

On the Chemistry of Pyrrole Pigments, XCVI [1]: An Efficient Synthesis of Corrphycenes

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Summary. By means of copper catalyzed intramolecular coupling of the easily accessible 1,2-bis-(1-iodo-dipyririn-9-yl)-ethanes and subsequent demetallation of the intermediate copper complexes corrphycenes could be prepared in nearly 40% overall yields.

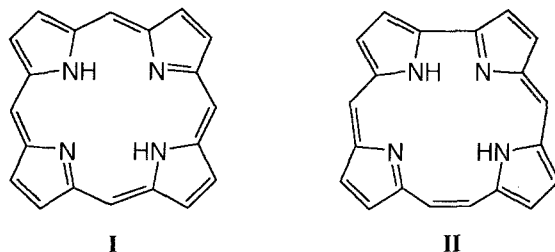
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Zur Chemie von Pyrrolpigmenten, 96. Mitt. [1]: Eine effiziente Synthese von Corrphycenen

Zusammenfassung. Durch Kupfer katalysierte intramolekulare Kupplung der leicht zugänglichen 1,2-bis-(1-Iod-dipyririn-9-yl)-ethane und anschließende Demetallierung der gebildeten Kupferkomplexe ergibt Corrphycene in Gesamtausbeuten von fast 40%.

Introduction

Porphyrin (I) is an extremely important and ubiquitously occurring structural unit, which is contained in a variety of natural compounds and artificial derivatives [2]. The structural variation of this fundamental tetrapyrrolic rings system has become highly attractive during the last decade. This has been due to a keen interest in the chemical and physical properties of these systems, which make them important with respect to material sciences and medicinal aspects. Among these novel systems, the extended and isomerized porphyrins should be mentioned [3, 4]. A very interesting group are those compounds in which the fundamental [18]-annulene system of the

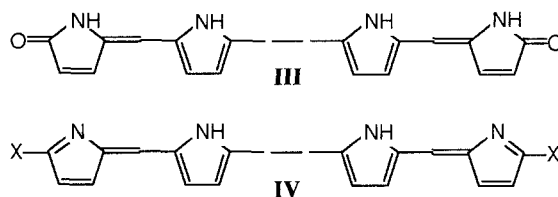


Scheme 1

porphyrin is left unaltered in a structural variation. One of these "isoporphyrins", which has been named corrphycene (**II**), has been recently prepared for the first time in a joint cooperation of the pioneer groups in this field [5].

It is interesting to note that in a reported synthesis of a corrphycene derivative [5] the final step involved the *McMurry* cyclization [6] of the corresponding α,ω -dialdehyde. The bipyrrolic unit had been assembled in a precursor derivative before. This synthesis strategy is found to be common to all the porphyrinoid systems involving a bipyrrolic fragment synthesized up to now [3, 4], and had provided an efficient access to these systems. However, in the case of the corrphycenes (**II**), this strategy provided yields in the order of a mere 3% in the cyclization key step [5].

Investigations of linear oligopyrroles derived from the natural open chain tetrapyrroles by contraction [7] or extension [8] of their *b*-methine bridges led our group to *b*-homo-rubinoïd systems of type **III** [9]. Potential precursors of **III**, which are of type **IV** ($X = \text{halogen}$), could also be envisaged as ideal precursor molecules for the synthesis of porphycenes. Such a synthetic approach involving these easily accessible educts will be described below.

