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# Narcissistic versus Social Self-Sorting of Oligophenyleneethynylene Derivatives: From Isodesmic Self-Assembly to Cooperative Co-Assembly

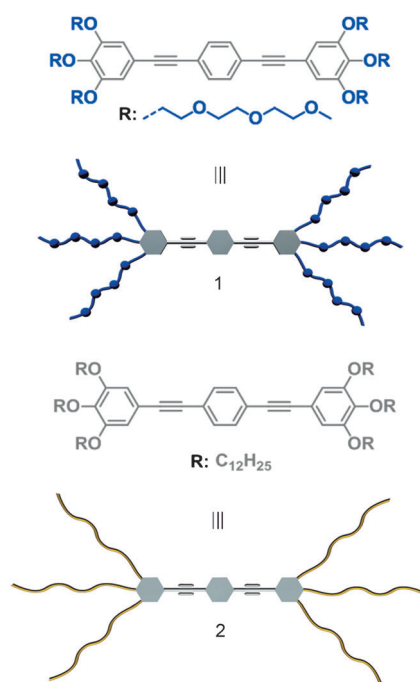
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Gustavo Fernández\*<sup>[a]</sup>**

Fundamental research in supramolecular chemistry has extensively focused on the properties of chemical substances, complexes or aggregates in isolation.<sup>[1]</sup> Only in the last decade, the extraordinary improvement of modern analytical techniques<sup>[2]</sup> and the curiosity of supramolecular chemists in the pursuit of systems with a higher level of complexity have awakened an increased interest in the study of multicomponent mixtures. These advances have brought about the emergence of the field of “self-sorting”,<sup>[3]</sup> which investigates the recognition phenomena between molecules within complex mixtures. Molecules that exhibit affinity for like species will give rise to “narcissistic” self-sorting,<sup>[4]</sup> whereas binding between unlike molecules can be termed “social” self-sorting.<sup>[5]</sup> These processes are commonplace in natural systems<sup>[6]</sup> and appear to have significant implications in the origin of life.<sup>[7]</sup> For instance, high-fidelity recognition events between complementary bases during the DNA replication are the basis for biological inheritance in living organisms.<sup>[8]</sup>

In contrast to their natural counterparts, social self-sorting is relatively scarce in artificial systems self-assembled through weak non-covalent forces. Systems involving discrete supramolecular structures,<sup>[9]</sup> extended supramolecular aggregates<sup>[10]</sup> or gel-phase materials<sup>[11]</sup> in organic solvents or binary mixtures of amphiphilic oligophenylenes,<sup>[12]</sup> perylene bisimides,<sup>[13]</sup> peptides,<sup>[14]</sup> bisurea bolaamphiphiles<sup>[15]</sup> or cyclodextrins<sup>[16]</sup> in aqueous media have been demonstrated to self-sort into a wide range of supramolecular architectures. However, the ability of directing competitive recognition events in a mixture of aggregates towards the formation of narcissistic or social self-sorted assemblies and their influence on the aggregation mechanisms has been virtually overlooked.

In this communication, we have exploited the well-known ability of oligophenyleneethynylenes (OPEs) to self-assemble into different supramolecular structures<sup>[17]</sup> for the inves-

tigation of the concentration-dependent narcissistic versus social self-sorting processes in aqueous mixtures of two OPE derivatives featuring polar or nonpolar peripheral chains (compounds **1** and **2** in Scheme 1, respectively). We



Scheme 1. Chemical structures and cartoon representation of the compounds investigated in the manuscript.

demonstrate that the transition from separate spherical assemblies formed by **1** and **2** (narcissistic self-sorting) to co-assembled ribbon-like structures can be accomplished by simply raising the concentration. This process, and this is to our knowledge unprecedented, is accompanied by a change in the aggregation mechanism from isodesmic to cooperative.

Linear OPE derivatives **1** and **2** (Scheme 1) have been readily synthesised in only five synthetic steps and fully characterised by NMR, UV/Vis, fluorescence and IR spectroscopy, and ESI and MALDI-TOF mass spectrometry (for characterisation details see Supporting Information).

