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Synthesis of Stannyl Porphyrins and Porphyrin Dimers via Stille Coupling and Their ^{119}Sn NMR and Fluorescence Properties

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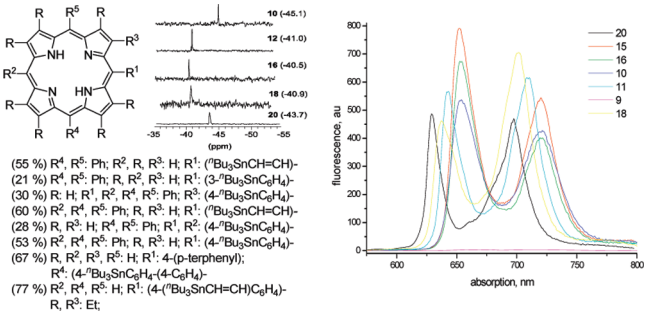

Free base stannyl porphyrins and free base porphyrin dimers have been successfully synthesized via copper-free Stille coupling in 21−67% yields. This approach provides an access to stannyl porphyrin synthons that were previously unavailable. Moreover, variation of the reaction conditions selectively provides access to either stannyl porphyrins or porphyrin dimers. Full $^{119/117}$Sn NMR analysis was used for characterization of the stannyl porphyrins and detailed ^{119}Sn-^{1}H-^{13}C NMR analyses were carried out on a series of the starting tin reagents and the stannyl porphyrins. These investigations indicate that significant structural information can be gathered by use of commonly known NMR techniques. Photophysical properties of the novel porphyrins prepared including absorption, emission, and fluorescence lifetimes were investigated. The stannyl porphyrins emitted in the visible region, and in all cases large Stokes shifts were observed. The emission intensities of the stannyl porphyrins were 100-fold higher than those of the starting bromoporphyrins. Measured fluorescence lifetime ($S_0 \rightarrow S_1$) of the stannyl and dimeric porphyrins were in the 7.7−12 ns region.

Introduction

Metal-catalyzed coupling reactions are an attractive synthetic tool for C−C bond formation and are used for modification of various organic molecules, especially heterocycles. Organotin compounds have found wide agricultural and industrial applications.[1] Recent studies have shown their potential use as antifungal agents and their relatively high in vitro antitumor activity. Stille coupling represents a simple approach to the synthesis of novel materials, including tin reagents and coupling products.[2] Tin compounds can be easily prepared starting from the corresponding bromides and can then be used for C−C bond formation in the presence of a catalyst.[3] Moreover, the precursors are commercially available, and the tin reagents are cheap to make

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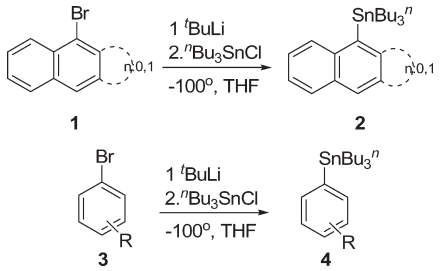
compared to the related boronates widely utilized for Suzuki coupling.[4] In addition, tin has three NMR active nuclei (spin 1/2) with relatively high natural isotope abundance of ^{115}Sn (0.34%), ^{117}Sn (7.68%), and ^{119}Sn (8.59%); they give a narrow signal over a wide NMR scale. Every type of tin compound has its characteristic chemical shift range, and these unique isotope properties can be used to study the organotin compounds.[5]

Porphyrins are naturally occurring pigments with a variety of applications in emerging areas of modern science: optoelectronics and nanotechnology as sensors and storage devices, as photocatalysts in green chemistry, and as photodynamic therapy agents for cancer treatments in medicine, to name a few.[6−8] These and many other possible applications require the development of new and more efficient methods to modify the porphyrin core to yield macrocycles with novel and improved physicochemical properties. The Stille reaction has been used in porphyrin chemistry to introduce some functional groups into the macrocycle.[9] However, the literature only reports examples associated with C−C bond formations starting from porphyrin bromides and the non-porphyrin tin counterparts.

SCHEME 1. Preparation of Mono- and Bis-tin Reagents 2 and 4



The synthesis of porphyrin dimers is often performed via metal catalyzed reactions, e.g., Suzuki or Sonogashira coupling.[10] Only a few examples have been reported so far for the synthesis of porphyrin dimers[11] and functional polymers[12] using a Stille approach. Moreover, to protect the porphyrin core from undesired metalation by copper (from CuI often used as a co-catalyst to increase the reaction rate[2b,c] or to improve the solubility of the starting porphyrins) the synthesis generally requires prior porphyrin metalation, preferably with zinc, that later has to be removed from a coupling product if necessary.

At present, there is no universal procedure for Stille coupling reactions of porphyrins in terms of the reaction conditions. Reported protocols employ a variety of solvents, catalysts, and additives for the reactions.[1c]Here we present results aimed at the development of a novel synthetic approach for the synthesis of free base stannyl porphyrins that can be used as coupling partners in Stille reactions. Depending on the reaction conditions either stannyl or dimeric porphyrins can be prepared and their physicochemical properties investigated.

Results and Discussion

1. Synthesis of Stannyl Porphyrins and Porphyrin Dimers. The mono- and bis-tin aromatic compounds **2** and **4** can be conveniently synthesized on a large scale via organolithium reactions starting from commercially available mono- or dibromoarenes **1** and **3** and tri(*n*-butyl)tin chloride (Scheme 1).

Generally, the reactions were carried out with an excess of *t*BuLi (2.5 equiv for mono and 4 equiv for dibromides) at −90 to −100 °C followed by addition of tri(*n*-butyl)tin chloride at −50 °C. The reaction of 1-bromonaphthalene gave the tin compound **2a** in 94% yield. 9-Bromoanthracene reacted in a similar manner to give the compound **2b** in 75% yield. However, attempts to synthesized the 9,10-bis-tin anthracene starting from the corresponding dibromide resulted in the formation of anthracene in 71%. Nevertheless, the 1,4- and 1,3-bis-tin substituted compounds **4a** and **4b** were prepared in 54% and 63% yield, respectively.

