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Identification of Stable Porphomethenes and Porphodimethenes from the Reaction of Sterically Hindered Aldehydes with Pyrrole

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Abstract—Use of pivalaldehyde in mixed acid-catalyzed condensations of an aryl aldehyde with pyrrole allows the isolation and structural characterization of stable porphomethenes (5,10,15,22-tetrahydroporphyrins) and porphodimethenes (both 5,10- and 5,15-diphydroporphyrins) as intermediates of porphyrin synthesis. Crystal structures reveal the importance of the absolute configuration at the sp^3-hybridized centers for the oxidation and stability of these (bio)synthetic intermediates.

The synthesis of porphyrins via the acid catalyzed condensation of pyrroles with aldehydes[1,2] and porphyrin biosynthesis[3] is believed to proceed first to a porphyrinogen and then via separate oxidation steps through a series of hydroporphyrins to porphyrin. Despite the importance and daily use of these reactions unambiguous proof for the porphomethene and porphodimethene type intermediates between porphyrinogen and porphyrin has been lacking. During recent studies on 5,10,15,20-tetra(*tert*-butyl)porphyrin[4] and the synthesis of hindered porphyrins[5] using pivalaldehyde[6] we noted a tendency towards formation of oxidation resistant hydroporphyrins.[5–7] For example, the main product of the reaction of pyrrole, pivalaldehyde and 2,5-dimethoxybenzaldehyde was the porphomethene **1**, that could not be oxidized to the respective porphyrin.[6]

In line with observations made by Buchler,[8] we assume that the stability towards oxidants is dependent on the relative configuration of the sp^3 hybridized meso carbon atoms in the intermediates. To date all 'stable' porphodimethenes exhibited a *syn* diaxial orientation of the substituents at the two sp^3 centers. This is conformationally a relaxed situation in which the substituents at the tetravalent centers are removed from the macrocycle as much as possible to minimize steric hindrance. Thus, we surmised that use of sterically hindered aldehydes in mixed pyrrole condensation reactions might result in the preferential formation of stable hydroporphyrin intermediates due to formation of tetrapyrrole intermediates in which steric strain is minimized in an oxidation resistant conformation (Scheme 1).

As a first test reaction pyrrole, pivalaldehyde and benzaldehyde (4:3:1) were reacted under Lindsey conditions[9] with TFA as acid catalyst and DDQ as oxidant. Chromatography on silica gel eluting with hexane/methylene chloride (1:0→1:1) resulted in the isolation of five different compounds (yields <1%) in the following order. The first yellow compound (λ_{max}=425 nm in CH_2Cl_2) was identified by NMR and X-ray crystallography as the porphomethene **2** (Fig. 1). Next, the orange–red porphodimethene **4** (λ_{max}=471, 686 nm, Fig. 2) was found, followed by the two symmetric porphyrins **7** and **10** and one porphyrin with both types of meso substituents **8** (λ_{max}=421, 523, 563, 600, 656 nm). Identification of the individual compounds on TLC or chromatographic columns is generally easy as the color of the different intermediates is quite different. Porphomethenes have a yellow–orange color, porphodimethenes are orange–red and porphyrins red. The absorption maxima are also quite typical as the hydroporphyrins exhibit a very broad absorption band between 400–500 nm, while porphyrins mostly have sharp Soret absorption bands around 400 nm.

Another test reaction was performed in a similar manner albeit using tolylaldehyde (to aid the NMR spectroscopic characterization) and silver(I) oxide (to aid removal of the oxidant from the reaction mixture). From this reaction we isolated again a small amount of a porphomethene **3**, that could not be characterized completely but that showed an absorption spectrum similar to **1** and **2**. In addition, the porphodimethene **5** with characteristics similar to **4** was obtained. Intriguingly, with **6** we also isolated a 5,10-dihydroporphyrin (λ_{max}=431 nm) whose constitution was determined using 2D-NMR experiments.[10] Finally, the formation of **7** and two silver porphyrins (**9**, λ_{max}=429, 549, 591 nm; **10**, λ_{max}=427, 542 nm) was noted. The structure of **11** was unambiguously determined by X-ray

