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Solvent Effects in Supramolecular Systems

Raffaello Papadakis and Ioanna Deligkiozi

Abstract

Today it is well-established that solvents demonstrate an important role in chemistry. Solvents are able to affect the reactivity, as well as the electronic, optical, and generally physicochemical properties of compounds in solution. Taking this into account, in this chapter we analyze the importance of solvent polarity in phenomena closely related to supramolecular systems as well as the aptitude of various supramolecules to interact with solvent molecules and thus to give rise to chromic effects such as solvatochromism. Main focus is placed on mechanically interlocked molecules, e.g., rotaxanes, catenanes, etc., exhibiting solvent-controlled shuttling movements, switching, and/or solvatochromism. The effect of solvents in various supramolecular architectures is a further focus of this chapter.

Keywords: solvents, medium responsiveness, supramolecular recognition, solvatochromism, supramolecules, mechanically interlocked molecules, shuttle movements, supramolecular architectures

1. Introduction

Fundamental nature's operations are dominated and regulated by noncovalent interactions. Solvation demonstrates a key role in all these processes as it drastically influences the energetics of host-guest (Ho-G) interactions as well as the supramolecular recognition phenomena. In many occasions solvents can influence and modulate the supramolecular structure of complex systems through various possible interactions with solutes.

In recent years a rapidly increasing interest and development in the field of supramolecular engineering have been observed. Specifically within the scope of modern materials and chemical science, the conducted research is continuously growing [1]. Fundamentally, the target is to create molecular systems by design, intending to regulate the interactions of complex building blocks in the solid and liquid state and to obtain desirable complex systems exhibiting multifunctional properties. Since the recent awarding of the Nobel Prize of chemistry to Jean-Pierre Sauvage, Fraser Stoddart, and Ben Feringa, this area has gained plenty of scientific attention [2]. The microenvironment-dependent complexation of supramolecular complexes provides a conventional tool for creating a vast variety of mechanically interlocked molecules, supramolecular architectures, and molecular machines. Rotaxanes and catenanes, which are at the heart of the development of "molecular machine" chemistry [3], are of principal importance. Under this framework, molecular machines that have been studied until today include molecular motors [4], shuttles [5], muscles [6], pumps [7], elevators [8], etc. Supramolecular chemistry showed an impulsive interest in

molecular-engineered compounds, whereby complexes are formed from small molecular building blocks held together by reversible intermolecular noncovalent interactions such as van der Waals interactions, hydrogen bonding, electrostatic, π - π stacking, and hydrophobic interactions. Their design, control, and function compose new relevant interdisciplinary key enabling areas (KEA) of science and technology. In all these solvents and solvation are demonstrating a fundamentally important role. Ordinarily, solvents are categorized into two main categories cited as polar and nonpolar, whereby their efficacy is often characterized by their dielectric constants. Solvents with a dielectric constant of less than 15 are usually regarded to be nonpolar. Nonpolar solvents contain bonds between atoms with similar electronegativities, such as carbon and hydrogen. Polar solvents have large dipole moments and they comprise bonds between atoms with very different electronegativities, such as oxygen and hydrogen. The aforementioned solvents are additionally divided into polar aprotic and polar protic. The solvation efficacy in a predefined medium plays a key role in thermodynamics and kinetics especially in supramolecular host-guest interactions. This is profoundly correlated to changes in solubility, stability constant, reactivity, redox potential, and some spectral parameters. Host-guest association behaviors can essentially be controlled only by applying diverse solvent system, thus altering by demand their solvation properties. Hence, the solvation environment plays a dynamic role for supramolecular solutes, being able thus to affect the thermodynamics of complex systems. In general, the interactions involved in supramolecular systems are quite weaker than covalent bonds, and thus they can be highly controlled and reversible. Acknowledging the importance of the above, this chapter discusses the impact of solvents in various types of supramolecular systems.

2. Supramolecular recognition

2.1 General aspects

One of the key roles of solvents which are dominant in supramolecular chemistry is their role in supramolecular recognition. This is essential for systems consisting of a host (Ho) and a guest (G) (**Figure 1**). In solution solvent molecules can interact with Ho and G molecules through various types of noncovalent weak interactions, and this process readily affects the mutual interactions between the Ho and G counterparts. Consequently, the thermodynamics of their binding can be significantly altered simply by changing solvents. The most dominant interactions in Ho-G-S system (where S is a solvent) can be electrostatic (i.e., ion-ion, ion-dipole, dipole-dipole, or dipole-induced dipole interactions), H-bonding, van der Waals, or π - π interactions. Inevitably, the type of developed interactions is influenced by the physicochemical properties of the Ho, G, and S molecules [9].

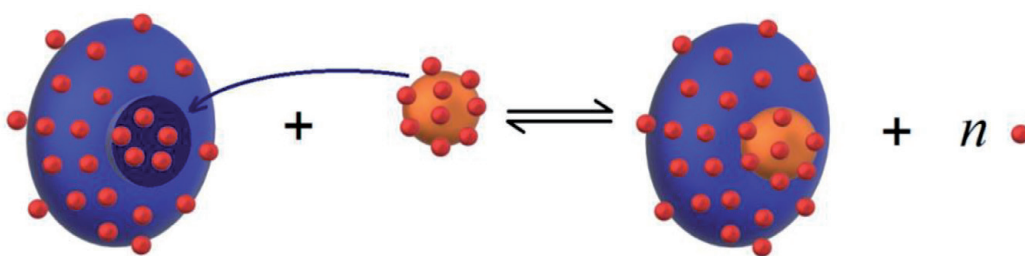


Figure 1. Illustration of the equilibrium of the binding between a solvated Ho (blue) and a solvated G (orange) molecule involving the release of solvent molecules (red).

From a thermodynamic perspective, the simple equilibrium of **Figure 1** is described by the equilibrium (association) constant which is connected to the thermodynamic activities of the Ho, G, and (Ho-G) species, i.e., $K_a = a_{[\text{Ho-G}]} / a_{[\text{Ho}]} \cdot a_{[\text{G}]}$. The association constant is in turn related to the changes in standard Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) upon binding of G to Ho, i.e., $RT \ln K_a = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, where R and T correspond to the ideal gas constant and temperature, respectively. Solvents are capable of influencing the above-described equilibrium by affecting the terms ΔH° and ΔS° [9, 10]. When it comes to Supramolecular Complexation (SC), a general classification of solvents is based on their aptitude to undertake to self-organization. Self-organized (structured) solvents are in general relatively polar solvents, e.g., water, alcohols, amides, etc., whereas the nonstructured are generally less polar, e.g., hydrocarbons, haloalkanes, etc. One might assume that the importance of nonstructured solvents would be minor in supramolecular complexation due to the weaker interaction with the Ho and G molecules; the situation however is much different. Of course highly structured/polar solvents like water exhibit major effects on the complexation of Ho and G. Surprisingly though, dramatic differences in the stabilization of a (Ho-G) complex can be observed when shifting from a haloalkane like chloroform to an aromatic solvent like benzene.

The tremendous impact of solvent polarity on the supramolecular assembling is easily manifested through the following example by Nishimura and coworkers [11]. In their work by employing dynamic covalent chemistry, they managed to develop a complementary capsule-guest supramolecular system (**Figure 2**) behaving very differently in two deuterated solvents of interest: CDCl_3 and C_6D_6 .

Specifically, the thermodynamics of the supramolecular recognition were different in these two solvents with K_a values differing by three orders of magnitude ($K_a(\text{C}_6\text{D}_6) / K_a(\text{CDCl}_3) = 1150$). It was also found that the supramolecular recognition effect was in both solvent cases enthalpy driven. Yet, $\Delta H(\text{kcal/mol})$ was determined to be -18.6 in deuterated benzene and -2.7 in deuterated chloroform which corresponds to a significant thermodynamic solvent effect. Interestingly, Kang and Rebek some years earlier designed and synthesized a dimeric supramolecular guest corresponding to various carboxylic acids such as 1-adamantanecarboxylic acid [12]. Working in the same two deuterated solvents, they discovered a reversed solvent effect (compared to that of Nishimura and coworkers). The supramolecular recognition effect in that case was found to be entropically favored with however two orders of magnitude difference in K_a : ($K_a(\text{CDCl}_3) / K_a(\text{C}_6\text{D}_6) = 243$). Through these stimulating examples, it is easily made understood that solvents have a drastic effect on supramolecular binding/recognition effects [9].

