ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 123 (1999) 87–91

Journal of Photochemistry and Photobiology A:Chemistry

Synthesis of covalently linked ferric tris(bipyridil) – viologen molecule and photo coloration in poly(vinylalcohol)

Jing-Ji Jin, Tadayoshi Uchida, Tetsuo Kuwabara, Michiko Hirai, Masato Nanasawa*

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Yamanashi University, Takeda 4, Kofu 400-8511, Japan

Received 13 January 1999; accepted 8 February 1999

Abstract

Three types of ferric tris(bipyridil) complexes appended a viologen, $\mathbf{1}^{3+}$, $\mathbf{2}^{3+}$, $\mathbf{3}^{3+}$, each having methylene, ethylene, and butylene spacer between ferric tris(bipyridil)- and viologen units, were synthesized and their photoinduced coloration properties were investigated in the thin poly(vinylalcohol) films. Upon photoirradiation, the colorless film of $\mathbf{1}^{3+}$ turned to red with increase in the absorption intensity around 530 nm, ascribing the ferrous tris(bipyridil) [Fe(II)bipy$_3$] complex. The coloration is interpreted in terms of the intramolecular electron transfer from the photogenerated viologen radical cation to the colorless Fe(III)bipy$_3$, since very little coloration of $\mathbf{4}^{3+}$ which has no viologen unit in a molecule was observed even in the presence of *N*, N′-dipropylviologen. Similar trends of $\mathbf{1}^{3+}$ were observed for $\mathbf{2}^{3+}$ and $\mathbf{3}^{3+}$. The order of absorption intensity around 530 nm is $\mathbf{1}^{3+} > \mathbf{2}^{3+} > \mathbf{3}^{3+}$, indicating that the electron transfer from the photogenerated viologen radical cation to Fe(III)bipy$_3$ is achieved effectively for the complex with a short alkyl spacer. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferric tris(bipyridine); Viologen; Photo-induced coloration; Intramolecular electron transfer

1. Introduction

It is well known that viologens composed of diquaternary salts of 4,4′-bipyridine undergo photoreduction accompanied by intense color development with reductive agents [1], however, the color species are generally observed within a flash-photolytic scale or anaerobic condition because the radical cation produced one-electron reduction is highly oxidation sensitive [2,3]. When viologens are embedded in appropriate polymer matrices, the resulting color can be observed visibly because the oxidation of viologen radical cation is restricted by the surrounding solid matrices [4–6]. The bleaching by both the reverse-electron transfer and air-oxidation depends on the kind of viologen, polymer matrix employed, and film preparation [7,8]. When the films are exposed in air, the bleaching proceeds predominantly by oxidation with molecular oxygen, in this case, the oxidation product seems to become an irreversible one on photoreaction [9]. In order to obtain long lived color species and to prevent air-oxidation, the viologen films free of oxygen were prepared by sandwiched method between two glass plates and the bleaching was performed by thermal back electron transfer [10]. One of other possible methods to produce a stable color form is the electron transfer process from photogenerated viologen radical cation to a reductive scavenger, e.g., a redox pigment; the color is persisted as reductive state of pigment and bleached by oxidation such as electrochemical reaction. In order to demonstrate the coloration by electron transfer, we have been interested in functionalized viologens bearing an electron accepting moiety. As an electron acceptor, we chose ferric tris(2,2′-bipyridine) [Fe(III)bipy$_3$], which is well known as oxidation-reduction indicator (redox potential, $E_{1/2} = 1.03$ V) and is enough to accept electron from viologen radical cation ($E_{1/2} = -0.5$ to -0.4 V) [11]. Since the film of Fe(III)bipy$_3$ with externally added viologen turned only faintly red for reasons to be discussed later, we would report here the synthetic studies on the Fe(III)bipy$_3$ complexes bearing viologen unit ($\mathbf{1}^{3+}$–$\mathbf{3}^{3+}$) and discuss their peculiar photocoloration by electron transfer in poly(vinylalcohol) (PVA). Reaction sequences and the structure of new photo-coloration compounds are described below. Schemes 1 and 2.