The porphyrin bromides **6**−**9** are thermally stable and easily accessible molecules.[4] They readily reacted with the corresponding tin reagents **2**, **4**, and **5** forming the stannyl porphyrins **10**−**16** in up to 60% yield. Moreover, the porphyrin free bases can be used under these reaction conditions and no palladium insertion was observed during these

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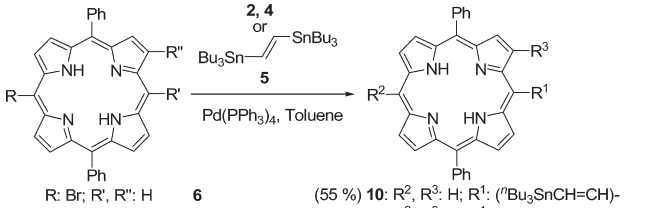
SCHEME 2. Synthesis of Stannyl Porphyrins 10−16



R: Br; R', R": H **6**
R, R': Ph; R": Br **7**
R: Br; R': Ph; R": H **8**
R, R': Br; R": H **9**

(55 %) **10**: R^2, R^3: H; R^1: (^{n}Bu$_3$SnCH=CH)-
(21 %) **11**: R^2, R^3: H; R^1: (3-^{n}Bu$_3$SnC$_6$H$_4$)-
(30 %) **12**: R^1, R^2: Ph; R^3: (4-^{n}Bu$_3$SnC$_6$H$_4$)-
(60 %) **13**: R^2: Ph; R^3: H; R^1: (^{n}Bu$_3$SnCH=CH)-
(50 %) **14**: R^3: H; R^1, R^2: (1-naphthalenyl)-
(28 %) **15**: R^3: H; R^1, R^2: (4-^{n}Bu$_3$SnC$_6$H$_4$)-
(53 %) **16**: R^2: Ph; R^3: H; R^1: (4-^{n}Bu$_3$SnC$_6$H$_4$)-

transformations for the whole series. The reactions exclusively gave tin products, when 2 (for monosubstitution) or 4 (for bisproducts) equiv of the tin compounds was used. No dimer formation was detected. Generally, these reactions proceeded under formation of the desired products only, and in the case of lower yields the starting materials were recovered. Noteworthy, conditions involving CsF and CuI in most cases resulted in complex mixtures with a very low yield of the tin adducts. Importantly, purification of all tin complexes has to be carried on aluminum oxide; use of silica gel causes a rapid hydrolysis of the stannyl groups. 5-Bromo-10,20-diphenylporphyrin **6** reacted with 1,3-bis(tri-*n*-butylstannyl)benzene **4b** and **5** to give compounds **11** and **10** (Scheme 2).

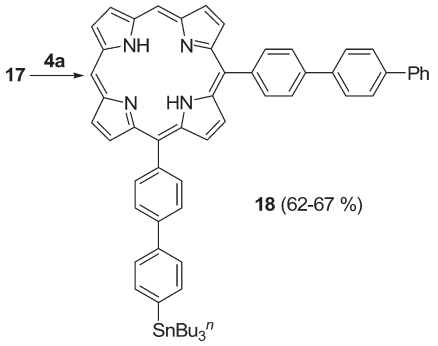
This approach can also be used for modification of the β-positions of porphyrins; e.g., 2-bromo-5,10,15,20-tetraphenylporphyrin **7** was converted into the tin compound **12** in 30% yield. 5-Bromo-10,15,20-triphenylporphyrin **8** and **5** provided compound **13** in 60% yield. Alternatively, this method can also be used for the synthesis of the dinaphthalene **14** (50%) via a reaction of 5,15-dibromo-10,20-diphenylporphyrin **9** with **2a**. The reaction of **9** with 1,4-bis(tri-*n*-butylstannyl)benzene **4a** provided an entry to the bisstannyl porphyrin **15**, however, only as a minor product. In this case, the product **15** turned out to be thermosensitive, and a partial hydrolysis of **15** led to compound **16** as the major product. These adducts **15** and **16** were isolated in 28% and 53% yield, respectively, with an overall yield of 81%.

Another example for the temperature sensitivity was demonstrated by the reaction of 5,10-bis(4-bromophenyl)-porphyrin **17** with **4a**. Here, curiously, the product of a double insertion **18** was isolated (Scheme 3). This reaction was repeated several times under slightly different conditions (90−110 °C); however, in all cases porphyrin **18** was formed (62−67%).

5-(4-Bromophenyl)-2,4,7,8,12,13,17,18-octaethylporphyrin **19**, prepared from 2,3,7,8,12,13,17,18-octaethylporphyrin and 4-bromophenyllithium,[13] was used for the synthesis of compound **20**. Porphyrin **20** (77%), isolated and purified on aluminum oxide, can also be hydrolyzed to **21** on silica gel (Scheme 4).

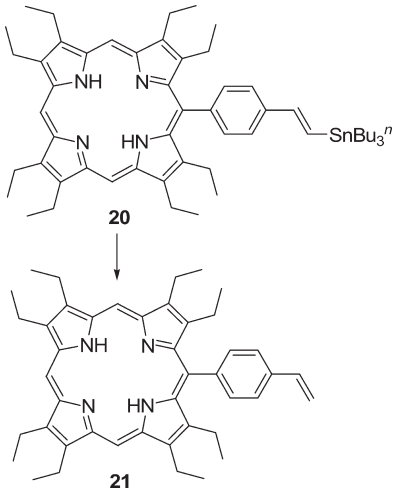
This methodology can be further extended and used for the synthesis of porphyrin dimers. This was achieved simply by reducing the number of tin reagent equivalents to 0.5

SCHEME 3. Formation of Porphyrin 18



18 (62-67 %)

SCHEME 4. Conversion of 20 into 21



20

21

equiv. The reaction mixtures were purified on silica to give the compounds **22**−**24** in 21−50% yield (Scheme 5).

Porphyrin **19** was treated with **4a** to give the dimer **22** (21%). The reaction of compound **6** with **4b** resulted in the formation of **24** in 28% yield. Because of the low solubility of **22** and **24** they could only be isolated in 21% and 28% yields, respectively. Surprisingly, zinc porphyrins did not undergo any transformations under these conditions. Neither dimer nor stannyl porphyrin formation was observed. However, 5-bromo-10,15,20-triphenylporphyrinatonickel reacted with **4a** to give **23** in 50% yield.

