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Synthesis of N-Confused Porphyrin Derivatives with a Substituted 3-C Position

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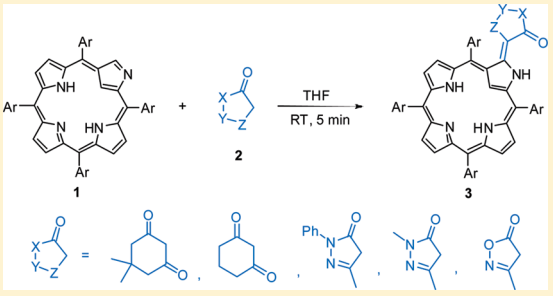
Supporting Information

ABSTRACT: Active methylene compounds such as 5,5-dimethylcyclohexane-1,3-dione, cyclohexane-1,3-dione, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 1,3-dimethyl-1*H*-pyrazol-5(4*H*)-one, and 3-methylisoxazol-5(4*H*)-one react with the 3-C position of N-confused porphyrin in THF for 5 min to afford a novel type of N-confused porphyrin derivatives in good yield without the need of any catalyst.

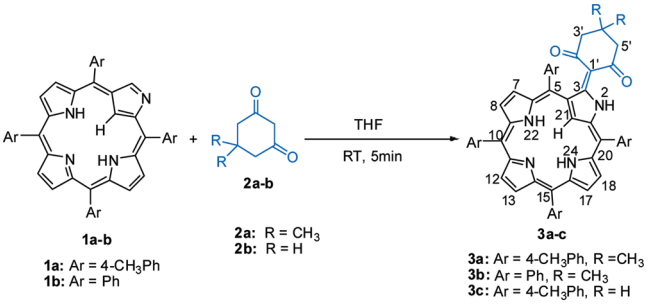


Chemical modification of N-confused porphyrin (Ncp) to generate novel Ncp derivatives with new structures and properties has attracted great attention since its first synthesis by the groups of Furuta[1] and Latos-Grażyński[2] independently in 1994 due to potential applications of this kind of porphyrin analogues as sensors[3] and catalysts,[4] in supramolecular chemistry[5] as well as in material[6] and medical science.[7]

The unusual reactivity of Ncp originated from the presence of *confused* pyrrole ring. There are three main reaction sites in the *confused* pyrrole ring, i.e., 2-N,[8] 21-C,[9] and 3-C.[10] At the external nitrogen of Ncp (2-N) an electrophilic reaction can take place yielding alkylation products, while acids (HBr,[10b] CF_3COOH,[10a] CF_3COOAg,[10d] $BF_3 \cdot O(C_2H_5)_2$[10e]) have been shown to catalyze substitution reactions at the position 3-C. The carbon−nitrogen double bond in the *confused* pyrrole ring is partially isolated from the macrocyclic conjugation pathway,[10d] and thus its reactivity resembles that of a C=N fragment in aza-aromatic systems rather than in a simple imine. The C=N in azines (quinolines, isoquinolines, and phenanthridine) can react with ketene,[11] 1,3-dipolar compounds (nitrilimine, nitrile oxide),[12] activated alkynes (dimethyl acetylenedicarboxylate, propiolate),[13] isocyanides,[14] trimethylsilyl cyanide,[15] active methylene compounds,[16] and chloroformylarylhydrazines.[17] Inspired by this reactivity pattern, we have reported the reactions of Ncp's with ketene,[18a] activated alkynes, and 1,3-dipolar compounds.[18b] The unusual reactivity of the peripheral carbon−nitrogen double bond of a free base Ncp drove us to a further study on the modification of Ncp's *via* the reaction at this site.

In the present work, we report a facile and catalyst-free method for direct coupling of active methylene compounds and Ncp at C-3 position (Scheme 1). It should be pointed out that the derivatization at C-3 position of Ncp generally is catalyzed by acids.[10]

Scheme 1. Synthesis of N-Confused Porphyrin Derivatives 3a−c



A solution of Ncp **1a** and 5,5-dimethylcyclohexane-1,3-dione **2a** in THF was stirred at room temperature for 5 min. Chromatographic separation of the reaction mixture afforded **3a**.