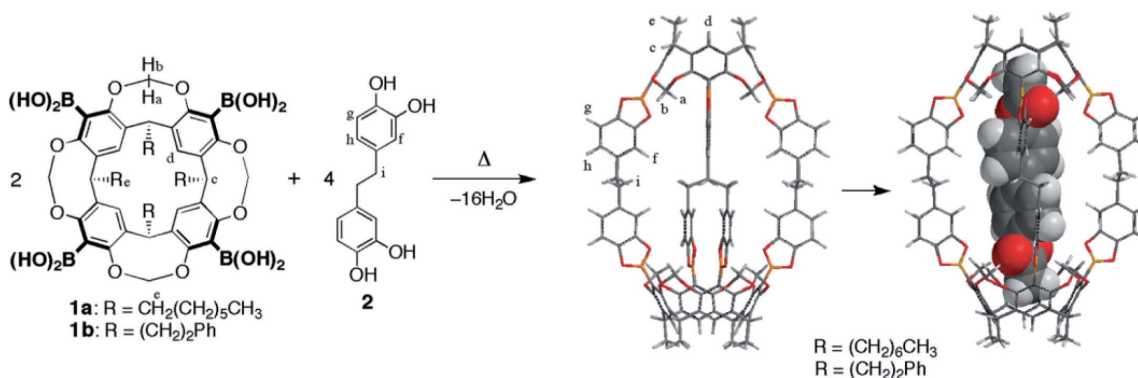


Figure 2.
 Supramolecular assembly exploiting dynamic covalent chemistry. Reprinted with permission from Nishimura and coworkers [11].

Large solvent effects are also encountered in supramolecular complexation (SC) involving ionic and neutral, e.g., hydrophobic, entities. These effects are largely dependent of the nature of the target guest molecule for a given host molecule. Noteworthy, ionic and neutral SC often exhibits opposite solvent polarity dependencies. Two characteristic such examples are the SC of aromatic hydrophobic molecules by a cyclophanes and that of potassium ions by the crown ether 18-crown-6. For instance, Smithrud and Diederich observed five orders of magnitude higher association constant in water compared to the solvent carbon disulfide for a cyclophane/pyrene SC system [13]. The hydrophobic 3D cyclophane developed by Smithrud and Diederich involved a large cavity accessible to solvent molecules, and the huge K_a determined in water was attributed to the solvophobic effect. In simple words pyrene prefers to be encapsulated in the hydrophobic cavity of the cyclophane instead of interacting with water. The effect becomes less and less important as one moves from water to apolar solvents [13]. The opposite effect is observed for the SC of potassium ions by ether 18-crown-6 [14]. In that case the association constant becomes larger in solvents of lower polarity, e.g., $\log K_a$ (H_2O) = 2.0, whereas $\log K_a$ (acetone) = 6.0 [14]. Interestingly, the $\log K_a$ exhibits a linear dependence to the surface tension of the medium as well as to other parameters/properties of solvents [15, 16].

The above-described examples are fundamental for the development of complex supramolecular systems with possibilities of external control and the design of molecular machines. Focus of the next section is the effect of solvents on some characteristic molecular machines and switches.

3. Nano-mechanical motions affected by solvents

3.1 Rotaxanes and catenanes

Rotaxanes, pseudorotaxanes, and catenanes are prominent members of the supramolecular family of compounds. They may be composed of both organic and inorganic (macro)molecules mechanically linked together. One of the latter parts may exhibit the ability to move in relation to the rest of the other parts. Due to this effect, many of these systems have been proposed for molecular machinery applications. In the case of rotaxanes bulky substitutes, the so-called stoppers are integrated in these systems preserving the stability of the supramolecular assembly. Pseudorotaxanes consist of the same structural units as rotaxanes, but do not include the aforementioned stoppering bulky substituents. In contrast, catenanes consist of two or more macrocyclic molecules tied together, forming chain-like supramolecular assemblies (**Figure 3**). The stability in all these systems is achieved through various types of weak interactions such as van der Waals forces, hydrophobic effects, hydrogen bonds, donor acceptor interactions, etc. Today a large number of scientific works have been published following the pioneering synthesis of the first rotaxane by Wasserman in 1960 [17]. Additional scientific support has been provided by a stream of publications by pioneering researchers such as Luttringhaus [18], Wasserman [17], Harrison [19], and Schill [20]. All of them dealt with the creation of functional molecular devices of high complexity and specialization.

Today multiple supramolecular structures have been created through the inclusion of a variety of linear axle-like molecules in the cavities of macromolecules such as crown ethers, cyclophanes, cyclodextrins (CD), etc. In this way numerous supramolecular systems exhibiting diverse one-, two-, and three-dimensional (1D, 2D, and 3D) architectures have been reported. The methodologies leading to catenanes and rotaxanes after assembling and pseudorotaxane formation are illustrated in the schematic representation of **Figure 3**.

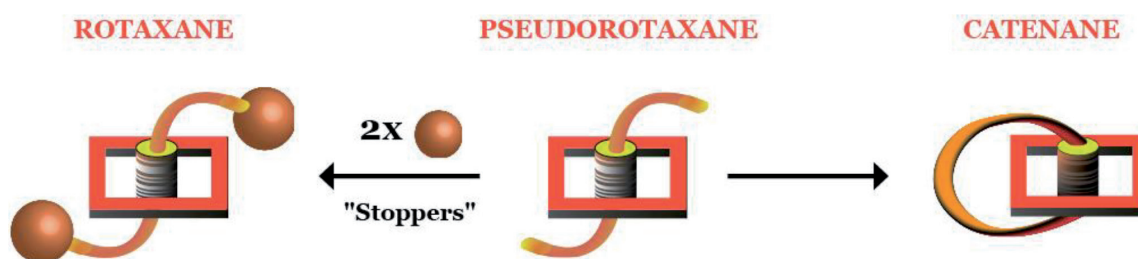


Figure 3.
 From pseudorotaxanes to rotaxanes and catenanes.

3.2 Molecular shuttles

Interlocking a part of a linear molecule of a rotaxane into the cavity of a macrocycle molecule is associated with a series of complex interaction phenomena. An important function that many of the aforementioned systems can undergo is that of molecular shuttling. This often happens when a macrocycle trapped onto a linear component (axle) is capable of moving reversibly between two or more Regions on the axle (often called stations), in response to external stimuli (e.g., electrochemical stimuli, irradiation, heating/cooling, and/or solvent polarity changes) [21].

As already mentioned the main forces that hold these supramolecular structures together are relatively weak, and therefore the systems can undergo the described shuttling movement under mild external changes in a fully controlled manner [21]. Across all the potential driving forces, all the kind of energy inputs, and all aforementioned parameters, it is noteworthy that a simple change in solvent polarity can be harvested in order to induce a controllable molecular machine function (**Figure 4**). In this section the stimulating role of solvents on the function of interlocked systems is reviewed.

One of the key/pioneering contributions in the field of solvent effects on the (multi)functional behavior of rotaxanes has been made by Leigh and coworkers. By applying chemistry similar to that occurring in natural systems and specifically

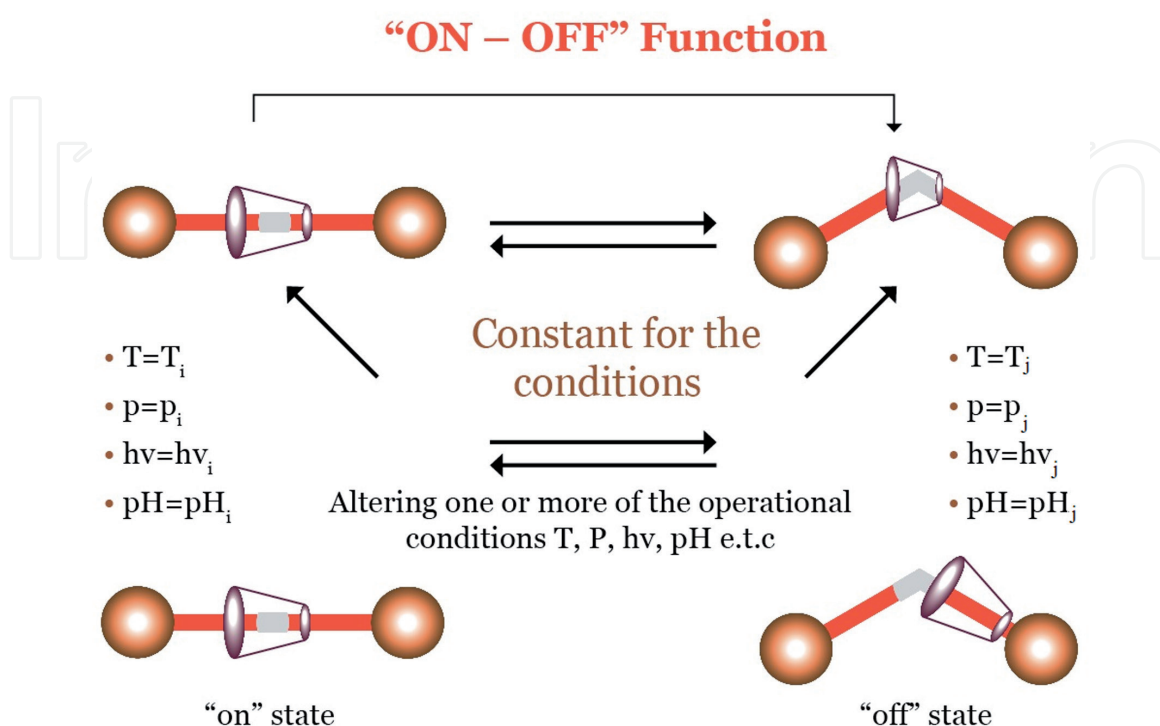


Figure 4.
 Schematic illustration of controllable switching of [2]rotaxanes through external stimuli.

in peptides, they managed to synthesize the rotaxanes of **Figure 5A** [22]. In both cases of rotaxanes of **Figure 5A**, the linear component consists of a glycylglycine chain and two diphenylmethane end groups (stoppers). The stabilization of these [2]rotaxanes is achieved through the development of hydrogen bonds between amide hydrogen of the macrocycle molecule with the carbonyl groups of the linear compound and vice versa. The resulted bonds are very stable when the rotaxanes are dissolved in non polar solvents such as CHCl_3 . However, when they are dissolved in polar solvents such as DMSO which can specifically interact with parts of these molecules, these bonds become unstable, and this results to a different molecular configuration for each of the two [2]rotaxanes. This solvent-driven feature is essential for triggering the switching ability of this supramolecular complex, thus functioning as a molecular machine, and has been a stimulating example for a number of later scientific works.

