Novel [2 + 2] Photocycloaddition-Induced Rearrangement of Bichromophoric Naphthalene-Tethered Resorcinol Ethers

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The first examples of sequential photocycloaddition−rearrangement reactions of naphthalene-tethered resorcinol ethers are described. Bichromophoric aromatic compounds with naphthalene and resorcinol ether moieties were irradiated in the presence/absence of a small amount of acid to give the corresponding cycloaddition−rearrangement products. From the determination of quantum yields, steady-state fluorescence spectral studies, and fluorescence lifetime measurements, the mechanism of this novel photoinduced multistep reaction was elucidated to involve the initial intramolecular exciplex formation, followed by the intramolecular [2 + 2] photocycloaddition between the two aromatic rings and the subsequent acid-catalyzed skeletal rearrangement of the resulting cyclobutane derivative leading to the final products.

Introduction

Photocycloadditions of aromatic compounds to olefins have been studied extensively, since these reactions provide us with a convenient direct access to various polyfunctionalized compounds in a single step.[1] Among them, the *meta*-arene photoaddition to olefin, giving rise to [3 + 2] cycloadducts, is reported amply in the literature.[2] It is also known that, depending on the substitution pattern and/or redox potentials of relevant arene and olefin, the major photochemical route can be switched to [2 + 2] cycloaddition or less frequently to [4 + 2] cycloaddition.[3] However, especially in the absence of electron-withdrawing substituents on the aromatic ring, the [2 + 2] cycloaddition products were not always fully characterized in earlier studies, simply because they were obtained as a complex mixture. Hence, it is not unreasonable that only recently people have recognized explicitly that the [2 + 2], as well as [3 + 2], cycloadditions are much more abundantly occurring photoreactions upon irradiation of arene with olefin.[4]

Earlier theoretical investigations predicted that polar transition states of similar structures are involved in both [2 + 2] and [3 + 2] photocycloadditions of alkenes to electronically excited benzene derivatives.[5] However, a more recent theoretical study[6] indicated the intervention of nonpolar diradical intermediates rather than polar

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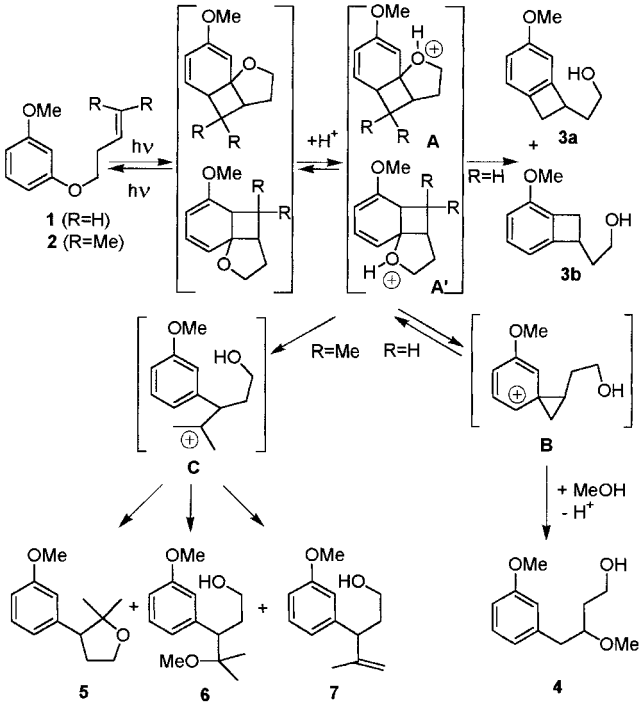
transition states but, unfortunately, could not make a plausible prediction about the competition between the branching two [2 + 2] and [3 + 2] cycloaddition pathways.

Recently, we have demonstrated that the efficiency and product yield of such photocycloaddition reactions of various arenes can be enhanced dramatically by adding a small amount of acid to the system.[7] We have also reported the intramolecular photocycloaddition reactions of several bichromophoric aromatic compounds, all of which possess an olefinic side chain tethered through an ether linkage to salicylic ester,[8] 3,5-dihydroxybenzonitrile,[9] 3,5-dihydroxybenzoic acid,[9,10] and resorcinol and 1,2,4-trihydroxyphenol.[11,12] It is noted that most of these substrates do not show any appreciable photoreactivity upon irradiation in neutral acetonitrile or methanol.

In sharp contrast, irradiation of resorcinol derivative **1** in acidic methanol afforded benzocyclobutenes **3a**,**b** and rearrangement product **4** in good quantum and chemical yields (Scheme 1).[11] Upon irradiation of dimethyl analogue **2** under identical conditions, only the rearrangement products **5**−**7** were obtained. From the examinations of the relevant electronic absorption and fluorescence spectra in the presence/absence of acid, we proposed the sequential photocycloaddition/acid-catalyzed rearrangement mechanism illustrated in Scheme 1 for these photoinduced reactions. In this mechanism, the initial [2 + 2] cycloaddition process is believed to be photoreversible at the excitation wavelength employed (λ = 254 nm) and therefore be nonproductive in the neutral media. However, in the acidic media, the photolabile cycloadducts is readily protonated to give oxonium intermediates **A** and **A′**, which in turn suffer the ring-opening of the tetrahydrofuran ring and/or the simultaneous alkyl shift to give **3a**,**b** and **4**, the latter being produced via the spiro cyclohexadienyl cation **B**. In the case of **2**, the acid-catalyzed ring opening of intermediates **A** and **A′** gives rise to stable tertiary carbenium ion **C**, which is either trapped by the intramolecular hydroxyl group or intermolecularly by solvent methanol or alternatively deprotonated to give products **5**, **6**, and **7**, respectively.

In our further attempts to expand the scope of this useful intramolecular arenic photocycloaddition, we found

Scheme 1. Photochemical Reactions of Resorcinol Derivatives Possessing an Olefinic Side Chain in Methanol and in the Presence of Acid[11]



that the olefin moiety can be replaced by a naphthalene chromophore. It is well documented that naphthalene derivatives undergo [2 + 2] photocycloaddition with a variety of olefins, but similar photoreactions between naphthalene and benzene chromophores have never been reported in the literature.[13,14] In the present study, we wish to elucidate the photochemical reactivity of resorcinol and 1,2,4-trihydroxybenzene derivatives carrying a naphthyl substituent and the detailed reaction mechanisms in the presence/absence of acid.

