Electronic Supplementary Information

Manifestation of π-π Stacking Interactions in Luminescence Properties and Energy Transfer in Aromatically-Derived Tb, Eu and Gd Tris(pyrazolyl)borate Complexes

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Table SI 1. Crystallographic data and structure refinement for complexes 1-3

Compound	**1** × $CHCl_3$	**2** × CH_2Cl_2	**2** × C_2H_3N	**3** × C_2H_3N
Empirical formula	$C_{29}H_{28}BCl_3EuN_9O_5$	$C_{29}H_{29}BCl_2GdN_9O_5$	$C_{30}H_{30}BGdN_{10}O_5$	$C_{30}H_{30}BN_{10}O_5Tb$
Moiety formula	$C_{28}H_{27}BEuN_9O_5$, $CHCl_3$	$C_{28}H_{27}BGdN_9O_5$, CH_2Cl_2	$C_{28}H_{27}BN_9O_5Gd$, C_2H_3N	$C_{28}H_{27}BN_9O_5Tb$, C_2H_3N
Mr	851.72	822.57	778.70	780.37
Color of crystal	colorless	colorless	colorless	colorless
Temperature, K	100(2)	100(2)	100(2)	100(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 11.0530(14)Å b = 11.1076(14)Å c = 15.203(3)Å α = 100.320(2)º β = 101.795(2)º γ = 106.355(2)º	a = 10.5915(8)Å b = 10.7225(8)Å c = 15.4145(12)Å α = 100.690(1)º β = 102.413(1)º γ = 100.304(1)º	a = 10.7488(16)Å b = 11.0512(17)Å c = 13.991(2)Å α = 99.728(2)º β = 103.413(2)º γ = 93.555(2)º	a = 10.7529(19)Å b = 11.044(2)Å c = 13.947(3)Å α = 99.580(2)º β = 103.408(2)º γ = 93.715(2)º
Volume, $Å^3$	1696.6(5)	1635.8(2)	1584.5(4)	1579.5(5)
Z	2	2	2	2
ρ_{calcd}, g/cm^3	1.667	1.670	1.632	1.641
μ_{calcd}, mm^{-1}	2.137	2.244	2.149	2.296
F(000)	848	818	778	780
Crystal size	0.55 × 0.45 × 0.35	0.40 × 0.25 × 0.15	0.50 × 0.25 × 0.10	0.56 × 0.30 × 0.11
θ range for data collection	1.99 to 31.39	2.68 to 31.39	2.16 to 31.38	2.82 to 31.73
Index ranges	$-16 \le h \le 15$ $-16 \le k \le 15$ $-21 \le l \le 21$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-22 \le l \le 22$	$-15 \le h \le 15$ $-16 \le k \le 16$ $-20 \le l \le 20$	$-15 \le h \le 15$ $-16 \le k \le 15$ $-20 \le l \le 20$
Reflections collected	9903	9771	9407	9798

Independent reflections	9375	9219	8906	9379
Completeness to θ_{max}	0.886	0.901	0.901	0.901
Absorption correction	'multi-scan'	'multi-scan'	'multi-scan'	'multi-scan'
max and min transmission	0.746 and 0.550	0.746 and 0.559	0.746 and 0.502	0.746 and 0.559
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/ parameters	9903 / 2 / 441	9771 / 2 / 432	9407 / 2 / 433	9798 / 2 / 433
Goodness-of-fit on F^2	1.030	1.058	1.073	1.042
Final R indices [I>2σ(I)]	R_1 = 0.0229 wR_2 = 0.0551	R_1 = 0.0238 wR_2 = 0.0586	R_1 = 0.0215 wR_2 = 0.0544	R_1 = 0.0207 wR_2 = 0.0491
R indices (all data)	R_1 = 0.0248 wR_2 = 0.0565	R_1 = 0.0259 wR_2 = 0.0599	R_1 = 0.0233 wR_2 = 0.0558	R_1 = 0.0219 wR_2 = 0.0499

1. Enhancement factor

Enhancement factor Y defined as

$$Y = \frac{I_1}{I_2} = \frac{I_\varphi}{I_{pure} \cdot \varphi} = \frac{\Phi_\varphi}{\Phi_{pure} \cdot \varphi} = \frac{q_\varphi}{\varphi} \qquad (1)$$

where:

I_1 – measured luminescence intensity of sample;

I_2 – calculated luminescence intensity for the sample with the same Eu^{3+} or Tb^{3+} concentrations in assumption of absence of interactions between different molecules in the crystal lattice. It can be calculated as $I_2 = I_{pure}*\varphi$ – where I_{pure} is measured luminescence intensity of pure Eu^{3+} or Tb^{3+} complexes, and φ is a molar fraction of Eu^{3+} or Tb^{3+} in Gd^{3+}-compound.[1,2]

Φ_φ - absolute quantum yield; the suffix φ defines the mole fraction of Eu^{3+} or Tb^{3+} in the sample.

q_φ- relative quantum yield of the sample with mole fraction of Eu^{3+} or Tb^{3+} equal to φ, determined as the ratio of the Φ_φ to Φ_{pure}, while for the pure compound, $q_{pure} = 1$.

