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A novel photoreaction of 1,2-diarylcyclopropanes with 9-cyanophenanthrene: the formation of (3+2) photocycloadducts

Hajime Maeda, Yasuo Miyata and Kazuhiko Mizuno*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

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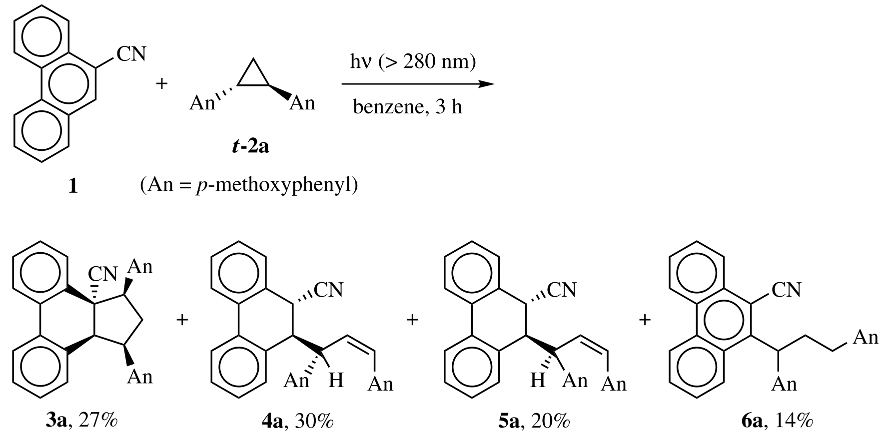
Abstract—Photoirradiation of a benzene solution containing 9-cyanophenanthrene (**1**) and *trans*-1,2-dianisylcyclopropane (***t*-2a**) by a high pressure mercury lamp through Pyrex filter gave (3+2) photocycloadduct **3a** and ring-opened photoadducts **4a**–**6a**. © 2002 Elsevier Science Ltd. All rights reserved.

Construction of five-membered ring compounds is important and fundamental architecture in organic syntheses. (3+2) Annulation/cycloaddition reactions of cyclopropane derivatives with alkenes are one of the strategies used to synthesize various cyclopentane rings, which have been developed by virtue of a variety of thermal reactions.[1] Photochemistry often provides clean and facile methodology to synthesis of organic molecules, however, so far a very limited number of literatures have described the (3+2) photocycloaddition of cyclopropanes to alkenes: photoreaction of methylenecyclopropanes with TCNE by the irradiation of their CT band,[2] photoreaction of triarylcyclopropanes with vinyl ethers via photoinduced electron transfer,[3] photocycloaddition of vinylidenecyclopropanes with electron-deficient alkenes,[4] and other miscellaneous reactions.[5,6] To the best of our knowledge, (3+2) photocycloaddition of cyclopropanes to aromatic rings has not been reported yet. We found that 1,2-diarylcyclopropanes having electron-donating substituents react with 9-cyanophenanthrene under photoirradiation to give an unprecedented (3+2) photocycloadduct onto aromatic ring.

Photoirradiation of a benzene solution containing 9-cyanophenanthrene (**1**) and *trans*-1,2-dianisylcyclopropane (***t*-2a**) by a high pressure mercury lamp through Pyrex filter for 3 h gave a (3+2) photocycload-



Scheme 1.

Keywords: (3+2) photocycloaddition; 9-cyanophenanthrene; 1,2-diarylcyclopropane; exciplex; 1,5-biradical.

* Corresponding author. Tel./fax: +81-72-254-9289; e-mail: mizuno@chem.osakafu-u.ac.jp

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duct **3a** and ring-opened photoadducts **4a**–**6a** in 27, 30, 20, 14% yields, respectively (Scheme 1). The structures of **3a**–**6a** were determined by their spectral data,[7] and confirmed by X-ray analysis of **3a** and **5a** (Figs. 1 and 2). It is noteworthy that the anisyl groups of **3a** both lay at *endo*-positions to the dihydrophenanthrene ring. Other stereoisomers of **3a**–**5a** were not obtained at all.

