amino]-4-phenyl-3-(1-hexenyl)-1*H*-pyrrole-2-carbonitrile (4i) (entry 19, Table I) were prepared from 1-phenyloct-3-en-1-yne (**2i**) (2.5 mmol, 0.46 g). Purification by column chromatography gave a mixture of **3i** and **4i** (0.54 g, 53%) as a pale yellow solid. The spectra are of the mixture. **3i** + **4i**: ^{1}H NMR ($CDCl_3$) δ [0.06 (s, **3i**), 0.12 (s, **4i**), 18 H, $SiCH_3$], 0.97 (t, J = 6.8 Hz, 3 H, CH_3), 1.3–1.5 (c, 4 H, CH_2), 2.3–2.5 (c, 2 H, $CH_2C{=}$), [6.98 (d, J = 16.4 Hz, **4i**), 6.95 (d, J = 16.5 Hz, **3i**), 1 H, CH=], [7.17 (d, J = 16.4 Hz, **4i**), 7.20 (d, J = 16.4 Hz, **3i**), 1 H, CH=], [8.21 (br s, **4i**), 8.54 (br s, **3i**), 1 H, NH]; IR (Nujol) 3240 (NH), 2200 (CN), 1590, 1570 (C=C); MS, m/z 409 (M^+); exact mass for $C_{23}H_{35}N_3Si_2$ (M^+), calcd 409.2370, found 409.2370.

5-[Bis(trimethylsilyl)amino]-3-hexyl-1*H*-pyrrole-2-carbonitrile (3k) and 5-[bis(trimethylsilyl)amino]-4-hexyl-1*H*-pyrrole-2-carbonitrile (4k) (entry 21, Table I) were prepared from 1-octyne (**2k**) (2.5 mmol, 0.37 mL). Purification by column chromatography gave a mixture of **3k** and **4k** (0.39 g, 47%; **3k**:**4k** = 73:27) as a pale yellow oil. The spectra are of the mixture. **3k** + **4k**: ^{1}H NMR ($CDCl_3$) δ [0.07 (s, **4k**), 0.08 (s, **3k**), 18 H, $SiCH_3$], 0.84–0.89 (m, 3 H, CH_3), 1.26–1.64 (m, 8 H, CH_2), [2.18–2.25 (m, **4k**), 2.51 (t, J = 7.5 Hz, **3k**), CH_2], [5.44 (d, J = 3.0 Hz, **3k**), 6.62 (d, J = 2.8 Hz, **4k**), 1 H, CH=], [7.89 (br s, **3k**), 8.10 (br s, **4k**), 1 H, NH]; ^{13}C NMR ($CDCl_3$) δ 13.99, 14.02, 22.53, 22.57, 25.13, 26.76, 28.58, 29.46, 30.06, 30.27, 31.51, 92.91, 93.47, 105.44, 115.38, 115.77, 118.61, 119.92, 137.46, 138.03, 140.49; IR (neat) 3280 (NH), 2200 (CN), 1590, 1570 (C=C); MS, m/z 335 (M^+); exact mass for $C_{17}H_{33}N_3Si_2$ (M^+), calcd 335.2214, found 335.2226.

5-[Bis(trimethylsilyl)amino]-3-[2-(acetyloxy)ethyl]-1*H*-pyrrole-2-carbonitrile (3l) and 5-[bis(trimethylsilyl)amino]-4-[2-(acetyloxy)ethyl]-1*H*-pyrrole-2-carbonitrile (4l) (entry 22, Table I) were prepared from 3-butyn-1-yl acetate (**2l**) (2.5 mmol, 0.29 g). Purification by column chromatography gave a mixture of **3l** and **4l** (0.35 g, 42%; **3l**:**4l** = 90:10) as a pale yellow oil. The spectra are of the mixture. **3l** + **4l**: ^{1}H NMR ($CDCl_3$) δ [(0.08, s, **3l**), 0.10 (s, **4l**), 18 H, $SiCH_3$], [(2.05, s, **3l**), (2.07, s, **4l**), 3 H, CH_3CO], [(2.61, t, J = 7.2 Hz, **4l**), (2.86, t, J = 6.9 Hz, **3l**), 2 H, $CH_2C{=}$], [(4.21, t, J = 7.2 Hz, **4l**), (4.23, t, J = 6.9 Hz, **3l**), 2 H, CH_2O], [(5.50, d, J = 2.4 Hz, **3l**), (6.68 (d, J = 2.8 Hz, **4l**), 1 H, CH=], 8.47 (br s, 1 H, NH); IR (neat) 3270 (NH), 2200 (CN), 1745 (CO), 1725 (CO), 1570 (C=C); MS, m/z 337 (M^+); exact mass for $C_{15}H_{27}N_3O_2Si_2$ (M^+), calcd 337.1642, found 337.1631.

5-[Bis(trimethylsilyl)amino]-3-(3-cyanopropyl)-1*H*-pyrrole-2-carbonitrile (3m) and 5-[bis(trimethylsilyl)amino]-4-(3-cyanopropyl)-1*H*-pyrrole-2-carbonitrile (4m) (entry 23, Table I) were prepared from 5-hexynenitrile (**2m**) (2.5 mmol, 0.23 mL). Purification by column chromatography gave a mixture of **3m** and **4m** (0.65 g, 82%; **3m**:**4m** = 95:5) as a pale yellow oil. The spectra of the major isomer (**3m**) were derived from the spectra of the mixture: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18 H, $SiCH_3$), 1.97 (quint, J = 7.1 Hz, 2 H, CH_2), 2.33 (t, J = 7.1 Hz, 2 H, CH_2), 2.69 (t, J = 7.1 Hz, 2 H, CH_2), 5.48 (m, 1 H, CH), 8.55 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 1.27, 16.17, 25.54, 26.03, 93.09, 105.42, 114.67, 119.30, 134.36, 141.02; IR (neat) 3270 (NH), 2245, 2205 (CN), 1565 (C=C); MS, m/z 318 (M^+); exact mass for $C_{15}H_{26}N_4Si_2$ (M^+), calcd 318.1696, found 318.1711.

5-[Bis(trimethylsilyl)amino]-*N-tert*-butyl-3,4-dipropyl-1*H*-pyrrole-2-carbonitrile (9). In a 10-mL reaction flask were placed 4-octyne (**2a**) (2.5 mmol, 0.38 mL), Me_3SiCN (12.5 mmol, 1.7 mL), *t*-BuNC (5 mmol, 0.58 mL), and $CpCo(CO)_2$ (0.1 mmol, 13 μL). The mixture was heated to reflux, with stirring, under N_2. After 20 h, the flask was cooled to room temperature and unreacted **1** and *t*-BuNC were evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford 5-[bis(trimethylsilyl)amino]-*N-tert*-butyl-3,4-dipropyl-1*H*-pyrrole-2-carbonitrile (**9**) (0.62 g, 64%) as a pale yellow solid. An analytical sample was obtained by recrystallization (hexane): mp 135–136 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 18 H, $SiCH_3$), 0.92 (t, J = 7.4 Hz, 3 H, CH_3), 0.97 (t, J = 7.4 Hz, 3 H, CH_3), 1.39–1.50 (m, 2 H, CH_2), 1.59 (sextet, J = 7.4 Hz, 2 H, CH_2), 1.77 (s, 9 H, *t*-Bu), 2.18–2.23 (m, 2 H, CH_2), 2.52 (t, J = 7.4 Hz, 2 H, CH_2); IR (Nujol) 2190 (CN), 1540 (C=C); MS, m/z 391. Anal. Calcd for $C_{21}H_{41}N_3Si$: C, 64.39; H, 10.55; N, 10.73. Found: C, 64.57; H, 10.31; N, 10.65.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of pure **3a** and **4c** and of mixtures of **3g** + **4g**, **3i** + **4i**, **3k** + **4k**, **3l** + **4l**, and **3m** + **4m** (15 pages). Ordering information is given on any current masthead page.

Photosensitized [2+2] Cycloreversion Reactions of Arylated Cage Compounds in Nonpolar Solvents. Highly Efficient Adiabatic Exciplex Isomerization

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Photosensitized [2+2] cycloreversion reactions of arylated cage compounds **1** to dienes **2** using several cyanoaromatics as sensitizers are reported. In acetonitrile, **1a** isomerized to **2a** via an efficient cation-radical chain process. In contrast, the isomerization of **1a** to **2a** proceeded via an exciplex in benzene. Interestingly, the exciplex emission maximum observed in the fluorescence quenching by **1a** was the same as that by **2a**. Such a coincidence was also observed in a series of arylated cage compounds **1a–d** and dienes **2a–d** in various solvents. These observations together with the results obtained from reaction and exciplex emission quenching experiments clearly demonstrated the occurrence of adiabatic exciplex isomerization of **1** to **2**. Efficiencies (A_e) of the adiabatic process obtained by comparing the intensities of the observed exciplex emissions with those of diene exciplex emissions were quite high and became almost quantitative in some cases. A_e values were found to increase as (1) the oxidation potentials ($E_{1/2}^{ox}$) of cage compounds **1a–d** decreased, (2) the reduction potentials ($E_{1/2}^{red}$) of sensitizers increased, and (3) the solvent polarity (E_T) increased.

