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BLUE EMITTING PENTACOORDINATED Al(III) COMPLEXES BASED ON 2-METHYL-QUINOLIN-8-OLATE AND SUBSTITUTED PHENOLATE LIGANDS. THE ROLE OF PHENOLATE DERIVATIVES ON EMISSION AND ABSORPTION PROPERTIES

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Synthesis and characterisation

General Information. All commercially available chemicals were used without further purification. The same procedure can be followed to produce the all the compounds (from **1** to **6**). Thus, only the synthesis of 1 is described in detail below:

*Preparation of **1**.* 4-Ethylphenol (0.576 g, 4.71 mmol) in toluene (10 mL) was added slowly to 10 mL of toluene solution containing aluminium isopropoxide (0.962 g, 4.71 mmol). After the mixture had been stirred at reflux for 15 min, a solution of 2-methyl-8-hydroxyquinoline (1.5 g, 9,42 mmol) was added. The resulting mixture was continuously stirred for 2 h at reflux and for 20 h at room temperature. The bright yellow product was collected by filtration, abundantly washed with toluene and dried in vacuum. Yield: 79%. Mp.: 250 °C. IR (KBr, cm^{-1}): ν 2969, 2925, 1608, 1579, 1509, 1459, 1291, 1271, 1116, 1048, 885, 836, 777, 670, 557. ^1H NMR ($CDCl_3$, ppm): δ 8.18 (d, 2H, J = 8.64 Hz, H^4), 7.44 (d, 2H, J = 7.83 Hz, H^6), 7.33 (t, 2H, J = 8.64 Hz, H^3), 7.18 (d, 2H, J = 7.83 Hz, $H^{5\ o\ 7}$), 7.08 (d, 2H, J = 7.83 Hz, $H^{7\ o\ 5}$), 6.65 (d, 4H, J = 8.25 Hz, $H^{3',5'}$), 6.28 (d, 4H, J = 8.25 Hz, $H^{2',6'}$), 2.98 (s, 6H, Ph-CH_3), 2.37 (q, 2H, J = 7.41 Hz, CH_2), 1.05 (t, 3H, J = 7.41 Hz, CH_2-CH_3). Anal. calcd. $C_{28}H_{25}N_2O_3Al$: C, 72.40; H, 5.42; N, 6.03%. Found: C, 72.25; H, 5.57; N, 5.86%.

*Preparation of **2**.* Green-yellow solid is abundantly washed with diethyl ether. Green-yellow solid. Yield: 69%. Mp. 254 °C. IR (KBr, cm^{-1}): 1611, 1589, 1503, 1458, 1315, 1270, 1115, 881, 839, 780, 749, 561. Anal. Calcd. for $C_{27}H_{20}N_3O_3Al$, C: 70.28; H: 4.37; N: 9.11%. Found: C: 70.31; H: 4.41; N, 9.20. The poor solubility of this complex does not allow collection of a ^1H NMR.

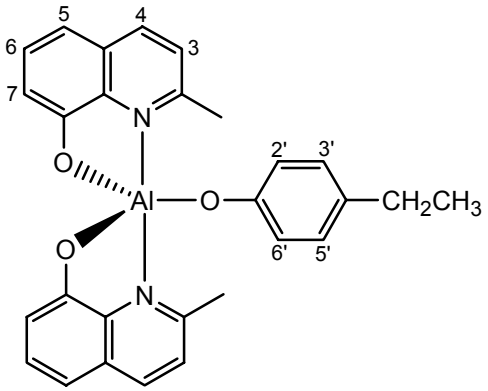
*Preparation of **3**.* Green-yellow solid is abundantly washed with diethyl ether. Yield: 61%. Mp. 252 °C. IR (KBr, cm^{-1}): 2219, 1604, 1579, 1509, 1460, 1323, 1273, 1115, 881, 836, 779, 749, 549. Anal.

Calcd. for $C_{26}H_{20}N_3O_5Al$, C: 64.86; H: 4.19; N: 8.73%. Found: C: 64.76; H: 4.21; N: 8.78%. The poor solubility of this complex does not allow collection of a ^{1}H NMR.

*Preparation of **4***. Bright yellow solid. Yield 92%. Mp > 350 °C. IR (KBr, cm^{-1}): ν 1608, 1579, 1501, 1460, 1294, 1271, 5 878, 832, 776, 746, 693, 556. Anal.Calcd. $C_{52}H_{40}N_4O_6Al_2$: C, 71.72; H, 4.63; N, 6.43%. Found: C, 71.35; H, 4.76; N, 6.64. The poor solubility of this complex does not allow collection of a ^{1}H NMR.

*Preparation of **5***. Bright yellow solid. Yield: 89%. Mp: 189 °C. IR (KBr, cm^{-1}): ν 2963, 1610, 15790, 1508, 1462, 1297, 1272, 1116, 889, 836, 780, 558. Anal Calcd. for $C_{55}H_{46}N_4O_6Al_2$: C, 72.36; H, 5.08; N, 6.14%. Found: C, 71.98; H, 5.07; N, 6.29%. The poor solubility of this complex does not allow collection of a ^{1}H NMR.

