Isomerization

Synthesis and Photoisomerization of Substituted Dibenzofulvene Molecular Rotors

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Abstract: The synthesis, spectral and structural characterization, and photoisomerization of a family of 2-substituted dibenzofulvene molecular actuators based on (2,2,2-triphenylethylidene)fluorene (TEF) are reported. The 2-substituted species investigated are nitro (NTEF), cyano (CTEF), and iodo (ITEF). X-ray structures of these three compounds and three intermediates were determined to assign alkene configuration and investigate the effects of the 2-substituents on steric gearing. The addition–elimination reaction of *Z*-**9** with trityl anion to form *Z*-**10** proceeded with complete retention of configuration. Rates of photoisomerization were measured at irradiation wavelengths between 266–355 nm in acetonitrile/dioxane solutions at room temperature. Photoisomerization quantum yields (ϕ) were calculated by means of a mathematical model that accounts for a certain degree of photodecomposition in the cases of CTEF and ITEF. Quantum yields vary significantly with substituent, having maximum values of ϕ =0.26 for NTEF, 0.39 for CTEF, and 0.50 for ITEF. NTEF is photochemically robust and has a large quantum yield for photoisomerization in the near-UV, making it a particularly promising drive rotor moiety for light-powered molecular devices.

Introduction

Currently there is keen interest in developing molecular devices that function as switches, actuators, shuttles, and motors.^[1–3] A wide variety of actuation methods have been demonstrated, including electrochemically^[2,4] or thermally^[5] driven reactions, as well as photoactivated^[1a,3,6,7] processes. In many cases, two or more methods are combined to drive a multistep process.^[3g,l,6d,f,m,7] Photoactivated devices are of particular interest because they potentially offer a high degree of positional control and much faster cycling rates than other methods. Of particular importance in this regard is the work of Feringa et al.^[3a,d,7] who developed a diverse family of rotary molecular motors that operate by photoactivation of an aromatic alkene and thermal relaxation of the resulting, strained photoisomer.

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A prototype for well-understood, photoactivated molecular devices is the *cis-trans* photoisomerization of stilbene, shown in Figure 1. Stilbene offers high photoisomerization quantum yields, typically ranging from 0.3–0.5.^[8] However, a potential



Figure 1. Structures of stilbene, fulvene, and dibenzofulvene (9-methylenefluorene, with numbering system for positions of substituents).

practical difficulty in many applications is that the *cis* and *trans* isomers of stilbene have significantly different geometries and absorption spectra. For example, to achieve fast, continuous rotary motion, two different excitation wavelengths would be required. Herein we consider the family of substituted dibenzo-fulvene actuators based on (2,2,2-triphenylethylidene)fluorene (TEF) shown in Figure 2. In these molecules a triphenylmethane (trityl) substituent is attached to the exocyclic C=C bond. This unique structure is a prototype for designed molecular motors, in which the dibenzofulvene rotor is sterically geared into a chiral trityl stator to produce directional rotation about the C-C bond between the rotor and stator.^[1c] Photoisomerization about the torsional angle θ interconverts the *E* and *Z* isomers shown in Figure 2 and serves to drive directional rotation about the adjacent single bond in the molecular motor design.

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Figure 2. Structures of previously reported (TEF and TTEF) and new 2-substituted dibenzofulvene rotors (NTEF, CTEF, and ITEF). Note: polarized photoisomerization of NTEF in a polymer matrix has been reported.^[9]

In 2-substituted TEF derivatives, the dibenzofulvene chromophore is preserved in both stereoisomers, which accordingly have very similar absorption spectra. The dibenzofulvene rotor moiety also allows for rotational symmetry about its photoisomerizable exocyclic double bond, facilitating its incorporation as a drive unit in rotary molecular devices. Theoretical studies on the fulvene parent chromophore, shown in Figure 1, predicted an extremely low photoisomerization quantum yield.^[10] However, our previous experimental studies on the dibenzofulvene derivative TTEF, shown in Figure 2, revealed photoisomerization quantum yields of 0.04-0.09.[11] Dibenzofulvene moieties have been used in many of Feringa's second-generation molecular motors,^[3d,7d-o,q-s] but these chromophores bear some resemblance to stilbene in that the photoactive C=C bond is conjugated to arene rings at both ends. In contrast, the dibenzofulvene chromophores in the 9-(2,2,2-triphenylethylidene)fluorenes shown in Figure 2 are not conjugated to the trityl phenyl rings. Herein we show that substituents on the dibenzofulvene chromophore can be used to tune both the absorption spectra and photoisomerization efficiencies of this family of compounds for potential application in light-driven molecular devices and that NTEF is of particular interest for this purpose.

Results

Synthesis

Current synthetic studies were modeled on the previously reported synthesis of (*E*)- and (*Z*)-2-*tert*-butyl-9-(2,2,2-tripheny-lethylidene)fluorene (TTEF) by the route shown in Scheme 1 (R = tBu).^[11] Thus, 2-*tert*-butylfluorene **1** was converted into the corresponding fluorenone **2** by aerobic oxidation in the presence of base. A Wittig reaction of **2** with bromomethylenetriphenylphosphorane gave the corresponding 9-bromomethylene derivative **3** as a mixture of the two stereoisomers (*E* and *Z*). Substitution of the bromide using an addition–elimination reaction with trityllithium gave both isomers of the target compound **4**=TTEF, after separation by chromatography and crystallization.

The key target compounds of the current synthesis are 2-nitro-9-(2,2,2-triphenylethylidene)fluorene (NTEF), 2-cyano-9-(2,2,2-triphenylethylidene)fluorene (CTEF), and 2-iodo-9-(2,2,2-



Scheme 1. Synthesis of E- and Z-TTEF.[11]

triphenylethylidene)fluorene (ITEF), the structures of which are shown in Figure 2. NTEF was selected for initial synthesis because it was expected to have the longest wavelength UV/Vis absorption. Unfortunately, the direct approach shown in Scheme 1 could not be applied to the synthesis of NTEF because 2-nitrofluorenone^[12] was found to have very low solubility in solvents suitable for the Wittig reaction step. Therefore, the alternate synthetic approach shown in Scheme 2 was pursued. This route involves four additional steps: reduction of the nitro group, protection of the resulting amine as a 2,5-dimethyl-1H-pyrrol-1-yl substituent, and later the deprotection and oxidation to the nitro group. This seven-step synthesis is considerably longer than the straightforward, three-step approach (Scheme 1), but it also produces two additional dibenzofulvenes (10 and 11) as potential candidates for photoisomerization studies.



Scheme 2. Synthesis of Z-NTEF; a) Zn, CaCl₂, EtOH, reflux; b) 2,5-hexanedione, benzene, AcOH, reflux; c) air, BnNMe₃OH, pyridine; d) BrCH₂PPh₃Br/ NaHMDS, THF, -60 °C to rt; e) Ph₃CLi, THF,-78 °C to rt; f) HONH₃Cl, Et₃N, *n*PrOH, reflux; (g) NaBO₃, AcOH, 60 °C.

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Whereas 2-aminofluorene 6 is commercially available, it can also be produced economically by the previously reported reduction of 2-nitrofluorene 5, which was prepared on large scale by the nitration of fluorene.^[13] The amino group of **6** was protected by Paal-Knorr condensation with 2,5-hexanedione,^[14] affording 7 in high yield. Oxidation of 7 to the corresponding fluorenone 8 was carried out by treatment with air in the presence of base. A Wittig reaction of 8 with bromomethylenetriphenylphosphorane proceeded efficiently, from which 9-bromomethylene derivative 9 was isolated as a 5:4 (Z/E) mixture by column chromatography. Fractional crystallization then gave pure Z-9 in 54% yield. The configuration of this intermediate was assigned by X-ray crystallography; the solid-state structure of Z-9 is displayed in Figure 3. As observed for other



Figure 3. Solid-state structures of synthetic intermediates Z-9, Z-10, and Z-11, and target compounds Z-NTEF, E-ITEF, and Z-ITEF.

9-bromomethylenefluorenes,^[11,15] steric compression by the bromine atom causes the ¹H NMR resonance of the aromatic proton in the 1-position of the fluorene ring system to shift downfield ($\delta = 8.43$ ppm for Z-9). The remaining ¹H NMR signals of Z-9 were assigned by 2D-NMR spectroscopy.

