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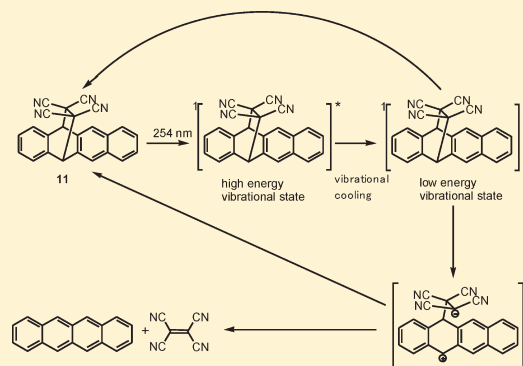
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Photo Retro-Diels–Alder Reactions

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S Supporting Information

ABSTRACT: Photo-retro-Diels–Alder (PrDA) reactions of a variety of Diels–Alder (DA) adducts were studied. Experimental results showed that the photoreactivity (quantum yield) depends on the electron-donating ability of the diene component and the electron-withdrawing ability of the dienophile component. The mechanism was studied by trapping the reaction intermediate, O₂ quenching, time-resolved absorption, and fluorescence spectroscopy. All the results support a mechanism that involves a charge-separated intermediate generated from a singlet excited state. The PrDA reaction may find applications in photoresponsive materials, photolithography, drug delivery, and mechanistic research.



INTRODUCTION

The retro-Diels–Alder (rDA) reaction, the reverse process of the Diels–Alder (DA) reaction, has evolved into a powerful synthetic tool and has been used for preparing many reactive, strained, and metastable chemicals.^{1–6} In addition, rDA reactions have been widely applied to many areas of materials science.^{7–14} According to the Woodward–Hoffmann rules,¹⁵ if a reversible DA process proceeds via a concerted mechanism, it is thermally allowed and photochemically forbidden. However, the Woodward–Hoffmann rules cannot be applied to a stepwise or a nonadiabatic mechanism, which are both common to organic photoreactions. In fact, photo-rDA (PrDA) reactions have been sparsely reported in literature.^{7,16–18} For example, Nozaki and Kato reported that the DA adduct of anthracene and styrene yielded anthracene under photoirradiation, while the adduct of anthracene and 2-butene is photostable.¹⁷ Jones et al. published PrDA reactions of a chiral compound that may be used as a chiral auxiliary.¹⁶ Recently, Nakagawa et al. demonstrated a photo-inducible HNO releasing agent based on a PrDA reaction.⁷

The PrDA reaction, which allows spatial and temporal control, may find applications in photoresponsive materials, photolithography, drug delivery, and mechanistic research. Although individual cases of PrDA reactions have been reported, no systematic study of PrDA reactions has been done either experimentally or theoretically, and no quantum yield of any PrDA reaction has been reported. Consequently, there was no guide to predict whether a compound could undergo PrDA reaction. All of these factors obstruct the wide application of PrDA reactions in chemistry and materials science. Herein, we report our study on the structure–reactivity relationship and the mechanism of the PrDA reaction,

which may help researchers design photoresponsive materials for different applications.

RESULTS AND DISCUSSION

In this work, a variety of normal-electron-demand DA adducts were prepared,^{19–23} and the electronic effects of the diene and dienophile components on the PrDA reactivity were studied (Scheme 1). Aromatic DA adducts were used because they can efficiently absorb at 254 nm, which was the wavelength chosen for measuring the quantum yields of these photoreactions. These DA adducts were prepared by mixing the corresponding dienophiles and aromatic dienes at room temperature or elevated temperatures. The details are given in Experimental Section.

Quantum yields of the retro-Diels–Alder reactions in acetonitrile were measured by the chemical actinometry method. The actinometer was uridine, which is hydrated under UV irradiation with a known quantum yield of 0.018 at 254 nm.^{24,25} Millimolar solutions of the DA adducts were irradiated at 254 nm in an inert atmosphere. The products were analyzed by the long-wavelength UV–vis absorption of the anthracene derivatives. An example is shown in Figure 1. The electronic effects of the diene component were examined by varying the 2,6-substituents of the anthracenes. Maleic anhydride was used as the common dienophile in this study because we found that the DA adduct of maleic anhydride and unsubstituted anthracene (**1** in Scheme 1) underwent PrDA reaction with a moderate quantum yield of 0.0057 under 254 nm UV irradiation. When electron donating substituents were introduced,

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Scheme 1. Structures of the Studied DA Adducts and an Example of a PrDA Reaction

