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Syntheses of dibenzo-18-crown-6 lariat isomers and their complexation with lanthanoid nitrates

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Two constitutional isomers of dibenzo-18-crown-6 derivatives (**6** and **7**) were synthesised and their binding behaviours towards trivalent lanthanoid cations (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} and Tb^{3+}) were investigated. Both isomers expressed better binding affinities towards Sm^{3+} and Tb^{3+} than a group of other lanthanoids, as measured by the ligand-to-metal charge-transfer (LMCT) band intensity at *ca.* 425 nm using UV–vis spectroscopic method. Additionally, the *trans* isomer **7** was shown to have a higher binding ability than the *cis* isomer **6** towards Tb^{3+}.

Keywords: dibenzo-18-crown-6; lanthanoid ion; complexation; selectivity; titration

Introduction

It is well known that crown ethers as ion acceptors have been successfully applied in various areas of science and technology because of their specific binding ability and high extraction efficiency. Great effort has been devoted to the synthesis and recognition on alkali, alkaline earth and heavy metal salts of crown ether, of which many significant results have been obtained (*1–8*). Among them, investigations on the resulting complexes of lanthanides and crown ethers are gaining importance, and recently much progress has been achieved in the coordination chemistry of lanthanides (*9*). However, most of them focused on the syntheses and structure studies of solid complexes of rare earth and crown ethers, (*10–14*) and less attention has been given to the binding behaviour of trivalent lanthanoid ions and crown ethers in solution. Recently, the complexation thermodynamics of lanthanoids by crown ethers was reviewed by Liu et al. indicating that the cavity size of crown ether, electron density, softness, spatial arrangement, additional binding site and other major factors govern the cation–ligand complexation (*15*). In the present work, we report the synthesis of novel *cis*- and *trans*-dibenzo-18-crown-6 lariat isomers (Chart 1) and investigate their complexation with lanthanides in acetonitrile by using absorption spectra. The absorption spectra of the resulting complexes of lariat ethers **6** and **7** with lanthanoid ions have an appearance of intramolecular ligand-to-metal charge-transfer (LMCT (*16*)) band at *ca.* 425 nm with colour changes from light yellow (nearly colourless) to orange yellow and show the relative large intensity changes upon complexation with Sm^{3+} and Tb^{3+} over other lanthanoid ions. The spectrum titration has been performed at 25 °C in acetonitrile to give the complex stability constants (K_S) and Gibbs free energy changes (ΔG^0) for the stoichiometric 1:1 complexation of **6** and **7** with Tb^{3+}, showing the relative higher host selectivity for **7**-Tb^{3+}/**6**-Tb^{3+} up to 1.95.

Experimental

General

Melting points, measured with an XT-4 apparatus, are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury VX300 spectrometer in $CDCl_3$ solution, using tetramethylsilane as an internal reference. FT-IR and ultraviolet spectra were recorded on Bio-Rad FTS 135 and Shimadzu UV-2401/PC instruments, respectively. Elemental analyses were performed on a Perkin–Elmer 2400C instrument.

Materials

The starting materials were commercially available unless noted otherwise. Dibenzo-18-crown-6 (**1**) and 2,14-dinitro-6,7,9,10,17,18,20,21-octahydro-5,8,11,16, 19,22-hexaoxadibenzo[*b*,*k*]cyclooctadecene (**2**); 2,13-dinitro-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxadibenzo[*b*,*k*]cyclooctadecene (**3**); 2,14-diamino-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19, 22-hexaoxadibenzo[*b*,*k*]-cyclooctadecene (**4**); 2,13-diamino-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19, 22-hexaoxadibenzo[*b*,*k*]

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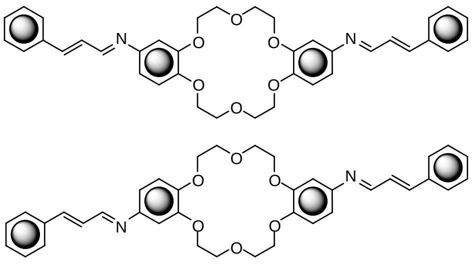


6 Cis Isomer

7 Trans Isomer

Chart 1. Structures of dibenzo-18-crown-6 lariat isomers.

