Photoinduced three-component coupling reactions of electron deficient alkenes, dienes and active methylene compounds

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Photoinduced three-component coupling reactions of electron deficient alkenes, dienes and active methylene compounds

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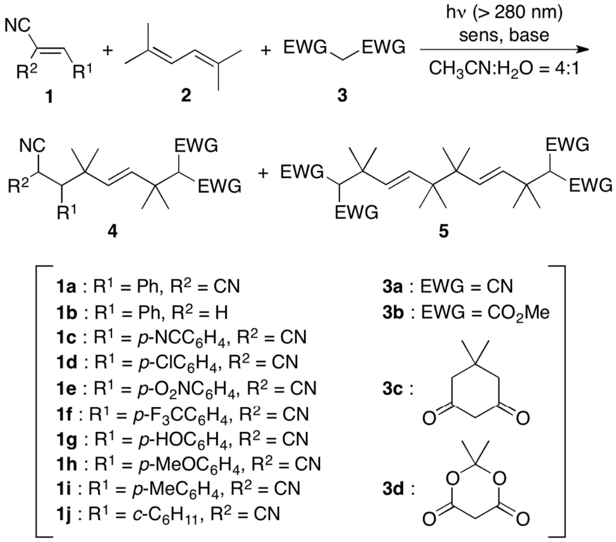
Irradiation of aqueous acetonitrile solutions, containing electron deficient alkenes, dienes and active methylene compounds along with sodium or cesium carbonate and catalytic amounts of phenanthrene or pyrene, gives rise to formation of novel three-component coupling products and diene dimers. Cinnamonitrile, and benzylidenemalononitrile and its derivatives serve as electron-acceptors, 2,5-dimethyl-2,4-hexadiene and malononitrile anion serve as electron donors in this process. Based on the results of UV-vis absorption spectroscopy and calculated ΔG values for single electron transfer (SET), a mechanism is proposed for the coupling reaction involving photoinduced electron transfer (PET) between the electron deficient alkenes and dienes or malononitrile anion via direct excitation of electron deficient alkenes or redox photosensitization using phenanthrene or pyrene serving as a photosensitizer.

Introduction

Coupling reactions, promoted by photoinduced electron transfer (PET) between electron donors and acceptors, have been extensively studied from both synthetic and mechanistic viewpoints.[1,2] Representative examples of these processes include photoaddition reactions in which alcohols,[3-23] amines[24-35] and cyanide anion[36-48] add to radical cations derived from alkenes, cycloalkanes and arenes. In addition, coupling reactions of nucleophile/olefin/arene systems, termed photo-NOCAS reactions, are familiar examples of three component versions of these PET induced processes.[49-56]

In recent studies we developed PET promoted photoallylation reactions of electron deficient alkenes by using allylsilanes as electron donors.[57-61] In addition, we demonstrated that anions generated from active methylene compounds can be used to trap alkene and diene radical cations[62,63] and that this process can be used as the foundation for the design of photochemical three component coupling reaction between cyanoarenes, dienes and active methylene compounds.[64,65] In the investigation described below, we developed a novel PET induced three component coupling reaction of electron deficient alkenes, dienes and active methylene compounds that generates highly substituted and functionalized alkenes.

Results and discussion



Scheme 1. PET-promoted three component coupling reactions of **1-3**.

Photoirradiation of an aqueous CH_3CN solution ($CH_3CN:H_2O$ = 4:1) containing benzylidenemalononitrile **1a** (R^1 = Ph, R^2 = CN), 2,5-dimethyl-2,4-hexadiene **2**, malononitrile **3a** (EWG = CN), a catalytic amount of phenanthrene and an excess of Na_2CO_3 using a 450 W high pressure mercury lamp for 20 h leads to the formation of the novel three component coupling product **4a** and the diene dimer **5a** (Scheme 1).

To explore this process further, the effects of molar ratios of substrates, photosensitizers, bases and irradiation times on the three component coupling reaction were investigated with yields of **4** and **5** determined based on **2** used (Table 1, full entries are shown in Table S1). The effects of the molar ratios of substrates **1a**, **2** and **3a** were determined in entries 1-4. The