The matrix-assisted laser desorption ionization−time-of-flight mass spectrometry (MALDI-TOFMS) of **3a** gave the molecular ion peak at *m*/*z* 808, which indicates the addition of one molecule of 5,5-dimethylcyclohexane-1,3-dione **2a** to **1a**. The

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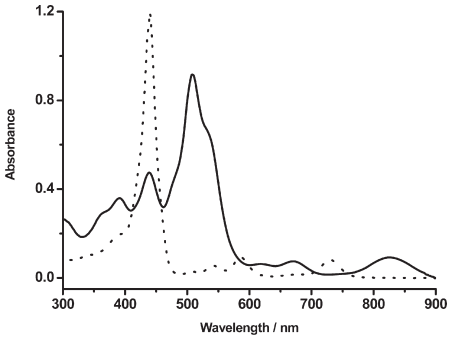


Figure 1. UV−vis−NIR spectra of **3a** (solid line) and **1a** (dotted line) in $CHCl_3$ (8.5×10^{-6} M).

UV−vis−NIR spectrum of **3a** (Figure 1), characterized by five major bands at ∼394, 439, 508, 674, and 824 nm, resembles that observed for Ncp's lactam derivative.[19]

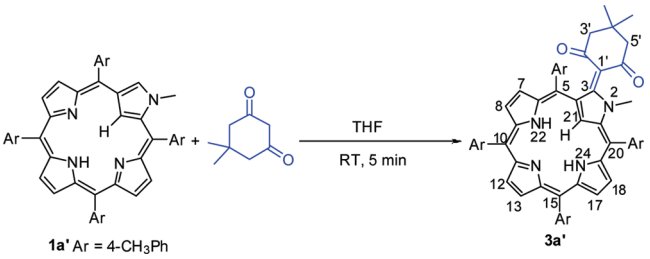
The ^{1}H NMR spectrum of **3a** (298 K, $CDCl_3$) (see Supporting Information, Figure S1) is characterized by six β-pyrrole proton signals in the region of 8.20−8.68 ppm, the inner CH signal (21-H) of the inverted pyrrole at −3.78 ppm, and the outer NH at 13.65 ppm assignment of which was confirmed by the deuterium exchange experiment with D_2O. Three singlets at 2.59, 2.69, and 2.72 ppm are assigned to four methyls of the *meso* *p*-tolyl substituents, and the singlet at 0.85 ppm represents two methyls of the dimethylcyclohexanedione fragment and splits into two singlets at 223 K. A decoalescence into four doublets is observed at low temperatures also for a multiplet at 2.02−2.04, which is assigned to the diastereotopic methylene groups of dimethylcyclohexane cycle. The signals of inner NHs, which are too broad to be observed at room temperature, appear at −0.77 and −1.03 ppm as two singlets at 223 K.

Further assignment of the proton signals in the NMR spectra of **3a** was conducted by means of combination of 2D homo- and heteronuclear experiments. In the low-temperature ^{1}H−^{1}H COSY spectrum (223 K, $CDCl_3$, see Supporting Information) the two inner NH protons at −0.77 and −1.03 ppm correlate to β-protons of pyrrole. The ^{1}H−^{1}H COSY map shows also correlations between 21-H and 2-NH, unequivocally indicating localization of the low-field resonating proton on the macrocycle's perimeter. Because of the signal overlap in the low field region, only a partial assignment of protons in **3a** can be performed. The ^{1}H NMR spectral pattern of **3a** resembles to some extent that of lactam Ncp derivative[19] with a striking difference regarding the position of the 2-NH resonance, which appears at 8.50 ppm for the 3-C=O containing compound[19] and at 13.65 in the spectrum of **3a**. Such a strong downfield shift can be attributed to an intramolecular hydrogen bond between 2-N and properly oriented carbonyl oxygen of the substituent in the position 3-C. Compounds **3b** and **3c** can be obtained in good yields by similar procedures.

To further elucidate the structure of product and find a plausible reaction mechanism, 2-N-CH_3-Ncp (**1a′**) was reacted with 5,5-dimethylcyclohexane-1,3-dione **2a** in THF at room temperature for 5 min affording **3a′** in 82% yield (Scheme 2).

