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Multifunctional "Clickates" as Versatile Extended Heteroaromatic Building Blocks: Efficient Synthesis via Click Chemistry, Conformational Preferences, and Metal Coordination

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Abstract: Click chemistry has been utilized to access 2,6-bis(1-aryl-1,2,3-triazol-4-yl)pyridines (BTPs) as versatile extended heteroaromatic building blocks for their exploitation in supramolecular chemistry, in particular foldamer and ligand design. In addition to their high-yielding synthesis using Cu^{I}-catalyzed Huisgen-type 1,3-dipolar cycloaddition reactions the formed triazole moieties constitute an integral part of the BTP framework and encode both its pronounced conformational preferences as well as its chelating ability. A diverse set of symmetrical and non-symmetrical BTPs carrying electron-donating and -withdrawing substituents at both terminal aryl and the central pyridine moieties has efficiently been synthesized and could furthermore readily be postfunctionalized with amphiphilic side chains and porphyrin chromophores. In both solution and solid state, the BTP scaffold adopts a highly conserved horseshoe-like *anti–anti* conformation. Upon protonation or metal coordination, the BTP scaffold switches to the chelating *syn–syn* conformation. Iron and europium complexes have been prepared, successfully characterized by single-crystal X-ray diffraction analysis, and investigated with regard to their spin state and luminescent properties. The extended heteroaromatic BTP scaffold should prove useful for the design of responsive foldamer backbones and the preparation of new magnetic and emissive materials.

Keywords: click chemistry · coordination chemistry · cycloaddition · foldamers · supramolecular chemistry

Introduction

The ability of the coordination chemist to prepare new metal complexes for various applications is inevitably tied to the accessibility of a versatile ligand set. Tridentate pyridine-centered heteroaromatic ligands, most notably terpyridines (tpy),[1] bis(oxazolinyl)pyridines (py-box),[2] and bis(pyrazolyl)pyridines,[3] represent a particularly privileged coordination framework, which has been utilized extensively for the design of various supramolecular architectures,[1b] optoelectronic[1b,4] and magnetic[5] materials as well as enantioselective catalysts.[6] However, variation of the ligand scaffold is often cumbersome, and therefore facile, modular, and versatile syntheses of these and related new ligand families are still needed.

The Cu^{I}-catalyzed Huisgen-type 1,3-dipolar cycloaddition of terminal alkynes and organic azides,[7,8] frequently referred to as the "click reaction",[9] provides an extremely efficient method to connect various functional entities.[10] Recently, this versatile reaction has been applied in various fields ranging from the biological[11] to the materials sciences.[12] While in most cases the formed 1,4-disubstituted 1,2,3-triazole serves as mere connecting unit, only occasionally the heterocycle itself is used as an integral structural element.[13]

The integration of several triazole building blocks within a larger structure constitutes a promising approach for the design of advanced chelating ligands, that is, "clickates".[14–16] Here, we report the facile and highly modular synthesis of

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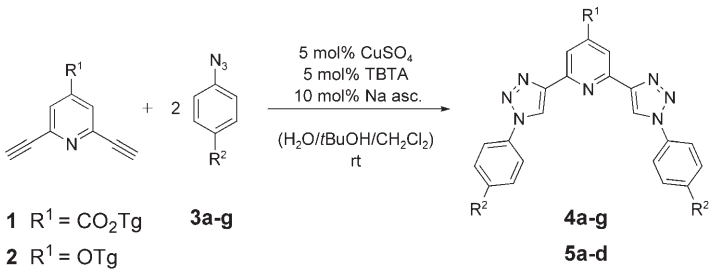
Supporting information for this article (68 pages of extensive synthetic details and characterization data) is available on the WWW under http://www.chemeurj.org/ or from the author.

2,6-bis(1-aryl-1,2,3-triazol-4-yl)pyridines (BTPs), featuring two integral triazole moieties bridged by a central pyridine core, thus creating a new ligand family and key building block for elongated heteroaromatic foldamer strands[17] (Figure 1). Our approach allows diverse substituents to be readily introduced at various positions in the ligand scaffold either during or after the "click reaction", thereby enabling the preparation of a multitude of symmetrical and non-symmetrical functional BTP derivatives with defined conformational preferences and rich coordination chemistry.[18]

Results and Discussion

Framework synthesis: 2,6-Diethynylpyridines carrying either electron-donating or electron-withdrawing groups were allowed to react with diverse electron-rich and electron-poor aryl azides (Scheme 1, Table 1).[19] Although frequently aliphatic azides and alkynes serve as substrates in the "click" reaction, we were pleased to note that after screening of the reaction conditions practically quantitative yields were obtained for aromatic substrates, independent of the electronic nature of the substituents. To maintain solubility of the products throughout the reaction (and for purposes of solvophobic foldamer design[20]) triethylene glycol side chains were introduced onto the pyridine components.



