Solvent-induced switching between two supramolecular assemblies of a guanosine–terthiophene conjugate†

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We report here our findings on a lipophilic guanosine derivative armed with a terthiophene unit that undergoes a pronounced variation of its supramolecular organisation by changing the polarity of the solvent. In chloroform the guanosine derivative, templated by alkali metal ions, assembles *via* H-bonding in G-quartet based D_4-symmetric octamers; the polar guanine bases are located into the inner part of the assembly and act as a scaffold for the terthienyl pendants. On the other hand, in the more polar (and H-bond competing) acetonitrile, different aggregates are observed in which the terthiophene chains are π–π stacked in a helicoidal (left-handed) arrangement in the central core, and the guanine bases (free from hydrogen bonding) are located at the periphery and exposed to the solvent. The system can be switched back and forth by subsequent addition of chloroform and acetonitrile. The solvent-induced switching can be easily followed by circular dichroism spectroscopy: the CD exciton-couplet in the guanine chromophore absorption region observed in chloroform disappears after addition of acetonitrile, indicating the disassembly of the G-quartet based octameric structure, while an intense quasi-conservative exciton splitting in the 300–450 nm spectral region becomes predominant in the CD spectrum. This latter strong bisignate optical activity can be ascribed to the helical packing of conjugated terthiophene moieties stabilised by π–π interactions. NMR spectra and photophysical investigations confirm the structures of the guanine-directed and thiophene-directed assemblies in chloroform and acetonitrile, respectively.

Introduction

In π-conjugated systems the control of molecular assembly into well-defined structures on the nanoscale is a key step to improve the performances of materials[1] to be used as components in electronic nanodevices,[2] such as solar cells, light-emitting diodes (LEDs), and field effect transistors (FETs). This control has enormous potential for materials science due to the possibility of bridging the gap between the molecular scale and the macroscopic one in terms of structural order, when precise control of such self-assembly processes are achieved.

Among weak interactions, π-stacking has been the first to be employed to drive the self-assembly of conjugated (macro)-molecular systems into well-defined nanoscale assemblies that feature a high degree of order at the supramolecular level.[3]

Further control of nanoarchitectures might be possible by incorporating more specific noncovalent interaction sites in the building blocks.[1b–e] Among the various noncovalent interactions, multiple hydrogen bonds have been widely adopted because of their directionality and selectivity.[4] Many examples of bottom-up nanostructurization of π-conjugated oligomers assisted by multiple hydrogen-bonding interactions have been reported. Typically the multiple hydrogen bonding units adopted are the ureidopyrimidone (or ureidotriazine), the melamine and barbituric (or cyanuric) moieties.[1b,5–7]

Guanine moiety is a versatile hydrogen bonding building block. In particular, lipophilic guanosines can undergo different self-assembly pathways originating diverse nanoarchitectures, and typical assemblies are the ribbons and the cyclic-quartet system reported in Fig. 1.[8] Furthermore, the easy functionalisation of guanosine in the sugar hydroxyl groups or in the aromatic base (in particular in C8) makes it a promising building block for the fabrication of complex architectures with functional units located in pre-programmed positions.[9,10]

Oligothiophenes are the most promising semiconducting materials for organic electronics.[11] In this context, the control of self-assembly through molecular engineering in thiophene-based architectures is an important issue in order to direct and improve the optical and electronic properties[12] and also oligothiophene–nucleoside conjugates have been proposed.[13,14] Although the supramolecular organisation in the thin films required for molecular electronics/photonics is governed by a multiplicity of interactions between solute, solvent and surface, a detailed knowledge of the self-assembly behaviour of these systems in solution is a pre-requisite for any futher investigation.

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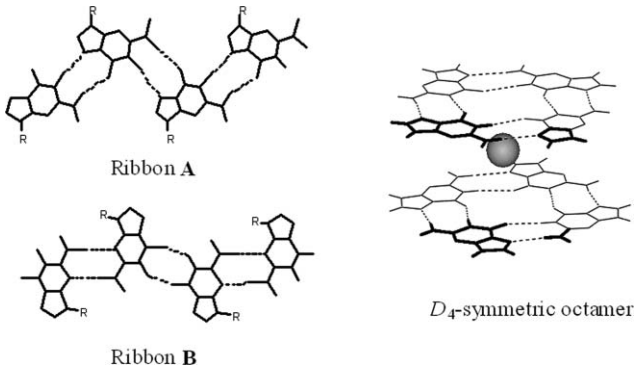
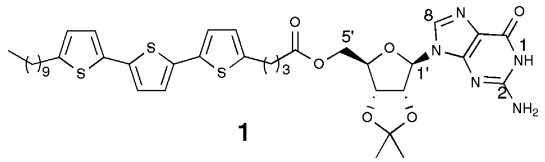


Fig. 1 A few supramolecular motifs from guanine derivatives.



