

With compliments of the Author

Azido- and Ethynyl-Substituted 2,2':6',2''-Terpyridines as Suitable Substrates for Click Reactions

Andreas Winter,^a Andreas Wild,^b Richard Hoogenboom,^a Martin W. M. Fijten,^a Martin D. Hager,^b Reza-Ali Fallahpour,^c Ulrich S. Schubert^{*a,b}

^a Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands

Fax +31(40)2474186; E-mail: u.s.schubert@tue.nl

^b Laboratory of Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany

^c HetCat, Gundeldingerstr. 174, 4053 Basel, Switzerland

Received 27 September 2008; revised 13 January 2009

Abstract: The click reaction of azido- and ethynyl-functionalized terpyridines has been exploited to obtain a series of 1*H*-1,2,3-triazole-substituted terpyridines. This protocol was extended towards the synthesis of terpyridine-based macroligands via end group modification of ethynyl-functionalized polymers. Finally, the combination of two orthogonal terpyridines within one click reaction highlights the potential of this approach with respect to the preparation of new building blocks for supramolecular assemblies and functional materials.

Key words: click reaction, complexes, cycloaddition, ligands, terpyridines

Supramolecular chemistry has evolved into one of the most active research areas in modern chemistry with the design and preparation of new functional ligands and their incorporation into supramolecular assemblies by transition metal complexation, π - π stacking, or hydrogen bonding as cornerstones of this field.¹ In general, supramolecular interactions are weaker than covalent bonds, and therefore they can be easily affected by external parameters (e.g., pH, temperature, solvent, redox processes, and shear forces) allowing the design of responsive and 'smart' materials with potential self-healing properties.²

The remarkably high binding affinity towards most transition metal ions, together with their chelating properties, make terpyridines attractive building blocks for the construction of supramolecular assemblies.³ Recently, oligopyridyl ligands and, in particular, their transition metal complexes have found applications as luminescent sensors in molecular biology and medical diagnostics, in photocatalysis, as active materials in self-assembled molecular devices, and as photoactive molecular wires and they have been used for storage applications in molecular electronics and photonics.^{4,5}

The basic principles and binding moieties known from supramolecular chemistry have successfully been introduced in the field of polymer chemistry, bringing together the characteristics from both fields: the intrinsic material

properties arising from the polymer backbone, as well as the reversible self-assembly properties of the supramolecular moieties attached to the polymeric structure.^{1b,c} We have introduced a range of polymeric materials into such assemblies by this approach.⁶ For this purpose, a variety of modified chelating ligands have been used successfully as initiators, monomers, or terminating agents.^{1a} Furthermore, the complexes have been utilized as supramolecular linkers between two polymeric chains to obtain well-defined homo and block copolymers, as well as chain-extended polymers.^{1a}

The Huisgen 1,3-dipolar cycloaddition, the so-called 'click' reaction,⁷ has been used in the field of polymer chemistry for the covalent linkage of suitable functionalized polymers as well as for end group modification reactions.⁸ Additionally, the click reaction has been introduced as a versatile tool for the attachment of organic substrates to surfaces and nanoparticles.⁹ In continuation of previous work we have now combined the wide scope¹⁰ of the click reaction with the chemistry of functionalized 2,2':6',2''-terpyridines to open new avenues towards new functional supramolecular materials.

In order to explore the applicability of this approach and to investigate the properties of such 1,2,3-triazol-1-yl-substituted terpyridines, we have synthesized a set of model compounds **2** starting from 4'-azido-2,2':6',2''-terpyridine (**1**)¹¹ and the corresponding ethynyl compounds (Scheme 1). As expected, a large range of functional groups can be easily clicked to the terpyridine moiety revealing the broad scope of this mild protocol. All synthesized 4'-substituted terpyridine derivatives **2** have been obtained in good yields (>65%) and the purity has been proven by NMR spectroscopy (Figure 1), mass spectrometry, and elemental analyses.

An excess of copper(I) iodide had to be used in all cases to avoid the deactivation of the catalyst by coordination to the chelating terpyridine moiety. During the workup procedure, the remaining copper ions were removed by repeated extraction with aqueous sodium hydroxyethylenediaminetriacetate (HEDTA) solution.

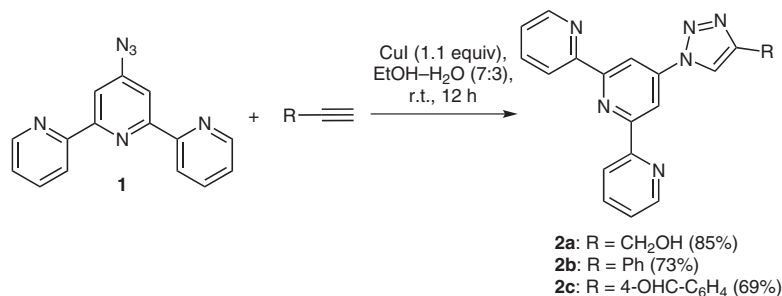
The application of the click reaction in the field of polymer chemistry has recently gained much attention, since the end group modification of functionalized polymers as

SYNTHESIS 2009, No. 9, pp 1506–1512

Advanced online publication: 25.03.2009

DOI: 10.1055/s-0028-1088159; Art ID: T16708SS

© Georg Thieme Verlag Stuttgart · New York



Scheme 1 Schematic representation of the synthesis of 4'-(1,2,3-triazol-1-yl)-2,2':6',2''-terpyridines **2** by click chemistry