*Preparation of **6***. Brigth yellow solid. Yield: 86%. M.p 300°C. IR (KBr, cm^{-1}): ν 2968, 1605, 1580, 1508, 1461, 1301, 1272, 1116, 891, 832, 777, 691, 558. Anal. Calcd. for $C_{64}H_{56}N_4O_6Al_2$: C, 74.55; H, 5.47; N, 5.43%. Found: C, 74.23; H, 5.31; N, 5.53%. The poor solubility of this complex does not allow collection of a ^{1}H NMR.



Chemical structure and proton numbering scheme for complex **1**.

Table S1. Cartesian coordinates of compounds **A**, **B, 2, 3**, **4** and Q'$_2$Al(μ-O)Q'$_2$Al complex computed at the B3LYP/6-31G* level of approximation. All the value is Angstrom.

Geometry of compound A

Al	-0.335077	-0.103861	-0.018771
O	-1.239598	-0.900540	-1.382564
N	-2.239722	0.269262	0.718866
N	1.464016	-0.867281	-0.750850
O	0.122487	-1.023512	1.483831
C	-2.568316	-0.875387	-1.309836
C	-3.427167	-1.419768	-2.252509
C	-4.828426	-1.335129	-2.071598

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C	-5.394714	-0.719961	-0.972657
C	-4.548551	-0.151033	0.014492
C	-3.144769	-0.239682	-0.165807
C	-4.975269	0.513061	1.190210
C	-4.047368	1.025432	2.071029
C	-2.658266	0.894931	1.817966
C	-1.628520	1.452438	2.760597
H	-4.365919	1.537647	2.973125
H	-6.039042	0.616527	1.391463
H	-6.472848	-0.664395	-0.853547
H	-5.474501	-1.771761	-2.828925
H	-3.011291	-1.909373	-3.127383
C	2.078367	-0.735361	-1.925928
C	3.313841	-1.393128	-2.156283
C	3.892463	-2.169082	-1.176559
C	3.253998	-2.322080	0.078495
C	2.022297	-1.635872	0.230241
C	1.266653	-1.703435	1.442712
C	1.773758	-2.465850	2.484503
C	3.003097	-3.149970	2.333390
C	3.739441	-3.092489	1.166558
C	1.444173	0.130599	-2.978357
H	3.795348	-1.271255	-3.121109
H	4.840144	-2.669939	-1.360372
H	4.680689	-3.625713	1.069619
H	3.372968	-3.739695	3.168230
H	1.214575	-2.531582	3.412454
O	0.038333	1.615418	-0.152988
C	1.136132	2.389647	-0.108117
C	1.246164	3.479235	-0.992104
C	2.359936	4.316740	-0.948639
C	3.385199	4.092579	-0.026287
C	3.277881	3.016832	0.857973
C	2.168065	2.172757	0.824263
H	0.438924	3.653637	-1.698242
H	2.424353	5.153855	-1.640158
H	4.251361	4.747641	0.005341
H	4.064253	2.831519	1.586231
H	2.083091	1.345680	1.524190
H	0.374870	-0.085148	-3.052728
H	1.554807	1.189492	-2.714666
H	1.915305	-0.031729	-3.951674
H	-1.031664	2.219221	2.255411
H	-2.100101	1.892595	3.643067
H	-0.939759	0.662024	3.074865

Geometry of compound B

Al	-0.540667	0.179654	0.002831
O	-1.546037	0.715566	1.422674

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N	-2.363558	-0.485369	-0.740085
N	1.103413	1.220991	0.764715
O	-0.290163	1.253735	-1.444101
C	-2.849198	0.452786	1.362334
C	-3.770791	0.769755	2.348679
C	-5.137214	0.442978	2.177580
C	-5.607386	-0.192903	1.045588
C	-4.694786	-0.533986	0.013694
C	-3.326186	-0.204062	0.184723
C	-5.021262	-1.188753	-1.198758
C	-4.035827	-1.468764	-2.120530
C	-2.687211	-1.106643	-1.873211
C	-1.596142	-1.409822	-2.861836
H	-4.276588	-1.972902	-3.050851
H	-6.053264	-1.470093	-1.395361
H	-6.660019	-0.436320	0.934329
H	-5.834393	0.704891	2.969386
H	-3.430439	1.269940	3.249818
C	1.751083	1.145433	1.926711
C	2.852242	2.003125	2.180836
C	3.266483	2.916708	1.237371
C	2.588627	3.014183	-0.002666
C	1.497020	2.126342	-0.179112
C	0.717573	2.120893	-1.378405
C	1.061488	3.013483	-2.382962
C	2.152270	3.897294	-2.207845
C	2.908854	3.912970	-1.052646
C	1.302638	0.129213	2.939412
H	3.363625	1.922530	3.134560
H	4.112419	3.569930	1.438563
H	3.741779	4.600176	-0.935972
H	2.395581	4.585133	-3.013587
H	0.480937	3.026119	-3.299981
O	0.137094	-1.447832	0.020529
C	1.361998	-2.004476	-0.000677
C	1.635276	-3.106556	0.829670
C	2.883884	-3.723868	0.802803
C	3.907235	-3.276160	-0.044490
C	3.623704	-2.185063	-0.874647
C	2.378728	-1.556183	-0.861414
H	0.845570	-3.471282	1.480951
H	3.065265	-4.577845	1.453407
C	5.267874	-3.935074	-0.045454
H	4.391655	-1.818571	-1.553695
H	2.180520	-0.721885	-1.529078
H	0.212054	0.125278	3.014987
H	1.622158	-0.875094	2.634995
H	1.733593	0.342700	3.921532
H	-0.835370	-2.046147	-2.397855
H	-1.995333	-1.915374	-3.744970