Isolation and unambiguous assignment of the configuration of Z-9 provided an opportunity to probe the stereoselectivity of the subsequent addition-elimination reaction. A reaction of Z-9 with trityllithium in THF gave only Z-10, as determined by X-ray crystallography (Figure 3; Table 1). None of the E isomer could be detected in the crude product by either NMR spec-

Table 1. Crystallographically determined bond angles of the photoactive double bond in the dibenzofulvene rotors. $^{\rm [a]}$						
\mathbf{R}^{1}	₽h₃ R²	$\begin{array}{l} \textit{E-TTEF:} \ \ \ \ R^1 = \textit{tBu}, \ \ R^2 = \textit{H} \\ \textit{Z-TTEF:} \ \ \ \ \ R^1 = \textit{H}, \ \ \ \ R^2 = \textit{tBu} \\ \textit{Z-NTEF:} \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	2 円 ^[b] 2			
Compound	α_1	α2	α3			
E-TTEF (mol 1) ^[c]	133.2(5)	133.7(5)	121.8(5)			
E-TTEF (mol 2) ^[c]	133.6(5)	134.8(5)	120.8(5)			
Z-TTEF (mol 1) ^[c]	134.1(4)	133.7(4)	121.7(4)			
Z-TTEF (mol 2) ^[c]	130.8(3)	132.6(3)	122.5(3)			
Z-NTEF	122.5(2)	129.7(2)	124.3(2)			
E-ITEF	131.4(1)	132.8(1)	122.1(1)			
Z-ITEF	134.8(7)	134.3(7)	121.5(7)			
Z-10	131.7(1)	133.3(1)	121.8(1)			
Z-11 (mol 1)	134.6(1)	134.9(1)	120.5(1)			
Z-11 (mol 2)	134.2(1)	133.7(1)	121.1(1)			
TEF (mol 1) ^[d]	134.7(3)	134.5(3)	120.8(3)			
TEF (mol 2) ^[d]	133.5(3)	134.3(3)	121.1(3)			
[a] Angles corresponding to C13-C14-C15 for α_{1} , C14-C13-C12 for α_{2} , and						

C14-C13-C1 for α_3 . [b] DMP = 2,5-dimethyl-1H-pyrrolyl. [c] mol = molecule; Ref. [11]. [d] Ref. [15].

troscopy or gas chromatography. Contrary to the effect of bromine in Z-9, the trityl group in Z-10 produces an upfield shift of the ¹H NMR resonance of the 1-position proton $(\delta = 6.10 \text{ ppm})$ and a weaker shielding effect is observed for the 3- and 4-position protons of the 2,5-dimethyl-1H-pyrrol-1yl group. Attempts to isolate E-10 from a reaction of E/Z-9 with trityllithium gave a sample of E-10 that was pure enough for spectroscopic comparison with the Z isomer.

As the protected intermediate was found to have very low solubility in ethanol,^[14] even at reflux, the deprotection of the amino group in Z-10 was accomplished by reaction of the 2,5dimethylpyrrole moiety with hydroxylamine hydrochloride in hot *n*-propanol. From this, amino derivative Z-11 was obtained in good yield, and an X-ray structure again confirmed the double bond configuration (see Figure 3 and Table 1). Finally, the amino group of Z-11 was cleanly oxidized to nitro using sodium perborate in hot acetic acid.^[16] This route gave pure samples of nitro target compound Z-NTEF for photoisomerization studies, and full details of the molecular structure were revealed by X-ray crystallography (see Figure 3 and Table 1).

The synthetic route shown in Scheme 2 gave pure Z-NTEF, but it did not readily produce pure samples of E-NTEF because of separation difficulties. So, the alternate route displayed in Scheme 3 was devised. Not only is this a shorter approach to the nitro derivatives (NTEF), it was also designed to produce samples of the E and Z isomers of the target CTEF and ITEF analogues. lodoarenes are readily converted into nitriles and amines, and the Z isomer of amine 11 was easily oxidized to Z-NTEF using the synthesis shown in Scheme 2.

The starting material for the synthesis shown in Scheme 3, 2-iodofluorene 12, was prepared in 77% yield by iodination of fluorene in acetic acid.^[17] The corresponding fluorenone 13^[18]

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Scheme 3. Synthesis of *E*-NTEF; a) air, BnNMe₃OH, pyridine; b) BrCH₂PPh₃Br/NaHMDS, THF, -60 °C to rt; c) Ph₃CLi, THF, -78 °C to rt; d) CuCN, DMF, reflux; (e) Ph₂C=NH, Pd₂(dba)₃, BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl), NaOtBu, [18]crown-6; f) NaBO₃, AcOH, 60 °C.

was then obtained from 12 by air oxidation.^[19] A Wittig reaction of 13 gave bromomethylene derivative 14 as a mixture of E and Z isomers and a reaction of this mixture with trityllithium gave target compound ITEF. Pure samples of E-ITEF and Z-ITEF were then obtained by crystallization of the resulting mixture of stereoisomers and unambiguously identified by X-ray crystallography (see Figure 3 and Table 1). The E/Z mixture was converted into CTEF by a Rosenmund-von Braun reaction^[20] with copper cyanide in DMF^[21] and both *E*-CTEF and *Z*-CTEF were isolated for photoisomerization studies. These stereoisomers were assigned by means of the observed shielding effect of the trityl group on the NMR resonances of the adjacent protons on the fluorene ring system. To obtain E-NTEF, ITEF was converted as a mixture of stereoisomers to the corresponding amine 11 by Pd-catalyzed coupling with benzophenone imine, followed by hydrolysis.^[22] Pure E-11 was obtained by crystallization of the resulting E/Z mixture, then it was oxidized to the desired E-NTEF target compound. This completed preparation of unambiguously assigned samples of both stereoisomers of all three target compounds, namely NTEF, CTEF, and ITEF.

Photoisomerization

Our previous studies of the photoisomerization of TTEF were performed in acetonitrile. A mixed solvent of 15% 1,4-dioxane and 85% acetonitrile (v/v) was used in the current studies investigating NTEF, CTEF, and ITEF. The 1,4-dioxane cosolvent was used to increase the solubility of these compounds in acetonitrile to allow for comparison with our previous experiments on TTEF under similar solvent conditions. Figure 4 shows the near-UV molar absorptivities of the *E* and *Z* isomers of NTEF, CTEF, and ITEF in the mixed solvents obtained from a series of absorption spectra measured at concentrations between 10^{-6} and 10^{-5} M.

Thermal isomerization data was previously reported for TTEF at elevated temperatures,^[11] however, no thermal isomerization



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Figure 4. Absorption spectra of *E* (blue trace) and *Z* (red trace) isomers of NTEF, CTEF, and ITEF in 15:85 (v/v) 1,4-dioxane/acetonitrile.

studies were performed in the current work. Neither NTEF nor ITEF in solution showed signs of thermal isomerization at room temperature over the course of months. Solutions of CTEF showed evidence of isomerization at room temperature that became detectable after 1–2 weeks. Crystalline CTEF showed no evidence of thermal isomerization at room temperature.

Compounds in solution were irradiated at various wavelengths in the UV region of 266-390 nm. Over the course of irradiation, 40 µL aliquots of the sample were extracted at time intervals to follow the progress of photoisomerization by means of chromatographic analysis, using either GC-MS or HPLC. Figure 5 shows typical chromatograms of aliguots removed from rotor molecule solutions at selected times during their irradiation. For the experiments shown in Figure 5, the initial solutions contained only the Z isomer of the dibenzofulvene rotor molecule. As the UV irradiation progresses, the Z isomer peak decreases and the peak corresponding to the E isomer increases. Dividing the peak area of a given isomer by the sum of the total integrated signals gives the mole fractions f_F and f_Z describing the isomeric distribution of the rotor molecule in solution. Figure 6 shows the evolution of these mole fractions as a function of the average number of absorbed photons per rotor molecule for experiments starting with both pure E and pure Z isomers. (The average number of absorbed photons is proportional to time as described in Equation (3) below.) Note that f_E and f_Z reach the same photostationary ratios at long irradiation times, regardless of the choice of starting stereoisomer.

