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Dynamic chirality, chirality transfer and aggregation behaviour of dithienylethene switches

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ABSTRACT

The synthesis and characterisation of a series of chiral and achiral low molecular weight organogelators (LMWGs) based on bis-amide substituted dithienylethene photochromic switches is reported. The LMWGs gelate a range of solvents depending on the specific functionalisation of the hydrogen bonding amide groups. In mixtures of chiral and achiral LMWGs the stereochemical outcome of the chiral aggregation is determined by the chiral LMWG molecules in most cases. However, for the first time we demonstrate that the stereochemical outcome of the aggregation can be influenced by the achiral LWMG molecules in some cases. Furthermore specific π–π (and/or van der Waals) interactions of chiral LMWGs **1**–**3o** with the solvent allow the solvent to influence the control of chirality of aggregation. This influence of the solvent has a dramatic effect on whether four- or two-gel states are available.

1. Introduction

The dynamic self-assembly of molecules into supramolecular systems, a phenomenon that is the basis of life itself, has at once inspired us to develop even more complex architectures and at the same time perplexed us in our efforts to understand the fundamental driving forces guiding these processes.[1] The control of the organisational processes involved in self-assembly by chemical or physical means represents a major scientific challenge and is key to the development of supramolecular devices of nanoscale dimensions. Smart molecular materials, based on small molecules into which responsive units are integrated, hold considerable promise in achieving molecular level control over micro- and indeed macroscopic structure. Central to the application of responsive molecular systems to smart supramolecular materials are properties such as rapid response and fatigue resistance. Photochromic molecular components[2] that react, reversibly, upon irradiation with different wavelengths of light, offer considerable opportunities to control the self-assembly of individual molecules into supramolecular structures. Low molecular weight organic gelators (LMWGs),[3] containing responsive perhydrodithienylcyclopentene photochromic switches (Fig. 1), offer such functionality.[4] As part of our continuing program of research on smart responsive materials based on functional LMWGs, recently, we reported a series of perhydrodithienylcyclopentene photochromic switches (e.g., Fig. 1), which incorporate hydrogen bonding (chiral) amide units to drive supramolecular assembly.[5] The primary focus of our earlier studies rested on the interrelationship between molecular and supramolecular chirality and how photochemically induced changes in the behaviour of the (LMWG) gelators can drive complex changes in supramolecular gel structures (Fig. 2).

Introducing chiral units into the structure of the gel forming monomers offers an additional point of control and can allow for new properties to be accessed.[6] Previously we have demonstrated transfer of chirality, using the sergeant soldier principal,[5a] where a chiral 'sergeant' molecule guides a racemic compound to form a chiral supramolecular co-assembled structure exhibiting dynamic chirality, e.g., an LMWG gel fibre.[5a] The supramolecular chirality of the assembly itself was found to be essential in transferring the chirality of the chiral sergeant molecules to the achiral soldiers.

This prompted us to explore chirality transfer via supramolecular assemblies in different environments, i.e., by varying the soldier molecules and solvents employed, to further our understanding of the effect of chiral selection during induction of aggregation. The solvent's ability to direct chiral assembly was found to be critically dependent on the substitution pattern of the sergeant and soldier molecules and as a result aggregation can result in a four state[5c] (Fig. 2) or two state aggregated system

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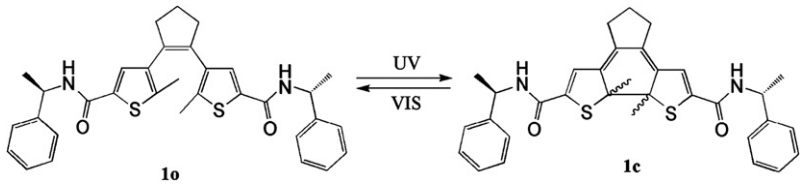

Figure 1. Structure of a chiral dithienylethene photochromic switch in the open **1o** and closed **1c** state.

depending on the combinations employed. These studies demonstrated the delicate balance involved in, and the opportunities available to alter and control, (chiral) aggregation.

In the present contribution we report the synthesis and characterisation of a series of perhydrodithienylcyclopentene photochromic switches bearing (chiral) amide side groups (Fig. 3). In these systems the gelation of organic solvents, from aprotic apolar to protic polar, is effected through intermolecular hydrogen bonding interactions between the amide units, but is influenced heavily by both steric and electronic properties of the amide substituents. We find that a soldier bearing non-innocent phenyl derived side groups could influence the direction of chiral induction, presumably through π–π interactions. Furthermore, it appears that van der Waals interactions can direct chiral aggregation of the soldiers through specific interactions with the chiral side-groups of the sergeant.

2. Results and discussion

Compounds **1**–**15**[7] were obtained, in good yields, by coupling[8] of dithienylcyclopentene diacid **A**,[9] with the corresponding amine using *N*-methylmorpholine and 2-chloro-4,6-dimethoxytriazine (Fig. 3). Compounds **1**–**15** differ in the substituent on the amide nitrogen (Fig. 3) ranging from linear alkyl chains to cyclic alkanes and aromatic amines. All compounds were characterised by HRMS, ^{1}H and ^{13}C NMR spectroscopies and exhibit the expected photochemical conversion from the open state to the closed state upon irradiation with UV (312 nm) light, which is reversed by visible irradiation (>400 nm, Fig. 1). In methanol solution at λ_{exc} 312 nm, the photostationary state (PSS) reached is >95% in favour of the closed state with the exception of **1** (77%) and **6** (87%) (for **8**, **14** and **15** the PSS in methanol could not be determined). Clear isosbestic points were maintained over three switching cycles. This indicates that amide derived perhydrodithienylcyclopentene switches show good switching behaviour in methanol solution.[10] For **11**, **13** and **14**, which bear aromatic groups attached directly to the amide nitrogen atom, a ~10 and 20 nm bathochromic shift in the λ_{max} of the lowest absorption bands of the open and closed form, respectively, are observed compared with the alkyl substituted amide switches (**1**–**10**, **12** and **15**), Table 1.

Compound **8** is insufficiently soluble in methanol to obtain an UV/vis spectrum. For **14** and **15** accurate determination of the PSS by ^{1}H NMR spectroscopy was precluded by low solubility. Molar absorptivities in parentheses ($\varepsilon=\times10^{4}$).

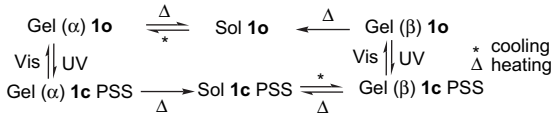

Figure 2. The four-gel-state cycle. The stable gel states formed by cooling solutions of the open form (**1o**) (gel state α) or at the $PSS_{365\ nm}$ (gel state β) are distinct. Once in the gel state the structure is effectively 'locked' so that a stable gel formed by cooling **1o** results in formation of gel (α) **1o**, which can then be irradiated to the meta-stable gel state (α) **1c**. Upon heating to dissolution and subsequent cooling to regelate the solution the stable gel (β) **1c** is formed, which can then be irradiated with UV light to meta-stable gel (β) **1o** and finally converted via a heating-cooling cycle to the original gel state (α). PSS=photostationary state, the suffixes 'o' and 'c' denote the open and closed forms of the photochromic switches. α and β refer to two distinct gel states.

2.1. Gelation behaviour

The aggregation (gelation) behaviour[3] of **1**–**15** was examined in a series of solvents (Table 2). It is apparent that the amide functionalized dithienylethene switches in the open state are capable of gelating both apolar and aprotic solvents with gelation occurring spontaneously upon cooling.[11] The driving force for gelation is expected to be due primarily to the hydrogen bonding interactions between the amide functional groups. Indeed it is clear that steric hindrance in proximity to the hydrogen bonding component (i.e.,

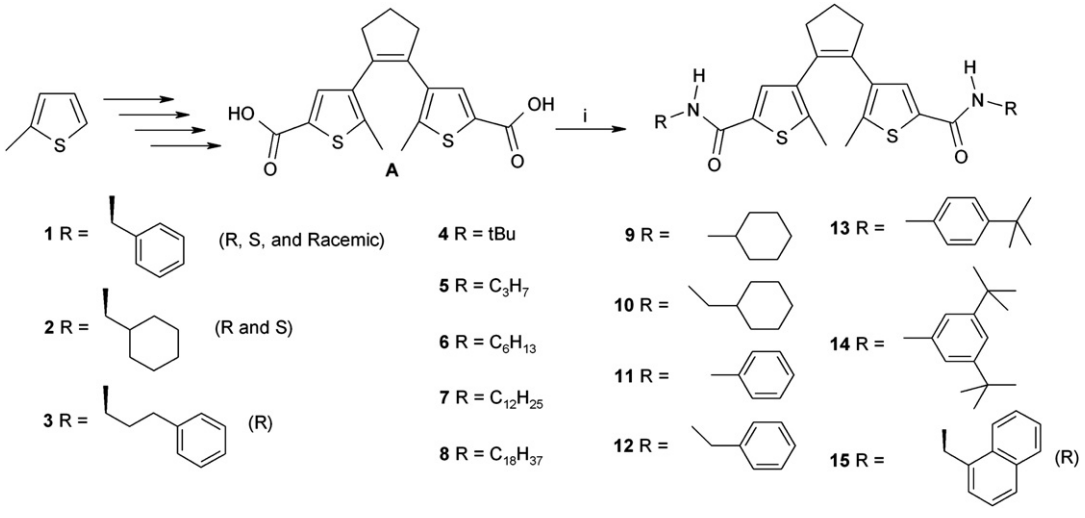

Figure 3. The switchable amide based gelators **1**–**15** were prepared from methylthiophene.[9] (i) 2 equiv 2-chloro-4,6-dimethoxytriazine, 4 equiv *N*-methylmorpholine, 2 equiv of the appropriate amine, DCM, 0 °C. See Section 4 for details.