Fortunately, this time we can give a full assignment for the protons based on ^{1}H NMR, COSY, NOESY, and their low temperature spectra (see Supporting Information, Figure S2). The obvious difference between the ^{1}H NMR spectra of **3a** and **3a′** is a lack of the low-field signal of 2-NH in the spectrum of **3a′** due to

Scheme 2. Synthesis of N-Confused Porphyrin Derivatives 3a′



methylation of outer nitrogen in this derivative and appearance of another methyl signal at about 3.2 ppm. A striking increase in the aromatic ring current effect on going from **1a′** to **3a′** is noteworthy. In the parent compound the π-electron delocalization pathway in the macrocycle includes the N(CH_3) fragment, which results in a weaker shielding/deshielding influence of the macrocyclic aromaticity on the proton chemical shifts than in the nonmethylated **1**. Thus in **1a′** 21-H resonates at about 0.7 ppm, 23-NH close to 3 ppm, and pyrrole signals are spread over the region from 7 to 8 ppm,[8b] whereas in the spectrum of **3a′** the internal CH signal appears near −4 ppm, inner NH's are shifted upfield by about 4 ppm and β-pyrrole protons downfield by about 1 ppm. Such an alteration of the spectral response is in line with the changes of the electronic structure of the molecule that take place upon introduction of double-bonded substituent onto the *confused* pyrrole.[8a]

Mechanistically, the reaction is originated from the mutual activation of the reactants by transfer of proton from **2a** to one of the basic sites of Ncp followed by nucleophilic attack on the 3-C position of the *confused* pyrrole resulting in the formation of intermediate **3′**, which undergoes a subsequent oxidehydrogenation in the presence of air to the corresponding product **3** (Scheme 3).

In addition to our studies on 5,5-dimethylcyclohexane-1,3-dione and cyclohexane-1,3-dione, we examined the reaction of 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, 1,3-dimethyl-1*H*-pyrazol-5(4*H*)-one, and 3-methylisoxazol-5(4*H*)-one. Thus reaction of these heterocyclic active methylene compounds with Ncp in THF for 5 min gave N-confused porphyrin derivatives with 3-C substituents (**3d**−**h**) in good yield (Scheme 4). The spectral characteristics of the products **3d**−**h** are similar to that of **3a**−**c** (see Supporting Information). Although the 2-NH of product **3d** is too broad to be observed in the room-temperature spectrum of ^{1}H NMR, its presence is apparent when the temperature is lowered to 252 K (see Supporting Information, Figure S3). Such behavior indicates involvement of this proton in a dynamic process slowing down at low temperature, which can be a keto−enolic tautomeric equilibrium related with proton transfer from 2-N onto oxygen of the substituent at 3-C (Scheme 5). The formation of the internal hydrogen bond in this system can facilitate the proton transfer process.

Other compounds bearing active methylene group such as acetylacetone, ethyl acetoacetate, diethyl malonate, and malononitrile in our hands do not react with Ncp under the reaction condition applied in the case of cyclic reagents **2**.

The reactions of Ncp **1** with active methylene compounds **2** can also take place in $CDCl_3$, DMF, and toluene, all giving good yields of the described products after 5 min.

