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Hinged bis-porphyrin scaffolds I. The synthesis of a new porphyrin diene and its role in constructing hinged porphyrin dyads and cavity systems

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ABSTRACT

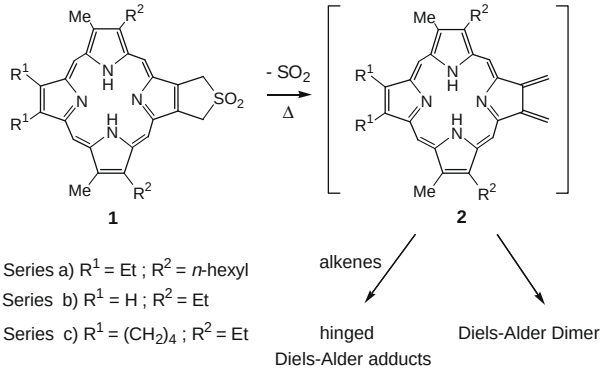
Norbornene building BLOCKs formed by the reaction of porphyrin 1,3-dienes with norbornadiene or dimethyl tricyclo[4.2.1.0^{2,5}]nona-2,7-diene-3,4-dicarboxylate were coupled with an ester-activated cyclobutene epoxide BLOCK to afford the first examples of hinged porphyrin-spacer-acceptor dyads. Similar dual coupling with a bis-(cyclobutene epoxide) formed doubly hinged POR-spacer-POR scaffolds separated by up to 16σ-bonds. The ability of the doubly hinged ZnPOR-16σ-ZnPOR scaffold to adopt cavity-shaped conformations was indicated by semiempirical AM1 calculations of these conformationally flexible bis-porphyrin scaffolds.

Molecular architectures containing in-built porphyrin components continue to attract attention as host–guest components[1,2] and in various aspects of energy and electron transfer.[3] Recently, two publications appeared from our respective laboratories, one dealing with the synthesis of the first porphyrin-1,3-diene **2a**[4] and the other describing the preparation of hinged scaffolds.[5] The present report combines these two concepts to produce a hinge-containing norbornene-fused porphyrin and its application to the synthesis of new classes of hinged bis-porphyrin scaffolds and porphyrin dyads (Scheme 1).

In this Letter, we report the preparation and stereoselective Diels–Alder reactions of porphyrin-1,3-diene **2a**. The porphyrin ring in **2a** contains two hexyl, two ethyl, and two methyl substituents designed to improve the lipophilicity of its derivatives over its earlier-described relative **2b** that contained only methyl and ethyl groups. The synthesis followed the previously reported multi-step protocol with only a few modifications such as the use of $PdCl_2$ rather than Pd/C for debenzylation. The 1,3-diene **2a** was generated in situ by ejection of SO_2 from **1a,** and in the presence of dienophilic alkene trapping agents formed hinged-adducts of type **4**/**6** (Scheme 2a and b); in the absence of a dienophilic trap, self-dimerization occurred to form a Diels–Alder adduct where one of the exocyclic olefinic π-bonds acted as the dienophile with the 1,3-diene of another.[4,6]

A key goal in this work was to prepare hinged norbornene building blocks suitable for cyclobutene bis-epoxide coupling procedures,[7,8] in which the porphyrins were south-facing relative to the scaffold positioned such that the methano-bridges were north-facing (Scheme 2).[9]

Direct reaction of a porphyrin 1,3-diene with norbornadiene was not suitable since we had shown previously that the adduct had the porphyrin ring in a north-facing relationship with the scaffold. Accordingly, the bicyclic diene **5** was employed as the dienophile in the expectation that reaction would occur preferentially at the ester-activated cyclobutene π-bond.[10] Reaction of **5** with por-



Scheme 1. Generation of porphyrin-1,3-dienes from sulfone precursors.