Results and Discussion

Photoreaction. When naphthalene-tethered resorcinol **8** (10 mM) was irradiated at λ = 254 nm in neutral acetonitrile, no appreciable decrease of the substrate was detected upon gas chromatographic examination of the irradiated solution. However, in the presence of sulfuric acid (6 mM) added to the sample solution, the substrate was smoothly consumed under the identical irradiation conditions to give two photoproducts **10** and **11** in good yields (Scheme 2), which were isolated from the solution

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Scheme 2. Photochemical Reactions of Bichromophoric Aromatic Compounds Possessing a Naphthyl and a Resorcinol Moiety

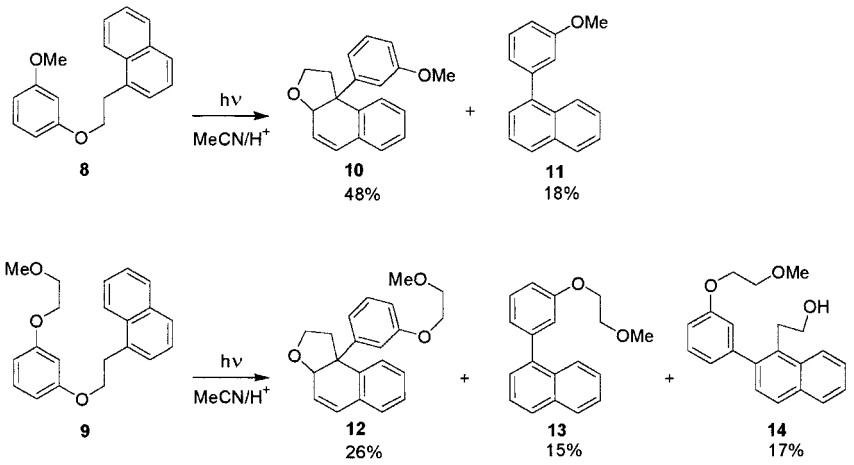


Table 1. Quantum Yields (Φ) for the Formation of 3−7, 10, and 12 (See Schemes 1 and 2)

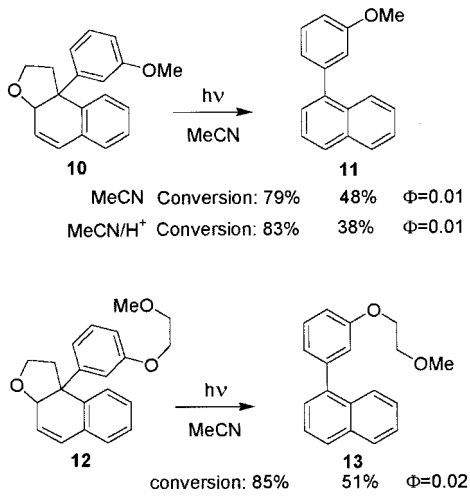
			Φ						
substrate	solvent	$[H_2SO_4]$, M	**3**	**4**	**5**	**6**	**7**	**10**	**12**
1	MeOH	6×10^{-3}	0.1	0.03					
2	MeOH	6×10^{-3}			0.075	0.065	0.07		
8	MeCN	6×10^{-3}						0.20	
9	MeCN	0							0.004
9	MeOH	0							0.02
9	MeCN	6×10^{-3}							0.14
9	MeOH	6×10^{-3}							0.13

irradiated for 3 h. The quantum yield (Φ) of **10** (Φ of **10** and **11** are combined, since **11** is derived photochemically from **10**, as described below), determined by using a conventional chemical actinometer, was fairly high (Φ = 0.20).[15] This value is comparable to those reported for the photocycloaddition of **1** and **2** (Table 1). However, it turned out that the irradiation in acetonitrile or in methanol is difficult to perform at higher substrate concentrations due to the low solubility of **8**. Hence, we have prepared the methoxyethyl ether **9** for the purpose of more detailed study on photobehavior of bichromophoric naphthalene-tethered resorcinol derivatives.

In the presence of acid, irradiation of **9** afforded three products **12**−**14** in good combined yields (ca. 60%) in both methanol and acetonitrile. The quantum yield of product **12** was almost the same (Φ = 0.13−0.14) in the two solvents (Table 1). In neutral media, only a slow, but steady, consumption of **9** was observed with an accompanying formation of **12** in a low quantum yield (Φ = 0.004−0.02, depending on the solvent used).

To clarify whether all of the obtained products are derived directly from **8** and **9** or in secondary photoreaction(s) of the primary product, the major products **10** and **12** were irradiated in neutral acetonitrile to give **11** and **13**, respectively, in good (40−50%) yields (Scheme 3). However, the quantum yields of **11** and **13** were low (Φ = 0.01−0.02) and independent of the acidity of the reaction media. The formation of **11** and **13** was rather surprising, since it requires a loss of C_2H_4O fragment from the tetrahydrofuran ring fused to dihydronaphthalene. Apart from the cheletropic elimination of molecules such as N_2, CO, CO_2, and SO_2 and elimination of anhydrides (in the case of ozonides), photochemical extrusion reactions from five-membered ring compounds are rare in the literature.[16] The positive result of the purpal test[17] clearly indicates the formation of acetaldehyde upon irradiation of **10** and **12**.

Scheme 3. Photochemical Reaction of Primary Photoproducts 10 and 11[a]



[a] Yields are given on the basis of transformed starting material.

