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Photoalkylation of 2,3-dicyanonaphthalene by methoxy-substituted 1,2-diarylcyclopropanes

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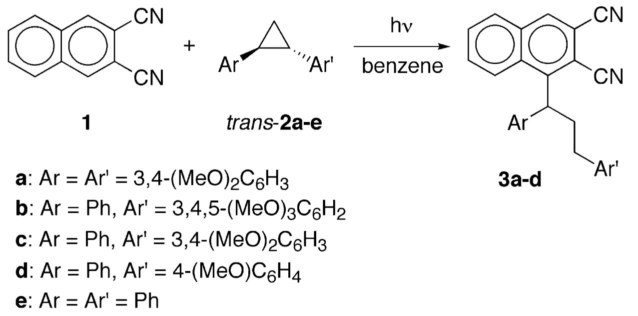
Abstract—Photoreaction of 2,3-dicyanonaphthalene with methoxy-substituted 1,2-diarylcyclopropanes in benzene gave alkylated naphthalene derivatives via excited singlet of 2,3-dicyanonaphthalene. Fluorescence of the photoalkylated products showed intense intramolecular exciplex emission.

(2π+2π) Photocycloaddition of alkenes to naphthalene rings is a useful synthetic pathway for the preparation of polycyclic compounds including cyclobutane rings.[1] The chemical conversion of the resulting cyclobutane rings gave substituted naphthalene derivatives.[2] On the other hand, photoreaction of naphthalene rings with cyclopropane derivatives have not been appeared in literatures, although a few examples of photocycloaddition reactions of anthracene and phenanthrene derivatives with cyclopropanes have been developed by us to give (4+3) and (2+3) photocycloadducts, respectively.[3] Here we describe the unprecedented direct photoalkylation of 2,3-dicyanonaphthalene by 1,2-diarylcyclopropanes.

Photoirradiation of a benzene solution containing 2,3-dicyanonaphthalene (**1**, 1.0×10^{-2} M) and *trans*-1,2-bis(3,4-dimethoxyphenyl)cyclopropane (*trans*-**2a**, 1.0×10^{-2} M) by a high-pressure Hg lamp through Pyrex filter under argon atmosphere for 120 h gave a photoalkylated naphthalene derivative **3a** as an isolable major product in 12% isolated yield (Scheme 1, Table 1, entry 1). Photoalkylated products were also obtained in the reaction of **1** with *trans*-1-(3,4,5-trimethoxyphenyl)-2-phenylcyclopropane (*trans*-**2b**), *trans*-1-(3,4-dimethoxyphenyl)-2-phenylcyclopropane (*trans*-**2c**), and *trans*-1-(4-methoxyphenyl)-2-phenylcyclopropane (*trans*-**2d**), in 19%, 28%, and 20% yields, respectively (entries 2–4). It is noteworthy that the single regioisomers were formed in the photoreactions with *trans*-**2b**–**d**. That is to say, the phenyl groups and the methoxy-substituted phenyl groups were attached to C1 and C3 positions of the propyl chains of **3b**–**d**, respectively, although each two regioisomers are possible in the photoreaction with unsymmetrical 1,2-diarylcyclopropanes. Photoalkylated product was not obtained in the photoreaction of **1** with *trans*-1,2-diphenylcyclopropane (*trans*-**2e**). The recovered 1,2-diarylcyclopropanes contained their *cis*-isomers (*cis*-**2a**–**e**).[4] To the best of our knowledge, this is the first example for the direct photoalkylation of naphthalene ring by cyclopropane derivatives.



Scheme 1.

The structures of alkylated products were determined by their spectral data.[5] Characteristic signals were observed at 5.2–5.3 ppm as triplet-like peaks in ^{1}H NMR spectra of **3a**–**d**, which were ascribable to diarylmethyne

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Keywords: Photoalkylation; 2,3-Dicyanonaphthalene; 1,2-Diarylcyclopropane; Exciplex; 1,5-Biradical.