All photoadducts **3a**–**6a** were produced at the initial stage of the photoreaction, and the yields of products were saturated in about 3 h irradiation (Table 1, runs 1–3). Since *cis*–*trans* photoisomerization of 1,2-diarylcyclopropane occurred during the irradiation,[8] *cis*/*trans* ratio (***c*-2a**/***t*-2a**) increased with increasing the irradiation time. In acetonitrile, any adduct was not obtained (run 4). The formation of **3a**–**6a** was not sensitized by the addition of benzophenone and was not quenched by the addition of isoprene or molecular dioxygen (runs 5–7).[9] The addition of methanol or methanol-d_4 decreased the yields of products, but any methanol-incorporated product was not observed (runs 8 and 9).

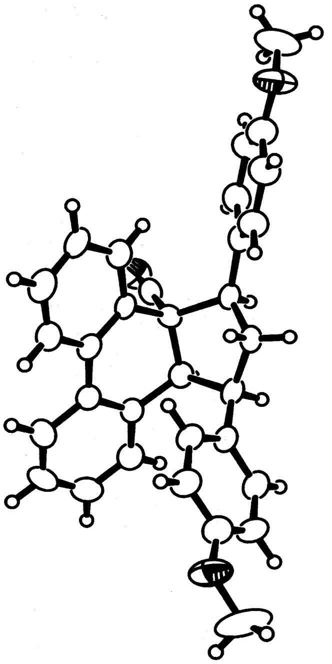


Figure 1. ORTEP drawing of **3a**. Orthorhombic, $Pna2_1$ (#33), $Z=8$, $R=0.087$, $R_w=0.107$, $a=14.0051(2)$, $b=14.4732(3)$, $c=23.9850(5)$ Å, $V=4861.7(1)$ Å^3, 1.250 g/cm^3.

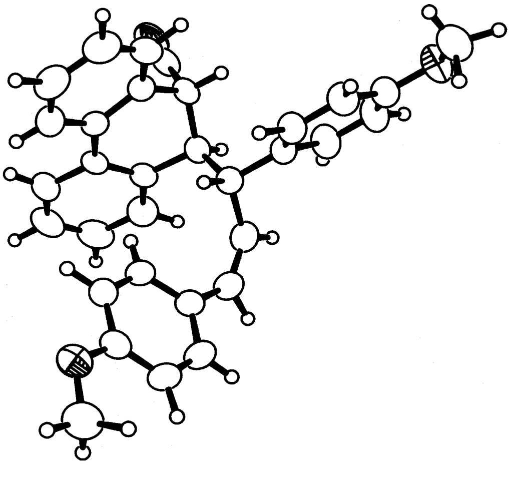


Figure 2. ORTEP drawing of **5a**. Monoclinic, $P2_1/n$ (#14), $Z=4$, $R=0.055$, $R_w=0.060$, $a=11.4829(8)$, $b=18.246(1)$, $c=12.0934(7)$ Å, $\beta=99.270(3)$°, $V=2500.7(3)$ Å^3, 1.215 g/cm^3.

Photoreaction of **1** with *trans*-1-anisyl-2-phenylcyclopropane (***t*-2b**) in benzene gave also the corresponding photoadducts **3b**–**6b**, and other regio- and stereoisomers were not obtained at all (Scheme 2).[10] It is noteworthy that the single regioisomers of each compound were formed among each two possible regioisomers (position of An and Ph). The structure of **4b** was confirmed by X-ray analysis (Fig. 3). Photoreaction of **1** with *trans*-1,2-diphenylcyclopropane (***t*-2c**) and photoreaction of unsubstituted phenanthrene with ***t*-2a**–**c** did not give any adduct.

