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One-Pot Synthesis of Cyanuric Acid-Bridged Porphyrin−Porphyrin Dyads

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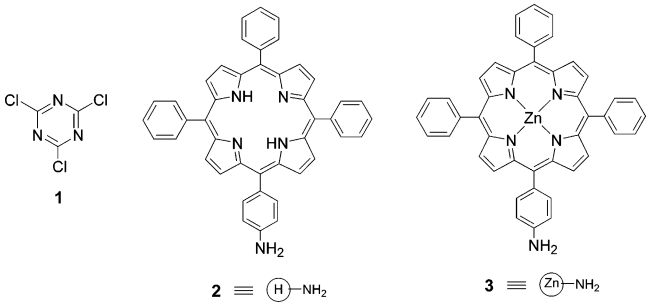
Abstract: Stepwise amination of cyanuric chloride (**1**) with 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**2**) and/or its zinc(II) complex (**3**) enables the synthesis of porphyrin−porphyrin dyads with predetermined free base−free base forms or free base−zinc and zinc−zinc metalation states. Furthermore, the use of aminopropyl-silanized silica gel as a scavenger for unwanted byproducts allowed the one-pot synthesis of title porphyrin compounds in high yield and purity with minimum use of preparative column chromatography.

Considerable effort has been devoted to the preparation of various types of covalently linked arrays of porphyrins and metalloporphyrins. The aim of the research is to utilize these compounds to elucidate or model the essential features of natural photosynthetic systems,[1] to mimic selectivity and reactivity performances of enzymes,[2] and to realize molecular-based material for optoelectronics,[3] photovoltaic energy conversion,[4] catalysis,[5] and optical sensing.[6]

In the past few years, there has been remarkable progress in the synthesis of multiporphyrin oligomers.[7] Nevertheless, gaining access to the compounds needed for the above applications in significant quantities often entails tremendous preparative efforts and reiterate purification steps. Thus, the development of new synthetic methodologies and/or the improvement of existing reactions in order to obtain target porphyrins in high yield and purity with minimal recourse to separation techniques still represents a challenging issue.

SCHEME 1. Building Blocks for the Synthesis of Porphyrin−Porphyrin Dyads



We describe here a modular approach for synthesizing porphyrin−porphyrin dyads that relies on the use of two essential building blocks: cyanuric chloride **1**, which provides the scaffold, and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin, used either as free base **2** or as zinc complex **3** (Scheme 1).[8]

Cyanuric chloride has been used as a template for the solution-phase synthesis of dendrimers,[9] macrocycles,[10] and combinatorial libraries,[11] taking advantage of the temperature-dependent stepwise substitution of its three chlorine atoms by different nucleophiles. Furthermore, near quantitative yields are routine for these reactions, which should also allow for a one-pot protocol. On the other hand, 5-(4-aminophenyl)-10,15,20-triphenylporphyrin **2** can be conveniently prepared on a multigram scale, as reported by Kruper,[12] making it a convenient building block for testing the feasibility of this project.

Initially, we devoted our attention to the reaction between cyanuric chloride and porphyrin **2** with the aim of preparing a derivative containing only one porphyrin group. The reaction of **2** with 1 equiv of cyanuric chloride (Scheme 2, i) in THF at 0 °C in the presence of 1.2 equiv of diisopropylethylamine (DIPEA) proceeded in several minutes, as witnessed by TLC analysis, which showed the complete disappearance of **2** and the formation of the monoadduct derivative, **4**.

