Communication

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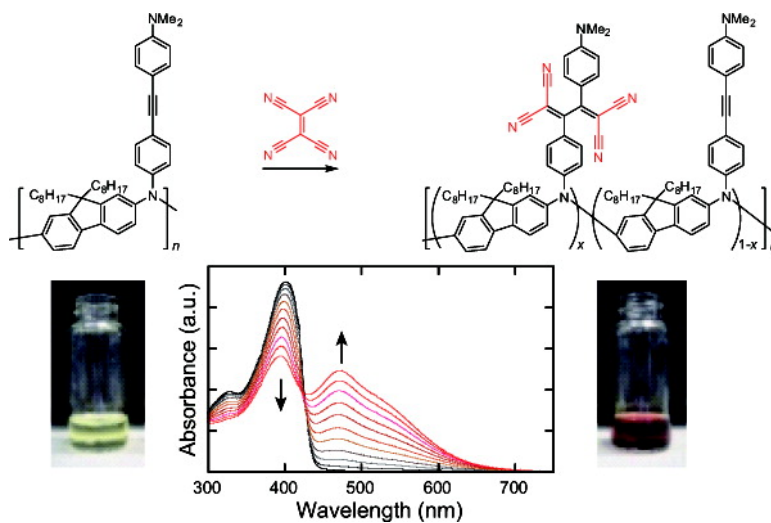# Click-Type Reaction of Aromatic Polyamines for Improvement of Thermal and Optoelectronic Properties

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Click chemistry can be defined as a highly efficient addition reaction, essentially yielding no byproducts. The most famous and well-studied click reaction is the copper(I)-catalyzed azide−alkyne cycloaddition reaction (CuAAC), forming a triazole ring,[1] which has been widely used for the preparation of functional materials.[2] However, the development of other click-type reactions has simultaneously been pursued,[3] because CuAAC has several limitations, such as the need for a metal catalyst to improve the reaction yield and regioselectivity, the explosive nature of the azide substances, and the poor optoelectronic properties of the triazole products. In particular, the last limitation is most significant when this click chemistry is applied to conjugated systems in optoelectronic devices. Indeed, there are some reports on the synthesis of conjugated molecules and polymers,[4,5] but the recently reported photovoltaic performance was not remarkable.[6]

One of the reactants in the click-type reactions usually contains a carbon-based multiple bond. Recently, it was found that electron-rich alkynes activated by aromatic amino substituents undergo a [2+2] cycloaddition reaction with a strong electron acceptor, tetracyanoethylene (TCNE), to form the cyclobutene rings, which spontaneously open to yield the donor-substituted 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) chromophores in quantitative yield at room temperature.[7] The advantages of this quantitative addition reaction are that metal catalysts are not necessary and the products feature strong charge-transfer (CT) interactions in the visible absorption region, potent redox activities, and related properties.[8] The controlled introduction of these chromophores into conjugated systems, especially into conjugated polymers, is useful for optimization of the electronic states, thereby leading to the enhanced performance of the optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells. We now report for the first time the application of this reaction as a new click-type reaction to improve the thermal and optoelectronic properties of conjugated polymers.

The fluorene-based aromatic polyamine bearing electron-rich alkyne side chains was designed as an active precursor[9] and was prepared by the palladium-catalyzed amination reaction between the dibromofluorene monomer and a tolane-based aniline monomer.[10] The molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymer, determined by gel permeation chromatography (GPC) (eluent, THF), were 13 300 and 3.43, respectively. The addition of a TCNE solution in 1,2-dichloroethane to the precursor polymer at room temperature results in an immediate color change from yellow to red, accompanying a gradual increase in a CT band with the most intense absorption centered at ∼470 nm (Figure 1). The presence of the isosbestic point (428 nm) in the UV−vis spectral change indicates the absence of any undesired side reactions. To reveal the quantitative yield of the polymer reaction, the full TCNE adduct ($x = 1$) was prepared and unambiguously characterized. In the ^{13}C NMR spectrum, 20 of the 22 desired peaks in the aromatic region were explicitly observed (Figure 2SI
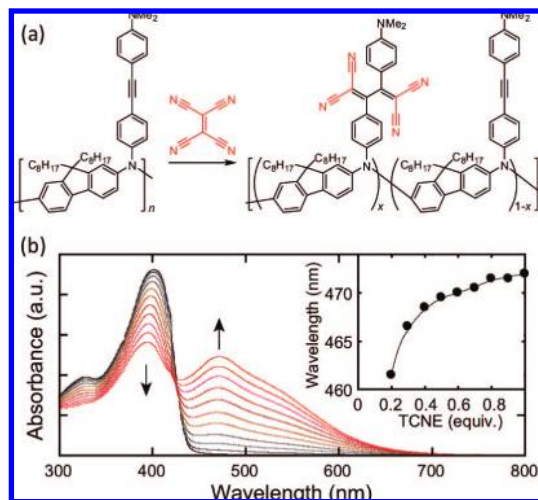

Figure 1. (a) Reaction of the aromatic polyamine containing electron-rich alkynes with TCNE. (b) Changes in the UV−vis spectral shape and (inset) the peak top value from 0 to 1 equiv TCNE addition in 1,2-dichloroethane.
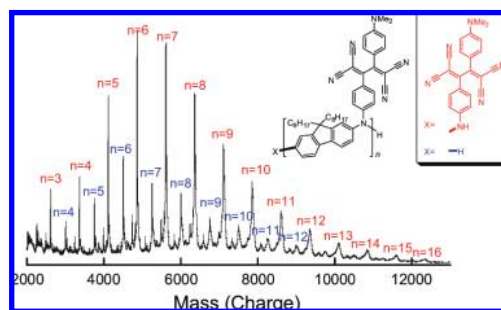

Figure 2. MALDI-TOF mass spectrum of the aromatic polyamine after reaction with an equivalent amount of TCNE ($x=1$) (matrix, dithranol).