Upon heating in acidic acetonitrile in the dark (82 °C, $[H_2SO_4]$ = 6 mM), **10** and **12** rearranged to **14** and **15**, respectively, in excellent yields (Scheme 4). These products were not found in appreciable amounts at least in the early stages of the photolyses of **8** and **9** and also

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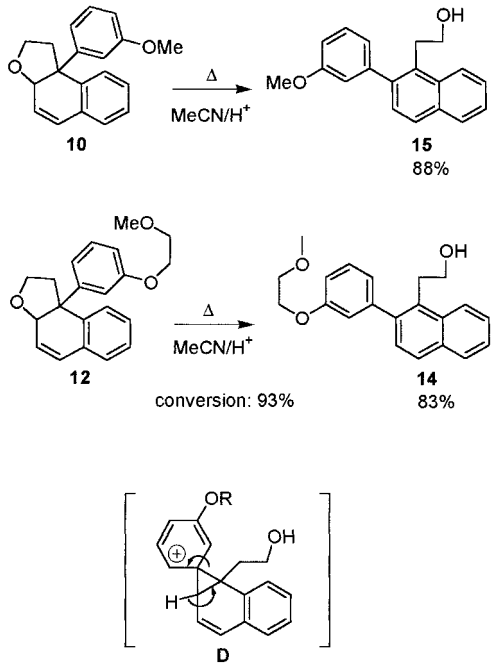
Scheme 4. Acid-Catalyzed Thermal Rearrangements of 10 and 11



upon photolyses of **10** and **12**. The formation of **14** and **15** is reasonably accounted for in terms of the acid-catalyzed thermal isomerization of **10** and **12**, respectively, through spirocyclohexadienyl intermediate **D**, a homologue of intermediate **B** in Scheme 1.

Previously, we proposed the mechanism outlined in Scheme 1 for the photochemical transformation of olefin-tethered resorcinols **1** and **2**.[11] In analogy, the formation of the primary photoproducts **10** and **12** are well interpreted by the mechanism depicted in Scheme 5. In this mechanism, the initial [2 + 2] photocycloaddition between the naphthalene to benzene rings and the subsequent protonation to the cycloadduct produced affords intermediate **E**, which in turn suffers successive ring opening to intermediate **F** and intramolecular trapping by the hydroxyl group, leading to the final product. From the fluorescence spectral examinations described below, it was revealed that an exciplex intervenes as a key intermediate in this photocycloaddition reaction and both exciplex and cycloadducts could be trapped by proton in the presence of acid leading to the efficient formation of intermediate **E**.

To the best of our knowledge, photochemical cycloaddition between naphthalene and benzene rings has never been reported in the literature. However, the present study unambiguously demonstrates that the olefinic moiety of **1** and **2** can be replaced by a naphthalene ring without damaging the photoreactivity for [2 + 2] cycloaddition. Interestingly, even in the absence of acid, the substrate **9** undergoes the photocycloaddition and subsequent rearrangement in low quantum yield (Table 1), which would be rationalized by the ligating stabilization of the protonated intermediate **E** by the adjacent methoxyethyl group.

In the case of olefin-tethered resorcinol substrates reported earlier,[11] an elongated tether or further alkoxylation of the resorcinol moiety did not spoil the photocycloaddition reaction. In the present study, we also prepared the corresponding naphthyl derivatives **16** (with an extra methylene in the tether) and **17** (with an additional methoxy group) (Chart 1), which were irradiated under the identical conditions to exhibit no appreciable photoreactivity. Furthermore, the anisylnaphthoxy analogue **18**, an isomer of **8**, also failed to give any photocycloadducts. These results clearly indicate that the photocycloaddition of naphthalene-tethered resorcinol is highly intolerable to the structural alterations at the tether or aromatic rings, and is specific to such compounds as **8** and **9**.

Fluorescence and Mechanistic Studies. To elucidate the origin of such a very strict structural requirement for photocycloaddition, we comparatively investigated the excited-state interactions of these reactive and nonreactive bichromophoric systems through the measurements of fluorescence spectra and lifetimes in various solvents. The results are summarized in Table 2. As already reported in the previous study,[11] compounds **1** and **2** showed exactly the same tendency as the reference compound *m*-dimethoxybenzene (**20**). Thus, slightly shorter lifetimes were obtained in MeOH than in MeCN, and the addition of sulfuric acid (0.1 M) shortened the lifetimes by 0.1−0.2 ns. It is interesting to note that the lifetimes of **1** in MeCN and MeOH (with and without acid) are the same as the respective lifetimes of **20** within the experimental error (ca. 0.1 ns), but the relevant values for **2** are appreciably shorter by 0.2−0.4 ns than those for **1** or **20**. This clearly indicates that the olefinic moiety of **1** does not interact with the aromatic moiety, whereas there must be some electronic interaction between the two moieties of **2** in the excited state, although no emission attributable to the intramolecular exciplex was observed at longer wavelengths. The apparently trivial, but consistent, decreases by 0.1−0.2 ns in the fluorescence lifetime of **1**, **2**, and **20** in the presence of sulfuric acid presumably support some interaction of acid with the fluorophore. This is also consistent with the slight

Scheme 5. Proposed Mechanism for the Photochemical Reaction of 8 and 9

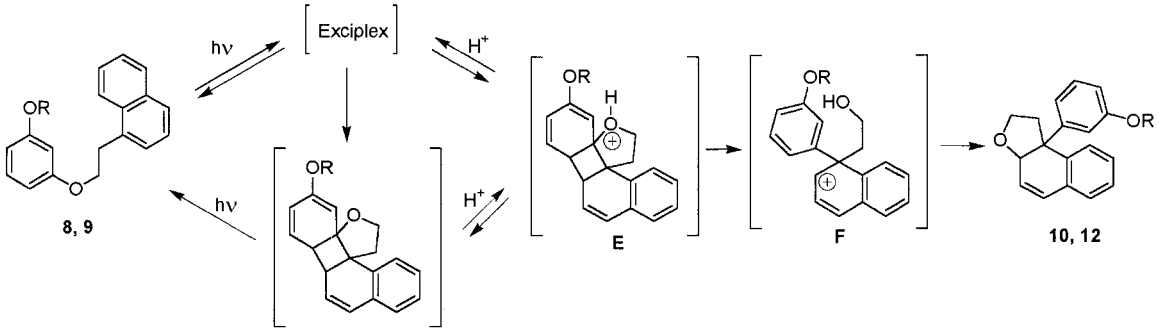
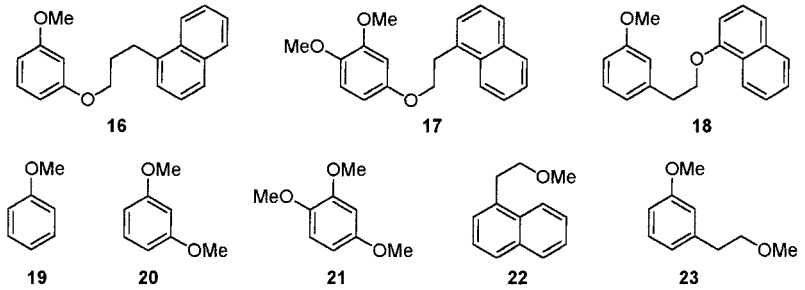