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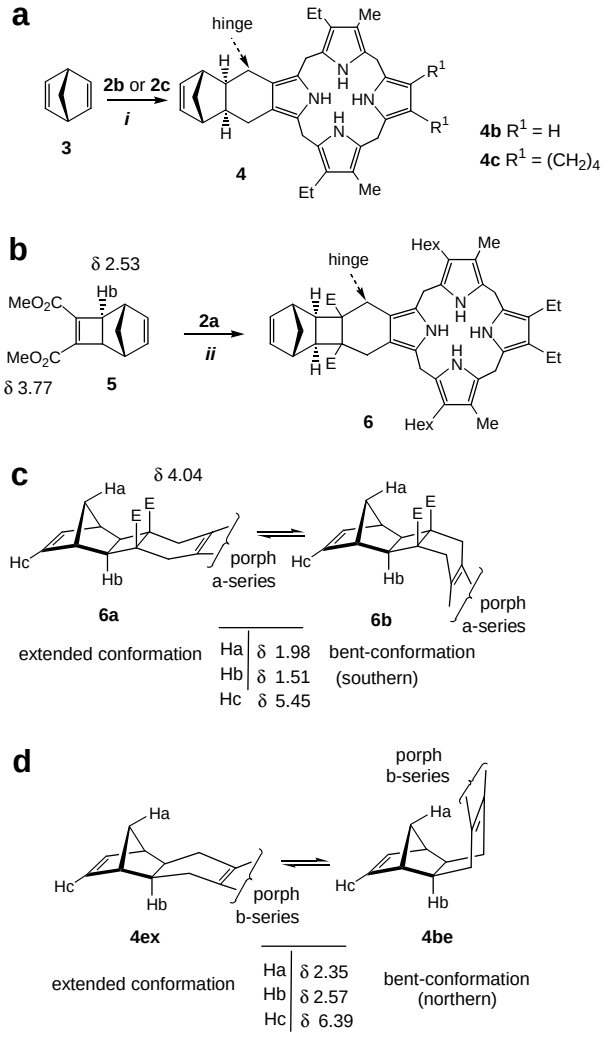


Scheme 2. Reagents and conditions: (i) 1,2,4-trichlorobenzene, 150 °C, 1 h, 55% (**4b**), 1,2,4-trichlorobenzene, 150 °C, 1 h, 35% (**4c**); (ii) 1,2,4-trichlorobenzene, 120 °C, 1 h, 89%.

phyrin 1,3-diene **2a**, generated in situ from its sulfone derivative **1a**, gave a single 1:1-adduct **6,** which by ^{1}H NMR spectroscopy showed that the norbornene π-bond (singlet, δ 5.45) had been retained.[11] The *endo*-facial selectivity for reactions at the cyclobutene π-bond of **5** has strong precedent,[10] and the resultant product **6** can exist in two conformations, the extended form **6a** or the bent conformation **6b** in which the porphyrin is south-facing relative to the alicyclic frame (Scheme 2c). The conformation of adduct **4** can similarly be in the extended form **4ex** or in the 'northern' directed bent conformation **4be** (Scheme 2d). Distinction between conformers **6a** and **6b**, assuming that they are not in equilibrium at room temperature, should be reflected in the chemical shift data for protons Ha and Hb since the anisotropy of the porphyrin ring should exhibit a pronounced geometry-dependant effect.[12] The chemical shift of the methyl esters in **6** at δ 4.04 indicates magnetic de-shielding of the ester methyl protons (from δ 3.77 in **5**), which could be associated with the bent conformation **6b** (Scheme 2c). On the other hand, the chemical shift of Hb (δ 1.51) is an intermediate value expected for the linear and bent conformations. For comparison, the corresponding isoindole bent and linear adducts of **5** have chemical shifts of Hb at δ 1.09 and δ 2.30, respectively,[13] where the value at higher field is caused by π-bond shielding. Variable temperature ^{1}H NMR spectroscopy showed that **6a**↔**6b** equilibrium is fast on the NMR time scale at room temperature, thus the ^{1}H NMR spectrum of **6** is averaged. A solution was cooled to 223 K, at which temperature the resonances of most protons severely broadened, but did not coalesce, indicating fast equilibrium even at low temperature. These results are further supported by the molecular modelling of **4**, **6,** and **14** employing the AM1 method (see modeling section, Figs. 1 and 2).[14] Finally, an X-ray structure of a related cycloadduct of **2b** features the bent conformation; however, these data cannot be directly compared to solution NMR results.[15] The observed fast interconversion between the two conformations strongly resembles the dynamic behavior of C_{60} ball-and-chain molecules in which a cyclohexene ring connects the polycyclic bridge to the fullerene cage.[16]