Amphiphilic OPE derivative **1** exhibits an emission maximum centered at about 391 nm in CHCl<sub>3</sub> (see Supporting

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Information). However, the fluorescence spectrum of **1** in water is concentration-dependent, red-shifted (458 nm) and remarkably quenched ( $\Phi_F=5\%$ ) compared to that measured in chloroform, which is indicative of the aggregation of the aromatic segments (Figure S1 and Table S1 in the Supporting Information).<sup>[18]</sup> Temperature-dependent UV/Vis studies in water show a simultaneous sharpening of the absorption bands at about 335 and 370 nm and a 10 nm blue-shift of the transition at 221 nm with an isosbestic point at 314 nm as the temperature increases from 283 to 343 K (Figure S2 in the Supporting Information). Analogous temperature-dependent UV/Vis experiments performed in THF/water (1:1) show comparable results, that is, the sharpening of the transitions at about 335 and 370 nm and a small decrease of the transition at 221 nm with increasing temperature (Figure 1a and Figure S3 in the Supporting Informa-

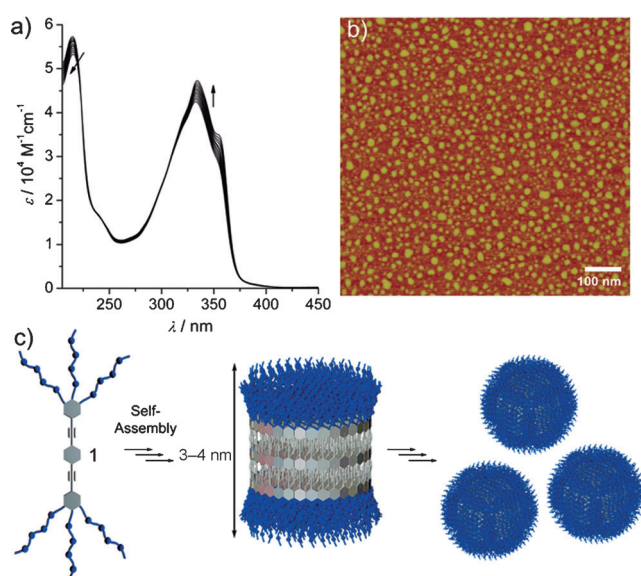


Figure 1. a) Temperature-dependent UV/Vis spectra of **1** ( $2 \times 10^{-4}$  M) in THF/water (1:1) between 283 and 343 K. Arrows indicate spectral changes upon increasing temperature. b) Height AFM image of **1** ( $1 \times 10^{-4}$  M, THF/water 1:1) onto silicon wafer. Z scale is 10 nm. c) Proposed self-assembly model of **1** in aqueous mixtures.

tion). The overall observations suggest a self-assembly process between well-defined species. The self-assembly mechanism has been studied in detail by monitoring the spectral changes as a function of temperature. The samples were cooled down slowly in small steps ( $1 \text{ K min}^{-1}$ ) to ensure that self-assembly takes place under thermodynamic control. For both experiments, no hysteresis in the molar absorption coefficient was observed when heating the solution again to 343 K, which demonstrates the reversibility of the self-assembly process both in water and 1:1 THF/water mixtures. The spectral changes at 338 nm have been successfully fitted to the isodesmic model,<sup>[19]</sup> in which each reversible step in the assembly pathway is characterised by a single binding constant ( $K$ ) (for details see Supporting Information). Application of this model to our temperature-dependent ex-

periments affords a binding constant ( $K_a$ ) of  $1.3 \times 10^5 \text{ M}^{-1}$  in water and  $2.2 \times 10^5 \text{ M}^{-1}$  in THF/water (1:1) at room temperature (Tables S2 and S3 in the Supporting Information). The equivalent values of binding constant indicate that the aggregation behaviour of **1** in pure water and THF/water (1:1) is identical in both media.