In the last two decades, an enormous amount of data on the photochemical behaviors of electron donor and electron acceptor pairs has been accumulated.[5] Irradiations of electron donor–acceptor systems produce sol-

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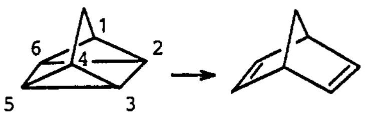
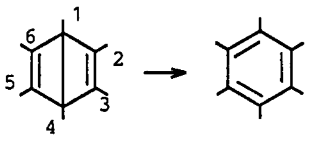
vent-separated ion-radical pairs (SSIRP) in polar solvents via a single-electron-transfer (SET) mechanism and exciplexes of those components in nonpolar solvents.[6] Electron-deficient species produced from such processes behave in a variety of ways depending on their structure and the surrounding media. Strained compounds possessing small rings, such as cyclopropyl and cyclobutyl frameworks, have been favorably subjected to photosensitized SET conditions.[7] Among them, quadricyclane (QC)-norbornadiene (ND)[8] and hexamethyl(Dewar benzene) (HMDB)-hexamethylbenzene (HMB)[9] are well-known systems showing cycloreversion reactions via photoinduced redox chain processes. SET or even partial charge transfer (CT) from the highest occupied molecular orbitals (HOMO) of QC or HMDB is thought to weaken the most strained carbon–carbon bonds (C_2–C_6 or C_3–C_5 for QC; C_1–C_4 for HMDB) to lower activation energies for isomerizations.[10] Apparently, the strain release is one of the driving forces for such bond-cleavage reactions. Thus, conversions of QC to ND and of HMDB to HMB were observed under conditions with electron acceptors as sensitizers in both polar[8,9,11] and nonpolar solvents.[12] Particularly interesting observations have been made in the HMDB–HMB system. In polar solvents, the quantum efficiency (Φ) for the conversion of HMDB to HMB was greater than 1.0, clearly indicating the cation-radical chain process.[9] On the other hand, HMDB isomerizes to HMB through an exciplex with electron acceptor in nonpolar solvents.[12a,c] Although most of the photochemical reactions proceed diabatically to give ground-state products, some photoreactions having small activation energies on the excited surfaces are known to occur occasionally via adiabatic processes.[13] Valence isomerization of HMDB to HMB, which occurs through an exciplex, is the reaction of this category and provides the first example for a unique exciplex–exciplex isomerization.[12a,c]

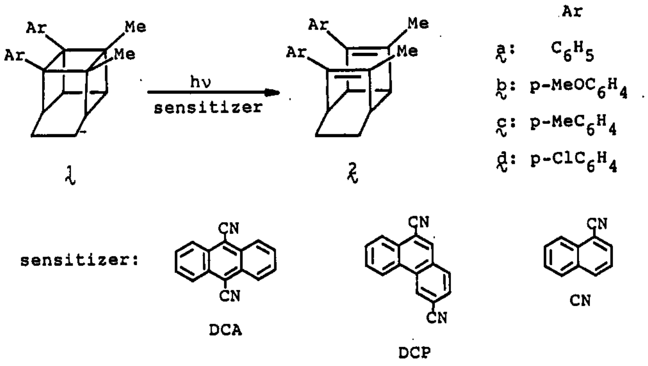


QC ND



HMDB HMB

Our studies on the photosensitized [2+2] cycloreversion reactions of arylated cage compounds 1 to dienes 2 have demonstrated that these compounds are suitable substrates for the investigation of SET and exciplex photochemistries since varying the substituent on phenyl groups can easily control their redox properties. Photosensitized isomerization of 1 to 2 proceeds by an efficient cation-radical chain mechanism in polar solvents.[14] We have also communicated that 1 isomerizes to 2 in nonpolar solvents by an



1 2

DCA DCP

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Table I. Photosensitized Isomerizations of Cage Compound 1a to Diene 2a[a]

entry	[1a]/mM	sens	10[sens]/mM	solv	[TMB][b]/mM	irrad time/min	conv of 1a to 2a[c]/%
1	35	DCA	4.0	MeCN	0	5	100
2	27	DCA	4.0	MeCN	25	5	8
3	35	DCA	4.6	C_6H_6	0	60	100
4	27	DCA	4.6	C_6H_6	25	60	69
5	35	DCP	5.9	C_6H_6	0	60	60
6	32	CN	65	C_6H_6	0	90	42

[a] Irradiated with light above 360 nm for DCA or above 300 nm for DCP and CN. [b] 1,2,4,5-Tetramethoxybenzene. [c] Determined by ^1H NMR analysis.

Table II. Limiting Quantum Yields (Φ_{lim}), Fluorescence Quenching Efficiencies ($k_q\tau$, k_q), Exciplex Emission Maxima (λ_{max}^{ex}, ν_{max}^{ex}) and Relative Intensities of Exciplex Emission for Photosensitized Cycloreversion Reaction of 1a to 2a

			$k_q\tau/M^{-1}$		$10^{-9}k_q/M^{-1}\ s^{-1}$				rel intens[c]	
sens ($E_{1/2}^{red\ a}$)	solv (E_T[b])	Φ_{lim} (i/s)	1a	2a	1a	2a	λ_{max}^{ex}/nm	$10^{-3}\nu_{max}^{ex}/cm^{-1}$	1a	2a
DCA (−0.95)	C_6H_{12} (31.2)		99	125			513	19.5	1.05	1.00
DCA	C_6H_6 (34.5)	1.1 (75)	94	120	7.6[e]	9.7[e]	542	18.5	0.52	0.52
DCA	Et_2O (34.6)		243	316			545	18.3	0.29	0.28
DCA	AcOEt (38.1)	1.3 (144)	158	182			575	17.4	0.02	0.02
DCA	$CHCl_3$ (39.1)		87	117			575	17.4	0.10	0.10
DCA	CH_2Cl_2 (41.1)		142	181	12.1[f]	15.5[f]	585	17.1	0.02	0.02
DCA	MeCN (46.0)	*d*	209	262	15.6[g]	19.6[g]	*i*			
DCP (−1.50)	C_6H_{12} (31.2)		85	97			420	23.8	0.71	1.00
DCP	C_6H_6 (34.5)	1.1 (39)	73	107	7.8[h]	11.4[h]	450	22.2	0.30	0.36
DCP	Et_2O (34.6)						451	22.2		
DCP	AcOEt (38.1)		100	119			472	21.2	0.15	0.19
DCP	$CHCl_3$ (39.1)						468	21.4		
DCP	CH_2Cl_2 (41.1)		90	115			478	20.9	0.17	0.18
CN (−1.90)	C_6H_6 (34.5)		50	75			400	25.0		

[a] Volts vs SCE in MeCN. [b] The transition energy (kcal/mol) for the charge-transfer band for pyridinium *N*-phenolbetaine. Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29. [c] I_{ex}/I_{mon} values for **1a** and **2a** are represented on the basis of the value of I_{ex}/I_{mon} for **2a** in cyclohexane. [d] See footnote 19. [e] τ = 12.4 ns: Ware, W. R.; Holmes, J. D.; Arnold, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 7861. [f] τ = 11.7 ns: Barber, R. A.; de Mayo, P.; Okada, K.; Wong, S. K. *Ibid.* **1982**, *104*, 4495. [g] τ = 13.4 ns, measured by oxygen quenching method of the fluorescence. [h] τ = 9.4 ns: Caldwell, R. A.; Ghali, N. I.; Chien, C. K.; DeMarco, D.; Smith, L. *J. Am. Chem. Soc.* **1978**, *100*, 2857. [i] No exciplex emission was observed.

adiabatic exciplex mechanism in a way similar to the HMDB–HMB system.[15] Adiabatic efficiencies (A_e) of the exciplex isomerization of 1 to 2 are in somes cases near 100%, whereas the maximum efficiency for the HMDB–HMB system is known to be 50%.[12c] To our knowledge, there are no reports beside these two systems for an adiabatic exciplex isomerization. Moreover, the systematic study focused on the influences of redox properties of electron donors as well as electron acceptors and solvent polarity on the adiabatic exciplex isomerization of a single system has not been so far conducted. We report herein the detailed results of the photosensitized isomerization of 1 to 2 using several solvents and sensitizers. The factors that control the efficiency of adiabatic exciplex isomerization are discussed.

Results and Discussion

Photosensitized reactions of a cage compound (**1a**) were explored with use of 9,10-dicyanoanthracene (DCA), 3,9-dicyanophenanthrene (DCP), and 1-cyanonaphthalene (CN) in acetonitrile and benzene (Table I). Complete conversion of **1a** to **2a** in benzene required longer irradiation time than that in acetonitrile (entries 1 and 3). Addition of 1,2,4,5-tetramethoxybenzene (TMB; $E_{1/2}^{ox}$ = +0.75 V vs SCE) into the solution efficiently quenched the reaction in acetonitrile while the degree of reaction quenching in benzene was rather low (entries 2 and 4). Similarly, both DCP and CN could sensitize the photoreactions of **1a** in benzene (entries 5 and 6). These preliminary observations imply that an efficient cation-radical chain reaction proceeds in acetonitrile (Scheme I).[16] The chain process in the DCA-sensitized reaction was confirmed by the fact that the double-reciprocal plots of the quantum yield (Φ) for the isomerization vs the concentration of **1a** ([**1a**]) gave a straight line with an intercept near to zero; the limiting quantum yield (Φ_{lim}) at infinite concentration is extremely high.[19] On the other hand, the isomerization of **1a** to **2a** in nonpolar solvent proceeded with Φ_{lim} a little over 1.0.[20] Double-reciprocal plots of the Φ vs [**1a**] for the reaction with DCA in benzene, in ethyl acetate, and with DCP in benzene afforded 1.1, 1.3, and 1.1 as Φ_{lim}, respectively. The values (i/s) obtained from the intercept (i) and slope (s) should be close to $k_q\tau$ values from sensitizer fluorescence quenching if the reactions proceed via typical singlet-sensitized mechanism.[21] In

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(15) Hasegawa, E.; Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1984**, *106*, 6852.

