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# Efficient synthesis and decomposition study of optically nonlinear adducts of tetracyanoquinodimethane

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**Abstract**—Described are the synthetic conditions resulting in a significant improvement in both yield and reaction time of *Z*-β-(1-substituted-4-pyridinium)-α-cyano-4-styryldicyanomethanide chromophores. A decomposition study of the zwitterionic chromophores in solution is also described. © 2003 Elsevier Science Ltd. All rights reserved.

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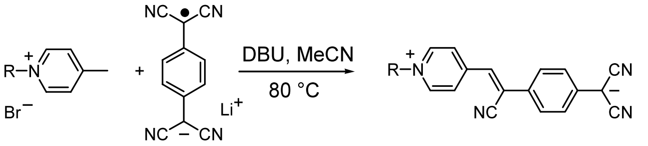
Organic nonlinear optical (NLO) materials are receiving much attention from the telecommunications industry for potential use in high-speed electro-optic (EO) modulators and switches.[1] Organic materials are able to achieve higher EO coefficients, lower dielectric constants (thus higher bandwidths), and are easier to prepare and process than the inorganic NLO crystals such as $LiNbO_3$ used presently in optical modulators.[1,2] When an NLO chromophore is incorporated into a polymer matrix and the required noncentrosymmetry is achieved, the material is optically nonlinear and would have an EO coefficient.[3] Some charge separated donor–(π-electron bridge)–acceptor type of chromophores have sufficiently large $\mu\beta$ values and thus exhibit the second-order NLO effect.[2–4] The scalar $\mu\beta$ represents the averaged orientation of the chromophore in poled media where $\mu$ is the ground state dipole moment and $\beta$ is the nonlinear second-order molecular hyperpolarizability.

Based on the structural similarity to one of the highest $\mu\beta$ chromophores,[5] chromophore **1** (Scheme 1) was selected for potential EO application. Chromophore **1** has previously been shown to a have large theoretical $\beta$ value ($1270\times10^{-30}$ cm$^5$ e.s.u.$^{-1}$ at 1.06 μm),[4,6] while $\mu$ varies depending on the orientation of the zwitterions.

Despite these attributes these NLO chromophores have long been neglected, presumably due to the lack of availablility. The literature procedures available reported low yields of only 15 to 30%, and the reaction times when repeated were upwards of 5 to 14 days.[4,7] In order to investigate the utility of these chromophores for EO device applications they need to be made more accessible. Thus, we report herein our findings that by varying the reaction conditions and with the use of an amine base, chromophores **1a** and **1b** were synthesized in 14 to 30 h with yields ranging from 68 to 97%.



**1a**, R = n-$C_8H_{17}$, 14 hours, 97%
**1b**, R = $C_3H_6OH$, 30 hours, 68%

**Scheme 1.** Synthesis of NLO chromophores **1a**,**b**.

**Table 1.** Molar equiv. of reactants used and the isolated yields for the syntheses of **1a** and **1b**[a]

| | Equiv.[b] pyridine salt[c] | Equiv. LiTCNQ | Equiv. DBU | % Yield |
|---|---|---|---|---|
| **1a** | 1 | 1 | 0.1 | 24[d] |
| **1a** | 1 | 1 | 2 | 20 |
| **1a** | 1 | 2 | 1 | 62[d] |
| **1a** | 1 | 2 | 2 | 97[e] |
| **1b** | 1 | 1 | 0.87 | 53[f] |
| **1b** | 1 | 2 | 1.54 | 68[f] |

[a] All reactions were carried out in MeCN at reflux under $N_2$.
[b] Molar equiv. of starting materials used in reaction.
[c] *N*-Alkyl-4-methylpyridinium bromide.
[d] After one purification.
[e] After four purifications.
[f] After two purifications.

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*Keywords*: synthesis; NLO chromophores; TCNQ adducts; decomposition study.

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The solvent selected for the reactions was MeCN since it resulted in the best yields by far. Reactions were also carried out using DMF, chlorobenzene and ethanol/chlorobenzene, but these only produced the chromophores in very low yields (0–2%).

The reaction of neutral TCNQ and a lepidinium salt in the presence of piperidine was found to proceed rapidly (e.g. 8 h).[8] However, it was later confirmed that a side reaction took place as the result of piperidine displacing cyano groups of TCNQ,[4] which is a known reaction for primary, secondary and tertiary amines with TCNQ.[9] Thus, in our work a number of tertiary amines were tested, including pyridine, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1-(2-hydroxyethyl)piperidine and 1,4-diazabicyclo[2.2.2]octane. It was found that the strongest base, DBU, led to the most drastic improvement in reaction time.