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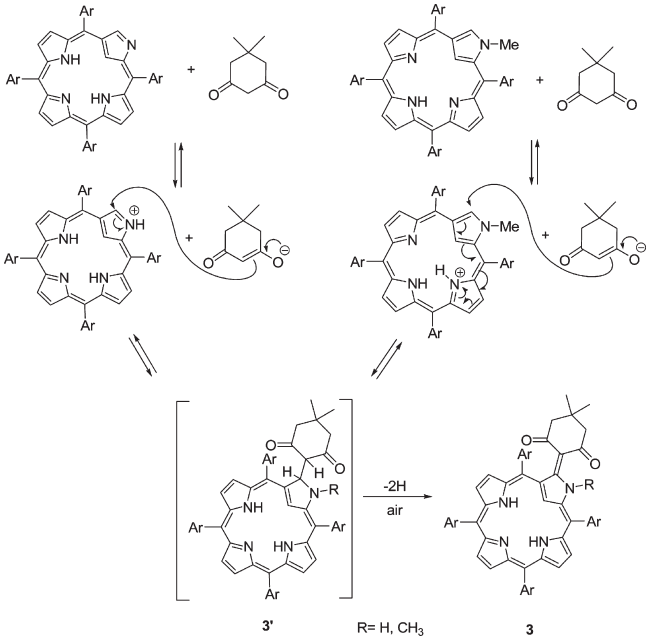
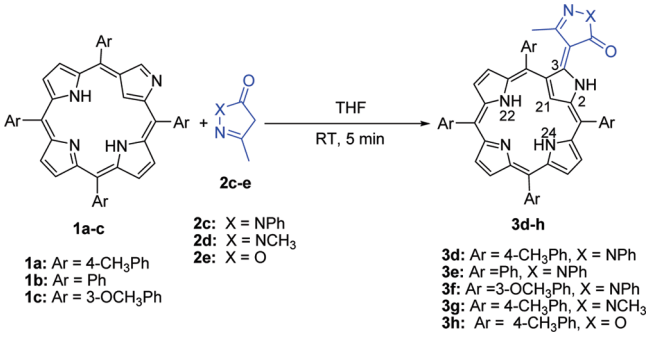
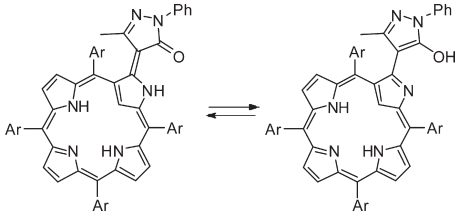
Scheme 3. Plausible Mechanism for the Reactions of Ncp with 2a



Scheme 4. Synthesis of N-Confused Porphyrin Derivatives 3d−h



Scheme 5. Keto-enolic Tautomery of 3d



In conclusion, a novel type of N-confused porphyrin derivatives with 3-C substituents were obtained in good yields by the reactions of Ncp with active methylene compounds without the need of any catalyst. This work demonstrates the reactivity of the peripheral C=N bond of N-confused porphyrins and provides a convenient method for the production of novel N-confused porphyrin derivatives, allowing fine-tuning of spectroscopic and redox properties of the system without changing main structural properties of the porphyrin skeleton or severely altering its aromaticity or coordination core.

EXPERIMENTAL SECTION

General Method for Synthesis of 3a−g. A solution of Ncp **1** (0.1 mmol) and active methylene compound **2** (0.1 mmol) in THF (5 mL) was stirred at room temperature for 5 min. After that time a TLC analysis revealed lack of Ncp reactant. The solvent was then evaporated under vacuum, and the residue was chromatographed on a silica gel column with dichloromethane/methanol (100:1 V/V) as eluent to afford Ncp derivative **3**.