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H	-1.099006	-0.484434	-3.170035
H	5.811127	-3.728755	-0.974183
H	5.895612	-3.578073	0.783094
H	5.189199	-5.023612	0.059418

Geometry of compound 2

Al	-0.679610	0.223587	0.009044
O	-1.750029	0.676603	1.403124
N	-2.402056	-0.651064	-0.741526
N	0.852921	1.418927	0.766804
O	-0.489855	1.261170	-1.467392
C	-3.018171	0.273041	1.333302
C	-3.981977	0.511540	2.300248
C	-5.302768	0.035135	2.120566
C	-5.684365	-0.673140	0.998463
C	-4.725437	-0.935968	-0.014068
C	-3.403037	-0.456601	0.166138
C	-4.962506	-1.646834	-1.215467
C	-3.940275	-1.836187	-2.120237
C	-2.642644	-1.324824	-1.865993
C	-1.514535	-1.523883	-2.839627
H	-4.112631	-2.381459	-3.042428
H	-5.955067	-2.042490	-1.417700
H	-6.702854	-1.031016	0.879845
H	-6.035667	0.238237	2.897040
H	-3.711028	1.066452	3.192794
C	1.482805	1.434838	1.941716
C	2.500002	2.392427	2.187539
C	2.851008	3.311476	1.223815
C	2.191228	3.313367	-0.029695
C	1.185043	2.328342	-0.197932
C	0.435523	2.219098	-1.410161
C	0.719665	3.107420	-2.436099
C	1.724939	4.089132	-2.269147
C	2.452776	4.205357	-1.101414
C	1.106592	0.414010	2.979556
H	2.998451	2.384518	3.151329
H	3.633140	4.041239	1.419320
H	3.219689	4.966403	-0.991557
H	1.923905	4.771343	-3.091446
H	0.159764	3.040952	-3.363523
O	0.166106	-1.335907	0.096051
C	1.418363	-1.788133	0.061171
C	1.783544	-2.867770	0.893681
C	3.071552	-3.382116	0.867830
C	4.040488	-2.836272	0.004997
C	3.680539	-1.765727	-0.833611
C	2.391711	-1.250938	-0.808631
H	1.028658	-3.288805	1.550833

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H	3.339751	-4.212290	1.514364
C	5.370319	-3.361966	-0.019244
H	4.420759	-1.343591	-1.506701
H	2.119815	-0.432380	-1.468361
H	0.020752	0.296170	3.020895
H	1.542838	-0.561480	2.731060
H	1.476846	0.708562	3.965287
H	-0.689141	-2.057868	-2.357392
H	-1.844364	-2.094048	-3.711747
H	-1.125110	-0.555250	-3.168927
N	6.454042	-3.788391	-0.036851

Geometry of compound 3

Al	-0.939510	0.248480	0.014441
O	-2.068699	0.551971	1.400875
N	-2.527124	-0.836188	-0.755519
N	0.425305	1.622021	0.790514
O	-0.863890	1.304425	-1.458131
C	-3.273676	-0.012303	1.318780
C	-4.267131	0.093128	2.279170
C	-5.513713	-0.549286	2.086128
C	-5.792096	-1.293344	0.956917
C	-4.799753	-1.423244	-0.049232
C	-3.551837	-0.778184	0.144751
C	-4.933960	-2.150595	-1.256653
C	-3.888911	-2.200776	-2.153719
C	-2.669922	-1.528575	-1.885567
C	-1.516637	-1.577486	-2.848662
H	-3.982518	-2.757969	-3.080055
H	-5.865599	-2.669545	-1.469544
H	-6.754770	-1.779218	0.827937
H	-6.272439	-0.448028	2.857699
H	-4.077197	0.672939	3.176771
C	1.037308	1.712786	1.971665
C	1.925024	2.788621	2.229273
C	2.168566	3.746778	1.270422
C	1.526584	3.669868	0.010193
C	0.651773	2.568429	-0.169653
C	-0.065115	2.370097	-1.389947
C	0.118198	3.288509	-2.412207
C	0.992737	4.386502	-2.233816
C	1.687596	4.589582	-1.057979
C	0.780459	0.650916	3.004789
H	2.410978	2.840339	3.198033
H	2.851967	4.567499	1.474830
H	2.354005	5.438812	-0.939422
H	1.115215	5.089141	-3.053811
H	-0.418589	3.154863	-3.346023
O	0.098691	-1.194179	0.108873

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C	1.393719	-1.486946	0.065434
C	1.890924	-2.530207	0.879704
C	3.232120	-2.878762	0.848191
C	4.099200	-2.188411	-0.004192
C	3.633986	-1.159725	-0.827692
C	2.291352	-0.813863	-0.794889
H	1.194146	-3.053474	1.527181
H	3.623737	-3.674900	1.469811
H	4.330964	-0.649819	-1.481831
H	1.915128	-0.024821	-1.438722
H	-0.285531	0.413182	3.049127
H	1.320405	-0.269263	2.749594
H	1.119689	0.979387	3.990873
H	-0.636661	-2.011200	-2.362147
H	-1.764568	-2.175648	-3.729092
H	-1.245920	-0.565258	-3.165271
N	5.509882	-2.547335	-0.034962
O	5.892094	-3.461284	0.702439
O	6.252300	-1.918160	-0.795449

