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Derivative of α,β-Dicyanostilbene: Convenient Precursor for the Synthesis of Diphenylmaleimide Compounds, *E*−*Z* Isomerization, Crystal Structure, and Solid-State Fluorescence

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A convenient and efficient procedure was developed for preparing 3,4-diaryl-substituted maleimides through the improved synthesized diaryl-substituted fumaronitrile. The synthesis of diphenyl-substituted fumaronitrile derivatives from phenylacetonitrile compounds was analyzed and improved. We found the stoichiometry of the sodium methoxide and the concentration of the starting material, phenylacetonitrile derivatives, were crucial for the high yield and easy purification of the products. Particularly, bis(4-bromophenyl)fumaronitrile, bis(3-trifluoromethylphenyl)fumaronitrile, and bis(4-methoxyphenyl)fumaronitrile were isolated in good yields of 70−90% by simple suction filtration. In addition, ^{1}H NMR provided compelling evidence that the *E*−*Z* isomerization was involved in the formation reaction of the maleimide compounds from either fumaronitrile or maleonitrile derivatives. Single-crystal X-ray structures of these three fumaronitrile derivatives, the first three of the kind, were obtained, revealing the nonplanar molecular structure. We ascribe the strong solid-state fluorescence of these diphenylfumaronitrile derivatives to the nonplanar structure that inhibits the close packing of the molecule aggregation and thus the fluorescence quenching.

1. Introduction

Recently, we reported an improved synthetic procedure in preparing *N*-methyl-3,4-bis(4-(*N*-(1-naphthyl)phenylamino)phenyl)maleimide (NPAMLMe) via the easily isolated intermediate bis(4-bromophenyl)fumaronitrile (or *trans*-4,4′-dibromo-α,β-dicyanostilbene) from (4-bromophenyl)acetonitrile (route B, Scheme 1).[1] Preparing diphenyl-substituted fumaronitrile compounds from phenyl-substituted acetonitrile derivatives by oxidative coupling reaction, in either Br_2- or I_2-containing alcoholic alkoxide or aqueous hydroxide, has been known to chemists and can be traced back to the late 19th century.[2] However, surveying the literature reveals that the reaction has been performed somewhat differently in many cases and the reaction yields varied even for the same parent compound, *trans*-α,β-dicyanostilbene. Considering *trans*-α,β-dicyanostilbene bearing different substituents, the synthetic yields differ widely and range from less than 20% to more than 80%.[2] This indicates that the reaction is sensitive to the reaction conditions and chemical structure. The essence of the synthesis seems illusive and yet to be developed. A systematic study of the reaction is thus needed to provide insightful information on the reaction, which is valuable for the efficient preparation of NPAMLMe, an unusual, nondoped, host emitter for red organic light-emitting diodes (OLEDs).[3] In addition, bis(4-bromophenyl)fumaronitrile is also a synthetic precursor for another efficient and bright host emitter, bis(4-(*N*-(1-naphthyl)phenylamino)phenyl)fumaronitrile (NPAFN), for nondoped red OLEDs.[4] Accordingly, we feel that the synthetic chemistry about α,β-

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(1) Yeh, H.-C.; Chan, L.-H.; Wu, W.-C.; Chen, C. T. *J. Mater. Chem.* **2004**, *14*, 1293.

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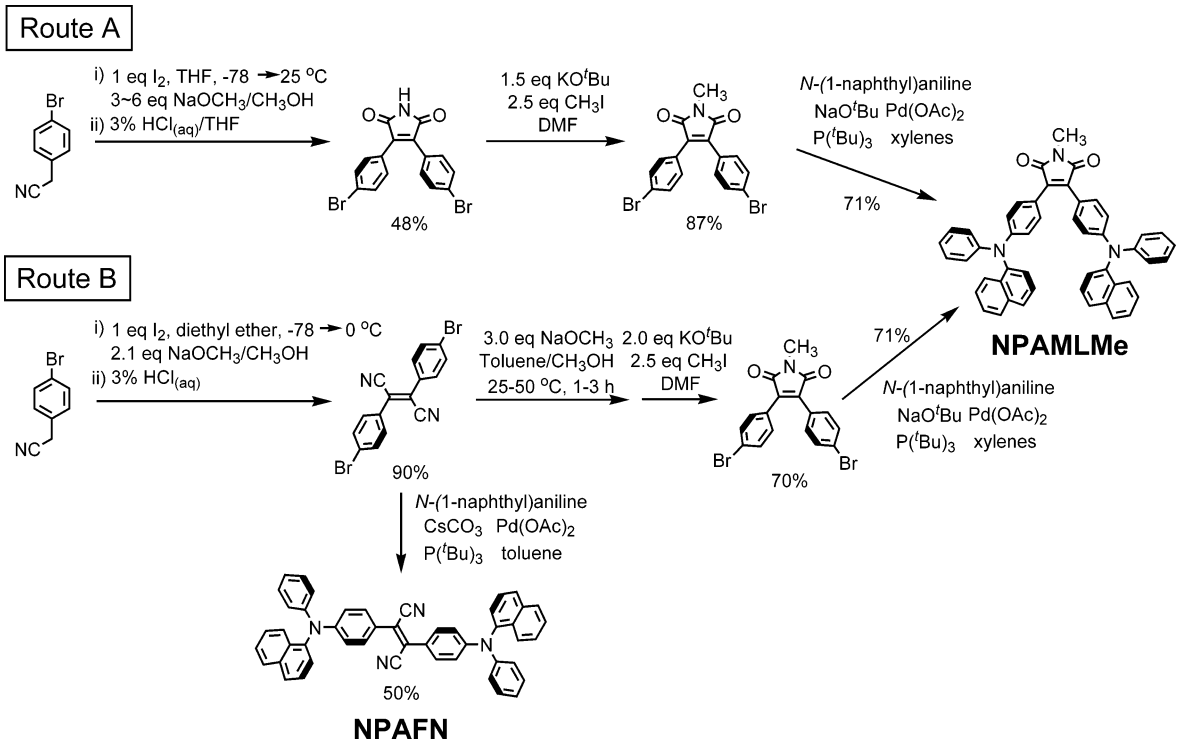
SCHEME 1

