ChemPubSoc Europe
DOI: 10.1002/chem.201504257
CHEMISTRY
A European Journal
Communication

Synthetic Methods

Chiroptical Probing of Lanthanide-Directed Self-Assembly Formation Using btp Ligands Formed in One-Pot Diazo-Transfer/Deprotection Click Reaction from Chiral Amines**

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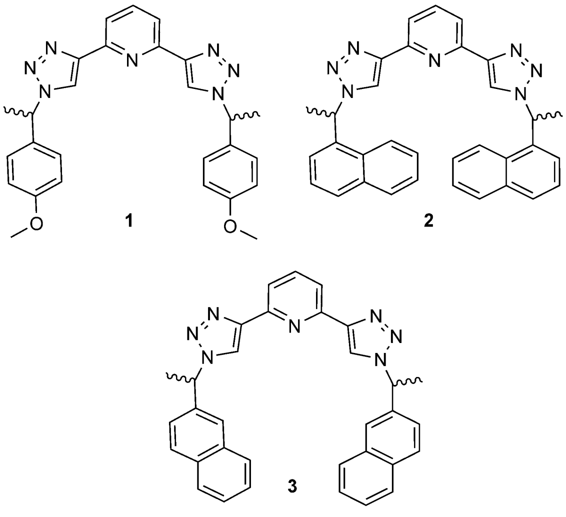
Abstract: A series of enantiomeric 2,6-bis(1,2,3-triazol-4-yl)pyridines (btp)-containing ligands was synthesized by a one-pot two-step copper-catalyzed amine/alkyne click reaction. The Eu^{III}- and Tb^{III}-directed self-assembly formation of these ligands was studied in CH_3CN by monitoring their various photophysical properties, including their emerging circular dichroism and circularly polarized luminescence. The global analysis of the former enabled the determination of both the stoichiometry and the stability constants of the various chiral supramolecular species in solution.

The development of highly organized self-assembly structures from simple starting materials is of great interest in supramolecular and materials chemistry. Recently, a new class of highly versatile and synthetically adaptable ligands based on the 2,6-bis(1,2,3-triazol-4-yl)pyridine (btp) motif have emerged as candidates for use in such self-assembly formations.[1] Synthesized by the CuAAC click reaction, the btp motif has been shown to coordinate a wide range of metals and have diverse applications including, but not limited to, catalysis,[2] enzyme inhibition,[3] luminescence-based molecular logic,[4] and nanomaterials.[5] The wide scope of CuAAC has allowed a wide range of functionalities to be introduced into btp arms, using various azide substrates.[6] We have recently reported the use of simple non-chiral btp ligands to give discrete d-metal ion complexes and metallogels.[7] We have also shown that such btp ligands can form stable complexes with f-metal ions;[8] however, only a few examples of f-btp systems have been developed to date.[9] Many beautiful examples of luminescent lanthanide (Ln^{III}) complexes with terdentate ligands have been reported.[10] Due to the remarkable photophysical properties of many of the lanthanides and building on pioneering work by Bünzli, Piguet and co-workers,[11] we[12] and others[13] have developed various amide derivatives of dipicolinic acid (dpa), synthesized from chiral amines, and used these in Ln^{III}-directed synthesis of supramolecular architectures. Moreover, chiral Ln^{III} complexes exhibit interesting chiroptical properties, which can be capitalized upon for sensing and imaging.[13a, 14] The btp ligands can be considered as structural analogues of these dpa derivatives, because the triazole units are considered an isostere for amide bonds.[15] With this in mind, we set out to develop a convenient methodology for introducing chirality into the btp motif in a one-pot synthesis from optically pure amines. Herein, we demonstrate such synthesis, using α-aryl amines, with the formation of ligands **1**–**3** (Scheme 1) and the subsequent use of chiral ligands to form optically active luminescent self-assembly structures through Ln^{III}-directed synthesis, the formation of which was both probed and quantified, among other techniques, by circular dichroism (CD) spectroscopy, in a manner recently developed within our laboratory.[16] This communication will focus the characterization and photo-



Scheme 1. Structures of chiral btp ligands **1**–**3**.

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[**] btp = 2,6-Bis(1,2,3-triazol-4-yl)pyridines.

Supporting information and ORCID(s) from the author(s) for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504257.

physical properties of ligands **1** and their Ln^{III} complexes (Ln = Eu, Tb). Details of the interactions of ligands **2** and Eu^{III} are given in Supporting Information.