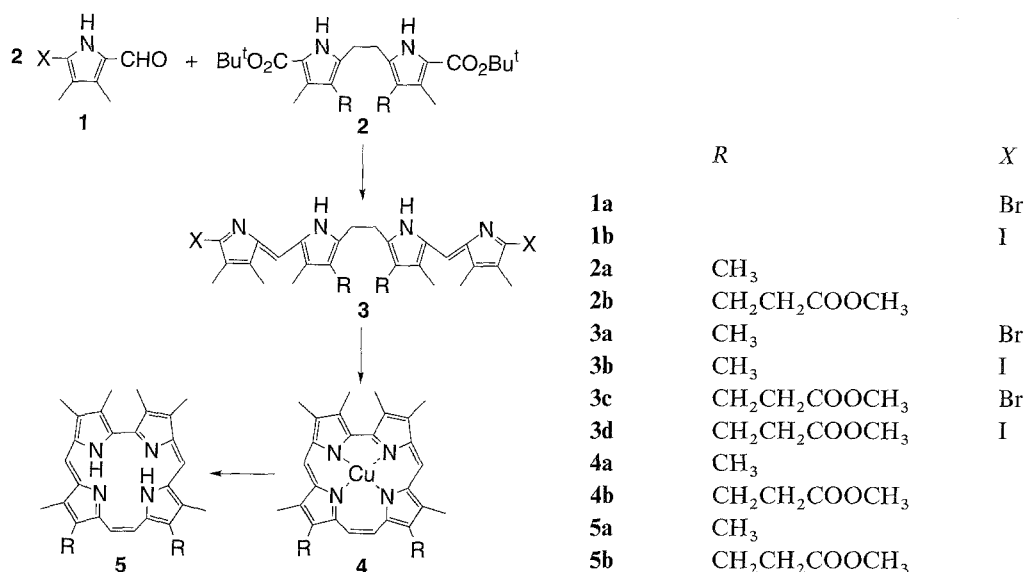


Scheme 2

Results and Discussions

The easily accessible bromo- or iodo-pyrrole aldehydes **1** [10] and the dipyrrolyl-ethane **2** [9] were condensed using trifluoroacetic acid as the catalyst to produce the corresponding *bis*-dipyrrolyl-ethanes **3** in favorable yields of up to 80%. Upon *Ullmann* type coupling [11] using copper in dimethyl formamide, **3** provided the corrphycenato copper(II) derivatives **4** in yields of about 50%. In this intramolecular coupling reaction, the bromo derivatives **3a** and **3c** gave the same cyclization results as their iodo analogs **3b** and **3d**. The copper chelates could be demetallated by means of sulfuric acid to yield the free bases **5** in about 80% yield. Otherwise, one could also execute the preparation of **5** from **3** without isolating the copper chelates. The products **5a** and **5b** were found to be analogous in their spectroscopic properties to the derivative described in Ref. [5] and displayed all characteristic data to assign their constitutions independently and unequivocally.

Accordingly, compared to the rather low yields of corrphycenes available *via* the *McMurry* cyclization route [5], the *Ullmann* cyclization route, which provides the bipyrrolic fragment in the final key step, made these interesting compounds accessible in about 40% overall yields. Functionalized derivatives like **5b**, which are analogous to the natural porphyrins, could be useful as models for comparative binding experiments using apomyoglobin. Possibly its free dicarboxylic acid derivative complexed with iron could constitute a heme oxygenase inhibitor.



Scheme 3

Experimental

¹H NMR and ¹³C NMR spectra were recorded on a Bruker-AC 200 instrument. UV/Vis and IR spectra were run on Hitachi-U-3210 and Biorad-FT-IR-45 spectrophotometers. Mass spectra were measured on Hewlett Packard 5989A and MAT 95 instruments, and melting points were determined by means of a Kofler hot stage microscope (Reichert, Vienna). Aluminum oxide (active, type 90, neutral) and silica GF₂₅₄ was used for column chromatography. Compound **2** was prepared according to Ref. [9].

5-Bromo-2-formyl-3,4-dimethyl-pyrrole (**1a**; C₇H₈BrNO)

To a solution of 5.2 g 5-bromo-2-(2-cyano-2-ethoxycarbonylvinyl)-3,4-dimethyl-pyrrole (17.5 mmol; [10]) in a mixture of 200 ml ethanol and 50 ml water, 80 g potassium hydroxide were carefully added in portions during 20 min. The mixture was then refluxed for 3 h under nitrogen protection. The reaction mixture was brought down to room temperature and chilled on ice. It was then acidified carefully with 6 N H₂SO₄ and extracted with 3 × 50 ml chloroform. The combined organic phases were washed with 50 ml water, 40 ml aqueous saturated sodium bicarbonate, and 30 ml brine. After drying over anhydrous sodium sulfate and removing the solvent, the residue was crystallized from 95% methanol, yielding 2.3 g (63%) **1a**. M.p.: 224 °C; ¹H NMR (200 MHz, δ, CDCl₃): 1.96 (s, CH₃), 2.27 (s, CH₃), 9.44 (s, CHO), 9.99 (br s, NH) ppm; ¹³C NMR (50 MHz, δ, CDCl₃): 9.21 (CH₃), 9.36 (CH₃), 125.55 (C_{pyrr}), 127.33 (C_{pyrr}), 129.54 (C_{pyrr}), 148.33 (C_{pyrr}), 176.33 (CHO) ppm; IR (KBr): ν = 3418, 3204, 3107, 2913, 2855, 1669, 1527, 1419, 1374 cm⁻¹; UV/Vis (CH₂Cl₂): λ_{max} = 307 (13600) nm (ε); UV Vis (MeOH): λ_{max} = 306 (1600) nm (ε); UV/Vis (DMSO): λ_{max} = 293 (79000) nm (ε); MS (70 eV, 186 °C): m/e (%) = 203 (100, M⁺ + 1), 202 (59, M⁺), 200 (57), 174 (28), 122 (36), 92 (36).

