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Preparation, characterization and photophysical properties of hybrid materials from rare earth complexes of phosphonato-substituted DOTAM derivatives

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Supporting Information

Experimental

General

All manipulations were performed using standard inert atmosphere techniques and freshly distilled and degassed solvents according to standard procedures. All chemicals used were of analytical grade and were purchased from Acros and Aldrich-Sigma Co, unless otherwise stated. Silica gel (0.04-0.063 mm, 230-400 mesh ASTM, Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, with fluorescence indicator F254).

All the spectrometers were available at the "Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne" (PACSMUB, Dijon, France) unless otherwise stated. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance 300 and a Bruker Avance II 600. CPMAS ^{31}P NMR spectra were recorded on a Bruker Avance II-500 instrument. All chemical shifts are reported as ppm in δ scale and referenced using residual solvent peak for ^{1}H and ^{13}C and phosphoric acid (H_3PO_4) for ^{31}P NMR as the internal standard. Coupling constants are expressed in Hz. UV-Vis spectra (electronic absorption and diffuse reflectance) were recorded on a Cary 50 and Cary 5E (Varian) spectrophotometers using either 1 cm quartz cells (Hellma) or a Labsphere DRA-CA-50 integration sphere. The samples for the diffuse reflectance measurements were prepared by abrasion of ca. 5-10 mg of the material with 300 mg of dry barium sulfate (Avacado) and the resulting powder was placed in a homemade sample holder. Mass spectra were obtained in linear mode with a Bruker Proflex III MALDI-TOF mass spectrometer using dithranol as matrix and accurate mass measurements (HRMS) were carried out using a Bruker microTOF-Q™ ESI-TOF mass spectrometer. IR spectra were registered on a Bruker IFS 66v Fourier transform spectrophotometer in the range of 4000 - 400 cm^{-1} as KBr pellets. Emission, excitation spectra were measured at room temperature by using a double monochromator Fluorolog FL-1039 instrument from HORIBA Jobin Yvon equipped with a Xe lamp as the excitation source. Emission quantum yield of the complex **$[Eu^{\cdot}L](CF_3SO_3)_3$** was measured relative to cresil violet (φ_f=0.54) {Magde, 1979 #61} in deoxygenated methanol and rodamine 101 ((φ_f=1) {Magde, 1999 #62} in deoxygenated ethanol. The obtained values are φ_f=0.041 and φ_f=0.049, respectively. The average value was calculated. The solution measurements were performed using deoxygenated (by Ar bubbling) anhydrous acetonitrile (spectrophotometric grade, Aldrich). Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method on Micromeritics ASAP2010 analyser. Powder X-ray diffraction analyses of **Ti1-Ti4** and **Zr1** were performed on INEL diffractometer ("Service d'analyse par Diffraction des Rayons X", Institut Carnot de Bourgogne, Dijon, France) with Cu tubes and curve counter detector CPS 120 INEL. All samples gave a diffraction pattern typical for amorphous powders without distinct sharp peaks. Microanalyses were performed on a Fisons EA 1108 CHNS instrument. Microanalyses of Ti, Zr, Eu, P were performed by the Service Central d'Analyse (CNRS, Vernaison, France).

