### Strength Enhancement of Nanostructured Organogels through Inclusion of Phthalocyanine-Containing Complementary Organogelator Structures and In Situ Cross-Linking by Click Chemistry

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Abstract: Stable photoactive organogels were successfully prepared by a two-step sequence involving: 1) formation of thermoreversible organogels by use of a combination of low-molecularweight organogelators (LMOGs) and Zn<sup>II</sup>-phthalocyanine (Zn<sup>II</sup>-Pc) moieties containing complementary organogelator structures, and 2) strength enhancement of the gels by in situ cross-linking with the aid of Cu<sup>I</sup>-catalysed azide-[3+2] alkyne cycloadditions (CuAACs). The optimum click reaction was carried out between a flexible C6 aliphatic diazide and a suitable dialkyne (molar ratio 1:1) added in a low proportion relative to the organogelator system [LMOG+Zn<sup>II</sup>Pc]. The dialkyne unit was incorporated into a molecule resembling the LMOGs structure in such a way that it could also participate in the self-assembly of [LMOG+Zn<sup>II</sup>Pc]. The significant compatibility of the multicomponent photoactive organogels towards this strengthening through CuAACs allowed their sol-to-gel transition temperatures  $(T_{gel})$  to be enhanced by up to 15°C. The  $T_{gel}$  values estimated by the "inverse flow method" were in good agreement with the values obtained by differential scanning calorimetry (DSC). Rheological measurements confirmed the viscoelastic, rigid, and brittle natures of all Pc-containing gels. Transmission and scanning electron microscopy (TEM, SEM) and atomic force microscopy (AFM) revealed the

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fibrilar nature of the gels and the morphological changes upon cross-linking by CuAAC. Emission of a red luminescence from the dry nanoscale fibrous structure-due to the self-assembly of the Pc-containing compounds in the organogel fibres-was directly observed by confocal laser scanning microscopy (CLSM). The optical properties were studied by UV/Vis and fluorescence spectroscopy. Fluorescence, Fouriertransform infrared (FTIR) and circular dichroism (CD) measurements were also carried out to complete the physicochemical characterization of selected gels. As a proof of concept, two different organogelators (cholesterol- and diamide-based LMOGs) were successfully used to validate the general strategy.

#### Introduction

Although gelation of liquids through the presence of small quantities of a second component has been known for several centuries,<sup>[1]</sup> gels have recently been reborn as a new field of supramolecular chemistry<sup>[2]</sup> because they represent a powerful approach to the development of new materials and devices of nanoscale dimensions with tailored functionality such as high strength or particular electronic or optical properties.

There are two types of gels: chemical gels,<sup>[3]</sup> which are polymer gels based on chemical bonding, and physical gels,<sup>[4]</sup> which are based on physical attractions. Systems based on both types of connections are also known.<sup>[5]</sup> In general, a gel is a viscoelastic solid-like (*soft*) material—constituting an elastic cross-linked network—and a solvent, which is the

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major component. A gel is usually prepared by heating a low-molecular-mass compound in an appropriate solvent (water for hydrogels, some organic solvent for organogels) and cooling the resulting isotropic supersaturated solution to room temperature.<sup>[4]</sup> When the hot solution is cooled, the molecules start to condense, and three situations are then possible: 1) a highly ordered aggregation giving rise to crystals (i.e., crystallization), 2) a random aggregation, resulting in an amorphous precipitate, or 3) an aggregation process intermediate between these two, yielding a gel. The solidlike appearance of a gel is a result of the entrapment and adhesion of the liquid in a solid 3D matrix of large surface area. The formation of the solid matrix is a consequence of cross-linking of the polymeric strands of (macro)molecules through physical or chemical forces.

Organogels based on low-molecular-mass organic gelators (LMOGs) are formed through self-assembled fibrillar networks (SAFINs) through the operation of a combination of weak noncovalent physical interactions such as H-bonding,  $\pi$ - $\pi$  stacking, dipole-dipole or donor-acceptor interactions, metal coordination, solvophobic forces (hydrophobic forces for hydrogels) and van der Waals interactions. This ends up in arrangements of gel fibres typically of micrometer scale lengths and nanometer scale diameters (ca. 10-100 nm).<sup>[6]</sup> Afterwards, the entanglement of such microheterogeneous fibrillar phases engenders complex nanoscale 3D networks,<sup>[7]</sup> which immobilize large volume of organic liquids in their interstices, typically through surface tension and capillary forces.<sup>[8]</sup> This process prevents the flow of solvent under gravity, and the mass appears like a solid. Organogels may hence immobilize up to  $10^5$  liquid molecules per gelator and increase the viscosity of the medium by a factor of  $10^{10}$ , with the potential to respond to a variety of external stimuli.<sup>[9]</sup>

Since the organogel networks involve weak interactions, they can be readily transformed into fluids (sols) by heating and are generally thermoreversible. (Gels based on strong chemical bonds, on the other hand, cannot be redissolved and do not show thermoreversible gel-sol transitions.) Gelators have been classified according to their driving forces for molecular aggregation into two major categories: non-hydrogen-bond-based gelators and hydrogen-bond-based gelators. Cholesterol derivatives<sup>[10]</sup> are typical examples of the former group, whereas aliphatic amide and urea<sup>[10]</sup> derivatives and saccharide-containing gelators<sup>[10]</sup> are the main representatives of the latter. These "intelligent"<sup>[2]</sup> systems, defining a metastable state between liquid and solid, have received increasing attention over the last 10-15 years<sup>[4]</sup> because of their unique supramolecular architectures and potential applications<sup>[11]</sup> as functional soft materials in the fabrication of sensors,<sup>[12]</sup> liquid crystalline substances,<sup>[13]</sup> electrophoretic and electrically conductive matrices,<sup>[14]</sup> biocatalytic vessels,<sup>[15]</sup> vehicles for drug delivery,<sup>[16]</sup> lubricating greases<sup>[17]</sup> and oil spill recovery agents,<sup>[18]</sup> optoelectronic materials,<sup>[19]</sup> templates for cell growth or the growth of sol-gel structures,<sup>[20]</sup> and in many other industrial fields such as cosmetics, oils and foods.<sup>[1]</sup> Supramolecular gel-phase materials based on LMOGs are a prime example of the way in which

bottom-up fabrication can be used for the assembly of nanoscale architectures. In the last decade, the enhancement of the thermostabilities of these gels has became an important task in macromolecular science and crucial for numerous applications.

