Maltose-based gelators having azobenzene as light-sensitive unit

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Three light-sensitive amphiphiles, based on azobenzene, have been synthesized as supramolecular gelators. A hydrophobic chain with an azobenzene group incorporated at different positions was click coupled to a maltose polar head by a copper(I)-catalyzed azide-alkyne [3+2] cycloaddition. The liquid crystalline and gel properties of these azo-amphiphilic materials have been studied. Two of these azo-gelators containing maltose give rise to stable gels in water or in a mixture of water and DMSO at room temperature. The chiral supramolecular assemblies of these gelators have been characterized by NMR, electron microscopy and circular dichroism (CD). The light-response of azo-amphiphiles in supramolecular gels has been studied. Also azo-gels which contained mixtures of the azo-amphiphilic compounds and a similar structural hydrogelator have been investigated.

Introduction

Research on supramolecular gels has increased in recent years by their potential applications as biomaterials, smart materials and electronic devices[1]. These types of gels are formed by self-aggregation of low molecular weight gelator molecules, a process that gives rise to a supramolecular structure that can trap organic or aqueous solvents by means of a combination of non-covalent interactions like H-bonding, π-π stacking, donor-acceptor interactions, solvophobic forces and van der Waals interactions[2]. Taking into account the reversibility of these interactions, supramolecular gels are responsive to external stimuli. The type of response depends on the applied stimulus and can affect the supramolecular structure at different hierarchical levels. For instance, by triggering adequate modifications, these materials can be cycled between free-flowing liquids and non-flowing materials. However other modifications can also be promoted, for example, on the chemical or physical properties, such color or conductivity or swelling and shrinking by extension or contraction of the network[3].

Changes on these supramolecular materials can be triggered by chemical or physical stimuli yielding to smart materials. Different supramolecular gels have been reported to be chemo-responsive by a host-guest complexation[4], a metal-ion interaction[5] and pH changes[6]. Apart from the response to temperature and mechanical stress, among the different physical stimuli, light is attractive because it is a remote stimulus that can promote spatially controlled changes As photoactive gels there are several examples of luminescent gels[7] and phototunable gels. On this last kind of materials there is a structure transformation through a photochemical process of a photochromic unit. The photochromic unit can be a gelator itself or added as a co-gelator. The gel response is a consequence of the ability of the photochromic unit to alternate between two different chemical forms with light, the two forms displaying different absorption spectra. Most often, the mechanisms involved at the molecular level are *trans-cis* isomerization, tautomerizations and electrocycling ring closures and openings. The photoinduced response in gels can be irreversible or reversible[8]. Azo dye systems are used in supramolecular assemblies to trigger reversible environmental changes thanks to the reversible *trans-cis* photochemical isomerization experimented by azobenzenes, where the isomer *cis* can promote a structural disruption[9].

Examples of *trans*-isomer organogels giving rise to a photo-stationary state of *trans-cis* mixtures which provide a sol state, have been described on aza-crown-appended cholesterol derivatives[10] and recently on hydrazine[11] or lipid derivatives[12]. In contrast, in organogels derived from bis-ureido-azobenzene derivatives the *trans-cis* isomerization is blocked in the gel state[3, 13]. The co-assembly of an azobenzene derivative with gels having a chiral nanotube structure has also been studied, in which reversible changes have been regulated by light switching[14]. Most reported examples are relative to organogels by the difficulty of incorporating a hydrophobic photoresponsive part, but few photoresponsive hydrogels based on peptide derivatives have also been reported[15].

Carbohydrates provide a water soluble hydrophilic building block and they can act as candidates in the preparation of

hydrogelators based on the H-bonding of hydroxyl groups[2c]. Azobenzene chromophores can be incorporated into the glyco-amphiphilic structure[16]. Reported azo-glycolipids can be classified into conventional single-head amphiphiles[17] and bolaamphiphiles[18]. Changes under irradiation on their structure[19] or gel-sol transition[20] have been described for sugar based azo-gelators.

Apart from their ability to self-assemble in solvents, glycolipids may exhibit liquid crystal (LC) phases due to the polar asymmetry of these compounds. The head groups are capable of H-bonding while the alkyl chains self-aggregate into microsegregated hydrophobic regions[21]. LC phases have been also observed on azo-glycoamphiphiles[22].

We have recently studied a series of disaccharide-based hydrogelators[23]. Some of them are efficiently synthesized by click chemistry of a hydrophilic maltose head and a palmitic hydrophobic chain. These structures can promote supramolecular interactions to establish a self-assembled 3D network. The triazole ring gives additional π-π stacking and its dipolar moment increases the hydrophilicity of the amphiphile contributing to the formation of hydrogels[2c, 24].

We report here gels in water and DMSO/water mixtures of new maltose-based photoactive gelators prepared by a copper(I)-catalyzed azide-alkyne [3+2] cycloaddition having an azobenzene group at different positions of the hydrophobic chain (Figure 1). The liquid crystalline behavior, chiral supramolecular structures and light-response capability of these gels have been explored.

Results and discussion

Synthesis of materials

The glyco azo-amphiphiles were synthesized by click coupling of maltosylazide and azo-contanining derivatives with a N-propargylamide end group using a copper(I)-catalyzed azide-alkyne [3+2] cycloaddition. The resulting triazole ring connects the maltose polar head with the hydrophobic part. The hydrophobic part consists of an azobenzene group and an alkyl chain with the azobenzene at different positions: directly linked to the triazole (**Malt-Tz-Azo-C_{16}**), in the middle of the chain (**Malt-Tz-C_5-Azo-C_8**) or at the end of the chain (**Malt-Tz-C_{10}-Azo-OCH_3**), see Figure 1.

The synthetic pathway of the azo-glycoamphiphiles is shown in Sheme 1. Peracetylated maltose and the azobenzene-containing carboxylic acids, shown in Figure 2, were used as starting materials. Compounds **HOOC-Azo-C_{16}**, **HOOC-C_5-Azo-C_8**, and **HOOC-C_{10}-Azo-OCH_3**, were prepared by an azo coupling reaction[25] by reaction of sodium phenoxide and ethyl p-aminobenzoate for **HOOC-Azo-C_{16}**, p-methoxyaniline for **HOOC-C_5-Azo-C_8** and (2R)-octyloxyaniline for **HOOC-C_{10}-Azo-OCH_3**, respectively. Compound (2R)-octyloxyaniline was prepared from 4-nitrophenol by etherification with (2R)-octanol and further reduction of the nitro group. The carboxylic aliphatic chains were introduced by a Williamson reaction, followed by the hydrolysis of the ester group to yield the desired acid.

Maltosylazide **1** (see scheme 1) was synthesized in a stereoselective manner by treating maltose octa-acetate with trimethylsilyl azide and tin tetrachloride, as a Lewis acid catalyst, employing the general procedure described by Paulsen[26]. This compound can react through a 1,3-dipolar cycloaddition with propargylamides of the azobenzene acids.

To introduce the alkyne, the propargylamide derivatives **2, 3** and **4,** were synthesized by EDC coupling reagent with hydroxybenzotriazole. Click reaction was carried out in DMF using CuBr and N-pentamethyldiethylenetriamine (PMDETA) to give the azo-glycosyl products in 80-90% of yield. All of the protected derivatives were deacetylated at room temperature with MeONa and Amberlyst IR120 in anhydrous THF to give the final product in 75-90% of yield.

Compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR and mass spectrometry (see experimental section and for characterization of intermediate compounds and Supporting Information, SI1). Peracetylated compounds (**OAc-Malt-Tz-Azo-C_{16}**, **OAc-Malt-Tz-C_5-Azo-C_8** and **OAc-Malt-Tz-C_{10}-Azo-OCH_3**) and azo-glycoamphiphilic compounds (**Malt-Tz-Azo-C_{16}**, **Malt-Tz-C_5-Azo-C_8**, and **Malt-Tz-C_{10}-Azo-OCH_3**) were characterized by additional bidimensional NMR experiments (COSY, TOCSY, NOESY, HSQC and HMBC) in order to corroborate their chemical structure. As example of the characterization studies, Figure 3 shows ^{1}H NMR experiments of **OAc-Malt-Tz-C_{10}-Azo-OCH_3** and **Malt-Tz-C_{10}-Azo-OCH_3** and Figure 4 shows a bidimensional TOCSY experiment of **OAc-Malt-Tz-C_{10}-Azo-OCH_3** where all the protons of the sugar rings can be assigned. The exact masses were determined for the azo-glycoamphiphiles by mass spectrometry (see Supporting Information SI2 for MicroTOF Mass Spectrometry of **Malt-Tz-C_{10}-Azo-OCH_3** as example) and the results also confirmed the proposed structures of these materials.

Thermal properties

It is known that carbohydrate amphiphiles usually have liquid crystal properties. These compounds have the ability to self-assemble and undergo microphase segregation due to hydrophobic interactions of aliphatic chains and the extensive hydrogen bonded network formed by the polar carbohydrate heads. Phase transition temperatures are dependent on the nature of the carbohydrate moiety, the length of the hydrophobic alkyl chain and the type of linker between the two parts, as was previously reported for **Malt-Tz-C_{16}** and analog compounds[21].

The thermal properties of the synthesized azo-glycolipids were studied by thermogravimetric analysis (TGA), polarized light microscopy and differential scanning calorimetry (DSC). Compounds were observed after drying under vacuum.

In peracetylated precursors, 5 % weight losses were observed at temperatures close to 300 ºC. However, thermogravimetric curves for deprotected azo-glycolipids display 5% weight losses at temperatures among 170-245 ºC (in samples previously dried and immediately analyzed). See Supporting Information for TGA analysis SI3.

The peracetylated precursors were studied by polarized optical microscopy and DSC as a function of temperature, see Table 1. On **OAc-Malt-Tz-Azo-C_{16}** and **OAc-Malt-Tz-C_{10}-Azo-OCH_3** mesomorphic behavior was not observed and compounds melted directly from a crystalline state to an isotropic liquid. **OAc-Malt-Tz-C_5-Azo-C_8** was an amorphous solid having a glass transition around 57ºC (DSC).

Decomposition of azo-glycolipids was observed by optical microscopy at temperatures above 170º C and the sample became

brown, most probably due to decomposition of the sugar units[27]. On an experiment performed up to 200º C, decomposition around 170º C- 175º C was confirmed by DSC for **Malt-Tz-Azo-C$_{16}$** and **Malt-Tz-C$_5$-Azo-C$_8$** while for **Malt-Tz-C$_{10}$-Azo-OCH$_3$**, the decomposition started at 120ºC, a decrease of the baseline was observed, according to TGA experiments. Then DSC studies of the azo-glycolipids were performed by heating the compounds to 120 ºC (maximum) in order to avoid the thermal decomposition of the samples. Under these conditions the second and successive scans were reproducible. By DSC measurements, **Malt-Tz-Azo-C$_{16}$** has a thermal transition at around 80ºC, however above at this temperature the sample is highly viscous and difficult to characterize by optical microscopy. Nevertheless by optical microscopy, at temperatures above approximately 140 ºC, the sample becomes more fluid and can be characterized as liquid crystal according to the optical observations. **Malt-Tz-C$_5$-Azo-C$_8$** has a glass transition, observed by DSC measurement at around 78º C and also exhibits a birefringent texture corresponding to a highly viscous mesophase (see Supporting Information SI 4). In **Malt-Tz-C$_{10}$-Azo-OCH$_3$** a glass transition was observed at 67ºC for the second and the third cycle.

Table 1 Thermal characterization of peracetylated compounds and azo-glycolipid compounds:

Compound	Thermal transition (ºC) [ΔH kJ/mol][a]
OAc-Malt-Tz-Azo-C$_{16}$[b]	Cr 171 [48.3] I
OAc-Malt-Tz-C$_5$-Azo-C$_8$[b]	g 57 I
OAc-Malt-Tz-C$_{10}$-Azo-OCH$_3$[b]	Cr 132[38.4] I
Malt-Tz-Azo-C$_{16}$[c]	Cr 58 [5,2] Cr´ 79 [3.3] Cr´´ 140[d] Sm
Malt-Tz-C$_5$-Azo-C$_8$[c]	g 78 Sm
Malt-Tz-C$_{10}$-Azo-OCH$_3$[c]	g 67 Sm + Dec.

[a]DSC termal cycles were carried out in nitrogen atmosphere (10ºC.min-1). [b]The heating cycles were carried out up to 200 ºC. Data corresponding to second heating scan. [c] The first and second heating cycles were carried out up to 120º. Cr = crystal, I = isotropic liquid, g = glassy state, Sm = smectic phase.[d] Data friom Polarized light microscopy.

In an effort to identify the mesophase by XRD, attemps to obtain oriented fibers of the compounds were made. A fiber of **Malt-Tz-C$_5$-Azo-C$_8$** compound was obtained around 160ºC; at lower temperatures any fiber can be drawn. Oriented fibers of **Malt-Tz-Azo-C$_{16}$** and **Malt-Tz-C$_{10}$-Azo-OCH$_3$** could not be obtained. X-ray patterns of **Malt-Tz-C$_5$-Azo-C$_8$** fiber was recorded at room temperature for 15 h. Bragg reflexions in low-angle region corresponding to second, third and fifth lamellar order were found. The lamellar spacing is close to 61.6 Å which is larger than the length of one molecule (44.1 Å) but smaller than twice the extended molecular length. This result indicates that an interdigitated bilayer is probably formed. In the high angle region a diffuse, broad maximum was found.

Gel properties

The solubility and gelation ability of the azo-glycolipids were examined in different solvents by dissolving the compound in the corresponding solvent with a concentration in the range of 0.5-5% wt. **Malt-Tz-Azo-C$_{16}$** and **Malt-Tz-C$_{10}$-Azo-OCH$_3$** azo-glycoamphiphiles are not soluble at room temperature (RT) in the selected solvents, except DMSO. However, **Malt-Tz-C$_5$-Azo-C$_8$** compound has a different behavior; it is soluble at RT in different solvents such as chloroform, THF, DMF, DMSO, methanol and the mixture of DMSO/water. It is not soluble in water at RT, but if the solution was heated and cooled down to RT the product remains soluble.

The results for the three compounds on the selected solvents are summarized in Table 2. If the compound was not soluble at RT the mixtures were first dissolved on heating and then cooled down to RT and a solution, a precipitate or a gel was observed depending on the solvent. **Malt-Tz-Azo-C$_{16}$** compound gelates in water in a minimum gelation concentration of 5 wt % to form a gel in absence of other organic solvents. This gel is opaque but in a mixture DMSO/water it becomes a little bit transparent as it can be seen at Figure 5. The minimum gelation concentration decreases until 1.5 wt % for the mixture of the two solvents (DMSO/water, 1:1 wt). **Malt-Tz-C$_{10}$-Azo-OCH$_3$** also formed a gel in a DMSO/water mixture (1:1 wt) at 2 wt % as minimum gelation concentration. This gel is also opaque. These molecules have a highly hydrophobic tail and the presence of an organic co-solvent as DMSO, in addition to water, is required for complete solubilization on cooling and subsequent gel formation. In all the cases, gels are stable at RT and thermoreversibles. Sol states were reached by heating the septum-capped test tube in a block heater, for **Malt-Tz-Azo-C$_{16}$** (5.0 wt % water) at 90ºC, **Malt-Tz-Azo-C$_{16}$** (1.5 wt % DMSO/water 1:1 wt) at 85ºC and for **Malt-Tz-C$_{10}$-Azo-OCH$_3$** (2.0 wt % DMSO/water 1:1 wt) at 100ºC. In contrast, **Malt-Tz-C$_5$-Azo-C$_8$** compound cannot form a gel even in mixtures of solvents.