Table 1
UV/vis maxima for **1**–**15o** and **1**–**15c** in MeOH solution

	PSS	Open	Isosbestic points	Closed
		λ_{max} (nm)	λ (nm)	λ_{max} (nm)
1	0.77	262 (2.8)	315	350 (0.51), 520 (0.57)
2	0.95	262 (2.0)	311	349 (0.44), 510 (0.54)
3	0.95	262 (2.9)	312	348 (0.69), 520 (0.76)
4	0.96	261 (2.5)	285	348 (0.63), 520 (0.70)
5	0.99	261 (2.7)	311	348 (0.74), 514 (0.79)
6	0.87	260 (2.4)	310	347 (0.56), 517 (0.59)
7	0.99	261 (2.5)	310	348 (0.67), 518 (0.71)
9	0.99	260 (2.7)	312	345 (0.67), 511 (0.74)
10	0.99	262 (2.1)	312	347 (0.54), 520 (0.59)
11	0.99	280 (3.1)	233, 241, 329	312 (1.3), 350 (1.1), 541 (1.1)
12	0.95	262 (2.8)	313	350 (0.65), 520 (0.68)
13	0.99	284 (2.8)	235, 248, 332	316 (1.2), 353 (1.2), 539 (1.1)
14	n.d.	283 (2.0)	224, 331	357, 540
15	n.d.	268 (3.6)	314	350, 514

the amide group) has a considerable influence on the gelation behaviour observed. Overall, reducing steric hindrance at the α-position facilitates gelation (**1o**–**3o**, **9o**, **11o**, **13o**–**15o**). This holds for further reduction in the steric hindrance also (**5o**–**9o**, **12o**), albeit with higher minimum gelation concentrations and a reduction in solvent scope.

Solvents are ordered according to dielectric constant. P=precipitate, S=solution, C=crystallisation, VS=viscous solution, G=gel. Number in bracket indicates minimal gelation concentration in milligrams per millilitre.

2.2. Effect of steric crowding on gelation by LMWGs

For the linear alkyl substituted LMWGs, **5**–**8o**, an increase in chain length results in a change in behaviour from gelation/precipitation for **5o** (C_3H_7), to gelation for **6o** (C_6H_{13}), to mostly viscous solutions for **7o** ($C_{12}H_{25}$) and **8o** ($C_{18}H_{37}$) indicating that, overall, gelation is disrupted by an increase in the contribution of van der Waals interactions between the alkyl chains. This is in agreement with recent findings for gelators derived from cyclohexane bis-ureas and bis-amides,[12] where the increase in chain length enhances the gelation properties, only where it facilitates anisotropic fibre growth.

Substitution at the amide position by an aromatic group (**11o**, **13o** and **14o**) provides for good gelation characteristics; however, direct comparison with the alkyl based gelators should be made with caution as the electronic effect (vide supra) of the aromatic substituent on the amide group and its affect on hydrogen bond strengths cannot be ignored. The contribution of secondary interactions, in particular π–π stacking, are unlikely to be significant considering the negligible effect that *tert*-butyl substitution on the phenyl ring has on gelation. Indeed comparison of **11o** and **13o** shows a benefit of reducing such interactions in terms of gelation.

The flexibility of the side group has a considerable effect on gelation behaviour. The cyclohexyl substituted LMWGs, **2o** ($-CH(CH_3)C_6H_{11}$), **9o** ($-C_6H_{11}$) and **10o** ($-CH_2C_6H_{11}$), demonstrate the importance of steric interactions in achieving gelation. Compounds **2o** and **9o**, both of which are substituted at the amide nitrogen with secondary carbon centres, are capable of gelating a broad range of solvents, whilst for **10o** gelation behaviour similar to that of **5o** (C_3H_7) is observed.

Similar trends with regard to the effect of steric crowding around the amide nitrogen atom can be seen in the alkyl phenyl derivatised LMWGs. Whereas for the alkyl phenyl bearing gelators **1o**, **3o** and **15o**, in which the amide nitrogen is substituted with a secondary carbon centre, very good gelation characteristics are observed (Table 1), a reduction in steric crowding at the C1 position (i.e., **12o** ($-CH_2C_6H_5$)) results in a near complete loss in gelation strength. For **4o**, bearing a *tert*-butyl group, gelation is inhibited, resulting in either precipitation or improved solubility at room temperature, indicating that over-crowding at the C1 position increases intermolecular separation and reduces potential hydrogen bonding interactions.

Overall, it is apparent that the ability of the compounds shown in Figure 3 to engage in gelation is critically dependent on the nature of the C1 atom of the alkyl amide substituent. Indeed the introduction of a methyl group at this position, e.g., **1**–**3o** and **15o**, introduces sufficient rigidity for hydrogen bonding between the amide units to form gel fibres.

In our earlier studies we demonstrated that molecular chirality can be extended to control chirality in supramolecular systems and vice versa.[5] In the following sections we will examine chiral aggregation phenomena in these remarkable LMWG based systems to attempt to understand how the stereochemical properties of the gel fibres, and hence the gel formed, is controlled by the stereochemistry at the amide-C1 position and what importance can we place on secondary interactions between the side chains in dictating the stereochemical outcome.

2.3. Soldier effect of 5–12o on the chiral aggregation of 1–3o

In our earlier reports we demonstrated that the chirality of the amide component of the LMWGs could be transferred to the photochromic component via the supramolecular structure of the gel fibres.[5a] In the present study, the transfer of the chirality of the amide component to the photochromic components of achiral LMWGS co-assembled within the same gel fibres, the effect of solvent on the transfer and the interaction between chiral and achiral molecular units of the gel fibres is examined.

LMWGs (chiral) **1o**–**3o** were co-assembled with achiral LMWGs **5o**–**12o**. The chirality is expected to be controlled by the chiral

Table 2
Gelation characteristics for dithienyl cyclopentenes **1o**–**15o**

Solvent	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Hexadecane	P	G (1)	G (1)	P	P	C	G (10)	VS (10)	G (5)	P	P	P	G (2)	G (2)	G (4)
Cyclohexane	G (4)	G (1)	G (1)	P	P	G (2)	VS	S	G (2)	G (2)	P	P	G (2)	G (2)	G (2)
Phenyloctane	G (2)	G (1)	G (1)	P	G (1)	G (5)	VS	VS (10)	G (5)	G (1)	G (3)	P	G (1)	G (1)	G (1)
Toluene	G (1)	G (1)	G (3)	P	G (1)	G (4)	VS (10)	VS (32)	G (3)	S	G (3)	P	G (3)	P	G (5)
Decalin	G (1)	G (1)	G (1)	P	G (3)	G (2)	VS (10)	VS (22)	G (2)	G (2)	G (1)	P	G (2)	G (2)	G (2)
Dibutylether	G (2)	G (5)	G (1)	P	P	G (10)	VS	VS (12)	G (2)	P	G (3)	P	G (2)	P	G (2)
Benzene	G (2)	G (3)	G (10)	S	G (10)	G (10)	VS	VS (10)	G (10)	P	G (3)	P	G (10)	G (10)	G (10)
Tetralin	G (4)	G (3)	S	S	S	G (4)	VS (10)	s	G (5)	S	G (3)	G (2)	G (2)	G (3)	G (2)
1,4-Dioxane	S	G (8)	S	S	S	S	P	P	P	C	S	S	P	P	S
Butylacetate	S	G (8)	P	S	S	VS (10)	P	P	P	C	S	S	VS (10)	P	G (10)
1,2-DCE	S	P	P	S	S	S	S	P	C	P	S	S	S	P	S
2-Octanol	S	P	S	S	S	S	S	S	S	S	S	S	S	P	P
Ethanol	S	S	S	S	S	S	S	P	S	C	S	S	S	P	S

'sergeant' molecules (i.e., **1o**–**3o**), which guide the assembly of the achiral 'soldier' molecules (i.e., **4**–**15**). The combination of sergeant LMWGs (**1o**–**3o**, 1 mg/ml) and soldier LMWGs (**5o**–**7o**, **9o**–**12o**) to form gels in a 1:1 ratio in toluene was examined and the chirality of the supramolecular assembly formed was determined by CD spectroscopy (Fig. 4 and Table 3).

It appears that after co-gelation of **1o** with the series of achiral gelators, **5o**–**7o** and **9o**–**12o**, in toluene, the CD signal observed indicates that the helicity of the gel fibres is the same as observed for gels of **1o** alone (i.e., negative). This indicates that **1o** is directing the chirality of the aggregates by chiral induction during co-aggregation occurring in the same manner in each case.

For **2o** a different situation is observed. Gel formation with **2o** shows positive helicity, however, the sign of the CD signal of the co-assemblies varies considerably with **5o**, **6o**, **10o**, **11o** and **12o** showing negative helicity and **7o** and **9o** positive helicity. This indicates that the chiral selection inverts for some of the soldier LMWGs. In the absence of strong interactions, over and above the hydrogen bonding amide groups of **7o** and **9o**, it is most probable that specific van der Waals interactions between the side chains has a considerable effect.

For **3o**, which shows positive helicity in the gel state in toluene, the sign of the CD absorption can be tuned upon addition of different (soldier) switches bearing either aromatic auxiliary groups (**11o**–**12o**, negative helicity) or non-aromatic auxiliary groups (**5o**–**7o**, **9o**–**10o**, positive helicity). It appears that when the soldier gelator is given a means to interact strongly with the sergeant, for example, via π–π interactions of the phenyls, it is not the chiral compound that is directing aggregation, but the achiral compound. This indicates that the phenyl derivatised switches **11** and **12** are capable of shielding the phenyl group of **3o** from the solvent, allowing it to assist in aggregation and lead to an inversion of the chiral selection. This is remarkable since the solvent is present in large excess compared to both **11o** and **12o**, but nevertheless the achiral LMWGs are still capable, presumably by means of pre-assembly with **3o**, to orientate the helicity in a direction opposite to that obtained on its own.