Compound **4** was rather reactive and was neither isolated nor characterized; instead, it was further reacted with an excess of piperidine at 80 °C in the presence of DIPEA for 24 h (Scheme 2, ii) to give compound **5**. Aqueous workup and preparative column chromatography gave **5** in almost quantitative yield, as confirmed by ^{1}H NMR spectroscopy and UV−vis spectrometry. In fact, the ^{1}H NMR resonance signals for the protons adjacent to the amino group of piperidine moved from 2.78 to 3.85 ppm upon attachment to the triazine ring. An analogous downfield displacement was observed for the aromatic protons

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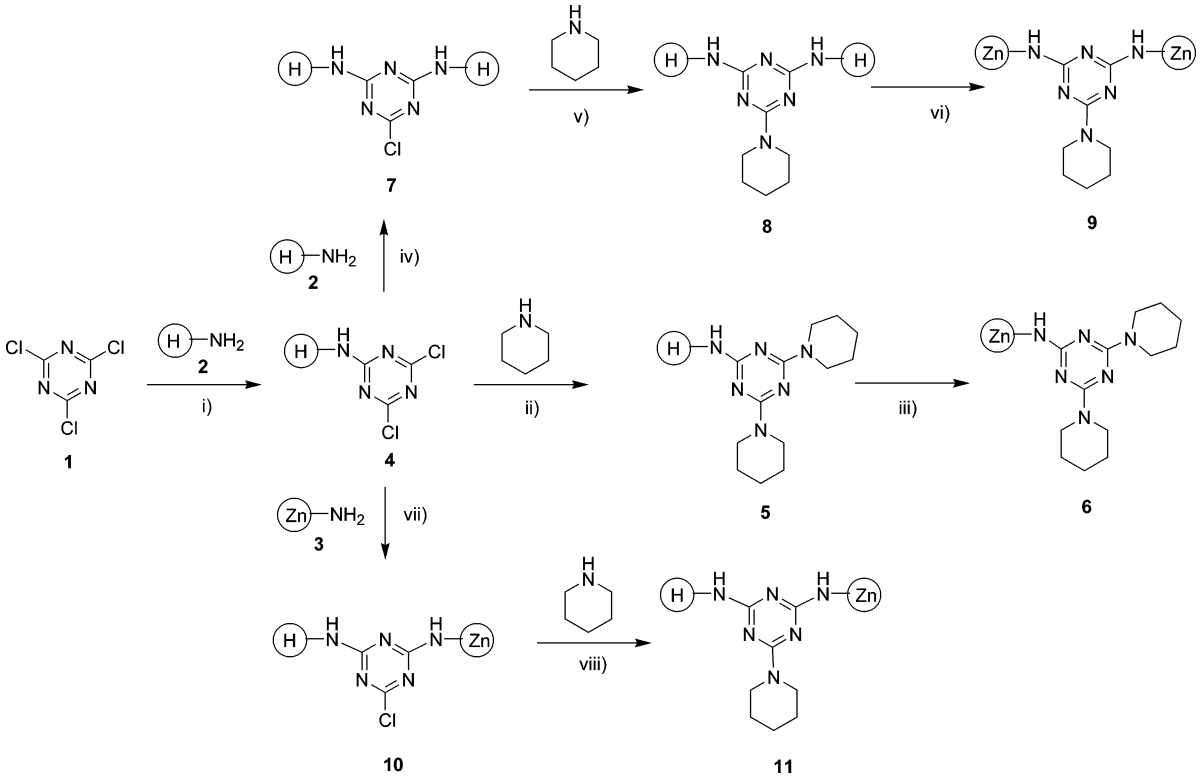
SCHEME 2. Synthesis of Porphyrin Monoadducts and Porphyrin–Porphyrin Dyads[a]



[a] Conditions: (i) THF, DIPEA, 0 °C; (ii) THF, excess piperidine, 80 °C; (iii) MeOH/$CHCl_3$ 1:1 (v/v), $Zn(Ac)_2$, 30 min, refluxing; (iv) *p*-aminoporphyrin **2**, THF, DIPEA, 25 °C; (v) THF, excess piperidine, DIPEA, 80 °C; (vi) MeOH/$CHCl_3$ 1:1 (v/v), $Zn(Ac)_2$, 30 min, refluxing; (vii) *p*-aminoporphyrin–Zn(II) (**3**), THF, DIPEA, 25 °C; (viii) excess piperidine, THF, DIPEA, 80 °C.

ortho to the amino group of **2**. The UV–vis spectrum in CH_2Cl_2 shows the Soret band at 419 nm and four Q-bands at 515, 552, 592, and 647 nm.