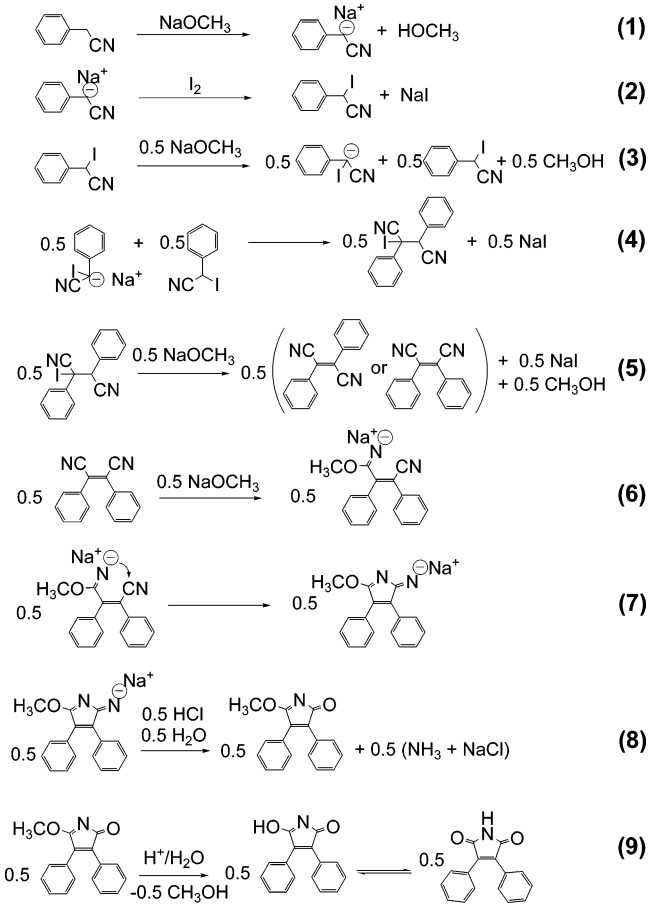


dicyanostilbene, either the *E*-isomer (diphenylfumaronitrile) or the *Z*-isomer (diphenylmaleonitrile), and diphenylmaleimide derivatives is vital for the development of potent materials such as NPAMLMe or NPAFN for nondoped red OLEDs. Here we present the analysis of the reaction conditions in depth to improve the synthesis and the purification process. We also provide a logical explanation for the unusually strong fluorescence observed for NPAFN in the solid state[4] by the X-ray structure determination of three diphenylfumaronitrile derivatives.

2. Results and Discussion

2.1. Opimization of the Synthesis of Fumaronitriles. On the basis of the scattered evidence found in the literature,[2] conceivable reactions involved in the synthesis can be divided into steps 1−9 as shown in Scheme 2. They are the deprotonation of a benzylic carbon (reactions 1, 3, and 5), halogenation of benzylic carbon (reaction 2), nucleophilic substitution with subsequent elimination reaction in forming diphenylfumaronitrile (*trans*-α,*β*-dicyanostilbene) or diphenylmaleonitrile (*cis*-α,*β*-dicyanostilbene) (reactions 4 and 5), methoxide-initiated intramolecular cyclization (reactions 6 and 7), and the next two hydrolysis steps leading to the maleimide ring (reactions 8 and 9). Although it is easy to perform (at room temperature requiring no heating or cooling) and has the advantage of a wide range of available phenylacetonitriles as the staring materials,[5] the one-step synthesis suffers from low to modest reaction yields. Furthermore, the purification often requires careful column chromatography that greatly limits the synthesis only suitable for small-scale preparation. Before the *N*-methylation of maleimide, the relatively high

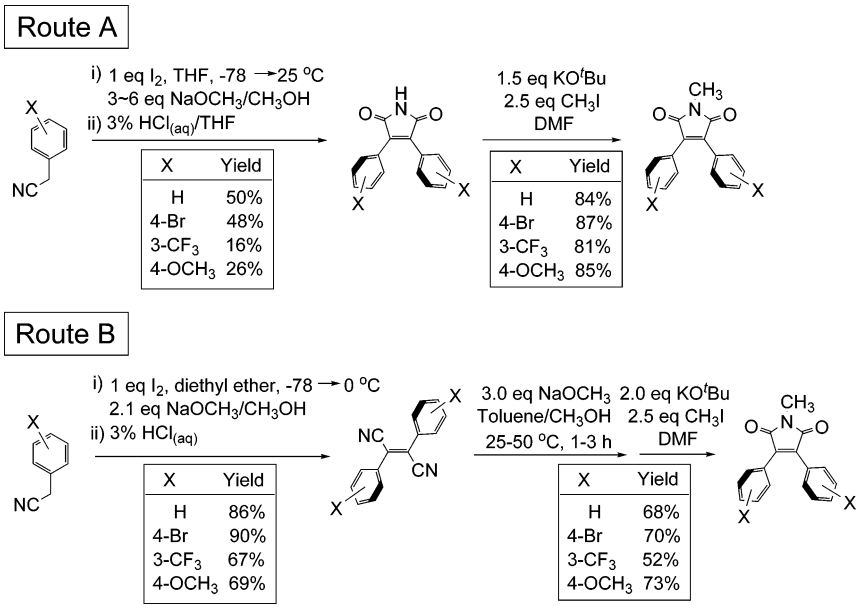
SCHEME 2



polarity of maleimide compounds is quite close to that of several other unidentified color species and makes the separation by chromatography rather difficult. Consider-

(5) Yeh, H.-C.; Wu, W.-C.; Chen, C.-T. *Chem. Commun.* **2003**, 404.

