Electronic Supplementary Information (ESI)

S1

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Synthesis and characterization

All chemicals were purchased from commercial sources and used without further purification. In particular, gallium(III) nitrate hydrate salts (99.9998% purity) were purchased from Acros Organics, dysprosium(III) nitrate pentahydrate salts (99.99% purity) were purchased from Alfa Aesar, and gadolinium(III) nitrate hexahydrate salts (99.999% purity) were purchased from Sigma-Aldrich.

2-Fluorobenzoic acid (HF-bz). Used as purchased. ^{1}H NMR (400 MHz, dmso-d_6) δ 13.26 (s, 1H), 7.88 (td, J = 7.7, 1.8 Hz, 1H), 7.70 – 7.59 (m, 1H), 7.36 – 7.27 (m, 2H).

2-Methylbenzoic acid (Hmbz). Used as purchased. ^{1}H NMR (400 MHz, dmso-d_6) δ 12.81 (s, 1H), 8.15 – 7.65 (m, 1H), 7.63 – 7.09 (m, 3H), 2.52 (s, 3H).

Benzoic Acid (Hbz). Used as purchased. ^{1}H NMR (400 MHz, dmso-d_6) δ 12.97 (s, 1H), 7.99 – 7.92 (m, 2H), 7.68 – 7.59 (m, 1H), 7.51 (t, J = 7.7 Hz, 2H).

Salicylhydroxamic acid (H₃shi). Used as purchased. ^{1}H NMR (400 MHz, dmso-d_6) δ 12.23 (s, 1H), 11.44 (s, 1H), 9.33 (s, 1H), 7.67 (dd, J = 7.9, 1.7 Hz, 1H), 7.38 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 6.93 – 6.81 (m, 2H).

Isophthalic acid (H₂iph). Used as purchased. ^{1}H NMR (400 MHz, dmso-d_6) δ 13.27 (s, 2H), 8.50 (t, J = 1.6 Hz, 1H), 8.18 (dd, J = 7.8, 1.7 Hz, 2H), 7.66 (t, J = 7.7 Hz, 1H).

5-iodoisophthalic acid (H₂I-iph). Synthesized as previously described. ^{1}H NMR (400 MHz, dmso-d_6) δ 13.54 (s, 2H), 8.43 (d, J = 1.6 Hz, 3H).

5-methoxysalicylhydroxamic acid (H₃moshi). Synthesized as previously described.[1] ^{1}H NMR (400 MHz, dmso-d_6) δ 11.75 (s, 1H), 11.41 (s, 1H), 9.33 (s, 1H), 7.24 (d, J = 3.1 Hz, 1H), 7.00 (dd, J = 9.0, 3.0 Hz, 1H), 6.84 (d, J = 9.0 Hz, 1H), 3.71 (s, 3H).

5-methylsalicylhydroxamic acid (H₃mshi). Synthesized as previously described.[1] ^{1}H NMR (400 MHz, dmso-d_6) δ 11.95 (s, 1H), 11.34 (s, 1H), 9.28 (s, 1H), 7.50 (d, J = 2.2 Hz, 1H), 7.19 (dd, J = 8.4, 2.2 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 2.22 (s, 3H).

5-iodosalicylhydroxamic acid (H₃I-shi). Synthesized as previously described.[2] ^{1}H NMR (400 MHz, dmso-d_6) δ 12.18 (s, 1H), 11.38 (s, 1H), 9.39 (s, 1H), 7.99 (dd, J = 10.6, 2.3 Hz, 1H), 7.82 – 7.54 (m, 1H), 6.77 (t, J = 8.8 Hz, 1H).

5-bromosalicylhydroxamic acid (H₃Br-shi). 5-bromosalicylic acid (20 g, 92 mmol) was dissolved in 250 mL of methanol. Anhydrous sodium sulphate was added to dry the solvent. To the stirring mixture, sulfuric acid (166 mmol) was added dropwise. The mixture was refluxed overnight (14 hours total). Then, the mixture was removed from the heat and allowed to cool to room temperature. The mixture was filtered via vacuum filtration to remove solid sodium sulfate. Saturated aqueous sodium bicarbonate was added dropwise, with stirring, until the mixture stopped bubbling. Then, bulk methanol was removed via rotary evaporation. 100 mL of water was added to the mixture, then the organic portion was extracted three times with 100 mL portions of ethyl acetate. The ethyl acetate was removed via rotary evaporation, yielding 9.5 g of off-white solid of methyl-5-bromosalicylate. Yield: 45% by mass. ^{1}H NMR (400 MHz, dmso-d_6) δ 10.51 (s, 1H), 7.83 (t, J = 1.9 Hz, 1H), 7.65 (dt, J = 8.9, 1.7 Hz, 1H), 6.97 (dd, J = 8.8, 1.0 Hz, 1H), 3.88 (d, J = 0.8 Hz, 3H).

Without further purification, 5.0 g of methyl-5-bromosalicylate (21.6 mmol) was suspended in 30 mL of methanol. Separately, hydroxylamine hydrochloride (130 mmol) and potassium hydroxide (130 mmol) were combined into 90 mL of methanol and stirred. The solution quickly formed a white solid (KCl). The solution was cooled on ice, and the precipitate was removed via vacuum filtration and discarded. To the filtrate, sodium sulphate was added to dry the solution. Then, the suspension of methyl-5-bromosalicylate was added and the resultant solution was stirred, covered, for 48 hours. The mixture was then filtered via vacuum filtration and a white precipitate (sodium sulphate) was discarded. To the filtrate, 100 mL of water was added. Then, the concentrated hydrochloric acid was added until pH ~1.0. White precipitate was formed which was collected via vacuum filtration. This solid was triturated in 50 mL of dichloromethane to dissolve unreacted methyl-5-bromosalicylate, then the solid was collected via vacuum filtration, and rinsed with additional dichloromethane. The white solid was dried *in vacuo* yielding 1.7 g of H₃Br-shi (34% yield from methyl-5-bromosalicylate

by mass, 16% yield total from 5-bromosalicylic acid). ^{1}H NMR (400 MHz, dmso-d_6) δ 11.72 (s, 2H), 9.44 (s, 1H), 7.85 (d, J = 2.5 Hz, 1H), 7.52 (dd, J = 8.9, 2.5 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H). ^{1}H NMR (700 MHz, dmso-d_6) δ 12.03 (s, 1H), 11.47 (s, 1H), 9.42 (s, 1H), 7.85 (d, J = 2.4 Hz, 1H), 7.52 (dt, J = 8.9, 1.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H).

5-chlorosalicylhydroxamic acid (H₃Cl-shi). Methyl-5-chlorosalicylate (5.6 g, 30 mmol) was dissolved in 90 mL of methanol producing a clear and colourless solution. Separately, hydroxylamine hydrochloride (90 mmol) and potassium hydroxide (90 mmol) were combined into 90 mL methanol and stirred. The solution quickly formed a white solid (KCl). The solution was cooled on ice, and the precipitate was removed via vacuum filtration and discarded. To the filtrate, the methyl-5-chlorosalicylate solution was added, and the two solutions were stirred for 20 hours. A cloudy yellow solution was formed. 50 mL of water was added. Then, the pH was adjusted to ~1.0 with concentrated hydrochloric acid, causing precipitation of a white solid. The solid was collected via vacuum filtration and rinsed with water then hexane. The product was dried *in vacuo* yielding 4.7 g of pale pink solid of H₃Cl-shi. Yield: 83% by mass. ^{1}H NMR (400 MHz, dmso-d_6) δ 12.18 (s, 1H), 11.41 (s, 1H), 9.43 (s, 1H), 7.74 (d, J = 2.6 Hz, 1H), 7.42 (dd, J = 8.8, 2.6 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H).

[LnGa₈(mshi)₈(OH)₄](PyH). H₃mshi (0.6 mmol), Ln(NO₃)₃·xH₂O (0.075 mmol) (Ln³⁺= Dy³⁺, Gd³⁺), and Ga(NO₃)₃·xH₂O (0.6 mmol) were dissolved in 10 mL of DMF. Concentrated aqueous NaOH solution (19.9 M, 2.1 mmol) was added slowly and the solution was stirred for two hours under ambient conditions. Then, the stirring was stopped, and the solution was set overnight to allow precipitate to congeal. The next day, the mixture was filtered via gravity filtration, the white precipitate was discarded, then 4 mL of pyridine was added to the filtrate and swirled gently to mix. The clear and colourless solution was left for slow evaporation. After one week, white crystalline compound was collected via filtration and dried *in vacuo*.

[DyGa₈(mshi)₈(OH)₄](pyH) · 1H₂O · 6DMF. Yield: 22%. ESI-MS, calc. for [M]⁻, C₆₄H₅₂DyGa₈N₈O₂₈, 2101.62; found, 2101.62. Anal. Calcd. for C₈₇H₁₀₂DyGa₈N₁₅O₃₅: C, 39.61; H, 3.90; N, 7.96. Found: C, 39.59; H, 4.03; N, 7.92. Single-crystal unit-cell parameters: a = 16.013 Å, b = 18.979 Å, c = 18.475 Å; α = 90°, β = 99.71°, γ = 90°; V = 5534.38 Å³.