It is apparent that secondary interactions of the gelator side groups are capable of tipping a delicate balance and thereby influence the helicity of the gel fibres formed. These results (Table 2) and our earlier reports,[5] open the possibility of combining changes in solvent properties with chiral dithienylethene switches **1o**–**3o** to determine the specific interactions present in the aggregated state.

2.4. Solvent effect on chiral aggregation of 1–3

The observation that secondary interactions between different gelator units can influence chiral self-assembly, it was anticipated that solvent could show a similar influence on the aggregation of inherently chiral (amide) dithienylethenes. Switches **1o**–**3o**, each incorporating different chiral amide side groups, were examined in a series of solvents to assess whether the expression of molecular chirality upon aggregation in the supramolecular assembly could be influenced by solvent (Fig. 5 and Table 4).

Table 3
Sign of CD signal (λ=318 nm) for mixtures of sergeants **1o**–**3o** and soldiers **5o**–**7o** and **9o**–**12o** (1:1) in toluene

	5	6	7	9	10	11	12
1	−	−	−	−	−	−	−
2	−	−	+	+	−	−	−
3	+	+	+	+	+	−	−

For all solvents examined, gels formed by **1o** show a negative exciton coupling (Fig. 2a) and although the intensity of the signal varies dramatically over the series of solvents, the maximum ($\lambda = 320$ nm) is relatively invariant.[13] This indicates that for **1o**, the helicity of the aggregates is solvent independent, which was confirmed by HPLC analysis of **1c** obtained by irradiation of gels of **1o** in toluene (−94% de), benzene (−53% de), decaline (−96% de), dibutylether (−93% de), and cyclohexane (−96% de). For all solvents examined, the UV/vis absorption shows a red shift upon aggregation (gelation), however, most of the absorption spectra are obscured at 300–320 nm due to the high gelator concentrations required to form gels.

In contrast to **1o**, for **2o** the sign of the CD absorption changes depending on the solvent employed (Fig. 5, centre).[14] For **2o** the CD absorption inverts (negative exciton coupling) upon changing from cyclohexane (−77% de), hexadecane (−25% de) or dibutylether (−44% de) to (positive exciton coupling) toluene (91% de), phenyloctane (85% de) or decaline (70% de). For **2o** the intensity of the signal varies considerably depending on the solvent employed, although the λ_{max} (317 nm) of the absorption is unaffected. It was anticipated that the change in signal would correspond to an inversion of the chirality of the diastereomer of **2c** obtained upon photochemical ring closure in the gel state. Indeed in each case the sign of the CD signal observed correlates well with the diastereomer of **2c** obtained, as determined by HPLC, although with varying maximum yields of induction. A simple correlation of CD exciton coupling sign and solvent properties, i.e., change in dielectric constant, aromatic versus non-aromatic, etc., is not apparent.[15]

The diastereomers of **2c** can be observed by ^{1}H NMR spectroscopy through the appearance of characteristic absorptions at 6.65 and 6.63 ppm (in chloroform-d_1) upon irradiation of **2o** with UV light. Irradiation of gels in either cyclohexane or toluene lead to the appearance of an intense purple colour. ^{1}H NMR spectra in chloroform-d_1, of the purple solid obtained by evaporation of the

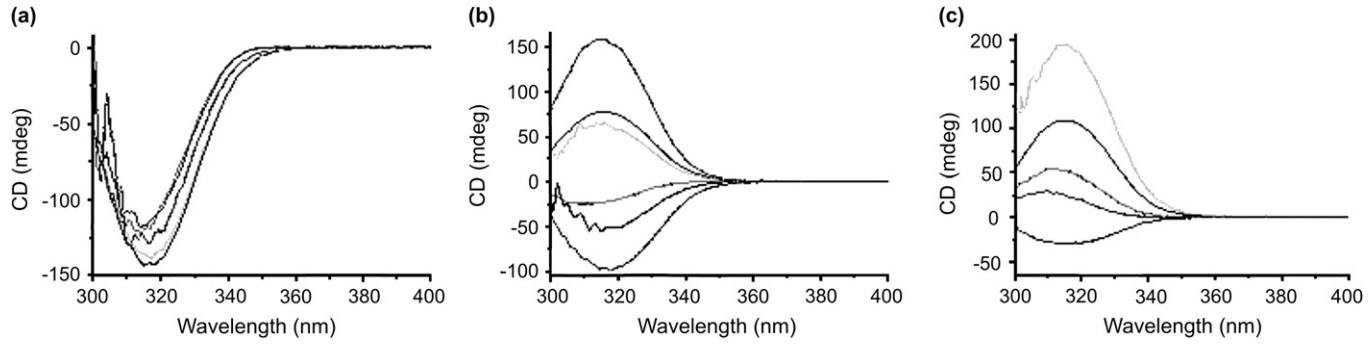

Figure 4. CD spectra for mixtures of **5o**–**12o** with (a) **1o**, (b) **2o**, and (c) **3o** in toluene (1 mg/ml, 1:1 ratio). For (a) **1o** all signals show negative sign (top to bottom **12**, **5**, **7**, **9**, **6**), whereas for (b) **2o** (top to bottom **7**, **2** (only), **9**, **10**, **6**, **12**) and (c) **3o** (top to bottom **9**, **3** (only), **10**, **7**, **12**) the sign changes from positive to negative. Spectra for compound **1o** have been reported earlier in Ref. 5c (and Fig. 2 therein).

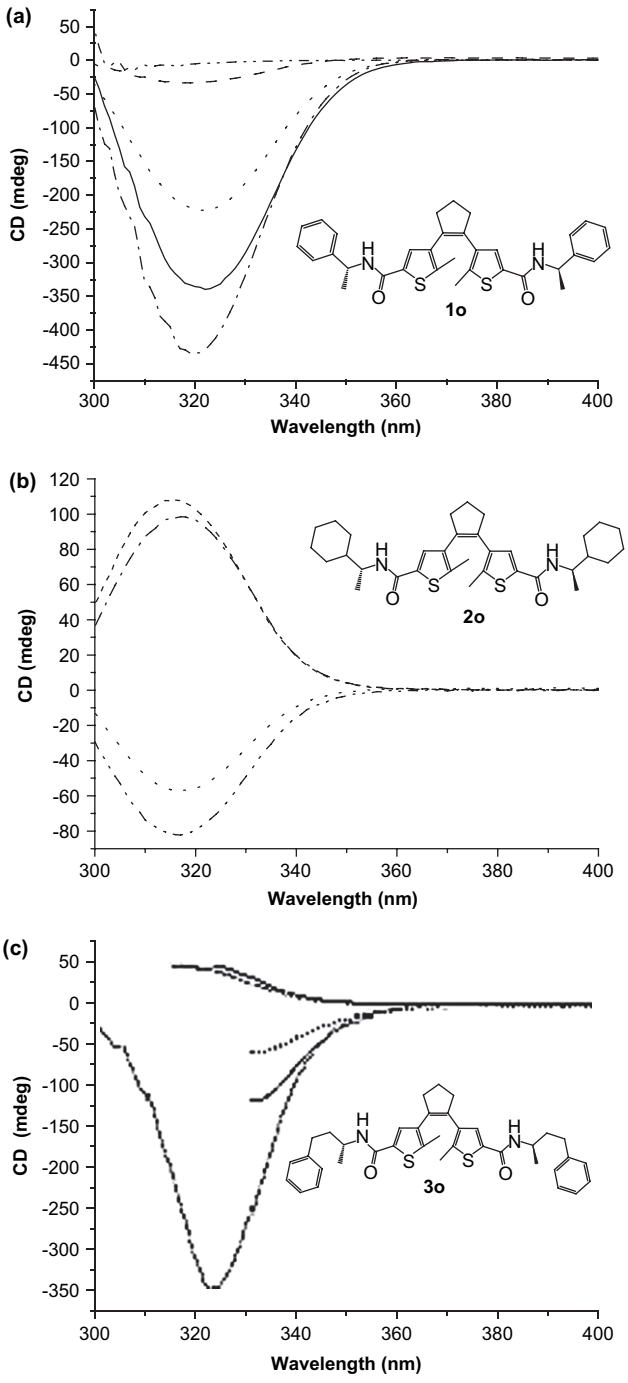

Figure 5. CD spectra for gels of (a) **1o**, (b) **2o** and (c) **3o** in selected solvents. Although the intensity changes dramatically for **1o** depending on the solvent employed, a negative exciton coupling is observed in every case. From bottom to top: phenyloctane, decaline, butylether, benzene and tetraline. For **2o** the CD absorption inverts upon changing from hexadecane or dibutylether (negative exciton coupling) to phenyloctane or decaline (positive exciton coupling). Tetraline, butylacetate, dioxane, and benzene all give very small CD signals even though the induced de is very high (vide infra). CD spectra for **3o** (lower) in selected solvents, phenyloctane (—), benzene (⁻··), hexadecane (– –), *n*-dibutylether (-··) and decaline (···).

solvent, show that for the gels prepared from toluene a single diastereomer (de >90%) is obtained as is evident from the absorptions for **2c** (thiophene proton) at 6.65 ppm and for the gels prepared from cyclohexane at 6.63 ppm. This is in agreement with HPLC data (vide supra) and indicates that the inversion in the sign of the CD signal is indeed correlated to the formation of a specific diastereomer.

Table 4
Sign in the CD spectrum of the exciton coupling for **1o**–**3o** in the gel state and observed diastereomeric ratio for **1c**–**3c** by HPLC

	1		2		3	
Benzene	−	−53%	nd	nd	+	40%
Decalin	−	−96%	+	70%	−	−77%
Dibutylether	−	−93%	−	−44%	−	−63%
Phenyloctane	ng		+	85%	+	92%
Hexadecane	ng		−	−25%	−	−23%
Cyclohexane	−	−96%	−	−77%	−	−92%
Toluene	−	−96%	+	91%	+	55%

ng=gelation not observed. nd=not determined due to the high concentration required for gelation. Note that the sign of the diastereomer observed has been assigned arbitrarily and is not related to the observed exciton coupling.

