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Donor−Acceptor Phthalocyanine Nanoaggregates

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Abstract: A novel donor−acceptor bisphthalocyanine (bis-Pc, **1**) in which two different Pc units (Zn(II)-Pc and Ni(II)-Pc) are linked via vinylene spacers to the pseudo*para* positions of a central [2.2]paracyclophane moiety is described. The synthesis of **1** is achieved by two successive Heck reactions of pseudo*para*-divinyl[2.2]paracyclophane **9** with, sequentially, a zinc(II)- and a nickel(II)-iodophthalocyanine (**4** and **5**, respectively). The self-assembly ability of **1**, which is the result of the complementary donor−acceptor character of its phthalocyanine units, has been assessed by a variety of techniques. It is revealed that **1** forms one-dimensional aggregates of nanometer-sized dimension, whereas equimolar mixtures of the donor and acceptor Pc subunits **2** and **3**, although strongly interacting, do not give large arrays. The aggregates of **1** represent a novel type of supramolecular polymers based mainly upon donor−acceptor interactions.

Introduction

Self-assembly and self-organization are based on the mutual noncovalent recognition of molecules containing specific structural information.[1] This strategy, originating from the natural world, has been elegantly applied using a wide variety of recognition motifs for the construction of numerous supramolecular architectures such as infinite arrays,[2] grids[3], cages,[4] tubes,[5] liquid crystals,[6] and monolayers.[7] The construction of precisely defined molecular materials[8] and molecular machines[9] designed to perform specific functions such as chemical sensing, electrical conductivity, mechanical movements, and so forth represents the next step forward in the field of supramolecular chemistry and requires (i) the incorporation of functional building blocks, (ii) a control of the supramolecular assembly process, and (iii) a function or property derived from the specific assembled architectures.

The aromatic macrocycles phthalocyanines (Pcs)[10] are one of the best known synthetic porphyrin analogues. They are highly versatile and stable chromophores with unique physicochemical properties that make them ideal building blocks in the construction of molecular materials having special electronic and optical properties. Interestingly, owing to their extended flat hydrophobic aromatic surface, these macrocycles can interact with each other by attractive $\pi-\pi$ stacking interactions,[11] leading to aggregation in solution. However, the formation of long-range ordered Pc aggregates is not so easily realized and requires additional structural features within the Pc ring such as the presence of long flexible hydrocarbon side chains[12] or/and crowned phthalocyanines.[13] While the former type of substituents promote a mesomorphic behavior, the crown ether

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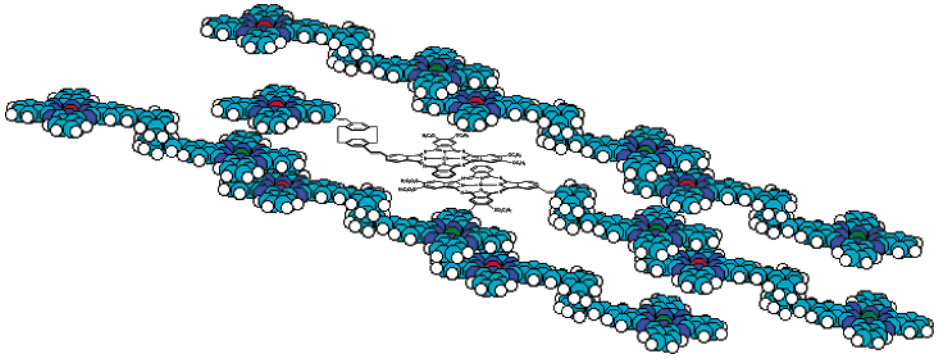

Figure 1. Computer generated model of the proposed phthalocyanine aggregate formed by self-association of **1**.

moieties help to form columnar aggregates in the presence of metal salts due to complexation of the cation by the crown ether subunits. Alternative molecular recognition motifs have also been used such as hydrogen-bonding[14] and metal−ligand[15] interactions to self-assemble phthalocyanine molecules forming either discrete supramolecular structures or infinite ill-defined aggregates.

In spite of the extensive research in the field of phthalocyanine assemblies, there are very few examples of supramolecular phthalocyanine heterodimers to be found in the literature. One such system is based on the recognition between the complementary peripheral substituents of a symmetrically substituted 18-crown-8-metallophthalocyanine and a tetra(alkylammonium) derivative.[16] In an alternative approach, noncovalent porphyrin heterodimers have been constructed using electrostatic interactions between macrocycles with opposite-charged substituents.[17] However, to our knowledge, donor−acceptor interactions[18] have never been explored in phthalocyanine systems and may constitute a new way of constructing functional supramolecular architectures based on these units.[19]

In this paper, we describe the first Pc supramolecular assembly (see Figure 1) driven by strong donor−acceptor interactions between Zn(II)- and Ni(II)-phthalocyanine rings possessing at the periphery alkoxy and alkylsulfonyl substituents, respectively.

We report here on the synthesis of the bisphthalocyanine system **1** (Chart 1) which consists of two Pc units, one of them electron-deficient and the other one electron-rich, conjugated to the pseudo*para* positions of a central [2.2]paracyclophane (pCp) moiety. We have introduced short alkyl chains in the peripheral alkoxy and alkylsulfonyl substituents, namely butoxy and propylsulfonyl, respectively, in order to minimize the formation of columnar assemblies driven by van der Waals interactions between the peripheral alkyl chains.[20] The aggregation behavior of compound **1** in comparison with that of a 1:1 molar mixture of monophthalocyanines **2** and **3** is described as well as the aggregate architectures formed by the self-assemby of **1**.

Results and Discussion

Synthesis and Characterization. Scheme 2 shows the convergent strategy used to synthesize compound **1**, which involves first the preparation of the iodophthalocyanine precursors **4**[21] and **5**[22] (Scheme 1) with different donor/acceptor character, by statistical crossover condensation of 4-iodophthalonitrile (**6**)[23] and 4,5-dibutoxyphthalonitrile (**7**)[24] or 4,5-dipropylsulfonylphthalonitrile (**8**),[22] respectively. The two differently substituted phthalocyanine fragments were connected to the pseudo*para*-divinyl[2.2]paracyclophane **9** by two successive Heck reactions.

Phthalocyanine **4** was prepared by heating a 1:3 mixture of phthalonitriles **6** and **7** in the presence of $Zn(OAc)_2$ in *N*,*N*-dimethylaminoethanol (DMAE). The electron-deficient phthalocyanine **5** was prepared in a similar way from phthalonitriles **6** and **8** using $NiCl_2$ and a mixture of *o*-dichlorobenzene and DMF as solvents in order to avoid nucleophilic attack to the sulfone groups.[25] The desired macrocycles were isolated from the statistical mixture of phthalocyanines by column chromatography on silica gel.

