Trifluoromethyl-Substituted Donor–Acceptor Norbornadiene, Useful Solar Energy Material

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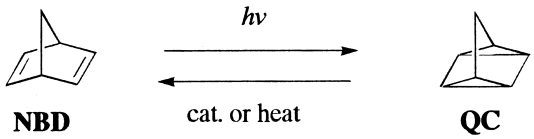
(Received Feburuary 9, 2001)

Trifluoromethyl (CF_3)-substituted donor–acceptor norbornadiene (NBD) derivatives were synthesized. The photoisomerization of CF_3-NBD derivatives proceeded smoothly. The thermal stability of quadricyclane (QC) derivatives obtained from CF_3-NBD derivatives was examined, and it was found that the CF_3 group increased the thermal stability of the QC derivatives. Furthermore, CF_3-NBD derivatives exhibited efficient fatigue resistance.

Photochemical valence isomerization between norbornadiene (NBD) and quadricyclane (QC) is of interest as a solar energy conversion and storage system,[1] because photoenergy can be stored as strain energy (about 20 kcal/mol) in a QC molecule (Scheme 1). Recently, this photochemical reaction has also been investigated as an optical waveguide utilizing photoinduced refractive index changes[2a–d] or as a photochromic system potentially applicable to data storage.[2e]

However, the photochemical reaction of NBD does not ordinarily occur upon irradiation with sunlight, because NBD does not efficiently absorb visible light. To solve this problem, there are two different methods used. One is the use of photosensitizers such as benzophenone derivatives in the NBD reaction system.[3] However, the wavelength which can be utilized is limited to the shorter region in visible light,[3a,b] and decomposition of the photosensitizer frequently results from by prolonged irradiation.[3f] The other is the introduction of suitable chromophores into the NBD molecule to extend the absorption to longer wavelength. To this end, many NBD derivatives have been synthesized.[4] Maruyama et al. and Mukai et al. reported the synthesis of the NBDs which have several chromophores on one of the two double bonds of the NBD molecule, but the quantum yield of the photoisomerization was relatively low.[4a–d] On the other hand, Yoshida et al. and Yonemitsu et al. have found that donor–acceptor (D–A) NBDs have C-T absorption in a visible region and photoisomerize to give QCs in high quantum yield.[4f–j] However, these NBDs do not absorb visible light efficiently (low $\varepsilon \sim 1000$) and the QCs that are obtained from NBDs whose absorption edge reaches above 500 nm are not stable enough, namely, they revert to the starting NBDs rapidly at room temperature.[4g]

It is known that a perfluoroalkyl group often serves to produce a stable valence isomer of aromatic compounds.[5] As in the case of NBDs, introduction of a CF_3 group would be expected to give the corresponding QCs with increased stability. Therefore, we synthesized new NBDs (**1**) containing a CF_3 group on the C-T acceptor site and examined the photoisomerization of these NBDs. We also examined the thermal stability of QCs obtained from CF_3-NBDs. Furthermore, we examined the durability of CF_3-NBDs.



Scheme 1.