(16) Similar observations were obtained for photosensitized isomerization of **1a** to **2a** using quinones[14b] and pyrylium salts[14c,d] in acetonitrile. The possibility of efficient SET from **1a** to the excited singlet of DCA ($^1DCA^*$) is supported by the free energy change for this process (ΔG = −15 kcal/mol) obtained by the equation[17] $\Delta G = 23.06(E_{1/2}^{ox} - E_{1/2}^{red} - C) - E_{0,0}$. $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ represent the oxidation potential of **1a** ($E_{1/2}^{ox}$ = +1.36 V vs SCE) and the reduction potential of DCA ($E_{1/2}^{red}$ = −0.95 V vs SCE), respectively. $E_{0,0}$ is the singlet excitation energy of DCA (67 kcal/mol),[18] and C is the Coulomb term (0.06 eV).[17] The fluorescence of DCA was efficiently quenched by **1a** in acetonitrile ($k_q = 15.6 \times 10^9\ M^{-1}\ s^{-1}$).

(17) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(18) Eriksen, J.; Foote, C. S. *J. Phys. Chem.* **1978**, *82*, 2659.

(19) $\Phi^{-1} = 0.00476[\mathbf{1a}]^{-1} - 0.0173$ (r = 0.997) was obtained from the double-reciprocal plots of Φ and [**1a**] in acetonitrile (see the Experimental Section).

(20) Since the quantum yields of the isomerization are a little over 1.0, the free ion radicals, if those are formed, might participate into the ion-radical chain process ($2^{\bullet+} + 1 \rightarrow 2 + 1^{\bullet+}$) as a minor reaction path. Probably, the main fate of the contact-ion radical pair (sensitizer$^{\bullet-}$ − $2^{\bullet+}$) would be a back electron-transfer process. These considerations are compatible with high A_e values in a relatively polar solvent, such as ethyl acetate.

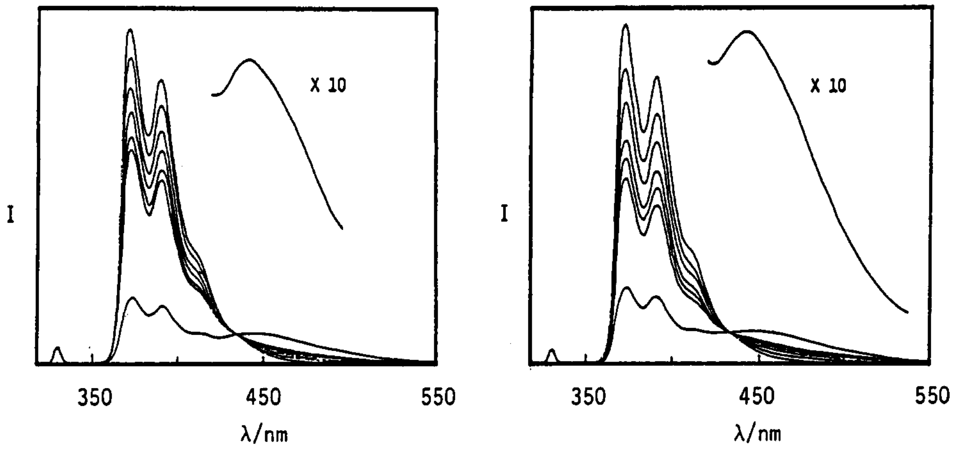

Figure 1. DCP fluorescence quenching by **1a** in benzene (left; [DCP] = 4.0 × 10^{-5} M; [**1a**] = 0, 1.63, 3.23, 4.80, 6.63, 7.97, 40.2 × 10^{-3} M) and by **2a** in benzene (right; [DCP] = 4.0 × 10^{-5} M; [**2a**] = 0, 1.57, 3.23, 4.90, 6.43, 8.07, 31.6 × 10^{-3} M).

Table III. Oxidation Potentials ($E_{1/2}^{ox}$) in Acetonitrile, Fluorescence Quenching Efficiencies ($k_q\tau$, k_q), Exciplex Emission Maxima (λ_{max}^{ex}, ν_{max}^{ex}), and Relative Intensities of Exciplex Emission for 1 and 2 in Benzene

		$k_q\tau/\mathrm{M}^{-1}$		$10^{-9}k_q/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$		λ_{max}^{ex}/nm		$10^{-3}\nu_{max}^{ex}/\mathrm{cm}^{-1}$		rel intens[b]	
compd	$E_{1/2}^{ox}$/V vs SCE	DCA	DCP	DCA	DCP	DCA	DCP	DCA	DCP	DCA	DCP
1a	+1.36	94	73	7.6	7.8	542	450	18.5	22.2	0.52	0.30
2a	+1.36	120	107	9.7	11.4	542	450	18.5	22.2	0.52	0.36
1b	+1.04	158	128	12.7	13.6	*a*	510		19.6		0.17
2b	+1.03	205	190	16.5	20.2	*a*	510		19.6		0.16
1c	+1.26	123	92	9.9	9.8	568	468	17.6	21.4	0.19	0.23
2c	+1.26	167	132	13.5	14.0	568	468	17.6	21.4	0.19	0.25
1d	+1.42	71	44	5.7	4.7	530	445	18.9	22.5	0.42	0.10
2d	+1.43	101	81	8.1	8.6	530	445	18.9	22.5	0.43	0.13

[a] No exciplex emission was observed. [b] I_{ex}/I_{mon} values for 1 and 2 are represented on the basis of the value of I_{ex}/I_{mon} for **2a** in cyclohexane.

above cases, values of 75, 144, and 39 M^{-1} were obtained for i/s while $k_q\tau$ values of 94, 158, and 73 M^{-1} were obtained respectively (Table II).

Scheme I

$$\text{sensitizer} \xrightarrow{h\nu} {}^{1}\text{sensitizer}^{*}$$

$$ {}^{1}\text{sensitizer}^{*} + \mathbf{1} \rightarrow \text{sensitizer}^{\bullet -} + \mathbf{1}^{\bullet +}$$

$$\mathbf{1}^{\bullet +} \rightarrow \mathbf{2}^{\bullet +}$$

$$\mathbf{2}^{\bullet +} + \mathbf{1} \rightarrow \mathbf{2} + \mathbf{1}^{\bullet +}$$

$$\text{sensitizer}^{\bullet -} + \mathbf{2}^{\bullet +} \rightarrow \text{sensitizer} + \mathbf{2}$$

Sensitizer fluorescence quenching experiments provided another interesting observation. A weak and new emission (542 nm) was observed in DCA fluorescence quenching by **1a** in benzene. When DCP was used as a sensitizer, a much stronger, broad, and structureless emission characteristic of an exciplex was clearly observed at 450 nm with an isoemissive point at 435 nm (left in Figure 1). Interestingly, a quite similar exciplex emission possessing the same emission maximum (450 nm) was observed in DCP fluorescence quenching by **2a** (right in Figure 1). To rule out the possibility of accidental coincidence of the exciplex emission maxima between **1a** and **2a**, fluorescence quenching experiments were conducted in several other solvents (Table II). Even in relatively polar solvents such as ethyl acetate and methylene chloride, weak exciplex emissions were also observed. No exciplex emission was observed in acetonitrile. The exciplex emission maximum was found to be red-shifted when the solvent becomes molar polar; plots of the wavenumber of exciplex emission (ν_{max}^{ex}) vs $[(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)]$[22] gave $\simeq$11 D as a dipole moment for the observed exciplex. It is quite interesting to notice that the exciplex emission maxima obtained from **1a** completely superimpose with those obtained from **2a** in all solvents used. Agreements of the exciplex maxima between the cage compounds **1** and dienes **2** were also observed in a series of substituted compounds (**1b–d**, **2b–d**), although their quenching efficiencies ($k_q\tau$, k_q) of sensitizer fluorescence were different from each other (Table III). These results clearly suggest that the observed emissions are of the sensitizer–**2** exciplexes[23] formed after very rapid adiabatic isomerization of **1** in the sensitizer–**1** exciplexes (Scheme II).

Scheme II

$$\text{sensitizer} \xrightarrow{h\nu} {}^{1}\text{sensitizer}^{*}$$

$$ {}^{1}\text{sensitizer}^{*} + \mathbf{1} \rightarrow {}^{1}(\text{sensitizer–}\mathbf{1})^{*}$$

$$ {}^{1}(\text{sensitizer–}\mathbf{1})^{*} \rightarrow \text{sensitizer} + \mathbf{1}$$

$$ {}^{1}(\text{sensitizer–}\mathbf{1})^{*} \rightarrow {}^{1}(\text{sensitizer–}\mathbf{2})^{*}$$

$$ {}^{1}(\text{sensitizer–}\mathbf{1})^{*} \rightarrow \text{sensitizer} + \mathbf{2}$$

$$ {}^{1}(\text{sensitizer–}\mathbf{2})^{*} \rightarrow \text{sensitizer} + \mathbf{2}$$

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(21) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 71.

(22) (a) Mataga, N.; Okada, T.; Yamamoto, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2562. (b) Mataga, N.; Okada, T.; Yamamoto, N. *Chem. Phys. Lett.* **1967**, *1*, 119. (c) Beens, H.; Knibbe, H.; Weller, A. *J. Phys. Chem.* **1967**, *47*, 1183.