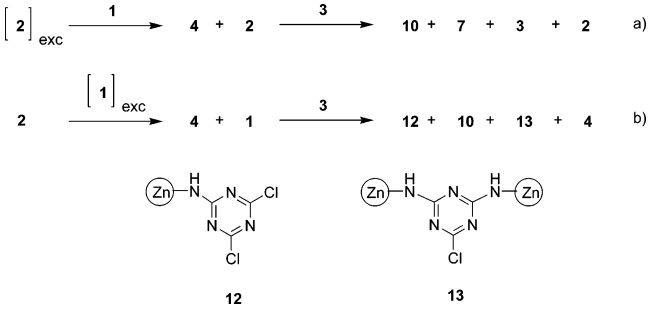
Compound **5** could be quantitatively converted into zinc complex **6** (Scheme 2, iii) by refluxing **5** with an excess of zinc acetate in methanol/chloroform for 30 min. The most relevant change in the ^{1}H NMR spectrum of **6**, with respect to that of **5**, is the expected disappearance of the pyrrolic proton signals at −2.75 ppm. Furthermore, the UV–vis spectrum in CH_2Cl_2 shows the Soret band at 420 nm and two Q-bands at 548 and 552 nm, which are characteristic for the zinc complex of porphyrin.

For the synthesis of the porphyrin–porphyrin dyad in free base–free base form (**7**), monoadduct **4** was reacted for 48 h at room temperature with a second equivalent of porphyrin **2** in the presence of 1.2 equiv of DIPEA (Scheme 2, iv). Monitoring the reaction by TLC analysis indicated the progressive disappearance of reactants **2** and **4** and the formation of the target dyad, **7**. Compound **7** was not isolated but was converted into **8** (76% yield) by using an excess of piperidine for 3 h at 80 °C in the presence of DIPEA (Scheme 2, v).

The structure of **8** was confirmed by ^{1}H NMR analysis, which clearly revealed a 2:1 ratio of porphyrin/piperidine. Using the same procedure as for **6**, compound **8** was quantitatively converted into the corresponding dyad **9** (Scheme 2, vi), possessing a zinc–zinc metalation state.

The reaction of **7** with porphyrin **2**, with the goal of obtaining a porphyrin triad, was not successful. Most likely, this is due to the low nucleophilicity of the amino group of **2**.

SCHEME 3. Expected Byproducts for Unsymmetrical Porphyrin–Porphyrin Dyads



Unsymmetrical dyads, possessing two different metal ions or a free base porphyrin and a metalated one, are the most challenging targets of our synthetic study. First, they are more complicated to synthesize with respect to the corresponding symmetrical dyads, and second, they are able to mimic the intramolecular energy transfer and charge separation systems involved in photosynthesis. To verify the potential of our approach, we tried to synthesize **11**, a dyad made of a free base and a zinc–porphyrin.

As described before, free base monoadduct **4** was prepared (Scheme 2, i), and zinc–porphyrin **3** was added to the reaction mixture at room temperature (Scheme 2, vii) to give dyad **10**. It turned out that **10** was too reactive to be isolated using chromatography on silica gel. Therefore, **10** was directly converted into **11** using piperidine.

To our disappointment, although compound **11** was the most abundant species in the reaction mixture, small amounts of other porphyrin derivatives (unreacted por-

phyrin or unwanted monoadducts or symmetrical dyads) were consistently present, and the chromatographic separation of **11** was rather laborious. These results, which represent a serious drawback for the one-pot approach, prompted us to look for a more careful choice of experimental conditions.

Scheme 3 depicts the distribution of products expected after addition of the second amine if an excess of porphyrin **2** (path a)[13] or cyanuric chloride **1** (path b)[14] was used in the first step.