Results and Discussion

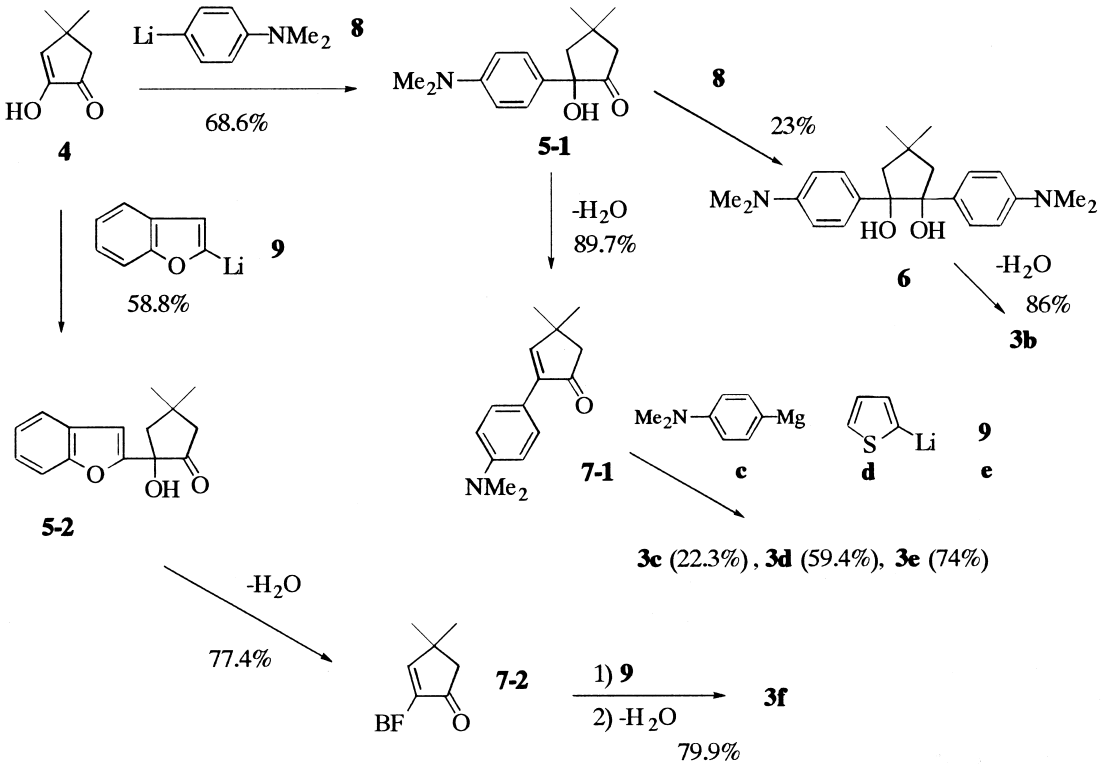
Synthesis of D–A NBDs Containing CF_3 Group. CF_3-NBDs (**1**) were synthesized according to the reaction sequences shown in Schemes 2 and 3.[6] As shown in Scheme 2, cyclopentadiene derivatives (**3b–f**) were synthesized from **4**.[7] 2-Hydroxy ketone (**5-1**) was obtained from the reaction of **4** with 4-(dimethylamino)phenyl lithium reagent (**8**) in 68.6% yield, then a second 4-dimethylaminophenyl group was introduced in 23% yield to give diol **6**. It seems that the relatively lower yield of **6** than that of **5-1** may be due to the steric effect of the substituent. Then, **6** was dehydrated by *p*-TsOH in toluene to give **3b** in 86% yield. **3c–e** were obtained in a similar way from **7-1**, which was obtained from dehydration of **5-1** in 89.7% yield, with a suitable phenyllithium reagent in 22.3, 59.4, and 74.0% yield, respectively. Similarly, addition of 2-lithiobenzofuran (**9**) to **4** gave **5-2** in 85.8% yield, followed by dehydration to give **7-2** in 77.4% yield, and finally, reaction with **9** to give **3f** in 79.9% yield. **3a** was prepared according to the literature.[8] As shown in Scheme 3 and Table 1, **1** was synthesized in good yields by the Diels–Alder reaction of hexafluoro-2-butyne (**2**) with **3**. This NBD synthesis strategy involves the facile introduction of a variety of substituents into the 2,3 positions, the C-T donor site, of the NBD framework.

Photochemical Property and Photoisomerization of CF_3-NBDs. Absorption spectra of the NBDs in the UV-visible region are shown in Fig. 1. Thus, CF_3-NBDs have a quite large absorption coefficient (ε value) in the visible region as compared with those of NBDs having other groups such as COOMe (**10**) or CN (**11**).[9] The absorption maxima of NBDs tend to red shift (**1a** < **c** < **d** < **b** < **e** < **f**) with the electron-donating ability of the donor group. Especially, **1f** having 2-benzofuryl as a donor group, has logε 4.30 at 414 nm and the

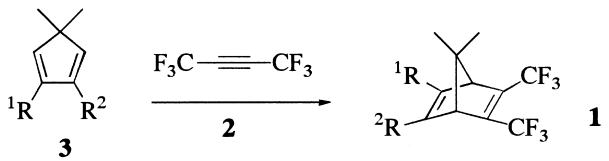
Table 1.

1	R1	R2	λ_{max}/nm[a] (log ε)	λ_{AE}/nm[a]	Yield/% from **3**
a	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	346 (3.71)	440	91
b	*p*-$Me_2NC_6H_4$	*p*-$Me_2NC_6H_4$	390 (3.93)	510	100
c	*p*-$Me_2NC_6H_4$	*p*-$MeOC_6H_4$	374 (3.93)	500	80.1
d	*p*-$Me_2NC_6H_4$	2-Thiophenyl	385 (3.89)	520	88.2
e	*p*-$Me_2NC_6H_4$	2-Benzofuryl	407 (4.11)	580	97.3
f	2-Benzofuryl	2-Benzofuryl	414 (4.30)	480	87

a) 1×10^{-4} mol dm^{-3} solution in acetonitrile.



Scheme 2.



Scheme 3.

absorption cut-off of **1e** reaches 580 nm (Table 1 and Fig. 1).

The photoisomerization of the CF_3-NBDs in CH_3CN solution (1×10^{-4} mol/L) was carried out by the irradiation of a 500-W xenon lamp. Changes in the UV spectra of **1a** are shown in Fig. 2. The maximum absorption of the NBDs decreased and the NBDs isomerized to the corresponding QCs after 10 min by irradiation. In addition, two isosbestic points at 219 and 240 nm were observed. This result means that the photoisomerization of the CF_3-NBD to the corresponding QCs occurred selectively without any side reactions. As shown in Fig. 3, the photoisomerization rate of CF_3-NBDs was higher

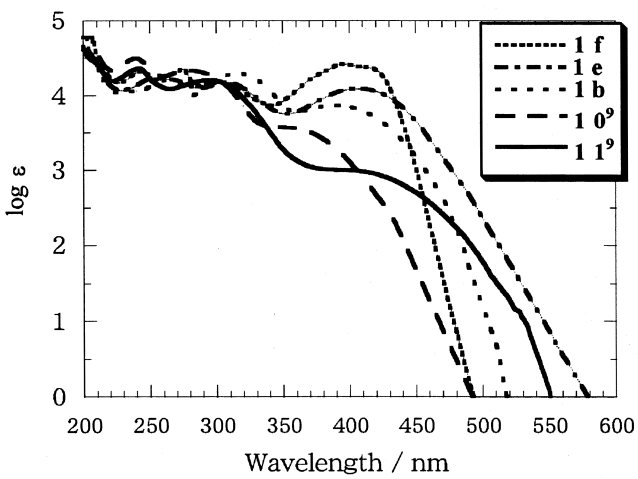


Fig. 1. Absorption spectra of NBD derivatives(1×10^{-4} mol dm^{-3} solution in acetonitrile).

