ELECTRONIC SUPPLEMENTARY INFORMATION

Tuning of bandgaps and emission properties of light-emitting diode materials through homogeneous alloying in molecular crystals

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S1. Experimental details

All the reagents are obtained from Sigma-Aldrich and were used as received without further purification. Gaq_3, Inq_3 and Crq_3 was synthesized by the reaction of M^{3+} salts with hydroxyquinoline which is further neutralized using potassium acetate. The precipitate obtained is vacuum dried.

$Ga Cl_3 + 3aqHQ \rightarrow Ga \quad q_3$ (yellow precipitate)

$Cr(NO_3)_3 + 3aqHQ \rightarrow Cr \quad q_3$ (brown precipitate)

$In Cl_3 + 3aqHQ \rightarrow In \quad q_3$ (yellow precipitate)

Crystals of pure Mq_3 and their alloys were obtained by two zone sublimation deposition method. In order to obtain single crystals of alloys, the mixtures of Mq_3 compounds of various composition ratios were taken in a glass boat. This mixture was placed in the hot end of a two-zone sublimation condensation apparatus with an Argon gas flow. The zones of the setup were kept at 390 °C and 100 °C and the samples were kept in the setup for ~5 hours before the temperature was lowered to room temperature. Needle like crystals were harvested from the walls of the glass tubes.

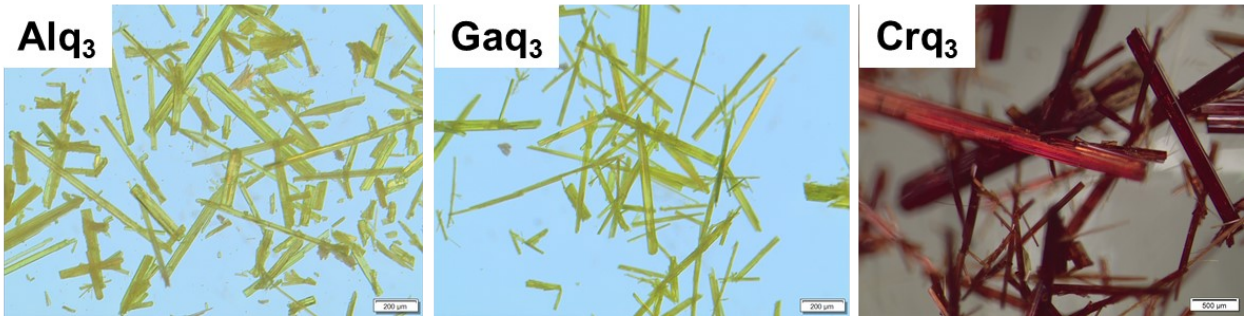

Figure S1: Optical microscopic images of the single crystals of grown by two zone vaporization condensation method in the study.

S2. Crystallographic data collection and structure refinement

The crystals were cooled to 100 K with a liquid nitrogen stream using an Oxford Instruments Cryojet-XL nitrogen gas-stream cooling device. X-ray diffraction data were collected on Agilent Supernova diffractometer using MoKα radiation (wavelength 0.71073 Å, Table S1-S6). The scan width was chosen to be 1° per frame and the crystal to detector distance was fixed at 53 mm (for MoKα data) during the data collection. Cell refinement, crystal face indexing, data integration and reduction were carried out using CrysAlisPro.1 Crystal structures were solved by direct methods and refined using SHELXS v.2013.12 accessed by OLEX2 package [1-3]. The hydrogen atoms were fixed to standard X-ray bond lengths and refined using a riding atom model.

Modeling molecular alloy crystal structures: The occupancies of central metal atoms in the binary alloy crystals were refined using PART command, using an occupancy free variable (FVAR). However, the occupancy values and the convergence of refinements depend on other variables such as atomic displacement parameters (ADPs) and the positions of the metal atoms. Two different refinement strategies were tested to model the binary alloy structures:

(i) The positions of the central metal atoms were refined freely, whereas their ADPs were constrained to be the same using EADP. The occupancies were refined with the help of an occupancy free variable (FVAR) using PART command.

(ii) The positions and atomic displacement parameters (ADPs) of the metal atoms occupying very close positions were constrained to be identical using the constraints EXYZ and EADP. The occupancies were refined with the help of an occupancy free variable (FVAR) using PART command.

After testing these two refinement methods, it was found that allowing the positions to be refined freely resulted in unreasonable ADPs or convergence issues. Hence, we adopted the strategy (ii) to model all the binary alloy structures in this study.

Modeling of ternary and quaternary alloy crystals: For ternary and quaternary alloy crystals, the occupancies of three/ four metal atoms occupying very close positions were found to be difficult to model. Attempts to refine the occupancies using SUMP restraint (the linear restraint that allows more than two atoms to be assigned to a particular site, with the sum of their site occupancy factors restrained to 1 resulted in unreasonable ADPs, in addition to some convergence issues. Hence to model these structures, the occupancies of central metal atoms were fixed to the values from the composition information obtained from energy-dispersive X-ray spectra (EDX) measured on the same single crystals. As in case of the binary alloy structures, the positions and atomic displacement parameters (ADPs) of the metal atoms occupying very close positions were constrained to be identical using the constraints EXYZ and EADP.

The crystallographic information files have been deposited in the CCDC database with CCDC deposition numbers 2073957-2073962, 2074033-2074036, 2074042-2074044, 2074050-2074051, 2074080-2074081.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst*. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). *Acta Cryst. A*, 71, 59-75.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). *Acta Cryst. A*, 71, 59-75.

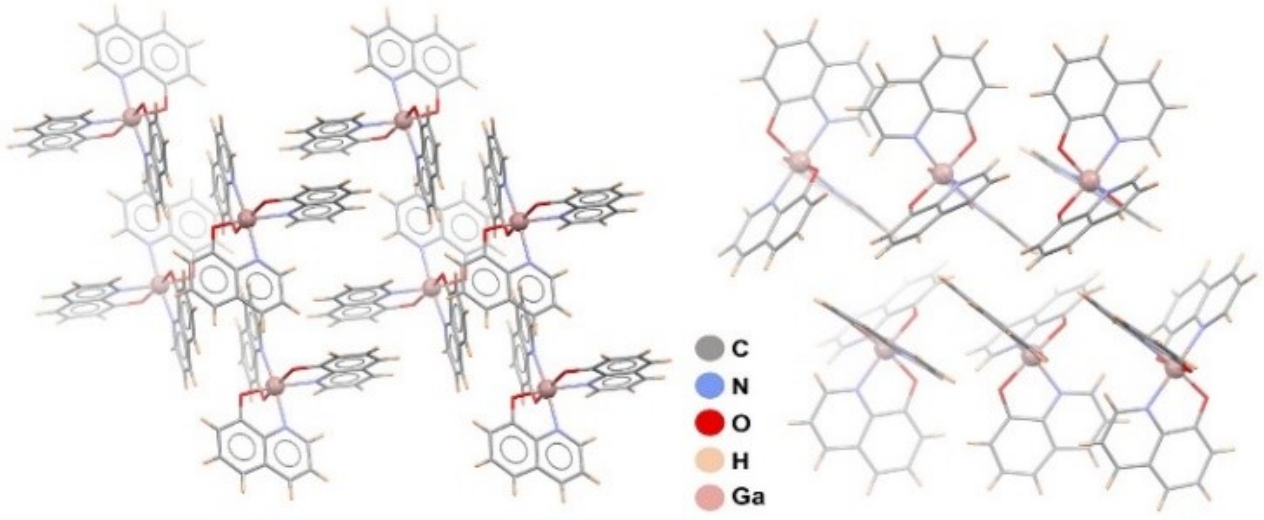

Figure S2: Crystal packing of mer-β Gaq_3 (left) in comparison with the new polymorph mer- ε Gaq_3 (right).