Compound **3o** shows a solvent dependence of the CD spectra of its gels (Fig. 5c). The high concentrations of **3o** and hence high UV absorption precluded observation of the entire CD exciton band of **3o** gel. Nevertheless the sign of the CD signal could be determined from the red edge of the CD signal and trends were observed. For aromatic solvents such as toluene, benzene and phenyloctane, a positive exciton coupling was observed, whereas for non-aromatic solvents such as decalin, *n*-dibutylether, cyclohexane and *n*-butylacetate, the exciton coupling was negative. This suggests that the phenyl side groups of **3o** play an important role in determining aggregation behaviour, as was observed in the behaviour of **3o** with achiral substituted dithienylethenes also (vide supra). If the aromatic side groups are shielded by the solvent, e.g., the phenyl can give π–π interactions with the aromatic solvent, the sign of the aggregates changes from negative to positive. Probably for **3o**, in contrast to **1o**, the more flexible longer C2 spacer positions the phenyl further away from the chiral groups adjacent to the amide functionality, which allows for control of the chiral induction exclusively by the chiral α-carbon in combination with the amide. Irradiation of gels of **3o** in benzene (40% de), phenyloctane (92% de) and toluene (55% de) results in stereochemical induction with an opposite sense to that of gels of cyclohexane (−92% de), decaline (−77% de), hexadecane (−23% de) and dibutyether (−61% de). Again verification of the differences in the diastereomers formed was obtained by ^{1}H NMR spectroscopy. Gels of **3o** in either cyclohexane or toluene were irradiated with λ=312 nm light and the solvent removed by evaporation to yield purple powders. The ^{1}H NMR spectra (in $CDCl_3$) of the powders showed that a different diastereomer (de >90%) of **3c** was formed (absorption at 6.60 ppm) in the toluene gel than that formed in a cyclohexane gel (6.58 ppm).[16]

In summary for **1o**, in all solvents examined, the sign of the CD absorption upon aggregation is always negative, and a single diastereomer is formed upon irradiation with UV light. For **2o** the sign for the CD absorption appears to be sensitive to van der Waals interactions while for **3o** in aromatic solvents positive exciton couplings are observed whereas in non-aromatic solvents an absorption with a negative exciton coupling is observed upon aggregation. The influence of achiral solvent on not only the formation of a gel state but also the supramolecular chirality of the gel is remarkable. In the next section we discuss how this influence could affect the four-gel-state chiral aggregation system reported recently.[5c]

2.5. Four-gel states versus two-gel states

The clear differences in the solvent dependence of the aggregation of **1o**–**3o** prompted us to investigate if the four different gel states found for **1** in toluene could be observed for compounds **2** and **3** also in other solvents. In addition to toluene used previously for **1**, cyclohexane was an obvious choice. It has a wider electronic

spectral window compared to toluene, but more importantly, it is possible to observe if the inversion of sign of CD signal for **2o** and **3o** (using either toluene or cyclohexane as solvent) correlates with the differences in helicity in **2c** and **3c** upon photochemical ring closure in the aggregated states. Figure 6 shows the results obtained for **1** in cyclohexane,[17] and Figures 7 and 8 and 9 and 10 show the results of similar experiments in both toluene and cyclohexane for **2** and **3**, respectively.

As described previously for gels of **1** formed in toluene,[5c] in cyclohexane (Fig. 6) the CD spectra after solvent gelation are similar in sign to those observed in toluene. Assembly of **1o** into the gel state in cyclohexane is stereoselective, leading to CD absorptions with a negative exciton coupling. Upon irradiation with UV light (λ=312 nm) the supramolecular chirality inverts to a meta-stable state (Fig. 6c and d, dashed line), and heating and subsequent cooling to release and reform the **1c** aggregates results in an inversion of helicity (Fig. 6c and d, solid line). It was thus possible to observe the inversion of chirality for cyclohexane gels containing **1c**, which leads to the four-gel states as described earlier[5c] for this system in toluene.

In toluene, **2o** assembles as gel fibres with *P* helicity (Fig. 7) as opposed to the *M* helicity of gel fibres formed by **1o**, despite both compounds having chiral side groups of *R* configuration. Upon irradiation (λ=312 nm) of the gel of **2o** an absorption appears at longer wavelengths, and after heating and subsequent cooling to release and reform the gel fibres the CD absorption changes but does not invert. Subsequent irradiation with visible light ($\lambda > 420$ nm) leads to a gel containing **2o**, however, no inversion of chirality is observed. Hence in contrast to **1**, for **2** in toluene only two aggregation states can be addressed. It is interesting to note that the UV/vis absorption spectra of the closed forms are not significantly different in the gel or solution state, especially in comparison with the changes observed for **1**.

The solubility of **2o** in cyclohexane is poor compared to that in toluene, however, CD spectra could be obtained for all four states (Fig. 8). The CD spectra appear similar to those of **1** and the signal for **2c** in cyclohexane inverts as expected. This indicates that the results obtained for the solvents examined indeed correlates to the sign of the stable open form. Depending on the direction of chiral selection either two or four chiral states can be addressed for **2**. In contrast to **2** in toluene, in cyclohexane, the UV/vis absorption spectra show significant changes for **2c** in the aggregated state. Very similar behaviour is observed for **3** in toluene (Fig. 9) and cyclohexane (Fig. 10) as observed for **2**. This indicates that the amide group by itself is not wholly responsible for the aggregation phenomena observed, and that a secondary interaction is involved, in particular in obtaining the four chiral gel states. For **1** and **3** the secondary interactions are most probably π–π interactions, however, for **2** this is not so apparent. The difference might be attributed to van der Waals interactions between the cyclohexane group or a steric effect, and this is currently under investigation.

The sequential processes shown in Figures 6, 8 and 10 complete a full cycle of four addressable chiral aggregated states and together comprise a four state chiroptical supramolecular switch (see Fig. 2). Despite the fact that there is no stereoselectivity in solution, after formation of chiral aggregates of **1o**–**3o** the molecular chirality can

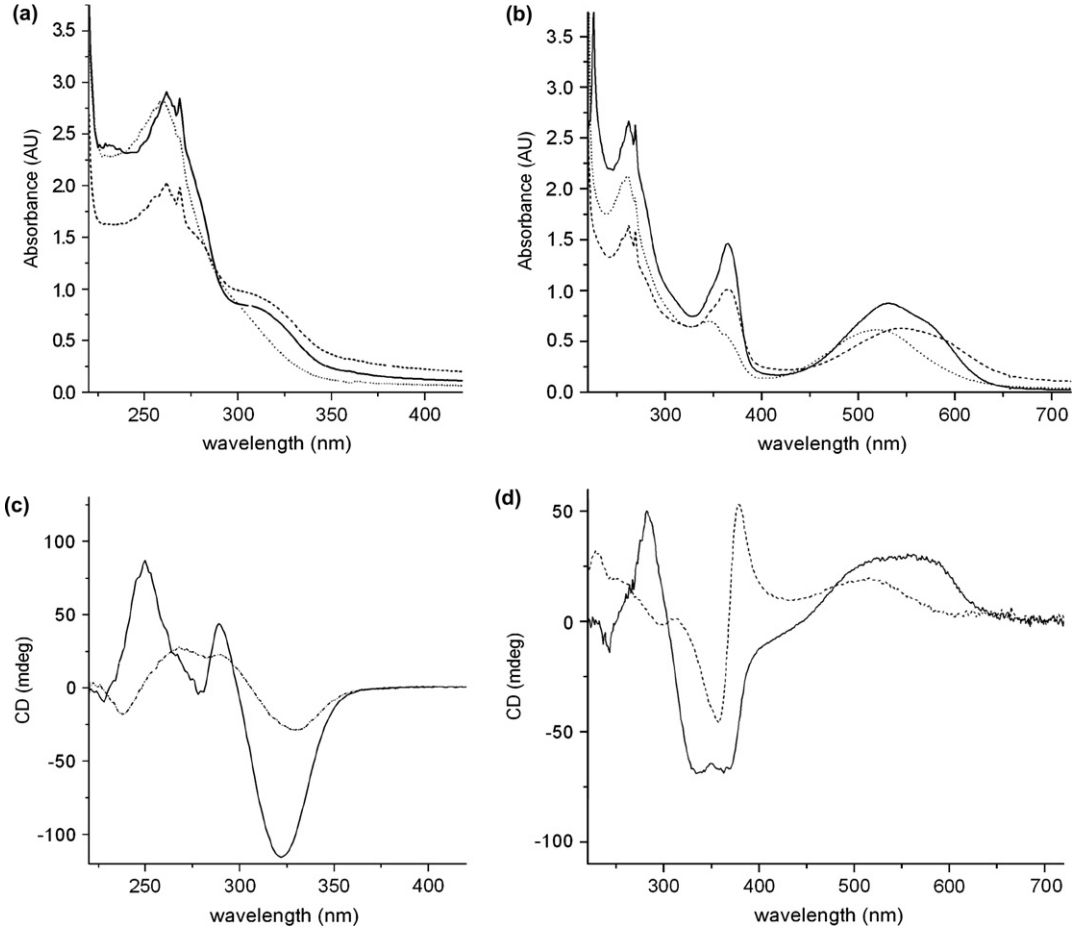

Figure 6. UV/vis (a/b) and CD spectra (c/d) of **1** in cyclohexane; (a/c) gel α **1o**—solid line, gel β **1o**—dashed line. (b/d) gel α **1c**—dashed and gel β **1c**—solid line (4 mg/ml). It is apparent for both CD and UV/vis spectra that the electronic character of the open and closed forms with respect to in solution are affected differently by incorporation into either the α or β gel states. The UV/vis spectra of (a) **1o** (dotted line) and (b) **1c** (dotted line) in solution are shown for comparison.

