NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Photoresponsive Supramolecular Gels based on Amphiphiles with Azobenzene and Maltose or Polyethyleneglycol polar head

María José Clemente,[a] Rosa MaríaTejedor,[b] Pilar Romero,[a] Juliette Fitremann,[c] and Luis Oriol*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In the context of exploring new materials based on low molecular weight amhiphiles, we prepared a new series of photoresponsive gelators with azobenzene as photosensitive unit, D-maltose or poly(ethylene glycol) (PEG) as polar head, and L-phenylalanine as linker. The gelation properties of the final amphiphiles and the intermediate molecules have been studied in different solvents. Organogels are obtained for all of them, except for compound with PEG_{16} polar head. Gelation in polar solvents, as DMSO, was achieved. The morphology of supramolecular structures was characterized by electronic microscopy. The chiro-optical properties of gels, due to the supramolecular chirality imposed by molecular chirality, were also studied. The modifications under irradiation have been monitored by UV-visible spectroscopy and electronic circular dicroism (ECD). Two of the obtained materials showed a gel-sol transition by irradiation with UV light and further thermal *cis-trans* isomerization to gel state at room temperature.

Introduction

Supramolecular gels based on low molecular weight molecules are sensitive to external stimuli due to the reversibility of the supramolecular interactions that support the gel structure. Compared with reversible gels based on polymers with non-covalent cross-linking, they are expected to be more sensitive, and dynamic. In addition they give rise to a variety of supramolecular aggregates (fibers, helices, tapes, tubes…). The formation, shape and polymorphism of these aggregates may be controlled by application of different stimuli or fields (such as light, temperature, shear, electric or magnetic field). As a consequence, when a photoresponsive group is inserted in the gel structure, the supramolecular assembly can be modulated by light.[1-2] If a photochromic unit is included in the molecular structure of the gelator, the supramolecular arrangement of the gel can be controlled as a consequence of the ability of the photochromic unit to alternate between two different chemical forms with light. Azobenzene hydrophobic groups are used in supramolecular assemblies to trigger reversible environmental changes, due to the reversible *trans-cis* photochemical isomerization experienced by azo-dyes.[3-4] Several examples of *trans*-isomer supramolecular gels giving rise to a photostationary state of *trans-cis* mixtures that provide a sol state have been described,[5-6]. Most of them are organogels, for example based on cholesterol derivatives,[7-14] on lipid,[15] and aminoacids[16-17] derivatives, uree or hydrazine-amide-containing compounds.[18] In water, most often, precipitation, full solubilisation or simple micellisation occur or even the formation of anisotropic fibrillary aggregates which however do not support a macroscopical gel. Thus, introducing the right balance of hydrophilic, hydrophobic parts, and interaction which enables the long-distance stacking to get hydrogels, can be hard to reach. However some examples of azobenzene hydrogels have been described, by appending hydrophilic blocks and blocks prone to develop strong hydrogen bonding, such as peptides,[19-20] or saccharidic blocks[21-22] or PEG.[23]

With the aim of finding new low molecular weight hydrogelators based on carbohydrates, we previously developed a series of hydrogelators based on the following bricks: maltose, cellobiose, lactose as the polar head- and triazole as the linker.[24-25] On the basis of the hydrogels obtained, we further introduced an azobenzene as photochromic group.[21] These structures gave rise to stable gels in water or in a mixture of water and DMSO, however the gel-sol transition under UV-irradiation failed. In this work, gelators based on phenylalanine as the linker have also been developed. Phenylalanine is quite often introduced in gelator structure, since it provides a flexible side aromatic group involved in π-π stacking and amide groups which enable directional hydrogel bonding.[26-27] Azobenzene has been introduced also in this case as a photoresponsive group. We selected both maltose and PEG chain with two different molecular weights as polar heads, with the objective to enable gelation in polar solvents. PEG has been described in a variety of supramolecular assemblies, including low molecular weight gelators,[29-33] to provide hydrophilicity and stealth in biological applications.[34-35] Moreover, it was previously used in our labs to synthesize amphiphilic block copolymers having the ability of self-assembling into different photoresponsive nano-objects in aqueous solutions.[36-37] The influence of the polar head on the supramolecular assembly and the photoresponse of the gels was

explored.

Accordingly, we describe here a series of gelators based on 4-[2-[4-(octadecyloxy)phenyl]diazenyl]benzoic acid (**HOOC-Azo-C_{18}**), on which the following bricks have been appended: phenylalanine, phenylalanine-PEG_8, phenylalanine-PEG_{16} and phenylalanine-maltose, see **Chart 1**. The synthetic strategy for grafting the disaccharide maltose is based on the formation of a maltosylamine, namely by introduction of amine in anomeric position. This strategy enables to keep both glycosidic units in their cyclic forms. The thermal properties and the gelation ability of the five molecules prepared including the precursors **HOOC-Azo-C_{18}** and **Phe-Azo-C_{18}** has been studied and compared with the final amphiphilic compounds **PEG_8-Phe-Azo-C_{18}, and Malt-Phe-Azo-C_{18}**. Chiroptical properties, highlighting the chiral supramolecular organization in the gel state, have been studied by ECD. Gel-sol transition and modification of the supramolecular arrangement by light has been studied by UV-visible and ECD spectroscopy and macroscopic observations.

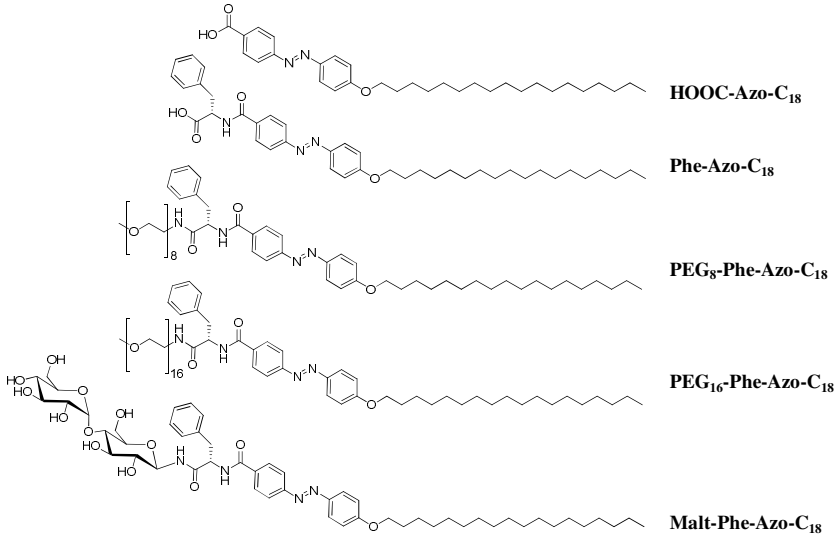


Chart 1 Chemical structure of synthetized materials

Results and discussion

Synthesis of Materials. The synthesis of the amphiphiles was approached according to the synthetic pathway described in **Scheme 1** and **Scheme 2**. The azobenzene carboxylic acid **HOOC-Azo-C_{18}** was prepared by the azo coupling of sodium phenoxide and ethyl *p*-aminobenzoate to obtain compound **1**. The carboxylic aliphatic chain was introduced by means of a Williamson reaction and subsequent hydrolysis of compound **2** gave rise to the desired acid compound **HOOC-Azo-C_{18}**.[38] This acid was used as precursor of **Phe-Azo-C_{18}** which was obtained by previous activation of **HOOC-Azo-C_{18}** with *N*-hydroxysuccinimide to obtain compound **3**, and further reaction with L-phenylalanine. This reaction was made in a mixture of water/THF to enhance the solubility of both compounds. In the subsequent synthetic step **Phe-Azo-C_{18}** was coupled with the corresponding amine-terminated PEG to obtain **PEG_n-Phe-Azo-C_{18}** (n=8 or 16) or with maltosylamine to obtain **Malt-Phe-Azo-C_{18}** (**Scheme 1** and **Scheme 2**, respectively). **PEG_n-Phe-Azo-C_{18}** (n=8 or 16) were synthesized using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), hydroxybenzotriazole and THF as solvent. Commercial PEGs were used for the synthesis of **PEG_8-Phe-Azo-C_{18}** (monodisperse amino-PEG with a molecular mass of 383.48) and for **PEG_{16}-Phe-Azo-C_{18}** (amino-PEG with an average molecular mass of 750 and an average degree of polymerization of 16).