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Table 1. Photoalkylation of 2,3-dicyanonaphthalene (**1**) by *trans*-1,2-diarylcyclopropanes (*trans*-**2a**–**e**); effects of irradiation time, additives, and solvents[a]

Entry	**2**	Solvent	Additive	Irradiation time (h)	Yield of **3** (%)[b]
1[c]	*trans*-**2a**	Benzene	—	120	12[d]
2	*trans*-**2b**	Benzene	—	120	19
3	*trans*-**2c**	Benzene	—	120	28
4	*trans*-**2d**	Benzene	—	120	20
5	*trans*-**2e**	Benzene	—	120	0
6	*trans*-**2c**	Benzene	—	5	8
7	*trans*-**2c**	Benzene	—	20	15
8	*trans*-**2c**	Benzene	—	50	20
9	*trans*-**2c**	Benzene	Benzophenone[e]	50	0
10	*trans*-**2c**	Benzene	Michler's ketone[e]	50	0
11	*trans*-**2c**	Ethyl acetate	—	50	10
12	*trans*-**2c**	Dichloromethane	—	50	3
13	*trans*-**2c**	Acetonitrile	—	50	0

[a] 300 W high-pressure mercury lamp, Pyrex filter, [**1**] = [*trans*-**2**] = 0.03 M.

[b] Yields based on **1** used. The yields were determined by ^{1}H NMR, using singlet peaks appeared at 8.22–8.25 ppm, ascribable to the hydrogens at C4 positions of naphthalene rings of **3a**–**d**.

[c] [**1**] = [*trans*-**2a**] = 0.01 M.

[d] Isolated yield.

[e] 5 equivalents based on **1**.

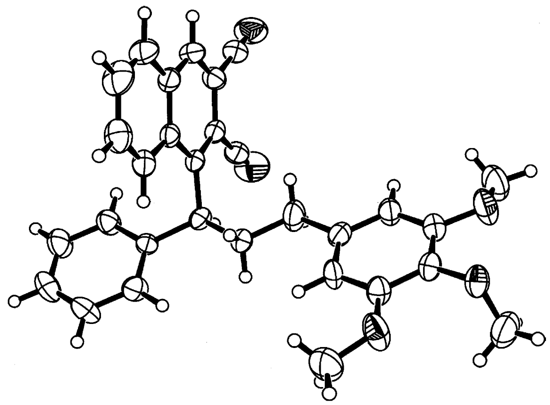


Figure 1. ORTEP drawing of **3b**. $C_{30}H_{26}N_2O_3$, FW = 462.55, monoclinic, *C*2/*c* (#15), *Z* = 8, *a* = 41.73(2) Å, *b* = 15.31(1) Å, *c* = 7.746(4) Å, β = 100.50(3)°, *V* = 4866(4) Å^3, D_{calcd} = 1.263 g cm^{-3}, Refl/Para = 6.59, *R*1 = 0.063, w*R*2 = 0.119, goodness of fit = 1.583, *μ* = 0.818.

hydrogens of **3a**–**d**. The structure of **3b** was confirmed by X-ray crystallographic analysis (Fig. 1). The C–C bond lengths and bond angles around the 1,3-diarylpropyl group were 1.51–1.55 Å and 107–109°, respectively. The trimethoxy-substituted phenyl group was attached to the C3 position of the propyl chain. The dicyanonaphthalene ring and 1,3-diarylpropyl chain located almost perpendicularly.

Effects of irradiation time, additives, and solvents were examined, and the results are summarized in Table 1. The yield of the photoalkylated product **3** increased with increasing the irradiation time (compare entries 6–8 and 3). During the initial stage of the photoreaction (~50 h), **3** was obtained as a major product with small amount of by-products such as 1,4-double alkylated product, although 30–50% of **1** and **2a**–**d** were still remained even after 120 h irradiation (entries 1–4). Further irradiation over 120 h gave a complex mixture containing unidentified by-products and the yield of **3** decreased. The photoalkylation of **1** by *trans*-**2a**–**d** did not proceed by use of triplet sensitizers such as benzophenone and Michler's ketone (entries 9 and 10). The photoreaction of **1** with *trans*-**2a**–**d** also proceeded in ethyl acetate and dichloromethane, but the efficiency was lower than that in benzene (entries 11 and 12). The photoalkylation in acetonitrile did not proceed at all, and the starting materials were recovered quantitatively (entry 13). Since *cis–trans* photoisomerization of **2a**–**e** took place during the photoirradiation,[4] the recovered **2a**–**e** were the mixture of the *trans* and *cis* isomers in all entries.