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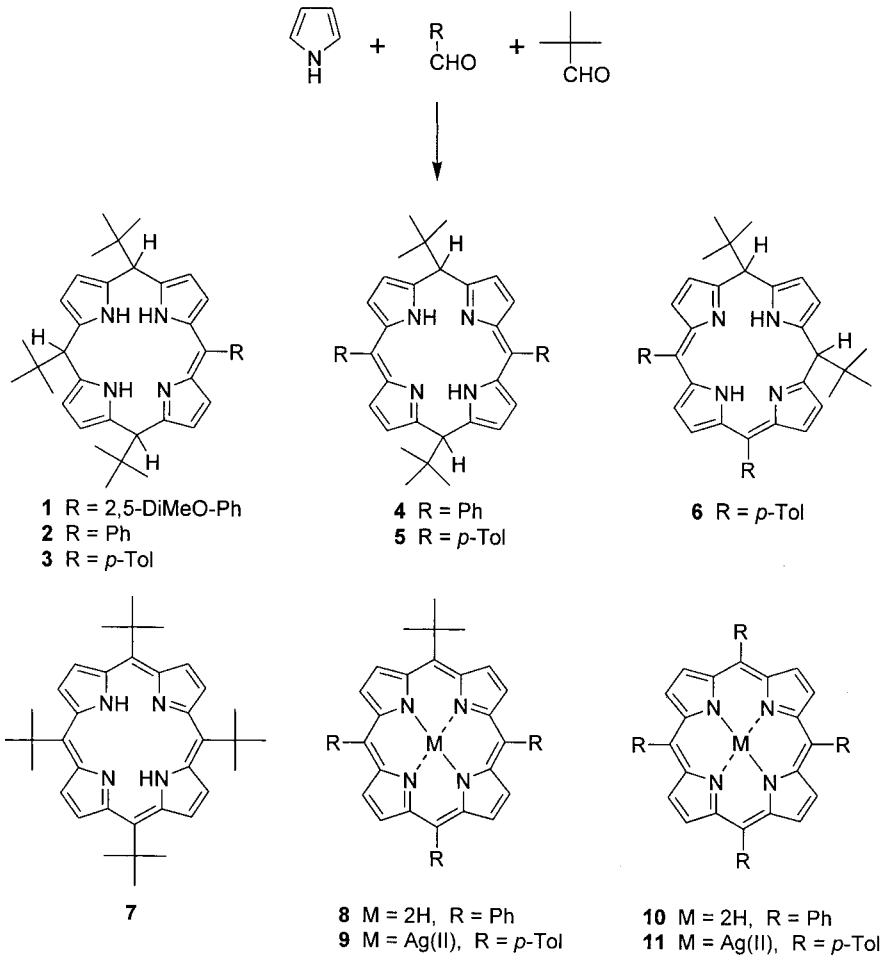


Scheme 1.

crystallography (not shown, average Ag–N bond length=2.0866(17) Å) and the structural data agree well with those of (5,10,15,20-tetraphenylporphyrinato)silver-(II).[11]

Use of the respective 5-substituted dipyrromethanes, reaction of pyrrole and aldehydes using other condensation methods (variation of concentration, acid, or chromatographic work-up) did not alter the products or their distribution significantly. All hydroporphyrins were resistant to oxidation with DDQ, *p*-chloranil, Ag_2O, PbO_4, MnO_4, $Ce(NH_4)NO_3$, and Br_2. Attempts to deprotonate the tetrapyrrolic intermediates with DBU to aid their oxidation to porphyrins resulted in the formation of blue colored and polar compounds. Thus, the remarkable stability of these compounds towards oxidants is so high that they rather undergo ring-opening reactions.