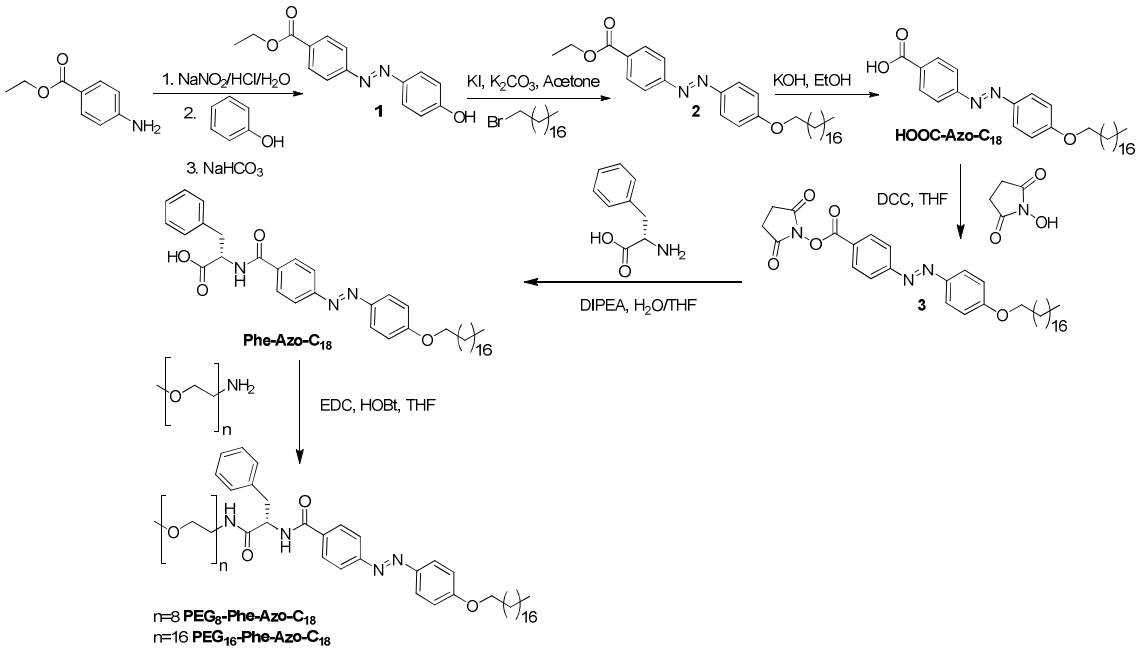
Malt-Phe-Azo-C_{18} was synthesized from peracetylated amino-maltose **5**, previously described.[24] The coupling to the azobenzene moiety of the acetylated maltosylamine was made with a chloride derivative of **Phe-Azo-C_{18}** (compound **6**) in a DMF/THF mixture yielding the peracetylated compound **OAc-Malt-Phe-Azo-C_{18}**. This compound was deprotected using MeONa in a mixture of MeOH and THF to obtain the aimed **Malt-Phe-Azo-C_{18}**. All the compounds were adequately characterized by ^{1}H NMR, ^{13}C NMR, IR and mass spectrometry, see experimental section. MALDI-TOF mass spectrometry experiments of **PEG_8-Phe-Azo-C_{18}** and **PEG_{16}-Phe-Azo-C_{18}** (see **Figure SI1** in Supporting Information) showed that in the case of **PEG_8-Phe-Azo-C_{18}** the sample is monodisperse, however **PEG_{16}-Phe-Azo-C_{18}** displays a pattern of peaks separated about 44 (-[O-CH_2-CH_2]-) due to the dispersity of the starting and commercial amine-ended PEG used in the synthesis.

^{1}H NMR spectra of **PEG_8-Phe-Azo-C_{18}**, **PEG_{16}-Phe-Azo-C_{18}**, **OAc-Malt-Phe-Azo-C_{18}** and **Malt-Phe-Azo-C_{18}** are shown in **Figure SI2** in Supporting Information. Spectra of **PEG_8-Phe-Azo-C_{18}** and **PEG_{16}-Phe-Azo-C_{18}** are in accordance with expected chemical structure. Moreover, **OAc-Malt-Phe-Azo-C_{18}** and **Malt-Phe-Azo-C_{18}** compounds were characterized by additional two-dimensional NMR experiments. The total deprotection of the acetylated groups was confirmed by ^{1}H NMR when spectra of **OAc-Malt-Phe-Azo-C_{18}** and **Malt-Phe-Azo-C_{18}** are compared, **Figure SI2** in the Supporting Information. As example, a two-dimensional TOCSY experiment of **OAc-Malt-Phe-Azo-C_{18}** is shown in **Figure SI3** in the Supporting Information.

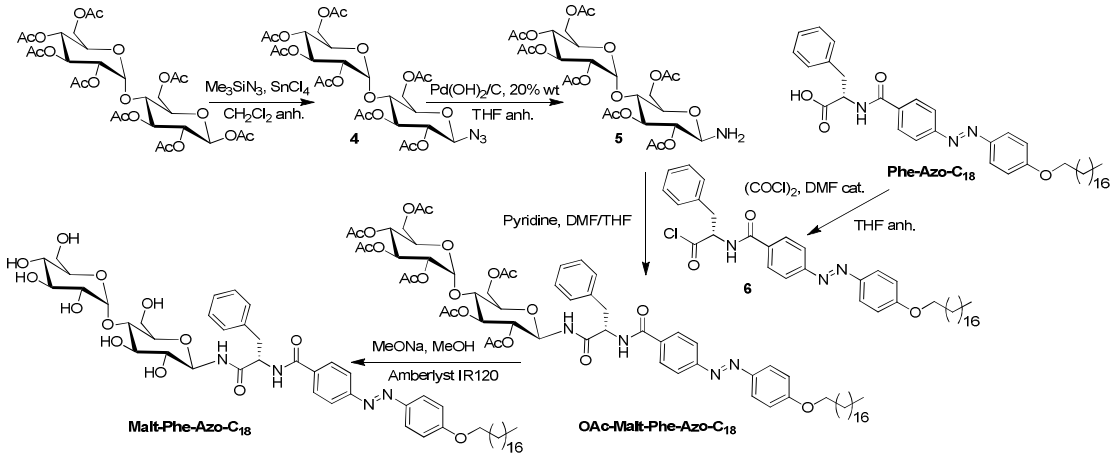
Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE



Scheme 1 Synthesis of **HOOC-Azo-C$_{18}$**, **Phe-Azo-C$_{18}$** and **PEG$_n$-Phe-Azo-C$_{18}$** (n=8 or 16).



Scheme 2 Synthesis of **Malt-Phe-Azo-C$_{18}$**.

Table 1 Thermogravimetric analysis and thermal transitions of the synthesized amphiphiles.

Compound	$T_{5\%\ lost}$, ºC	Tonset, ºC	Thermal transition, ºC [ΔH, kJ/mol]
HOOC-Azo-C_{18}	325	340	Cr 111[11.7] S_1 138.6 [9.7] S_2 146.4 [9.8] S_3 204 [7.7] S_4 237.2 [19.1]
Phe-Azo-C_{18}	250	245	Cr 137 [5.6] Cr' 153 [28.3] I
PEG_8-Phe-Azo-C_{18}	305	325	Cr 87 [1.0] Cr' 97 [2.7] Cr'' 116 [32.6] I
PEG_{16} -Phe -Azo -C_{18}	315	320	Cr 27 [53.4] Cr' 84 [4.2] Cr'' 106 [33.5] I
Malt-Phe-Azo-C_{18}	220	235	Cr 112 [22.8] Cr' 175 Dec

[a] $T_{5\%lost}$, temperature at which 5% of the initial mass is lost; T_{onset}, onset of the thermal decomposition process. Cr, crystalline; S, smectic mesophase; I, isotropic liquid phase.

Table 2 Solubility and gelation properties of synthesized compounds in different solvents.

Solvent	HOOC-Azo-C_{18}	Phe-Azo-C_{18}	PEG_8-Phe-Azo-C_{18}	PEG_{16}-Phe-Azo-C_{18}	Malt-Phe-Azo-C_{18}
Hexane	I	I	I	I	I
Toluene	P	Gel (5)	S	S	I
Dochloromethane	I	Gel (5)	S	S(heat)	I
Chloroform	I	S	S	S	I
THF	P	S(heat)	S	S	Gel (1.3)
1-Dodecanol	Gel (5)	Gel (10)	Gel (5)	I	Gel (0.5)
Acetone	I	P	Gel (8)	S	I
DMF	Gel (2)	S(heat)	S	S	S(heat)
DMSO	Gel (6)	Gel (10)	Gel (5)	S	P
Methanol	I	I	Gel (5)	S	I
Water	I	I	I	I	I

[a] I, insoluble at rt; P, insoluble at rt and soluble on heating; S(heat), soluble at rt after heating; S, soluble at rt; Gel (minimum gel concentration, wt%).

Thermal properties. The thermal properties of the synthesized amphiphilic azocompounds were studied by thermogravimetric analysis (TGA), polarized light microscopy provided with a thermal stage and differential scanning calorimetry (DSC). Weight losses were observed in TGA at temperatures ranging from 200 to 325 °C as it has been summarized in **Table 1**. Acid compound **HOOC-Azo-C_{18}** has a high stability while introduction of L-phenylalanine makes that the temperature at which 5 % of the initial mass is lost decreases from 325°C to 250°C (first decomposition process of that compound). However, linking a PEG moiety produces an increase of the thermal stability. Temperatures for 5 % weight loses for **PEG_8-Phe-Azo-C_{18}** and **PEG_{16}-Phe-Azo-C_{18}** are around 310°C. In the case of **Malt-Phe-Azo-C_{18}** thermal stability is lower than the PEG-analogs and it can be expected from the introduction of a sugar polar head.[39]

In the case of **HOOC-Azo-C_{18}** smectic mesomorphism was observed as was previously reported.[40] However, the derivative **Phe-Azo-C_{18}** is not mesogenic, as a consequence of the phenyl lateral ring that decreases the aspect ratio. The final amphiphiles **PEG_8-Azo-Phe-C_{18}** and **PEG_{16}-Azo-Phe-C_{18}** and the sugar derivative **Malt-Phe-Azo-C_{18}** are crystalline materials. The thermal transitions were characterized by DSC and gathered in **Table 1**. The melting transition of **PEG_8-Azo-Phe-C_{18}** and **PEG_{16}-Azo-Phe-C_{18}** is detected at temperature around 110 °C and both exhibit polymorphic transitions before melting. In the case of the sugar derivative, **Malt-Phe-Azo-C_{18}**, the sample was previously dried and immediately analyzed. When this compound was studied by optical microscopy, the sample becomes brown above 170-175 °C due to decomposition of the sugar units. On a DSC experiment performed until 200°C, decomposition was detected at around 175°C as a decrease of the baseline.

