Saptarshi Datta

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

1.1.Introduction

In recent years, expeditiously growing interest and improvement in supramolecular engineering were observed due to its vast application in biology, material science and chemistry [1]. Fundamentally, the goal is to design supramolecular systems, modifying the interactions between individual building units in the solution as well as solid-state to gain beneficial complicated structures showing multi-functional properties. This field has developed rapid interest since the latest Nobel Prize in Chemistry was awarded to Ben Feringa Jean-Pierre Sauvage and Fraser Stoddart.[2] The self-assembly of supramolecular complexes affords a beneficial aid for growing an extensive kind of molecules that are mechanically interlocked or vary in their supramolecular architectures or can be the pioneer in forming molecular machines involving rotaxanes and catenanes.[3] A few examples of recent studies of molecular machines are molecular automobiles [4], shuttles [5], mussles[6], pumps [7], elevators [8] and so on. Supramolecular chemistry offered a spontaneous interest in molecular-engineered complexes, which are constructed from small molecular blocks held collectively with the aid of reversible intermolecular non-covalent

interactions, including Hydrogen bonding, electrostatic, π - π stacking, and solvatochromic interactions. Controlling their layout and function offers a promising interdisciplinary course of interest. The interactions between solvents and solutes broadly appear as one of chemistry's most crucial subjects. They are significant in controlling solubility, structure and reactivity.[9] Even though chemists and biologists have used solvents daily in laboratories, selecting the appropriate solvent for a specific solute is a conjecture. At the same time, the role of unique solvents for solutes has become nicely documented. Through a long time of research, chemists achieved an immoderate degree of expertise in perceptions of the properties of solvents, their chemical structure, and their role in controlling chemical reactions. The numerous exciting solvent-induced outcomes in supramolecular chemistry make these "commonly forgotten" areas, without a doubt, worth revisiting.

1.2.Solute−Solvent Interactions in Biology and Chemistry

Commonly, chemical reactions are executed in a solvent medium, which strongly affects the reaction rate by controlling the reactivity of reactants and intermediates. For example, S_N1 reactions favour polar, protic solvents, which stabilise the carbocation formed in the rate-determining step, while S_N2 reactions usually proceed faster in apolar, aprotic solvents, which helps solvation of the transition state. The course of investigation on physical-organic aspects of the effect of the solvent on chemical structure and reactivity of organic systems affects polymer science, too. The solvent quality essentially guides the conformations in the solution state of artificial polymers. Small globular debris is found in minute contamination solvents, while other prolonged chains are present in pure(desired) solvents. The overall outcome of techniques, such as material processing, annealing, moulding, and electrospinning, rely on solute−solvent interactions. Additionally, the non-covalent chemistry amongst solvents and solutes is paramount in material science, leading to its applicability in industries. Solute-solvent interactions are of critical significance in biology.[10] The tertiary structure of folded biomacromolecules, like polypeptides[11] or polynucleotides [12], stabilises biomacromolecules, like polypeptides[11] or polynucleotides [12], stabilises by interactions of the biomolecule with water. Another fascinating effect solvents have on the biological system is the liquid−liquid phase separation in cell structures [13], while the stabilising role of water to balance between dipoles in proteins is still an exciting topic.[14], As a solvent, water plays a vital role in controlling the structure and function of

DNA[15–17] and proteins[18– 20], thus serving as a critical element inside the living system. In artificial supramolecular structures, the solvents can affect the structures with specific interactions of enthalpic and entropic contributions. [21,22] Using polar solvents, a comprehensive description of solvation is acquired from the multiple directional interactions among constituents.[23–25] The solvent contribution's enthalpic origin can be determined in cooperative systems that display sharp transitions amongst states upon binding subtle amounts of H-bonding cosolvent.[26–29] Such enthalpic contributions are responsible for the early irreproducibility of Pasteur's enantiomeric separation, where the dehydration of conglomerate tartaric acid salt forms a racemic mixture at ambient temperature.[30] However, this thesis will not cover those existing biological systems; instead, it will focus on the synthetic supramolecular self-assemblies.

1.3.Solute−Solvent Interactions in Supramolecular Chemistry

After their first intellectual idea, "*Hochmolekulare Verbindungen*" by Staudinger in 1920,[31]

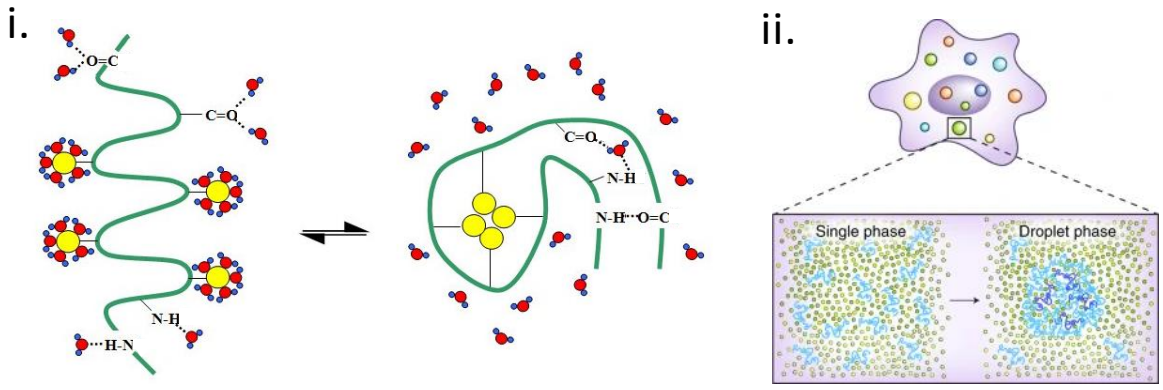


Figure 1.1. The stability of the tertiary structure of folded biomacromolecules, 1.2. Liquid−liquid phase transition in cellular systems

macromolecules ruled the initial century of polymer chemistry. Later, reviews began to emerge on polymeric aggregates of repeating monomers that have not been held together with covalent bonds; however, as an alternative with the aid of supramolecular, non-covalent interactions. [32-35] Those examples initiate the journey of present-day supramolecular chemistry with the pioneering contributions of Lehn, Aida, Stupp, and others.[36] In supramolecular self-assemblies, the repeating units(monomers) are held collectively through one or multiple non-covalent interactions,

viz hydrogen bonding, π-stacking, charge-transfer interactions, metal−ligand coordination, ionic interactions, and solvophobic interactions. [37-38] The energy of these interactions is generally within tens to hundreds of kJ/mol, contrasting to covalently linked polymers. These soft interactions make the backbone of supramolecular self-assemblies fantastically dynamic and exceptionally responsive to diverse external factors and stimuli.[37,38] This stimuli-responsiveness offers processing of functional smart materials, reversibly tunable through external conditions.[39]

Mastering the approach to apply external stimuli to regulate supramolecular assemblies is especially desirable because creating new opportunities to design beneficial materials is essential. Regarding this, the most popular stimuli are temperature,[40] pH,[41] light[42] and redox or electro-chemical actuators.[43] On the contrary, the solvent's role is typically of little significance, although some widely recognised outcomes have been verified, along with the effect on polarity[44,45] or self-assembly guided by solvophobic interactions.[46] There are a few good examples of supramolecular systems that might be appreciably caused via a minor change in the solvent, including its assembly packing.[47] In this context, Meijer and co-workers investigated the effect of water in supramolecular self-assemblies in oils and determined its function in the helicity of self-assembly(Figure 1.2).[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

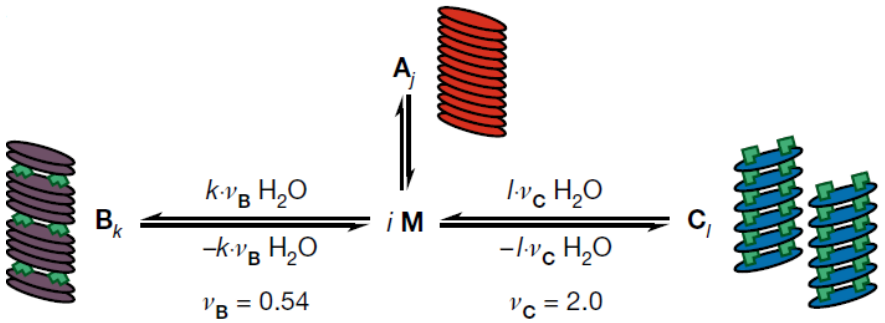


Figure 1.2. Schematic representation of three cooperative, competitive pathways. The variables *j*, *k* and *l* correspond to the degrees of polymerization of **A**, **B** and **C**, respectively. The coloured discs represent aggregated monomer units, and the green blocks represent water molecules.Figure taken from ref.[48]

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.

Supramolecular self-assemblies are usually prepared and studied in the solution state. Many solvent molecules surround each constituent monomer unit or self-assembled architecture in the solution. Here, the solute-solute interactions are of similar energy to the net energy of interactions offered by multiple solute−solvent interactions. For this reason, solvent effect on self-assembly mechanism and structure are more responsive than covalent polymeric systems. This dynamic nature of supramolecular self-assemblies offers a strong dependency on the external conditions beneath which they have been analysed. Consequently, studying the interactions between supramolecular self-assemblies and their solvents is tough but might also offer appealing possibilities to make the most of those interactions to design advanced reversible materials.

Not only that, but the strength of these weak interactions also depends on the solvent environment.[55] The degree of self-assembly highly depends on the solvent system composition in binary solvent structures. However, looking at every solvent impact in every weak interaction at a time is complex. Chemists are capable of empirically determining solvent outcomes in chromatography and the phenomenon of solvatochromism in polarised compounds.[56] The outcomes depend on several factors, with arbitrary coefficients, based on linear free energy relationships(discussed later).[57] Solvent has a significant impact on the solubilities of low-molecular-weight compounds and the macroscopic properties of their self-assemblies,[58] consisting of wetting,[59] alteration of morphology,[60] and gel formation.[61] However, we have little expertise on the impacts of solvent-solute interactions on the molecular stage for low-molecular-weight compounds and their self-assemblies.

1.4.Good and Poor Solvent in Supramolecular Self-Assemblies

Solvent polarity is often used qualitatively in discussions of complicated supramolecular formation with various nonbonding interactions. The solvent polarity interacts with the polar residues in molecules, resulting in hydrogen bonding and dipole-dipole interactions are adjusted by using additional polar solvents. However, apparent relationships among solvent polarity and π–π interactions have seldom been discussed in the literature. The formation of supramolecular self-

assemblies depends on the solvent effect in terms of the various strong and weak interactions, whereby the polar solvent might be used to strengthen a few interactions 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 the restrictions related to the solubilities and the complexity of the self-assembly process, it is challenging to collect self-assembly constants in all solvents using a particular supramolecular probe(monomer). Consequently, peripheral substituents(usually long alkyl chains) that ensure the well-solubility of monomers in organic solvents are attached to a poorly soluble large π-aromatic core to be used to survey numerous solvents(Figure 1.3). If peripheral substituents contain secondary non-covalent interaction, it may lead to different self-assembly outcomes. To split the susceptible interactions at the peripheral substituents from that of the mainframes, it is far acceptable to put together the same supramolecular composed of a non-substituted π-core. Therefore, evaluating various solvents has been challenging even when using an identical supramolecular system.

