Chapter 9

Experimental description

9.1 General conditions

All the commercially available chemicals were used without further purification. All solvents utilised for photophysical characterisation were Fluka spectroscopic grade solvents. IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped for reflectance measurements. ^{1}H NMR spectra were recorded on a Bruker WH-300 spectrometer in $CDCl_3$ solutions, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer CHNS/O.

Thermal analysis was monitored with a Zeiss Axioscope polarising microscope equipped with a Linkam CO 600 heating stage and a Perkin-Elmer DSC-6 differential scanning calorimeter with a heating and cooling rate of 10.0 °C min^{-1} following calibration with indium. Absorption spectra were recorded with a Perkin-Elmer Lambda 900 spectrophotometer. Corrected luminescence spectra were obtained with a Perkin-Elmer LS-50B spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube. Photoluminescent quantum yields were measured with the method described by Demas and Crosby[1] using $[Ru(bipy)_3]Cl_2$ (bipy = 2,2′-bipyridine; Φ_{PL}= 0.028 in aerated water [2]) and cresyl violet perchlorate (CV) (MeOH, Φ_{PL}= 0,54[3]) as standard. The experimental uncertainty in the band maximum for absorption and luminescence spectra is 2 nm; that for luminescence intensity is 15%. All emissions are confirmed by excitation spectra. Films were obtained by spin coating on quartz support.

Mass spectrometry

The MALDI mass spectra were acquired on a 4700 proteomics analyzer mass spectrometer from Applied Biosystems (Foster City, CA) equipped with a 200-Hz Nd:YAG laser at 355-nm wavelength. The MS spectra, internally calibrated, were acquired in reflectron mode (20-keV accelerating voltage), with 400-ns delayed extraction, averaging 2000 laser shots with a mass accuracy of 10 ppm. 2,7-Dimethoxynaphthalene (DMN; Sigma-Aldrich Corp., Saint Louis, MO) was used as matrix. The DMN was recrystallized from CH_3OH to remove the impurities. A 0.45-μL aliquot of a premixed solution of DMN and sample (400:1) dissolved in MeOH/CH_3Cl (1:1) was spotted on the matrix target, dried at room temperature, and analyzed into the mass spectrometer. The MS/MS experiments were acquired at the collision energy of 1 kV, defined by the potential difference between the source acceleration voltage (8 kV) and the floating collision cell (7 kV); 3400 laser shots were averaged, while the pressure inside the collision cell was 8×10^{-7} Torr.

Computational Details

Molecular geometries were optimized using the Kohn-Sham Density Functional Theory (DFT)[4] with the 6-31G(d) basis set and the Becke three-parameters hybrid exchange-correlation functional known as B3LYP.[5] Analytical evaluation of the energy second derivative matrix w.r.t. Cartesian coordinates (Hessian matrix) at the same level of approximation confirmed the nature of minima of the energy surface points associated to the optimized structures.

Time dependent density functional theory (TD-DFT)[6,7] allowed the computation of vertical excitation energies, oscillator strengths and excited state compositions in terms of monoelectronic excitations between occupied and virtual orbitals. These computations were performed at the B3LYP/6-31G(d) level of approximation. All the calculations were performed using the

Gaussian98 program.[8] **Figure 5.15** has been produced by the program Molekel 4.3 for Windows platforms.[9]

Crystallography

X-ray data for **Q'$_2$GaC$_6$H$_5$** and **Q'$_2$GaC$_6$H$_4$CN** were collected on a Bruker-Nonius X8 Apex CCD area detector equipped with graphite monochromator and Mo-Kα radiation (λ = 0.71073), and data reduction was performed using the SAINT programs; absorption corrections based on multiscan were obtained by SADABS.[10] X-ray data for **Q'$_2$GaC$_6$H$_4$NO$_2$** were collected on a Siemens R3m/V automated four-circle diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073).

The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using a method based upon azimuthal (Ψ) scan data. All structures were solved by Patterson method (SHELXS/L program in the SHELXTL-NT software package)[11] and refined by full-matrix least squares based on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as idealized atoms riding on the respective carbon atoms with C-H bond lengths appropriate to the carbon atom hybridization.

Thickness measurements

The thickness of the thin solid film applied in the reported devices was collected with a VEECO DEKTAK 3 ST Surface Profilometer Measurement System (sub micron up to 262 μm). Accurate step heights and surface roughness permit scans from 50 with a maximum 8000 data points.

Ellipsometric data were collected with J.A. Woollam VWASE32 M-2000DI™ Spectroscopic Ellipsometer. Backside corrected ellipsometric data, 50°-70° in 5°

increments. Model 6 Gaussians. 1 High energy pole, e1 offset. Four data sets fitted simultaneously. MSE = 3.785.

Light-Current-Voltage measurements

The L-I-V data were collected with a Keithley Instruments Model 2400 Source Meterwith digital I/O interface and Keithley Instruments Model 6514 Programmable Electrometer coupled with a calibrated silicon photodiode in front of the light-emitting pixel at 4 cm of distance. Output spectra were registered with Oriel 77400 MS125 CCD spectrograph coupled with a Jobin Yvon SPEX fiber.

