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Multicolour Self-Assembled Fluorene Co-Oligomers: From Molecules to the Solid State via White-Light-Emitting Organogels

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Abstract: Five fluorene-based co-oligomers have been prepared to study their self-assembly in a wide range of concentrations, from dilute solutions to the solid state. Subtle changes to the chemical structures, introduced to tune the emission colours over the entire visible range, induce strong differences in aggregation behaviour. Only two of the fluorescent co-oligomer derivatives self-assemble to form soluble fibrils from which fluorescent organogels emerge at higher concentrations. In contrast, the other compounds form precipitates. Mixed fluorescent co-oligomer systems exhibit partial energy transfer, which allows the creation of white-light-emitting gels. Finally, a mechanism for the hierarchical self-assembly of this class of materials is proposed based on experimental results and molecular modelling calculations.

Keywords: energy transfer · fluorene · gels · liquid crystals · self-assembly

Introduction

π-Conjugated polymers and oligomers play a prominent role in organic electronic devices.[1] The macroscopic properties of these devices strongly depend on the chemical structure and the morphologies of the π-conjugated materials used and consequently a lot of research has focussed on the influence of these two factors.[2] Among the most studied classes of π-conjugated materials are polyfluorene and its copolymers.[1e,3] They are known to exhibit a richly varied phase behaviour and supramolecular chemistry.[4] Additionally, they allow easy band-gap tuning over a wide range when appropriate co-monomers are used,[3c,d] which results in emission colours that span the entire visible spectrum and reach even into the near infrared region.[5] Despite these promising prospects, only a few studies that have focussed on fluorene-based co-oligomers and their supramolecular chemistry have so far been published.[6] Such studies are interesting because they allow the effect of the chemical structure and the supramolecular state on, for example, the optical properties to be systematically investigated.

Recently we reported the synthesis and aqueous self-assembly of a set of fluorene co-oligomers equipped with hydrophilic tetra(ethylene glycol) wedges that form fluorescent nanoparticles with tuneable emission colours.[6e] Herein we describe a series of five fluorene-based (co)oligomers (**1**–**5**; Scheme 1) equipped with 3,4,5-tridodecylbenzamide wedges at the periphery that form self-assembled structures in an apolar solvent. The conjugated parts of the molecules consist of two chiral dialkylfluorene units linked by a central aromatic moiety (fluorene, naphthalene, quinoxaline, benzothiadiazole or thienopyrazine) that was chosen to cover a wide range of electron-accepting capability to vary the absorption and emission wavelengths with only minor changes in the shape and size of the molecules. Amide linkers between the chromophores and the wedges were chosen to introduce hydrogen bonding as a non-covalent ordering interaction. Our fluorene-based (co)oligomers can be classified as so-called polycatenars, which are known to exhibit a rich variety of thermotropic and lyotropic liquid crystalline (LC) mesophases.[7,8] We have studied the self-assembly of the

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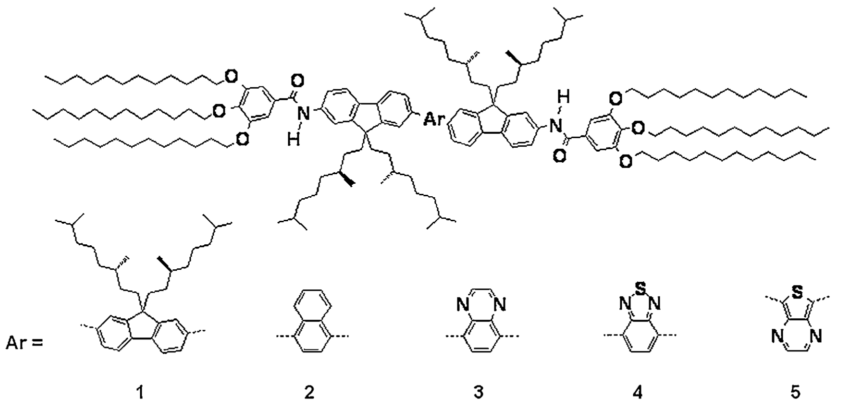


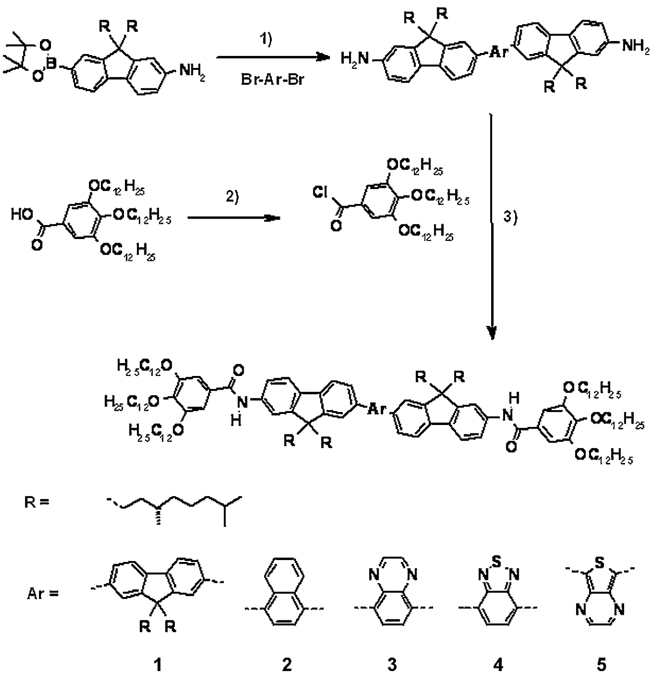
Scheme 1. Chemical structures of oligofluorenes **1**–**5**.

polycatenars **1**–**5** as a function of concentration going from dilute solution to the solid state. In dilute solution at low temperatures, some of these oligomers exhibited the so-called β-phase-type organisation. In concentrated solutions, a lyotropic organogel is formed in which the emission colour can be tuned by energy transfer to yield white emissive gels. Such an organogel[9,10] has recently been reported for an oligo(*p*-phenylenevinylene) system.[11]