Scheme 1. Synthesis of 2,6-bis(-1aryl-1,2,3-triazol-4-yl)pyridines (BTPs) **4a–g** and **5a–d** (Tg = -$(CH_2CH_2O)_3CH_3$, TBTA = tris(benzyltriazolylmethyl)amine, Na asc. = sodium ascorbate).

Table 1. Synthesis of 2,6-bis(1-aryl-1,2,3-triazol-4-yl)pyridines (BTPs) as outlined in Scheme 1.

Compound	R^1	R^2	Yield[%][a]
4a	CO_2Tg[b]	CH_3	quant.[c]
4b	CO_2Tg	I	98
4c	CO_2Tg	NO_2	95
4d	CO_2Tg	$N(CH_3)_2$	95
4e	CO_2Tg	CO_2Et	quant.
4f	CO_2Tg	OCH_3	88[c]
4g	CO_2Tg	n-$C_{10}H_{21}$	96
5a	OTg	CH_3	quant.[c]
5b	OTg	I	85
5c	OTg	NO_2	86
5d	OTg	$N(CH_3)_2$	94

[a] Yield of isolated product. [b] Tg = -$(CH_2CH_2O)_3CH_3$. [c] 20 mol % Na asc. were used.

Non-symmetrical BTPs carrying two different triazole fragments were also generated in excellent yields by a sequential coupling approach (Scheme 2). The mono-protected 2,6-diethynyl-pyridine **6** was coupled to the first azide fragment to furnish monocycloadduct **7**, which was deprotected and subsequently coupled to another azide fragment to yield non-symmetrical, donor–acceptor substituted BTP **9** in 98% overall yield. The triisopropylsilyl (TIPS) protecting group proved stable under the applied click reaction conditions, yet it could easily be removed in the consequent activation step allowing for successive cycloaddition. This repetitive synthetic route provides the basis for the preparation of more complex structures, in particular larger oligomers (foldamers).[21]

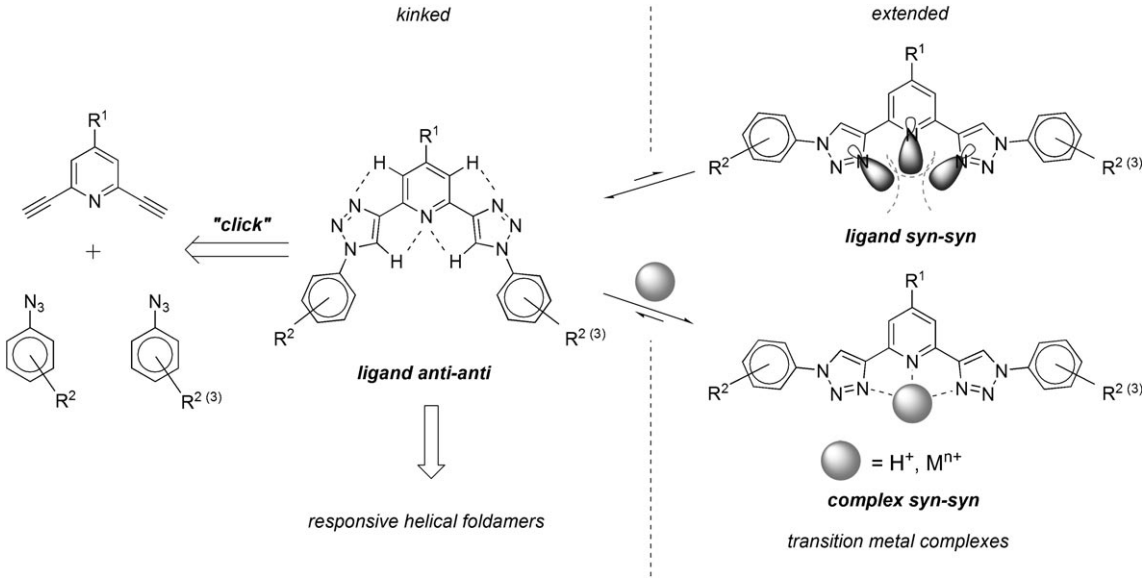
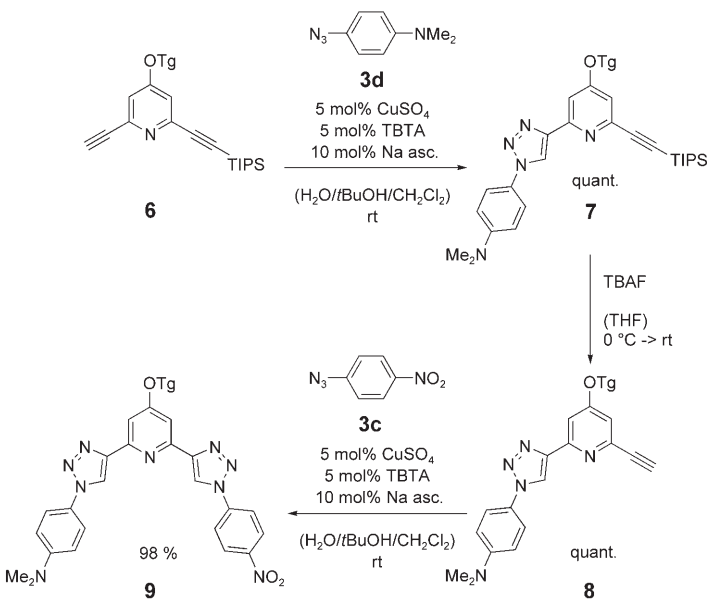


