

SUPPORTING INFORMATION

Eu³⁺-and Tb³⁺-Dipicolinate Complexes Covalently Grafted into Kaolinite as Luminescent Functionalized Clay Hybrid Materials

Denis Talarico de Araujo,^{†,*} Katia J. Ciuffi,[†] Eduardo J. Nassar,[†]
Miguel A. Vicente,^{‡,*} Raquel Trujillano,[‡] Paulo S. Calefi,[†]
Vicente Rives,[‡] Emerson H. de Faria^{†,*}

[†]Universidade de Franca, Parque Universitário, 201, 14404-600, Franca, SP, Brazil

[‡]GIR-QUESCAT, Departamento de Química Inorgánica, Universidad de Salamanca, 37008 Salamanca, Spain

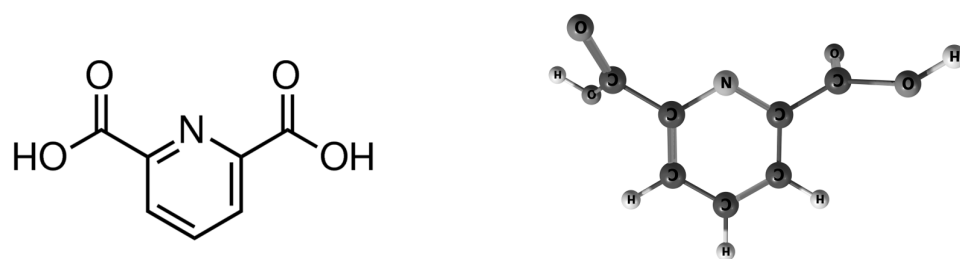


Figure S1. Formula and structure of dipicolinic acid.

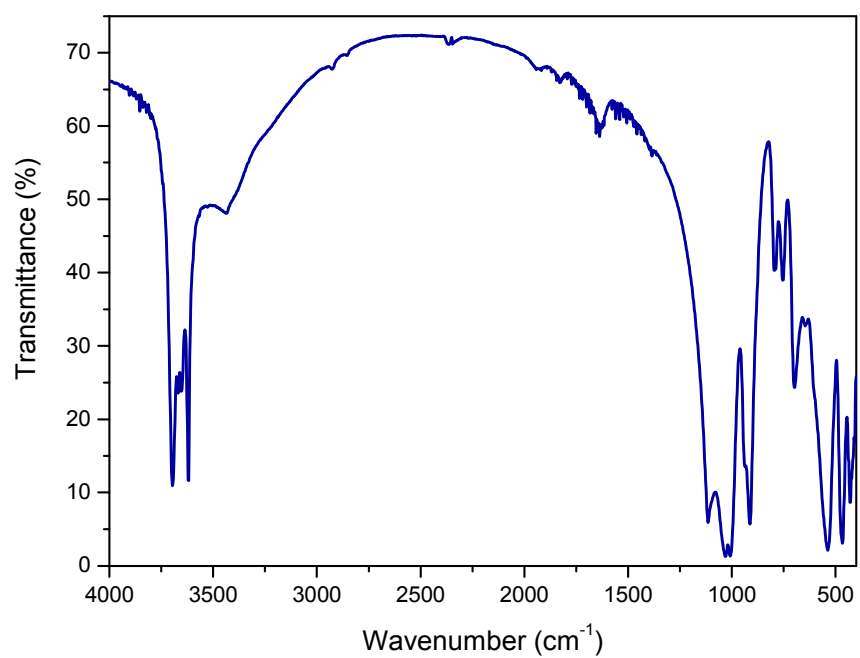
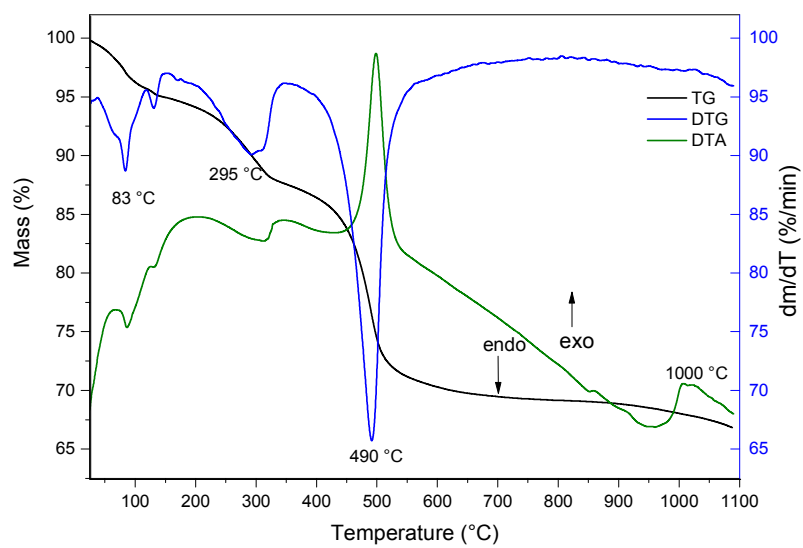
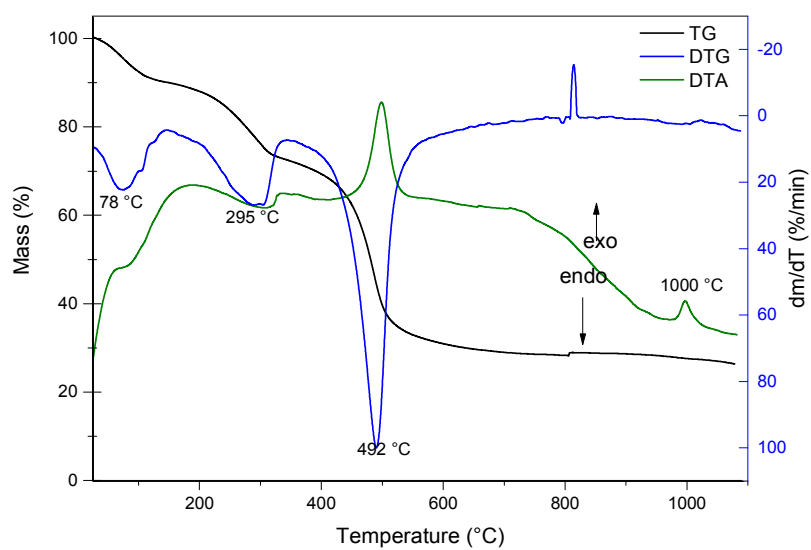