The fluorescence of **1** in benzene was quenched by ***t*-2a**–**c** at nearly diffusion-controlled rates.[11] ΔG values for single electron transfer from ***t*-2a**–**c** to **1** in acetonitrile estimated by Rehm–Weller equation were negative (−103.2 kJ/mol for ***t*-2a**, −83.9 kJ/mol for ***t*-2b**, and −53.1 kJ/mol for ***t*-2c**).[12]

From these results, we propose a possible mechanism for the formation of photoadducts shown in Scheme 3. Excited singlet **1** interacts with **2a** to produce a singlet exciplex, which forms 1,5-biradical **7**.[13] 1,5-Biradical **7** may have a partially charge separated character, but the formation of complete charge separated species such as zwitterionic intermediate **8** seems unlikely from the controlled experiments in the presence of methanol. Intramolecular C–C coupling of **7** gives (3+2) photocycloadduct **3a**, where intramolecular hydrogen transfer of **7** affords **4a**–**6a**. In acetonitrile, electron transfer from **2a** to **1** to give radical ion pair and the following back electron transfer may retard the formation of **7**.[14,15]

Three possible structures of singlet exciplexes **9a**–**c** are proposed on the basis of sandwich-type π–π interaction in the excited state (Scheme 4).[16] Initial C–C bond formation at the 10-position of phenanthrene ring from **9a** results in the formation of *threo*-1,5-biradical **7a**, while **9b** and **9c** forms *erythro*-1,5-biradical **7b**. (3+2) Photocycloadduct **3a** should be formed from **7b** because two anisyl groups of **3a** have *endo*,*endo*-configuration.[17] The *endo*,*endo*-configuration of **3a** and *cis*-configuration of the double bonds of **4a** and **5a** may support an assumption that the π–π interaction also act at the second C–C bond formation (ring closure) of **7b** to form **3a**.[18] It is not clear why the other isomer **7a** did not give the corresponding (3+2) photocycloadduct, but we suggest the most favorable conformation of **7a** may

Table 1. (3+2) Photocycloaddition of ***t*-2a** with **1**[a]

Run	Solvent	Atmosphere	Additive	Irrad time	Yields (%)[b]			
					3a	**4a**	**5a**	**6a**
1	Benzene-d_6	Ar	–	15 min	6	5	3	4
2	Benzene-d_6	Ar	–	1 h	19	23	13	10
3	Benzene-d_6	Ar	–	3 h	27	30	20	14
4	Acetonitrile-d_3	Ar	–	3 h	0	0	0	0
5	Benzene-d_6	Ar	PhCOPh[c]	3 h	6	8	5	4
6	Benzene-d_6	Ar	Isoprene[d]	3 h	26	28	22	11
7	Benzene-d_6	O_2	–	3 h	23	25	17	12
8	Benzene-d_6	Ar	CD_3OD[e]	3 h	22	18	15	11
9	Benzene-d_6	Ar	CH_3OH[e]	3 h	15	15	12	10

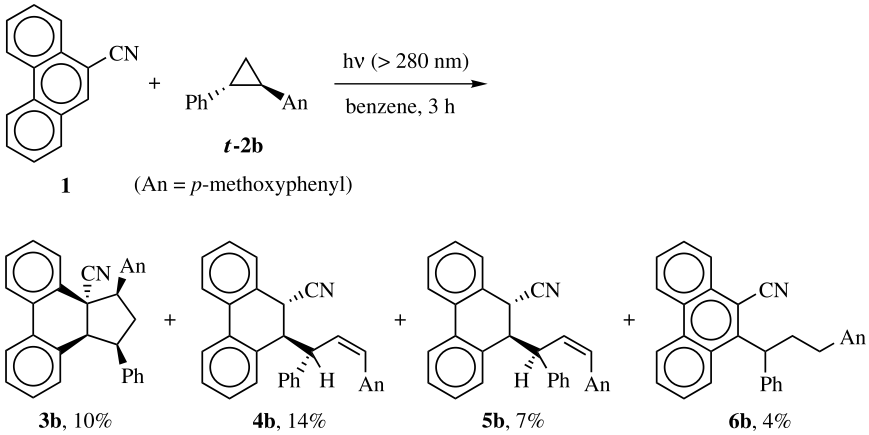
[a] [**1**]=[***t*-2a**]=0.05 mol dm^{-3}.