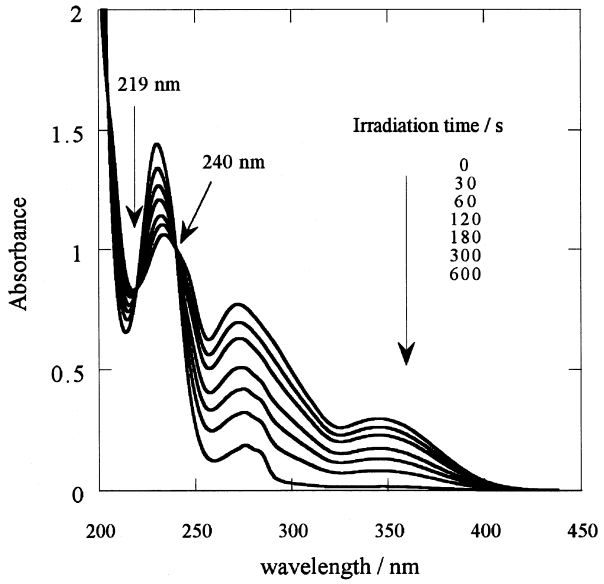


Fig. 2. Change in UV spectra of **1a** upon irradiation with a xenon lamp(1×10^{-4} mol dm^{-3} solution in acetonitrile).

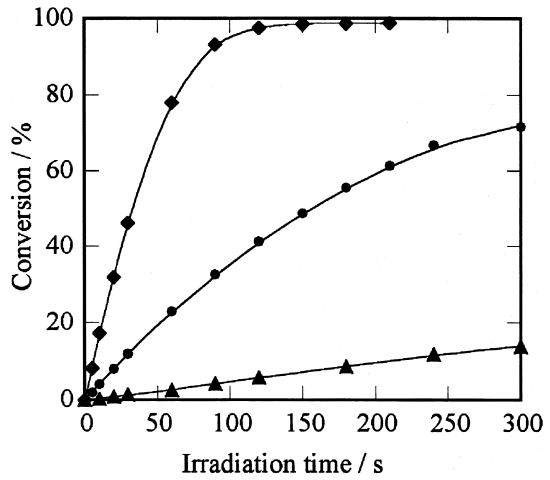


Fig. 3. Rates of photoisomerization of NBDs in solution: (●)**1a**; (◆)**1f**; (▲)**10**[9].

than that of the other D–A NBD (**10**)[9] bearing ester groups on the C-T acceptor site. It seems that the higher photoisomerization rate of CF_3-NBDs is attributable to its large absorption in the visible region.

The quantum yields of **1a** and **1f** of photoisomerization from NBDs to QCs in CH_3CN solution (1×10^{-4} mol/L) were evaluated with a chemical actinometer. The quantum yield at 354 nm of **1a** and at 400 nm of **1f** were 0.7 and 0.6, respectively. These results suggest that CF_3-NBDs have high photochemical reactivity.

Thermal Stability of the QCs. Next, we examined the thermal stability of QCs at room temperature (20 °C) in a PMMA solid film (Table 2). As shown in Table 2, the CF_3 group increased the thermal stability of QCs. In particular, **1b**, **d**, **e**, and **f** not only have larger absorption in the visible region but also produce far more stable QCs than **10**[9] and **11**.[9] The thermal reversion rate of the QCs to the corresponding NBDs obeyed the first-order kinetics. The rate constants are shown in Table 2.

Table 2. Thermal Stability of QC Derivatives at Room Temperature (20 °C) in the Dark

No. of NBDs	$T_{1/2}$ of QCs	k/min^{-1}	Temp/°C
10[9]	6.5 h	1.45×10^{-2}	35
11[9]	11 min	14.7×10^{-2}	25
1a	stable	5.38×10^{-2}	130
1b	1.1 year	6.44×10^{-2}	70
1c	stable	20.3×10^{-2}	130
1d	500 h	0.325×10^{-4}	20
1e	31 h	3.78×10^{-4}	20
1f	72 h	1.27×10^{-4}	20

Table 3. Stored Thermal Energy in the CF_3-QC Derivatives

No. of NBDs	**1a**	**1c**	**1e**	**1f**
Stored thermal energy/kJ mol^{-1}	80	78	76	63

It was reported that the QC groups contained in polymer chains were more stable than monomer QC, and that the rigidity of the polymer chains was intimately reflected in the stability of the QC.[10] Furthermore, it was reported that the CF_3 group was rigid and spherical, and showed as large a steric effect as an *s*-butyl group.[11] On the other hand, it was reported that QCs containing a CF_3 group and a ketone group on the C-T acceptor site were rather unstable.[5c] Therefore, it seems that both CF_3 groups introduced into the acceptor olefin parts are necessary and the large steric effect of these CF_3 groups contributes to the stability of QC as the rigidity of the polymer chain.