Geometry of compound 4

C	-0.735705	0.120657	-0.353339
C	-3.561921	0.499609	-0.358797
C	-1.383783	0.799774	-1.400513
C	-2.762535	0.991328	-1.406202
C	-1.543358	-0.355921	0.693904
C	-2.924048	-0.174336	0.698082
H	-3.247732	1.518471	-2.223265
H	-0.798315	1.165182	-2.240488
H	-1.077481	-0.857331	1.538671
H	-3.518642	-0.536308	1.532784
O	-4.888939	0.718583	-0.378859
Al	-6.356911	-0.198129	-0.040847
N	-7.483966	1.528496	0.215221
C	-7.382922	2.534059	1.083062
C	-8.298136	3.615528	1.021193
C	-9.294736	3.642069	0.069699
C	-9.414423	2.583872	-0.863775
C	-8.462229	1.540728	-0.735440
C	-10.387555	2.489242	-1.892468
C	-10.375498	1.393082	-2.732181
C	-9.423514	0.353543	-2.604965
C	-8.457274	0.410443	-1.611983
O	-7.520758	-0.511786	-1.404907
C	-6.286848	2.486222	2.110664
H	-6.292696	3.383711	2.734764
H	-5.313928	2.397157	1.616808
H	-6.406905	1.604054	2.748094
H	-8.197457	4.423665	1.738420

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H	-9.992857	4.474997	0.028354
H	-11.126173	3.277161	-2.007770
H	-11.119854	1.318610	-3.520877
H	-9.439364	-0.496302	-3.279928
O	-6.719842	-0.738374	1.657979
C	-6.362789	-1.979565	1.979920
C	-6.550566	-2.559759	3.225913
C	-6.134372	-3.891054	3.462030
C	-5.535312	-4.659229	2.483180
C	-5.325890	-4.100810	1.195845
C	-5.740997	-2.765653	0.959583
N	-5.587041	-2.130932	-0.240315
C	-5.028687	-2.772216	-1.266388
C	-4.589301	-4.112106	-1.109907
C	-4.730523	-4.763942	0.094725
H	-7.022694	-1.979888	4.012685
H	-6.296355	-4.316673	4.449034
H	-5.223402	-5.680268	2.682850
H	-4.389708	-5.790502	0.207716
H	-4.136508	-4.612445	-1.959691
C	-4.863412	-2.044710	-2.571194
H	-4.044244	-1.318642	-2.499524
H	-5.776653	-1.496791	-2.818196
H	-4.630417	-2.743998	-3.378908
C	0.733402	-0.082965	-0.353177
C	3.557919	-0.474884	-0.353882
C	1.311312	-1.263243	0.147506
C	2.689474	-1.459307	0.151020
C	1.610818	0.892439	-0.857814
C	2.990691	0.705758	-0.866369
H	3.119202	-2.384667	0.525151
H	0.665601	-2.055691	0.517755
H	1.205886	1.828853	-1.233307
H	3.641990	1.477507	-1.268262
O	4.882957	-0.704636	-0.368080
Al	6.359733	0.199135	-0.031504
N	7.514295	-1.078065	-1.192816
C	7.468989	-1.382451	-2.488907
C	8.390593	-2.315717	-3.028114
C	9.335657	-2.917034	-2.225347
C	9.395085	-2.609085	-0.844379
C	8.440797	-1.666893	-0.383288
C	10.311237	-3.157095	0.090675
C	10.243648	-2.760315	1.411604
C	9.289255	-1.821761	1.871501
C	8.377474	-1.264389	0.987810
O	7.443030	-0.375133	1.314711
C	6.428202	-0.716779	-3.345100
H	6.473684	-1.081134	-4.374683
H	5.429991	-0.908428	-2.938775

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H	6.575015	0.368296	-3.340227
H	8.336181	-2.548152	-4.086739
H	10.038953	-3.632082	-2.646028
H	11.051005	-3.879625	-0.241575
H	10.944509	-3.178734	2.129504
H	9.260667	-1.528930	2.916256
O	6.811601	1.621718	-1.072274
C	6.455881	2.824393	-0.626122
C	6.701905	4.019341	-1.286260
C	6.280969	5.245639	-0.720125
C	5.620597	5.309004	0.491137
C	5.349206	4.107897	1.195752
C	5.769133	2.878604	0.627387
N	5.556605	1.665385	1.218018
C	4.931460	1.596117	2.392707
C	4.484582	2.783199	3.028233
C	4.684886	4.013725	2.443418
H	7.222769	3.999440	-2.238332
H	6.489282	6.164475	-1.262247
H	5.306015	6.260341	0.910224
H	4.337097	4.919279	2.935060
H	3.977233	2.700841	3.983921
C	4.698377	0.244789	3.008123
H	3.884755	-0.273427	2.485604
H	5.597490	-0.371151	2.922592
H	4.422433	0.339837	4.061979