Recently we have shown that the scaffolding of a terthiophene unit is achieved by taking advantage of the self-assembly of the diad guanosine derivative **1** into highly directional H-bonded networks.[14] Reversible interconversion fuelled by cation complexation and release allows switching between ribbons and quartet-based assemblies in solution, thus controlling the inter-oligothiophene interactions. Our next challenge is to verify and extend the validity of our strategy in order to introduce a control of the organisation by the appropriate choice of solvent. We report here on the interconversion, fuelled by solvent polarity variation,‡ between two different supramolecular assemblies from derivative **1**, *i.e.* G-quartet octamers scaffolded by the guanine unit and oligomeric stacks directed by the oligothiophene fragments.

Results and discussion

We have recently shown that derivative **1** can form in THF either a ribbon-like motif or a G-quartet based columnar structure in the absence or presence of alkali metal ions, respectively.[14]

In the present work we investigated the self-assembly in two solvents chosen for their different polarity and ability to dissolve supramolecular guanosine architectures. Namely, the "good" solvent $CHCl_3$, where lipophilic guanosine H-bonded structures are typically obtained, and the more polar acetonitrile (ACN), whose ability to compete with H-bonds tends to disassemble them ("poor" solvent).

The UV-vis spectrum of **1** in $CHCl_3$ (not shown) shows an absorption band at 250 nm related to the guanine chromophore, and a large band in the 300–450 nm region ($\lambda_{max} = 370$ and $\varepsilon = 29150$ $M^{-1}cm^{-1}$ at 22 °C) due to the terthiophene moiety π–π* transition, which is polarized parallel to the conjugated π-system. The corresponding CD spectrum (Fig. 2, black line) shows only a weak Cotton effect in the region of the guanine chromophore that can be ascribed to the intrinsic chirality of the molecule. After addition of 0.125 eq. of potassium picrate (KPic) to the chloroform

‡ When this paper was in preparation, Rivera *et al.* reported a solvent-induced switching between two distinct cation templated G-quartet based assemblies obtained from a lipophilic 8-substituted guanosine derivative.[15]

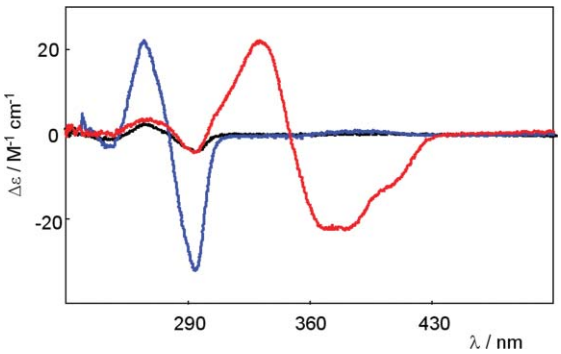


Fig. 2 CD spectra of 0.3 mM solutions of (a) **1** in $CHCl_3$ (black line), (b) **1**–KPic in $CHCl_3$ (blue line), (c) **1**–KPic in ACN–$CHCl_3$ 9 : 1 (red line).

solution of **1**, a strong negative exciton couplet centred at 275 nm appears,[14] whose shape and intensity, diagnostic of a chiral stack of at least two G-quartets,[10,16] are reminiscent of those reported for D_4-symmetric octamers[17] (Fig. 2, blue line).

This couplet does not change with guanosine concentration in the range 3–0.3 mM, suggesting that in these conditions all guanosines are self-assembled in the cation-templated G-quartet based complex (a partial disassembly is observed in 0.03 mM solutions, where CD band intensity reduces to *ca.* 80%, see Fig. S1 in the ESI†). The weak optical activity detectable at 350–430 nm (and totally absent before KPic addition) is likely due to weak dissymmetric interactions between terthienilic pendants, arising from the chirally rotated supramolecular arrangement of guanosines **1**.[18]§

In the absence of added salts, the ^{1}H NMR spectrum of **1** in $CDCl_3$ shows broad signals, if compared to the one recorded in the strongly competing solvent DMSO-d_6,[14] as expected for associated molecules. Indeed, in the 0.3 mM chloroform solution (Fig. 3,

