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Communication
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Light harvesting and energy transfer in a ruthenium–coumarin-2 copolymer†

Xavier Schultze, Jason Serin, Alex Adronov and Jean M. J. Fréchet*

University of California, Berkeley, CA 94720-1460, USA. E-mail: frechet@cchem.berkeley.edu; Fax: +1(510) 643-3079; Tel: +1(510) 643-3077

Received (in Cambridge, UK) 26th April 2001, Accepted 15th May 2001
First published as an Advance Article on the web 7th June 2001

Copolymers containing Ru(bpy)$_3$ and coumarin-2 chromophores prepared using both grafting and copolymerization approaches exhibit Förster-type energy-transfer efficiencies ranging from 70% to above 98%.

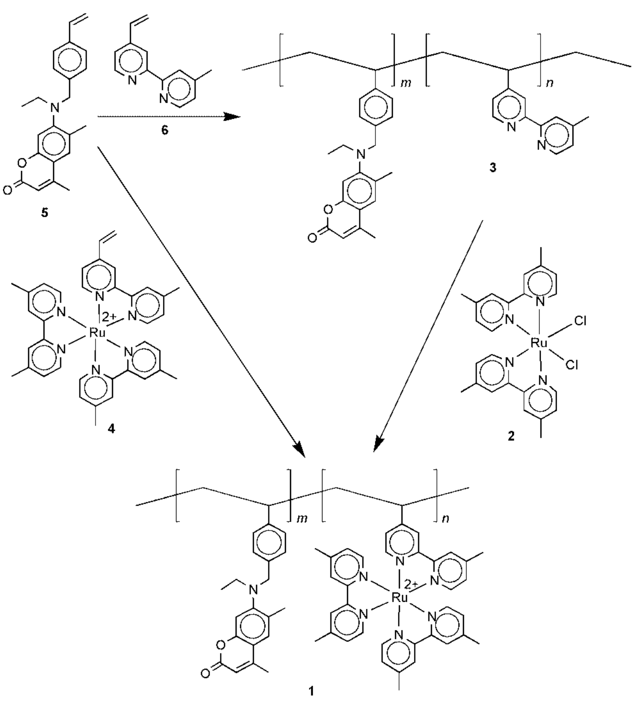
Molecular assemblies capable of harvesting light and transforming the absorbed energy have attracted great interest in recent years because of their applicability in such domains as light emitting diodes, fluorescent labeling of biological molecules, and photonic devices.[1] We have recently described several dendritic systems containing light-harvesting dyes at the periphery that efficiently absorb and channel light to a different dye at the focal point by a Förster-type mechanism.[2] Although these systems exhibit extremely high energy-transfer efficiencies, the demanding multi-step synthesis required for their preparation may limit their use to speciality applications. To circumvent this limitation, we have explored analogous light-harvesting linear polymers in which the donor–acceptor ratios were optimized by mimicking the dendrimer models and found that their antenna properties,[3] although less impressive than those of the corresponding dendrimers, are nevertheless very good.

Ruthenium-containing macromolecules are attracting widespread interest due to their photochemical and electrochemical properties.[4,5] We now report our results concerning the synthesis and characterization of a linear Ru(bpy)$_3$–coumarin-2 copolymer (**1**) that exhibits the energy transfer efficiency generally observed with light harvesting dendrimers,[5] without requiring the multi-step synthesis involved in the design of these molecules. Two strategies were used (Scheme 1): (i) grafting the ruthenium complex **2** on a bipyridine–coumarin-2 functionalized copolymer (**3**), and (ii) copolymerization of a ruthenium functionalized monomer (**4**) with a coumarin-2 functionalized monomer (**5**). The first route enabled us to obtain a copolymer that exhibits an energy transfer efficiency of 70% between the coumarin-2 and the Ru(bpy)$_3$ units. More interestingly, the copolymerization route afforded a better performing copolymer that displays quantitative energy transfer efficiency.