2. Experimental

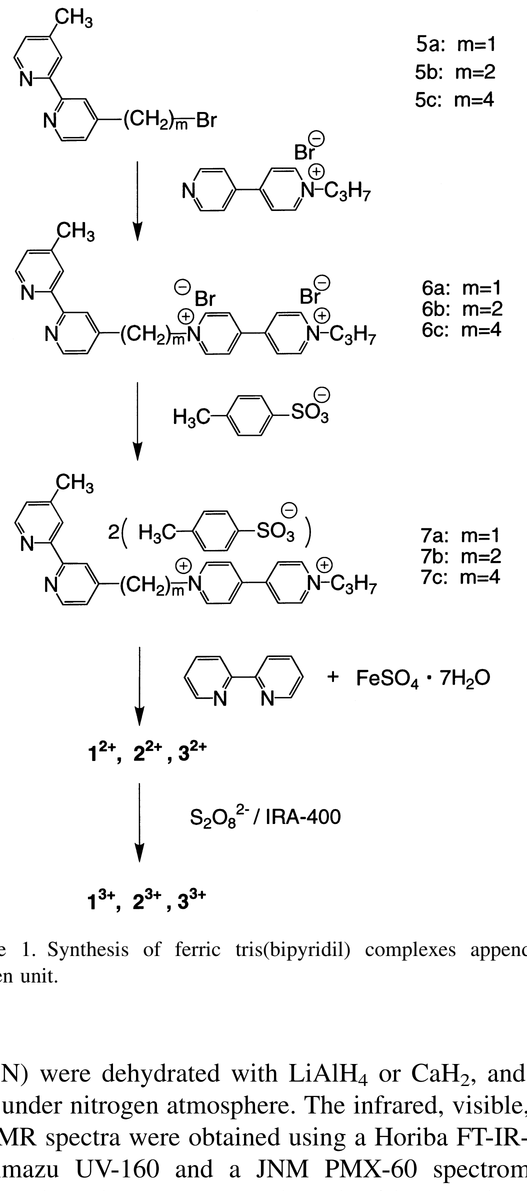
2.1. Materials

All reagents employed were of highest purity, unless otherwise noted. Tetrahydrofuran (THF) and acetonitrile

---

*Corresponding author.

PII: S1010-6030(99)00041-6



Scheme 1. Synthesis of ferric tris(bipyridil) complexes appended a viologen unit.

(MeCN) were dehydrated with $LiAlH_4$ or CaH_2, and distilled under nitrogen atmosphere. The infrared, visible, and ^1H NMR spectra were obtained using a Horiba FT-IR-720, a Shimazu UV-160 and a JNM PMX-60 spectrometer. Elemental analyses were conducted with a Carbo Elba EA1108.

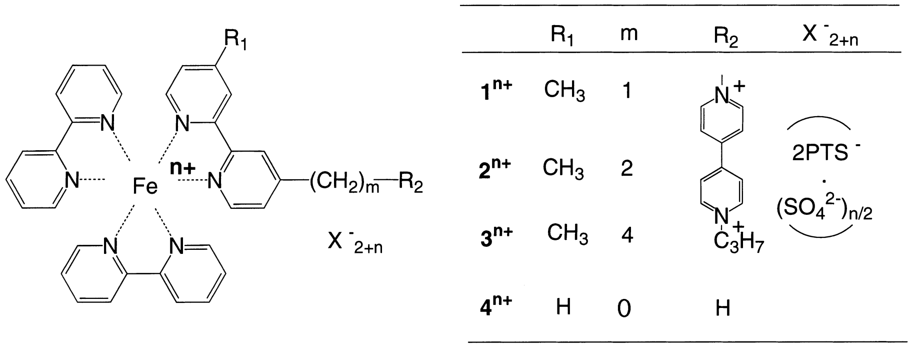
*2.1.1. Synthesis of [(4′-methyl-2,2′-bipyridil-4-yl)-methyl]-1′-propyl-4,4′-bipyridinium bis(p-toluenesulfonate) (**7a**)*

