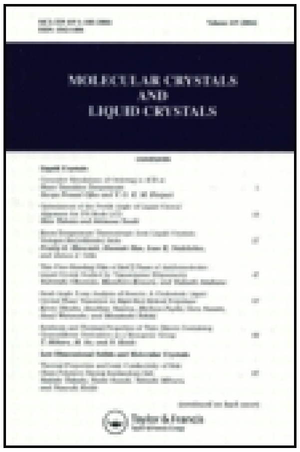


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Near-IR Dyes for the 1.3 to 1.5 Micron Region: The Use of Substituted Dithiolene Complexes

U. T. Mueller-westerhoff [a] , D. I. Yoon [a] & K. Plourde [a]

[a] University of Connecticut, Storrs, CT, 06269-3060

Version of record first published: 04 Oct 2006.

To cite this article: U. T. Mueller-westerhoff , D. I. Yoon & K. Plourde (1990): Near-IR Dyes for the 1.3 to 1.5 Micron Region: The Use of Substituted Dithiolene Complexes, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 291-302

To link to this article: http://dx.doi.org/10.1080/15421409008047466

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 291–302
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

NEAR-IR DYES FOR THE 1.3 TO 1.5 MICRON REGION: THE USE OF SUBSTITUTED DITHIOLENE COMPLEXES

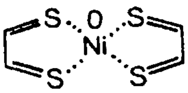
U. T. MUELLER-WESTERHOFF*, D. I. YOON, AND K. PLOURDE
University of Connecticut, Storrs, CT 06269-3060

Abstract Nickel complexes of the dithiolenes type with broad but also intense electronic transitions in the NIR region of the electromagnetic spectrum have been syntyhesized. These complexes are extremely useful in certain applications involving NIR lasers.

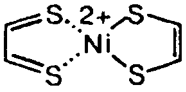
INTRODUCTION

For quite a few years, we have investigated several approaches to create materials which show intense electronic transitions in the 1.0 to 1.6 micron region of the Near-IR. Of the several choices in the types of compounds which one might consider as candidates for NIR dyes we have chosen the class of square planar transition metal dithiolene complexes, especially those of Ni, because already the unsubstituted parent Ni dithiolene shows a transition at the NIR edge of the visible and the dithiolene absorption can be shifted by proper substitution. In addition, the dithiolenes show much higher thermal and photochemical stability than other dyes which absorb in this spectral region. This is a consequence of the high degree of electron delocalization in these systems. One notable characteristic, in which the dithiolenes differ from purely organic dyes such as the cyanines, is the shape of the intense Near-IR band: in all known dithiolenes the band is very broad and shows no vibrational fine structure.

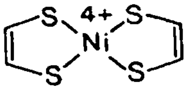
A qualitative description of the bonding in dithiolenes, as exemplified by the neutral d^8 complex $Ni(S_2C_2H_2)_2$, involves the structures 1 to 3, in which the metal assumes formal oxidation states of 0, 2+, and 4+ while the ligands are either neutral "dithiodiketones" or dinegative "dithiolates".



1

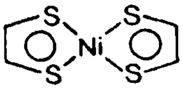


2



3

Dithiolenes are best considered to be a resonance hybrid of the limiting structures 1 - 3. The electron delocalization is not limited to the ligand, but includes the metals to give rise to cyclic delocalization ("aromaticity"). To symbolize this electron delocalization in dithiolenes, they can be represented, similar to the description of benzene, by formulas such as 4, containing a ring inside the framework given by the metal, sulfur, and carbon atoms. It is worth noting that dithiolenes are not unique in this regard: complexes with o-benzoquinones and o-phenylenediamines appear to possess some delocalization because they have been shown to also undergo reversible redox chemistry. Special to the dithiolenes is the extent of delocalization which is made possible by the stronger overlap involving sulfur d-orbitals.