In order to corroborate the presence of π-π stacking and H-bonding interactions ^{1}H-NMR experiments have been performed to study the groups involved in the self-assembly. As an example, Figure 6a collects the ^{1}H NMR spectra of **Malt-Tz-C$_{10}$-Azo-OCH$_3$** compound (2.9 mg) in 0.40 mL of DMSO-d$_6$ at RT. The spectra were recorded upon successive addition of 0.04 mL of water to the DMSO-d$_6$ solution. A displacement of the signals was observed as consequence of aggregation, up to 0.16 mL of water (1:0.4 DMSO/water). A shielding for the H signal of the triazole ring ($\Delta^1H_{Tz}\delta$ = 0.072 ppm) and for the H signals of the azobenzene aromatic ring ($\Delta^1H_{arom}\delta$ = 0.036 ppm in both signals) was found. This fact supports the contribution of π-π stacking to the aggregation of the amphiphiles promoted by water addition. Moreover, a simultaneous deshielding for the NH signal is also

detected ($\Delta^1H_{NH}\delta$ = 0.075 ppm), which can be assigned to self-assembly through hydrogen bonding.

Different solubility and ability to gelate has been observed in the synthesized compounds and that fact can be related to the position of the azobenzene inside the hydrophobic chain, when the azobenzene group is located in the middle (**Malt-Tz-C$_5$-Azo-C$_8$**), the compound is soluble in several organic solvents and surprisingly soluble in water while when the azobenzene is located at the edge a gel could be formed; if it is directly linked to the sugar polar head the compound (**Malt-Tz-Azo-C$_{16}$**) gelates only in water but when the azobenzene is at the end of the hydrophobic chain (**Malt-Tz-C$_{10}$-Azo-OCH$_3$**), the gel had to be formed in a mixture of a soluble solvent, DMSO, and a insoluble solvent, water.

The self-assembled structure of the gels derived from **Malt-Tz-Azo-C$_{16}$** and **Malt-Tz-C$_{10}$-Azo-OCH$_3$** were studied by electron microscopy (SEM and TEM), which revealed a characteristic fibrillar network of supramolecular gels[2,3,8].

SEM measurements of the xerogels show bundles of fibers which form the tridimensional network responsible for the gel structure. The fibers of **Malt-Tz-Azo-C$_{16}$** gel, either in water or in a mixture of DMSO/water 1:1 wt, show diameters around 40-60 nm. However, fibers from gels in water seem to be shorter than in the mixture of solvents where they have several μm of length. Moreover, in the gel from the mixture of solvents, some wider fibers can also be measured around 100 nm of diameter (see Supporting Information SI5). **Malt-Tz-C$_{10}$-Azo-OCH$_3$** xerogels images shows fibers diameters mainly around 200- 250 nm but narrower fibers of around 80 nm can be also observed (see Figure 7a).

Fibrillar structures have also been observed by TEM but in this technique, a dried dilute solution of the gel must be used (0.1 wt % concentration in water or in DMSO/water) and negative staining with uranyl acetate was made. The observed fibers have over 10-20 nm diameter either for **Malt-Tz-Azo-C$_{16}$** samples or **Malt-Tz-C$_{10}$-Azo-OCH$_3$**, see Supporting Information SI5.

Torsion was detected on the microphotographs, specifically on **Malt-Tz-Azo-C$_{16}$** (see TEM microphotograph in Supporting Information SI5) and **Malt-Tz-C$_{10}$-Azo-OCH$_3$** DMSO/water gels; Figure 7.b shows a single **Malt-Tz-C$_{10}$-Azo-OCH$_3$** twisted ribbon observed by SEM. This torsion could be related to the molecular chirality of the molecules which is traduced into the chiral helicity of the supramolecular arrangement.

Additionally, in order to obtain hydrogels having a lower ratio of azo-derivatives, mixtures were prepared with an azo-glycolipid (**Malt-Tz-C$_5$-Azo-C$_8$** or **Malt-Tz-Azo-C$_{16}$**) and a previously known hydrogelator **Malt-Tz-C$_{16}$**, see Figure 1. **Malt-Tz-C$_5$-Azo-C$_8$** and **Malt-Tz-Azo-C$_{16}$** azo-glycolipids where selected because of their structural similarity with the hydrogelator and their solubility or ability to gelify in water. **Malt-Tz-C$_{10}$-Azo-OCH$_3$** was not used because is not soluble in water. In these cases, CD and absorption spectra could be recorded from 200 to 600 nm, to investigate both regions corresponding to triazole and azobenzene groups, in contrast to gels made from DMSO/water mixtures, where only region of azobenzene group can be observed. **Gel I** was formed by **Malt-Tz-C$_5$-Azo-C$_8$** and **Malt-Tz-C$_{16}$** (1:10 molar ratio), 1 wt % of **Malt-Tz-C$_{16}$** hydrogelator on water. In this mixture, the azo-amphiphile **Malt-Tz-C$_5$-Azo-C$_8$** is able to gelate. Other mixtures, increasing the azo-compound, avoid the gel formation. To compare the influence of the azoamphiphile, **Gel II** was formed by **Malt-Tz-Azo-C$_{16}$** and **Malt-Tz-C$_{16}$**, in the same ratio (1:10 molar ratio), 1 wt % of **Malt-Tz-C$_{16}$** hydrogelator on water. Microscopical observations show a similar fibrillar structure formed in these mixtures compared to **Malt-Tz-C$_{16}$** compound alone[23].

Study and control of the chiral supramolecular arrangement

The presence in the supramolecular gels of photoactive units as the azobenzene moieties allows the control of their nanostructure and subsequently of the gel properties. If a chiral organization is expected in the gel the CD spectroscopy is a great interest in order to characterize the chiral assemblies and potential changes of the organization. With this purpose UV-vis and CD spectra of the azo-gelators, were registered simultaneously in DMSO solutions as well as in gel states

In DMSO solutions with similar absorbance values to gel states (5 10^{-5} M), the $\lambda_{máx}$ in the UV absorption spectrum appears at 362 nm for all compounds **Malt-Tz-Azo-C$_{16}$**, **Malt-Tz-C$_5$-Azo-C$_8$** and **Malt-Tz-C$_{10}$-Azo-OCH$_3$** (see Supporting Information SI6) and the solutions were CD silent. These spectroscopic results point to the azobenzene chromophores are isolates in the DMSO solutions. No aggregation is detected. However, a **Malt-Tz-C$_5$-Azo-C$_8$** water solution, with a similar absorption to **Gel I** (4.5 10^{-5} M) exhibit a maximum absorption of the π-π* band of the azobenzene groups at 343 nm, i.e. it is blue-shifted concerning maximum absorption of the isolate azobenzene groups. Moreover, in the water solution of **Malt-Tz-C$_5$-Azo-C$_8$** , CD was observed. These results indicate azobenzene chromophores are H-aggregate in the water solution (see Supporting Information SI7).

