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Star-shaped electrochemiluminescent metallodendrimers with central polypyridyl Ru(II) complexes: Synthesis and their photophysical and electrochemical properties

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Abstract

Several dendritic bridging ligands were designed and synthesized to develop more sensitive and efficient electrochemiluminescent (ECL) polynuclear Ru(II) complexes. Various types of novel two-armed, four-armed and six-armed tris(bipyridyl)ruthenium core dendrimers were synthesized by coordinating dendritic polybipyridyl ligands with Ru(II) complexes, and the effect of the ligand and the dendritic network on the ECL characteristics were studied. Their electrochemical redox potentials, UV, photoluminescence (PL), and relative ECL intensities were also investigated in detail. The synthesized metallodendrimers exhibited strong metal-to-ligand charge transfer (MLCT) absorption at 428–451 nm and emission at 591–601 nm. Most of the newly synthesized metallodendrimers showed enhanced ECL intensities compared to the reference complex, $[Ru(o\text{-phen})_3](PF_6)_2$. In particular, the ECL intensities of the six-armed heptanuclear ruthenium complexes were almost four times greater than that of $[Ru(o\text{-phen})_3]^{2+}$. These metallodendrimers could be utilized as efficient ECL materials and light emitting devices.

Keywords: Electrochemiluminescence; Ruthenium(II) complexes; Polyester; Metallodendrimer

1. Introduction

Dendrimers, with highly branched and regularly repeated architectures, have become an attractive research subject worldwide since the mid-1980s [1,2]. Rapid progress in this area has been attributed to numerous reasons such as the ability of dendrimers to control functional unit positioning, their ease of construction, and their well-behaved solubility features compared to polymers [3]. Dendrimers could be designed with ease by assembling the appropriate molecular units to perform useful functions such as catalysis, light emitting, and reversible redox processes [4–6]. The electrochemiluminescence (ECL) emitted by transition metal complexes has been recognized as a powerful method of analyzing a wide range of compounds such as oxalate, alkylamine, amino acid, NADH, and organic acids [6]. Among the numerous electrogenerated chemiluminescent materials, the ECL system associated with tris(2,2′-dipyridyl)ruthenium, $[Ru(bpy)_3]^{2+}$, has been used as the most intense and best model so far. The ECL emission of the $Ru(bpy)_3^{2+}$/tripropylamine (TPA) system arises when the deprotonated TPA radical ($TPA^{\cdot}$) formed from the reduction of $Ru(bpy)_3^{3+}$ or via direct electrode oxidation reacts with another $Ru(bpy)_3^{2+}$ or an additional $Ru(bpy)_3^{3+}$ to form $[Ru(bpy)_3^{2+}]^*$, which then decays to produce an orange emission. A simplified ECL reaction scheme is shown below [7]

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$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^- \quad (1)$$

$$Ru(bpy)_3^{3+} + TPA \rightarrow Ru(bpy)_3^{2+} + TPA^{\cdot} \quad (2a)$$

$$TPA \rightarrow TPA^{\cdot} + e^- \quad (2b)$$

$$Ru(bpy)_3^{3+} + TPA\cdot \rightarrow [Ru(bpy)_3^{2+}]^* + \text{oxidized products of TPA} \quad (3)$$

$$[Ru(bpy)_3^{2+}]^* \rightarrow Ru(bpy)_3^{2+} + \text{light}(610\ \text{nm}) \quad (4)$$

Previously, a series of dendrimers peripherally functionalized with the Ru complex has been explored as a strategy for developing highly efficient ECL materials [8]. From ECL studies on polyamidoamine (PAMAM) and polyamine (PA) metallodendrimers, it was noted that the dendrimers with multiple $[RuL_3]^{2+}$ pendant units could produce higher ECL intensities compared to their monomeric $[RuL_3]^{2+}$ complex: the ECL intensities of metallodendrimers become larger as the multiplicity of peripheral Ru(II) units increases. In addition, the ECL intensities of metallodendrimers were strongly affected by the length of the spacer connecting the metal complexes to the dendrimers as well as by the nature of the ligand of the $[RuL_3]^{2+}$ pendant units. However, these PAMAM and PA metallodendrimers exhibited strong ECL background signals, probably due to the inter- or intramolecular interaction of amine groups in the core with peripheral Ru(II) complexes. Since the number of inner amine groups in metallogendrimers is likely to affect their background ECL signals, it seems probable that the background signal can be controlled by eliminating the amine moieties from the dendrimer network.

Towards this end, a series of new star-shaped metallodendrimers has been designed with central polypyridyl Ru(II) complexes connected with an ester linkage between the metal core and the peripheral metal complexes through the bridging ligand. Herein, synthesis and characteristics of metallodendrimers are described. In addition, the relationship between their architectures and ECL characteristics, along with their electrochemical properties, are discussed.

2. Results and discussion

The formulas of polynuclear complexes, and the abbreviations used in this study, are shown in Fig. 1. By changing the number of bipyridyl-moiety-containing ester bridging ligands; i.e., 2,2′-bipyridine-4,4′,-diylbis(methylene) di-2,2′-bipyridine-5-carboxylate [bpy-$(CH_2OCO\text{-bpy})_2$], a complex containing multi-nuclear ruthenium can be extended to trimers (**A**), pentamers (**B**), and up to heptamers (**C**) depending on the number of ruthenium in the metallodendrimer complex. All these multinuclear ruthenium complexes can be prepared by modifying the method developed in our laboratory.

The synthetic strategy employed for one of the targeted complex molecules, heptamer, is shown in a retrosynthetic analysis in Scheme 1. As shown in Scheme 1, the targeted polynuclear ruthenium complexes (**C**) can be synthesized from the complexation of polypyridyl Ru(II) complexes with self-assembled dendritic bridging ligands (**D**). The dendritic bridging ligand (**D**) can be prepared through the esterification of the $[Ru(bpy\text{-}(CH_2OH)_2)_3](PF_6)_2$(**E**) with 2,2′-bipyridine-5-carboxylic acid (**F**). The alkoxy part of the esterification, i.e. $[Ru(bpy\text{-}(CH_2OH)_2)_3](PF_6)_2$(**E**) can be obtained from the reaction of the dichloro(*p*-cymene)ruthenium(II) dimer with 4,4′-bis(hydroxymethyl)-2,2′-bipyridine (**H**). Synthesis of trimer- and pentamer-type metallodendrimers is also possible with a minor modification of the synthetic path.

2.1. Synthesis of mono-ruthenium complexes centered on metallodendrimers for either ECL materials or precursors for complexes containing star-shaped multi-ruthenuim

At first, two bipyridyl ligands, 2,2′-bipyridine-5-caboxylic acid (**F**, Eq. (1) in Scheme 2) and 4,4′-bis(hydroxy-

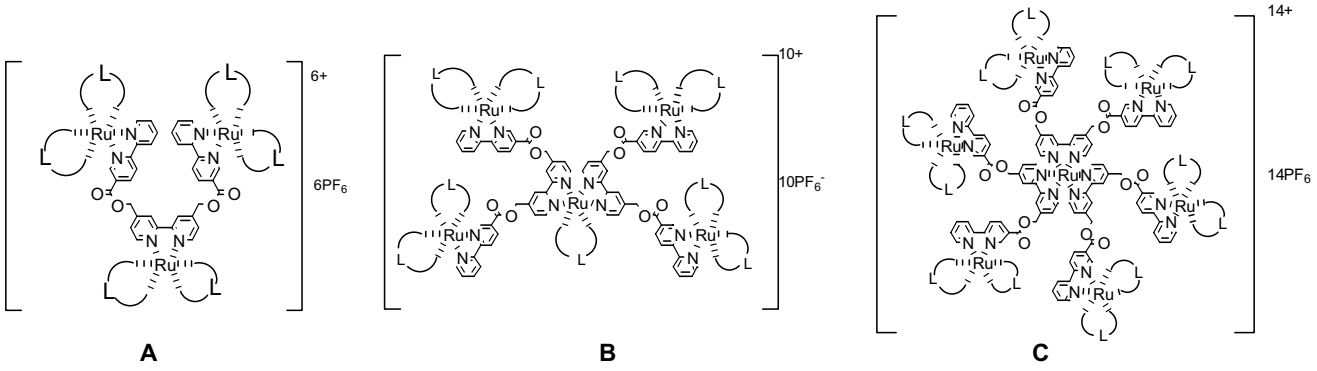
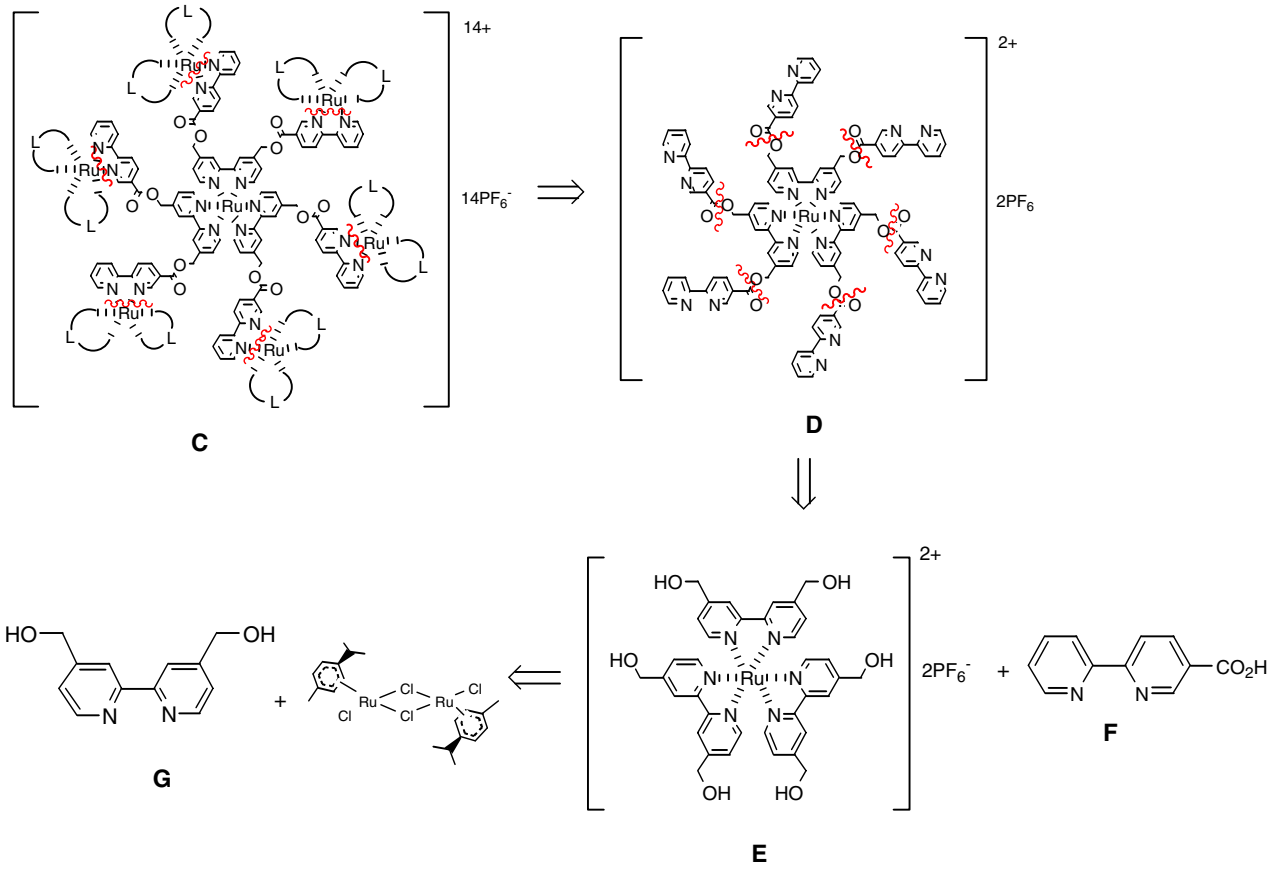