The [2.2]paracyclophane **9** was prepared in good yield in two steps which involve the bromination of commercially available [2.2]paracyclophane using the Reich and Cram conditions[26] and a subsequent Stille reaction in hot toluene using vinyltributyltin as nucleophile and $Pd(PPh_3)_4$ as catalyst (Scheme 2). [2.2]Paracyclophane **9** was further reacted with phthalocyanine **4** in the presence of $Pd(OAc)_2$, Et_3N, and $Bu_4N^+Br^-$ yielding 56% of

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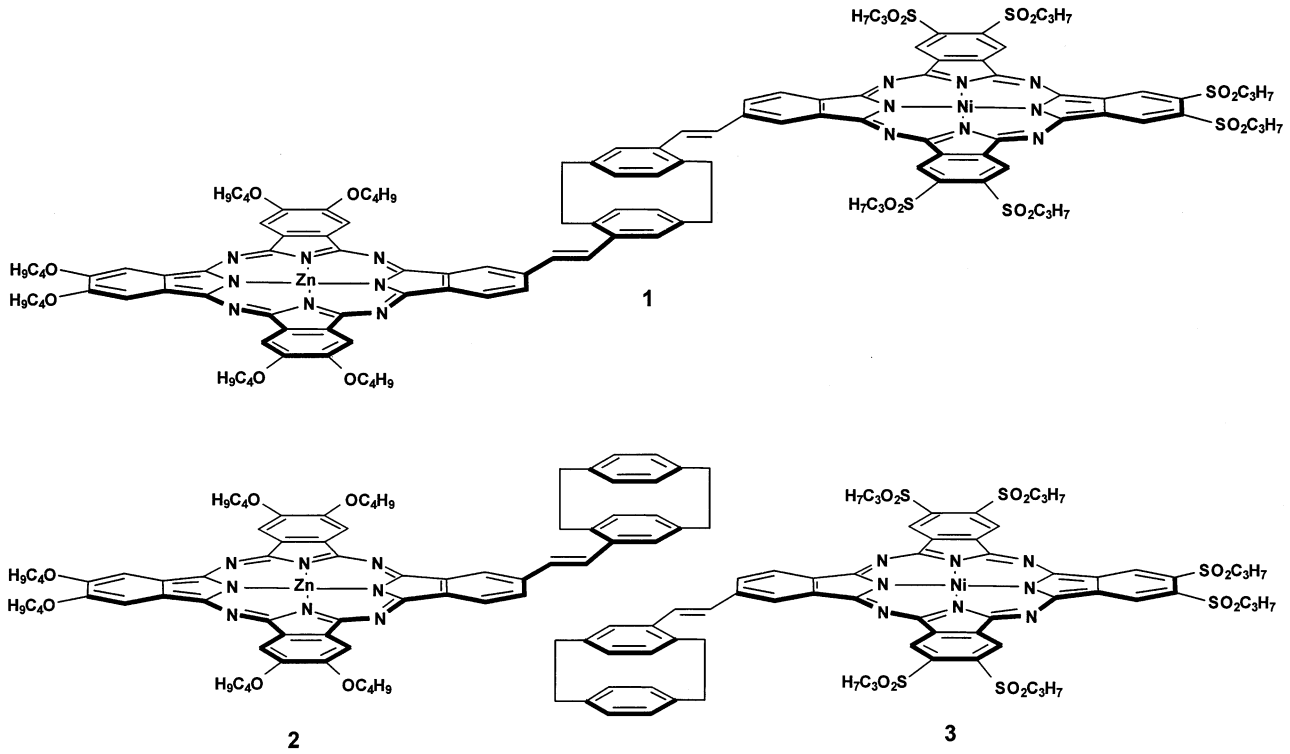
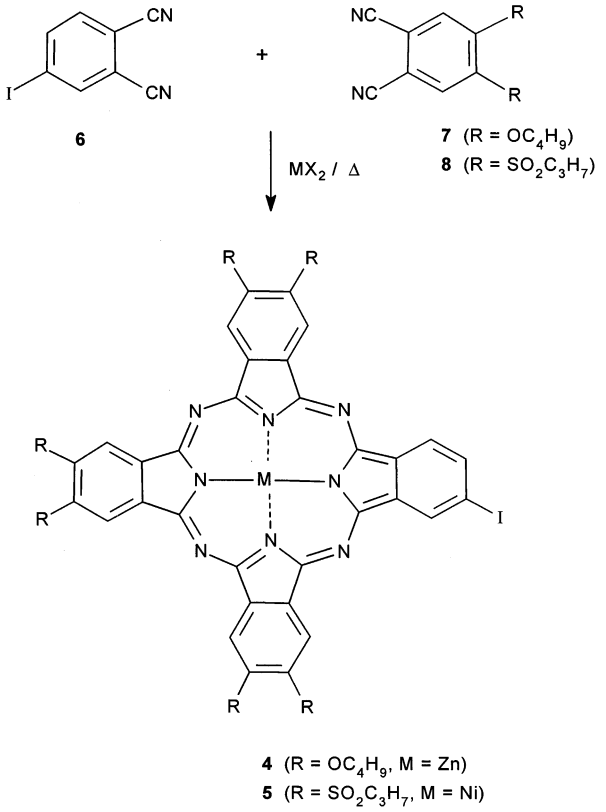
Chart 1



Scheme 1. Synthesis of Iodophthalocyanine Precursors **4** and **5** by Statistical Condensation



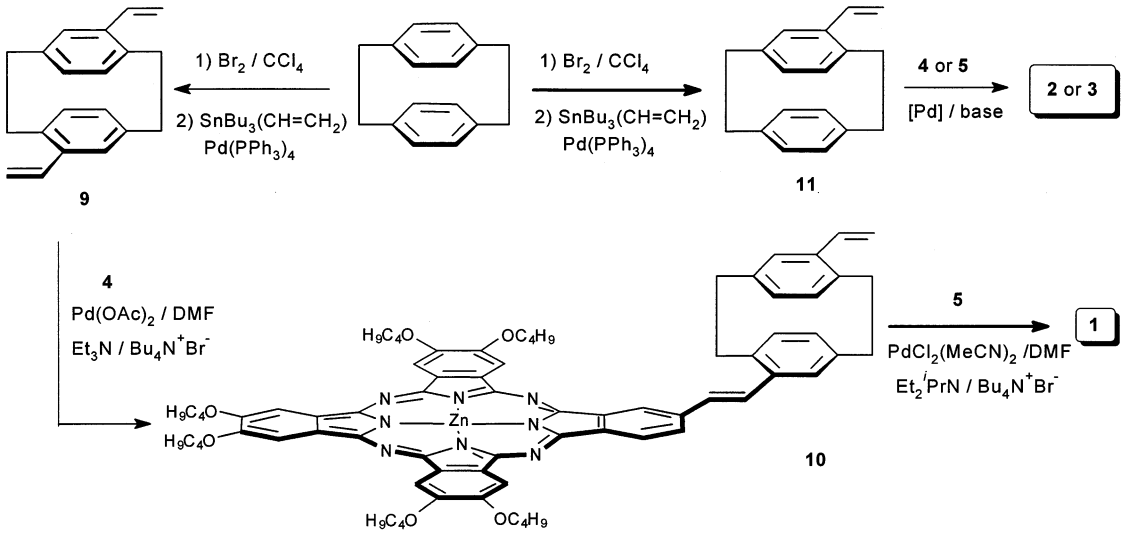
derivative **10**. The second phthalocyanine unit was introduced by an additional Heck reaction using milder conditions, namely $Pd(MeCN)_2Cl_2$ and a less nucleophilic base such as $Et_2{}^iPrN$.