As a part of our extensive research program directed towards the synthesis, applications and supramolecular aspects of Pcs and their derivatives,<sup>[21]</sup> we became interested in the noncovalent inclusion of Pcs in self-assembled polymeric supramolecular networks for study of the reciprocal effects both on the photophysical properties of the metallophthalocyanines (MPcs) and on the physicochemical properties of the 3D organogel networks. In this regard, large fibrous networks made of LMOGs have been shown to provide specific molecular environments for incorporated photoactive dye molecules, and therefore to improve the functionality of these smart materials.<sup>[22]</sup> Our previous contribution described the physicochemical characterization of mesogenic octakis(alkyloxy)-substituted Zn<sup>II</sup>-phthalocyanines noncovalently incorporated into an organogel and their remarkable morphological effect on the nanoscaled fibres.<sup>[23]</sup> Novel, unique fibrous organic-inorganic hybrid materials-1D aggregates of inorganic materials based on electrostatic and/or hydrogen-bonding interactions-have also been fabricated recently.[24]

The overall objective of this work was the fabrication of stable photoactive organogels by combining LMOGs with Pc-containing complementary organogelator structures.

### **Results and Discussion**

Organogels consisting of combinations of LMOGs and complementary LMOG structures containing  $Zn^{II}$ -Pc moieties:  $5\alpha$ -Cholestan-3 $\beta$ -yl *N*-(2-anthryl)carbamate (**1**, Figure 1) is a renowned LMOG for both alkanes and alkanols at concentrations in the 0.5–2.0 wt % range,<sup>[25]</sup> but it does not gel aromatic solvents such as benzene, styrene or toluene, in which precipitation occurs upon cooling of the isotropic solutions to room temperature. Nevertheless, we found that stable gels were obtained in various aromatic solvents when **1** and the  $Zn^{II}$ -Pc-containing complementary cholestanyl structure **3** were mixed in a molar ratio of 20:1. In order to demonstrate the scope of this method for the preparation of photoactive organogels, the strategy was also applied to the different, well-known LMOG **2**,<sup>[26]</sup> with the Zn<sup>II</sup>-Pc-containing analogues **7–9**.

Synthesis:<sup>[27]</sup> All synthesized compounds here were satisfactorily characterized by UV/Vis, FTIR, MALDI-TOF MS and NMR. The synthesis of **1** was carried out by means of a condensation reaction between  $5\alpha$ -cholestan- $3\beta$ -yl chloroformate and the corresponding 2-aminoanthracene as previously reported.<sup>[25]</sup> The UV/Vis absorption of **1** in CH<sub>2</sub>Cl<sub>2</sub> solution showed the expected bands corresponding to a weak perturbed <sup>1</sup>L<sub>a</sub> transition at about 394 nm and a strong perturbed <sup>1</sup>B<sub>b</sub> transition at about 263 nm.<sup>[25]</sup>

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Figure 1. Organogelators (1, 2) and novel Zn<sup>II</sup>-Pc-containing complementary organogelator structures (3-9) used in this work.

LMOG **2**, first described by Hanabusa and co-workers,<sup>[26]</sup> was easily synthesized by DCC coupling between (1R,2R)-(-)-1,2-diaminocyclohexane and undec-10-ynoic acid.

The photoactive building blocks **3–6** were obtained in one-step fashion and in modest yields through DCC-assisted coupling between the appropriate  $Zn^{II}$ -Pc acid derivatives **12** or **13** and the corresponding 3 $\beta$ -cholest-5-en-3-yl *N*-(2-aminoalkyl)carbamates<sup>[28]</sup> (**10** or **11**; Scheme 1).

The  $Zn^{II}$ -Pc acid derivatives  $12^{[21f,29]}$  and 13 thus emerge as powerful Pc-based scaffolds for DCC-mediated coupling reactions in the construction of novel photoactive materials. Acids 12 and 13 were each synthesized similarly, by two-step

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oxidation of the corresponding alcoholic precursors  $16^{[21a]}$  and 19, respectively (Scheme 2). Compounds 16 and 19 were first converted into the corresponding aldehydes 17<sup>[21a]</sup> and 20 by Parikh–Doering and IBX-mediated oxidations,<sup>[30]</sup> respectively, and were further oxidized to the desired acids with sodium chlorite and sulfamic acid as a chloride scavenger.<sup>[30]</sup> The alcohol precursors 16 and 19 were obtained by statistical crossover condensation of the appropriate phthalonitriles, 15<sup>[21f,29]</sup> and 18 respectively, with 4-tert-butylphthalonitrile (14) in the presence of Zn-(AcO)<sub>2</sub>. The absorption spectra of the investigated Zn<sup>II</sup>-Pccontaining compounds in solution each exhibited a strong band in the 650-680 nm region (Q-band) and a Soret transition (B-band) in the 300-400 nm region.<sup>[27]</sup>

On the other hand, the  $Zn^{II}$ -Pc dimers **7** and **8** were readily obtained by DCC-coupling be-

tween (1R,2R)-(-)-1,2-diaminocyclohexane<sup>[31]</sup> (21) and the appropriate Zn<sup>II</sup>–Pc acids 12 and 13, respectively (Scheme 3). In contrast, Zn<sup>II</sup>–Pc dimer 9 was synthesized by palladium-catalysed Sonogashira<sup>[32]</sup> coupling between dialkyne 22<sup>[33]</sup> and unsymmetrical iodo-substituted Zn<sup>II</sup>–Pc 23<sup>[34]</sup> (Scheme 3).

Organogels made of LMOGs 1 and 2 and the complementary organogelator structures 3–9, containing  $Zn^{II}$ –Pc moieties: Even though many ALS compounds—containing aromatic (A), linking (L) and steroidal groups (S)—have been reported as effective organogelators,<sup>[35]</sup> Zn<sup>II</sup>–Pc 3–6 were



Scheme 1. Synthesis of Zn<sup>II</sup>-Pc-containing complementary organogelator structures 3-6.

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Scheme 2. Synthesis of Zn<sup>II</sup>-Pc acid derivatives 12 and 13.