9.2 Preparation of charged hexacoordinated [Q'$_2$Ga(N,N)][X] compounds

Synthesis of ***[Q'$_2$Ga(bipy)][NO$_3$]***

An ethanol (3 ml) solution of gallium(III) nitrate hydrate (0.150 g, 0.58 mmol) was prepared at room temperature under stirring. Hence the 2,2'-bipyridine (0.091 g, 0.58 mmol) solved in ethanol (3 ml) was added. After 30 min the ethanol (3 ml) solution of 2-methyl-8-hydroxyquinoline (0.186 g, 1.172 mmol) was dropped into the cloudy white reaction mixture. The mixture was allowed to stir over night. The suspension was filtered to give a yellow solid. The product was purified by washing with water and ethanol and recrystallized from dichloromethane/diethyl ether. Yield: 45%. M. p.: 176°C, dec.. IR (KBr, cm^{-1}): 3063 (-CH_3), 1602, 1570, 1507, 1463, 1445, 1431, 1383 (NO_3^-), 1277, 1114, 1032, 837, 754, 733, 641, 522. ^{1}H NMR (Acetone, ppm): 8.71 (d, *J*= 4.13 Hz, 2H, H$^{a,a'}$); 8.41 (d, *J*= 8.03 Hz, 2H, H^4); 8.33 (d, *J*= 8.36 Hz, 2H, H$^{d,d'}$); 7.85 (td, *J*= 7.8 Hz, 2H, H$^{c,c'}$); 7.5 (m, 4H, H$^{3,6,b,b'}$); 7.23 (d, *J*= 8.26 Hz, 2H, H$^{7\ or\ 5}$); 7.16 (d, *J* = 7.7 Hz, 2H,

$H^{5\ or\ 7}$); 3.12 (s, -CH_3, 6H). Anal. Calcd. for $C_{30}H_{24}N_5O_5Ga$: C, 59.69; H, 4.01; N, 11.61%. Found: C, 59.35; H, 3.85; N, 11.25%.

Synthesis of ***[Q'$_2$Ga(bipy)][PF$_6$]***

Compound ***[Q'$_2$Ga(bipy)][NO$_3$]*** (0.135 g, 0.2 mmol) was solved, under stirring, in the minimum quantity of chloroform (2 ml) at room temperature. Thus, a solution of ammonium hexafluorophosphate in acetone (0.163 g, 1 mmol, 3 ml) in molar ratio 1:5 was added to the reaction mixture. The suspension was stirred 12 h at room temperature. Hence the product, collected by filtration, was purified washing with small amounts of water, ethanol and diethyl ether. The yellow solid was recrystallized from dichloromethane/diethyl ether. Yield: 73%. M. p.: 262-264°C. IR (KBr, cm^{-1}): 3120 (-CH_3), 3070, 1602, 1570, 1508, 1464, 1447, 1431, 1384, 1335, 1279, 1113, 1065, 1032, 845 (PF_6^-), 771, 754, 645, 558. ^{1}H NMR (Acetone, ppm): 8.69 (d, *J*= 4, 2H, $H^{a,a'}$); 8.46 (d, *J*= 8.37 Hz, 2H, H^4); 8.39 (d, *J*= 8 Hz, 2H, $H^{d,d'}$); 7.95 (td, *J*= 7.8 Hz, 2H, $H^{c,c'}$); 7.5 (m, 4H, $H^{3,6,b,b'}$); 7.25 (d, *J*= 7.27 Hz, 2H, $H^{7\ or\ 5}$); 7.12 (d, *J* = 7.7 Hz, 2H, $H^{5\ or\ 7}$); 3.12 (s, -CH_3, 6H). Anal. Calcd. $C_{30}H_{24}N_4O_2GaPF_6$: C, 52.43; H, 3.52; N, 8.15%. Found: C, 52.05; H, 3.20; N, 7.85%.

Synthesis of ***[Q'$_2$Ga(phen)][NO$_3$]***

The compound was synthesised following the procedure described for the complex ***[Q'$_2$Ga(bipy)][NO$_3$]***. Yellow solid, yield: 50%. M. p.: 208 °C, dec.. IR (KBr, cm^{-1}): 3036 (-CH_3), 1567, 1606, 1463, 1428, 1382 (NO_3^-), 1337, 1275, 1106, 872, 857, 837, 755, 725, 644. ^{1}H NMR (Acetone, ppm): 9.07 (dd, *J*= 8.36 Hz, 2H, $H^{a,a'}$); 8.63 (d, *J*= 8.47 Hz, 2H, H^4); 8.48 (s, 2H, $H^{d,d'}$); 8.37 (dd, *J*= 4.91 Hz, 2H, $H^{c,c'}$); 8.07 (dd, *J*= 8.25 Hz, 2H, $H^{b,b'}$); 7.69 (d, *J*= 8.47 Hz, 2H, H^3); 7.49 (t, *J*= 8.03 Hz, 2H, H^6); 7.32 (d, *J*= 8.15 Hz, 2H, $H^{7\ or\ 5}$); 6.85 (d, *J*= 7.69 Hz, 2H, $H^{5\ or\ 7}$); 2.87 (s, -CH_3, 6H). Anal. Calcd. for $C_{32}H_{24}N_5O_5Ga$: C, 61.17; H, 3.85; N, 11.15%. Found: C, 60.95; H, 3.85; N, 8.70%.

Synthesis of ***[Q′$_2$Ga(phen)][PF$_6$]***

This compound was synthesised with the same procedure reported for the complex ***[Q′$_2$Ga(bipy)][PF$_6$]***. Yellow solid, yield: 50%. M. p.: 208°C, dec.. IR (KBr, cm^{-1}): 3069 (-*CH*$_3$), 1613, 1602, 1570, 1509, 1464, 1447, 1429, 1383, 1318, 1278, 1111, 1032, 844 (*PF*$_6^-$), 770, 753, 645, 557. ^{1}H NMR (Acetone, ppm): 9.07 (dd, *J*= 9 Hz, 2H, H$^{a,a'}$); 8.63 (d, *J*= 9 Hz, 2H, H^4); 8.48 (s, 2H, H$^{d,d'}$); 8.37 (dd, *J*= 5 Hz, 2H, H$^{c,c'}$); 8.07 (dd, *J*= 8 Hz, 2H, H$^{b,b'}$); 7.69 (d, *J*= 9 Hz, 2H, H^3); 7.49 (t, *J*= 8 Hz, 2H, H^6); 7.32 (d, *J*= 8 Hz, 2H, H$^{7 \text{ or } 5}$); 6.85 (d, *J*= 8 Hz, 2H, H$^{5 \text{ or } 7}$); 2.87 (s, -*CH*$_3$, 6H). Anal. Calcd. for $C_{32}H_{24}N_4O_2GaPF_6$: C, 54.08; H, 3.41; N, 7.89%. Found: C, 53.90; H, 3.15; N, 7.90%.

