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Exploring Solvent-Solute Interactions: Unveiling Their Impact on Supramolecular Self-Assemblies

1. Introduction

Because of its widespread application in biology, material science, and chemistry, supramolecular engineering has seen a rapid increase in interest and advancement in recent years [1]. Fundamentally, the goal is to create supramolecular systems by modifying the interactions between individual building units in solution and solid-state to achieve beneficial complicated structures with multi-functional properties. Since the recent Nobel Prize in Chemistry was awarded to Ben Feringa, Jean-Pierre Sauvage, and Fraser Stoddart, this field has seen a surge in interest. [2] The self-assembly of supramolecular complexes aids in the development of a diverse range of molecules that are mechanically interlocked or differ in their supramolecular architectures or can be the first to form molecular machines involving rotaxanes and catenanes. [3] Recent studies of molecular machines include molecular automobiles [4], shuttles [5], mussels [6], pumps [7], elevators [8], and so on. Supramolecular chemistry sparked an interest in molecular-engineered complexes, which are made up of small molecular blocks held together by reversible intermolecular non-covalent interactions such as hydrogen bonding, electrostatic interactions, π-

π stacking, and solvatochromic interactions. Controlling their layout and function opens up an exciting interdisciplinary field of study. One of chemistry's most important topics appears to be the interactions between solvents and solutes. They play an important role in controlling solubility, structure, and reactivity. [9] Even though chemists and biologists use solvents on a daily basis in their laboratories, choosing the best solvent for a specific solute is a guess. Simultaneously, the role of unique solvents for solutes has been well documented. Chemists have gained a high level of expertise in perceptions of solvent properties, chemical structure, and role in controlling chemical reactions through extensive research. The numerous exciting solvent-induced results in supramolecular chemistry make these "often overlooked" areas well worth revisiting.

2. Solute−Solvent Interactions in Biology and Chemistry

Chemical reactions are typically carried out in a solvent medium, which has a strong influence on the reaction rate by controlling the reactivity of reactants and intermediates. For example, polar, protic solvents are preferred for S_N1 reactions, which help to stabilize the carbocation formed in the rate-determining step, whereas apolar, aprotic solvents are preferred for S_N2 reactions, which aid in the solvation of the transition state. The investigation into the physical-organic aspects of the effect of the solvent on the chemical structure and reactivity of organic systems has an impact on polymer science as well. The quality of the solvent essentially guides the conformation of artificial polymers in solution. In minute contamination solvents, small globular debris can be found, whereas longer chains can be found in pure (desired) solvents. Solutesolvent interactions govern the overall outcome of techniques such as material processing, annealing, moulding, and electrospinning. Furthermore, non-covalent chemistry between solvents and solutes is critical in material science, leading to its application in industries. Solute-solvent interactions are extremely important in biology. [10] The tertiary structure of folded biomacromolecules, such as polypeptides[11] or polynucleotides [12], is stabilized by interactions between the biomolecule and water. Another fascinating effect that solvents have on biological systems is liquid-liquid phase separation in cell structures [13], while the stabilizing role of water in protein dipole balance remains an exciting topic. [14], Water, as a solvent, plays an important role in controlling the structure and function of DNA[15-17] and proteins[18-20], making it an essential component of

the living system. Solvents can affect artificial supramolecular structures through specific interactions of enthalpic and entropic contributions. [21,22] The multiple directional interactions among constituents in polar solvents yield a comprehensive description of solvation. [23–25] The enthalpic origin of the solvent contribution can be determined in cooperative systems that exhibit sharp transitions between states when small amounts of H-bonding cosolvent are bound. [26–29] Such enthalpic contributions account for the early irreproducibility of Pasteur's enantiomeric separation, in which dehydration of conglomerate tartaric acid salt results in a racemic mixture at room temperature. [30] This thesis, however, will not cover those existing biological systems; instead, it will concentrate on synthetic supramolecular self-assemblies.

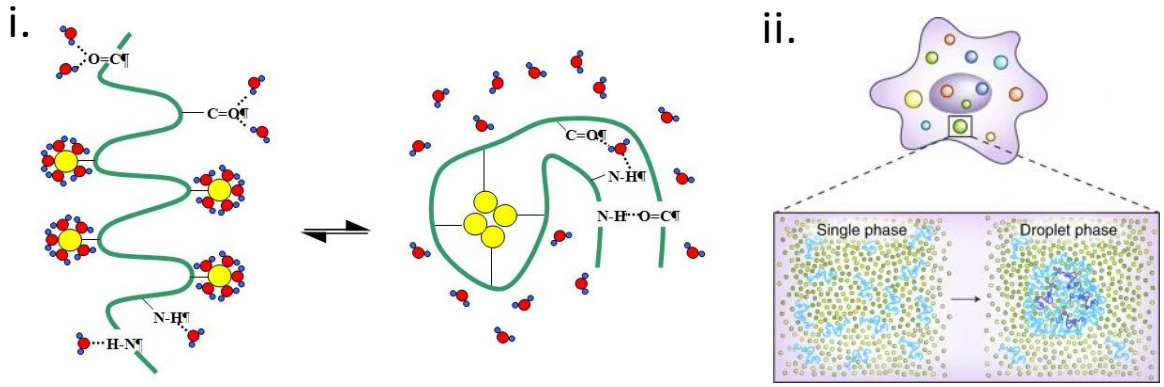

Figure 1. The stability of the tertiary structure of folded biomacromolecules, 1.2. Liquid−liquid phase transition in cellular systems

3. Solute−Solvent Interactions in Supramolecular Chemistry

After Staudinger's initial intellectual idea, "*Hochmolekulare Verbindungen*," in 1920,[31] macromolecules ruled the first century of polymer chemistry. Later, reviews began to emerge on polymeric aggregates of repeating monomers that were not held together by covalent bonds but rather by supramolecular, non-covalent interactions. [32-35] With the pioneering contributions of Lehn, Aida, Stupp, and others, these examples kick off the journey of modern supramolecular chemistry. [36] The repeating units (monomers) in supramolecular self-assemblies are held together by one or more non-covalent interactions, such as hydrogen bonding, -stacking, charge-transfer interactions, metal-ligand coordination, ionic interactions, and solvophobic interactions.

[37-38] In contrast to covalently linked polymers, the energy of these interactions is typically in the tens to hundreds of kJ/mol range. These soft interactions make the backbone of supramolecular self-assemblies extremely dynamic and responsive to a wide range of external factors and stimuli. [37,38] This stimuli-responsiveness enables the processing of functional smart materials that can be reversibly tunable via external conditions. [39] Mastering the approach of using external stimuli to regulate supramolecular assemblies is especially desirable because it is critical to create new opportunities to design beneficial materials. Temperature, pH, light, and redox or electro-chemical actuators are the most commonly used stimuli in this regard. [43] On the contrary, the solvent's role is typically of minor importance despite the fact that some widely accepted outcomes, such as the effect on polarity[44,45] or self-assembly guided by solvophobic interactions, have been validated. [46] There are a few good examples of supramolecular systems that could be significantly influenced by a minor change in the solvent, such as its assembly packing. [47] Meijer and colleagues investigated the effect of water in supramolecular self-assemblies in oils and determined its role in the helicity of self-assembly in this context (Figure 2). [48] They have concluded that the role of water in oils results from the potential enthalpy of molecularly dissolved water, which is the frequently unconsidered manifestation of hydrophobic effects.[49,50] Although those underlying consequences have existed for decades, [51-54] the results describe the acute effect of water on self-assembly in oils, even with a minuscule quantity of water.

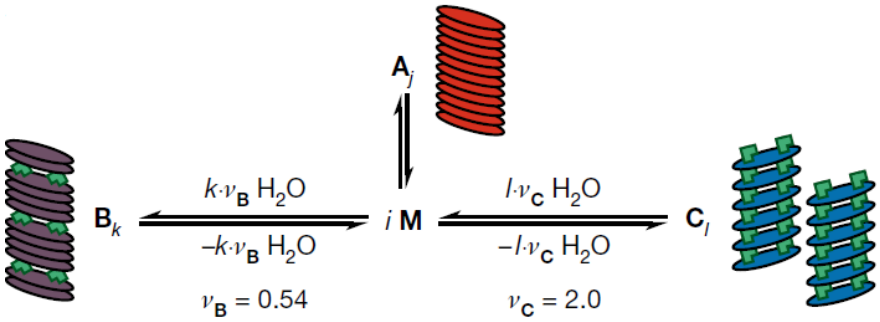

Figure 1. Schematic representation of three cooperative, competitive pathways. The variables *j*, *k* and *l* correspond to the degrees of polymerization of **A**, **B** and **C**, respectively. The coloured discs represent aggregated monomer units, and the green blocks represent water molecules.Figure taken from ref.[48]

Typically, supramolecular self-assemblies are prepared and studied in solution. Each constituent monomer unit or self-assembled architecture in the solution is surrounded by many solvent molecules. In this case, the energy of solute-solute interactions is comparable to the net energy of

interactions provided by multiple solute-solvent interactions. As a result, the effect of solvents on the self-assembly mechanism and structure is more responsive than that of covalent polymeric systems. Because of their dynamic nature, supramolecular self-assemblies are highly dependent on the external conditions under which they have been studied. As a result, while studying the interactions between supramolecular self-assemblies and their solvents is difficult, it may also offer appealing opportunities to use those interactions to design advanced reversible materials.

Furthermore, the strength of these weak interactions is affected by the solvent environment. [55] In binary solvent structures, the degree of self-assembly is highly dependent on the solvent system composition. Looking at every solvent impact in every weak interaction at the same time, on the other hand, is difficult. Chemists can determine solvent outcomes in chromatography and the phenomenon of solvatochromism in polarised compounds empirically. [56] The outcomes are determined by a number of variables with arbitrary coefficients and are based on linear free-energy relationships (discussed later). [57] Solvent has a significant impact on the solubility of low-molecular-weight compounds as well as the macroscopic properties of their self-assemblies, including wetting, morphology change, and gel formation[58]. [61] However, we know little about how solvent-solute interactions affect the molecular stage of low-molecular-weight compounds and their self-assemblies.

