Electronic Supplementary Information

Anisotropic Convergence of Dendritic Macromolecules Facilitated by a Heteroleptic Metal-Organic Polyhedron Scaffold

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1. Abbreviations


2. Materials and methods

All solvents, organic and inorganic reagents are commercially available, and were used without further purification. Carbazole dendrons 2, 3, and linker ligand (3,3’-(ethyne-1,2-diyl)dibenzoic acid) $\text{H}_2\text{L}$ were synthesized according to previously reported procedures.\textsuperscript{1a,b} $\text{H}_2\text{iP}\text{G}1$ was prepared and characterized by the modified procedure of a literature (Scheme S1).\textsuperscript{1c} Dimethyl 5-iodoisophthalate, 4, was prepared and characterized according to a literature procedure.\textsuperscript{1d} Silica-gel column chromatography was performed using Wakogel silica gel C-200 (64–210 µm). Microwave synthesis was performed using Biotage model Initiator+. NMR spectroscopic measurements were performed using JEOL model ECS-400 (400 MHz for $^1\text{H}$, 100 MHz for $^{13}\text{C}$) spectrometer. NMR spectra were calibrated as below; $d_6$-DMSO: $\text{CHD}_2\text{CD}_3\text{SO} = 2.50$ ppm for $^1\text{H}$, $(\text{CD}_3)_2\text{SO} = 39.52$ ppm for $^{13}\text{C}$; DClaq/$d_6$-DMSO: $\text{CHD}_2\text{CD}_3\text{SO} = 2.50$ ppm for $^1\text{H}$. ESI-TOF mass spectra were recorded on a Bruker model microTOF II. MALDI-TOF mass spectra were recorded on a Bruker model solariX XR using DCTB as a matrix. FT-ICR mass spectra were recorded on a Bruker model solariX XR using DCTB as a matrix. Analytical SEC was performed at 313 K on a Shimadzu model HPLC Prominence system with two polystyrene gel columns in series (Shodex KF-804L) equipped with a refractive index detector (Shimadzu RID-10A) and an UV detector (Shimadzu SPD-20A). The mobile phase was THF at a flow rate of 1.0 mL/min. Single-crystal X-ray crystallographic analysis was performed using Rigaku model XtaLab P200 diffractometer equipped with a Dectoris PILATUS 200 K detector, using a VariMax Mo Optic with Mo–Kα radiation ($\lambda = 0.71075$ Å) and a confocal monochromator. The obtained data were calculated using a CrystalStructure crystallographic software package, SHELXL-2013,\textsuperscript{2} except for refinement. All non-hydrogen atoms were refined using anisotropic thermal parameters. The solvent molecules were severely disordered and the SQUEEZE command was employed in the refinement.\textsuperscript{3}
3. Preparation of dendritic macroligands $\text{H}_2\text{IpG}_n$ ($n = 1–3$)

**Scheme S1.** Synthetic routes for dendritic macroligands $\text{H}_2\text{IpG}_n$ ($n = 1–3$).

Reagents and conditions: (a) (i) Cu, K$_2$CO$_3$, DMSO, 120 °C, 16 h, (ii) KOH$_{aq.}$, THF/MeOH, r.t., 1.5 h (44%); (b) (i) CuI, trans-1,2-diaminocyclohexane, K$_3$PO$_4$, 1,4-dioxane, 140 °C (microwave), 15 h, (ii) KOH$_{aq.}$, THF, r.t., 3 h (67%); (c) (i) CuI, trans-1,2-diaminocyclohexane, K$_3$PO$_4$, 1,4-dioxane, 140 °C (microwave), 15 h, (ii) KOH$_{aq.}$, THF/MeOH, r.t., 3 h (26%).
5-(9H-Carbazol-9-yl)isophthalic acid (H2IpG1): 1 (4.18 g, 25.0 mmol, 1.0 eq), 4 (24.0 g, 75.0 mmol, 3.0 eq), Cu (7.94 g, 125.0 mmol, 5.0 eq), and K2CO3 (5.18 g, 37.5 mmol, 1.5 eq) were placed in a dried flask. The inner gas was replaced by N2, then anhydrous DMSO (350 mL) was added to the mixture. The mixture was stirred at 120 °C for 16 h. After cooling down to room temperature, water (200 mL) and AcOEt (200 mL) were added to the reaction mixture. The resulting mixture was filtered through Celite, then an organic phase was separated and washed with water. After drying over Na2SO4, the organic phase was filtered and evaporated under reduced pressure. The residue was purified by column chromatography (SiO2, CH2Cl2) to afford a colorless solid (4.20 g). The resulting product (dimethylester) was used for the next reaction without further purification. To the mixture of the dimethylester (123 mg, 0.34 mmol, calculated as a pure compound), MeOH (1 mL), and THF (3 mL) in flask was added 1 M KOHaq. (2.05 mL). After stirred at room temperature for 1.5 h, the reaction mixture was acidified with conc.HClaq. (ca. 0.2 mL). The resulting precipitate was collected by filtration, successively washed with water and CHCl3/n-hexane = 1/100, then dried under reduced pressure at 60 °C affording H2IpG1 (109 mg, 0.32 mmol, 44%, 2 steps) as a colorless solid.