Results and Discussion

Synthesis: The fluorene-based oligomers **1**–**5** were prepared in a similar manner to that described earlier for fluorene-based bolaamphiphiles (Scheme 2).[6e] Suzuki reaction of the dibromide co-monomer derivatives[4e,12] (Br–Ar–Br, Ar = fluorene, naphthalene, quinoxaline, benzothiadiazole or thienopyrazine, respectively) with an aminofluorene boronic ester[13] yielded the bis(aminofluorene) oligomers. Subsequent coupling of the resulting diamino chromophores with tris(dodecyloxy)benzoic acid chloride prepared in situ from the corresponding acid[14] led to the products **1**–**5**. All five compounds were purified by recycling GPC[15] and fully characterised by ^{1}H and ^{13}C NMR and IR spectroscopies, UV/Vis and photoluminescent (PL) spectrophotometry, mass spectrometry and elemental analysis (see the Supporting Information).

Solid-state phase behaviour: The phase behaviour of the different oligomers in the solid state was elucidated by differential scanning calorimetry (DSC), polarised optical microscopy (POM), variable-temperature infrared (VT-IR) spectroscopy and two-dimensional wide-angle X-ray scattering (2D-WAXS). DSC revealed that at room temperature **1**–**5** are crystalline solids that melt by several phase transitions upon heating (Figure 1, Table 1 and the Supporting Information). The temperatures of the first transition and the isotropisation both depended on the chemical structures and were the lowest for **1**, which has the highest density of flexible side chains. When the two fluorene units were connected by a benzene-type ring, as in **2**–**4**, melting occurred at more elevated temperatures, whereas the transition temperatures of **5** were intermediate between the values obtained for **1** and **2**–**4**. Upon cooling from the isotropic melt, most of the samples showed significant undercooling even at low cooling rates, which is a sign of crystallisation rather than the formation of a thermotropic LC phase.[16] This conclusion was further supported by the high enthalpies of melting (45–75 kJ mol^{-1}), which are about one order of magnitude higher than the values usually found for LC isotropic transitions in polycatenars.[7] Slow cooling below the isotropisation temperatures resulted in spherulitic or fan-like textures that could not be deformed by applying pressure, as was shown by POM. We assume that the phase transitions observed at lower temperatures are due to changes from one crystalline structure to another. Presumably, the arrangements of molecules in these phases are very similar because no changes are evident from the POM or X-Ray scattering measurements (see below).



Scheme 2. Synthesis of **1**–**5**. Reagents and conditions: 1) dioxane/H_2O, Na_2CO_3, [Pd(PPh$_3$)$_4$], reflux, 3 d, 43-65 %; 2) CH_2Cl_2, oxalyl chloride, room temperature, overnight, product used in situ; 3) CH_2Cl_2, Et_3N, room temperature, 6 h, 52–83 %.

The role of hydrogen bonding in the solid state was elucidated by VT-IR spectroscopy (see the Supporting Information). At room temperature, the vibrations arising from amide functionalities revealed hydrogen bonding (ν_{NH} =

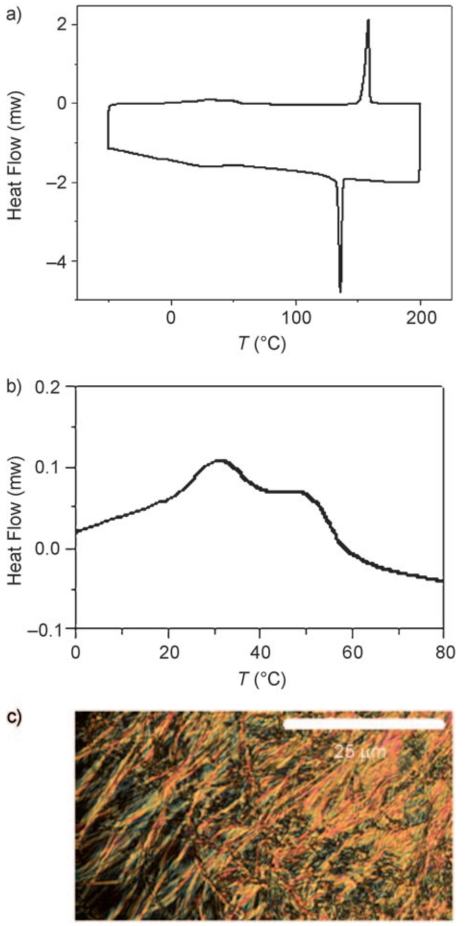


Figure 1. a) DSC trace (heating/cooling rate 10 °C min^{-1}; second run; *endo* up) of **1**. b) Magnification of the transitions in the lower-temperature region. c) POM image (crossed polars) of **1** cooled from the isotropic melt at 159 °C at a rate of 2 °C min^{-1}.

Table 1. Solid-state characteristics of **1**–**5**.

Compound	Transition temperatures [°C] (Enthalpies[a] [kJmol^{-1}])	Orthorhombic unit cell	
		a [nm]	*b* [nm]
1	31, 47 (13.2),[b] 134 (46.9)	2.10	4.74
2	80 (23.8), 219 (69.1)	1.85	4.44
3	74 (33.0), 223 (75.3)	1.80	4.89
4	82 (25.6), 223 (57.6)	1.76	4.85
5	43, 50 (21.6),[b] 186 (53.6)	n.d.[c]	n.d.[c]

[a] Only transitions with $\Delta H > 2$ kJ mol^{-1} are considered. [b] These phase transitions were not sufficiently resolved to be integrated separately. Their combined ΔH values are therefore given. [c] n.d. = not determined.

3298, $\nu_{C=O} = 1643$, amide II = 1536 and amide III = 1221 cm^{-1}). Upon heating, shifts in the absorptions were observed that are characteristic of decreasing hydrogen-bond strength,[17] whereas free amide bonds were found in the isotropic melt.

