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Peripheral Substitution of a Near-IR-Absorbing Soluble Phthalocyanine Using "Click" Chemistry

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Abstract: A series of near-IR-absorbing soluble phthalocyanines (Pcs) with eight alkyne moieties as side chains of the chromophore have been synthesized. One of these Pcs has been used as a scaffold for functional group modification using alkyne–azide click chemistry with various azides. This led to a small library of Pcs with photo and thermal crosslinkable, dendritic, and hydrophilic moieties starting from a single Pc molecule. A patterned thin film was fabricated by photocrosslinking one of these Pc derivatives.

Keywords: click chemistry · crosslinking · phthalocyanine · synthetic methods · thin films

Introduction

We report herein the use of an octaalkynyl-substituted phthalocyanine (Pc) precursor for the creation of a small library of peripherally substituted Pc derivatives by "click" chemistry methodology. Pcs are highly conjugated synthetic porphyrin analogues that exhibit high extinction coefficients, LUMO energies and hole mobilities, and strong π–π interactions.[1] Near-IR-absorbing (and emitting) Pcs, in particular, have potential application in both detecting and treating cancer since mammalian tissues are transparent in the near-IR spectrum (700–900 nm).[2] These molecules are also used as xerographic materials,[3] in photovoltaic windows,[4] and in organic solar cells.[5] These applications require optimization of chemical, physical, and photophysical properties such as absorption, solubility, partition ratio, and electrochemical potentials. The behavior of Pcs as materials is also highly dependent on short- and long-range organization of the molecules induced by either self-assembly (bottom-up)[6,7] or nanopatterning (top-down) approaches,[8,9] both of which can be facilitated by modification of Pc with suitable functional groups. Hence, the application of Pcs for advanced technologies demands synthetic methods that can generate numerous precisely tailored Pc derivatives with high fidelity. Though there are many reports on the peripheral modification of Pcs,[7,10–21] a general method remains scarce. A practical route for phthalocyanine modification would 1) circumvent the low yielding Linstead cyclization step, which is often accompanied by tedious purification; 2) allow modification with substituents that would otherwise not survive the Linstead cyclization conditions; and 3) be amenable to scale up.

The Cu^{I}-catalyzed azide–alkyne cycloaddition (CuAAC) "click" reaction[22] has recently been demonstrated by us and others as a mild and straightforward method for functional modification of Pcs.[8,23–27] Here, we disclose the synthesis of a series of near-IR-absorbing soluble Pc derivatives that bear eight alkynyl arylthio moieties as side chains of the chromophore. Substitution at the β positions of Pcs with arylthio moieties shift the absorption towards the near-IR region around 30 nm relative to analogous aryloxy-substituted Pcs.[23] The clickable phthalocyanines (**3b–3d**) reported here were readily soluble in most organic solvents (e.g., CH_2Cl_2, $CHCl_3$, and THF), a significant improvement over a previous method.[24] We further demonstrate with one of these Pcs (**3d**) the click modification approach to produce a small library of Pc derivatives by reaction with a variety of azides, therefore producing seven different Pcs from a single Linstead cyclization reaction.[25]

Results and Discussion

Click chemistry modification of Pcs can be approached either from azide- or alkyne-terminated Pcs as a partner in the CuAAC reaction. Since the acetylenic functional group can easily be carried through the synthetic steps leading to the Pc chromophore, we chose to use alkyne-terminated Pcs as one of the clickable partners in the CuAAC reaction. Phthalonitrile (Pn) **1** was synthesized by nucleophilic substitution on 4,5-dichlorophthalonitrile with 4-hydroxythiophenol (Scheme 1). Due to the higher nucleophilicity of sulfur relative to oxygen, the S-arylation isomer was obtained exclusively. The phenolic sites of Pn **1** provide facile access to alkylated derivatives using either Williamson ether or Mitsunobu conditions.[26,27] To determine a suitable alkyne-linker length that would result in sufficient solubility of the corre-

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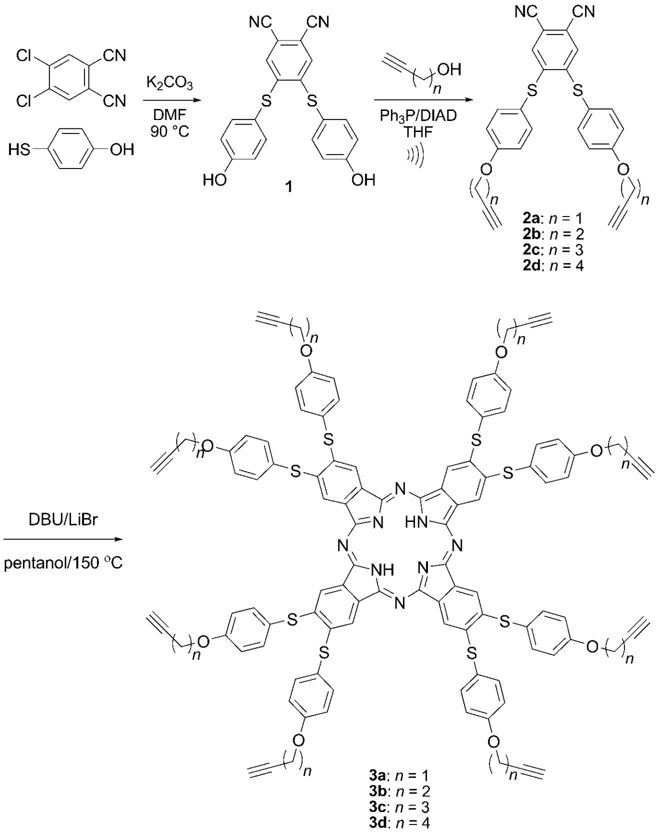


Scheme 1. Synthesis of “clickable” phthalocyanines **3a–3d**.

sponding clickable phthalocyanine, a series of phthalonitriles **2a–2d** were synthesized using a Mitsunobu protocol between phthalonitrile **1** and a series of ω-alkyn-1-ols in the presence of diisopropyl azodicarboxylate (DIAD) and triphenyl phosphine under sonication conditions (Scheme 1). In all cases colorless solids were obtained in acceptable yields.