1H NMR (400 MHz, d6-DMSO, 298 K): δ (ppm) = 13.4–13.8 (br, 2H, -CO2H), 8.58 (t, J = 1.4 Hz, 1H, Ar-H), 8.31 (d, J = 1.4 Hz, 2H, Ar-H), 8.24–8.30 (m, 2H, Ar-H), 7.40–7.51 (m, 4H, Ar-H), 7.30–7.38 (m, 2H, Ar-H).

13C NMR (100 MHz, d6-DMSO, 298 K): δ (ppm) = 165.9, 139.9, 137.7, 133.5, 131.0, 128.6, 126.6, 123.1, 120.7, 120.6, 109.4.

ESI-TOF mass: calcd. for [C20H13NO4 – H]–: m/z = 330.08, found: m/z = 330.05.

IR (ATR): ν (cm–1) = 2978, 2360, 2341, 1311, 1239, 979, 851, 756.

5-(9'H-[9,3':6',9''-Tercarbazol]-9'-yl)isophthalic acid (H2IpG2): 2 (100 mg, 0.20 mmol, 1.0 eq), 4 (96 mg, 0.30 mmol, 1.5 eq), CuI (3.8 mg, 0.02 mmol, 0.1 eq), (±)trans-1,2-diaminocyclohexane (2.4 µL, 0.02 mmol, 0.1 eq), dry K3PO4 (127 mg, 0.60 mmol 3.0 eq), and 1,4-dioxane (10 mL) were placed in a pressure tube. After bubbled with nitrogen for 1 min, the mixture was stirred at 140 °C for 15 h using a microwave reactor. After cooling down to room temperature, the resulting mixture was quenched with 0.5 N HClaq and diluted with CH2Cl2 (60 mL). The resulting mixture was filtered through Celite. The filtrate was washed with water and dried over Na2SO4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (SiO2, AcOEt/n-hexane = 1/9–2/3) to afford a colorless solid (101 mg). The resulting product (dimethylester) was used for the next reaction without further purification. To the mixture of the dimethylester (97.3 mg, 0.14 mmol, calculated as a pure compound), MeOH (1 mL), and THF (3 mL) in a flask was added 1 M KOHaq. (2.13 mL). After stirred at room temperature for 3 h, the reaction mixture was acidified with conc.HClq. (ca. 0.2 mL). The resulting precipitate was collected by filtration, washed with water, then dried under reduced pressure at 40 °C affording H2IpG2 (73 mg, 0.32 mmol, 67%, 2 steps) as a colorless solid.
\(^1\)H NMR (400 MHz, \(d_6\)-DMSO, 300 K, Fig. S1): \(\delta\) (ppm) = 14.0–13.4 (br, 2H, -CO\(_2\)H), 8.71 (d, \(J = 1.8\) Hz, 2H, Ar-H), 8.67 (t, \(J = 1.8\) Hz, 1H, Ar-H), 8.54 (d, \(J = 1.8\) Hz, 2H, Ar-H), 8.24–8.28 (m, 4H, Ar-H), 7.76 (d, \(J = 8.8\) Hz, 2H, Ar-H), 7.71 (dd, \(J = 8.8, 1.8\) Hz, 2H, Ar-H), 7.38–7.46 (m, 8H, Ar-H), 7.24–7.31 (m, 4H, Ar-H).

