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Direct β-amination reaction in porphyrin systems—a simple route to compounds containing two nitrogen substituents at both β-positions of the same pyrrole unit

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ABSTRACT

The direct β-amination of porphyrin derivatives is described. 2-Nitro-*meso*-tetraarylporphyrins (zinc and copper complexes) react with *N*,*N*,*N*-trimethylhydrazinium iodide (TMHI) in the presence of a base (KOH/DMSO system, ca 70–80 °C) to give products of nucleophilic aromatic substitution of hydrogen. In this process, the nucleophilic replacement of a H-atom by an NH_2 group takes place. The products obtained, bearing two neighbouring nitrogen substituents on the same pyrrole ring, are valuable intermediates for various synthetic uses.

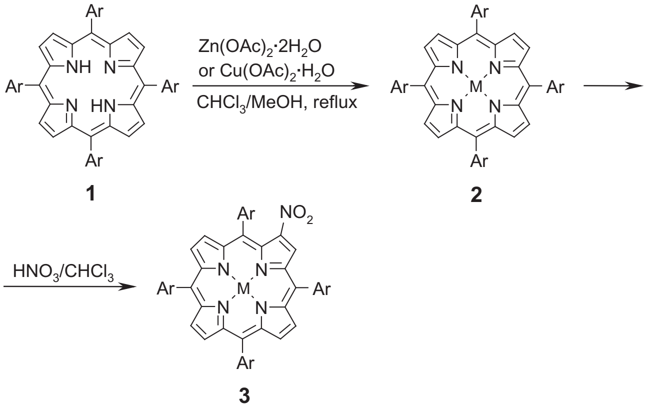
β-Functionalized porphyrins are very useful and versatile intermediates for the synthesis of more complex moieties (e.g., Lacerda et al.;[1] Alonso et al.;[2] Silva et al.;[3] Silva et al.;[4] Wang et al.;[5] Ostrowski and Wyrębek[6]). Among others, β-amino derivatives appear to be very attractive starting materials.[7] They were used for the preparation of *N*-linked bis-porphyrins (e.g., Tröger's base analogues[7a]), new porphyrins with extended π-system (pyrazine- and quinoxaline-fused porphyrins,[7b] pyridine-fused porphyrins,[2,7c,7d] imidazole-fused porphyrins,[7e,7f] etc.), or porphyrins conjugated with a fused peripheral *N*-heterocyclic carbene moiety (NHC).[7e,7f] β-Amino functionalization also offers the possibilities for modulation of physico-chemical properties of the parent compounds (e.g., sensitivity to oxidation and very interesting electrochemical properties[7b]).

Simple β-aminoporphyrins are usually prepared by reduction of the corresponding nitro-derivatives. Their synthesis could be possible, as well, by the aromatic nucleophilic substitution of hydrogen in appropriate electrophilic porphyrin systems. However, in the literature there are only occasional known examples of this type of nucleophilic substitution in β-positions of porphyrins by nitrogen nucleophiles.[7b,7e,7f,8]

In continuation of our ongoing research, investigations towards the synthesis of β-amino-porphyrins via vicarious nucleophilic substitution of hydrogen[9] were undertaken. We have already successfully applied this methodology for the amination of porphyrins in *meso*-aryl rings.[10]

Herein, electrophilic β-nitroporphyrins were used as the starting materials, which can be easily prepared according to literature methods (Scheme 1).[11] Some are known compounds and they were previously used in our laboratory.

Initially, the NH groups inside the core ring were protected to avoid *N*-anion generation under the strong basic conditions employed.[10,12] *N*,*N*,*N*-Trimethylhydrazinium iodide ($[Me_3N^+{-}NH_2]I^-$)



a: M = Zn, Ar = Ph; **b:** M = Cu, Ar = 3-F-C_6H_4; **c:** M = Cu, Ar = 3-Cl-C_6H_4; **d:** M = Cu, Ar = 3-Me-C_6H_4; **e:** M = Cu, Ar = 3-MeO-C_6H_4

Scheme 1.