Figure 1. "Clickates" based on 2,6-bis(1,2,3-triazol-4-yl)pyridines (BTPs) provide a highly functional kinked foldamer building block and extended ligand scaffold, readily accessible via "click chemistry".



Scheme 2. Synthesis of non-symmetrical BTP **9** (Tg = -$(CH_2CH_2O)_3CH_3$, TBTA = tris(benzyltriazolylmethyl)amine, Na asc. = sodium ascorbate, TBAF = tetra(*n*-butyl)ammonium fluoride).

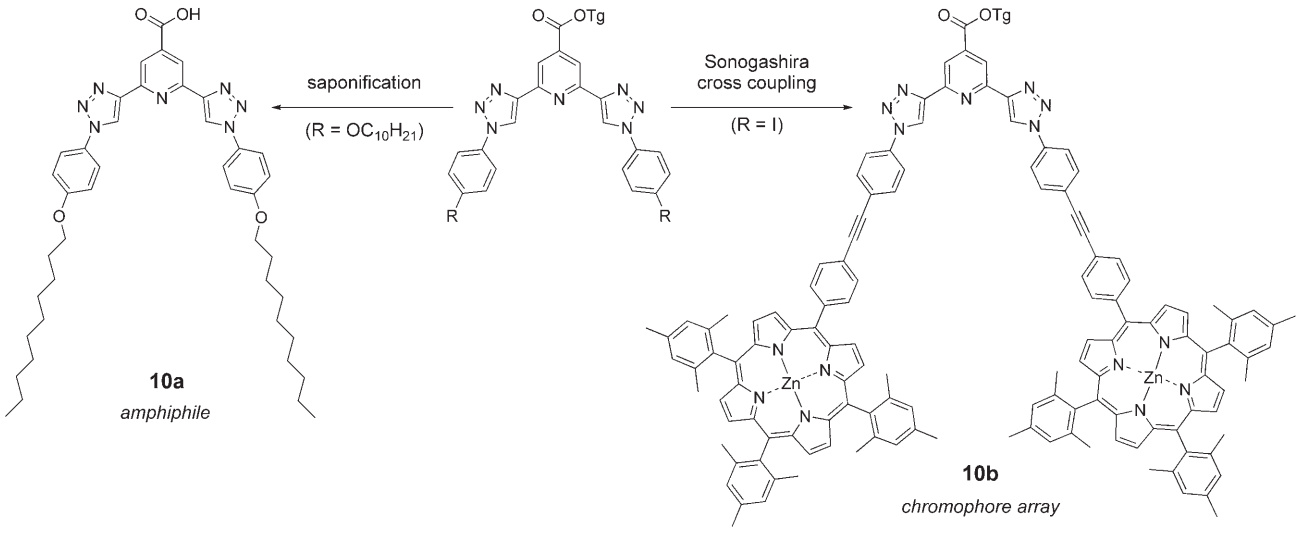
The BTP framework proved chemically robust and could be further functionalized, both at its central pyridine as well as at the terminal aryl moieties (Scheme 3). For example, the bisalkylated BTP ester **4g** could be easily saponified to yield the free carboxylic acid **10a**, while Pd^0-catalyzed cross-coupling of **4b** with the appropriate porphyrin-based acetylene readily provided **10b**, in which two zinc porphyrins are linked by the BTP scaffold. In both structures conformational switching of the BTP scaffold by changing pH or complexation of metal ions (vide infra) can be utilized either to alter self-assembly behavior or to tune distances and relative orientation of large chromophores.[21]