Measurement of Stored Thermal Energy in the CF_3-QCs. The stored thermal energy in the CF_3-QCs obtained from **1a**, **c**, **e**, and **f** was measured on DSC. The irradiated **1a**, **c**, **e**, and **f** released 80, 78, 76, and 63 kJ/mol of thermal energy, respectively (Table 3). The value of stored thermal energy in these QCs was lower than that reported (about 84 kJ/mol) for other QCs. It is possible that the stored thermal energy in the QCs obtained from the NBDs, which absorb longer wavelength light, was lower than that from other NBDs.

Examination of Durability of the CF_3-NBDs. We also examined the ability of the CF_3-NBDs to turn over the cycles of photochemical valence isomerization (NBDs → QCs) and thermal reversion isomerization (QCs → NBDs). Few studies concerning the reversibility of NBD compounds have been reported so far.[4g, 12] Fatigue resistance of NBDs **1a**, **b**, **c**, and **f** in PMMA solid film is shown in Fig. 4. While **1b** and **c** having a *p*-(dimethylamino)phenyl group showed low fatigue resistance, **1a** and **f** having *p*-methoxyphenyl groups and 2-benzofuryl groups, respectively, showed excellent fatigue resistance. After 10^3 times of the cycle, the loss in extinction was 30% and 3% for **1a** and **f**, respectively. These results possibly indicate that the dimethylaminophenyl group seems to be more labile for photo or thermal degradation than the methoxylphenyl and benzofuryl groups.

Conclusion

From all these results, the following conclusions can be ob-

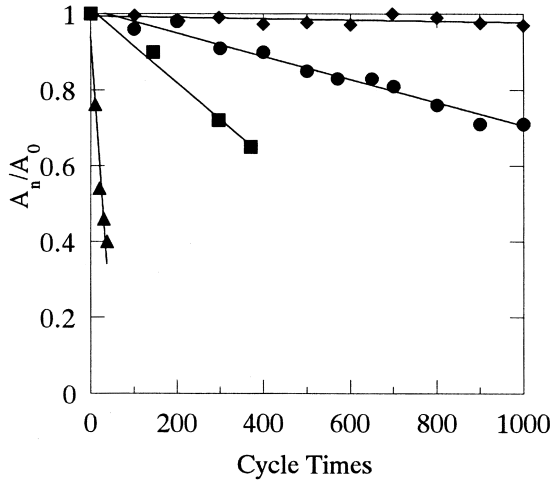


Fig. 4. Durability of CF_3-NBD derivatives: (●)**1a**; (▲)**1b**; (■)**1c**; (◆)**1f**.

tained. 1) CF_3-substituted donor–acceptor NBD derivatives were synthesized. 2) This NBD synthesis strategy involves the facile introduction of a variety of substituents into the 2,3 positions, the C-T donor site, of the NBD framework. 3) The photoisomerization of CF_3-NBD derivatives proceeded smoothly. 4) The CF_3 group increased the thermal stability of QC derivatives. 5) CF_3-NBD derivatives exhibited efficient fatigue resistance.

Experimental

Apparatus. Melting points were determined with a Yanaco MP-500D hot stage microscope and not corrected. Infrared spectra were obtained on a Perkin Elmer 1600 FT-IR either neat or in KBr pellets. Absorption was expressed as reciprocal centimeters (cm^{-1}). ^1H NMR were recorded at 200 MHz on a Varian Gemini-200 instrument and indicated in parts per million (ppm) downfield from tetramethylsilane as the internal standard (δ). ^{19}F NMR spectra were measured at 188 MHz on a Varian Gemini-200 instrument and indicated in parts per million (ppm) upfield from CCl_3F as the internal standard. Low- and high-resolution mass spectral analyses were performed under 70 eV electron-impact (EI) conditions on a Kratos CONCEPT-1H double-focusing magnetic sector spectrometer. Elemental analyses were made at Toray Research Center, Inc., Tokyo.

Synthesis of CF_3-NBD Derivatives. Synthesis of 1a. **3a** (306 mg, 1 mmol), which was prepared according to the literature,[8] was placed in a stainless steel tube with toluene (5 mL). To this tube, **2** (0.2 mL) was introduced by a vacuum line. The mixture was stirred at 100 °C for 6 h in the tube. After the tube was cooled in an ice bath, it was opened and the mixture was extracted with ether. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 30:1) to give **1a** (427 mg, 91%), as slightly yellow needles, mp 80–81 °C. ^1H NMR ($CDCl_3$) δ 1.26 (s, 3 H), 1.36 (s, 3 H), 3.69 (s, 2 H), 3.80 (s, 6 H), 6.81 (d, J = 9.0 Hz, 4 H), 7.18 (d, J = 9.0 Hz, 4 H); ^{19}F NMR ($CDCl_3$) δ −61.46 (bs); IR (KBr) 1607, 1514, 1302, 1253, 1180, 1138, 1036 cm^{-1}. Found: C, 64.17; H, 4.73%. Calcd for $C_{25}H_{22}F_6O_2$: C,64.10; H, 4.73%.