5-Iodo-2-formyl-3,4-dimethyl-pyrrole (**1b**; C₇H₈INO)

This compound was prepared as above by hydrolysis of 5-iodo-2-(2-cyano-2-ethoxycarbonylvinyl)-3,4-dimethyl-pyrrole [10] in 80% yield. M.p.: 178–180 °C; ¹H NMR (200 MHz, δ, CDCl₃): 1.97 (s, CH₃), 2.26 (s, CH₃), 9.37 (s, CHO), 9.51 (NH) ppm; ¹³C NMR (50 MHz, δ, CDCl₃): 9.45 (CH₃), 10.22 (CH₃),

122.55 (C_{pyrr}), 129.33 (C_{pyrr}), 131.22 (C_{pyrr}), 145.66 (C_{pyrr}), 176.54 (CHO) ppm; IR (KBr): $\nu = 3222, 2998, 1652, 1626, 1454, 1414, 1367, 1223 \text{ cm}^{-1}$; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 286 (13300) \text{ nm} (\epsilon)$; UV/Vis (MeOH): $\lambda_{\text{max}} = 282 (22300) \text{ nm} (\epsilon)$; UV/Vis (DMSO): $\lambda_{\text{max}} = 296 (15700) \text{ nm} (\epsilon)$; MS (70 eV, 206 °C): $m/e (\%) = 249 (95, M^+), 220 (12), 193 (3.4), 122 (8.2), 93 (9.5)$.

1,2-bis-(1-Bromo-2,3,7,8-tetramethyldipyrinyl)-ethane (3a; C₂₈H₃₄N₄Br₂)

To a round-bottom flask filled with argon, 497 mg **2a** (1.20 mmol) and then 10 ml trifluoroacetic acid were added. The mixture was stirred for 30 min at room temperature under an argon atmosphere. To this solution, a mixture of 485 mg **1a** (2.4 mmol, 2.0 mole equivalents) and 50 ml methanol was added. The mixture was further stirred for 1 hour and then treated with 100 ml dichloromethane and 30 ml 15% aqueous ammonia. The organic layer was separated and the water phase was extracted three times with 50 ml dichloromethane. The combined organic layers were washed with 50 ml water and 30 ml brine. After drying over anhydrous sodium sulfate and removing the solvent, the residue was purified by means of flash chromatography on aluminum oxide (type 90, neutral) using methylene chloride/ethyl acetate ($v/v = 6/4$) as the eluent. The yellow band was purified by silica gel column chromatography using dichloromethane/ethyl acetate/tetrachloromethane ($v/v/v = 2/2/1$), crystallization from dichloromethane-hexane, and finally from methanol, yielding 840 mg (70%) **3a** M.p. 230 °C; $^1\text{H NMR}$ (200 MHz, δ , CDCl_3): 1.87 (s, CH_3 -8,13), 1.92 (s, CH_3 -2,19), 2.10 (s, CH_3 -3,18), 2.11 (s, CH_3 -7,14), 2.92 (s, CH_2 - CH_2), 6.67 (s, $-\text{CH}=-5, 16$) ppm; NOE (CDCl_3): $-\text{CH}=-5, 16 \leftrightarrow \text{CH}_3$ -3,7,14,18; $-\text{CH}_2$ - CH_2 - $\leftrightarrow \text{CH}_3$ -8,10; CH_3 -8 $\leftrightarrow \text{CH}_2$ - CH_2 -, CH_3 -7; $^{13}\text{C NMR}$ (50 MHz, δ , CDCl_3): 8.70 (CH_3 -8,13), 9.72 (CH_3 -2,19), 10.15 (CH_3 -3, 18), 10.60 (CH_3 -7, 14), 26.46 (CH_2 - CH_2), 116.46 ($-\text{CH}=-5, 16$), 117.40 (C_{pyrr}), 126.48 (C_{pyrr}), 127.40 (C_{pyrr}), 126.48 (C_{pyrr}), 131.17 (C_{pyrr}), 139.47 (C_{pyrr}), 145.02 (C_{pyrr}), 148.46 (C_{pyrr}) ppm; $^{13}\text{C NMR}$ (90 MHz, δ , CDCl_3): 8.69 (CH_3 -8, 13), 9.70 (CH_3 -2, 19), 10.11 (CH_3 -3, 18), 10.57 (CH_3 -7, 14), 26.46 (CH_2 - CH_2), 117.64 ($-\text{CH}=-5, 16$), 118.48 (C_{pyrr}), 127.45 (C_{pyrr}), 128.49 (C_{pyrr}), 131.17 (C_{pyrr}), 139.44 (C_{pyrr}), 139.72 (C_{pyrr}), 145.05 (C_{pyrr}), 148.43 (C_{pyrr}) ppm; IR (KBr): $\nu = 2910, 2853, 1603, 1544, 1484, 1212 \text{ cm}^{-1}$; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 276 (29000), 342 (68000), 452 (34500), 484 (34000) \text{ nm} (\epsilon)$; UV/Vis (MeOH): $\lambda_{\text{max}} = 321 (42700), 449 (49700), 484 (52000) \text{ nm} (\epsilon)$; UV/Vis (DMSO): $\lambda_{\text{max}} = 276 (78900), 342 (6000), 452 (36000), 487 (36000) \text{ nm} (\epsilon)$; MS (EI, 70 eV): $m/e (\%) = 586 (5, M^+), 584 (7), 503 (3), 423 (5), 409 (3), 304 (6), 293 (20, 1/2M^+), 292 (98), 291 (100), 211 (23), 197(18), 132 (5)$.

