Supplementary Supporting Information

Ammonia-Free and One-Pot Synthesis of Di-Chloro Silicon Phthalocyanine and Naphthalocyanine

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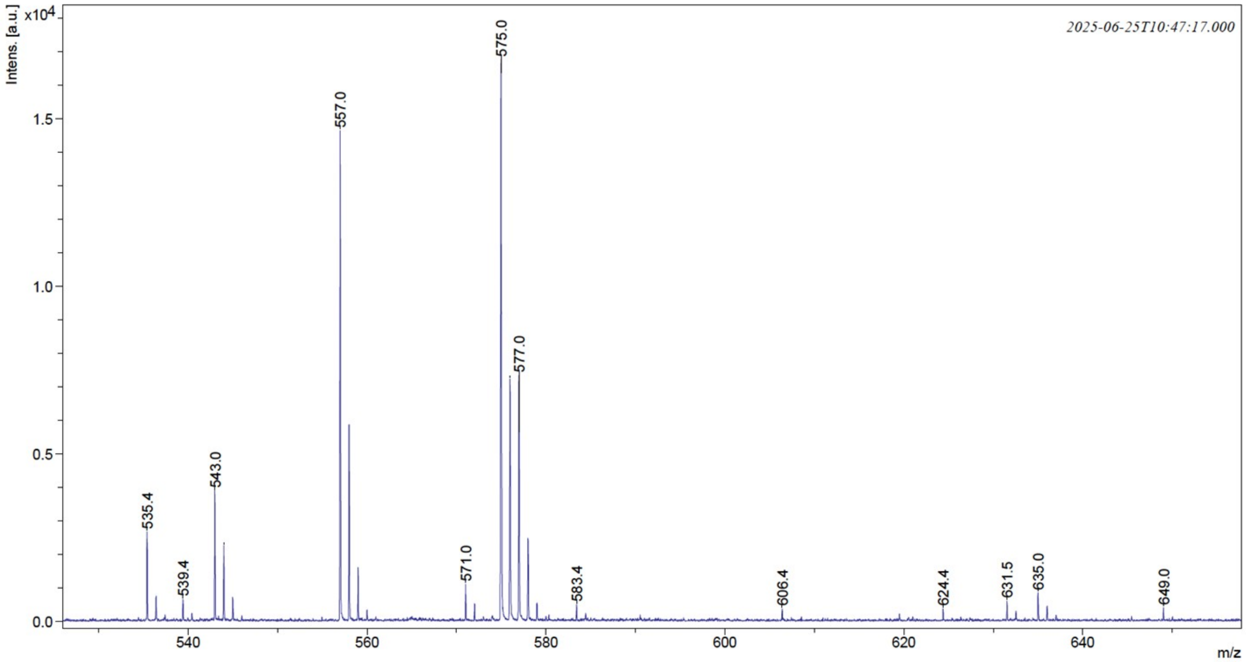
SUPPORTING INFORMATION/ASSOCIATED CONTENT

