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

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A series of octakis(alkyloxy)-substituted Zn(II)-phthalocyanines were efficiently incorporated into an organogel made of (1*R*,2*R*)-*trans*-1,2-bis(dodecanoylamino)cyclohexane by means of multiple cooperative non-covalent interactions, and SEM revealed the formation of unique brush-like nanostructures.

Stimuli-responsive organic gels[1] have received increasing attention over the last 10–15 years[2] because of their unique supramolecular architectures and potential applications as functional soft materials.[3] These "intelligent"[4] viscoelastic materials, which define a metastable state between liquid and solid, consist of an organic liquid and a low molecular-mass compound self-assembled by virtue of multiple non-covalent interactions into gel fibers, often of micrometre scale lengths and nanometre scale diameters.[5] The entanglement of such microheterogeneous fibrillar phases engenders complex nanoscale 3D-networks, which immobilizes large volumes of organic liquid into the interstices, typically by surface tension and capillary forces.[6] It has been already pointed out that these large fibrous networks made of low molecular-mass organic gelators (LMOGs) could provide a specific molecular environment for the incorporation of photoactive molecules.[7] In fact, many dyes-based LMOGs have been reported, mostly metalloporphyrins.[8] In spite of the intense research in this field, only a few reports on phthalocyanines (Pcs) incorporated in gel formulations[9] or Pc-based LMOGs have been published.[10]

As part of our extensive research program directed towards the synthesis of symmetrically and unsymmetrically substituted Pcs and their use as functional materials,[11] we became interested in the non-covalent inclusion of Pcs in self-assembled polymeric supramolecular networks to study the reciprocal effects on both the photophysical properties of the metallo-Pcs (MPcs) and the physicochemical properties of the 3D-organogel network. In this regard, one of our major interests lies in improving the morphology of supramolecular phthalocyanine-based systems for applications in the photovoltaic field.[11e] In this paper we report the characterization of new photoactive organogels made by inclusion of mesogenic octakis(alkyloxy)-substituted Zn(II)-Pcs **1** into the fibrillar network created by the self-assembly of (1*R*,2*R*)-*trans*-bis(dodecanoylamino)-cyclohexane (**2**)[12] (Fig. 1). As far as we are aware, this is the first report describing the physicochemical properties of photoactive hybrid organogels formed by the entanglement of Zn(II)-Pcs into a 3D-organic gel network through a subtle balance of non-covalent interactions operating cooperatively.

MPcs [M = Co(II), Ni(II), Cu(II), Zn(II)] substituted with eight alkoxy chains in the peripheral positions (2,3,9,10,16,17,23,24) have been reported to stack one above another into columns that are ordered in a hexagonal 2D-lattice, thus forming hexagonal columnar mesophases ($\mathrm{Col_h}$).[13] It occurred to us that these Zn(II)-Pcs bearing long alkoxy chains could help the stabilization of the macrocycles into an organogel made of long alkyl chain-containing LMOGs by means of hydrophobic interactions between the alkyl chains. Thus, to test this idea we chose the well-known LMOG **2**[12] for two reasons: (1) it possesses the necessary long alkyl chains, and (2) it undergoes a self-assembly process *via* the formation of four hydrogen bonds per LMOG molecule, which would define a marked area of backbone polar groups (amides) being very different to that defined by the aromatic–aromatic interactions between the Pc cores. LMOG **2** can gelate a wide range of organic solvents including hydrocarbons, alcohols, ketones, and aromatic solvents. On the other hand, Zn(II)-Pcs **1** were found to be highly soluble in non-polar solvents and unable to form gels in non-polar, polar aprotic and polar protic solvents.[14]

In preliminary studies we found that when toluene-soluble Zn(II)-Pcs lacking the long alkoxy chains† were mixed with LMOG **2** (3 wt%) in a ratio **2** : Zn(II)-Pc = 10 : 1, an evident phase separation occurred within 1–24 h after the gel formation. In all cases the organogels collapsed after two weeks at 293 K. At higher concentrations of Zn(II)-Pcs the gel formation did not take place. However, when a mixture of **2** (3 wt%) and **1b** (molar ratio **2** : **1b** = 10 : 1) in toluene was heated in a septum-capped test tube until the

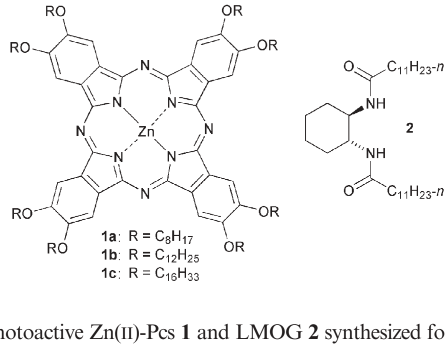

Fig. 1 Photoactive Zn(II)-Pcs **1** and LMOG **2** synthesized for this work.

