Supporting Information for

Synthesis of unsymmetrical carboxyphthalocyanines by palladium-catalyzed hydroxycarbonylation of iodo-substituted precursors

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1. General experimental details and techniques

UV-Vis spectra were recorded on a Hewlett-Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. NMR spectra were recorded on a BRUKER AC-300 (300 MHz) instrument with solvent used as internal reference. Chemical shifts are measured in ppm relative to tetramethylsilane (TMS). For target compound **2**, due to aggregation at NMR concentrations, multiple scans (i.e., over 1000) had to be run in order to observe its aromatic protons with a satisfactory signal to noise ratio. Mass spectra were obtained on a Bruker Ultraflex III MALDI-TOF spectrometer. Column chromatography was carried out on silica gel Merck-60 (230-400 mesh, 60 Å) or reverse phase silica gel (LiChroprep RP-18, 25-40 μm), and TLC on aluminum sheets pre-coated with silica gel 60 F254 or 60 RP-18 $F_{254}S$ (Merck). Chemicals were purchased from Sigma-Aldrich and Alfa-Aesar, and used without further purification.

2. Synthetic procedures

2.1 In the route towards compound 1 (TT1)

Apart from the hydroxycarbonylation step (described in the main text), the synthetic procedures to prepare 4-iodophthalonitrile[1] and the tri-*tert*-butyl iodo-Pc precursor,[2] have been previously described in the literature.

2.2. In the route towards compound 2

3,6-Bis(4-methylphenylsulfonyloxy)phthalonitrile

Synthesized as reported in the literature.[3]

1 S. M. Marcuccio, P. I. Svirskaya, S. Greenberg, A. B. P. Lever, C. C. Leznoff and K. B. Tomer, *Can. J. Chem.*, 1985, **63**, 3057.
2 E. M. Maya, P. Vazquez and T. Torres, *Chem. Eur. J.*, 1999, **5**, 2004.

3,6-Bis[(tert-butylphenyl)sulfanyl]phthalonitrile (4)

Procedure adapted from: K. Sakamoto, E. Ohno-Okumura, T. Kato and Hisashi Soga, *J. Porphyrins Phthalocyanines*, 2010, **14**, 47. *Tert*-buthylbenzenethiol (2.52 g, 15.1 mmol) was dissolved in DMSO under a argon atmosphere, and 3,6-bis(4-methylphenylsulfonyloxy)phthalonitrile (2.83 g, 6.05 mmol) was added. The mixture was stirred for 15 min, and finely ground anhydrous potassium carbonate (3.33 g, 24.2 mmol) was added slowly for two hours while stirring. The mixture was stirred under argon atmosphere for 15 h. Water was added and the aqueous phase extracted using DCM (3 x 50 mL). The extracts were further treated with 5% aqueous sodium carbonate (2 x 250 ml) and then dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under vacuum. The desired product was purified by column chromatography over silica gel with hexane/THF (3:1) as eluent. Yield: 51%. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm)= 7.41 (m, 8H), 6.95 (s, 2H), 1.31 (s, 18H). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3040, 2960, 2210, 1600, 1500, 1460, 1210, 808, 735, 529, 433. MS (MALDI-TOF, DCTB): *m/z* = 456.3 [M^+].

Zinc(II) iodophthalocyanine 3

A mixture of phthalonitrile **4** (0.46 g, 1.0 mmol), 4-iodophthalonitrile (0.05 g, 0.2 mmol) and zinc(II) acetate (0.06 g, 0.32 mmol) in DMAE (5mL) was stirred at 140 ^{o}C under argon atmosphere for 24 h. After cooling down to room temperature, DMAE was evaporated under vacuum. The resultant oily crude mixture was treated with methanol/water (3:1) and then filtered under vacuum. The green solid obtained was washed thoroughly with methanol/water (3:1) and with methanol, and then purified by column chromatography over silica gel using hexane/dioxane (3:1) as eluent. As final product, a mixture of iodophthalocyanine **3** and the symmetrical phthalocyanine substituted with eight *tert*-buthylphenylsulfanyl groups was obtained. The proportion of **3** in this mixture was estimated to be

3 G. Mbambisa, P. Tau, E. Antunes and T. Nyokong, *Polyhedron*, 2007, **26**, 5355.

35% by mass spectrometry. This value was used to calculate the yield of this step and the subsequent hydroxycarbonylation reaction.[4] Yield: 11%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 8.0-7.0 (m, 33H; arom. H), 1.35-1.20 (m, 54H; -CH_3). MS (MALDI-TOF, DCTB): *m/z* = 1888.5 [symmetrical Pc^+], 1686.4 [Iodo-Pc **3**$^+$].