Chart 1



decrease (5−15%) in the (steady-state) fluorescence intensity reported previously.[11]

Among the naphthalene derivatives employed in this study (**8**, **9**, **16**−**18**), only **8** and **9** undergo efficient photocycloaddition in the presence and even in the absence (in the case of **9**) of added acid, while the analogues **16**−**18** are completely unreactive photochemically. It is therefore intriguing and crucial to compare the fluorescence behavior of these compounds. Although naphthalene derivatives are known in general to be highly fluorescent and frequently form exciplexes,[13,18] no appreciable fluorescence from exciplex was detected with most of the present substrates, except for **17**, which gave very strong exciplex fluorescence and much smaller (by a factor of 20−50:1) monomer fluorescence. Fluorescence lifetime of the reference compound **22**, excited at 280 nm, was not significantly affected by changing solvent or by adding 0.1 M sulfuric acid. This seems reasonable since the fluorescing naphthyl group is electronically isolated from the ether oxygen that would be solvated in methanol or protonated in highly acidic media. In contrast, compound **8** gave fairly shorter lifetimes of 8.9 and 9.6 ns in neutral acetonitrile and methanol than those obtained for **22** (12.2 and 12.5 ns, respectively), which is reasonably attributed to the intramolecular quenching of the excited naphthyl by the anisyloxy group probably through the charge-transfer interactions. The yet shorter lifetime (8.0 ns) of **8** in acidic methanol may be ascribed to the equilibrium shift caused by protonation to the initial photoadduct giving intermediate **E**. The excitation of **8** at 230 nm, which leads to an increased excitation of the ansyloxy chromophore, provides us with further information about the excited-state interaction of the two tethered chromophores. Upon excitation at 230 nm, both chromophores are competitively activated and the fluorescence decay profile becomes double-exponential, giving short and long lifetimes of varying contributions shown in parentheses of Table 2.

All of the long lifetimes are consistent with those obtained by the 280 nm excitation. The short lifetimes of **8**, measured in neutral and acidic acetonitrile and/or methanol, also nicely coincide with those of reference **20** measured under the comparable conditions. The relative contribution of naphthalene fluorescence (longer lifetime) decreases from 70% in neutral acetonitrile to 61% in neutral methanol and then to 56% in acidic methanol in good agreement with the declining tendency of lifetime (i.e., 9.7, 9.2, and 7.9 ns, respectively).

In the case of **8** and **9**, added acid enhances the quenching of naphthalene fluorescence and the formation of product. In this context, it is noted that photochemically unreactive **16** exhibits completely different fluorescence behavior. Possessing a resorcinol moiety connected with a longer tether, **16** gives the fluorescence lifetimes around 13 ns, which are comparable to those observed for reference **22** (12−13 ns) and are totally insensitive to the solvent or acidity change. These observations immediately mean that no excited-state interaction exists between the naphthalene and resorcinol moieties. Probably, the "rule of three" upon exciplex formation, which is abundantly exemplified in the literature, is very strictly applied in the present case and hinders the desirable approach of the naphthalene and resorcinol moieties in **16**.[13,19]

However, no photoproduct is formed upon irradiation of **18**, although the "rule of three" does not formally prohibit an association of the two chromophores in **18**. The fluorescence lifetimes of **18** (7−8 ns) in neutral media are much shorter than those of reference **22** (12−13 ns) and are sensitive to added acid to give a yet shorter lifetime of 5 ns in acidic methanol. These results are not unexpected, as the alkoxynaphthalene chromophore in **18** should be different in fluorescence properties from that of the alkylnaphthalene chromophore in **8**, **16**, or **22**, and the protonation to the ether oxygen can easily alter the fluorescence behavior. Probably incidentally, reference compound **23** gives exactly the same lifetime (5 ns). We tentatively conclude that added acid quenches the excited alkoxynaphthalene moiety of **18** to give the shorter lifetimes around 5 ns, while the excited alkylanisole moiety is not quenched by acid but gives lifetimes around 1−2 ns, which are shorter than that of reference **23**, probably through interaction with the naphthyl chromophore.

Introduction of an extra methoxy to **8** dramatically alters the fluorescence behavior of **17**, which is distinctly different from that of **8**, **9**, **16**, or **18**. Thus, the naphthalene fluorescence of **17** was very efficiently quenched intramolecularly by the trialkoxybenzene moiety to leave an extremely weak monomer fluorescence at 328 and 334 nm, which is ca. 1000 times smaller in intensity than that of **16**. Instead, much stronger (by a factor of 5−20, compared to monomer fluorescence of **17**) exciplex emission emerged at a longer wavelength, which varies from

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Table 2. Fluorescence Spectra and Lifetimes of Various Bichromophoric Arenes