Conformational preferences: In analogy to the known conformational preference of 2,2′-bipyridines,[22] the BTP skeleton is expected to predominantly adopt the *anti–anti* conformation due to favorable electrostatic interactions, whereas repulsive interactions due to lone pair repulsion disfavor the *syn–syn* conformation (Figure 1). DFT calculations on a 4-(2-pyridyl)-1,2,3-triazole model system were carried out and predict a significant stabilization of the *anti* conformer by 6.4 kcal mol^{-1} over the *syn* conformer in the gas phase.[19] Experimental verification of the predicted strong conformational preference for the *anti–anti* conformation was obtained both in the solid state and in solution (Figure 2). Several independent single-crystal X-ray structural analyses reveal the highly conserved horseshoe-type flat arrangement of the BTP core. In NMR measurements on the non-symmetrical BTP derivative **9** in solution practically no NOE between the distant pyridyl and triazolyl protons could be detected.

The repulsive interaction between the lone pairs of adjacent N atoms can be overcome by protonation and metalation, respectively, thereby taking advantage of the chelating effect. Hence, as anticipated and conceptually envisaged in Figure 1, the *anti–anti* conformation of the BTP skeleton can be switched to the *syn–syn* conformation by protonation as shown by NOE experiments on BTP derivative **5b** (Figure 3).[19]

Coordination chemistry: First investigations into the coordination chemistry of the BTP scaffold were performed to compare it with well-known tridentate polyazaromatic ligands, such as bis(pyrazolyl)pyridines, from which the parent BTP can be derived via formal replacement of a C–H group within the pyrazole residue by a nitrogen atom.

To clarify the influence of this modification on the ligand field strength, subsequent to initial UV/Vis titrations,[19] the iron complex $[Fe(\mathbf{5c})_2](OTf)_2$ (OTf = trifluoromethanesulfonate) was synthesized (Scheme 4). While the triethylene



Scheme 3. Postfunctionalization of the BTP scaffold (Tg = -$(CH_2CH_2O)_3CH_3$).

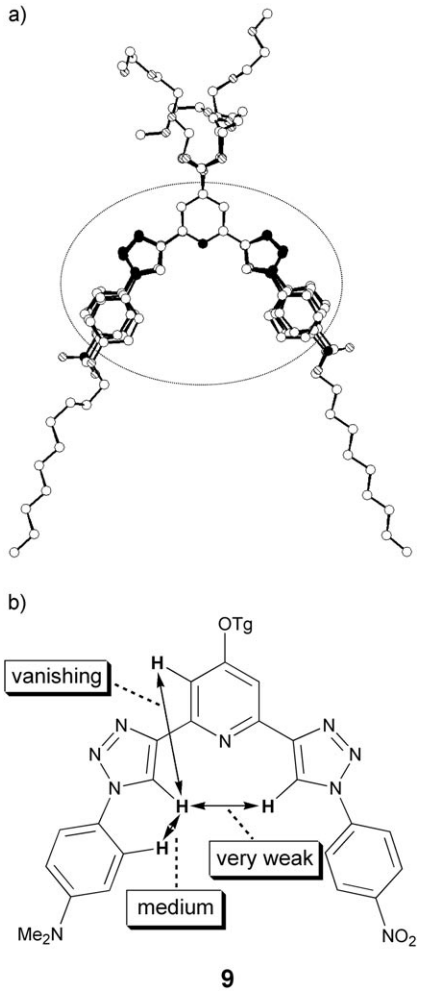


Figure 2. Conformational preference of BTPs for the *anti–anti* conformation in the solid: a) top view overlay of four independent crystal structures of **4a**, **4c**, **5b**, and **10a** (oval denotes highly conserved horseshoe-like conformation) as well as in solution: b) intensity of NOE contacts in compound **9** (CH_2Cl_2, 27 °C).