2. ^{119}Sn NMR Studies. According to the literature, tin NMR studies were only carried out for a series of (porphyrinato)tin(IV) complexes with axial ligation at tin(IV) to investigate their axial ligation properties.[14] ^{119}Sn (8.59%) with a nuclear spin of 1/2 gives a narrow signal and is slightly more sensitive than ^{117}Sn or ^{115}Sn. Thus, in our studies of the organotin compounds synthesized, main attention was given to ^{119}Sn NMR studies; in some cases for a better clarity ^{117}Sn analysis was performed as well. The tin reagents **2**, **4**, and **5** and the stannyl porphyrins **10**−**12**, **15**, **16**, **18**, and **20** exhibit resonances in the approximate range of δ −35 to −65 ppm compared to the starting compound

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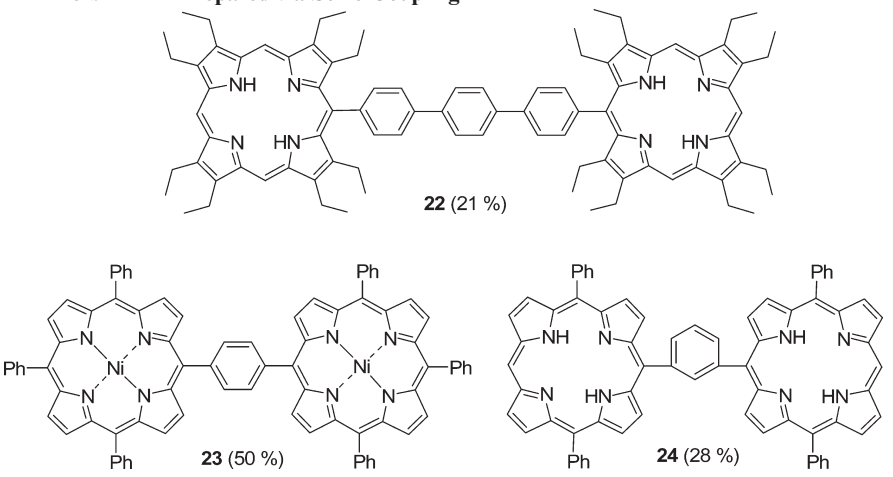
SCHEME 5. Porphyrin Dimers 22−24 Prepared via Stille Coupling



$^{n}Bu_3SnCl$ with a chemical shift of 144.9 ppm.[15] The data for the proton decoupled ^{119}Sn NMR are summarized in Table 1 and illustrated in Figure 1.

The ^{119}Sn NMR resonances of the organostannanes can be correlated with the substitution pattern at the tin atom. Thus, visible changes in the chemical shifts are observed in the case of the double bond pattern of **5** compared to aromatic substituents for the **2** and further for **4**. In all cases, resonances for the tin atoms of the porphyrins appear slightly downfield from their tin reagents.

Tin NMR remains the main tool for the structure determinations of organotin compounds (e.g., substitution pattern on tin, coordination number, influence of solvent) depending on the Sn chemical shifts.[5a,16] Despite $^{117/119}Sn$ NMR literature data available,[5,16−19] there is still a lack of information describing in detail proton-tin spin−spin interactions for systems in which two pairs of H and Sn nuclei (H^1/Sn^1 and H^2/Sn^2, respectively) correlate to one another by a number of $^{n}J(^{1}H-^{117/119}Sn)$ couplings. Bearing the same spins, ^{117}Sn and ^{119}Sn are also present in almost equal isotopic ratios that complicate the matter. Additionally, a quite insignificant isotope shift and a small difference in J values are observed for the ^{117}Sn and ^{119}Sn nuclei. Thus, there are only a few papers discussing in details an influence of tin NMR active nuclei on ^{1}H NMR $^{n}J(^{119}Sn-^{1}H)$ coupling constants.[18,19]

For the symmetric olefin **5** with the two sets of the satellite signals centered with a major (H,H)-singlet (6.96 ppm), a J value for $(^{117/119}Sn-^{1}H)$ was determined to be ca. 106 Hz (Figure 2A).

In $^{n}Bu_3Sn$ the (Sn,H) spin−spin couplings are calculated to be around 54 Hz for $(^{119}Sn-^{1}H)$ (Figure 2B) and ∼52 Hz for $(^{117}Sn-^{1}H)$ in accordance with those reported for $^{n}Bu_4Sn$ in the literature.[18] Figure 2C presents ^{1}H (for simplicity, only the resonance at 7.28 ppm (Hx) is shown) and proton coupled ^{119}Sn spectra. In this case a number of the spin−spin coupling systems can be considered as three separate resonances centered around 7.28 ppm[20] of ^{1}H NMR with a difference of ∼2 Hz (usually invisible $^{n}J(^{115}Sn-^{1}H)$ couplings satellites are suppressed[19c]): (i) protons attached to non-NMR-active tin ±80%; (ii) protons attached to NMR active tin, i.e., $^{1}H-^{119}Sn$; (iii) protons attached to NMR-active tin, i.e., $^{1}H-^{117}Sn$. In the first case, the signal is a doublet with $J \approx 19.3$ Hz for *trans* spin−spin (H,H) coupling.

TABLE 1. ^{119}Sn NMR Data for the Tin Reagents 2, 4, and 5 and Stannyl Porphyrins 10−12, 15, 16, 18, and 21

reagent	^{119}Sn	porphyrin	^{119}Sn
$^{n}Bu_3SnCl$	144.9	**10**	−45.1
2a	−39.7	**12**	−41.0
2b	−49.8	**15**	−40.6
4a	−43.9	**16**	−40.5
4b	−43.3	**18**	−40.9
5	−63.3	**20**	−43.7

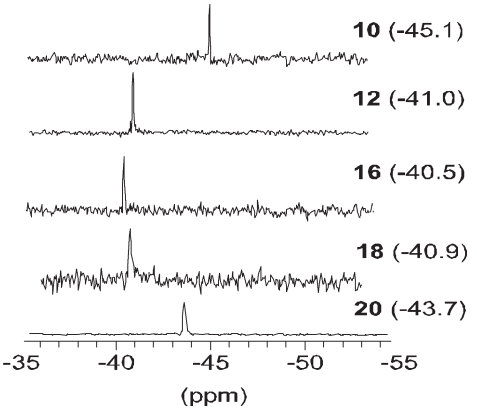


FIGURE 1. Proton decoupled ^{119}Sn NMR spectra for the porphyrins **10**, **12**, **16**, **18**, and **20**.

(15) For all ^{119}Sn NMR, $^{n}Bu_4Sn$ was used as external reference compounds.

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(20) The exact position of the dominant resonance depends on concentration of the sample and the deuterated solvent $CDCl_3$ or CD_2Cl_2 and the temperature of the probe for 400 MHz (296 K) and 600 MHz (300 K).

