One Step Reaction for Screening of Chromophores to Improve Luminescence of Lanthanide Complexes

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Abstract: A stable cyclen-based Eu(III) complex precursor is synthesized as a fast-screening tool and template to select suitable chromophores for sensitizing Eu(III) luminescence by a one-step coupling reaction. A library of chromophores has been synthesized and screened by either Sonogashira or Suzuki reaction to confirm proof of concept and the ease of this methodology. The photophysical properties of these corresponding complexes as well as their potential properties for biological applications has been assessed.

Introduction

Luminescent lanthanide ions possess fascinating optical properties that make them ideal tags/probes in biological applications.[1] They have characteristic emission bands and large Richardson shifts,[2] making them easily distinguishable from organic moiety signals. Their long-lived luminescence lifetimes (μs – ms) allow the use of time-gated technique to eliminate the short-lived (ns) background fluorescence to improve the signal-to-noise ratio significantly. The f-f transitions of lanthanide ions are Laporte-forbidden, so they have low molar absorption coefficients ($\varepsilon < 10\ M^{-1}cm^{-1}$) and requires the use of an organic chromophore as sensitizer to absorb light energy and transfer the energy to the lanthanide ions (so-called antenna effect). More importantly, as the lanthanide ions are good triplet state quenchers, photobleaching – which is particularly frustrating in time-lapse microscopy – of the chromophore could be substantially reduced.[3] Despite some good chromophores being published, complexes with suitable absorption wavelength, satisfactory brightness ($B = \varepsilon \times \Phi$)[4] and stability for bioapplications are still rare.

In 2015, Borbas's group reported a fast method for antenna testing.[5] To overcome the difficulty of synthesizing complexes with coumarin chromophores with the chelate of 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A), they screened the chromophores' performance in a dipicolinate (dpa) framework. It is regarded that the photophysical properties of the chromophore in the dipicolinate system would be maintained in the DO3A system. An in-depth study on the photophysical properties of the optimized chromophores are presented in a recent publication.[6]

However, to obtain a highly luminescent lanthanide complex in aqueous solutions, two more factors need to be considered: First, vibrational energy transfer to higher harmonics of water deactivates the excited state of the lanthanide.[3] Normally in an octadentate lanthanide complex, one water molecule is coordinated onto the lanthanide ion, whereas the luminescence of nonadentate lanthanide complexes is regarded as less effected in aqueous solutions due to the additional coordination. Second, the sensitization efficiency exhibits a $1/r^6$ dependence with r, the distance between the chromophore and the lanthanide ion;[7] hence for most highly luminescent lanthanide complexes, the chromophore is directly coordinated onto the metal ion.[8]

Based on Parker's work on a series of nonadentate lanthanide complexes with a pyridylmethylphosphinate chromophore[9] to shift the maximum absorbance to around 350 nm,[10] we incorporated the brightest pyridylmethylphosphinate chromophore (Φ = 55% in methanol for Eu(III)) onto our chiral DO3A chelators[11] and a highly luminescent Eu(III) complex (Φ = 22% in water) with very efficient energy transfer (η_{sens} = 73%) was obtained; the luminescent quantum yield is much higher than the 6.9% obtained for the achiral DO3A complex. Further examination revealed no change to the coordination center with no water molecules coordinated to the metal ion. Upon further studies, the complex was stable even in the presence of 1000 equivalents of competitive ligand of diethylenetriaminepentaacetic acid (DTPA).[11] While introducing chiral moieties on the DO3A backbone is a proven strategy to improve a complex's luminescent properties,[11] structural modification to the chromophore is always an alternative especially if the intrinsic properties of the backbone is already optimized.

As a result, we herein present a one-step reaction screening of chromophores for a DO3A-based Eu(III) system. Eu(III) was selected due to the hypersensitive and visible emission luminescent profile relative to the other lanthanides[12] where its ideal excitation state and longer emission window in the red region allows easy detection. As shown in **Figure 1**, we designed a europium complex **EuBR** with a bromide on the 4-position of the pyridylmethylphosphinate moiety. As this complex is very stable, we hypothesized it could sustain coupling reaction conditions, such as Sonogashira[13] or Suzuki[14] reactions, and the performance of the chromophores with an expanded electronic conjugation as a Eu(III) antenna could be tested easily by optical spectroscopy.