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Figure 5. Chromatograms showing isomerization progress of NTEF (top panel) during 266 nm irradiation as measured by GC-MS, and for CTEF (middle panel) and ITEF (bottom panel) during 310 nm irradiation as measured by HPLC. HPLC chromatograms were detected by UV absorption at wavelengths where both isomers have equal absorptivity. In each case the initial solution contained only the Z isomer, and individual chromatograms are labeled according to the irradiation time (in units of average photons absorbed per rotor molecule; see Equation (3)). Peaks assigned to the rotor molecule isomers Z and E are labeled. The peaks labeled D are assigned to unidentified photodecomposition products.

Photoisomerization kinetic model

The photoisomerization reaction in this family of rotor molecules can be expressed as:

$$E_{\underline{\underbrace{k_{ZZ}}}}^{\underline{k_{ZZ}}} Z \tag{1}$$

where k_{EZ} and k_{ZE} are the effective rate constants that depend upon the irradiation intensity.

The corresponding rate equation is:

$$\frac{d[E]}{dt} = k_{ZE}[Z] - k_{EZ}[E]$$
⁽²⁾

The rate constants k_{EZ} and k_{ZE} include the photon flux, absorption cross section of the molecule, and the photoisomerization quantum yield. To express Equation (2) in a way that is more directly related to the photoisomerization quantum yields, we transform the irradiation time, t, into the average number of



Figure 6. Photoisomerization progress quantified by isomer fraction f_E and f_Z for NTEF, CTEF, and ITEF during 355 nm irradiation, plotted as a function of the average number of photons absorbed per rotor molecule. Photodecomposition is ignored in this analysis. The solid traces and symbols • and • correspond to experiments in which only the Z isomer was initially present. The dashed traces and crossed symbols \otimes and \boxtimes correspond to experiments in which only the E isomer was initially present. The solid and dashed traces are obtained by least squares optimization of $\phi_{\rm EZ}$ and $\phi_{\rm ZE}$ in a fit to the kinetic model represented by Equations (1), (2), and (4).

photons absorbed per molecule, x(t). For an optically dense sample, in which all photons are absorbed, it is:[11]

$$\mathbf{x}(t) = \frac{\mathbf{v}_i \mathbf{E}_i \lambda_i t}{hc} (C V N_A)^{-1}$$
(3)

where λ_{l} , E_{l} , v_{l} , h, and c are the laser wavelength, pulse energy, laser pulse repetition frequency, Planck's constant, and the speed of light, respectively. The number of rotor molecules in the sample solution is CVN_A , where C is the solution concentration, V is the volume (taking into account the volume decrease due to the removal of aliquots for chromatographic analysis), and N_A is Avogadro's number. Equation (2), expressed in terms of x and the isomer mole fractions f_E and $f_{Z'}$ becomes:

$$\frac{df_E}{dx} = \frac{\phi_{ZE}\varepsilon_Z f_Z - \phi_{EZ}\varepsilon_E f_E}{\varepsilon_Z f_Z + \varepsilon_E f_E}$$
(4)

where ε_E and ε_Z are the measured molar absorptivities of the E and Z isomer, respectively, at the irradiation wavelengths shown in Table 2; ϕ_{EZ} and ϕ_{ZE} are the absolute photoisomerization quantum yields for $E \rightarrow Z$ and $Z \rightarrow E$, respectively. Kinetic

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Table 2. Molar absorptivities, photostationary isomeric ratios $f_E f_Z (t = \infty)$, and fitted photoisomerization quantum yields for rotor molecules at irradiation wavelengths λ .^[a]

Cmpnd	λ [nm]	$\varepsilon_E^{[c]}$	$\varepsilon_Z^{[c]}$	$f_E:f_Z(t=\infty)$	$\phi_{\scriptscriptstyle EZ}$	$\phi_{\rm ZE}$
TTEF ^[b]	266		_	0.59:0.41	0.07 ± 0.05	0.10±0.02
	280	-	-	0.44:0.55	0.05 ± 0.01	0.04 ± 0.01
	320	-	-	0.56:0.43	0.07 ± 0.01	0.09 ± 0.01
NTEF	266	17200	17700	0.38:0.62	0.25 ± 0.05	0.17 ± 0.01
	290	29400	30 500	0.38:0.62	0.26 ± 0.03	0.17 ± 0.03
	340	23 500	23800	0.40:0.60	0.31 ± 0.03	0.21 ± 0.03
	355	17700	18100	0.33:0.67	0.21 ± 0.05	0.12 ± 0.01
	390	3600	5400	0.48:0.52	0.21 ± 0.03	0.20 ± 0.03
CTEF	266	28100	28100	0.53:0.47	0.35 ± 0.02	0.42 ± 0.03
	310	16400	14200	0.47:0.53	0.34 ± 0.02	0.29 ± 0.02
	355	1440	1550	0.62:0.38	0.31 ± 0.03	0.33 ± 0.03
ITEF	266	28 200	28600	0.49:0.51	0.50 ± 0.04	0.46 ± 0.04
	310	15 300	16200	0.52:0.48	0.49 ± 0.02	0.49 ± 0.02
	355	480	640	0.52:0.48	0.55 ± 0.04	0.45 ± 0.04
[a] Quantum yields are obtained by fits to experimental kinetics data using the kinetic model represented by Equations (1), (2), and (4), in which photodecomposition is ignored. [b] Isomer fractions f_E and f_2 deter- mined by ¹ H NMR spectroscopy. ^[11] [C] [Lmol ⁻¹ cm ⁻¹]. For TTEF, molar ab- sorbtivities reported for λ_{max} values. ^[11]						

modeling of forward and reverse reactions of the measured $E \rightarrow Z$ photoisomerization data is accomplished by numerical integration of Equation (4) to obtain $f_E(x)$ with the constraint that $f_Z(x) = 1 - f_E(x)$. Optimization of ϕ_{EZ} and ϕ_{ZE} in a fit of $f_E(x)$ to the experimental data by nonlinear least-squares fitting gives the traces shown in Figure 6, and the corresponding quantum yields are reported in Table 2.

Irradiation of CTEF and ITEF gave rise to minor photoproducts that appear at shorter elution times in the chromatograms in Figure 5. In the case of CTEF, the photoproducts appear as two peaks. The ratio of the product peaks areas in relation to each other as a function of irradiation time shows a trend similar to that of the *E* and *Z* isomers of the parent CTEF. Irradiation of ITEF led to the development of one major and numerous minor photodecomposition peaks. Given their tiny quantities, no attempt was made to isolate or characterize these photoproducts. In an attempt to account for photodecomposition mathematically, Equation (1) was modified by introducing a photodecomposition product, *D*, into the previous kinetic model:

$$E_{\overbrace{\phi_{ZE}}}^{\phi_{EZ}} Z \tag{5}$$

$$E \xrightarrow{\phi_D} D \tag{6}$$

$$Z \xrightarrow{\phi_D} D$$
 (7)

Equation (4) now becomes:

$$\frac{df_E}{dx} = \frac{\phi_{ZE}\varepsilon_Z f_Z - \phi_{EZ}\varepsilon_E f_E - \phi_D \varepsilon_E f_E}{\varepsilon_Z f_Z + \varepsilon_E f_E + \varepsilon_D f_D}$$
(8)

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$$\frac{df_D}{dx} = \frac{2\phi_D(\varepsilon_E f_E + \varepsilon_Z f_Z)}{\varepsilon_Z f_Z + \varepsilon_E f_E + \varepsilon_D f_D}$$
(10)

where ϕ_D is the photodecomposition quantum yield and ε_D is the molar absorptivity of the decomposition product *D*. The quantity f_D represents the mole fraction of *D* such that $f_E + f_Z +$ $f_D = 1$; f_D was measured experimentally as the sum of the areas of all decomposition chromatogram peaks (see Figure 5) divided by the sum of all chromatogram peaks *D*, *Z*, and *E*. The detection wavelength for the HPLC chromatographic analysis was chosen such that both *E* and *Z* isomers have the same absorptivity at that wavelength; however, the absorption spectrum of the decomposition product is unknown. Therefore, the accuracy of f_D is dependent upon the relation between the molar absorptivities of the photoproducts, ε_D and the values ε_E and ε_Z at the HPLC detection wavelength.