2D-WAXS experiments were performed by using extruded filaments containing aligned molecules of **1**–**4**. The structural analysis revealed a qualitatively similar supramolecular organisation in the bulk for all compounds, with differences only in their degrees of internal order. Therefore, the discussion will be limited to the example of **1** and a comparison with the other compounds will be provided thereafter.

The appearance of a high number of reflections in the 2D-WAXS pattern for **1** indicated a well-ordered bulk structure (Figure 2). After annealing at elevated temperatures (125 °C), new higher-order reflections were observed that indicated an enhanced order. However, the supramolecular organisation did not change qualitatively. The scattering angle of the equatorial reflections yielded an orthogonal unit cell with *d* spacings of $a = 2.10$ and $b = 4.74$ nm. The unit cell parameter *a* is related to the distance orthogonal to the chromophore long axis, whereas *b* correlates to the distance parallel to it. The equatorial position and the anisotropic shape of these reflections indicate alignment along the extrusion direction of the fibres. The meridional reflections (related to the *c* axis) revealed a period of 0.5 nm along the extrusion direction. A stacking distance of 0.44 nm between the molecules was determined from the positions of the off-meridional reflections. This value corresponds well with the values typically found for π-stacked polyfluorenes.[18] Additional off-meridional reflections related to a *d* spacing of 1.0 nm suggest a more complex packing. Interestingly, this spacing of 1.0 nm is twice the distance of 0.5 nm between individual molecules and has therefore been attributed to a structural organisation in which every second molecule is in an identical positional order, which suggests an alternating arrangement of the molecules in the unit cell (see below).[19]

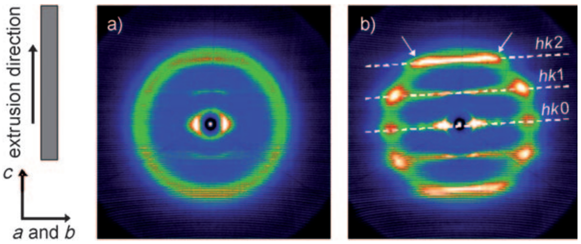


Figure 2. 2D-WAXS pattern for **1** recorded at 30 °C a) prior to and b) after annealing at 125 °C. On the left the extruded filament is assigned by the three planes *a*, *b* and *c*. Plane *c* is oriented along the extrusion direction, whereas *a* and *b* are distributed perpendicular to the filament axis. In (b), Miller's indexes are assigned to the intralamellar correlations, and the white arrows indicate off-meridional reflections.

The distribution of reflections in the 2D-WAXS patterns for compounds **2**–**4** (see the Supporting Information) shows a lamellar organisation identical to that found for **1**. In all cases, orthorhombic unit cells were determined (Table 1). The spacing along the stacking direction could only be determined for **2** and **3** and was identical to that of **1**. For **2**, the corresponding reflections were too diffuse to allow a quantitative evaluation.

Based on the WAXS and VT-IR data we have proposed a supramolecular organisation in which the molecules of **1**–**4** stack on top of each other in a quasi-1D lamellar superstructure (see the Supporting Information). This organisation is caused by the combined effects of several non-covalent interactions, such as π stacking, hydrogen bonding and microphase separation between the aromatic and aliphatic moieties. The spacing of 0.5 nm along the *c* axis corresponds to the intralamellar period and the additional meridional reflections of 1.0 nm indicate an alternating or shifted arrangement of the chromophores. This arrangement is presumably necessary to reduce steric repulsion between the branched alkyl side chains attached to the fluorene units (see below).

Optical properties in the molecularly dissolved state: All compounds easily dissolve in organic solvents of low polarity, such as THF, toluene, dichloromethane and chloroform. As an example of a good solvent, the spectral properties in chloroform (Figure 3 and Table 2) will be discussed. The compounds show maxima in different parts of the UV and visible regions of their absorption spectra. When excited at their respective absorption maxima, the compounds emit light covering the whole visible range, from blue (**1**, **2**) to green (**3**) and yellow (**4**) through to red (**5**), with moderate-to-high quantum yields. These spectral features qualitatively resemble the properties of their parent polymers[21] and show that it is possible to easily modulate the emission wavelength over the entire visible spectrum by using fluorene co-oligomers.[6c]

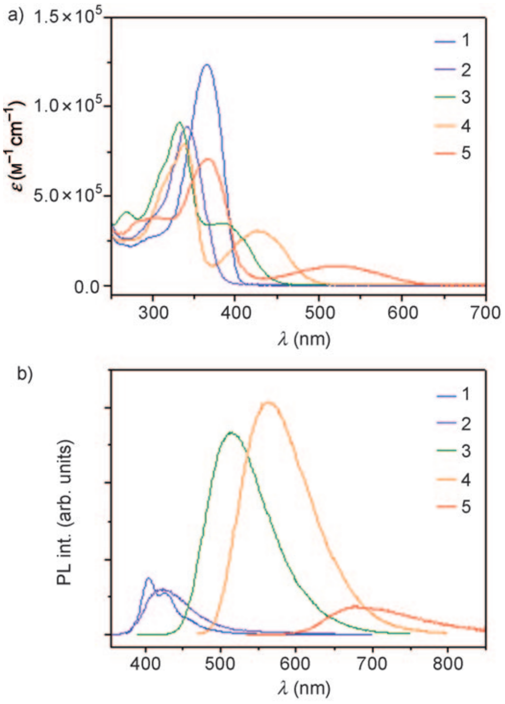


Figure 3. a) UV/Vis absorption and b) photoluminescence spectra of dilute (μm range) solutions of **1**–**5** in chloroform. The PL spectra are weighted according to the respective quantum yields.

Table 2. Spectral properties of dilute solutions of **1**–**5** in chloroform (in the μm range) at room temperature.