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Table 1. PET-promoted three component coupling reaction of **1**-**3**.[a]

entry	1	3	molar ratio of **1**:**2**:**3**	sens[b]	base	time (h)	yields[c] (%)	
							4	**5**
1	**1a**	**3a**	1:1:20	phenanthrene	Na_2CO_3	20	28	15
2	**1a**	**3a**	2:1:20	phenanthrene	Na_2CO_3	20	30	14
3	**1a**	**3a**	5:1:20	phenanthrene	Na_2CO_3	20	28	25
4	**1a**	**3a**	2:1:5	phenanthrene	Na_2CO_3	20	13	6
5	**1a**	**3a**	2:1:20	phenanthrene	Na_2CO_3	40	42	18
6	**1a**	**3a**	2:1:20	pyrene	Na_2CO_3	40	58	18
7	**1a**	**3a**	2:1:20	anthracene	Na_2CO_3	20	28	5
8	**1a**	**3a**	2:1:20	naphthalene	Na_2CO_3	20	23	17
9	**1a**	**3a**	2:1:20	none	Na_2CO_3	20	29	11
10	**1a**	**3a**	2:1:20	phenanthrene	K_2CO_3	20	14	10
11	**1a**	**3a**	2:1:20	phenanthrene	Cs_2CO_3	20	43	18
12	**1a**	**3a**	2:1:20	phenanthrene	NaOH	20	23	11
13	**1a**	**3a**	2:1:20	pyrene	Cs_2CO_3	40	53	18
14	**1b**	**3a**	2:1:20	pyrene	Na_2CO_3	20	39	42
15	**1c**	**3a**	2:1:20	phenanthrene	Na_2CO_3	20	46	16
16	**1d**	**3a**	2:1:20	none	Na_2CO_3	20	27	28
17	**1e**	**3a**	2:1:20	pyrene	Na_2CO_3	20	0	0
18	**1f**	**3a**	2:1:20	none	Na_2CO_3	20	28	19
19	**1g**	**3a**	2:1:20	phenanthrene	Na_2CO_3	20	20	6
20	**1h**	**3a**	2:1:20	phenanthrene	Na_2CO_3	20	34	16
21	**1i**	**3a**	2:1:20	none	Na_2CO_3	20	21	8
22	**1j**	**3a**	2:1:20	phenanthrene	Na_2CO_3	20	5	33
23	**1a**	**3b**	2:1:20	phenanthrene	Na_2CO_3	20	0	0
24	**1a**	**3c**	2:1:20	phenanthrene	Na_2CO_3	20	0	15
25	**1a**	**3d**	2:1:20	phenanthrene	Na_2CO_3	20	0	28

[a] **1** (1-5 mmol), **2** (1 mmol), **3** (5-20 mmol), sens (0.25 mmol), base (10 mmol), CH_3CN (10 mL), H_2O (2.5 mL), Pyrex vessel, 450 W high pressure mercury lamp, rt. [b] sens = photosensitizer. [c] Determined by using ^1H NMR analysis, based on **2** used.

results show that when the molar ratio of **1**:**2**:**3** is 2:1:20, **4a** is generated in a maximum 30% yield. Observations made in additional optimization studies show that the yield of **4a** reaches a maximum value of 42% when the solution is irradiated for 40 h (entry 5) and that the yield decreases upon prolonged irradiation. Moreover, when pyrene is used as a photosensitizer instead of phenanthrene (entry 6), the yield of **4a** increases to 58% using a 40 h irradiation period, but when anthracene and naphthalene are used as photosensitizers photoreactions occur in only moderate yields (entries 7, 8). It is known that photocycloaddition reaction of arenes with alkenes gives various photocycloadducts,[66-68] however, formation of such products as well as other side-products and unidentified polymers are not observed. Unexpectedly, the photoreaction proceeds in the absence of photosensitizer (entry 9), giving **4a** in 29% yield using a 20 h irradiation period. The effect of the nature of the base on the efficiency of the process was explored (entries 2, 10-12). Among photoreactions using Na_2CO_3, K_2CO_3, Cs_2CO_3, NaOH and *t*-BuOK as bases, the most highly efficient was the one employing Cs_2CO_3. Finally, experiments using Cs_2CO_3 as the base and exploring the effect of photosensitizer and irradiation time demonstrated that a maximum yield of **4a** of 53% is obtained using pyrene as a photosensitizer and a 40 h irradiation time (entry 13).

The effect of substituents on electron deficient alkenes on the efficiency of the process was probed using either phenanthrene or pyrene as the photosensitizer, or in the absence of a photosensitizer (entries 14-22, full data is given in Table S1). The results show that cinnamonitrile (**1b**) and benzylidenemalononitriles **1c-d,f-i** containing cyano, chloro, trifluoromethyl, hydroxy, methoxy and methyl as *p*-phenyl substituents react to generate the corresponding adducts **4b-d,f-i** and **5a**, however, the best conditions (phenanthrene, pyrene, or no photosensitizer) for production of **4** and **5** are different depending on the each of substrates. On the other hand, the *p*-nitro derivative **1e** does not react to form either **4e** or **5a** (entry 17). Finally, the alkyl substituted acrylonitrile derivative **1j** reacts to form **5a** along with only a minor amount of **4j** (entry 22).

