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Gelators

Pseudopeptide-Based Hydrogels Trapping Methylene Blue and Eosin Y

Lorenzo Milli, Nicola Zanna, Andrea Merlettini, Matteo Di Giosia, Matteo Calvaresi, Maria Letizia Focarete, and Claudia Tomasini*[a]

Abstract: We present herein the preparation of four different hydrogels based on the pseudopeptide gelator Fmoc-L-Phe-D-Oxd-OH (Fmoc = fluorenylmethyloxycarbonyl), either by changing the gelator concentration or adding graphene oxide (GO) to the water solution. The hydrogels have been analysed by rheological studies that demonstrated that pure hydrogels are slightly stronger compared to GO-loaded hydrogels. Then the hydrogels efficiency to trap the cationic methylene blue (MB) and anionic eosin Y (EY) dyes has been analyzed. MB is efficiently trapped by both the pure hydrogel and the GO-loaded hydrogel through π–π interactions and electrostatic interactions. In contrast, the removal of the anionic EY is achieved in less satisfactory yields, due to the unfavourable electrostatic interactions between the dye, the gelator and GO.

Introduction

Adsorption is a very efficient and low-cost method for water purification. Many types of materials were used as adsorbent: carbon, silica gel,[1] activated alumina[2] or polymeric materials. Often these adsorbent materials suffer from low efficiencies, high operational costs and the generation of secondary waste. To overcome these drawbacks, polymeric hydrogels (chemical hydrogels) have been proposed as innovative adsorbents.[3–9] More recently the use of physical gels has been introduced, as they usually are biocompatible,[10] and may be used in medicine as scaffolds or drug-delivery systems.[11–16]

In this paper we show the possibility to employ the peptide-based hydrogelator Fmoc-L-Phe-D-pGlu-OH (Fmoc = fluorenylmethyloxycarbonyl; Figure 1)[17] as a dye adsorbant. This molecule belongs to a group of foldamers containing the 4-carboxy-5-methyl-oxazolidin-2-one unit (Oxd)[18] or the *p*-glutamic acid unit (pGlu).[19] These molecules cause a local constraint in the pseudopeptide chain that favours the formation of secondary structures,[20–22] fibers[23–25] and gels.[26–28] Thus we prepared hydrogels based on Fmoc-L-Phe-D-pGlu-OH to test them for the adsorption of Methylene Blue (MB), a cationic dye, and Eosin Y (EY), an anionic dye, as these molecules may be used as model pollutants.

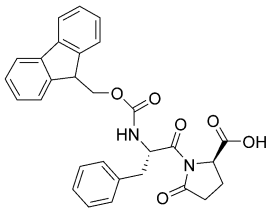

Figure 1. Chemical structure of the gelator Fmoc-L-Phe-D-pGlu-OH, described in this work.

In addition, we prepared composite GO-hydrogels based on Fmoc-L-Phe-D-pGlu-OH to test if the introduction of graphene oxide (GO) could improve or reduce the capacity of these hydrogels to trap the dyes. Indeed graphene oxide is particularly attractive for the doping due to its low cost, large specific surface area in aqueous solutions (736.6 $m^2 g^{-1}$)[29] and its high performance as an adsorbent in polymer/hydrogel composites.[30–38]

Results and Discussion

Fmoc-L-Phe-D-pGlu-OH was synthesized by standard reactions.[17] To prepare the hydrogels, we applied a new method to avoid the use of toxic substances:[39] the gelation trigger is a pH slow variation induced by the hydrolysis of glucono-δ-lactone (GdL), which is a non-toxic food additive with the E575 code.

Fmoc-L-Phe-D-pGlu-OH was added to water, together with NaOH, which is required to dissolve the peptide, as it is insoluble at pH ≈ 4, while it is soluble at pH ≈ 10. Then GdL was added to slowly decrease the solution pH. When the pK_a value of the molecule was reached, the molecule precipitated getting organized into fibers that in turn trap the water molecules, yielding a hydrogel.[40] The composite GO-hydrogel was obtained following the same method, but replacing water with a GO suspension in water (1 mg mL^{-1}).

[a] *L. Milli, Dr. N. Zanna, A. Merlettini, M. Di Giosia, Dr. M. Calvaresi, Prof. M. L. Focarete, Prof. C. Tomasini*
Dipartimento di Chimica Ciamician, Università di Bologna
Via Selmi, 2-40126 Bologna (Italy)
E-mail: claudia.tomasini@unibo.it

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Using this technique, we prepared four hydrogels **A**, **B**, **C** and **D** by using Fmoc-L-Phe-D-pGlu-OH in 1 or 2% w/w concentration and pure water or GO/water suspension (Figure 2). The most common diagnostic test of gelation is tube inversion.[41,42] In this test, a sample tube containing the hydrogel is turned upside down to ascertain if the sample would flow under its own weight. A gel is assumed to be a sample that has a yield stress that prevents it from flowing down the tube, while a sol is taken to be a sample that flows down the tube.