cyclooctadecene (**5**) were prepared according to the modified literature procedures (*17*, *18*). Lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd and Tb) were prepared by dissolving the corresponding oxides of 99.9% purity (Baotou Rare Earth Chemical Co., Baotou, Inner Mongolia, China.) in 50% aqueous nitric acid by heating for *ca.* 10 min. After evaporation, the solid residue was dehydrated with P_2O_5 *in vacuo* for several days to give a powdery product. The lanthanoid nitrates obtained were dissolved in anhydrous acetonitrile and refluxed for 24 h over molecular sieves for further removal of water. The concentrations of the lanthanoid nitrate solutions in acetonitrile were determined by EDTA titration using xylenol orange as the indicator.

Synthesis of cis-*isomer 6*

2,14-Diamino-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxadibenzo[*b*,*k*]cyclooctadecene (**4**) (0.50 g, 1.28 mmol) and cinnamic aldehyde (1.5 ml, excess) were added to absolute ethanol (200 ml), and the mixture was refluxed with stirring for 4 h under nitrogen protection. After cooling, the solution was filtered and the collected precipitates were washed with cold ethanol to give 0.72 g of yellow product, yield 91%: mp 198.0–199.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.288$ (dd, $J = 2.3$, 4.7 Hz, 2H, C**H**=N), 7.531 (dd, $J = 2$, 5.2 Hz, 4H, C**H**=C**H**), 7.423–7.342 (m, 6H, Ar**H**), 7.111 (m, 4H, Ar**H**), 6.775–6.884 (m, 6H, Ar*H*), 4.202 (m, 8H, 2 × OC**H₂**), 4.041 (t, $J = 4.6$ Hz, 8H, OC**H₂**C**H₂**O). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 160.0$, 149.3, 147.7, 145.3, 143.5, 135.9, 129.7, 129.1, 128.8, 127.7, 113.8, 113.0, 107.5, 77.8, 77.4, 76.9, 70.1, 69.2, 68.7. IR (KBr): ν_{max}/cm^{-1}: 3033, 2923, 2881, 1627, 1607, 1585, 1509, 1451, 1423, 1364, 1321, 1261, 1228, 1164, 1136, 1060, 1042, 987, 953, 932, 906, 832, 806, 784, 749, 691, 647, 507. UV–vis λ_{max}(CH_3CN)/nm (ε/M^{-1} cm^{-1}) 294.0 (37,400), 358 (28,900). Anal. Calcd for $C_{38}H_{38}O_6N_2$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.55; H, 6.37; N, 4.67%.

Synthesis of trans-*isomer 7*

Compound **7** was prepared **6** to give 0.75 g (yield 93%) of **7** from 0.51 g (1.30 mmol) of **2**, 13-diamino-6,7,9,10,17,18,20,21-octahydro-5,8,11,16,19,22-hexaoxadibenzo[*b*,*k*]cyclooctadecene (**5**) and 1.5 ml of cinnamic aldehyde: mp 185.5–187.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 8.289$ (dd, $J = 2.3$, 4.7 Hz, 2H, C**H**=N), 7.531 (dd, $J = 2$, 5.3 Hz, 4H, C**H**=C**H**), 7.424–7.342 (m, 6H, Ar**H**), 7.113 (m, 4H, Ar**H**), 6.777–6.885 (m, 6H, Ar**H**), 4.204 (m, 8H, 2 × OC**H₂**), 4.041 (t, $J = 4.7$ Hz, 8H, OC**H₂**C**H₂**O). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 160.0$, 149.3, 147.7, 145.2, 143.5, 135.9, 129.7, 129.1, 128.8, 127.7, 113.7, 113.0, 107.5, 77.7, 77.3, 76.9, 70.0, 69.1, 68.8. IR (KBr): ν_{max}/cm^{-1}: 3030, 2928, 2876, 1627, 1607, 1587, 1510, 1452, 1423, 1364, 1322, 1261, 1230, 1164, 1137, 1062, 1042, 990, 926, 878, 830, 808, 783, 750, 692, 650, 528. UV–vis λ_{max}(CH_3CN)/nm (ε/M^{-1} cm^{-1}) 294.0 (46,900), 358 (36,300). Anal. Calcd for $C_{38}H_{38}O_6N_2$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.71; H, 6.14; N, 4.63%.