[b] Yields were determined by ^{1}H NMR.

[c] 0.13 mol dm^{-3}.

[d] 0.5 mol dm^{-3}.

[e] 5 Vol % (=1.2 mol dm^{-3}).



Scheme 2.

not be suitable for the ring closure rather than intramolecular hydrogen transfer in terms of the maximum stabilization due to the π–π orbital interaction. As a possible explanation for the excellent regioselectivity in the photoreaction of **1** with ***t*-2b**, it is proposed that the structures of singlet exciplexes formed from **1** and **2b** may be restricted by the dipole moments of each molecule, which act to offset each other.[16e,i]

In conclusion, we have developed the first example of (3+2) photocycloaddition of 1,2-diarylcyclopropanes to phenanthrene ring. This new strategy for the one-pot construction of cyclopentane frameworks will be useful for the synthesis of polycyclic organic molecules. Further details for the reaction mechanisms and synthetic applications are now under investigation.

Acknowledgements

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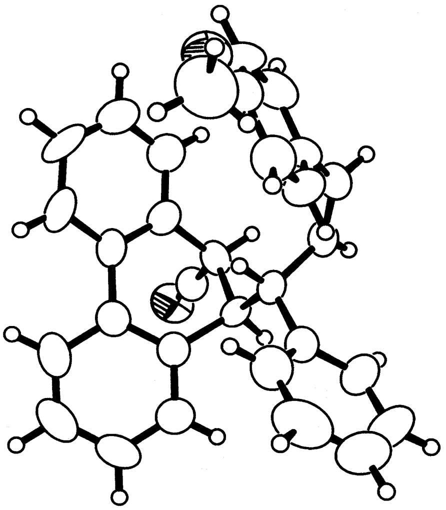
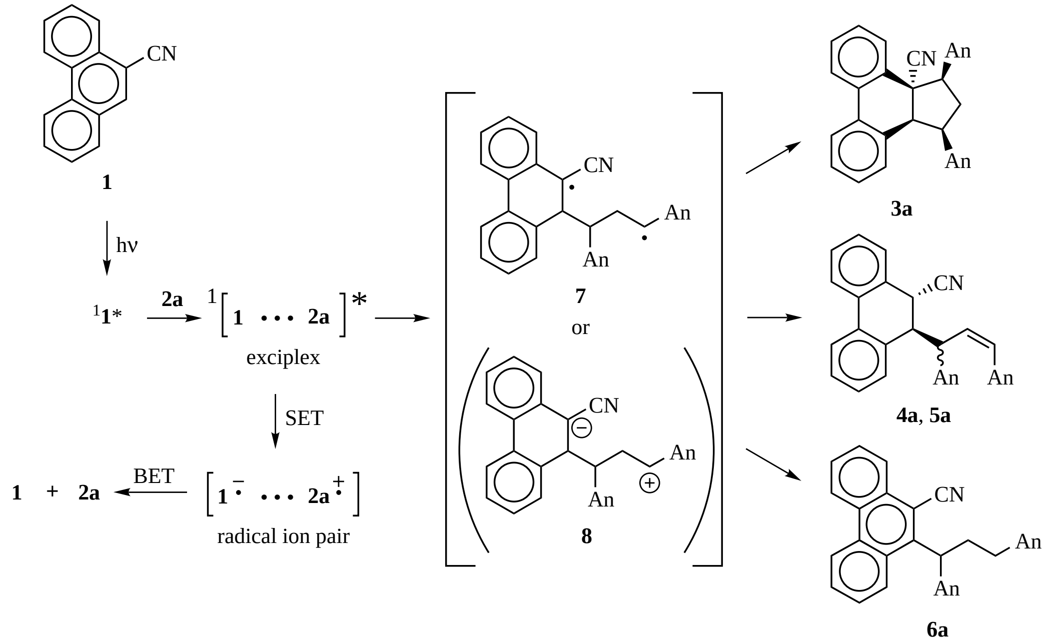
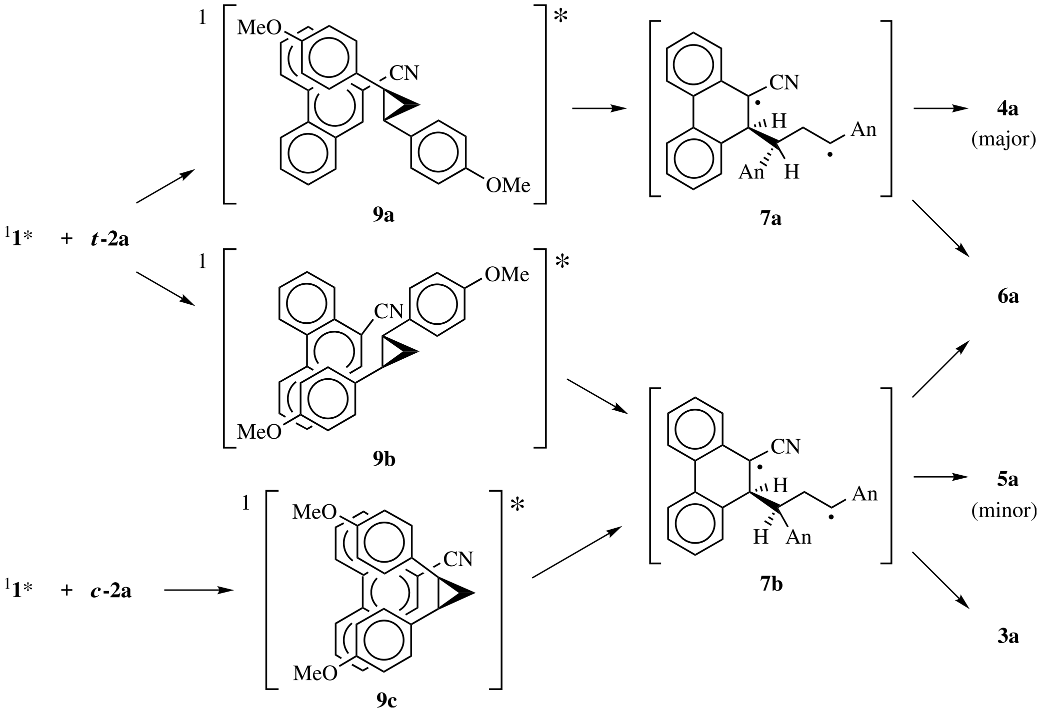


Figure 3. ORTEP drawing of **4b**. Triclinic, $P\bar{1}$ (#2), $Z=4$, $R=0.070$, $R_w=0.084$, $a=11.333(2)$, $b=15.031(2)$, $c=15.232(2)$ Å, $\alpha=72.3(2)°$, $\beta=77.255(2)°$; $\gamma=84.287(2)°$, $V=2410.2(1)$ Å^3, 1.178 g/cm^3.



Scheme 3.



Scheme 4.

