A Dual pH-Responsive Supramolecular Gelator with Aggregation-Induced Emission Properties

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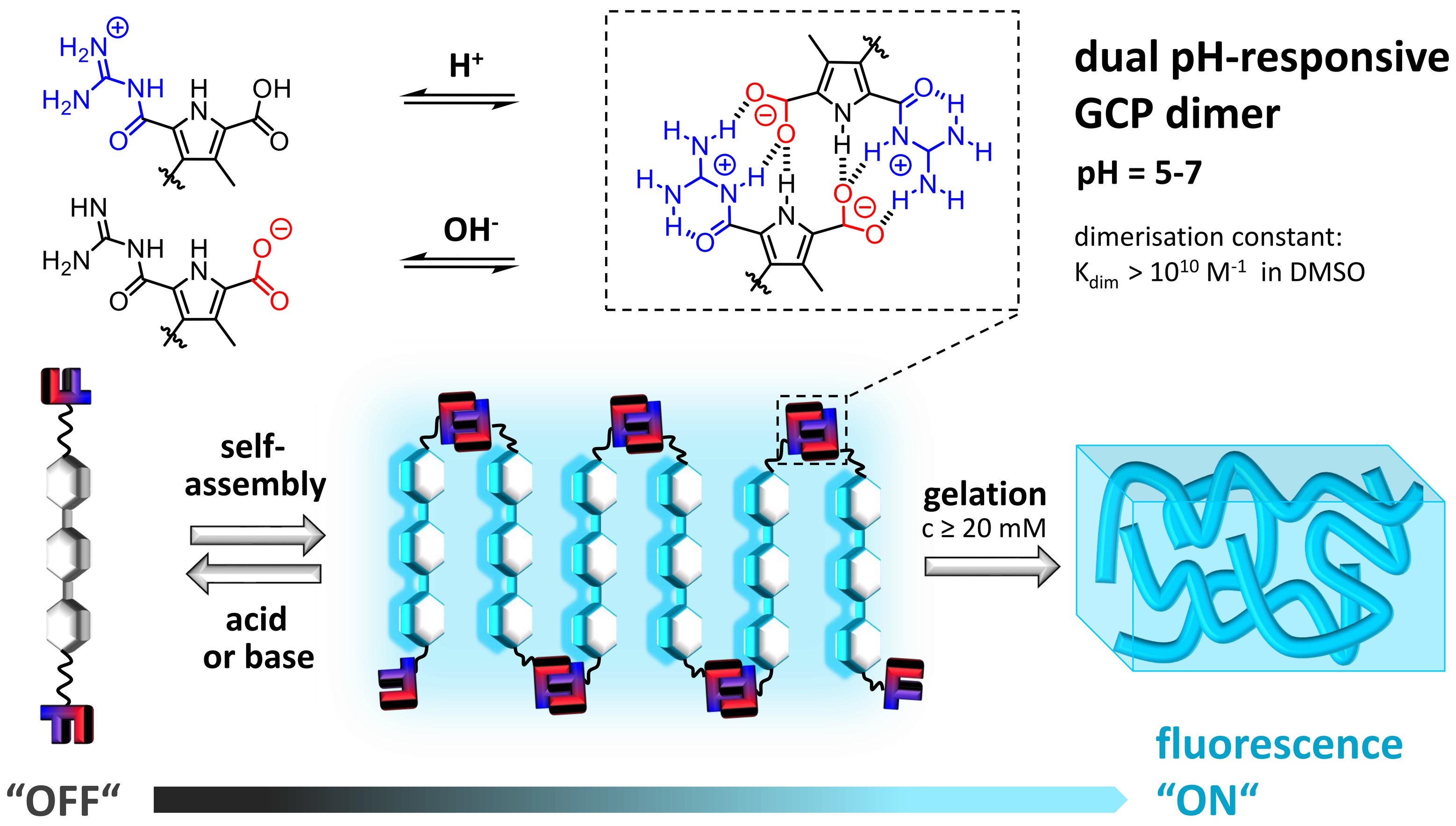
Concept

Multi-stimuli responsive supramolecular gels show great potential as novel smart materials, since their physicochemical properties can be triggered by external stimuli.