Compounds	Absorption		Photoluminescence	
	λ_{max} [nm]	ε [M^{-1}cm^{-1}]	λ_{max} [nm]	ϕ_{PL} [%]
1	366	123000	405, 426	8[a]
2	342	89100	423	10[a]
3	332, 385	91200, 36300	515	55[a]
4	338, 427	79400, 30900	563	70[b]
5	367, 520	70800, 11200	675	10[c]

Reference compounds for quantum yield determination (see ref. [20]): [a] Quinine bisulfate in 1 N H_2SO_4. [b] *N,N'*-Bis(pentylhexyl)perylenebisimide in dichloromethane. [c] Rhodamine 101 in ethanol.

Self-assembly in an apolar solvent: Methylcyclohexane (MCH) is known to be a poor solvent for poly(dialkylfluorene)s,[22] which is why it was chosen to study the self-assembly of **1**–**5**. At sufficiently low concentrations (10 μm and below) the compounds were molecularly dissolved in MCH at room temperature. Although none of the absorption spectra changed significantly on changing the solvent from chloroform to MCH, the emission maxima of **1**–**5** shifted to the blue (<10 nm for **1** and **2** and ca. 30 nm for **3**–**5**, Table 3), most likely due to solvatochromism.[23] These solvent effects were significantly larger for those compounds containing a more polar central unit. This might be due to the greater differences in the solvation of the ground and excited states when a more polar solvent is used. Remarkably, the choice of solvent also had a strong influence on some of the fluorescence quantum yields, which increased by up to a factor of 10 in MCH for **1**. No circular or linear dichroic (CD or LD) effects were found in dilute (<10 μm) solutions at room temperature.

Table 3. Spectral properties of dilute solutions of **1**–**5** in MCH (in the μm range) at room temperature.

Compound	UV absorption		Photoluminescence	
	λ_{max} [nm]	ε [M^{-1}cm^{-1}]	λ_{max} [nm]	ϕ_{PL} [%]
1	362	123000	402, 424	84[a]
2	338	83200	420	60[a]
3	331, 389	85200, 34600	483	48[a]
4	337, 431	93300, 36400	529	71[b]
5	366, 528	72400, 12900	649	35[c]

Reference compounds for quantum yield determination (see ref. [20]): [a] Quinine bisulfate in 1 N H_2SO_4. [b] *N,N'*-Bis(pentylhexyl)perylenebisimide in dichloromethane. [c] Rhodamine 101 in ethanol.

Because the molecules were molecularly dissolved at room temperature, we slowly cooled the solutions of **1**–**5** to induce self-assembly. Upon cooling, spectral changes were observed in both the absorption and emission spectra (Figure 4a,b). Precipitation was observed for compounds **2**–**4**, which also had the highest melting temperatures in the bulk (see above).[24] Both observations may reflect distinct differences in the π-stacking abilities in the molecules. Because this precipitation precluded a reproducible investigation, we will confine the following discussion to compounds **1** and **5**. In the case of **1**, sharpening of the π–π* absorption band and the emergence of a distinct vibronic splitting pattern was observed. Furthermore, the peak maxima were shifted to the red, whereas the onset of absorption hardly changed. Simi-

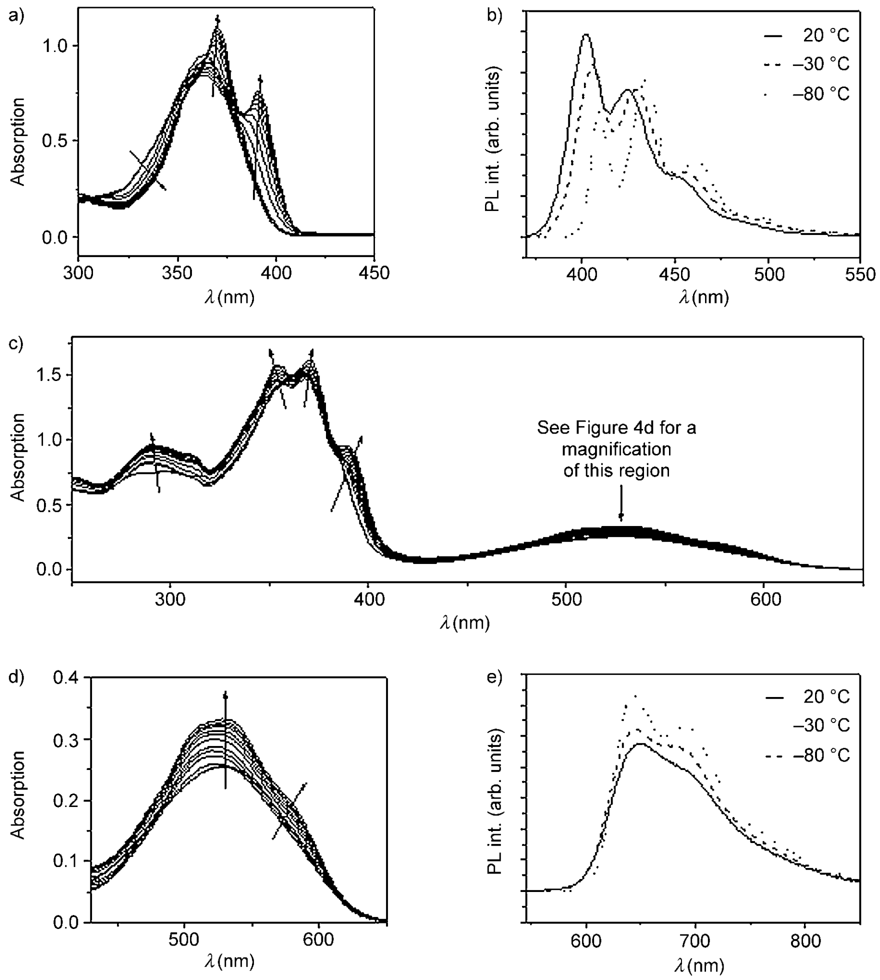


Figure 4. a,b) Temperature dependence of the UV/Vis absorption and PL spectra of **1** in MCH (7 μM for absorption, 0.7 μM for PL). c,d,e) The corresponding spectra for **5** (21 μM for absorption, 7 μM for PL). The arrows in the absorption spectra indicate spectral changes upon cooling from room temperature to −90 °C. Excitation wavelengths: $\lambda_{exc}=366$ nm (**1**) and 520 nm (**5**).