The styrene functionalized coumarin-2 monomer (**5**) was synthesized by coupling coumarin-2 with vinyl benzyl chloride as described elsewhere.[3] The 4-vinyl-4′-methylbipyridine monomer (**6**) was obtained using a modified literature procedure.[6] Copolymerization of these two monomers using a 3 to 1 feed ratio (mol fraction of **5** = 0.75) was carried out at 90 °C with AIBN as the initiator in a minimum amount of dichlorobenzene. The polymer was precipitated twice into Et$_2$O to remove the unreacted monomers. Molecular weights ranging from 5000 to 15 000 Daltons were obtained along with a polydispersity of 1.6, typical of AIBN initiated polymerizations. Elemental analysis of copolymer **3** showed that the resulting polymer was composed of *ca.* 25% of the bipyridine monomer and 75% of the coumarin-2 monomer, as expected from the feed ratio.

To perform grafting of the ruthenium complex, we used the method reported by Fraser and co-workers.[7] Two equiv. of dichloride **2** were refluxed in MeOH in the presence of an excess of AgPF$_6$ for 12 h and the solution was then added to a suspension of copolymer **3** in dimethoxyethane. After 48 h at reflux, the reaction mixture was filtered, concentrated, redissolved in dichloromethane and extensively washed with water to remove any unreacted ruthenium complex. A dark red polymer was obtained after precipitation in Et$_2$O.

The UV spectra of the polymer before and after the grafting reaction with ruthenium complex **2** are given in Fig. 1. The starting polymer displays two strong absorption bands at 290 and 350 nm, which are characteristic of the coumarin-2 and the bipyridine units. After reaction with the ruthenium complex a new absorption band was observed at 465 nm, which indicates successful grafting of the ruthenium bis(bipyridine) onto the



Scheme 1

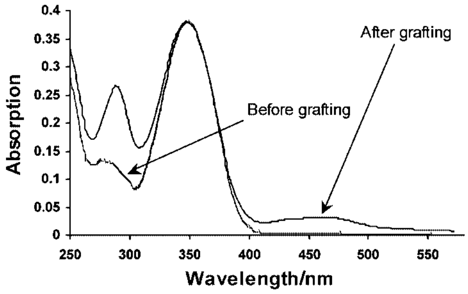


Fig. 1 Normalized UV-Vis spectra of copolymer **3** before and after grafting.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b1/b103792g/

DOI: 10.1039/b103792g

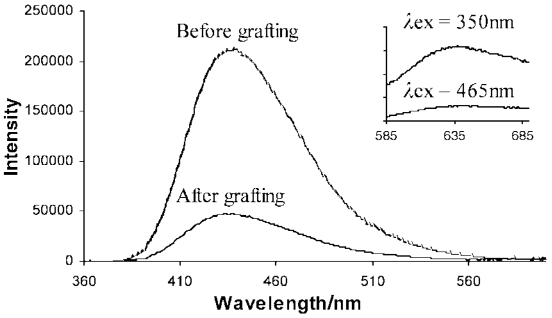

Fig. 2 Fluorescence spectrum of copolymer **3**, in the region of coumarin-2 emission, before and after grafting. Inset shows the spectrum of the same copolymer in the region where the Ru(bpy)$_3$ acceptor complex emits.

polymer. The absorption band at 290 nm is further increased due to the two additional bipyridine ligands introduced by the reaction. Fluorescence resonance energy transfer studies were carried out to determine the efficiency of energy transfer from the coumarin-2 chromophore to the ruthenium complex. The efficiency was calculated by comparing the coumarin-2 emission in the starting polymer **3** (a donor model compound) to the emission of this dye in the polymer obtained after grafting of ruthenium (Fig. 2). Based on the quenching of this emission, an energy transfer efficiency of 70% was determined for the grafted copolymer. Additionally, a 5-fold increase of the ruthenium emission was observed upon excitation of the coumarin-2 units (λ_{ex} = 350 nm) over excitation of the ruthenium complex directly (λ_{ex} = 465 nm), this type of amplification is the direct result of energy transfer (Fig. 2, inset).