The **self-complementary guanidiniocarbonyl pyrrole carboxylate (GCP) zwitterion** is an outstanding binding motif for the formation of **dual-pH switchable gels.**[1] The GCP zwitterions self-assemble into extremely stable dimers held together by H-bond assisted ion pairs even in polar solvents such as DMSO ($K_{dim} > 10^{10}$ M^{-1}). These zwitterionic species are only present in a pH range around 5-7 enabling the bidirectional pH-responsiveness.[2]

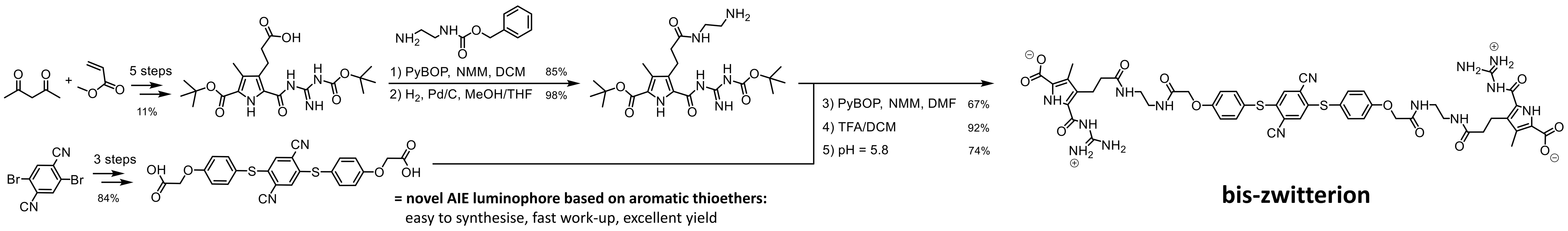
» In this work we extended the features of GCP based gels by incorporating fluorophores with aggregation-induced emission (AIE) properties. In the gel state the rotation of the phenyl rings of the AIE cores is hindered and the emission is boosted.[3]



Synthesis

GCP binding motif: (Schmuck group)[2]

AIE luminophore: (Voskuhl group)[4]