In order to maximize the yield the syntheses of **1a** and **1b** were repeated several times, using the different amounts of starting materials for each reaction. Table 1 outlines the variables and resulting yields. The conditions providing the highest yield for **1a** used 1 equiv. of *N*-octyl-4-methylpyridinium bromide, 2 equiv. of lithium–TCNQ adduct (LiTCNQ) and 2 equiv. of DBU. Once the reactants were dissolved in refluxing MeCN, DBU was added slowly in intervals of three drops every 15 min over a period of 1.5 h. The reaction proceeded for 14 h and the product that had precipitated from solution was collected. After washing the crude product repeatedly with boiling methanol, **1a** was obtained in 97% yield.[10]

The IR spectrum of **1a** showed C≡N peaks at 2132 and 2175 cm$^{-1}$, reinforcing that the compound was zwitterionic in character.[4,8] The UV–vis absorption spectrum showed $\lambda_{max}$ to be 654 nm (Fig. 1). The chromophore **1a** was also characterized by MS and NMR.[11]

Chromophore **1b** was synthesized in the same manner using 1 equiv. of 1-(3-hydroxypropyl)-4-methylpyridinium bromide, 2 equiv. of LiTCNQ and 1.54 equiv. of DBU. The reaction was stopped after 30 h. The more soluble **1b** was purified by dissolving in methanol and precipitating into diethyl ether, then by placing the mixture in a freezer for 12 h before filtering and drying the product. After purifying twice the final product had a yield of 68%. IR and UV–vis spectra of **1b** were similar to those of **1a**, showing C≡N peaks at 2128 and 2175 cm$^{-1}$ in IR and $\lambda_{max}$ at 653 nm. Chromophore **1b** was also characterized by MS and NMR.[12]

To compare with the results achieved using LiTCNQ, two additional reactions were carried out using neutral TCNQ. The first involved 1 equiv. of *N*-octyl-4-methylpyridinium bromide, 2 equiv. of DBU and 2 equiv. of TCNQ. The reaction proceeded for 18.5 h and had a yield of only 34%. The second reaction used 1 equiv. of *N*-octyl-4-methylpyridinium bromide, 2 equiv. of DBU, 1 equiv. of LiTCNQ and 1 equiv. of neutral TCNQ. The reaction proceeded for 16 h and had a final yield of 50%. The results suggested that using LiTCNQ instead of the neutral analogue led to higher yields. The results overall indicated that using both LiTCNQ and DBU in excess relative to the pyridinium salt provided shorter reaction times and higher yields than reported previously for type 1 chromophores. Based on these results we propose the reaction mechanism shown in Scheme 2. This radical mechanism seemingly explains why the second equiv. of LiTCNQ is required to achieve a yield greater than 50%, as well as the need for the second equiv. of DBU. A one-electron transfer from the first adduct to LiTCNQ is facilitated by the formation of the known TCNQ dianion.

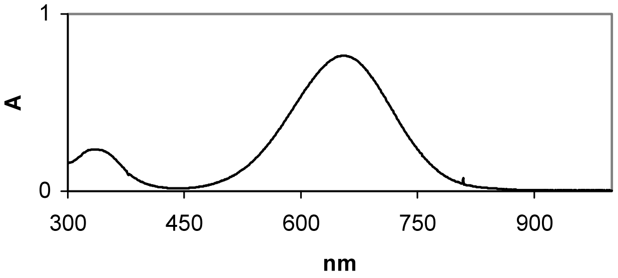
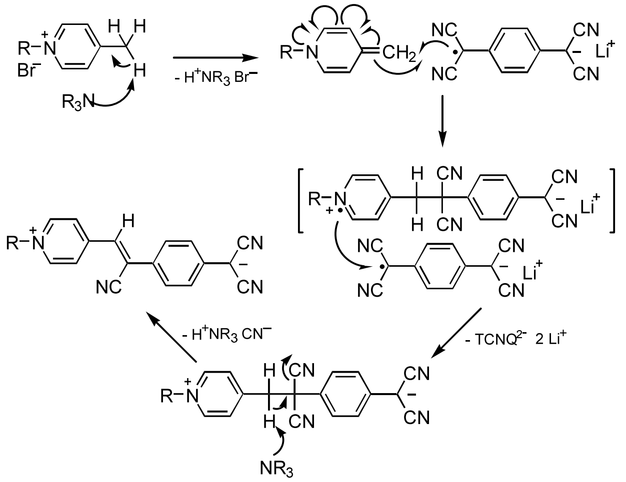
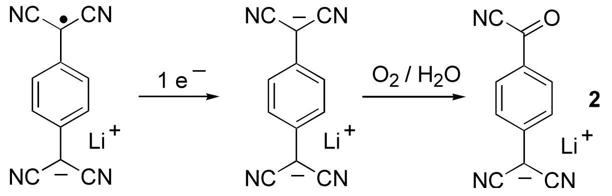


**Figure 1.** UV–vis absorption spectrum of **1a** in DMF (4.4× 10$^{-4}$ M, 0.1 cm path length), $\lambda_{max}$=654 nm.