Data for 3a: yield 85%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −3.78 (s, 1H, 21-CH), 0.85 (s, 6H, $-CH_3$), 2.02−2.04 (m, 4H, $-CH_2$), 2.59 (s, 3H, $-CH_3$), 2.69 (s, 6H, $-CH_3$), 2.72 (s, 3H, $-CH_3$), 7.55−7.58 (m, 6H, ArH), 7.78 (d, J = 8.0 Hz, 2H, ArH), 7.98−8.02 (m, 4H, ArH), 8.21 (d, J = 5.0 Hz, 1H, pyrrH), 8.26 (d, J = 4.5 Hz, 1H, pyrrH), 8.30−8.35 (m, 6H, ArH + pyrrH), 8.55 (d, J = 4.5 Hz, 1H, pyrrH), 8.62 (d, J = 5.0 Hz, 1H, pyrrH), 13.65 (br, 1H, 2-NH); ^{1}H NMR (500 MHz, $CDCl_3$, 223 K) δ −3.84 (s, 1H, 21CH), −1.03 (s, 1H, −NH), −0.77 (s, 1H, −NH), 0.80 (s, 3H, $-CH_3$), 0.83 (s, 3H, $-CH_3$), 1.66 (d, J = 15.5 Hz, 1H, $-CH_2$), 1.78 (d, J = 15.5 Hz, 1H, $-CH_2$), 2.19 (d, J = 15.0 Hz, 1H, $-CH_2$), 2.38 (d, J = 15.0 Hz, 1H, $-CH_2$), 2.58 (s, 3H, $-CH_3$), 2.68 (s, 6H, $-CH_3$), 2.69 (s, 3H, $-CH_3$), 7.54−7.69 (m, 7H), 7.84−7.91 (m, 3H), 8.09−8.12 (m, 3H), 8.21−8.22 (m, 2H), 8.27 (d, J = 5.0 Hz, 1H), 8.31−8.34 (m, 2H), 8.58−8.59 (m, 3H), 8.67 (d, J = 5.0 Hz, 1H), 13.52 (br, 1H, 2-NH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 21.3, 21.5, 21.7, 28.6, 29.1, 29.5, 51.2, 92.6, 102.6, 117.1, 119.9, 120.6, 125.3, 126.3, 126.5, 127.2, 127.5, 127.9, 128.0, 129.9, 134.0, 134.5, 134.8, 135.0, 136.0, 137.4, 137.6, 137.7, 137.9, 138.2, 138.5, 139.9, 140.5, 143.2, 145.4, 157.2, 159.3, 194.7. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 394 (4.62), 439 (4.74), 508 (5.03), 674 (3.93), 824 (4.03). MS (MALDI-TOF): m/z 808.2 (808.4 for $C_{56}H_{48}N_4O_2$). ESI-HRMS calcd for $[C_{56}H_{49}N_4O_2]^+$ (M + H): 809.3777, found 809.3755.

Data for 3b: yield 80%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −3.90 (s, 1H, 21CH), 0.78 (s, 6H, $-CH_3$), 1.97 (s, 4H, $-CH_2$), 7.50−7.55 (m, 1H), 7.65−7.75 (m, 8H), 7.81−7.84 (m, 1H), 7.93 (t, J = 7.0 Hz, 2H), 8.05−8.13 (m, 4H), 8.17 (d, J = 4.5 Hz, 1H), 8.23 (d, J = 4.0 Hz, 1H), 8.26−8.28 (m, 2H), 8.35−8.37 (m, 2H), 8.41 (d, J = 7.0 Hz, 2H), 8.53 (d, J = 4.0 Hz, 1H), 8.64 (d, J = 4.5 Hz, 1H), 13.70 (br, 1H, −NH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 29.3, 29.7, 51.3, 93.1, 102.7, 117.2, 120.0, 120.3, 125.5, 126.3, 126.4, 126.9, 127.2, 127.6, 127.8, 127.9, 128.0, 128.1, 129.0, 129.8, 130.0, 134.2, 134.5, 134.9, 135.0, 135.9, 136.8, 137.4, 138.5, 140.3, 140.6, 140.9, 141.3, 143.0, 145.6, 157.0, 159.1, 195.0. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 390 (4.35), 436 (4.45), 508 (4.75), 668 (3.76), 819 (3.74). ESI-HRMS calcd for $[C_{52}H_{41}N_4O_2]^+$ (M + H): 753.3151, found 753.3159.

Data for 3c: yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −3.94 (s, 1H, 21CH), 1.33−1.51 (m, 1H), 1.60−1.70 (m, 1H), 1.99−2.00 (m, 2H), 2.04−2.19 (m, 2H), 2.57 (s, 3H, $-CH_3$), 2.65 (s, 6H, $-CH_3$), 2.67 (s, 3H, $-CH_3$), 7.50−7.53 (m, 6H), 7.72 (d, J = 8.0 Hz, 2H), 7.96 (t, J = 7.5 Hz, 4H), 8.18 (d, J = 5.0 Hz, 1H), 8.23−8.25 (m, 3H), 8.27−8.31 (m, 4H), 8.53 (d, J = 4.5 Hz, 1H), 8.63 (d, J = 5.0 Hz, 1H), 13.54 (br, 1H, −NH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 19.3, 21.3, 21.5, 21.7, 37.2, 93.4, 104.8, 117.3, 119.9, 120.6, 126.4, 126.6, 127.3, 127.4, 127.9, 128.0, 128.4, 128.8, 128.9, 129.3, 129.7, 129.8, 132.7, 133.1, 133.8, 133.9, 134.2, 134.5, 134.8, 134.9, 135.0, 136.2, 137.5, 137.6, 137.7, 137.8, 138.0, 138.2, 138.3, 138.4, 138.7, 139.9, 140.8, 143.4, 146.9, 157.2, 159.1, 195.5. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 391 (4.55), 439 (4.68), 510 (4.90), 669 (3.88), 821 (3.93). ESI-HRMS calcd for $[C_{54}H_{45}N_4O_2]^+$ (M + H): 781.3464, found 781.3469.