An investigation exploring reactions using other active methylene compounds (entries 23-25) show that the photoreaction using dimethyl malonate **3b** gives neither **4b** nor **5b**, and that photoreactions by using dimedone **3c** or Meldrum's acid **3d** do not produce **4c-d** but do generate dimers **5c-d**. Because the pK_a values of the active methylene compounds are 11.0 for **3a**, 15.9 for **3b**, 11.2 for **3c**, and 7.3 for **3d** in DMSO,[69,70] the findings suggest that, a pK_a value of the active methylene compound of around 11 is optimal for this process. In addition, steric effects arising from substituents on the active methylene compounds might also govern the efficiencies of this process.

To gain insight into the detailed mechanism of this three component process, UV-vis absorption spectra of the electron deficient alkenes **1a-j** and photosensitizers (1.0×10^{-4} M CH_3CN) were recorded (Figure 1). Because 8-fold molar excesses of the alkenes **1a-j** over the photosensitizer are used in these photoreactions, the alkenes absorb a portion of the light under the irradiation conditions (>280 nm). In addition, because adduct **4a** has a weak absorption band at 280-320 nm, it can also absorb light under the irradiation conditions. In fact,

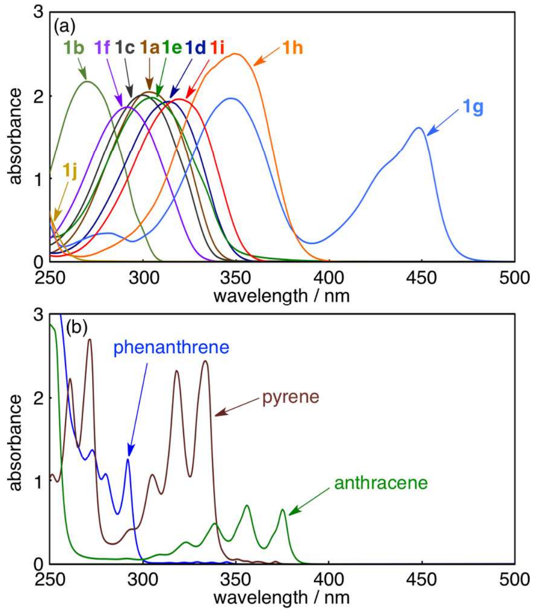


Figure 1. UV-vis absorption spectra of (a) **1a-j** and (b) photosensitizers, [**1a-j**] = [sens] = 1.0×10^{-4} M in CH_3CN, optical path = 1 cm.

exposure of **4a** to the photoreaction conditions in the presence of a base for 20 h results in its partial decomposition.

In the photosensitized reactions, single electron transfer (SET) from singlet excited state of the photosensitizer (^{1}sens*) to the ground state of the alkene **1** is likely a key step. Fluorescence quenching experiments were carried out to demonstrate the feasibility of these SET processes. Fluorescence of pyrene and phenanthrene in CH_3CN was efficiently quenched by adding **1a-j**, however, Stern-Volmer analysis was difficult because absorption bands of sens and **1a-j** are overlapped. Evidence for SET from excited singlet state of photosensitizers to the ground state of **1a** comes from a consideration of free energy changes (ΔGs) for SET estimated by using the Rehm-Weller equation,[71] $\Delta G = 96.48(E^{ox}(D/D^+)-E^{red}(A^-/A)-e^2/\varepsilon r)-E_{0\text{-}0}$; $e^2/\varepsilon r = 0.056$, where the oxidation potentials of the additives (E^{ox}), reduction potentials of **1** (E^{red}) and singlet excitation energy of the photosensitizers ($E_{0\text{-}0}$) are given in Table 2. The ΔG values are negative, indicating that SET takes place exergonically. Another key step in the mechanistic pathway, involving SET from diene **2** to the radical cation of the photosensitizer (sens$^{\bullet+}$), should also take place exergonically when phenanthrene is used because the oxidation potential of **2** is sufficiently low (E^{ox} = 0.86 V vs Ag/Ag$^+$ [74]). In the absence of photosensitizer, direct excitation of alkene **1** followed by SET from diene **2** to the resulting excited singlet state of **1** (^{1}**1***) can occur. A rough estimate suggests that the ΔG value for the SET process should be negative but it is difficult to determine the exact ΔG value because the alkenes **1** are non-fluorescent[75] and, hence, their $E_{0\text{-}0}$ values cannot be readily obtained experimentally.