4. Good and Poor Solvent in Supramolecular Self-Assemblies

In discussions of complicated supramolecular formation with various nonbonding interactions, solvent polarity is frequently used qualitatively. By using additional polar solvents, the solvent polarity interacts with the polar residues in molecules, resulting in hydrogen bonding and dipole-dipole interactions. However, apparent relationships between solvent polarity and - interactions have received little attention in the literature. The formation of supramolecular self-assemblies is

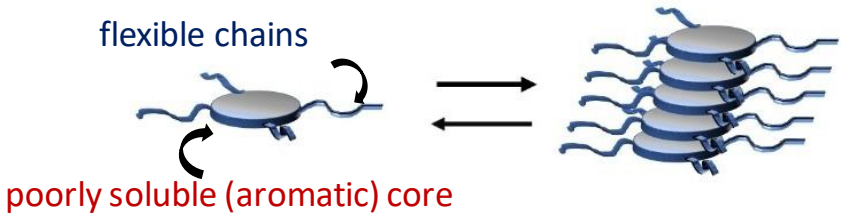

Figure 3. A schematic representation of design strategy of supramolecular self-assembly probe.

dependent on the solvent effect in terms of the various strong and weak interactions, with the polar solvent being used to strengthen some but weaken others.

Although it is tough to characterise macroscopic observations of the formation of supramolecular self-assemblies, solvent-based self-association constants may be correlated with the solvent effect.[62]. Since the association consistent is related to the Gibbs free of self-assembly(ΔG), the ΔG values may be used as indexes for the solvents used. In order to quantify the degree of the solvent-dependent self-assembly constants, the monomer and corresponding assembly must be in equilibrium.[63] Consequently, the monomers must be soluble in the solvent to stay as a solvated monomer beneath a dilute concentration, whereas the corresponding self-assembly is higher. When an exceptionally "good" solvent can dissolve as non-aggregated monomers even at higher concentrations, a completely "poor" solvent gives precipitates, even in a dilute condition. Various analytical techniques like vapour pressure osmometry or NMR spectroscopy [64] require tens of millimolar to sub-millimolar samples, whereas micromolar concentrations are utilised in UV-vis absorption spectroscopy. Suitable concentrations also rely upon the monomers' molecular weights and molar extinction coefficients. Due to solubility constraints and the complexity of the self-assembly process, it is difficult to collect self-assembly constants in all solvents using a specific supramolecular probe (monomer). As a result, peripheral substituents (usually long alkyl chains) that ensure monomer solubility in organic solvents are attached to a poorly soluble large -aromatic core that will be used to survey various solvents (Figure 3). Secondary non-covalent interaction between peripheral substituents may result in different self-assembly outcomes. To separate the susceptible interactions at the peripheral substituents from those at the mainframes, the same supramolecular composed of a non-substituted -core is far more acceptable. As a result, even when using the same supramolecular system, evaluating different solvents has been difficult.

5. Thermodynamic Aspect of Solvent-Solute Interactions in Supramolecular Self-Assembly

The balance of solute-solute non-covalent interactions and solvent-solute weak interactions determines whether monomers self-assemble or not. Despite the fact that this effect has been recognized since the early stages of supramolecular self-assembled systems, systematic and

quantitative research has only recently been mentioned. [65] Empirical solvent polarity parameters are useful in explaining the binding strengths (free energy of self-assembly) in supramolecular self-assemblies using linear free energy relationships in self-assembly equilibria (LFER). For all intermolecular interactions in supramolecular assemblies of solvatochromic dyes, LFER relates the Gibbs free energy of self-assembly to the standard solvent polarity scales, including $E_T(30)$, π^*, α or β. [67] LFERs can aid in understanding the nature of specific intermolecular interactions in supramolecular self-assembly because several solvent parameters are related to multiple solvent-solute interactions. Würthner defined LFER for supramolecular systems assembled through non-covalent interactions such as hydrogen bonding, halogen bonding, $\pi-\pi$ -stacking, and so on. Understanding those relationships provides a useful tool for selecting the best solvent to investigate a specific self-assembled system.

Because of their strong $\pi-\pi$ -stacking interactions in various solvents, perylene bisimides (PBI) proved to be ideal dyes for self-assembly research. [72] Furthermore, aggregation approaches for PBIs are simple to analyze. Figure 4 depicts how the Gibbs free energy of self-assembly varies with solvent polarity, beginning with the non-polar aliphatic solvent n-hexane and progressing to the very polar solvent water. [73,74] It is not possible to cover this entire range with a single dye molecule. It is, however, accessible with two dyes that differ in their solubilizing substituent chains. Based on nearly identical values for intermediate polarity solvents (toluene, THF, and diethyl ether), it can be assumed that substituent chains do not significantly contribute to intermolecular interactions. With this wealth of data, a relationship can be drawn between these two PBI dyes in which the aggregation increases or decreases for stacking interactions with increasing solvent polarity, as shown in Figure 4. Red dye with oligo ethylene glycol chains shows increasing binding energy with increasing solvent polarity, whereas blue dye with aliphatic chains shows decreasing binding power with increasing solvent polarity. This result is most likely defined by intermolecular interactions between the dyes and between the dyes and the solvent. Aromatic solvents and THF have the lowest binding energy and are, therefore, preferred for dissolving PBI molecules. Strong binding energy has been found for a PBI dye with alkoxy chains instead of alkyl chains, and from LFER, it can be concluded that chloroform is the best solvent for solubilizing red dye (open blue diamond). The solvents with the lowest binding free energy, on the other hand, are suitable for self-assembly. Thus, LFER can aid in the discovery of suitable solvents for studying

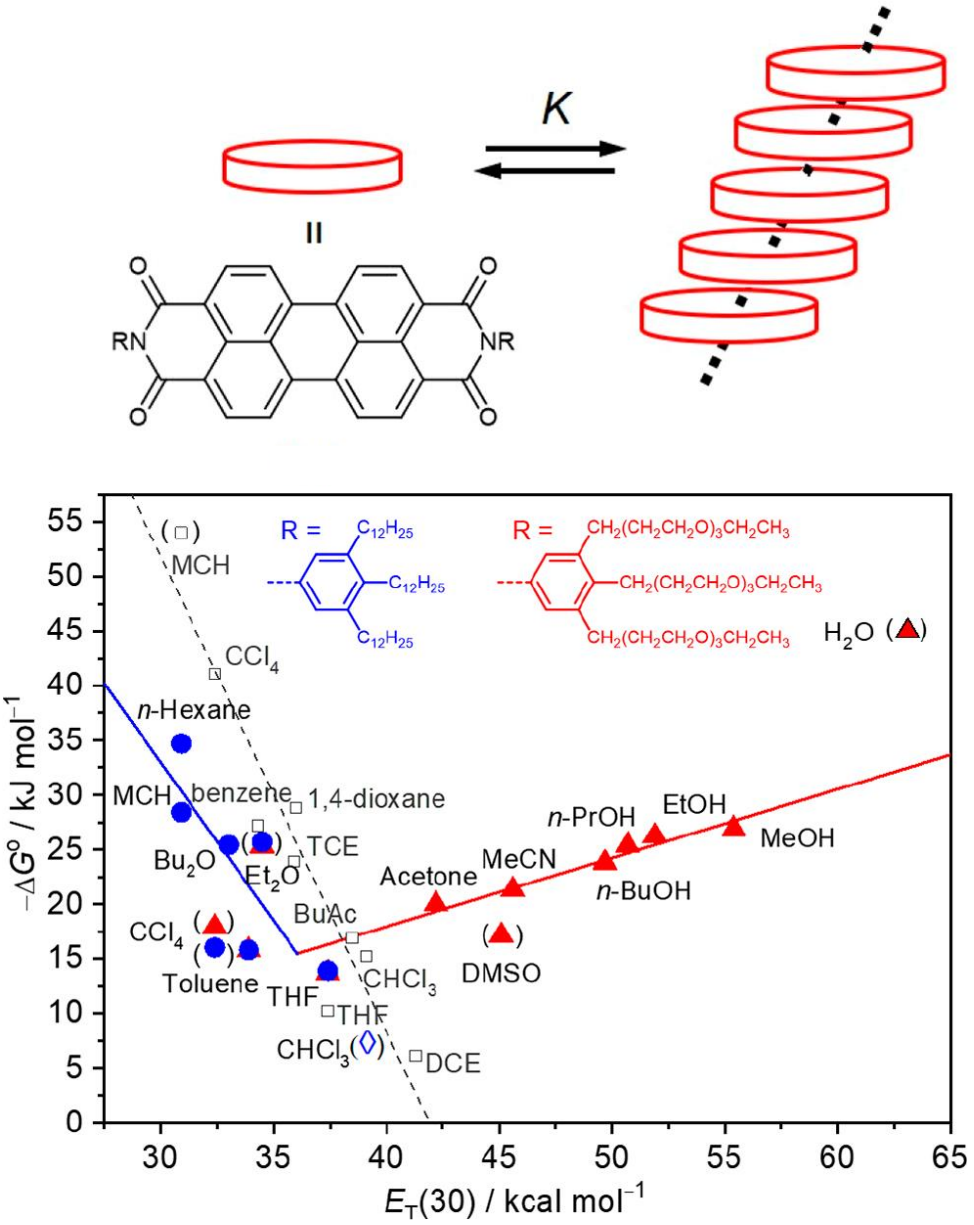

Figure 4.. LFER between the Gibbs free energy of self-assembly for the isodesmic aggregation of two different PBI dyes (blue and red as well as for merocyanine (gray) with the $E_T(30)$ polarity scale. Figure taken from ref.[68]

supramolecular self-assemblies. The solvent properties of a couple of solvents in a solvent system cannot be understood completely based on the ratio of the solvents in the mixture. As a result, many LFERs have been studied with various solvent combinations (Figure 5). Furthermore, these LFERs aid in the discovery of the best conditions for the desired self-assembly process. In this case, the solvent mixture includes a "good" solvent that dissolves the monomers and a "poor" solvent that dissolves only the substituent chains but not the aromatic cores. A simple LFER can

define the effect of a good solvent on self-assembly in a poor solvent for many solvent combinations.

$$\Delta G = \Delta G^{o}_{poor\ solvent} - m f_{good\ solvent}$$

where ΔG is the Gibbs free energy of the self-assembly at a fraction of good solvent *f*, $\Delta G^{o}_{poor\ solvent}$ is the Gibbs free energy of the self-assembly in the poor solvent, and $f_{good\text{-}solvent}$ is the volume fraction of the good solvent.[75,76] This simple relationship has been applied to diverse self-assembled systems in different solvent mixtures.