The corresponding octaalkynyl Pcs were synthesized by Linstead macrocyclization[25] of Pns **2a–2d** (Scheme 1). Since unprotected terminal alkynes are less tolerant to hard nucleophilic bases such as alkoxide, 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was used as an alternate non-nucleophilic base.[28] Pc **3a** could not be purified or characterized due to its low solubility in common organic solvents (THF, CH_2Cl_2, $CHCl_3$, dimethylacetamide (DMAc), and *N*-methylpyrrolidone (NMP)). Pcs **3b–3d** were readily soluble in CH_2Cl_2, $CHCl_3$, and THF, and their purification was accomplished by a combination of precipitation and flash chromatography. Due to solution-phase aggregation, NMR spectra could not be obtained for Pc **3b** and only ^{1}H NMR spectra could be obtained for Pcs **3c** and **3d**. Pcs **3b–3d** exhibit intense Q and B bands in the UV/Vis spectra, the former of which are split due to the electronic transition from a doubly degenerate HOMO to LUMO of the molecule in these unmetalated macrocycles (Figure 1a).[29] The spectra were consistent with non-aggregated Pc cores with

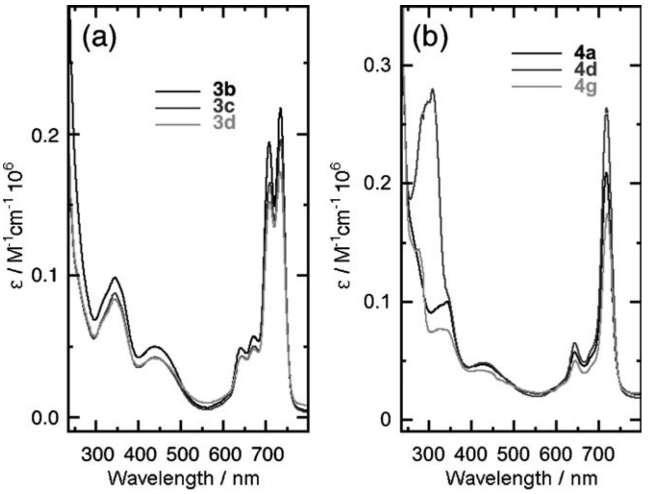


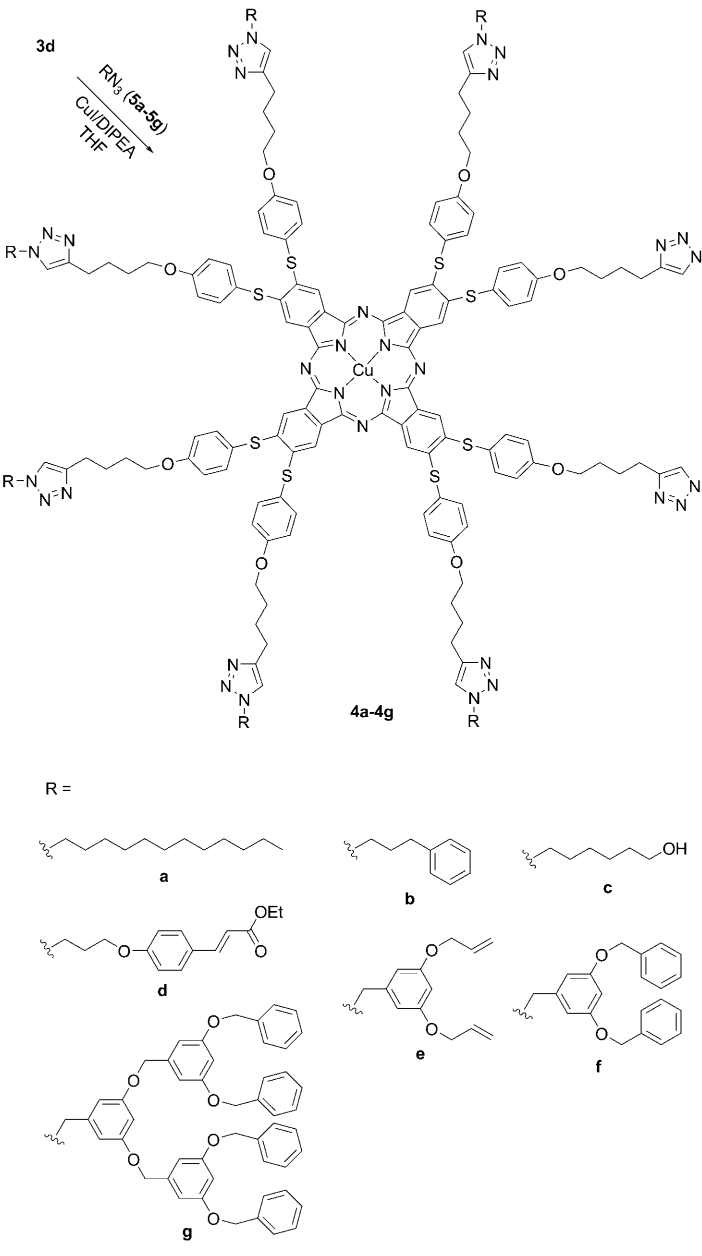
Figure 1. UV/Vis spectroscopy of a) clickable (**3a–3c**) and b) clicked Pcs (**4a**, **4d**, and **4g**).

Q-band absorptions at 709 and 735 nm, vibrational bands at 642 and 673 nm, and B-bands at 345 and 441 nm.