9.3 Preparation of Q′$_2$GaL^n compounds

An ethanol solution (5 ml) of suitable phenol (1.95 mmol) and sodium hydroxide (1.95 mmol), was added to an aqueous solution (20 mL) of gallium(III) nitrate hydrate (1.95 mmol). After several minutes, 2-methyl-8-hydroxyquinoline (3.9 mmol), dissolved in ethanol (5 mL), was slowly dropped to the reaction mixture that was refluxed six hours and allowed to stir overnight at room temperature. After cooling, a yellow solid was filtered, washed with water, ethanol and diethyl ether. The crude product was recrystallized from $CHCl_3$/Et_2O (1:3) solution.

Synthesis of ***Q′$_2$GaOC$_6$H$_5$***

Yellow solid, yield: 50%. M. p.: 267°C. IR (KBr, cm^{-1}): 3052 (-*CH*$_3$), 2992, 2928, 1610, 1591, 1576, 1506, 1466, 1431, 1282, 1114, 883, 834, 753, 648. ^{1}H NMR ($CDCl_3$, ppm): 8.19 (d, *J*= 8.27 Hz, 2H, H^4), 7.46 (t, *J*= 7.93 Hz, 2H, H^6), 7.33 (d, *J*= 8.28 Hz, 2H, H^3), 7.15 (m, 5H, H^{5,7,c}), 6.80 (d, *J*= 2.07 Hz, 2H, H$^{b,b'}$), 6.52 (d, *J*= 2.42 Hz, 2H,

$H^{a,a'}$), 3.15 (s, 6H, *–CH₃*). Anal. Calcd. for $C_{26}H_{21}O_3N_2Ga$: C, 65.17; H, 4.42; N, 5.85%. Found: C 65.03; H, 4.42; N, 5.57%.

Synthesis of ***Q'₂GaOC₆H₄CN***

Yellow solid, yield: 55%. M. p.: 264°C. IR (KBr, cm^{-1}): 3046 (*-CH₃*), 2221 (*–CN*), 1598, 1576, 1504, 1465, 1432, 1303, 1269, 1115, 860, 845, 835, 755, 651, 530. ^1H NMR ($CDCl_3$, ppm): 8.25 (d, *J*= 8.41 Hz, 2H, H^4), 7.49 (t, *J*= 8.07 Hz, 2H, H^6), 7.38 (d, *J*= 8.42 Hz, 2H, H^3), 7.21 (d, *J*= 7.37 Hz, 2H, $H^{5 \text{ or } 7}$), 7.17 (d, *J*= 7.71 Hz, 2H, $H^{7 \text{ or } 5}$), 7.10 (d, *J*= 8.77 Hz, 2H, $H^{b,b'}$), 6.48 (d, *J*= 8.77 Hz, 2H, $H^{a,a'}$), 2.98 (s, 6H, *–CH₃*). Anal. Calcd. for $C_{27}H_{20}N_3O_3Ga$: C, 64.32; H, 4.00; N, 8.33 %. Found: C, 64.15; H, 3.90; N, 8.31 %.

Synthesis of ***Q'₂GaOC₆H₄NO₂***

Yellow solid, yield 60%. M. p.: 273 °C. IR (KBr, cm^{-1}): 3063 (*-CH₃*), 1586, 1496, 1451, 1430, 1342, 1303 (*–NO₂)*, 1270, 1115, 869, 852, 834, 755, 674, 531. ^1H NMR ($CDCl_3$, ppm): 8.26 (d, *J*= 8.53 Hz, 2H, H^4), 7.75 (d, *J*= 8.87 Hz, 2H, $H^{b,b'}$), 7.50 (t, *J*= 7.84 Hz, 2H, H^6), 7.39 (d, *J*= 8.53 Hz, 2H, H^3), 7.22 (d, *J*= 8.18 Hz, 2H, $H^{5 \text{ or } 7}$), 7.18 (d, *J*= 7.51 Hz, 2H, $H^{7 \text{ or } 5}$), 6.45 (d, *J*= 9.2 Hz, 2H, $H^{a,a'}$), 2.99 (s, 6H, *–CH₃*). Anal. Calcd. for $C_{26}H_{20}N_3O_5Ga$: C, 59.58; H, 3.85; N, 8.02%. Found: C, 59.34; H, 3.83; N, 8.32%.

Synthesis of ***Q'₂GaOC₆H₄C₆H₄OGaQ'₂***

The complex was synthesised following the procedure illustrated in the previous compounds with Ga:HL^n:HQ' in 2:1:4 molar ratio.

Light green solid, yield 40%. M. p.: > 350 °C. IR (KBr, cm^{-1}): 3065 (*-CH₃*), 1604, 1576, 1498, 1467, 1432, 1343, 1269, 1115, 858, 832, 754, 649, 610. ^1H NMR (*d_6*-DMSO, ppm): 8.54 (d, *J*= 8.7 Hz, 2H, H^4), 7.70 (d, *J*= 8.3 Hz, 2H, $H^{b,b'}$), 7.43 (t, *J*= 7.93 Hz, 2H, H^6), 7.39 (d, *J*= 7.56 Hz, 2H, H^3), 7.26 (d, *J*= 8.31 Hz, 2H, $H^{5 \text{ or } 7}$), 6.92

(d, *J*= 7.55 Hz, 2H, $H^{7 \text{ or } 5}$), 6.78 (d, *J*= 7.93 Hz, 2H, $H^{a,a'}$), 3.04 (s, 6H, $-CH_3$). Anal. Calcd. for $C_{52}H_{40}N_4O_6Ga_2$: C, 65.31; H, 4.22; N, 5.86%. Found: C, 64.88; H, 4.23; N, 5.80%.