4

We can thus regard the dithiolenes as subject to some of the rules of substituent effects which are well established in the organic chemistry of aromatic compounds. This will guide us in the design of dithiolenes with particular properties.

If we analyze our earlier work in terms to see structural factors contribute to the desired shift of the electrinic transitions, we can extract a strategy for the design of NIR dyes. This has been done is two recent publications from this group,[1,2] and only a summary is given here. The following factors are important in any attempt to shift the absorption maximum of the dithiolenes to lower energy:

1. Coplanarity of ligand pi-system and dithiolene;
2. Presence of an extended pi-system;
3. Presence of electron donating substituents;
4. Fixing of the substituents into rigid coplanarity with the ligand;

   Attachment of sterically bulky substituents to increase solubility;

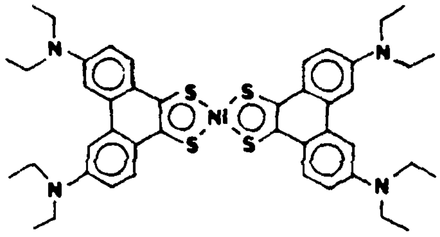
SYNTHESIS OF NEW DITHIOLENES WITH NEAR-IR ABSORPTION

With the above options and constraints in mind, new types of ligands can be designed. While it may be relatively simple to produce dithiolenes with one of these properties, to combine all of them into a particular ligand structure amounts to a major synthetic effort. We have explored several approaches to the preparation of near-IR dyes based on the planar dithiolenes of Ni as the central core. Of the many possible planar ring systems, the phenanthrene derivatives proved to be a good basis for amino-substituted aromatic ligands for new dithiolenes.

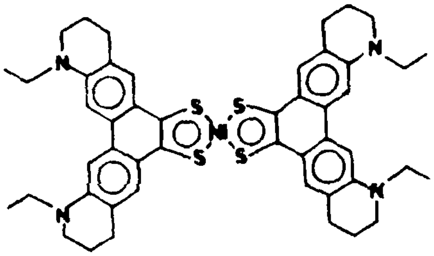
However, a new approach to dithiolenes with strong Near-IR absorption is based on using totally different electron donor functions as substituents in dithiolene ligands: this involves the synthesis of metallocene-substituted dithiolenes. This area is still almost unexplored but our research group has contributed to both areas, metallocene and dithiolene chemistry, with some success. It has become clear that the chemistry of metallocenes and of related compounds offers great structural variety and that its combination with the chemistry of dithiolenes may provide an important alternative to the first approach.

DITHIOLENES WITH PHENANTHRENE-BASED SUBSTITUENTS

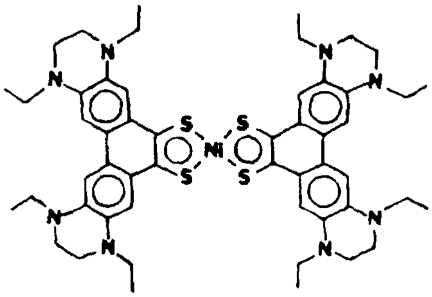
In the series of phenanthrene-based dithiolenes, we have investigated three main examples. In the first two, two dialkylamino substituents in the 3 and 6 positions are the electron donor functionalities, which in the first case, the bis-3,6-diethylaminophenanthrene based system 5, are free to rotate, while they are fixed in the second example, compound 6, in which a saturated six-membered ring holds the substituent in conjugation with the phenanthrene rings. The third target was compound 7, which is structurally related to 6, but which contains four nitrogen donor groups.