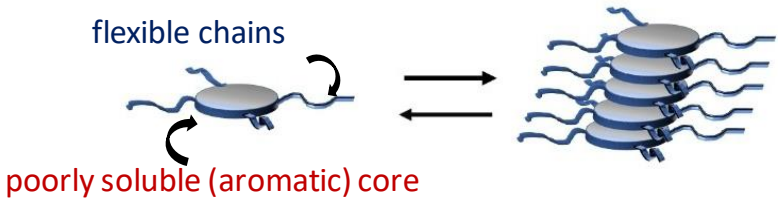


Figure 1.3. A schematic representation of design strategy of supramolecular self-assembly probe.

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

It has been seen that the balance between solute-solute non-covalent interactions and solvent-solute weak interactions dictates whether monomers self-assemble or not. Even though this effect has been recognised at a very early stage of supramolecular self-assembled systems, systematic and quantitative research has been mentioned relatively recently.[65]

In the equilibria of the self-assembly process,[66] empirical solvent polarity parameters are beneficial to explain the binding strengths (free energy of self-assembly) in supramolecular self-assemblies with the aid of linear free energy relationships (LFER). LFER relates the Gibbs free energy of self-assembly to the standard solvent polarity scales, including $E_T(30)$, π^*, α or β, for all intermolecular interactions in supramolecular assemblies of solvatochromic dyes. [67] Because several solvent parameters are related to multiple solvent−solute interactions, LFERs can help one understand the nature of specific intermolecular interactions in supramolecular self-assembly. Würthner described LFER for supramolecular systems assembled by non-covalent interactions,[68] which include hydrogen bonding,[69] halogen bonding,[70] $\pi-\pi$-stacking,[71] and so on. Understanding those relationships offers a valuable tool for choosing the appropriate solvent for investigating a specific self-assembled system.

Perylene Bisimides (PBI) proved to be ideal dyes for self-assembly research due to their sturdy $\pi-\pi$-stacking interactions in various solvents.[72] Moreover, it is straightforward to analyse aggregation approaches for PBIs. Figure 1.4 describes how Gibbs free energy of self-assembly varies with solvents of various polarities, starting from the non-polar aliphatic solvent n-hexane to the very polar solvent water.[73,74] Covering this entire range with a single dye molecule is not viable. However, it can be accessible with two dyes that vary in solubilising substituent chains. Primarily based on almost the same values for the solvents of intermediate polarity (toluene, THF, and diethyl ether), it can be assumed that the substituent chains do not contribute notably to the intermolecular interactions.

With this ample information set, the relation can be drawn with these two PBI dyes wherein the aggregation's increase or decrease is consistent for $\pi-\pi$ stacking interactions with increasing solvent polarity, as seen in Figure 1.4. Red dye bearing the oligo ethylene glycol chains indicates

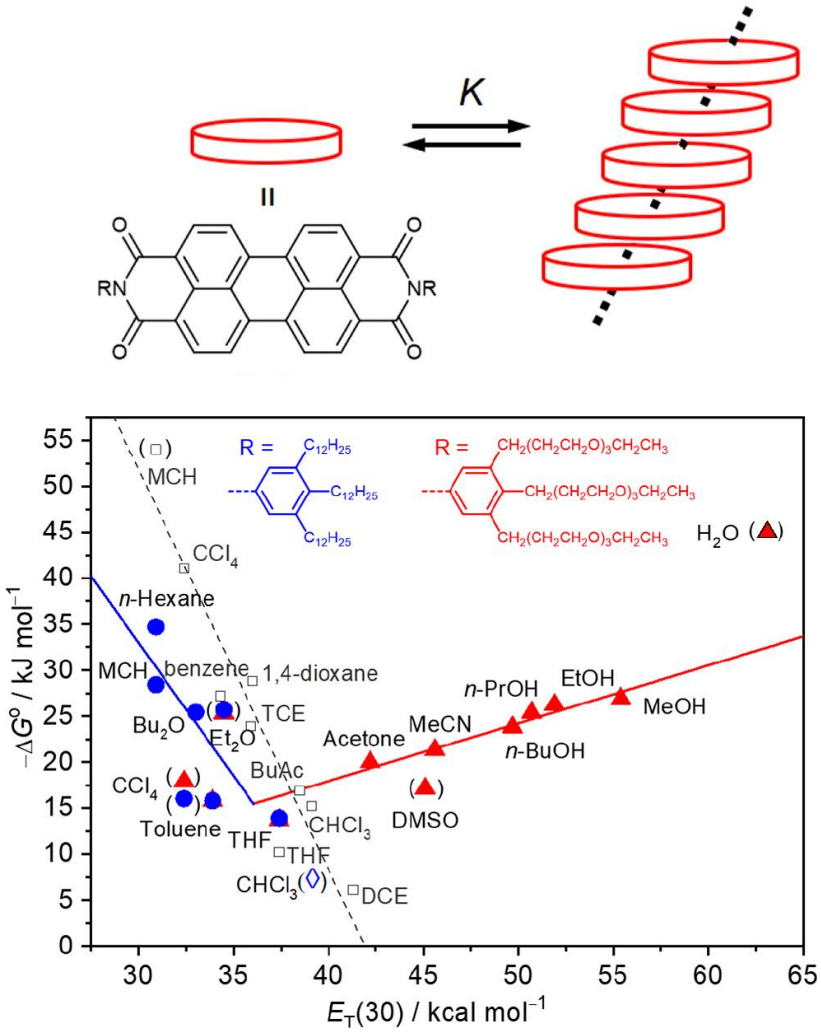


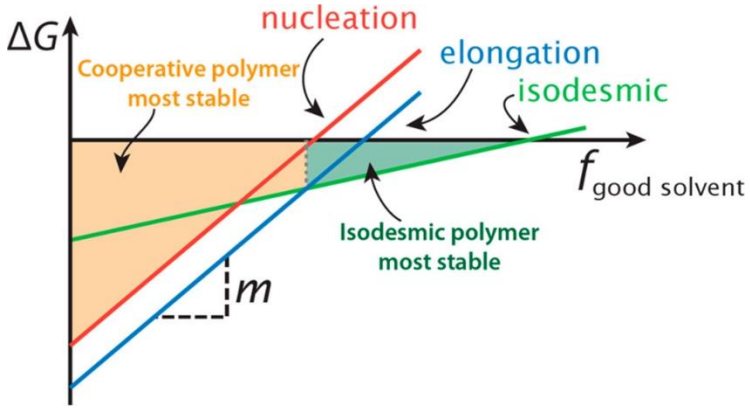
Figure 1.4.. LFER between the Gibbs free energy of self-assembly for the isodesmic aggregation of two different PBI dyes (blue and red as well as for merocyanine (gray) with the $E_T(30)$ polarity scale. Figure taken from ref.[68]

increased binding energy with growing solvent polarity, whilst blue dye bearing aliphatic chains show decreasing binding power with growing solvent polarity. This result is probably defined by contributions from several intermolecular interactions, each between the dyes and among the dyes and the solvent. The weakest binding energy is found for those solvents that are quality desirable to dissolve PBI molecules, i.e., aromatic solvents and THF. However, for a PBI dye bearing alkoxy chains in place of alkyl chains, strong binding energy has been found, and from LFER, it can be concluded that the best solvent for solubilising red dye is chloroform (open blue diamond). Whereas the solvents having the lowest binding free energy are suitable for self-assembly. Thus, LFER can help to find appropriate solvents for studying supramolecular self-assemblies.

For a solvent system that consists of a couple of solvents, the solvent properties can not be understood absolutely based on the ratio of the solvents within the mixture. Therefore, many LFERs have been studied with solvent combinations(Figure 1.5). Further, these LFERs help discover the most suitable conditions for the desired self-assembly process. Here, the solvent mixture entails a "good" solvent that solubilises the monomers and a "poor" solvent that only solubilises the substituent chains but not aromatic cores. For many solvent combinations, the effect of a good solvent on self-assembly in a poor solvent may be defined by a simple LFER,

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

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.



Here, the *m*-value signifies the denaturing ability of a good solvent for a specific chromophore and

Figure1.5.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]

a specific pair of good and bad solvents. In supramolecular self-assemblies, *m*-values have been reported for limited systems. Typical *m*-values for a binary mixture of $CHCl_3$ and MCH is around 60 kJ/mol for OPV, ureidotriazines,[77] perylenes,[78] and a BTA.[79]. However, LFERs can

quantify the effect of a good solvent on supramolecular self-assembly in poor solvents, but it does not provide a molecular-level understanding of different solvent-induced interactions.

1.5.1. Solvent-Induced Helicity in Self-Assemblies

Besides controlling balance among several non-covalent interactions, solvents can also effectively direct supramolecular polymer structure and morphology. One of the most common examples is the usage of chiral solvents to bias helical preference when achiral monomers form supramolecular self-assemblies.

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 1.6).[80] This indicates that the helical induction

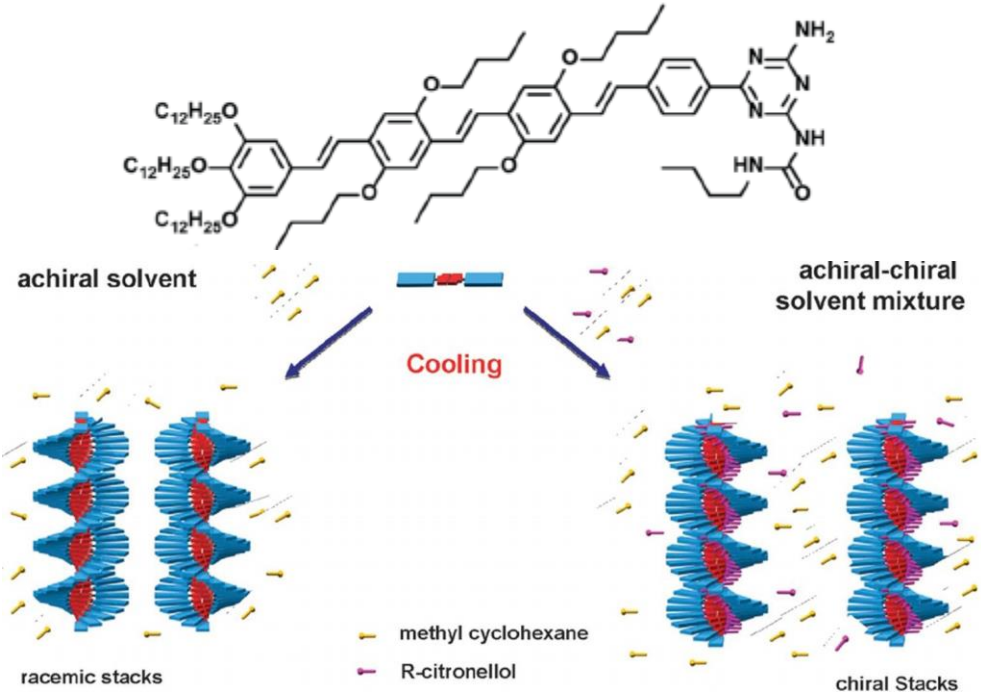


Figure 1.6. (R)-Citronellol as cosolvent in MCH induces the formation of supramolecular polymers of OPV derivatives of a preferred handedness. Figure taken from ref.[80]

inside the OPV assembly is primarily based on enthalpic interactions, which contrasts with the lack of any directional interactions in aliphatic solvents.

1.5.2. 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 1.7).[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.