The absorption spectrum of **Malt-Tz-C$_{10}$-Azo-OCH$_3$** gel (2 wt % DMSO/water (1:1)) (Figure 8) exhibits a $\lambda_{máx}$ at 335 nm, blue shifted respect to $\lambda_{máx}$ of the free azobenzene units in DMSO solutions. This fact points to the association of the azobenzene moieties in H-aggregates. Moreover a negative Cotton effect is detected in the CD spectrum corresponding with the absorption band of the azobenzene units. The UV-vis and CD spectra of the **Malt-Tz-Azo-C$_{16}$** gel (1.5 wt % DMSO/water (1:1 wt) cannot be registered due to the sample crystallization.

The presence of azobenzene groups can be used to induce modifications of the supramolecular structure of the gel by the irradiation with UV light. However, after the UV irradiation at 365 nm for 150 minutes no changes were detected in the UV-vis and CD spectra of **Malt-Tz-C$_{10}$-Azo-OCH$_3$** gel (2 wt % DMSO/water (1:1)) (Figure 8). In this conditions the gel is stable, and indicate that the *trans-cis* isomerization of the azobenzene groups do not occur, probably because the dense packing of the azobenzene groups prevents the *trans-cis* reactivity[28].

The π-π* band of the azobenzene units in the UV-vis spectra **Gel I** (**Malt-Tz-C$_5$-Azo-C$_8$** as photoactive compound) and **Gel II** (**Malt-Tz-Azo-C$_{16}$** as photoactive compound) show a hypsochromic shift in relation to the band of free azobenzene chromophores suggesting a H-aggregation. Both gels show CD signals due to triazole group and azobenzene group (Figure 9), however some differences are noteworthy. At shorter wavelength **Gel I** exhibit a Cotton effect around 240 nm due to the absorption band of the triazole group which is directly bonded to the chiral

group (maltose unit). At longer wavelength negative Cotton effect associated with the π–π* absorption band of the azobenzene moiety is detected. Moreover, the CD spectrum of the fresh **Gel II** seems to show two positive couplets corresponding to triazole groups (shorter wavelength) and azobenzene units (longer wavelength). **Gel II**, surprisingly after storage for 6 h, the ellipticity values of the negative bands increase and a new CD band is detected at 365 nm. Probably a reorganization of the sample occurs[13b] in the sandwich formed under measurement conditions.

Both **Gel I** and **Gel II** were irradiated with UV light at 365 nm in order to evaluate the effect on the supramolecular organization of the *trans-cis* isomerization of the azobenzene groups. The UV-vis spectra of **Gel I** (Figure 9), after 365 nm irradiation, shows clearly the presence of *cis*-azoisomer: the absorption at 365 nm decreases and at 450 nm increases. The photostatonary state is reached after irradiation for 2 minutes. The *trans-cis* isomerization reduce the *trans*-azoisomer concentration and, consequently, the negative CD signal related to azobenzene group disappears, while negative signal corresponding to the triazole, only decreases. It can be deduced that gel-sol transition does not happen because not fully extinction of signals was reached. This fact was macroscopically corroborated with a gel irradiation on a tube, gel disruption was not detected and only a color change from red to yellow was obtained, probably due to a partial disruption of the aggregates[13b]. When the sample was kept 24 h under dark conditions, a total recovery of the initial UV-vis and CD spectra was obtained. After irradiation for 150 minutes **Gel II** show no evidence of *trans-cis* isomerization but an increasing of the CD band at 365 nm was observed (see Figure 9). This band could be probably caused by a photoinduced reorganization of the chiral supramolecular structure or simple reorganization with time which involves azobenzene groups. By storing the sample 24h in darkness, CD and absorption signals were not modified.

Gel I works as a photoresponsive mixture while **Gel II** has no response to light. This fact can be due to the presence of the azobenzene in the middle of the hydrophobic chain in contrast to the azobenzene derivative of **Gel II,** which has the azobenzene directly linked to the sugar polar head.

Experimental section

Characterization data (elemental analysis, ^{1}H and ^{13}C NMR, FTIR and MS) for the intermediate compounds (1-4) are collected in the Supporting Information, see SI1. Only data corresponding to the azobenzene acid precursors, peracetylated and final azo-amphiphilic glycolipids are included in this section.

HOOC-Azo-C$_{16}$ ($C_{29}H_{42}N_2O_3$): ^{1}H NMR (400MHz, DMSO-d$_6$, 70ºC, δ ppm): 0.85 (t, 3H, J= 6.8 Hz) –$(CH_2)_{12}$-C*H*$_3$, 1.17-1.52 (m, 24H) -(C*H*$_2$)$_{12}$-CH$_3$, 1.69-1.80 (m, 2H) –O-CH$_2$-C*H*$_2$-, 4.10 (t, 2H, J=6,6 Hz) –O-*CH*$_2$-CH$_2$-, 7.10-7.14 (m, 2H) *Har*, 7.86-7.92 (m, 4H) *Har*, 8.09-8.12 (m, 2H) *Har*.^{13}C NMR (100 MHz, DMSO-d$_6$, 70ºC, δ ppm): 14.2 –$(CH_2)_{12}$-*C*H$_3$, 22.4, 25.8, 29.0, 29.0, 29.3, 29.3, 29.3, 31.6 -(*C*H$_2$)$_{15}$-, 68.7 –O-*C*H$_2$, 115.4, 122.5, 125.3, 130.9 *C*Har, 132.8, 146.8, 155.2, 162.6, *C*ar, 167.1 *C*OOH. ESI: 467.2 [M+H]$^+$. IR (KBr, cm^{-1}): 2953, 2919, 2868, 2850, 1680, 1601, 1582, 1501, 1470, 1418, 1404, 1303, 1290, 1248, 1143, 1107, 1026, 941, 864, 838, 809, 775, 721, 544.

HOOC-C$_5$-Azo-C$_8$ ($C_{26}H_{36}N_2O_4$):^{1}H NMR (400MHz, DMSO-d$_6$, 50ºC, δ ppm): 0.85 (t, 3H, J= 6.8 Hz) –$(CH_2)_5$-C*H*$_3$, 1.26 (d, 3H, J=6.4 Hz) –CH-C*H*$_3$, 1.20-1.80 (m, 16H) -(C*H*$_2$)-, 2.24 (t, 2H, J=7.3 Hz) –C*H*$_2$-COOH, 4.05 (t, 2H, J=6.4 Hz) –O-C*H*$_2$-CH$_2$-, 4.55 (m, 1H) –O-C*H*-CH$_3$, 7.07-7.10 (m, 4H) *Har*, 7.79-7.82 (m, 4H) *Har*.^{13}C NMR (100 MHz, DMSO-d$_6$, 50ºC, δ ppm): 13.9 -CH$_2$-*C*H$_3$, 19.4 *C*H$_3$-O- 21.9, 24.2, 24.7, 25.0, 28.3, 28.6, 31.2, 33.5, 35.7, -(*C*H$_2$)-, CO-*C*H$_2$-CH$_2$-, 67.7 O-*C*H$_2$-CH$_2$, 73.4 -O-*C*H-CH$_3$, 114.9, 115.7, 124.0, 124.1 *C*Har x8, 145.8, 146.0, 160.0, 160.8 *C*ar x4, 174.4 NH-*C*O-Car. ESI: 441.1 [M+H]$^+$, 463.1 [M+Na]$^+$. IR (KBr, cm^{-1}): 2936, 2859, 2868, 1706, 1600, 1578, 1498, 1473, 1464, 1314, 1257, 1241, 1206, 1146, 1111, 1059, 1042, 1006, 972, 961, 935, 854, 845, 553.

