Synthesis of Functionalized Fluorescent Europium(III) Terpyridyl Chelates

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Abstract: The synthesis of substituted terpyridines via triazine intermediates is described. The intermediates allow the facile introduction of cyano groups, which are converted into amino diacetic acid moieties. Together with the terpyridine nitrogen atoms they shield coordinated europium(III) ions completely from the solvent. The terpyridines may be further functionalized for specific applications using ligands, bromo substituents, and standard transition metal mediated coupling methods. This makes the title compounds valuable intermediates for the preparation of luminescent probes in biochemistry, medicinal diagnostics or materials science.

Key words: heterocycles, pyridines, Diels–Alder reaction, ligands, lanthanide

Europium chelates are widely used due to their unique luminescence properties for various bioanalytical applications such as non-radioactive labeling in time-resolved fluorescence immunoassays or DNA hybridization assays.[1] Furthermore, some recent examples demonstrated the application of europium chelates as luminescent chemosensors for different chemical analytes.[2] The main advantages of Eu^{3+} luminescence based probes are their long emission wavelengths excitation lifetimes, which allow easy separation of the output signal from short-lived background noise in the sample. However, solvated lanthanide metal ions have only weak absorption and fluorescence and a light harvesting ligand, a molecular antenna, is needed to enhance the photophysical properties. Light energy absorbed by the ligand is intramolecularly transferred to the Eu^{3+} ion and emitted as the characteristic spectrum of Eu^{3+}. In aqueous solution it is important to exclude water molecules from the coordination sphere of the Eu^{3+} in order to prevent vibronic quenching. Terpyridine polyaminocarboxylates are well known as perfect chelating ligands for Eu^{3+}.[3] The terpyridine moiety coordinates directly to the europium ion, harvesting light energy and efficiently transfers the energy to Eu^{3+}. Additional imidodiacetic acid moieties occupy the remaining coordination sites of Eu^{3+}, which results both in the high stability of the complex and effective protection of the central ion from water coordination.

In this paper we report an efficient synthesis of terpyridines[4] bearing carboxylic or bis(carboxymethyl)aminomethyl groups which are able to chelate lanthanide ions.[5] The procedure is based on transformations of the cyano group of dicyanoterpyridines, which are available starting materials according to a recently introduced synthetic methodology for the formation of 1,2,4-triazine rings.[6] One main advantage of the approach is the potential wide variation of aromatic substituents in the terminal rings of the terpyridine system. The bromoaryl moieties used in this paper allow a further transformation by standard methods of transition-metal mediated coupling reactions with carbon or heteroatom nucleophiles.[7] This makes the title compounds key intermediates for the synthesis of complex luminescence probes for applications in biochemistry, medicinal diagnostics or material science.

The starting material 2,6-bis[6-(4-bromophenyl)-1,2,4-triazin-3-yl 4-oxide]-pyridine (**2**) was prepared by the reaction of two equivalents of 1-(4-bromophenyl)-1-hydrazono-2-oximinoethane (**1**) with pyridine-2,6-dicarboxaldehyde in acetic acid, followed by treatment with Pb_3O_4 without isolation of the intermediate products (Scheme 1). The *N*-oxide group in the 1,2,4-triazine moieties of **2** facilitates nucleophilic substitution of hydrogen. Desoxygenative cyanation of **2** by treatment with cyanohydrine in the presence of triethylamine in dichloromethane solution gave 2,6-bis[6-(4-bromophenyl)-5-cyano-1,2,4-triazin-3-yl]-pyridine (**3**).

A Diels–Alder reaction with norbornadiene converts compound **3** into 5,5″-di(4-bromophenyl)-6,6″-dicyano terpyridine **4**. The use of other dienophiles, such as cyclopentene, allows the introduction of other substituents, such as in **9** (Scheme 2). The regioselective introduction of the cyano group in the positions 6,6″ of the terpyridine system sets the stage for the synthesis of terpyridine ligands with additional coordination sites with a suitable geometry. The reduction of the dinitrile **4** with diborane as its THF complex, affords 6,6″-bis(aminomethyl)terpyridine **5**, which already may serve as a pentadentate aza ligand itself. Alkylation of the aminomethyl compound **5** with methyl bromoacetate gave the tetra ester **6**, which was hydrolyzed to the tetracarboxylic acid **7**. Acid **7** with its tridentate terpyridine and four carboxy groups is a suitable chelating ligand for Eu(III) ions. The Eu(III) complex **8** was obtained from **7** and Eu(III) chloride.