glycol side chains at the BTP scaffold are certainly advantageous for solubility, foldamer design, and subsequent surface attachment, they naturally hamper crystallization due their inherent flexibility and poor packing ability and therefore rarely allow single-crystal X-ray diffraction analysis. Nonetheless, the molecular structure of $[Fe(\mathbf{5c})_2](OTf)_2$ (Figure 4) could be determined. It shows unexpectedly short Fe–N bonds averaging 1.93 Å, which point to a low-spin state at 116 K (high-spin complexes of the type $[Fe(L)_2]^{2+}$ typically exhibit bond lengths between 2.1 and 2.2 Å),[23] consistent with the red-brown color of the compound. No thermochromic effects are observed on warming to room temperature and accordingly, ^{1}H NMR spectroscopic investigations performed in CD_3CN solution at room temperature again indicate a low-spin state,[19] a finding that is surprising, considering that related systems with bis(pyrazolyl)pyridine ligands usually switch from their low-spin ground states into the high-spin states at temperatures significantly below room temperature[3] or even at 30 K after irradiation, referred to as light-induced excited spin state trapping (LIESST).[24] Thus, the ligand field strength of **5c** is higher than that of bis(pyrazolyl)pyridine and more comparable to that of terpyridine.[25] Future research will aim at tuning the electronic properties of the BTP ligand framework (R and R′ substituents in Scheme 4) to obtain iron complexes that undergo spin crossovers in an accessible temperature range or induced by light, which can subsequently be attached to surfaces via the readily adjustable tether at the pyridyl moiety.[21]

Another area where terpyridine, bis(pyrazolyl)pyridine, and their related bis(benzimidazolyl)pyridine derivatives have been extensively employed is the sensitization of lanthanide (Ln) luminescence, whose direct excitation is not possible due to Laporte-forbidden 4f–4f transitions.[26] Suitable organic chromophores (ligands) with a significant absorption cross-section in the UV(Vis) are thus required as antennae that efficiently transfer their excitation energy to the excited state(s) of the lanthanide ion and thus lead to "sensitized" light emission. Ideally, ligands should: 1) form stable complexes (for practical applications under physiological conditions), 2) enable efficient ligand-to-lanthanide energy transfer (through compatible energy levels), and 3) prevent nonradiative deactivation of the lanthanide excited states, for instance by O–H oscillators of coordinated or closely diffusing water molecules.[27] A strategy that has been successfully pursued in the past relies on the organization of three tridentate binding sites around nine-coordinate

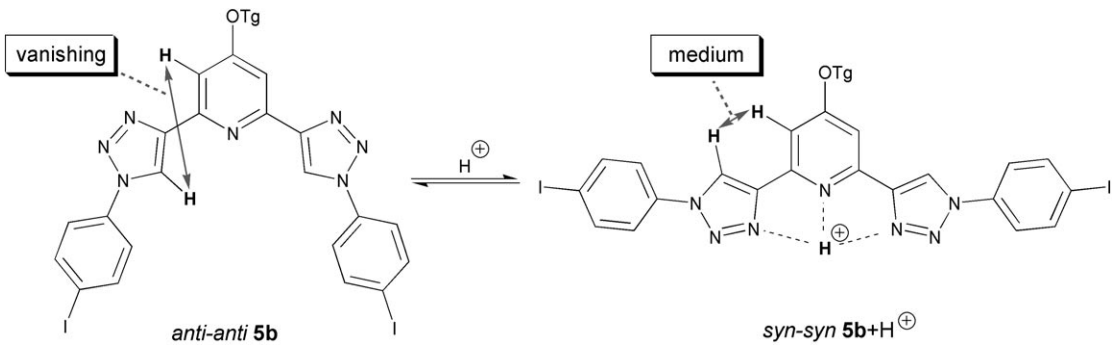
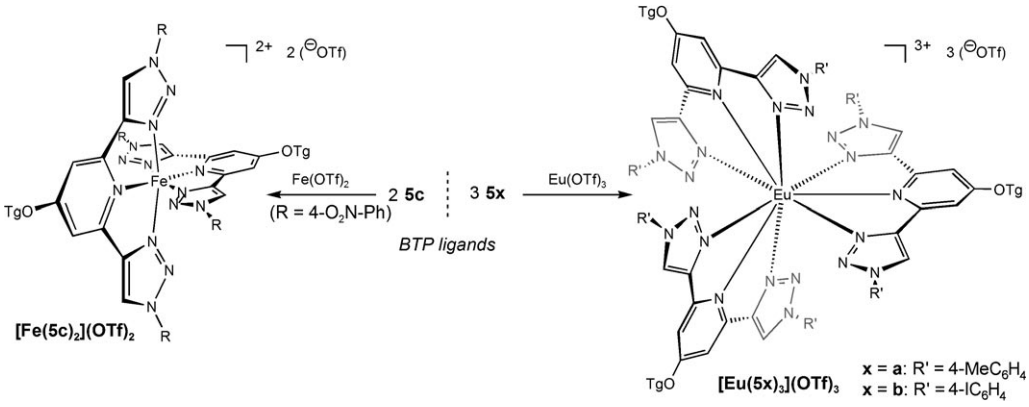


Figure 3. Conformational switching from the *anti–anti* to the *syn–syn* conformation induced by protonation, as revealed from the relative intensities of NOE contacts in compound **5b** before and after addition of trifluoroacetic acid (TFA) in CD_2Cl_2 at 27 °C (Tg = -$(CH_2CH_2O)_3CH_3$).



