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A Novel Modular Approach to Triazole-Functionalized Phthalocyanines Using Click Chemistry

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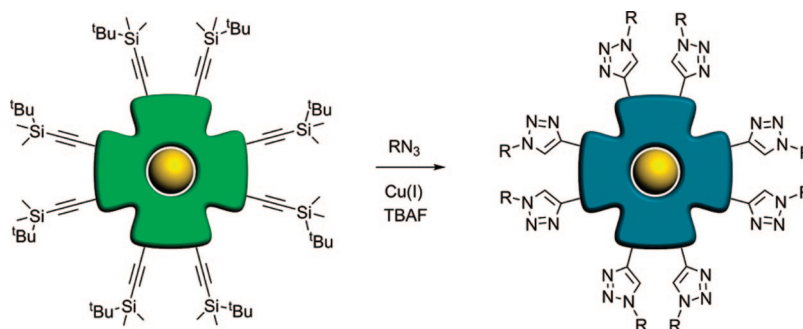
A novel, elegant, and significantly improved protocol for the synthesis of a protected octaacetylene phthalocyanine is described. Inexpensive, mild, and environmentally benign iodination of 1,2-dibromobenzene and subsequent optimized chemoselective palladium-catalyzed cyanation are employed to effectively build up the key intermediate 4,5-dibromophthalonitrile in two steps. Introduction of the *tert*-butyldimethylsilyl-protected acetylene moieties via a Sonogashira cross-coupling provides the desired phthalonitrile precursor that, after cyclization, yielded the protected octaacetylene phthalocyanine. Subsequently, in situ deprotection and "clicking" are employed as a highly efficient and quantitative route to a novel class of octatriazole-functionalized phthalocyanines. The ability of such triazole-derived phthalocyanines to form well-defined supramolecular structures upon doping with zinc(II) triflate is demonstrated.

Introduction

Phthalocyanines (Pcs)[1−5] belong to a "magic pool" of compounds that are an inevitable part of modern science. Man's analogues of nature's porphyrins have recently attracted an increasing interest as building blocks for the construction of molecular devices such as organic field effect transistors,[6,7] optical switching and limiting devices,[8,9] sensors,[6,7] organic light-emitting devices,[10] low band gap molecular solar cells,[11,12]

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SCHEME 1. Postmodification of Octaacetylene Pc 1 via Click Chemistry Using Dodecylazide as a Model Substrate: Traces Yielding Clicking of 1a (Right) and Efficient in Situ Deprotection and Clicking of 1b (Left)
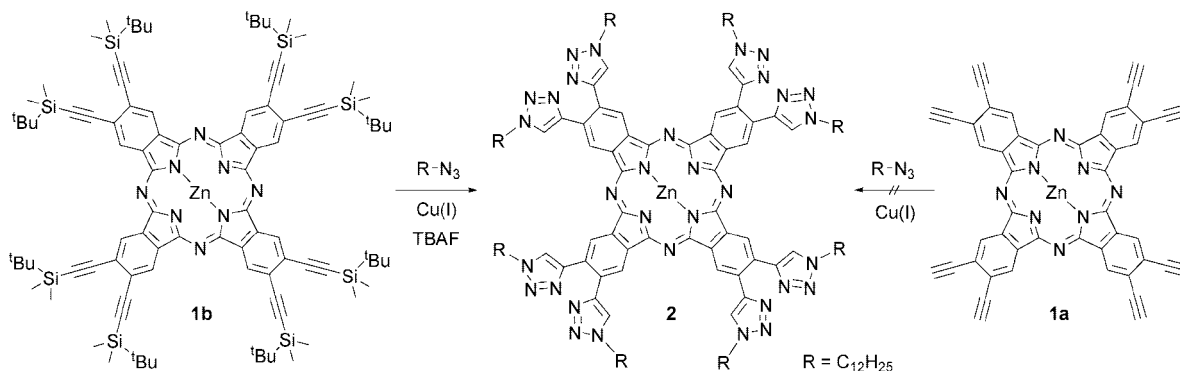

nonlinear optical materials,[8,13] etc. This is due to their outstanding dye properties and the ability to self-assemble, by means of π−π interactions, into highly ordered arrays that can be tuned by careful design of their periphery (e.g., equipping them with specific molecular-recognition sites). These arrays exhibit unique photophysical and (opto)electronic properties as a result of excitonic interactions between adjacent dye units.[14]