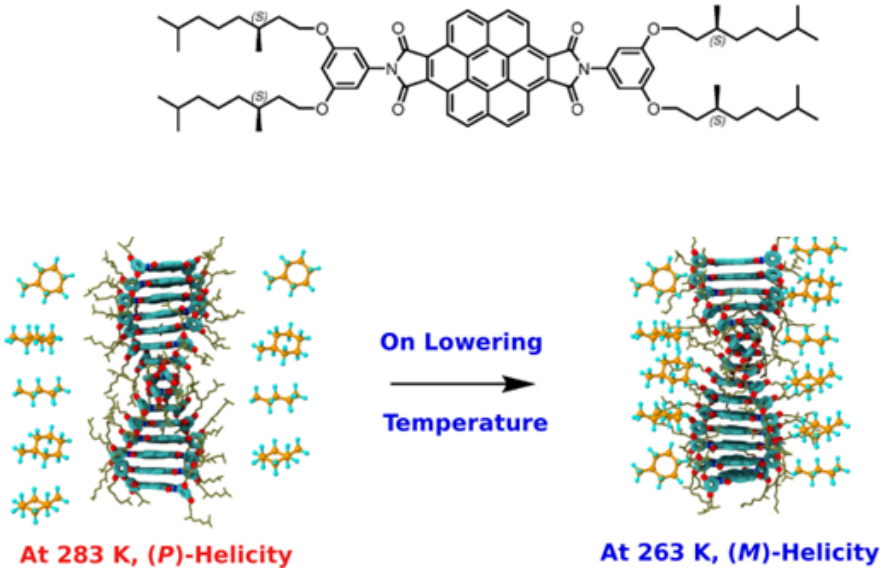


Figure 1.7. Self-assembled corine bisimide: molecular structure and schematic representation of solvent molecule incorporation in molecular pockets of self-aseembly on lowering the temperature to inverse the helicity Figure taken from ref.[81]

1.6. 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.

1.6.1. 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 1.8).

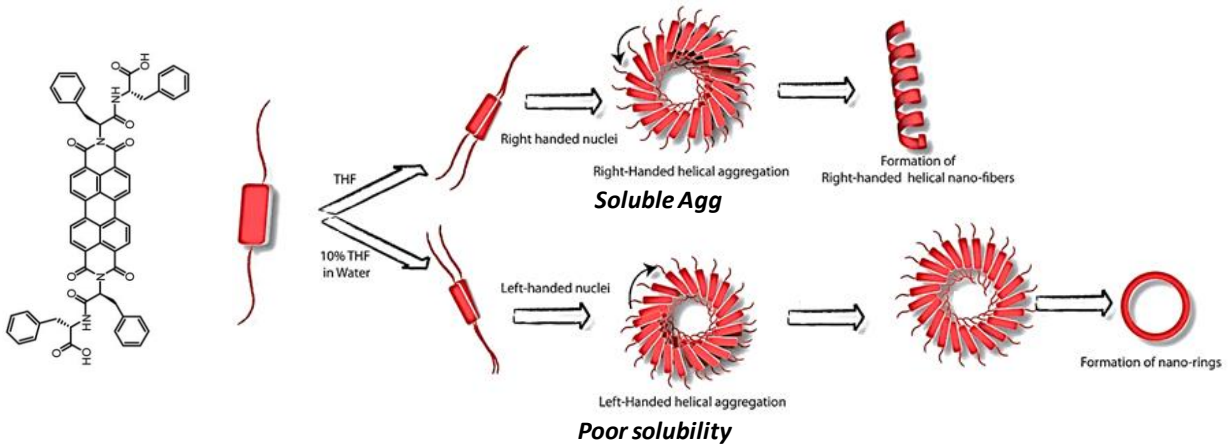


Figure 1.8. Schematic presentation of the thermodynamic and kinetic control of the self-assembly process in different solvent composition to show the formation mechanism for helical nano-fibers and nano-rings. Figure taken from ref.[84]

1.6.2. 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 1.9).[85] The degree of superhelical twisting could be controlled by cautious control of the amount of $CHCl_3$ in n-decane.

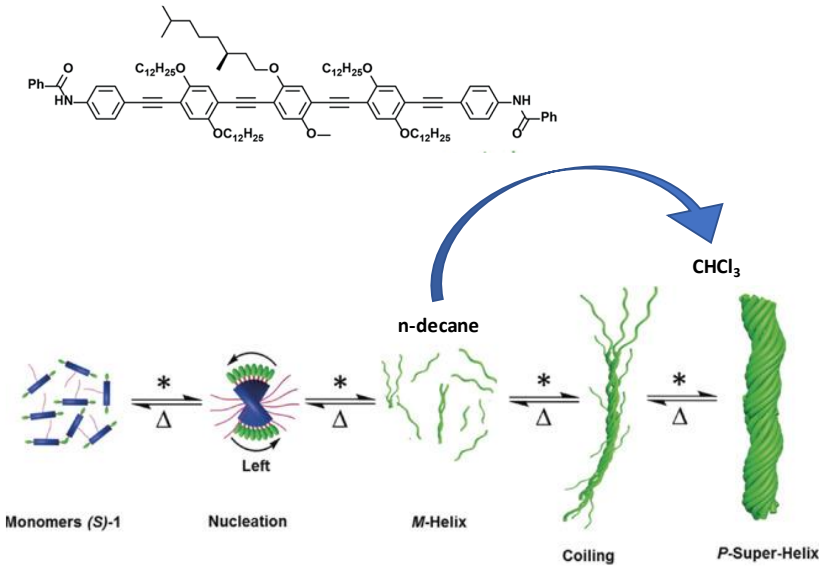


Figure 1.9. Schematic presentation of the solvent and temperature induced chiral inversion in superhelix. Figure taken from ref.[85]

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

One of the most suitable solvent-induced assets of self-assemblies is their capability to undergo significant adjustments in their morphologies and secondary structures in reaction to the pH of the solvent medium. For example, H-bonding interactions are strongly responsive to the medium's pH, resulting in a collapse or generation of the self-assemblies due to adding acid or base.[86] In this context, self-assembled peptides have been appreciably investigated for their pH-responsiveness that can be probed for several applications, starting from drug delivery structures (DDS) [87], used as injectable gels in tissue engineering [88,89] to biosensing.[90] Drugs can be delivered to a targeted organ through a pH-responsive DDS while protecting its function during its journey via physiological obstacles. Most significantly, pH-responsive DDS is considered appropriate for chemo-therapeutics. [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

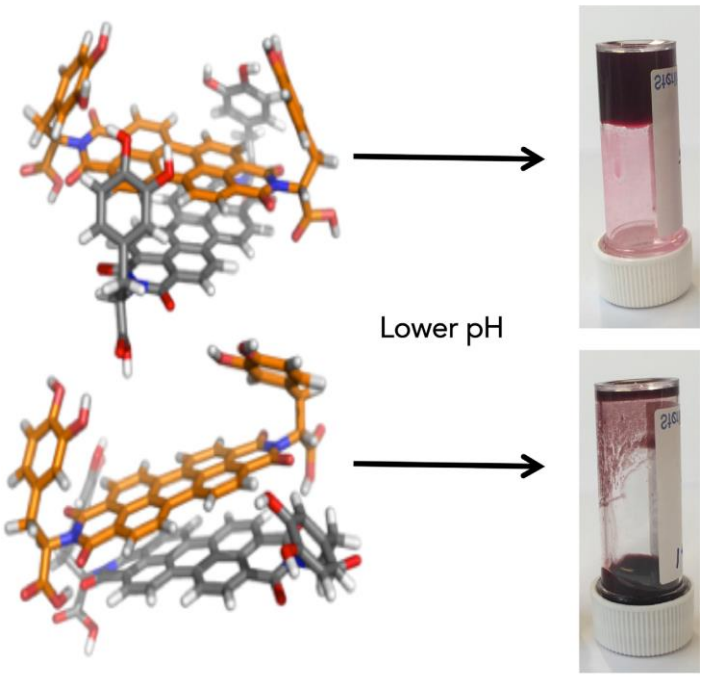


Figure 1.10 .Chemical structure of PBI-DOPA at different degrees of deprotonation A1 and A2. Photographs of the solution of A2 upon a decrease in pH to 3.3 (left) and of the solution of A1 upon a decrease in pH to 3.3 . The scale bar represents 1.5 cm. Figure taken from ref.[95]

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 pretty hard to control the packing, which is vital because the conductivity and optoelectronic properties are immediately affected by packing. Adam and co-workers reported a strategy to control the packing of a single PBI chromophore functionalised with an amino acid through a minute change in the pH of the medium.[95] While H-aggregated PBIs form a gel at a decreased pH, different starting conditions result in the formation of J-aggregates incapable of forming a gel while the pH is reduced. By drying these aggregates, the solid films also show exclusive photoconductive properties.

1.8. Role of Solvent-Solute Interactions in Supramolecular Gelation

Gels are a unique outcome of solvent-solute interactions that are frequently less difficult to understand than accurately defined.[96,97] Since the introduction of the gel concept by Thomas Graham in 1861, the definition of the gel has evolved notably.[98] The numerous various tries

made to define gels. Dr. Dorothy Jordan Lloyd proposed that gels should be composed of additives, one liquid at the temperature of attention and the other solid. The system should also have solid-like mechanical properties.[97] This definition is beneficial in figuring out a gel; however, it is vague because not all colloids are gels.[99] Over several decades, the definition of a gel advanced to the point in which Hermans depicted gels as "coherent colloid disperse structures of at the least two components that show off mechanical properties feature of the strong state" and "both the dispersed factor and dispersing medium amplify themselves continuously during the entire system".[100] Because of the uniqueness of this definition, Ferry offers an extra descriptive one: "A gel is a drastically diluted system which exhibits no constant state flow."[101] A substance may be characterised as a gel if: (1) it has a microscopic structure with macroscopic dimensions, which is unchanged at the time scale of an analytical test, and (2) it is solid in its rheological conduct, notwithstanding being ordinarily liquid. Flory labelled gels into four classes: (1) ordered lamellar gel mesophases; (2) completely disordered covalently linked polymeric networks; (3) predominantly disordered aggregating systems with locally ordered domains; (4) disordered particulate structures.[102] Herein, molecular gels live in class three and perhaps.[99]

1.8.1. 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.

1.8.2. Designing the Gelators

The rational design of small-molecular gelators has remained elusive, notwithstanding the hastily growing investigation into such gels over the last decade.[110] Gelation via small molecules is still an empirical technology, and maximum new gelators are determined coincidentally. Each class of molecular gelators can gel a limited set of solvents. No general law can be applied to all gelator–solvent mixtures. Every work has shown that a given gelator can form gel in limited solvents! The diversity of attractive and repulsive forces that could be performed between gelators and solvents is large. In that regard, a current analysis of fifty different gelators with a noticeably diverse set of solvents has been carried out.[111] The analysis of solvent parameters with gelating factors explains why selective gelators form gels only in specific solvents. For instance, the molecules that act as gelators of benzene have strong H-bonding interactions, while molecules that remain as sols tend to engage mainly through dispersive forces.

