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Second-Order Self-Organization in Coordination-Driven Self-Assembly: Exploring the Limits of Self-Selection

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Abstract

Self-organization during the self-assembly of a series of functionalized bispyridyl organic donors with complementary di-Pt(II) acceptors into supramolecular rhomboids and rectangles is explored. The connectivity and location of functional groups on the organic donors ensures that they do not interfere sterically or electronically with their respective binding sites. Carefully controlled reaction conditions are employed so that the only means of self-organization during self-assembly is through “second-order” effects arising from the distal functional groups themselves. With the selection of functionalized systems studied the extent of second-order self-organization varies from essentially zero to quite pronounced.

Keywords

Coordination-driven self-assembly; self-organization

Introduction

Self-assembly¹ and self-organization² are related concepts that account for much of the beauty and complexity of the natural world across all length scales. Beginning with seminal studies of molecular recognition in the 1960's and 1970's by Pedersen, Lehn, Sauvage, Dietrich, Cram and others,³ chemists have developed a variety of means of using noncovalent interactions – e.g. hydrogen bonding, charge-charge, donor-acceptor, metal-ligand coordination, etc. – to drive the self-assembly of pre-designed molecules into particular shapes and topologies. While it may not always be possible to predict *a priori* the exact shapes or constitutions of supramolecular assemblies, it is often possible and desirable to limit the range of potential assemblies by using relatively few, specifically designed complimentary pairs of component molecules: one hydrogen bond donor and one hydrogen bond acceptor, one π -electron rich donor and one π -electron poor acceptor, a metal with one free Lewis acidic site and a ligand with one free Lewis basic site, etc. Much more complicated systems and situations arise when multiple components are combined into one complex mixture. The presence of many species in one mixture, whether their self-assembly protocols are independent (orthogonal) or competitive (communicative), presents a situation wherein self-organization becomes a possibility.

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Self-organization is the process where complimentary components of a multi-component mixture selectively recognize each other to form well-defined assemblies of discrete structures at the expense of a random, statistical mixture of products. Such “order out of chaos” self-organization processes are present throughout nature, from the formation of galaxies to weather patterns to biological systems.⁴ Proteins, for example, are able to perform incredibly complex and specific functions throughout the body – perhaps the ultimate complex mixture – alongside other proteins performing entirely different tasks. These diverse functions are largely carried out simultaneously despite the fact that all proteins are built from collections of the same 21 amino acid building blocks. No system, however, is truly perfect and it is possible, even necessary at times, to disrupt this elegant self-organization such as through the introduction of pharmaceuticals into the body. Recently, chemists have explored the concepts of self-organization in purely synthetic systems. Initial studies by Lehn,⁵ Schneider,⁶ and Raymond⁷ involving transition metal mediated self-organization of helices demonstrated how the information encoded within specific building blocks can govern the exclusive assembly of multiple, discrete homohelical constructs from within a complex mixture and without any evidence of heterohelical assemblies.

More recently, a number of studies have shown that self-organization in synthetic systems is not always exclusively self-selective and is often more statistical. Stack⁸ and Davis⁹ have both studied chiral self-organization and have found examples where exclusively homochiral assemblies form when cations (Cu^{II} or Ba^{II}) are added to racemic mixtures of diiminopyridine ligands or a guanosine-quartet precursor, respectively. Slight modifications of either the precursors or cations, however, results in mixtures of homochiral and heterochiral assemblies, though a preference for homochiral assemblies was observed in each case. Lehn,¹⁰ Raymond,¹¹ Nitschke,¹² Severin,¹³ Barboiu,¹⁴ and Isaacs¹⁵ have performed similar investigations of the effects that size, geometry, concentration, and “external effectors” (e.g. cations of different charge or metals with varying coordination number/geometry) have on the extent of self-organization. These studies have found that a range of potential outcomes, from statistical dynamic combinatorial libraries to exclusive “narcissistic” self-organization,¹⁶ can be observed. Isaacs^{15a} has recently posed the question of whether self-organization in designer systems should be expected or surprising, is it the “exception or the rule?” By investigating the simultaneous self-assembly of nine components in the presence of barium picrate Isaacs observed near exclusive self-organization of eight¹⁷ supramolecules and, after thoroughly investigating the effects of different conditions, determined that only small differences in equilibrium constant (<10 fold) are necessary to promote such discriminating results. It was noted, however, that the variety of complimentary components that were chosen to fit criteria that were deemed sufficient for exclusive self-organization and a number of conditions were noted when such exclusivity would likely not be observed, ultimately concluding that self-organization should neither be expected nor surprising. These collective observations suggest that there is a self-organization “spectrum” from statistical (no organization) to exclusive (organization of either pure homo or pure hetero assemblies) and that where a mixture falls on that spectrum depends upon size, shape, geometry, concentration, k_{eq} , and various external effectors.

We have previously explored^{18–21} the concept of self-organization during the self-assembly of square planar $\text{Pt}(\text{II})$ acceptors and pyridyl donors into supramolecular polygons and polyhedra. For example, mixing a single ditopic 4,4'-bipyridine donor with three different di- $\text{Pt}(\text{II})$ acceptors of varying geometries (0° , 60° , and 90°) resulted in the exclusive formation of discrete assemblies of supramolecular rectangles, triangles, and squares, respectively, from within the complex mixture.¹⁸ Extending these studies into the third dimension, mixtures of two different tritopic donors with one ditopic acceptor or, alternatively, one tritopic donor with two ditopic acceptors resulted, in each case, in the exclusive formation of discrete M_3L_2 polyhedra.¹⁹ Size selective self-sorting has also been observed during the self-assembly of 2D

metallacycles when linear ditopic bispyridyl donors of different length were combined with 0° or 60° di-Pt(II) acceptors.²⁰ In both cases only those metallacycles with identical length bispyridyl donors were found and no mixed donor assemblies were observed. Recently we have examined the self-organization of supramolecular squares composed of a 90° di-Pt(II) acceptor and asymmetric (4-ethynylpyridyl)-substituted-pyridine donors, with the substituents being -CH₃ or -Cl groups located at the α or β position(s).²¹ With such asymmetric ligands we were able to study the effects of steric interactions on self-organization processes. It was observed that as steric bulk around the pyridyl donor nitrogen atom increased the extent of self-organization increased as well.

These studies reflect, to the best of our knowledge, the only reported examples of self-organization involving square platinum-pyridine complexes, which have proven to be especially versatile and powerful in molecular self-assembly. Across these four studies, the only variables investigated have been the effects of geometry, dimensionality, size, and sterics on the self-organization of Pt(II)-pyridine based metallacycles and metallacages while the concentration, temperature, the oxidation state and coordination number of the metal, and k_{eq} were kept constant and no external effectors were introduced into the systems. Though important, these studies leave the door open for further investigations wherein the size, geometry, dimensionality, and sterics around the coordination site of all building blocks are kept constant. Such studies, in which all variables that have been heretofore considered contributory to self-organization are kept constant allows for the influence of purely second order effects to be investigated, further exploring the limits of self-organization. In this article we report the effects of second order interactions – those far removed from the principle determinants/directors of molecular self-assembly processes – on the self-organization of supramolecular rhomboids and rectangles and show that these secondary effects can, but don't always, play a role in self-organization processes.

