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# Lewis Acid Assisted Diels–Alder Reaction with Regio- and Stereoselectivity: *Anti*-1,4-Adducts with Rigid Scaffolds and Their Application in Explosives Sensing

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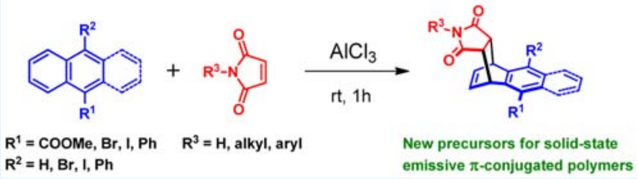
*Supporting Information*

**ABSTRACT:** Unusual *anti*-1,4-adducts of anthracene derivatives and *anti*-adducts of inert arenes with rigid scaffolds have been obtained via $AlCl_3$-assisted Diels–Alder reaction in good to excellent yields under mild conditions. Further derivation of 1,4-adducts gave $\pi$-conjugated polymers which could act as sensors of explosive species. This highly efficient synthesis method provides versatile approaches to solid-state emissive $\pi$-conjugated polymers.



The Diels–Alder (D–A) reaction, which is among the most powerful and well understood reactions in organic chemistry,[1] has been widely used as a versatile tool for synthesis of functional materials,[2] nature products,[3] and unique topological polymers.[4] As a class of aromatic hydrocarbons with inner-ring dienes, arenes have the potential to react with dienophile to yield D–A adducts. Among all of the arenes, D–A reactions of anthracene derivatives were studied most intensively and generally generate adducts bridging the center ring (9,10-adduct) due to the high localization of $\pi$-electron density at 9,10-position.[5−7] Hence, there are only a few reports of 1,4-adduction, and among them, *syn*-1,4-adducts are generally favored because of secondary orbital interactions.[8] Besides anthracene derivatives, D–A reactions involving other arenes like naphthalene and phenanthrene are much less studied due to the low reactivity of these arenes.[9] Reactions from limited reports in the literature usually suffer from harsh conditions, long reaction time, and relatively low yields.[10,11] Recently, our group reported the first method for synthesis of unusual *anti*-1,4-adducts between bulky *N*-phenylmaleimides and anthracene derivatives under thermal conditions.[12] However, limited substrate scope and relatively low yields of *anti*-1,4-adducts still restrict the utility of the D–A reaction in synthetic organic chemistry.

Luminescent $\pi$-conjugated polymers have attracted much attention due to their wide applications in light-emitting devices (LEDs), wavelength-tunable lasers, and ultrasensitive sensors.[13] An effective strategy to attain highly luminescent $\pi$-conjugated polymers in the solid state is to inhibit interchain $\pi$–$\pi$ interactions by rigid protecting frameworks such as triptycene,[14] supramolecular encapsulation,[15] and cyclic side chains.[16] Similar to triptycene, the D–A adducts of anthracene also contain rigid scaffolds. In contrast to 9,10-adducts, the 1,4-adduction retains the aromatic naphthyl structure (Figure 1), which renders 1,4-adducts useful for further derivation as new precursors for solid-state emissive organic materials.

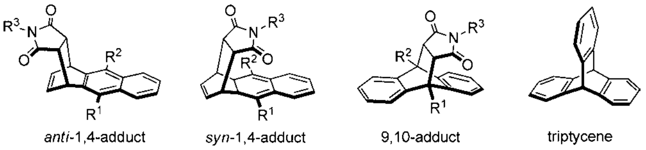


**Figure 1.** D–A adducts of anthracene derivatives and triptycene.

Since Yates and Eaton first reported the remarkable acceleration of the D–A reaction with $AlCl_3$,[10e] Lewis acids have been used widely in D–A reactions to activate dienophiles, lower the activation barrier, and increase both the reaction rate and selectivity at the same time under certain circumstances.[1,17] Herein, we report a $AlCl_3$-assisted D–A reaction to achieve unusual regio- and stereoselectivity between *N*-maleimides and arene derivatives in good to excellent yields. *Anti*-1,4-adducts of anthracene derivatives and *anti*-adducts of inert arenes with rigid scaffolds were obtained under mild conditions, and the resultant *anti*-1,4-adduct could be further derived in the synthesis of solid emissive $\pi$-conjugated polymers which could act as sensors of explosive species.