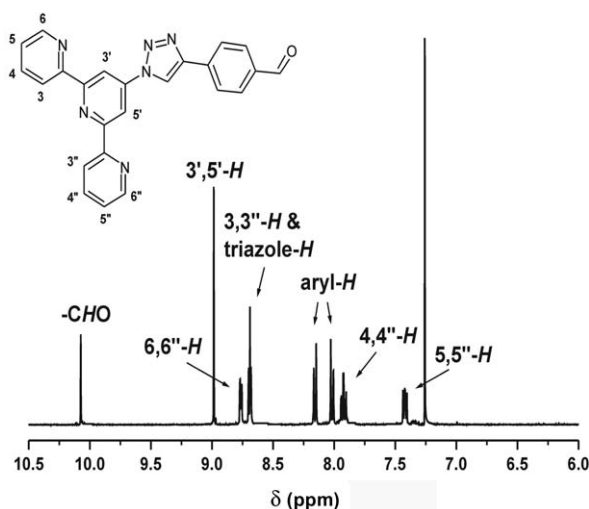
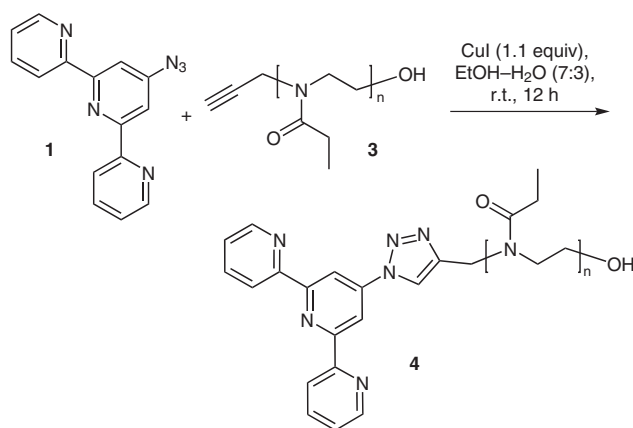


Figure 1 ¹H NMR spectrum (400 MHz, CDCl₃, r.t., aromatic region) of **2c**

well as the coupling of different polymer chains can be performed in high yields and under mild conditions.⁸ 2-Oxazolines are known as versatile monomers in living cationic ring-opening polymerizations (CROP).¹² The resulting poly(2-oxazoline)s consist of a poly(ethyleneimine) chain with narrow molecular weight distributions (PDI ≤ 1.20), bearing the 2-substituent of the starting oxazoline monomer as amidic side chains. Overall, the properties of the polymers are strongly dependent on the 2-substituent and can therefore, be easily tuned.¹³ Due to their manifold properties, (co)poly(2-oxazoline)s are currently of significant interest in chemical and medicinal research.¹⁴

We recently reported the cationic ring-opening polymerization of 2-ethyl-2-oxazoline in acetonitrile at 140 °C with propargyl tosylate as initiator (monomer to initiator ratio 20:1) using microwave irradiation¹⁵ yielding the desired ethynyl-functionalized poly(2-ethyl-2-oxazoline) **3**.¹⁶ Subsequently, the click reaction of polymer **3** with 4'-azido-2,2':6',2''-terpyridine (**1**) afforded the new terpyridyl-functionalized macroligand **4** (Scheme 2).

Size exclusion chromatography (SEC) was carried out with chloroform–triethylamine–propan-2-ol (94:4:2) as eluent and indicated the purity of the polymeric systems **3** and **4** with monomodal distributions. As illustrated in



Scheme 2 Schematic representation of the click reaction of ethynyl-functionalized poly(2-ethyl-2-oxazoline) **3**

Figure 2 (top), no signal for the ethynyl-functionalized poly(2-ethyl-2-oxazoline) **3** were detected with a UV detector. The high similarity of the two size exclusion chromatography traces obtained for **4** (RI and UV detector) lets us to conclude that a fully terpyridine-functionalized material has been synthesized. Since size exclusion chromatography alone is not a proof of quantitative attachment of the aromatic groups, MALDI-TOF mass spectrometry (Figure 2, bottom) was also performed. For both polymers **3** and **4** only one distribution was observed in the spectra, with the spacing between the peaks corresponding to one monomer unit (2-ethyl-2-oxazoline, $M = 99.13$ g/mol). The end group analysis of **4** revealed that the peak molar masses correspond exactly to the expected structure of the terpyridine-functionalized polymer with a sodium ion, since sodium iodide was used as an additive for the MALDI-TOF MS measurements.

The fluorescent Kröhnke-type derivative **5**¹⁷ was used as an example for ethynyl-functionalized terpyridines and, therefore, as a substrate for click reactions with organic azide compounds. A modified procedure for the one-pot click reaction of aromatic boronic acids was used for the synthesis of the 1,2,3-triazol-4-yl-substituted terpyridine derivatives **6** (Scheme 3).¹⁸ The selective in situ formation of the azide in the presence of other functional groups highlights the feasibility of modifications of the products after the click reaction, e.g. by palladium(0)-catalyzed cross-coupling reactions.

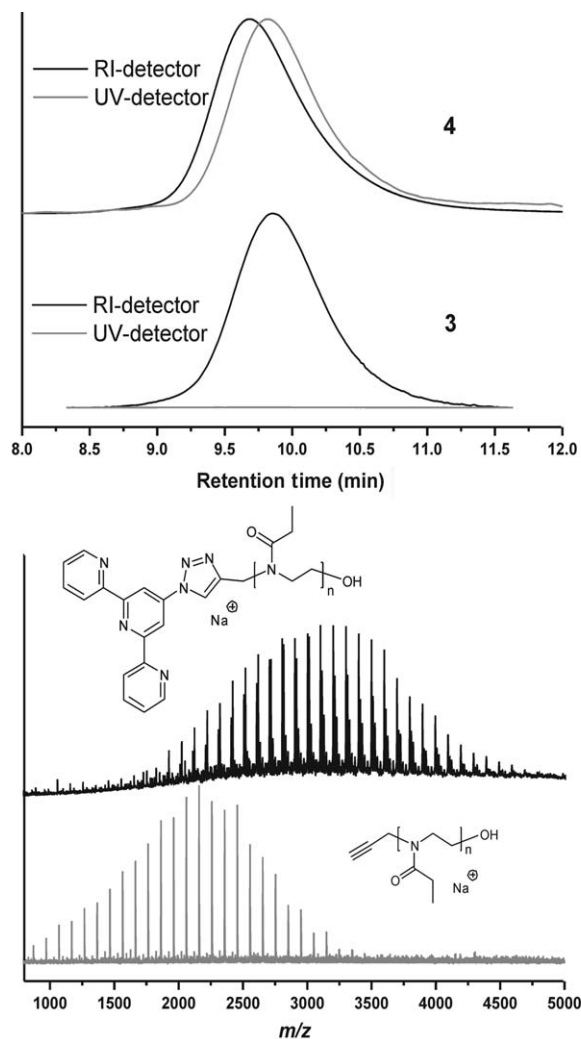
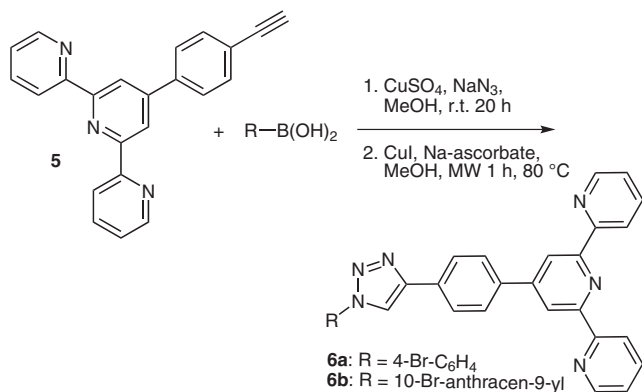
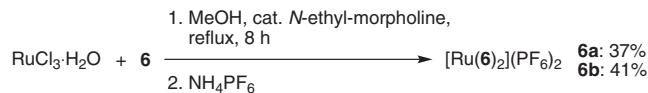


