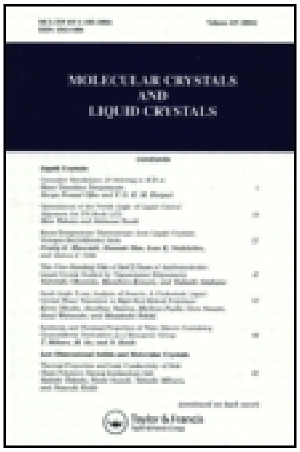

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Photoconductivity of Rh(I) Aryldiisocyanide Polymers and Oligomers

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Photoconductivity of Rh(I) Aryldiisocyanide Polymers and Oligomers

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We have shown that stacked-layer, three dimensional Rh(I) organometallic coordination polymers having bifunctional bridging aryl diisocyanides and interlayer Rh---Rh interactions demonstrate photoconductive properties. Thin films of these materials can be prepared from dilute solutions containing small oligomers. These have revealed photoconductivities in the visible and near infrared regions.

Keywords: photoconductivity, organometallic polymers, aryldiisocyanides, Rh(I) polymers, Rh(I) oligomers, photoelectric

INTRODUCTION

We have investigated the molecular design and preparation of various coordination polymeric systems using organotransition metal complexes and a series of bifunctional stereochemically rigid aryldiisocyanide ligands.[1-10] Aside from the versatile coordination chemistry shown by these ligands, the existence of extensive "p-π" orbitals can allow for electron delocalization throughout these networks suggesting the existence of numerous electronic properties of interest. In fact, aryldiisocyanides have recently been shown to bridge between macromolecular square-planar phthalocyanine systems resulting in new one-dimensional compounds showing significant electric conductivity.[11] The above approach to the molecular design of organometallic polymers has produced, among others, air-stable Rh(I) aryldiisocyanide polymers, $[\mathrm{Rh}((\mathrm{CN})_2\mathrm{Ar})_2^+\,\mathrm{Cl}^-]_n$.[1-5] These networks have been shown to be particularly ordered by powder X-ray diffractometry.[1-5] They are composed of rhodium atoms in a two-dimensional, approximately square-planar geometry. Three-dimensional systems are then formed via stacking involving Rh(I)---Rh(I) interactions having interlayer spacings of 3.31 to 3.53Å[4,5] (Figure 1).

In anticipation of anisotropic properties for these systems, we investigated their dark electrical conductivity and semiconductive behavior. The results of this investigation have been recently reported.[10] It may be noted that similar properties have been observed with Rh(I) tetrakismonoisocyanide cations having both simple anions,[12] as well as TCNQ$^{\bar{\cdot}}$ as a radical anion.[13] This data as well as our own may suggest that these systems are one-dimensional metals wherein the metallic behavior has been quenched by disorder and imperfections. An alternative explanation for the electrical properties of these materials may be the existence of small band-gap intrinsic or extrinsic semiconductor systems, with the latter being dominated by Rh(II) impurities.

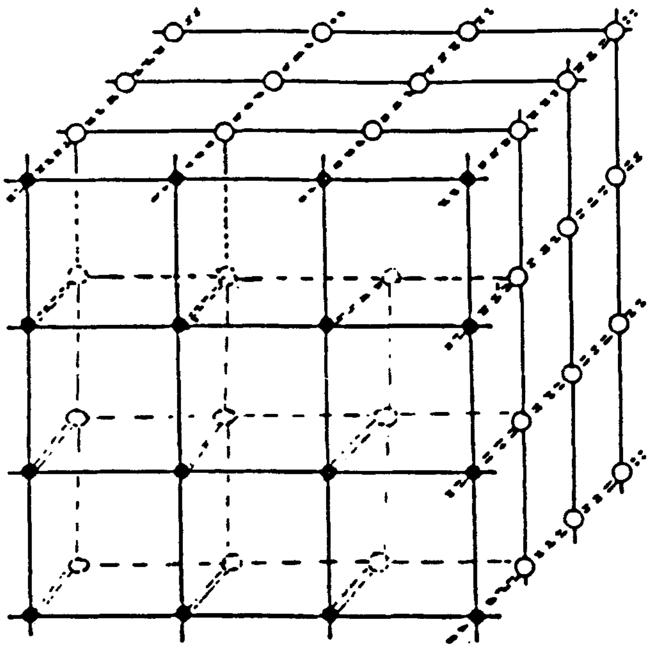

FIGURE 1 Schematic representation of the three-dimensional [Rh(4,4'-diisocyanobiphenyl)$_2^+$Cl$^-$]$_n$ network structure.