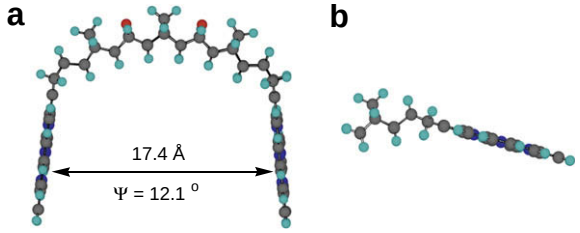


Figure 1. (a) AM1-optimized structure of **14** (substituents are removed) and (b) transition state for interconversion from **6a** to **6b**.

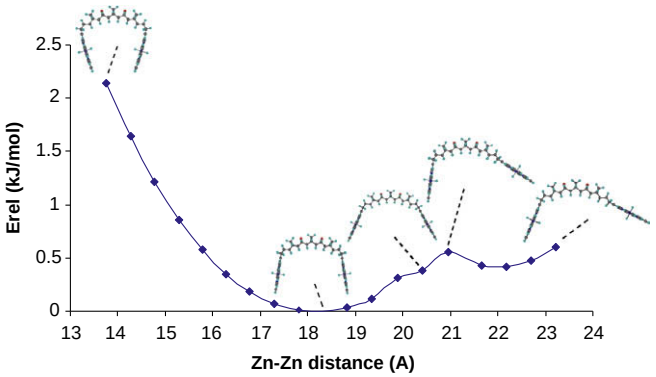
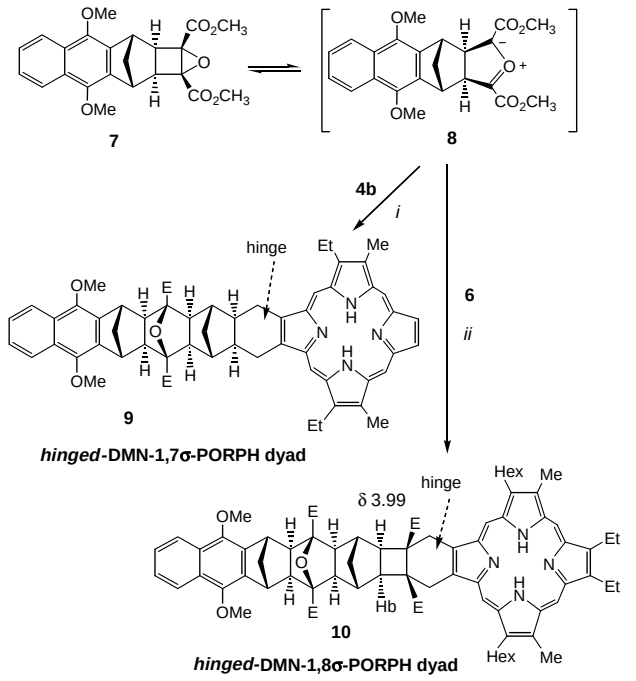