[GdGa₈(mshi)₈(OH)₄](pyH) · 2H₂O · 7DMF. Yield: 28%. ESI-MS, calc. for [M]⁻, C₆₄H₅₂DyGa₈N₈O₂₈, 2095.62; found, 2095.62. Anal. Calcd. for C₉₀H₁₁₁GdGa₈N₁₆O₃₇: C, 39.55; H, 4.11; N, 8.23. Found: C, 39.55; H, 4.15; N, 8.22. Single-crystal unit-cell parameters: a = 16.237 Å, b = 19.100 Å, c = 18.976 Å; α = 90°, β = 99.91°, γ = 90°; V = 5742.33 Å³.

[Ln₂Ga₈(shi)₈(I-iph)₄]Na₂ was synthesized similarly to the previously described procedure.[2] Solid Ln(NO₃)₃·xH₂O (0.125 mmol) (Ln³⁺= Dy³⁺, Gd³⁺), Ga(NO₃)₃.·xH₂O (0.5 mmol), H₂I-iph (0.25 mmol), and H₃shi (0.5 mmol) were dissolved under stirring in 10 mL of DMF. Then concentrated aqueous NaOH solution (2.0 mmol, ~19.9 M) was added and the solution was stirred for one hour. The stirring was stopped and the solution was set overnight to allow precipitate to congeal. The next day, the mixture was filtered via gravity filtration, and a white precipitate was discarded. The yellow filtrate was set for slow evaporation yielding crystals after two weeks.

[Dy₂Ga₈(shi)₈(I-iph)₄]Na₂ · 10H₂O · 15DMF. Yield: 47%. ESI-MS, calc. for [M]²⁻, C₈₈H₄₄Dy₂Ga₈I₄N₈O₄₀, 1621.52; found, 1621.83. Anal. Calcd. for C₁₃₃H₁₆₉Dy₂Ga₈I₄N₂₃Na₂O₆₅: C, 34.98; H, 3.73; N, 7.06. Found: C, 35.03; H, 3.84; N, 7.08. Single-crystal unit-cell parameters: a = 17.659 Å, b = 17.659 Å, c = 30.392 Å; α = 90°, β = 90°, γ = 90°; V = 9789.80 Å³.

[Gd₂Ga₈(shi)₈(I-iph)₄]Na₂ · 5H₂O · 10DMF. Synthesized as previously described.[2] ESI-MS, calc. for [M]²⁻, C₈₈H₄₄Gd₂Ga₈N₈O₄₀I₄, 1617.52; found, 1616.51. Anal. Calcd. for C₁₁₈H₁₂₈Dy₂Ga₈N₁₈Na₂O₅₅: C, 34.65; H, 3.18; N, 6.04. Found: C, 34.57; H, 3.05; N, 6.15. Single-crystal unit-cell parameters: a = 17.507 Å, b = 17.507 Å, c = 31.378 Å; α = 90°, β = 90°, γ = 90°; V = 9617.15 Å³.

[Ln₂Ga₈(shi)₈(iph)₄]Na₂ was synthesized similarly to the previously described procedure.[2] Solid Ln(NO₃)₃·xH₂O (0.125 mmol) (Ln³⁺= Dy³⁺, Gd³⁺), Ga(NO₃)₃·xH₂O (0.5 mmol), H₂iph (0.25 mmol), and H₃shi (0.5 mmol) were dissolved with stirring in 10 mL of DMF. Then concentrated aqueous NaOH solution (2.0 mmol, 19.9 M) was added and the solution was stirred for one hour. The stirring was stopped and the solution was set overnight to allow precipitate to congeal. The next day, the

mixture was filtered via gravity filtration, and a white precipitate was discarded. The yellow filtrate was set for slow evaporation yielding crystals after two weeks.

[Dy$_2$Ga$_8$(shi)$_8$(iph)$_4$]Na$_2$ ·5H$_2$O ·10DMF. Yield: 38%. ESI-MS, calc. for [M]$^{2-}$, C$_{88}$H$_{48}$Dy$_2$Ga$_8$N$_8$O$_{40}$, 1369.73; found, 1364.72. Anal. Calcd. for C$_{118}$H$_{128}$Dy$_2$Ga$_8$N$_{18}$Na$_2$O$_{55}$: C, 39.29; H, 3.58; N, 6.99. Found: C, 39.23; H, 3.50; N, 6.95. Single-crystal unit-cell parameters: a = 14.705 Å, b = 21.951 Å, c = 21.811 Å; α = 90°, β = 106.64°, γ = 90°; V = 6745.62 Å^3.

[Gd$_2$Ga$_8$(shi)$_8$(iph)$_4$]Na$_2$ ·4H$_2$O ·11DMF. Synthesized as previously described.[2] ESI-MS, calc. for [M]$^{2-}$, Gd$_2$Ga$_8$C$_{88}$H$_{48}$N$_8$O$_{40}$, 1365.73; found, 1364.72. Anal. Calcd. for C$_{121}$H$_{133}$Gd$_2$Ga$_8$N$_{19}$Na$_2$O$_{55}$: C, 39.80; H, 3.67; N, 7.29. Found: C, 39.71; H, 3.69; N, 7.19. Single-crystal unit-cell parameters: a = 14.799 Å, b = 22.004 Å, c = 21.956 Å; α = 90°, β = 106.93°, γ = 90°; V = 6839.86 Å^3.

[Ln$_2$Ga$_8$(moshi)$_8$(iph)$_4$]Na$_2$. H$_3$moshi (0.6 mmol), Ln(NO$_3$)$_3$·xH$_2$O (0.15 mmol) (Ln^{3+}= Dy^{3+}, Gd^{3+}), Ga(NO$_3$)$_3$.xH$_2$O (0.6 mmol), and isophthalic acid (0.3 mmol) were dissolved in 30 mL of DMF. Concentrated aqueous NaOH solution (19.9 M, 2.4 mmol) was added slowly and the solution was stirred for two hours under ambient conditions. The solution was filtered then the filtrate was left for slow evaporation, producing crystalline compound within 2-4 weeks. Compound was collected via filtration and dried *in vacuo*. The crystalline solid was collected in each case.

[Dy$_2$Ga$_8$(moshi)$_8$(iph)$_4$]Na$_2$ ·9H$_2$O ·8DMF. Yield: 27%. ESI-MS, calc. for [M]$^{2-}$, C$_{96}$H$_{64}$Dy$_2$Ga$_8$N$_8$O$_{48}$, 1490.30; found, 1490.30. Anal. Calcd. for C$_{120}$H$_{138}$Dy$_2$Ga$_8$N$_{16}$Na$_2$O$_{65}$: C, 38.20; H, 3.69; N, 6.07. Found: C, 38.13; H, 3.63; N, 6.07. Single-crystal unit-cell parameters: a = 22.924 Å, b = 23.319 Å, c = 31.462 Å; α = 90°, β = 108.84°, γ = 90°; V = 15917.30 Å^3.

[Gd$_2$Ga$_8$(moshi)$_8$(iph)$_4$]Na$_2$ ·5H$_2$O ·8DMF. Synthesized as previously described.[1] ESI-MS, calc. for [M]$^{2-}$, Gd$_2$Ga$_8$C$_{96}$H$_{64}$N$_8$O$_{48}$, 1484.3; found, 1484.2. Anal. Calcd. for Gd$_2$Na$_2$Ga$_8$C$_{111}$H$_{115}$N$_{13}$O$_{61}$: C, 39.05; H, 3.55; N, 6.07. Found: C, 39.01; H, 3.48; N, 6.03. Single-crystal unit-cell parameters: a = 23.013 Å, b = 23.428 Å, c = 31.581 Å; α = 90°, β = 108.88°, γ = 90°; V = 16110.06 Å^3.

[Ln$_2$Ga$_8$(mshi)$_8$(iph)$_4$]Na$_2$. H$_3$mshi (0.6 mmol), Ln(NO$_3$)$_3$·xH$_2$O (0.15 mmol) (Ln^{3+}= Dy^{3+}, Gd^{3+}), Ga(NO$_3$)$_3$.xH$_2$O (0.6 mmol), and isophthalic acid (0.3 mmol) were dissolved in 30 mL of DMF. Concentrated aqueous NaOH solution (19.9 M, 2.4 mmol) was added slowly and the solution was stirred for two hours under ambient conditions. The solution was filtered and the filtrate was left for slow evaporation. After about one week, an amorphous, powdery precipitate was formed. The mixture was filtered again, the filtrate was collected and set for slow evaporation, producing crystalline compound within 2-3 weeks. Pale white crystalline compound was collected via filtration and dried *in vacuo*.