The strong visible absorptions (Figure 2) observed for the $[Rh((CN)_2Ar)_2^+Cl^-]_n$ polymers can be accounted for by the presence of extensive columnar metal chains. The gross electronic spectral features of these polymers are similar to those reported[27] for oligomers of the type $[Rh(CNR)_4]_n^{n+}$ in which the visible bands have been assigned to transitions associated with weak intermetallic interactions. These electronic spectra may be understood in terms of a band diagram (Figure 3). This diagram is derived by the n-way splitting of the monomeric $[ML_4(D_{4h})]$ a_{1g} (HOMO) and a_{2u} (LUMO) levels of an isolated columnar metal chain section $[(ML_4)_n$-eclipsed$]$ of the polymers. Here the bonding dz^2 and antibonding $(P_{Z\text{-}\pi}{}^*)$ bands are comprised of n-filled ($2n$-electrons) and empty levels, respectively. The higher energy band in the spectra of the polymers may be assigned to either top-to-top or bottom-to-bottom transitions (see Figure 3).

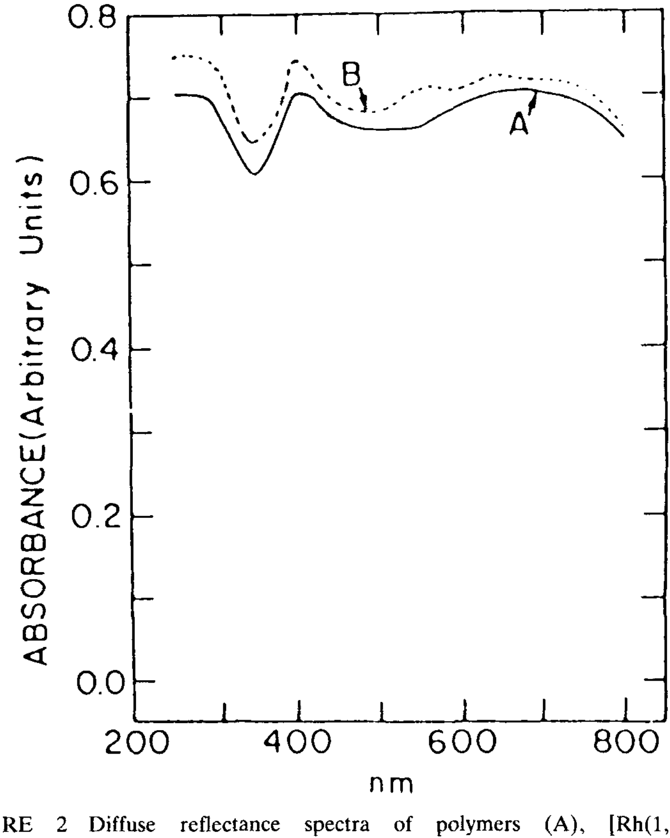

FIGURE 2 Diffuse reflectance spectra of polymers (A), $[Rh(1,4\text{-diisocyanobenzene})_2^+Cl^-]_n$ and (B), $[Rh(4,4'\text{-diisocyanobiphenyl})_2^+Cl^-]_n$.

