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Photocatalytic Styrene Polymerization by Novel Bichromophoric Pd Catalyst Having Long Excited-state Lifetime

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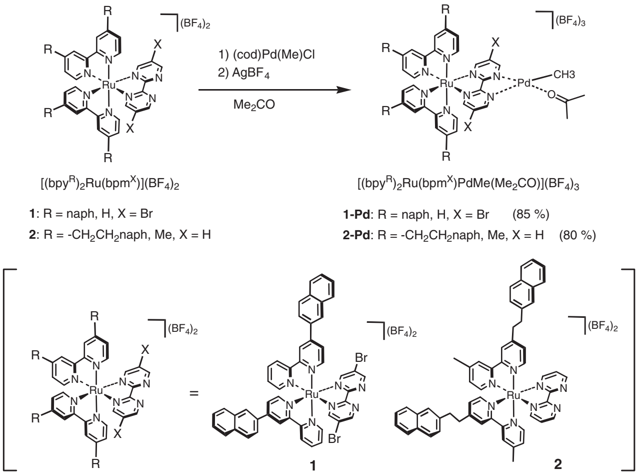
The reaction of the novel bichromophoric Pd complexes with styrene resulted in the formation of polymer or dimer by UV–vis light irradiation, depending upon the connectivity of the naphthyl moiety. The Pd complex having the bichromophore with a Ru(II)–polypyridyl and a naphthyl moiety connected by a single σ bond contained long-lived ^{3}MLCT emitting species.

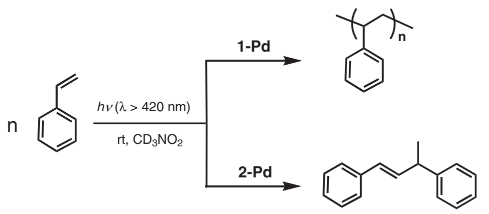
Utilization of abundant and inexhaustible solar energy in chemical reactions has attracted much attention because of recent serious issues such as global climate variation and shortage of fossil fuels.[1] In the field of coordination chemistry, several systematic studies on catalytic transformation promoted by visible light, such as CO_2 reduction and hydrogen production from water, have been presented,[2] but the variety of reactions is still limited. In these studies, Ru(II)–polypyridyl complexes are widely used as a visible-light-absorbing photoactive component because they show outstanding photophysical properties such as long excited-state lifetimes and high luminescent efficiencies.[3] Additionally, there have been increasing attempts to control the photophysical properties of Ru(II)–polypyridyl complexes through various modifications, especially with focus on extending the excited-state lifetime. Chromophores with long excited-state lifetime are highly desirable for use in diffusion-rate-limited multicomponent systems, which are involved in photoinduced energy and/or electron-transfer processes.[4] One method to extend the lifetime is the use of a bichromophoric system, in which peripheral arene units such as naphthalene, anthracene, and pyrene are linked to the Ru(II)–polypyridyl moiety. Syntheses and photochemical processes of such bichromophores have been reported recently.[5] However, these works mainly focus on clarifying the mechanism responsible for the lifetime extension by kinetic measurements. We have been interested in utilizing light energy for catalytic transformation of organic molecules. In our previous papers, we described that Pd catalysts, which possess the Ru(II)–polypyridyl moiety bridged by various 2,2′-bipyrimidines (bpm^X), $[(bpy)_2Ru(bpm^X)PdMe(Me_2CO)]^{3+}$, catalyzed selective dimerization of α-methylstyrene upon visible-light irradiation.[6] In this communication, we extend our earlier studies to the bichromophoric system to achieve a new type of catalytic transformation.



Scheme 1. Synthesis of bichromophoric Pd complexes.

Novel bichromophoric Ru complexes $[(bpy^R)_2Ru(bpm^X)](BF_4)_2$ (**1**: R = naph, H, X = Br, **2**: R = –CH$_2$CH$_2$naph, Me, X = H) have been synthesized through the reaction of the corresponding dichloride complex, $(bpy^R)_2RuCl_2$, with bpm^X in DMF according to a modified procedure of a published method.[7] The corresponding Pd complexes were then prepared by treatment of **1**/**2** with (cod)PdMeCl, followed by Cl$^-$ abstraction by $AgBF_4$ (Scheme 1). The Pd complexes possess two types of bichromophoric Ru moieties: Ru–polypyridyl with naphthalenes directly linked by a σ C(sp^2)–C(sp^2) bond and with naphthalenes linked by an ethylene chain. We previously showed that introduction of the electron-withdrawing Br group on bipyrimidines led to the preferential MLCT transition toward the bipyrimidine ligand, which resulted in the drastic acceleration of photocatalytic dimerization of α-methylstyrene.[6] Since the directly linked naphthyl moiety was shown to act as a slightly electron-withdrawing group as revealed by CV data,[8] 5,5′-dibromobipyrimidine was adopted as the bridging ligand of **1**. All the novel Ru···Pd complexes were unambiguously determined on the basis of ^{1}H and ^{13}C NMR spectral data.[9]

