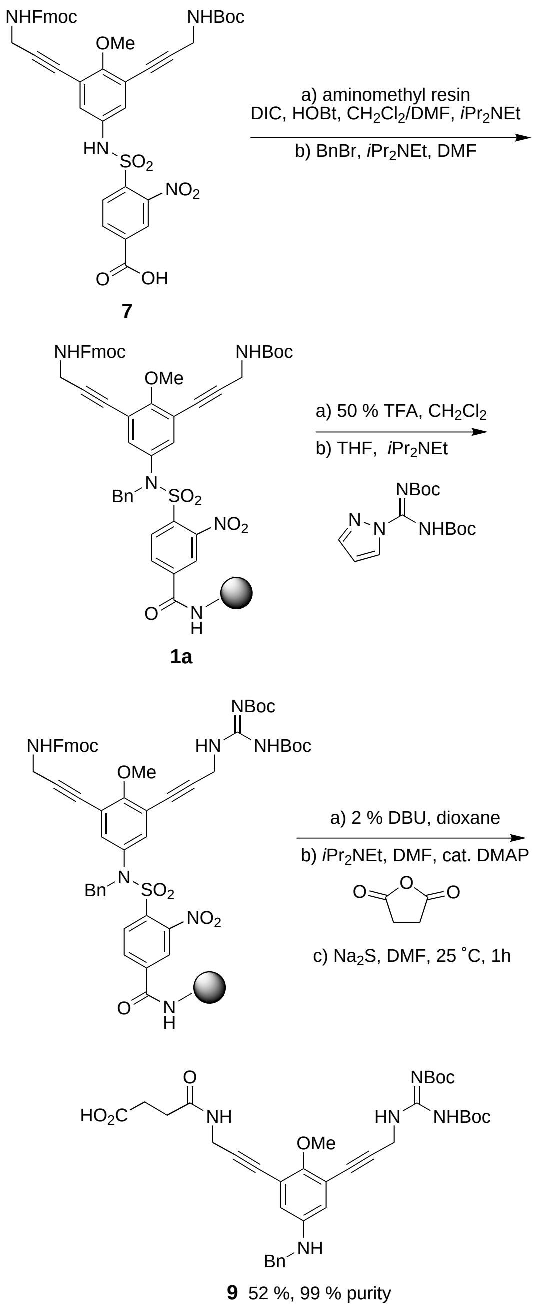

Scheme 2. Attachment of **7** to the resin, N-alkylation, and functionalization of the linker scaffold **1a**. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DIC = diisopropylcarbodiimide; DMAP = 4-dimethylaminopyridine; HOBt = 1-hydroxy-1*H*-benzotriazole; TFA = trifluoroacetic acid.

cleavage of the linker fragment. Only one compound **9** (Table 1) is shown in Scheme 2, but a small library of homo- and heterodimeric ureas, pyridinium salts, carboxylic acids, and guanidines has been prepared. Full details of this library synthesis will be submitted shortly in the full account of this work.

The specific design of the linker scaffold **1** is special because it is the first to be produced to address the problem of making libraries of pharmacophores to mimic or disrupt protein–protein interactions. The most relevant prior research in this area involves scaffolds that do not have custom-made cleavable linkers, but have either flexible amines[8–10] or carbohydrate scaffolds.[11, 12] Many other linker scaffold systems using other skeletons attached to orthogonally cleavable linking groups could be envisaged. Indeed, slight modifications of the approaches presented here could be used to produce systems with longer or shorter arms, and more or less rigidity. It is likely that this type of work will evolve into an important area of solid-phase synthesis.

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First Generation Light-Harvesting Dendrimers with a $[Ru(bpy)_3]^{2+}$ Core and Aryl Ether Ligands Functionalized with Coumarin 450

Xiaoli Zhou, Daniel S. Tyson, and Felix N. Castellano*

Dendritic macromolecules are well defined, treelike structures that are typically prepared by a series of repetitive synthetic steps.[1–3] Dendrimer chemistry continues to rapidly develop as a field, since dendritic molecules are both fundamentally interesting and have many potential applications. Of particular interest are dendrimers that can be fabricated to control patterns of energy migration throughout the structure, enabling efficient light harvesting.[4, 5] Dendritic molecules constructed around Ru^{II} polypyridyl complexes that display metal-to-ligand charge transfer (MLCT) excited

