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Generation of quinone methide from aminomethyl(hydroxy)arenes precursors in aqueous solution

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Abstract—*o*-Quinone methides (QMs) are an important reactive intermediate for organic synthetic and biological standpoints of view. Photochemical and thermal transformation of *N*,*N*-dialkyl-9-aminomethyl-10-phenanthrols and their naphthalene analogs, which act as QM precursors, has been studied. These precursors readily reacted with alkyl vinyl ethers to give 2-alkoxydibenzo[*f*,*h*]chroman and 2-alkoxybenzo[*f*]chroman, respectively. Thermal and photochemical generation of QM was accelerated by the presence of water molecule in reaction solvents and by the formation of anionic micelle and vesicle.

1. Introduction

Photochemical reactions in aqueous solution have been received much attention from viewpoints of environmentally benign process. However, the advantages of use of water as reaction solvent are still low, because many reactions in aqueous solution are inefficient than those in organic solvents. Recently, much attention has been paid to the water-enhancing effect on the generation of *o*-quinone methide and the analogs (QMs), which are one of the important reactive intermediates from synthetic and biological standpoints of view.[1] Wan et al., for example, have reported on the photochemical generation of QMs by the elimination of water from *o*-(hydroxymethyl)phenol derivatives.[2] They proposed that an intramolecular proton transfer in the excited state of *o*-hydroxystyrene was accelerated by intervention of water molecule that was named ESIPT (exited state intramolecular proton transfer) mechanism, resulting in more effective reaction in aqueous organic solvent than water-free solvents.[3] Yate[4] and our group[5] have reported the nucleophilic addition to QM via proton transfer in aqueous solution. Also, Nakatani and his co-workers have reported on the photochemical generation of QM from *N*,*N*-dimethyl-6-phenyl-2-(aminomethyl)phenol which is highly accelerated in aqueous solvents.[6] Freccero has reported the photochemical generation of QM using (2-hydroxybenzyl)trimethylammonium salts as more effective precursors in water.[7] In order to develop the efficient generation of QMs in aqueous solution, we will report on solvent and micelle effects on the photochemical and thermal transformations from aminomethyl(hydroxy)arenes (**1**) to QMs.

2. Results and discussion

2.1. Products

N,*N*-Dialkyl-9-aminomethyl-10-phenanthrols (**1a–b**) and *N*,*N*-dialkyl-1-aminomethyl-2-naphthols (**1c–e**) were easily prepared by Mannich reactions of 9-phenanthrol and 2-naphthol with the alkylamines in the presence of formalin, respectively. The thermal reaction of *N*,*N*-dimethyl-9-aminomethyl-10-phenanthrol (**1a**) with ethyl vinyl ether (**2a**) proceeded in aqueous MeOH, MeCN, DMF, and THF solutions at 50 °C to give 2-ethoxydibenzo[*f*,*h*]chroman (**3a**), but did not proceed in water-free MeOH and THF solutions (Table 1). 9,10-Phenanthrenequinone (**4**) was produced as a by-product from the thermal reaction of **1a–b** in MeCN–H_2O and DMF–H_2O.

The photoreactions of **1** with vinyl ethers (**2**) were carried out by irradiating a degassed solution containing **1** and **2** by a high-pressure mercury lamp through a Pyrex filter ($\lambda > 280$ nm) at 20 °C (Scheme 1). The photoreaction of **1a**

Keywords: Quinone methide; Cycloaddition; Micelle effect; Photochemical generation.
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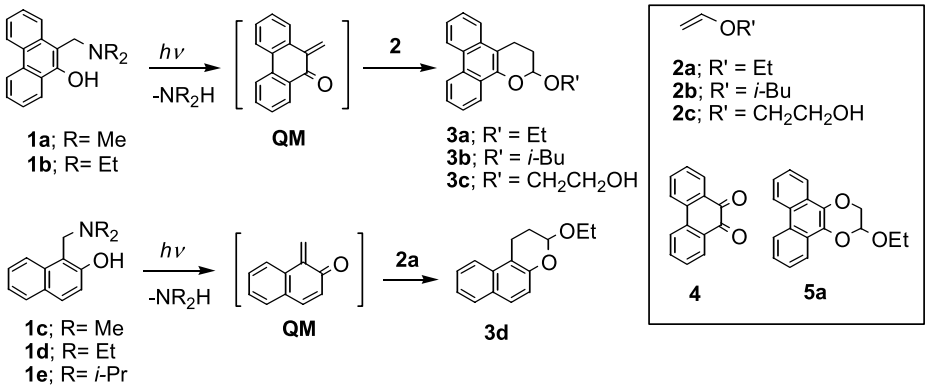
Table 1. Photoreaction of **1** with **2a** in aqueous solution