Geometry of the Q'$_2$Al(μ-O)Q'$_2$Al

O	0.000000	0.000000	0.000000
Al	0.000000	0.000000	1.711235
O	-0.633998	1.463987	2.615407
C	-1.906732	1.447678	2.993378
C	-2.548374	2.483099	3.659490
C	-3.912339	2.365829	4.015664
C	-4.655989	1.239537	3.722955
C	-4.036679	0.158800	3.042919
C	-4.667204	-1.054900	2.674746
C	-3.953168	-2.030281	2.014781
C	-2.583791	-1.836482	1.696678
N	-1.973822	-0.702685	2.036100
C	-2.667722	0.273837	2.687357
H	-1.988072	3.380092	3.904289
H	-4.383905	3.194553	4.538110
H	-5.702697	1.168187	4.004598
H	-5.716077	-1.209689	2.917631
H	-4.426909	-2.963603	1.727702
C	-1.793336	-2.889491	0.970712
H	-2.368932	-3.814307	0.875230
H	-1.521297	-2.541264	-0.031796

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H	-0.862672	-3.093110	1.508056
O	0.633998	-1.463987	2.615407
C	1.906732	-1.447678	2.993378
C	2.548374	-2.483099	3.659490
C	3.912339	-2.365829	4.015664
C	4.655989	-1.239537	3.722955
C	4.036679	-0.158800	3.042919
C	4.667204	1.054900	2.674746
C	3.953168	2.030281	2.014781
C	2.583791	1.836482	1.696678
N	1.973822	0.702685	2.036100
C	2.667722	-0.273837	2.687357
H	1.988072	-3.380092	3.904289
H	4.383905	-3.194553	4.538110
H	5.702697	-1.168187	4.004598
H	5.716077	1.209689	2.917631
H	4.426909	2.963603	1.727702
C	1.793336	2.889491	0.970712
H	2.368932	3.814307	0.875230
H	1.521297	2.541264	-0.031796
H	0.862672	3.093110	1.508056
Al	0.000000	0.000000	-1.711235
O	0.633998	1.463987	-2.615407
C	1.906732	1.447678	-2.993378
C	2.548374	2.483099	-3.659490
C	3.912339	2.365829	-4.015664
C	4.655989	1.239537	-3.722955
C	4.036679	0.158800	-3.042919
C	4.667204	-1.054900	-2.674746
C	3.953168	-2.030281	-2.014781
C	2.583791	-1.836482	-1.696678
N	1.973822	-0.702685	-2.036100
C	2.667722	0.273837	-2.687357
H	1.988072	3.380092	-3.904289
H	4.383905	3.194553	-4.538110
H	5.702697	1.168187	-4.004598
H	5.716077	-1.209689	-2.917631
H	4.426909	-2.963603	-1.727702
C	1.793336	-2.889491	-0.970712
H	2.368932	-3.814307	-0.875230
H	1.521297	-2.541264	0.031796
H	0.862672	-3.093110	-1.508056
O	-0.633998	-1.463987	-2.615407
C	-1.906732	-1.447678	-2.993378
C	-2.548374	-2.483099	-3.659490
C	-3.912339	-2.365829	-4.015664
C	-4.655989	-1.239537	-3.722955
C	-4.036679	-0.158800	-3.042919
C	-4.667204	1.054900	-2.674746
C	-3.953168	2.030281	-2.014781

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C	-2.583791	1.836482	-1.696678
N	-1.973822	0.702685	-2.036100
C	-2.667722	-0.273837	-2.687357
H	-1.988072	-3.380092	-3.904289
H	-4.383905	-3.194553	-4.538110
H	-5.702697	-1.168187	-4.004598
H	-5.716077	1.209689	-2.917631
H	-4.426909	2.963603	-1.727702
C	-1.793336	2.889491	-0.970712
H	-2.368932	3.814307	-0.875230
H	-1.521297	2.541264	0.031796
H	-0.862672	3.093110	-1.508056

Table S2. Complete list of the computed excited state energies and oscillator strengths of **A, B, 2**, **3** and **4.**

Compound A

Excited State	eV	nm	f
1	3.0127	411.54	0.0004
2	3.1185	397.58	0.0098
3	3.1718	390.89	0.0738
4	3.2455	382.02	0.0047
5	3.3880	365.95	0.0019
6	3.4415	360.26	0.0058
7	3.9974	310.16	0.0003
8	4.1549	298.40	0.0001
9	4.2129	294.29	0.0009
10	4.2193	293.85	0.0003
11	4.2533	291.50	0.0005
12	4.3696	283.74	0.0008
13	4.5794	270.74	0.0043
14	4.6270	267.96	0.0062
15	4.7251	262.39	0.0008
16	4.7491	261.06	0.0009
17	4.9094	252.54	0.0032
18	4.9840	248.77	0.0039
19	5.0671	244.68	0.1193
20	5.0858	243.78	0.1159
21	5.1642	240.08	0.7270
22	5.2225	237.40	0.0105
23	5.3592	231.34	0.0005
24	5.3819	230.37	0.0005
25	5.3826	230.34	0.0060
26	5.4800	226.25	0.0021
27	5.5467	223.53	0.0043
28	5.6082	221.08	0.0138
29	5.6217	220.55	0.0126
30	5.6497	219.45	0.0292