The most soluble Pc in the series (**3d**) was chosen as the scaffold for the synthesis of a small library of Pc derivatives using click chemistry. Initially, we investigated click conditions using the reaction between Pc **3d** and azide **5d** as a model. The catalyst generally employed for these reactions, $Cu(Ph_3P)_3Br$,[30] failed to provide fully clicked Pc as assayed by MALDI mass spectrometry, even with a large excess of azide. However, using CuI as catalyst led to a complete reaction when an excess of azide (10 equiv with respect to alkyne) was used in presence of diisopropylethylamine (DIPEA) as a base. Beneficially, the copper-mediated click reaction resulted in metalated Pcs starting from octaalkynyl Pc **3d** in a single step (Scheme 2). Copper Pcs have high charge carrier mobility, which is crucial for certain applications such as field-effect transistors.[31]

To demonstrate the generality and functional group tolerance of the click reaction on acetylene-terminated phthalocyanine **3d**, we chose alkyl azides **5a** and **5b**, hydroxy azide **5c**, crosslinkable azides **5d** and **5e**, and dendritic azides **5f** and **5g** to prepare a small library of peripherally modified Pcs directly from Pc **3d**. The synthesis of azides **5a–5g** was accomplished by reaction of corresponding chlorides or bromides with sodium azide in DMF. The CuAAC conditions determined optimum for the click reaction between **3d** and **5d** (CuI/DIPEA/THF) were used for the synthesis of all clicked Pcs **4a–4g**. Excess copper from the clicked Pcs **4a–4g** were removed by repeated washing of the Pc solution in CH_2Cl_2 with ethylenediaminetetraacetic acid (EDTA) and then dilute acid. All clicked Pcs were obtained as green solids in moderate to excellent yields after purification by flash column chromatography followed by precipitation in hexanes.

Pcs **4a–4g** were structurally characterized by ^{1}H NMR, MALDI-TOF MS, UV/Vis spectroscopy, and gel permeation chromatography (GPC). The appearance of the Q and B



Scheme 2. Click reaction between phthalocyanine **3d** and azides **5a–5g**.

bands in the UV/Vis spectra were identical for all clicked Pcs, consistent with the identical nature of the central Pc chromophore in all eight compounds (Figure 1b). The absorptivities of the Q-bands of **4a–4g** were all around $10^5\,\text{M}^{-1}\text{cm}^{-1}$ as determined by Beer's law analysis (see the Supporting Information). Metalation of the macrocycle by copper was confirmed by the collapsed Q-band at 719 nm for all clicked Pcs. Representative examples of UV/Vis spectra (Figure 1b) illustrate that the contrasting portion of the absorbance profile lies to the blue of 400 nm. Although compound **4a** contains no chromophoric portions other than the Pc macrocycle, and hence exhibits no additional absorbance, more dramatic is the cinnamate chromophore on compounds **4d** that gives rise to a strongly absorbing band at around 309 nm. The band arising from absorption of the benzylaryl ether dendrons at 280 nm in **4g** is also evident.

The GPC traces of octaalkynyl Pcs **3b–3d** were indicative of monodisperse materials, and a hydrodynamic size increase was observed commensurate with the increase in molecular weight on proceeding from **3b**→**3c**→**3d** (Figure 2a).

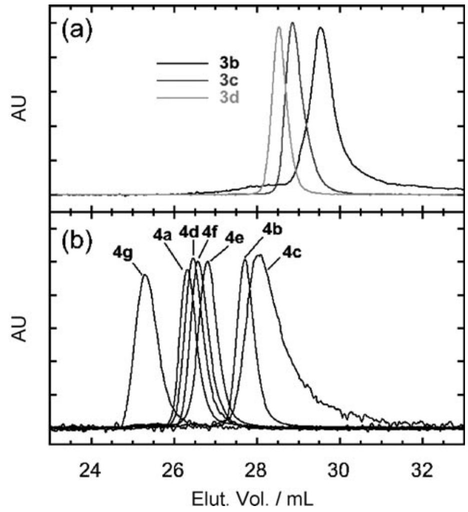


Figure 2. GPC chromatograms of a) clickable (**3a–3c**) and b) clicked Pcs (**4a–4g**).

The GPC traces of **4a–4g** indicate materials with larger hydrodynamic sizes than the corresponding starting material **3d** (Figure 2b). As expected, compounds **4b** and **4c** were among the smaller of the clicked derivatives, and exhibited similar elution volumes. The largest of the clicked derivatives was second-generation dendrimer **4g**.

Thin films of **4a–4g** were prepared to investigate the nature of the Pcs in the condensed state. Spin-coated films on quartz substrates were fabricated from CH_2Cl_2 solutions ($\approx 10^{-3}\,\text{M}$) of octa-substituted Pcs **4a–4g**. All compounds formed crack-free solid films exhibiting a broadened Q-band region indicative of aggregation (Figure 3a). Although we have previously observed varying degrees of frustration of aggregation with dendritic substituents on the periphery of Pc chromophores,[26,27] the presence of second-generation dendrons on the periphery of **4g** is clearly insufficient to maintain site isolation of the core chromophore. It is likely that the presence of the linker between the Pc and the dendrons contributes to mitigating the site-isolation effect of the dendritic periphery. Indeed, in octa-substituted dendritic Pcs that exhibited effective site isolation,[26,27] the dendrons were directly attached to the hydroquinone moieties of the phthalonitrile precursor analogous to **1**.