larly, the photoluminescent spectrum of **1** was also shifted to the red ($\Delta\lambda \approx 10$ nm between 25 and −80 °C) and its vibronic fine structures sharpened. In addition, CD and LD effects were observed upon cooling to −10 °C (see the Supporting Information), which suggests that elongated aligned aggregates were formed.[25] The absorption and fluorescence spectra at low temperatures are similar to the optical properties reported for polyfluorenes present in the so-called β phase. In this phase, which is usually only found for polymers with unbranched alkyl substituents,[22b,26] the fluorene repeat units are more planarised with respect to each other in an alternating arrangement. Our results suggest that this planarisation phenomenon takes place concomitantly with aggregation.[27]

The main absorption band of **5** (at 320–400 nm) shows a very similar temperature dependence to that found for **1**, whereas less pronounced changes were evident from its lowest-energy band (Figure 4c,d). Although the fluorescence spectra sharpened somewhat, no shift occurred upon cooling (Figure 4e). Again CD and LD effects were observed upon cooling (see the Supporting Information), which suggests comparable aggregation and conformation changes to those of **1**.

At a concentration of 2.5 mM, **1** and **5** formed stable blue and red fluorescent organogels at room temperature, whereas precipitation was found for all other compounds. The gels exhibited birefringence viewed under crossed polars, which points to a lyotropic organisation (Figure 5). In the case of **1**, upon increasing the concentration from 0.25 to 5 mM, a low-energy shoulder in the absorption spectrum and a redshift of around 5 nm in the photoluminescence spectrum were observed. Remarkably, compared with a dilute solution at room temperature, neither the absorption nor the fluorescence spectrum of **5** was significantly affected on increasing the concentration, even though a gel was formed. In the case of **1**, the fraction of aggregated molecules could be estimated from the intensity of the low-energy shoulder relative to that in the fully aggregated state (Figure 6a; see the Supporting Information). This reveals that at room temperature the gelation process took place in a rather narrow concentration window (between 0.4 and 2 mM) with hardly any aggregated species in more dilute solutions and almost full aggregation under more concentrated conditions. A similar transition was observed by concentration-dependent IR spectroscopy at room temperature, which reveals the presence of hydrogen bonds between the amide functionalities that were broken at a concentration below 1 mM (Figure 6a; see the Supporting Information).[28]

Variable-temperature (VT) UV/Vis absorption spectroscopy showed that the gels formed by **1** could be melted (Figure 6b). At elevated temperatures, the absorption spectra closely resembled those recorded in dilute solutions at room temperature. This observation demonstrates that heating allows the transformation of gels into the molecularly dissolved state. Remarkably, even at very low temperature gradients ($2\,^{\circ}\mathrm{C\,h^{-1}}$), the curves for cooling and heating did not overlap, which suggests that the gelation process takes place under kinetic rather than thermodynamic conditions.[29]

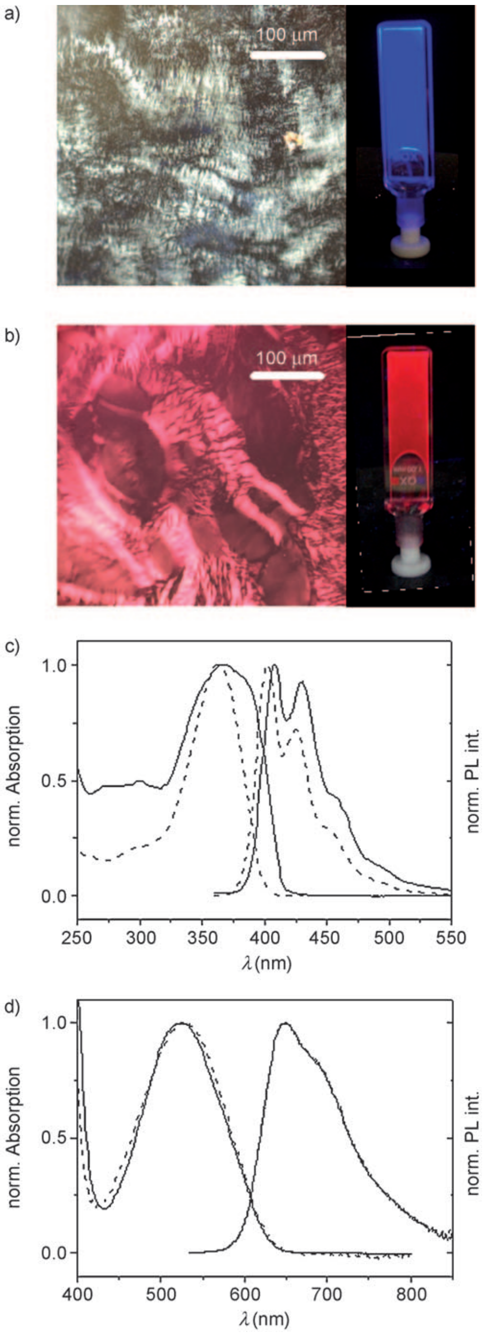


Figure 5. a,b) POM images (crossed polars) and photographs under UV illumination (365 nm) of organogels (2.5 mM) formed by **1** and **5** in MCH. c,d) Normalised absorption and fluorescence spectra of **1** and **5** in the gel state (2.5 mM; solid line) and in dilute solution in MCH (0.7 (**1**) and 7 µM (**5**); dashed line) at room temperature.

Atomic force microscopy measurements of thin deposits prepared by drop casting from solutions of **1** or **5** in MCH on glass substrates (AFM) showed a fibrillar morphology with ribbons of a constant thickness of around 20 nm and a height of 4.3 nm (Figure 7).[30] In the case of **1**, additional clustering into thicker structures and overlap between crossing fibres were observed. When the gels were spin-coated, the fibres did not cluster, but aligned themselves.