(23) One may suspect that the exciplex emission maxima for **1** were accidentally the same as those for **2** since their electron-donating abilities are quite similar to each other (compare $E_{1/2}^{ox}$). However, we feel that the exciplex emissions for **1**, if those are observed, would exist in a shorter wavelength region than those for **2**, considering the fact that CT absorption for **1b** and tetracyanoethylene (TCNE) in methylene chloride was observed in an obviously different region (λ_{max} = 700 nm) from that for **2b** (λ_{max} = 740 nm).[14b]

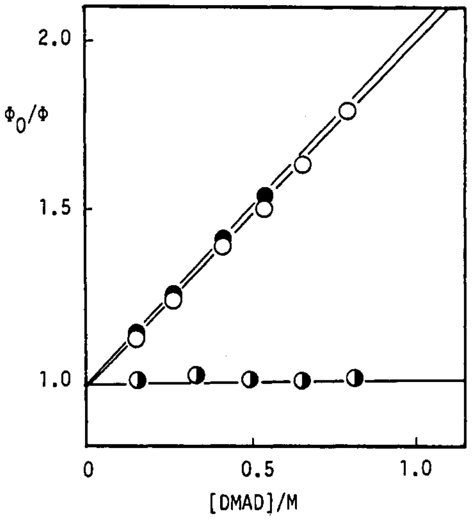

Figure 2. Stern–Volmer plots for exciplex emission quenching (○ for **1a**, ● for **2a**) and reaction quenching (◑) by DMAD for DCA with **1a** and **2a** in benzene.

In this context, it is also interesting to compare the emission intensities of the exciplexes formed from **1** with those from **2**. The intensity ratio of sensitizer–**2a** exciplex vs monomer (sensitizer) fluorescence at the concentration of **2a** that quenches about 50% of monomer fluorescence is dependent on the solvent polarity (E_T); the relative value based on that for **2a** in cyclohexane as a standard of intensity ratio of the exciplex decreases as the solvent polarity increases as shown in Table II. These observations suggest that the increase in the solvent polarity affects the electronic structure of the exciplex and leads the transformation into the contact-ion-radical pairs (CIRP).[6,20] Furthermore, the relative intensity of sensitizer–**2** exciplex varies depending on the substituent of the phenyl groups (Table III). Similar solvent and substituent effects on the relative intensity of the exciplex emission formed from **1** were observed (Tables II and III). The relative intensities from **1** are similar to those from **2** in many cases. These results suggest the occurrence of highly efficient adiabatic exciplex isomerization.

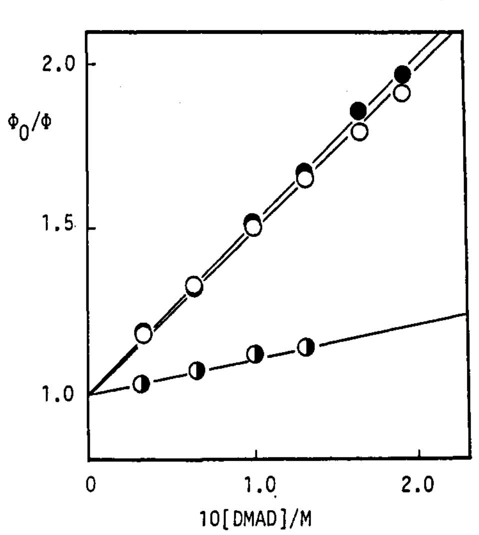

Figure 3. Stern–Volmer plots for exciplex emission quenching (○ for **1a**, ● for **2a**) and reaction quenching (◑) by DMAD for DCP with **1a** and **2a** in benzene.

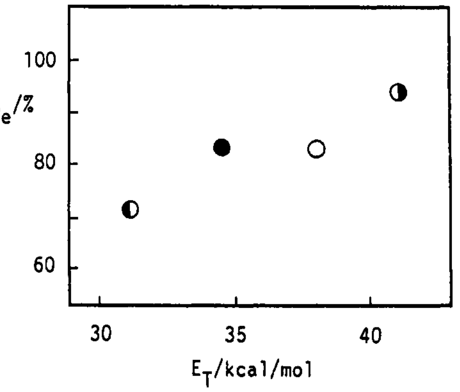

Figure 4. Plots of adiabatic efficiencies (A_e) for DCP and **1a** vs solvent E_T values (see footnote *b* in Table II; ◐ for C_6H_{12}; ● for C_6H_6; ○ for AcOEt; ◑ for CH_2Cl_2).

Table IV. Adiabatic Efficiencies (A_e) in Photosensitized Isomerizations of Cage Compounds 1 to Dienes 2

cage compd ($E_{1/2}^{\text{ox}\,a}$)	solv ($E_T{}^b$)	A_e/% sensitizer ($E_{1/2}^{\text{red}\,a}$) DCA(−0.95)	DCP(−1.50)	CN(−1.90)
1a (+1.36)	C_6H_{12} (31.2)	100	71	
1a	C_6H_6 (34.5)	100	82	60
1a	Et_2O (34.6)	100		
1a	AcOEt (38.1)	90	81	
1a	$CHCl_3$ (39.1)	99		
1a	CH_2Cl_2 (41.1)	99	94	
1b (+1.04)	C_6H_6 (34.5)		100	
1c (+1.26)	C_6H_6 (34.5)	95	97	
1d (+1.42)	C_6H_6 (34.5)	96	74	

[a] Volts vs SCE in MeCN. [b] Kilocalories per mole. See footnote *b* in Table II.

To obtain definitive experimental support for the adiabatic exciplex isomerization, quenching experiments of the exciplex were conducted. Since Caldwell and coworkers have reported that dimethyl acetylenedicarboxylate (DMAD) quenched the exciplexes through CT interaction,[24] we applied this method to our systems. As results, it was found that DMAD quenched the exciplex emission of **1a** and **2a** with nearly the same efficiency for DCA ($k_q\tau$ = 1.0 M^{-1} for **1a** and 1.1 M^{-1} for **2a**; Figure 2) and for DCP ($k_q\tau$ = 4.9 M^{-1} for **1a** and 5.0 M^{-1} for **2a**; Figure 3). Quenching of monomer fluorescence was negligible for DCA and was inefficient ($k_q\tau \simeq 0.15$ M^{-1}) for DCP in the concentration range of DMAD used. In contrast to exciplex emission quenching, almost no quenching was observed for DCA-sensitized isomerization of **1a** to **2a** (Figure 2) while DCP-sensitized reaction was quenched with low efficiency ($k_q\tau$ = 1.1 M^{-1}; Figure 3). The observations that (1) nearly the same efficiencies were obtained in the exciplex emission quenching both for **1a** and **2a**[25] and (2) the efficiency of the reaction quenching was even lower than that of emission quenching are interpreted by the proposal that the emissive exciplex is that of **2a** with sensitizer, which is generated by an adiabatic isomerization of a short-lived exciplex of **1a** with sensitizer.

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(24) (a) Caldwell, R. A.; Smith, L. *J. Am. Chem. Soc.* **1974**, *96*, 2994. (b) Caldwell, R. A.; Creed, D.; DeMarco, D. C.; Melton, L. A.; Ohta, H.; Wine, P. H. *Ibid.* **1980**, *102*, 2369.

(25) Exciplex emission quenchings were also conducted using 1,4-dimethoxybenzene (DMB) as a quencher. The situation is rather complicated in this case since DMB is a more efficient quencher ($k_q\tau$ = 178 M^{-1} in benzene) than **1a** ($k_q\tau$ = 94 M^{-1}) toward ^{1}DCA*. Therefore, relative intensities of exciplex emissions at varied concentrations of DMB were corrected for DCA monomer fluorescence quenching by DMB.[24] Then, 47.5 and 47.9 M^{-1} were obtained in benzene as slopes of Stern–Volmer plots for DCA–**1a** and for DCA–**2a** systems, respectively.

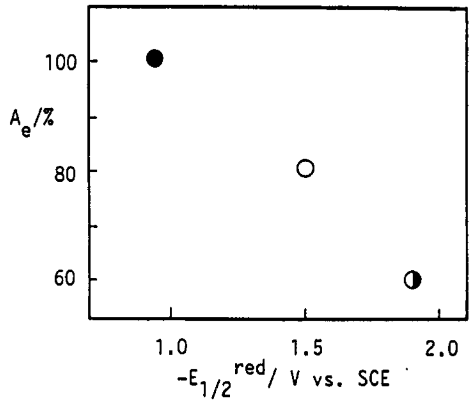

Figure 5. Plots of adiabatic efficiencies (A_e) for **1a** in benzene vs reduction potentials ($E_{1/2}^{red}$) of sensitizers (● for DCA; ○ for DCP; ◑ for CN).

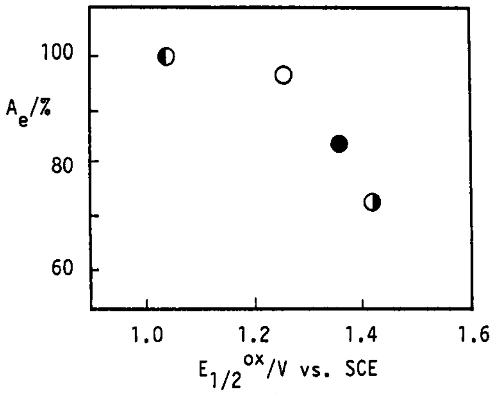

Figure 6. Plots of adiabatic efficiencies (A_e) for DCP in benzene vs oxidation potentials ($E_{1/2}^{ox}$) of cage compounds **1** (● for **1a**; ◐ for **1b**; ○ for **1c**; ◑ for **1d**).