Results and Discussion

We have recently reported the synthesis of a series of functionalized 120° and 180° ditopic bispyridyl donors (Figure 1). Three different types of functionalized 120° donors were prepared by covalently attaching a dibenzo[24]crown-8 (**DB24C8**) derivative,²² a redox-active ferrocene derivative,²³ or a Fréchet-type dendritic derivative²⁴ to a 3,5-bis(4-ethynylpyridyl)-phenol. A series of 180° donors bearing C₆H₁₃, C₁₂H₂₅, and C₁₈H₃₇ straight chain hydrophobic functionalities (C₆, C₁₂, and C₁₈) or methylated di-, tetra-, and hexaethyleneglycol hydrophilic functionalities (DEG, TEG, and HEG) has also been prepared.²⁵ The placement of **DB24C8**, ferrocenyl, dendritic, and hydrophobic/hydrophilic functionalities onto their respective 120° and 180° donors was chosen to be sufficiently far from donor binding sites that they do not interfere structurally (sterically) or electronically with their pyridyl donor moieties and their ability to undergo self-assembly with complementary di-Pt(II) acceptors wouldn't be compromised. Indeed, when mixed with a 60° di-Pt(II) acceptor the functionalized 120° donors self-assemble into bisfunctionalized rhomboids^{22b,23a,24b} and when mixed with a molecular “clip” the 180° donors form hydrophobic and hydrophilic rectangles,²⁵ all in essentially quantitative isolated yields (>95%). Upon the successful self-assembly of functionalized metallacyclic rhomboids and rectangles the possibility of “mixed-functionality” metallacycles and the prospect of self-organization became of immediate interest. Furthermore, the range of different donor functional groups allows for a variety of different potential second order self-organization effects to be studied: mixtures of unrelated functionalities (**DB24C8**/ferrocenyl), structurally related moieties that vary in size (dendritic), and size related functionalities that vary in their affinity for water (hydrophobic/hydrophilic) have all been investigated.

Mixed Functionality Rhomboids

The self-assembly of mixed crown ether and ferrocene functionalized rhomboids (Scheme 1A) was undertaken first. It is important to reiterate that the distal location of the **DB24C8** and ferrocenyl functionalities and the rigidity of the 120° donor backbone ensure that the functional group cannot interfere directly with their respective coordination sites. It is equally important to note that the experimental conditions of each self-assembly were kept the same as in the original reports of their self-assembly^{22,23} and no “external effectors” were added to the mixture in hopes to amplify the formation of one species over another. In this way, the only means for self-organization to occur is through second order effects resulting from the presence of the functional groups. With the knowledge from previous studies^{22,23} that quantitative self-assembly does occur in each individual functionalized system, four outcomes may be expected upon mixing **DB24C8** donor **1**, ferrocenyl donor **2**, and 60° di-Pt(II) acceptor **6** in a 1:1:2 ratio: (1) exclusive heteromeric formation of mixed rhomboids containing one **DB24C8** and one ferrocenyl moiety (“social” self-organization); (2) exclusive homomeric formation of discrete bis**DB24C8** and bisferrocenyl rhomboids (“narcissistic” self-organization); (3) a purely statistical mixture of heteromeric and homomeric rhomboids (orthogonal self-assembly of individual components); and (4) a mixture possessing either slightly more heteromeric or homomeric rhomboids (self-amplified organization). Scheme 2 displays a generic representation of all four possible outcomes.

One equivalent, each, of **DB24C8** donor **1** and ferrocenyl donor **2** were added to 2.0 equiv of di-Pt(II) acceptor **6** in 2:1 CD₃COCD₃/D₂O and the solution was heated at 55° for 18h. The homogeneous clear orange solution was then cooled down to room temperature and the composition of this complex mixture was then examined by both ¹H and ³¹P {1H} NMR spectroscopy as well as high-resolution electrospray ionization mass spectrometry (ESI-MS).

The ¹H NMR spectrum for the **DB24C8**/ferrocenyl mixture showed the formation of a highly symmetric specie(s) as indicated by the presence of sharp proton signals (Figure 2A). It is not possible, however, to determine the relative ratios of heteromeric and homomeric rhomboids by integration because no noticeable shifts of proton signals associated with homomeric **DB24C8** rhomboids or homomeric ferrocenyl rhomboids occur upon formation of heteromeric **DB24C8**-ferrocenyl rhomboids. The ³¹P NMR spectrum (Figure 2B) displayed a single sharp peak at 15.5 ppm that is also indicative of the formation of discrete heteromeric and/or homomeric species as opposed to the formation of any oligomeric assemblies. Previous self-assembly of purely homotopic **DB24C8** and ferrocenyl rhomboids indicate that the ³¹P NMR signals associated with the formation of their rhomboids appear at 12.6 and 12.2 ppm, respectively.^{22,23,26} The appearance of one single peak in the ³¹P NMR of the mixed **DB24C8**-ferrocenyl assembly implies that either: (1) only heterotopic mixed rhomboids are formed (“social” self-organization) or (2) that the ³¹P signals associated with individual **DB24C8** and ferrocenyl rhomboids occur at the same chemical shift and it is not possible to determine whether narcissistic, social, or statistical organization is occurring.

ESI-MS, on the other hand, allows for facile resolution of peaks corresponding to individual bis**DB24C8**, bisferrocenyl, and **DB24C8**/ferrocenyl rhomboids, as there is significant variation in their molecular weight of their nitrate salts (3839.69, 3591.20, and 3342.71 g/mol, respectively). The full ESI mass spectrum is displayed in Figure 3. It is clearly evident from these ESI-MS results that [M – 2NO₃]²⁺ peaks, where M represents the fully intact supramolecular assembly, associated with homomeric **DB24C8**, homomeric ferrocenyl, and heteromeric **DB24C8**-ferrocenyl rhomboids were all observed (*m/z* 1857.5, 1609.4, and 1733.4, respectively) and their isotopic distributions agree with theory (see Supporting Information), indicating that interpretation (2) of the ³¹P NMR spectroscopic results is true and that all three assemblies are formed. It is interesting to note that the relative intensities of ESI-MS peaks associated with homotopic rhomboid assemblies are larger than the peak

corresponding to the heterotopic, mixed assembly. While the intensities of mass spectral peaks are often not quantitative, this result is suggestive that some form of second-order self-organization may be favoring the formation of homotopic rhomboids (bis**DB24C8** and bisferrocenyl) rather than heterotopic assemblies (**DB24C8**-ferrocenyl). It remains difficult, however, to conclusively state this preference for amplified self-organization without corroborative evidence from NMR studies or another analytical technique. The potential observation of second-order amplified self-organization is surprising given that the structural, physical, and electronic properties of the **DB24C8** and ferrocenyl functionalities are, to the best of our knowledge, unrelated and non-interacting.

Dendritic 120° bispyridyl donors **3a–c** share much greater structural similarity than dissimilar **DB24C8** and ferrocenyl donors **1** and **2** in that they differ only in the generation of the attached dendritic wedge. As representative examples of the complex self-assembly of mixed dendronized assemblies we have chosen to focus on mixtures of the [G1]/[G2] (**3b** and **3c**) and [G2]/[G3] donors (**3c** and **3d**) (Scheme 1B). It is hypothesized that those donors with the largest dendritic wedges may have the greatest possibility to direct self-organization phenomena given the greater number of intermolecular dendron-dendron interactions.

Dendrons **3b** and **3c** were mixed with 60° di-Pt(II) acceptor **6** in a 1:1:2 ratio and stirred at room temperature in CD₂Cl₂ for 18h. The same conditions were used for the mixed self-assembly of dendrons **3c** and **3d** with acceptor **6**. Each case yielded clear, homogeneous solutions that were both analyzed by multinuclear NMR spectroscopies (¹H and ³¹P {¹H}) as well as ESI-MS. The [G1]/[G2] (**3b/3c**) and [G2]/[G3] (**3c/3d**) assemblies displayed sharp signals in both their ¹H (see Supporting Information) and ³¹P NMR spectra (Figure 4), indicating the formation of discrete supramolecular species. However, the lack of observable shifts of proton signals in the ¹H NMR spectra of both mixtures precluded quantitative determination of the ratios of homomeric and heteromeric products formed upon self-assembly, as did significant overlap of signals in the ³¹P NMR spectra.