Scheme 3. Synthesis of Zn<sup>II</sup>–Pc dimers **7–9**.

unable to form organogels after dissolution in hot solvents with subsequent cooling to room temperature. Cooling below room temperature (5°C) did not afford organogels either, despite the facts that 1) these compounds could in principle facilitate the formation of 1D superstructures, because of their propensities to form hydrogen-bonded and  $\pi$ stacked structures,<sup>[36]</sup> and 2) they are structurally similar to Zn<sup>II</sup>-porphyrin-appended cholesterol derivatives, which were able to form transparent gels in several aromatic solvents such as toluene, benzene and *p*-xylene.<sup>[28]</sup> However, when 1 and the Zn<sup>II</sup>-Pc-containing complementary cholestanyl structure 3 were mixed in toluene at an optimum<sup>[27]</sup> molar ratio of 20:1, a stable dark green organogel was obtained within minutes after a heating-cooling cycle (Figure 2). The existence of the gel state was verified by the absence of flow upon turning the test vial upside-down and was further confirmed by rheological experiments (see Table 1, entry 1). Unfortunately, this gel remained homogenous only for 17 days when stored in the dark in sealed glass vials at 293 K, after which precipitation was observed. The use of higher concentrations of 3 caused the collapse of the gel within the first hour, whereas the use of lower concentrations did not afford any stable gel upon cooling. An analogous situation was also observed in other solvents such as acetonitrile, 1,2-dichloroethane, o-, m- or p-xylene, benzene, chlorobenzene, or ethylbenzene.<sup>[27]</sup> Although the use of a mixture of MPcs isomers should affect the gel properties,<sup>[38]</sup> we did not address this issue because of serious difficulties in the separation of the pure isomers.

Appropriate control experiments<sup>[27]</sup> showed that both cholesterol and Pc units were necessary for the observed stabilization phenomenon. Based on previous studies of cholester-



Figure 2. Digital photographs. a) Organogelator 1 in toluene solution at room temperature. b) Effect of the inclusion of the  $Zn^{II}$ -Pc-containing complementary organogelator structure 3 ([1]=12.12 mgmL<sup>-1</sup>, 20.0 mM, [3]=2.52 mgmL<sup>-1</sup>, 2.0 mM) after a heating-cooling cycle allowing the formation of a stable organogel. c) Photoactive organogel made of [1+3] under irradiation at 356 nm. d) Solution obtained by means of the thermally induced phase transition of the gel made from [1+3].

ol-based LMOGs,<sup>[25]</sup> one of the possible configurations for the aggregates are outlined (Figure 3), which combine the described self-assembly pattern of the cholesterol-based LMOG **1** with the integration of the complementary LMOG structures **3–6**, containing Zn<sup>II</sup>–Pc moieties, which would allow stabilizing  $\pi$  interactions between aromatic residues through the gel network.

An interesting, albeit weak, influence of the separation distance between the Pc moiety and the  $3\beta$ -cholest-5-en-3-yl skeleton on gel stability was found when **3** was replaced by its higher analogue **5**. Thus, photoactive organogels made of [1+5] or [1+6] (molar ratio [1]/[5 or 6] = 20:1) were found to remain stable for around three weeks. The mechanical strengths of these gels (Table 1, entries 3 and 4) proved to be similar to those of the gels made of [1+3] or [1+4] (molar ratio [1]/[3 or 4] = 20:1; Table 1, entries 1 and 2). No odd-even effect on the gel stability of the aliphatic segment (n=2, 3) between the two NHCO functions was observed on comparing **3** with **4** or **5** with **6**.

At this point we decided to investigate whether this stabilizing effect was strictly dependent on the organogelator structure. To this end, we chose the LMOG **2**, which self-assembles spontaneously into ordered fibrous nano-aggregates at low concentrations in a variety of organic solvents.<sup>[26]</sup> The

Table 1. Properties of organogels based on 1 or 2 in toluene in sealed glass vials, with the effects of the incorporation of compounds 3–9.<sup>[a]</sup>

Entry	Compound <sup>[b]</sup>	Molar ratio	$MGC^{[c]} [g dm^{-3}]$	$\Delta \tau^{[d]} [d]$	$[d]  \lambda_{Abs}^{[e]} [nm] \qquad T_{gel}^{[f]} [^{\circ}C]$		[℃]	$\Delta H^{[i]} \left[ J  g^{-1}  ight]$	$G'^{[j]}$ [×10 <sup>3</sup> Pa]	$G''^{[k]} [\times 10^3 \text{ Pa}]$
						DSC <sup>[g]</sup>	IFM <sup>[h]</sup>			
1	[1+3]	20:1	14.64	17	672	41	40	0.47	$14.53 \pm 0.05$	$7.61\pm0.04$
2	[1+4]	20:1	14.63	19	672	45	43	0.70	$15.32 \pm 0.09$	$8.27\pm 0.06$
3	[1+5]	20:1	14.78	23	672	48	47	0.44	$16.89 \pm 1.03$	$9.35\pm0.05$
4	[1+6]	20:1	14.81	28	672	51	49	1.03	$16.73 \pm 1.24$	$9.12\pm0.12$
5	[2+8]	22:1	15.28	31	671	57	56	0.91	$17.38 \pm 1.76$	$10.13\pm0.13$
6	[ <b>2</b> <sup>[j]</sup> +9]	22:1	15.46	36	671	49	51	1.07	$17.58 \pm 1.12$	$10.02\pm0.13$

[a] The gels were prepared with 2 mL of solvent. The state of each sample was determined by visual inspection after the sample had been allowed to stand for 2 h at room temperature, although gelation in each case occurred within 10 min. The intensity of the characteristic greenish colour and the transparency of the photoactive organogels depended both on the solvent and on the organogelator system (for an example, see inset of Figure 3). Neither  $\alpha$  values nor relaxation times were obtained. [b] Components of the hybrid organogels. [c] MGC is defined here as the minimum concentration of the organogelator system at which gelation was observed to restrict the flow of the medium. [d] Temporal stability defined as the time after gel formation at which phase separation of the sample was macroscopically observed. The experimental error was 5–12 h. [e] Absorption wavelength maximum of the photoactive organogels. [f] Sol-to-gel transition temperature (average of three independent measurements). [g]  $T_{gel}$  determined by DSC, which corresponds to the maximum of the observed endothermic peak. [h]  $T_{gel}$  determined by IFM in a sealed vial, allowing measurements above the boiling point of the solvents. The estimated error for the  $T_{gel}$  values obtained by DSC and the "inverse flow method" were ±2 and ±1°C, respectively. [i] Enthalpic change. [j] G' = average storage modulus. [k] G'' = average loss modulus.