To confirm the proposed complete chelation of the Eu(III) ion by ligand **7** the number of water molecules within the coordination sphere of complex **8** was estimated by a known procedure[8] and compared with the complex **11** having fewer coordination sites. The lifetimes of emission

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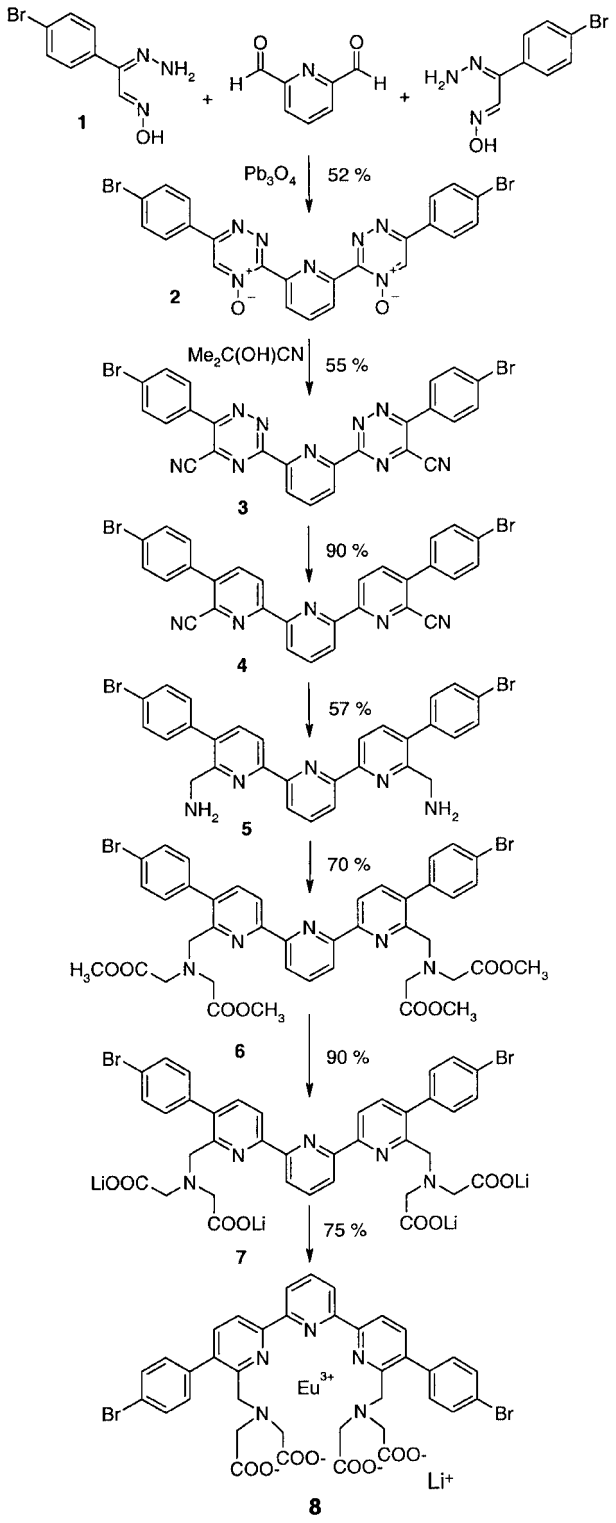
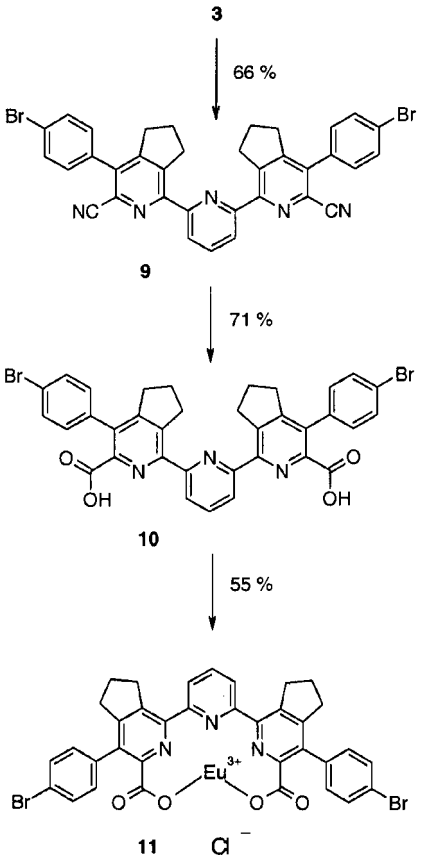