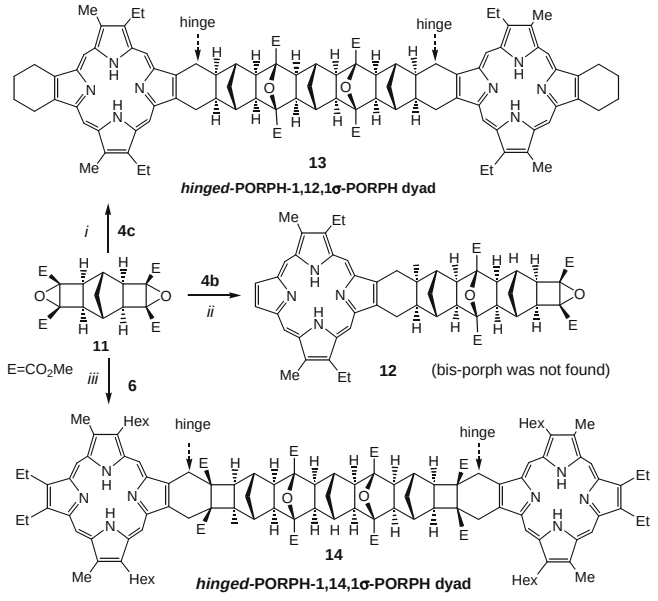
Figure 2. AM1 Bending potential of **14**.

Mixed chromophore dyad formation was relatively straightforward using cycloaddition coupling[17] of the cyclobutene epoxide **7**[18] with the norbornene BLOCKs **4b** and **6,** and yielded *hinged*-**POR**-1,7σ-**DMN** dyad **9** and *hinged*-**POR**-1,8σ-**DMN** dyad **10**, respectively (Scheme 3). Both reactions proceeded with *exo,exo*-selectivity where the 1,3-dipole **8**, formed in situ by thermal ring-opening of the epoxide, attacked the norbornene from the *exo*-face. Single adducts were obtained in both cases. These products are the first examples of porphyrin dyads containing cyclohexene hinges positioned between the porphyrin and its linked chromophore (Schemes 4 and 5).

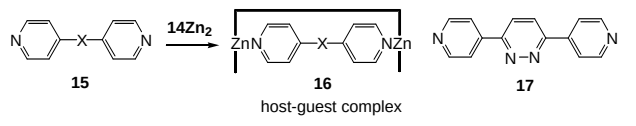
The norbornene BLOCKs **4** and **6** were also valuable reagents for the construction of bis-porphyrin scaffolds. Again the stereoselectivity of the dipolar cycloaddition reaction was employed, this time using the bis-epoxide **11**[7] as a dual cyclobutene epoxide. Reaction between **4b** and **11** rapidly formed a 1:1-adduct **12**, but the dual adduct was not formed by continued heating of the reaction mixture. It was necessary to introduce more solubilizing substituents such as cyclohexane on the porphyrin ring (**4c**). The resultant dual hinged-**POR**-1,12,1σ-**POR** product **13** possesses ^{1}H, ^{13}C NMR, and MS spectral data required for the 2:1 adduct. Similar reaction of bis-epoxide **11** with norbornene **6** afforded the longer framed dual



Scheme 3. Reagents and conditions: (i) THF, 140 °C, 24 h, 150 °C, 25 h, 48%; (ii) 1,2,4-trichlorobenzene, 145 °C, 2 h, 60%.



Scheme 4. Reagents and conditions: (i) THF, 140 °C, 40 h, 40%; (ii) THF, 140 °C, 24 h, 51%; (iii) 1,2,4-trichlorobenzene, 150 °C, 3 h, 28%.



Scheme 5. Schematic representation of complexation of **14Zn$_2$** with bis-(4-pyridyl) guests.

hinged-**POR**-1,14,1σ-**POR 14**. These two bis-porphyrin dyads had distinctly different geometries where the porphyrin rings are capable of forming dual-hinged U-shaped cavity systems. In this conformation Zn-metallated porphyrin derivatives of **14** may act as a host for certain bis-(4-pyridyl)-substituted guests such as **15** and **17** to form host–guest complexes of type **16**, which possess the 'southern' cavity shape of **14**. The calculated AM1 structure of **14** shows almost parallel porphyrin walls and ideal interporphyrinic geometry for ligation (Fig. 1).[19] Results of these binding studies will be reported at a later date.