Figure 3. Plausible configuration for the aggregates made of LMOG structures **1** and Pc-containing complementary LMOG structures **3–6**.

gelation mechanism of 2 differs remarkably from that of 1, because the extended supramolecular structure of 2 is stabilized by two cooperating noncovalent forces: the solvophobic interaction of the long hydrocarbon chains and two hydrogen bonds between adjacent molecules with two equatorial amide NH and amide CO groups aligned antiparallel to each other and perpendicularly to the cyclohexyl ring.<sup>[26]</sup> Although no gel formation was observed upon cooling the isotropic toluene solutions containing only the Pc-containing analogues 7-9, the combination of 2 and analogues 8 or 9 (Table 1, entries 5-6) in an optimum molar ratio of 22:1  $([2] = 12.0 \text{ mg mL}^{-1} = 25.1 \text{ mM}; [8] = 3.28 \text{ mg mL}^{-1} = 1.79 \text{ mM};$  $[9] = 3.46 \text{ mg mL}^{-1} = 1.79 \text{ mM}$ ) resulted in the formation of photoactive organogels. These gels, in contrast to the gels formed from 1 and 3-6, were found to remain stable for 31 and 36 days, respectively (Table 1, entries 5-6), after which time partial crystallization was observed. Nevertheless, both their thermostabilities and their mechanical strengths were found to be slightly lower than those of the gel made only of 2.<sup>[27]</sup> Once again, the preservation of the original organogelator structure, and therefore the major interactions responsible for the gelation process, along with a considerable

separation between the Pc moiety and the hydrogen bonds region, were found to be crucial for the effective integration of the Pc-containing analogues in the nanoscale-fibres of the gels. Indeed, no organogel formation was observed for the combination of **2** and the analogue **7**, lacking the flexible aliphatic chains between the dye and the NHCO functions, which most likely provide a suitable space for the groups to interact and to organize their individual patterns of interaction efficiently.

Along with insignificant contributions from linear dichroism (no changes in the intensities of the signals were observed when rotated by 90°), the gels made of  $2^{[26]}$  exhibited strong circular dichroism (CD) peaks for the amide units, due to the formation of chiral aggregates (molar ellipticity values:  $[\theta]_{201} = +4.20 \times 10^4 \text{ cm}^2 \text{ dmol}^{-1};$  $[\theta]_{213} = -1.73 \times$ 10<sup>5</sup> cm<sup>2</sup> dmol<sup>-1</sup>). However, the CD spectra of the photoactive loose organogels ([2+8] or [2+9]) in acetonitrile at 20°C showed no additional peaks due to the absorption of the Pc units, and the CD signals disappeared when the isotropic state was reached (49-57 °C). No further investigation into the dependence of the CD spectra on cooling rate, aging or thermal history was carried out.<sup>[35]</sup> Thus, as is also the case with the analogous porphyrin system,<sup>[28]</sup> the positions of the chromophores appear to be barely affected by the helical-like self-assembly of 2. In addition, highly chirally-oriented aggregates are very unlikely to exist in the solution state, because the CD pattern is not maintained at the sol-to-gel transition temperatures  $(T_{gel})$ .

*Characterization of photoactive organogels*: All gels were characterized through a combination of rheological experiments and different techniques including FTIR, differential scanning calorimetry (DSC), electron microscopy and UV/ Vis and fluorescence spectroscopy.

*Thermal analysis*: The thermal properties of the gels were examined by DSC and by determination of their  $T_{gel}$  values (Table 1). The  $T_{gel}$  values—defined as the temperatures at which the organogels are destroyed—of samples with similar

thermal histories were first calculated by the "inverse flow method" (IFM).<sup>[27]</sup> As  $T_{gel}$  determined by IFM depends on factors such as aging, cooling rate, thermal history and degree of hysteresis, among others,<sup>[25,38]</sup> the values were further correlated with the endothermic transitions observed by modulated DSC.<sup>[27]</sup> The  $T_{gel}$  values increased in an approximately linear manner as with the concentration of the gelator system [LMOG+Zn<sup>II</sup>Pc], probably due to the formation of more closely packed 3D-networks (Figure 4). From the sol-to-gel phase diagram (Figure 4), the calculated



Figure 4. Onset sol-to-gel transition temperatures determined by IFM for gels made at different concentrations of [1+3] in toluene, [2+9] in CH<sub>3</sub>CN, and [2+9] in toluene. The differences in  $T_{gel}$  for the materials prepared in CH<sub>3</sub>CN and toluene did not exceed 5 °C. Inset: digital photographs of the organogels. Collapse of the gels took place within 1 h at concentrations higher than the maximum values outlined in the graphic.

thermodynamic parameters were found to be consistent with the FTIR spectroscopic measurements and showed a consistent compensation of the entropic change by the enthalpic contribution in the gelation process.<sup>[39]</sup> In addition, all photoactive gels were found to be fully thermoreversible.

*Rheological behaviour*: Oscillatory rheological measurements<sup>[27]</sup> confirmed the viscoelastic, rigid and brittle natures of the gels (Table 1), which did not flow upon inversion of the test tubes but did exhibit fully reversible sol-to-gel phase transitions upon repeated heating–cooling cycles without the gelation ability being affected. The storage moduli (*G'*) were uniformly found to be of greater magnitude than the corresponding loss moduli (*G''*). At its  $T_{gel}$ , the elastic properties of each gel decreased strongly and the soft solid (*G'* > *G''*) was transformed into a viscoelastic liquid (*G''* > *G'*). All the photoactive gels were stable over a wide frequency range (0.1 to 100 rads<sup>-1</sup>), and dynamic strain sweep (DSS) measurements showed that they break at less than 0.5% strain. The material rigidity as indicated by *G'* was found to follow a relative uniform trend with respect to  $T_{gel}$ .

