

Molecular Engineering of Noncovalent Dimerization

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ABSTRACT: Dimers are probably the simplest model to facilitate the understanding of fundamental physical and chemical processes that take place in much-expanded systems like aggregates, crystals, and other solid states. The molecular interplay within a dimer differentiates it from the corresponding monomeric state and determines its features. Molecular engineering of noncovalent dimerization through applied supramolecular restrictions enables additional control over molecular interplay, particularly over its dynamic aspect. This Perspective introduces the recent effort that has been made in the molecular engineering of noncovalent dimerization, including supramolecular dimers, folda-dimers, and macrocyclic dimers. It showcases how the variation in supramolecular restrictions endows molecular-based materials with improved performance and/or functions like enhanced emission, room-temperature phosphorescence, and effective catalysis. We particularly discuss pseudostatic dimers that can sustain molecular interplay for a long period of time, yet are still flexible enough to adapt to variations. The pseudostatic feature allows for active species to decay along an alternate pathway, thereby spinning off emerging features that are not readily accessible from conventional dynamic systems.

1. INTRODUCTION

Organic molecular-based functional materials are recognized as crucial drivers of emerging technologies for their rapid development and applications as dyes and semiconductors in optoelectronics,^{1,2} as probes and medicine in theragnostics,^{3,4} as active intermediates and catalysts in chemical reactions,^{5,6} as switches and rotors in molecular machines,^{7–9} etc. To customize a molecular-based system toward desired functions, it typically requires careful consideration of two aspects: (i) the intrinsic features of a single molecule species determined by its atomic arrangement and connection; and (ii) the coherent features of molecular ensembles determined by the interplay among them.¹⁰ The latter, in terms of material design, is practically more important as most materials are present as an ensemble of molecules. The attention to this importance has been particularly drawn by the extensive reports of aggregation-induced phenomena, which offer functionalities that are not accessible by single molecular species.^{11–13} However, the term of “aggregation” depicts a coarse-grain picture for molecular ensembles, without explicit information on the number and arrangement of molecules involved. As more knowledge is gained on molecular self-assembly,^{10,14–17} now it comes to a point that the interplay among molecules can be introduced, controlled, and understood in more subtle ways and, more importantly, with a precision at molecular scale.

Noncovalent dimerization is employed in this Perspective to showcase the recent effort that has been made in the pursuit of precise control, either spatially or temporally, over molecular interplay. Dimers are probably the simplest system to enable the presence of molecular interplay experimentally and theoretically.^{18,19} The premise behind control is variability, which is one of the key features of noncovalent systems on the

basis of dynamic and reversible interactions.²⁰ Therefore, through the molecular engineering of noncovalent dimerization, one could readily elucidate how the change of molecular interplay leads to the variability of functions. Moreover, on account of its normally good dispersion in solvent, the investigation of a minimal molecular system like a dimer is more feasible with the help of plentiful characterization techniques.

The task of dimerization is to drive monomers into dimeric entities, i.e., discrete pairs of monomeric species, and to sustain their spatial proximity and interaction for a certain period of time. In contrast to isodesmic or cooperative self-assembly,²¹ which typically leads to expanded molecular systems like oligomers, supramolecular polymers, or random aggregates,^{11,22,23} dimerization can be regarded as a special case of anticooperative self-assembly^{24,25} that prohibits growth beyond dimers. For a molecule inclining to aggregation, the challenge of dimerization becomes to isolate pairs of monomers out of their aggregates. To address this challenge, the volume-exclusion strategy is often employed by introducing bulky groups during the molecular design (Figure 1a).^{26–29} Selectively tethered bulky groups allow for the interplay of two molecules along a specific direction while sterically blocking others. However, this strategy is diffusion controlled and does not work for molecules that are well solvated and dispersed in solution. In other words, it works for molecular

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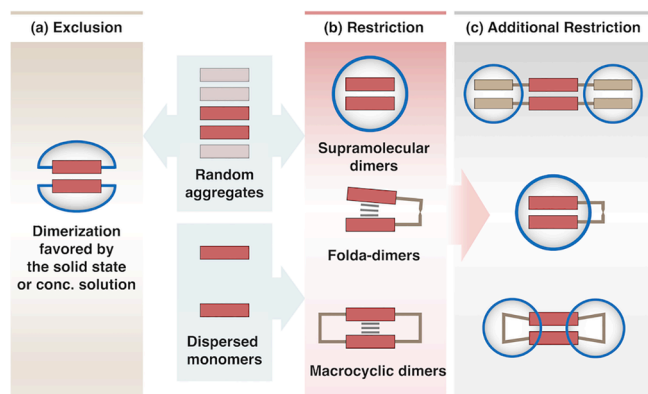


Figure 1. Typical pathways toward noncovalent dimers with variable degrees of restriction.

moieties intrinsically prone to assembly or upon conditions that favor their aggregation such as concentrated solution or solid states.^{30,31}

An alternative strategy, instead of the passive exclusion, is to actively bring two molecular moieties to close proximity through single or multiple linkages. An advantage of this strategy is that noncovalent molecular interplay can be held between two moieties no matter whether they are prone to aggregation or not. In other words, this type of noncovalent dimerization is concentration independent and can take place in a broad range of concentrations. Moreover, it can even enforce repelling moieties into their dimeric form and generate features that are inaccessible by normal methods.^{32–34} According to the fashion of linkages, products from this prelinked noncovalent dimerization are divided into three catalogues in this Perspective (Figure 1b): (i) *supramolecular dimers* in which the dimerization of two moieties is associated with supramolecular binding events; (ii) *folda-dimers* in which two interacting moieties are tethered by a single and switchable covalent bridge; and (iii) *macrocyclic dimers* in which two interacting moieties are settled by multiple covalent linkages into a macrocyclic form.

The control over the dimeric molecular interplay can be realized in each type of noncovalent dimer through a variation in the degree of restriction (Figure 1b,c). For instance, additionally introduced supramolecular restriction can augment the interplay and generally endow the dimers with shorter spatial distance and more persistent interaction.^{35,36} As a result, the additional restriction turns a dynamic supramolecular dimer into a less dynamic one;³⁷ makes an adaptive folda-dimer, which is tethered by a switchable linkage, less labile;³⁸ and strengthens the coupling within a macrocyclic dimer even though the dimeric moieties have been settled by multiple covalent linkages (Figure 1c).³⁹ We classify those dimers generated by the additional restriction as “pseudostatic dimers”, on the one hand, for their more persistent interplay compared with typical dynamic noncovalent dimers, and on the other hand, for their noncovalent nature against completely static species.

Well-controlled restriction leads to well-regulated dimeric interplay and subsequently well-defined dimer functions. Besides the ground state, the influence from the applied restriction is particularly imposed on dimers' excited states, and also extended to dimers with different redox states (Figure 2). For instance, excited dimers can be generated by a direct excitation from ground-state dimers,⁴⁰ which should differ-

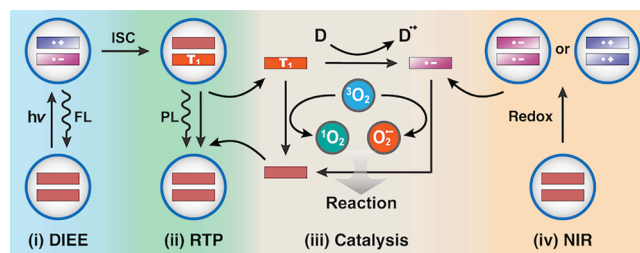


Figure 2. Exemplified functions and relevant pathways for noncovalent dimers with a variable extent of restriction applied on their ground states, excited states, and redox states. (i) Dimerization-induced enhanced emission (DIEE); (ii) room-temperature phosphorescence (RTP); (iii) catalysis; (iv) near-infrared (NIR) probes.

entiate from the formation of excimers or exciplexes that are initially excited from a monomer.⁴¹ If a dimer is sustained with strong restriction, as will be introduced later, its pseudostatic excited state can remain as a dimeric form before relaxation to the ground state. On account of the restriction, the relaxation will mainly choose a radiative pathway of high efficiency, which could lead to dimerization-induced enhanced emission (DIEE)^{40,42–47} or room-temperature phosphorescence (RTP).^{35,38} If a dimer is dynamically and loosely held with weak restriction, its excited dimer may have more chances to dissociate into an excited monomer, which then behaves as a supramolecular catalyst to trigger subsequent reactions.^{48,49} Similar profiles could also be found for the redox products of noncovalent dimers, working either as stable near-infrared (NIR) probes or catalytic supramolecular radicals depending on oxygen content.^{50,51}

The perspective we therefore aim to convey is that an active and precise control over the dynamics of molecular interplay is an effective way to endow molecular-based materials with improved performance and/or new functions. The rest of this Perspective will expand and demonstrate this idea with recent progress that has been made in the molecular engineering of noncovalent dimerization, from dynamic supramolecular dimers, adaptive folda-dimers, and macrocyclic dimers to their corresponding pseudostatic counterparts. Dimeric systems and accompanying features generated through various restriction methods are mainly introduced, along with a few emerging cases of discrete dimers in solid states mentioned in the end.

2. SUPRAMOLECULAR DIMERIZATION

The basic idea of supramolecular dimerization is to associate a dimerization process with a thermodynamically favorable supramolecular binding event. The formation of a dimer from two molecular moieties in solution has to overcome the penalty from a loss of translational entropy.⁵² The associated supramolecular binding, of adequately high binding affinity, will append a change of free energy that is large enough to pay off the entropic penalty, thereby favoring the dimerization with preorganized and less diffusion-controlled features. A broad range of supramolecular dimers have been achieved by association with various types of supramolecular binding events such as macrocyclic complexations,^{53,54} capsulation through hydrogen bonding,⁵⁵ or halogen and chalcogen bonding,⁵⁶ antielectrostatic hydrogen bonding,^{57–59} metal-coordination,^{60–63} metal–metal interaction,⁶⁴ micellization,^{65,66} and so on. This Perspective mainly employs macrocyclic-based, particularly cucurbituril-based, host–guest

systems to exemplify the molecular engineering of supramolecular dimerization.

Host–guest inclusion as a supramolecular binding system is a good candidate to perform supramolecular dimerization through a simple mix-and-match fashion at low molar concentration. Typical hosts like cyclodextrin,^{67,68} cucurbit[*n*]urils (CB[*n*]),^{54,69} pillararenes,⁷⁰ molecular cages,^{71,72} etc., can provide a confined and isolated cavity space for accommodating guest molecules, including a dimer. Kim et al. in 2000 found that cucurbit[8]uril (CB[8]), a macrocyclic host with eight repeat units, was capable of encapsulating two guest molecules in aqueous solution.^{53,73,74} Biedermann et al. then revealed that the main driving force for cucurbituril-based binding was the release of energetically frustrated cavity-bound water (so-called “high-energy water”).^{14,75,76} This means once the combined shape and size of two molecular moieties match the cavity of CB[8], they are likely to be dragged into the macrocycle and sustained as a dimer even if the two moieties are not inclined to dimerization. Moreover, the macrocyclic backbone as a shielding layer can mechanically prevent further aggregation of guests and sustain dimers as discrete entities.⁷⁷

The pursuit of radical dimers is a good illustration of the advantage of supramolecular dimerization. Effective spin–spin coupling between two radical species results in narrow bandgaps and significant absorption in the near-infrared region, which has shown a promising potential as NIR reagents for photothermal conversion and therapy.^{78,79} However, the intermolecular spin–spin interaction is often not strong enough to generate and sustain a long-lasting radical pair against the thermal fluctuation in solution.⁸⁰ Moreover, it is difficult for a highly reactive radical species to meet with another radical before being promptly diminished by other quenchers.