We started our investigation by screening different kinds of commonly used Lewis acid based on the D–A reaction between **1i** and **2d**.[18] After exploration, we found that using 5 equiv of $AlCl_3$ in $CHCl_3$ furnished good yield of the desired *anti*-1,4-adduct after 1 h of stirring at room temperature. Addition of excess $TiCl_4$ with prolonged reaction time resulted in poor yield of the desired adduct, while other Lewis acids showed no activity. We attribute this result to the larger $\pi/\sigma$-binding enthalpy of $AlCl_3$ compared to other Lewis acids used in this experiment,[19] which leads to much stronger complex formation with carbonyl group. This strong binding affinity enables effective activation of

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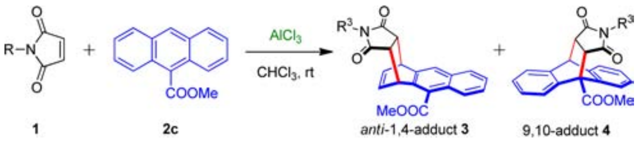
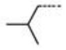
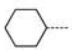
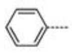
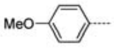
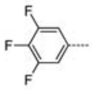
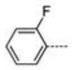
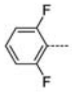
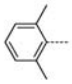
the maleimides and results in high reactivity. With the optimized conditions in hand, we tested the Lewis acid assisted D−A reaction between **2c** and both alkyl- and aryl-substituted maleimides (Table 1). No *syn*-1,4-adduction was detected in this D−A reaction, and the *anti*-1,4-adduct was obtained as the major product even when maleimide without substituent was used (entry 1). The ratio of *anti*-1,4-adducts increased dramatically when bulky alkyl substituents were introduced onto the maleimides (entries 2−4). As for aryl-substituted maleimides, the reaction demonstrated good compatibility as well as high regioselectivity as shown in entries 5−10. The introduction of an electron-donating substituent onto the *para*-position would decrease the ratio of the 1,4-adduct with prolonged duration time because of reduced reactivity (entry 6), while the electron-withdrawing substituent showed no significant influence of the regioselectivity (entry 7). Maleimides with substituents on the *ortho*-position of the phenyl ring provided excellent regioselectivity (entries 8−10). However, in the absence of $AlCl_3$, even bulky substituted maleimides resulted in a very low ratio of the *anti*-1,4-adduct (Table 1, control experiment).[18] Based on the results of NMR binding experiments,[18] we propose that the regio- and stereoselectivity should be attributed to the binding of $AlCl_3$ on the carbonyl group of maleimides as well as **2c**, which significantly increases the steric repulsion between two reactants and decreases the π-electron density at the 9,10-position of **2c**, thus suppressing both 9,10-/*syn*-1,4-cycladductions and giving *anti*-1,4-adducts through kinetic control.

**Table 1. Substrate Scope of the Maleimides**[a]

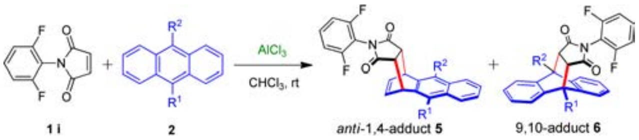


| entry | 1 | R | ratio of 3/4[b] | |
|---|---|---|---|---|
| | | | Lewis acid-assisted reaction[c] | control experiment[d] |
| 1 | **1a** | H— | 66:34, **3a**:**4a** | <1:99 |
| 2 | **1b** | $C_{12}H_{25}$— | 94:6, **3b**:**4b** | <1:99 |
| 3 | **1c** |  | 93:7, **3c**:**4c** | <1:99 |
| 4 | **1d** |  | 96:4, **3d**:**4d** | 4:96 |
| 5 | **1e** |  | 94:6, **3e**:**4e** | 2:98 |
| 6[e] | **1f** |  | 72:28, **3f**:**4f** | 2:98 |
| 7 | **1g** |  | 94:6, **3g**:**4g** | 2:98 |
| 8 | **1h** |  | >99:1, **3h**:**4h** | 3:97 |
| 9 | **1i** |  | >99:1, **3i**[f]:**4i** | 22:78 |
| 10 | **1j** |  | >99:1, **3j**:**4j** | 26:74 |