Diethyl 4-amino-1-naphthylphosphonate (1). A 500 ml round bottom flask equipped with a reflux condenser and a magnetic stirrer bar was charged with 1-bromonaphthylamine (20.00 g, 90 mmol), $Pd(OAc)_2$ (414 mg, 1.84 mmol) and PPh_3 (1.41 g, 5.36 mmol). The reaction vessel was evacuated and purged with N_2 three times. Subsequently, abs. ethanol (360 ml), diethyl phosphite (13.7 ml, 1.2 mmol) and triethylamine (18.8 ml, 1.5 mmol) were added *via* syringe. The reaction mixture was stirred at reflux for 24 h. After cooling, the volatiles were evaporated under reduced pressure and the residue was purified by column chromatography on silica (CH_2Cl_2–MeOH 100–3.5) to yield the product as a pink solid in 88% yield (22.12 g). Found: C, 60.47, H, 6.35, N, 5.20. Calc. for $C_{14}H_{18}NO_3P$: C, 60.21; H, 6.50; N 5.02%. δ_H (300 MHz, $CDCl_3$) 1.28 (6H, t, J 7.1), 4.04 (2H, m), 4.10 (2H, m), 4.56 (2H, br s), 6.75 (1H, dd, J 6.9, 1.3), 7.50 (1H, dt, J 6.9, 1.3), 7.58 (1H, dt, J 6.9, 1.3), 7.83 (1H, d, J 8.2), 8.06 (1H, dd, J 15.8, 7.9), 8.47 (1H, dd, J 8.5, 1.3). δ_P {^1H} (121 MHz, $CDCl_3$) 21.33. δ_C {^1H} (75 MHz, $CDCl_3$) 16.55 (2C, d, J_{C-P} 6.7), 61.99 (2C, d, J_{C-P} 5.2), 107.70 (1C, d, J_{C-P} 17.2), 112.54 (1C, d, J_{C-P} 191.7), 121.29 (1C, s), 123.23 (1C, d, J_{C-P} 13.5), 125.34 (1C, s), 127.40 (1C, d, J_{C-P} 3.7), 127.53 (1C, s), 134.27 (1C, d, J_{C-P} 12.0), 136.80 (1C, d, J_{C-P} 10.3), 147.35 (1C, d, 1C, J_{C-P} 3.0).

Diethyl 4-bromoacetamido-1-naphtylphosphonate (2). A 500 ml round bottom flask equipped with a reflux condenser and a magnetic stirrer bar was charged with a solution of diethyl 4-amino-1-naphthylphosphonate (17.99 g; 64 mmol) in 150 ml of CH_2Cl_2 and a solution of K_2CO_3 (22.6 g; 163 mmol) in 80 ml H_2O. The flask was cooled to 0°C and a solution of bromoacetyl bromide (10.2 ml; 120 mmol) in 25 ml CH_2Cl_2 was added dropwise to this mixture. After stirring at 0-5°C for 2 h, the organic layer was washed with water (3x50 ml), dried over $MgSO_4$ and solvent was evaporated *in vacuo*. The residue was washed with pentane (3x50 ml) to give the product as a pink solid (23.5 g; 91% yield). Found C 47.93, H 4.84, N 3.76. Calc. for $C_{16}H_{19}BrNO_4P$: C 48.02, H 4.79, N 3.50%. ν_{max}/cm^{-1} (KBr) 3262, (NH) 1697 (amide I), 1538 (amide II), 1215 (PO), 1017, 955 (POC). δ_H (300 MHz, C_6D_6) 1.00 (6H, t, *J* 7.2), 3.52 (2H, s), 3.95 (4H, m), 7.12 (1H, m), 7.31 (1H, dt, *J* 7.0, 1.0), 7.70 (1H, d, *J* 7.6), 8.18 (1H, m), 8.21 (1H, dd, J_{H-P} 15.6, 8.1), 8.68 (1H, s), 8.96 (1H, d, *J* 8.4). δ_P {^{1}H} (121 MHz, $CDCl_3$) 18.56. δ_C {^{1}H} (75 MHz, $CDCl_3$) 16.41 (2C, d, J_{C-P} 6.6), 29.65 (1C, s), 62.62 (2C, d, J_{C-P} 5.5), 118.96 (1C, d, J_{C-P} 16.4), 121.75 (1C, s), 121.30 (1C, d, J_{C-P} 186.7), 126.73 (1C, s), 127.02 (1C, s, J_{C-P} = 4.2), 127.11 (1C, d, J_{C-P} 10.0), 127.59 (1C, s), 133.26 (1C, d, J_{C-P} 12.3), 134.21 (1C, d, J_{C-P} 8.9), 136.88 (1C, d, J_{C-P} 4.0), 165.49 (1C, s).