SCHEME 3



ing the large amount of the material demanded in the fabrication of OLEDs, an improved synthesis of maleimide compounds, which is convenient to perform and suitable for large-scale preparation, becomes a quest.

In our recent process of improving the reaction yield of one-step synthesis of 3,4-bis(4-bromophenyl)maleimide, we frequently encountered better results (higher reaction yield and cleaner reaction product) by performing the reaction first at low temperature and then warming to room temperature (−78 → +25 °C) and controlling the stoichiometric amount of sodium methoxide base to no more than 3 equiv in the reaction.[5] However, the further reduction of the amount of sodium methoxide base often dramatically decreases the reaction yield. More recently, we have found that what we obtained is mainly bis(4-bromophenyl)fumaronitrile instead of 3,4-bis(4-bromophenyl)maleimide from those unsatisfactory synthetic experiments.[1] We deduced that an insufficient amount of sodium methoxide (≤3 equiv) will bring the reaction to fumaronitrile instead of maleimide because it needs 2.0 equiv of sodium methoxide to generate the former and 2.0 equiv or more of sodium methoxide to obtain the latter. This is quite consistent with the stoichiometry of sodium methoxide in Scheme 2. On the other hand, lowering the temperature in the early stage of the reaction can statistically reduce the chance of generating downstream product of maleimide even in the circumstance of insufficient sodium methoxide. Here, another key issue is that we switch the solvent from THF to diethyl ether. We have found that diethyl ether is a better solvent than THF in obtaining cleaner product. This is partially due to the diaryl-substituted fumaronitriles usually having a lower solubility in ether than in THF, which facilitates the precipitation of the desired product for easy isolation (by filtration) and prevents the fumaronitrile from further reacting with sodium methoxide in solution.

Regarding the product purification, we have found that the concentration of the reaction is critical for a quick and easy isolation of the product and should be adjusted accordingly on the basis of the solubility of the fumaronitrile products. The product often can be easily obtained with good to high yields by simple filtration of the reaction solution if the reaction concentration is set above the saturation point of the product. For instance, 0.25 M is the optimum concentration for bis(4-bromophenyl)fumaronitrile, and a higher concentration of 1.0−2.0 M is necessary for the high-yield synthesis of diphenylfumaronitrile, bis(3-trifluoromethylphenyl)fumaronitrile, and bis(4-methoxyphenyl)fumaronitrile due to the higher solubility of the products. Following our improved reaction conditions and the simple isolation method, bis(4-bromophenyl)fumaronitrile, diphenylfumaronitrile, bis(3-trifluoromethylphenyl)fumaronitrile, and bis(4-methoxyphenyl)fumaronitrile can be obtained directly in pure form from the reaction with good to high yields of 90%, 86%, 67%, and 69%, respectively.

2.2. Synthesis of *N*-Methylated Maleimide from Fumaronitrile. With readily available fumaronitrile derivatives in pure form, a one-step synthesis procedure becomes possible for the preparation of *N*-methyl-3,4-diaryl-substituted maleimides. For the sake of easy column chromatography in the later step of the synthesis, the *N*-methylation of maleimide with iodimethane was performed without the isolation of the pure maleimide product from the previous reaction. However, removal of the ionic species (by extraction) generated from the acidic hydrolysis procedure is necessary to increase the reaction yield. We were able to prepare *N*-methyl-3,4-diaryl-substituted maleimides in reasonable yields of 52−73% after the column chromatography purification. Such results are satisfactory considering the moderate purity of the maleimide reactants. It is worth noting that the column chromatography performed at this stage on *N*-methylated maleimide is significantly easier than that before *N*-methylation due to the relatively low polarity of the *N*-methylated maleimide and the distant separation from other side products during column chromatography.

The advantage of the new synthesis (route B in Scheme 3) is its relatively high yield and the ease of purification, namely, chromatography once instead of twice including

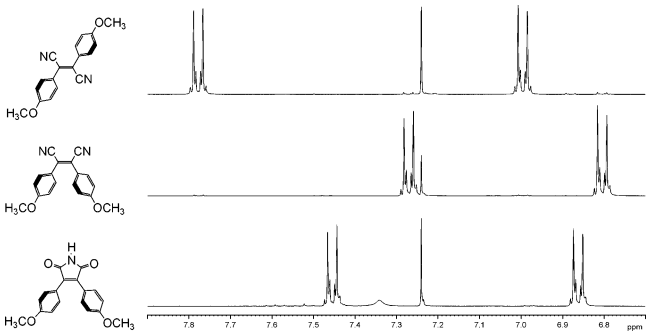


FIGURE 1. Aromatic region of ^{1}H NMR spectra (in $CDCl_3$) of bis(4-methoxyphenyl)fumaronitrile (top), bis(4-methoxyphenyl)maleonitrile (middle), and bis(4-methoxyphenyl)maleimide (bottom).

a difficult one. The overall yield of the preparation of the *N*-methylated maleimide compounds (from acetonitrile derivatives) is around 35−63%, a substantial improvement from those of route A in Scheme 3. More importantly, the most desired compound *N*-methyl-3,4-bis(4-bromophenyl)maleimide, the precursor for synthesizing NPAMLMe, is particularly beneficial to the improved synthetic procedure with an overall isolated yield of ∼63%, the highest among all *N*-methyl-3,4-diarylmaleimide compounds reported so far. The overall yield of the synthesis of *N*-methyl-3,4-bis(4-bromophenyl)maleimide has never been over 45% through route A of Scheme 3.