In 2003 Da Ros et al. published a [2]rotaxane which performs a solvent-induced shuttling movement as shown in **Figure 5B** [23]. This [2]rotaxane consists of fullerene C_{60} group behaving as both a stoppering unit and a photoactive group. The amphiphilic nature of the rotaxane thread was used to shuttle the macrocycle from close to the fullerene spheroid (in nonpolar solvents) to far away (in polar solvents). The rotaxane is based on hydrogen bond-directed assembly of a benzylic amide macrocycle around a dipeptide thread, solvent-switchable molecular shuttles in a similar fashion to the work by Leigh et al. [22]. In nonpolar solvents, e.g., CH_2Cl_2 or CHCl_3 , the macrocycle forms hydrogen bonds with the peptide residue. In polar aprotic solvents such as DMSO, the hydrogen bonding between the macrocycle $>\text{NH}$ group and the peptide carbonyl group is disrupted by the competing solvent interactions, and thus the macrocycle selectively stops over the alkyl chain [23].

In 2005 Gschwind and coworkers published a series of [2]rotaxanes, containing a phenol-involving linear part, amide-involving macrocycles, and triphenylmethane-stoppering units [24]. The dumbbell molecule **1** of **Figure 6** offers three diamide stations to the macrocyclic molecule in the protonated form of the [2]rotaxane. It was found that electrostatic interactions can modulate exceptionally well the speed of the mechanical motion between a fast- and a slow-motion state as a response to a reversible external solvent-provided stimulus. The electrostatic interactions in these rotaxanes are controllably regulated through solvent effects

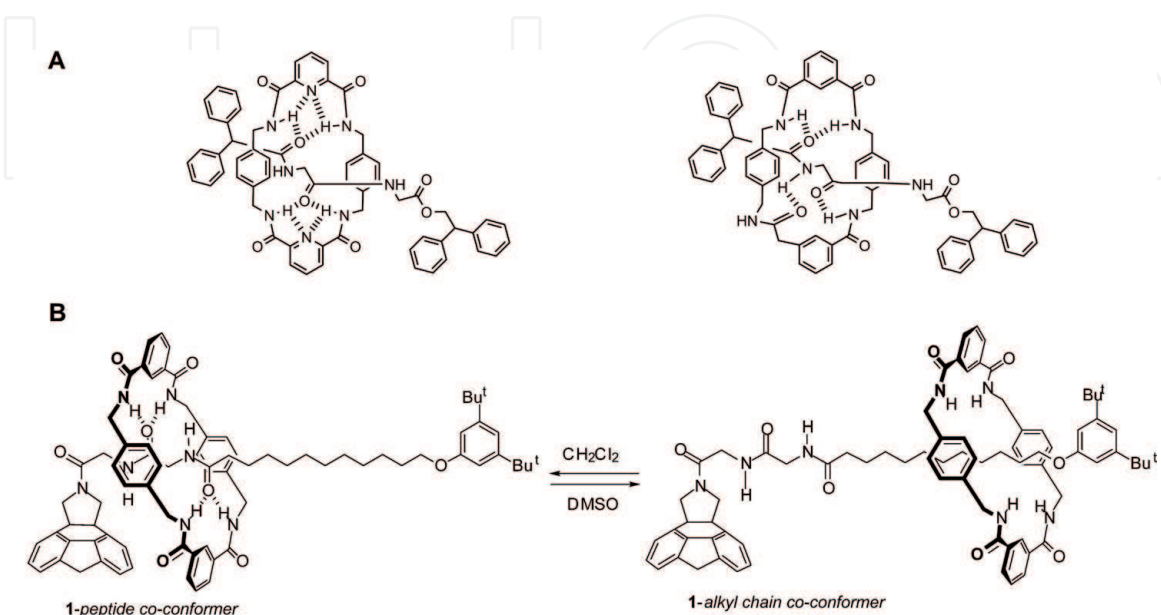


Figure 5. (A) The two rotaxanes by Leigh et al. [22] and (B) the solvent-switchable [2]rotaxane containing C_{60} stoppering unit by Da Ros et al. Reprinted with permission from Da Ros et al. [23].

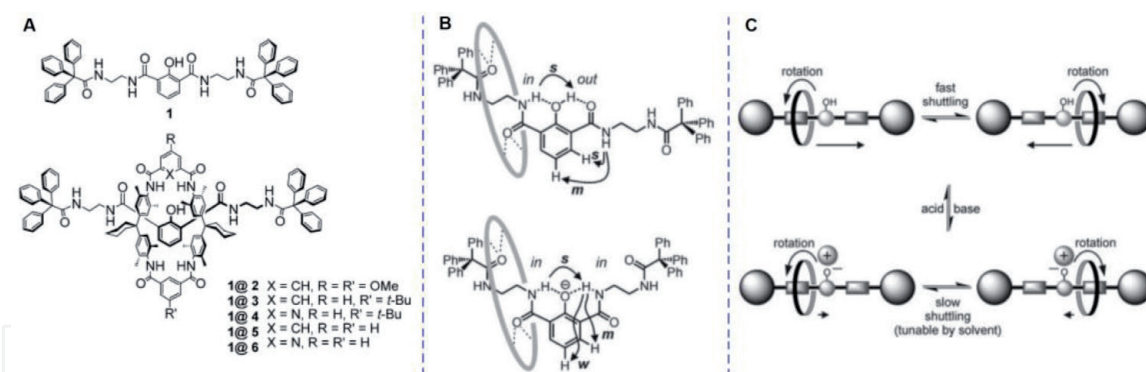


Figure 6. (A) Various [2] rotaxanes by Gschwind and coworkers [24]. (B) Interactions in a [2] rotaxane. (C) Cartoon representation illustrating the dynamic processes in the acid-/base-regulated switching of [2] rotaxanes depicted in (A). Reprinted with permission from Gschwind and coworkers [24].

induced by altering the proportion of polar solvent in a binary solvent mixture. For example, when different amounts of DMSO are added to dichloromethane, solvent-driven shuttling modifications occur (**Figure 6C**). It was further found that the molecular wheel shuttling in deprotonated rotaxanes is hindered by the counter-cation held through electrostatic forces close to the anion at the axle-center region. Thus, the shuttling speed can easily be regulated by addition of acids and bases enabling a fast- and a slow-motion mode parallel to the on-off switching function.

Cai and coworkers have a long-standing interest in the effects of solvents in the shuttling movements in mechanically interlocked compounds [25–27]. In 2012 they reported a [2] rotaxane molecular shuttle controlled by solvent. The rotaxane involved α -cyclodextrin (α -CD), dodecamethylene, and bipyridinium moieties as shown in **Figure 7** [26]. Cai et al. discovered that the molecular shuttling in this [2] rotaxane can be driven by both solvent and temperature changes. They indeed demonstrated the shuttling process of α -CD along the linear thread in solvents of different polarities such as DMSO and H_2O . The energy barrier in water was shown to be 4.0 kcal/mol higher than in DMSO. Water interacts favorably with the bipyridinium moieties, however, negligibly with the alkyl chain, and this yields to a higher free energy barrier in the case of water.