Computational AM1 results indicate that the polycyclic framework of **6** is a flexible and dynamic molecular system, which is in accordance with the NMR results. Hence, the activation barrier required for the **6a↔6b** interconversion was calculated to be very low, 0.30 kcal mol^{-1} (the transition state for this process is depicted in Fig. 1b).

Similarly, bis-adduct **14** has three possible conformations of porphyrin rings, bent–bent, bent-extended and extended-extended, which are very close in energies, showing a very shallow bending potential (Fig. 2). The extended-extended conformer is predicted to be the most stable (by 0.87 kcal mol^{-1}, compared to the bent–bent conformer). A similar low activation barrier was found for the **4ex↔4be** interconversion of adduct **4** (1.65 kcal mol^{-1}), with a small thermodynamic preference for the bent conformer (4.3 kcal mol^{-1}).

In summary, porphyrin-functionalized norbornenes were formed by the cycloaddition reaction of porphyrin 1,3-dienes with norbornene dienophiles. Coupling with bis-(cyclobutene epoxide) yielded doubly hinged POR-spacer-POR scaffolds. VT-NMR and modeling studies of the doubly hinged ZnPOR-16σ-ZnPOR scaffold suggest conformational flexibility and the ability to adopt cavity-shaped conformation, a feature important for host-guest complexation.