A one-pot amine/alkyne CuAAC methodology has been previously reported,[17] but relies on the relatively unstable TfN_3 as a diazo-transfer reagent. In contrast, a salt of imidazole-1-sulfonyl azide, $ImSO_2N_3{\cdot}HCl$, was reported as a more robust shelf-stable diazotransfer agent,[18] and consequently Stonehouse and co-workers employed this to form triazoles,[19] whereas Xie and Maisonneuve presented a route to form triazoles from aldehydes and amines also using $ImSO_2N_3$.[20] However, it has recently been reported that $ImSO_2N_3{\cdot}HCl$ is less stable than originally thought,[21] and $ImSO_2N_3{\cdot}H_2SO_4$ was proposed as an alternative. Our work presented herein makes use of $ImSO_2N_3{\cdot}H_2SO_4$ in a modular and mild one-pot diazo-transfer/deprotection click reaction, which has two steps, catalyzed by Cu^{II} and Cu^{I}, respectively. The reaction mixture underwent dramatic color change during the course of the reaction, allowing it to be monitored by the naked eye, as shown in Figure 1 for the formation of **1 a** (*S*,*S*) and **1 b** (*R*,*R*) (from *S*- and *R*-amines, respectively). The initial mixture, a bright cyan color, changed into a lilac suspension after stirring for 5 h in the presence of K_2CO_3, corresponding with the conversion of the amine to azide (as was monitored by TLC; this color change was not observed if insufficient amount of base was added). Subsequent addition of sodium ascorbate (to reduce $Cu^{II} \rightarrow Cu^{I}$) and degassing of the reaction mixture resulted in formation of a dull pale yellow suspension, Figure 1(c), while addition of the protected dialkyne, 2,6-bis(TMS-ethynyl)pyridine, gave an orange color upon successful formation of **1** after 18 h.[22] After aqueous workup and precipitation from CH_3OH or flash chromatography, **1 a** and **b** were isolated in moderate overall yields of approximately 50%, with retention of stereochemistry, as was confirmed by X-ray crystallography (Figure 2) and circular dichroism (CD; Figure 3 a), in which opposite ellipticities were seen for the enantiomers, **1 a** displaying positive signals centered at 300 and 236 nm, which correspond closely to the main absorbance bands (see below). Both enantiomers of ligand **1** crystallized in the orthorhombic $C222_1$ space group, Figure 2. The structures were identical, but mirror images of each other. There were two molecules in the asymmetric unit of the structure and, as a result of nonclassical triazolyl hydrogen bonding to the pyridyl nitrogen of the adjacent molecule, a double helix structure occurred in the solid state. These hydrogen bonds had C−H⋅⋅⋅N distances ranging from 2.458(2)–2.608(3) Å (Table S2 in the Supporting information). The btp motifs of the two molecules were nearly orthogonal to each other (85°).

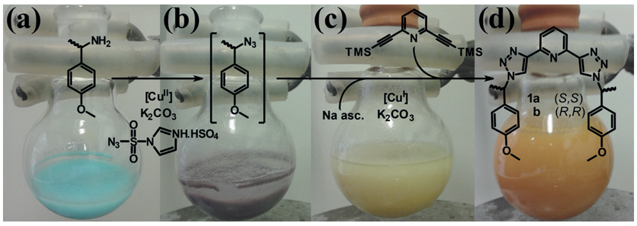

Figure 1. Schematic representation of synthesis of chiral btp ligands **1**. (a) Cyan mixture of amine, $CuSO_4{\cdot}5\,H_2O$, $ImSO_2N_3{\cdot}H_2SO_4$, and K_2CO_3 in CH_3OH ($t = 0$ h). (b) Lilac suspension upon formation of the azide ($t = 5$ h). (c) Dull yellow suspension after addition of sodium ascorbate and degassing mixture ($t = 5.5$ h). (d) Orange reaction mixture upon completion of CuAAC reaction ($t = 18$ h).

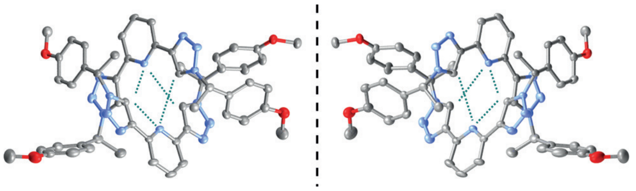

Figure 2. X-ray crystal structures of the *S*,*S*- (left) and *R*,*R*-enantiomers (right) of ligand **1**, shown with thermal ellipsoids at 50%. Hydrogen bonding between triazoles and adjacent pyridines is shown by a dashed line. Hydrogen atoms have been omitted for clarity. Selected crystallographic and refinement data: **1 a** (CCDC 1019214): $a = 10.0935(15)$, $b = 27.370(4)$, $c = 36.577(6)$ Å; $Z = 16$; GOF, $R1$, $wR2 = 1.045$, 0.0392, 0.1032; Flack = 0.1(2). **1 b** (CCDC 1019215): $a = 10.0910(15)$, $b = 27.262(4)$, $c = 36.585(6)$; $Z = 16$; GOF, $R1$, $wR2 = 1.045$, 0.0481, 0.1287; Flack = 0.3(2). CCDC 1019214 and 1019215 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