In kinetic modeling that accounts for photodecomposition, the value of ε_D was arbitrarily chosen to be equal to the average of ε_E and ε_Z at both the photoisomerization and HPLC



Figure 7. Photoisomerization progress quantified by isomer fraction f_{ε} and f_Z for irradiation of NTEF (355 nm), CTEF (266 nm), and ITEF (266 nm), plotted as a function of the average number of photons absorbed per rotor molecule. Photodecomposition is accounted for in this analysis. The solid traces and symbols \bullet and \blacksquare correspond to experiments in which only the *Z* isomer was initially present. The dashed traces and crossed symbols \otimes and \boxtimes correspond to experiments in which only the *Z* isomer was initially present. The dashed traces and crossed symbols \otimes and \boxtimes correspond to experiments in which only the E isomer was initially present. The solid and dashed traces are obtained by least squares optimization of $\phi_{\varepsilon Z'}$ $\phi_{ZE'}$ and ϕ_D in a fit to the kinetic model represented by Equations (5)–(10).

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detection wavelengths. Equations (8), (9), and (10) were integrated numerically and $\phi_{\rm EZ'}$ $\phi_{\rm ZE'}$ and $\phi_{\rm D}$ were optimized in a simultaneous fit to the measured f_E and $f_{Z'}$ shown in Figure 7. The decomposition is manifest in the negative slope at long irradiation times of what was previously represented as a photostationary plateau in Figure 6. This photodecomposition decline in both f_F and f_Z is most noticeable for ITEF. There was no measurable decomposition for NTEF. Again, the final values of f_F and f_7 are the same, regardless of the identity of the starting isomer. Table 3 gives the optimized values of $\phi_{\it EZ'}$ $\phi_{\it ZE'}$ and $\phi_{\it D}$

Table 3. Optimized photoisomerization and photodecomposition quan-
tum yields of CTEF and ITEF for the model described by Equations (5)-
(10) accounting for photodecomposition.

Compound	λ [nm]	$\phi_{\scriptscriptstyle EZ}$	$\phi_{\it ZE}$	$\phi_D imes 10^2$
CTEF	266	0.40±0.01	0.45 ± 0.01	0.32±0.03
	310	0.31 ± 0.01	0.32 ± 0.01	0.189 ± 0.005
	355	0.37 ± 0.04	0.40 ± 0.04	0.180 ± 0.001
ITEF	266	0.48 ± 0.06	0.44 ± 0.06	4.5 ± 0.6
	310	0.49 ± 0.01	0.50 ± 0.01	0.98 ± 0.02
	355	$\textbf{0.55}\pm\textbf{0.09}$	0.45 ± 0.07	0.13 ± 0.09
1				

after decomposition has been taken into account, and can be compared to the quantum yields in Table 2, which ignore photodecomposition. With the exception of ITEF at 266 nm excitation, ϕ_{D} is two orders of magnitude smaller than ϕ_{EZ} and ϕ_{ZE} . The inclusion of the additional photodecomposition quantum yield ϕ_D into the kinetic model resulted in fitted photoisomerization quantum yields ϕ_{EZ} and ϕ_{ZE} for ITEF to increase by no more than 0.02, and those for CTEF to increase an average of 0.05.

Discussion

Synthesis

The key target molecule NTEF was synthesized by the two different routes shown in Scheme 2 and 3. In principle, both routes produce both the E and Z stereoisomers, but for practical reasons involving separation procedures (crystallization and chromatography), the route in Scheme 2 more readily yielded Z-NTEF, whereas the shorter route in Scheme 3 fortuitously gave more E-NTEF. lodo target compound ITEF, an intermediate in Scheme 3, was also converted into cyano target compound CTEF in one step and good yield.

An important finding of these synthetic studies is that nucleophilic substitution of bromine in 9-bromomethylenefluorenes by trityllithium is highly stereoselective and gives complete retention of configuration, as demonstrated clearly in the conversion of Z-9 into Z-10 (Scheme 2). This is consistent with rate-determining attack by trityl anion to produce the intermediate fluorenyl anion, that very rapidly eliminates bromide to form Z-10. The retention product is formed via the least-motion geometry for the fast elimination step in this addition-elimination (add-E1) process.^[23]

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X-ray structures

The solid-state structures of the new compounds were analyzed carefully to understand the effects of substituents on bond angles and steric gearing between the trityl group and the dibenzofulvene rotor, which is relevant to possible use of substituted dibenzofulvenes in designed molecular motors.^[1c] Table 1 gives selected bond angle data for the crystallographically determined structures of three of the key target compounds, the Z nitro compound (Z-NTEF) and both stereoisomers of the iodo analogue (E-ITEF and Z-ITEF). Also provided in Table 1 are corresponding data for intermediates Z-10, and Z-11, as well as for the unsubstituted parent compound TEF (9-(2,2,2-triphenylethylidene)fluorene).[15]

Not only do the crystal structures of these compounds, along with other spectroscopic data, unambiguously prove the E/Z configurations of the compounds used in photoisomerization experiments, they also show the effects of substituents on ground-state structures. Of particular interest are the bond angles about the photoactive, exocyclic C=C double bond. The previously reported structure of TEF^[15] showed an unusual distribution of strain for an overcrowded alkene. No significant twisting of the C=C double bond was observed. Instead, steric gearing between the trityl group and the fluorene moiety causes in-plane distortion, as shown by bond angles α_1 , α_2 , and α_3 listed in Table 1. In particular, bond angles α_1 and α_2 are 133–135°; α_{3} , corresponding to α_{2} , but on the side opposite the trityl group, is only 121–122 $^\circ$ (range for the two symmetry-nonequivalent molecules, denoted mol 1 and mol 2, in the asymmetric unit).

The previously reported structures of (E)- and (Z)-2-tertbutyl-9-(2,2,2-triphenylethylidene)fluorene (TTEF)^[11] show no significant changes in C=C double bond angles relative to the unsubstituted parent compound TEF, as seen in Table 1. Angles α_1 and α_2 on the same side as the trityl group range from 131–135° and α_3 is 121–123°. This indicates that there is no significant steric repulsion between the bulky trityl and tertbutyl groups. The corresponding bond angles fall in the same ranges for the 2-iodo (E- and Z-ITEF), 2-(2,5-dimethyl-1H-pyrrol-1-yl) 10, and 2-amino 11 analogues, as also shown in Table 1. The exception is the 2-nitro analogue Z-NTEF, which has decreased bond angles for α_1 and α_2 (both ca. 123°) and an increased α_3 angle (124°). This may be due either an electronic perturbation of sp² carbon geometry in the dibenzofulvene π -system, or to an attractive, dipole-induced dipole interaction between the nitroaromatic dipole and the trityl group. Not shown Table 1 are the corresponding double bond angles for 9-bromomethylene compound Z-14 ($\alpha_1 = 125^\circ$, $\alpha_2 = 130^\circ$, $\alpha_3 =$ 122°), that suggest decreased steric interaction between the bromo group and the fluorene moiety, relative to the corresponding trityl-fluorene interactions in all the other structures discussed herein.

Photoisomerization

Photoisomerization quantum yields for the well-studied stilbene molecule are relatively independent of substitution,

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varying only by about ten% from typical values of $\phi_{EZ} \approx 0.5$ and $\phi_{ZE} \approx 0.3$.^[8] For the dibenzofulvene derivatives studied herein, changing the substituent has a larger effect on the photoisomerization efficiency, as seen in Table 2. The compounds show a wide range of quantum yields with TTEF having a photoisomerization quantum yield of about $0.07^{[11]}$ and increasing in the order of TTEF <NTEF <CTEF <ITEF, where ITEF has a quantum yield of about 0.50. There is no consistent wavelength dependence of the quantum yields for λ_{ex} > 266 nm. The maximum quantum yields (average of ϕ_{EZ} and ϕ_{ZE}) are 0.26 for NTEF at 340 nm, 0.43 for CTEF at 266 nm (corrected for photodecomposition), and 0.50 for ITEF at 355 nm. NTEF favors the Z isomer in the photostationary state at all the excitation wavelengths investigated, whereas the others show nearly a 1:1 photostationary isomer ratio.