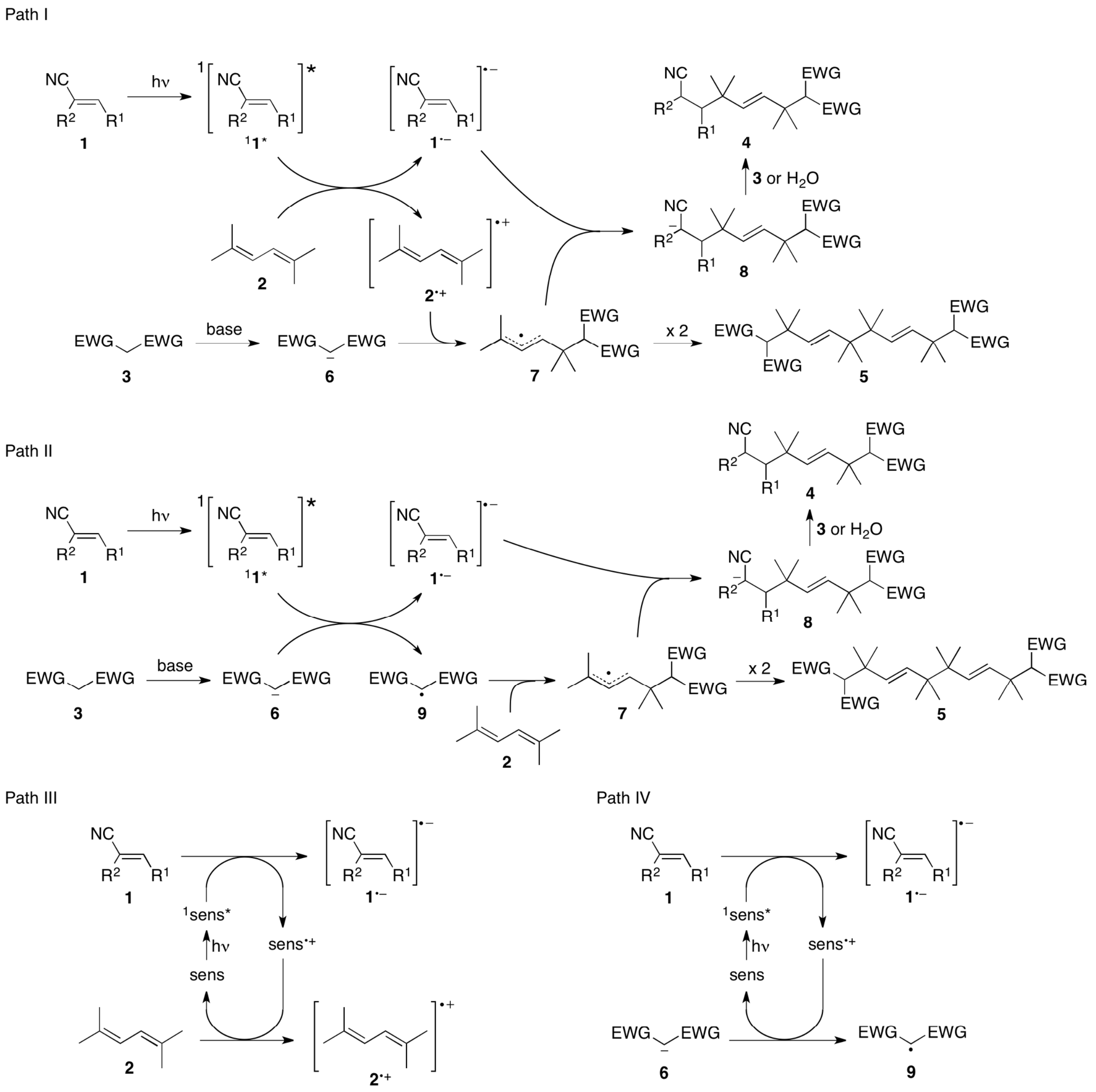
The observations described above suggest that the possible mechanisms for the three component coupling reactions shown in Scheme 2 are plausible. In one route, Path I in Scheme 2, **1** directly absorbs light and SET from **2** to ^{1}**1*** occurs to give radical anion **1**$^{\bullet-}$ and radical cation **2**$^{\bullet+}$. The anion **6**, generated by deprotonation reaction of the active methylene compound **3** with the base, nucleophilically adds to **2**$^{\bullet+}$ to give radical **7**. The resulting radical **7** couples with **1**$^{\bullet-}$ to give anion **8**, which is then protonated with **3** or H_2O to give the three component coupling product **4**. The formation of diene dimer **5** strongly suggests the intermediacy of radical **7**. An alternative mechanism is shown in Path II in Scheme 2. In this route, SET from the anion **6** to ^{1}**1*** occurs to produce **1**$^{\bullet-}$ and radical **9**, which couples with **2** to form radical **7**. Although this pathway is also energetically favorable, the fact that the concentration of **6** is much lower than that of **2** suggests that path I is kinetically preferred.[64] The sensitized mechanism for the photoreaction taking place in the presence of photosensitizer is shown in Paths III and IV. In these processes, SET from excited singlet state of ^{1}sens* to **1** occurs to give sens$^{\bullet+}$ and **1**$^{\bullet-}$. This is followed by a second SET from **2** or **6** to sens$^{\bullet+}$ giving **2**$^{\bullet+}$ or **9** and neutral sens. Thus, if an electron is injected to **1** from **6** (Paths II and IV), the resulting **1**$^{\bullet-}$ react with **7** and reproduces **6** which is an electron source like a chain mechanism. In that sense, this reaction may be regarded as an electron-catalyzed reaction.[76]