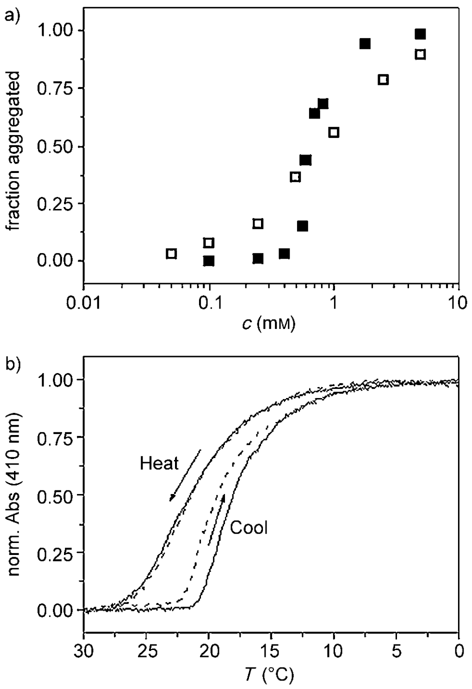


Figure 6. a) Concentration dependence of the fraction of aggregated **1** at room temperature (20 °C) determined by UV/Vis spectrophotometry (■) and IR spectroscopy (□). b) VT-UV/Vis absorption (cooling rates 10 °C h^{-1} (solid line) and 2 °C h^{-1} (dotted line)) of **1** (concentration = 500 µM, monitored at $\lambda = 410$ nm).

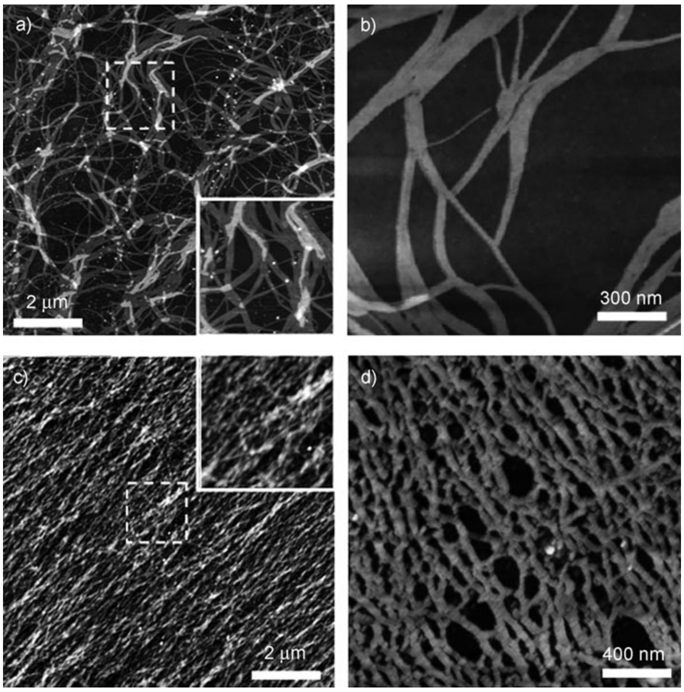


Figure 7. AFM height images of **1** drop cast (a,b) and spin-coated (c) from solutions in MCH and **5** (d) drop cast from MCH solution. The height scale is 25 nm (a,b,c) or 10 nm (d), respectively.

To relate the structures observed by AFM to those present in solution and in the gel, the fluorescence, CD and LD spectra of films of **1** on glass substrates were recorded and revealed features that were comparable to those found in MCH solutions upon cooling (see the Supporting Information). This finding suggests that a similar supramolecular organisation is present in both cases. Thermal annealing of these films above the melting temperature of **1** intensified the spectral features that indicate aggregation, pointing to reorganisation processes that lead to a higher degree of internal order. Similar fluorescence spectra were also obtained when **1** was melted from the solid state.

Interestingly, white emissive organogels could be prepared by partial energy transfer in a similar approach to that reported earlier for bolaamphiphilic fluorene co-oligomers,[6e] hydrogen-bonded supramolecular π-conjugated oligomers[13] and oligo(*p*-phenylenevinylene) organogels.[11] Mixing small amounts of **3** (green), **4** (yellow) and **5** (red) into a gel of **1** (molar ratio **1**/**3**/**4**/**5** = 4.5:0.7:0.2:0.1) in a similar fashion to that described for the bolaamphiphilic fluorene co-oligomer analogues[6e] resulted in partial energy transfer from the blue-emitting donor to the embedded energy acceptors upon excitation of **1** (Figure 8). The fluorescence lifetime of **1** in the MCH gel revealed a biexponential decay with lifetimes of $\tau = 0.93$ (94.5 %) and 1.81 ns (5.5 %), whereas for the white-light-emitting gel shorter decay times were observed with $\tau = 0.28$ (95.4 %) and 1.10 ns (5.6 %), respectively (Figure 8b). This decrease in the fluorescence lifetime of **1** shows that the emission is quenched by approximately a factor of three in the mixed gel, which indicates energy transfer. Under crossed polars and as a spin-coated film, this white emissive gel had an appearance similar to the two gels formed by **1** and **5** (see the Supporting Information).