4-bromomethyl-4′-methyl-2,2′-bipyridine (**5a**) was prepared by formylation, reduction, and then bromination starting from 4,4′-dimethyl-2,2′-bipyridin, [12] yield 60.0%, mp 76–77°C. The solution of *N*-propyl-4,4′-bipyridinium bromide (1.0 g, 3.6 mmol) and **5a** (0.89 g, 3.4 mmol) in MeCN (50 ml) was heated to reflux under nitrogen atmosphere until bromoalkyl material was consumed with monitoring by TLC, which generally required for 60–70 h. The reaction mixture was cooled at room temperature, the resulting yellow precipitate was separated by filtration, and then recrystallized from a mixture of methanol (MeOH) and diethyl ether (Et_20) to afford a yellow solid of **6a** in 70% yield. Bromide anion in compound **6a** was exchanged with p-toluenesulfonate ion (PTS^-) as follows: dibromide (**6a**, 0.55 g, 1 mmol) in water (10 ml) was added an anion exchange resin (10 g, Amberlite IRA 400), loaded with PTS^- by exchanging the OH type with PTS, and the reaction mixture was gently stirred for 24 h in a dark place. The resin was filtered off, and the filtrate was lyophilized to leave a pale red powder of **7a** in 80% yield, mp 270°C.

IR (neat, cm^{-1}):1600, 1460 (C=C, C=N), 1176 (S=O). ^1H-NMR(D_2O, TMS), σ(ppm): 0.9 (3H, t, CH_3), 2.0 (2H, m, $-CH_2-$), 2.3 (6H, s, CH_3), 2.4 (3H, s, 4′-CH_3), 4.6 (2H, t, N-CH_2), 6.0 (2H, s, 4-CH_2-N), 7.2–9.2 (22H, py-H, Ar–H).

*2.1.2. Synthesis of [(4′-methyl-2,2′-bipyridil-4-yl)-ethyl]-1′-propyl-4,4′-bipyridinium PTS^-_2 (**7b**)*

4-bromoethyl-4′-methyl-2,2′-bipyridine (**5b**) was prepared by metoxymethylation and then bromination starting from 4,4′-dimethyl-2,2′-bipyridin:), [13] yield 56%, yellow oil. Compound **7b** was synthesized from **5b** (0.94 g, 3.4 mmol) by a similar method to **7a**, Yield 14%, mp 275°C. 1H-NMR (D_2O): 1.1 (3H, t, -CH_3), 2.0 (2H, m, -CH_2-), 2.4 (6H, s, CH_3), 2.6 (3H, s, 4′-CH_3), 3.8 (2H, t, -CH_2-), 4.7 (2H, t, N-CH_2-), 5.4 (2H, t, -CH_2-N), 7.2–9.6 (22H, py-H, Ar–H) ppm.



n = 2 or 3. PTS⁻ : *p*-toluenesulfonate

Scheme 2. Structure of ferric tris(bipyridil) complexes appended a viologen unit.

*2.1.3. [(4′-methyl-2,2′-bipyridil-4-yl)-butyl]-1′-propyl-4,4′-bipyridinium PTS₂- (**7c**)*

To the solution of diisopropylamine (1.94 ml) in THF (15 ml) was added successively a solution of butyllithium/hexane (1.5 mol/l, 9.3 ml) and 4,4′-dimethyl-2,2′-bipyridin (2.5 g) in THF (50 ml) at 0°C. After the reaction mixture stirring for 15 min at 0°C, 3-bromopropyl t-butyldimethylsilyl ether (2.2 ml), prepared from t-butyldimethylsilyl chloride, [14] was added. The reaction mixture was stirred for 14 h at room temperature, and then diluted with saturated NH_4Cl solution. The product, 4′-(4-methyl-2,2′-bipyridil-4-yl)butyl t-butyldimethylsilyl ether, was extracted with Et_2O, and then purified by column chromatography (Wako-gel C-300, AcOEt) to afford pale yellow oil in 62% yield. The silyl compound was converted to 4-bromobutyl-4′-methyl-2,2′-bipyridine (**5c**) by hydrolysis with tetrabutylammonium fluoride in THF (43% yield) and bromination with HBr/AcOH (92% yield). The product was purified by column chromatography, mp, 48–51°C (lit 50–52°C) [12]. Compound **7c** was synthesized from **5c** (1.04 g, 3.4 mmol) by a similar method to **7a**. Yield 24%, mp 270°C.

