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Synthesis and Resonance Energy Transfer Study on a Random Terpolymer Containing a 2-(Pyridine-2-yl)thiazole Donor-Type Ligand and a Luminescent [Ru(bpy)$_2$(2-(triazol-4-yl)pyridine)]$^{2+}$ Chromophore

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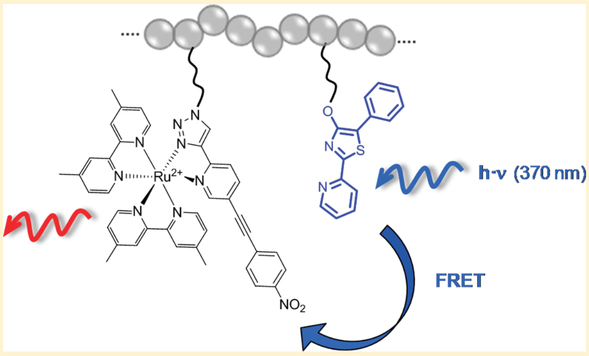
Supporting Information

ABSTRACT: A statistical terpolymer, containing a 2-(pyridine-2-yl)-1,3-thiazole donor-type system and an acceptor-type [Ru(bpy)$_2$-(2-(triazol-4-yl)pyridine)]$^{2+}$ chromophore as well as methyl methacrylate as comonomer, was synthesized using the controlled reversible addition−fragmentation chain transfer polymerization (RAFT) approach. Additionally, the appropriate donor- and acceptor-type copolymers were synthesized, whereas only a maximum content of 5 mol % of the ruthenium(II) chromophore could be incorporated into the macromolecules caused by its nitro-functionalization. The resulting terpolymer exhibited a direct Förster resonance energy transfer from the thiazole to the ruthenium(II) subunit as indicated by emission spectroscopy of the Ru(II) phosphorescence as well as lifetime measurements and quantum yield determinations of the thiazole fluorescence. The efficiency of the energy transfer was found to be higher than 70%.



INTRODUCTION

Relating to artificial photosynthetic systems which are capable to harvest and exploit photons enabled by solar energy, ruthenium(II) complexes coordinated by *N*-heterocycles, such as 2,2′-bipyridines (bpy) and 2,2′:6′,2″-terpyridines (tpy), have been widely studied due to their predictable coordination behavior as well as their interesting photophysical and electrochemical properties.[1−19] Ruthenium−polypyridine complexes have particularly drawn significant interest, since they are able to catalyze reduction and oxidation processes under visible light irradiation enclosing a broad range of substrates. These privileges could be utilized for applications including, e.g., the photocatalytic decomposition of water and the implementation in photovoltaic devices.[20−26] The light sensitizing feature of ruthenium coordination compounds has been further used as luminescent chemosensors as well as for the production of singlet molecular oxygen.[27−31]

Thus, considerable effort in the synthesis of metal-containing polymers has been accomplished for combining the beneficial properties of a metal ion complex, which provides the optoelectronic capacity, and a polymer backbone enhancing the processability of the materials. Applications in the field of supramolecular chemistry, conducting and photoresponsive materials, and catalysis were established.[5,7,32−37] In particular, the work of Fréchet and Meyer is noteworthy regarding the synthesis of linear macromolecules containing bipyridine-functionalized ruthenium(II) complexes. Fréchet et al. synthesized polymers containing coumarin and Ru(dmbpy)$_3^{2+}$ (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) chromophores using a grafting as well as a copolymerization approach utilizing free radical polymerization procedures. The resulting bichromophoric macromolecules exhibited enhanced absorption and luminescence properties compared to the single Ru(II) complexes due to an efficient (>95%) energy transfer between the coumarin donor dyes and the ruthenium subunit.[38,39] Meyer et al. established a molecular assembly that combined both the light-harvesting and electron transfer properties of a natural photosynthetic system within a single macromolecule.[33] The

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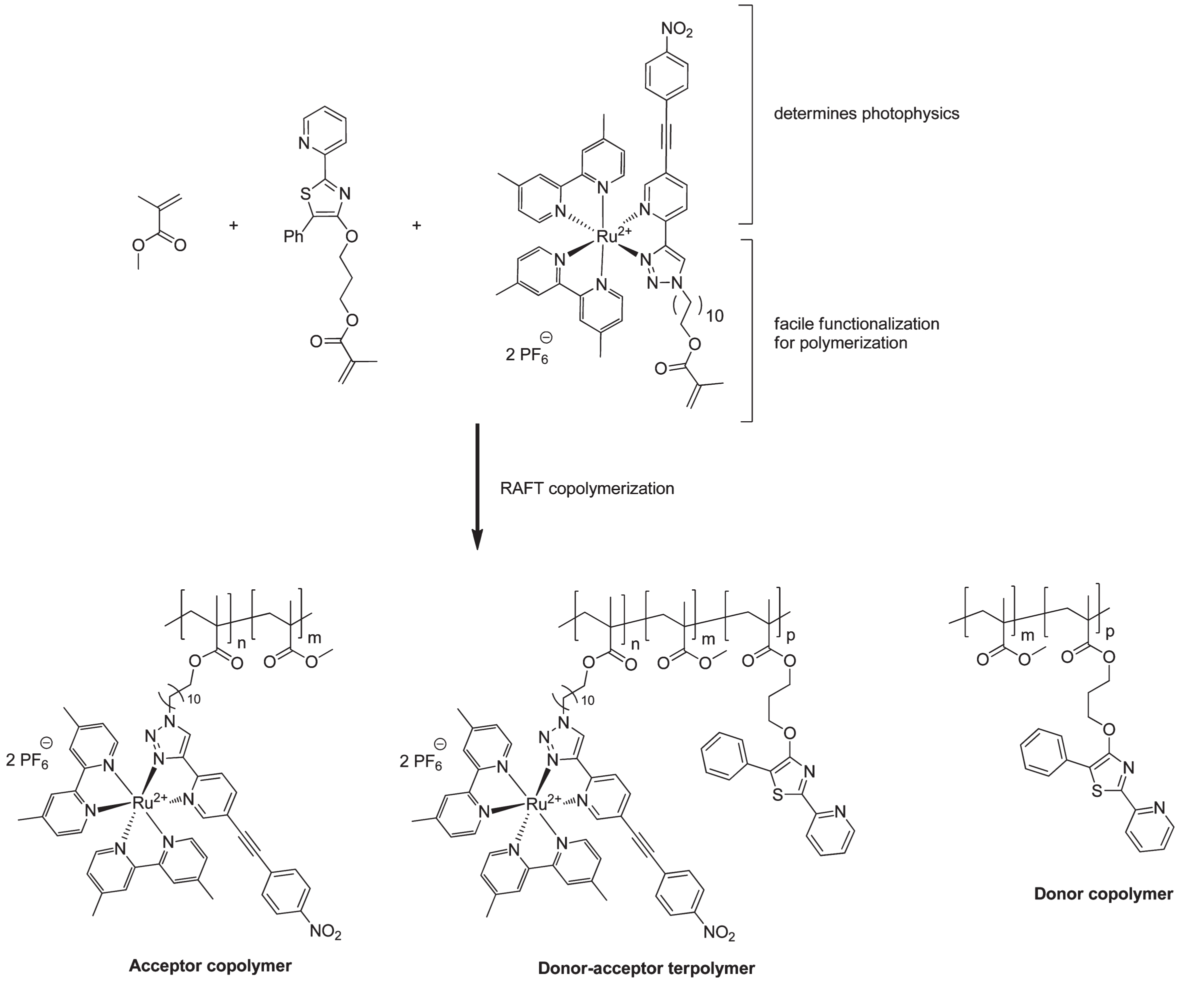
Scheme 1. Schematic Representation of the Various Synthesized Polymer Systems