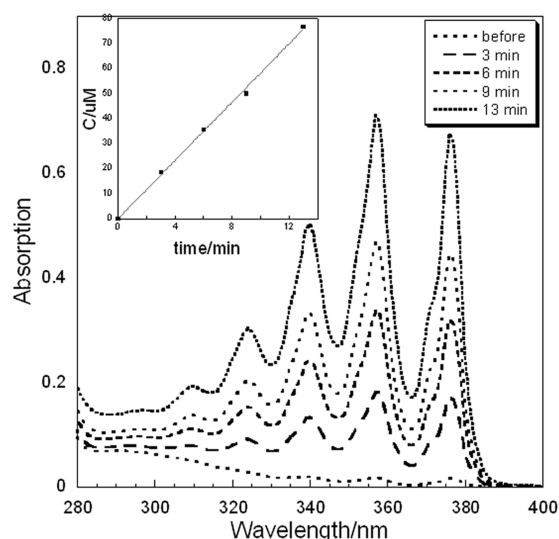
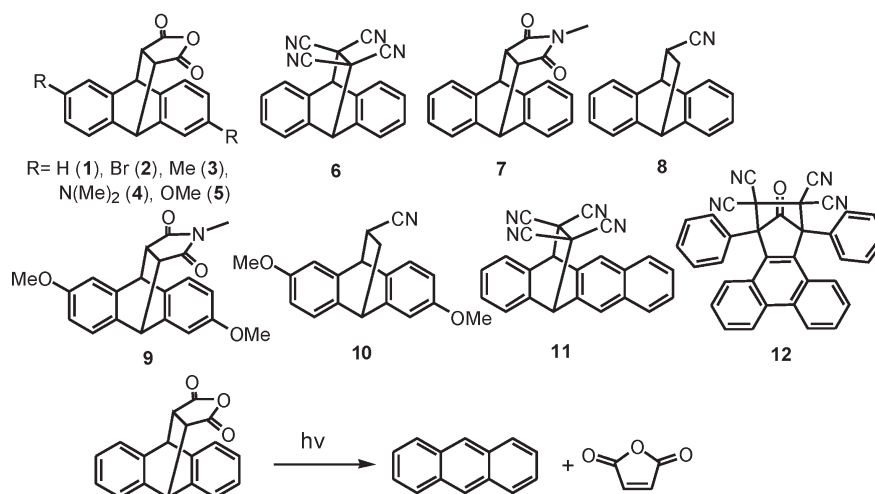


Figure 1. UV absorption change during photoirradiation of TCNE/anthracene adduct (**6**). (The linear relationship shown in the inset figure indicates a “total absorption” condition in the early stage of the reaction, during which period the quantum yield can be calculated with chemical actinometry.)

Table 1. Quantum Yields and Hammett Para Substituent Constants of the DA Adducts of Substituted Anthracenes and Maleic Anhydride

DA adducts	substituent	Hammett constant σ_p	Φ
2	Br	+0.232	X^a
1	H	0	0.0057 ± 0.0005
3	Me	−0.170	0.0068 ± 0.0020
4	$N(Me)_2$ ²⁷	−0.205	0.016 ± 0.001
5	OMe	−0.268	0.023 ± 0.003

^aThe quantum yield is too low to be measured because prolonged irradiation caused unidentified side reactions.

the PrDA reactivity was enhanced. DA adducts of 2,6-dimethyl- (**3**), tetramethyldiamino- (**4**), and dimethoxyanthracenes (**5**) showed

Table 2. Quantum Yields of the DA Adducts Studied To Understand the Electronic Effects of the Dienophile

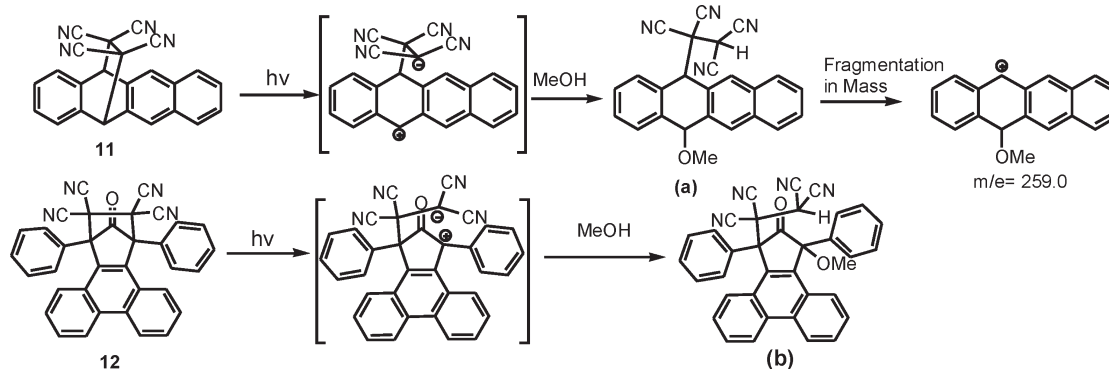
DA adducts	Φ
6	0.021 ± 0.001
1	0.0057 ± 0.0005
7	X^a
8	X^a
9	0.0094 ± 0.0002
10	0.0015 ± 0.0002