2.3. ^{1}H NMR Characterization of Fumaronitrile, Maleonitrile, and Maleimide. Due to the relatively large size of the single crystal, we were able to take the ^{1}H NMR spectra of the individual crystals in solution. This helps in the spectroscopic differentiation of two isomers (fumaronitrile and maleonitrile) in addition to maleimide derivative. The 4-methoxy-substituted compounds turned out to be the ideal case in our synthesis, generating a sufficient amount of the *Z*-isomer in conjunction with the *E*-isomer, and they were separable by column chromatography. Figure 1 shows the ^{1}H NMR spectra in the aromatic region of the three species. It is evident that the *E*-isomer has a more pronounced difference in chemical shifts of phenyl ring signals than the other two compounds. This is quite consistent with the maleimide structurally resembling the *Z*-isomer than the *E*-isomer. Another characteristic feature of the maleimide compound is the humplike signal due to the imide hydrogen around 7.35 ppm (Figure 1), which is unique among the three compounds. Similar ^{1}H NMR spectral patterns were also observed for the other three sets of the compound and thus can be used as a common identification marker.

Synthetically, the *E*-isomers of α,*β*-dicyanostilbene derivatives were the compounds we adopted in the synthesis of maleimide compounds. With the geometry concern, it is intriguing to ask how it could be possible to form the maleimide compound with the *E*-isomer (fumaronitrile) that has nitrile groups on the opposite side of the C−C double bond. It is possible unless an *E*−*Z* isomerization process takes place before the intramolecular cyclization reaction. This has been supposed to be the case, a long-time postulation.[2g,6a,b] With the complete ^{1}H NMR data of the three species, we attempted to offer the spectroscopic evidence to support the case.

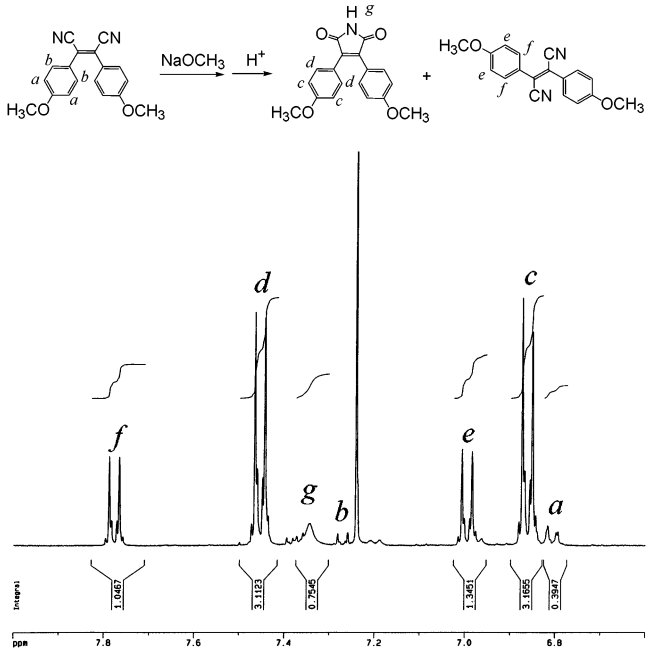


FIGURE 2. ^{1}H NMR spectrum (in $CDCl_3$) of the reaction products (from the reaction shown above) providing evidence of possible *E*−*Z* isomerization under the reaction conditions (see the text for details).

We first tried to isolate the *Z*-isomer of 4-methoxy-substituted α,*β*-dicyanostilbene, i.e., bis(4-methoxyphenyl)maleonitrile, from the reaction with an *E*-isomer reactant. We quenched the reaction (by acidic hydrolysis) of maleimide formation halfway toward completion (cut the reaction time in half). After the removal of ionic species by extraction, the crude reaction mixture was taken for ^{1}H NMR examination for the presence of the *Z*-isomer in the reaction mixture. From several attempts, all we found in the ^{1}H NMR spectra were the signals caused by the reactant bis(4-methoxyphenyl)fumaronitrile and the product bis(4-methoxyphenyl)maleimide. There was no detectable signal of bis(4-methoxyphenyl)-maleonitrile. After several failed attempts, we changed the reactant to the *Z*-isomer and looked for the signals of the *E*-isomer instead in ^{1}H NMR spectra (Figure 2). In addition to the unreacted *Z*-isomer reactant and the maleimide product, we saw the signals due to the *E*-isomer of 4-methoxy-substituted α,*β*-dicyanostilbene. This is alternative evidence of the *E*−*Z* isomerization between malenitrile and fumaronitrile under the reaction conditions (diethyl ether in the presence of sodium methoxide and modest heating).[6c] In addition, we noticed that the reaction of forming bis(4-methoxyphenyl)maleimide, in fact, ran much faster than that using the *E*-isomer as the reactant. Such an observation is also in

(6) (a) Baguley, M. E.; France, H.; Linstead, R. P.; Whalley, M. *J. Chem. Soc.* **1955**, 3521. (b) Fitzgerald, J.; Tayloer, W.; Owen, H. *Synthesis* **1991**, 686. (c) The base sensitivity of the isomerization of fumaronitrile and maleonitrile has been noted again recently (Huisgen, R.; Li, X.; Giera, H.; Langhals E. *Helv. Chim. Acta* **2001**, *84*, 981). The central C−C double bond of either fumaronitrile or maleonitrile is susceptible to base, such as fluoride, alkoxide, or even a polar solvent molecule such as acetonitrile. It is conceivable that the base acts as a nucluophile in transforming the double bond to a rotary C−C single bond. The C−C double bond can thus be recovered after the elimination of the substituted base but with alternative isomer structure (from *cis* to *trans* form or from *trans* to *cis* form).