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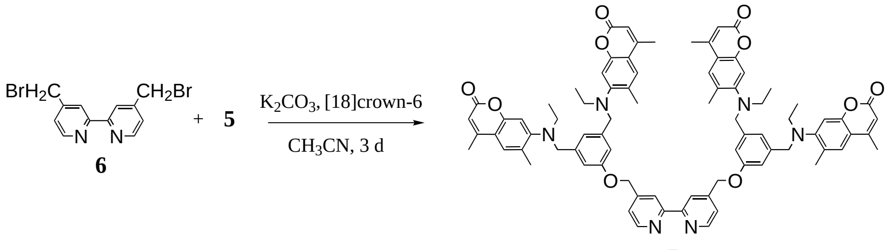
states are especially intriguing because of their outstanding photochemical, photophysical, and electrochemical properties.[6] In this regard, many large polynuclear dendritic arrays of MLCT complexes have been synthesized and their photophysical and electrochemical properties generally display novel characteristics.[7] Very recently, it has been reported that a single $[\mathrm{Ru(bpy)_3}]^{2+}$ core (bpy = 2,2′-bipyridine) can be tethered to a well defined array of benzyl, 4′-*tert*-butylphenyloxy, or naphthyl peripheral units.[8, 9] The dendritic wedges employed in these studies have been shown to improve the luminescence properties of the metal complex and can modulate the rate of intermolecular electron transfer reactions from the $[\mathrm{Ru(bpy)_3}]^{2+}$ core.[8, 9]

In addition to metal-containing photoactive dendrimers, there have been marked advances in the development of purely organic light-harvesting dendrimers.[4, 5, 10] In the latter, light is primarily absorbed by the peripheral antenna units (energy transfer donors) and is transferred rapidly and efficiently to a single fluorescent moiety, whose emission is sensitized. A recent strategy using long-range Förster-type resonance energy transfer[11] has been shown to funnel the photonic energy to the final acceptor, independent of the dendritic architecture.[10] Molecules based on dendritic architectures permit large cross-sections for photon collection, a feature particularly suited to light-harvesting purposes.

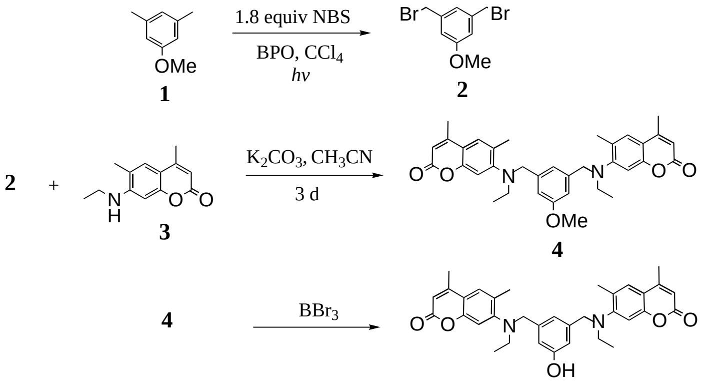
Continuing our efforts in the field of hybrid organic/inorganic light-harvesting systems based on long-range resonance energy transfer,[12] we report the synthesis and photophysical characterization of a new bipyridine ligand, bpy-$(\mathrm{C\text{-}450})_4$, which carries a first-generation poly(aryl ether) dendritic wedge containing coumarin 450 (C-450) units in the 4,4′-positions, and two associated $\mathrm{Ru^{II}}$ complexes, $[\mathrm{Ru(bpy)_2\{bpy(C\text{-}450)_4\}}]^{2+}$ and $[\mathrm{Ru\{bpy(C\text{-}450)_4\}_3}]^{2+}$, which possess four and twelve C-450 peripherial units, respectively. The singlet C-450 fluorescence substantially overlaps the absorption spectrum of the $[\mathrm{Ru(bpy)_3}]^{2+}$ core (Förster distance $R_0 = 41.2$ Å in $\mathrm{CH_3CN}$, assuming an orientation factor $\kappa^2 = 2/3$); such conditions are favorable for Förster-type singlet–singlet resonance energy transfer. Importantly, the C-450 fluorescence displays a large Stokes shift which lowers the probability for self-quenching by energy transfer between the donors.[13] Excitation of the C-450 antennae initiates nonradiative energy transfer to the central $[\mathrm{Ru(bpy)_3}]^{2+}$ complex, which then displays its characteristic long lifetime, sensitized photoluminescence. This hybrid architecture harvests near-visible light and converts the blue nanosecond C-450 fluorescence to an orange, long lifetime MLCT-based emission.