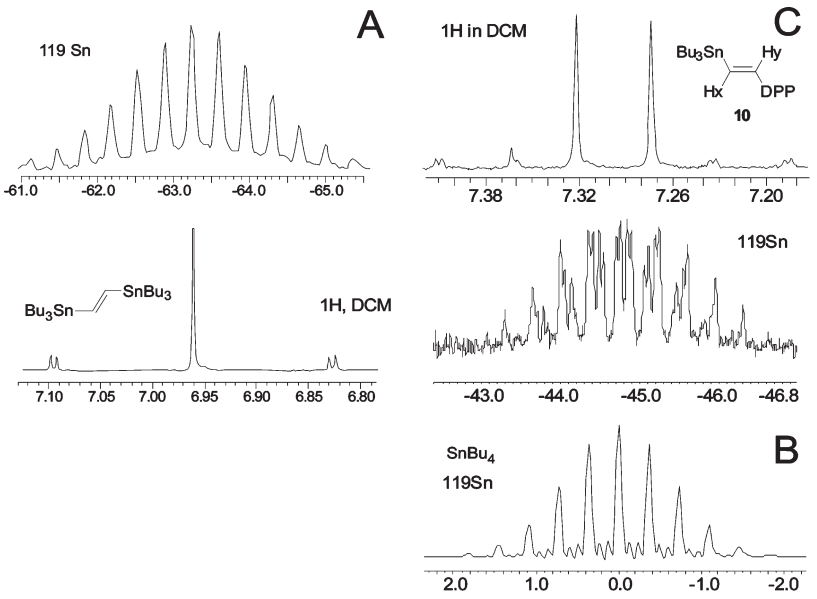

FIGURE 2. Proton coupled ^{119}Sn (149.3 MHz) and ^{1}H (400 MHz) NMR spectra in CD_2Cl_2: (A) ^{119}Sn, ^{1}H for **5**; (B) ^{119}Sn spectrum of the external reference compound $^{n}Bu_3Sn$; (C) ^{1}H (for Hx) and ^{119}Sn for the porphyrin **10**.

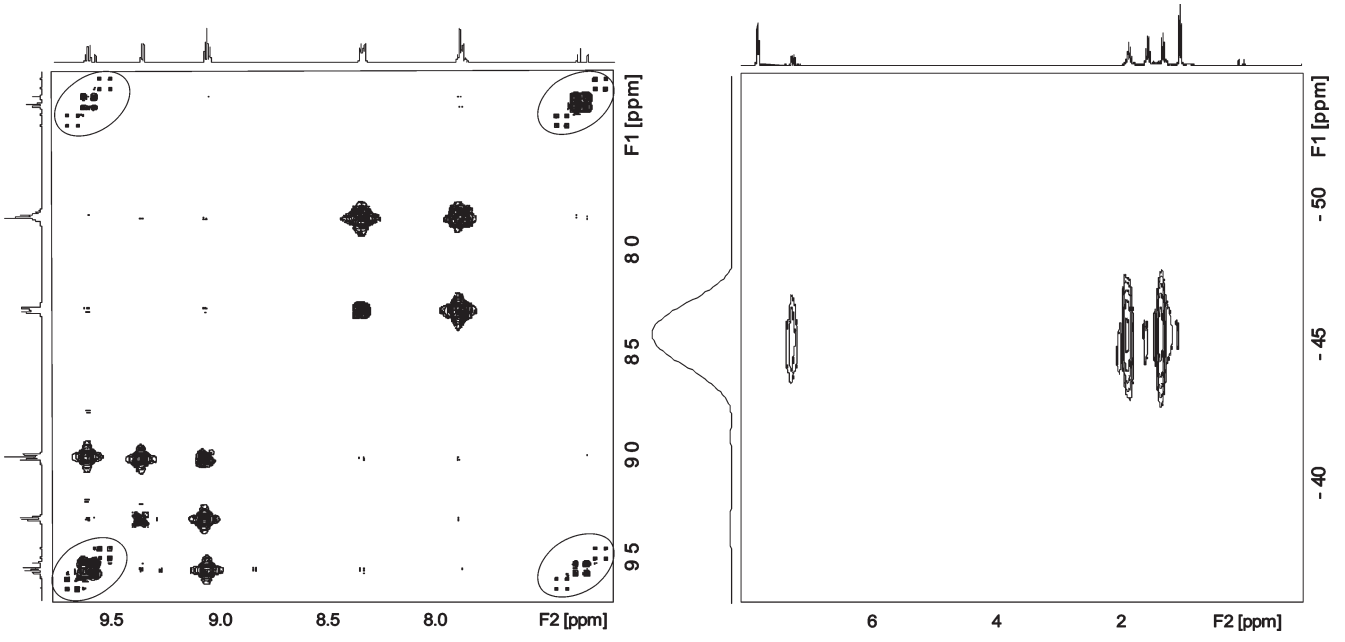

FIGURE 3. 2D (H,H) TOCSY (600 MHz, $CDCl_3$): (A) double bond Hx and Hy, aromatic and porphyrin Hs [7−9 ppm]; (B) ^{1}H, ^{119}Sn HSQC spectra for **10**.

In the other two cases, the signal is double doublet, which is a (Sn,H) spin coupling of 71.5 Hz and a (H,H) spin coupling of 19.3 Hz (Figure 3A).[21]

The *J* value can also be estimated for the alkyl chains of the -$SnBu_3$ as 8.2 Hz for the (H,H) of $Sn(CH_2Pr)_3$ and ca. 50 Hz for ($^{117/119}$Sn−^{1}H) spin−spin couplings. This is in accordance with the data for Bu_4Sn. Thus, the complexity of the proton coupled ^{119}Sn NMR spectrum of the compound **10** can be explained as a number of the spin−spin coupling contributions originating from *ddtr* (Figure 2C).