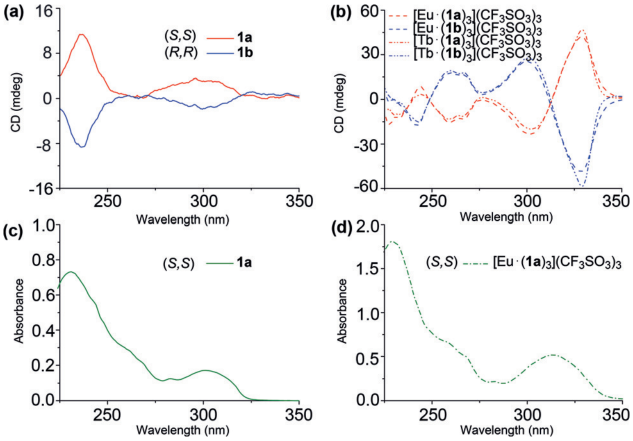

Figure 3. (a) CD spectra of ligands **1 a** and **b**; and (b) CD spectra of the Eu^{III} and Tb^{III} complexes ($[Ln{\cdot}(\mathbf{1})_3](CF_3SO_3)_3$). (c) UV/Vis absorbance spectrum of **1 a**. (d) UV/Vis absorbance spectrum of $[Eu{\cdot}(\mathbf{1\,a})_3](CF_3SO_3)_3$. All data recorded in CH_3CN at room temperature.

Ln^{III} complexes were prepared by reacting **1** with $Ln(CF_3SO_3)_3$ in 3:1 stoichiometry in CH_3OH and isolated as solids upon ether diffusion, using both Eu^{III} and Tb^{III}. The Tb^{III} complexes were highly luminescent in CH_3CN solution upon excitation of the ligand (antenna), displaying characteristic green Tb^{III} emission, demonstrating successful sensitization of the Tb^{III} $^5D_0$ excited state. The quantum yield of $[Tb{\cdot}(\mathbf{1\,b})_3](CF_3SO_3)_3$ was determined as 67 ± 12% by a relative method, compared to $Cs_3[Tb{\cdot}(\mathbf{dpa})_3]$.[23] The Eu^{III} analogue was also emissive, giving rise to metal-based emission in the red; however, in contrast to the Tb^{III}, the quantum yield was significantly less, which is consistent with our previous observations.[8a] The hydration states, or the numbers of metal-bound water molecules (q), were determined for both complexes by measuring their lanthanide centered luminescence lifetimes upon excitation of the ligand in both H_2O and D_2O. The results showed a q of zero for both pair of enantiomers indicating that they were coordinatively saturated in solution; confirming the 3:1 stoichiometry (Table S3 in the Supporting Information).

The UV/Vis absorbance spectra of ligands **1 a** and **b** were measured in CH_3CN, showing a band centered at 300 nm, with a slight shoulder at 283 nm, as well as a broader band with a maximum at 230 nm, Figure 3(c). The UV/Vis spectra of the Ln^{III} complexes of **1** resembled those of the ligands, but the band centered at 300 nm underwent a redshift to 315 nm; the spectrum of $[Eu\cdot(\mathbf{1a})_3](CF_3SO_3)_3$ is shown in Figure 3 d. The corresponding CD spectra of the $[Ln\cdot(\mathbf{1})_3](CF_3SO_3)_3$ complexes is shown in Figure 3 b; these display significantly different features to those seen for the ligands. Furthermore, the CD spectra of the complexes were, within error, nearly identical for both Eu^{III} and Tb^{III} complexes demonstrating that both adopted the same geometry in solution. The dramatic differences in the CD spectra of the ligands versus those seen for the Ln^{III} complexes are the result of exciton coupling between the chromophores in adjacent ligands, brought together by the metal-directed self-assembly formation.[24] The spectra of the complexes of **1 a** showed a large positive exciton couplet with a Davydov splitting of approximately 27 nm, representing a Cotton effect splitting of the 315 nm-centered absorbance band, a broad negative band centered at 260 nm, with a shoulder at 267 nm, as well as a positive band centered at 242 nm. The complexes of **1 b** gave equal and opposite spectra of those seen for **1 a**.