7
bpy(C-450)$_4$

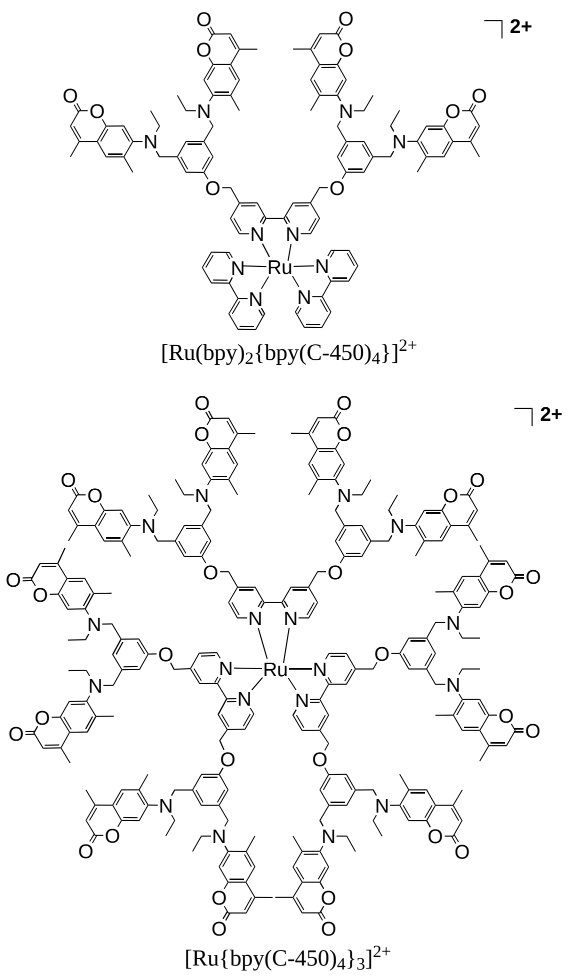
(1)

The synthesis of the dendritic wedge was modeled after the “reversed” convergent growth of laser dye-labeled poly(aryl ether) dendrimers developed by Fréchet and co-workers, Scheme 1.[10] Compound **5** represents a first generation dendritic wedge and contains two peripheral C-450 chromophores. Equation 1 presents the one-pot synthesis of bpy-$(\mathrm{C\text{-}450})_4$ prepared from the dye-labeled phenol **5** and 4,4′-bis(bromomethyl)-2,2′-bipyridine. This step doubles the number of peripheral C-450 chromophores to four. The dendritic metal-organic light harvesting complexes, $[\mathrm{Ru(bpy)_2\{bpy(C\text{-}450)_4\}}]^{2+}$ and $[\mathrm{Ru\{bpy(C\text{-}450)_4\}_3}]^{2+}$, are shown in Scheme 2. Both metal complexes were prepared according to standard procedures and purified by gel filtration chromatography on Sephadex LH-20. Analytically pure samples were obtained using reversed-phase HPLC. Since two monomer wedges are covalently attached to a single diimine ligand, and three such diimine ligands are converged onto a single $\mathrm{Ru^{II}}$ metal center in $[\mathrm{Ru\{bpy(C\text{-}450)_4\}_3}]^{2+}$, the number of peripheral organic chromophores using the above hybrid design obey the growth model 6×2^n, where n is the generation number of the wedge. Molecular modeling of $[\mathrm{Ru\{bpy(C\text{-}450)_4\}_3}]^{2+}$ using a Merck force field (MMFF94, Spartan 5.0) shows that the donor–acceptor distances range from 7.7 to 16.4 Å, well within the Förster distance.



