Light-Harvesting Polymers

Star-Shaped Light-Harvesting Polymers Incorporating an Energy Cascade**

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The photosynthetic apparatus of both photosynthetic bacteria and higher plants involves a reaction center surrounded by intricate arrays of pigments that form an energy gradient for efficient light collection.[1] Artificial systems that can mimic this remarkable natural process have attracted great interest. Among them, polymers used to simulate the process are known as "light-harvesting" or "antenna" polymers.[2] Owing

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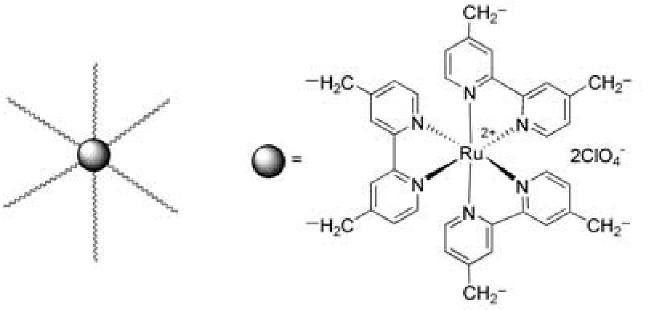
to their structural features, multiarmed star-shaped polymers are particularly attractive as artificial light-harvesting systems.[3] Compared with linear light-harvesting polymers, the condensed packing of chromophores around a central energy-trap core will lower the average donor–acceptor distance, thus leading to a faster rate and higher efficiency of energy transfer.[4] Star-shaped polymers with an encapsulated lumophore core may also have potential uses in molecular-scale optoelectronics, photonics, security devices, luminescence-based sensors, and other emerging areas of technology.[5] A tetrahedral starlike arrangement of chromophores has previously been shown to exhibit advantages for collection of diffuse light through exciton interactions.[6] Dendritic light-harvesting systems that exhibit cascade-energy-transfer behavior have also been reported recently.[7] However, the multistep syntheses required for such systems have so far limited their widespread application and there remains a need for simpler synthetic strategies to create light-harvesting arrays.

During the last two decades, controlled/living radical polymerization has emerged as one of the most effective synthetic routes to well-defined polymers.[8] Among them, reversible addition–fragmentation chain-transfer (RAFT) polymerization appears to be one of the most efficient and could potentially be applied to any classical radical system.[9] The RAFT process involves performing a conventional radical polymerization in the presence of certain thiocarbonylthio compounds (S=C(Z)-SR), so-called RAFT agents. Light-harvesting polymers with defined properties can be synthesized by RAFT polymerization with specially functionalized RAFT agents.[3,10] We report herein the synthesis by RAFT methods of well-defined star-shaped light-harvesting block copolymers that contain an energy cascade of chromophores from the periphery to the core.

Hexa(dithiobenzoate)-functionalized Ru^{II} tris(bipyridine) (Ru-hexa-RAFT) was synthesized as previously reported.[3] It was used to control the polymerization of a styrene-functionalized coumarin monomer (st-coumarin).[11] The resulting star-shaped polymer **1** has an average length of two st-coumarin repeat units in each arm. Polymer **1** was subsequently used as a macro-RAFT agent to control the polymerization of acenaphthylene to obtain the star-shaped diblock copolymer **2** with a narrow polydispersity and an average length of 36 acenaphthenyl repeat units in each arm. The ratio of the acenaphthenyl to coumarin chromophores in each arm of polymer **2** was designed to provide selective excitation of acenaphthenyl units of this polymer at 295 nm. To avoid the competing quenching effect of the dithiobenzoyl groups on excited chromophores observed previously,[3,10] a triblock copolymer, **3**, with an average length of 44 *N*-isopropylacrylamide (NIPAM) repeat units in each arm was similarly synthesized by using polymer **2** as the macro-RAFT agent and NIPAM monomer.

The numbers of st-coumarin, acenaphthenyl, and NIPAM repeating units in the polymers are calculated based on gravimetric determinations. These values agreed with compositions determined spectrophotometrically by comparing the absorption spectra of the polymers with the corresponding model compounds. The agreement obtained indicates that incorporating the chromophores in the polymer does not perturb their absorption spectra, that is, there is no evidence for ground-state electronic interactions between chromophores. This observation has also been reported in previous work on related polymers.[3,10] The composition of polymer **1** was also characterized by NMR spectroscopy. The block copolymers **2** and **3** displayed narrow molecular-weight distributions by gel permeation chromatography (GPC).