Synthesis of 1b. The Diels–Alder reaction of **2** with **3b** was carried out in the same way as above to give **1b** in 100% yield as yellow needles, mp 126–127 °C. ^1H NMR ($CDCl_3$) δ 1.22 (s, 3 H), 1.32 (s, 3 H), 2.91 (s, 12H), 3.77 (s, 2 H), 6.34 (d, J = 9.0 Hz, 4 H), 7.13 (d, J = 9.0 Hz, 4 H); ^{19}F NMR ($CDCl_3$) δ −60.21 (bs); IR (KBr) 1610, 1524, 1345, 1299, 1175, 1133 cm^{-1}. Found: C, 65.53; H, 5.67%. Calcd for $C_{27}H_{28}F_6N_2$: C,65.58; H, 5.71%.

Synthesis of 1c. The Diels–Alder reaction of **2** with **3c** was carried out in the same way as above to give **1c** in 80.1% yield as yellow needles, mp 110–111 °C. ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.27 (s, 3 H), 2.87 (s, 6 H), 3.59 (d, J = 3.5 Hz, 1 H), 3.63 (d, J = 3.5 Hz, 1 H), 3.71 (s, 3 H), 6.54 (d, J = 8.9 Hz, 2 H), 6.73 (d, J = 8.9 Hz, 2 H), 7.08 (d, J = 8.9 Hz, 2 H), 7.22 (d, J = 8.9 Hz, 2 H); ^{19}F NMR ($CDCl_3$) δ −61.26 (q, J = 9.0 Hz, 3F), −61.50 (q, J = 9.0 Hz, 3F); IR (KBr) 1609, 1522, 1508, 1298, 1175, 1139 cm^{-1}. Found: C, 64.82; H, 5.20; N, 2.91%. Calcd for $C_{26}H_{25}F_6NO$: C, 64.86; H, 5.28; N, 2.91%.

Synthesis of 1d. The Diels–Alder reaction of **2** with **3d** was carried out in the same way as above to give **1d** in 88.2% yield as yellow needles, mp 56–57 °C. ^1H NMR ($CDCl_3$) δ 1.25 (s, 3 H), 1.33 (s, 3 H), 2.98 (s, 6 H), 3.66 (d, J = 3.6 Hz, 1 H), 3.71 (d, J = 3.6 Hz, 1 H), 6.72 (d, J = 8.9 Hz, 2 H), 6.95 (dd, J = 5.1, 3.7 Hz, 1 H), 7.04 (dd, J = 3.7, 1.2 Hz, 1 H), 7.15 (dd, J = 5.1, 1.2 Hz, 1 H), 7.27 (d, J = 8.7 Hz, 2 H); ^{19}F NMR ($CDCl_3$) δ −61.25 (q, J = 6.6 Hz, 3F), −61.34 (q, J = 6.6 Hz, 3F); IR (KBr) 1610, 1525, 1346, 1298, 1175, 1132 cm^{-1}. Found: C, 60.38; H, 4.60; N, 3.06%. Calcd for $C_{23}H_{21}F_6NS$: C, 60.38; H, 4.63; N, 3.06%.

Synthesis of 1e. The Diels–Alder reaction of **2** with **3e** was carried out in the same way as above to give **1e** in 97.3% yield as orange viscous oil. ^1H NMR ($CDCl_3$) δ 1.28 (s, 3 H), 1.31 (s, 3 H), 3.03 (s, 6 H), 3.78 (d, J = 3.6 Hz, 1 H), 3.95 (d, J = 3.6 Hz, 1 H), 6.70–6.80 (m, 3 H), 7.10–7.43 (m, 3 H), 7.45–7.60 (m, 3 H); ^{19}F NMR ($CDCl_3$) δ −61.00 (q, J = 9.4 Hz, 3F), −61.48 (q, J = 9.4 Hz, 3F); IR (KBr) 1676, 1609, 1345, 1297, 1176, 1136 cm^{-1}; MS m/z 491 (M^+; 100), 476 (M^+−Me; 36), 461 (8), 448 (11), 422 (6), 385 (11), 261 (37). HRMS Found: m/z 491.16766. Calcd for $C_{27}H_{23}F_6NO$: M, 491.16838.

Synthesis of 1f. The Diels–Alder reaction of **2** with **3f** was carried out in the same way as above to give **1f** in 87% yield as yellow needles, mp 105–106 °C. ^1H NMR ($CDCl_3$) δ 1.29 (s, 3 H), 1.34 (s, 3 H), 4.16 (s, 2H), 7.22–7.40 (m, 6 H), 7.55 (d, J = 8.2 Hz, 2 H), 7.61–7.68 (m, 2 H); ^{19}F NMR ($CDCl_3$) δ −61.57 (s); IR (KBr) 1681, 1451, 1352, 1297, 1172, 1133, 749 cm^{-1}. Found: C, 66.55; H, 3.75%. Calcd for $C_{27}H_{18}F_6O_2$: C, 66.40; H, 3.71%.

