Amino-Functionalization of Vinyl-Substituted Aromatic Diimides by Quantitative and Catalyst-Free Hydroamination

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Abstract:

Development of facile and versatile synthetic tools for decorating π-conjugated molecules has attracted considerable interest because of their potential application in creating novel π-electron materials. Reported herein are quantitative catalyst-free hydroamination reactions of a series of aromatic diimide compounds having vinyl groups at the π-core, which have been confirmed by NMR, UV–vis absorption spectroscopy, mass analysis, and single crystal X-ray structural analysis. Kinetic studies revealed that the hydroamination reaction of a vinyl-substituted naphthalenediimide with an aliphatic amine proceeded rapidly under benign conditions. Similary, the two vinyl groups attached to aromatic diimides reacted with amines simultaneously, resulting in the formation of amine bisadducts and macromolecules.

1. Introduction

The continual emergence of novel π-conjugated molecules has been achieved through sophisticated synthetic methods for the expansion of the π-core and the introduction of functional groups around the π-core. Aromatic diimide derivatives, as represented by benzenediimide (BDI), naphthalenediimide (NDI), and perylenediimide (PDI), have been extensively studied as excellent dyes and building blocks in the fields of organic electronics, supramolecular chemistry, and so forth.[1] Functionalization of the diimide π-core is known to induce significant changes in its conformation and physicochemical properties.[2] It often requires, however, numerous synthetic efforts and sometimes metal catalysts to attach functional groups to the π-core.

We recently found that hydroamination reaction of an ethynyl-substituted NDI and PDI occurred quantitatively without an external catalyst.[3] This facile decoration method of the diimide π-cores (electron acceptors) with various amines (electron donors) would offer a versatile platform to create functional π-electron materials. However, the scope of such a hydroamination reaction on electron-withdrawing π-systems, particularly its utilization for the synthesis of amine multi-adducts and macromolecules, is still very limited,[3] [4] [5] because the following hydroamination reactions become much slower than the first reaction ($k_1 \gg k_2$; Scheme 1a). In light of these limitations, we envisioned to design novel aromatic diimide compounds in which hydroamination reactions occur simultaneously ($k_1 \approx k_2$) to foster facile and more versatile synthetic tools for π-electron materials.

Herein, we report quantitative hydroamination reactions of vinyl-substituted aromatic diimide compounds, which proceeded simultaneously ($k_1 \approx k_2$) to afford diimide-based macromolecules as well as discrete amine multi-adducts, without an external catalyst. We designed a series of aromatic diimide compounds of which the π-core is substituted with vinyl groups (**vNDI1**, **vNDI2**, **vBDI2**, and **vPDI2**; Scheme 1b). The reaction of **vNDI1** with different amines was studied in detail, as a prototype

example, by NMR, UV–vis absorption spectroscopy, and mass analysis. We then examined the simultaneous addition of amines to the two vinyl groups of **vNDI2**, **vBDI2**, and **vPDI2** for the formation of bisadducts and macromolecules.
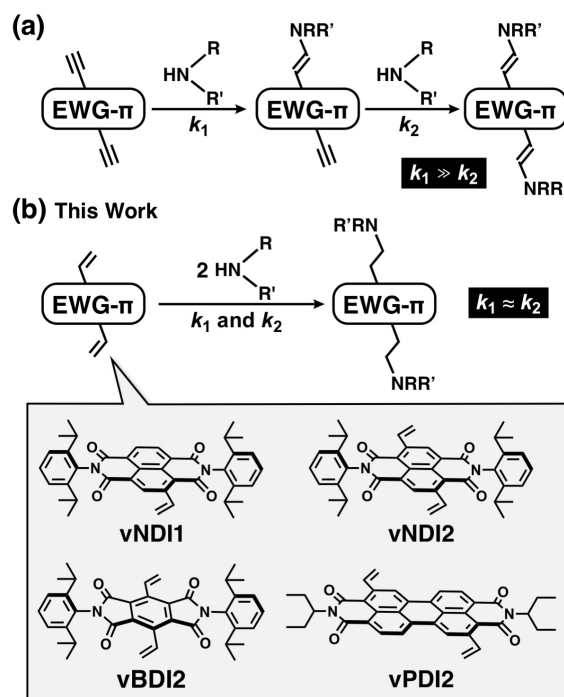

Scheme 1. (a) Stepwise hydroamination of terminal alkyne (ethynyl group) attached to electron-withdrawing π-systems (EWG-π), in which the first step is much faster than the second step ($k_1 \gg k_2$). (b) Simultaneous hydroamination of terminal alkene (vinyl group) attached to EWG-π with equal rate constants in the first and second steps ($k_1 \approx k_2$) and the structures of aromatic diimide compounds in this study.

