

# The Solvent Effect on Weak Interactions in Supramolecular Polymers: Differences between Small Molecular Probes and Supramolecular Polymers

Akiharu Satake\*[a]

[a] Professor Dr., AS, Satake  
Department of Chemistry, Faculty of Science Division II  
Tokyo University of Science  
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan  
E-mail: asatake@rs.tus.ac.jp

**Abstract:** In this minireview, weak interactions that occur in supramolecular polymers are discussed. Combination of weak and strong interactions plays an important role in the construction of supramolecular polymers. It is beneficial to separate the contributions of the weak interactions, as well as each solvent effect on the weak interactions. However, it is generally difficult to observe each solvent effect separately at work in each interaction. Small molecular probes are useful to estimate the contributions of the weak interaction. But, the results should be treated with caution when applied to supramolecular polymer systems. To overcome the problems, a new solvent parameter, solvation ability (SA), is introduced, which was determined on the balance point of extended and stacked forms of porphyrin-based interconvertible supramolecular polymers.

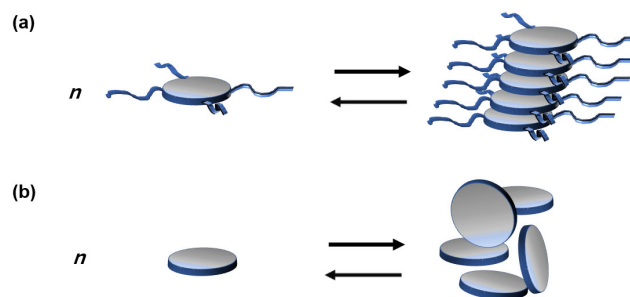
## 1. Introduction

Van der Waals interaction is a general term that includes weak interactions, such as aromatic–aromatic ( $\pi$ – $\pi$ ) and CH– $\pi$  interactions, and dispersion, at work in all organic compounds and residues. Although weak interactions may be literally weak, compared with ionic, hydrogen, and coordination bonds, they play a leading role in, especially, noncharged and nonpolar compounds and residues. Furthermore, a weak interaction works independently in the presence of other weak and stronger interactions in a system. The combination of these weak and strong interactions plays an important role in the construction of higher-order structures of large biopolymers, such as proteins, and the self-assembly of functional molecular systems.

The strength of these weak interactions varies in different solvents.<sup>[1]</sup> In binary solvent systems, the degree of change in the strength of weak interactions depends on the type of solvents and the solvent system composition. However, it is difficult to observe each solvent effect separately at work in each weak interaction. Chemists are able to empirically determine solvent effects in chromatography and the phenomenon of solvatochromism in polarized compounds.<sup>[2]</sup> The effects differ because of several factors, with arbitrary coefficients, based on linear solvation energy relationships.<sup>[3]</sup> Chemists also have knowledge regarding solvent effects pertaining to the solubilities of low-molecular-weight compounds and the macroscopic physical properties of polymers,<sup>[4]</sup> such as wetting,<sup>[5]</sup> change in morphology,<sup>[6]</sup> and gel formation.<sup>[7]</sup> However, we have little

knowledge of the effect/s on solvent–solute interactions at the molecular level for low-molecular-weight compounds and polymers in solution.

In this minireview, I focus on weak interactions at work in supramolecular polymers (anisotropic one-dimensional aggregates, composed of synthetic molecules) (Figure 1a). Isotropic supramolecular assemblies (Figure 1b) such as micelles and vesicles are not addressed here. Supramolecular polymers are employed as smart functional materials. Studying supramolecular polymers is also useful to realize natural molecular composites and their systems, as well as to construct artificial molecular systems, in which various molecules and supramolecules work synergistically.



**Figure 1.** (a) Supramolecular polymer and (b) isotropic aggregate.

Supramolecular polymers are often assembled from units composed of large aromatic groups (e.g., porphyrin, perylene bisimide, hexabenzocoronene; Figure 2) and some peripheral substituent groups (R groups in Figure 2). As substituents, linear and branched alkyl chains, or oligoether chains, are connected to a main aromatic framework directly, or through amide, ester, ether, or benzene groups. When these units form supramolecular polymers, the latter are stabilized by both aromatic–aromatic ( $\pi$ – $\pi$ ) interaction between the main polymer chains and other interactions among the peripheral substituents, such as hydrogen bonding, dipole–dipole interaction, and dispersion. Therefore, the anisotropic structure of a supramolecular polymer is based on the combination of these different weak interactions.<sup>[8]</sup> For the design of new supramolecular polymers, it is beneficial to separate the

contributions of the weak interactions, as well as each solvent effect on the weak interactions.