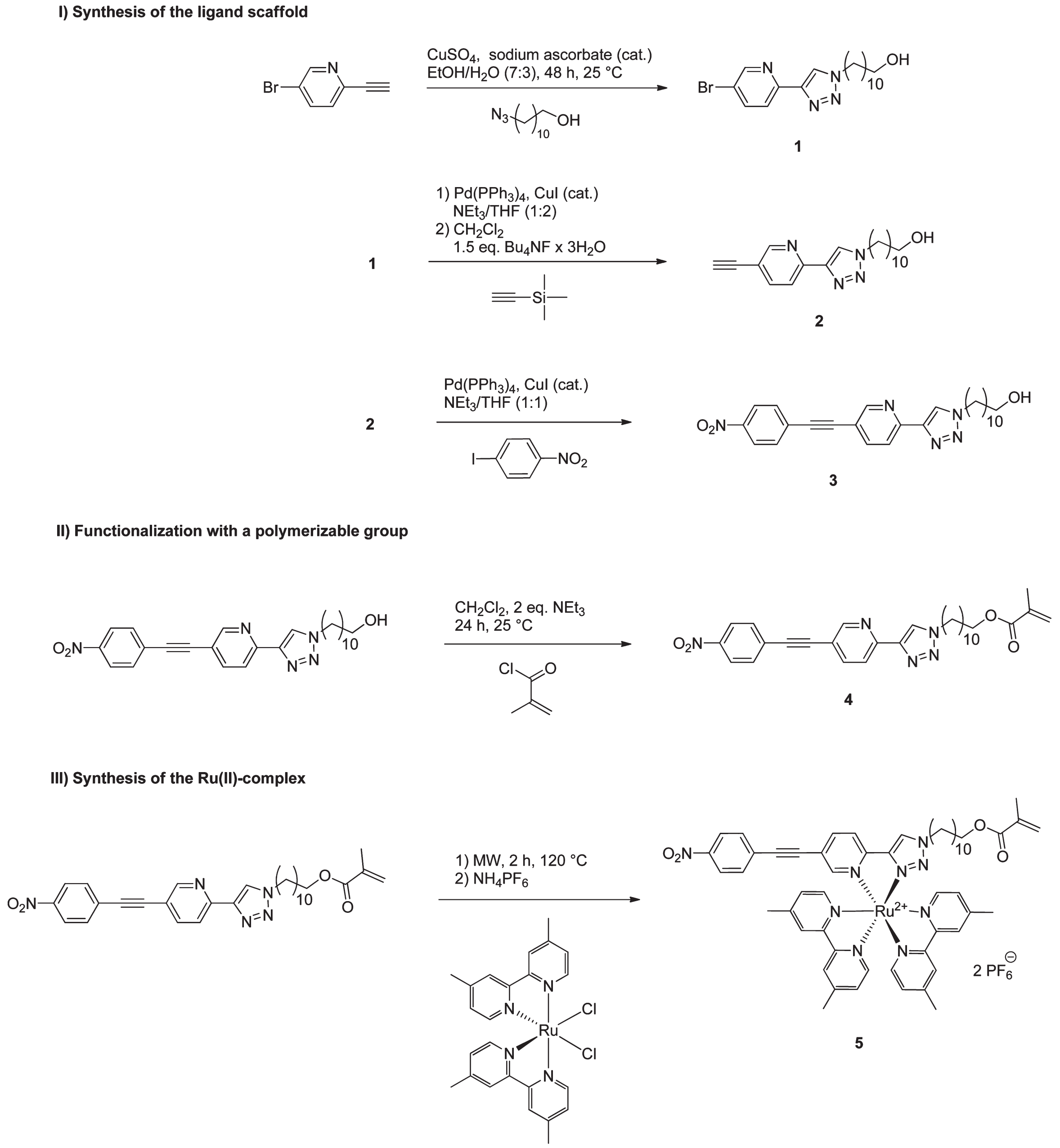


support material in these studies was a mixed styrene-based copolymer, which was prepared by free radical random copolymerization of styrene with *p*-(chloromethyl)styrene. This copolymer pictured a versatile precursor for the addition of a variety of functional groups by nucleophilic substitution of chloride from the pendant chloromethyl groups.[40]

However, the functionalization of polypyridine-based chelators with polymerizable groups can be synthetically troublesome and, therefore, requires new approaches in the preparation of analogous bidentate chelating ligands that also possess well-defined coordination properties and can be prepared as well as modified with high effectiveness.[41] In this respect the Cu^{I}-catalyzed 1,3-cycloaddition of organic azides with terminal alkynes (the CuAAC reaction) has a great potential due to its mild reaction conditions and wide range of usable substrates.[42,43] The development of the CuAAC reaction resulted in an increased interest toward the coordination chemistry of 1,4-functionalized 1*H*-[1,2,3]triazoles due to their potential as *N*-donor ligands.[44−49]

In this contribution, the synthesis of a light-harvesting terpolymer by controlled reversible addition−fragmentation chain transfer (RAFT) radical polymerization is reported, comprising a luminescent ruthenium(II) complex coordinated by a 2-(1*H*-[1,2,3]triazol-4-yl)pyridine system (trzpy) and a 2-(pyridine-2-yl)thiazole donor-type system (Scheme 1). This terpolymer is designed in order to mimic natural strategies for light harvesting and—potentially—to be incorporated in supramolecular systems for conversion of energy from sunlight into chemical energy.[12,50−52] The thiazole dye absorbs light and transfers a fraction of the excitation energy to a ruthenium(II) complex, where a metal-to-ligand charge-transfer (MLCT) state is directly excited for charge separation. Hence, the transition metal complex can act as a primary electron donor when, in perspective, combined with an electron acceptor, e.g., a semiconductor nanoparticle.[50,53] Thus, the photoinduced molecular processes resemble those in natural light harvesting, where the capability of the special pair to harvest sunlight is increased by dressing it with extended antenna structures.[54−56] For the system under investigation the main focus is on the energy transfer taking place in the random donor−acceptor terpolymer. The donor and acceptor units are designed for efficient Förster resonance energy transfer (FRET) as reported by Schäfer et al.[57] The successful incorporation of the donor and acceptor has been confirmed by size exclusion chromatography (SEC) coupled with a photodiode array detector. The trzpy ligand coordinated to the ruthenium(II) ion included two features at the same time: (i) affording the polymerizable group and (ii) an electron-withdrawing moiety on the pyridine, which is responsible for the

Scheme 2. Schematic Representation of the Synthesis of the Acceptor-Type Ruthenium(II) Complex

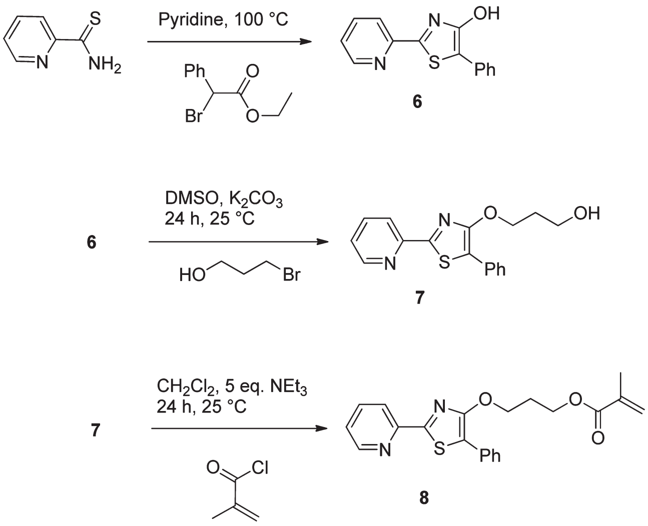


ruthenium complex luminescence. The latter consideration facilitated the energy transfer studies with respect to emission spectroscopy of the acceptor-type ruthenium subunit. The blue-fluorescent thiazole was characterized by a good stability toward the radical polymerization conditions as well as a considerable high luminescence quantum yield.[58]

RESULTS AND DISCUSSION

Synthesis of the Monomers. The general synthesis route of the acceptor-type ruthenium(II) complex **5** is depicted in Scheme 2. In the first three steps, copper(I)-catalyzed azide—alkyne coupling (CuAAC) and Pd(0)-catalyzed Sonogashira coupling were used to set up the trzpy scaffold bearing an electron-withdrawing 4-nitrophenylacetylene moiety on the 5-position of the pyridine ring. The copper(I)-catalyzed 1,3-dipolar cycloaddition of 2-ethynyl-5-bromopyridine and 11-azidoundecan-1-ol yielded **1** under typical CuAAC reaction conditions, whereas 10 mol % of $CuSO_4$ and 0.5 equiv of sodium ascorbate served as Cu(I) source.[43] Consecutive Sonogashira cross-coupling with trimethylsilylacetylene and $Pd^0(PPh_3)_4$, as catalytic active palladium(0) source, as well as subsequent deprotection of the trimethylsilyl-group by potassium fluoride afforded **2** in moderate yield (47%). The following Sonogashira coupling with 4-nitro-1-iodobenzene provided component **3**. The purity of the compounds has been proven by NMR spectroscopy, mass spectrometry, and elemental analysis. The hydroxyl moiety was changed to methyl methacrylate in order to introduce a polymerizable group. The straightforward esterification of **3** with methacryloyl chloride gave **4** in good yield (89%).