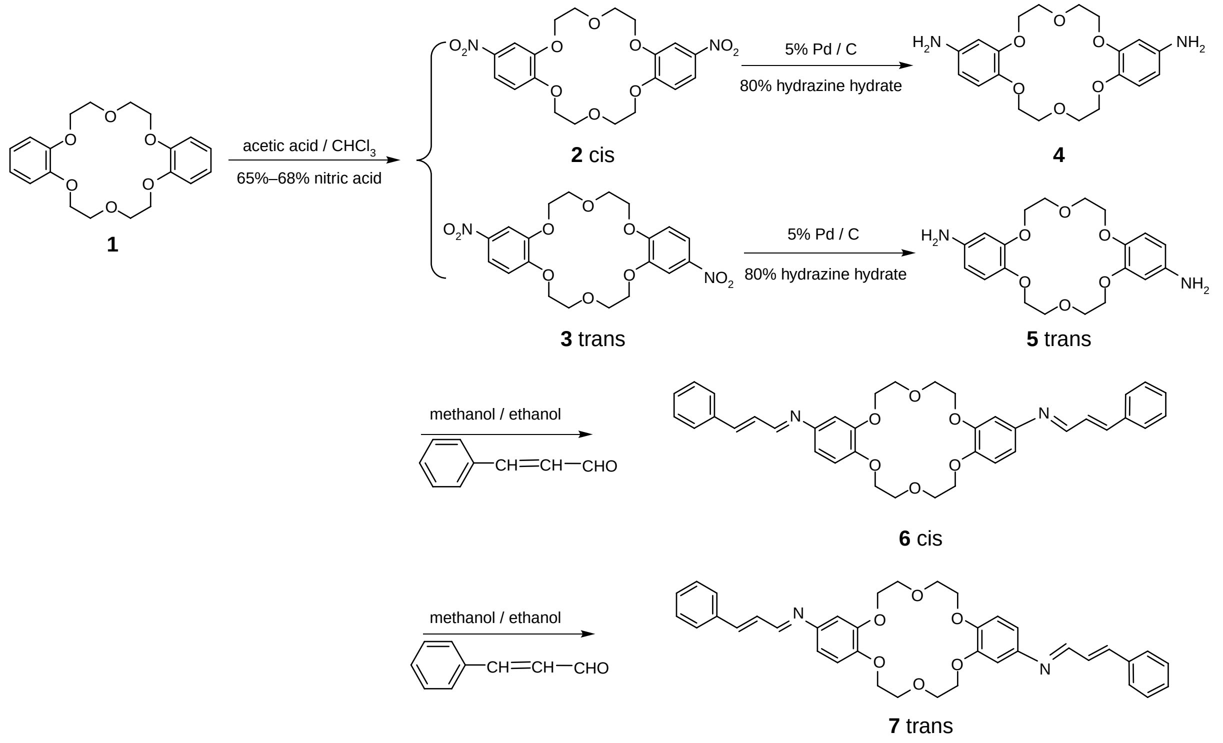
Results and discussion

Synthesis

The synthetic pathway for the target compounds is shown in Scheme 1. Among a number of methods that have been suggested in the literature for the synthesis of **4** and **5**, the method we chose is shown in Scheme 1. Here, 5% Pd–C catalyst was chosen to give pure products **4** and **5** in high yields. The two isomers were synthesised from their precursors. The separation of the isomers was done in the process of the syntheses of their precursors (**2** and **3**). For convenience, we synthesised the products separately and therefore did not attempt to synthesise the isomeric mixture and separate them. Dibenzo-18-crown-6 (**1**) was nitrated with a mixture of nitric acid and acetic acid in a chloroform–acetic acid solution to give a mixture of two geometric isomers **2** and **3** with high yield (42 and 45%, respectively, with a total yield of 87%). The separation of **2** and **3** by fractional crystallisation from water/ethanol, benzene and chloroform was the key step to give the final products as a pure isomer. The NMR spectra of the nitroproducts agreed with the literature (*18*). In the final step, we obtained the products in high yield (93 and 91%, respectively).