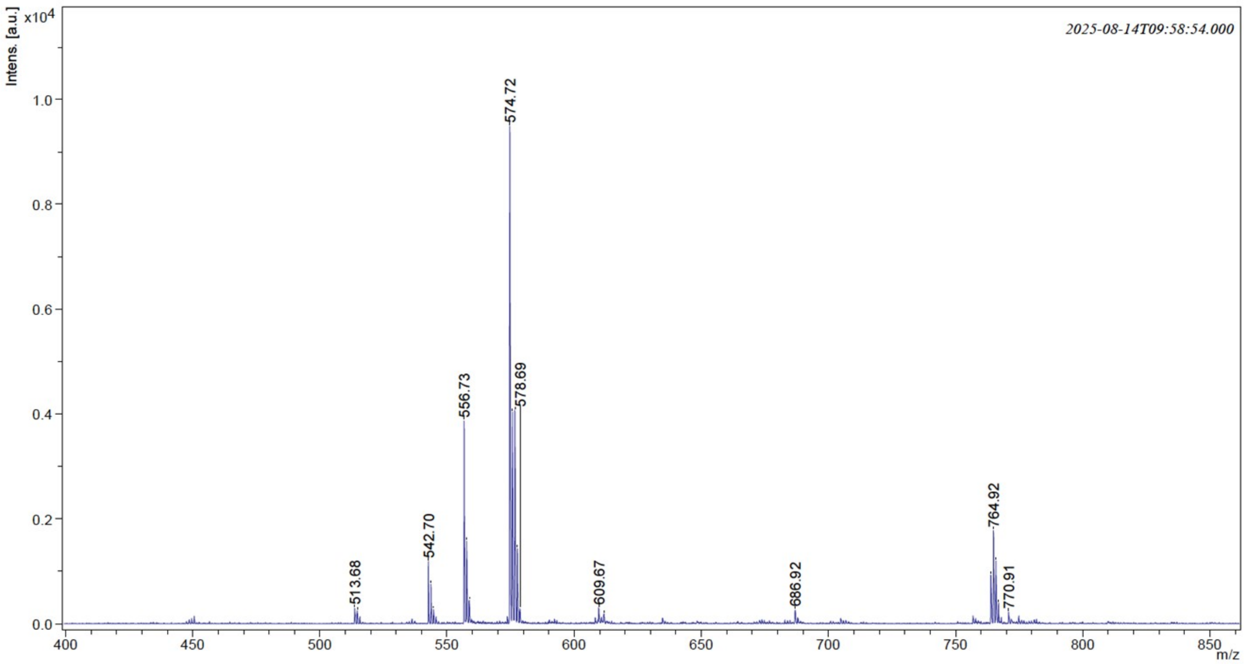
Characterization

The molecular weight of both crude materials (Cl_2-SiPc and Cl_2-SiNc) was assessed using matrix-assisted laser desorption/ionization and time-of-flight (TOF) mass spectrometry (MALDI-TOF MS), using a dithranol-tetrahydrofuran matrix. Secondly, the optical behavior of compounds **1** and **2** was assessed by UV-Visible spectroscopy in 1,2-dichlorobenzene solution using a Perkin-Elmer Lambda 25 spectrometer in a PerkinElmer quartz cuvette with a 10 mm path length.