Gelation properties. The solubility and gelation ability of the amphiphiles and the precursors **HOOC-Azo-C_{18}** and **Phe-Azo-C_{18}** were examined in different solvents by placing 5 mg of compound in the corresponding amount of solvent in a septum-capped test tube. If the compound was not soluble at rt, mixtures were first heated and then cooled down to rt. A solution, precipitate or a gel was then observed depending on the solvent. The formation of a gel was registered if the tube was turned upside down and no flow was observed.

All the compounds are not soluble in water even upon heating. However, they are able to form organogels in different solvents (at different minimum concentrations) except **PEG_{16}-Phe-Azo-C_{18}** that exhibit a good solubility in most of tested solvents, except hexane and 1-dodecanol. **HOOC-Azo-C_{18}**, **Phe-Azo-C_{18}**, **PEG_8-Phe-Azo-C_{18}** and **Malt-Phe-Azo-C_{18}** are able to form gels in 1-dodecanol at different concentrations. The lowest minimum gel concentration was reached in 1-dodecanol at 0.5 wt% for **Malt-Tz-Azo-C_{18}** compound. **HOOC-Azo-C_{18}**, **Phe-Azo-C_{18}** and **PEG_8-Phe-Azo-C_{18}** were also able to form gels in DMSO. Gelation in DMSO is not often described. DMSO displays a low toxicity and it has a low vapor pressure. These facts open its interest to many applications. Otherwise, to our knowledge, gels of **HOOC-Azo-C_{18}** have never been described yet. This compound is mostly known for its use in liquid crystals and Langmuir-Blodgett films.[40]

The gelation ability for the synthetized molecules is different according to the molecular structure. The addition of phenylalanine block to **HOOC-Azo-C_{18}** enables to switch from an insoluble compound in toluene and CH_2Cl_2 to gelation in these same solvents. **Phe-Azo-C_{18}** is also able to gelate in DMSO and 1-dodecanol. The introduction of the PEG_8 chain enables the gelation in methanol and acetone. Increasing the PEG chain up to 16 units tends to make soluble the molecule in nearly all the organic solvents tested. Otherwise, both PEG_8 and PEG_{16} ensure a very broad enlargement of solubility in both polar and apolar solvents compared with **HOOC-Azo-C_{18}** and **Phe-Azo-C18**. Introducing the maltose unit suppresses the gelation in DMSO, but it adds the gelation in THF. All gels are orange in color due to the azobenzene group, as can be seen for the examples selected in **Figure 1,** an opaque gel of **Phe-Azo-C_{18}** in dichloromethane at 5 wt % and a transparent gel of **Malt-Phe-Azo-C_{18}** in THF at 1.3 wt%.

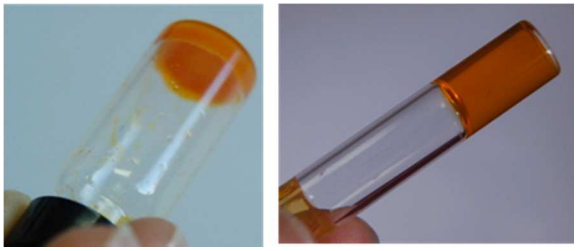


Fig.1 Opaque gel of **Phe-Azo-C_{18}** in dichloromethane at 5 wt% (left), and transparent gel of **Malt-Phe-Azo-C_{18}** in THF at 1.3 wt% (right).

Morphological study. In order to investigate the supramolecular organization of the gels derived from the synthesized amphiphiles, xerogels, formed by the removal of swelling agents, were first obtained from these compounds and studied by microscopic techniques.

Xerogels obtained from gels in 1-dodecanol of **HOOC-Azo-C_{18}**, **Phe-Azo-C_{18}**, **PEG_8-Phe-Azo-C_{18}** and **Malt-Phe-Azo-C_{18}** (at their minimum gel concentration) were first investigated by scanning electronic microscopy (SEM). For **HOOC-Azo-C_{18}** sample, non-well defined structures are observed (**Figure 2a**). Ribbons, having lengths and widths of around several micrometers are detected for **PEG_8-Phe-Azo-C_{18}** (**Figure 2c**). However, for **Phe-Azo-C_{18}** and **Malt-Phe-Azo-C_{18}** widths of the ribbons are at the nanometer scale, ranging from 50 to 200 nm for **Phe-Azo-C_{18}** (**Figure 2b)** and from 90 to 160 nm in the case of **Malt-Phe-Azo-C_{18}** (**Figure 2d).** Xerogels derived from gels in DMSO were also studied for the different compounds as can be seen in the Supporting Information, **Figure SI4**. Differences on the morphology or in the size of the fibrillar structure were observed depending on the solvent.

The self-assembly of the gelators, was also studied in diluted and negative stained samples of the amphiphiles by transmission electronic microscopy (TEM), using first in 1-dodecanol as solvent. Samples obtained from solutions 10 times more diluted than the minimum gel concentration were studied (see **Figure 3** for **Phe-Azo-C_{18}** sample and **Figure SI5** in Supporting Information for **HOOC-Azo-C_{18}**, **PEG_8-Phe-Azo-C_{18}** and **Malt-Phe-Azo-C_{18}** samples). For **Phe-Azo-C_{18}** sample, twisted ribbons are observed having widths of approx. 20-30 nm (**Figure 3**) with a torsion pitch around 50 nm, see close up in **Figure 3**. Microphotographs of the rest of amphiphiles also showed ribbons of different widths: approx. 0.5 mm for **HOOC-Azo-C_{18}**, around 100 to 300 nm for **PEG_8-Phe-Azo-C_{18}**, and 50 to 150 nm for **Malt-Phe-Azo-C_{18}** (see SI).

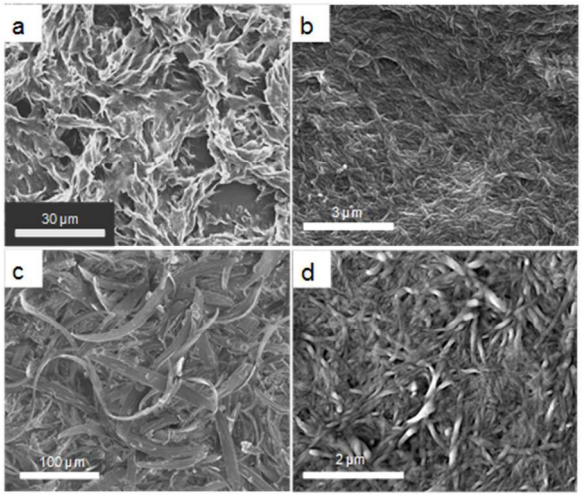


Fig. 2 SEM image of xerogel (1-dodecanol) obtained from: a) **HOOC-Azo-C_{18}** at 5 wt %; b) **Phe-Azo-C_{18}** at 10 wt %; c) **PEG_8-Phe-Azo-C_{18}** at 5 wt % and, d) **Malt-Phe-Azo-C_{18}** at 0.5 wt %.

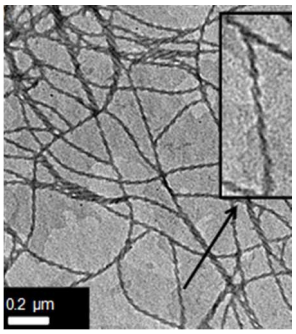


Fig. 3 TEM image of **Phe-Azo-C_{18}** (sample obtained from a solution at 1 wt % in 1-dodecanol).

The amphiphilic structure of **PEG_{16}-Phe-Azo-C_{18}** should promote aggregation and self-assembly, although gelification was not observed in the tested solvents. Self-assembly of **PEG_{16}-Phe-Azo-C_{18}** compound was studied in DMSO solutions (0.5%) by carefully addition of water. Turbidity was monitored as a means of detecting aggregation threshold.[41] (see **Figure SI6** in Supporting Information). The final dispersion was then dialyzed against water for 2 days to remove the organic solvent. The morphological analysis of the dialyzed aggregate solution was then performed by TEM on a sample stained with uranyl acetate. Fibrillar aggregates with a length around 100 nm were observed, see **Figure 4a**. **PEG_8-Phe-Azo-C_{18}** compound was also studied in DMSO, where this compound forms a gel in a concentration of 5 wt % and consequently should aggregate in this solvent even at a lower concentration. For the study of supramolecular aggregation, diluted sample at 0.1 wt % was prepared, heated to complete solubility and then cooled to obtain a clear solution. A drop of the solution was placed onto a copper grid and negative stained by uranyl acetate (**Figure 4b**). Fibrillar aggregates have a length of several microns in this case.