[a] The 1,4- and 9,10-adducts were obtained as two pairs of enantiomers due to the desymmetrization from the methoxy carbonyl group. [b] Determined by $^1H$ NMR integration with complete conversion of **1**. [c] Reaction conditions: **1** (0.1 mmol), **2c** (0.105 mmol), and $AlCl_3$ (0.5 mmol) in 1 mL of $CHCl_3$ at room temperature for 1 h. [d] Reaction conditions: **1** (0.06 mmol) and **2c** (0.06 mmol) in 0.6 mL of TCE-$d_2$ (1,1,2,2-tetrachloroethane-$d_2$) at 110 °C. [e] The reaction time was 6 h with 92% conversion of **1f**. [f] The isolated yield of **3i** was 96%.

The synthetic versatility of the $AlCl_3$-assisted D−A reaction was further demonstrated by applying various anthracene derivatives to reaction conditions (Table 2). In entries 1 and 2, reaction between **1i** and anthracene without substitution or with one bromine atom substitution led to similar results with the control experiments, and 9,10-adducts were obtained as the dominant product. However, when an electron-withdrawing substituent was introduced onto the 9-position (entry 3) or bulky substituents were introduced onto both the 9- and 10-positions of anthracene (entry 4−6), the *anti*-1,4-adduct became the only product and the regioselectivity was improved significantly compared with the control experiment. It is worth mentioning that in entries 4 and 5 halo-substituted anthracene derivatives were successfully converted directly into target *anti*-1,4-adducts **5d** and **5e** in excellent yields on a gram scale. Compared with 9,10-adducts, these 1,4-adducts retained two $sp^2$ C−Br or C−I bonds which could serve as precursors for polymer synthesis (vide infra). The reaction between strong Lewis base substituted anthracene and **1i** resulted in complete recovery of the starting material (entry 7). The relative configuration of isolated products in Tables 1 and 2 was assigned based on single crystal X-ray diffraction analysis and NOESY experiments of **3i** as a representative example.[12,18]

**Table 2. Substrate Scope of the Anthracene Derivatives**

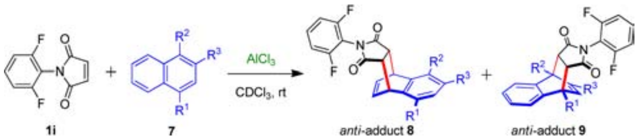


| entry | 2 | R | ratio of 5/6[a] | |
|---|---|---|---|---|
| | | | Lewis acid assisted reaction[b] | control experiment[c] |
| 1 | **2a** | $R^1 = R^2 = H$ | <1:99, **5a**:**6a** | 2:98 |
| 2 | **2b** | $R^1$ = Br<br>$R^2$ = H | <1:99, **5b**:**6b** | 6:94 |
| 3 | **2c** | $R^1$ = COOMe<br>$R^2$ = H | >99:1, **3i**:**4i** | 22:78 |
| 4 | **2d** | $R^1 = R^2$ = Br | >99:1, **5d**[d]:**6d** | 28:72 |
| 5 | **2e** | $R^1 = R^2$ = I | >99:1, **5e**[d]:**6e** | 55:45 |
| 6 | **2f** | $R^1 = R^2$ = Ph | >99:1, **5f**[d]:**6f** | >99:1 |
| 7 | **2g** | $R^1$ = $CH_2OH$<br>$R^2$ = H | N.A. | <1:99 |

[a] Determined by $^1H$ NMR integration with complete conversion of **1i**. [b] Reaction conditions: **1i** (0.1 mmol), **2** (0.105 mmol), and $AlCl_3$ (0.5 mmol) in 1 mL of $CHCl_3$ at room temperature for 1 h. [c] Reaction conditions: **1** (0.06 mmol) and **2c** (0.06 mmol) in 0.6 mL of TCE-$d_2$ at 110 °C. [d] The isolated yields of **5d**, **5e**, and **5f** were 98%, 95%, and 96%, respectively.