**Scheme 2.** Proposed reaction mechanism.



**Scheme 3.** Formation of by-product **2** from LiTCNQ.

For each synthesis outlined in Table 1, an additional peak would begin to form around 490 nm during the course of the reaction. This peak is attributed to the oxidation of TCNQ$^{2-}$ formed during the reaction following the one-electron transfer to the second equiv. of LiTCNQ as shown in Schemes 2 and 3.[13] The product, α,α-dicyano-*p*-toluoylcyanide anion (**2**, Scheme 3) has been shown to form readily and irreversibly in the presence of trace amounts of oxygen and it absorbs in the same region by UV–vis ($\lambda_{max}=490$ nm).[13–15]

The stability of the NLO chromophore is important when considering the lifetime of an EO device. It was hypothesized that light, temperature and atmospheric oxygen would each influence the chromophore decomposition, thus studies to investigate each were designed and carried out.

Each reaction used chromophore **1a** in DMF at the same concentration ($4.4\times10^{-4}$ M). All the reactions were carried out in a closed system under nitrogen, at 125°C and in the dark unless stated otherwise (i.e. depending on the variable being investigated).

Figure 2 shows the effects of air on the chromophore decomposition. For this reaction the vessel was open to air, protected from light and maintained at 125°C. The peak at 490 nm began to form after only 90 min. The chromophore peak at 654 nm had disappeared completely within 144 min.

The relative effects of temperature, light and atmospheric oxygen are demonstrated in Figure 3. The absence of an inert atmosphere led to the fastest rate of decomposition. The presence of light (from a 60 W white light lamp) focused on the reaction vessel increased the rate of decomposition as well but to a lesser degree. There was no reaction at room temperature (under nitrogen and in the dark) after 45 h. A closer look at the temperature dependence is demonstrated in Figure 4. At both room temperature and 65°C the chromophore appears stable even after 45 h. At 80°C and above, the rate of decomposition increases with temperature.

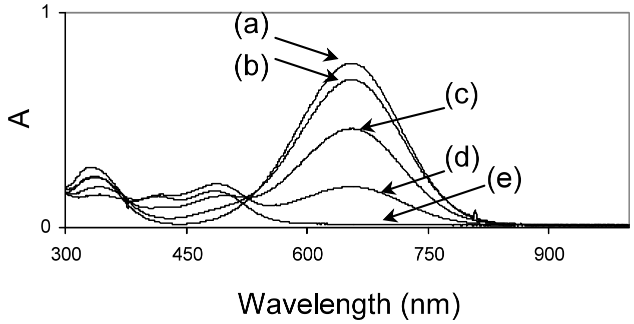


**Figure 2.** UV–vis absorption spectra of **1a** in DMF ($4.4\times10^{-4}$ M, 0.1 cm path length) at 125°C, in the dark, with the vessel open to air, heated for a period of (a) 2 min; (b) 50 min; (c) 90 min; (d) 122 min; (e) 144 min.

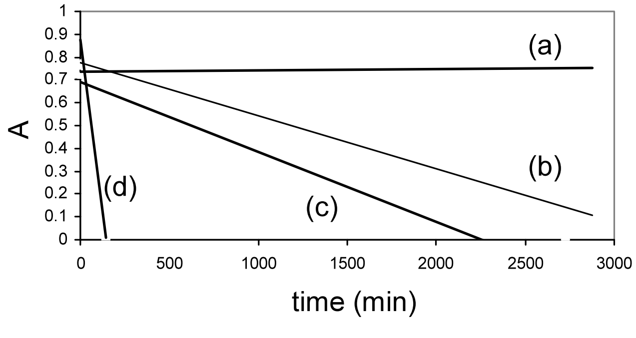


**Figure 3.** Absorbance of $\lambda_{max}$ (654 nm) versus time for **1a** under different conditions: (a) 25°C, under $N_2$ (g), dark; (b) 125°C, under $N_2$ (g), dark; (c) 125°C, under $N_2$ (g), exposed to light; (d) 125°C, no $N_2$ (g), dark.