2. Results and Discussion

The synthetic procedures and full characterization data of the vinyl-substituted aromatic diimide compounds are shown in the Supporting Information (Experimental Section; Figures S1–S8). The ^{1}H NMR signals corresponding to the terminal vinyl protons of **vNDI1** appear at 5.79 ppm and 6.18 ppm in chloroform-*d* (CDCl$_3$) at 298 K (Figure 1a), while those of styrene, a typical vinyl-substituted aromatic compound, appear at 5.25 ppm and 5.76 ppm.[6] The significant downfield shifts of the terminal

vinyl protons of **vNDI1** indicate deshielding by the electron-withdrawing nature of NDI and are comparable to those of methyl acrylate (5.82 ppm and 6.41 ppm) which has been reported to react with amines.[7] Indeed, when dibutylamine (**DBA**) was added to a solution of **vNDI1** at 298 K, the ^{1}H NMR of **vNDI1** was fully converted, as shown in Figure 1b. After careful characterization, we confirmed that the product was an amine monoadduct, **vNDI1–DBA** (Figures S9 and S10).[8] Note that this aza-Michael addition reaction proceeded, without an external catalyst, almost quantitatively (isolated yield: 94%) at room temperature. Purification such as column chromatography was not required after the reaction.
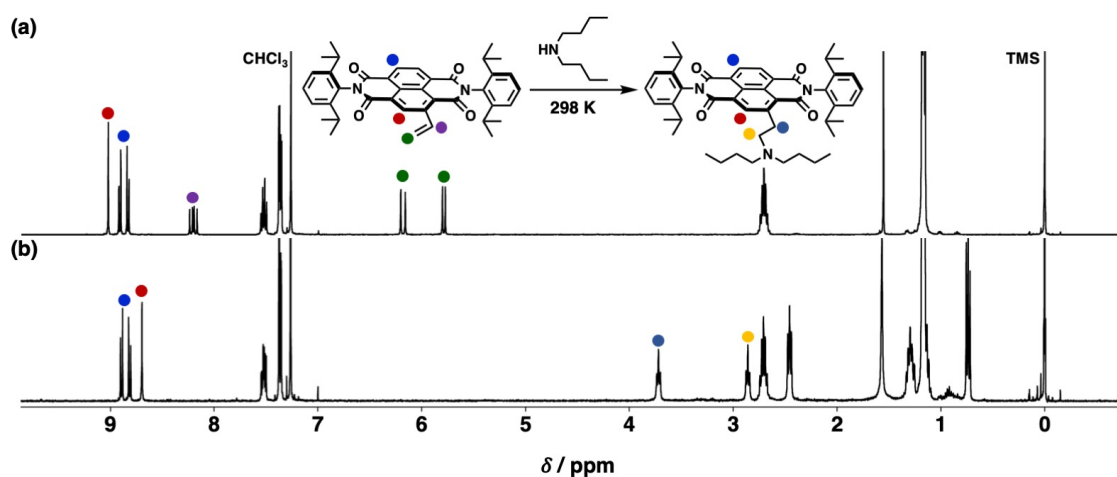

Figure 1. ^{1}H NMR spectra of (a) **vNDI1** and (b) **vNDI1–DBA** in CDCl$_3$ at 298 K.

The reaction kinetics were followed with UV–vis absorption spectroscopy. The UV–vis absorption spectrum of **vNDI1** in 1,2-dimethoxyethane (DME) at 298 K changed upon addition of excess **DBA** with isosbestic points (Figure 2). The change in the absorption spectrum (from yellow to brown color) became saturated over time, indicating the quantitative formation of **vNDI1–DBA**.[9] The UV–vis absorption spectral shape of **vNDI1–DBA** was fairly consistent with the corresponding oscillator strengths calculated by TDDFT (Figure S12). The time course of the absorbance at 405 nm (A_{405}) is described by Equation (1):

$$A_{405} = \varepsilon_{\textbf{vNDI}}C_0 \exp(-k_{\text{obs}}t) + \varepsilon_{\textbf{vNDI–DBA}}C_0\{1 - \exp(-k_{\text{obs}}t)\} \qquad (1)$$