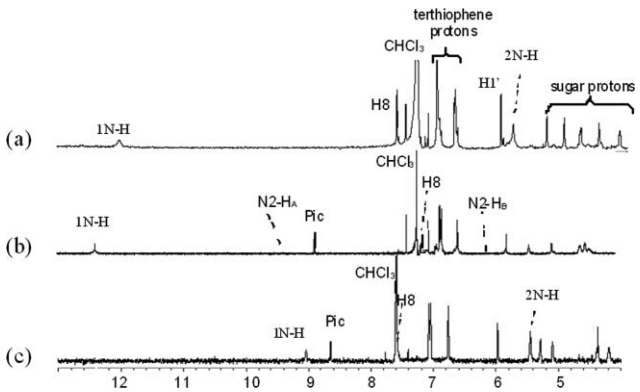


Fig. 3 ^{1}H NMR spectra of 0.3 mM solutions of (a) **1** in $CDCl_3$, (b) **1**–KPic in $CDCl_3$, (c) **1**–KPic in ACN-d_3/$CDCl_3$ 9 : 1.

§ Because picrate and terthiophene absorb in the same spectral region (picrate in ACN: $\lambda_{max} = 375$ nm, $\varepsilon = 16900$ M^{-1} cm^{-1}), the potassium-templated assembly of **1** has been obtained also with the UV/vis transparent potassium formate. CD and ^{1}H NMR spectra recorded after addition of 0.125 eq. of solid potassium formate to a $CDCl_3$ solution of **1** (see Fig. S2 and S3 in the ESI†) are superposable on those obtained after KPic addition, supporting that the weak CD signal observed at 300–450 nm is not due to optical activity induced on the achiral picrate anion possibly interacting with the guanosine supramolecular aggregate.

spectrum (a)) N1-H resonance is shifted downfield at 11.9 ppm revealing the presence of dimeric guanosines where the imino protons are H-bonded;[19] upon increasing guanosine concentration (from 0.3 to 15 mM) progressive line broadening of all signals is observed, as well as deshielding of both the imino N1-H and amino N2–H protons (see Fig. S4†). This behaviour indicates that, in this solvent, the H-bond donor groups of the guanine bases are progressively involved in H-bonding during the self-assembly process, as typically observed for guanosine derivatives when forming ribbon-like self-assembled structures in solution.[14,20]

After addition of 0.125 eq. of KPic (Fig. 3, spectrum (b)) only one set of sharp signals is observed in the ^{1}H NMR spectrum, and the N2-H signal splits in two broad bands at 9.4 (N2-H_A) and 6.1 ppm (N2-H_B), well visible for concentrations higher than 3 mM (see Fig. S3 in the ESI†). The N2-H splitting and the downfield resonance of N2-H_A are typical of G-quartet formation, where the latter proton is involved in H-bonding.[21] Furthermore, the presence of only one set of signals indicates that all complexed guanosines must be equivalent and adopt the same conformation around the glycosidic bond. A 8 : 1 guanosine/picrate ratio can be inferred from integration. These spectral features represent the unambiguous signature of a discrete D_4-symmetric octamer arising from two G-quartets stacked in a head-to-head (or tail-to-tail) orientation.[10,14,17] ^{1}H NMR spectra do not change in the range of guanosine concentration 0.3–15 mM, confirming that in these conditions all guanosines are self-associated in the $\mathbf{1}_8$–KPic octamer. Additional structural information on the assembled species were obtained by NOESY experiments, carried out on a 15 mM chloroform solution of **1**–KPic at −15 °C (Fig. S5†). An inter-base cross-peak was observed between H8 and N2–H_A, due to the G-quartet formation,[21] while an inter-quartet NOE cross peak between H8 and H5′/5″ confirmed the octameric (quartet-based) nature of the complex.[17b] A cross peak between H8 and H1′ stronger than that observed between H8 and H2′ suggested that guanosines adopt a *syn* conformation with respect to the glycosidic bond.

When diluting a chloroform solution of **1**–KPic (3 mM), with the "poor" solvent acetonitrile up to 0.3 mM, the system exhibits new, dramatically different chiroptical properties (Fig. 2, red line). The CD exciton-couplet in the guanine chromophore absorption region disappears, indicating the disassembly of the G-quartet based octameric structure, while an intense quasi-conservative exciton splitting in the 300–450 nm spectral region, characterised by a first negative and a second positive Cotton effect, becomes predominant in the CD spectrum.[22] This strong bisignate optical activity can be ascribed to (highly) ordered helical packing of (mainly planar) conjugated terthiophene moieties stabilised by π–π interactions, and the negative CD couplet is diagnostic of a left-handed π-stacked assembly.[1c,23,¶] The intensity of the observed molar CD signal is concentration dependent (see Fig. S6†), thus confirming that it arises from intermolecular interactions.