We have performed a preliminary investigation of the utility of the crosslinking residues installed on the periphery of the Pc core in cinnamate derivative **4d**. Robust condensed structures were fabricated from thin films (about 60 nm thick as determined by ellipsometry) of **4d** spin-cast from approximately $10^{-3}\,\text{M}$ CH_2Cl_2 solutions onto quartz (500 rpm

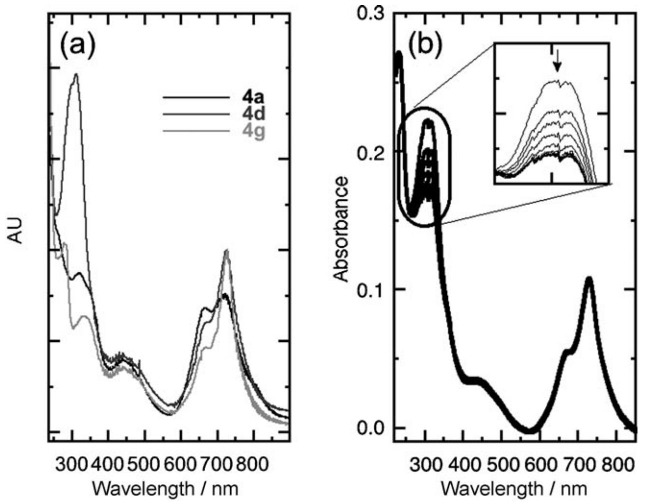


Figure 3. a) UV/Vis spectroscopy of thin films of clicked Pcs (**4a**, **4d**, and **4g**) spin-coated on quartz; b) UV absorption spectra of a spin-cast film of **4e** before, during (10 min intervals, 0→90 min), and after irradiation and wet development (bold trace).

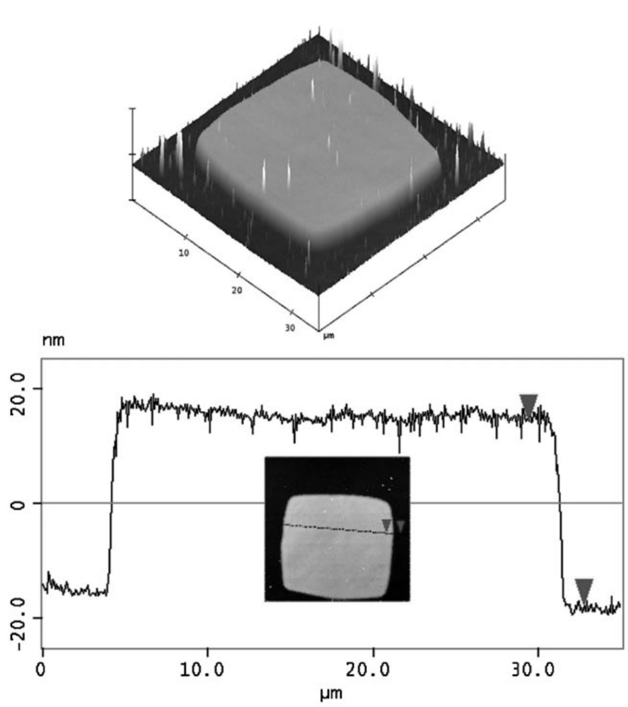


Figure 4. AFM images (full images in the Supporting Information) of patterned Pc **4d** showing 30 µm square features in a thin film.

for 1 min). The conditions necessary for successful crosslinking of these films were investigated by subjecting them to irradiation ($\lambda = 310$ nm, 6 mm slits) using a 75 W Xe arc lamp. The solid state [2+2] photodimerization of the cinnamate residues was easily monitored by changes in the UV absorbance (see the Supporting Information).[32] Continuous irradiation resulted in a decrease in the cinnamate peak in the UV for **4d** (32% overall decrease at 312 nm, λ_{max}) after 90 min. The decrease in cinnamate absorbance is most likely due to both $E \rightarrow Z$ isomerization, as well as [2+2] photodimerization. Subsequent wet development (CH_2Cl_2 for 2 min) resulted in negligible change in absorbance for the film of **4d**, indicating the formation of an insoluble crosslinked network (Figure 3b).

With the conditions for effective crosslinking determined, we next produced features from these thin films with pattern sizes in the 30 µm range and characterized them by optical microscopy and AFM. Films with around 30 µm feature sizes were produced by irradiation (310 nm for 90 min) of a film masked with a transmission electron microscopy (TEM) copper grid and subsequent wet development in CH_2Cl_2. Patterns of **4d** were visualized by atomic force microscopy (AFM). The positive tone images possessed resolved features with sharp edges with the dimensions of the copper grid pattern used as a mask. AFM images (Figure 4) of the patterned thin film confirmed the feature dimensions (30×30 µm) as well as the thickness (≈ 32 nm). The similar surface roughness of the films before and after crosslinking and wet development (≈ 0.9 nm RMS) is evidence of complete polymerization of the pendant cinnamate residues.

Conclusion

We have demonstrated the modification of a phthalocyanine by click reaction as a simple and general route to numerous Pc derivatives. Synthesis of a series of near-IR-absorbing alkyne-terminated Pcs has been reported and the suitable length of alkyne linker necessary to impart solubility has been optimized. Click conditions have been optimized for the preparation of fully clicked Pc derivatives that led to a small library of Pc derivatives starting from a single Pc. We have demonstrated that the Pc bearing a cinnamate residue can be photochemically polymerized to obtain an insoluble network. We have also shown that the crosslinking ability of the Pc can be utilized to obtain features by photopatterning.

Experimental Section

All reactions were run under a nitrogen or argon atmosphere unless otherwise specified. All chemicals were purchased from Aldrich, Acros Organics, TCI America, and Alfa Aesar and used without further purification. Azides 1-azidododecane (**5a**),[24] 3-azidopropylbenzene (**5b**),[33] 6-azidohexan-1-ol (**5c**),[34] ethyl 4-(3-azidopropoxy)cinnamate (**5d**),[35] and 3,5-dibenzyloxybenzyl azide (**5f**),[34] and 3,5-(di(3,5-dibenzyloxy)benzyloxy)benzyl azide (**5g**)[36] were prepared according to the literature. Anhydrous THF was distilled from sodium and benzophenone under argon. ^{1}H NMR spectra were recorded on commercial instrumentation in $CDCl_3$ and were calibrated using TMS as internal standard. Gel permeation chromatography (GPC) was performed in a tetrahydrofuran mobile phase with a Waters 2695 isocratic pump running three Jordi Gel DVB columns (pore sizes 100, 500, 1000 Å) with a Waters 2996 Photodiode Array UV/Vis detector. Mass spectra were obtained from the Mass Spectrometry Facility, Department of Chemistry and Biochemistry, University of Arizona. Flash column chromatography and TLC were performed using silica gel 60 and Silica Gel 60 F_{254} plates respectively from EMD.