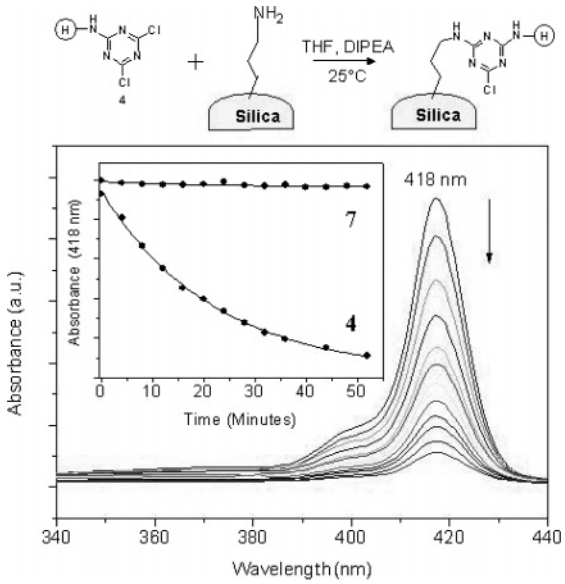
Both pathways result in a complicated mixture of products impossible to separate after the reaction with piperidine. We reasoned that this problem could be resolved by using a supported scavenger capable of removing the remaining excess reagents or byproducts from the reaction. We decided to use commercially available aminopropyl-silanized silica gel, which possesses 0.9 ± 0.1 mmol[15] of amino groups per gram of material, which could serve as a scavenger for cyanuric chloride.

However, since compound **4** could also potentially react with amino-silica, we carried out a preliminary experiment to estimate the extent of such a reaction. An excess of amino-silica was added to a cuvette containing a solution of **4** (0.01 mM) in THF in the presence of an equivalent amount of DIPEA at room temperature. The suspension was then stirred vigorously for 1 min, and after 2 min, when the silica settled down, the UV−vis spectrum was recorded. This was repeated until the Soret band of **4** had virtually disappeared. The obtained results are reported in Scheme 4 (the inset shows the decrease of the absorbance at 418 nm versus time for monomer **4**).

These results indicate that it is possible to scavenge selectively cyanuric chloride from a solution containing monomer **4** using aminopropyl-silanized silica gel. Interestingly, the inset also reports the data from an analogous experiment performed with dyad **7** (4 μM) showing that it is not reactive, at least at room temperature, with amino-silica. Therefore, it is also possible to scavenge monoadducts from a solution of porphyrin dyads. This reactivity also suggests the use of **4**, and eventually of **7** (at higher temperature), for the preparation of porphyrin monolayers or thin films on surfaces or nanoparticles.[16]

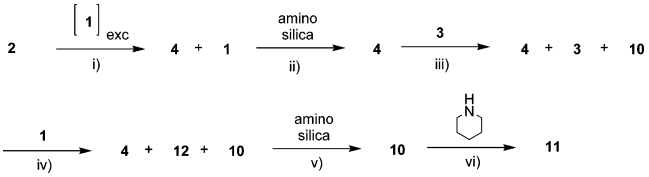
After these positive tests, we carried out the synthesis of unsymmetrical dyad **11** according to the following protocol (Scheme 5). The first step was carried out in the presence of an excess of cyanuric chloride **1** in order to form quantitatively **4** from **2** (Scheme 5, i). A sufficient amount of amino-silica and DIPEA was then added to scavenge the unreacted **1**, and the reaction mixture was filtered (Scheme 5, ii). Scavenging and filtration were conveniently performed at 0 °C in order to minimize the reaction of monomer **4** with amino-silica. Subsequently, zinc−porphyrin **3** was added to the reaction mixture (Scheme 5, iii), and the reaction was monitored by TLC. A typical TLC result after a 24 h reaction is reported in Scheme 6 (lane a), showing that the unsymmetrical dyad was the main product, but some unreacted zinc−porphy-

SCHEME 4. Quenching of 4 and 7 with Amino-Silica[a]