By diluting the 0.3 mM ACN–$CHCl_3$ 9 : 1 solution of **1**–KPic up to 0.03 mM with $CHCl_3$, the system is switched back to the octameric structure: the exciton CD couplet centred at 275 nm appears again (the intensity recovered being 50% of the intensity recorded for $\mathbf{1}_8$–KPic in pure $CHCl_3$ at the same concentration, see Fig. S6†).

Hence, an interesting reversible solvatochromic effect came out for guanosine **1** in the presence of KPic, and representative CD spectra of this reversible switching are reported in Fig. 2, where equimolar 0.3 mM solutions in two limiting solvent conditions are compared (blue and red lines). By moving from the "good" solvent $CHCl_3$ to the "poor" solvent ACN–$CHCl_3$ 9 : 1, the cation-templated H-bonded octameric architecture disaggregates and it is replaced by a different chiral superstructure (named ππT3 in the following), where self-assembly of derivative **1** is driven by interchain (face-to-face) π–π interactions of the terthienilic side-arms.

The solvent-induced switching for **1**–KPic 0.3 mM was monitored also by ^{1}H NMR spectroscopy (Fig. 3, spectrum (c)). On passing from the less polar $CDCl_3$ to the more polar ACN-d_3/$CDCl_3$ 9 : 1 solvent, N1-H signal moves upfield from 12.4 to 9 ppm, while a new peak, corresponding to the two amino protons N2-H, appears at 5.4 ppm. These features confirm that the octameric complex disaggregates and that, in the new assembled species, neither imino N1-H nor amino protons N2-H are involved in intermolecular H-bonding.

Potassium picrate does not play any fundamental role in the self-assembly process occurring in ACN–$CHCl_3$ 9 : 1. As a confirmation, aggregation of derivative **1** in this solvent mixture was examined by CD/UV and NMR spectroscopy in the absence of KPic, and related spectra are similar to those recorded on **1**–KPic (*vide infra* and see Fig. S7 in the ESI†).

NOESY experiments carried out on **1** in ACN-d_3/$CDCl_3$ 9 : 1 show cross-peaks with the same phase as the diagonal (negative), indicating the existence of large ($M_w > 1000$, $\varpi\tau_c > 1$), slowly tumbling aggregates as the main species in solution,[24] and confirming that the system is not molecularly dissolved. Furthermore, NOE cross-peaks are observed between the terthiophene ring protons H^{int} (see Chart 1) and the methylene hydrogens Hα of the aliphatic chains (Fig. S8†): since these NOE interactions are not detected in the chloroform solution they are supposed to originate from inter-molecular interactions occurring in the associated species present in ACN-d_3/$CDCl_3$ 9 : 1. The intense intramolecular cross-peak between H8 and H1′ (stronger than between H8 and H2′) indicates that also in poor solvent conditions guanosine **1** adopts the *syn* conformation observed in $CDCl_3$.

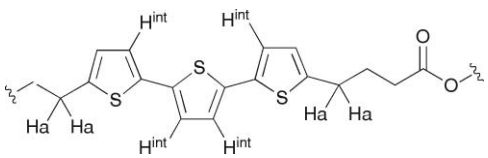


Chart 1

A measure of the optical activity induced on the intrinsically achiral terthiophene fragment in the new helicoidal π-stacked arrangement can be obtained from the chiral anisotropy factor g ($= \Delta\varepsilon/\varepsilon$): it reaches a value of approximately $+2 \times 10^{-3}$ (at *ca.* 325 nm) in the 0.3 mM ACN–$CHCl_3$ 9 : 1 solutions. Its value however critically depends on the self-assembly protocol adopted (and in particular on temperature, concentration, synthetic batch of compound *etc.*) indicating that exact organisation of terthienilic fragments is a sensitive function of experimental conditions and