Morphologies: To gain visual insights into the microscopic morphologies of the gels, we took transmission and scanning electron micrographs (TEM, SEM), which proved to be complementary, as well as atomic force micrographs (AFM) (Figure 5).<sup>[27]</sup> Similarly to other ALS-based gelators,<sup>[36]</sup> all the xerogels consist of entangled fibre-like aggregates with numerous junction zones.<sup>[4b]</sup> For the gels made of [2+8] and [2+9], most of the fibres presented relatively uniform diameters of  $180\pm30$  nm (Figure 5A–J) and lengths on the micron scale. The dimensions of the unit fibre were about 30 nm height × 40 nm width (Figure 5L-M). The high aspect ratios of the bundled fibres must arise from a strong anisotropic growth process, indicating that the fibres have well-ordered molecular packing. No significant morphological differences between the single-component (only 2; Figure 5A) and the dual-component gels (Figure 5B-D) were observed for these gels. Hence, the influence of added complementary organogelator structures containing Zn<sup>II</sup>-Pc moieties is not so great as to change the superstructure, at least at the molar ratios indicated earlier. Nevertheless, remarkable changes in the fibre morphologies were observed for specimens prepared at different concentrations and solvents.<sup>[27]</sup> Reductions of only 1 mol% (with respect to the optimum values) in the concentrations of complementary organogelator structures containing Zn<sup>II</sup>-Pc moieties, for instance, generated thinner and less knotted fibrillar aggregates (Figure 5E, G-H), supporting their low stabilities towards mechanical agitation. In addition, the more densely intertwined fibrous structure of the gel made of [2+8] in toluene (Figure 5A) or o-, m-, p-xylene (Figure 5J) in relation to the gel in 1,2-dichloroethane (Figure 5I) seems to reflect the increased thermal stability and intermolecular cohesiveness of the former case with respect to the latter, as supported by  $T_{gel}$  measurements ( $T_{gel}$  (xylene)=55°C;  $T_{gel}$  (1,2-dichloroethane) = 44 °C).<sup>[27]</sup> Some pictures revealed an expected helicity (anticlockwise) of fibres for the hybrid gels made of 2 (Figure 5F).<sup>[26]</sup> In addition, a red luminescence emitted by the dry nanoscale fibrous structure (Figure 5K) could be directly observed by confocal laser scanning microscopy (CLSM), and was probably due to the self-assembly of the Pc-containing compounds in the organogel fibres. Similarly, the gels made of 1 and 3-6 were found to consist of entangled fibres with diameters of  $90 \pm 40$  nm (Figure 5N–P) and lengths in the micron scale.

*FTIR experiments*: In order to assist understanding of the precise roles of the CO, NH and aromatic residues of the organogelator systems in the gelation process, temperaturecontrolled FTIR studies were carried out.<sup>[27]</sup> The intensities of the bands were found to be stronger in the gel samples, indicating that the components interact more efficiently in the gel phase. The results also demonstrated the necessity for participation of hydrogen-bonded amides, van der Waals, and aromatic interactions in different extensions during the gelation phenomenon. Hydrogen bonding in the **2**-based hybrid gels thus uniformly shifted both carbonyl and NH resonances to lower energy relative to the spectra recorded

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Figure 5. A) Negative TEM image of the xerogel made up of  $2 (12 \text{ mgmL}^{-1})$  in toluene. B) Negative TEM image of the xerogel made up of [2+8] (Table 1, entry 5). C) Negative TEM image of the xerogel made up of [2+9] (Table 1, entry 6). D) Negative SEM image of the xerogel made up of [2+9] (Table 1, entry 6). D) Negative SEM image of the xerogel made up of [2+8]. F) Negative TEM image showing the detail of the helicoidal fibres from the xerogel made up of [2+8] (Table 1, entry 5). G) Negative TEM image of the xerogel made up of [2+8] (molar ratio: [2+8]=22:0.99). H) Negative SEM image of the xerogel made up of [2+8] (molar ratio: [2+8]=22:0.99). H) Negative SEM image of the xerogel made up of [2+8] (molar ratio: [2+8]=22:1). J) Negative TEM image of the xerogel made up of [2+8] in *o*-, *m*-, *p*-xylene (molar ratio: [2+8]=22:1). K) Emitted red luminescence captured by CLSM of dry gel fibres made of [2+9] (Table 1, entry 6). L) Atomic force microscopy height image of the gel made of [2+8] (Table 1, entry 5) showing the presence of parallel fibre bundles. M) 3D atomic force microscopy image of the xerogel made up of [2+8] (Table 1, entry 5). N) Negative TEM image of the xerogel made up of [1+3] (Table 1, entry 1). O) Negative TEM image of the xerogel made up of [1+4] (Table 1, entry 2). P) Negative TEM image of the xerogel made up of [1+6] (Table 1, entry 4). The physicochemical properties of the specimens are given in Table 1.

in the solid state: from 1636–1665 to 1628–1637 cm<sup>-1</sup> for amide I bands, from 1542–1558 to 1535–1544 cm<sup>-1</sup> for amide II bands, and from 3296–3334 to 3273–3295 cm<sup>-1</sup> for NH stretching bands. The same tendency was observed when the concentrations of the organogelator systems were increased. In addition to signals routinely observed at about 1270 (Ar– O) and 1090 cm<sup>-1</sup> (Ar-O-C), slight shifts of the aromatic C– H stretching frequencies to lower wavenumber (from ca. 3075–3078 to 3069–3073 cm<sup>-1</sup>) were also observed at higher concentrations, probably due to increasing  $\pi$ – $\pi$  stacking interactions. The gel-to-sol phase transitions occurred with increasing temperature, and the IR bands arising from hydro-

gen amide groups sharply decreased (homogeneous solutions), whereas those from the free groups increased (amide ca. 1660 cm<sup>-1</sup>). Bands in the region of the antisymmetric and symmetric stretching vibrations of C–H (ca. 2845–2935 cm<sup>-1</sup>) were also observed for the gel states, thus indicating significant electrostatic interactions between the alkyl segments. In the case of **1**-based hybrid gels, however, stretching frequencies of N–H bonds (carbamate groups) in solution were found to be at about 3438–3460 cm<sup>-1</sup>, with C= O stretching at about 1725–1735 cm<sup>-1</sup>, which were not very different from those in the gel state. This is in good agreement with the work of Weiss and co-workers,<sup>[25]</sup> in which it

was shown that there is no clear evidence of H-bonding from N-H to other carbamate during the formation of the gel made of **1**. Hydrogen bonding here is thus subordinated to other van der Waals forces (e.g.  $\pi$ - $\pi$  and/or  $\pi$ ···H-N interactions) in the promotion of gelation.