Zinc(II) carboxyphthalocyanine 2

This procedure has been described in the main text of the article.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 8.0-7.0 (m, 33H; arom. H), 1.35-1.20 (m, 54H; -CH_3). FT-IR [(KBr) ν_{max}/cm^{-1}]: 3061, 2964, 2905, 2867, 1720, 1647, 1490, 1460, 1395, 1365, 1269, 1233, 1119, 1015, 832. UV/Vis (THF), λ_{max} (nm) (log ε)= 380 (4.17), 448 (4.0), 678 (4.30), 716 (4.17). MS (MALDI-TOF, dithranol): *m/z* = 1603.5 [M-H]$^-$.

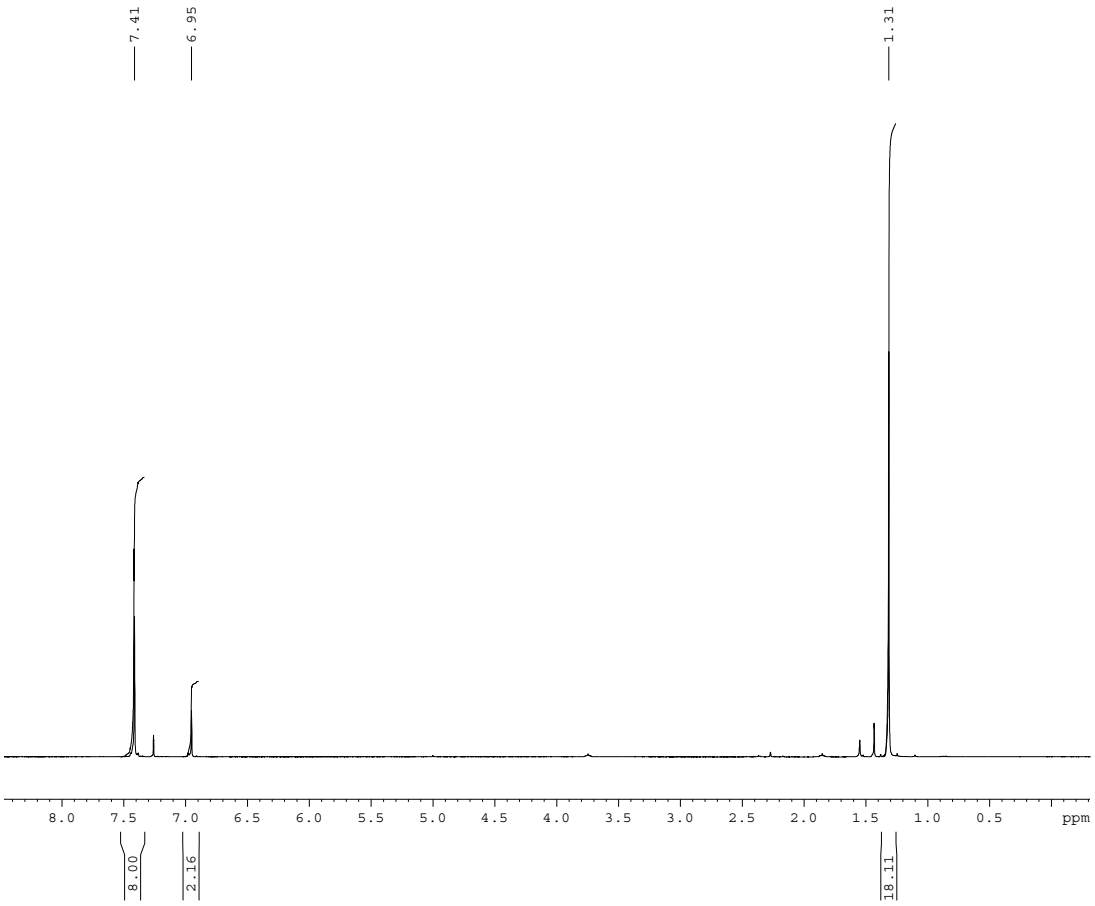
3. Characterization of compounds

The spectroscopic data obtained for all compounds prepared in the synthetic route towards **1** (not shown herein), including 4-iodophthalonitrile[1] and the tri-*tert*-butyl iodo-Pc precursor,[2] were coincident with those previously reported in the literature. Concerning the carboxyphthalocyanine **2**, its ^{1}H NMR spectrum in $CDCl_3$ shows two broad multiplets corresponding to the aromatic and *tert*-butyl protons. The poor resolution of the spectrum is probably a consequence of aggregation at NMR concentrations, for which multiple scans (i.e., 1024) had to be run in order to observe with low but reasonable intensity the aromatic signals of the compound. The low resolution of the spectrum could not be improved under other conditions such as high temperature or the use of THF-d8 as solvent.

