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Self-assembly of Diacetylene-Bridged Phenylenevinylene Oligomers in Water and Organic Solvents

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Abstract: We investigate here the self-assembly in aqueous and organic media of a new kind of rod-like π -conjugated molecules in which two OPV fragments are connected through a diacetylene bond. Optical spectroscopy and AFM measurements indicated that, in water, strong hydrophobic interactions between π -cores promote aggregation into robust, uniform micellar structures. In apolar solvents, in contrast, a fibrillar morphology is obtained by coiling of columnar stacks. These stacks are formed via a nucleation-elongation process with degrees of cooperativity of 0.006, that is influenced by the low rotation barriers around the σ -bonds in the diacetylene linker.

Organic π -conjugated molecules, having either disk- or rod-like shape, are endowed with highly appealing electronic and optical properties that are attributed to electron delocalization throughout the planar conjugated system. Furthermore, their organization into ordered self-assembled architectures is known to facilitate long-range intermolecular transport of excitons and charge carriers, which increases their applied potential in various fields related to flexible molecular electronics and light-energy conversion devices.^[1–3] Therefore, controlling their ordered assembly through multiple hierarchical levels and scale dimensions,^[4] that span from the molecule to nanostructured networks and ultimately to the morphology of the device active layer, is essential to establish structure–property relationships and thereof enhance device performance.^[5]

In order to reach such control, noncovalent interactions between individual molecules, like H-bonding, π – π stacking, dipole–dipole interactions, or van der Waals forces, play a crucial role in regulating self-assembly, so they must be considered in first instance.^[6] These interactions are intrinsically encoded in the molecular structure, but solvent effects may also influence self-assembly, and should be taken into account in the design of a given morphology. Apolar organic solvents typically favor directional intermolecular interactions with a large enthalpic contribution. Aqueous media, in contrast, provides a stronger entropic component due to the preference of water for maintaining its own H-bonded network, where apolar moieties are not efficiently solvated and therefore excluded and forced to self-

aggregate.^[7] Hence, the kind of assemblies obtained in each solvent system may be radically different and afford rather distinct final properties. Additionally, the regulation of cooperative effects^[8] that may arise between the repeating units along self-assembly is of equal importance to determine the degree of order in the final nanostructures, and hence to define an optimal homogeneous function. Three main mechanisms govern supramolecular polymerization processes:^[9] *ring-chain* polymerization, in which ditopic monomers establish an equilibrium between cycles and polymers, *isodesmic* polymerization, in which the equilibrium constant for all binding events is equal, and *cooperative* polymerization, where a endergonic nucleation or activation step is required before the exergonic elongation of the polymer. The latter mechanism usually leads to assemblies with a higher degree of internal order.

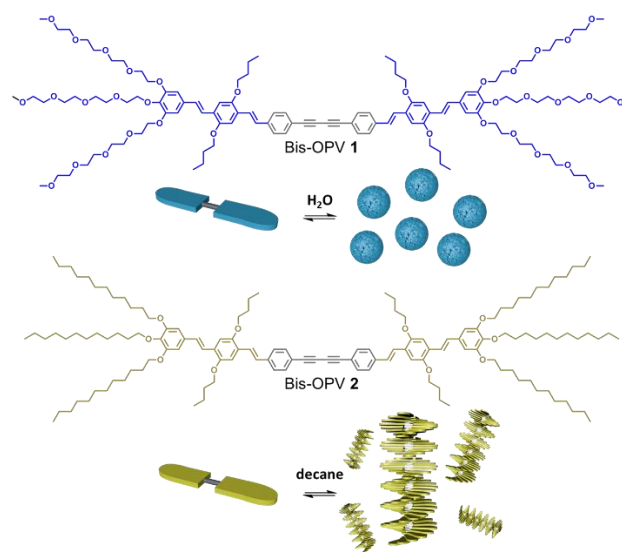


Figure 1. Chemical structures of bis-OPVs **1** and **2** and models of the corresponding supramolecular assemblies formed in aqueous or alkane media.

