Bull. Chem. Soc. Jpn., **75**, 1159–1162 (2002) 1159

Development of New Three Component Photo-Polymerization Systems Efficient Even Near the Infrared Region

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(Received November 9, 2001)

Several visible light initiators of polymerization have been reported mainly as a two component system consisting of a radical-generator and a sensitizing dye possessing absorption bands from 400 to 550 nm. Electron transfer from the excited dye to the radical-generator has been proposed for the two component system. For the purpose of improving the sensitivity and extending light wave length up to near the infrared region, a three component visible light-initiating system has been explored— the combination of a bimolecular visible light-initiating system and electron-donating subsidiary additives. We think if electron transfer from the donor to the excited dye takes place, the dye radical would be generated before the de-excitation of the dye. The generated dye radical should be a better electron donor to the radical-generator because the de-excitation process is blocked by filling the singly occupied HOMO of the excited dye. We tested electron donors such as ferrocene, ruthenocene, (*E*)-9-julolidinylruthenocenylethylene (*E*-**J-Ru**), and *p*-dimethylaminocinnamylruthenocen (*E*-**DA-Ru**) as the electron-donating additives, various sensitizing dyes, and radical generators. When *E*-**J-Ru** or *E*-**DA-Ru**, the cyanine dyes, and 2,4,6-tris(trichloromethyl)-1,3,5-triazine **TCT** were selected, the new three component system worked more efficiently than the corresponding two component system, even near the infrared region.

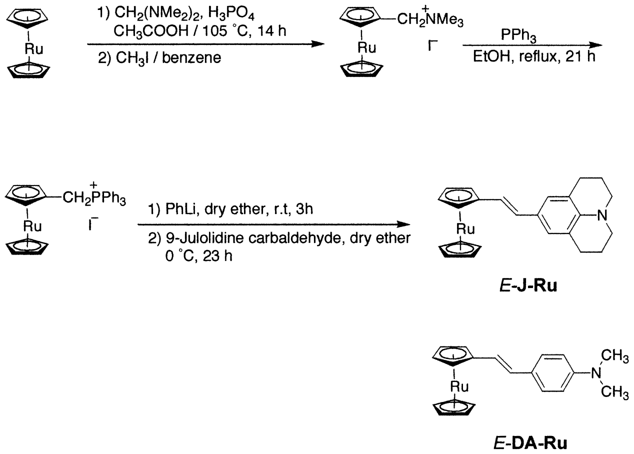
Among recent image recording processes, photo-polymerization is receiving much attention as a widely applicable process replacing the silver salts process, and various efforts have been exerted for sensitivity enhancement as a primary requirement.[1] Furthermore, as the visible light-polymerization system is usually initiated by light up to 550 nm, extension of the light range to the near infrared region is an urgent necessity from the viewpoint of semiconductor laser directing imaging processes.[1,2] Two component photo-initiating systems consisting of radical generators and sensitizing dyes are basic for use in the visible light region.[3,4] For the purpose of improving both sensitivity and for light range extension, a combination of the two component visible light-initiating system and electron donating subsidiary additives is proposed here. Although the combination of sensitizing dye-radical generator-reductant is known as a typical three component system,[5] we would like to demonstrate a new three component system in which electron donors play an important role in maintaining the electron donating ability of the excited dye by dye radical formation.

Experimental

Measurements. Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a JASCO FT/IR-5000 spectrometer. UV/vis spectra were measured with a HITACHI UV-288 spectrophotometer. ^{1}H (chemical shifts referenced to $CDCl_3$ at δ 7.26) and ^{13}C (chemical shifts referenced to $CDCl_3$ at δ 77.00) NMR spectra were recorded on a Varian VXR-200 spectrometer, or a Varian VXR-500 spectrometer. Elemental analysis was performed by a Yanagimoto C.H.N. corder MI-2 type. Cyclic voltammograms were recorded on a Yanaco Polarographic Analyzer P-1100.