HOOC-C$_{10}$-Azo-OCH$_3$ ($C_{24}H_{32}N_2O_4$): ^{1}H NMR (400MHz, DMSO-d$_6$, 45ºC, δ ppm): 1.17-1.53 (m, 14H) -(C*H*$_2$)$_7$-, 1.68-1.77 (m, 2H) C*H*$_2$-CH$_2$-O, 2.15 (t, 2H, J= 7.6 Hz) –C*H*$_2$-CO, 3.84 (s, 3H) O-C*H*$_3$, 4.05 (t, 2H, J=6.8 Hz) –O-C*H*$_2$-CH$_2$-, 7.03-7.12 (m, 4H) C*Har*, 7.76-7.85 (m, 4H) C*Har*. ^{13}C NMR (100 MHz, DMSO-d$_6$, 45ºC, δ ppm): 25.0, 25.9, 29.0, 29.1, 29.2, 29.3 -(*C*H$_2$)$_8$-, 34.4 CH$_2$-*C*H$_2$-CO, 56.0 -O-*C*H$_3$, 68.5 -O-*C*H$_2$-CH$_2$-, 115.0, 115.5, 124.5, 124.5, *C*Har, 146.7, 146.8, 161.4, 161.9 *C*ar, 174.9 *C*O-NH. ESI: 413.1 [M+H]$^+$, 435.1 [M+Na]$^+$. IR (KBr, cm^{-1}): 2936, 2916, 2848, 1709, 16202, 1582, 1497, 1469, 1465, 1317, 1296, 1278, 1246, 1151, 1107, 1029, 1018, 843, 823, 558.

Synthesis of Hepta-O-acetyl-β-maltosyl azide 1:Trimethylsilyl azide (543 µl, 4.13 mmol) and tin tetrachloride (173 µl, 1.48 mmol) were added, at room temperature and under argon, to a solution of β-D-maltose octaacetate (2.00 g, 2.95 mmol) in dry CH_2Cl_2 (6 mL, 0.5 M). The reaction mixture was stirred at room temperature and the reaction was monitored by TLC (6:4 hexane/ethyl acetate). After 24 h, CH_2Cl_2 was added and the solution was washed with saturated Na_2CO_3 and twice with water. The organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The product was purified by flash chromatography using hexane/ethyl acetate 6:4. A white solid was obtained (1.59 g, 80%). For characterization data see Supporting Information.

Synthesis of Propargylamide azo derivatives 2, 3 and 4: Azobenzene acids (1.05 g, 2.25 mmol) and hydroxybenzotriazole (0.35 g, 2.60 were dissolved in 20 mL of anhydrous tetrahydrofuran. Propargylamine (0.16 mL, 2.50 mmol) was added. The solution was cooled to 0 ºC. A solution of EDC (418 mg, 2.18 mmol) in 15 mL of anhydrous THF was added. The reaction mixture was stirred for 2 days at room temperature or under slightly heating. The reaction was monitored by TLC with hexane/ethyl acetate 7:3 as eluent. The mixture was filtered and

the solvent was removed under reduced pressure. 250 mL of dichoromethane 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 resulting white solid was purified by recrystallization or flash chromatography. A red solid was obtained (yield around 40-70% depending on the compound). For characterization data see Supporting Information.

Synthesis of acetylated maltose conjugates OAc-Malt-Tz-Azo-C_{16}, OAc-Malt-Tz-C_5-Azo-C_8, and OAc-Malt-Tz-C_{10}-Azo-OCH_3: Propargyl derivatives (433 mg, 0.83 mmol), maltosylazide (562 mg, 0.85 mmol), copper(I) bromide (27.1 mg, 0.19 mol) and N-pentamethyldiethylenetriamine (PMDETA) (35 µL, 0.17 mmol) were dissolved in anhydrous dimethylformamide (6mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 days. The reaction was monitored by TLC with hexane/ethyl acetate 1:1 as eluent. The catalyst was removed by filtration and the solvent was removed under reduced pressure. The reaction was poured into 150 mL of water. The aqueous phase was extracted three times, each with 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 solid was purified by flash chromatography using initially dichloromethane/ethyl acetate 6:4 and then increasing the polarity. A red solid was obtained (819 mg, 82-90%).

OAc-Malt-Tz-Azo-C_{16} ($C_{58}H_{80}N_6O_{19}$):^{1}H (400 MHz, $CDCl_3$, 25ºC, δ ppm): 0.87 (t, 3H, J=6.7 Hz) -$(CH_2)_{11}$-C*H*$_3$, 1.18-1.40 (m, 22H) -CH_2-(C*H*$_2$)$_{11}$-CH_3, 1.41-1.52 (m, 2H) -C*H*$_2$-$(CH_2)_{11}$-CH_3, 1.78-1.86 (m, 2H) –O-CH_2-C*H*$_2$-, 1.85 (s, 3H) C*H*$_3$-CO-O-C2′, 2.01 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 2.12 (s, 3H), 2.17 (s, 3H), *CH*$_3$-CO-O-, 3.97-3.99 (m, 2H) *H5′, H5*, 4.05- 4.10 (m, 4H) –O-C*H*$_2$-CH_2, *H4′*, *H6b,* 4.23-4.27 (m, 2H) *H6a*, *H6′a*, 4.49 (dd, 1H, $J_{5′,6′b}$=1,8 Hz, $J_{6′a,6′b}$=12.5 Hz) *H6′b*, 4.69-4.79 (m, 2H) NH-C*H*$_2$-triazole, 4.88 (dd, 1H, $J_{1,2}$= 3.9 Hz, $J_{2,3}$= 10.5 Hz) *H2*, 5.07 (dd, 1H, $J_{3,4}$= 9.8 Hz, $J_{4,5}$= 9.8 Hz) *H4*, 5.34 (dd, 1H, $J_{1′,2′}$= 9.1 Hz, $J_{2′,3′}$=9.3 Hz) *H2′*, 5.37 (dd, 1H, $J_{2,3}$=10.5 Hz, $J_{3,4}$= 9.8 Hz) *H3*, 5.44 (d, 1H, $J_{1,2}$=3.9 Hz) *H1*, 5.46 (dd, 1H, $J_{2′,3′}$=9.3 Hz, J $_{3′,4′}$=9.1 Hz) *H3′*, 5.87 (d, 1H, $J_{1′,2′}$= 9.1 Hz) *H1′*, 6.91 (t, 1H, J=5.5 Hz) -N*H*-CO, 6.99-7.01 (m, 2H) *Har*, 7.81 (s, 1H) C*H*-triazole, 7.90-7.93 (m, 6H) *Har*. ^{13}C (100 MHz, $CDCl_3$, 25ºC, δ ppm): 14.1 $(CH_2)_{14}$-*C*H_3, 20.2, 20.6, 20.7, 20.8, 20.8, *C*H_3-CO-O-22.7, 26.0, 29.2, 29.4, 29.5, 29.5, 29.6, 29.7, 30.9, 31.9 -(*C*H_2)$_{14}$-CH_3, 35.4 triazole-*C*H_2-NH, 61.5 *C6*, 62.4 *C6′*, 67.9 *C4*, 68.4 O-C*H*$_2$-$(CH_2)_{14}$, 68.8 *C5*, 69.2 *C3*, 70.0 *C2*, 70.9 *C2′*, 72.4 *C4′*, 75.0 *C3′*, 75.4 *C5′*, 85.4 *C1′*, 95.9 *C1*, 114.8 *C*Har, 121.2 *C*H triazole, 122.6, 125.2, 127.9 *C*Har, 134.9 *C*ar, 145.1 CHtriazole-*C*triazole-CH_2, 146.8, 154.6, 162.3 *Car*, 166.8 NH-*C*O-Car, 169.1 CH_3-*C*O-O-C2′, 169.4 CH_3-*C*O-O-C4, 169.9, 169.9 CH_3-*C*O-O-C3/C3′, 170.3, 170.5, 170.6 CH_3-*C*O-O-C2/C6/C6′.MALDI-TOF (DCTB+NaTFA): 1187,6 $[M+Na]^+$. IR (KBr, cm^{-1}): 3351, 2922, 2851, 1749, 1644, 1604, 1532, 1503, 1470, 1370, 1234, 1141, 1036, 859.