UV absorption and fluorescence spectra of **1** and **3a**–**c** were measured in benzene (Figs. 2 and 3). Absorption maxima of **3a** ($\lambda_{\max}$ = 347 nm, ε = 2.2 × 10^3), **3b** ($\lambda_{\max}$ = 346 nm, ε = 2.1 × 10^3), and **3c** ($\lambda_{\max}$ = 346 nm, ε = 1.9 × 10^3) were shifted to longer wavelength than **1** ($\lambda_{\max}$ = 343 nm, ε = 2.5 × 10^3). The 3–4 nm bathochromic shift was attributable to the effect of the introduction of alkyl chains to 2,3-dicyanonaphthalene chromophore, hence intramolecular CT interaction between 2,3-dicyanonaphthalene and methoxy-substituted phenyl ring at ground state was negligible. Fluorescence spectra of **3a**–**c** showed intense intramolecular exciplex emission. Fluorescence maxima of **3a** and **3c** appeared both at 474 nm, and that of **3b** appeared at 496 nm, due to the excited-state interaction between dicyanonaphthyl group and methoxy-substituted phenyl groups. The longer wavelength of the intramolecular exciplex of **3b** than those of **3a** and **3c** was explained by the formation of more stabilized exciplex depending on the number of methoxy groups. Fluorescence lifetimes of **3b**,**c** (λ_{em} > 420 nm) were calculated by single components, whose values were 21.0 and 26.6 ns in aerated benzene, whereas that of **3a** was consisted from two components whose values were 23.4 and 7.24 ns. The longer component (23.4 ns) corresponds to the intramolecular exciplex between dicyanonaphthyl group and dimethoxyphenyl group at C3 position of the propyl

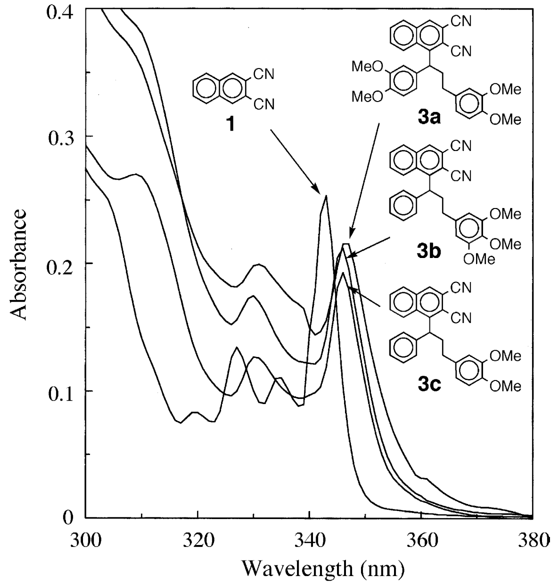


Figure 2. UV absorption spectra of **1** and **3a**–**c** (1.0×10^{-4} M) in benzene.

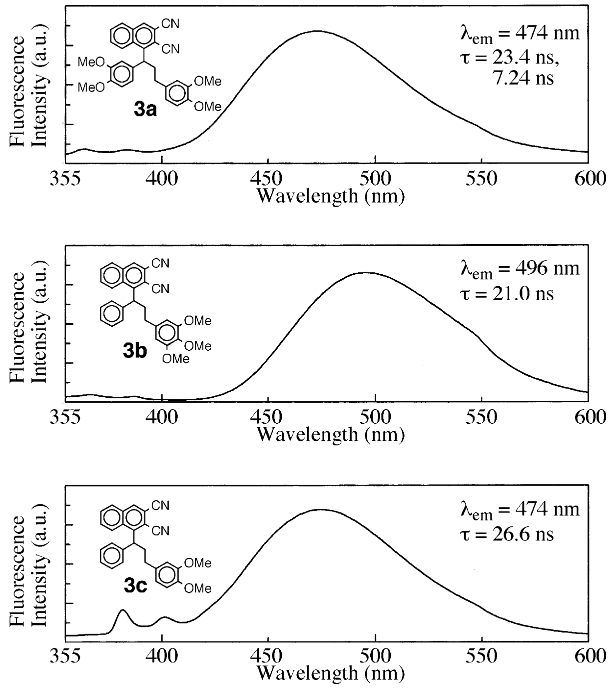


Figure 3. Fluorescence spectra (λ_{ex} = 346 nm) and fluorescence lifetimes (λ_{ex} = 346 nm, λ_{em} > 420 nm) of **3a**–**c** in benzene (1.0×10^{-4} M).

chain, whereas the shorter component (7.24 ns) corresponds to that between dicyanonaphthyl group and dimethoxyphenyl group at C1 position.

