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Photoreversible Supramolecular Polymerisation and Hierarchical Organization of Hydrogen-Bonded Supramolecular Co-polymers Composed of Diarylethenes and Oligothiophenes

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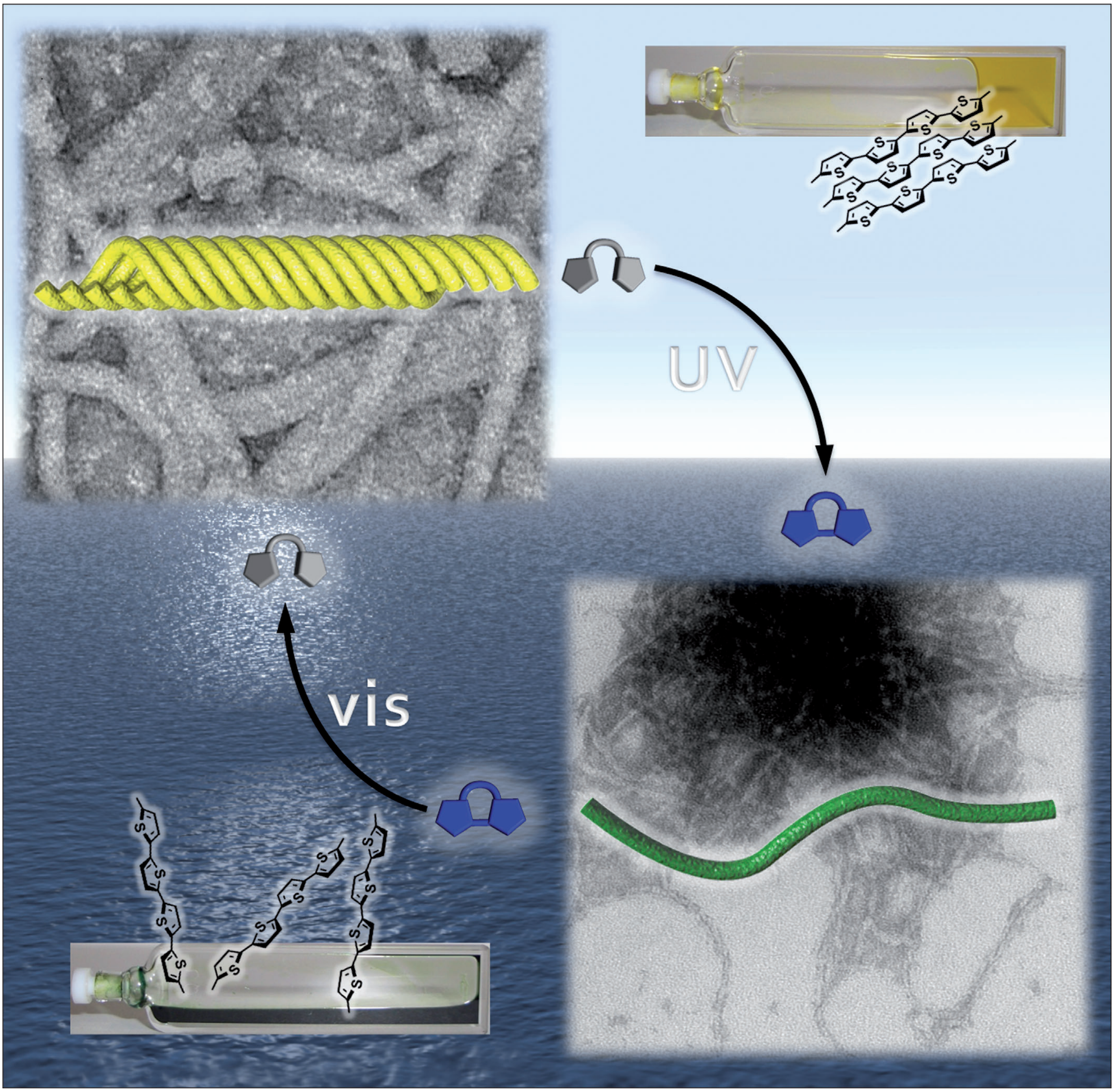

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Abstract: Diarylethene **1** equipped with two monotopic melamine hydrogen-bonding sites and oligothiophene-functionalized ditopic cyanurate (OTCA) were mixed in a nonpolar solvent to form AA-BB-type supramolecular co-polymers (SCPs) bearing photoswitchable moieties in their main chains and extended π systems as side chains. UV/Vis, fluorescence, dynamic light scattering (DLS), TEM, and AFM studies revealed that the two functional co-monomers formed flexible quasi-one-dimensional SCPs in solution that hierarchically self-organized into helical nanofibers through H-aggregation of the oligothiophene side chains. Upon irradiating the SCPs with UV light, a transition occurred from the H-aggregated state to non-aggregated monomeric oligothiophene side chains, as shown by spectroscopic studies, which indicates the formation of small oligomeric species held together only by hydrogen-bonding interactions. TEM and AFM visualized unfolded fibrils corresponding to elongated single SCP chains formed upon removal of solvent. The helical nanofibers were regenerated upon irradiating the UV-irradiated solution with visible light. These results demonstrated that the supramolecular polymerisation followed by hierarchical organization can be effectively controlled by proper supramolecular designs using diarylethenes and π-conjugated oligomers.