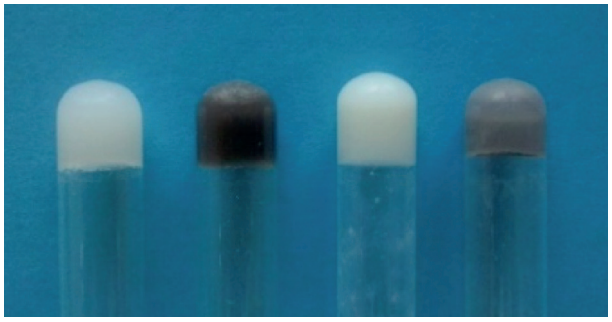

Figure 2. Photographs of hydrogels **A**–**D** prepared with Fmoc-L-Phe-D-pGlu-OH at different concentrations. From left to right: **A**, 1% gelator/H_2O; **B**, 1% gelator/GO/H_2O; **C**, 2% gelator/H_2O; **D**, 2% gelator/GO/H_2O.

The first analysis useful to understand the strength of the hydrogel is the measurement of its melting point (T_{gel}), which is the range of temperatures over which the gel decomposes (Table 1). T_{gel} was determined by heating the test tubes (diameter: 8 mm) containing the gel with a glass ball (diameter: 5 mm, weight: 165 mg) on the top of it.

Table 1. T_{gel} of hydrogels **A**–**D** in H_2O or GO/H_2O as a function of increasing amounts of gelator (expressed in % w/w).

Hydrogel	Gelator conc. [% w/w]	GO [1 mg mL^{-1}]	T_{gel} [°C]
A	1	no	44–83[a]
B	1	yes	50–75[a]
C	2	no	55–94[a]
D	2	yes	61–85[a]

[a] The gel is not thermoreversible and syneresis occurs on heating.

At room temperature the ball is suspended atop the gel. The T_{gel} is the range of temperatures between the point reached when the ball starts to penetrate inside the gel and the point reached when the ball touches the test-tube bottom, which indicates the total hydrogel disruption. All our samples give syneresis with water ejection after heating. Pure hydrogels **A** and **C** show final melting points higher than the corresponding GO-loaded hydrogels, while **B** and **D** have a higher initial melting point with respect to **A** and **C**. All these data suggest that pure hydrogels are stronger than the GO-doped ones, which in turn are more elastic and resistant to deformation. This property contrasts the initial ball penetration and enhances the initial melting temperatures of hydrogels **B** and **D**. More details both on the nature and on the strength of these gels have been obtained by rheological studies.

Strain sweep and gelation kinetics experiments have been performed: the strength of the hydrogels **A**, **B**, **C** and **D** was evaluated in terms of storage modulus and linear viscoelastic region (G′ and LVE, Table 2 and Figure S1).

Table 2. Storage modulus (G'), linear viscoelastic region (LVE) and gelation time of hydrogels **A**–**D**.

Hydrogel	G' [Pa]	LVE [γ %]	Gelation time [min]
A	5000	1.5	450
B	4000	3	450
C	6000	1	400
D	4000	3	400

[a] The gel is not thermoreversible and syneresis occurs on heating.

Hydrogel **C**, obtained from the gelator at 2% w/w concentration, was characterized by the highest storage modulus among the analyzed samples, with values of almost 6000 Pa, and LVE region of 1% (Figure 3A, Table 2). The addition of GO to this hydrogel (**D**) led to a lower storage modulus value (around 4000 Pa) and a more extended LVE region, up to 3% (Figure 3A, Table 2). Considering the hydrogels **A** and **B**, obtained with the gelator at 1% w/w concentration either with or without GO addition, **A** was characterized by a storage modulus of 5000 Pa and LVE region of 1.5% while the GO-loaded **B** by a storage modulus of 4000 Pa and LVE region of

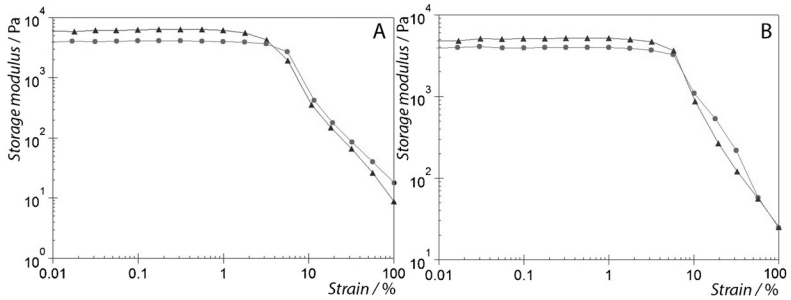

Figure 3. Strain-dependence of storage modulus of hydrogel obtained starting from 2% w/w (A) and 1% w/w (B) of gelator concentration loaded with GO (●) and without GO (▲). The analyses were performed about 20 hours after the gelation had begun.