In the following sections, the solvent effect in the formation of supramolecular polymers is selectively reviewed. Solvent effects in weak interactions, collected in small molecular probes, are also discussed. Then, a new solvent parameter (the so-

called solvation ability) measured in a supramolecular polymer system recently developed by our group is introduced. In the final section, the present situation and an outlook for the solvent effect on weak interactions in supramolecular polymers are described.

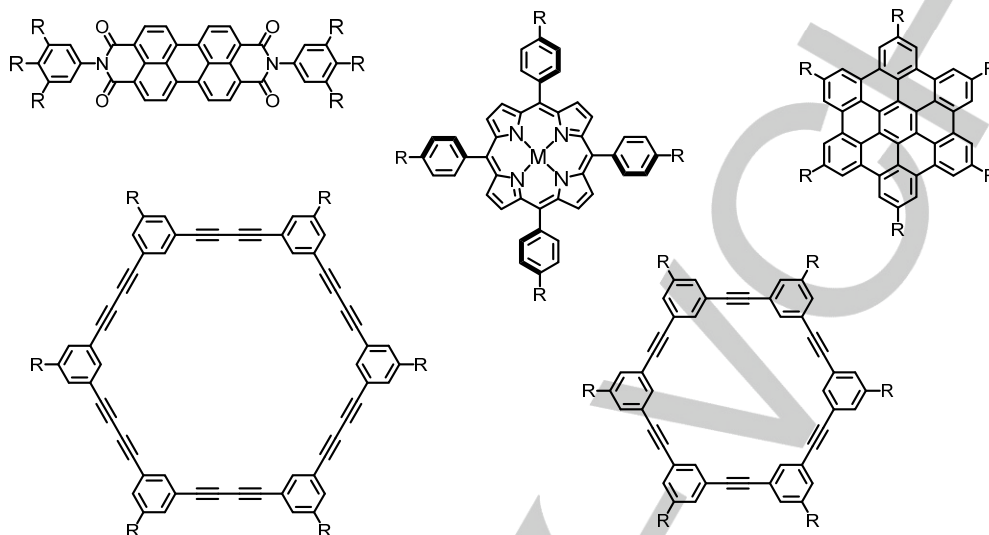


Figure 2. Components of supramolecular polymers.

## 2. Solvent effect pertaining to self-association constants in the formation of supramolecular polymers

Numerous comprehensive reviews<sup>[9]</sup> and articles have been published on supramolecular polymers, and solvent effects in the formation of supramolecular polymers have been widely described. Macroscopic phenomena in supramolecular polymers have often been reported after direct observation with a scanning probe microscope in solution<sup>[10]</sup> and gel formation. However, it is difficult to digitize macroscopic observations of the formation of supramolecular polymers. Therefore, when using macroscopic phenomena, it is difficult to arrange solvents accurately in the order of their roles for the macroscopic phenomena.

Degrees of solvent polarity are nonetheless frequently used qualitatively in discussions of supramolecular complex formation. In supramolecular complex formation, there are various nonbonding interactions. The degree of solvent polarity is affected by polar residues in molecules. As a result, hydrogen bonding, dipole–dipole interaction, and interactions associated with charged residues must be decreased by the use of additional polar solvents.

However, in the literature, obvious relationships between solvent polarity and aromatic–aromatic ( $\pi$ – $\pi$ ) interaction or dispersion have seldom been discussed. A discussion of solvent polarity, in the formation of supramolecular polymers, addresses the solvent effect in terms of the various weak and strong interactions. The polar solvent and solvent system used may function to strengthen some interactions, yet weaken others.

Although it is difficult to digitize macroscopic observations of the formation of supramolecular polymers, solvent-dependent self-association constants in the formation of such polymers can

be indexed for the solvent effect.<sup>[11]</sup> During the formation of supramolecular polymers, monomer units associate, successively, to give dimer, trimer, tetramer, and larger oligomers. Although the association constants are defined for each step, they are assumed to be equal (an isodesmic model) for the sake of simplifying calculations. Since the association constant is related to the Gibbs free energy change ( $\Delta G$ ), the  $\Delta G$  values can be used as indexes for the solvents used (solvent index).