Figure 2 Top: Normalized size exclusion chromatograms (SEC, CHCl_3 - Et_3N -*i*-PrOH, 94:4:2) of the starting polymer **3** and the macroligand **4**. Bottom: MALDI-TOF mass spectra of the starting polymer **3** (gray curve) and the macroligand **4** (black curve)



Scheme 3 Schematic representation of the one-pot click reaction with 4'-(4-ethynylphenyl)-2,2',6',2''-terpyridine (**5**)

The subsequent coordination of **6** to ruthenium (II) ions afforded the desired homoleptic complexes of the general formula $[\text{Ru}(\mathbf{6})_2](\text{PF}_6)_2$ in moderate yields (Scheme 4).^{1b}



Scheme 4 Schematic representation of the synthesis of homoleptic ruthenium(II)-bis(terpyridine) complexes $[\text{Ru}(\mathbf{6})_2](\text{PF}_6)_2$

The shift of the signals in the ^1H NMR spectra compared to the uncomplexed ligands revealed the coordination of the chelating ligand **6** to the ruthenium(II) core. In particular the protons in 6/6''-position, directed towards the shielding region of the central pyridine ring of the orthogonal second ligand, experience a considerable upfield shift of about 1.5 ppm (see Figure 3 for **6a**).

The $[\text{M} - \text{PF}_6]^+$ and $[\text{M} - 2 \text{PF}_6]^+$ peaks were detected by MALDI-TOF mass spectrometry.¹⁹ No dissociation of the complex occurred during the laser desorption/ionization process, indicating the high stability of these complexes. However, for all herein described terpyridine ligands as well as ruthenium(II) complexes a characteristic fragmentation of the triazole moiety was observed. Obviously, such 1,4-diaryl-substituted 1*H*-1,2,3-triazole derivatives tend to eliminate nitrogen under the conditions of MALDI-TOF mass spectrometry. This effect has previously been described only for a variety of benzotriazole derivatives.²⁰

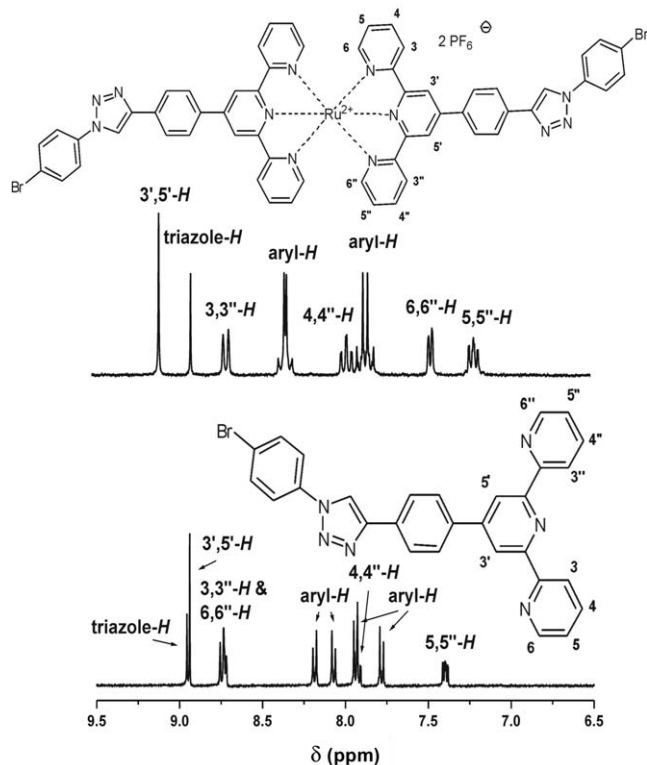


Figure 3 Aromatic region of the ^1H NMR spectra of terpyridine **6a** (bottom, $\text{THF}-d_8$) and the corresponding ruthenium(II) complex $[\text{Ru}(\mathbf{6a})_2](\text{PF}_6)_2$ (top, CD_3CN); for both spectra: 400 MHz, r.t.

The UV/Vis absorption spectra (MLCT band at ~ 500 nm, Figure 4) additionally proved the formation of rutheni-

um(II)–bis(terpyridine) complexes. Since in the present cases this band appears to be indifferent from the nature of the lateral aromatic substituent, we could assume that π -conjugation is interrupted by the triazole moiety²¹ and thus, the ruthenium–terpyridine unit and the aryl substituent might have to be considered as ‘isolated’ chromophores.²² The complexes showed only very weak emission at room temperature, since, in contrast to analogue bipyridine-based complexes, the photoluminescence is strongly quenched by the transition metal ion.

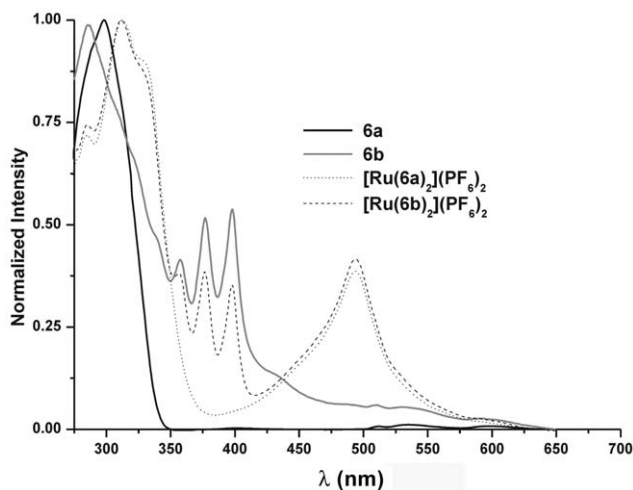
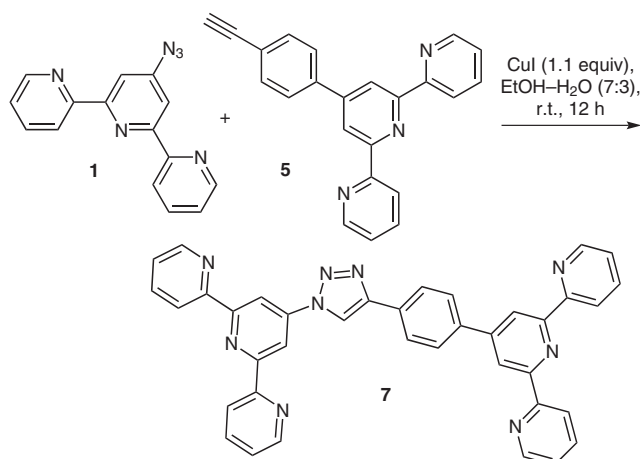