The two monophthalocyanine-[2.2]paracyclophane systems **2** and **3** were prepared by means of the same synthetic methodology (Scheme 2). Thus, a Heck reaction between the monovinyl[2.2]paracyclophane **11** and the iodophthalocyanine **4** or **5** in the appropriate conditions (depending on the substituents at the periphery, OC_4H_9 or $SO_2C_3H_7$) afforded compounds **2** and **3**, respectively, in good yields.

All the compounds were characterized by mass spectrometry and UV−vis spectroscopy and, when it was possible, by NMR spectroscopy. The ^{1}H NMR spectra of phthalocyanine derivatives **3** and **5** bearing sulfone groups showed well-resolved sets of resonances. The high-resolution found in these spectra is indicative of a low degree of aggregation in solution, that has to be attributed to the high polarity of the sulfonyl groups surrounding the Pc core.[25] The aromatic phthalocyanine protons for the isoindole units bearing sulfone groups appear as six singlets in the range of δ 9.8 to 10.2 ppm (see Supporting Information). The alkoxy substituted phthalocyanines are, in general, more prone to aggregation, which results in ^{1}H NMR spectra with broadened signals, as was observed for compound **4**. In contrast, the ^{1}H NMR spectra in $CDCl_3$ of hexabutoxyphthalocyanines **2** and **10**, in which a paracyclophane subunit has been attached, showed resolved sets of resonances assigned to the Pc ring protons in the range of 7.5 to 8.5 ppm (see Supporting Information) which indicates that the presence of such a bulky substituent has significantly reduced the macrocycle aggregation in solution.

The ^{1}H NMR spectrum in $CDCl_3$ of bisphthalocyanine **1** showed the typical broadened resonances of phthalocyanine aggregates (see Supporting Information). As this phenomenon is not observed with compounds **2** and **10**, these results suggest that inter- or intramolecular interactions are occurring between the differently substituted, donor and acceptor, phthalocyanine units. For this reason, monophthalocyanines **2** and **3** have been prepared, to more closely study the inter- or intramolecular nature of these interactions.

Scheme 2. Synthesis of Bis- and Monophthalocyanine-[2.2]Paracyclophanes **1**, **2**, and **3**



The same conclusions concerning the aggregation properties of the molecules were also obtained using UV−vis spectroscopy. The shape and location of the so-called Q-band is known to be a sensitive probe in determining the aggregation properties of these macrocycles.[27] The UV−vis spectra of compounds **1**, **2**, and **3** in $CHCl_3$ are shown in Figure 2. Compound **2** exhibits an intense Q-band absorption centered at 692 nm, typical of monomeric metallophthalocyanines.[10] The intrinsic lack of symmetry of compound **3** is also reflected in its UV−vis spectrum, showing a split Q-band. Interestingly, a new broad blue shifted absorption centered at ca. 639 nm is observed in the spectrum of compound **1**, indicative of cofacial aggregation. Additionally, the UV−vis spectrum of compound **1** reveals a broad low intensity band at around 740 nm assignable to a charge-transfer (CT) band[28] which is a consequence of the electronic coupling between the donor and acceptor phthalocyanine units of the molecule. The CT band can be more clearly observed by subtracting the UV−vis spectra of monophthalocyanines **2** and **3** from the spectrum of **1** (see Figure S2 in the Supporting Information). The subtracted spectrum also shows the characteristic aggregation band at 638 nm due to the cofacial aggregation of phthalocyanines.

Aggregation Studies. Prior to any binding analyses, UV−vis and ^{1}H NMR dilution studies were carried out with the monomers **2** and **3** in order to evaluate the contribution of the self-association processes. No significant changes in the absorption spectra of these compounds in $CHCl_3$ were detected in the range of 5×10^{-6} to 1×10^{-4} molar concentration. These results indicate that aggregation of these [2.2]paracyclophane-phthalocyanines is not significant in this range of concentration in contrast with the usual behavior of peripherally alkoxy substituted phthalocyanines.[12a] To evaluate more precisely the

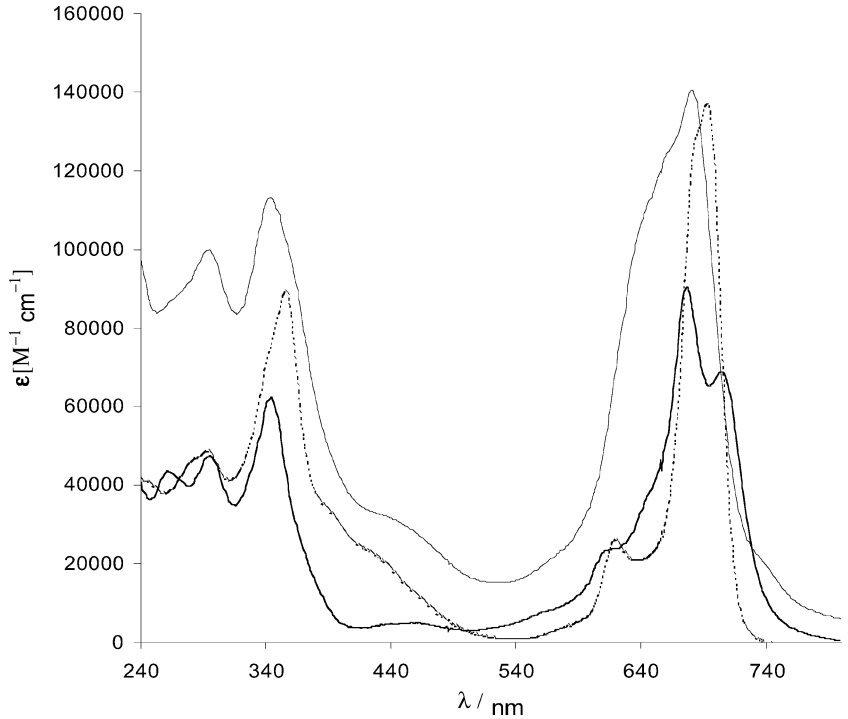


Figure 2. Electronic absorption spectra in $CHCl_3$ of **1** (7.5×10^{-6} M, plain line), **2** (8.1×10^{-6} M, dashed line), and **3** (6.9×10^{-6} M, solid line).

Table 1. Association Constants (M^{-1}) and Free Energy of Formation (kJ/mol) at 298 K

	solvent	K_a	$-\Delta G°$
2	$CHCl_3$	$1 \times 10^{4a,b}$	
3	$CHCl_3$	1175^a	17.5 ± 1
2•3	$CHCl_3$	$2 \times 10^{7\ c}$	42 ± 4
1	toluene	$3 \times 10^{9\ c}$	54 ± 10
1	$CHCl_3$	$1.1 \times 10^{6\ c}$	34 ± 2
1	DMF	$9.2 \times 10^{4\ c}$	28 ± 2

[a] Determined by ^{1}H NMR. [b] Upper estimated value. [c] Determined by UV−vis spectroscopy.