Synthesis of ***Q′₂GaOC₆H₄(CH₂)₃C₆H₄OGaQ′₂***

The synthetic protocol followed those of the previous compound. The characterization of the collected powder reveals the presence of impurities as GaQ'_3 and HQ′ .

Synthesis of ***Q′₂GaOC₆H₄C(CH₃)₂C₆H₄C(CH₃)₂C₆H₄OGaQ′₂***

The synthesis followed the same procedure mentioned for the previous compounds. In the obtained product was found GaQ'_3 and unreacted biphenol ligand as impurities.

9.4 Preparation of polymetallic gallium complexes with $H_2TPP(OH)_4$

Synthesis of ***ZnTPP(OH)₄·2H₂O***

To a solution of **$H_2TPP(OH)_4$** (0.510 g, 0.751 mmol) in 10 mL of THF was added a methanol solution (3 mL) of zinc(II) acetate dihydrate (0.164 g, 0.751 mmol). The reaction mixture was stirred under ambient temperature for 20 h. The solvents were evaporated under reduced pressure. The violet solid was collected with water and filtered washing with water and small amounts of diethyl ether. Violet solid, yield 51%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3331, 1607, 1587, 1509, 1468, 1437, 1348, 1267, 1229, 1171, 1101, 984, 968, 844, 804, 729, 598. ^{1}H NMR (MeOD, ppm): 8.86 (s, 8H, H^{β}), 8.00 (d, *J*= 8.2 Hz, 8H, $H^{3',5'}$), 7.18 (d, *J*= 8.2 Hz 8H, $H^{2',6'}$). Anal. Calcd. for $C_{44}H_{32}N_4O_6Zn$: C 67.92; H 4.15; N 7.20%. Found: C 67.03; H 4.41; N 7.15%.

Synthesis of ***ZnTPP(OH)$_3$(OGaQ′$_2$)·2H$_2$O***

To an aqueous solution of gallium(III) nitrate hydrate (0.029 g, 0.13 mmol, 10 mL) was added an ethanol solution of **ZnTPP(OH)$_4$** (0.100 g, 0.13 mmol, 8 mL) activated with sodium hydroxyde (0.005 g, 0.13 mmol) in 1:1 molar ratio. After same minute an ethanol (4 mL) solution of 2-methyl-8-hydroxyquinoline (0.041 g, 0.255 mmol), 1:2 molar ratio, was slowly dropped to the reaction mixture. The suspension was refluxed for 5 h, and allowed to stir overnight at ambient temperature. The reaction mixture was dried by evaporation under reduced pressure. The solid was collected with water, then filtered and washed with small amounts of acetone, ethanol and chloroform. Dark blue solid, yield 36%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3400, 3056, 1607, 1577, 1508, 1467, 1431, 1391, 1339, 1268, 1170, 1113, 997, 835, 810, 798, 753. ^{1}H NMR (MeOD, ppm): 8.86 (s, 8H, H$^{\beta}$), 8.35 (d, *J*= 8.36 Hz, 2H, H^4), 8.00 (d, *J*= 8.4 Hz, 8H, H$^{3',5'}$), 7.56 (d, *J*= 8.46 Hz, 2H, H^3), 7.41 (t, *J*= 8.02 Hz, 2H, H^6), 7.19 (d, *J*= 8.46 Hz, 10 H, H$^{2',6',5 \text{ or } 7}$), 7,02 (d, *J*= 7.07 Hz, 2 H, H$^{5 \text{ or } 7}$), 3.09 (s, 6H, -*CH*$_3$). Anal. Calcd. for $C_{64}H_{47}N_6O_8GaZn$: C 66.08; H 4.07; N 7.22%. Found: C 66.57; H 3.97; N 7.43%.

Synthesis of ***ZnTPP(OH)$_2$(OGaQ′$_2$)$_2$·2H$_2$O***

The product was obtained following the synthetic protocol described for the previous compound but with **ZnTPP(OH)$_4$**:Ga:HQ′ in 1:2:4 molar ratio. Dark blue solid, yield 57%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3435, 1609, 1577, 1507, 1467, 1431, 1384, 1339, 1269, 1169, 1113, 997, 835, 810, 798, 753. Anal. Calcd. for $C_{84}H_{62}N_8O_{10}Ga_2Zn$: C 65.16; H 4.04; N 7.24%. Found: C 63.95; H 3.95; N 7.31%.

Synthesis of ***ZnTPP(OH)(OGaQ′$_2$)$_3$·2H$_2$O***

The product was obtained following the synthetic protocol described for the previous compound but with **ZnTPP(OH)$_4$**:Ga:HQ′ in 1:3:6 molar ratio. Dark blue solid, yield 30%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3391, 1609, 1576, 1507, 1466,

1431, 1340, 1269, 1169, 1113, 997, 835, 810, 797, 753. Anal. Calcd. for $C_{104}H_{77}N_{10}O_{14}Ga_3Zn$: C 63.56; H 3.95; N 7.13%. Found: C 60.81; H 3.87; N 6.89%. Because of the poor solubility ^{1}H NMR spectra were not collected.