For both the [G1]/[G2] and the [G2]/[G3] mixed assemblies their ESI-MS results show the formation of heteromeric as well as homomeric rhomboid products (see Table 1). The full ESI-MS spectrum of the [G1]/[G2] mixture is shown in Figure 4A and that of the [G2]/[G3] spectrum is shown in Figure 4B. The high-resolution experimental results of each peak match their theoretical distribution (see Supporting information) confirming the [2+2] molecularity of each rhomboid. As stated previously, an orthogonal self-assembly wherein there is no self-organization would lead to a statistical distribution of homomeric and heteromeric assemblies, with the heteromeric assemblies formed in a 2:1 ratio over both homomeric assemblies. While ESI-MS results cannot be evaluated quantitatively, the relative intensities of peaks in the full spectrum of the [G1]/[G2] mixture do suggest a nearly statistical distribution of homomeric and heteromeric assemblies. Figure 5A shows, for example, that the intensity of [G1]-[G2] heteromeric [M – 2NO₃]²⁺ and [M – 3NO₃]³⁺ peaks is greater than the intensity of the [M – 2NO₃]²⁺ and [M – 3NO₃]³⁺ peaks of either homodendritic ([G1]-[G1] or [G2]-[G2]) assembly. However, it can also be seen that peaks corresponding to the larger [G2]-[G2] rhomboids are less intense than those of the [G1]-[G1] assemblies. It has been observed previously that larger dendritic metallacycles are less stable under the experimental ionization conditions than smaller metallacycles^{24b}, which likely explains this relative difference in intensities. Similar results are observed for the [M – 3NO₃]³⁺ peaks of the [G2]/[G3] mixture (Figure 5B), which are also suggestive of a roughly statistical distribution. However, the trend in intensities of the [M – 2NO₃]²⁺ peaks of the [G2]/[G3] mixture are not supportive of a statistical ratio of homomeric and heteromeric assemblies. This discrepancy is most likely due to the relative instabilities of the [G3]-[G3] and [G2]-[G3] rhomboids, the largest of those investigated, under mass conditions. All together, the collective ESI-MS results show that both homomeric and

heteromeric metallacyclic rhomboids are self-assembled in both the [G1]/[G2] and [G2]/[G3] complex mixtures and are suggestive, though not conclusive, that their ratios are near statistical.

Mixed Functionality Rectangles

The potential for self-organization of hydrophobic/hydrophilic/amphiphilic rectangles was also investigated (Scheme 1C). As before, all experimental conditions were kept constant for each self-assembly. In the case of hydrophobic and hydrophilic 180° donors, however, the additional variable of chain length could be investigated. It is important to reiterate that the overall size, shape, geometry, and binding constant of the rigid ditopic bipyridyl moiety are kept constant, as is the di-Pt(II) molecular clip (**7**). Pairs of similar length hydrophobic and hydrophilic donors – C₆/DEG, C₁₂/TEG, and C₁₈/HEG – were combined in a 1:1:2 ratio with molecular clip **7**. Again, purely amphiphilic (social self-organization), discrete hydrophobic and hydrophilic (narcissistic self-organization), statistical (orthogonal), and non-statistical (amplified) mixtures of rectangles could be expected.

Each hydrophobic/hydrophilic pair of donors was added to the molecular clip in a 1:1:2 ratio and heated at 55° C in CD₃COCD₃/D₂O (1.2:1) for 18 h. Upon cooling and exchange of the nitrate counterions with hexafluorophosphate (PF₆[−]) anions, the mixtures were analyzed by ¹H and ³¹P NMR spectroscopy and ESI-MS. The ¹H NMR for each mixture showed sharp peaks indicating the formation of highly symmetric species (see Supporting Information). As with the complex rhomboid mixtures, however, integration of specific peaks cannot be used to provide details of relative ratios of species in the mixtures on account of negligible shifts of proton signals associated with homomeric and heteromeric rectangles. By contrast, ³¹P NMR spectra revealed that peaks corresponding to heteromeric (amphiphilic) rectangles appear at slightly different chemical shifts than their homomeric (hydrophobic and hydrophilic) counterparts (Figure 6).

The ³¹P NMR spectrum for the C₆/DEG mixture, for example, showed three distinct peaks at 8.60, 8.56, and 8.53 ppm, corresponding to hydrophobic, amphiphilic, and hydrophilic rectangles, respectively (Figure 6A). Though integration of ³¹P NMR is not as quantitative as integration of ¹H NMR signals, integration values of 1.0, 1.6, and 1.0 do suggest a nearly statistical mixture of rectangles with a slight deviation toward narcissistic self-organization. In the ESI-MS of the C₆/DEG mixture, peaks at *m/z* = 1664.4, 1682.4, and 1700.4 in agreement with the [M – 2PF₆]²⁺ peaks of the hydrophobic, amphiphilic, and hydrophilic rectangles, respectively, were found and their isotopic distributions are in agreement with theory. It is interesting to note the difference in intensity of these peaks when viewed at the same scale (Figure 7A): the amphiphilic rectangle dominates over the two homomeric rectangles, in line with a roughly statistical distribution. These collective results strongly suggest that a near statistical mixture is obtained from the combination of bispyridyl donors functionalized with the shortest hydrophobic and hydrophilic chains.

Examination of the ³¹P NMR and ESI-MS spectral results for the C₁₂/TEG mixture revealed somewhat different results from those of the C₆/DEG mixture. It is immediately clear from the relative heights of phosphorous signals of the ³¹P NMR spectrum (Figure 6B) that with these slightly longer hydrophobic and hydrophilic chains there is an amplification of homomeric species (C₁₂-C₁₂ at 8.63 ppm and TEG-TEG at 8.57 ppm) relative to the heteromeric amphiphilic rectangle (C₁₂-TEG at 8.59 ppm). Integration of signals corresponding to hydrophobic, amphiphilic, and hydrophilic species revealed an approximate ratio of 1.1:0.7:1.0. This ratio indicates a respective increase of 12% and 9% in narcissistic hydrophobic and hydrophilic self-organization and concomitant 19% decrease in the amount of social self-organization. Peaks associated with each type of rectangle were observed (Figure 7B) in the ESI-MS: *m/z* = 1832.7, 1854.5, and 1876.6 g/mol were found, consistent with the [M-2PF₆]²⁺ peaks of the hydrophobic, amphiphilic, and hydrophilic rectangles, respectively.

Again, the isotopically resolved peaks match their theoretical distributions. When viewed together, it is apparent that the intensity of the central heteromeric peak is very nearly the same as for the two homomeric rectangles flanking it. While not quantitative, this observation supports an amplification of homomeric rectangles and provides further evidence of some extent of self-organization in the C₁₂/TEG mixture.

The trend of increased self-organization with increased chain length is continued in the C₁₈/HEG mixture. In the ³¹P NMR spectrum (Figure 6C) of these longest hydrophobic and hydrophilic functionalized rectangles it is clear that there is considerable, though still not pure, narcissistic self-organization. Only two phosphorous signals are visible in the spectrum, though there appears to be a slight shoulder on the signal associated with the homomeric hydrophobic rectangle, likely indicative of an unresolved signal for the amphiphilic rectangle. Integration of the two signals gives values of 1.0 and 1.4. Assuming that the relative amounts of homomeric hydrophobic and hydrophilic rectangles is roughly equal, and that the difference between integration values of the signals at 8.64 ppm (purely hydrophobic) and 8.59 ppm (purely hydrophilic along with some amphiphilic) is equal to the amount of amphiphilic rectangle in the mixture, then the relative ratio of hydrophobic, amphiphilic, and hydrophilic rectangles is approximated as 1.0:0.4:1.0. Further investigation of the C₁₈/HEG mixture using ESI-MS showed peaks corresponding to the loss of two PF₆⁻ counterions ([M – 2PF₆]²⁺) for the hydrophobic, amphiphilic, and hydrophilic rectangles at *m/z* = 2000.7, 2026.4, and 2052.5 g/mol, respectively (Figure 7C). When viewed at the same intensity scale, the central peak of the amphiphilic rectangle is now very near the baseline while the flanking homomeric rectangles are significantly larger. It is therefore believed that a considerable amount of narcissistic self-organization takes place during the self-assembly of supramolecular rectangles from a complex mixture of **4c**, **5c**, and **7**.

The trend of increasing self-organization from a roughly statistical mixture (the C₆/DEG mixture) to a highly amplified homomeric mixture (the C₁₈/HEG mixture) is interesting because the functionality that determines this tendency toward self-organization is far removed from those factors that govern the self-assembly of the underlying rectangles. As opposed to variations in reaction conditions, binding interactions, or the size, shape, or geometry of constituent building blocks, the observed range of self-organization results purely from second order effects. The results, however, can be explained in terms of a “pre-assembly” organization phenomenon that biases the resulting self-assembly of supramolecular rectangles. It is well known and well established in both natural and synthetic systems that molecules possessing long hydrophobic or hydrophilic chains readily aggregate into structures such as spheres, micelles, vesicles, etc.²⁷ Such hydrophobic/hydrophilic self-aggregation is largely dependent upon the length of the chains, with longer chains aggregating more readily, and also upon solvent wherein the aggregation of hydrophobic molecules is more facile in polar solvents (especially water) and aggregation of hydrophilic molecules is more prevalent in nonpolar solvents. While solvent has not been investigated as a variable in the studies presented here²⁸, chain length has.