^aThe quantum yield is too low to be measured because prolonged irradiation caused unidentified side reactions.

quantum yields of 0.0068, 0.0157, and 0.023, respectively. When the substituent was Br, a weak electron withdrawing group, DA adduct **2** was photostable. The quantum yields of the DA adducts and the Hammett para-substituent constants²⁶ of the corresponding substituents are listed in Table 1. The trend of the PrDA reactivity is consistent with the trend of the Hammett substituent constants (Table 1). The low reactivity of **2** may also be due to intersystem crossing, which is enhanced by the heavy bromine atoms.

The electronic effects of the dienophile component were also studied. DA adducts of dienophiles including acrylonitrile, *N*-methyl maleimide, maleic anhydride and tetracyanoethylene (TCNE) were prepared using unsubstituted anthracene as the common diene. Among the dienophiles, TCNE, with four CN groups, has the strongest electron withdrawing ability. TCNE/anthracene adduct **6** underwent PrDA reaction quickly with a quantum yield of 0.021 (Table 2). The UV absorption change of **6** during the photoirradiation is shown in Figure 1 as an example. Maleic anhydride is less electron deficient than TCNE. As described above, maleic anhydride/anthracene adduct **1** was also photoactive. However, the quantum yield (0.0057) was significantly smaller than that of the TCNE adduct. When the electron-withdrawing ability of the dienophile was further reduced, as in *N*-methylmaleimide/anthracene adduct **7** and acrylonitrile/anthracene adduct **8**, the adducts are photostable.

The results indicate that the PrDA reactivity of a DA adduct depends on both the electron-donating ability of the diene and

Scheme 2. Trapping the Charge-Separated Intermediate in the PrDA Reactions of **11** and **12**

the electron-withdrawing ability of the dienophile. If this structure–reactivity relationship holds, DA adducts of weakly electron-withdrawing dienophiles may become photoactive when a strong electron-donating diene is used, and adducts of weakly electron-donating dienes may become photoactive when a strong electron-withdrawing dienophile is used. To test this, adducts of *N*-methylmaleimide/2,6-dimethoxyanthracene (**9**) and acrylonitrile/2,6-dimethoxyanthracene (**10**) were studied because we showed that the adducts of *N*-methylmaleimide/anthracene (**7**) and acrylonitrile/anthracene (**8**) are photostable. When the electron-rich dimethoxyanthracene was used as the diene, the DA adduct of *N*-methylmaleimide (**9**) underwent PrDA reaction with a moderate quantum yield of 0.0094. Even acrylonitrile adduct **10** is photoactive, although the quantum yield was low ($\Phi = 0.0015$).

The structure–reactivity relationship indicates that the mechanism may involve a charge separated intermediate, on which a positive charge is localized on the diene and a negative charge on the dienophile. One might think that the structure–reactivity relationship could be a result of the relative thermal stabilities of the DA adduct because the mechanism could be a nonadiabatic one. However, we found that the DA adduct of naphthacene and TCNE (**11**) has a PrDA quantum yield of 0.18, which is much higher than that of **6** (0.021), while **11** is obviously more thermally stable than **6**, which slowly decomposes at room temperature. The higher photoreactivity of **11** than **6** can be contributed to the extended aromatic structure that stabilizes the positive charge in the intermediate. In addition, the charge-separated intermediate was supported by conducting the PrDA reaction of **1** in dichloromethane. Dichloromethane is a less polar solvent than acetonitrile, and thus is expected to destabilize the charge-separated intermediate. If the path of the PrDA reaction involves the charge-separated intermediate, this shall lower the quantum yield because less charge-separated intermediates will be produced from the excited state. Indeed, the quantum yield of the reaction in dichloromethane was 0.0016, which is lower than that in acetonitrile (0.0057).

