



## A Novel Approach to Synthesis of Tricyanovinylthiophene for Heterocyclic Imidazole Nonlinear Optical Chromophores

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**Abstract:** A new synthetic method for tricyanovinylation has been developed to prepare a series of novel NLO imidazole chromophores containing a tricyanovinyl acceptor coupled with thiophene spacer.

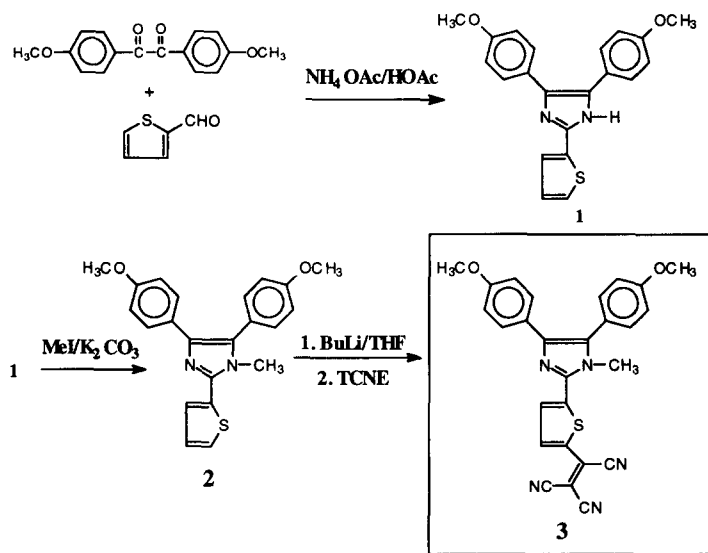
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Heterocyclic compounds, especially five-membered ring heterocyclic azole derivatives have been used as nonlinear optical (NLO) chromophores since those compounds exhibited excellent thermal stability in guest-host systems,<sup>1-5</sup> excellent solubility in common organic solvents and outstanding miscibility with high performance polymers (up to 50% without phase separation).<sup>6</sup> We have recently reported the incorporation of NLO imidazole chromophores into polyimides leading to NLO side chain polymers.<sup>7</sup> Previous approaches to further enhance the molecular nonlinearity have led only limited success. Attempts to optimize the conjugation pathway by maximizing the coplanarity of aromatic rings at the 4 and 5 positions of the imidazole have resulted in low solubility due to high rigidity imposed by highly fused aromatic rings.<sup>8</sup>

Our novel approach to the design of a new imidazole system, **3** (Scheme 1), with enhanced molecular nonlinearity and excellent solubility is based upon two principles: (1) the two separate aromatic rings at the 4 and 5 positions of the imidazole ring should interact sterically leading to twisting and poor crystal packing, therefore, enhancing solubility; (2) the incorporation of the highly efficient tricyanovinyl acceptor coupled with thiophene should give chromophores with superior molecular nonlinearity. Previous studies by Katz et al. revealed that tricyanovinyl acceptors are superior to dicyanovinyl acceptors by a factor of 2-3 in enhancing molecular nonlinearity.<sup>9</sup> Rao and Jen et al. recently demonstrated that tricyanovinyl acceptors combined with thiophenes dramatically enhance molecular nonlinearity by a factor of 4-5 relative to dicyanovinyl acceptors, and by a factor of 10-11 relative to nitro acceptors.<sup>10</sup>

There have been two synthetic routes widely used in the preparation of tricyanovinyl derivatives: direct reaction of tetracyanoethylene (TCNE) with activated aromatic rings, or stepwise conversions starting with aldehydes (from aldehyde first to dicyanovinyl by condensing with malonitrile, then to tricyanovinyl by nucleophilic substitution of dicyanovinyl with sodium cyanide, followed by oxidation with Pb(OAc)<sub>4</sub>).<sup>11</sup> However, our attempts to apply existing methods of tricyanovinylation to imidazole-thiophenes failed to give the desired product that these two routes are found inapplicable to imidazole-thiophenes.

In this communication, we wish to report a novel approach to tricyanovinylation of imidazole-thiophenes by direct reaction of tetracyanoethylene with the thienyllithium of imidazole.