To be able to measure the solvent-dependent self-association constants, the monomer units and corresponding supramolecular polymer must be in equilibrium in the solvent.<sup>[12]</sup> Thus, the unit components should be soluble in the solvent, as follows: monomer, under dilute conditions, and the corresponding supramolecular polymer should be formed at higher concentration. It is inappropriate that either a very “good” solvent is able to dissolve components as monomers, even at higher concentration, or that a very “poor” solvent gives precipitates, even in dilute solution. The degrees of the high and low concentrations used here depend on the methods selected to measure the equilibria between monomers and supramolecular polymers. Various levels of concentration are required for various analytical techniques:<sup>[13]</sup> approximately, from tens of millimolar to sub-millimolar concentrations of samples are used in vapor pressure osmometry and nuclear magnetic resonance (NMR) spectroscopy, whereas micromolar concentrations are used in ultraviolet–visible (UV–Vis) absorption spectroscopy. Appropriate concentrations also depend on the molecular weights and molar extinction coefficients of the monomers.

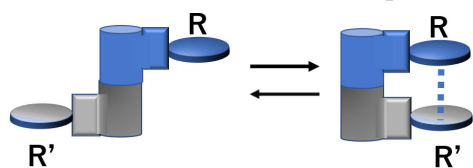
Due to the limitations associated with the solubilities as well as the supramolecular complex formation, it is difficult to collect self-association constants in different solvents using only one type of supramolecular probe. The solubilities of

components of a supramolecular probe generally vary significantly in various solvents. Therefore, to survey various solvents, peripheral substituent groups are replaced on a large  $\pi$ -aromatic framework. For example, a component having hydrophobic linear and branched alkyl groups could be dissolved in hydrophobic solvents and chlorinated hydrocarbons, whereas a component having oligoether groups could be dissolved in hydrophilic solvents and chlorinated hydrocarbons. If peripheral substituents differ in supramolecular polymers, then weak interactions among the peripheral parts will differ, even in structures having the same  $\pi$ -aromatic framework. To separate the weak interactions on the peripheral parts from those among the main frames, it is desirable to prepare the same type of supramolecular polymer composed of a nonsubstituted  $\pi$ -aromatic framework. However, the solubility of a large  $\pi$ -aromatic compound with no or less substitution decreases significantly, and the configuration of the aggregated structure may not be same as the configuration having substituent groups (see Figures 1a and 1b). In such a case, it is difficult to compare the solvent-dependent self-association constants. Therefore, when using the same supramolecular system, the assessment of a wide variety of solvents has been difficult.

Yet another problem is associated with the use of the solvent-dependent  $\Delta G$  values as a solvent index. Here, the data are sometimes collected under different concentrations, as well as by different methods. When data are collected under different conditions, the accuracy thereof and errors therein may vary.

### 3. Solvent effect on weak interactions determined using small molecular probes: differences between small molecular probes and supramolecular polymers

Measurement of the solvent effect on weak interactions has been achieved using small molecular probes that have a hinge region, referred to as molecular torsion balance and molecular seesaw balance (Figure 3). There are several good reviews of small molecular probes.<sup>[14]</sup> Here, the fundamental principle is described briefly.



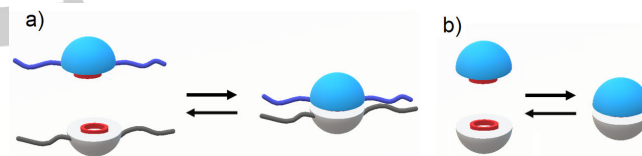
**Figure 3.** Design of small molecular probes having a hinge region. (Only two conformers exist.)

When the exchange rate between two conformers is slower than the NMR time scale, signals corresponding to each conformer can be observed separately in the NMR spectra. If there is a weak interaction at work in only one conformer, but not in the other, the solvent effect on the weak interaction can be estimated from the integration ratios of the conformers in the  $^1\text{H}$  NMR spectra collected in various solvents. Since the integration ratios can be converted to an equilibrium constant, and then to  $\Delta G$ , the solvent effects can be indexed as  $\Delta G$  values. In small molecular probe system, the control molecules having no

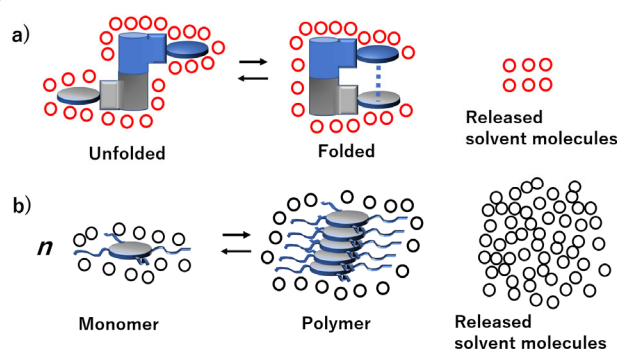
substituent groups can be easily prepared. Therefore, the solvent effect on the weak interactions can be separated from other interactions by subtraction of the data obtained for the control molecules. Since low-molecular-weight compounds are usually readily soluble in most solvents, and because a relatively new NMR technique is available in which a nondeuterated solvent may be used,<sup>[15]</sup> we consider this method to be useful for discussing solvent effects at work in each weak interaction by energy unit.