In spite of their enormous potential, the synthesis of large Pcs bearing sensitive functional groups remains a challenge. This drawback arises from the fact that cyclic rearrangement of the corresponding precursors (e.g., phthalonitriles, phthalimides, etc.) to form Pcs usually requires high reaction temperatures (>140 °C) and a presence of a strong nucleophile. Moreover, yields of functionalized Pcs obtained in such a way are in many cases unsatisfactory and purifications cumbersome.

Another frequently overlooked drawback is that the synthetic routes toward substituted phthalonitriles—the most commonly used precursors to Pcs—are limited to few reactions only, and these are exclusively indelicate. Most often they are synthesized by cyanation of corresponding *ortho*-substituted aryl halides requiring the use of highly toxic (NaCN, KCN) or heavy metal containing (CuCN, $Zn(CN)_2$) cyanide sources and/or high temperatures (150−250 °C) to obtain reasonably good yields. This significantly lowers an overall efficiency when cyanation cannot be employed prior to incorporation of sensitive functional groups.[15]

In order to overcome these problems, we have been looking for an alternative: a general and relatively easily applicable route toward functionalized Pcs that would also be suitable for sensitive groups. The recently discovered copper(I)-catalyzed modification of the 1,3-dipolar cycloaddition of azides and alkynes leading to 1,2,3-triazole derivatives,[16] belonging to the pool of "click chemistry" reactions,[17] is an excellent candidate for efficient postmodification. Moreover, the synthesis of octaacetylene Pc 1a and its protected analogue 1b,[18] as well as

SCHEME 2. Three-Step Harsh Original Procedure (Top) and a New Two-Step Route (Bottom) Affording the Key Intermediate 3
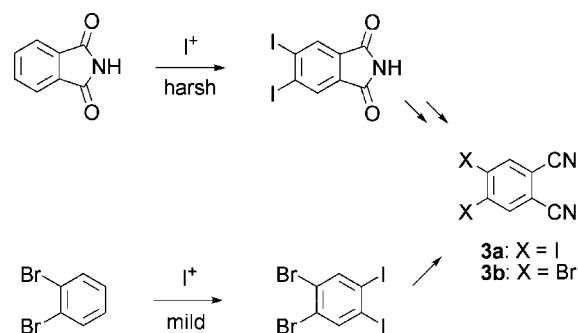
an example of application of click chemistry in phthalocyanine postmodification[19] have recently been reported. Here, we would like to describe our recently developed approach to octatriazole-functionalized Pcs using copper(I)-catalyzed cycloaddition of azides to octaacetylene Pc 1 (Scheme 1). A novel and significantly improved protocol for the preparation of 1 is also reported.

Results and Discussion

In the previously reported original synthesis of 1, Leznoff et al. introduced 4,5-diiodophthalonitrile (3a) as a key intermediate to attach acetylene moieties.[18,20] Since the original three-step procedure—starting from phthalimide—involved a harsh iodination step (reflux in fuming sulfuric acid) and a multistep poorly reproducible crystallization procedure of the corresponding product (from a mixture containing hydrolysis products of the phthalimide moiety), we have designed and optimized a novel two-step route to the analogous 4,5-dibromophthalonitrile (3b), starting from a commercially available 1,2-dibromobenzene and using the cheapest iodination method to date followed by subsequent chemoselective cyanation (Scheme 2).