1	Solvent	Time (h)	Method[a]	3 (Yields/%)[b]
1a	MeCN–H_2O (6:4)	10	A	**3a** (74) [0]
1a	DMF–H_2O (6:4)	10	A	**3a** (30) [0]
1a	MeOH–H_2O (6:4)	10	A	**3a** (25) [0]
1a	THF–H_2O (6:4)	10	A	**3a** (4) [0]
1b	MeCN–H_2O (6:4)	10	A	**3a** (78)
1c	MeCN–H_2O (6:4)	20	A	**3d** (20, 17[c])
1d	MeCN–H_2O (6:4)	20	A	**3d** (30)
1e	MeCN–H_2O (6:4)	20	A	**3d** (43)
1a	MeCN–H_2O (6:4)	10	B	**3a** (50)[d] [0]
1a	MeOH–H_2O (6:4)	10	B	**3a** (84) [0]
1a	DMF–H_2O (6:4)	10	B	**3a** (66)[e] [0]
1a	THF–H_2O (6:4)	10	B	**3a** (70) [0]
1b	MeCN–H_2O (6:4)	10	B	**3a** (72)
1c	MeCN–H_2O (6:4)	10	B	**3d** (15)
1d	MeCN–H_2O (6:4)	10	B	**3d** (44)
1e	MeCN–H_2O (6:4)	10	B	**3d** (58)

[a] Method A: photoreaction at room temperature. Method B: thermal reaction at 50 °C.
[b] The values in the blanket are the yields in the solvents in the absence of water.
[c] The value is the reported yield (Ref. 6).
[d] Accompanied by the formation of 9,10-phenanthrenequinone (**4**) in 32% yield.
[e] Accompanied by the formation of **4** in 6% yield.



Scheme 1. Photoreactions of **1** with vinyl ethers (**2**).

with ethyl vinyl ether (**2a**) in MeCN–H_2O (6:4) gave selectively **3a** in 74% yield without the formation of **4**. However, the photoreaction of **1a** at higher temperature in MeCN–H_2O gave **3a** and 2-ethoxy-4-oxodibenzo[*f*,*h*]-chroman (**5a**) which was formed as a consequence of the photoreaction of **4** with **2a**. As shown in Table 1, the reaction yields were depending on the solvent used. The photoreaction of **1a** with **2a** proceeded more efficiently in aqueous MeCN solution compared with that in MeOH–H_2O and THF–H_2O. It is noteworthy that no reaction occurred entirely in the water-free solvents and even in MeOH regardless of the presence of OH group. Therefore, the presence of water was requisite for the efficient formation of **3** in the photochemical and thermal reactions.

The photochemical and thermal reactions of *N*,*N*-dimethyl-1-aminomethyl-2-naphthol (**1c**) with enamines have been previously reported.[8] However, the yields of the cyclo-adducts were relatively low compared with the case of **1a**. Also, Nakatani et al. have reported that the photoreaction of **1c** with **2a** in MeCN–H_2O (6:4) gave 2-ethoxybenzo[*f*]-chroman (**3d**) but the yield was still low.[6] In order to improve the chemical yields of **3d**, we performed the reaction of *N*,*N*-dialkyl-1-aminomethyl-2-naphthols (**1d–e**) containing more electron-donating alkyl groups on the amino group. The yields were slightly improved in thermal and photochemical reactions.

2.2. Micelle effect

The photocycloaddition of **1a** with **2a** proceeded efficiently in aqueous solution of sodium dodecylsulfate (SDS) that formed a micelle (aggregation number, AN, is 62) in concentrations higher than critical micelle concentration (CMC = 8.1 mM). Figure 1 shows the dependence of the yields of **3a** on the concentration of SDS. In the case of the photochemical reaction, the reaction yields were remarkably enhanced in the presence of SDS of concentrations higher than CMC to reach maximum yield at >9 mM. In the thermal reaction, however, the yield increased gradually, showing no sharp enhancing effect at CMC. It might be due to the disorder of the micelle structure in higher temperature. The formation of **3** occurred effectively in aqueous solution of sodium 1,2-bis(alkyloxycarbonyl)-ethanesulfonate (BES_n: $n=10$ for decyl and 12 for dodecyl groups), which was tend to form a vesicle in aqueous solution.[9,10] Figure 2 shows the dependence of the yields of **3** on the concentration of BES_n. The yields reached to 60%