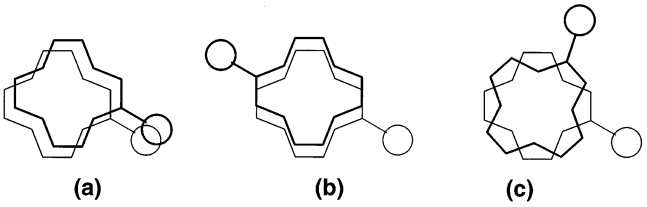


Figure 3. Schematic representation of some of the possible conformations of a noncovalent dimer of **3**: parts a and b represent cofacial conformations, and part c represents a staggered conformation.

self-association constants, ^{1}H NMR studies in the range of 1×10^{-4} to 1×10^{-3} M concentrations were carried out. In these studies, a 1:1 homodimer complex was assumed as the only type of association event occurring in solution. Several aromatic signals of compounds **2** and **3** were monitored as a function of concentration, and quantitative analysis of the data was accomplished using a custom written global[29] nonlinear regression analysis program within the Matlab 5.3 package[30] (see Supporting Information). The 1:1 self-dimerization of compound **3** was found to be $K_{dimer} = 1175\ M^{-1}$ in $CHCl_3$ (Table 1). In the case of compound **2**, the spectra throughout the ^{1}H NMR binding study were too broad to obtain any accurate result. However, the upper limit of the value of the dimerization constant of this compound can tentatively be estimated to be in the order of $10^4\ M^{-1}$ considering the results reported in the literature[12a] and the particular structural features of **2**, namely, the presence of both a very bulky substituent (the paracyclophane) and short alkoxy chains.

Upon dilution, both the chemical shifts and the number of peaks changed, in particular in the aromatic region of the spectra. The spectrum of the most diluted sample (8.25×10^{-5} M) showed the expected three singlets for compound **3**. Upon increasing the concentration, the aromatic resonances shifted to higher field and doubled in number (from 3 to 6 resonances). This doubling might be a consequence of the formation of a noncovalent dimer with low symmetry, as the one depicted schematically in Figure 3c, in which the macrocycles have adopted a staggered geometry that accounts for the observed breaking of symmetry.

Having previously analyzed the tendency of monomeric phthalocyanines **2** and **3** to self-associate, we have carried out further binding studies to determine the heteroassociation constants of the differently substituted phthalocyanine units present in **1**, **2** and **3**.

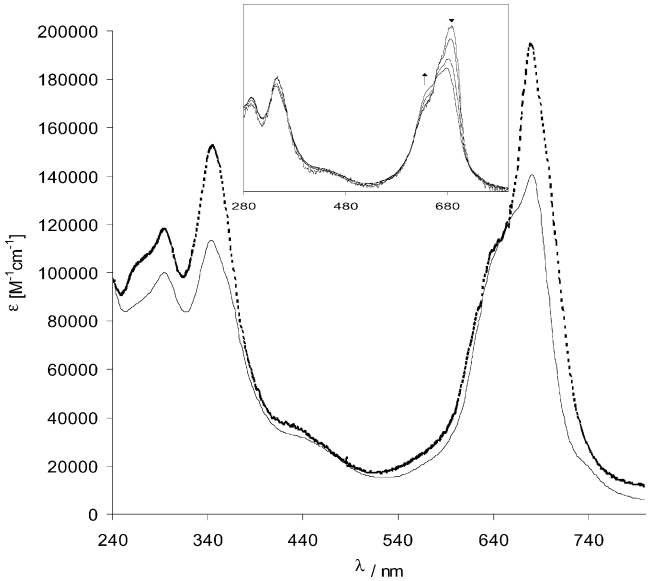


Figure 4. Electronic absorption spectra in $CHCl_3$ of **1** (solid line, 7.5×10^{-6} M) and an equimolar mixture of **2** and **3** (dotted line, 4×10^{-6} M). Inset: concentration dependence (from 1×10^{-6} to 1×10^{-4} M) of the electronic spectrum of **1** in chloroform solution.

The UV−vis spectrum of an equimolar mixture of donor and acceptor phthalocyanines **2** and **3** in $CHCl_3$ showed remarkably similar features to those seen for compound **1** (see Figure 4), namely the appearance of a blue shifted maximum absorption centered at 639 nm and a low intensity charge transfer band at around 740 nm, thus confirming the intermolecular nature of this CT band. This result indicates that, in addition to the hydrophobic effect, which is known to induce phthalocyanines to form aggregates in solution, the two Pc halves of compound **1** may be considered as donor and acceptor subunits that interact with each other mainly in an intermolecular fashion.

UV−vis spectroscopy was found to be an ideal technique[31] for studying the interaction between **2** and **3**. The concentration of compound **2** was kept constant at 1.5 μM in $CHCl_3$, to which was added increasing concentrations of the monophthalocyanine−cyclophane **3**. The heterodimer **2•3**/monomer **3** ratio was monitored as a function of the concentration of **3** by plotting the absorption ratio at 639 and 705 nm [A(639)/A(705)] versus concentration of monomer **3** (Figure 5). These two maxima were chosen since they are characteristic absorptions of the dimeric and the monomeric species, respectively. Upon aggregation, a decrease in the intensity of the maxima at 705 nm (assigned to the monomeric phthalocyanine **3**) and concomitant increase of the maxima at 639 nm (assigned to the heterodimer formed between **2** and **3**) are observed.[32] The formation of higher aggregates ($n = 3$, 4, etc.) has been neglected, taking into account the low concentration used. The dimerization constant in $CHCl_3$ calculated[29,30] (see Supporting Information) from the

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(30) *Matlab*, version 5.3.0.620a (R11); The Mathworks, Inc.: Natick, MA, 1999.

(31) To determine the exact association constants, ^{1}H NMR binding studies in $CDCl_3$ were performed in which the concentration of **3** was held constant at 1 mM in the presence of increasing concentrations of **2**. Unfortunately, the ^{1}H NMR signals were not sufficiently resolved at relatively low concentrations to obtain any accurate data from this experiment.
(32) However, it is necessary to point out that both the absorption spectra of monomeric phthalocyanines **2** and **3** and the heterodimer **2•3** appear in the same spectral region, and therefore, it is very difficult to obtain clean spectra for each species. Most probably, a small contribution of the other species to the selected maxima absorption (mainly the one at 639 nm) cannot be discarded, obviously contributing to the experimental small error of this analysis.