5



6



7

Bis-(3,6-diethylaminophenanthrene-9,10-dithiolato) Nickel (5)

After many different attempts to prepare compound 5, the following sequence of reactions proved to be successful:

Starting from commercially available 3-chloro-aniline or the much more costly 3-bromo-aniline), acetylation and reduction by LAH produced the n-ethyl derivative, which was converted to N,N-diethyl 3-chloro-aniline either by a second acetylation and again reduction by LAH or by direct alkylation using iodoethane and di-isopropyl ethylamine in acetonitrile. Its Vilsmeier formylation was followed by coupling using $Ni(Ph_3P)_4$ in DMF to yield the biphenyl derivative. This dialdehyde was cyclized to the substituted phenanthrene by hydrazine in acetic acid under reflux. The product was quite sensitive to oxidation, but it was nevertheless possible to brominate it in good yields by bromine in 48% HBr, yielding the 9,10-dibromo derivative. Its conversion to the bis-benzylmercapto derivative was achieved in standard ways using CuBr as a catalyst and lutidine as solvent. Cleavage by sodium dissolving in EtOH or by sodium in liquid ammonia led to the dithiolate, which was converted to the desired complex 5. For some not evident reasons, the cleavage reaction gave poor yields and the resulting dithiole was very prone to polymerization. This only allowed the formation of the dithiolene in small quantities of a very hard to purify material. No full characterization was possible for these reasons. The NIR spectrum of 5 in methylene chloride solution (Figure 1) showed a strong, broad absorption centered at 1340nm.

Bis-(1,12-diethyl-1,2,3,4;9,10,11,12-octahydro-1,12-diaza-pentaphene-6,7-dithiolato)nickel (6)

Our next goal was the synthesis of compound 6, a fixed derivative with the same electronic structure as compounds 5. As one might expect, the general synthetic scheme has some similarity with that outlined for 5, but there exist notable and significant differences. The synthesis can be summarized as follows:

Initial attempts to substitute tetrahydroquinoline, N-acetyl-tetrahydro quinoline, or 6-formyl-tetrahydroquinoline, even when some procedures which claim meta-directing substitution were followed, showed that is was not possible to introduce a halogen substituent in position 7. It was thus necessary to again start from the commercially available 3-chloroaniline and to introduce first the quinoline ring system following a Skraup synthesis. As expected, both possible isomers with the halogen in the 5- or 7-position were formed, but their separation was easy to achieve by fractional crystallization from HNO_3 as the nitrate salts. The free base was regenerated by strong alkali.

When 7-chloro-quinoline was reduced by pyridine-borane in acetic acid, a mixture of three products was obtained: the partially reduced 7-chloro dihydroquinoline, the completely reduced 7-chloro tetrahydroquinoline, and its N-ethyl derivative, which appeared to be formed by acylation under reducing conditions. The first two products were obtained as a hard to separate mixture. However, the acetylation of this mixture and reduction by sodium borohydride in the presence of Raney nickel in warm EtOH led to N-acetyl-tetrahydroquinoline as the only product.

The reduction of 7-chloroquinoline was also carried out in a two-step procedure, first using DIBALH to obtain the dihydro derivative and then reducing with $NaBH_4$ or $NaBH_3CN$ in acetic acid, which led to the N-acetyl tetrahydroquinoline.

The Ni(0) mediated coupling of again produced considerable amounts of dehalogenated product, and the coupled biphenyl derivative was obtained only in very small yield. Much more advantageous was the coupling of the acetyl derivative and subsequent reduction with LAH. This generated the benzidine derivative with fixed amino groups.

This product is a strong electron donor and as such is very air sensitive. Even under nitrogen and in the dark, it turns deep red or black within a short while. Immediate reaction with oxalyl chloride and aluminum chloride to generate the more stable phenanthrenequinone derivative was therefore indicated. Sulfurization of the dione to produce the dithione was sluggish and required drastic conditions, which resulted in considerable loss of material. The only choice to generate the dithione turned out to be the reaction with P_4S_{10} in boiling dioxane. Reaction of this solution with $NiCl_2$ in water is similar to the now superseded low-yield procedure used earlier for related dithiolenes such as the frequently used JUL2. It was therefore not surprising that it produced an impure dithiolene and in low yield.