To determine the structure of the charge-separated intermediate, the adduct **11** was irradiated in a solution of 25% of methanol in acetonitrile for an extended time. Large amount of methanol was used to trap the intermediate. The product was analyzed by GC-MS. Besides the expected PrDA products, a product showed a fragment with $m/e = 259.0$, which is the mass of the cation resulting from the fragmentation of the trapped intermediate (**a** in Scheme 2). The molecular peak was not observed perhaps due to its low stability under the GC-MS conditions. More convincing evidence was obtained from the reaction of **12**, which is a DA adduct of TCNE

and phenylcyclo. Irradiation of **12** in the presence of an excess amount of methanol gave the trapped intermediate (**b** in Scheme 2) as the major product, which was isolated and analyzed by ^1H NMR.

Furthermore, oxygen quenching experiments were conducted to understand the excited states involved in the reaction. A solution of **11** saturated with air was irradiated for 5 min and was compared to a carefully degassed solution irradiated under the same conditions. The UV absorption of naphthacene, the product of the PrDA reaction, was only slightly lower than that of the degassed sample, which is due to the oxidation of naphthacene. We conclude that oxygen does not quench the PrDA reaction, and thus the reaction does not involve a triplet state. This result is consistent with the charge-separated intermediate shown in Scheme 2. The intermediate must be in a singlet state because all the electrons are paired. Therefore, it is unlikely that it is from a triplet excited state.

The excited states of **11** were further studied by femtosecond time-resolved absorption spectroscopy. The transient absorption spectra were recorded following a 266 nm excitation. Figure 2 shows the transient absorption spectra in a spectral region of 525–720 nm at a delay time of 3, 13, and 210 ps, respectively, after the excitation. The broad band spectra have an absorption maximum at ~ 610 nm with their spectral shape almost unchanged with the delay time. Figure 2 displays the corresponding kinetic decay curve probed at 580 nm. The decay process can be fit well into a biexponential decay with time constants of 8.3 ± 0.6 and 546 ± 12 ps. Previous study on the excited states in a photodecarbonylation reaction of an α -diketone, which has a structure similar to those of the DA adducts described here, showed a relaxation time of 5.4 ps for a vibrational cooling process in the S_1 state, and a lifetime of 218 ps for the S_1 state.²⁸ The criteria for vibrational cooling in the S_1 state of this kind of compound is the invariance of the transient absorption spectra with the delay time. In addition, a 12 ps time constant has also been observed in the fluorescence decay of the S_1 state of naphthacene, which was assigned to a vibrational cooling process.²⁹ Therefore, we assign the two constants, 8.3 and 546 ps, to the vibrational cooling and excited-state decay of S_1 state, respectively.

The assignment of the S_1 excited state was supported by time-resolved fluorescence spectroscopy. Although the fluorescence is very weak, we have successfully acquired the time-resolved fluorescence spectra excited at 291 nm on a streak camera. This excitation wavelength locates at the red band side of the absorption spectrum of **11**. Figure 3 shows the time-resolved fluorescence spectra at the initial time, 100 ps, and 200 ps delay after the excitation, and the kinetics of the fluorescence decay is also shown

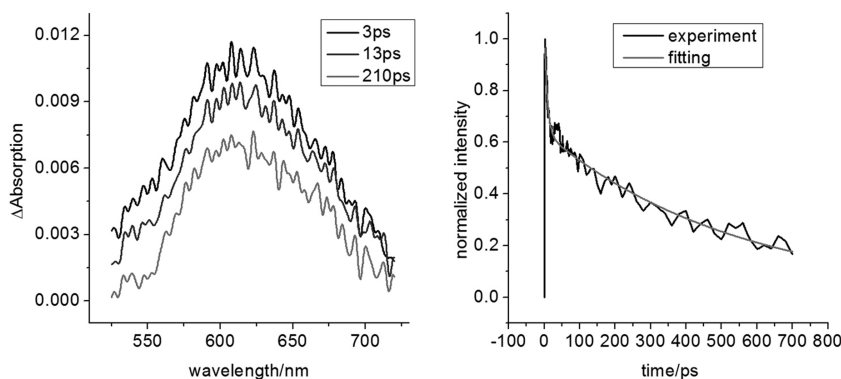


Figure 2. Absorption difference spectra obtained from the pump–probe spectrometry of **11** (left) and the biexponential decay of the absorption at 580 nm (right).