The m-value denotes a good solvent's denaturing ability for a specific chromophore and a specific pair of good and bad solvents. m-values for limited systems have been reported in supramolecular self-assemblies. For OPV, ureidotriazines, perylenes, and a BTA, typical m-values for a binary mixture of $CHCl_3$ and MCH are around 60 kJ/mol. LFERs, on the other hand, can quantify the effect of a good solvent on supramolecular self-assembly in poor solvents, but they do not provide a molecular-level understanding of various solvent-induced interactions.

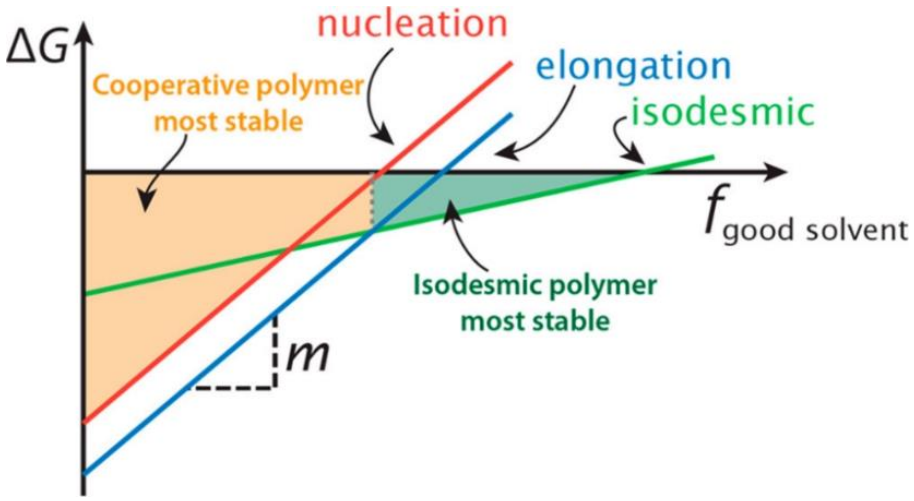

Figure 5.Representation of the changes in Gibbs free energies (ΔG) upon the addition of a good solvent of the various aggregation pathways in a competitive supramolecular self-assemblies involving a cooperative and isodesmic pathway. As a fraction of good solvent, $f_{good\text{-}solvent}$, is added, the change in stability of the aggregates is given by their m-value. When the elongation or isodesmic pathway is lower in ΔG, the cooperative or isodesmic assembly, respectively, are the most stable self-assemblies, as indicated by the shaded areas and dashed lines. Figure taken from ref.[61]

5.1. Solvent-Induced Helicity in Self-Assemblies

Solvents can effectively direct supramolecular polymer structure and morphology in addition to controlling the balance of several non-covalent interactions. The use of chiral solvents to bias helical preference when achiral monomers form supramolecular self-assemblies is one of the most common examples.

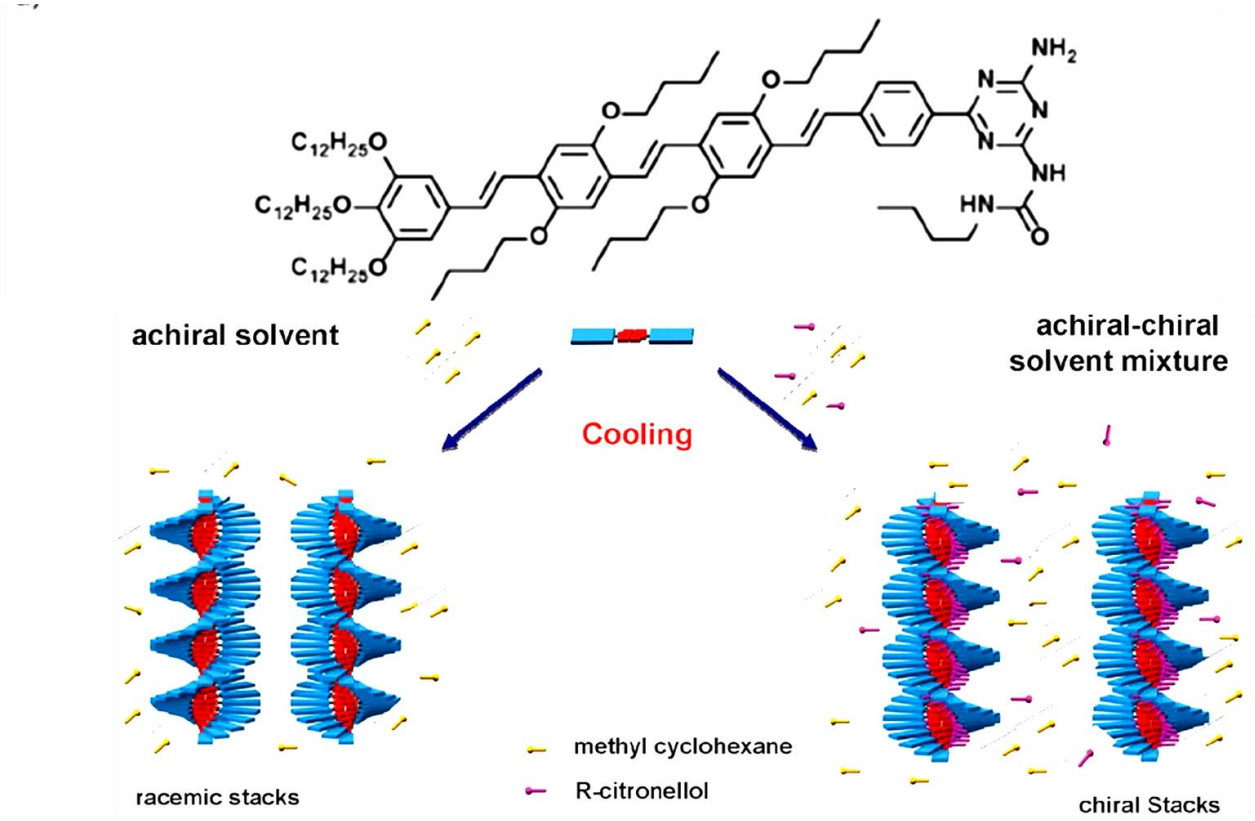

Figure 6. (R)-Citronellol as cosolvent in MCH induces the formation of supramolecular polymers of OPV derivatives of a preferred handedness. Figure taken from ref.[80]

George and co-workers reported one such example of solvent-induced helicity in OPV derivatives, where adding a minute amount of chiral (R)-citronellol solvent can bias helical preference in self-assembly in MCH. They also showed that this helical biasing only happens whilst the solvent includes hydrogen-bonding moieties (Figure 6).[80] This indicates that the helical induction inside the OPV assembly is primarily based on enthalpic interactions, which contrasts with the lack of any directional interactions in aliphatic solvents.

5.2. Solvents or Cosolvents as Structural Components in Self-Assembly

Besides helical induction by chiral solvents, solvents can play an active role in self-assembly by acting as a structural component of the assembly. Meijer and co-workers have presented an excellent example of stereomutation under thermodynamic control in the self-assembled coronene bisimide system, where the substituents form "molecular pockets" within the assembly(Figure 7).[81] Unique chiroptical studies reveal that solvent molecules intercalate or form clathrates inside the molecular pockets at low temperature (263 k), thereby triggering the stereomutation.