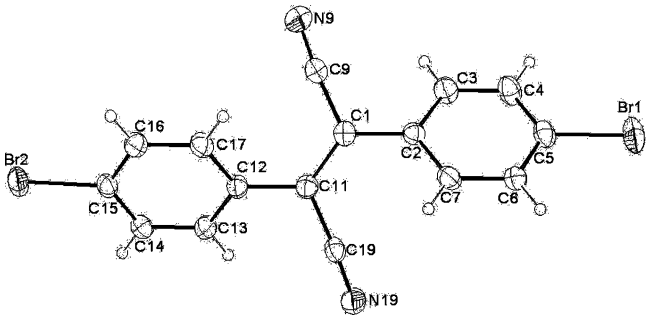


FIGURE 3. X-ray crystal structure of bis(4-bromophenyl)-fumaronitrile with a 30% thermal ellipsoid.

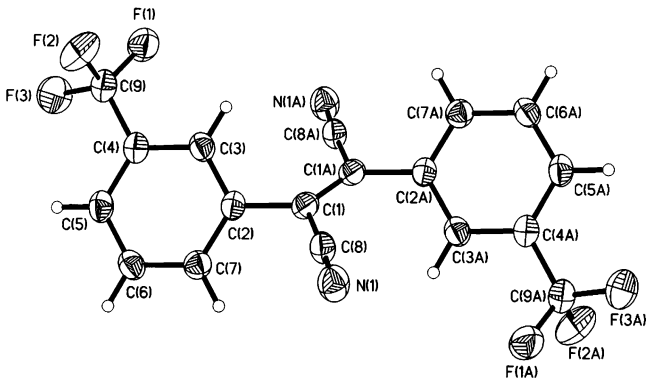


FIGURE 4. X-ray crystal structure of bis(3-trifluoromethylphenyl)fumaronitrile with a 50% thermal ellipsoid.

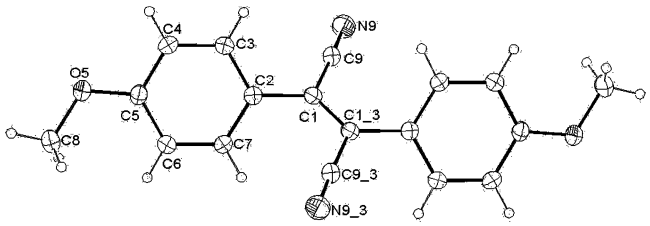


FIGURE 5. X-ray crystal structure of bis(4-methoxyphenyl)-fumaronitrile with a 30% thermal ellipsoid.

accord with the requirement of *E*−*Z* isomerization if the *E*-isomer is the reactant.

2.4. X-ray Crystal Structure and Solid-State Fluorescence. The single-crystal X-ray structures were obtained for verifying the *E*-isomer configuration of bis(4-bromophenyl)fumaronitrile, bis(3-trifluoromethylphenyl)fumaronitrile, and bis(4-methoxyphenyl)fumaronitrile (Figures 3−5). We note that there has been only one preceding report on the crystal structure of the parent compound, diphenylfumaronitrile, in the early 1960s.[7]

However, this crystal structure was poorly refined. For instance, the C−C double bond of the central CN−HC=CH−CN unit was determined to be 1.46 Å, which is way too long for a typical sp^2−sp^2-connected C−C double bond (i.e., 1.34 Å for ethylene).[8] Interestingly enough, except the bromo-substituted compound, these crystals belong to the same symmetrical subgroup (2/*m* point group) of the monoclinic system, two independent half-molecules are in the asymmetric unit, and each full

FIGURE 6. Fluorescence image of NPAFN in dichloromethane solution (in vial) and as a solid powder (on glass slide).

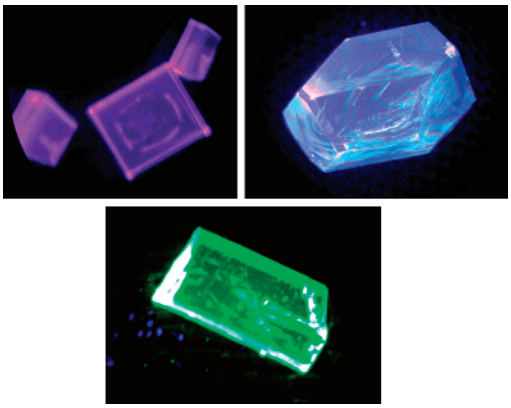


FIGURE 7. Fluorescence images of the single crystal of bis(3-trifluoromethylphenyl)fumaronitrile (top left), bis(4-bromophenyl)fumaronitrile (top right), and bis(4-methoxyphenyl)-fumaronitrile (bottom).

molecule is generated through a crystallographic center of inversion because of the symmetrical configuration imposed by the occupation of the special position in the monoclinic crystal. Consequently, there is no doubt about the *E*-configuration (fumaronitrile), instead of the *Z*-configuration (maleonitrile), of the three structures reported here.

The bond lengths of the central C−C double bond are 1.341(5), 1.344(7), and 1.360(3) Å for bromo, trifluoromethyl, and methoxy, respectively. The 1.341(5) Å bond length of bis(4-bromophenyl)fumaronirile and bis(3-trifluoromethylphenyl)fumaronitrile and 1.344(7) Å bond length of bis(3-trifluoromethylphenyl)fumaronitrile are rather similar to the 1.338 Å bond length of the central C−C double bond of the unsubstituted parent *trans*-stilbene.[9] On the other hand, the bond distance 1.360(3) Å of bis(4-methoxyphenyl)fumaronitrile is rather close to the bond distance 1.362(2) Å of the central C−C double bond of 2,3-bis(4-methylphenyl)maleonitrile (a *Z*-form isomer).[10] We tried to connect the difference in chemical reactivity of the diphenylfumaronitrile bearing a different substituent to the bond length of the central C−C double bond. Chemically, we have noticed that NPAFN is the one among five diphenylfumaronitrile derivatives (the parent and 4-bromo, 3-CF_3, 4-methoxy, and 4-(1-naphthyl)phenylamino derivatives) most susceptible to the

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(8) Costain, C. C.; Stoicheff, B. P. *J. Chem. Phys.* **1959**, *30*, 777.
(9) Hoekstra, A.; Meertens, P.; Vos, A. *Acta Crystallogr., Sect. B* **1975**, *31*, 2813.
(10) Faulmann, C.; Cassoux, P.; Pullen, A. E. *Acta Crystallogr., Sect. B* **2000**, *56*, 384.