Keywords: diarylethenes • oligothiophenes • photoresponsive assemblies • self-assembly • supramolecular polymers

Introduction

Main-chain supramolecular polymers, in which noncovalent interactions are the driving force for polymerisation, are probably one of the most promising applications of supramolecular chemistry owing to their extreme sensitivity to external stimuli arising from the reversible nature of these interactions.[1] Among the many supramolecular polymers based on various noncovalent interactions, those based on multiple hydrogen bonds, pioneered by Lehn[2] and Meijer,[3] are within the main stream of research investigations.[1] The high directionality and selectivity of multiple hydrogen bonds allow fine control over polymer architectures and properties.[4] Another distinct advantage of multiple hydrogen bonds in supramolecular polymer research is that more than one functional molecular element can be readily incorporated into a polymer chain, affording complex and multifunctional polymeric materials.[5] Furthermore, the incorporation of secondary interaction sites, such as extended π systems, organize supramolecular polymer chains into complex higher-order nanostructures.[6,7] Although many of the supramolecular polymers feature dynamic and reversible monomerisation/polymerisation triggered by changes in the external environment, such as temperature, solvent, and concentration, the design of the supramolecular polymers for which higher-level organization could be controlled with accessible external stimuli may open new possibilities in their applications.[8]

Light is arguably the most useful external stimulus, because of its non-invasive character, high spatial and temporal resolution, and its ability to excite selected chromophores absorbing at a certain wavelength.[9] Thus, various photochromic molecules have been functionalized with specific noncovalent interaction sites, and the impact of photoinduced mechanical motion on their aggregation has been investigated.[10,11] While many of these systems were characterized by the photoinduced disassembling/assembling of molecular building blocks, some of them displayed photoreversible transformations between two well-defined self-assembled nanostructures.[12] However, there are no examples of phototransformable nanostructures composed of electronically active π-conjugated molecular elements, despite their potential utility in smart nanoelectronics and nanophotonics.[13]

To photochemically transform the robust supramolecular nanostructures that are stabilized by strong π–π stacking interactions, a rational co-assembly of proper photochromic molecules and functional π-conjugated molecules is required. We have previously exploited azobenzene/perylene bisimide bichromophoric supramolecular co-polymers connected through melamine–imide multiple hydrogen-bonding interactions to fabricate supramolecular dye assemblies, the nanostructures of which could be controlled by external light input.[14] Owing to the attractive interchain J-type π–π stacking interaction between the perylene chromophores embedded in the main chain, the hydrogen-bonded co-poly-

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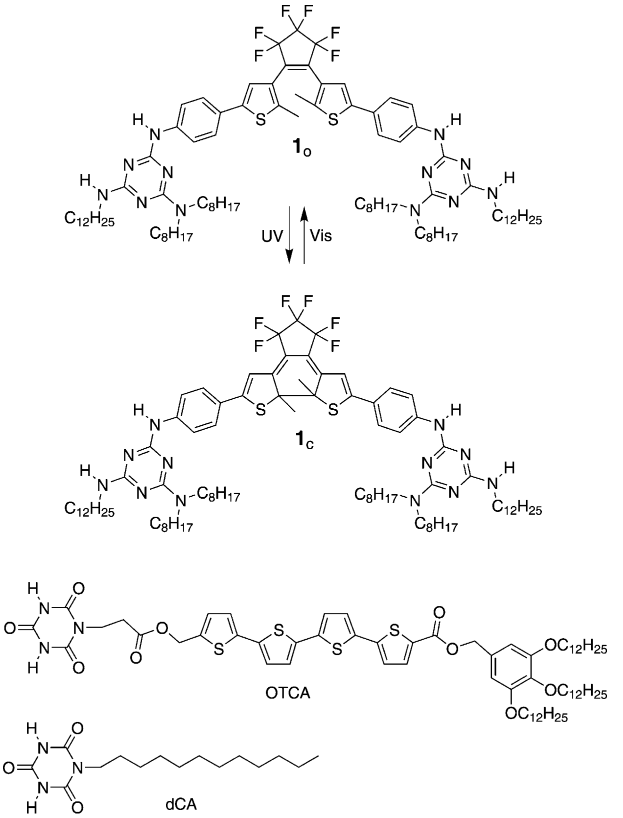
mers afforded unique coil-shaped nanostructures. Despite the favourable chromophore packing within these nanostructures, the photoisomerisation of their constituent azobenzene moieties was severely suppressed due to tight molecular packing (H-aggregation). In this context, diarylethenes (DAEs) were particularly appealing, because of their known ability to photoisomerise even in the crystalline state.[15] Several DAE derivatives suitable for supramolecular assembly have already been designed and shown to exhibit unique photoresponsive aggregation properties.[16] Such photoresponsive aggregation of these supramolecular DAE systems is based on conformational changes upon ring-closing/ring-opening reactions and/or modification of the electron density of DAE moieties.

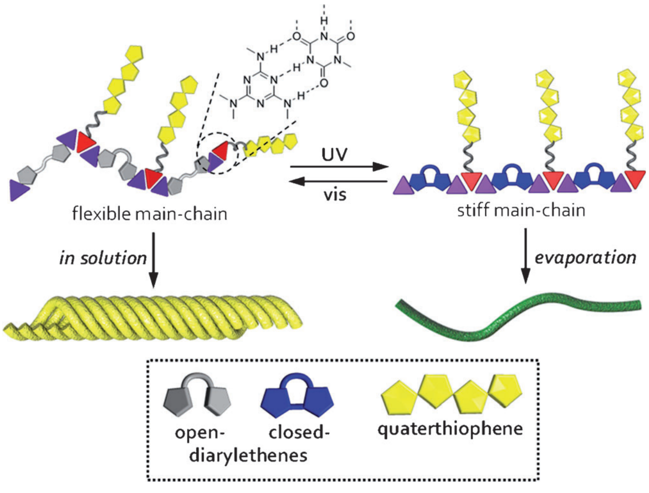
Here we report a supramolecular polymer system in which DAEs form part of the main chain of hydrogen-bonded supramolecular polymers[17] bearing π-electronic side chains.[18] For this supramolecular polymer system, it is possible to modulate the conformational flexibility of the main chain by reversible ring-closing and ring-opening photoreactions of the DAE moieties. The π-electronic side chains enable higher-order organization of the supramolecular polymers by interchain π–π stacking, thus rendering the impact of the flexibility change detectable by spectroscopy and microscopy, as well as imparting fruitful optical and electronic properties to the supramolecular polymers. As a consequence of distinct functional properties in the main chain and the side chain, a high level of control over the supramolecular polymerisation, that is, a reversible transition between helically intertwined secondary structures and small oligomeric species,[19,20] was achieved by modifying the external light input.