We previously reported that the unichromophoric complexes, which do not have the peripheral aromatic chromophores, catalyze styrene dimerization to give 1,3-diphenyl-1-butene selectively.[10] In order to investigate the bichromophoric effect, catalytic reaction with styrene was conducted using **1-Pd** and **2-Pd** as catalysts. A nitromethane solution of styrene which contains a catalytic amount of the Ru···Pd complex (2 mol %) was irradiated by Xe lamp (150 W, $\lambda > 420$ nm) at room temperature under N_2 atmosphere. Under these conditions, **1-Pd** promoted the polymerization of styrene selectively although conversion was relatively low mainly due to catalyst decomposition (42% conversion after 12 h). The reaction mixture became emulsive with the formation of polymer, which also seems to hinder the reaction owing to inefficient light transmittance. The styrene polymer was collected by precipitation,



Scheme 2. Photocatalytic reaction with styrene.

Table 1. Products formed in the reaction of styrene[a]

Entry	Catalyst	Conv. /%	Product /%
1	**1-Pd**	40	polymer (33%)[b]
2	**2-Pd**	8	dimer (4%)[c]
3	$[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{Br}})\mathrm{PdMe}(\mathrm{Me_2CO})]^{3+}$	48	dimer (48%)[c]
4	$[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{Br}})\mathrm{PdMe}(\mathrm{Me_2CO})]^{3+}$ + 2 naphthalene	43	dimer (40%)[c]
5	**1** + $[(\mathrm{bpm})\mathrm{PdMe}(\mathrm{Me_2CO})]\mathrm{BF_4}$	0	N. R.[d]

[a]After 8 h of irradiation in CH_3NO_2 solution. [b]Isolated yield. [c]NMR yield. [d]N. R.: no reaction.

washed with MeOH, extracted with $CHCl_3$, and then filtered. GPC measurement of the isolated polymer showed molecular weight of $M_w = 3900$ with molecular weight distribution of $M_w/M_n = 1.4$.[13] In contrast to the above-mentioned reaction, styrene dimer was formed in the reaction of **2-Pd** under the same condition (Scheme 2). To be mentioned is that the reactions proceed similarly under UV-light irradiation (high-pressure Hg lamp) giving polymer or dimer depending on the catalyst used. The reactions did not proceed in dark (<5% conversion).

To confirm the bichromophoric effect of **1-Pd**, we have conducted the reaction using 1:1 mixture of (1) $[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{Br}})\mathrm{PdMe}(\mathrm{Me_2CO})](\mathrm{BF_4})_3$ ($\mathrm{bpm}^{\mathrm{Br}}$ = 5,5′-dibromo-2,2′-bipyrimidine) + naphthalene (1:2 molar ratio) (Table 1, Entry 4) and (2) **1** + $[(\mathrm{bpm})\mathrm{PdMe}(\mathrm{Me_2CO})]\mathrm{BF_4}$ (Table 1, Entry 5). In the reactions using the catalysts other than **1-Pd**, the main product was the styrene dimer. These results clearly indicate that the direct connection of naphthalene to Ru(II)–polypyridyl chromophore through a σ bond is necessary for an active polymerization catalyst.[11]

Photophysical data of the bichromophoric Ru complexes and those of the reference unichromophoric complexes are summarized in Table 2. UV–vis absorption spectra of the Ru···Pd complexes, **1-Pd** and **2-Pd**, in deaerated acetonitrile show extended absorption from the UV to visible region, which is dominated by ^{1}MLCT and ^{1}LC bands (Figure S1).[13] Marked increase of ε of the MLCT band in **1-Pd** and **2-Pd** upon introducing the naphthyl moiety indicates the intraligand electron delocalization in the MLCT excited state.[12]

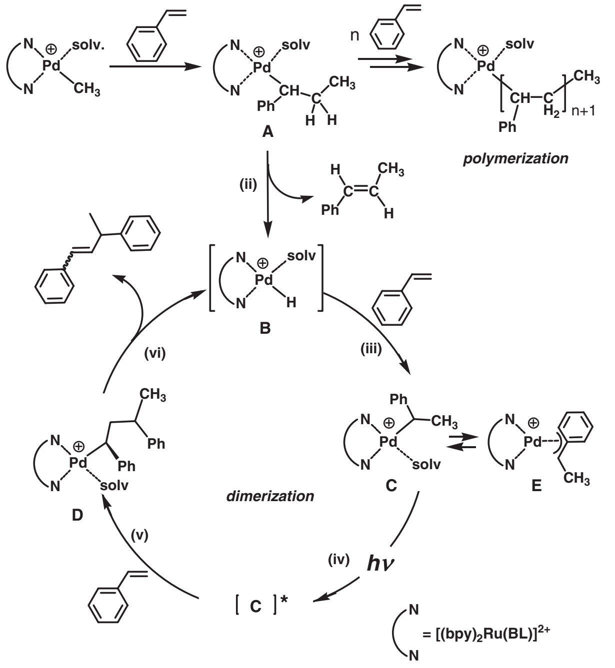
Luminescence spectra of **1-Pd** and **2-Pd** showed marked differences. When the ^{1}MLCT absorption is excited ($\lambda_{ex} = 450$ nm), the phosphorescence typical of ^{3}MLCT is observed around 650 nm, but **1-Pd** has much weaker luminescence compared to those of $[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm})]^{2+}$ and **2-Pd** (Figure S2).[13] In the luminescence spectra obtained by excitation of the aromatic chromophores ($\lambda_{ex} = 300$ nm), no fluorescence from the naphthalene moiety but the phosphorescence originating from the Ru(II) ^{3}MLCT state was observed. This indicates the efficient energy transfer from the naphthalene moiety to the Ru center for both complexes. Thus the UV-light irradiation also promoted the catalytic reaction by energy transfer.