Scheme 1 Synthesis of europium complex **8**. For reaction conditions and reagents, see text and experimental part.

of both complexes in water and in D_2O were determined. O–D oscillators quench lanthanide luminescence less efficient then O–H oscillators and Equation 1 allows the number of water molecules within the lanthanide coordination sphere to be estimated.



Scheme 2 Synthesis of europium complex **11**. For reaction conditions and reagents, see text and experimental part.

$$q = A'[(1/\tau_{H2O} - 1/\tau_{D2O})-0.25]$$

Equation 1 Estimation of the number of water molecules *q* in the coordination sphere; τ_{H2O} and τ_{D2O} experimental lifetimes in milliseconds obtained in water and deuterium oxide respectively; A′ is a normalizing factor which is approximately 1.2 for Eu^{3+} species.

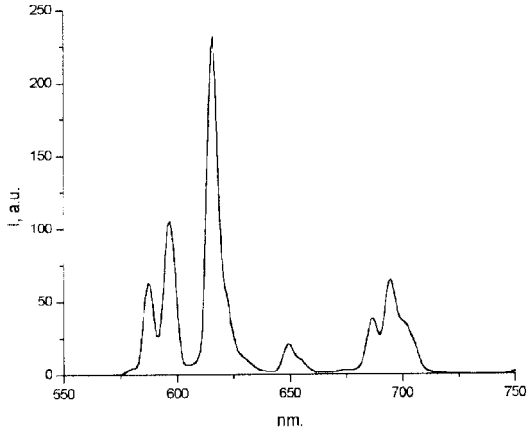


Figure 1 Emission spectrum of compound **8** in water λ_{ex} 344 nm, total decay time 5 ms, delay time 0.1 ms, gate time 1.0 ms, excitation slit width of 2.5 nm, emission slit width 5 nm.

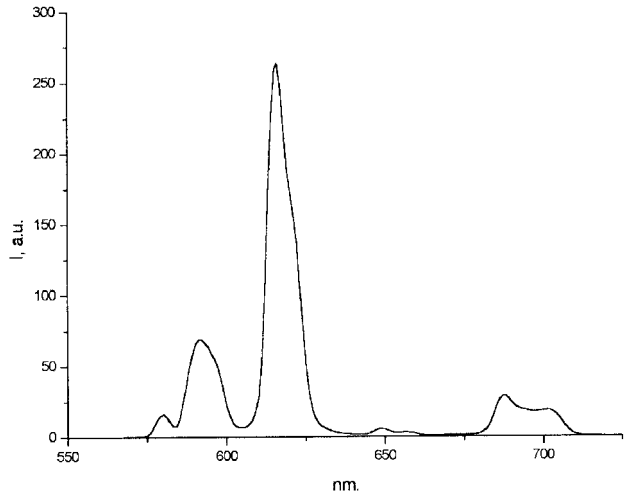


Figure 2 Emission spectrum of compound **11** in water λ_{ex} 336 nm, total decay time 5 ms, delay time 0.1 ms, gate time 1.0 ms, excitation slit width of 5 nm, emission slit width 5 nm.