^{1}H-NMR (D_2O): 1.1 (3H, t, $-CH_3$), 1.7–2.3 (12H, m, $–CH_2–$, CH_3), 2.6 (3H, s, 4′-CH_3), 3.8 (2H, t, 4-CH^2-), 4.7 (2H, t, $N'CH^{2'}$), 5.4 (2H, t, $'CH_2'N$), 7.2–9.3 (22H, py-H, Ar–H) ppm.

2.1.4. Syntheses of Fe(II)bipy₃ complexes ($\mathbf{1}^{2+}$–$\mathbf{4}^{2+}$)

Compound **7a–c** (0.19 mmol) and 2,2′-bipyridine (0.06 g, 0.38 mmol) was added to $Fe_2SO_47H_2O$ (0.54 g, 0.19 mmol) in water (10 ml), and the reaction mixture was stirred for 1 h. An insoluble precipitate was separated by filtration and the filtrate was lyophilized. The residue was purified by several times precipitation of MeOH solution with Et_20 to afford a red powder of $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$.

$\mathbf{1}^{2+}$: Yield, 96%. IR, 1176 (S=O) cm^{-1}. $\lambda_{max} = 527$ nm ($\varepsilon = 8400/H_2O$). Anal. Found: C, 59.80%; H, 4.86%; N9.16%. Calcd. for $FeC_{59}H_{56}N_8O_{10}S_3$: C, 59.59%; H, 4.75%; N,9.42%.

$\mathbf{2}^{2+}$: Yield, 96%. $\lambda_{max} = 527$ nm ($\varepsilon = 8200/H_2O$). Anal. Found: C, 60.10%; H, 5.41%; N, 9.10%. Calcd for $FeC_{60}H_{58}N_8O_{10}S_3$: C, 59.89%; H, 4.86%; N, 9.31%.

$\mathbf{3}^{2+}$: Yield, 86%. $\lambda_{max} = 527$ nm ($\varepsilon = 8100/H_2O$). Anal. Found: C, 60.75%; H, 5.60%; N, 8.70%. Calcd for $FeC_{62}H_{62}N_8O_{10}S_3$: C, 60.48%; H, 5.08%; N, 9.10%.

$\mathbf{4}^{2+}$: Yield, 83%. $\lambda_{max} = 527$ nm ($\varepsilon = 10\,000/H_2O$). Anal. Found: C, 61.65%; H, 5.10%; N, 12.25%. Calcd for $FeC_{36}H_{36}N_6O_4S$: C, 61.36%; H,5.15%; N, 11.93%.

The complex ($\mathbf{1}^{2+}$–$\mathbf{4}^{2+}$) was oxidized with an anion exchange resin (Amberlite IRA 400), loaded with peroxodisulfate [15]. The mixture of Fe(II)bipy₃ complex (0.1 g) and the resin (10 g) in water (10 ml) was gently stirred for 2 h in a dark place and the aqueous solution was lyophilized to leave a pale red powder of $\mathbf{1}^{3+}$–$\mathbf{4}^{3+}$.

$\mathbf{1}^{3+}$: Yield, 86%. $\lambda_{max} = 527$ nm ($\varepsilon = 540/H_2O$).

$\mathbf{2}^{3+}$: Yield, 95%. $\lambda_{max} = 527$ nm ($\varepsilon = 600$).

$\mathbf{3}^{3+}$: Yield, 96%. $\lambda_{max} = 527$ nm ($\varepsilon = 550$).

$\mathbf{4}^{3+}$: Yield, 86%. $\lambda_{max} = 527$ nm ($\varepsilon = 330$).