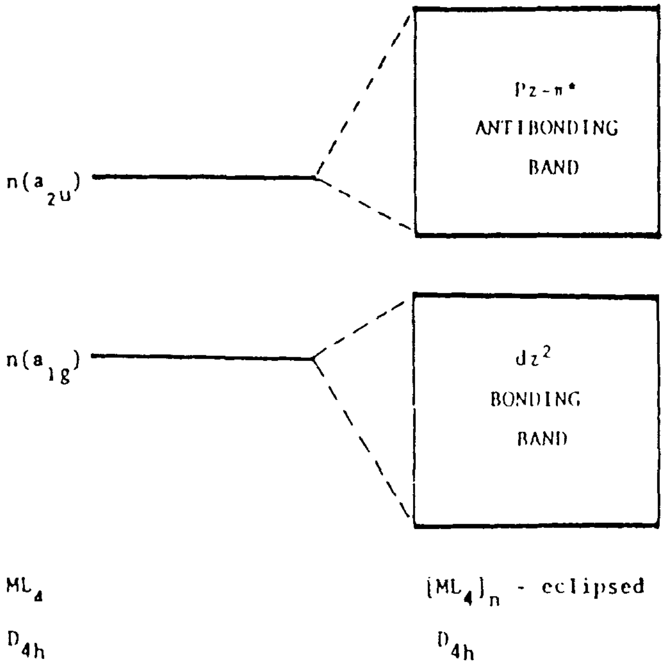

FIGURE 3 Proposed relative energy band diagram for polymers [Rh(1,4-diisocyanobenzene)$_2^+$Cl$^-$]$_n$ and [Rh(4,4'-diisocyanobiphenyl)$_2^+$Cl$^-$]$_n$.

These transitions are expected to be of comparable energies to those assigned as $^1A_{1g} \rightarrow {}^1A_{2u}$ in the case of the mononuclear complexes, [Rh(CNR)$_4$)]$^+$. The broad absorptions oberved for the lower energy transitions associated with Rh(I)---Rh(I) interactions are most probably due to band-gap transitions, and may be viewed as consisting of a multitude of transitions occuring between the upper region of the bonding and the lower region of the antibonding bands.

The spectral absorptions in the ultraviolet, visible, and near infrared regions noted for [Rh((CN)$_2$Ar)$_2^+$Cl$^-$]$_n$[2,5] led us to consider the possible photoelectric properties of these systems. Materials demonstrating photoconductive properties are of current interest in their potential application in numerous devices, i.e., photoelectrochemical devices,[14] vidicon television pickup tubes,[15] xerographic photoreceptors,[16] etc. Metallophthalocyanines,[17,18] arylethynl copper polymers,[19] and metalloporphyrin films[20] have all been reported to be photoconductive organometallic systems. Very recently, reports revealing photoconductive behavior for copper phthalocyanine,[21] lead phthalocyanine[22] and μ-cyanophthalocyaninato Co(III) polymers[23] have appeared, further stimulating interest in photoelectric properties of organometallic systems. The former report compared the photoelectric behavior of monomeric and polymeric copper phthalocyanine in order to investigate the influence of polymerization on these properties.

We report here that $[Rh((CN)_2Ar)_2^+Cl^-]_n$ polymers,[5] which precipitate out of concentrated oligomeric solutions, show photoconductive behavior. Thin films prepared by evaporation of these same oligomeric solutions on conductive glass reveal photoconductive properties as well, in the visible and near infrared regions. Our results reported here, demonstrate somewhat similar trends to those of the monomeric and polymeric copper phthalocyanine systems.[21]

EXPERIMENTAL

Powdered $[Rh((CN)_2Ar)_2^+Cl^-]_n$ polymers were synthesized from $[Rh(CO)_2Cl]_2$ and the respective aryldiisocyanides;[24] their preparation has been previously reported.[5] These polymers are best formulated as $[Rh((CN)_2Ar)_2^+Cl^-.\times H_2O]_n$, x = 0–10, unless they are handled in a dry box or dried under high vacuum (80°C/0.1 torr) in order to remove the associated water molecules. Photoconductivity measurements were performed on compressed pellets (10 ton $cm^{-2}min^{-1}$) of these materials.

All thin films were prepared from $2.6\times10^{-3}M$ CH_2Cl_2 solutions of $[Rh(CO)_2Cl]_2$ to which a $1.0\times10^{-2}M$ CH_2Cl_2 solution of the respective aryldiisocyanide had been dropped rapidly via a dropping funnel. The allowed reaction time controlled the extent of oligomerization as could be observed by diffuse reflectance spectroscopy using a Cary 15 spectrophotometer fitted with a diffuse reflectance measurement apparatus. $MgCO_3$ was taken as the standard material for which was assumed 100% reflectivity or 0% absorbance (there are small deviations from these percentages but they are negligible in the region of measurement).[25] During measurement this standard was placed directly behind the translucent films in order to reflect the light back into the diffuse reflection sphere. All samples measured were then compared to this standard and plotted accordingly in absorbance terms. This technique was used to measure the spectral response of all films and pellets. In order to extend these measurements into the near-infrared (in the range 700–1100 nm), a silicon photodiode was used. The films were prepared by dipping conductive glass slides (tin oxide coated glass) into the above solutions followed by evaporation. Films prepared using this method were observed via electron microscopy to be $<0.1\mu$ in thickness. They were then sputtered with a Au target producing a 800-1000Å layer. Unavoidable pinholes in the thin films prepared in this manner resulted in contact between the gold sputtered layer and the conductive glass. This led to a large shorting current which prevented us from observing the voltage dependence of the photoconductivity. Significantly thicker films, wherein pinholes may have been eliminated, could not be prepared due to polymer precipitation as fine powders from the oligomeric solutions during additional dipping of the glass slides.