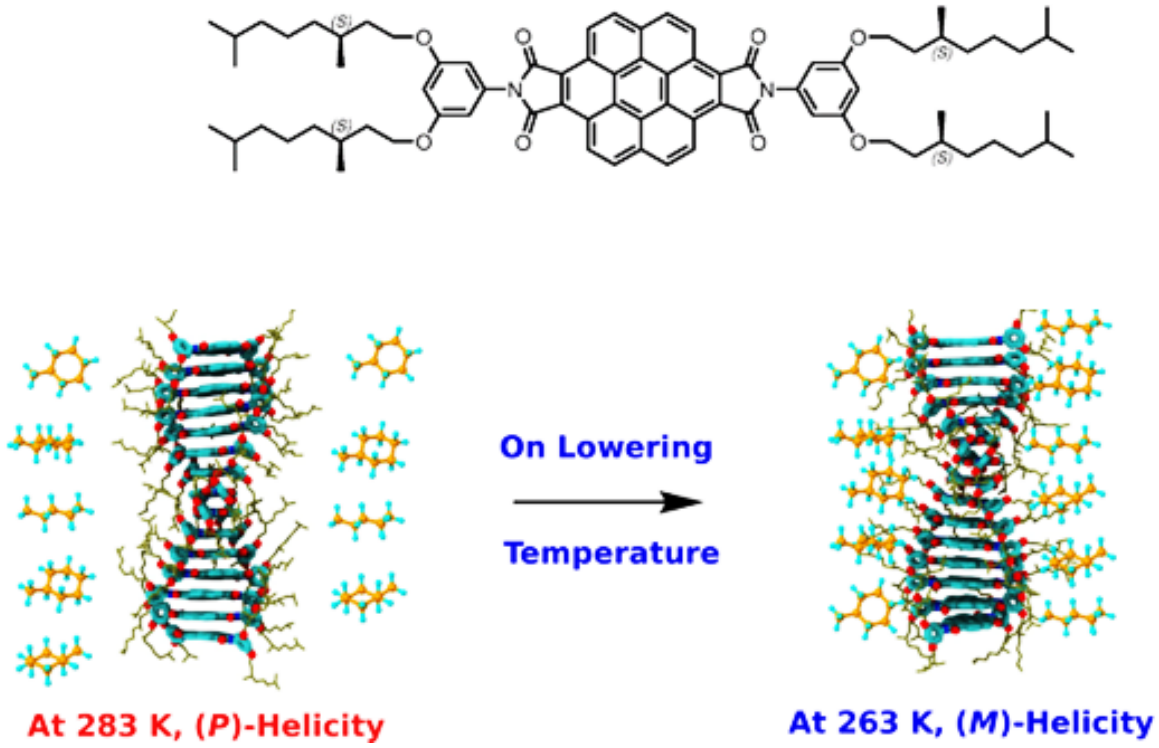

Figure 7. Self-assembled corine bisimide: molecular structure and schematic representation of solvent molecule incorporation in molecular pockets of self-aseembly on lowering the temperature to inverse the helicity Figure taken from ref.[81]

6. Kinetic Control of Solvent-Solute Interactions in Supramolecular Self-Assembly

Besides influencing the thermodynamic aspects of supramolecular self-assemblies, solvents additionally affect their kinetic properties. Typically, poor solvents are found to be put in kinetic traps in supramolecular systems. Würthner is one of the pioneers in apprehending the kinetic trapping of monomers in ill-defined aggregates in poor solvents.[82] Adding THF to MCH

solutions of trapped merocyanine-based monomers drags the dynamics to form supramolecular self-assembly.

6.1. Trapping of Kinetic State by Poor Solvent

Rybtchinski reported fluorinated, amphiphilic PBIs that prefer to assemble via more cooperative pathways as the water volume fraction in the water−THF mixture has increased. [83] Diverse pathways were additionally discovered in the aqueous polymerisation of N-phenylalanyl-adorned PBIs.[84] In aqueous solutions containing 10 vol % THF, the monomers are assembled into concentric rings of left-handed supramolecular helix due to the poor solubility of the growing assemblies. In comparison, in THF, long fibres with a right-handed helicity were acquired because the growing assemblies remained soluble in the more apolar solvent (Figure 8).

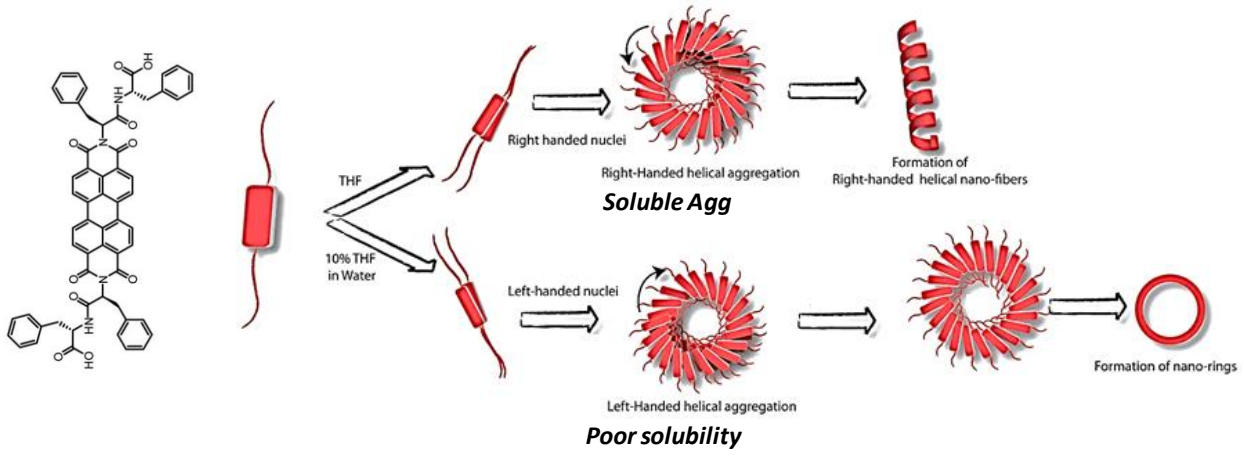

Figure 8. Schematic presentation of the thermodynamic and kinetic control of the self-assembly process in different solvent composition to show the formation mechanism for helical nano-fibers and nano-rings. Figure taken from ref.[84]

6.2. Solvents-Driven Hierarchical Self-Assembly

In addition to distinguishing between several unique self-assembled structures, solvents may be used for controlling numerous degrees of hierarchical self-assembly. The group of Ajayaghosh reported chiral oligo(phenylene ethynylene)s that assemble into helical supramolecular polymers,

which reassemble into superhelices of contrary handedness (Figure 9).[85] The degree of superhelical twisting could be controlled by cautious control of the amount of $CHCl_3$ in n-decane.

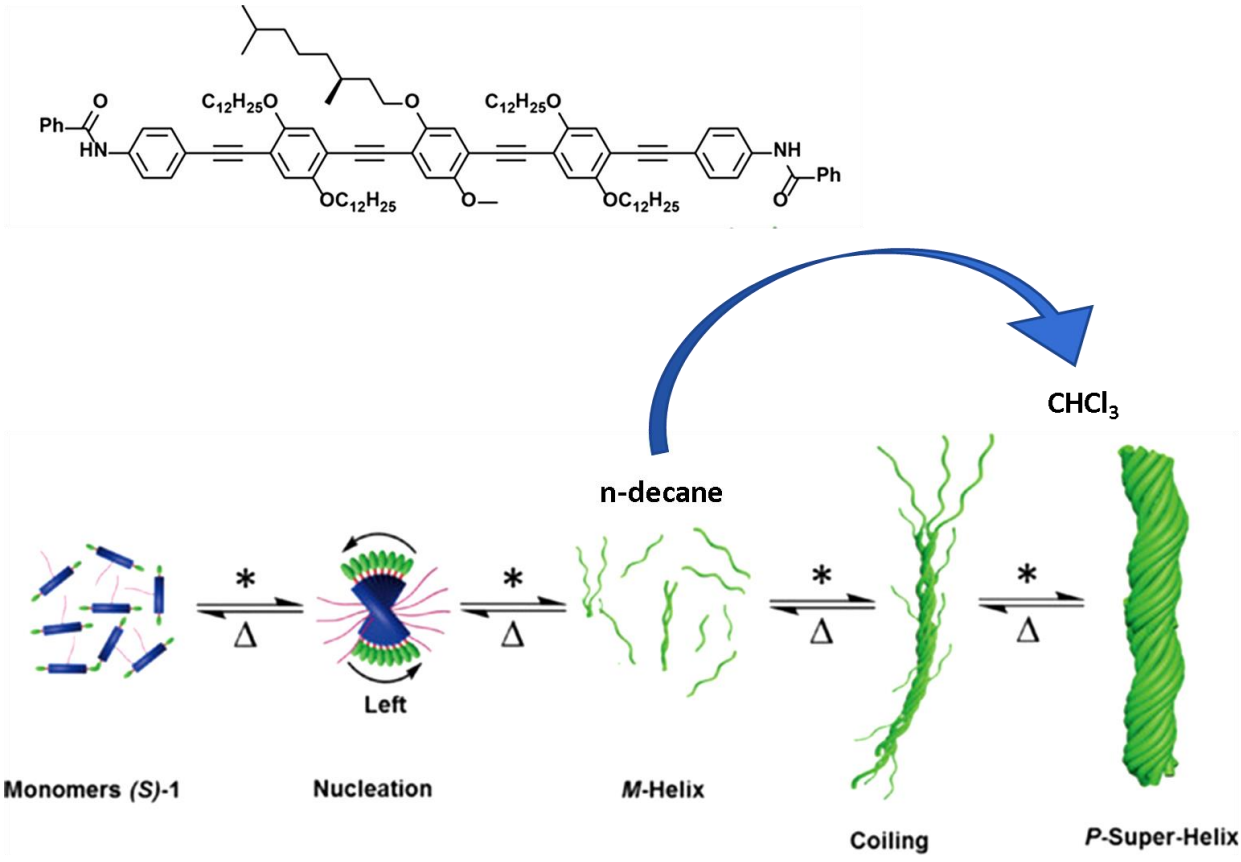

Figure 9. Schematic presentation of the solvent and temperature induced chiral inversion in superhelix. Figure taken from ref.[85]

7. Role of pH of the Medium to Control the Self-Assembly

The ability of self-assemblies to undergo significant changes in their morphologies and secondary structures in response to the pH of the solvent medium is one of their most suitable solvent-induced assets. For example, H-bonding interactions are highly sensitive to the pH of the medium, resulting in the collapse or generation of self-assemblies when acid or base is added. [86] In this context, self-assembled peptides have been extensively studied for their pH-responsiveness, which can be