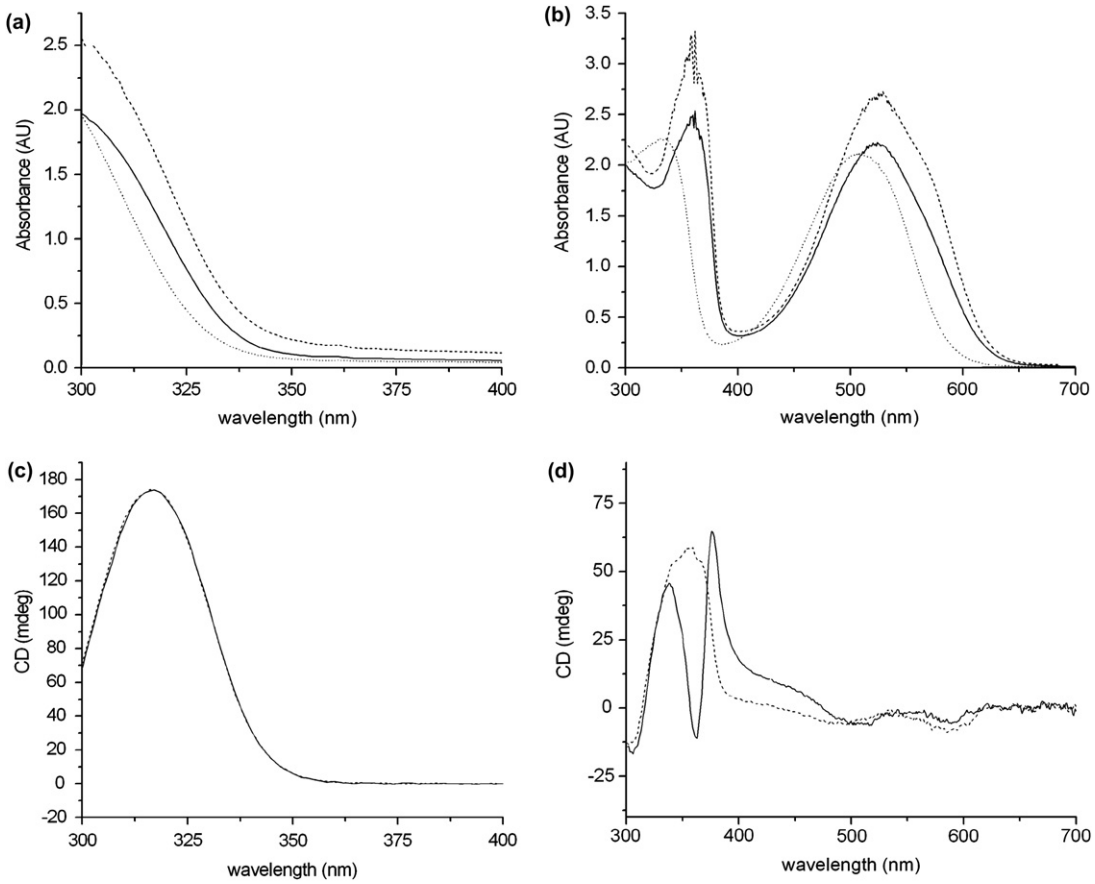

Figure 7. UV/vis (a/b) and CD spectra (c/d) for **2** in toluene (1 mg/ml). (a/c) solid line is gel α **2o**, dashed is gel β **2o**. (b/d) gel α **2o**—dashed line and gel β **2c**—solid line.[20] The UV/vis spectra for (a) **2o** and (b) **2c** in solution are also shown (dotted lines).

be locked subsequently with near absolute stereocontrol in the aggregates. In turn, the molecular chirality obtained governs both the stability and helicity of the aggregate. Transfer of molecular chirality to supramolecular chirality and back is thus established. Of particular significance is that meta-stable chiral aggregates can be obtained in a reversible manner and that the aggregation process can be controlled by an external—i.e., light—signal.

3. Conclusions

It is demonstrated in this study for the first time that the stereochemical outcome of the supramolecular aggregation of LMWG can be influenced by an achiral LMWG as well as the nature of the solvent. Compounds **2** and **3** show different (i.e., solvent dependent) aggregation during chiral dynamic selection, which reveals that the (phenyl) side group is important during chiral selection. For **3o** in aromatic solvents the phenyl side group is presumed to have π–π interaction with the solvent, leaving this auxiliary group unable to participate in the selection upon aggregation. This leads to chiral selection exclusively by the chirality adjacent to the amide functionality in combination with the hydrogen bonding between amides. In non-aromatic solvents the phenyl side groups are free to participate in chiral selection together with the amides, leading to the four-state-gel system. Although it is unclear at present what the additional interaction is for **2**, it shows similar solvent dependent behaviour.

The delicate balance that exists between molecular chirality and the stability of supramolecular aggregates in natural systems, such as actin filaments and the process of protein folding, relies on the interplay of molecular and supramolecular chirality. In the present study the presence of a photo-reponsive unit, i.e., the dithienylethene unit, in the LMWGs presents a distinct opportunity in understanding such delicate processes through the ability to switch between stable and meta-stable states in a fully reversible light controlled manner. The meta-stable states, which are inaccessible via direct aggregation are especially attractive as components in functional materials. Furthermore the control of chirality at several hierarchical levels in a synthetic system allows for furthering of our understanding of complex (bio-)molecular supramolecular processes.

4. Experimental section

4.1. General

Reagents and solvents were obtained from commercial sources (Aldrich, Acros Chimica, Fluka) and used without further purification unless stated otherwise. Melting points were determined using a Büchi melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer (at 300 MHz) or a Varian 500 spectrometer (at 500 MHz) at ambient temperature. The splitting patterns are designated as follows: s (singlet); d (doublet); dd (doublet of doublets); t (triplet); q (quartet); m (multiplet) and br (broad peak). ^{13}C NMR spectra were recorded on a Varian VXR-300 (at 75.4 MHz). Chemical shifts are denoted in δ (ppm) referenced to the residual protic solvent peaks. Coupling constants *J*, are denoted in hertz. Masses were recorded with an MS-Jeol mass spectrometer, with ionisation according to CI^{+}, DEI or EI^{+}

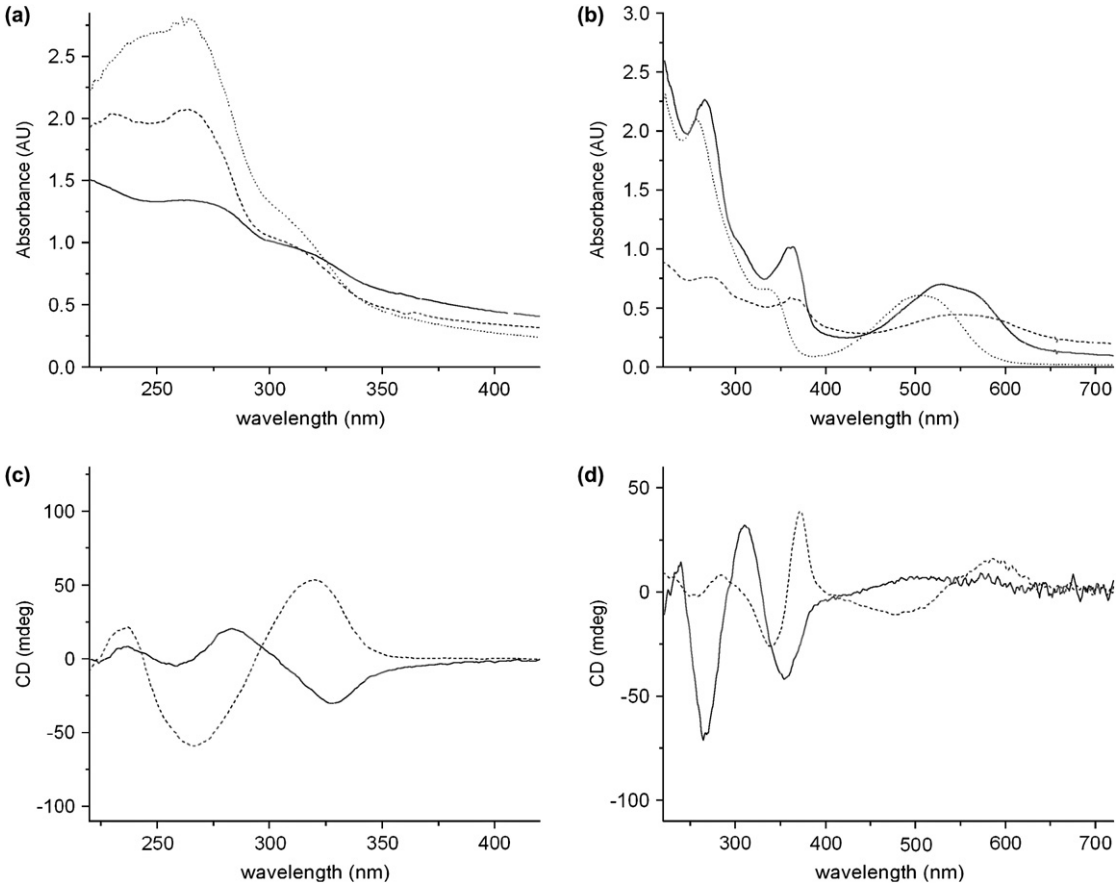

Figure 8. UV/vis (a/b) and CD spectra (c/d) for **2** in cyclohexane (1 mg/ml). (a/c) gel α **2o**—solid line, gel β **2o**—dashed line. (b/d) gel α **2o**—dashed line and gel β **2c**—solid line. The UV/vis spectra of (a) **2o** and (b) **2c** in solution are also shown (dotted lines).

procedures. Aldrich, silica gel, Merck grade 9385, (230–400 mesh) was used for column chromatography. Solvents were distilled and dried before use, if necessary, using standard methods. For all spectroscopic measurements Uvasol (Merck) grade solvents or better were employed. The compounds synthesised are light sensitive and were handled, therefore, exclusively in the dark using brown glassware, and column chromatography was performed under yellow light. Irradiations were performed with a high pressure mercury/xenon lamp (200 W, Oriel) or a xenon lamp (300 W, Oriel) and the appropriate highpass or bandpass filters (Andover corporation). Additionally, UV light was obtained from a spectroline longlife filter nominally at 312 and 365 nm. UV/vis measurements were performed on a Hewlett–Packard HP 8453 diode array spectrophotometer. CD spectra were recorded on a JASCO J-715 spectropolarimeter. Electrochemical data were obtained as reported earlier.[18]

4.2. Determination of critical gelation concentration

The following procedure was used for all compounds and solvents. A 2 ml vial with screw cap was charged with 1.0 mg of compound and 0.10 ml of solvent was added. The mixture was heated until the powder dissolved with subsequent cooling to room temperature resulting in gelation (G), precipitation (P), crystallisation (C) or the compound remaining dissolved (S). By inverting the vial, 'the inverted test tube method',[19] it could be established if gelation was successful. Gelation is considered successful if the solvent showed no gravitational flow during inversion. If successful, a subsequent addition of 0.10 ml of the appropriate solvent and repetition of the previous steps was carried out until either a gel was no longer obtained or until the total volume exceeded 1.0 ml.