Scheme 3. Schematic Representation of the Synthesis of a Polymerizable Donor-Type Thiazole Ligand



The heteroleptic ruthenium(II) complex **5** was synthesized by heating *cis*-dichlorobis(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II) $Ru(dmbpy)_2Cl_2$[45] and ligand **4** under microwave irradiation (120 °C). The methacryl moiety was found to be stable under these conditions as confirmed by preliminary experiments. After the reaction was completed, a 10-fold excess of NH_4PF_6 was added to precipitate the ruthenium(II) complex. Precipitation occurred usually within 30 min, and the complex was finally purified by recrystallization from ethanol and subsequent washing with cold ethanol (yield >90%). The verification of the structure was carried out by ^{1}H and ^{13}C NMR spectroscopy as well as by high-resolution mass spectrometry (HR-ESI MS).

The 4-hydroxythiazole **6** was prepared by a cyclization process of pyridine-2-carbothioamide with ethyl 2-bromophenylacetate.[59] Williamson-type etherification of **6** with 3-bromopropan-1-ol as electrophile yielded **7** in good yield (68%) under mild conditions. Subsequently, the hydroxyl group was reacted with methacryloyl chloride under basic conditions to yield the polymerizable ester **8** (Scheme 3). All compounds had to be purified by column chromatography to ensure a proper reagent grade for the following radical polymerization reactions. The confirmation of the structures was performed by NMR spectroscopy, mass spectrometry, and elemental analysis.

Synthesis of the Polymers. Two copolymers and one terpolymer were synthesized based on a poly(methyl methacrylate) (PMMA) backbone, where **8** served as the donor and **5** as the acceptor unit, respectively (Scheme 4). In general, statistical RAFT copolymerizations were performed in concentrated solutions (∼2 M solution of the monomer) to allow the polymerizations to proceed in a controlled manner.[60] 2-Cyanobutan-2-yl benzodithioate (CBBD) was used as RAFT agent, since it is known to provide a narrow molar mass distribution, in particular for PMMA, as it has been described in the literature.[61,62] The conversion of the reactions was driven to roughly 80% using a standard reaction time of 16 h. Because of the insolubility of **5** in commonly utilized solvents for radical polymerization (i.e., toluene, ethanol), the RAFT polymerizations were performed in *N*,*N*-dimethylacetamide (DMA), as described elsewhere.[63] After the reaction, **9b** was precipitated into cold diethyl ether yielding the desired donor-type copolymer. The polymers **9a,c** were further purified by preparative SEC due to remaining monomer **5** (see SEC graphs in the Supporting Information). Selected characterization data of the final products are summarized in Table 1.

A noteworthy synthesis issue appeared concerning the copolymerization of the heteroleptic ruthenium(II) complex **5** and MMA. It was found after optimization of the reaction conditions (Table 2) that initiation of the polymerization only occurred if the molar content of **5** did not exceed 5 mol %. This fact was attributed to the retardation nature of the NO_2 group.[64] Consequently, the ruthenium(II) content of the terpolymer **9c** was kept below 5 mol % to ensure an efficient initiation of the reaction.

Energy Transfer Studies. When considering the emission and absorption spectra of the donor—acceptor pair **5** and **8** (Figure 1), it is apparent that the requirements for FRET are met, which were a significant emission quantum yield of the donor and a spectral overlap of the donor emission and the acceptor absorption band. The overlap between the donor (**8**) emission and the acceptor (**5**) extinction (hatched region in Figure 1) resulted in an overlap integral value of $J = 4.6\ M^{-1}\ cm^{-1}\ nm^4$ (compare Table 3). The Förster radius, which corresponds to the distance between donor and acceptor at which the efficiency of FRET drops to 50%, was calculated to $R_0 = 4$ nm. The average distance between the donor and the acceptor units had to be smaller than R_0 in order to obtain efficient FRET, which was achieved by copolymerizing **5** and **8** in a polymer backbone delivering **9c**. In the terpolymer the thiazoles were randomly distributed in the vicinity of the Ru(II) complexes. Because of the fact that the geometrical constraints discussed above were met, FRET from the thiazole to the MLCT band of **5** (centered at 450 nm) was expected to occur in the polymer.

In order to verify the appearance of FRET in the donor—acceptor polymer **9c**, excitation spectra were recorded of the donor-type polymer **9b**, the acceptor-type polymer **9a**, and the donor—acceptor polymer **9c** (see Figure 2). For recording the luminescence excitation spectra of the Ru(II) subunit the emission was monitored at 620 nm, where no donor fluorescence from subunit **8** appeared. Therefore, a difference in the luminescence excitation spectra of **9a** and **9c** indicated contributions from thiazole excitation to the luminescence of the ruthenium(II) unit as seen in the additional excitation band at 380 nm in **9c** (see Figure 2). This excitation band is spectrally centered, where the thiazole emission is excited in the donor-type polymer **9b** as indicated by the dashed line in Figure 2. These findings point toward FRET; i.e., excitation of the donor led to amplified luminescence of the acceptor.

The additional excitation band in the luminescence of the Ru(II) subunit is accompanied by a reduction of the donor-based quantum yield in the donor—acceptor polymer **9c** compared to that of **9b** (Table 3). While measuring the donor-based quantum yield in donor-type polymer **9b** was straightforward, the quantum yield measurement in the donor—acceptor polymer **9c** required adequate care: because of overlapping donor and acceptor absorptions (see Figures 1 and 2), it was not possible to exclusively excite donor molecules in the donor—acceptor polymer in order to directly measure the donor-based emission quantum yields. Taking into account these overlapping absorptions, the molar extinction coefficients of donor and acceptor at the excitation wavelength had to be considered as well as the ratio of donors and acceptors within the polymer chain. Considering these properties, the quantum yield measurement in the

Scheme 4. Schematic Representation of the Synthesis of the Statistical Copolymers 9a−c