4,5-Bis(4-hydroxyphenylthio)phthalonitrile (1): A mixture of 4-hydroxythiophenol (9.6 g, 76 mmol), K_2CO_3 (35.0 g, 250 mmol), and DMSO (200 mL) was stirred at room temperature under argon for 30 min. Dichlorophthalonitrile (5.0 g, 25 mmol) was then added and the reaction mixture was maintained at 90 °C with stirring for 12 h. The reaction mixture was allowed to cool to room temperature before being poured into 1 M HCl (750 mL) to induce precipitation. The precipitate was filtered, washed with water (1000 mL), and redissolved in ethyl acetate (350 mL). The resulting solution was washed (H_2O) until the aqueous layer became neutral, dried ($MgSO_4$), and the solvent was removed under reduced pressure to obtain a yellow solid. The yellow solid was powdered using a mortar and pestle, and then dispersed in CH_2Cl_2 (600 mL) with vigorous stirring. The precipitate was filtered to obtain **1** (8.77 g, 91 %) as a yellow powder: m.p. 268–270 °C; ^1H NMR (500 MHz, $[D_6]$DMSO) $\delta = 10.23$ (s, 2H), 7.44–7.42 (d, $J = 9.0$ Hz, 4H), 6.95 (s, 2H), 6.95–6.94 ppm (d, $J = 9$ Hz, 4H); ^{13}C NMR (125 MHz, $[D_6]$DMSO) $\delta = 159.7$, 143.8, 137.3, 128.5, 117.6, 115.6, 115.2, 110.6 ppm; MS (ESI, negative mode): m/z: 412.7 $[M+HCl]^-$; $C_{20}H_{13}N_2O_2S_2Cl$ requires 412.0. elemental analysis calcd for $C_{20}H_{12}N_2O_2S_2$: C 63.81, H 3.21, N 7.44; found: C 63.10, H 3.53, N 7.29.

4,5-Bis(4-(prop-2-ynyloxy)phenylthio)phthalonitrile (2a): A solution of 2-propyn-1-ol (0.5, 9 mmol), phthalonitrile **1** (1.0 g, 2.6 mmol), triphenyl phosphine (2.4 g, 9.3 mmol), and DIAD (1.9 g, 9.3 mmol) in THF (20 mL) was sonicated at room temperature under argon for 3 h. The reaction mixture was diluted with CH_2Cl_2 (300 mL), washed with water (3 × 100 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure to obtain crude product as a yellow solid. The crude product was powdered using a mortar and pestle, dispersed in hexanes (500 mL) with vigorous stirring and then filtered to obtain a colorless solid that was purified by flash chromatography (SiO_2, 70 % CH_2Cl_2 in hexanes) to afford **2a** (0.51 g, 42 %) as a colorless solid: m.p. 176–178 °C; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.49$–7.48 (d, $J = 8.8$ Hz, 4H), 7.11–7.10 (d, $J = 8.8$ Hz, 4H), 6.88 (s, 2H), 4.77–4.76 (d, $J = 2.5$ Hz, 4H), 2.58–2.57 ppm (t, $J = 4.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 160.0$, 144.8, 137.6, 129.4, 119.7, 117.5, 115.9, 111.7, 78.1, 76.8, 56.4 ppm; MS (ESI, positive mode): m/z: 475.1 $[M+Na]^+$; $C_{26}H_{16}N_2O_2S_2Na$ requires 475.0; elemental analysis calcd for $C_{26}H_{16}N_2O_2S_2$: C 69.00, H 3.56, N 6.19; found: C 68.52, H 3.80, N 6.09.

4,5-Bis(4-(but-3-ynyloxy)phenylthio)phthalonitrile (2b): Following the procedure for **2a**, 3-butyn-1-ol (0.6, 9 mmol), phthalonitrile **1** (1.0 g, 2.6 mmol), triphenyl phosphine (2.4 g, 9.3 mmol), and DIAD (1.9 g, 9.3 mmol), after flash chromatography (SiO_2, CH_2Cl_2), afforded **2b** (0.34 g, 27 %) as a colorless solid: m.p. 158–160 °C; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.47$–7.46 (d, $J = 8.5$ Hz, 4H), 7.04–7.02 (d, $J = 8.5$ Hz, 4H), 6.85 (s, 2H), 4.18–4.15 (t, $J = 13.5$ Hz, 4H), 2.75–2.72 (t, $J = 16.5$ Hz, 4H), 2.06 ppm (t, $J = 2.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 160.9$, 144.9, 137.7, 129.3, 119.1, 117.2, 115.9, 111.9, 80.3, 70.6, 66.6, 20.0 ppm; MS (ESI, positive mode) m/z: 503.0 $[M+Na]^+$; $C_{28}H_{20}N_2O_2S_2Na$ requires 503.0; elemental analysis calcd for $C_{28}H_{20}N_2O_2S_2$: C 69.97, H 4.19, N 5.83; found: C 69.74, H 4.43, N 5.84.