where $\varepsilon_{\textbf{vNDI1}}$ and $\varepsilon_{\textbf{vNDI1–DBA}}$ are absorption coefficients at 405 nm due to **vNDI1** and **vNDI1–DBA**, respectively, C_0 is the initial concentration of **vNDI1** (40 μM), k_{obs} is a pseudo-first-order rate constant for the formation of **vNDI1–DBA**. The time profile of the absorbance changes at 405 nm is well fitted by Equation (1) to give k_{obs} to be 4.25×10^{-3} s^{-1}. The reaction rate at 298 K is comparable to that of conventional uncatalyzed click reactions.[10]
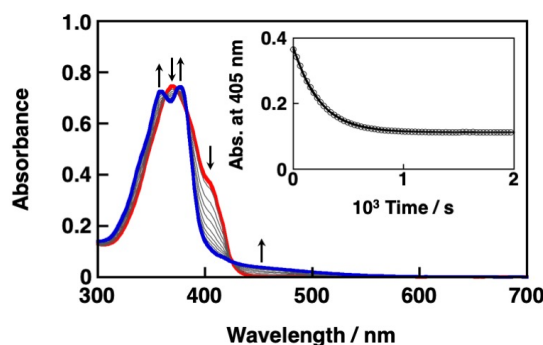
Figure 2. UV–vis absorption spectral changes observed upon addition of **DBA** (96 mM) to a DME solution of **vNDI1** (40 μM) at 298 K. Inset: Time profile of the absorbance change at 405 nm in the reaction of **vNDI1** (40 μM) and **DBA** (96 mM) at 298 K, fitted by pseudo-first order kinetic curve with R^2 value of over 0.999.

The reactivity of **vNDI1** with different amines was similarly studied by ^{1}H NMR and UV–vis spectroscopy (Figures S13–S15). The quantitative formation of a single aza-Michael product was confirmed even when an aromatic amine such as aniline, which is less nucleophilic than aliphatic amines, was used. The rate constants (k_{obs} in s^{-1}) of each product are summarized in Table 1. The reaction rate depends on not only the nucleophilicity of amine, but also the polarity of the reaction solvent (Figure S16). The k_{obs} value is 30-fold larger in DME than that in toluene, probably because the ionic intermediate is stabilized in polar environments to reduce the reaction barrier (Figure

S16c). The reaction of **vNDI1** with a primary amine (*n*-butylamine) was faster than in the case of a secondary amine (**DBA**), which may be due to less steric hindrance.[11]

**Table 1:** Scope of amines in the reaction with **vNDI1** at 298 K.

Amine	Product [a] (monoadduct)	Purity / % [a]	k_{obs} / s^{-1}
dibutylamine	**vNDI1–DBA**	≥95	1.41 ($\pm$ 0.04) $\times$ 10^{-4} in toluene [b]
			2.30 ($\pm$ 0.07) $\times$ 10^{-3} in methanol [b]
			4.25 ($\pm$ 0.13) $\times$ 10^{-3} in DME [b]
n-butylamine	**vNDI1–BA**	≥95	7.97 ($\pm$ 0.24) $\times$ 10^{-3} in DME [b]
dibenzylamine	**vNDI1–DBzl**	≥95	1.85 ($\pm$ 0.06) $\times$ 10^{-4} in DME [b]
aniline	**vNDI1–Ani**	≥95	2.68 ($\pm$ 0.20) $\times$ 10^{-4} in DME [c]

[a] The ^{1}H NMR spectrum of each product is shown in Figure 2b (**vNDI1–DBA**), Figure S13 (**vNDI1–BA**), Figure S14 (**vNDI1–DBzl**), and Figure S15 (**vNDI1–Ani**). The purity was determined by ^{1}H NMR. [b,c] The rate constant was determined by UV–vis absorption spectroscopy at 298 K; [nucleophile] = 96 mM for [b] and 5.5 M for [c].

When **vNDI2**, having two vinyl groups, and **DBA** were mixed at 298 K, the reaction proceeded almost quantitatively to give an amine bisadduct, **vNDI2–(DBA)₂** (Figure 3a). The formation of **vNDI2–(DBA)₂** was confirmed by NMR spectroscopy (Figure S17), mass analysis (Figure S18), and single crystal X-ray structural analysis. The C=C double bonds of the vinyl groups in **vNDI2** (bond lengths: 1.33 Å) were converted to C–C single bonds (bond lengths: 1.54 Å), and the new C–N bonds were formed by the addition of **DBA** (Figures 3b and 3c). The aza-Michael product exhibited a characteristic conformation such that the amine moieties enfold the NDI π-core.