Dynamic light scattering (DLS) experiments support the formation of supramolecular associates of **1** in both water and THF/water (1:1) mixtures. For both solvents, the CONTIN analysis of the autocorrelation function from DLS experiments shows a sharp peak corresponding to an average hydrodynamic radius of about 5 nm at a concentration of  $1 \times 10^{-3}$  M (Figure S4 in the Supporting Information). The aggregate morphology on substrates has been visualised by atomic force microscopy (AFM) on silicon wafer under ambient conditions and scanning electron microscopy (SEM) experiments. AFM images of **1** spin-coated from water and THF/water (1:1) solutions onto silica wafer reveal the appearance of discrete globular objects with sizes between 3–10 nm, which are in agreement with the values observed by DLS (Figure 1b and Figure S5 in the Supporting Information). SEM images confirm the presence of small spherical associates with comparable sizes (Figure S6 and S7 in the Supporting Information). The overall results support the non-cooperative (isodesmic) formation of spherical micelles that are stabilised by  $\pi$ – $\pi$  and hydrophobic interactions between the aromatic OPE segments and shielded from the aqueous environment by the peripheral triethyleneglycol (TEG) chains (Figure 1c). This unusual non-cooperative micellar formation has also been observed in the aqueous self-assembly of related rectangular OPE amphiphilic derivatives into highly-organised micellar, vesicular and 2D assemblies.<sup>[20]</sup>

The ability of polar OPE **1** to self-assemble into well-defined supramolecular structures prompted us to investigate to what extent these would be influenced by the presence of a structurally related OPE derivative. Owing to its nonpolar nature, OPE **2** is expected to aggregate in aqueous mixtures driven by the hydrophobic effect. In fact, addition of water to a dilute ( $10^{-5}$  M) solution of **2** in THF induces aggregation, as evidenced by the decrease in absorption at 345 nm and the appearance of a red-shifted shoulder at about 405 nm in UV/Vis experiments when the water content exceeds 30% (Figure 2a). Equivalent results are observed at  $1 \times 10^{-4}$  M until at higher concentration ( $10^{-3}$  M) the compound precipitates. DLS experiments reveal that the associates formed in THF/water (1:1) at a concentration of  $1 \times 10^{-4}$  M are relatively small and monodisperse, with a very narrow distribution of sizes ranging from 3 to 30 nm (Figure S8 in the Supporting Information). AFM and SEM imaging show the appearance of spherical objects with diameters ranging from 4 to 50 nm (Figure 2b, and Figures S9 and S10 in the Supporting Information). The diameter of the smallest aggregates (ca. 4 nm) approximately match the length of a molecule of **2**, whereas the agglomeration of some of these small aggregates driven by the hydrophobic effect ultimately gives rise to larger nanoparticles with sizes up to 50 nm (Figure 2b,c).

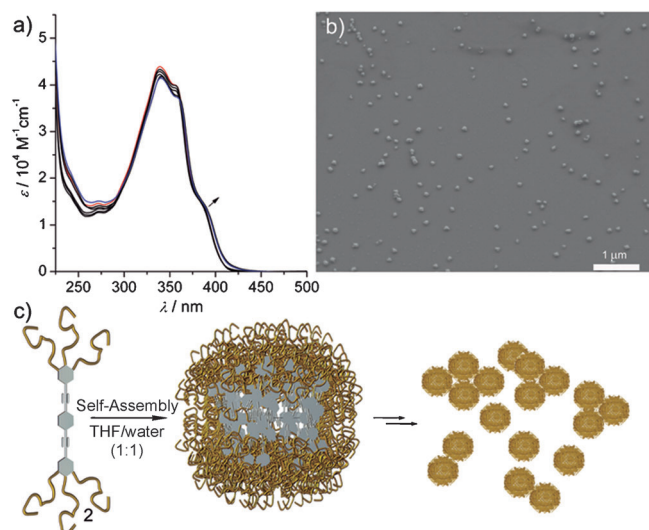


Figure 2. a) UV/Vis spectra of **2** in THF/water mixtures (0 to 90% water) at  $1 \times 10^{-5}$  M. b) SEM image obtained by spin-coating a solution of **2** in THF/water (1:1;  $1 \times 10^{-5}$  M) on a silicon wafer. c) Cartoon representation of the self-assembly of **2** in THF/water mixtures above 30% water.