4,5-Bis(4-(pent-4-ynyloxy)phenylthio)phthalonitrile (2c): Following the procedure for **2a**, 4-pentyn-1-ol (0.8, 9 mmol), phthalonitrile **1** (1.0 g, 2.6 mmol), triphenyl phosphine (2.4 g, 9.3 mmol), and DIAD (1.9 g, 9.3 mmol), after flash chromatography (SiO_2, 70 % CH_2Cl_2 in hexanes), afforded **2c** (0.61 g, 45 %) as a colorless solid: m.p. 136–138 °C; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.46$–7.45 (d, $J = 11.5$ Hz, 4H), 7.02–7.00 (d, $J = 11.5$ Hz, 4H), 6.85 (s, 2H), 4.14–4.12 (t, $J = 12$ Hz, 4H), 2.45–2.41 (t, $J = 16.5$ Hz, 2H), 2.07–2.01 (m, 4H), 1.99 ppm (t, $J = 3$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 161.4$, 144.9, 137.7, 129.2, 118.5, 117.1, 116.0, 111.5, 83.6, 69.6, 66.9, 28.5, 15.6 ppm; MS (ESI, positive mode): m/z: 531.1 $[M+Na]^+$; $C_{30}H_{24}N_2O_2S_2Na$ requires 531.1; elemental analysis calcd for $C_{30}H_{24}N_2O_2S_2$: C 70.84, H 4.76, N 5.51; found: C 70.94, H 5.10, N 5.60.

4,5-Bis(4-(hex-5-ynyloxy)phenylthio)phthalonitrile (2d): Following the procedure for **2a**, 5-hexyn-1-ol (1.6, 16 mmol), phthalonitrile **1** (1.8 g, 4.7 mmol), triphenyl phosphine (4.4 g, 16.0 mmol), and DIAD (3.4 g, 16.0 mmol), after flash chromatography (SiO_2, CH_2Cl_2), afforded **2d** (1.7 g, 69 %) as a colorless solid: m.p. 118–120 °C; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.46$–7.44 (d, $J = 9.0$ Hz, 4H), 7.01–6.99 (d, $J = 9$ Hz, 4H), 6.85 (s, 2H), 4.07–4.05 (t, $J = 12.5$ Hz, 4H), 2.31–2.29 (m, 4H), 1.98–1.95 (m, 6H), 1.77–1.75 ppm (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 161.1$, 144.5, 137.2, 128.74, 117.9, 116.6, 115.5, 111.0, 83.8, 68.7, 67.6, 28.1, 25.0, 18.1 ppm; MS (ESI, positive mode): m/z: 559.1 $[M+Na]^+$; $C_{32}H_{28}N_2O_2S_2Na$ requires 559.1; elemental analysis calcd for $C_{32}H_{28}N_2O_2S_2$: C 71.61, H 5.26, N 5.22; found: C 71.66, H 5.55, N 5.15.

2,3,9,10,16,17,23,24-Octa(4-(prop-2-ynyloxy)phenthio)phthalocyanine (3a): A mixture of phthalonitrile **2a** (0.20 g, 0.44 mmol), DBU (0.06 g, 0.44 mmol), LiBr (3.8 mg, 0.04 mmol), and 1-pentanol (10 mL) was maintained at 145 °C under argon for 48 h. The dark green reaction mixture was allowed to cool to room temperature before precipitating into methanol to obtain a green precipitate. The precipitate was insoluble in CH_2Cl_2, chloroform, THF, ethyl acetate, methanol, acetone, NMP, and hexanes. No characterization data was obtained on this material.

2,3,9,10,16,17,23,24-Octa(4-(but-3-ynyloxy)phenthio)phthalocyanine (3b): Following the procedure for **3a**, phthalonitrile **2b** (0.20 g, 0.44 mmol), DBU (0.06 g, 0.4 mmol), LiBr (3.8 mg, 0.04 mmol), and 1-pentanol (10 mL), after flash chromatography (SiO_2, EtOAc–hexanes, gradient from 0:100 to 30:70, CH_2Cl_2, then THF), followed by precipitation in hexanes afforded **3b** (0.04 g, 43 %) as a green solid: m.p. 360 °C dec.; MS (MALDI): m/z: 1986.0 $[M+Cu]^+$; $C_{112}H_{82}N_8O_8S_8Cu$ requires 1986.3; elemental analysis calcd for $C_{112}H_{82}N_8O_8S_8$: C 69.90, H 4.29, N 5.82; found: C 69.99, H 4.09, N 5.84.

2,3,9,10,16,17,23,24-Octa(4-(pent-4-ynyloxy)phenthio)phthalocyanine (3c): Following the procedure for **3a**, phthalonitrile **2c** (0.2 g, 0.4 mmol), DBU (0.06 g, 0.4 mmol), and LiBr (3.4 mg, 0.04 mmol), after flash chromatography (SiO_2, EtOAc–hexanes, gradient from 0:100 to 30:70, CH_2Cl_2, then THF), followed by precipitation in hexanes afforded **3c** (0.05 g, 26 %) as a green solid: m.p. 350 °C dec.; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 8.84$ (s, 8H), 7.64–7.62 (d, $J = 9.0$ Hz, 16H), 7.07–7.05 (d, $J = 9.0$ Hz, 16H), 4.19–4.18 (t, $J = 12.0$ Hz, 16H), 2.45–2.44 (m, 16H), 2.08–2.03 (m, 8H), 1.97 ppm (m, 16H); MS (MALDI): m/z: 2035.5 $[M]^+$; $C_{120}H_{98}N_8O_8S_8$ requires 2035.5; elemental analysis calcd for $C_{120}H_{98}N_8O_8S_8$: C 70.77, H 4.85, N 5.50; found: C 70.47, H 5.00, N 5.50.