Furthermore, we examined the scope of other arenes with respect to **1i** (Table 3). In the absence of $AlCl_3$, only trace

### Table 3. Substrate Scope of the Naphthalene Derivatives[a]



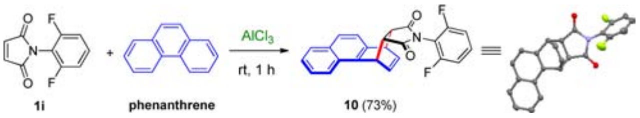
| entry | 7 | R | ratio of 8/9[b] |
|---|---|---|---|
| 1 | **7a** | R$^1$ = R$^2$ = R$^3$ = H | –, **8a**[d] |
| 2 | **7b** | R$^1$ = Cl<br>R$^2$ = R$^3$ = H | 67:33, **8b**:**9b** |
| 3 | **7c** | R$^1$ = Br<br>R$^2$ = R$^3$ = H | 77:23, **8c**:**9c** |
| 4 | **7d** | R$^1$ = R$^2$ = H<br>R$^3$ = Br | 95:5, **8d**:**9d** |
| 5[c] | **7e** | R$^1$ = R$^2$ = Br<br>R$^3$ = H | >99:1, **8e**[d]:**9e** |

[a] Reaction conditions: **1i** (0.1 mmol), **2** (0.105 mmol), and AlCl$_3$ (0.5 mmol) in 1 mL of CHCl$_3$ at room temperature for 1 h. [b] Determined by $^1$H NMR integration with complete conversion of **1i**. [c] The reaction time were 4 h. [d] The isolated yields of **8a** and **8e** was 99% and 98%, respectively.

*syn*-adducts were detected for naphthalene or phenanthrene after 3 days of heating at 100 °C. However, after treatment with 5 equiv of AlCl$_3$, the reaction with naphthalene and its derivatives proceeded smoothly to afford the corresponding *anti*-adducts in nearly quantitative yields. The reaction between **1i** and **7e** requires more time because of the relatively low reactivity of the diene (entry 5). The *anti*-configuration of the adduct **8a**, which was in accordance with literature reports,[10a,e] was confirmed by NOESY experiments.[18] Regioisomers were obtained when halogen atoms were introduced onto the 1- or 2-position of the naphthalene, and the reaction with 2-subsituted naphthalene turned out to show better regioselectivity. Similarly, the reaction with **7e** gave pure *anti*-5,8-adduct **8e**, which could also be further functionalized by various reactions.

In the case of phenanthrene, the AlCl$_3$-assisted D–A reaction also produced *anti*-adduct in good yield (73%) under similar conditions. The *anti*-configuration of the adduct was confirmed by single-crystal X-ray diffraction analysis as shown in Scheme 1.[20] To the best of our knowledge, this is the first Diels–Alder adduct obtained from phenanthrene and *N*-maleimides.

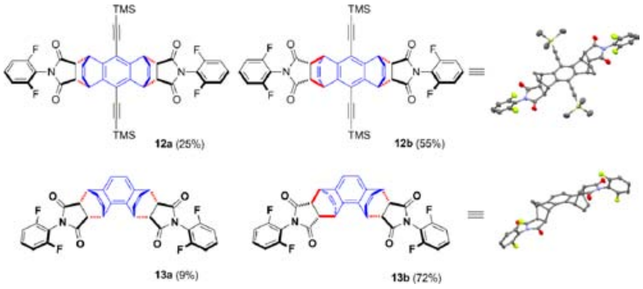
### Scheme 1. D–A Reaction between 1i and Phenanthrene[a]



[a] Isolated yield. Inset: single-crystal structure of **10**.