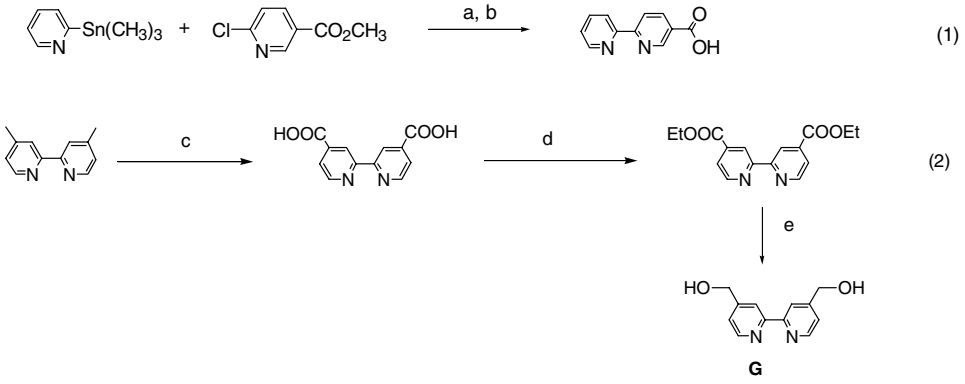
Fig. 1. Schematic representation of polynuclear ruthenium complexes along with their abbreviations.



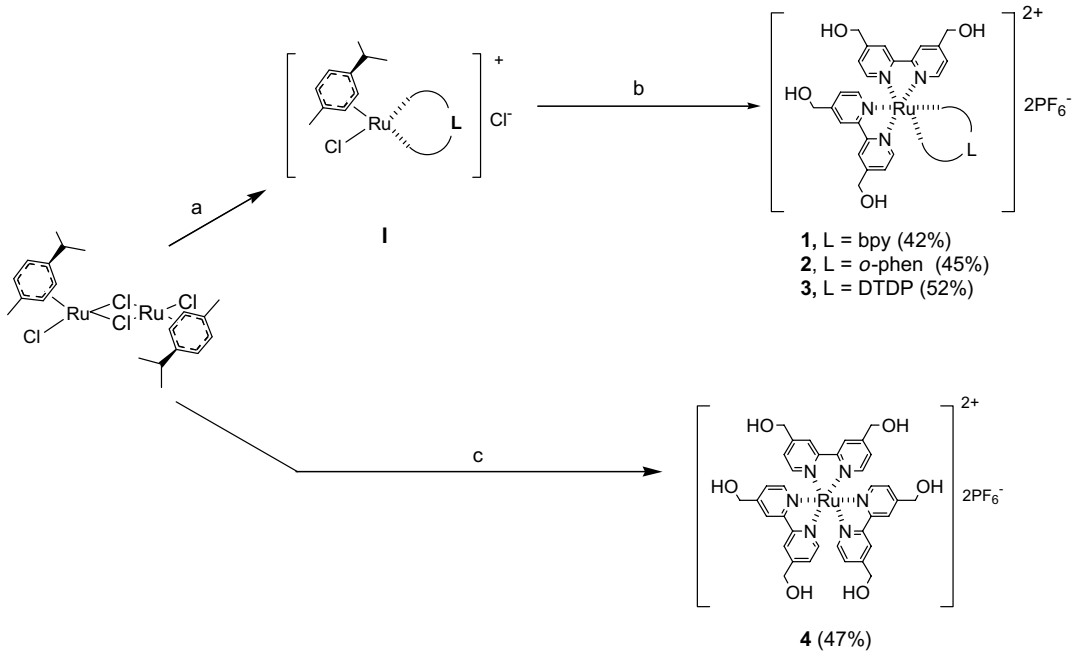
Scheme 1. Retrosynthetic analysis of star-shaped heptamer-type metallodendrimers.

methyl)-2,2′-bipyridine (**G**, Eq. (2) in Scheme 2) were prepared using known literature methods [9,10] as shown in Scheme 2. These ligands were used to introduce the peripheral ruthenium complexes to the core ruthenium complex through esterification.

As an initial step in the metallodendrimer synthesis, four kinds of core Ru(II) complexes $[Ru(bpy\text{-}(CH_2OH)_2)_n\text{-}L_{3-n}](PF_6)_2$ (L = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (*o*-phen), 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren-2-one (DTDP, $n = 2$, 3) were synthesized, and were used either as ECL materials or as precursors of the synthesis of the metallodendrimers containing multinuclear ruthenium complexes. Thus, the sequential reactions of $[RuCl_2(p\text{-cymene})]_2$ with an elected ligand (L = bpy, *o*-phen, DTDP) in ethanol, H_2O, or H_2O/EtOH were employed. When 2 equiv. of the elected ligand was applied to $[RuCl_2(p\text{-cymene})]_2$ in the EtOH solution at room temperature, $[RuCl_2(p\text{-cymene})L]$ (**I**) was obtained



Scheme 2. Preparation of bipyridyl ligands. Reagents and conditions: (a) $(PPh_3)_2PdCl_2$, *m*-xylene, reflux, 12 h (84%). (b) 1 N NaOH, MeOH, 5 h. (c) CrO_3, H_2SO_4, 75 °C, 4 h, then stirring at room temperature, 10 h. (d) (1) $SOCl_2$, reflux, 6 h, (2) EtOH/$CHCl_3$ (v/v = 1:50), reflux, 4 h. (e) $NaBH_4$, EtOH, reflux, 4 h (48% for c–e steps).



Scheme 3. Syntheses of mono-ruthenium complexes. Reagents and conditions: (a) L (bpy, *o*-phen, DTDP, 2 equiv.), EtOH, room temperature, 2 h. (b) (1) **G** (4 equiv.), H_2O, reflux, 24 h, (2) excess aq. NH_4PF_6. (c) (1) **G** (8 equiv.), EtOH/H_2O (v/v = 1:2), reflux, 24 h, (2) excess aq. NH_4PF_6.

selectively. After [$RuCl_2$(*p*-cymene)L] was refluxed with 6 equiv. of bpy-$(CH_2OH)_2$ in an aqueous solution, followed by addition of NH_4PF_6, **1**–**3** were obtained with 42–52% yields (Scheme 3). A symmetrical complex **4** was obtained in a 47% yield by refluxing [$RuCl_2$(*p*-cymene)]$_2$ with 8 equiv. of bpy-$(CH_2OH)_2$ in aqueous EtOH (v:v = 2:1), followed by addition of NH_4PF_6 (Scheme 3). All the newly synthesized compounds were fully identified with ^{1}H NMR, IR, UV–Vis, and FAB mass.

2.2. Synthesis of dendritic bridging ligands

Prior to the synthesis of the metallodendrimers, the bridging ligands **5**–**9** were synthesized successfully with 42–80% yields via the esterification of 2,2′-bipyridine-5-carboxylic acid with 4,4′-bis(hydroxymethyl)-2,2′-bipyridine [(bpy-$(CH_2OH)_2$)] (Eq. (1) in Scheme 4) or core Ru(II) complexes [Ru(bpy-$(CH_2OH)_2)_nL_{3-n}$]$(PF_6)_2$ in CH_2Cl_2 or CH_2Cl_2/CH_3CN (Eqs. (2) and (3) in Scheme 4). 2,2′-bipyridine-4,4′-diylbis(methylene) di-2,2′-bipyridine-5-carboxylate (**5**) could be utilized as a bridging ligand for the synthesis of trimers. The mono-ruthenium complexes, **6**–**8** and **9** acted as core complexes on pentamers and heptamers, respectively.