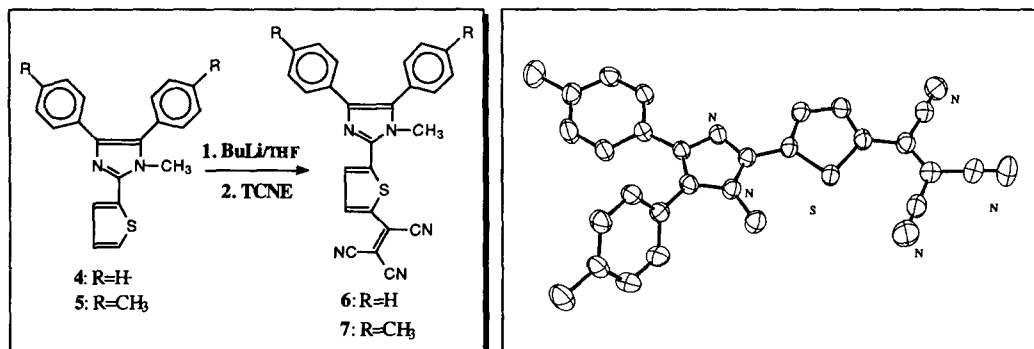


Scheme 1

The synthesis of novel chromophore 3 using the new methodology was achieved in four steps, as illustrated in Scheme 1, starting with commercially available and inexpensive 4,4'-dimethoxybenzil. The benzoin was converted into 4,4'-dimethoxybenzil using cupric acetate oxidation. The heterocyclic compound, 2-(2'-thienyl)-4,5-bis(4'-methoxyphenyl)imidazole, **1**, was prepared in 94% yield by treatment of 4,4'-dimethoxybenzil and 2-thiophenecarboxaldehyde with ammonium acetate in glacial acetic acid. The alkylation of **1** with methyl iodide in the presence of potassium carbonate in DMAc led to the formation of 1-methyl-2-(2'-thienyl)-4,5-bis(4'-methoxyphenyl)imidazole, **2**, in a yield of 71 %. This alkylation at the 1-position of the azole ring is necessary to ensure the formation of a monoanion species of thiophene (thienyllithium) in the following step. Treatment of **2** with *n*-butyl lithium in THF-hexane in-situ generated a solution of the red anion at low temperature, which upon the addition of tetracyanoethylene, led to the formation of the desirable 1-methyl-2-[2'-(5'-tricyanovinyl)thienyl]-4,5-bis(4'-methoxyphenyl)-imidazole, **3**, in 65 %.<sup>12</sup>

This new method has been extended to other substituents on 4,5 aromatic rings. For example, chromophores **6** (R=H) and **7** (R=CH<sub>3</sub>) have been prepared in a similar fashion (Scheme 2). All new chromophores are very soluble in most common organic solvents such as THF, chloroform and methylene dichloride.

The general molecular structure of this new series of chromophores has been established by x-ray crystallographic study of **7**.<sup>13</sup> The two aromatic rings at the 4 and 5 positions of the azole ring sterically interact leading to a dihedral angle of 60.32°, with one aromatic ring twisted more than the other relative to imidazole ring (59.34° vs. 12.40°).



In conclusion, a novel tricyanovinylolation has been developed that permits the direct synthesis of a series of novel heterocyclic imidazole NLO chromophores by reaction of tetracyanoethylene with a thienyllithium of imidazoles. Efforts are underway to extend this new methodology to prepare other potentially important NLO chromophores containing tricyanovinyl acceptors which can not be synthesized by previously known methods otherwise because of low reactivity.

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- see 2 and 3.
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12. A typical procedure for the preparation of **3**: To the mixture of 5 mL THF and 1.2 mL of n-butyllithium (1.6 M in hexane) was added dropwise over 3 minutes 0.565 g (1.50 mmol) **2** in 3 mL THF at -50 °C. After addition, the mixture was allowed to warm to 0 °C for 15 minutes, and cooled again to -50 °C, followed by dropwise addition of 0.22 g (1.65 mmol) TCNE in 3 mL THF. The mixture was allowed to warm to room temperature and stirred overnight at room temperature. A blue solid was collected after the mixture was poured into 200 mL water. The second fraction (eluted with benzene) from a silica-gel column chromatography was recrystallized from methylene dichloride/methanol to give dark green needle crystals. <sup>1</sup>H NMR 400 MHz(CDCl<sub>3</sub>/TMS), δ: 8.08(d, J=4.46Hz, 1H), 7.65(d, J=4.38Hz, 1H), 7.45(d, J=8.80Hz, 2H), 7.28(d, J=8.58Hz, 2H), 7.03(d, J=8.66 Hz, 2H), 6.79(d, J=8.82 Hz, 2H), 5.29(s, 0.5H, CH<sub>2</sub>Cl<sub>2</sub>), 3.90(s, 3H), 3.78(s, 3H), 3.71(s, 3H) ppm. <sup>13</sup>C NMR 400 MHz (CDCl<sub>3</sub>/TMS), δ: 160.51, 159.07, 147.63, 141.01, 140.55, 139.19, 133.76, 133.01, 132.27, 132.06, 131.87, 128.26, 125.97, 121.36, 114.87, 113.98, 113.78, 112.84, 112.42, 112.18, 81.98, 55.39, 55.21, 33.38 ppm. Anal. for C<sub>27</sub>H<sub>19</sub>N<sub>5</sub>O<sub>2</sub>S·1/4CH<sub>2</sub>Cl<sub>2</sub>: C: 65.89, H: 4.10, N: 13.94, Calc. C: 65.62, H: 3.94, N: 14.05.
13. Empirical formula: C<sub>27</sub>H<sub>19</sub>N<sub>5</sub>S; FW=445.54; space group and cell dimensions: monoclinic, P2<sub>1</sub>/c, a=13.0458(11), b=9.1717(8), c=18.796(3), β=97.456(11)°, V=2229.9(5) Å<sup>3</sup>, cell dimensions were obtained from 25 reflections with 2θ in the range 24.60 to 60.50°; T=298 K, graphite monochromated Cu-Kα radiation, λ=1.54056 Å, Z=4, D<sub>c</sub>=1.327 Mg/m<sup>3</sup>, F(000)=928.00, dark blue prism with dimensions 0.31 x 0.22 x 0.12 mm, μ(Cu-Kα)=1.44 mm<sup>-1</sup>, absorption corrections were made based on ψ<sub>0</sub> scans, the minimum and maximum transmission factors were 0.614757 and 0.7132273, respectively; intensity data were collected on a Nonius diffractometer using the 2θ scan mode in the range of 3° < 2θ < 150°, ± h, +k, +l, three standard reflections showed no significant variation in intensity; 5637 reflections measured, 4583 unique (R<sub>int</sub> = 0.026) which were used in all calculations. The structure was solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by full-matrix least squares, on F<sup>2</sup> (program NRCVAX<sup>14</sup>). The last least square cycle was calculated with 52 atoms, 237 parameters and 3419 with I ≥ 2.5σ(F) out of 4583 reflections. R(F) was 0.066, R<sub>w</sub> 0.071 and GoF 2.26. The maximum Δσ = 0.000, the deepest hole is -0.360 e/Å<sup>3</sup> and the highest peak is 0.490 e/Å<sup>3</sup>.
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