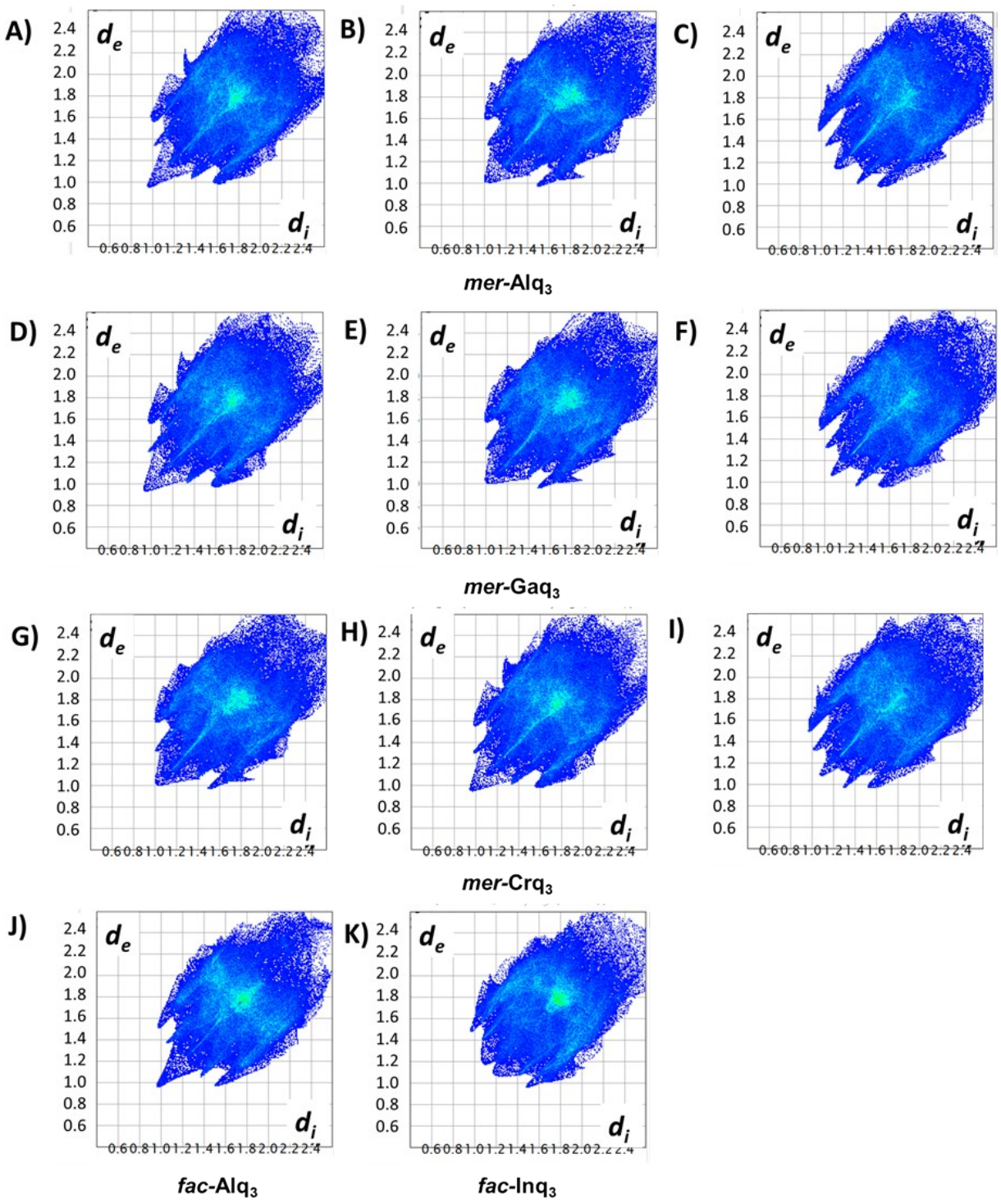

Figure S3: Hirshfeld fingerprint plots for the crystal structures of Mq_3 compounds discussed in this study. Note that *mer* forms of Mq_3 have three molecules in the asymmetric unit.

Table S1. Percentage contributions of different intermolecular atom…atom contacts estimated by Hirshfeld fingerprint analysis for the crystal structures of Mq_3 compounds discussed in this study.

	% C…C	% C…H	% O…H	% H…H	Molecular volume in Å^3 (Hirshfeld surface)
Mer-Alq_3 molecule 1	6.5	34.5	10.3	46.2	535.17
molecule 2	5.1	33.1	10.3	48.5	537.52
molecule 3	6.9	33.0	10.3	46.7	548.70
Mer-Gaq_3 molecule 1	5.4	33.8	11.1	46.5	529.35
molecule 2	7.1	34.0	10.9	44.5	526.76
molecule 3	5.4	35.7	11.2	43.7	540.41
Mer-Crq_3 molecule 1	7.0	33.5	10.9	45.2	530.03
molecule 2	5.3	33.3	11.2	47.1	531.52
molecule 3	5.4	35.0	33.3	44.7	543.54
Fac-Alq_3	5.1	33.2	12.6	46.1	528.80
Fac-Inq_3	7.4	32.7	11.6	45.2	526.23

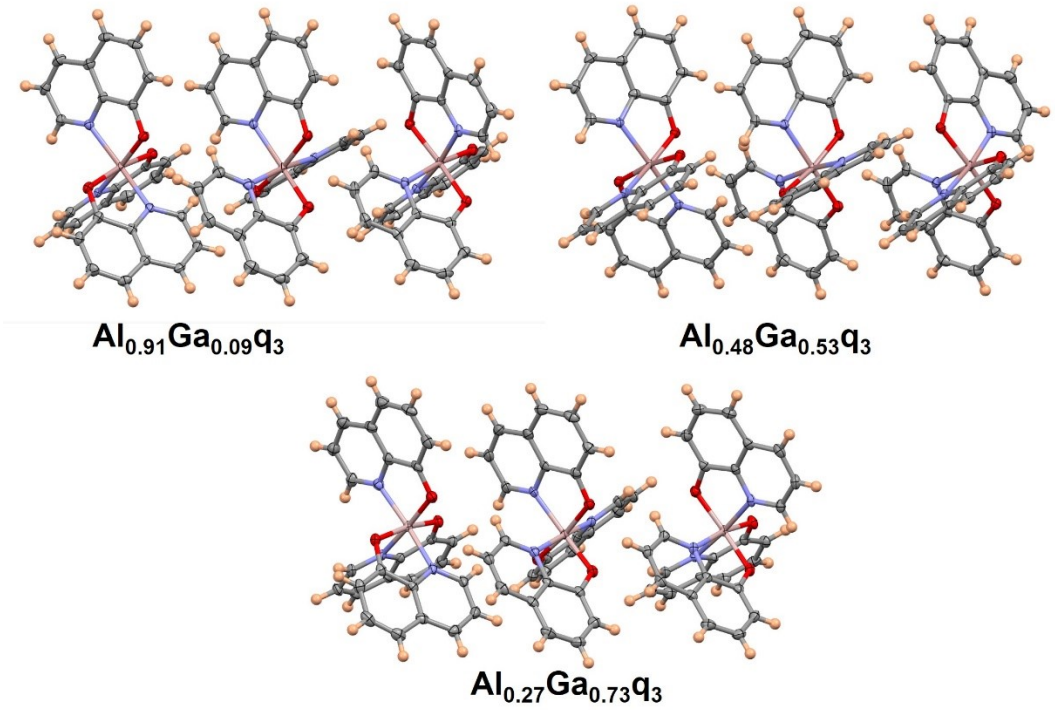

Figure S4: Asymmetric units of Alq_3-Gaq_3 molecular alloys with thermal ellipsoids at the 50% probability level.

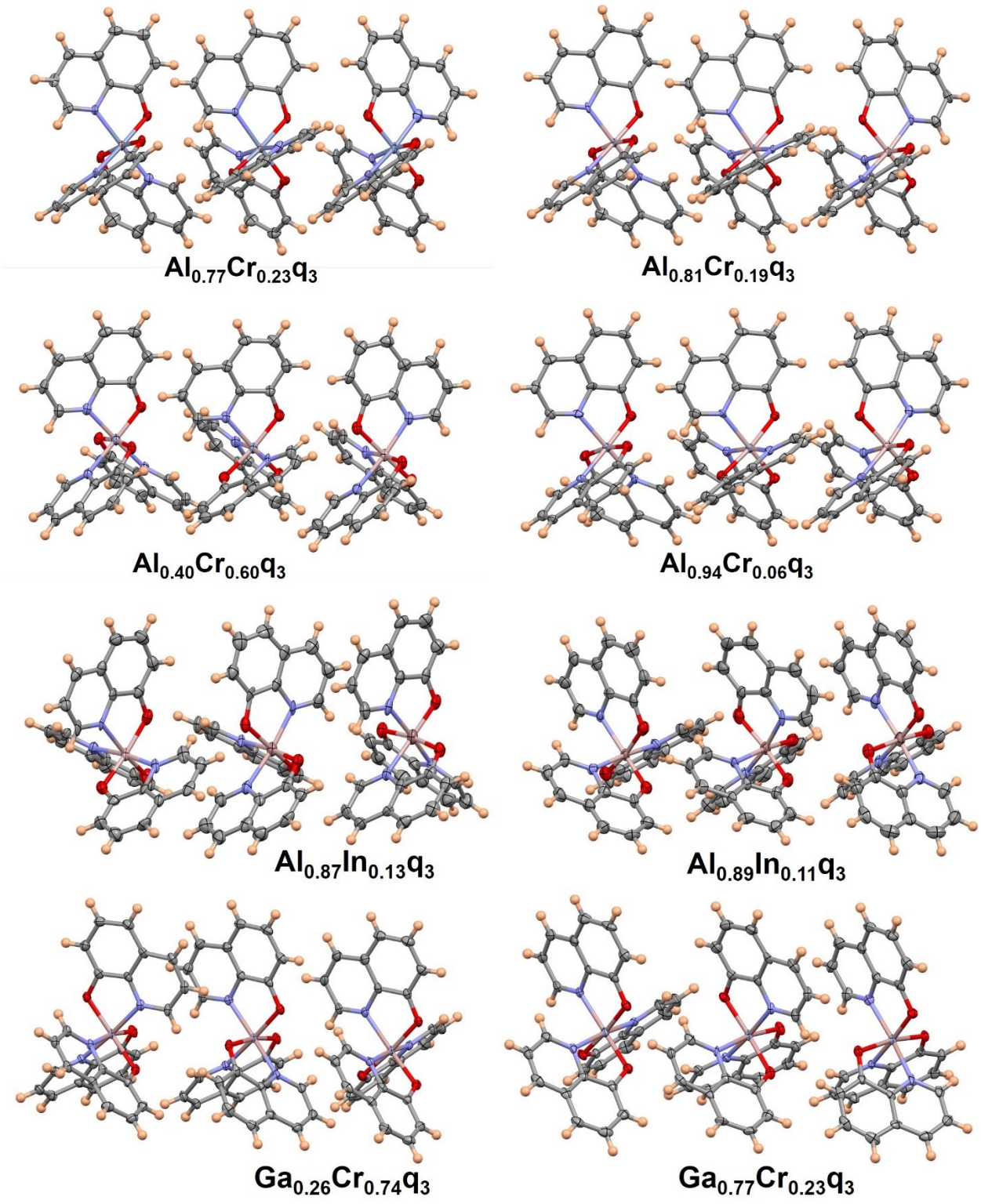

Figure S5: Asymmetric units of Alq_3-Crq_3, Alq_3-Inq_3 and Gaq_3-Crq_3 molecular alloys with thermal ellipsoids at the 50% probability level.