Figure S2: FTIR spectrum of natural kaolinite.



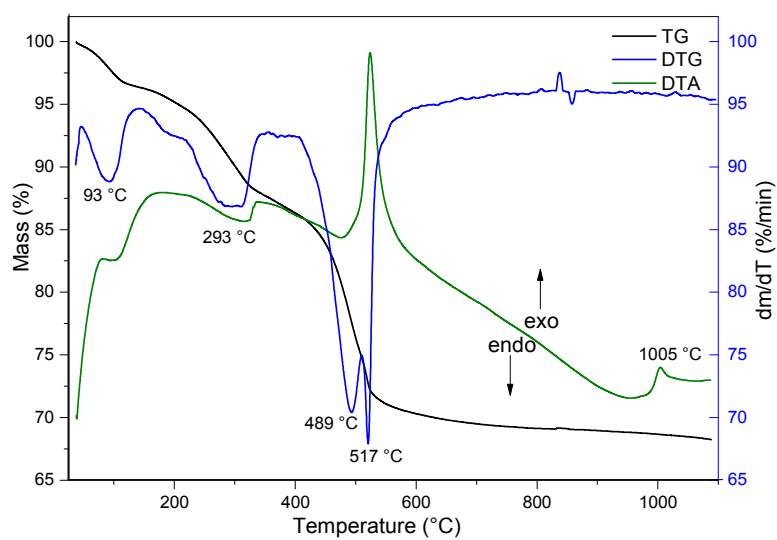


Figure S3. TG (black), DTG (blue), and DTA (green) curves of, from top to bottom, Eu(Ka-dpa)-1, Eu(Ka-dpa)-2 and Tb(Ka-dpa), recorded under air atmosphere and at a heating rate of 20 °C/min.

Table S1. Reaction Ratio (α) for the Different Solids

Sample	α^*
Ka-dpa	86
(Ka-dpa)Eu-1	96
(Ka-dpa)Eu-2	77
(Ka-dpa)Eu-3	75
(Ka-dpa)Tb	77

*The reaction ratio (α) was determined by using the relation $\alpha = I/(I + I_0)$, where I is the d_{001} intensity of the products, and I_0 is the d_{001} intensity of pure kaolinite.

Table S2. Assignment of the Infrared Absorption Bands for Ka-dpa before and after Complexation with Eu^{3+} or Tb^{3+} Ions

	Ka-dpa (cm^{-1})	Ln(Ka-dpa)* (cm^{-1})
$\nu(\text{OH})_{\text{intra}}$	3620	3629
$\nu(\text{OH})_{\text{inter}}$	3698	3698
Si-O	1029, 1050, 1088	1025, 1046, 1091
$\nu \text{ Al-OH}_{\text{intra}}$	912	912
$\nu \text{ Al-OH}_{\text{inter}}$	—	—
SiO_2 or quartz	795	795
$\delta \text{ Si-O-Al}$	755	760
$\delta \text{ Si-O-Si}_{\text{out of plane}}$	685	698
$\delta \text{ Si-O-Al}_{\text{oct}}$	536	536
$\delta \text{ Si-O-Si}_{\text{in plane}}$	467	467
Si-O	432	432
$\nu_{\text{as}} \text{ COO}$	1487, 1545, 1684	1575, 1548
$\nu_{\text{sym}} \text{ COO}$	1334	1400
$\nu \text{ C=C or C=N}_{(\text{aro})}$	1614	1618
$\beta \text{ C-H}$	1295, 1161, 1117, 1090	1295, 1161, 1117, 1090

*Ln = Eu^{3+} or Tb^{3+}