[Dy$_2$Ga$_8$(mshi)$_8$(iph)$_4$]Na$_2$ ·13H$_2$O ·10DMF. Yield: 56%. ESI-MS, calc. for [M]$^{2-}$, C$_{96}$H$_{64}$Dy$_2$Ga$_8$N$_8$O$_{40}$, 1426.30; found, 1426.30. Anal. Calcd. for C$_{126}$H$_{160}$Dy$_2$Ga$_8$N$_{18}$Na$_2$O$_{63}$: C, 39.17; H, 4.17; N, 6.53. Found: C, 39.10; H, 4.14; N, 6.46. Single-crystal unit-cell parameters: a = 19.389 Å, b = 19.389 Å, c = 20.045 Å; α = 90°, β = 90°, γ = 90°; V = 7535.50 Å^3.

[Gd$_2$Ga$_8$(mshi)$_8$(iph)$_4$]Na$_2$ ·10H$_2$O ·9DMF. Synthesized as previously described.[1] ESI-MS, calc. for [M]$^{2-}$, Gd$_2$Ga$_8$C$_{96}$H$_{64}$N$_8$O$_{40}$, 1421.3; found, 1420.3. Anal. Calcd. for Gd$_2$Na$_2$Ga$_8$C$_{123}$H$_{147}$N$_{17}$O$_{59}$: C, 39.65; H, 3.98; N, 6.40. Found: C, 39.66; H, 4.00; N, 6.38. Single-crystal unit-cell parameters: a = 19.494 Å, b = 19.494 Å, c = 19.490 Å; α = 90°, β = 90°, γ = 90°; V = 7406.47 Å^3.

[LnGa$_4$(shi)$_4$(bz)$_4$]Na. Solid Ln(NO$_3$)$_3$·xH$_2$O (0.25 mmol) (Ln^{3+}= Gd^{3+}, Dy^{3+}), H$_3$shi (1.0 mmol), and Ga(NO$_3$)$_3$·xH$_2$O (1.0 mmol) were dissolved completely in 15 mL of DMF. Then sodium benzoate (3.0 mmol) was added and the solution was stirred overnight. The solution was filtered and the clear and colourless filtrate was set to crystallize, yielding crystalline material after about four weeks. Pale pink solid was collected by filtration and dried *in vacuo*.

[DyGa$_4$(shi)$_4$(bz)$_4$]Na ·4H$_2$O ·4DMF. Synthesized as previously described.[3] ESI-MS, calc. for [M]$^-$, DyGa$_4$C$_{56}$H$_{36}$N$_4$O$_{20}$, 1524.8; found, 1524.8. Anal. Calcd. for DyNaGa$_4$C$_{68}$H$_{72}$N$_8$O$_{28}$: C, 42.68; H, 3.79; N, 5.86 %. Found: C, 42.78; H, 3.92; N, 5.90 %. Single-crystal unit-cell parameters: a = 23.816 Å, b = 23.816 Å, c = 16.452 Å; α = 90°, β = 90°, γ = 90°; V = 9339.93 Å^3.

[GdGa$_4$(shi)$_4$(bz)$_4$]Na ·4H$_2$O ·5DMF. Yield: 40%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{36}$GdGa$_4$N$_4$O$_{20}$, 1521.82; found, 1521.64. Anal. Calcd. for C$_{71}$H$_{79}$GdGa$_4$N$_9$NaO$_{29}$: C, 43.03; H, 4.02; N, 6.36. Found:

C, 42.92; H, 3.99; N, 6.30. a = 23.732 Å, b = 23.732 Å, c = 16.100 Å; α = 90°, β = 90°, γ = 90°; V = 9067.61 Å^3.

[LnGa$_4$(Cl-shi)$_4$(bz)$_4$]Na. Solid Ln(NO$_3$)$_3$·xH$_2$O (0.125 mmol) (Ln^{3+}= Gd^{3+}, Dy^{3+}), H$_3$Cl-shi (0.5 mmol), and Ga(NO$_3$)$_3$·xH$_2$O (0.5 mmol) were dissolved completely in 10 mL of DMF. Then sodium benzoate (2.0 mmol) was added and the solution was stirred overnight. The solution was filtered and the clear red filtrate was set to crystallize, yielding crystalline material after about four weeks. Pale brown solid was collected by filtration and dried *in vacuo*.

[DyGa$_4$(Cl-shi)$_4$(bz)$_4$]Na · 7H$_2$O · 4DMF. Yield: 53%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{32}$Cl$_4$DyGa$_4$N$_4$O$_{20}$, 1663.66; found, 1663.48. Anal. Calcd. for C$_{68}$H$_{74}$Cl$_4$DyGa$_4$N$_8$NaO$_{31}$: C, 38.79; H, 3.54; N, 5.32. Found: C, 38.77; H, 3.42; N, 5.16. Single-crystal unit-cell parameters: a = 14.551 Å, b = 24.421 Å, c = 24.195 Å; α = 90°, β = 91.18°, γ = 90°; V = 8596.34 Å^3.

[GdGa$_4$(Cl-shi)$_4$(bz)$_4$]Na · 5H$_2$O · 3DMF. Yield: 54%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{32}$Cl$_4$GdGa$_4$N$_4$O$_{20}$, 1657.66; found, 1657.48. Anal. Calcd. for C$_{65}$H$_{63}$Cl$_4$GdGa$_4$N$_7$NaO$_{28}$: C, 39.21; H, 3.19; N, 4.92. Found: C, 39.11; H, 3.19; N, 5.26. Single-crystal unit-cell parameters: a = 14.547 Å, b = 24.447 Å, c = 24.207 Å; α = 90°, β = 91.13°, γ = 90°; V = 8607.06 Å^3.

[LnGa$_4$(Br-shi)$_4$(bz)$_4$]Na. Solid Ln(NO$_3$)$_3$·xH$_2$O (0.125 mmol) (Ln^{3+}= Gd^{3+}, Dy^{3+}), H$_3$Br-shi (0.5 mmol), and Ga(NO$_3$)$_3$·xH$_2$O (0.5 mmol) were dissolved completely in 10 mL of DMF. Then sodium benzoate (2.0 mmol) was added and the solution was stirred overnight. The solution was filtered and the clear and pale red filtrate was set to crystallize, yielding crystalline material after about four weeks. Pale pink solid was collected by filtration and dried *in vacuo*.

[DyGa$_4$(Br-shi)$_4$(bz)$_4$]Na ·5H$_2$O ·4DMF. Yield: 35%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{32}$Br$_4$DyGa$_4$N$_4$O$_{20}$, 1841.46; found, 1841.27. Anal. Calcd. for C$_{68}$H$_{70}$Br$_4$DyGa$_4$N$_8$NaO$_{29}$: C, 36.34; H, 3.14; N, 4.99. Found: C, 36.20; H, 3.10; N, 4.96. Single-crystal unit-cell parameters: a = 14.674 Å, b = 24.527 Å, c = 24.320 Å; α = 90°, β = 91.50°, γ = 90°; V = 8756.83 Å^3.

[GdGa$_4$(Br-shi)$_4$(bz)$_4$]Na ·5H$_2$O ·4DMF. Yield: 40%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{32}$Br$_4$GdGa$_4$N$_4$O$_{20}$, 1837.46; found, 1837.26. Anal. Calcd. for C$_{68}$H$_{70}$Br$_4$GdGa$_4$N$_8$NaO$_{29}$: C, 36.43; H, 3.15; N, 5.00. Found: C, 36.26; H, 3.08; N, 4.99. Single-crystal unit-cell parameters: a = 14.655 Å, b = 24.578 Å, c = 24.318 Å; α = 90°, β = 91.44°, γ = 90°; V = 8756.13 Å^3.

[LnGa$_4$(I-shi)$_4$(bz)$_4$]Na. Solid Ln(NO$_3$)$_3$·xH$_2$O (0.125 mmol) (Ln^{3+}= Dy^{3+}), H$_3$I-shi (0.5 mmol), and Ga(NO$_3$)$_3$·xH$_2$O (0.5 mmol) were dissolved completely in 20 mL of DMF. Then sodium benzoate (2.0 mmol) was added and the solution was stirred overnight. The solution was filtered and the clear and pale red filtrate was covered with perforated aluminium foil and set to crystallize, yielding crystalline material after about four weeks. Pale pink solid was collected by filtration and dried *in vacuo*.

[DyGa$_4$(I-shi)$_4$(bz)$_4$]Na ·4H$_2$O ·4DMF. Yield: 67%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{32}$I$_4$DyGa$_4$N$_4$O$_{20}$, 2029.41; found, 2029.20. Anal. Calcd. for C$_{68}$H$_{68}$I$_4$DyGa$_4$N$_8$NaO$_{28}$: C, 33.78; H, 2.84; N, 4.64. Found: C, 33.80; H, 2.72; N, 4.59. Single-crystal unit-cell parameters: a = 14.833 Å, b = 24.546 Å, c = 24.468 Å; α = 90°, β = 92.05°, γ = 90°; V = 8902.58 Å^3.