Results and Discussion

Design and synthesis: We have designed a supramolecular co-polymer (SCP) system consisting of diarylethene **1** functionalized at its ends with two monotopic melamine hydrogen-bonding modules and oligothiophene-functionalized ditopic cyanurate OTCA (Scheme 1).[21] Complementary triple hydrogen-bonding interactions between these ditopic comonomers were expected to afford quasi-one-dimensional AA+BB-type SCPs possessing photoswitchable DAE moieties in their main chains with oligothiophene (OT) moieties as side chains (Scheme 2).[22] It was anticipated that photocyclisation of the DAE moieties residing in the main chains would decrease the conformational flexibility of the SCPs by restricting the conformational freedom associated with rotation of the thiophene rings.[15a] The OT moieties not only imparted favourable optical and electronic properties to the SCPs, but also enabled their higher-order nanostructurisation, thus amplifying the impact of photoswitching.



Scheme 1. Structure of melamine-appended diarylethene **1** in its open ($\mathbf{1}_o$) and closed forms ($\mathbf{1}_c$) and oligothiophene-functionalized cyanurate (OTCA) and dodecylated cyanurate (dCA).



Scheme 2. Schematic representation of the photoresponsive hierarchical organization of supramolecular co-polymers of **1** and OTCA.

Diarylethene **1** was synthesized from 1,2-bis[5-(4-aminophenyl)-2-methylthien-3-yl]perfluorocyclopentene[23] by reaction with 1,3,5-trichloro-2,4,6-triazine and subsequent reactions with *n*-dodecylamine and di-*n*-octylamine. The synthesis of oligothiophene-functionalized cyanurate OTCA has been reported previously.[21]

Photoisomerisation of melamine-appended DAE 1 and its aggregation with non-chromophoric cyanurate dCA: ^{1}H NMR spectra of **1** in $CDCl_3$ (Figure 1 A) revealed that **1**

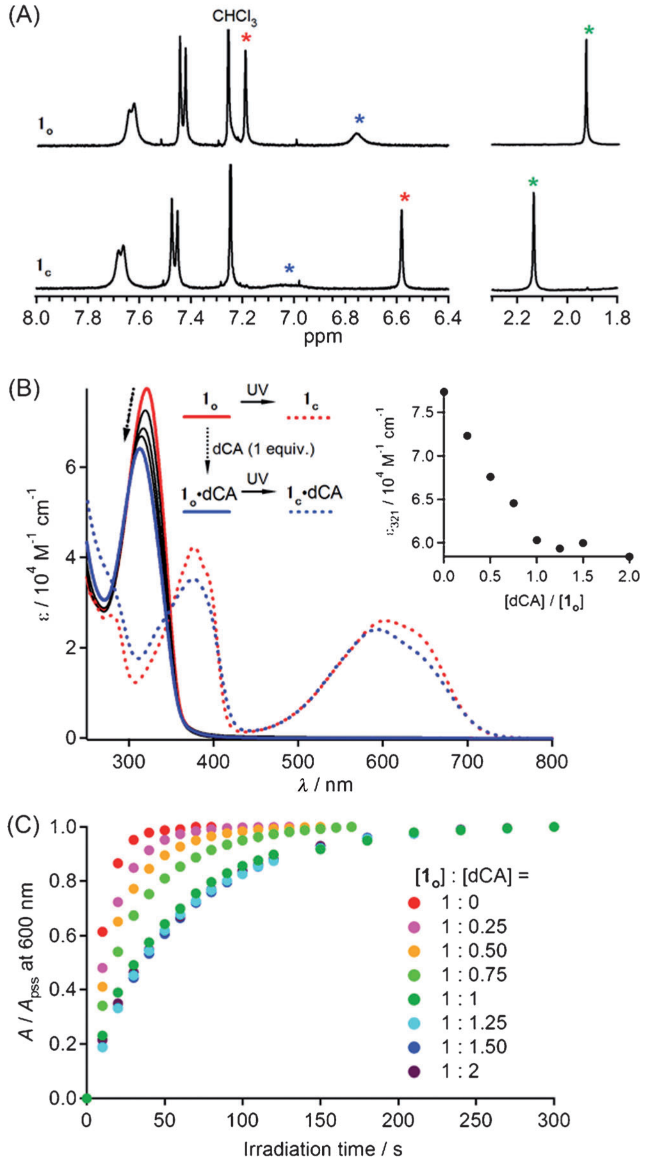


Figure 1. A) ^{1}H NMR spectra of $\mathbf{1}_o$ (top) in CDCl$_3$ (5×10^{-3} M), and of $\mathbf{1}_c$ (bottom), obtained by photoirradiation of $\mathbf{1}_o$ at 313 nm for 1 h. B) Red to blue solid curves: UV/Vis spectral changes of $\mathbf{1}_o$ (1×10^{-5} M) in cyclohexane upon addition of dCA (0, 0.25, 0.5, 0.75 and 1 equiv). The dotted arrow indicates the direction of increasing dCA. Inset shows the plot of ε at 321 nm versus equivalents of dCA (0–2 equiv). Red and blue dotted curves: UV/Vis spectra of solutions with 0 and 1 equiv of dCA recorded after photoirradiation at 313 nm for 80 (0 equiv) or 300 s (1 equiv). C) Time-course changes of the absorbance at 600 nm relative to that after reaching the photostationary state during photoirradiation of $\mathbf{1}_o$ (1×10^{-5} M) in cyclohexane in the presence of varying amounts of dCA (0–2 equiv). Photoirradiation was performed in a $\phi=5$ mm NMR tube or a 1 cm quartz cuvette using a fluorimeter equipped with a 150 W xenon lamp (band width = 20 nm).