Table S2. Crystal data and structure refinement for the Mq_3 series of compounds

Stoichiometric ratio used for alloy crystallization	Alq_3	Gaq_3	Crq_3
Empirical formula	$C_{12}H_{12}N_3O_3Al$	$C_{27}H_{18}GaN_3O_3$	$C_{27}H_{18}CrN_3O_3$
Formula weight	306.30	502.16	484.44
Temperature/K	100(1)	100.01(10)	100(1)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.3849(5)	13.3947(4)	13.4826(9)
b/Å	15.5506(6)	15.5684(6)	15.7428(14)
c/Å	18.6315(4)	18.6801(5)	18.5238(7)
α/°	95.044(3)	94.969(3)	94.860(5)
β/°	109.792(3)	109.651(3)	109.436(5)
γ/°	114.085(4)	113.851(3)	114.310(8)
Volume/Å^3	3213.8(2)	3241.3(2)	3264.5(4)
Z	9	6	6
ρ_{calc}g/cm^3	1.4242	1.544	1.478
μ/mm^{-1}	0.132	1.310	0.562
F(000)	1429.0	1536.0	1494.0
Crystal size/mm^3	0.25 × 0.14 × 0.1	0.19 × 0.11 × 0.06	0.22 × 0.11 × 0.06
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.98 to 52	6.606 to 52.998	3.436 to 51.996
Index ranges	-16 ≤ h ≤ 15, -18 ≤ k ≤ 18, -23 ≤ l ≤ 22	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -23 ≤ l ≤ 21	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22
Reflections collected	46405	53536	40042
Independent reflections	12017 [R_{int} = 0.0973, R_{sigma} = 0.1118]	13414 [R_{int} = 0.0532, R_{sigma} = 0.0587]	12844 [R_{int} = 0.1250, R_{sigma} = 0.1963]
Data/restraints/parameters	12017/0/919	13414/0/769	12844/0/919
Goodness-of-fit on F^2	1.071	1.064	0.936
Final R indexes [I>=2σ (I)]	R_1 = 0.0661, wR_2 = 0.1555	R_1 = 0.0536, wR_2 = 0.1309	R_1 = 0.0930, wR_2 = 0.1814
Final R indexes [all data]	R_1 = 0.1225, wR_2 = 0.1930	R_1 = 0.0781, wR_2 = 0.1431	R_1 = 0.2161, wR_2 = 0.2276
Largest diff. peak/hole / e Å^{-3}	0.72/-0.69	2.02/-0.68	1.35/-0.45

Inq_3 single crystals obtained were too weakly diffracting to obtain full data for structure solution. However, the cell parameters were obtained from a SC-XRD dataset, which confirmed that Inq3 crystallizes in fac-δ form (Z=2) with the following cell parameters:

a = 6.196(7) Å, *b* = 13.44(2) Å, *c* = 14.73(3) Å, α =65.65(17)°, β =88.03(12)°, γ=83.53(11)°, Volume= 1110(3) Å^3

Table S3. Crystal data and structure refinement for the Alq_3-Gaq_3 binary alloys

Stoichiometric ratio used for alloy crystallization	Alq3-Gaq3(9:1)	Alq3-Gaq3(1:1)	Alq3-Gaq3(1:3)
Empirical formula	$C_{27}H_{18}Al_{0.91}Ga_{0.09}N_3O_3$	$C_{27}H_{18}Al_{0.48}Ga_{0.53}N_3O_3$	$C_{27}H_{18}Al_{0.27}Ga_{0.73}N_3O_3$
Formula weight	463.21	481.88	490.70
Temperature/K	100.01(10)	100.00(10)	99.94(19)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.3967(6)	13.3851(4)	13.3810(4)
b/Å	15.5597(7)	15.5551(5)	15.5698(5)
c/Å	18.6662(5)	18.6583(5)	18.6754(4)
α/°	95.000(3)	94.960(2)	94.984(2)
β/°	109.813(3)	109.741(2)	109.719(2)
γ/°	113.987(4)	113.903(3)	113.790(3)
Volume/Å^3	3227.9(3)	3228.32(18)	3237.2(2)
Z	6	6	6
ρ_{calc}g/cm^3	1.4296	1.487	1.5101
μ/mm^{-1}	0.236	0.753	0.995
F(000)	1438.6	1485.0	1508.7
Crystal size/mm^3	0.25 × 0.1 × 0.06	0.28 × 0.12 × 0.1	0.25 × 0.14 × 0.11
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.3 to 54	6.612 to 62.008	3.3 to 54
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -24 ≤ l ≤ 23	-19 ≤ h ≤ 19, -21 ≤ k ≤ 22, -26 ≤ l ≤ 26	-16 ≤ h ≤ 17, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24
Reflections collected	42561	84947	56372
Independent reflections	13933 [R_{int} = 0.0794, R_{sigma} = 0.0959]	18704 [R_{int} = 0.0731, R_{sigma} = 0.0869]	13945 [R_{int} = 0.0639, R_{sigma} = 0.0703]
Data/restraints/parameters	13933/0/920	18704/0/812	13945/0/920
Goodness-of-fit on F^2	1.052	1.037	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0596, wR_2 = 0.1358	R_1 = 0.0556, wR_2 = 0.0971	R_1 = 0.0425, wR_2 = 0.0852
Final R indexes [all data]	R_1 = 0.0971, wR_2 = 0.1629	R_1 = 0.1098, wR_2 = 0.1193	R_1 = 0.0676, wR_2 = 0.0981
Largest diff. peak/hole / e Å^{-3}	0.75/-0.49	0.72/-0.63	0.87/-0.54
Percentage of Al	0.9118(12)	0.4751(14)	0.2687(14)
Percentage of Ga	0.0882(12)	0.5249(14)	0.7313(14)

Table S4. Crystal data and structure refinement for the Alq_3-Crq_3 binary alloys

Stoichiometric ratio used for alloy crystallization	Alq3-Crq3(95:5)	Alq3-Crq3(9:1)	Alq3-Crq3(3:1)	Alq3-Crq3(1:1)
Empirical formula	$C_{27}H_{18}Al_{0.94}Cr_{0.06}N_3O_3$	$C_{27}H_{18}Al_{0.81}Cr_{0.19}N_3O_3$	$C_{27}H_{18}Al_{0.77}Cr_{0.23}N_3O_3$	$C_{27}H_{18}Al_{0.4}Cr_{0.6}N_3O_3$
Formula weight	461.01	464.21	465.22	474.56
Temperature/K	100(1)	100.00(11)	100(1)	100.00(10)
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1	P-1
a/Å	13.4084(6)	13.4069(6)	13.4034(8)	13.4728(12)
b/Å	15.5505(9)	15.5667(9)	15.5617(12)	15.6445(19)
c/Å	18.6432(5)	18.6269(6)	18.6118(7)	18.5794(6)
α/°	95.029(4)	95.032(4)	94.972(5)	95.013(6)
β/°	109.772(3)	109.659(4)	109.711(5)	109.452(6)
γ/°	114.071(5)	114.181(5)	114.128(7)	114.370(10)
Volume/Å^3	3222.7(3)	3222.5(3)	3219.4(4)	3246.3(6)
Z	6	6	6	6
ρ_{calc}g/cm^3	1.425	1.4351	1.440	1.456
μ/mm^{-1}	0.159	0.215	0.233	0.394
F(000)	1432.0	1441.9	1443.0	1468.0
Crystal size/mm^3	0.26 × 0.13 × 0.11	0.3 × 0.27 × 0.12	0.2 × 0.08 × 0.05	0.14 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.296 to 53.994	3.3 to 54	3.452 to 51.998	6.896 to 53.996
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-17 ≤ h ≤ 16, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24	-10 ≤ h ≤ 16, -18 ≤ k ≤ 18, -22 ≤ l ≤ 14	-16 ≤ h ≤ 14, -18 ≤ k ≤ 19, -22 ≤ l ≤ 23
Reflections collected	53059	56151	20022	20588
Independent reflections	13808 [R_{int} = 0.2480, R_{sigma} = 0.2384]	13898 [R_{int} = 0.0946, R_{sigma} = 0.1292]	10587 [R_{int} = 0.0847, R_{sigma} = 0.1717]	11360 [R_{int} = 0.0538, R_{sigma} = 0.1054]
Data/restraints/parameters	13808/0/920	13898/0/920	10587/0/920	11360/0/764
Goodness-of-fit on F^2	0.911	1.052	0.908	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0862, wR_2 = 0.1788	R_1 = 0.0925, wR_2 = 0.2194	R_1 = 0.0712, wR_2 = 0.1346	R_1 = 0.1167, wR_2 = 0.2746
Final R indexes [all data]	R_1 = 0.2070, wR_2 = 0.2266	R_1 = 0.1705, wR_2 = 0.2876	R_1 = 0.1595, wR_2 = 0.1698	R_1 = 0.1599, wR_2 = 0.3000
Largest diff. peak/hole / e Å^{-3}	0.67/-0.52	1.70/-0.75	0.61/-0.33	1.71/-0.90
Percentage of Al	0.935(3)	0.809(4)	0.768(3)	0.396(7)
Percentage of Cr	0.065(3)	0.191(4)	0.232(3)	0.604(7)

Table S5. Crystal data and structure refinement for the Alq_3-Inq_3 binary alloys

Stoichiometric ratio used for alloy crystallization	Alq3-Inq3(9:1)	Alq3-Inq3(9:1)
Empirical formula	$C_{27}H_{18}Al_{0.89}In_{0.12}N_3O_3$	C27H18Al0.87In0.13N3O3
Formula weight	470.09	470.51
Temperature/K	100(1)	99.98(12)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	13.4101(13)	13.3999(10)
b/Å	15.6147(17)	15.6033(13)
c/Å	18.6245(10)	18.6507(8)
α/°	95.104(7)	95.062(5)
β/°	109.621(7)	109.708(5)
γ/°	114.045(10)	114.012(8)
Volume/Å^3	3237.0(6)	3236.1(5)
Z	6	6
ρ_{calc}g/cm^3	1.447	1.4485
μ/mm^{-1}	0.250	0.257
F(000)	1454.0	1455.6
Crystal size/mm^3	0.2 × 0.15 × 0.11	0.21 × 0.14 × 0.1
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.288 to 54	3.28 to 54
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -25 ≤ l ≤ 24
Reflections collected	40517	56377
Independent reflections	13918 [R_{int} = 0.1923, R_{sigma} = 0.3085]	13930 [Rint = 0.2247, Rsigma = 0.3270]
Data/restraints/parameters	13918/0/884	13930/0/920
Goodness-of-fit on F^2	0.899	0.987
Final R indexes [I>=2σ (I)]	R_1 = 0.1108, wR_2 = 0.2364	R1 = 0.1092, wR2 = 0.2323
Final R indexes [all data]	R_1 = 0.2792, wR_2 = 0.3033	R1 = 0.2731, wR2 = 0.3376
Largest diff. peak/hole / e Å^{-3}	1.38/-0.66	2.20/-1.40
Percentage of Al	0.8922(13)	0.8740(17)
Percentage of In	0.1185(15)	0.1260(17)