[LnGa$_4$(shi)$_4$(F-bz)$_4$]Na. Solid Ln(NO$_3$)$_3$·xH$_2$O (0.25 mmol) (Ln^{3+}= Dy^{3+}), Ga(NO$_3$)$_3$·xH$_2$O (1.0 mmol), HF-bz (1.0 mmol), and H$_3$shi (1.0 mmol) were dissolved with stirring in 15 mL of DMF. Then concentrated aqueous NaOH solution (4.0 mmol, 19.9 M) was added and the solution was stirred overnight. Then the stirring was stopped, and the solution was set overnight to allow precipitate to congeal. The next day, the mixture was filtered via gravity filtration, the white precipitate was discarded, and the clear reddish filtrate was set for slow evaporation. Pale red, crystalline solid was collected after about two weeks and dried *in vacuo*.

[DyGa$_4$(shi)$_4$(F-bz)$_4$]Na ·4H$_2$O ·4DMF. Yield: 18%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{32}$F$_4$DyGa$_4$N$_4$O$_{20}$, 1597.79; found, 1597.79. Anal. Calcd. for C$_{68}$H$_{68}$F$_4$DyGa$_4$N$_8$NaO$_{28}$: C, 41.13; H, 3.45; N, 5.64. Found: C, 41.22; H, 3.52; N, 5.84. Single-crystal unit-cell parameters: a = 21.243 Å, b = 33.431 Å, c = 22.779 Å; α = 90°, β = 99.388°, γ = 90°; V = 15960.00 Å^3.

[LnGa$_4$(shi)$_4$(mbz)$_4$]Na. Solid Ln(NO$_3$)$_3$·xH$_2$O (0.25 mmol) (Ln^{3+}= Dy^{3+}), Ga(NO$_3$)$_3$·xH$_2$O (1.0 mmol), Hmbz (1.0 mmol), and H$_3$shi (1.0 mmol) were dissolved with stirring in 15 mL of DMF. Then concentrated aqueous NaOH solution (4.0 mmol, 19.9 M) was added and the solution was stirred

overnight. Then the stirring was stopped, and the solution was set overnight to allow precipitate to congeal. The next day, the mixture was filtered via gravity filtration, the white precipitate was discarded, and the clear and colourless filtrate was set for slow evaporation. White crystalline solid was collected after about two weeks and dried *in vacuo*.

[DyGa$_4$(shi)$_4$(mbz)$_4$]Na ·4H$_2$O ·5DMF. Yield: 17%. ESI-MS, calc. for [M]$^-$, C$_{60}$H$_{44}$DyGa$_4$N$_4$O$_{20}$, 1581.89; found, 1581.89. Anal. Calcd. for C$_{75}$H$_{87}$DyGa$_4$N$_9$NaO$_{29}$: C, 44.09; H, 4.29; N, 6.17. Found: C, 44.05; H, 4.22; N, 5.95. Single-crystal unit-cell parameters: a = 14.254 Å, b = 16.862 Å, c = 17.182 Å; α = 90°, β = 90.158°, γ = 90°; V = 4129.60 Å^3.

[LnGa$_4$(Cl-shi)$_4$(F-bz)$_4$]Na. Solid Ln(NO$_3$)$_3$·xH$_2$O (0.25 mmol) (Ln^{3+}= Dy^{3+}), Ga(NO$_3$)$_3$·xH$_2$O (1.0 mmol), HF-bz (1.0 mmol), and H$_3$Cl-shi (1.0 mmol) were dissolved with stirring in 15 mL of DMF. Then concentrated aqueous NaOH solution (4.0 mmol, 19.9 M) was added and the solution was stirred overnight. Then the stirring was stopped, and the solution was set for four hours to allow precipitate to congeal. The next day, the mixture was filtered via gravity filtration, the white precipitate was discarded, and the clear reddish filtrate was set for slow evaporation. Red, crystalline solid was collected after about two weeks and dried *in vacuo*.

[DyGa$_4$(Cl-shi)$_4$(F-bz)$_4$]Na ·5H$_2$O ·4DMF. Yield: 18%. ESI-MS, calc. for [M]$^-$, C$_{56}$H$_{28}$Cl$_4$F$_4$DyGa$_4$N$_4$O$_{20}$, 1735.63; found, 1735.44. Anal. Calcd. for C$_{68}$H$_{66}$Cl$_4$F$_4$DyGa$_4$N$_8$NaO$_{29}$: C, 38.14; H, 3.11; N, 5.23. Found: C, 38.15; H, 3.05; N, 5.36. Single-crystal unit-cell parameters: a = 14.254 Å, b = 16.862 Å, c = 17.182 Å; α = 90°, β = 90.16°, γ = 90°; V = 4129.60 Å^3.

Photophysical characterization

Excitation and emission spectra, luminescence lifetimes, and quantum yields were collected on powder samples in the solid state placed into 2.4 mm i.d. quartz capillaries. Steady-state emission and excitation spectra were measured on a custom-designed Horiba Scientific Fluorolog 3 spectrofluorimeter equipped with a visible photomultiplier tube (PMT) (220–850 nm, R928P; Hamamatsu) and a NIR PMT (950–1650 nm, H10330-75; Hamamatsu) upon excitation with a continuous Xenon lamp. All excitation and emission spectra were corrected for the instrumental functions. Luminescence lifetimes (τ_{obs}) were determined under excitation at 355 nm provided by a Nd:YAG laser (YG 980; Quantel). Dy^{3+} signal was detected in the range 575-577 nm using an iHR320 monochromator (Horiba Scientific) equipped with a Hamamatsu R928P PMT. The output signal from the detector was fed into a 500 MHz bandpass digital oscilloscope (TDS 754C; Tektronix), transferred to a PC for data processing with the program Origin 8$^\circledR$. Luminescence lifetimes are averages of at least three independent measurements. Absolute quantum yields of Dy^{3+} emission under ligand-centred excitation (Q_{Dy}^L) at 330–350 nm were determined with the Fluorolog 3 spectrofluorimeter based on an absolute method with the use of an integration sphere (Model G8, GMP SA, Renens, Switzerland). Each sample was measured several times under comparable experimental conditions, varying the position of samples. Estimated experimental error for quantum yield determination is ~10 %. Ligand-centred quantum yields (Q_L^L) were calculated from the corresponding emission spectra taking into account the values of Q_{Dy}^L.

Phosphorescence spectra of Gd^{3+} MCs were measured on powder samples at 77 K on a Horiba-Jobin-Yvon Fluorolog 3 spectrofluorimeter in time-resolved mode.

Diffuse reflectance spectra. For the collection of diffuse reflectance spectra, MCs (5 wt.%) were thoroughly grounded and dispersed in MgO. Measurements were performed on a Jasco V670 UV-visible spectrophotometer in reflectance (R) mode using a horizontal integration sphere accessory at room temperature. To reflect absorbance, diffuse reflectance spectra are presented as Kubelka-Munk function (($1-R)^2/2R$) vs. wavelength.
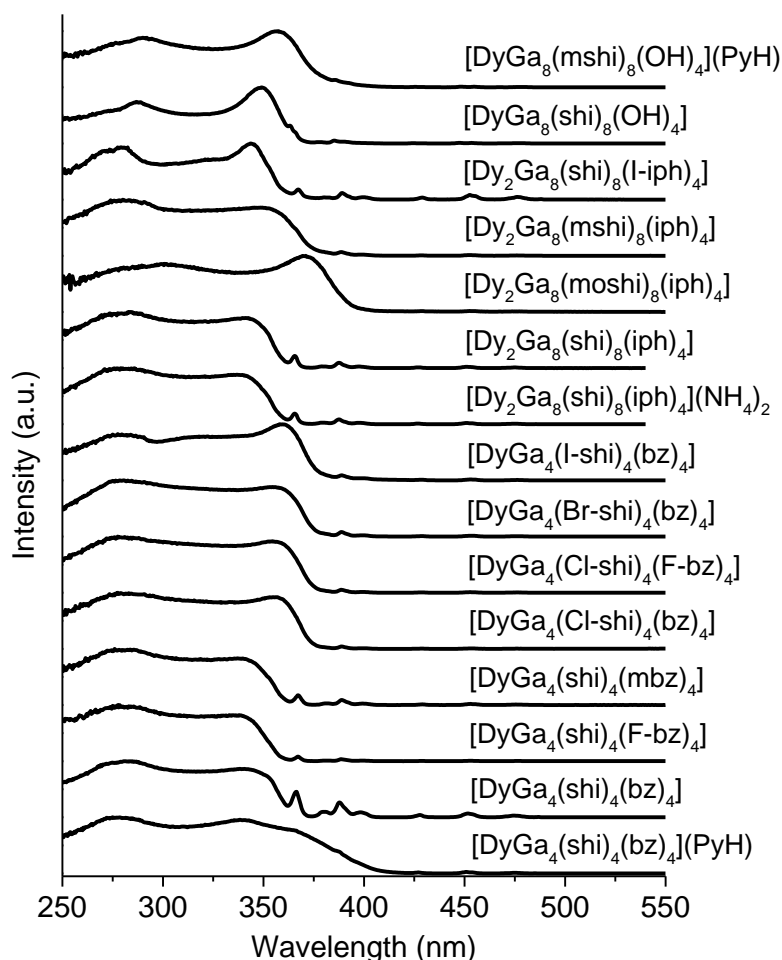
Figure S1. Corrected and normalized excitation spectra of Dy^{3+} MCs in the solid state upon monitoring emission at 575 nm at room temperature.