4.3. Syntheses

*4.3.1. Compound **1**, 1,2-bis(2′-methyl-5′-{[((R)-1-phenylethyl)-amino]carbonyl}thien-3′-yl)cyclopentene*

1,2-Bis[5′-carboxylic-acid-2′-methyl-thien-3′-yl]cylopentene (**A**) (0.50 g, 1.44 mmol) was suspended in CH_2Cl_2 (5 ml) and placed in an ice bath. Subsequently *N*-methylmorpholine (0.31 ml, 2.9 mmol) was added and the suspension became a solution. Then 2-chloro-4,6-dimethoxytriazine (0.50 g, 2.9 mmol) was added, and a white precipitate was formed immediately after this addition. The reaction mixture was stirred for 2 h at 0 °C, and then another 2 equiv of *N*-methylmorpholine (0.31 ml, 2.9 mmol) was added followed by (*R*)-phenylethylamine (0.37 ml, 2.9 mmol). Stirring was continued for 1 h at 0 °C. The reaction mixture was stirred overnight at room temperature. CH_2Cl_2 (50 ml) was added and the solution was washed with, respectively, 1 M aq HCl (2×20 ml), brine (1×20 ml), saturated aqueous bicarbonate solution (1×20 ml) and H_2O (1×20 ml). The organic phase was dried (Na_2SO_4) and evaporation of the solvent afforded a solid product. After purification by column chromatography (silica gel, CH_2Cl_2/MeOH 60:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.28 g, 35%), mp 207 °C (dec); $[\alpha]_D^{23}$ −83.5 (*c* 0.99, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.55 (d, *J*=6.9 Hz, 6H), 1.90 (s, 6H), 1.97–2.07 (m, 2H), 2.74 (t, *J*=7.4 Hz, 4H), 5.19–5.29 (m, 2H), 7.18 (s, 2H), 7.26–7.38 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.7 (q), 21.7 (q), 22.8 (t), 38.5 (t), 49.1 (t), 126.3 (d), 127.5 (d), 128.7 (d), 129.4 (d), 134.2 (s), 134.7 (s), 136.3 (s), 139.9 (s), 143.0 (s), 160.8 (s); MS (EI): 554 [M^+]; HRMS calcd for $C_{33}H_{34}N_2O_2S_2$ 554.206, found 554.205.

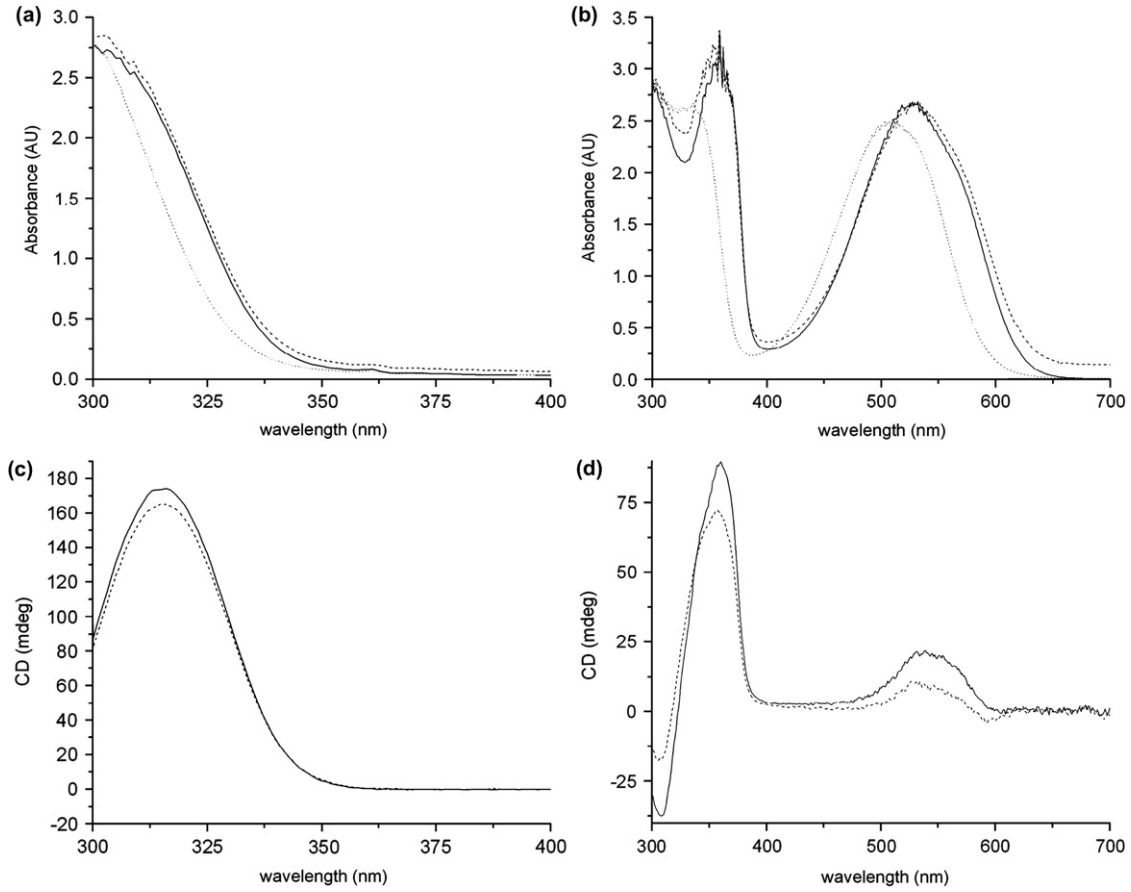

Figure 9. UV (a/b) and CD spectra (c/d) for **3** (1 mg/ml) in toluene. (a/c) solid line is gel α **3o**, dashed is gel β **3o**, (b/d) dashed is gel α **3c** and solid line is gel β **3c** for **3**. The UV/vis spectra of (a) **3o** and (b) **3c** in solution are also shown (dotted lines).

*4.3.2. Compound **2**, 1,2-bis(2′-methyl-5′-{[((R)-1-cyclohexylethyl)-amino]carbonyl}thien-3′-yl)cyclopentene*

As for **1**, except from **A** (1.34 g, 3.85 mmol) and (*R*)-cyclohexylamine (1.1 ml, 7.7 mmol). After purification by column chromatography (silica gel, CH_2Cl_2/MeOH 60:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.59 g, 44%), mp 209 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.93 (d, *J*=5.6 Hz, 2H), 1.15–1.46 (m, 8H), 1.22 (d, *J*=4.4 Hz, 6H), 1.62–1.77 (m, 12H), 1.94 (s, 6H), 2.00–2.10 (m, 2H), 2.78 (t, *J*=7.2 Hz, 4H), 3.93–4.02 (m, 2H), 5.52 (d, *J*=9.0 Hz, 2H), 7.17 (s, 2H); ^{13}C NMR (74.5 MHz, $CDCl_3$): δ_C 14.7 (q), 17.9 (q), 22.9 (t), 26.2 (t), 26.4 (t), 29.1 (t), 38.4 (t), 43.2 (d), 49.8 (d), 129.1 (d), 134.6 (s), 134.8 (s), 136.3 (s), 139.4 (s), 161.0 (s); MS (EI): 566 [M^+]; HRMS calcd for $C_{33}H_{46}N_2O_2S_2$ 566.300, found 566.299.

*4.3.3. Compound **3**, 1,2-bis(5′-[((R)-(−)-1-methyl-3-phenylpropyl-amino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene*

As for **1**, except from **A** (0.75 g, 2.4 mmol) and (*R*)-(−)-1-methyl-3-phenylpropylamine (0.72 g, 4.8 mmol). After purification by column chromatography (silica gel, CH_2Cl_2/MeOH 100:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (308 mg, 0.50 mmol, 21%), mp 159.4–160.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.97 (s, 6H), 2.11 (m, 2H), 2.73 (t, *J*=7.5 Hz, 2H), 2.83 (t, *J*=7.5 Hz, 2H), 4.22 (m, 2H), 5.58 (d, *J*=8.4 Hz, 2H), 7.16 (s, 2H), 7.23 (d, *J*=7.2 Hz, 4H), 7.31 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.7 (q), 21.0 (q), 22.9 (t), 32.4 (t), 38.5 (t), 38.6 (t), 45.7 (d), 125.9 (d), 128.3 (d), 128.5 (d), 129.2 (d), 134.5 (s), 134.7 (s), 136.3 (s), 139.6 (s), 141.7 (s), 161.1 (s); IR: ν 1308, 1460, 1560, 1623, 2873, 2962, 3067 cm^{-1}; MS (EI): 610 [M^+]; HRMS calcd for $C_{37}H_{42}S_2N_2O_2$ 610.269, found 610.267.