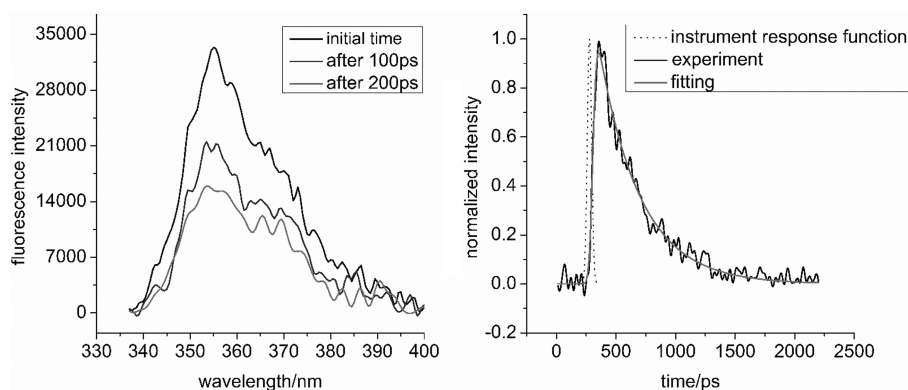
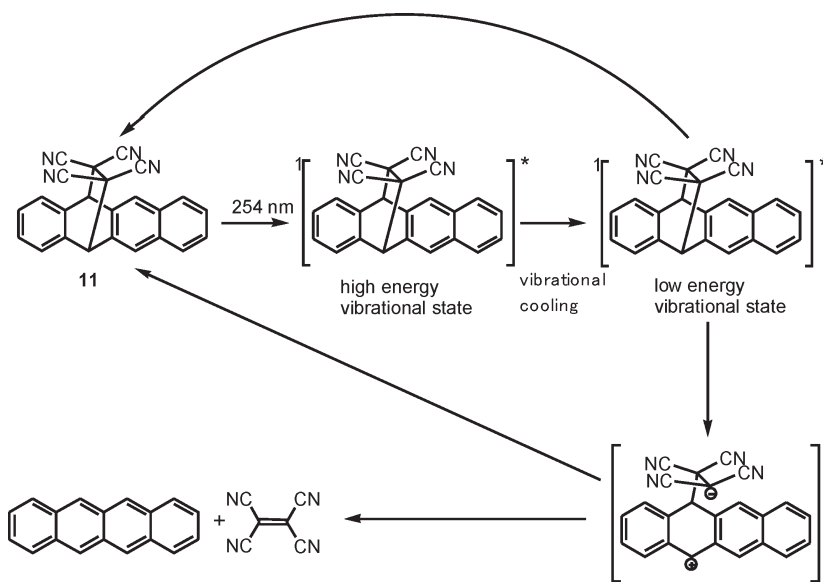


Figure 3. Time-resolved fluorescence spectra of **11** (left) and the exponential decay of the fluorescence (right).

Scheme 3. Proposed Mechanism of the PrDA Reaction of **11**



in Figure 3. Limited by the temporal resolution, the fast decay component was not observed by the streak camera, and thus the corresponding kinetics was fitted to a monoexponential decay with a time constant of 346 ± 4.3 ps. It is noteworthy that the shapes of the

time-resolved fluorescence spectra are also independent of the delay time, which is similar to the time-resolved absorption spectra. In addition, the decay-time constant is close to the value obtained from the time-resolved absorption study. (The discrepancy between the

two lifetimes may be due to the different fitting models used, i.e., biexponential and monoexponential models.) Therefore, the fluorescence study supports that the transient absorption is from the S_1 state. On the basis of all the results, we propose that the PrDA reaction follows the mechanism shown in Scheme 3.

In conclusion, we have shown that a variety of aromatic DA adducts undergo PrDA reactions. The photoactivity depends on the electron-withdrawing ability of the dienophile component and the electron-donating ability of the diene component. The mechanism was studied by trapping the reaction intermediate, O_2 quenching, time-resolved absorption and fluorescence spectroscopy. All the results support a mechanism that involves a charge-separated intermediate generated from a singlet excited state. It may be worth mentioning that we used 254 nm irradiation for all of the adducts so that their photoactivities could be compared. However, if a high reaction yield is desired, 254 nm may not be a suitable wavelength for some of the DA adducts due to the strong absorption of the products at this wavelength. For readers who are interested in a high reaction yield, a suitable wavelength must be carefully chosen so that only the reactant absorbs strongly at this wavelength, while the products do not or only weakly absorb.

EXPERIMENTAL SECTION

General Information. All starting materials for preparing the DA adducts were purchased without further purification. HPLC grade solvents were used without further purification except degassing. Acetonitrile was distilled over molecular sieve under nitrogen before being used. TCNE/anthracene (**1**),¹⁹ acrylonitrile/anthracene (**8**),²⁰ TCNE/phencyclone (**12**)³⁰ tetramethyl-2,6-diaminoanthracene,²¹ 2,6-dimethoxyanthracene,^{22,23} and 2,6-dimethylantracene²³ were synthesized following literature procedures.