Table S1. Relative integral intensities of the ligand-centred bands in the range 360–445 nm and Dy^{3+}-centred $^4F_{9/2}\rightarrow^6H_J$ (J = 15/2, 13/2, 11/2) transitions normalized to the $^4F_{9/2}\rightarrow^6H_{13/2}$ band in the emission spectra of Dy^{3+}/Ga^{3+} MCs recorded under excitation at 340 nm.

Metallacrown	$\pi\pi^*$ (blue)	$^4F_{9/2}\rightarrow^6H_{15/2}$ (blue)	$^4F_{9/2}\rightarrow^6H_{13/2}$ (yellow)	$^4F_{9/2}\rightarrow^6H_{11/2}$ (red)	Total
$[DyGa_4(shi)_4(bz)_4](PyH)$[3,4]	0.007	0.856	1.000	0.078	1.940
$[DyGa_4(shi)_4(bz)_4]$[3]	0.123	0.844	1.000	0.076	2.043
$[DyGa_4(shi)_4(F-bz)_4]$	0.151	0.889	1.000	0.057	2.097
$[DyGa_4(shi)_4(mbz)_4]$	0.279	0.879	1.000	0.059	2.217
$[DyGa_4(Cl-shi)_4(bz)_4]$	2.064	0.824	1.000	0.054	3.941
$[DyGa_4(Cl-shi)_4(F-bz)_4]$	1.756	0.866	1.000	0.052	3.674
$[DyGa_4(Br-shi)_4(bz)_4]$	0.403	0.859	1.000	0.053	2.315
$[DyGa_4(I-shi)_4(bz)_4]$	0.090	0.910	1.000	0.050	2.050
$[Dy_2Ga_8(shi)_8(iph)_4](NH_4)_2$[3,5]	0.191	0.817	1.000	0.075	2.083
$[Dy_2Ga_8(shi)_8(iph)_4]$	0.153	0.816	1.000	0.079	2.049
$[Dy_2Ga_8(moshi)_8(iph)_4]$[1]	1.807	0.871	1.000	0.093	3.772
$[Dy_2Ga_8(mshi)_8(iph)_4]$	0.606	0.824	1.000	0.050	2.480
$[Dy_2Ga_8(shi)_8(I-iph)_4]$	0.090	0.860	1.000	0.042	1.991
$[DyGa_8(shi)_8(OH)_4]$[3,6]	0.535	1.171	1.000	0.065	2.771
$[DyGa_8(mshi)_8(OH)_4](PyH)$	0.604	1.112	1.000	0.052	2.768

Determination of the singlet state (S₁) energy levels: diffuse reflectance and ligand-centred emission spectra

Energy levels of the lowest singlet state (S_1) were determined from the red edge (10% of the maximum) of the diffuse reflectance spectra of the MCs (**Figure S2**) or organic ligands (**Figure S3**), or from the intersection of the corresponding diffuse reflectance and ligand-centred emission spectra (**Figure S4, S5**).
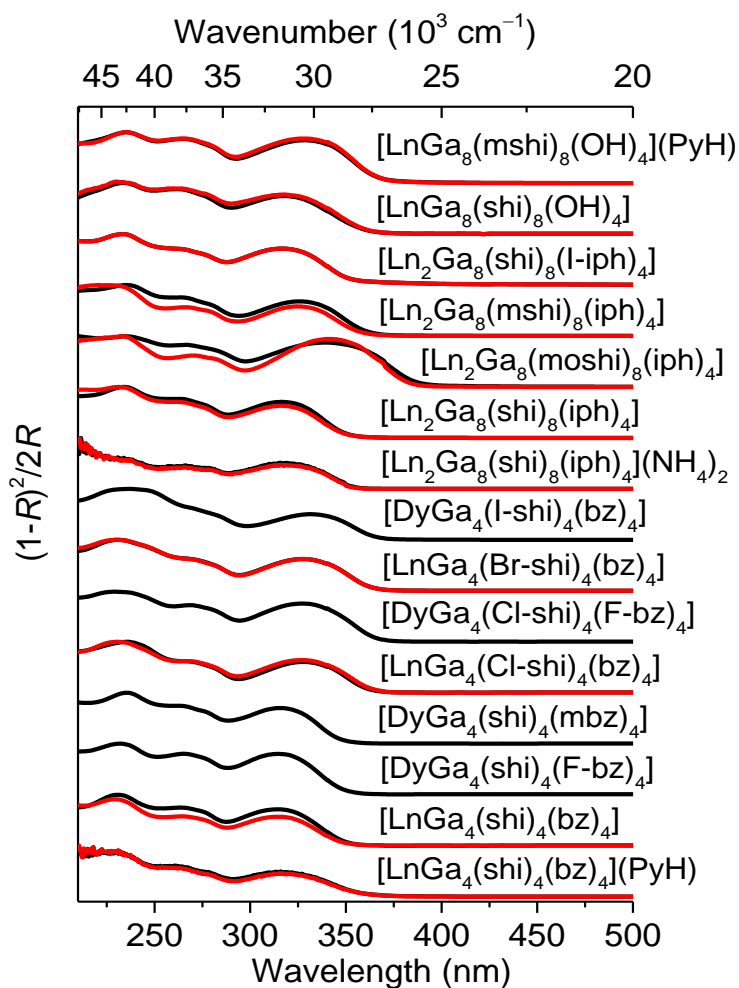