2.2. Film preparation and measurement

The solution of Fe(III)bipy₃ complex (3.0×10^{-6} mol) and PVA (Mn: 20 000, 0.2 g) in water (0.2 ml) was spread homogeneously on a glass plate (1.3×3.8 cm^2), followed by drying in a dark place. The film (0.06–0.09 mm-thickness) was stored in a desiccator of 58% RH (saturated NaBr solution) at least overnight before use. The film was irradiated at a distance of 10 cm from a 75 W mercury lamp (Toshiba SHL-100UV) for 2 min, the resulting color development was determined by transmission.

3. Result and discussion

2,2′-bipyridinium derivatives as electron donating viologen are accessible due to the same skeleton of Fe(III)bipy₃ [16], however, its photo-sensitivity is small compared with those of 4,4-ones, [17] therefore 4,4′-viologen was employed as an electron donor. These compounds possess three different spacers, $–CH_2–$, $–CH_2CH_2–$, and $–(CH_2)_4–$ between electron donating and accepting moiety. In order to couple these two parts, the ω-(haloalkyl) group was derived at the 4-position of 2,2′-bipyridil ligand. 4-(Hydroxymethyl)-4′-methyl-2,2′-bipyridine was prepared by the method adopted from Ciana, followed by bromination with 48% aqueous HBr solution. Although, it was reported that the free base of **5a** polymerized by quaternization of bromomethyl group [12], the compound could be obtained in 60% yield by isolation under neutral condition, and then purified by column chromatography with neutral alumina. 4-(4-Bromobutyl)-4′-methyl-2,2′-bipyridine (**5c**) was prepared by the method adopted for 3-(ω-hydroxyalkyl)pyridine using ω-bromoalkyl tert-butyl-dimethylsilyl ether [14].

A large excess of ω-bromoalkyl compounds (**5a–c**) in Menschutkin reaction of 1-propyl-4,4′-bipyridinium bromide induced *N*-quaternization of 2,2′-bipyridine moiety, which are often difficult to separate from the desired product. In order to minimize the by-product, about 0.92 equivalent of **5a–c** were employed in the Menschutkin reaction, so that yields (**6a–c**) were relatively small; especially, in the case of the reaction with **6b**, dehydrobromination of bromoethyl group caused the decrease in yield of **6c**. With the intention of increasing solubility and compatibility of $\mathbf{1}^{3+}$–$\mathbf{3}^{3+}$ to polymer matrix, bromide anions in **6a–c** were exchanged by PTS$^-$ ion and then converted to Fe(II)bipy₃ complexes. In this case, it is impossible to isolate Fe(II)-(bipy)₂-precursor as is distinct from Ru(bipy)₂, [13] so that

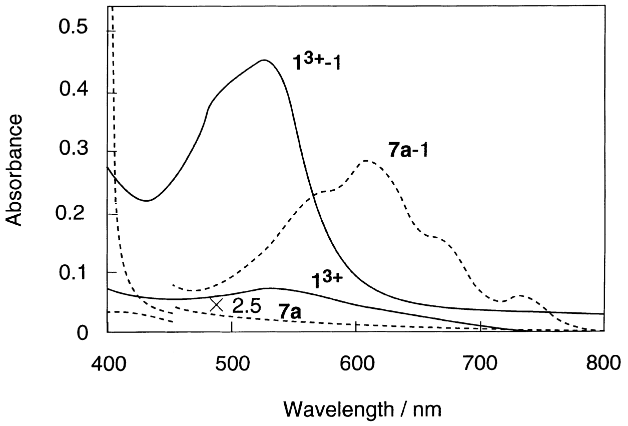


Fig. 1. Absorption spectra of **7a** and $\mathbf{1}^{3+}$ in PVA matrix before and after 2 min irradiation.