3% (Figure 3B, Table 2). Hydrogels were also characterized by means of frequency sweep experiments (Figure S1, Supporting Information) showing that for all the studied hydrogels both the storage and loss moduli were almost independent from the applied frequency, indicating the "solid-like" rheological behaviour of the analyzed hydrogels in the range from 0.1 to 100 rad s^{-1}.

Although the introduction of GO in the hydrogels is not crucial for the modification of their mechanical properties, pure hydrogels **A** and **C** are slightly stronger compared to GO-loaded hydrogels **B** and **D**. The presence of GO might cause a partial loss of the 3D non-covalent interactions in the gel network, which are essential to obtain a solid and strong gel.

To further investigate this aspect, gelation kinetics experiments have been performed (Figure 4). The gelation behaviour was investigated in terms of both total gelation time and starting point of the gelation process, that is, the first point at which the storage modulus and loss modulus start to significantly differentiate and increase. Figures 4A,B show that the gelation kinetics always follow a one-step mechanism. Comparing the gelation behavior of hydrogels **C** and **D** (2% w/w gelator concentration either with or without GO), we could notice that the gelation mechanism is triggered earlier for hydrogel **C** than for the GO loaded sample **D** (around 50 and 100 min, respectively), while the total gelation time is about 400 min for both samples (Figure 4A, Table 2). A similar behaviour was found for hydrogels **A** and **B** (1% w/w gelator concentration with and without GO), as the gelation process started earlier for hydrogel **A** compared to the GO-loaded hydrogel **B** (around 100 and 150 min, respectively). In this case for both hydrogels the total gelation time was about 450 min (Figure 4B, Table 2).

These results suggest that, in both cases, GO interferes with the formation of the non-covalent interactions between dipeptides that lead to the gel formation, slows down the gelation process and leads to the formation of a weaker hydrogel compared to the plain one, thus confirming the results obtained with the strain sweep experiments.

SEM images of the xerogels obtained drying a sample of Fmoc-L-Phe-D-pGlu-OH hydrogels **A** and **B** do not show a dramatic difference between the two fibers network (Figure 5).

Due to the interest in the preparation of new materials able to trap aromatic pollutants,[43,44] we wondered if our hydrogels could be usefully applied to filter polluted water. This is only a basic study on the behaviour and properties of the materials that in the future could be used to build devices able to clean water. For this reason we chose to check the ability of both hydrogels, even though the GO-loaded hydrogel **B** showed worse mechanical properties compared with hydrogel **A**. Indeed pollutant molecules can interact with GO either through π–π interactions with the GO aromatic region or through hydrogen bond and electrostatic interactions due to its hydrophilic functional groups.

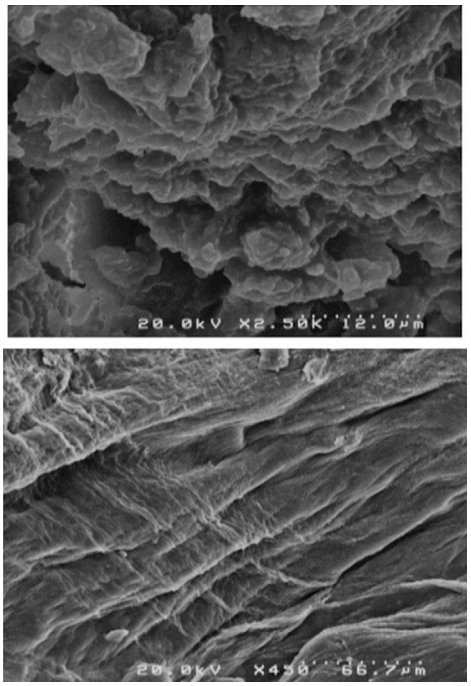

Figure 5. SEM images of the xerogels obtained drying a sample of Fmoc-L-Phe-D-pGlu-OH hydrogels **A** and **B** at 1% concentration either without GO (left) or with GO (right).