Figure 4 UV/Vis absorption spectra of terpyridines **6** (THF) and their corresponding homoleptic ruthenium(II) complexes $[\text{Ru}(\mathbf{6})_2](\text{PF}_6)_2$ (MeCN); for all spectra: 10^{-6} M, r.t.

The combination of the two orthogonally substituted substrates **1** and **5** within one click reaction yielded directly the new 1,4'-(triazol-4-yl-phenyl)-bridged bis(terpyridine) derivative **7** (Scheme 5). Due to the highly rigid structure and the absence of any solubilizing side chains, only very low solubility of the bis(terpyridine) **7** in common organic solvents was observed.²³ Nonetheless, this example shows that the click chemistry approach is also suited for the straightforward construction of π -conjugated rigid-linear terpyridyl derivatives with potential in the design of new functional materials by transition metal ion complexation.

In conclusion, the azide–alkyne click reaction has been applied for the synthesis of a series of 1*H*-1,2,3-triazole-substituted terpyridines. Two independent approaches have been carried out to obtain a diverse set of functionalized terpyridine derivatives, including end group modified polymers, in good yields. Furthermore, ruthenium(II) model complexes have been synthesized to highlight the potential of the herein described terpyridines as chelating ligands for the coordination of transition metal ions. In addition, the combination of the building blocks within one click reaction has enabled the realization of a new type of bridged bis(terpyridine)s that represent potentially interesting substrates for the design of supramolecular assemblies, including block copolymers or chain-extended polymers, by metal complexation.



Scheme 5 Schematic representation of the click reaction of the two orthogonal terpyridyl derivatives **1** and **5**

The ¹H and ¹³C NMR spectra were recorded at 25 °C on a Varian Mercury 400 MHz instrument with TMS as standard. Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Voyager-DE PRO biospectrometry workstation (Applied Biosystems) time-of-flight mass spectrometer, with dithranol as matrix. Elemental analyses were obtained on a EuroVector EuroEA3000 elemental analyzer for CHNS-O. UV/Vis absorption and photoluminescence spectra were recorded at r.t. at concentrations of 10^{-6} M on an Analytik Jena SPECORD 250 and Jasco FP-6500 spectrophotometer, respectively. Size exclusion chromatography (SEC) was measured on a Shimadzu system equipped with a SCL-A10 system controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10A UV-detector at 254 nm and a PLgel 5 mm Mixed-D column at 50 °C utilizing a CHCl_3 – Et_3N –*i*-PrOH (94:4:2) mixture as eluent at a flow rate of 1 mL/min. The molar masses were calculated against polystyrene standards.

Unless stated otherwise, all reagents were purchased from commercial sources and used without further purification. The solvents were received from Biosolve and were dried and distilled according to standard procedures. All reactions were performed under an atmosphere of argon unless specified. Column chromatographic separations were performed on alumina (neutral, Macherey & Nagel, 0.063–0.200 mm). Preparative size exclusion chromatography was carried out using BioBeads SX-5, swollen with CH_2Cl_2 . The terpyridines **1**¹¹ and **5**^{17d} as well as the poly(2-ethyl-2-oxazoline) **3**¹⁶ were synthesized following previously published methods.

Safety comment: NaN_3 is very toxic, personal protection precautions should be taken. As low molecular weight organic azides are potential explosives, care must be taken during their handling. Generally, when the total number of carbon (N_C) plus oxygen (N_O) atoms is less than the total numbers of nitrogen atoms (N_N) by a ratio of three, i.e. $(N_C + N_O)/N_N \leq 3$, the compound is considered as an explosive hazard. Therefore, the compounds were prepared prior to use and used immediately.

Click Reactions Involving 4'-Azido-2,2':6',2''-terpyridine (**1**); General Procedure

To a suspension of 4'-azido-2,2':6',2''-terpyridine (**1**, 50 mg, 0.18 mmol) and an alkyne derivative (0.25 mmol) in $\text{EtOH-H}_2\text{O}$ (7:3, 10 mL) was added CuI (37.7 mg, 0.20 mmol). The mixture was stirred at r.t. for 15 h. The brown precipitate was filtered off, washed with H_2O (10 mL) and vigorously stirred with aq HEDTA (20 mL) for 2 h. The product was extracted into CHCl_3 (3 × 20 mL). The com-

bined organic phases were washed with H₂O (3 × 20 mL) and dried (MgSO₄). The solvent was evaporated and the crude product **2** was purified by column chromatography (neutral alumina, CH₂Cl₂–MeOH, 98:2).

[1-(2,2':6',2''-Terpyridin-4'-yl)-1H-1,2,3-triazol-4-yl]methanol (**2a**)

According to the general protocol for the click reaction, **1** (50 mg, 0.18 mmol), propargyl alcohol (2 mL, excess), and CuI (37.7 mg, 0.20 mmol) were reacted to yield **2a** (51 mg, 85%) as a white solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.90 (s, 2 H, H^{3',5'-tpy}), 8.73 (d, ³J = 4.1 Hz, 2 H, H^{6',6''-tpy}), 8.65 (d, ³J = 7.5 Hz, 2 H, H^{3,3''-tpy}), 8.15 (s, 1 H, H^{triaz}), 7.89 (m_c, 2 H, H^{4,4''-tpy}), 7.39 (m_c, 2 H, H^{5,5''-tpy}), 4.33 (s, 2 H, H^{CH₂}), 2.46 (br s, 1 H, H^{OH}).

