substituted Zn(II)-phthalocyanines noncovalently incorporated into an organogel and their remarkable morphological effect on the nanoscale-fibers

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Reactions requiring anhydrous conditions were carried out under argon atmosphere. Starting materials and reagents are commercially available (Aldrich, Acros or Fluka) and were used without further purification. Solvents used were dried by standard distillation procedures or were of p.a. grade. The synthesis of Zn(II)-Pcs 1a-c and LMOG 2 are summarized in Scheme S1.

Zn(II)-Pcs 1a-c were synthesized by the cyclotetramerization of the corresponding phthalonitrile precursors 5a-c and zinc as metal ion template. The phthalonitriles were prepared by the 3-steps standard procedure: (1) alkylation of catechol (Williamson etherification reaction) to yield 1,2-dialkoxybenzenes 3a-c, (2) dibromination of the 1,2-dialkoxybenzenes to yield 1,2-dibromo-4,5-dialkoxybenzenes 4a-c, (3) substitution of the bromine atoms by cyano groups (Rosenmund-Von Braun reaction) to afford substituted phthalonitriles 5a-c. Precursors 3a, 3c, 4a and 5a can also be obtained from commercial suppliers. All compounds displayed spectroscopic data identical to the reported in the literature.

LMOG 2 was synthesized as reported in the literature by condensation reaction between (1R,2R)-trans-1,2-diaminocyclohexane and lauroyl chloride under basic conditions.

Scheme S1. Schematic preparation of (top) Zn(II)-Pcs 1a-c [Q-band absorption maxima in toluene], and (bottom) LMOG 2.

2. Gelation Experiments and Determination of $T_{gel}$.

A weighted amount of 2+1 and the appropriate solvent (2 mL) were placed in a screw-capped glass vial (3 cm length and 1 cm diameter) and heated with a heat-gun until the solid was completely dissolved (isotropic solution). The resulting solution was cooled down to room temperature and left for 1 h, after which time the state of the solution was monitored visually by
turning the test vial upside-down. The material was classified as “gel” if it did not exhibit gravitational flow.

Gel-to-sol phase transition temperatures ($T_{gel}$) were determined by the “inverse flow method”.$^4$ A sealed vial containing the gel was immersed upside-down in a thermostated oil bath. The temperature of the batch was raised at a rate of 2 °C min$^{-1}$. $T_{gel}$ was defined herein as the temperature at which the gel was broken. The experimental error of $T_{gel}$ in at least two independent measurements was ± 1 °C.

3. Control Experiments.

The inclusion of Zn(II)-Pcs 6 lacking the long alkoxy chains (Fig. S1) in the organogels made with LMOG 2 (3 wt.-%) in a ratio 2:Zn(II)-Pc = 10:1, resulted in evident phase separation and subsequent disruption of the gels was observed after 3 weeks. The use of much lower π-systems such as 1,2-bis(dodecyloxy)benzene 7 lead to the formation of very weak gels comparing with those obtained by inclusion of Zn(II)-Pcs 1 as indicated by rheological measurements ($G' = 5.3–7.8 \times 10^3$ Pa; $G'' = 7.4–9.3 \times 10^3$ Pa).

Fig. S1. Zn(II)-Pcs 6, 1,2-bis(dodecyloxy)benzenes 7, and known LMOGs 8 and 9 used for control experiments.

Equally, very fragile gels were obtained when Zn(II)-Pcs 1 were mixed with LMOG lacking long aliphatic chains such as bis-urea 8$^5$ and sacaride 9.$^6$ The organic gels made with different concentrations of 1 and 8 or 9 were easily disrupted on minor shaking and rheological data were not obtained.

4. Rheological Experiments.

Oscillatory rheology experiments were performed with an AR 2000 rheometer to determine the storage modulus ($G'$, elastic component) and loss modulus ($G''$, viscous component) of the samples. The material is considered a gel if $G' > G''$ (soft solid). Samples were kept at room temperature for 48 h before measurement to ensure consistency in the crosslinking reactions. The data were found to be highly reproducible for independent batches. The elastic and viscous limits are defined by a tan δ value between 0 and $\infty$ respectively. Tan δ values of the photoactive gels were found to be only slightly different than the one for the gel made merely with 2. The following experiments were carried out for each sample, using ca. 2 mL total gel volume:
a) Dynamic Strain Sweep (DSS): plot of $G'$ and $G''$ with strain. The results showed that the organogels were within the linear viscoelastic regime at 1% strain (cross point between $G'$ and $G''$ is indicated below with a red arrow).

b) Dynamic Frequency Sweep (DFS): plot of $G'$ and $G''$ with frequency. The results show that the organogels here are viscoelastic for frequencies ranging from 0.1 to 100 rad/sec.

c) Dynamic Time Sweep (DTS): plot of $G'$ and $G''$ with time keeping the strain and frequency values constant and within the linear viscoelastic regime (strain = 1% strain; frequency = 10 rad/sec).

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It is worth to mention that our thermoset SIN-like system -it flows at elevated temperatures- possesses dual phase continuity, in which both gelation and phase separation are controlled by the kinetics of polymerization and the concentration of the components, as well as the thermodynamics of mixing.