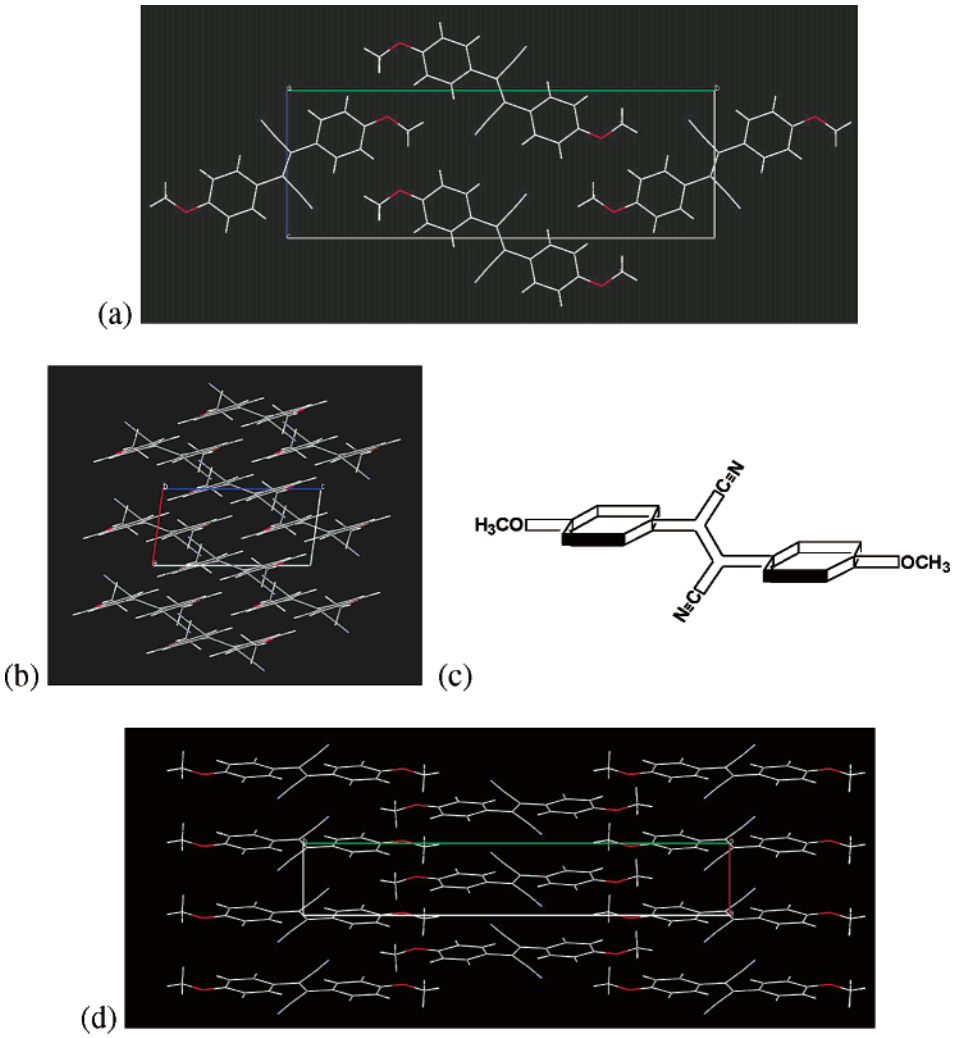

FIGURE 8. Crystal packing diagrams of bis(4-methoxyphenyl)fumaronitrile viewing along the *a*-axis, (a) *b*-axis (b), and *c*-axis (d) (three or four layers of the stacking molecules are included in the diagrams). A perspective view of the nonplanar molecule (c).

E−*Z* isomerization in solution (such as chloroform). Bis-(4-methoxyphenyl)fumaronitrile shows such isomerization as well but to a much less extent. There is no sign of *E*−*Z* isomerization of bis(4-bromophenyl)fumaritrile and bis(3-trifluoromethylphenyl)fumaronitrile by ^{1}H NMR spectroscopy (see section 2.3). The bond distance seems to follow the trend of the susceptibility of *E*−*Z* isomerization. The long central C−C double bond of bis(4-methoxyphenyl)fumaronitrile may be due to the electron-donating effect of the methoxy substituent. Such an effect is supposed to be much stronger for NPAFN, an amino-donor-bearing diphenylfumaronitrile derivative. Nevertheless, the crystal structure of NPAFN is needed to confirm our speculation.

Fluorescencewise, previously we have reported that NPAFN is unusual because it is brightly fluorescent but only in the solid state (Figure 6).[4] Unfortunately, we were not able to obtain a single crystal suitable for X-ray structure determination probably due to the amorphous nature of NPAFN.[4] However, the nonplanar structure observed here (see below) for diphenylfumaronitrile-type molecules is quite inspiring in the explanation of the unusual fluorescence of NPAFN. Similar to that of NAPNF, Figure 7 shows the conspicuous fluorescence of bis(3-trifluoromethylphenyl)fumaronitrile, bis(4-bromophenyl)fumaronitrile, and bis(4-methoxyphenyl)fumaronitrile in the solid state. Recent measurements showed the solid-state fluorescence quantum yields are 19%, 22%, 32%, and 49% for NPAFN and 3-trifluoromethylphenyl-, 4-bromophenyl-, and 4-methoxyphenyl-substituted diphenylfumaronitrile fluorophores, respectively.