Thus we checked the efficiency of hydrogels **A**–**B** in trapping MB, that is, a cationic aromatic heterocycle with strong absorption at 664 nm (Figure 6). Both Fmoc-L-Phe-D-pGlu-OH and GO are rich in aromatic groups that, in principle, should favour the absorption of aromatic dyes through π–π interactions. Moreover, the gelator contains two carboxylic groups, whereas GO

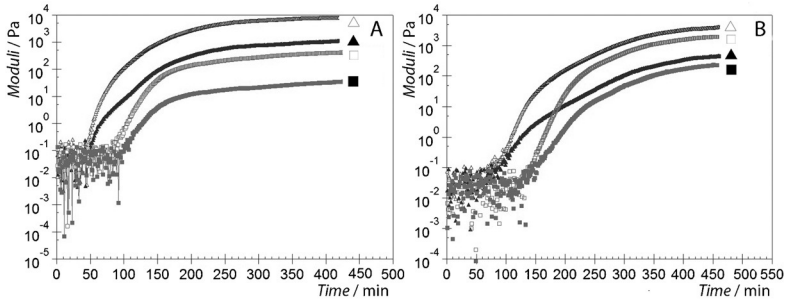

Figure 4. Time-dependence of storage modulus (△, □) and loss modulus (▲, ■) for hydrogel obtained starting from Fmoc-L-Phe-D-pGlu-OH at 2% w/w (A) and 1% w/w (B) of gelator concentration loaded with (■, □) and without GO (▲, △).

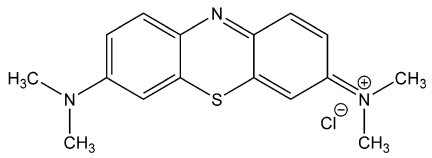

Figure 6. Chemical structure of MB.

is rich in basic groups, such as epoxides, hydroxyl or carboxylic groups: this excess of negative charges should favour the absorption of cationic MB.

We prepared hydrogels **A**–**B** in glass columns for flash chromatography (internal diameter 1.0 cm, equipped with a glass frit, Figure S2, Supporting Information), so that the dye aqueous solution could freely flow after interaction with hydrogels. First we allowed 0.5 mL of a water solution of gelator at 1% w/w concentration to gelate on the bottom of the glass column, using the GdL method. After eight hours, we added another layer of hydrogel prepared with 1.0 mL of a water solution containing 1% w/w gelator either without GO or with GO. The gelation trigger was again the GdL methodology. When the hydrogel was formed (16 hours) we added to the column about 50 mL of a 0.13 mM blue solution of MB in water. The liquid flowed slowly through hydrogels **A** and **B**, producing transparent water, which was analysed by UV/Vis spectroscopy to check the amount of dye present in each portion of eluted solutions. The results are reported in Figure 7.

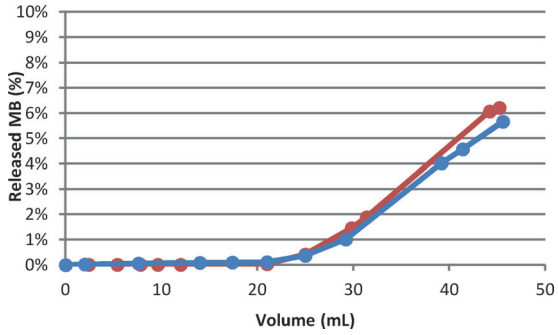

Figure 7. A) Graph of the released dye by the pure hydrogel **A** (red) and of the GO doped hydrogel **B** (blue), based on UV/Vis analysis at 664 nm.

Both hydrogels **A** and **B** clean completely the first 20 mL of dye solution, then a very modest amount of MB is slowly released, reaching an overall amount of 5.7% for **A** and 6.2% for **B**, respectively. This preliminary result is very interesting, as both hydrogels **A** and **B** efficiently trap MB. The gelator Fmoc-L-Phe-D-Oxd-OH is the principal responsible for this effect, as it holds the dye both by π–π interactions between the aromatic groups and by electrostatic interactions between the carboxylic groups of the gelator and the ammonium groups of MB. In contrast, the presence of GO does not show significant effects, as the two results are very similar.

After these satisfactory results, we checked how these systems would behave with very concentrated solutions, so we prepared two solutions of MB in water at different concentrations: 5 mL of a 1.26 mM solution (2 mg in 5 mL) and 10 mL of a 0.63 mM solution (2 mg in 10 mL). We also replaced the glass columns with medical-grade disposable hypodermic plastic syringes to avoid the presence of the glass frit. In a typical run, we prepared 0.5 mL of a water solution of gelator at 1% w/w concentration and allowed it to gelate on the bottom of the syringe, using the GdL method. This layer was built to act as a support for the next layer. After eight hours, we added another layer of hydrogel prepared with 1.0 mL of a water solution containing 1 or 2% w/w gelator with or without GO. The gelation trigger was again the GdL methodology. After 16 hours, the syringe was ready for elution of dye containing water solutions (Figure 8).