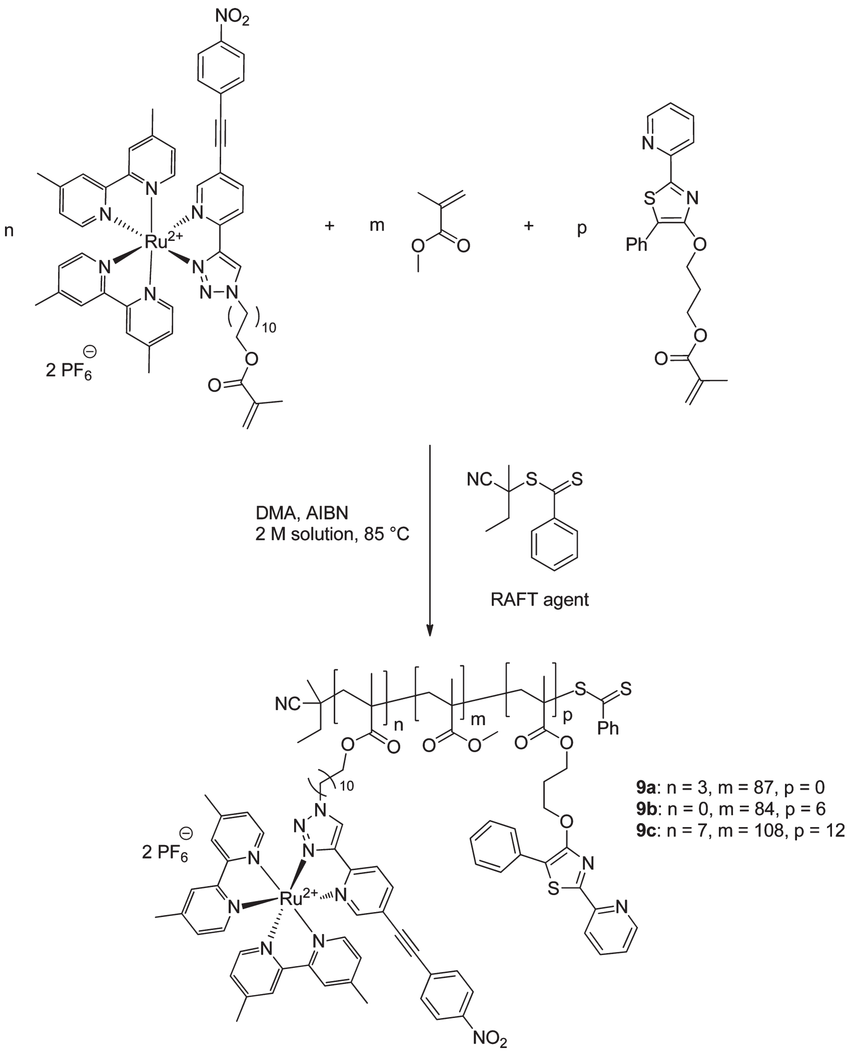


Table 1. Selected Characterization Data for the Polymers 9a−c

polymer	Ru(II) content [mol %][a]	dye content [mol %][a]	$M_{n,theo}$	$M_{n,NMR}$ [g mol^{-1}][a]	DP[a,b]	$M_{n,SEC}$ [g mol^{-1}][c]	PDI[d]
9a	3		8 500	9 000	90	5 000	1.32
9b		7	11 700	12 000	90	15 100	1.13
9c	6	10	11 200	12 800	127	8 000	1.32

[a] Determined by ^{1}H NMR spectroscopy. [b] Degree of polymerization. [c] Determined by SEC using PMMA calibration. [d] Polydispersity index determined by SEC.

donor−acceptor polymer **9c** followed the same procedure as the emission quantum yield measurements of **8** and **9b**.

In the work presented here the donor-type polymer **9b**, lacking acceptor molecules, was synthesized as reference system for **9c**. It is expected that the fluorescence quantum yield and the lifetime of the reference polymer are practical for calculating the transfer efficiency for energy transfer in the donor−acceptor polymer **9c**. The importance of using such a reference system instead of the monomeric unit **8** is obvious from Table 3. Upon integration into the polymer, the fluorescence quantum yield of the thiazole increased compared to the monomeric fluorophore. Such behavior is in agreement with the measured fluorescence lifetimes, whereas the emission spectrum of **9b** was similar to that of **8** (see Figure 3). The reason for the increased lifetime was attributed to random coiling of the polymer in solution changing sufficiently the environment of individual dyes.[65] Nevertheless, choosing **9b** as reference was a critical step for the analysis of the excitation energy transfer in the donor−acceptor polymer **9c**: the lengths of **9b** and **9c** are not identical, and additionally, the reference polymer could exhibit a different coiling compared to the donor−acceptor polymer. Nonetheless, energy transfer efficiencies were calculated as described in the Experimental Section using the quantum yields and lifetime measurements from the reference system **9b** and the donor−acceptor polymer **9c**.

Table 2. Optimization of the Reaction Conditions of the Copolymerization of 5 and MMA

M/I ratio[a]	Ru(II) content [mol %]	t_R [h]	AIBN [mol %]	conv [%]
100	10	18	0.25	0
200	10	18	0.25	0
50	10	18	0.25	0
100	10	18	0.5	0
100	10	18	1	0
100	6	18	0.25	0
100	4	18	0.25	85

[a] Monomer/initiator ratio (MMA/CBBD).

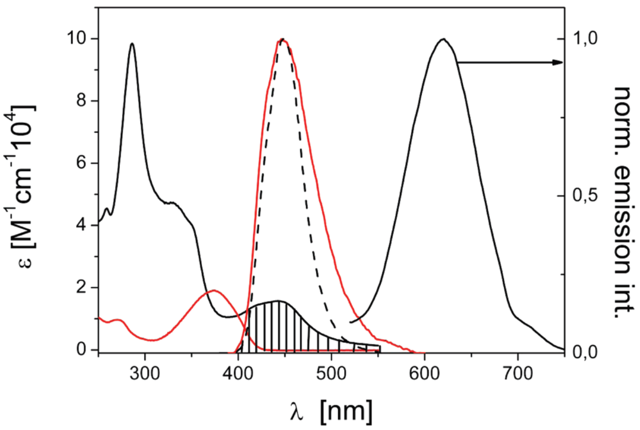


Figure 1. Extinction and emission spectra of **8** (red) and **5** (black) at room temperature measured in dichloromethane (excitation at 370 and 462 nm, respectively). The hatched region indicates the donor–acceptor spectral overlap, and the dashed line displays the integrand of the overlap integral.

Table 3. Representation of the Photophysical Properties from 8–9c

compd	$\lambda_{abs,max}$ (nm) [log ε]	$\lambda_{em,max}$ (nm) [excitation]	Φ[a]	τ (ns)[b]	J (M^{-1} cm^{-1} nm^4)
8	375 [5.14]	447 [370]	0.40	1.8	
9a	286 [5.47]	620 [460]			
	330 [5.17]				
	443 [4.68]				
9b	375 [5.14]	447 [370]	0.58	2.7	0.064[c]
9c	285	449 [370]	0.06	–[e]	4.6[d]
	350				
	442				

[a] Emission quantum yield measured in dichloromethane at room temperature. [b] Lifetime measured in dichloromethane at room temperature. [c] Overlap integral considering homotransfer for **9b**. [d] Overlap integral of emission from **8** with absorption of **9a**. [e] No single-exponential decay was observed.

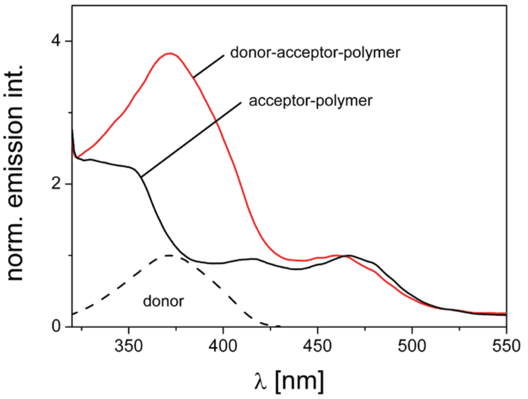


Figure 2. Excitation spectra of the donor–acceptor polymer **9c** (red) and the acceptor polymer **9a** (black) recorded by monitoring the luminescence of **5** at 620 nm (solid), normalized to maximal intensity in the MLCT excitation band at 460 nm. The donor polymer fluorescence excitation spectrum from **9b** recorded at 450 nm (dashed) was normalized to the maximal emission intensity. The spectra were taken in dichloromethane at room temperature.