Table S6. Crystal data and structure refinement for the Gaq_3-Crq_3 binary alloys

Stoichiometric ratio used for alloy crystallization	Gaq3-Crq3(1:1)	Gaq3-Crq3(9:1)
Empirical formula	$C_{27}H_{18}Cr_{0.74}Ga_{0.26}N_3O_3$	$C_{27}H_{18}Cr_{0.23}Ga_{0.78}N_3O_3$
Formula weight	489.08	498.11
Temperature/K	100.01(10)	100.01(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	13.4304(3)	13.4017(7)
b/Å	15.5926(5)	15.5902(9)
c/Å	18.5705(3)	18.6416(7)
α/°	94.833(2)	94.981(4)
β/°	109.506(2)	109.585(4)
γ/°	114.045(2)	114.021(5)
Volume/Å^3	3236.16(15)	3237.0(3)
Z	6	6
ρ_{calc}g/cm^3	1.506	1.5330
μ/mm^{-1}	0.762	1.141
F(000)	1505.0	1528.5
Crystal size/mm^3	0.19 × 0.13 × 0.1	0.17 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.616 to 55.998	3.3 to 52
Index ranges	$-17 \le h \le 17$, $-20 \le k \le 20$, $-24 \le l \le 24$	$-17 \le h \le 17$, $-20 \le k \le 19$, $-24 \le l \le 24$
Reflections collected	76466	42649
Independent reflections	15576 [R_{int} = 0.0451, R_{sigma} = 0.0345]	12724 [R_{int} = 0.0968, R_{sigma} = 0.1452]
Data/restraints/parameters	15576/0/920	12724/0/920
Goodness-of-fit on F^2	1.139	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0661, wR_2 = 0.1870	R_1 = 0.0711, wR_2 = 0.1684
Final R indexes [all data]	R_1 = 0.0777, wR_2 = 0.1924	R_1 = 0.1183, wR_2 = 0.2012
Largest diff. peak/hole / e Å^{-3}	2.80/-1.28	2.69/-1.55
Percentage of Ga	0.262(7)	0.770(8)
Percentage of Cr	0.738(7)	0.230(8)

Table S7. Crystal data and structure refinement for the Alq_3-Gaq_3-Crq_3 ternary alloys and Alq_3-Gaq_3-Crq_3-Inq_3 quaternary alloy crystals.*

Stoichiometric ratio used for alloy crystallization	Alq3-Gaq3-Crq3(1:1:1)	Alq3-Gaq3-Crq3(1:1:1)	Alq3-Gaq3-Inq3-Crq3 (1:1:1:1)
Empirical formula	$C_{27}H_{18}Al_{0.23}Cr_{0.51}Ga_{0.26}N_3O_3$	$C_{20}H_{20}N_3O_3AlCrGa$	$C_{27}H_{18}Al_{0.14}Cr_{0.54}Ga_{0.14}In_{0.18}N_3O_3$
Formula weight	483.25	481.28	494.73
Temperature/K	100.0(4)	99.99(10)	100.00(10)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	13.4222(7)	13.4296(15)	13.4055(7)
b/Å	15.6206(8)	15.589(3)	15.6401(10)
c/Å	18.5990(4)	18.5731(10)	18.6009(6)
α/°	95.021(3)	94.902(9)	94.842(4)
β/°	109.472(4)	109.511(8)	109.500(4)
γ/°	114.159(5)	114.214(14)	113.676(5)
Volume/Å^3	3238.8(3)	3228.8(9)	3257.2(3)
Z	6	6	6
ρ_{calc}g/cm^3	1.487	1.4850	1.513
μ/mm^{-1}	0.659	0.613	0.707
F(000)	1490.0	1486.5	1518.0
Crystal size/mm^3	0.16 × 0.1 × 0.07	0.2 × 0.12 × 0.08	0.15 × 0.1 × 0.08
Radiation	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.292 to 53.998	3.3 to 52	6.584 to 58.83
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	-16 ≤ h ≤ 17, -19 ≤ k ≤ 18, -24 ≤ l ≤ 23	-17 ≤ h ≤ 16, -19 ≤ k ≤ 20, -25 ≤ l ≤ 23
Reflections collected	41246	36489	42679
Independent reflections	13935 [R_{int} = 0.0583, R_{sigma} = 0.0695]	12696 [R_{int} = 0.2736, R_{sigma} = 0.4993]	15344 [R_{int} = 0.1195, R_{sigma} = 0.2095]
Data/restraints/parameters	13935/0/919	12696/0/853	15344/0/919
Goodness-of-fit on F^2	1.099	0.920	0.986
Final R indexes [I>=2σ (I)]	R_1 = 0.0880, wR_2 = 0.2280	R_1 = 0.1245, wR_2 = 0.2854	R_1 = 0.0756, wR_2 = 0.1181
Final R indexes [all data]	R_1 = 0.1222, wR_2 = 0.2499	R_1 = 0.3058, wR_2 = 0.4091	R_1 = 0.1931, wR_2 = 0.1620
Largest diff. peak/hole / e Å^{-3}	3.02/-0.80	4.04/-1.79	0.89/-0.53
Percentage of Al	0.24	0.29	0.14
Percentage of Cr	0.5	0.48	0.54
Percentage of Ga	0.26	0.23	0.14
Percentage of In	---	---	0.18

* The occupancy values of metal atoms are fixed to the compositions obtained from EDX spectra

Table S8. Gaq_3-Inq_3 binary alloys: single crystals of Gaq_3-Inq_3 binary alloys obtained were too weakly diffracting to obtain full data for structure solution. However, the cell parameters were obtained from SC-XRD datasets showed mer-ε form (Z=6) with the following cell parameters (for the different crystals tested):

Crystal	Ga-Inq3 (50:50) Crystal-1	Ga-Inq3 (50:50) Crystal-2	Ga-Inq3 (90:10) Crystal-1	Ga-Inq3 (90:10) Crystal-2	Ga-Inq3 (90:10) Crystal-3
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
a/Å	13.419	13.437	13.400	13.483	13.510
b/Å	15.706	15.710	15.574	15.656	15.780
c/Å	18.664	18.642	18.689	18.632	18.612
α/°	94.987	94.709	95.043	95.171	94.836
β/°	109.445	109.491	109.708	109.297	109.461
γ/°	113.450	113.800	113.831	114.727	114.970
Volume/Å^3	3291.68	3285.20	3243.09	3250.13	3272.01
Presumed crystal form	*mer*-ε	*mer*-ε	*mer*-ε	*mer*-ε	*mer*-ε
Z	6	6	6	6	6
Presumed space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1

Alq_3-Inq_3 binary alloys: good quality single crystals of Alq_3-Inq_3 binary alloys could be only for very low composition of In (as given in Table 4). Alloy crystal phases of Alq_3-Inq_3 50:50 and 30:0 binary phases were characterized by powder XRD Lebail fitting as given below.

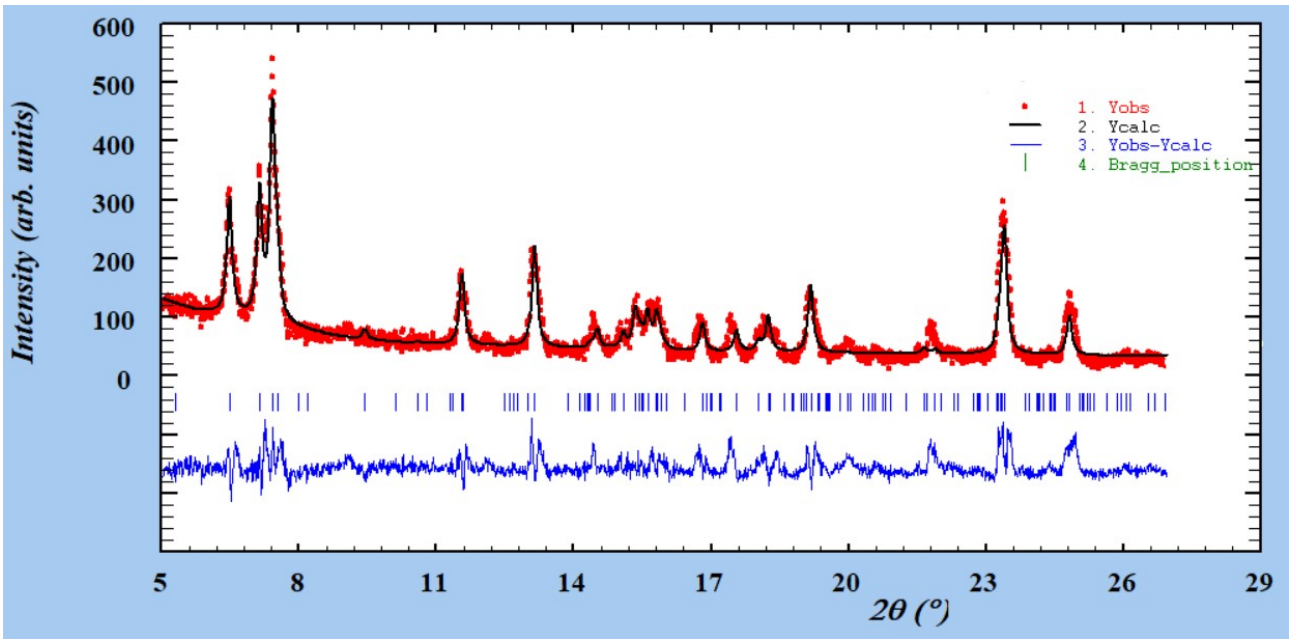

Figure S6. Le Bail fitting PXRD profile for the Alq_3-Inq_3 (30:70) binary alloy sample. Cell parameters: a= 13.458 Å, b= 15.534 Å, c= 18.606 Å, α= 95.104°, β= 110.973°, γ= 114.223°.