Photochemical Reaction Conditions. Millimolar solutions of the adducts in acetonitrile or acetonitrile/methanol mixture were irradiated under 254 nm UV light in an inert atmosphere at room temperature. The power of the UV lamp is only 8 W, and the reaction was conducted in a ventilation hood. Under these conditions, the photo heating effect can be ignored and the “total absorption” required for measuring quantum yield with chemical actinometry can be achieved. Quantum yields were measured by chemical actinometry using uridine as the chemical actinometer.^{24,25} For each solution, the absorption at 254 nm was well above 2. Except the solution for the oxygen quenching experiment, all solutions were carefully degassed before irradiation. The reaction time was controlled so that less than 5% of starting material reacted, which lowers the error caused by the absorption of the product. The concentrations of the products were analyzed by the long-wavelength absorption of the anthracene products. Multiple measurements were conducted to obtain a reliable value. For each sample, if an approximate linear relationship is obtained from the data at different time intervals, the first data was used to calculate the quantum yield using the following equation.²⁵ (For the readers who are not familiar with the concept of the quantum yield, the quantum yield is defined as the number of the photoevents divided by the number of the photons absorbed. Unlike the reaction rate, it is independent of the absorption at the irradiation wavelength. Therefore, although the DA adducts

have different molar absorption coefficients at 254 nm, their quantum yields are comparable.)

$$\Phi = (\varepsilon^\circ t^\circ \Phi^\circ / \Delta A^\circ) (\Delta A / \varepsilon t)$$

ε° , t° , Φ° , and ΔA° are the molar absorption coefficient, irradiation time, quantum yield, and absorption change of the standard, and ε , t , Φ , and ΔA are the molar absorption coefficient, irradiation time, quantum yield, and absorption change of the PrDA product. For the TCNE adduct, the backward DA reaction also occurs at room temperature unless one of the products is stabilized or reacts with other reagents. Previous work by Brown and Cookson showed that this problem can be solved by adding a small amount of methanol, which prevents the reverse reaction by quickly reacting with TCNE and allows the analysis of the aromatic dienes.²⁰ Therefore, 5% of methanol was added to the acetonitrile solution of the TCNE adducts immediately before the photoreaction. Except in the reaction of **12**, such amount of methanol did not produce detectable amount of trapped intermediate in the experimental condition for quantum yield measurement, and thus did not significantly alter the results.

In the trapping experiment of **12**, a 1 mM solution of **12** in 1:3 methanol/MeCN was irradiated at either 254 or 365 nm under nitrogen using an 8 W UV lamp. After 6 h reaction, two major products were isolated by filtration and column chromatography. One is phencyclone, which is the product of the corresponding PrDA reaction; the other is the methanol trapped product. The ^1H NMR of the trapped product matches the previously reported data of the same structure.³⁰ [^1H NMR: 3.15 (s, 3H), 8.77 (1H, d, $J = 8.43$ Hz), 8.73 (1H, d, $J = 8.02$ Hz), 8.30 (1H, d, $J = 7.58$ Hz), 8.15 (s, 1H), 8.00 (1H, d, $J = 7.81$ Hz), 7.89 (d, 1H, $J = 7.03$ Hz), 7.68–7.58 (m, 7H), 7.53 (1H, m), 7.34–7.29 (3H, m), 7.16–7.14 (2H, m)].

Femtosecond Time-Resolved Absorption Spectroscopy. A millimolar solution of **11** was used due to its relatively high quantum yield. The spectrometer employs a regenerative amplifier Ti:sapphire femtosecond laser with 1 kHz repetition (Hurricane, Spectra Physics) as the primary beam source. The excitation pulses with a wavelength of 266 nm are generated by sum frequency of 800 nm pulses and 400 nm pulses in a type II BBO crystal. A dual beam configuration was adopted for the detection. The spectra were recorded by a charge-coupled device spectrometer (Acton). The detailed setup has been published previously.³¹

Picosecond Time-Resolved Fluorescence Spectroscopy. Picosecond time-resolved fluorescence spectra were measured using a streak camera system. The sample, filled in a revolving spinning cell, was excited by 120 fs pulses, frequency doubled from a Ti:sapphire laser oscillator (Mira 900F, Coherent). Fluorescence was collected at the magic angle polarization to the excitation light field. The time-resolved emission spectra were dispersed by a C5094 imaging spectrograph and recorded using a Hamamatsu C5680 synchroscan streak camera. The temporal observation windows applied were 2.2 ns. The instrument response functions (IRF) were 20 ps.

