Dithienylcyclopentene optical switches
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Preface

Be it small children or a multinational company, hierarchy is a key element in the control of vast numbers of individuals, components, or units. Modern society is dependent on hierarchical structures and strict organization layers for control and management. These structures are observed at the microscopic level too. Chemists are interested in how changes at the molecular level affect supramolecular processes, organization, and functions, e.g. how an individual molecule interacts with neighboring molecules and the surrounding solvent environment. Control over these interactions is desirable and therefore we are interested in addressing molecular components by means of one or more external triggers. With external triggers, the molecules become responsive to influences from outside and as a consequence, for instance, their order and organisation can be controlled. From the many phenomena that can be explored, in the current program we chose to examine self assembly and dynamic chirality (handedness).

Figure 1 Small molecules in solution (left) can self assemble to form fibers (right) or more complex supramolecular structures by means of a trigger. Typical triggers are light, temperature, and electrochemical potential.

Self-assembly of (small) molecules into more complex structures is occurring all around and within us (Figure 1). Without it, the cell membrane would not prevent the contents of the cell from leaking out, or give the three dimensional structures that enzymes need to achieve function. Artificial systems that mimic these self assembly phenomena are the low molecular mass organogelators (LMOGs), in which small molecules assemble into fibers and intertwine further into bundles to immobilize solvents by gelation. This assembly is a temperature-dependent reversible process, e.g. the temperature change acts as a trigger to which the system responds. Upon heating, the aggregates dissolve and upon subsequent cooling they form again.
Chirality has intrigued organic chemists since Pasteur discovered the molecular chirality of tartaric acid and van ‘t Hoff proposed the tetrahedral model of carbon. Chirality spans the spectrum of science from left handed neutrinos in space to α-amino acids in your body, and considerable effort is directed to control (and manipulate) the formation (or destruction) of chirality. Usually the chirality is fixed, for instance in the tetrahedral arrangement of groups around an asymmetric carbon atom, but it is also possible to have a chiral dynamic equilibrium. In such a dynamic equilibrium, the chirality is not fixed but inverting rapidly from one state to the other. The basic stereochemical phenomena we examine in this thesis comprises a P to M helix inversion of a triene structure (Figure 2).

**Figure 2** The dynamic equilibrium between a P and M helix which interconvert rapidly into each other in solution.

With the incorporation of a responsive part, these small molecules can (dis)-assemble on command. Several responsive systems that can be addressed by chemical and physical triggers have been developed previously. The aim of this thesis work is to study reversibly responsive low molecular weight organogelators, which had been discovered before the start of this PhD period. Marrying (dynamic) chirality and self-assembly into one system, as is shown in Figure 3, was the primary focus of the project. A literature
overview on responsive molecular gels is given in Chapter 1. The remaining chapters of this thesis can be divided into three separate, but nevertheless intimately intertwined, topics.

In Chapter 2, the basic properties that are common for all perhydrodithienylcyclopentene switches are addressed. An overview of the recent literature on dithienylethene switches and our contribution towards elucidating and understanding their properties is presented. Light, $\gamma$-irradiation, and electrochemistry will be investigated as potential triggers. Furthermore, (near)-IR, Raman, fluorescence, and phenomena in the crystalline state are explored.

In chapters 3 and 4 the first steps towards responsiveness are described. Chapter 3 is focused around the synthesis and characterization of the amide-derivatized switches. Several closely related compounds were prepared and their properties, e.g. gelation capability and UV/Vis spectroscopic behavior are investigated. Chapter 4 addresses the possibility to change macroscopic properties by altering a molecular property, namely the control of gelation by changing between open and closed forms of the switch. It is demonstrated that it is possible to non-destructively switch with light between the solution and gel phase. This process could be extended to defined, inhomogeneous pattern formation.

In chapters 5 and 6, the influence of chirality on aggregation is explored. In Chapter 5 the importance of molecular chirality in self-assembly is examined. It was observed that chirality has a subtle influence on aggregation behavior, which leads to a four state switchable system. Several related switches were tested and the influences of the solvent is explored. Chapter 6 takes the studies described in Chapter 5 one step further, and introduces the concept of transfer of chirality upon self-assembly to achiral complementary amide derived switches. Whereas in the previous system only one dynamic self-assembling gelator shows chiral selection behavior, multiple systems can be influenced simultaneously. To rationalize the stereoselection process, sergeant-soldiers effects are explored. Since choice of solvent plays such a critical role, this thesis will end with chirality transfer from chiral solvents to achiral (non-complementary) amide-derived perhydrodithienyl switches.