1,2-bis-(1-Iodo-2,3,7,8-tetramethyldipyrinyl)-ethane (3b; C₂₈H₃₄N₄I₂)

This compound was prepared as above by treatment of **2a** with TFA and condensation with **1b** in 80% yield. M. p.: 223 °C (dec.); $^1\text{H NMR}$ (200 MHz, δ , CDCl_3): 1.89 (s, CH_3 -8, 13), 1.90 (s, CH_3 -2, 19), 1.91 (s, CH_3 -3, 18), 2.13 (s, CH_3 -7, 14), 2.94 (s, CH_2 - CH_2 -), 6.62 (s, $-\text{CH}=-5, 16$) ppm; NOE (CDCl_3): $-\text{CH}=-5, 16 \leftrightarrow \text{CH}_3$ -3, 7, 14, 18; $-\text{CH}_2$ - CH_2 - $\leftrightarrow \text{CH}_3$ -8, 10; CH_3 -8 $\leftrightarrow \text{CH}_2$ - CH_2 -, CH_3 -7; $^{13}\text{C NMR}$ (50 MHz, δ , CDCl_3): 8.82 (CH_3 -2, 19), 8.94 (CH_3 -8, 13), 10.19 (CH_3 -3, 18), 12.38 (CH_3 -7, 14), 26.45 ($-\text{CH}_2$ - CH_2), 117.33 ($-\text{CH}=-5, 16$), 127.94 (C_{pyrr}), 128.86 (C_{pyrr}), 131.87 (C_{pyrr}), 132.03 (C_{pyrr}), 133.05 (C_{pyrr}), 137.34 (C_{pyrr}), 147.00 (C_{pyrr}), 161.35 (C_{pyrr}) ppm; IR (KBr): $\nu = 3195, 2906, 2851, 1601, 1580, 1543, 1438, 1363, 1357, 1263, 1209 \text{ cm}^{-1}$; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 348 (13400), 474 (35900) \text{ nm} (\epsilon)$; UV/Vis ($\text{CH}_2\text{Cl}_2 + 1 \text{ drop TFA}$): $\lambda_{\text{max}} = 304 (2900), 377 (12300), 474 (130700), 530 (48200) \text{ nm} (\epsilon)$; UV/Vis ($\text{CH}_2\text{Cl}_2 + \text{Zn}^{2+}$): $\lambda_{\text{max}} = 378 (35600), 479 (46600), 507 (32700) \text{ nm} (\epsilon)$; UV/Vis ($\text{CH}_2\text{Cl}_2 + \text{Fe}^{2+}$): $\lambda_{\text{max}} = 473 (89200), 504 (41800), 530 (33000) \text{ nm} (\epsilon)$; UV/Vis ($\text{CH}_2\text{Cl}_2 + \text{Ni}^{2+}$): $\lambda_{\text{max}} = 306 (29500), 363 (28600), 473 (49200), 502 (26700), 523 (31400) \text{ nm} (\epsilon)$; UV/Vis ($\text{CH}_2\text{Cl}_2 + \text{Cu}^{2+}$): $\lambda_{\text{max}} = 349 (20500), 434 (20600), 515 (10400) \text{ nm} (\epsilon)$; UV/Vis (MeOH): $\lambda_{\text{max}} = 460 (32700), 473 (23800), 516 (34400) \text{ nm} (\epsilon)$; UV/Vis (MeOH + TFA): $\lambda_{\text{max}} = 374 (10700), 470 (65400), 519 (92900) \text{ nm} (\epsilon)$; UV/Vis (MeOH + Zn^{2+}): $\lambda_{\text{max}} = 311 (1700), 373 (5000), 480 (20400), 528 (85800) \text{ nm} (\epsilon)$; UV/Vis (MeOH + Fe^{2+}): $\lambda_{\text{max}} = 302 (8800), 470 (32800), 524 (29400) \text{ nm} (\epsilon)$; UV/Vis (MeOH + Cu^{2+}): $\lambda_{\text{max}} = 342 (11000), 432 (13000), 530 (7000) \text{ nm} (\epsilon)$; UV/Vis (DMSO): $\lambda_{\text{max}} = 315 (16400), 355 (14900), 467 (39600), 505 (42500) \text{ nm} (\epsilon)$; UV/Vis