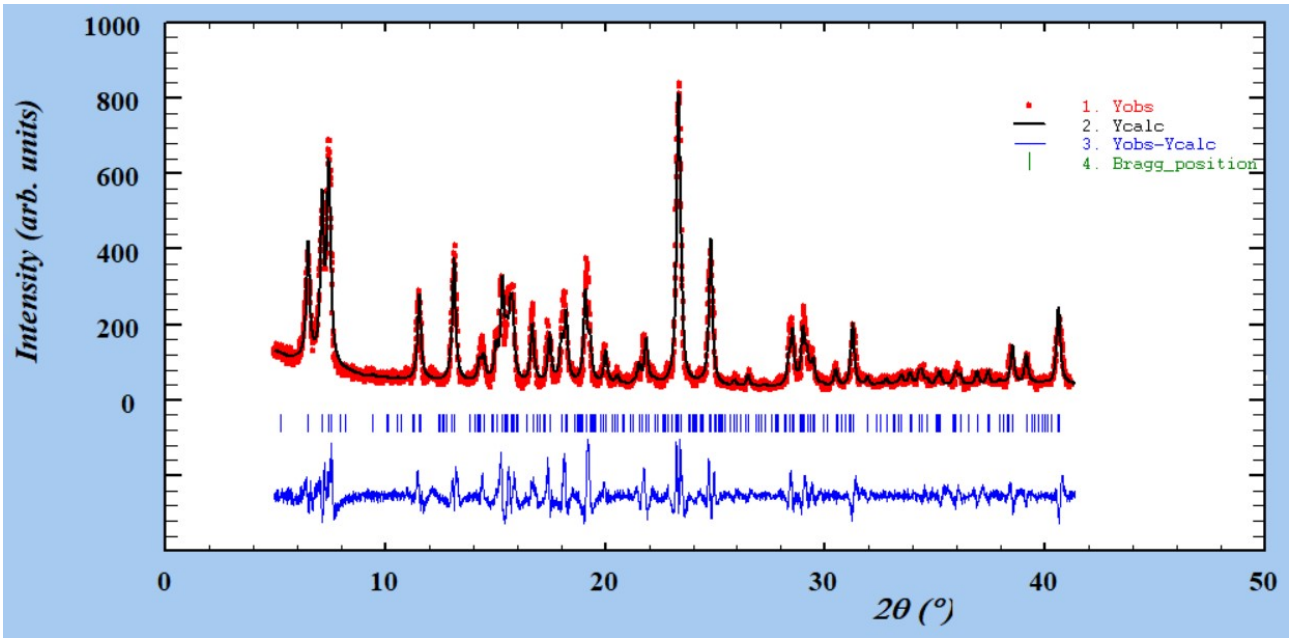

Figure S7. Le Bail fitting PXRD profile for the Alq_3-Inq_3 (50:50) binary alloy sample. Cell parameters: a= 13.480 Å, b= 15.534 Å, c= 18.671 Å, α= 95.349°, β= 110.507°, γ= 114.219°.

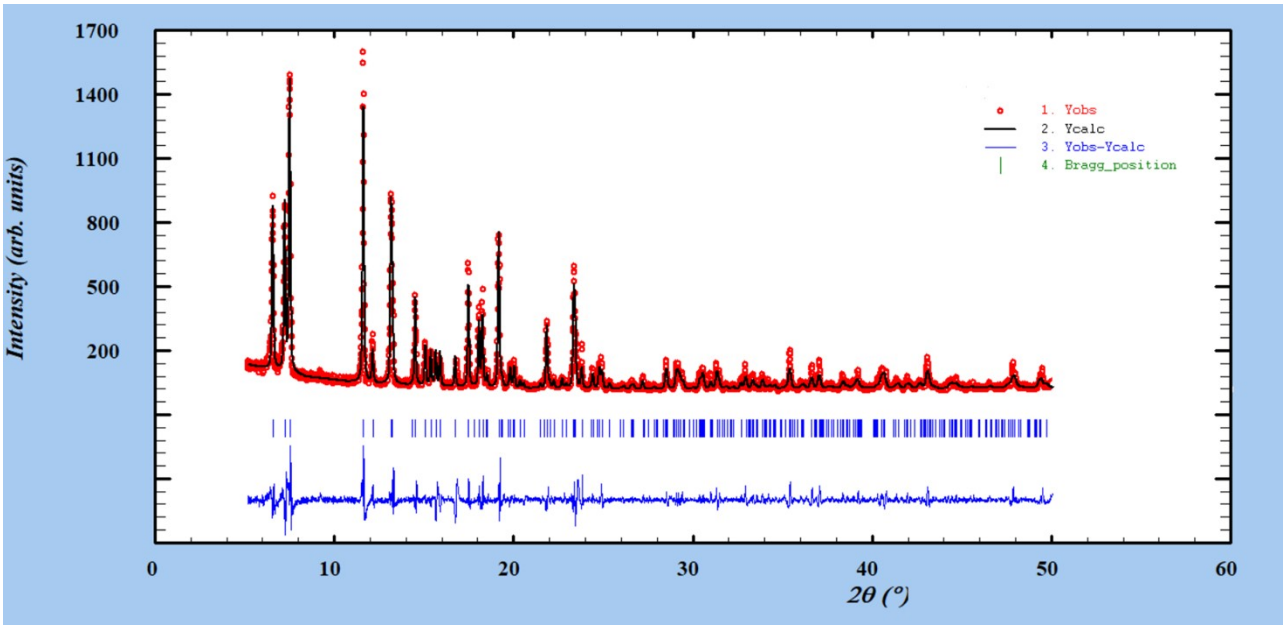

Figure S8. Le Bail fitting PXRD profile for the Inq_3 sample (fitted to cell parameters corresponding to fac-δ form).

Table S9: Average metal-oxygen and metal nitrogen bond distances observed in the Mq_3 crystal structures and their alloys.

	Composition	Metal-N	e.s.d.	Metal-O	e.s.d.
Alq_3	---	2.027	0.013	1.861	0.0185
Gaq_3	---	2.075	0.016	1.948	0.014
Crq_3	---	2.041	0.009	1.956	0.0115
Alq_3-Gaq_3	91:09 (Al:Ga)	2.041	0.016	1.873	0.014
Alq_3-Gaq_3	48:52 (Al:Ga)	2.058	0.015	1.910	0.015
Alq_3-Gaq_3	27:73 (Al:Ga)	2.066	0.015	1.929	0.014
Alq_3-Crq_3	40:60 (Al:Cr)	2.046	0.011	1.931	0.007
Alq_3-Crq_3	77:23 (Al:Cr)	2.030	0.013	1.889	0.010
Alq_3-Crq_3	81:19 (Al:Cr)	2.032	0.014	1.887	0.011
Alq_3-Crq_3	94:06 (Al:Cr)	2.029	0.012	1.875	0.014
Gaq_3-Crq_3	77:23 (Ga:Cr)	2.068	0.015	1.949	0.012
Gaq_3-Crq_3	26:74 (Ga:Cr)	2.061	0.010	1.955	0.011

S3: Raman spectroscopic studies of solid solutions

Raman spectra were recorded on a Renishaw inVia Reflex Micro Raman spectrometer using a 785 nm laser operated at 10% power. The spectra of the single crystal samples were recorded with an exposure time of 1 s using a 50× objective. The instrument was calibrated using a silicon standard.

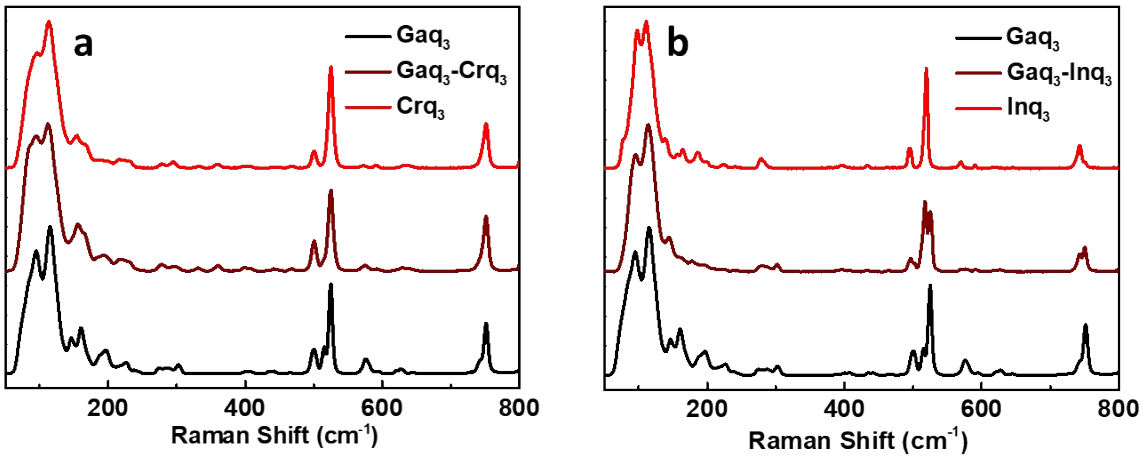

Figure S9. Raman spectra collected from crystals of (a) Gaq_3-Crq_3 (b) Gaq_3-Inq_3 alloy crystals