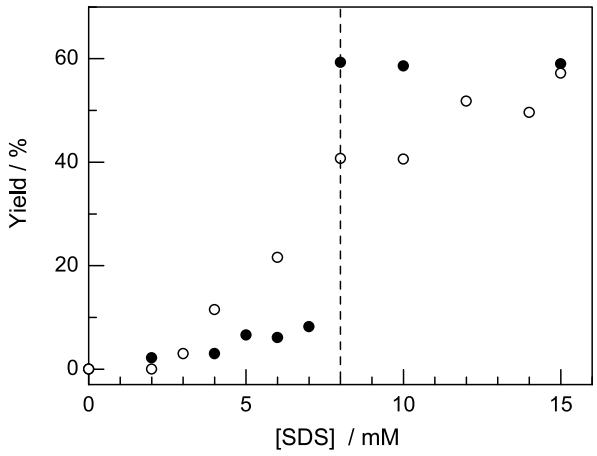


Figure 1. Dependence of the yields on the concentration of SDS in the photochemical (●) and thermal (○) reactions of **1a** with **2a** in aqueous solution.

by the addition of BES_n in concentrations higher than 0.9 mM for BES_{10} and 1.0 mM for BES_{12} to the solution. The advantage of the use of BES_n vesicle is to lower the surfactant concentration than the case of SDS micelle.

However, the reaction in nonionic surfactant such as poly(ethyleneglycol) dodecyl ether (PED; CMC = 0.09 mM, AN = 400) was ineffective (Fig. 3), and the reactions in aqueous solution of cationic surfactant such as hexadecyltrimethylammonium chloride (CTAC; CMC = 1.3 mM, AN = 78) did not occur at all (Table 2). Also, the photoreaction of **1a** with CH_2=CH–OR (**2b**; R = *i*-Bu and **2c**; R = $-CH_2CH_2OH$) in aqueous SDS solution gave the corresponding 2-alkoxydibenzo[*f*,*h*]chroman (**3b**–**c**). But, the photoreaction of **1a** with such other alkenes as 2,3-dimethyl-2-butene and acrylonitrile gave no products.

Although micelle and vesicle operate mainly to dissolve **1** into aqueous solution, the yields were depending on the surfactant used. Anionic surfactants is well known to construct the rigid micelle compared with cationic and nonionic surfactants, because surrounding water molecule

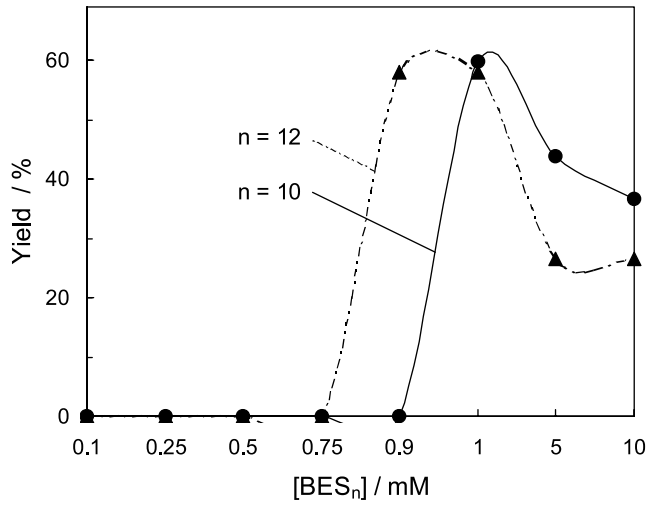


Figure 2. Dependence of the yields on the concentration of BES_n: $n = 10$ (●), $n = 12$ (▲) in the photoreaction of **1a** with **2a** in aqueous solution.

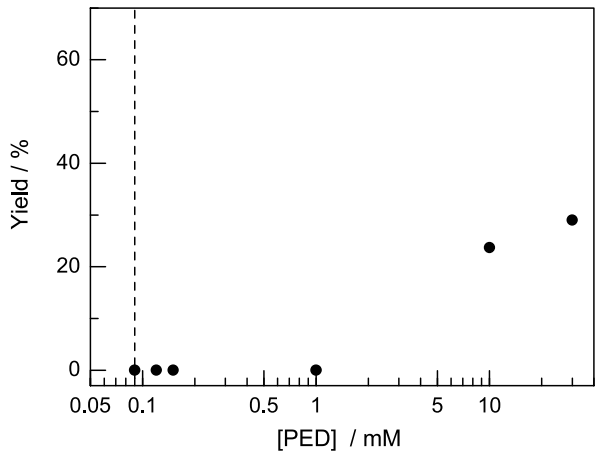


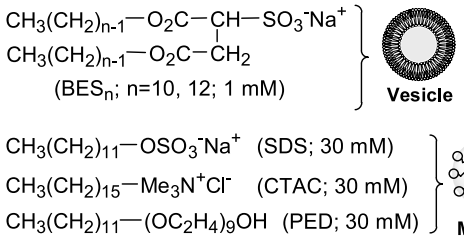
Figure 3. Dependence of the yields on the concentration of PED in the photochemical reactions of **1a** with **2a** in aqueous solution.