1.8.3. Role of Solvent

The impact of solvent chemistry on the potential of small molecules to bring together and self-assemble into long fibres is as essential as the structure of the gelator! The initial works on the role of solvent and molecular structure responsible for fibrillar self-assemblies confirmed that the gelation number (i.e., the highest number of solvent molecules gelled by each gelator molecule) could be correlated with Hildebrand solubility parameters, keeping primary functional groups in the solvent molecule to be fixed.[112] Various primary alcohols were gelled via trehalose-based gelators in the concerned work. The authors discovered that after the substituent is short, the ability to gel solvents turned inversely proportional to the Hildebrand solubility parameter of the solvent.[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 modify the morphology of the gels also. In a study with dipeptide (diphenylalanine) gelators, converting the solvent from toluene to ethanol brought about an alternate gel morphology from fibres to microcrystals (Figure 1.11).[119] Morphological alteration induced by solvents has also been reported with morphs of *CAB* gelators [120] and *HSA*.[121,122]

HSA-based gels in various alkanes and thiols have fibrillar morphologies, with a hexagonal sub-cellular spacing and a multi-lamellar morphology in which the gap between lamellae is more than the length of two *HSA* molecules. On the other hand, in solvents with nitriles, aldehydes and ketones functionalities, HSA aggregates less effectively in spherulitic objects having a triclinic, parallel subcell with interdigitation in the lamellar architecture.[112] Thus, it is clear that versatile solvent properties are crucial in dictating non-covalent interactions driving self-assemblies leading to gelation.[123-128]

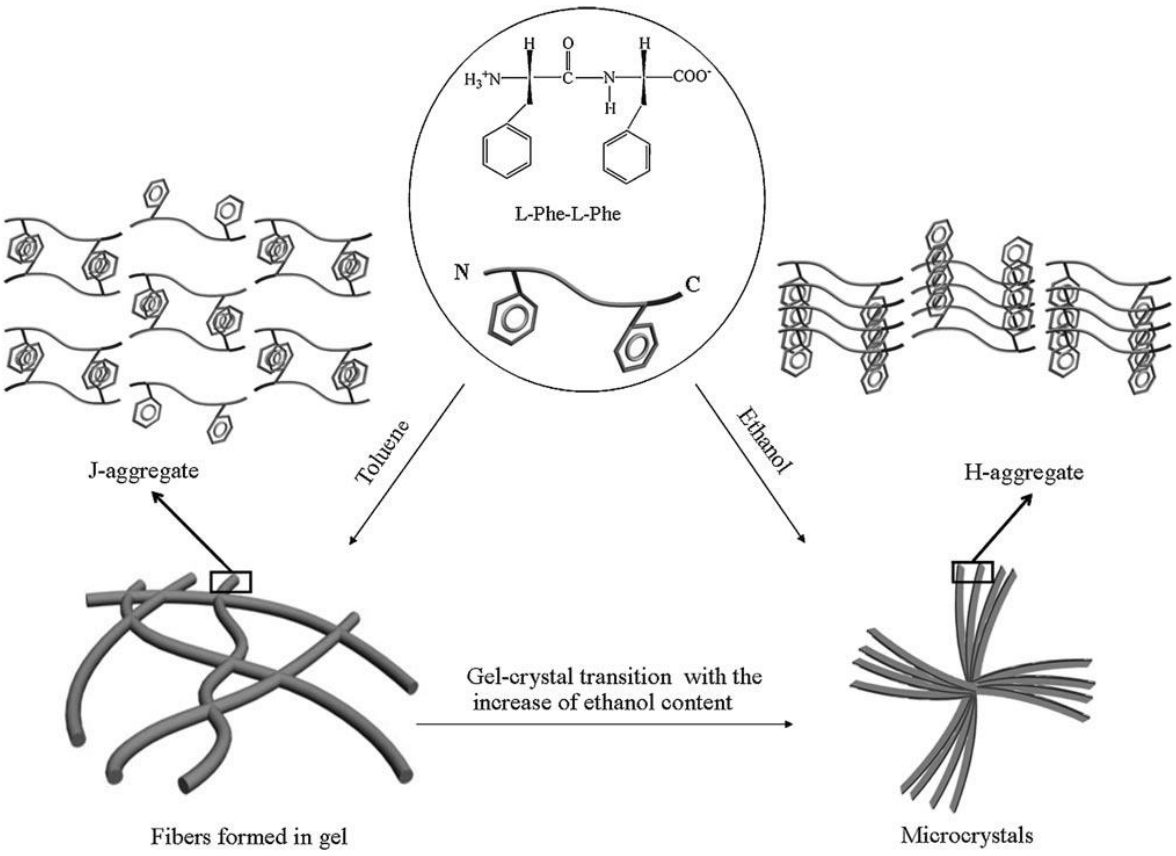


Figure 1.11.. Schematic illustration of the structural transition of *diphenylalanine* induced by varying the *ethanol* content in the mixed solvents, and the proposed molecular packing in the gel and in the microcrystal. SEM images are of samples formed in *toluene* and *ethanol*. Figure taken from ref.[119]

1.9. Role of Solvent-Solute Interactions in Supramolecular Polymorphism

Polymorphism is a broad term exposed to examination across various exploration disciplines, including chemistry, biology, crystallography and materials sciences. Since polymorphism in a chemical system was first reported more than two centuries back, there is still an ongoing debate

on the proper definition.[129] Polymorphism has been defined as the manifestation of more than one crystalline phase arising from distinct packing arrangements of the same molecule in the solid state.[130-132] In a polymorphic system, the molecules, atoms, or ions alter their mutual arrangement, critically affecting various properties like morphologies, electric conductivities, and crystal properties. [130-132] Polymorphs that diverge in their molecular arrangement can be called packing polymorphs,[129] and a molecule exhibiting several possible conformations is known as conformational polymorphism[133]. Multiple polymorphs having comparable energies are often isolated concomitantly in the same crystallising medium,[134] making control over polymorphs a real challenge.[135] This unforeseen phenomenon is widespread in crystal engineering but has also been a topic of interest in various self-assembled systems, counting lyotropic liquid crystals,[136] block copolymers,[137] and self-assembled dendrimer systems.[138] Inspired by supramolecular assemblies in nature, the non-covalent synthesis of complex architectures from the same molecules offers excellent potential for developing advanced materials.[139,140] Despite several advances in polymorphs that have been theoretically predicted [141], the identification, isolation, and characterisation of a rational design to access their complex energetic landscapes 16 to develop reversibly responsive solids is challenging.[142-143] Thus, several strategies to access polymorphism and tune their phase behaviour can pave away plausible design of new responsive, functional materials.[144-149]

1.9.1. Supramolecular Polymorphism: Mechanistic Insight

Therefore, control over the polymorphism of organic systems is highly desirable but very difficult in practical situations due to the complex interplay between thermodynamics and kinetics within the same crystallisation process.[131] Thermodynamic considerations deal with the stability of the respective polymorphs, which usually differ only by a few kJ mol^{-1} [150-151], while kinetic pathways determine how fast a specific polymorph is formed, which depends on their activation barriers.[131] The formation of a particular polymorph is usually under kinetic control and thus can be critically tuned as a function of variable experimental conditions like solvent environment, temperature, and heating-cooling rates.[131] The crystallisation of a particular polymorph can be explained from the molecular point of view as a supramolecular reaction initiated by nuclei due to non-covalent interactions that develop into a 3D structure. [130,131,152] To gain mechanistic

insights into polymorphism, the thermodynamics, kinetics, initial nucleation event, and transformations between certain polymorphs must be studied adequately. [131,153]

1.9.2. Molecular Packing Effectuated by Solvent-Solute Interactions

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

1.9.3. Solvent-Induced Liquid Crystalline Systems

In 2015, Saito and co-workers [159] reported a self-assembled lyotropic liquid crystal system that shows reversible polymorphism using cyclic ethynylhelicene oligomers cyclobis[(M)-D-n] (n = 4 and 6) where two flexible linkers connect two oligomer moieties. Growing such a self-aggregated material framework, which displays dynamic and reversible polymorphism by various hierarchical bottom-up small oligomers, can be a basis for understanding biological processes and creating stimuli-responsive functional materials. LLCs are alluring for a material framework because of their anisotropic nature, especially when they display dynamic and reversible polymorphism. The cyclic molecular structure was intended to control molecular to macroscopic self-assembly properties. Temperature and solvent-dependent CD and UV−vis studies reveal the cyclic oligomer's structural change between molecularly dissolved random coils formation level and intramolecularly attached homo-double helix. 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]

1.9.4. Supramolecular Polymorphism Utilising Pathway Complexity

Supramolecular Polymorphism [169] has been reported in a typical metal-ligand complex system utilising the self-assembly of a chiral Pd-II complex [170,171] where the hidden kinetic pathways [172,173] play substantial significance in supramolecular polymerisation processes, allowing new self-assembly pathways with promising functional materials. The supramolecular polymerisation of the complex developed into a pair of competing aggregates assigned as Agg I and Agg II. The kinetic [174-177] one (Agg II) is created through a "hidden" pathway inaccessible by standard thermal polymerisation protocols. Variable temperature spectroscopic studies [178] revealed that

the thermally-controlled self-assembly process prefers stable cooperative [179-180] AggI with no sign of the kinetic state. That is affirmed by the fact that the kinetic pathway exhibits lower T_e than the thermodynamic ones. This incident is in clear contrast to the typical supramolecular self-assembled polymeric behaviour. When the monomer is injected into a large amount of aggregating solvent MCH, a "hidden" rapid kinetic polymerisation pathway (Agg II) is revealed that is also cooperative. [181] When the packing mode remains conserved, this kinetic pathway rapidly converts into clustered superstructures (Agg IIc) [182-184]. After the monomers get involved in the kinetic aggregate formation (Agg II), the rapid clustering step is sequestered from the coupled polymerisation equilibria in the solution, which hinders the thermodynamic pathway, even in the presence of seeds. [185-187] The exceptional kinetic stability of Agg II could be an outcome of a cooperative mechanism in the nucleation of Agg I. The dramatic influence of a hidden kinetic pathway on developing two polymorphs [188] is extraordinary. The formation of a cluster in a solution where fast kinetics isolates monomers from the equilibria can 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.

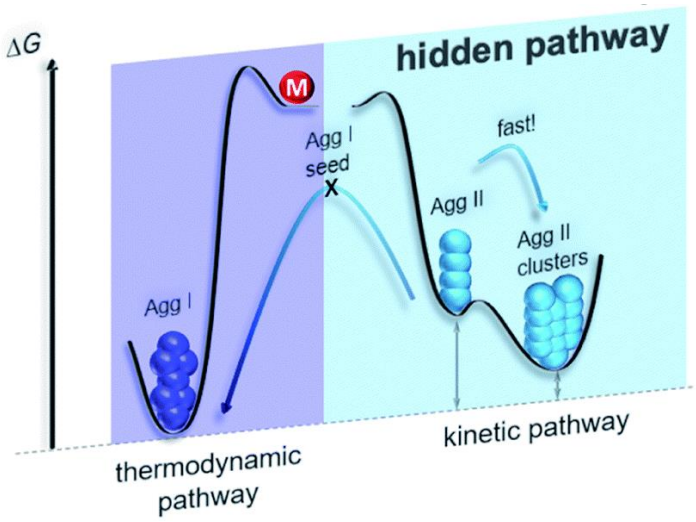


Figure. 1.12. Energy landscape outlining its complex self-assembly behaviour that incorporates a hidden pathway. Figure taken from ref.[189]

1.10. 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]

1.10.1. 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.