In the photoreactions of **1b** and **1j** whose absorption bands appear at only shorter wavelengths regions (Figure 1(a)), the

Table 2. Free energy change (ΔG) for photoinduced single electron transfer from excited singlet state of photosensitizers (^{1}sens*) to electron deficient alkenes (**1**).

Entry	sens	$E_{0\text{-}0}$ of sens[a] (kJ/mol)	$E_{1/2}^{ox}$ of sens[b] (V)	**1**	$E_{1/2}^{red}$ of **1**[c] (V)	ΔG[d] (kJ/mol)
1	phenanthrene	346.9	1.17	**1a**	–1.45	–99.5
2	phenanthrene	346.9	1.17	**1c**	–1.13	–130.4
3	phenanthrene	346.9	1.17	**1d**	–1.37	–107.2
4	phenanthrene	346.9	1.17	**1h**	–1.59	–86.0
5	phenanthrene	346.9	1.17	**1i**	–1.51	–93.7
6	pyrene	322.2	0.78	**1a**	–1.45	–112.5
7	pyrene	322.2	0.78	**1c**	–1.13	–143.3
8	pyrene	322.2	0.78	**1d**	–1.37	–120.2
9	pyrene	322.2	0.78	**1h**	–1.59	–98.9
10	pyrene	322.2	0.78	**1i**	–1.51	–106.7

[a] Singlet excitation energy.[72] [b] Oxidation potential vs Ag/Ag$^+$ in CH_3CN.[73] [c] Reduction potential vs Ag/Ag$^+$ in CH_3CN.[73] [d] Free energy change estimated by Rehm-Weller equation, $\Delta G = 96.48(E^{ox}(D/D^+)-E^{red}(A^-/A)-e^2/\varepsilon r)-E_{0\text{-}0}$; $e^2/\varepsilon r = 0.056$ [71] for single electron transfer from excited singlet of photosensitizer, ^{1}sens* to ground state of **1**.



Scheme 2. Proposed mechanisms for the three component coupling reaction.

yields of products are higher when photosensitizers are present than the reactions in the absence of photosensitizers. This fact means that the hydrocarbons act as photosensitizers as the routes of Paths III and IV in the reactions of **1b** and **1j**. On the other hand, since absorption bands of **1c-i** shift to longer wavelengths regions, 8-fold molar excesses of **1c-i** over the photosensitizers absorb the light under the reaction conditions. Consequently, the mechanism for direct excitation of **1c-i** (Paths I and II) preferentially involves rather than the photosensitized mechanism (Paths III and IV). It is still unclear why higher product yields for reactants **1c,g,h** are obtained in the presence of phenanthrene, and why those for **1d,f,i** are given without any sensitizer, even after taking into consideration of electron-donating and -accepting substituents. In the presence of pyrene, higher yields are obtained from **1a,b,j**, but low or negligible yields are observed from **1c,d,f-i**. In the case of pyrene acting as a photosensitizer, the oxidation potential of pyrene (E^{ox} = 0.78 V vs Ag/Ag^{+} [73]) is lower than that of **2** (E^{ox} = 0.86 V vs Ag/Ag^{+} [74]), indicating that hole transfer from cation radical of pyrene (pyrene$^{\bullet+}$) to **2** is an unfavorable process. When presence of pyrene accelerates the photoreaction, pyrene may contribute higher harvesting ability of light, and formation of radical cation complex with **2** ([pyrene ••• **2**]$^{\bullet+}$) to overcome this unfavorable hole transfer. Finally, in photoreactions of **1e**, usual workup of photolysates does not give any product nor recovery of substrate, probably due to some side reactions involving the nitro group.[77,78]

Conclusions

In this effort, a new, PET promoted three component coupling reaction of electron-deficient alkenes, dienes and active methylene compounds was developed. In this process, cinnamonitrile, and benzylidenemalononitrile and its derivatives serve as electron acceptors, 2,5-dimethyl-2,4-hexadiene and malononitrile anion serve as electron donors, Na_2CO_3 or Cs_2CO_3 is used as a suitable base, and phenanthrene or pyrene acts as the photosensitizer. UV-vis absorption spectroscopic data and the results of calculated ΔG values combine to suggest that the three component coupling reaction proceeds by PET from diene or malononitrile anion to the electron-deficient alkenes in the absence or presence of photosensitizers as the major pathway.