In the literature, some solvent effects in dispersion,<sup>[16]</sup> OH- $\pi$  interactions,<sup>[17]</sup> and nonpolar cohesive interactions<sup>[18]</sup> have been reported as relationships between  $\Delta G$  values and solvent parameters. However, the energy differences among various solvents in weak interactions seem very small. The solvent effects observed in low-molecular-weight compounds may be underestimated compared with those observed in the formation of supramolecular polymers, in which solvent replacement has a dramatic effect on the system.

Another approach to investigate weak interactions between substituents relies on equilibria between monomer and dimer (Figure 4).<sup>[19]</sup> Dimerization constants were determined in series of substituted and non-substituted probes. Contributions of the weak interactions between substituents are estimated by the difference between dimerization energies. In this approach, however, available solvents are limited. Many solvents give only either monomer or dimer. Therefore, comprehensive assessment of solvents is not expected at present.



**Figure 4.** Design of small molecular probes based on monomer/dimer equilibria (a) with and (b) without substituents.



**Figure 5.** Schematic images of released solvent molecules after formation of (a) a folded state of covalently linked small molecular probe, and (b) supramolecular polymer. Open circle: solvent molecule.

Some differences between small molecular probes and supramolecular polymers are now considered. (1) In small molecular probes, weak interaction works on only one side of the substituents introduced into the probes (Figures 3 and 4a). On the other hand, in supramolecular polymers, weak interactions occur on both sides of the main frames and peripheral substituents (Figure 1a). (2) In small molecular

probes, two interactive parts are covalently connected through a rigid and structurally restricted moiety. In such a restricted system, the two interactive parts may not approach each other to take the maximum interaction.<sup>[14d]</sup> (3) In structurally restricted systems, the difference in the numbers of solvent molecules accessible between two conformers is small compared with that between monomers and supramolecular polymers; thus, in small molecular probes, the entropy term of solvent molecules is underestimated (Figure 5). (4) In rigid and structurally restricted systems, interaction between solute (probe) and solvent is regulated and, therefore, the strength of the interaction depends on the intrinsic shapes of the solvent molecules.<sup>[20]</sup>

Typical examples of solvent-shape-mediated transformation are chiral induction in helical<sup>[21]</sup> and supramolecular polymers,<sup>[22]</sup> and inversion of helicity in chiral polymers.<sup>[23]</sup> Since the shapes of solvent molecules are independent of solvent polarity and other physical properties, the relationship between the strengths of interactions and the solvent parameters cannot be discussed in rigid and structurally restricted systems.

For the above reasons, indications are that the solvent effect on weak interactions should be measured in supramolecular systems, but not in small molecular probes.

#### 4. Solvation/desolvation indicator using supramolecular porphyrin polymers

We recently developed a solvation/desolvation indicator using porphyrin-based supramolecular polymers. We have reported that a monoimidazole-substituted bisporphyrin<sup>[24]</sup> and porphyrin-phthalocyanine<sup>[25]</sup> composite give two types of coordination dimers, respectively, which can be interconverted by adding or removing coordinating solvent. In these systems, complementary imidazole-to-zinc coordination bonds are utilized to give the coordination dimers. Although the complementary coordination bonds are labile, the self-association constants are very large (typically  $> 10^8 \text{ M}^{-1}$ )<sup>[13]</sup> in the absence of strongly coordinating solvent, such as pyridine and methanol (a primary alcohol).<sup>[26]</sup> In other words, the systems give coordination dimers in most solvents, excluding pyridine and primary alcohols.

This technique was applied to supramolecular polymer systems. Two imidazolylporphyrinatozinc molecules were connected through a 1,3-butadiyne moiety to give bisporphyrins **1Zn<sub>2</sub>** and **2Zn<sub>2</sub>**<sup>[26]</sup> (Figure 6). The bisporphyrins give two types of coordination polymers, extended and stacked, as shown in Figure 7. An extended polymer is formed in a “good” solvent to gain in solvation by expanding the surface areas of the supramolecular polymer, whereas a stacked polymer is formed in a “poor” solvent. (Note that the expressions of “good” and “poor” used here are based on our experience, not on physical parameters.)