Materials. Sensitizing dyes **1**–**6** were purchased from Hayashibara Biochemical Laboratories. The radical-generating reagent, **TCT**, was purchased from Midori Kagaku Co., Ltd. The polymer for photographic measurement was a matrix polymer: polyacrylate caboset XPD-2000 (B.F. Goodrich, MW. 30,000, acid value 75). As a poly-functional monomer, pentaerythritol triacrylate (PETA) was purchased from Shin Nakamura Kagaku Kogyo Co., Ltd. Ferrocene and ruthenocene were purchased from Aldrich Chemical Company Inc.

Triphenyl(ruthenocenylmethyl)triphenylphosphonium iodide was prepared according to the literature method.[6] The route of synthesis of the new compound *E*-**J-Ru** is shown in Scheme 1.



Scheme 1. Preparation of *E*-**J-Ru** and *E*-**DA-Ru**.

Synthesis of (*E*)-9-Julolidinylruthenocenylethylene (*E*-J-Ru). Phenyllithium-cyclohexane 1.6 M solution (2.9 mL) was added to a suspension of tripenyl(ruthenocenylmethyl)phosphonium iodide (0.694 g, 1.10 mmol) in freshly distilled ether (10 mL) under an atmosphere of argon. The mixture was stirred for 3 h at rt. under an atmosphere of argon, after formation of the corresponding phosphorane was complete. A solution of julolidine-9-carbaldehyde (0.29 g, 1.44 mmol) in freshly distilled ether was added slowly at 0 °C, and the mixture was stirred for 23 h at 10 °C under an atmosphere of argon. The mixture was filtered and the precipitate was washed with ether, then the organic layer was evaporated under reduced pressure. The residue was chromatographed on silica gel eluting with hexane : AcOEt = 9 : 1, then only *E*-**J-Ru**) (0.141 g, 0.328 mmol, 30% yield) was obtained as pale yellow plates, which gradually decomposed on heating at 114 °C for elimination of crystal water: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (4H, qa, J = 5.5 Hz, 6.5 Hz), 2.74 (4H, t, J = 5.5 Hz), 3.13 (4H, t, J = 6.5 Hz), 4.50 (5H, s, Cp), 4.56 (2H, m, substituted Cp), 4.82 (2H, m, substituted Cp), 6.44 (1H, d, J = 16.5 Hz, olefin), 6.49 (1H, d, J = 16.5 Hz, olefin), 6.82 (2H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.11, 27.68, 50.03, 68.76, 70.18, 70.92, 88.97, 120.31, 121.50, 124.66, 125.42, 126.49, 142.20; FT IR (KBr) ν_{max} 1605, 1313 , 1100, 957, and 806 cm^{-1}; UV (CH_2Cl_2) λ_{max} 328 nm (log ε = 4.22); mp 136–137 °C (from EtOH); Anal. Calcd for $C_{24}H_{25}$ NRu·1/2H_2O: C, 65.88; H, 5.99; N,3.20%. Found: C, 65.72; H, 5.70;N, 2.97%:

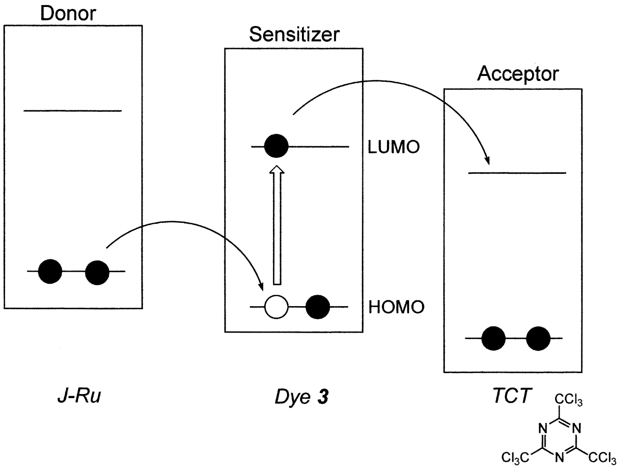
Measurement of Photographic Sensitivity. The photosensitive layer was prepared by coating 2-ethoxyethanol solution of the photosensitive composition onto a grained aluminum plate; the coating was dried to form a 1-2 µm-thick layer. Furthermore, an aqueous solution of poly(vinyl alcohol) was coated on it in order to eliminate inhibition of polymerization by oxygen. Test plates were prepared which possess photosensitive layers consisting of different concentrations of sensitized dye and *E*-**J-Ru** or *E*-**DA-Ru**. The photographic sensitivity (E, mJ/cm^2) was measured by counting the minimum exposing light intensity after exposing the photosensitive layer through a 21step tablet (Kodak no. 2 step tablet) with a 150 W xenon arc lamp. Use of an appropriate glass filters allowed selection of the wavelength of the exposing light. The exposed photosensitive layer was developed in an aqueous alkaline solution, and the plate was toned by printing ink. The sensitivity was defined as the minimum E for polymerization of the layer, and is calculated from

$$E = I_0 \times T \times t \qquad (1)$$

where I_0 is the incident light intensity (mJ/cm^2·s), T is the transmittance of the step at which the photosensitive layer begins to be polymerized and t is exposure time(s).

Results and Discussion

Our strategy for construction of the three component visible light initiating polymerization system is as follows: Generally, electron transfer from the excited dye to the activator is a common process, but deactivation of the excited dye to ground state blocks free radical generation from a two component dye-**TCT** system. Electrons involved in the reaction are generated in the half occupied LUMO of excited dyes upon irradiation. To initiate the radical reaction, the electrons should attack **TCT** before any deactivation takes place. If an excited dye accommodates an electron in its half filled HOMO, the deactivation process through de-excitation should be blocked due to formation of the corresponding radical with filled HOMO. The radical probably has a longer lifetime than the excited dye, and the radial should have a high probability of electron transfer to **TCT**. The concept of the three component system is shown in terms of HOMO and LUMO energy levels in Scheme 2.



Scheme 2. The concept of three component system in terms of HOMO and LUMO energy levels.

In order to maximize sensitivity of the three component system, we tested electron donors such as ferrocene, ruthenocene, *E*-**J-Ru**, and *E*-**DA-Ru** as the additives and sensitizing dyes: 2-[3-(1-ethyl-3,3-dimethyl-2,3-dihydro-1*H*-indol-2-ylidene)-1-propenyl] -1-ethyl-3,3-dimethyl-3*H*-indolium iodide (**1**), 2-[5-(1-ethyl-3,3-dimethyl-2,3-dihydro-1*H*-indol-2-ylidene)-1,3-pentadienyl]-1-ethyl-3,3-dimethyl-3*H*-indolium iodide (**2**), 2-[7-(1-ethyl-3,3-dimethy-2,3-dihydro-1*H*-indol-2-ylidene)-1,3, 5-heptatrienyl]-1-ethyl-3,3-dimethyl-3*H*-indolium iodide (**3**), 3-Ethyl-2-[3-(3-ethyl-3*H*-benzothiazol-2-ylidene)-1-propenyl]benzothiazol-3-ium iodide (**4**), 2-(4-butylaminocinnamyl)-6-methyl-4*H*-pyran-4-ylidene]propanedinitrile (**5**), and 3,3′-carbonylbis(7-dibutylamino-2*H*-chromen-2-one) (**6**) shown in Fig. 1. An appropriate sensitizing dye was selected from **3**–**6** by comparing the sensitivities measured both in the presence and absence of *E*-**J-Ru**. Only cyanine **3** increased in sensitivity by addition of *E*-**J-Ru**. Light absorption properties and oxidation potentials of these sensitizing dyes are summarized in Table 1. Oxidation potentials of electron donors used here are summarized in Table 2.