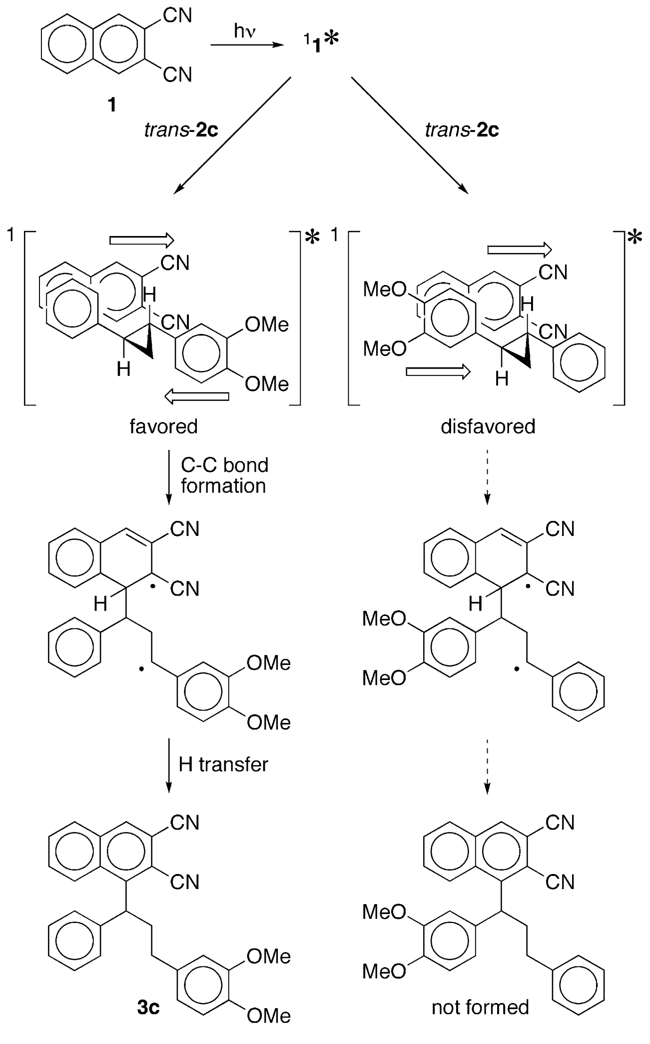
Rate constants for fluorescence quenching of **1** by *trans*-**2a**–**e** calculated by Stern–Volmer plots were shown in Table 2. The fluorescence of **1** in benzene was efficiently quenched by *trans*-**2a**–**e** at nearly diffusion controlled rates. Emission of exciplexes between **1** and *trans*-**2a**–**e** was not observed. *Trans*-**2d** has the largest k_q value among these substrates, and the k_q values decreased in the order of *trans*-**2d** > *trans*-**2c** > *trans*-**2e** > *trans*-**2a** > *trans*-**2b**. It is assumed that both electron-donating ability of the aromatic rings of **2** and the steric effect of methoxy group(s) influenced the k_q values.

Table 2. Rate constants for fluorescence quenching of 2,3-dicyanonaphthalene (**1**) by 1,2-diarylcyclopropanes (*trans*-**2a**–**e**) calculated by Stern–Volmer plots[a]

2	k_q (M^{-1} s^{-1})
trans-**2a**	8.2×10^9
trans-**2b**	6.9×10^9
trans-**2c**	9.9×10^9
trans-**2d**	1.17×10^{10}
trans-**2e**	8.9×10^9

[a] In benzene, τ(**1**) = 15.6 ns.