Acknowledgments

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11. All new compounds provided spectroscopic data consistent with the structure. Data of representative products: Compound **1a** mp 288–289 °C, ^{1}H NMR ($CDCl_3$) δ: −4.6 (2H, br s), 0.82 (6H, t, J = 7.14 Hz), 1.25–1.38 (8H, m), 1.53 (4H, quint, J = 7.2 Hz), 1.84 (6H, t, J = 7.60 Hz), 2.03 (4H, quint, J = 7.1 Hz), 3.50 (6H, s), 3.69 (4H, t, J = 7.67 Hz), 3.95 (4H, q, J = 7.55 Hz), 5.23 (4H, s), 9.16 (2H, s), 9.91 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 12.7, 14.3, 19.3, 20.2, 23.1, 28.3, 31.4, 33.4, 34.2, 54.2, 96.3, 98.3, 134.1, 138.7, 142.2, 144.7 (2C), 143.2, 145.2 (2C); HRMS (EI) calcd. for $C_{40}H_{52}N_4O_2S$: 652.3811, found: 652.3824; **6** mp 221–223 °C, ^{1}H NMR ($CDCl_3$) δ: −3.85 (2H, s), 0.92 (6H, t, J = 7.5 Hz), 1.27 (1H, d, J = 9.9 Hz), 1.38 (4H, sext, J = 7.5 Hz), 1.51 (2H, s), 1.52–1.55 (4H, m), 1.74–1.76 (4H, m), 1.91 (6H, t, J = 7.5 Hz), 1.98 (1H, d, J = 9.5 Hz), 2.28–2.31 (4H, m), 3.29 (2H, s), 3.62 (6H, s), 4.04 (6H, s), 4.06–4.07 (4H, m), 4.07–4.08 (4H, m), 4.35 (2H, d, J = 14.3 Hz), 4.71 (2H, d, J = 14.3 Hz), 5.45 (2H, s), 10.01 (2H, s), 10.08 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 12.4, 14.7, 19.9, 20.5, 23.4, 27.3, 30.4, 32.7, 33.6, 35.3, 44.1, 44.5, 46.0, 52.0, 52.5, 96.9, 97.3, 136.0, 137.5, 138.3, 141.5, 141.6, 141.8, 144.2, 143.0, 145.1, 175.2; HRMS (EI) calcd for M+H: $C_{53}H_{67}N_4O_4$: 823.5162, found: 823.5153; **9** mp >350 °C, ^{1}H NMR ($CDCl_3$) δ: −3.92 (2H, br s), 1.52 (1H, dd, J = 14.3 Hz, J = 2.3 Hz), 1.84 (6H, t, J = 6 Hz), 1.94 (1H, dd, J = 14.0 Hz, J = 1.9 Hz), 2.34 (2H, br s), 2.43 (2H, s), 2.52 (4H, br s), 2.62 (1H, dd, J = 14.0 Hz, J = 1.9 Hz), 2.88 (1H, dd, J = 14.3 Hz, J = 2.3 Hz), 3.27 (2H, d, J = 14.3 Hz), 3.64 (6H, s), 3.71 (2H, s), 4.01 (6H, s), 4.10 (4H, q, J = 9 Hz), 4.12 (6H, s), 4.56 (2H, d, J = 14.3 Hz), 7.41 (2H, m), 8.05 (2H, m), 9.39 (2H, s), 10.03 (2H, s), 10.17 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 11.4, 17.5, 19.8, 26.7, 30.3, 42.0, 43.0, 44.7, 46.0, 52.4, 55.5, 56.9, 61.4, 90.1, 95.7, 100.6, 122.1, 125.4, 128.0, 134.4, 144.1, 169.8 (8C unaccounted); MS (ES) calcd for $C_{58}H_{58}N_4O_7$, $(M+H)^+$ 923.4384, found: 923.4387; *Compound* **10** mp 276–278 °C, ^{1}H NMR ($CDCl_3$) δ: −3.82 (2H, s), 0.93 (6H, t, J = 7.0 Hz), 1.13 (2H, s), 1.15 (1H, d, J = 10.1 Hz), 1.40 (4H, sext, J = 7.3 Hz), 1.55–1.56 (4H, m), 1.56 (2H, s), 1.65 (2H, s), 1,77 (4H, pent, J = 7.4 Hz), 1.87 (1H, d, J = 9.0 Hz), 1.89 (6H, t, J = 7.9 Hz), 2.31–2.32 (4H, m), 2.35 (1H, d, J = 9.0 Hz), 2.54 (1H, d, J = 10.1 Hz), 2.62 (2H, s), 3.29 (2H, s), 3.53 (6H, s), 3.64 (6H, s), 3.90 (6H, s), 3.99 (6H, s), 4.04–4.05 (2H, m), 4.06–4.07 (4H, m), 4.21–4.22 (2H, m), 4.22 (2H, d, J = 14.6 Hz), 4.60 (2H, d, J = 14.6 Hz), 7.14 (2H, dd, J = 6.4 Hz, J = 3.2 Hz), 