2. Figures

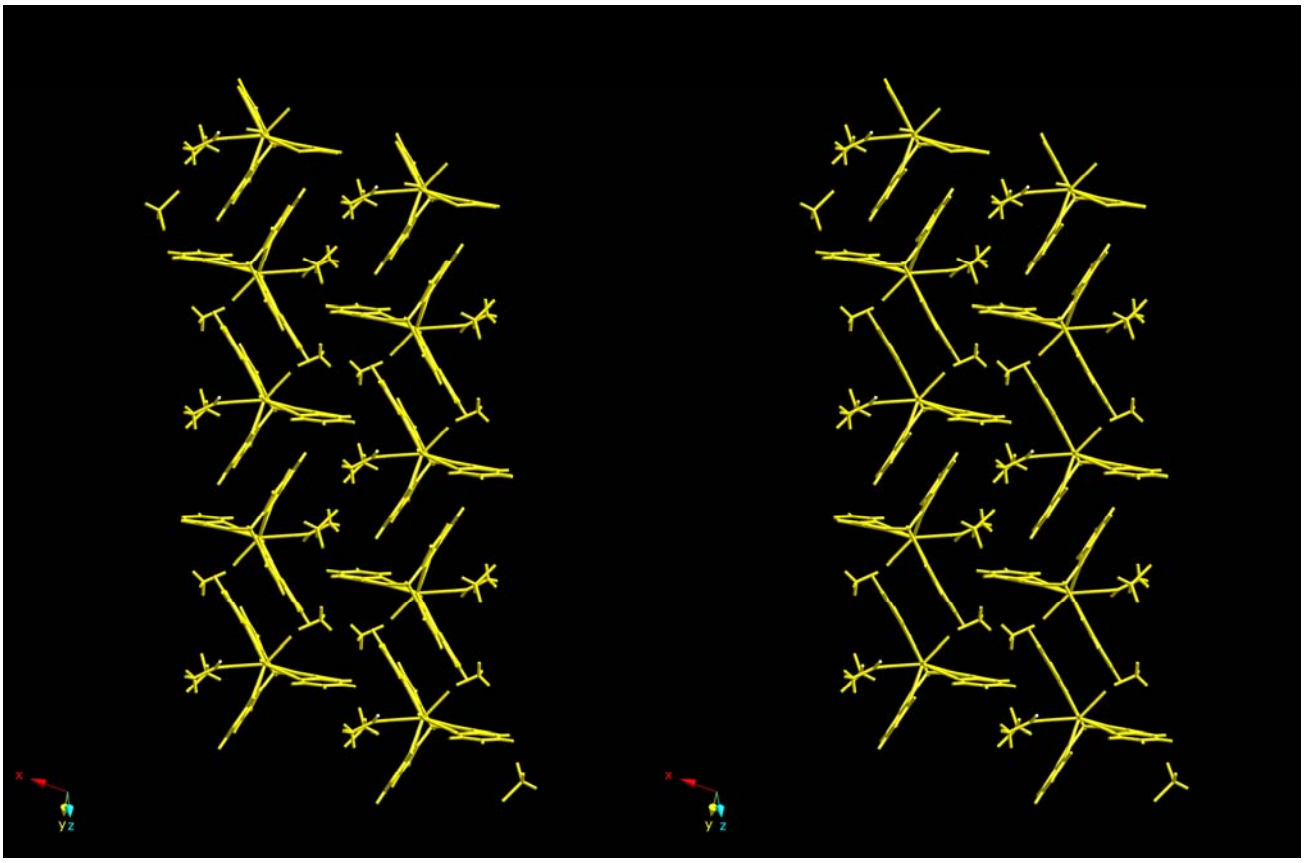

Figure SI 1. Fragment of a pair of parallel stacks in the Gd^{3+} compound **2** (inverse stereoview, stick structure).

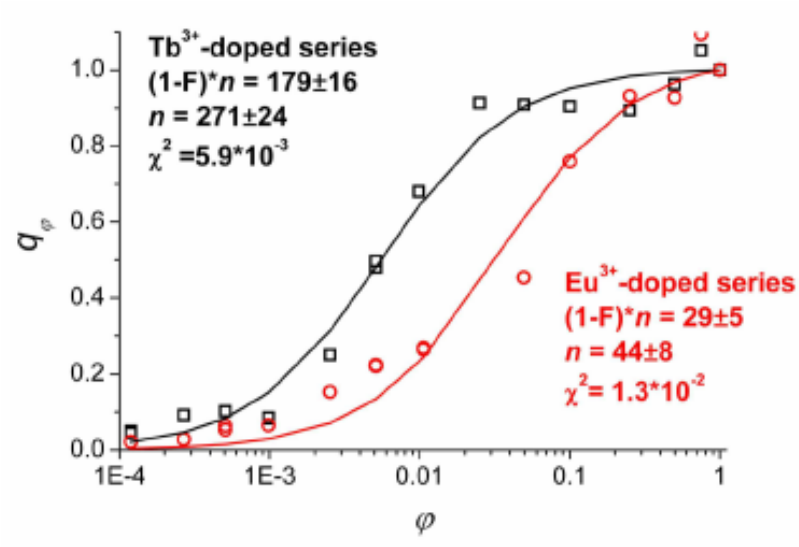

Figure SI 2. Dependence of relative quantum yields (q_φ) on φ for Eu^{3+} and Tb^{3+} in $Tp^{Py}Gd(CH_3CO_2)_2(H_2O)$ (**2**). Solid lines represent the best fits the "hopping" model of equation (4) from the main text.

References for Supporting Information

1. Y. Chen and W.-M. Cai, *Spectrochim. Acta*, 2005, **A62**, 863.

2. Z. Wang, W. Shu, Z. Zhou, Y. Liu and H. Chen, *J. Cent. South Univ. Technol.*, 2003, **4**, 342.