Synthesis of ***ZnTPP(OGaQ′$_2$)$_4$·2H$_2$O***

The synthesis followed the procedure described in the previous compounds but with **ZnTPP(OH)$_4$**:Ga:HQ′ in 1:4:8 molar ratio. Dark blue solid, yield 20%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3051 (-*CH*$_3$), 1596, 1574, 1507, 1463, 1431, 1384, 1340, 1321, 1304, 1279, 1171, 882, 749, 642, 521. ^{1}H NMR (MeOD, ppm): 8.86 (s, 8H, H$^{\beta}$), 8.42 (d, *J*= 8.5 Hz, 8H, H^4), 7.99 (d, *J*= 8.11 Hz, 8H, H$^{b,b'}$), 7.62 (d, *J*= 8.11 Hz, 8H, H^3), 7.53 (t, *J*= 8.84 Hz, 8H, H^6), 7.25 (d, *J*= 8.11 Hz, 8H, H$^{5 \text{ or } 7}$), 7,17 (d, *J*= 8.11 Hz, 8H, H$^{a,a'}$), 7.84 (d, *J*= 7.73 Hz, 8H, H$^{5 \text{ or } 7}$), 3.18 (s, 24H, -*CH*$_3$). Anal. Calcd. for $C_{124}H_{92}N_{12}O_{14}Ga_4Zn$: C 64.24; H 4.00; N 7.25%. Found: C 63.99; H 4.17; N 7.68%.

Synthesis of ***ClGaTPP(OGaQ′$_2$)$_4$·2H$_2$O***

H$_2$TPP(OH)$_4$ (0.101 g, 0.130 mmol) was activated with sodium hydroxyde (0.0208 g, 0.521 mmol) in ethanol (20 mL). After 75 minutes an ethanol solution gallium(III) nitrate hydrate (0.147 g, 0.7651 mmol, 5 mL) was slowly added. The mixture was allowed to stir for 30 minutes. Successively a solution of 2-methyl-8-hydroxyquinoline (0.165 g, 1.04 mmol) and ammonium acetate (0.109 g, 1.04 mmol) in ethanol was slowly dropped to the reaction mixture. After 16 h reflux a dark violet solid was observed. A catalytic amount of LiCl was added. The reaction mixture was allowed to stir at ambient temperature for 20 h. The solid was collected by filtration and washed with water, ethanol and chloroform to obtain a dark violet solid. Yield 65%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3049 (-*CH*$_3$), 2921, 2851, 1600, 1576, 1507, 1467, 1431, 1342, 1269, 1169, 1114, 834, 803, 753, 646. Anal. Calcd. for $C_{124}H_{92}N_{12}O_{14}Ga_5Cl$: C 62.44; H 3.88; N 7.04%. Found: C 66.19; H 4.40; N 6.22%. Because of the poor solubility ^{1}H NMR data were not collected.

9.4.1 Preparation of ***ZnTPP(OGaQ′$_2$)$_4$·2H$_2$O*** *with different synthetic procedure*

Synthesis of ***H$_2$TPP(OGaQ′$_2$)$_4$·2H$_2$O***

To an aqueous solution of gallium(III) nitrate hydrate (0.127 g, 0.565 mmol, 8 mL) was added an ethanol solution (10 mL) of **H$_2$TPP(OH)$_4$** (0.110 g, 0.141 mmol) activated with sodium hydroxyde (0.022 g, 0.565 mmol). After 15 minutes an ethanol (3 mL) mixture of 2-methyl-8-hydroxyquinoline (0.180 g, 1.13 mmol) and ammonium acetate (0.087 g, 1.13 mmol, 7 mL) was slowly dropped to the reaction mixture, so after a reflux of 5h, the reaction mixture was allowed to stir at ambient temperature for 20 h. Therefore the mixture was dried by evaporation under reduced pressure. The solid was collected with water, then filtered and washed with acetone and chloroform to obtain a purple solid. Dark purple solid, yield 40%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3435 (*NH*), 3049 (*-CH$_3$*), 2920, 2851, 1600, 1576, 1507, 1467, 1431, 1342, 1269, 1169, 1114, 834, 753. Anal. Calcd. for $C_{124}H_{94}N_{12}O_{14}Ga_4$: C 66.05; H 4.20; N 7.45%. Found: C 65.90; H 4.04; N 7.18%. Because of the poor solubility ^{1}H NMR data were not collected.

Synthesis of ***ZnTPP(OGaQ′$_2$)$_4$·2H$_2$O***

To a methanol (10 mL) suspension of **H$_2$TPP(OGaQ′$_2$)$_4$·2H$_2$O** (0.059 g, 0.026 mmol) was slowly dropped a methanol solution (5 mL) of zinc acetate dihydrate (0.0064 g, 0.03 mmol) (1:1.1 molar ratio). The dark purple suspension was stirred at ambient temperature for 24 h then filtered and washed with methanol and acetone. The obtained mater liquor was evaporated under reduced pressure. Consequently the solid was collected with water and washed with small amounts of diethyl ether to give dark blue-violet solid. Yield 50%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3050 (*-CH$_3$*), 1609, 1576, 1507, 1465, 1431, 1339, 1270, 1169, 1113, 997, 835, 753. Anal. Calcd. for $C_{124}H_{94}N_{12}O_{14}Ga_4Zn$: C 64.24; H 4.00; N

7.26%. Found: C 68.10; H 4.09; N 7.54%. Because of the poor solubility ^{1}H NMR data were not collected.

9.5 Preparation of $Q'_2GaL'^n$

Gallium compounds series in which the monodentate or bidentate ligand is a carboxylic acids derivatives were synthesised with a procedure analogue to those described for Q'_2GaL^n compounds. Only $Q'_2GaOOCC_6H_4O(CH_2)_7CH_3$ compound was obtained with a different synthetic pathway.

Synthesis of $Q'_2GaOOCC_6H_4NO_2$.