compd	solvent	$[H_2SO_4]$/M	λ_{em}/nm[a]	λ_{ex}/nm[b]	τ/ns[c]
1	MeCN	0	300	270	2.1
	MeOH	0		270	1.9
	MeOH	0.1		270	1.8
2	MeCN	0	300	270	1.8
	MeOH	0		270	1.6
	MeOH	0.1		270	1.5
8	MeCN	0	320, 326, 335, 340	280	9.8
				230	9.7 (70%), 2.1 (30%)
	MeOH	0		280	9.6
				230	9.2 (61%), 1.7 (39%)
	MeOH	0.1		280	8.0
				230	7.9 (56%), 1.7 (44%)
9	MeCN	0	321, 328, 338, 340	280	10.3
				230	10.0 (59%), 1.9 (41%)
	MeOH	0		280	9.8
				230	9.8 (55%), 1.9 (45%)
	MeOH	0.1		280	8.6
				230	8.2 (49%), 1.4 (51%)
16	MeCN	0	327, 336	280	13.3
				230	13.3 (37%), 1.0 (63%)
	MeOH	0		280	13.1
				230	13.1 (36%), 1.2 (64%)
	MeOH	0.1		280	13.3
				230	13.5 (31%), 1.0 (69%)
17	C_5H_{12}	0	328; *395*	280	6.5 [6.4]
				230	6.2 [6.6]
	MeCN	0	328, 334; *444*	280	7.2 [7.1]
				230	7.3 (53%), 1.3 (47%) [7.1 (45%), 1.1 (55%)]
	MeOH	0	328, 339; *450*	280	5.4 [5.4]
				230	5.3 (55%), 1.0 (45%) [5.2 (61%), 1.1 (39%)]
	MeOH	0.1	328, 339; *453*	280	1.0 [1.0]
				230	0.9 [0.9]
18	MeCN	0	326, 339, 354	280	6.7
				230	6.5 (74%), 1.4 (26%)
	MeOH	0		280	7.7
				230	7.8 (75%), 2.0 (25%)
	MeOH	0.1		280	5.0
				230	4.9 (77%), 2.1 (23%)
19	P[d]	0			7.5[d]
20	MeCN	0	300	270	2.2
	MeOH	0		270	1.9
	MeOH	0.1		270	1.7
21	MeCN	0	325	280	0.8
	MeOH	0		280	0.8
	MeOH	0.1		280	0.7
22	MeCN	0	321, 326, 335, 340	280	12.2
	MeOH	0		280	12.5
	MeOH	0.1		280	13.0
23	MeCN	0	295	270	4.9
	MeOH	0		270	5.0
	MeOH	0.1		270	4.9

[a] Fluorescence maxima; values in italic after a semicolon are those for exciplex emissions. [b] Excitation wavelength used. [c] Relative amplitudes for double-exponential decay in the parentheses, and values obtained with a Y-44 filter in brackets. [d] In polar solvent.[23]

395 nm in pentane to 450 nm in methanol, indicating its charge-transfer character.

Both of the time-resolved fluorescence profiles obtained with **16** and **17** upon excitation at 230 nm can be fitted to a double-exponential decay curve, giving two lifetimes. However, the origins of the two lifetimes are completely different. The long lifetime of 13 ns obtained for **16** upon excitation at 230 and 280 nm is assigned to the singlet naphthalene moiety, while the short lifetime of 1 ns is attributed to the singlet *m*-anisyloxy moiety, since the latter lifetime appears only upon excitation at 230 nm which is absorbed by both *m*-anisyloxy and naphthalene moieties (cf. the data for **20** and **22**).

Similarly, **17** gave two lifetimes of 5−7 ns and 1 ns upon excitation at 230 nm, which might be assigned to the fluorescence from the naphthalene and trialkoxybenzene moieties, as is the case with **16**. However, it turned out that this assignment is erroneous and two exciplexes with different lifetimes exist in the system, since the use of a short-cut filter Y-44 (50% transmission at 440 nm and 0% at 410 nm) to completely eliminate the originally weak monomer fluorescence of naphthalene and trialkoxybenzene moieties did not alter the lifetimes or their relative contribution. Probably, the reduced oxidation potential of trialkoxybenzene moiety in **17** is responsible for such an efficient fluorescence quenching and formation of exciplexes with different structures and lifetimes.[20] Clearly, we do not have enough data for discussing in detail the structural differences of the two exciplexes, but it seems reasonable to conclude that the short-lived species is produced more favorably by excitation at shorter wavelength (230 nm), is more populated in polar solvents than in pentane (probably more polarized and/or solvated), and is not subjected to acid quenching (probably as a result of the short lifetime and/or heavy solvation). It is also mentioned that the two exciplex species do not appear to have significant difference in spectral profile (and therefore in conformation or degrees of stacking and charge transfer), since the relative contribution of the two species is practically independent of the observation wavelength (with and without Y-44). The intervention of stable exciplexes with strong charge-transfer character may hinder the photocycloaddition of **17**.

Conclusion

The [2 + 2] photocycloaddition between naphthalene and benzene rings was shown to occur for the first time upon irradiation of naphthalene-tethered resorcinol ethers **8** and **9** in the presence of sulfuric acid. The added acid traps the initially generated "labile" tetrahydrofuran derivatives **10** and **12** and accelerates their thermal rearrangement to the corresponding final products **11** and **13**/**14**, respectively. However, this photocycloaddition reaction is not very tolerant to the structural modifications in tether or chromophore, as the analogues **16**−**18** are totally inactive photochemically.

The photophysical properties of naphthyl derivatives **8** and **9** were compared with those of olefinic analogues **1** and **2**. Although the photochemical reactivity is essentially the same for **1**/**2** and **8**/**9**, the fluorescence

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behavior, particularly in the presence of added acid, is quite different in both cases, showing practically no effect for **1**/**2** but significant quenching for **8**/**9**. Similar fluorescence quenching by acid was observed also for **17** and **18**. Hence, the presence of acid not only accelerates the transformation of the primary photocycloadduct to the final products (as in photoreactions of **8** and **9**) but also quenches the exciplex fluorescence (of **17**).

We have demonstrated in the present study that the intramolecular [2 + 2] photocycloaddition of aromatic substrates is not restricted to the conventional olefin−benzene pair but can be extended to unprecedented naphthalene-benzene pair. Fluorescence spectral and lifetime measurements may provide us with some criteria for judging the photoreactivity of a given bichromophoric substrate. Thus, highly efficient intramolecular fluorescence quenching and subsequent formation of an emissive exciplex seems unfavorable, while moderately quenched fluorescence and shortened lifetime without accompanying formation of emissive exciplex appears to be more suitable for the product formation. In this connection, it is important to examine the effect of added acid as a trapping agent for "labile" photoproduct, even if the bichromophoric system does not appear to give any photoproduct in neutral media.

Experimental Section

General Methods. Irradiations of the solution were carried out in quartz tubes (i.d. 1 cm), with a Rayonet apparatus (model RPR-100) from the Southern New England Ultraviolet Co. RPR-2537 A lamps were used. Solutions were degassed with argon before irradiation.