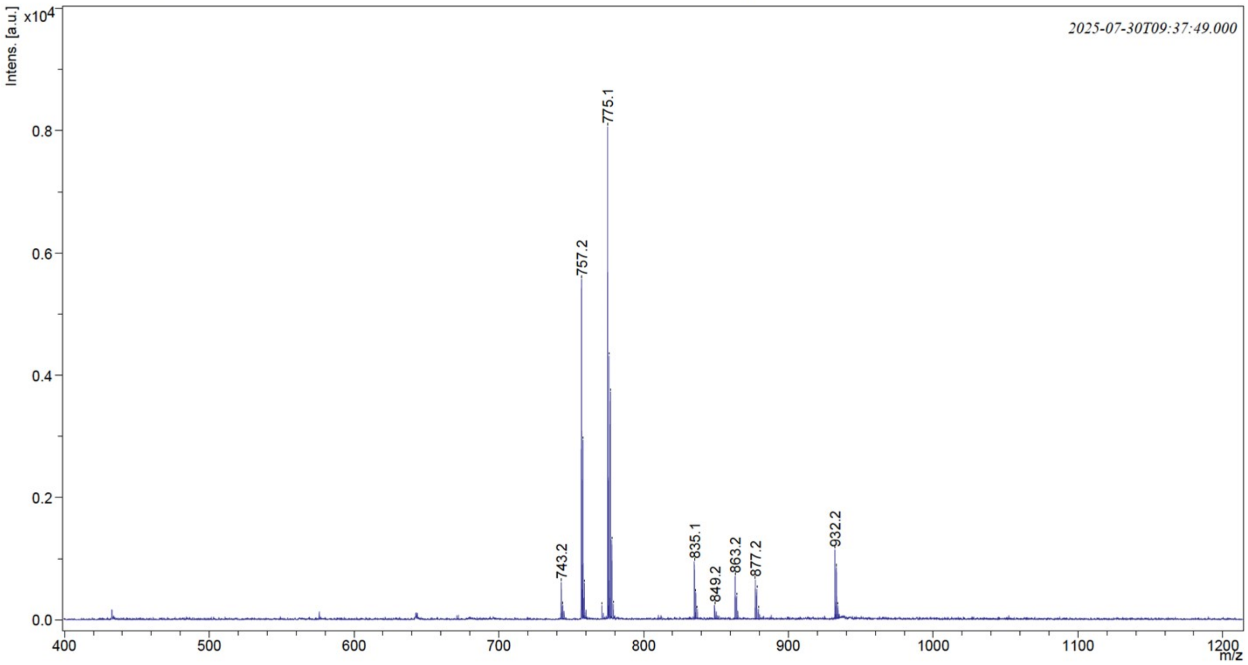
1 Mass Spectrometry Spectra



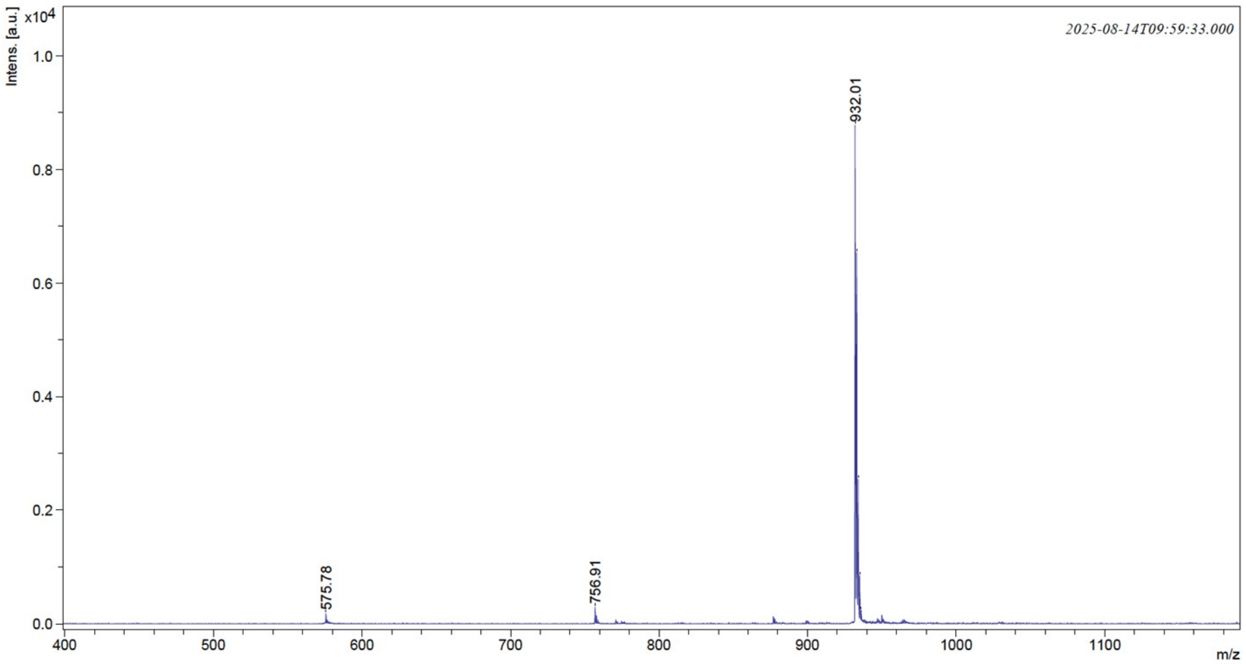
Supporting Figure 1. MALDI-TOF mass spectrometry of Cl_2-SiPc using a dithranol/THF matrix. Intense 575.0 m/z peak represents a monochlorinated isotopic pattern due to the M+2 doublet which is separated by 2 Da.



