Supporting Information

Single-component panchromatic white light generation, tuneable excimer-like visible orange and NIR emission in a Dy quinolinolate complex

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Table 1. Crystal data and refinement details for 1.

CCDC no	1990016
Empirical formula	C ₃₆ H ₁₈ Cl ₉ DyN ₄ O ₄
Formula weigth (g mol ⁻¹)	1052.10
Т (К)	100(2)
λ (Å)	1.54184
Crystal system	orthorhombic
Space group	Pca2 ₁
a (Å)	25.4963(3)
b (Å)	9.6756(1)
c (Å)	28.9159(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	7133.32(13)
Z	8
ρ_{calc} (g cm ⁻³)	1.959
μ (mm ⁻¹)	17.834
F (000)	4104.0
Crystal dimensions (mm ³)	0.273 x 0.095 x 0.049
2θ max (°)	134.746
Reflections collected	72278
Independent reflections	12770
Observed reflections $[I_0>2\sigma(I_0)]$	12142
Parameters refined	974
Final R indexes $[I_0>2\sigma(I_0)]$	$R_1 = 0.0480; wR_2 = 0.1181$
R indexes (all data)	$R_1 = 0.0502; wR_2 = 0.1208$
Goodness-of-fit on F ²	1.055



Figure S1. Experimental powder-XRD pattern of **1** (blue) compared to the simulated one retrieved from single-crystal XRD data (grey).



Figure S2. Thermogravimetric analysis (TGA, black curve), differential thermogravimetric curve (DTA, red curve) and simultaneous differential thermal analysis (SDTA, blue curve) of **1**. The thermogravigram shows two small weight losses (ca. 1% wt.) accompanied by exothermic peaks at ca. 64 and 116 °C which can be attributed to the loss of adsorbed methanol and water molecules. A relevant weight loss, also related to an exothermic peak, begins at ca. 250°C followed by the endothermic thermal decomposition of the sample at temperatures above 400°C. The residual mass (ca. 17% wt.) is attributed to residual dysprosium oxide. The thermal analysis was performed under air flux. It is worth pointing out that the thermal stability of **1** exceeds that of the best performing materials used as emissive layers in OLED devices.¹



Figure S3. Crystal packing of **1** evidencing the three configurations used for DFT calculations in different colors: single molecule "monomer" (blue); "dimer" (green) and "inter-dimer" (pink). A simplified scheme is also depicted on the right.



LUMO+5

LUMO+6



LUMO+3



LUMO+1



LUMO





Figure S4. Set of DFT-calculated frontier MOs for 1' as "monomer".



Figure S5. Set of DFT-calculated frontier MOs for 1' in a "dimer" configuration.



Figure S6. Extended set of frontier MOs for 1' in the "inter-dimer" configuration.