Figure S2. Normalized to the maximum diffuse reflectance spectra presented as Kubelka-Munk function for studied Dy^{3+} (black traces) and Gd^{3+} (red traces) MCs.
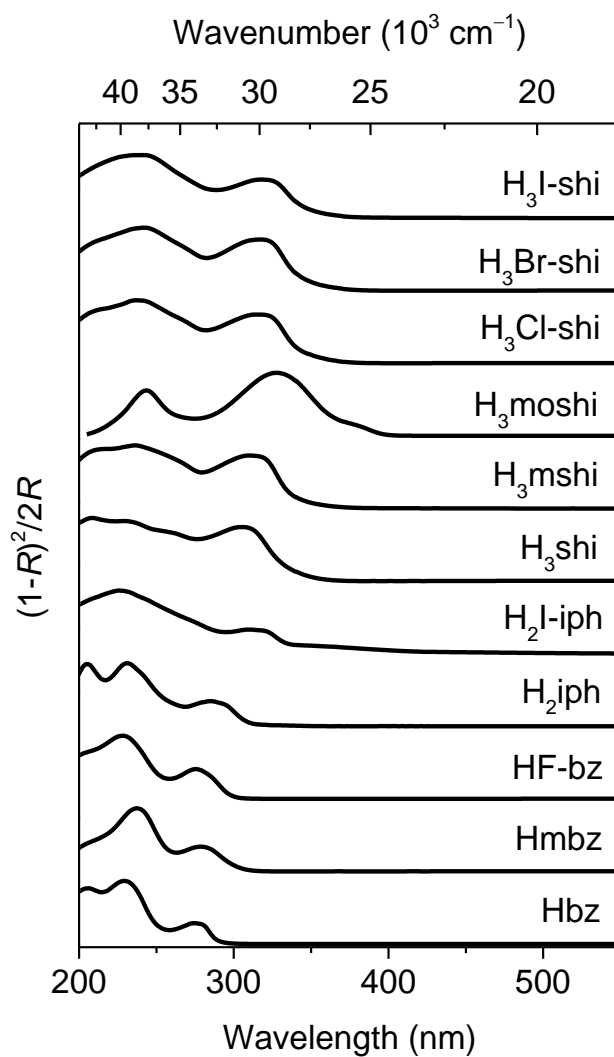
Figure S3. Normalized to the maximum diffuse reflectance spectra presented as Kubelka-Munk function for organic ligands used to assemble MCs.
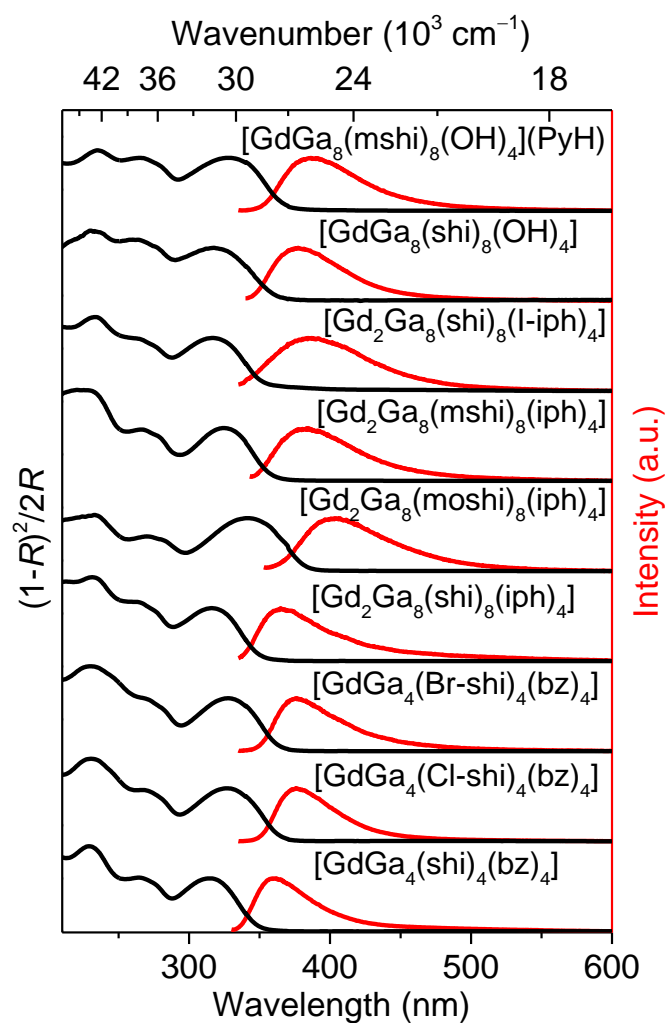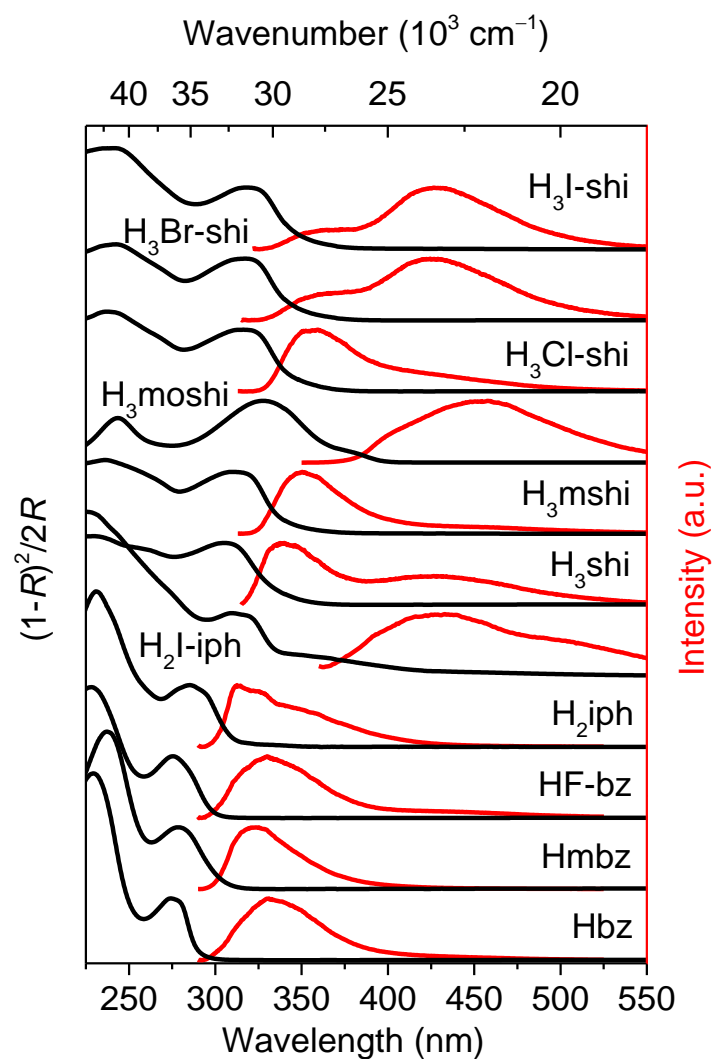
Figure S4. Normalized to the maximum of the low-energy band diffuse reflectance spectra presented as Kubelka-Munk function (black traces) and normalized to the maximum emission spectra upon excitation at 320 nm for all Gd^{3+} MCs except $[Gd_2Ga_8(moshi)_8(iph)_4]$ that was excited at 340 nm.

Figure S5. Normalized to the maximum of the low-energy band diffuse reflectance spectra presented as Kubelka-Munk function (black traces) and normalized to the maximum emission spectra upon excitation at 280 nm for Hbz, Hmbz, HF-bz, H$_2$iph, at 300 nm for H$_3$shi, H$_3$mshi, H$_3$Cl-shi, H$_3$Br-shi, H$_3$I-shi or at 340 nm for H$_3$moshi, H$_2$I-iph.

Determination of the triplet state ($^3T_1$) energy levels: phosphorescence spectra

Energy levels of the triplet state ($^3T_1$) were determined as a 0-0 transition from the Gaussian decomposition of the phosphorescence spectra of the Gd^{3+} MCs (**Figure S6**) or corresponding organic ligands (**Figure S7**).
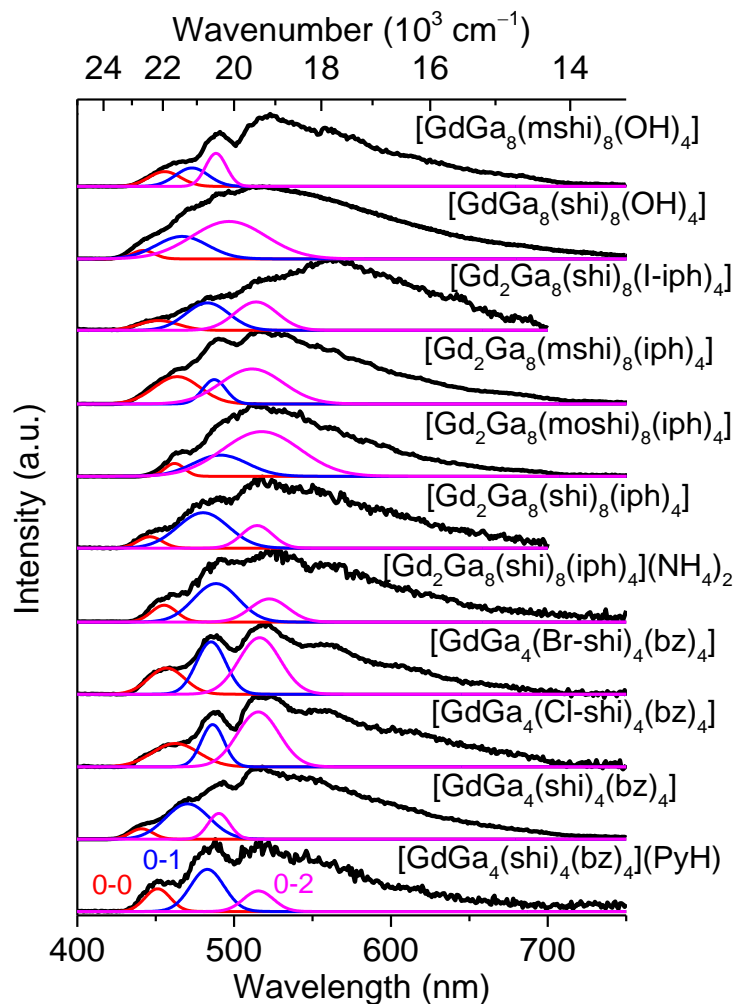

Figure S6. Corrected and normalized phosphorescence spectra of the Gd^{3+} MCs in the solid state upon excitation at 320-340 nm and application of a time delay of 200 µs at 77K (black traces), and 0-0 (red), 0-1 (blue), 0-2 (magenta) components obtained from their Gaussian decomposition.
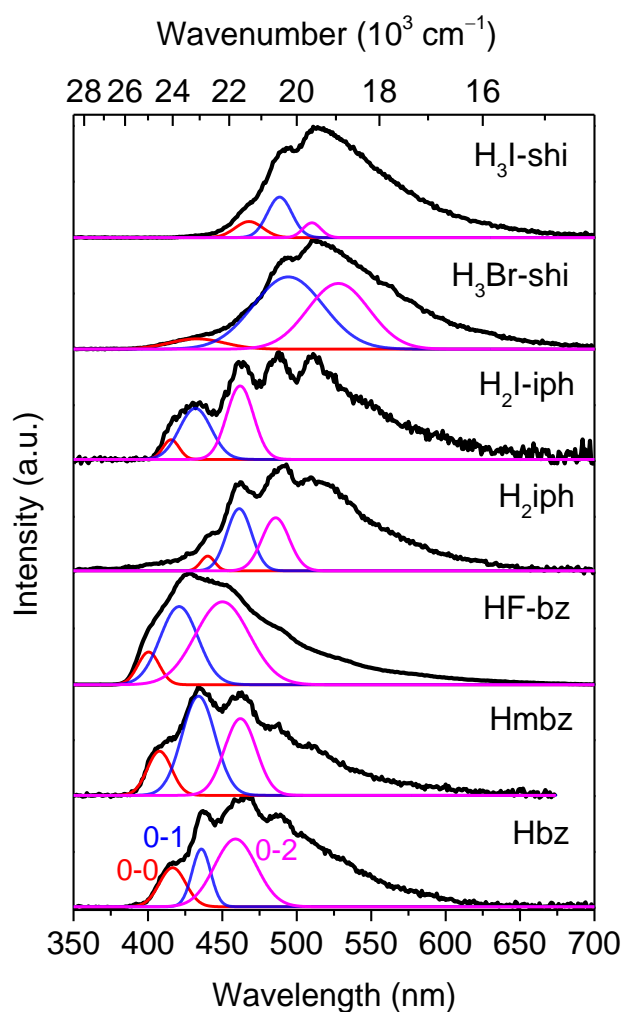
Figure S7. Corrected and normalized phosphorescence spectra of the ligands used to assemble MCs in the solid state upon excitation at 320 nm and application of a time delay of 200 µs at 77K (black traces) and 0-0 (red), 0-1 (blue), 0-2 (magenta) components obtained from their Gaussian decomposition.