Ferrocene is a promising donor because its oxidation potential (0.49 V), except its d–d absorption bands (500 nm) should present an obstacle for utilization of light in this visible region. We selected *E*-**DA-Ru** from p-substitutedcinnamylruthenocenes as an efficient electron- donating subsidiary additive because its oxidation potential was 0.48 V, the lowest in the series. On this line, *E*-**J-Ru** was prepared here and its oxidation potential was measured to be 0.34 V.[7] From **3**–**6** , **3** as an appropriate sensitizing dye was selected by comparing sensitivities measured both in the presence and absence of *E*-**J-Ru**. The sensitivity was increased only by the addition of *E*-**J-Ru** to **3**, as shown in Table 3. For radical generators, **TCT** was selected from **TCT**, ferrocenium salt, *N*-phenylglycine, borate

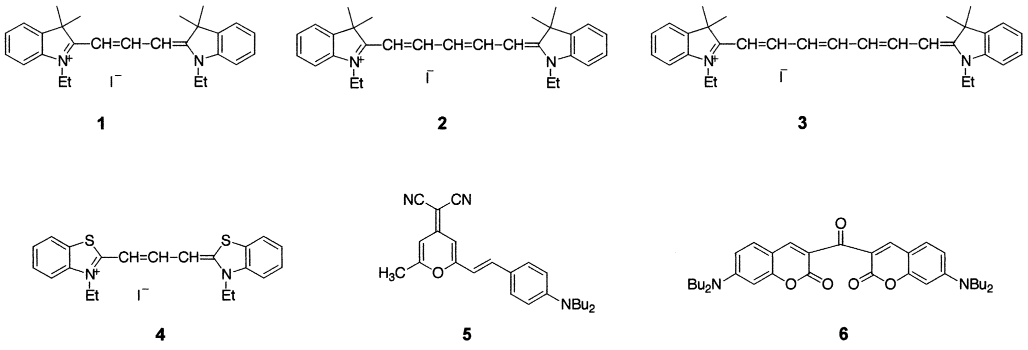


Fig. 1. Sensitizing dyes.

Table 1. Light Absorption Properties and Oxidation Potentials (E_{pa}) of Sensitizing Dyes

Dye	λ_{max}/nm[a)]	ε_{max}	Oxidation potential/V[b)]
1	546	133,000	1.16
2	640	241,000	0.87
3	742	286,000	0.65
4	557	153,000	0.95
5	485	51,000	0.96
6	463	96,200	1.35

a) Solvent for **1**, **2**, **3**, and **4** was MeOH. That for **5** and **6** was CH_2Cl_2.
b) Reference electrode was used Ag/AgCl in *N*,*N*-dimethylformamide containing 0.1 M *n*-Bu_4NClO_4.

Table 2. Oxidation Potentials (E_{pa}) of Electron Donors

Electron donor	Oxidation potential/V[a)]
E-**J-Ru**	0.34
E-**DA-Ru**	0.48
Ruthenocene	1.08
Ferrocene	0.49

a) Reference electrode was used Ag/AgCl in *N*,*N*-dimethylformamide containing 0.1 M *n*-Bu_4NClO_4.

Table 3. Sensitivity of Photoinitiating System with Various Dyes[a)]

Entry	Dye	Rutenocene compound	Exposing wavelength/nm[b)]	Sensitivity mJ/cm^2
1	**3**	none	≥ 680	230
2	**3**	*E*-**J-Ru**	≥ 680	81
3	**4**	none	540	0.7
4	**4**	E-**J-Ru**	540	1.5
5	**5**	none	490	1.7
6	**5**	E-**J-Ru**	490	3.5
7	**6**	none	490	0.6
8	**6**	E-**J-Ru**	490	0.5

a) Composition of the photosensitive layer (parts by weight): matrix polymer (100), polyfunctional monomer (100), TCT (8), sensitizing dye (2), ruthenocene compound (0.5). b) Glass filters were used for selection of wavelength as follows: R-68 (≥ 680 nm); Y-52 and KL-54 (540 nm); Y-47 and KL-49 (490 nm).