Various solvents can therefore be easily assessed, based on these indicators, using a conventional UV–Vis spectrometer. We tested 67 types of solvents and determined relationships between the “good” and “poor” properties obtained. The various physical parameters,<sup>[27]</sup> such as refractive index  $n$  and dielectric constant  $\epsilon$ , induced polarizability and dispersion interaction functions  $(n^2-1)/(n^2+1)$ ,<sup>[27]</sup> and dipolar–dipolar interaction function  $(\epsilon-1)/(\epsilon+1) - (n^2-1)/(n^2+1)$ <sup>[27]</sup> and empirical solvent polarities (such as  $\pi^*$ ,<sup>[28]</sup> and  $E_{\text{T}(30)}$ )<sup>[29]</sup> were examined. No relationship was observed between the collected data and any of the solvent parameters. The results of our analyses indicated that “good” or “poor” properties are independent of physical parameters or empirical solvent polarities.

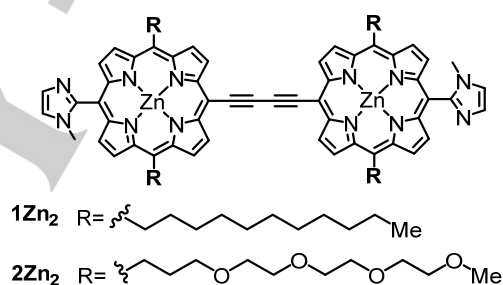


Figure 6. Structures of bisporphyrins **1Zn<sub>2</sub>** and **2Zn<sub>2</sub>**.

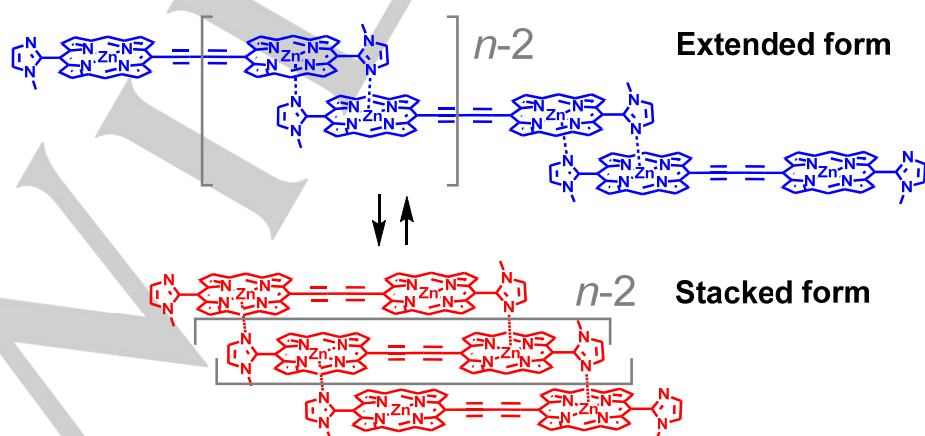


Figure 7. Structures of supramolecular polymers composed of bisporphyrins **1Zn<sub>2</sub>** and **2Zn<sub>2</sub>**. Substituent groups are omitted.



In the supramolecular polymer, the labile but strong coordination bonds and aromatic–aromatic ( $\pi$ – $\pi$ ) interactions work simultaneously among the components, bisporphyrins **12n<sub>2</sub>** and **22n<sub>2</sub>**. The contributions of the two types of coordination bonds and  $\pi$ – $\pi$  interactions vary depending on the solvent used. To separate the contributions, solvent dependencies were examined by making use of dimer systems, which afford only extended or stacked dimers, respectively.<sup>[30]</sup> Upon comparison of the two dimers, only a small solvent effect was observed in both the coordination bonds and the  $\pi$ – $\pi$  interaction. The effect of the coordination bonds per unit porphyrin in the dimer systems is almost the same as that in the supramolecular polymer, with indications that the  $\pi$ – $\pi$  interaction in the dimer system is much smaller than that in the polymer system. This fact indicates that  $\pi$ – $\pi$  interactions among inside porphyrin parts in a supramolecular polymer are strongly solvent-dependent and constitute a major driving force in the construction of solvent-dependent supramolecular polymers. Therefore, the solvent-dependent properties in supramolecular systems require examination, which is not required in dimer systems.

The phenomenon of interconversion between extended and stacked supramolecular polymers is useful in assessing the solvent effect on the weak interactions in supramolecular polymers as a solvation/desolvation indicator. Such a system resolves the problems with regard to solvent parameters determined by self-association constants in the formation of supramolecular polymers (described in Section 2).