can stabilize micelles by the formation of hydrogen bond with the anionic site on the surface of the micelles (Scheme 2). In anionic micelle, therefore, the hydrophilic OH and NR_2 groups of **1** might be fixed on the surface of a

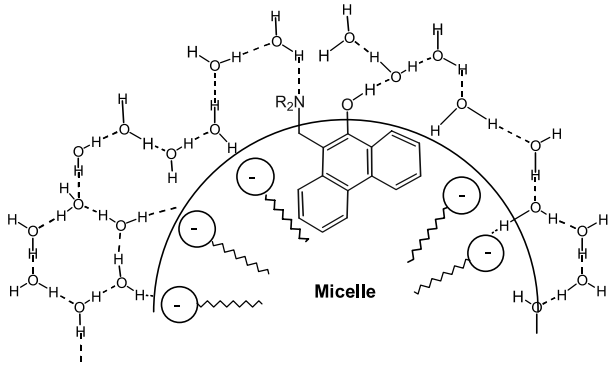
Table 2. Photoreaction of **1a** with **2a**–**c** in aqueous surfactant solution[a]

Solvent/surfactant[b]	**2**	Method[c]	**3** (Yields/%)
H_2O/SDS (30 mM)	**2a**	A	**3a** (61)
H_2O/SDS (30 mM)	**2a**	B	**3a** (72)
H_2O/BES_{12} (1 mM)	**2a**	A	**3a** (58)
H_2O/BES_{12} (1 mM)	**2a**	B	**3a** (41)
H_2O/BES_{10} (1 mM)	**2a**	A	**3a** (58)
H_2O/PED (30 mM)	**2a**	A	**3a** (29)
H_2O/CTAC (30 mM)	**2a**	A	**3a** (0)
H_2O/SDS (30 mM)	**2b**	A	**3b** (29)
H_2O/SDS (30 mM)	**2c**	A	**3c** (43)

[a] Reaction time was 10 h.
[b] The surfactants are as follows:



[c] Method A: photoreaction at room temperature. Method B: thermal reaction at 50 °C



Scheme 2. Schematic representation of micelle surface.

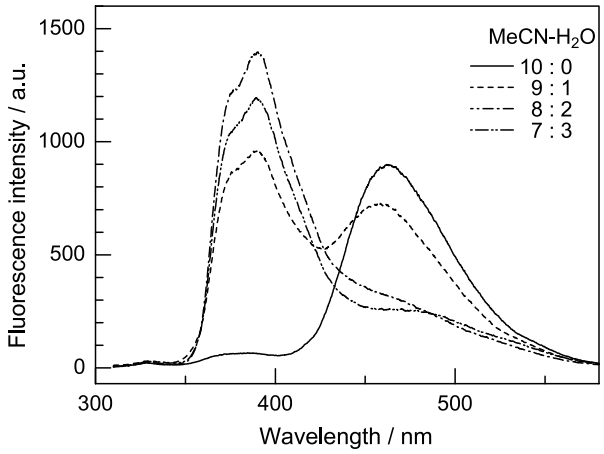


Figure 4. Fluorescence spectra of **1a** in MeCN and MeCN–H_2O (1:1): The excitation at 300 nm, the concentration of **1a** $=1\times10^{-5}$ M.

micelle, while the residual aromatic moiety was oriented toward hydrophobic domain. This causes to induce effective assistance of surrounding water molecule, resulting in the efficient elimination of amine from **1**.

By contrast, the cationic and nonionic surfactants seem unfavorable to form a micelle with a dense of hydrophobic domain, because of little stabilizing effect by surrounding water. Therefore, the hydrophilic OH and NR_2 groups of **1** might arrange randomly in the micelle, resulting that the effect of surrounding water molecule is little. Similar specific enhancing effects of anionic surfactants have already been elucidated on *tetra-O*-acetylriboflavin-photosensitized ring-splitting reaction of pyrimidine cyclobutanes[11] and dehydrogenation of benzyl alcohols[12] in aqueous solution. Thus, the assistance of surrounding water is favorable for the elimination of the amine from **1**.