Table 4. Sensitivity of Photoinitiating System in Three Component System with **1**[a)] or **3**[b)], **TCT**, and Various Donors[c)]

Cyanine dye	Electron donor	Sensitivity mJ/cm^2	Relative efficiency ratio[d)]
1	none	103	1
1	*E*-**J-Ru**	4.5	23
3	none	270	1
3	*E*-**J-Ru**	23	11
3	Ruthenocene	160	1.7
3	Ferrocene	220	1.2

a) Glass filter Y52, KL54, HA 30 (transparent at 540 nm).
b) Glass filter R-68 (transparent > 680 nm) was used.
c) Composition of the photosensitive layer (parts by weight): matrix polymer (100), polyfunctional monomer (100), **TCT** (8), sensitizing dye (1), electron donor (1).
d) The relative efficiency ratio of three conponent system to the correspoding two component system.

salt, and diphenyliodonium salt by comparing sensitivities. Sensitivities were measured in three component systems, cyanine **3**-**TCT**- above donors, summarized in Table 4. Colorless *E*-**J-Ru** and **DA-Ru** were found to be efficient donors. Surprisingly even considering its visible light absorption, brownish ferrocene was the least efficient, inferior to that of ruthenocene possessing a high oxidation potential (1.08 V).

Stern–Volmer plots of fluorescence efficiencies of cyanine-**3** against TCT were nonlinear (Fig. 2). In the presence of E-**J-Ru** (1.06×10^{-4} M), the slopes of the Stern–Volmer plots became lower. Considering the quenching of the excited state of the cyanine dye-**3**, we ascribe the slope change to lower slope to the block of the back path from an intermediate possessing long a lifetime to the fluorescent singlet state. These findings suggest that quenched states of cyanine-**3** probably are both singlet and triplet excited states.

Cyanines **1**–**3**, which possess different methine chain lengths, were prepared to test absorbing light effects on the sensitivity (Fig. 3). In all cases tested, the photo-sensitivities are higher in the presence of *E*-**J-Ru** or *E*-**DA-Ru** as shown in Table 5. *E*-**J-Ru** appears to be very efficient and an ideal donor without exceptions. In the case of cyanine **1** possessing a mono-methine chain, the relative efficiency ratio of the three component system to the corresponding two-component system is 23 (Table 4). As shown in Fig. 4, the color fading rate of cyanine **3** in the three component system was slower than that in the two component system, implying that cyanine **3** was sta-

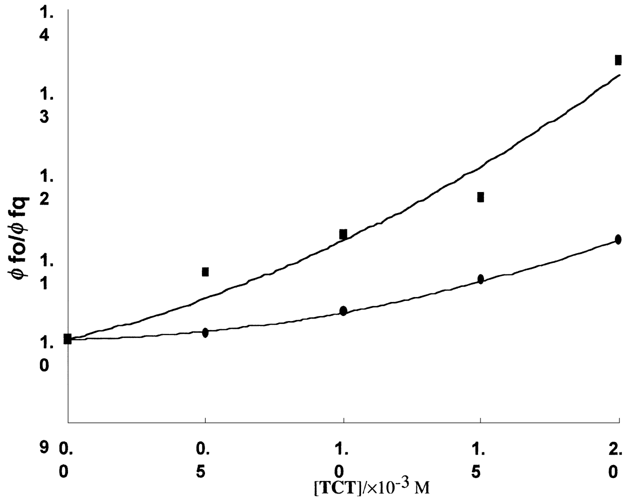


Fig. 2. Stern–Volmer plots for quenching of fluorescence of cyanine **3** (1.0×10^{-7} M) by TCT (■) and that of cyanine **3** (1.0×10^{-7} M) by **TCT** in the presence of *E*-**J-Ru** (1.0×10^{-5} M) (●).
Conditions: Solvent = Methanol, Temperature = 25°C.

