Table I. Characteristic Data of (Substituted) Poly-1,2-azepines

| polymer | GPC[a] | UV[b] | IR[c] |
|---|---|---|---|
| **7a** | 30.0 | 202, 245, 320 (w, sh) | 750, 690 |
| **7b** | 32.0[d] | 200, 240 (w), 340 (sh) | 845 |
| **7c** | 33.0[d] | n.a. | 835 |
| **7d** | 30.5 | 202, 280 | 780, 730 |
| **7e** | 30.2 | n.a. | 815 |
| **7f** | 30.5 | n.a. | 850 (w) |
| **7g** | 30.5 | 195, 240, 320 (w, sh) | 810, 740, 670 (all w) |
| emeraldine[e] | 30.5 | | |

[a] GPC with DMF/0.05 M LiBr, retention time of peak is given. [b] UV-vis spectra of ultrathin films on fused silica. [c] IR out-of-plane vibrations in the region below 900 $cm^{-1}$. [d] These Rt's are overshadowed by hydrophobic interactions as proven with the corresponding azides and anilines. [e] Emeraldine and polyanilines have been studied in great detail.[16]

are broadened, while a long tail into the near infrared appears, characteristic of the presence of undefined defect levels in the band gap of the virgin polymer. These slightly oxidized poly-1,2-azepines are the main products in the photolysis of **1**, as found in most studies published to date.[1-13] We have performed most of our analyses on these, inadvertently, slightly oxidized polymers.

The most significant data on the spectroscopic analyses are given in Table I. Independent of their structure, a low average molecular weight for **7a-g** is found with GPC ($\overline{DP}$ about equal to emeraldine, i.e., 8-10). The out-of-plane C-H resonances in the IR fingerprint region indicate that no aromatic substitution of the phenyl azides occurs, thus excluding the formation of substituted polyanilines.[3,4,16] Additional evidence for ring expansion during polymerization is found from $^1H$ and $^{13}C$ NMR spectroscopy, although this analysis is hampered by the presence of paramagnetic species.[17] The NMR spectra show very broad and low sensitivity resonances for the atoms of the azepine ring mainly by paramagnetic broadening. Powder ESR spectra of **7a** show a single isotropic Gaussian signal with a $g$ factor of 2.0035 and a peak-to-peak line width of 6 G.

In contrast to neutral azepines[18] the slightly oxidized poly-1,2-azepine **7a** is not reduced by $H_2$ and Pd/C. However, upon exposure of **7** to hydrogen chloride the corresponding HCl salts are isolated from this heterogeneous reaction.[19]

The ease of oxidation of **7** prompted us to investigate the possible formation of conducting polymers.[20] Upon oxidative doping of the polymer films with $I_2$ or $AsF_5$ specific conductivities up to $10^{-2}$ S/cm are found. UV-vis spectra of ultrathin, doped samples (Figure 2) show that the extension of the conjugation is limited and that the conductivity with $I_2$ is reversible due to evaporation of the dopant.[21] Polymer **7f** is clearly a much better C-T donor for $I_2$ than **7g**. These results show again that conductivity can be obtained from precursors lacking delocalization, as shown before.[22]

The formation of conducting poly-1,2-azepines suggests that the charged species formed are stabilized by conjugation or even aromaticity. The species to be expected are radical cations and dications of azepines. Delocalization of these species and 6-$\pi$ electron aromaticity of the dication is evident both from theoretical studies and from experiments.[23] However, extended conjugation is excluded owing to steric hindrance between the individual azepine rings (ortho-substituted aromatics). Hence, a moderate conductivity is expected and found.

Two remarkable deductions can be drawn from the comparison of polymerizations carried out in nitrogen and in air. Firstly, the rate of polymer formation is identical in both cases, indicating that **2** and not **3** is the intermediate, as already suggested by Platz.[4] Secondly, the polymerization performed in air is accompanied by simultaneous photooxidation of **7**, furnishing carbonyl-containing polymers (strong IR absorption at 1750 $cm^{-1}$), presumably by oxidation of the ketene-aminal group. In the case of alkoxy-substituted phenylazides **1c-e** and especially **1f** the photooxidation is most pronounced.[24]

On the basis of the evidence presented, poly-1,2-azepines are established to be the primary products of the photopolymerization of phenyl azides. The polymers are easily oxidized to delocalized charged species, yielding conducting polymers that can be formed in films with pattern structures.

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**Registry No. 1a** (homopolymer), 115483-22-2; **1b** (homopolymer), 115483-23-3; **1c** (homopolymer), 115483-25-5; **1d** (homopolymer), 115483-27-7; **1e** (homopolymer), 115483-28-8; **1f** (homopolymer), 115483-30-2; **1g** (homopolymer), 115483-31-3; **7a** (SRU), 115483-32-4; $I_2$, 7553-56-2; $AsF_5$, 7784-36-3.