Alternatively, $^3T_1$ energy levels were determined as the centre of gravity (C_g) of phosphorescent spectra (**Table 2**). C_g was calculated in the wavenumber basis after magnitude correction[7] using the formula:

$$C_g = \frac{\int_0^\infty f|S(f)|df}{\int_0^\infty |S(f)|df},$$ **(S1)**

where f is the spectral frequency (wavenumber) and $S(f)$ is the intensity of emission at that wavenumber over the entire dataset.

In general, the energies of S_1 and $^3T_1$ states determined using different methodologies either coincide or follow similar trends (**Figure S8**).
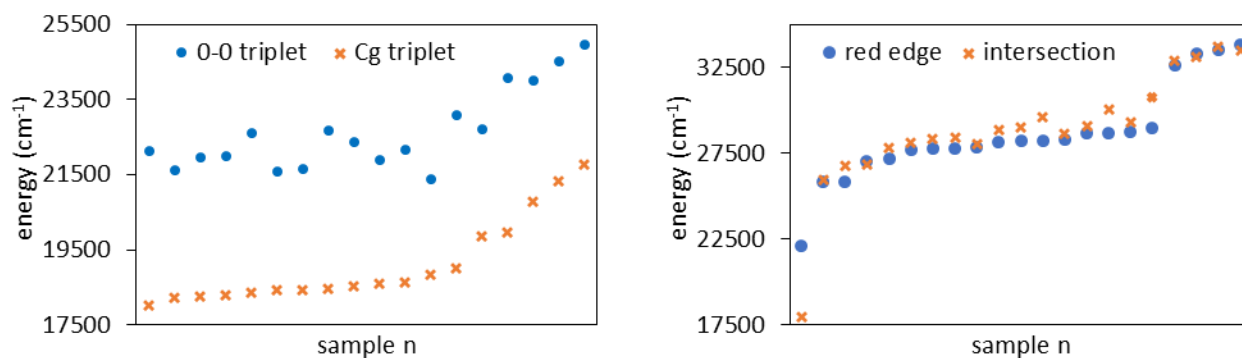

Figure S8. Comparison between two methodologies for determining energies of the (left) $^3T_1$ states from the phosphorescence spectra of Gd^{3+} MCs (*vide supra*), and (right) S_1 states from the red edge of the diffuse reflectance spectra or from the intersection of diffuse reflectance and ligand-centred emission spectra. Data correspond to **Table S2**.

Table S2. Singlet (S_1) and triplet ($^3T_1$) state energies of organic building blocks used to assemble MCs, and the associated values for the Gd^{3+} MCs.

Ligand	$^3T_1$ (cm^{-1})^a	$^3T_1$ (cm^{-1})^b	S_1 (cm^{-1})^c	S_1 (cm^{-1})^d
Hbz	24010	20796	33500	33730
Hmbz	24520	21327	33330	33110
HF-bz	24970	21774	33840	33500
H$_2$iph	22720	19860	32630	32895
H$_2$I-iph	24070	19962	27060	26850
H$_3$shi	-	-	28940	30720
H$_3$mshi	-	-	28690	30075
H$_3$moshi	-	-	25840	25970
H$_3$Cl-shi	-	-	28250	29630
H$_3$Br-shi	23100	19015	28210	29030
H$_3$I-shi	21370	18842	28290	28650
Metallacrown^e	$^3T_1$ (cm^{-1})^a	$^3T_1$ (cm^{-1})^b	S_1 (cm^{-1})^c	S_1 (cm^{-1})^d
[GdGa$_4$(shi)$_4$(bz)$_4$](PyH)[4]	22170	18653	28290	-
[GdGa$_4$(shi)$_4$(bz)$_4$]	22680	18456	28735	29280
[GdGa$_4$(shi)$_4$(F-bz)$_4$]	-	-	28695	-
[GdGa$_4$(shi)$_4$(mbz)$_4$]	-	-	28860	-
[GdGa$_4$(Cl-shi)$_4$(bz)$_4$]	21620	18220	27820	28050
[GdGa$_4$(Cl-shi)$_4$(F-bz)$_4$]	-	-	27470	-
[GdGa$_4$(Br-shi)$_4$(bz)$_4$]	21890	18611	27700	28090
[GdGa$_4$(I-shi)$_4$(bz)$_4$]	-	-	27625	-
[Gd$_2$Ga$_8$(shi)$_8$(iph)$_4$](NH$_4$)$_2$[6]	21980	18306	28650	-
[Gd$_2$Ga$_8$(shi)$_8$(iph)$_4$][2]	22385	18537	28650	29110
[Gd$_2$Ga$_8$(moshi)$_8$(iph)$_4$]	21640	18445	25870	26810
[Gd$_2$Ga$_8$(mshi)$_8$(iph)$_4$][1]	21570	18420	27780	28370
[Gd$_2$Ga$_8$(shi)$_8$(I-iph)$_4$]	22130	18008	28170	28860
[GdGa$_8$(shi)$_8$(OH)$_4$][5,7]	22620	18354	27815	28410
[GdGa$_8$(mshi)$_8$(OH)$_4$](PyH)	21945	18266	27210	27820

^{a} Determined from the Gaussian fitting of the 0-0 phonon line of the phosphorescence spectra measured at 77 K (**Figure S7**). ^{b} Determined as the centre of gravity (C_g) of the phosphorescence spectra measured at 77K (**Figure S7**). ^{c} Determined from the red edge (10% of the maximum) of the solid-state diffuse reflectance spectra (**Figure S3**). ^{d} Determined from the intersection of the diffuse reflectance and the corresponding ligand-centred emission spectra (**Figure S5**). ^{e} This section is partially reproduced from **Table 2** for the ease of comparison.
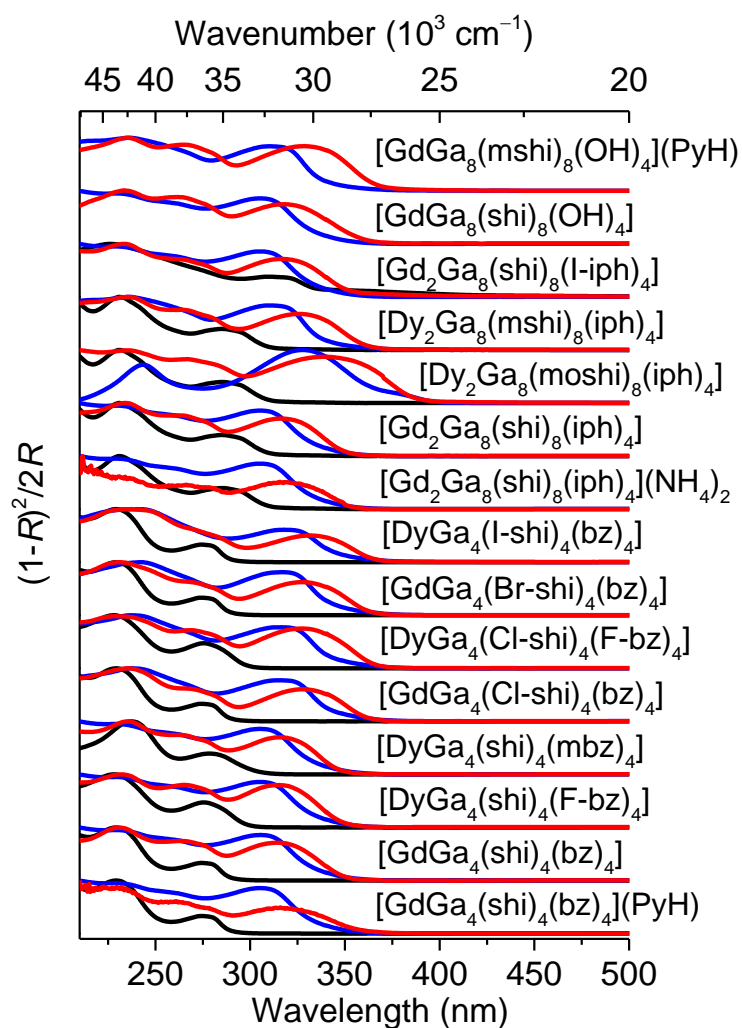
Figure S9. Comparison of normalized diffuse reflectance spectra presented as Kubelka-Munk function of $LnGa_4(L')_4(L'')_4$, $Ln_2Ga_8(L')_8(L''')_4$ and $LnGa_8(L')_8(OH)_4$ MCs (red traces, Ln = Gd^{3+} or Dy^{3+}) with those of the corresponding constituent organic ligands (blue traces: H_3L' = H_3shi, H_3mshi, H_3moshi, H_3Cl-shi, H_3Br-shi, H_3I-shi; black traces: HL'' = Hbz, F-bz, mbz or H_2L''' = H_2iph, H_2I-iph) in the solid state at room temperature.
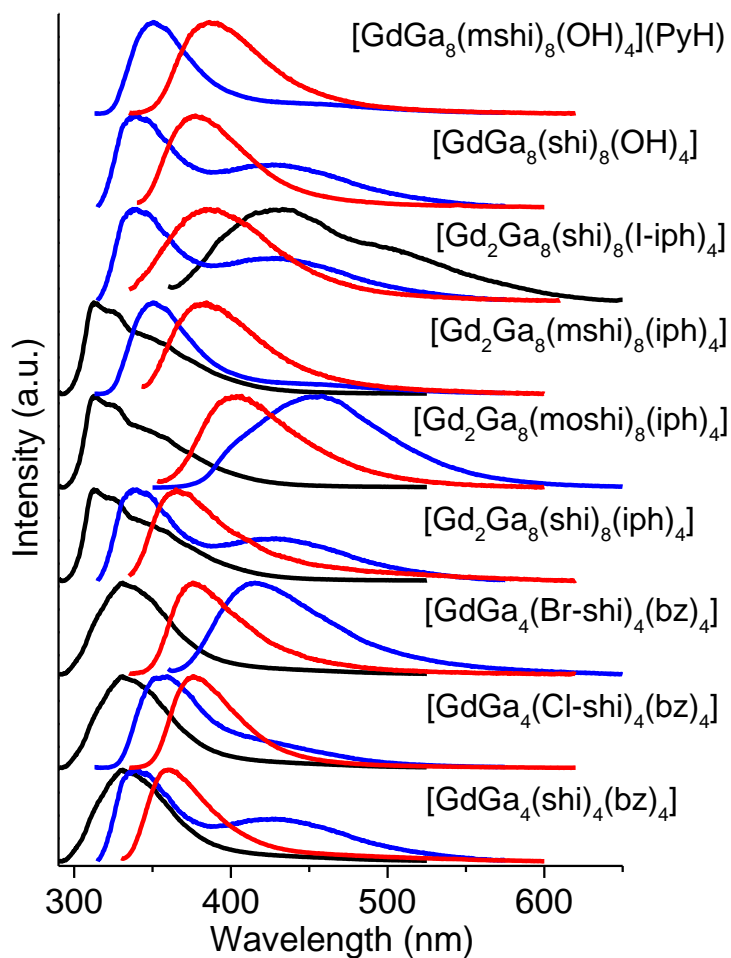
Figure S10. Comparison of corrected and normalized emission spectra of $GdGa_4(L')_4(L'')_4$, $Gd_2Ga_8(L')_8(L''')_4$ and $GdGa_8(L')_8(OH)_4$ MCs (red traces) with those of the corresponding constituent organic ligands (blue traces: H_3L' = H_3shi, H_3mshi, H_3moshi, H_3Cl-shi, H_3Br-shi, H_3I-shi; black traces: HL'' = Hbz or H_2L''' = H_2iph, H_2I-iph) in the solid state at room temperature.