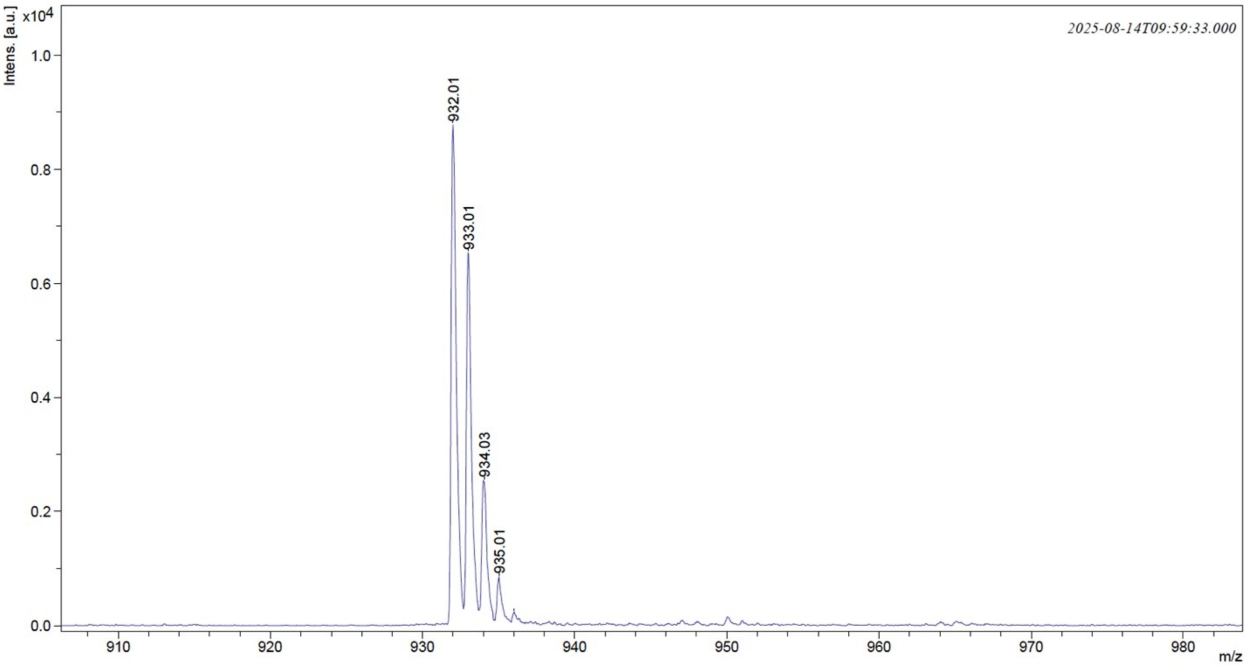
Supporting Figure 2. MALDI-TOF mass spectrometry of Cl_2-SiPc after additional work-up using a dithranol/THF matrix. The M+ fragment persists at 574.72 m/z. A weakly ionized M+ peak appears at 609.67 m/z.



Supporting Figure 3. MALDI-TOF mass spectrometry of Cl_2-SiNc using a dithranol/THF matrix. The intense peak at 775.1 m/z represents the monochlorinated species.



Supporting Figure 4. MALDI-TOF mass spectrometry of Cl_2-SiNc after additional work-up using a dithranol/THF matrix. The 932.01 m/z monoisotopic peak represents a fragment of dithranol or another matrix-related species.



Supporting Figure 5. Zoom in of MALDI-TOF mass spectrometry of Cl_2-SiNc after additional work-up using a dithranol/THF matrix. The peaks ranging from 932 to 935 m/z represent the isotopic envelope of Cl_2-SiNc, where the splitting pattern is chlorine driven and broadened by carbon and silicon isotopes.