General Synthetic Procedures for DA Adducts of Maleic Anhydride and Substituted Anthracenes. The substituted anthracene was mixed with 1 equiv of maleic anhydride. The mixture was dissolved in just enough xylene and heated at 180 °C (bath temperature) for 45 min in a sealed tube under nitrogen. After cooling to room temperature, the tube was placed in an ice bath for 10 min. The precipitate was collected by filtration and then washed with a small amount of ethyl acetate and hexanes to

yield the crude product. Recrystallization in toluene yielded the pure product.

2,6-Dibromoanthracene/Maleic Anhydride Adduct 2. ^1H NMR (500 MHz, CDCl_3): δ/ppm = 7.55 (d, 1H, J = 1.75 Hz), 7.49 (d, 1H, J = 1.74 Hz), 7.37 (m, 2H), 7.26 (d, 1H, J = 7.64 Hz), 7.21 (d, 1H, J = 7.94), 4.78 (m, 2H), 3.53 (m, 2H). HRMS (DART): 431.8990 (M^+ , expected = 431.8997), 432.9062 ($\text{M} + \text{H}^+$, expected = 432.9075), 449.9305 ($\text{M} + \text{NH}_4^+$, expected = 449.9340).

2,6-Dimethylantracene/Maleic Anhydride Adduct 3. ^1H NMR (500 MHz, CDCl_3): δ/ppm = 7.25 (m, 1H), 7.20 (d, 1H, J = 7.41), 7.20 (m, 1H), 7.14 (m, 1H), 6.98 (m, 2H), 4.73 (m, 2H), 3.50 (m, 2H), 2.32 (s, 3H), 2.29 (s, 3H). HRMS (DART): 304.1099 (M^+ , expected = 304.1099), 305.1171 ($\text{M} + \text{H}^+$, expected = 305.1178), 322.1445 ($\text{M} + \text{NH}_4^+$, expected = 322.1443).

Tetramethyl-2,6-diaminoanthracene/Maleic Anhydride Adduct 4. ^1H NMR (500 MHz, CDCl_3): δ/ppm = 7.20 (d, 1H, J = 8.26 Hz), 7.14 (d, 1H, J = 8.27 Hz), 6.78 (d, 1H, J = 2.12 Hz), 6.67 (d, 1H, J = 2.45 Hz), 6.46 (dd, 2H, J_1 = 2.3 Hz, J_2 = 8.3 Hz), 4.62 (m, 2H), 3.49 (m, 2H), 2.92 (s, 6H), 2.90 (s, 6H). HRMS (DART): 362.1637 (M^+ , expected = 362.1630), 363.1710 ($\text{M} + \text{H}^+$, expected = 363.1709).

2,6-Dimethoxyanthracene/Maleic Anhydride Adduct 5. ^1H NMR (500 MHz, CDCl_3): δ/ppm = 7.27 (m, 1H), 7.23 (d, 1H, J = 8.24 Hz), 6.96 (d, 1H, J = 2.47 Hz), 6.89 (d, 1H, J = 2.45 Hz), 6.70 (m, 2H), 4.722 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.51 (m, 2H). HRMS (DART): 336.0991 (M^+ , expected = 336.0998), 337.1064 ($\text{M} + \text{H}^+$, expected = 337.1076), 354.1337 ($\text{M} + \text{NH}_4^+$, expected = 354.1341).

Synthesis of *N*-Methylmaleimide/Anthracene DA Adduct (7). Anthracene (500 mg, 2.81 mmol), *N*-methylmaleimide (494 mg, 4.45 mmol), and chlorobenzene (2 mL) were added to a sealed tube equipped with a magnetic stirrer. The mixture was purged with nitrogen and sealed and then allowed to reflux for 24 h at 160 °C. The reaction mixture was cooled to room temperature. The precipitate was collected by filtration and washed with methanol to yield a white solid as the product (520 mg, 70% yield). ^1H NMR (500 MHz, CDCl_3): δ/ppm = 7.37 (dd, 2H, J_1 = 8.57 Hz, J_2 = 2.12 Hz), 7.25 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.2 Hz), 7.17 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.25 Hz), 7.12 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.27 Hz), 4.78 [m (the doublets of the two protons on the respective chiral centers overlap), 2H], 3.21 [m (the doublets of the two protons on the respective chiral centers overlap), 2H], 2.50 (s, 3H). HRMS (DART): 289.1116 (M^+ , expected = 289.1103), 290.1179 ($\text{M} + \text{H}^+$, expected = 290.1181), 307.1445 ($\text{M} + \text{NH}_4^+$, Expected = 307.1147).