Experimental

Materials and equipment

CH_3CN, *i*-PrOH and EtOH were distilled from CaH_2. Electron-deficient alkenes **1a,c-e,g-i**,[79] **1f**[80] and **1j**[81] were prepared using literature procedures. Cinnamonitrile (**1b**), 2,5-dimethyl-2,4-hexadiene (**2**), active methylene compounds (**3a-d**) and other chemicals were purchased and used after purification by distillation or recrystallization. Melting points were determined on a Yanagimoto Micro Melting Point apparatus, Yanaco MP-500. ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JMN FX-270 (270 MHz and 68 MHz, respectively) or a JEOL JMN LA-400 (400 MHz and 100 MHz, respectively) spectrometer with Me_4Si as an internal standard. IR spectra were determined using a Shimadzu FTIR-8300 spectrometer. UV absorption spectra were recorded using a Hitachi U-2900 spectrophotometer. Fluorescence spectra were recorded using a Hitachi F-2500 spectrofluorometer. Low- and high-resolution mass spectra were recorded on a JEOL JMS-AM50 and a JEOL JMS-SM102A instruments, respectively. HPLC separations were performed on recycling preparative HPLC instruments, Japan Analytical Industry Co. Ltd., LC-918 equipped with a JAIGEL SIL S-043-15 column (silica gel, normal phase, eluent: hexane:AcOEt = 3:1) or Japan Analytical Industry Co. Ltd., LC-908 equipped with a JAIGEL-H (GPC, eluent: $CHCl_3$) column. Column chromatography was conducted by using Kanto-Chemical Co. Ltd., silica gel 60 N (spherical, neutral, 0.04–0.05 mm). Thin-layer chromatography was done with Merck Kiesel gel 60 F_{254} plate, and spots were detected by using UV light and phosphomolybdic acid ethanol solution with heating.

Photoreactions

As a representative example, the procedure for reaction listed as entry 11 in Table 1 is shown below. A CH_3CN (10 mL) and H_2O (2.5 mL) solution containing benzylidenemalononitrile (**1a**, 311 mg, 2 mmol), 2,5-dimethyl-2,4-hexadiene (**2**, 109 mg, 1 mmol), malononitrile (**3a**, 1.327 g, 20 mmol), pyrene (54 mg, 0.25 mmol) and Na_2CO_3 (1.052 g, 10 mmol) in a cylindrical Pyrex vessel (ϕ = 12 mm) was degassed by argon bubbling for 10 min and then the vessel was sealed. The solution was irradiated by using a 450 W high-pressure mercury lamp (Ushio, UM-452) at rt for 40 h, maintained by using circulated cooling water. The solution was neutralized by adding 1 N HCl. The aqueous layer was washed with Et_2O (10 mL × 2). The combined organic layers were washed with H_2O (1 mL) and brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. ^{1}H NMR analysis of the crude mixture by using trioxane as an internal standard indicated the presence of (*E*)-2,2,5,5-tetramethyl-6-phenylhept-3-ene-1,1,7,7-tetracarbonitrile (**4a**, 189 mg, 0.57 mmol, 58% yield) and (3*E*,7*E*)-2,2,5,5,6,6,9,9-octamethyldeca-3,7-diene-1,1,10,10-tetracarbonitrile (**5a**, 31 mg, 0.088 mmol, 18% yield) based on diene **2**. Products **4a** and **5a** could be isolated by using silica gel column chromatography (hexane:AcOEt = 2:1–1:5) and/or HPLC. Determination of recovery yields of substrates **1-3** from photolysates was difficult, because ^{1}H NMR analysis of crude reaction mixture has no clear resonance ascribable to substrates **1-3**.

(*E*)-2,2,5,5-Tetramethyl-6-phenylhept-3-ene-1,1,7,7-tetracarbonitrile (4a)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (s, 3H), 1.18 (s, 3H), 1.42 (s, 6H), 3.13 (d, *J* = 6.3 Hz, 1H), 3.62 (s, 1H), 4.21 (d, *J* = 6.1 Hz, 1H), 5.59 (d, *J* = 15.9 Hz, 1H), 5.85 (d, *J* = 15.9 Hz, 1H), 7.33-7.37 (m, 2H), 7.39-7.43 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), δ 24.1, 24.4, 24.6, 25.4, 28.0, 35.1, 39.9, 40.3, 55.7, 111.75, 111.78, 112.9, 113.0, 128.8, 128.9, 129.3, 132.0, 135.0, 137.8 ppm; IR (neat) 714, 988, 1169, 1373, 1709, 2253, 2909, 2974, 3031 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 110 (99), 175 (100), 265 (6), 330 (M^+, 5); HRMS (EI) calcd for $C_{21}H_{22}N_4$: 330.1844, found: 330.1835.