underwent a reversible photochromic ring-opening ($\mathbf{1}_o\rightarrow\mathbf{1}_c$; subscripts o and c denote the open and closed forms, respectively) and ring-closing reaction ($\mathbf{1}_c\rightarrow\mathbf{1}_o$) upon irradiation with UV and visible light, respectively. In the NMR spectra, a prominent higher-field shift was observed for the proton resonance of the thiophene rings (marked by red star) upon ring-closing. In contrast, lower-field shifts were observed for the inner NH protons (marked by green star) and the methyl protons of the DAE core (marked by blue star). In the photostationary state (PSS), no proton resonances of $\mathbf{1}_o$ were observed, demonstrating the quantitative formation of $\mathbf{1}_c$. The UV/Vis spectrum of the PSS state of **1** in CHCl$_3$ thus corresponded to that of pure $\mathbf{1}_c$ (Figure S1 in the Supporting Information), allowing the determination of isomerisation yields by UV/Vis measurements in the following experiments.

The photochromic reaction of **1** also occurred in nonpolar solvents such as cyclohexane as shown by UV/Vis measurements (Figure 1B). The quantum yields of the ring-closing and the ring-opening reactions in cyclohexane were measured to be 0.58 and 0.0021, respectively. The relatively low quantum yield of the ring-opening reaction might be due to a substituent effect.[24] The reversible photochromic reaction in cyclohexane could be repeated at least ten times without degradation.

To confirm the hydrogen-bonding capability of **1** with ditopic cyanurates, we first investigated the complexation of $\mathbf{1}_o$ with monododecylated cyanurate (dCA) as a non-chromophoric co-monomer. Upon increasing the amount of dCA in a solution of $\mathbf{1}_o$ ($c=1\times10^{-5}$ M) in cyclohexane, a hypochromic effect was observed for the π–π transition of $\mathbf{1}_o$ at 321 nm (Figure 1B). This indicates that the electron density of the amino groups is affected by hydrogen-bonding interactions and/or complexation with dCA induces π–π stacking of the DAE moieties. Plots of the spectral change versus the equivalents of dCA displayed a kink at molar ratio 1:1 (inset in Figure 1B), confirming the quantitative complexation of these two ditopic co-monomers.[25] Such quantitative complexation in DAD–ADA (D = donor; A = acceptor) hydrogen-bonding systems at micromolar concentrations, the binding constants of which are only about 2×10^5 M^{-1}, are often observed for those containing π-conjugated systems, because additional π–π stacking interactions and/or the formation of cyclic species stabilize the resulting co-assemblies.[7c,d,h,i,14,22g,26]

Figure 1C shows progress of the ring-closing photoreaction of $\mathbf{1}_o$ in cyclohexane in the presence of varying amounts of dCA. The ring-closing reaction was suppressed with increasing content of dCA, which can be attributed to the induced π–π stacking interaction and/or the conformational fixation upon hydrogen bonding.[15a] This suppression levelled off when the amount of dCA reached one equivalent,[25] further confirming the 1:1 complexation. The quantum yield of the ring-closing reaction for the 1:1 mixture then diminished to 0.16. The absorption spectrum at the PSS state also showed a hypsochromic effect compared to pure $\mathbf{1}_c$, indicating the interaction with dCA through hydrogen bonding (Figure 1B). The quantum yield of the ring-opening reaction for the 1:1 mixture was 0.0020, almost identical to that of $\mathbf{1}_c$ alone. Despite the quantitative complexation of **1** with dCA, atomic force microscopy showed no well-defined nanostructured aggregates, either in the open or in the closed state, in films spin-coated from a 1×10^{-4} M solution.

Photoresponsive supramolecular co-polymerisation of 1 and OTCA: Oligothiophene-functionalized cyanurate (OTCA) was previously shown to form H-aggregates in nonpolar solvents.[21] The formation of H-aggregates was evidenced by a prominent hypsochromic shift (414→378 nm) of the absorption band and a bathochromic shift (513→540 nm) of the emission band originating from the π—π* transition of the OT moiety upon decreasing the solvent polarity. When aliquots of $\mathbf{1}_o$ were added to a solution of H-aggregated OTCA ($c = 1\times10^{-5}$ M) in cyclohexane, the absorption band of the OT moiety at 378 nm decreased and a new band appeared at 415 nm (Figure 2A). In the fluorescence spectra, the emission of the H-aggregates at 540 nm shifted to a more bluish band at 513 nm with more significant vibronic components, characteristic of the free OT moiety (Figure 2B). These observations demonstrated that $\mathbf{1}_o$ disrupted the H-aggregates of OTCA by its complementary triple hydrogen-bonding interaction. Both these spectral changes levelled off close to a 1:1 molar ratio (insets). The quantitative complexation suggests that the resulting 1:1 co-assemblies are further stabilized by π–π stacking interactions between the DAE moieties and also probably by the formation of cyclic species.