Yellow-greenish solid, yield 55%. M. p. : 267-270 °C. IR (KBr, cm^{-1}): 3051 (-CH_3), 1734 (C=O), 1660, 1603, 1577, 1527, 1508, 1467, 1453, 1431, 1392, 1340, 1322, 1272, 1115, 1014, 834, 793, 755, 724, 647, 528. ^{1}H NMR (CD_3Cl, ppm): 8.28 (d, *J*= 8.49 Hz, 2H, H^4), 8.14 (d, *J*= 8.49 Hz, 2H, $H^{b,b'}$), 8.08 (d, *J*= 8.49 Hz 2H, $H^{a',a'}$), 7.50 (t, *J*= 8.49 Hz, 2H, H^6), 7.43 (d, *J*= 8.16 Hz, 2H, H^3), 7.20 (t, *J*= 7.19 Hz, 4H, $H^{5,7}$), 3.14 (s, 6H, -CH_3). Anal. Calcd. for $C_{27}H_{20}N_3O_6Ga$: C 58.73; H 3.65; N 7.61%. Found: C 57.93; H 3.54; N 7.59%.

Synthesis of $Q'_2GaOOCC_6H_4O(CH_2)_5CH_3$.

Light green solid, yield 42%. M. p.: 197-200 °C. IR (KBr, cm^{-1}): 3045 (-CH_3), 2950-2856 (aliphatic-CH_2-), 1655 (*C=O*), 1606, 1577, 1508, 1431, 1390, 1341, 1271, 1247, 1170, 1114, 836, 780, 753, 667. ^{1}H NMR (CD_3Cl, ppm): 8.22 (d, *J*= 8.38 Hz, 2H, H^4), 7.87 (d, *J*= 8.72 Hz, 2H, $H^{a,a'}$), 7.46 (t, *J*= 8.04 Hz, 2H, H^6), 7.37 (d, *J*= 8.39 Hz, 2H, H^3), 7.16 (d, *J*= 8.04 Hz, 4H, $H^{5\text{ or }7}$), 6.76 (d, *J*= 8.72 Hz, 2H, $H^{b,b'}$), 3.91 (t, *J*= 6.38 Hz, 2H, -O$CH_2$$CH_2$-), 3.04 (s, 6H, -$CH_3$), 1.78 (q, 2H, -OCH$_2$$CH_2$-), 1.32 (m, 4H, -$CH_2CH_2$$CH_2CH_3$), 1.29 (m, 2H, -$CH_2$$CH_3$), 0.87 (t, *J*= 6.38 Hz, 3H, -CH_2CH_3).

Anal. Calcd. for $C_{33}H_{33}N_2O_5Ga$: C 65.26; H 5.48; N 4.61%. Found: C 65.66; H 5.29; N 4.37%.

Synthesis of ***Q'$_2$GaOOCC$_6$H$_4$O(CH$_2$)$_7$CH$_3$***

Q'$_2$GaOC$_6$H$_5$ complex (0.154 g, 0.321 mmol) was dissolved in 10 mL of chloroform, then an ethanol solution (50 mL) of *p*-octyloxybenzoic acid (0.803 g, 3.21 mmol), activated with NaOH (0.128 g, 3.21 mmol) was slowly added. To obtain a reaction mixture with **Q'$_2$GaOC$_6$H$_5$**:sodium *p*-octyloxybenzoate in 1:10 molar ratio then the reaction mixture was allowed to stir for 72 hours at room temperature. The suspension was filtered, washed with water, ethanol and diethyl ether. The obtained powder was recrystallized from chloroform/diethyl ether. Green solid, yield 30%. M. p.: 185–187°C. IR (KBr, cm^{-1}): 3057 (-*CH$_3$*), 2924-2854 (aliphatic -*CH$_2$*-), 1642 (*C=O*), 1605, 1576, 1508, 1467, 1452, 1430, 1343, 1271, 1248, 1170, 1115, 834, 782, 754, 666, 526 . ^{1}H NMR (CD_3Cl, ppm): 8.23 (d, *J*= 8.44 Hz, 2H, H^4), 7.87(d, *J*= 8.7 Hz, 2H, H$^{a,a'}$), 7.46 (t, *J*= 8 Hz, 2H, H^6), 7.38 (d, *J*= 8.4 Hz, 2H, H^3), 7.16 (d, *J*= 7.43 Hz, 4H, H$^{b,b',5 \text{ or } 7}$), 6.76 (d, *J*= 8.9 Hz; 2H, H$^{7 \text{ or } 5}$), 3.9 (t, *J*= 6.58 Hz, 2H, -O*CH$_2$*CH$_2$-), 3 (s, 6H, -*CH$_3$*), 1.73 (q, *J*= 6.65 Hz, 2H, -OCH$_2$*CH$_2$*-), 1.39 (q, 2H, -OCH$_2$CH$_2$*CH$_2$*CH$_2$-), 1.23 (m, 4H, -CH$_2$*CH$_2$CH$_2$*CH$_3$), 0.86 (t, *J*= 6.41 Hz, 3H, -CH$_2$*CH$_3$*). Anal. Calcd. for $C_{27}H_{20}N_3O_6Ga$: C 66.16; H 5.87; N 4.41%. Found: C 66.22; H 5.32; N 5.32%.