1.10.2. 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 narrate 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 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

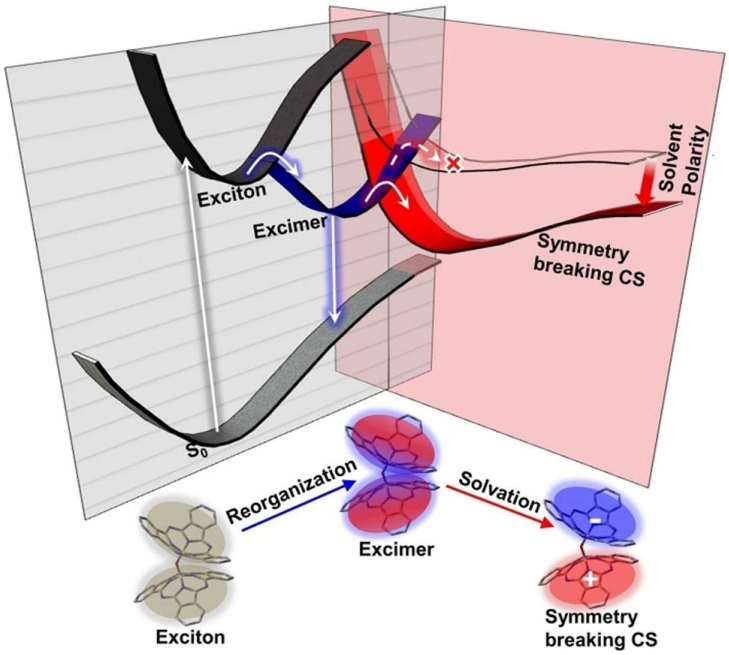


Figure 1.13. Schematic representation of µ-OSubPc2 photophysics. Direct excitation is to a Frenkel exciton state, where excitation is shared over the dimer. This is followed by sequential formation of the µ-OSubPc2 excimer and its decay by symmetry breaking charge separation to forma charge separated state, which is accessible only in polar solvent. The first step thus involves an evolution in the wavefunction of the Frenkel exciton state to favour charge resonance forms in the excimer. This involves evolution on intramolecular coordinates. The excimer subsequently decays along a solvation coordinate in polar solvents, with the initial step arising from an asymmetric fluctuation in the solvent environment. Figure taken from ref. [236]

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.

1.11. Conclusions

This chapter briefly discussed the importance of solvent-solute interactions in controlling the supramolecular self-assemblies with plausible thermodynamic and kinetic factors with suitable examples. We also discussed the role of solvent in supramolecular polymorphism, supramolecular gelation and photoinduced charge transfer. The effect of the pH of the medium on the outcome of self-assembly has also been studied. We dedicated our work to investigating the solvent's role in controlling the assembly structures and pathways.

1.12. References

1. M. Baroncini, L. Casimiro, C. de Vet, J. Groppi, S. Silvi and A. Credi, *ChemistryOpen*, 2018, **7**, 169–179.
2. J.-P. Sauvage, *Angew. Chem. Int. Ed.*, 2017, **56**, 11080–11093.
3. C. Pezzato, C. Cheng, J. F. Stoddart and R. D. Astumian, *Chem. Soc. Rev.*, 2017, **46**, 5491–5507.

4. T. van Leeuwen, A. S. Lubbe, P. Štacko, S. J. Wezenberg and B. L. Feringa, *Nat Rev Chem*, 2017, **1**, 0096.
5. S. Silvi, M. Venturi and A. Credi, *J. Mater. Chem.*, 2009, **19**, 2279.
6. M. C. Jiménez, C. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem. Int. Ed.*, 2000, **39**, 3284–3287.
7. C. J. Bruns and J. F. Stoddart, *The Nature of the Mechanical Bond: From Molecules to Machines*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2016.
8. P. Ghosh, G. Federwisch, M. Kogej, C. A. Schalley, D. Haase, W. Saak, A. Lützen and R. M. Gschwind, *Org. Biomol. Chem.*, 2005, **3**, 2691.
9. Y. Marcus, *Chem. Soc. Rev.*, 1993, **22**, 409.
10. P. Ball, *Chem. Rev.*, 2008, **108**, 74–108.
11. K. A. Dill, S. Bromberg, K. Yue, H. S. Chan, K. M. Ftebig, D. P. Yee and P. D. Thomas, *Protein Science*, 2008, **4**, 561–602.
12. I. Tinoco and C. Bustamante, *Journal of Molecular Biology*, 1999, **293**, 271–281.
13. S. F. Banani, H. O. Lee, A. A. Hyman and M. K. Rosen, *Nat Rev Mol Cell Biol*, 2017, **18**, 285–298.
14. H.-X. Zhou and X. Pang, *Chem. Rev.*, 2018, **118**, 1691–1741.
15. M. Kulkarni and A. Mukherjee, *Progress in Biophysics and Molecular Biology*, 2017, **128**, 63–73.
16. W. Fuller, T. Forsyth and A. Mahendrasingam, *Phil. Trans. R. Soc. Lond. B*, 2004, **359**, 1237–1248.
17. T. Siebert, B. Guchhait, Y. Liu, B. P. Fingerhut and T. Elsaesser, *J. Phys. Chem. Lett.*, 2016, **7**, 3131–3136.
18. S.-H. Chong and S. Ham, *J. Phys. Chem. Lett.*, 2016, **7**, 3967–3972.
19. S.-H. Chong and S. Ham, *Sci Rep*, 2017, **7**, 8744.
20. H. Oshima, T. Hayashi and M. Kinoshita, *Biophysical Journal*, 2016, **110**, 2496–2506.
21. C. A. Hunter, *Angew. Chem. Int. Ed.*, 2004, **43**, 5310–5324.
22. K. Kanagaraj, M. Alagesan, Y. Inoue and C. Yang, in *Comprehensive Supramolecular Chemistry II*, Elsevier, 2017, pp. 11–60.
23. D. Chandler, *Nature*, 2005, **437**, 640–647.
24. R. Cabot and C. A. Hunter, *Chem. Soc. Rev.*, 2012, **41**, 3485.

25. S. Otto, *Chem. Sci.*, 2013, **4**, 2953.
26. N. J. Van Zee, B. Adelizzi, M. F. J. Mabesoone, X. Meng, A. Aloi, R. H. Zha, M. Lutz, I. A. W. Filot, A. R. A. Palmans and E. W. Meijer, *Nature*, 2018, **558**, 100–103.
27. S. Dong, J. Leng, Y. Feng, M. Liu, C. J. Stackhouse, A. Schönhals, L. Chiappisi, L. Gao, W. Chen, J. Shang, L. Jin, Z. Qi and C. A. Schalley, *Sci. Adv.*, 2017, **3**, eaao0900.
28. E. Yashima, T. Matsushima and Y. Okamoto, *J. Am. Chem. Soc.*, 1997, **119**, 6345–6359.
29. K. Venkata Rao, D. Miyajima, A. Nihonyanagi and T. Aida, *Nature Chem*, 2017, **9**, 1133–1139.
30. Biot, *J. Prakt. Chem.*, 1843, **29**, 447–451.
31. H. Staudinger, *Ber. dtsch. Chem. Ges. A/B*, 1920, **53**, 1073–1085.
32. T. Aida, A. Takemura, M. Fuse and S. Inoue, *J. Chem. Soc., Chem. Commun.*, 1988, 391.
33. Y. Ducharme and J. D. Wuest, *J. Org. Chem.*, 1988, **53**, 5787–5789.
34. C. Fouquey, J.-M. Lehn and A.-M. Levelut, *Adv. Mater.*, 1990, **2**, 254–257.
35. J. A. Zerkowski, C. T. Seto, D. A. Wierda and G. M. Whitesides, *J. Am. Chem. Soc.*, 1990, **112**, 9025–9026.
36. T. Aida and E. W. Meijer, *Isr. J. Chem.*, 2020, **60**, 33–47.
37. L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4098.
38. T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma and E. W. Meijer, *Chem. Rev.*, 2009, **109**, 5687–5754.
39. T. Aida, E. W. Meijer and S. I. Stupp, *Science*, 2012, **335**, 813–817.
40. S. Kiyonaka, K. Sugiyasu, S. Shinkai, I. Hamachi, *J. Am. Chem. Soc.* ,2002, **124**, 10954; S. Valkama, H. Kosonen, J. Ruokolainen, T. Haatainen, M. Torkkeli, R. Serimaa, G. Ten Brinke, O. Ikkala, *Nature Materials* 2004, **3**, 872; J. H. van Esch, B. L. Feringa, *Angew. Chem. Int. Ed.*, 2000, **39**, 2263; *Angew. Chem.*, 2000, **112**, 2351.
41. A. Aggeli, M. Bell, L. M. Carrick, C. W. G. Fishwick, R. Harding, P. J. Mawer, S. E. Radford, A. E. Strong, N. Boden, *J. Am. Chem. Soc.*, 2003, **125**, 9619.
42. B. J. B. Folmer, E. Cavini, R. P. Sijbesma, E. W. Meijer, *Chem. Commun.*, 1998, 1847.; J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, B. L. Feringa, *Science*, 2004, **304**, 278.

43. Y. Liu, A. H. Flood, J. F. Stoddart, *J. Am. Chem. Soc.* 2004, *126*, 9150; J. P. Sauvage, *Chem. Commun.* 2005, 1507.
44. D. B. Smithrud, F. Diederich, *J. Am. Chem. Soc.* 1990, **112**, 339.
45. D. J. Cram, H. J. Choi, J. A. Bryant, C. B. Knobler, *J. Am. Chem. Soc.* 1992, **114**, 7748;
46. J. C. Nelson, J. G. Saven, J. S. Moore, P. G. Wolynes, *Science* 1997, **277**, 1793.
47. K. T. Chapman, W. C. Still, *J. Am. Chem. Soc.* 1989, **111**, 3075; Y. Tokunaga, D. M. Rudkevich, J. Santamaria, G. Hilmersson, J. Rebek, Jr., *Chem. Eur. J.* 1998, **4**, 8; R. K. Castellano, R. Clark, S. L. Craig, C. Nuckolls, J. Rebek Jr., *Proc. Natl. Acad. Sci.USA* 2000, **97**, 12418; D. Lopez, J.-M. Guenet, *Macromolecules* 2001, **34**, 1076; A. Scarso, L. Trembleau, J. Rebek Jr., *J. Am. Chem. Soc.* 2004, **126**, 13512.
48. N. J. Van Zee, B. Adelizzi, M. F. J. Mabesoone, X. Meng, A. Aloi, R. H. Zha, M. Lutz, I. A. W. Filot, A. R. A. Palmans and E. W. Meijer, *Nature*, 2018, **558**, 100–103.
49. D. Chandler, *Nature*, 2005, **437**, 640–647.
50. F. Biedermann, W. M. Nau and H.-J. Schneider, *Angew. Chem. Int. Ed.*, 2014, **53**, 11158–11171.
51. S. D. Christian, A. A. Taha and B. W. Gash, *Q. Rev., Chem. Soc.*, 1970, **24**, 20.
52. R. Wolfenden and A. Radzicka, *Science*, 1994, **265**, 936–937.
53. E. N. Lassettre, *Chem. Rev.*, 1937, **20**, 259–303.
54. A. Louhichi, A. R. Jacob, L. Bouteiller and D. Vlassopoulos, *Journal of Rheology*, 2017, **61**, 1173–1182.
55. M. S. Cubberley, B. L. Iverson, *J. Am. Chem. Soc.* 2001, **123**, 7560–7563
56. C. Reichardt, *Chem. Rev.* 1994, **94**, 2319–2358.
57. A. F. M. Barton, *Chem. Rev.* 1975, *75*, 731–753; J.-Y. Hwang, A. Nish, J. Doig, S. Douven, C.-W. Chen, L.-C. Chen, R. J.Nicholas, *J. Am. Chem. Soc.* 2008, **130**, 3543–3553.
58. Y. Si, Z. Dong, L. Jiang, *ACS Cent. Sci.* 2018, *4*, 1102–1112.
59. J. Zhang, X. Chen, W. Li, B. Li, L. Wu, *Langmuir* 2017, **33**, 12750–12758.
60. S. Yao, U. Beginn, T. Gress, M. Lysetska, F. Würthner, *J. Am. Chem. Soc.*2004, **126**, 8336–8348.
61. K. V. Rao, M. F. J. Mabesoone, D. Miyajima, A. Nihonyanagi, E. W. Meijer, T. Aida, *J. Am. Chem. Soc.* 2020, **142**, 598–605.