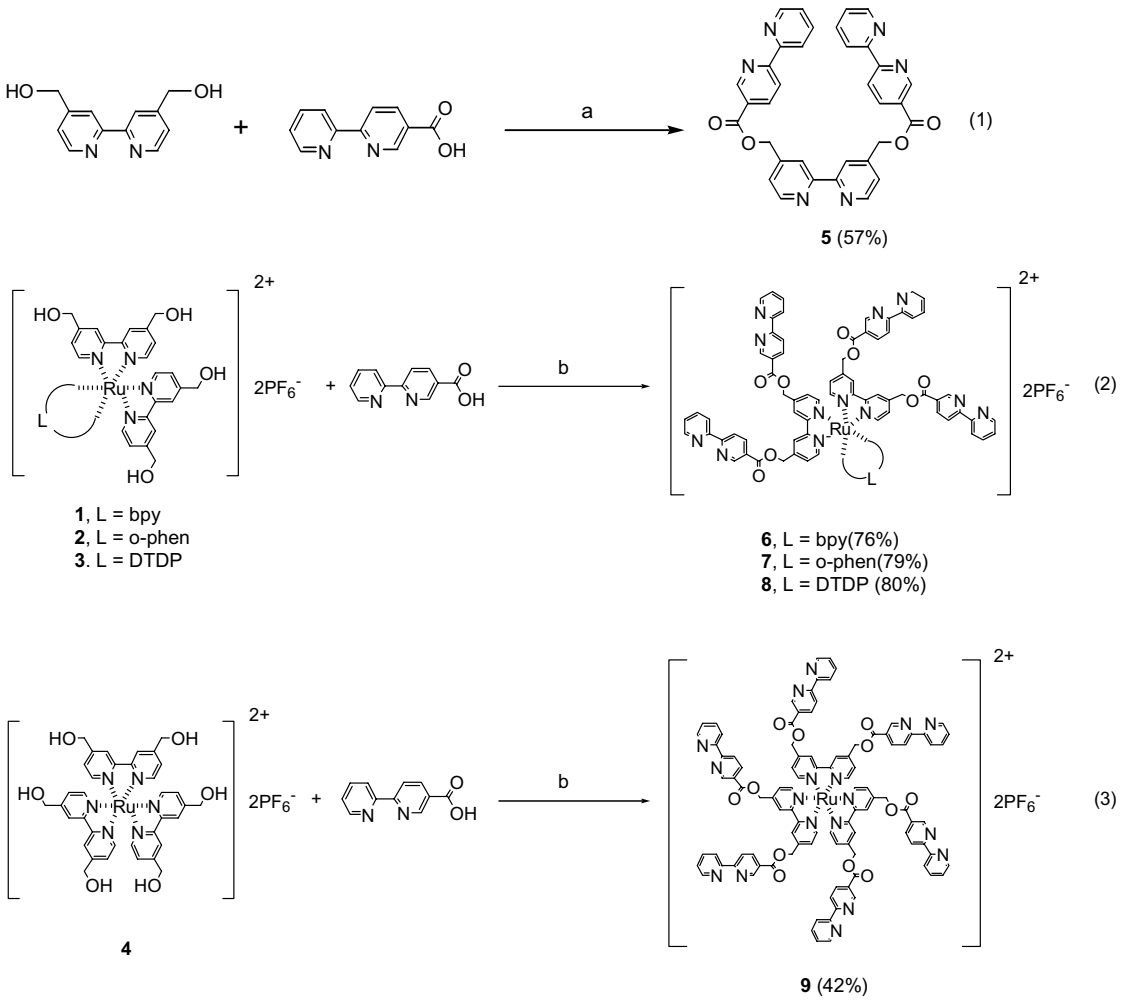
2.3. Syntheses of complexes containing star-shaped multinuclear ruthenuim; trimers, pentamers, and heptamers

As shown in Scheme 5, metallodendrimers, **10**–**18** were obtained with reasonably good yields via the complexation of the bridging ligands **5**–**9** to [*cis*-$Ru(L)_2(acetone)_2]^{2+}$ (L = bpy, *o*-phen, DTDP) in DMF at reflux and were fully characterized with ^{1}H NMR, IR, UV–Vis, and MALDI-TOF mass (Fig. 2).

2.4. Absorption and emission spectra of metallodendrimers

The absorption and emission spectral data of the monomer Ru(II) complexes in acetone are listed in Table 1. The most intense band, at around 457 nm, can be assigned to the metal-to-ligand charge transfer (MLCT) transition. The mononuclear Ru(II) complexes containing the bridging ligand with liberated bipyridyl groups (i.e., bipyridyl moieties which are not ligated to ruthenium metal), **6**–**9**, showed more intense absorption compared to **1**–**4**, which do not contain liberated bipyridyl groups. The absorption of the mononuclear Ru(II) complexes might be affected by the nature of the ligand. The luminescence spectra of these complexes exhibited an emission at a wavelength of around 591–599 nm. This suggests that the lowest excited state mostly has a metal-to-ligand charge-transfer character.

The absorption and emission spectral data of the metallodendrimers (the trimer, pentamer and heptamer) were obtained in acetone at room temperature, as summarized in Table 2. It shows that the metallodendrimers exhibit an intense absorption band at 430–450 nm, which is clearly blue-shifted from those of the monomers. Moreover, their molar absorptivities increase linearly three or sevenfold due to the increase in multiplicity (Table 2 and Fig. 3). However, the emissions of the metallodendrimers were observed at 585–601 nm, which is close to the emissions of the monomers.

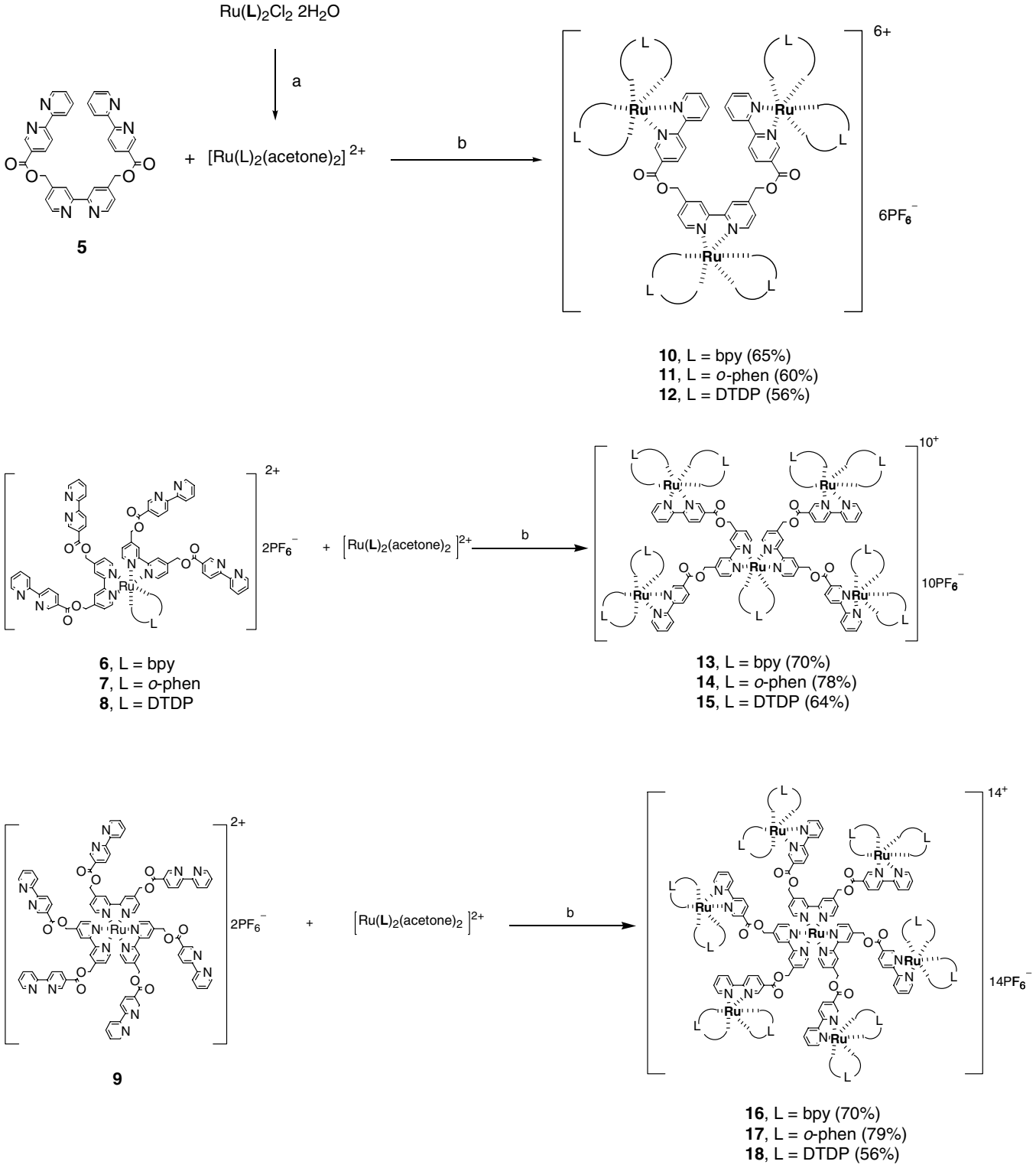


Scheme 4. Syntheses of dendritic bridging ligands. Reagents and conditions: (a) DCC, DMAP, CH_2Cl_2/CH_3CN (v/v = 1:1), room temperature, 24 h. (b) DCC, DMAP, CH_2Cl_2/CH_3CN (v/v = 1:1), room temperature, 2 h.