Scheme 1. Synthesis of the C-450 dye-labeled dendritic wedge. **5**

Figure 1 displays the absorption and uncorrected emission spectra of $[\mathrm{Ru(bpy)_2\{bpy(C\text{-}450)_4\}}]^{2+}$ and $[\mathrm{Ru\{bpy(C\text{-}450)_4\}_3}]^{2+}$ in $\mathrm{CH_3CN}$. The electronic spectra for each complex contains typical $[\mathrm{Ru(bpy)_3}]^{2+}$ visible absorption bands at 460 nm with extinction coefficients of 14200 and 15100 $\mathrm{M^{-1}\,cm^{-1}}$ for $[\mathrm{Ru(bpy)_2\{bpy(C\text{-}450)_4\}}]^{2+}$ and $[\mathrm{Ru\{bpy(C\text{-}450)_4\}_3}]^{2+}$, respectively. In both complexes, the C-450 units are largely responsible for the broad absorption band centered at 343 nm. The molar extinction coefficients at 343 nm increase from ~8000 $\mathrm{M^{-1}\,cm^{-1}}$ for $[\mathrm{Ru(bpy)_3}]^{2+}$,



$[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$

$[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$

Scheme 2. Stuctures of the first generation metal–organic light-harvesting dendrimers.

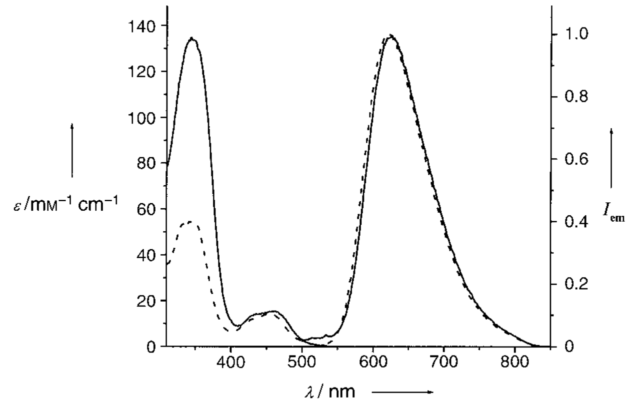


Figure 1. Absorption (left side) and uncorrected emission (right side) spectra of $[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$ (----) and $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ (——) in CH_3CN at 20 °C.

to 53200 $\text{M}^{-1}\text{cm}^{-1}$ for $[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$, and 136000 $\text{M}^{-1}\text{cm}^{-1}$ for $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$. The C-450 chromophores account for 85 % and 94 % of the light absorbed at 343 nm in $[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$ and $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$, respectively. Since the lowest energy C-450 absorption bands are well removed from the $[Ru(bpy)_3]^{2+}$ transitions, good photoselectivity in this wavelength region can be achieved. The enhanced absorption cross-sections between 300 and 380 nm from the C-450 chromophores provide an antenna system for the efficient harvesting of near-visible light. Excitation at wavelengths between 300 and 550 nm results in the observation of $[Ru(bpy)_3]^{2+}$ MLCT-based emission centered near 620 nm in both light-harvesting complexes (Figure 1).

The absorption and corrected excitation spectra of $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ in CH_3CN are presented in Figure 2. For brevity, $[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$ is omitted from this discussion, however, the experimental results are similar to that observed with $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$. The absorption and corrected excitation spectra of $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ are nearly superimposible at all wavelengths between 310 and 550 nm, which suggests an energy transfer efficiency close to unity. By directly comparing the magnitude of the absorption and corrected excitation spectra,[5, 10, 12] the energy transfer efficiency of $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ was determined to be ~95 ± 10 %. We realize that this is a crude estimate of the energy transfer efficiency and further experimentation is required to obtain a more reliable value. In addition, there is always a minor amount of residual C-450 fluorescence (Figure 3) which is present in all analytically pure samples, suggesting that the transfer efficiency is less than unity.

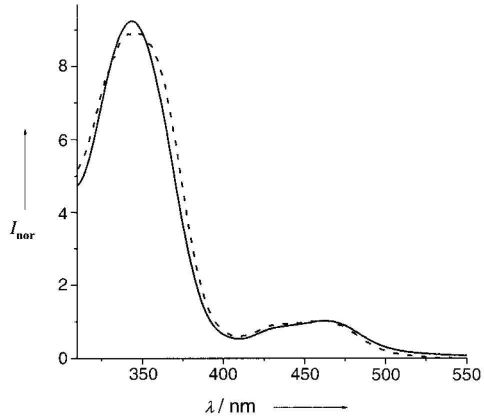


Figure 2. Absorption (——) and corrected excitation (----) spectra of $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ in CH_3CN normalized at 460 nm. The excitation spectrum was detected at 610 nm.