UV–vis spectroscopy

The absorption spectra of **6** and **7** were measured in acetonitrile in the presence and absence of lanthanide ions (La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} and Tb^{3+}) at 25 °C as shown in Figures 1 and 2. The spectra changed with the addition of an equimolar amount each of the lanthanide ions. All the spectrum lines have an isobestic point at 365 nm and a slight hypsochromic shift at 294 and 358 nm as compared with the free ligands, as well as an appearance of a LMCT



Scheme 1. Synthetic routes of dibenzo-18-crown-6 lariat isomers.

band at *ca.* 425 nm owing to an efficient metal coordination and according to conformational changes of the ligands. This means that the two lariat ethers form complexes with lanthanide ions.

The absorption behaviour reflects the manner of host–guest complexation. The spectroscopic changes are associated with metal cation complexation by lariat ethers. In the complexation of crown ethers and metal ions, phenolic oxygen atoms participated in the complexation of metal cations (*14*). Since the metal cation withdraws the non-bonding electrons of the two oxygen atoms connected to the benzene ring upon complexation, this process reduces the electron-donating character of the oxygen to the crown ether benzene ring

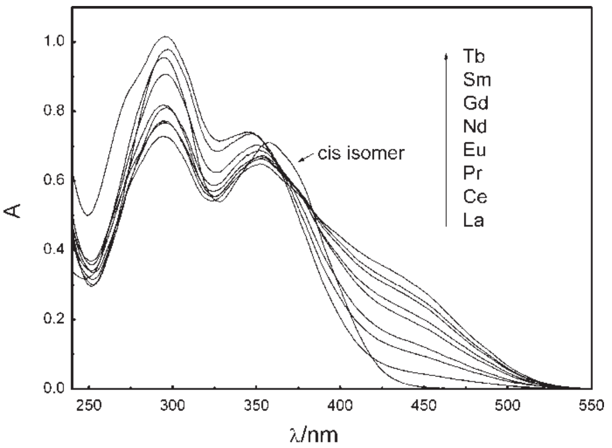


Figure 1. UV–vis spectral changes of acetonitrile solution of *cis* isomer **6** (4.0×10^{-5} M) in the absence and presence of lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd and Tb), respectively. The concentration of lanthanoid(III) nitrates is 5.0×10^{-4} M.

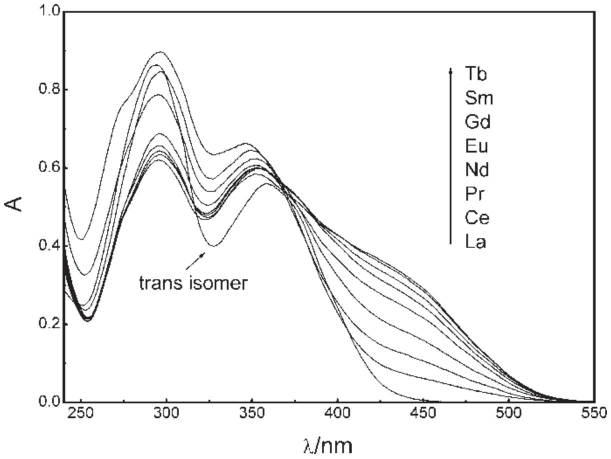


Figure 2. UV–vis spectral changes of acetonitrile solution of *trans* isomer **7** (4.0×10^{-5} M) in the absence and presence of lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd and Tb), respectively. The concentration of lanthanoid(III) nitrates is 5.0×10^{-4} M.

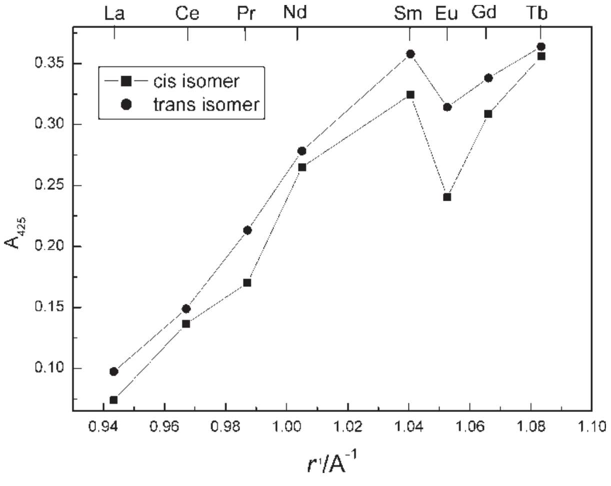


Figure 3. Dependence of A_{425} on the reciprocal ionic radius of lanthanide ions. The concentration of lanthanoid(III) nitrates is 5.0×10^{-4} M; [**6**] = [**7**] = 4.0×10^{-5} M.

and the conjugate system of the arms. As a consequence, the absorption maximum shifts to a shorter wavelength, (*4*) hence a hypsochromic shift was observed in the experiment.