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Compound B

Excited State	eV	nm	f
1	2.8861	429.59	0.0006
2	3.0039	412.74	0.0004
3	3.1648	391.76	0.0839
4	3.2433	382.27	0.0046
5	3.3867	366.08	0.0019
6	3.4409	360.32	0.0055
7	3.9785	311.64	0.0004
8	4.1190	301.01	0.0003
9	4.1404	299.45	0.0001
10	4.2076	294.67	0.0009
11	4.2141	294.21	0.0006
12	4.2529	291.53	0.0007
13	4.5740	271.06	0.0040
14	4.6253	268.05	0.0060
15	4.7272	262.28	0.0009
16	4.7500	261.02	0.0010
17	4.8812	254.00	0.0038
18	4.9594	250.00	0.0060
19	4.9765	249.14	0.0120
20	5.0713	244.48	0.2196
21	5.1615	240.21	0.6850

Compound 2

Excited State	eV	nm	f
1	3.1604	392.31	0.0792
2	3.2389	382.79	0.0043
3	3.3339	371.88	0.0037
4	3.3995	364.71	0.0019
5	3.4393	360.49	0.0010
6	3.4865	355.60	0.0068
7	4.2134	294.26	0.0005
8	4.2227	293.61	0.0001
9	4.4832	276.55	0.0007
10	4.5487	272.57	0.0028
11	4.6119	268.83	0.0021
12	4.6429	267.04	0.0006
13	4.6503	266.61	0.0062
14	4.7028	263.64	0.0008
15	4.7106	263.20	0.0047
16	4.7163	262.88	0.0017
17	4.7524	260.88	0.0009
18	4.8943	253.32	0.0059
19	4.9304	251.47	0.0040
20	5.0687	244.60	0.4404
21	5.0930	243.44	0.0613
22	5.1269	241.83	0.1485
23	5.1628	240.15	0.5620

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24	5.1906	238.86	0.2465
25	5.2481	236.25	0.0196
26	5.2947	234.16	0.0001
27	5.4035	229.45	0.0005
28	5.4311	228.29	0.0015

Compound 3

Excited State	eV	nm	f
1	3.1619	392.12	0.0806
2	3.2397	382.70	0.0059
3	3.3817	366.63	0.0034
4	3.4442	359.97	0.0035
5	3.5491	349.33	0.0011
6	3.6256	341.97	0.0016
7	3.6688	337.94	0.0063
8	3.8088	325.52	0.0003
9	3.8145	325.03	0.0039
10	4.1213	300.84	0.3927
11	4.2163	294.06	0.0004
12	4.2248	293.47	0.0009
13	4.3682	283.83	0.0001
14	4.5164	274.52	0.0014
15	4.5410	273.03	0.0013
16	4.5808	270.66	0.0042
17	4.6560	266.29	0.0071
18	4.6744	265.24	0.0002
19	4.7025	263.66	0.0005
20	4.7464	261.22	0.0009
21	4.7975	258.43	0.0006
22	4.8603	255.09	0.0002

Compound 4

Excited State	eV	nm	f
1	2.4005	516.49	0.0025
2	2.4012	516.33	0.0000
3	2.5081	494.33	0.0000
4	2.5082	494.32	0.0005
5	3.1605	392.29	0.0000
6	3.1618	392.13	0.1667
7	3.2392	382.75	0.0173
8	3.2427	382.34	0.0000
9	3.3868	366.07	0.0040
10	3.3876	366.00	0.0000
11	3.4376	360.67	0.0000
12	3.4376	360.67	0.0111
13	3.5436	349.88	0.0000
14	3.5436	349.88	0.0000
15	3.6149	342.98	0.0000
16	3.6149	342.98	0.0000

17	3.6241	342.10	0.0000
18	3.6245	342.07	0.0007
19	3.7251	332.83	0.0001
20	3.7251	332.83	0.0000
21	3.7272	332.64	0.0038
22	3.7280	332.58	0.0000
23	3.7967	326.55	0.0001
24	3.7967	326.55	0.0000
25	3.8285	323.84	0.0000

TABLE S3. The lowest energy excited states with main contribution from *q'3* and *ph3* occupied orbitals and *q'4* virtual orbitals (see Table 5) and computed for the series of compounds **A**, **B**, **2**, **3** and **4** characterised by their energy (nm), oscillator strength (in parenthesis) and main composition.