The hydrophobic/hydrophilic balance seems to play a crucial role in the self-assembly and the dimensions of the aggregates of these amphiphilic molecules. In case of **PEG_8-Phe-Azo-C_{18}**, having a higher hydrophobic content (60/40 molecular weight hydrophobic/hydrophilic part ratio) than **PEG_{16}-Phe-Azo-C_{18}**, the network is consistent enough to entrap the solvent. Meanwhile for **PEG_{16}-Phe-Azo-C_{18}**, with a higher hydrophilic content (44/56 molecular weight hydrophobic/hydrophilic part ratio taking as reference n=16), the aggregates cannot form a consistent network to entrap the solvent.

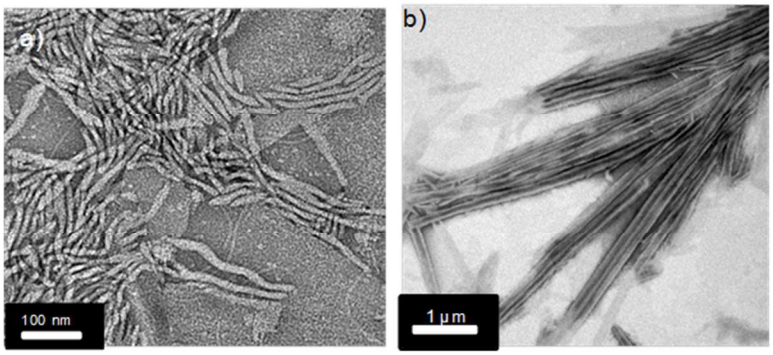


Fig. 4 a) TEM images of a **PEG_{16}-Phe-Azo-C_{18}** dialyzed sample; b) TEM image of **PEG_8-Phe-Azo-C_{18}** at 0.1wt % in DMSO.

Irradiation studies. Irradiation experiments in solution as well as in gel state were carried out. The modification of the supramolecular arrangement by light has been studied by UV-visible and ECD spectroscopy, and macroscopic observations.

Solutions of PEG derivatives in DMSO were irradiated at 365 nm, around the maximum corresponding to the π–π* transition of the *trans*-isomer. As an example, **Figure SI7** displays the corresponding spectra of **PEG_8-Phe-Azo-C_{18}** in DMSO at 10^{-4} M. Evolution of the sample was monitored by UV-vis spectroscopy in order to check *trans-cis* isomerization. The band is approximately symmetrical and has a maximum at 365 nm corresponding to the π-π* transition of *trans*-isomer, which is in accordance with a relatively low aggregation. Under irradiation, **PEG_8-Phe-Azo-C_{18}** solution exhibits a decrease of the absorbance at λ_{max} due to the decrease of the *trans*-isomer and the absorbance at 445 nm, corresponding to the n–π* transition, increases due to the appearance of the *cis*-isomer. Photostationary state was reached at around 6 min. Partial recovery of the initial UV-vis spectrum was achieved when samples were kept in the dark for 24 h.

Photoirradiation was also carried out in the gel state using a 5 wt % DMSO gel (the same solvent that solution studies) of **PEG_8-Phe-Azo-C_{18}** in DMSO. **Malt-Phe-Azo-C_{18}** was studied at 0.5 wt% in 1-dodecanol, due to the very low minimum concentration of gelification in this solvent. UV-vis spectra of the studied gels were analyzed before and after irradiation to explore the changes caused by the *trans-cis* isomerization. In addition, studies by electronic circular dichroism (ECD) were performed in order to get more insight into the chiral supramolecular organization and modification by irradiation. The circular dichroism spectra were registered in a small amount of the gels and sandwich between two fused silica discs. We confirmed that the contribution of the linear dichroism to the ECD spectra was negligible by comparing several ECD spectra recorded at different angles around the incident light beam.

Before irradiation UV-vis absorption spectrum in gel state of **PEG_8-Phe-Azo-C_{18}** at 5 wt % in DMSO (**Figure 5, top**) shows a slightly broaden curve compared with solution and the λ_{max} value appears at 362 nm (in solution 365 nm). The λ_{max} value for a **Malt-Phe-Azo-C_{18}** organogel at 0.5 wt % in 1-dodecanol (**Figure 6, top**) appears at around 339 nm. The broadness of the UV-vis bands and the blue-shifted maxima, in particular for **Malt-Phe-Azo-C_{18}**, are a consequence of the aggregation of azobenzene chromophores in the gel structure.

In the case of **PEG_8-Phe-Azo-C_{18}** gel at 5 wt % in DMSO, under UV irradiation (**Figure 5, top**) at 365 nm (using the same irradiation conditions as in solution) a decrease in the *trans*-azobenzene UV band was observed. After irradiation for 45 min, UV-vis spectrum is more similar to the one exhibited by the *cis*-isomer, however, the *trans* to *cis* isomerization was clearer appreciated when the sample was irradiated for 3h. As it is expected from the results and the evaluation of the degree and rate constant of isomerization (see in Supporting Information, **Table SI1** and **Figure SI8**), the photoisomerization is more hindered in the case of gel than in solution, due to the self-assembly of the chromophores, which gives account of the slower conversion. For **Malt-Phe-Azo-C_{18}** gel at 0.5 wt % in 1-dodecanol gel under irradiation at 365 nm is detected a less hindered *trans*-to-*cis* conversion with respect to **PEG_8-Phe-Azo-C_{18}** gel (**Figure 6, top**). Partial recovery of the initial UV-vis spectrum was achieved when gel samples were kept in the dark for 24 h at rt (see **Figure 5, top** and **Figure 6, top**).

Both organogel **PEG_8-Phe-Azo-C_{18}** at 5 wt% in DMSO (**Figure 5, bottom**) and **Malt-Phe-Azo-C_{18}** gel at 0.5 wt% in 1-dodecanol (**Figure 6, bottom**), show a positive exciton couplet corresponding to the π–π* transition of the azobenzene units**.** These results indicate a chiral organization of the azobenzene moieties imposed by the molecular quirality of L-phenylalanine (and maltose in case of **Malt-Phe-Azo-C_{18}**). As expected, the ellipticity values of non-irradiated samples are higher than the irradiated material as a consequence of the decrease of the chiral aggregation due to the increase of the *cis*-azobenzene moieties. Once irradiated, the gel samples partially recovered its original ECD spectra after 24h at darkness at rt (see **Figure 5, bottom** and **Figure 6, bottom**).

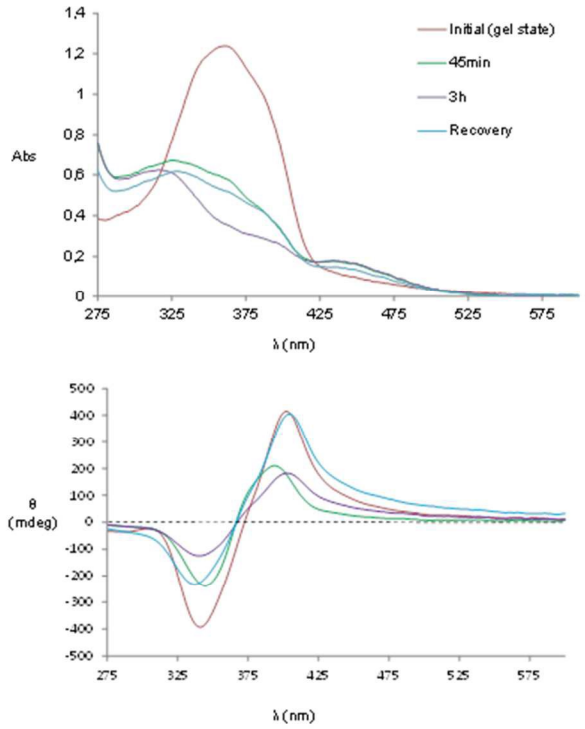


Fig. 5 Absorption spectra (top) and ECD spectra (bottom) of **PEG$_8$-Phe Azo-C$_{18}$** gel (5 wt % in DMSO) measured at rt, without irradiation, after 45 min of irradiation, 3 h of irradiation and recovery after 3h of irradiation and keeping the sample in dark for 24h at rt.

Irradiation of the **PEG$_8$-Phe-Azo-C$_{18}$** gel (5 wt % in DMSO) and **Malt-Phe-Azo-C$_{18}$** gel (0.5 wt % in 1-dodecanol) were carried out in a 1mm thickness cuvette, in order to check if a gel to sol transition is photoinduced. In fact, this transition was observed in both cases, by using irradiation conditions similar to UV-vis and ECD studies. For **PEG$_8$-Phe-Azo-C$_{18}$** gel (5 wt % in DMSO), after 45 min of irradiation a partial dark red solution was observed at the bottom of the cuvette and after 3h almost all the gel became sol state (**Figure 7a**). Gel was reformed after 96 h and sol state was again obtained under irradiation at 365 nm. For **Malt-Phe-Azo-C$_{18}$** gel (0.5 wt % in 1-dodecanol) a gel to sol transition was reached after 10 min of irradiation at 365 nm (**Figure 7b**). Gel was reformed after 6 h and the process was reversible by cycles of irradiation at 365 nm and subsequent thermal back *cis-trans* isomerization in darkness. Therefore, in both cases a gel-sol photoresponse was achieved under UV light, however this process is faster in the case of the maltose derivative.