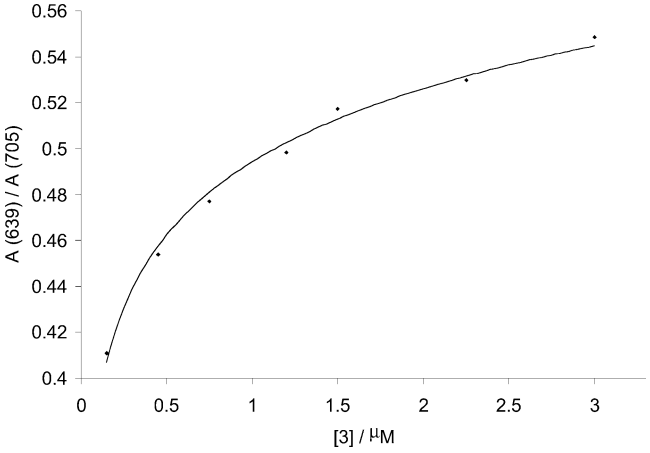

Figure 5. Ratio of the absorbances at 639 and 705 nm plotted versus the concentration of monomer **3** in chloroform.

UV−vis studies is $K_{dimer} = 2 \times 10^7$ M^{-1} (Table 1). This large dimerization value certainly demonstrates the strong preference for the qualitative formation of a heterodimer by intermolecular interactions of the donor and acceptor phthalocyanines **2** and **3**.

The aggregation of bisphthalocyanine **1** was also studied by UV−vis spectroscopy. Dilution experiments carried out in solvents with different dielectric constants (namely toluene, $CHCl_3$ and DMF) in the range of concentration 1×10^{-6} to 1×10^{-4} M showed a clear concentration dependency. The different absorption spectra of compound **1** in $CHCl_3$ are shown in the inset of Figure 4. As the concentration is increased, a decrease in the absorption maxima at 692 nm (corresponding to the monomer) and an increase of the absorption at 639 nm due to the aggregate are observed. The data from these dilution studies were fitted[29,30] (see Supporting Information) to a 1:1 dimerization binding model, assuming no higher aggregates, to give $K_{dimer} = 1.1 \times 10^6$ in $CHCl_3$ (Table 1). This value is an order of magnitude (ca. 8 kJ mol^{-1}) lower than that observed for the heterodimerization of **2** and **3**. This suggests that **1** cannot assemble to form a perfectly cofacial "double dimer" (Figure 6b) (due to the cyclophane step that forces the phthalocyanine units to offset) and rather prefers to assemble into an "elongated dimer" (Figure 6a) in which only two phthalocyanines interact, with the possibility of further aggregation in one dimension. Possible staggered conformations cannot be ruled out from the latter assembly.

The donor−acceptor nature of the dimerization is highlighted by the sensitivity to the solvent polarity. The influence of the solvent polarity in the association constant can also give valuable information about the nature of the interactions controlling the complexation.[33] In general, complexes involving nonpolar interactions are stabilized by polar solvents and complexes involving polar interactions (electrostatics) are more stable in nonpolar solvents. A higher association constant was measured for compound **1** in toluene ($K_{dimer} = 3 \times 10^9$ M^{-1}, $\Delta G = -54$ kJ mol^{-1}). This trend is in line with the idea that polar interactions play an important role in the complex formation between the two phthalocyanine surfaces, one with acceptor and the other one with donor character.

The aggregation of the bisphthalocyanine-[2.2]paracyclophane **1** was found also to be temperature dependent. The heat of association (W) can be estimated by UV−vis spectroscopy by plotting the ratio of absorbances of the aggregate (639 nm) and the monomer (692 nm) versus the temperature for four different concentrations of **1** in toluene (see Supporting Information). The aggregation number is related to this absorbance ratio; that is, at a fixed ratio the weight fraction of the monomer, m_1, is constant. For a constant m_1, the following relationship holds for linear aggregates of uniform structure:[34]

$$W = R[\Delta \ln c/\Delta(1/T)]$$

where $W(\Delta H)$ is the heat of association, R is the gas constant, $\Delta \ln c$ is the difference between two Pc concentrations, and $\Delta(1/T)$ is related to the temperature difference that has to be applied to maintain a constant m_1. The temperature (T) values at which the absorbance ratio equals 0.8 were obtained by intrapolation of the data points at each concentration c and plotted as $\ln c$ versus $1/T$ (see Supporting Information). A straight line was obtained from which a value of $W = -30$ kJ mol^{-1} was determined. In combination with ΔG measurements obtained by binding studies, the entropy of association can be calculated as $\Delta S \approx 80$ J K^{-1} mol^{-1}. This tentatively suggests that desolvation of the monomer **1** is an important factor in driving the self-association of this compound in toluene.[35]

Higher values of heats of associations (−125 kJ/mol) have been reported for liquid-crystalline phthalocyanines, which form larger linear aggregates in a chloroform solution, as a consequence of additional van der Waals interactions between the peripheral substituents.[13a] However, in our system, we have tried to minimize the contribution of the peripheral substituents to the aggregation, and therefore, the heat of association comes primarily from the donor−acceptor interactions between different types of Pc macrocycles.

Electron Microscopy Studies. Considering the complexation studies mentioned above, we believed the interaction between the different phthalocyanine units of compound **1** could result in the formation of a large phthalocyanine array (see Figure 1 and Figure 6a). To investigate the formation of these aggregates, several samples of different concentration in hot *n*-butanol were studied by transmission electron microscopy (TEM). *n*-Butanol was chosen as the solvent for technical reasons, among others, its high boiling point. The formation of large aggregates was not observed in the low concentration samples. However, as the concentration of **1** reached approximately 1 mM, aggregates became visible (Figure 7). A unique feature of these aggregates is that they are very monodisperse in both shape and size (typical dimensions 290×90 nm^2). In contrast and as expected, no aggregates were detected when using an equimolar mixture of phthalocyanines **2** and **3**. Indeed, the presence of the bulky paracyclophane unit prevents the formation of large phthalocyanine nanoaggregates.

Phthalocyanines **2** and **3**, in the presence of **1**, could eventually act as stoppers of an infinite array made of compound **1** units, preventing the growth of the aggregate. The effect of the addition of these monophthalocyanines on the aggregates

(33) (a) Breault, G. A.; Hunter, C. A.; Mayers, P. C. *J. Am. Chem. Soc.* **1998**, *120*, 3402. (b) Cubberley, M. S.; Iverson, B. L. *J. Am. Chem. Soc.* **2001**, *123*, 7560.

(34) Ölschläger, H. J. *Colloid Interface Sci.* **1969**, *31*, 503.

(35) For an example of desolvation effects in self-assembly, see: Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **1999**, *121*, 11538.