Regarding the π -conjugated systems studied in the last years,^[10] linear rod-like oligomers have gained considerable attention due to their well-defined molecular structure, tunable optoelectronic properties, and suitability for light and flexible next-generation devices. These include thiophene, phenylene-vinylene, phenylene-ethynylene, and phenylene oligomers. Among them, the electronic properties of oligo(*p*-phenylenevinylene)s (OPVs) are particularly sensitive to the incorporation of donor and acceptor groups, and to molecular organization, which is mainly driven by π – π stacking between the planar conjugated cores.^[11]

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Here, we report on the self-assembly of a new class of rod-like π -conjugated molecules that are constituted by two short OPV segments connected through a rigid diacetylene linker (bis-OPVs **1** and **2**; Figure 1). Both compounds are therefore endowed with an extended planar π -conjugated core, comprising 6 phenylene-vinylene units, which should provide a strong driving force for self-assembly through π - π stacking interactions. On the other hand, the solubility of these molecules and their corresponding assemblies in water or in organic solvents is controlled by the peripheral substituents attached at the oligomer edges, either tetraethylene glycol tails (**1**) or dodecyl chains (**2**).

Diacetylene-bridged compounds **1** and **2** were produced by direct Glaser homocoupling of ethynyl-substituted precursors **3** and **4**^[12] in the presence of Cu^{2+} (see S.I. for experimental details). The absorption and emission spectra of **1** and **2** do not change significantly when compared with these precursors, suggesting that the extension of π -conjugation through the bis-ethynylene bridge is not efficient.

Bis-OPV **1**, having a hydrophobic core and peripheral ethylene glycol tails, is soluble in water. Contrary to the ^1H NMR spectra recorded in organic solvents, like $\text{CDCl}_2\text{CDCl}_2$ (TCE-D_2), the broad features observed in water indicated, however, that **1** is strongly aggregated in aqueous media within the 283–343 K temperature range (see Figure S1A). As shown in Figure 2a, the absorption of **1** in water shows a broadened band centred at 422 nm, which is slightly blue-shifted when compared to organic solvents like THF or TCE, where **1** is molecularly dissolved. Likewise, the emission of **1** in water is strongly quenched and red-shifted when compared to THF, as shown as well in Figure 2a, which is quite typical of strongly aggregated π -conjugated cores.

Temperature-dependent experiments were carried out at low concentrations to see if the aggregates of **1** in water could be denatured at high temperatures (Figure 2b). A transition between 20 °C and 60 °C was indeed observed by ^1H NMR (Figure S1A)

and optical spectroscopy experiments (Figure 2b), but it was ascribed to the typical LCST desolvation process of the ethylene glycol chains, rather than to deaggregation. Therefore, the strong hydrophobic forces between π -conjugated cores seem to hamper aggregate dissociation in water even at low concentrations. Such strong association was also observed by Meijer and coworkers when analysing the temperature-dependent self-assembly of related tri- and penta-phenylene-vinylene bolaamphiphiles substituted with peripheral tetraethylene glycol chains.^[13]

AFM experiments were then conducted to characterize the morphology of the aggregates of bis-OPV **1** in water. Diluted aqueous solutions were dropcasted onto mica at room temperature and, after solvent evaporation, surface analysis revealed round objects with a rather uniform height between 10 and 15 nm (Figures 2c–f). Considering a fully extended molecular length of 7.0 nm, this would be consistent with the self-assembly of the coil-rod-coil molecule **1** in discrete micelles, where the aromatic hydrophobic rods would be excluded from the water network and the peripheral ethylene glycol tails would be located at the outer side, facing the aqueous solvent, and at the inner core, possibly encapsulating some water molecules as well.