Attempts to recrystallize this material led to further losses. Extraction with methylene chloride and precipitation of the product from the concentrated solution by addition of methanol led to the crude complex 6, which was filtered and washed several times with methanol. This product clearly is not analytically pure and only a qualitative Near-IR spectrum was recorded (Figure 1). The maximum is found at 1380 nm (in methylene chloride). It is worth noting that the Near-IR peak is much sharper than that of the electronically very similar complex 5, in which the amino groups are free to rotate. Apparently, the fixation of the donor substituents does has the effect of narrowing the absorption band while maintaining the transition moment. The result is a more intense peak.

1,4,9,12-tetraethyl-1,2,3,4;9,10,11,12-octahydro-1,4,9,12-tetraaza-pentaphene-6,7-dithiolato nickel (7)

In making this complex one of our targets, we looked at the fact that its non-planar analog was the dithiolene with the longest wavelength absorption known so far. It was therefore surmised that the planar system would allow another substantial gain in bathochromic shift.

The synthesis of this complex was, by necessity, closely related to the methods used in the perparation of the dithiolenes described above. Starting from commercially available 4-chloro-1,2-phenylenediamine, double acetylation and LAH reduction led to the N,N'-diethyl derivative which was cylized with oxalyl chloride in methylene chloride to give the cyclic oxamide. This compound was amenable to Ni(0) mediated coupling to the biphenyl derivative, which was then reduced by LAH and subjected to a double Friedel-Crafts reaction with oxalyl chloride and aluminum chloride in methylene chloride to yield red-black crystals of the phenanthrenequinone derivative. Thionation of this quinone with P_4S_{10} or Lawesson's reagent in refluxing dioxane and addition of aqueous nickel chloride to this solution led to the dithiolene complex 7.

This dithiolene, obtained as a microcrystalline, black powder, showed an intense absorption maximum at 1,440nm in methylene chloride solution (Figure 2). Compared to the absorption maximum, under the same conditions, of its non-planar analog (1,370nm) the shift by 70 nm

(0.044eV) is less than what we know to occur when two phenyl groups are forced into coplanarity and thus reinforces the caveat applied there that we can not expect a phenanthrene ring to act like two separate, but coplanar, phenyl substituents. However, this is a substantial step toward the 1,500 nm target we had set out to meet.

Unfortunately, this complex also proved to be a very unstable and apparently air sensitive compound. For example, a solution in CH_2Cl_2 lost 50% of its characteristic Near-IR absorption during a few hours in a closed spetrometric cuvette.

The above work was geared to the synthesis of Near-IR dyes with benzenoid ligands carrying donor substituents. This approach was chosen, because we had seen that strong donor groups alone would destabilize the HOMO to such an extent that it would become non-bonding or even anti-bonding and thus produce a high degree of reactivity in the resulting dithiolenes. Whereas benzenoid aromatics extend the overall delocalized pi-system and thus lead to the wanted bathochromic shift, they alone will not suffice to bring the absorption maximum to the desired 1.500 nm range. Coplanarity of the aromatic substituent with the dithiolene core was recognized as an essential ingredient of the ligand structure to effect low energy transitions. Thus, the combination of coplanar pi-systems linked to the dithiolene core and the presence of donor substituents on the ligand was deemed to be the best compromise to generate the necessary shifts while stability was maintained.

The results confirm our expectations in part. It is possible to approach the 1.500 nm range, but the stability of the dithiolene products is not at all what we would want it to be. We attribute their high degree of reactivity to the presence of the amino functions. These donor groups certainly are conjugated to the dithiolenes as evidenced by the resulting bathochromic shifts, but they nevertheless remain susceptible to oxidation. They may therefore possess a more negative effect in adding to the reactivity than their positive effect of shifting the Near-IR transition would merit.