The relative ratios of hydrophobic, amphiphilic, and hydrophilic rectangles change from 1.0:1.6:1.0 to 1.0:0.4:1.0 in going from mixtures containing donors with the shortest (C₆/DEG) to the longest (C₁₈/HEG) hydrophobic and hydrophilic functionalities. The trend toward self-organization arises because the longer chains likely undergo a self-organization phenomenon prior to the introduction of the di-Pt(II) molecular clip, with hydrophobic donors and hydrophilic donors forming separate aggregates at thermodynamic equilibrium. When the di-Pt(II) acceptor is then added to the system it is more likely to encounter aggregates of hydrophobic or hydrophilic donors rather than a continuous, completely randomized mixture of different donors (Scheme 3). In other words, it is more likely that di-Pt(II) acceptors will undergo self-assembly with donors of like philicity, resulting in a less than statistical mixture

of supramolecular rectangle products. The Pt-N coordinative bond is, however, dynamic and it is unlikely that donors of different philicity are exclusively segregated in solution, giving rise to some amounts of heteromeric rectangles even in the case of the C₁₈/HEG mixture. The drive toward pre-organized aggregation is less strong for the shortest chains, leading to a near statistical mixture of heteromeric and homomeric rectangles.

As a means of testing this hypothesis, two additional complex mixtures were prepared. The first was a combination of the C₆ and C₁₈ donors **4a** and **4c** with molecular clip **7** in a 1:1:2 ratio while the other was a mixture of the DEG and HEG donors **5a** and **5c** with molecular clip **7**, also in a 1:1:2 ratio. Assuming that any enthalpic gain from aggregation of long chain (C₁₈ or HEG) donors in their respective mixtures will be outweighed by the entropic gain of a more randomized mixture, there should be little to no donor pre-organization and a more statistical mixture of supramolecular rectangles should be obtained. Indeed, the ³¹P NMR spectra of the C₆/C₁₈ and DEG/HEG mixtures revealed three phosphorous signals each (Figure 8). In the case of the hydrophobic C₆/C₁₈ mixture, the middle heteromeric C₆-C₁₈ signal at 8.60 ppm is of roughly the same intensity of as the homomeric peaks (C₆-C₆ and C₁₈-C₁₈ at 8.62 and 8.59 ppm, respectively) while the ³¹P NMR spectrum of the hydrophilic DEG/HEG mixture reveals a heteromeric DEG-HEG peak at 8.56 ppm that is of notably greater intensity than homomeric DEG-DEG and HEG-HEG peaks at 8.58 and 8.54 ppm, respectively. The increased similarity of homomeric and heteromeric rectangles in these two mixtures, however, results in an increase in signal overlap prohibiting integration of the ³¹P NMR spectra.

ESI-MS analysis of the mixtures also revealed peaks associated with homomeric and heteromeric rectangles for each complex mixture. The [M – 2PF₆]²⁺ peaks of the hydrophobic C₆, C₆/C₁₈, and C₁₈ rectangles were observed at *m/z* = 1664.4, 1832.6, and 2000.8 g/mol, respectively, and the hydrophilic DEG, DEG/HEG, and HEG rectangles at *m/z* = 1700.5, 1876.6, and 2052.7 g/mol, respectively. It should be noted, however, that when viewed on the same scale (Figure 9), the intensity of the heteromeric peak for the hydrophobic C₆/C₁₈ mixture is only slightly above those of the mixtures homomeric peaks, indicative of a greater than statistical amount of homomeric rectangles. This is not the case with the hydrophilic DEG/HEG mixture, where peak intensities suggest a more statistical distribution. It is likely that the high concentration of D₂O present during self-assembly results in some amounts of pre-organized aggregation of hydrophobic donors in the hydrophobic mixture while disfavoring aggregation of the hydrophilic donors. Such a situation would be consistent with the slightly non-statistical distribution of rectangles in the C₆/C₁₈ mixture and essentially statistical distribution of rectangles in the DEG/HEG mixture.

Conclusion

Herein we have explored the limits of self-organization through the controlled self-assembly of a collection of supramolecular rhomboids and rectangles within complex mixtures of di-Pt (II) acceptors and bipyridyl donors containing various crown ether, ferrocenyl, dendritic, and hydrophobic/hydrophilic functionalities. The functional groups were all spatially and electronically isolated from the pyridyl moieties of the donor molecules. By keeping constant the reaction conditions – i.e. temperature, concentration, and reaction time – and structural and thermodynamic variables – i.e. size, geometry, *k*_{eq}, and oxidation state and coordination geometry of the metal – of underlying molecular acceptors and donors, the extent to which second order interactions are able to influence, if at all, self-organization during self-assembly was investigated. In this manner the second order effects of seemingly unrelated (crown ether/ferrocene), structurally related though different sized (dendritic), and size related though different affinity for water (hydrophobic/hydrophilic) functionalities were studied. Collective NMR spectroscopic and ESI-MS results of the different complex mixtures suggest that while the mixed dendrimer assemblies do not undergo observable second-order self-organization,

the hydrophobic/hydrophilic complex mixtures do show evidence of self-organization as a function of chain length and the crown ether/ferrocene assemblies may, surprisingly, undergo some amplified self-organization. In the case of the mixed phobicity metallacyclic rectangles the self-organization phenomena, which is supported by both NMR and ESI-MS results, can be attributed to a pre-assembly aggregation of like donors.

These studies reveal, similar to previous investigations of self-organization phenomena where reaction conditions and/or structural parameters were varied, that there exists a spectrum from statistical mixtures to purely narcissistic self-organization along which every complex mixture ultimately falls. While it may not always be possible to predict where a particular mixture will appear on that spectrum, it is important to investigate the wide range of potential variables that may influence self-organization in an effort to better understand which direct such processes more strongly than others. The discovery that second-order interactions can play a role in self-organized self-assembly reveals that control over organization doesn't rest solely on, in this case, the reaction conditions or nature of the donor-acceptor interaction. It is likely that similar results may be obtained for investigations of self-assembly involving hydrogen bonding, solvophobic, π -donor and π -acceptor and other noncovalent interactions. Being able to better understand and control self-organized self-assembly is important not only for the bottom-up development of molecular materials but also for our understanding of biological systems.

In this regard, labeling the effects described herein as "second order" may be somewhat of a misnomer: it almost goes without saying that complex functional biological systems take advantage of every potential director of self-organization whether they be proximal to primary binding sites or distal to them. Enzyme-substrate interactions, drug molecules, membranes, etc. all take advantage of the different interactions present within their structures and their assembly and function are not solely dictated by a single interaction phenomena. While considerable progress has been made in designing synthetic analogues of biological systems it is important to continue to explore the wide variety of means by which such abiological molecules can be induced to interact, self-assemble, and ultimately function.

Experimental

DB24C8 functionalized donor **1**,^{22a} ferrocene functionalized donor **2**,^{23a} dendronized donors **3a-c**,^{24a} hydrophobic donors **4a-c**,²⁵ hydrophilic donors **5a-c**,²⁵ 60° acceptor **6**,²⁹ and the 0° molecular clip **7**³⁰ were synthesized according to published literature procedures. Isolated yields of the mixed metallacycle products are given as percents by mass. Integration values for ¹H NMR spectral results for each mixed metallacycle system are normalized to a donor-A/donor-B/acceptor ratio of 3:3:6.