The emission lifetimes of complex **8** in H_2O and D_2O are 1.4 and 2.5 ms, respectively. From Equation 1 the number of water molecules within the coordination sphere $q = 0.08$, is estimated. This confirms a nearly complete shielding of the Eu^{3+} ion in **8** by the ligand (Figure 1 and Figure 3). The emission lifetimes in H_2O and D_2O for complex **11**, which has two carboxyl groups less available for europium ion binding, are 0.25 and 1.93 ms, respectively. From Equation 1 a value of $q = 3.88$ is calculated, which indicates the presence of four water molecules in the europium coordination sphere of complex **11** (Figure 2 and Figure 4).

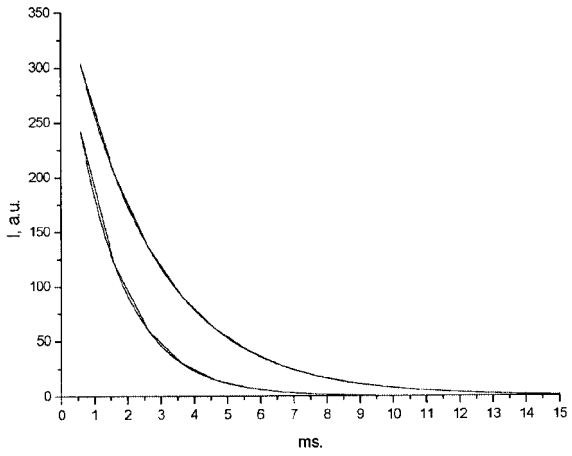


Figure 3 Emission life times of complex **8** in water (lower) and D_2O (upper curve), respectively.

In conclusion, we have reported a feasible synthetic route to functionalized terpyridienes, such as **7** and **10**, which serve as europium(III) complex ligands. The preparation of ligands that fully or partially shield the europium ion from the solvent is possible using the same intermediates. The bromoaryl substituents of the ligands are well suited for further functionalization by transition metal mediated

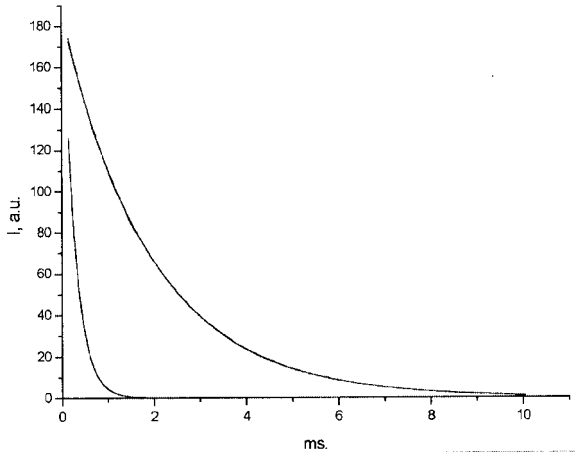


Figure 4 Emission life times of complex **11** in water (lower) and D_2O (upper curve), respectively.

coupling reactions. This renders the described compounds valuable synthetic intermediates for the preparation of luminescent probes for applications in biochemistry, medicinal diagnostics or material science.

NMR: Bruker Avance DRX 300. ^1H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra at 75 MHz. The multiplicity of the ^{13}C signals was determined with the DEPT technique and quoted as: (+) for CH_3 or CH, (–) for CH_2 and (C_{quat}) for quaternary carbons. UV/VIS: Varian Cary 50 Bio. Mass spectra: Varian CH-5. Starting hydrazone **1** was synthesized according to the described method.[9] Luminescent measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature. Distilled, deionized water was used without deaeration. Deuterium oxide 99.9% was purchased from Deutero GmbH.