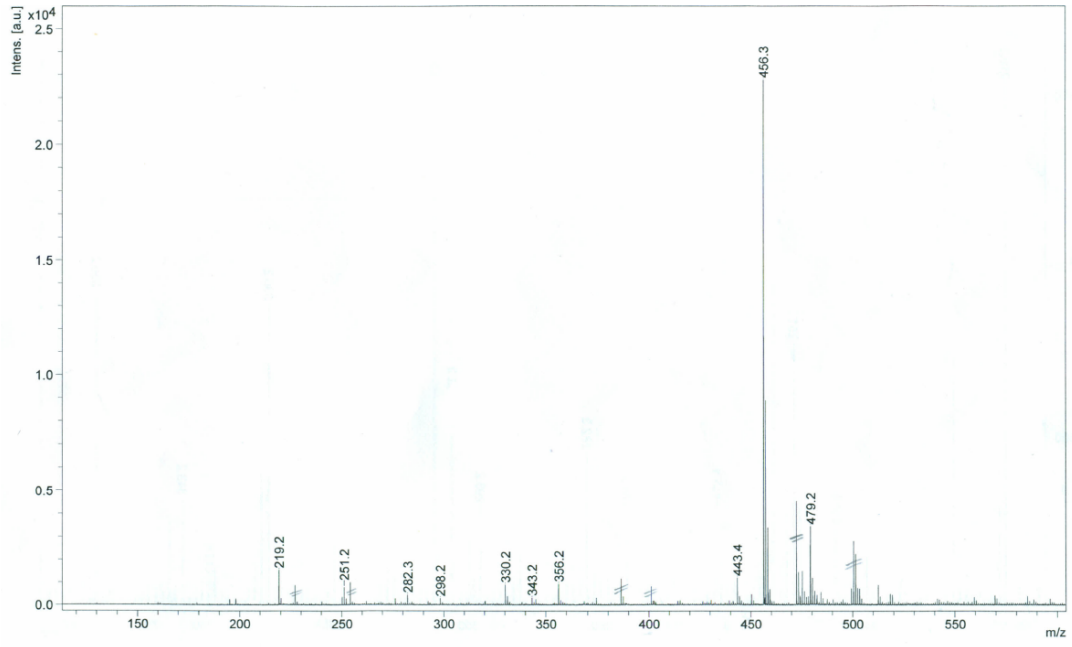
4 The ^{1}H NMR spectrum of the mixture in $CDCl_3$ shows broad signals due to aggregation, and therefore does not provide information to estimate the proportion of the iodophthalocyanine **3** by this technique. MALDI-TOF mass spectrometry, on the other hand, is not a quantitative method for determining the proportion of different compounds in a mixture. Yet, because the structures of both compound **3** and the symmetrical octakis[(tert-butylphenyl)sulfanyl]phthalocyanine are very similar, it is reasonable to assume that their efficiency to fly and being ionized in the mass spectrometer should be rather similar. Our estimation also matches the qualitative observations made by TLC. As a result, although the estimated yields contain a significant error, they should not deviate much from the actual yields of both reactions.

Phthalonitrile 4

^{1}H NMR (in $CDCl_3$)