The arrangement used for photoconductivity measurements for both the thin films and pellets has been reported earlier.[26] A potentiostat was used to convert current to voltage and to apply a voltage bias (1.2 Volts for the pellet and less than a few millivolts for the films). The light source was a 250W tungsten-halogen projector. A silicon photodiode was used to verify that the intensity of this source was constant throughout the experiments. The power per unit surface of the source was measured with a YSI-Kettering model 65A radiometer. We attempted to obtain photoconductive spectra using either a monochromator or bandpass filters; in both cases the signal was attenuated to values below the noise level. Therefore action spectra were obtained using a series of cut-off filters at 420, 495, 610, 695, 780, 850, and 1000 nm. These measurements were initially obtained as bar graphs of photocurrent normalized to incident power and were then smoothed into curves for the sake of clarity. The light beam was modulated using a mechanical chopper (21 Hz for the pellet and 40 Hz for the films, Model PAR 192) and the ac signal was detected with a Brookdeal 9505 SC lock-in amplifier.

RESULTS AND DISCUSSION

The only polymeric sample which displayed a measurable photocurrent was the $[\mathrm{Rh(4,4'\text{-}diisocyanobiphenyl)}_2^+\mathrm{Cl}^-]_n$ pellet, whose spectral profile is shown in Figure 4. These measurements were all taken under an applied external field. When the same pellet was measured in the absence of such a field no observable photocurrent was detected. While the photoresponse was reproduced at the time of measurement, no response was detected some weeks later. The poor photoresponse, which we attribute to recombination in the pellet, prompted us to prepare thinner samples to enhance the ability of charge carriers

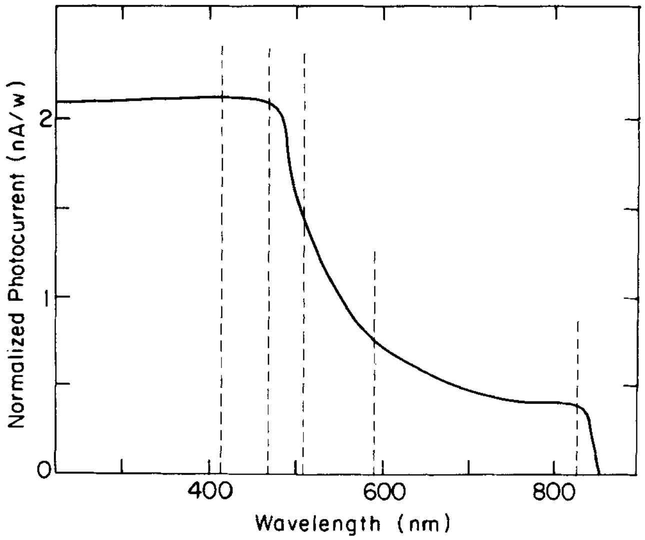

FIGURE 4 Photoconductivity spectrum of polymeric pellet of $[Rh(4,4'\text{-diisocyanobiphenyl})_2^+Cl^-]_n$.
Vertical lines show the intervals of measurement.

to reach the metal contacts. The ability to prepare soluble $[Rh((CN)_2Ar)_2^+Cl^-]_n$ oligomers having metal-metal interactions suggested that we could "freeze-out" these systems, not allowing them to undergo further polymerization, by rapid evaporation as thin films on microscope slides. Further polymerization leads to powdered precipitates which are not amenable to thin film preparation. Therefore, investigation of the photoconductivity of these thin film samples is limited to metal-metal interacted oligomers and does not allow for the study of the polymers as films.