*4.3.4. Compound **4**, 1,2-bis(5′[(tert-butylamino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene*

As for **1**, except from **A** (0.50 g, 1.44 mmol) and *tert*-butylamine (0.32 ml, 3.0 mmol). After purification by column chromatography (silica gel, CH_2Cl_2/MeOH 25:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.32 g, 48%), mp 143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.41 (s, 18H), 1.92 (s, 6H), 1.99–2.09 (m, 2H), 2.76 (t, *J*=7.5 Hz, 4H), 5.56 (s, 2H), 7.09 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.7 (q), 28.9 (q), 38.4 (t), 51.8 (t), 124.0 (s), 128.8 (d), 134.7 (s), 135.7 (s), 136.2 (s), 139.4 (s), 161.1 (s); IR: ν 1535, 1559, 1622, 2851, 2913, 2958, 3291 cm^{-1}; MS (DEI): 458 [M^+]; HRMS calcd for $C_{25}H_{34}S_2N_2O_2$ 458.206, found 458.205.

*4.3.5. Compound **5**, 1,2-bis(5′-[(propylamino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene*

As for **1**, except from **A** (0.75 g, 2.4 mmol) and propylamine (0.28 g, 4.8 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 100:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (158 mg, 0.37 mmol, 15%), mp176.0–177.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.93 (t, *J*=7.5 Hz, 6H), 1.54–1.62 (m, 4H), 1.92 (s, 6H), 2.03 (m, 2H), 2.76 (t, *J*=7.2 Hz, 4H), 3.32 (m, 4H), 5.77 (m, 2H), 7.16 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 11.4 (q), 14.7 (q), 22.8 (t), 22.9 (t), 23.0 (t), 38.4 (t), 41.6 (t), 129.2 (d), 134.4 (s), 134.7 (s), 136.2 (s), 139.6 (s), 161.7 (s), IR: ν 1308, 1362, 1460, 1560, 1623, 2873, 2962, 3067 cm^{-1}; MS (EI): 430 [M^+-1]; HRMS calcd for $C_{23}H_{30}S_2N_2O_2$ 430.174, found 430.175.

*4.3.6. Compound **6**, 1,2-bis(5′-[(hexylamino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene*

As for **1**, except from **A** (0.500 g, 1.44 mmol) and hexylamine (0.22 ml, 2.9 mmol). After purification, column chromatography

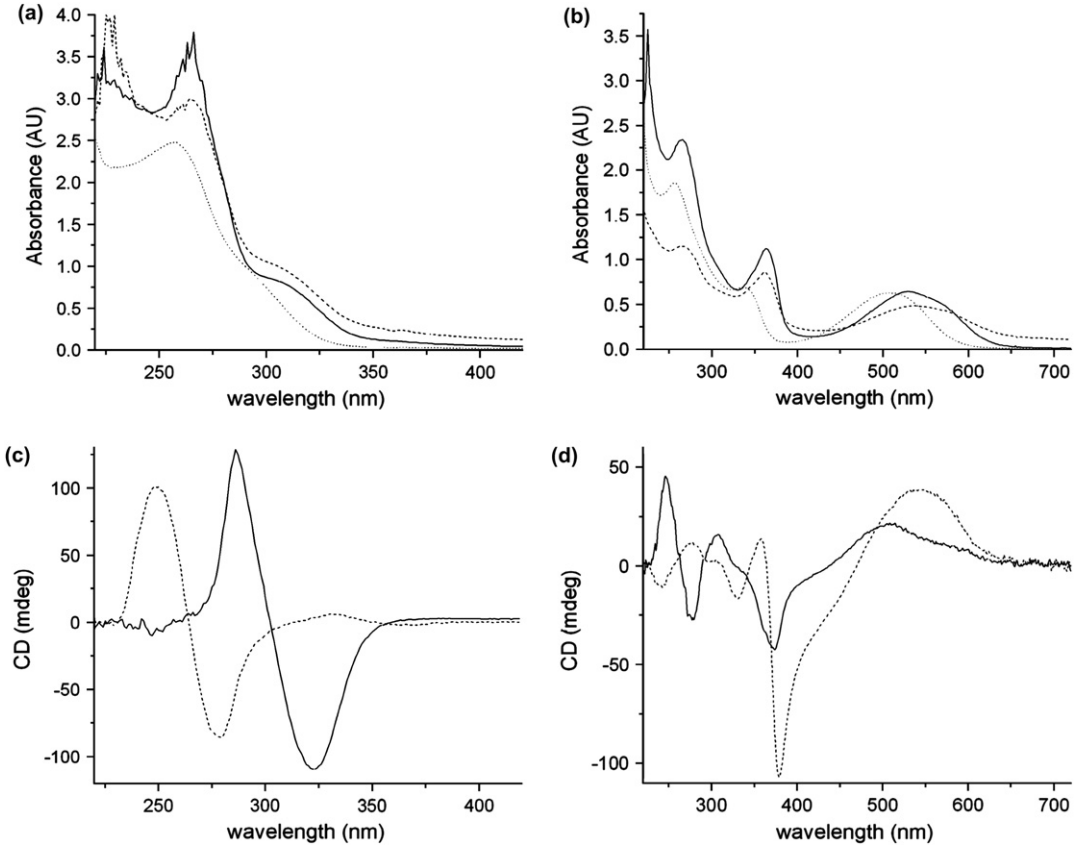

Figure 10. UV (a/b) and CD spectra (c/d) for **3** (3 mg/ml) in cyclohexane. (a/c) solid line is gel α **3o**, dashed is gel β **3o**, (b/d) dashed is gel α **3c** and solid line is gel β **3c** for **3**. The UV/vis spectra of (a) **3o** and (b) **3c** in solution are also shown (dotted lines).

(silica gel, CH_2Cl_2/MeOH 10:1) and stirring in excess hexane with a few drops of MeOH, an off-white solid was obtained (0.386 g, 0.75 mmol, 52%), mp 124–127 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.87 (t, J=6.8 Hz, 6H), 1.27–1.36 (m, 12H), 1.52–1.58 (m, 6H), 1.98 (s, 6H), 2.01–2.07 (m, 2H), 2.75–2.80 (m, 4H), 3.33–3.37 (m, 4H), 5.72 (t, J=5.5 Hz, 2H), 7.16 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.0 (q), 14.7 (q), 22.5 (t), 22.9 (t), 26.6 (t), 29.6 (t), 31.5 (t), 38.4 (t), 40.0 (t), 129.2 (d), 134.4 (s), 134.7 (s), 136.2 (s), 139.5 (s), 161.7 (s); IR: ν 1306, 1373, 1535, 1616, 2855, 2954, 3064, 3295 cm^{-1}; MS (EI): 514 [M$^+$]; HRMS calcd for $C_{29}H_{42}N_2O_2S_4$ 514.269, found 514.269.

4.3.7. Compound **7**, 1,2-bis(5′[(dodecylamino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.200 g, 0.6 mmol) and dodecylamine (0.26 ml, 1.2 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 40:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.22 g, 53%), mp 102 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.41 (t, J=6.6 Hz, 6H), 1.24 (m, 18H), 1.56 (m, 4H), 1.92 (s, 6H), 1.97–2.07 (m, 2H), 2.77 (t, J=7.5 Hz, 4H), 3.35 (m, 4H), 5.77 (m, 2H), 7.17 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.1 (q), 14.6 (q), 22.7 (t), 22.8 (t), 26.8 (t), 26.9 (t), 29.3 (t), 29.4 (t), 29.5 (t, 2×), 29.6 (t, 2×), 31.9 (t), 38.4 (t), 40.0 (t), 129.3 (d), 134.4 (s), 134.7 (s), 136.2 (s), 139.5 (s), 161.8 (s); IR: ν 1535, 1561, 1618, 2852, 2922, 3298 cm^{-1}; MS (DEI): 682 [M$^+$]; HRMS calcd for $C_{41}H_{66}S_2N_2O_2$ 682.457, found 682.452.

4.3.8. Compound **8**, 1,2-Bis(2′-methyl-5′-octyldecylcarbonyl-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.50 g, 1.44 mmol) and octyldecylamine (0.77 g, 2.9 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 40:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.55 g, 45%), mp 116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 0.86 (t, J=6.3 Hz, 6H), 1.24 (m, 60H), 1.29 (m, 4H), 1.91 (s, 6H), 1.99–2.08 (m, 2H), 2.76 (t, J=7.5 Hz, 4H), 3.35 (q, J=6.6 Hz, 4H), 5.77 (t, J=5.1 Hz, J=5.4 Hz, 2H), 7.18 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.1 (q), 14.7 (q), 22.7 (t), 22.9 (t), 29.3 (t), 29.4 (t), 29.6 (t), 29.7 (t, m), 31.9 (t), 38.5 (t), 40.0 (t), 129.3 (d), 134.4 (s), 134.7 (s), 136.3 (s), 139.5 (s), 161.7 (s); MS (EI): 851 [M$^+$].

4.3.9. Compound **9**, 1,2-bis(5′-[(cyclohexylamino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.500 g, 1.44 mmol) and cyclohexylamine (0.31 ml, 2.9 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 60:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.068 g, 0.13 mmol, 9%), mp 256–260 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.14–1.23 (m, 8H), 1.34–1.43 (m, 4H), 1.61 (q, J=4.3 Hz, 4H), 1.63–1.69 (m, 4H), 1.91 (s, 6H), 1.96 (d, 4H), 2.05 (m, 2H), 2.76 (t, J=7.5 Hz, 4H), 3.83–3.90 (m, 2H), 5.55 (d, J=7.5 Hz, 2H), 7.15 (s, 2H); ^{13}C NMR (75.4 MHz, DMSO): δ_C 14.2 (q), 22.3 (t), 24.9 (t), 25.2 (t), 32.5 (t), 38.3 (d), 48.2 (t), 128.6 (d), 134.0 (s), 136.0 (s), 138.5 (s), 146.2 (s), 159.9 (s); IR: ν 1324, 1374, 1529, 1613, 2850, 2925, 3075, 3275 cm^{-1}; MS (EI): 510 [M$^+$]; HRMS calcd for $C_{29}H_{38}N_2O_2S_4$ 510.237, found 510.237.