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7. **Data for 3a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (td, J=13.1, 10.6 Hz, 1H), 2.56 (ddd, J=13.0, 7.5, 5.7 Hz, 1H), 3.65 (s, 3H), 3.87 (s, 3H), 3.95 (td, J=11.0, 7.7 Hz, 1H), 4.20 (dd, J=13.4, 5.3 Hz, 1H), 4.24 (d, J=11.2 Hz, 1H), 6.43 (d, J=9.0 Hz, 2H), 6.48 (d, J=8.8 Hz, 2H), 6.79 (dd, J=8.1, 1.1 Hz, 1H), 6.94 (d, J=9.0 Hz, 2H), 6.96–7.13 (m, 4 H), 7.30 (td, J=7.7, 1.5 Hz, 1H), 7.46 (d, J=8.3 Hz, 2H), 7.49 (d, J=8.1 Hz, 1H), 7.63 (d, J=8.1 Hz, 1H). **Data for 4a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (dd, J=10.5, 1.7 Hz, 1H), 3.57 (t, J=10.9 Hz, 1H), 3.742 (s, 3H), 3.745 (s, 3H), 4.27 (d, J=1.8 Hz, 1H), 5.93 (t, J=11.4 Hz, 1H), 6.40 (dd, J=7.6, 1.3 Hz, 1H), 6.54–6.60 (m, 3H), 6.68–6.78 (m, 5H), 6.80–6.87 (m, 2H), 6.90 (td, J=7.5, 1.3 Hz, 1H), 6.94 (td, J=7.5, 1.3 Hz, 1H), 7.23 (td, J=7.8, 1.2 Hz, 1H), 7.27 (td, J=7.6, 1.5 Hz, 1H), 7.70 (t, J=6.5 Hz, 2H). **Data for 5a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.34 (dd, J=10.8, 1.8 Hz, 1H), 3.53 (t, J=11.0 Hz, 1H), 3.57 (d, J=1.5 Hz, 1H), 3.74 (s, 3H), 3.82 (s, 3H), 5.75 (t, J=11.1 Hz, 1H), 6.19 (d, J=11.4 Hz, 1H), 6.30 (dt, J=8.4, 2.5 Hz, 2H), 6.50 (dt, J=8.8, 2.5 Hz, 2H), 6.86–6.97 (m, 5H), 7.22–7.44 (m, 5H), 7.67 (t, J=8.4 Hz, 2H). **Data for 6a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25–2.37 (m, 1H), 2.69–2.82 (m, 2H), 2.85–2.95 (m, 1H), 3.74 (s, 3H), 3.76 (s, 3H), 5.35 (t, J=7.2 Hz, 1H), 6.72 (dt, J=8.6, 2.5 Hz, 2H), 6.82 (dt, J=9.0, 2.6 Hz, 2H), 6.95 (dt, J=8.6, 2.5 Hz, 2H), 7.27 (d, J=8.9 Hz, 2H), 7.38–7.47 (m, 1H), 7.68 (t, J=7.8 Hz, 1H), 7.768 (t, J=3.8 Hz, 1H), 7.768 (t, J=5.6 Hz, 1H), 8.02 (d, J=7.7 Hz, 1H), 8.39–8.44 (m, 1H), 8.68–8.75 (m, 2H).
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9. Photoreaction in the presence of isoprene did produce a complex mixture of (2+2) photocycloadducts with isoprene.
10. **Data for 3b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (td, J=13.2, 10.6 Hz, 1H), 2.58 (ddd, J=12.8, 7.9, 5.6 Hz, 1H), 3.87 (s, 3H), 3.99 (td, J=10.7, 7.8 Hz, 1H), 4.22 (dd, J=13.4, 6.0 Hz, 1H), 4.29 (d, J=11.0 Hz, 1H), 6.58 (dd, J=7.8, 1.7 Hz, 2H), 6.79 (dd, J=8.1, 1.1 Hz, 1H), 6.86–7.04 (m, 8H), 7.09 (td, J=7.5, 1.6 Hz, 1H), 7.31 (td, J=7.6, 1.4 Hz, 1H), 7.48 (d, J=8.4 Hz, 1H), 7.48 (d, J=8.4 Hz, 2H), 7.63 (dd, J=8.0, 1.4 Hz, 1H). **Data for 4b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28 (dd, J=10.6, 1.8 Hz, 1H), 3.62 (t, J=10.9 Hz, 1H), 3.75 (s, 3H), 4.28 (d, J=1.8 Hz, 1H), 5.97 (t, J=11.4 Hz, 1H), 6.37 (dd, J=7.7, 0.9 Hz, 1H), 6.58 (d, J=8.8 Hz, 2H), 6.56–6.62 (m, 1H), 6.76 (d, J=8.6 Hz, 2H), 6.81–6.90 (m, 4H), 6.94 (td, J=7.5, 1.2 Hz, 1H), 7.12–7.30 (m, 5H), 7.70 (t, J=8.0 Hz, 2H). **Data for 5b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (dd, J=10.8, 1.8 Hz, 1H), 3.53 (d, J=1.8 Hz, 1H), 3.58 (t, J=11.1 Hz, 1H), 3.74 (s, 3H), 5.79 (t, J=11.1 Hz, 1H), 6.21 (d, J=11.5 Hz, 1H), 6.24–6.37 (m, 1H), 6.30 (d, J=8.4 Hz, 2H), 6.50 (dt, J=8.8, 2.4 Hz, 2H), 6.88–7.00 (m, 4H), 7.21–7.57 (m, 6H), 7.67 (dd, J=10.3, 7.3 Hz, 2H). **Data for 6b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27–2.38 (m, 1H), 2.70–2.85 (m, 2H), 2.89–3.02 (m, 1H), 3.74 (s, 3H), 5.41 (t, J=7.4 Hz, 1H), 6.72 (dt, J=8.6, 2.3 Hz, 2H), 6.95 (dt, J=8.6, 2.3 Hz, 2H), 7.16–7.45 (m, 6H), 7.68 (t, J=7.4 Hz, 1H), 7.78 (t, J=3.8 Hz, 1H), 7.78 (t, J=5.4 Hz, 1H), 8.00 (d, J=7.9 Hz, 1H), 8.40–8.44 (m, 1H), 8.68–8.75 (m, 2H).
11. Emission of exciplex between **1** and ***t*-2a** was not observed both in benzene and cyclohexane.
12. Rehm–Weller Equation: $\Delta G = E^{ox}(D) - E^{red}(A) - E_{0-0} - e^2/\varepsilon r$. $e^2/\varepsilon r$: Coulomb energy, 0.06 eV. E_{0-0}: singlet energy of **1**, 2.89 eV. E^{red} of **1**=−1.92 eV. E^{ox} of ***t*-2a**=0.55 eV. E^{ox} of ***t*-2b**=0.75 eV. E^{ox} of ***t*-2c**=1.07 eV. See: Rehm, D.; Weller, A. *Isr. J. Chem*. **1970**, *8*, 259–271.
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15. We have previously reported that (2σ+4π) photocycloaddition of 1,2-diarylcyclopropanes to 9,10-dicyanoanthracene occurred in degassed acetonitrile, but did not proceed in benzene. The difference of the reactivity is now under investigation. (a) Ref. 8f; (b) Ichinose, N.; Mizuno, K.; Hiromoto, Z.; Otsuji, Y. *Tetrahedron Lett*. **1986**, *27*, 5619–5620.
16. Caldwell, Pac, and we have independently suggested the sandwich-type singlet exciplexes might be formed in the (2+2) photocycloaddition of polyaromatic compounds with arylalkenes. See: (a) Pac, C.; Mizuno, K.; Sugioka, T.; Sakurai, H. *Chem. Lett*. **1973**, 187–188; (b) Mizuno,

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17. An alternative pathway where the concerted two C–C bond formation from **1** and ***c*-2a** via **9c** produces **3a** cannot be ruled out.
18. PM3 calculation by MOPAC suggested that *exo*,*endo*-isomer of **3a** is the most stable thermodynamically among four possible stereoisomers of **3a**.