2,3,9,10,16,17,23,24-Octa(4-(hex-5-ynyloxy)phenthio)phthalocyanine (3d): Following the procedure for **3a**, phthalonitrile **2d** (1.77 g, 3.30 mmol), DBU (0.50 g, 3.3 mmol), LiBr (0.02 g, 0.3 mmol), and 1-pentanol (50 mL), after flash chromatography (SiO_2, EtOAc–hexanes, gradient from 0:100 to 30:70, CH_2Cl_2, then THF), followed by precipitation in hexanes afforded (0.66 g, 37 %) as a green solid: m.p. 320 °C dec.; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 8.72$ (s, 8H), 7.62–7.60 (d, $J = 9.0$ Hz, 16H), 7.04–7.02 (d, $J = 9$ Hz, 16H), 4.09–4.06 (t, $J = 12.5$ Hz, 16H), 2.29–2.25 (m, 16H), 1.98–1.92 (m, 24H), 1.77–1.71 ppm (m, 16H); MS (MALDI): m/z: 2147.7 $[M]^+$; $C_{127}H_{114}N_8O_8S_8$ requires 2147.6; elemental analysis calcd for $C_{128}H_{114}N_8O_8S_8$: C 71.54, H 5.35, N 5.21; found: C 71.67, H 5.70, N 5.47.

Copper 2,3,9,10,16,17,23,24-Octa(4-(4-(1-dodecyl-1H-1,2,3-triazol-4-yl)-butoxy)phenthio)phthalocyanine (4a): A mixture of **3d** (30.0 mg, 14.0 µmol), CuI (4.2 mg, 22 µmol), compound **5a** (0.2 g, 1 mmol), DIPEA (30.0 mg, 0.2 mmol), and dry THF (15 mL) was degassed and back filled with argon three times and then stirred for 48 h under argon. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with EDTA (0.1 M, 4 × 100 mL), HCl (1 N, 4 × 100 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated and crude product was subjected to flash chromatography (SiO_2, MeOH–CH_2Cl_2, gradient from 0:100 to 4:96), followed by precipitation in hexanes afforded **4a** (43 mg, 79 %) as a green solid: m.p. 320 °C dec.; ^1H NMR (500 MHz, $CDCl_3$) δ 7.44–6.58 (m, 48H), 4.26 (brs, 16H), 4.03 (brs, 16H), 2.76 (brs, 16H), 1.84 (brs, 32H), 1.23–1.20 (m, 160H), 0.67 ppm (brs, 24H); MS (MALDI): m/z: 3898.8 $[M^+]$; $C_{224}H_{312}N_{32}O_8S_8Cu$ requires 3898.2; elemental analysis calcd for $C_{224}H_{312}N_{32}O_8S_8Cu$: C 68.61, H 8.01, N 11.47; found: C 68.96, H 8.06, N 11.49.

Copper 2,3,9,10,16,17,23,24-Octa(4-(4-(1-(3-phenylpropyl)-1H-1,2,3-triazol-4-yl)butoxy)phenthio)phthalocyanine (4b): Following the procedure for **4a**, compound **3d** (30.0 mg, 14.0 μmol), CuI (4.2 mg, 22 μmol), **5b** (0.2 g, 1 mmol), DIPEA (30.0 g, 0.2 mmol), and dry THF (15 mL), after flash chromatography (SiO_2, MeOH–CH_2Cl_2, gradient from 0:100 to 4:96), followed by precipitation in hexanes afforded **4b** (42 mg, 87%) as a green solid: m.p. 280 °C dec.; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.46–6.84$ (brm, 88H), 4.26 (brm, 16H), 4.03 (brs, 16H), 2.76 (brs, 16H), 1.97 (brs, 16H), 1.23 (brm, 32H), 0.83 ppm (brm, 16H); MS (MALDI): *m/z*: 3563.7 $[M+Cu^+]$; $C_{200}H_{200}N_{32}O_8S_8Cu_2$ requires 3563.2; elemental analysis calcd for $C_{200}H_{200}N_{32}O_8S_8Cu$: C 68.63, H 5.76, N 12.81; found: C 68.24, H 6.10, N 12.57.

Copper 2,3,9,10,16,17,23,24-Octa(4-(4-(1-(6-hydroxyhexyl)-1H-1,2,3-triazol-4-yl)butoxy)phenthio)phthalocyanine (4c): Following the procedure for **4a**, compound **3d** (30.0 mg, 14.0 μmol), CuI (4.2 mg, 22 μmol), **5c** (0.2 g, 1 mmol), DIPEA (30.0 mg, 0.2 mmol), and dry THF (15 mL), after flash chromatography SiO_2, MeOH–CH_2Cl_2, gradient from 0:100 to 25:75), followed by precipitation in water and hexanes afforded **4c** (22.4 mg, 49%) as a green solid: m.p. 330 °C dec.; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.65–6.55$ (m, 48H), 4.28 (brs, 16H), 4.01 (brs, 16H), 3.51–3.46 (m, 8H) , 3.34 (brs, 8H) , 2.74 (brs, 16H), 1.97–1.47 (m, 64H), 1.45–1.16 ppm (m, 32H); MS (MALDI): *m/z*: 3355.8 $[M^+]$; $C_{176}H_{216}N_{32}O_{16}S_8Cu$ requires 3355.4; elemental analysis calcd for $C_{176}H_{216}N_{32}O_{16}S_8Cu$: C 62.99, H 6.49, N 13.36; found: C 62.60, H 6.36, N 13.32.

Copper 2,3,9,10,16,17,23,24-Octa(4-(4-(1-(3-(4-(3-ethoxy-3-oxoprop-1-en-1-yl)-phenoxy)propyl)-1H-1,2,3-triazol-4-yl)butoxy)phenthio)phthalocyanine (4d): Following the procedure for **4a**, compound **3d** (30.0 mg, 14.0 μmol), CuI (4.2 mg, 22 μmol), compound **5d** (0.3 g, 1 mmol), DIPEA (30.0 mg, 0.2 mmol), and dry THF (15 mL), after flash chromatography (SiO_2, MeOH–CH_2Cl_2, gradient from 0:100 to 4:96), followed by precipitation in hexanes afforded **4d** (59 mg, 95%) as a green solid: m.p. 220 °C dec.; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.23–6.79$ (m, 80H), 4.47 (brs, 16H), 4.16 (brs, 16H), 4.07 (brs, 32H), 2.82 (brs, 16H), 2.32 (brs, 16H), 1.59 (brs, 16H), 1.51 (brs, 32H), 1.25 (brs, 24H); MS (MALDI): *m/z*: 4475.9 $[M+Cu]^+$; $C_{240}H_{248}N_{32}O_{32}S_8Cu_2$ requires 4475.5; elemental analysis calcd for $C_{240}H_{248}N_{32}O_{32}S_8Cu$: C 65.32, H 5.66, N 10.16; found: C 64.90, H 5.40, N 9.90.