Aromatic iodides are widely used in organic synthesis, and many different synthetic methods have been reported for their effective preparation. However, direct iodination methods of deactivated arenes are less numerous and include use of expensive (silver salts, triflic acid) or hazardous (fuming sulfuric

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SCHEME 3. Iodination of 1,2-Dibromobenzene Using Strongly Electrophilic I⁺ Intermediates
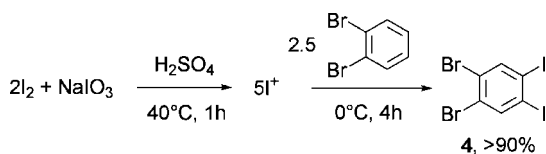
TABLE 1. Palladium-Catalyzed Cyanation of 4[a]

entry	M	CN (equiv)	Ad.[b]	t (h)	t (°C)	yield (%)[c]		
						3b	5	4
1[d]	K	2.0	CuI	72	70	10	20	60
2	Zn	3.0	py	16	110	30	20	40
3	Zn	6.0	py	8	120	20	15	55
4	Zn	8.0	py	16	120	15	11	64
5	Zn	2.4	py	36	120	61	13	17
6	Zn	2.4	−	48	120	55	25	10
7	Zn	2.4	py	48	120	73	4	1
8	Zn	2.8[e]	py	48	120	47	6	0
9	Zn	2.4	py	60	120	65	[f]	[f]
10	Zn	2.8[e]	py	60	120	52	[f]	0
11	Zn	2.8[e]	py	90	130	0	0	0

[a] **4** (1 equiv), Pd(PPh₃)₄ (0.01 equiv), and DMF. [b] Additive: CuI (0.01 equiv) or pyridine (1 equiv). [c] Isolated yield. [d] THF was used as a solvent. [e] Catalyst (0.012 equiv) and cyanide were added in two portions. [f] Yield not determined.

acid, iodine(I) chloride) reagents.[21] Recently, an easy, inexpensive, and effective oxidative iodination of deactivated arenes in 90% (v/v) concentrated sulfuric acid has been described using strongly electrophilic I⁺ intermediates, simply generated from diiodine and NaIO₃ as an oxidant.[21a] We used and optimized these reaction conditions for diiodination of 1,2-dibromobenzene to afford 1,2-dibromo-4,5-diiodobenzene (**4**) in >90% yield (Scheme 3). We discovered that low temperature (0 °C) and vigorous stirring were important parameters to obtain high selectivity (iodination takes place preferably at positions 4 and 5), and the crude product could be easily separated from the reaction mixture by filtration. Furthermore, since 2 equiv of I⁺ intermediates was sufficient for complete conversion (otherwise a product of trisubstitution was formed in the reaction mixture which complicated purification of the product), the reaction waste only composed of the NaHSO₄/H₂SO₄ mixture could be disposed after dilution without a problem.

To provide the key intermediate **3b**, the scope and limitations of chemoselective cyanation of **4** were investigated. Since aromatic iodides are significantly more reactive in transition metal catalyzed cross-coupling reactions than bromides, palladium-catalyzed cyanation[22a] of **4** was chosen and optimized for the preparation of **3b**. An overview of the results is summarized in Table 1.

Initially, we compared two of the most commonly used catalyzed cyanation procedures (entries 1 and 2). Prompted by the promising result of the latter (50% conversion of **4** to the mono- and bisubstituted products), we decided to optimize these reaction conditions. Increasing the amount of a cyanide had a

negative effect on the yield of the desired product (entries 2, 3, and 4), which is in agreement with the observations reported in the literature,[22] where a higher concentration of the cyanides in the solution led to the formation of palladium(II) cyanide species which are almost inactive in a cyanation reaction. Thus, only a slight excess (2.4 equiv/2.8 equiv in the case of multiple additions) of cyanide species was used for further experiments.

Crucial parameters for cyanation of *ortho*-substituted aryl halides are the reaction time and temperature. Typically, longer reaction times (>1 day) and higher temperatures (>120 °C) are required for effective cyanation. However, the cyclic rearrangement of phthalonitriles to form phthalocyanines (or polymerization) that occurs under similar conditions makes the reaction very delicate. We investigated the influence of the reaction time on the yield of the desired product (entries 5, 7, and 9). We found that prolongation of the reaction time after 48 h—when maximum (73%) efficiency was achieved—led to partial decomposition of the product, and in the final case (entry 11) no product could be isolated at all.