Table S10. Raman peak positions and their corresponding vibrational assignments of mer-Alq_3.[1]

Mer Alq_3	**Vibration Assignments**
118 cm^{-1}	Al-HQ deformation + Al-N stretching
153 cm^{-1}	8-HQ wagging
166 cm^{-1}	Butterfly mode
195 cm^{-1}	8-HQ wagging
238 cm^{-1}	Ring torsion
314 cm^{-1}	Al-N stretching + C-C-O bending
503 cm^{-1}	Ring deformation
525 cm^{-1}	Ring deformation + Al-O stretching
540 cm^{-1}	Al-O str.+ Al-N str.+ ring deformation
576 cm^{-1}	Ring deformation + Al-O-C bending
645 cm^{-1}	Al-O stretching+ ring deformation
756 cm^{-1}	CH wagging

Table S11. Raman peak positions and their corresponding vibrational assignments of fac-Alq_3.[2]

Fac-Alq_3	**Vibration Assignments**
118 cm^{-1}	Al-HQ deformation + Al-N stretching
166 cm^{-1}	Butterfly mode
183 cm^{-1}	Ring torsion
195 cm^{-1}	8-HQ wagging
224 cm^{-1}	8-HQ wagging
292 cm^{-1}	Ring torsion
503 cm^{-1}	Ring deformation
535 cm^{-1}	Ring deformation + Al-O stretching
548 cm^{-1}	Al-O str.+ Al-N str.+ ring deformation
576 cm^{-1}	Ring deformation + Al-O-C bending

1) Halls, M. and R. Aroca *Can. J. Chem*. **1998**, *76*, 1730-1736.
2) Hung, Shang-Yu, Kao, Ruei-Lin, Lin, Ku-Yen, Yang, Chun-Chuen, Lin, Kuen-Song, Chao, Yu-Chiang, Chiu, Kuan-Cheng. *Materials Chemistry and Physics,* **2015**, *154*, 100-106.

S4. Diffuse reflectance spectroscopic studies of solid solutions

For the diffuse reflectance spectroscopy, a Shimadzu UV-3600 spectrophotometer was used. The finely powdered samples were spread onto a layer of $BaSO_4$ powder and the spectra are measured in the wavelength range of 200 nm to 900 nm. The band gaps of the samples were estimated using Tauc plots[1,2] assuming direct allowed transition, i.e. plot of $[F(R)\cdot h\nu]^2$ against $h\nu$ where F(R) is the Kubelka-Munk function and $h\nu$ is incident photon energy. In case of Crq_3 and its alloy crystals, there is a fair amount of absorption below the band gap energy and therefore a modified Tauc plot is used in these cases.[3]

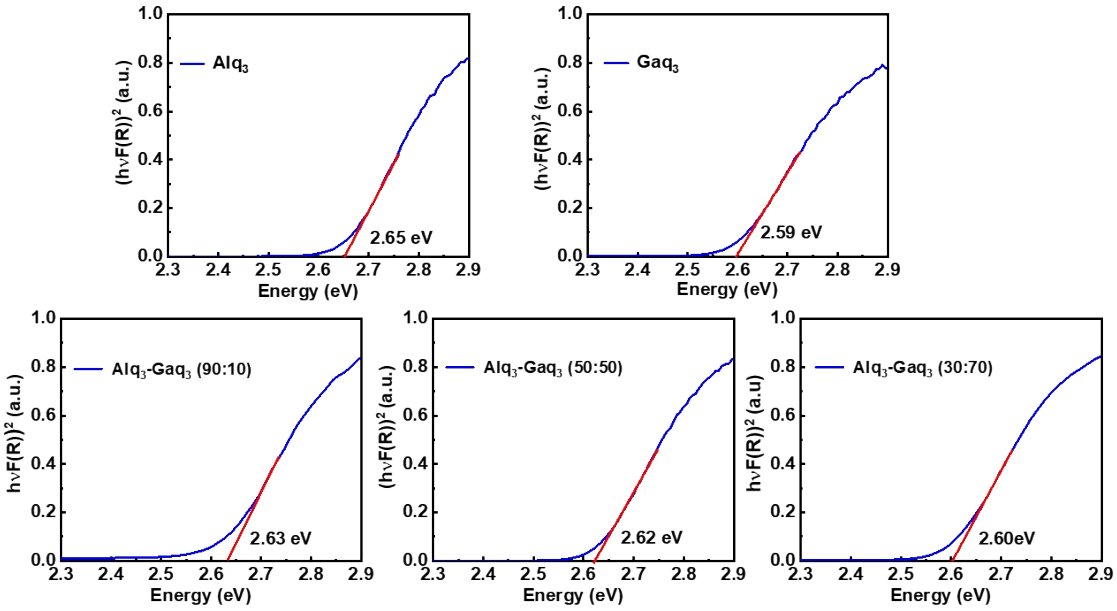

Figure S10. Tauc's plots obtained from the diffuse reflectance spectra of pure Alq_3 and Gaq_3 and their alloys of varying compositions.

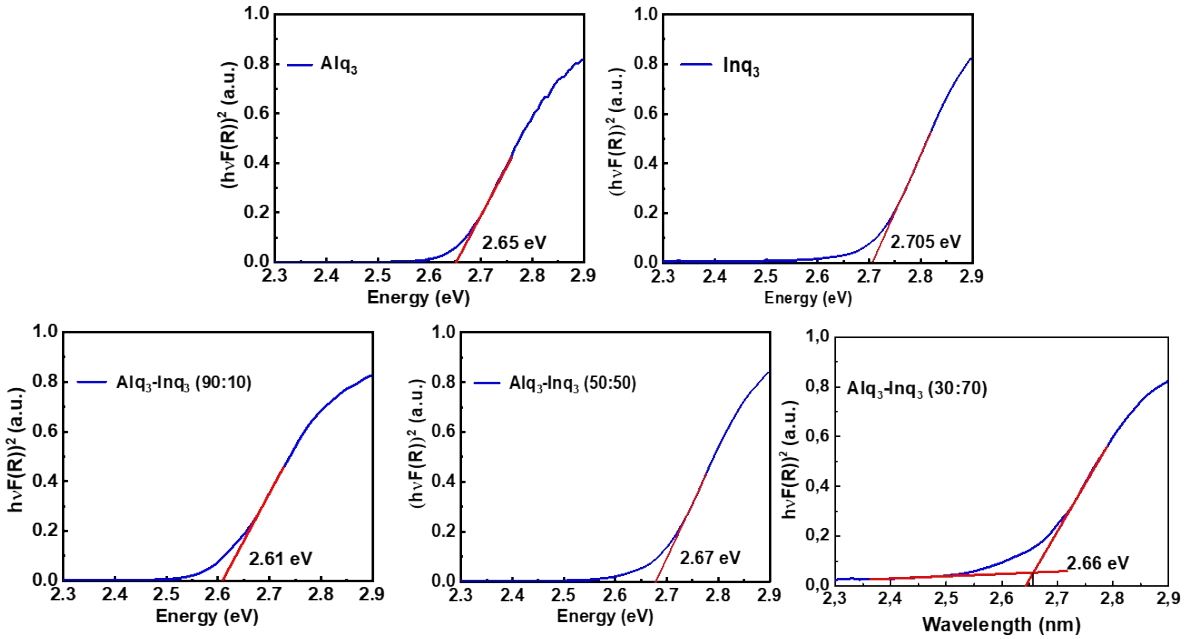

Figure S11. Tauc's plots obtained from the diffuse reflectance spectra of pure Alq_3 and Inq_3 and their alloys of varying compositions.

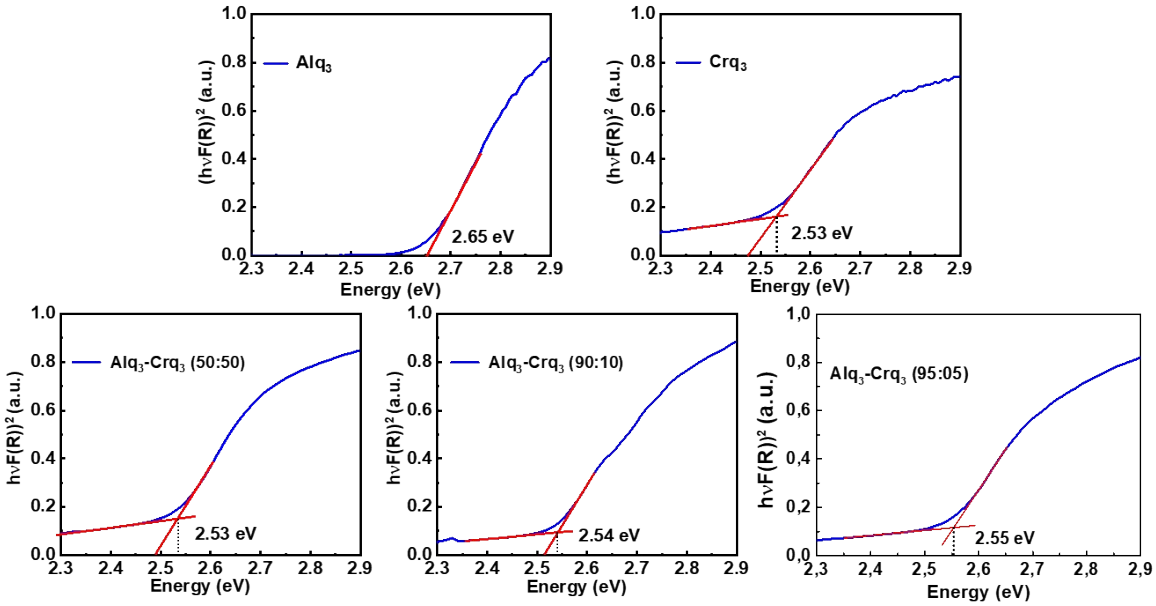

Figure S12. Tauc's plots obtained from the diffuse reflectance spectra of pure Alq_3 and Crq_3 and their alloys of varying compositions.