Upon ligand excitation (of both **1 a** and **b**), a broad ligand-centered fluorescence band (max. at 335 nm) was observed. As was referred above, the ligands were capable of sensitizing the characteristic Ln^{III} luminescence. For the Eu^{III} complexes, emission bands were observed at $\lambda = 593$, 617, 650, and 694 nm, arising from the $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 1$–4), whereas for Tb^{III} complexes emission bands were observed at $\lambda = 487$, 541, 580, and 619 nm, which represent the $^5D_4 \rightarrow {}^7F_J$ transitions ($J = 6$–3). Emission related to the $^5D_0 \rightarrow {}^7F_0$ transition in the complexes $[Eu\cdot(\mathbf{1})_3](CF_3SO_3)_3$ was not observed, and the $^5D_0 \rightarrow {}^7F_2$ transition was quite weak compared to the $^5D_0 \rightarrow {}^7F_1$ transition. The former observation is consistent with the tris-btp complex adopting D_3 symmetry in solution.[25] Moreover, the chirality of the lanthanide complexes was further probed by using circular polarized luminescence (CPL). All the Ln^{III} complexes exhibit CPL spectra with each pair of enantiomer displaying signals of equal magnitude and opposite sign for each band characteristic of a specific f–f electronic transition (Figure 4 a and b). This demonstrates that the chirality of the ligands is transferred to the Ln^{III} complexes. These measurements further confirmed the enantiomeric and chiral nature of these compounds. However, the Ln^{III} complexes possess quite low luminescence dissymmetry factors, g_{lum}, compared to previous work by Muller[13a] and by our group,[12c,f,g] suggesting that the twist away from symmetrical arrangement is small. For instance, g_{lum} for the most intense transitions in the Eu^{III} complex, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, are -0.016 and $+0.023$ for **1 a**. The dissymmetry factor for the $^5D_0 \rightarrow {}^7F_3$ transition of the Tb^{III} complexes was the largest observed, with a value of $+0.085$ for **1 a** and -0.081 for **1 b**. These values are comparable with chiral organic fluoro-

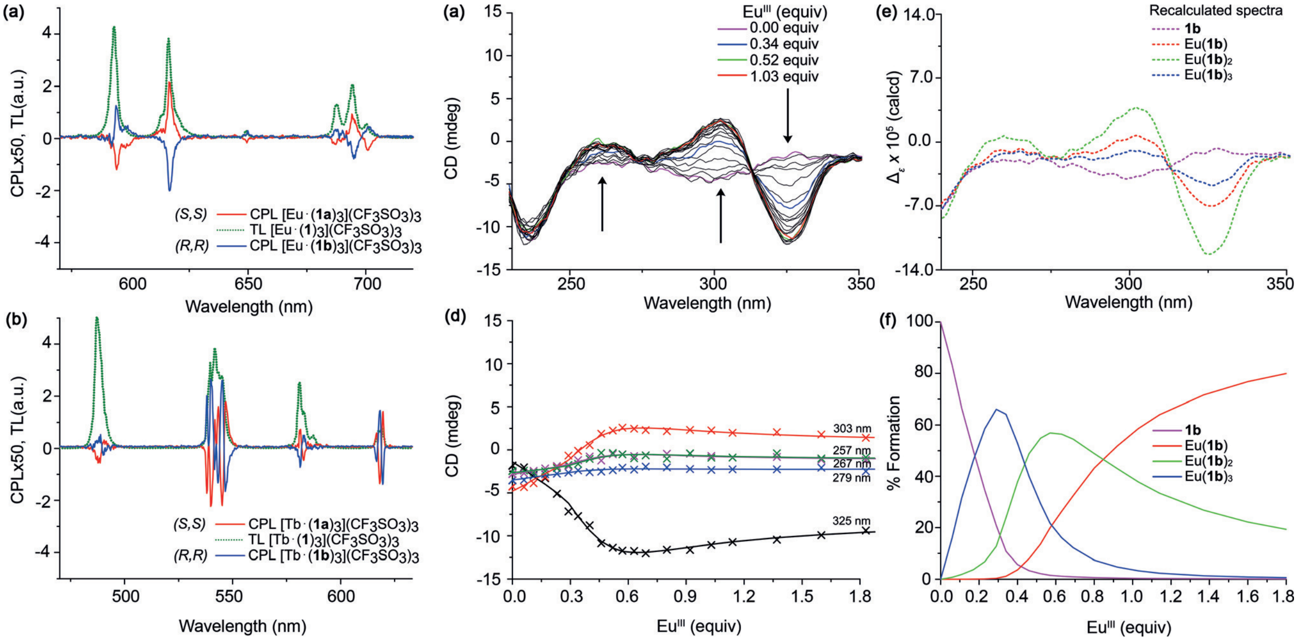

Figure 4. (a–b) Circularly polarized luminescence spectra of both enantiomers and total luminescence spectra of (a) $[Eu\cdot(\mathbf{1})_3](CF_3SO_3)_3$ and (b) $[Tb\cdot(\mathbf{1})_3](CF_3SO_3)_3$ in CH_3CN at room temperature. (c) CD titration data upon addition of a solution of $Eu(CF_3SO_3)_3$ to a solution of ligand **1 b** in CH_3CN ($[\mathbf{1b}] \approx 1 \times 10^{-5}$ M), spectra at 0.0, 0.3, 0.5, and 1.0 equivalents are highlighted. (d) Experimental (×) and calculated (——) binding isotherms at various wavelengths. (e) Recalculated spectra of various $Eu(\mathbf{1})_n$ stoichiometries. (f) Calculated speciation distribution diagram.

phores[26] (see Table S4 in the Supporting Information for full details).