Figures 5, 6 and 7 show the photoresponse (normalized photocurrent, nA/W) as a function of wavelength for three different films of $[Rh(1,4\text{-diisocyanobenzene})_2^+Cl^-]_n$. Superimposed on each of these figures are the respective diffuse reflectance spectra and it is the latter which we would like to discuss first. In order to understand the reflectance data of the films, it is useful to discuss the spectral absorbance of the solutions from which these films were prepared as well as that of soluble monoisocyanide oligomers, $[Rh(CNPh)_4]_n^{n+}$. For the latter it has been shown that these complexes undergo oligomerization via metal-metal interactions as viewed by the appearance of ~600 and ~750 nm absorptions.[27] We have made similar observations for solutions of $[Rh((CN)_2Ar)_2^+Cl^-]_n$ employing aryl-

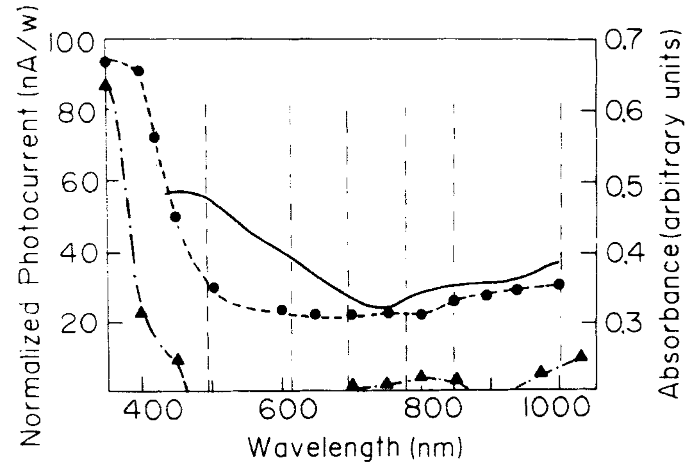

FIGURE 5 Photoconductivity spectrum of [Rh(1,4-diisocyanobenzene)$_2^+$ Cl$^-$]$_n$, Film 3 (unbroken curve). Diffuse reflectance spectrum of Film 1 (broken dotted curve) and uncoated conductive glass (broken triangular curve).

diisocyanide ligands. These latter spectra can be measured at relatively high concentrations ($\sim 2.6 \times 10^{-3}$M).[5] Our results suggest the beginning of metal-metal bond formation in solution at these concentrations. With more dilute solutions ($\sim 2.6 \times 10^{-5}$M) the absence of any bands in the visible region indicates that sufficiently soluble

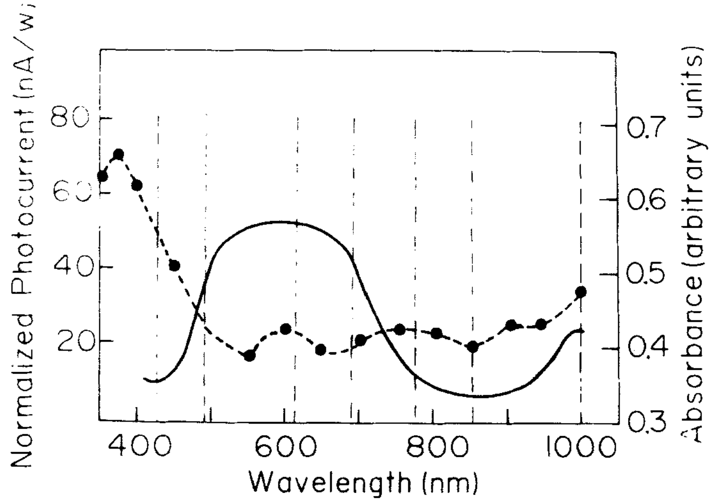

FIGURE 6 Photoconductivity spectrum of [Rh(1,4-diisocyanobenzene)$_2^+$ Cl$^-$]$_n$, Film 2 (unbroken curve). Diffuse reflectance spectrum of Film 2 (broken curve).