Radical dimers with enhanced stability could be achieved by the combination of a supramolecular host–guest binding with spin–spin coupling. Through the inclusion by CB[8], Kim et al. reported the stabilized radical dimers of methylated viologen in 2002.⁸¹ Discrete dimers for tetrathiafulvalene radical cations were successfully prepared and stabilized by various supramolecular hosts such as CB[8] by Kim et al.,⁸² self-assembled coordination cages by Fujita et al.,⁸³ and [3]catenanes by Stoddart et al.⁸⁴ Recently, Zhang et al. reported the application of a radical dimer in NIR-II photothermal therapy⁵¹ (Figure 3) on the basis of the supramolecular dimerization between *N,N'*-dimethylated dipyridinium thiazolo[5,4-*d*]thiazole radical cation (MPT^{•+}) and CB[8]. On the one hand, the formation of a supramolecular radical dimer stabilized the radical and improved its redox reversibility. On the other hand, the supramolecular radical dimer exhibited a strong absorption at NIR-II biowindow (1000–1350 nm) owing to the intermolecular spin–spin coupling. Combining the enhanced stability and strong NIR-II absorption of the supramolecular radical dimer, 2MPT^{•+}-CB[8] exhibited an efficient and reliable NIR-II photothermal conversion. On account of the large penetration depth and maximum permissible exposure to human skin of NIR-II light, the supramolecular radical dimer showed a high inhibition rate toward HepG2 cancer cells with NIR-II irradiation penetrating through a 5 mm-thick chicken breast tissue. The supramolecular radical dimer as a novel candidate for NIR photothermal reagents features in metal-free composition, facile fabrication, considerable aqueous solubility,

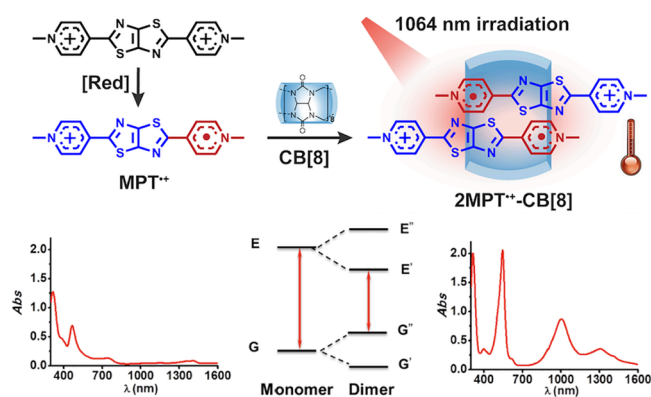


Figure 3. Supramolecular radical dimers, 2MPT^{•+}-CB[8], exhibiting strong absorption at NIR-II biowindow (1000–1350 nm) with an application in photothermal therapy. Adapted with permission from ref 51. Copyright (2019) Wiley-VCH.

and more importantly, strong long-wavelength absorption for biosafety.

Dynamic Dimers. Supramolecular dimerization, on the one hand, requires an engagement with a supramolecular event of high thermodynamic stability; on the other hand, it allows for large degree of variation in the kinetic aspect and offers a means to control the molecular interplay by imposing varied restriction on dimers. The variation in restriction can be performed by the introduction of a different number of binding or restriction sites.

A dimer sustained by only one CB[8] macrocycle is generally more dynamic than those bearing multiple restriction sites. Zhang et al. reported a supramolecular dimerization of two MPT²⁺ guests with one CB[8], yielding a 2MPT²⁺-CB[8] dimer with two guests arranged in a parallel and staggered conformation (Figure 4).⁵⁰ Owing to their acceptor–donor–

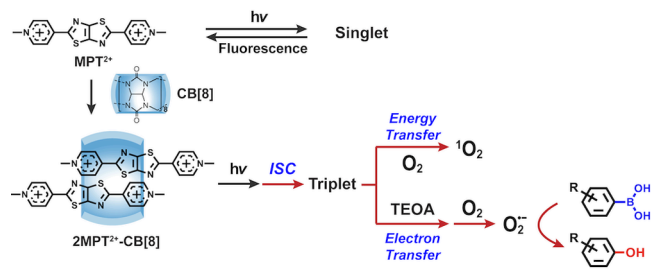


Figure 4. A dynamic supramolecular CT dimer, 2MPT²⁺-CB[8], performed as an efficient photocatalyst by effectively generating and releasing triplet species for subsequent reactions. The triplet generation is assisted by host-sustained discrete CT pair that promotes the intersystem crossing. The release of triplet species is favored by the dynamic nature of this supramolecular dimer loosely restricted by one macrocycle. Adapted with permission from ref 50. Copyright (2021) Wiley-VCH.

acceptor structures, two MPT²⁺ guests were coupled with each other as a discrete charge-transfer (CT) pair inside cavity. Upon excitation, the CT interaction was known to promote the intersystem crossing process and generated triplets through a charge separation and recombination mechanism.^{49,85,86} The supramolecular CT dimer of 2MPT²⁺-CB[8] thereby behaved as a triplet generator, displaying an increasing yield of triplets upon photoexcitation. As this CT pair was associated with only one CB[8] macrocycle, the resulting triplets were loosely

restricted and could move in and out of the host cavity at a fast exchange rate. This dynamic nature of $2\text{MPT}^{2+}\text{-CB}[8]$ is also demonstrated by their susceptibility to the change of conditions, such as host–guest ratio, solvent, pH, humidity, etc.⁸⁷

The loosely bound and temporally escaped single triplet species can trigger subsequent physical processes or chemical reactions. As for excited $2\text{MPT}^{2+}\text{-CB}[8]$ dimers, the resulting fast-exchanging triplets were prone to accept an electron transfer from electron donors and generate radical cations that further reacted with oxygen to produce superoxide ions. Superoxide ions could oxidize arylboronic acids into phenols. As a result, the supramolecular dimer $2\text{MPT}^{2+}\text{-CB}[8]$ could serve as an efficient photocatalyst for the oxidative hydroxylation of arylboronic acids (Figure 4).⁵⁰ Providing that MPT is a fluorescent dye with over 90% quantum yield, this finding demonstrates the great power of supramolecular dimerization in terms of dramatically changing the photo-physical and photochemical properties of a molecular system.

Pseudostatic Dimers. By appending additional restriction sites, one can turn a supramolecular dimer from a dynamic pair into a pseudostatic one that maintains as an interacting pair for a longer period of time. Pseudostatic features were initially pointed out by Scherman et al.^{37,40,88} when comparing doubly restricted dimers with a singly restricted counterpart. The pseudostatic concept is thereby a relative description of dynamics depending on specific time scales. For a supramolecular complex that is pseudostatic under an equilibrium state, it typically displays a slow exchanging rate which can be qualitatively elucidated from the pattern and the line width of NMR signals and quantified through variable-temperature NMR.^{37,40} A pseudostatic system is often formed in a quantitative manner insensitive to the mixing ratio of starting materials.

In Scherman's work, a series of arylviologen derivatives were found to bind with $\text{CB}[8]$ at a "1:1" stoichiometry, whereas exhibiting sharp proton NMR signals at slow exchanging limit and showing exclusive complexation products insensitive to the mixing ratio.³⁷ These complexes were verified to be supramolecular dimers composed of two arylviologens simultaneously restricted by two $\text{CB}[8]$ macrocycles (Figure 5a). They further developed a modular strategy to ease the design and preparation of multiple restricted dimers universally feasible for a variety of molecular moieties. By using bis(*N*-arylpriidinium) (BAP) as a restricting or clamping module and attaching multiple BAP units onto one chromophore moiety, supramolecular dimers of more than ten chromophore moieties were fabricated upon complexation with $\text{CB}[8]$ macrocycles (Figure 5b).^{40,45,88} The doubly or triply restricted dimers can sustain a long-lived interchromophore coupling and generally display significant dimerization-induced enhanced emission.

This modular strategy toward pseudostatic dimers can readily construct and provide a series of dimer-based fluorescent dyes whose emission wavelength covers a broad range of spectra and displays fluorescent quantum yields generally larger than 80% (Figure 5b).⁴⁰ Unlike the direct inclusion in $\text{CB}[8]$ cavity, by separating functional and clamping modules, the supramolecular dimerization can be extensively applied to various chromophores or fluorophores even if their size and shape do not perfectly match the cavity of macrocycles. Moreover, a precise control over the stacking and alignment of the two functional moieties can be achieved by a

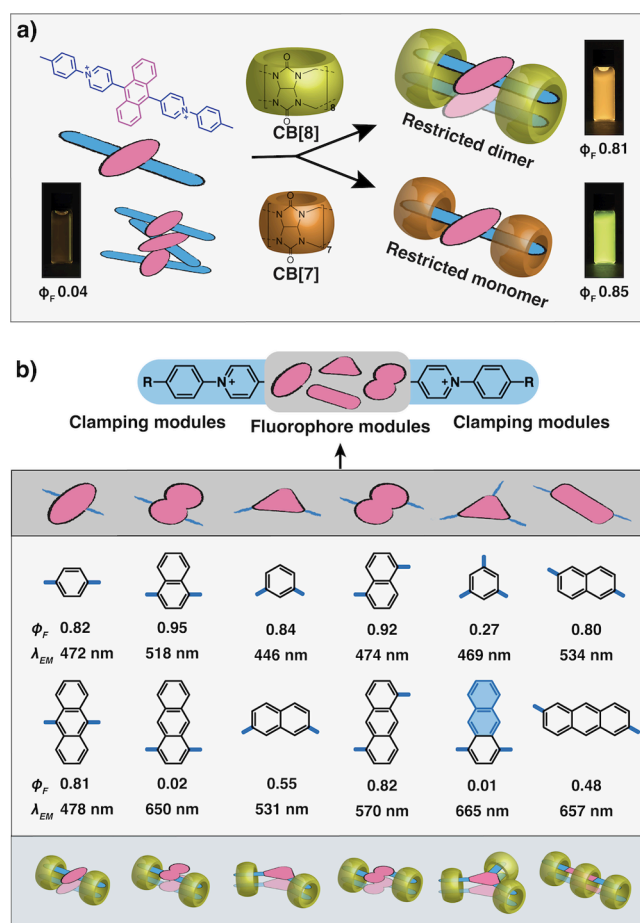


Figure 5. Pseudostatic supramolecular dimers of various chromophores constructed by the introduction of multiply $\text{CB}[8]$ restriction as exemplified in detail by (a) 9,10-anthracene moiety and universally demonstrated by (b) another ten chromophore moieties, generally exhibiting enhanced fluorescence quantum yield (ϕ_F) and bathochromic shifts in adsorption and emission. Panel (a) is adapted with permission from ref 88. Copyright (2019) Royal Society of Chemistry. Panel (b) is adapted with permission from ref 40. Copyright (2019) Royal Society of Chemistry. <https://creativecommons.org/licenses/by/3.0/>.

variation in their clamping modules. For instance, a triply restricted stacking and directional alignment of two 2,6-anthracene moieties along their long molecular axis led to extremely large bathochromic shifts in absorption and emission, which is significantly different from those of random aggregates.⁸⁸ Utilizing multiple supramolecular restrictions thereby not only strengthens the interplay within the dimeric pair, but also can precisely define their spatial alignment.