¹³C NMR (100 MHz, CDCl₃): δ = 155.9, 155.5, 149.1, 141.3, 137.2, 136.0, 123.8, 121.2, 118.5, 117.9, 52.9.

MS (MALDI-TOF, dithranol): *m/z* = 302.34 ([M – N₂]⁺), 331.29 ([M + H]⁺).

Anal. Calcd for C₁₈H₁₄N₆O: C, 65.44; H, 4.27; N, 25.44. Found: C, 65.22; H, 3.98; N, 25.51.

4'-(4-Phenyl-1H-1,2,3-triazol-1-yl)-2,2':6',2''-terpyridine (**2b**)

According to the general protocol for the click reaction, **1** (50 mg, 0.18 mmol), phenylacetylene (25.5 mg, 0.25 mmol), and CuI (37.7 mg, 0.20 mmol) were reacted to yield **2b** (49.5 mg, 73%) as an off-white solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.91 (s, 2 H, H^{3',5'-tpy}), 8.76 (d, ³J = 3.4 Hz, 2 H, H^{6',6''-tpy}), 8.67 (d, ³J = 7.8 Hz, 2 H, H^{3,3''-tpy}), 8.55 (s, 1 H, H^{triaz}), 7.96 (d, ³J = 7.4 Hz, 2 H, H^{o-aryl}), 7.91 (m_c, 2 H, H^{4,4''-tpy}), 7.49 (m_c, 3 H, H^{m,p-aryl}), 7.40 (m_c, 2 H, H^{5,5''-tpy}).

¹³C NMR (100 MHz, CDCl₃): δ = 156.1, 155.7, 149.2, 146.5, 137.0, 134.8, 130.1, 129.2, 128.5, 127.4, 123.6, 122.6, 120.9, 118.9.

MS (MALDI-TOF, dithranol): *m/z* = 349.07 (M – N₂)⁺, 377.04 ([M + H]⁺), 412.98 ([M + K]⁺).

Anal. Calcd for C₂₃H₁₆N₆: C, 73.39; H, 4.28; N, 22.33. Found: C, 73.17; H, 4.37; N, 22.54.

4-[1-(2,2':6',2''-Terpyridin-4'-yl)-1H-1,2,3-triazol-4-yl]benzaldehyde (**2c**)

According to the general protocol for the click reaction, **1** (50 mg, 0.18 mmol), 4-ethynylbenzaldehyde (32.5 mg, 0.25 mmol), and CuI (37.7 mg, 0.20 mmol) were reacted to yield **2c** (50.3 mg, 69%) as an off-white solid.

¹H NMR (400 MHz, CDCl₃): δ = 10.01 (s, 1 H, H^{CHO}), 8.98 (s, 2 H, H^{3',5'-tpy}), 8.76 (m_c, 2 H, H^{6',6''-tpy}), 8.69 (d, ³J = 7.9 Hz, 2 H, H^{3,3''-tpy}), 8.69 (s, 1 H, H^{triaz}), 8.16 (d, ³J = 8.2 Hz, 2 H, H^{aryl}), 8.02 (d, ³J = 8.2 Hz, 2 H, H^{aryl}), 7.93 (m_c, 2 H, H^{4,4''-tpy}), 7.42 (m_c, 2 H, H^{5,5''-tpy}).

¹³C NMR (100 MHz, CDCl₃): δ = 155.9, 155.3, 189.9, 149.3, 146.1, 137.3, 136.8, 136.2, 135.9, 130.1, 128.2, 123.5, 122.5, 121.2, 118.9.

MS (MALDI-TOF, dithranol): *m/z* = 404.14.

Anal. Calcd for C₂₄H₁₆N₆O: C, 71.28; H, 3.99; N, 20.78. Found: C, 70.93; H, 4.21; N, 21.01.

4'-[4-Poly(2-ethyloxazoline)-1H-1,2,3-triazol-1-yl]-2,2':6',2''-terpyridine (**4**)

A soln of **1** (20 mg, 75 μmol), acetylene-functionalized poly(2-ethyl-2-oxazoline) (**2**,¹⁶ 100 mg, 44 μmol, *M_n* = 2,300 g/mol, PDI = 1.08) and CuI (23 mg, 121 μmol) in a mixture of EtOH (3 mL) and H₂O (1 mL) was stirred at r.t. for 24 h. After evaporation of the solvent and redissolution in CHCl₃ (2 mL), the crude mixture was precipitated into Et₂O (20 mL). The resulting green powder was redissolved in CHCl₃ (20 mL) and washed with aq HEDTA (10 mL). The resulting colorless organic phase was concentrated and

the terpyridine-functionalized polymer **4** was collected by precipitation into Et₂O.

¹H NMR (400 MHz, CDCl₃): δ = 8.90 (br, 2 H, H^{3',5'-tpy}), 8.73–8.59 (br, 4 H, H^{6',6''-tpy}, H^{3,3''-tpy}), 8.04–7.84 (br, 3 H, H^{triaz}, H^{4,4''-tpy}), 7.47–7.35 (br, 2 H, H^{5,5''-tpy}), 4.68 (br, 2 H, H^a), 3.64–3.18 (br, 80 H, H^b, H^c), 2.53–2.08 (br, 40 H, H^d), 1.35–0.90 (br, 60 H, H^e).

MS (MALDI-TOF, dithranol): *m/z* = *M_n* = 3,050 g/mol; *M_w* = 3,250 g/mol; PDI = 1.07.

GPC (CHCl₃–Et₃N–*i*-PrOH): *M_n* = 2,300 g/mol; *M_w* = 2,480 g/mol; PDI = 1.08.

Click Reaction of Aromatic Boronic Acids; General Procedure

NaN₃ (78 mg, 1.2 mmol) and anhyd CuSO₄ (80 mg, 0.5 mmol) were placed in an oven-dried round-bottomed flask. Subsequently, anhyd MeOH (3 mL) and the aromatic boronic acid (1.0 mmol) were added. The mixture was stirred vigorously at r.t. till full conversion of the boronic acid (TLC monitoring). Then H₂O (0.3 mL), sodium ascorbate (5 mol%), CuI (10 mol%), and 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (**5**, 333 mg, 1 mmol) were added. The resulting mixture was heated under microwave irradiation at 80 °C for 1 h. Subsequently H₂O (15 mL) was added and the formed precipitate was collected by filtration. The precipitate was washed with dil aq NH₃ soln (15 mL), extracted with toluene (2 × 20 mL), and purified by precipitation into MeOH, followed by recrystallization and/or preparative size exclusion chromatography.