The two silver porphyrins **9** and **11** have to be the result of metalation with Ag_2O followed by disproportionation.[12]

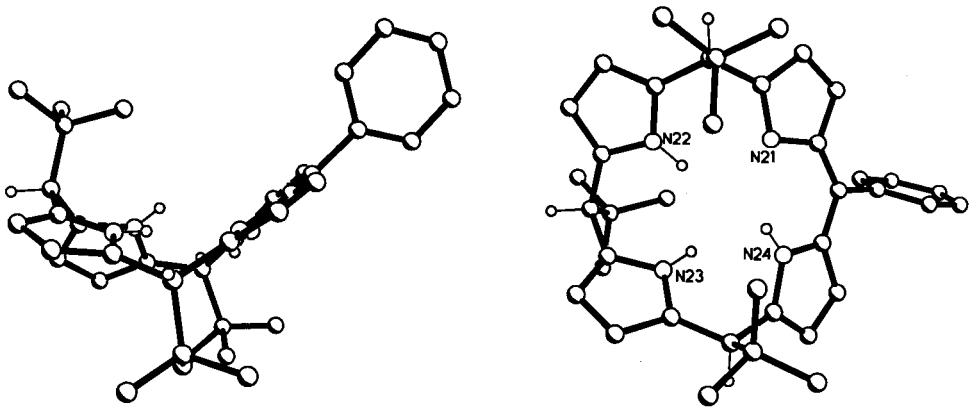


Figure 1. Side and top view of the molecular structure of **2** in the crystal.

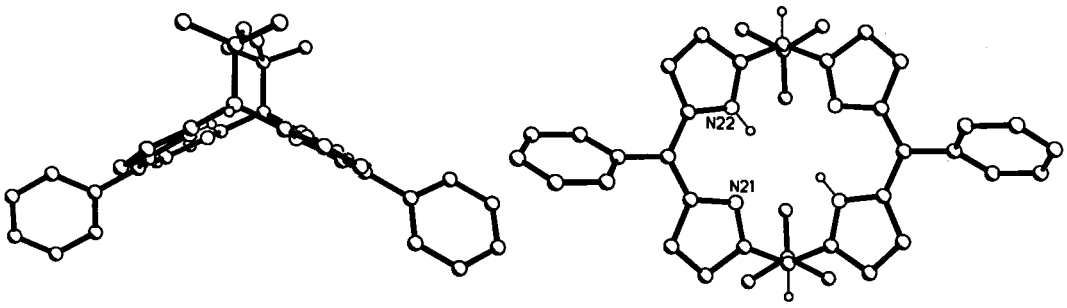
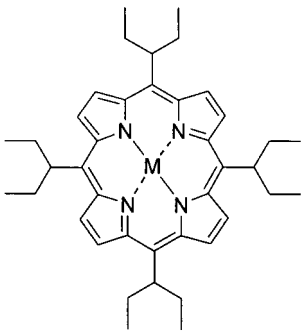


Figure 2. Side and top view of the molecular structure of **4** in the crystal.

This mechanism involves metallation of the free base precursors by CF_3COOAg^I to a Ag^I_2Por complex, that then undergoes disproportionation to give Ag^{II}Por and Ag^0. Silver porphyrins have only been rarely investigated and are normally prepared from Ag^I acetate in pyridine or AgCl in DMF.[13] We found, that use of Ag_2O in methylene chloride with TFA catalysis allows the preparation of Ag^{II} porphyrins in 60–70% yield with simpler work-up than existing methods. For example, the free base **12** was converted cleanly to **13** using this method (Scheme 2).

The crystal structures of the hydroporphyrins **1**,[6] **2** and **4** reveal several interesting features with implications for the porphyrinogen→porphyrin oxidation mechanism. All structures show the bulky *tert*-butyl residues in axial positions and each has a *syn* diaxial orientation of the 5,15 substituents. This is best evidenced in the side views given in Figs. 1 and 2. As **1** had an ↑↑↑-orientation (*syn* triaxial) of the *tert*-butyl groups[6] with respect to the macrocycle plane and **2** an ↑↓↑-orientation, the presence of the 5,15 *syn* diaxial feature appears to be critical for the oxidation resistance. In all hydroporphyrins (**1**–**6**) oxidation occurred at those meso positions that carried the sterically less demanding aryl substituent but not at those bearing a *tert*-butyl group. Again, this is best evidenced in the side views of the crystal structures where the dipyrromethene unit(s) in **2** and **4** have coplanar pyrrole rings while the dipyrromethane halves have tilted arrangements of the pyrrole rings. The roof-type conformation of the macrocycle in the crystal structure of **4** is rather similar to those obtained upon reaction of 5,10,15,20-tetra(*tert*-butyl)porphyrin **7** with nucleophiles[4] or by reductive alkylation of metal complexes of



12 M = 2H
13 M = Ag(II)

Scheme 2.