Efficiencies of the adiabatic process for exciplex isomerization of **1** to **2** were obtained in several solvents by applying the method reported by Jones for the HMDB–HMB system[12c] (Table IV). Taylor first observed that the ratio of emission intensities upon CN fluorescence quenching by HMDB and HMB increased with solvent polarity; the maximum value of 28% as I_{ex}(HMDB) to I_{ex}(HMB) was observed in dimethoxyethane.[12a] Jones obtained 72% as A_e for the HMDB–HMB system on excitation of CT complex of HMDB and fumaronitrile in isopropyl ether[11d] while the A_e value for exciplex isomerization of HMDB to HMB never exceeded 50% in cyclohexane.[12c] In the case of **1a**, quite high A_e values (>90%) were obtained for DCA in all solvents used. In DCP sensitization, the A_e value increased (71–100%) as solvent became more polar (Figure 4) as have been observed by Taylor[12a] and Jones[12c] in the HMDB–HMB system. More polar solvents that can stabilize CT character appear to favor adiabatic exciplex isomerization. Redox potentials ($E_{1/2}^{red}$ and $E_{1/2}^{ox}$) of electron acceptors and donors can control the degree of CT interaction in exciplexes. An increase in $E_{1/2}^{red}$ of sensitizer, making it a better electron acceptor, resulted in a high A_e value for the conversion of **1a** to **2a** (Figure 5). For instance, when DCA was used as a sensitizer in benzene, the high A_e values over 95% were obtained for **1** (Table IV). On the other hand, the higher yield for an adiabatic process was obtained as $E_{1/2}^{ox}$ of **1** decreases, that is, as it becomes a better electron donor for DCP (Figure 6). These observations suggest that CT interaction between **1** and sensitizer is a crucial factor for an efficient adiabatic process.

Table V. Photosensitized Isomerization of Cage Ketone 3 to Dienone 4 in Benzene[a]

entry	sens	[TMB]/mM	irrad time/min	conv of **3** to **4**[b]/%
1	DCA	0	5	100
2	DCA	10	5	22
3	DCP	0	180	23
4	DCP	10	180	17

[a] Irradiated with light above 360 nm similar to photosensitized reactions of **1**. [**3**] = 10 mM; [DCA] = 0.98 mM; [DCP] = 0.50 mM. [b] Determined by ^{1}H NMR analysis.

We have previously shown by means of the CIDNP technique that the cation radical of **1a** has a shallow energy minimum on the potential energy surface and undergoes very rapid cycloreversion to the cation radical of **2a**.[26] Increasing CT interaction in the exciplex of **1** leads to the greater resonance contribution[27] of the SET state, which has a smaller activation energy for the cycloreversion than the corresponding neutral one.[28] The higher A_e values obtained in exciplexes possessing greater CT interaction would be partly due to this kinetic factor. Furthermore, the following thermodynamic factor should also be important. In the adiabatic isomerization, the product exciplex should be stable enough to be favorably produced at the same time as the completion of the isomerization. Therefore, the product exciplex must have lower energy than the reactant exciplex. The energies (H_{ex}) of exciplexes may be roughly estimated by the redox potentials and heats of formation of the neutral components.[29] Therefore, the energy difference (ΔH_{ex}(P,R)) between the product (P) and the reactant (R) exciplexes consisting of the same sensitizer (S) may be expressed by the eq 1, where

$$\Delta H_{ex}(\mathrm{P,R}) = H_{ex}(\mathrm{S{-}P}) - H_{ex}(\mathrm{S{-}R}) = \Delta H(\mathrm{P,R}) + \Delta E_{1/2}^{ox}(\mathrm{P,R}) \quad (1)$$

H_{ex}(S–P) and H_{ex}(S–R) are exciplex energies of the product and the reactant exciplexes, respectively; ΔH(P,R) and $\Delta E_{1/2}^{ox}$(P,R) are the differences of heat of formations and oxidation potentials between product and reactant, respectively. In the present case, **1**–**2**, $\Delta H(\mathrm{P,R}) \simeq -32$ kcal/mol[30c] and $23.06\Delta E_{1/2}^{ox}(\mathrm{P,R}) = 0$–$0.2$ kcal/mol. Therefore, the transformation of cage exciplex to diene exciplex is thermodynamically favorable.[31] The high exothermicity as well as the small activation energy for the exciplex isomerization apparently accelerates the adiabatic exciplex isomerization. In addition to the above factors, it should be also noted that the substrate must be consecutively bound with sensitizer for an adiabatic exciplex isomerization.[12a,c] In other words, an efficient CT interaction between sensitizer and substrate in the exciplex

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(26) Roth, H. D.; Schilling, M. L. M.; Mukai, T.; Miyashi, T. *Tetrahedron Lett.* **1983**, *24*, 5815.

(27) (a) Förster, T. *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 1. (b) Weller, A. *Ibid.* p 23.

(28) Mukai, T.; Yamashita, Y. *Tetrahedron Lett.* **1978**, 357.

(29) The exciplex energy (H_{ex}) discussed here should not be same as the excitation energy[27] of the exciplex, which does not account for heats of formations of each component.

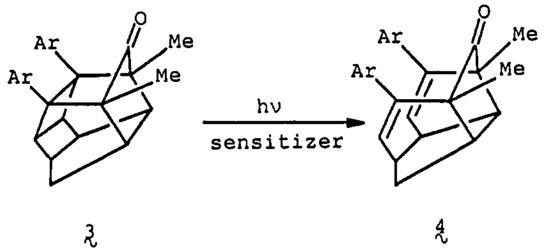
(30) (a) $-\Delta H$ = 21.2 kcal/mol for QC–ND: Kabakoff, D. S.; Bunzli, J. C. G.; Oth, J. F. M.; Hammond, W. B.; Berson, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1510. (b) $-\Delta H$ = 59.5 kcal/mol for HMDB–HMB: Oth, J. F. M. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1185. (c) $-\Delta H$ = 32 kcal/mol for **1c**–**2c** was obtained by differential thermal analysis: Miyashi, T.; Mukai, T. Unpublished result.

(31) It may be of interest to compare ΔH_{ex}(P,R) values of other exciplex isomerization systems. The values of ΔH_{ex}(P,R) are −32 kcal/mol for the **1**–**2** system, −59 kcal/mol[9,30b] for the HMDB–HMB system, and −6 kcal/mol[30a,32] for the QC–ND system. In the QC–ND case, the emission from product exciplex was not observed.[12a] This may be due to the low exothermicity in the exciplex conversion of QC to ND.

(32) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308.

must be maintained during isomerization. Therefore, $E_{1/2}^{\mathrm{ox}}$ values of product as well as reactant should be low, and the $\Delta E_{1/2}^{\mathrm{ox}}$(P,R) value should not be highly positive.

Considerable interest in the correlation between the A_e value and $\Delta E_{1/2}^{\mathrm{ox}}$(P,R) led us to explore another example of adiabatic exciplex isomerization. Recently, we have found that arylated cage ketone **3**[33] ($E_{1/2}^{\mathrm{ox}}$ = +1.10 V vs SCE) isomerizes to dienone **4** ($E_{1/2}^{\mathrm{ox}}$ = +1.25 V vs SCE) upon photosensitized irradiation with DCA and DCP (Table V). Oxidation potentials of **3** and **4** and fluorescence quenching data[34] indicated that these substances would be as good electron donors as **1** and **2**. Similar to the **1**–**2** system, the exciplex emission ($\lambda_{\max}^{\mathrm{ex}}$ = 485 nm) observed on DCP fluorescence quenching by **3** in benzene was identical with that for DCP and **4** although the intensity of the former emission was apparently lower than that of the latter one. The A_e value for DCP in benzene was obtained to be 39% from the exciplex emission intensities at the same stage of monomer fluorescence quenching. Calculations of $\Delta E_{1/2}^{\mathrm{ox}}$(P,R) values for **1**–**2**, HMDB–HMB, **3**–**4**, and QC–ND gave 0–0.01, 0.04,[9] 0.15, and 0.65 V,[32] respectively. The A_e value has a tendency to decrease in the order named. Increase in $\Delta E_{1/2}^{\mathrm{ox}}$(P,R) is apparently disadvantageous for an adiabatic exciplex isomerization since this may lead to (1) the weaker binding of sensitizer with product than that with reactant[12a] and (2) the decrease in exothermicity for the CT reaction compared to the neutral reaction,[31] which may also cause the increase in activation energy.

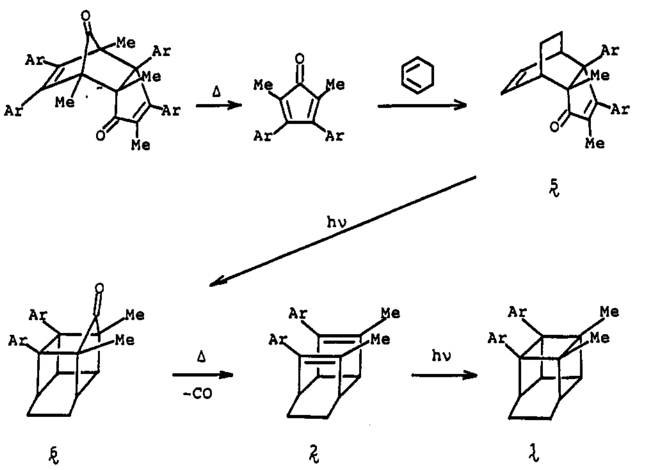


Ar = p-MeOC$_6$H$_4$

Conclusion

We have found that cage compounds **1** adiabatically isomerize to dienes **2** through exciplex formation with some cyanoaromatics. Notably, efficiencies of the adiabatic process for the reaction reached about 100% under conditions employing moderately polar solvents and better electron acceptors. We were able to study the effect of electron-donating ability of substrate on the adiabatic process systematically by varying the substituent on phenyl groups of **1** and **2**, which must be a particular advantage of the cage compound **1**–diene **2** system, unlike other systems. As a result, we conclude the following factors to be important for efficient adiabatic exciplex isomerization: (1) a sufficient CT from reactant to sensitizer in the exciplex, which lowers the activation energy, (2) a high exothermicity in the exciplex transformation, which can be achieved by the large difference of heat of formation and the similar electron-donor character between reactant and product, and (3) high and similar electron-donating abilities of product as well as reactant, which can lead to consecutive binding with sensitizer by CT interaction during isomerization.