2.5. Electrochemical and ECL characteristics

Cyclic voltammograms of the metallodendrimers were obtained in a 50 mM phosphate buffer at pH 7, with aqueous acetonitrile (80% (v/v)). They showed a quasi-reversible one-electron process for Ru(II)/Ru(III) oxidation–reduction, with half-wave potentials within the range of $1.21 < E_{1/2} < 1.25$ V vs. Ag/AgCl (3 M NaCl) ($E_{1/2} = (E_{pa}+E_{pc})/2$) (Table 3). This behavior was confirmed by the fact that the separation of the anodic and cathodic peak potentials, ΔE_p, and the ratio of the anodic to cathodic currents, I_{pa}/i_{pc} were close to 70–160 mV and 1.0, respectively. All the metallodendrimers showed similar electrochemical properties. However, their oxidation potentials (1.25–1.30 V vs. 1.16 V) shifted anodically compared to that of $[Ru(o\text{-phen})_3](PF_6)_2$. The cyclic voltammograms obtained for all the metallodendrimers tested showed only single quasi-reversible waves. This indicates that the Ru(II) centers in the metallodendrimers were electrochemically equivalent to one another.

The ECL measurement experiments were carried out in Ru(II) complex solutions that contained tripropylamine as a coreactant. ECL emissions were obtained for each metallodendrimer upon sweeping of the potential from 0.7 V to 1.4 V with a scanning rate of 100 mV/s. In contrast to the previous polyamidoamine (PAMAM) and polyamine (PA) metallodendrimers [8], serious background signals were not obtained with the present metallodendrimers that were based on the ester linkage instead of the amine group between the metal core and the peripheral metal complexes through the bridging ligand. As summarized in Table 3, most of the metallodendrimers showed significantly higher ECL responses compared to that of the $[Ru(o\text{-phen})_3](PF_6)_2$ complex except for trimer-*o*-phen, which produced only a 10% higher ECL intensity (entry 2). The ECL intensities of heptamer, **16**–**18**, exhibited the strongest intensities in the ECL. As a result, the ECL intensity of metallodendrimers increases as the number of peripheral Ru(II) units in metallodendrimers increases. For example, the ECL intensities of trimer-DTDP (entry 3), pentamer-DTDP (entry 6), and



Scheme 5. Syntheses of star-shaped multi-nuclear ruthenium complexes; trimers, pentamers, and heptamers. Reagents and conditions: (a) $AgPF_6$, acetone, room temperature, 2 h. (b) (1) DMF, 120 °C, 4 h, (2) excess aq. NH_4PF_6.

heptamer-*o*-phen (entry 8) showed around two, three, and fourfold higher ECL intensities, respectively, relative to that of the $[Ru(o\text{-phen})_3](PF_6)_2$ complex. However, the ECL intensity of the metallodendrimer with seven $[Ru(bpy)_3]^{2+}$ units was only around four times higher than that of the reference monomer species, the $[Ru(o\text{-phen})_3](PF_6)_2$ complex. This is similar those previously observed for the PAMAM metallodendrimers, in which the ECL intensity of the dendrimer with four $[Ru(bpy)_3]^{2+}$ units was 2.5 times higher than that of the

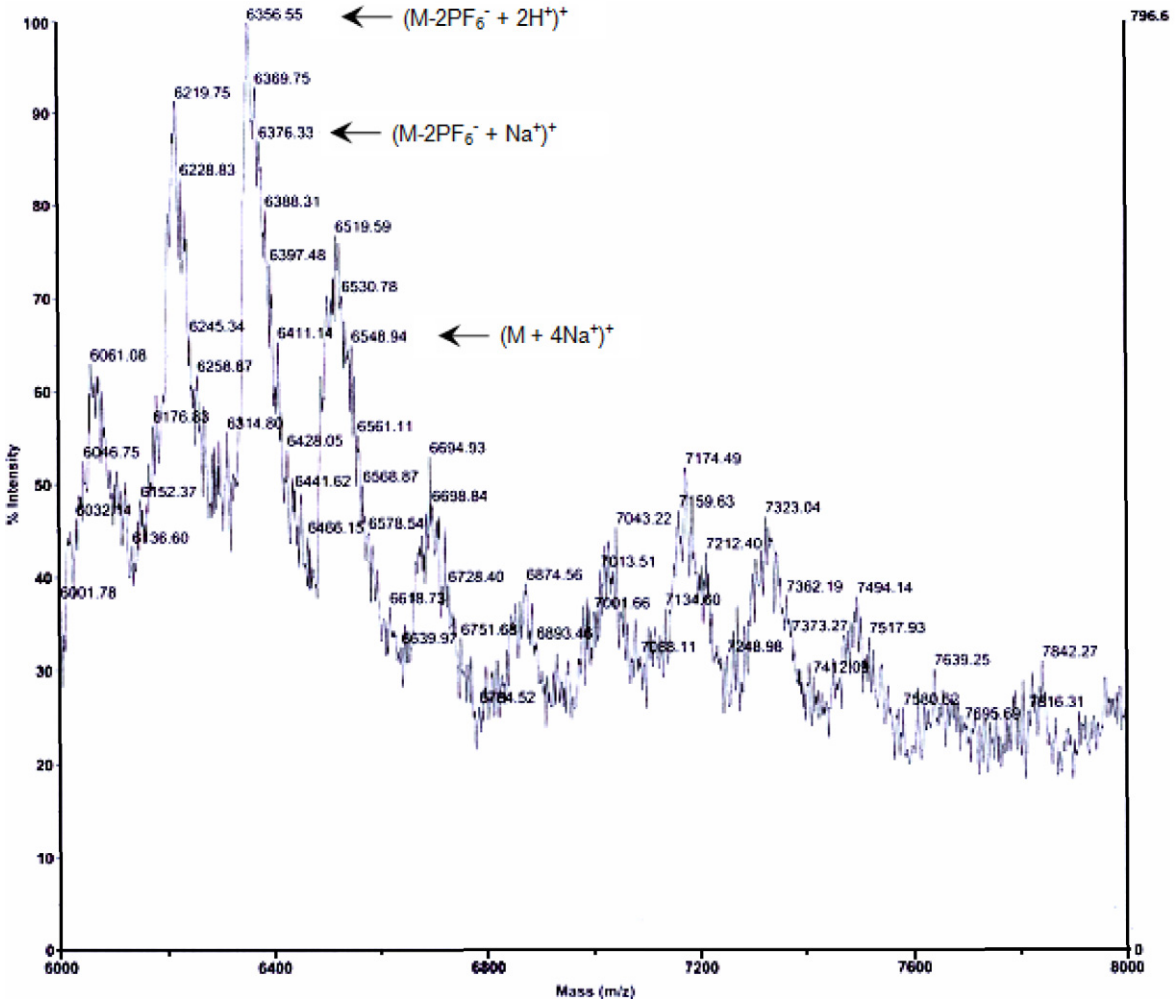


Fig. 2. MALDI-TOF MS data of $[Ru(bpy(CH_2OCO\text{-}bpyRu(o\text{-}phen)_2)_2)_3](PF_6)_{14}$(heptamer-*o*-phen; **17**).

Table 1
UV and PL spectra data of mononuclear ruthenium complexes

Entry	Ru(II) Cpd	Absorption[a]		Emission[a]
		λ_{max}, UV (nm)[a]	ε (M^{-1} cm^{-1})	PL (nm)[a]
1	$[Ru(bpy\text{-}(CH_2OH)_2)_2(bpy)](PF_6)_2$ (**1**)	457	11 200	598
2	$[Ru(bpy\text{-}(CH_2OH)_2)_2(o\text{-phen})](PF_6)_2$ (**2**)	454	12 400	591
3	$[Ru(bpy\text{-}(CH_2OH)_2)_2(DTDP)](PF_6)_2$ (**3**)	457	10 000	591
4	$[Ru(bpy\text{-}(CH_2OH)_2)_3](PF_6)_2$ (**4**)	458	10 000	596
5	$[Ru(bpy\text{-}(CH_2OCO\text{-}bpy)_2)_2(bpy)](PF_6)_2$ (**6**)	458	12 400	599
6	$[Ru(bpy\text{-}(CH_2OCO\text{-}bpy)_2)_2(o\text{-phen})](PF_6)_2$ (**7**)	456	13 600	596
7	$[Ru(bpy\text{-}(CH_2OCO\text{-}bpy)_2)_2(DTDP)](PF_6)_2$ (**8**)	457	15 200	593
8	$[Ru(bpy\text{-}(CH_2OCO\text{-}bpy)_2)_3](PF_6)_2$ (**9**)	460	14 400	599

[a] Recorded in acetone at room temperature.

reference monomer species [8]. In addition, a similar result was also observed for the carbosilane-based metallodendrimers, in which the ECL intensity of the dendrimer with eight $[Ru(bpy)_3]^{2+}$ units was five times higher than that of the reference monomer species [11].

3. Conclusion

Novel star-shaped metallodendrimers and polynuclear ruthenium complexes were synthesized with reasonably good yields from the reactions of $[Ru(L)_2(acetone)_2]^{2+}$

Table 2
UV and PL spectra data of metallodendrimers

Entry	Ru(II) Cpd	Absorption[a]		Emission[a]
		λ_{max}, UV (nm)[a]	ε (M^{-1} cm^{-1})	PL (nm)[a]
1	Trimer-bpy (**10**)	448	29 600	593
2	Trimer-*o*-phen (**11**)	441	33 600	585
3	Trimer-DTDP (**12**)	451	24 400	587
4	Pentamer-bpy (**13**)	440	51 200	595
5	Pentamer-*o*-phen (**14**)	434	57 600	590
6	Pentamer-DTDP (**15**)	441	56 800	591
7	Heptamer-bpy (**16**)	439	59 600	598
8	Heptamer-*o*-phen (**17**)	434	70 400	595
9	Heptamer-DTDP (**18**)	428	77 600	601

[a] Recorded in acetone at room temperature.