Synthesis of 2-Hydroxy-4,4-dimethyl-2-[4-(dimethylamino)phenyl]-cylopentan-1-one (5-1). A solution of **4** (5.0 g, 40 mmol) in ether (150 mL) was added dropwise at 0 °C to an ether solution (350 mL) of lithium reagent (**8**) obtained from 4-bromo-*N*,*N*-dimethylaniline (22.8 g, 114 mmol) with *n*-BuLi (1.59 M, 75 mL, 120 mmol). The mixture was stirred for 18 h at room temperature, then poured into ice-water, and extracted with ether. The ether layer was washed with brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 5:1) to give **5-1** (6.79 g, 68.6%) as colorless viscous oil. ^1H NMR ($CDCl_3$) δ 1.10 (s, 3 H), 1.20 (s, 3 H), 2.23 (d, J = 13.8 Hz, 1H), 2.35 (d, J = 15.8 Hz, 1H), 2.38 (d, J = 13.8 Hz, 1H), 2.45 (d, J = 15.8 Hz, 1H), 2.70 (s, 1 H), 2.93 (s, 6 H), 6.70 (d, J = 9.1 Hz, 2 H), 7.22 (d, J = 9.1 Hz, 2 H); IR (KBr) 3448, 2950, 1741, 1618, 1528, 1365 cm^{-1} ; MS m/z 247 (M^+; 17), 229 (M^+−H_2O; 81), 214 (M^+−H_2O−Me; 83), 186 (71), 163 (100), 148 (36). HRMS Found: m/z 247.15777. Calcd for $C_{15}H_{21}NO_2$: M, 247.15723.

Synthesis of 4,4-Dimethyl-1,2-bis[4-(dimethylamino)phenyl]cyclopentane-1,2-diol (6). A solution of **5-1** (822 mg, 3.3 mmol) in THF (10 mL) was added dropwise at 0 °C to a solution

of **8** (10 mmol) in THF (30 mL). The mixture was stirred for 15 h. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 4:1) to give **5-1** (309 mg, 38%) and **6** (283 mg, 23%) as colorless needles, mp 175–176 °C. ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 6 H), 1.74 (s, 2 H), 1.89 (d, J = 13.9 Hz, 2H), 2.76 (d, J = 13.9 Hz, 2H), 2.93 (s, 12H), 6.63 (d, J = 9.0 Hz, 4 H), 7.08 (d, J = 9.0 Hz, 4 H); IR (KBr) 3535, 3285, 2947, 2864, 1610, 1516, 1475, 1440, 1336, 1199, 1142, 1055, 967, 936, 819 cm^{-1}. Found: C, 74.87; H, 8.79; N, 7.61%. Calcd for $C_{23}H_{32}N_2O_2$: C, 74.96; H, 8.77; N, 7.60%.

Synthesis of 3b. A solution of **6** (282 mg, 0.76 mmol) and *p*-TsOH·H_2O (260 mg, 1.37 mmol) in toluene (10 mL) was refluxed for 30 min. The mixture was poured into 10% NaOH solution and extracted with ether. The ether layer was washed with brine, and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 10:1) to give **3b** (156 mg, 86%) as slightly yellow needles (sensitive to air). ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6 H), 2.93 (s, 12H), 6.19 (s, 2 H), 6.65 (d, J = 8.9 Hz, 4 H), 7.08 (d, J = 8.9 Hz, 4 H); IR (KBr) 2950, 2858, 1617, 1516, 1352, 1225, 1195, 814 cm^{-1}; MS *m/z* 332 (M$^+$; 20), 317 (M$^+$−Me; 9), 295 (4), 281 (14), 264 (4). HRMS Found: *m/z* 332.22434. Calcd for $C_{23}H_{28}F_6N_2$: M, 332.22525.

Synthesis of 4,4-Dimethyl-2-[4-(dimethylamino)phenyl]-2-cyclopenten-1-one (7-1). A solution of **5-1** (1.31 g, 5.3 mmol) and *p*-TsOH·H_2O (1.11 g, 5.8 mmol) in toluene (50 mL) was refluxed for 20 min. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 10:1) to give **7-1** (1.089 g, 89.7%) as colorless needles, mp 87–88 °C. ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 6 H), 2.44 (s, 2 H), 2.97 (s, 6 H), 6.72 (d, J = 9.1 Hz, 2 H), 7.41 (s, 1H), 7.65 (d, J = 9.1 Hz, 2 H); IR (KBr) 2962, 1695, 1614, 1522, 1360, 819 cm^{-1}. Found: C, 78.76; H, 8.14; N, 5.99%. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11%.