The aggregation ability of OPE derivatives **1** and **2** can be ultimately exploited to investigate their self-sorting behaviour in aqueous mixtures driven by geometrical complementarity and the hydrophobic effect. Self-sorting experiments have been carried out in THF/water mixtures for an adequate comparison of the behaviour of **1** and **2** in isolation and in their mixtures. In the light of previous results, both **1** and **2** form spherical aggregates at concentrations as low as  $1 \times 10^{-5}$  M in THF/water (1:1) (see Figures 1 and 2 and Table S3 in the Supporting Information). At this concentration, the UV/Vis spectra of mixtures of **1** and **2** at different mole fractions (0–100%) in THF/water (1:1) correspond to the sum of the spectra of both compounds in isolation and are characterised by the lack of any new spectral signature (Figure 3a). These findings along with the appearance of two isosbestic points at 300 and 350 nm indicate that no mixing between the individual aggregates of **1** and **2** takes place. Equivalent spectral changes are observed when the concentration is raised to  $1 \times 10^{-4}$  M (Figure S11 in the Supporting Information). However, a subsequent tenfold increase in concentration (1 mM) strongly influences the behaviour of the mixture. Addition of increasing amounts of water (10–80%) to an equimolar mixture of **1** and **2** in THF induces remarkable spectral changes. Depletion of the absorption band at 335 nm is accompanied by the emergence of a new red-shifted transition between 400–500 nm with an isosbestic point at 365 nm when the water content exceeds 30%, indicating that a co-assembly process occurs (Figure 3b). This co-assembly process takes place only when **1** and **2** are present in comparable ratios ( $1/2 = 2.5:1 \rightarrow 1:2.5$ ), indicating the lack of a precise stoichiometry. At high ratios of **1** (70% or above), no appreciable spectral changes occur whereas the mixture precipitates at high ratios of **2** (80% or above) (Figure S12 in the Supporting Information).

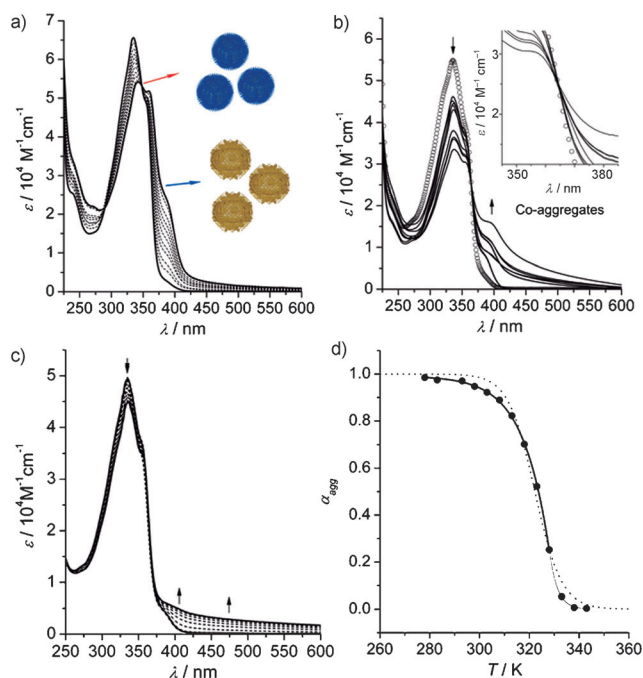


Figure 3. a) UV/Vis spectra of mixtures of **1** and **2** ( $1 \times 10^{-5}$  M, 298 K) at different mole fractions (0–100%) in THF/water (1:1). b) UV/Vis spectra of a 1:1 mixture of **1** and **2** in THF (1 mM, 298 K) and after subsequent additions of water up to 80%. c) Temperature-dependent (283–343 K) UV/Vis spectra of a 1:1 mixture of **1** and **2** in THF/water (6:4). Arrows indicate spectral changes upon water addition (b) or temperature decrease (c). d) Fitting of  $\alpha_{\text{agg}}$  data against  $T$  ( $\lambda = 400$  nm) in the framework of the nucleation–elongation model. The grey line corresponds to the nucleation regime and the black line to the elongation regime. The dotted line represents the fit to the isodesmic model.