¶ The zero-crossing occurs close to the absorption maximum of the terthiophene chromophore (λ_{max} = 365 nm, ε = 23060 M^{-1} cm^{-1} at 22 °C) suggesting exciton coupling as a result of a chiral aggregation.[22]

operative methodology. Nevertheless, although a standardised preparation of samples is adopted, it has been noticed that subsequent experiments led to slightly different CD spectra with variations in the crossover of the exciton couplet and in the intensity of the double-signed signal (Fig. S9†). As reported very recently by Meijer *et al.*,[25] oligothiophenes (and other π-conjugated systems) can self-assemble through nucleation-growth mechanism, a cooperative kinetically driven self-assembly process where tiny amounts of impurities also have a decisive influence on the resulting supramolecular organisation. Hence, in this light, observed differences in CD spectra could be explained by the presence of traces of impurities that are out of control. Furthermore, UV/CD analysis performed as a function of time confirmed that the supramolecular helicoidal system generated in the poor solvent conditions is a non-equilibrium state. Spectra of **1**–KPic (or **1**) recorded on ACN–$CHCl_3$ 9 : 1 solutions after one night show an increased Cotton effect (with respect to the freshly prepared samples), possibly due to larger dimensions of aggregates (see Fig. S10†); after three days, CD and UV spectra show parallel decreasing of intensity and solutions become turbid; after four months both CD and UV absorptions go to zero (and a fine orange powder appears on the bottom of the vial).

These observations suggest that **1** self-organises in kinetically stable superstructures, as soon as the ACN–$CHCl_3$ 9 : 1 solution is prepared, in the form of microcrystalline aggregates that, on growing with time, become insoluble and precipitate.‖ Further evidence of this behaviour comes from the results obtained with DLS experiments on the same samples used for the CD analysis. The chloroform solution of **1**–KPic (or **1**) shows very weak scattering and is not possible to evidence any defined peak ascribable to large aggregates. This is perfectly in accordance with the formation of octamers (or ribbon-like oligomers) in this medium, that are too small to be detected as a precise signal with this methodology. On the contrary, in ACN–$CHCl_3$ 9 : 1 solutions a family of aggregates with an average diameter of 80 nm has been evidenced (see Fig. S11†): this is in line with the hypothesis of the formation of bigger π-stacked aggregates in these poor solvent conditions, clearly detectable by the instrument. Slightly different degrees of polydispersity characterise different samples, although the value of the average diameter is always confirmed.

Variable-temperature CD/UV experiments have been performed on freshly prepared solutions of **1** in ACN–$CHCl_3$ 9 : 1, either in the presence or in the absence of KPic (Fig. 4 and S12†).

By cooling samples from the room temperature to 5 °C a strong enhancement of the Cotton effect is observed, that can be rationalised as an increased π–π stacked chiral aggregation, while by heating both samples from 5 °C up to 50 °C the Cotton effect in the visible spectral region gradually decreases and eventually disappears, indicating that conversion of the chiral aggregate to the molecularly dissolved species has occurred. For compound **1** (in the absence of salts) hypochromic and hypsochromic (*ca.* 8 nm) effects are evident at the 360 nm absorption band by moving from the molecularly-dissolved state to the ordered assembled form, supporting a prevalent face-to-face (H-type) aggregation.[26]**

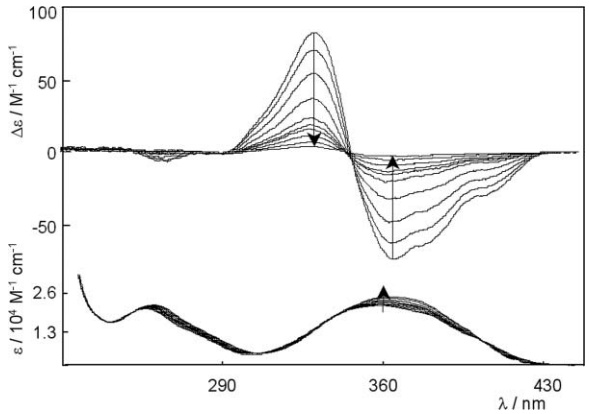


Fig. 4 CD/UV spectra recorded at variable temperatures, from 5 to 50 °C (increment 5 °C), of a 0.3 mM ACN–$CHCl_3$ 9 : 1 solution of **1**. Arrows indicate increasing temperatures.

The observed assembly–disassembly transition is not completely reversible, as expected for kinetically controlled non-equilibrium systems. In fact, by cooling samples a second time, CD intensities weaker than the original ones are obtained. Further evidence of this temperature-dependent aggregation has been obtained from NMR spectroscopy. ^{1}H NMR spectrum of **1** recorded at 5 °C, compared to the one recorded at 25 °C, show line-broadening of all guanosine signals (that are partially lost down the baseline), presumably due to the progressive formation of solid microaggregates (Fig. S7†). Moreover, both imino N1-H and amino N2-H protons are shifted upfield by *ca.* 0.3 ppm at low temperature: this spectral behaviour rules out any involvement of these H-bonding donnor groups in stabilising the helical packing formed in the "poor" solvent mixture.††

A new chiral superstructure has emerged for the guanosine–terthiophene conjugate derivative **1** in ACN–$CHCl_3$ 9 : 1, where the terthiophene chains are π–π stacked in a helicoidal (left-handed) arrangement in the central core and the guanine bases, free from hydrogen bonding, are located at the periphery and exposed to the solvent. No significant optical activity was detected in the guanine absorption region even at 5 °C, demonstrating that in the terthiophene-directed assembled species guanosine moieties are not so close to give chiral interchromophoric interactions. A possible model in agreement with the experimental data is reported in Fig. 5.