UV/Vis measurements: The cooperative natures of the multiple noncovalent interactions were also supported by single UV/Vis measurements,<sup>[27]</sup> which showed the typical Soret (ca. 349 nm) and Q-bands (ca. 672 nm) for the Zn<sup>II</sup>-Pc-containing gels, and confirmed their higher temporal stabilities (ca. 2-5 weeks) in comparison with the common decomposition of Zn<sup>II</sup>-Pc solutions after exposure to light for several days (colour change from blue-green to yellowish) due to the efficient generation of singlet oxygen. We did not find any noteworthy dependence of the spectral shapes and intensities either on cooling rate or upon aging within the stability period of each gel. In the case of the 1-based hybrid gels in toluene, the UV/Vis spectra at 293 K also each showed a characteristic red-shifted band at about 420 nm together with an excitonic band at about 396 nm, characteristic of aggregated anthryl-containing molecules in a gel state group. The UV/Vis spectra showed almost no influence of chain length on the positions of the Q-bands, which are dependent on the aggregation state and the crystalline phases present. Additional temperature-dependent UV/Vis absorption and fluorescence spectroscopy provided more insights into the photochemical properties of the organic gels. Upon cooling of the isotropic solutions, the spectral shape is slightly broadened, and the Soret and Q bands are slightly blueshifted (<5 nm) relative to those in homogeneous solution. According to the molecular exciton theory, both shifts can point to stacking of Zn<sup>II</sup>-Pc molecules.<sup>[40]</sup> Close to the gelto-sol phase transitions, shoulder-like absorption patterns were also observed around 349 nm in some spectra, probably due to molecules that were not yet taking part in the formation of the 1D structure.

Fluorescence measurements: The steady-state fluorescence emission spectra of toluene gels made of [1+3] or [2+8] systems at 293 K were also closely consistent with those of 3 or 8, respectively, in homogeneous solutions, showing characteristic Q-band emissions at about 672 nm. No additional bands attributable to different aggregates were observed. Similarly to the UV/Vis measurements, emission spectra (position, shape and intensity) of the hybrid gels were found to be independent of the cooling rate (slowly or rapidly cooled gels<sup>[41]</sup>). In general, strong aggregates of MPcs tend to exhibit blue shifts, and selection rules dictate that these species are non-fluorescent. Nevertheless, another possible geometry is the clamshell arrangement, in which the Pc molecules are constrained over one another but the rings are no longer parallel and emission is not categorically excluded. Although we have no conclusive data as yet, such an orientation effect could occur in the cases of the gels made of [1+3] or [2+8] in toluene (Table 1), which were characterized at 293 K by short fluorescence lifetimes ( $\tau = 1.1$  and

2.2 ns, respectively) and low fluorescence quantum yields  $(\Phi_{\rm f}=0.36 \text{ and } 0.43, \text{ respectively})$ . These values were close to those observed for **3** or **8** in solution ( $\tau = 1.3$  and 1.5 ns, respectively).<sup>[27]</sup> Interestingly, we also found that the fluorescence intensities of photoactive Pc-based references [for example, (tBu)<sub>4</sub>ZnPc, (tBu)<sub>3</sub>ZnPcI, (tBu)<sub>3</sub>Pc-acetylene] in toluene solution or embedded in gels made of 1 or 2 (at the same molar concentrations as those used for making the hybrid gels) decreased on addition of methyl viologen (MV<sup>2+</sup>) as electron transfer quenching reagent, and linear Stern-Volmer plots due to intermolecular collisional quenching were obtained.<sup>[27]</sup> In contrast, the fluorescence intensities of toluene gels made of [1+3] or [2+8] remained virtually intact while MV<sup>2+</sup> concentration was increased up to 1.5 mm.<sup>[27]</sup> In agreement with previous studies in our group,<sup>[23]</sup> this difference in fluorescence quenching behaviour suggests the absolute suppression of collision between Zn<sup>II</sup>-Pc moiety and MV<sup>2+</sup> when incorporated into fibrous assemblies.

Strengthening of photoactive multicomponent organogels through in situ cross-linking with the aid of Cu<sup>I</sup>-catalysed azide-alkyne [3+2] cycloadditions (CuAACs): The relatively low thermal and temporal stabilities of the prepared Pcbased photoactive organogels could jeopardize the potential applications of such materials. For this reason, we were interested in investigating strengthening of such materials without loss of their main physicochemical properties. Several examples of in situ enhancement of organogel thermostability have been described; they include post-polymerization of gel fibres made up of polymerizable LMOGs,<sup>[42]</sup> the use of host-guest interactions,<sup>[43]</sup> the addition of polymers<sup>[44]</sup> and the employment of metal ion coordination.<sup>[45]</sup> In addition, CuAAC<sup>[46]</sup> has recently been used to modify the properties of organic gels while retaining their overall structures and thermoreversibilities.<sup>[33,47]</sup> CuAAC has emerged as the best example of click chemistry,<sup>[48]</sup> characterized by extraordinary reliability and functional group tolerance.<sup>[10]</sup> The above organic gels were thus prepared in the presence of tiny amounts of mixtures consisting of the suitable complementary diacetylenes 24 and 25 (5 mol % with respect to 1 and 2, respectively, in the hybrid gels) and a linear diazide such as 26 or 27 (Figure 6) in a diacetylene/diazide molar ratio of 1:1. In view of the objectives described above, the CuAAC here would represent a much more challenging process than that in previous studies,<sup>[34,49]</sup> since the cycloaddition reaction would have to occur in an already multicomponent preformed organic gel (e.g., [1+3] or [2+8]) in which the appropriate "clickable" acetylene monomer (24 or 25) should be at least partially associated with the gel fibres by virtue of multiple noncovalent interactions.