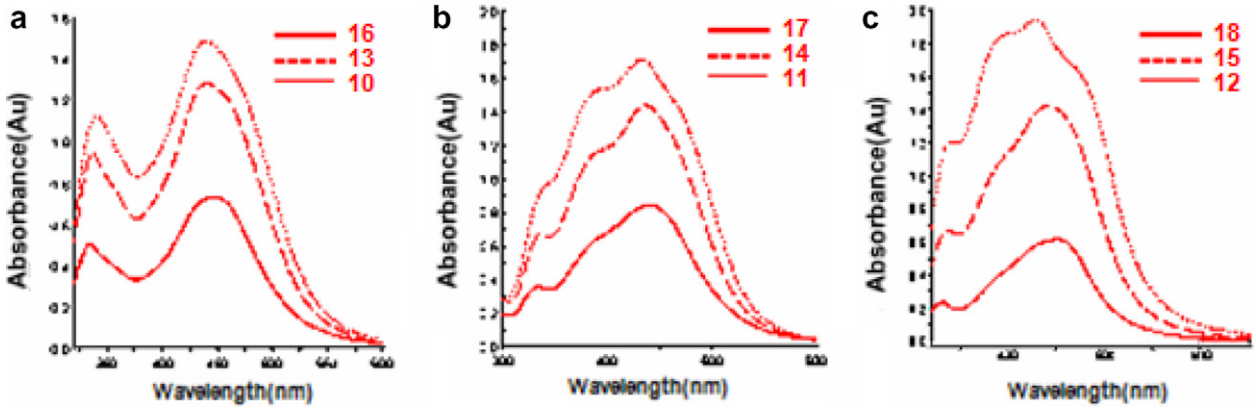


Fig. 3. UV spectral data of metallodendrimers, L = (a) bpy, (b) *o*-phen, (c) DTDP. Concentrations were 0.05 mM in acetone.

Table 3
CV and ECL data of metallodendrimers

Entry	Compound	E_{pa} (V)[a]	E_{pc} (V)[a]	ΔE_p (mV)[a]	ECL[b]
1	Trimer-bpy (**10**)	1.30	1.15	150	1.9
2	Trimer-*o*-phen (**11**)	1.25	1.18	70	1.1
3	Trimer-DTDP (**12**)	1.28	1.20	80	2.2
4	Pentamer-bpy (**13**)	1.31	1.15	160	1.5
5	Pentamer-*o*-phen (**14**)	1.25	1.17	80	2.9
6	Pentamer-DTDP(**15**)	1.30	1.18	120	2.9
7	Heptamer-bpy (**16**)	1.30	1.14	160	3.3
8	Heptamer-*o*-phen (**17**)	1.27	1.18	90	3.8
9	Heptamer-DTDP (**18**)	1.30	1.20	100	3.4

[a] Measured in acetonitrile/H_2O at pH 7 containing 50 mM phosphate buffer as a supporting electrolyte at a glassy carbon electrode vs. Ag/AgCl (3 M NaCl).
[b] ECL relative to $[Ru(o\text{-phen})_3](PF_6)_2$.

and dendritic bridging ligands. Their solubility in solvents such as acetonitrile, acetone, etc., was improved compared to that of the polymeric compound. The absorption spectra of the metallodendrimers exhibited an intense band at 430–450 nm, which was blue-shifted from that of the monomers, and the molar absorptivity is improved linearly three to sevenfold with respect to the increase in the multiplicities. The emissions of the metallodendrimers were observed at 585–601 nm, which resembled those of the monomers. Most of the metallodendrimers showed greater ECL intensities than did the standard $[Ru(o\text{-phen})_3](PF_6)_2$ complex. Especially, the ECL intensities of heptamer were almost four-times greater than that of the $[Ru(o\text{-phen})_3](PF_6)_2$ complex. These results indicate that the increase in the multiplicity of the peripheral Ru(II) complexes can improve the ECL intensity. The types of ligands in the metallodendrimers do not strongly affect the latter's ECL intensities unlike the monomeric Ru(II) complexes. Since the present

polynuclear ruthenium complexes show strong ECL signals, these Ru(II) metallodenrimers, which are based on the ester linkage between the metal core and peripheral metal complexes can be utilized not only as highly efficient ECL materials but also as intense light-emitting materials.

4. Experimental

4.1. Materials and instrumentation

All the reactions were carried out under a dry nitrogen atmosphere, unless otherwise stated. The solvents were purchased and dried using the standard method. Most of the chemical reagents were purchased from Aldrich Chemical Co. and were used as received without further purification in most cases. 2,2′-Bipyridine-5-caboxylic acid [9], 1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]-phenanthren-2-one (DTDP) [12], 4,4′-bis(hydroxymethyl)-2,2′-bipyridine(bpy-$(CH_2OH)_2$) [10], and *cis*-$Ru(L)_2Cl_2 \cdot 2H_2O$ (L: bpy, *o*-phen, DTDP) [13] were prepared using the known literature methods.

^1H NMR spectra were recorded on a 400 MHz Jeol instrument. Chemical shifts were reported in ppm relative to a residual solvent as an internal standard. GC/MS was recorded on an HP 5973 mass spectrometer connected with HP 6890 GC and MALDI-TOF mass was recorded on a JMS-DX303 (JEOL Co.). Infrared spectra (IR) were recorded on a MB104 FT-IR (ABB Bomen Inc.) and UV–Vis spectra were recorded on a Sinco S-3100. Emission spectra were obtained with the use of a Perkin Elmer luminescence spectrometer LS 50B (excitation source at 400 nm).

4.2. Electrochemical and ECL measurements

Cyclic voltammetric experiments were performed with an EG&G 273A potentiostat (Oak Ridge, TN, USA). A conventional three-electrode system was employed with a platinum wire as counter electrode, glassy carbon (0.07 cm^2) electrode as a working electrode, and an Ag/AgCl (3 M NaCl) reference electrode. The photon counting system used was a Hamamatsu Photonics HC 135-02 photon counting module (Hamamatuse City, Japan) in conjunction with a computer for recording the output. The electrochemical cell was also used in the ECL experiments. The ECL cell was placed directly in front of the photomultiplier tube (PMT) window. Prior to the electrochemical and ECL experiments, the working electrode was polished with 0.05 μm alumina, sonicated, and rinsed with methanol followed by water. Ru(II) complex solution and tripropylamine (TPA) solutions were prepared in the same 50 mM pH 7.0 phosphate buffer containing acetonitrile (v/v, 80%). TPA solutions (3 mM, 5 mM, or 7 mM) were mixed with 0.5 mM synthesized Ru(II) complex solutions (1/1, v/v) and also blank solutions were prepared by mixing the given concentration of Ru(II) complex solution and the same buffer (1:1, v/v) without TPA. During the course of the ECL measurement, the potential of the working electrode was cycled from 0.7 V to 1.4 V with a scanning rate of 100 mV/s. ECL measurements were also performed for blank solutions in all studies. Corrected ECL signals were obtained by subtracting the ECL signals for blank solutions from the observed ECL signals for TPA.

4.3. Synthesis

4.3.1. General procedure for the syntheses of $[Ru(bpy\text{-}(CH_2OH)_2)_nL_{3-n}](PF_6)_2$; mono-ruthenium complexes

For the unsymmetrically ligated complexes such as $[Ru(bpy\text{-}(CH_2OH)_2)_2L](PF_6)_2$, a solution of $[RuCl_2(p\text{-cymene})]_2$ (122.4 mg, 0.2 mmol) and L (L = bpy, *o*-phen, DTDP, 0.4 mmol) dissolved in ethanol (10 mL) was stirred for 2 h. Then, L′ (L′ = bpy-$(CH_2OH)_2$, 259.0 mg, 1.2 mmol) in distilled water (10 mL) was added to the solution, after which the solution was refluxed for 24 h. For the symmetrically ligated complex, $[Ru(bpy\text{-}(CH_2OH)_3)(PF_6)_2$, a solution of $[RuCl_2(p\text{-cymene})]_2$ (122.4 mg, 0.2 mmol) and bpy-$(CH_2OH)_2$ (345.6 mg, 1.6 mmol) in aqueous ethanol ($EtOH:H_2O$ = 5:10 mL) was refluxed for 24 h. The reaction was monitored by TLC (eluant; sat. aq. KNO_3 solution:$H_2O:CH_3CN$ = 1:3:6). After the solution was cooled to room temperature, the ethanol was removed under reduced pressure and the residue was treated with a saturated aqueous solution of NH_4PF_6, which resulted in a red precipitate. The red solid was filtered and recrystallized from acetone/ethyl acetate. Dark red crystals were obtained with 42–52% yields.

4.3.2. $[Ru(bpy\text{-}(CH_2OH)_2)_2(bpy)](PF_6)_2$ (**1**)

Yield: 42%, UV (acetone) $\lambda_{max}(\varepsilon)$ 457 nm (11 200 $M^{-1}\,cm^{-1}$); FT-IR (KBr) 3394 (br), 3078, 2968, 2925, 1618, 1469, 1054, 838 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 3.78 (br s, 4H), 4.86 (s, 8H), 7.40–7.43 (m, 6H), 7.46 (ddd, J = 1.4, 5.6, 8.1 Hz, 2H), 7.71 (d, J = 5.6 Hz, 2H), 7.73 (d, J = 5.6 Hz, 2H), 7.82 (ddd, J = 0.7, 1.4, 5.6 Hz, 2H), 8.11 (ddd, J = 1.4, 8.1, 8.1 Hz, 2H), 8.54–8.57 (m, 6H); FAB MS m/z 835 $(M-PF_6)^+$, 689 $(M-PF_6-H^+)^+$.