A determination of the position and the values of ^{n}J in ^{13}C reveals two interesting features. The isotopic difference on the order of ∼2 Hz in ^{1}H NMR is also preserved in the ^{13}C NMR, and a strong upfield shift for -$Sn(CH_2Pr)_3$ (10.2 ppm, the first ^{13}C resonance signal) that was confirmed by DEPT and HSQC (similar results were found for the compound **5** as well) was found. It is known that *J* coupling constants

(21) These experimental results are in accordance with theories proposed in the literature: "the schematic representation of the outcome of a ^{1}H−^{119}Sn HMQC-NMR experiment performed on a fictitious organotin compound in which two pairs of ^{1}H and ^{119}Sn nuclei, respectively, H^1/Sn^1 and H^2/Sn^2, are mutually correlated to one another by a ^{n}J(^{1}H−^{119}Sn) scalar coupling. It is assumed that proton H^1 appears as a ^{1}H singlet and proton H^2 displays a ^{n}J(^{1}H−^{1}H) doublet in the standard proton spectrum".[19c]

TABLE 2. Photophysical Data of Compounds 10, 11, 15, 16, 18, 20, 22, 24, and Foscan in THF[a]

entry	absorption λ_{max}/nm [log(ε)]	excitation λ_{ex}/nm	emission at 298 K λ_{em}/nm (τ_f, ns)
Foscan	373 (5.0), 408 (5.4), 419 (5.4), 516 (4.7), 541 (4.7), 600 (4.6), 652 (4.9)	373	655 (8.8)
10	415 (5.6), 511 (4.8), 547 (4.7), 592 (4.7), 645 (4.6)	415	653, 721 (7.7 ± 0.1)
11	412 (5.4), 440 (5.1), 509 (4.6), 545 (4.5), 585 (4.5), 643 (4.6)	412	643, 709 (10.1 ± 0.1)
15	417 (5.4), 427 (5.4), 515 (4.7), 550 (4.7), 593 (4.6), 654 (4.6)	417, 427	652, 720 (10.6 ± 0.1)
16	417 (5.3), 427 (5.4), 516 (4.7), 551 (4.6), 593 (4.5), 648 (4.5)	417, 427	652, 722 (9.5 ± 0.1)
18	408 (5.9), 501 (4.9), 536 (7.8), 578 (4.8), 642 (4.7)	408	637, 702 (10.3 ± 0.2)
20	406 (5.5), 502 (4.8), 533 (4.7), 577 (4.7), 630 (4.6)	405	629, 697 (10.7 ± 0.1)
22	407 (5.5), 502 (4.8), 535 (4.6), 549 (4.6), 577 (4.6), 626 (4.5)	406	630, 698 (12 ± 0.5)
24	408 (5.8), 420 (5.7), 508 (4.9), 540(4.7), 584 (4.7), 640 (4.5)	409	643, 709 (10.9 ± 0.1)

[a]Concentration for all samples: 7.39×10^{-7} in THF. Laser: 370 nm (pulse < 1 ns); 635 nm (< 200 ps)

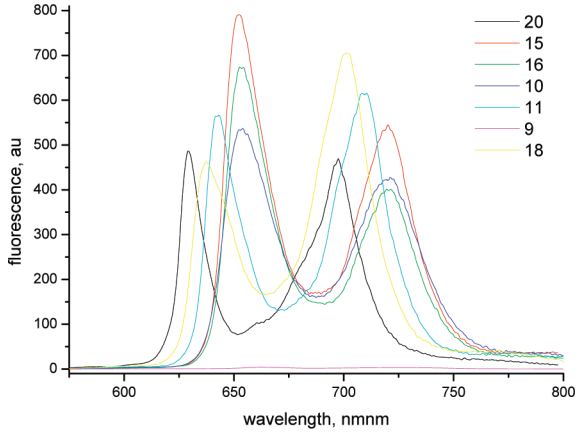

FIGURE 4. Emission spectra at the excitation energies of the Soret bands for the porphyrins **9**−**11**, **15**, **16**, **18**, and **20**.

for directly bonded (Sn,C) are very large; the values of the J ($^{117/119}$Sn−^{13}C) are ca. 336 Hz for the ^1J, ~53 Hz for the ^2J, and ~21 Hz for the ^3J, respectively.

3. Photophysical Studies of the Stannyl Porphyrins and Porphyrin Dimers. Emission and absorption spectra, and the fluorescence lifetime characteristics for the series of the stannyl compounds prepared were recorded. All stannyl porphyrins exhibited a large bathochromic shift of the last Q-bands ~650 nm in CH_2Cl_2 compared to ~635 nm in THF. However, due to their relative low solubility and in some cases unwanted protonation (e.g., dication formation), the spectra for these compounds were recorded in THF. The stannyl compounds showed a much higher emission intensity (90- to 110-fold) compared to the corresponding bromides (as an example, the bromoporphyrin **9** is shown in Figure 4).[22]

The porphyrins were excited at the energies of the Soret bands, resulting in a deviation of the mirror image rules of the emission spectra.[23] Such exceptions of the mirror rules are often associated with the different geometry of the excited state compared to the ground states.[23,24] The stannyl porphyrins emitted in the UV−vis region, and in all cases large Stokes shifts were observed (Table 2). Fluorescence lifetime measurements were carried out in THF and excitation of the porphyrins was performed by 635 nm laser with pulse rate of < 200 ps. The laser (635 nm) targeted the lower-energy Q-band in absorption spectra, which originates from the lowest singlet excited state S_1. Fluorescence lifetime results are presented in Table 2.

We have compared the obtained results for the stannyl porphyrins and the dimers with the lifetime of Foscan (2,3-dihydro-5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin), which is used as an approved drug in photodynamic therapy.[25] Photophysical properties were studied in THF at the same concentrations. We found that the Q-bands in the absorption spectra for the porphyrin synthesized and the lifetimes of the novel compounds **22** and **24** are comparable to those of Foscan. Thus, their electronic absorption properties and a longer fluorescence lifetime make these novel porphyrin dimers promising test compounds for use in PDT.

Conclusions

We have shown that the novel stannyl porphyrins **10**−**13**, **15**, **16**, **18**, and **20** can be easily prepared and characterized using the Stille coupling reaction in 21−67% yields. The compounds are stable and can be stored in solid form for several months. However, these materials are readily hydrolyzed on silica gel and can only be purified on aluminum oxide or via recrystallization. These porphyrins can be used further as building blocks in coupling reactions and thus offer significant synthetic potential. In addition, this approach can also be applied for the synthesis of dimeric porphyrins simply by reducing the equivalents of tin reagent. As an illustration, dimers **22**−**24** were prepared in 21−50% yields. Attempts to use conditions employing CuI/CsF for the synthesis of these compounds led to complex mixtures of the monomeric porphyrins and polymerization products.

We found that ^{119}Sn NMR can easily be used for analysis and characterization of the stannyl porphyrins. It gives a narrow signal and can be recorded within a short period of time. However, tin NMR active nuclei complicate ^{1}H spectra. A complex analysis including various NMR techniques as well as a series of compounds with increasing spin−spin complexity modes is necessary to reveal the mystery of the tin influence. These investigations indicate that structural information can be gathered by a use of standard NMR methods.