The luminescence quantum yields of $[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$ and $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$, measured in deaerated CH_3CN, are very similar to that observed for the "naked" $[Ru(bpy)_3]^{2+}$ complex, within experimental error (Table 1). The presence of four or twelve C-450 units tethered to the $[Ru(bpy)_3]^{2+}$ core through poly(aryl ether) spacers does not appear to provide any additional nonradiative decay pathways which could potentially shorten the MLCT excited states.

Complete spectroscopic and photophysical data for the compounds in this study are presented in Table 1. Using our N_2 pumped dye laser apparatus (instrument response function (IRF) = 15 ns), the excited state lifetimes of $[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$ and $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ measured at 610 nm in deaerated CH_3CN are 1.00 ± 0.05 and 1.04 ± 0.05 μs, respectively, and follow single exponential decays, regardless

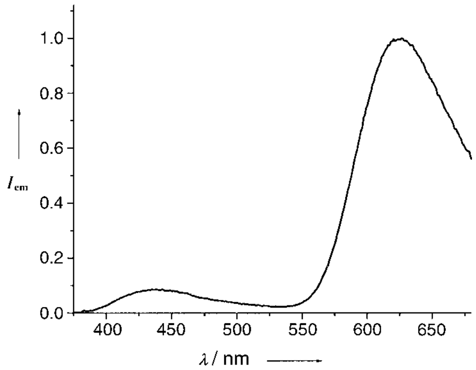


Figure 3. Uncorrected emission spectrum of $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ in CH_3CN, excited at 343 nm.

of excitation wavelength (350–480 nm). These values resemble that observed for $[Ru(bpy)_3]^{2+}$ in deaerated CH_3CN as measured in our laboratory ($\tau = 920 \pm 50$ ns). However, air-equilibrated solutions of the same complexes are quite different. For example, $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ displays the longest excited state lifetime, which can be most likely attributed to shielding of the $[Ru(bpy)_3]^{2+}$ core by the dendrimer branches, hindering the access of dioxygen. This effect has been previously observed in related dendritic metal complexes and it should be noted that the extent of shielding generally increases with increasing dendrimer generation.[8, 9] $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$, a first generation dendrimer, displays similar sensitivity to dioxygen as a second generation Ru^{II} core dendrimer that contains 24 peripheral benzyl units, suggesting that higher generations of the C-450 labeled molecules may provide more complete shielding of the metal core in fewer generations. We would like to note that $[Ru(bpy)_3]^{2+}$ is not necessarily the perfect model of the dendrimer core, therefore the lifetimes contrasted in aerated solution should be viewed with caution.

In an attempt to estimate the rate of singlet energy transfer, time-correlated single-photon counting measurements were employed. With 343 nm pulsed excitation from a H_2 lamp, no measurable rise time was observed for the MLCT-based emission at 620 nm, indicating that the rate is rapid, $> 10^9\,s^{-1}$. However, we do observe some residual coumarin emission with complex kinetic behavior. At present, we are unable to resolve these components due to the time resolution limits of our single photon counting experiment.

Light-harvesting systems based on hybrid organic/inorganic designs may be applicable to single molecule spectroscopy.[14] The MLCT-based orange emission of nanomolar concentrations of $[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$ (in CH_3CN) can be detected with the naked eye in a darkened room with 4 Watt long-wave black-light excitation. For this first generation light-harvesting system, the sensitized $[Ru(bpy)_3]^{2+}$-based emission can be detected to a 250 femtomolar concentration using a conventional single photon counting fluorimeter. Lower detection limits may be achieved by utilizing higher generation (2nd and 3rd) laser-dye labeled dendrimers. Alternatively, detection limits in the present system could be markedly improved by using a pulsed laser excitation source in conjunction with gated detection, as routinely employed in time-resolved luminescence-based immunoassays.[15]

The present dendritic hybrid light-harvesting system exhibits a high quantum yield sensitized emission with a ~275 nm (~13025 cm^{-1}) Stokes shift (relative to C-450 excitation) that has a single exponential decay and a long lifetime. Due to the increased absorption coefficients and high efficiency of energy transfer, excitation of the C-450 units yielded substantially more MLCT-based emission than was observed from direct excitation of the inorganic core. The well defined, highly soluble structures permitted exact analytical characterization of the macromolecules. This hybrid design permits the attachment of more peripheral chromophores in fewer generations than is possible with a pure organic structure. In the current system, the Ru^{II} MLCT core is somewhat protected from dioxygen quenching in the first generation, suggesting that higher generations will provide a larger degree of shielding and allow their use under ambient conditions. The long lifetimes associated with these new structures permit bimolecular solution chemistry commonly associated with $[Ru(bpy)_3]^{2+}$, such as electron transfer reactions.[6, 9] The current approach could potentially be extended to other donor–acceptor organic–inorganic pairs to harvest visible light and exhibit sensitized long lifetime emission in the red to near IR range.