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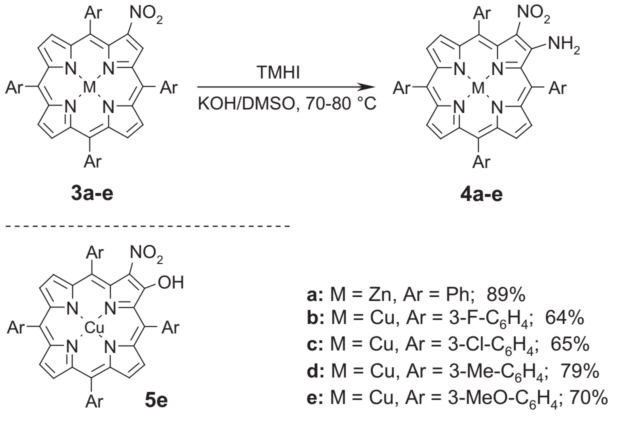
was chosen as the aminating agent, which has been previously successfully applied in several reactions. We also used other aminating reagents (sulfenamides, hydroxylamine, and 4-amino-4*H*-1,2,4-triazole) which were tested for various porphyrin systems in our laboratory, but only with moderate success.[13] Similarly, in the present case, when using the above listed reagents, we did not observe promising results. It should be mentioned, however, that for 4-amino-4*H*-1,2,4-triazole Richeter et al. reported good yields of the β-amination of two similar porphyrinates.[7e,7f]

In the first experiment, β-nitroporphyrin-zinc(II) **3a** was reacted with TMHI to give the expected 2-amino-3-nitro-substituted product **4a** (KOH/DMSO, 70–80 °C, 1.5 h).[14] The yield of this product was very high (89%). In its ^{1}H NMR spectrum the characteristic signal of the β-proton neighbouring the NO_2 group had disappeared. This provided clear evidence that the substitution occurred on the same pyrrole ring containing the NO_2 group. Additionally, a broad singlet was observed at 6.54 ppm (NH_2) and three doublets: 8.98 ppm (*J* = 4.9 Hz, 1H), 8.84 ppm (*J* = 4.9 Hz, 1H), and 8.54 ppm (*J* = 4.9 Hz, 1H) due to three of the remaining β-protons. The other three β-protons appeared as a multiplet at 8.75–8.81 ppm. These signals confirmed the structure of product **4a**. Three similar compounds were obtained by Crossley et al.[7b] and Richeter et al.[7e, 7f] They used other *N*-nucleophiles, generated from amides and from 4-amino-4*H*-1,2,4-triazole.

Amination of several other porphyrin complexes with the use of TMHI gave good yields of the expected products:[14] [2-amino-3-nitro-5,10,15,20-tetrakis(3-fluorophenyl)porphyrinato]copper(II) (**4b**, 64%), [2-amino-3-nitro-5,10,15,20-tetrakis(3-chlorophenyl)-porphyrinato]copper(II) (**4c**, 65%), [2-amino-3-nitro-5,10,15,20-tetrakis(3-methylphenyl)porphyrinato]copper(II) (**4d**, 79%), and [2-amino-3-nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]copper(II) (**4e**, 70%) (Scheme 2). It is worth noting that labile groups such as F or Cl in *meso*-aryl rings did not enter into an S_NAr substitution reaction with the hydrazinium anion.

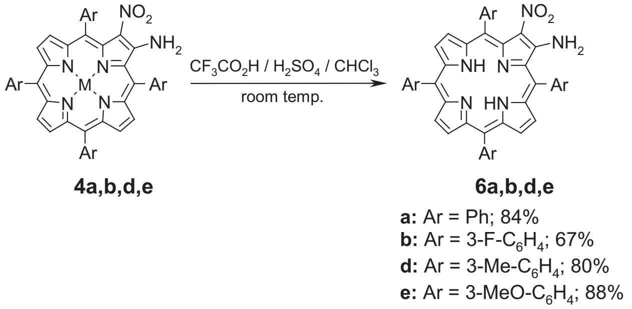
In the reaction of **3e**, the desired product **4e** was accompanied by small amounts of [2-hydroxy-3-nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]copper(II) (**5e**, 6%). Probably, this is due to an OH^-addition to the nitroporphyrin complex and subsequent oxidation of the σ^H-adduct formed, according to the oxidative nucleophilic substitution mechanism (ONSH).[10b,15,16]