A triplet generated from a pseudostatic dimer will adopt a relaxation pathway different from those generated in a dynamic dimer according to their different exchanging rates. For example, a supramolecular dimer capable of room-temperature phosphorescence (RTP) was reported by Tian and Ma et al. using two $\text{CB}[8]$ macrocycles to construct a pair of triazine derivatives (TBP).³⁵ Single crystal analysis of the dimer showed that two TBP molecules were aligned in a parallel and partially overlapped conformation (Figure 6). Upon photoexcitation, the CT interaction between two TBPs promoted intersystem crossing to generate triplets. In contrary to triplets produced by dynamic $2\text{MPT}^{2+}\text{-CB}[8]$ dimers,⁵⁰ the triplets generated in doubly restricted $(\text{TBP})_2\text{-CB}[8]_2$ complexes

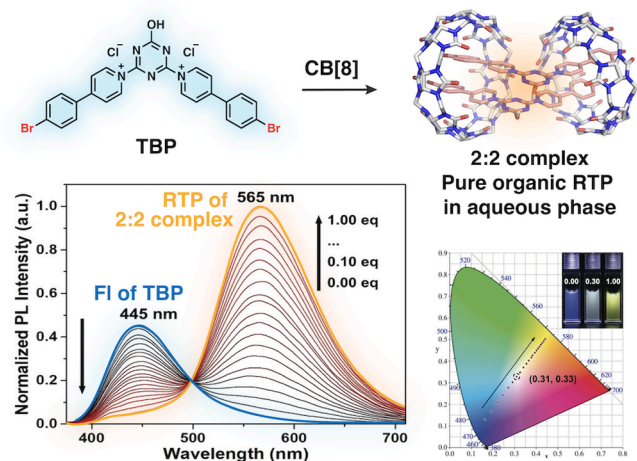


Figure 6. Single crystal structure of $(\text{TBP})_2\cdot\text{CB}[8]_2$ and photoluminescence emission spectra and chromaticity coordinates of TBP with different ratios of $\text{CB}[8]$. Adapted with permission from ref 35. Copyright (2020) Wiley-VCH.

exhibited less chance to escape the initial dimeric state but mainly relaxed along a radiative pathway leading to RTP in solution. Owing to its pseudostatic feature, the formation of this doubly restricted dimer is not susceptible to the mixing ratio of TBP and $\text{CB}[8]$. This feature enables a further development of a dual-emitting hydrogel, which is composed of restricted dimers to emit RTP and an excess amount of TBP monomers to emit fluorescence. To achieve RTP in solution is a challenging topic; the restricted supramolecular dimerization provides a feasible way to tackle this problem and provide new guidelines for the design of luminescent materials in solution. Besides RTP, through the formation of similar pseudostatic dimers, more emerging features have been achieved including enhanced emission,^{40,42–47} red-shifted absorption,^{37,45} directional self-sorting,⁸⁹ and a negative $\text{p}K_a$ shift.⁹⁰

A noncovalent dimer itself can function as a supramolecular linker, for instance, to dimerize large molecular systems like proteins as reported by Brunsveld et al.^{91,92} Being endowed with a pseudostatic feature, a supramolecular linker is kinetically steady and capable of sustaining hierarchical structures. Flood et al. and Zhang et al. have utilized doubly restricted dimeric motifs to strengthen anion–anion interaction⁹³ and CT interactions,⁹⁴ respectively, which were then performed as linkers to trigger effective supramolecular polymerization. In contrary to the complete static behaviors performed by covalent linkages,³³ a pseudostatic dimer is still of dynamic nature and convertible in responsive to the change of equilibrium. Heterodimers bearing a coupling of different moieties were thereby realized by simply mixing two pseudostatic homodimers.³² However, in order to produce exclusive heterodimeric species with minimized equilibrium byproducts, shape-complementary moieties were introduced onto clamping modules and promoted the quantitative formation of heterodimers via a social self-sorting. Following this method, an exclusive heterocoupling of naphthalene and anthracene moieties was successfully generated and exhibited a highly efficient intermolecular energy transfer upon photoexcitation.³² A rapidly changing linker is not steady enough to hold a hierarchical structure, while a completely static connection is too rigid for adaptive structure adjustment. Therefore, pseudostatic dimerization literally fills the demand

for a system that can sustain a long-lived connection yet still along with adaptive and self-correction features. This is an essential step toward the fabrication of higher-ordered molecular architectures.

3. FOLDA-DIMERS

Endowing a pair of molecular moieties with controllable features does not necessarily require a noncovalent connection or encapsulation. Covalent but switchable linkages are as well employed to fabricate folda-type dimers that are adaptive to external stimuli.

Ferrocene (Fc) can be utilized as a molecular rotor^{95,96} with a rotational barrier of two cyclopentadienyl (Cp) rings of ca. 1 kcal mol⁻¹, similar to the thermal fluctuation at room temperature of ca. 0.6 kcal mol⁻¹. Attachment of a moiety onto each Cp ring of Fc facilitates the formation of dimeric entities such as π -dimers,⁹⁷ π -pimers,⁹⁸ or diradicals.⁹⁹ Following this idea, Bucher et al.⁹⁷ and Takeuchi et al.⁹⁸ reported the synthesis of Fc derivatives having two connected viologens and naphthalenediimide (NDI), respectively. They demonstrated that the rotational dynamics could be controlled through redox stimuli. For instance, different redox states of NDI determined the pivoting motion of Fc (Figure 7a). At

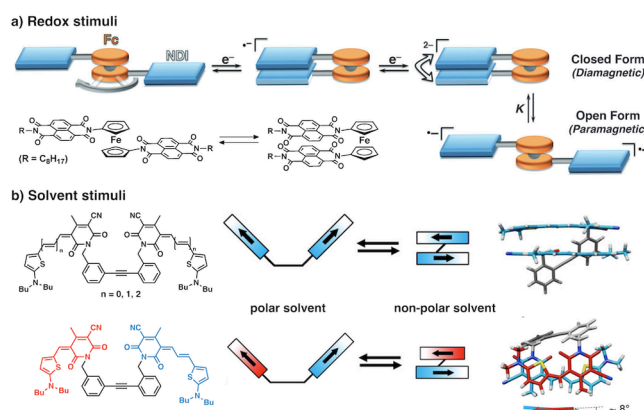


Figure 7. Folda-dimers allowed for intramolecular dimerization controlled by (a) redox stimuli and (b) solvent polarity. Panel (a) is adapted with permission from ref 98. Copyright (2013) Wiley-VCH. Panel (b) is adapted with permission from ref 103 and ref 104. Copyright (2019) Wiley-VCH.

room temperature, the rotation of NDIs was smooth in the neutral state, forbidden in the one-electron reduced state owing to the electron-rich π -bonding with a stabilization energy of 5.7 kcal mol⁻¹, and became stepwise between two equilibrated forms upon two-electron reduction.⁹⁸

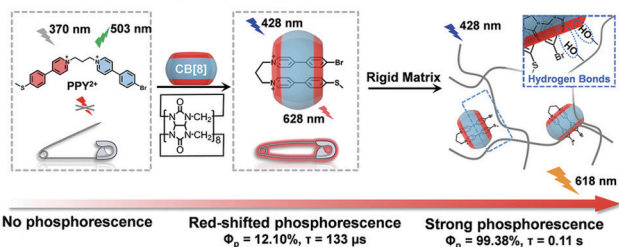
Besides redox control, the dimeric interplay within a folda-dimer can be tuned by the polarity of solvent. Würthner et al. developed a series of bis(merocyanine) derivatives with rotatable spacers.¹⁰⁰ A cofacial π -stacking of two, either homo- or hetero-, chromophores, was generated through a folding process triggered by lowering the polarity of solvent (Figure 7b). Through a modular molecular engineering, the dimeric coupling of dye's transition dipole moments could be systematically investigated with variables like chromophore types, conjugation length, and spacers.^{101–104} It thereby provided various folda-dimers with different coupling strength to enable the experimental study of the interplay between exciton and vibrational coupling.¹¹

It is noteworthy that the role of rotary or foldable linkers in the above cases is to bring the two interacting moieties to close proximity so that their dimerization is not limited by diffusion and at the same time remains certain degree of freedom for coupling. However, the linkage itself is not directly responsible for the coupling. Therefore, the strength and dynamics of dimeric interplay are determined by the intrinsic noncovalent affinity of the two moieties involved.

Restricted Folda-Dimers. Besides intrinsic affinities, a long-lasting proximity of the two moieties in a folda-dimer can be enforced and retained by the introduction of additional supramolecular restrictions like host–guest encapsulation. The resulting folda-dimers may lose their adaptive features while acquiring pseudostatic features that lead to specific photo-physical or catalytic properties.¹⁰⁵

Two phenylpyridinium (PhPyd) moieties were bridged via a flexible alkyl-spacer into a folda-dimer, as reported by Liu et al.³⁸ Upon photoexcitation, this molecule was mainly relaxed through a fluorescent radiation, suggesting weak interaction between two linked PhPyds. No phosphorescence was observed even if PhPyds were modified with heavy atoms like bromine or sulfur (Figure 8a).³⁸ However, in the presence

a) Ultralong efficient phosphorescence



b) Induced turn formation with structural chirality

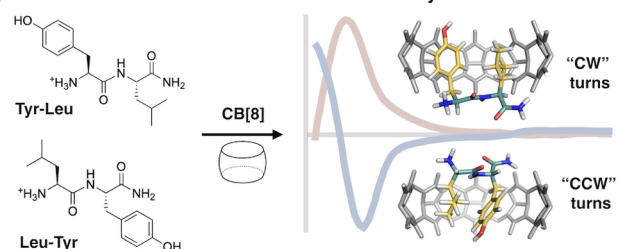


Figure 8. Restricted folda-dimerization through a self-inclusion folding into CB[8] cavity, leading to (a) ultralong efficient phosphorescence and (b) structural chirality. Panel (a) is reprinted with permission from ref 38. Copyright (2021) Wiley-VCH. Panel (b) is reprinted with permission from ref 109. Copyright (2021) American Chemical Society.

of CB[8] macrocycles, the bromine and sulfur modified PhPyds folda-dimers displayed a red-shifted RTP in solution. It was demonstrated by NMR that the two neighboring PhPyds were folded into one CB[8] cavity in a self-inclusion form. The narrow line width and split pattern of certain complexing signals in proton NMR spectra suggested a slow-exchange rate at the NMR time-scale. It is thought that this pseudostatic dimerization strengthened the interaction between two PhPyds and promoted charge-transfer during excitation for subsequent efficient intersystem crossing. A further transfer of these restricted folda-dimers into a rigid matrix led to ultrahigh phosphorescence quantum yield (ca. 99%), which enabled an application in targeted phosphorescent imaging of mitochon-

dria.³⁸ The two RTP cases, either the previous one displayed in the doubly restricted dimer³⁵ or this one performed in the restricted folda-dimer, both demonstrate the power of pseudostatic dimerization in sustaining long-lived excited states, which should increase our capability in engineering the relaxation pathway of excited species.

A macroscopic physical property such as circular dichroism (CD) of a molecular system comes from the ensemble average of the contribution from all possible states or conformations within a certain period of time. Therefore, by confining a molecular system at a specific conformation, for instance, through restricted dimerization, one may control the system to display desired functions. Urbach et al. found that a folda-dimer of oligopeptides could be readily produced by the binding of CB[8] with a specific peptide sequence,^{106,107} Scherman et al.^{108,109} then observed intense CD signals for these peptide-based folda-dimers owing to the pseudostatic secondary structure induced by the restricted folding. Moreover, the secondary chirality can be simply inverted by changing the sequence (Figure 8b).¹⁰⁹ This restricted turn-type motif is thermodynamically and kinetically stable enough to manipulate the folding of a peptide sequence, offering a facile way to perform artificial protein folding.

The selected conformation, spatial proximity, and long-lasting interaction favored by the restricted folda-dimer can facilitate chemical reactions in a microenvironment.⁵ The intramolecular Diels–Alder reaction of *N*-allyl-2-furfurylamine derivatives was accelerated by more than 1000 times by a tight and self-inclusion folding inside a CB[7] cavity.¹¹⁰ Fujita et al. found that a crowded dimerization of reagents in a coordinated cage eased the hydration of amide bonds.¹¹¹ Attaching restricted folda-dimers to the reaction center is an alternative way to regulate their reactivity. For the Fenton oxidation of a 1,4-diketopyrrolo[3,4-*c*]pyrrole derivative (DPP), its radical cation (DPP^{•+}) is the key intermediate to determine the reaction rate. Zhang et al. found a close contact of the carbonyl groups to the spin center of DPP^{•+} can enhance the reactivity of radical cations. This is realized by a self-inclusion complexation of DPP side groups with CB[8], which accelerated the Fenton oxidation by more than 100 times (Figure 9).¹¹² By contrast, a loose binding over alkyl chains with smaller CB[7] macrocycles, which were slightly far away from the radical cation center, only displayed mild catalytic effect. In other words, the restricted folda-dimer may play up

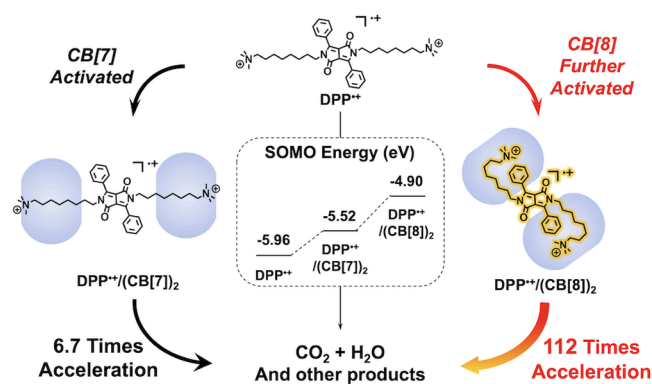


Figure 9. Fenton oxidation of DPP derivatives activated by the association with cucurbiturils. Reprinted with permission from ref 112. Copyright (2018) Royal Society of Chemistry.

the electronic effect and further activate radical cations, thus providing a new way for supramolecular catalysis.