Mixed DB24C8-ferrocene rhomboid

Acceptor **6** (4.51 mg, 3.8 μ mol) was added to a 2-dram vial. **DB24C8** functionalized donor **1** (1.46 mg, 1.9 μ mol) and ferrocene functionalized donor **2** (0.99 mg, 1.9 μ mol) were added to a separate glass vial, dissolved in 0.5 mL of a CD₃COCD₃/CD₂Cl₂ (1:1 v/v) solution, and transferred to the vial containing acceptor **6**. The donor vial was then washed with 3 $\times$ 0.2 mL of the mixed solvent system to ensure quantitative transfer to the vial containing acceptor **6**. The resulting suspension was stirred at room temperature for 18 h, yielding a homogeneous clear solution. The sample was then dried under a stream of N₂(g). Yield 6.3 mg (pale orange solid) 93%. ¹H NMR (1:1 CD₃COCD₃/CD₂Cl₂, 300 MHz) δ 9.41-9.30 (m, 12H, H _{α} -Py), 8.87-8.76 (m, 24H, H₄-**6** and H _{α} -Py), 7.91 (d, 12H, J = 5.4 Hz, H₁-**6**), 7.86 (d, 12H, J = 5.4 Hz, H₂-**6**), 7.80-7.72 (m, 24H, H _{β} -Py), 7.60-7.45 (m, 21H, H _{β} -**2**, H _{α} -**2**, H₁₀-**6**), 7.28 (s, 6H, H _{β} -**1**), 6.98-6.80 (m, 12H, H _{α} -**1**, ArH-**1**), 6.85-6.72 (m, 12H, ArH-**1**), 5.01 (t, 6H, J = 2.1 Hz, H _{c} -**2**), 4.88 (t, 6H, J = 2.1 Hz, H _{d} -**2**), 4.50 (s, 6H, PhOCH₂), 4.26 (s, 15H, H _{c} -**2**), 4.09-4.03 (m, 24H, α -CH₂-**1**), 4.02-3.97 (m, 24H, β -CH₂-**1**), 3.79-3.70 (m, 24H, γ -CH₂-**1**), 1.42-1.22 (m,

144H, PCH_2CH_3 -**6**), 1.13-0.91 (m, 216H, PCH_2CH_3 -**6**). $^{31}\text{P}\{^1\text{H}\}$ NMR (1:1 $\text{CD}_3\text{COCD}_3/\text{CD}_2\text{Cl}_2$, 121.4 MHz) δ 15.47 (br, $1J_{\text{Pt-P}} = 1354.48$ Hz). MS (ESI) calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 1609.1, found 1609.4 (ferrocene-ferrocene); calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 1733.5, found 1733.4 (**DB24C8**-ferrocene); calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 1857.9, found 1857.5 (**DB24C8**-**DB24C8**).

General procedure for preparation of mixed dendritic rhomboids

Acceptor **6** (2.0 equiv) was added to a 2-dram glass vial. Two different generation dendronized 120° donors (**3a** and **3b** or **3b** and **3c**, 1.0 equiv each) were then added to a separate glass vial, dissolved in CD_2Cl_2 (0.5 mL), and transferred to the vial containing acceptor **6**. Quantitative transfer was ensured by washing the donor vial with additional CD_2Cl_2 (3×0.2 mL). The reaction mixture was allowed to stir at room temperature for 18 h, resulting in a clear homogeneous solution, which was transferred directly to an NMR tube for spectroscopic analysis. Following spectroscopic analysis the samples were dried under a stream of $\text{N}_2(\text{g})$ and weighed.

[G1]/[G2] mixed assembly

Reaction scale: acceptor **6** (4.98 mg, 4.3 μmol), donor **3a** (1.29 mg, 2.15 μmol), donor **3b** (2.18 mg, 2.15 μmol). Yield 8.1 mg (pale yellow solid), 96%. ^1H NMR (CD_2Cl_2 , 300 MHz) δ 9.38 (d, 12H, $J = 5.7$ Hz, H_α -Py), 8.85 (s, 12H, H_4 -**6**), 8.69 (d, 12H, $J = 5.7$ Hz, H_α -Py), 7.96 (d, 12H, $J = 5.4$ Hz, H_2 -**6**), 7.78 (dd, 12H, $J = 11.3, 5.4$ Hz, H_1 -**6**), 7.66 (s, 12H, H_{10} -**6**), 7.59 (d, 24H, $J = 5.7$ Hz, H_β -Py), 7.48-7.32 (m, 126H, PhH and ArH), 6.73 (m, 12H, H_b), 6.63-6.55 (m, 6H, H_a), 5.15 (s, 12H, OCH_2Ar), 5.08 (s, 12H, OCH_2Ph), 5.06 (s, 24H, OCH_2Ph), 5.03 (s, 12H, OCH_2Ph), 1.43-1.30 (m, 144H, PCH_2CH_3 -**6**), 1.20-1.05 (m, 216H, PCH_2CH_3 -**6**). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.4 MHz) δ 14.72 (br, $1J_{\text{Pt-P}} = 1365.2$ Hz). MS (ESI) calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 1689.9, found 1699.6 ([G1]-[G1]); calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 1911.7, found 1911.2 ([G1]-[G2]); calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 2124.2, found 2124.7 ([G2]-[G2]); calcd for $[\text{M} - 3\text{NO}_3]^{3+} m/z$ 1111.6, found 1112.4 ([G1]-[G1]); calcd for $[\text{M} - 3\text{NO}_3]^{3+} m/z$ 1253.6, found 1253.4 ([G1]-[G2]); calcd for $[\text{M} - 3\text{NO}_3]^{3+} m/z$ 1395.6, found 1395.8 ([G2]-[G2]).

[G2]/[G3] mixed assembly

Reaction scale: acceptor **6** (3.01 mg, 2.6 μmol), donor **3b** (1.33 mg, 1.3 μmol), donor **3c** (2.41 mg, 1.3 μmol). Yield 6.4 mg (pale yellow solid), 95%. ^1H NMR (CD_2Cl_2 , 300 MHz) δ 9.37 (d, 12H, $J = 6.0$ Hz, H_α -Py), 8.86 (s, 12H, H_4 -**6**), 8.68 (d, 12H, $J = 5.8$ Hz, H_α -Py), 7.95 (d, 12H, $J = 5.7$ Hz, H_2 -**6**), 7.79-7.73 (m, 12H, H_1 -**6**), 7.66 (s, 12H, H_{10} -**6**), 7.58 (d, 24H, $J = 6.0$ Hz, H_β -Py), 7.50-7.25 (m, 198H, ArH), 6.76-6.65 (m, 60H, ArH and H_b), 6.56-6.53 (m, 30H, ArH and H_a), 5.14 (s, 12H, OCH_2Ar), 5.08 (s, 24H, OCH_2Ph), 5.06 (s, 24H, OCH_2Ph), 5.04-4.92 (m, 84H, OCH_2Ph), 1.42-1.27 (m, 144H, PCH_2CH_3 -**6**), 1.20-1.00 (m, 216H, PCH_2CH_3 -**6**). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.4 MHz) δ 13.25 (br, $1J_{\text{Pt-P}} = 1370.68$ Hz). MS (ESI) calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 2124.4, found 2124.7 ([G2]-[G2]); calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 2548.0, found 2547.9 ([G2]-[G3]); calcd for $[\text{M} - 2\text{NO}_3]^{2+} m/z$ 2971.7, found 2972.2 ([G3]-[G3]); calcd for $[\text{M} - 3\text{NO}_3]^{3+} m/z$ 1394.9, found 1395.8 ([G2]-[G2]); calcd for $[\text{M} - 3\text{NO}_3]^{3+} m/z$ 1678.0, found 1677.9 ([G2]-[G3]); calcd for $[\text{M} - 3\text{NO}_3]^{3+} m/z$ 1960.9, found 1961.3 ([G3]-[G3]).

General procedure for preparation of mixed functionality supramolecular rectangles

1.0 equiv each of a hydrophobic donor (**4a-c**) and a hydrophilic donor (**5a-c**) were added to a glass vial. To another glass vial was added 2.0 equiv of 0° molecular clip **7**. The mixed donors were taken up in 0.5 mL $\text{CD}_3\text{COCD}_3/\text{D}_2\text{O}$ (1.2:1) and transferred to the vial containing acceptor **7**. This process was repeated (3×0.4 mL) to ensure quantitative transfer. The glass vial was sealed with Teflon tape and heated at 55 – 60°C for 18 h, after which time a

homogeneous orange solution had formed. The solution was concentrated under a stream of $N_2(g)$ and a saturated H_2O solution of KPF_6 was added in order to exchange the NO_3^- anions to PF_6^- counterions. The product was washed several times with H_2O and the resulting solid was collected.