4. Solvatochromic supramolecular systems

4.1 Generalities

Solvatochromism is a well-studied phenomenon occurring in many diverse systems. It is described as the change in color ($\chi\rho\acute{\omega}\mu\alpha$, Greek word for color) induced by solvents. In a broader context, the term solvatochromism covers changes in the electronic (UV-Vis), FTIR, Raman, or EPR spectra induced by solvents [28]. A

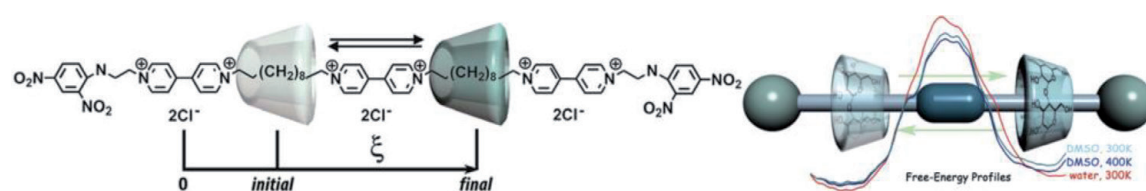


Figure 7. Solvent-induced shuttle movement in a [2] rotaxane. Reprinted with permission from Cai and coworkers [26].

vast number of solvatochromic compounds have been reported to date exhibiting large structural diversity [29]. The most frequently studied class of solvatochromic dyes involves dyes bearing a **D- π -A** structure where **A** is an electron-withdrawing moiety, **D** is an electron-donating group, and π is a conjugated system (often aromatic), separating **A** and **D**. **D- π -A** dyes have recently received much attention as they can be used in hi-tech applications including materials with nonlinear optical (NLO) properties [30, 31], chromotropic sensors and molecular switches [32, 33]. They serve also in many cases as multifunctional building blocks for supramolecular architectures, e.g., in rotaxanes [34]. Some examples of such dyes are depicted in **Figure 8**. The common characteristic of the compounds **I–IV** is that their **D** part (an iodine anion in **I**, a phenolate in **II**, a carbanion in **III**, and an iron(II) cation in **IV**) is capable of transferring an electron pair (in **II** and **III**) or a single electron (in **I** and **IV**) to the electron-deficient positively charged pyridinium ring. The π -system through which the charge transfer occurs is either the aromatic backbone of pyridine itself (the cases of dyes **I**, **III**, and **IV**) or another π -system in conjugation with the pyridine ring (the case of dye **II**). This charge transfer (CT) is induced by light. The required energy of light for the CT transition depends strongly on solvent polarity [28]. Noteworthy, solvent polarity can affect CT energy in various ways. When the increase of medium polarity leads to a drop of the CT energy of a dye, the corresponding effect is called positive solvatochromism. In those cases bathochromic shifts in the electronic spectra of the compound are induced by an increase in solvent polarity (**Figure 9A**). When the opposite effect is observed, the observed phenomenon is called negative solvatochromism (**Figure 9B**). The main focus of this section is the solvatochromism in supramolecular systems.

4.2 Supramolecules involving solvatochromic entities

When conducting a deep literature search, it is easily made obvious that there are not many examples of solvent-switchable supramolecular structures such as rotaxanes and catenanes exhibiting also solvatochromism. As mentioned above, solvatochromic supramolecular assemblies exhibit a strong change in position and sometimes the intensity of their absorption spectra, which is achieved by changing

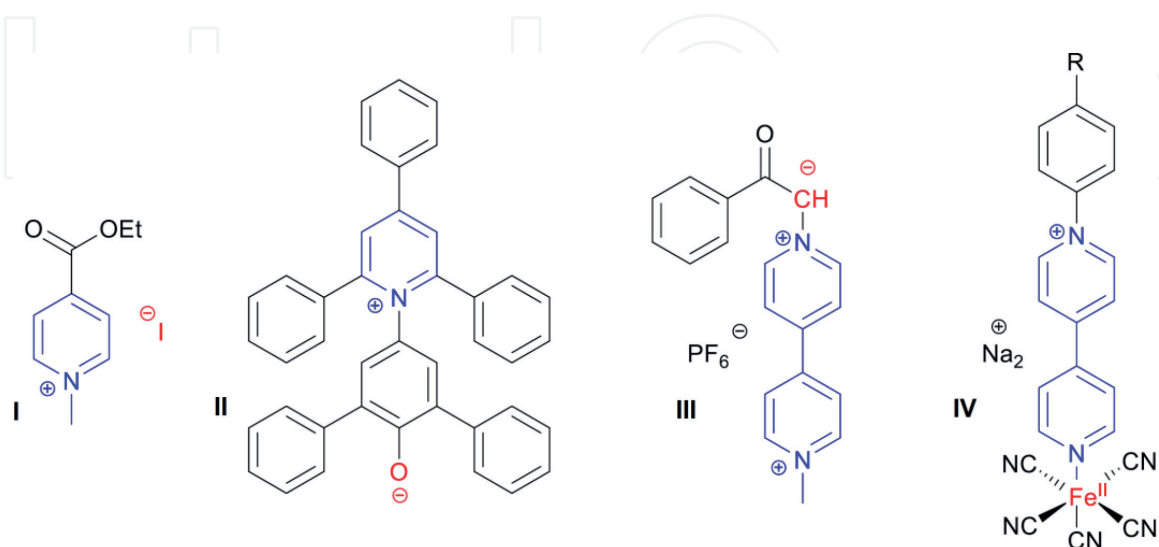


Figure 8. Various pyridinium-based solvatochromic **D- π -A** dyes. **I**, Kosower salt [28]; **II**, Reichardt's betaine [28]; **III**, betaine of *N*-aryl and *N*'-phenacetyl-4,4'-bipyridines [35, 36]; and **IV**, pentacyanoferrate(II) complexes with *N*-aryl-4,4'-bipyridines (monoquats) ligands ($\text{R} = \text{OMe}, \text{Me}, \text{H}, \text{Cl}, \text{Br}, \text{CN}$) [37, 38].



Figure 9. Plots of CT energy as a function of solvent polarity corresponding to (A) positive and (B) negative solvatochromism (G corresponds to ground and E to excited state).

the polarity of the solvent (solvatochromic effect). This phenomenon is pronounced in electron acceptor-donor systems.

An interesting example combining solvent-controlled shuttle movement in a rotaxane (see previous section) and solvatochromic behavior was reported by Günbaş et al. in 2011 (**Figure 10**) [39]. The solvatochromic behavior of their [2] rotaxane and its dumbbell-like precursor molecule was investigated in a variety of solvents of different polarities. It was observed that both compounds exhibited solvatochromic shifts in their absorption spectra when increasing the polarity of the solvent. Spectroscopic data showed a wavelength shift of 575 nm in toluene to 621 nm in DMSO for the molecule which corresponds to a positive solvatochromic shift. The observed values were attributed to the pyrrolidine group. For the [2] rotaxane, however, the solvatochromic changes were smaller. The absorbance was shifted from 608 to 621 nm when the solvent was changed from the nonpolar toluene to the highly polar DMSO. In general, both in the case of the [2] rotaxane and the dumbbell molecule, solvatochromic shifts were observed, indicating that polar solvent interacts stronger with the molecules and also stabilizes the excited state. Of course, this effect is stronger for the dumbbell molecule than for [2] rotaxane, an effect which could be attributed to interactions developed among the chromophore linear molecule and the macrocycle molecule.

In 2007, Toma and his scientific team published a paper in which they disclosed the solvatochromic properties of a [2] rotaxane, which involved a β -cyclodextrin

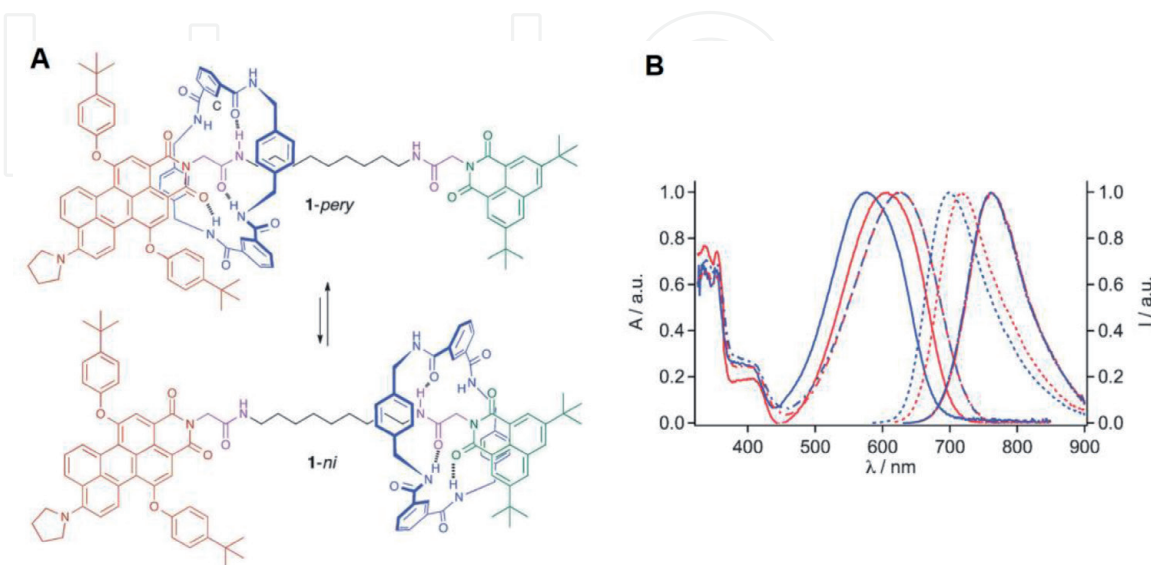


Figure 10. (A) Shuttle movement in a [2] rotaxane and (B) solvatochromic shifts observed. Reprinted with permission from Günbaş et al. [39].

(β -CD) macrocycle [40]. The linear molecule of their rotaxane consisted of *trans*-1,4-di-[(4-pyridyl) ethylene] benzene (**Figure 11**) and *trans* ferrocyanide(II) anions ligated by the pyridyl groups of the linear molecule which act as stoppering groups. The UV-Vis absorption spectral analysis of $\{[\text{Fe}^{\text{II}}(\text{CN})_5]_2(\text{BPEB})\}$ (dumbbell) and the corresponding β -CD-involving rotaxane indicated that the dumbbell molecule exhibited two absorption bands, one around 352 nm and the other at 454 nm.