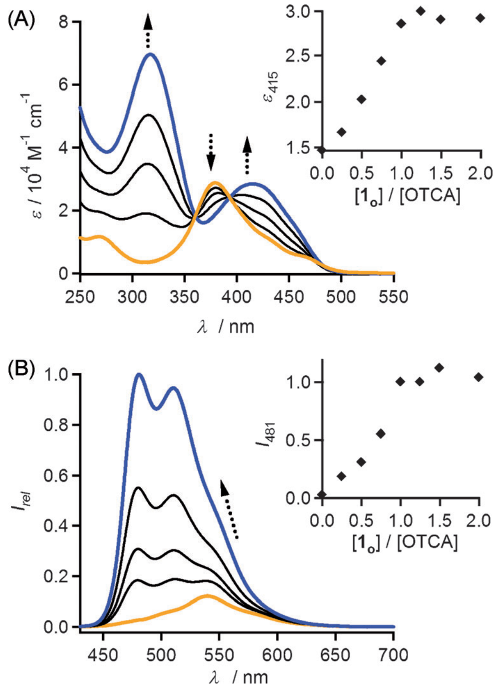


Figure 2. A) UV/Vis and B) fluorescence titration experiments of OTCA (1×10^{-5} M) with $\mathbf{1}_o$ (0 to 2 equiv) in cyclohexane. Only the spectra at OTCA:$\mathbf{1}_o$=1:0 (yellow), 1:0.25 (black), 1:0.5 (black), 1:0.75 (black) and 1:1 (blue) are shown for clarity. The arrows indicate the direction of spectral change upon increasing $\mathbf{1}_o$. Insets show changes in ε at 415 nm for A) and relative fluorescence intensity at 481 nm for B) with increasing [$\mathbf{1}_o$].

Upon increasing concentration of the 1:1 mixture, their higher-order organization was indicated by concentration-dependent changes in the UV/Vis and fluorescence spectra (Figure 3). Because of the slow progress of this higher-order organization towards equilibrium (Figure S2 in Supporting Information), the spectra were recorded after aging for 3 h. A hypsochromic shift of the absorption and a bathochromic shift of the emission of the OT moieties upon increasing the concentration from 1×10^{-5} to 1×10^{-4} M unequivocally indicate a transition from the free to the H-aggregated state. For this spectral change, the transition from the co-assembled state (complementarily hydrogen-bonded $\mathbf{1}_o$ and OTCA) to the self-sorted state (simple mixture of $\mathbf{1}_o$ and H-aggregated OTCA) was clearly excluded by the AFM study described later. For a 1×10^{-4} M solution, the formation of large aggregates with average size of 600 nm was confirmed by dynamic light scattering (DLS) measurements (Figure S3 in the Supporting Information). If only complementary hydrogen-bonding interactions between melamine and cyanurate moieties, the binding constants of which are about 2×10^{5} M^{-1},[22d] are responsible for the co-assembling of $\mathbf{1}_o$ and OTCA, the degree of polymerisation (DP) for $(\mathbf{1}_o+\mathrm{OTCA})_n$ at 1×10^{-4} M is only 2.6. Thus, cooperative H-aggregation of OT moieties promotes the supramolecular co-polymerisation, leading to the formation of the higher-order aggregates.[7d,26]

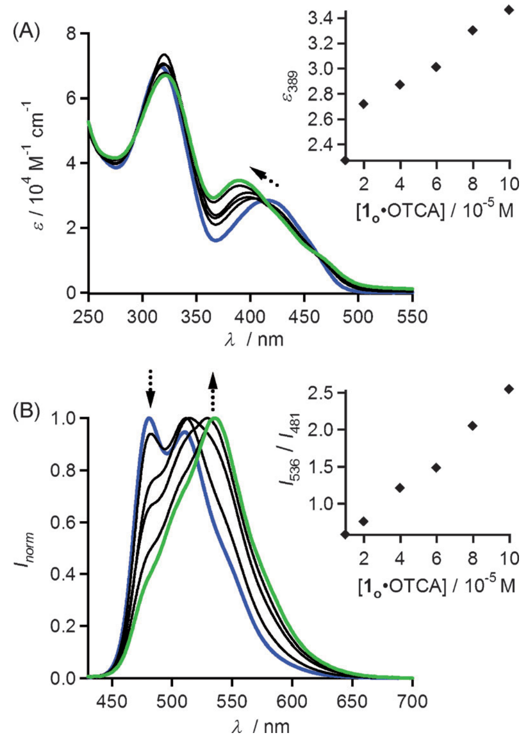


Figure 3. A) UV/Vis and B) normalized fluorescence spectra of a 1:1 mixture of $\mathbf{1}_o$ and OTCA in cyclohexane for concentrations from 1×10^{-5} M (blue) to 1×10^{-4} M (green). The arrows indicate the changes upon increasing the concentration. Insets show changes in ε at 389 nm in A) and the ratio of fluorescence intensities at 536 nm (H-aggregate) and 481 nm (monomer) in B) with increasing concentration of the mixture.

Upon irradiating a 1×10^{-4} M solution of SCPs $(\mathbf{1}+\text{OTCA})_n$ with UV light, $\mathbf{1}_o$ was almost completely converted to $\mathbf{1}_c$, as confirmed by UV/Vis measurements (Figure 4A and 4B). In contrast to the spectral changes accompanying the ring-closing reaction of $\mathbf{1}_o$ alone, no well-defined isosbestic point was observed at around 350 nm (inset in Figure 4A), implying that the ring-closing of the DAE moieties in the SCPs induced a change in the overlapping absorption band of the OT moiety. A more impressive change could be seen in the corresponding fluorescence spectra (Figure 4C and 4D). Significant quenching of the OT emission was observed upon UV irradiation due to Förster resonance energy transfer (FRET) to the closed DAE moiety, the visible absorption band of which overlaps considerably with the emission band of the OT moiety. More importantly, normalized fluorescence spectra clearly showed the unstructured emission band of the H-aggregated OT moiety gradually changing to that with the vibronic progression of the monomeric OT moiety (Figure 4C). This finding implies that the ring-closing reaction of the DAE moieties in the SCPs prevent their higher-order organization. Without additional π–π stacking interaction between OT moieties, the co-assemblies cannot elongate to form SCPs, and may exist as small hydrogen-bonded oligomers. Indeed, for the UV-irradiated solution, no large aggregates could be detected by DLS analysis.