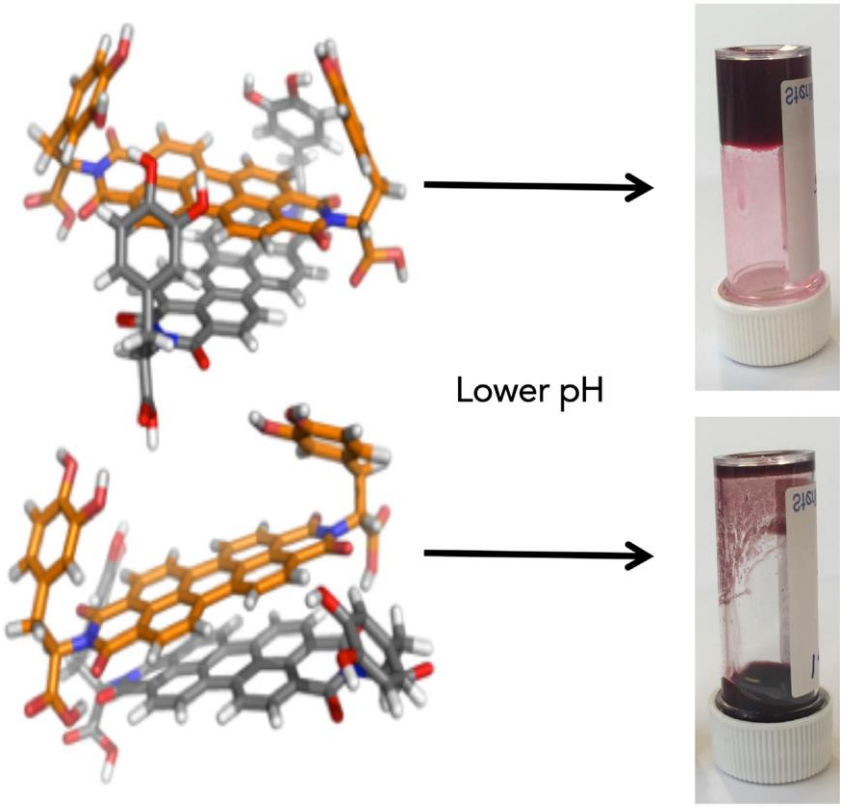

Figure 10 .Chemical structure of PBI-DOPA at different degrees of deprotonation A1 and A2. Photographs of the solution of A2 upon a decrease in pH to 3.3 (left) and of the solution of A1 upon a decrease in pH to 3.3 . The scale bar represents 1.5 cm. Figure taken from ref.[95]

probed for a variety of applications ranging from drug delivery structures (DDS) [87] to injectable gels in tissue engineering [88,89]. [90] Drugs can be delivered to a specific organ via a pH-responsive DDS, while its function is protected via physiological obstacles. Most importantly, pH-responsive DDS is thought to be suitable for chemotherapeutics. [91-93] An especially crucial advantage of peptides is that they are amphiphilic, encompassing both hydrophilic and hydrophobic amino acid residues, which performs a vital function in the self-assembly process and its turnability with the alteration of pH [94]. One of the compelling examples of such pH-responsive systems has been reported with perylene bisimides (PBS), which is regarded as one of the fascinating examples of beneficial π-conjugated molecules that can self-assemble into various systems. However, it is difficult to control the packing, which is critical because packing has an immediate effect on conductivity and optoelectronic properties. Adam and colleagues described a method for controlling the packing of a single PBI chromophore functionalized with an amino acid

using a minute change in the medium's pH. [95] While H-aggregated PBIs form a gel at a lower pH, different starting conditions result in the formation of J-aggregates that are incapable of forming a gel at a lower pH. By drying these aggregates, the solid films also show exclusive photoconductive properties.

8. Role of Solvent-Solute Interactions in Supramolecular Gelation

Gels are a distinct result of solvent-solute interactions that are frequently easier to understand than precisely defined. [96,97] Since Thomas Graham introduced the gel concept in 1861, the definition of the gel has evolved significantly. [98] The numerous attempts made to define gels. Dr. Dorothy Jordan Lloyd proposed that gels be made up of additives, one of which should be liquid at the temperature of interest and the other solid. The system's mechanical properties should be similar to those of a solid. [97] This definition is useful for determining a gel; however, it is ambiguous because not all colloids are gels. [99] Over the course of several decades, the definition of a gel evolved to the point where Hermans depicted gels as "coherent colloid disperse structures of at least two components that exhibit mechanical properties of the strong state" and "both the dispersed factor and dispersing medium amplify themselves continuously throughout the entire system." [100] Because of the uniqueness of this definition, Ferry adds another: "A gel is a drastically diluted system with no constant state flow." [101] A substance is defined as a gel if it: (1) has a microscopic structure with macroscopic dimensions that remains unchanged at the time scale of an analytical test, and (2) is solid in its rheological conduct despite being normally liquid. Flory organized gels into

8.1. Supramolecular Gels

Unlike polymeric gels, supramolecular gels are produced from low molecular weight gelators (LMWGs). The molecules self-assemble via non-covalent interactions that usually lead to elongated fibrillar structures.[103,104] Unlike general crystallisation methods wherein macroscopic phase separation occurs between bulk solids and liquid, the gelation here involves microscopic segment separation. The precise non-covalent interactions promote preferential 1-dimensional (1D) growth. Those interactions include Hydrogen bonding,[105,106] π-π stacking, electrostatic interactions, and van der Waals interactions[107]. The junction zones and branching among these fibres are responsible for the robustness of the gel matrixes.[108] Those junction

zones integrate 1D fibres into 3-dimensional networks that suffuse the entire system and entrap the liquid macroscopically through capillary forces and surface tension.[109] The process of self-assembly in supramolecular gels is complex. Stability parameters must influence solubility and those opposing forces that govern the formation of elongated aggregates. Though the gelator–gelator interactions have attained paramount importance in gelation studies, the solvent–gelator-specific (i.e., H-bonding) and non-specific (dipole-dipole, dipole-induced dipole) intermolecular interactions are similarly critical.

8.2. Designing the Gelators

Despite the hastily expanding research into such gels over the last decade, the rational design of small-molecular gelators has remained elusive. [110] Gelation via small molecules is still an empirical technology, with the maximum number of new gelators discovered by chance. Each type of molecular gelator can only gel a limited number of solvents. There is no general rule that can be applied to all gelator-solvent mixtures. Every study has demonstrated that a given gelator can form gel in a limited number of solvents! There is a wide range of attractive and repulsive forces that can be applied between gelators and solvents. In this regard, a recent study of fifty different gelators with a noticeably diverse set of solvents was conducted. [111] The study of solvent parameters in conjunction with gelating factors explains why selective gelators form gels.

8.3. Role of Solvent

The effect of solvent chemistry on the ability of small molecules to bind together and self-assemble into long fibres is as important as the gelator structure! The first studies on the role of solvent and molecular structure in fibrillar self-assemblies confirmed that the gelation number (the highest number of solvent molecules gelled by each gelator molecule) could be correlated with Hildebrand solubility parameters while keeping primary functional groups in the solvent molecule fixed. [112] In the study, various primary alcohols were gelled using trehalose-based gelators. The authors discovered that when the substituent is short, the ability to gel solvents becomes inversely proportional to the solvent's Hildebrand solubility parameter. [113] Similar observations had also been reported for *HSA*,[114] and its derivatives,[115] bi-component dendritic gels,[116] *L-lysine*-based gelators,[117] and di-peptides.[118]

Changing the solvent can also affect the morphology of the gels. Converting the solvent from toluene to ethanol resulted in an alternate gel morphology from fibres to microcrystals in a study with dipeptide (diphenylalanine) gelators (Figure 11). [119] Solvent-induced morphological changes in CAB gelators [120] and HSA have also been reported. [121,122] HSA-based gels in various alkanes and thiols have fibrillar morphologies with hexagonal sub-cellular spacing and multi-lamellar morphologies with gaps greater than the length of two HSA molecules. HSA aggregates less effectively in spherulitic objects with a triclinic, parallel subcell with interdigitation in the lamellar architecture in solvents with nitriles, aldehydes, and ketones functionalities. [112] As a result, it is clear that the versatile solvent properties are crucial in dictating non-covalent interactions driving self-assemblies leading to gelation.[123-128]