OAc-Malt-Tz-C_5-Azo-C_8 ($C_{55}H_{74}N_6O_{20}$):^{1}H (400 MHz, $CDCl_3$, 25ºC, δ ppm): 0.90 (t, 3H, J=7.0 Hz) -$(CH_2)_5$-C*H*$_3$, 1.27- 1.89 (m, 16H) -(C*H*$_2$)-, 1.35 (d, 3H, J= 6.2 Hz) C*H*$_3$-CH-O, 1.87 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 2.13 (s, 3H), 2.15 (s, 3H) C*H*$_3$-CO-O-, 2.26 (t, 2H, J=7,6 Hz) CO-C*H*$_2$-$(CH_2)_3$-, 3.96- 4.02 (m, 2H) *H5*, *H5′*, 4.04 (t, 2H, J=6.4 Hz) –O-C*H*$_2$-CH_2, 4.05-4.11 (m, 1H) *H6b*, 4.15 (dd, 1H, $J_{3′,4′}$= 8.8 Hz, $J_{4′,5′}$= 9.8 Hz) *H4′*, 4.25-4.30 (m, 2H) *H6a*, *H6′a*, 4.43-4.58 (m, 4H) *H6′b*, O-C*H*-CH_3-, Ctriazole-C*H*$_2$-NH- 4.90 (dd, 1H, $J_{1,2}$= 3.9 Hz, $J_{2,3}$= 10.5 Hz) *H2*, 5.09 (dd, 1H, $J_{3,4}$= 9.9 Hz, $J_{4,5}$= 9.9 Hz) *H4,* 5.34 (dd, 1H, $J_{1′,2′}$= 9.3 Hz, $J_{2′,3′}$=9.5 Hz) *H2′*, 5.39 (dd, 1H, $J_{2,3}$=10.5 Hz, $J_{3,4}$= 9.9 Hz) *H3*, 5.46 (d, 1H, $J_{1,2}$=3.9 Hz) *H1*, 5.47 (dd, 1H, $J_{2′,3′}$=9.5 Hz, J $_{3′,4′}$=8.8 Hz) *H3′*, 5.87 (d, 1H, $J_{1′,2′}$= 9.3 Hz) *H1′*, 6.11 (t, 1H, J=5.7 Hz) CH_2-N*H*-CO, 6.98-6.99 (m, 4H) Har, 7.73 (s, 1H) CH-triazole, 7.85-7.80 (m, 4H) Har. ^{13}C (100 MHz, $CDCl_3$, 25ºC, δ ppm): 14.1 $(CH_2)_5$-C*H*$_3$, 19.7 CH-C*H*$_3$, 20.2 C*H*$_3$-CO-O-C2′, 20.6, 20.7, 20.8, 20.8, C*H*$_3$-CO-O-22.6, 25.2, 25.5, 25.7, 28.9, 29.2, 31.8 -(C*H*$_2$)-, 34.9 Ctriazole-C*H*$_2$-NH, 36.3 –CO-C*H*$_2$-CH_2-, 36.4 CH_3-CH-C*H*$_2$-, 61.4 *C6*, 62.4 *C6′*, 67.9 *C4*, O-C*H*$_2$-CH_2, 68.8 *C5*, 69.2 *C3*, 70.0 *C2*, 70.9 *C2′*, 72.4 *C4′*, 74.2 O-*CH*-CH_3, 75.1 *C3′*, 75.4 *C5′*, 85.3 *C1′*, 95.9 *C1*, 114.8, 115.2 *C*Har, 120.7 *C*Htriazole, 124.3, 124.3, CHar, 145.2 CHtriazole-*Ctriazole*-CH_2, 146.8, 147.0, 160.4, 160.9 *Car*, 169.1 CH_3-*C*O-O-C2′, 169.4 CH_3-*C*O-O-C4, 169.9, 169.9 CH_3-*C*O-O-C3/C3′, 170.3, 170.5, 170.6 CH_3-*C*O-O-C2/C6/C6′, 172.8 NH-*C*O-CH_2.

MALDI-TOF (DCTB+NaTFA): 1161,5 [(M+Na]. IR (KBr, cm^{-1}): 3326, 2935, 2858, 1748, 1599, 1499, 1373, 1234, 1147, 1036, 841.

OAc-Malt-Tz-C_{10}-Azo-OCH_3 ($C_{53}H_{70}N_6O_{20}$):^{1}H (400 MHz, $CDCl_3$, 25ºC, δ ppm): 1.31- 1.72 (m, 14H) –(C*H*$_2$)$_7$-, 1.77- 1.87 (m, 2H) –O-CH_2-C*H*$_2$-(CH_2)-, 1.87 (s, 3H) C*H*$_3$-CO-O-C2′, 2.03 (s, 3H), 2.05 (s, 6H), 2.09 (s, 3H), 2.013 (s, 3H), 2.16 (s, 3H), C*H*$_3$-CO-O-, 2.20 (t, 2H, J= 7,5 Hz) CO-C*H*$_2$-CH_2-, 3.91 (s, 3H) -O-C*H*$_3$, 3.97-4.02 (m, 2H) *H5*, *H5′*, 4.05 (t, 2H, J= 6,8 Hz) –O-C*H*$_2$-CH_2, 4.06-4.12 (m, 1H) *H6b*, 4.16 (dd, 1H, $J_{3′,4′}$= 9.1 Hz, $J_{4′,5′}$= 9.1 Hz) *H4′*, 4.25-4.30 (m, 2H) *H6a*, *H6′a*, 4.47-4.58 (m, 3H) *H6′b*, Ctriazole-C*H*$_2$-NH-, 4.91 (dd, 1H, $J_{1,2}$= 4.2 Hz, $J_{2,3}$= 10.6 Hz) *H2*, 5.10 (dd, 1H, $J_{3,4}$= 9.8 Hz, $J_{4,5}$= 9.8 Hz) *H4*, 5.34 (dd, 1H, $J_{1′,2′}$= 9.1 Hz, $J_{2′,3′}$= 9.1 Hz) *H2′*, 5.40 (dd, 1H, $J_{2,3}$= 9.8 Hz, $J_{3,4}$= 9.8 Hz) *H3*, 5.46-5.50 (m, 2H) *H1*, *H3′*, 5.86 (d, 1H, $J_{1′,2′}$= 9.1Hz) *H1′,* 6.08 (t, 1H, J= 5.6Hz) CH_2-*NH*-CO, 6.99-7.03 (m, 4H) *Har*, 7.72 (s, 1H) C*H*-triazole, 7.87-7.90 (m, 4H) *Har*. ^{13}C (100 MHz, $CDCl_3$, 25ºC, δ ppm): 20.2 *C*H_3-CO-O-C2′, 20.6, 20.7, 20.8, 20.8, *C*H_3-CO-O- 25.5, 26.0, 29.2, 29.3, 29.3, 29.3, 29.4, 29.5, -(*C*H_2)-, 34.8 Ctriazole-*C*H_2-NH, 36.5 –CO-*C*H_2-CH_2-, 55.6 –O-*C*H_3, 61.4 *C6*, 62.4 *C6′*, 67.9 *C4*, 68.3 O-*C*H_2-CH_2, 68.8 *C5*, 69.2 *C3*, 70.0 *C2*, 71.0 *C2′*, 72.4 *C4′*, 75.1 *C3′*, 75.4 *C5′*, 85.3 *C1′*, 95.9 *C1*, 114.2, 115.6 *C*Har, 120.8 *C*Htriazole, 124.3, 124.3 *C*Har, 145.3 CHtriazole-*C*triazole-CH_2, 146.9, 147.1 *Car* 161.2 *Car*-O-CH_2, 161.5 *Car*-O-CH_3, 169.1 CH_3-*C*O-O-C2′, 169.4 CH_3-*C*O-O-C4, 169.9, 169.9 CH_3-*C*O-O-C3/C3′, 170.3, 170.5, 170.6 CH_3-*C*O-O-C2/C6/C6′, 173.2 NH-*C*O-CH_2. MALDI-TOF (DCTB+NaTFA): 1133,5 $[M+Na]^+$. IR (KBr, cm^{-1}): 3360, 2926, 2851, 1748, 1652, 1601, 1582, 1501, 1370, 1238, 1147, 1038, 840.