To investigate the formation of the Ln^{III} complexes of **1**, the changes in the UV/Vis absorption, fluorescence emission, and the Ln^{II}-centered emission were all monitored, upon addition of $Ln(CF_3SO_3)_3$ in CH_3CN solution at room temperature. Upon the addition of either Eu^{III} or Tb^{III}, the absorbance band of **1**, centered at 300 nm, was redshifted by 15 nm, whereas the more absorbing band at 231 nm was only shifted slightly approximately 3 nm with concomitant hypochromic effect (an example is shown in Figure 5 a). All spectral changes were complete upon addition of 0.5 equivalents. Simultaneously, the ligand fluorescence was quenched, and the characteristic Ln^{III}-centered emission spectra were sensitized, reaching a maximum at 0.5 equivalents (see the Supporting Information).

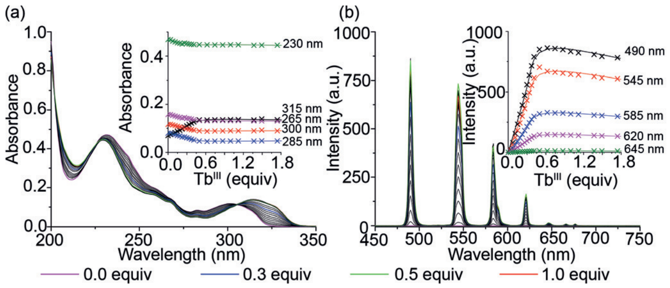

Figure 5. (a) UV/Vis absorption and (b) Tb^{III}-centered luminescence titration results upon addition of a solution of $Tb(CF_3SO_3)_3$ to ligand **1 a** in CH_3CN ([**1 a**] $\approx 1\times10^{-5}$ M). Spectra at 0.0, 0.3, 0.5, and 1.0 equivalents are highlighted. Insets show experimental (×) and calculated (——) binding isotherms.

Global stability constants of each species were estimated by fitting both the UV/Vis absorbance and the Ln luminescence data using the non-linear regression analysis program ReactLab Equilibria (Jplus Consulting Pty Ltd), using the following equilibria: $Ln + \mathbf{1} \leftrightarrow Ln(\mathbf{1})$ ($\log\beta_{1:1}$); $Ln + 2(\mathbf{1}) \leftrightarrow Ln(\mathbf{1})_2$ ($\log\beta_{1:2}$); $Ln + 3(\mathbf{1}) \leftrightarrow Ln(\mathbf{1})_3$ ($\log\beta_{1:3}$). For the absorbance data of **1 a**, upon addition of $Eu(CF_3SO_3)_3$ in CH_3CN, values of $\log\beta$ for the various equilibria were found to be 6.7, 13.4, and 20.9, respectively, whereas for the luminescence titrations, the binding constants for **1 a** in these three equilibria were determined as 7.0, 13.8, and 19.0 respectively, with very similar results for the *R,R*-enantiomer (Table S5 in the Supporting Information; experimental binding isotherms and calculated fitting curves are shown in Supporting Information as well).

Given the remarkable changes observed between the CD spectra of the ligands and those of their corresponding complexes (c.f. Figure 3), with the occurrence of bisignate Cotton effects for both complexes, we also carried out CD titrations upon the addition of $Ln(CF_3SO_3)_3$ solution with ligands **1**. The overall CD changes are shown in Figure 4 c. The ligand spectrum featured bands centered at 300 and 235 nm of equal signs. Throughout the course of the titration, minimal changes were observed in the band centered at 235 nm; however, the band at higher wavelength (300 nm) underwent a redshift of 15 nm and exhibited an intense Cotton effect, giving a bisignate CD couplet of the same sign as the respective ligand band (e.g., a negative couplet for **1 b**); a minor band of opposite sign to the original spectrum centered at 260 nm also developed. Spectral changes were largely complete upon addition of 0.5 equivalents, as can be seen from the binding isotherms at various wavelengths (Figure 4 d); the final spectra matching those observed for the isolated complexes shown in Figure 3 b. These data were fitted to the same theoretical models used above using non-liner regression analysis and gave excellent fits (c.f. Figure 4 d). In all cases, binding constants could be determined that complemented those which were seen in both the absorption and the emission spectra discussed above (Table S5 in the Supporting Information), that is, $\log\beta_{1:1} = 7.7$, $\log\beta_{1:2} = 14.9$, and $\log\beta_{1:3} = 21.0$. Furthermore, these results allowed the calculation of a speciation distribution diagram for each of the complex stoichiometries formed (for example Figure 4 f; see the Supporting Information for the fitting of the titration data of **1 a**, as well as data for Tb^{III} titrations and data for titrations of **2** with Eu^{III}). Because significant changes occurred in the CD spectra for each $Ln(\mathbf{1})_n$ stoichiometry, the recalculated spectra of these stoichiometries can be used as a "fingerprint" for each species in solution. Figure 4 e demonstrates this, and the potential for employing CD titrations to probe the metal-directed self-assembly of supramolecular systems—a phenomenon not much employed to date.