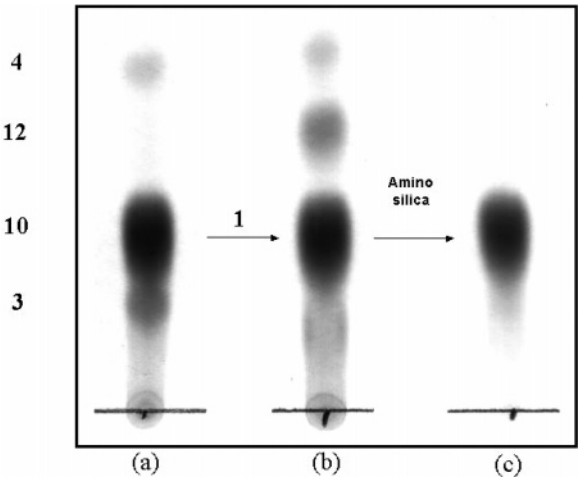
[a] Reactions of **4** (0.01 mM) and **7** (4 μM) in THF in the presence of DIPEA (1 equiv) with amino-silica (10 mg). The mixture was stirred for 1 min and settled in 2 min.

SCHEME 5. One-Pot Synthesis of Compound 11[a]



[a] Conditions: (i) THF, DIPEA, 0 °C; (ii) THF, DIPEA, amino-silica, 0 °C; (iii) zinc−aminoporphyrin (**3**), THF, DIPEA, 25 °C; (iv) THF, DIPEA, 25 °C; (v) THF, DIPEA, amino-silica, 25 °C; (vi) excess piperidine, THF, DIPEA, 80 °C.

SCHEME 6. TLC of Scavenging of Heterodimer 10 Undesired Byproducts with Amino-Silica



(13) If an excess of **2** is present after the first step, it will compete in the second step with zinc−porphyrin **3** in the reaction with monomer **4**, resulting in the formation of some homodimer **7**. Consequently, corresponding amounts of **2** and **3** will be left unreacted.

(14) If cyanuric chloride **1** is in excess with respect to porphyrin **2**, it will quickly react with zinc−porphyrin **3** at the second step, producing the corresponding monomer **12**. Then **3** can react not only with **4** to produce the desired heterodimer **10** but also with **12** to give zinc homodimer **13**. Furthermore, a corresponding amount of **4** will be left unreacted.

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rin **3** and some porphryin **4** were still present. Extended reaction times did not improve the yield significantly.

Since zinc−porphyrin **3** itself is not reactive with amino-silica gel, a sufficient amount of cyanuric chloride was added in order to form quantitatively the corresponding monomer **12** (Scheme 5, iv), as shown by TLC analysis (Scheme 6, lane b). The reaction mixture was then treated with amino-silica (Scheme 5, v), which reacts only with cyanuric chloride and porphyrins **4** and **12**, leaving a solution of pure **10** (Scheme 6, lane c).

Finally, the reaction with an excess of piperidine (Scheme 5, vi) gave the unsymmetrical dyad **11**, which can be eventually purified by preparative chromatography. The structure of compound **11** was confirmed by ^{1}H NMR and UV−vis spectroscopy.

In conclusion, we have demonstrated that cyanuric chloride can be conveniently used as a scaffold for the modular assembly of porphyrin−porphyrin dyads in free base−free base, free base−zinc, and zinc−zinc metalation states. Taking advantage of the stepwise reactivity of cyanuric chloride and of amino-silica as a scavenger for cyanuric chloride and porphyrin monoadducts, we have been able to synthesize the unsymmetrical dyad **11**, using a one-pot procedure, in a pure form without the use of chromatographic separations.

Current work is focused on studying the photophysical and recognition properties of the reported compounds and on the preparation of more-elaborate structures. These results will be reported in due course.

Experimental Section

Materials and Instrumentation. All reagents were the best available purity and used without further purification. Porphyrin **2** was prepared according to the literature procedure.[12] ^{1}H NMR spectra were recorded with a spectrometer operating at 250 MHz. UV−vis spectra were recorded on a spectrophotometer equipped with a thermostated cell holder.