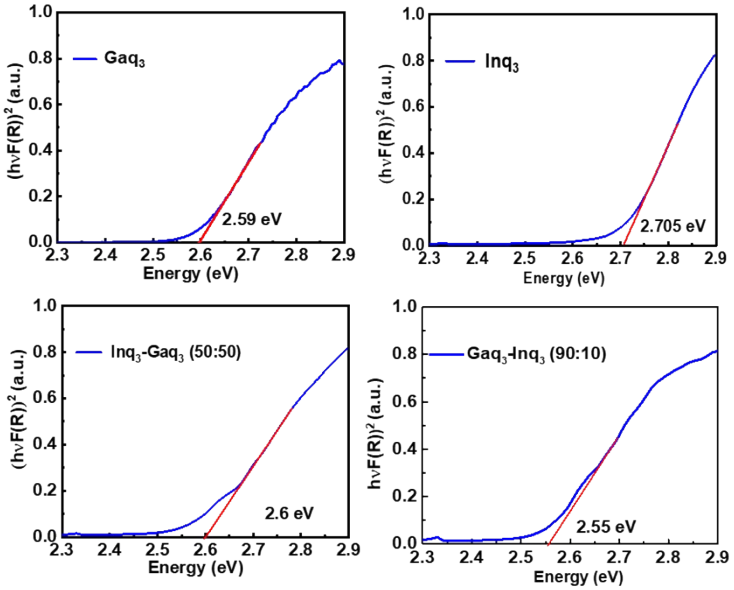

Figure S13. Tauc's plots obtained from the diffuse reflectance spectra of pure Gaq_3 and Inq_3 and their alloys of varying compositions.

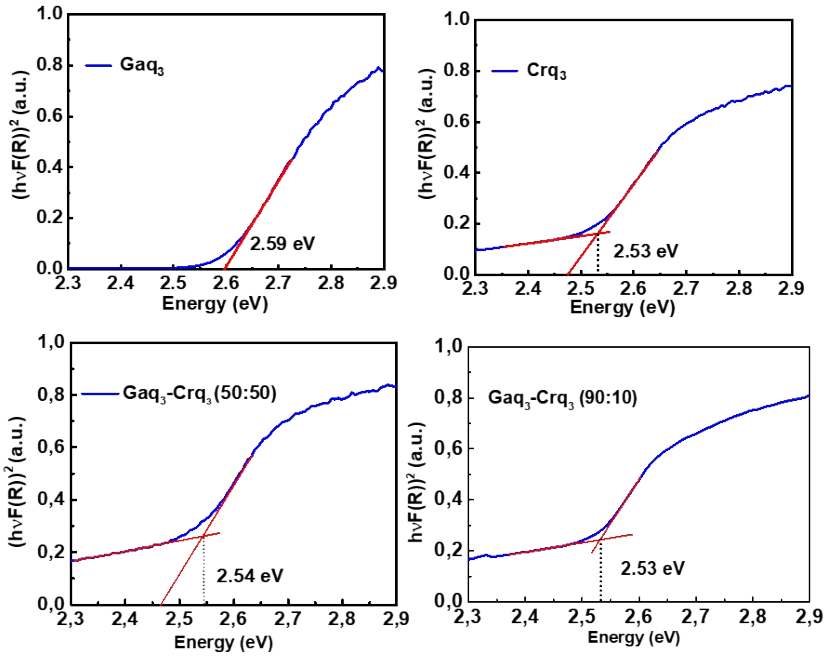

Figure S14. Tauc's plots obtained from the diffuse reflectance spectra of pure Gaq_3 and Crq_3 and their alloys of varying compositions.

1) J. Tauc, R. Grigorovici, A. Vancu, *physica status solidi (b)* **1966**, *15*, 627-637

2) E. A. Davis, N. F. Mott, *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics* **1970**, *22*, 0903-0922.

3) Patrycja Makuła, Michał Pacia, and Wojciech Macyk, *J. Phys. Chem. Lett.* **2018**, *23*, 6814–6817.

S5. Photoluminescence studies

Photoluminescence (PL) measurements on the samples were performed in solid state using FluoroMax-3 fluorometer, Jobin Yvon, Horiba. The single crystals of Mq_3 and their alloy samples were placed on a quartz plate with minimum amount of paratone oil to hold the crystal. The emission was collected with an excitation wavelength of 370 nm.

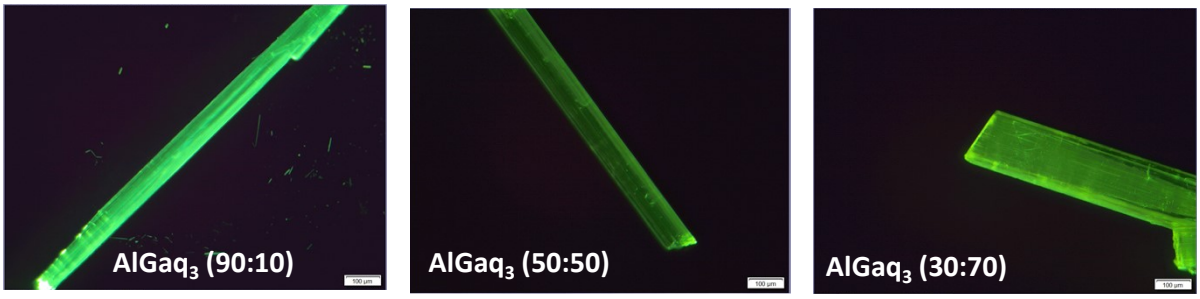

Figure S15: Optical microscopic images of single crystals of Alq_3-Gaq_3 alloy crystals of varying compositions, under UV light (395 nm).

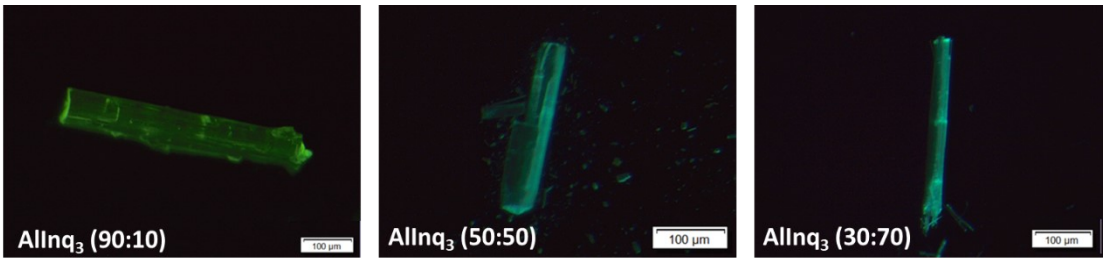

Figure S16. Optical microscopic images of single crystals of Alq_3-Inq_3 alloy crystals of varying compositions, under UV light (395 nm).

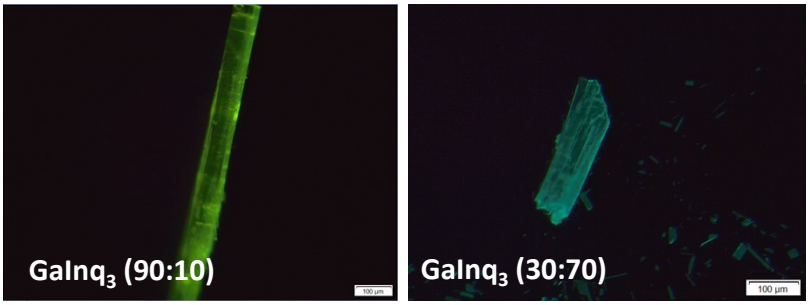

Figure S17. Optical microscopic images of single crystals of Gaq_3-Inq_3 alloy crystals of varying compositions, under UV light (395 nm).

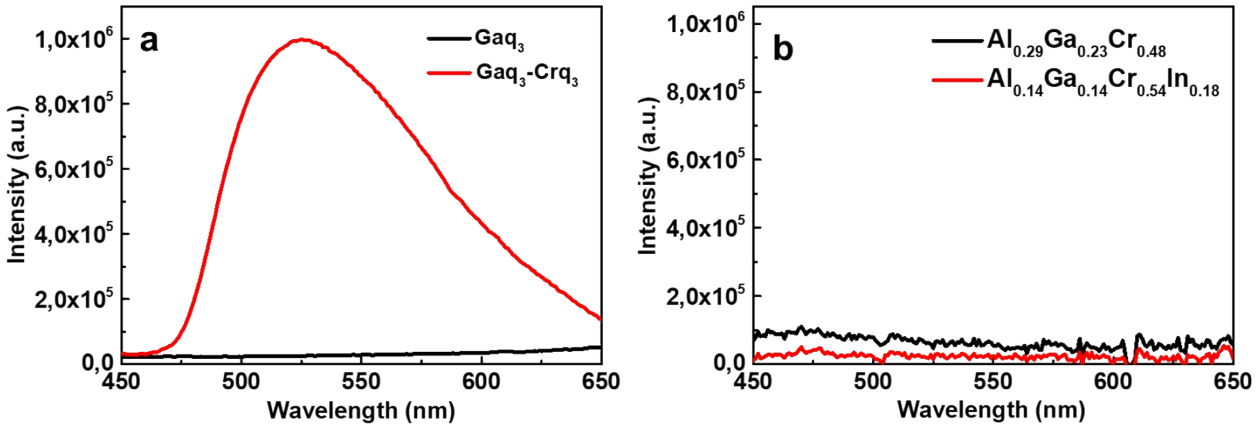

Figure S18. Photoluminescence spectra of (a) Gaq_3-Crq_3 95:5 alloy crystal (b) ternary and quaternary alloy crystals (background corrected spectra). The sample is excited at λ =370 nm.