1,4,7,10-tetrakis({4-[diethoxyphosphoryl)-1-naphtyl]amino}-2-oxoethyl)-1,4,7,10-tetraazacyclotetradecane (L). A 50 ml round bottom flask equipped with a reflux condenser and a magnetic stirrer bar was charged with a solution of cyclen (0.261 g; 1.5 mmol) in 15 ml of CH_3CN, diethyl 4-bromoacetamido-1-naphtylphosphonate (2.658 g; 6.6 mmol) and N(*i*-Pr)$_2$Et (2.35 mL; 14.2 mmol). The reaction mixture was stirred at room temperature for 24 h. After evaporation of the volatiles *in vacuo*, the residue was purified by column chromatography on silica (CH_2Cl_2–MeOH 20:1) to afford the product as a pink solid (1.89 g; 89% yield). Found C 59.04, H 6.46, N 7.54. Calcd for $C_{72}H_{92}N_8O_{16}P_4$: C 59.66, H 6.40, N 7.73%. ν_{max}/cm^{-1} (KBr) 3260 (NH), 1690 (amide I), 1526 (amide II), 1226 (PO), 1015, 953 (POC). δ_H (300 MHz, $CDCl_3$) 1.21 (24H, t, *J* = 7.2), 3.06 (16H, br. s), 3.39 (8H, s), 4.03 (16H, m), 7.40 (4H, t, *J* 7.5), 7.49 (4H, t, *J* 7.5), 7.89 (8H, m), 8.03 (4H, dd, J_{H-P} 15.3, 7.6), 8.46 (4H, d, *J* 8.4), 9.89 (4H, s). δ_P {^{1}H} (121 MHz, $CDCl_3$) 18.45. δ_C {^{1}H} (75 MHz, $CDCl_3$) 16.25 (8C, d, J_{C-P} 6.7), 53.13 (8C, s), 58.94 (4C, s), 62.25 (8C, d, J_{C-P} 5.2), 118.08 (4C, d, J_{C-P} 16.5), 120.73 (4C, d, J_{C-P} 186.0), 121.74 (4C, s), 126.36 (4C, s), 127.09 (4C, s), 126.72 (4C, d, J_{C-P} 13.5), 127.31 (4C, s), 133.38 (4C, d, J_{C-P} 12 H), 134.46 (4C, d, J_{C-P} 9.0), 137.37 (4C, d, J_{C-P} 2.2), 169.94 (4C, s). MALDI-TOF: 1449.55 $[M+H]^+$.

Preparation of the complexes [Eu·L]X$_3$ (X = SO$_3$CF$_3$, NO$_3$). Lanthanide complexes were prepared by refluxing the Ln salt (triflate or nitrate) and L taken in 1:1 ratio in dry methanol. The reaction progress was controlled by MALDI-TOF spectrometry. After complete disappearance of L signal (2-3 d), solvent was evaporated *in vacuo*. The solid was washed with Et_2O, THF and CH_2Cl_2 and dried for 2 h at 298-313 K under vacuum (1 mbar).

[Eu·L](CF$_3$SO$_3$)$_3$ prepared from 700 mg (0.483 mmol) of **L** in 93% yield (928 mg). Found C, 43.36, H, 4.72, N, 5.25, S, 4.31. Calc. for $C_{75}H_{92}EuF_9N_8O_{25}P_4S_3 \cdot H_2O$ C, 43.58, H, 4.58, N, 5.42, S, 4.65%. ν_{max}/cm^{-1} (KBr) 3445 (OH), 3284 (ν NH), 1628 (CO), 1566 (NH), 1445 (Ar), 1283, 1247, 1225 (PO, SO), 1031, 980 (POC). MALDI-TOF m/z 1600.60 (100) $[M\text{-}3CF_3SO_3\text{-}2H]^+$. ESI-MS m/z 533.83 $[M\text{-}3CF_3SO_3]^{3+}$, 811.23 $[M\text{-}3CF_3SO_3\text{+}Na\text{-}2H]^{2+}$.