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solid dissolved and the solution was cooled to 293 K, a robust dark-green gel was formed within 10 min and determined by a 'stable to inversion of the test-tube' criterion. Interestingly we found that this gel displayed good stability over time when stored in dark in sealed glass vials at 293 K as no changes in either appearance or melting temperature were detected after up to 6 months. A molar ratio **2** : **1b** = 10 : 1 was found to be optimum since a higher concentrations of **1** decreased the stability of the gels drastically. At ratios > 10 : 4 gels were not formed.

Table 1 outlines the physicochemical properties of the organogels. The thermal properties were examined by the determination of their gel melting temperatures (T_{gel}), where the T_{gel} is defined as the organogel-destruction temperature and determined by the inverse flow method.† As expected, T_{gel} values of the gels increased with the concentration of the LMOG **2** while keeping the ratio **2** : **1** = 10 : 1. For instance, for **1b** and concentration values (wt%) of **2** = 3, 4, 6, the T_{gel} (°C) values were 49, 63, 72, respectively. A similar trend was found for **1a** and **1c**.

Rheological oscillatory measurements confirmed the gel state of the samples that did not flow upon inversion of the test tube ($G' > G''$), but the gels did exhibit fully reversible gel-to-sol phase transitions upon repeated heating–cooling cycles without affecting the gelation ability. Although the method of placement of the samples between the rheometer plates made difficult the reproducibility of the absolute values of G' and G'' between runs on the same sample, the values of tan δ, the ratio between G'' and G', were reproducible, as they should be if the same type of gel network is formed in each run. The results show a brittle nature for the gels with the storage moduli being an order of magnitude greater than the respective loss moduli. The length of the side chains was also found to have an influence on material rigidity as indicated by G', which was found to be higher for a length of 12 carbon atoms. In general, the blue-green solutions of the Zn(II)-Pcs **1** turned yellow after standing for several days. The reason for this behavior is that MPcs containing diamagnetic metal ions efficiently generate singlet-oxygen and this species has a bleaching action. Very interestingly, such decomposition as confirmed by UV-vis measurements was not observed in the hybrid MPc-gels that were exposed to the light for more than one month. The high stability of these hybrid systems can be attributed to the cooperative strong van der Waals interactions between the alkyl chains and to the π–π stacking interactions between the Pc cores. UV-vis spectra at 293 K of toluene gels containing **2** and **1a–c** (Table 1) were very similar to those of **1a–c** in a toluene solution.† The chain length has hardly any influence on the position of the Q-bands.

Table 1 Physical data for gels made of **2** (3 wt%) in toluene and effect of the incorporation of photoactive building blocks **1** (ratio **2** : **1** = 10 : 1)

Entry	Components	$T_{\mathrm{gel}}{}^{a}$/°C	G' ($\times 10^3$)^b/Pa	G'' ($\times 10^3$)^c/Pa	$\lambda_{\mathrm{Abs}}{}^{d}$/nm
1	**2 + 1a**	43	14.7	7.86	671
2	**2 + 1b**	49	16.8	9.24	671
3	**2 + 1c**	46	15.2	8.36	672

^{a} Gel-sol transition temperature determined by the inverse flow method. ^{b} G' = average storage modulus (±1.1 Pa) ^{c} G'' = average loss modulus (±0.04 Pa) ^{d} Absorption wavelength maximum of the gels containing **1** (Q-band, 293 K).

A quick look at the solvent and metal nature revealed similar results with other non-polar (*e.g.* benzene) or polar (*e.g.* ethyl acetate) solvents working at the minimum gelation concentration of **2**,[12] and other transition metals (*e.g.* Ni, Cu). Appropriate control experiments (see ESI†) demonstrated the positive effect of the long alkyl chains and the extended aromatic system on the gel stability. Thus, in Zn(II)-Pcs bearing alkoxy chains of four or fewer carbon atoms appreciable disruption of the gel was observed after three weeks. The use of much lower π-systems such as 1,2-bis(dodecyloxy)benzene led to the formation of very weak gels.

The FT-IR spectra of the toluene gels mode of **2** + **1** (Table 1) are characterized by broad bands at 3377 and 1639 cm^{-1}, which are assigned to N–H and C=O intermolecular hydrogen bonding stretching vibration, respectively. The absorption bands assignable to amide-I and amide-II were located at 1648 cm^{-1} and 1506 cm^{-1} respectively. In addition, signals at 1609 (arom. C=C), 1276 (Ar–O) and 1093 (Ar–O–C) were routinely observed. Fig. 2 shows a plausible mechanism of the formation of the photoactive stable gels involving the main intermolecular non-covalent interactions in agreement with the experimental data. Zn(II)-Pcs are firmly included into the organogel with the long alkoxy chains placed in the hydrophobic portion of the network made of **2**, keeping the extended aromatic systems far away from the hydrogen bond zone. Induced CD peaks corresponding to the absorption peaks for the Zn(II)-Pcs **1** were not observed in the toluene gels in contrast to the CD spectrum of **2** in the gel state.[12]