2,3,7,8,12,13,17,18-octaethylporphyrins.[8a] These are conditions where putatively the sterically most relaxed and thus thermodynamically most stable form on the conformational landscape is entered.

A possible explanation of the formation of the hydroporphyrins **1**–**6** involves the steric demand of the various meso substituents. Alkyl substituents, especially bulky ones like *tert*-butyl tend to ruffle a porphyrin, resulting in large displacements of the meso carbons from the mean plane.[5a,14] If oxidation proceeds first at the meso aryl substituted positions, this will result in a roof type structure of the porphomethene and -dimethene intermediates. An ↑↓-orientation of the 5,15 substituents in e.g. **2** or **4** and or a pseudoplanar macrocycle conformation,[8b,15] as putatively required for oxidation, is not possible for bulky alkyl residues and thus for aryl/*tert*-butyl combinations with 2 or 3 *tert*-butyl groups no further oxidation is possible. Note, that the currently accepted mechanism for in vivo synthesis of porphyrins requires the cofacial removal of three of the four meso hydrogen atoms, i.e. an arrangement of ↑↓↑↑ in our terminology.[3] The preferential oxidation of the meso aryl quadrants in the precursors might be due to the smaller steric demand of sp^2 hybridized substituents. For the porphyrinogen obtained from reaction of pyrrole with pivalaldehyde two conformations with yet unknown configurations have to exist. One is passed through during synthesis of **7** and undergoes oxidation while the other is obtained upon reduction of **7** to the respective porphyrinogen and is stable against oxidants.[7]

Currently, there is renewed interest in porphomethenes and -dimethenes[16] as examples of 'calixphyrins'[17] and the stability and structural properties of the hydroporphyrins discussed here, together with recent advances in the synthesis of porphodimethenes[5b,17,18] allows an interesting entry into conformationally designed receptors for small molecules and anions. Further studies are aimed at elucidating the exact relationship between the configuration of the intermediates and their oxidation to porphyrins.

Experimental

General experimental conditions and techniques were as follows: All chemicals used were of analytical grade and were purchased from Aldrich Co. Melting points were measured on a Reichert Thermovar apparatus and are uncorrected. Silica gel 60 (Merck, 230–400 mesh) or neutral

alumina (Alfa, 60 mesh) (Brockmann Grade III, i.e. deactivated with 7% water) were used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates. ^{1}H NMR spectra were recorded at a frequency of 250 MHz (Bruker, AC 250) or 500 MHz (Bruker, AMX 500) while ^{13}C NMR spectra were recorded with a Bruker AM 270 instrument. All chemical shifts are given in ppm, referenced on the δ scale downfield from the TMS signal as internal standard. Electronic absorption spectra were recorded on a Specord S10 (Carl Zeiss) spectrophotometer using dichloromethane as solvent. Mass spectra were recorded using a Varian MAT 711 mass spectrometer using the EI technique with a direct insertion probe and excitation energy of 80 eV.

Condensation reactions

Individual reactions were performed on a mmol scale and 4 equiv. of pyrrole were reacted with 3 equiv. of pivalylaldehyde and 1 equiv. of arylaldehyde under Lindsey-conditions[8] using trifluoroacetic acid as acid catalyst. Oxidation was performed with either DDQ (for the benzaldehyde reaction) or silver(I) oxide (for the tolylaldehyde reaction). Chromatography was laborious and involved first filtration of the crude reaction mixture through a short plug of alumina. After concentration of the filtrate, the residue was taken up in a minimum volume of methylene chloride and applied to the top of a silica gel column. For separation of the individual compounds the column was developed using a gradient method. Elution started first with neat *n*-hexane and then gradually the content of methylene chloride was increased until a ratio of 1:1 (v/v) was obtained. Compounds eluted in the following order: yellow porphomethenes with neat hexane, followed by porphodimethenes (10:1). Increase of the methylene chloride content to 1:1 eluted then the asymmetric substituted porphyrins or silver porphyrins followed by the symmetric (silver) porphyrins. The individual fractions were rechromatographed on silica gel under the same conditions and recrystallized. The individual yields of the isolated products were about 1%. Compounds **7**[4] and **10**[19] gave analytical data identical to literature values.