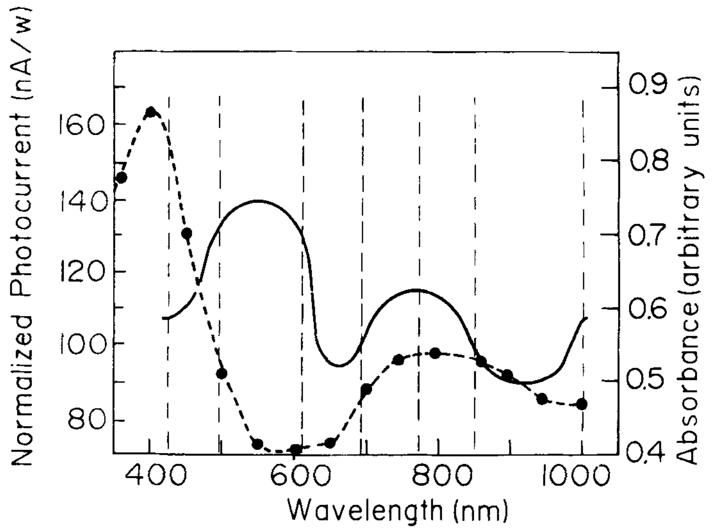

FIGURE 7 Photoconductivity spectrum of [Rh(1,4-diisocyanobenzene)$_2^+$Cl$^-$]$_n$, Film 3 (unbroken curve). Diffuse reflectance spectrum of Film 3 (broken curve).

oligomers are formed through the linking ligand rather than by intermetallic interactions.[5] Thin films prepared from these same solutions after different reaction times have also shown these spectral features, measured using diffuse reflectance spectroscopy and an appropriate standard material.

Our experiments have shown that the reflectivity of these samples is constant in the region of measurement. Therefore it appears that the spectral features identified using diffuse reflectance spectroscopy (see experimental section) correspond to absorbances as depicted in Figures 5–7. Photoacoustic spectroscopic measurements gave absorbance spectra corroborating the above.

The size of metal-metal linked oligomers would be expected to increase with both reaction time (prior to film preparation) and solution concentration. The reflectance spectra support this. Film 1 (Figure 5) was prepared using the shortest reaction time (~5 min.) and no defined absorbance maxima is observed in the visible range. Therefore, it appears that only oligomerization via the linking diisocyanide has taken place without the formation of Rh---Rh interacted oligomers. Figure 5 also shows that the spectral contribution of the tin oxide coated glass upon which the films were evaporated is virtually negligible in the visible and near-infrared range. Film 2 (Figure 6) was prepared using a reaction time approximately twice that of

Film 1. The presence of low-intensity absorbance bands at ~600 and ~750 nm are visible in the absorbance spectrum of this film. Based on spectral assignments for the extensively investigated monoisocyanide $[Rh(CNPh)_4]_n^{n+}$ oligomers, we assign these absorbance bands to mixed oligomeric dimer-trimer systems (via Rh---Rh interactions). The preparation of the third film $[Rh(1,4\text{-diisocyanobenzene})_2^+Cl]_n$ (Figure 7) employed reaction times twice that of Film 2 and its spectrum displays a heightened absorbance maxima at ~750 nm. This is indicative of the predominant presence of metal-metal interacted trimers in this film. As higher oligomeric species are known to absorb in the 600-750 nm region,[27] mixtures with higher oligomers are possible in both the two latter films.

We now consider the photoconductivity spectra in Figures 5–7. These have also been reproduced in Figure 8 for the sake of convenient comparison. Although one may intuitively expect increases in photoconductivity to occur at wavelengths of peak absorption, this is by no means a necessary requirement. We have observed only partial correlation between the photoconductivity and absorption spectra. For example, the decrease in photoconductivity for Films 2 and 3 (Figures 6 and 7, respectively) upon approaching the ultraviolet range, contrasts the films' absorption in the same region. Furthermore, Film 3 displays a maximum in photoconductivity at ~600 nm where an absorption minimum exists. As of yet we have no explanation for the heightened photoconductivity signal of Film 3 (Figure 8) compared to Films 1 and 2. However, the general trend in Figure 8 is clear; as the size of the metal-metal interacted oligomers increases, a shift in photoconductive response from ~400 nm (Film 1) to 600 nm (Film 2) to 750 nm (Film 3) occurs. All films show increases in photoconductivity at ~1000 nm suggesting that this may be due to an infrared absorption of the monomeric unit itself.