(DMSO + TFA): $\lambda_{\max} = 377$ (9700), 454 (60700), 524 (58800) nm (ϵ); UV/Vis (DMSO + Zn²⁺): $\lambda_{\max} = 315$ (9500), 386 (12100), 395 (12000), 531 (104600) nm (ϵ); UV/Vis (DMSO + Ni²⁺): $\lambda_{\max} = 312$ (15500), 388 (13400), 476 (37800), 508 (45100) nm (ϵ); UV/Vis (DMSO + Fe²⁺): $\lambda_{\max} = 309$ (145300), 490 (37500) nm (ϵ).

1,2-bis-(1-Bromo-2,3,7-trimethyl-8-(2-methoxycarbonyl)ethyl)-dipyrrinyl)-ethane (3c; C₃₄H₄₀N₄O₄Br₂)

This compound was prepared as above by treatment of **2b** with TFA and condensation with **1a** in 80% yield. M. p.: 170 °C (dec.); ¹H NMR (200 MHz, δ , CDCl₃): 1.99 (s, CH₃-2, 19), 2.19 (s, CH₃-3, 18), 2.20 (s, CH₃-7,14), 2.43 (t, $J = 7.5$ Hz, 2CH₂CH₂COO), 2.78 (t, $J = 7.50$ Hz, 2CH₂CH₂COO), 2.99 (-CH₂-CH₂-), 3.65 (s, 2OCH₃), 6.60 (s, CH= at 5, 19) ppm; NOE (CDCl₃): -CH=-5, 16 \leftrightarrow CH₃-3, 7, 14, 18; -CH₂-CH₂- \leftrightarrow CH₂CH₂COO \leftrightarrow CH₃-7,14; ¹³C NMR (50 MHz, δ , CDCl₃): 9.89 (CH₃-2, 19), 10.25 (CH₃-3,18), 12.47 (CH₃-7,14), 19.51 (CH₂CH₂COO), 26.67 (-CH₂-CH₂-), 34.60 (CH₂CH₂COO), 51.73 (OCH₃), 117.25 (-CH=-5,16), 121.67 (C_{pyrr}), 127.61 (C_{pyrr}), 131.30 (C_{pyrr}), 135.88 (C_{pyrr}), 137.43 (C_{pyrr}), 146.95 (C_{pyrr}), 147.88 (C_{pyrr}), 148.65 (C_{pyrr}), 173.22 (COOCH₃) ppm; IR (KBr): $\nu = 3315, 2988, 2980, 1730, 1600, 1588, 1433, 1430, 1361, 1210$ cm⁻¹; UV/Vis (CH₂Cl₂): $\lambda_{\max} = 295$ (10800), 474 (27300) nm (ϵ); UV/Vis (CH₂Cl₂ + TFA): $\lambda_{\max} = 375$ (13000), 475 (83100), 505 (28100), 530 (28700) nm (ϵ); UV/Vis (MeOH): $\lambda_{\max} = 313$ (8900), 375 (9000), 505 (31000) nm (ϵ); UV/Vis (MeOH + TFA): $\lambda_{\max} = 303$ (6700), 374 (9100), 506 (33800) nm (ϵ); UV/Vis (DMSO): $\lambda_{\max} = 314$ (11200), 465 (39600), 495 (38500) nm (ϵ); UV/Vis (DMSO + TFA): $\lambda_{\max} = 381$ (13500), 477 (50900), 521 (52900) nm (ϵ).