Because the shoulder peak at 425 nm is induced only by the complex formation between crown ethers and lanthanide ions (Ln^{3+}), we use the absorbance intensity at 425 nm to represent the relative absorption selectivity of complexation between crown ethers and lanthanide ions (Ln^{3+}). Figure 3 shows the dependence of the absorption at 425 nm (A_{425} for the charge-transfer band of the complex formation) on the reciprocal ionic radius. It can be easily recognised that high absorption intensity change selectivity for Tb^{3+} is obtained by both the *cis* and *trans* isomers. As can be seen from Figure 3, A_{425} of **6** shows a characteristic peak at Sm^{3+} and gradually increases with the increasing atomic number or the increasing ionic radius from La^{3+} to Tb^{3+}. Lariat ether **7** gives the same trend as **6** except for Eu^{3+}. Both **6** and **7** give high absorption selectivities for Sm^{3+} and Tb^{3+}. The regular trend of the complexation ability may be attributable to the conformational change of the introduction of the rigid arm, the efficient participation on the nitrogen donor atom in the complex formation and the lariat ligation effect of the arm moiety. The introduction of the rigid arms also induces their fitted cavity's change. Our previous thermodynamic studies on 18-crown-6 series gave a similar results (*15*). Since both the *cis* and *trans* isomers give the highest absorption selectivity for Tb^{3+}, we further examined the complexation stoichiometry of the isomers with Tb^{3+} and the influences of linkage difference between the two isomers upon complexation with Tb^{3+}.

Spectrophotometric titrations

To further investigate the binding ability of Tb^{3+} by the two lariat ethers, the differential UV–vis spectral titration experiments were performed. In the spectrophotometric titration experiments, the absorption intensity of crown ethers gradually changed upon addition of varying amounts of Tb^{3+}, accompanied by obvious colour changes from light yellow (nearly colourless) to orange yellow as detected by the naked eye. Figure 4 shows the UV–vis spectral changes of the acetonitrile solution of *trans* lariat ethers (4.0×10^{-5} M) in the absence and presence of $TbNO_3$.

From Figure 4(a), we can see that the absorbance at 358 and 294 nm decreases with an increasing concentration of Tb^{3+}, and isobestic point at 365 nm and LMCT absorption band (shoulder at 425 nm) of the lanthanide ions coordination process appeared. A new peak emerged at 425 nm, and increased in intensity with increasing concentration of Tb^{3+}, which indicates the formation of the inclusion complex with Tb^{3+}. The absorption at 358 nm from b to g shifted slightly to a shorter wavelength by 10 nm in Figure 4(a). The hypsochromic shift is attributed to the decrease in conjugation between the phenolic oxygen lone pairs, the aromatic rings and double linkages due to the coordination with Tb^{3+}.

With the assumption of the 1:1 binding stoichiometry, the complexation can be expressed by Equation (1).

$$H + G \underset{}{\overset{K_S}{\rightleftharpoons}} HG \tag{1}$$

The stability constant (K_S) may be determined using a non-linear least squares method according to the curve