A rigorous theoretical understanding of the mechanism of photoisomerization for the compounds studied herein is beyond the scope of this study; here we speculate on important key processes. As a reference point for this discussion, Figure 8 provides an idealized, schematic representation of the



Figure 8. Schematic singlet potential energy surfaces plotted along the θ photoisomerization coordinate (defined in Figure 2). Photoisomerization via the singlet mechanism occurs by 1) excitation from the ground singlet state, S_{or} to the first excited singlet state, S_1 , 2) structural relaxation on the S_1 surface, followed by intersystem crossing to the S_o surface at the conical intersection, and relaxation on the S_o surface either 3a) returning to the initial isomer with no net change in θ or 3b) successful photoisomerization with θ changing by 180°.

potential energy surfaces likely to be important in the photoisomerization dynamics. Figure 8 depicts the energy along the θ torsion coordinate defined in Figure 2, which is the reaction coordinate for photoisomerization. The qualitative surfaces in Figure 8 are analogous to those believed important in stilbene, and extending the stilbene photoisomerization picture to dibenzofulvene, the singlet mechanism consists of excitation from the ground singlet state, S₀, to the first excited singlet state, S_1 , followed by structural relaxation along θ on S_1 . The system crosses to the S_0 surface at a conical intersection at some critical torsion angle (shown as $\theta \approx 90^{\circ}$ in Figure 8). Subsequent structural relaxation on the S₀ surface results in either a return to the original configuration at $\theta = 0$, or to $\theta = 180^{\circ}$ for a successful isomerization event. Within this dynamical picture, if the minimum energy conical intersection of S_1 and S_o occurs at θ significantly less than 90°, or if the S₁ excited state dynamics do not efficiently convey the system to a conical intersection configuration near $\theta = 90^{\circ}$, then the photoisomerization quantum yield will be small. Bearpark et al.^[10] performed S₁ excited state dynamics calculations on fulvene, that predicted a very low photoisomerization quantum yield, likely measurable only upon excitation at the 0–0 vibrational origin.

Subsequent to our earlier experimental study that showed significant quantum yields for the dibenzofulvene derivative TTEF,^[11] S₁-S₀ transitions in fulvene were examined in greater detail by Bearpark^[24] and Sumita and Saito.^[25] Although Figure 8 depicts the potential energy surfaces only along the exocyclic double bond torsion angle θ , the S₁/S₀ conical intersection is actually a high-dimensional space in the nuclear coordinates. Theoretical studies by Bearpark examined the multidimensional surfaces for fulvene S1 and S0 to determine the fulvene S₁/S₀ surface crossing dynamics.^[24] Figure 1 of reference [24a] and Figure 2(b) of reference [24c] depict the S1 and S₀ surfaces along the nuclear coordinates of the exocyclic double bond torsion angle, θ , and the "bond inversion" or "delocalization" coordinate in which the single and double bond character of the C-C bonds of fulvene is interchanged. Reference [24a] shows that the θ -torsion and bond inversion coordinates are the two involved in the S1-S0 conical intersection. The global energy minimum in the surface crossing seam for fulvene is located at $\theta = 63^{\circ}$, ^[24,25] so that crossing to the S₀ surface at this point results in a return to the original configuration at $\theta = 0^{\circ}$, with no isomerization. Trajectory calculations on the fulvene S_1 and S_0 surfaces performed by Sumita and Saito show that crossing between $80^{\circ} < \theta < 0^{\circ}$ is required for relaxation along the S₀ surface to result in complete 180° rotation about the double bond.^[25] For fulvene, the topography of the S_1 and S_0 surfaces leads to a lowest energy S_1/S_0 curve crossing at $\theta = 63^{\circ}$, making photoisomerization inefficient.

As our previous studies of a dibenzofulvene derivative showed significant photoisomerization quantum yields,^[11] Sumita and Saito theorized that the addition of benzene rings to fulvene may affect the S_1/S_0 degeneracy space in such a way as to favor surface crossing at θ closer to 90° before relaxing along the S_0 surface.^[25] The addition of the benzene moieties to fulvene is at the location of two C–C bonds involved in the bond inversion coordinate. It is reasonable to expect that addition of the highly aromatic benzene moieties to form dibenzofulvene will cause motion along the bond inversion coordinate to be more energetically costly. This modification of the fulvene surfaces could shift the energetically accessible region of the conical intersection seam to angles closer to 90°, promoting relaxation dynamics that successfully achieve isomerization.

Our experimentally measured photoisomerization quantum yield increases in the order TTEF < NTEF < CTEF < ITEF, indicating that the substituent identity also affects the location of the conical intersections of the S₁ and S₀ surfaces. The triplet mechanism for the photoisomerization of dibenzofulvene, or even fulvene, is not as well understood as the singlet mechanism, and therefore not much can be conjectured herein. That ITEF shows the highest photoisomerization quantum yields measured in this family ($\phi_{EZ} \approx \phi_{ZE} \approx 0.5$) suggests the iodo substituent could enable access to triplet surface photoisomerization pathways that augment those available in the singlet

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mechanism. Considering that the photodecomposition quantum yield is also increased for ITEF, the mechanisms made available by the iodo substituent may include other pathways that lead to photodecomposition rather than photoisomerization. The photolability of iodine in iodoaryl compounds is well known.^[26] Whereas the photoisomerization quantum yields for CTEF and ITEF are larger than for NTEF, the latter is deemed most useful for practical applications. NTEF absorbs more strongly in the near-UV, has a substantial photoisomerization quantum yield ($\phi = 0.1-0.3$), and no photodecomposition was detected at the wavelengths studied. NTEF has also been shown to undergo angular distribution hole-burning in a thin polymer matrix when irradiated with polarized laser light.^[9]

Conclusion

We have synthesized and studied a family of dibenzofulvene compounds that efficiently function as light-driven molecular actuators. X-ray structures and ¹H NMR data have been used to assign all alkene configurations of intermediates and products. The X-ray data show small geometric effects of 2-substituents, suggesting negligible differences in steric gearing between the trityl group and the neighboring aromatic ring. The additionelimination reaction of Z-9 with the trityl anion to form Z-10 has been shown to proceed with complete retention of configuration, consistent with a least-motion reaction mechanism. Rates of photoisomerization were measured at irradiation wavelengths between 266-355 nm in acetonitrile/dioxane solutions at room temperature. Photoisomerization quantum yields ϕ were calculated by means of a mathematical model that accounts for a small degree of photodecomposition in the cases of CTEF and ITEF. The isomerization quantum yield, absorption spectrum, and photodurability of the compound are dependent on the substituent. While ITEF gives the largest ϕ , it also displays the highest rate of photodecomposition. The compound NTEF demonstrates high photostability, a broad absorption spectrum encompassing the near-visible region, and photoisomerization quantum yields in the range of 0.1–0.3, making it an exceptional candidate as a light-powered molecular actuator. With appropriate functionalization, these molecules could be readily incorporated into molecular devices and motors as drive and control elements.

Experimental Section

Synthesis and characterization

General methods: All reactions were carried out under dry nitrogen using commercially available, high-purity solvents, unless noted otherwise. Anhydrous THF and toluene were obtained by distillation from sodium benzophenone ketyl. Pyridine was heated at reflux over CaH₂, distilled, and stored over 4 Å molecular sieves under nitrogen. Flash chromatography was conducted on alumina (80–200 mesh). NMR spectra were recorded with TMS as an internal reference. Melting points were measured in open glass capillary tubes and are uncorrected. Mass spectra were recorded by gas chromatography-mass spectrometry (GC-MS) with electron impact ionization (70 eV), matrix assisted laser desorption mass spectrometry (MALDI-MS) recorded with no matrix and analyzed by time of flight (TOF), or electrospray mass spectrometry (ESI-MS) with positive ion detection. Samples for microanalysis were dried under vacuum (0.5–1.0 mm) at 65–80 $^\circ$ C for 48–72 h.