In fact, all three molecules do not have a flat conformation (neither does diphenylfumaronitrile despite its poor X-ray data). There are considerable deviations from planarity: 40° and 44° (bromo compound), 42° (trifluoromethyl compound), and 66° (methoxy compound) were determined for the torsion angle between the plane of the phenyl ring and the central CN−HC═CH−CN unit. We believe such nonplanarity is due to the necessity of avoiding close contacts between the *ortho* hydrogen of the benzene ring and the adjacent CN group. This is accordant with the small torsion angle of 3−7° observed for nearly flat *trans*-stilbene.[9] It is interesting to note that whereas a parallel orientation was found for bis(4-methoxyphenyl)fumaronitrile as well as bis(3-trifluoromethylphenyl)fumaronitrile, the pair of the phenyl rings of each bis(4-bromophenyl)fumaritrile were nearly perpendicular to each other, forming an edge-to-face (or T-shaped) contact between the molecules (see the Supporting Information).

Due to the prominent nonplanarity, the crystal structure of bis(4-methoxyphenyl)fumaronitrile is the best among the three crystals illustrating a stacking feature of this type of the molecules and the influence on the molecular contact. The stacking structure of molecules of bis(4-methoxyphenyl)fumaronitrile is clearly seen, and it is along the *a* axis of the unit cell (Figure 8a,b). However, the spacing (repeating distance) in each molecule stack is large, 3.907(1) Å, which is equivalent to the length of the *a* axis of the unit cell (Figure 8d). The large spacing is due to the erection of the CN group in a large angle out of the plane of parallel phenyl rings (Figure 8b−d). Quantitatively, the closest contact happens to be the oxygen atom of the methoxy group and the hydrogen atom of the methoxy group of the neighboring molecule (2.87 Å), although it is unlikely relevant to the fluorescence quenching. The closest interatomic interaction keen to the fluorescence quenching is found between the C5 carbon and the hydrogen atom on C3 in Figure 5, which is 3.54 Å in distance. The shortest distance considered for direct $\pi-\pi$ interaction is 3.60 Å between the C2 carbon in Figure 5 and the vicinal C3 carbon of the nearest neighboring molecules. Both distances are considered to be too long for an effective distance of $\pi-\pi$ interaction, 3.36 Å, a nonbonded interplanar spacing of graphite.[11] Therefore, we can conclude that there is no intimate $\pi-\pi$ interaction between the molecules in the solid state and hence there is only limited fluorescence quenching in the solid state.

The nonplanar molecular structure of three fumaronitrile compounds in conjunction with their solid-state fluorescence strongly implies that NPAFN may possess a similar nonplanar structure. The nonplanar structure greatly prevents π-conjugated molecules from close stacking, which induces the fluorescence quenching in the solid state. In the case of NPAFN, the nonplanar 1-naphthylphenylamino groups can further push the molecules away from tight stacking.

In summary, we have analyzed the reaction of forming 3,4-diphenylmaleimide from phenylacetonitrile reactants. We can perform the reaction in one step or in two steps, which is more favorable via the formation of diphenylfumaronitrile. The stoichiometry of the sodium methoxide base is the key controlling factor in addition to the near-saturation concentration of the reactant, which facilitates the handy isolation of pure diphenylfumaronitrile derivatives. The successful synthesis and characterization of four 3,4-diphenylmaleimide and four diphenylfumaronitrile compounds illustrate our points. The *E*−*Z* (or fumaronitrile−maleonitrile) isomerization process in the synthesis of maleimide from phenylacetonitrile was implied by the ^{1}H NMR evidence. The nonplanar molecular structure of diphenylfumaronitrile derivatives was revealed by X-ray structure determination and was ascribed to be the reason for strong fluorescence observed in the solid state.

3. Experimental Section

The quantum yields of red emitting fluorene derivatives were determined by the integrating-sphere method described by de Mello et al. on vacuum-deposited thin films.[12] Whereas the improved synthesis and characterization of bis(4-bromophenyl)fumaronitrile and *N*-methyl-3,4-bis(4-bromophenyl)-maleimide have been described before,[1] those of the corresponding parent diphenylfumaronitrile and *N*-methyl-3,4-diphenylmaleimide together with their 3-trifluoromethyl and 4-methoxy derivatives are reported here.

3.1. General Procedure for the Synthesis of Diphenyl-Substituted Fumaronitrile Derivatives. The following procedure was applied to the reaction with a solvent volume of 100 mL for phenylacetonitrile (1 M), 400 mL for 4-bromophenylacetonitrile (0.25 M), and 50 mL for both 3-trifluoromethylphenylacetonitrile and 4-methoxyphenylacetonitrile (2 M). Acetonitrile derivatives and 1 equiv of iodine were dissolved in dry diethyl ether. Sodium methoxide (2−2.2 equiv)−methanol solution was added slowly (over a period of 30 min) into the reaction solution at dry ice temperature under a nitrogen atmosphere. The reaction solution was allowed to warm by replacing the dry ice bath with an ice−water bath before the temperature rose above 0 °C. During this time, more and more precipitation was formed in the solution. The reaction solution was stirred for another 3−4 h, and then the reaction was quenched with 3−6% hydrochloric acid at less than 10 °C. The solution was filtered to isolate the solid, which was rinsed with cold methanol−water solution to wash away ionic substances. A second crop of the pure product could often be isolated by filtration of the original filtrate after further concentration. The reported reaction yields of the following fumaronitrile derivatives do not include the product isolated from the filtrate.

3.1.1. Diphenylfumaronitrile. An off-white solid. Yield: 86% (9.9 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80−7.84 (m, 4H), 7.50−7.56 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 131.9, 131.6, 129.1, 128.6, 125.5, 116.5. FAB-MS: calcd MW = 230.08, *m*/*e* = 230.10 (M^+). Anal. Found (Calcd) for $C_{16}H_{10}N_2$: C, 83.19 (83.46); H, 4.47 (4.38); N, 12.14 (12.17).