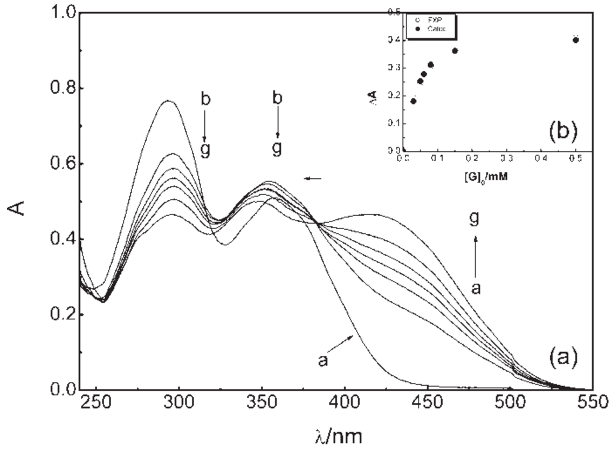


Figure 4. (a) UV–vis spectral changes of acetonitrile solution of *trans* isomer **7** (4.0×10^{-5} M) in the absence and presence of $TbNO_3$. The concentration of Tb^{3+} was 0–0.8 mM from *a* to *g*. (b) Least-squares curve-fitting analyses for complexations of Tb^{3+} with **7**; the lines represent the fit to a 1:1 binding model.

Table 1. Complex stability constants (K_S) and Gibbs free energy changes ($-\Delta G^0$) for 1:1 inclusion complexation of Tb^{3+} with *cis–trans* isomers in acetonitrile at 25.0 °C.

Host	Guest	$K_\mathrm{S}/\mathrm{M}^{-1}$	$\log K_\mathrm{S}$	$-\Delta G^0/\mathrm{kJ\,mol}^{-1}$	α
Cis isomer **6**	Tb^{3+}	31,700	4.5002	25.691	12,080
Trans isomer **7**	Tb^{3+}	61,900	4.7908	27.349	10,360

fitting Equation (2), (*19*)

$$\Delta A = 1/2\left\{\alpha([\mathrm{H}]_0+[\mathrm{G}]_0+1/K_\mathrm{S}) \pm \sqrt{\alpha^2([\mathrm{H}]_0+[\mathrm{G}]_0+1/K_\mathrm{S})^2-4\alpha^2[\mathrm{H}]_0[\mathrm{G}]_0}\right\} \tag{2}$$

where $[\mathrm{G}]_0$ and $[\mathrm{H}_0]$ refer to the total concentrations of Tb^{3+} and crown ethers, respectively. α is the proportionality coefficient for the effective UV intensity change induced by guest complexation, which may be taken as a sensitivity factor for the absorbance change. ΔA denotes the change in absorbance upon stepwise addition of guest. In the control experiments, we noticed that the NO_3^- in acetonitrile exhibited a relatively weak absorption below 300 nm when its concentration was less than 0.1 mM, but a relatively large absorption when its concentration was larger than 0.5 mM. Therefore, in the titration experiments of crown ethers and $\mathrm{Tb(NO_3)_3}$, we chose the absorption at 425 nm where NO_3^- did not show any significant changes even at a concentration up to 10 mM in order to perform the curve fitting. For each isomer–Tb^{3+} combination examined, the plot of ΔA at 425 nm as a function of $[\mathrm{G}]_0$ gave an excellent fit to the theoretical curve, verifying the validity of the 1:1 complex stoichiometry assumed above. As shown in Figure 4(b), the observed ΔA values (open circle) are plotted against $[\mathrm{G}]_0$ to give an excellent fit without serious deviations from the calculated values (small dots). In the repeated measurement, the K_S value was reproducible within an error of ±5%.

The K_S and α values obtained by the curve fitting are listed in Table 1, along with the free energy changes ($-\Delta G^0$) of complex formation. Therefore, we can conclude that both **6** and **7** form a 1:1 complex with Tb^{3+}. Table 1 indicates that the *trans* isomer has a better binding affinity for Tb^{3+} than the *cis* isomer. The *trans* isomer gave 1.95 times K_S as the *cis* isomer, indicating that the *trans* isomer is more suitable for the complexation with Tb^{3+}. This may be attributed to the minute conformational difference between the two isomers.

In conclusion, we synthesised two *cis*/*trans* isomers of dibenzo-18-crown-6 derivatives in high yields and investigated their binding behaviours towards lanthanoid cations. By the measurement of the LMCT band intensity using UV–vis spectroscopy, the lariat crown ether isomers gave better binding affinities towards Sm^{3+} and Tb^{3+} and appreciable solution colour changes. The spectrum titration experiments showed a relative higher host selectivity for **7**-Tb^{3+}/**6**-Tb^{3+} up to 1.95. This kind of *cis*/*trans* host design may have potential applications in rare metal separation technology.

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Note

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