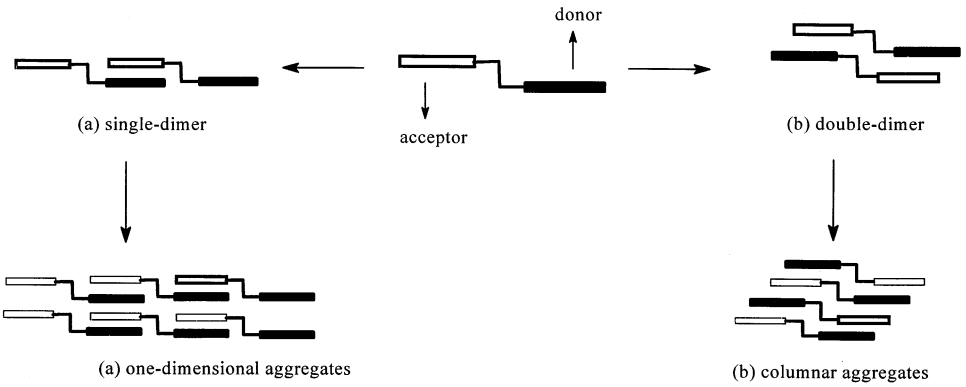

Figure 6. Schemetic representation of the type of aggregates that bisphthalocyanine **1** could form by donor−acceptor interactions: (a) one-dimensional aggregates or (b) columnar aggregates.

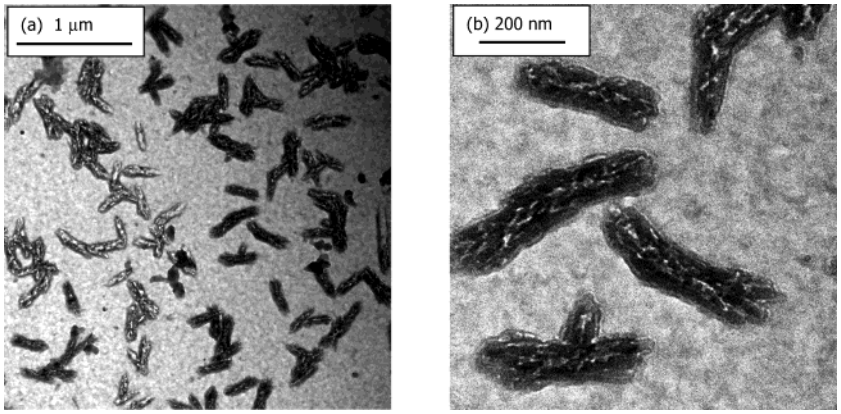

Figure 7. (a,b) Transmission electron micrographs of **1**. Samples were prepared from hot *n*-butanol solutions (1×10^{-3} M).

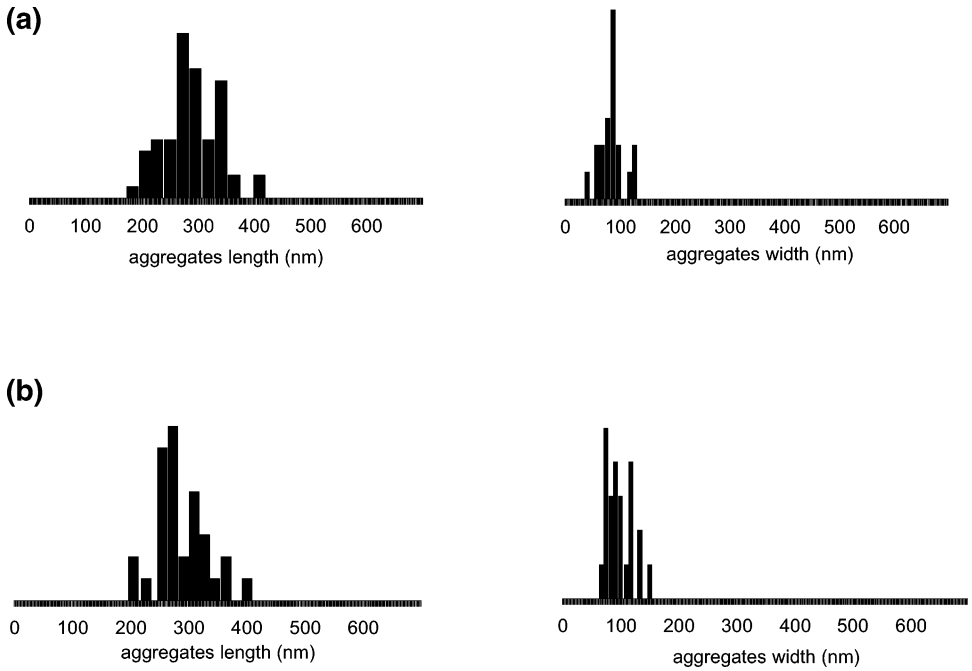

Figure 8. Size distribution diagrams of lengths and widths of aggregates formed by (a) bisphthalocyanine **1** and (b) a 2:1:1 mixture of **1**, **2**, and **3** (each diagram contains around 150 data points).

size of the bisphthalocyanine **1** was investigated also by means of TEM in different samples in which the bisPc/monoPcs ratio was changed. Using a 2:1:1 mixture of **1**, **2**, and **3**, well-defined aggregates were observed with the same shape as those obtained with compound **1**. Figure 8 presents the size distribution diagram of lengths and widths of the aggregates formed by (a) pure bisphthalocyanine **1** and (b) the 2:1:1 mixture of **1**, **2**, and **3**. They both show similar lengths, widths, and size dispersities of the structures. This result indicates that the size of the bisphthalocyanine **1** aggregates is not dramatically modified by

addition of monophthalocyanines **2** and **3**, probably due to the higher tendency of these molecules to form discrete dimers rather than to be incorporated within the phthalocyanine aggregate.

Conclusions

In conclusion, heteroassociation between electron-rich Zn(II)-hexabutoxyphthalocyanines and electron-deficient Ni(II)hexa-(alkylsulfonyl)phthalocyanines has been observed for the first time. Donor−acceptor interactions have been shown to be the main driving force for the association of bisphthalocyanine **1**, which forms one-dimensional nanoaggregates through intermolecular interactions between its complementary, donor and acceptor, Pc fragments. We believe that this novel recognition motif and the formation of these novel $\pi-\pi$ supramolecular polymers represent a useful tool to control the organization of phthalocyanines into functional supramolecular systems.

Experimental Section

Melting points were determined on a Büchi apparatus and are uncorrected. Infrared spectra were recorded on a Bruker (FT-IR) spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker AC-200 (200 MHz) and AC-300 (300 MHz). UV/vis spectra were recorded on a Perkin-Elmer 8453 spectrophotometer. The mass spectra were determined on a VG AutoSpec spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

Transmission electron microscopy was carried out with a Philips TEM 201 instrument. Small drops of the samples in hot *n*-butanol, at concentrations of approximately 10^{-5}, 10^{-4}, and 10^{-3}, were placed on carbon-coated grids. The material was allowed to adsorb for 1 min, and then the grids were blotted dry by touching the edges with filter paper. Finally, the structures were visualized by TEM.