Data for 3a′: yield 82.0%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −3.57 (s, 1H, 21CH), 0.80 (s, 3H, $-CH_3$), 0.82 (s, 3H, $-CH_3$), 1.68 (d,

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J = 16.0 Hz, 2H, $-CH_2$), 1.84 (d, J = 16.0 Hz, 2H, $-CH_2$), 2.59 (s, 3H, $-CH_3$), 2.62 (s, 3H, $-CH_3$), 2.64 (s, 6H, $-CH_3$), 3.17 (s, 3H, $-CH_3$), 7.52 (d, J = 7.5 Hz, 4H, ArH), 7.57 (d, J = 7.5 Hz, 2H, ArH), 7.68 (d, J = 8.0 Hz, 2H, ArH), 7.90 (d, J = 8.0 Hz, 2H, ArH), 7.94 (d, J = 8.0 Hz, 2H, ArH), 8.10 (d, J = 5.0 Hz, 1H, pyrrH), 8.15 (d, J = 5.0 Hz, 1H, pyrrH), 8.21 (br, 2H, pyrrH), 8.30 (d, J = 7.5 Hz, 2H, ArH), 8.32 (d, J = 7.5 Hz, 2H, ArH), 8.52 (d, J = 5.0 Hz, 1H, pyrrH), 8.61 (d, J = 5.0 Hz, 1H, pyrrH); ^{1}H NMR (500 MHz, $CDCl_3$, 223 K) δ −3.65 (s, 1H, 21CH), −0.53 (s, 1H, −NH), −0.45 (s, 1H, −NH), 0.79 (s, 3H, $-CH_3$), 0.86 (s, 3H, $-CH_3$), 1.44 (br, 1H, $-CH_2$), 1.52 (br, 1H, $-CH_2$), 1.94 (br, 1H, $-CH_2$), 2.11 (br, 1H, $-CH_2$), 2.63 (s, 6H, $-CH_3$), 2.68 (s, 6H, $-CH_3$), 3.18 (s, 3H, $-NCH_3$), 7.54−7.72 (m, 8H), 7.82−7.84 (m, 2H), 8.03−8.05 (m, 1H), 8.15−8.22 (m, 3H), 8.27 (br, 2H), 8.31−8.39 (m, 4H), 8.56 (d, J = 4.5 Hz, 1H), 8.64 (d, J = 4.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 21.2, 21.4, 21.5, 26.5, 30.4, 31.3, 38.2, 50.9, 86.2, 103.4, 118.3, 118.4, 121.5, 126.7, 126.9, 127.0, 128.0, 128.8, 128.9, 130.1, 130.9, 133.3, 134.2, 134.8, 134.9, 135.0, 135.4, 135.6, 137.1, 137.4, 137.8, 137.9, 138.3, 138.5, 139.1, 140.0, 144.4, 145.3, 150.8, 159.3, 159.5, 193.0. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 393 (4.47), 439 (4.60), 508 (4.88), 673 (3.79), 827 (3.88). ESI-HRMS calcd for $[C_{57}H_{51}N_4O_2]^+$ (M + H): 823.3934, found 823.4000.