*Synthesis*: Enantiomerically pure dialkyne **25** was prepared by DCC coupling of undec-10-ynoic acid and (1R,2R)-1,2-di-aminocyclohexane.<sup>[34]</sup> Diazide **26** was prepared by nucleo-philic substitution of the appropriate dichloride,<sup>[47]</sup> giving spectroscopic data identical with those reported in the liter-



Figure 6. Cross-linkers **24–27** used to amplify the thermostabilities of the photoactive organogels through CuAAC reactions. Control experiments and additional trials with an expanded collection of polyvalent azides are described in the Supporting Information.<sup>[43]</sup>

ature. Dialkyne **24** was synthesized by DCC coupling between 3,5-bis(prop-2-ynyloxy)benzoic acid (**28**)<sup>[50]</sup> and 3βcholest-5-en-3-yl *N*-(2-aminoethyl)carbamate (**10**, n=2;<sup>[28]</sup> Scheme 4).



Scheme 4. Synthesis of diacetylene-containing complementary organogelator structure 24.

Cross-linking of preformed organogels through CuAAC: In order to test the compatibilities of the CuAACs with the entangled supramolecular gel networks, we chose the hybrid LMOG systems [1+3] and [2+8] as models. The nanoscaledfibres were prepared in the presence of low concentrations of the alkyne-containing "clickable" compounds 24 or 25, together with the diazides 26 or 27 (Figure 6). CH<sub>3</sub>CN/2,6lutidine (1:0.01, v/v, 0.1 M in diacetylene) was used as a solvent system. With a cautious level of click connectivity, the multicomponent system was subsequently subjected to CuAAC, permitting the strengthening of the photoactive organogels while preserving their photochemical properties. The use of an optimized gelator system/diacetylene/diazide molar ratio of 20:1:1 for [1+3]/24/26, [1+3]/24/27, [2+8]/25/ 26 and [2+8]/25/27 afforded the strongest materials. The use of larger amounts of cross-linkers ended either in partially gelled materials or in macroscopically phase-separated materials. Cu<sup>I</sup> catalyst was introduced by layering a stock solution of CuI in CH<sub>3</sub>CN (1.5 M) on top of the pre-set organogel,<sup>[50]</sup> and allowing this to diffuse into the material for 10 days to complete the reaction, as indicated by preliminary GC-MS experiments. The resulting materials were then broken up by vigorous stirring and exposed to oxygen for 3 h to ensure quenching of the click reaction by oxidation of

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the catalyst. A further heating– cooling cycle allowed the gel state to be restored for physical characterization.

NMR spectroscopy confirmed the presence of triazole moieties in the cross-linked gels, whereas FTIR spectroscopy showed that the cross-linking reaction had consumed most of the azide groups.<sup>[27]</sup> When no copper catalyst was employed, the azide peak remained unchanged, and when

an approximately 2:1 ratio of azide to alkyne was used, the IR spectrum still displayed an azide resonance, which could potentially be functionalized after cross-linking, providing another means of tailoring the properties of these materials.

*Characterization of crosslinked photoactive organogels*: The resulting cross-linked photoactive organogels were characterized similarly to their precursor gels.

*Thermal and mechanical analysis*: Interestingly, all crosslinked organogels displayed thermoreversibility, together with better stability over time (>3 months) than their precur-

sors under identical storage conditions. The enhanced stabilities of the gels after CuAAC were simultaneously accompanied by enhancements both of thermoresistance and the mechanical strength, as demonstrated by  $T_{gel}$  determination and oscillatory shear measurements (Table 2). The  $T_{gel}$ values were thus enhanced by up to 15°C after CuAAC, whereas the storage moduli (G') were uniformly found to be one order of magnitude greater than those of the precursor gels and their viscoelastic natures were retained (G'' > G'). In general, relatively uniform trends between  $T_{gel}$  and material rigidity (G') were observed upon cross-linking. Stressstrain curves consistently showed the transformation of hard, brittle materials (high elastic modulus, small elongation) into soft, tough materials (low elastic modulus, large elongation) as temperature increased. Appropriate control experiments<sup>[27]</sup> demonstrated the successful modification of the photoactive organogels only when the appropriate catalyst and clickable monomers were used.

*Morphologies*: TEM pictures revealed significant morphological differences in the stabilized xerogels (Figure 7B–L) in relation to the non-cross-linked materials (Figure 7A). Patches of agglomerated fibres with non-uniform diameters (20–180 nm) and lengths in the micron scale were consistently found after CuAAC (Figure 7B–E). The denser and

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Table 2. Physical data for organogels after CuAAC cross-linking under  $N_2^{.\left[a\right]}$ 

Entry	Components	Molar ratio	$\Delta \tau^{[b]} [d]$	$\lambda_{Abs}^{[c]}[nm]$	$T_{\rm gel}{}^{\rm [d]}[{}^{\rm o}{\rm C}]$	$G^{\prime \left[ \mathrm{e}  ight]} \left[   imes 10^4  \mathrm{Pa}  ight]$	$G''^{\rm [f]}  [ \times  10^4  { m Pa}]$
1	[1+3+24+26]	18.1:1.8:1:1	94	673	56	$30.27 \pm 1.32$	$9.23\pm0.28$
2	[1+3+24+27]	18.1:1.8:1:1	103	673	59	$33.02 \pm 2.03$	$11.16 \pm 1.14$
3	[2+8+25+26]	18.7:1.3:1:1	121	677	71	$37.51 \pm 1.78$	$12.31 \pm 1.03$
4	[2+8+25+27]	18.7:1.3:1:1	118	677	73	$39.44 \pm 1.52$	$12.31 \pm 1.03$

[a] Each reaction was performed in degassed CH<sub>3</sub>CN (2.0 mL) and 2,6-lutidine (0.02 mL). Note: the  $T_{gel}$  values of the materials prepared in CH<sub>3</sub>CN did not overly differ from those in toluene (±5°C), and the former were chosen for testing the cross-linking because CH<sub>3</sub>CN in combination with 2,6-lutidine has been found to be a good solvent system for CuAAC. [b] Temporal stability defined as the time after gel formation at which phase separation of the sample is macroscopically observed. The experimental error was 5–12 h. [c] Absorption wavelength maxima of the photoactive modified organogels. [d] Sol-to-gel transition temperature determined by IFM in sealed vials, allowing measurements above the boiling point of the solvents. [e] G' = average storage modulus. [f] G'' = average loss modulus.