2.3. Spectroscopic analysis

As has been reported for the formation of QM in the photochemical and thermal reactions of **1c**,[3,6] it is suggested that the QM intermediates, 9-methylene-10-phenanthrone, were formed by the elimination of R_2NH in the cases of the phenanthrene analogs, **1a–b** (Scheme 1). It is well known that the QMs generated from various precursors undergo thermally the cycloaddition reaction with C=C double bonds.[1] Figure 4 shows the fluorescence spectra of **1a** in MeCN and aqueous MeCN. The emission was observed at 460 nm in MeCN. As an increase of the water contents in MeCN, the emission of 460 nm decreased and new emission appeared at 380 nm. It is well known that the phenolic compounds in the excited singlet state are readily converted in the presence of a base to the excited singlet state of the phenolate anion. Therefore, it is safely assigned that the emission at 460 nm comes from the excited singlet states of the zwitter ion (**6**) transformed by the intramolecular proton transfer from the OH to the NH_2 groups of **1a**. Moreover, it is suggested that the emissions at 380 nm come from the excited singlet states of the intermediate (**7**) generated by the protonation on the oxy anion of **6**, since, the emissions at 380 nm observed in the MeCN–H_2O solution was similar to the fluorescence of 9-phenanthrol ($\lambda_{max}=384$ nm). The photochemically and thermally activated **7** induced the Hofmann elimination of R_2NH to give QM intermediate. Similar mechanism has been reported for the photochemical and thermal generation of QM from (2-hydroxybenzyl)-trimethylammonium iodide (Scheme 3).[5]

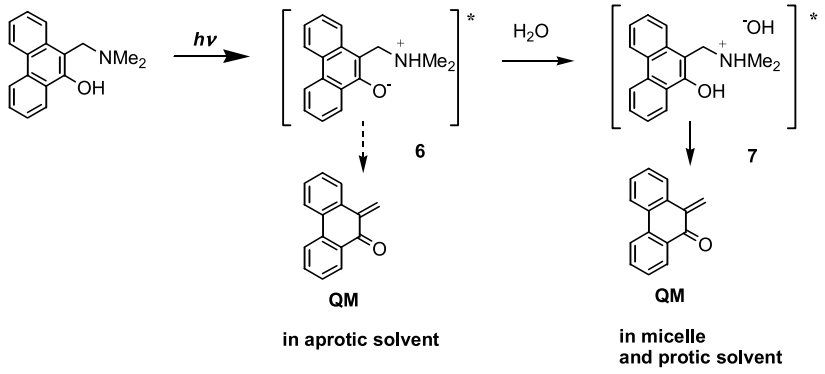
2.4. Participation of water molecule

It has been reported that a water molecule accelerates the intramolecular proton transfer in *o*-hydroxystyrene by ESIPT mechanism. As mentioned above, however, the fluorescence spectra of **1** showed the formation of the zwitter ion (**6**) in MeCN. In contrast to the case of *o*-hydroxystyrene, the proton transfer of **1** proceeds smoothly even in water-free solvents because of the stronger basicity of the amino group than the vinyl group. In the case of **1**, therefore, the enhancing effect of water molecule operates for the elimination step of R_2NH rather than the proton transfer step.

As a conclusion, the recent research of QM intermediate is aimed to the utilization for the bio-molecules involving nucleic acids and peptides.[1] Among a variety of methods to generate QM, therefore, the attention will be focused on the precursor acting in aqueous solution under mild conditions. The photochemical generation of QM from **1** in micelle meets the above requirements.

3. Experimental

9-Bromophenanthrene, 2-naphthol, the amines, and the surfactants were purchased from Wako Chemicals and were used. Commercially available ethyl vinyl ether, isobutyl



Scheme 3. Photochemical generation of *o*-QM.

vinyl ether, and ethylene glycol monovinyl ether were used after distillation to remove the stabilizer (KOH).

^{1}H and ^{13}C NMR spectra were measured on a Bruker AC 250P spectrometer. MS spectra were obtained on a Hitachi M2000A spectrometer. Fluorescence spectra were measured on a Shimadzu RF5300PC fluorometer.