Scheme III



Experimental Section

General Procedures. All melting points are uncorrected. UV spectra were recorded on a Hitachi 340 spectrometer. Fluorescence spectra were measured on a Hitachi MPF-4 spectrophotometer equipped with Ushio 150-W Xe lamp. ^{1}H NMR were obtained at 60 MHz on a Varian EM-360, at 90 MHz on a Varian EM-390, or at 100 MHz on a JEOL PS 100 spectrometer. ^{13}C NMR spectra were obtained at 50 MHz on a Varian XL-200 spectrometer. NMR multiplicities were reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra (MS) were recorded on a Hitachi M-52 mass spectrometer. Elemental analyses were performed by the Instrumental Analyses Center for Chemistry, Faculty of Science, Tohoku University. Redox potentials ($E_{1/2}^{\mathrm{ox}}$ and $E_{1/2}^{\mathrm{red}}$; V vs SCE) were measured on a Yanaco P-1000 voltammetric analyzer by cyclic voltammetry (Pt electrode, scan rate 100 mV/s) in acetonitrile containing tetraethylammonium perchlorate (0.1 M). All of **1** and **2** gave irreversible waves, and their $E_{1/2}^{\mathrm{ox}}$ were obtained as anodic peak potential − 0.03 V, assuming one-electron oxidation process.

9,10-Dicyanoanthracene (DCA) was prepared[35] and purified by sublimation and recrystallization from benzene. 3,9-Dicyanophenanthrene (DCP) was prepared[36] and purified by sublimation and recrystallized from chlorobenzene. 1-Cyanonaphthalene (CN) was commercially available and was sublimed prior to use. 1,2,4,5-Tetramethoxybenzene (TMB) was prepared[37] and recrystallized from methanol. Dimethyl acetylenedicarboxylate (DMAD) was commercially available and was distilled before use. Acetonitrile was distilled over phosphorus pentoxide and then calcium hydride. Benzene was treated with concentrated sulfuric acid, 5% aqueous sodium hydroxide, and calcium chloride and then distilled over calcium hydride. Other solvents were spectroscopic grade and were used without further purification.

Preparation of Cage Compounds 1 and Dienes 2. Cage compounds **1** were synthesized by the sequence shown in Scheme III.[28,38] Dienones **5** were obtained by Diels–Alder reaction of 2,5-dimethyl-3,4-diarylcyclopentadienones, which were generated in situ by decomposition of corresponding dimers, and 1,3-cyclohexadiene followed by Cope rearrangement. Direct irradiation of **5** afforded cage ketones **6**. Thermal decarbonylation of **6** and subsequent irradiation of resulting dienes **2** produced cage compounds **1**. Typical experiments for **1a** and **2a** are described below.

Preparation of Dienone 5a. A solution of 898 mg (1.72 mmol) of 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer[39] and 940 mg (11.73 mmol) of 1,3-cyclohexadiene in 4 mL of tetrachloroethylene was refluxed under nitrogen for 20 h. The red oil ob-

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[33] Yamashita, Y.; Ikeda, H.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 6682.

[34] Fluorescence quenching efficiencies ($k_q\tau$) in benzene were the following: DCA, 130 M^{-1} for **3**, 171 M^{-1} for **4**; DCP, 105 M^{-1} for **3**, 135 M^{-1} for **4**.

[35] Beyer, H.; Fritsch, H. *Chem. Ber.* **1941**, *74*, 494.

[36] Caldwell, R. A.; Ghali, N. I.; Chien, C. K.; DeMarco, D.; Smith, L. *J. Am. Chem. Soc.* **1978**, *100*, 2857.

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[39] Allen, C. F. H.; von Allan, J. *J. Am. Chem. Soc.* **1942**, *64*, 1260.

tained after removal of solvent in vacuo was chromatographed on a silica gel column (Wakogel Q-22). Elution with benzene–petroleum ether (1:1) gave 320 mg (27%, mp 161 °C) of a Diels–Alder cycloadduct. Elution with benzene–ether (8:2) gave 810 mg (69%) of **5a** as colorless solid. Recrystallization from methanol–benzene gave pure **5a** as colorless prisms. **5a** was also obtained in good yield by refluxing in toluene instead of tetrachloroethylene: mp 162–163 °C; IR (KBr; ν/cm^{-1}) 3050, 2950, 1688, 1635, 1370, 1325, 745, 700, 694; UV (ethanol; λ/nm (log ϵ)) 262 (4.08), 268 (4.09), 274 (sh, 4.07); MS (25 eV, 80 °C; *m/e* (relative intensity)) 340 (M$^+$, 12), 312 (48), 261 (19), 260 (M$^+$ − C$_6$H$_8$, 100), 232 (16); ^{1}H NMR (CDCl$_3$, 60 MHz; δ) 0.97 (s, 3 H), 1.00–1.40 (m, 2 H), 1.70 (s, 3 H), 1.70–2.20 (m, 2 H), 2.55 (m, 1 H), 2.97 (m, 1 H), 5.83–6.25 (m, 2 H), 6.30–6.50 (m, 2 H), 7.00–7.30 (m, 8 H); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 9.26 (q), 19.04 (t), 21.40 (q), 21.45 (t), 35.15 (d), 43.15 (d), 53.81 (s), 61.72 (s), 126.60 (d), 127.76 (d, 2 C), 127.88 (d, 2 C), 128.15 (d), 128.22 (d, 2 C), 130.47 (d, 2 C), 131.55 (d), 134.45 (d), 135.67 (s), 138.62 (s), 138.87 (s), 173.49 (s), 213.75 (s). Anal. Calcd for C$_{25}$H$_{24}$O: C, 88.20; H, 7.10. Found: C, 88.08; H, 7.28.

Preparation of Cage Ketone 6a. A solution of 700 mg (2.06 mmol) of **5a** in 300 mL of methanol was irradiated through a Pyrex filter with Rayonet RUL-3500 Å lamps under nitrogen for 2 h. Removal of methanol gave 700 mg (100%) of colorless solid (mp 125–127 °C), which was recrystallized from chloroform–ethanol to give **6a** as colorless columns: mp 134 °C; IR (KBr; ν/cm^{-1}) 3050, 2950, 1688, 1635, 1370, 1325, 745, 700, 694; UV (cyclohexane; λ/nm (log ϵ)) 225 (4.06), 255 (sh, 2.76), 262 (2.76), 268 (sh, 2.67), 273 (2.54); MS (13.5 eV, 80 °C; *m/e* (relative intensity)) 340 (M$^+$, 2), 313 (35), 312 (M$^+$ − CO, 100); ^{1}H NMR (CDCl$_3$, 100 MHz; δ) 0.87 (s, 3 H), 1.19 (s, 3 H), 1.50–2.00 (m, 4 H), 2.09 (m, 1 H), 2.46 (dd, 1 H, *J* = 5.5, 5.0 Hz), 3.31 (m, 1 H), 3.38 (dd, 1 H, *J* = 5.5, 5.5 Hz), 6.79–7.18 (m, 10 H); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 9.79 (q), 11.76 (q), 15.39 (t), 16.65 (t), 33.64 (d), 36.06 (d), 37.40 (d), 38.74 (d), 50.57 (s), 51.92 (s), 56.67 (s), 56.85 (s), 125.71 (d), 125.96 (d), 127.16 (d, 2 C), 127.20 (d, 2 C), 127.42 (d, 2 C), 127.60 (d, 2 C), 136.60 (s), 139.43 (s), 219.76 (s). Anal. Calcd for C$_{25}$H$_{24}$O: C, 88.20; H, 7.10. Found: C, 87.96; H, 7.11.

Preparation of Diene 2a. A solution of 1.42 g (4.17 mmol) of **6a** in 40 mL of dry benzene was passed through a quartz column heated at 480 °C under nitrogen. Evaporation of benzene in vacuo gave 1.3 g of crude **2a** as yellow oil, which was crystallized from ethanol to give 1.00 g (77%) of **2a**. Recrystallization from benzene–ethanol gave pure **2a** as colorless needles. **2a** was also obtained in a similar yield by heating of neat **6a** under nitrogen at above 300 °C: mp 56–57 °C; IR (KBr; ν/cm^{-1}) 3050, 2900, 1650, 1596, 1490, 1440, 770, 755, 735, 692, 680; UV (cyclohexane; λ/nm (log ϵ)) 251 (4.34), 268 (sh, 4.18), 280 (sh, 3.90), 296 (sh, 2.62); MS (25 eV, 90 °C; *m/e* (relative intensity)) 313 (M$^+$ + 1, 26), 312 (M$^+$, 100), 297 (24), 182 (23), 170 (12), 169 (23), 168 (12), 143 (12), 142 (11), 129 (27), 102 (10), 91 (10); ^{1}H NMR (CDCl$_3$, 100 MHz; δ) 1.53–1.62 (br s, 4 H), 1.80 (s, 3 H), 1.90 (t, 3 H, *J* = 1.5 Hz), 2.46–2.64 (m, 2 H), 2.83–2.97 (m, 2 H), 6.70–6.85 (m, 2 H), 6.92–7.30 (m, 8 H); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 14.24 (q), 18.51 (q), 24.36 (t), 25.60 (t), 39.92 (d), 40.57 (d), 42.46 (d), 44.84 (d), 125.25 (d), 125.91 (d, 2 C), 126.17 (d), 127.41 (d, 2 C), 128.14 (d, 2 C), 128.46 (d, 2 C), 132.26 (s), 134.79 (s), 135.69 (s), 139.96 (s), 140.73 (s), 141.58 (s). Anal. Calcd for C$_{24}$H$_{24}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.88.