	A	**B**	**2**	**3**		**4**
S_1	412 (0.0004) *ph3 – q'4* (HOMO-LUMO)	460 (0.0158) *ph3 – q'4* (HOMO-LUMO)	392 (0.0792) Q' localised (HOMO-LUMO)	392 (0.0806) *q'3 – q'4* (HOMO-LUMO)	S_1	516 (0.0025) *ph3 – q'4* (HOMO-LUMO)
S_2	398 (0.0098) *ph3 – q'4*	441 (0.0191) *ph3 – q'4*	383 (0.0043) Q' localised	383 (0.0059) *q'3 – q'4*	S_2	516 (0.0000) *ph3 – q'4*
S_3	391 (0.0738) *q'3 – q'4*	396 (0.0984) *q'3 – q'4*	372 (0.0037)	367 (0.0034) *q'3 – q'4*	S_3	494 (0.0000) *ph3 – q'4*
S_4	382 (0.0047) *q'3 – q'4*	384 (0.0033) *q'3 – q'4*	365 (0.0019)	360 (0.0035) *q'3 – q'4*	S_4	494 (0.0005) *ph3 – q'4*
S_5	366 (0.0019) *q'3 – q'4*	372 (0.0020) *q'3 – q'4*	360 (0.0010)	349 (0.0011) *ph3 – q'4*	S_5	392 (0.0000) *q'3 – q'4*
S_6	360 (0.0058) *q'3 – q'4*	361 (0.0011) *q'3 – q'4*	356 (0.0068)	342 (0.0016) *q'3 – ph4*	S_6	392 (0.1667) *q'3 – q'4*
S_7				338 (0.0063) *ph3 – q'4*	S_7	383 (0.0173) *q'3 – q'4*
					S8	382 (0.0000) *q'3 – q'4*
					S9	366 (0.0040) *q'3 – q'4*
					S10	366 (0.0000) *q'3 – q'4*
					S11	361 (0.0000) *q'3 – q'4*
					S12	361 (0.0111) *q'3 – q'4*
					S13	350 (0.0000) *q'3 – q'4*
					S14	350 (0.0000) *q'3 – q'4*
					S15	343 (0.0000) *q'3 – q'4*
					S16	343 (0.0000) *q'3 – q'4*
					S17	342 (0.0000) *ph3 – q'5*
					S18	342 (0.0007) *ph3 – q'5*

S19	333 (0.0001) *q'3 – q'4*
S20	333 (0.0000) *q'3 – q'4*
S21	333 (0.0038) *ph3 – q'5*

TABLE S4. Results from the decomposition displayed in Figure 5. Each curve is described in terms of λ_{max}, relative intensity (I_{max}) and full width at half maximum (FWHM).

		1	**2**	**3**	**4**
	λ_{max} (nm, eV)	477 nm ; 2.60 eV	471 nm ; 2.63 eV	472 ; 2.62 eV	470 nm ; 2.63 eV
Gaussian 1	Relative I_{max}	5.05	4.23	4.77	10.01
	FWHM (nm)	49.4	55.0	58.6	50.8
	λ_{max} (nm, eV)	518 nm ; 2.39 eV	518 nm ; 2.39 eV	519 nm ; 2.39 eV	515 nm ; 2.41 eV
Gaussian 2	Relative I_{max}	5.32	2.40	3.32	7.01
	FWHM (nm)	49.4	55.0	58.6	50.8
	λ_{max} (nm, eV)	567 nm ; 2.19 eV	565 nm ; 2.19 eV	571 nm ; 2.17 eV	565 nm ; 2.19 eV
	I_{max}	1.00	1.00	1.00	1.00
Gaussian 3	FWHM (nm)	49.4	55.0	58.6	50.8

The fluorescence emission spectrum of bis(2-methyl-8-hydroxyquinolinato)aluminium(III)-μ-oxo-bis(2-methyl-8-hydroxyquinolinato)aluminium(III)

The phenolate-based ligand (L) influence on the emission process has been definitely ruled out by comparing the fluorescence emission spectra of the six studied compounds **1-6** with the dinuclear complex whose chemical formula is reported in Figure S1.

This compound is well known as a relatively stable product of the reaction between $AlCl_3$ and 2-methyl-8-hydroxyquinoline, and its structure has been characterised by single-crystal X-ray analysis [1]. Geometry optimisation at the B3LYP/6-31G(d) level of approximation generated the structure reported in Figure S1. It is in good agreement with the experimental X-Ray structure, with differences limited to the relative orientation of the equatorial planes of the aluminium coordination sphere (each aluminium atom is pentacoordinated in a trigonal bipyramidal geometry; see Table S1 for the computed geometry). The presence of a *μ*-oxo bridge in place of the aromatic L ligand

makes it possible to confidentially assign the emission process to the 2-methyl-quinolin-8-olate chelants.

Table S5

Compound	*Solution (CH_2Cl_2)*	
	Abs/nm	*Em/nm*
$Q'_2Al(\mu\text{-}O)Q'_2Al$	260, 355	510