Scheme 4. Preparation of iron and europium complexes (Tg = -$(CH_2CH_2O)_3CH_3$, OTf = trifluoromethanesulfonate).

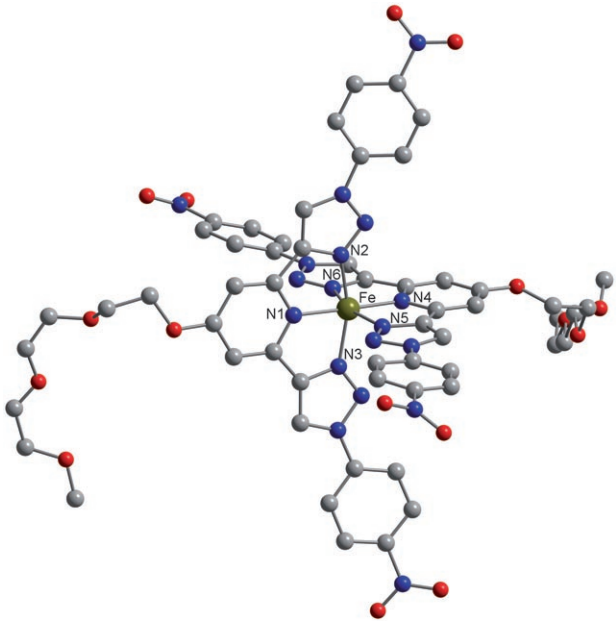


Figure 4. Molecular structure of $[Fe(\mathbf{5c})_2](OTf)_2$ (hydrogen atoms, anions, co-crystallized $[Fe(OTf)(H_2O)(MeCN)_4]OTf$ and solvent molecules have been omitted for clarity. OTf = trifluoromethanesulfonate). Selected bond lengths [Å] and angles [°]: N1–Fe 1.913(4), N2–Fe 1.921(3), N3–Fe 1.945(3), N4–Fe 1.908(4), N5–Fe 1.937(4), N6–Fe 1.936(4); N1-Fe-N2 80.0(2), N1-Fe-N3 81.1(2), N1-Fe-N4 178.2(2), N1-Fe-N5 101.2(2), N1-Fe-N6 98.4(2), N2-Fe-N3 160.9(2), N2-Fe-N4 99.1(2), N2-Fe-N5 91.5(2), N2-Fe-N6 91.8(2), N3-Fe-N4 99.9(2), N3-Fe-N5 89.5(2), N3-Fe-N6 93.7(2), N4-Fe-N5 80.4(2), N4-Fe-N6 80.0(2), N5-Fe-N6 160.4(2).