It thus appears that the approach of using the typical manipulation of aromatic compounds as ligand for dithiolenes has reached its limit. It it fortunate that we have arrived at this

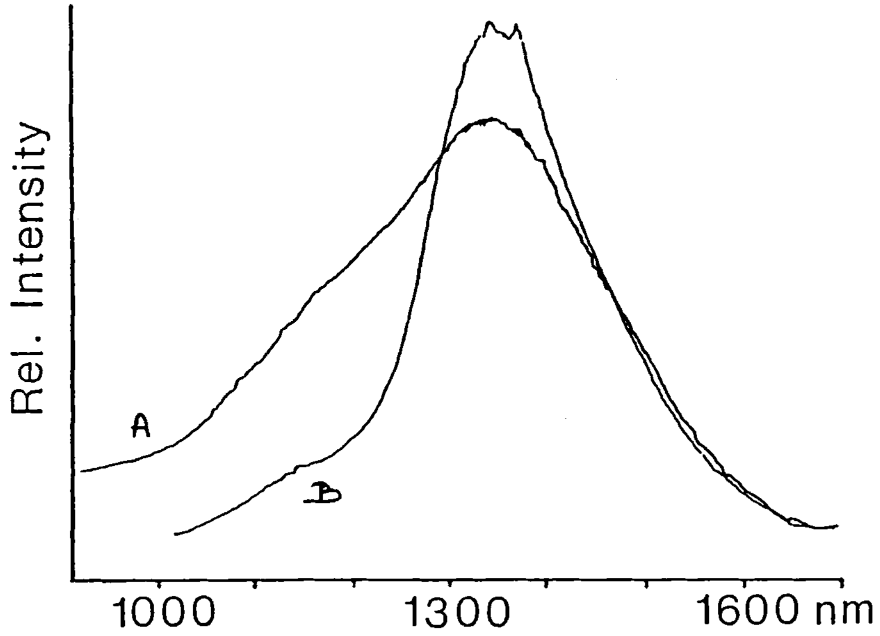


FIGURE 2 NIR Spectra of Dithiolenes 5 (A) and 6 (B).

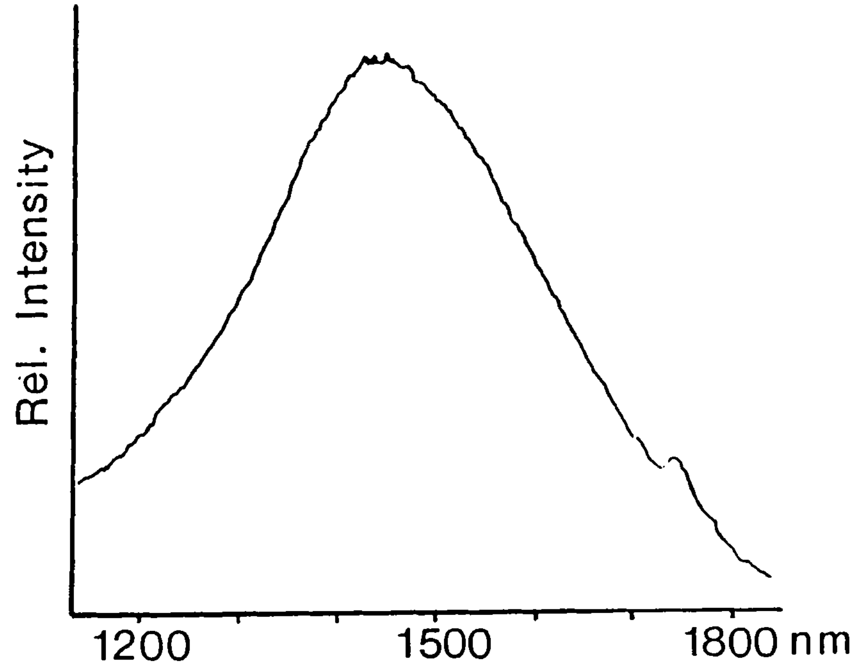


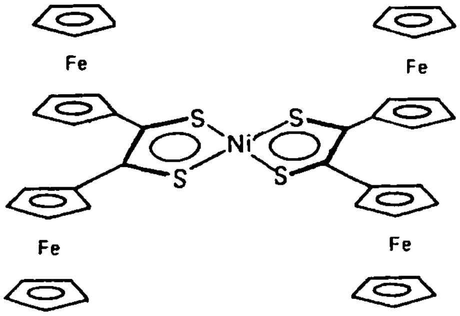
FIGURE 2 NIR Spectrum of the Dithiolene 7

conclusion at the same time at which a new avenue has opened for further progress in this area. This new approach is based on metallocenes as the donor ligands.