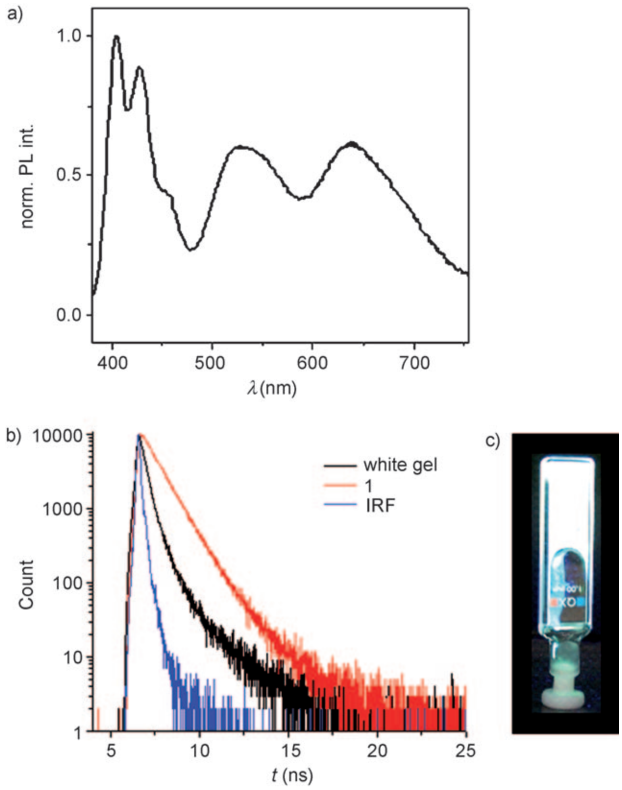


Figure 8. a) PL spectrum of a gel containing **1** (4.5 mM) and **3**–**5** (excitation wavelength: $\lambda_{exc} = 375$ nm). b) PL lifetime–decay ($\lambda_{exc} = 400$ nm) monitored at 415 nm of a gel containing **1** and **1** and **3**–**5**. c) Photograph of the same mixture under UV illumination ($\lambda_{exc} = 365$ nm; molar ratio **1**/**3**/**4**/**5** = 4.5:0.7:0.2:0.1).

Molecular modelling: Molecular mechanics (MM) and molecular dynamics (MD) calculations were carried out to provide some insight into the differences in the self-assembly of **1**–**5**. MM calculations indicate that in the case of **1**, neighbouring fluorene units are preferentially oriented with the methylene bridges in an *anti* conformation (Figure 9 and the Supporting Information). This arrangement is more stable by 18 kcal mol^{-1} than the *syn* conformation, which is disfavoured by the steric hindrance between the alkyl groups. In agreement with earlier results on polyfluorene,[31] a relatively small tilt angle (36°) is found between the fluorene units. The torsion barrier between two neighbouring fluorene units is estimated to be less than 2 kcal mol^{-1} between the most stable conformation and a fully co-planar arrangement. In the case of the fluorene co-oligomers **3**–**5**, similar small torsion angles were found ranging from 34 to

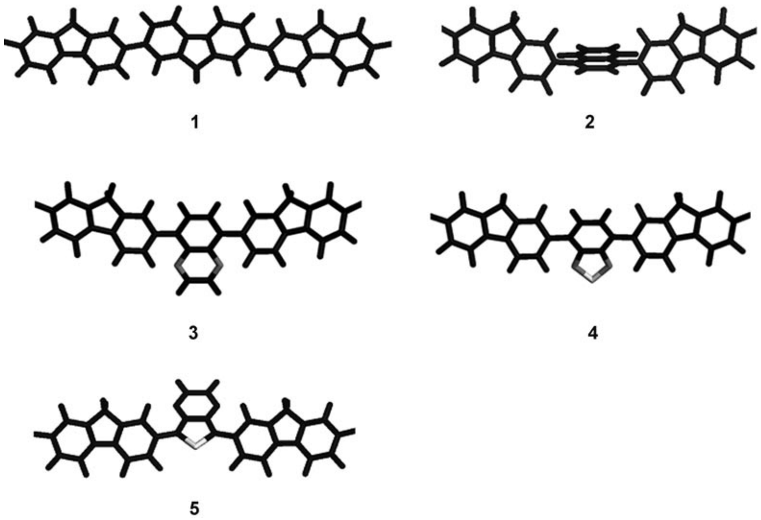

1
2
3
4
5

Figure 9. Calculated single molecule conformations of **1**–**5** in a vacuum. The 3,4,5-tridodecylbenzamide wedges and alkyl chains have been omitted for clarity.

40° (Figure 9 and the Supporting Information). Remarkably, the naphthalene–fluorene co-oligomer (**2**) has an energy minimum associated with a torsion angle of approximately 71° between the two units. The naphthalene co-monomer is therefore almost perpendicular to the conjugated plane of the fluorene units. Looking at the conformations, compounds **1** and **5** are linear conjugated molecules: the most stable conformations correspond to those in which the bridging carbon atom of one fluorene unit (C-9) is *anti* to C-9 of the neighbouring fluorene unit in the case of **1** or *anti* to the sulfur atom of the neighbouring thiophene unit in the case of **5** (Figure 9).[18] In contrast, the *para* substitution of the phenylene core in **2**, **3** and **4** leads to curved conformers (i.e., with a banana shape). The differences in the shapes of the molecules (almost linear for **1** and **5** versus slightly curved for **2**, **3** and **4**, see the Supporting Information) and in the torsion angles between neighbouring units (less than 40° for **1** and **5** and greater than or equal to 40° for **2**, **3** and **4**) may explain the differences in the aggregation between the different compounds: while **1** and **5** lead to fibres in solution, precipitation occurs with the oligomers **2**–**4**.