$\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ were synthesized from the mixture of **7a–c** and 2 equivalent 2,2′-bipyridine. However, the complex formation was not quantitative and the reaction product was contaminated by the compound containing more than 1 equivalent of **7a–c**. The by-product were isolated by precipitation of MeOH solution with ether, and the purity was ascertained above 95% by the result of elemental analyses. Usually Fe(II)bipy$_3$ complexes are oxidized by mixing with aqueous solution of oxidation agent such as peroxydisulfate [18], however, a remaining trace amount of oxidation agent affects seriously on photo-reduction of viologens, thereby the oxidation was conducted with anion exchange resin lorded with peroxydisulfate. The reversibility of Fe(III)-bipy$_3$ on redox reaction was assured by that the parent absorptivity of Fe(II)bipy$_3$ was attained by reduction with hydroxylamine.

A transparent PVA film of **7a** turned intense blue upon near-UV irradiation (dotted line in Fig. 1), which color gradually faded, reaching to the original one after 20 h. The band at 570 nm is ascribed to the viologen radical cation dimer and the band at 610 nm is ascribed to the monomer [1,19]. The mechanism of radical formation has been well discussed in solution [20,21] and solid phase [4,5]: the viologen radical cation in compound **7a** might be mainly formed by intramolecular electron transfer from counter anion, which is stabilized by polymer matrix through restriction of both back electron transfer and air-oxidation, as a diffusion controlled in solid state. The photosensitivity of **7a–c** was similar to that of conventional viologen such as *N*,N′-dipropyl-4,4′-bipyridinium (PV^{2+}), and the absorption maxima were not affected by different alkyl spacer of 2,2′-bipyridine units.

When the film of $\mathbf{1}^{3+}$ was irradiated with the similar conditions, the absorption spectra was much different to that of **7a** (solid line in Fig. 1). The absorption shape is apparently distinct from that of viologen radical cation dimer [22] and coincides with that of $\mathbf{1}^{2+}$. Since the spectra of $\mathbf{4}^{3+}$ in PVA did not change by near UV irradiation, Fe(III) complex might be inactive for photoreaction [23]. Thus, photo-excited viologen units convert into $\mathrm{V}^{+\bullet}$ by one electron transfer from counter anion, however, the oxidation is restricted in PVA matrix as mentioned above, so that the photogenerated $\mathrm{V}^{+\bullet}$ might mainly react intramolecularly with Fe(III)bipy$_3$ to form a red Fe(II)bipy$_3$ species ($E_{1/2}, \mathrm{V}^{2+}/\mathrm{V}^{+\bullet} = 0.44$, Fe(III)bipy$_3$/Fe(II)bipy$_3$ = +1.03 V, respectively). Table 1 indicates the absorption changes (ΔA) at 530 nm after 2 min irradiation for compound $\mathbf{1}^{3+}$–$\mathbf{3}^{3+}$ and a mixture of $\mathbf{4}^{3+}$–PV^{2+}. The values for $\mathbf{4}^{3+}$–PV^{2+} film is small, even with 50 fold PV^{2+}, in spite of the appearance of an absorption of $\mathrm{V}^{+\bullet}$. From a space filling molecular model, the mean distance between PV^{2+} and $\mathbf{4}^{3+}$ in the polymer film is estimated to be 18 Å. Since the distance to proceed an effective intermolecular reaction for $\mathrm{V}^{+\bullet}$ is less than 10 Å [24], the photogenerated $\mathrm{V}^{+\bullet}$ in the mixture of $\mathbf{4}^{3+}$–PV^{2+} hardly reduce Fe(III)bipy$_3$ in polymer matrix.

The absorption of $\mathbf{2}^{3+}$ and $\mathbf{3}^{3+}$ in PVA film is small compared with that of $\mathbf{1}^{3+}$, and its magnitude decreased with the increase in the methylene spacer. The straight distances of V^{2+}–Fe(III)bipy$_3$ in $\mathbf{1}^{3+}$, $\mathbf{2}^{3+}$, and $\mathbf{3}^{3+}$ are estimated to be 1.27, 2.54, and 5.08 Å, respectively; these values are exponentially correlated to their absorption increase upon irradiation. This means that the efficiency of intraelectron transfer depends on the chain-length of methylene spacer.

Although the behavior of the surrounding PVA matrix oxidized by viologen anion radical is not yet examined in this study, [5,20,21] the system synthesized here will be useful to develop novel type of photo-redox functional materials using viologen as photo-electron inducer, since the viologen has been examined only as an electron mediator in photo-redox process.