3.1.2. Bis(3-trifluoromethylphenyl)fumaronitrile. A white solid. Yield: 67% (12.3 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (s, 2H), 8.03 (d, 2H, J = 7.9 Hz), 7.84 (d, 2H, J = 7.9 Hz), 7.71 (t, 2H, J = 7.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 132.3, 132.1 (q, $^2J_{CF}$ = 33.2 Hz), 131.8, 130.1, 128.6 (q, $^3J_{CF}$ = 3.6 Hz), 125.6 (q, $^3J_{CF}$ = 3.5 Hz), 123.2 (q, $^1J_{CF}$ = 271.2 Hz), 115.6. FAB-MS: calcd MW = 366.06, *m*/*e* = 365.99 (M^-). Anal. Found (Calcd) for $C_{18}H_8F_6N_2$: C, 58.94 (59.03); H, 2.29 (2.20); N, 7.55 (7.65).

3.1.3. Bis(4-methoxyphenyl)fumaronitrile. Unlike the other three fumaronitrile compounds isolated from the reaction solution, the product was found to be a mixture of fumaronitrile and maleonitrile with a molar ratio of about 19:1 determined by ^{1}H NMR. A lemon yellow solid. Yield: 69% (10.0 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78 (d, 4H, J = 8.9 Hz), 6.99 (d, 4H, J = 8.9 Hz), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$): δ (ppm) 162.0, 130.4, 124.6, 122.7, 117.3, 114.6, 55.5. FAB-MS: calcd MW = 290.11, *m*/*e* = 290.10 (M^+). Anal. Found (Calcd) for $C_{18}H_{14}N_2O_2$: C, 74.08 (74.47); H, 4.83 (4.86); N, 9.15 (9.65). A pure sample of bis(4-methoxyphenyl)maleonitrile was isolated by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.28 (d, 4H, J = 9.0 Hz), 6.80 (d, 4H, J = 9.0 Hz), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.4, 130.9, 123.2, 122.9, 117.3, 114.5, 55.3. FAB-MS: calcd MW = 290.11, *m*/*e* = 290.10 (M^+). Anal. Found (Calcd) for $C_{18}H_{14}N_2O_2$: C, 74.13 (74.47); H, 4.78 (4.86); N, 9.45 (9.65).

3.2. General Procedure for the Synthesis of *N*-Methylated Diphenylmaleimide Derivatives. The following procedure was applied to the reaction proceeding in toluene (50 mL) containing fumaronitrile compounds (0.2 M). Sodium methoxide (3 equiv)−methanol solution was added to the reaction solution. The solution mixture was then stirred for another 1−3 h depending on the substituent of the fumaroni-

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(12) de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.

triles. We found electron-donating substituents, such as methoxy, required a longer time (i.e., 3 h) and a higher temperature (i.e., 50 °C) to drive the reaction toward completion. On the other hand, room temperature and a short period of reaction time (i.e., 1 h) were enough for an electron-withdrawing-substituent-containing fumaronitrile, such as bis(3-trifluoromethylphenyl)fumaronitrile. The reaction was quenched by water and then extracted by dichloromethane. After the removal of the solvent, the solid residue was treated at 0 °C with 2.0 equiv of potassium *tert*-butoxide in DMF. After 1−2 h of stirring, 2.5 equiv of iodomethane was added to the solution. The solution was then stirred at room temperature for about 10 h. After the removal of volatiles under reduced pressure, the residue was redissolved in dichloromethane and extracted with water. The desired product in dichloromethane was isolated by column chromatography (silica gel, ethyl acetate/hexanes).

3.2.1. *N*-Methyl-3,4-diphenylmaleimide. An apple green solid. Yield: 68% (1.8 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.43−7.46 (m, 4H), 7.30−7.36 (m, 6H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.8, 136.3, 129.8, 129.7, 128.7, 128.5, 24.2. FAB-MS: calcd MW = 263.09, *m*/*e* = 264.3 ($M^+ + 1$). Anal. Found (Calcd) for $C_{17}H_{13}NO_2$: C 77.79 (77.55), H 5.11 (4.98), N 4.93 (5.32).

3.2.2. *N*-Methyl-3,4-bis(3-trifluoromethylphenyl)maleimide. A green-yellow solid. Yield: 52% (2.1 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.71 (s, 2H), 7.64 (t, 4H, J = 9.0 Hz), 7.49 (t, 2H, J = 7.80 Hz), 3.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.7, 135.6, 132.5, 131.2, 129.1, 128.1, 126.8, 126.7, 123.2, 24.5. FAB-MS: calcd MW = 399.07, *m*/*e* = 400.3 ($M^+ + 1$). Anal. Found (Calcd) for $C_{19}H_{11}F_6NO_2$: C 57.13 (57.15), H 2.67 (2.78), N 3.33 (3.51).

3.2.3. *N*-Methyl-3,4-bis(4-methoxyphenyl)maleimide. A golden yellow solid. Yield: 73% (2.4 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45 (d, 4H, J = 9.0 Hz), 6.85 (d, 4H, J = 9.0 Hz), 3.81 (s, 6H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 184.3, 180.6, 171.4, 160.7, 134.3, 131.4, 121.4, 114.1, 55.2, 39.6, 24.1. FAB-MS: calcd MW = 323.12, *m*/*e* = 324.2 ($M^+ + 1$). Anal. Found (Calcd) for $C_{19}H_{17}NO_4$: C 70.19 (70.58), H 5.14 (5.30), N 4.20 (4.33).

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Supporting Information Available: CIF files for bis(4-bromohenyl)fumaronitrile, bis(3-trifluoromethylphenyl)fumaronitrile, and bis(4-methoxyphenyl)fumaronitrile and X-ray crystal strucure data and crystal packing diagrams of bis-(4-bromophenyl)fumaronitrile and bis(3-trifluoromethylphenyl)fumaronitrile (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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