4.3.3. $[Ru(bpy\text{-}(CH_2OH)_2)_2(o\text{-phen})](PF_6)_2$ (**2**)

Yield: 45%, UV (acetone) $\lambda_{max}(\varepsilon)$ 453 nm (12 400 $M^{-1}\,cm^{-1}$); FT-IR (KBr) 3359 (br), 1614, 1422, 1054, 839 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 3.72 (br s, 4H), 4.73 (s, 4H), 4.83 (s, 4H), 7.15–7.17 (m, 2H), 7.40–7.45 (m, 4H), 7.72–7.78 (m, 4H), 8.10 (dd, J = 1.3, 5.3 Hz, 2H), 8.23 (s, 2H), 8.46 (br s, 2H), 8.50–8.51 (m, 2H), 8.60 (dd, J = 1.3, 8.0 Hz, 2H); FAB MS m/z 859 $(M-PF_6)^+$, 714 $(M-2PF_6)^+$.

4.3.4. $[Ru(bpy\text{-}(CH_2OH)_2)_2(DTDP)](PF_6)_2$ (**3**)

Yield: 52%, UV (acetone) $\lambda_{max}(\varepsilon)$ 457 nm (10 000 $M^{-1}\,cm^{-1}$); FT-IR (KBr) 3363 (br), 2972, 2933, 2874, 1747, 614, 1426, 1046, 835, 737 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 1.65–1.72 (m, 12H), 4.74 (s, 4H),

4.83 (s, 4H), 7.20 (d, $J = 5.7$ Hz, 2H), 7.40 (d, $J = 5.7$ Hz, 2H), 7.46 (d, $J = 5.7$ Hz, 2H), 7.72 (dd, $J = 5.7$, 8.4 Hz, 2H), 7.75 (d, $J = 5.7$ Hz, 2H), 8.10 (d, $J = 5.7$ Hz, 2H), 8.48 (s, 2H), 8.51 (s, 2H), 8.82 (d, $J = 8.4$ Hz, 2H); FAB MS m/z 969 $(M-PF_6)^+$, 824 $(M-2PF_6)^+$.

4.3.5. *[Ru(bpy-(CH$_2$OH)$_2$)$_3$](PF$_6$)$_2$(**4**)*

A solution of $[RuCl_2(p\text{-cymene})]_2$ (122.4 mg, 0.2 mmol) and 4,4′-bis(hydroxymethyl)-2,2′-bipyridine (172 mg, 0.8 mmol) dissolved in ethanol (5 mL) and distilled water (10 mL) was stirred for 24 h. After the solution was cooled to room temperature, the ethanol was removed under reduced pressure and the residue was treated with a saturated aqueous solution of NH_4PF_6. The resulting precipitate was filtered and recrystallized from acetone/ethyl acetate. Dark red crystals were obtained with a 47% yield.

UV (acetone) $\lambda_{max}(\varepsilon)$ 458 nm (10000 M^{-1} cm^{-1}); FT-IR (KBr) 3363 (br), 2921, 2850, 1618, 1422, 1058, 835 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 3.37 (br s, 6H), 4.79 (s, 12H), 7.34 (d, $J = 5.8$ Hz, 6H), 7.65 (d, $J = 5.8$ Hz, 6H), 8.47 (s, 6H); FAB MS m/z 895 $(M-PF_6)^+$, 748 $(M-2PF_6-2H^+)^+$.

4.3.6. *Synthesis of Dendritic Bridging Ligand; bpy-(CH$_2$OCO–bpy)$_2$ (**5**)*

2,2′-Bipyridine-5-carboxylic acid (250 mg, 1.25 mmol), 4,4′-bis(hydroxymethyl)-2,2′-bipyridine (108 mg, 0.50 mmol), and dimethylaminopyridine (DMAP) (30 mg, 0.25 mmol) were dissolved in CH_2Cl_2 (15 mL) at 0 °C. Then, *N*,*N*′-dicyclohexylcarboimide (DCC, 257 mg, 1.25 mmol) dissolved in CH_2Cl_2 (5 mL) was added. This solution was stirred at 0 °C for 1 h, after which the solution was stirred for over night at room temperature. The precipitated DCU was filtered off. After CH_2Cl_2 was distilled off at low pressure, the product was purified using silica gel column chromatography (MeOH:CH_2Cl_2 = 5:95) and obtained with a 57% yield.

TLC (10% methanol/dichloromethane, ammonia water) R_f 0.62; FT-IR (KBr) 3058, 2933, 2854, 1723, 1590, 1555, 1457, 1281, 1117, 823, 757; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (s, 4H), 7.36–7.39 (m, 2H), 7.42–7.43 (m, 2H), 7.85–7.88 (m, 2H), 8.47–8.56 (m, 8H), 8.72–8.73 (m, 4H), 9.37 (s, 2H); HRMS calc. for 580.1859, found 580.1858.

4.3.7. *General procedure for the synthesis of [Ru(bpy-(CH$_2$OCO-bpy)$_2$)$_2$(L)](PF$_6$)$_2$*

2,2′-Bipyridine-5-carboxylic acid (120 mg, 0.6 mmol), $[Ru(bpy\text{-}(CH_2OH)_2)_2L](PF_6)_2$ (0.1 mmol), and DMAP (6.0 mg, 0.05 mmol) were dissolved in CH_3CN (5 mL) at 0 °C. Then, DCC (124 mg, 0.6 mmol) dissolved in CH_2Cl_2 (5 mL) was added and the solution was stirred for 1 h. The solution was warmed up to room temperature and stirred for 4 h additionally. The precipitated DCU was filtered off. After CH_2Cl_2 was distilled off at low pressure, the resulting solid was filtered and recrystallized from acetone/ethyl acetate. Yellow red crystals were obtained with 76–80% yields.

4.3.8. *[Ru(bpy-(CH$_2$OCO-bpy)$_2$)$_2$(bpy)](PF$_6$)$_2$ (**6**)*

Yield: 76%, UV (acetone) $\lambda_{max}(\varepsilon)$ 458 nm (12400 M^{-1} cm^{-1}); FT-IR (KBr) 3062, 3003, 2960, 1727, 1594, 1461, 1375, 1281, 1109, 839, 753; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.66 (s, 8H), 7.51–7.57 (m, 6H), 7.72–7.84 (m, 10H), 7.94–7.99 (m, 4H), 8.18 (dd, $J = 7.6$, 7.6 Hz, 2H), 8.38–8.41 (m, 4H), 8.52 (br s, 8H), 8.71 (br s, 4H), 8.86 (d, $J = 8.0$ Hz, 2H), 8.99 (s, 4H), 9.30 (s, 4H); MALDI TOF MS m/z 1731.6 $((M^+ + Na^+)^+$, calc. 1731.2), 1564.5 $((M-PF_6^- + H^+)^+$, calc. 1564.3), 1417.5 $((M-2PF_6^-)^+$, calc. 1418.3).

4.3.9. *[Ru((bpy-(CH$_2$OCO-bpy)$_2$)$_2$(o-phen)](PF$_6$)$_2$ (**7**)*

Yield: 79%, UV (acetone) $\lambda_{max}(\varepsilon)$ 456 nm (13600 M^{-1} cm^{-1}); FT-IR (KBr) 3052, 2999, 2960, 1723, 1590, 1273, 1109, 839, 753; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.62 (s, 4H), 5.72 (s, 4H), 7.48 (br s, 4H), 7.56 (m, 2H), 7.81 (br s, 2H), 7.95 (br s, 10H), 8.28 (d, $J = 5.6$ Hz, 2H), 8.41–8.58 (m, 10H), 8.70 (br s, 4H), 8.83 (d, $J = 8.0$ Hz, 2H), 9.04 (br s, 4H), 9.08 (br s, 4H), 9.20 (s, 4H), 9.27 (s, 4H); MALDI TOF MS m/z 1755.2 $((M^+ + Na^+)^+$, calc. 1755.3), 1587.2 $((M-PF_6^-)^+$, calc. 1587.3).

4.3.10. *[Ru(bpy-(CH$_2$OCO-bpy)$_2$)$_2$(DTDP)](PF$_6$)$_2$ (**8**)*

Yield: 80%, UV (acetone) $\lambda_{max}(\varepsilon)$ 457 nm (15,200 M^{-1} cm^{-1}); FT-IR (KBr) 2929, 2847, 1720, 1590, 1277, 1113, 839, 753; ^{1}H NMR (400 MHz, CD_3CN) δ 1.66 (s, 6H), 1.72 (s, 6H), 5.54 (s, 4H), 5.62 (s, 4H), 7.37 (d, $J = 4.2$ Hz, 2H), 7.41–7.44 (m, 4H), 7.59 (d, $J = 5.8$ Hz, 4H), 7.76 (dd, $J = 5.2$, 8.5 Hz, 2H), 7.86–7.90 (m, 6H), 8.15 (d, $J = 4.2$ Hz, 2H), 8.37–8.51 (m, 12H), 8.66–8.69 (m, 8H), 8.86 (d, $J = 8.5$ Hz, 2H), 9.25 (d, $J = 1.1$ Hz, 2H), 9.29 (d, $J = 1.1$ Hz, 2H); MALDI TOF MS m/z 1865.7 $((M^+ + Na^+)^+$, calc. 1865.5), 1699.6 $((M-PF_6^- + 2H^+)^+$, calc. 1699.4).