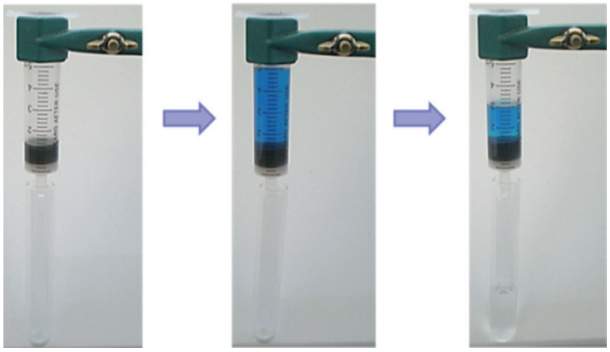

Figure 8. Example of MB solution in water flowing through a disposable hypodermic plastic syringes loaded with hydrogel: the recovered water is colourless.

We made several trials, in which we changed both the MB concentration and the hydrogel (Table 3). The results show that both hydrogels **A** and **B** are far less efficient compared with the results reported in Figure 6 in the presence of concentrated solutions, even though the moles of gelator are always much higher that the moles of eluted MB. Interestingly, in this case the GO-doped hydrogel **B** is more efficient than **A**, suggesting that GO may help the trapping. Finally, excellent results have been obtained with 2% hydrogels **C** and **D**, as they both efficiently trap all the dye.

In addition to MB, which is a cationic dye, we checked the ability of these hydrogels to trap Eosin Y (EY), an anionic dye

Table 3. Adsorption of MB by hydrogels **A**–**D**.

Hydrogel	Gelator [μmol]	GO [mg]	MB [μmol]	MB solution [mL]	Detained MB [%]
A	29.2	0	6.3	5	11
A	29.2	0	6.3	10	40
B	29.2	1	6.3	5	80
B	29.2	1	6.3	10	82
C	48.6	0	6.3	5	100
C	48.6	0	6.3	10	100
D	48.6	1	6.3	5	100
D	48.6	1	6.3	10	100

(Figure 9), to understand how important the electrostatic interactions are compared with the π–π aromatic interactions in the process of dye removal. Thus, we prepared two solutions of EY in water at different concentrations: 5 mL of a 0.62 mM solution (2 mg in 5 mL) and 10 mL of a 0.31 mM solution (2 mg in 10 mL).

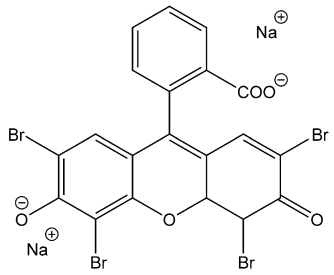

Figure 9. Chemical structure of EY.

Although a large excess of gelator compared to EY (nearly 10:1 ratio) has been used to prepare hydrogels **A** and **B**, a reduced efficiency is always observed for the dye removal (Table 4). This outcome may be attributed to the unfavourable electrostatic interactions between the gelator, EY and GO that have all negative charges. Despite this disadvantageous effect, satisfactory results have been obtained with hydrogels **C** and **D**, probably thanks to the high number of π–π aromatic interactions between EY and the gelator, which is in large excess compared to the dye (>15:1 ratio).

Table 4. Adsorption of EY by hydrogels **A**–**D**.

Hydrogel	Gelator [μmol]	GO [mg]	MB [μmol]	MB solution [mL]	Detained MB [%]
A	29.2	0	3.1	5	22
A	29.2	0	3.1	10	83
B	29.2	1	3.1	5	29
B	29.2	1	3.1	10	17
C	48.6	0	3.1	5	95
C	48.6	0	3.1	10	90
D	48.6	1	3.1	5	94
D	48.6	1	3.1	10	87

Conclusions

In conclusion we prepared four different hydrogels based on the pseudopeptide Fmoc-L-Phe-D-Oxd-OH, either by changing the gelator concentration or adding GO to the water solution. Rheological studies have been carried out on all these hydrogels and demonstrated that, although the introduction of GO in the hydrogels is not crucial for the modification of their mechanical properties, pure hydrogels **A** and **C** are slightly stronger compared to GO-loaded hydrogels **B** and **D**, which, in turn, are more elastic. The presence of GO might cause a partial loss of the 3D non-covalent interactions in the gel network, which are essential to obtain a solid and strong gel.

Then we checked the ability of hydrogels **A**–**D** to trap the cationic dye methylene blue (MB) and the anionic dye eosin Y (EY). A preliminary test made on the ability of hydrogels **A** and **B** to trap MB, showed that both hydrogels are very efficient. Indeed both the gelator and GO are rich in aromatic groups that favour the absorption of aromatic dyes through π–π interactions. In addition, the gelator contains two carboxylic groups and GO is rich in epoxides, hydroxyl and carboxylic groups: all these groups efficiently interact with the cationic MB by electrostatic interactions that enhance the material efficiency. To further validate the importance of electrostatic interactions to trap dyes, we tested the removal of the anionic EY. As we expected, all the trails furnished less satisfactory results, both with pure and with GO-loaded hydrogels.

These preliminary studies on the properties and the behaviour of four peptide-based hydrogels towards dye adsorption could be profitably applied to the preparation of devices able to trap aromatic dyes.