Synthesis of *N*-methyl maleimide/2,6-dimethoxyanthracene DA adduct (9). *N*-Methylmaleimide (213 mg, 1.9 mmol), 2,6-dimethoxyanthracene (203 mg, 0.95 mmol), and chlorobenzene (1.5 mL) were added to a sealed tube equipped with a magnetic stirrer. The mixture was purged with nitrogen, sealed, and heated to reflux for 2 h at 160 °C. The reaction mixture was cooled to room temperature. The white crystalline precipitate was collected and was added some dichloromethane. The cloudy solution (or dispersion) was filtered and the filtrate was added dropwise into methanol to yield the product as a white precipitate (290 mg, 97% yield). ^1H NMR (500 MHz, CDCl_3): δ/ppm = 7.25 (s, 1H), 7.14 (d, 1H, J = 8.12 Hz), 6.94 (d, 1H, J = 2.49 Hz), 6.82 (d, 1H, J = 2.49 Hz), 6.66 (dd, 1H, J_1 = 2.5 Hz, J_2 = 8.13 Hz), 6.62 (dd, 1H, J_1 = 8.13 Hz, J_2 = 2.5 Hz), 4.66 (m, 2H), 3.77 (s, 3H), 3.73 (s, 3H), 3.18 (m, 2H), 2.54 (s, 3H). HRMS

(DART): 349.1309 (M^+ , expected = 349.1314), 350.1381 ($\text{M} + \text{H}^+$, expected = 350.1392), 367.1652 ($\text{M} + \text{NH}_4^+$, expected = 367.1658).

Synthesis of Acrylonitrile/2,6-Dimethoxyanthracene DA Adduct (10). Acrylonitrile (5 mL, 76.32 mmol), 2,6-dimethoxyanthracene (1 g, 4.2 mmol), *m*-xylene (15 mL), and hydroquinone (50 mg, 0.45 mmol) were added to a sealed tube equipped with a magnetic stirrer. The mixture was degassed, sealed, and then heated at 175 °C for 3 days. After the reaction was cooled to room temperature, the solvent was evaporated under reduced pressure to yield a brown thick oil. About 4 mL of toluene was added to the oil and the solution was kept below 0 °C overnight to yield light brownish precipitates. The precipitate contained the product and some hydroquinone. So it was further purified by adding a small volume of methanol to form a paste, followed by adding water to the paste. The pure product was collected by filtration as a light brown solid (80 mg, 7% yield). ^1H NMR (500 MHz, CDCl_3): δ/ppm = 7.19 (dd, 2H, $3J_1$ = 5.7 Hz, J_2 = 2.47 Hz), 6.98 (d, 1H, J = 2.47 Hz), 6.85 (d, 1H, J = 2.48 Hz), 6.7 (dd, 1H, J_1 = 5.63 Hz, J_2 = 2.48 Hz), 6.64 (dd, 1H, J_1 = 5.84 Hz, J_2 = 2.49 Hz), 4.45 (d, 1H, J = 2.48 Hz), 4.28 (t, 1H, J = 2.62 Hz), 3.78 (s, 3H), 3.76 (s, 3H), 2.90 (m, 1H), 2.19 (m, 1H), 1.95 (m, 1H). HRMS (DART): 291.1256 (M^+ , expected = 291.1259), 292.1333 ($\text{M} + \text{H}^+$, expected = 292.1338), 309.1605 ($\text{M} + \text{NH}_4^+$, expected = 309.1603).

Synthesis of TCNE/Naphthacene Adduct (11). Naphthacene (150 mg, 0.69 mmol) and 10 mL of toluene were added to a round-bottom flask equipped with a magnetic stir bar. The flask was sealed and purged with Nitrogen then heated to 60 °C. Tetracyanoethylene (104 mg, 0.8 mmol) was added to 6 mL of toluene and stirred, leaving a small fraction of undissolved solid left. The liquid portion of this solution was extracted and injected dropwise into the hot naphthacene solution. The resulting mixture was maintained at 60 °C with stirring for 30 min, then cooled to 0 °C, and vacuum filtered to obtain a white solid. (108 mg, 44% yield) ^1H NMR (CDCl_3 , 500 MHz): δ/ppm = 8.05 (s, 2H), 7.91 (q, 2H, J = 3.31, 6.18), 7.63 (m, 4H), 7.49 (q, 2H, J = 3.25, 5.46), 5.17 (s, 2H). HRMS (DART): 374.1404 ($\text{M} + \text{NH}_4^+$, expected = 374.1406).

■ ASSOCIATED CONTENT

Supporting Information. UV–vis spectra and molar absorption coefficients of the DA adducts and the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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