4. MACROCYCLIC DIMERS

Two types of pseudostatic dimers are introduced so far: one can be regarded as a dimer restricted by multiple noncovalent linkages; the other folda-type can be taken as a dimer sustained via a combination of covalent and noncovalent connections. It is the introduction of noncovalent components that endows the system with dynamic features, whereas the presence of multivalency makes it less dynamic.

If all the multiple connections are covalent as typically exemplified by cyclophanes,^{113,114} it results in macrocyclic dimers with settled spatial alignments. Settled dimeric alignment is not necessarily equivalent to an effective interplay of dimeric moieties. Instead, optimized spatial coupling is hardly achieved in the macrocyclic dimer on account of its limited degree of structural freedom. For instance, Young, Wasielewski et al. reported a series of cycloalkanes containing two coplanar oriented extended viologens, whose planar distance was variable according to the substitution fashion of their xylylene linkers (Figure 10).³³ Upon photoexcitation, the

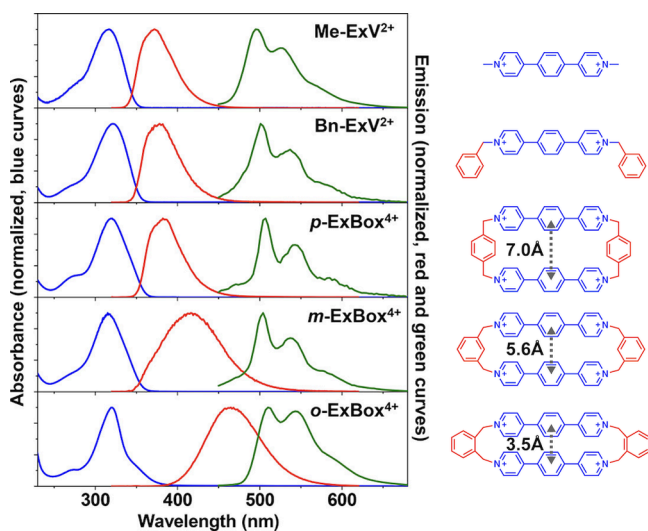


Figure 10. Normalized absorption (blue line) and fluorescence (red line) spectra of a series of extended viologen derivatives in CH_3CN at 295 K and phosphorescence (green line) spectra in glassy PrCN at 77 K. Adapted with permission from ref 33. Copyright (2017) American Chemical Society.

charge-transfer of these cyclophanes exhibited distance dependence leading to variation in emission (red line in Figure 10). However, the absorption of all relevant species was unified (blue line in Figure 10) and insensitive to their planar distance, which suggested ineffective π -stacking or orbital hybridization between coplanar oriented viologen derivatives. This is contrary to the pseudostatic supramolecular dimers of extended viologens as mentioned above,^{40,45} where the noncovalent dimeric interplay is sustained via multiple $\text{CB}[8]$ bindings and displays significant bathochromic shifts in both absorption and emission. The supramolecular restriction still allows the dimerized chromophores to self-optimize their alignments toward an effective π -stacking.

To Squeeze a Macrocyclic Dimer. Properties of a macrocyclic dimer, however, can still be regulated by introducing additional supramolecular restrictions. Recently,

Stoddart et al. reported the formation of ring-in-ring(s) complexes by threading a cyclophane-based dimer through $\text{CB}[8]$ macrocycles (Figure 11a–d).³⁹ The introduced supra-

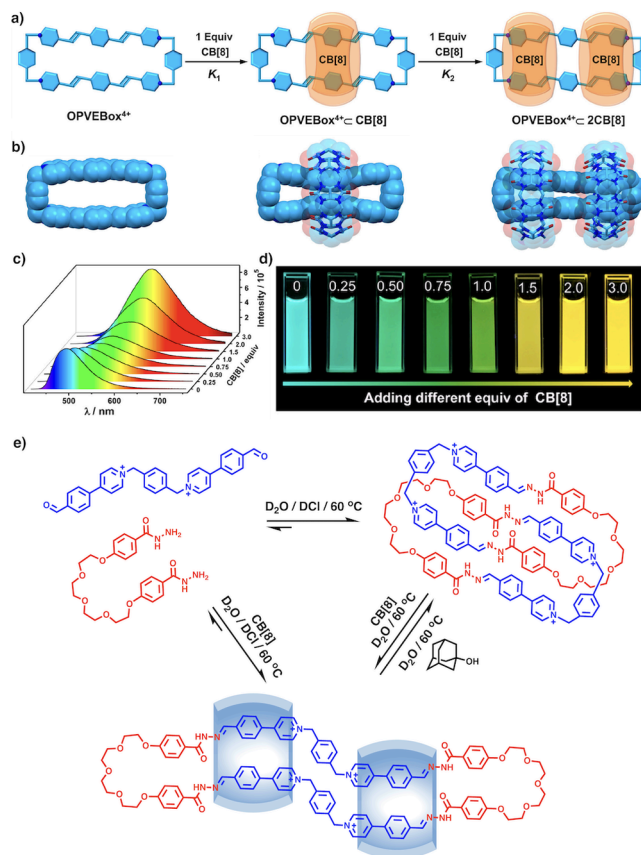


Figure 11. Schematic diagram of (a) ring-in-ring(s) complexes with an extended tetracationic cyclophane threaded through one or two $\text{CB}[8]$ macrocycles and their corresponding space-filling representations (b). Color-tunable emission (c) and fluorescence photographs (d) of a series of cyclophane solutions with the addition of different equivalents of $\text{CB}[8]$ macrocycles. Adapted with permission from ref 39. Copyright (2020) American Chemical Society. (e) Synthesis of an ultralarge macrocycle driven by the preferable formation of ring-in-ring(s) complexes. Adapted with permission from ref 115. Copyright (2022) Royal Society of Chemistry. <https://creativecommons.org/licenses/by/3.0/>.

molecular restriction “squeezes” the extended tetracationic cyclophane ring mechanically, thereby narrowing the planar distance between two extended viologen moieties and facilitating their effective π -stacking. Compared with uncomplexed cyclophanes, the resulting ring-in-ring complexes exhibited significant bathochromic shifts in absorption as well as in emission along with increased fluorescence lifetime. Moreover, the bathochromic effect was augmented when more $\text{CB}[8]$ macrocycles were bound to squeeze the cyclophane backbone. As a consequence, color-tunable emissions were realized in one single chromophore from sky blue, to cyan, green, and yellow, by simply adding different amounts of supramolecular cofactors like $\text{CB}[8]$ macrocycles. This work opens up a feasible approach to attain tunable multicolor dyes based on single chromophores without introducing irreversible chemical reactions.

Conformation of the squeezed inner ring in a ring-in-ring complex is often thermodynamically unfavorable by itself. By

associating with supramolecular binding events, however, such uncomfortable conformations become attainable owing to the favorable free energy changes contributed by the associated bindings. In other words, the propensity toward the formation of ring-in-ring complexes can be used as a driving force to catalyze the direct synthesis of specific products that are not achievable under normal reaction conditions. Li et al. recently demonstrated this idea and used it to successfully synthesize an ultralarge macrocycle.¹¹⁵ A dihydrazide with a glycol spacer and a cationic bisaldehyde with a *p*-xylene linker, as shown in Figure 11e, typically condensed in a [1 + 1] manner into macrocycles, which actually led to a quantitative formation of [2]catenanes consisting of two interlocked macrocycles. In the presence of CB[8], the same reagents and conditions resulted in a ring-in-ring product containing an ultralarge macrocycle as the inner ring. Products of both reactions were confirmed unambiguously by single crystal XRD analysis. It was found that cationic bisaldehydes were prone to form a pseudostatic supramolecular dimer as clamped by two CB[8] macrocycles. In this preorganized complex, two bisaldehydes had to adopt an expanded conformation which only allowed for condensation in a [2 + 2] manner, thereby generating a macrocyclic dimer with an ultralarge backbone containing over one hundred atoms. However, this ultralarge and flexible backbone had to be sustained by outer rings, as it would turn back to [2]catenane products when withdrawing CB[8] by competitive guests such as adamantan-1-ol.¹¹⁵ We foresee this flaw could be solved by employing dynamic covalent linkages that are capable of performing subsequent reactions toward robust covalent bonds.

5. DISCRETE DIMERS IN SOLID STATES

The dimers that have been introduced so far are all constructed with the help of third-party linkers, either covalently or noncovalently. This prelinking design can minimize the concentration effect and allow for effective dimerization taking place in a broad range of conditions, which is particularly helpful for dimeric moieties of weak attraction or even repulsion. For moieties that are of a strong attraction between each other and prone to aggregation, a steric spacer, instead of a linker, is needed to ensure an anticooperative dimerization with only dimeric products, i.e., discrete dimers, by blocking unlimited aggregation.

Perylene bisimide (PBI) derivatives, for instance, are a typical class of fluorophores that are inclined to aggregate and often suffer from aggregation-caused emission quenching, particularly, in solid states. In order to prevent its unlimited aggregation, Würthner et al. bridged the two bay positions of PBIs by a macrocyclic spacer, which sterically blocked one π -face of the PBIs and allowed the other face to dimerize freely with only a second PBI (Figure 12a).¹¹⁶ The bridging unit substituted from bay positions, meanwhile, evokes a twist of the chromophore core. As a result, the dimeric π -stacking exhibited a chiral recognition with self-recognition prevailing over self-discrimination.¹¹⁶ Although the distortion of the core was demonstrated to be alleviated by lengthening the bridge unit,¹¹⁷ it inevitably led to photophysical properties different from typical planar PBI cores. By substituting at the two imide positions, Stoddart et al. further developed a series of PBI derivatives showing a rigid structure with a cyclic triangular geometry.¹¹⁸ This way of substitution not only favored the formation of discrete PBI–PBI π -dimers, but also maintained an undistorted planar fluorophore core, which was confirmed

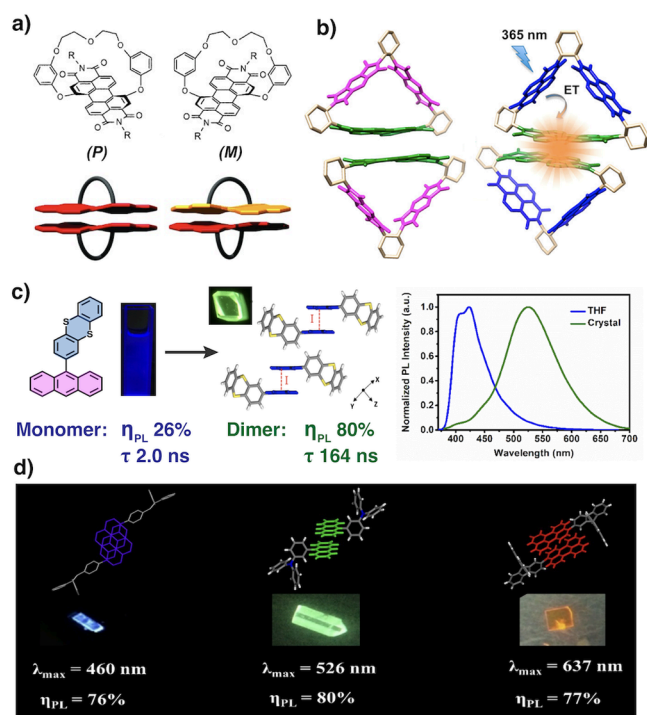


Figure 12. (a) Schematic representation of chiral PBIs modified from bay positions of the PBI core and their competitive homo- and heterodimerization products. Reprinted with permission from ref 116. Copyright (2010) Wiley-VCH. (b) Triangular PBIs modified from two imide positions. Reprinted with permission from ref 28. Copyright (2019) American Chemical Society. (c) Photophysical properties of TA-AN in its dispersed solution and dimerized crystal state. Adapted with permission from ref 121. Copyright (2016) Royal Society of Chemistry. (d) Emissive crystals of discrete π -dimers achievable for a variety of fluorophores that generally exhibited high-efficiency dimer-based emissions. Adapted with permission from ref 123. Copyright (2019) American Chemical Society.

by single crystal XRD analysis (Figure 12b).²⁸ In the solid state, the discrete dimers formed by these triangular PBIs exhibited enhanced fluorescence efficiency of at least an order of magnitude higher than the reference PBI.