Copper 2,3,9,10,16,17,23,24-Octa(4-(4-(1-(3,5-bis(allyloxy)benzyl)-1H-1,2,3-triazol4-yl)butoxy)phenthio)phthalocyanine (4e): Following the procedure for **4a**, compound **3d** (30 mg, 14.0 μmol), CuI (4.2 mg, 22 μmol), compound **5e** (0.3 g, 1 mmol), DIPEA (30.0 mg, 0.2 mmol), and dry THF (15 mL), after flash chromatography (SiO_2, MeOH–CH_2Cl_2, gradient from 0:100 to 4:96), followed by precipitation in hexanes afforded **4e** (34 mg, 64%) as a green solid: m.p. 230 °C dec.; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.85–6.05$ (m, 72H), 5.88 (brs, 16H), 5.28–5.17 (m, 48H), 4.34 (brs, 32H), 3.95 (brs, 16H), 2.72 (brs, 16H), 1.83 (brs, 16H), 1.55 ppm (brs, 16H); MS (MALDI): *m/z*: 4171.5 $[M]^+$; $C_{232}H_{232}N_{32}O_{24}S_8Cu$ requires 4171.5; elemental analysis calcd for $C_{232}H_{232}N_{32}O_{24}S_8Cu$: C 66.78, H 5.60, N 10.74; found: C 66.47, H 5.82, N 10.39.

Copper 2,3,9,10,16,17,23,24-Octa(4-(4-(1-(3,5-bis(benzyloxy)benzyl)-1H-1,2,3-triazol-4-yl)butoxy)phenthio)phthalocyanine (4f): Following the procedure for **4a**, compound **3d** (30.0 mg, 14.0 μmol), CuI (4.2 mg, 22 μmol), **5f** (0.4 g, 1 mmol), DIPEA (30.0 mg, 0.23 mmol), and dry THF (15 mL), after flash chromatography (SiO_2, MeOH–CH_2Cl_2, gradient from 0:100 to 4:96), followed by precipitation in hexanes afforded **4f** (60 mg, 87%) as a green solid: mp. 330 °C dec.; ^{1}H NMR (500 MHz, $CDCl_3$ $\delta = 7.44–6.46$ (m, 152H), 5.38–5.28 (m, 16H), 4.97–4.82 (m, 32H), 3.97 (brs, 16H), 2.72–2.71 (m, 16H), 2.03 (m, 16H), 1.55 ppm (m, 16H); MS (MALDI): *m/z*: 4973.7 $[M]^+$; $C_{296}H_{264}N_{32}O_{24}S_8Cu$ requires 4973.5; elemental analysis calcd for $C_{296}H_{264}N_{32}O_{24}S_8Cu$: C 71.48, H 5.35, N 9.01; found: C 71.66, H 5.07, N 9.32.

Copper 2,3,9,10,16,17,23,24-Octa(4-(4-(1-(3,5-bis((3,5-bis(benzyloxy)benzyl)oxy)benzyl)-1H-1,2,3-triazol-4-yl)butoxy)phenthio)phthalocyanine (4g): Following the procedure for **4a**, phthalocyanine **3d** (30.0 mg, 13.9 μmol), CuI (4.2 mg, 22 μmol), **5g** (0.9 g, 1 mmol), DIPEA (30.0 mg, 0.23 mmol), and dry THF (15 mL), after flash chromatography (SiO_2, MeOH–CH_2Cl_2, gradient from 0:100 to 4:96), followed by precipitation in hexanes afforded **4g** (85 mg, 73%) as a green solid: m.p. 330 °C dec.; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.85–5.95$ (m, 208H), 5.54–4.32 (m, 184H), 3.95 (brs, 16H), 2.69 (brs, 16H), 1.79 (brs, 16H), 1.53 ppm (brs, 16H); MS (MALDI): *m/z*: 8434.1 $[M+Cu]^+$; $C_{520}H_{456}N_{32}O_{56}S_8Cu_2$ requires 8433.0; elemental analysis calcd for $C_{520}H_{456}N_{32}O_{56}S_8Cu$: C 74.62, H 5.49, N 5.36; found: C 74.22, H 5.80, N 5.42.

3,5-Diallyloxybenzyl azide (5e): A mixture 3,5-diallyloxybenzyl bromide[37] (2.2 g, 7.8 mmol), NaN_3 (2.5 g, 39.2 mmol), and DMF (15 mL) was stirred at room temperature under argon for 16 h. Reaction mixture was diluted with CH_2Cl_2 (150 mL) and filtered. The organic layer was washed with water (2 × 100 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure to obtain **5e** (1.4 g, 73%) as a colorless liquid: ^{1}H NMR (500 MHz, CDCl3) $\delta = 6.46–6.45$ (s, 3H), 6.07–5.99 (m, 2H), 5.42–5.38 9 (d, $J = 18.5$ Hz, 2H), 5.29–5.26 (d, $J = 12$ Hz, 2H), 4.51–4.50 (d, $J = 5$ Hz, 4H), 4.23 ppm (s, 2H); ^{13}C NMR (125 MHz, CDCl3) $\delta = 160.4$, 137.9, 133.4, 118.1, 107.4, 102.0, 69.3, 55.2 ppm; MS (ESI): *m/z*: 246.1 $[MH^+]$; $C_{13}H_{16}N_3O_2$ requires 246.1. The product tends to decompose and hence it was immediately used for the click reaction.

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