The products described in this communication represent valuable intermediates for further syntheses, which sometimes can be realized under acidic conditions. To avoid potential problems in these transformations, we decided to convert the above chelates into the free porphyrin bases. Therefore, the synthesized compounds were demetallated in reactions carried out in $H_2SO_4/CF_3COOH/CHCl_3$ mixture at room temperature (Scheme 3).[17] Thus, a new set of valuable products (**6a**,**b**,**d**,**e**) was obtained and the yields of the decomplexation were very good (67–88%). The structures of the final products were confirmed by ^{1}H NMR, UV–vis, and MS methods. Interestingly, in the ^{1}H NMR spectra, diagnostic signals originating from the β-protons, situated at the opposite side to the substituted pyrrole ring, appeared as AB systems in all cases in the region 8.61–8.66 ppm.



a: M = Zn, Ar = Ph; 89%
b: M = Cu, Ar = 3-F-C_6H_4; 64%
c: M = Cu, Ar = 3-Cl-C_6H_4; 65%
d: M = Cu, Ar = 3-Me-C_6H_4; 79%
e: M = Cu, Ar = 3-MeO-C_6H_4; 70%

Scheme 2.



a: Ar = Ph; 84%
b: Ar = 3-F-C_6H_4; 67%
d: Ar = 3-Me-C_6H_4; 80%
e: Ar = 3-MeO-C_6H_4; 88%

Scheme 3.

In conclusion, the described amination represents an important tool in porphyrin chemistry. This method is of high utility because the corresponding amino-/nitro–moieties allow for various synthetic transformations. Currently, we are investigating the utility of these compounds and results concerning the synthesis of new attractive porphyrin hybrids will be reported in due course.

Acknowledgments

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11. *Substrates*: [2-Nitro-5,10,15,20-tetrakis(3-chlorophenyl)porphyrinato]copper(II) (**3c**) and [2-nitro-5,10,15,20-tetrakis(3-methylphenyl)porphyrinato]-copper(II) (**3d**) were obtained according to known procedures[18] (yields: 80% and 85%, respectively). (2-Nitro-5,10,15,20-tetraphenylporphyrinato)zinc(II) (**3a**) was prepared according to a modified literature procedure[19] (0.13 mmol of **2a** in 180 ml of $CHCl_3$; addition of 32.5 ml of 50% HNO_3; 0.5 min); yield—35%. Synthesis of **3b**: 5,10,15,20-Tetrakis(3-fluorophenyl)porphyrin (**1b**)[20] was converted into complex **2b** according to a procedure applied for similar

compounds[21] (with the use of $Cu(OAc)_2{\cdot}H_2O$); yield—97%. Then, the above complex was nitrated (also according to a procedure described for similar compounds:[18] 30% HNO_3, rt, 15 min) to give [2-nitro-5,10,15,20-tetrakis(3-fluorophenyl)porphyrinato]copper(II) (**3b**); yield—93%. Synthesis of **3e**: 5,10,15,20-Tetrakis(3-methoxyphenyl)porphyrin (**1e**)[22] was converted into complex **2e** according to a procedure applied for similar compounds[21] (with the use of $Cu(OAc)_2{\cdot}H_2O$); yield—75%. Then, the above complex was nitrated (also according to a procedure described for similar compounds:[18] 20% HNO_3, rt, 5 min) to give [2-nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]-copper(II) (**3e**); yield—89%. Data for new compounds: *[5,10,15,20-Tetrakis(3-fluorophenyl)porphyrinato]copper(II) (**2b**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 570 (3.13), 537.5 (4.06), 499.5 (3.28), 413.5 nm (5.34, Soret band). MS (FD) m/z (% rel int.): 751 (4), 750 (20), 749 (56), 748 (44), 747 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{44}H_{24}N_4F_4Cu$ [M^+]: 747.1233; Found: 747.1275. *[5,10,15,20-Tetrakis(3-methoxyphenyl)porphyrinato]copper(II) (**2e**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} (*log* ε): 591.5 (3.76), 549 (3.96), 514 (3.43), 424.5 nm (5.11, Soret band). MS (APPI) m/z (% rel int.): 800 (9), 799 (30), 798 (66), 797 (58), 796 (100) [isotope $(M+H)^+$]. HR-MS (FD) calculated for $C_{48}H_{36}N_4O_4Cu$ [M^+]: 795.2033; Found: 795.1981. *[2-Nitro-5,10,15,20-tetrakis(3-fluorophenyl) porphyrinato]copper(II) (**3b**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 589.5 (4.04), 547 (4.27), 513 (3.79), 419.5 nm (5.36, Soret band). MS (FD) m/z (% rel int.): 796 (7), 795 (28), 794 (65), 793 (45), 792 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{44}H_{23}N_5O_2F_4Cu$ [M^+]: 792.1084; Found: 792.1108. *[2-Nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]-copper(II) (**3e**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 591.5 (3.99), 548.5 (4.18), 511 (3.64), 422.5 nm (5.32, Soret band). MS (APPI) m/z (% rel int.): 845 (8), 844 (26), 843 (57), 842 (58), 841 (100) [isotope $(M+H)^+$]. MS (FD) m/z (% rel int.): 844 (1), 843 (15), 842 (54), 841 (52), 840 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{48}H_{35}N_5O_6Cu$ [M^+]: 840.1883; Found: 840.1852.