Experimental Section

Materials

All chemicals and solvents were purchased by Sigma–Aldrich, VWR or Iris Biotech and used as received. Acetonitrile was distilled under an inert atmosphere before use. MilliQ water (Millipore, resistivity = 18.2 $m\Omega\,cm^{-1}$) was used throughout. GO was purchased by Cheap Tubes (thickness 0.7–1.2 nm, lateral dimensions 300–800 nm, number of layers = 1, purity >99 wt%, prepared by modified Hummers method).

Synthesis of Fmoc-L-Phe-D-pGlu-OH

To a stirred solution of Fmoc-L-Phe-OH (1 mmol, 0.39 g) and HBTU (1.1 mmol, 0.42 g) in dry acetonitrile (10 mL) under an inert atmosphere, D-Oxd-OBn (1 mmol, 0.24 g) in dry acetonitrile (5 mL) was added at room temperature, followed by a solution of triethylamine (2.2 mmol, 0.30 mL). The solution was stirred for 40 min under an inert atmosphere, then acetonitrile was removed under reduced pressure and replaced with ethyl acetate. The mixture was washed with brine, 1 N aqueous HCl (3×30 mL) and with 5% aqueous $NaHCO_3$ (1×30 mL), dried over sodium sulphate and concentrated in vacuo. Fmoc-L-Phe-D-Oxd-OBn was obtained pure after silica gel chromatography (cyclohexane/ethyl acetate 9:1→7:3 as the eluent) in 60% yield (0.6 mmol, 0.36 g).

To remove the Bn protective group, Fmoc-L-Phe-D-Oxd-OBn (0.36 g, 0.6 mmol) was dissolved in MeOH (30 mL) under nitrogen. C/Pd (35 mg, 10% w/w) was added under nitrogen. A vacuum was created inside the flask using the vacuum line. The flask was then filled with hydrogen using a balloon (1 atm). The solution was stirred for 4 h under a hydrogen atmosphere. The product was obtained pure as a solid in 98% yield (0.59 mmol, 0.30 g) after filtration through filter paper and concentration in vacuo. For the characterization, see ref. [17]

Conditions for the gel formation

A portion of Fmoc-L-Phe-D-pGlu-OH (10–20 mg, depending on the final concentration, ranging from 0.5% to 2% w/w) was placed in a test tube (diameter: 8 mm), then MilliQ water (≈0.95 mL) and aqueous NaOH 0.5 N (1.0 equiv) were added and the mixture was

stirred and sonicated in turn for about 30 min, until sample dissolution. Glucono-δ-lactone (GdL: 1.1 equiv) was added in one portion to the mixture. After a rapid mixing to allow the GdL complete dissolution, the sample was allowed to stand quiescently until gel formation, which occurs over a number of hours, reaching slowly pH ≈ 5. This method may be applied also to prepare gels in syringes, as the gelation procedure is slow enough to transfer the mixture anywhere before solidification. In the case of composite hydrogels, we followed the same steps using 1 mL of GO solution in water (1 mg mL^{-1}) instead of 1 mL of MilliQ water.

Conditions for T_{gel} determination

T_{gel} was determined by heating some test tubes (diameter: 8 mm) containing the gel and a glass ball (diameter: 5 mm, weight: 165 mg) on the top of it. When the gel is formed, the ball is suspended atop. The T_{gel} is a range of temperatures in which the first point indicates when the ball starts to penetrate inside the gel, while the second point indicates when the ball touches the bottom of the test tube. Some hydrogel samples melt, producing a clear solution, while in other cases the gelator shrinks and water is ejected, as syneresis occurs.

Rheology

Rheology experiments were carried out on an Anton Paar Rheometer MCR 102 using a parallel plate configuration (25 mm diameter). Experiments were performed at a constant temperature of 23 °C controlled by the integrated Peltier system and a Julabo AWC100 cooling system. To keep the sample hydrated a solvent trap was used (H-PTD200). All the analyses (Frequency, Amplitude and Time sweeps analyses) were performed with a fixed gap value of 0.5 mm on gel samples prepared directly on the upper plate of the rheometer once the gelation reaction was completed. The samples were prepared the day before the analysis and left overnight to complete the gelation process (around 20 hours). Oscillatory amplitude sweep experiments (γ: 0.01–100 %) were carried out to determine the linear viscoelastic (LVE) range at a fixed frequency of 1 rad s^{-1}. Once the LVE of each hydrogel was established, frequency sweep tests were performed (ω: 0.1—100 rad s^{-1}) at constant strain within the LVE region of each sample. Time-sweep oscillatory tests were carried out at fixed frequency (1 rad s^{-1}) and strain amplitude (within the LVE region). In this case the gelator solution (≈ 0.5 mL, fresh prepared) was placed in between the two parallel plates and the dynamic moduli were monitored (1 measurement point every 60 seconds) until a plateau was reached.