We then focused on the study of the self-assembly of lipophilic bis-OPV **2**, endowed with dodecyl tails at both edges of the π -conjugated rod. Compound **2** is very soluble in organic solvents of moderate or low polarity, from THF to dodecane. The absorption and emission spectra of **2** in different solvents was first recorded (Figure 3a). A very small hypsochromic shift (<10 nm) was noted when comparing absorption maxima as the solvent polarity is reduced. The differences in fluorescence emission were more pronounced, thus allowing the calculation of the orientational polarizability in different solvents as well as the difference in dipole moment between the ground and excited states ($\Delta\mu$) (see S. I.).¹⁴

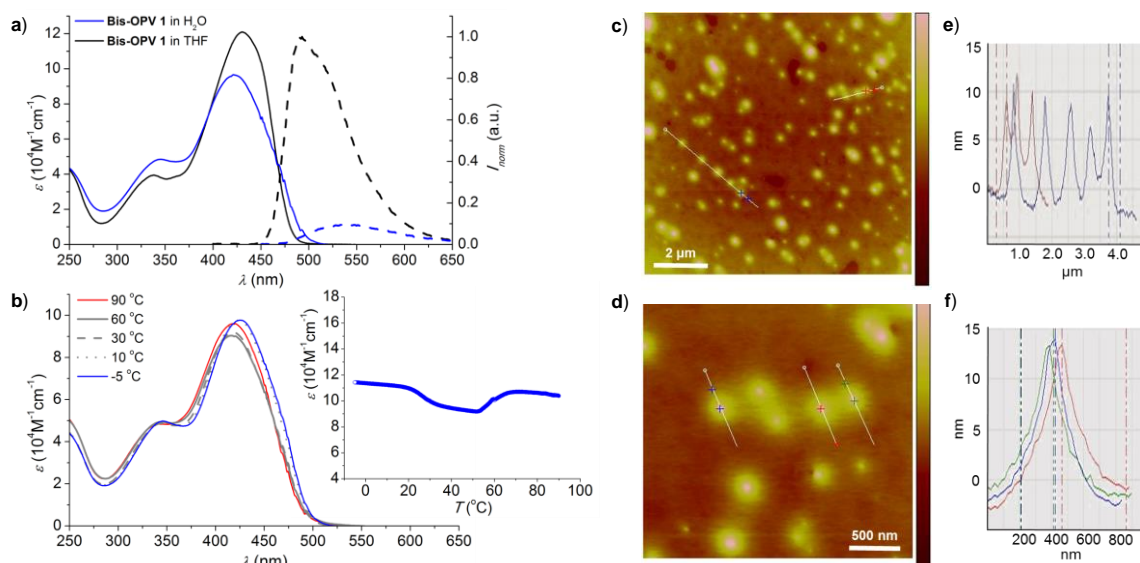


Figure 2. (a) UV-vis and emission spectra of bis-OPV **1** in water and THF at $2.0 \cdot 10^{-4}$ M (298 K). (b) Temperature-dependent UV-vis experiment of bis-OPV **1** in water at $2.0 \cdot 10^{-4}$ M. Inset shows the cooling curve at 425 nm. (c, d) Height AFM images of bis-OPV **1** ($2.0 \cdot 10^{-4}$ M, water) onto mica. Z scale is 30 nm. (e, f) Height profiles of the aggregates along the white lines in (c) and (d).