2 Synthesis on 500 mg Scale

2.1 Larger scale synthesis of dichloride-silicon phthalocyanine (1)

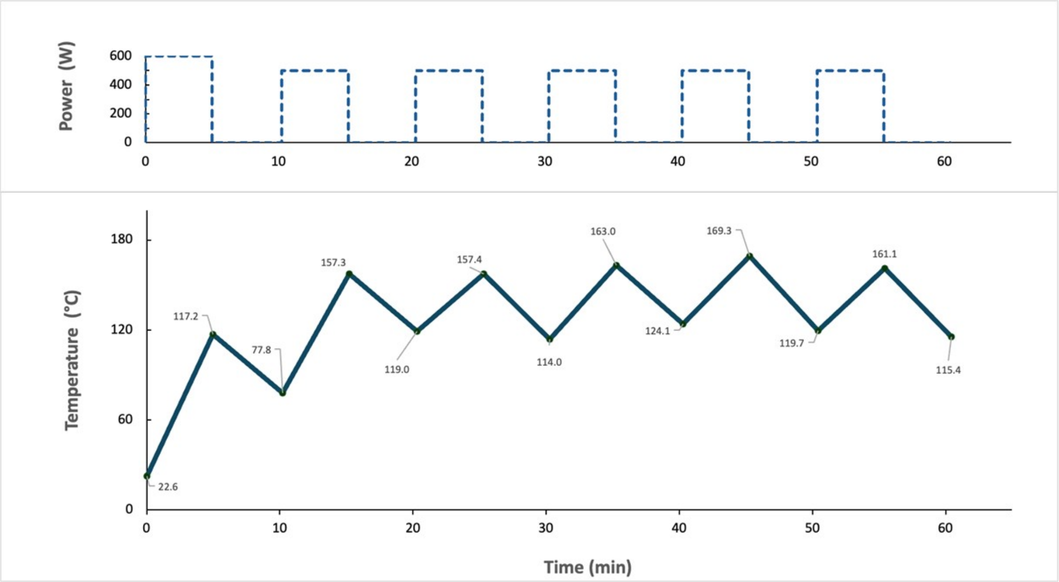
An oven-dried, 50 mL three-neck round bottom flask was charged with phthalonitrile (500 mg, 3.90 mmol). After purging the flask with argon for 10 minutes, LiHMDS (394 mg, 2.34 mmol) was added under inert atmosphere and the flask was sealed with rubber septa and placed under positive argon pressure. Next, anhydrous tetralin solvent (8 mL) was added via a needle syringe transfer and the solution was set to stir rigorously (370 RPM) at room temperature for 24 hours. After that, the flask was connected to a water condenser and continued remaining under positive argon pressure. Silicon tetrachloride (0.63 mL, 5.46 mmol) was slowly added dropwise to the stirring reaction mixture (370 RPM), which was immediately heated to 200°C. After 24 hours, the deep turquoise solution was allowed to cool to room temperature which was then admixed with hexanes (20 mL) and methanol (50 mL). After drying under vacuum, the resulting mass was a deep bluish-green solid (crude: 237 mg (40%)).