The fluorescence intensity of modified PBIs, although increased by an order of magnitude, was still quite weak considering that the reference PBI was almost completely quenched in solid state.²⁸ However, the finding of achieving enhanced solid-state emission through the pursuit of discrete dimers or oligomers is inspiring. Along this line, Yang et al. developed a series of highly emissive organic crystals consisting of discrete pairwise fluorophore dimers.^{119–122} For example, an anthracene moiety was tethered by a bent thianthrene group (TA-AN) that only allowed for a pairwise stacking of anthracenes in its crystal state (Figure 12c).¹²¹ In contrast with short-life blue emission of 26% efficiency in its dispersed solution, the crystal of discrete TA-AN dimers exhibited excimer fluorescence with bathochromic emission, significantly enhanced luminous efficiency (up to 80%), and elongated lifetime (164 ns). Besides bent thianthrene, other steric tethering groups such as triphenylamine,¹²³ spirofluorene,¹²³ 2-(*p*-tolyl)ethene-1,1-diyl)dibenzene,¹²⁴ and tetra-phenyl ethylene¹²⁰ were demonstrated to play the same role in ensuring discrete fluorophore dimerization in crystal states. On the other hand, highly emissive crystals with different wavelengths were also obtained through a variation in the π -conjugation of

fluorophore moieties, while the tethering group remained unchanged (Figure 12d).¹²³

It is noteworthy that crystals of discrete dimers should be distinguished from the classic bimolecular cocrystals extensively reported before.^{125,126} Both types of crystals consist of pairwise entities as their minimized repeated unit. However, the repeated dimeric units in a classic bimolecular crystal will continue to interact with other pairs in a coherent fashion, in contrast to the localized dimeric interplay within the crystal of discrete dimers. With regard to fluorophore dimers, the extensive stacking in bimolecular crystals often results in emission quenching according to the energy gap law, while discrete and localized dimerization without unlimited stacking can uphold the emission.

In addition, the restriction offered by rigid crystal frameworks that limited the nonradiative decay is another key request toward high-efficiency emission. In other words, the dimerized systems which adopt a passive exclusion design by tethering steric repulsive groups may perform quite differently in solution and in crystal states. This could be an advantage if a self-adaptive system is desired to react according to external stimuli such as pressure,¹²⁰ temperature,¹¹⁹ and vapors.¹²⁴ However, discrete dimers achieved by this means may not meet the need in material applications which mostly require consistent performance. An alternative way to address this problem is to transfer pseudostatic dimers that are designed and fabricated by active restriction strategy from solution to solid states, a positive attempt of which has been carried out by Liu et al. in their restricted folda-dimers, as mentioned in Figure 8a.³⁸

6. PERSPECTIVES AND OUTLOOK

“One begets two; two begets three; three begets everything.” This is how Taoism, a Chinese philosophy, interprets the formation of our material universe. This Perspective, with a similar logic yet only regarding to the formation of organic functional materials, briefly introduces various approaches toward a molecular system consisting of “two” key components, i.e., dimerization. We particularly emphasize the important roles of supramolecular restrictions in defining dimeric features. Effective dimerization can be generally performed through an association with energy-favorable prelinking processes such as covalent bonding or noncovalent binding. We attempt to demonstrate that it is the number of, rather than the type of, linkages that mainly determines the dynamic property of a dimerized system. On the one hand, a dimer prelinked by single covalent bridge can be a switchable folda-dimer and become less dynamic by appending supramolecular restrictions.^{38,109} On the other hand, a dimer restricted by multiple noncovalent linkages can be rather static, denoted here as pseudostatic, yet still be adaptive to variations.^{32,40} We highlight the recent progress in fabricating pseudostatic supramolecular systems that can sustain molecular interplay for a long period of time. This elongated association allows for active species like radicals and excimers to decay along an alternate pathway thereby spinning off emerging properties such as RTP in solutions, DIEE, and highly efficient catalysis that are not readily accessible from conventional dynamic systems.

There is still plenty of room left for the precision chemistry of noncovalent dimerization, as we can envision at least in the following four aspects:

1. Toward quantification. Noncovalent dimers in the current stage are only described with qualitative terms like “dynamic”, “pseudostatic”, and “static” due to the lack of kinetic data from the literature. Although whether it is fast or slow, dynamic or static highly depends on the time scale of studied physicochemical properties, it is crucial to quantify the kinetic aspects of specific objects like photoexcited dimers in order to provide quantitative insights into their relaxation and catalytic features. We thereby anticipate more effort being made to enrich the kinetic database so that quantitative criteria can be established for dimeric molecular systems.
2. Toward interface. Despite the deep dive in solutions and solid states, dimerization at the interface is important yet rarely explored, particularly in pseudostatic systems. Recent attempts of using noncovalent dimers as single-(supra)molecular circuits have provided valuable information on charge transport^{127,128} and quantum interference.¹²⁹ With a complexation nature that is neither fast exchanging nor completely static, it is anticipated that pseudostatic chromophore dimers at the interface would be robust yet self-adaptive tectons or linkers for the fabrication of optical molecular devices. This lays the foundations for the further construction of photon-based molecular integrated circuits that not only generate less heat and allow for higher data transfer rates than electronic systems, but also would be capable in manipulation of the quantum state of light for optical quantum computing.¹³⁰
3. Toward customization. In terms of spatial alignments in dimerization, many cases display a dimeric cofacial stacking of chromophores, which is not necessarily the most desired geometry. Singlet fission that can generate two triplet excitons from one high-energy singlet exciton, for instance, requires the chromophore dimerization in close proximity but often suffers from their cofacial stacking.¹³¹ It is thereby desired to develop a more flexible dimerization that can customize the position and alignment of functional moieties. Moreover, although customizable positioning of (bio)molecular entities has been realized through DNA engineering with a spatial resolution at the molecular level,¹³² noncovalent dimerization with tunable dynamics may further allow for manipulation over functional molecules with adequate temporal resolution. This will append another dimension during the survey of energy landscapes for molecular coupling and provide additional understanding for dimer-based physical processes.¹³³
4. Toward oligomers. In order to fill the gap between “two” and “everything”, it is highly desirable to expand our capability from “two”, i.e., dimers, to “three”, which can be regarded as oligomers in a general sense. Although a supramolecular trimer has recently been demonstrated using a cucurbituril homologue larger than CB[8],¹³⁴ the idea of simply expanding the cavity size of macrocycles may not work for bigger oligomers. The driving force stemmed from the release of “high energy” water will drop dramatically when the cavity is too big to generate a “frustrated” water network. To address this point, rather than expanding macrocycles, we anticipate more effort be made in developing diverse frameworks, either organic or inorganic, which possess anisotropic inner-space with the size of at least one dimension small

enough to comfort the oligomerization. It is anticipated that next-generation pigments would be prepared from only one single dye, but could display various colors by simply mixing with different molecular “containers”, where the color is mainly determined by the degree of oligomerization.

To make a long story short, noncovalent dimerization is a field that we can continue to make full use of the power of imagination, though lots of beautiful chemistry has been discovered in this regard. Various tailor-made architectures can be envisioned, and more importantly, ensembles with emerging functions may be achieved through noncovalent dimerization. Bridging the gap between tailor-made architectures and emerging functions will enrich the realm of molecular engineering for functional supramolecular systems.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

BAP, bis(*N*-arylpyridinium); CD, circular dichroism; Cp, cyclopentadienyl; CT, charge-transfer; DIEE, dimerization-induced enhanced emission; DPP, 1,4-diketopyrrolo[3,4-*c*]pyrrole derivative; Fc, ferrocene; MPT^{•+}, *N,N'*-dimethylated dipyrrolium thiazolo[5,4-*d*]thiazole radical cation; MPT²⁺, *N,N'*-dimethylated dipyrrolium thiazolo[5,4-*d*]thiazole cation; NDI, naphthalenediimide; NIR, near-infrared; NMR,

nuclear magnetic resonance; PBI, perylene bisimide; PhPyd, phenylpyridinium; RTP, room-temperature phosphorescence; XRD, X-ray diffraction.

REFERENCES

- (1) Ostroverkhova, O. Organic Optoelectronic Materials: Mechanisms and Applications. *Chem. Rev.* **2016**, *116*, 13279–13412.
- (2) Xiang, D.; Wang, X.; Jia, C.; Lee, T.; Guo, X. Molecular-Scale Electronics: from Concept to Function. *Chem. Rev.* **2016**, *116*, 4318–4440.
- (3) Gao, M.; Yu, F.; Lv, C.; Choo, J.; Chen, L. Fluorescent Chemical Probes for Accurate Tumor Diagnosis and Targeting Therapy. *Chem. Soc. Rev.* **2017**, *46*, 2237–2271.
- (4) Balachandran, Y. L.; Jiang, X. Aggregation-Induced Fluorogens in Bio-Detection, Tumor Imaging, and Therapy: A Review. *CCS Chem.* **2022**, *4*, 420–436.
- (5) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. Functional Molecular Flasks: New Properties and Reactions within Discrete, Self-Assembled Hosts. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418–3438.
- (6) Raynal, M.; Ballester, P.; Vidal-Ferran, A.; van Leeuwen, P. W. N. M. Supramolecular Catalysis. Part 1: Non-Covalent Interactions as a Tool for Building and Modifying Homogeneous Catalysts. *Chem. Soc. Rev.* **2014**, *43*, 1660–1733.
- (7) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. Artificial Molecular Machines. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391.
- (8) Dattler, D.; Fuks, G.; Heiser, J.; Moulin, E.; Perrot, A.; Yao, X.; Giuseppone, N. Design of Collective Motions from Synthetic Molecular Switches, Rotors, and Motors. *Chem. Rev.* **2020**, *120*, 310–433.
- (9) Browne, W. R.; Feringa, B. L. Making Molecular Machines Work. *Nat. Nanotechnol.* **2006**, *1*, 25–35.
- (10) Cademartiri, L.; Bishop, K. J. M.; Snyder, P. W.; Ozin, G. A. Using Shape for Self-Assembly. *Philos. Trans. R. Soc. A* **2012**, *370*, 2824–2847.
- (11) Bialas, D.; Kirchner, E.; Röhr, M. I. S.; Würthner, F. Perspectives in Dye Chemistry: A Rational Approach toward Functional Materials by Understanding the Aggregate State. *J. Am. Chem. Soc.* **2021**, *143*, 4500–4518.
- (12) Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718–11940.
- (13) Würthner, F. Aggregation-Induced Emission (AIE): A Historical Perspective. *Angew. Chem., Int. Ed.* **2020**, *59*, 14192–14196.
- (14) Biedermann, F.; Nau, W. M.; Schneider, H.-J. The Hydrophobic Effect Revisited—Studies with Supramolecular Complexes Imply High-Energy Water as a Noncovalent Driving Force. *Angew. Chem., Int. Ed.* **2014**, *53*, 11158–11171.
- (15) Hong, F.; Zhang, F.; Liu, Y.; Yan, H. DNA Origami: Scaffolds for Creating Higher Order Structures. *Chem. Rev.* **2017**, *117*, 12584–12640.
- (16) Lutz, J.-F.; Lehn, J.-M.; Meijer, E. W.; Matyjaszewski, K. From Precision Polymers to Complex Materials and Systems. *Nat. Rev. Mater.* **2016**, *1*, 16024.
- (17) Mattia, E.; Otto, S. Supramolecular Systems Chemistry. *Nat. Nanotechnol.* **2015**, *10*, 111–119.
- (18) Engels, B.; Engel, V. The Dimer-Approach to Characterize Opto-Electronic Properties of and Exciton Trapping and Diffusion in Organic Semiconductor Aggregates and Crystals. *Phys. Chem. Chem. Phys.* **2017**, *19*, 12604–12619.
- (19) Fink, R. F.; Seibt, J.; Engel, V.; Renz, M.; Kaupp, M.; Lochbrunner, S.; Zhao, H.-M.; Pfister, J.; Würthner, F.; Engels, B. Exciton Trapping in π -Conjugated Materials: A Quantum-Chemistry-Based Protocol Applied to Perylene Bisimide Dye Aggregates. *J. Am. Chem. Soc.* **2008**, *130*, 12858–12859.
- (20) Lehn, J.-M. From Supramolecular Chemistry towards Constitutional Dynamic Chemistry and Adaptive Chemistry. *Chem. Soc. Rev.* **2007**, *36*, 151–160.