The development of photochemically stable light-harvesting complexes that possess long excited state lifetimes is important for the analytical applications of fluorescence spectroscopy, such as lifetime-based chemical sensing.[16] In addition, long lifetime extrinsic luminescence probes with large absorption cross-sections have potential applications in biological systems where low analyte concentrations require

Table 1. Spectroscopic and photophysical data at room temperature in CH_3CN.

Complex	λ_{max} (ε) [nm] ([$M^{-1}cm^{-1}$])	$\lambda_{em\,max}$ [nm]	τ_{em}[a] (deaerated) [μs]	τ_{em}[a] (air equil.) [ns]	Φ_r[b]	Energy transfer efficiency [%]
$[Ru(bpy)_3]^{2+}$	452 (13000)	615	0.920 ± 0.05	165 ± 15	0.062 ± 0.006	NA
$[Ru(bpy)_2\{bpy(C\text{-}450)_4\}]^{2+}$	343 (53200), 455 (14200)	621	1.00 ± 0.05	277 ± 15	0.071 ± 0.007	96 ± 10
$[Ru\{bpy(C\text{-}450)_4\}_3]^{2+}$	343 (136000), 462 (15100)	625	1.04 ± 0.05	306 ± 15	0.073 ± 0.007	95 ± 10
$bpy(C\text{-}450)_4$	343 (39000)	450	NA	3.9 ± 0.2[c](75%) 1.6 ± 0.1 (25%)	NA	NA

[a] Lifetimes represent an average of at least six measurements with an uncertainty of less than 5%. Here, the data were obtained using excitation at 458 ± 2 nm. [b] Errors represent reproducibility within 2σ, including the uncertainty in the measurement of the standard. [c] Measured by time-correlated single photon counting (TCSPC) with excitation at 343 nm. Decays were complex and two lifetimes were observed. Numbers in parenthesis indicate relative amplitudes of each decay component.

detection. Such long-lived luminophores are amenable to situations where off gating can be used to suppress autofluorescence in biological systems or scattered light in opaque samples.

Experimental Section

All manipulations were performed under an inert and dry argon atmosphere using standard techniques. 4,6-Dimethyl-7-ethylaminocoumarin (Coumarin 2 or Coumarin 450), 3,5-dimethylanisole, 4,4′-dimethyl-2,2′-bipyridine, anhydrous THF, and anhydrous CH_2Cl_2 were purchased and used as received. Potassium carbonate was ground and dried in an oven (140 °C) at least 12 h before use. Acetonitrile was dried over CaH_2 and 4 Å molecular sieves and distilled from CaH_2 immediately before use. Diisopropylamine was also distilled from CaH_2 immediately before use. Water was deionized with a Barnstead E-Pure system. $[Ru(bpy)_2]Cl_2 \cdot 2H_2O$[17] and $[Ru(DMSO)_4]Cl_2$[18] were prepared according to published procedures. 3,5-Bis(*N*-(4,6-dimethyl-7-ethylaminocoumarin)methyl)phenol, **5**, was synthesized as described.[10] Commercially available $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (Aldrich) was converted into the corresponding PF_6^- salt by metathesis with NH_4PF_6 (Aldrich) in water. Reversed-phase HPLC (C18, semi-preparative) was performed with a Waters HPLC system equipped with a diode array absorption detector.

^1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) spectrometer. All chemical shifts are referenced to residual solvent signals previously referenced to TMS. Direct insertion probe (DIP) mass spectra were obtained in-house using a Shimadzu GC-MS QP5050A equipped with a QP5000 direct sample inlet device. Fast atom bombardment (FAB) mass spectra were measured at the mass spectrometry facilities of either the University of Maryland (College Park) or at the University of Illinois at Urbana-Champaign. All photophysical measurements were performed on optically dilute samples (optical density ~ 0.1) in Optima Grade CH_3CN (Fisher), as described previously.[19]

Full details of the syntheses and characterization of the materials are given in the Supporting Information.

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