During the addition of β -CD to the linear molecule solution, a wavelength shift was observed denoting the formation of the [2] rotaxane, which was attributable to the metal-to-ligand charge transfer (MLCT). The formation of [2] rotaxane resulted in a decrease in the energy of MLCT, i.e., a bathochromic shift from 454 to 479 nm. Commonly, the reaction of the iron complex (II) with N-heterocyclic substituents results in deep chromatic shifts of MLCT when the final products are dissolved in less polar solvents. In these systems the hydrophobic forces increase the solvatochromic effect. Thus, for the [2] rotaxane, the low-wavelength shift values are attributed to the inclusion of the β -CD cavity and to the selective solubilization of the rotaxane. This behavior could be related to the stabilization of the energy levels of the complex between β -CD and the ligand leading to a decrease in the energy of MLCT [41].

Various other similar examples of solvation effects on rotaxane have been reported in the literature; one of these examples is the [2] rotaxane reported by Baer and Macartney in 2000 [41]. Cyclodextrin (CD) inclusion complexes with linear guest parts have been studied extensively using a variety of spectroscopic techniques. There have also been several reports of cyclodextrin (α - or β -CD)-based rotaxanes, polyrotaxanes, and catenanes using linear parts (L) containing biphenyl, stilbene, and azobenzene dyes. These [2] rotaxanes can be formed rapidly by the addition of $[\text{Fe}^{\text{II}}(\text{CN})_5]^{3-}$ stoppering units, and a cyclodextrin macrocyclic unit can be threaded by the linear Skeleton. It has been proven that such [2] rotaxanes exhibit intense metal-to-ligand charge transfer (MLCT) transition bands in the visible spectrum. This transition as mentioned above is prone to changes in energy and intensity induced by solvents (solvatochromism). Different ligands acting as the axial parts for series of rotaxanes have been exploited so far such as *trans*-1,2-bis(4-pyridyl) ethylene ligand (BPE, **Figure 12**) which can nicely provide a conjugated bridging of inner sphere and intervalence electron transfer between transition metal centers [42]. The 4,4'-azopyridine ligand (AZP, **Figure 12**) has been employed as a bridging ligand as well mainly for ruthenium amines and porphyrins [43, 44]. The APA and PCA, i.e., 4-acetylpyridine azine and 4-pyridinecarboxaldehyde azine, respectively, are interesting examples of azines which have also been reported as building blocks of [2], rotaxanes of this class [45] (structures depicted in **Figure 12** correspond to some prominent examples of such ligands/linear skeletons). Spectroscopic studies conducted in order to validate the maximum wavelength difference for CD-free

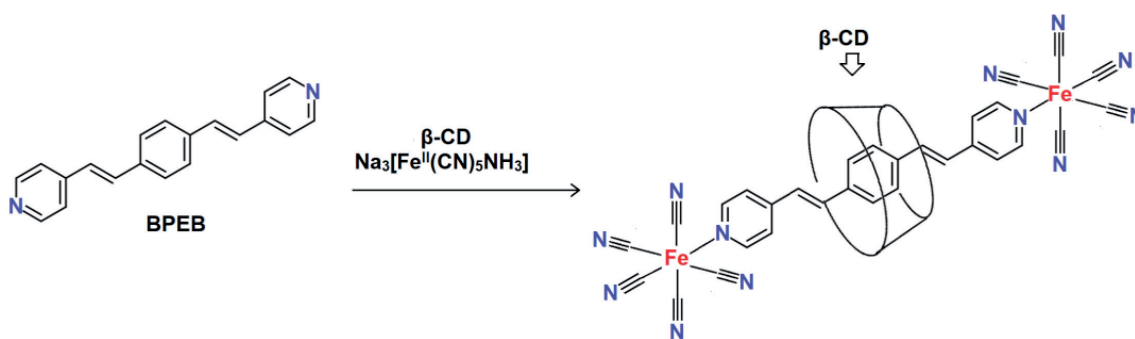


Figure 11. Pioneering solvatochromic [2] rotaxane synthesis by Toma and coworkers [40].

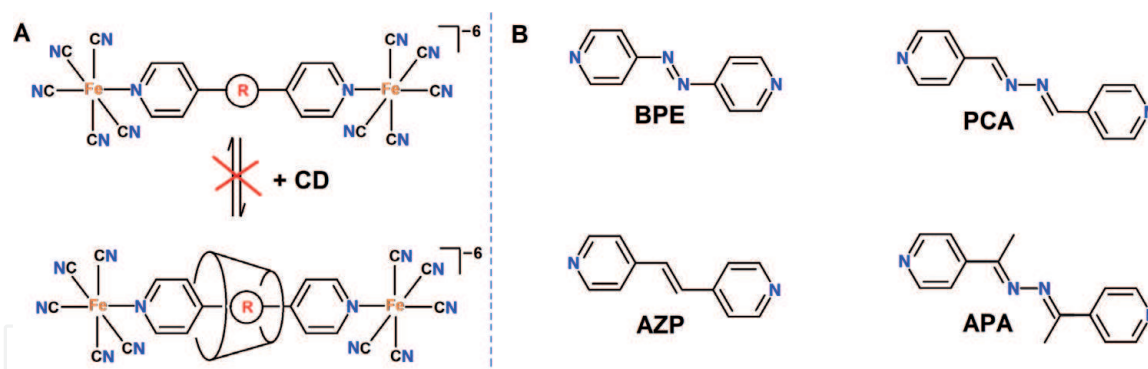


Figure 12. Pyridine-involving ligands BPE, PCA, AZP, and APA (left) and the corresponding dumbbells and cyclodextrin-involving [2]rotaxanes (right).

dumbbells and CD-involving rotaxanes resulted in the following $\lambda_{\text{max}}(\text{nm})$ $\{\text{Fe}(\text{CN})_5\text{L}_3- / (\text{Fe}(\text{CN})_5\{\text{L}, \text{CD}\}_3-)\}$: (i) BPE, 460/496 (α -CD) and 478 (β -CD); (ii) AZP, 596/698 (α -CD) and 644 (β -CD); (iii) PCA 508/536 (α -CD) and 518 (β -CD); and (iv) APA 448/456 (α -CD) and 458 (β -CD). It is evident in all cases that the spectra are affected by the presence of α - or β -CD, resulting in bathochromic shifts in the MLCT band in the visible spectrum. This effect constitutes an important response (of high sensitivity) to the polarity of their environment. This effect is much connected to solvatochromism. Indeed the aptitude of both non-rotaxanated dumbbells and the corresponding rotaxanes to yield solvatochromic shifts is very large [41].

In 2012 Deligkiozi et al. reported the synthesis of a [2]rotaxane consisting of a fully conjugated arylazo-based linear part entrapped in α -cyclodextrin and stoppered by bulky dinitrophenyl end groups [46]. Recording the UV-Vis spectra of both compounds, a broadband in the region 300–400 nm was observed, which was attributed to the π - π^* transition of the group ($-\text{N}=\text{N}-$). Comparing the spectra of the [2]rotaxane and the dumbbell precursor, a bathochromic shift was observed. Specifically, the maximum wavelength of the dumbbell precursor was positioned at 337 nm, whereas that of the [2]rotaxane was centered at 351 nm. This shift is attributed to the interaction of the α -CD cavity and the ($-\text{N}=\text{N}-$) group of the dumbbell-like compound, which causes a decrease in the energy difference between the ground and excited states of the azo-compound leading to bathochromism. Both compounds were found to undergo *E-Z* reversible isomerizations, and in the case of the [2]rotaxane, light-induced shuttle movement was reported [46]. Interestingly the same complexes were found to be photoconductive in the solid state, and this was accredited to the extended π -conjugation in these molecules [47, 48]. These findings enforced the same group to develop a system involving the same π -conjugated backbone, however involving strong electron-donating groups (pentacyanoferrate(II) stoppering groups). This led to the formation of strong **D- π -A** systems (Figure 13) [49]. More recently, Papadakis et al. exploited the solvatochromism of two CD-containing [2]rotaxanes and their CD-free linear precursor in order to investigate preferential solvation (PS) effects in water/ethylene glycol (EG) mixtures [50]. Pentacyanoferrate(II) groups which served as strong electron donors facilitated charge transfer to the viologen electron-deficient parts. It was proven that the pentacyanoferrate(II) units were able to trigger an intense solvatochromic behavior in such systems in neat solvents, solvent mixtures, and other types of aqueous media. In order to study the solvatochromic behaviors, aqueous/ethylene glycol (EG) mixtures were used as the media, and alteration of the polarity was achieved through changing solvent/cosolvent mole ratio. The medium-responsive behavior of these compounds (Figure 13) is mainly pronounced in very polar media such as water, aqueous EG mixtures, and neat EG (see Figure 13).