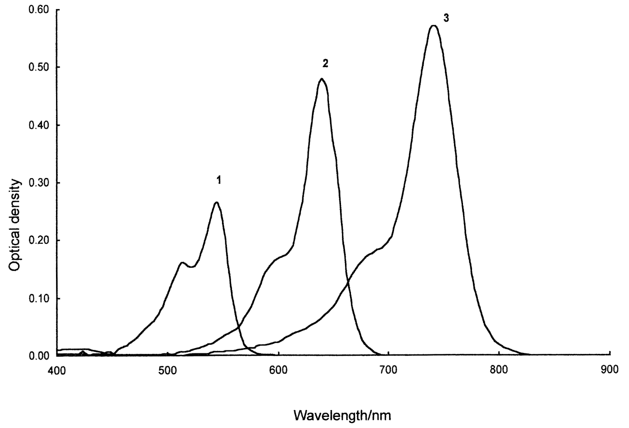


Fig. 3. Absorption spectra of cyanine dyes **1**, **2**, and **3** (2.0×10^{-6} M) in MeOH.

bilized by *E*-**J-Ru**. Further, the relative efficiency ratio was remarkably increased to 11 (Table 4). It is notable that cyanine **3** provides an efficient system even near the infrared region. This efficient electron donator system which works under a near infrared region seems to be consequently related to an artificial photosynthetic system similar to that of green plants.[8]

This investigation was partially supported by a Grant-in-Aid for Scientific Research from Hayashibara Biochemical Laboratories, Inc. We thank the Okayama NMR Center for NMR spectra, recorded on a Varian VXR-500 spectrometer. We appreciate encouragement from and discussion with Dr. M. Hayami of Hayashibara Biochemical Laboratories.

Table 5. Sensitivity of Photoinitiating System with Cyanine Dyes[a)]

Entry	Dye	Rutenocene compound	Exposing wavelength/nm[b)]	Sensitivity mJ/cm^2
1	**1**	none	540	103
2	**1**	*E*-**DA-Ru**	540	92
3	**1**	*E*-**J-Ru**	540	4.5
4	**2**	none	640	140
5	**2**	*E*-**DA-Ru**	640	130
6	**2**	*E*-**J-Ru**	640	18
7	**3**	none	780	> 100
8	**3**	*E*-**J-Ru**	780	11

a) Composition of the photosensitive layer (parts by weight): matrix polymer (100), polyfunctional monomer (100), TCT (8), sensitizing dye (1), ruthenocene compound (1). b) Glass filters were used for selection of wavelength as follows: Y-52 and KL-54 (540 nm); R-61 and KL-63 (640 nm); R-68 and KL-78 (780 nm).

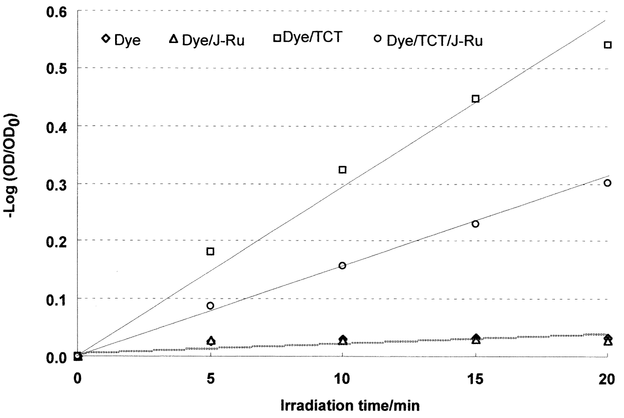


Fig. 4. Consumption of cyanine **3** vs time by irradiation with visible light for **3** itself, **3** and *E*-**J-Ru, 3** and TCT, and **3** and *E*-**J-Ru**-**TCT** systems.
Conditions: Solvent was methanol; Concentrations of Dye **3**, **TCT**, and *E*-**J-Ru** were 1.0×10^{-6} M, 1.0×10^{-4} M, and 1.0×10^{-5} M, respectively; Lamp = Xenon, Glass filter R-68 was used for cutting UV light; Before irradiation the solutions were bubbled with N_2 gas for 10 min.

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