5,10,15-Tri(*tert*-butyl)-5,10,15,22-tetrahydro-20-phenylporphyrin (2). Yield: 5 mg yellow crystals from CH_2Cl_2/MeOH.; mp 220–230°C.; UV/Vis (CH_2Cl_2): λ_{max} (rel. int.)=425 nm (1); ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=0.65–0.72 (m, 9H, C(C*H*$_3$)$_3$), 0.90–1.05 (m, 18H, C(C*H*$_3$)$_3$), 3.65 (s, 1H, C$_m$–*H*), 4.01 (s, 2H, C$_m$–H), 5.80–5.85 (m, 2H, H$_{\beta\text{-pyrrole}}$), 6.13–6.15 (m, 4H, H$_{\beta\text{-pyrrole}}$), 6.23–6.27 (m, 2H, H$_{\beta\text{-pyrrole}}$), 7.35–7.51 (m, 5H, H$_{phenyl}$), 9.23 (br, s, 2H, N*H*); HRMS [$C_{38}H_{46}N_4$]: calcd 558.3722, found 558.3734.

5,15-Di(*tert*-butyl)-5,15-dihydro-10,20-diphenylporphyrin (4). Yield: 4 mg orange-red crystals from CH_2Cl_2/MeOH; mp 250–260°C; UV/Vis (CH_2Cl_2): λ_{max} (rel. int.)=471 nm (1) 686 (0.015); ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=1.09 (s, 18H, C(C*H*$_3$)$_3$), 3.91 (s 2H, C$_m$–H), 5.75–5.96, 6.23–6.51 (each d, *J*=4.1 Hz, 4H, H$_\beta$), 7.10–7.15 (m, 6H, H$_{phenyl}$), 7.24–7.28 (m, 4H, H$_{phenyl}$), 11.0 (s, 2H, N*H*); MS (80 eV); *m*/*z* (%): 576 (3) [M^+], 518 (1) [$M^+-C_4H_9$), 463 (100) [$M^+-2\times C_4H_9$); HRMS [$C_{40}H_{40}N_4$]: calcd 576.3253, found 576.3282.

5,15-Di(*tert*-butyl)-5,15-dihydro-10,20-di(*p*-tolyl)porphyrin (5). Yield: 4 mg red-brown crystals from CH_2Cl_2/MeOH; mp 250–255°C; UV/Vis (CH_2Cl_2): λ_{max} (rel. int.)=451 nm (1); ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=1.12 (s, 18H, C(C*H*$_3$)$_3$), 2.40 (s, 6H, C*H*$_3$–C$_6$H$_6$), 3.84 (s, 2H, C$_m$–H), 5.88–6.15, 6.42–6.74 (each d, *J*=4.1 Hz, 4H, H$_\beta$), 7.19–7.23 (m, 4H, H$_{phenyl}$), 7.34–7.37 (m, 4H, H$_{phenyl}$), 11.2 (s, 2H, N*H*); HRMS [$C_{42}H_{44}N_4$]: calcd 604.3566, found 604.3545.