Synthesis of azo-glycosyl conjugates : The protected triazole-disaccharide-heptaacetate derivatives (**OAc-Malt-Tz-Azo-C_{16}**, **OAc-Malt-Tz-C_5-Azo-C_8** and **OAc-Malt-Tz-C_{10}-Azo-OCH_3**) (197.7 mg, 0.17 mmol) were dissolved in 7.5 mL of anhydrous THF. Sodium methoxide (81.0 mg, 1.50 mmol) was 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 to reach pH= 6-7, the resin was filtered off and the solvent was evaporated in vacuo. The resulting solid was purified by flash chromatography using initially dichloromethane/methanol acetate 9:1 and then increasing the polarity. A red solid was obtained (75-90%).

Malt-Tz-Azo-C16 ($C_{44}H_{66}N_6O_{12}$):^{1}H (400 MHz, DMSO-d_6, 25ºC, δ ppm): 0.85 (t, 3H, J=7.0 Hz) -$(CH_2)_{13}$-C*H*$_3$, 1.20-1.40 (m, 26H) -CH_2-(C*H*$_2$)$_{13}$-CH_3, 1.73-1.76 (m, 2H) -C*H*$_2$-$(CH_2)_{13}$-CH_3, 3.04-3.87 (m, 12H) *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, 4.56 (d, 2H, J=5.5 Hz) Ctriazole-C*H*$_2$-NH, 5.04 (d, 1H, $J_{1,2}$= 3.6 Hz) *H1*, 5.56 (d, 1H, $J_{1',2'}$= 9.2 Hz) *H1´*, 7.12- 7.15 (m, 2H) *Har*, 7.68-7.93 (m, 4H) *Har*, 8.08-8.09 (m, 2H) *Har*, 8.18 (s, 1H) C*H*-triazole, 9.28 (t, 1H, J=5.5 Hz) CH_2-N*H*-CO. ^{13}C (100 MHz, DMSO-d_6, 25ºC, δ ppm): 14.4 $(CH_2)_{14}$-*C*H_3, 22.5, 25.8, 28.9, 29.2, 29.4, 29.5, 31.7, -(*C*H_2)$_{14}$-CH_3, 35.4 triazole-*C*H_2-NH, 60.70, 61.3, 70.4, 71.5, 73.1, 73.7, 74.1, 77.1, 78.6, 79.7 *C2*, *C3*, *C4*, *C5*, *C6*, *C3´*, *C4´*, *C5´*, *C6´*, 68.5 O-*C*H_2-$(CH_2)_{14}$, 71.5 *C2´*, 87.7 *C1´*, 101.7 *C1*, 115.6 *C*Har, 122.4 *C*Htriazole, 125.3, 129.1 *C*Har, 135.5 *C*ar, 145.4 CHtriazole-*C*triazole-CH_2, 146.5, 153.9, 162.4 *Car*, 165.4 NH-*C*O-ar. MicrOTOF-Q: $[M+Na]^+$ 893.461 calcd.: 893.463.IR (KBr, cm-1): 3320 (wide band), 2918, 2849, 1577, 1418, 1251, 1040, 850.

Malt-Tz-C5-Azo-C8 ($C_{41}H_{60}N_6O_{13}$):^{1}H (400 MHz, MeOD, 25ºC, δ ppm): 0.92 (t, 3H, J=6.8 Hz) -$(CH_2)_5$-C*H*$_3$, 1.31- 1.88 (m, 16H) -C*H*$_2$-, 1.35 (d, 3H, J= 5.8 Hz) C*H*$_3$-CH-O, 2.29 (t, 2H, J=7.4 Hz) CO-C*H*$_2$-$(CH_2)_3$-, 3.29- 3.91 (m, 10H) *H3*, *H4*, *H5*, *H6a*, *H6b*, *H3´*, *H4´*, *H5´*, *H6´a*, *H6´b*, 3.48 (dd, 1H, $J_{1,2}$=3.8 Hz, $J_{2,3}$= 9.7 Hz) *H2*, 3.95 (dd, 1H, $J_{1',2'}$= 9.1 Hz, $J_{2',3'}$= 9.1 Hz) *H2´*, 4.08 (t, 2H, J= 6.5 Hz) –O-C*H*$_2$-, 4.47 (s, 2H) Ctriazole-C*H*$_2$-NH-, 4.51-4.60 (m, 1H) O-C*H*-CH_3, 5.24 (d, 1H, $J_{1,2}$= 3.8 Hz) *H1*, 5.62 (d, 1H, $J_{1',2'}$= 9.1 Hz) *H1´*, 7.02-7.06 (m, 4H) *Har*, 7.83-7.86 (m, 4H) *Har*, 8.08 (s, 1H) C*H*-triazole.^{13}C (100 MHz, MeOD, 25ºC, δ ppm): 13.0 CH_2-*C*H_3, 18.6 O-CH-*C*H_3, 22.2, 25.1, 25.2, 25.3, 28.6, 29.0, 29.5, 31.6 -(*C*H_2)-, 34.2 Ctriazole-*C*H_2-NH, 35.4 –CO-*C*H_2-CH_2-, 36.2 CH_3-CH-*C*H_2-, 67.8 O-*C*H_2-CH_2, 72.2 *C2´*, 72.8 *C2*, 60.4, 61.3, 70.1, 73.5, 73.7, 73.8, 76.8, 78.2, 78.9 *C3*, *C4*, *C5*, *C6*, *C3´*, *C4´*, *C5´*, *C6´*-O-*C*H-CH_3, 88.0 *C1´*, 101.5 *C1*, 114.4, 115.4 *C*H ar, 122.0 *C*Htriazole, 123.9, 123.9 *C*Har, 145.0 CHtriazole-*C*triazole-CH_2, 146.6, 146.8, 160.5, 161.3 *C*ar, 174.7 NH-*C*O-CH_2. MicrOTOF MS: 845.4309 $[M+H]^+$, 867.4118 $[M+Na]^+$. Calcd: 845.4218 $[M+H]^+$, 867.4110 $[M+Na]^+$. IR (KBr, cm^{-1}): 3364, 2928, 2857, 1652, 1598, 1498, 1248, 1148, 1039, 840.