Synthesis of Compound 8. A suspension of 3-methoxyphenol (3 g, 16.1 mmol), 2-(1-naphthyl)-ethyl tosylate (5 g, 15.3 mmol) and K_2CO_3 (5 g, 36.2 mmol) in DMF (20 mL) was heated at 80 °C for 4 h. After evaporation of the solvent, the residue was treated with water and CH_2Cl_2. The aqueous phase was extracted twice with CH_2Cl_2. The organic phase was then washed subsequently with 10% NaOH and with water. After drying with $MgSO_4$ and evaporation of the solvent, the residue was subjected to flash chromatography (petroleum ether/ethyl acetate 5:1). Yield: 2.4 g (56%). Mp: 108 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.13 (m, 1H), 7.90 (m, 1H), 7.81 (m, 1H), 7.45−7.62 (m, 4H), 7.22 (d/d, J = 7/14 Hz, 1H), 6.50−6.59 (m, 3H), 4.32 (t, J = 7.5 Hz, 2H), 3.81 (s, 3H), 4.33 (t, J = 7.5 Hz, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.8, 160.0, 134.0, 133.8, 132.0, 129.9, 128.8, 127.3, 127.0, 126.1, 125.6, 125.5, 123.5, 106.6, 106.4, 100.9, 68.0, 55.2, 32.8. IR (KBr): ν 3040, 3005, 2934, 2841, 1510, 1169, 1036, 837, 792, 768. MS *m*/*z* (relative intensity): 278 (M^+, 51), 155 (100), 154 (62), 141 (31), 128 (13), 115 (21). UV (2.52×10^{-5} M, MeCN): λ (ϵ) 282 (9200), 224 (81 000). Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.01; H, 6.47. Found: C, 82.02; H, 6.62.

Synthesis of Compound 9. A suspension of resorcinol monoacetate (technical grade, 7.3 g, 48.0 mmol), 2-methoxyethyl tosylate (10 g, 43 mmol), and K_2CO_3 (14.5 g, 105 mmol) in 60 mL of DMF was heated at 80 °C for 4 h. After evaporation of the solvent, the residue was treated with 20% NaOH (120 mL). After careful acidification with hydrochloric acid, the resulting mixture was extracted with CH_2Cl_2. The organic phase was dried with $MgSO_4$. The solvent was evaporated, and the crude material was used for further conversion.

A suspension of 3-(2-methoxyethoxy)phenol (9 g, ∼ 60 mmol), 2-(1-naphthyl)ethyl tosylate (14 g, 42.9 mmol), and K_2CO_3 (16 g, 116 mmol) in 60 mL of DMF was heated at 80 °C for 4 h. After evaporation of the solvent, the residue was treated with water and CH_2Cl_2. The aqueous phase was extracted twice with CH_2Cl_2. The organic phase was then washed subsequently with 10% NaOH and with water. After drying with $MgSO_4$ and evaporation of the solvent, the residue was subjected to flash chromatography (petroleum ether/ethyl acetate 5:1). Yield: 4.15 g (30%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.12 (m, 1H), 7.90 (m, 1H), 7.80 (m, 1H), 7.43−7.58 (m, 4H), 7.19 (m, 1H), 7.52−6.60 (m, 3H), 4.32 (t, J = 7.5 Hz, 2H), 4.10 (m, 2H), 3.74 (m, 2H), 360 (t, J = 7.5 Hz, 2H), 3.47 (s, 3H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.0 (2×), 134.0, 133.8, 132.0, 129.8, 128.8, 127.3, 127.0, 126.2, 125.5 (2×), 123.5, 107.1, 107.0, 101.6, 70.9, 67.9, 67.1, 59.1, 32.7. IR (film): ν 3046, 2926, 2878, 1593, 1493, 1127, 777. MS *m*/*z* (relative intensity): 322 (M^+, 32), 155 (100), 154 (58), 141 (21), 115 (16). UV (3.88×10^{-5} M, MeCN): λ(ϵ) 282 (9200), 224 (69 000), 202 (52 000). HRMS: calcd for $C_{21}H_{22}O_3$ 322.1569, found 322.1581.

Synthesis of Compound 16. Compound **16** was synthesized from 3-methoxyphenol (2.2 g, 17.7 mmol) and 3-(1-naphthyl)propan-1-yl tosylate (6 g, 17.6 mmol) in the same way as compound **9**. Yield: 2.04 g (40%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.13 (m, 1H), 7.90 (m, 1H), 7.78 (m, 1H), 7.38−7.60 (m, 4H), 7.25 (m, 1H), 6.54−6.63 (m, 3H), 4.06 (t, J = 7.5 Hz, 2H), 3.83 (s, 3H), 3.33 (t, J = 7.5 Hz, 2H), 2.30 (pen, J = 7.5 Hz, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 160.8, 160.3, 137.5, 133.9, 131.8, 129.8, 128.7, 126.7, 126.2, 125.8, 125.5, 125.4, 123.7, 106.7, 106.2, 101.0, 67.0, 55.2, 30.1, 29.2. IR (film): ν 3044, 2940, 2874, 2836, 1597, 1493, 1154, 779. MS *m*/*z* (relative intensity): 292 (M^+, 23), 168 (100), 152 (85), 141 (70), 115 (32). UV (2.64×10^{-5} M, MeCN): λ (ϵ) 282 (7700), 224 (70 000). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 82.28; H, 6.54.

Synthesis of Compound 17. Compound **17** was synthesized from 3,4-dimethoxyphenol and 2-(1-naphthyl)ethyl tosylate in the same way as compound **9**. Yield: 2.65 g (56%). Mp: 66 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.13 (m, 1H), 7.90 (m, 1H), 7.80 (m, 1H), 7.44−7.60 (m, 4H), 6.77 (d, J = 8.5 Hz, 1H), 6.55 (d, J = 3.0 Hz, 1H), 6.42 (d/d, J = 3.0/8.5 Hz, 1H), 4.29 (t, J = 7.5 Hz, 2H), 3.85 (s, 6H), 3.60 (t, J = 7.5 Hz, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 153.3, 149.8, 143.4, 134.0, 133.8, 132.0, 128.7, 127.2, 127.0, 126.0, 125.5, 125.4, 123.5, 111.8, 103.9, 100.7, 68.4, 56.3, 55.7, 32.8. IR (KBr): ν 3043, 3005, 2914, 2839, 1596, 1516, 1231, 1200, 1139, 1036, 795. MS *m*/*z* (relative intensity): 308 (M^+, 12), 155 (100), 153 (26), 127 (8), 115 (10). UV (2.42×10^{-5} M, MeCN): λ (ϵ) 283 (11 000), 224 (82 000). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.92; H, 6.49. Found: C, 77.64; H, 6.55.