Determination of CIE 1931 coordinates and CCT

CIE 1931 coordinates (x, y) were calculated from the emission spectra using standard equations.[8] Correlated Colour Temperature (CCT) values were estimated from CIE 1931 (x, y) values using McCamy's approximation:[9]

$$n = \frac{x - 0.3320}{0.1858 - y} \qquad \textbf{(S2a)}$$

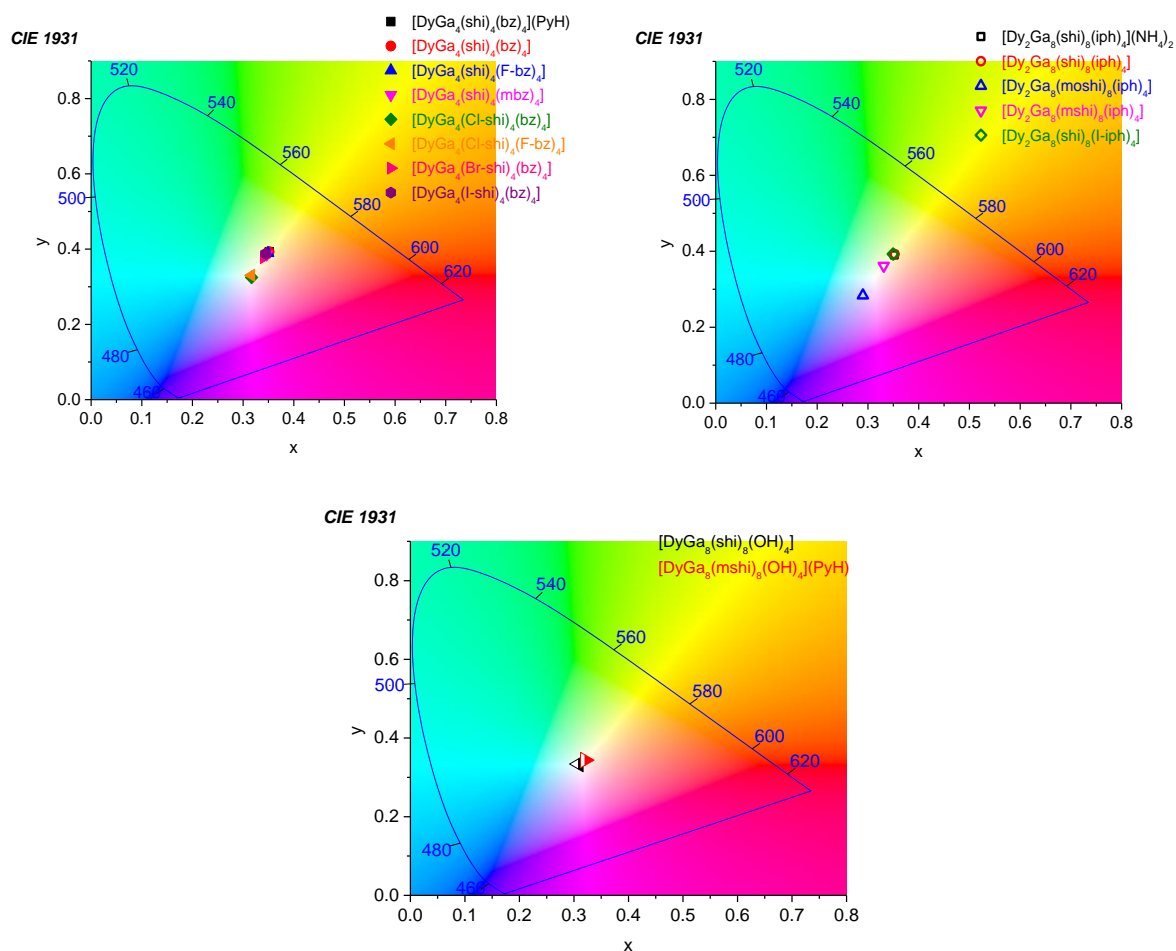$$CCT = 437 \times n^3 + 3601 \times n^2 + 6861 \times n + 5517 \qquad \textbf{(S2b)}$$

Figure S11. CIE 1931 diagram depicting the chromaticity coordinates (calculated from 370-700 nm) for each of the Dy^{3+} complexes presented herein, separated by the compound topology type: A (top left), B (top right), or C (bottom).
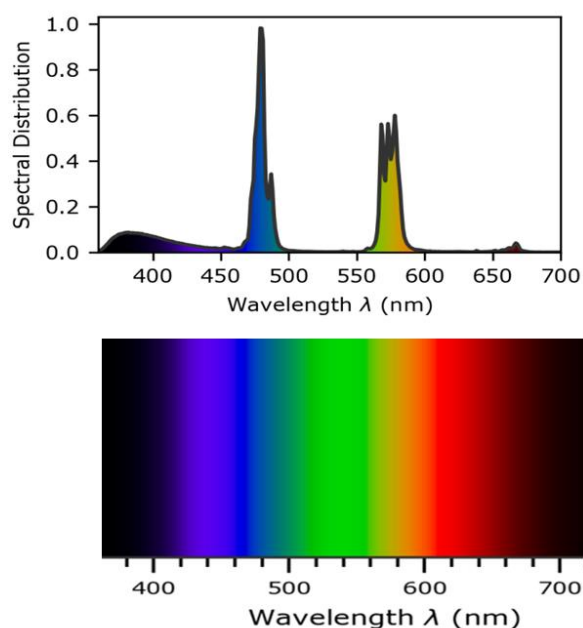
Figure S12. (Top) An example of a visible emission profile of a molecular Dy^{3+} compound ($[DyGa_8(Shi)_8(OH)_4]$), colorized by the approximate visual perception of a typical human eye. Black corresponds to the range of wavelengths invisible to a human eye highlighting that the large part of the ligand-centred emission here does not contribute to the colour perception of a human. (Bottom) Approximate colorimetric appearance *vs*. wavelength.

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