In summary, by using a one-pot two-stage reaction strategy, we demonstrated the convenient synthesis of enantiomers of chiral btp ligands **1**–**3** from chiral amines and a protected bis-alkyne, with retention of stereochemistry. Focusing on **1 a** and **b**, both were fully characterized, including by X-ray crystallography. The Eu^{III} and Tb^{III} complexes of these were prepared, exhibiting characteristic Ln^{III}-centered luminescence. The chiral nature of the ligands was probed further using CD and CPL spectroscopies. Conventional spectroscopic titrations and data fitting gave reasonably high global stability constants for the 1:1, 1:2, and 1:3 ligand/metal stoichiometric self-assemblies in solution. Furthermore, by carrying out CD titrations, we were also able to probe the formation of each of these species in solution by observing the chiroptical spectroscopic changes. This allowed us to identify the fingerprint spectra for each of the stoichiometries and determine the stepwise stability constants, which were comparable to those obtained by conventional methods, allowing a new approach to probing self-assembly formation in real time.

Experimental Section

General experimental procedure: To a suspension of $ImSO_2N_3{\cdot}H_2SO_4$ (0.24 mmol, 65 mg), K_2CO_3 (0.40 mmol, 55 mg), and $CuSO_4{\cdot}5H_2O$ (0.04 mmol, 10 mg) in CH_3OH (1.7 mL) was added the chiral amine (0.20 mmol). Significant color change was observed after 5 h (6 h for **4**), then 0.5 mL of an aqueous solution of sodium ascorbate (0.09 mmol, 18 mg) and K_2CO_3 (0.20 mmol, 28 mg) was added along with 0.75 mL *t*BuOH, and the reaction mixture degassed with argon. 2,6-Bis(TMS-ethynyl)pyridine (0.11 mmol, 30 mg) in DMF (0.3 mL) was added by syringe, and the reaction mixture was stirred at room temperature for 18 h. Reaction mixture was concentrated, aqueous EDTA/NH_4OH (1:9, pH 9) solution added, and product was extracted into CH_2Cl_2. Product was isolated upon trituration with CH_3OH or flash chromatography. Full experimental details and characterization are provided in the Supporting Information.

Acknowledgements

This research was supported by the Irish Research Council for Science, Engineering & Technology (IRCSET) and the Irish Research Council (IRC; PhD Scholarship J.P.B.), University of Dublin and Science Foundation Ireland (SFI;SFI PI Awards 10/IN.1/B2999 and 13/IA/1865), for funding. We thank Dr. Oxana Kotova and Dr. Jennifer Jones for useful discussions.

Keywords: chirality · circular dichroism · click chemistry · lanthanides · 1,2,3-triazoles

[1] J. P. Byrne, J. A. Kitchen, T. Gunnlaugsson, *Chem. Soc. Rev.* **2014**, *43*, 5302.

[2] T. Karthikeyan, S. Sankararaman, *Tetrahedron: Asymmetry* **2008**, *19*, 2741.

[3] S. Wang, J. A. Cuesta-Seijo, D. Lafont, M. M. Palcic, S. Vidal, *Chem. Eur. J.* **2013**, *19*, 15346.

[4] a) G. C. Midya, S. Paladhi, S. Bhowmik, S. Saha, J. Dash, *Org. Biomol. Chem.* **2013**, *11*, 3057; b) S. J. Bradberry, J. P. Byrne, C. P. McCoy, T. Gunnlaugsson, *Chem. Commun.* **2015**, *51*, 16565.

[5] N. Chandrasekhar, R. Chandrasekar, *Angew. Chem. Int. Ed.* **2012**, *51*, 3556; *Angew. Chem.* **2012**, *124*, 3616.

[6] a) J. D. Crowley, P. H. Bandeen, *Dalton Trans.* **2010**, *39*, 612; b) J. D. Crowley, P. H. Bandeen, L. R. Hanton, *Polyhedron* **2010**, *29*, 70.

[7] J. P. Byrne, J. A. Kitchen, O. Kotova, V. Leigh, A. Bell, J. J. Boland, M. Albrecht, T. Gunnlaugsson, *Dalton Trans.* **2014**, *43*, 196.