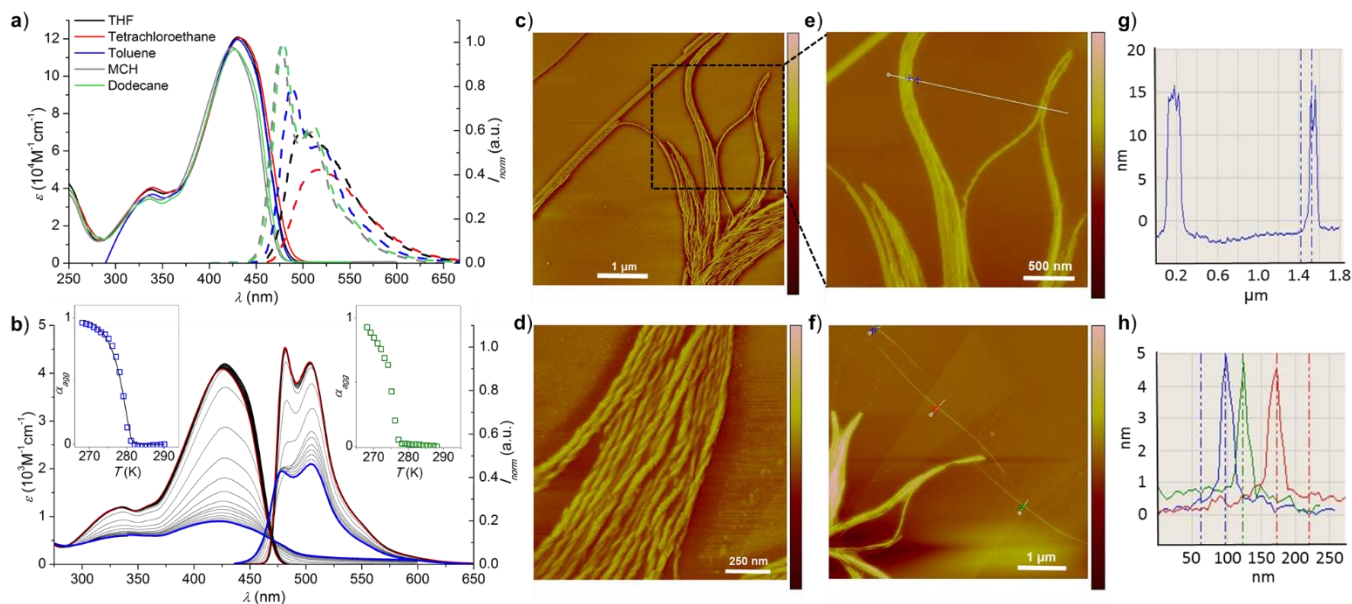


Figure 3. (a) Solvent-dependent UV-vis and emission spectra of bis-OPV **2** at $1.0 \cdot 10^{-5}$ M (298 K). (b) Temperature-dependent UV-vis ($5.0 \cdot 10^{-4}$ M) and emission ($2.0 \cdot 10^{-4}$ M) changes of **2** in decane, from 29 °C (red line) to -5 °C (blue line). Insets: blue and green squares represent the spectral trends at 428 and 504 nm, while the black line shows the fitting to the ten Eikelder–Markvoort–Meijer model at 428 nm. (c, d) Phase and (e, f) height AFM images of bis-OPV **2** dropcasted onto Highly Oriented Pyrolytic Graphite (HOPG; $2.0 \cdot 10^{-4}$ M, MCH). Z scale is 100 nm in (e) and 50 nm in (f). (g, h) Height profiles of the aggregates along the yellow lines in (e) and (f), respectively.

As shown in Figure 3a, fluorescence emission maxima experienced a blue shift of about 40 nm when going from THF to toluene, and then to methylcyclohexane (MCH) or dodecane. Emission in these aliphatic solvents is characterized by two maxima at 473 and 502 nm.

Compound **2** was then subjected to different conditions in apolar solvents with the aim to force its aggregation. We noted, however, that this product exhibits an extraordinary solubility, actually comparable to that of its smaller precursor **4**, despite the double extension of the π -conjugated surface. For instance, bis-OPV **2** could be dissolved in toluene- D_8 or even cyclohexane- D_{12} at millimolar NMR concentrations, displaying sharp and well-resolved proton signals (see Figures S1B-C). We only managed to monitor the aggregation of this compound by ^1H NMR at rather low temperatures and relatively high concentrations. For instance, as shown in Figure S1C, bis-OPV **2** exhibited a sharp transition from a well-resolved to a very broad NMR spectrum, which is consistent with the formation of polymeric assemblies, within a temperature range of less than 5 K: 248–243 K at $1.0 \cdot 10^{-2}$ M and 223–218 K at $2.5 \cdot 10^{-4}$ M. The dependence with concentration confirms the intermolecular nature of this process. When turning our attention to optical spectroscopy, we could only observe aggregation in highly apolar solvents (decane or dodecane) and relatively high concentrations for these techniques (*i.e.* $> 10^{-4}$ M). Below such concentration, bis-OPV **2** revealed the typical temperature-dependent trends of monomeric OPV/OPE compounds: a red-shift and an increase in absorption intensity is noted when the temperature is decreased, which is simply a consequence of molecular planarization.^[12] However, when cooling concentrated solutions, compound **2** strongly aggregates

when crossing a certain temperature threshold, as noted in the sudden drop in absorption and emission intensity (Figure 3b).