(*E*)-2,2,5,5-Tetramethyl-6-phenylhept-3-ene-1,1,7-tricarbonitrile (4b)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.04 (s, 3H), 1.36 (s, 3H), 1.37 (s, 3H), 2.68 (dd, *J* = 16.8, 10.0 Hz, 1H), 2.75 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.94 (dd, *J* = 9.9, 5.5 Hz, 1H), 3.55 (s, 1H), 5.41 (d, *J* = 16.1 Hz, 1H), 5.69 (d, *J* = 15.9 Hz, 1H), 7.13-7.17 (m, 2H), 7.28-7.37 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 23.7, 24.8, 25.0, 26.5, 35.3, 39.5, 40.1, 52.1, 111.75, 111.79, 119.4, 127.6, 128.2, 129.0, 130.4, 138.2, 139.3 ppm; IR (neat) 706, 737, 1169, 1470, 1659, 2249, 2905, 3032 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 110 (99), 175 (100), 305 (M^+, 8); HRMS (EI) calcd for $C_{20}H_{23}N_3$: 305.1892, found: 305.1896.

(*E*)-6-(4-Cyanophenyl)-2,2,5,5-tetramethylhept-3-ene-1,1,7,7-tetracarbonitrile (4c)

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 3H), 1.19 (s, 3H), 1.417 (s, 3H), 1.424 (s, 3H), 3.20 (d, *J* = 5.9 Hz, 1H), 3.65 (s, 1H), 4.28 (d, *J* = 6.1 Hz, 1H), 5.63 (d, *J* = 15.9 Hz, 1H), 5.81 (d, *J* = 15.9 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), δ 24.0, 24.4, 24.8, 25.0, 28.2, 35.1, 40.1, 40.5, 55.6, 111.66, 111.70, 112.2, 112.4, 113.2, 117.9, 130.2, 132.6, 132.9, 137.0, 140.1 ppm; IR (neat) 1469, 1504, 1609, 1709, 2230, 2909, 2974 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 110 (100), 175 (62), 354 (M$^+$, 9); HRMS (EI) calcd for $C_{22}H_{21}N_5$: 355.1797, found: 355.1805.

(*E*)-6-(4-Chlorophenyl)-2,2,5,5-tetramethylhept-3-ene-1,1,7,7-tetracarbonitrile (4d)

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.14 (s, 3H), 1.16 (s, 3H), 1.41 (s, 6H), 3.12 (d, *J* = 5.9 Hz, 1H), 3.64 (s, 1H), 4.22 (d, *J* = 5.9 Hz, 1H), 5.60 (d, *J* = 15.9 Hz, 1H), 5.82 (d, *J* = 15.9 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$), δ 24.0, 24.4, 24.7, 25.3, 28.1, 35.1, 40.0, 40.4, 55.2, 111.68, 111.72, 112.6, 112.7, 129.1, 130.6, 132.4, 133.4, 135.1, 137.5 ppm; IR (neat) 1169, 1470, 1493, 1597, 2253, 2912, 2974 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 110 (100), 175 (85), 364 (M$^+$, 0.3); HRMS (EI) calcd for $C_{21}H_{21}ClN_4$: 364.1455, found: 364.1473.

(*E*)-2,2,5,5-Tetramethyl-6-(4-(trifluoromethyl)phenyl)hept-3-ene-1,1,7,7-tetracarbonitrile (4f)

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.16 (s, 3H), 1.18 (s, 3H), 1.412 (s, 3H), 1.417 (s, 3H), 2.17 (s, 1H), 3.21 (d, *J* = 5.9 Hz, 1H), 3.65 (s, 1H), 4.28 (d, *J* = 5.9 Hz, 1H), 5.62 (d, *J* = 16.1 Hz, 1H), 5.83 (d, *J* = 15.9 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$), δ 24.0, 24.4, 24.7, 25.2, 28.1, 35.1, 40.0, 40.4, 55.4, 111.70, 111.75, 112.4, 112.6, 123.7 ($^1J_{C\text{-}F}$ = 272.6 Hz), 125.9, 129.8, 131.2 ($^2J_{C\text{-}F}$ = 33.0 Hz), 132.7, 137.3, 138.9 ppm; HRMS (EI) calcd for $C_{22}H_{21}F_3N_4$: 398.1718, found: 398.1733.

(*E*)-6-(4-Hydroxyphenyl)-2,2,5,5-tetramethylhept-3-ene-1,1,7,7-tetracarbonitrile (4g)

Isolation of pure product was failed.