62. Y. Tobe, N. Utsumi, K. Kawabata, A. Nagano, K. Adachi, S. Araki, M. Sonoda, K. Hirose and K. Naemura, *J. Am. Chem. Soc.*, 2002, **124**, 5350–5364.
63. C. Shao, M. Grüne, M. Stolte and F. Würthner, *Chem. Eur. J.*, 2012, **18**, 13665–13677.
64. A. Satake and Y. Kobuke, *Tetrahedron*, 2005, **61**, 13–41.
65. P. A. Korevaar, C. Schaefer, T. F. A. de Greef and E. W. Meijer, *J. Am. Chem. Soc.*, 2012, **134**, 13482–13491.
66. C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry: REICHARDT:SOLV.EFF. 4ED O-BK*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010.
67. Corwin. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165–195.
68. F. Würthner, *J. Org. Chem.*, 2022, **87**, 1602–1615.
69. L. J. Prins, D. N. Reinhoudt and P. Timmerman, *Angew. Chem. Int. Ed.*, 2001, **40**, 2382–2426.
70. P. Metrangolo, F. Meyer, T. Pilati, G. Resnati and G. Terraneo, *Angew. Chem. Int. Ed.*, 2008, **47**, 6114–6127.
71. C. A. Hunter, *Chem. Soc. Rev.*, 1994, **23**, 101.
72. A. Nowak-Król and F. Würthner, *Org. Chem. Front.*, 2019, **6**, 1272–1318.
73. Z. Chen, B. Fimmel and F. Würthner, *Org. Biomol. Chem.*, 2012, **10**, 5845.
74. D. Görl, X. Zhang and F. Würthner, *Angew. Chem. Int. Ed.*, 2012, **51**, 6328–6348.
75. M. F. J. Mabesoone, A. R. A. Palmans and E. W. Meijer, *J. Am. Chem. Soc.*, 2020, **142**, 19781–19798.
76. J. S. Moore and C. R. Ray, in *Poly(arylene etynylene)s*, ed. C. Weder, Springer Berlin Heidelberg, Berlin, Heidelberg, 2005, vol. 177, pp. 91–149.
77. P. A. Korevaar, C. Schaefer, T. F. A. de Greef and E. W. Meijer, *J. Am. Chem. Soc.*, 2012, **134**, 13482–13491.
78. J. Buendía, E. E. Greciano and L. Sánchez, *J. Org. Chem.*, 2015, **80**, 12444–12452.
79. F. García, P. A. Korevaar, A. Verlee, E. W. Meijer, A. R. A. Palmans and L. Sánchez, *Chem. Commun.*, 2013, **49**, 8674.
80. S. J. George, Ž. Tomović, A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2011, **47**, 3451.

81. C. Kulkarni, P. A. Korevaar, K. K. Bejagam, A. R. A. Palmans, E. W. Meijer and S. J. George, *J. Am. Chem. Soc.*, 2017, **139**, 13867–13875.
82. A. Lohr, T. Gress, M. Deppisch, M. Knoll and F. Würthner, Synthesis, 2007, 2007, 3073–3082.
83. E. Krieg, H. Weissman, E. Shimoni, A. Bar On (Ustinov) and B. Rybtchinski, J. Am. Chem. Soc., 2014, 136, 9443–9452.
84. S. Ahmed, B. Pramanik, K. N. A. Sankar, A. Srivastava, N. Singha, P. Dowari, A. Srivastava, K. Mohanta, A. Debnath and D. Das, Sci Rep, 2017, 7, 9485.
85. M. Hifsudheen, R. K. Mishra, B. Vedhanarayanan, V. K. Praveen and A. Ajayaghosh, *Angew. Chem. Int. Ed.*, 2017, **56**, 12634–12638.
86. R. Narayanaswamy and V. P. Torchilin, *Molecules*, 2019, **24**, 603.
87. L. Saunders and P. X. Ma, *Macromol. Biosci.*, 2019, **19**, 1800313.
88. X. Du, J. Zhou, J. Shi and B. Xu, *Chem. Rev.*, 2015, **115**, 13165–13307.
89. J. D. Tang, C. Mura and K. J. Lampe, *J. Am. Chem. Soc.*, 2019, **141**, 4886–4899.
90. S. Wong, M. S. Shim and Y. J. Kwon, *J. Mater. Chem. B*, 2014, **2**, 595–615.
91. F. Raza, Y. Zhu, L. Chen, X. You, J. Zhang, A. Khan, M. W. Khan, M. Hasnat, H. Zafar, J. Wu and L. Ge, *Biomater. Sci.*, 2019, **7**, 2023–2036.
92. L. Mei, K. Xu, Z. Zhai, S. He, T. Zhu and W. Zhong, *Org. Biomol. Chem.*, 2019, **17**, 3853–3860.
93. K. M. Hainline, F. Gu, J. F. Handley, Y. F. Tian, Y. Wu, L. de Wet, D. J. Vander Griend and J. H. Collier, *Macromol. Biosci.*, 2019, **19**, 1800249.
94. A. Dehsorkhi, V. Castelletto and I. W. Hamley, *J. Pept. Sci.*, 2014, **20**, 453–467.
95. E. R. Draper, B. J. Greeves, M. Barrow, R. Schweins, M. A. Zwijnenburg and D. J. Adams, *Chem*, 2017, **2**, 716–731.
96. R. G. Weiss and P. Te'rech, in *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*, ed. R. G. Weiss and P. Te´rech, *Springer*, Dordrecht, The Netherlands, 2006, pp. 1–12.
97. D. Jordan Lloyd, *Colloid Chemistry*, The Chemical Catalog Company Inc., New York, 1926.
98. T. Graham, *Philos. Trans. R. Soc. London*, 1861, **151**,183–224.
99. R.B.Dean, *Modern Colloids*, D. Van Nostrand Co., New York, 1948.

100. P. H. Hermans, in Colloid Science, ed. H. R. Kruyt, Elsevier, Amsterdam, 1949, ch. XII, vol II, p. 484.
101. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.
102. P. J. Flory, *Faraday Discuss*., 1974, **57**, 7–18.
103. Y. Wu, S. Wu, G. Zou and Q. Zhang, *Soft Matter*, 2011, **7**, 9177–9183.
104. A. Bui and N. Virgilio, *Ind. Eng. Chem. Res*., 2013, **52**, 14185–14191.
105. R. Y. Wang, P. Wang, J. L. Li, B. Yuan, Y. Liu, L. Li and X. Y. Liu, *Phys. Chem. Chem. Phys*., 2013, **15**, 3313–3319.
106. F. P. Duval, J. P. M. van Duynhoven and A. Bot, *J. Am. Oil Chem. Soc*., 2006, **83**, 905–912.
107. D. Farbi, J. Guan and A. Cesaro, *Thermochim. Acta*, 1998, **321**, 3–16.
108. P. Terech, I. Furman and R. G. Weiss, *J. Phys. Chem*., 1995, **99**, 9558–9566.
109. R. G. Weiss, *J. Am. Chem. Soc*., 2014, **136**, 7519–7530.
110. Y. Lan, M. G. Corradini and M. A. Rogers, *Cryst. Growth Des*., 2014, **14**, 4811–4818.
111. G. Zhu and J. S. Dordick, *Chem. Mater*., 2006, **18**, 5988–5995.
112. J. Gao, S. Wu and M. A. Rogers, *J. Mater. Chem*., 2012, **22**, 12651–12658.
113. M. George and R. G. Weiss, *Langmuir*, 2003, **19**, 1017–1025.
114. Y. Lan, M. G. Corradini, X. Liu, T. E. May, F. Borondics, R. G. Weiss and M. A. Rogers, *Langmuir*, 2014, **30**, 14128–14142.
115. A. R. Hirst and D. K. Smith, *Langmuir*, 2004, **20**,10851–10857.
116. M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Langmuir*, 2003, **19**, 8622–8624.
117. P. Zhu, X. Yan, Y. Su, Y. Yang and J. Li, *Chem. – Eur. J*., 2010, **16**, 3176–3183.
118. I. Furman and R. G. Weiss, *Langmuir*, 1993, **9**, 2084–2088.
119. J. Gao, S. Wu, T. Emge and M. A. Rogers, *CrystEngComm*, 2013, **15**, 4507–4515.
120. S. Wu, J. Gao, T. Emge and M. A. Rogers, *Soft Matter*, 2013, **9**, 5942–5950.
121. R. Wang, C. Geiger, L. Chen, B. Swanson and D. G. Whitten, *J. Am. Chem. Soc*., 2000, **122**, 2399–2400.
122. Y. Jeong, K. Hanabusa, H. Masunaga, I. Akiba, K. Miyoshi, S. Sakurai and K. Sakurai, *Langmuir*, 2005, **21**, 586–594.

123. G. Qing, X. Shan, W. Chen, Z. Lv, P. Xiong and T. Sun, *Angew. Chem.*, 2014, **126**, 2156–2161.
124. X. Wang and M. Liu, *Chem. – Eur. J.*, 2014, **20**, 10110–10116.
125. M.-M. Su, H.-K. Yan, L.-J. Ren, P. Zheng and W. Wang, *Soft Matter*, 2014, **11**, 741–748.
126. X. Chen, P. Fei, K. A. Cavicchi, W. Yan and N. Ayres, *Colloid Polym. Sci.*, 2014, **292**, 477–484.
127. D. Dasgupta, S. Srinivasan, C. Rochas, A. Ajayaghosh and J.-M. Guenet, *Soft Matter*, 2011, **7**, 9311–9315.
128. M. Bielejewski, J. Kowalczuk, J. Kaszyn´ska, A. Łapin´ski, R. Luboradzki, O. Demchuk and J. Tritt-Goc, *Soft Matter*, 2013, **9**, 7501–7514.
129. (a) A. J. Cruz-Cabeza, S. M. Reutzel-Edens and J. Bernstein, *Chem. Soc. Rev.*, 2015, **44**, 8619–8635. (b) P. A. Gale and J. W. Steed, Eds., *Supramolecular Chemistry: From Molecules to Nanomaterials*, John Wiley & Sons, Ltd, Chichester, UK, 2012. (c) R. Hilfiker, Ed., *polymorphism: in the Pharmaceutical Industry*, Wiley, 1st edn., 2006. (d)
130. J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press: New York, 2002. 1
131. G. R. Desiraju, J. J. Vittal and A. Ramanan, *Crystal Engineering: A Textbook*, Co-Published with Indian Institute of Science (IISc), Bangalore, India, 2011.
132. Supramolecular Chemistry, 2nd Edition | Wiley, https://www.wiley.com/en-us/Supramolecular+Chemistry%2C+2nd+Edition-p-9781118681503, (accessed 6 October 2022).
133. A. J. Cruz-Cabeza and J. Bernstein, *Chem. Rev.*, 2014, **114**, 2170–2191.
134. J. Bernstein, R. J. Davey and J. Henck, *Angewandte Chemie Intl Edit*, 1999, **38**, 3440–3461.
135. N. P. Rath, V. S. S. Kumar, M. Janka and G. K. Anderson, *Inorganica Chimica Acta*, 2007, **360**, 2997–3001.
136. (a) N. Saito, K. Kanie, M. Matsubara, A. Muramatsu and M. Yamaguchi, *J. Am. Chem. Soc.*, 2015, **137**, 6594–6601. (b) D. Jurašin, A. Pustak, I. Habuš, I. Šmit and N. Filipović-Vinceković, *Langmuir*, 2011, **27**, 14118–14130. (c) D. Jurašin, A. Pustak, I. Habuš, I. Šmit and N. Filipović-Vinceković, *Langmuir*, 2011, **27**, 14118–14130. (d) I. W. Hamley, M. J.