Although the grafting route enabled us to obtain a polymer displaying good energy transfer characteristics, the functionalization of the polymer, estimated from the relative UV-Vis absorbance of the coumarin-2 and Ru(bpy)$_3$ units, was not quantitative (*ca.* 30%) and some insoluble material was also formed, decreasing the polymer yield. Therefore the copolymerization of monomers **4** and **5** was studied. The ruthenium-containing monomer **4** was prepared using a modified literature procedure.[8] Polymerization of the monomers was then performed at 90 °C with AIBN in DMF (mol fraction of **5** = 0.75). The resulting polymer was purified by precipitation in Et$_2$O and extensive washing with MeOH. The UV-visible spectrum of the polymer showed that incorporation of the ruthenium monomer **4** was as expected from the feed ratio, *ca.* 25%, with the remainder of the polymer repeat units consisting of the coumarin-containing monomer **5,** therefore the copolymerization route is much more effective for the introduction of the Ru(bpy)$_3$ complex than the grafting reaction.

The absorption spectrum of the copolymer (Fig. 3) is similar to that of the material obtained by the grafting route except that it displays stronger bipyridine and ruthenium metal to ligand charge transfer bands at 290 and 465 nm. Excitation of this polymer at 350 nm results in an emission spectrum (Fig. 4) that is totally quenched at 440 nm (the coumarin emission), indicating that quantitative energy transfer between the coumarin-2 and the Ru(bpy)$_3$ units occurs in this copolymer. Furthermore, the intensity of the ruthenium emission at 630 nm is increased by a factor of 2.7 when the polymer is illuminated at 350 nm *vs.* 465 nm. This increase is lower than that observed for the grafted copolymer, again indicating that, as a result of incomplete grafting, a higher concentration of donors relative to acceptors was present in that case.

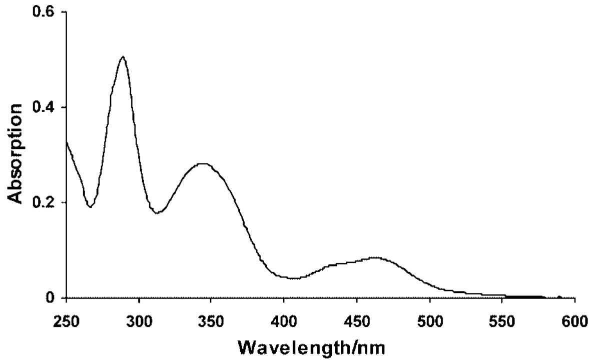

Fig. 3 UV spectrum of polymer **1**, obtained by the copolymerization route.

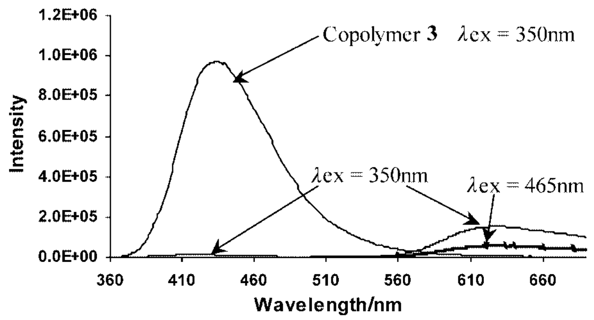

Fig. 4 Fluorescence spectrum of polymer **1**, obtained by the copolymerization route.

In conclusion, readily accessible linear copolymers containing coumarin-2 and Ru(bpy)$_3$ units can provide quantitative energy transfer from the coumarin-2 units to the ruthenium centers. This finding opens interesting perspectives in the field of solar energy conversion.[9] The application of such a system to photovoltaic devices is currently under investigation.

Financial support of this research by the AFOSR (F-49620-01) and the U. S. Department of Energy (# DE-AC03-76SF00098). Fellowship support from the Eastman Kodak Company is also gratefully acknowledged (A. A).

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