[8] a) J. P. Byrne, J. A. Kitchen, J. E. O'Brien, R. D. Peacock, T. Gunnlaugsson, *Inorg. Chem.* **2015**, *54*, 1426; b) E. P. McCarney, J. P. Byrne, B. Twamley, M. Martínez-Calvo, G. Ryan, M. E. Möbius, T. Gunnlaugsson, *Chem. Commun.* **2015**, *51*, 14123.

[9] a) Y. Li, J. C. Huffman, A. H. Flood, *Chem. Commun.* **2007**, 2692; b) R. M. Meudtner, M. Ostermeier, R. Goddard, C. Limberg, S. Hecht, *Chem. Eur. J.* **2007**, *13*, 9834; c) N. Chandrasekhar, R. Chandrasekar, *J. Org. Chem.* **2010**, *75*, 4852; d) E. Brunet, H. M. H. Alhendawi, O. Juanes, L. Jimenez, J. C. Rodriguez-Ubis, *J. Mater. Chem.* **2009**, *19*, 2494; e) L. Munuera, R. K. O'Reilly, *Dalton Trans.* **2010**, *39*, 388.

[10] a) N. Martin, J.-C. G. Bünzli, V. McKee, C. Piguet, G. Hopfgartner, *Inorg. Chem.* **1998**, *37*, 577; b) A. Escande, L. Guénée, K.-L. Buchwalder, C. Piguet, *Inorg. Chem.* **2009**, *48*, 1132; c) N. M. Shavaleev, S. V. Eliseeva, R. Scopelliti, J.-C. G. Bünzli, *Inorg. Chem.* **2010**, *49*, 3927; d) A. de Bettencourt-Dias, P. S. Barber, S. Bauer, *J. Am. Chem. Soc.* **2012**, *134*, 6987; e) A. de Bettencourt-Dias, P. S. Barber, S. Viswanathan, D. T. de Lill, A. Rollett, G. Ling, S. Altun, *Inorg. Chem.* **2010**, *49*, 8848; f) A. de Bettencourt-Dias, S. Viswanathan, A. Rollett, *J. Am. Chem. Soc.* **2007**, *129*, 15436; g) E. S. Andreiadis, D. Imbert, J. Pecaut, R. Demadrille, M. Mazzanti, *Dalton Trans.* **2012**, *41*, 1268; h) S. Di Pietro, D. Imbert, M. Mazzanti, *Chem. Commun.* **2014**, *50*, 10323.

[11] a) F. Renaud, C. Piguet, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *Chem. Eur. J.* **1997**, *3*, 1646; b) T. Le Borgne, J.-M. Benech, S. Floquet, G. Bernardinelli, C. Aliprandini, P. Bettens, C. Piguet, *Dalton Trans.* **2003**, 3856.

[12] a) S. J. Bradberry, A. J. Savyasachi, M. Martinez-Calvo, T. Gunnlaugsson, *Coord. Chem. Rev.* **2014**, *273–274*, 226; b) M. Martínez-Calvo, O. Kotova, M. E. Möbius, A. P. Bell, T. McCabe, J. J. Boland, T. Gunnlaugsson, *J. Am. Chem. Soc.* **2015**, *137*, 1983; c) O. Kotova, J. A. Kitchen, C. Lincheneau, R. D. Peacock, T. Gunnlaugsson, *Chem. Eur. J.* **2013**, *19*, 16181; d) C. Lincheneau, J. P. Leonard, T. McCabe, T. Gunnlaugsson, *Chem. Commun.* **2011**, *47*, 7119; e) C. Lincheneau, C. Destribats, D. E. Barry, J. A. Kitchen, R. D. Peacock, T. Gunnlaugsson, *Dalton Trans.* **2011**, *40*, 12056; f) F. Stomeo, C. Lincheneau, J. P. Leonard, J. E. O'Brien, R. D. Peacock, C. P. McCoy, T. Gunnlaugsson, *J. Am. Chem. Soc.* **2009**, *131*, 9636; g) J. P. Leonard, P. Jensen, T. McCabe, J. E. O'Brien, R. D. Peacock, P. E. Kruger, T. Gunnlaugsson, *J. Am. Chem. Soc.* **2007**, *129*, 10986.

[13] a) K. T. Hua, J. Xu, E. E. Quiroz, S. Lopez, A. J. Ingram, V. A. Johnson, A. R. Tisch, A. de Bettencourt-Dias, D. A. Straus, G. Muller, *Inorg. Chem.* **2011**, *50*, 647; b) C.-T. Yeung, W. T. K. Chan, S.-C. Yan, K.-L. Yu, K.-H. Yim, W.-T. Wong, G.-L. Law, *Chem. Commun.* **2015**, *51*, 592; c) G. Zhang, G. Gil-Ramírez, A. Markevicius, C. Browne, I. J. Vitorica-Yrezabal, D. A. Leigh, *J. Am. Chem. Soc.* **2015**, *137*, 10437.