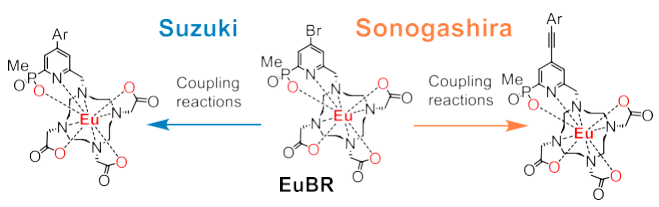
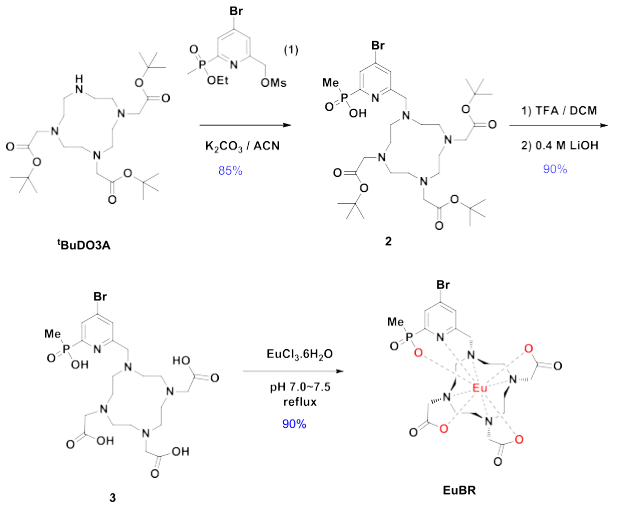


Figure 1. EuBR as key intermediate for screening of chromophores.(the counterions are not depicted for clarity)

Results and Discussion

Synthesis of EuBR

The key intermediate EuBR was synthesized from the starting material of ^{t}BuDO3A compound (**Scheme 1**). It was reacted with **1** to obtain **2**, which was purified by adjusting the pH. It was first dissolved in dilute hydrochloric acid and the impurities from the compound **1** was extracted away by ethyl acetate, then the pH of the aqueous layer was adjusted to 8 by sodium bicarbonate, and the product was extracted by dichloromethane, dried and concentrated to obtain the desired product with good purity. **2** was deprotected by trifluoroacetic acid first to remove the ^{t}Butyl esters, then the phosphate ester was removed by sodium hydroxide. Complexation with Eu(III) chloride hexahydrate was performed at neutral condition.



Scheme 1. The synthesis of **EuBR** (the counterions are not depicted for clarity)

Synthesis of EuL1 - EuL16

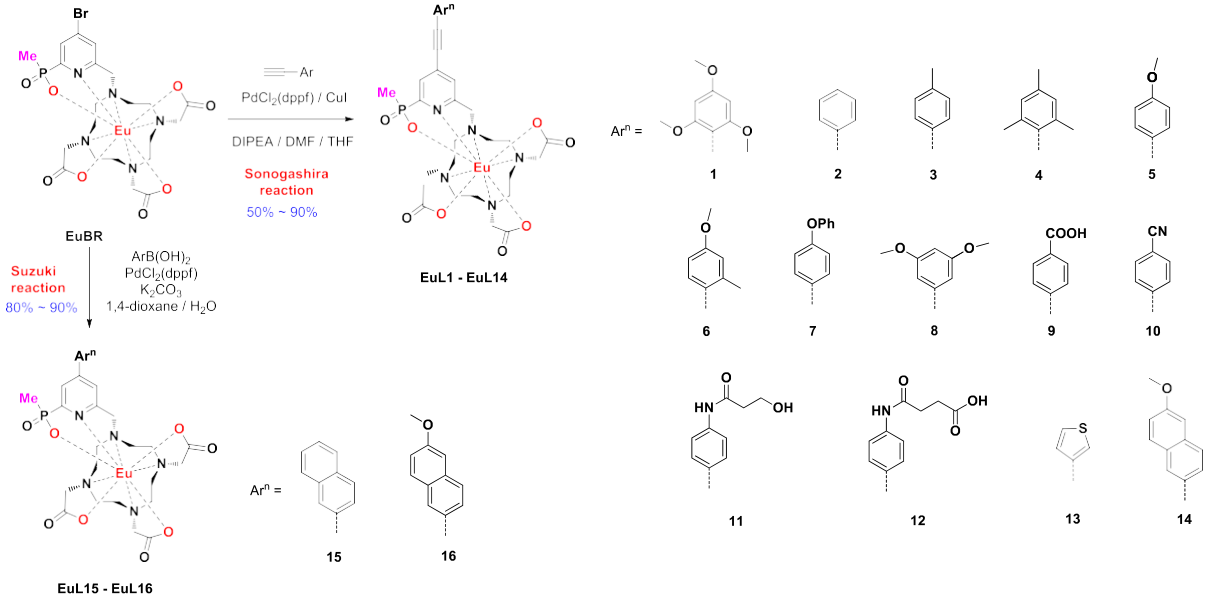
The complexes of **EuL1 - EuL14 (Scheme 2)** were synthesized from **EuBR**, it was reacted with alkynyl compounds through Sonogashira reactions. Using $PdCl_2$(dppf) and CuI as co-catalyst and DIPEA as base in a mixed DMF and THF solution, the reaction was carried out at 60 – 70°C overnight, which was monitored by reversed-phase HPLC. After the starting material of **EuBR** reacted completely, the resultant solution was purified by reversed-phase semi-preparative HPLC to obtain pure complexes. Complexes **EuL15** and **EuL16** were synthesized through Suzuki reactions. It should be noted that as there was no competitive reaction with Suzuki reactions, so ideally, multi-aromatic boronic acids could be reacted with **EuBR** in one batch, and hence only a one-pot reaction is required to obtain a series of complexes with different chromophores. Nonetheless, the Sonogashira reaction is relatively more difficult, as undesired coupling reactions may take place between the alkynyl compounds, especially when the reaction mixtures were not degassed completely.