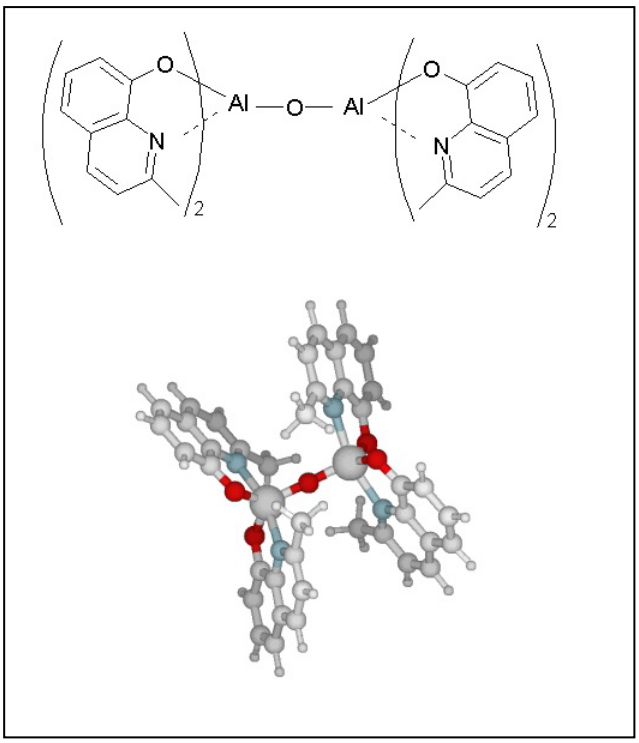

Fig. S1. The $Q'_2Al(\mu\text{-}O)Q'_2Al$ complex

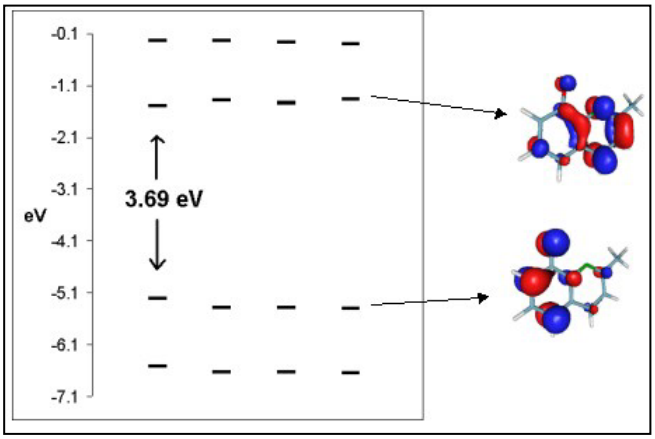

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Fig. S2. The highest occupied and lowest virtual Kohn-Sham orbitals of Q'$_2$Al(μ-O)Q'$_2$Al

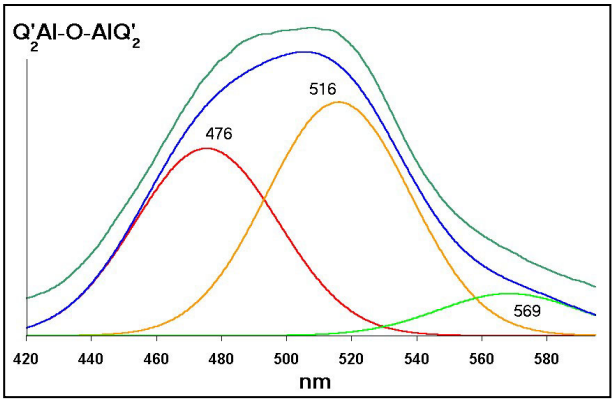

Fig. S3. Decomposition of the fluorescence emission spectrum, of the Q'$_2$Al(μ-O)Q'$_2$Al. The higher green curve in each graph is the experimental spectrum. The lower blue one is the corresponding combination of the Gaussian curves. The experimental curve has been shifted at higher values to be distinguished from the fitted curve.

Figure S2 shows that the four highest occupied orbitals and the four lowest unoccupied orbitals are localised on the four 2-methyl-quinolin-8-olate chelants. The experimental spectral data are reported in Table S5. The experimental emission spectrum in CH_2Cl_2 solution has been decomposed with three Gaussian curves placed at 476 nm, 516 nm and 569 nm (Figure S3). These values are comparable to the values found in the **1-4** complexes (Figure 5 and Table S4), with relative peak intensities (4.46 : 5.56 : 1.00) being very similar to the case of the complex **1** (5.05; 5.32; 1.0), whereby the Gaussian curve in the middle is somewhat more intense. These findings allows excluding that the unusual pattern of the emission spectrum of complex **1** is associated to the L ligand. Likewise, we have a further confirm that the fluorescence emission spectra are associated to phenomena related to the 2-methyl-quinolin-8-olate chelants.

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References

[1] Kushi, Y.; Fernando, Q. *J. Amer. Chem. Soc.* **1970**, *92*, 91

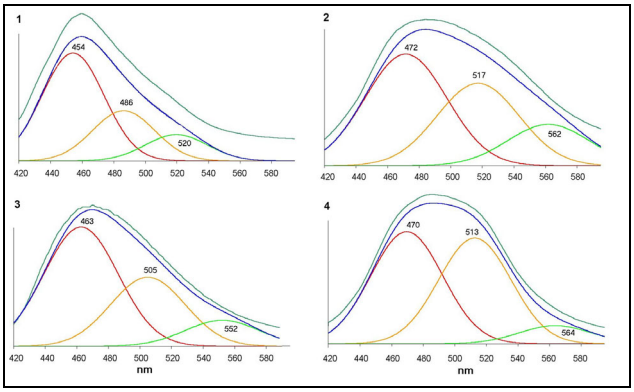

Fig. S4 Decomposition of the experimental fluorescence emission spectra for the complexes **1-4**. All the emission spectra have been recorded from KBr pellets, with an excitation wavelength of 355 nm. Table 7 (see the paper) reports data about the used three Gaussian curves and a comparison with the spectra in solution. The higher green curve in each graph is the experimental spectrum. The lower blue one is the corresponding combination of the Gaussian curves. The experimental curve has been shifted at higher values to be distinguished from the fitted