- (21) De Greef, T. F. A.; Smulders, M. M. J.; Wolfs, M.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. Supramolecular Polymerization. *Chem. Rev.* **2009**, *109*, 5687–5754.
- (22) Yang, L.; Tan, X.; Wang, Z.; Zhang, X. Supramolecular Polymers: Historical Development, Preparation, Characterization, and Functions. *Chem. Rev.* **2015**, *115*, 7196–7239.
- (23) Würthner, F.; Kaiser, T. E.; Saha-Möllner, C. R. J-Aggregates: From Serendipitous Discovery to Supramolecular Engineering of Functional Dye Materials. *Angew. Chem., Int. Ed.* **2011**, *50*, 3376–3410.
- (24) Vonhausen, Y.; Lohr, A.; Stolte, M.; Würthner, F. Two-Step Anti-Cooperative Self-Assembly Process into Defined π -Stacked Dye Oligomers: Insights into Aggregation-Induced Enhanced Emission. *Chem. Sci.* **2021**, *12*, 12302–12314.
- (25) Gershberg, J.; Fennel, F.; Rehm, T. H.; Lochbrunner, S.; Würthner, F. Anti-Cooperative Supramolecular Polymerization: A New K₂-K Model Applied to the Self-Assembly of Perylene Bisimide Dye Proceeding via Well-Defined Hydrogen-Bonded Dimers. *Chem. Sci.* **2016**, *7*, 1729–1737.
- (26) Gemen, J.; Ahrens, J.; Shimon, L. J. W.; Klajn, R. Modulating the Optical Properties of BODIPY Dyes by Noncovalent Dimerization within a Flexible Coordination Cage. *J. Am. Chem. Soc.* **2020**, *142*, 17721–17729.
- (27) Gut, D.; Rudi, A.; Kopilov, J.; Goldberg, I.; Kol, M. Pairing of Propellers: Dimerization of Octahedral Ruthenium(II) and Osmium(II) Complexes of Eilatin via π - π Stacking Featuring Heterochiral Recognition. *J. Am. Chem. Soc.* **2002**, *124*, 5449–5456.
- (28) Mohan Nalluri, S. K.; Zhou, J.; Cheng, T.; Liu, Z.; Nguyen, M. T.; Chen, T.; Patel, H. A.; Krzyaniak, M. D.; Goddard, W. A.; Wasielewski, M. R.; Stoddart, J. F. Discrete Dimers of Redox-Active and Fluorescent Perylene Diimide-Based Rigid Isosceles Triangles in the Solid State. *J. Am. Chem. Soc.* **2019**, *141*, 1290–1303.
- (29) Shao, C.; Grüne, M.; Stolte, M.; Würthner, F. Perylene Bisimide Dimer Aggregates: Fundamental Insights into Self-Assembly by NMR and UV/Vis Spectroscopy. *Chem.—Eur. J.* **2012**, *18*, 13665–13677.
- (30) Martin, R. B. Comparisons of Indefinite Self-Association Models. *Chem. Rev.* **1996**, *96*, 3043–3064.
- (31) Chen, Z.; Lohr, A.; Saha-Möllner, C. R.; Würthner, F. Self-Assembled π -Sacks of Functional Dyes in Solution: Structural and Thermodynamic Features. *Chem. Soc. Rev.* **2009**, *38*, 564–584.
- (32) Wu, G.; Huang, Z.; Scherman, O. A. Quantitative Supramolecular Heterodimerization for Efficient Energy Transfer. *Angew. Chem., Int. Ed.* **2020**, *59*, 15963–15967.
- (33) Wu, Y.; Zhou, J.; Phelan, B. T.; Mauck, C. M.; Stoddart, J. F.; Young, R. M.; Wasielewski, M. R. Probing Distance Dependent Charge-Transfer Character in Excimers of Extended Viologen Cyclophanes Using Femtosecond Vibrational Spectroscopy. *J. Am. Chem. Soc.* **2017**, *139*, 14265–14276.
- (34) Jon, S. Y.; Ko, Y. H.; Park, S. H.; Kim, H.-J.; Kim, K. A Facile, Stereoselective [2 + 2] Photoreaction Mediated by Cucurbit[8]uril. *Chem. Commun.* **2001**, 1938–1939.
- (35) Wang, J.; Huang, Z.; Ma, X.; Tian, H. Visible-Light-Excited Room-Temperature Phosphorescence in Water by Cucurbit[8]uril-Mediated Supramolecular Assembly. *Angew. Chem., Int. Ed.* **2020**, *59*, 9928–9933.
- (36) Wang, Q.; Zhong, Y.; Miller, D. P.; Lu, X.; Tang, Q.; Lu, Z.-L.; Zurek, E.; Liu, R.; Gong, B. Self-Assembly and Molecular Recognition in Water: Tubular Stacking and Guest-Templated Discrete Assembly of Water-Soluble, Shape-Persistent Macrocycles. *J. Am. Chem. Soc.* **2020**, *142*, 2915–2924.
- (37) Wu, G.; Olesinska, M.; Wu, Y.; Matak-Vinkovic, D.; Scherman, O. A. Mining 2:2 Complexes from 1:1 Stoichiometry: Formation of Cucurbit[8]uril-Diarylvologen Quaternary Complexes Favored by Electron-Donating Substituents. *J. Am. Chem. Soc.* **2017**, *139*, 3202–3208.
- (38) Ma, X.-K.; Zhang, W.; Liu, Z.; Zhang, H.; Zhang, B.; Liu, Y. Supramolecular Pins with Ultralong Efficient Phosphorescence. *Adv. Mater.* **2021**, *33*, 2007476.
- (39) Wu, H.; Wang, Y.; Jones, L. O.; Liu, W.; Song, B.; Cui, Y.; Cai, K.; Zhang, L.; Shen, D.; Chen, X.-Y.; Jiao, Y.; Stern, C. L.; Li, X.; Schatz, G. C.; Stoddart, J. F. Ring-in-Ring(s) Complexes Exhibiting Tunable Multicolor Photoluminescence. *J. Am. Chem. Soc.* **2020**, *142*, 16849–16860.
- (40) Wu, G.; Bae, Y. J.; Olesińska, M.; Antón-García, D.; Szabó, I.; Rosta, E.; Wasielewski, M. R.; Scherman, O. A. Controlling the Structure and Photophysics of Fluorophore Dimers Using Multiple Cucurbit[8]uril Clampings. *Chem. Sci.* **2020**, *11*, 812–825.
- (41) Birks, J. B. Excimers. *Rep. Prog. Phys.* **1975**, *38*, 903–974.
- (42) Schoder, S.; Schröder, H. V.; Cera, L.; Puttreddy, R.; Güttler, A.; Resch-Genger, U.; Rissanen, K.; Schalley, C. A. Strong Emission Enhancement in pH-Responsive 2:2 Cucurbit[8]uril Complexes. *Chem.—Eur. J.* **2019**, *25*, 3257–3261.
- (43) Mohanty, J.; Thakur, N.; Dutta Choudhury, S.; Barooh, N.; Pal, H.; Bhasikuttan, A. C. Recognition-Mediated Light-Up of Thiazole Orange with Cucurbit[8]uril: Exchange and Release by Chemical Stimuli. *J. Phys. Chem. B* **2012**, *116*, 130–135.
- (44) Zhang, B.; Dong, Y.; Li, J.; Yu, Y.; Li, C.; Cao, L. Pseudo[n,m]rotaxanes of Cucurbit[7/8]uril and Viologen-Naphthalene Derivative: A Precise Definition of Rotaxane. *Chin. J. Chem.* **2019**, *37*, 269–275.
- (45) Olesińska, M.; Wu, G.; Gómez-Coca, S.; Antón-García, D.; Szabó, I.; Rosta, E.; Scherman, O. A. Modular Supramolecular Dimerization of Optically Tunable Extended Aryl Viologens. *Chem. Sci.* **2019**, *10*, 8806–8811.
- (46) Zhang, X.; Sun, T.; Ni, X.-L. Fluorescence Visualization of Cucurbit[8]uril-Triggered Dynamic Host-Guest Assemblies. *Org. Chem. Front.* **2021**, *8*, 32–38.
- (47) Mohanty, J.; Dutta Choudhury, S.; Upadhyaya, H. P.; Bhasikuttan, A. C.; Pal, H. Control of the Supramolecular Excimer Formation of Thioflavin T within a Cucurbit[8]uril Host: A Fluorescence On/Off Mechanism. *Chem.—Eur. J.* **2009**, *15*, 5215–5219.
- (48) Jiao, Y.; Xu, J.-F.; Wang, Z.; Zhang, X. Visible-Light Photoinduced Electron Transfer Promoted by Cucurbit[8]uril-Enhanced Charge Transfer Interaction: Toward Improved Activity of Photocatalysis. *ACS Appl. Mater. Interfaces* **2017**, *9*, 22635–22640.
- (49) Uchikura, T.; Oshima, M.; Kawasaki, M.; Takahashi, K.; Iwasawa, N. Supramolecular Photocatalysis by Utilizing the Host-Guest Charge-Transfer Interaction: Visible-Light-Induced Generation of Triplet Anthracenes for [4 + 2] Cycloaddition Reactions. *Angew. Chem., Int. Ed.* **2020**, *59*, 7403–7408.
- (50) Tang, B.; Xu, W.; Xu, J.-F.; Zhang, X. Transforming a Fluorochrome to an Efficient Photocatalyst for Oxidative Hydroxylation: A Supramolecular Dimerization Strategy Based on Host-Enhanced Charge Transfer. *Angew. Chem., Int. Ed.* **2021**, *60*, 9384–9388.
- (51) Tang, B.; Li, W.-L.; Chang, Y.; Yuan, B.; Wu, Y.; Zhang, M.-T.; Xu, J.-F.; Li, J.; Zhang, X. A Supramolecular Radical Dimer: High-Efficiency NIR-II Photothermal Conversion and Therapy. *Angew. Chem., Int. Ed.* **2019**, *58*, 15526–15531.
- (52) Siebert, X.; Amzel, L. M. Loss of Translational Entropy in Molecular Associations. *Proteins* **2004**, *54*, 104–115.
- (53) Kim, H.-J.; Heo, J.; Jeon, W. S.; Lee, E.; Kim, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. Selective Inclusion of a Hetero-Guest Pair in a Molecular Host: Formation of Stable Charge-Transfer Complexes in Cucurbit[8]uril. *Angew. Chem., Int. Ed.* **2001**, *40*, 1526–1529.
- (54) Barrow, S. J.; Kasera, S.; Rowland, M. J.; del Barrio, J.; Scherman, O. A. Cucurbituril-Based Molecular Recognition. *Chem. Rev.* **2015**, *115*, 12320–12406.
- (55) Conn, M. M.; Rebek, J. Self-Assembling Capsules. *Chem. Rev.* **1997**, *97*, 1647–1668.
- (56) Zhu, Y.-J.; Gao, Y.; Tang, M.-M.; Rebek, J.; Yu, Y. Dimeric Capsules Self-Assembled Through Halogen and Chalcogen Bonding. *Chem. Commun.* **2021**, *57*, 1543–1549.
- (57) Zhao, W.; Flood, A. H.; White, N. G. Recognition and Applications of Anion-Anion Dimers Based on Anti-electrostatic Hydrogen Bonds (AEHBs). *Chem. Soc. Rev.* **2020**, *49*, 7893–7906.