Preparation of Cage Compound 1a. A solution of 350 mg (1.12 mmol) of **2a** in 300 mL of dry ether was irradiated through a quartz filter with Rayonet RUL-3000 Å lamps under nitrogen for 2 h. Ether was evaporated in vacuo at room temperature to give 350 mg of yellow oil, which was crystallized from ethanol to give 242 mg (69%) of crude **1a**. Recrystallization from benzene–ethanol gave pure **1a** as colorless prisms: mp 63–64 °C; IR (KBr; ν/cm^{-1}) 2950, 1600, 1490, 1440, 760, 730, 695; UV (cyclohexane; λ/nm (log ϵ)) 240 (sh, 4.05), 270 (sh, 3.21); MS (25 eV, 90 °C; *m/e* (relative intensity)) 313 (M$^+$ + 1, 12), 312 (M$^+$, 100), 297 (27), 221 (10), 182 (48), 170 (21), 169 (64), 168 (49), 167 (20), 143 (25), 142 (38), 141 (12), 129 (49), 91 (56); ^{1}H NMR (CDCl$_3$, 100 MHz; δ) 0.79 (s, 3 H), 1.32 (s, 3 H), 1.50–2.00 (m, 4 H), 2.35 (m, 1 H), 2.81 (dd, 1 H, *J* = 6.9, 6.0 Hz), 2.98 (m, 1 H), 3.14 (dd, 1 H, *J* = 6.9, 6.9 Hz), 6.80–7.20 (m, 10 H); ^{13}C NMR (CDCl$_3$, 50 MHz, δ) 11.67 (q), 15.00 (t), 15.09 (q), 17.47 (t), 36.54 (d), 37.61 (d), 38.46 (d), 39.84 (d), 47.58 (s), 53.19 (s), 58.26 (s), 61.03 (s), 125.18 (d), 125.40 (d), 126.88 (d, 2 C), 127.17 (d, 2 C), 127.31 (d, 2 C), 127.99 (d, 2 C), 140.08 (s), 142.60 (s). Anal. Calcd for C$_{24}$H$_{24}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.87.

Dienes **2b–d** and cage compounds **1b–d** were similarly synthesized. Physical data for those compounds are as follows.

2b: mp 83–84 °C (chloroform–methanol); colorless crystal; IR (KBr; ν/cm^{-1}) 2950, 2900, 2870, 1610, 1570, 1510, 1460, 1280, 1255, 1170, 1030, 818; UV (cyclohexane; λ/nm (log ϵ)) 255 (4.44), 270 (sh, 4.32), 300 (sh, 3.44), 310 (sh, 3.01); MS (25 eV, 90 °C; *m/e* (relative intensity)) 373 (M$^+$ + 1, 33), 372 (M$^+$, 100), 357 (11); ^{1}H NMR (CDCl$_3$, 60 MHz; δ) 1.56 (br s, 4 H), 1.80 (s, 3 H), 1.89 (br s, 3 H), 2.54 (m, 2 H), 2.88 (m, 2 H), 3.69 (s, 3 H), 3.76 (s, 3 H), 6.63 (d, 2 H, *J* = 9.5 Hz), 6.82 (d, 2 H, *J* = 9.0 Hz), 6.84 (d, 2 H, *J* = 9.5 Hz), 7.25 (d, 2 H, *J* = 9.0 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 14.07 (q), 18.54 (q), 24.39 (t), 25.62 (t), 39.94 (d), 40.74 (d), 42.51 (d), 44.87 (d), 55.15 (q), 55.25 (q), 112.90 (d, 2 C), 113.68 (d, 2 C), 127.15 (d, 2 C), 128.94 (s), 129.50 (d, 2 C), 131.51 (s), 134.16 (s), 134.33 (s), 138.23 (s), 139.37 (s), 157.23 (s), 157.96 (s). Anal. Calcd for C$_{26}$H$_{28}$O$_2$: C, 83.83; H, 7.58. Found: C, 83.76; H, 7.68.

1b: mp 97.5–98 °C (acetone); colorless crystal; IR (KBr; ν/cm^{-1}) 2920, 2830, 1615, 1510, 1460, 1285, 1240, 1175, 1030, 820, 795; UV (cyclohexane; λ/nm (log ϵ) 233 (3.98), 272 (sh, 3.52), 282 (sh, 3.46), 288 (sh, 3.32); MS (25 eV, 90 °C; *m/e* (relative intensity)) 373 (M$^+$ + 1, 18), 372 (M$^+$, 100), 357 (20), 199 (11), 198 (10), 173 (16), 132 (15), 121 (13); ^{1}H NMR (C$_6$D$_6$, 60 MHz; δ) 0.93 (s, 3 H), 1.27 (s, 3 H), 1.56–2.00 (m, 4 H), 2.32 (m, 1 H), 2.79 (dd, 1 H, *J* = 6.0, 6.0 Hz), 3.00–3.30 (m, 2 H), 3.26 (s, 3 H), 3.31 (s, 3 H), 6.60–7.30 (m, 8 H); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 11.57 (q), 15.02 (t), 15.12 (q), 17.40 (t), 36.45 (d), 37.54 (d), 38.36 (d), 39.65 (d), 47.51 (s), 52.95 (s), 55.01 (q), 55.13 (q), 57.39 (s), 60.42 (s), 112.78 (d, 2 C), 113.51 (d, 2 C), 127.90 (d, 2 C), 128.14 (d, 2 C), 132.17 (s), 135.01 (s), 157.09 (s), 157.38 (s). Anal. Calcd for C$_{26}$H$_{28}$O$_2$: C, 83.83; H, 7.58. Found: C, 83.78; H, 7.82.

2c: mp 78.5–79 °C (ethanol); colorless prisms; IR (KBr; ν/cm^{-1}) 2940, 2900, 2870, 1510, 1445, 818; UV (acetonitrile; λ/nm (log ϵ)) 253 (4.44); MS (25 eV, 90 °C; *m/e* (relative intensity)) 341 (M$^+$ + 1, 23), 340 (M$^+$, 100), 325 (22), 196 (14), 183 (19), 182 (13), 157 (10), 143 (27), 105 (13); ^{1}H NMR (CDCl$_3$, 90 MHz; δ) 1.53 (br s, 4 H), 1.78 (s, 3 H), 1.85 (s, 3 H), 2.20 (s, 3 H), 2.28 (s, 3 H), 2.40–2.63 (m, 2 H), 2.78–2.97 (m, 2 H), 6.67 (d, 2 H, *J* = 8.4 Hz), 6.80 (d, 2 H, *J* = 8.4 Hz), 7.03 (d, 2 H, *J* = 8.4 Hz), 7.08 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 14.13 (q), 18.52 (q), 20.95 (q), 21.23 (q), 24.36 (t), 25.64 (t), 39.96 (d), 40.65 (d), 42.48 (d), 44.93 (d), 125.89 (d, 2 C), 128.13 (d, 2 C), 128.37 (d, 2 C), 128.83 (d, 2 C), 131.77 (s), 133.04 (s), 134.59 (s), 134.68 (s), 135.67 (s), 138.77 (s), 139.57 (s), 139.93 (s). Anal. Calcd for C$_{26}$H$_{28}$: C, 91.71; H, 8.29. Found: C, 91.61; H, 8.36.

1c: mp 66–67 °C (acetone–ethanol); colorless prisms; IR (KBr; ν/cm^{-1}) 2960, 2900, 2860, 1514, 1440, 1365, 1175, 1105, 820, 810, 790; UV (acetonitrile; λ/nm (log ϵ)) 227 (4.23), 273 (sh, 3.26); MS (25 eV, 90 °C; *m/e* (relative intensity)) 341 (M$^+$ + 1, 24), 340 (M$^+$, 100), 325 (32), 196 (22), 184 (15), 183 (20), 182 (23), 157 (25), 156 (20), 143 (30), 116 (11), 105 (18); ^{1}H NMR (CDCl$_3$, 90 MHz; δ) 0.80 (s, 3 H), 1.31 (s, 3 H), 1.40–2.10 (m, 4 H), 2.23 (s, 3 H), 2.27 (s, 3 H), 2.33 (m, 1 H), 2.79 (dd, 1 H, *J* = 7.1, 5.7 Hz), 3.00 (m, 1 H), 3.12 (dd, *J* = 7.1, 6.0 Hz), 6.80 (d, 2 H, *J* = 9.0 Hz), 6.92 (d, 2 H, *J* = 9.0 Hz), 6.99 (s, 4 H); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 11.60 (q), 15.02 (t), 15.14 (q), 17.45 (t), 21.04 (q), 21.09 (q), 36.52 (d), 37.56 (d), 38.41 (d), 39.72 (d), 47.46 (s), 53.07 (s), 57.82 (s), 60.76 (s), 126.83 (d, 2 C), 127.07 (d, 2 C), 128.04 (d, 2 C), 128.70 (d, 2 C), 134.40 (s), 134.74 (s), 136.90 (s), 139.64 (s). Anal. Calcd for C$_{26}$H$_{28}$: C, 91.71; H, 8.29. Found: C, 91.69; H, 8.47.

2d: mp 111–111.5 °C (ethanol); colorless crystal; IR (KBr; ν/cm^{-1}) 2920, 1650, 1490, 1450, 1080, 1000, 840, 825, 790, 740, 730, 605, 585, 518; UV (cyclohexane; λ/nm (log ϵ)) 218 (4.23), 225 (sh, 4.15), 256 (4.43), 274 (sh, 4.28), 296 (sh, 3.48), 305 (sh, 2.89); MS (25 eV, 90 °C; *m/e* (relative intensity)) 384 (M$^+$ + 4, 1), 383 (M$^+$ + 3, 7), 382 (M$^+$ + 2, 79), 381 (M$^+$ + 1, 18), 380 (M$^+$, 100), 367 (12), 365 (23), 216 (28), 204 (23), 203 (47), 143 (32), 136 (15); ^{1}H NMR (CDCl$_3$, 60 MHz; δ) 1.56 (br s, 4 H), 1.77 (s, 3 H), 1.90 (br s, 3 H), 2.55 (m, 2 H), 2.85 (m, 2 H), 6.75 (d, 2 H, *J* = 9.0 Hz), 7.08 (d, 2 H, *J* = 9.0 Hz), 7.21 (s, 4 H); ^{13}C NMR (CDCl$_3$, 50 MHz, δ) 14.24 (q), 18.47 (q), 24.26 (t), 25.53 (t), 39.87 (d), 40.42 (d), 42.37 (d), 44.79 (d), 127.02 (d, 2 C), 127.68 (d, 2 C), 128.43 (d, 2 C), 129.62 (d, 2 C), 131.10 (s), 131.80 (s), 133.21 (s), 133.65 (s), 134.01 (s), 138.82 (s), 139.86 (s), 141.66 (s). Anal. Calcd for C$_{24}$H$_{22}$Cl$_2$: C, 75.59; H, 5.81; Cl, 18.60. Found: C, 75.58; H, 6.02; Cl, 18.48.