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## Ruthenium(II)-Polypyridine Cage Complexes: Luminescence and Photochemical Properties

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Ruthenium(II)-polypyridine complexes have long since attracted the attention of many researchers because of a unique combination of ground and excited state properties and in the last 10 years have extensively been used as mediators in the interconversion of light and chemical energy.[2-5] A quite important property for luminescent compounds or photosensitizers is their

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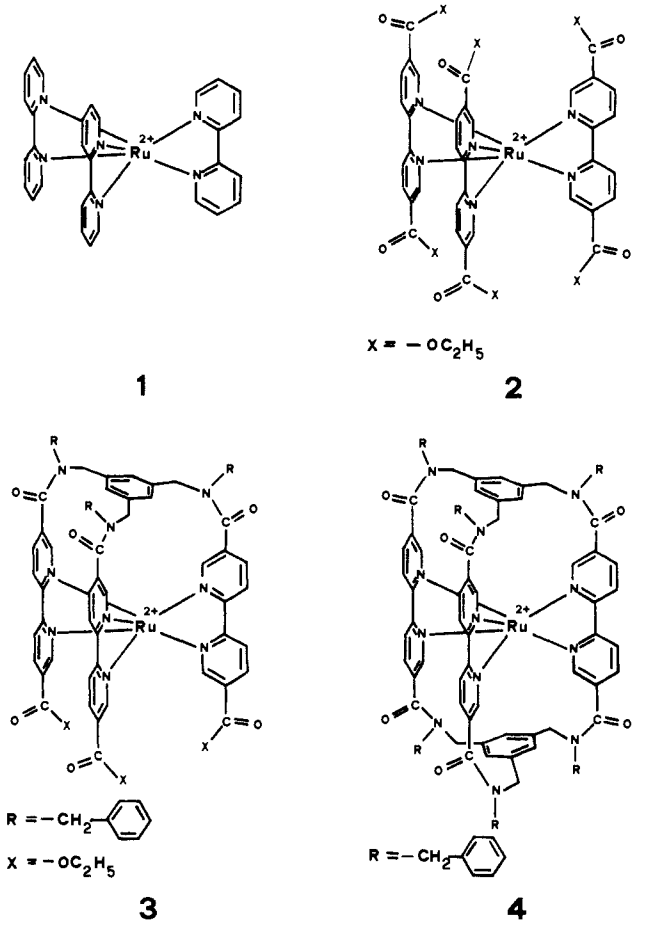


**Figure 1.** Structural formulas of the complexes studied.

stability toward photodecomposition. For most practical applications, in fact, turnover numbers of the order of $10^6$ or more may be required, especially when the species are expensive. Ruthenium(II)–polypyridine complexes, however, undergo ligand photosubstitution reactions with non-negligible quantum yields. For $Ru(bpy)_3^{2+}$ (**1**, bpy = 2,2-bipyridine) in aqueous solution, the quantum yield of photodecomposition, $\Phi_p$, is in the range $10^{-5}$–$10^{-3}$, depending on pH and temperature.[6] In solutions containing $X^-$ ions like $Cl^-$, $Br^-$, and $NCS^-$, $\Phi_p$ may be as high as $10^{-1}$ for solvents of low dielectric constant.[7]

A way to prevent ligand photodissociation without changing other properties is to link the ligands together by covalent bonds so as to make a cage.[8] In this way, the first coordination sphere of the metal (and thus, the energy level diagram near the equilibrium nuclear configuration) is unchanged, but processes that require extensive nuclear motions, such as photochemical reactions and radiationless decays via strongly distorted structures, may be prevented. Following this research line, our groups have recently synthesized the first noncryptand type, spacered tris-bpy-ligand[9] and the first closed cage ruthenium(II)–polypyridine complex.[10] In this paper, we report data concerning the photophysical and photochemical behavior of that cage complex[10] and of some related species.

The complexes examined are those shown in Figure 1, where the sketches do not show the true molecular geometry (approximately octahedral coordination symmetry) but underline the relationships among the ligands. The preparation of ligands and complexes (as $PtF_6^-$ salts) is described elsewhere.[9,10]

**Table I.** Spectroscopic, Photophysical, and Photochemical Data[a]

| complex | absorption 298 K $\lambda_{max}$, nm ($\epsilon$) | emission 298 K $\lambda_{max}$, nm | emission 298 K $\tau$, $\mu$s | emission 90 K $\lambda_{max}$, nm | emission 90 K $\tau$, $\mu$s | photochemistry[b] 298 K $\Phi_p$ |
|---|---|---|---|---|---|---|
| **1** | 452 (13000) | 615 | 0.80 | 582 | 4.8 | 0.017 |
| **2** | 500 (10000) | 665 | 0.09 | 657 | 0.57 | |
| **3** | 477 (9500) | 640 | 0.45 | 620 | 1.9 | |
| **4** | 455 (10400) | 612 | 1.70 | 597 | 4.8 | $<10^{-6}$[c] |

[a] Propionitrile–butyronitrile (4:5 v/v) deaerated solutions, unless otherwise specified. [b] Aerated $CH_2Cl_2$ solution containing 0.01 M $Cl^-$. [c] Estimated from the decrease of the MLCT absorption band.