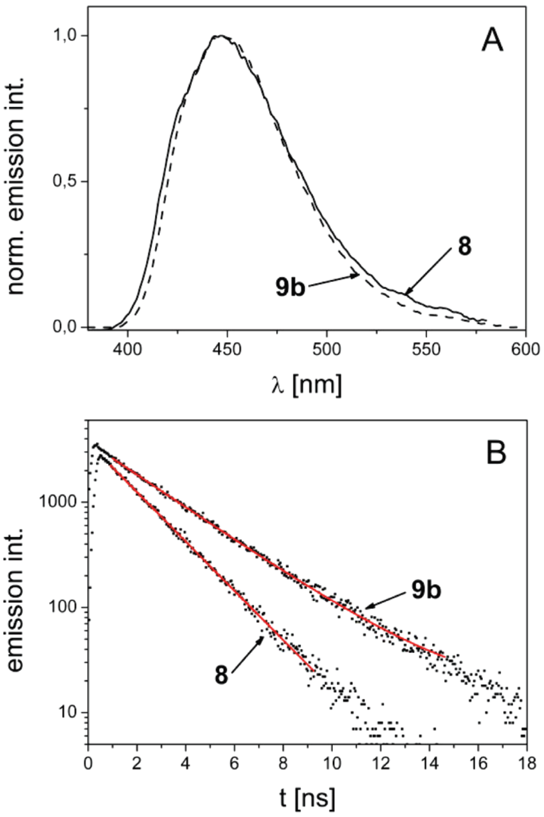


Figure 3. In panel A, the dashed line denotes the emission spectra of the reference polymer **9b** and the solid line the emission of the monomer **8** in dichloromethane, excited at 375 nm. In panel B, the red line fits the monoexponential decay of the measured data (dotted).

Time-resolved measurements of the donor lifetime in **9b** and **9c** (see Figure 4) revealed that the donor emission decayed more rapidly in the presence of an acceptor as the interaction between the donor and the acceptor quenched the donor emission. On the basis of the temporal emission profiles of the donor in **9b** and **9c**, the FRET efficiency *E* was calculated to be 70% (see Experimental Section for details). Although there are many possibilities for excitation quenching in polymers—such as energy migration, exciton–exciton annihilation,[66–68] and excimer formation[69]—it was assumed that this shortening of the donor decay time in the donor–acceptor polymer is dominated by FRET. Because of the overlap between donor emission and

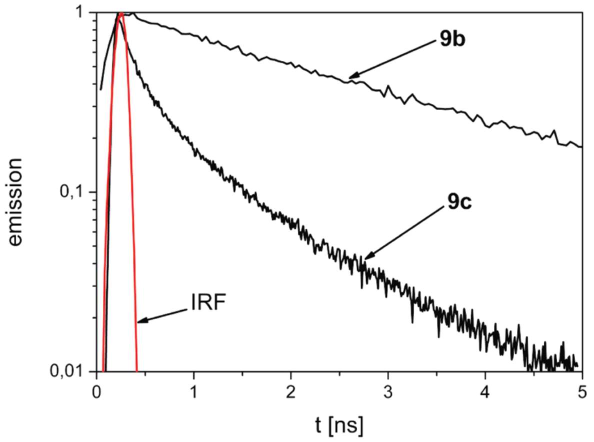


Figure 4. Donor decay profile of the reference polymer **9b** and the donor−acceptor polymer **9c** in dichloromethane at room temperature, excited at 290 nm. The instrument response function (IRF) was measured by scattered light.

donor absorption (see Figure 1) homoenergy transfer, i.e., FRET between dyes of the same type, is not excluded, but the calculated overlap integral for such energy transfer, and consequently the resulting transfer rate, was 2 orders of magnitude smaller than FRET between donor and acceptor molecules of the type **8** and **5** (see Table 3). Thus, in polymer **9c** no considerable homoenergy transfer will occur, even if there is a higher number of donor than acceptor molecules. Along the same lines contributions from back-energy transfer, i.e., FRET from the acceptor to the donor subunit, were excluded. Excimer formation was excluded as well because it typically causes an additional emission band beyond the red end of the fluorescence, which was not observed for **9c**.[70] Comparing the FRET results presented here to analogous work on other polymers and dendrimers,[65,71,72] it can be stated that in **9** effects, such as energy migration, excimer formation, or local concentration quenching, were avoided.[73] These effects cause a reduction of the emission quantum yield and a nonexponential emission decay. Neither of these effects were observed in the reference polymer **9b**. Probably this is caused by the low concentration of donor units in the polymer backbone compared to dendritic systems.[65]

Additionally, Figure 4 shows a nonexponential donor emission in the presence of acceptor units in the terpolymer. This is due to the fact that no fixed donor−acceptor distances existed within the polymer. This situation resulted in different FRET rates for individual donor−acceptor pairs and, therefore, different decay rates for individual photoexcited donors.

Moreover, preliminary solvent-dependent donor lifetime measurements were carried out and are depicted in Figure 5. The measured donor lifetimes in presence of the ruthenium(II) acceptor were shortened (non-single-exponential decay) compared to the donor alone lifetimes (single-exponential decay) due to the resonance energy transfer. The shape of the decay curves of the polymers themselves in different solvents are very similar, and thus, no significant change in the conformation of the polymers can be concluded. A comparison of the transfer efficiencies in the different solvents was not possible because the avalanche photodiode detects scattered photons from the excitation pulse as well. This may result in incorrect calculated transfer efficiencies.

Of course, any description of donor quenching in donor−acceptor polymers is incomplete using Förster's theory only; for

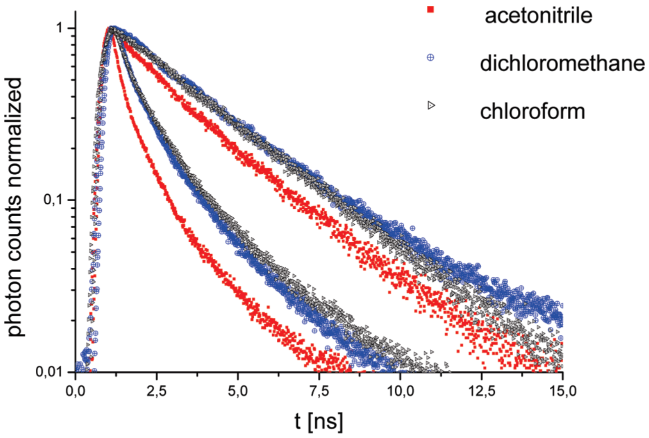


Figure 5. Donor fluorescence curves of compound **9b** (donor alone polymer) and of **9c** (donor−acceptor polymer) in different solvents: acetonitrile (red squares), dichloromethane (blue circles), chloroform (black triangles). The longer living fluorescence (single-exponential decay) stems from the donor alone polymer and the shortened fluorescence (non-exponential decay) from the donor−acceptor polymer. Excitation wavelength: 290 nm.

example, Dexter type energy transfer can also occur at donor−acceptor distances smaller than 10 Å, when donor emission and acceptor absorption spectrally overlap.[70] Furthermore, translational diffusion can cause an enhancement of the FRET efficiency compared to systems with a static distance distribution of donor and acceptor as reported by Lakowicz et al.[74] and Thomas et al.[75] Regardless of a possibly incomplete description of the excitation energy transfer only by FRET, the donor−acceptor polymers designed for efficient FRET allow enhanced light harvesting in a Ru(II) complex, whereupon energy is focused into the ^{1}MLCT band. By considering the charge separating character of the MLCT states, this process increased the accessibility of Ru(II) complexes as primary electron donors in photocatalytic systems.

■ CONCLUSIONS

Polymers containing a 1,3-thiazole dye (energy donor) and a ruthenium(II) chromophore (energy acceptor) were synthesized using a controlled RAFT polymerization procedure. The terpolymer was able to relay the absorbed energy by energy transfer from the thiazole donor to the ruthenium(II) acceptor. The ruthenium(II) content in the macromolecules was limited to 5 mol % at most, since for higher metal content the polymerization could not be initiated. The donor−acceptor functionalized terpolymer displayed a reasonable energy transfer efficiency of over 70%. Those polymeric systems will be practical, e.g., in terms of the synthesis of artificial photosynthetic systems, in which they can act as light-harvesting antennas.