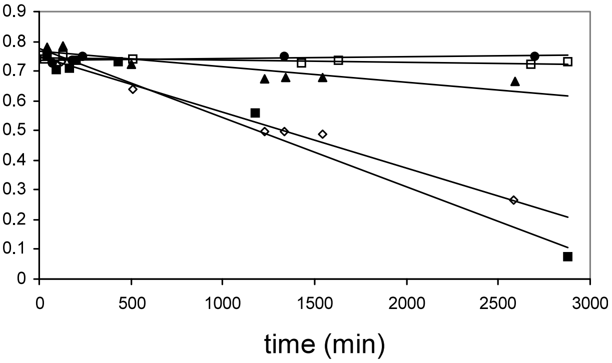


**Figure 4.** Absorbance of $\lambda_{max}$ (654 nm) versus time of **1a** at various temperatures, in the absence of light, under $N_2$ (g); (●) 25°C; (□) 65°C; (▲) 80°C; (◇) 100°C; (■) 125°C.

The results show that exposure to atmosphere oxygen had the largest impact on chromophore decomposition. Although the decomposition product could not be isolated and therefore could not be characterized, the peak absorbing at 490 nm suggests that the product is either structurally similar to, or may in fact be, **2**. The presence of light and temperatures above 80°C also impact decomposition, but the effects are secondary compared to exposure to $O_2$/moisture. If the chromophore decomposes to **2**, the likely pathway would be attack of $O_2$ or/and $H_2O$ at the allylic bridge, similar to the one found for other TCNQ-tertiary amine adducts.[17] Since the chromophore syntheses were done without absolute exclusion of oxygen, water or light, there is still room for further improvement in the reaction yields.

In summary, the yields and reaction times for the syntheses of chromophores **1a** and **1b** were significantly improved by varying the amount of reactants and with the use of a strong tertiary amine base, making this interesting class of NLO chromophores available in tens of grams for the first time. This new method should also be applicable to similar NLO chromophores that are difficult to make such as those derived from TCNQ and lepidinium derivatives.[16] Further studies involving chromophore **1** and corresponding EO devices may now be possible.

The decomposition studies in solution revealed that chromophore stability is maximized in the absence of oxygen, light and at temperatures below 65°C. These results need to be followed up by the equivalent investigation in the solid state so that chromophore and hence device lifetimes can be maximized.

## Acknowledgements

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10. Compound **1a** was prepared by first dissolving LiTCNQ (2.570 mmol) in 20 mL of MeCN, followed by addition of a solution of *N*-octyl-4-methylpyridinium bromide (1.283 mmol) in 5 mL of MeCN. At reflux DBU (2.570 mmol) was added in increments of three drops every 15 min. After 14 h the reaction was stopped and the precipitate was filtered, washed with MeCN and dried under vacuum. The crude product was purified by washing with boiling methanol (70 mL) in a beaker, followed by filtering the undissolved portion. The process was repeated four times before the undissolved product was pure as analyzed by UV–vis.
11. Compound **1a**: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 0.83 (m, 3H), 1.24 (m, 10H), 1.89 (m, 2H), 4.48 (t, 2H, $J=7.2$ Hz), 6.84 (d, 2H, $J=8.6$ Hz), 7.56 (d, 2H, $J=8.5$ Hz), 7.83 (s, 1H), 8.29 (d, 2H, $J=6.4$ Hz), 8.95 (d, 2H, $J=6.6$ Hz); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 13.9, 22.0, 25.4, 28.2, 28.4, 30.4, 31.1, 59.9, 116.8, 118.4, 119.6, 121.0, 123.1, 125.1, 125.5, 127.4, 144.2, 147.1, 149.5; MS (EI, *m*/*e*) 382 ($M^{+\cdot}$); IR (KBr, cm$^{-1}$): 2132, 2175 (C≡N).
12. Compound **1b**: $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 2.10 (m, 2H), 3.49 (m, 2H), 4.60 (m, 2H), 4.80 (s, 1H), 6.87 (d, 2H, $J=8.7$ Hz), 7.59 (d, 2H, $J=7.3$ Hz), 7.82 (s, 1H), 8.31 (d, 2H, $J=6.4$ Hz), 8.98 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 33.0, 57.1, 57.8, 116.7, 118.4, 119.4, 121.0, 123.1, 124.9, 125.5, 127.3, 144.3, 146.9, 149.3; MS (SI, *m*/*e*) 329 ($M+H^+$); IR (KBr, cm$^{-1}$): 2129, 2176 (C≡N).
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