Table I collects some relevant spectroscopic, photophysical, and photochemical data of the complexes studied. Compared to $Ru(bpy)_3^{2+}$, ethyl ester substituents on the bpy rings (complex **2**) cause a red shift in the MLCT absorption and emission bands because the substituted bpy ligand is a better electron acceptor than bpy.[11] The MLCT absorption and emission bands of the one-side-capped complex **3** are blue-shifted compared to those of complex **2** because the CO groups connected to the cap must assume an orthogonal orientation with respect to the aromatic rings,[10] thereby reducing delocalization of the promoted electron. For the same reason, it turns out that the closed cage complex **4** exhibits absorption and emission spectra very similar to those of $Ru(bpy)_3^{2+}$. This trend in the spectroscopic results is in qualitative agreement with the values of the first one-electron reduction potential (−1.350, −0.735, −0.855, and −1.010 V for **1**, **2**, **3**, and **4**, respectively). More detailed electrochemical data and a full discussion of the correlation between spectroscopic and electrochemical results will be reported in a subsequent paper.

The values obtained for the emission lifetimes are quite interesting (Table I). At low temperature, the lifetime is apparently controlled by the energy gap between ground and excited state.[5,12] At room temperature, when the lifetime is controlled by thermally activated $^3CT \rightarrow {}^3MC$ radiationless decay processes,[5] the cage compound **4** is considerably longer lived than the other complexes. A detailed examination of the temperature dependence of the luminescence intensity and lifetime in the temperature range 90–350 K is now in progress in our laboratories.

The most interesting result is the extraordinary stability of the cage complex **4** toward photodecomposition, about $10^4$ times higher than that of $Ru(bpy)_3^{2+}$ (Table I). It is generally agreed[2-7] that for $Ru(bpy)_3^{2+}$ the ligand photosubstititon reaction proceeds via a thermally activated radiationless transition from the luminescent metal-to-ligand charge-transfer ($^3CT$) level to a distorted metal-centered ($^3MC$) level, with subsequent cleavage of one Ru–N bond and formation of an intermediate containing a monodentate bpy ligand. Such an intermediate can undergo either loss of bpy or chelate ring closure with reformation of $Ru(bpy)_3^{2+}$.[7] The photochemical stability of the cage complex **4** may be due to one or more of the following reasons: (i) more difficult access to the labile $^3MC$ level; (ii) lower tendency of $^3MC$ to undergo ligand dissociation; (iii) more favorable conditions for recoordination in a primary photoproduct. Previous attempts to obtain complexes more photostable than $Ru(bpy)_3^{2+}$ were based on an increase in the energy gap between the luminescent $^3CT$ and the labile $^3MC$ excited states. Starting from $Ru(bpy)_3^{2+}$, this was done either lowering $^3CT$ by substituting bpy with ligands that are easier to reduce[5,12-14] or raising $^3MC$ by replacing Ru with Os (thereby

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increasing the ligand field strength).[12] In both cases, however, the excited state lifetime was compromised. By contrast, caging increases both the photochemical stability and the excited state lifetime.

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## Stereochemical Assignment of Neocarzinostatin Chromophore. Structures of Neocarzinostatin Chromophore–Methyl Thioglycolate Adducts†

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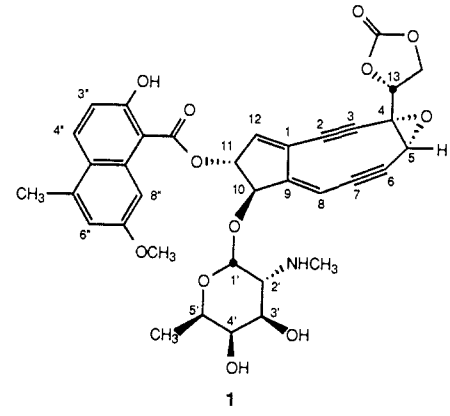
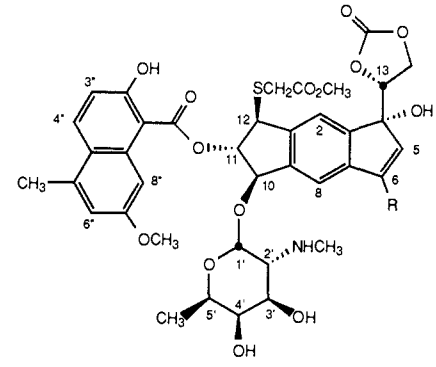
The nonprotein component of the antitumor antibiotic neocarzinostatin[1] (neocarzinostatin chromophore, **1**)[2,3] undergoes rapid and irreversible reaction with thiols to produce a species which is capable of cleaving DNA upon aerobic incubation.[4] Goldberg and co-workers first demonstrated that reaction of **1** with methyl thioglycolate produces a 1:1 adduct with the added incorporation of two hydrogen atoms.[5] Subsequently, we proposed structure **2** (planar form) for this adduct and presented the mechanism outlined in Scheme I to account for its formation.[6] We describe herein the isolation and complete characterization of **2** and a new product, the bisthiol adduct **3**. The full stereochemical assignment of **2** and, by induction, of **1** is also reported.