Temperature-dependent UV/Vis studies on a 1:1 mixture of **1** and **2** in THF/water (1:1) reveal only partial dissociation of the co-aggregates into monomeric species when the temperature is increased up to 343 K (Figure S13 in the Supporting Information). However, when mixture of **1** and **2** in THF/water (6:4) is slowly cooled down in small steps ( $1 \text{ K min}^{-1}$ ) from 343 to 283 K, a reversible co-assembly process between monomeric (333 nm) and aggregated (400–500 nm) species with an isosbestic point at about 361 nm (Figure 3c) can be observed.<sup>[21]</sup> The plot of fraction of aggregated molecules ( $\alpha_{\text{agg}}$ ) against temperature at  $\lambda = 400$  nm is clearly non-isodesmic (see dotted line in Figure 3d), which suggests a cooperative co-assembly process between **1** and **2** as described by the nucleation–elongation model developed by Schenning, Meijer and van der Schoot (for details see the Supporting Information).<sup>[22]</sup> This mechanism involves a highly favourable cooperative growth (elongation) that can only take place after an initial critical-sized aggregated species (nucleus) has been formed (nucleation). Application of this model to our experimental data points affords good fits to both nucleation (grey plot in Figure 3d) and elongation (black plot in Figure 3d) regimes and enables the calculation of the thermodynamic parameters of the co-assembly process (for details see Figure S14 and Table S4 in the Supporting Information). Interestingly, the nucleus size ( $\langle N_n(T_c) \rangle$ )



was calculated to be around six molecules, which indicates that an initial unfavourable nucleation process involving six molecules of **1** and/or **2** induces an increase in local concentration<sup>[23]</sup> of monomeric units that ultimately “activates” the co-assembly process (see model in Figure 4c bottom). DLS

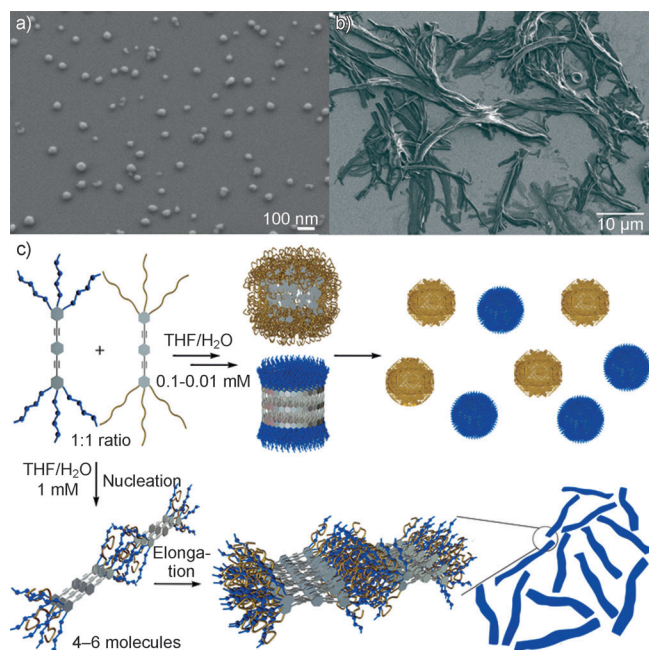


Figure 4. SEM images obtained by spin-coating a 1:1 mixture of **1** and **2** in THF/water at a) 0.1 mM and b) 1 mM on a silicon wafer. c) Cartoon representation of the concentration-dependent self-sorting behaviour of a 1:1 mixture of **1** and **2** in THF/water (1:1). Narcissistic self-sorting at concentrations between 0.01 and 0.1 mM (top) and social self-sorting at 1 mM (bottom).

studies performed on an equimolar mixture of **1** and **2** in THF/water (1:1) at 1 mM reveal the formation of co-aggregates with a remarkably large size, as evidenced by the appearance of a broad distribution of sizes ranging from about 40 nm to 5 μm with a maximum at approximately 1 μm (Figure S15 in the Supporting Information).