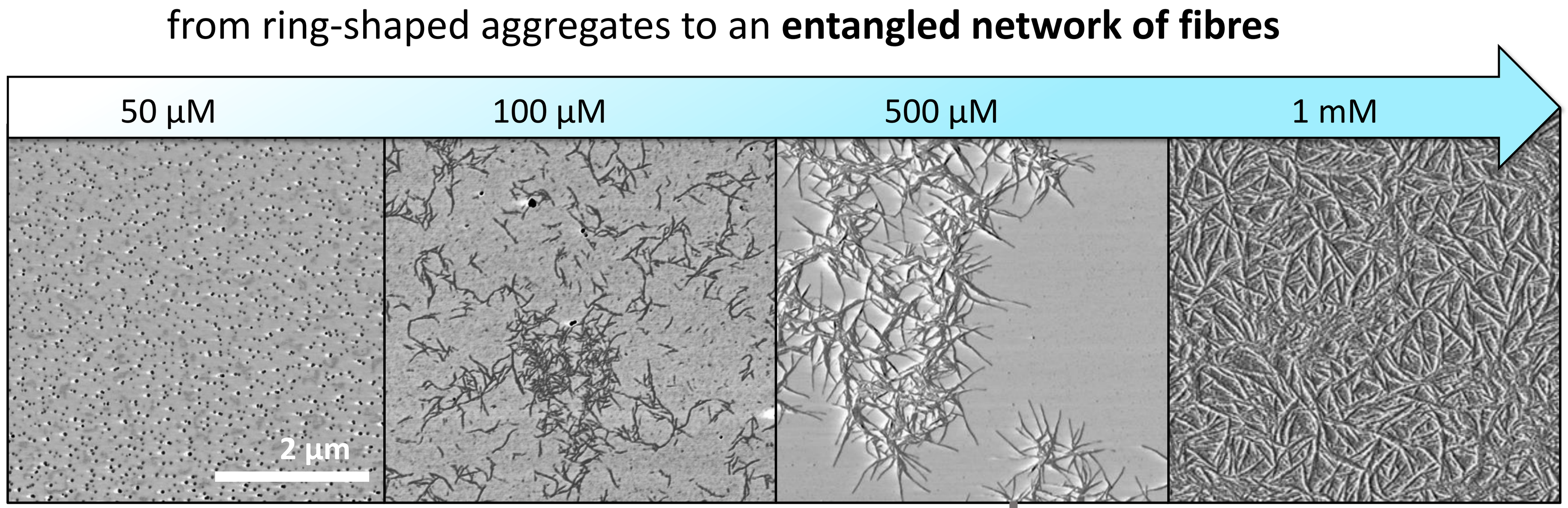


Results

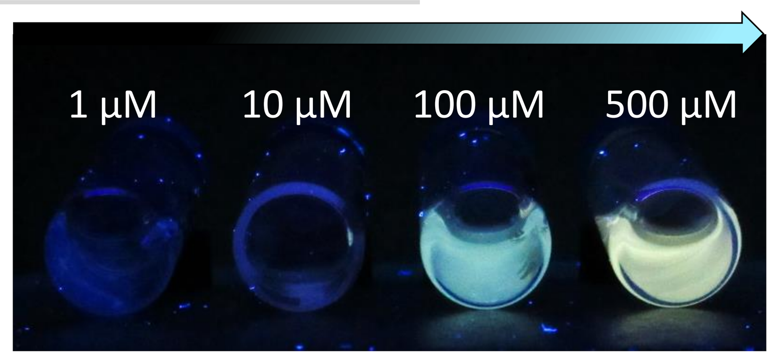
Upon increasing the concentration of the bis-zwitterion above the critical gelation concentration (cgc) of 20 mM a gel is formed in DMSO.
The self-assembly behaviour, the pH-switchability and the fluorescence properties of the gelator molecules were investigated in dilute solution and in the gel state:

Low concentration << cgc (20 mM):

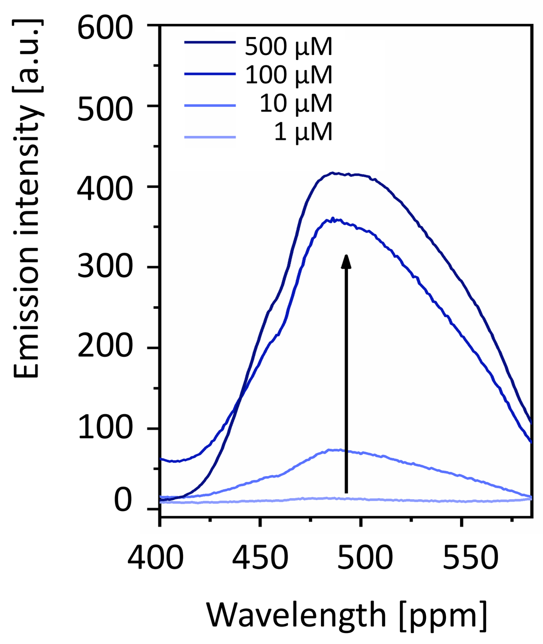
AFM: - morphological changes with increasing concentration (50 µM → 1 mM): from ring-shaped aggregates to an **entangled network of fibres**



Fluorescence emission:

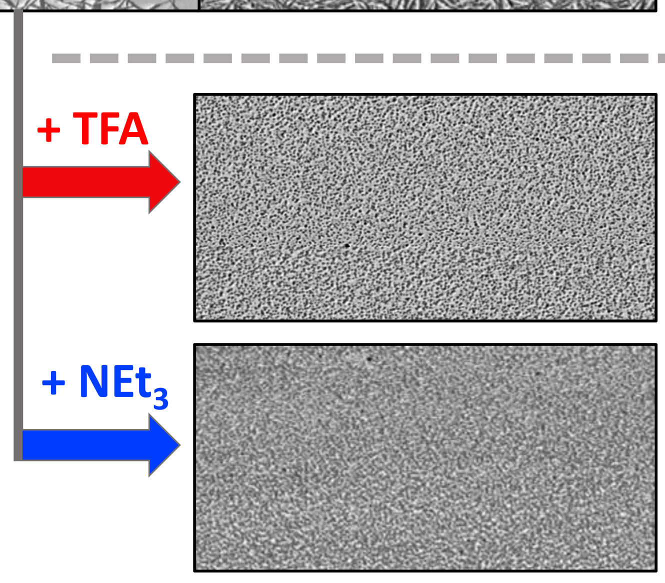


- already weak fluorescence for samples with c ≥ 0.1 mM with an emission maximum at **λ_{em} = 490 nm**