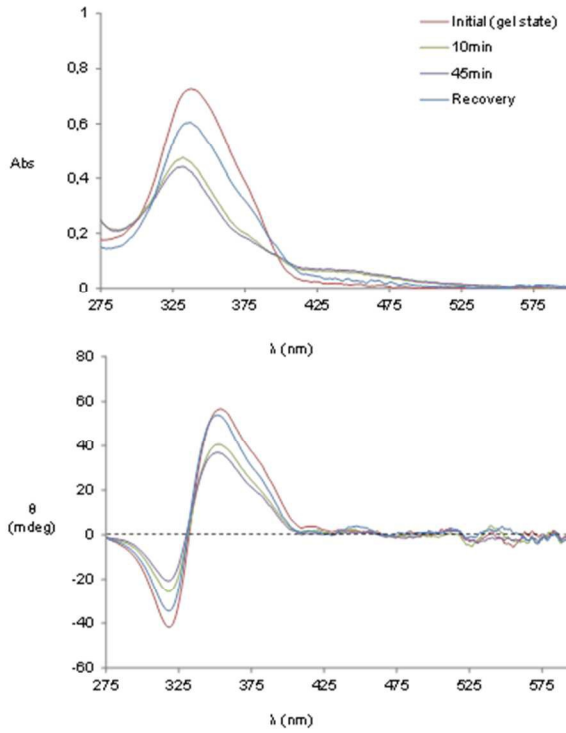


Fig. 6 Absorption spectra (top) and ECD spectra (bottom) of **Malt -Phe – Azo-C$_{18}$** gel (0.5 wt % in 1 dodecanol) measured at rt, without irradiation, after 10 min, after 45 min of irradiation and recovery after 45h of irradiation and keeping the sample in dark for 24h at rt.

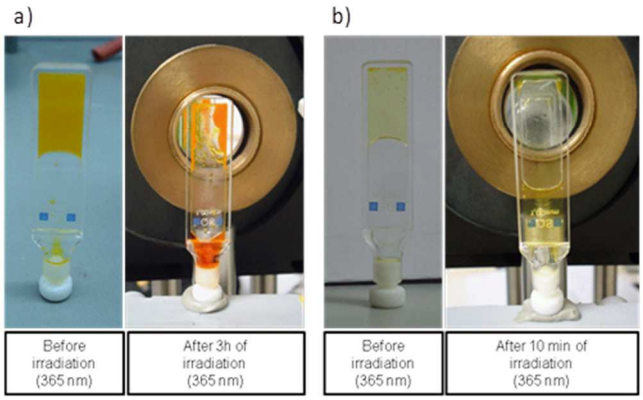


Fig. 7 a) **PEG$_8$-Phe-Azo-C$_{18}$** gel (5 wt % in DMSO) before irradiation and after 3h of irradiation at 365 nm. b) **Malt-Phe-Azo-C$_{18}$** gel (0.5 wt % in 1-dodecanol) before irradiation and after 10 min of irradiation at 365 nm.

Conclusions

Amphiphilic molecules, based on a photoresponsive azobenzene hydrophobic block and poly(ethylene glycol) or maltose as polar heads, which are connected by L-phenylalanine have been designed and synthesized. Precursors **HOOC-Azo-C$_{18}$** and **Phe-Azo-C$_{18}$,** and the amphiphiles **PEG$_8$-Phe-Azo-C$_{18}$** and **Malt-Phe-Azo-C$_{18}$** form gels in different organic solvents, including polar solvents such as DMSO. The gelation ability can be moved toward more apolar solvents with phenylalanine while adding PEG units moved the gelation toward more polar solvents. The molecular weight of PEG is a key factor for balancing gel formation and full solubility. While **PEG$_8$-Phe-Azo-C$_{18}$** is able to

form organogels in polar solvents, **PEG$_{16}$-Phe-Azo-C$_{18}$** is soluble in main solvents. For this compound, gelation was not observed however when it is first dissolved in an organic solvent it forms fibrillar self-assembled structures in aqueous solution. The morphology of the gels depends on the gelator and the gel medium as it has been confirmed by different microscopic techniques. The photoisomerization of the azobenzene units, has been studied in solution and gel state. Two gels, **PEG$_8$-Phe-Azo-C$_{18}$** gel at 5 wt % in DMSO and **Malt-Phe-Azo-C$_{18}$** gel at 0.5 wt % in 1-dodecanol were able to switch reversibly from the gel to the sol state, under irradiation at UV light. **Malt-Phe-Azo-C$_{18}$** gel (0.5 wt% in 1-dodecanol) shows a faster response to the irradiation than the **PEG$_8$-Phe-Azo-C$_{18}$** gel (5 wt% in DMSO). In the maltose derivative, despite the apparent slight modifications of UV-vis and ECD spectra, the gel-sol transition is photoinduced in a few minutes, and this fact evidences than slight changes into the supramolecular organization of amphiphiles may lead to significant changes at the macroscale. The gel-sol transition is reversible by thermal back cis-to-trans isomerization in both switchable organogels.

Experimental Section

Characterization data (elemental analysis, ^{1}H and ^{13}C NMR, FTIR and MS) for the intermediate compounds are collected in the Supporting Information. Only data corresponding to the final compounds are included in this section.

Syntheses

4-hydroxy-4´-(ethyloxycarbonyl)azobenzene (1)

Ethyl 4-aminobenzoate (9.26 g) was dissolved in 45 mL of water and cooled in a water-ice bath. 20 mL of HCl (37%) solution was added dropwise and later was also added dropwise a $NaNO_2$ (4.68 g in 30 mL of water) solution. 6.30 g of phenol (66.94 mmol) was added 30 min later, and the mixture was stirred at 5° C for 1 h. The product precipitated upon addition of a concentrated $NaHCO_3$ aqueous solution to achieve pH 7-8. It was filtered and washed with water. The product was finally purified by flash chromatography using dichloromethane as eluent. A red solid was obtained (6.55 g, 45%). For characterization data, see Supporting Information.

4-(octadecyloxy)-4'-(ethyloxycarbonyl)azobenzene (2)

Compound 1 (1.84 g, 7.4 mmol) was dissolved in acetone (30 mL), under an argon atmosphere, KI (0.28 g, 1.85 mmol) and K_2CO_3 (1.89 g, 1.48 mmol) was added. Once the solvent is refluxing, the octadecyl bromide (2.72 g, 8.88 mmol) was added dropwise. The mixture was stirred for 24 h. The reaction was monitored by TLC (hexane/ethyl acetate, 7:3). The solvent was partially removed. Dichloromethane (60 mL) was added and washed three times with water and dried with anhydrous MgSO4. The product was recrystallized in ethanol yielding an orange solid (2.08 g, 55%). For characterization data, see Supporting Information.

4-(octadecyloxy)-4'-(hydoxycarbonyl)azobenzene (HOOC-Azo-C$_{18}$)

Compound 2 (2.08 g, 3.9 mmol) and KOH (1.58 g, 27.3 mmol) were dissolved in ethanol (50 mL) and stirred and heated under reflux for 24 h. The reaction is monitored by TLC with dichloromethane as eluent. 70 mL of water was added and the product finally precipitated upon addition of HCl (37%) until pH 2. It was filtered and washed with water. It was obtained as an orange powder which was recrystallized in acetic acid (1.55 g, 80%).

^{1}H NMR (400 MHz, DMSO, 90°C, δ ppm): 0.87 (t, 3H, J=7.2 Hz, CH_3-CH_2-), 1.47-1.27 (m, 30 H, –$(CH_2)_{15}$-), 1.80-1.76 (m,2H, $(CH_2)_{15}$-CH_2-CH_2-O-), 4.13 (t, 2H, J=6.4 Hz, CH_2-CH_2-O-), 7.13-7.11 (m, 2H, CHar), 7.91-7.86 (m, 4H, CHar), 8.12-8.10 (m, 2H, CHar).

^{13}C (100 MHz, DMSO, 90°C, δ ppm): 14.0, CH_3, 22.3, 25.8, 28.9, 29.1, 29.3, 29.3, 31.6, CH_2, 68.9 O-CH_2, 115.7, 122.4, 125.2, 130.8, CHar, 132.9, 147.0, 155.3, 162.6, 167.7 Car, CO.

ESI+: 495.4 $[M + H]^+$.

IR (KBr, cm^{-1}): 2918, 2849, 1680, 1602, 1583, 1501, 1471, 1419, 1290, 1249, 1143, 837, 544.