To further increase the yield of **3b** we applied stepwise addition of the catalyst and cyanide source (entries 8 and 10). This, however, led to the decrease of the reaction yield of **3b** probably due to contamination of the system with oxygen during the addition. A significant effect of an additive was observed. Addition of 1 equiv of pyridine to the reaction mixture led to an 18% increase of the yield of **3b** as a result of the increased reactivity of the Zn(CN)₂/pyridine complex (entries 6 and 7).

Sonogashira cross-coupling was used to attach acetylene moieties at positions 4 and 5 of **3b**. Due to the lower reactivity of **3b** compared to **3a**, reflux and a prolonged reaction time were necessary to obtain comparable yields of **6**. Moreover, due to the fragility of the acetylenes (even those protected with a bulky *tert*-butyldimethylsilyl groups) to hard nucleophilic alkoxides that are widely used in phthalocyanine synthesis, an alternative route using gaseous ammonia was proposed by Leznoff et al. in the synthesis of **1a**, providing after zinc insertion its protected derivative **1b** in 24% yield.[18] In order to make this route synthetically more attractive, we performed the cyclic rearrangement of **6** in an analogous manner to the previously described cyclizations of acetylene-containing phthalonitriles[23] using ZnCl₂ as a template. This resulted in a significantly improved efficiency of this reaction affording **1b** in 65% yield. Deprotection of **1b** using an excess of TBAF afforded **1a** in quantitative yield[24] (in overall 37% yield starting from 1,2-dibromobenzene) (Scheme 4).

Despite the poor solubility of **1a** in all organic solvents, we decided to investigate the possibility of its use as a unique precursor for preparation of a wide spectrum of novel triazole-functionalized Pcs via click chemistry. Not only would such an approach represent a highly efficient, mild, and selective way to potentially interesting Pc derivatives (including those bearing sensitive groups) but also building in of a triazole moiety (stable heterocyclic ligand) could open up new pathways to the controlled self-organization of such molecules upon doping with Lewis acids (e.g., metals) at the supramolecular level. Moreover, plausible oxidative coupling through the carbon atoms of two

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(24) Precipitation in methanol instead of column chromatography was used as a purification technique due to restricted solubility of **1a** which also prevents characterization of the compound.

SCHEME 4[a]

$$3 \xrightarrow{a \text{ or } b} 6 \xrightarrow{c \text{ or } d} 1b \xrightarrow{e} 1a$$
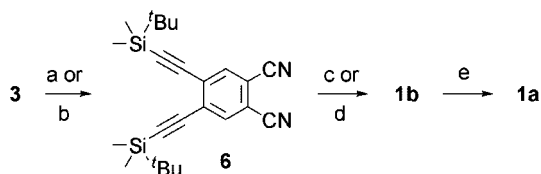
[a] (a) **3a**, *tert*-butyldimethylsilylacetylene, Pd(PPh$_3$)$_4$, CuI, Et$_3$N, r.t., 14 h, 90%.[18] (b) **3b**, *tert*-butyldimethylsilylacetylene, Pd(PPh$_3$)$_4$, CuI, Et$_3$N, reflux, 36 h, 87%. (c) *i* NH$_3$, DMAE, reflux, 4 h, *ii* Zn(OAc)$_2$, DMF, toluene, reflux, 12 h, 24%.[18] (d) ZnCl$_2$, DMAE, reflux, 12 h, 65%. (e) TBAF, THF, r.t., 12 h, quantitative.[18,24]

triazoles in *ortho* position in **2** would afford a flat superconjugated Pc system that is expected to absorb in near-infrared.