C₆/DEG mixed assembly

Reaction scale: acceptor **7** (14.42 mg, 12.4 μ mol), donor **4a** (3.0 mg, 6.2 μ mol), donor **5a** (3.2 mg, 6.2 μ mol). Yield 21.7 mg (orange solid), 96%. 1H NMR (CD_3COCD_3 , 300 MHz) δ 9.56 (s, 6H, H_{9-7}), 9.24 (dd, 12H, $J = 15.9$, 5.4 Hz, H_α -Py-**4a**), 9.13 (d, 12H, $J = 5.5$ Hz, H_α -Py-**5a**), 8.53 (s, 6H, H_{10-7}), 8.27 (s, 12H, H_β -Py-**5a**), 8.15 (dd, 12H, $J = 15.9$, 5.6 Hz, H_β -Py-**4a**), 7.89-7.78 (m, 24H, $H_{2,4,5,7-7}$), 7.58-7.49 (m, 12H, $H_{3,6-7}$), 7.32-7.22 (m, 12H, ArH), 4.55-4.45 (m, 12H, $H_{glycol-5a}$), 4.31 (t, 12H, $J = 6.3$ Hz, $ArOCH_2-4a$), 3.98-3.91 (m, 12H, $H_{glycol-5a}$), 3.72-3.66 (m, 12H, $H_{glycol-5a}$), 3.55-3.49 (m, 12H, $H_{glycol-5a}$), 3.30 (s, 18H, $-OCH_3-5a$), 1.97-1.85 (m, 12H, $H_{alkane-4a}$), 1.79-1.50 (m, 156H, PCH_2CH_3-7 and $H_{alkane-4a}$), 1.44-1.28 (m, 24H, $H_{alkane-4a}$), 1.10-0.90 (m, 236H, PCH_2CH_3-7 and $-CH_3-4a$). $^{31}P\{^1H\}$ NMR (CD_3COCD_3 , 121.4 MHz) δ 8.60, 8.56, 8.53 (all singlets, $^1J_{Pt-p} = 1330.55$ Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 1664.6, found 1664.4 (C₆-C₆); calcd for $[M - 2PF_6]^{2+}$ m/z 1682.6, found 1682.4 (C₆-DEG); calcd for $[M - 2PF_6]^{2+}$ m/z 1700.6, found 1700.4 (DEG-DEG).

C₁₂/TEG mixed assembly

Reaction scale: acceptor **7** (10.7 mg, 9.2 μ mol), donor **4b** (3.0 mg, 4.6 μ mol), donor **5b** (3.2 mg, 4.6 μ mol). Yield 17.3 mg (orange solid), 94%. 1H NMR (CD_3COCD_3 , 300 MHz) δ 9.55 (s, 6H, H_{9-7}), 9.29-9.19 (m, 12H, H_α -Py-**4b**), 9.13 (d, 12H, $J = 5.7$ Hz, H_α -Py-**5b**), 8.54 (s, 6H, H_{10-7}), 8.31-8.21 (m, 12H, H_β -Py-**5b**), 8.20-8.11 (m, 12H, H_β -Py-**4b**), 7.88-7.80 (m, 24H, $H_{2,4,5,7-7}$), 7.55-7.52 (m, 12H, $H_{3,6-7}$), 7.31-7.25 (m, 12H, ArH), 4.54-4.49 (m, 12H, $H_{glycol-5b}$), 4.32 (t, 12H, $J = 6.2$ Hz, $ArOCH_2-4b$), 3.99-3.93 (m, 12H, $H_{glycol-5b}$), 3.73-3.67 (m, 12H, $H_{glycol-5b}$), 3.64-3.55 (m, 48H, $H_{glycol-5b}$), 3.49-3.44 (m, 12H, $H_{glycol-5b}$), 3.28 (s, 18H, $-OCH_3-5b$), 2.00-1.87 (m, 12H, $H_{alkane-4b}$), 1.75-1.50 (m, 156H, PCH_2CH_3 and $H_{alkane-4b}$), 1.41-1.22 (m, 96H, $H_{alkane-4b}$), 1.07-0.92 (m, 236H, PCH_2CH_3 and $-CH_3-4b$). $^{31}P\{^1H\}$ NMR (CD_3COCD_3 , 121.4 MHz) δ 8.63, 8.59, 8.57 (all singlets, $^1J_{Pt-p} = 1324.10$ Hz). MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 1832.8, found 1832.7 (C₁₂-C₁₂); calcd for $[M - 2PF_6]^{2+}$ m/z 1854.7, found 1854.5 (C₁₂-TEG); calcd for $[M - 2PF_6]^{2+}$ m/z 1876.7, found 1876.6 (TEG-TEG).

C₁₈/HEG mixed assembly

Reaction scale: acceptor **7** (8.37 mg, 7.2 μ mol), donor **4c** (3.0 mg, 3.6 μ mol), donor **5c** (3.1 mg, 3.6 μ mol). Yield 15.0 mg (orange solid), 96%. 1H NMR (CD_3COCD_3 , 300 MHz) δ 9.55 (s, 6H, H_{9-7}), 9.27-9.18 (m, 12H, H_α -Py-**4c**), 9.15-9.09 (m, 12H, H_α -Py-**5c**), 8.54 (s, 6H, H_{10-7}), 8.31-8.18 (m, 12H, H_β -Py-**5c**), 8.14-8.05 (m, 12H, H_β -Py-**4c**), 7.88-7.80 (m, 24H, $H_{2,4,5,7-7}$), 7.56-7.50 (m, 12H, $H_{3,6-7}$), 7.30-7.24 (m, 12H, ArH), 4.54-4.48 (m, 12H, $H_{glycol-5c}$), 4.32 (t, 12H, $J = 6.9$ Hz, $ArOCH_2-4c$), 3.99-3.93 (m, 12H, $H_{glycol-5c}$), 3.73-3.68 (m, 12H, $H_{glycol-5c}$), 3.65-3.51 (m, 96H, $H_{glycol-5c}$), 3.48-3.43 (m, 12H, $H_{glycol-5c}$), 3.27 (s, 18H, $-OCH_3-5c$), 2.00-1.89 (m, 12H, $H_{alkane-4c}$), 1.75-1.52 (m, 156H, PCH_2CH_3 and $H_{alkane-4c}$), 1.43-1.25 (m, 168H, $H_{alkane-4c}$), 1.08-0.92 (m, 236H, PCH_2CH_3 and $-CH_3-4c$). $^{31}P\{^1H\}$ NMR (CD_3COCD_3 , 121.4 MHz) δ 8.64 (s), 8.59 (s with a broad shoulder) $^1J_{Pt-p} = 1325.62$ Hz. MS (ESI) calcd for $[M - 2PF_6]^{2+}$ m/z 2001.0, found 2000.7 (C₁₈-C₁₈); calcd for $[M - 2PF_6]^{2+}$ m/z 2026.4, found 2026.4 (C₁₈-HEG); calcd for $[M - 2PF_6]^{2+}$ m/z 2052.8, found 2052.5 (HEG-HEG).

C₆/C₁₈ mixed assembly

Reaction scale: acceptor **7** (19.3 mg, 16.6 μ mol), donor **4a** (4.0 mg, 8.3 μ mol), donor **4c** (6.8 mg, 8.3 μ mol). Yield 31.8 mg (yellow solid), 97%. ¹H NMR (CD₃COCD₃, 300 MHz) δ 9.55 (s, 6H, H₉-**7**), 9.20 (dd, 24H, J = 36.0, 5.1 Hz, H _{α} -Py), 8.54 (s, 6H, H₁₀-**7**), 8.29-8.20 (m, 12H, H _{β} -Py), 8.13 (d, 12H, J = 5.1 Hz, H _{β} -Py), 7.88-7.81 (m, 24H, H_{2,4,5,7}-**7**), 7.53 (s, 12H, ArH), 7.31-7.24 (m, 12H, H_{3,6}-**7**), 4.31 (t, 24H, J = 6.6 Hz, ArOCH₂), 2.00-1.85 (m, 24H, H_{alkane}), 1.75-1.51 (m, 192H, PCH₂CH₃ and H_{alkane}), 1.43-1.24 (m, 168H, H_{alkane}), 1.08-0.92 (m, 216H, PCH₂CH₃), 0.91-0.84 (m, 36H, -CH₃). ³¹P{¹H} NMR (CD₃COCD₃, 121.4 MHz) δ 8.62, 8.60, 8.59 (all singlets, ¹J_{Pt-p} = 1331.27 Hz). MS (ESI) calcd for [M – 2PF₆]²⁺ m/z 1664.6, found 1664.4 (C₆-C₆); calcd for [M – 2PF₆]²⁺ m/z 1832.8, found 1832.6 (C₆-C₁₈); calcd for [M – 2PF₆]²⁺ m/z 2001.0, found 2000.8 (C₁₈-C₁₈).