Malt-Tz-C10-Azo-OCH3 ($C_{39}H_{56}N_6O_{13}$):^{1}H (400 MHz, DMSO-d_6, 25ºC, δ ppm: 1.27- 1.56 (m, 14H) –(C*H*$_2$)$_7$-, 1.71- 1.78 (m, 2H) –O-CH_2-C*H*$_2$-(CH_2)-, 2.11 (t, 2H, J= 7.4 Hz) CO-C*H*$_2$-CH_2-, 3.07- 3.90 (m, 12H) *H2*, *H3*, *H4*, *H5*, *H6a*, *H6b*, *H2´*, *H3´*, *H4´*, *H5´*, *H6´a*, *H6´b*, 3.85 (s, 3H) ar-O-C*H*$_3$, 4.05 (t, 2H, J= 6.0 Hz) –O-C*H*$_2$-CH_2, 4.30 (d, 2H, J= 3.9 Hz) Ctriazole-C*H*$_2$-NH-, 4.54-4.60 (m, 1H) O*H*, 4.60-4.67 (m, 1H) O*H*, 4.95-5.02 (m, 2H) O*H*, 5.07 (d, 1H, J_{1-2}=2.6 Hz) *H1*, 5.50-5.51 (m, 1H) O*H*, 5.58-5.63 (m, 2H) *H1´*,O*H*, 5.79-5.80 (m, 1H) O*H*, 7.09-7.13 (m, 4H) *Har,* 7.82-7.85 (m, 4H) *Har*, 8.08 (s, 1H) C*H*-triazole, 8.33 (t, 1H, J= 5.6 Hz) CH_2-N*H*-CO.^{13}C (100 MHz, DMSO-d_6, 25ºC, δ ppm): 25.6, 25.9, 29.1, 29.2, 29.2, 29.3, 29.4, 29.5, -(*C*H_2)-, 34.5 Ctriazole-*C*H_2-NH, 35.7 –CO-*C*H_2-CH_2-, 56.1 –O-*C*H_3, 68.4 O-*C*H_2-CH_2, 60.7, 61.2, 70.3, 72.0, 72.9, 73.7, 74.0, 77.2, 78.4, 79.6 *C2*, *C3*, *C4*, *C5*, *C6*, *C2´*, *C3´*, *C4´*, *C5´*, *C6´*, 87.6 *C1´*, 101.4 *C1*, 115.0, 115.4 *C*Har, 122.3 *C*Htriazole, 124.6, 124.6 *C*Har, 145.5 CHtriazole-Ctriazole-CH_2, 146.5, 146.7 *C*ar**,** 161.4 *C*ar-O-CH_2**,** 161.9 *C*ar-O-CH_3**,** 172.6 NH-*C*O-CH_2. MicrOTOF MS: 817.3968 $[M+H]^+$, 839.3773 $[M+Na]^+$. Calcd: 817.3978 $[M+H]^+$, 839.3797 $[M+Na]^+$. IR (KBr, cm^{-1}): 3376 (wide band), 2920, 2850, 1642, 1582, 1602, 1253, 1148, 1025, 840.

Characterization Techniques

^{1}H and ^{13}C NMR spectra were recorded on a BRUKER AV-400 spectrometer. IR spectra were measured on Thermo NICOLET Avatar 360 FT-IR spectrophotometer using KBr pellets. Mass Analysis was performed using a MALDI+/TOF Brüker Microflex system with a different matrix depending on the compound (DCTB or DHB) and MicroTOF Brüker equipment for exact mass measurements. Elemental analysis was performed using a Perkin Elmer CHN2400 microanalyzer.

The mesogenic behavior was studied by optical microscopy with an Olympus BH-2 polarizing microscope equipped with a Linkam THMS hot-stage central processor and a CS196 cooling system. Differential scanning calorimetry (DSC) was performed using a DSC 2910 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. Thermogravimetric analysis (TGA) was performed using a TGA Q5000IR from TA Instruments at a rate of 10 ºC/min under a nitrogen atmosphere. XRD measurements of the oriented fiber sample were performed with an evacuated Pinhole camera (Anton-Paar) operating with a point-focused Ni-filteres Cu-Kα beam. Sample was held in Lidemann glass capillaries and the patterns were collected on flat photographic films perpendicular to the X-ray beam.

CD spectra were registered using a Jasco J-810 equipment. In order to probe no contribution of lineal dichroism in the circular dichroism, CD spectra of the samples were registered by rotating the sandwich every 60 degrees around the light beam axis. Sample preparation for CD measurement: **Malt-Tz-Azo-C16** and **Malt-Tz-C10-Azo-OCH3** gels were heated and a drop of hot solution was placed over a UV fused silica sandwich with a 0.025 mm Teflon spacer and left to cool at room temperature for 10 min. Gel I and Gel II mixed hydrogels were placed onto the sandwich with a 0.025 mm spacer at room temperature.

SEM measurements were performed using a FESEM Carl

Zeiss MERLIN at the laboratory of 'Servicio de Microscopia de la Universidad de Zaragoza'. The sample was fixed onto glass and coated with platinium. TEM measurements were performed using a TECNAI G^2 20 (FEI COMPANY) at the laboratory of Advanced Microscopy of the 'Instituto de Nanociencia de Aragon'. For TEM sample preparation, a drop of the solution (0.1% wt 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.

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.

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Conclusions

Three maltose-based azo-amphiphiles have been synthesized and gel-forming properties have been determined. Azobenzene chromophore was placed at different positions of the hydrophobic chain and a maltose sugar head was linked by a copper(I)-catalyzed azide-alkyne [3+2] cycloaddition in good yield. Mesomorphic fluid state was found for these compounds. While one was soluble in water, two of the three compounds synthesized, having the azobenzene close to the triazole group or at the end of the chain, form gels in pure water or in a mixture of DMSO and water at different minimum concentrations from 5 to 1.5 wt %. Gels are stable at room temperature. Torsion on the resulting self-assembled fibrillar network was observed by different electronic microcopies and a chiral arrangement was confirmed by CD.

The designed molecules have a photosensitive group and a modulation of the supramolecular arrangement with light has been tested. No changes were obtained in DMSO/water gels due to their high ordered organization. Moreover, hydrogels formed by combination of azobenzene compounds synthesized in this paper and a hydrogelator previously prepared, were also studied. The tridimensional network of the hydrogel has been successfully doped with a similar structure having a photoresponsive unit. Reversible modifications in the azobenzene structure under irradiation with UV light were performed when the water soluble azobenzene derivative was used**.** The CD signal related to azobenzene group disappeared and the photostationary state was reached. It indicates that some structural modifications have been promoted and make this material capable of switching one part of this structure while the gel structure remains inalterable. This mixture forms a rewritable supramolecular hydrogel to be applied in the field of soft matterials.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Characterization data of intermediate compounds (1-4). MicroTOF Mass Spectrometry of **Malt-Tz-C_{10}-Azo-OCH_3**. Thermogravimetric analysis of peracetylated precursors and azo-glycolipids. Microphotograph of **Malt-Tz-C_5-Azo-C_8**. SEM and TEM images of the synthesized azo-glycolipids. . Absorption spectra of **Malt-Tz-Azo-C_{16}**, **Malt-Tz-C_5-Azo-C_8** and **Malt-Tz-C_{10}-Azo-OCH_3** in DMSO solution (5 10^{-5}). SI7. CD and absorption spectra of **Malt-Tz-C_5-Azo-C_8** in a 4.5 10^{-5} M water solution.

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