Calc.	_ 20	Maior contributions
abs. (nm)	J	Major contributions
Monomer		
499	0.0018	H-1->LUMO (97%)
457	0.0182	H-2->L+1 (6%), HOMO->LUMO (6%), HOMO->L+1 (85%) LLCT
440	0.0022	HOMO->LUMO (88%), HOMO->L+1 (5%)
418	0.0536	H-3->LUMO (65%), H-2->LUMO (24%), HOMO->LUMO (4%) ILCT
401	0.0469	H-3->L+1 (12%), H-2->L+1 (73%), HOMO->L+1 (8%) ILCT
334	0.1844	H-1->L+2 (10%), H-1->L+4 (4%), HOMO->L+4 (13%), HOMO->L+5 (65%) ILCT
330	0.0118	H-1->L+2 (66%), H-1->L+4 (9%), HOMO->L+5 (12%),
325	0.0121	H-9->L+1 (4%), H-2->L+3 (6%), HOMO->L+3 (81%)
317	0.0432	H-1->L+2 (13%), H-1->L+4 (62%), H-1->L+5 (7%)
Intra-dimer		
488	0.0014	H-3->LUMO (80%), H-1->L (13%)
480	0.0032	H-1->L+1 (5%), H-2->L+1 (89%)
426	0.0376	H-5->L+2 (8%), H-4->L+2 (14%), H-1->L+2 (64%) LL'CT
411	0.0613	H-7->LUMO (74%), H-6->LUMO (4%), H-5->LUMO (10%) ILCT
410	0.0508	H-6->L+1 (61%), H-5->L+1 (16%), H-4->L+1 (10%), H-1->L+1 (4%) ILCT
406	0.0136	H-5->L+3 (4%), HOMO->L+3 (86%)
397	0.0131	H-3->L+2 (92%)
390	0.0011	H-6->L+1 (6%), H-3->L+1 (10%), H-2->L+1 (4%), H-1->L+1 (70%)
383	0.0330	H-6->L+2 (6%), H-5->L+2 (16%), H-4->L+2 (40%), H-1->L+2 (28%)
Inter-dimers		
498	0.0036	H-4->LUMO (10%), H-4->L+1 (86%)
487	0.0028	H-3->L+3 (45%), H-2->L+3 (47%)
479	0.0063	H-1->L+5 (6%), HOMO->L+4 (4%), HOMO->L+5 (80%)
476	0.0464	H-8->L+2 (12%), H-6->L+2 (8%), H-3->L+2 (36%), H-2->L+2 (35%) LL'CT
470	0.0504	H-11->LUMO (6%), H-9->LUMO (24%), H-5->LUMO (57%), H-5->L+1 (4%) LLCT
447	0.0228	H-7->L+4 (4%), H-1->L+3 (6%), H-1->L+4 (68%), HOMO->L+4 (11%)
428	0.0439	H-8->L+2 (33%), H-7->L+2 (10%), H-6->L+2 (26%), H-3->L+2 (12%), H-2->L+2 (13%)
420	0.0727	H-10->L+3 (23%), H-7->L+3 (41%), H-6->L+3 (5%), H-1->L+3 (14%) ILCT
417	0.0524	H-11->L+1 (50%), H-9->LUMO (8%), H-9->L+1 (25%)
415	0.0160	H-8->L+5 (15%), H-6->L+5 (51%), H-1->L+5 (21%)

 Table S2. TD-DFT calculated lowest energy transitions for 1' in different configurations.

^aCalculated oscillator strength



Figure S7. Emission decay dynamics for $[Gd(5,7ClQ)_2(H5,7ClQ)_2Cl]$ at 620 nm (blue dots) and 520 nm (green dots, also shown in the inset). Solid black curves represent the best fit to data. Excitation wavelength was 370 nm. Both decays clearly display two signal components whose dynamics significantly differs. The slow component, representing the majority of the signal (>70%) at 620 nm was fitted with a monoexponential function yielding a time constant of $\tau = 307$ ns. This signal is attributed to the LLCT/LL'CT state associated with the "excimer-like" (EL) emission (See Figure 4f). On the other hand, the fast component ($\tau = 1.6$ ns), which dominates the decay at 520 nm, can be reliably associated to the ligand-centered "locally-excited" (LE) fluorescence from ILCT states.

Dy³⁺ sensitization efficiency

The dysprosium sensitization efficiency η_{sens} , was calculated through the equation:

$$\eta_{sens} = \frac{1}{1 + \frac{\tau_{Dy}}{\tau_{Gd}}}$$
 Equation S1

Where τ_{Dy} and τ_{Gd} represent the decay time constant of the ligand states in **1** and in the reference Gd analog, respectively. As already discussed in the manuscript, and as evidenced by the double component decay dynamics in the visible range, more than one ligand states, which could be labelled as ILCT and LLCT/LL'CT, actively feed the $Dy^{3+} H_{5/2} + F_{7/2}$ levels. Despite the estimation of the sensitization efficiency is complicated because of the multiple energy transfer pathways, the single contributions could be separately evaluated. In the present case, the instrumental temporal resolution limits hamper the evaluation of η_{sens} from the ILCT state which is associated with a sub-ns decay in **1** (Figure 4d). Instead, a value of $\eta_{sens} = 98.2\%$ is retrieved through equation S1 for the energy transfer from the LLCT/LL'CT states, by taking $\tau_{Dy} = 5.5$. ns and $\tau_{Gd} = 307$ ns.



Figure S8. Excitation spectra of **1** in CH₃OH solution monitored at 543 nm (blue) and in the crystalline state monitored at 620 nm (yellow) and at 990 nm (pink) corresponding to $Dy^{3+6}H_{5/2} \rightarrow {}^{6}H_{15/2}$ transition. The sharp peak at 463 nm is a typical artefact related to the excitation source.

References

1. S. Lee, H. Kim, Y. Kim Progress in organic semiconducting materials with high thermal stability for organic light-emitting devices *InfoMat* 2021, **3**, 61.