2,6-Bis[6-(4-bromophenyl)-1,2,4-triazin-3-yl 4-oxide]-pyridine (2)

A solution of pyridine 2,6-dicarboxaldehyde (0.675 g, 5 mmol) in HOAc (10 mL) was added to a stirred solution of isonotrosoacetophenone hydrazone **1** (2.42 g, 10 mmol) in HOAc (10 mL) and the reaction mixture was stirred at r.t. for 4 h. To the resulting suspension Pb_3O_4 (6.85 g, 10 mmol) was added and the mixture was stirred at r.t. for 5 h. The obtained precipitate was separated by filtration, washed with HOAc (5 mL) and then heated to reflux for 5 min in HOAc (10 mL), cooled, filtered, and washed with EtOH (20 mL) to give **2** (1.5 g, 2.6 mmol, 52%). No further purification was required before the next step; mp 292 °C (decomp.).

IR (KBr): 3057, 1654, 1551, 1585, 1421, 1365, 1237, 1074, 826 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 7.80–7.86 (m, 4 H), 8.18–8.22 (m, 4 H), 8.29 (s, 3 H), 9.25 (s, 2 H).

MS (EI, 70 eV): *m/z* (%) = 581 (51) [M(2 ^{81}Br)]$^+$, 579 (100) [M ($^{81}Br^{79}Br$)]$^+$, 577 (52) [M (2 ^{79}Br)]$^+$, 561 (35) [M (^{79}Br) – O]$^+$, 545 (9) [M(^{79}Br) – 2 O]$^+$.

Anal. Calcd for $C_{23}H_{13}Br_2N_7O_2$, (579.21): C, 47.70; H, 2.26; N, 16.93. Found: C, 47.62; H, 2.95; N, 17.08.

2,6-Bis[5-cyano-6-(4-bromophenyl)-1,2,4-triazine-3-yl]pyridine (3)

To a solution of 1,2,4-triazine-4-oxide **2** (1.40 g, 2.42 mmol) in CH_2Cl_2 (30 mL) acetone cyanohydrine (0.88 mL, 9.68 mmol) and Et_3N (0.68 mL, 4.84 mmol) were added. The reaction mixture was

refluxed for 1 h, concentrated by rotary evaporation to a volume of about 10 mL and filtered through a short silica column (CH_2Cl_2–EtOAc, 10:1). The solvent was removed under reduce pressure, the residue was stirred in EtOAc (10 mL) and filtered to give **3** (795 mg, 55%); mp 242–243 °C.

IR (KBr): 3084, 2239, 1585, 1479, 1376, 1180, 1074, 1005, 829 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.78–7.85 (m, 4 H), 8.04–8.12 (m, 4 H), 8.32 (t, 1 H, *J* = 8.0 Hz), 8.92 (d, 2 H, *J* = 8.0 Hz).

^{13}C NMR: δ = 114.2 (C_{quat}), 127.0 (+), 127.7 (C_{quat}), 129.7 (C_{quat}), 130.6 (+), 132.6 (C_{quat}), 132.9 (+), 139.4 (+), 152.1 (C_{quat}), 156.7 (C_{quat}), 160.6 (C_{quat}).

MS (EI, 70 eV): *m*/*z* (%) = 599 (51) $[M]^+$, 597 (100), $[M]^+$, 595 (49) $[M]^+$.

Anal. Calcd for $C_{25}H_{11}Br_2N_9$ (597.23): C, 50.28; H, 1.86; N, 21.11. Found: C, 50.17; H, 2.09; N, 20.95.

5,5″-Bis(4-bromophenyl)-6,6″-dicyano-2,2′,6′2″-terpyridine (4)
Dicyanotriazine **3** (1.65 g, 2.76 mmol) and bicyclo[2.2.1]hepta-2,5-diene (2.54 g, 3 mL, 27.6 mmol) in toluene (10 mL) was heated under reflux for 24 h. Upon cooling a precipitate of **4** formed, which was collected by filtration, washed with EtOH and dried to give **4** (1.47 g, 90%).

^1H NMR ($CDCl_3$): δ = 7.49–7.56 (m, 4 H), 7.67–7.74 (m, 4 H), 8.00 (d, 2 H, *J* = 8.5 Hz), 8.06 (t, 1 H, *J* = 8.0 Hz), 8.61 (d, 2 H, *J* = 8.0 Hz), 8.85 (d, 2 H, *J* = 8.5 Hz).