intertwined fibrous morphologies of the xerogels after crosslinking, in relation to the straight-fibre networks of noncross-linked gels, could be related to the increased thermal stability and intermolecular cohesiveness after CuAAC, as determined by  $T_{\rm gel}$  measurements (Table 2). Less homogeneous networks characterized by shorter fibres were observed for phase-separated materials obtained at higher concentrations of the clickable monomers (Figure 7F–G). Very interestingly, the observation of the cross-linked xerogels under SEM (Figure 7H–L) revealed the occasional presence of two new morphological moieties forming sheet-like structures, combined with thick entangled strands of about 5  $\mu$ m pressive architectures resembles the tentacles of the sea anemone (Figure 7I–J), whereas the other is made up of agglomerates of tubular structures of about 1  $\mu$ m in length, 0.5  $\mu$ m in width and 0.4  $\mu$ m in diameter, greatly resembling a bunch of silk cocoons (Figure 7K, L). As these aggregates were not observed in all crosslinked samples, we presume that the less stable fibrils of

in diameter. One of these im-

the cross-linked gels undergo some morphological changes during the freeze-drying treatment and aggregate into the tentacle- and cocoon-like forms.

*FTIR experiments*: FTIR spectroscopy showed comparable evidence for the participation of hydrogen-bonded amides and van der Waals and aromatic interactions in the gelled states of both non-cross-linked and cross-linked materials, indicating that the greater part of the original noncovalent pattern is still retained upon stabilization.



Figure 7. A) Negative TEM image of the xerogel made up of [2+8] (molar ratio 22:1) in CH<sub>3</sub>CN/2,6-lutidine 1:0.01, 0.1 M). B)–E): Negative TEM images of the cross-linked xerogels (Table 2, entries 1, 2, 3, 4, respectively). F) and G): Negative TEM images of the xerogels made of [1+3+24+26] (molar ratio 18.1:1.8:3:3) and [2+8+25+27] (molar ratio 18.7:1.3:3:3), respectively. H) Negative SEM image of the cross-linked xerogel (Table 2, entry 3) showing the presence of new structural moieties. I)–L) Zoom-in on H), showing the sea anemone-like structures (I–J) and the silk cocoon-like structures (K–L).

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*UV/Vis and fluorescence measurements*: Slight bathochromic shifts in the positions both of the Soret bands and of the Q-bands of the Pc moieties were observed in the UV/Vis spectra after CuAAC. This phenomenon could be explained by the cross-linking process, which can ultimately promote the agglomeration of the Pcs moieties. The fluorescence intensities of cross-linked gels remained virtually unchanged while the quenching (MV<sup>2+</sup>) concentrations were increased up to 1.5 mm. These foregoing results thus show only a small influence of the cross-linking process on the optical properties of the gels. First-round experiments essentially showed no improvement in fluorescence lifetimes.

Figure 8 provides an overview of the procedure developed for the preparation of standard functional organogels and their further stabilization, if necessary, by in situ cross-linking through CuAAC. System **4** represents a standard organogel formed upon cooling of the isotropic solution of the appropriate LMOG (system **2**). If further strength enhancement of the material is required, a well-defined concentration of a suitable diacetylene-containing complementary LMOG structure, linear diazide and Cu<sup>I</sup> catalyst can be swollen into the organogel network or premixed with the LMOG prior to gel formation (system **3**) in the heatingcooling process. The subsequent cross-linking reaction should enhance the thermostability of the organogel while preserving its thermoreversibility (system **5**).<sup>[33]</sup> On the other hand, the organogel **4** may be prepared in the presence of the appropriate Pc-containing complementary organogelator structures to afford a multicomponent photoactive viscoelastic material (system **6**). Also in this case, suitably designed clickable monomers (diacetylene-containing complementary LMOG structure and linear diazide) and the Cu<sup>I</sup> catalyst can be incorporated into the gel network (system **7**) in order to achieve further cross-linking to generate a new photoactive organogel with enhanced thermostability and mechanical properties.

Interestingly, all attempts to incorporate the [1,3,5]-triazole-based polymeric structure (system 9), made by CuAAC of the appropriate monomers in solution, into the photoactive organogels failed to form stable gels, due to evident and fast phase-separation processes. The explanation was found to lie in the structural differences between the preformed



Figure 8. Schematic illustration of the synthesis of standard organogels and Pc-based photoactive organogels, and their further stabilization by in situ cross-linking achieved through CuAAC.

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polymer 9 and the cross-linked material (system 10) obtained by in situ CuAAC of the clickable monomers, which could be extracted by evaporation of the solvent system under vacuum followed by a washing protocol with the remaining solid material. MALDI-TOF experiments indicated that the system 10 was made up of a mixture of short oligomers whereas the system 9, prepared in CH<sub>3</sub>CN solution, proved to be a polydisperse polymer of much higher MW.<sup>[27,49]</sup> In summary, a photoactive gel could in principle be fabricated by the self-assembly process of a LMOG in the presence of a small amount of a suitable complementary organogelator structure containing a dye (e.g., MPc). The amount of dye can be optimized in order to minimize the negative effect on the thermostability of the organogel, and in some cases to maximize a possible positive effect. Further thermal/mechanical stabilization can be achieved by CuAAC-mediated cross-linking of a suitable complementary diacetylene and a linear diazide previously incorporated into the multicomponent gel network.

#### Conclusion

In summary, photoactive organogels can be prepared through the association of LMOGs with suitably designed Zn<sup>II</sup>–Pc-containing complementary organogelator structures through a subtle balance of noncovalent interactions operating cooperatively. The above findings consistently support the view that these new multicomponent photoactive materials define a unique chemical system driven by two competing and antagonistic interactions: self-assembly versus phase separation. As a whole, this class of hybrid organogels, in which cross-linked materials are generated by swelling the appropriate monomers and activators into preformed supramolecular assembled networks, can be considered to consist of thermoplastic semi-interpenetrating supramolecular polymer networks prepared by a sequential process.<sup>[51]</sup> Therefore, these systems with enhanced mechanical properties due to their peculiar entanglement behave as thermosets at ambient temperatures, but flow at elevated temperatures. The physicochemical characterization of these soft materials shows that maintaining the original molecular network constructed in the gel phase is crucial for the improvement of gel stability by post-modification. Studies directed towards the use of this procedure for the integration of other functional photoactive-based systems into both organo- and hydrogels, as well as the study of electron transfer reactions between these organogels and electron acceptors, are underway in our laboratories.

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