Compound 3

HOOC-Azo-C$_{18}$ (2.49 g, 5.04 mmol) was dissolved in 240 mL of anhydrous THF. This solution was heated until the benzoic acid derivative HOOC-Azo-C$_{18}$ was dissolved and N-hydroxysuccinimide (0.81 g, 7.13 mmol) in 40 mL of THF solution was added. The mixture was cooled to room temperature and then placed in a water-ice bath. Dicyclohexylcarbodiimide (DCC) (6.60 g, 32 mmol) was dissolved in 35 mL of THF and added to the mixture and was stirred for 96 h at room temperature. The reaction mixture was filtered and the solvent was distilled off. The product was recrystallized from isopropanol to obtain a red solid (2.56 g, 86%). For characterization data, see Supporting Information.

Phe-Azo-C$_{18}$

L-Phenylalanine (0.66 g, 3.99 mmol) and diisopropylethylamine (1.40 mL, 8.12 mmol) were dissolved in 25 mL of water and 30 mL of THF. A solution of 3 (2.40 g, 4.06 mmol) in 100 mL of THF was added. The mixture was stirred at room temperature for 60 h. The reaction was monitored by TLC using hexane/ethyl acetate 1:1 as eluent. A solution of HCl (37%) was added until pH = 4. The solvent was partially removed and the resulting aqueous phase was extracted with dichloromethane (3 × 250 mL). The organic layer was dried with anhydrous MgSO4 and finally the solvent was evaporated. The product was purified by flash chromatography using dichloromethane and increasing the polarity with methanol. A red solid was obtained (1.502 g, 58%).

^{1}H (300 MHz, CDCl3, δ ppm): 0.88 (t, 3H, J= 6.7 Hz, CH_2-CH_3), 1.26-1.50 (m, 30H, -$(CH_2)_{15}$-), 1.78-1.87 (m, 2H, –O-CH_2-CH_2), 3.24-3.46 (m, 2H, –CH-CH_2-ar), 4.05 (t, 2H, J=6.6 Hz, -O-CH_2-CH_2-), 5.07-5.17 (m, 1H, -CH-CH_2-ar), 6.59 (d, 1H, J=7.2 Hz, NH-CO-), 6.99-7.02 (m, 2H, Har-C-O-CH_2-), 7.22-7.73 (m, 6H, Har), 7.80-7.94 (m, 5H, Har).

^{13}C (75 MHz, CDCl3, δ ppm): 14.1 CH_2-CH_3, 22.7, 26.0, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9,-CH_2-, 37.2 –CH-CH_2-ar, 53.7 -CH-CH_2-ar, 68.5 O-CH_2-CH_2-, 114.8, 122.7, 125.2, 127.4, 128.0, 128.8, 129.4 CHar, 134.3, 135.5, 146.8, 155.8, 162.3 Car, 167.0 NH-CO, 174.3 COOH.

MALDI-TOF (DCTB+NaTFA): 686.7 $[M+2Na]^+$, 664.6 $[M+Na]^+$, 642.6 $[M+H]^+$.

Anal.Calcd. for $C_{40}H_{55}N_3O_4$: C, 74.85; H, 8.64; N, 6.55. Found:

C, 74.75; H, 8.65; N, 6.44.
IR (KBr, cm-1): 3316, 2919, 2850, 1644, 1527, 1252, 1143, 838.

PEG_8-Phe-Azo-C_{18} and PEG_{16}-Phe-Azo-C_{18}

Phe-Azo-C_{18} (305 mg, 0.47 mmol) and hydroxybenzotriazole (80 mg, 0.59 mmol) were dissolved in 20 mL of anhydrous THF. Methyl-PEGn-amine (n=8, from Fisher Scientific or n=16, from Fluka) (0.50 mmol) was added. The solution was cooled to 0 °C. 1-Ethyl-3-(3-dimethyllaminopropyl)carbodiimidehydrochloride (101 mg, 0.52 mmol) was added. The reaction mixture was stirred for 2 days at room temperature. The reaction was monitored by TLC with hexane/ethyl acetate 1:9 as eluent. The mixture was filtered and the solvent was removed under reduced pressure. 250 mL of dichloromethane were added and the organic phase was washed three times with 1M $KHSO_4$ solution, and three times with 1M $NaHCO_3$ solution. The organic layer was dried over anhydrous $MgSO_4$. The solution was filtered and the solvent was removed under reduced pressure. The product was purified by flash chromatography using dichloromethane and increasing the polarity with methanol. A red solid was obtained (0.401 mg, 85% for **PEG_8-Phe-Azo-C_{18}**, 315 mg, 84% **PEG_{16}-Phe-Azo-C_{18}**).

PEG_8-Phe-Azo-C_{18}. ^{1}H(500 MHz, CDCl3 δ ppm): 0.87 (t, 3H, J= 6.7Hz, CH_2-CH_3), 1.16-1.53 (m, 30H, -$(CH_2)_{15}$-), 1.78-1.85 (m, 2H, -O-CH_2-CH_2), 3.10-3.29 (m, 2H, -CH-CH_2-ar), 3.36 (s, 3H,–O-CH_3), 3.32-3.73 (m, 32H, –$(O$-CH_2-$CH_2)_7$-O, -O-CH_2-CH_2-NH-), 4.05 (t, 2H, J= 6,5Hz, -O-CH_2-CH_2-), 4.77-4.86 (m, 1H, -CH-CH_2-ar), 6.28 (s, 1H, CH_2-CH_2-NH-CO), 6.97-7.07 (m, 3H, Har-C-O-CH_2-, ar-CH-NH-CO), 7.20-7.37 (m, 5H, Har), 7.85-7.99 (m, 6H, Har).
^{13}C (125 MHz, CDCl3 δ ppm): 14.1 CH_2-CH_3, 22.7, 26.0, 29.2, 29.4, 29.4, 29.5, 29.5, 29.6, 29.7, 31.9 -CH_2-, 38.9 –CH-CH_2-ar, 39.4 –O-CH_2-CH_2-NH, 55.1 -CH-CH_2-ar, 59.0 -O-CH_3, 68.5 O-CH_2-CH_2-, 69.5, 70.3, 70.5, 70.5, 71.9 –$(O$-CH_2-$CH_2)_n$-O, -O-CH_2-CH_2-NH-, 114.7, 122.6, 125.0, 127.0, 128.0, 128.7, 129.4 CHar, 134.9, 136.7, 146.8, 154.6, 162.2, 166.2, 170.6 Car, ar-CH-NH-CO, CH_2-CH_2-NH-CO-.
MALDI-TOF (DCTB+NaTFA): 1029.8 [M (n=8) +Na]$^+$.
Anal. Calcd for $C_{57}H_{90}N_4O_{11}$: C, 67.96; H, 9.01; N, 5.56. Found: C, 68.08; H, 9.59 ; N, 5.58.
IR (KBr, cm-1): 3301, 2920, 2850, 1636, 1530, 1251, 1143, 1105, 859, 837, 698.

PEG_{16}-Phe-Azo-C_{18}. ^{1}H(300 MHz, CDCl3 δ ppm): 0.81 (t, 3H, J= 6.7Hz, CH_2-CH_3), 1,04-1,40 (m, 30H, -$(CH_2)_{15}$-), 1.70-1.81 (m, 2H, –O-CH_2-CH_2), 3.04-3.22 (m, 2H, –CH-CH_2-ar), 3.31 (s, 3H, –O-CH_3), 3.32-3.70 (m, nH, –$(O$-CH_2-$CH_2)_n$-O-, -O-CH_2-CH_2-NH-), 3.98 (t, 2H, J= 6.5Hz, -O-CH_2-CH_2-), 4.73-4.84 (m, 1H, -CH-CH_2-ar), 6.60 (s, 1H, CH_2-CH_2-NH-CO-), 6.92-6.95 (m, 2H, Har-CO-CH_2-), 7,04 (d, 1H, J= 7.6 Hz, ar-CH-NH-CO), 7.16-7.26 (m, 5H, Har), 7.82-7.87 (m, 6H, Har).
^{13}C (100 MHz, CDCl3, δ ppm): 14.1 CH_2-CH_3, 22.7, 26.0, 29.2, 29.4, 29.4, 29.5, 29.5, 29.6, 29.7, 31.9,-CH_2-, 38.9 –CH-CH_2-ar, 39.4 –O-CH_2-CH_2-NH, 54.9 -CH-CH_2-ar, 59.1 –O-CH_3, 68.5 O-CH_2-CH_2-, 69.5, 70.3, 70.5, 71.9 –$(O$-CH_2-$CH_2)_n$-O-, -O-CH_2-CH_2-NH-, 114.7, 122.5, 125.0, 126.9, 128.0, 128.5, 129.4 CHar, 134.3, 136.7, 146.8, 154.6, 162.2, 166.2, 170.6 Car, ar-CH-NH-CO, CH_2-CH_2-NH-CO-.
MALDI-TOF (DCTB+NaTFA): 1249.8 [M (n=13) +Na]$^+$, 1293.8 [M (n=14) +Na]$^+$, 1337.8 [M (n=15) +Na]$^+$, 1381.9 [M (n=16) +Na]$^+$, 1425.9 [(M (n=17) +Na]$^+$, 1469.9 [M (n=18) +Na]$^+$, 1513.9 [M (n=19) +Na]$^+$, 1558.0 [M (n=20) +Na]$^+$, 1603.0 [M (n=21) +Na]$^+$, 1646.0 [M (n=22) +Na]$^+$, 1690.0 [M (n=23) +Na]$^+$, 1734.0 [M (n=24) +Na]$^+$.
IR (KBr, cm^{-1}): 3300, 2920, 2850, 1636, 1531, 1251, 1144, 1107, 838.