\(^{13}\)C NMR (100 MHz, \(d_6\)-DMSO, 300 K, Fig. S2): \(\delta\) (ppm) = 165.9, 141.0, 139.8, 137.3, 133.7, 131.3, 130.0, 129.1, 126.2, 126.1, 126.0, 124.0, 122.5, 120.4, 119.6, 111.1, 109.7.

ESI-TOF mass: calcd. for \([\text{C}_{44}\text{H}_{27}\text{N}_3\text{O}_4 - \text{H}]^-\): \(m/z = 660.19\), found \(m/z = 660.12\).

IR (ATR): \(\nu\) (cm\(^{-1}\)) = 2976, 2359, 2342, 1310, 1238, 1136, 978, 849, 789.
Figure S1. $^1$H NMR spectra of H$_2$IpG2 (400 MHz, $d_6$-DMSO, 300 K).

Figure S2. $^{13}$C NMR spectra of H$_2$IpG2 (100 MHz, $d_6$-DMSO, 300 K).
5-(6',6'''-Di(9H-carbazol-9-yl)-9''H-[9,3':9',3'':6'',9''':3''',9'''':6'',9''':3'',9''':3''''-quinquecarbazol]-9''-yl)isophthalic acid (H$_2$IpG3): 3 (200 mg, 0.17 mmol, 1.0 eq), 4 (82 mg, 0.26 mmol, 1.5 eq), CuI (3.2 mg, 0.02 mmol, 0.1 eq), (±)-trans-1,2-Diaminocyclohexane (2.0 µL, 0.02 mmol, 0.1 eq), dry K$_3$PO$_4$ (110 mg, 0.50 mmol, 3.0 eq), and 1,4-dioxane (10 mL) were placed in a pressure tube. After bubbled with nitrogen for 1 min, the mixture was stirred at 140 °C for 15 h using a microwave reactor. After cooling down to room temperature, the resulting mixture was quenched with 0.5 N HClaq and diluted with CH$_2$Cl$_2$ (60 mL). The resulting mixture was filtered through Celite. The filtrate was washed with water and dried over Na$_2$SO$_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (SiO$_2$, AcOEt/n-hexane = 1/8–1/4 with 1% CHCl$_3$) to afford a colorless solid (111 mg). The resulting product (dimethylester) was used for the next reaction without further purification. To the mixture of dimethylester (105 mg, 78 µmol, calculated as a pure compound) and THF (0.7 mL) in flask was added 1 M KOHaq. (0.62 mL). After stirred at room temperature for 3 h, the reaction mixture was acidified with conc.HClaq. (ca. 0.05 mL). The resulting precipitate was collected by filtration, washed with water, then dried under reduced pressure at 40 °C affording H$_2$IpG3 (57 mg, 43 µmol, 26%, 2 steps) as a colorless solid.

$^1$H NMR (400 MHz, $d_6$-DMSO, 343 K, Fig. S3): $\delta$ (ppm) = 13.82–13.67 (br, 2H, -CO$_2$H), 9.01 (s, 2H, Ar-H), 8.72 (s, 1H, Ar-H), 8.71 (s, 4H, Ar-H), 8.62 (s, 2H, Ar-H), 8.24 (d, $J$ = 7.6 Hz, 8H, Ar-H), 7.98 (d, $J$ = 8.8 Hz, 2H, Ar-H), 7.89 (d, $J$ = 8.8 Hz, 2H, Ar-H), 7.76 (d, $J$ = 8.8 Hz, 4H, Ar-H), 7.68 (d, $J$ = 8.8 Hz, 4H, Ar-H), 7.43–7.36 (m, 16H, Ar-H), 7.28–7.4 (m, 8H, Ar-H).

$^{13}$C NMR (100 MHz, $d_6$-DMSO, 343 K, Fig. S4) : $\delta$ (ppm) = 165.6, 141.1, 140.8, 140.2, 137.1, 133.8, 131.2, 129.6, 129.4, 129.2, 126.2, 125.8, 125.4, 124.0, 123.3, 122.3, 120.4, 120.0, 119.9, 119.4, 111.2, 109.4.

ESI-TOF mass: calcd. for [C$_{92}$H$_{37}$N$_7$O$_4$]–: $m/z$ = 1321.43, found: $m/z$ = 1321.28.