Synthesis of 3c. A solution of **7-1** (229 mg, 1.0 mmol) in THF (3 mL) was added dropwise at 0 °C to a solution of Grignard reagent, which was formed by treatment of Mg (36.3 mg, 1.5 mmol) with 4-bromoanisole (280.6 mg, 1.5 mmol) in THF (2 mL), and stirred for 19 h at room temperature. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 10:1) to give **7-1** (25.7 mg 11.2%) and **3c** (72.5 mg, 22.3%) as slightly yellow viscous oil (sensitive to air). ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 6 H), 2.93 (s, 6 H), 3.79 (s, 3 H), 6.20 (d, J = 2.6 Hz, 1 H), 6.22 (d, J = 2.6 Hz, 1 H), 6.62 (d, J = 8.8 Hz, 2 H), 6.78 (d, J = 8.9 Hz, 2 H), 7.04 (d, J = 8.9 Hz, 2 H), 7.12 (d, J = 8.8 Hz, 2 H); IR (KBr) 2957, 1609, 1508, 1351, 1245, 1176, 1039, 821 cm^{-1}; MS *m/z* 319 (M$^+$; 100), 304 (M$^+$−Me; 57), 290 (7), 274 (3), 245 (5), 214 (20). HRMS Found: *m/z* 319.19425. Calcd for $C_{22}H_{25}NO$: M, 319.19361.

Synthesis of 3d. A solution of **7-1** (229 mg, 1.0 mmol) in THF (3 mL) was added dropwise at −78 °C to a solution of 2-lithiothiophene (3 mmol) in THF (3 mL) and stirred for 1 h at room temperature. The mixture was poured into ice-water and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. A mixture of the crude product and *p*-TsOH (190 mg, 1 mmol) in toluene (10 mL) was refluxed for 15 min. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 20:1) to give **3d** (175.1 mg, 59.4%) as slightly yellow needles (sensitive to air). ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 6 H), 2.97 (s, 6 H), 6.17 (d, J = 2.5 Hz, 1 H), 6.40 (d, J = 2.5 Hz, 1 H), 6.63 (dd, J = 1.1, 3.6 Hz, 1 H), 6.70 (d, J = 8.6 Hz, 2 H), 6.89 (dd, J = 5.1, 3.6 Hz, 1 H), 7.12 (dd, J = 5.1, 1.1 Hz, 1 H), 7.15 (d, J = 8.6 Hz, 2 H); IR (KBr) 2928, 2810, 1620, 1525, 1445, 1364, 1228, 1197, 814 cm^{-1}; MS *m/z* 295 (M$^+$; 100), 280 (M$^+$−Me; 60), 266 (8), 250 (4), 235 (10), 221 (12). HRMS Found: *m/z* 295.13981. Calcd for $C_{19}H_{21}NS$: M, 295.13947.

Synthesis of 3e. A solution of **7-1** (229 mg, 1.0 mmol) in THF (3 mL) was added dropwise at −78 °C to a solution of 2-lithiobenzofuran (**9**, 2 mmol) in ether (2 mL) and stirred for 15 min at this temperature. The mixture was poured into ice-water and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. A mixture of the crude product and *p*-TsOH (190 mg, 1 mmol) in toluene (10 mL) was refluxed for 15 min. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 20:1) to give **3e** (243.3 mg, 74.0%) as slightly yellow viscous oil (sensitive to air). ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 6 H), 2.99 (s, 6 H), 6.16 (d, J = 2.6 Hz, 1 H), 6.19 (s, 1H), 6.74 (d, J = 8.9 Hz, 2 H), 6.85 (d, J = 2.6 Hz, 1 H), 6.89 (dd, J = 5.1, 3.6 Hz, 1 H), 7.04–7.32 (m, 2 H), 7.26 (d, J = 8.9 Hz, 2 H), 7.37–7.48 (m, 2 H); IR (KBr) 2960, 2859, 1612, 1512, 1450, 1352, 1256, 1163, 814 cm^{-1}; MS *m/z* 329 (M$^+$; 100), 314 (M$^+$−Me; 45), 300 (6), 284 (3), 255 (9). HRMS Found: *m/z* 329.17769. Calcd for $C_{23}H_{23}NO$: M, 329.17796.

Synthesis of 3f. Synthesis of (2-Benzofuryl)-2-hydroxy-4,4-dimethylcylopentan-1-one (5-2). A solution of **4** (9.0 g, 71 mmol) in THF (80 mL) was added dropwise at 0 °C to a solution of **9** (237 mmol) in ether (240 mL). The mixture was stirred for 1 h at room temperature. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 10:1–5:1) to give **5-2** (16.94 g, 85.8%) as colorless viscous oil. ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 3 H), 1.21 (s, 3 H), 2.21 (dd, J = 14.3, 1.7 Hz, 1H), 2.37 (dd, J = 17.4, 1.7 Hz, 1H), 2.60 (d, J = 17.4 Hz, 1H), 2.63 (d, J = 14.3 Hz, 1H), 3.32 (s, 1 H), 6.69 (d, J = 0.9 Hz, 1 H), 7.15–7.35 (m, 2 H), 7.42–7.55 (m, 2 H); IR (neat) 3348, 2959, 1752, 1457, 1251 cm^{-1} ; MS *m/z* 244 (M$^+$; 11), 226 (M$^+$−H_2O; 45), 211 (M$^+$−H_2O−Me; 42), 183 (39), 160 (83). HRMS Found: *m/z* 244.11034. Calcd for $C_{15}H_{16}O_3$: M, 244.10994.