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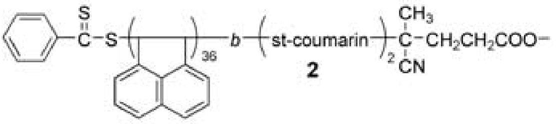

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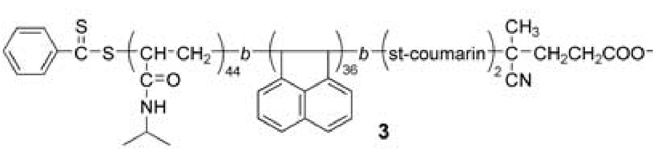

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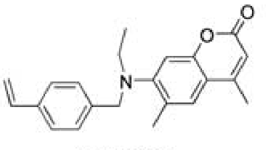
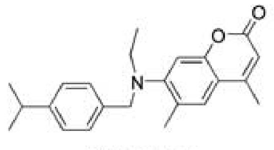
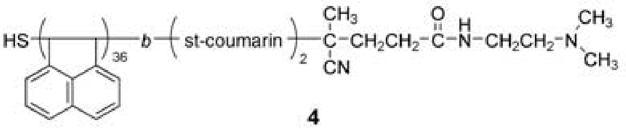


st-coumarin



IPB-coumarin



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To investigate the energy-transfer process between acenaphthenyl and coumarin units in the star-shaped polymers, a linear block copolymer, **4**, was synthesized through hydrolysis of the star-shaped diblock copolymer **2** with an amine.[12]

Acenaphthene, a 4-isopropylbenzyl-functionalized coumarin compound (IPB-coumarin), tris(bipyridine) Ru^{II} dichloride, and 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid[3] were selected as model compounds to characterize the electronic interaction between the photoexcited donor chromophore with the ground-state acceptor. Energy transfer between an electronically excited donor and ground-state acceptor is commonly described by the induced dipole–dipole (Förster) mechanism.[13] The strength of the electronic interaction is characterized by the Förster critical transfer distance determined from the spectroscopic and photophysical properties of the donor and acceptor and defined as the distance at which the rate of energy transfer equals the rate of other excited-state relaxation processes of the donor. Assuming an orientation factor (κ^2) equal to 2/3 (corresponding to a random distribution of transition dipole orientations), we calculated the Förster critical distances between these chromophores in degassed dichloromethane solutions as shown in Table 1.

Table 1: The Förster critical transfer distances (R_0 [Å]) between relevant chromophores in degassed dichloromethane solution.

	Acenaphthenyl	Coumarin	Ru^{II} complex	Dithiobenzoyl
acenaphthenyl	13.7	29.2	23.2	24.6
coumarin	29.2	13.0	39.7	16.0
Ru^{II} complex	23.2	39.7	NA	NA
dithiobenzoyl	24.6	16.0	NA	NA

The Förster critical transfer distance between acenaphthenyl and coumarin chromophores (29.2 Å) exceeds that for the acenaphthenyl and Ru^{II} complex moieties (23.2 Å). Owing to the polymer structure, the interchromophoric distance between acenaphthenyl and coumarin units can be expected to be smaller than that between the acenaphthenyl units and the Ru^{II} complex core in the star-shaped block copolymers. Thus, the rate of energy transfer from excited acenaphthenyl molecules to the coumarin units should be faster than that between the excited acenaphthenyl molecules and Ru^{II} complex cores, thus leading to a sequential energy-transfer process.

A comparison of the absorption and emission spectra from degassed dichloromethane solutions of the polymers is shown in Figure 1. Photoexcitation of acenaphthenyl units in the linear polymer **4** at 295 nm, in which absorption is almost exclusively (> 95 %) due to the acenaphthenyl donor, results in fluorescence being predominantly emitted from the coumarin acceptor at 440 nm. After the Ru^{II} core has been introduced into the star-shaped polymers, the coumarin emission is dramatically quenched, whereas significant emission from the Ru^{II} complex core is observed at 615 nm in polymers **2** and **3**. It should be noted that emission from the star-shaped polymers at 415 nm arises largely from acenaphthenyl excimers.[14] Figure 1 also shows that removal of the competing quenching effect of the dithiobenzoyl end groups in the triblock copolymer **3** increases the efficiency of the energy transfer from acenaphthenyl units to the Ru^{II} moieties.

The excitation spectrum of **4**, monitored at 435 nm, contains a major contribution attributable to acenaphthenyl chromophore absorption at 295 nm, which confirms that energy transfer occurs. By comparing the excitation spectrum with the normalized absorption spectrum,[15] the efficiency of energy transfer from the acenaphthenyl to coumarin units in this linear polymer was determined to be 67 %.