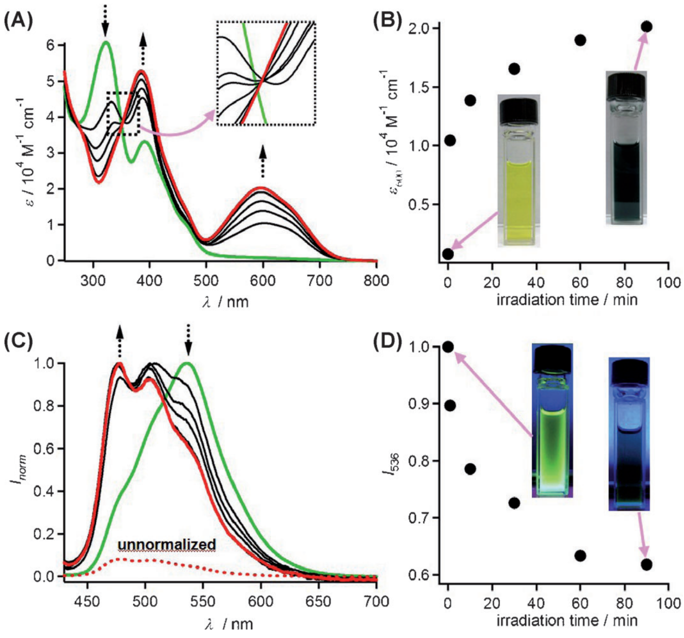


Figure 4. A) UV/Vis and C) normalized fluorescence spectra of a 1:1 mixture of $\mathbf{1}_o$ and OTCA (1×10^{-4} M) in cyclohexane upon photoirradiation at 313 nm (green to red spectra). The photoirradiation was performed in a 1 mm quartz cuvette using a 150 W xenon lamp equipped with fluorimeter (band width = 20 nm). Fluorescence spectra were recorded with the front-face geometry. The arrows indicate the changes upon photoirradiation. In C), the un-normalized spectrum recorded after 90 min of UV irradiation is shown by the red dotted curve. B) Time-course changes in ε at 600 nm in A). D) Time-course changes in fluorescence intensity at 536 nm in C).

TEM and AFM Studies of photoreponsive supramolecular co-polymers: The change in the nanostructure of the SCPs of **1** and OTCA upon UV irradiation was investigated by transmission electron microscopy (TEM). For this purpose, aliquots were taken from the 1×10^{-4} M solution of the SCPs in cyclohexane before and after exposure to UV light to achieve PSS state (photoconversion yield = 87 %), and deposited on TEM grids. TEM images of the SCPs without irradiation showed bundled nanofibers, the longest of which had lengths on the order of micrometers (Figure 5A). The widths of the nanofibers were quite uniform at 20 nm (Figure 5B), suggesting that the SCPs form a well-defined secondary structure. Interestingly, these nanofibers were completely absent in the TEM images of UV-irradiated SCPs, and neuron-like clumps of thinner fibrils were seen instead (Figure 5C). These fibrils were at most about 200 nm long, with a width of 5 nm (Figure 5D). The width is consistent with the extended molecular length of OTCA (ca. 5 nm), suggesting that the observed fibrils correspond to the linearly extended supramolecular co-polymer chains of $\mathbf{1}_c$ and OTCA. Since the distance between the two melamine hydrogen-bonding sites of $\mathbf{1}_c$ (based on the nitrogen atoms of the outer hydrogen-bonding NH groups) is about 2.5 nm, the DP for the 200 nm length fibril is roughly estimated to be 80. If such extended SCPs exist in solution, we should detect them by DLS. The absence of any large aggregates in the DLS experiments of $\mathbf{1}_c$ and OTCA thus suggests that these fibrils visualized by TEM are formed by an increase of the DP by solvent evaporation.

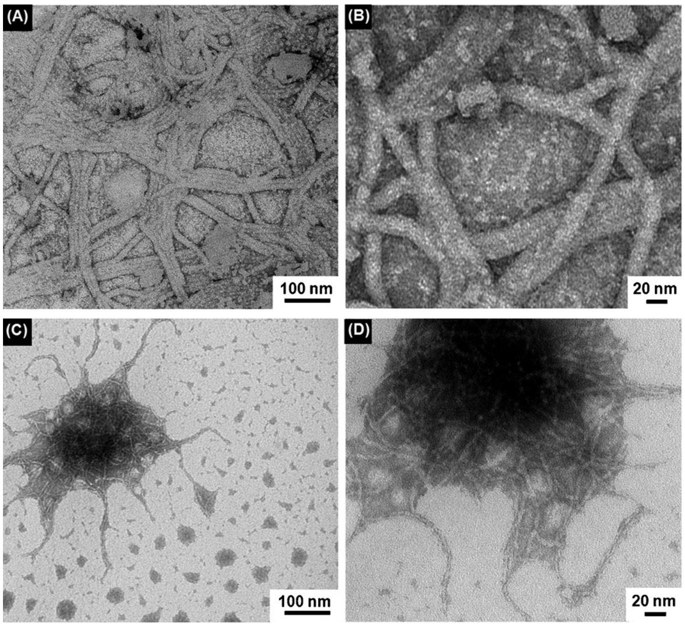


Figure 5. TEM images of A,B) $(\mathbf{1}_o+\text{OTCA})_n$ and C,D) $(\mathbf{1}_c+\text{OTCA})_n$. The samples were prepared by drop-casting of their cyclohexane solutions ($c = 1\times10^{-4}$ M) onto carbon-coated TEM grid and staining with uranyl acetate.