Table 1
Photo-induced absorption change of V^{2+}–Fe(III)bipy$_3$ in PVA matrix

	$\mathbf{1}^{3+}$	$\mathbf{2}^{3+}$	$\mathbf{3}^{3+}$	$\mathbf{4}^{3+}$	$\mathbf{4}^{3+}$	$\mathbf{4}^{3+}$	$\mathbf{4}^{3+}$
V^{2+} [a]	0	0	0	0	3	10	50
ΔA [b]	0.38	0.31	0.15	0.02	0.04	0.05	0.06

[a] Amount of *N*,N'-dipropylviologen added to Fe(III)bipy$_3$ (molar ratio).

[b] Absorption difference at 530 nm before and after 2 min irradiation. Absorption difference was normalized to 0.1 mm film thickness.

References

[1] E.M. Kosower, J.L. Cotter, J. Am. Chem. Soc. 86 (1964) 5524.
[2] A.L. Rieger, J.O. Edwards, J. Org. Chem. 53 (1988) 1481.
[3] T. Watanabe, K. Honda, J. Phys. Chem. 86 (1982) 2617.
[4] H. Kamogawa, T. Masui, M. Nanasawa, Chem. Lett. (1980) 1145.
[5] M. Kaneko, A. Yamada, Makromol. Chem. 182 (1981) 1111.
[6] L.A. Vermenlen, M.E. Thompson, Nature 358 (1992) 656.
[7] H. Kamogawa, K. Kikushima, M. Nanasawa, J. Polym. Sci. Polym. Chem. Ed. 27 (1989) 393.
[8] M. Nanasawa, M. Kaneko, H. Kamogawa, Bull. Chem. Soc. Japan 66 (1993) 1764.
[9] A.W. Mau, J.M. Overbeek, J.W. Londer, W.H.F. Sasse, J. Chem. Soc. Farady Trans. 2(82) (1986) 869.
[10] M. Nanasawa, Y. Matsukawa, J.-J. Jin, Y. Haramoto, J. Photochem. Photobiol. A: Chem. 109 (1997) 35.
[11] D.R. Lide, Handbook of Chemistry and Physics, CRC Press, 1993, 8–17.
[12] L.D. Ciana, I. Hamachi, T.J. Meyer, J. Org. Chem. 54 (1989) 1731.
[13] E.H. Yonemoto, R.L. Riley, Y.I. Kim, S.J. Atherton, R.H. Schmehl, T.E. Mallouk, J. Am. Chem. Soc. 114 (1992) 8081.
[14] M.T.D. Coleman, D.J. Fanekner, G.M. Dubowchik, G.P. Roth, C. Palson, G. Fairchild, J. Org. Chem. 58 (1993) 5925.
[15] D. Sansoni, K. Dorfner, Angew. Chem. 71 (1959) 160.
[16] C.M. Elliott, R.A. Freitag, D.D. Blaney, J. Am. Chem. Soc. 107 (1985) 4648.
[17] H. Kamogawa, M. Nanasawa, Chem. Lett. (1988) 373.
[18] K. Tsukahara, R.G. Wilkins, Inorg. Chem. 24 (1985) 3399.
[19] A. Yasuda, H. Kondo, M. Itabashi, J. Seto, J. Electroanal. Chem. 210 (1986) 265.
[20] T.W. Ebbesen, G. Levery, L.K. Patterson, Nature 298 (1982) 545.
[21] T.W. Ebbesen, G. Ferraudi, J. Phys. Chem. 87 (1983) 3717.
[22] W. Geuder, S. Hunig, A. Suchy, Tetrahedron 42 (1986) 1665.
[23] J.H. Baxendale, N.K. Bridge, J. Phys. Chem. 59 (1955) 783.
[24] C.K. Ryu, R. Wang, R.H. Schmehl, S. Ferrere, M. Jundwikow, J.W. Merkert, C.E.L. Headford, C.M. Elliot, J. Am. Chem. Soc. 114 (1992) 430.