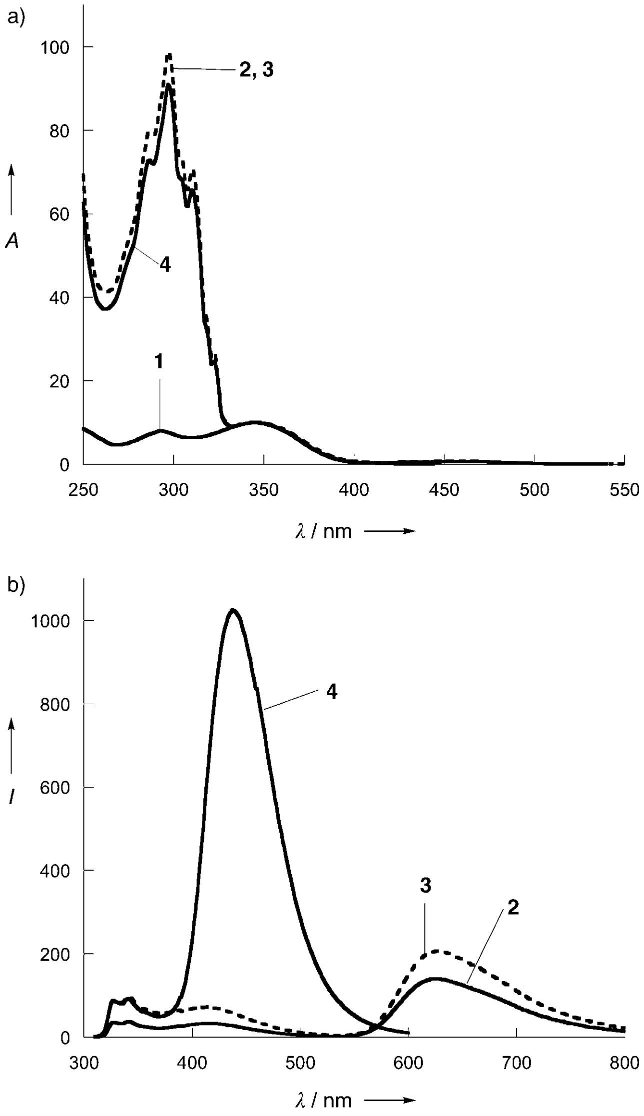

Figure 1. a) Absorption (normalized at $\lambda = 350$ nm) and b) luminescence spectra of polymers **1**–**4** in dichloromethane. For luminescence measurements, all degassed solutions have the same absorbance at the excitation wavelength of 295 nm. Fluorescence in **1** is totally quenched by the adjacent dithiobenzoyl end group.

When the Ru^{II} complex emission is monitored at 615 nm, the excitation spectra of **2** and **3** exhibit major contributions due to the absorption of coumarin chromophores at 345 nm and acenaphthenyl chromophores at 295 nm. The efficiencies of energy transfer from coumarin units to the Ru^{II} complex core, determined as described above, in both star-shaped polymers are 90 %. This is a consequence of the relatively large R_0 (39.7 Å) and short donor-to-acceptor separations. The efficiencies from acenaphthenyl to the Ru^{II} complex core in polymers **2** and **3** are 47 % and 62 %, respectively. The higher efficiency in **3** relative to **2** is the result of a decrease in the competing dithiobenzoyl quenching effect that results from insertion of the photo-inactive NIPAM spacers in the triblock copolymer.

The excited acenaphthenyl units can conceivably pass their excitation energy to the Ru^{II} complex core either in a stepwise cascade fashion through coumarin sequences or by a direct one-step energy-transfer process. In the present case, we believe that the former path is favored for the following reason: Energy transfer between excited acenaphthenyl and coumarin units is kinetically favored as a result of the larger

Förster critical distance and shorter interchromophoric distance in comparison with those of excited acenaphthenyl units and the Ru^{II} core. This conclusion is also supported by the measured energy-transfer efficiencies. The efficiency of energy transfer from the acenaphthenyl to coumarin units is 67 % in the linear model polymer, **4**. The transfer efficiency from coumarin units to the Ru^{II} core is 90 %. Hence, the theoretical efficiency for the overall energy-transfer process from acenaphthenyl to the Ru^{II} complex through a cascade route in **3** can be expected to be 60 % (i.e., 67 × 90 %), which agrees well with the measured value, 62 %. The sequence of the energy-transfer processes is depicted schematically in Figure 2.

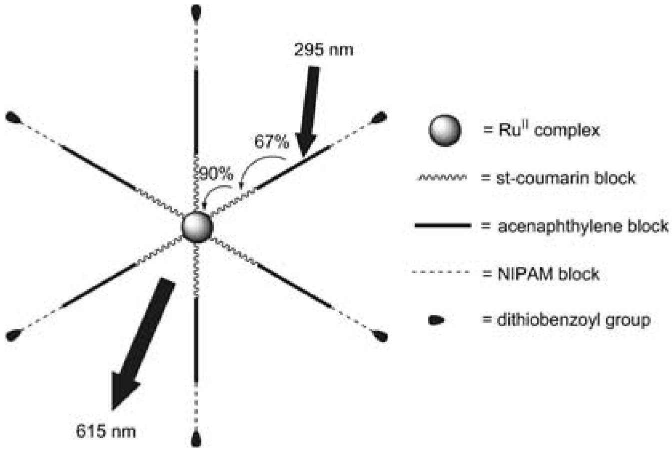

Figure 2. Schematic representation of the energy-transfer processes within the star-shaped block copolymer **3**.