IR (ATR): $\nu$ (cm$^{-1}$) = 2926, 2359, 2342, 1586, 1559, 1425, 1308, 1254, 1028, 844, 771, 762.
Figure S3. $^1$H NMR spectra of H$_2$IpG3 (400 MHz, $d_6$-DMSO, 343 K).

Figure S4. $^{13}$C NMR spectra of H$_2$IpG3 (100 MHz, $d_6$-DMSO, 343 K).
4. Metal complexation behaviors of macroligands H$_2$IpG$_n$ (n = 1–3)

4-1. Complexation reaction of H$_2$IpG$_n$ and Cu(OAc)$_2$·H$_2$O (n = 1–3)

To a DEF solution of H$_2$IpG$_n$ (40 µL, 25 mM, 1.0 µmol, 1.0 eq, where n = 1–3) was added a DEF solution of Cu(OAc)$_2$·H$_2$O (50 µL, 20 mM, 1.0 µmol, 1.0 eq) at room temperature to obtain a clear blue solution. The resulting mixture (20 µL) was diluted with THF (1.0 mL), which was subjected to SEC analysis. The SEC traces are shown in Fig. S5.

![Image]

**Figure S5.** SEC analyses for homoleptic cuboctahedral MOPs (Cu$_{24}$IpG$_{n24}$). a) Schematic illustration of coordination-driven self-assembly of H$_2$IpG$_n$ and Cu(OAc)$_2$·H$_2$O in DEF at room temperature, b–d) SEC traces of the H$_2$IpG$_n$ (dashed lines) and mixtures of H$_2$IpG$_n$ (1 eq) and Cu(OAc)$_2$·H$_2$O (1 eq) (solid lines), where b) n = 1, c) n = 2 and d) n = 3, recorded at 313 K with a UV detector using THF as the eluent.

In the case of Cu$^{II}$-complexation with H$_2$IpG$_1$, monodisperse SEC peak locating shorter elution time ($t = 17.2$ min) than that of free ligand was observed (Fig. S5b), suggesting formation of a homoleptic cuboctahedral MOP, Cu$_{24}$IpG$_{124}$. Formation of Cu$_{24}$IpG$_{124}$ is supported by MALDI-TOF mass spectrum (Fig. S6). On the other hand, in the cases of Cu$^{II}$-complexation with H$_2$IpG$_3$ or H$_2$IpG$_2$, SEC traces showed significant broadening and no sharp peaks corresponding to cuboctahedral MOPs were detected (Figs. S5c and S5d). These observations suggest homoleptic cuboctahedral MOPs, namely Cu$_{24}$IpG$_{324}$ or Cu$_{24}$IpG$_{224}$, are hardly formed and/or not stable enough to be clearly detected by SEC.
Figure S6. MALDI-TOF mass spectra (negative, matrix DCTB) of the equimolar mixture of H$_2$IpG1 and Cu(OAc)$_2$·H$_2$O in THF. a) Whole spectrum. b) Experimental and theoretical spectra of the major signal. THF was used as the solvent instead of DEF for the mass analysis analyte.

4-2. Complexation reaction of H$_2$IpG1, H$_2$L and Cu(OAc)$_2$·H$_2$O

To a DEF solution of H$_2$IpG1 (0.7 mL, 25 mM, 17.5 µmol, 1.0 eq) was added DEF solutions of H$_2$L (0.7 mL, 25 mM, 17.5 µmol, 1.0 eq) and Cu(OAc)$_2$·H$_2$O (1.75 mL, 20 mM, 35.0 µmol, 2.0 eq) at room temperature to give a clear blue solution. A small aliquot (20 µL) of the resulting mixture was collected and diluted with THF (1.0 mL), which was subjected to SEC analysis (Fig. S13). FT-ICR mass spectrometry (Fig. S7) was carried out regarding the reaction mixture for which THF was used as the solvent instead of DEF. The result of the mass spectrometry supported the formation of Cu$_{12}$IpG1$_6$L$_6$. In order to isolate the product, the reaction mixture was poured into MeOH (5 mL). The product thus precipitated out was washed with DEF (1 mL × 3) then Et$_2$O (1 mL × 2) successively, then dried under vacuum at room temperature to afford Cu$_{12}$IpG1$_6$L$_6$ (7.6 mg) as a pale blue solid. $^1$H NMR spectrometry was carried out for the product that was digested in the mixed solvent of $d_6$-DMSO/DClaq (60/1, v/v) (Fig. S8).