The schematic structure shown is consistent with a H-type aggregate, where the terthiophene backbones are assumed to be almost planar, parallel to each other, and packed at the π–π stacking distance. Interacting terthiophenes are rotated counterclockwise with respect to each other, in agreement with the observed exciton-type splitting Cotton effects; the twist between the long axis of

‖ The presence, in the poor solvent solution, of microcrystalline solid–NMR silent but UV/CD active–can explain also the signal/noise ratio in ^{1}H NMR spectra lower than those recorded in $CDCl_3$.

** In the case of **1**–KPic the hypsochromic effect is almost negligible, while a red-shifted absorption band arises at 420 nm upon lowering the temperature, as expected for imperfectly aligned face-to-face intermolecular geometries (Fig. S12†).[27] These data suggest that in the presence of KPic the terthiophene moieties interact less efficiently in the π-stacked aggregate.

†† The same variable temperature experiments were performed on **1** in the "good" solvent $CDCl_3$ (0.3 mM). An ^{1}H NMR spectrum recorded at 5 °C does not show a pronounced line broadening, if compared to the one recorded at 25 °C, while the downfield shift of both imino and amino protons reveals progressive H-bonding of guanine bases (in ribbon-like architectures) even at this low concentration (Fig. S13†).

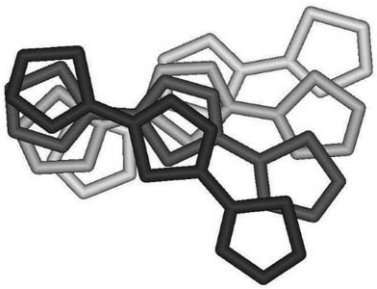


Fig. 5 Left-handed chiral stacking of terthyenyl units.

neighbor molecules in the stack could avoid sterically unfavorable interactions between guanosines (in their *syn* conformation).

CD spectra of thin films of **1**–KPic prepared by drop casting from chloroform and from ACN–$CHCl_3$ 9 : 1 solutions are shown in Fig. 6. Their band-shapes are similar to the corresponding spectra recorded in solution, indicating that the two different chiral supramolecular orders present in the two solvents are also maintained in the solid state upon solvent removal.

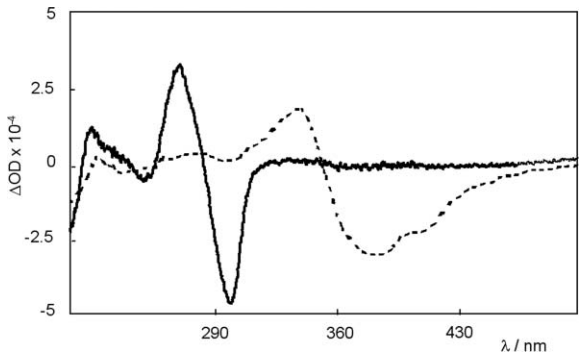
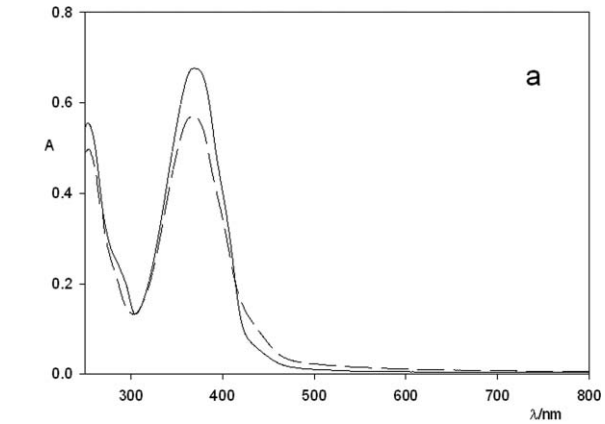


Fig. 6 CD spectra of drop-cast films obtained from **1**–KPic (150 μL of 0.3 mM solutions) in $CHCl_3$ (solid line) and ACN–$CHCl_3$ 9 : 1 (dashed line).