4.3.11. *[Ru(bpy-(CH$_2$OCO-bpy)$_2$)$_3$](PF$_6$)$_2$ (**9**)*

2,2′-Bipyridine-5-carboxylic acid (155.9 mg, 0.8 mmol), $[Ru(bpy\text{-}(CH_2OH)_3)(PF_6)_2$ (104.0 mg, 0.1 mmol), and DMAP (6.0 mg, 0.05 mmol) were dissolved in CH_3CN (5 mL) at 0 °C. Then, DCC (146 mg, 0.8 mmol) dissolved in CH_2Cl_2 (5 mL) was added and the solution was stirred for 1 h. The solution was warmed up to room temperature and stirred for 4 h additionally. The precipitated DCU was filtered off. After CH_2Cl_2 was distilled off at low pressure, the resulting solid was filtered and recrystallized from acetone/ethyl acetate. Yellow red crystals were obtained with a 42% yield.

UV (acetone) $\lambda_{max}(\varepsilon)$ 460 nm (14400 M^{-1} cm^{-1}); FT-IR (KBr) 3058, 3007, 1723, 1590, 1551, 1277, 1109, 839, 753; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.66 (s, 12H), 7.40–7.53 (m, 6H), 7.74 (d, $J = 5.8$ Hz, 6H), 7.84 (d, $J = 5.8$ Hz, 6H), 7.95 (dd, $J = 7.8$, 7.8 Hz, 6H), 8.38 (d, $J = 7.8$ Hz, 6H), 8.49–8.54 (m, 12H), 8.69–8.71 (m, 6H), 9.00 (s, 6H), 9.30 (br s, 6H); MALDI TOF MS m/z 2155.5 $(M^+ + Na^+)^+$, calc. 2155.3.

4.3.12. Synthesis of star-shaped multi-nuclear ruthenium complexes; trimers, pentamers, and heptamers

4.3.12.1. General procedure for the synthesis of [Ru(L)$_2$(bpy-(CH$_2$OCO-bpyRu(bpy)$_2$)$_2$)](PF$_6$)$_6$; trimers. *Cis*-Ru(L)$_2$Cl$_2$· 2H$_2$O(L=bpy, phen, DTDP, 0.30 mmol) and AgPF$_6$ (151 mg, 0.6 mmol) were dissolved in degassed acetone (10 mL) and the mixture was stirred for 2 h at room temperature. After the AgCl was removed by filteration, the dendritic ligand, **5** (29 mg, 0.05 mmol) was added to the filtrate and the mixture was refluxed for 4 h. After it cooled down, excess aqueous NH_4PF_6 was added to the mixture for the anion exchange, and evaporated until the solid precipitated. The resulting solid was filtered and recrystallized from acetone/ethyl acetate. Brown crystals were obtained with 56–65% yields.

*4.3.12.2. [Ru(bpy)$_2$(bpy-(CH$_2$OCO-bpyRu(bpy)$_2$)$_2$)](PF$_6$)$_6$ (trimer-bpy; **10**).* Yield: 65%, UV (Acetone) $\lambda_{max}(\varepsilon)$ 448 nm (29 600 M^{-1} cm^{-1}); PL (acetone) 593 nm; FT-IR (KBr) 3121, 3081, 2334, 1727, 1598, 1465, 1289, 1133, 839, 753 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 5.44–5.54 (m, 4H), 7.38–7.49 (m, 2H), 7.50–7.65 (m, 14H), 7.87–7.93 (m, 2H), 7.98–8.11 (m, 16H), 8.15–8.25 (m, 12H), 8.32 (s, 2H), 8.65–8.82 (m, 16H), 8.88 (d, $J = 8.6$ Hz, 4 H); MALDI TOF MS *m*/*z* 2546.1 ((M−PF_6^-)$^+$, calc. 2546.7).

*4.3.12.3. [Ru(o-phen)$_2$(bpy-(CH$_2$OCO-bpyRu(o-phen)$_2$)$_2$)](PF$_6$)$_6$ (trimer-o-phen; **11**).* Yield: 60%, UV (acetone) $\lambda_{max}(\varepsilon)$ 441 nm (33 600 M^{-1} cm^{-1}); PL (acetone) 585 nm; IR (KBr) 3121, 3082, 2358, 1986, 1731, 1622, 1427, 1286, 1128, 838, 718 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 5.37–5.39 (m, 4H), 7.23–7.28 (m, 2H), 7.48–7.59 (m, 4H), 7.72–7.77 (m, 4H), 7.86–7.97 (m, 8H), 8.05–8.06 (m, 2H), 8.10–8.34 (m, 16H), 8.37–8.42 (m, 10H), 8.56–8.63 (m, 6H), 8.71–8.89 (m, 16H); MALDI TOF MS *m*/*z* 2691.5 ((M−PF_6^-)$^+$, calc. 2691.3).

*4.3.12.4. [Ru(DTDP)$_2$(bpy-(CH$_2$OCO-bpyRu(DTDP)$_2$)$_2$)](PF$_6$)$_6$ (trimer-DTDP; **12**).* Yield: 56%, UV (acetone) $\lambda_{max}(\varepsilon)$ 451 nm (24 400 M^{-1} cm^{-1}); PL (acetone) 587 nm; IR (KBr) 3101, 2972, 2937, 2873, 1747, 1602, 1427, 1290, 1124, 842 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.54–1.17 (m, 72H), 5.35 (br s, 4H), 7.22 (br s, 2H), 7.28–7.46 (m, 4H), 7.58–7.93 (m, 20H), 8.07–8.21 (m, 10H), 8.48–8.65 (m, 10H) 8.77–8.88 (m, 10H); MALDI TOF MS *m*/*z* 3352.7 ((M−PF_6^-+H^+)$^+$, calc. 3352.7).

4.3.13. General procedure for the synthesis of [Ru(L)(bpy-(CH$_2$OCO-bpyRu(L)$_2$)$_2$)$_2$](PF$_6$)$_{10}$; pentamers

Cis-Ru(L)$_2$Cl$_2$ · 2H$_2$O (L = bpy, phen, DTDP, 0.3 mmol) and AgPF$_6$ (151 mg, 0.6 mmol) were dissolved in degassed acetone (10 mL) and the mixture was stirred for 2 h at room temperature. After the AgCl was removed by filtration, the dendritic ligand, [Ru(bpy-(CH$_2$OCO-bpy)$_2$)$_2$(L)](PF$_6$)$_2$ (0.05 mmol) dissolved in DMF (5 mL) was added to the filtrate and the mixture was refluxed for 4 h. After it cooled down, excess aqueous NH_4PF_6 was added and evaporated until the solid precipitated. The solid was filtered and recrystallized from acetone/ethyl acetate. Brown crystals were obtained with 64–78% yields.

*4.3.13.1. [Ru(bpy)(bpy-(CH$_2$OCO-bpyRu(bpy)$_2$)$_2$)$_2$](PF$_6$)$_{10}$ (pentamer-bpy; **13**).* Yield: 70%, UV (acetone) λ_{max} (ε) 440 nm (51 200 M^{-1} cm^{-1}); PL (acetone) 595 nm; IR (KBr) 3121, 3081, 1735, 1598, 1465, 1285, 1125, 835, 757 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 5.49 (br s, 8H), 7.34–7.65 (m, 28H), 7.78–7.80 (m, 2H), 7.93–8.21 (m, 42H), 8.31–8.33 (m, 4H), 8.64–8.87 (m, 36H); MALDI TOF MS *m*/*z* 4378.2 ((M−PF_6^-)$^+$, calc. 4379.5).

*4.3.13.2. [Ru(o-phen)(bpy-(CH$_2$OCO-bpyRu(o-phen)$_2$)$_2$)$_2$](PF$_6$)$_{10}$ (pentamer-o-phen; **14**).* Yield: 78%, UV (acetone) λ_{max} (ε) 434 nm (57 600 M^{-1} cm^{-1}); PL (acetone) 590 nm; FT-IR (KBr) 3085, 1731, 1602, 1422, 1285, 1125, 838 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 5.31 (br s, 4H), 5.40 (br s, 4H), 7.14 (br s, 2H), 7.43–7.48 (m, 8H), 7.58–7.63 (m, 2H), 7.68–7.76 (m, 6H), 7.83–8.09 (m, 20H), 8.15–8.38 (m, 34H), 8.47–8.83 (m, 40H); MALDI TOF MS *m*/*z* 4597.5 ((M−PF_6^-+2H^+)$^+$, calc. 4595.5), 4453.3 ((M−2PF_6^-+3H^+)$^+$, calc. 4453.5).

*4.3.13.3. [Ru(DTDP)(bpy-(CH$_2$OCO-bpyRu(DTDP)$_2$)$_2$)$_2$](PF$_6$)$_{10}$ (pentamer-DTDP; **15**).* Yield: 64%, UV (acetone) λ_{max} (ε) 441 nm (56 800 M^{-1} cm^{-1}); PL (acetone) 591 nm; FT-IR (KBr) 3101, 2975, 1751, 1606, 1427, 1289, 1124, 842; ^{1}H NMR (400 MHz, acetone-d_6) δ 1.54–1.74 (m, 108H), 5.38–5.40 (m, 8H), 7.16 (br s, 2H), 7.38–7.49 (m, 10H), 7.58–7.63 (m, 6H), 7.70–8.01 (m, 22H), 8.08–8.25 (m, 20H), 8.43–8.61 (m, 18H), 8.72–8.87 (m, 16H); MALDI TOF MS *m*/*z* 5584.3 ((M−PF_6^-+2H^+)$^+$, calc. 5586.1) 4282.9 ((M−10PF_6^-)$^+$, calc. 4281.1).