3.1. Preparation of aminomethyl(hydroxy)arenes (1a–e)

Into a flask containing sodium (4.1 g) and pyridine (75 ml) MeOH (75 ml) was added slowly and then CuI (11.4 g) was added into the solution under stirring. Then 9-bromophenanthrene (15.45 g) in pyridine (75 ml) was added into the solution under heating at 80 °C. After heating for 18 h, the reaction was quenched by 10% aqueous HCl solution (75 ml). The extraction with Et_2O of the solution gave the crude 9-methoxyphenanthrene which was purified by column chromatography on SiO_2 and recrystallized from MeOH (yield 86.0%, 10.7 g). The solution of acetic acid (150 ml) of 9-methoxyphenanthrene (7.5 g) was heated at 60 °C and an aqueous solution of HBr (48%, 11.4 ml) was added. After heating at 130 °C for 2 h, the water (150 ml) was added, and the precipitate was obtained by filtration and washing with water to give 9-phenanthrol in 92% yield (6.42 g).

The preparation of **1** was performed by Mannich reaction. Into a reaction mixture of 9-phenanthrol (30 mmol, 5.82 g) and aqueous Me_2NH solution (40%, 40 mmol), a formalin solution (37%, 30 mmol) was slowly added. After stirring at room temperature for 18 h, the solution was extracted with $CHCl_3$. The evaporation of the solvent left the crude *N*,*N*-dimethyl-9-aminomethyl-10-phenanthrol (**1a**) that was subjected to column chromatography on Al_2O_3. Also, *N*,*N*-diethyl-9-aminomethyl-10-phenanthrol (**1b**) and *N*,*N*-dialkyl-1-aminomethyl-2-naphthols (**1c–e**) were prepared according to the method to prepare **1a**.

3.1.1. *N*,*N*-Dimethyl-9-aminomethyl-10-phenanthrol (1a). Yield 76%. ^{1}H NMR δ=2.45 (s, 6H), 4.14 (s, 2H), 7.44–7.53 (m, 3H), 7.83 (d, J=8.1 Hz, 1H), 8.38–8.42 (m, 2H), 8.61–8.66 (m, 2H); ^{13}C NMR δ=44.73, 58.45, 106.34, 121.17, 122.21, 122.67, 122.91, 123.15, 125.81, 126.29, 126.71, 126.80, 130.81, 131.91, 152.79. Exact mass calcd for $C_{17}H_{17}NO$: 251.1310. Found 251.1302.

3.1.2. *N*,*N*-Diethyl-9-aminomethyl-10-phenanthrol (1b). Yield 68%. ^{1}H NMR δ=1.15 (d, J=7.5 Hz, 3H), 2.70 (q, J=7.5 Hz, 4H), 4.23 (s, 2H), 7.40–7.61 (m, 5H), 8.37–8.41 (m, 1H), 8.61–8.66 (m, 2H); ^{13}C NMR δ=11.23, 47.04, 52.87, 106.14, 120.93, 122.10, 122.19, 122.62, 122.69, 123.03, 125.54, 126.45, 126.63, 126.91, 127.07, 130.34, 131.85, 153.05. Exact mass calcd for $C_{19}H_{21}NO$: 279.1623. Found 279.1549.

3.1.3. *N*,*N*-Dimethyl-1-aminomethyl-2-naphthol (1c). Yield 63%. ^{1}H NMR δ=2.36 (s, 6H), 4.04 (s, 2H), 7.06–7.78 (m, 7H); ^{13}C NMR δ=44.57, 57.79, 111.29, 119.15, 120.84, 122.74, 126.19, 128.35, 128.79, 129.10, 132.47, 156.71. Exact mass calcd for $C_{13}H_{15}NO$: 202.1154. Found 202.1165.

3.1.4. *N*,*N*-Diethyl-1-aminomethyl-2-naphthol (1d). Yield 68%. ^{1}H NMR δ=1.12 (d, J=7.2 Hz, 6H), 2.65 (q, J=7.2 Hz, 4H), 4.15 (s, 2H), 7.07 (d, J=8.8 Hz, 1H), 7.18–7.26 (m, 1H), 7.35–7.42 (m, 2H), 7.46–7.76 (m, 3H); ^{13}C NMR δ=11.23, 46.32, 52.21, 111.20, 118.54, 119.32, 120.69, 122.13, 126.16, 128.26, 128.62, 132.53, 157.04. Exact mass. calcd for $C_{15}H_{19}NO$: 229.1467. Found 229.1466.