S6. Energy-dispersive X-ray spectroscopy (EDX) measurements

Elemental mapping was obtained on a TALOS F200A with a TWIN lens system, X-FEG electron source. Spatially resolved elemental analysis, with a spatial resolution better than 2 nm, was obtained using the same TALOS microscope in STEM mode. Exposure times of 5 minutes were used to create elemental distribution maps with satisfactory counting statistics. STEM pictures were obtained using a High Angle Annular Dark Field detector (HAADF). RG overlays of the STEM EDX elemental maps were made using the FIJI (v.1.49q) software.[1]

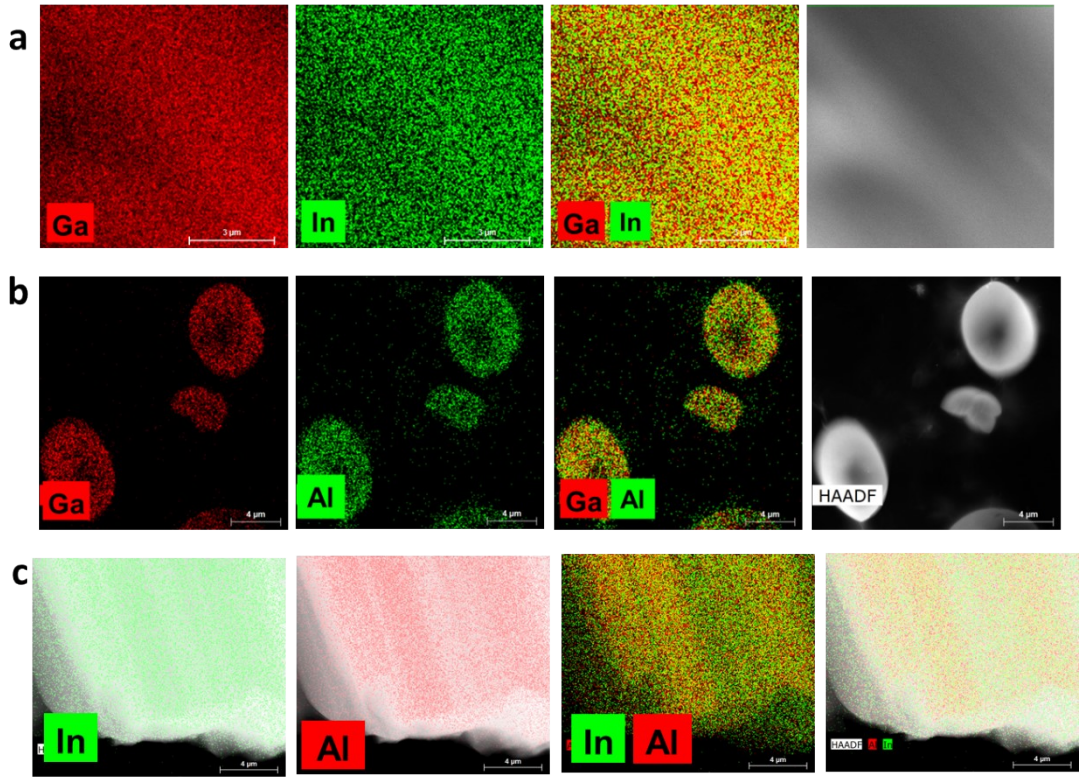

Figure S19. EDX maps of the a) $Ga_{0.92}In_{0.8}$ b) $Al_{0.52}Ga_{0.48}$ c) $Al_{0.72}In_{0.28}$ alloy crystal highlighting regions of different elemental contents and overlapped map showing nearly homogenous distribution of the individual components in the alloy crystal.

Elemental analysis

EDX measurements were performed on the Nova NANO SEM 600 using a high-resolution scanning electron microscope. The microscope was operated in high vacuum. It is equipped with an EDAX detector for energy dispersive X-Ray spectroscopy (EDX) measuring of samples.

Table S12: Elemental analysis of Alq_3-Gaq_3 alloy crystal from the EDX measurement.

Sample	Element	Point 1		Point 2		Point 3		Average atomic % with esd
		Wt %	At %	Wt %	At %	Wt %	At %	**At %**
$Al_{0.91}Ga_{0.09}$	Al	78.87	90.61	80.93	91.64	79.89	91.12	**91.1(4)**
	Ga	21.13	9.39	19.07	8.34	20.11	8.88	**8.9(4)**
$Al_{0.89}Ga_{0.11}$	Al	74.78	88.46	78.37	90.35	76.73	89.5	**89.4(8)**
	Ga	25.22	11.54	21.63	9.65	23.27	10.5	**10.6(8)**
$Al_{0.78}Ga_{0.22}$	Al	56.59	77.11	60.35	79.73			**78(1)**
	Ga	43.41	22.89	39.65	20.27			**22(1)**
$Al_{0.59}Ga_{0.41}$	Al	29.35	51.78	37.19	60.47	42.89	66	**59 (5)**
	Ga	70.65	48.22	62.81	39.53	57.11	34	**41 (5)**
$Al_{0.49}Ga_{0.51}$	Al	22.17	42.39	28.53	50.78	28.22	50.39	**48(4)**
	Ga	77.83	57.61	71.47	49.22	71.78	49.61	**52(4)**

Table S13: Elemental analysis of Alq_3-Inq_3 alloy crystal from the EDX measurement.

Sample	Element	Point 1		Point 2		Point 3		Average Atomic % with esd
		Wt %	At %	Wt %	At %	Wt %	At %	**At %**
$Al_{0.86}In_{0.14}$	Al	61.07	86.97	58.98	85.95			**86.5(5)**
	In	38.93	13.03	41.02	14.05			**13.5(5)**
$Al_{0.86}In_{0.14}$	Al	57.10	84.99	55.70	84.25	64.07	88.35	**86(2)**
	In	42.90	15.01	44.30	15.75	35.93	11.65	**14(2)**
$Al_{0.49}In_{0.51}$	Al	18.63	49.35	17.99	48.28			**48.8(5)**
	In	81.37	50.65	82.01	51.72			**51.2(5)**
$Al_{0.27}In_{0.73}$	Al	8.44	28.19	7.67	26.13			**27(1)**
	In	91.56	71.81	92.33	73.87			**73(1)**

Table S14: Elemental analysis of Alq_3-Crq_3 alloy crystal from the EDX measurement.

Sample	Element	Point 1		Point 2		Point 3		Average Atomic % with esd
		Wt %	At %	Wt %	At %	Wt %	At %	
$Al_{0.22}Cr_{0.78}$	Al	15.28	25.79	10.13	17.85	13.20	22.66	**22(3)**
	Cr	84.72	74.21	89.87	82.15	86.80	77.34	**78(3)**
$Al_{0.85}Cr_{0.15}$	Al	73.93	84.53	74.85	85.15			**84.8(3)**
	Cr	26.07	15.47	25.15	14.85			**15.2(3)**
$Al_{0.89}Cr_{0.11}$	Al	80.46	88.81	75.94	85.88	83.69	90.82	**89(2)**
	Cr	19.54	11.19	24.06	14.12	16.31	9.18	**11(2)**

Table S15: Elemental analysis of Gaq_3-Inq_3 alloy crystal from the EDX measurement.

Sample	Element	Point 1		Point 2		Point 3		Average Atomic % with esd
		Wt %	At %	Wt %	At %	Wt %	At %	
$Ga_{0.88}In_{0.12}$	Ga	81.37	87.79	82.88	88.85	81.85	88.13	**88.3(4)**
	In	18.63	12.21	17.12	11.15	18.15	11.87	**11.7(4)**
$Ga_{0.51}In_{0.49}$	Ga	40.69	53.05	38.57	50.84	36.25	48.36	**51(2)**
	In	59.31	46.95	61.43	49.16	63.75	51.64	**49(2)**

Table S16: Elemental analysis of Gaq_3-Crq_3 alloy crystal from the EDX measurement.

Sample	Element	Point 1		Point 2		Point 3		Average Atomic % with esd
		Wt %	At %	Wt %	At %	Wt %	At %	
$Ga_{0.62}Cr_{0.38}$	Ga	66.73	59.93	70.08	63.59	67.88	61.18	**62(2)**
	Cr	33.27	40.07	29.92	36.41	32.12	38.82	**38(2)**
$Ga_{0.51}Cr_{0.49}$	Ga	55.75	48.45	59.09	51.86	60.55	53.37	**51(2)**
	Cr	44.25	51.55	40.91	48.14	39.45	46.63	**49(2)**

Table S17: Elemental analysis of Alq_3-Gaq_3-Crq_3 ternary alloy crystal from the EDX measurement.

Sample	Element	Point 1		Point 2		Point 3		Point 4		Average Atomic % with esd
		Wt %	At %	Wt %	At %	Wt %	At %	Wt %	At %	
$Al_{0.29}Ga_{0.23}Cr_{0.48}$	Al	20.64	35.52	13.07	24.36	15.56	28.48			**29(5)**
	Ga	28.17	18.76	34.49	24.89	35.90	25.43			**23(2)**
	Cr	51.20	45.72	52.44	50.75	48.54	46.09			**48(3)**
$Al_{0.23}Ga_{0.26}Cr_{0.50}$	Al	12.02	22.88	11.46	21.79	13.19	24.4	13.09	24.54	**24(1)**
	Ga	38.86	28.62	36.55	26.9	31.63	22.64	36.85	26.75	**26(2)**
	Cr	49.12	48.5	51.99	51.31	55.18	52.96	50.06	48.71	**50(2)**

Table S18: Elemental analysis of Alq_3-Gaq_3-Crq_3-Inq_3 quaternary alloy crystal from the EDX measurement.

Sample	Element	Point 1		Point 2		Average Atomic % with esd
		Wt %	At %	Wt %	At %	
AlGaCrIn	Al	4.77	11.09	7.62	17.3	**14(3)**
	Ga	17.01	15.32	14.30	12.56	**14(1)**
	Cr	46.64	56.32	44.21	52.07	**54(2)**
	In	31.58	17.27	33.86	18.06	**17.7(4)**

1) C. A. Schneider, W. S. Rasband, K. W. Eliceiri, *Nature Methods* **2012**, *9*, 671-675.