Photophysical properties of EuL1 - EuL16

A library of compounds was explored by the above screening reactions, with variations among the conjugation length, electron-donating or -withdrawing properties or functional groups for further chemical conjugation. The ligands could be divided into three main categories: **L1-L10** studies the effect of the different substituents of an alkynyl phenyl ring; **L11-L12** are functionalized phenyl rings for potential conjugations; and **L13-16** explores other conjugated systems. The photophysical data of the complexes are summarized in **Table 1**.

UV-visible absorption

The structural changes on the phenyl ring were adequately reflected in the absorption maxima. Using **EuL2** as a reference structure, its absorption maximum is at a relatively high energy at 303 nm, assigned as the π-π^* transition of the local excited state of the ligand. The addition of one electron-donating methoxy substituent on the para-position (relative to the alkynyl group hereafter) in **EuL5** caused a red-shift in the absorption maximum to 332 nm. A phenoxy group of **EuL7** led to a shift to 328 nm while a weakly donating methyl substituent in **EuL3** caused a similar shift to 330 nm. A combination of the methoxy and the methyl group in **EuL6** shifted the maximum further to 338 nm. Further substituents at



Scheme 2. One-step reaction screening of chromophores (the counterions are not depicted for clarity).

Table 1. Photophysical properties of **EuL1-EuL16**

Complex	λ_{abs} (max)	τ_{HEPES} (ms)	τ_{H2O} (ms)	τ_{D2O} (ms)	q_{H2O}[a],[b]	Φ_{HEPES}	τ_{rad} (ms)	Φ^{Eu}_{Eu}	η_{sens}
EuL1	353	1.00	1.01	1.44	0.06, 0	0.069	4.22	0.24	0.29
EuL2	303	1.27				[c]			
EuL3	330	1.27	1.04	1.92	0.23, 0.15	0.19	4.30	0.29	0.64
EuL4	332	1.23	1.02	1.95	026, 0.17	0.24	4.45	0.28	0.87
EuL5	332	1.25	1.15	1.37	0, 0	0.20	4.28	0.29	0.69
EuL6	338	1.25	1.16	1.42	0, 0	0.16	4.39	0.29	0.54
EuL7	328	1.24	1.12	1.96	0.16, 0.08	0.23	4.29	0.29	0.79
EuL8	308	1.20	1.17	1.95	0.11, 0.04	0.20	4.63	0.26	0.75
EuL9	321	1.25	1.23	1.98	0.07, 0	0.20[d]	4.18	0.30	0.660
EuL10	300	1.27	1.27	2.00	0.04, 0	0.24 [d]	4.44	0.29	0.85
EuL11	337	1.23	1.14	1.90	0.12, 0.05	0.17	4.29	0.29	0.60
EuL12	330	1.20	1.03	1.91	0.24, 0.15	0.20	4.27	0.28	0.71
EuL13	318	1.22	1.11	1.99	0.18, 0.10	0.23	4.42	0.28	0.82
EuL14	335	0.57	0.57	0.81	0.32, 0.23	0.073	4.30	0.13	0.55
EuL15	306	1.27	1.25	1.98	0.05, 0	0.18	4.58	0.28	0.65
EuL16	327	1.09	1.11	1.64	0.05, 0	0.13	4.32	0.25	0.50