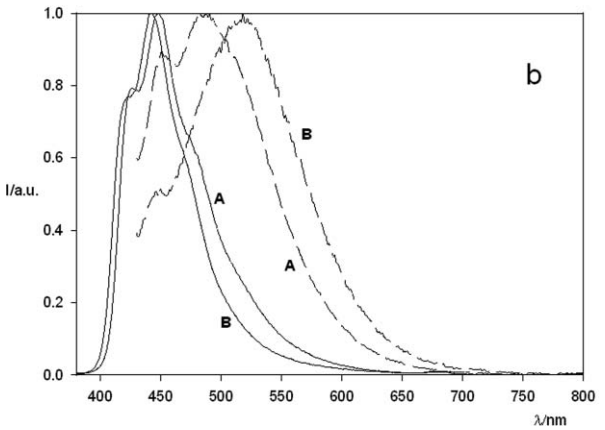


Fig. 7 (a) Absorption spectra of **1**–KPic in $CHCl_3$ (solid line), **1**–KPic in ACN–$CHCl_3$ 9 : 1 (dashed line); (b) emission spectra of **1**–KPic in $CHCl_3$ (A) exciting at 340 nm (solid line), and at 420 nm (dashed line) and of **1**–KPic in ACN–$CHCl_3$ 9 : 1 (B) exciting at 340 nm (solid line), and at 420 nm (dashed line).

In order to get additional information on the self-assembly behaviour of these systems, a careful photophysical characterisation was carried out. Suitable concentrations for this kind of experiments are quite dilute, therefore 0.03 mM solutions were used even if, as noted above, in these conditions the self-assembly is only partial. The absorbtion spectra profiles of solutions of **1**–KPic in the two different solvents in study are quite similar, as shown in Fig. 7a, but in the "poor" solvent system ACN–$CHCl_3$ 9 : 1 the shoulder around 400–500 nm is more pronounced indicating a higher degree of π–π stacking interactions between the terthienyl moieties in ππT3.[28] It is reasonable to assume, therefore, that the absorbance in this area is prevalently determined by the aggregated terthienyls, while the peak centred a 360 nm is due both to ππT3 and the species with non-interacting terthyenilic arms (named freeT3 in the following). We have then compared the profiles and the relative intensities of the emissions and the luminescence lifetimes exciting at two different wavelengths: 340 nm (where the absorption of freeT3 is maximum) and 420 nm (where the absorption of ππT3 species is prevalent).

The normalised emission spectra shown in Fig. 7b clearly evidence that there are two different peaks, one centred at 440 nm typical of freeT3, and a red shifted one as expected for ππT3 aggregates.[28] Most interestingly, this last peak, by excitation at 420 nm, is centred at 490 nm in $CHCl_3$ and at 520 nm in ACN–$CHCl_3$ 9 : 1: this further red shift of the band is a clear indication of the formation of larger and more conjugated associated species in this latter environment, as expected when increasing π–π stacking interactions between terthiophene fragments.

It has to be noted that peaks of both freeT3 and ππT3 species are always present (either in chloroform or in ACN–$CHCl_3$ 9 : 1), and their luminescence intensity ratio depends on the excitation wavelength and solvent. The dependence on the excitation wavelength is proof that two different species are always present in solution, absorbing in the same range with different molar extinction coefficients. Therefore it is not possible to excite them selectively, but it is only possible to preferentially excite one or the other. The emission lifetimes can help us to understand the dependence of the peak intensity ratio on the solvent. In fact, a very short lifetime (< 0.5 ns) and a longer one (around 2.5 ns) were detected in both solvents. The first one is ascribable to freeT3, while the longer one is to ππT3. However, their percentage ratio is totally different exciting at the two different wavelengths. In particular, by exciting at 420 nm the percentage of the ππT3

species is higher in the poor solvent than in $CHCl_3$, perfectly in line with the intensity peaks ratio in the emission spectra (Fig. 7b).