To examine the photoinduced nanostructure transition of our SCPs, they were imaged with atomic force microscopy (AFM) after different periods of exposure to UV light. The SCPs were spin-coated onto highly oriented pyrolytic graphite (HOPG). Without UV irradiation, SCPs $(\mathbf{1}_{\mathrm{o}}+\mathrm{OTCA})_n$ formed many bundled nanofibers (Figure S4 in the Supporting Information), consistent with TEM observations. Photoconversion of 50% of $\mathbf{1}_{\mathrm{o}}$ to $\mathbf{1}_{\mathrm{c}}$ resulted in the dispersion of the nanofibers, most likely due to the decrease in the concentration of $(\mathbf{1}_{\mathrm{o}}+\mathrm{OTCA})_n$ (Figures S5 and S6 in the Supporting Information). AFM imaging of the isolated nanofibers with a phase mode sensitive to the mechanical and chemical properties of materials revealed a helical morphology with an average helical pitch of (10±2) nm (Figure 6A and 6B). The helical sense appears to be unbiased, which is reasonable in the absence of any chiral sources. The average height of the nanofibers, estimated by cross-sectional analysis, was (8.2±0.1) nm (see Figure 6D, described later), considerably shorter than the width measured by TEM (20 nm).[27] The significant difference between these two measurements was attributed to the presumably hollow structure of the helices, which made them susceptible to deformation through evaporation processes.[14] The dimensions of the nanofibers are unambiguously different from those of previously reported nanostructures of self-aggregated OTCA,[21] indicating the formation of SCPs $(\mathbf{1}_{\mathrm{o}}+\mathrm{OTCA})_n$. The observed helical morphology is reminiscent of that found by Würthner and co-workers for merocyanine supramolecular polymer nanorods,[28] suggesting helical folding and intertwining of the SCP chains.

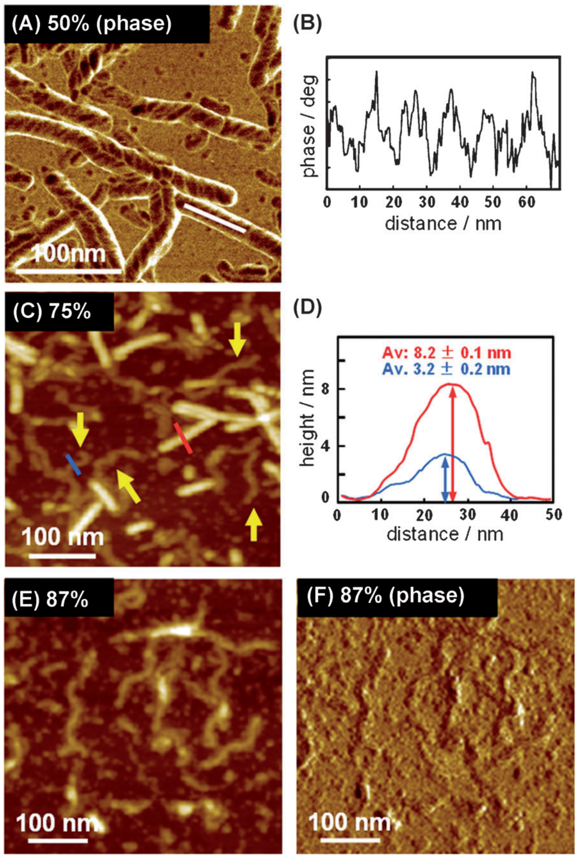


Figure 6. AFM images showing photoconversion of $(\mathbf{1}_{\mathrm{o}}+\mathrm{OTCA})_n$ to $(\mathbf{1}_{\mathrm{c}}+\mathrm{OTCA})_n$. A) Phase image obtained at 50% photoconversion to $\mathbf{1}_{\mathrm{c}}$. B) Cross sectional analysis along the white line in A). C) Height image obtained at 75% photoconversion to $\mathbf{1}_{\mathrm{c}}$. The yellow arrows denote fibrils of $(\mathbf{1}_{\mathrm{c}}+\mathrm{OTCA})_n$. D) Superimposed cross-sectional curves along the red and the blue lines in C). E) Height image and F) phase image, both at 87% photoconversion to $\mathbf{1}_{\mathrm{c}}$.

The images obtained at 75% photoconversion to $\mathbf{1}_{\mathrm{c}}$ displayed short, curved fibrils (Figure 6C). The average height of the fibrils was (3.2±0.1) nm (Figure 6D). At 87% photoconversion to $\mathbf{1}_{\mathrm{c}}$, almost all the nanofibers disappeared, leaving only curved fibrils and small particles (Figure 6E and 6F). The lengths of fibrils are about 100 nm, shorter than those observed by TEM. This is reasonable, because spin-coating enables a faster evaporation of solvent compared to drop-casting employed for the preparation of the TEM samples. When extensively UV-irradiated solutions were irradiated with visible light for the ring-opening reaction, helical nanofibers of $(\mathbf{1}_{\mathrm{o}}+\mathrm{OTCA})_n$ were regenerated, accompanying the nearly complete reconversion of $\mathbf{1}_{\mathrm{c}}$ to $\mathbf{1}_{\mathrm{o}}$ (Figure S7 in the Supporting Information), thus demonstrating the photoreversibility of the present system.