NMR experiments support the existence of a co-assembly process between **1** and **2**. Addition of 30% D<sub>2</sub>O to a 2 mM solution of nonpolar OPE derivative **2** in [D<sub>8</sub>]THF induces a turbidity that ultimately results in the precipitation of the compound. However, the addition of polar OPE **1** in a 1:1 ratio enhances the solubility and stability of **2** at high water content, which speaks in favour of a co-assembly process. <sup>1</sup>H NMR experiments reveal a strong and continuous upfield shift of most of the resonances when D<sub>2</sub>O is added to a 4 mM solution of a 1:1 mixture of **1** and **2** in [D<sub>8</sub>]THF (Figure S16 in the Supporting Information). An increase in water content appears to induce a rearrangement of the molecules of polar OPE **1** around the nonpolar molecules of **2** to shield them from the polar environment, thereby strengthening the  $\pi$  stacking between them. This observation is in sharp contrast to the behaviour of polar OPE **1** in

isolation, in which no significant signal shifts can be observed above about 30% D<sub>2</sub>O in [D<sub>8</sub>]THF at 4 mM (Figure S17).

Final evidence demonstrating a concentration-dependent self-sorting behaviour between **1** and **2** has been provided by SEM studies. The images obtained from a 1:1 THF/water mixture on silicon wafer at either 10<sup>−4</sup> or 10<sup>−5</sup> M show that the 1:1 mixture of **1** and **2** self-assembles into independent spherical aggregates with sizes between 5 and 50 nm (Figure 4a and the model shown in Figure 4c). These results are in accordance with previous UV/Vis studies and clearly indicate that up to a concentration of 0.1 mM narcissistic self-sorting dominates. At a higher concentration (1 mM) the equilibrium is shifted towards the formation of co-assemblies, as demonstrated by SEM studies. The images display long ribbon-like aggregates with widths of about 2 μm and lengths of several microns (Figure 4b and Figure S18 in the Supporting Information). Polarized optical microscopy (POM) investigations on the same mixture show a clear spherulitic growth, which is indicative of the formation of a lyotropic lamellar (L $\alpha$ ) mesophase<sup>[24,25]</sup>—an emergent property of the mixture (Figure S19 in the Supporting Information and model in Figure 4c bottom). These results can be rationalised by considering the intercalation of nonpolar molecules of **2** in the  $\pi$  stack formed by **1** driven by cooperative hydrophobic and  $\pi$ – $\pi$  interactions. Further lateral interaction between the alternated  $\pi$  stacks most likely driven by van der Waals and solvophobic interactions between the alkyl chains of **2** ultimately yields larger ribbon-like associates (Figure 4b and Figure S18 in the Supporting Information).

In conclusion, we have described the self-assembly of two structurally related OPE derivatives substituted with polar or nonpolar chains (**1** and **2**) and their narcissistic versus social self-sorting behaviour in aqueous media that can be controlled by concentration changes. At relatively low concentration (0.01–0.1 mM) the 1:1 mixture of **1** and **2** in THF/water (1:1) self-assembles in a non-cooperative fashion into independent spherical associates that coexist in the aqueous medium, as demonstrated by DLS, UV/Vis and SEM experiments. By simply raising the concentration to 1 mM, the mixture undergoes a cooperative co-assembly process driven by geometrical complementarity and the hydrophobic effect, giving rise to micrometric-sized aggregates with lyotropic liquid-crystalline behaviour, as demonstrated by DLS, UV/Vis, NMR, SEM, and POM studies. Overall, our findings should provide rational guidelines for the design of narcissistic and co-assembled aggregates exhibiting emergent properties with relevance to the fields of self-assembly in water<sup>[26,12a]</sup> and systems chemistry<sup>[27]</sup> and potential applications in optoelectronic devices or biomedicine.

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