The foregoing findings consistently support the view that these new materials define a chemical system driven by two competing antagonistic interactions: self-assembly *vs.* phase separation. Thus, they can be considered as thermosets formed by simultaneous interpenetrating supramolecular networks, in which the supramolecular self-assemblies of both LMOG and MPcs occur simultaneously *via* non-interfering reactions.[15] To gain visual insights into the microscopic morphology of the toluene hybrid gels containing **1**, we took transmission and scanning electron micrographs (TEM and SEM respectively, Fig. 3). As expected, LMOG **2** self-assembles into well-resolved nanoscale fibrous structures with regular fiber diameters of *ca.* 40–120 nm, creating a closely packed 3D-network structure (a). However, when the gels were formed in the presence of Zn(II)-Pc **1b**, a much less uniform material with

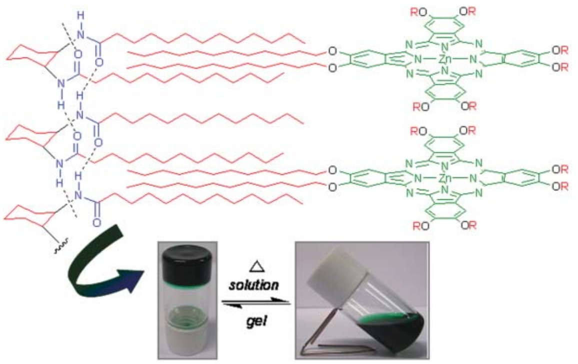

Fig. 2 Top: proposed interactions pattern for formation of stable gels. Zones of main possible interactions are colored: hydrogen bonds (blue), hydrophobic forces (red), aromatic π–π (green) interactions. Bottom: thermally induced phase transition of the dark-green organogel made with **2 + 1b** ([**2**] = 3 wt%, molar ratio **2** : **1b** = 10 : 1).

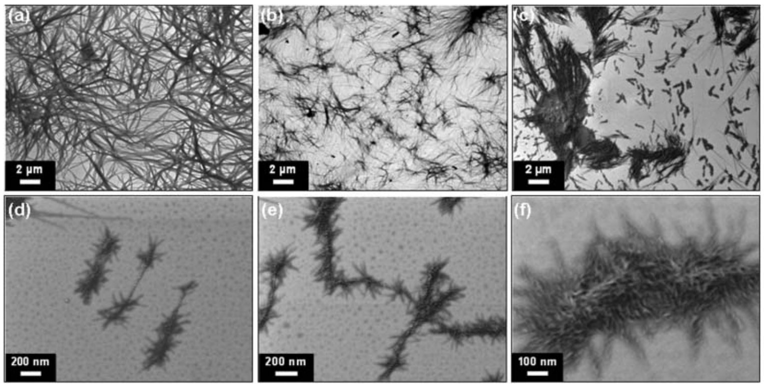

Fig. 3 Electron microscopy photographs: (a) TEM image of the toluene gel made of **2** (3 wt%), (b) TEM image of the toluene gel made of **2** (3 wt%) + **1b** (molar ratio **2** : **1b** = 10 : 1), (c–f) SEM images of the sample (b), (d–f) enlarged views of individual nanobrushes in (c).

junction zones of higher density was observed under TEM without staining (b). Interestingly, the observation of the xerogels under SEM revealed the formation of a new morphological moiety along thin strands with diameters of *ca.* 30 nm. The new induced morphology bears a striking resemblance to laboratory brushes. In most cases it is clearly seen that the individual nanobrushes are formed by a twisted left-handed fibrillar backbone with a diameter of *ca.* 25 nm and surrounding small left-helical fibers emerging from the ends of the fibrillar spine (Fig. 3f). The same type of nanoscale structures could be also found with the other Zn(II)-Pcs (**1a**, **1c**) although in an appreciably lower concentration per surface unit. The (*R*)-chiral centers in **2** induce the anti-clockwise helicity of the strands, in good agreement with previous observations.[12] We believe that the induced morphological variations could be useful as well to control the catalytic and photophysical functions of the MPcs. Generally strong aggregates of MPcs tend to exhibit a blue shift, and due to selection rules these species are non-fluorescent. However, another possible geometry is the clamshell arrangement, whereby the Pc molecules are held over one another but the rings are no longer parallel and emission is not categorically excluded.† In fact, such an orientation effect could occur in the case of the gel made of **2** + **1c** in toluene, which was characterized by a short lifetime (τ = 1.1 ns) and low quantum yield (Φ_f = 0.37).† The fluorescence intensity of the gel remained virtually unchanged while increasing the concentration of an added electron transfer quenching reagent (MV^{2+}) up to 2.5 mM,† suggesting an absolute reduction in collisions between **1c** and MV^{2+} through incorporation into nanofibrous assemblies.[7] No accurate fluorescence data were obtained for gels containing **1a–b**.

In summary, we have reported the physicochemical characterization of new optical active organogels made by simple association of a bis(amide)cyclohexane-based LMOG with a series of octakis(alkyloxy)-substituted Zn(II)-Pcs, which revealed a noteworthy stabilization and morphological effect. We are currently continuing our experiments involving lyotropic MPcs, which will allow us to study the effect of the supramolecular environment created by an LMOG on the liquid crystalline properties of the MPcs, if any, and *vice versa.*[16]

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