With the aim to determine the morphology of the aggregates of **2**, AFM experiments were carried out from diluted solutions in MCH or dodecane that were drop-casted onto HOPG. In contrast to the assemblies formed by **1** in water, AFM analysis (Figures 3c-h and S2A) revealed the formation of large fibrillar objects with a consistent height of 10–15 nm, which suggested they were actually formed by bundles of stacks. As a matter of fact, a closer inspection of the surface also revealed the existence of smaller fibrils with a uniform height of 4.8 nm (Figures 3f,h), which is only slightly larger than the length of the rigid aromatic rod of **2** (3.8 nm), calculated from computational models. Thus, we suppose the larger fibres are formed by a coiling process from these fibrils which, at the same time are constituted by stacked columns of **2**. Further magnification of the AFM images confirmed the coiled morphology of the self-assembled fibres (Figures 3d and S2A).

In order to investigate in more detail the sharp aggregation transition observed and to determine the supramolecular polymerization mechanism, cooling curves were recorded at a 0.1 K/min rates for $5.0 \cdot 10^{-4}$ M solutions of **2** in decane. The non-sigmoidal trends obtained could be fitted to a cooperative nucleation–elongation model,^[9a,15] where the polymerization is divided in a nucleation and an elongation phase (Figure 4).

$$K_n = e^{\left(\frac{-(\Delta H_n^0 - \Delta H_n^0) - T\Delta S^0}{RT}\right)} \quad (1)$$

$$K_e = e^{\left(\frac{-(\Delta H_e^0 - T\Delta S^0)}{RT}\right)} \quad (2)$$

$$\sigma = \frac{K_n}{K_e} = e^{\left(\frac{\Delta H_n^\circ}{RT}\right)} \quad (3)$$

The fit provided the elongation temperature ($T_e = 280.6 \pm 0.3$ K), the nucleation and elongation enthalpies ($\Delta H_n^\circ = -15.0 \pm 3.4$ kJmol⁻¹, $\Delta H_e^\circ = -185.0 \pm 20.3$ kJmol⁻¹), the polymerization entropy ($\Delta S^\circ = -0.59 \pm 0.07$ Jmol⁻¹K⁻¹), as well as the corresponding nucleation and elongation constants ($K_n = 3.2$ M⁻¹, $K_e = 533.3$ M⁻¹). The degree of a cooperativity was calculated as $\sigma = 0.006$. This model has been also applied to other oligo(*p*-phenylenevinylene)s (OPVs)¹⁶ and oligo(*p*-phenyleneethynylene)s (OPEs), affording related cooperative parameters.¹⁷

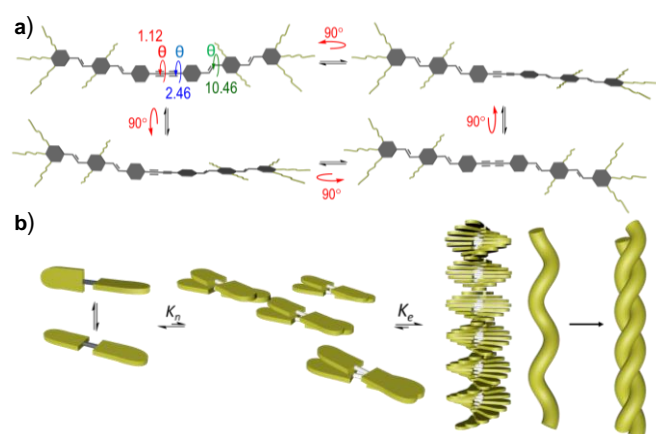


Figure 4. (a) π -conjugated conformations adopted by bis-OPV **2**, obtained by 90° rotation around the σ -bonds. (b) Cooperative self-assembly process of bis-OPV **2** in decane.