1d: mp 110–111 °C (acetone); colorless prisms.; IR (KBr; ν/cm^{-1}) 2950, 2860, 1495, 1390, 1365, 1088, 1010, 825, 810, 750, 515; UV (cyclohexane; λ/nm (log ϵ)) 231 (4.29), 246 (4.19), 271 (3.65), 280 (3.49); MS (25 eV, 90 °C; m/e (relative intensity)) 383 ($M^+ + 3$, 6), 382 ($M^+ + 2$, 77), 381 ($M^+ + 1$, 15), 380 (M^+, 100), 367 (24), 365 (50), 255 (13), 218 (13), 216 (47), 205 (29), 204 (40), 203 (78), 202 (23), 178 (13), 177 (33), 176 (41), 167 (27), 143 (63), 141 (14), 136 (26), 125 (26); ^{1}H NMR (CDCl$_3$, 60 MHz; δ) 0.81 (s, 3 H), 1.34 (s, 3 H), 1.42–2.00 (m, 4 H), 2.50 (m, 1 H), 2.93 (dd, 1 H, J = 6.9, 6.0 Hz), 3.12 (m, 1 H), 3.23 (dd, 1 H, J = 6.9, 6.9 Hz), 6.90–7.50 (m, 8 H); ^{13}C NMR (CDCl$_3$, 50 MHz; δ) 11.55 (q), 14.80 (t), 15.00 (q), 17.25 (t), 36.49 (d), 37.44 (d), 38.41 (d), 39.92 (d), 47.61 (s), 53.19 (s), 57.73 (s), 60.39 (s), 127.65 (d, 2 C), 128.07 (d, 2 C), 128.29 (d, 2 C), 128.43 (d, 2 C), 131.10 (s), 131.25 (s), 138.14 (s), 140.56 (s). Anal. Calcd for $C_{24}H_{22}Cl_2$: C, 75.59; H, 5.81; Cl, 18.60. Found: C, 75.53; H, 6.04; Cl, 18.48.

Photosensitized Isomerization of Cage Compound 1a to Diene 2a. The general procedure was as follows. An acetonitrile or benzene (2–3 mL) solution of **1a** (27–35 mM) containing sensitizer (0.40–0.59 mM for DCA and DCP and 6.5 mM for CN) with or without 1,2,4,5-tetramethoxybenzene (25 mM) was irradiated with a Ushio 300-W Xe lamp through a Corning 0-51 glass filter (λ > 360 nm) for DCA or Corning 0-54 glass filter (λ > 300 nm) for DCP or CN. The photolysate was concentrated in vacuo to afford the residue, which was analyzed by ^{1}H NMR to obtain the conversion of **1a** to **2a**.

Quantum Yield Measurements. Stock solutions (5 mL) containing **1a** and sensitizer were prepared. These solutions (3 mL) were irradiated with a Ushio 150-W Xe lamp on a Hitachi MPF-4 spectrophotometer (λ = 405 ± 10 nm for DCA; 334 ± 10 nm for DCP). Aliquots (1 mL) were removed and diluted to 10 mL (solution A). Same dilutions of stock solutions (1 mL) were conducted (solution B). The conversion of **1a** to **2a** was determined by analyses of UV spectra of solutions A and B. The number of photons absorbed by the solution was determined by using a potassium ferrioxalate actinometer. The results were obtained as follows. In acetonitrile with DCA (0.37 mM), Φ = 0.95, 1.24, 1.61, 1.83, 2.17, 2.54, 4.69, and 6.20 for [**1a**] = 4.48, 5.63, 7.30, 8.90, 10.3, 12.5, 18.8, and 24.7 mM. In benzene with DCA (0.55 mM), Φ = 0.322, 0.357, 0.484, 0.642, 0.816, and 0.918 for [**1a**] = 5.89, 6.83, 11.4, 21.4, 43.5, and 88.0 mM. In ethyl acetate with DCA (0.51 mM), Φ = 0.443, 0.639, 0.780, and 0.857 for [**1a**] = 3.71, 6.59, 10.8 and 13.5 mM. In benzene with DCP (2.3 mM), Φ = 0.211, 0.255, 0.364, 0.455, and 0.583 for [**1a**] = 6.40, 8.58, 13.1, 19.7, and 32.3 mM. Slopes and intercepts were obtained by a least-squares treatment.

Fluorescence Quenching of Sensitizers. Fluorescence quenching of sensitizer was conducted by using aerated solutions (DCA, 0.027–0.060 mM; DCP, 0.040–0.053 mM and 0.007 mM for cyclohexane; CN, 0.084 mM) at room temperature. Fluorescence intensities were measured at five or more quencher concentrations. Slopes ($k_q\tau$) of Stern–Volmer plots were determined by a least-squares treatment, and quenching rate constants (k_q) were calculated from the known singlet lifetimes (τ) of sensitizers in aerated solutions.

Exciplex Emission Quenching by Dimethyl Acetylenedicarboxylate in Benzene. Exciplex emissions (λ = 540 and 550 nm for DCA; 450 nm for DCP) observed from sensitizer fluorescence quenching by **1a** or **2a** were quenched by addition of DMAD. The results were obtained as follows. In the case of DCA (0.055 mM) and **1a** (8.75 mM), I_0/I = 1.12, 1.23, 1.39, 1.49, 1.62, and 1.79 for [DMAD] = 0.131, 0.261, 0.392, 0.522, 0.653, and 0.784 M. In the case of DCA (0.055 mM) and **2a** (8.74 mM), I_0/I = 1.14, 1.25, 1.42, and 1.55 for [DMAD] = 0.131, 0.261, 0.392, and 0.522 M. In the case of DCP (0.040 mM) and **1a** (13.0 mM), I_0/I = 1.17, 1.33, 1.48, 1.66, 1.75, and 1.91 for [DMAD] = 0.0326, 0.0652, 0.0978, 0.130, 0.163, and 0.196 M. In the case of DCP (0.040 mM) and **2a** (12.9 mM), I_0/I = 1.18, 1.31, 1.50, 1.64, 1.84, and 1.97 for [DMAD] = 0.0326, 0.0652, 0.0978, 0.130, 0.163, and 0.196 M. Slopes ($k_q\tau$) were obtained by a least-squares treatment. Monomer fluorescence quenching by DMAD was also conducted as described below. In the case of DCA (0.050 mM), I_0/I = 1.01, 1.00, 1.00, 1.02, and 1.01 for [DMAD] = 0.131, 0.261, 0.392, 0.522, and 0.653 M. In the case of DCP (0.040 mM), I_0/I = 1.01, 1.02, 1.03, and 1.06 for [DMAD] = 0.0652, 0.130, 0.196, and 0.228 M.

Reaction Quenching by Dimethyl Acetylenedicarboxylate in Benzene. In the case of DCA, solutions (3 mL) of **1a** (15.8 mM) and DCA (0.60 mM) containing different concentrations of DMAD were irradiated with 150-W Xe lamp (λ = 405 ± 10 nm) for 90 min. The photolysates were concentrated in vacuo to the residues, which were analyzed by ^{1}H NMR to obtain the conversion of **1a** to **2a**. The ratio of the conversion from the reaction without DMAD to that from the reaction with DMAD was obtained as Φ_0/Φ. The results were obtained as follows: Φ_0/Φ = 0.99, 1.02, 1.00, 0.99, and 0.99 for [DMAD] = 0.163, 0.327, 0.490, 0.653, and 0.816 M. In the case of DCP, solutions (5 mL) of **1a** (16.1 mM) and DCP (0.80 mM) containing different concentrations of DMAD were irradiated with 300-W Xe lamp through Corning O-52 glass filters (λ > 340 nm) for 30 min. Similar to the DCA case, the results were obtained as follows: Φ_0/Φ = 1.03, 1.05, 1.12, and 1.13 for [DMAD] = 0.0326, 0.0652, 0.0978, and 0.130 M.

Determination of Adiabatic Efficiencies. Adiabatic efficiencies (A_e) were determined by the equation $A_e = 100(I_{ex}(1)/I_{mon})/(I_{ex}(2)/I_{mon})^{12c}$ in which I_{ex} and I_{mon} represent the maximum intensities of observed exciplex emission and that of monomer fluorescence, respectively. It should be noted that $I_{ex}(1)$ and $I_{ex}(2)$ must be compared at the same extent of sensitizer fluorescence quenching. Practically, plots of log $(100I_{ex}/I_{mon})$ vs percent of quenched sensitizer for **1** and **2** were constructed. Thus, A_e was obtained as 100×10^a, $a = \log [(I_{ex}(1)/I_{mon})/(I_{ex}(2)/I_{mon})]$ at the same percent of quenched sensitizer, which is within 40–50%. When the values slightly above 100 were obtained (105 for DCA–**1a** in cyclohexane, 101 for DCA–**1a** in ether, 102 for DCP–**1b** in benzene), A_e values are reported as 100% in the text.