NOTE: The isolation yield of the product was calculated to be 40% based on the integral ratio of $^1$H NMR signals of the digested sample with respect to an internal standard (p-dimethoxybenzene) added at a predetermined concentration.
Figure S7. FT-ICR mass spectra (negative, matrix DCTB) of the mixture of $\text{H}_2\text{IpG}1$ (1 eq), $\text{H}_2\text{L}$ (1 eq) and $\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}$ (2 eq) in THF. Experimental and theoretical spectra of a) whole area and b) the major signal area. THF was used as the solvent instead of DEF for the mass analysis analyte.

Figure S8. Partial $^1$H NMR spectrum (400 MHz, $d_6$-DMSO/DClaq = 60/1, 358 K) of the digested product of $\text{Cu}_{12}\text{IpG}1_6\text{L}_6$. The signals corresponding to $\text{H}_2\text{IpG}1$ and $\text{H}_2\text{L}$ were marked with green triangles and blue circles, respectively.

4-3. Complexation reaction of $\text{H}_2\text{IpG}2$, $\text{H}_2\text{L}$ and $\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}$

To a DEF solution of $\text{H}_2\text{IpG}2$ (1.0 mL, 25 mM, 25.0 μmol, 1.0 eq) was added DEF solutions of $\text{H}_2\text{L}$ (1.0 mL, 25 mM, 25.0 μmol, 1.0 eq) and $\text{Cu(OAc)}_2\cdot\text{H}_2\text{O}$ (2.5 mL, 20 mM, 50.0 μmol, 2.0 eq) at room temperature to give a clear blue solution. A small aliquot (20 μL) of the resulting mixture was collected and diluted with THF (1.0 mL), which was subjected to SEC analysis (Fig. S13). FT-ICR mass spectrometry (Fig. S9) was carried out regarding the reaction mixture for which THF was used as the solvent instead of DEF. The result of the mass spectrometry supported the formation of $\text{Cu}_{12}\text{IpG}2_6\text{L}_6$. In order to isolate the product,
the reaction mixture was poured into MeOH (5 mL). The product thus precipitated out was washed with DEF (1 mL) then Et₂O (1 mL × 2) successively, then dried under vacuum at room temperature to afford Cu₁₂IpG₂,L₆ (22.34 mg) as a pale blue solid. ¹H NMR spectrometry was carried out for the product that was digested in the mixed solvent of d₆-DMSO/DClaq (60/1, v/v) (Fig. S10).

NOTE: The isolation yield of the product was calculated to be 65% based on the integral ratio of ¹H NMR signals of the digested sample with respect to an internal standard (p-dimethoxybenzene) added at a predetermined concentration.

**Figure S9.** FT-ICR mass spectra (negative, matrix DCTB) of the mixture of H₂IpG₂ (1 eq), H₂L (1 eq) and Cu(OAc)₂·H₂O (2 eq) in THF. Experimental and theoretical spectra of a) whole area and b) the major signal area. THF was used as the solvent instead of DEF for the mass analysis analyte.

**Figure S10.** Partial ¹H NMR spectrum (400 MHz, d₆-DMSO/DClaq = 60/1, 358 K) of the digested product of Cu₁₂IpG₂,L₆. The signals assignable to H₃IpG₂ and H₃L were marked by green triangles and blue circles, respectively.
4-4. Complexation of $\text{H}_2\text{IpG}_3$, $\text{H}_2\text{L}$ and Cu(OAc)$_2$·$\text{H}_2\text{O}$

To a DEF solution of $\text{H}_2\text{IpG}_3$ (0.7 mL, 25 mM, 17.5 μmol, 1.0 eq) was added DEF solutions of $\text{H}_2\text{L}$ (0.7 mL, 25 mM, 17.5 μmol, 1.0 eq) and Cu(OAc)$_2$·$\text{H}_2\text{O}$ (1.75 mL, 20 mM, 35.0 μmol, 2.0 eq) at room temperature to give a clear blue solution. A small aliquot (20 μL) of the resulting mixture was collected and diluted with THF (1.0 mL), which was subjected to SEC analysis (Fig. S13). MALDI-TOF mass spectrometry (Fig. S11) was carried out regarding the reaction mixture for which THF was used as the solvent instead of DEF. The result of the mass spectrometry supported the formation of Cu$_{12}$IpG$_3$L$_6$. In order to isolate the product, the reaction mixture was poured into MeOH (5 mL). The product thus precipitated out was washed with DEF (1 mL) then Et$_2$O (1 mL × 2) successively, then dried under vacuum at room temperature to afford Cu$_{12}$IpG$_3$L$_6$ (19.34 mg) as a pale blue solid. $^1$H NMR spectrometry was carried out for the product that was digested in the mixed solvent of $d_6$-DMSO/DClaq (60/1, v/v) (Fig. S12).