Hepta-O-acetyl-β-maltosylazide (4) and hepta-O-acetyl-β-maltosyl amine (5) have been previously described.[18]

Compound 6

Phe-Azo-C_{18} (740 mg, 1.15 mmol) was dissolved in 25 mL of anhydrous THF. Oxalyl chloride (0.30 mL, 2.81 mmol) and anhydrous DMF (0.3 mL) were added. The reaction mixture was stirred overnight. The solvent was removed under reduced pressure. The product was used without further purification.

OAc-Malt-Phe-Azo-C_{18}

Compound 6 (0.94 mmol) was dissolved in 10 mL of anhydrous DMF. Pyridine (0.1 mL, 1.24 mmol) was added and the solution was cooled to 0 °C. A solution of compound 7 (1.15 mmol) in 10 mL of anhydrous DMF and 15 mL of THF was added. 20 mL of THF were added to complete solubilization. The reaction mixture was stirred for 48 h at room temperature and poured into 150 mL of water. The aqueous phase was extracted with 3 × 150 mL of hexane/ethyl acetate 1:1. The organic phase was dried with anhydrous $MgSO_4$. The solution was filtered and the solvent was removed under reduced pressure. The resulting product was purified by flash chromatography with dichloromethane/ethyl acetate 8:2 as eluent. A red solid was obtained (646.2 mg, 54%). For characterization data, see Supporting Information.

Malt-Phe-Azo-C_{18}

OAc-Malt-Phe-Azo-C_{18} (131.1 mg, 0.10 mmol) were dissolved in 5 mL of anhydrous methanol. Sodium methoxide (50.0 mg, 0.92 mmol) was then added. The solution was stirred at room temperature until the reaction was complete (TLC, dichloromethane/ethyl acetate 1:1). Amberlyst IR 120 (H^+ form) was added to exchange sodium ions until pH 7-6. The resin was filtered off and the solvent was evaporated in vacuum to give a red solid (58 mg, 60%).
^{1}H NMR (500 MHz, DMSO, δ ppm): 0.85 (t, 3H, J = 6.7 Hz, -$(CH_2)_{15}$-C*H*$_3$), 1.17-1.49 (m, 30H, CH_2-(C*H*$_2)_{15}$-CH_3), 1.70-1.78 (m, 2H, –CH_2-C*H*$_2$-$(CH_2)_{15}$), 2.99-3.92 (m, 14H, CH-C*H*$_2$-Car-, *H2*, *H3*, *H4*, *H5*, *H6a*, *H6b*, *H2´*, *H3´*, *H4´*, *H5´*, *H6´a*, *H6´b*), 4.09 (t, 2H, J = 6.4 Hz, –O-C*H*$_2$-CH_2), 4.16-4.31 (m, 2H, O*H*), 4.49-4.72 (m, 2H, O*H*), 4.77-4.90 (m, 2H, NH-C*H*-CH_2, *H1´*), 5.01-5.09 (m, 1H, *H1*), 5.09-5.22 (m, 1H, O*H*), 5.29-5.45 (m, 2H, O*H*), 7.06-7.41 (m, 7H, *Har*), 7.78-7.99 (m, 6H, *Har*), 8.36-8.46 (m, 1H, N*H*-CO), 8.56 (t, 1H, N*H*-C1´).
^{13}C NMR (125 MHz, DMSO, δ ppm): 13.5 -$(CH_2)_{12}$-*C*H$_3$,21.7, 25.2, 28.4, 28.7, 31.0 -CO-*C*H$_2$-(*C*H$_2)_{13}$-CH_3, 37.3 CH-*C*H$_2$-Car,54.6, 54.7 *C*H-CH_2-Car, 68.1, –O-*C*H$_2$-CH_2, 61.0, 70.2, 71.7, 72.0, 72.2, 72.4, 73.3, 76.9, 77.1, 79.3, *C2*, *C3*, *C4*, *C5*, *C6*, *C2´*, *C3´*, *C4´*, *C5´*, *C6´*, 79.9*C1´*, 100.6 *C1*, 115.0, 121.6, 124.6, 125.9, 127.8, 128.3, 129.0 *C*Har, 135.6, 137.9, 138.0, 146.2, 153.6, 165.4, 171.6 *C*ar, CH-NH-*C*O-Car, C1´-NH-*C*O.
MicroTOF MS: 987.5253 [M+ Na]$^+$, calcd: 987.5403.

IR (KBr, cm^{-1}): 3307, 2917, 2849, 1635, 1539, 1250, 1034, 856, 836.

Techniques

^1H and ^{13}C NMR spectra were recorded on BRUKER AV-300, AV-400 or AV-500 spectrometers. IR spectra were measured on Thermo NICOLET Avatar 360 FT-IR spectrophotometer using KBr pellets. Mass Spectrometrywas performed using a MALDI$^+$/TOF Brüker Microflex system with a DIT + NaFTA matrix and MicroTOFBrüker equipment for exact mass measurements. Elemental analysis was performed using a Perkin Elmer CHN2400 microanalyzer.

The thermal and mesogenic behavior was studied by optical microscopy with an Olympus BH-2 polarizing microscope equipped with a Linkam THMS hot-stage central processor. Differential scanning calorimetry (DSC) was performed using a DSC Q2000 from TA Instruments with samples sealed in aluminum pans and a scanning rate of 10 ºC/min under a nitrogen atmosphere. Temperatures were read at the maximum of the transition peaks and. Thermogravimetric analysis (TGA) was performed using a TGA Q5000IR from TA Instruments at a rate of 10 ºC/min under a nitrogen atmosphere. Circular dichroism was measured using a Jasco J-810 equipment. The ECD spectra of the samples were registered by rotating the sandwich every 60 degrees around the light beam axis.**PEG$_8$-Phe-Azo-C$_{18}$**gel (5 wt % in DMSO) was placed onto between two fused silica slides at room temperature with a 25 µm spacer. In the case of **Malt-Phe-Azo-C$_{18}$** gel (0.5 wt % in 1-dodecanol) w a 100 µm spacer was used. Spacers were selected in order to reach absorption below 2.

SEM measurements were performed using a QUANTA FEG 250 and TEM measurements were performed using a TECNAI G^2 20 (FEI COMPANY), 200 kV, both at the Laboratory of Advanced Microscopy (LMA) of the 'Instituto de Nanociencia de Aragon'. For SEM the sample was fixed onto glass and coated with platinum. For TEM sample preparation, a drop of the solution (gel diluted) was placed on a copper grid and left to dry for 15 min. The copper grid was then placed again over a drop of 1% uranyl acetate solution as a negative stain for 30 s and was then left to dry.

Irradiation with UV light was carried out using an Hg lamp (1000 W, Oriel) with an infrared water filter and an absorption filter 365 nm ± 5nm. (intensity was 3.4 ± 0.3 mW/cm^2).

Gelation test: The gelator and the solvent were placed in a septum-capped test tube. The resulting mixture was heated until a clear solution was obtained. The solution was cooled to room temperature and if the tube was turned upside down and the solution did not flow, the formation of a gel was registered.

Aggregation study of **PEG$_{16}$-Phe-Azo-C$_{18}$**: The sample was first dissolved in DMSO (0.5 wt %) and water was carefully added to the solution (20 µL of Milli-Q water to 1.0 mL of solution) with slight shaking. Turbidity (as a modification of the apparent optical density of the sample) of the solution was measured after every addition of water at a wavelength of 650 nm using a quartz cell (path length 1 cm) with a UV/vis spectrophotometer. The solution was left to equilibrate till the turbidity value remains constant. The cycle of water addition, equilibration and turbidity measurement was continued until the increase in turbidity upon water addition was very small. The solution was then dialyzed against water for 2 days to remove the organic solvent using a regenerated cellulose membrane with a molecular weight cutoff of 1000 a. m. u.