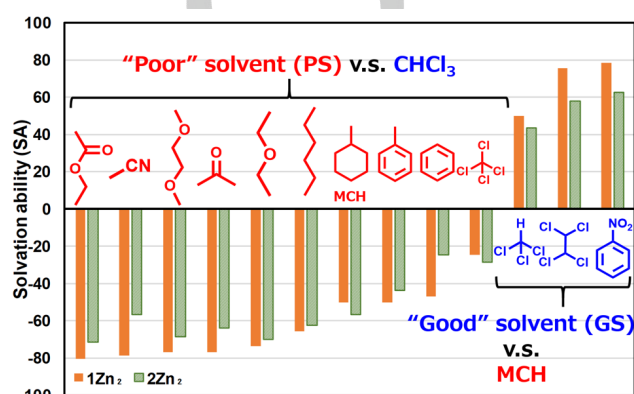
Both types of bisporphyrin coordination polymers are formed in micromolar concentrations as monomer units. Therefore, assessments of solvent effects were carried out under the same dilute conditions of  $2 \times 10^{-6}$  M. Since no precipitation of supramolecular polymer was observed under the dilute conditions, any “poor” solvent other than water could be used. Due to the unique properties of supramolecular complex formation in highly diluted concentrations, various solvents can be assessed for one supramolecular probe. When two types of supramolecular probes having different substituents are used for solvent, the substituent effect becomes obvious. Since the directional and strong complementary coordination bonds are used to construct the main chains of supramolecular polymers, we assume that the same types of supramolecular polymers will be formed from components that have different side chains.

However, the supramolecular probe presents a problem. The energy difference between the two states (extended and stacked) is difficult to measure because only one state is observed in a single solvent; this is because the energy differences between the two states is very large. In supramolecular polymers, either the extended or stacked form is produced exclusively in a supramolecular polymer. Therefore, a positive allosteric effect is at work in the formation of both types of polymers.

Although the energy differences between the two states are difficult to determine experimentally, the balance point, in which extended and stacked polymers exist comparably, can be achieved by mixing two “good” and “poor” solvents. This method closely resembles neutralization by mixing acid and base. Therefore, for solvents whose solvation abilities are unknown, the orders of solvation can be assigned by assessment to give the balance point using the standard solvent. In fact, this idea was established by tournament-style assessment<sup>[31]</sup> using chloroform and methylcyclohexane as standard “good” and “poor” solvents, respectively, to give a solvent parameter.<sup>[31]</sup>

The new solvent parameter is known as the solvation ability (SA), the value of which is defined as the volume percentage of added standard solvent to prepare the balance point between extended and stacked polymers (Figure 8). If chloroform is used as standard, the sign of SA is negative, whereas in the case of methycyclohexane, the sign of SA is positive.

Sugimoto et al. compared SA values obtained with physical parameters of solvents as well as the empirical solvent polarities.<sup>[31]</sup> Overall, no relationship was observed. Therefore, the solvation ability of solvents for supramolecular polymers is considered to be independent of either the solvent parameters or the solvent polarities, as are customarily used.



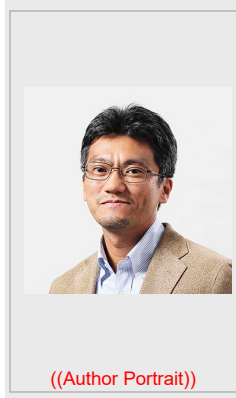
**Figure 8.** Solvation ability (SA) of solvents for **1Zn<sub>2</sub>** and **2Zn<sub>2</sub>** from reference,<sup>[31]</sup> copyright © 2020, American Chemical Society.

## 5. Summary and Outlook

Aromatic–aromatic ( $\pi$ – $\pi$ ) interaction plays a significant role in supramolecular polymers, but not in the corresponding dimers. Therefore, solvent effects in various weak interactions, determined using low-molecular-weight compounds and self-assembled dimer systems, should be treated with caution when applied to supramolecular polymer systems. Supramolecular probes should be used to assess the solvent effect in the formation of supramolecular polymers. This should lead to the opening of a new scientific field, with regard to weak interactions—weak interactions occur in dynamic and smart molecular systems in nature.

As an outlook, the contribution of each weak interaction and their solvent effects should be separated in supramolecular systems. Such information will assist in the design of more complicated, or combinational, supramolecular systems composed of aromatic frameworks with functional groups and substituents. The accumulation of fundamental new techniques will contribute to the construction of higher-order artificial supramolecular systems in which more than two supramolecular systems interact and are regulated dynamically in response to outer stimuli.