(Z)-2-Nitro-9-(2,2,2-triphenylethylidene)fluorene (Z-NTEF):^[16] A solution of NaBO₃·4H₂O (0.55 g, 3.59 mmol) in AcOH, (15 mL) was stirred at 60 °C and a hot solution of Z-11 (0.30 g, 0.69 mmol) in AcOH (20 mL) was added dropwise over 1.5 h. The reaction mixture was stirred for 2 h at 60 $^\circ\text{C}$ then concentrated to dryness by rotary evaporation. The residue was partitioned between 15 mL of CH₂Cl₂ and 50 mL of H₂O, then the aqueous layer was separated and extracted with CH_2CI_2 (3×10 mL). The combined organic solutions were dried over Na2SO4 and concentrated by rotary evaporation. The resulting brown solid was dried in vacuo, then recrystallized from a (1:1:1, v/v/v) mixture of EtOH/cyclohexane/CH₂Cl₂ (20 mL). Filtration and drying at ca. 0.1 mm over P₂O₅ gave Z-NTEF (0.21 g, 65%) as yellow-brown crystals, m.p. > 300 °C (dec). ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 8.06$ (dd, ³J(H,H) = 8.4, ⁴J(H,H) = 1.8 Hz, 1 H, H3), 8.03 (s, 1 H, C=CH), 7.87 (d, ³J(H,H)=8.0 Hz, 1 H, H8), 7.80 (d, ${}^{3}J(H,H) = 8.0$ Hz, 1H, H5), 7.75 (d, ${}^{3}J(H,H) = 8.4$ Hz, 1H, H4), 7.45 (m, 2H, H6,7), 7.37 (d, ⁴J(H,H) = 1.1 Hz, 1H, H1), 7.28 ppm (m, 15 H, ArH); ¹³C NMR (75 MHz, CD_2CI_2): $\delta = 146.9$, 143.0, 130.7, 130.6, 129.1, 128.9, 128.8, 127.4, 124.0, 121.4, 121.0, 119.7 ppm; GC-MS: m/z (%) 465 (59) [M⁺], 388 (11), 370 (16), 341 (43), 270 (20), 252 (28), 207 (16), 165 (100); IR (KBr): ñ=3052, 1597, 1518, 1335, 701 cm⁻¹; UV/Vis (CH₃CN): $\lambda_{max}(\varepsilon) = 296$ nm (1,500 mol⁻¹ m³ cm⁻¹); fluorescence (CH₃CN, λ_{ex} 338): λ_{em} = 376, 392 nm; elemental analysis calcd (%) for C₃₉H₃₁NO₂·H₂O: C 84.32, H 5.04, N 2.98; found: C 84.27, H 5.32, N 2.94.

(E/Z-14):^[27] (E/Z)-9-Bromomethylene-2-iodofluorene Bromomethyltriphenylphosphonium bromide (17.8 g, 40.7 mmol) was dried by gentle heating at ca. 0.1 mm Hg. The flask was cooled under a nitrogen atmosphere, anhydrous THF (200 mL) was added, and the resulting suspension was cooled to $-60\,^{\circ}C$ (CHCl₃/dry-ice bath) and stirred for 10 min before a 2 M solution of NaHMDS in THF (20 mL, 40 mmol) was added. After 50 min a solution of 2-iodofluorenone 13 (10.4 g, 34 mmol)^[18] in anhydrous THF (100 mL) was added. The reaction mixture was allowed to warm to room temperature overnight then water (500 mL) was added. The resulting mixture was extracted with CH₂Cl₂ (2×500 mL) then the combined organic solutions were dried over Na₂SO₄. Rotary evaporation gave a brown solid (13 g) consisting of a 1.3:1 mixture of Z-14 and E-14 (by ¹H NMR analysis). Purification by flash chromatography, eluting with 7:3 (v/v) hexane/CH₂Cl₂, gave 1:1 E-14/Z-14 (by ¹H NMR analysis) as light yellow crystals (7.8 g, 61%), m.p. 85– 87 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.91 (s, 0.5 H, Z-H1), 8.56 (d, ³J(H,H) = 7.3 Hz, 0.5 H, E-H8)), 7.3–7.9 ppm (m, 7 H, C=CH, ArH) ; $^{13}{\rm C}~{\rm NMR}$ (126 MHz, CDCl_3): $\delta\!=\!138.2,~138.1,~137.9,~137.3,~134.5,$ 129.6, 129.4, 128.8, 127.80, 127.76, 125.7, 121.4, 121.3, 120.1, 119.9, 107.1, 107.0, 92.0 ppm; GC-MS: *m/z* (%) 384 (100) [*M*+2], 382 (89) [*M*⁺], 257 (3), 255 (3), 176 (43); elemental analysis calcd (%) for C₁₄H₈Brl: C 43.90, H 2.10; found: C 44.21, H 2.48.

(*E*)- and (*Z*)-2-Iodo-9-(2,2,2-triphenylethylidene)fluorene (*E*-ITEF and *Z*-ITEF): Triphenylmethane (6.81 g, 22.5 mmol) was dried by gentle heating at ca. 0.1 mm Hg. The flask was cooled under a nitrogen atmosphere, anhydrous THF (200 mL) was added, and the resulting suspension was cooled to -78 °C. After 5 min, a 1.6 M solution of *n*-butyllithium in hexane (12 mL, 19 mmol) was added. The resulting solution was stirred for 5 min, the cooling bath was replaced with an ice bath, the reaction mixture was stirred at 0 °C for 80 min, then the cooling bath was replaced with a dry ice/acetone bath. A solution of *E*/*Z*-**14** (7.12 g, 18.6 mmol) in anhydrous THF (20 mL) was added to the stirred solution. The reaction mix-

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ture was allowed to warm to room temperature overnight then water (400 mL) was added. The mixture was extracted with dichloromethane (2×300 mL). The combined organic solutions were dried (Na₂SO₄) and concentrated to dryness to give a brown gum. Purification by flash chromatography eluting with 9:1 (v/v) hexane/CH₂Cl₂ gave of an off-white solid (9.94 g, 98%). A solution of part of this mixture (6 g) in boiling toluene (70 mL) was concentrated to 50 mL and cooled to room temperature. Hexane (5 mL) was added and the solution was allowed to stand at room temperature for 2 min then filtered. A solution of the residue in hot toluene (25 mL) was cooled and stored for 6 h at -20 °C, yielding pure E-ITEF (0.6 g) as white needles, m.p. 262 °C. ¹H NMR (300 MHz, CD_2CI_2 : $\delta = 8.08$ (d, ${}^{4}J(H,H) = 1.4$ Hz, 1H, H1), 7.76 (s, 1H, C=CH), 7.69 (d, ${}^{3}J(H,H) = 7.8$ Hz, 1 H, H3), 7.63 (d, ${}^{3}J(H,H) = 7$ Hz, 1 H, H4), 7.46 (d, ³J(H,H) = 8 Hz, 1 H, H5), 7.2-7.3 (m, 15 H, ArH), 7.17 (t, ³J(H,H) = 8 Hz, 1 H, H6), 6.71 (t, ³J(H,H) = 8 Hz, 1 H, H7), 6.46 ppm (d, 3 J(H,H) = 8 Hz, 1 H, H8); 13 C NMR (126 MHz, CD₂Cl₂): δ = 146.7, 142.8, 141.0, 140.5, 138.5, 137.5, 136.9, 135.1, 130.3, 129.4, 128.4, 128.28, 128.25, 126.78, 126.77, 121.2, 119.4, 92.0, 61.9 ppm; IR (KBr): ñ = 3088, 3058, 3022, 1962, 1885, 1593, 1491, 1445, 1260, 1035, 1004, 830, 764, 702 cm⁻¹; GC-MS: *m/z* (%) 547 (30) [*M*+1], 546 (100) [*M*⁺], 545 (14), 420 (17), 342 (27), 166 (27); UV/Vis (CH₃CN): $\lambda_{max}(\varepsilon) =$ (13000), 306 (15000), 292 (16000), 266 nm 320 (26000 mol⁻¹ m³ cm⁻¹); elemental analysis calcd (%) for $C_{33}H_{23}I$: C 72.53, H 4.24; found: C 72.78, H 4.61. The mother liquor from the first crystallization was concentrated to dryness by rotary evaporation. A solution of this solid (1:1 E-ITEF/Z-ITEF by ¹HNMR analysis) in boiling toluene (5 mL) was cooled, stored at -20 °C, and filtered. A solution of the residue in boiling toluene (2 mL) was cooled, stored at -20 °C, and filtered. Evaporation of the filtrate gave a mixture (0.73 g) of 7:5 Z-ITEF/E-ITEF, by ¹H NMR analysis. A solution of this solid in toluene (1 mL) was stored at -20° C and filtered. Drying under vacuum (ca. 0.1 mm, 28 °C) gave pure Z-ITEF (90 mg) as yellow crystals, m.p. 267 °C. ¹H NMR (300 MHz, CD₂Cl₂): δ = 7.88 (s, 1H, C=CH), 7.78 (d, ³J(H,H) = 8 Hz, 1H, H4), 7.70 (d, ³J(H,H) = 8 Hz, 1 H, H5), 7.52 (d, ${}^{3}J(H,H) = 8$ Hz, 1 H, H8), 7.24–7.42 (m, 18 H, ArH,H3,6,7), 6.72 ppm (s, 1 H, H1); 13 C NMR (126 MHz, CD₂Cl₂): $\delta =$ 146.7, 141.3, 140.7, 140.4, 138.0, 137.4, 137.2, 137.1, 137.0, 130.3, 128.4, 128.3, 127.7, 127.0, 120.8, 120.2, 119.7, 91.5, 62.0 ppm; IR (KBr): ñ = 3109, 3058, 3017, 1598, 1491, 1271, 1153, 1035, 999, 907, 810, 753, 728, 697 cm⁻¹; GC-MS: *m/z* (%) 547 (30) [*M*+1], 546 (100) $[M^+]$, 420 (17), 342 (27), 166 (27); UV/Vis (CH₃CN): $\lambda_{max}(\varepsilon) = 310$ (13000), 292 (15000), 264 nm (26000 mol⁻¹ m³ cm⁻¹); elemental analysis calcd (%) for C33H23I: C 72.53, H 4.24; found: C 72.90, H 3.90.