From these results, the regioselective photoalkylation of **1** was explained as shown in Scheme 2, which was exemplified by the photoreaction of **1** with *trans*-**2c**. Excited singlet state of **1** (^{1}**1***) interacts with **2** to produce a sandwich-type singlet exciplex.[6] C–C bond formation from the singlet exciplex forms 1,5-biradical, which has distonic tertiary cyano-substituted radical and methoxy-substituted benzyl radical.[7] Intramolecular hydrogen transfer of the 1,5-biradical gives the alkylated naphthalene derivative **3**. Some charge-separated interaction



Scheme 2.

might be required for the C–C bond formation because photoreaction between **1** and *trans*-**2e** did not proceed. As a possible explanation for the excellent regioselectivity in the photoreaction of **1** with **2b**–**d**, it is proposed that the formation of the singlet exciplex may be restricted in directions of favorable π–π overlapping by offset the dipole moments of each molecule.[8] In polar solvents, electron transfer from **2** to $^{1}\mathbf{1}^{*}$ to give radical ion pair and the following rapid back electron transfer may retard the formation of 1,5-biradical. After the formation of some amounts of products **1** and **3a**–**d** competitively absorb UV light under the present irradiation conditions. The low chemical yields of **3** may be due to some disturbance by **3** itself. The formation of trichromophoric complex between **2** and **3** and less reactivity of **3** will be also included. Indeed, double alkylated products at 1,4-positions of naphthalene ring were produced in small amounts especially in the photoreaction of **1** with **2c**–**d**.

In conclusion, we developed a novel photoalkylation of **1** by methoxy-substituted 1,2-diarylcyclopropanes via excited singlet state. Fluorescence of the photoalkylated products showed typical intramolecular exciplex emission due to the intramolecular interaction between electron-deficient and electron-rich aromatic groups. The formation of the stable intramolecular exciplex of the products rather disturb the photoalkylation.