2.2 Larger scale synthesis of dichloride-silicon naphthalocyanine (2)

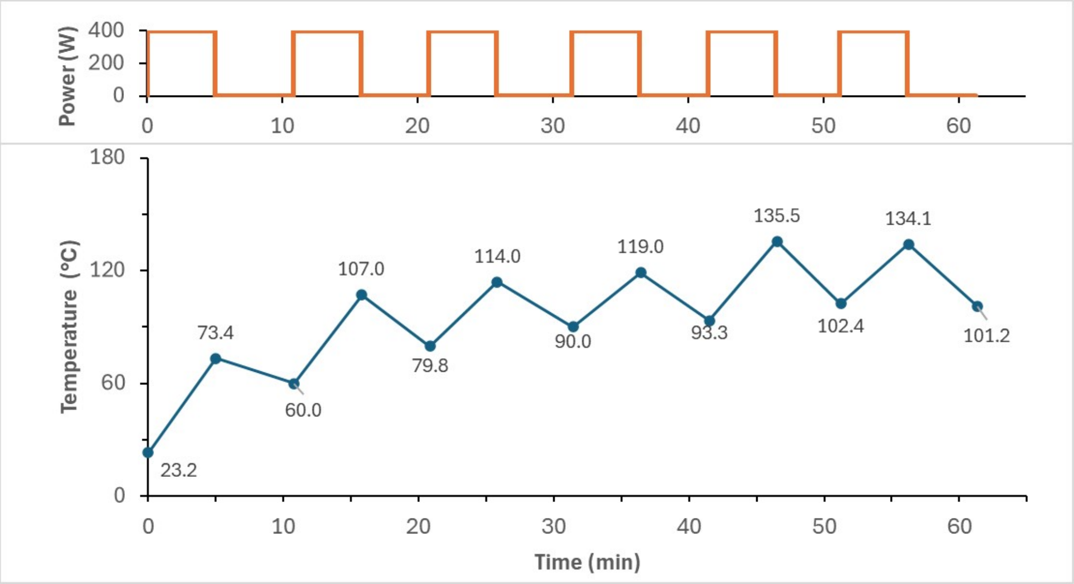
An oven-dried, 50 mL three-neck round bottom flask was charged with dicyanonapthalene (500 mg, 2.80 mmol). After purging the flask with argon for 10 minutes, LiHMDS (283 mg, 1.68 mmol) was added under inert atmosphere and the flask was sealed with rubber septa and placed under positive argon pressure. Next, anhydrous tetralin solvent (8 mL) was added via a needle syringe transfer and the solution was set to stir rigorously (370 RPM) at room temperature for 24 hours. After that, the flask was connected to a water condenser and continued remaining under positive argon pressure. Silicon tetrachloride (0.45 mL, 3.93 mmol) was slowly added dropwise to the stirring reaction mixture (370 RPM), which was immediately heated to 200°C. After 24 hours, the deep yellow-brown solution was allowed to cool to room temperature which was then admixed with hexanes (20 mL), followed by methanol (30 mL), and dried under vacuum. The remaining mass was a deep green solid (crude: 174 mg (31%)).