Photophysical analyses were carried on for the series of the stannyl porphyrins and dimers. Emission spectra for the stannyl porphyrins were recorded in THF and showed an increased intensity for the latter compared to the starting

(22) The intensity comparison of the tin bromides and corresponding bromides were calculated as the integral function under the intensity curves.

(23) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic-Plenum Publishers: New York, 1999.

(24) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1–13.

(25) (a) Kessel, D.; Dougherty, T. J. *Rev. Contemp. Pharmacother.* **1999**, *10*, 19–24. (b) Wiehe, A.; Simonenko, E. J.; Senge, M. O.; Röder, B. *J. Porphyrins Phthalocyanines* **2001**, *5*, 758–761. (c) Wiehe, A.; Shaker, Y. M.; Brandt, J. C.; Mebs, S.; Senge, M. O. *Tetrahedron* **2005**, *61*, 5535–5564.

bromides. The fluorescence lifetimes were measured for the stannyl and dimeric porphyrins and compared with commonly used PDT drug Foscan.

Experimental Section

All solvents were distilled prior to use. All reagents were purchased from Sigma-Aldrich and were used without any further purification. *trans*-1,2-Bis(tri-*n*-butylstannyl)ethylene **5** was purchased from TCI Europe. Bromoporphyrins **6**−**9**, **17**, and **19** were synthesized according to the procedures previously reported.[7a,10c] General experimental and analytical techniques used were as described earlier.[10d] All photophysical measurements were performed in THF at concentration for all samples: 7.39×10^{-7} M. All fluorescence spectra were recorded on Perkin-Elmer Precisely LS55 spectrometer. Lifetime measurements were carried out on Fluorolog Horiba Jobin Yvon spectrometer using a laser beam: 370 nm (pulse <1 ns) and 635 nm (<200 ps). For the spectroscopic analyses statistical measurements were carried out for each compound reported (five times at the same concentrations) and average data were collected and used.

General Procedure for the Synthesis of Mono- and Bis-tin Reagents 2 and 4. To a solution of bromide **1** or **3** (8 mmol) in anhydrous THF (35−50 mL) was added 11.8 mL (for monobromide **1**) or 18.8 mL (for dibromide **3**) of *t*BuLi (1.7 M in pentane) dropwise (40 min to 1 h) at −90 to −100 °C. A white or yellow precipitation was observed. The mixture was stirred for 1 h, and tri(*n*-butyl)tin chloride (12 mmol for monobromide **1** and 27 mmol for dibromide **3**) was added at −50 °C and stirred at the same temperature for 30 min, resulting in a clear solution. The cold bath was removed, and stirring was continued for 8−12 h. The reaction mixture was quenched with NH_4Cl (satd), extracted with ether (3×50 mL), and dried over Na_2SO_4. The volatiles were removed, and *n*-hexane (50 mL) was added. The solution was quickly passed through a silica plug and eluted with *n*-hexane to give colorless or light yellow oils in 54−94% yield (all tin compounds **2** and **4** have a high R_f (0.9−1)). Alternatively, they can be purified by distillation.

General Procedure for the Synthesis of the Stannyl Porphyrins 10−16, 18, and 20. A heterogeneous solution of a bromoporphyrin **6**−**9** (0.12 mmol), $Pd(PPh_3)_4$ (46.2 mg, 0.03 mmol) and tin reagent **2** or **4** (0.24 mmol for monobromides and 0.48 mmol for dibromides) in toluene (20 mL) was heated under argon at 90−110 °C for 24−72 h (TLC control). The reaction mixture was filtered through a plug of aluminum oxide and washed with ethyl acetate. After removal of the solvents under reduced pressure the residue was chromotographed on aluminum oxide or recrystallized from CH_2Cl_2/MeOH to give **10**−**16** in 21−60% yields.

(*E*)-5-[2-(Tri-*n*-butylstannyl)vinyl]-10,20-diphenylporphyrin 10. Violet solid (51.3 mg, 55%); mp 240 °C; R_f 0.6 (ethyl acetate/hexane, 1:7, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.87 (br, 2H), 1.06 (tr, J = 7.3 Hz, 9H), 1.34 (m, 6H), 1.58 (m, 6H), 1.88 (m, 6H), 7.25 (d, J = 19.0 Hz, 1H), 7.83 (m, 6H), 8.28 (m, 4H), 8.99 (d+d, J = 4.6 Hz, 4H), 9.32 (d, J = 4.6 Hz, 2H), 9.53 (d+d, J = 4.6 Hz, 19.0 Hz, 3H), 10.17 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.2, 13.9, 27.5, 29.5, 104.5, 119.6, 121.1, 126.8, 129.9, 130.7, 131.1, 131.4, 134.7, 141.9, 146.9, 148.7; UV−vis (THF) λ_{max} (log ε) 415 (5.6), 513 (4.7), 549 (4.7), 591 (4.6) nm; HRMS ($C_{46}H_{50}N_4Sn$) calcd for [M + H] 779.3136, found 779.3159.

5-[3-(Tri-*n*-butylstannyl)phenyl]-10,20-diphenylporphyrin 11. Purple solid (25.0 mg, 21%); mp 198 °C; R_f 0.5 (CH_2Cl_2/hexane, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.95 (s, 2H), 0.91 (s, 9H), 1.18 (tr, J = 7.8 Hz, 6H), 1.37 (q, J = 7.8 Hz, 6H), 1.65 (m, 6H), 7.83 (m, 8H), 8.18 (d, J = 6.8 Hz, 1H), 8.29 (m, 5H), 8.94 (br, 4H), 9.06 (d, J = 4.9 Hz, 2H), 9.37 (d, J = 4.9 Hz, 2H), 10.25 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.9, 13.8, 27.4, 29.2, 104.7, 119.6, 121.4, 126.0, 126.8, 127.7, 130.6, 131.4, 134.2, 134.7, 135.7, 139.8, 141.8, 141.9, 142.6, 146.4; UV−vis (THF) λ_{max} (log ε) 412 (5.4), 440 (5.1), 509 (4.6), 545 (4.5), 585 (4.5), 643 (4.6) nm; TOF MS ES+ ($C_{50}H_{52}N_4Sn$) calcd for [M + H] 829.3292, found 829.3292.