5. FT-IR Spectroscopy.

FT-IR spectra of solid samples were obtained using KBr pellets or high pressure diamond ATR accessory (Bio-Rad) at room temperature over the wavenumber range 4000–1000 cm$^{-1}$. 
Spectra of the gels at different temperatures were obtained on a Bruker Vector 22 spectrophotometer equipped with a variable temperature cell controller (SPECAC) with the samples sandwiched between KBr pellets (4 cm⁻¹ resolution, 16 scans). The results (Fig. S2) indicated that the addition of Zn(II)-Pcs 1 almost does not disarrange the aggregation mode of the gelator molecules, as well as a clear increase in the intensity of the signals going from solution to gel state.

**Fig. S2.** Representative FT-IR of: (A) LMOG 2 in the solid state (KBr), (B) LMOG 2 in the gel state (toluene, 3 wt.% thick film), (C) toluene gel made of 2 (3 wt.%) + 1b (ratio 2:1b = 10:1) at different temperature during the gelation. Spectra (A-C) have been included for comparative purposes.

6. **UV-Vis Spectroscopy.**

UV-Vis spectra at different temperatures were recorded in a 2101Pc UV-Vis scanning spectrophotometer equipped with a temperature controlled cell holder (TCC–260). The gels were prepared in quartz cuvettes of 1 cm optical path and the UV-Vis spectra recorded at temperatures ranging from 20 °C to 80 °C at 10 °C intervals. The absorption spectrum obeys the Beer-Lambert law up to at least 0.1 mM Zn(II)-Pc 1. As a consequence, stock (1 mM) solutions of 1 were routinely prepared in toluene and stored in the dark at 3–4 °C.
Fig. S3. Representative UV-Vis spectra of 1b, toluene gels in the absence and presence of 1b as indicated in Table 1.

Valduga et al.\textsuperscript{7} have reported the preparation of Zn(II)-Pcs associated in a monomeric state with cationic micelles, unilamellar liposomes, and low-density lipoproteins, in which the distribution of Zn(II)-Pc in the hydrophobic phases appears to be controlled by the nature of the lipid environment.

7. Fluorescence Spectroscopy.

Fluorescence studies were carried out with a Perkin-Elmer MPF-4 spectrophotofluorimeter. The samples were thermostated at 293 K and the absorbance was maintained below 0.1 to avoid inner-filter artifacts (Ex Slit = 20 and Em Slit = 20 with medium PMT Voltage). Pc-containing samples were excited at 600 nm wavelength and their fluorescence emission was recorded in the 600–800 nm range. Bandwidths were fixed at 5 nm for excitation and emission.

Steady-state fluorescence quenching measurements of 1c in a toluene solution using methyl viologen (MV\textsuperscript{2+}) as an electron transfer quenching reagent showed a decrease of the fluorescence intensity by addition of MV\textsuperscript{2+}, giving a standard linear Stern-Volmer plot due to intramolecular collisional quenching. The data were analyzed by Stern-Volmer formalism:\textsuperscript{8} \(F_0/F = 1 + K_{SV}[Q]\), which relates the decrease in fluorescence intensity \((F_0/F)\) to quencher concentration \([Q]\); \(K_{SV}\) is the Stern-Volmer quenching constant.

The fluorescence quantum yields (\(\Phi_F\)) (± 10\%) were estimated in reference to a methanolic solution of cresyl violet perchlorate as a standard (\(\Phi_F = 0.54\))\textsuperscript{9} according to the following equation\textsuperscript{10} reported by Williams \textit{et al}:

\[
\Phi_X = \Phi_{ST} \left( \frac{\text{Grad}_X}{\text{Grad}_{ST}} \right) \left( \frac{\eta_X^2}{\eta_{ST}^2} \right)
\]

where the subscripts ST and X denote standard and test respectively, \(\Phi\) the fluorescence quantum yield, \(\text{Grad}\) the gradient from the plot of integrated fluorescence intensity \(vs\) absorbance, and \(\eta\) the refractive index of the solvent.

TEM images were obtained with a Philips CM120 transmission electron microscope operating at an accelerating voltage of 100 kV. The specimens were prepared as follow: 5–10 μL of the polymeric gel suspension was allowed to adsorb for 3–5 minutes onto copper grids (300 mesh) coated with both formvar and silicon monoxide. The samples were finally dried at low pressure (>10⁻⁵ Torr) before taking the electronic pictures. The relatively large size of the polymer pieces made negative staining unnecessary for visualization.

SEM images were taken with a Zeiss Gemini 1530 field emission scanning electron microscope equipped with a digital camera. The aperture size was 25 μm and the accelerating voltage of the scanning electron microscope was 5.80 kV. Samples of the xerogels were prepared by the freeze-drying (FD) method from their gel phases.¹¹

Fig. S5. Additional SEM images: (left) toluene gel made of 2 (3 wt.-%) + 1b (molar ratio 2:1b = 10:1) showing the coexistence of nanobrushes and fibrillar sheets, (center) detail of a single nanobrush, (right) toluene gel made of 2 (4 wt.-%) + 1c (molar ratio 2:1b = 2:1).
Fig. S6. Images of the toluene gel made of 2 (3 wt.-%) + 1b (molar ratio 2:1b = 10:1) obtained by polarizing optical microscopy.

9. References.