Krysmann, V. Castelletto and L. Noirez, Adv. Mater., 2008, 20, 4394–4397. (e) S. S. Zhu and T. M. Swager, *Adv. Mater.*, 1995, **7**, 280–283.

137. (a) J. Hwang, T. Heil, M. Antonietti and B. V. K. J. Schmidt, *J. Am. Chem. Soc.*, 2018, **140**, 2947–2956. (b) L. Yin, T. P. Lodge and M. A. Hillmyer, *Macromolecules*, 2012, **45**, 9460–9467.
138. (a) D. Sahoo, M. R. Imam, M. Peterca, B. E. Partridge, D. A. Wilson, X. Zeng, G. Ungar, P. A. Heiney and V. Percec, *J. Am. Chem. Soc.*, 2018, **140**, 13478–13487. (b) H.-J. Sun, S. Zhang and V. Percec, *Chem. Soc. Rev.*, 2015, **44**, 3900–3923. (c) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam and V. Percec, Chem. Rev., 2009, 109, 6275–6540.
139. Z. B. Henson, K. Müllen and G. C. Bazan, *Nature Chem*, 2012, **4**, 699–704.
140. C. Sutton, C. Risko and J.-L. Brédas, *Chem. Mater.*, 2016, **28**, 3–16.
141. P. M. Piaggi and M. Parrinello, *Proc. Natl. Acad. Sci. U.S.A.*, 2018, **115**, 10251–10256.
142. J. D. Dunitz, *Pure and Applied Chemistry*, 1991, **63**, 177–185.
143. R. Dubey, M. S. Pavan and G. R. Desiraju, *Chem. Commun.*, 2012, **48**, 9020.
144. G. E. Purdum, N. G. Telesz, K. Jarolimek, S. M. Ryno, T. Gessner, N. C. Davy, A. J. Petty, Y. Zhen, Y. Shu, A. Facchetti, G. E. Collis, W. Hu, C. Wu, J. E. Anthony, R. T. Weitz, C. Risko and Y.-L. Loo, *J. Am. Chem. Soc.*, 2018, **140**, 7519–7525.
145. D. R. Islamov, V. G. Shtyrlin, N. Yu. Serov, I. V. Fedyanin and K. A. Lyssenko, *Crystal Growth & Design*, 2017, **17**, 4703–4709.
146. M. Jin, T. Seki and H. Ito, *J. Am. Chem. Soc.*, 2017, **139**, 7452–7455.
147. F. C. Pigge, *CrystEngComm*, 2011, **13**, 1733.
148. D. Yan and D. G. Evans, *Mater. Horiz.*, 2014, **1**, 46–57.
149. C. P. Brock, W. B. Schweizer and J. D. Dunitz, *J. Am. Chem. Soc.*, 1991, **113**, 9811–9820.
150. M. R. Caira, in *Design of Organic Solids*, eds. E. Weber, Y. Aoyama, M. R. Caira, G. R. Desiraju, J. P. Glusker, A. D. Hamilton, R. E. Meléndez and A. Nangia, Springer Berlin Heidelberg, Berlin, Heidelberg, 1998, vol. 198, pp. 163–208.
151. J. D. Dunitz, in *Perspectives in Supramolecular Chemistry*, ed. G. R. Desiraju, John Wiley & Sons, Ltd., Chichester, UK, 2007, pp. 1–30.
152. B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658.
153. N. M. Ahmad, *ChemInform*, , DOI:10.1002/chin.200836252.

154. L. Bouteiller, O. Colombani, F. Lortie and P. Terech, *J. Am. Chem. Soc.*, 2005, **127**, 8893–8898.
155. T. Pinault, B. Isare and L. Bouteiller, *Chem. Eur. J. of Chem. Phys.*, 2006, **7**, 816–819.
156. F. García, P. A. Korevaar, A. Verlee, E. W. Meijer, A. R. A. Palmans and L. Sánchez, *Chem. Commun.*, 2013, **49**, 8674.
157. M. J. Hollamby, K. Aratsu, B. R. Pauw, S. E. Rogers, A. J. Smith, M. Yamauchi, X. Lin and S. Yagai, *Angew. Chem. Int. Ed.*, 2016, **55**, 9890–9893.
158. C. Kulkarni, P. A. Korevaar, K. K. Bejagam, A. R. A. Palmans, E. W. Meijer and S. J. George, *J. Am. Chem. Soc.*, 2017, **139**, 13867–13875.
159. Q. Wang, W.-W. Zhang, C. Zheng, Q. Gu and S.-L. You, *J. Am. Chem. Soc.*, 2021, **143**, 114–120.
160. N. Saito, K. Kanie, M. Matsubara, A. Muramatsu and M. Yamaguchi, *J. Am. Chem. Soc.*, 2015, **137**, 6594–6601.
161. (a) H. Sugiura, Y. Nigorikawa, Y. Saiki, K. Nakamura and M. Yamaguchi, *J. Am. Chem. Soc.*, 2004, **126**, 14858–14864, (b) H. Sugiura and M. Yamaguchi, *Chem. Lett.*, 2007, **36**, 58–59, (c)H. Sugiura, R. Amemiya and M. Yamaguchi, *Chem. Asian J.*, 2008, **3**, 244–260.
162. N.Saito, *Hierarchical Bottom-Up Methodology for Integrating Dynamic Ethynylhelicene Oligomers*, Springer Japan, Tokyo, 2013.
163. (a) K. Van, T. Norisuye and A. Teramoto, *Molecular Crystals and Liquid Crystals*, 1981, **78**, 123–134. (b) K. Van and A. Teramoto, *Polym J*, 1982, **14**, 999–1005. (c) Teramoto, K. Yoshiba, N. Nakamura, J. Nakamura and T. Sato, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 2001, **365**, 373–380. (d) K. Yoshiba, A. Teramoto, N. Nakamura and T. Sato, *Macromolecules*, 2003, **36**, 2108–2113. (e) R. Valluzzi and D. L. Kaplan, *Biopolymers*, 2000, **53**, 350–362. (f) R. Valluzzi and D. Kaplan, *Macromolecules*, 2003, **36**, 3580–3588. (h) J. Huang, P. Cebe and D. L. Kaplan, *Macromol. Rapid Commun.*, 2009, **30**, 336–344.
164. (a) G. Zanchetta, *Liquid Crystals Today*, 2009, **18**, 40–49. (b) J. E. Lydon, *Liquid Crystals Today*, 2003, **12**, 1–9. (c) F. Livolant and A. Leforestier, *Progress in Polymer Science*, 1996, **21**, 1115–1164. (d) G. Zanchetta, F. Giavazzi, M. Nakata, M. Buscaglia, R. Cerbino, N. A. Clark and T. Bellini, *Proc. Natl. Acad. Sci. U.S.A.*, 2010, **107**, 17497–17502. (e) G. Zanchetta, T. Bellini, M.

Nakata and N. A. Clark, *J. Am. Chem. Soc.*, 2008, **130**, 12864–12865. (f) M. Nakata, G. Zanchetta, B. D. Chapman, C. D. Jones, J. O. Cross, R. Pindak, T. Bellini and N. A. Clark, *Science*, 2007, **318**, 1276–1279. (g) T. E. Strzelecka, M. W. Davidson and R. L. Rill, *Nature*, 1988, **331**, 457–460. (h) E. Senechal, G. Maret and K. Dransfeld, *International Journal of Biological Macromolecules*, 1980, **2**, 256–262.

165. (a) M. K. Okajima, D. Kaneko, T. Mitsumata, T. Kaneko and J. Watanabe, *Macromolecules*, 2009, **42**, 3057–3062. (b) S. Inatomi, Y. Jinbo, T. Sato and A. Teramoto, *Macromolecules*, 1992, **25**, 5013–5019.
166. (a) D. Popp, A. Yamamoto, M. Iwasa and Y. Maéda, *Biochemical and Biophysical Research Communications*, 2006, **351**, 348–353. (b) T. Oda, K. Makino, I. Yamashita, K. Namba and Y. Maéda, *Biophysical Journal*, 1998, **75**, 2672–2681. (c) R. Furukawa, R. Kundra and M. Fechheimer, *Biochemistry*, 1993, **32**, 12346–12352. (d) A. Suzuki, T. Maeda and T. Ito, *Biophysical Journal*, 1991, **59**, 25–30. (e) A. Kerst, C. Chmielewski, C. Livesay, R. E. Buxbaum and S. R. Heidemann, *Proc. Natl. Acad. Sci. U.S.A.*, 1990, **87**, 4241–4245. (f) J. Newman, N. Mroczka and K. L. Schick, *Macromolecules*, 1989, **22**, 1006–1008.
167. (a) A. El-ghayoury, L. Douce, A. Skoulios and R. Ziessel, *Angewandte Chemie International Edition*, 1998, **37**, 2205–2208. (b) L. Douce and R. Ziessel, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 2001, **362**, 133–145.
168. (a) S. Sasaki, K. Tokuma and I. Uematsu, *Polymer Bulletin*, 1983, **10**, 539–546. (b) C.-C. Yen, Y. Taguchi, M. Tokita and J. Watanabe, *Macromolecules*, 2008, **41**, 2755–2758. (c) C.-C. Yen, Y. Taguchi, M. Tokita and J. Watanabe, *Molecular Crystals and Liquid Crystals*, 2010, **516**, 91–98.
169. J. Matern, K. K. Kartha, L. Sánchez and G. Fernández, *Chem. Sci.*, 2020, **11**, 6780–6788.
170. A. Langenstroer, K. K. Kartha, Y. Dorca, J. Droste, V. Stepanenko, R. Q. Albuquerque, M. R. Hansen, L. S´anchez and G. Fern´andez, *J. Am. Chem. Soc.*, 2019, **141**, 5192–5200.
171. N. K. Allampally, M. J. Mayoral, S. Chansai, M. C. Lagunas, C. Hardacre, V. Stepanenko, R. Q. Albuquerque and G. Fern´andez, *Chem.–Eur. J.*, 2016, **22**, 7810–7816.
172. G. Ghosh, T. Ghosh and G. Fern'andez, *Chem Plus Chem*, 2020, **85**, 1022–1033.
173. Y. Chen, C.-M. Che and W. Lu, Chem. Commun., 2015, 51, 5371–5374.