Data for 3d: yield 85.0%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −4.26 (s, 1H, 21CH), 1.76 (s, 3H, $-CH_3$), 2.52 (s, 3H, $-CH_3$), 2.68 (s, 3H, $-CH_3$), 2.69 (s, 3H, $-CH_3$), 2.72 (s, 3H, $-CH_3$), 7.08 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.49−7.53 (m, 6H), 7.71−7.72 (m, 1H), 7.76 (d, J = 7.5 Hz, 3H), 7.83−7.86 (m, 4H), 7.95 (t, J = 8.0 Hz, 2H), 8.13 (d, J = 4.5 Hz, 1H), 8.21 (d, J = 4.5 Hz, 1H), 8.32−8.34 (m, 2H), 8.49−8.52 (m, 3H), 8.66 (d, J = 4.5 Hz, 1H); ^{1}H NMR (500 MHz, $CDCl_3$, 252 K) δ −4.74 (s, 1H, 21CH), −2.20 (br, 1H, −NH), −1.99 (br, 1H, −NH), 1.68 (s, 3H, $-CH_3$), 2.56 (s, 3H, $-CH_3$), 2.74 (s, 6H, $-CH_3$), 2.77 (s, 3H, $-CH_3$), 7.15−7.18 (m, 2H), 7.21−7.39 (m, 5H), 7.43−7.46 (m, 2H), 7.50−7.56 (m, 2H), 7.75−8.07 (m, 11H), 8.48−8.60 (m, 5H), 13.04 (br, 1H, −NH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 15.8, 21.4, 21.5, 21.8, 94.7, 96.8, 118.0, 118.9, 119.2, 120.5, 122.9, 123.5, 123.7, 126.0, 126.1, 127.8, 127.9, 128.0, 128.1, 128.6, 129.7, 130.1, 133.3, 133.9, 134.0, 134.5, 134.8, 135.2, 135.8, 136.5, 136.9, 137.1, 137.8, 137.9, 138.3, 139.1, 139.2, 139.5, 139.7, 139.9, 141.9, 143.3, 146.0, 156.2, 157.8, 167.4. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 391 (4.56), 460 (4.63), 531 (4.81), 711 (4.09), 830 (4.03). ESI-HRMS calcd for $[C_{58}H_{47}N_6O]^+$ (M + H): 843.3733, found 843.3741.

Data for 3e: yield 79%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −4.15 (s, 1H, 21CH), 1.78 (s, 3H, $-CH_3$), 7.05 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 2H), 7.74−7.76 (m, 6H), 7.85 (t, J = 7.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.96 (t, J = 7.5 Hz, 2H), 8.09−8.10 (m, 2H), 8.13−8.15 (m, 2H), 8.22 (d, J = 5.0 Hz, 1H), 8.26−8.27 (m, 1H), 8.29 (d, J = 4.5 Hz, 2H), 8.43−8.44 (m, 2H), 8.56 (d, J = 5.0 Hz, 1H), 8.61 (d, J = 7.5 Hz, 2H), 8.74 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 15.8, 95.1, 97.1, 118.4, 118.8, 119.1, 120.9, 122.7, 123.7, 126.1, 126.3, 127.0, 127.2, 127.3, 128.1, 128.2, 128.5, 128.8, 129.0, 129.2, 129.8, 133.8, 134.6, 134.9, 135.3, 136.7, 136.9, 137.3, 138.3, 139.1, 139.4, 139.5, 140.8, 141.2, 141.8, 143.3, 145.8, 156.5, 158.2, 167.3. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 384 (4.41), 460 (4.48), 531 (4.64), 714 (4.00), 817 (3.91). ESI-HRMS calcd for $[C_{54}H_{39}N_6O]^+$ (M + H): 787.3107, found 787.3115.