Synthesis of 2-(2-Benzofuryl)-4,4-dimethyl-2-cyclopenten-1-one (7-2). A solution of **5-2** (6.49 g, 26.6 mmol) and *p*-TsOH·H_2O (465 mg, 2.7 mmol) in toluene (260 mL) was refluxed for 40 min. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 20:1) to give **7-2** (4.66 g, 77.4%) as colorless needles, mp 65–66 °C. ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 6 H), 2.48 (s, 2 H), 2.97 (s, 6 H), 7.22 (dd, J = 7.2, 1.3 Hz, 1 H), 7.30 (dd, J = 7.7, 1.6 Hz, 1 H), 7.42–7.49 (m, 2 H), 7.57–7.63 (m, 1 H), 7.80 (s, 1H); IR (neat) 2956, 1713, 1449, 1364, 1250, 1112 cm^{-1}. Found: C, 79.57; H, 6.26%. Calcd for $C_{23}H_{32}N_2O_2$: C, 79.62; H, 6.24; N.

Synthesis of 3f. A solution of **7-2** (485 mg, 2.1 mmol) in THF (3 mL) was added dropwise at −78 °C to a solution of **9** (4.2 mmol) in ether (5 mL) and stirred for 1 h at room temperature. The mixture was poured into ice-water and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo. A mixture of the crude product and *p*-TsOH (5 mg, 0.026 mmol) in toluene (10 mL) was refluxed for 30 min. After normal workup, the product was separated by column chromatography (SiO_2, hexane–EtOAc, 50:1) to give **3f** (547 mg, 79.9%) as slightly yellow viscous oil (sensitive to air). ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 6 H), 6.70 (d, J = 0.9 Hz, 2 H), 6.82 (s, 2 H), 7.17–7.34 (m, 4 H), 7.45–7.64 (m, 4 H); IR (neat) 2962, 1451, 1256, 749 cm^{-1}; MS *m/z* 326 (M$^+$; 100), 311 (M$^+$−Me; 35), 297 (5), 281 (5), 252 (5), 239 (9). HRMS Found: *m/z*

326.12959. Calcd for $C_{23}H_{18}O_2$: M, 326.13068.

Typical Procedure for the Photoisomerization of CF_3-NBDs in Solution. A solution of CF_3-NBDs in MeCN (1.0×10^{-4} mol dm^{-3}) was charged into a quartz cell, and then the solution was irradiated by a 500-W xenon lamp (Ushio Electric Co., UXL-500D-O) with a UV transmitting filter (Hoya: UV-34) and a thermal-ray cut filter (ULTRAFINE TECHNOLOGY) in air. The conversion and the photoisomerization rates from NBDs to QCs were calculated by the disappearance of the maximum absorption of the NBDs, as measured by a UV spectrophotometer.

Typical Procedure for the Preparation of the PMMA Solid Film Doped with CF_3-NBDs. A PMMA (Wako Pure Chemical LTD., 250 mg) solution incorporating with **1c** (12.2 mg, 0.025 mmol) in $CHCl_3$ (2.5 mL) was degassed three times by consecutive freeze-pump-thaw cycles and cast on a quartz plate under argon atmosphere and dried in vacuo at 80 °C for 1 day.

Determination of the Quantum Yield for the Photoisomerization of CF_3-NBDs in Solution. The monochromatic light (**1a**: 354 nm; **1f**: 400 nm) was isolated by passing the light through a monochromator (JASCO, M10-T) from a 150-W xenon lamp. The quantum yield was measured in MeCN solution of CF_3-NBDs according to the method of Hatchard and Parker,[13] which used a potassium tris(oxalato)ferrate(II) aqueous solution as photon counter.

Measurement of Stored Energy in CF_3-QCs. A solution of NBDs in MeCN was irradiated for enough time to change from NBDs to QCs by a 500-W xenon lamp. After evaporation of the solvent, QCs (5 mg) was packed in an aluminum sample tube for DSC analysis. The sample was heated at 2 °C/min under nitrogen.

Examination of the Durability of CF_3-NBDs. The experiment was performed under argon atmosphere. Initially, the PMMA solid film doped with NBDs was irradiated by a 500-W xenon lamp until the absorbance of the maximum absorption of NBDs disappeared. Then, the irradiated film was heated on a hot plate until the absorbance of NBDs was reversed (**1a**: irradiated for 10 min, then heated at 130 °C for 40 min; **1b**: irradiated for 2 min, then heated at 100 °C for 10 min; **1c**: irradiated for 1 min, then heated at 120 °C for 20 min; **1f**: irradiated for 1 min, then heated at 80 °C for 15 min). The durability was evaluated from the differences in the absorbance values between NBDs and QCs at maximum absorption of NBDs on the 1st and n th cycles of reactions.

We would like to thank Professors Itumaro Kumadaki of Setsunan University, Sadao Miki of Kyoto Institute of Technology, and Tadatomi Nishikubo of Kanagawa University for helpful discussions.

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9 Compounds **10** and **11** were synthesized according to Ref. 4g (Chart 1).

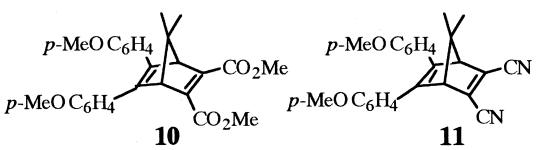

Chart 1.

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