Copper(I)-catalyzed cycloaddition of azides and alkynes is an extremely versatile reaction that can proceed even in heterogeneous systems (i.e., in systems where either catalyst or substrates have restricted solubility). Unfortunately, this was not the case when **1a** was treated with dodecylazide and a copper(I) catalyst to provide **2** (Scheme 1). The reaction proceeded very slowly, and only traces of product were detected even after few weeks. This could be because of extremely low solubility of **1a** which forms unreactive aggregates where the formation of copper(I) acetylide(s) (first step in the proposed mechanism of click cycloaddition)[16b] cannot occur. To prevent this problem, we decided to use an in situ deprotection and clicking approach where **1b** (soluble protected analogue of **1a**) was treated with TBAF in the presence of a copper(I) species so that formation of copper(I) acetylide(s) of **1a** could occur prior to aggregation and precipitation of **1a**. In this case, "activated" **1a** with an unspecified number of acetylenes bearing copper(I) instead of a proton precipitated out and quantitatively (each acetylene of **1a** underwent cycloaddition)[25] reacted with dodecylazide over a period of 24 h. Strict oxygen-free conditions were crucial to obtain pure **2**, otherwise broadening and a red shift of UV–vis absorption maximum of **2** were observed, which were attributed to the partial oxidative coupling of neighboring groups in **2** extending the π conjugation of the Pc.[26,27]

2a was isolated by precipitation from CH$_2$Cl$_2$ in MeOH and characterized by ^{1}H NMR (significant broadening of the peaks indicated very strong aggregation that could be suppressed by addition of TFA),[28] UV, IR (showing complete disappearance of acetylene stretches), and MALDI-TOF mass spectrometry techniques.

As previously mentioned, **2** could serve as a model compound for controlling the self-assembly properties of triazole-derivatized Pcs upon doping with Lewis acids. To illustrate this, **2** was successfully titrated with zinc(II) triflate, and this process was monitored using UV–vis spectroscopy. The resulting titration curves together with the Job plot are depicted in Figure 1. To our surprise, these preliminary results showed that **2** forms a very well-defined 1:1 complex with zinc(II) triflate as seen by a significant blue shift of the absorption maximum (697 to 657 nm) and a precise isosbestic point. The former absorption
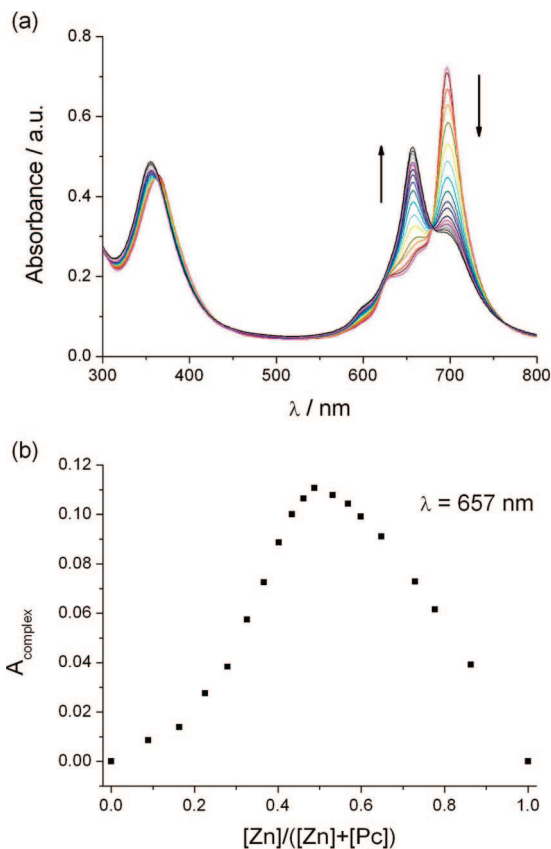

FIGURE 1. (a) UV–vis titration of **2** ([Pc]$_0$ = 6.76 μM) with Zn(OTf)$_2$ in THF and (b) Job plot at absorption maximum of the complex (657 nm).

shift is indicative of a cofacial geometry, the precise architecture of which is currently being investigated.

Conclusion

In summary, a novel improved protocol for the synthesis of **1a** using mild, easy, and inexpensive iodination of 1,2-dibromobenzene and subsequent chemoselective cyanation has been reported. Although **1a** does not undergo copper(I)-catalyzed click cycloadditions with azides due to solubility restrictions, an in situ deprotection and clicking procedure of its protected derivative **1b** has been developed to overcome this problem. Using this method, octatriazole Pc **2** was synthesized in an excellent yield for the first time. Upon the basis of the demonstrated versatility of click chemistry, this route is of great potential for the highly efficient, mild, and easy construction of novel functionalized Pcs, in particular those bearing sensitive groups. In addition, preliminary studies show the ability of **2** to form well-defined supramolecular structures upon doping with zinc(II) triflate.