5,10-Di(*tert*-butyl)-5,10,-dihydro-15,20-di(*p*-tolyl)porphyrin (6). Yield: 3 mg red-purple crystals from CH_2Cl_2/MeOH; mp 245–250°C; UV/Vis (CH_2Cl_2): λ_{max} (rel. int.)=431 nm (1); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=0.89 (s, 18H, C(C*H*$_3$)$_3$), 2.42 (s, 6H, C*H*$_3$–C$_6$H$_6$), 3.8 (s, 2H, C$_m$–*H*), 5.8 (d, *J*=2.5 Hz, 2H, H$_{\beta\text{-pyrrole}}$), 6.14 (d, *J*=2.3 Hz, 2H, H$_\beta$), 6.4 (d, *J*=4.4 Hz, 2H, H$_\beta$), 6.71 (d, *J*=4.4 Hz, 2H, H$_\beta$), 7.22 (d, *J*=8.1 Hz, 4H, H$_{m\text{-phenyl}}$), 7.32 (d, *J*=6.9 Hz, 4H, H$_{o\text{-phenyl}}$), 11.2 (s, 1H, N*H*), 13.47 (s, 1H, N*H*); ^{13}C NMR ($CDCl_3$): δ=22.65 (*C*H$_3$–C$_6$H$_6$), 28.24 (C(*C*H$_3$)$_3$), 37.04 (*C*(CH$_3$)$_3$), 51.97, 138.53 (*C*$_m$), 105.08, 136.94, 151.83, 177.3 (*C*$_a$), 120.75, 127.08, 130.29, 134.61 (*C*$_\beta$), 128.26 (*C*$_{m\text{-phenyl}}$), 131.34 (*C*$_{o\text{-phenyl}}$), 134.71 (*C*$_{p\text{-phenyl}}$), 138.67 (*C*$_{p\text{-phenyl}}$); HRMS [$C_{42}H_{44}N_4$]: calcd 604.3566, found 604.3598.

5-(*tert*-Butyl)-5,10,15-triphenylporphyrin (8). Yield: 3 mg purple crystals from CH_2Cl_2/MeOH; mp >300°C; UV/Vis (CH_2Cl_2): λ_{max} (rel. int.)=421 nm (1), 523 (0.035), 563 (0.018), 600 (0.009), 656 (0.004); ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=−1.79 (br. s, 2H N*H*), 2.38 (s, 9H, C(C*H*$_3$)$_3$), 7.69–7.75 (m, 9H, H$_{phenyl}$), 8.08–8.12 (m, 6H, H$_{phenyl}$), 8.52–8.54 (d, *J*=4.3 Hz, 2H, H$_{\beta\text{-pyrrole}}$), 8.59–8.61 (d, *J*=4.3 Hz, 2H, H$_{\beta\text{-pyrrole}}$), 8.87–8.89 (d, *J*=4.3 Hz, 2H, H$_{\beta\text{-pyrrole}}$), 9.52–9.54 (d, *J*=4.3 Hz, 2H, H$_{\beta\text{-pyrrole}}$); HRMS [$C_{42}H_{34}N_4$]: calcd 594.2783, found 594.2765.

{5-(*tert*-Butyl)-5,10,15-tri(*p*-tolyl)porphyrinato}silver(II) (9). Yield: 6 mg purple crystals from CH_2Cl_2/MeOH; mp >300°C; UV/Vis (CH_2Cl_2): λ_{max} (rel. int.)=429 nm (1), 549 (0.082), 591 (0.031); MS (80 eV); *m*/*z* (%): 743 (75) [M^+], 697 (95) [$M^+-C_3H_{10}$] 636 (100) [M^+−Ag]; HRMS [$C_{45}H_{38}N_4Ag$]: calcd 741.2147, found 741.2108.

(5,10,15,20-Tetratolylporphyrinato)silver(II) (11). Yield: 10 mg purple crystals from CH_2Cl_2/MeOH; mp >300°C; UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=427 nm (5.24), 542 (4.38); MS (80 eV); *m*/*z*(%): 777 (100) [M^+], 670 (10) [M^+−Ag]; HRMS [$C_{48}H_{36}N_4Ag$]: calcd 775.1991, found 775.1942.

{5,10,15,20-Tetrakis(1-ethylpropyl)porphyrinato}silver-(II) (13). To a solution of the free base **12** (0.25 mmol) in 50 ml dichloromethane 3 equiv. of Ag_2O are given and the mixture treated with 3 drops of trifluoroacetic acid. Stirring for 20 min is followed by filtration of the mixture through silica gel, evaporation of the solvation and recrystallization. Yield: 110 mg (0.1578 mmol, 63%) red crystals from CH_2Cl_2/MeOH; mp >300°C; UV/Vis (CH_2Cl_2): λ_{max} (log ϵ)=424 nm (5.07), 479 (4.21), 544 (4.24); MS

(80 eV); *m/z*(%): 695 (100) [M^+], 666 (10) [$M^+-C_2H_5$], 651 (41) [$M^+-C_3H_8$]; HRMS [$C_{40}H_{52}N_4Ag$]: calcd 695.3243, found 695.3274.