[Eu·L](NO$_3$)$_3$ prepared from 200 mg (0.138 mmol) of **L** in 79% yield (200 mg). Found C, 46.93, H, 5.03, N, 8.28. Calc. for $C_{72}H_{92}EuN_{11}O_{25}P_4 \cdot 3H_2O$ C, 46.96, H, 5.36, N, 8.37%. ν_{max}/cm^{-1} (KBr) 3424 (OH), 3258 (ν NH), 1627 (CO), 1565 (NH), 1451 (Ar), 1384 (NO), 1324 (PO), 1228 (PO), 1047, 1018, 967 (POC). MALDI-TOF m/z 1600.60 (100) $[M\text{-}3NO_3\text{-}2H]^+$.

Materials preparation. The immobilization of the europium complexes was carried out by sol-gel process using **[Eu·L]X$_3$ (X = SO$_3$CF$_3$, NO$_3$)** and M(OR)$_4$ (M = Ti, Zr; R = *i*-Pr, *t*-Bu) as molecular precursors in organic medium in the presence of small amount (2-20 equiv) of water. The typical synthetic procedure is described in detail for material **Ti1**.

Material Ti1. Freshly distilled trimethylsilylbromide (232 μl, 1.76 mmol) was added to a suspension of **[Eu·L](SO$_3$CF$_3$)$_3$** (300 mg, 0.15 mmol) in 2 ml of CH_3CN. The reaction was monitored by ^1H NMR analysis. After disappearance of the signals of ethoxy group (3 d), all volatiles were evaporated *in vacuo* and 7.5 ml of a 0.8 M solution of Ti(O-*i*-Pr)$_4$ in THF were added with stirring. A pale-pink suspension was stirred for 30 min and kept in ultrasonic bath for 5 min. A solution of 216 μl of water in 0.5 ml of THF was added with stirring at room temperature. After 30 min of stirring, the gel was kept aside for 2 d. The solid was separated by centrifugation, carefully washed with CH_2Cl_2 (2x10 ml), MeOH (3x10 ml), H_2O(3x10 ml), MeOH(1x10 ml), CH_2Cl_2 (2x10 ml). The material was powdered and dried for 2 d at 60°C *in vacuo* to give 647 mg of material **Ti1** as a white powder Found: C, 11.26; H, 1.59; Eu 1.80; N, 2.14; P, 1.61; S, 0.63; Ti 40.20. Calc. for $C_{57}H_{112}EuF_9N_8O_{147}P_4STi_{51}$: C, 11.28; H, 1.86; Eu 2.50; N, 1.85; P, 2.04; S, 0.53; Ti 40.23%. . ν_{max}/cm^{-1} (KBr) 3500 (OH), 1622 (CO), 1557 (NH), 1423 (Ar), 1249, 1175 (PO, SO), 1031 (POTi). ^{31}P CP MAS NMR δ_P $\{^1H\}$ (202 MHz) 13.6. UV-Vis diffuse reflectance/nm 320.

Material Ti2 was prepared from 100 mg (0.049 mmol) of **[Eu·L](SO$_3$CF$_3$)$_3$** and 278 mg (0.98 mmol) of Ti(O-*i*-Pr)$_4$ under the same conditions as described for the synthesis of **Ti1**. 139 mg of a white powder were obtained. Found: C, 17.57; H, 3.20; Eu 3.05; N, 2.77; P, 2.71; S, 0.63; Ti 30.68. Calc. for $C_{57}H_{102}EuF_9N_8O_{90}P_4STi_{25}$: C, 17.55; H, 2.64; Eu 3.90; N, 2.87; P 3.18; S, 0.82; Ti 30.68%.