SEM analysis

Scanning electron micrographs of gold-sputtered samples were recorded using a Hitachi 6400 field-emission gun scanning electron microscope.

Preparation of glass columns to trap dyes

In a typical run, we prepared 0.5 mL of a water solution of gelator at 1% w/w concentration and allowed it to gelate on the bottom of a glass chromatography column (1.0 cm diameter, equipped with a glass frit), using the GdL method. This layer was built to act as a support for the next layer. After 8 h, we added another layer of hydrogel prepared with 1.0 mL of a water solution containing 1% w/w gelator with or without GO. The gelation trigger was again the GdL methodology. When the hydrogel was formed (16 h) we added to the column a solution (50 mL) of methylene blue (2 mg) in water.

Preparation of disposable syringes to trap dyes

In a typical run, we prepared 0.5 mL of a water solution of gelator at 1% w/w concentration and allowed it to gelate on the bottom of the syringe, using the GdL method. This layer was built to act as a support for the next layer. After 8 h, we added another layer of hydrogel prepared with 1.0 mL of a water solution containing 1 or 2% w/w gelator either with or without GO. The gelation trigger was again the GdL methodology. After 16 h, the syringe was ready for elution of dye-containing water solutions.

UV/Vis analysis

The kinetics of MB detaining solutions was studied by UV/Vis spectroscopy (Cary 300 bio) following the absorption intensity of MB at 664 nm. The amount of MB or EY found in the final solutions was also detected by UV/Vis spectroscopy (Cary 300 bio). The absorption intensity of EY was followed at 525 nm.

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Keywords: dye adsorption · gelators · graphene oxide · hydrogels · pseudopeptides

[1] S. K. Parida, S. Dash, S. Patel, B. K. Mishra, *Adv. Colloid Interface Sci.* **2006**, *121*, 77–110.
[2] T. F. Lin, J. K. Wu, *Water Res.* **2001**, *35*, 2049–2057.
[3] R. F. Gomes, A. C. N. de Azevedo, A. G. B. Pereira, E. C. Muniz, A. R. Fajardo, F. H. A. Rodrigues, *J. Colloid Interface Sci.* **2015**, *454*, 200–209.
[4] E. Karadag, D. Saraydin, O. Guven, *Polym. Bull.* **1996**, *752*, 745–752.
[5] H. Kaşgöz, *Polym. Bull.* **2006**, *56*, 517–528.
[6] Y. S. Jeon, J. Lei, J. H. Kim, *J. Ind. Eng. Chem.* **2008**, *14*, 726–731.
[7] A. Bhatnagar, M. Sillanpää, *Adv. Colloid Interface Sci.* **2009**, *152*, 26–38.
[8] B. Özkahraman, I. Acar, S. Emik, *Polym. Bull.* **2011**, *66*, 551–570.
[9] S. Deng, H. Xu, X. Jiang, J. Yin, *Macromolecules* **2013**, *46*, 2399–2406.
[10] B. Adhikari, A. Banerjee, *Soft Matter* **2011**, *7*, 9259–9266.
[11] N. A. Peppas, J. Z. Hilt, A. Khademhosseini, R. Langer, *Adv. Mater.* **2006**, *18*, 1345–1360.
[12] T. R. Hoare, D. S. Kohane, *Polymer* **2008**, *49*, 1993–2007.
[13] H. Wang, X. Yuan, Y. Wu, H. Huang, X. Peng, G. Zeng, H. Zhong, J. Liang, M. M. Ren, *Adv. Colloid Interface Sci.* **2013**, *195–196*, 19–40.
[14] L. Yu, J. Ding, *Chem. Soc. Rev.* **2008**, *37*, 1473–1481.
[15] K. Raemdonck, J. Demeester, S. De Smedt, *Soft Matter* **2009**, *5*, 707–715.
[16] J. T. A. Jones, T. Hasell, X. Wu, J. Bacsa, K. E. Jelfs, M. Schmidtmann, S. Y. Chong, D. J. Adams, A. Trewin, F. Schiffman, F. Cora, B. Slater, A. Steiner, G. M. Day, A. I. Cooper, *Nature* **2011**, *474*, 367–371.
[17] L. Milli, N. Castellucci, C. Tomasini, *Eur. J. Org. Chem.* **2014**, 5954–5961.
[18] S. Lucarini, C. Tomasini, *J. Org. Chem.* **2001**, *66*, 727–732.
[19] C. Tomasini, M. Villa, *Tetrahedron Lett.* **2001**, *42*, 5211–5214.
[20] N. Castellucci, G. Falini, L. Milli, M. Monari, S. Abbate, G. Longhi, E. Castiglioni, G. Mazzeo, C. Tomasini, *ChemPlusChem* **2014**, *79*, 114–121.
[21] L. Milli, M. Larocca, M. Tedesco, N. Castellucci, E. Ghibaudi, A. Cornia, M. Calvaresi, F. Zerbetto, C. Tomasini, *J. Org. Chem.* **2014**, *79*, 5958–5969.
[22] G. Longhi, S. Abbate, F. Lebon, N. Castellucci, P. Sabatino, C. Tomasini, *J. Org. Chem.* **2012**, *77*, 6033–6042.