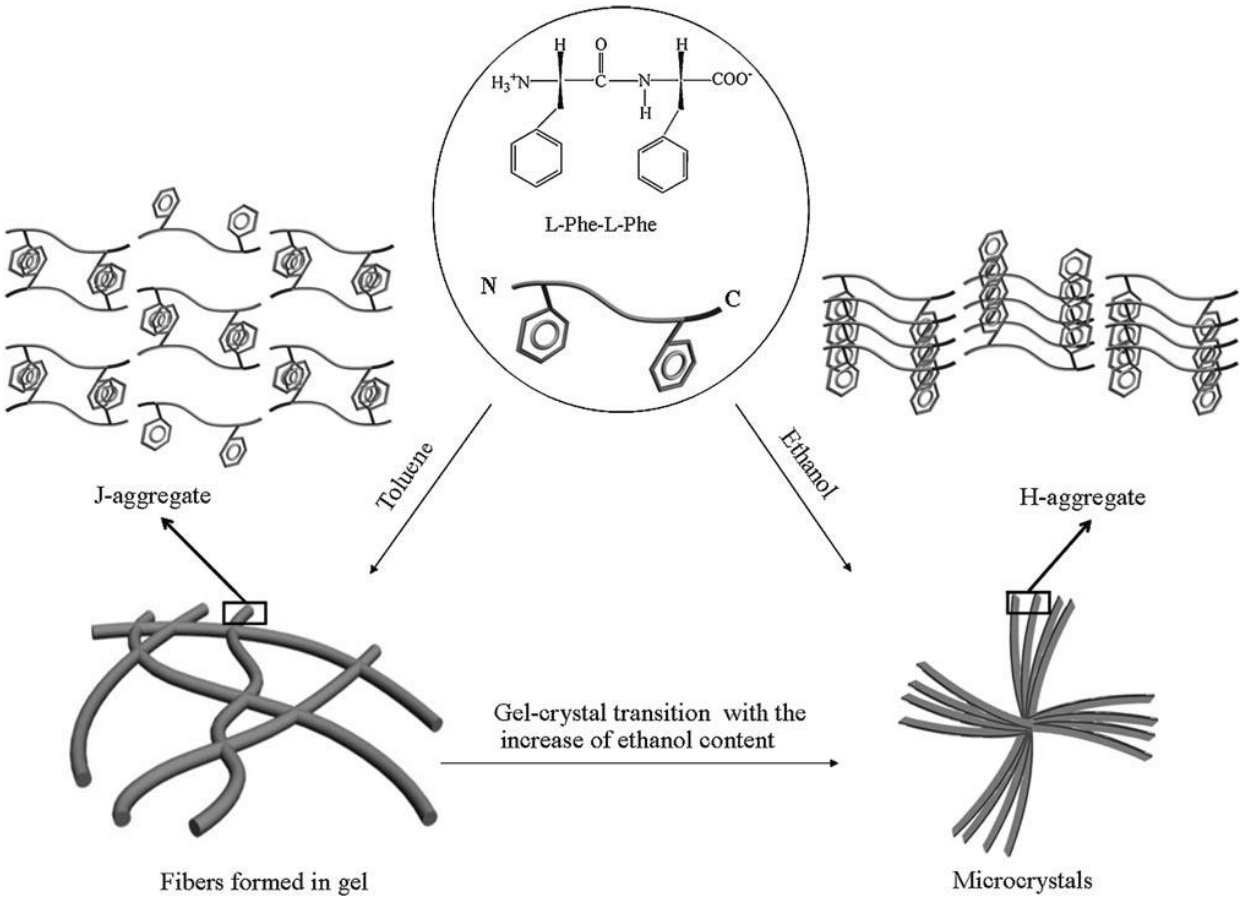

Figure 11.. Schematic illustration of the structural transition of *diphenylalanine* induced by varying the *ethanol* content in the mixed solvents, and the proposed molecular packing in the gel and in the microcrystal. SEM images are of samples formed in *toluene* and *ethanol*. Figure taken from ref.[119]

8.4. Functional Materials based on Supramolecular Geels

Supramolecular gelation, which is based on the interaction of solvents and solutes via supramolecular self-assembly, has practical applications in a variety of fields. It aids in the recovery of spilled oils from water surfaces by acting as an effective absorbent. These gels enable precise control over medication release in drug delivery, improving therapeutic outcomes. Simple products such as cosmetics and paints that use supramolecular self-assembled gels to provide desired textures and properties are examples of everyday applications. Because of their unique molecular interactions, these versatile gels have a wide range of applications, from environmental cleanup to everyday consumer products.

We have utilised this unique outcome of solvent-solute interaction, i.e. gelation, by reporting a phase selective organogelator that can efficiently congeal heavy crude oil from an oil-water biphasic mixture and can be used at extreme conditions(Figure 12).[128b]

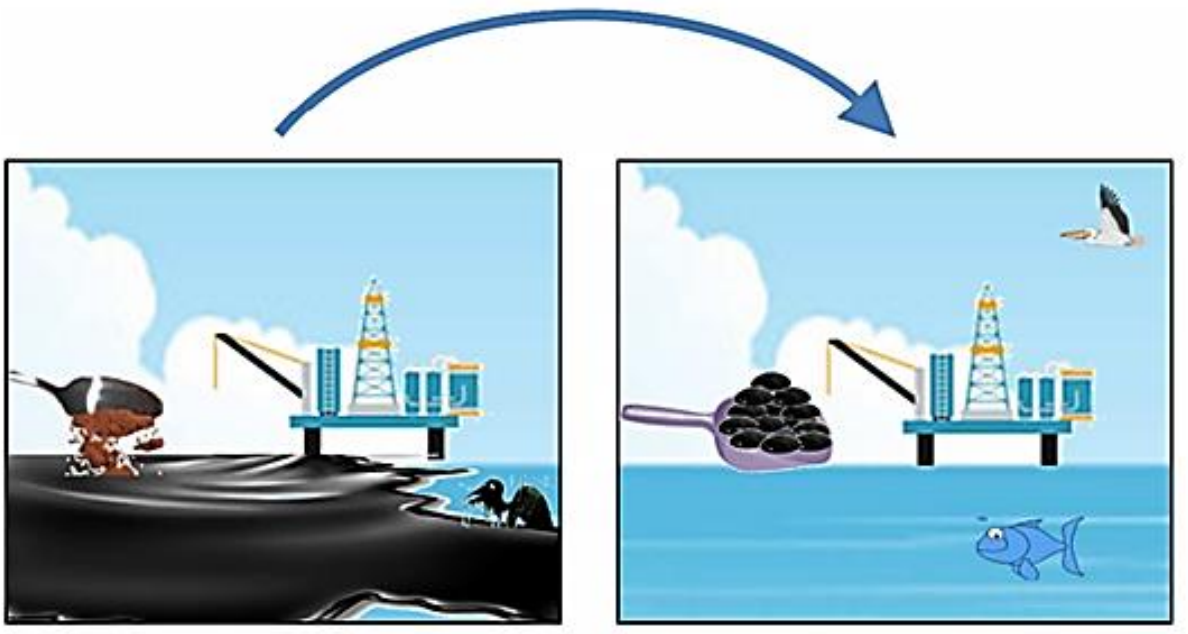

Figure 12. Near Instantaneous Gelation of Crude Oil using Naphthalene Diimide based Powder Gelator[128b]

9. Role of Solvent-Solute Interactions in Supramolecular Polymorphism

Polymorphism is a broad term that has been investigated in a variety of exploration disciplines, including chemistry, biology, crystallography, and materials sciences. Since the first report of polymorphism in a chemical system more than two centuries ago, there has been an ongoing debate about the proper definition. [129] Polymorphism is defined as the appearance of more than one crystalline phase in the solid state due to different packing arrangements of the same molecule. [130-132] In a polymorphic system, molecules, atoms, or ions change their mutual arrangement, which has a significant impact on various properties such as morphologies, electric conductivities, and crystal properties. [130-132] Polymorphs that differ in their molecular arrangement are referred to as packing polymorphs[129], and a molecule with multiple possible conformations is referred to as conformational polymorphism[133]. Multiple polymorphs with comparable energies are frequently isolated concurrently in the same crystallising medium,[134] making polymorph control a real challenge. [135] This unexpected phenomenon is common in crystal engineering, but it has also piqued the interest of researchers in self-assembled systems such as lyotropic liquid crystals, block copolymers, and self-assembled dendrimer systems. [138] Non-covalent synthesis of complex architectures from the same molecules, inspired by supramolecular assemblies in nature, has great potential for developing advanced materials.[139,140] Despite several theoretically predicted advances in polymorphs [141], the identification, isolation, and characterisation of a rational design to access their complex energetic landscapes 16 in order to develop reversibly responsive solids is difficult. [142-143] As a result, several strategies for accessing polymorphism and tuning its phase behaviour can pave the way for the design of new responsive, functional materials.[144-149]

9.1. Supramolecular Polymorphism: Mechanistic Insight

Controlling the polymorphism of organic systems is thus highly desirable but difficult in practice due to the complex interplay of thermodynamics and kinetics within the same crystallisation process. [131] Thermodynamic considerations address the stability of the respective polymorphs, which usually differ by only a few kJ mol1 [150-151], whereas kinetic pathways govern how quickly a specific polymorph is formed, which is determined by their activation barriers.[131] The formation of a specific polymorph is usually under kinetic control and can thus be fine-tuned as a

function of variable experimental conditions such as solvent environment, temperature, and heating-cooling rates. [131] From a molecular standpoint, the crystallization of a specific polymorph can be explained as a supramolecular reaction initiated by nuclei due to non-covalent interactions that develop into a 3D structure. [130,131,152] The thermodynamics, kinetics, initial nucleation event, and transformations between specific polymorphs must all be thoroughly studied in order to gain mechanistic insights into polymorphism.[131,153]

9.2. Molecular Packing Effectuated by Solvent-Solute Interactions

Solvent-solvent interactions can also have a significant impact on the nature of molecular packing. Several promising early reports describe the strong dependence of a molecular assembly's structure and morphology on the solvent's molecular geometry,[154,155] ability to preferentially solvate one part of the molecule,[156] or tendency to interdigitate/penetrate within an assembled structure. [157,158] By eliminating the need for careful manipulation of the self-assembly conditions, this approach overlooks different competing assembly pathways; a specific polymorph can be generated in the appropriate solvent. However, reversible transformation between polymorphs would necessitate an impractical and time-consuming process of changing the solvent.