DEG/HEG mixed assembly

Reaction scale: acceptor **7** (13.5 mg, 11.6 μ mol), donor **5a** (3.0 mg, 5.8 μ mol), donor **5c** (5.0 mg, 5.8 μ mol). Yield 22.2 mg (orange solid), 95%. ¹H NMR (CD₃COCD₃, 300 MHz) δ 9.56 (s, 6H, H₉-**7**), 9.17 (dd, 24H, J = 24.9, 5.7 Hz, H _{α} -Py), 8.53 (dd, 24H, J = 24.7, 5.7 Hz, H _{β} -Py), 7.89-7.79 (m, 24H, H_{2,4,5,7}-**7**), 7.53 (s, 12H, ArH), 7.31-7.24 (m, 12H, H_{3,6}-**7**), 4.54-4.46 (m, 24H, H_{glycol}), 3.98-3.92 (m, 24H, H_{glycol}), 3.73-3.66 (m, 24H, H_{glycol}), 3.65-3.42 (m, 120H, H_{glycol}), 3.30 (s, 18H, -OCH₃), 3.27 (s, 18H), 1.78-1.52 (m, 144H, PCH₂CH₃), 1.09-0.86 (m, 216H, PCH₂CH₃). ³¹P{¹H} NMR (CD₃COCD₃, 121.4 MHz) δ 8.58, 8.56, 8.54 (all singlets, ¹J_{Pt-p} = 1325.33 Hz). MS (ESI) calcd for [M – 2PF₆]²⁺ m/z 1700.0, found 1700.5 (DEG-DEG); calcd for [M – 2PF₆]²⁺ m/z 1876.6, found 1876.6 (DEG-HEG); calcd for [M – 2PF₆]²⁺ m/z 2052.8, found 2052.7 (HEG-HEG).

Supplementary Material

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References

- (a) Lehn JM. Angew Chem Int Ed 1990;29:1304. (b) Lindsey JS. New J Chem 1991;15:153. (c) Philp D, Stoddart JF. Angew Chem Int Ed 1996;35:1154. (d) Rebek J Jr. Acc Chem Res 1999;32:278. (e) Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J. Nature 2003;423:705. [PubMed: 12802325]
- (a) Orr GW, Barbour LT, Atwood JL. Science 1999;285:1049. [PubMed: 10446047] (b) Storhoff JJ, Mirkin CA. Chem Rev 1999;99:1849. [PubMed: 11849013] (c) Lehn JM. Science 2002;295:2400. [PubMed: 11923524] (d) Lehn JM. Proc Natl Acad Sci USA 2002;99:4763. [PubMed: 11929970] (e) Lehn JM. Rep Prog Phys 2004;67:249. (f) Hollingsworth MD. Science 2002;295:2410. [PubMed: 11923527]
- (a) Dietrich B, Lehn JM, Sauvage JP. Tetrahedron Lett 1969;34:2889. Pederson, C. J Ger Offen. 1970. Application: DE 70-2015732 (c) Lehn JM, Sauvage JP, Dietrich B. J Am Chem Soc 1970;92:2916. (d) Cram DJ, Cram JM. Acc Chem Res 1978;11:8. (e) Lehn JM. Acc Chem Res 1978;11:49. (f) Pederson CJ, Lehn JM, Cram DJ. Resonance 2001;6:71.
- Gleick, J. Chaos: Making a New Science. Penguin; New York, NY: 1988. Kauffman, S. At Home in the Universe. Oxford University Press; 1995.
- (a) Krämer R, Lehn JM, Marquis-Rigault A. Proc Natl Acad Sci USA 1993;90:5394. [PubMed: 11607405] (b) Smith V, Lehn JM. Chem Commun 1996:2733. (c) Funeriu DP, Lehn JM, Fromm KM, Fenske D. Chem Eur J 2000;6:2103.

6. (a) Albrecht M, Schneider M, Röttele H. *Angew Chem Int Ed* 1999;38:557. (b) Albrecht M, Schneider M. *Eur J Inorg Chem* 2002:1301.
7. (a) Caulder DL, Raymond KN. *Angew Chem Int Ed Engl* 1997;36:1440. (b) Ziegler M, Miranda JJ, Anderson UN, Johnson DW, Leary JA, Raymond KN. *Angew Chem Int Ed* 2001;40:733.
8. Masood MA, Enemark EJ, Stack TDP. *Angew Chem Int Ed* 1998;37:928.
9. Shi X, Fettingner JC, Davis JT. *J Am Chem Soc* 2001;123:6738. [PubMed: 11439079]
10. (a) Giuseppone N, Schmitt J-L, Lehn J-M. *Angew Chem Int Ed* 2004;43:4902. (b) Giuseppone N, Lehn JM. *J Am Chem Soc* 2004;126:11448. [PubMed: 15366885] (c) Giuseppone N, Fuks G, Lehn JM. *Chem Eur J* 2006;12:1723.
11. (a) Caulder DL, Powers RE, Parac TN, Raymond KN. *Angew Chem Int Ed* 1998;37:1840. (b) Bruckner C, Powers RE, Raymond KN. *Angew Chem Int Ed* 1998;37:1837.
12. (a) Schultz D, Nitschke JR. *Proc Natl Acad Sci USA* 2005;102:11191. [PubMed: 16061815] (b) Schultz D, Nitschke JR. *Angew Chem Int Ed* 2006;45:2453. (c) Hutin M, Frantz R, Nitschke JR. *Chem Eur J* 2006;12:4077. (d) Nitschke JR. *Acc Chem Res* 2007;40:103. [PubMed: 17309191]
13. (a) Severin K. *Chem Eur J* 2004;10:2565. (b) Saur I, Severin K. *Chem Commun* 2005:1471. (c) Saur I, Scopelliti R, Severin K. *Chem Eur J* 2006;12:1058.
14. (a) Barboiu M, Petit E, Vaughan G. *Chem Eur J* 2004;10:2263. (b) Dumitru F, Petit E, van der Lee A, Barboiu M. *Eur J Inorg Chem* 2005:4255. (c) Barboiu M, Petit E, van der Lee A, Vaughan G. *Inorg Chem* 2005;44:5649. [PubMed: 16060614] (d) Legrand YM, van der Lee A, Barboiu M. *Inorg Chem* 2007;46:9540. [PubMed: 17718483]
15. (a) Wu A, Isaacs L. *J Am Chem Soc* 2003;125:4831. [PubMed: 12696902] (b) Mukhopadhyay P, Wu A, Isaacs L. *J Org Chem* 2004;126:10035. (c) Lui SM, Ruspici C, Mukhopadhyay P, Chakrabarti S, Zavalij P, Isaacs L. *J Am Chem Soc* 2005;127:15959. [PubMed: 16277540] (d) Mukhopadhyay P, Zavalij PY, Isaacs L. *J Am Chem Soc* 2006;128:14903.
16. Taylor PN, Anderson HL. *J Am Chem Soc* 1999;121:11538.
17. While the simultaneous self-assembly of nine components was studied only eight supramolecules were obtained because two of the nine components were complementary constituents that self-assemble to form one single supramolecule.
18. Addicott C, Das N, Stang PJ. *Inorg Chem* 2004;43:5335. [PubMed: 15310211]
19. Yang HB, Ghosh K, Northrop BH, Stang PJ. *Org Lett* 2007;9:1561. [PubMed: 17378574]
20. Zheng YR, Yang HB, Northrop BH, Ghosh K, Stang PJ. *Inorg Chem* 2008;47:4706. [PubMed: 18433099]
21. Zhao L, Northrop BH, Zheng YR, Yang HB, Lee HJ, Lee YM, Park JY, Chi KW, Stang PJ. *J Org Chem* 2008;73:6580–6586. [PubMed: 18683976]
22. (a) Yang HB, Ghosh K, Northrop BH, Zheng YR, Lyndon MM, Muddiman DC, Stang PJ. *J Am Chem Soc* 2007;129:114187. (b) Ghosh K, Yang H-B, Northrop BH, Lyndon MM, Zheng Y-R, Muddiman DC, Stang PJ. *J Am Chem Soc* 2008;130:5320. [PubMed: 18341280]
23. (a) Yang HB, Ghosh K, Zhao Y, Northrop BH, Lyndon MM, Muddiman DC, White HS, Stang PJ. *J Am Chem Soc* 2008;130:839. [PubMed: 18166061] (b) Ghosh K, Zhao Y, Yang HB, Northrop BH, White HS, Stang PJ. *J Org Chem*. 2008In Press
24. (a) Yang HB, Das N, Huang F, Hawkrigide AM, Muddiman DC, Stang PJ. *J Am Chem Soc* 2006;128:10014. [PubMed: 16881621] (b) Yang HB, Hawkrigide AM, Huang SD, Das N, Bunge SD, Muddiman DC, Stang PJ. *J Am Chem Soc* 2007;129:2120. [PubMed: 17256935]
25. Northrop BH, Glöckner A, Stang PJ. *J Org Chem* 2008;73:1787. [PubMed: 18247491]
26. In the original reports of the self-assembly of **DB24C8** and ferrocene functionalized rhomboids their ^{31}P NMR spectra were recorded after evaporating to dryness and re-dissolving in CD_2Cl_2 whereas in the current study their spectra were obtained in a mixture of 2:1 $\text{CD}_3\text{COCD}_2/\text{D}_2\text{O}$. The different solvents account for the difference in their ^{31}P NMR chemical shifts: 12.6 and 12.2 ppm in CD_2Cl_2 (original studies) and 15.5 in $\text{CD}_3\text{COCD}_3/\text{D}_2\text{O}$ (current study).
27. See, for example, (a) Jones MN, Champman DM. *Micelles, Monolayers and Biomembranes* Wiley-Liss New York 1995 (b) Discler DE, Eisenberg A. *Science* 2002;297:967. [PubMed: 12169723] (c) Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, Yin Y, Kim F, Han H. *Adv Matter* 2003;15:353. (d) Xia Y, Gates B, Yin YD, Lu Y. *Adv Matter* 2000;12:693.