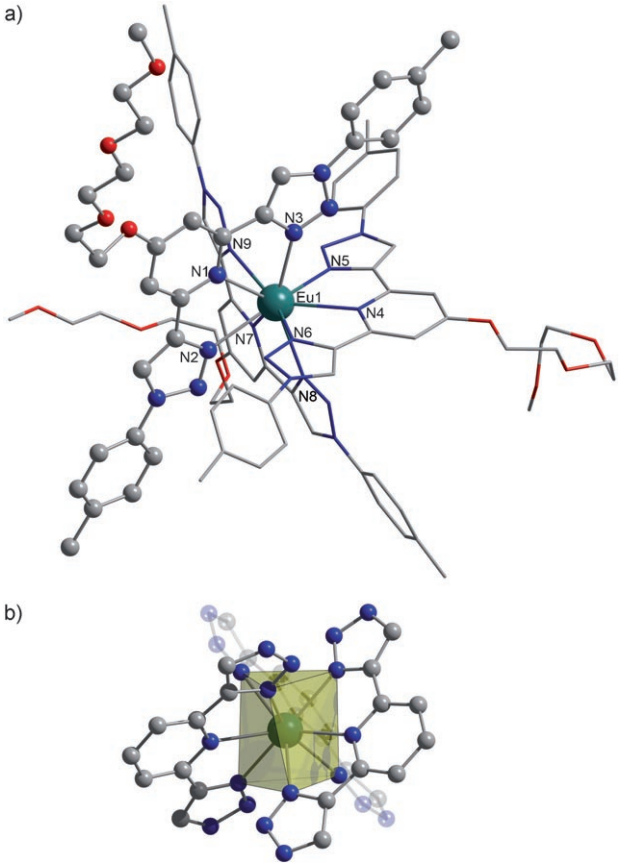


Figure 5. a) Molecular structure of $[Eu(\mathbf{5a})_3](OTf)_3$ (Hydrogen atoms, anions, and co-crystallized solvent molecules have been omitted for clarity. OTf = trifluoromethanesulfonate). b) Tricapped, trigonal prismatic coordination of the metal center. Selected bond lengths [Å] and angles [°]: N1–Eu1 2.574(8), N2–Eu1 2.531(8), N3–Eu1 2.513(8), N4–Eu1 2.598(8), N5–Eu1 2.520(8), N6–Eu1 2.514(8), N7–Eu1 2.572(8), N8–Eu1 2.507(8), N9–Eu1 2.499(7); N1-Eu-N2 62.9(3), N1-Eu-N3 64.2(2), N1-Eu-N4 122.4(3), N1-Eu-N5 136.7(3), N1-Eu-N6 74.2(3), N1-Eu-N7 119.8(3), N1-Eu-N8 135.7(2), N1-Eu-N9 74.3(3), N2-Eu-N3 127.1(3), N2-Eu-N4 135.4(3), N2-Eu-N5 147.2(3), N2-Eu-N6 78.8(3), N2-Eu-N7 74.6(3), N2-Eu-N8 78.3(3), N2-Eu-N9 89.0(3), N3-Eu-N4 74.7(3), N3-Eu-N5 79.4(3), N3-Eu-N6 85.2(3), N3-Eu-N7 137.5(2), N3-Eu-N8 146.3(3), N3-Eu-N9 79.1(2), N4-Eu-N5 63.9(3), N4-Eu-N6 63.5(3), N4-Eu-N7 117.8(3), N4-Eu-N8 71.7(3), N4-Eu-N9 135.6(3), N5-Eu-N6 127.3(3), N5-Eu-N7 72.6(2), N5-Eu-N8 87.6(3), N5-Eu-N9 76.6(3), N6-Eu-N7 137.2(3), N6-Eu-N8 78.2(3), N6-Eu-N9 148.4(3), N7-Eu-N8 64.1(3), N7-Eu-N9 63.8(3), N8-Eu-N9 128.0(3).

Ln^{III} ions.[28,29] To test the potential of BTPs in this context a threefold excess of **5b** was allowed to react with $Eu(OTf)_3$ for the synthesis of compound $[Eu(\mathbf{5b})_3](OTf)_3$ (Scheme 4), which was fully characterized; however, severe disordering of the cations within its crystals prohibited the exact analysis of the molecular structure.[19] However, when **5a** was employed as the ligand, the crystal structure of the resulting complex $[Eu(\mathbf{5a})_3](OTf)_3$ (Scheme 4) could be determined and the result is displayed in Figure 5a.

The metal center is coordinated by all nine N atoms of the three terdentate ligands with a tricapped trigonal prismatic geometry (Figure 5b). The two triangular faces of the

trigonal prism are not exactly eclipsed but slightly staggered and are formed by the six coordinating N atoms belonging to the triazole units, while the pyridyl donors form the three caps. Comparing this structure with the related structure of $[Eu(L')_3](PF_6)_3$ (L′ = 2,6-bis(1*H*-pyrazol-3-yl)pyridine)[28b] it can be noted that the Eu–$N_{pyridyl}$ distances are very similar in both complexes, whereas the Eu–$N_{triazole}$ distances in $[Eu(\mathbf{5a})_3]^{3+}$ are somewhat shorter than the Eu–$N_{pyrazole}$ distances in $[Eu(L')_3]^{3+}$. This is a reflection of the fact that in $[Eu(L')_3]^{3+}$ the ligands are not exactly planar but exhibit slight twists between the adjacent aromatic rings, and interestingly the same observation has been made for $[Eu(terpy)_3]^{3+}$ as well.[29] The ligand scaffolds in $[Eu(\mathbf{5a})_3]^{3+}$ are merely planar, however, which indicates that the binding pockets provided by the BTPs are more favorable for the formation of complexes $[Ln(BTP)_3]^{3+}$, thus leading to stronger metal–ligand interactions. In summary, the BTP ligand provides superior donor capabilities and enhanced steric freedom in comparison to established tridentate azaaromatic ligands such as terpy (in the case of $[Eu(BTP)_3]^{3+}$) and bis(pyrazolyl)pyridines (in the case of $[Fe(BTP)_2]^{2+}$), respectively.