174. W. Wagner, M. Wehner, V. Stepanenko, S. Ogi and F. Wurthner, *Angew. Chem., Int. Ed.*, 2017, **56**, 16008–16012.
175. H. Wang, Y. Zhang, Y. Chen, H. Pan, X. Ren and Z. Chen, *Angew. Chem., Int. Ed*., 2020, **59**, 5185–5192.
176. Z. Wang, J. Pan, Q. Li, Y. Zhou, S. Yang, J.-J. Xu and D. Hua, *Adv. Funct. Mater*., 2020, **30**, 2000220
177. S. Ogi, V. Stepanenko, K. Sugiyasu, M. Takeuchi and F. Würthner, *J. Am. Chem. Soc*., 2015, **137**, 3300–3307.
178. A. Langenstroer, Y. Dorca, K. K. Kartha, M. J. Mayoral, V. Stepanenko, G. Fern´andez and L. S´anchez, *Macromol. Rapid Commun*., 2018, **39**, 1800191.
179. Z. Chen, Y. Liu, W. Wagner, V. Stepanenko, X. Ren, S. Ogi and F. Würthner, *Angew. Chem., Int. Ed.*, 2017, **56**, 5729–5733.
180. S. Ogi, V. Stepanenko, J. Thein and F. Würthner, *J. Am. Chem. Soc*., 2016, **138**, 670–678.
181. Y. Liu, Y. Zhang, F. Fennel, W. Wagner, F. Würthner, Y. Chen and Z. Chen, *Chem. Eur. J*., 2018, **24**, 16388–16394.
182. K. Aratsu, R. Takeya, B. R. Pauw, M. J. Hollamby, Y. Kitamoto, N. Shimizu, H. Takagi, R. Haruki, S.-I. Adachi and S. Yagai, *Nat. Commun*., 2020, **11**, 1623.
183. A. Suzuki, K. Aratsu, S. Datta, N. Shimizu, H. Takagi, R. Haruki, S.-I. Adachi, M. Hollamby, F. Silly and S. Yagai, *J. Am. Chem. Soc*., 2019, **141**, 13196–13202.
184. S. Yagai, M. Yamauchi, A. Kobayashi, T. Karatsu, A. Kitamura, T. Ohba and Y. Kikkawa, *J. Am. Chem. Soc*., 2012, **134**, 18205–18208.
185. S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu and M. Takeuchi, *Nat. Chem*., 2014, **6**, 188–195.
186. J. S. Valera, R. G´ omez and L. S´anchez, *Small*, 2017, **14**, 1702437.
187. T. Fukui, N. Sasaki, M. Takeuchi and K. Sugiyasu, *Chem. Sci.*, 2019, **10**, 6770–6776.
188. A. Langenstroer, K. K. Kartha, Y. Dorca, J. Droste, V. Stepanenko, R. Q. Albuquerque, M. R. Hansen, L. S´anchez and G. Fern´andez, *J. Am. Chem. Soc*., 2019, **141**, 5192–5200.
189. (a) Y. Kubota, S. Tanaka, K. Funabiki and M. Matsui, *Org. Lett*., 2012, **14**, 4682–4685; (b) Z. Wu, J. Sun, Z. Zhang, H. Yang, P. Xue and R. Lu, *Chem. – Eur. J*., 2017, **23**, 1901–1909; (c) Z. Yu, Y. Wu, L. Xiao, J. Chen, Q. Liao, J. Yao and H. Fu, *J. Am. Chem. Soc*., 2017, **139**, 6376–6381; (d) H. Shimogawa, Y. Murata and A. Wakamiya, *Org. Lett.*, 2018,

20, 5135–5138; (e) N. Zhao, C. Ma, W. Yang, W. Yin, J. Wei and N. Li, *Chem. Commun.*, 2019, **55**, 8494–8497; (f) J. M. Wong, R. Zhang, P. Xie, L. Yang, M. Zhang, R. Zhou, R. Wang, Y. Shen, B. Yang, H.-B. Wang and Z. Ding, *Angew. Chem., Int. Ed.*, 2020, **59**, 17461–17466; (g) S. Ohtani, M. Nakamura, M. Gon, K. Tanaka and Y. Chujo, *Chem. Commun*., 2020, **56**, 6575– 6578.

190. (a) D. Li, H. Zhang and Y. Wang, *Chem. Soc. Rev.*, 2013, **42**, 8416. (b) D. Frath, J. Massue, G. Ulrich and R. Ziessel, *Angew. Chem. Int. Ed.*, 2014, **53**, 2290–2310.
191. H. Lu, J. Mack, Y. Yang and Z. Shen, *Chem. Soc. Rev.*, 2014, **43**, 4778–4823.
192. (a) D. Tian, F. Qi, H. Ma, X. Wang, Y. Pan, R. Chen, Z. Shen, Z. Liu, L. Huang and W. Huang, *Nat Commun*, 2018, **9**, 2688. (b) H. Wang, Y. Zhang, Y. Chen, H. Pan, X. Ren and Z. Chen, *Angew. Chem. Int. Ed.*, 2020, **59**, 5185–5192.
193. I. Helmers, G. Ghosh, R. Q. Albuquerque and G. Fernández, *Angew. Chem. Int. Ed.*, 2021, **60**, 4368–4376.
194. R. A. Nathan, R. E. Schwerzel, A. H. Adelman and R. E. Wyant, *Solar Energy Collection and Retrieval Employing Reversible Photochemical Isomerization*, U.S. Pat. n.d., 4004572, 1977
195. R. J. Das and K. Mahata, *Org. Lett.*, 2018, **20**, 5027–5031.
196. R. J. Das and K. Mahata, *Soft Matter*, 2019, **15**, 5282–5286.
197. I. Debnath, T. Roy, J. Matern, S. A. H. Jansen, G. Fernández and K. Mahata, *Org. Chem. Front.*, 2021, **8**, 5432–5439.
198. M. R. Caira, in *Design of Organic Solids*, eds. E. Weber, Y. Aoyama, M. R. Caira, G. R. Desiraju, J. P. Glusker, A. D. Hamilton, R. E. Meléndez and A. Nangia, Springer Berlin Heidelberg, Berlin, Heidelberg, 1998, vol. 198, pp. 163–208.
199. H. Leonhardt and A. Weller, *Berichte der Bunsengesellschaft für physikalische Chemie*, 1963, **67**, 791–795.
200. D. P., *Journal of Molecular Structure*, 1976, **33**, 154–155.H. Masuhara and N. Mataga, *Acc. Chem. Res.*, 1981, **14**, 312–318.
201. N. Mataga, *Pure and Applied Chemistry*, 1984, **56**, 1255–1268.
202. T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, 1980, 694–695.
203. S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1983, **105**, 1386–1387.

204. S. L. Mattes and Samir. Farid, *J. Am. Chem. Soc.*, 1986, **108**, 7356–7361.
205. R. Gould, R. H. Young, R. E. Moody and S. Farid, *J. Phys. Chem.*, 1991, **95**, 2068–2080.
206. H. Kobashi, S. Okabe, Y. Ohsugi and H. Shizuka, *BCSJ*, 1990, **63**, 2173–2182.
207. H. Kobashi, M. Funabashi, T. Kondo, T. Morita, T. Okada and N. Mataga, *BCSJ*, 1984, **57**, 3557–3565.
208. H. Kobashi, H. Suto and H. Shizuka, *BCSJ*, 1990, **63**, 1441–1446.
209. J. W. Verhoeven, H. J. van Ramesdonk, M. M. Groeneveld, A. C. Benniston and A. Harriman, ChemPhysChem, 2005, **6**, 2251–2260.
210. T. V. Duncan, T. Ishizuka and M. J. Therien, *J. Am. Chem. Soc.*, 2007, **129**, 9691–9703.
211. M. Di Valentin, A. Bisol, G. Agostini, A. L. Moore, T. A. Moore, D. Gust, R. E. Palacios, S. L. Gould and D. Carbonera, *Molecular Physics*, 2006, **104**, 1595–1607.
212. G. Jones and L. N. Lu, *J. Org. Chem.*, 1998, **63**, 8938–8945.
213. G. Jones and V. I. Vullev, *Org. Lett.*, 2002, **4**, 4001–4004.
214. A. Knorr, E. Galoppini and M. A. Fox, *J. Phys. Org. Chem.*, 1997, **10**, 484–498.
215. M. A. Fox and E. Galoppini, *J. Am. Chem. Soc.*, 1997, **119**, 5277–5285.
216. E. Galoppini and M. A. Fox, *J. Am. Chem. Soc.*, 1996, **118**, 2299–2300.
217. T. Morita and S. Kimura, *J. Am. Chem. Soc.*, 2003, **125**, 8732–8733.
218. S. Yasutomi, T. Morita, Y. Imanishi and S. Kimura, *Science*, 2004, **304**, 1944–1947.
219. Y. K. Shin, M. D. Newton and S. S. Isied, *J. Am. Chem. Soc.*, 2003, **125**, 3722–3732.
220. G. Jones, D. Yan, J. Hu, J. Wan, B. Xia and V. I. Vullev, *J. Phys. Chem. B*, 2007, **111**, 6921–6929.
221. H.-J. Wolff, D. Burssher and U. E. Steiner, *Pure and Applied Chemistry*, 1995, **67**, 167–174.
222. E. Vauthey and D. Phillips, *Chemical Physics*, 1990, **147**, 421–430.
223. G. Rabassa, *World Literature Today*, 2005, **79**, 37.
224. T. L. Netzel, *Tetrahedron*, 2007, **63**, 3491–3514.
225. C. Reichardt, *Pure and Applied Chemistry*, 2004, **76**, 1903–1919.
226. J. Wan, A. Ferreira, W. Xia, C. H. Chow, K. Takechi, P. V. Kamat, G. Jones and V. I. Vullev, *Journal of Photochemistry and Photobiology A: Chemistry*, 2008, **197**, 364–374.
227. A. Nowak-Król, B. Fimmel, M. Son, D. Kim and F. Würthner, Faraday Discuss., 2015, **185**, 507–527.

228. F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat and D. Schmidt, *Chem. Rev.*, 2016, **116**, 962–1052.
229. E. Vauthey, *ChemPhysChem*, 2012, **13**, 2001
230. O. Yushchenko, D. Villamaina, N. Sakai, S. Matile, E. Vauthey, *J. Phys. Chem. C*, 2015, **119**, 14999.
231. V. Markovic, D. Villamaina, I. Barabanov, L.M.L. Daku, E. Vauthey, *Ang. Chem. Int. Ed.*, 2011, **50**, 7596.
232. F. Terenziani, A. Painelli, C. Katan, M. Charlot, M. Blanchard-Desce, *J. Am. Chem. Soc*., 2006, **128**, 15742.
233. B. Dereka, A. Rosspeintner, Z. Li, R. Liska, E. Vauthey, *J. Am. Chem. Soc*., 2016, **138**, 4643.
234. B. Dereka, A. Rosspeintner, M. Krzeszewski, D.T. Gryko, E. Vauthey, *Ang. Chem. Int. Ed.*, 2016, **55**, 15624.
235. B. Dereka, M Koch, E. Vauthey, *Acc. Chem. Res*., 2017, **50**, 426.
236. P. Roy, G. Bressan, J. Gretton, A. N. Cammidge and S. R. Meech, *Angew. Chem.*, 2021, **133**, 10662–10666.