4.3.10. Compound **10**, 1,2-bis(5′-[(1-cyclohexylmethylamino)-carbonyl]-2′-methyl-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.450 g, 1.29 mmol) and cyclohexylmethylamine (0.30 ml, 2.6 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 100:1) and stirring in excess hexane with a few drops of MeOH, an off-white solid was obtained (0.180 g, 0.32 mmol, 51%), mp 215–217 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 0.94 (q, J=11.7 Hz, 4H), 1.13–1.23 (m, 4H), 1.54

(s, 4H), 1.65 (d, 2H), 1.73 (d, J=6.3 Hz, 8H), 1.94 (s, 6H), 2.04 (t, J=7.5 Hz, 2H), 2.75 (t, J=7.5 Hz, 4H), 3.20 (t, J=6.5 Hz 4H), 5.76 (t, J=6.0 Hz, 2H), 7.16 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.7 (q), 22.9 (t), 25.8 (t), 26.4 (t), 30.8 (t), 38.0 (d), 38.4 (t), 46.1 (t), 129.3 (d), 134.4 (s), 134.7 (s), 136.3 (s), 139.6 (s), 161.8 (s); IR: ν 1308, 1372, 1533, 1612, 2849, 2960, 3057, 3240 cm^{-1}; MS (EI): 538 [M$^+$]; HRMS calcd for $C_{31}H_{42}N_2O_2S_4$ 538.269, found 538.269.

4.3.11. Compound **11**, 1,2-bis(5′-(anilinocarbonyl)-2′-methyl-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.50 g, 1.44 mmol) and aniline (0.28 ml, 2.9 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 50:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.27 g, 37%), mp 150 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.01 (s, 6H), 2.04–2.14 (m, 2H), 2.82 (t, J=7.5 Hz, 4H), 7.12 (t, J=7.2 Hz, 4H), 7.33 (t, J=7.2 Hz, 4H), 7.51 (s, 2H), 7.56 (d, J=7.8 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.7 (q), 22.9 (t), 38.4 (t), 127.6 (d), 127.9 (d), 128.7 (d), 129.5 (d), 134.0 (s), 134.7 (s), 136.3 (s), 138.1 (s), 140.1 (s), 161.6 (s); MS (DEI): 498 [M$^+$]; HRMS calcd for $C_{29}H_{26}S_2N_2O_2$ 498.144, found 498.143.

4.3.12. Compound **12**, 1,2-bis(5′-[(benzylamino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene

This compound was prepared as described for **1**, starting from **A** (0.50 g, 1.44 mmol) and benzylamine (0.31 ml, 2.9 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 50:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.18 g, 23%), mp 204 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.92 (s, 6H), 1.99–2.07 (m, 2H), 2.75 (t, J=7.5 Hz, 4H), 4.57 (d, J=5.4 Hz, 4H), 6.02 (t, J=7.3 Hz, 2H), 7.19 (s, 2H), 7.28–7.36 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.8 (q), 22.9 (t), 38.4 (t), 43.9 (t), 120.1 (d), 124.4 (d), 129.0 (d), 130.2 (d), 134.5 (s), 134.9 (s), 136.6 (s), 137.7 (s), 140.9 (s), 159.9 (s); MS (DEI): 526 [M$^+$]; HRMS calcd for $C_{31}H0_{30}S_2N_2O_2$ 526.175, found 526.174.

4.3.13. Compound **13**, 1,2-bis(5′-[((p)-tert-butylphenylamino)-carbonyl]-2′-methyl-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.500 g, 1.44 mmol) and (*p*)-*tert*-butylphenylamine (0.37 ml, 2.9 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 30:1) and stirring in excess ether with a few drops of MeOH, a white solid was obtained (0.092 g, 0.15 mmol, 26%), mp 160–174 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.26–1.31 (m, 18H), 2.00 (s, 6H), 1.96–2.15 (m, 2H), 2.79 (t, J=7.5 Hz, 4H), 7.29 (s, 2H), 7.32 (q, J=3.7 Hz, 4H), 7.46 (q, J=6.8 Hz, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.8 (q), 22.9 (t), 31.3 (q), 34.4 (t), 38.3 (s), 119.9 (d), 125.9 (d), 130.0 (d), 134.6 (s), 134.9 (s), 1345.0 (s), 136.5 (s), 140.7 (s), 147.4 (s), 159.7 (s); IR: ν 1319, 1362, 1526, 1646, 2868, 2962, 3057, 3387 cm^{-1}; MS (EI): 610 [M$^+$]; HRMS calcd for $C_{37}H_{42}N_2O_2S_2$ 610.269, found 610.268.

4.3.14. Compound **14**, 1,2-bis(5′-[((m)-(m)-di-tert-butylphenyl-amino)carbonyl]-2′-methyl-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.500 g, 1.44 mmol) and (2,5)-di-*tert*-butylphenylamine (0.237 mg, 2.9 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 30:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.039 g, 0.05 mmol, 7%), mp 214–215 °C (dec); ^{1}H NMR (500 MHz, DMSO): δ_H 1.24–1.31 (m, 36H), 1.93 (s, 6H), 2.08 (m, 2H), 2.84 (t, J=8.7 Hz, 4H), 7.13 (s, 2H), 7.57 (s, 4H), 7.79 (s, 2H), 9.79 (s, 2H); ^{13}C NMR (188.5 MHz, DMSO): δ_C 13.8 (q), 22.1 (t), 30.7 (q), 30.8 (q), 30.8 (q), 34.1 (t), 38.0 (s), 114.3 (d), 114.4 (s), 114.4 (d), 116.4 (d), 116.8 (s), 117.1 (d), 129.1 (s), 129.3 (d), 133.9 (s), 135.5 (s), 135.6 (s), 137.6 (s), 139.3 (s), 150.1 (s), 158.9 (s); IR: ν 1322, 1361, 1513, 1630, 2865, 2961, 3079, 3249 cm^{-1}; MS (EI): 723 [M$^+$−1]; HRMS calcd for $C_{45}H_{58}N_2O_2S_2$ 722.393, found 722.394.

4.3.15. Compound **15**, 1,2-bis(2′-methyl 5′-{[((R)-(+)-1-naphthylethyl)amino]carbonyl}-thien-3′-yl)cyclopentene

As for **1**, except from **A** (0.500 g, 1.44 mmol) and *R*-(+)-naphthylethylamine (0.186 ml, 2.9 mmol). After purification, column chromatography (silica gel, CH_2Cl_2/MeOH 30:1) and stirring in excess ether with a few drops of MeOH, an off-white solid was obtained (0.073 g, 0.11 mmol, 19%), mp 244–247 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.72 (d, J=11 Hz, 6H), 1.84 (s, 6H), 1.90–2.15 (m, 2H), 2.68 (t, J=12.3 Hz, 4H), 5.90 (d, J=12.5 Hz, 2H), 6.03 (t, J=7.3 Hz, 2H), 7.09 (s, 2H), 7.40–7.52 (m, 8H), 7.81 (q, J=16.2 Hz, 4H), 8.12 (d, J=12.5 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ_C 14.7 (q), 20.8 (q), 22.8 (t), 38.5 (t), 45.1 (d), 122.7 (d), 123.4 (d), 125.2 (d), 125.9 (d), 126.7 (d), 128.5 (d), 128.8 (d), 129.4 (d), 131.1 (s), 133.9 (s), 134.1 (s), 134.6 (s), 136.2 (s), 138.0 (s), 140.0 (s), 160.7 (s); IR: ν 1334, 1371, 1530, 1615, 2842, 2947, 3050, 3280 cm^{-1}; MS (EI): 654 [M$^+$−1]; HRMS calcd for $C_{41}H_{38}N_2O_2S_2$ 654.236, found 654.237.

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7. For **2** only the *R*- and *S*-enantiomer and for **3** only the *R*-enantiomer were prepared. However, for **1** the racemic, *R*- and *S*-enantiomer of the compound, which were examined previously[5c] were prepared. For both **1** and **2** the *S*-enantiomer showed similar (but as expected opposite) behaviour to the *R*-enantiomers. For clarity only the *R*-enantiomer will be discussed in the present work.
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10. For electrochemical properties compounds **1**–**13** show very similar behavior. For all compounds in the open state an irreversible wave at 1.29 (3) V (vs SCE) was observed, which did not result in switching to the closed form, with the exception of **11o**, where the oxidation falls outside the potential window of methanol. In the closed state all compounds, including **11c**, show a quasi reversible oxidation at 0.74 (2) V (vs SCE) and an irreversible oxidation at 0.83 (2) V (vs SCE).
11. 30–120 s after cooling to rt, and even faster by quenching in either ice-water (0 °C), cold methanol (−40 °C) or even liquid nitrogen (−192 °C).

12. Zweep, N. Ph.D. thesis, University of Groningen: Groningen, The Netherlands, 2006.
13. The zero point crossing on the *y*-axis is obsecured by the solvent absorption, but extrapolation of the lines point to a common CD minimum at λ=297 nm.
14. All samples were prepared similarly, although at different minimal gelation concentrations according to Table 1. The concentrations needed for gelation of **2o** in benzene, tetralin, 1,4-dioxane and butylacetate are too high to allow for measurement of CD spectra.
15. As for **1o**, the zero point crossing on the *y*-axis is obsecured by the solvent absorption for **2o**, but extrapolation of the lines point to a common CD minimum at λ=295 nm.
16. Irradiation of **3o** in chloroform-d_1 and in hot toluene showed racemic **3c** with signals for the thiophene proton matching those of the gels.
17. For the spectrum of **1o** in toluene see Ref. 5c.
18. The absorbance between 325–380 nm is close to the limit of the dynamic range of the spectrophotometer; the unusual shape of the CD signal for gel β **2c** is due to the high absorbance.
19. For redox properties of related diarylcyclopentenes in solution, see: (a) Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem.—Eur. J.* **2005**, *11*, 6414–6429; (b) Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem.—Eur. J.* **2005**, *11*, 6430–6441.
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