UV–vis absorption spectral changes of **vNDI2** in DME were observed upon the addition of **DBA** at 298 K (Figure S19). The spectra changed sequentially until **vNDI2** was fully converted to **vNDI2–(DBA)₂**. Mass spectrometry during the reaction indicated the simultaneous existence of unreacted **vNDI2**, the monoadduct (**vNDI2–DBA**), and **vNDI2–(DBA)₂** (Figure S20). These results indicate that the rate constants for the formation of the monoadduct and the bisadduct are almost the same ($k_1 \approx k_2$), which is

significantly different from the stepwise reaction of ethynyl-substituted NDI with **DBA** ($k_1 \gg k_2$).[3] The rate constant for the formation of **vNDI2–(DBA)₂** under pseudo-first-order conditions was roughly determined to be $k_{obs} = 1.1 \times 10^{-3}$ s^{-1} based on the time profile of the absorbance changes at 408 nm,[12] which was in the same order as that of **vNDI1–DBA** (4.25×10^{-3} s^{-1}) under the same experimental conditions.
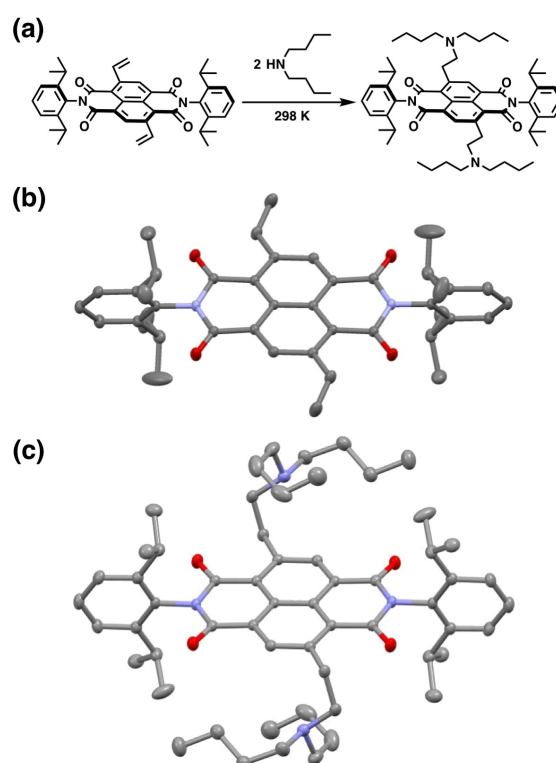

Figure 3. (a) Reaction of **vNDI2** with **DBA**. Crystal structures of (b) **vNDI2** and (c) **vNDI2–(DBA)₂**. Hydrogen atoms are omitted for clarity. The pertinent crystallographic data are summarized in Tables S1 and S2.

We confirmed that the other vinyl-substituted aromatic diimides (**vBDI2** and **vPDI2**) also reacted with **DBA** simultaneously to afford the corresponding bisadducts, **vBDI2–(DBA)₂** and **vPDI2–(DBA)₂**, quantitatively (Experimental Section and Figures S21–S24). In both cases, the reaction was much slower than in the case of **vNDI2**. The time profile of the UV–vis absorbance change in the reaction of **vBDI2** with **DBA** (Figure S25) indicated the monoadduct formation was faster than the bisadduct

formation ($k_1 > k_2$), probably because of the electronic effect of the amine unit on the BDI π-core. In contrast, the UV–vis absorption spectrum of **vPDI2** did not significantly change even after the formation of **vPDI2–(DBA)₂**, and its time profile obeyed pseudo-first order kinetics (Figure S26; $k_1 \approx k_2$), indicating that the electronic effect of the amine unit on the PDI π-core was small.