[14] a) R. Carr, N. H. Evans, D. Parker, *Chem. Soc. Rev.* **2012**, *41*, 7673; b) K. Matsumoto, K. Suzuki, T. Tsukuda, T. Tsubomura, *Inorg. Chem.* **2010**, *49*, 4717; c) G. Muller, C. L. Maupin, J. P. Riehl, H. Birkedal, C. Piguet, J.-C. G. Bünzli, *Eur. J. Inorg. Chem.* **2003**, *2003*, 4065; d) R. S. Dickins, J. A. K. Howard, C. L. Maupin, J. M. Moloney, D. Parker, J. P. Riehl, G. Siligardi, J. A. G. Williams, *Chem. Eur. J.* **1999**, *5*, 1095; e) R. S. Dickens, J. A. K. Howard, C. L. Maupin, J. M. Moloney, D. Parker, R. D. Peacock, J. P. Riehl, G. Siligardi, *New J. Chem.* **1998**, *22*, 891; f) D. G. Smith, B. K. McMahon, R. Pal, D. Parker, *Chem. Commun.* **2012**, *48*, 8520.

[15] a) J. M. Holub, K. Kirshenbaum, *Chem. Soc. Rev.* **2010**, *39*, 1325; b) V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, *2006*, 51; c) N. G. Angelo, P. S. Arora, *J. Am. Chem. Soc.* **2005**, *127*, 17134.

[16] O. Kotova, S. Blasco, B. Twamley, J. E. O'Brien, R. Peacock, J. A. Kitchen, M. Martinez-Calvo, T. Gunnlaugsson, *Chem. Sci.* **2015**, *6*, 457.

[17] H. S. G. Beckmann, V. Wittmann, *Org. Lett.* **2006**, *8*, 1.

[18] E. D. Goddard-Borger, R. V. Stick, *Org. Lett.* **2007**, *9*, 3797.

[19] N. M. Smith, M. J. Greaves, R. Jewell, M. W. D. Perry, M. J. Stocks, J. P. Stonehouse, *Synlett* **2009**, *2009*, 1391.

[20] S. Maisonneuve, J. Xie, *Synlett* **2009**, *2009*, 2977.

[21] E. D. Goddard-Borger, R. V. Stick, *Org. Lett.* **2011**, *13*, 2514.

[22] If the reaction proceeds under ambient atmosphere, a small amount of the Glaser coupling product is observed in the reaction mixture, but inert atmosphere produced only the desired btp product **1** (see the Supporting Information).

[23] a) G. A. Crosby, J. N. Demas, *J. Phys. Chem.* **1971**, *75*, 991; b) A. S. Chauvin, F. Gumy, D. Imbert, J. C. G. Bünzli, *Spectrosc. Lett.* **2004**, *37*, 517; c) A.-S. Chauvin, F. Gumy, D. Imbert, J.-C. G. Bünzli, *Spectrosc. Lett.* **2007**, *40*, 193.

[24] a) N. Berova, L. D. Bari, G. Pescitelli, *Chem. Soc. Rev.* **2007**, *36*, 914; b) S. G. Telfer, N. Tajima, R. Kuroda, M. Cantuel, C. Piguet, *Inorg. Chem.* **2004**, *43*, 5302.

[25] Relative intensities of bands related to various transitions in Eu^{III} complexes give insight into the geometry of the metal ion. The absence of the $^5D_0 \rightarrow {}^7F_0$ emission band is consistent with the absence of an inversion center in the structure. Of the possible point groups for a 1:3 tris-chelate complex, only D_3 symmetry fulfills this criterion. This phenomenon is discussed in the following references: R. D. Peacock, *Struct. Bonding (Berlin)* **1975**, *22*, 83; A. S. Souza, Y. A. R. Oliveira, M. A. Couto dos Santos, *Opt. Mater.* **2013**, *35*, 1633. Moreover, the intensity of the hypersensitive electric dipole transition band ($^5D_0 \rightarrow {}^7F_2$) is determined by geometry, being absent at octahedral geometry and non-zero for lower symmetries. In this case, this band is of lower intensity than the $^5D_0 \rightarrow {}^7F_1$, which is relatively unusual; ligand-polarization theory supports the assignment of trigonal antiprismatic geometry about the metal ion, in which the ligators are closest to octahedral positions. See S. F. Mason, R. D. Peacock, B. Stewart, *Mol. Phys.* **1975**, *30*, 1829 for further discussion of ligand polarization theory.

[26] G. Muller, *Dalton Trans.* **2009**, 9692.

Received: October 22, 2015