Synthesis of Compound 18. Compound **18** was synthesized from α-naphthol (2.35 g, 16.3 mmol) and 2-(3-methoxyphenyl)ethyl tosylate (5 g, 16.3 mmol) in the same way as compound **9**. Yield: 2.8 g (62%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.26 (m, 1H), 7.77 (m, 1H), 7.20−7.50 (m, 5H), 6.90−6.97 (m, 2H), 6.75−6.81 (m, 2H), 4.33 (t, J = 7.0 Hz, 2H), 3.78 (s, 3H), 3.20 (t, J = 7.0 Hz, 2H). ^{13}C NMR (62 MHz, $CDCl_3$): δ 159.7, 154.5, 140.1, 134.5, 129.5, 127.4, 126.3, 125.8, 125.1, 122.1, 121.4, 120.2, 114.8, 111.9, 104.6, 68.8, 55.1, 35.9. IR (film): ν 3052, 2953, 2873, 2834, 1595, 1460, 1268, 1100, 772. MS *m*/*z* (relative intensity): 278 (M^+, 90), 194 (30), 170 (35), 144 (44), 135 (86), 126 (36), 121 (100), 115 (44), 105 (97). UV (2.36×10^{-5} M, MeCN): λ (ϵ) 294 (6300), 281 (6700), 229 (3200), 211 (49 000). Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.01; H, 6.47. Found: C, 82.06; H, 6.22.

Compounds 22 and 23. These compounds were synthesized according to ref 21.

Photochemical Transformations on Preparative Scale. A solution of **8** (1.2×10^{-2} M) or **9** (1×10^{-2} M) and H_2SO_4 (6×10^{-3} M) in acetonitrile (120 mL) was distributed into eight quartz tubes. After percolation with argon for 0.5 h, the solutions were irradiated for 3 h. The solvent was evaporated in the presence of $NaHCO_3$. The residue was subjected to flash chromatography (petroleum ether/ethyl acetate: first 5:1, then 1:1, and finally pure ethyl acetate).

Compound 10. Yield: 190 mg (48%). ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.01−7.22 (m, 5H), 6.85 (d/m, J = 8.0 Hz, 1H), 6.80 (t, J = 2.5 Hz, 1H), 6.75 (d/d, J = 2.5/8.0 Hz, 1H), 6.68 (d, J = 10.0 Hz, 1H), 6.08 (d/d, J = 4.5/10.0 Hz, 1H), 4.56 (d, J =

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4.5 Hz, 1H), 3.93 (d/t, J = 6.5/7.5 Hz, 1H), 3.71 (s, 3H), 3.66 (d/t, J = 6.5/7.5 Hz, 1H), 2.95 (d/d/d, J = 6.5/7.5/13.0 Hz, 1H), 2.69 (d/d/d, J = 6.5/7.5/13.0 Hz, 1H). ^{13}C NMR (126 MHz, CD_3COCD_3): δ 160.5, 149.2, 141.7, 132.2, 130.3, 130.1, 129.2, 129.0, 128.2, 127.5, 126.7, 119.8, 114.1, 111.8, 82.6, 66.5, 55.3, 53.8, 41.3. IR (film): ν 3025, 2938, 2872, 2834, 1582, 1485, 1256, 1159, 1051, 750. MS *m/z* (relative intensity): 278 (M^+, 100), 249 (31), 247 (31), 202 (24), 189 (29), 178 (24), 171 (51), 170 (55), 141 (25), 135 (49), 115 (36). UV (2.09×10^{-5} M, MeCN): λ (ϵ) 266 (11 000), 218 (38 000). Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.01; H, 6.47. Found: C, 82.14; H, 6.20.

Compound 11.[22] Yield: 60 mg (18%). ^{1}H NMR (500 MHz, CD_3COCD_3): δ 7.97 (d, J = 8.0 Hz, 1H), 7.91 (t, J = 9.0 Hz, 2H), 7.40−7.50 (m, 5H), 7.00−7.10 (m, 3H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, CD_3COCD_3): δ 160.6, 142.8, 140.9, 1.34,8, 132.2, 130.2, 129.2, 128.5, 127.5, 126.9, 126.7, 126.5, 126.3, 123.0, 116.3, 113.7, 55.5.

Compound 12. Yield: 102 mg (26%). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.13−7.21 (m, 5H), 6.74−6.90 (m, 3H), 6.68 (d, J = 10.0 Hz, 1H), 6.09 (d/d, J = 4.5/10.0 Hz, 1H), 4.56 (d, J = 4.5 Hz, 1H), 4.00−4.10 (m, 2H), 3.93 (d/t, J = 6.5/7.5 Hz, 1H), 3.60−3.72 (m, 3H), 3.32 (s, 3H), 2.95 (d/d/d, J = 6.5/7.0/13.0 Hz, 1H), 2.70 (d/d/d, J = 6.5/7.0/13.0 Hz, 1H). ^{13}C NMR (63 MHz, CD_3COCD_3): δ 159.7, 148.2, 141.6, 132.2, 130.3, 130.1, 129.2, 129.0, 128.2, 127.4, 126.7, 119.9, 114.7, 112.3, 82.6, 71.6, 67.8, 66.5, 58.8, 53.7, 41.3. IR (film): ν 3032, 2927, 2874, 1580, 1451, 1256, 1127, 1053, 752. MS *m/z* (relative intensity): 322 (M^+, 100), 294 (15), 263 (18), 247 (16), 202 (17), 171 (27), 170 (36), 141 (57), 115 (30). UV (2.92×10^{-5} M, MeCN): λ (ϵ) 265 (8500), 219 (33 000). Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.26; H, 6.83. Found: C, 78.13; H, 6.98.