Data for 3f: yield 87%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −4.18 (s, 1H, 21CH), 1.83 (s, 3H, $-CH_3$), 3.99 (s, 3H, -OCH_3), 4.01 (s, 6H, -OCH_3), 4.09 (s, 3H, -OCH_3), 7.05−7.09 (m, 2H), 7.28−7.33 (m, 4H), 7.36−7.38 (m, 1H), 7.57−7.69 (m, 7H), 7.86−7.88 (m, 2H), 7.93 (d, J = 8.0 Hz, 2H), 8.05−8.09 (m, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.19−8.21 (m, 1H), 8.22−8.27 (m, 3H), 8.32 (d, J = 4.5 Hz, 1H), 8.59 (d, J = 5.0 Hz, 1H), 8.77 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 15.9, 55.5, 55.6, 55.7, 95.3, 97.3, 113.4, 113.9, 115.1, 117.9, 118.4, 118.7, 119.1, 120.4, 120.6, 120.8, 121.2, 122.5, 122.9, 123.6, 123.7, 124.9, 126.2, 127.3, 128.0, 128.1, 128.3, 128.5, 128.7, 129.7, 130.2, 130.5, 133.4, 134.2, 136.7, 136.8, 137.9, 138.9, 139.4, 139.7, 141.7, 141.9, 142.3, 143.4, 146.0, 156.0, 157.7, 158.3, 158.4, 159.4, 159.9, 171.5. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 401 (4.49), 456 (4.51), 529 (4.65), 706 (3.78), 822 (3.66). ESI-HRMS calcd for $[C_{58}H_{47}N_6O_5]^+$ (M + H): 907.3530, found 907.3527.

Data for 3g: yield 80%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −4.35 (s, 1H, 21CH), 1.66 (s, 3H, $-CH_3$), 2.54 (s, 3H, $-CH_3$), 2.67 (s, 3H, $-CH_3$), 2.68 (s, 3H, $-CH_3$), 2.70 (s, 3H, $-CH_3$), 3.39 (s, 3H, $-CH_3$), 7.49−7.63 (m, 8H), 7.75−7.79 (m, 6H), 8.07 (d, J = 5.0 Hz, 1H), 8.17 (d, J = 4.5 Hz, 1H), 8.30−8.31 (m, 2H), 8.46 (d, J = 8.0 Hz, 2H), 8.49 (d, J = 5.0 Hz, 1H), 8.62 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 16.0, 21.5, 21.6, 21.8, 31.5, 95.0, 95.8, 117.8, 118.6, 120.1, 122.7, 123.6, 125.8, 126.0, 127.7, 127.8, 127.9, 128.0, 129.6, 130.0, 132.6, 133.3, 133.9, 134.3, 134.8, 135.1, 135.9, 136.6, 137.0, 137.2, 137.6, 137.7, 137.8, 138.1, 138.9, 139.1, 139.8, 139.9, 141.6, 143.7, 144.4, 155.5, 156.9, 168.0. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 387 (4.65), 476 (4.73), 533 (4.82), 710 (4.09), 829 (4.04). ESI-HRMS calcd for $[C_{53}H_{45}N_6O]^+$ (M + H): 781.3577, found 781.3563.

Data for 3h: yield 90%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ −4.28 (s, 1H, 21CH), 1.65 (s, 3H, $-CH_3$), 2.56 (s, 3H, $-CH_3$), 2.67 (s, 3H, $-CH_3$), 2.68 (s, 3H, $-CH_3$), 2.69 (s, 3H, $-CH_3$), 7.53−7.56 (m, 6H), 7.75 (d, J = 7.5 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H), 7.91−7.95 (m, 4H), 8.16 (d, J = 4.5 Hz, 1H), 8.27−8.28 (m, 3H), 8.43 (d, J = 8.0 Hz, 2H), 8.58 (d, J = 4.5 Hz, 1H), 8.67 (d, J = 5.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ 13.8, 21.4, 21.5, 21.7, 86.2, 93.5, 118.4, 119.7, 120.4, 122.3, 123.5, 126.4, 126.7, 127.9, 128.0, 128.1, 128.6, 128.8, 129.9, 130.1, 133.6, 133.8, 134.3, 134.5, 135.0, 135.3, 135.5, 136.8, 137.2, 137.6, 138.0, 138.1, 139.7, 140.2, 140.3, 142.6, 142.8, 156.8, 157.7, 177.5. UV−vis−NIR ($CHCl_3$) λ_{max}/nm (log ε): 380 (4.73), 450 (4.88), 528 (5.06), 690 (4.26), 824 (4.23). ESI-HRMS calcd for $[C_{52}H_{42}N_5O_2]^+$ (M + H): 768.3260, found 768.3265.

■ ASSOCIATED CONTENT

Supporting Information. Analytical data and spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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