4'-[4-[1-(4-Bromophenyl)-1H-1,2,3-triazol-4-yl]phenyl]-2,2':6',2''-terpyridine (**6a**)

According to the general protocol for the click reaction, NaN₃ (78 mg, 1.2 mmol), 4-bromophenylboronic acid (200 mg, 1 mmol), and **5** (333 mg, 1 mmol) were reacted to yield **6a** (329 mg, 62%) as an off-white solid.

¹H NMR (400 MHz, THF-*d*₆): δ = 8.96 (s, 1 H, H^{triaz}), 8.94 (s, 2 H, H^{3',5'-tpy}), 8.75 (d, ³J = 8.0 Hz, 2 H, H^{6',6''-tpy}), 8.73 (d, ³J = 5.4 Hz, 2 H, H^{3,3''-tpy}), 8.19 (d, 2 H, H^{aryl}), 8.07 (d, 2 H, H^{aryl}), 7.93 (t, ³J = 8.2 Hz, 2 H, H^{4,4''-tpy}), 7.94 (d, 2 H, H^{aryl}), 7.78 (d, 2 H, H^{aryl}), 7.34 (t, ³J = 6.2 Hz, 2 H, H^{5,5''-tpy}).

¹³C NMR (100 MHz, THF-*d*₆): δ = 156.1, 156.0, 149.2, 149.0, 147.5, 138.1, 136.5, 132.7, 131.7, 127.4, 126.1, 123.7, 121.5, 121.4, 120.7, 118.3, 118.0.

MS (MALDI-TOF, dithranol): *m/z* = 530.89 ([M + H]⁺).

Anal. Calcd for C₂₉H₁₉BrN₆: C, 65.55; H, 3.60; N, 15.81. Found: C, 65.67; H, 3.69; N, 15.62.

4'-[4-[1-(10-Bromoanthracen-9-yl)-1H-1,2,3-triazol-4-yl]phenyl]-2,2':6',2''-terpyridine (**6b**)

According to the general protocol for the click reaction, NaN₃ (78 mg, 1.2 mmol), (10-bromoanthracen-9-yl)boronic acid (301 mg, 1 mmol), and **5** (333 mg, 1 mmol) were reacted to yield **6b** (360 mg, 57%) as an off-white solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.84 (s, 2 H, H^{3',5'-tpy}), 8.77 (d, ³J = 4.4 Hz, 2 H, H^{6',6''-tpy}), 8.71–8.67 (m, 4 H, H^{3,3''-tpy}, H^{anthracene}), 8.30 (s, 1 H, H^{triaz}), 8.19 (d, 2 H, H^{aryl}), 8.09 (d, 2 H, H^{aryl}), 7.91 (dt, ³J = 7.8 Hz, ⁴J = 1.8 Hz, 2 H, H^{4,4''-tpy}), 7.70 (dt, ³J = 7.8 Hz, ⁴J = 1.2 Hz, 2 H, H^{anthracene}), 7.59 (dt, ³J = 7.7 Hz, ⁴J = 1.2 Hz, 2 H, H^{anthracene}), 7.42 (d, ³J = 8.7 Hz, 2 H, H^{anthracene}), 7.38 (m_c, 2 H, H^{5,5''-tpy}).

¹³C NMR (100 MHz, CDCl₃): δ = 156.2, 156.1, 149.6, 149.2, 147.5, 138.6, 136.9, 130.8, 130.3, 129.0, 128.7, 128.4, 128.2, 128.0, 127.8, 126.5, 126.5, 124.5, 123.9, 122.6, 121.4, 118.7.

MS (MALDI-TOF, dithranol): *m/z* = 630.97 ([M + H]⁺).

Anal. Calcd for C₃₇H₂₃N₆Br: C, 70.37; H, 3.67; N, 13.31. Found: C, 70.56; H, 3.77; N, 13.22.

4'-{4-[1-(2,2':6',2''-Terpyridin-4'-yl)-1H-1,2,3-triazol-4-yl]phenyl}-2,2':6',2''-terpyridine (7)

To a suspension of 4'-azido-2,2':6',2''-terpyridine (**1**, ¹¹ 50 mg, 0.18 mmol) and 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (**5**, ^{17d} 67 mg, 0.20 mmol) in EtOH–H₂O (7:3, 10 mL) was added CuI (94.3 mg, 0.50 mmol). The mixture was stirred at r.t. for 15 h. The brown precipitate was filtered off, washed with H₂O (10 mL) and vigorously stirred with aq HEDTA (20 mL) at 40 °C for 2 h. The product was extracted into CHCl₃ (3 × 20 mL). The combined organic phases were washed with H₂O (3 × 20 mL) and dried (MgSO₄). The solvent was evaporated and the crude product was purified by column chromatography (neutral alumina, CH₂Cl₂–MeOH, 98:2) to yield **7** (52 mg, 47%) as a pale brown solid.

¹H NMR (400 MHz, CDCl₃): δ = 8.91 (s, 2 H, H^{tpy}), 8.83 (s, 2 H, H^{3',5'-tpy}), 8.75 (m, 4 H, H^{tpy}), 8.72 (m, 2 H, H^{tpy}), 8.64 (d, ³J = 7.5 Hz, 2 H, H^{tpy}), 8.40 (s, 1 H, H^{triazol}), 8.17 (d, 2 H, H^{aryl}), 8.04–7.93 (d, 4 H, H^{tpy}, H^{aryl}), 7.88 (m, 2 H, H^{4,4'-tpy}), 7.36 (m, 4 H, H^{tpy}).

¹³C NMR spectroscopy could not be performed due to the low solubility.

MS (MALDI-TOF, dithranol): *m/z* = 594.22 [M – N₂ + H]⁺, 608.17 ([M + H]⁺).

Anal. Calcd for C₃₈H₂₅N₉: C, 75.11; H, 4.15; N, 20.75. Found: C, 75.39; H, 4.37; N, 21.01.

Synthesis of Ru(II)–Bis(terpyridine) Complexes; General Procedure

A suspension of **6** (0.07 mmol) and RuCl₃·H₂O (0.1 mmol) in MeOH (3 mL) was refluxed for 4 h and filtered.²³ The residue was washed with MeOH (2 mL) and H₂O (2 mL) and subsequently suspended with **6** (0.05 mmol) in MeOH (5 mL) containing *N*-ethylmorpholine (1 drop). After 8 h at reflux, the soln was filtered and the complex precipitated using methanolic NH₄PF₆ soln. The precipitate was filtered off and washed with H₂O (5 mL) and MeOH (5 mL). Purification was carried out by precipitation of the crude product (MeCN soln into Et₂O) and/or recrystallization (MeCN) to yield the desired complex [Ru(**6a**)₂](PF₆)₂.