■ EXPERIMENTAL SECTION

Materials and Instrumentation. All reagents were acquired from commercial sources and used without further purification. Solvents were dried and distilled according to standard procedures and stored under nitrogen. All reactions were performed in air-dried flasks under a nitrogen atmosphere, unless stated otherwise. For the Pd^0-catalyzed cross-coupling and the RAFT polymerization procedures, the solvents were degassed by bubbling with nitrogen 0.5 h before use. Purification of the reaction products was carried out by column chromatography using

40−63 μm silica gel. Analytical thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel 60 F254, and visualization was accomplished with UV light (254 nm). Preparative size exclusion chromatography (SEC) was carried out on Bio-Rad S-X1 beads (size exclusion 600−14 000 g/mol), swollen in dichloromethane. The conversion of the copolymerization reactions was determined by ^{1}H NMR spectroscopy. The heteroleptic ruthenium(II) complexes were synthesized by microwave-assisted reactions using a Biotage Initiator ExpEU (maximum power: 400 W; working frequency: 2450 MHz) with closed reaction vials. During the experiments the temperature and the pressure profiles were detected. 1D (^{1}H and ^{13}C) and 2D (^{1}H−^{1}H COSY) nuclear magnetic resonance spectra were recorded on a Bruker AC 300 (300 MHz) at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the signal of the applied solvent.

5-Bromo-2-ethynylpyridine,[45] 2-cyanobutan-2-yl benzodithioate,[61] dichloro(cycloocta-1,5-diene)ruthenium(II),[45] *cis*-dichlorobis(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II),[45] and 5-phenyl-2-(pyridin-2-yl)-1,3-thiazol-4-ol[59] were synthesized according to literature reports.

Photophysical Measurements and Calculations. Measurements of the fluorescence intensity were carried out on a Perkin-Elmer lambda16 UV/vis spectrometer in the perpendicular excitation−emission geometry, while the absorbance at the excitation wavelength was <0.05. The calculation of fluorescence quantum yields was done according to following equation[76]

$$\Phi = \Phi_{\mathrm{r}} \frac{I}{I_{\mathrm{r}}} \frac{A_{\mathrm{r}}}{A} \frac{n^2}{{n_{\mathrm{r}}}^2} \qquad (1)$$

where Φ is the quantum yield, I is the corrected integrated emission intensity, A is the absorbance at the excitation wavelength, and n is the refractive index of the solvent, i.e., in this study dichloromethane of spectroscopic grade from Sigma-Aldrich. The subscript "r" refers to a reference fluorophore of known quantum yield, whereas quinine sulfate (Φ = 0.55) was used in our investigations.[76]

The fluorescence decay curves were obtained by a Hamamatsu streak scope C4334 in time-correlated single photon counting (TCSPC) modus. Triggering was carried out by the Hamamatsu trigger unit C4792-01. After excitation with a frequency-tripled Ti-sapphire laser (Tsunami, Newport Spectra-Physics GmbH), i.e., λ_{ex} = 290 nm, in perpendicular direction the fluorescence emission wavelength were separated by a Chromex 250IS imaging spectrograph. The repetition rate of the laser was adjusted to 0.8 MHz by a pulse selector (model 3980, Newport Spectra-Physics GmbH). All measurements were carried out at concentrations below 10^{-6} M. Solvent-dependent donor lifetime measurements were performed with a time-correlated single-photon counting module from Becker & Hickl using an avalanche photodiode as detector. The solvents were acetonitrile, dichloromethane, and chloroform.

In order to quantify the efficiency of FRET the time-dependent intensity decay curve of the donor-alone polymer **9b** was measured and compared to the respective intensity decay of **8** incorporated into the donor−acceptor polymer **9c** using eq 2, which can be derived from ref 77. Here, τ_{D} and τ_{DA} refer to the donor lifetime in the donor-alone polymer **9b** and to the donor lifetime in the donor−acceptor polymer **9c**, respectively. I_{DA} is the time-dependent intensity of the donor fluorescence in presence of an acceptor, which is normalized to the amplitude I_{DA}^0. The resultant efficiency E is 0.7.

$$E = 1 - \frac{\tau_{DA}}{\tau_{\mathrm{D}}} = 1 - \frac{1}{\tau_{\mathrm{D}}} \int \frac{I_{DA}(t)\,\mathrm{d}t}{I_{DA}^0} \qquad (2)$$

In analogy to the determination of the transfer efficiency based on time-resolved measurements, the emission quantum yield of the donor was measured in **9b** (donor-only polymer) and in the donor−acceptor polymer **9c** in order to calculate the transfer efficiency from eq 3, where Φ_{DA} and Φ_{D} refer to the donor emission quantum yield of **8** in **9c** and **9b**, respectively (see Table 3).

$$E = 1 - \frac{\Phi_{DA}}{\Phi_{\mathrm{D}}} \qquad (3)$$

The obtained value of 90% for the transfer efficiency E is only an estimate because of the uncertainty for the measured quantum yields. But the significant reduction of the donor fluorescence quantum yield upon incorporation into the donor−acceptor polymer from Φ = 0.58 (**9b**) to 0.06 (**9c**) proved FRET to take place. A more accurate value for E is achieved from the time-resolved measurements. Consequently, the value E = 0.7 in this article was discussed and assumed.

Synthesis of 11-(4-(5-Bromopyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)undecan-1-ol (1). Sodium azide (590 mg, 9 mmol) was dissolved in dimethyl sulfoxide (20 mL), and 11-bromo-1-undecanol (1.5 g, 6 mmol) was added subsequently. After stirring 24 h at room temperature, water (30 mL) was added to quench the reaction, and the suspension was extracted three times with diethyl ether. The organic phases were combined, washed with brine, and dried over Na_2SO_4. The solution was subsequently concentrated *in vacuo* to yield 11-azido-1-undecanol as slight yellow oil (1.25 g, 98%).

To a solution of the organic azide, 2-ethynyl-5-bromopyridine (1.07 g, 5.9 mmol) and $CuSO_4$ (88 mg, 0.59 mmol, dissolved in 1 mL water) in an EtOH/water mixture (7:3 ratio, 50 mL) was added sodium ascorbate (570 mg, 2.9 mmol, dissolved in 2 mL of water), and the reaction was stirred for 72 h at room temperature. The yellow precipitate was filtered and recrystallized from ethanol, yielding the pure product as white solid (1.55 g, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.63 (s, 1H), 8.12−8.08 (m, 2H), 7.91 (dd, J = 8.5 Hz, J = 2.1 Hz, 1H), 4.42 (t, J = 7.2 Hz, 2H, N−CH_2), 3.67−3.61 (m, 2H, O−CH_2), 1.98−1.93 (m, 2H), 1.59−1.54 (m, 2H), 1.39−1.27 (m, 14H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 150.4, 148.9, 147.4, 139.4, 121.9, 121.3, 119.3, 62.8, 50.5, 32.7, 30.0, 29.4, 29.3, 29.2, 28.8, 26.3, 25.7. ESI-TOF MS: m/z = 418.33 (15%, $[M + Na]^+$), 394.14 (100%, $[M]^+$). Anal. Calcd for $C_{18}H_{27}BrN_4O$: C, 54.69%; H, 6.88%; N, 14.17%. Found: C, 54.76%; H, 7.08%; N, 14.02%.

Synthesis of 11-(4-(5-Ethynylpyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)undecan-1-ol (2). To a solution of 11-(4-(5-bromopyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)undecan-1-ol (**1**, 1.5 g, 3.79 mmol), CuI (34 mg, 0.18 mmol), and tetrakis(triphenylphosphine)palladium(0) (220 mg, 0.18 mmol) in NEt_3/THF (1:1 ratio, 50 mL) was added trimethylsilylacetylene (280 mg, 2.8 mmol), and the mixture was stirred 48 h at 40 °C. After removal of the solvent under reduced pressure, the residue was purified by gel filtration on silica ($CHCl_3$/EtOAc 2:1 ratio).