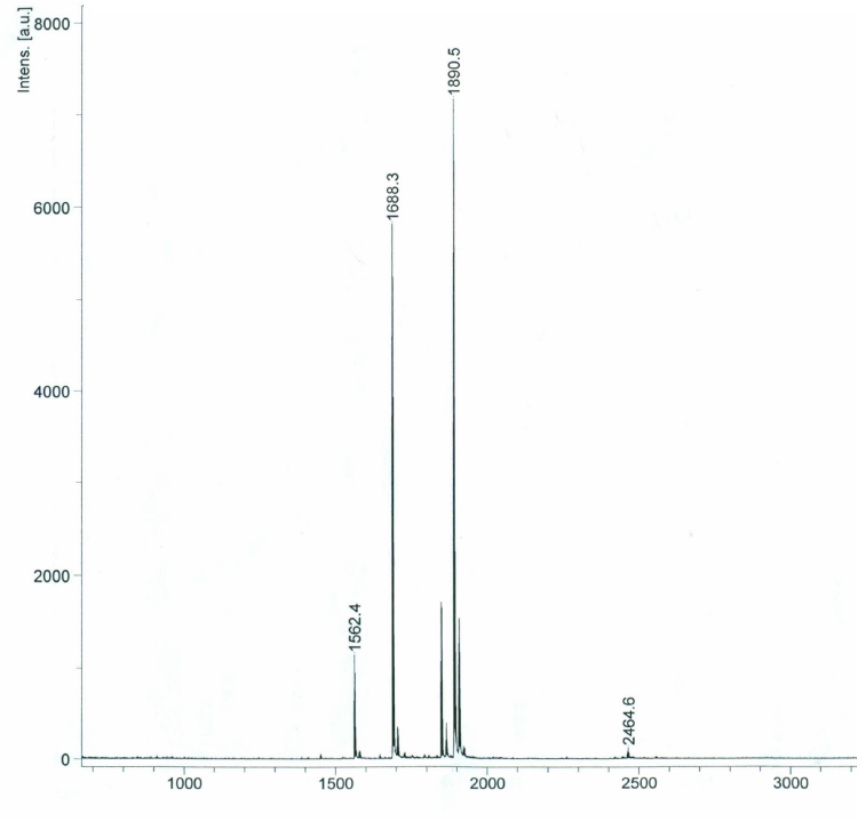


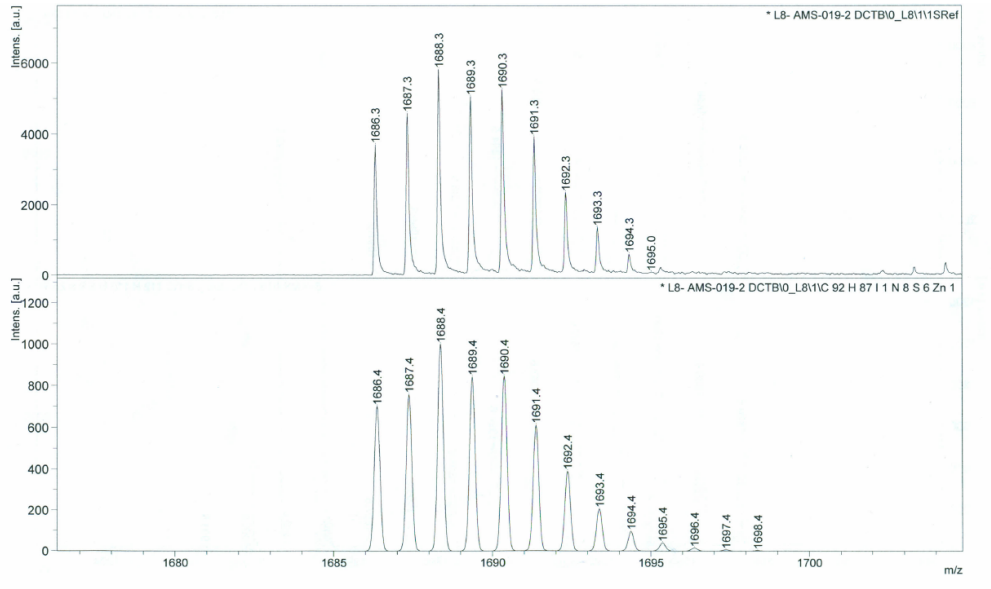
MALDI-TOF MS (matrix: DCTB)



Iodophthalocyanine 3 (as a mixture with octakis[(tert-butylphenyl)sulfanyl]phthalocyanine)