$[Eu(\mathbf{5b})_3](OTf)_3$ displays a characteristic red-orange emission both in the solid state (crystal and powder) and in solution (Figure 6). The BTP scaffold efficiently absorbs in the UV and sensitizes the typical narrow lanthanide ion emission, in agreement with the few reported spectra of EuL_3^{3+} ions.[30] Again, substitution of the BTP ligand framework should allow convenient tuning of the luminescence properties of the respective lanthanide complexes and their covalent attachment to either biomacromolecules (labeling for diagnostics) or solid substrate surfaces.[21]

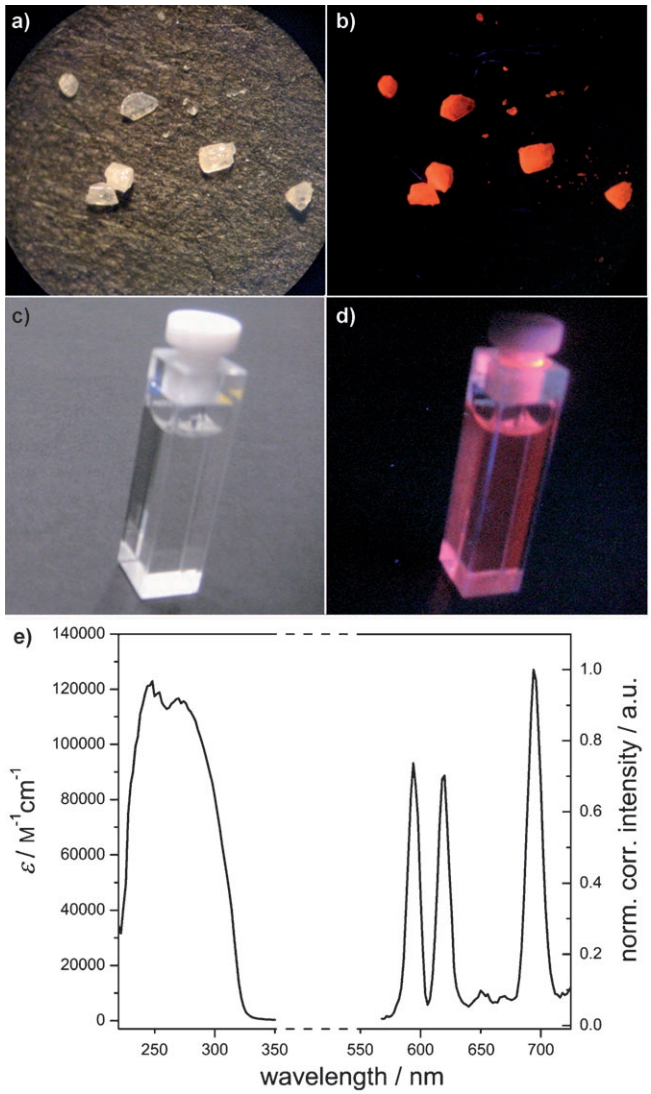


Figure 6. Emission properties of europium complex $[Eu(\mathbf{5b})_3](OTf)_3$: Microscope views showing $[Eu(\mathbf{5b})_3](OTf)_3$ single crystals a) in daylight, and b) exposed to excitation by a 254 nm UV lamp as well as cuvettes containing CH_2Cl_2 solutions of $[Eu(\mathbf{5b})_3](OTf)_3$ c) in daylight, and d) exposed to excitation by a 254 nm UV lamp. e) Absorption and emission (λ_{exc} = 265 nm) spectra of $[Eu(\mathbf{5b})_3](OTf)_3$ in CH_2Cl_2 at 25 °C.

Conclusion

We have developed "clickates" based on the BTP motif as a new privileged framework for supramolecular chemistry. While our approach benefits from its synthetic ease and versatility, the resulting BTP derivatives display strong yet switchable conformational preferences and reveal rich coordination chemistry. Ongoing efforts in our laboratories are primarily focused on constructing larger oligomers and polymers as new responsive foldamer backbones and exploring the coordination chemistry to utilize the BTP scaffold for the generation of magnetic and emissive materials, as well as switchable amphiphiles, chromophore arrays, and supramolecular polymers.[21]

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