^{13}C NMR ($CDCl_3$): δ = 116.9 (C_{quat}), 128.2 (+), 129.0 (+), 130.3 (+), 131.3 (C_{quat}), 132.4 (+), 134.0 (C_{quat}), 137.9 (C_{quat}), 138.3 (+), 138.6 (+), 140.7 (C_{quat}), 153.3 (C_{quat}), 156.0 (C_{quat}).

IR (KBr): 3080, 2230, 1584, 1433, 1072, 813 cm^{-1}.

MS (CI, NH_3): *m*/*z* (%) = 595 (50), 593 (100), 591 (47) $[M]^+$.

Anal. Calcd for $C_{29}H_{15}Br_2N_5$ (593.28): C, 58.71; H, 2.55; N, 11.80. Found: C, 58.73; H, 2.57; N, 11.55.

6,6″-Bis(aminomethyl)-5,5″-bis(4-bromophenyl)-2,2′:6′,2″-terpyridine·5HCl (5)
Dinitrile **4** (617 mg, 1.04 mmol) was dissolved in anhyd THF (10mL) and degassed, then a BH_3·THF solution was added (1 M, 10.4 mL, 10.4 mmol) and the reaction mixture was stirred at r.t. for 24 h. The excess of borane was destroyed with MeOH (5 mL). The solvent was removed by rotary evaporation, the residue was dissolved in HCl-saturated EtOH (10 mL) and refluxed for 2 h yielding, after cooling, a precipitate, which after filtration gave **5** (462 mg, 57%); mp > 300 °C.

IR (KBr): 3032, 2885, 1610, 1453, 1277, 1074, 1000, 822 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 4.27 (br q, 4 H, *J* = 5.6 Hz), 7.48–7.57 (m, 4 H), 7.75–7.82 (m, 4 H), 8.03 (d, 2 H, *J* = 8.0 Hz), 8.24 (t, 1 H, *J* = 7.8 Hz), 8.59 (br t, 6 H, *J* = 5.2 Hz), 8.74 (d, 2 H, *J* = 8.2 Hz), 8.95 (d, 2 H, *J* = 7.7 Hz).

^{13}C NMR: δ = 40.7 (–), 119.8 (+), 122.0 (C_{quat}), 122.2 (+), 131.1 (+), 131.7 (+), 134.7 (C_{quat}), 136.0 (C_{quat}), 138.3 (+), 139.1 (+), 149.6 (C_{quat}), 153.4 (C_{quat}), 153.9 (C_{quat}).

MS (ESI): *m*/*z* = 600, 602, 604 $[MH]^+$.

6,6″-[*N*,*N*]bis(methoxycarbonylmethyl)aminomethyl]-5,5″-bis(4-bromophenyl)-2,2′:6′,2″-terpyridine (6)
A mixture of the bis-amine **5** (405 mg, 0.52 mmol), sodium carbonate (772 mg, 7.28 mmol) and methyl bromoacetate (318 mg, 2.08 mmol) in anhyd CH_3CN was heated under reflux for 24 h. The mixture was concentrated in vacuum, mixed with water and extracted with CH_2Cl_2 (3 × 10 mL). The organic extract was dried over sodium sulfate and evaporated. Purification by column chromatography (EtOAc–hexane, 1:1) yielded **6** (325 mg, 70%); R_f 0.45; mp 124–126 °C.

IR (KBr): 2949, 1744, 1436, 1200, 1002, 816 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 3.57 (s, 12 H), 3.67 (s, 8 H), 4.01 (s, 4 H), 7.41–7.47 (m, 4 H), 7.51–7.58 (m, 4 H), 7.69 (d, 2 H, *J* = 8.0 Hz), 7.93 (t, 1 H, *J* = 8.0 Hz), 8.48 (d, 2 H, *J* = 8.0 Hz), 8.55 (d, 2 H, *J* = 8.0 Hz).