1,2-bis-(1-Iodo-2,3,7-trimethyl-8-(2-methoxycarbonyl)ethyl)-dipyrrinyl)-ethane (3d; C₃₄H₄₀N₄O₄I₂)

This compound was prepared as above by treatment of **2b** with TFA and condensation with **1b** in 80% yield. M. p.: 170 °C (dec.); ¹H NMR (200 MHz, δ , CDCl₃): 1.88 (s, CH₃-2, 19), 2.10 (s, CH₃-3, 18), 2.16 (s, CH₃-7, 14), 2.42 (t, $J = 7.50$ Hz, 2CH₂CH₂COO), 2.70 (t, $J = 7.50$ Hz, 2CH₂CH₂COO), 2.98 (s, -CH₂-CH₂-), 3.64 (s, 2OCH₃), 6.59 (s, -CH=-5, 19) ppm; NOE (CDCl₃): -CH=-5, 16 \leftrightarrow CH₃-3, 7, 14, 18; -CH₂-CH₂- \leftrightarrow -CH₂CH₂COO \leftrightarrow CH₃-7, 14; ¹³C NMR (50 MHz, δ , CDCl₃): 9.78 (CH₃-2, 19), 10.15 (CH₃-3, 18), 12.37 (CH₃-7, 14), 19.49 (-CH₂CH₂COO), 26.57 (-CH₂-CH₂-), 34.70 (CH₂CH₂COO), 51.63 (OCH₃), 117.20 (-CH= at 5, 16), 121.69 (C_{pyrr}), 128.61 (C_{pyrr}), 132.30 (C_{pyrr}), 137.88 (C_{pyrr}), 138.43 (C_{pyrr}), 140.95 (C_{pyrr}), 147.68 (C_{pyrr}), 148.55 (C_{pyrr}), 173.22 (COOCH₃) ppm; IR (KBr): $\nu = 3236, 2947, 2908, 1738, 1606, 1551, 1484, 1361, 1219$ cm⁻¹; UV/Vis (CH₂Cl₂): $\lambda_{\max} = 294$ (10600), 472 (26300) nm (ϵ); UV/Vis (CH₂Cl₂ + TFA): $\lambda_{\max} = 373$ (11000), 474 (82100), 502 (28100), 529 (29700) nm (ϵ); UV/Vis (CH₂Cl₂ + Zn²⁺): $\lambda_{\max} = 482$ (54600), 509 (39100), nm (ϵ); UV/Vis (CH₂Cl₂ + Fe²⁺): $\lambda_{\max} = 277$ (137800), 351 (99100), 474 (82200), 500 (40600), 525 (31400) nm (ϵ); UV/Vis (CH₂Cl₂ + Ni²⁺): $\lambda_{\max} = 284$ (128500), 367 (12700), 474 (68000), 520 (33500) nm (ϵ); UV/Vis (CH₂Cl₂ + Cu²⁺): $\lambda_{\max} = 271$ (14800), 352 (20300), 436 (16500), 486 (14900), 518 (13800), 540 (14200) nm (ϵ); UV/Vis (MeOH): $\lambda_{\max} = 312$ (8600), 370 (7000), 500 (30000) nm (ϵ); UV/Vis (MeOH + TFA): $\lambda_{\max} = 301$ (6600), 372 (8100), 516 (32800) nm (ϵ); UV/Vis (MeOH + Zn²⁺): $\lambda_{\max} = 312$ (8200), 390 (8400), 512 (32600), 523 (43800) nm (ϵ); UV/Vis (MeOH) + Ni²⁺): $\lambda_{\max} = 405$ (9200), 474 (22500), 500 (26300) nm (ϵ); UV/Vis (MeOH + Cu²⁺): $\lambda_{\max} = 280$ (125000), 390 (9300), 470 (8200), 514 (11300) nm (ϵ); UV/Vis (MeOH) + Fe²⁺): $\lambda_{\max} = 294$ (177200), 470 (20900), 500 (26700) nm (ϵ); UV/Vis (DMSO): $\lambda_{\max} = 313$ (10200), 461 (38600), 493 (37500) nm (ϵ); UV/Vis (DMSO + TFA): $\lambda_{\max} = 380$ (12500), 476 (50700), 520 (52800) nm (ϵ); UV/Vis (DMSO + Zn²⁺): $\lambda_{\max} = 312$ (6500), 388 (9600), 529 (10800) nm (ϵ); UV/Vis (DMSO + Ni²⁺): $\lambda_{\max} = 449$ (33100), 513 (30100) nm (ϵ); UV/Vis (DMSO + Cu²⁺): $\lambda_{\max} = 489$ (26200), 539 (31600) nm (ϵ); UV/Vis + Fe²⁺): $\lambda_{\max} = 295$ (98300), 322 (17600), 487 (39000), 512 (12200) nm (ϵ).