28. Previous investigations of the self-assembly of hydrophobic and hydrophilic rectangles (see Ref. 25) have shown that the mixture of $\text{CD}_3\text{COCD}_3/\text{D}_2\text{O}$ used in this study is optimal for achieving quantitative self-assembly of rectangular metallacycles, therefore we chose not to vary the solvent in the current study.
29. Kryschenko YK, Seidel SR, Arif AM, Stang PJ. *J Am Chem Soc* 2003;125:5193. [PubMed: 12708871]
30. Kuehl CJ, Huang SD, Stang PJ. *J Am Chem Soc* 2001;123:9634. [PubMed: 11572685]

Figure 1.

Chemical structures of **DB24C8** functionalized 120° bispyridyl donor **1**, ferrocenyl functionalized 120° donor **2**, dendronized 120° donors **3a–c**, hydrophobic 180° donors **4a–c**, hydrophilic 180° donors **5a–c**, as well as 60° and 0° di-Pt(II) acceptors **6** and **7**.

Figure 2. (A) Full ^1H NMR spectrum of the **DB24C8**/ferrocene mixed rhomboid self-assembly. (B) Full ^{31}P NMR spectrum of the mixed assembly wherein a single, sharp ^{31}P signal (inset) indicates the formation of discrete supramolecular products.

Figure 3. Full ESI mass spectrum of the complex mixture of **DB24C8** and/or ferrocene functionalized supramolecular rhomboids. The ESI-MS results show the presence of both homotopic and heterotopic assemblies and is suggestive of the preferred formation of homotopic species.

Figure 4. ^{31}P NMR spectra of (A) the [G1]–[G2] mixed dendron rhomboid assemblies and (B) the [G2]–[G3] mixed dendron rhomboid assemblies. Both spectra indicate that only discrete supramolecular species and no oligomeric are obtained, however, differences between homotopic and heterotopic assemblies cannot be resolved.

Figure 5.

Full ESI mass spectra of (A) the [G1]-[G2] and (B) the [G2]-[G3] mixed assemblies. The different intensities of mass spectral peaks are suggestive of a statistical mixture of homotopic and heterotopic assemblies.

Figure 6. Full spectra and close-up views of the ^{31}P NMR spectra of the C_6/DEG (A), C_{12}/TEG (B), and C_{18}/HEG (C) mixtures showing the relative contributions of purely hydrophobic (dark blue), purely hydrophilic (light blue) and mixed amphiphilic (red) metallacycles rectangles.

Figure 7.

ESI-MS results for the C_6/DEG (A), C_{12}/TEG (B), and C_{18}/HEG (C) mixtures. The series of spectra show that with an increase in hydrophobic/hydrophilic chain length comes a decline in the presence of mixed functionality rectangles.

Figure 8. Full spectrum and close-up views of the ^{31}P NMR spectra of the purely hydrophobic C_6/C_{18} mixture (A) and purely hydrophilic DEG/HEG mixture (B).

Figure 9. ESI-MS results for the hydrophobic C_6/C_{18} mixture (A) and hydrophilic DEG/HEG mixture (B).

Scheme 1.

Potential second-order self-organization effects are investigated through the self-assembly of (A) unrelated **DB24C8** and ferrocene functionalized bispyridyl donors **1** and **2** with 60° di-Pt(II) acceptor **6**, (B) related though different generation dendronized 120° bispyridyl donors **3a** and **3b** (or **3b** and **3c**) with 60° di-Pt(II) acceptor **6**, and (C) like sized hydrophobic (**4a–c**) and hydrophilic (**5a–c**) 180° bispyridyl donors with a 0° di-Pt(II) molecular clip. In each case the donor:donor:acceptor ratio is 1:1:2.

Scheme 2.

Schematic representation of the four general types of self-organization that are possible when two ditopic bispyridyl donors are combined with a di-Pt(II) acceptor in a 1:1:2 ratio: "social," exclusive formation of heterotopic metallacycles; "narcissistic," exclusive formation of only homotopic metallacycles; "statistical" formation of homotopic and heterotopic assemblies; and "amplified" formation of slightly more homotopic than heterotopic metallacycles or vice versa (the ratio of 2:1:2 is only one representative example of such self-organization).

Scheme 3.

Schematic representation of the pre-assembly aggregation phenomena that likely explains the trend toward greater self-organization upon increasing chain length in mixtures of hydrophobic (dark blue) and hydrophilic (light blue) bispyridyl donors and a di-Pt(II) acceptor.

Observed and calculated $[M - 2NO_3]^{2+}$ and $[M - 3NO_3]^{3+}$ peaks (m/z) for the $[G1]/[G2]$ and the $[G2]/[G3]$ mixed dendronized rhomboids indicating that both homotopic and mixed heterotopic assemblies are obtained.

Table 1

	Rhomboid	$[M - 2NO_3]^{2+}$		$[M - 3NO_3]^{3+}$	
		Found	Calculated	Found	Calculated
[G1]/[G2] Mixed Assembly	[G1]-[G1]	1698.9	1699.6	1111.6	1112.4
	[G1]-[G2]	1911.7	1911.2	1253.6	1253.4
	[G2]-[G2]	2124.2	2124.7	1395.6	1395.8
[G2]/[G3] Mixed Assembly	[G2]-[G2]	2124.4	2124.7	1394.9	1395.8
	[G2]-[G3]	2548.0	2547.9	1678.0	1677.9
	[G3]-[G3]	2971.7	2972.2	1960.9	1961.3