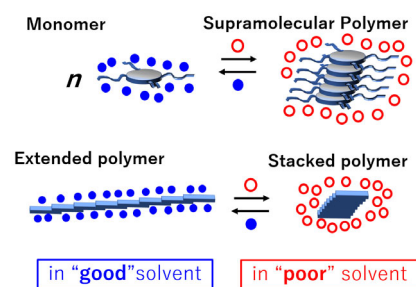
Akiharu Satake completed his PhD at the Waseda University (Japan) under the supervision of Prof. Isao Shimidzu in 1995. After working at RIKEN, he went to Nara Institute of Science and Technology as an assistant professor. He studied supramolecular chemistry with Prof. Yoshiaki Kobuke from 1999 to 2009. He went to Tokyo University of Science in 2010 as an associate professor, and he was promoted to full professor in 2015. His research fields are coordination chemistry, solution chemistry, and supramolecular chemistry.



**Keywords:** aggregation • pi interactions • porphyrinoid • solvent effects • supramolecular chemistry

- [1] a) M. S. Cubberley, B. L. Iverson, *J. Am. Chem. Soc.* **2001**, *123*, 7560-7563; b) F. Würthner, S. Yao, T. Debaerdemaeker, R. Wortmann, *J. Am. Chem. Soc.* **2002**, *124*, 9431-9447; c) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem. Int. Ed.* **2003**, *42*, 1210-1250; d) J. Aimi, Y. Nagamine, A. Tsuda, A. Muranaka, M. Uchiyama, T. Aida, *Angew. Chem. Int. Ed.* **2008**, *47*, 5153-5156; e) S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu, M. Takeuchi, *Nat. Chem.* **2014**, *6*, 188-195; f) T. Haino, *Chem. Rec.* **2015**, *15*, 837-853; g) H.-J. Schneider, *Acc. Chem. Res.* **2015**, *48*, 1815-1822; h) D. Zhang, T. K. Ronson, J. R. Nitschke, *Acc. Chem. Res.* **2018**, *51*, 2423-2436; i) M. Morisue, I. Ueno, *J. Phys. Chem. B* **2018**, *122*, 5251-5259.
- [2] a) C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319-2358; b) M. J. Kamlet, J. L. Abboud, R. W. Taft, *J. Am. Chem. Soc.* **1977**, *99*, 6027-6038.
- [3] a) A. F. M. Barton, *Chem. Rev.* **1975**, *75*, 731-753; b) M. Vitha, P. W. Carr, *J. Chromatogr. A* **2006**, *1126*, 143-194.
- [4] 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.
- [5] Y. Si, Z. Dong, L. Jiang, *ACS Cent. Sci.* **2018**, *4*, 1102-1112.
- [6] J. Zhang, X. Chen, W. Li, B. Li, L. Wu, *Langmuir* **2017**, *33*, 12750-12758.
- [7] S. Yao, U. Beginn, T. Gress, M. Lysetska, F. Würthner, *J. Am. Chem. Soc.* **2004**, *126*, 8336-8348.
- [8] K. V. Rao, M. F. J. Mabeoone, D. Miyajima, A. Nihonyanagi, E. W. Meijer, T. Aida, *J. Am. Chem. Soc.* **2020**, *142*, 598-605.
- [9] a) T. Aida, E. W. Meijer, S. I. Stupp, *Science* **2012**, *335*, 813-817; b) L. Yang, X. Tan, Z. Wang, X. Zhang, *Chem. Rev.* **2015**, *115*, 7196-7239; c) E. Yashima, N. Ousaka, D. Taura, K. Shimomura, T. Ikai, K. Maeda, *Chem. Rev.* **2016**, *116*, 13752-13990.
- [10] M. Numata, *Chem. Asian J.* **2015**, *10*, 2574-2588.
- [11] a) Y. Tobe, N. Utsumi, K. Kawabata, A. Nagano, K. Adachi, S. Araki, M. Sonoda, K. Hirose, K. Naemura, *J. Am. Chem. Soc.* **2002**, *124*, 5350-5364; b) D. Zhao, J. S. Moore, *Chem. Commun.* **2003**, 807-818; c) Z. Chen, A. Lohr, C. R. Saha-Moller, F. Würthner, *Chem. Soc. Rev.* **2009**, *38*, 564-584.
- [12] C. Shao, M. Grüne, M. Stolte, F. Würthner, *Chem. Eur. J.* **2012**, *18*, 13665-13677.
- [13] A. Satake, Y. Kobuke, *Tetrahedron* **2005**, *61*, 13-41.
- [14] a) F. Biedermann, H.-J. Schneider, *Chem. Rev.* **2016**, *116*, 5216-5300; b) J. w. Hwang, P. Li, K. D. Shimizu, *Org. Biomol. Chem.* **2017**, *15*, 1554-1564; c) M. A. Strauss, H. A. Wegner, *Eur. J. Org. Chem.* **2019**, 295-302; d) A. E. Aliev, W. B. Motherwell, *Chem. Eur. J.* **2019**, *25*, 10516-10530.