Bisphthalocyaninato-[2.2]paracyclophane (1). A solution of hexa-(butoxy)phthalocyaninatozinc(II)-[2.2]paracyclophane (**10**) (40 mg, 0.032 mmol), hexa(propylsulfonyl)iodophthalocyanatonickel(II) (**5**)[22] (45 mg, 0.034 mmol), $Et_2{}^iPrN$ (0.1 mL), tetra-*n*-butylammonium bromide (12.6 mg, 0.039 mmol), and $Pd(CH_3CN)_2Cl_2$ (0.5 mg, 0.0030 mmol) in 5 mL of anhydrous DMF was heated at 80 °C for 12 h under argon atmosphere. After the solution cooled to room temperature, the solvent was evaporated and the residue was triturated with methanol, filtered, and finally purified by column chromatography (SiO_2, $CHCl_3$/ethyl acetate/acetone 30:1:1) to afford **1** (27 mg, 34%) as a green solid; mp > 250 °C; IR (KBr) ν = 3442 (ArC−H), 2958, 2920 (CH), 1605 (C═C), 1263 (ArO−C), 1145, 1097, 1046 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) = 298 (4.99), 347 (5.05), 639 (5.02), 679 nm (5.15); MALDI-TOF MS *m*/*z* = 2471 [M$^+$]. Calculated for $C_{126}H_{132}N_{16}S_6O_{18}NiZn$ (2474.96): C, 61.20; H, 5.33; N, 9.05; S, 7.78. Found: C, 61.01; H, 5.29; N, 9.04; S, 7.68.

Hexa(butoxy)phthalocyaninatozinc(II)-[2.2]paracyclophane (2). A solution of hexa(butoxy)iodophthalocyaninatozinc(II) (**4**)[21] (60 mg, 0.053 mmol), 4-vinyl[2.2]-paracyclophane (**11**) (15 mg, 0.064 mmol), K_2CO_3 (37 mg, 0.27 mmol), tetra-*n*-butylammonium bromide (17 mg, 0.053 mmol), LiCl (2 mg, 0.047 mmol), and palladium(II) acetate (1.3 mg, 0.0053 mol) in 3 mL of anhydrous DMF was heated at 100 °C for 8 h. After the reaction mixture cooled to room temperature, the solvent was removed under reduced pressure. CH_2Cl_2 was added, and the organic layer was washed several times with water, dried (Na_2SO_4), filtered, and evaporated. The crude was purified by column chromatography on silica gel with hexane/dioxane (4:1) as eluent. The product was obtained as a green solid: 39 mg (60%); mp >250 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.5 (br s, 2H, arom. Pc), 8.4 (br s, 2H, arom. Pc), 7.8−7.6 (m, 5H, arom. Pc), 7.5 (m, 1H; vinyl), 7.3 (m, 1H, vinyl), 6.9 (m, 1H, arom. pCp), 6.8 (s, 1H, arom. pCp), 6.6 (m, 5H, arom. pCp), 4.3−3.9 (2 × m, 12H, OCH_2), 3.8 (m, 1H, pCp−CH_2), 3.5 (br. s, 1H, pCp−CH_2), 3.2 (m, 6H, pCp−CH_2), 2.1−1.8 (2 × m, 24H, CH_2), 1.2 ppm (m, 18H, CH_3); IR (KBr) ν = 3442 (ArC−H), 2957, 2920, (CH), 1605 (C═C), 1279 (ArO−C), 1097, 1048, 743 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) = 291 (4.68), 355 (4.95), 622 (4.4), 692 nm (5.14); MS (FAB) *m*/*z* = 1240.5 [M + H$^+$], 1137.4 [M − C_8H_7]$^+$. Calculated for $C_{74}H_{80}N_8O_6Zn$ (1242.87): C, 71.45; H, 6.44; N, 9.01. Found: C, 44; H, 6.27; N, 9.11.

Hexa(propylsulfonyl)phthalocyaninatonickel(II)-[2.2]paracyclophane (3). A solution of hexa(propylsulfonyl)iodophthalocyaninatonickel(II) (**5**)[22] (50 mg, 0.037 mmol), 4-vinyl[2.2]paracyclophane (**11**) (9.6 mg, 0.040 mmol), $Et_2{}^iPrN$ (0.1 mL), tetra-*n*-butylammonium bromide (11.2 mg, 0.040 mmol), and $Pd(CH_3CN)_2Cl_2$ (0.6 mg, 0.0035 mmol) in anhydrous DMF (3 mL) was heated at 80 °C for 12 h under an argon atmosphere. The solvent was evaporated, and the solid residue was triturated with methanol, filtered, and purified by column chromatography (SiO_2, $CHCl_3$/Et_2O 30:1) to yield **3** (20 mg, 37%) as a blue solid. Mp >250 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ = 10.1−9.8 (six s, 6H, arom. Pc), 9.0 (m, 2H, arom. Pc), 8.41 (d, *J* = 7.8 Hz, 1H, arom. Pc), 7.61 and 7.33 (AB system, *J* = 15.6 Hz, 2H, vinyl), 6.91 (s, 1H, arom. pCp), 6.77 (d, 1H, arom. pCp), 6.6 (m, 5H, arom. pCp), 4.1 (m, 12H, SO_2CH_2), 3.7 (m,1H, pCp−CH_2), 3.3−3.0 (m, 7H, pCp−CH_2), 2.2 (m, 12H, CH_2), 1.2 ppm (m, 18H, CH_3); IR (KBr) $\bar{\nu}$ = 3452 (ArC−H), 2967, 2933 (CH), 1604 (C═C), 1295, 1145, 1086 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) = 267 (4.63), 300 (4.66), 347 (4.79), 615 (4.37), 677 (4.96), 705 nm (4.81); MS (FAB) *m*/*z* = 1439 [M + H$^+$]. Calculated for $C_{68}H_{68}N_8S_6O_{12}Ni$ (1440.38): C, 56.65; H, 4.72; N, 7.78; S, 13.37. Found: C, 56.59; H, 4.44; N, 7.83; S 13.31.

4,12-Divinyl[2.2]paracyclophane (9). A mixture of 4,12-dibromo-[2.2]-paracyclophane[26] (80 mg, 0.22 mmol) and $[Pd(PPh_3)_4]$ (24 mg, 0.021 mmol) in toluene (20 mL) was stirred under argon. Then tributyl-(vinyl)tin (0.27 mL, 0.88 mmol) was added. The reaction mixture was heated at 100 °C for 48 h. After removal of the solvent, CH_2Cl_2 was added and the organic layer was washed with water, dried (Na_2SO_4), and filtered. The solvent was removed in vacuo, and the residue was purified by column chromatography using hexane/ether 150:1 as eluent. Compound **9** was obtained as a white solid (43 mg, 75%). Mp 164 °C; ^{1}H and ^{13}C NMR ($CDCl_3$) are in agreement with those reported in ref 36; IR (KBr) $\bar{\nu}$ = 3092−3010, 2934−2851, 1622, 1588, 980, 770 cm^{-1}; MS *m*/*z* (%) = 260 (30) [M$^+$], 131 (55), 130 (61), 129 (100), 128 (37), 115 (60). Calculated for $C_{20}H_{20}$ (260.16): C, 92.25; H, 7.75. Found: C, 92.07; H, 7.68.