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14. *General procedure for the amination of β-nitro-5,10,15,20-tetraarylporphyrin complexes*. To a stirred solution of zinc(II) or copper(II) complex **3a**–**e** (0.20 mmol) in DMSO (4 ml), *N*,*N*,*N*-trimethylhydrazinium iodide (TMHI; 122 mg, 0.60 mmol) [for **3a**: 200 mg, 0.99 mmol] and KOH (120 mg, 2.14 mmol) [for **3a**: 170 mg, 3.03 mmol] were added. The reaction was carried out under argon in a flask equipped with a reflux condenser at 75 °C for 45 min (for **3a**—1.5 h). The reaction mixture was cooled to room temperature and was poured into a 3% aqueous solution of HCl (50 ml) with ice. The product was extracted with $CHCl_3$ (3 × 15 ml), the combined organic layers were washed with H_2O (3 × 50 ml), and dried over $MgSO_4$. After evaporating the solvent, the crude residue was chromatographed (silica gel, 230–400 mesh) to give: **4a**—131 mg (eluent: $CHCl_3$), yield 89%; **4b**—104 mg (eluent: $CHCl_3$), yield 64%; **4c**—114 mg (eluent: $CHCl_3$), yield 65%; **4d**—125 mg (eluent: $CHCl_3$), yield 79%; **4e**—120 mg (eluent: $CHCl_3$/MeOH, 250:1), yield 70%. In the last reaction, the desired product **4e** was accompanied by [2-hydroxy-3-nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]copper(II) (**5e**), 10.5 mg (eluted with $CHCl_3$/MeOH, 100:1), yield 6%. Data for new compounds: *[2-Amino-3-nitro-5,10,15,20-tetraphenylporphyrinato]zinc(II) (**4a**)*: mp >300 °C. ^{1}H NMR (200 MHz, $CDCl_3$): 8.98 (d, J = 4.9 Hz, 1H, H^{β}-pyrrole), 8.84 (d, J = 4.9 Hz, 1H, H^{β}-pyrrole), 8.81–8.75 (m, 3H, H^{β}-pyrrole), 8.54 (d, J = 4.9 Hz, 1H, H^{β}-pyrrole), 8.27–8.09 (m, 8H, H-Ph), 7.93–7.62 (m, 12H, H-Ph), 6.54 (br s, 2H, NH_2). UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 609 (4.07), 567.5 (4.29), 531.5 (3.70), 442 nm (5.34, Soret band). MS (FD) m/z (% rel int.): 743 (2), 742 (7), 741 (21), 740 (47), 739 (39), 738 (69), 737 (50), 736 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{44}H_{28}N_6O_2Zn$ [M^+]: 736.1565; Found: 736.1602. *[2-Amino-3-nitro-5,10,15,20-tetrakis(3-fluorophenyl)porphyrinato]copper(II) (**4b**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 608.5 (4.08), 561 (4.07), 521 (3.73), 432 nm (5.18, Soret band). MS (FD) m/z (% rel int.): 811 (4), 810 (21), 809 (53), 808 (38), 807 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{44}H_{24}N_6O_2F_4Cu$ [M^+]: 807.1193; Found 807.1202. *[2-Amino-3-nitro-5,10,15,20-tetrakis(3-chlorophenyl)porphyrinato]copper(II) (**4c**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 606 (4.15), 562.5 (4.30), 522 (3.85), 438 (5.31, Soret band), 321 nm (4.37). MS (FD) m/z (% rel int.): 880 (4), 879 (5), 878 (12), 877 (20), 876 (23), 875 (61), 874 (29), 873 (100), 872 (21), 871 (53) [isotope M^+]. HR-MS (FD) calculated for $C_{44}H_{24}N_6O_2{}^{35}Cl_3{}^{37}Cl_1Cu$ [M^+]: 872.9981; Found: 