3.1.5. *N*,*N*-Diisopropyl-1-aminomethyl-2-naphthol (1e). Yield 21%. ^{1}H NMR δ=1.14 (d, J=6.6 Hz, 6H), 3.18 (sept, J=6.6 Hz, 1H), 4.23 (s, 2H), 7.03 (d, J=8.8 Hz, 1H), 7.16–7.25 (m, 1H), 7.35–7.42 (m, 2H), 7.58–7.76 (m, 3H); ^{13}C NMR δ=21.32, 44.65, 51.11, 111.01, 116.64, 120.72, 120.90, 122.16, 126.16, 126.39, 127.71, 129.60, 157.22. Exact mass calcd for $C_{17}H_{23}NO$: 257.1780. Found 257.1788.

3.2. Preparation of BES_n

Decanol (3.3 mmol) was heated with maleic anhydride (1.5 mmol) in the presence of H_2SO_4 (0.1 ml) in benzene (50 ml) at 110 °C on Dean-Stark apparatus. After the neutralization with aqueous $NaHCO_3$ solution, the solution was extracted with benzene. Evaporation of the benzene solution left the crude didecyl maleate that was purified by the recrystallization from hexane. An aqueous solution (50 ml) containing of $NaHSO_3$ (17.5 g) and didecyl maleate (1 mmol) was refluxed for 3 h under bubbling with air. After the neutralization with $NaHCO_3$, the solution was evaporated. The resulting residue was solved into hot methanol, and filtrated. The filtrate was evaporated to give a crude BES_{10} which was purified by recrystallization from hexane.

3.2.1. Didecyl maleate. Yield 78%. ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.9 Hz, 6H), 1.30 (br s, 28H), 1.66 (t, J=7.0 Hz, 4H), 4.17 (t, J=6.8 Hz, 4H), 6.23 (s, 2H).

3.2.2. Sodium 1,2-bis(decylcarbonyl)ethanesulfonate (BES_{10}).[9,10] Yield 16%. ^{1}H NMR (CD_3OD) δ=0.89 (br t, 6H), 1.26–1.31 (m, 28H), 1.63 (br s, 4H), 3.00–3.20 (m, 2H), 4.15–4.20 (m, 5H).

In a similar manner, BES_{12} was prepared using dodecanol instead of decanol.

3.2.3. Didodecyl maleate. Yield 18%. ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.9 Hz, 6H), 1.26 (br s, 28H), 1.60–1.75 (m, 4H), 4.17 (t, J=6.7 Hz, 4H), 6.22 (s, 2H).

3.2.4. Sodium 1,2-bis(dedecylcarbonyl)ethanesulfonate (BES_{12}). Yield 36%. ^{1}H NMR (CD_3OD) δ=0.90 (br t, 6H), 1.30 (br s, 36H), 1.64 (br s, 4H), 3.00–3.20 (m, 2H), 4.15–4.20 (m, 5H).

3.3. General procedure for the reaction of 1 with 2

MeCN–H_2O (6:4), DMF–H_2O (6:4), MeOH–H_2O (6:4), and THF–H_2O (6:4) solutions (100 ml) of **1** (1 mmol) were bubbled with argon gas for 15 min and then **2a** (15 mmol, 1.08 g) was introduced into the solution. Irradiation was performed by an Eikosha high-pressure mercury lamp through a Pyrex filter for 10–20 h at room temperature

(Method A). After the photoreaction, the solvent was evaporated from the photolysate. The crude products were purified by a column chromatography on silica-gel to give **3**. The structure was assigned by ^{1}H NMR and MS spectra. The **2a** was purified by distillation since commercially available **2a** was stabilized by 0.1% NaOH. Under irradiation without the remove of NaOH, **1a** was turned to 9,10-phenanthrenequinone that underwent the formation of the cycloadduct (**5a**) with **2a**.

In the cases of aqueous surfactant solutions, aqueous solution (100 ml) containing **1a** (1 mmol, 251 mg) and the surfactant (SDS 30 mM, 864 mg; PED 30 mM, 1.747 g; CTAC: 30 mM, 960 mg) was bubbled with argon gas for 30 min under cooling with ice and then **2** (15 mmol) was introduced into the solution. Irradiation was performed, as described above (Method A). After the irradiation, the photolysates were extracted with $CHCl_3$. The $CHCl_3$ solution was washed with saturated aqueous NaCl solution to remove the surfactant and was subjected to a column chromatography on silica-gel to give **3a**.