Dissociation of **1** from its protein complex was achieved with >85% efficiency by a modification of the procedure of Goldberg et al.[5,7] A freshly prepared solution of **1** ($6.6 \cdot 10^{-4}$ M) in 0.5 M methanolic acetic acid was deoxygenated at −78 °C and treated with excess distilled, deoxygenated methyl thioglycolate (**4**, 300 equiv) with reaction at −78 °C for 2 h followed by slow warming to 0 °C (10 °C/h). Volatiles were removed at 0 °C, 0.05 mm to provide a mixture containing **2** and **3** (ca. 1:1) as the major products. Preparative thin-layer chromatography (48:48:4 ethanol:benzene:acetic acid, $R_f$ values 0.31 and 0.43 for **2** and **3**, respectively) with subsequent and final purification over Sephadex LH-20 (dichloromethane) provided **2** and **3** as amorphous films.[8]



**1**



**2** R = H

**3** R = $SCH_2CO_2CH_3$

High resolution FABMS (calcd for $[M + H]^+$, $C_{38}H_{42}NO_{14}S$: 768.2326; found: 768.2429) of **2** confirmed its formulation as **1** + $HSCH_2CO_2CH_3$ + $H_2$. The FTIR spectrum (neat film) showed that the carbonate and naphthoate groups had been preserved (1807 and 1644 $cm^{-1}$, respectively) and indicated incorporation of **4** (1738 $cm^{-1}$). All carbon-bound proton resonances were well-resolved in the 400 MHz $^1H$ NMR spectrum ($CDCl_3$). In addition to readily discernible signals for the *N*-methylfucosamine, naphthoate, methyl thioglycolate, and carbonate appendages, seven resonances attributable to the rearranged core were visible: two aromatic and three nonaromatic singlets ($\delta$ 7.77, 7.23, 5.78, 5.24, 4.63) and two coupled olefinic doublets ($\delta$ 6.94, 6.30, $J$ = 5.6 Hz). 2D-COSY revealed a coupling pathway linking the five singlets (C2–C12–C11–C10–C8–C2).[9] Whereas vanishingly small positive NOEs were observed in $CDCl_3$ ($\omega\tau_c \approx 1$), large negative NOEs could be obtained in dimethyl-$d_6$ sulfoxide (DMSO-$d_6$):$D_2O$ (2:1, 23 °C, Figure 1).[10] Qualitatively similar information was obtained in a two-dimensional version of the CAMELSPIN experiment ($CDCl_3$).[11,12] The NOE studies corroborate the linkage established in the 2D-COSY experiment and further define the substitution pattern along the entire periphery of the nucleus, confirming the two-dimensional structure of **2** previously set forth.[6] The data also allow complete determination of the stereochemistry of the left-hand portion of the molecule. The trans,trans-arrangement of the substituents at C10, C11, and C12 was apparent from proton–proton coupling constants ($J_{10,11}$ and $J_{11,12} \leq 1$ Hz)[13] and multiple confirming NOEs (Figure

† Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

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(7) Neocarzinostatin powder (0.500 g) was suspended in ice-cold 0.5 M methanolic acetic acid solution (20 mL), and the mixture was gently agitated for 2 h. The suspension was centrifuged and filtered, and the clear filtrate was stored on ice in the dark. The extraction was repeated by resuspending the protein pellet in fresh cold solvent. The filtrates were combined, and the content of **1** was determined by UV absorbance at 340 nm.[2a] We are indebted to Dr. Matthew Suffness, the National Cancer Institute, and Kayaku Co., Ltd. for generous supplies of neocarzinostatin powder.

(8) We obtained 1.5–2.5 mg (5–10%) each of pure **2** and **3**. These yields are for scrupulously purified samples and, as such, represent lower limits on the actual values.

(9) For clarity, we have numbered **2** and **3** to correspond with **1**.

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