NOTE: The isolation yield of the product was calculated to be 55% based on the integral ratio of $^1$H NMR signals of the digested sample with respect to an internal standard ($p$-dimethoxybenzene) added at a predetermined concentration.

Figure S11. MALDI-TOF mass spectra (negative, matrix DCTB) of the mixture of $\text{H}_2\text{IpG}_3$ (1 eq), $\text{H}_2\text{L}$ (1 eq) and Cu(OAc)$_2$·$\text{H}_2\text{O}$ (2 eq) in THF. a) Whole spectrum. b) Experimental and theoretical spectra of the major signal. THF was used as the solvent instead of DEF for the mass analysis analyte.
Figure S12. Partial $^1$H NMR spectrum (400 MHz, $d_6$-DMSO/DClaq = 60/1, 358 K) of the digested product of Cu$_{12}$IpG$_3$L$_6$. The signals assignable to H$_3$IpG$_3$ and H$_3$L were marked by green triangles and blue circles, respectively.

Figure S13. a) Schematic illustration of the syntheses of heteroleptic bipolar MOPs (Cu$_{12}$IpG$_n$L$_6$). H$_2$IpG$_n$, H$_3$L, and Cu(OAc)$_2$·H$_2$O were reacted in DEF at room temperature, b–d) SEC traces of the H$_3$IpG$_n$ (dashed line) and mixtures (solid line) of H$_3$IpG$_n$ (1 eq), H$_3$L (1 eq), and Cu(OAc)$_2$·H$_2$O (2 eq), where b) $n = 1$, c) $n = 2$ and d) $n = 3$, recorded at 313 K with a UV detector using THF as the eluent.
Figure S14. Stacked SEC traces of isolated samples of Cu₁₂IpG₆L₆ (solid lines, n = 1; green, 2; red, 3; blue), H₂IpGₙ (dashed line, n = 1; green, 2; red, 3; blue), and H₂L (black dashed line), recorded at 313 K with a UV detector using THF as the eluent.

4-5. Complexation of H₂IpG₃ with variable H₂L stoichiometry

Mixtures of H₂IpG₃ (4.5 mM), H₂L (0, 0.3, 0.6, 1.0, 1.2, and 1.5 eq), and equimolar amount of Cu(OAc)₂·H₂O relative to the total amount of organic ligands (H₂IpG₃ and H₂L) in DEF were prepared. A small aliquot (40 µL) of the each resulting mixture was collected and diluted with THF (1.0 mL), then subjected to SEC analysis (Fig. S15).

Figure S15. SEC traces of the mixtures of a) H₂IpG₃ and H₂L (x eq) in the presence of Cu(OAc)₂·H₂O (equimolar amount to the total amount of ligand molecules, i.e. 1 + x eq), recorded at 313 K with a UV detector using THF as the eluent.
4-6. Complexation reaction of H$_2$Ip$_t$Bu, H$_2$L and Cu(OAc)$_2$$\cdot$H$_2$O$^{1b,4}$

To a DEF solution of H$_2$Ip$_t$Bu (25 µL, 20 mM, 0.05 µmol, 1.0 eq) was added DEF solutions of H$_2$L (25 µL, 20 mM, 0.05 µmol, 1.0 eq) and Cu(OAc)$_2$$\cdot$H$_2$O (50 µL, 20 mM, 0.1 µmol, 2.0 eq) at room temperature. To the mixture was successively added DEF (10 µL) to give a clear blue solution. A small aliquot (40 µL) of the resulting mixture was collected and diluted with THF (1.0 mL), which was subjected to SEC analysis (Fig. S16).