Recent comparative studies on the photoconductivity of monomeric copper phthalocyanine, monoCuPc, and polymeric phthalocyanine systems, polyCuPc,[21] have evidenced a broad photoconductivity band which decreases upon going to longer wavelengths (visible → near-infrared) for the polymeric system. The monoCuPc complex was characterized by an increase in photoconductivity upon going to longer wavelengths and distinct photoconductivity peaks at ~850 nm and ~1050 nm were observed.[21] Film 1 for which spectral evidence has shown the absence of oliomeric species through Rh—Rh interactions shows a minimal relative photoconductivity in the ~500–800 nm range with significantly increasing photoconductivity in the near infrared at ~1000 nm. This behavior bears similarity to the monoCuPc

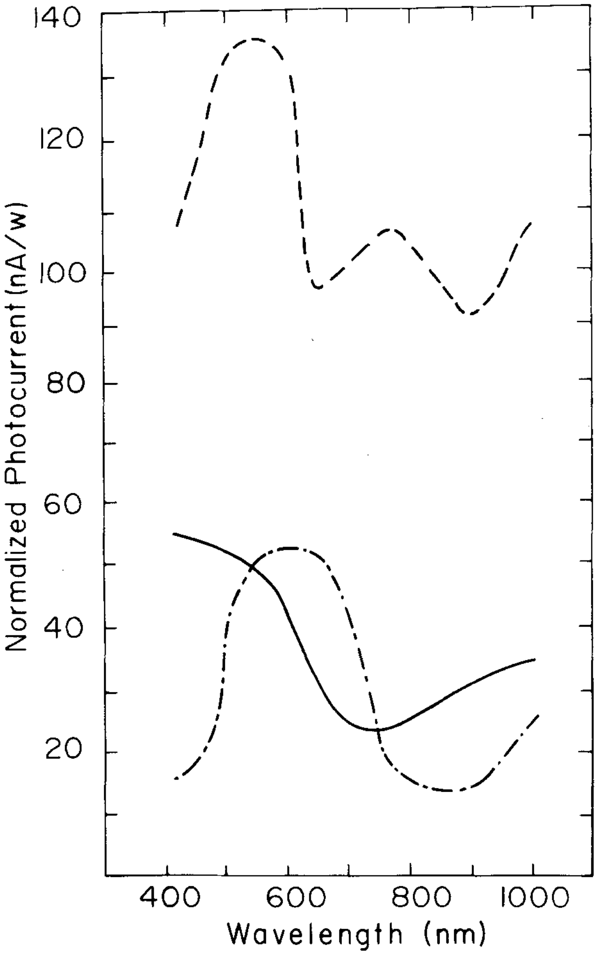

FIGURE 8 Comparison of action spectra of the three [Rh(1,4-diisocyanobenzene)$_2^+$Cl$^-$]$_n$ films; Film 1 (———), Film 2 (- — - — -), and Film 3 (- - - -).

complex. Films 2 and 3 most probably represent intermediate stages for which no comparison is available in the CuPc system, and show different photoconductivity maxima in the visible region. However, the polymeric Rh(I)-4,4′-diisocyanobiphenyl pellet has indeed shown a steady decrease in photoconductivity as a function of longer wavelengths similar to polyCuPc. It should be noted, however, that not all organometallic polymers follow the trends of decreasing photoconductivity in the near-infrared regions. Both polymeric [PcGeS]$_x$[28]

and $[\mathrm{PcCoCN}]_x$[22] show defined photoconductivity maxima at ~1000 nm.

CONCLUSIONS

We have observed different visible and near-infrared photoconductive reponses for the Rh(I) aryldiisocyanide polymeric pellet and various thin films described here. By varying reaction times and/or reactant concentrations, thin films containing various $[\mathrm{Rh}((\mathrm{CN})_2\mathrm{Ar})_2^+\mathrm{Cl}^-]_n$ oliogmeric lengths (via metal-metal interactions) have been prepared. It is difficult to extrapolate and draw conclusions for films of longer oligomers, however, on the basis of the data at hand, we have observed a general trend worth noting for the photoresponses in these films. In these samples, the maximal photoconductive response is red shifted with increasing degrees of metal-metal oligomerization. These films then demonstrate photoconductivity in defined spectral regions. This property of spectral selectivity suggests their potential use as optical filters and as novel photoconductive materials.