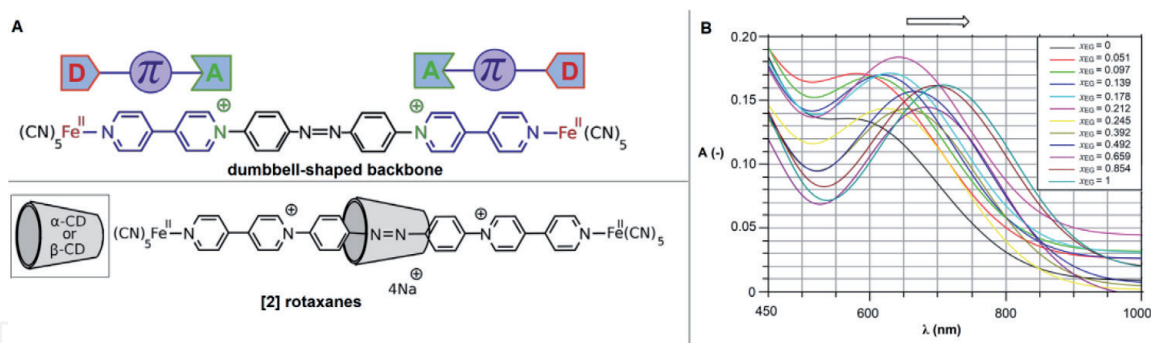


Figure 13.

A) The dumbbell-shaped push-pull backbone developed by Deligkiozi et al. (top) and the corresponding cyclodextrin involving [2]rotaxanes (bottom). B) The bathochromic shifts of the MLCT band of the [2] rotaxane with α -cyclodextrin depicted in A observed in aqueous ethylene glycol mixtures. Reprinted with permission from: [34] and [50].

In some cases rotaxanes and catenanes can also exhibit solvent-dependent emission of light. A representative example is that by Baggerman et al. involving [2]rotaxanes and [3]rotaxanes bearing a tetraphenoxy perylene diimide core [51]. In their work Baggerman et al. observed the influence of hydrogen bonding developed between the amide and the wheel macrocycle of these rotaxanes on the optical behavior of the chromophore (peryene). Specifically, they showed that both absorption and fluorescence spectra are bathochromically shifted upon rotaxanation. All systems including the wheel-free axle (WFA) exhibited fluorosolvatochromism with red shifts of up to 47 nm (WFA case) and a reduced fluorosolvatochromism when going to the [2] rotaxanes and [3] rotaxanes [51]. On the other hand, Boer et al. very recently exploited the solvent-dependent excimer and exciplex emissive behavior of naphthalene diimide metallomacrocycles and catenanes and thus managed to perform a solution speciation of the metallosupramolecular complexes and their solvent-dependent nature [52].

4.3 Supramolecular solvatochromism

Solvatochromism derived by an interaction of solvent molecules with a supramolecular system is characterized by various authors as “supramolecular solvatochromism.” In many cases the systems involve transition metals coordinated to ligands forming supramolecular architectures in which solvent molecules can be trapped or simply interact with parts of the system giving rise to different responses, e.g., in their electronic spectra.

A characteristic early such example is that reported by Lee and Kimizuka in 2002 [53]. In their studies they developed a lipid-packaged 1D supramolecular complex bearing platinum. The anionic lipids acted as counter anions of the positively charged Pt complex. The electronic spectra of the as described supramolecular complex were found to be readily influenced by solvent polarity and that the packaging of the complex is vital for the overall medium-responsive properties. Some years later, Kuroiwa et al. reported on the supramolecular solvatochromism of lipid-packaged, mixed-valence linear platinum complexes (**Figure 14**) which were investigated in dispersions employing the solvents CHCl_3 , chlorocyclohexane, and methylcyclohexane [54]. It was found that solid samples were all indigo-colored but displayed supramolecular thermochromism, attributed to heat-induced dissociation and concomitant recovery of coordination chains. The reassembled supramolecular complexes exhibited color changes depending on the solvent employed, and the CT energy measured was found to decrease as the polarity of the organic medium

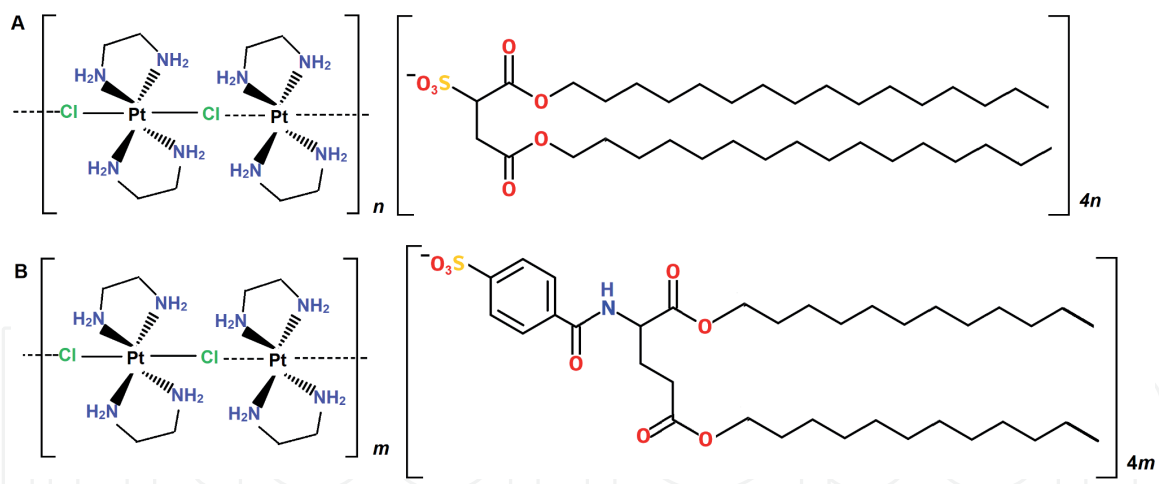


Figure 14.
 Structure of the two Pt(IV) complexes of Kuroiwa et al. [54].

increases following the sequence: methylcyclohexane, benzene, chlorocyclohexane, CHCl_3 , and 1,2-dichloroethane.

Such approaches gain more and more the attention of materials scientist as it could be envisioned that through mixing optical sensors and solvatochromic species or even aggregachromic compounds, the effects of various stimuli on the rheology of viscoelastic gels (VEGs) could be facilitated and this is considered as an important step before the development of new products based on VEGs becomes reality [55]. More recently, Nikolayenko et al. reported the supramolecular solvatochromic behavior of a dinuclear copper(II)-involving metallacycle [56]. The authors exploited the intense solvatochromic behavior of the Cu^{II} complex and the capacity of the macrocycle to trap small solvent molecules like tetrahydrofuran, diethyl ether, and pentane at temperatures well above their boiling points. The latter effect is attributed to the suitable guest shape and size which drastically limit lattice diffusion. Solvent exchange was found to induce intense color changes (**Figure 15B**) and sizable shifts in the visible region of the diffuse reflectance spectra (**Figure 15B**). The high intensity of the supramolecular solvatochromic effect is furthermore excellently illustrated through microphotographs of the variable colors of crystals.

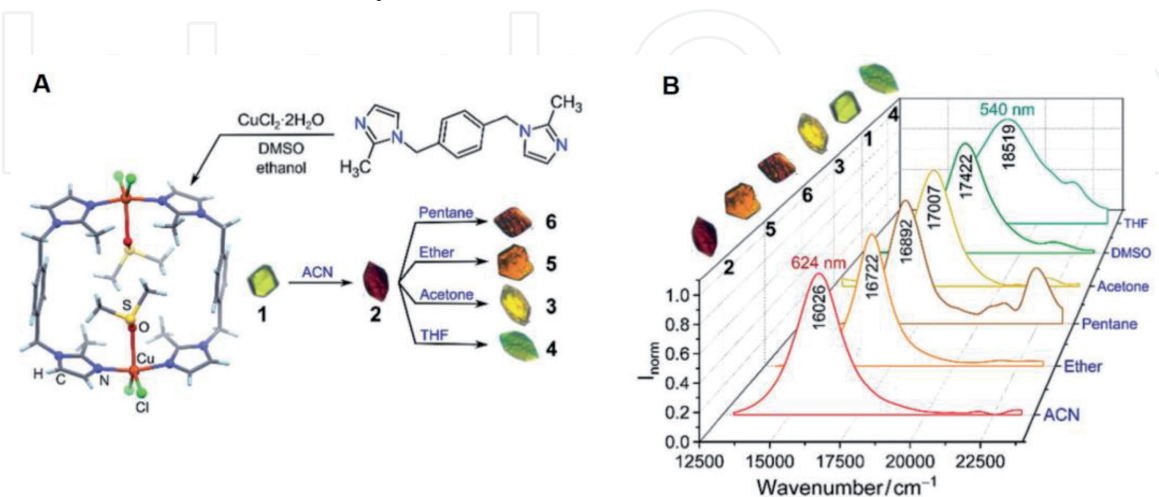


Figure 15.
 A) Synthesis of $[\text{Cu}_2\text{Cl}_4\text{L}_2] \cdot 2\text{DMSO}$ (1) from 1,10-[1,4-phenylenebis(methylene)]bis(2-methyl-1H-imidazole) and copper(II) chloride dihydrate. B) Visible-region diffuse reflectance spectra (bottom) quantitatively illustrate the broad-spectrum (540–624 nm) solvatochromism of 1–6. Reprinted with permission from: Nikolayenko et al. [56].