^{13}C NMR: δ 51.4 (+), 54.4 (–), 57.6 (–), 119.7 (+), 121.2 (+), 122.1 (C_{quat}), 131.2 (+), 131.5 (+), 137.4 (C_{quat}), 137.8 (+), 138.1 (C_{quat}), 138.8 (C_{quat}), 154.2 (C_{quat}), 154.9 (C_{quat}), 171.7 (C_{quat}).

MS (ESI): *m*/*z* = 888, 890, 892 $[MH]^+$, 910, 912, 914 $[MNa]^+$.

Anal. Calcd for $C_{41}H_{39}Br_2N_5O_8$ (889.60): C, 55.36; H, 4.42; N, 7.87. Found: C, 55.45; H, 4.62; N, 7.78.

6,6″-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-5,5″-bis(4-bromophenyl)-2,2′:6′,2″-terpyridine tetralithium salt (7)
Compound **6** (200 mg, 0.22 mmol) was dissolved in a mixture of THF (4 mL) and MeOH (1 mL). An aq solution of LiOH (1 M, 2 mL, 2 mmol) was added and the solution was heated under reflux for 30 min. The reaction mixture was cooled to r.t., the precipitate was separated by filtration and washed with THF to give **7** (170 mg, 0.20 mmol, 90%); mp > 300 °C.

IR (KBr): 2924, 1592, 1435, 1414, 999, 816 cm^{-1}.

^1H NMR (MeOD): δ = 3.17 (s, 8 H), 3.95 (s, 4 H), 7.31–7.39 (m, 4 H), 7.63–7.70 (m, 4 H), 7.91 (d, 2 H, *J* = 8.0 Hz), 8.21 (t, 1 H, *J* = 8.0 Hz), 8.36 (d, 2 H, *J* = 8.0 Hz), 8.45 (d, 2 H, *J* = 8.0 Hz).

^{13}C NMR: δ = 57.4 (–), 59.4 (–), 120.4 (+), 122.0 (C_{quat}), 122.7 (+), 130.6 (+), 131.4 (+), 136.3 (C_{quat}), 136.7 (C_{quat}), 138.9 (+), 139.5 (+), 154.3 (C_{quat}), 155.5 (C_{quat}), 155.7 (C_{quat}), 178.7 (C_{quat}).

MS (ESI): *m*/*z* = 832, 838, 844, 850 (for isotopes ^{79}Br, ^7Li).

{6,6″-[N,N-bis(carboxymethyl)aminomethyl]-5,5″-bis(4-bromophenyl)-2,2′:6′,2″-terpyridine}europium(III) Monolithium Salt (8)
A solution of ligand **7** (86 mg, 0.1 mmol) in MeOH (2mL) was added to a solution of europium(III) chloride hexahydrate (40 mg, 0.11 mmol) in MeOH. The reaction mixture was stirred at r.t. for 6 h. Complex **8** crystallizes from the reaction mixture, was separated by filtration and washed with MeOH to give **8** (74 mg, 75%).

IR (KBr): 2921, 1603, 1440, 1400, 1004, 816 cm^{-1}.

MS (FAB): *m*/*z* = 985, 987, 989, 991 $[C_{37}H_{27}{}^{79}Br_2{}^{151}EuLiN_5O_8]$ 978, 980, 982, 984. $[C_{37}H_{27}{}^{79}Br_2{}^{151}EuN_5O_8]$, (for all isotopes of Br and Eu).

HRMS: *m*/*z* calcd for $C_{37}H_{28}{}^{79}Br_2{}^{151}EuN_5O_8H^+$, 979.9579; found, 979.9559.

2,6-Bis[6-cyano-5-(4-bromophenyl)-3,4-cyclopentenopyridyl-2]pyridine (9)
1-(4-Morpholino)cyclopentene (1.05 mL, 1.00 g, 6.56 mmol) was added to a solution of dicyanotriazine **3** (980 mg, 1.64 mmol) in toluene and the reaction mixture was heated to reflux for 12 h. The resulting precipitate was separated by filtration, then heated to reflux in HOAc for 30 min. Crystals of the product were separated by filtration and recrystallized from DMSO to give **9** (730 mg, 66%); Mp 325 °C (dec.).