- (58) Lee, S.; Chen, C.-H.; Flood, A. H. A Pentagonal Cyanostar Macrocycle with Cyanostilbene CH Donors Binds Anions and Forms Diallylphosphate [3]Rotaxanes. *Nat. Chem.* **2013**, *5*, 704–710.
- (59) Fatila, E. M.; Twum, E. B.; Karty, J. A.; Flood, A. H. Ion Pairing and Co-facial Stacking Drive High-Fidelity Bisulfate Assembly with Cyanostar Macrocylic Hosts. *Chem.—Eur. J.* **2017**, *23*, 10652–10662.
- (60) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. Supramolecular Coordination: Self-Assembly of Finite Two- and Three-Dimensional Ensembles. *Chem. Rev.* **2011**, *111*, 6810–6918.
- (61) Sharma, V. K.; Mahammed, A.; Mizrahi, A.; Morales, M.; Fridman, N.; Gray, H. B.; Gross, Z. Dimeric Corrole Analogs of Chlorophyll Special Pairs. *J. Am. Chem. Soc.* **2021**, *143*, 9450–9460.
- (62) Schmidt, B. M.; Osuga, T.; Sawada, T.; Hoshino, M.; Fujita, M. Compressed Corannulene in a Molecular Cage. *Angew. Chem., Int. Ed.* **2016**, *55*, 1561–1564.
- (63) Kishi, N.; Li, Z.; Sei, Y.; Akita, M.; Yoza, K.; Siegel, J. S.; Yoshizawa, M. Wide-Ranging Host Capability of a Pd^{II}-Linked M₂L₄ Molecular Capsule with an Anthracene Shell. *Chem.—Eur. J.* **2013**, *19*, 6313–6320.
- (64) Chan, A. K.-W.; Ng, M.; Low, K.-H.; Yam, V. W.-W. Versatile Control of Directed Supramolecular Assembly via Subtle Changes of the Rhodium(I) Pincer Building Blocks. *J. Am. Chem. Soc.* **2018**, *140*, 8321–8329.
- (65) Catti, L.; Narita, H.; Tanaka, Y.; Sakai, H.; Hasobe, T.; Tkachenko, N. V.; Yoshizawa, M. Supramolecular Singlet Fission of Pentacene Dimers within Polyaromatic Capsules. *J. Am. Chem. Soc.* **2021**, *143*, 9361–9367.
- (66) Yoshizawa, M.; Catti, L. Bent Anthracene Dimers as Versatile Building Blocks for Supramolecular Capsules. *Acc. Chem. Res.* **2019**, *52*, 2392–2404.
- (67) Del Valle, E. M. M. Cyclodextrins and Their Uses: A Review. *Process Biochem.* **2004**, *39*, 1033–1046.
- (68) Rekharsky, M. V.; Inoue, Y. Complexation Thermodynamics of Cyclodextrins. *Chem. Rev.* **1998**, *98*, 1875–1918.
- (69) Assaf, K. I.; Nau, W. M. Cucurbiturils: from Synthesis to High-Affinity Binding and Catalysis. *Chem. Soc. Rev.* **2015**, *44*, 394–418.
- (70) Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F. Pillararenes, A New Class of Macrocycles for Supramolecular Chemistry. *Acc. Chem. Res.* **2012**, *45*, 1294–1308.
- (71) Rizzuto, F. J.; von Krbeek, L. K. S.; Nitschke, J. R. Strategies for Binding Multiple Guests in Metal-Organic Cages. *Nat. Rev. Chem.* **2019**, *3*, 204–222.
- (72) Dalgarno, S. J.; Power, N. P.; Atwood, J. L. Metallo-Supramolecular Capsules. *Coord. Chem. Rev.* **2008**, *252*, 825–841.
- (73) Heitmann, L. M.; Taylor, A. B.; Hart, P. J.; Urbach, A. R. Sequence-Specific Recognition and Cooperative Dimerization of N-Terminal Aromatic Peptides in Aqueous Solution by a Synthetic Host. *J. Am. Chem. Soc.* **2006**, *128*, 12574–12581.
- (74) Kim, J.; Jung, I.-S.; Kim, S.-Y.; Lee, E.; Kang, J.-K.; Sakamoto, S.; Yamaguchi, K.; Kim, K. New Cucurbituril Homologues: Syntheses, Isolation, Characterization, and X-ray Crystal Structures of Cucurbit[n]uril (n = 5, 7, and 8). *J. Am. Chem. Soc.* **2000**, *122*, 540–541.
- (75) Biedermann, F.; Uzunova, V. D.; Scherman, O. A.; Nau, W. M.; De Simone, A. Release of High-Energy Water as an Essential Driving Force for the High-Affinity Binding of Cucurbit[n]urils. *J. Am. Chem. Soc.* **2012**, *134*, 15318–15323.
- (76) Biedermann, F.; Vendruscolo, M.; Scherman, O. A.; De Simone, A.; Nau, W. M. Cucurbit[8]uril and Blue-Box: High-Energy Water Release Overwhelms Electrostatic Interactions. *J. Am. Chem. Soc.* **2013**, *135*, 14879–14888.
- (77) Dsouza, R. N.; Pischel, U.; Nau, W. M. Fluorescent Dyes and Their Supramolecular Host/Guest Complexes with Macrocycles in Aqueous Solution. *Chem. Rev.* **2011**, *111*, 7941–7980.
- (78) Jung, H. S.; Verwilt, P.; Sharma, A.; Shin, J.; Sessler, J. L.; Kim, J. S. Organic Molecule-Based Photothermal Agents: an Expanding Photothermal Therapy Universe. *Chem. Soc. Rev.* **2018**, *47*, 2280–2297.
- (79) Li, X.; Zhang, D.; Yin, C.; Lu, G.; Wan, Y.; Huang, Z.; Tan, J.; Li, S.; Luo, J.; Lee, C.-S. A Diradicaloid Small Molecular Nanotheranostic with Strong Near-Infrared Absorbance for Effective Cancer Photoacoustic Imaging and Photothermal Therapy. *ACS Appl. Mater. Interfaces* **2021**, *13*, 15983–15991.
- (80) Cui, Z.; Abdurahman, A.; Ai, X.; Li, F. Stable Luminescent Radicals and Radical-Based LEDs with Doublet Emission. *CCS Chemistry*. **2020**, *2*, 1129–1145.
- (81) Jeon, W. S.; Kim, H.-J.; Lee, C.; Kim, K. Control of the Stoichiometry in Host-Guest Complexation by Redox Chemistry of Guests: Inclusion of Methylviologen in Cucurbit[8]uril. *Chem. Commun.* **2002**, 1828–1829.
- (82) Ziganshina, A. Y.; Ko, Y. H.; Jeon, W. S.; Kim, K. Stable π -Dimer of a Tetrathiafulvalene Cation Radical Encapsulated in the Cavity of Cucurbit[8]uril. *Chem. Commun.* **2004**, 806–807.
- (83) Yoshizawa, M.; Kumazawa, K.; Fujita, M. Room-Temperature and Solution-State Observation of the Mixed-Valence Cation Radical Dimer of Tetrathiafulvalene, [(TTF)₂]^{••}, within a Self-Assembled Cage. *J. Am. Chem. Soc.* **2005**, *127*, 13456–13457.
- (84) Spruell, J. M.; Coskun, A.; Friedman, D. C.; Forgan, R. S.; Sarjeant, A. A.; Trabolsi, A.; Fahrenbach, A. C.; Barin, G.; Paxton, W. F.; Dey, S. K.; Olson, M. A.; Benitez, D.; Tkatchouk, E.; Colvin, M. T.; Carmielli, R.; Caldwell, S. T.; Rosair, G. M.; Hewage, S. G.; Duclairoir, F.; Seymour, J. L.; Slawin, A. M. Z.; Goddard, W. A.; Wasielewski, M. R.; Cooke, G.; Stoddart, J. F. Highly Stable Tetrathiafulvalene Radical Dimers in [3]Catenanes. *Nat. Chem.* **2010**, *2*, 870–879.
- (85) Spent, P.; Young, R. M.; Wasielewski, M. R.; Würthner, F. Guest and Solvent Modulated Photo-Driven Charge Separation and Triplet Generation in a Perylene Bisimide Cyclophane. *Chem. Sci.* **2016**, *7*, 5428–5434.
- (86) Weiss, E. A.; Ratner, M. A.; Wasielewski, M. R. Direct Measurement of Singlet-Triplet Splitting within Rodlike Photo-generated Radical Ion Pairs Using Magnetic Field Effects: Estimation of the Electronic Coupling for Charge Recombination. *J. Phys. Chem. A* **2003**, *107*, 3639–3647.
- (87) Jiang, T.; Wang, X.; Wang, J.; Hu, G.; Ma, X. Humidity- and Temperature-Tunable Multicolor Luminescence of Cucurbit[8]uril-Based Supramolecular Assembly. *ACS Appl. Mater. Interfaces* **2019**, *11*, 14399–14407.
- (88) Wu, G.; Szabó, I.; Rosta, E.; Scherman, O. A. Cucurbit[8]uril-Mediated Pseudo[2,3]rotaxanes. *Chem. Commun.* **2019**, *55*, 13227–13230.
- (89) Kotturi, K.; Masson, E. Directional Self-Sorting with Cucurbit[8]uril Controlled by Allosteric π - π and Metal-Metal Interactions. *Chem.—Eur. J.* **2018**, *24*, 8670–8678.
- (90) Yin, H.; Cheng, Q.; Rosas, R.; Viel, S.; Monnier, V.; Charles, L.; Siri, D.; Gignes, D.; Ouari, O.; Wang, R.; Kermagoret, A.; Bardelang, D. A Cucurbit[8]uril 2:2 Complex with a Negative pK_a Shift. *Chem.—Eur. J.* **2019**, *25*, 12552–12559.
- (91) Uhlenheuer, D. A.; Young, J. F.; Nguyen, H. D.; Scheepstra, M.; Brunsveld, L. Cucurbit[8]uril Induced Heterodimerization of Methylviologen and Naphthalene Functionalized Proteins. *Chem. Commun.* **2011**, *47*, 6798–6800.
- (92) Zhang, L.; Wu, Y.; Brunsveld, L. A Synthetic Supramolecular Construct Modulating Protein Assembly in Cells. *Angew. Chem., Int. Ed.* **2007**, *46*, 1798–1802.
- (93) Zhao, W.; Tropp, J.; Qiao, B.; Pink, M.; Azoulay, J. D.; Flood, A. H. Tunable Adhesion from Stoichiometry-Controlled and Sequence-Defined Supramolecular Polymers Emerges Hierarchically from Cyanostar-Stabilized Anion-Anion Linkages. *J. Am. Chem. Soc.* **2020**, *142*, 2579–2591.
- (94) Liu, Y.; Yu, Y.; Gao, J.; Wang, Z.; Zhang, X. Water-Soluble Supramolecular Polymerization Driven by Multiple Host-Stabilized Charge-Transfer Interactions. *Angew. Chem., Int. Ed.* **2010**, *49*, 6576–6579.
- (95) Muraoka, T.; Kinbara, K.; Aida, T. Mechanical Twisting of a Guest by a Photoreversible Host. *Nature* **2006**, *440*, 512–515.