Crystal structure determinations

The crystals were immersed in hydrocarbon oil (Paraton N®), a single crystal selected, mounted on a glass fiber and placed in the low-temperature N_2 stream.[20] Intensity data for **4** were collected using an Siemens R3m/V instrument with graphite filtered Mo-K_α radiation (λ=0.71073 Å) at 126 K with ω-scans. Data for **2** were collected with an Siemens P4 diffractometer equipped with a rotating anode ($2\theta-\theta$ scans, Ni filtered Cu-K_α radiation, λ=1.54178 Å) at 129 K while data for **11** were collected at 85 K with a Siemens SMART system complete with 3-circle goniometer and CCD detector utilizing Mo-K_α radiation (λ=0.71073 Å). The intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied for **2** and **4** using the program XABS2[21a] and for **11** with the program SADABS,[21b] extinction effects were disregarded. The structures were solved with Direct Methods using the SHELXTL PLUS program system[22a] and refined against $|F^2|$ with the program XL-97 using all data.[22b] Nonhydrogen atoms were refined with anisotropic thermal parameters. Except for disordered groups, hydrogen atoms were generally placed into geometrically calculated positions and refined using a ridging model.[†]

Crystal data for 2. $C_{38}H_{46}N_4$. F_W=558.79, yellow plate from CH_2Cl_2/CH_3OH, crystal size 0.8×0.6×0.01 mm, monoclinic, $P2_1/n$, a=11.602(3), b=19.688(4), c=14.406(5) Å, β=99.33(2)°, V=3247(2) Å^3, Z=4, d_{calcd}=1.143 Mg m^{-3}, μ(Cu-K_α)=0.510 mm^{-1}, T_{min}=0.69, T_{max}=0.99, θ_{max}=56.45°, 4726 reflections collected, 4309 independent reflections, R_{int}=0.0233, 3148 reflections with $I>2.0\sigma(I)$, 391 parameters, R_1 ($I>2.0\sigma(I)$)=0.0643, R_1 (all data)=0.0932, wR_2 (all data)=0.1967, S=1.066, ρ_{max}=0.266 e Å^{-3}.

Crystal data for 4. $C_{40}H_{40}N_4$. F_W=576.76, orange–red block from CH_2Cl_2/CH_3OH, crystal size 1×1×1 mm, monoclinic, C_2/c, a=21.182(12), b=12.735(7), c=12.283(6) Å, β=105.19(4)°, V=3198(3) Å^3, Z=4, d_{calcd}=1.198 Mg m^{-3}, μ(Mo-K_α)=0.070 mm^{-1}, T_{min}=0.93, T_{max}=0.93, θ_{max}=27.51°, 4138 reflections collected, 3663 independent reflections, R_{int}=0.0264, 2677 reflections with $I>2.0\sigma(I)$, 202 parameters, R_1 ($I>2.0\sigma(I)$)=0.0626, R_1 (all data)=0.0870, wR_2 (all data)=0.1911, S=0.956, ρ_{max}=0.383 e Å^{-3}.

Crystal data for 11. $C_{48}H_{36}AgN_4\cdot 1/2CH_2Cl_2$. F_W=860.60, purple trapezoid from CH_2Cl_2/CH_3OH, crystal size 0.5×0.4×0.06 mm, monoclinic, $P2_1/c$, a=14.5231(6), b=8.6074(3), c=15.7568(6) Å, β=94.852(1)°, V=1962.64(13) Å^3, Z=2, d_{calcd}=1.456 Mg m^{-3}, μ(Mo-K_α)=0.691 mm^{-1}, T_{min}=0.72, T_{max}=0.96, θ_{max}=28.29°, 4743 reflections collected, 4135 reflections with $I>2.0\sigma(I)$, 267 parameters, R_1 ($I>2.0\sigma(I)$)=0.0294, R_1 (all data)=0.0364, wR_2 (all data)=0.0921, S=1.097, ρ_{max}=0.577 e Å^{-3}. The structure contains a disordered methylene chloride of solvation. Cl1 was refined as disordered over two split positions with equal occupancy. Due to crystallographically required disorder the total occupancy assigned was 0.5.

[†] Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 147599-147601.

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