[Ru(**6a**)₂](PF₆)₂

According to the general protocol for the complexation reaction, **6a** (74 mg, 1.40 mmol) and RuCl₃·H₂O (25 mg, 0.10 mmol) were reacted to yield [Ru(**6a**)₂](PF₆)₂ (38 mg, 37%) as a red solid.

¹H NMR (400 MHz, CD₃CN): δ = 9.10 (s, 4 H, H^{3',5'-tpy}), 8.91 (s, 2 H, H^{triazol}), 8.70 (d, ³J = 8.0 Hz, 4 H, H^{3,3'-tpy}), 8.34 (m, 8 H, H^{aryl}), 7.97 (t, ³J = 7.9 Hz, 4 H, H^{4,4'-tpy}), 7.86 (m, 8 H, H^{aryl}), 7.46 (d, ³J = 5.6 Hz, 4 H, H^{6,6'-tpy}), 7.20 (t, ³J = 6.2 Hz, 4 H, H^{5,5'-tpy}).

MS (MALDI-TOF, dithranol): *m/z* = 1307.78 ([M – PF₆]⁺), 1164.01 ([M – 2 PF₆]⁺), 1114.33 ([M – 2 PF₆ – 2 N₂]⁺).

Anal. Calcd for C₅₈H₃₈Br₂F₁₂N₁₂P₂Ru: C, 47.92; H, 2.63; N, 11.56. Found: C, 48.28; H, 2.90; N, 11.86.

[Ru(**6b**)₂](PF₆)₂

According to the general protocol for the complexation reaction, **6b** (88 mg, 1.40 mmol) and RuCl₃·H₂O (25 mg, 0.10 mmol) were reacted to yield [Ru(**6b**)₂](PF₆)₂ (47 mg, 41%) as a red solid.

¹H NMR (400 MHz, CD₃CN): δ = 9.12 (s, 4 H, H^{3',5'-tpy}), 8.82 (s, 2 H, H^{triazol}), 8.77–8.70 (m, 8 H, H^{3,3'-tpy}, H^{anthracene}), 8.19 (m, 8 H, H^{aryl}), 7.99 (t, ³J = 8.4 Hz, 4 H, H^{4,4'-tpy}), 7.84 (t, ³J = 6.8 Hz, 4 H, H^{anthracene}), 7.70 (t, ³J = 8.0 Hz, 4 H, H^{anthracene}), 7.50–7.46 (m, 8 H, H^{6,6'-tpy}, H^{anthracene}), 7.23 (t, ³J = 6.3 Hz, 4 H, H^{5,5'-tpy}).

MS (MALDI-TOF, dithranol): *m/z* = 1362.03 ([M – 2 PF₆]⁺), 1338.22 ([M – 2 PF₆ – N₂]⁺), 1314.15 ([M – 2 PF₆ – 2 N₂]⁺).

Anal. Calcd for C₇₄H₄₆Br₂F₁₂N₁₂P₂Ru: C, 53.73; H, 2.80; N, 10.16. Found: C, 54.02; H, 3.17; N, 10.42.

Acknowledgment

Financial support of this work by the *Nederlandse Organisatie voor Wetenschappelijk Onderzoek* (VICI award for U. S. Schubert), and the *Fonds der Chemischen Industrie* is kindly acknowledged. The authors would also like to thank T. Erdmenger, N. Herzer, A. Baumgärtl and R. Eckardt for the help with MALDI-TOF MS measurements and elemental analyses.

References

- (a) Schubert, U. S.; Hofmeier, H.; Newkome, G. R. *Modern Terpyridine Chemistry*; Wiley-VCH: Weinheim, **2006**. (b) Newkome, G. R.; Wang, P.; Moorefield, C. N.; Cho, T. J.; Mohoapatra, P. P.; Li, S.; Hwang, S.-H.; Lukoyanova, O.; Echegoyen, L.; Palagallo, J. A.; Lancu, V.; Hla, S.-W. *Science* **2006**, *312*, 1782. (c) Bonnet, S.; Collin, J.-P.; Koizumi, M.; Mobian, P.; Sauvage, J.-P. *Adv. Mater. (Weinheim, Ger.)* **2006**, *18*, 1239. (d) Brunsveld, L.; Folmer, B. J. B.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2001**, *101*, 4071.
- (a) Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 1072. (b) Yuan, Y. C.; Yin, T.; Rong, M. Z.; Zhang, M. Q. *EXPRESS Polym. Lett.* **2008**, *2*, 238. (c) Bergman, S. D.; Wudl, F. *J. Mater. Chem.* **2008**, *18*, 41.
- (a) Constable, E. C. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69. (b) Schubert, U. S.; Eschbaumer, C.; Andres, P.; Hofmeier, H.; Weidl, H. C.; Herdtweck, E.; Dulkeith, E.; Morteaux, A.; Hecker, N. E.; Feldmann, J. *Synth. Met.* **2001**, *121*, 1249.
- (a) Erkkila, K. E.; Odom, D. T.; Barton, J. K. *Chem. Rev.* **1999**, *99*, 2777. (b) Barigeletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1. (c) Andres, P. R.; Schubert, U. S. *Adv. Mater. (Weinheim, Ger.)* **2004**, *16*, 1043. (d) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373. (e) Schmittel, M.; Kalsani, V.; Mal, P.; Bats, J. W. *Inorg. Chem.* **2006**, *45*, 6370. (f) Hwang, S. H.; Moorefield, C. N.; Dai, L.; Newkome, G. R. *Chem. Mater.* **2006**, *18*, 4019.
- (a) Ziessel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178–180*, 1251. (b) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219–221*, 545. (c) Flood, A. H.; Stoddart, J. F.; Steuerman, D. W.; Heath, J. R. *Science* **2004**, *306*, 2055. (d) Ciofini, I.; Lainé, P. P.; Bedioui, F.; Adamo, C. *J. Am. Chem. Soc.* **2004**, *126*, 10763. (e) Duprez, V.; Biancardo, M.; Spanggaard, H.; Krebs, F. C. *Macromolecules* **2005**, *38*, 10436. (f) Benniston, A.; Harriman, A.; Li, P.; Patel, P. V.; Sams, C. A. *J. Org. Chem.* **2006**, *71*, 3481.
- (a) Hofmeier, H.; Hoogenboom, R.; Wouters, M. E. L.; Schubert, U. S. *J. Am. Chem. Soc.* **2005**, *127*, 2913. (b) Lohmeijer, B. G. G.; Schubert, U. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 3825. (c) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4016. (d) Schmatloch, S.; van den Berg, A. M. J.; Alexeev, A. S.; Hofmeier, H.; Schubert, U. S. *Macromolecules* **2003**, *36*, 9943. (e) Meier, M. A. R.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, *24*, 852. (f) Winter, A.; Schubert, U. S. *Macromol. Chem. Phys.* **2007**, *208*, 1956.
- (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596. (b) Chan, T. R.; Hilgraf, R.; Sharpless, K. B.; Fokin, V. V. *Org. Lett.* **2004**, *6*, 2853. (c) Huisgen, R.; Szeimies, G.; Möbius, L. *Chem. Ber.* **1967**, *100*, 2494. (d) Huisgen, R.; Knorr, R.; Möbius, L.; Szeimies, G. *Chem. Ber.* **1965**, *98*, 4014. (e) Boyer, J. H.; Hamer, J. *J. Am. Chem. Soc.* **1955**, *77*, 951.