Material Ti3. **[Eu·L](SO$_3$CF$_3$)$_3$** (100 mg, 0.049 mmol) was reacted with trimetylsilyl bromide as described above. After evaporation of all volatiles *in vacuo*, the residue was dissolved in 2.6 ml of MeOH to give a transparent solution, and 583 µl of Ti(O-*i*-Pr)$_4$ were added with stirring. After 30 min of stirring at room temperature, 700 µl of water were added, and the solution was stirred for additional 30 min. The gel was allowed to age for 3 d. Addition of 7 ml of water led to the formation of fine suspension which could not have been centrifugated. The solution was concentrated *in vacuo*, then 15 ml of toluene were added and the mixture was placed in Dean-Stark apparatus and refluxed for 24 h to complete the co-condensation reaction. The solid was separated by centrifugation, carefully washed with CH_2Cl_2 (2x10 ml), MeOH (3x10 ml), H_2O(3x10 ml), MeOH(2x10 ml), CH_2Cl_2 (2x10 ml) . The material was powdered and dried for 2 d at 60°C in vacuo to give 222 mg of a white powder. ν_{max}/cm^{-1} (KBr) 3500 (OH), 1623 (CO), 1558 (NH), 1399 (Ar), 1255, 1136 (PO, SO), 1032 (POTi). ^{31}P CP MAS NMR δ_P {^{1}H} (202 MHz) 13.6. Found: C, 14.77; H, 2.20; Eu 2.22; N, 1.88; P, 1.99; S, 0.42; Ti 35.24. Calc. for $C_{72}H_{162}EuF_9N_8O_{143}P_4STi_{44}$: C, 14.66; H, 2.27; Eu 2.58; N, 1.90; P 2.10; S, 0.54; Ti 35.70%.

Ti4 was prepared from 52 mg (0.028 mmol) of **[Eu·L](NO$_3$)$_3$** and 318 mg (1.12 mmol) of Ti(O-*i*-Pr)$_4$ under the same conditions as described for the synthesis of **Ti3**. 120 mg of white powder were obtained. ν_{max}/cm^{-1} (KBr) 3500 (OH), 1623 (CO), 1561 (NH), 1460 (Ar), 1395 (NO), 1079, 1038 (POTi).Found: C, 14.54; H, 2.72; Eu 2.14; N, 2.46; P, 1.74; Ti 38.04. Calc. for $C_{86}H_{192}EuN_{11}O_{173}P_4Ti_{56}$: C, 14.54; H, 2.72; Eu 2.14; N, 2.17; P 1.74; Ti 37.73 %.

Zr1. **[Eu·L](SO$_3$CF$_3$)$_3$** (100 mg, 0.049 mmol) was reacted with trimethylsilyl bromide as described above. After evaporation of all volatiles *in vacuo*, 894 ml (938 mg) of Zr(O-*n*-Bu)$_4$ in *n*-BuOH (0.8 w, 748 mg (1.95 mmol) of Zr(O-*n*-Bu)$_4$) and 2 ml of *n*-BuOH were added with stirring. After 30 min of stirring at room temperature, 700 µl of water were added, and the mixture was stirred for additional 30 min giving a white suspension. The suspension was kept aside for 3 d, after that 27 ml of water was added and the solid was separated by centrifugation, carefully washed with CH_2Cl_2 (2x10 ml), MeOH (3x10 ml), H_2O(3x10 ml), MeOH(2x10 ml), CH_2Cl_2 (2x10 ml). The material was powdered and dried for 2 d at 60°C *in vacuo* to give 384 mg of a white powder. ν_{max}/cm^{-1} (KBr) 3450 (OH), 1618 (CO), 1558 (NH), 1421 (Ar), 1255, 1171 (PO, SO), 1032 (POTi). Found: C, 9.50; H, 1.55; Eu 1.55; N, 1.24; P, 1.39; S, 1.53; Zr 41.80. Calc. for $C_{67}H_{264}EuF_9N_8O_{195}P_4SZr_{38}$: C, 9.68; H, 3.20; Eu 1.83; N, 1.35; P 1.49; S, 1.16; Zr 41.70 %. UV-Vis diffuse reflectance/nm 320.