General Procedures. Compound 5. A solution of porphyrin **2** (25 mg, 40 μmol) in THF (1.0 mL) was added to a THF (1.0 mL) solution of cyanuric chloride **1** (7.3 mg, 40 μmol) and DIPEA (6.2 mg, 48 μmol) cooled at 0 °C. After the mixture was stirred for 10 min, the solution was left to reach room temperature. After 15 min, the reaction was complete, as witnessed by TLC analysis (silica gel, 2:1 (v/v) petroleum ether/ethyl acetate), showing the disappearance of porphyrin **2** (R_f = 0.33) and the formation of derivative **4** (R_f = 0.7). Product **4** was not isolated, but it was reacted further with an excess of piperidine (8.1 mg, 0.1 mmol) in the presence of DIPEA (6.2 mg, 48 μmol) and stirred at 80 °C for 24 h. After removal of the solvent, the residue was partitioned between $CHCl_3$ (15 mL) and water (20 mL × 4). The organic phase was dried on $MgSO_4$ and evaporated, producing a dark-red solid which was purified by column chromatography on silica gel (eluent, 3:2 (v/v) hexanes/diethyl ether). A dark-red solid was obtained (33 mg, 93% yield): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.95 (d, 2H), 8.86 (m, 6H), 8.23−7.74 (m, 19H), 7.07 (s, broad, 1H), 3.85 (s, 8H), 1.68 (s, 12H), −2.75 (s, 2H); UV−vis (CH_2Cl_2, nm) λ 419 (Soret band, ϵ = 220 400 M^{-1} cm^{-1}), 515 (ϵ = 9300 M^{-1} cm^{-1}), 552 (ϵ = 5300 M^{-1} cm^{-1}), 592 (ϵ = 3000 M^{-1} cm^{-1}), 647 (ϵ = 2800 M^{-1} cm^{-1}).

Compound 6. To a solution of **5** (6.4 mg, 7.3 μmol) in $CHCl_3$ (5 mL) was added a saturated solution of zinc acetate (0.5 mL) in CH_3OH, and the mixture was refluxed for 1 h. The solvent was evaporated, and the residue was purified by a short column chromatography on silica gel in order to remove zinc acetate excess (eluent, chloroform). Product **6** (TLC eluent, 99:5 (v/v) CH_2Cl_2/CH_3OH, R_f = 0.74) was obtained in 95% yield: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 9.08 (d, 2H), 8.99 (m, 6H), 8.24−7.74 (m, 19H), 7.07 (s, broad, 1H), 3.84 (s, 8H), 1.67 (s, 12H); UV−vis (CH_2Cl_2, nm) λ 420 (Soret band, ϵ = 337 000 M^{-1} cm^{-1}), 548 (ϵ = 14 000 M^{-1} cm^{-1}), 552 (ϵ = 2400 M^{-1} cm^{-1}).

Compound 8. To a solution of porphyrin **2** (25 mg, 40 μmol) in THF (1.5 mL) cooled at 0 °C were added cyanuric chloride **1** (7.3 mg, 40 μmol) and DIPEA (6.2 mg, 48 μmol). After the mixture was stirred for 15 min, the solution was left to reach room temperature. After 15 min, monomer **2** was no longer present. More porphyrin **2** (25 mg, 40 μmol) was then added with 1.2 equiv of DIPEA, and the reaction was monitored by TLC (eluent, 2:1 (v/v) petroleum ether/ethyl acetate, compound **7**, R_f = 0.57). After 24 h, an excess of piperidine (8.6 mg, 0.1 mmol) was added with 1.2 equiv of DIPEA, and the mixture was stirred at 80 °C. A purple solid formed. After 3 h, the solvent was evaporated, and the solid was subjected to column chromatography on silica gel (eluent, 2:1 (v/v) petroleum ether/ethyl acetate). Compound **8** was recovered from the fraction giving a single spot in the TLC with R_f = 0.48 (same eluent as that of the column chromatography): yield 76%; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.98 (d, 4H), 8.96 (m, 12H), 8.23−7.68 (m, 38H), 7.07 (s, broad, 2H), 3.99 (s, 4H), 1.75 (s, 6H), −2.75 (s, 4H); UV−vis (CH_2Cl_2, nm) λ 420 (Soret band, ϵ = 524 000 M^{-1} cm^{-1}), 516 (ϵ = 38 200 M^{-1} cm^{-1}), 552 (ϵ = 28 000 M^{-1} cm^{-1}), 591 (ϵ = 21 000 M^{-1} cm^{-1}), 647 (ϵ = 20 100 M^{-1} cm^{-1}).