Compound 13. Yield: 52 mg (15%). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 7.88−8.00 (m, 3H), 7.39−7.60 (m, 5H), 7.00−7.09 (m, 3H), 4.20 (m, 2H), 3.74 (m, 2H), 3.35 (s, 3H). ^{13}C NMR (63 MHz, CD_3COCD_3): δ 159.9, 142.9, 140.9, 134.8, 132.3, 130.2, 129.2, 128.5, 127.6, 127.0, 126.7, 126.5, 126.3, 123.1, 116.8, 114.4, 71.7, 68.2, 58.9. IR (film): ν 3059, 2926, 2878, 1577, 1485, 1224, 1129, 781. MS *m/z* (relative intensity): 278 (M^+, 100), 220 (50), 203 (53), 202 (50), 189 (35), 165 (15). Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.01; H, 6.47. Found: C, 81.74; H, 6.73.

Compound 14. Yield: 66 mg (17%). ^{1}H NMR (250 MHz, CD_3COCD_3): δ 8.23 (d, J = 8.5 Hz, 1H), 7.92 (d/d, J = 1.5, 8.0 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.48−7.63 (m, 2H), 7.30−7.41 (m, 2H), 6.91−7.01 (m, 3H), 4.15−4.20 (m, 2H), 3.70−3.90 (m, 4H), 3.36 (s, 3H), 3.26−3.36 (m, 2H). ^{13}C NMR (63 MHz, CD_3COCD_3): δ 159.7, 144.9, 140.8, 134.2, 133.6, 132.5, 130.0, 129.4, 129.0, 127.2, 127.1, 126.3, 125.4, 122.5, 116.2, 114.0, 71.7, 68.1, 63.1, 58.9, 33.9. IR (film): ν 3404, 3052, 2927, 2880, 1594, 1466, 1293, 1095, 1038, 823, 706. MS *m/z* (relative intensity): 322 (M^+, 60), 292 (43), 259 (37), 245 (36), 233 (46), 215 (100), 203 (40), 202 (54), 189 (22). Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.26; H, 6.83. Found: C, 78.06; H, 7.38.

Irradiation of 10 and 12. Solutions of **10** (160 mg, 0.58 mmol) or **12** (160 mg, 0.50 mmol) in acetonirile (50 mL) were distributed into three quartz tubes and irradiated for 4.5 h. The solvent was evaporated and the residue was subjected to flash chromatography (petroleum ether/ethyl acetate 5:1): **10**, 34 mg (conversion 79%); **11**, 51 mg (yield 48%); **12**, 24 mg (conversion 85%); **13**, 60 mg (yield 51%).

A solution of **10** (160 mg, 0.58 mmol) and H_2SO_4 (6×10^{-3} M) in acetonitrile (53 mL) was distributed into three quartz tubes and irradiated for 4.5 h. The solvent was evaporated in the presence of $NaHCO_3$, and the residue was subjected to flash chromatography (petroleum ether/ethyl acetate 5:1): **10**, 27 mg (conversion 83%); **11**, 42 mg (yield 38%).

Acid-Catalyzed Rearrangement of 10 and 12. Solutions of **10** (100 mg, 0.43 mmol) or **12** (100 mg, 0.31 mmol) and H_2SO_4 (6×10^{-3} M) in 16 mL of acetonitrile were heated under reflux for 5 to 6 h. The solvent was evaporated in the presence of $NaHCO_3$, and the residue was subjected to flash chromatography (petroleum ether/ethyl acetate 2:1): **15**, 88 mg (yield 88%); **12**, 7 mg (conversion 93%); **14**, 78 mg (83%).

Compound 15. ^{1}H NMR (500 MHz, CD_3COCD_3): δ 8.24 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.60 (d/d/d, J = 1.0, 7.0, 8.0 Hz, 1H), 7.53 (d/d/d, J = 1.0, 7.0, 8.0 Hz, 1H), 7.38 (m, 1H), 7.33 (d, J = 8.5 Hz, 1H), 6.94−7.00 (m, 3H), 3.85 (s, 3H), 3.74−3.80 (m, 2H), 3.30 (t, J = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, CD_3COCD_3): δ 160.4, 144.9, 140.9, 134.2, 133.3, 132.5, 130.0, 129.4, 129.0, 127.2, 127.1, 126.3, 125.4, 122.4, 115.7, 113.4, 63.1, 55.5, 33.9. IR (KBr): ν 3231, 3058, 3007, 2963, 2934, 2830, 1590, 1460, 1217, 1020, 833, 793, 754, 704. MS *m/z* (relative intensity): 278 (M^+, 42), 247 (100), 232 (21), 216 (26), 215 (52), 203 (33), 202 (32), 189 (10). Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.01; H, 6.47. Found: C, 81.70; H, 6.28.

Determination of the Quantum Yields. Solutions (Schemes 1−3, Table 1) possessing an optical density of 3.5 (λ = 254 nm, optical path = 0.5 cm) were irradiated until the conversion reached between 10 and 20%. *N*,*N*-Dimethyluracil (formation of the monohydrate) was used as actinometer.[15]

Fluorescence Lifetime Measurements of Bichromophoric Aromatic Compounds and Related Compounds. Absorption spectra were recorded on a JASCO V-550 spectrometer fitted with an ETC-505T temperature controller, and fluorescence spectra on JASCO FP-777. Fluorescence lifetime measurements were performed for an argon-saturated solution of sensitizers (ca. 0.1 mM) on a Horiba NAES-550 fitted with SCN-121A (optical chamber), NFL-111A (pulsed H_2 light source), SGM-121A (monochromator), SSU-111A (photomultiplier), LPS-111 (lamp power supply), and Advantec LCH-111 Labo Thermo-Cool temperature controller. The radiation from the lamp was made monochromatic by 10 nm monochromator (centered at 230 or 270/280 nm) and the emission from the sample solution was detected through a Toshiba UV31 or UV33 filter, unless otherwise stated. There must be some ambiguity in smaller components of fluorescence lifetimes, especially for the shorter lifetimes obtained, since our instrument does not measure the lifetime in a range of <1 ns much correctly, which will be studied with ps fluorescence spectrometer in due course.

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Supporting Information Available: UV and fluorescence spectra of compounds **8**, **9**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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