5. Solvent effects on supramolecular architecture

In the previous sections, the role of solvents in supramolecular functions and processes has been discussed. As described, in those cases solvents are capable of influencing the thermodynamics of supramolecular binding processes as well as the energetics of supramolecular systems so as to induce solvatochromism or some nano-mechanical functions like molecular shuttle movements in rotaxanes and catenanes or other conformational changes.

In this section focus is placed on the effect of solvents in supramolecular architectures. Their regulating role in metallosupramolecular solids has been thoroughly investigated in recent years [57] as well as their aptitude to affect crystal growth and assembly and dynamic transformations. Many solvents especially those bearing N, O, or S atoms exhibit aptitude to coordinate (i.e., to specifically interact) with metals in various coordination complexes, and thus they are capable of forming new complexes. In these complexes solvent molecules can demonstrate a stabilizing role as building blocks and variation of the solvent can lead to alternative molecular architectures. A very nice example illustrating this ability of solvents is that of the assembly of the ligand 1,4-benzene dicarboxylic acid (*bda*) with Mg^{II} in the solvents dimethyl acetamide (DMA), EtOH, and dimethylformamide (DMF). In the case of DMA, polymeric 2D layers (**Figure 16a**) of the type $[\text{Mg}_3(\text{bda})_3(\text{DMA})_4]_n$ are obtained. The situation is very different when EtOH or DMF are used as solvents.

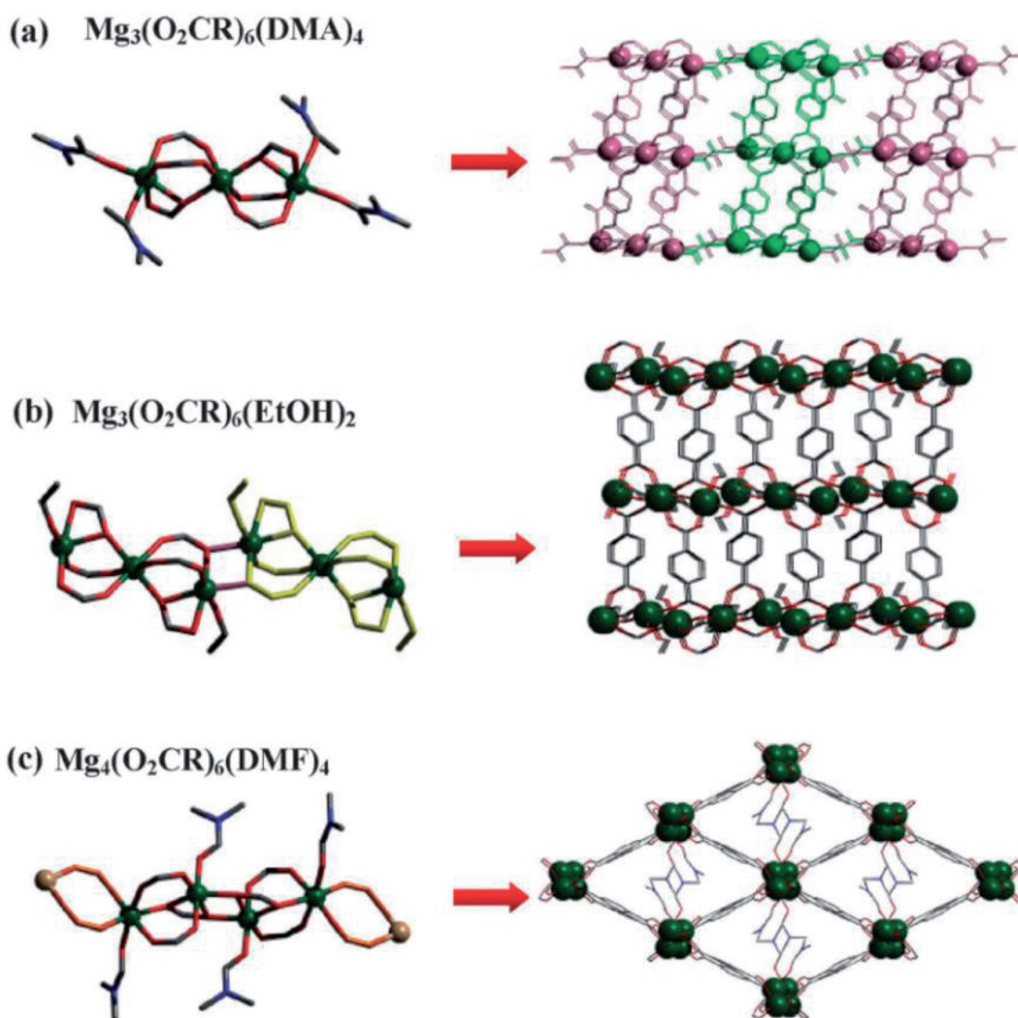


Figure 16.

Different supramolecular architectures involving Mg^{II} , the ligand *bda* and one of the solvents DMA (a), EtOH (b), and DMF (c). Reprinted with permission from: Li et al. [57].

In the latter two cases, 3D frameworks are obtained instead of the following: $[\text{Mg}_3(\text{bda})_3(\text{EtOH})_2]_m$ and $[\text{Mg}(\text{bda})(\text{DMF})]_k$, respectively (**Figure 16b,c**). Note that n , m , and k correspond to the number of repeated units in each case [58–60].

Another important feature of the solvents which readily affects the supramolecular architecture of coordination complexes is the steric effect they might introduce. Noro et al. reported the steric effect of different solvents with sp^1 -, sp^2 -, or sp^3 -hybridized coordinating atoms on the assembly of $\text{Cu}^{\text{II}}(\text{PF}_6)_2$ and the ligand 1,2-bis(4-pyridyl)ethane (*bpe*) [61]. As depicted in **Figure 17A**, solvents with sp^1 - or sp^2 -hybridized coordinating atoms such as MeCN (sp^1 N) and DMF or acetone (sp^2 O carbonyl atom) are able to directly ligate Cu^{II} . The coordination of the solvents in these two cases happens axially with a Jahn-Teller distortion. On the other hand, alcohols, THF, and dioxane (which all have sp^3 O atoms) preferably form H-bonds with the H-atoms of coordinated water molecules already coordinated at the axial positions. This stimulating divisibility is achieved through the variation of the steric effect introduced by different solvents.

Synergistic solvent effects can also drastically influence the structure of supramolecular coordination polymers illustrated in 3D pillar-layered coordination polymers prepared by Wang et al. [62]. These complexes comprise Co^{II} metal centers and *meso*- α,β -bi(4-pyridyl)glycol (*bpg*) and azide (N_3^-) ligands. Their general formula is $[\text{Co}(\text{bpg})(\text{azide})_2]_n$ (S represents a solvent and x the corresponding stoichiometric number), and they are prepared through a reaction of Co^{II} , azide, and *bpg* in the following solvent mixtures: MeOH– H_2O , DMSO– H_2O , and DMF– H_2O . The use of different solvent systems was found to drastically influence the 2D $[\text{Co}(\text{azide})_2]_m$ layers involved in the 3D networks. In the case of the protic mixture MeOH–water, a square net was observed without incorporation of solvent. On the other hand from DMSO– H_2O and DMF– H_2O , the aforementioned 2D layers obtained were of honeycomb and *kagomé* geometry, respectively, and solvent molecules were incorporated in the 3D polymers (DMSO and DMF, respectively) (see **Figure 17B**) [62].

Moreover, the protic or aprotic nature of the solvent can have a significant impact on the crystal structures of coordination compounds. A characteristic example is that of $\text{Mn}(\text{OAc})_2$ and its complexation with the ligand 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazole (*ppt*). The use of binary solvent mixtures involving a protic and an aprotic solvent (viz., DMF–EtOH and toluene–MeOH) or neat MeCN led to three different 2D systems according to Lin et al. [63]. What is noteworthy is that in the case of MeCN (aprotic) as a solvent, the obtained supramolecular system did not incorporate any solvent molecule: $[\text{Mn}(\text{ppt})_2]_n$. Strikingly, in the case of the aforementioned binary solvent mixtures, two supramolecular 2D polymers involving the corresponding

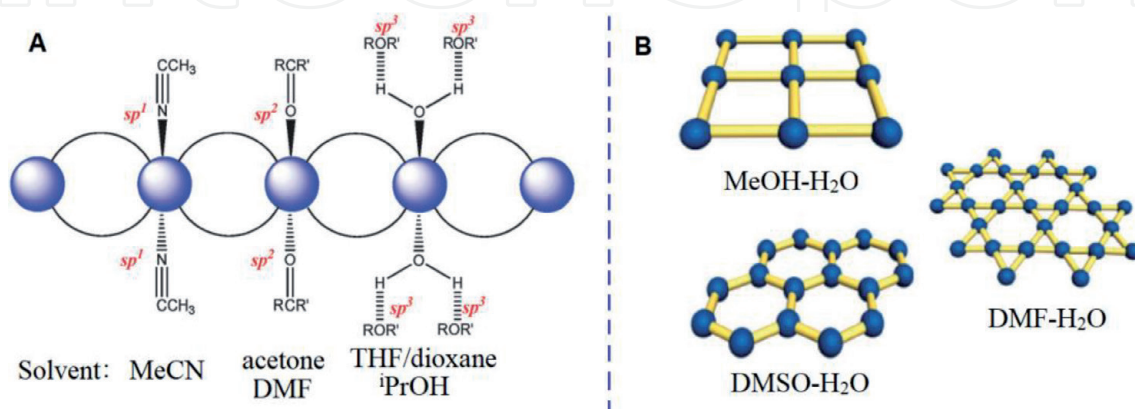


Figure 17.
 A) Illustration depicting the steric effect introduced by various types of solvents in the polymeric supramolecular architecture involving Cu^{II} and *bpe*. B) Three different 2D polymeric $[\text{Co}(\text{azide})_2]_m$ layers involved in the complexes obtained by Wang et al. [62] Reprinted with permission from: Li et al. [57].