Compound 9. Compound **9** was obtained from compound **8** by reaction with an excess of zinc acetate in $CHCl_3$, following the procedure described for compound **6**: yield 92%; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 9.01 (d, 4H), 8.91 (m, 12H), 8.20−7.71 (m, 38H), 7.07 (s, broad, 2H), 3.98 (s, 4H), 1.71 (s, 6H); UV−vis (CH_2Cl_2, nm) λ 421 (Soret band, ϵ = 551 000 M^{-1} cm^{-1}), 588 (ϵ = 52 900 M^{-1} cm^{-1}), 548 (ϵ = 71 800 M^{-1} cm^{-1}), 507 (ϵ = 54 000 M^{-1} cm^{-1}).

Compound 11. A solution of porphyrin **2** (14 mg, 22 μmol) in THF (1.5 mL) was added to a THF (1.0 mL) solution of cyanuric chloride **1** (4.9 mg, 26 μmol) and DIPEA (3.4 mg, 26 μmol) cooled at 0 °C. After the mixture was stirred for 15 min, the solution was left to reach room temperature. After 15 min, the reaction was complete, as determined by TLC analysis (silica gel, 2:1 (v/v) petroleum ether/ethyl acetate), showing the disappearance of porphyrin **2** (R_f = 0.33) and the formation of derivative **4** (R_f = 0.7). To scavenge the excess of cyanuric chloride, amino-silica (70 mg) was added, the was suspension stirred at 0 °C for 5 min, and then it was rapidly filtered. To the resulting solution, which contains only monomer **4**, was added a THF (1.5 mL) solution of zinc−porphyrin **3** (15.3 mg, 22 μmol) and 1.2 equiv of DIPEA, and the mixture was stirred at room temperature for 48 h. TLC analysis showed the presence of heterodimer **10** as the main product with small amounts of zinc−porphyrin **3** and monomer **4**. Thus, 0.1 equiv of cyanuric chloride and DIPEA was added to the reaction mixture in order to form the corresponding zinc−porphyrin monomer **12** from unreacted **3**. Then amino-silica (100 mg) was added in order to scavenge monomers **4** and **12**, the heterodimer **10** not being reactive under these conditions. After 1.5 h, the silica was filtered off, and the solution was reacted further with an excess of piperidine (8.1 mg, 0.1 mmol) in the presence of DIPEA (6.2 mg, 48 μmol) and stirred at 80 °C for 12 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (eluent, 1:2 (v/v) ethyl acetate/petroleum ether). A dark-red solid was obtained (19 mg, 58% yield): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.97−8.83 (m, 16H), 8.28−7.76 (m, 38H), 7.07 (s, broad, 2H), 4.02 (s, 4H), 1.81 (s, 6H), −2.74 (s, 2H); UV−vis (CH_2Cl_2, nm) λ 420 (Soret band, ϵ = 925 000 M^{-1} cm^{-1}), 515 (ϵ = 99 500 M^{-1} cm^{-1}), 550 (ϵ = 109 000 M^{-1} cm^{-1}), 589 (ϵ = 86 000 M^{-1} cm^{-1}).

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Supporting Information Available: Figures S1−5 of ^{1}H NMR data for compounds **5**, **6**, **8**, **9**, and **11** and HPLC traces for compounds **8**, **9**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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