Acknowledgments

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References and notes

1. (a) Gilbert, A. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York and London, 1984; pp 1–60; (b) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811–860; (c) Mizuno, K.; Maeda, H.; Sugimoto, A.; Chiyonobu, K. In *Understanding and Manipulating Excited-State Processes*; Ramamurthy, V., Schanze, K. S., Eds.; Molecular and Supramolecular Photochemistry; Marcel Dekker: New York, 2001; Vol. 8, pp 127–241; (d) Chamberlain, T. R.; McCullough, J. J. *Can. J. Chem.* **1973**, *51*, 2578–2589; (e) McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1980**, *102*, 7780–7782; (f) McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1982**, *104*, 4644–4658; (g) Gilbert, A.; Heath, P.; Kashoulis-Koupparis, A.; Ellis-Davies, G. C. R.; Firth, S. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 31–36; (h) Albini, A.; Fasani, E.; Giavarini, F. *J. Org. Chem.* **1988**, *53*, 5601–5607; (i) Wagner, P. J.; Sakamoto, M. *J. Am. Chem. Soc.* **1989**, *111*, 9254–9256; (j) Al-Jalal, N. A. *J. Photochem. Photobiol. A* **1990**, *51*, 429–436; (k) McCullough, J. J.; McMurry, T. B.; Work, D. N. *J. Chem. Soc., Perkin Trans. 1* **1991**, 461–464; (l) Mizuno, K.; Nakanishi, K.; Yasueda, M.; Miyata, H.; Otsuji, Y. *Chem. Lett.* **1991**, 2001–2004; (m) Mella, M.; Fasani, E.; Albini, A. *J. Org. Chem.* **1992**, *57*, 6210–6216; (n) Döpp, D.; Erian, A. W.; Henkel, G. *Chem. Ber.* **1993**, *126*, 239–242; (o) Weng, H.; Roth, H. D. *Tetrahedron Lett.* **1996**, *37*, 4895–4898; (p) Mizuno, K.; Konishi, S.; Takata, T.; Inoue, H. *Tetrahedron Lett.* **1996**, *37*, 7775–7778; (q) Noh, T.; Kim, D.; Kim, Y.-J. *J. Org. Chem.* **1998**, *63*, 1212–1216.
2. (a) Pac, C.; Mizuno, K.; Okamoto, H.; Sakurai, H. *Synthesis* **1978**, 589–590; (b) Akhtar, I. A.; McCullough, J. J. *J. Org. Chem.* **1981**, *46*, 1447–1450; (c) Chow, Y. L.; Buono-Core, G. E.; Liu, X.-Y.; Itoh, K.; Qian, P. *J. Chem. Soc., Chem. Commun.* **1987**, 913–915; (d) Chow, Y. L.; Liu, X.-Y.; Hu, S. *J. Chem. Soc., Chem. Commun.* **1988**, 1047–1048; (e) Chow, Y. L.; Liu, X.-Y. *Can. J. Chem.* **1991**, *69*, 1261–1272; (f) Chow, Y. L.; Buono-Core, G. E.; Zhang, Y.-H.; Liu, X.-Y. *J. Chem. Soc., Perkin Trans. 2* **1991**, 2041–2045; (g) Chow, Y. L.; Johansson, C. I. *Can. J. Chem.* **1994**, *72*, 2011–2020.
3. (a) Ichinose, N.; Mizuno, K.; Hiromoto, Z.; Otsuji, Y. *Tetrahedron Lett.* **1986**, *27*, 5619–5620; (b) Mizuno, K.; Ichinose, N.; Otsuji, Y. *J. Org. Chem.* **1992**, *57*, 1855–1860; (c) Maeda, H.; Miyata, Y.; Mizuno, K. *Tetrahedron Lett.* **2002**, *43*, 1481–1486.
4. *cis*–*trans*-Photoisomerization of 1,2-diarylcyclopropanes are known to be sensitized by cyanoaromatic compounds such as 1,4-dicyanonaphthalene and 9,10-dicyanoanthracene. See: (a) Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, 2101–2104; (b) Mizuno, K.; Hiromoto, Z.; Ohnishi, K.; Otsuji, Y. *Chem. Lett.* **1983**, 1059–1060; (c) Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1985**, 455–458; (d) Ref. 3b; (e) Tamai, T.; Ichinose, N.; Tanaka, T.; Sasuga, T.; Hashida, I.; Mizuno, K. *J. Org. Chem.* **1998**, *63*, 3204–3212.
5. Data for **3a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.30–2.39 (m, 1H), 2.70–2.82 (m, 2H), 2.83–2.95 (m, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 3.835 (s, 3H), 3.843 (s, 3H), 5.17–5.25 (m, 1H), 6.47 (s, 1H), 6.58 (d, $J = 8.2$ Hz, 1H), 6.71 (d, $J = 7.7$ Hz, 1H), 6.74–6.87 (m, 3H), 7.52–7.61 (m, 1H), 7.69 (t, $J = 7.6$ Hz, 1H), 7.93 (d, $J = 7.7$ Hz, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 8.24 (s, 1H). Data for **3b**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.35–2.46 (m, 1H), 2.73–2.86 (m, 2H), 2.92–3.04 (m, 1H), 3.73 (s, 6H), 3.79 (s, 3H), 5.28 (dd, $J = 8.7$, 5.8 Hz, 1H), 6.18 (s, 2H), 7.23–7.35 (m, 5H), 7.57 (t, $J = 7.0$ Hz, 1H), 7.68 (t, $J = 7.7$ Hz, 1H), 7.93 (d, $J = 7.3$ Hz, 1H), 8.04 (d, $J = 8.1$ Hz, 1H), 8.23 (s, 1H). Data for **3c**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.29–2.42 (m, 1H), 2.68–2.85 (m, 2H), 2.90–3.01 (m, 1H), 3.72 (s, 3H), 3.83 (s, 3H), 5.23–5.31 (m, 1H), 6.48 (s, 1H), 6.59 (d, $J = 8.2$ Hz, 1H), 6.71 (d, $J = 7.7$ Hz, 1H), 7.12–7.43 (m, 5H), 7.51–7.60 (m, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.93 (d, $J = 7.7$ Hz, 1H), 8.02 (d, $J = 8.4$ Hz, 1H), 8.22 (s, 1H). Data for **3d**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.26–2.37 (m, 1H), 2.65–2.79 (m, 2H), 2.89–2.98 (m, 1H), 3.76 (s, 3H), 5.27 (dd, $J = 9.0$, 5.7 Hz, 1H), 6.63 (d, $J = 7.5$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.92–7.45 (m, 5H), 7.49–7.58 (m, 1H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.93 (d, $J = 7.1$ Hz, 1H), 8.02 (d, $J = 7.7$ Hz, 1H), 8.25 (s, 1H).
6. UV absorption spectrum of **1** shifted to bathochromic region in ranges of 1–3 nm when large excess of *trans*-**2a**–**d** were added to the solution. Therefore, formation of contact CT between **1** and *trans*-**2a**–**d** at ground state and their excitation may be included.
7. The 1,5-biradical may have a partially charge separated character, but the formation of complete charge separated species such as zwitterionic intermediate seems unlikely.
8. (a) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45–50; (b) Maeda, H.; Waseda, S.; Mizuno, K. *Chem. Lett.* **2000**, 1238–1239.