2-[4-(Tri-*n*-butylstannyl)phenyl]-5,10,15,20-tetraphenylporphyrin 12. Amorphous solid (35.3 mg, 30%); R_f 0.5 (CH_2Cl_2/hexane, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.60 (br, 2H), 1.02 (tr, J = 7.0 Hz, 9H), 1.14 (m, 6H), 1.46 (m, 6H), 1.66 (m, 6H), 7.28 (m, 5H), 7.56 (m, 1H), 7.77 (m, 10H), 7.93 (m, 2H), 8.25 (m, 6H), 8.79 (m, 7H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.6, 13.8, 27.6, 29.2, 119.7, 119.9, 120.4, 121.4, 126.0, 126.6, 126.7, 126.8, 127.4, 127.6, 127.7, 128.8, 129.8, 130.9, 132.5, 134.5, 134.6, 134.7, 135.5, 135.9, 139.0, 140.5, 141.9, 142.4, 142.6; UV−vis (CH_2Cl_2) λ_{max} (log ε) 421 (5.3), 517 (4.2), 551 (4.0), 595 (3.9), 656 (3.9) nm; HRMS ($C_{62}H_{60}N_4Sn$) calcd for [M + H] 981.3918, found 981.4046.

(*E*)-5-[2-(Tri-*n*-butylstannyl)vinyl]-10,15,20-triphenylporphyrin 13. Purple solid (61.5 mg, 60%); R_f 0.5 (ethyl acetate/hexane, 1:7, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.65 (br, 2H), 1.09 (tr, J = 7.3 Hz, 9H), 1.39 (m, 6H), 1.61 (m, 6H), 1.92 (m, 6H), 7.34 (d, J = 19.6 Hz, 1H), 7.83 (m, 9H), 8.27 (m, 6H), 8.88 (br, 4H), 8.96 (m, 2H), 9.54 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 10.0, 13.5, 27.4, 29.4, 119.8, 120.0, 120.5, 126.55, 126.6, 127.5, 127.6, 130.9 (br), 134.4, 141.9, 142.1, 146.2, 149.1; UV−vis (CH_2Cl_2) λ_{max} (log ε) 422 (5.2), 520 (3.8), 557 (3.6), 595 (3.3), 656 (3.4) nm; HRMS ($C_{52}H_{54}N_4Sn$) calcd for [M + H] 855.3449, found 855.3415.

5,15-Di(1-naphthalenyl)-10,20-diphenylporphyrin 14. Purple solid (50.1 mg, 37%); mp >300 °C; R_f 0.4 (CH_2Cl_2/hexane, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.48 (s, 2H), 7.15 (m, 4H), 7.52 (m, 2H), 7.74 (m, 6H), 7.90 (m, 2H), 8.20 (m, 6H), 8.32 (m, 4H), 8.61 (d, J = 3.9 Hz, 4H), 8.77 (d, J = 3.9 Hz, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ117.2, 119.7, 123.8, 125.2, 125.8, 126.2, 127.2, 127.4, 128.2, 130.7 (br), 132.3 (m), 134.0, 136.4, 138.9, 141.5; UV−vis (THF) λ_{max} (log ε) 419 (6.0), 514 (5.0), 547 (4.8), 590 (4.8) nm; TOF MS ES+ ($C_{70}H_{46}N_8$) calcd for [M + H] 715.2862, found 715.2862.

5,15-Bis[4-(tri-*n*-butylstannyl)phenyl]-10,20-diphenylporphyrin 15. Violet solid (40.1 mg, 28%); mp >300 °C; R_f 0.7 (CH_2Cl_2/hexane, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.75 (br, 2H), 1.03 (tr, J = 7.3 Hz, 18H), 1.30 (m, 12H), 1.50 (m, 12H), 1.76 (m, 12H), 7.82 (m, 10H), 8.23 (m, 8H), 8.89 (d+d, J = 4.7 Hz, 17.0 Hz, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.4, 13.4, 27.1, 28.9, 119.6, 119.9, 126.2, 126.3, 127.2, 130.8 (br), 133.8, 134.2, 134.3, 140.8, 141.2, 141.8; UV−vis (CH_2Cl_2) λ_{max} (log ε) 420 (5.6), 517 (4.6), 552 (4.5), 593 (4.4), 648 (4.4) nm; TOF MS LD+ ($C_{68}H_{82}N_4Sn_2$) calcd for [M + H] 1195.4662, found 1195.4655.

5-[4-(Tri-*n*-butylstannyl)phenyl]-10,15,20-triphenylporphyrin 16. Violet solid (57.5 mg, 53%); mp >300 °C; R_f 0.6 (CH_2Cl_2/hexane, 3:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.59 (br, 2H), 1.05 (tr, J = 7.3 Hz, 9H), 1.35 (m, 6H), 1.53 (m, 6H), 1.80 (m, 6H), 7.87 (m, 9H), 8.24 (d, J = 7.8 Hz, 2H), 8.34 (m, 4H), 8.67 (m, 2H), 8.95 (br, 4H), 9.08 (br, 2H), 9.34 (br, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.9, 13.9, 27.5, 29.3, 119.7, 120.3, 120.7, 126.8 (m), 127.8, 131.1 (br), 133.0, 134.3, 134.7 (m), 141.4, 141.7, 142.3; UV−vis (CH_2Cl_2) λ_{max} (log ε) 421 (4.9), 514 (4.1), 549 (4.0), 592 (3.9), 647 (3.9) nm; HRMS ($C_{56}H_{56}N_4Sn$) calcd for [M + H] 905.3605, found 905.3622.

5-[4-(Tri-*n*-butylstannyl)biphen-4′-yl]-10-[4-(*p*-terphenyl)]porphyrin 18. Violet solid (79 mg, 67%); mp >300 °C; R_f 0.4 (CH_2Cl_2/hexane, 2:3, v/v); recrystallization (CH_2Cl_2/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ −3.27 (br, 2H), 0.98 (tr, J = 7.6 Hz, 9H), 1.19 (m, 6H), 1.44 (m, 6H), 1.66 (m, 6H), 7.51 (m, 3H), 7.77 (m, 4H), 7.90 (m, 4H), 8.03 (m, 6H), 8.36 (m, 4H), 9.08 (m, 2H), 9.17 (m, 2H), 9.42 (br, 2H), 9.51 (br, 2H), 10.30 (br, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.6, 13.6, 27.3, 29.0, 104.1,

125.1, 125.2, 126.7, 127.0, 127.25, 127.3, 122.75, 127.6, 127.62, 128.8, 128.9, 131.3, 135.0, 135.1, 137.0, 139.6, 139.8, 140.4, 140.5, 140.6, 140.7, 140.9, 141.1, 141.3; UV−vis (CH_2Cl_2) λ_{max} (log ε) 410 (3.3), 504 (2.3), 537 (2.2), 578 (2.2), 634 (2.1) nm; HRMS ($C_{62}H_{60}N_4Sn$) calcd for [M + H] 981.3918, found 981.3959.