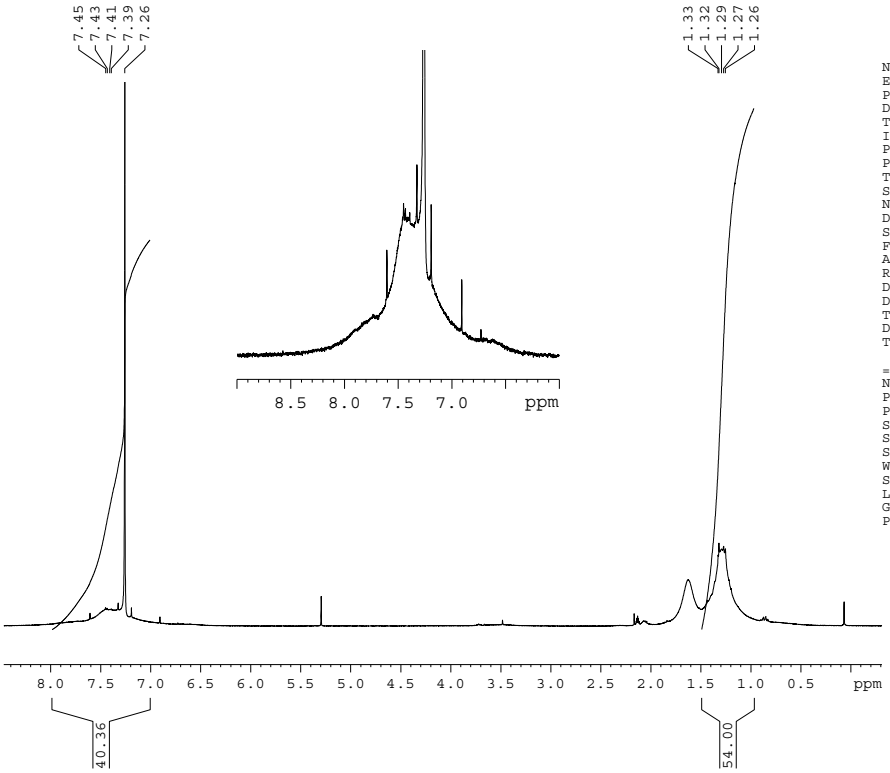
MALDI-TOF MS (matrix: DCTB)





Carboxyphthalocyanine 2

^{1}H NMR (in $CDCl_3$)

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TD                        32768
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FIDRES                0.188846 Hz
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RG                          512
DW                     80.800 usec
DE                      6.00 usec
TE                      300.0 K
D1                  1.00000000 sec
TD0                           1

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SI                        32768
SF                  300.2300086 MHz
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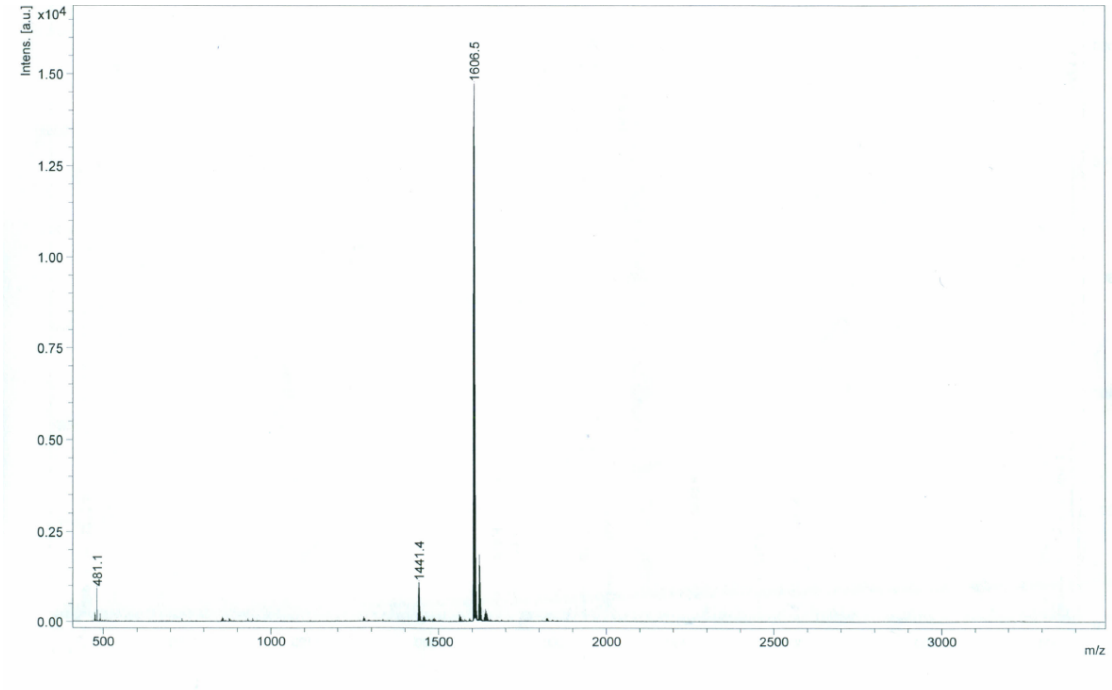
MALDI-TOF MS (matrix: dithranol, positive mode)



MALDI-TOF MS (matrix: dithranol, negative mode)