2,3,6,7,11,12,17,18-Octamethyl-corrphycenato-copper(II) (4a; C₂₈H₂₈CuN₄)

General procedure: 200 mg metallic copper dust (Aldrich) and 0.3 mmol **3** in 100 ml dimethyl formamide were stirred for 3 days under reflux. Then the solvent was removed under vacuum. The

residue was taken up in 200 ml dichloromethane and the mixture was filtered to remove the solid residue. The solution was washed with 50 ml 10% aqueous HCl, 2 × 50 ml water, and 50 ml brine. After drying over anhydrous sodium sulfate and removing the solvent *in vacuo*, the residue was purified by flash chromatography on silica (type G60) using dichloromethane/ethyl acetate/tetrachloromethane ($v/v/v = 2/1/1$) as the eluent. The yellow-red band was further purified by silica gel column chromatography using dichloromethane/ethyl acetate/tetrachloromethane ($v/v/v = 2/2/1$). To further purify **4**, the material was dissolved in the minimum amount of dichloromethane, and hexane was added until **4** started to precipitate. The mixture was kept for 4 h at ambient temperature, the solid was filtered off, and washed with small amount of methanol (-10°C).

Yield: 50% (starting from **3a** or **3b**); M.p.: 250°C (dec.); $^1\text{H NMR}$ (200 MHz, δ , $\text{CDCl}_3 + 1$ drop *TFA*-d): 3.47 (br s, 2CH_3), 3.52 (br s, 4CH_3), 3.59 (br s, 2CH_3), 10.42 (br s, $-\text{CH}=\text{CH}-$), 10.73 (br s, $2-\text{CH}=\text{}$) ppm; IR (KBr): $\nu = 3315, 2958, 2880, 1590, 1488, 1453, 1430, 1261, 1200\text{ cm}^{-1}$; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 389 (19800), 423 (19800), 471 (2100), 524 (1800), 559 (2500), 603 (1200)\text{ nm}$ (ϵ); UV/Vis (acetone): $\lambda_{\text{max}} = 397 (19400), 434 (6400), 568 (1500), 624 (1000)\text{ nm}$ (ϵ); UV/Vis (*DMSO*): $\lambda_{\text{max}} = 404 (15000), 506 (1800), 574 (940)\text{ nm}$ (ϵ); UV/Vis (MeOH): $\lambda_{\text{max}} = 404 (26500), 568 (2300), 592 (1500)\text{ nm}$ (ϵ); MS (EI): m/e (%) = 486 (23, $\text{M}^+ + 2$), 485 (78, $\text{M}^+ + 1$), 484 (70, M^+), 483 (100, $\text{M}^+ - 1$), 482 (22), 468 (18), 241 (20), 233 (10), 226 (13), 97 (11), 85 (12), 83 (11), 77 (12), 71 (16), 69 (11), 57 (22), 55 (13), 44 (75), 43 (12), 41 (14).

2,3,6,7,11,18-Hexamethyl-12,17-bis-(2-methoxycarbonyl)ethyl-corrphycenato-copper(II)
(**4b**; $\text{C}_{34}\text{H}_{36}\text{CuN}_4\text{O}_4$)

Prepared according to the above general procedure from **3c** or **3d**. Yield: 50%; M.p.: 250°C (dec.); $^1\text{H NMR}$ (200 MHz, δ , $\text{CDCl}_3 + 1$ drop *TFA*-d): 3.51 (br s, 2CH_3), 3.65 (br s, $2\text{CH}_2\text{COO}, 2\text{CH}_3$), 3.73 (br s, $2\text{CH}_2\text{CH}_2\text{COO}, 2\text{CH}_3$), 4.31 (2OCH_3), 10.42 (br s, $-\text{CH}=\text{CH}-$), 10.73 (br s, $2-\text{CH}=\text{}$) ppm; IR (KBr): $\nu = 3368, 3115, 2968, 2870, 1730, 1590, 1458, 1450, 1400, 1201, 1200, 970\text{ cm}^{-1}$; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 435 (23300), 555 (2000), 593 (1000)\text{ nm}$ (ϵ); UV/Vis (acetone): $\lambda_{\text{max}} = 405 (35200), 433 (62600), 552 (5100), 591 (2300)\text{ nm}$ (ϵ); UV/Vis (*DMSO*): $\lambda_{\text{max}} = 417 (61400), 435 (116900), 553 (9800), 593 (4500)\text{ nm}$ (ϵ); MS (EI): m/e (%) 629 (37), 628 (69), 627 (71, M^+), 626 (67), 555 (22), 554 (23), 482 (37), 470 (4), 469 (5), 468 (9), 467 (5), 466 (5), 453 (3), 452 (4), 442 (4), 441 (9), 234 (3), 233 (5), 227 (3), 226 (7), 225 (4), 219 (4), 218 (4), 208 (3), 207 (13), 201 (6), 199 (9), 197 (3), 173 (15), 171 (17), 157 (4), 155 (4), 125 (20), 113 (21), 111 (28), 107 (3), 105 (3), 99 (30), 97 (71), 95 (24), 85 (72), 83 (63), 69 (64), 57 (95); Ms (high resolu., EI): $m/e = 627.2028$.