- [15] T. R. Hoye, B. M. Eklov, T. D. Ryba, M. Voloshin, L. J. Yao, *Org. Lett.* **2004**, *6*, 953-956.
- [16] L. Yang, C. Adam, G. S. Nichol, S. L. Cockcroft, *Nat. Chem.* **2013**, *5*, 1006-1010.
- [17] J. M. Maier, P. Li, E. C. Vik, C. J. Yehl, S. M. S. Strickland, K. D. Shimizu, *J. Am. Chem. Soc.* **2017**, *139*, 6550-6553.
- [18] L. Yang, C. Adam, S. L. Cockcroft, *J. Am. Chem. Soc.* **2015**, *137*, 10084-10087.
- [19] a) L. Yang, J. B. Brazier, T. A. Hubbard, D. M. Rogers, S. L. Cockcroft, *Angew. Chem. Int. Ed.* **2016**, *55*, 912-916; b) S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **2017**, *8*, 405-410; c) A. C. N. Kwamen, M. Schlottmann, D. Van Craen, E. Isaak, J. Baums, L. Shen, A. Massomi, C. Räuber, B. P. Joseph, G. Raabe, C. Göb, I. M. Oppel, R. Puttreddy, J. S. Ward, K. Rissanen, R. Fröhlich, M. Albrecht, *Chem. Eur. J.* **2020**, *26*, 1396-1405.
- [20] a) T. V. Nguyen, D. J. Sinclair, A. C. Willis, M. S. Sherburn, *Chem. Eur. J.* **2009**, *15*, 5892-5895; b) P. Spenst, R. M. Young, B. T. Phelan, M. Keller, J. Dostál, T. Brixner, M. R. Wasielewski, F. Würthner, *J. Am. Chem. Soc.* **2017**, *139*, 2014-2021; c) H. Kar, G. Ghosh, S. Ghosh, *Chem. Eur. J.* **2017**, *23*, 10536-10542.
- [21] M. M. Green, C. Khatri, N. C. Peterson, *J. Am. Chem. Soc.* **1993**, *115*, 4941-4942.
- [22] S. Xue, P. Xing, J. Zhang, Y. Zeng, Y. Zhao, *Chem. Eur. J.* **2019**, *25*, 7426-7437.
- [23] a) N. Suzuki, M. Fujiki, R. Kimpinde-Kalunga, J. R. Koe, *J. Am. Chem. Soc.* **2013**, *135*, 13073-13079; b) Y. Nagata, T. Nishikawa, M. Sugimoto, *J. Am. Chem. Soc.* **2014**, *136*, 15901-15904; c) C. Kulkarni, P. A. Korevaar, K. K. Bejagam, A. R. A. Palmans, E. W. Meijer, S. J. George, *J. Am. Chem. Soc.* **2017**, *139*, 13867-13875.
- [24] A. Satake, J. Tanihara, Y. Kobuke, *Inorg. Chem.* **2007**, *46*, 9700-9707.
- [25] A. Satake, T. Sugimura, Y. Kobuke, *J. Porphyrins Phthalocyanines* **2009**, *13*, 326-335.
- [25] A. Satake, Y. Suzuki, M. Sugimoto, T. Shimazaki, H. Ishii, Y. Kuramochi, *Chem. Eur. J.* **2018**, *24*, 14733-14741.
- [27] J.-L. M. Abboud, R. Notari, *Pure Appl. Chem.* **1999**, *71*, 645-718.
- [28] C. Laurence, P. Nicolet, M. T. Dalati, J.-L. M. Abboud, R. Notario, *J. Phys. Chem.* **1994**, *98*, 5807-5816.
- [29] C. Reichardt, in *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH, Weinheim, **2004**, pp. 389-469.
- [30] A. Satake, Y. Suzuki, M. Sugimoto, Y. Kuramochi, *Chem. Eur. J.* **2020**, *26*, 669-684.
- [31] M. Sugimoto, Y. Kuramochi, A. Satake, *ACS Omega* **2020**, *5*, 6045-6050.

## Entry for the Table of Contents



Solvents affect strengths of non-bonding interactions, which control formation of supramolecular polymers in solution. Solvent effects and parameters measured in supramolecular polymer systems are selectively reviewed. A new solvent scale, solvation ability (SA), based on the balance point between extended and stacked polymers is introduced.

## The Graphic Art in Frontispiece

## The Solvent Effect on Weak Interactions in Supramolecular Polymers: Differences between Small Molecular Probes and Supramolecular Polymers

Akiharu Satake\*[a]