[a] Determined by Parker's equation.[17] [b] Determined by Horrocks' equation.[18] [c] Did not measure due to very weak luminescence. [d] Measured against quinine sulfate (0.1 N H_2SO_4, λ_{ex} = 310 nm, Φ = 0.53).[11] Estimated errors of quantum yield or lifetime are ±15% and ±10%, respectively.

the meta-positions in **EuL1** from **EuL5** shifted the maximum to 353 nm whereas three methyl substituents in **EuL4** also led to a large devitation from **EuL1**. These wavelength shifts are consistent with the introduction of an intraligand charge-transfer state that is also observed in Maury's[15] and Takalo's[16] studies on extended families of their respective antennae, hence the lack of any electronic extension *para* to the alkynyl group on **EuL2** resulted in no ILCT transitions. Conversely, and expectedly, introducing methoxy groups at ortho-positions in **EuL8** resulted in a negligible shift of 5 nm to 308 nm to the local excited state.[15] The addition of a carboxylic acid in **EuL9** also gave a red-shift of 18 nm whereas the strongly electron-withdrawing cyano group in **EuL10** even caused a slight blue shift from the **EuL2** template to 300 nm. Both **EuL11** and **EuL12** featured a moderate electron withdrawing amide group and their shift in absorption is relatively similar at 337 nm and 330 nm respectively; as we purposely designed an aliphatic linker to segregate the conjugation system with the strongly electron-withdrawing functional groups.

In **EuL13**, changing the phenyl ring to a thiophene ring with better electron localization resulted in a modest red-shift to 318 nm. Extending the conjugation using a fused ring using a 2-methoxylnaphthalene group in **EuL14** resulted in a red-shift of the absorption maximum to 335 nm. The methoxy substituent proved to be significant when comparing between **EuL15** and **EuL16** – which were synthesized by Suzuki reaction and lack the alkynyl bridge – and the electron donating group resulted in a further 21 nm red-shift of the absorption maximum to 327 nm for **EuL16** while that of **EuL15** was only at 306 nm. Since the absorption properties of the complex determine the excitation wavelength(s) used; therefore, by simply conjugating the designed substrates with Sonogashira or Suzuki reactions, one would be able to quickly determine whether high energy excitation could be avoided.

Luminescence lifetimes and quantum yields

Except for **EuL14**, all complexes exhibited luminescence lifetimes – measured at the $^5D_0 \rightarrow {}^7F_2$ transition in both 0.1 HEPES buffer (pH 7.4) and milli-Q water – longer than 1 ms. The number of water molecules coordinated to the inner sphere of Eu(III) (*q*) was determined by Parker's[14] and Horrocks'[19] modified equations, which explains the short lifetimes and low quantum yield of **EuL14** as it has the highest *q* values, indicating increased non-radiative quenching by high energy O-H oscillators. The luminescent quantum yields of the complexes are also quite impressive, sitting in the range between 17% to 25%, with a few exceptions in **EuL1**, **EuL14** and **EuL16**. Delving deeper into the intrinsic quantum yields – defined as the quantum yield *via* direct excitation of the Eu(III) center and obtained through calculations – and the sensitization efficiencies reveals more information behind the mediocre quantum yields. The intrinsic quantum yields of **EuL1**, **EuL6** and **EuL16** are in fact quite similar to those of other compounds, only to find their sensitization efficiencies at 29%, 54% and 50% respectively, suggesting that the coordination environment is not responsible for the low quantum yields but instead the chromophore. For **EuL14**, the intrinsic quantum yield (13%) is significantly lower than the rest of the compounds, reinforcing our proposal that the Eu(III) center is in an environment with dominant non-radiative transitions. For the other