In short, the high solubility and relatively low propensity to aggregation in apolar solvents exhibited by bis-OPV **2** is remarkable and rather unexpected for a system comprising 6 phenylenevinylene units, in comparison to other oligomers reported in the literature. For instance, related OPVs with 6 continuously connected phenylenevinylene segments and similar peripheral tails already showed signs of stacking interactions at room temperature in toluene, a better solvating agent for π -surfaces.^[18] However, once the T_e is reached, compound **2** aggregates abruptly and the cooled concentrated solutions led to big amounts of a yellow precipitate, suggesting complete polymerization into large, insoluble aggregates. We attribute this supramolecular behaviour to the special characteristics of the diacetylene linker. The π -conjugated core of the bis-OPV compounds studied here presents three types of σ -bonds with markedly different rotation barriers (Figure 4a): 1) the more rigid sp^2 - sp^2 bond between vinyl and phenyl units (ca. 10.46 KJ·mol⁻¹),^[19a] 2) the sp - sp^2 bond between ethynyl and phenyl units (ca. 2.46 KJ·mol⁻¹),^[19b,c] and 3) the sp - sp bond between two ethynyl groups (ca. 1.12 KJ·mol⁻¹).^[19d,e] As a result of the relatively low rotation barriers of the sp - sp^2 bonds and, particularly, the sp - sp diacetylene bond, compound **2** exchanges dynamically in solution between 4 main types of similarly populated π -conjugated conformations, obtained by fast 90° rotation of any of these bonds. Two of these conformations are planar, and can therefore lead to

the π - π stacked nuclei required for polymerization (Figure 4b), but the two other conformations maintain the two OPV segments in orthogonal planes, which impedes π - π stacking interactions. Therefore, fast rotation around these bonds renders bis-OPV **2** an average cylindrical shape, which must strongly hinder nuclei formation. Only when the temperature is low enough and conformational exchange is slowed down, discrete π - π stacked species are formed in which planar conformations are immobilized, which can then serve as nuclei for elongation.

Finally, we tested photopolymerization of bis-OPV **2** during aggregation by UV light irradiation. However, no photoreactivity was noted at short irradiation times and the compound decomposed at long irradiation times.

In summary, we investigated here the self-assembly of a novel type of rod-like π -conjugated molecules in which two OPV segments are linked through a diacetylene bond. The supramolecular behaviour of these bis-OPVs strongly differs in aqueous or organic media. In water, the strong hydrophobic interactions between the π -cores in **1** promote aggregation into very robust and uniform micellar structures. In alkane media, in sharp contrast, a fibrillar morphology is obtained through a coiling process of columnar stacks of **2**. These stacks are, at the same time, formed via a highly cooperative nucleation-elongation mechanism that is influenced by the low rotation barriers around the sp - sp^2 bonds and, particularly, the sp - sp diacetylene bond.

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Keywords: cooperativity • oligo(phenylenevinylene)s • π -conjugated molecules • self-assembly • supramolecular polymers

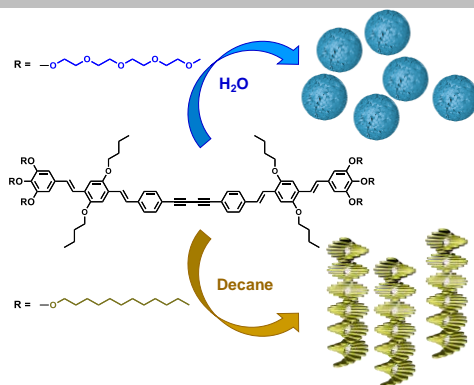
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COMMUNICATION

Novel rod-like, diacetylene-linked oligo(phenylenevinylene) molecules exhibit distinct self-assembly as function of the solvent environment. In water, these π -conjugated molecules aggregate into robust, uniform micellar structures. In alkanes a coiled-coil morphology is instead formed *via* a nucleation-elongation process with degrees of cooperativity of 0.006. Stacking interactions in these apolar media seem to be greatly affected by the low rotation barriers around the σ -bonds in the diacetylene linker.



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