- (8) Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1369.
- (9) (a) Haensch, C.; Hoepfener, S.; Schubert, U. S. *Nanotechnology* **2008**, *19*, 035703. (b) Sommer, W. J.; Weck, M. *Langmuir* **2007**, *23*, 11991. (c) Nandivada, H.; Jiang, X.; Lahann, J. *Adv. Mater. (Weinheim, Ger.)* **2007**, *19*, 2197. (d) Devaraj, N. K.; Collman, J. P. *QSAR Comb. Sci.* **2007**, *26*, 1253.
- (10) (a) Hawker, C. J.; Wooley, K. L. *Science* **2005**, *309*, 1200. (b) Aucagne, V.; Hanni, K. D.; Leigh, A. D.; Lusby, P. J.; Walker, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 2186. (c) Dichtel, W. R.; Miljanic, O. S.; Spruell, J. M.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10388. (d) Mobian, P.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **2006**, *47*, 4907. (e) Devaraj, N. K.; Dinolfo, P. H.; Chidsey, C. E. D.; Collman, J. P. *J. Am. Chem. Soc.* **2006**, *128*, 1794. (f) Wu, P.; Fokin, V. V. *Aldrichimica Acta* **2007**, *40*, 7. (g) Monkowius, U.; Ritter, S.; König, B.; Zabel, M.; Yersin, H. *Eur. J. Inorg. Chem.* **2007**, *29*, 4597. (h) David, O.; Maisonneuve, S.; Xie, J. *Tetrahedron Lett.* **2007**, *48*, 6527.
- (11) Fallahpour, R.-A.; Neuburger, M.; Zehnder, M. *Synthesis* **1999**, 1051.
- (12) (a) Tomalia, D. A.; Sheetz, D. P. *J. Polym. Sci., Part A: Polym. Chem.* **1966**, *4*, 2253. (b) Kagiya, T.; Narisawa, S.; Maeda, T.; Fukui, K. *J. Polym. Sci., Part B: Polym. Lett.* **1966**, *4*, 441. (c) Seeliger, W.; Aufderhaar, E.; Diepers, W.; Feinauer, R.; Nehring, R.; Thier, W.; Hellmann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 875. (d) Bassiri, T. G.; Levy, A.; Litt, M. *J. Polym. Sci., Part B: Polym. Lett.* **1967**, *5*, 871.
- (13) (a) Hoogenboom, R.; Fijten, M. W. M.; Thijs, H. M. L.; Van Lankvelt, B. M.; Schubert, U. S. *Designed Monomers Polym.* **2005**, *8*, 659. (b) Beck, M.; Birnbrich, P.; Eicken, U.; Fischer, H.; Fristad, W. E.; Hase, B.; Krause, H. J. *Angew. Makromol. Chem.* **1994**, *223*, 217.
- (14) (a) Adams, N.; Schubert, U. S. *Adv. Drug Delivery Rev.* **2007**, *59*, 1504. (b) Aoi, K.; Okada, M. *Prog. Polym. Sci.* **1996**, *21*, 151. (c) Kobayashi, S.; Uyama, H. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 192.
- (15) Wiesbrock, F.; Hoogenboom, R.; Abeln, C. H.; Schubert, U. S. *Macromol. Rapid Commun.* **2004**, *25*, 1895.
- (16) Fijten, M. W. M.; Haensch, C.; Van Lankvelt, B. M.; Hoogenboom, R.; Schubert, U. S. *Macromol. Chem. Phys.* **2008**, *209*, 1887.
- (17) (a) Wang, J.; Hanan, G. S. *Synlett* **2005**, 1251. (b) Smith, C. B.; Raston, C. L.; Sobolev, A. N. *Green Chem.* **2005**, *7*, 650. (c) Winter, A.; van den Berg, A. M. J.; Hoogenboom, R.; Kickelbick, G.; Schubert, U. S. *Synthesis* **2006**, 2873. (d) Winter, A.; Egbe, D. A. M.; Schubert, U. S. *Org. Lett.* **2007**, *9*, 2345.
- (18) Tao, C.-Z.; Cui, X.; Li, J.; Liu, A.-X.; Liu, L.; Guo, Q.-X. *Tetrahedron Lett.* **2007**, *48*, 3525.
- (19) This fragmentation in MALDI-TOF mass spectrometry is often observed for Ru(II)-bis(terpyridine) complexes, see, for example: Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 411.
- (20) Vagin, S.; Frickenschmidt, A.; Kammerer, B.; Hanack, M. *Eur. J. Org. Chem.* **2005**, 3271.
- (21) Li, Y.; Huffman, J. C.; Flood, A. H. *Chem. Commun.* **2007**, 2692.
- (22) A detailed investigation of the electrooptical properties of 1*H*-1,2,3-triazole-containing terpyridine derivatives, supported by DFT calculations is currently ongoing will be published elsewhere.
- (23) Winter, A.; Hummel, J.; Risch, N. *J. Org. Chem.* **2006**, *71*, 4862.