Hexa(butoxy)phthalocyaninatozinc(II)-vinyl[2.2]paracyclophane (10). A solution of hexa(butoxy)iodophthalocyaninatozinc(II) (**4**)[21] (52 mg, 0.045 mmol), 4,12-divinyl[2.2]paracyclophane (**9**) (11.9 mg, 0.045 mmol), K_2CO_3 (32 mg, 0.23 mmol), tetra-*n*-butylammonium bromide (14.4 mg, 0.045 mmol), LiCl (2 mg, 0.047 mmol), and palladium(II) acetate (1.1 mg, 0.0045 mmol) in 4 mL of anhydrous DMF was heated at 100 °C for 8 h. After the reaction mixture cooled to room temperature, the solvent was removed under reduced pressure. CH_2Cl_2 was added, and the organic layer was washed several times with water, dried (Na_2SO_4), filtered, and evaporated. The crude was purified by chromatography on silica gel with hexane/dioxane (4:1) as eluent. The product was obtained as a green solid: 20 mg (56%); mp > 250 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS) δ 8.5 = (br. s, 2H, arom. Pc), 8.3 (br. s, 2H, arom. Pc), 7.8−7.7 (m, 5H, arom. Pc), 7.50 (d, *J* = 15.8 Hz, 1H, vinyl), 7.19 (d, *J* = 15.8 Hz, 1H, vinyl), 6.98 (s, 1H, arom. pCp), 6.94 (dd, *J* = 17.4, 10.9 Hz, 1H, vinyl H_{gem}), 6.8 (m, 3H, arom. pCp), 6.68 (s, 1H, arom. pCp), 6.50 (dd, *J* = 7.3, 4.9 Hz, 1H, arom. pCp), 5.64 (d, *J* = 17.4 Hz, 1H, vinyl H_{trans}), 5.39 (d, *J* = 10.9 Hz, 1H, vinyl H_{cis}), 4.2−3.9 (2 × m, 12 H, OCH_2), 3.8 (m, 1H, pCp−CH_2), 3.6 (m, 1H, pCp−CH_2), 3.1 (m, 6H, pCp−CH_2), 2.0−1.7 (2 × m, 24H, CH_2), 1.2 ppm (m, 18H, CH_3); IR (KBr) $\bar{\nu}$ = 3442 (ArC−H), 2957, 2920, (CH), 1605 (C═C), 1279 (ArO−C), 1097, 1048, 743 cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ϵ) = 276 (4.79), 356 (4.92),

(36) Alay, A. A.; Hopf, H.; Ernst, L. *Eur. J. Org. Chem.* **2000**, 3021.

620 (4.26), 692 nm (4.94); MS (FAB) $m/z = 1266.6$ [M^+], 1136.3 [$M - C_{10}H_{10}]^+$. Calculated for $C_{76}H_{82}N_8O_6Zn$ (1268.52): C, 71.89; H, 6.46; N, 8.83. Found: C, 71.88; H, 6.44; N, 8.62.

4-Vinyl[2.2]paracyclophane (11). To a stirred solution of 4-bromo-[2.2]-paracyclophane[37] (100 mg, 0.35 mmol) and [$Pd(PPh_3)_4$] (18 mg, 0.018 mmol) in toluene (20 mL), tributyl(vinyl)tin (0.20 mL, 1.05 mmol) was added. The mixture was heated at 100 °C for 24 h. After removal of the solvent under reduced pressure, dichloromethane was added and the solution was washed with water and dried (Na_2SO_4); the solvent was evaporated. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 1:1) to give **11** (71 mg, 87%) as a white solid. Mp 70 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS) $\delta = 6.81$ (dd, $J = 17.8$, 11.3 Hz, 1H, vinyl H_{gem}), 6.73 (d, $J = 7.7$ Hz, 1H, arom.), 6.6−6.4 (m, 6H, arom. H), 5.55 (d, $J = 17.8$ Hz, 1H, vinyl H_{trans}), 5.29 (d, $J = 11.3$ Hz, 1H, vinyl H_{cis}), 3.5 (m, 1H, pCp−CH_2), 3.2−2.8 ppm (m, 7H, pCp−CH_2); ^{13}C NMR ($CDCl_3$, 300 MHz, 25 °C, TMS) $\delta = 139.3$, 137.2, 135.1, 134.7, 133, 131.9, 131.8, 130.1, 129.5, 114.2, 35.4, 35.2, 34.6, 33.6 ppm; IR (KBr) $\bar{\nu} = 3090-3009$, 2927−2851, 1621, 1590, 989, 906 cm^{-1}; MS (EI) m/z (%) = 234.1 (24) [M^+], 129.1 (100) [$M - C_8H_8]^+$, 105.1 (34) [$C_8H_8]^+$. Calculated for $C_{18}H_{18}$ (234.34): C, 92.17; H, 7.68. Found: C, 92.01; H, 7.59.

^{1}H NMR Dilution Studies of Phthalocyanines 2 and 3. Stock chloroform solutions of compounds **2** and **3** (1.11 mM and 2.64 mM, respectively) were prepared in volumetric flasks (2 mL). For each compound, an aliquot of the stock solution (1 mL) was transferred to a dry vial using a syringe and diluted with chloroform (1 mL). This solution was then used as the stock in the preparation of a third dilution. This procedure was repeated to give a total of five different concentrations. An aliquot of each concentration (0.5 mL) was then transferred to a dry NMR sample tube. The NMR spectra were referenced to TMS, and the aromatic signals were recorded as a function of the concentration ($T = 298$ K). The dilution data were analyzed using a custom written global[29] nonlinear regression analysis program within the Matlab 5.3[30] package (see also Supporting Information).

UV/vis Titration of Donor and Acceptor Phthalocyanines (2 and 3). A stock 1.5 μM solution of compound **2** was prepared in chloroform and then used as solvent for the preparation of a stock 69.5 μM solution of **3**. This procedure ensures a constant concentration of **2** throughout the titration. The titration was performed by adding the required volumes of the solution of the acceptor phthalocyanine **3** to 2 mL of the donor phthalocyanine **2** solution. The Q-band absorptions were monitored as a function of the concentration of **3**, and the data were analyzed by a custom written global[29] nonlinear regression analysis program within the Matlab 5.3[30] package (see also Supporting Information).

UV/vis Dilution Studies of Bisphthalocyanine 1. Stock solutions of compound **1** in different solvents (chloroform, DMF, and toluene) were prepared in a volumetric flask (2 mL). More diluted solutions were prepared in 2 mL volumetric flasks by diluting the required amounts of the stocks. This procedure was repeated for the three different solvents giving in each case a total of eight concentrations. The Q-band absorptions were monitored as a function of the concentration of **1**, and the data were analyzed a custom written global[29] nonlinear regression analysis program within the Matlab 5.3[30] package (see also Supporting Information).

Supporting Information Available: Details on calculations of binding constants, ^{1}H NMR spectra of compounds **1**, **2**, and **3**, figures showing the temperature dependence of association for compound **1**, and the UV−vis spectrum of bisphthalocyanine **1** obtained upon subtracting the absorption spectra of the reference molecules **2** and **3** showing both the aggregation and CT bands. This material is available free of charge via the Internet at http://pubs.acs.org.

JA030038M

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