9.3. Solvent-Induced Liquid Crystalline Systems

Saito and colleagues [159] reported a self-assembled lyotropic liquid crystal system with reversible polymorphism using cyclic ethynylhelicene oligomers cyclobis[(M)-D-n] (n = 4 and 6) with two flexible linkers connecting two oligomer moieties in 2015. Growing a self-aggregated material framework with dynamic and reversible polymorphism via various hierarchical bottom-up small oligomers can serve as a foundation for understanding biological processes and developing stimuli-responsive functional materials. Because of their anisotropic nature, LLCs are appealing for a material framework, especially when they exhibit dynamic and reversible polymorphism. The purpose of the cyclic molecular structure was to control molecular to macroscopic self-assembly properties. The cyclic oligomer's structural change between molecularly dissolved random coils formation level and intramolecularly attached homo-double helix is revealed by temperature and solvent-dependent CD and UV-vis studies. Hetero-double helix was achieved using the mixture of cyclobis[(M)-D-4] and (P)-D-5 in toluene solvent, which is known to be a weaker helix-forming solvent than trifluoromethyl benzene. [160] Early reports showed that the

hetero-double helices were thermodynamically more stable than homo-double helices, similar to the formerly grown self-assembly. [161] If the concentration of cyclobis[(M)-D-4] and (P)-D-5 in toluene is increased, the trimolecular complex self-assembled to form LLCs, composed of anisotropically aligned fibres, having a total molecular weight of over 10,000 Da. The apparent molecular weights of the heteroaggregate were determined by VPO studies (60 °C) in fluorobenzene. The formation of the trimolecular complex LLC is more favourable than the complex bimolecular formation. The outcome contrasts with other acyclic systems that undergo gelation with randomly oriented fibres. Another noticeable fact is that the LLC generation by self-assembling synthetic double-helix-forming molecules has not been previously reported. The results are comparable with the properties of biological double-helical molecules and polymers [162] such as DNA and RNA, [163] polysaccharides,[164] and actin [165] that form LLCs in aqueous media. The LLCs transformed into turbid gels consisting of randomly ordered bundles upon cooling to −60 °C, which did not show a gravitational flow when the glass tube was reverted upside down, and the LLCs were regenerated by heating to 25 °C. Similar observations were seen on repeating the cooling/heating cycle, and the DSC thermograms showed broad endothermic and exothermic events between −10 and −60 °C in heating and cooling runs, respectively. The AFM results showed that the thin fibres of 7−8 nm width in the LLC self-assembled to form a randomly oriented and entangled three-dimensional network of bundles of mostly 40−300 nm width upon cooling. It is speculated that cooling promoted the aggregation of thin fibres expelling solvents, which resulted in bundle formation, and the anisotropy of the LLC state was lost, leading the system to change into the turbid gel. This work is an example of an LLC formed by aggregating synthetic double-helix organic molecules. [162,166] With temperature changes, this self-assembled system showed a reversible polymorphic interchange between two ordered structures,[167] the LLC and a turbid gel. The results are similar to actin's self-assembly properties and reversible polymorphism, which play a vital role in biological systems.[168]

9.4. Supramolecular Polymorphism Utilising Pathway Complexity

Supramolecular Polymorphism [169] has been reported in a typical metal-ligand complex system using self-assembly of a chiral Pd-II complex [170,171], where hidden kinetic pathways [172,173] play a significant role in supramolecular polymerisation processes, allowing new self-assembly pathways with promising functional materials. The complex's supramolecular polymerisation

resulted in a pair of competing aggregates known as Agg I and Agg II. The kinetic [174-177] one (Agg II) is produced via a "hidden" pathway that standard thermal polymerisation protocols do not allow access to. Thermally-controlled self-assembly prefers stable cooperative [179-180] AggI with no sign of the kinetic state, according to variable temperature spectroscopic studies [178]. This is supported by the fact that the kinetic pathway has a lower Te than the thermodynamic pathways. This occurrence stands in stark contrast to the usual supramolecular self-assembled polymeric behaviour. When the monomer is injected into a large amount of the aggregating solvent MCH, a "hidden" cooperative rapid kinetic polymerisation pathway (Agg II) is revealed. [181] This kinetic pathway rapidly converts into clustered superstructures when the packing mode is conserved (Agg IIc). [182-184] The rapid clustering step is sequestered from the coupled polymerisation equilibria in the solution after the monomers become involved in the kinetic aggregate formation (Agg II), which hinders the thermodynamic pathway even in the presence of seeds. [185-187] Agg II's exceptional kinetic stability could be the result of a cooperative mechanism in the nucleation of Agg I. The dramatic impact of a hidden kinetic pathway on the development of two polymorphs [188] is astounding. The formation of a cluster in a solution with fast kinetics isolates monomers from the equilibria and allows them to resist relaxing into the thermodynamic minimum.

Another solvent-induced pathway complexity example involved supramolecular polymorphism manifested N,O-bidentate[189] boron difluoride complexes.[190,191] It is indeed known that some BF_2 complexes show supramolecular polymorphism.[192,193] Inspired by the enchanting aggregation behaviours of PNI [194-196] and preliminary reports of BF_2-complexes based supramolecular polymorphism, Mahata and group reported a new N,O bidentate boron difluoride complex $PNIBF_2$, that displays polymorphic aggregation.[197] Boron fluoride coordination influences delicate alteration in structural rigidity to control its self-assembly and optical properties, depending upon solvent nature and sample preparation.[198] The lowering of solubility in organic solvents influences the structural change to self-assemble into three supramolecular polymorphs. In a non-polar solvent mixture,99/1 (v/v) MCH-chloroform or MCH–DCE, the complex forms a linear emissive nano aggregates Agg1. Contrarily, in a polar solvent mixture of 76/24 (v/v) water–THF, it aggregates into nanoellipsoids Agg2, which are kinetically controlled assembly and could be transformed into thermodynamically stablenanospheres Agg3 with the aid

of heating followed by slow cooling. However, it is also possible to kinetically lock these aggregates by exposing them to a more hydrophobic environment of 95:5 (v/v) water/THF mixture, which remains stable even at high temperatures. Various supramolecular self-assemblies from a single complex offer a new dimension to explore supramolecular polymorphism by creating functional supramolecular systems.

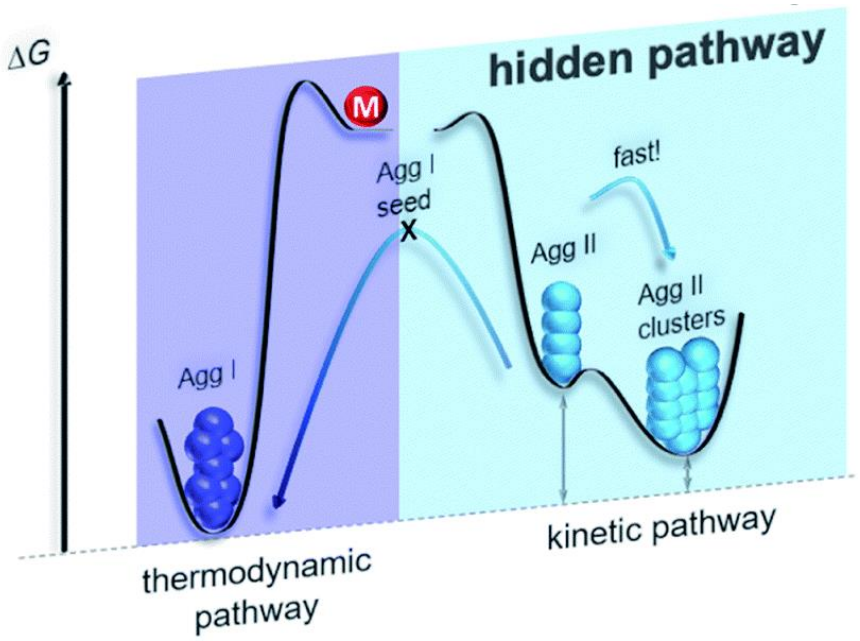

Figure. 13. Energy landscape outlining its complex self-assembly behaviour that incorporates a hidden pathway. Figure taken from ref.[189]

We describe how subtle changes in the *trans*-azobenzene side-chain conformation induced by protic solvent can give rise to differently assembled polymorphs that are also stable in solid films. To our great satisfaction, we can reversibly switch between these polymorphs with the aid of two external stimuli: temperature and medium pH. This reversibility is also reproducible in a solid silica gel matrix (Figure 14).[198b]

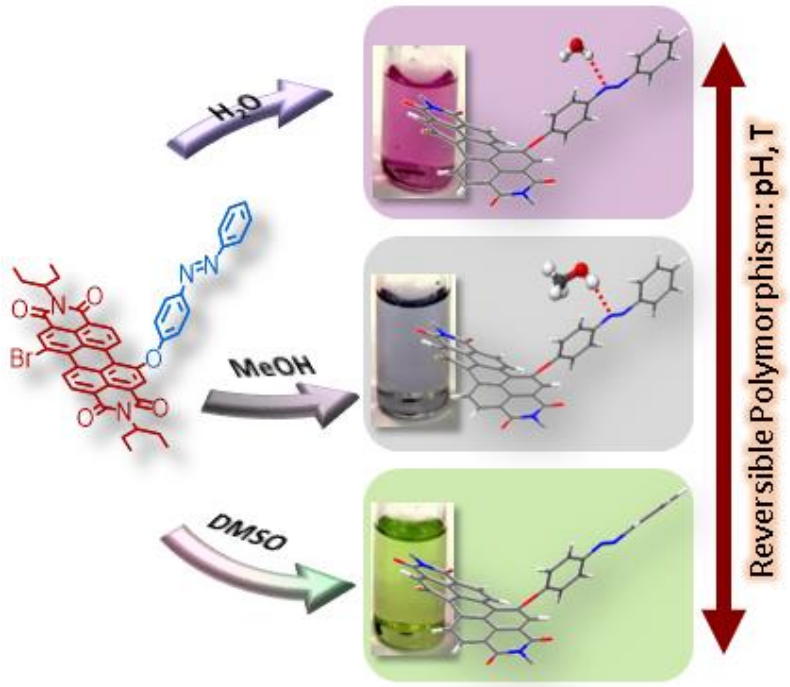

Figure 14. Reversible Supramolecular Polymorphism in Solution and Solid Matrix by Manipulating Side-group Conformation[198b]

10. Effect on Solvent-Solute Interaction in Photoinduced Electron Transfer

Photoinduced electron-transfer reactions have attracted tremendous interest in recent years, intending to investigate molecules' oxidation and reduction mechanisms in the excited state. Because most electron-transfer reactions take place in condensed media, the impact of the medium is of great importance for knowledge of the reaction's mechanism and the nature of intermediates. The ion pair generated between a donor and acceptor has been recognised as a critical intermediate in PET.[199] Opposing forces of the stabilisation received from the Coulombic interaction of the ions in an ion pair and the solvation of the ions have an important impact on the ion pair's nature, contact ion pair(CIP) or a solvent-separated ion pair(SSIP). Regarding this, solvent polarity has determined exciting features in the distribution of these intermediates.[200-206] In polar solvents, triplet ion pairs, generally observable inside the nanosecond time domain in a bimolecular PET, are particularly SSIP, while in less polar solvents, CIPs are anticipated within a similar timescale.