4.3.13.4. General procedure for synthesis of [Ru(bpy-(CH$_2$OCO-bpyRu(L)$_2$)$_2$)$_3$](PF$_6$)$_{14}$; heptamers. *Cis*-Ru(L)$_2$Cl$_2$ · 2H$_2$O (L = bpy, phen, DTDP, 0.30 mmol) and AgPF$_6$ (151 mg, 0.6 mmol) were dissolved in degassed acetone (10 mL) and the mixture was stirred for 2 h at room temperature. After the AgCl was removed by filtration, the dendritic ligand, [Ru(bpy-(CH$_2$OCO-bpy)$_2$)$_3$]-(PF$_6$)$_2$ (0.05 mmol) dissolved in DMF (5 mL) was added to the filtrate and the mixture was refluxed for 4 h. After it cooled down, excess aqueous NH_4PF_6 was added and evaporated until the solid precipitated. The solid was filtered and recrystallized from acetone/ethyl acetate. Brown crystals were obtained with 56–79% yields.

*4.3.13.5. [Ru(bpy(CH$_2$OCO-bpyRu-(bpy)$_2$)$_2$)$_3$](PF$_6$)$_{14}$ (heptamer-bpy; **16**).* Yield: 70%, UV (acetone) $\lambda_{max}(\varepsilon)$ 439 nm (59 600 M^{-1} cm^{-1}); PL (acetone) 598 nm; IR (KBr) 3121, 3077, 2365, 1735, 1602, 1465, 1290, 1128, 838, 761; ^{1}H NMR (400 MHz, CD_3CN) δ 5.43 (s, 12H), 7.32–7.49 (m, 36H), 7.71–7.87 (m, 42H), 8.04–8.12 (m, 30H), 8.47–8.58 (m, 48H); MALDI TOF MS *m*/*z* 6425.0

$((M+3Na^+)^+$, calc. 6425.1), 6448.1 $((M+4Na^+)^+$, calc. 6448.3), 5342.6 $((M-7PF_6^-+H^+)^+$, calc. 5342.4), 5048.2 $((M-9PF_6^-)^+$, calc. 5051.5).

*4.3.13.6. [Ru(bpy-(CH$_2$OCO-bpyRu(o-phen)$_2$)$_2$)$_3$] (PF$_6$)$_{14}$ (heptamer-o-phen; **17**).* Yield: 79%, UV (acetone) λ_{max} (ε) 439 nm (70 400 $M^{-1}\,cm^{-1}$); PL (acetone) 595 nm; FT-IR (KBr) 3089, 1990, 1731, 1618, 1430, 1286, 1128, 838; ^{1}H NMR (400 MHz, CD_3CN) δ 5.42 (br s, 12H), 7.41–7.46 (m, 12H), 7.55–7.57 (m, 6H), 7.67–7.7.89 (m, 32H), 7.99–8.12 (m 12H), 8.14–8.36 (m, 48H), 8.48–8.51 (m, 10H), 8.59–8.71 (m, 36H); MALDI TOF MS *m/z* 6548.9 $((M+4H^+)^+$, calc. 6648.7), 6376.3 $((M-2PF_6^-+Na^+)^+$, calc. 6377.7), 6356.5 $((M-2PF_6^- +2H^+)^+$, calc. 6356.7).

*4.3.13.7. Tris{4,4′-bis[(methyl 2,2′-bipyridine-5-carboxylate)bis(1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta-[1]phenanthren-2-one)ruthenium(II)]-2,2′-bipyridine} ruthenium(II) teradecakis(hexafluorophosphate) [Ru(bpy-(CH$_2$OCO-bpyRu(DTDP)$_2$)$_2$)$_3$](PF$_6$)$_{14}$ (heptamer-DTDP; **18**).* Yield: 56%, UV (acetone) λ_{max}(ε) 428 nm (77 600 $M^{-1}\,cm^{-1}$); PL (acetone) 601 nm; FT-IR (KBr) 3097, 2976, 2878, 1747, 1602, 1465, 1426, 1379, 1281, 1125, 1050, 842; ^{1}H NMR (400 MHz, CD_3CN) δ 1.56–1.69 (m, 144H), 5.32 (br s, 12H), 7.35–7.41 (m, 12H), 7.61 (br s, 18H), 7.72–7.79 (m, 18H), 7.87 (br s, 6H), 7.98–8.25 (m, 32H), 8.43 (br s, 6H), 8.56–8.71 (m, 22H), 8.79–8.87 (m, 18H); MALDI TOF MS *m/z* 6513.25 $(M-10PF_6^-)^+$, calc. 6515.5.

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References

[1] G.R. Newkome, E. He, C.N. Moorefield, Chem. Rev. 99 (1999) 1689–1746.
[2] (a) D.A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, Polym. J. 17 (1985) 117–132;
(b) G.R. Newkome, C.D. Weis, C.N. Moorefield, I. Weis, Macromolecules 30 (1997) 2300–2304;
(c) G.R. Newkome, Z. Yao, G.R. Baker, V.K. Gupta, J. Org. Chem. 50 (1985) 2003–2004.
[3] (a) A.W. Bosman, H.M. Janssen, E.W. Meijer, Chem. Rev. 99 (1999) 1665–1688;
(b) D.A. Tolmalia, A.M. Naylor, W.A. Goddard III, Angew. Chem., Int. Engl. 29 (1990) 138–175.
[4] (a) P. Bhyrappa, J.K. Young, J.S. Moore, K.S. Suslick, J. Am. Chem. Soc. 118 (1996) 5708–5711;
(b) T.R. Krishna, N. Jayaraman, Tetrahedron 60 (2004) 10325–10334;
(c) A.W. Freeman, S.C. Koene, P.R.J. Malenfant, M.E. Thompson, J.M.J. Frechet, J. Am. Chem. Soc. 122 (2000) 12385–12386;
(d) N.D. McClenaghan, F. Loiseau, F. Puntoriero, S. Serroni, S. Campagna, Chem. Commun. (2001) 2634–2635.
[5] (a) S.-C. Lo, E.B. Namdas, P.L. Burn, I.D. Samuel, Macromolecules 36 (2003) 9721–9730;
(b) J.A. Barron, S. Bernhard, P.L. Houston, H.D. Abruna, J.L. Ruglovsky, G.G. Malliaras, J. Phys. Chem. A. 107 (2003) 8130–8133;
(c) G.R. Newkome, E. He, L.A. Godinez, G.R. Baker, J. Am. Chem. Soc. 122 (2000) 9993–10006;
(d) E.C. Constable, P. Harverson, J.J. Ramsden, Chem. Commun. (1997) 1683–1684.
[6] (a) W.-Y. Lee, Mikrochim. Acta 127 (1997) 19–39;
(b) W.-Y. Lee, T.A. Nieman, Anal. Chem. 67 (1995) 1789–1796;
(c) A.W. Knight, G.M. Greenway, Analyst 121 (1996) 101R–106R;
(d) R.D. Gerardi, N.W. Barnett, S.W. Lewis, Anal. Chim. Acta 378 (1999) 1–41;
(e) I. Rubinstein, A.J. Bard, Anal. Chem. 55 (1983) 1580–1582;
(f) J.B. Noffsinger, N.D. Danielson, Anal. Chem. 59 (1987) 865–868;
(g) S.N. Brune, D.R. Bobbitt, Talanta 38 (1991) 419–424;
(h) S.N. Brune, D.R. Bobbitt, Anal. Chem. 64 (1992) 166–170;
(i) K. Uchikura, M. Kirisawa, Chem. Lett. (1991) 1373–1376;
(j) T.M. Downey, T.A. Nieman, Anal. Chem. 64 (1992) 261–268;
(k) A.F. Martin, T.A. Nieman, Anal. Chim. Acta 281 (1993) 475–481;
(l) X. Chen, M. Sato, Anal. Sci. 11 (1995) 749–754;
(m) M. Zorzi, P. Pastore, F. Magno, Anal. Chem. 72 (2000) 4934–4939;
(n) N.E. Tokel, A.J. Bard, J. Am. Chem. Soc. 94 (1972) 2862–2863.
[7] (a) I. Rubinstein, A.J. Bard, Anal. Chem. 55 (1983) 1580–1582;
(b) J.B. Noffsinger, N.D. Danielson, Anal. Chem. 59 (1987) 865–868;
(c) W. Miao, J.–P. Choi, A.J. Bard, J. Am. Chem. Soc. 124 (2002) 14478–14485.
[8] (a) D.N. Lee, H.S. Park, E.H. Kim, Y.M. Jun, J.-Y. Lee, W.-Y. Lee, B.H. Kim, Bull. Korean Chem. Soc. 27 (2006) 99–105;
(b) D.N. Lee, J.K. Kim, H.S. Park, Y.M. Jun, R.Y. Hwang, W.-Y. Lee, B.H. Kim, Synth. Met. 150 (2005) 93–100.
[9] C.A. Panetta, H.J. Kumpaty, N.E. heimer, M.C. Leavy, C.L. Hussey, J. Org. Chem. 64 (1999) 1015–1021.
[10] S. Bernhard, P. Belser, Synthesis (1996) 192–194.
[11] G.D. Storrier, K. Takada, H.D. Abruña, Langmuir 15 (1999) 872–884.
[12] I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C.A. Bignozzi, P. Qu, G.J. Meyer, Inorg. Chem. 40 (2001) 6073–6079.
[13] B.P. Sullivan, D.J. Salmon, T.J. Meyer, Inorg. Chem. 17 (1978) 3334–3341.