2,3,6,7,11,12,17,18-Octamethyl-corrphycene (**5a**; $\text{C}_{28}\text{H}_{30}\text{N}_4$)

General procedure: 10 mg **4** were stirred at ambient temperature for 5 h with a mixture of 20 ml dichloromethane, 20 ml methanol, and 17 g 98% sulfuric acid. Then, 100 ml dichloromethane and 50 ml water were added. The organic layer was separated and washed with 20 ml water, 20 ml satd. aqueous sodium bicarbonate, and 20 ml brine. After drying over anhydrous sodium sulfate and removing the solvent *in vacuo*, the residue was flash chromatographed over silica (type G-60) using dichloromethane as the eluent. The yellow-red band was collected. After removing the solvent, the residue was crystallized from methanol. Yield: 80%; m. p.: 280°C (dec.); $^1\text{H NMR}$ (200 MHz, δ , CDCl_3): -2.10 (br s, 2NH), 3.35 (s, 2CH_3), 3.52 (s, 4CH_3), 3.64 (s, 2CH_3), 9.87 (s, $-\text{CH}=\text{CH}-$), 9.90 (s, $2-\text{CH}=\text{}$) ppm; $^{13}\text{C NMR}$ (50 MHz, δ , $\text{CDCl}_3 + 1$ drop *TFA*-d): 11.93 (4CH_3), 13.52 (4CH_3), 98.51, 103.44, 133.01, 136.99, 138.64, 139.23, 140.11, 141.88, 144.30, 144.65 ppm; UV/Vis (CH_2Cl_2): $\lambda_{\text{max}} = 408 (82800), 510 (8800), 545$ (sh, 2500), 632 (2000) nm (ϵ); UV/Vis (*DMSO*): $\lambda_{\text{max}} = 408 (56000), 510 (6300), 546$ (sh, 1700), 632 (1000) nm (ϵ); IR (KBr) $\nu = 3355, 2955, 2854, 1730, 1600, 1445, 1321, 1200, 1080\text{ cm}^{-1}$; MS (FAB): m/e (%) = 424 (55), 423 (100), 422 (60, M^+), 421 (41), 409 (31), 383 (30), 369 (58), 339 (52), 313 (71), 285 (48), 257 (35), 243 (38), 237 (43), 219 (53).

2,3,6,7,11,18-Hexamethyl-12,17-bis-(2-methoxycarbonylethyl)-corrphycene (5b; C₃₄H₃₈N₄O₄)

Prepared according to the above general procedure. Yield: 82%; M. p.: 270 °C (dec.); ¹H NMR (200 MHz, δ, CDCl₃): -2.23 (br, s, 2NH), 3.20 (t, *J* = 8.0 Hz s, 2CH₂CH₂COO), 3.36 (s, 2CH₃), 3.48 (s, 2CH₃), 3.56 (s, 2CH₃), 3.76 (s, 2OCH₃), 4.32 (t, *J* = 8.0 Hz, 2CH₂CH₂COO), 9.78 (s, -CH=CH-), 9.81 (s, 2-CH=) ppm; UV/Vis (CH₂Cl₂): λ_{max} = 411 (93000), 512 (8600), 550 (sh, 3600), 628 (1050) nm (*ε*); UV/Vis (DMSO): λ_{max} = 411 (88200), 512 (300), 550 (sh, 2700), 629 (900), nm (*ε*); IR (KBr): ν = 3445, 3289, 2948, 2916, 2857, 1733, 1595, 1435, 1365, 1288, 1186, 1174, 955 cm⁻¹; MS (FAB): *m/e* (%) = 568 (40), 567 (100), 566 (71, M⁺), 565 (19), 507 (9), 460 (13), 369 (9), 307 (84), 289 (48), 273 (13).

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