[207-209] In polar solvents such as acetonitrile, the SSIP may dissociate into solvated ions. Femtosecond transient absorption studies have shown that, in non-polar media, CIP decays through intra-ion-pair proton transfer while, in polar solvents, the character of ion pair is SSIP, which further dissociates into a free anion and cation radicals.[207] Chloranil durene system in 1,2-dichloromethane solvent found the presence of each CIP and SSIP in equilibrium.[208]

10.1. Solvent-Controlled Electron Transfer Kinetics

Moreover, the electron-transfer kinetics of a donor-acceptor dyad is based on the solvent polarity. Modifications of the polarity of the media shift the energy of the charge-separated state, which essentially modifies the electron-transfer kinetics. For solar-energy-conversion applications, it is very critical to design systems that, upon photoexcitation, generate long-lived CT states. Therefore, electron donor-acceptor systems with rapid PET and slow recombination benefit slight-harvesting programs [209]. Moreover, triplet formation, [209-213] localised electric fields [214-219], and media viscosity of the media [220-222] favour the formation of lengthy-lived CT species.

The dependence of the CT rates on media polarity [209,223–225] offers the turnability of the CT kinetics. Typically, a decrease in the solvent polarity results in the destabilisation of long-lived CT states and lowers the reorganisation energy.

10.2. Solvent Effect on Donor-Acceptor Dyads

An electron donor-acceptor dyad mediates ultrafast intramolecular photoinduced charge separation and recombination simultaneously in a polar solvent. Contrarily, non-polar media inhabits the initial PET by inflicting enough destabilisation of the CT state and shifting the energy above the lowest locally excited singlet state. Additionally, femtosecond transient-absorption spectroscopy reveals that the charge recombination for the solvents mediating PET is slower than the rate separation. This behaviour of donor-acceptor systems is crucial for Solar energy harvesting systems. [226]

Würthner and co-workers stated foldamer systems comprised of perylene bisimide (PBI) dyes connected through 1,2-bis(phenylethynyl)benzene and phenylethynylbis(phenylene)indane and investigated their photo-physics effectuated by solvent-induced interactions.[227] UV/vis

absorption and fluorescence spectra reveal that each foldamer exists in a π-stacked folded H-aggregated state in THF and random non-assembled conformations in chloroform.[228] Time-resolved fluorescence and transient absorption spectroscopy show unique relaxation pathways for the photoexcited molecules in specific solvents. Photoinduced electron transfer states for the open conformations (in chloroform) and relaxes to excimer states with bathochromic emission for the stacked conformations (in THF).[227] Cyclic voltammetry and Rehm–Weller evaluation successfully narrates the photophysical process in the solvent-dependent model system to the strategies used in organic solar cells.[226]

Vauthey and co-workers have reported several examples of PET between identical chromophores.[229,230] In such instances, it has become unfathomable whether the excited state symmetry is broken or not upon photoexcitation, i.e. whether separate units of the system act as acceptor (A) or donor (D) or both the electron and hole transfers are equiprobable. From polarised transient absorption measurements with a biperylene system, it has been concluded that symmetry

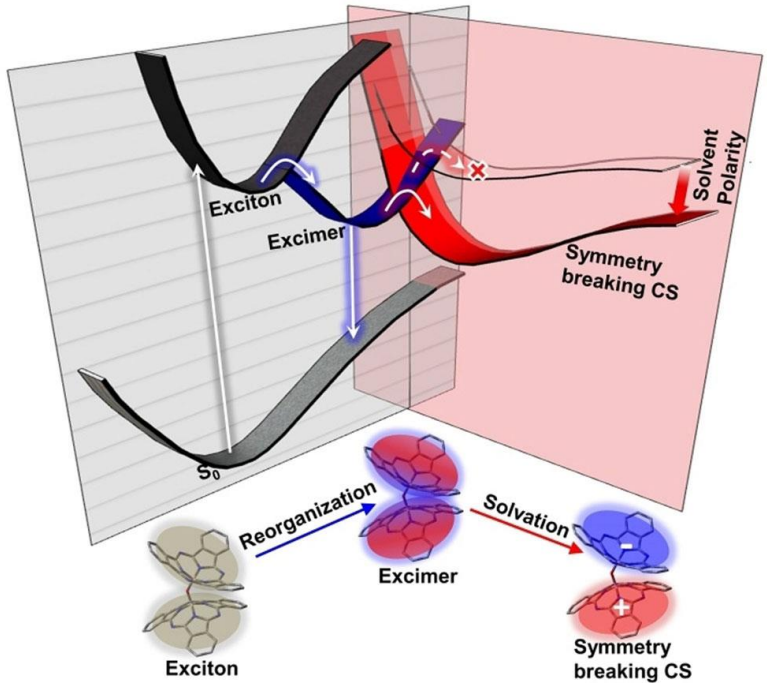

Figure 15. The photophysics of μ -OSubPc2 is depicted schematically. Direct excitation leads to a Frenkel exciton state, in which excitation is distributed across the dimer. This is followed by the sequential formation of the -OSubPc2 excimer and its decay to the forma charge separated state via symmetry breaking charge separation, which is only accessible in polar solvent. The first step is thus an evolution of the Frenkel exciton state's wavefunction to favor charge resonance forms in the excimer. This involves intramolecular coordinate evolution. In polar solvents, the excimer decays along a solvation coordinate, with the initial step caused by an asymmetric fluctuation in the solvent environment. Figure taken from ref. [236]

is not broken on photoexcitation and that solvent fluctuations control the direction of charge separation entirely.[231] The strong fluorescence solvatochromism associated with many quadrupolar molecules with an AA-D-A or D-A-D motif has resulted in excited-state symmetry breaking driven through solvent fluctuations. [232] However, the exact reason for symmetry breaking has been unknown due to the shortage of characteristics of spectroscopic signatures in the UV and visible regions. Direct evidence of symmetry breaking has been revealed by IR spectroscopy, i.e., C≡C- or -C≡N- stretching modes, localised inside the centre or at the edges of the D-A branches of the molecules.[233-235] It has been seen that SB is mediated via solvent fluctuations. The excited state remains symmetric in a non-polar solvent at its complete lifetime. However, the excited state evolves to an asymmetric one on a timescale similar to the solvation time when a polar solvent has been used. The localisation of excitation, i.e., whether it is partly or absolutely recites on one branch, depends on several factors, including the solvent polarity. SB in such molecules alters basicities to vary hydrogen-bond accepting strengths, leading to a noticeable amplification of the SB in protic solvents due to forming a rigid H-bonded complex.[234] Such complex formation results in the excited states' decay more rapidly. The mechanism of H-bond-caused non-radiative deactivation can be elucidated by tracking the vibrational modes of the solvent molecules.

11. Summary and Future Aspect

he precise manipulation of solvent-solute interactions within the realm of supramolecular self-assemblies is of paramount importance in contemporary supramolecular chemistry, serving as a pivotal mechanism for tailoring material properties and functionalities. Recent advancements in this field have provided significant insights into the fundamental principles underlying these interactions and have opened doors to a multitude of innovative applications with futuristic implications. Solvent-solute interactions are, fundamentally, the driving force behind the formation and stability of supramolecular assemblies. They are rooted in both thermodynamic and kinetic factors, offering scientists the ability to finely tune self-assembling materials with remarkable precision. Recent studies have revealed the profound influence of solvent choice on supramolecular polymorphism. For example, in the pharmaceutical industry, varying solvent conditions during crystallization processes have been shown to yield distinct crystal structures of the same active pharmaceutical ingredient, thereby altering its solubility and bioavailability. In the

realm of supramolecular gelation, the choice of solvent has a direct impact on the mechanical properties and responsiveness of the resulting gels. This property has found practical applications in fields as diverse as drug delivery and environmental remediation. For instance, supramolecular gels have been engineered to encapsulate and release drugs in a controlled and sustained manner, optimizing therapeutic efficacy and minimizing side effects. Additionally, they have proven invaluable in oil-spill recovery, where tailored solvent-solute interactions enable efficient and selective absorption of oil from water surfaces. Solvent-dependent photoinduced charge transfer processes are at the forefront of emerging photovoltaic technologies. Researchers are leveraging these interactions to design innovative materials for next-generation solar cells. By carefully selecting solvents and solutes that facilitate efficient charge separation and transfer upon exposure to light, scientists aim to enhance the energy conversion efficiency of solar cells, making sustainable energy production more accessible. Moreover, pH-dependent self-assembly outcomes represent another dimension of solvent-solute interactions. Researchers are actively exploring the role of pH in modulating self-assembled structures and properties. This control has profound implications for drug delivery systems, where pH-responsive gels can release drugs selectively in specific physiological environments, such as acidic tumour tissues.

Looking to the future, the potential for solvent-solute interactions in supramolecular chemistry appears limitless. Emerging research is focused on sustainable and eco-friendly solvents, aligning with the growing global emphasis on environmental sustainability. Moreover, recent advancements in nanomedicine have harnessed the power of supramolecular gels to create highly efficient controlled drug release systems. Additionally, adaptive materials based on solvent-responsive supramolecular assemblies are being explored for applications in soft robotics, wearable technology, and beyond.

In conclusion, the intricate world of solvent-solute interactions within supramolecular self-assemblies holds the key to groundbreaking innovations across a spectrum of scientific disciplines and technological domains. As we delve deeper into the complexities of these interactions, we can anticipate an exciting future where tailored materials, advanced pharmaceuticals, and sustainable technologies are not just possibilities but realities, all owing their existence to the remarkable role of solvents in supramolecular chemistry.

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