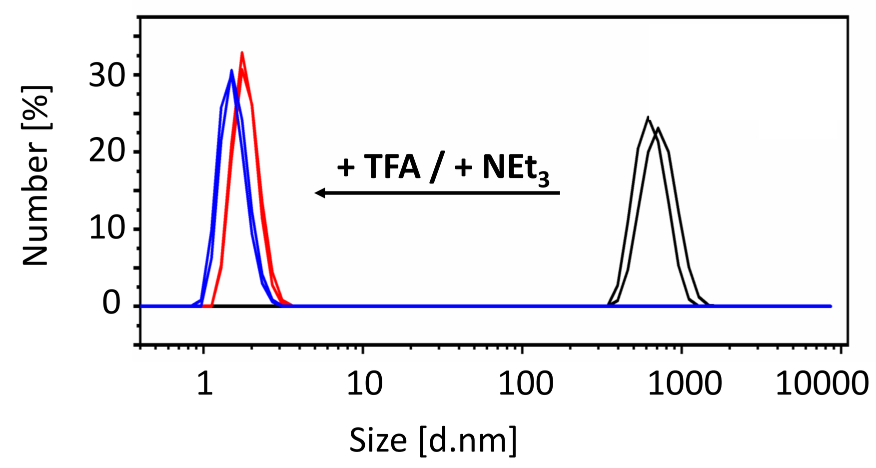


Response to acid (TFA) and base (NEt_3):

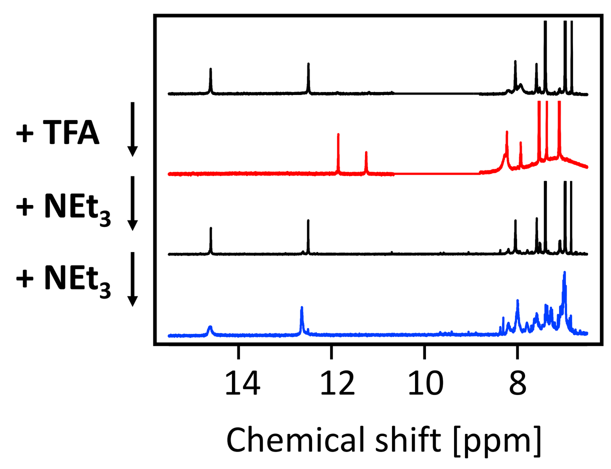
- transition from large **zwitterionic aggregates** to **protonated**/**deprotonated monomers** with a hydrodynamic diameter around 1.7 nm (DLS)
- monitoring of the species by characteristic ^1H-NMR shift changes of the GCP-NH protons



DLS: (c = 500 µM, DMSO)



NMR: (c = 1 mM, DMSO-d_6)

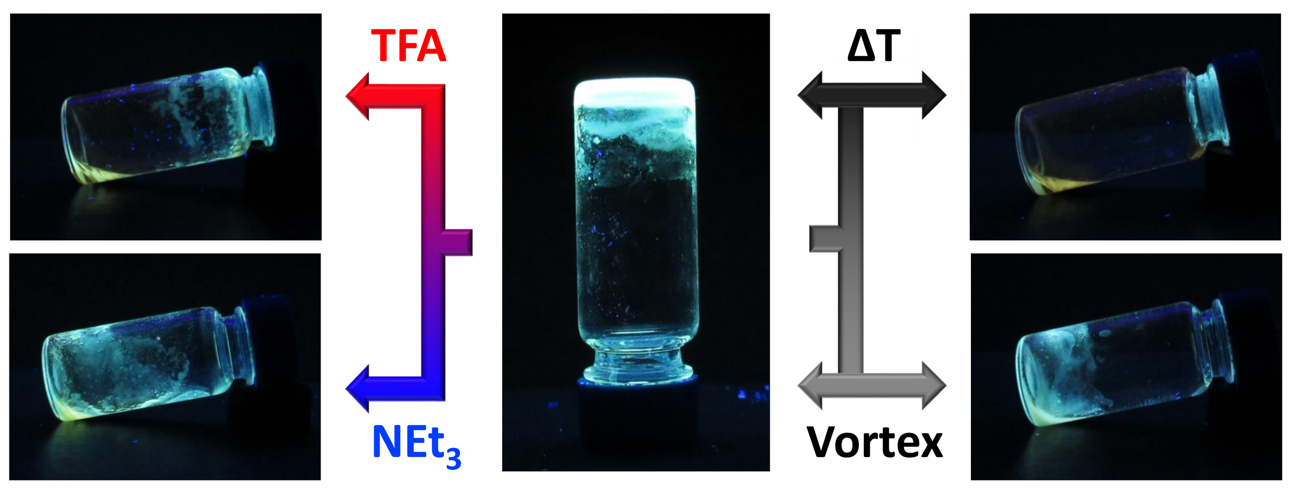


High concentration ≥ cgc (20 mM):