IR (KBr): 2943, 2870, 2228, 1565, 1489, 1403, 1093, 1006, 828 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.12 (q, 4 H, *J* = 7.5 Hz), 2.92 (t, 4 H, *J* = 7.5 Hz), 3.46 (t, 4 H, *J* = 7.5 Hz), 7.33–7.41 (m, 4 H), 7.65–7.72 (m, 4 H), 8.05 (t, 1 H, *J* = 8.0 Hz), 8.31 (d, 2 H, *J* = 8.0 Hz).

^{13}C NMR: δ = 25.2 (–), 32.5 (–), 34.0 (–), 117.1 (C_{quat}), 122.8 (C_{quat}), 123.7 (C_{quat}), 124.0 (+), 129.9 (C_{quat}), 130.6 (+), 132.2 (+), 133.3

(C_{quat}), 137.2 (+), 137.7 (C_{quat}), 143.3 (C_{quat}), 152.7 (C_{quat}), 155.6 (C_{quat}).

MS (CI): *m*/*z* = 672, 674, 676 $[MH]^+$.

Anal. Calcd for $C_{35}H_{23}Br_2N_5$ (673.42): C, 62.43; H, 3.44; N, 10.40. Found: C, 62.46; H, 3.59; N, 10.43.

2,6-Bis[5-(4-bromophenyl)-6-carboxy-3,4-cyclopentenopyridyl-2]-pyridine (10)

A mixture of dicyanoterpyridine **9** (640 mg, 0.95 mmol) and H_2SO_4 (3 mL) was stirred at 100 °C for 2 h. Water (3mL) was added very carefully and the reaction mixture was stirred at 100 °C for 24 h. After cooling the reaction mixture was diluted with water (10 mL), the precipitate was filtered, washed with water, and recrystallized from DMSO to give **10** (480 mg, 71%); mp 183–185 °C (dec.).

IR (KBr): 2957, 1711, 1570, 1429, 1012, 947, 834 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 2.02 (q, 4 H, *J* = 7.5 Hz), 2.81 (t, 4 H, *J* = 7.5 Hz), 3.89 (t, 4 H, *J* = 7.5 Hz), 7.32–7.41 (m, 4 H), 7.63–7.73 (m, 4 H), 8.15 (dd, 1 H, *J* = 8.5 Hz, 6.7 Hz), 8.31 (d, 2 H, *J* = 7.7 Hz).

^{13}C NMR: δ = 24.7 (–), 31.8 (–), 33.2 (–), 121.2 (C_{quat}), 123.1 (+), 130.6 (+), 130.7 (C_{quat}), 131.2 (+), 135.8 (C_{quat}), 137.6 (+), 140.0 (C_{quat}), 147.7 (C_{quat}), 149.6 (C_{quat}), 155.7 (C_{quat}), 155.9 (C_{quat}), 167.8 (C_{quat}).

ESI-MS: *m*/*z* = 666, 668, 670 $[MH - CO_2]^+$, 710, 712, 714 $[MH]^+$, 732, 734, 736 $[MNa]^+$.

{2,6-Bis[5-(4-bromophenyl)-6-carboxy-3,4-cyclopentenopyridyl-2]-pyridine}europium(III) chloride (11)

The solution of **10** (125 mg, 0.176 mmol) and europium(III) chloride hexahydrate (65 mg, 0.176 mmol) in MeOH (5 mL) was stirred at r.t. for 1 h. The solvent was removed by rotary evaporation under reduce pressure. The precipitate was stirred at r.t. in EtOH (3mL) for 15 min, filtered and washed with EtOH to give **11** (87 mg, 55%).

IR (KBr): 2961, 1616, 1560, 1427, 1010 cm^{-1}.

FAB-MS: *m*/*z* = 859, 861, 863, 864 8 ($C_{35}H_{23}{}^{79}Br_2{}^{151}EuN_3O_4H^+$) (for all isotopes of Br and Eu).

HR-MS: *m*/*z* calcd for $C_{35}H_{23}{}^{79}Br_2{}^{151}EuN_3O_4H^+$, 858.9330; found, 858.9322.

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