METALLOCENE-SUBSTITUTED DITHIOLENES

While the above work on dithiolenes with benzenoid ligands was in progress, we have also begun to explore a very different approach to the synthesis of dithiolenes using donor ligands other than the ones described above. Our experience with metallocenes and metallocenophanes has led us to explore the synthesis of dithiolenes which contain organometallic ligands. Ferrocene and ruthenocene are the classical organometallics and their chemistry has been widely investigated. Ferrocene and several of its analogs are strong electron donors which can be reversibly oxidized at low potentials. They also are able to stabilize adjacent positive charges as in carbenium ions and can be used as the donor component in charge transfer complexes. Our own work has helped in understanding the properties of cyclic, binuclear metallocene systems[3] and it is this class of ferrocene and ruthenocene derivatives we eventually want to utilize as ligands in dithiolenes.

As a trial balloon, we undertook the synthesis of the tetra-ferrocenyl dithiolene 8 and were most pleasantly surprised by the results. First of all, the new complex showed an absorption maximum at 1,310nm (0.95eV) in CH_2Cl_2 solution - at much lower energy than we had expected, because there exists no possibility for the ferrocenes to arrange themselves in a way that the ligands could maximize their overlap with the dithiolene core. The donor potential of the ferrocene substituents thus cannot possibly be fully utilized, and yet we see a drastic shift. Furthermore, the product appears to be perfectly stable in the solid state and in solution. Solid samples were exposed to laboratory environment for several months without any apparent change in composition or in loss of absorption at 1310nm.



8

The synthesis of 8 was simple compared to the long and tedious routes which had to be taken in the preparation of the phenanthrene-based dithiolenes. The oxidation of diferrocenyl ethane by manganese dioxide led to the red dione, which was reacted with P_4S_{10} in dioxane to yield the brown dithione. Its reaction with $NiCl_2$ in methanol generated the grey-green dithiolene.

The apparent thermal and photochemical stability of the tetraferrocenyl dithiolene substantiates to some degree the suspicion that donor strength (and thereby increase in the HOMO energy of the resulting dithiolene) is not the only important criterion for the stability of the dithiolenes, but that the presence of highly oxidation sensitive amino groups in the compounds 5-7 may be the cause of their high reactivity. The metallocene-substituted dithiolene shows the electron donor effect of the metallocenes in the very large shift it produces in the Near-IR transition, but without an increase in reactivity.

These latest results appear to open up an entirely new set of possibilities. Knowing the relative donor potentials of metallocenes and metallocenophanes and adding to this what we have learned about the importance of co-planarity between substituents and the dithiolene central core, we may envision some interesting compounds to investigate. Our present work is following along these lines.

We can now state that dithiolenes indeed have come through with almost all of what we expected of them and they represent a class of materials which are of interest beyond just a special synthesis of a dye with particular properties. Our search for dyes with still lower energy absorption mamima with continue to rely on dithiolenes as the central core.

REFERENCES

1. U. T. Mueller-Westerhoff and B. Vance, in '*Comprehensive Coordination Chemistry*, (Pergamon, Oxford, 1987), Vol. 2, Chap. 16.5, pp. 595 - 631.
2. U. T. Mueller-Westerhoff, K. Plourde, B. Vance, and D. I. Yoon, *Tetrahedron*, in press.
3. U. T. Mueller-Westerhoff, *Angew. Chem. Int. Ed. Engl.*, **25**, 702 (1986).