Experimental Section

General. All chemicals and solvents were purchased from commercial sources and used without further purification unless stated otherwise. Solvents were distilled prior to use: THF (Na), CH$_2$Cl$_2$, 2-(dimethylamino)ethanol (DMAE), Et$_3$N, MeOH, and pyridine (CaH$_2$). All cross-coupling and click reactions were performed under an argon atmosphere using Schlenk techniques and deoxygenated solvents (freeze–pump–thaw in three cycles, <0.4 mbar). For more detailed instructions and instrumentation, see Supporting Information.

(25) We believe that a certain number of molecules of dodecylazide reacted with insoluble copper(I)$_x$ derivative of **1a** and thereby solubilized it. Remaining "free" acetylenes underwent copper(I) acetylide formation and subsequent cycloaddition with dodecylazide in solution.

(26) Optimizing conditions for controlled and quantitative oxidative coupling of *ortho*-bis(triazole) moieties in **2** are currently under intense investigation.

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(28) The reduced aggregation of **2** is a result of mutual electrostatic repulsion between the positively charged protonated Pcs.

1,2-Dibromo-4,5-diiodobenzene (4). A mixture of a fine-grounded I_2 (3.43 g, 13.5 mmol), $NaIO_3$ (1.34 g, 6.76 mmol), and 160 mL of 90% H_2SO_4 (v/v) was stirred at 40 °C for 1 h in the dark. The resulting dark solution was then cooled to 0 °C, and 1,2-dibromobenzene (4.00 g, 16.9 mmol) was added in one portion. The solution was vigorously stirred at 0 °C for 4 h before it was poured on ice (400 g). The white precipitate was filtered off and washed with an excess of water (1 L) before it was dissolved in chloroform (0.5 L), washed with 10% aq. $NaHSO_3$, and dried over Na_2SO_4. After filtration, the solvent was evaporated and the residue dried under vacuum to give 8.16 g of the crude product. Crystallization from chloroform/hexanes or chromatography over a short plug of silica (hexanes) afforded pure product as a white crystalline solid in >90% yield. Characterization was in agreement with the literature.[29]

Procedure for Cyanation of 4 using KCN. 4 (1.0 g, 2.05 mmol), KCN (0.27 g, 4.10 mmol), CuI (0.039 g, 0.205 mmol), and $Pd(PPh_3)_4$ (0.24 g, 0.205 mmol) were placed in a Schlenk tube equipped with a stirrer, and the system was evacuated and filled with argon in three cycles. After THF (25 mL) was added with a syringe, the mixture was heated to reflux for 72 h under an argon atmosphere. The reaction was quenched using 10% aq. NH_3, and the crude products were extracted with chloroform. The combined organic layers were washed with 10% aq. NH_4Cl and dried over Na_2SO_4. After filtration, the solvent was evaporated, and the residue was purified by chromatography over silica gel using hexane/dichloromethane 4/1 and 2/1 as eluents.

General Procedure for Cyanation of 4 using $Zn(CN)_2$. 4 (1.0 mmol), $Zn(CN)_2$, and $Pd(PPh_3)_4$ (0.10 mmol) were placed in a Schlenk tube equipped with a stirrer, and the system was evacuated and filled with argon in three cycles. After DMF (20 mL, extra dry, <0.01% H_2O) and pyridine (1 mmol) were added with a syringe, the mixture was heated under an argon atmosphere. The reaction was quenched using 10% aq. NH_3, and the crude products were extracted with chloroform. Combined organic layers were washed with 10% aq. NH_4Cl and dried over Na_2SO_4. After filtration, the solvent was evaporated, and the residue was purified by chromatography over silica gel using hexane/dichloromethane 4/1 and 2/1 as eluents.