872.9976. *[2-Amino-3-nitro-5,10,15,20-tetrakis(3-methylphenyl)porphyrinato]copper(II) (**4d**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 605 (3.42), 562.5 (3.57), 524.5 (3.14), 439.5 nm (4.62, Soret band). MS (FD) m/z (% rel int.): 795 (7), 794 (28), 793 (54), 792 (48), 791 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{48}H_{36}N_6O_2Cu$ [M^+]: 791.2196; Found: 791.2238. *[2-Amino-3-nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]copper(II) (**4e**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 604.5 (3.84), 561.5 (4.00), 440 nm (5.06, Soret band). MS (ESI) m/z (% rel int.): 881 (4), 880 (7), 879 (6.5), 878 (11) [isotope $(M+Na)^+$]; 860 (6), 859 (16), 858 (43), 857 (74), 856 (71), 855 (100) [isotope M^+]. HR-MS (ESI) calculated for $C_{48}H_{36}N_6O_6Cu$ [M^+]: 855.1992; Found: 855.1946. *[2-Hydroxy-3-nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]copper(II) (**5e**)*: mp >300 °C. UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 605 (3.88), 557.5 (3.95), 430.5 nm (4.97, Soret band). MS (ESI) m/z (% rel int.): 861 (17), 860 (28), 859 (62), 858 (94), 857 (100), 856 (97) [isotope M^+ and $(M+H)^+$]. HR-MS (ESI) calculated for $C_{48}H_{35}N_5O_7Cu$ [M^+]: 856.1832; Found: 856.1821.
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17. *General procedure for the demetallation of 2-amino-3-nitro-5,10,15,20-tetraarylporphyrinates.* To a stirred solution of 2-amino-3-nitro-5,10,15,20-tetraarylporphyrinate (**4a**,**b**,**d**,**e**; 0.03 mmol) in 1 ml of $CHCl_3$ in a round-bottomed flask, concentrated H_2SO_4 (1 ml) and CF_3COOH (1.5 ml) were added dropwise. The reaction was continued with stirring at room temperature for 10–15 min. Then, the mixture was poured into H_2O (20 ml). The aqueous phase was extracted with $CHCl_3$ (3 × 10 ml), the combined organic layers were washed with H_2O (3 × 50 ml), and dried over $MgSO_4/Na_2CO_3$. After evaporating the solvent, the residue was chromatographed (silica gel, 230–400 mesh; eluent: $CHCl_3$/*n*-hexane, 2:1) to yield the respective 2-amino-3-nitro-5,10,15,20-tetraarylporphyrins: (a) 17 mg of **6a**, 84%; (b) 15 mg of **6b**, 67%; (c) 17.5 mg of **6d**, 80%; (d) 21 mg of **6e**, 88%. Data for new compounds: *2-Amino-3-nitro-5,10,15,20-tetraphenylporphyrin (**6a**)*: This compound has been already described in the literature;[7b] the additional data are given below for more detailed and accurate characterizarion of the product. mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.96 (d, J = 5.2 Hz, 1H, H^{β}-pyrrole), 8.78 (d, J = 5.2 Hz, 1H, H^{β}-pyrrole), 8.76 (d, J = 4.8 Hz, 1H, H^{β}-pyrrole), 8.63 and 8.61 (AB, J = 4.6 Hz, 2H, H^{β}-pyrrole), 8.59 (d, J = 4.8 Hz, 1H, H^{β}-pyrrole), 8.36 (d, J = 7.2 Hz, 2H, H-Ph), 8.24–8.15 (m, 6H, H-Ph), 7.94–7.89 (m, 3H, H-Ph), 7.81–7.63 (m, 9H, H-Ph), 6.81 (br s, 2H, NH_2), −2.32 and −2.54 (2 × s, 2H, 2 × NH). UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 661 (3.49), 604.5 (3.62), 568.5 (3.81), 529.5 (4.05), 431 nm (5.26, Soret band). MS (FD) m/z (% rel int.): 677 (2), 676 (13), 675 (50), 674 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{44}H_{30}N_6O_2$ [M^+]: 674.2430; Found: 674.2405. *2-Amino-3-nitro-5,10,15,20-tetrakis(3-fluorophenyl)porphyrin (**6b**)*: mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.97 (d, J = 5.1 Hz, 1H, H^{β}-pyrrole), 8.79 (d, J = 5.1 Hz, 1H, H^{β}-pyrrole), 8.77 (d, J = 5.1 Hz, 1H, H^{β}-pyrrole), 8.63 and 8.61 (AB, J = 4.7 Hz, 2H, H^{β}-pyrrole), 8.60 (d, J = 5.0 Hz, 1H, H^{β}-pyrrole), 8.15–7.86, 7.78–7.61, and 7.56–7.47 (3 × m, 15H, H-Ar(F)), 7.38 (td, J = 8.4, 2.2 Hz, 1H of H-Ar(F)), 6.88 (br s, 2H, NH_2), −2.40 and −2.63 (2 × s, 2H, 2 × NH). UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 669 (3.48), 606.5 (3.98), 571 (4.07), 532.5 (4.38), 434.5 nm (5.36, Soret band). MS (ESI) m/z (% rel int.): 749 (16), 748 (51), 747 (100) [isotope $(M+H)^+$]. HR-MS (ESI) calculated for $C_{44}H_{27}N_6O_2F_4$ [$(M+H)^+$]: 747.2132; Found: 747.2138. *2-Amino-3-nitro-5,10,15,20-tetrakis(3-methylphenyl)porphyrin (**6d**)*: mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.96 (d, J = 5.0 Hz, 1H, H^{β}-pyrrole), 8.78 (d, J = 5.0 Hz, 1H, H^{β}-pyrrole), 8.76 (d, J = 5.0 Hz, 1H, H^{β}-pyrrole), 8.63 and 8.61 (AB, J = 4.8 Hz, 2H, H^{β}-pyrrole), 8.59 (d, J = 5.0 Hz, 1H, H^{β}-pyrrole), 8.18–8.11 (m, 2H, H-Ar(CH_3)), 8.05–7.94 (m, 6H, H-Ar(CH_3)), 7.79 (apparent t, J = 7.8 Hz, 1H, H-Ar(CH_3)), 7.74–7.51 (m, 6H, H-Ar(CH_3)), 7.46 (d, J = 7.8 Hz, 1H, H-Ar(CH_3)), 6.83 (br s, 2H, NH_2), 2.68 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 2.64 (s, 6H, 2 × CH_3), −2.35 and −2.58 (2 × s, 2H, 2 × NH). UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 668.5 (3.47), 609.5 (3.83), 573.5 (3.92), 534 (4.19), 437.5 nm (5.21, Soret band). MS (FD) m/z (% rel int.): 733 (3), 732 (15), 731 (55), 730 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{48}H_{38}N_6O_2$ [M^+]: 730.3056; Found: 730.3042. *2-Amino-3-nitro-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin (**6e**)*: mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 9.01 (d, J = 5.0 Hz, 1H, H^{β}-pyrrole), 8.83–8.77 (m, 2H, H^{β}-pyrrole), 8.66 and 8.64 (AB, J = 4.6 Hz, 2H, H^{β}-pyrrole), 8.63 (d, J = 5.0 Hz, 1H, H^{β}-pyrrole), 7.97–7.60 (m, 16H, H-Ar(OCH_3)), 5.92 (br s, 2H, NH_2), 4.02 (s, 3H, OCH_3), 4.01 (s, 6H, 2 × OCH_3), 3.99 (s, 3H, OCH_3), −2.36 and −2 60 (2 × s, 2H, 2 × NH). UV–vis ($CHCl_3$), λ_{max} ($\log\varepsilon$): 673.5 (3.67), 650.5 (3.69), 605 (3.80), 575 (3.94), 532.5 (4.19), 436 nm (5.21, Soret band). MS (FD) m/z (% rel int.): 797 (3), 796 (15), 795 (54), 794 (100) [isotope M^+]. HR-MS (FD) calculated for $C_{48}H_{38}N_6O_6$ [M^+]: 794.2853; Found: 794.2828.
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