For the deprotection, the product was dissolved in dichloromethane (30 mL) and treated with tetrabutylammonium fluoride trihydrate (1.8 g, 1.5 equiv). After 4 h, the solvent was removed and the crude product was finally purified by column chromatography on silica (EtOAc) yielding the product as off-white powder (580 mg, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.66 (s, 1H), 8.16−8.14 (m, 2H), 7.85 (dd, J = 8.2 Hz, J = 2.0 Hz, 1H), 4.41 (t, J = 7.1 Hz, 2H, N−CH_2), 3.64−3.59 (m, 2H, O−CH_2), 3.25 (s, 1H, C≡C−H), 1.95−1.92 (m, 2H), 1.56−1.51 (m, 2H), 1.33−1.25 (m, 14H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 152.4, 149.7, 147.7, 139.9, 122.3, 119.3, 118.0, 80.8, 80.5, 62.9, 50.5, 32.7, 30.1, 29.4, 29.3, 29.2, 28.8, 26.3, 25.6. ESI-TOF MS: m/z = 340.24 (100%, $[M]^+$). Anal. Calcd for $C_{20}H_{28}N_4O$: C, 70.56%; H, 8.29%; N, 16.46%. Found: C, 70.22%; H, 7.98%; N, 16.41%.

Synthesis of 11-(4-(5-((4-Nitrophenyl)ethynyl)pyridine-2-yl)-1*H*-1,2,3-triazol-1-yl)undecan-1-ol (3). 11-(4-(5-Ethynylpyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)undecan-1-ol (**2**, 450 mg, 1.32 mmol), 4-nitro-1-iodobenzene (336 mg, 1.35 mmol), tetrakis(triphenylphosphine)palladium(0) (30 mg, 0.026 mmol), and CuI (5 mg, 0.026 mmol) were dissolved in a NEt_3/THF mixture (3:7, 30 mL), and the solution was stirred for 72 h at room temperature. The solution was evaporated under reduced pressure, and the pure product was isolated by column chromatography over silica ($CHCl_3$/EtOAc 8:1 ratio) as a slight yellow powder (560 mg, 92%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.74 (s, 1H), 8.26−8.22 (m, 2H), 8.19−8.17 (m, 2H), 7.92 (dd, *J* = 8.2 Hz, *J* = 2.1 Hz, 1H), 7.71−7.68 (m, 2H), 4.42 (t, *J* = 7.1 Hz, 2H, N−CH$_2$), 3.63 (t, *J* = 6.6 Hz, 2H, O−CH$_2$), 1.99−1.93 (m, 2H), 1.58−1.53 (m, 2H), 1.34−1.27 (m, 14H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 152.0, 149.9, 147.5, 147.3, 139.6, 132.3, 129.4, 123.7, 122.4, 119.5, 118.0, 91.2, 90.8, 62.9, 50.5, 32.7, 30.1, 29.4, 29.3, 29.2, 28.8, 26.3, 25.6. ESI-HRMS calcd for $C_{26}H_{32}N_5O_3$ [M + H]$^+$: 462.2500. Found: 462.2486.

Synthesis of 11-(4-(5-((4-Nitrophenyl)ethynyl)pyridine-2-yl)-1*H*-1,2,3-triazol-1-yl)undecyl Methacrylate (4). 11-(4-(5-((4-Nitrophenyl)ethynyl)pyridine-2-yl)-1*H*-1,2,3-triazol-1-yl)undecan-1-ol (**3**, 400 mg, 0.88 mmol) and triethylamine (240 μL, 1.76 mmol) were dissolved in dry dichloromethane (10 mL). The solution was cooled to 0 °C, methacryloyl chloride (200 μL, 2 mmol) was added, and subsequently the solution was stirred for 2 h at 0 °C and further 24 h at room temperature. The reaction mixture was washed with saturated NaHCO$_3$ solution, and after drying of the organic layer over MgSO$_4$, the solvent was removed *in vacuo*. The crude product was purified by column chromatography on silica (EtOAc/CHCl$_3$ 3:1) providing the pure product as slight yellow solid (410 mg, 88%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.75 (s, 1H), 8.27−8.24 (m, 2H), 8.21−8.17 (m, 2H), 7.94 (dd, *J* = 8.2 Hz, *J* = 2.1 Hz, 1H), 7.72−7.69 (m, 2H), 6.09 (s, 1H, *C* = CH$_2$), 5.54 (s, 1H, *C* = CH$_2$), 4.42 (t, *J* = 7.1 Hz, 2H, N−CH$_2$), 4.13 (t, *J* = 6.7 Hz, 2H, O−CH$_2$), 2.01−1.97 (m, 2H), 1.93 (s, 3H, CH$_3$), 1.70−1.64 (m, 2H), 1.35−1.26 (m, 14H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 167.5, 151.7, 149.8, 147.3, 139.8, 136.5, 132.4, 129.3, 125.1, 123.7, 122.6, 119.7, 118.1, 91.0, 64.8, 50.6, 30.2, 29.41, 29.38, 29.31, 29.1, 28.9, 28.5, 26.4, 25.9, 18.3. ESI-HRMS calcd for $C_{30}H_{35}N_5NaO_4$ [M + Na]$^+$: 552.2587. Found: 552.2580.

Synthesis of Bis(4,4′-dimethyl-2,2′-bipyridine)-[11-(4-(5-((4-nitrophenyl)ethynyl)pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-undecyl methacrylate]ruthenium(II) Hexafluorophosphate (5). *cis*-Dichlorobis(4,4′-dimethyl-2,2′-bipyridine)ruthenium(II) (87 mg, 0.16 mmol) and 11-(4-(5-((4-nitrophenyl)ethynyl)pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)undecyl methacrylate (**4**, 85 mg, 0.16 mmol) were suspended in ethanol (10 mL). After heating under microwave irradiation at 125 °C for 2 h, the red solution was filtered and treated with a 10-fold excess of NH$_4$PF$_6$. Subsequently, precipitation occurred within 30 min, and the red precipitate was filtered off after 1 day. The precipitate was washed twice with cold ethanol, and recrystallization from ethanol yielded the pure product as red powder (184 mg, 89%). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz): δ = 8.75 (s, 1H), 8.29−8.07 (m, 8H), 7.73−7.46 (m, 7H), 7.31−7.26 (m, 3H), 7.16 (d, *J* = 5.9 Hz, 1H), 6.07 (s, 1H, C=C−H), 5.56 (m, 1H, C=C−H), 4.39 (t, *J* = 7.4 Hz, 2H, N−CH$_2$), 4.12 (t, *J* = 6.7 Hz, 2H, C(O)O−CH$_2$), 2.61−2.56 (m, 12H, CH$_3$), 1.92−1.87 (m, 2H), 1.67−1.59 (m, 6H), 1.34−1.24 (m, 14H). ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz): δ = 156.9, 156.7, 156.3, 152.8, 151.0, 150.8, 150.7, 150.6, 150.5, 147.9, 147.0, 140.4, 132.7, 128.8, 128.7, 128.6, 128.0, 127.7, 126.0, 124.9, 124.85, 124.6, 124.5, 124.2, 124.1, 123.7, 122.4, 121.5, 93.5, 87.9, 64.7, 29.5, 29.4, 29.38, 29.34, 29.2, 28.8, 28.6, 26.2, 26.0, 21.1, 21.06, 21.02, 18.0. ESI-TOF MS: *m*/*z* = 1144.33 (5%, [M−PF$_6$]$^+$), 499.69 (100%, [M−2PF$_6$]$^{2+}$). ESI-HRMS calcd for $C_{54}H_{59}N_9O_4Ru$ [M−2PF$_6$]$^{2+}$: 499.6861. Found: 499.6881.