In conclusion, star-shaped block copolymers have been synthesized to obtain light-harvesting systems with an energy gradient from the periphery to the core. Photophysical data suggest that the transfer of excitation energy in the block copolymers occurs mainly through a stepwise energy cascade from the initially excited acenaphthenyl units to the coumarin chromophores and hence to the Ru^{II} complex core.

Experimental Section

Solutions for luminescence measurements were degassed by multiple freeze–pump–thaw cycles at $\approx 10^{-6}$ torr. Emission and excitation spectra were recorded on a Varian Cary Eclipse fluorometer and were corrected for the wavelength dependence of the sensitivity of the detector and the output of the excitation light source by using a calibrated standard lamp source. Molecular-weight determinations were performed in THF at 25 °C with a Waters GPC instrument with a refractive-index detector. Molecular weights are reported as linear polystyrene equivalents.

IPB-coumarin: A mixture of coumarin-2 (0.20 g, 0.92 mmol; Exciton, laser grade), 4-ispropyl benzyl chloride (0.17 g, 1.01 mmol), K_2CO_3 (0.38 g, 2.67 mmol), KI (0.05 g, 0.28 mmol) in CH_3CN (10 mL) was stirred under nitrogen at 85 °C for 24 h. Purification was performed with column chromatography on silica gel (Kieselgel-60, 70–230 mesh) with a mixture of ethyl acetate and *n*-hexane in a ratio of 1:4 as eluent. Yield: 0.25 g, 78 %. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 1.03 (t, 3H, $J = 6.94$ Hz), 1.21 (s, 3H), 1.24 (s, 3H), 2.37 (b, 3H), 2.41 (b, 3H), 2.87 (m, 1H), 3.05 (q, 2H, $J = 6.94$, 14.25 Hz), 4.16 (s, 2H), 6.11 (b, 1H), 6.92(s, 1H), 7.10–7.26(m, 4H), 7.35 ppm (s, 1H). UV/Vis (DCM): λ_{max} ($\log\varepsilon$): 347 (4.16).

1: A mixture of Ru-hexa-RAFT[3] (30 mg, 11.9 μmol), 2,2′-azobis(isobutyronitrile) (AIBN; 0.5 mg, 3.7 μmol), st-coumarin (477 mg, 1.43 mmol) and solvent (1 mL, acetonitrile/chlorobenzene = 1:2, *v*/*v*) was degassed through three freeze–pump–thaw cycles, sealed under vacuum, and heated at 70 °C for 8 h. The polymer was purified by precipitation into MeOH (20 mL). Yield: 78 mg (10 %). $\bar{M}_n$ (by calculation) = 6500; $\bar{M}_n$ (by ^{1}H NMR spectroscopy) = 6200; $\bar{M}_n$ (by UV/Vis spectroscopy) = 6500; $\bar{M}_n$ is the number-average molecular weight.

2: Polymer **2** was prepared from polymer **1** (17 mg, 2.6 μmol equivalent Ru-hexa-RAFT), AIBN (0.5 mg, 3.7 μmol), acenaphthylene (474 mg, 3.12 mmol) and chlorobenzene (1 mL) at 70 °C for 16 h. Yield: 120 mg (18 %). $\bar{M}_n$ (by calculation) = 39300; $\bar{M}_n$ (by UV/Vis) = 43000; $\bar{M}_n$ (by GPC) = 5300, $\bar{M}_w/\bar{M}_n$ (by GPC) = 1.13; $\bar{M}_w$ is the weight-average molecular weight.

3: Polymer **3** was prepared from polymer **2** (40 mg, 0.9 μmol equivalent Ru-hexa-RAFT), AIBN (0.5 mg, 3.7 μmol), NIPAM (49 mg, 432 mmol) and solvent (1 mL, acetonitrile/chlorobenzene = 1:1, *v*/*v*) at 70 °C for 16 h. Yield: 67 mg (55 %). $\bar{M}_n$ (by calculation) = 69100; $\bar{M}_n$ (by GPC) = 3700, $\bar{M}_w/\bar{M}_n$ (by GPC) = 1.16.[16]

4: Polymer **4** was prepared from the hydrolysis of polymer **2** (40 mg) by using *N*,*N*-dimethylethylenediamine (0.5 mL) in chlorobenzene (1 mL) under nitrogen. Yield: 30 mg (75 %). $\bar{M}_n$ (by calculation) = 6100; $\bar{M}_n$ (by GPC) = 7100, $\bar{M}_w$/ $\bar{M}_n$ (by GPC) = 1.21.

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