3 Microwave Procedure

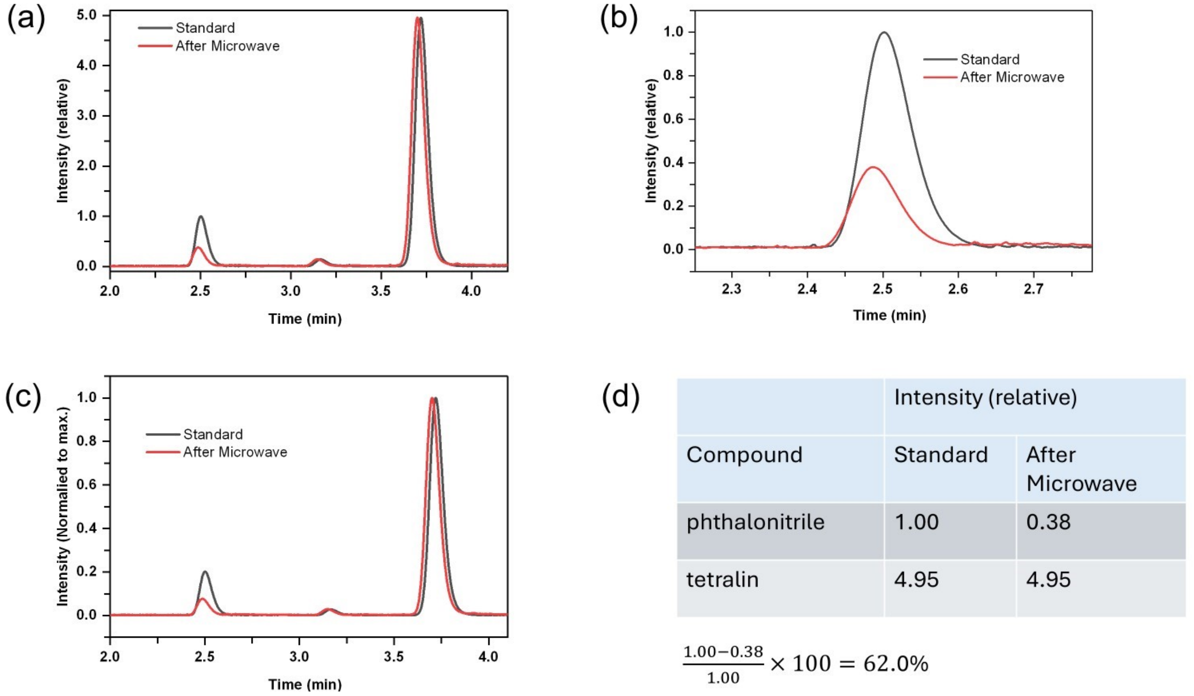
Phthalonitrile (250 mg, 1.95 mmol) was added to a 65 mL borosilicate round-bottom pressure vessel and purged under argon for 30 minutes. Subsequently, LiHMDS (197 mg, 1.17 mmol) was added under inert atmosphere, and the flask was sealed with rubber septa and placed under positive argon pressure. Next, anhydrous tetralin solvent (6 mL) was added via syringe and the solution was sonicated for 3 minutes to incorporate all reagents. After 30 minutes, the reaction was sonicated for 2 minutes, repeating the series of sonication steps for 5 hours. Following sonication, the reaction was left overnight under inert atmosphere without additional stirring. After 24 hours, silicon tetrachloride (0.31 mL, 2.73 mmol) was added dropwise, and the vessel was closed under argon and sonicated for 2 minutes. Finally, the vessel was placed in a BP310 microwave oven and irradiated for the indicated time and power, using the Fluke 62 Max Mini Infrared Thermometer to measure the temperature of the reaction mixture (**Fig.S6 and Fig.S7**). After irradiation, the vessel was removed from the oven and allowed to cool to room temperature for 30 minutes. To obtain the mass, the reaction mixture was admixed with hexanes (20 mL). The solid was further washed with hexanes (20 mL) and methanol (50 mL) under vacuum filtration. After complete drying, the resulting solid was deep bluish-teal in colour, similar to the benchtop procedure (crude: 8 mg (3%)).



Supporting Figure 6. Microwave heating cycle Protocol 1: Wattage, temperature, and time throughout the irradiation of the optimized benchtop conditions to form Cl_2-SiPc from phthalonitrile.



Supporting Figure 7. Microwave heating cycle protocol 2: Wattage, temperature, and time throughout the irradiation of the optimized benchtop conditions to form Cl_2-SiPc from phthalonitrile.



	Intensity (relative)	
Compound	Standard	After Microwave
phthalonitrile	1.00	0.38
tetralin	4.95	4.95

$$\frac{1.00-0.38}{1.00} \times 100 = 62.0\%$$

Supporting Figure 8. Comparison of phthalonitrile intensity after microwave-assisted synthesis of Cl_2-SiPc. Panels (a) and (b) show the relative intensity, while (c) show the normalized intensity, measured by HPLC-PDA. These were compared to a reference standard representing the initial phthalonitrile content (0.250g, 1.95 mmol, RT: 2.5 min, λ_{max}: 291nm) in tetralin (6 mL, RT:3.7 min, λ_{max}: 274nm). Panel (d) shows the phthalonitrile's peak relative intensity, which was used to estimate conversion.