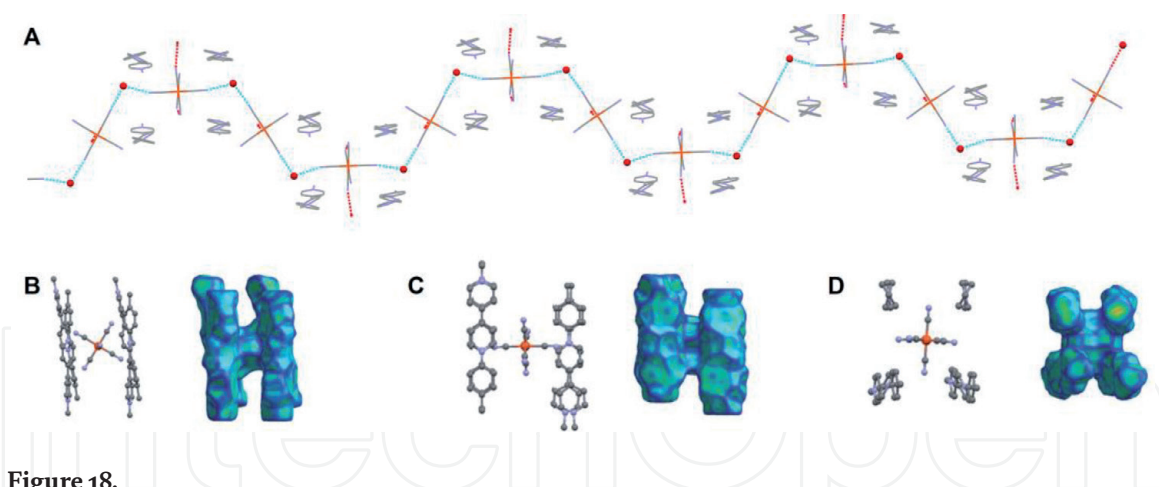


Figure 18.

(A) The zigzag $(\cdots\text{HOH}\cdots\text{HCF}\cdots)_n$ polymers involved in a viologen/HCF CTC reported by Papadakis et al. (hydrogen atoms have been omitted). A cluster consisting of four viologen molecules around a HCF anion and the corresponding Hirshfeld surface representations shown along the b-(B), a-(C) and c-(D) axis. Reprinted with permission from: Papadakis et al. [65].

solvents were obtained: $[\text{Mn}(\text{ppt})_2(\text{DMF})_{1/2}(\text{H}_2\text{O})_3]_m$ and $[\text{Mn}(\text{ppt})_2(\text{toluene})_{1/2}(\text{MeOH})_{3/2}]_k$, respectively. This interesting phenomenon was attributed to the fact that when only an aprotic solvent is utilized, the neighboring 2D polymer grid-sheets in $[\text{Mn}(\text{ppt})_2]_n$ are stacked in a staggered mode, and this leads to a very compact 3D structure leaving out the solvent molecules. This effect is avoided when a protic solvent is employed as cosolvent [63].

In all above examples, the coordination of solvent molecules to the metal centers was found to affect the structure of the supramolecular coordination systems. Secondary interactions, which were already mentioned, mainly account to the H-bonding of a coordinating solvents and non-coordinating cosolvent. There are several cases however where secondary interactions alone can lead to stabilized 3D supramolecular coordination structures. The supramolecular charge transfer complexes (CTCs) of viologens with various electron donors have been reported long ago [64]. Such CTCs involving $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ (HCF) as a strong electron donor have been given some attention; however, their supramolecular structure has been scarcely investigated so far. An example pertaining to this category of supramolecular CTCs was recently reported by Papadakis et al. [65]. As depicted in **Figure 18**, the nonsymmetric dicationic viologen molecules tend to aggregate around the anionic HCF donor. However, the stability of a crystalline structure of such a CTC is achieved only if water is introduced in the reaction mixture. Water is found to readily form H-bonds with CN groups of HCF, and this results in the formation of a zigzag 2D polymer of the type: $(\cdots\text{HOH}\cdots\text{HCF}\cdots)_n$. The 3D supramolecular structure comprises the described 2D polymers and cationic channels of viologens perpendicular to these 2D polymers (**Figure 18**). Attempts to remove (by drying) or replace water (employing even another protic solvent) in these structures failed. Apparently the stabilizing interaction in these supramolecular systems is H-bonding which is stronger when H_2O is utilized. The importance of H_2O and the formation of a CTC in a similar fashion have been also reported earlier by Abouelwafa et al. [66]. In the aforementioned example, a symmetric viologen was utilized instead [66].

6. Applications of solvent effects in supramolecular systems

Except of publications that are indicative of scientific activity for furthering the knowledge base, patents are indicative of technology development for commercial

Keyword	Simple	Total
Supramolecular complexes	4682	16,727
Solvatochromism	296	806
Rotaxane/catenane	165	587
Solvatochromic Rotaxanes/catenanes	4	7

Table 1.
Summary of the patent search results.

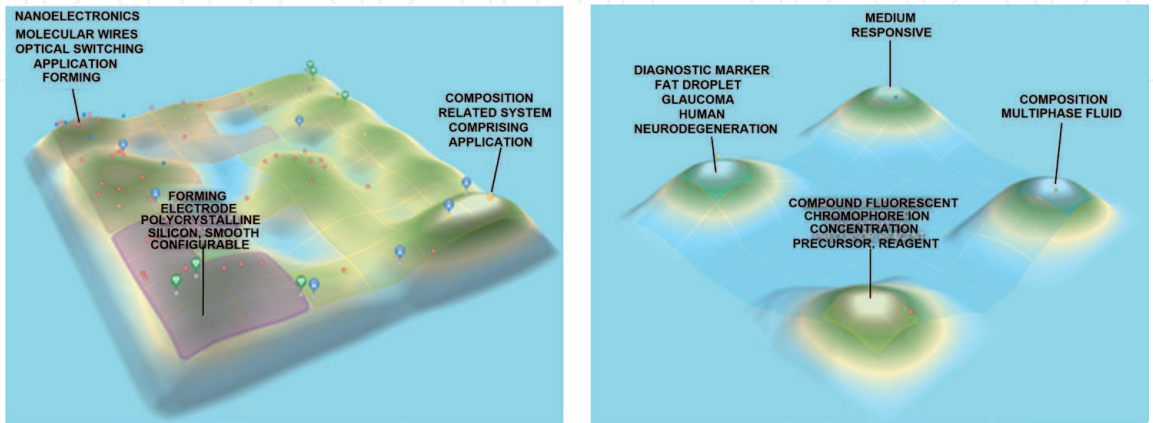


Figure 19.
Patent search results: rotaxane/catenane (left) and solvatochromic rotaxane/catenane (right).

or market potential. On this basis a patent search has been conducted so as to map the transition between science, technology, and market. For this purpose, we used the same parameters for our patent data extraction through Patsnap, a patent search engine and analytic portal. Using this patent search engine, an extended patent search in available patent libraries such as the European Patent Office, USPTO, and FPO was conducted. From this analysis it is evident that the sector supramolecular chemistry has started to grow significantly in recent years. The patent search followed a four-level approach starting by available patents using the following keywords: supramolecular complexes, solvatochromism, rotaxane/catenane, and solvatochromic rotaxane/catenane (**Table 1**). This refinement drives us to the specific market and indicates us the freedom to operate since by this procedure we conclude on the presence of very few patents that are mainly filled in the United States and China. The corresponding landscape is shown in **Figure 19**.

7. Conclusion

In this chapter, we reviewed some important examples of how solvents can influence supramolecular processes and structures. The impact of solvents on supramolecular binding is the starting point through which it is made clear that altering solvent polarity can drastically influence supramolecular binding processes. Solvents can also affect the relative supramolecular conformations of complex systems allowing the development of medium responsive molecular machines and switches. Moreover, solvents can give rise to supramolecular solvatochromic phenomena leading to optical changes and this observation has significantly assisted in the development of solvent (environment) sensing supramolecular systems. Last but not least, various metal ion-involving supramolecular architectures can be drastically influenced by specific solvents or solvent/cosolvent mixtures. This key effect

enables the design of new supramolecular architectures encompassing modulation possibilities based on either the coordination of solvents to metal centers or the secondary interactions between them. In any case, the role of solvents in supramolecular chemistry is obviously enormous. Thus, it is highly important that solvent effects are taken seriously into account when designing new supramolecular systems.

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