Based on a proposed reaction mechanism reported previously,[6] the reason for the product variation can be attributed to the excited-state lifetime. We have conducted time-resolved fluorescence experiments for **1**, **2**, and their Pd complexes. The decay profiles collected around 650 nm could be well fitted with a single exponential function for **2** and **2-Pd** but with a biexponential function for **1** and **1-Pd** (Table 2). Unichromophoric Ru complexes with various bipyrimidine ligands possess the excited-state lifetime of around 90 ns (Table 2), and those of the corresponding Ru···Pd complexes do not vary much. The lifetime values for **1** and **1-Pd** contained long emitting species (>1 µs) with a relative contribution of 16% and 27%, respectively. We previously claimed that excitation of the Pd–alkyl intermediate accelerates the second insertion step of α-methylstyrene which is the rate-determining step in the catalytic cycle (Scheme 3).[6] If the lifetime of the Pd–alkyl species **A** is comparable to the corresponding starting compound **1-Pd** or **2-Pd**, it can be expected that the long excited-state species **A*** should largely contribute in the reaction of **1-Pd**, and the insertion of styrene is accelerated prior to the β-H elimination step, resulting in the polymer chain growth.

Table 2. Electronic absorption and luminescence data[a]

Complex	Absorption (^{1}MLCT)	Luminescence at 298 K[b]		
	λ_{max} /nm ($\varepsilon/10^4\,\mathrm{M^{-1}\,cm^{-1}}$)	λ_{max} /nm	ϕ^c	τ /ns
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{H}})](\mathrm{BF_4})_2$	423 (1.20)	659	0.09	90.3
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{Br}})](\mathrm{BF_4})_2$	416 (1.40), 498 (sh)	661	0.14	94.8
$[(\mathrm{bpy}^{\mathrm{naph}})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{H}})](\mathrm{PF_6})_2$	461 (2.37)	669	0.22	—[d]
$[(\mathrm{bpy}^{\mathrm{naph}})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{Br}})](\mathrm{BF_4})_2$ (**1**)	431 (1.91), 498 (sh)	645	0.19	76.0 (84%), 1.29 × 10^3 (16%)
$[(\mathrm{bpy}^{\mathrm{CH_2CH_2naph}})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{H}})](\mathrm{BF_4})_2$ (**2**)	436 (1.59)	705	0.02	67.5
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{H}})\mathrm{PdMe}(\mathrm{Me_2CO})](\mathrm{BF_4})_3$	425 (1.70)	647	0.11	105.2[e]
$[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{Br}})\mathrm{PdMe}(\mathrm{Me_2CO})](\mathrm{BF_4})_3$	418 (1.20), 498 (sh)	697	0.02	—[d]
$[(\mathrm{bpy}^{\mathrm{naph}})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{Br}})\mathrm{PdMe}(\mathrm{Me_2CO})](\mathrm{BF_4})_3$ (**1-Pd**)	433 (1.82), 500 (sh)	654	0.21	94.3 (73.1%), 1.01 × 10^3 (26.9%)
$[(\mathrm{bpy}^{\mathrm{CH_2CH_2naph}})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{H}})\mathrm{PdMe}(\mathrm{Me_2CO})](\mathrm{BF_4})_2$ (**2-Pd**)	431 (1.70)	696	0.03	61.1

[a]Measurements were carried out in deaerated CH_3CN solution at room temperature. [b]Luminescence irradiated at 450 nm. [c]Relative quantum yield vs. $[(\mathrm{bpy})_3\mathrm{Ru}]^{2+}$. [d]Not measured. [e]Data for MeCN coordinated complex $[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{bpm}^{\mathrm{H}})\mathrm{PdMe}(\mathrm{MeCN})](\mathrm{PF_6})_2(\mathrm{BF_4})$.



Scheme 3. Proposed reaction mechanism of styrene polymerization and dimerization.

In summary, we have synthesized novel Pd complexes which possess a bichromophoric moiety consisting of naphthyl and Ru(II)–polypyridyl chromophores. The complexes were active toward catalytic polymerization/dimerization of styrene under both UV–vis light irradiated condition. The reaction pathway to give either a polymer or a dimer seems to be determined by the excited-state lifetime of the catalysts.

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9 Complexes were spectroscopically determined using mixtures of stereoisomers based on the geometry of naphthyl ligand. Physical properties of the single isomer of **1** isolated by column chromatography showed similar properties as those of a nonisolated mixture (including excited-state lifetime). Thus mixtures of the isomers were used for the reactivity studies.

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