4-7. Complexation reaction of H$_2$Ip$_t$Bu and Cu(OAc)$_2$$\cdot$H$_2$O$^{1b,4}$

To a DEF solution of H$_2$Ip$_t$Bu (25 µL, 20 mM, 0.05 µmol, 1.0 eq) was added DEF solutions of Cu(OAc)$_2$$\cdot$H$_2$O (25 µL, 20 mM, 0.05 µmol, 1.0 eq) at room temperature. To the mixture was successively added DEF (60 µL) to give a clear blue solution. A small aliquot (40 µL) of the resulting mixture was collected and diluted with THF (1.0 mL), which was subjected to SEC analysis (Fig. S16).

Figure S16. SEC traces of the mixtures of H$_2$Ip$_t$Bu and 1.0 eq (blue) or 0 eq (black) of H$_2$L in the presence of Cu(OAc)$_2$$\cdot$H$_2$O (equimolar amount to the total amount of ligand molecules), recorded at 313 K with a UV detector using THF as the eluent.
4-5. Single-crystal X-ray crystallography for Cu$_{12}$IpG$_2$L$_6$

To a DEF solution of H$_2$IpG$_2$ (250 μL, 25 mM, 6.25 μmol, 1.0 eq) was added DEF solutions of H$_2$L (250 μL, 25 mM, 6.25 μmol, 1.0 eq) and Cu(OAc)$_2$·H$_2$O (625 mL, 20 mM, 13.5 μmol, 2.0 eq) at room temperature to give a clear blue solution. The solution was left at room temperature for one day. Blue precipitate formed was removed by decantation. The supernatant clear solution (700 μL) was layered by MeOH (700 μL). Blue block crystals, which are suitable for single crystal X-ray analysis, were obtained after leaving the sample for 3 days at room temperature. The single-crystal X-ray diffractions were collected at 93 K (Figs. S17 and S18).

**Figure S17.** a) ORTEP view (50% probability level) of Cu$_{12}$IpG$_2$L$_6$. The peripheral carbazole moieties adopt two different disordering patterns: mode A and B. The structure of disordering mode A is shown here. (C: gray, Cu: pale green, N: pale blue, O: red). H-atoms are omitted for clarity. b–c) Disordering patterns of G$_2$ dendrons of Cu$_{12}$IpG$_2$L$_6$ viewed from the polar axis: b) mode A, c) mode B. Occupancies of G$_2$ dendrons; b) 54%, c) 46%. (C of G$_2$ moiety is highlighted as green color, other C: gray, Cu: pale green, N: pale blue, O: red). Coordinating molecules at axial positions of each Cu$^{II}$-paddlewheel cluster are represented by oxygen atoms.
Figure S18. Space filling model of Cu_{12}IpG_{26}L_6. C atoms are colored for clarity. (C: blue, yellow, or green, Cu: pale green, H: white, N: pale blue, O: red).

Crystal data for C_{360}H_{198}Cu_{12}N_{18}O_{60}: \( F_w = 6498.16 \), crystal dimensions 0.1 \( \times \) 0.1 \( \times \) 0.1 mm, trigonal, space group \( R-3c \), \( a = b = 32.3220(8) \) Å, \( V = 71027(4) \) Å\(^3\), \( Z = 6 \), \( \rho_{\text{calc}} = 0.911 \) gcm\(^{-3}\), \( \mu = 0.5806 \) mm\(^{-1}\), \( T = 93 \) K, \( \lambda(\text{MoKα}) = 0.71073 \) Å, \( 2\theta_{\text{max}} = 61.5^\circ \), 215055/23234 reflection collected/unique (\( R_{\text{int}} = 0.1507 \)), \( R_1 = 0.0915 \) (\( I > 2\sigma(I) \)), \( wR_2 = 0.3313 \) (for all data), GOF = 1.023, largest diff. peak and hole 1.88/–0.37 eÅ\(^{-3}\). The contribution of solvent electron density was removed by the SQUEEZE function. CCDC deposit number 1827025.
Figure S19. SEC traces of the reaction mixture of a) H$_2$I$p$G$_2$ (1 eq), H$_2$L (1 eq), and Cu(OAc)$_2$·H$_2$O (2 eq), and b) the single crystals of Cu$_{12}$I$p$G$_2$L$_6$, recorded at 313 K with a UV detector using THF as the eluent.
5. References