(E)and (Z)-2-Cyano-9-(2,2,2-triphenylethylidene)fluorene (E-CTEF and Z-CTEF):^[21] A mixture of 2:1 E-ITEF/Z-ITEF (2.1 g, 3.8 mmol), CuCN (0.52 g, 5.8 mmol), and DMF (35 mL) was stirred and heated under reflux for 4 h. A solution of ferric chloride (FeCl₃·6H₂O, 5.0 g, 19 mmol) in 2.5 N aq HCl (30 mL) was added. The reaction mixture was stirred at 100 °C for 1 h then poured into water (100 mL) and filtered. The residue was washed with water $(2 \times 50 \text{ mL})$ and dried to give an off-white solid, that was purified by flash chromatography, eluting with EtOAc, yielding a pale yellow solid (1.25 g, 73%) of 5:3 E-CTEF/Z-CTEF, by ¹H NMR analysis. A solution of this solid in toluene (20 mL) was cooled to -20 °C to give pure E-CTEF (0.2 g) as an off-white powder, mp 262–263 $^\circ\text{C}.$ ¹H NMR (300 MHz, CD_2CI_2): δ = 8.08 (s, 1 H, H1), 7.91 (s, 1 H, C=CH) 7.82 (d, ³J(H,H) = 8 Hz, 1 H, H3), 7.74 (d, ³J(H,H) = 8 Hz, 1 H, H4) 7.67 (d, ³J(H,H) = 8 Hz, 1 H, H5), 7.24-7.34 (m, 16 H, ArH, H6), 6.82 (t, ${}^{3}J(H,H) = 8$ Hz, 1H, H7), 6.53 ppm (d, ${}^{3}J(H,H) = 8$ Hz, 1H, H8); ^{13}C NMR (100 MHz, CDCl₃): $\delta\,{=}\,146.5,\,$ 142.7, 141.8, 141.2, 140.2, 136.9, 136.2, 131.8, 130.3, 128.7, 128.4, 128.3, 127.9, 126.9, 124.1, 120.4, 120.2, 119.7, 110.2, 62.0 ppm; IR (KBr): ñ = 3078, 3047, 2218, 1281, 1184, 1035, 896, 728, 697, 630, 538 cm⁻¹; MALDI-MS: *m*/*z* = 447 [*M*+1], 446 [*M*⁺], 445; UV/Vis (dioxane/CH₃CN, 1:3, v/v); $\lambda_{max}(\varepsilon) = 327$ (15000), 312 (17000), 294 (18000), 269 nm (31 000 mol⁻¹ m³ cm⁻¹); fluorescence (CH₃CN, λ_{ex} 266): λ_{em} = 442 nm; elemental analysis calcd (%) for C₃₄H₂₃N·2/3 H₂O: C 89.25, H 5.36, N 3.06; found: C 89.28, H 5.80, N 3.17. Evaporation of the mother liquor from crystallization of E-CTEF gave a residue that was dissolved in boiling toluene (2 mL) then hexane (1 mL) was added. The resulting solid was collected by filtration, washed with hexane $(2 \times 0.5 \text{ mL})$, and dried under vacuum to give an off-white powder (0.1 g). To a solution of this solid in boiling chloroform (1 mL) hexane (1 mL) was added. The resulting off-white precipitate was collected by filtration, washed with hexane (1 mL), and dried overnight (ca. 0.1 mm Hg, 28 °C) to give pure Z-CTEF (72 mg) as an offwhite powder, m.p. 263–265 °C. ¹H NMR (400 MHz, CD_2CI_2): $\delta = 7.97$ (s, 1 H, C=CH), 7.84 (d, ³J(H,H) = 8 Hz, 1 H, H7), 7.78 (d, ³J(H,H) = 8 Hz, 1 H, H6), 7.73 (d, ³J(H,H) = 8 Hz, 1 H, H3), 7.41-7.47 (m, 3 H, H4,5,8), 7.25-7.33 (m, 15 H, ArH), 6.52 ppm (s, 1 H, H1); ¹³C NMR (100 MHz, CD₂Cl₂): *δ* = 146.5, 145.7, 142.1, 141.6, 137.3, 136.8, 135.9, 132.0, 131.5, 130.3, 128.9, 128.7, 128.6, 128.5, 127.2, 120.7, 120.5, 119.9, 109.5, 62.2 ppm; IR (KBr) ñ=2914, 2848, 1189, 1148, 1086, 1035, 901, 769, 728, 702, 661 cm⁻¹; MALDI-MS: *m*/*z*=447 [*M*+1], 446 [*M*⁺], 445; UV/Vis (dioxane/CH₃CN, 1:3, v/v): $\lambda_{max}(\varepsilon) = 329$ (11000), 314 (14000), 293 (18000), 267 (30000) 259 nm (23 000 mol⁻¹ m³ cm⁻¹); fluorescence (CH₃CN, λ_{ex} 330 nm): λ_{em} = 440 nm; elemental analysis calcd (%) for C₃₄H₂₃N: C 91.65, H 5.20, N 3.14; found: C 91.80, H 4.82, N 3.30.