(*E*)-6-(4-Methoxyphenyl)-2,2,5,5-tetramethylhept-3-ene-1,1,7,7-tetracarbonitrile (4h)

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.16 (s, 3H), 1.18 (s, 3H), 1.44 (s, 6H), 3.11 (d, *J* = 6.1 Hz, 1H), 3.66 (s, 1H), 3.86 (s, 3H), 4.22 (d, *J* = 6.1 Hz, 1H), 5.61 (d, *J* = 16.1 Hz, 1H), 5.87 (d, *J* = 16.1 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$), δ 24.1, 24.4, 24.6, 25.6, 28.0, 35.1, 40.1, 40.3, 55.1, 55.2, 111.74, 111.77, 112.95, 113.0, 114.1, 126.8, 130.5, 131.9, 137.9, 159.8 ppm; IR (neat) 1516, 1612, 1732, 2253, 2839, 2909, 2974 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 138 (100), 189 (79), 360 (M$^+$, 1); HRMS (EI) calcd for $C_{22}H_{24}N_4O$: 360.1950, found: 360.1961.

(*E*)-2,2,5,5-Tetramethyl-6-(p-tolyl)hept-3-ene-1,1,7,7-tetracarbonitrile (4i)

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.13 (s, 3H), 1.16 (s, 3H), 1.41 (s, 6H), 2.37 (s, 3H), 3.09 (d, *J* = 6.3 Hz, 1H), 3.63 (s, 1H), 4.19 (d, *J* = 6.3 Hz, 1H), 5.58 (d, *J* = 15.9 Hz, 1H), 5.84 (d, *J* = 15.9 Hz, 1H), 7.19-7.25 (m, 4H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.0, 24.1, 24.4, 24.6, 25.5, 28.1, 35.1, 40.0, 40.3, 55.5, 111.72, 111.74, 112.9, 113.0, 129.2, 129.5, 131.88, 131.92, 137.9, 138.8 ppm; IR (neat) 1396, 1470, 1516, 2253, 2909, 2974 cm^{-1}; MS (EI) *m/z* (relative intensity, %) 95 (96), 109 (100), 175 (87), 344 (M$^+$, 6); HRMS (EI) calcd for $C_{22}H_{24}N_4$: 344.2001, found: 344.2001.

(3*E*,7*E*)-2,2,5,5,6,6,9,9-Octamethyldeca-3,7-diene-1,1,10,10-tetracarbonitrile (5a)

Spectral and analytical data of this product have already been reported.[62]

2,2'-((3*E*,7*E*)-2,5,5,6,6,9-Hexamethyldeca-3,7-diene-2,9-diyl)bis(5,5-dimethylcyclohexane-1,3-dione) (5c)

Colorless powder; mp 150-158 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.84 (s, 6H), 0.95 (s, 12H), 1.09 (s, 6H), 1.15 (s, 12H), 2.39 (d, *J* = 14.2 Hz, 4H), 2.54 (d, *J* = 13.7 Hz, 4H), 2.95 (s, 2H), 5.30 (d, *J* = 16.2 Hz, 2H), 5.47 (d, *J* = 16.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 23.2, 27.3, 27.5, 30.2, 30.5, 39.9, 40.8, 54.8, 75.4, 133.4, 136.4, 207.3 ppm; IR (neat) 1697, 2870, 2970 cm^{-1}; MS (FAB+) *m/z* (relative intensity, %) 55 (100), 136 (40), 249 (85), 499 (M$^+$, 2); HRMS (FAB+) calcd for $C_{32}H_{51}O_4$: 499.3787, found: 499.3792.

5,5'-((3*E*,7*E*)-2,5,5,6,6,9-Hexamethyldeca-3,7-diene-2,9-diyl)bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (5d)

Colorless powder; mp 140-143 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.93 (s, 12H), 1.32 (s, 12H), 1.70 (s, 6H), 1.73 (s, 6H), 3.26 (s, 2H), 5.41 (d, *J* = 16.1 Hz, 2H), 5.55 (d, *J* = 16.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 22.8, 26.7, 27.9, 29.1, 40.7, 40.8, 57.1, 104.8, 132.3, 136.4, 164.6 ppm; IR (neat) 1200, 1277, 1389, 1466, 1747, 1774, 2874, 2974 cm^{-1}; MS (FAB+) *m/z* (relative intensity, %) 119 (84), 137 (77), 154 (100), 195 (41), 507 (M$^+$, 2); HRMS (FAB+) calcd for $C_{28}H_{43}O_8$: 507.2958, found: 507.2954.

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For Graphical Abstract

Photoinduced three-component coupling reactions of electron deficient alkenes, dienes and active methylene compounds
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In this effort, we developed a novel three component coupling reactions of electron deficient alkenes, dienes and active methylene compounds via photoinduced electron transfer.