[23] G. Angelici, G. Falini, H.-J. Hofmann, D. Huster, M. Monari, C. Tomasini, *Angew. Chem. Int. Ed.* **2008**, *47*, 8075 – 8078; *Angew. Chem.* **2008**, *120*, 8195 – 8198.
[24] G. Angelici, G. Falini, H.-J. Hofmann, D. Huster, M. Monari, C. Tomasini, *Chem. Eur. J.* **2009**, *15*, 8037 – 8048.
[25] N. Castellucci, G. Angelici, G. Falini, M. Monari, C. Tomasini, *Eur. J. Org. Chem.* **2011**, 3082 – 3088.
[26] N. Castellucci, G. Falini, G. Angelici, C. Tomasini, *Amino Acids* **2011**, *41*, 609 – 620.
[27] N. Zanna, A. Merlettini, G. Tatulli, L. Milli, M. L. Focarete, C. Tomasini, *Langmuir* **2015**, *31*, 12240 – 12250.
[28] N. Castellucci, G. Sartor, N. Calonghi, C. Parolin, G. Falini, C. Tomasini, *Beilstein J. Org. Chem.* **2013**, *9*, 417 – 424.
[29] P. Montes-Navajas, N. G. Asenjo, R. Santamaría, R. Menéndez, A. Corma, H. García, *Langmuir* **2013**, *29*, 13443 – 13448.
[30] M. Yu, A. Song, G. Xu, X. Xin, J. Shen, H. Zhang, Z. Song, *RSC Adv.* **2015**, *5*, 75589 – 75599.
[31] Y. Wang, P. Zhang, C. F. Liu, C. Z. Huang, *RSC Adv.* **2013**, *3*, 9240 – 9246.
[32] X. Wang, Z. Liu, X. Ye, K. Hu, H. Zhong, J. Yu, M. Jin, Z. Guo, *Appl. Surf. Sci.* **2014**, *308*, 82 – 90.
[33] J. A. González, M. E. Villanueva, L. L. Piehl, G. J. Copello, *Chem. Eng. J.* **2015**, *280*, 41 – 48.
[34] S. Hu, A. Trinchi, P. Atkin, I. Cole, *Angew. Chem. Int. Ed.* **2015**, *54*, 2970 – 2974; *Angew. Chem.* **2015**, *127*, 3013 – 3017.
[35] H. Gao, Y. Sun, J. Zhou, R. Xu, H. Duan, *ACS Appl. Mater. Interfaces* **2013**, *5*, 425 – 432.
[36] H. Guo, T. Jiao, Q. Zhang, W. Guo, Q. Peng, X. Yan, *Nanoscale Res. Lett.* **2015**, *10*, 272.
[37] S. Chowdhury, R. Balasubramanian, *Adv. Colloid Interface Sci.* **2014**, *204*, 35 – 56.
[38] Q. Y. Cheng, D. Zhou, Y. Gao, Q. Chen, Z. Zhang, B. H. Han, *Langmuir* **2012**, *28*, 3005 – 3010.
[39] D. J. Adams, M. F. Butler, W. J. Frith, M. Kirkland, L. Mullen, *Soft Matter* **2009**, *5*, 1856 – 1862.
[40] H. Frisch, P. Besenius, *Macromol. Rapid Commun.* **2015**, *36*, 346 – 363.
[41] M. Yamanaka, H. Fujii, *J. Org. Chem.* **2009**, *74*, 5390 – 5394.
[42] A. Takahashi, M. Sakai, T. Kato, *Polym. J.* **1980**, *12*, 335 – 341.
[43] D. Fowler, C. E. Steadman, D. Stevenson, M. Coyle, R. M. Rees, U. M. Skiba, M. A. Sutton, J. N. Cape, A. J. Dore, M. Vieno, D. Simpson, S. Zaehle, B. D. Stocker, M. Rinaldi, M. C. Facchini, C. R. Flechard, E. Nemitz, M. Twigg, J. W. Erisman, K. Butterbach-Bahl, J. N. Galloway, *Atmos. Chem. Phys. Discuss.* **2015**, *15*, 1747 – 1868.
[44] V. K. Sharma, T. J. McDonald, H. Kim, V. K. Garg, *Adv. Colloid Interface Sci.* **2015**, *225*, 229 – 240.

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