In order to extend the utility of the simultaneous and rapid amine addition reactions of vinyl-substituted aromatic diimides, we finally performed polymerization of **vNDI2** with an equimolar amount of diamine (Figure 4a). The reaction of **vNDI2** with *N,N'*-dimethylethylenediamine in DME at 323 K proceeded with the solution color change from yellow to brown, followed by the formation of a brown precipitate within 2 h. A matrix-assisted laser desorption/ionization time-of-flight mass (MALDI TOF–MS) spectrometry measurement confirmed the formation of oligomers and polymers (Figure 4b).[13] The insoluble precipitate was separated from the filtrate in over 85% yield. MALDI TOF–MS and gel permeation chromatography (GPC) analysis of the filtrate indicated the elongation of the oligomer chain up to heptamer (Figure S27a and S27b). The number average molecular weight (M_n) and polydispersity index of the filtrate were 1.35 kDa and 3.63, respectively. The ¹H NMR spectrum of the filtrate in CDCl₃ indicated the presence of vinyl terminated oligomers. The degree of oligomerization was determined to be 3.5 based on the ratio of the integration values of the terminal vinyl protons and the isopropylphenyl protons (Figure S27c), which was consistent with the GPC results.
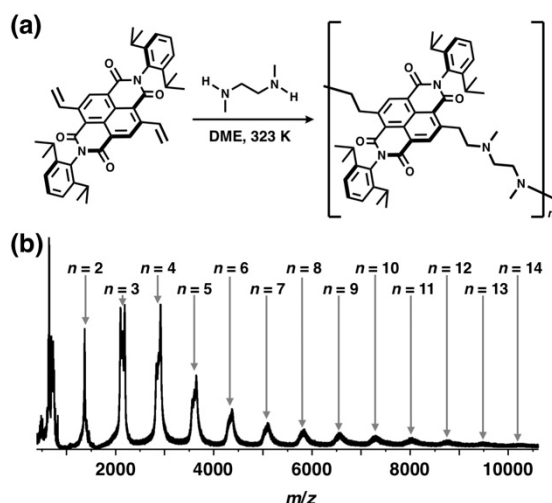
Figure 4. (a) Reaction of **vNDI2** with *N,N'*-dimethylethylenediamine in DME at 323 K. (b) MALDI TOF–MS chart after the reaction (positive ion, linear mode).

The reaction between **vBDI2** and *N,N'*-dimethylethylenediamine in DME at 348 K also resulted in the formation of oligomers and polymers (Experimental Section and Figure S28). In contrast to the case of **vNDI2**, all the obtained product was soluble in organic solvents and analyzed by GPC, ^{1}H NMR, and MALDI TOF–MS. The M_n and polydispersity index of the product were 1.79 kDa and 1.80, respectively. Further elongation of the polymer chain is expected by optimizing spacer length of diamines or the imide *N*-substituents of the aromatic diimides, which is under progress in our group.

3. Conclusions

In summary, we demonstrated hydroamination reactions of a series of vinyl-substituted aromatic diimides which afforded the corresponding aza-Michael products quantitatively and without a catalyst. The reaction of a vinyl-substituted naphthalenediimide with various amines proceeded in accordance with pseudo-first-order kinetics in the presence of excess amine in different solvents at 298 K. Similarly, the reaction of an aromatic diimide having two vinyl groups with a monoamine and a diamine respectively afforded an amine bisadduct and an amino-bridged macromolecule. We believe that such catalyst-free, spontaneous

hydroamination offers versatile synthetic tools for π-core-decoration of the aromatic diimides and their macromolecules.

Acknowledgements

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[6] Similar downfield shift of the terminal vinyl carbon of vNDI1 at 123 ppm (Figure S1) was also observed compared to that of styrene at 114 ppm.

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[8] The product is fairly stable under ambient atmosphere and even in the silica-gel column.

[9] The weak absorption band over 450 nm probably be assigned to intramolecular charge-transfer band between the amine unit and the NDI π-core, but the electronic effect of the amine unit on the NDI π-core is not significant judging from the results of cyclic voltammetry (Figure S11).

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[11] The secondary amine moiety in **vNDI1–BA** did not react with **vNDI1**, judging from the reaction progress followed by ^{1}H NMR spectroscopy.

[12] Note that the determination of the pseudo-first-order rate constant includes the assumption that the absorption coefficient at 408 nm due to the monoadduct is almost the same as that of the bisadduct, **vNDI2–(DBA)₂**. Appearance of isosbestic points in the UV–vis absorption spectral changes indicates that this assumption is roughly valid. See Figure S19 for details.

[13] Some oligomers' peaks are split into several peaks, which are assigned to the oligomers with different terminal groups, *i.e.* vinyl and diamino groups.