compounds, the intrinsic quantum yields and the sensitization efficiencies are near 30% and 70%-80%, again demonstrating that the coordination environment, the Eu-chromophore distance particularly, is retained after the coupling reactions, offering a robust and stable scaffold that allows fair comparison between chromophores. Among the complexes, **EuL4** and **EuL10** have the highest quantum yields at *ca.* 24% and similar luminescence lifetimes; however, for a luminescent lanthanide complex to be used in biological applications, the excitation wavelength must also be considered as that tissue damage by high energy UV could be alleviated and the excitation light could also penetrate better through the biological tissues with a lower excitation energy. Therefore, since the absorption maximum of **EuL10** is at 300 nm, compared to that of **EuL4** at 332 nm, **EuL4** would be more suitable for biological applications. Furthermore, not only does **EuL12** have decent overall luminescent properties, it also bears a carboxylic acid for conjugation, thus becoming another good candidate for future development into more sophisticated bio-probes with enhanced cellular-related properties such as cellular localization, penetration and up-take.

Conclusions

We have successfully developed a stable system for the screening of luminescence sensitizers for Eu(III) by performing Sonogashira and Suzuki coupling reactions. Various chromophores were readily incorporated by reacting appropriate substrates with our scaffold **EuBR** and their photophysical properties could be characterized much quicker than the conventional way of synthesizing all complexes from an intermediate at an earlier stage of the synthetic route. Our work also demonstrated the potential of fast-screening chromophores for designated applications without using expensive hardware for optimization of photophysical properties by computational means. With a library of data of carefully designed complexes obtained with less synthetic work, the most suitable design could be screened conveniently and the biggest advantage of our screening strategy lies in the retention of coordination mode of the Eu(III)-based scaffold which directly influences the photophysical properties.

Experimental Section

Materials and general methods

Unless noted otherwise, all chemicals were of reagent–grade and were purchased from Sigma–Aldrich or Acros Organics and used without further purification. Davisil silica gel (40–63 m) was obtained from Grace Davison. High–performance liquid chromatography (HPLC) was performed using an Agilent 1100 Series or Waters ACQUITY UPLC H-class system apparatus with a UV visible detector with UV detection from 220 to 360 nm by a Vision HT C18 HL 5 mm column. Reverse–phase semi–preparative purification was performed on the Waters system with UV detection from 220 to 360 nm using the columns of Waters XBridge® Prep C18 5 μm OBD™ (19 x 250 mm) or (19 x 100 mm). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer (at 400 MHz, 100 MHz and 162 MHz respectively). The ^{1}H and ^{13}C NMR chemical shifts were referenced to solvent residual peaks. Mass spectra, reported as *m/z*, were obtained on a Micromass Q–TOF 2 mass spectrometer; HRMS were performed on an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS.

Synthetic procedures

Synthesis of compound **1**: A solution of ethyl (4-bromo-6-(hydroxymethyl)pyridin-2-yl)(methyl)phosphinate[8b] (335 mg) in dichloromethane (5 ml) was cooled to 0 – 10°C by ice/water bath, then methanesulfonyl chloride (0.13 ml) was added dropwise within 5 min. After reacting for 20 min, the mixture was quenched by adding 20 ml of water, diluted with 20 ml of dichloromethane, the organic phase was washed with 20 ml of water again, then washed with 20 ml of brine, dried with anhydrous magnesium sulfate. After filtration and concentration, the obtained intermediate (400 mg) was used to the next step reaction directly without any further purification.

Synthesis of compound **2**: Into a mixture of ^{t}BuDO3A (420 mg), K_2CO_3 (322 mg) and dry acetonitrile (5 ml), compound **1** (380 mg) was added, then reacting at room temperature for 12 h. A filtration was performed, the filtrate was concentrated, the residue was dissolved into 60 ml of 1% of HCl, extracted with ethyl acetate (20 ml) for two times, then the aqueous solution was adjusted pH to 8.0 by the solution of sodium bicarbonate, extracted with dichloromethane (20 ml) for two times, the combined dichloromethane solution was washed with brine (10 ml), dried with anhydrous magnesium sulfate, after filtration and concentration, this resulted in the compound **2** (534 mg, yield 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.04 (d, *J* = 5.2 Hz, 1H), 4.22 – 4.18 (m, 1H), 4.01 – 3.95 (m, 1H), 3.87 (s, 2H), 3.41 – 2.14 (m, 22H), 1.74 (d, *J* = 15.3 Hz, 3H), 1.56 -1.39 (m, 27H), 1.25 (dd, *J* = 13.7, 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.00, 171.03, 163.85, 160.63, 133.94, 129.59, 128.97, 128.55, 81.92, 80.54, 61.45, 61.39, 58.77, 56.71, 56.33, 56.03, 55.94, 53.22, 52.73, 52.36, 51.82, 28.25, 28.03, 16.33, 12.92. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.89. HRMS (ESI-TOF): *m/z*: calcd for C35H62BrN5O8P: 790.35198 $[M+H]^+$; found: 792.3504.