(E-11):[22] (E)-2-Amino-9-(2,2,2-triphenylethylidene)fluorene [18]Crown-6 (0.51 g, 5.3 mmol) was dried at ca. 0.1 mm Hg overnight. Under a nitrogen atmosphere Pd₂(dba)₃ (0.19 g, 0.21 mmol), BINAP (0.39 g, 0.63 mmol), 2:1 E-ITEF/Z-ITEF (2.1 g, 3.8 mmol), and 0.51 g (5.3 mmol) of NaOEt were dried at ca. 0.1 mm Hg for 30 min in a second flask before being stored under nitrogen. A solution of the [18]crown-6 in anhydrous THF (3 mL) was added to the second flask, followed by benzophenone imine (1 mL, 8.8 mmol), then the reaction mixture was stirred at room temperature for 72 h. The reaction mixture was diluted with dichloromethane (20 mL) and filtered. The filtrate was concentrated to dryness, giving a brown gum. A solution of the crude product in THF (20 mL) was stirred for 20 min with 2 M aqueous HCl (1 mL), diluted with water, then extracted with EtOAc (2×50 mL). The combined extracts were shaken with 20% aqueous NaHCO₃solution (30 mL) and the layers were separated. The organic layer was evaporated, giving a yellow solid (1.56 g, 63%) after drying at ca. 0.1 mm Hg. The product was purified by flash chromatography, eluting with hexane/CH₂Cl₂, 7:3 (v/v), to give a yellow solid that was recrystallized from chloroform, washed with hexane, and dried under vacuum (ca. 0.1 mm Hg, 28°C) to give pure E-11 as a yellow solid (0.45 g), m.p. 262-265 °C.¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.78$ (d, ³J(H,H) = 8 Hz, 1 H, H4), 7.64 (s, 1 H, C=CH), 7.50 (d, ${}^{3}J(H,H) = 8$ Hz, 1 H, H5), 7.44 (t, ³J(H,H) = 8 Hz, 1 H, H6), 7.19–7.45 (m, 15 H, PhH), 7.12 (t, ³J(H,H) = 8 Hz, 1 H, H7), 6.63 (m, 2 H, H1,3), 6.40 ppm (d, ³J(H,H) = 8 Hz, 1 H, H8); ¹³C NMR (126 MHz, CD₂Cl₂): $\delta = 147.0$, 139.1, 138.3, 135.7, 130.3, 129.6, 129.5, 128.4, 128.3, 128.22, 128.16, 128.1, 126.7, 125.6, 119.5, 118.8, 113.9, 61.7 ppm; IR (KBr): ñ = 3420, 3344, 3324, 3058, 3027, 1956, 1619, 1593, 1485, 1454, 1291, 1034, 810, 764, 707 cm⁻¹; MS (ESI): m/z (%) 465 (100) $[M^+]$; elemental analysis calcd (%) for C₃₃H₂₅N: C 91.00, H 5.79, N 3.20; found: C 91.40, H 5.49, N 2.95.

(E)-2-Nitro-9-(2,2,2-triphenylethylidene)fluorene (E-NTEF):^[16] A solution of NaBO₃·4H₂O (1.2 g, 7.9 mmol) in AcOH (10 mL) was stirred at 60 °C as a solution of E-11 (0.25 g, 0.57 mmol) in hot AcOH (10 mL) was added dropwise over 1.5 h. The reaction mix-

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ture was stirred for 2 h at 60° C then poured into water (100 mL). The resulting solid was collected by filtration, washed with water (2×50 mL), and dried under vacuum. A solution of the crude product in CH₂Cl₂ (200 mL) was filtered through alumina (10 g), eluting with EtOAc (200 mL). Rotary evaporation gave a yellow solid (0.20 g, 75%), that was dissolved in $CHCl_3$ (1 mL) then hexane (1 mL) was added to give of pure E-NTEF (0.12 g, 56%) as yellow crystals, m.p. 254 °C. ¹H NMR (400 MHz, CD_2CI_2): $\delta = 8.62$ (s, 1 H, H1), 8.27 (d, ${}^{3}J(H,H) = 8$ Hz, 1 H, H3), 8.0 (s, 1 H, C=CH), 7.85 (d, ${}^{3}J(H,H) =$ 8 Hz, 1 H, H4), 7.77 (d, ³J(H,H) = 8 Hz, 1 H, H5), 7.26-7.30 (m, 16 H, PhH,H6), 6.84 (t, ${}^{3}J(H,H) = 8$ Hz,1 H, H7), 6.56 ppm (d, ${}^{3}J(H,H) = 8$ Hz, 1 H, H8); ¹³C NMR (125 MHz, CD₂Cl₂): δ = 146.5, 142.3, 139.7, 137.1, 137.0, 132.6, 130.4, 130.3, 130.2, 128.8, 128.6, 128.5, 128.4, 126.9, 123.7, 120.7, 119.8, 115.8, 62.0 ppm; IR (KBr): ñ = 3119, 3063, 3017, 1952, 1885, 1808, 1593, 1516, 1445, 1419, 1143, 907, 820, 759, 733, 697 cm⁻¹; MALDI-MS: *m*/*z*=466 [*M*+1], 465, [*M*⁺], 464; UV/Vis (dioxane/CH₃CN, 1:3, v/v): $\lambda_{max}(\varepsilon) = 334$ (24000), 298 (29000), 289 nm (29000 mol⁻¹ m³ cm⁻¹); fluorescence (dioxane/CH₃CN, 1:3 (v/v), λ_{ex} 266): λ_{em} = 471 nm; elemental analysis calcd (%) for C₃₃H₂₃NO₂·¹/₂H₂O: C 83.52, H 5.10, N 2.95; found: C 83.19, H 5.27, N 2.90.

Crystallographic structure determination

X-ray crystallographic data was collected at 100(1) K on a Bruker APEX CCD diffractometer with Mo K radiation (0.71073 Å) and a detector-to-crystal distance of 4.94 cm. Data collection was optimized utilizing the APEX2 software with a 0.5° rotation about between frames, and exposure times of 10 or 20 s per frame. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed using SAINTPLUS, and corrected for absorption using SADABS. The structures were solved using direct methods followed by successive least squares refinement on F^2 using the SHELXTL 6.10 software package.^[28] All nonhydrogen atoms were refined anisotropically and hydrogen atoms placed in CCDC 784492 (E-ITEF), calculated positions. 784493 (Z-10), 784494 (Z-11), 784495 (Z-9), 784496 (Z-ITEF), and 784497 (Z-NTEF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Irradiation

Photoisomerization excitation wavelengths used were generated either as harmonics of a pulsed Nd:YAG laser (10 Hz repetition rate) or from a Nd:YAG-pumped, frequency-doubled dye laser. Light pulses ca. 5 ns in duration of energies 0.3–0.5 mJ pulse⁻¹ irradiated a sample of an approximately 0.4 mm solution in a 1 cm square fused silica cuvette, giving a laser fluence of 0.4-0.6 mJ cm⁻² pulse⁻¹. The optical density of the solution was high enough that more than 99.5% of the laser energy was absorbed in the laser path, with the exception of CTEF and ITEF at 355 nm irradiation. For these two cases, where the optical density of the sample solution was low, the energy absorbed by the solution was determined by subtraction of the measured pulse energy after sample absorption from the measured energy before passing through the sample, with the minor energy loss due to reflection at the cuvette surface taken into account. Solvent-saturated nitrogen gas bubbled through the solution deoxygenated the samples prior to irradiation, and continuous stirring during irradiation ensured that all molecules were equally exposed to laser excitation.

Chromatographic analysis

The isomeric composition of NTEF as a function of irradiation time was measured using a gas chromatograph (Varian CP-3800) with a tandem mass spectrometer detector (Saturn 2200) with front injector temperature of 290 °C, oven temperature starting at 80 °C ramping up to 290°C at 15° per minute, and a flow rate of 6 mLmin⁻¹. Peak identities were verified by mass spectrometry and by comparison with the chromatographic spectra of samples with known isomer purity. Photoisomerization of CTEF and ITEF was measured using an HPLC (Waters 1525) with a reverse-phase column (Symmetry C18 5 μ m). A flow rate of 1 mLmin⁻¹ of 9:1 (v/ v) methanol/water was sufficient to separate the E and Z isomers of CTEF, where they were detected by absorption spectroscopy at 320 nm. ITEF was analyzed using a 100% methanol mobile phase, at a flow rate of 1 mLmin⁻¹, and a detection wavelength of 298 nm. In each case, the detection wavelength was chosen such that the molar absorptivities of the E and Z isomers were equivalent. Isomer peaks were verified by comparison with the chromatograms of samples with known isomer purity.

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FULL PAPER

A useful twist: 2-Substituted dibenzofulvene molecular actuators based on (2,2,2-triphenylethylidene)fluorene are reported. The 2-nitro compound is photochemically robust and has a large quantum yield for photoisomerization in the near-UV, making it a promising drive rotor moiety for light-powered molecular devices. The 2-cyano and 2-iodo analogues (*E* and *Z* isomers of the latter shown in picture) have higher quantum yields but absorb light at shorter wavelengths and undergo minor competing photodecomposition.



Isomerization

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Synthesis and Photoisomerization of Substituted Dibenzofulvene Molecular Rotors