Synthesis of 3-((5-Phenyl-2-(pyridine-2-yl)thiazol-4-yl)oxy)-propan-1-ol (7). To a solution of 5-phenyl-2-(pyridin-2-yl)thiazol-4-ol (**6**, 4.0 g, 15.8 mmol) and 3-bromopropan-1-ol (2.60 g, 18.9 mmol) in dimethyl sulfoxide (100 mL) was added fine ground K$_2$CO$_3$ (2.60 g, 18.9 mmol). The purple mixture was stirred for 24 h at room temperature followed by addition of 200 mL of H$_2$O. The solution was extracted with CHCl$_3$ (3 × 100 mL). The combined organic phases were washed with H$_2$O (3 × 100 mL) to remove the dimethyl sulfoxide, dried over MgSO$_4$, and concentrated *in vacuo*. The brown oil was purified using gel filtration (silica, CHCl$_3$) to yield the pure ether as a yellow oil (3.35 g, 68%). ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 8.59 (d, *J* = 4.8 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.82−7.71 (m, 3H), 7.44−7.34 (m, 2H), 7.33−7.24 (m, 2H), 4.69 (t, *J* = 5.9 Hz, 2H, O−CH$_2$), 3.87 (t, *J* = 5.9 Hz, 2H, CH$_2$−OH), 2.90 (s, 1H, OH), 2.10 (p, *J* = 5.9 Hz, 2H, CH$_2$). ^{13}C NMR (CDCl$_3$, 63 MHz): δ = 160.9, 159.2, 150.9, 149.5, 137.0, 131.5, 128.7, 126.97, 126.96, 124.3, 118.9, 115.0, 67.7, 59.2, 32.8. EI MS: *m*/*z* = 312.09 (100%, [M]$^+$), 254.05 (75%, [M−C$_3$H$_6$O]$^+$). Anal. Calcd for $C_{17}H_{16}N_2O_2S$: C, 65.36%; H, 5.16%; N, 8.97%; S, 10.26%. Found: C, 65.38%; H, 5.18%; N, 9.10%; S, 9.92%.

Synthesis of 3-((5-Phenyl-2-(pyridin-2-yl)thiazol-4-yl)oxy)-propyl Methacrylate (8). To a solution of 3-((5-phenyl-2-(pyridin-2-yl)thiazol-4-yl)oxy)propan-1-ol (**7**, 1.40 g, 4.48 mmol) and triethylamine (2.24 g, 22.4 mmol) in dry CH$_2$Cl$_2$ (30 mL) was added methacryloyl chloride (0.94 g, 8.96 mmol). The reaction was stirred for 24 h at ambient temperature, and subsequently, the organic phase was thoroughly washed with water (3 × 20 mL) and saturated NaHCO$_3$ solution to hydrolyze the excess acid chloride. After drying of the organic phase over MgSO$_4$ and evaporation of the solvent (T < 40 °C), the crude product was purified using column chromatography on silica (CHCl$_3$) yielding the pure product as yellow oil (1.5 g, 88%). ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 8.60 (d, *J* = 4.70 Hz, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.83−7.67 (m, 3H), 7.45−7.32 (m, 2H), 7.32−7.19 (m, 2H), 6.13 (s, 1H, C=C−H), 5.55 (s, 1H, C=C−H), 4.64 (t, *J* = 6.3 Hz, 2H, O−CH$_2$), 4.40 (t, *J* = 6.3 Hz, 2H, C(O)O−CH$_2$), 2.26 (p, *J* = 6.3 Hz, 2H, CH$_2$), 1.95 (s, 3H, CH$_3$). ^{13}C NMR (63 MHz, CDCl$_3$): δ = 167.4, 160.5, 158.9, 151.2, 149.4, 136.9, 136.3, 131.6, 128.8, 126.94, 126.85, 125.5, 124.2, 118.9, 114.8, 67.1, 61.7, 29.0, 18.3. EI MS: *m*/*z* = 380.12 (30%, [M]$^+$), 254.05 (10%, [M−C$_7$H$_{11}$O$_2$]$^+$). Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 66.29%; H, 5.30%; N, 7.36%; S, 8.43%. Found: C, 66.41%; H, 5.32%; N, 7.22%; S, 7.98%.

General RAFT Copolymerization Procedure. The respective methacrylate-functionalized monomer, methyl methacrylate (125 μL, 1.163 mmol), 2-cyanobutan-2-yl benzodithioate (2.7 mg, 1.6 μmol, 1 mol %), and 2,2′-azobis(2-methylpropionitrile) (0.5 mg, 0.4 μmol, 0.25 mol %) were dissolved in *N*,*N*-dimethylacetamide (600 μL) in a 2 mL microwave vial. The vial was sealed, and the solution was degassed for 0.5 h under nitrogen. Subsequently, the reaction mixture was stirred at 85 °C (oil bath temperature) for 16 h. The crude product was precipitated in cold diethyl ether and purified by preparative size exclusion chromatography (BioBeads S-X1, CH$_2$Cl$_2$ as eluent) yielding the pure desired copolymer.

Synthesis of Polymer 9a. According to the general procedure, bis(4,4′-dimethyl-2,2′-bipyridine)-[11-(4-(5-((4-nitrophenyl)ethynyl)-pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)undecyl methacrylate]ruthenium-(II) hexafluorophosphate (**5**, 60 mg, 0.047 mmol) was reacted to yield the product as red solid (106 mg, 45%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.80 (br), 8.35−8.10 (br), 7.70−7.50 (br), 7.45−7.25 (br), 7.15−7.08 (br), 4.40 (br), 3.95 (br), 3.58 (s), 2.60−2.45 (br), 2.05−1.65 (br), 1.45−1.15 (br), 1.0 (s), 0.8 (s). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 178.1, 177.8, 176.9, 157.0, 156.6, 156.3, 152.9, 150.9, 150.8, 147.8, 147.1, 140.4, 132.7, 128.8, 128.7, 128.0, 127.7, 126.0, 124.9, 124.6, 124.2, 124.1, 123.7, 122.4, 121.5, 93.7, 87.7, 54.4−51.8, 44.9, 44.5, 29.4, 21.5, 21.2, 18.7, 16.5.

Synthesis of Polymer 9b. According to the general procedure, 3-((5-phenyl-2-(pyridin-2-yl)thiazol-4-yl)oxy)propyl methacrylate (**8**, 35 mg, 0.093 mmol) was reacted to yield the product as orange solid (81 mg, 51%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.59 (br), 8.15−8.0 (br), 7.8−7.70 (br), 7.40−7.30 (br), 4.60 (br), 4.20 (br), 3.70−3.45 (br), 2.2−1.70 (br), 1.48−1.30 (br), 1.0 (br), 0.83 (br). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 178.1, 177.8, 176.9, 160.4, 158.7, 151.1, 149.3, 148.3, 137.1, 131.5, 128.9, 128.7, 126.9, 124.2, 123.1, 119.0, 114.7, 66.9, 65.8, 54.3−51.7, 44.8, 44.5, 18.7, 16.4, 15.2.

Synthesis of Polymer 9c. According to the general procedure, bis(4,4′-dimethyl-2,2′-bipyridine)-[11-(4-(5-((4-nitrophenyl)ethynyl)-pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)undecyl methacrylate]ruthenium-(II) hexafluorophosphate (**5**, 60 mg, 0.047 mmol) and 3-((5-phenyl-2-(pyridin-2-yl)thiazol-4-yl)oxy)propyl methacrylate (**8**, 35 mg, 0.093 mmol) were reacted to yield the product as red solid (42 mg, 36%). ^{1}H NMR

(CDCl$_3$, 300 MHz): δ = 8.58 (br), 8.30−7.90 (br), 7.85−7.30 (br), 7.20−7.0 (br), 4.51 (br), 4.15 (br), 3.55 (s), 2.50 (br), 1.92−1.70 (br), 1.34−1.24 (br), 1.0 (br), 0.83 (br). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 178.1, 177.8, 177.0, 151.1−150.0, 149.5, 137.0, 136.70, 136.24, 132.9, 131.6, 128.8−126.9, 124.3, 123.6, 118.9, 67.0, 54.4, 51.8, 44.9, 44.5, 29.7−28.5, 26.3, 26.0, 21.2, 18.7, 16.5.

■ ASSOCIATED CONTENT

Supporting Information. SEC traces of all polymers as well as UV/vis absorption and emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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