Synthesis of the ligands **3**. The compound **2** (500 mg) was dissolved in dichloromethane (3 ml) and TFA (3 ml), after stirring at room temperature for 12 h (monitored by HPLC), the reaction mixture was concentrated (crude NMR showed the tetra-butyl groups were removed completely (^{1}H NMR (400 MHz, D_2O) δ 7.42 (d, *J* = 5.4 Hz, 1H), 7.35 (s, 1H), 3.55 – 2.36 (m, 26H), 1.12 (d, *J* = 15.0 Hz, 3H), 0.55 (t, *J* = 7.0 Hz, 3H)). Then the residue was dissolved in 2 ml of water and 2 ml of methanol, LiOH (100 mg) was added, the mixture was reacted at room temperature for 2 h (HPLC showed the deprotection was completely). Then the solution was adjusted pH to 7.0 by 2% of HCl, after concentration, the obtained solid was passed through a C18 column to remove the inorganic salts, after freeze drying to get the ligand **3** as a white solid (319 mg, yield 85%). ^{1}H NMR (400 MHz, D_2O) δ 7.91 (s, 1H), 7.89 (s, 1H), 3.89 – 2.05 (m, 24H), 1.47 (d, *J* = 14.4 Hz, 3H). ^{13}C NMR (100 MHz, D_2O) δ 180.43, 179.87, 179.75, 179.16, 161.04, 159.57, 159.12, 134.48, 134.35, 129.35, 127.82, 127.62, 58.86, 58.09, 51.61, 51.40, 50.34, 49.42, 49.01, 16.17, 15.17. ^{1}H NMR (400 MHz, MeOD) δ 7.80 (d, *J* = 4.9 Hz, 1H), 7.66 – 7.56 (m, 1H), 4.23 (s, 2H), 3.18 – 1.90 (m, 24H), 1.29 (d, *J* = 14.5 Hz, 3H). ^{13}C NMR (100 MHz, MeOD) δ 171.06, 163.39, 161.92, 155.20, 152.93, 145.21, 134.10, 133.98, 132.28, 128.62, 127.87, 127.67, 126.21, 125.68, 56.53, 54.51, 49.79, 49.46, 15.60, 14.59. ^{31}P NMR (162 MHz, MeOD) δ 25.90. HRMS (ESI-TOF): *m/z*: calcd for C21H34BrN5O8P: 594.13288 $[M+H]^+$; found: 594.1325.

Synthesis of the complex **EuBR**: The ligand **3** (100 mg) was dissolved in 2 ml of water, then added the europium salt of $EuCl_3$. $6H_2O$ (65 mg), then the pH of the solution was adjusted to 7.0, after reacting at 80°C for 12 h, which was monitored by HPLC to get fully complexation. The mixture was then cooled down and adjusted the pH to 10 (by 0.01 M NaOH solution), then filtered through a 0.2 μm of filter to remove the free europium ion. Then the salt impurities were removed by C18 column on a semi-prep HPLC system. The freeze dried product was in the form of white solid (112 mg, yield 90%). HRMS of **EuBR** (ESI-TOF): *m/z*: calcd for C21H31BrEuN5O8P: 744.03065 $[M+2H]^+$; found: 744.0284. To check the

purity of **EuBR**, Lu(III) complex was also obtained through the same procedure. NMR of **LuBR**: ^{1}H NMR (400 MHz, D_2O) δ 8.08 (s, 1H), 7.90 (s, 1H), 4.10 – 2.29 (m, 24H), 1.72 (d, *J* = 14.8 Hz, 3H). ^{31}P NMR (162 MHz, D_2O) δ 34.49. HRMS of **LuBR** (ESI-TOF): *m/z*: calcd for $C_{21}H_{31}BrLuN_5O_8P$: 766.0502 $[M+2H]^+$; found: 766.0493.