Compared with 9,10-adducts, 1,4-adducts and compound **10** retained naphthyl structures which could be further used as dienes to obtain diadducts with novel rigid structures. To our delight, when treated with 2.5 equiv of **1i**, anthracene derivatives **2d** converted completely to diadducts in good yield after being stirred for 48 h at room temperature. However, the two isomers could not be separated due to poor solubility, and thus, **12a** and **12b** were obtained after Sonogashira coupling reaction with TMSA (Scheme 2). Under similar conditions, the reaction between phenanthrene and **1i** gave diadducts **13a** and **13b** in 9% and 72% yields, respectively. The major products of both reactions were confirmed to be the *anti*-diadducts **12b** and **13b** by single-crystal X-ray diffraction analysis.[20]

### Scheme 2. Structure of Diadducts[a]



[a] Isolated yields. Inset: single-crystal structures of **12b** and **13b**.

Inspired by the unique structure of 1,4-adducts with rigid scaffolds similar to triptycene, we further derived the adducts by synthesizing $\pi$-conjugated polymers. The polymer from **5d** and the control polymer (**P1** and **P2** in Figure 2) were prepared via Sonogashira reaction, and the absorption and fluorescence spectra of **P1** ($M_n$ = 13 kDa) and **P2** ($M_n$ = 26 kDa) in dichloromethane and thin films are shown in Figure 2. Similar to pentiptycene polymers,[21] **P1** showed a relatively smaller red shift (11 nm) than **P2** (23 nm) in fluorescence bands in the thin film, which indicated efficient isolation of the $\pi$-conjugated backbone by rigid scaffolds. The new broad bands at longer wavelength in thin films were ascribed to the possible formation of exciplexes between naphthalene units and adjacent polymer chains.[21b] 2,4-dinitrotoluene (**DNT**) quenching experiments for **P1** and **P2** were conducted in film state, and **P1** showed much faster quenching response than **P2**(Figure 2). These results supported the idea that easily accessible 1,4-adducts could serve as new monomers for synthesizing solid-state fluorescent $\pi$-conjugated polymers.

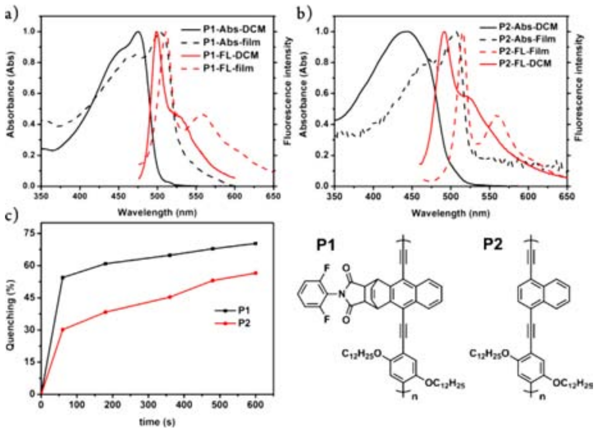


**Figure 2.** Absorption and fluorescence spectra of **P1** (a) and **P2** (b) in dichloromethane (full lines) and in spin-cast films (dash lines) and the fluorescence quenching (%) upon exposure to DNT vapor against time (c). Insets: structures of **P1** and **P2**.

In conclusion, we discovered a new method to achieve unusual regio- and stereoselectivity between *N*-maleimides and arene derivatives by AlCl$_3$-assisted D–A reaction. This efficient method with wide substrate scope enables 1,4-adduction of anthracene derivatives as well as adduction of inert arenes to generate adducts with rigid scaffolds with high regio- and stereoselectivity in good to excellent yields. Polymerization of *anti*-1,4-adducts gave $\pi$-conjugated polymers, which could act as sensors of explosive species. This highly efficient synthesis method provides new approaches to obtaining solid-state emissive materials. Further studies will focus on the photophysical properties of the $\pi$-conjugated polymers in condensed phases and their applications as fluorescent materials.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02487.

Experimental procedures, product characterizations, and $^{1}$H, $^{13}$C and $^{19}$NMR spectra (PDF)
X-ray data for compound **10** (CIF)
X-ray data for compound **12a** (CIF)
X-ray data for compound **13a** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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