(***E***)**-5-[4-(1-Tri-*n*-butylstannylvinyl)phenyl]-2,3,7,8,12,13,17,18-octaethylporphyrin 20.** Violet amorphous solid (86 mg, 77%); eluent (ethyl acetate/hexane, 1:10, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −3.05 (br, 2H), 1.04 (tr, J = 7.3 Hz, 9H), 1.18 (m, 12H), 1.49 (m, 6H), 1.71 (m, 6H), 1.92 (m, 18H), 2.87 (m, 4H), 4.10 (m, 12H), 7.26 (m, 2H), 7.76 (d, J = 7.9 Hz, 2H), 8.20 (d, J = 7.9 Hz, 2H), 9.96 (s, 1H), 10.20 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 9.8, 13.9, 18.1, 18.5, 18.55, 18.6, 19.8, 19.9, 20.9, 27.5, 29.3, 29.7, 95.3, 96.7, 118.8, 124.0, 124.2, 130.3, 133.6, 138.8, 141.0, 141.2, 141.9, 142.2, 142.6, 142.7, 142.8, 143.5, 144.1, 145.7, 146.1; UV−vis (CH_2Cl_2) λ_{max} (log ε) 406 (5.2), 506 (4.3), 537 (4.2), 570 (4.2), 622 (4.1) nm; HRMS ($C_{56}H_{78}N_4Sn$) calcd for [M + H] 927.5327, found 927.5303.

5-(4-Vinylphenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 21. Violet solid; mp >219 °C; R_f 0.2 (CH_2Cl_2/hexane, 3:2, v/v); ^{1}H NMR (600 MHz, $CDCl_3$) δ −3.03 (br, 2H), 1.19 (tr, J = 7.6 Hz, 6H), 1.19 (m, 18H), 2.86 (m, 4H), 4.09 (m, 12H), 5.54 (d, J = 10.3 Hz, 1H), 6.12 (d, J = 17.6 Hz, 1H), 7.11 (m, 1H), 7.76 (d, J = 7.3 Hz, 2H), 8.20 (d, J = 7.3 Hz, 2H), 9.96 (s, 1H), 10.20 (s, 2H); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 17.9, 18.2, 18.3, 18.4, 19.5, 19.6, 19.7, 20.7, 96.6, 114.1, 124.1, 133.5, 136.9, 137.5, 140.8, 141.8, 142.1, 142.5, 142.6, 143.3, 144.0, 145.6; UV−vis (CH_2Cl_2) λ_{max} (log ε) 407 (5.1), 506 (4.2), 538 (4.1), 572 (4.1), 622 (3.9) nm; HRMS ($C_{44}H_{52}N_4$) calcd for [M + H] 637.4265, found 637.4266.

4,4′′-Bis[5-(2,3,7,8,12,13,17,18-octaethylporphyrinyl)]-*p*-terphenyl 22. Violet solid (33 mg, 21%); mp >300 °C; R_f 0.3 (CH_2Cl_2/hexane, 3:2, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −3.00 (br, 4H), 1.37 (m, 12H), 1.92 (m, 36H), 2.98 (m, 8H), 4.10 (m, 24H), 7.56 (m, 2H), 7.74 (m, 2H), 8.65 (m, 8H), 9.96 (s, 2H), 10.20 (s, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.2, 18.4, 18.5, 19.7, 19.8, 95.8, 97.0, 117.1, 128.6, 130.4, 130.5, 130.9, 134.1, 141.3, 142.0, 142.5, 143.1, 144.7, 146.0; UV−vis (CH_2Cl_2) λ_{max} (log ε) 407 (5.2), 505 (4.3), 540 (4.1), 573 (4.1), 624 (3.9) nm; HRMS ($C_{90}H_{102}N_8$) calcd for [M + H] 1295.8300, found 1295.8304.

1,4-Bis[5-(10,15,20-triphenylporphyrinatonickel(II)yl)]benzene 23. Purple solid (76 mg, 50%); mp >300 °C; R_f 0.6 (CH_2Cl_2/hexane, 1:2, v/v); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.73 (m, 19H), 8.11 (m, 15H), 8.60 (d, J = 4.9 Hz, 4H), 8.86 (dd, J = 4.9 Hz, 8H); ^{13}C NMR (150.9 MHz, CD_2Cl_2) δ 115.6, 119.8, 119.9, 126.6, 126.7, 126.8, 127.6, 127.7, 131.8, 132.1 (m), 133.5, 133.6 (m), 140.6, 140.7, 142.4, 142.7, 143.2, 146.7; UV−vis (CH_2Cl_2) λ_{max} (log ε) 413 (5.1), 443 (5.1), 535 (4.6) nm; HRMS ($C_{76}H_{46}N_8Ni_2$) calcd for [M^+] 1186.2567, found 1186.2552.

1,3-Bis[5-(10,20-diphenylporphyrinyl)]benzene 24. Purple solid (17 mg, 28%); mp >300 °C; R_f 0.2 (CH_2Cl_2/hexane, 2:3, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ −2.94 (br, 4H), 7.84 (m, 12H), 8.27 (m, 8H), 8.67 (m, 2H), 9.06 (d+d, J = 4.9 Hz, 8H), 9.37 (d+d, J = 3.9 Hz, 8H), 10.24 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 104.5, 119.3, 119.6, 124.3, 126.4, 127.3, 130.7, 130.9 (br), 133.3, 134.2 (m), 139.5, 140.4, 145.7 (br), 146.7 (br); UV−vis (THF) λ_{max} (log ε) 408 (5.8), 420 (5.7), 508 (4.9), 540 (4.7), 581 (4.7), 640 (4.5) nm; TOF MS ES+ ($C_{70}H_{46}N_8$) calcd for [M + H] 999.3925 found 999.3924.

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Supporting Information Available: Characterization data including 1D and 2D NMR spectra of compounds **10**−**16**, **18**, **20**−**22**, **24**. This material is available free of charge via the Internet at http://pubs.acs.org.