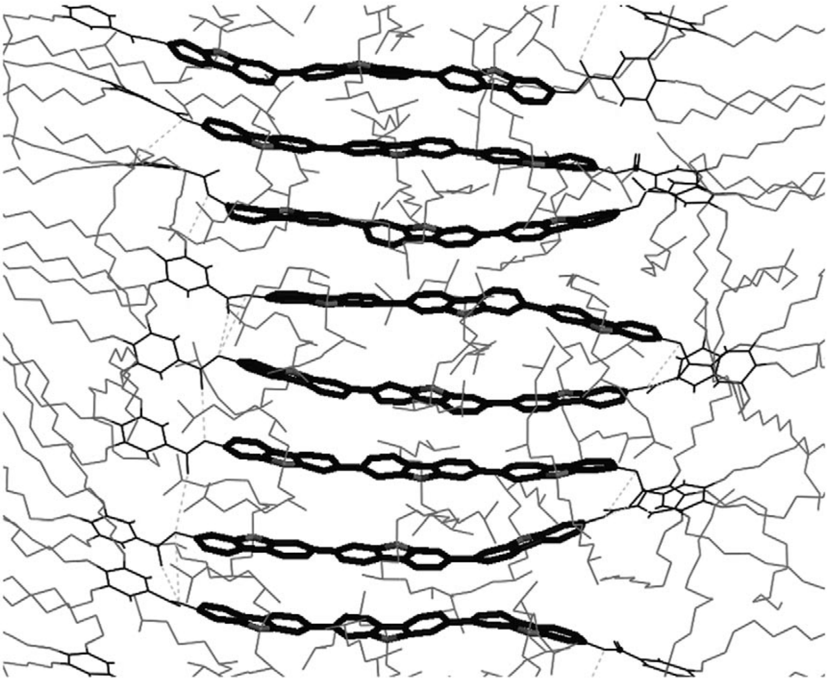


Figure 10. Snapshot at the end of the MD run showing the calculated supramolecular packing of a cluster of **1**. Fluorenes are displayed in black, alkyl groups in grey and hydrogen bonds by dotted lines.

To gain more insight into the supramolecular structure of the fluorene derivatives, MD calculations were carried out on clusters of **1** and compared with the data obtained from X-ray diffraction and AFM measurements. The fluorene units of adjacent molecules tend to be in a face-to-face configuration at a distance of around 0.5 nm, which is in agreement with the results of the XRD measurements. In terms of packing configurations, the neighbouring fluorenes are packed in an alternating orientation,[18b] that is, with the C-9 atoms pointing in opposite directions, and with a slight shift along the molecular axis. Such a configuration leads to the doubling of the distance between equivalent sites along the π stack (Figure 10). Note that the length of the fully extended molecule **1** with alkyl groups is around 6.8 nm (with a conjugated terfluorene core of 2.35 nm). This is larger than the *b* unit cell spacing observed in the XRD experiments, which suggests interdigitation of the alkyl groups in the solid state. Moreover, the molecular modelling studies suggest that the additional reflection peak along the *a* axis (at 1.0 nm) is likely to originate from the "flipped" configuration of the face-to-face fluorene units.[18b,32] This specific packing originates from the balance between the steric hindrance of alkyl substituents at C-9, hydrogen-bonding and π–π interactions with the alkyl chains displaying a Y-shaped configuration with respect to the fluorene planes.

The combined results of WAXS, AFM, optical spectroscopy and molecular modelling have allowed us to propose a self-assembly process for **1** as a function of the concentration (Figure 11). Whereas in very dilute solutions, molecularly dissolved species are predominant, increasing the concentration causes aggregation, first into one-dimensional fibres. The fluorene repeat units adopt a planarised conformation in these aggregates. With increasing length, the fibres entangle and cluster into ribbons, thereby forming a lyotropic organogel.

Conclusions

Five fluorene-based polycatenars have been synthesised that exhibit emission over the entire visible spectrum. Two of these fluorene co-oligomers self-assemble in a manner that is dependent on the concentration. The solid-state phase behaviour is qualitatively uniform and governed by the combined effects of several supramolecular interactions, most notably hydrogen bonding, π stacking and microphase separation due to mutual repulsion of alkyl chains and the aromatic backbones. The self-assembly in methylcyclohexane, an apolar solvent, was sensitive to apparently minor changes in the chemical structures. Depending on the ability of the aromatic parts to form stacks, either precipitation or the for-

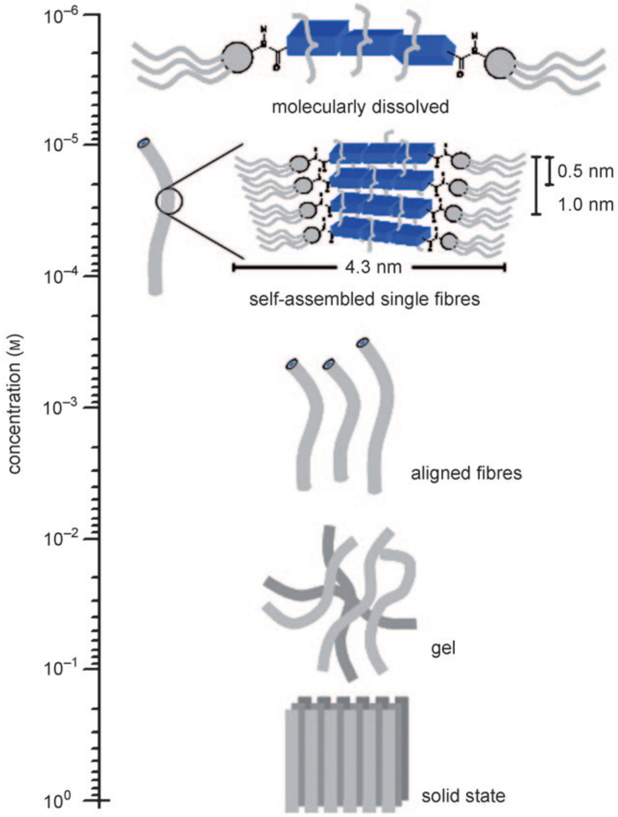


Figure 11. Proposed self-assembly mechanism of **1** in solution in MCH and its concentration dependence at room temperature.

mation of lyotropic organogels were observed. Interestingly, blue and red luminescent gels were obtained at high concentrations, whereas white emissive organogels were obtained by mixing different fluorene-based oligomers. This shows that in the self-assembled state the emission colour can be tuned by partial energy transfer in a modular approach.

The supramolecular chemistry of these closely related conjugated oligomers strongly depends on apparently small differences in their chemical structures. Their varying aggregation behaviour in solution suggests that similarly subtle adaptations in conjugated polymers might have a comparably strong influence. This could have important implications for solution-processed organic electronic devices; chemical modifications to adjust the electronic properties of the materials might unintentionally also alter their self-assembly behaviour.

Experimental Section

Full experimental details for this paper are given in the Supporting Information.

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