- (96) Gardner, A. B.; Howard, S.; Waddington, T. C.; Richardson, R. M.; Tomkinson, J. The Dynamics of Ring Rotation in Ferrocene, Nickelocene and Ruthenocene by Incoherent Quasi-Elastic Neutron Scattering. *Chem. Phys.* **1981**, *57*, 453–460.
- (97) Iordache, A.; Oltean, M.; Milet, A.; Thomas, F.; Baptiste, B.; Saint-Aman, E.; Bucher, C. Redox Control of Rotary Motions in Ferrocene-Based Elemental Ball Bearings. *J. Am. Chem. Soc.* **2012**, *134*, 2653–2671.
- (98) Takai, A.; Yasuda, T.; Ishizuka, T.; Kojima, T.; Takeuchi, M. A Directly Linked Ferrocene-Naphthalenediimide Conjugate: Precise Control of Stacking Structures of π -Systems by Redox Stimuli. *Angew. Chem., Int. Ed.* **2013**, *52*, 9167–9171.
- (99) Koivisto, B. D.; Ichimura, A. S.; McDonald, R.; Lemaire, M. T.; Thompson, L. K.; Hicks, R. G. Intramolecular π -Dimerization in a 1,1'-Bis(verdazyl)ferrocene Diradical. *J. Am. Chem. Soc.* **2006**, *128*, 690–691.
- (100) Bialas, D.; Kirchner, E.; Würthner, F. Folding-Induced Exciton Coupling in Homo- and Heterodimers of Merocyanine Dyes. *Chem. Commun.* **2016**, *52*, 3777–3780.
- (101) Fimmel, B.; Son, M.; Sung, Y. M.; Grüne, M.; Engels, B.; Kim, D.; Würthner, F. Phenylene Ethynylene-Tethered Perylene Bisimide Folda-Dimer and Folda-Trimer: Investigations on Folding Features in Ground and Excited States. *Chem.—Eur. J.* **2015**, *21*, 615–630.
- (102) Shang, C.; Wang, G.; Wei, Y.-C.; Jiang, Q.; Liu, K.; Zhang, M.; Chen, Y.-Y.; Chang, X.; Liu, F.; Yin, S.; Chou, P.-T.; Fang, Y. Excimer Formation of Perylene Bisimide Dyes within Stacking-Restrained Folda-Dimers: Insight into Anomalous Temperature Responsive Dual Fluorescence. *CCS Chem.* **2021**, 1921–1932.
- (103) Kirchner, E.; Bialas, D.; Wehner, M.; Schmidt, D.; Würthner, F. Bis(merocyanine) Homo-Folda-Dimers: Evaluation of Electronic and Spectral Changes in Well-Defined Dye Aggregate Geometries. *Chem.—Eur. J.* **2019**, *25*, 11285–11293.
- (104) Kirchner, E.; Bialas, D.; Würthner, F. Bis(merocyanine) Hetero-Folda-Dimers: Evaluation of Exciton Coupling between Different Types of π -Stacked Chromophores. *Chem.—Eur. J.* **2019**, *25*, 11294–11301.
- (105) Zhang, Z.-J.; Zhang, Y.-M.; Liu, Y. Controlled Molecular Self-Assembly Behaviors between Cucurbituril and Bispyridinium Derivatives. *J. Org. Chem.* **2011**, *76*, 4682–4685.
- (106) Smith, L. C.; Leach, D. G.; Blaylock, B. E.; Ali, O. A.; Urbach, A. R. Sequence-Specific, Nanomolar Peptide Binding via Cucurbit[8]uril-Induced Folding and Inclusion of Neighboring Side Chains. *J. Am. Chem. Soc.* **2015**, *137*, 3663–3669.
- (107) Hirani, Z.; Taylor, H. F.; Babcock, E. F.; Bockus, A. T.; Varnado, C. D.; Bielański, C. W.; Urbach, A. R. Molecular Recognition of Methionine-Terminated Peptides by Cucurbit[8]uril. *J. Am. Chem. Soc.* **2018**, *140*, 12263–12269.
- (108) Wu, G.; Clarke, D. E.; Wu, C.; Scherman, O. A. Oligopeptide-CB[8] Complexation with Switchable Binding Pathways. *Org. Biomol. Chem.* **2019**, *17*, 3514–3520.
- (109) Clarke, D. E.; Wu, G.; Wu, C.; Scherman, O. A. Host-Guest Induced Peptide Folding with Sequence-Specific Structural Chirality. *J. Am. Chem. Soc.* **2021**, *143*, 6323–6327.
- (110) Palma, A.; Artelsmair, M.; Wu, G.; Lu, X.; Barrow, S. J.; Uddin, N.; Rosta, E.; Masson, E.; Scherman, O. A. Cucurbit[7]uril as a Supramolecular Artificial Enzyme for Diels-Alder Reactions. *Angew. Chem., Int. Ed.* **2017**, *56*, 15688–15692.
- (111) Takezawa, H.; Shitozawa, K.; Fujita, M. Enhanced reactivity of twisted amides inside a molecular cage. *Nat. Chem.* **2020**, *12*, 574–578.
- (112) Tang, B.; Li, W.-L.; Jiao, Y.; Lu, J.-B.; Xu, J.-F.; Wang, Z.; Li, J.; Zhang, X. A Supramolecular Radical Cation: Folding-Enhanced Electrostatic Effect for Promoting Radical-Mediated Oxidation. *Chem. Sci.* **2018**, *9*, 5015–5020.
- (113) Ghasemabadi, P. G.; Yao, T.; Bodwell, G. J. Cyclophanes Containing Large Polycyclic Aromatic Hydrocarbons. *Chem. Soc. Rev.* **2015**, *44*, 6494–6518.
- (114) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. Cyclobis(paraquat-p-phenylene). A Tetracationic Multipurpose Receptor. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1547–1550.
- (115) Chen, Q.; Lei, Y.; Wu, G.; Li, Q.; Pan, Y.; Li, H. Ultramacrocyclization in Water via External Templatation. *Chem. Sci.* **2022**, *13*, 798–803.
- (116) Safont-Sempere, M. M.; Osswald, P.; Radacki, K.; Würthner, F. Chiral Self-Recognition and Self-Discrimination of Strapped Perylene Bisimides by π -Stacking Dimerization. *Chem.—Eur. J.* **2010**, *16*, 7380–7384.
- (117) Safont-Sempere, M. M.; Osswald, P.; Stolte, M.; Grüne, M.; Renz, M.; Kaupp, M.; Radacki, K.; Braunschweig, H.; Würthner, F. Impact of Molecular Flexibility on Binding Strength and Self-Sorting of Chiral π -Surfaces. *J. Am. Chem. Soc.* **2011**, *133*, 9580–9591.
- (118) Wang, Y.; Wu, H.; Stoddart, J. F. Molecular Triangles: A New Class of Macrocycles. *Acc. Chem. Res.* **2021**, *54*, 2027–2039.
- (119) Shen, Y.; Liu, H.; Cao, J.; Zhang, S.; Li, W.; Yang, B. Unusual Temperature-Sensitive Excimer Fluorescence from Discrete π - π Dimer Stacking of Anthracene in a Crystal. *Phys. Chem. Chem. Phys.* **2019**, *21*, 14511–14515.
- (120) Liu, H.; Gu, Y.; Dai, Y.; Wang, K.; Zhang, S.; Chen, G.; Zou, B.; Yang, B. Pressure-Induced Blue-Shifted and Enhanced Emission: A Cooperative Effect between Aggregation-Induced Emission and Energy-Transfer Suppression. *J. Am. Chem. Soc.* **2020**, *142*, 1153–1158.
- (121) Liu, H.; Yao, L.; Li, B.; Chen, X.; Gao, Y.; Zhang, S.; Li, W.; Lu, P.; Yang, B.; Ma, Y. Excimer-Induced High-Efficiency Fluorescence due to Pairwise Anthracene Stacking in a Crystal with Long Lifetime. *Chem. Commun.* **2016**, *52*, 7356–7359.
- (122) Shen, Y.; Liu, H.; Zhang, S.; Gao, Y.; Li, B.; Yan, Y.; Hu, Y.; Zhao, L.; Yang, B. Discrete Face-to-Face Stacking of Anthracene Inducing High-Efficiency Excimer Fluorescence in Solids via a Thermally Activated Phase Transition. *J. Mater. Chem. C* **2017**, *5*, 10061–10067.
- (123) Shen, Y.; Zhang, Z.; Liu, H.; Yan, Y.; Zhang, S.; Yang, B.; Ma, Y. Highly Efficient Orange-Red/Red Excimer Fluorescence from Dimeric π - π Stacking of Perylene and Its Nanoparticle Applications. *J. Phys. Chem. C* **2019**, *123*, 13047–13056.
- (124) Liu, H.; Shen, Y.; Yan, Y.; Zhou, C.; Zhang, S.; Li, B.; Ye, L.; Yang, B. One Stimulus In Situ Induces Two Sequential Luminescence Switchings in the Same Solvent-Fuming Process: Anthracene Excimer as the Intermediate. *Adv. Funct. Mater.* **2019**, *29*, 1901895.
- (125) Dar, A. A.; Rashid, S. Organic Co-Crystal Semiconductors: a Crystal Engineering Perspective. *CrystEngComm* **2021**, *23*, 8007–8026.
- (126) Patrick, C. R.; Prosser, G. S. A Molecular Complex of Benzene and Hexafluorobenzene. *Nature* **1960**, *187*, 1021–1021.
- (127) Chen, H.; Stoddart, J. F. From Molecular to Supramolecular Electronics. *Nat. Rev. Mater.* **2021**, *6*, 804–828.
- (128) Yu, H.; Li, J.; Li, S.; Liu, Y.; Jackson, N. E.; Moore, J. S.; Schroeder, C. M. Efficient Intermolecular Charge Transport in π -Stacked Pyridinium Dimers Using Cucurbit[8]uril Supramolecular Complexes. *J. Am. Chem. Soc.* **2022**, *144*, 3162–3173.
- (129) Chen, H.; Hou, S.; Wu, Q.; Jiang, F.; Zhou, P.; Zhang, L.; Jiao, Y.; Song, B.; Guo, Q.-H.; Chen, X.-Y.; Hong, W.; Lambert, C. J.; Stoddart, J. F. Promotion and Suppression of Single-Molecule Conductance by Quantum Interference in Macrocyclic Circuits. *Matter* **2021**, *4*, 3662–3676.
- (130) Toninelli, C.; Gerhardt, I.; Clark, A. S.; Reserbat-Plantey, A.; Götzinger, S.; Ristanović, Z.; Colautti, M.; Lombardi, P.; Major, K. D.; Deperasińska, I.; Pernice, W. H.; Koppens, F. H. L.; Kozankiewicz, B.; Gourdon, A.; Sandoghdar, V.; Orrit, M. Single Organic Molecules for Photonic Quantum Technologies. *Nat. Mater.* **2021**, *20*, 1615–1628.
- (131) Johnson, J. C.; Nozik, A. J.; Michl, J. The Role of Chromophore Coupling in Singlet Fission. *Acc. Chem. Res.* **2013**, *46*, 1290–1299.
- (132) Rosier, B. J. H. M.; Markvoort, A. J.; Gumí-Audenis, B.; Roodhuizen, J. A. L.; den Hamer, A.; Brunsveld, L.; de Greef, T. F. A.

Proximity-Induced Caspase-9 Activation on a DNA Origami-Based Synthetic Apoptosome. *Nat. Catal.* **2020**, *3*, 295–306.

(133) Young, R. M.; Wasielewski, M. R. Mixed Electronic States in Molecular Dimers: Connecting Singlet Fission, Excimer Formation, and Symmetry-Breaking Charge Transfer. *Acc. Chem. Res.* **2020**, *53*, 1957–1968.

(134) Liu, F.; Chowdhury, S.; Rosas, R.; Monnier, V.; Charles, L.; Karoui, H.; Gimes, D.; Ouari, O.; Chevallier, F.; Bucher, C.; Kermagoret, A.; Liu, S.; Bardelang, D. Triple Stack of a Viologen Derivative in a CB[10] Pair. *Org. Lett.* **2021**, *23*, 5283–5287.

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