For the case of BES_n, BES_n (0.1–10 mmol, 0.05–5 g for BES_{10}, 0.056–5.6 g for BES_{12}) was solved in MeOH and heated at 40 °C and then cooled to room temperature. After the addition of **1** (0.1 mmol), MeOH was removed by a rotary evaporator to produce a thin film of BES_n and then the film was dried in vacuo. The BES_n film containing **1** was suspended in water (10 ml) and the solution was sonicated at 30 °C for 10 min, giving clear ($\sim$1 mM for BES_n) to slightly turbid ($>$ 5 mM for BES_n) solutions. The obtained solution was bubbled with argon gas for 30 min. After **2a** (1.5 mmol) was introduced into the solution, irradiation was performed. The follow-up process was similar to the method described above.

The thermal reactions of **1** with **2a** were performed for a solution (50 ml) containing **1** (0.2 mmol) and **2a** (3.0 mmol) at bath temperature at 50 °C for 3 h (Method B).

3.3.1. 2-Ethoxydibenzo[*f,h*]chroman (3a). ^{1}H NMR δ= 1.14 (t, J=7.2 Hz, 3H), 2.12–2.26 (m, 4H), 2.90–3.18 (m, 2H), 3.60–3.78 (m, 1H), 3.88–4.00 (m, 1H), 5.41 (t, J= 2.6 Hz, 1H), 7.15–7.60 (m, 4H), 7.73–7.85 (m, 1H), 8.30–8.46 (m, 1H), 8.53–8.59 (m, 2H). ^{13}C NMR δ=15.15, 18.13, 26.56, 63.94. 97.09, 121.79, 122.37, 122.37, 122.72, 124.00, 126.38, 126.38, 126.84, 130.51, 130.82, 131.53, 131.84, 144.80, 152.50. Exact MS calcd for $C_{19}H_{18}O_2$: 278.1307. Found 278.1304.

3.3.2. 2-Isobutoxydibenzo[*f,h*]chroman (3b). ^{1}H NMR δ=0.78 (d, J=6.7 Hz, 3H), 0.83 (d, J=6.7 Hz, 3H), 1.83 (d, J=6.7 Hz, 1H), 2.13–2.31 (m, 2H), 2.99–3.16 (m, 2H), 3.43 (dd, J=9.4, 6.7 Hz, 1H), 3.67 (dd, J=9.5, 6.7 Hz, 1H), 5.45 (dd, J=3.5, 2.6 Hz, 1H) 7.49–7.64 (m, 4H), 7.86–7.90 (m, 1H), 8.29–8.33 (m, 1H), 8.59–8.64 (m, 2H); ^{13}C NMR δ=17.56, 21.03, 28.88, 42.28, 70.80, 109.57, 117.31, 123.38, 123.55, 128.71, 129.92, 131.03, 133.42, 156.74. Exact MS calcd for $C_{21}H_{22}O_2$: 306.1620. Found 306.1584.

3.3.3. 2-(2-Hydroxyethoxy)dibenzo[*f,h*]chroman (3c). ^{1}H NMR δ=1.70 (br s, 1H), 2.20–2.35 (m, 4H), 3.10–3.20 (m, 2H), 3.65–3.74 (m, 1H), 3.80–3.92 (m, 1H), 3.96–4.08 (m, 1H), 5.54 (t, J=3.1 Hz, 1H), 7.15–7.60 (m, 4H), 7.73–7.85 (m, 1H), 8.30–8.46 (m, 1H), 8.53–8.59 (m, 2H); ^{13}C NMR δ=17.96, 26.43, 61.68, 69.96, 97.64, 121.64, 122.41, 122.80, 124.23, 126.53, 126.93. Exact MS calcd for $C_{19}H_{18}O_3$: 294.1283. Found 294.1281.

3.3.4. 2-Ethoxybenzo[*f*]chroman (3d). ^{1}H NMR δ=1.18 (t, J=7.5 Hz, 3H), 2.07–2.21 (m, 2H), 3.05–3.13 (m, 2H), 3.61–3.70 (m, 1H), 3.87–3.96 (m, 1H), 5.31 (t, J=2.5 Hz, 1H), 7.06 (d, J=8.9 Hz, 1H), 7.33 (dd, J=6.8, 1.0 Hz, 1H), 7.48 (dd, J=6.8, 1.3 Hz, 1H), 7.63 (d, J=8.9 Hz, 1H), 7.82 (d, J=5.2 Hz, 1H), 7.85 (d, J=5.2 Hz, 1H); ^{13}C NMR δ= 15.10, 17.43, 26.37, 29.23, 30.85, 63.75, 96.81, 114.37, 119.04, 121.95, 123.27, 126.20, 127.66, 128.33, 129.25. Exact mass calcd for $C_{15}H_{16}O_2$: 228.1150. Found 228.1148.

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