Electronic properties of nanostructures: Because our SCPs contained oligothiophene semiconductors, their intrinsic charge carrier mobilities were evaluated by flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements, which provided information on the short-range (ca. 10 nm) dynamics of mobile charge carriers.[29] To prepare films capable of exhibiting detectable TRMC signals, a 1:1 mixture of $\mathbf{1}_{\mathrm{o}}$ and OTCA was dissolved in cyclohexane at a high concentration (1×10^{-2} M) with heating. After the resulting homogeneous solution was cooled to room temperature, it formed a gel on standing for several minutes, as a result of the formation of elongated nanofibers.[10c,30] UV irradiation of the gel prepared in a 1 mm cuvette converted it to a solution together with a photochromic reaction (Figure 7A). Irradiation of the resulting sol with visible light reformed the original gel state. Although it was not possible to obtain images of the nanostructures formed in these condensed materials, the observed photoreversible sol–gel transition is consistent with the photoreversible supramolecular polymerisation seen in the above-described microscopic studies. We therefore prepared films from the gel and the sol for TRMC studies. Both films, upon excitation with a 355 nm laser pulse, exhibited TRMC signals given by $\phi\Sigma\mu$ (ϕ, photocarrier generation yield; $\Sigma\mu$, sum of the mobilities of photogenerated charge carriers) with a maximum value of $1.9\times10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ (Figure 7B). Since films of $\mathbf{1}_{\mathrm{o}}$ or $\mathbf{1}_{\mathrm{c}}$ alone showed negligible TRMC signals, the foregoing results indicate that both the films contained oligothiophene stacks as pathways for mobile charge carriers. For the film prepared from the sol, nonspecific aggregation of $(\mathbf{1}_{\mathrm{c}}+\mathrm{OTCA})_n$ might have occurred by π–π stacking of the OT moieties upon evaporating the solution. This was confirmed by fluo-

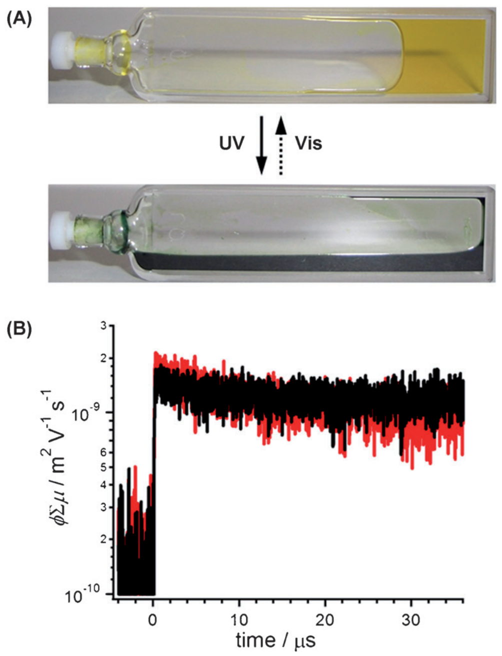


Figure 7. A) UV-induced gel-to-sol transition of the cyclohexane gel containing 1:1 mixture of $\mathbf{1}_o$ and OTCA ($c=1\times10^{-2}$ M). The resulting sol could be converted to the gel state by irradiation with visible light as formally shown by the dotted arrow. B) Conductivity transients observed for thin films of $(\mathbf{1}_o+\text{OTCA})_n$ (black line) and $(\mathbf{1}_c+\text{OTCA})_n$ (red line). The transients were recorded under 355 nm laser pulse excitation at 9.1×10^{15} photons cm^{-2}.

rescence measurements on the film prepared from the sol, which exhibited the luminescence at around 540 nm characteristic of H-aggregated OT moieties. From the values of ϕ measured by photocurrent integration (1.9×10^{-4}), the sum of the mobilities of photogenerated charge carriers $\Sigma\mu$ was estimated to be 0.1 cm^{2}V^{-1}s^{-1} for both films, comparable to that of regioregular poly(3-hexylthiophene) films.[31]

Conclusion

Photoreponsive and electroactive supramolecular co-polymers (SCPs) could be prepared by mixing two complementary, multiple-hydrogen-bonding modules functionalized by diarylethene (DAE) or oligothiophene (OT) moieties. From the spectroscopic and the microscopic investigations, it can be concluded that DAE can work as photoresponsive comonomer that lead to the formation of flexible and rigid supramolecular polymer chains by being incorporated into appropriate supramolecular polymer backbone (Scheme 2). The flexible open-form DAE moieties in $(\mathbf{1}_o+\text{OTCA})_n$ impart the SCP chains with sufficient conformational flexibility to fold and intertwine into thermodynamically stable helical nanofibers through interchain π–π stacking interactions (H-aggregation) between the pendent OT moieties. The ring-closing reaction of the DAE moieties reduced the conformational flexibility of the SCP chains, disabling them from organizing into higher-order structures. Without such a higher-order organization capability, SCPs of $(\mathbf{1}_c+\text{OTCA})_n$ are not formed in solution due to weak triple hydrogen-bonding interaction between melamines and cyanurates, and only when evaporation of the solvent occurs do they elongate to form fibrils with several hundreds of nanometers in length. Both the helically organized nanofibers and the photogenerated fibrils showed comparable charge transport capabilities, as shown by FP-TRMC, due to the nonspecific association of the latter in the condensed state. However, the high level of control over self-assembled nanostructures by the photochromic reaction of DAE demonstrated here affords a promising prospect of the use of supramolecular polymer chemistry for the spatiotemporally controlled generation of novel photo- and electroactive nanoarchitectures.[32]

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