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References

1. A. Efraty, I. Feinstein, L. Wackerle and F. Frolow, *Angew. Chem. Intl. Ed.*, **19**, 633 (1980).
2. A. Efraty, I. Feinstein, F. Frolow and L. Wackerle, *J. Am. Chem. Soc.*, **102**, 6341 (1980).
3. A. Efraty, I. Feinstein, F. Frolow and A. Goldman, *J. Chem. Soc. Chem. Commun.*, **864** (1980).
4. A. Efraty, I. Feinstein and F. Frolow, *Inorg. Chem.*, **21**, 485 (1982).
5. I. Feinstein-Jaffe, F. Frolow, L. Wackerle, A. Goldman and A. Efraty, submitted.
6. A. Efraty, I. Feinstein and L. Wackerle, *Inorg. Chim. Acta*, **54**(5), L211 (1981).
7. A. Efraty and I. Feinstein, *Inorg.*, **21**, 3115 (1982).
8. I. Jaffe, M. Segal and A. Efraty, *J. Organometal Chem.*, **294**, C17 (1985).
9. I. Feinstein-Jaffe and A. Efraty, *J. Mol. Cat.*, **35**, 285 (1986).
10. I. Feinstein-Jaffe and A. Efraty, *Macromolecules*, 19, 2076 (1986).

11. M. Hanack, K. Mitulla and O. Schneider, *Chemica Scripta*, **17**, 139 (1981); C. Hedtmann-Rein, U. Keppeler, X. Munz and M. Hanack, *Mol. Cryst. Liq. Cryst.*, **118**, 361 (1985); M. Hanack, *Mol. Cryst. Liq. Cryst.*, **105**, 133 (1984); M. Hanack, *Israel J. of Chem.*, **25**, 205 (1985).
12. J. G. Gordon, II, R. Williams, C.-H. Hsu, E. Cuellar, S. Samson, K. Mann, H. B. Gray, U. Hadek and R. Somoano, *Ann. N.Y. Acad. Sci.*, **313**, 58 (1978).
13. T. Iinuma and T. Tanaka, *Inorg. Chim. Acta*, **49**, 79 (1981).
14. N. Minami, *J. Chem. Soc.*, Faraday Trans. 2, **78**, 1871 (1982); H. Meier, W. Albrecht, U. Tschirwitz, N. Geheeb and E. Zimmerhackl, *Chem.-Ing.-Tech.*, **51**, 653 (1979).
15. H. Meier and W. Albrecht, *Ber. Bunsenges. Phys. Chem.*, **73**, 86 (1969).
16. J. W. Weigl, J. Mammino, G. L. Whittaker, R. W. Radler and J. F. Byrne, *Current Problems in Electrophotography* (W.F. Berg and K. Hauffe, eds.), W. deGruyter, Berlin, 1972, pp. 287.
17. S. Meshitsuka and K. Tamaru, *J. Chem. Soc. Farad. Trans.*, **73**, 760 (1977).
18. J. Langton and P. Day, *J. Chem. Soc.*, Faraday Trans. 2, **78**, 1633 (1982).
19. Y. Okamoto and S. K. Kundu, *J. Phys. Chem.*, **77**, 2677 (1973).
20. K. Yamashita, K. Maenobe and J. Fajer, *Chem. Lett.*, **307** (1980).
21. H. Meier, W. Albrecht and E. Zimmerhackl, *Polym. Bull.*, **13**, 43 (1985).
22. J. P. Dodelet, H.-P. Pommier and M. Ringuet, *J. Appl. Phys.*, **53**(6), 4270 (1982).
23. H. Meier, W. Albrecht, E. Zimmerhackl, M. Hanack and J. Metz, *Syn. Met.*, **11**, 333.(1985).
24. A. Efraty, I. Feinstein, L. Wackerle and A. Goldman, *J. Org. Chem.*, **45**, 4059 (1980).
25. T. Surles, J. O. Erickson and D. Porter, *Inter. Laboratory* May–June, 29 (1975).
26. A. Natansohn and H. Flashier, *J. Polym. Sci., Polym. Let. Ed.*, **22**, 579 (1984).
27. K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray and J. R. Gordon II, *Inorg. Chem.*, **17**, 828 (1978); K. R. Mann, J. R. Gordon II and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 3553 (1975); J. G. Gordon II, R. Williams, C.-H. Hsu, E. Cuellar, S. Samson, K. Mann, H. B. Gray, V. Hadek and R. Somoano, *Annals N.Y. Acad. Sci.*, **313**, 587 (1978); K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray and J. G. Gordon II, *Inorg. Chem.*, **17**, 828 (1978).
28. H. Meier, W. Albrecht, E. Zimmerhackl, M. Hanack and K. Fischer, *J. Mol. Electron.*, **1**, 47 (1985).