4,5-Bis(*tert*-butyldimethylsilylethynyl)phthalonitrile (6). 3b (0.56 g, 1.96 mmol), *tert*-butyldimethylsilylacetylene (0.73 g, 5.20 mmol), CuI (0.15 g, 0.785 mmol), and $Pd(PPh_3)_4$ (0.23 g, 0.196 mmol) were placed in a Schlenk tube equipped with a stirrer, and the system was evacuated and filled with argon in three cycles. After Et_3N (25 mL) was added with a syringe, the mixture was heated to 60 °C for 36 h under an argon atmosphere. The reaction was quenched using 10% aq. NH_3, and the crude product was extracted with chloroform. Combined organic layers were washed with 10% aq. NH_4Cl and dried over Na_2SO_4. After filtration, the

solvent was evaporated and the residue purified by chromatography over silica gel using hexane/CH_2Cl_2 2/1 as eluent to afford 0.69 g (87% yield) of the product as an off-white solid. Characterization was in agreement with the literature.[18]

2,3,9,10,16,17,23,24-Octakis(*tert*-butyldimethylsilylethynyl)phthalocyanato Zinc(II) (1b). A mixture of **6** (525 mg, 1.30 mmol), $ZnCl_2$ (44.2 mg, 0.325 mmol), and DMAE (4 mL) was heated to 140 °C overnight. The solvent was evaporated, and the residue was dried under vacuum. Column chromatography over silica ($CHCl_3$ followed by $CHCl_3$/EtOH 99/1) and crystallization from CH_2Cl_2/MeOH afforded 355 mg (65% yield) of the product as a dark green solid. Characterization was in agreement with the literature.[18]

2,3,9,10,16,17,23,24-Octakis(1-dodecyl-1*H*-1,2,3-triazole-4-yl)phthalocyanato Zinc(II) (2). 1b (17.3 mg, 0.0103 mmol), dodecylazide (138 mg, 0.658 mmol), and CuI (62 mg, 0.329 mmol) were placed in a Schlenk tube equipped with a stirrer, and the system was evacuated and filled with argon in three cycles. Then THF (10 mL) and 1,1,4,7,7-pentamethyldiethylenetriamine (114 mg, 0.658 mmol) were added with a syringe, and the mixture was stirred until all CuI dissolved (10 min). TBAF (1 M, 0.66 mL) was added dropwise (the first portion of 0.11 mL over 1 h and the second portion of 0.55 mL over 1.5 h), and the reaction mixture was stirred for 24 h under an argon atmosphere before it was quenched with 10% aq. NH_3. The crude product was extracted with CH_2Cl_2, and the combined organic layers were washed with 10% aq. NH_4Cl and dried over Na_2SO_4. After filtration, the solvent was evaporated, and the desired product was obtained after five precipitations from CH_2Cl_2 in MeOH as a dark green solid in >90% yield. IR (neat, cm^{-1}) 2956, 2922, 2851, 1258, 1094, 1017, and 798. UV−vis (THF) 698, 665, 629, and 370 nm. ^1H NMR (500 MHz, $CDCl_3$ + TFA) δ 9.98 (br, 8H, C_{Ar}-*H*), 8.74 (br, 8H, C_{Ar}-*H*), 4.72 (br, 16H, C*H*$_2$), 2.16 (br, 16H, C*H*$_2$), 1.45−1.30 (br, 144H, C*H*$_2$), 0.88 (br, 24H, C*H*$_3$). MALDI-TOF MS *m*/*z* calcd for $C_{144}H_{216}N_{32}Zn + H^+$ 2458.72, found 2458.96. GPC (THF): t_R = 8.42 min, M_n = 2566 g/mol, M_w/M_n = 1.12.

Supporting Information Available: Complete Experimental Section including characterization of all compounds, copies of ^1H NMR (**5**, **2**) and ^{13}C NMR (**5**) spectra, copies of IR (**1b**, **2**), UV−vis (**1b**, **2**), MALDI-TOF (**2**) spectra, and GPC chromatograms (**1b**, **2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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