General procedure of the Sonogashira reactions for chromophore screening: Into a nitrogen protected flask was added **EuBR** (5 mg), dry DMF (1 ml) and THF (1 ml), then added the alkyne compound (1.5 eq.), then added DIPEA (0.3 ml), after that, the catalysts of $PdCl_2$(dppf) (0.05 eq.) and CuI (0.1 eq.) were added into the reaction mixture together, then set the reaction temperature at 60 – 70°C for overnight. HPLC showed the starting material of **EuBR** was consumed completely, the reaction mixture was concentrated and the residue was purified by semi-prep-HPLC. The yields were around 50% - 90%, which depended on the isolation efficiency.

General procedure of the Suzuki reactions for chromophore screening: Into a nitrogen protected solution of **EuBR** (5 mg) in 1,4-dioxane (1 ml) and water (1 ml) was added K_2CO_3 (1.9 mg), then the borane compound was added, the catalyst of $PdCl_2$(dppf) (0.05 eq.) was added at last, after reacting at 60 – 70°C for overnight, the temperature was cooled down and the mixture was washed with ethyl acetate (1 ml) for two times. The aqueous solution was purified by semi-prep-HPLC directly. The isolated yields for **EuL15** and **EuL16** were 80% and 90% respectively.

Photophysical measurements

0.1 M HEPES solution was prepared by diluting stock 1 M buffer from Fisher Scientific with milli-Q water. Solution samples of ca. 0.1 absorbances at 350 nm (310 nm for EuL9 and EuL10) were prepared for visible photoluminescence measurements. Separate samples were used for 1) UV-vis, emission and excitation scans; 2) luminescence lifetime measurements and 3) quantum yield measurements. All room temperature solution measurements were done a quartz cuvette (Starna) of 1 cm path length. UV-vis spectra were recorded with an HP UV-8453 spectrophotometer. Room temperature photoluminescence measurements data obtained with Edinburgh Instruments FLSP920 spectrophotometer equipped with a Xe900 continuous xenon lamp (450 W), xenon flashlamp (60 W) and a Hamamatsu R928P cooled at -20°C. Luminescence lifetimes of visible emissions were measured with FLSP290 and fitted with Origin. All photophysical measurements were averages of triplicate.

The intrinsic quantum yield of the complex was also calculated using the below equations to gain more insight into the sensitization processes:[20]

$$\Phi_L^{Ln} = \Phi_{Ln}^{Ln} \cdot \eta_{sens} \quad (1)$$

$$\Phi_{Ln}^{Ln} \quad \frac{\tau_{obs}}{\tau_{rad}} \quad (2)$$

$$\frac{1}{\tau_{rad}} = {}_{MD} \cdot n^3 \left(\frac{I_{tot}}{I_{MD}}\right) \quad (3)$$

The overall quantum yield (Φ_L^{Ln}) is the product of intrinsic quantum yield (Φ_L^{Ln}) and sensitization efficiency (η_{sens}). The reciprocal of the radiative lifetime ($1/\tau_{rad}$) could be calculated by equation (3), where AMD denotes the spontaneous emission probability of the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_0$ for Eu(III)) which is a constant equal to 14.65 s^{-1}, n is the refractive index of the medium and I_{tot} and I_{MD} are the integrated intensities of the total $^5D_0 \rightarrow {}^7F_J$ transitions and the magnetic dipole transition respectively.

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Keywords: Lanthanide complex • europium complex • one step reaction • screening chromophore • DO3A

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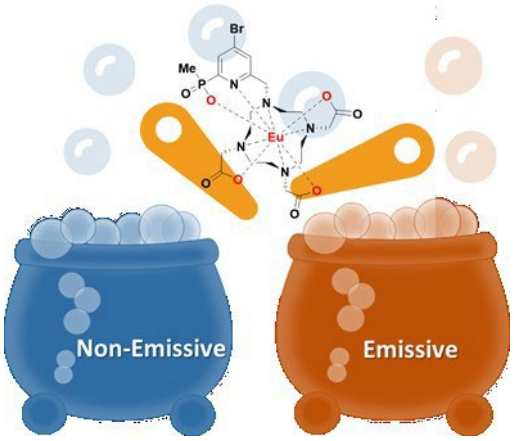

A stable lanthanide template as a fast-screening tool to select suitable chromophores for sensitizing of Eu(III) luminescence by a one-step coupling reaction.