The last piece of photophysical evidence of the formation of larger and more conjugated aggregates in ACN–$CHCl_3$ 9 : 1 solution was obtained *via* emission anistropy measurements. The value of the emission anisotropy of a species in solution depends on its possibility of depolarisation *via* rotation or energy transfer. Therefore, even if the mobility of the self-assembled structures in the poor solvent should be minor than in $CHCl_3$, since their dimensions are bigger, the higher degree of conjugation greatly favours the energy transfer between the chromophores and this should cause an appreciable decrease of the anisotropy signal. As shown by Fig. 8 this is exactly the case if we compare the anisotropy values for the two different solvents by exciting preferentially the aggregates at 420 nm. At 450 nm, corresponding to the emission of freeT3, the values are the same, but in the range of the ππT3 emission maximum there is an appreciable anisotropy decrease in the poor solvent. The same films were photophysically characterised and they all presented a broad emission band centred around 500–520 nm due to strong intermolecular interactions, as expected for the solid state.[28b,d]

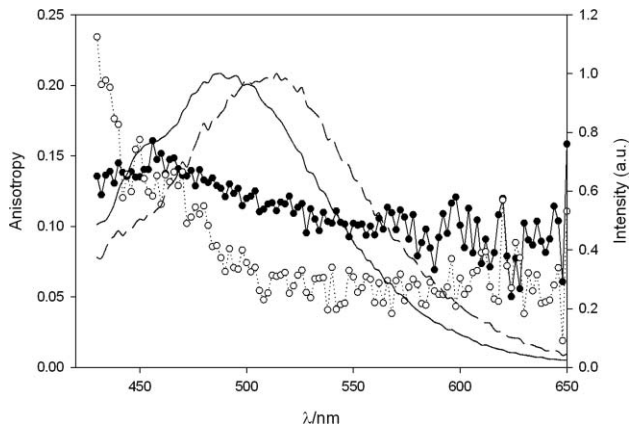


Fig. 8 Emission spectra of **1**–KPic in $CHCl_3$ (solid line), and of **1**–KPic in ACN–$CHCl_3$ 9 : 1 (dashed line), anisotropy of the same solutions in $CHCl_3$ (black dots), and in ACN–$CHCl_3$ 9 : 1 (white dots); $\lambda_{exc} = 420$ nm.

3. Conclusions

In summary, we have shown, by using CD, NMR and fluorescence emission spectroscopies, that the lipophilic guanosine derivative **1** armed with a terthiophene unit undergoes a pronounced variation of its supramolecular organisation by changing the polarity of the solvent. In chloroform, the guanosine derivative, templated by alkali metal ions, assembles *via* H-bonding in G-quartet-based D_4-symmetric octamers; the polar guanine bases are located in the inner part of the assembly and act as a scaffold for the terthienyl pendants. On the other hand, in the more polar (and H-bond competing) acetonitrile, different aggregates are observed, where the terthiophene chains are π–π stacked in a helicoidal (left-handed) arrangement in the central core and the guanine bases, free from hydrogen bonding, are located at the periphery and exposed to the solvent. The system can be switched from one state (guanine-directed) to the other (thiophene-directed) by subsequent addition of chloroform and acetonitrile.

The amphiphilicity of **1** must be taken into account for understanding the solvent-induced switching described here. The amphiphilic character can in fact balance various competing intermolecular forces, such as π–π-stacking, van der Waals interactions and H-bonding. The combinations of all these effects may allow fine tuning of the self-aggregating behaviour. This findings extend the comprehension of the experimental tools suitable for controlling the supramolecular organisation of multifunctional derivatives. The possibility to relay on non-disruptive techniques to precisely characterize self-aggregating assemblies is particularly valuable and can allow a much deeper understanding of these very fascinating but complex systems.

Experimental

Derivative **1** was prepared as reported in ref. 14. Solvents were purchased from Aldrich Chemical Co (Aldrich or Fluka catalogues). CD spectra were recorded on a JASCO J-710 Spectropolarimeter (cell path length = 0.01, 0.1 or 1 cm). NMR spectra were recorded on Varian Inova (300 MHz) or Varian Mercury (600 MHz) instruments.

UV-vis absorption spectra were performed at room temperature by means of a Perkin-Elmer Lambda 45 spectrophotometer. Steady-state and time-resolved fluorescence measurements were performed with an Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for TCSPC (time-correlated single-photon counting) data acquisition and Glan–Thompson polarizing prisms. For excitation in the TCSPC experiments, an LDH-P–C-405 pulsed diode laser was used. All the fluorescence emission and excitation spectra recorded were corrected for the non-linear response of the photomultiplier and for the wavelength-dependent excitation intensity, respectively.

Dynamic light scattering measurements (DLS) were recorded with a Malvern Nano ZS instrument with a 633 nm laser diode. The width of DLS hydrodynamic diameter distribution is indicated by PdI (polydispersion index). For all the measurements, quartz cuvettes with an optical path length of 1 cm were used.

The details of sample preparation are reported in the ESI.†

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