(Supporting Information)). In the IR spectra before and after the reaction, a weak alkyne vibrational peak at 2207 cm^{-1} was replaced by a strong cyano one at 2217 cm^{-1} (Figure 3SI). GPC showed a reasonable increase in the molecular weight (M_n = 14 400) and a noticeable decrease in the polydispersity (M_w/M_n = 2.00).[11] Furthermore, strong evidence was obtained from the MALDI-TOF mass spectra. Two sets of polymer peak profiles were observed for both the precursor ($x = 0$) and the TCNE adduct ($x = 1$) (Figure 1SI and Figure 2). The observed peak values and the intervals substantiated the polymer structures. After the polymer reaction, the peak interval was expanded in accordance with the molecular weight of TCNE. Importantly, the addition of 1.5 equiv of TCNE provided the same MALDI-TOF mass spectrum as Figure 2, indicating that the products are inert to excess TCNE. The blue set of peaks suggests that the termination process of the polycondensation is debromination and hydrogenation.
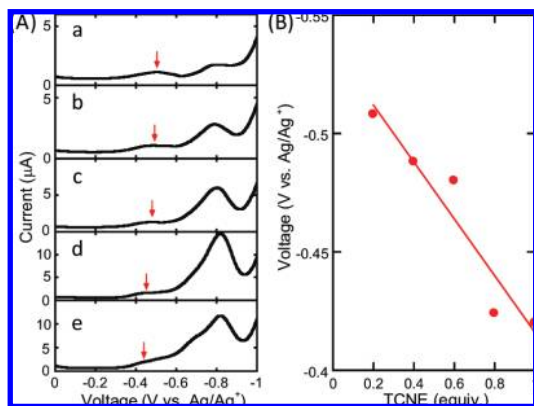
Figure 3. (A) Differential pulse voltammetry (DPV) and (B) the $E_{red,1}$ of the aromatic polyamine with addition of different amounts of TCNE (a, 0.2 equiv; b, 0.4 equiv; c, 0.6 equiv; d, 0.8 equiv; e, 1.0 equiv).

Very interestingly, when the most intense CT absorption is noted, the peak top values shifted bathochromically with increasing amount of TCNE addition, and the shift was almost saturated at the equivalent amount of TCNE (Figure 1b, inset). The possibility of the intermolecular aggregation was ruled out (Figure 4SI). If the side-chain chromophores do not interact with each other, the peak top values should be constant (Figure 5SI). This result suggests that this click-type reaction can affect the electronic state of the whole conjugated polymers. To prove this idea, electrochemical measurements were performed for the polymers with different TCNE addition amounts. Cyclic voltammetry (CV) of the precursor polymer ($x = 0$) displayed only reversible oxidation steps, whereas the TCNE adducts showed reversible reduction steps together with anodically shifted oxidations (Figure 6SI). Since it was difficult to discuss the exact potentials from the CV measurements, differential pulse voltammetry (DPV) was also measured. As reported for the small chromophores,[7] two well-resolved reduction steps ascribed to the TCBD moieties of the polymers appeared (Figure 3A), while the oxidation potentials were still elusive. The first reduction potential, $E_{red,1}$, which is associated with the LUMO level of the polymers, shifted anodically in a linear fashion with increasing amount of the TCNE addition (Figure 3B). This result is consistent with the UV−vis spectral change and again suggests that this click-type reaction can be employed for tuning the energy levels of the conjugated polymers.

Since the thermostability of organic materials is highly important in practical applications, the detailed thermal properties of the polymers with addition of different amounts of TCNE were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal stability of the aromatic polyamines is quite high. Thus, the decomposition temperature (T_d) of the precursor polymer ($x = 0$) was 291 °C. Remarkably, the T_d value was further improved with increasing amount of the TCNE addition, reaching 409 °C for the full adduct ($x = 1$) (Figure 7SI and Table 1). Similarly, the glass transition temperature (T_g) of the precursor polymer ($x = 0$), determined by the second heating scan during the DSC measurements, was 125 °C, and this value increased to some extent with the increasing amount of the TCNE addition (Figure 8SI and Table 1). All these enhancements in thermal properties upon TCNE addition most likely originate from the strong interactions between the cyano functions. Previously, the antiparallel dipolar alignment and multipolar interactions of the cyano functions were demonstrated for the X-ray crystal structures of the small TCBD molecules.[7] These interactions are expected to be effective even in the amorphous solid states of the polymers.

Table 1. Summary of the Thermal Properties of the Aromatic Polyamines with Addition of Different Amounts of TCNE

TCNE addition x (equiv)	T_g (°C)[a]	T_d (°C)[b]
0	125	291
0.2	129	368
0.4	141	381
0.6	146	387
0.8	149	400
1.0	152	409

[a] Glass transition temperature determined by DSC measurements. [b] Decomposition temperature determined by derivative thermogravimetry.

In summary, the quantitative addition reaction between electron-rich alkynes and TCNE was found to serve as a new click-type reaction to improve the thermal and optoelectronic properties of the aromatic polyamine. Advanced studies of device fabrication using these polymers are currently under way. Since the addition amount of the acceptor molecule can be regulated, fine-tuning of the electronic states of the conjugated systems will be possible. These findings should be applicable to a variety of conjugated molecules and polymers.

Supporting Information Available: Experimental details on synthesis and measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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