7.70 (2H, dd, J = 6.4 Hz, J = 3.2 Hz), 10.01 (2H, s), 10.08 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 12.5, 14.8, 19.2, 20.5, 23.4, 27.1, 29.0, 31.5, 32.6, 33.6, 35.2, 40.5, 42.4, 43.2, 49.9, 52.7, 52.9, 54.4, 55.4, 55.8, 61.7, 90.3, 96.9, 97.2, 122.5, 125.7, 128.3, 134.7, 139.8, 144.4, 150.1, (6C unaccounted), 170.2, 174.8; HRMS (EI) calcd for $C_{76}H_{88}N_4O_{11}$: 1232.6450 found: 1232.6461; *Compound* **12** mp >350 °C, ^{1}H NMR ($CDCl_3$) δ: −3.90 (2H, br s, NH), 1.25 (2H, d, J = 11.2 Hz), 1.84 (6H, t, J = 6 Hz), 2.02 (2H, br s), 2.12 (2H, d, J = 11.5 Hz), 2.27 (2H, s), 2.32 (2H, br s), 2.37 (2H, s), 2.48 (2H, d, J = 11.5 Hz), 2.50 (2H, d, J = 11.2 Hz), 2.71 (2H, br s), 3.25 (2H, dd, J = 14.2 Hz, J = 2.1 Hz), 3.59 (6H, s), 3.79 (6H, s), 4.05 (6H, s), 4.06 (4H, q, J = 6 Hz), 4.56 (2H, dd J = 14.2 Hz, J = 2.1 Hz), 9.36 (2H, s), 9.97 (2H, s), 10.01 (2H, s); ^{13}C NMR ($CDCl_3$) δ: 13.6, 20.1, 23.3, 26.5, 26.6, 38.6, 42.8, 44.0, 44.1, 49.5, 52.4, 54.3, 56.3, 63.6, 90.3, 90.4, 97.4, 98.6, 137.1, 139.6, 140.2, 140.7, 140.8, 141.8, 141.9, 143.1, 164.4, 169.5; HRMS (ES) calcd for $C_{54}H_{56}N_4O_{10}$: 920.3996 found: 920.3989; *Compound* **13** mp >350 °C, ^{1}H NMR ($CDCl_3$) δ: −3.98 (4H, br s), 1.70 (12H, t, J = 6 Hz), 1.80 (2H, dd, J = 9.1 Hz, J = 2.1 Hz), 2.02 (2H, br s), 2.10 (4H, br s), 2.12 (2H, br s), 2.29 (4H, br s), 2.33 (4H, br s), 2.43 (4H, br s), 2.44 (2H, dd, J = 9.1 Hz, J = 2.1 Hz), 2.49 (8H, br s), 3.17 (4H, dd, J = 14.1 Hz, J = 2.2 Hz), 3.56 (12H, s), 3.98 (8H, q, J = 9 Hz), 4.00 (12H, s), 4.08 (8H, br s), 4.53 (4H, dd, J = 14.1 Hz, J = 2.2 Hz), 10.41 (4H, s), 10.51 (4H, s); ^{13}C NMR ($CDCl_3$) δ: 11.8, 16.5, 20.1, 22.7, 23.3, 26.6, 28.4, 28.5, 44.2, 45.7, 52.3, 55.3, 56.5, 66.1, 90.3, 97.3, 98.6, 136.9, 139.6, 140.0, 140.6, 141.8, 143.0, 155.8, 156.3, 172.9; HRMS (ES) calcd for $C_{97}H_{106}N_8O_{10}$ $(M+2H)^+$: 1542.8031, found: 1542.8030; **14** mp >330 °C, ^{1}H NMR ($CDCl_3$) δ: −4.08 (4H, s), 0.75 (4H, s), 0.77 (4H, s), 0.84 (12H, t, J = 7.4 Hz), 1.30 (8H, sext, J = 7.4 Hz), 1.33 (2H, s), 1.37 (2H, s), 1.40 (4H, s), 1.44–1.46 (8H, m), 1.61 (2H, d, J = 11.3 Hz), 1.64–1.65 (8H, m), 1.85 (12H, t, J = 7.4 Hz), 2.06 (2H, d, J = 11.3 Hz), 2.17–2.19 (8H, m), 2.35 (4H, s), 3.59 (12H, s), 3.63 (12H, s), 3.86(12H, s), 3.92–3.94 (4H, m), 4.01–4.02 (8H, m), 4.02–4.03 (4H, m), 4.03 (4H, d, J = 14.5 Hz), 4.42 (4H, d, J = 14.5 Hz), 9.83 (4H, s), 9.97 (4H, s); ^{13}C NMR ($CDCl_3$) δ: 12.4, 14.8, 19.2, 20.5, 23.4, 26.9, 28.7, 31.2, 32.5, 33.4, 34.9, 40.3, 40.7, 41.4, 49.6, 52.5, 52.6, 54.1, 54.9, 55.1, 90.4, 96.7, 97.1, 135.4, 138.4, 140.9, 142.1, 142.4, 143.3, 147.2, 148.3, 169.8, 174.7; HRMS (ES) calcd for $C_{125}H_{152}N_8O_{18}$: 2053.1225, not found, calcd for (M+2H)/2 (doubly charged): 1027.5691, found: 1027.5684.
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