Synthesis of ***HOOC$_6$H$_2$(OC$_6$H$_{13}$)$_3$***

The methyl 3,4,5-trihydroxybenzoate, was solved under stirring in cyclohexanone (1 g, 5.43 mmol, 50 mL), then potassium carbonate (3.827 g, 27.7 mmol) was added to the solution, methyl ester:K_2CO_3 in 1:5.1 molar ratio. An excess of the liquid 1-bromo-hexane, $C_6H_{13}Br$ (2.36 mL, 16.8 mmol, 1:3.1 molar ratio) was slowly dropped in the reaction mixture. So a catalytic amount of potassium iodide was added. The brown reaction mixture was allowed to stir

for 72 h at 150°C. The reaction mixture was filtered to separate the salts in excess so the cyclohexanone of the mater liquor was removed azeotropically with water by evaporation under reduced pressure four times. The obtained solid was recrystallised from chloroform/methanol mixture for two times to give a white product that was suspended in ethanol and stirred under reflux for 24 h then an aqueous solution of potassium hydroxide, was added (in 1:2 molar ratio). After 24 hours under reflux the desired compound was precipitated by adding an acidic aqueous solution (10 mL) of HCl:H_2O in 2:10 volume ratio. Suddenly a white product was precipitated, then filtered, washed with water ethanol and petroleum ether. Final the purification was obtained by precipitation at -15 °C two times, from a solution of the white product in petroleum ether. Yield 50%. M. p.: 157- 160°C. IR (KBr, cm^{-1}): 2931-2859 (aliphatic -CH_2-), 2638, 1687 (C=O), 1586, 1502, 1431, 1381, 1330, 1272, 1231, 1113, 997, 923, 863, 767, 729,. ^{1}H NMR (CD_3Cl, ppm): 7.32 (s, 2H, $H^{a,a'}$), 4 (m, 6H, -O$CH_2$$CH_2$-), 1.8 (m, 6H, -$OCH_2CH_2$-), 1.5 (m, 6H, -$OCH_2CH_2CH_2$-), 1.31 (m, 12H, (-$CH_2CH_2CH_3$), 0.92 (m, 9H, -$CH_2CH_3$). Anal. Calcd. for $C_{26}H_{44}O_5$: C 71.51; H 10.15%. Found: C 70.50; H 9.17%.

Synthesis of ***$HOOC_6H_2(OC_{14}H_{29})_3$***

The synthesis was performed following the synthetic protocol described for ***$HOOC_6H_2(OC_6H_{13})_3$***. White solid, yield 60%. DSC: 74 °C liquid, interval of mesomorphysme in the cooling run at 45°-Tc. IR (KBr, cm^{-1}): 2919-2849 (aliphatic -CH_2-), 2640, 1682 (C=O), 1587, 1505, 1468, 1431, 1381, 1334, 1276, 1228, 1122, 989, 969, 863, 767, 719. ^{1}H NMR (CD_3Cl, ppm): 7.32 (s, 2H, $H^{a,a'}$), 4.03 (m, 6H, -O$CH_2$$CH_2$-), 1.8 (m, 6H, -$OCH_2CH_2$-), 1.5 (m, 6H, -$OCH_2CH_2CH_2$-), 1.31 (m, 60H, (-$CH_2CH_2CH_3$), 0.9 (m, 9H, -$CH_2CH_3$). Anal. Calcd. for $C_{25}H_{43}O_5$: C 81.45; H 12.55%. Found: C 80.21; H 12.01%.

Synthesis of ***Q′$_2$GaOOCC$_6$H$_2$(OC$_6$H$_{13}$)$_3$***

The **HOOC$_6$H$_2$(OC$_6$H$_{13}$)$_3$** ligand (0.120 g, 2,84 mmol) was suspended in ethanol (10 mL) with potassium hydroxide (0.032 g, 5.68 mmol) in 1:2 molar ratio, small amounts of diethyl ether were added to the suspension, then the reaction mixture was allowed to stir for 24 hours at room temperature. The mixture with the activated ligand was slowly added to an ethanolic solution (5 mL) of gallium(III) nitrate hydrate (0.073 g, 2,84 mmol) under energetic stirring, after 15 minutes an ethanolic solution (5 mL) of 2-methyl-8-hydroxyquinoline (0.090 g, 5.68 mmol) was slowly added to the reaction mixture. That suspension was refluxed for six hours then was allowed to stir overnight. The reaction mixture was dried by evaporation under reduced pressure to give a solid again dissolved in chloroform to be filtered on Celite powder. The obtained chloroform solution was dried by evaporation under reduced pressure. The green solid was dissolved in small amounts of chloroform then a small quantity of methanol was added to induce crystallization at -15 °C. A green microcrystalline precipitates was obtained. The green solid was washed with small amounts of very cold diethyl ether and acetone to obtain the desired compound. Green solid, yield 30%. M. p.: 160–164°C. IR (KBr, cm^{-1}): 3064 (-*CH$_3$*), 2931-2859 (aliphatic –*CH$_2$*–), 1649 (*C=O*), 1586, 1507, 1452, 1431, 1389, 1342, 1270, 1227, 1115, 837, 780, 754, 651, 573, 527. ^{1}H NMR (CD$_3$Cl, ppm): 8.29 (d, *J*= 8.54 Hz, 2H, H^4), 7.47(d, *J*= 7.94 Hz, 2H, H^6), 7.40 (t, *J*= 8.55 Hz, 2H, H^3), 7.17 (m, 6H, H$^{a,a',7,5}$), 3.92 (t, *J*= 6.72 Hz, 2H, -O*CH$_2$*CH$_2$-, central aliphatic tail), 3.87 (t, *J*= 6.71 Hz, 4H, -O*CH$_2$*CH$_2$-, lateral aliphatic tails), 3.06 (s, 6H, -*CH$_3$*), 1.72 (m, 6H, -OCH$_2$*CH$_2$*-), 1.41 (m, 6H, -OCH$_2$CH$_2$*CH$_2$*-), 1.31 (m, 12H, -*CH$_2$CH$_2$*CH$_3$, 0.85 (t, *J*= 4.88 Hz, 9H, -CH$_2$*CH$_3$*). Anal. Calcd. for C$_{45}$H$_{57}$N$_2$O$_7$Ga: C 66.91; H 7.11; N 3.46%. Found: C 66.32; H 6.69; N 3.04%.