Gel-sol transition: - **switching from highly fluorescent gel to weak emissive sol**

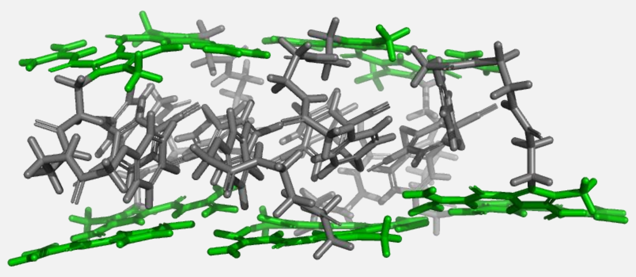
triggered by:

- **addition of acid**
- **addition of base**
- **heating > 100 °C**
- **strong shaking**



Molecular Modelling:

- Molecular Mechanics calculation of a short section of a fibre:



Correlation between formation of fibres and occurrence of fluorescence emission

» **AIE effect is caused by the restriction of intramolecular rotation (RIR) in the fibrillar aggregates**[5]

Summary

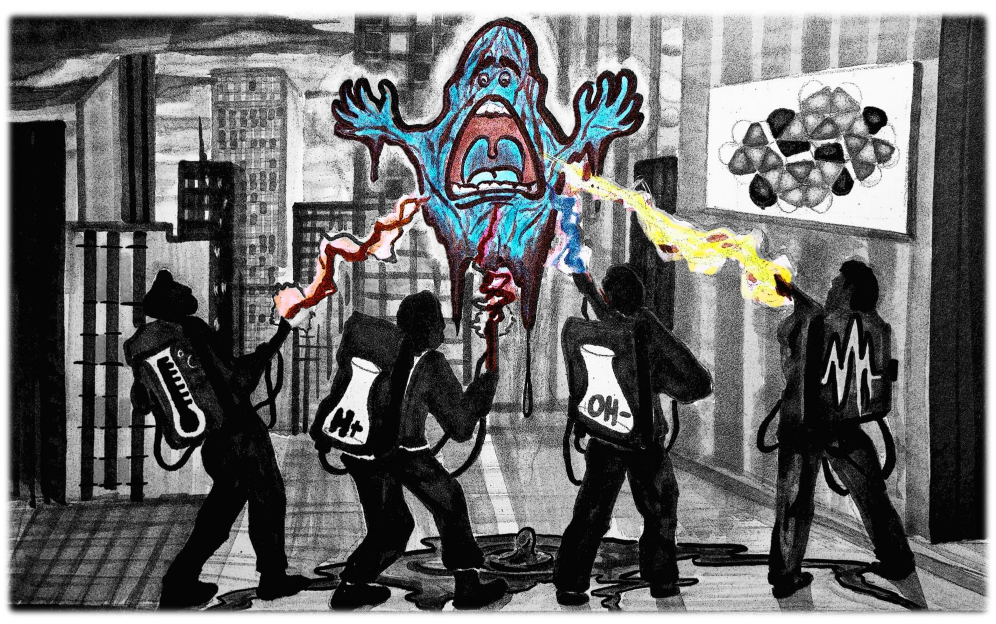
The gel-sol phase transition of the supramolecular gelator can be triggered by several external stimuli:

- acid, base, temperature and mechanical stress

The phase transition goes along with a change in the emission properties:

- **fibrillar gel network:** strong cyane fluorescence
- **sol:** loss of fluorescence

» **First dual pH-responsive gelator with AIE properties**



"We ain't afraid of no ghost!"

Artistic Illustration designed by Christian Thomas, AtMe-Art (Hamburg)

Outlook

Incorporation of longer linkers with hydrophilic groups
(e.g. triethylene glycol, lysine …)

» formation of hydrogels?
» stronger differentiation between the fluorescence emission of sol and gel ("OFF" ↔ "ON")?

Literature

[1] Y. Hisamatsu et al., *Angew. Chem. Int. Ed.* **2013**, *52*, 12550.
[2] C. Schmuck, *Eur. J. Org. Chem.* **1999**, *9*, 2397.
[3] M. Externbrink et al., *Soft Matter* **2018**, *14*, 6166.
[4] S. Riebe et al., *Chem. Eur. J.* **2017**, 23, 13660.
[5] J. Mei et al., *Chem. Rev.* **2015**, 115, 11718.