Acknowledgment

Financial support from the Spanish Government (MAT2011-27978-C02-01) is gratefully acknowledged. The authors acknowledge the Laboratory of Advanced Microscopy Laboratory (LMA) of the Universidad de Zaragoza (Unizar) and CEQMA (CSIC-Unizar) for the NMR, MS, EA and thermal analysis general facilities. The authors additionally acknowledge the use of the Servicio General de Apoyo a la Investigación of the Universidad de Zaragoza

Notes and references

[a] *Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza-CSIC, Dpto. Química Orgánica, Facultad de Ciencias, Pedro Cerbuna 12, 50009 Zaragoza, Spain. Tel: +34 876 55 3785; E-mail: loriol@unizar.es*

[b] *Centro Universitario de la Defensa, Academia General Militar, Carretera de Huesca s/n, 50090 Zaragoza, Spain.*

[c] *Université de Toulouse, Laboratoire des IMRCP, UMR CNRS 5623, Bât. 2r1, Université Paul Sabatier, 118 route de Narbonne, F-31062, Toulouse Cedex 9, France.*

† Electronic Supplementary Information (ESI) available: [Characterization data of compounds 1- 4 and **OAc-Malt-Phe-Azo-C$_{18}$**. MALDI-TOF MS of **PEG$_8$-Phe-Azo-C$_{18}$**, **PEG$_{16}$-Phe-Azo-C$_{18}$** and **Malt-Phe-Azo-C$_{18}$**.^1H NMR of **PEG$_8$-Phe-Azo-C$_{18}$**, **PEG$_{16}$-Phe-Azo-C$_{18}$**, **OAc-Malt-Phe-Azo-C$_{18}$** and **Malt-Phe-Azo-C$_{18}$**. TOCSY spectrum of **OAc-Malt-Phe-Azo-C$_{18}$**. SEM images of **HOOC-Azo-C$_{18}$** and **Phe-Azo- C$_{18}$** in DMSO. TEM images of **HOOC-Azo-C$_{18}$**, **PEG$_8$-Phe-Azo-C$_{18}$**, **Malt-Phe-Azo-C$_{18}$**. Turbidity curve of **PEG$_{16}$-Phe-Azo-C$_{18}$**. Absorption spectra of a 10^{-4} M solution of **PEG$_8$-Phe-Azo-C$_{18}$** in DMSO at different irradiation times at 365 nm. Degree of isomerization for azobenzene moieties for **PEG$_8$-Phe-Azo-C$_{18}$** gel and solution and **Malt-Phe-Azo-C$_{18}$** gel. The dependence of ln $[(A_\infty-A_t)/(A_\infty-A_0)]$ on irradiation time for **PEG$_8$-Phe-Azo-C$_{18}$** gel and solution and **Malt-Phe-Azo-C$_{18}$** gel]. See DOI: 10.1039/b000000x/

1 R. G. Weiss and P. Terech, *Molecular gels*, Springer: Dordrecht, 2006.
2 S. S. Babu, V. K. Praveen and A. Ajayaghosh, *Chem. Rev.*, 2014, **114**, 1973.
3 J. Griffith, *Chem. Soc. Rev,* 1972, **1**, 481.
4 S. Mahesh, A. Gapal, R. Thirumalai and A. Ajayaghash, *J. Am. Chem. Soc.,* 2012, **134**, 7227.
5 W. Chen, W. Gong, J. Ye, Y. Lin and G. Ning, *RSC Adv.*, 2012, **2**, 809.
6 S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu and A. Kitamura, *J. Am. Chem. Soc.*, 2005, **127**, 11134.
7 Y. Wu, S. Wu, X. Tian, X. Wang, W. Wu, G. Zou and Q. Zhang, *Soft Matter*, 2011, **7**, 716.
8 J. Wang, G. Yang, H. Jiang, G. Zou and Q. Zhang, *Soft Matter*, 2013, **9**, 9785.
9 N. Koumura, M. Kudo and N. Tamaoki, *Langmuir*, 2004, **20**, 9897.
10 T. Jiao, Y. Wang, F. Gao, J. Zhou and F. Gao, *Prog. in Nat. Sci.: Mat. Inter.*, 2012, **22**, 64–70.
11 J. H. Jung, Y. Ono and S. Shinkai, *Tetrahedron Lett.*, 1999, **40**,8395.
12 K. Murata, M. Aoki, T. Nishi, A. Ikeda and S. Shinkai, *J. Chem. Soc., Chem. Commun.,* 1991, **24**, 1715.
13 K. Murata, M. Aoki and S. Shinkai, *Chem. Lett,* 1992, **5**, 739.

14 K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda and S. Shinkai, *J. Am. Chem. Soc.*, 1994, **116**, 6664.

15 P. F. Duan, Y. G. Li, L. C. Li, J. G. Deng and M. H. Liu, *J. Phys. Chem. B,* 2011, **115**, 3322.

16 L. Li, H. Jiang, B. W. Messmore, S. R. Bull and S. I. Stupp, *Ang. Chem. Int. Ed.*, 2007, **46**, 5873.

17 Y. C. Huang, Z. J. Qiu, Y. M. Xu, J. F. Shi, H. K. Lin and Y. Zhang . *Org. Biomol. Chem,*. 2011, **9**, 2149.

18 X. Ran, H. T. Wang, P. B. Zhang, L. Bai, C. X. Zhao, Z. X. Yu and M. Li. *Soft Matter,* 2011, **7**, 8561.

19 Y. Lin, Y. Qiao, P. Tang, Z. Li and J. Huang, *Soft Matter*, 2011, **7**, 2762.

20 X. Li, Y. Gao, Y. Kuang and B. Xu, *Chem. Com.*, 2010, **46**, 5364.

21 M. J. Clemente, R. M. Tejedor, P. Romero, J. Fitremann, and L. Oriol. *RSC Adv.* 2012, **2**, 11419.

22 Y. Ogawa, C. Yoshiyama and T. Kitaoka, *Langmuir*, 2012, **28**, 4404.

23 R. Yang, S. Peng, W. Wan and T. C. Hughes, *J. Mater. Chem. C*, 2014, **2**, 9122–9131.

24 M. J. Clemente, J. Fitremann, M. Mauzac, J. L. Serrano and L.Oriol, *Langmuir* 2011, **27**, 15236.

25 M. J. Clemente, P. Romero, J. L. Serrano, J. Fitremann and L. Oriol, *Chem. Mat.* 2012, **24**, 3847.

26 A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith. *Angew. Chem. Int. Ed.,* 2008, **47**, 8002.

27 N. Tzokova, C. M. Fernyhouph, P.D. Topham, N. Sandon, D. J. Adams, M. F. Butler, S. P. Armes and A. J. Ryan, *Langmuir,* 2009, **25**, 2479.

28 A. Brizard, M. Stuart, K. van Bommel, A. Friggeri, M. de Jong, and J. van Esch, *Ang. Chem. Int. Ed,* 2008, **47**, 2063.

29 H. G. Borner, B. M. Smarsly, J. Hentschel, A. Rank, R. Schubert, Y. Geng, D. E. Discher, T. Hellweg, and A. Brandt, *Macromolecules*, 2008, **41**, 1430.

30 I. W. Hamley, A. Ansari, V. Castelletto, H. Nuhn, A. Rosler, and H. A. Klok, *Biomacromolecules*, 2005, **6**, 1310.

31 J. Hentschel, E. Krause and H. G. Borner, *J. Am. Chem. Soc,*. 2006, **128**, 7722.

32 P. Jing, J. S. Rudra, A. B. Herr and J. H. Collier, *Biomacromolecules,* 2008, **9**, 2438.

33 M. Suzuki, R. Yanagida, C. Setoguchi, H. Shirai, and K. Hanabusa, *J. Polym. Sci. Part A: Polym. Chem.,*. 2008, **46**, 353.

34 K. Knop, R. Hoogenboom, D. Fischer and U. S. Schubert. *Angew. Chem. Int. Ed.*, 2010, **49**, 6288.

35 M. J. Roberts, M. D. Bentley and J. M. Harris. *Adv. Drug Deliv. Rev,* 2002, **54**, 459.

36 J. del Barrio, L. Oriol, R. Alcala and C. Sanchez, *Macromolecules*, 2009, **42**, 5752.

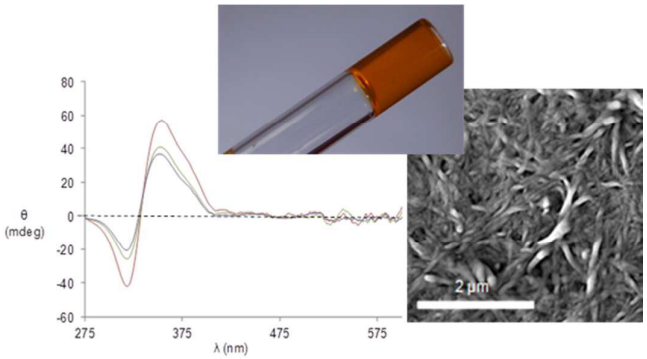
37 J. del Barrio, L. Oriol, C. Sanchez, J. L. Serrano, A. Di Cicco, P. Keller and M. H. Li, *J. Am. Chem. Soc,* 2010, **132**, 3762.

38 M. Sano, D. Y. Sasaki, M. Isayame and T. Kunitake, *Langmuir* 1992, **8**, 1893.

39 J. W. Goodby, V. Gortz, S. J. Cowling, G. Mackenzie, P. Martin, D. Plusquellec, T. Benvegnu, P. Boullanger, D. Lafont, Y. Queneau, S. Chambert and J. Fitremann, *Chem. Soc. Rev,* 2007, **36**, 1971.

40 M. Sano and T. Kunitake, *Langmuir,* 1992, **8**, 320.

41 L. F. Zhang and A. Eisenberg, *Macromolecular Symp,* 1997, **113**, 221.



Photoresponsive supramolecular gelators have been synthesized using PEG or D-maltose as polar head. Incorporation of azobenzene photoresponsive moieties allows controlling the supramolecular gel structure, including a reversible gel-sol transition using light as external stimulus.