Synthesis of ***Q′$_2$GaOOCC$_6$H$_2$(OC$_{14}$H$_{29}$)$_3$***

The synthesis was performed as illustrated for the previous compound. Green solid, yield 12%. DSC: heating run 67.5 °C (ΔH= 14.4 J/g); 143.9 °C (ΔH= 16.5 J/g); cooling run 141.5 °C (ΔH= -15.8 J/g); 46.1°C (ΔH= -15.9 J/g). IR (KBr, cm^{-1}): 3060 (-*CH*$_3$), 2917-2851 (aliphatic –*CH*$_2$–), 1649 (*C*=*O*), 1579, 1507, 1468, 1427, 1381, 1341, 1271, 1218, 1115, 836, 754, 719, 651, 528. ^{1}H NMR (CD$_3$Cl, ppm): 8.25 (d, *J*= 8.55 Hz, 2H, H^4), 7.47(d, *J*= 7.94 Hz, 2H, H^6), 7.40 (t, *J*= 8.55 Hz, 2H, H^3), 7.17 (m, 6H, H$^{a,a',7,5}$), 3.92 (d, *J*= 6.72 Hz, 2H, -O*CH*$_2$CH$_2$-, central aliphatic tail), 3.86 (t, *J*= 6.72 Hz, 4H, -O*CH*$_2$CH$_2$-, lateral aliphatic tails), 3.06 (s, 6H, -*CH*$_3$), 1.72 (m, 6H, -OCH$_2$*CH*$_2$-), 1.42 (m, 6H, -OCH$_2$CH$_2$*CH*$_2$-), 1.22 (m, 60H, -(*CH*$_2$)$_{10}$CH$_3$), 0.88 (t, *J*= 6.72 Hz, 9H, -CH$_2$*CH*$_3$). Anal. Calcd. for C$_{69}$H$_{105}$N$_2$O$_7$Ga: C 72.42; H 9.25; N 2.45%. Found: C 72.39; H 9.01; N 3.32%.

Synthesis of ***Q′$_2$GaOOCC$_6$H$_4$COOGaQ′$_2$.***

The synthetic procedure adopted was the same mentioned in the previous paragraphs with Ga:HL′^{n}:HQ′ in 2:1:4 molar ratio. The spectroscopic characterization of the collected green solid revealed the presence of *GaQ′*$_3$ and unreacted ligand as impurities.

Synthesis of ***Q′$_2$GaOOCC≡CCOOGaQ′$_2$.***

The synthesis of this compound is reported in literature[12] with a different procedure. In the present study the complex was obtained following the procedure previously illustrated with Ga:HL′^{n}:HQ′ in 2:1:4 molar ratio. Yellow solid, yield 32%. M. p.: 337-340 °C. IR (KBr, cm $^{-1}$): 3047 (-*CH*$_3$), 1658 (C=O), 1577, 1508, 1467, 1431, 1432, 1391, 1320, 1272, 1136, 1115, 836, 755, 649, 528. Anal. Calcd. for C$_{40}$H$_{32}$N$_4$O$_6$Ga$_2$: C 62.01; H 3.78; N 6.57%. Found: C 61.11; H 3.78; N 6.75%. ^{1}H NMR spectra were not registered because of the poor solubility of this compound.

Synthesis of ***Q′$_2$GaOOC(CH$_2$)$_{12}$COOGaQ′$_2$.***

Light green solid, yield 40%. M. p.: 169-175 °C. IR (KBr, cm $^{-1}$): 3069 (-CH_3), 2925-2852 (–CH_2– aliphatic), 1665 (C=O), 1577, 1508, 1466, 1431, 1380, 1342, 1272, 1114, 836, 754, 651, 528. ^{1}H NMR (CD_3Cl, ppm): 8.23 (d, *J*= 8.14 Hz, 4H, H^4), 7.42 (t, *J*= 8.81 Hz, 8H, $H^{6,3}$), 7.13 (t, *J*= 7.83 Hz, 8H, $H^{5,7}$), 3.05 (s, 12H, -CH_3), 2.14 (m, 4H, -OOC$CH_2$$CH_2$-), 1.43 (m, 4H, -OOC$CH_2$$CH_2$$CH_2$-), 1.10 (s, 16H, -$(CH_2)_8$-). Anal. Calcd. for $C_{54}H_{56}N_4O_8Ga_2$: C 63.06; H 5.49; N 5.45%. Found: C 62.29; H 5.31; N 6.11%.

9.6 Preparation of polymetallic gallium complexes with H_2TPP(COOH)$_4$

Synthesis of ***ZnTPP(COOH)$_4$·2H$_2$O***

The synthesis was performed in the same manner described for the preparation of **ZnTPP(OH)$_4$·2H$_2$O** compound. Dark violet solid, yield 79%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3125, 2889, 2814, 1697 (C=O), 1606, 1544, 1408, 1274, 1175, 1102, 1073, 997, 960, 865, 797, 767, 719. Anal. Calcd. for $C_{48}H_{32}O_{10}N_4Zn$: C 64.29; H 3.62; N 6.29%. Found: C 62.61; H 3.75; N 6.51%. Because of the poor solubility wasn't possible to register ^{1}H NMR spectra.

Synthesis of ***ZnTPP(COOGaQ′$_2$)$_4$·2H$_2$O***

This complex was prepared following the procedure illustrated for the synthesis of ***ZnTPP(OGaQ′$_2$)$_4$·2H$_2$O***. Brown solid, yield 63%. M. p.: >350 °C. IR (KBr, cm^{-1}): 3052 (-CH_3), 1715 (C=O), 1605, 1576, 1508, 1428, 1341, 1273, 1178, 1114, 998, 871, 835, 797, 774, 755, 720, 650. Anal. Calcd. for $C_{128}H_{92}O_{18}N_{12}Ga_4Zn$: C 63.21; H 3.82; N 6.92%. Found: C 58.10; H 3.79; N 7.21%. ^{1}H NMR data collection wasn't permitted because of the poor solubility.

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